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A Tutorial for NEWTON-X

Tutorial based on NEWTON-X version 2.2 build 08, 2019

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Please cite this tutorial as:

- Matthias Ruckebauer, Daniele Fazzi, Wilmer Arbelo-González, Ljiljana Stojanović, and Mario Barbatti, **A Tutorial for NEWTON-X**, version 2.2, www.newtonx.org, 2019.

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1. Before starting

1.1 Programs necessary to follow this tutorial

- NEWTON-X.¹⁻³ The variable \$NX should be defined, pointing to the binaries. The latest update in this tutorial is based on NEWTON-X version indicated in the cover. Nevertheless, parts of it can still refer to older versions. Changes between versions are indicated in proper places.
- COLUMBUS⁴⁻⁵ for spectrum and dynamics using MRCI or MCSCF methods. The variable \$COLUMBUS should also be defined, pointing to the binaries.
- TURBOMOLE⁶ for spectrum and dynamics using TD-DFT or RI-CC2/ADC(2) methods. The TURBOMOLE addresses should be in \$path.
- GAUSSIAN 09 for spectrum and dynamics using TD-DFT. \$g09root should be defined, and g09.login should have been sourced.
- TINKER⁷ for QM/MM dynamics. Tinker executable 'testgrad.x' should be in the standard path or available.
- EZDYSON⁸⁻⁹ for photoelectron spectrum. NEWTON-X reads the C_{klm} partial wave coefficients from EZDYSON. These coefficients are defined, however, in slightly different ways in the different versions of EZDYSON. NEWTON-X uses them as defined in version 3.2.
- PERL 5.8 or higher.
- MOLDEN, VMD or another molecular visualization program able to read sequential xyz files.
- GNUPLOT.

1.2 How to use this tutorial

The Tutorial is divided into several sections with different jobs. Advanced jobs may refer to basic jobs. The chapters referring to different third-party programs are, however, independent of each other. Thus, if you want to learn how to using NEWTON-X with GAUSSIAN 09, you may skip Chapters 2 and 3 and study Chapters 4 to 6.

In \$NX/./test-nx, there are many examples of input jobs for NEWTON-X. You may consider to study them as well.

1.3 Notation

1. The basic instructions are sequentially numbered.

This kind of font indicates what is seen in the screen
and the command lines that you should type <ENTER> ! Comments come here

Important information related to NEWTON-X but not necessarily connected to the current job comes in boxes like this. It is advisable to read the boxes, but you can follow the tutorial without them.

1.4 Preparing the jobs

2. Create a directory TUTORIAL. Inside TUTORIAL, new subdirectories will be created for each job.

You should organize your jobs using the suggested structure of directories. Such structure will make it easier to copy files between different jobs.

2. Initial conditions and spectrum simulation: TD-DFT – Turbomole

In this section, we will simulate the absorption spectrum with TURBOMOLE. The system is pyrazine and two singlet excited states will be included. The initial geometry distribution will be generated by a Wigner distribution in the ground vibrational state of the ground electronic state. The transition energies and moments will be also computed at TD-DFT(B3-LYP)/SV(P). Theoretical details about the spectrum simulation are discussed in Ref.¹⁰.

2.1 Geometry file creation

1. In the TUTORIAL directory (see Section 1.4) create a subdirectory called PYRAZINE_TDDFT_SPEC:

```
> mkdir PYRAZINE_TDDFT_SPEC
```

2. Move to this directory and create a file called pyrazine.xyz containing the geometry in XYZ format:

```
> cd PYRAZINE_TDDFT_SPEC
> vi pyrazine.xyz
```

```
10
```

N	-0.000000	2.421234	1.397837
N	-0.000000	0.003637	0.002163
C	0.000000	1.241014	2.044972
C	-0.000000	0.033417	1.347829
C	-0.000000	2.391454	0.052171
C	0.000000	1.183858	-0.644972
H	0.000000	1.271951	3.113613
H	-0.000000	-0.907483	1.855431
H	-0.000000	3.332354	-0.455431
H	0.000000	1.152921	-1.713613

This initial geometry can be created by hand with a text editor (like VI) or with any molecular editor like MOLDEN. It is the simple xyz Cartesian format in Angstrom. The first line contains the number of atoms, and it is followed by a blank line.

3. Convert geometry into NEWTON-X format.

```
> $NX/xyz2nx < pyrazine.xyz <ENTER>
```

The NEWTON-X geometry file is called 'geom' and looks like

N	7.0	0.00000000	4.57546916	2.64152911	14.00307401
N	7.0	0.00000000	0.00687293	0.00408748	14.00307401
C	6.0	0.00000000	2.34517659	3.86443703	12.00000000
C	6.0	0.00000000	0.06314898	2.54702768	12.00000000
C	6.0	0.00000000	4.51919312	0.09858890	12.00000000
C	6.0	0.00000000	2.23716740	-1.21882044	12.00000000
H	1.0	0.00000000	2.40363904	5.88387585	1.00782504
H	1.0	0.00000000	-1.71489434	3.50625645	1.00782504
H	1.0	0.00000000	6.29723644	-0.86063986	1.00782504
H	1.0	0.00000000	2.17870494	-3.23825927	1.00782504

The second column contains the atomic number, and the following three columns contain the x, y and z coordinates in atomic units (Bohr). The last column contains the atomic masses, which can be eventually changed to simulate isotopic effects. The file can be freely formatted.

The conversion back from NEWTON-X format to xyz can be done with

```
> $NX/nx2xyz
```

After running this program, the xyz-format geometry is written to file 'geom.xyz'.

2.2 Normal-modes step

4. Create a new directory to run normal-mode calculation:

```
> mkdir FREQ-DFT <ENTER>
```

5. Move to this directory and copy the geom file there.

```
> cd FREQ-DFT
> cp ../geom .
```

6. Transform the geometry into TURBOMOLE format.

```
> $NX/nx2tm
```

nx2tm program converts NEWTON-X "geom" file into TURBOMOLE "coord" file (atomic units). The back conversion can be done with

```
> $NX/tm2nx
```

7. Prepare the input and run a normal mode calculation at DFT(B3-LYP)/SV(P) level with TURBOMOLE. To do that, follow specific TURBOMOLE documentation (www.turbomole.com). Let the geometry be optimized to have only real frequencies. The TURBOMOLE output containing the normal modes and frequencies can have any name. Here we will suppose it is called "force.out".

NEWTON-X can read normal modes and frequencies from the outputs of the following programs: GAMESS, TURBOMOLE, COLUMBUS, GAUSSIAN, MOLDEN, DFTB, and ACES2.

Note that the normal modes and harmonic frequencies are used only to set the width of the random number distributions. For this reason, they do not need to be calculated at the same level as the one that will be used in the dynamics. It is, however, absolutely necessary that the order of atoms and geometry orientation in the "geom" file and in the normal modes are exactly the same. Using NEWTON-X conversion tools (like nx2tm) assures that.

2.3 Energy and transition moment input

8. Move to the parent directory (TUTORIAL/PYRAZINE_TDDFT_SPEC) and create a new subdirectory called JOB_AD.

```
> cd ..
> mkdir JOB_AD
```

The directory must be named JOB_AD since NEWTON-X will search for it.

9. Move into JOB_AD and copy the TURBOMOLE geometry file there.

```
> cd JOB_AD
> cp ../FREQ-DFT/coord .
```

10. In this directory, prepare a TURBOMOLE input for single point calculation at TD-DFT(B3-LYP)/SV(P) without symmetry, with two singlet excited states, and transition moments (oscillator strengths) calculations. Follow the TURBOMOLE documentation (www.turbomole.com).

This is the basic procedure for any program. If, for example, the initial conditions should be generated using RI-CC2 energies, JOB_AD should contain a TURBOMOLE input for single point calculations at RI-CC2 level.

Before submitting running any NEWTON-X job is highly advisable to run the job in JOB_AD directory just to test whether the input and outputs are OK. In the current case, just copy the content of the JOB_AD into a test directory and run the TURBOMOLE job. Check whether the three roots and the oscillator strengths are computed and show reasonable values.

2.4 NEWTON-X input

11. Move to directory TUTORIAL/PYRAZINE_TDDFT_SPEC and create a subdirectory called IC-TDDFT.

```
> cd ..
> mkdir IC-TDDFT
```

12. Move to this directory and copy the optimized DFT geometry file there.

```
> cd IC-TDDFT
> cp ../FREQ-DFT/coord .
```

13. Convert the new TURBOMOLE geometry file into NEWTON-X format.

```
> $NX/tm2nx
> rm -f coord ! We do not need this file anymore.
```

14. Copy the JOB_AD directory and the normal modes file into IC-TDDFT.

```
> cp -rf ../JOB_AD .
> cp ../FREQ-DFT/force.out .
> ls
force.out geom JOB_AD
```

15. Run the nxinp program and select option 1: Generate initial conditions.

nxinp is the input tool for NEWTON-X. All input procedures, from the initial condition generation, through the dynamics inputs, to the statistical analysis options are performed with it.

> \$NX/nxinp

```

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

MAIN MENU

1. GENERATE INITIAL CONDITIONS

2. SET BASIC INPUT

3. SET GENERAL OPTIONS

4. SET NONADIABATIC DYNAMICS

5. GENERATE TRAJECTORIES AND SPECTRUM

6. SET STATISTICAL ANALYSIS

7. EXIT

```

Select one option (1-7): 1 <ENTER>

16. Select the adequate options for the initial condition properties.

nxinp will guide you through a set of questions. Each of them contains a short explanation and the available options. Most of the times, the default value is the best option. To accept the default you can just press <ENTER>.

```

...
nact: Distribution:
      1 - Classic harmonic oscillator
      2 - Q/P-uncorrelated quantum harmonic oscillator (Wigner)
      3 - Q/P-correlated quantum harmonic oscillator
      4 - Pick points from previous dynamics
      5 - Random-velocities generation
      6 - Single point on a previous calculation
The current value of nact is: 2
Enter the new value of nact : <ENTER>
Setting nact = 2

numat: Number of atoms.
The current value of numat is: 10
Enter the new value of numat : <ENTER>
Setting numat = 10

npoints: Number of initial conditions to be generated
The current value of npoints is: 1
Enter the new value of npoints : 50 <ENTER>
Setting npoints = 50

```

npoints sets the number of initial conditions that should be generated. This number depends on how many points you want to compute to generate the spectrum and how many trajectories you want to simulate.

In real applications, you will need much more than 50 points. 500 may be a good number.

You can also run several short jobs with few points in each one and merge them afterward using the tool “merge_initcond.pl.” Thus, with 10 computers running 50 points each, you can quickly have 500 points. See in section 2.5 a note about how to split and merge the jobs.

```
file_geom: File containing the equilibrium geometry.
The current value of file_geom is: 'geom'
Enter the new value of file_geom : <ENTER>
Setting file_geom = 'geom'
```

```
iprogram: Read vibrational modes from:
  1 - GAMESS output
  2 - TURBOLMOLE output
  3 - COLUMBUS output
  4 - GAUSSIAN output
  5 - MOLDEEN file
  6 - DFTB output
  7 - ACES2 output
```

```
The current value of iprog is: 2
Enter the new value of iprog : <ENTER>
Setting iprog = 2
```

```
file_nmodes: File containing the normal modes.
The current value of file_nmodes is: 'force.out'
Enter the new value of file_nmodes : <ENTER>
Setting file_nmodes = 'force.out'
```

```
anh_f: Multiply harmonic frequencies by this factor.
The current value of anh_f is: 1
Enter the new value of anh_f : <ENTER>
Setting anh_f = 1
```

```
chk_e: Restrict (or do not) the statistical distribution:
  0 - Do not check the energies.
  1 - Check the energies between states NIS and NFS.
The current value of chk_e is: 0
Enter the new value of chk_e : 1 <ENTER>
Setting chk_e = 1
```

The next keywords define the restriction on the statistical distribution.

```
nis: Initial state (State in which the previous dynamics run. Ground state = 1.).
The current value of nis is: 1
Enter the new value of nis : <ENTER>
Setting nis = 1
```

```
nfs: Final state.
The current value of nfs is: 2
Enter the new value of nfs : 3 <ENTER>
Setting nfs = 3
```

The Wigner distribution will be generated in the ground electronic state (nis = 1) and transition energies between the ground and the second excited (nfs = 3) states will be computed. Indeed, with nfs = N, transition information for all states below N will also be computed and collected.

```

kvert: Center of the restriction:
      0 - Provide the energy for center of restriction
      1 - Use the vertical excitation energy of the equilibrium geometry
The current value of kvert is: 1
Enter the new value of kvert : <ENTER>
Setting kvert = 1

de: Width of restriction (center +/- de/2).
The current value of de (eV) is: 0.5
Enter the new value of de (eV) : 100 <ENTER>
Setting de = 100

```

This large “de” implies that this restriction will not be used. It can be imposed later on.

```

prog: Program and method to compute vertical excitation energies:
      1 - COLUMBUS
      2.0 - TURBOMOLE RI-CC2
      2.1 - TURBOMOLE TD-DFT
      5 - DFTB
The current value of prog is: 1
Enter the new value of prog : 2.1 <ENTER>      ! Turbomole TD-DFT
Setting prog = 1

iseed: Random number seed.
      0 - default seed value.
     -1 - set random seed.
     >0 - (integer) set specific value for the seed.
The current value of iseed is: 0
Enter the new value of iseed : <ENTER>
Setting iseed = 0

lvprt: Print level.
      1 - standard level
      2 - debug level
The current value of lvprt is: 1
Enter the new value of lvprt : <ENTER>
Setting lvprt = 1

```

17. Exit nxinp.

2.5 Running NEWTON-X: initial conditions

18. Run the initial condition generation program.

```
> $NX/initcond.pl > initcond.log &
```

In general, with $chk_e = 1$, you might want to submit this job to a batch system. Files “pini” and “pini-ew” in $\$NX/./batch/$ directory are templates that can be adapted to your own batch system.

Splitting and merging jobs:

To split the job among several computers, just prepare the input as it was done until here. Then run

```
> $NX/split_initcond.pl
```

This program will create a directory called INITIAL_CONDITIONS and inside it a sequence of subdirectories called I1, I2, ..., each one containing a complete set of input files.

Copy each directory to a different computer and run the job normally.

To merge the jobs, after the calculations, copy the directories I1, I2, ... back to INITIAL_CONDITIONS directory and from inside this directory run

```
> $NX/merge_initcond.pl
```

This program will ask for the number of jobs to be merged, and it will create a new directory called I_merged with merged results. Move to this directory and proceed with the spectrum simulation as explained below.

2.6 Checking the results

19. Normal job termination is indicated at the end of initcond.log file by:

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

20. The primary information is written to the final_output files.

21. Both final_output.1.2 and final_output.1.3 contains the same 50 geometries and velocities generated according to the Wigner distribution. final_output.1.2 contains transition energies and oscillator strengths to excitations into state 2 (first excited state), while final_output.1.3 contains the same information to excitations into state 3 (second excited state).

2.7 Generating the spectrum

22. Go to directory TUTORIAL/PYRAZINE_TDDFT_SPEC and create the directory SPECTRUM.

```
> mkdir SPECTRUM !This name is not compulsory.
```

23. Move to this directory and copy final_output files there.

```
> cd SPECTRUM
> cp ../IC_TDDFT/final_output* .
```

24. Run nxinp and select option 5: “Generate Trajectories and Spectrum”.

```
> $NX/nxinp
```

1. GENERATE INITIAL CONDITIONS
2. SET BASIC INPUT
3. SET GENERAL OPTIONS
4. SET NONADIABATIC DYNAMICS
5. GENERATE TRAJECTORIES AND SPECTRUM
6. SET STATISTICAL ANALYSIS
7. EXIT

Select one option (1-7): 5

25. Go through the next options.

```
type: What do you want to do?
      1 - Generate spectrum
      2 - Select initial conditions for multiple initial states
      3 - Generate trajectories
      4 - Return to main menu
The current value of type is: 3
Enter the new value of type : 1
Setting type = 1
```

If for this first option you are asked for “kindjob” instead “type,” this means you are using an old version of NEWTON-X. Contact the distributors to get an updated version of the program.

```
nis: Initial state.
The current value of nis is: 1
Enter the new value of nis : <ENTER>
Setting nis = 1
```

```
nfs: Array of final states (comma or dash separated, e.g., 2-4 or 2,3,4).
For trajectories generation only one final state is allowed.
The current value of nfs is: 2
Enter the new value of nfs : 2,3 <ENTER> !Spectrum including both states
Setting nfs = 2,3
```

If nfs should be given as a ‘space separated’ list, this means that you are using an old version of NEWTON-X. Contact the distributors to get an updated version of the program.

```
screen: Energy restriction
        0 - don't apply any restriction
        1 - use the original energy restriction written in the final_output files
        2 - apply new energy restriction
The current value of screen is: 0
Enter the new value of screen : <ENTER>
Setting screen = 0
```

```
os_condon: Oscillator strength:
-1 - try to read from final_output file.
x - oscillator strength is always x (Condon approximation).
The current value of os_condon is: -1
Enter the new value of os_condon : <ENTER>
Setting os_condon = -1
```

If the oscillator strength is not available, but the transition energy is, it is still possible to simulate the spectrum by giving a value to the oscillator strength in os_condon option. In this case, all transitions will be computed with the same oscillator strength. For only one final state this option is not bad, but it can be completely inadequate when more than one final state is selected.

```
prob_kind: Formula to calculate the transition probabilities:
           A - Einstein-coefficient A (spontaneous emission)
           B - Einstein-coefficient B (induced absorption or induced emission)
           F - Oscillator strength (photoabsorption cross section)
The current value of prob_kind is: B
Enter the new value of prob_kind : <ENTER>
Setting prob_kind = F
```

```
norm: Normalization of transition intensities:
```

```

    local - Use energy-restricted data set
    global - Use complete data set
The current value of norm is: local
Enter the new value of norm : <ENTER> ! with no energy restriction, doesn't
Setting norm = local ! matter.

seed: Seed for the random number generation
    0 - a default random number seed is used
    1 - a randomized seed is used
    Any other positive integer is used as the random number seed
The current value of seed is: 0
Enter the new value of seed : <ENTER>
Setting seed = 0

l_shape: Line shape:
    gauss - Normalized Gaussian function.
    lorentz - Normalized Lorentzian function.
The current value of l_shape is: lorentz
Enter the new value of l_shape : <ENTER>
Setting l_shape = lorentz

delta: Phenomenological broadening of the spectrum.
The current value of delta (eV) is: 0.05
Enter the new value of delta (eV) : <ENTER>
Setting delta = 0.05

```

“delta” is possibly the only option that you need to play with. It controls the width of the Gaussian curve attributed to each one of the 100 transitions (50 initial conditions x 2 final states).

```

temp: Temperature.
The current value of temp (K) is: 0
Enter the new value of temp (K) : <ENTER>

nref: Refraction index.
The current value of nref is: 1
Enter the new value of nref : <ENTER>

eps: Distance between consecutive points in the spectrum.
The current value of eps (eV) is: 0.005
Enter the new value of eps (eV) : <ENTER>
Setting eps = 0.005

kappa: The range of the spectrum is defined between
Emin-kappa*delta and Emax+kappa*delta, where kappa is an integer.
The current value of kappa is: 3
Enter the new value of kappa : <ENTER>
Setting kappa = 3

```

26. Exit nxinp.

27. The simulated cross section using a Lorentzian line shape with phenomenological broadening $\delta = 0.05$ eV is written to cross-section.dat. Looking in this file, we see:

```

! DE (eV) Wavelength(nm) cross-section(Å2.molecule-1)
3.1914 3.8849e+02 0.0003
3.1964 3.8789e+02 0.0003
3.2014 3.8728e+02 0.0003
...
3.8014 3.2615e+02 0.0304
3.8064 3.2573e+02 0.0306
...

```

28. Run Gnuplot to visualize the spectrum.

```
> gnuplot  
gnuplot> plot 'cross-section.dat' using 1:3 with lines
```

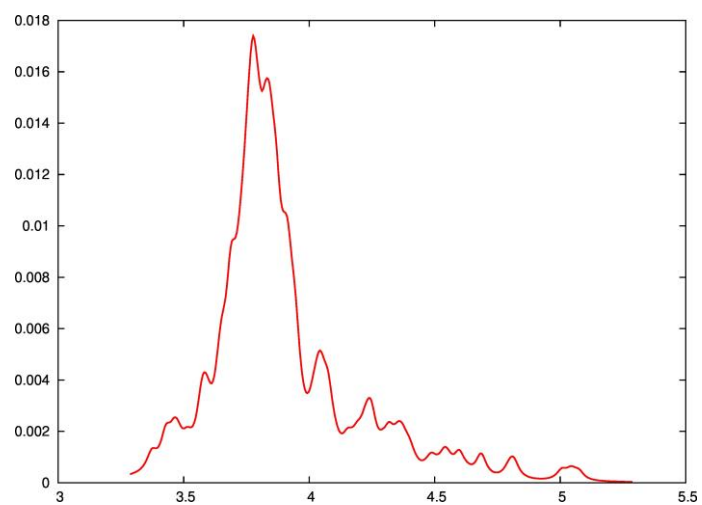


Fig. 1. Photoabsorption cross-section in $\text{\AA}^2 \cdot \text{molecule}^{-1}$ as a function of the excitation energy in electron-Volts.

3. Surface hopping dynamics: TDDFT – Turbomole

In this section, we will prepare the inputs and run dynamics simulations. The system is pyrazine, and the dynamics will be initiated in the second excited state. The initial conditions were generated in Chapter 2 of this tutorial. The surface hopping¹¹ dynamics will be performed at TDDFT level using TURBOMOLE. The trajectory time will be 100 fs with 0.5 fs time step.

The TDDFT will use the B3-LYP functional and the SV(P) basis set. The dynamics will start in S_2 , with initial conditions selected in the interval of 3.5 to 4 eV.

3.1 Copying the initial conditions

1. Go to TUTORIAL directory (see section 1.4) create a subdirectory called PYRAZINE_TDDFT_DYN:

```
> mkdir PYRAZINE_TDDFT_DYN
```

2. Move to this directory and copy the initial conditions file for the second excited state there.

```
> cd PYRAZINE_TDDFT_DYN
> cp ../PYRAZINE_TDDFT_SPEC/IC_TDDFT/final_output.1.3 final_output ! note the new
name
```

3. Create a subdirectory called JOB_AD.

The directory must be named JOB_AD since NEWTON-X will search for it.

3.1 Preparing electronic structure input

4. Move to JOB_AD and create an input for single point TDDFT/B3LYP/SV(P) calculation. Use C_1 point group (no symmetry) and request the calculation of two excited states belonging to representation a .

Before submitting running any NEWTON-X job is highly advisable to run the job in JOB_AD directory just to test whether the input and outputs are OK. In the current case, just copy the content of the JOB_AD into a test directory and run the TURBOMOLE job. Check whether the three roots are computed and show reasonable values.

3.2 NEWTON-X input

5. Run nxinp.

> \$NX/nxinp

```

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

MAIN MENU

1. GENERATE INITIAL CONDITIONS

2. SET BASIC INPUT

3. SET GENERAL OPTIONS

4. SET NONADIABATIC DYNAMICS

5. GENERATE TRAJECTORIES AND SPECTRUM

6. SET STATISTICAL ANALYSIS

7. EXIT

```

Select one option (1-7): 2 <ENTER>

6. Select option 2: “set basic input” and answer the questions to set the dynamics options.

```

nat: Number of atoms.
The current value of nat is: 10
Enter the new value of nat : <ENTER>
Setting nat = 10

nstat: Number of states.
The current value of nstat is: 2
Enter the new value of nstat : 3 <ENTER>      ! 3 states will be computed
Setting nstat = 3

nstatdyn: Initial state (1 - ground state).
The current value of nstatdyn is: 3
Enter the new value of nstatdyn : <ENTER>      ! dynamics will start in state 3
Setting nstatdyn = 3

dt: Time step for the classical equations.
The current value of dt (fs) is: 0.5
Enter the new value of dt (fs) : <ENTER>
Setting dt = 0.5

tmax: Total duration of the trajectory.
The current value of tmax (fs) is: 100
Enter the new value of tmax (fs) : <ENTER>
Setting tmax = 100

prog: Quantum chemistry program and method
      0 - ANALYTICAL MODEL
      1 - COLUMBUS
      2.0 - TURBOMOLE RI-CC2
      2.1 - TURBOMOLE TD-DFT

```

```

2.2 - TURBOMOLE ADC (2)           ! NX > 1.4
3  - ACES2 EOM-CCSD (in development)
4  - MOPAC (in development)
5  - DFTB
6  - GAUSSIAN                     ! NX < 1.2
6.0 - GAUSSIAN(03) CASSCF         !
6.5 - GAUSSIAN(09) TDDFT         !
7  - TINKER
8  - DFTB+
10.0 - GAMESS
10.1 - GAMESS ARBITRARY ADIABATIC METHOD
20 - HYBRID GRADIENT
The current value of prog is: 1
Enter the new value of prog : 2.1 <ENTER>
Setting prog = 2.1

thres: Threshold to initiate nonadiabatic coupling calculation.
      0 - Only adiabatic dynamics.
     100 - Only nonadiabatic dynamics
The current value of thres (eV) is: 0
Enter the new value of thres (eV) : 100 <ENTER>
Setting thres = 100

Would you like to generate internal coordinate file? (default=y) n <ENTER>

```

7. In the main nxinp menu you have the option to set more general options if you select either option 3 or option 4. Normally, this is not necessary, and the default values are good enough.

8. Select option 5: “generate trajectories and spectrum.”

```

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

MAIN MENU

1. GENERATE INITIAL CONDITIONS

2. SET BASIC INPUT

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5. GENERATE TRAJECTORIES AND SPECTRUM

6. SET STATISTICAL ANALYSIS

7. EXIT

```

Select one option (1-7): 5 <ENTER>

9. Select the job options.

```

type: What do you want to do?
      1 - Generate spectrum
      2 - Select initial conditions for multiple initial states
      3 - Generate trajectories
      4 - Return to main menu
The current value of type is: 3
Enter the new value of type : <ENTER>
Setting type = 3

```

If for this first option you are asked for “kindjob” instead “type,” this means you are using an old version of NEWTON-X. Contact the distributors to get an updated version of the program.

```

Would you like to apply energy and probability restrictions (y/n)? (default=n) y
<ENTER>

```

```

nis: Initial state.
The current value of nis is: 1
Enter the new value of nis : <ENTER>
Setting nis = 1

```

```

nfs: Array of final states (comma or dash separated, e.g., 2-4 or 2,3,4).
For trajectories generation only one final state is allowed.
The current value of nfs is: 2
Enter the new value of nfs : 3 <ENTER>
Setting nfs = 3

```

The next keywords will allow setting the initial condition restrictions between 3.5 and 4 eV. If nfs should be given as a ‘space separated’ list, this means that you are using an old version of NEWTON-X. Contact the distributors to get an updated version of the program.

```

screen: Energy restriction
        0 - don't apply any restriction
        1 - use the original energy restriction written in the final_output files
        2 - apply new energy restriction
The current value of screen is: 0
Enter the new value of screen : 2 <ENTER>
Setting screen = 2

```

```

e_center: Center of the energy restriction.
          x - value of the center of restriction
          ref n - use the vertical excitation of final_output.nis.n file
The current value of e_center (eV) is: 0.0
Enter the new value of e_center (eV) : 3.75 <ENTER>
Setting e_center = 3.75

```

```

e_var: Width of the energy restriction.
The current value of e_var (eV) is: 0.5
Enter the new value of e_var (eV) : 0.25 <ENTER>
Setting e_var = 0.25

```

```

os_condon: Oscillator strength:
-1 - try to read from final_output file.
      x - oscillator strength is always x (Condon approximation).
The current value of os_condon is: -1
Enter the new value of os_condon : <ENTER>
Setting os_condon = -1

```

```

prob_kind: Formula to calculate the transition probabilities:
           A - Einstein-coefficient A (spontaneous emission)
           B - Einstein-coefficient B (induced absorption or induced emission)
           F - Oscillator strength (photoabsorption cross section) ! NX < 1.2
           E - Fluorescence (radiative decay rate) ! Options for NX > 1.4
           F - Absorption (photoabsorption cross section) !
The current value of prob_kind is: F

```

```

Enter the new value of prob_kind : <ENTER>
Setting prob_kind = F

norm: Normalization of transition intensities:
      local - Use energy-restricted data set
      global - Use complete data set
The current value of norm is: local
Enter the new value of norm : <ENTER>
Setting norm = local

seed: Seed for the random number generation
      0 - a default random number seed is used
      1 - a randomized seed is used
      Any other positive integer is used as the random number seed
The current value of seed is: 0
Enter the new value of seed : <ENTER>
Setting seed = 0

Will the trajectories run in a batch system? n <ENTER>

Processing data: This may take some minutes. Please, wait...

```

In general, you might want to submit this job to a batch system. In this case, answer “y” to “Will the trajectories run in a batch system?”. You will be asked the name of the submission script and `nxinp` will look for its existence in the input directory. Files “`pmold`” and “`pmold-ew`” in `$NX/./batch/` directory are templates that can be adapted to your own batch system.

10. Exit `nxinp`.

11. Now the input directory should contain a new directory called `TRAJECTORIES`, which was created by `nxinp`.

```
> ls
control.dyn  final_output  intcfl  JOB_NAD  mkdir.log  mkd.inp  TRAJECTORIES
```

12. Move to `TRAJECTORIES` and list the content. You will see that 2 directories named `TRAJ1` to `TRAJ2` were created. Each one of these directories contains a complete set of input files to run one independent trajectory with different initial conditions (geometry and velocities).

The number of `TRAJn` directories is controlled by the number of initial conditions in the `final_output` file and by the energy restrictions imposed. In this case, only two trajectories were created because our restriction 3.75 ± 0.25 eV is a too low energy window to sample the S_2 state. You can see a summary of the sampling process in `mkdir.log`.

Each accepted initial condition card is split into a `geom` and `veloc` files that appear inside `TRAJn`. The `TRAJn` structure of directories (see Fig. 9) is very important in `NEWTON-X`. Several tools to control the jobs and to perform statistical analysis use it.

Each `TRAJn` directory can be copied to a different computer or submitted to a different node of a batch system. They should, however, be grouped again after having finished the dynamics calculations.

3.3 Running `NEWTON-X`: dynamics simulations

13. Move to `TRAJ1` and run this trajectory.

```
> cd TRAJ1  
> $NX/moldyn.pl > moldyn.log &
```

14. Move to TRAJ2 and run that trajectory.

If the jobs should be submitted to a batch system, you can either go to each TRAJn directory and run

```
> qsub pmold      ! pmold is the submission script
```

or in the TRAJECTORIES directory you can run

```
> $NX/submit.pl
```

In this case, you will be asked for the initial and final trajectory number that should be submitted, and the submission of all these trajectories will be done automatically.

For a discussion about how to visualize the results and how to perform statistical analysis, see sections 8.5 and 8.6.

4. Initial conditions and spectrum simulation: TD-DFT – Gaussian 09

In this section, we will simulate the absorption spectrum with GAUSSIAN09. The system is the five-membered heterocycle ring **thiophene** (e.g. *IT*) and ten singlet excited states will be included. The initial geometry distribution will be generated by a Wigner distribution in the ground vibrational state of the ground electronic state. The transition energies and moments will be also computed at TD-DFT(ω B97XD)/6-31G*. Theoretical details about the structure of the excited state of *IT* can be found in Refs.¹²⁻¹³.

4.1 Molecular structure optimization and geometry file creation

1. Chemical structure of the thiophene molecule:



2. In the TUTORIAL directory (see section 1.4) create a subdirectory called 'OPT-DFT'

```
> mkdir OPT-DFT <ENTER>
```

3. In the directory 'OPT-DFT' prepare the input and run a geometry optimization calculation at DFT(ω B97XD)/6-31G* level with GAUSSIAN 09. To do that, follow specific GAUSSIAN09 documentation (http://www.gaussian.com/g_prod/g09.htm).

4. In the TUTORIAL directory create another subdirectory called THIOPHENE_TDDFT_SPEC:

```
> mkdir THIOPHENE_TDDFT_SPEC <ENTER>
```

5. Once optimized the molecular structure, move to the subdirectory called THIOPHENE_TDDFT_SPEC and create a file called 'thiophene.xyz' containing the optimized DFT geometry in XYZ format:

```
> cd THIOPHENE_TDDFT_SPEC <ENTER>
> vi thiophene.xyz <ENTER>
```

9

```
S      0.000000    1.192685    0.000000
C      1.237296   -0.008625    0.000000
C      0.713548   -1.267517    0.000000
C     -0.713772   -1.267466    0.000000
C     -1.236952   -0.008600    0.000000
H      2.279067    0.280785    0.000000
H      1.319826   -2.165766    0.000000
H     -1.320853   -2.165283    0.000000
```

```
H      -2.278765    0.280547    0.000000
```

6. Convert the optimized geometry (file name ‘thiophene.xyz’) into NEWTON-X format.

```
> $NX/xyz2nx < thiophene.xyz <ENTER>
```

The NEWTON-X geometry file is called ‘geom’ and looks like

```
s 16.0 0.00000000 2.25384801 0.00000000 31.97207180
c 6.0 2.33815059 -0.01629889 0.00000000 12.00000000
c 6.0 1.34841030 -2.39526000 0.00000000 12.00000000
c 6.0 -1.34883360 -2.39516362 0.00000000 12.00000000
c 6.0 -2.33750052 -0.01625164 0.00000000 12.00000000
h 1.0 4.30681247 0.53060675 0.00000000 1.00782504
h 1.0 2.49410968 -4.09270461 0.00000000 1.00782504
h 1.0 -2.49605043 -4.09179187 0.00000000 1.00782504
h 1.0 -4.30624177 0.53015700 0.00000000 1.00782504
```

The second column contains the atomic number, and the following three columns contain the x, y and z coordinates in atomic units (Bohr). The last column contains the atomic masses, which can be eventually changed to simulate isotopic effects. The file can be freely formatted. The conversion back from NEWTON-X format to xyz can be done with.

```
> $NX/nx2xyz
```

After running this program, the xyz-format geometry is written to file ‘geom.xyz.’

4.2 Normal modes step

7. In the TUTORIAL directory create another subdirectory called ‘FREQ-DFT’ to run normal mode calculation:

```
> mkdir FREQ-DFT <ENTER>
```

8. Move to this directory and copy the ‘thiophene.xyz’ file there.

```
> cd FREQ-DFT <ENTER>
```

```
> cp ../THIOPHENE_TDDFT_SPEC/thiophene.xyz . <ENTER>
```

9. Prepare the input and run a normal mode calculation at DFT(ω B97XD)/6-31G* level with GAUSSIAN 09. To do that, follow specific GAUSSIAN 09 documentation (http://www.gaussian.com/g_prod/g09.htm). The GAUSSIAN 09 output containing the normal modes and frequencies can have any name. Here we will suppose it is called “freq.out.”

4.3 Energy and transition moment input

10. The TUTORIAL directory now looks like:

```
> ls <ENTER>
```

```
FREQ-DFT OPT-DFT THIOPHENE_TDDFT_SPEC
```


11. Move to the directory 'THIOPHENE_TDDFT_SPEC' and create a new subdirectory called JOB_AD.

```
> cd THIOPHENE_TDDFT_SPEC <ENTER>
> mkdir JOB_AD <ENTER>
```

The directory must be named JOB_AD since NEWTON-X will search for it.

12. Move into JOB_AD and prepare two files named, 'basis' and 'gaussian.com' respectively. 'basis' contains the basis set information while 'gaussian.com' contains the TD-DFT Gaussian09 input, like:

```
> cd JOB_AD <ENTER>
> vi basis <ENTER>
6-31G*
> vi gaussian.com <ENTER>
%chk=gaussian
%rwf=gaussian
%nproc=2
%mem=400mw
#TD(NStates=10) 6-31G* wB97XD NoSymm

thiophene wb97xd/6-31gs

0      1
S      0.000000    1.192685    0.000000
C      1.237296   -0.008625    0.000000
C      0.713548   -1.267517    0.000000
C     -0.713772   -1.267466    0.000000
C     -1.236952   -0.008600    0.000000
H      2.279067    0.280785    0.000000
H      1.319826   -2.165766    0.000000
H     -1.320853   -2.165283    0.000000
H     -2.278765    0.280547    0.000000
```

For Gaussian 09 calculations it is mandatory that the 'JOB_AD' directory contains the above two files, 'basis' and 'gaussian.com.'

To prepare a GAUSSIAN09 input for single point calculation at TD-DFT(ω B97XD)/6-31G* without symmetry, with ten singlet excited states, and transition moments (oscillator strengths) calculations follow the GAUSSIAN09 documentation (http://www.gaussian.com/g_prod/g09.htm).

Before submitting running any NEWTON-X job is highly advisable to run the job in JOB_AD directory just to test whether the input and outputs are OK. In the current case, just copy the content of the JOB_AD into a test directory and run the GAUSSIAN09 job. Check whether the roots and the oscillator strengths are computed and show reasonable values.

From a general point of view, at this stage we have:

- 1) optimized the molecular structure;*
- 2) computed the normal modes;*
- 3) converted the optimized structure file 'name.xyz' into NEWTON-X format 'geom';*

4) created the directory (e.g., *THIOPHENE_TDDFT_SPEC*) in which the spectrum will be computed using the *NEWTON-X* program interfaced with *GAUSSIAN09*.

4.4 NEWTON-X input

12. Move to directory *TUTORIAL/THIOPHENE_TDDFT_SPEC* and create a subdirectory called *IC-TDDFT*.

```
> cd TUTORIAL/THIOPHENE_TDDFT_SPEC <ENTER>
> mkdir IC-TDDFT <ENTER>
```

13. Move to this directory and copy the optimized DFT geometry file in *NEWTON-X* format (*geom*) there.

```
> cd IC-TDDFT <ENTER>
> cp ../geom . <ENTER>
```

14. Copy the *JOB_AD* directory and the normal modes file into *IC-TDDFT*.

```
> cp -rf ../JOB_AD .
> cp ../../FREQ-DFT/freq.out .
> ls <ENTER>
freq.out geom JOB_AD ! for a further check
> ls JOB_AD/ <ENTER>
basis gaussian.com
```

15. Run the *nxinp* program and select option 1: Generate initial conditions.

nxinp is the input tool for *NEWTON-X*. All input procedures, from the initial condition generation, through the dynamics inputs, to the statistical analysis options are performed with it.

```
> $NX/nxinp
```

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

MAIN MENU

1. GENERATE INITIAL CONDITIONS

2. SET BASIC INPUT

3. SET GENERAL OPTIONS

4. SET NONADIABATIC DYNAMICS

5. GENERATE TRAJECTORIES AND SPECTRUM

6. SET STATISTICAL ANALYSIS

7. EXIT
```

Select one option (1-7): 1 <ENTER>

16. Select the adequate options for the initial condition properties.

nxinp will guide you through a set of questions. Each of them contains a short explanation and the available options. Most of the time, the default value is the best option. To accept the default you can just press <ENTER>.

```
...
nact: Distribution:
      1 - Classic harmonic oscillator
      2 - Q/P-uncorrelated quantum harmonic oscillator (Wigner)
      3 - Q/P-correlated quantum harmonic oscillator
      4 - Pick points from previous dynamics
      5 - Random-velocities generation
      6 - Single point on a previous calculation
The current value of nact is: 2
Enter the new value of nact : <ENTER>
Setting nact = 2

numat: Number of atoms.
The current value of numat is: 9
Enter the new value of numat : <ENTER>
Setting numat = 9

npoints: Number of initial conditions to be generated
The current value of npoints is: 1
Enter the new value of npoints : 50 <ENTER>
Setting npoints = 50
```

npoints sets the number of initial conditions that should be generated. This number depends on how many points you want to compute to generate the spectrum and how many trajectories you want to simulate.

In real applications, you will need much more than 50 points. 500 may be a good number. You can also run several short jobs with few points in each one and merge them afterward using the tool "merge_initcond.pl." Thus, with 10 computers running 50 points each, you can quickly have 500 points. See in section 4.5 a note about how to split and merge the jobs.

```
file_geom: File containing the equilibrium geometry.
The current value of file_geom is: 'geom'
Enter the new value of file_geom : <ENTER>
Setting file_geom = 'geom'

iprogram: Read vibrational modes from:
          1 - GAMESS output
          2 - TURBOLMOLE output
          3 - COLUMBUS output
          4 - GAUSSIAN output
          5 - MOLDEN file
          6 - DFTB output
          7 - ACES2 output
The current value of iprogram is: 2
Enter the new value of iprogram : 4 <ENTER>
Setting iprogram = 4

file_nmodes: File containing the normal modes.
The current value of file_nmodes is: gaussian.log
Enter the new value of file_nmodes : freq.out <ENTER>

anh_f: Multiply harmonic frequencies by this factor.
The current value of anh_f is: 1
Enter the new value of anh_f : <ENTER>
Setting anh_f = 1
```

```

chk_e: Restrict (or do not) the statistical distribution:
      0 - Do not check the energies.
      1 - Check the energies between states NIS and NFS.
The current value of chk_e is: 0
Enter the new value of chk_e : 1 <ENTER>
Setting chk_e = 1

```

The next keywords define the restriction on the statistical distribution.

```

nis: Initial state (State in which the previous dynamics run. Ground state = 1.).
The current value of nis is: 1
Enter the new value of nis : <ENTER>
Setting nis = 1

```

```

nfs: Final state.
The current value of nfs is: 2
Enter the new value of nfs : 11 <ENTER>
Setting nfs = 11

```

The Wigner distribution will be generated in the ground electronic state (nis = 1), and transition energies between the ground and the tenth excited (nfs = 11) states will be computed. Indeed, with nfs = N, transition information for all states below N will also be computed and collected.

```

kvert: Center of the restriction:
      0 - Provide the energy for center of restriction
      1 - Use the vertical excitation energy of the equilibrium geometry
The current value of kvert is: 1
Enter the new value of kvert : <ENTER>
Setting kvert = 1

```

```

de: Width of restriction (center +/- de/2).
The current value of de (eV) is: 0.5
Enter the new value of de (eV) : 100 <ENTER>
Setting de = 100

```

This large “de” implies that this restriction will not be used. It can be imposed later on.

```

prog: Program and method to compute vertical excitation energies:
      1 - COLUMBUS
      2.0 - TURBOMOLE CC2
      2.1 - TURBOMOLE TDDFT
      2.2 - TURBOMOLE ADC2
      5 - DFTB
      6.5 - GAUSSIAN 09
      9 - DFT-MRCI
      10 - GAMESS MCSCF
      20 - HYBRID ENERGY

```

```

The current value of prog is: 1
Enter the new value of prog : 6.5 <ENTER> ! Gaussian09 TDDFT
Setting prog = 6.5

```

```

iseed: Random number seed.
      0 - default seed value.
     -1 - set random seed.
     >0 - (integer) set specific value for the seed.
The current value of iseed is: 0
Enter the new value of iseed : <ENTER>
Setting iseed = 0

```

```

lvprt: Print level.
      1 - standard level
      2 - debug level
The current value of lvprt is: 1
Enter the new value of lvprt : <ENTER>
Setting lvprt = 1

```

17. Exit nxinp.

4.5 Running NEWTON-X: initial conditions

18. Run the initial condition generation program.

```
> $NX/initcond.pl > initcond.log &
```

In general, with $chk_e = 1$, you might want to submit this job to a batch system. Files “pini” and “pini-ew” in $\$NX/./batch/$ directory are templates that can be adapted to your own batch system.

Splitting and merging jobs:

To split the job among several computers, just prepare the input as it was done until here.

Then run

```
> $NX/split_initcond.pl
```

This program will create a directory called INITIAL_CONDITIONS and inside it a sequence of subdirectories called I1, I2, ..., each one containing a complete set of input files.

Copy each directory to a different computer and run the job normally.

To merge the jobs, after the calculations, copy the directories I1, I2, ... back to INITIAL_CONDITIONS directory and from inside this directory run

```
> $NX/merge_initcond.pl
```

This program will ask for the number of jobs to be merged, and it will create a new directory called I_merged with merged results. Move to this directory and proceed with the spectrum simulation as explained below.

4.6 Checking the results

19. Normal job termination is indicated in the end of initcond.log file by:

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

20. The main information is written to the final_output file.

21. Each final_ouput.1.# file (# = 1,11 in this case) contains the same 50 geometries and velocities generated according to the Wigner distribution. For instance, final_output.1.2 contains transition energies and oscillator strengths to excitations into state 2 (first excited state S_1), while final_output.1.3 contains the same information to excitations into state 3 (second excited state S_2) and so on.

4.7 Generating the spectrum

22. Go to directory TUTORIAL/THIOPHENE_TDDFT_SPEC and create the directory SPECTRUM.

```
> mkdir SPECTRUM !This name is not compulsory.
```

23. Move to this directory and copy each final_output files there.

```
> cd SPECTRUM <ENTER>
> cp ../IC_TDDFT/final_output* . <ENTER>
```

24. Run nxinp and select option 5: “Generate Trajectories and Spectrum.”

```
> $NX/nxinp
```

1. GENERATE INITIAL CONDITIONS
2. SET BASIC INPUT
3. SET GENERAL OPTIONS
4. SET NONADIABATIC DYNAMICS
5. GENERATE TRAJECTORIES AND SPECTRUM
6. SET STATISTICAL ANALYSIS
7. EXIT

```
Select one option (1-7): 5 <ENTER>
```

25. Go through the next options.

```
type: What do you want to do?
      1 - Generate spectrum
      2 - Select initial conditions for multiple initial states
      3 - Generate trajectories
      4 - Return to main menu
The current value of type is: 3
Enter the new value of type : 1 <ENTER>
Setting type = 1
```

If for this first option you are asked for “kindjob” instead “type,” this means you are using an old version of NEWTON-X. Contact the distributors to get an updated version of the program.

```
nis: Initial state.
The current value of nis is: 1
Enter the new value of nis : <ENTER>
Setting nis = 1
```

```
nfs: Array of final states (comma or dash separated, e.g., 2-4 or 2,3,4).
For trajectories generation only one final state is allowed.
The current value of nfs is: 2
Enter the new value of nfs : 2-11 <ENTER> !Spectrum including each state
Setting nfs = 2-11
```

If nfs should be given as a ‘space separated’ list, this means that you are using an old version of NEWTON-X. Get an updated version at www.newtonx.org.

```
screen: Energy restriction
        0 - don't apply any restriction
        1 - use the original energy restriction written in the final_output files
        2 - apply new energy restriction
The current value of screen is: 0
Enter the new value of screen : <ENTER>
Setting screen = 0
os_condon: Oscillator strength:
```

```
-1 - try to read from final_output file.
x - oscillator strength is always x (Condon approximation).
The current value of os_condon is: -1
Enter the new value of os_condon : <ENTER>
Setting os_condon = -1
```

If the oscillator strength is not available, but the transition energy is, it is still possible to simulate the spectrum by giving a value to the oscillator strength in os_condon option. In this case, all transitions will be computed with the same oscillator strength. For only one final state this option is not bad, but it can be completely inadequate when more than one final state is selected.

```
prob_kind: Formula to calculate the transition probabilities:
  A - Einstein-coefficient A (spontaneous emission)
  B - Einstein-coefficient B (induced absorption or induced emission)
  E - Fluorescence (radiative decay rate)
  F - Absorption (photoabsorption cross section)
The current value of prob_kind is: F
Enter the new value of prob_kind : <ENTER>
Setting prob_kind = F

norm: Normalization of transition intensities:
  local - Use energy-restricted data set
  global - Use complete data set
The current value of norm is: local
Enter the new value of norm : <ENTER> ! with no energy restriction, doesn't
Setting norm = local ! matter.

seed: Seed for the random number generation
  0 - a default random number seed is used
  1 - a randomized seed is used
  Any other positive integer is used as the random number seed
The current value of seed is: 0
Enter the new value of seed : <ENTER>
Setting seed = 0

l_shape: Line shape:
  gauss - Normalized Gaussian function.
  lorentz - Normalized Lorentzian function.
The current value of l_shape is: lorentz
Enter the new value of l_shape : <ENTER>
Setting l_shape = lorentz

delta: Phenomenological broadening of the spectrum.
The current value of delta (eV) is: 0.05
Enter the new value of delta (eV) : <ENTER>
Setting delta = 0.05
```

“delta” is possibly the only option that you need to play with. It controls the width of the Gaussian curve attributed to each one of the 100 transitions (50 initial conditions \times 2 final states).

```
temp: Temperature.
The current value of temp (K) is: 0
Enter the new value of temp (K) : <ENTER>

nref: Refraction index.
The current value of nref is: 1
Enter the new value of nref : <ENTER>

eps: Distance between consecutive points in the spectrum.
The current value of eps (eV) is: 0.005
Enter the new value of eps (eV) : <ENTER>
Setting eps = 0.005

kappa: The range of the spectrum is defined between
```

E_{min}-kappa*delta and E_{max}+kappa*delta, where kappa is an integer.
 The current value of kappa is: 3
 Enter the new value of kappa : <ENTER>
 Setting kappa = 3

Processing data: This may take some minutes. Please, wait...

26. Exit nxinp.

27. The simulated cross section using a Lorentzian line shape with phenomenological broadening $\delta = 0.05$ eV is written to cross-section.dat. Looking at this file, we see:

```
!      DE/eV      lambda/nm      sigma/A^2      +/-error/A^2
5.1006  2.4308E+02  0.00477581     0.00049100
5.1056  2.4284E+02  0.00491096     0.00053555
5.1106  2.4260E+02  0.00505910     0.00058786
5.1156  2.4236E+02  0.00522267     0.00064969
5.1206  2.4213E+02  0.00540474     0.00072344
5.1256  2.4189E+02  0.00560926     0.00081227
5.1306  2.4166E+02  0.00584135     0.00092032
5.1356  2.4142E+02  0.00610763     0.00105312
5.1406  2.4119E+02  0.00641675     0.00121801
5.1456  2.4095E+02  0.00677996     0.00142465
5.1506  2.4072E+02  0.00721155     0.00168546
5.1556  2.4048E+02  0.00772885     0.00201555
...
> gnuplot
gnuplot> plot 'cross-section.dat' using 1:3 with lines
```

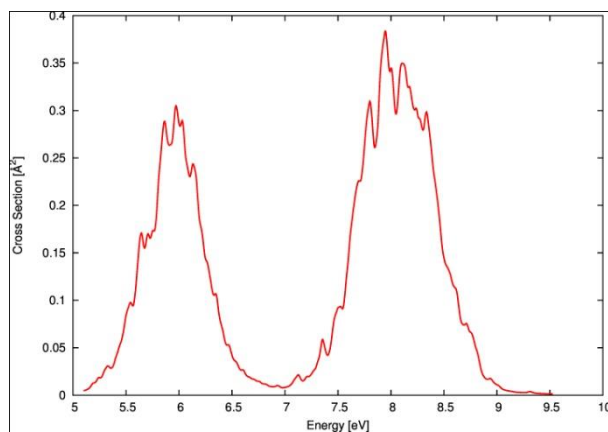


Fig. 2. Photoabsorption cross section in $\text{\AA}^2 \cdot \text{molecule}^{-1}$ as a function of the excitation energy in electron-Volts of 1T ($\omega\text{B97XD}/6\text{-}31\text{G}^*$).

Your spectrum should not look exactly the one in Fig. 2. This one was done with 300 points instead of 50.

5. Steady photoelectron spectrum: TD-DFT – Gaussian 09

In this section, we will simulate a steady photoelectron spectrum (SPES) with GAUSSIAN 09. The system is imidazole. We are going to compute the HeI (21.2 eV) SPES for ionization from the ground state of the neutral molecule into the ground and 20 states of the cation. The initial geometry distribution will be generated by the Wigner distribution function corresponding to the electronic and vibrational ground states of the neutral molecule. The ionization potentials (IPs) and Dyson orbitals (DOs) will be computed at TD-DFT(CAM-B3LYP)/aug-cc-pVDZ level.

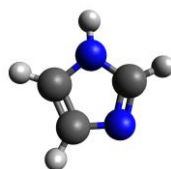


Fig. 3. Imidazole.

The photoionization spectrum is computed in two steps: first, the relevant transition energies and Dyson orbitals between the N - and $(N-1)$ -electron systems are generated for an ensemble of nuclear geometries. This step is explained in detail Sections **Error! Reference source not found.** to 5.4. Then, in the second step, the spectrum is generated by computing the ionization probabilities for each point in the ensemble. This is explained in Section 5.5.

Although in the example that we will work out here, the nuclear ensemble is generated via a harmonic-oscillator Wigner distribution, the program is completely general and takes ensembles generated in any other way, including by trajectory runs.

5.1 Setting files and directories for energies and transition dipoles

1. Before starting, you should optimize imidazole geometry in the ground state with DFT, at CAM-B3LYP/aug-cc-pVDZ level with GAUSSIAN 09 and make a normal mode analysis (vibrational frequencies). To do that, follow specific GAUSSIAN 09 documentation at www.gaussian.com. To proceed, we will suppose 1) that the GAUSSIAN 09 output with the normal modes is written to a file named 'freq.log' and 2) that the imidazole's optimized structure is written to a file named imidazole.xyz looking like:

9

```

N      0.741641    0.815030    0.000057
N     -0.112197   -1.223606   -0.000099
C      0.995650   -0.523144    0.000004
C     -0.625405    0.972029   -0.000058
C     -1.131408   -0.300404    0.000026
H      1.428625    1.552969    0.000654
H      2.002726   -0.925512   -0.000027
H     -1.098087    1.946179   -0.000158
H     -2.172403   -0.604490   -0.000012

```

2. In the TUTORIAL directory create another subdirectory called IMIDAZOLE_TDDFT_SPES and move there:

```

> mkdir IMIDAZOLE_TDDFT_SPES <ENTER> !This name is not compulsory.
> cd IMIDAZOLE_TDDFT_SPES <ENTER>

```

3. In this directory, create another subdirectory called IP+DO and move there:

```

> mkdir IP+DO <ENTER> !This name is not compulsory.
> cd IP+DO <ENTER>

```

4. Copy imidazole.xyz and freq.log to this directory.

```

> ls <ENTER>
freq.log  imidazole.xyz

```

5. Convert imidazole.xyz into NEWTON-X format.

```

> $NX/xyz2nx < imidazole.xyz <ENTER>
> ls <ENTER>
freq.log  geom  imidazole.xyz

```

The NEWTON-X geometry file is called 'geom' and looks like

```

N      7.0    1.40149838    1.54018349    0.00010771    14.00307401
N      7.0   -0.21202160   -2.31228023   -0.00018708    14.00307401
C      6.0    1.88150582   -0.98859889    0.00000756    12.00000000
C      6.0   -1.18184417    1.83686860   -0.00010960    12.00000000
C      6.0   -2.13805126   -0.56768129    0.00004913    12.00000000
H      1.0    2.69971000    2.93468610    0.00123588     1.00782504
H      1.0    3.78460366   -1.74896421   -0.00005102     1.00782504
H      1.0   -2.07508370    3.67774532   -0.00029858     1.00782504
H      1.0   -4.10524672   -1.14232055   -0.00002268     1.00782504

```

The second column contains the atomic number, and the following three columns contain the x, y and z coordinates in atomic units (Bohr). The last column contains the atomic masses, which can be eventually changed to simulate isotopic effects. The file can be freely formatted. The conversion back from NEWTON-X format to xyz can be done with

```

> $NX/nx2xyz

```

After running this program, the xyz-format geometry is written to file 'geom.xyz'.

6. Create a new subdirectory called JOB_N.

```

> mkdir JOB_N <ENTER> !This name is compulsory.

```

The directory must be named JOB_N since NEWTON-X will search for it. It will contain a GAUSSIAN template for a single-point job for the initial N-electron system (DFT for neutral imidazole in the ground state, in our example).

12. Move into JOB_N and prepare two files named, 'basis' and 'gaussian.com'. 'basis' contains the basis set information, while 'gaussian.com' contains the DFT GAUSSIAN 09 input:

```
> cd JOB_N <ENTER>
> vi basis <ENTER>
aug-cc-pVDZ
> vi gaussian.com <ENTER>
%chk=gaussian
%rwf=gaussian
%nproc=4
%mem=5000mb
#p CAM-B3LYP/aug-cc-pVDZ gfinput NoSymm

Ground state of imidazole at CAM-B3LYP/aug-cc-pVDZ level

0 1
N 0.741641 0.815030 0.000057
N -0.112197 -1.223606 -0.000099
C 0.995650 -0.523144 0.000004
C -0.625405 0.972029 -0.000058
C -1.131408 -0.300404 0.000026
H 1.428625 1.552969 0.000654
H 2.002726 -0.925512 -0.000027
H -1.098087 1.946179 -0.000158
H -2.172403 -0.604490 -0.000012
```

For GAUSSIAN 09 calculations, it is mandatory that the 'JOB_N' directory contains the above two files, 'basis' and 'gaussian.com.' To prepare a GAUSSIAN 09 input for single point calculation at DFT (CAM-B3LYP)/aug-cc-pVDZ level without symmetry, follow the GAUSSIAN 09 documentation (www.gaussian.com).

It is important that you include gfinput keyword in the GAUSSIAN input; otherwise you will not be able to generate MOLDE files later to visualize the Dyson orbitals.

13. Move back to the directory IP+DO and create a new subdirectory called JOB_N-1.

```
> cd ../ <ENTER>
> mkdir JOB_N-1 <ENTER> !This name is compulsory.
```

The directory must be named JOB_N-1 since NEWTON-X will search for it. It will contain a GAUSSIAN template for a single-point job for the target (N-1)-electron system (TD-DFT for imidazole cation, in our example).

14. Move into JOB_N-1 and prepare two files named again, 'basis' and 'gaussian.com.' 'basis' contains the basis set information and **must** be the same as in JOB_N. 'gaussian.com' contains the TD-DFT GAUSSIAN 09 input:

```
> cd JOB_N-1 <ENTER>
> vi basis <ENTER>
aug-cc-pVDZ
```

```
> vi gaussian.com <ENTER>

%chk=gaussian
%rwf=gaussian
%nproc=4
%mem=5000mb
#p TD(NStates=20) CAM-B3LYP/aug-cc-pVDZ NoSymm

First 20 states of imidazole at CAM-B3LYP/aug-cc-pVDZ level

1  2
N   0.741641   0.815030   0.000057
N  -0.112197  -1.223606  -0.000099
C   0.995650  -0.523144   0.000004
C  -0.625405   0.972029  -0.000058
C  -1.131408  -0.300404   0.000026
H   1.428625   1.552969   0.000654
H   2.002726  -0.925512  -0.000027
H  -1.098087   1.946179  -0.000158
H  -2.172403  -0.604490  -0.000012
```

For GAUSSIAN 09 calculations, it is mandatory that the ‘JOB_N-1’ directory contains the above two files, ‘basis’ and ‘gaussian.com.’ To prepare a GAUSSIAN 09 input for single point calculation TD-DFT(CAM-B3LYP)/aug-cc-pVDZ without symmetry, with 20 doublet excited states, follow the GAUSSIAN 09 documentation.

Before submitting running any NEWTON-X job is highly advisable to run the jobs in JOB_N and JOB_N-1 directories, just to test whether the inputs and outputs are OK. Just copy the content of the JOB_N or JOB_N-1 into a test directory and run the GAUSSIAN 09 jobs. Check whether the roots and the oscillator strengths are computed and show reasonable values.

5.2 NEWTON-X input

15. At this point, directory IP+DO and its subdirectories should contain:

```
> ls <ENTER>
freq.log geom JOB_N JOB_N-1
> ls JOB_N/ <ENTER>
basis gaussian.com
> ls JOB_N-1/ <ENTER>
basis gaussian.com
```

16. Still in directory IP+DO, run the nxinp program, and select option 1: Generate initial conditions.

nxinp is the input tool for NEWTON-X. All input procedures, from the initial condition generation, through the dynamics inputs, to the statistical analysis options are performed with it.

```
> $NX/nxinp <ENTER>
```

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

MAIN MENU

1. GENERATE INITIAL CONDITIONS
2. SET BASIC INPUT
3. SET GENERAL OPTIONS
4. SET NONADIABATIC DYNAMICS
5. GENERATE TRAJECTORIES AND SPECTRUM
6. SET STATISTICAL ANALYSIS
7. EXIT

Select one option (1-7): 1 <ENTER>

17. Select the adequate options for the initial condition properties.

nxinp will guide you through a set of questions. Each of them contains a short explanation and the available options. Most of the time, the default value is the best option. To accept the default you just press <ENTER>.

```
...
nact: Distribution:
      1 - Classic harmonic oscillator
      2 - Q/P-uncorrelated quantum harmonic oscillator (Wigner)
      3 - Q/P-correlated quantum harmonic oscillator
      4 - Pick points from previous dynamics
      5 - Random-velocities generation (not valid for photoionization)
      6 - Single point on a previous calculation
The current value of nact is: 2
Enter the new value of nact : <ENTER>
Setting nact = 2

numat: Number of atoms.
The current value of numat is: 9
Enter the new value of numat : <ENTER>
Setting numat = 9

npoints: Number of initial conditions to be generated
The current value of npoints is: 1
Enter the new value of npoints : 50 <ENTER>
Setting npoints = 50
```

npoints sets the number of initial conditions that should be generated. This number depends on how many points you want to compute to generate the SPES. In real applications, you will need much more than 50 points. 500 may be a good number.

```
file_geom: File containing the equilibrium geometry.
The current value of file_geom is: 'geom'
Enter the new value of file_geom : <ENTER>
Setting file_geom = 'geom'

iprogr: Read vibrational modes from:
      1 - GAMESS output
      2 - TURBOLMOLE output
      3 - COLUMBUS output
```

```

    4 - GAUSSIAN output
    5 - MOLDEN file
    6 - DFTB output
    7 - ACES2 output
The current value of iprog is: 4
Enter the new value of iprog : <ENTER>
Setting iprog = 4

file_nmodes: File containing the normal modes.
The current value of file_nmodes is: gaussian.log
Enter the new value of file_nmodes : freq.log <ENTER>

anh_f: Multiply harmonic frequencies by this factor.
The current value of anh_f is: 1
Enter the new value of anh_f : <ENTER>
Setting anh_f = 1

temp: Temperature.
The current value of temp [K] is: 0.0
Enter the new value of temp [K] :
Setting temp = 0.0

```

'temp' is the (environment) temperature used by the Wigner distribution function. With temp=0 [K], the Wigner reduces to the standard Wigner function used in the previous versions of NEWTON-X before version 2.0.

```

Are these initial conditions for ionization cross-sections (y/n)? y <ENTER>

prog: Program and method to compute vertical excitation energies:
    6.5 - GAUSSIAN 09 TDDFT
The current value of prog is: 6.5
Enter the new value of prog : <ENTER>

iseed: Random number seed.
    0 - default seed value.
   -1 - set random seed.
   >0 - (integer) set specific value for the seed.
The current value of iseed is: 0
Enter the new value of iseed : <ENTER>
Setting iseed = 0

nis_mol: Initial state of the N-electron species (Ground state = 1).
         (use nis_mol = 1 within Koopmans approximation)
The current value of nis_mol is: 1
Enter the new value of nis_mol : <ENTER>
Setting nis_mol = 1

nfs_cat: Maximum electronic state of the N-1 electron system (Ground state = 1).
The current value of nfs_cat is: 1
Enter the new value of nfs_cat : 21 <ENTER>
Setting nfs_cat = 21

```

Since the ground state of the cation is 1, the 20th excited state computed with TDDFT will correspond to nfs_cat=21 in this example.

```

ip_type: Method to calculate the ionization potentials (IPs).
    1 - IP = -E[MO] (Koopmans approximation)
    2 - IP = E[N] - E[N-1]
    3 - IP computed with the Outer Valence Green's Function (OVGF) method
The current value of ip_type is: 2
Enter the new value of ip_type : <ENTER>
Setting ip_type = 2

do_type: Method to calculate the Dyson orbitals (DOs).
    1 - DO = MO (Koopmans approximation)
    2 - DOs computed accurately

```

```
The current value of do_type is: 2
Enter the new value of do_type : <ENTER>
Setting do_type = 2
```

```
Do you want to use only the equilibrium geometry (y/n)? n <ENTER>
```

Before doing a full calculation of the SPES, it is advisable to do a first test only with the equilibrium geometry (choosing 'y'). Here, we suppose the tests have been done, and the answer to the previous question is 'n'. This option overpowers npoints.

```
lvprt: Print level.
      1 - standard level
      2 - debug level
The current value of lvprt is: 1
Enter the new value of lvprt : <ENTER>
Setting lvprt = 1
```

```
Do you want to create a 'do.par' file (y/n)? y <ENTER>
```

The 'do.par' file sets a few parameters related with the computation of the DOs.

```
njobs_dyson: Number of DOs to be computed at the same time.
The current value of njobs_dyson is: 1
Enter the new value of njobs_dyson : 8 <ENTER>
Setting njobs_dyson = 8
```

'njobs_dyson' sets the number of DOs that will be computed at the same time on a single computer.

```
eps_ciscffs: Threshold of the electronic expansion coefficients.
The current value of eps_ciscffs is: 1.0E-2
Enter the new value of eps_ciscffs : <ENTER>
Setting eps_ciscffs = 1.0E-2
```

```
eps_overlap: Threshold of the Slater Determinant overlaps.
              (for writing purposes only)
The current value of eps_overlap is: 1.0E-1
Enter the new value of eps_overlap : <ENTER>
Setting eps_overlap = 1.0E-1
```

18. Exit nxinp.

5.3 Running NEWTON-X: energies and transition moments for an ensemble of geometries

19. At this point, directory IP+DO should contain:

```
> ls <ENTER>
freq.log geom initqp_input JOB_N JOB_N-1
```

Besides, you may also have a do.par file. You may change any options by directly editing initqp_input and do.par files.

20. Run the initial condition generation program.

```
> $NX/initcond.pl > initcond.log & <ENTER>
```

In general, if you are dealing with hundreds of nuclear geometries, you might want to submit this job to a batch system. Files “pini” and “pini-ew” in \$NX/./batch/ directory are templates that can be adapted to your batch system.

Splitting and merging jobs:

To split the job between several computers, just prepare the input as it was done until here.

Then run

```
> $NX/split_initcond.pl
```

This program will create a directory called INITIAL_CONDITIONS and inside it a series of subdirectories called I1, I2, ..., each one containing a complete set of input files.

Copy each directory to a different computer and run the job normally.

To merge the jobs, after the calculations, copy the directories I1, I2, ... back to INITIAL_CONDITIONS directory and from inside this directory run

```
> $NX/merge_initcond.pl
```

This program will ask for the number of jobs to be merged, and it will create a new directory called I_merged with merged results. Move to this directory and proceed with the SPES simulation as explained below.

5.4 Checking the results

21. Normal job termination is indicated at the end of initcond.log file by:

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

22. There are three relevant outputs after running the initial condition generation program: ‘GEOMETRIES,’ ‘ip.dat,’ and ‘MO_DYSON.’

23. GEOMETRIES contains a set of files like:

```
geom.0 geom.1 geom.2 ... geom.49 geom.50
```

Each of these files contains the nuclear geometry of the corresponding initial condition in NEWTON-X format.

24. ip.dat contains the IPs for every nuclear geometry generated and electronic state of the cation considered. It looks like this:

```
Initial condition = 0 ! 0 is the equilibrium geometry
Electronic state = 1
E_N(1) = -226.134588196 [a.u.] ! Ground state energy of neutral imidazole
IP1 = E_N-1(1) - E_N(1) = 8.9790842 [eV]
IP2 = E_N-1(2) - E_N(1) = 10.3044842 [eV]
IP3 = E_N-1(3) - E_N(1) = 10.6173842 [eV]
IP4 = E_N-1(4) - E_N(1) = 14.0329842 [eV]
IP5 = E_N-1(5) - E_N(1) = 14.2048842 [eV]
IP6 = E_N-1(6) - E_N(1) = 14.7364842 [eV]
IP7 = E_N-1(7) - E_N(1) = 14.8954842 [eV]
IP8 = E_N-1(8) - E_N(1) = 15.0144842 [eV]
.
.
Initial condition = 1
Electronic state = 1
.
```


25. MO_DYSON contains a set of compressed files with names of the form `dyson_mo_ic.nis.nfs.gz`, where `ic` is the number of the initial condition, `nis` is the electronic state of the N -electron molecule (before the ionization) and `nfs` is the state of the $(N-1)$ -electron molecule after the ionization. Each of these files contains the corresponding DO in both the atomic and molecular orbital basis sets. After uncompressing (gunzip), they look like this:

```

    0.95661948383739      0.95661948801718
151      Linear Combination of Molecular Orbitals
    0.02479467089699      0.00000000000000      0.00001739644645
   -0.06220374938866     -0.00000000000000     -0.00010166649522
   -0.10326132366492      0.00000000000000      0.00003001393284
    0.02591635000685     -0.00000000000000      0.00001311495108
   -0.02053397116999     -0.00000000000000      0.00006969760828
    0.12477724143098      0.00000000000000      0.00802239939626
    0.00005213656696     -0.00000000000000      0.01943804377759
    0.00397114452823      0.00000000000000     -0.00240958300748
    0.04617580206270     -0.00000000000000      0.01260762001680
    0.00003394245454      0.00000000000000     -0.01037320924134
   -0.04130474527755     -0.00000000000000     -0.00729114309321
    0.03695263197019      0.00000000000000     -0.00183624726465
    0.00000827274935      0.00000000000000     -0.00007412163866
   -0.00162728613971     -0.00000000000000      0.01357692592388
    0.00000186372661      0.00000000000000      0.00362389373215
    0.00000349260005      0.00000000000000      0.00013507795176
   -0.00475436160369      0.00000000000000      0.99951558442769
    0.00049298128014     -0.00000000000000     -0.00000107762265
   -0.00768736429118      0.00000000000000      0.00000000000000
    .
    .
    .

```

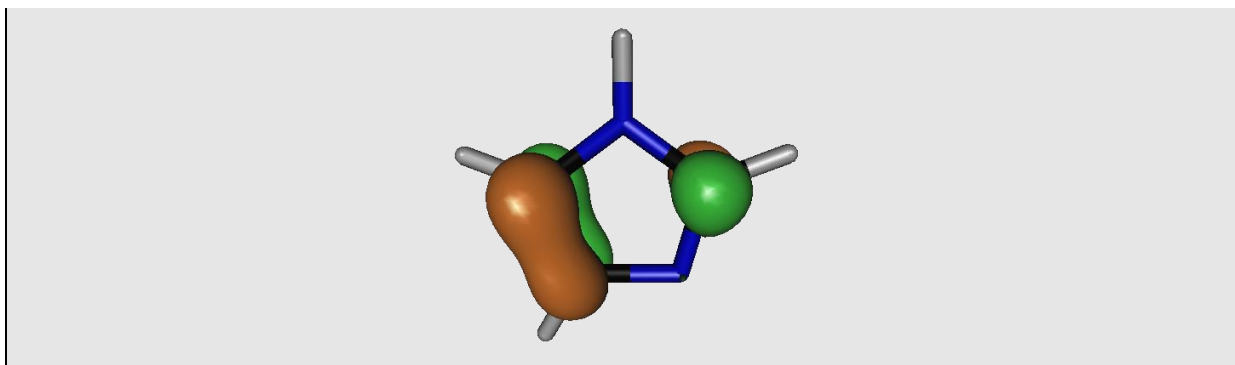
In the first column, the DO is represented in the atomic basis set: the first element is the norm of the DO (0.9566, in this case), the second element is the size of the basis set (N_{bf}), and the remaining N_{bf} elements are the atomic orbital coefficients. In columns two and three, the DO is represented as a linear combination of α (column 2) and β (column 3) molecular orbitals. The first element of column 2 is the norm of the DO computed in the molecular basis set, written for testing purposes only.

You can visualize the DO using MOLDEN. To do that, from the IP+DO directory run

```
> $NX/do_nx2molden.pl
```

This program will ask you for which geometry (ic), initial state (nis), and final state (nfs) you want to make a MOLDEN file. It will also ask whether your calculations have been done with (5d,7f) or (6d,10f) basis (pure vs. Cartesian functions). Check your GAUSSIAN output to figure this out. Then, do_nx2molden.pl creates a MOLDEN_VIEW directory with a file named molden_dyson.ic.nis.nfs, which can be visualized with MOLDEN.

In our example, the Dyson orbital for the equilibrium geometry for ionization from ground state of the neutral to the ground state of the cation will look like (molden_dyson.0.1.01):



5.5 Generating the spectrum

26. Go to directory TUTORIAL/IMIDAZOLE_TDDFT_SPES and create the directory SPES.

```
> mkdir SPES !This name is not compulsory.
```

27. Move to this directory and copy each of the relevant outputs mentioned before.

```
> cd SPES <ENTER>
> cp -rf ../IP+DO-TDDFT/GEOMETRIES . <ENTER>
> cp -rf ../IP+DO-TDDFT/MO_DYSON . <ENTER>
> cp ../IP+DO-TDDFT/ip.dat . <ENTER>
```

28. The SPES directory now looks like this:

```
> ls <ENTER>
  GEOMETRIES  ip.dat  MO_DYSON
```

29. Run nxinp and select option 5: “Generate Trajectories and Spectrum”.

```
> $NX/nxinp <ENTER>
```

1. GENERATE INITIAL CONDITIONS
2. SET BASIC INPUT
3. SET GENERAL OPTIONS
4. SET NONADIABATIC DYNAMICS
5. GENERATE TRAJECTORIES AND SPECTRUM
6. SET STATISTICAL ANALYSIS
7. EXIT

```
Select one option (1-7): 5 <ENTER>
```

30. Go through the next options.

```
type: What do you want to do?
      1 - Generate absorption or emission spectrum
      2 - Generate ionization spectrum
      3 - Select initial conditions for multiple initial states
      4 - Generate trajectories
```

```

5 - Return to main menu
The current value of type is: 4
Enter the new value of type : 2 <ENTER>

nfs: Maximum electronic state of the (N-1)-electron system (Ground state = 1).
The current value of nfs is: 1
Enter the new value of nfs : 21 <ENTER>
Setting nfs = 21

prob_kind: Formula to calculate the transition probabilities:
A - Einstein-coefficient A (spontaneous emission)
B - Einstein-coefficient B (induced absorption or induced emission)
E - Fluorescence (radiative decay rate)
F - Absorption (photoabsorption cross-section)
I - Ionization (photoionization cross-section)
The current value of prob_kind is: I
Enter the new value of prob_kind : <ENTER>
Setting prob_kind = I

ics_comp: Compute photoionization spectra and cross-sections using:
1 - the norm of the Dyson orbitals
2 - the 'ezDyson' program
The current value of ics_comp is: 1
Enter the new value of ics_comp : <ENTER>
Setting ics_comp = 1

```

If you select ics_comp = 2, then you should also prepare an input file for EZDYSON. NEWTON-X will use this file as a template to run that program. This input file must be named 'ezdyson.xml' and should be located in the same directory as GEOMETRIES (in our example, SPES). To prepare an EZDYSON input file, follow the documentation at <http://iopenshell.usc.edu/downloads>.

```

ics_kind: Type of experiment to be simulated:
1 - Ep (photon energy) ranging from Ep_min to Ep_max
2 - Ep fixed and Ek (kinetic energy) ranging from Ek_min to Ek_max
The current value of ics_kind is: 2
Enter the new value of ics_kind : <ENTER>
Setting ics_kind = 2

ics_proc: Type of weighting used in the simulation:
1 - Using a normalized step function
2 - Using a normalized peaked function
The current value of ics_proc is: 2
Enter the new value of ics_proc : <ENTER>
Setting ics_proc = 2

Ephoton: Fixed value of the photon energy:
The current value of Ephoton (eV) is: 10.0
Enter the new value of Ephoton (eV) : 21.2 <ENTER>
Setting Ephoton = 21.2

Ek_min: Minimum value of the photoelectron kinetic energy:
- Ek_min = 0.1 eV (use with ezDyson and Coulomb)
- Ek_min = 0.01 eV (use with ezDyson and Spherical)
- Ek_min = 0.0 eV (use with the DO norms)
The current value of Ek_min (eV) is: 0.0
Enter the new value of Ek_min (eV) : <ENTER>
Setting Ek_min = 0.0

Do you want to use only the equilibrium geometry (y/n): n <ENTER>

l_shape: Line shape:
gauss - Normalized Gaussian function (use for ionizations).
lorentz - Normalized Lorentzian function.
The current value of l_shape is: lorentz
Enter the new value of l_shape : gauss <ENTER>

```

```

Setting l_shape = gauss

delta: Phenomenological broadening of the spectrum.
The current value of delta (eV) is: 0.05
Enter the new value of delta (eV) : 0.15 <ENTER>
Setting delta = 0.15

eps: Distance between consecutive points in the spectrum.
The current value of eps (eV) is: 0.005
Enter the new value of eps (eV) : <ENTER>
Setting eps = 0.005

kappa: The range of the spectrum is defined between
Emin-kappa*delta and Emax+kappa*delta, where kappa is an integer.
The current value of kappa is: 3
Enter the new value of kappa : 5 <ENTER>
Setting kappa = 5

```

31. Exit nxinp.

32. Run NEWTON-X to compute the photospectrum:

```
> $NX/ixsec.pl > ixsec.log & <ENTER>
```

You may also distribute this run among a cluster of computers. To do so, before running ixsec.pl, run

```
>$NX/split_intensities.pl
```

This program will ask in how many independent jobs you want to split the input files; then it will create a directory named IONIZATION_INTENSITIES, with a series of subdirectories named I1, I2, Move to each of these directories and run ixsec.pl from there. After finishing, go to IONIZATION_INTENSITIES and run

```
>$NX/merge_intensities.pl
```

to put all jobs together. The merged results will be written to directory I_merged.

5.6 Analysing the photospectrum

33. After running ixsec.pl, two types of results are written. First, into general.dat. This file contains all information about the transition intensities. For instance, the example below tells that, for geometry 1, the transition from the ground state of the neutral system to state 21 of the cation has an IP of 17.2843 eV and squared norm of the Dyson orbital 0.027 au².

St.Ini(N)	St.Fin(N-1)	IP (eV)	Ep (eV)	DO ^2

Initial Condition 1				
1	1	8.4612	21.2000	0.9575702466
1	2	9.9345	21.2000	0.9248608099
...				
1	20	17.2354	21.2000	0.2077824379
1	21	17.2843	21.2000	0.0268793849
Initial Condition 2				
1	1	9.1990	21.2000	0.9584798618
...				

The information in `general.dat` is enough to recompute the spectrum with other variables if you wish. If during the execution of `ixsec.pl` NEWTON-X detects the existence of `general.dat`, it does not compute the intensity, but just reads it from that file.

34. The second type of results is written to `spectrum*` files. They contain the photoelectron spectrum profile. Each `spectrumN.dat` file contains the spectrum for a target state `N`. `spectrum.dat` contains the total spectrum summed over all states. It looks like:

E_k (eV)	BE (eV)	Intensity (arb. units)
1.790	19.410	0.0000000000
1.795	19.405	0.0000000000
1.800	19.400	0.0000000000
1.805	19.395	0.0000000000
1.810	19.390	0.0000000000
...		
3.145	18.055	0.7649114716
3.150	18.050	0.7658365222
3.155	18.045	0.7658156567
3.160	18.040	0.7649138631
...		
13.485	7.715	0.0000000000

In this example, the spectrum has a peak for the electron kinetic energy $E_k = 3.15$ eV (binding energy $E_b = 18.05$ eV), with relative intensity 0.77. If you want absolute intensities, you should run the spectrum with `ics_comp = 2`.

35. Run GNUPLOT to visualize the spectrum.

```
> gnuplot
gnuplot> plot 'spectrum.dat' using 1:3 with lines
```

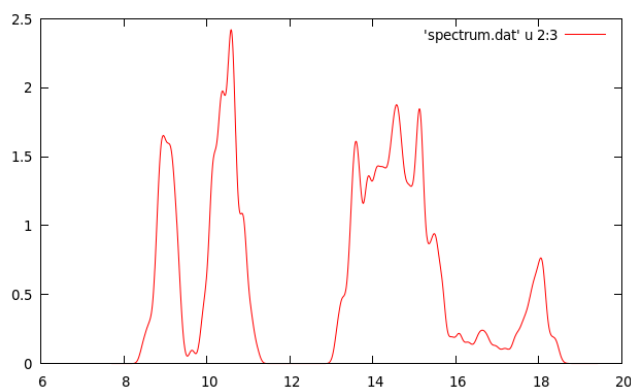


Fig. 4. Photoelectron spectrum of imidazole (intensity in arbitrary units) as a function of the binding energy in electron-Volts.

6. Surface hopping dynamics: TD-DFT – Gaussian 09

In this section, we will prepare the inputs and run dynamics simulations. The system is thiophene ring (*IT*), and the dynamics will be initiated in the second excited state (state 3, S_2). The initial conditions were generated in Chapter 4 of this tutorial. The surface hopping¹¹ dynamics will be performed at TDDFT level using GAUSSIAN 09. The trajectory time will be 300 fs with 0.5 fs time step.

The TDDFT will use the ω B97XD functional and the 6-31G* basis set. The dynamics will start in S_2 , with initial conditions selected in the interval of 5.5 to 6.5 eV.

(An energy width of ± 0.5 eV allows to generate trajectories belonging to the whole first absorption band, see Fig. 2. This will generate a large number of trajectories and, for practical reasons, only a few of them will be computed and analyzed in this tutorial).

6.1 Copying the initial conditions

1. Go to TUTORIAL directory create a subdirectory called THIOPHENE_TDDFT_DYN:

```
> mkdir THIOPHENE_TDDFT_DYN <ENTER>
```

2. Move to this directory and copy the initial conditions file for the first excited state there.

```
> cd THIOPHENE_TDDFT_DYN
> cp ../THIOPHENE_TDDFT_SPEC/IC_TDDFT/final_output.1.3 final_output ! note the new
name
```

3. Create a subdirectory called JOB_AD.

4. Check the content of the THIOPHENE_TDDFT_DYN directory:

```
> ls <ENTER>
final_output  geom  JOB_AD
```

The directory must be named JOB_AD since NEWTON-X will search for it.

6.2 Preparing electronic structure input

5. Move to JOB_AD and create the file ‘basis’ and the input file ‘gaussian.com’ for single point TDDFT/ ω B97XD/6-31G* calculation. Use C_1 point group (no symmetry) and request the calculation of three excited states specifying we are interested in the second root (i.e., S_2).

```

> ls <ENTER>
basis gaussian.com

> cat gaussian.com

%chk=gaussian
%rwf=gaussian
%nproc=2
%mem=400mw
#TD(NStates=3,Root=2) 6-31G* wb97XD scf(MaxCycle=512) NoSymm

thiophene wb97xd/6-31gs

0      1
  S      0.000000    1.192685    0.000000
  C      1.237296   -0.008625    0.000000
  C      0.713548   -1.267517    0.000000
  C     -0.713772   -1.267466    0.000000
  C     -1.236952   -0.008600    0.000000
  H      2.279067    0.280785    0.000000
  H      1.319826   -2.165766    0.000000
  H     -1.320853   -2.165283    0.000000
  H     -2.278765    0.280547    0.000000

```

Before submitting running any NEWTON-X job is highly advisable to run the job in JOB_AD directory just to test whether the input and outputs are OK. In the current case, just copy the content of the JOB_AD into a test directory and run the GAUSSIAN 09 job. Check whether the three roots are computed and show reasonable values.

6.3 NEWTON-X input

6. Run nxinp.

```
> $NX/nxinp
```

```

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

MAIN MENU

1. GENERATE INITIAL CONDITIONS

2. SET BASIC INPUT

3. SET GENERAL OPTIONS

4. SET NONADIABATIC DYNAMICS

5. GENERATE TRAJECTORIES AND SPECTRUM

6. SET STATISTICAL ANALYSIS

7. EXIT

```


Select one option (1-7): 2 <ENTER>

7. Select option 2: “set basic input” and answer the questions to set the dynamics options.

```

nat: Number of atoms.
The current value of nat is: 9
Enter the new value of nat : <ENTER>
Setting nat = 9

nstat: Number of states.
The current value of nstat is: 2
Enter the new value of nstat : 3 <ENTER> ! 3 states will be computed
Setting nstat = 3

nstatdyn: Initial state (1 - ground state).
The current value of nstatdyn is: 3
Enter the new value of nstatdyn : <ENTER> ! dynamics will start in state 3 (e.g.
S2)
Setting nstatdyn = 3

dt: Time step for the classical equations.
The current value of dt (fs) is: 0.5
Enter the new value of dt (fs) : <ENTER>
Setting dt = 0.5

tmax: Total duration of the trajectory.
The current value of tmax (fs) is: 100
Enter the new value of tmax (fs) :300 <ENTER>
Setting tmax = 300

prog: Quantum chemistry program and method
  0 - ANALYTICAL MODEL
  1 - COLUMBUS
  2.0 - TURBOMOLE CC2
  2.1 - TURBOMOLE TDDFT
  2.2 - TURBOMOLE ADC2
  3 - ACES2 EOM-CCSD (in development)
  4 - MOPAC (in development)
  5 - DFTB
  6.0 - GAUSSIAN(03) CASSCF
  6.5 - GAUSSIAN(09) TDDFT
  7 - TINKER
  8 - DFTB+
  10.0 - GAMESS
  10.1 - GAMESS ARBITRARY ADIABATIC METHOD
  20 - HYBRID GRADIENT
The current value of prog is: 1
Enter the new value of prog : 6.5 <ENTER>
Setting prog = 6.5

thres: Threshold to initiate nonadiabatic coupling calculation.
  0 - Only adiabatic dynamics.
  100 - Only nonadiabatic dynamics
The current value of thres (eV) is: 100
Enter the new value of thres (eV) : <ENTER>
Setting thres = 100

Would you like to generate internal coordinate file? (default=y) y <ENTER>

```

8. In the main nxinp menu you have the option to set more general options if you select either option 3 or option 4. Normally, this is not necessary, and the default values are good enough.

9. Select option 5: “generate trajectories and spectrum.”

```

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

```

MAIN MENU

1. GENERATE INITIAL CONDITIONS
2. SET BASIC INPUT
3. SET GENERAL OPTIONS
4. SET NONADIABATIC DYNAMICS
5. GENERATE TRAJECTORIES AND SPECTRUM
6. SET STATISTICAL ANALYSIS
7. EXIT

Select one option (1-7): 5 <ENTER>

10. Select the job options.

```

type: What do you want to do?
      1 - Generate spectrum
      2 - Select initial conditions for multiple initial states
      3 - Generate trajectories
      4 - Return to main menu
The current value of type is: 3
Enter the new value of type : <ENTER>
Setting type = 3

```

If for this first option you are asked for "kindjob" instead "type," this means you are using an old version of NEWTON-X. Contact the distributors to get an updated version of the program.

```

Would you like to apply energy and probability restrictions (y/n)? (default=n) y
<ENTER>

```

```

nis: Initial state.
The current value of nis is: 1
Enter the new value of nis : <ENTER>
Setting nis = 1

```

```

nfs: Array of final states (comma or dash separated, e.g., 2-4 or 2,3,4).
For trajectories generation only one final state is allowed.
The current value of nfs is: 2
Enter the new value of nfs : 3 <ENTER>
Setting nfs = 3

```

The next keywords will allow setting the initial condition restrictions between 5.5 and 6.5 eV.

If nfs should be given as a 'space separated' list, this means that you are using an old version of NEWTON-X. Contact the distributors to get an updated version of the program.

```

screen: Energy restriction
      0 - don't apply any restriction
      1 - use the original energy restriction written in the final_output files
      2 - apply new energy restriction
The current value of screen is: 0
Enter the new value of screen : 2 <ENTER>
Setting screen = 2

e_center: Center of the energy restriction.
      x      - value of the center of restriction
      ref n - use the vertical excitation of final_output.nis.n file
The current value of e_center (eV) is: 0.0
Enter the new value of e_center (eV) : 6.0 <ENTER>
Setting e_center = 6.0

e_var: Width of the energy restriction.
The current value of e_var (eV) is: 0.5
Enter the new value of e_var (eV) : <ENTER>
Setting e_var = 0.5

os_condon: Oscillator strength:
-1 - try to read from final_output file.
      x - oscillator strength is always x (Condon approximation).
The current value of os_condon is: -1
Enter the new value of os_condon : <ENTER>
Setting os_condon = -1

prob_kind: Formula to calculate the transition probabilities:
      A - Einstein-coefficient A (spontaneous emission)
      B - Einstein-coefficient B (induced absorption or induced emission)
      E - Fluorescence (radiative decay rate)
      F - Absorption (photoabsorption cross section)
The current value of prob_kind is: F
Enter the new value of prob_kind : <ENTER>
Setting prob_kind = F

norm: Normalization of transition intensities:
      local - Use energy-restricted data set
      global - Use complete data set
The current value of norm is: local
Enter the new value of norm : <ENTER>
Setting norm = local

seed: Seed for the random number generation
      0 - a default random number seed is used
      1 - a randomized seed is used
      Any other positive integer is used as the random number seed
The current value of seed is: 0
Enter the new value of seed : <ENTER>
Setting seed = 0

Will the trajectories run in a batch system? n <ENTER>

      Processing data: This may take some minutes. Please, wait...

```

In general, you might want to submit this job to a batch system. In this case, answer “y” to “Will the trajectories run in a batch system?”. You will be asked the name of the submission script and nxinp will look for its existence in the input directory. Files “pmold” and “pmold-ew” in \$NX/./batch/ directory are templates that can be adapted to your batch system.

11. Exit nxinp.

12. Now the input directory should contain a new directory called TRAJECTORIES, which was created by nxinp.

```
> ls
control.dyn  final_output  geom  intcfl  JOB_AD  mkdir.log  mkd.inp  TRAJECTORIES
```

13. Move to TRAJECTORIES and list the content. You will see that 176 directories named TRAJ1, TRAJ2, ..., TRAJ176 were created. Each one of these directories contains a complete set of input files to run one independent trajectory with different initial conditions (geometry and velocities).

The number of TRAJn directories is controlled by the number of initial conditions in the final_output file and by the energy restrictions imposed.

Each accepted initial condition card is split into a geom and veloc files that appear inside TRAJn. The TRAJn structure of directories (see Fig. 9) is very important in NEWTON-X. Several tools to control the jobs and to perform statistical analysis use it.

Each TRAJn directory can be copied to a different computer or submitted to a different node of a batch system. They should, however, be grouped again after having finished the dynamics calculations.

6.4 Running NEWTON-X: dynamics simulations

14. Move to TRAJ1 and run this trajectory.

```
> cd TRAJ1
> $NX/moldyn.pl > moldyn.log &
```

15. Move to TRAJ2 and run that trajectory; redo the same until TRAJ10.

If the jobs should be submitted to a batch system you can either go to each TRAJn directory and run

```
> qsub pmold      ! pmold is the submission script
```

or in the TRAJECTORIES directory you can run

```
> $NX/submit.pl
```

In this case, you will be asked the initial and final trajectory number that should be submitted, and the submission of all these trajectories will be done automatically.

6.5 Checking the results

16. For each TRAJn, the dynamics output is in three directories:

- a. RESULTS: the dynamics information;
- b. INFO_RESTART: stored information to restart the trajectory;
- c. DEBUG: error messages, convergence information and additional electronic structure files like molecular orbital files.

and the content of each TRAJn directory looks like:

```
> ls TRAJ1/
control.dyn  DEBUG  geom  INFO_RESTART  intcfl  JOB_AD  moldyn.log  RESULTS
veloc
```

17. Go to directory TRAJ1/RESULTS.

```
> cd TRAJ1/RESULTS
```

18. If it finished with error, nx.log should finish like:

```
moldyn.pl:  ::ERROR::  step =      123 time = 61.5 fs
Trying to save TEMP directory to ../DEBUG
```

In this example, the job finished with an error after 123 steps (61.5 fs). The last GAUSSIAN09 calculation was written into TRAJ1/DEBUG/TEMP and you can check what was wrong. More error messages are also written to DEBUG/runnx.error file.

19. If the job ended normally, the file nx.log should finish with:

```
moldyn.pl: End of dynamics
===== NEWTON-X ends here =====
```

20. Plot the energies (Fig. 10):

```
> $NX/plot
Number of states: 3
```

The energy information used by plot program is in the file RESULTS/en.dat. It looks like:

!Time (fs)	E0 (au)	E1 (au)	E2 (au)	E(current) (au)	Etot (au)
0.00	-552.894216	-552.674187	-552.668582	-552.668582	-552.649141
0.50	-552.900033	-552.680213	-552.674932	-552.674932	-552.649355
1.00	-552.905180	-552.685933	-552.680921	-552.680921	-552.649487
1.50	-552.907398	-552.689155	-552.684274	-552.684274	-552.649503
2.00	-552.906227	-552.689465	-552.684475	-552.684475	-552.649437
2.50	-552.902523	-552.687756	-552.682277	-552.682277	-552.649348
3.00	-552.897612	-552.685315	-552.678932	-552.678932	-552.649260
3.50	-552.892784	-552.683324	-552.675698	-552.675698	-552.649198
4.00	-552.888995	-552.682629	-552.673522	-552.673522	-552.649162
4.50	-552.886775	-552.683658	-552.672935	-552.672935	-552.649155
5.00	-552.886234	-552.686446	-552.674047	-552.674047	-552.649172
5.50	-552.887131	-552.690695	-552.676617	-552.676617	-552.649199
6.00	-552.888979	-552.695879	-552.680169	-552.680169	-552.649241
6.50	-552.891112	-552.701298	-552.684037	-552.684037	-552.649291
...					

If you give one more state (4, in this example), the total energy is also printed.

You can run the plot program for a sequence of trajectories either to see them on screen or only to generate pictures. To do so, go to TRAJECTORIES directory and run:

```
> $NX/plotall
```

In GNUPLOT the basic script (plot.gpi) can be:

```
set terminal postscript enhanced color solid
set xlabel 'time / fs'
set ylabel 'Energy / Hartree'
set key right bottom

plot\
'en.dat' u 1:2 t 'S_{0}' w p pt 6 ps 2, \
'en.dat' u 1:3 t 'S_{1}' w p pt 6 ps 2, \
```

```
'en.dat' u 1:4 t 'S_{2}' w p pt 6 ps 2, \
'en.dat' u 1:5 t 'current' w p pt 7 lt 7 ps 2
```

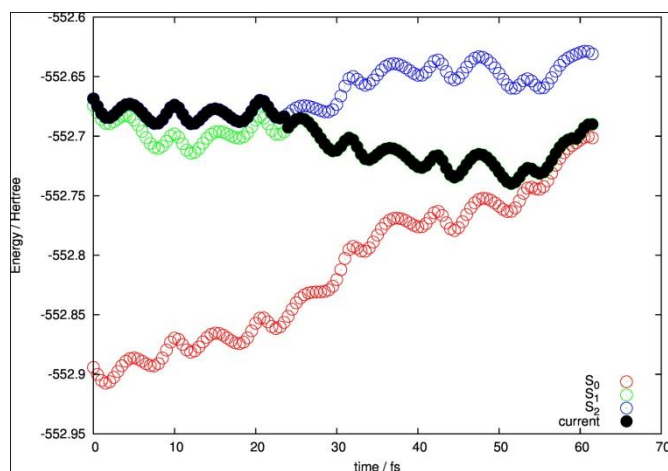


Fig. 5. Potential energies of the three states (S_0 , S_1 and S_2) for TRAJ1, as a function of time, plotted with GNUPLOT. The black circles indicate the current state of the system at each time step.

21. Visualize the dynamics:

```
> molder dyn.mld &
```

dyn.mld file is a simple multiple-xyz format file with all geometries along the trajectory. It can be opened by most programs for dynamics visualization. A good option is VMD (www.ks.uiuc.edu/Research/vmd), which allow quite complete control of the timeline and excellent rendering quality.

To save disk space, dyn.mld is not automatically created starting from NEWTON-X version 1.2.5. In these new versions, you can get the xyz file by moving to the RESULTS directory and running

```
> $NX/dynout2xyz.pl
```

A file called dyn.xyz (multiple xyz format) is created and can be visualized with programs like Molden or VMD.

22. Geometry, velocities, energies and other quantities are written in a more verbose way in file dyn.out.

The first time-step looks like:

```
*** Molecular Dynamics ***
Output printed at each kt= 1 steps ( 0.50 fs).
STEP          0      Molecular dynamics on state 3      TIME =          0.00 fs
Type of dyn. =  2      N. of hoppings =  0      N. of rejec. hoppings =  0

Initial geometry:
s  16.0  -0.01344068   2.19466790  -0.00363459  31.97207180
c   6.0   2.40677418   0.05835506  -0.07775881  12.00000000
c   6.0   1.36330143  -2.41575449   0.06668980  12.00000000
c   6.0  -1.44655585  -2.34258424  -0.07326877  12.00000000
```

```

c      6.0   -2.27564538   0.01234952   0.03977154   12.00000000
h      1.0    4.17763770   0.69542380   0.53765428   1.00782504
h      1.0    2.43927573  -3.87923298  -0.16835954   1.00782504
h      1.0   -2.52844608  -4.11962585   0.27288499   1.00782504
h      1.0   -4.22150801   0.40278622   0.04398443   1.00782504

```

Initial velocity:

```

-0.00008485   0.00001268   -0.00004137
-0.00023103  -0.00003321   0.00016062
0.00023174   0.00001566   -0.00023973
-0.00011618  -0.00044362   -0.00007019
0.00029570   0.00058595   -0.00009650
0.00014906  -0.00028854   0.00109718
0.00106823  -0.00159003   0.00048862
-0.00002047  0.00060141   0.00140778
-0.00063164  -0.00057783   0.00158049

```

```

      Time      Etot          Ekin          Epot E0,      E1, ...
%      0.0    -552.649141      0.019442    -552.894216  -552.674187  -552.668582
Etot variation = 0.000000 au      Worse conservation = 0.000000 au

```

```

Wave function state 1:      0.0000000000000000      0.0000000000000000
Wave function state 2:      0.0000000000000000      0.0000000000000000
Wave function state 3:      1.0000000000000000      0.0000000000000000

```

...

The last time-step looks like:

```

STEP      123      Molecular dynamics on state 2      TIME =      61.50 fs
Type of dyn. =      4      N. of hoppings =      1      N. of rejec. hoppings =      0

```

New geometry:

```

s      16.0   0.70340260   3.07317235  -0.05504104   31.97207180
c      6.0    2.29325059   0.25270304  -0.16881052   12.00000000
c      6.0    0.91275966  -2.38661106   0.23034902   12.00000000
c      6.0   -1.57197537  -3.13649503  -0.00236842   12.00000000
c      6.0   -3.42722163  -1.43306138   0.14777090   12.00000000
h      1.0    4.12022179  -0.25329381  -0.44739620   1.00782504
h      1.0    2.12132046  -4.26057143   0.63263093   1.00782504
h      1.0   -1.83590406  -5.26397036  -0.16118117   1.00782504
h      1.0   -5.30394868  -0.89750746   0.23519054   1.00782504

```

New velocity:

```

0.00036909   0.00043416   0.00004654
-0.00024132  0.00006964  -0.00064342
0.00032666  -0.00049094   0.00045817
-0.00001929  -0.00003415  -0.00032210
-0.00071953  -0.00073804   0.00044689
0.00076679   0.00128969   0.00193094
-0.00311104  0.00164735  -0.00003364
-0.00068100  -0.00061212   0.00012677
-0.00087992  -0.00184894  -0.00239036

```

```

      Time      Etot          Ekin          Epot E0,      E1, ...
%      61.50   -552.627499      0.062561    -552.701426  -552.690060  -552.630923
Etot variation = 0.003809 au      Worse conservation = 0.021642 au

```

```

Wave function state 1:      0.0000000000000000      0.0000000000000000
Wave function state 2:      0.57219705163435      -0.82011522798407
Wave function state 3:      0.00115939315479      -0.00045026337002

```

“*Etot variation*” gives $E_{tot}(t)-E_{tot}(t-\Delta t)$. When this quantity is larger than a threshold, the trajectory breaks with “*Etot_jump*” error message. This threshold can be controlled with the keyword “*Etot_jump*” in the advanced input.

“*Worse conservation*” gives $\text{MAX}[E_{tot}(t)-E_{tot}(0)]$ until time t . When this quantity is larger than a threshold, the trajectory breaks with “*Etot_drift*” error message. This threshold can be controlled with the keyword “*Etot_drift*” in the advanced input.

In surface hopping approach, the time-dependent wavefunction is written as ¹¹

$$\Psi(t) = \sum_{n=1}^{Nstat} \chi_n(t) \psi_i(\mathbf{R}(t)),$$

where ψ_i is the electronic wavefunction (in the adiabatic representation, in this example). The time-dependent coefficients χ_n are complex numbers: The real and imaginary parts of them are given in *dyn.out*. For example, the line in the last time-step means

Wave function state 2: 0.57219705163435 -0.82011522798407

$$\text{Re}(\chi_0) = 0.572197 \text{ and } \text{Im}(\chi_0) = -0.82011$$

The normalization of these coefficients is an important check of the quality of the dynamics, and it will be discussed below.

23. Energy information is also written in a different format in file *typeofdyn.log*. It looks like:

```
...
Time = 22.50 Threshold=**** PES = 3 DE_inf = 0.39 DE_sup = ----- Type = 2 Next type = 2
Time = 23.00 Threshold=**** PES = 3 DE_inf = 0.37 DE_sup = ----- Type = 2 Next type = 2
Time = 23.50 Threshold=**** PES = 3 DE_inf = 0.34 DE_sup = ----- Type = 2 Next type = 2
Time = 24.00 Threshold=**** PES = 2 DE_inf = 4.32 DE_sup = 0.31 Type = 2 Next type = 4
Time = 24.50 Threshold=**** PES = 2 DE_inf = 4.26 DE_sup = 0.28 Type = 4 Next type = 4
Time = 25.00 Threshold=**** PES = 2 DE_inf = 4.19 DE_sup = 0.26 Type = 4 Next type = 4
...
```

At time 23.50 fs the molecule was on surface 3 (S_2). The energy gap to S_1 *DE_inf* was 0.34 eV. At time 24.00 fs, the molecule was on surface 2 (S_1). Therefore a surface-hopping took place. The energy gap with S_0 was 4.32eV and with S_2 was 0.31eV.

24. Gradients, oscillator strengths, and non-adiabatic coupling vectors and log information are written to *nx.log* (and also in the standard output).

25. The information about the integration of the time-dependent Schrödinger equation is in *sh.out* file. It looks like:

```
...
substep      step  surf  populations      Total pop
...
|v.h|=      0.000000    0.000000  -0.001959
      941         48     3    0.0000000000    1.0000000000
                0.103439012
                0.896560988
...
```

NEWTON-X keeps two related timelines. The first is composed by the steps used to integrate Newton’s equations. For step n , the time is $n.\Delta t$ ($\Delta t = 0.5$ fs in this example). The second timeline is counted in substeps, which are used to integrate the time-dependent Schrödinger

equation. The number of substeps per step is defined by keyword “ms,” which can be changed in the advance input. The default is $ms = 20$. At the end of a trajectory with N steps, we will have $N.ms$ substeps.

At the substep 941, still during step 48, with the molecule still on surface 3 (S_2), the population of the second excited state (S_2) was:

$$|\chi_2|^2 = 0.896560988.$$

The population is defined as the diagonal terms of the matrix $\chi_i\chi_j^*$. These terms are written in sh.out. Note that

$$\sum_{n=1}^{Nstat} |\chi_n|^2 = 1.$$

The normalization factor is also printed there (“Total pop”). When it deviates more than “pop_dev” (a keyword defined in the advance input, whose default is 0.05), the job breaks with an error message.

The inner products of the nuclear velocity and the non-adiabatic coupling vectors, which are proportional to the hopping probability, are also printed:

$$\mathbf{v} \cdot \mathbf{h}_{10} = 0.000000,$$

$$\mathbf{v} \cdot \mathbf{h}_{20} = 0.000000,$$

$$\mathbf{v} \cdot \mathbf{h}_{21} = -0.001959.$$

26. The hopping probability is written in tprob file. It looks like:

random number	substep	step	probabilities		
...					
0.511167348	945	48	0.000000000	0.001554715	0.000000000
0.001460153	946	48	0.000000000	0.001609113	0.000000000
0.834699438	1068	54	0.000000000	0.000000000	0.000046495
0.894276913	1069	54	0.000000000	0.000000000	0.000111712
...					

In the substep 945 (during step 48), the hopping probabilities were:

$$P_{2 \rightarrow 0} = 0.000000000,$$

$$P_{2 \rightarrow 1} = 0.001554715,$$

$$P_{2 \rightarrow 2} = 0.000000000.$$

These probabilities were compared with the random number 0.511167348 to decide whether a hopping occurs or not. Since the random number was larger than the probabilities, the molecule stays on S_2 surface in the next substep (946).

In the substep 946, the random number (0.001460153) was smaller than $P_{2 \rightarrow 1}$ (0.001609113); therefore the molecule hops to surface S_1 .

In the fewest-switches approach under adiabatic representation, the hopping probability from state j to state i is given by:

$$P_{j \rightarrow i}(t) = \begin{cases} -2 \frac{\operatorname{Re}(\chi_i^* \chi_j e^{i\gamma_{ji}})}{|\chi_{ji}|^2} \mathbf{v}(t) \cdot \mathbf{h}_{ji}(t) \delta t, & \text{if } P_{j \rightarrow i} > 0. \\ 0, & \text{if } P_{j \rightarrow i} \leq 0. \end{cases}$$

In this equation, $\delta t = \Delta t/\text{ms}$. Due to this definition, the probability becomes zero for some time intervals (not reported in the above example...have a look by yourself in the tprob file!).

27. Points close to conical intersections (energy gaps smaller than “e_ci”, which is keyword defined in advanced input. The default is 0.2 eV) are written to “report.ci” file.

6.6 Statistical analysis of the trajectories

28. After running your trajectories, you can perform a series of statistical analysis on them.

29. Go to TRAJECTORIES directory, run nxinp, and select option 6: “Set statistical analysis.”

```

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

                                MAIN MENU

                                1. GENERATE INITIAL CONDITIONS

                                2. SET BASIC INPUT

                                3. SET GENERAL OPTIONS

                                4. SET NONADIABATIC DYNAMICS

                                5. GENERATE TRAJECTORIES AND SPECTRUM

                                6. SET STATISTICAL ANALYSIS

                                7. EXIT

```

Select one option (1-7): 6 <ENTER>

30. First, perform a general diagnostic of errors.

```

What do you want to do?
 1 - Generate input for diagnostic (only statistics on errors)
 2 - Generate input for statistical analysis (statistics on wavefunction,
energies, etc.)
 3 - Return to main menu

```

Enter the option (default = 1): 1 <ENTER>

```

ad: Path to the trajectories. The default is the current directory.
The current value of ad is: /home/TUTORIAL/THIOPHENE_TDDFT_DYN_S2/TRAJECTORIES

```

```

Enter the new value of ad : <ENTER>
Setting ad = /home/TUTORIAL/THIOPHENE_TDDFT_DYN_S2/TRAJECTORIES

itraj: Initial trajectory to be checked.
The current value of itraj is: 1
Enter the new value of itraj : <ENTER>
Setting itraj = 1

ftraj: Final trajectory to be checked. There is not sensible default value.
The current value of ftraj is:
Enter the new value of ftraj : 10 <ENTER> ! We run 10 trajs out of 176 generated
Setting ftraj = 10

tmin: Initial time. It must be common to all trajectories.
The current value of tmin (fs) is: 0.0
Enter the new value of tmin (fs) : <ENTER>
Setting tmin = 0.0

Etot_dev: Maximal allowed total energy variation.
The current value of Etot_dev (eV) is: 0.5
Enter the new value of Etot_dev (eV) : <ENTER>
Setting Etot_dev = 0.5

pop_dev: Maximal allowed variation in the norm of the adiabatic population.
The current value of pop_dev is: 0.1
Enter the new value of pop_dev : 0.05 <ENTER>
Setting pop_dev = 0.05

```

31. Exit nxinp and run:

```
> $NX/diagnostic.pl
```

32. The result is the file diag.log. It contains a summary of what happened to the trajectories. It looks like:

```

DIAGNOSTIC OF NEWTON-X TRAJECTORIES

Diagnostic of trajectories 1 to 10

Path to the trajectories: /home/TUTORIAL/THIOPHENE_TDDFT_DYN/TRAJECTORIES
Initial time (fs): 0.0
Max. Energy deviation(eV): 0.5
Max. population deviation: 0.1
Number of states: 3
Normal termination: 0
Error termination: 10

TRAJECTORY 1:
moldyn.pl: ::ERROR:: step = 123 time = 61.5 fs
Energy conservation failed at 61.50 fs
Suggestion: make analysis until time (fs): 61.50

TRAJECTORY 2:
moldyn.pl: ::ERROR:: step = 110 time = 55 fs
Energy conservation failed at 55.00 fs
Suggestion: make analysis until time (fs): 55.00
...

Maximum time reached (fs): 192.00

Distribution of trajectories:
Number of trajs finished between 0.0 and 48 fs: 1
Number of trajs finished between 48 and 96 fs: 8
Number of trajs finished between 96 and 144 fs: 0
Number of trajs finished between 144 and 192 fs: 1

```

...

In this case study, all the 10 trajectories finished in error.

1 trajectory in the time interval between 0.0 and 48.0 fs, 8 trajectories in the 48-96 fs interval and 1 trajectory in the 144-192 fs range.

One of the most often reason for finishing in error is the connection with the adequacy of electronic structure method to compute the energies and gradients for some specific nuclear geometry.

For instance, dynamics trajectories performed with TD-DFT will crash as soon as the molecule enters in a region of strong multireference character (e.g., S_0/S_1 crossing seam). Trajectories performed with CASSCF may crash if the molecule dissociates and the necessary anti-bonding orbitals are not in the active space.

The dynamics information until these critical points, however, usually is correct and can be useful for the global statistical analysis.

For each trajectory, diagnostic.pl program prints until which time the calculation is reliable according to the criteria defined in its input. The log file, for example, says that for trajectory 1, data until 61.50 fs can be used.

It is not mandatory to run diagnostic.pl before the statistical analysis but it is quite advisable.

If the statistical analysis program finds the diag.log file, it will automatically use the “suggested time” to decide which data to use from each trajectory. You can change these suggested times in diag.log if you want.

33. Run nxinp and select option 6: “Set statistical analysis”.

```
MAIN MENU
```

1. GENERATE INITIAL CONDITIONS
2. SET BASIC INPUT
3. SET GENERAL OPTIONS
4. SET NONADIABATIC DYNAMICS
5. GENERATE TRAJECTORIES AND SPECTRUM
6. SET STATISTICAL ANALYSIS
7. EXIT

```
Select one option (1-7): 6 <ENTER>
```

34. Make the input for statistical analysis. Start making the “wave function analysis”.

```
What do you want to do?
1 - Generate input for diagnostic (only statistics on errors)
```

2 - Generate input for statistical analysis (statistics on wavefunction, energies, etc.)
 3 - Return to main menu

Enter the option (default = 2): 2 <ENTER>

itrj: Initial trajectory to be analysed.
 The current value of itrj is: 1
 Enter the new value of itrj : <ENTER>
 Setting itrj = 1

jtrj: Final trajectory to be analysed.
 The current value of jtrj is: 10
 Enter the new value of jtrj : 10 <ENTER>
 Setting jtrj = 10

tmin: Initial time for the analysis.
 The current value of tmin (fs) is: 0
 Enter the new value of tmin (fs) : <ENTER>
 Setting tmin = 0

tmax: Final time for the analysis.
 The current value of tmax (fs) is: 100
 Enter the new value of tmax (fs) : 300 <ENTER>
 Setting tmax = 300

dt: Time step in which outputs are written.
 If TRAJ1/control.dyn is found, default is DT*KT,
 otherwise default is 0.5 fs.
 The current value of dt (fs) is: 0.5
 Enter the new value of dt (fs) : <ENTER>
 Setting dt = 0.5

proptype: Kind of properties to be analysed.
 1. Energy.
 2. Wave function.
 3. Internal coordinates.
 4. Internal forces (only for COLUMBUS dynamics).
 5. Velocity autocorrelation.
 The current value of proptype is: 1
 Enter the new value of proptype : 2 <ENTER>

nstat: Number of states to be analysed.
 The current value of nstat is: 2
 Enter the new value of nstat : 3 <ENTER>
 Setting nstat = 3

complete_data: Complete data for broken trajectories.
 0. Do not complete data. (default)
 Other positive value. If the last time in the trajectory
 is larger than complete_data, repeat last set of data until
 tmax. Neglect trajectories whose last time is
 smaller than complete_data. (Only for proptype = 2.)
 The current value of complete_data is: 0
 Enter the new value of complete_data : <ENTER>
 Setting complete_data = 0

35. Exit nxinp and run:

```
> $NX/analysis.pl > analysis.log &
```

analysis.pl program makes averages over trajectories for several different properties.

36. If everything runs normally, analysis.log ends with:

```
analysis: End of analysis
===== NEWTON-X ends here =====
```

37. Go to the directory ANALYSIS and look at file prop.2. It looks like:

```
!Traj Time/fs SA SB SA.SB a0 a1 a2
  1 0.00 3 3 3.3 0.0000 0.0000 1.0000
  1 0.50 3 3 3.3 0.0000 0.0048 0.9952
  1 1.00 3 3 3.3 0.0000 0.0464 0.9536
...
  1 24.00 3 3 3.3 0.0000 0.2126 0.7874
  1 24.50 3 2 3.2 0.0000 0.3576 0.6424
  1 25.00 2 2 2.2 0.0000 0.5168 0.4832
...
```

Trajectory 1 starts at time 0 fs in surface 3 (given by SA) and ends this time stem still on surface 3 (given by SB). In this step, all population is in surface 3 ($a_2 = |\chi_{22}|^2 = 1.0000$).

At time 24.50 fs, TRAJ1 starts on surface 3 and ends on surface 2, meaning that a hop between S_2 and S_1 took place. Now $a_2 = |\chi_{22}|^2 = 0.6424$.

This description continues for all trajectories until TRAJ10, for which only data until 62.0 fs was used (because of the instruction in diag.log).

38. Look at mean_value.2.

```
!Time/fs N NO <a0> da0 N1 <a1> da1 N2 <a2> da2
  0.00 10 0.000 0.000 0.000 0.000 0.000 0.000 1.000 1.000 0.000
  0.50 10 0.000 0.000 0.000 0.000 0.002 0.003 1.000 0.998 0.003
  1.00 10 0.000 0.000 0.000 0.000 0.021 0.031 1.000 0.979 0.031
  1.50 10 0.000 0.000 0.000 0.000 0.077 0.146 1.000 0.923 0.146
...
 24.00 10 0.000 0.000 0.000 0.700 0.746 0.394 0.300 0.254 0.394
 24.50 10 0.000 0.000 0.000 0.900 0.790 0.351 0.100 0.210 0.351
 25.00 10 0.000 0.000 0.000 0.900 0.835 0.327 0.100 0.165 0.327
 25.50 10 0.000 0.000 0.000 0.900 0.859 0.318 0.100 0.141 0.318
```

This file contains the average over all trajectories as a function of time.

A time 1 fs, 10 trajectories were used to compute the averages. The fraction of trajectories on state S_2 was $N_2 = 1$, and the average adiabatic population was $\langle |\chi_{22}|^2 \rangle = 0.979$ with standard deviation $da_2 = 0.031$.

At time 24.50fs, 10 trajectories were used to compute the averages. The fraction of trajectories on state S_2 was $N_2 = 0.1$, and the average adiabatic population was $\langle |\chi_{22}|^2 \rangle = 0.210$ with standard deviation $da_2 = 0.351$, while the fraction of trajectories on state S_1 was $N_1 = 0.9$ and the average adiabatic population was $\langle |\chi_{11}|^2 \rangle = 0.790$ with standard deviation $da_1 = 0.351$.

39. Go to TRAJECTORIES directory, run nxinp again, select Statistical analysis option and choose analysis of “Internal coordinates.”

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

MAIN MENU

1. GENERATE INITIAL CONDITIONS
2. SET BASIC INPUT
3. SET GENERAL OPTIONS
4. SET NONADIABATIC DYNAMICS
5. GENERATE TRAJECTORIES AND SPECTRUM
6. SET STATISTICAL ANALYSIS
7. EXIT

Select one option (1-7): 6 <ENTER>

What do you want to do?

- 1 - Generate input for diagnostic (only statistics on errors)
- 2 - Generate input for statistical analysis (statistics on wavefunction, energies, etc.)
- 3 - Return to main menu

Enter the option (default = 2): <ENTER>

Would you like to delete old input files? (prop.inp) y <ENTER>

itrj: Initial trajectory to be analysed.

The current value of itrj is: 1

Enter the new value of itrj : <ENTER>

Setting itrj = 1

jtrj: Final trajectory to be analysed.

The current value of jtrj is: 10

Enter the new value of jtrj : 10 <ENTER>

Setting jtrj = 10

tmin: Initial time for the analysis.

The current value of tmin (fs) is: 0

Enter the new value of tmin (fs) : <ENTER>

Setting tmin = 0

tmax: Final time for the analysis.

The current value of tmax (fs) is: 100

Enter the new value of tmax (fs) : 300 <ENTER>

Setting tmax = 300

dt: Time step in which outputs are written.

If TRAJ1/control.dyn is found, default is DT*KT,

otherwise default is 0.5 fs. The current value of dt (fs) is: 0.5

Enter the new value of dt (fs) : <ENTER>

Setting dt = 0.5

proptype: Kind of properties to be analysed.

- 1. Energy.
- 2. Wave function.
- 3. Internal coordinates.
- 4. Internal forces (only for COLUMBUS dynamics).
- 5. Velocity autocorrelation.

The current value of proptype is: 1

Enter the new value of proptype : 3 <ENTER>

nstat: Number of states to be analysed.
The current value of nstat is: 2
Enter the new value of nstat : 3 <ENTER>
Setting nstat = 3

nic: Number of internal coordinates to be analyzed (Maximum = 100).
The current value of nic is: 1
Enter the new value of nic : 1 <ENTER>
Setting nic = 1

The internal coordinates are defined in the intcfl file in the JOB_NAD directory. The coordinate number one in this example corresponds to the CS stretching.

iclist: Array with the number of internal coordinates to be analyzed.
Example: if the stretch corresponds coordinate 1 and the torsion to 12,
and one wants to analyse both, iclist = 1,12 and nic = 2.
The current value of iclist is: 1
Enter the new value of iclist : <ENTER>
Setting iclist = 1

bmat: Internal coordinates options
0. Get the internal coord. from output files. COLUMBUS only.
1. Run cart2int.x program from COLUMBUS to get the internal
coordinates. In this case, an intcfl file with definition
of the internal coordinates is required.
The current value of bmat is: 0
Enter the new value of bmat : <ENTER>
Setting bmat = 0

40. Exit nxinp and run:

```
> $NX/analysis.pl > analysis.log &
```

analysis.pl program makes averages over trajectories for several different properties.

41. If everything runs normally, analysis.log ends with:

```
analysis: End of analysis
===== NEWTON-X ends here =====
```

42. Go to the directory ANALYSIS and look at file prop.3. It looks like:

```
! Traj Time/fs R_CN (Angstrom)
  1   0.00   1.7087400
  1   0.50   1.7079124
  1   1.00   1.7071965
...
  4  25.50   2.1650025
  4  26.00   2.1732732
  4  26.50   2.1811207
...
 10  60.50   1.6632894
 10  61.00   1.6499948
 10  61.50   1.6368442
```

TRAJ1 starts with CS bond length 1.708740 Å. In the next step, this distance is 1.7079124 Å. This information is printed for all trajectories until the last one, TRAJ10, for which only data until 61.50 fs is printed due to the restriction in diag.log.

If you had asked the analysis of more internal coordinates, they would also have appeared in this file as additional columns.

43. Look at mean_value.3.

```

0.00 10      1.729985    0.053
0.50 10      1.731448    0.053
1.00 10      1.732855    0.053
...
74.00 2      2.643658    0.402
74.50 2      2.653141    0.420
75.00 2      2.662796    0.438
...

```

At time 0 fs, the average CS distance was 1.729985 Å with standard deviation of 0.053. 10 trajectories were used to compute the average. At 75.00 fs, this average bond length increased to 2.6627 Å, and only two trajectories were used.

44. Plot the CS distance for all trajectories as a function of time.

```

> gnuplot
gnuplot> plot[x=1:100] 'prop.3' using 2:3

```

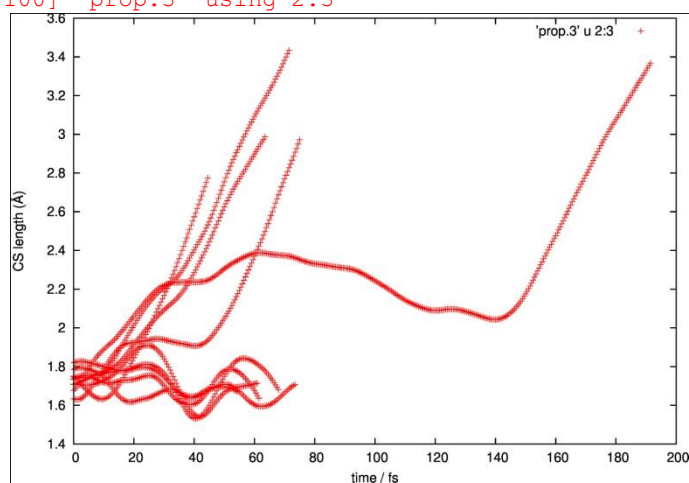


Fig. 6. CS distance (Å) as a function of time (fs) for all 10 trajectories.

Fig. 12 shows that the trajectories split in two. Five of them keeps the CS distance oscillating below 2 Å, while other part shows dissociation.

7. Initial conditions and spectrum simulation: MCSCF – Columbus

In this section, we will prepare initial conditions for dynamics using COLUMBUS. The system is methaniminium cation CH_2NH_2^+ and the dynamics will be initiated in the second excited state. The initial condition will be generated by a Wigner distribution in the ground vibrational state of the ground electronic state. The transition energies and moments will be also computed with two aims: 1) to have better control of the initial conditions and 2) to simulate the absorption spectrum.

The distribution will be created using normal modes obtained at DFT level with TURBOMOLE.

The energies and transition moments will be calculated at MCSCF level using a complete active space composed of twelve electrons in eight orbitals [CASSCF(12,8)]. Three singlet states will be included in the state-average procedure (SA-3), and the 6-31G* basis set will be used.

7.1 Geometry file creation

1. In the TUTORIAL directory (see section 1.4) create a subdirectory called CNH4_MCSCF_IC:

```
> mkdir CNH4_MCSCF_IC
```

2. Move to this directory and create a file called cnh4.xyz containing the geometry in XYZ format:

```
6
```

```
N      0.051443      -0.125748      0.596619
C      0.067113      -0.025698     -0.683445
H      0.002169       0.695516      1.199263
H      0.087711     -1.030762      1.065358
H      0.027120       0.954772     -1.143351
H      0.120118     -0.922908     -1.288953
```

This initial geometry can be created by hand using any text editor or with any molecular editor like MOLDEN. It is the simple xyz Cartesian format in Angstrom. The first line contains the number of atoms and it is followed by a blank line.

These values are the ground state geometry optimized at the same CASSCF level that will be used in the dynamics.

Because COLUMBUS will be used, the hydrogen atoms must appear at the end of the file.

3. Convert geometry into NEWTON-X format.

```
> $NX/xyz2nx < cnh4.xyz <ENTER>
```

The NEWTON-X geometry file is called 'geom' and looks like

N	7.0	0.09721318	-0.23762928	1.12744652	14.00307401
C	6.0	0.12682519	-0.04856218	-1.29152388	12.00000000
H	1.0	0.00409882	1.31433476	2.26627863	1.00782504
H	1.0	0.16574977	-1.94785789	2.01323485	1.00782504
H	1.0	0.05124937	1.80425760	-2.16062026	1.00782504
H	1.0	0.22699012	-1.74404337	-2.43576817	1.00782504

The second column contains the atomic number, and the following three columns contain the x, y and z coordinates in atomic units. The last column contains the atomic mass, which can be eventually changed to simulate isotopic effects. The file can be freely formatted.

The conversion back from NEWTON-X format to xyz can be done with

```
> $NX/nx2xyz
```

After running this program, the xyz-format geometry is written to file 'geom.xyz'.

7.2 Normal modes step

4. Create a new directory to run normal mode calculation:

```
> mkdir FREQ-DFT <ENTER>
```

5. Move to this directory and copy the geom file there.

```
> cd FREQ-DFT
> cp ../geom .
```

6. Transform the geometry into TURBOMOLE format.

```
> $NX/nx2tm
```

nx2tm program converts NEWTON-X "geom" file into TURBOMOLE "coord" file (atomic units). The back conversion can be done with

```
> $NX/tm2nx
```

7. Prepare the input and run a normal mode calculation at DFT(B3-LYP)/SV(P) level with TURBOMOLE. To do that, follow specific TURBOMOLE documentation (www.turbomole.com). Let the geometry be optimized to have only real frequencies. The TURBOMOLE output containing the normal modes and frequencies can have any name. Here we will suppose it is called "force.out."

NEWTON-X can read normal modes and frequencies from the outputs of the following programs: GAMESS, TURBOMOLE, COLUMBUS, GAUSSIAN, MOLDEN, DFTB, and ACES2.

Note that the normal modes and harmonic frequencies are used only to set the width of the random number distributions. For this reason, they do not need to be calculated at the same level as the one that will be used in the dynamics. It is, however, absolutely necessary that the order of atoms and geometry orientation in the "geom" file and in the normal modes are exactly the same. Using NEWTON-X conversion tools (ie nx2tm) assures that.

7.3 Energy and transition moment input

8. Move to the parent directory (TUTORIAL/CNH4_MCSCF_IC) and create a new subdirectory called JOB_AD.

```
> cd ..
> mkdir JOB_AD
```

The directory must be named JOB_AD since NEWTON-X will search for it.

9. Move into JOB_AD and copy the geom file there.

```
> cd JOB_AD
> cp ../geom .
```

10. In this directory, prepare a COLUMBUS input for single point calculation at SA-3-CASSCF(12,8)/6-31G* without symmetry. The orbital occupation and DRT tables are given in the Appendix “Methaniminium at CAS(12,8)”. The mocoef file containing the initial molecular orbitals coefficients should be provided. Important: even though the simulation will be performed at MCSCF level, the full MRCI input must be prepared. In the MRCI input section select “Excitation level = 0”, “NROOT = 3”, and transition moments at CI level between the ground and the two excited states. Follow the Columbus tutorial (www.univie.ac.at/columbus/tutorial).

This is the basic procedure for any program. If, for example, the initial conditions should be generated using DFT energies, JOB_AD should contain a TURBOMOLE input for single point calculations at DFT level.

Before submitting running any NEWTON-X job is highly advisable to run the job in JOB_AD directory just to test whether the input and outputs are OK. In the current case, just copy the content of the JOB_AD into a test directory and run the COLUMBUS job. Check whether the three roots and the oscillator strengths are computed and show reasonable values.

7.4 NEWTON-X input

11. Move to directory TUTORIAL/CNH4_MCSCF_IC and create a new subdirectory called IC_MCSCF.

```
> mkdir IC_MCSCF
```

12. Move to this directory and copy the geom file, JOB_AD directory, and the Turbomole output (force.out) there.

```
> cd IC_MCSCF
> cp ../geom .
> cp -rf ../JOB_AD .
> cp ../FREQ-DFT/force.out .
> ls
force.out  geom  JOB_AD
```

13. Run the nxinp program and select option 1: Generate initial conditions.

nxinp is the input tool for NEWTON-X. All input procedures, from the initial condition generation, through the dynamics inputs, to the statistical analysis options are performed with it.

> \$NX/nxinp

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

MAIN MENU

1. GENERATE INITIAL CONDITIONS
2. SET BASIC INPUT
3. SET GENERAL OPTIONS
4. SET NONADIABATIC DYNAMICS
5. GENERATE TRAJECTORIES AND SPECTRUM
6. SET STATISTICAL ANALYSIS
7. EXIT

Select one option (1-7): 1 <ENTER>

14. Select the adequate options for the initial condition properties.

nxinp will guide you through a set of questions. Each of them contains a short explanation and the available options. Most of the time, the default value is the best option. To accept the default you can just press <ENTER>.

```
...
nact: Distribution:
      1 - Classic harmonic oscillator
      2 - Q/P-uncorrelated quantum harmonic oscillator (Wigner)
      3 - Q/P-correlated quantum harmonic oscillator
      4 - Pick points from previous dynamics
      5 - Random-velocities generation
      6 - Single point on a previous calculation
The current value of nact is: 2
Enter the new value of nact : <ENTER>
Setting nact = 2

numat: Number of atoms.
The current value of numat is: 6
Enter the new value of numat : <ENTER>
Setting numat = 6

npoints: Number of initial conditions to be generated
The current value of npoints is: 1
Enter the new value of npoints : 100 <ENTER>
Setting npoints = 100
```

npoints sets the number of initial conditions that should be generated. This number depends on how many points you want to compute to generate the spectrum and how many trajectories you want to simulate.

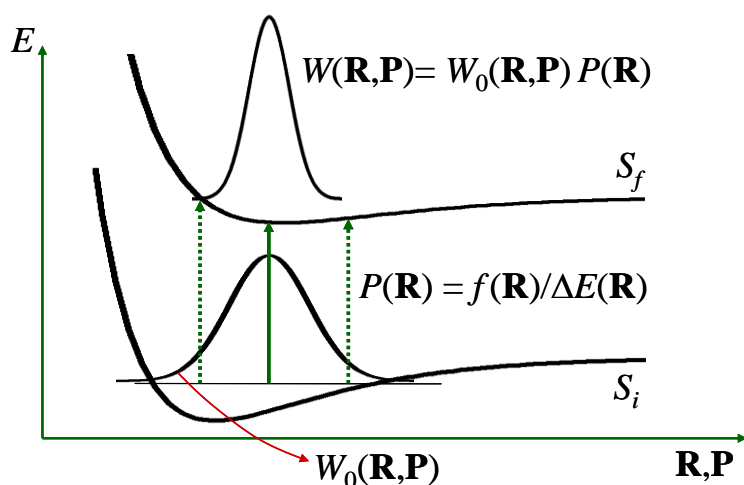


Fig. 7. Initial conditions generation for excited state dynamics: first, a ground state distribution of nuclear geometries and velocities is generated (W_0 , nact option). After that, the distribution is transformed according to the transition probabilities $f/\Delta E$ (chk_e = 1 option).

```
file_geom: File containing the equilibrium geometry.
The current value of file_geom is: 'geom'
Enter the new value of file_geom : <ENTER>
Setting file_geom = 'geom'

iprogram: Read vibrational modes from:
  1 - GAMESS output
  2 - TURBOLMOLE output
  3 - COLUMBUS output
  4 - GAUSSIAN output
  5 - MOLDEN file
  6 - DFTB output
  7 - ACES2 output
The current value of iprogram is: 2
Enter the new value of iprogram : <ENTER>
Setting iprogram = 2

file_nmodes: File containing the normal modes.
The current value of file_nmodes is: 'force.out'
Enter the new value of file_nmodes : <ENTER>
Setting file_nmodes = 'force.out'

anh_f: Multiply harmonic frequencies by this factor.
The current value of anh_f is: 1
Enter the new value of anh_f : <ENTER>
Setting anh_f = 1

chk_e: Restrict (or do not) the statistical distribution:
  0 - Do not check the energies.
  1 - Check the energies between states NIS and NFS.
The current value of chk_e is: 0
Enter the new value of chk_e : 1 <ENTER>
Setting chk_e = 1
```

The default 0 for `chk_e` means that the initial conditions will be generated without checking the transition energies and moments. In this case, the `JOB_AD` input (section 7.3) is not necessary and can be skipped. Since energies will not be computed, the generation of the initial condition is very fast, only a few seconds. The result, however, will not allow generating the spectrum and to initiate the trajectories according to the transition energy (to simulate a monochromatic photo-excitation. for example).

When `chk_e = 1`, NEWTON-X generates the “`npoints`” initial conditions uses the `JOB_AD` input to compute the energies and transition moments for each one (Fig. 7). Depending on the molecule and on the theoretical method this can be quite computationally expensive.

The next keywords define the restriction on the statistical distribution.

```
nis: Initial state (State in which the previous dynamics run. Ground state = 1.).
The current value of nis is: 1
Enter the new value of nis : <ENTER>
Setting nis = 1

nfs: Final state.
The current value of nfs is: 2
Enter the new value of nfs : 3 <ENTER>
Setting nfs = 3
```

The Wigner distribution will be generated in the ground electronic state (`nis = 1`) and transition energies between the ground and the second excited (`nfs = 3`) states will be computed. Indeed, with `nfs = N`, transition information for all states below `N` will also be computed and collected.

```
kvert: Center of the restriction:
      0 - Provide the energy for center of restriction
      1 - Use the vertical excitation energy of the equilibrium geometry
The current value of kvert is: 1
Enter the new value of kvert : <ENTER>
Setting kvert = 1

de: Width of restriction (center +/- de/2).
The current value of de (eV) is: 0.5
Enter the new value of de (eV) : 100 <ENTER>
Setting de = 100
```

This large “`de`” implies that this restriction will not be used. It can be imposed later on.

```
prog: Program and method to compute vertical excitation energies:
      1 - COLUMBUS
      2.0 - TURBOMOLE RI-CC2
      2.1 - TURBOMOLE TD-DFT
      5 - DFTB
The current value of prog is: 1
Enter the new value of prog : <ENTER>
Setting prog = 1

iseed: Random number seed.
      0 - default seed value.
     -1 - set random seed.
     >0 - (integer) set specific value for the seed.
The current value of iseed is: 0
Enter the new value of iseed : <ENTER>
Setting iseed = 0

lvprt: Print level.
      1 - standard level
```

```

    2 - debug level
The current value of lvprt is: 1
Enter the new value of lvprt : <ENTER>
Setting lvprt = 1

mem:   COLUMBUS core memory (1 GB = 134 Mwords).

The current value of mem is: 200
Enter the new value of mem : <ENTER>

```

15. Exit nxinp.

7.5 Running NEWTON-X: initial conditions

16. Run the initial condition generation program.

```
> $NX/initcond.pl > initcond.log &
```

In general, with `chk_e = 1`, you might want to submit this job to a batch system. Files “pini” and “pini-ew” in `$NX/./batch/` directory are templates that can be adapted to your batch system.

You can split the job into several computers. To do that, see the note “Splitting and merging jobs” in section 2.5.

7.6 Checking the results

17. Normal job termination is indicated at the end of `initcond.log` file by:

```

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

```

18. The main information is written to the `final_output` files.

19. Both, `final_output.1.2` and `final_output.1.3` contains the same 100 initial conditions generated according to the Wigner distribution. `final_output.1.2` contains transition energies and oscillator strengths to excitations into state 2 (first excited state), while `final_output.1.3` contains the same information to excitations into state 3 (second excited state).

20. `final_output.1.2`, for example, has the following structure:

```

! The first card is the information for the initial geometry (geom)
Equilibrium geometry with null velocity:
Geometry in COLUMBUS and NX input format:
N    7.0    0.09721318    -0.23762928    1.12744652    14.00307401
C    6.0    0.12682519    -0.04856218    -1.29152388    12.00000000
H    1.0    0.00409882     1.31433476     2.26627863     1.00782504
...
Velocity in NX input format:
    0.00000000    0.00000000    0.00000000
...
Reference energy (au):    -94.432419    ! CAS(12,8)/6-31G* ground state energy
Vibrational energy (eV):    1.4587    ! Harmonic zero point energy
Vertical excitation (eV):    9.2106    ! ΔE between S0 and S1
Oscillator strength:    0.0000    ! S0->S1 oscillator strength
Accept initial conditions between -90.7894 eV and 109.2106 eV. ! kvert and de

```


choices are
reflected here

! npoints = 100 cards are given next. Each one contains random geometry, random velocity, energy and oscillator strength information.

```

Initial condition = 1                ! Initial condition 1
Geometry in COLUMBUS and NX input format:
N      7.0    0.13997128   -0.23122935    1.15406634    14.00307401
...
Velocity in NX input format:
  -0.000073416    0.000060077   -0.000254145
...
Epot of initial state (eV):    2.8428  Epot of final state (eV):    12.0552
Vertical excitation (eV):    9.2124  Is Ev in the required range?  YES
Ekin of initial state (eV):    0.5082  Etot of initial state (eV):    3.3510
Oscillator strength:          0.1295

```

“Epot of initial state” is the energy of state “nis” (in this case nis = 1) calculated in eV in relation to the reference energy given above.

“Epot of final state” is the energy of state 2 (this file is final_output.1.2). In final_output.1.3, the energy of state 3 is given.

“Vertical excitation”= “Epot of final state” – “Epot of initial state”

“Ekin” is the kinetic energy.

“Etot of initial state”= “Epot of initial state”+ “Ekin”

```

...
...
Initial condition = 100              ! Initial condition 100
Geometry in COLUMBUS and NX input format:
N      7.0    0.13840985   -0.25156066    1.10567304    14.00307401
...
Velocity in NX input format:
  0.000174253    0.000281108   -0.000102347
...
Epot of initial state (eV):    0.6489  Epot of final state (eV):    9.4031
Vertical excitation (eV):    8.7542  Is Ev in the required range?  YES
Ekin of initial state (eV):    0.7481  Etot of initial state (eV):    1.3970
Oscillator strength:          0.0027

```

If you have a final_output file and for any reason, you would like to update the energy and oscillator strength values on it (for example, because in the first run ckq_e was set to zero), you can use the option NACT = 6. It will read the geometries and velocities from your file (which should be renamed final_output.old) and perform single point calculations for each of the geometries contained there at the level set in JOB_AD directory.

7.7 Generating the spectrum

21. Go to directory TUTORIAL/CNH4_MCSCF_IC and create the subdirectory SPECTRUM.

```
> mkdir SPECTRUM
```

22. Move to this directory and copy final_output files there.

```
> cd SPECTRUM
> cp ../IC_MCSCF/final_output* .
```

23. Run nxinp and select option 5: “Generate Trajectories and Spectrum”.

```
> $NX/nxinp
```

1. GENERATE INITIAL CONDITIONS
2. SET BASIC INPUT
3. SET GENERAL OPTIONS
4. SET NONADIABATIC DYNAMICS
5. GENERATE TRAJECTORIES AND SPECTRUM
6. SET STATISTICAL ANALYSIS
7. EXIT

```
Select one option (1-7): 5
```

24. Go through the next options.

```
type: What do you want to do?
      1 - Generate spectrum
      2 - Select initial conditions for multiple initial states
      3 - Generate trajectories
      4 - Return to main menu
The current value of type is: 3
Enter the new value of type : 1
Setting type = 1
```

If for this first option you are asked for “kindjob” instead “type,” this means you are using an old version of NEWTON-X. Contact the distributors to get an updated version of the program.

```
nis: Initial state.
The current value of nis is: 1
Enter the new value of nis : <ENTER>
Setting nis = 1
```

```
nfs: Array of final states (comma or dash separated, e.g., 2-4 or 2,3,4).
For trajectories generation only one final state is allowed.
The current value of nfs is: 2
Enter the new value of nfs : 2,3 <ENTER> ! Spectrum including both states
Setting nfs = 2,3
```

If nfs should be given as a ‘space separated’ list, this means that you are using an old version of NEWTON-X. Contact the distributors to get an updated version of the program.

```
screen: Energy restriction
        0 - don't apply any restriction
        1 - use the original energy restriction written in the final_output files
        2 - apply new energy restriction
The current value of screen is: 0
Enter the new value of screen : <ENTER>
Setting screen = 0
```

```
os_condon: Oscillator strength:
-1- try to read from final_output file.
```

x - oscillator strength is always x (Condon approximation).
 The current value of os_condon is: -1
 Enter the new value of os_condon : <ENTER>
 Setting os_condon = -1

If the oscillator strength is not available, but the transition energy is, it is still possible to simulate the spectrum by giving a value to the oscillator strength in os_condon option. In this case, all transitions will be computed with the same oscillator strength. For only one final state this option is not bad, but it can be completely inadequate when more than one final state is selected.

prob_kind: Formula to calculate the transition probabilities:
 A - Einstein-coefficient A (spontaneous emission)
 B - Einstein-coefficient B (induced absorption or induced emission)
 F - Oscillator strength (photoabsorption cross section)
 The current value of prob_kind is: B
 Enter the new value of prob_kind : B <ENTER>
 Setting prob_kind = B

norm: Normalization of transition intensities:
 local - Use energy-restricted data set
 global - Use complete data set
 The current value of norm is: local
 Enter the new value of norm : <ENTER>
 Setting norm = local

seed: Seed for the random number generation
 0 - a default random number seed is used
 1 - a randomized seed is used
 Any other positive integer is used as the random number seed
 The current value of seed is: 0
 Enter the new value of seed : <ENTER>
 Setting seed = 0

l_shape: Line shape:
 gauss - Normalized Gaussian function.
 lorentz - Normalized Lorentzian function.
 The current value of l_shape is: lorentz
 Enter the new value of l_shape : <ENTER>
 Setting l_shape = lorentz

delta: Phenomenological broadening of the spectrum.
 The current value of delta (eV) is: 0.05
 Enter the new value of delta (eV) : <ENTER>
 Setting delta = 0.05

“delta” is possibly the only option that you need to play with. It controls the width of the Gaussian curve attributed to each one of the 200 transitions (100 initial conditions x 2 final states).

temp: Temperature.
 The current value of temp (K) is: 0
 Enter the new value of temp (K) : <ENTER>

nref: Refraction index.
 The current value of nref is: 1
 Enter the new value of nref : <ENTER>

eps: Distance between consecutive points in the spectrum.
 The current value of eps (eV) is: 0.005
 Enter the new value of eps (eV) : <ENTER>
 Setting eps = 0.005

kappa: The range of the spectrum is defined between
 Emin-kappa*delta and Emax+kappa*delta, where kappa is an integer.

```
The current value of kappa is: 3
Enter the new value of kappa : <ENTER>
Setting kappa = 3
```

25. Exit nxinp.

26. The simulated spectrum using the “gaussian broadening” method as a function of excitation energy is written to spectrum.dat. Looking at this file, we see:

```
! DE(eV)  Wavelength(nm)  cross-section(Å2.molecule-1)
7.3546   1.6858e+02         0.0004
7.3596   1.6847e+02         0.0004
7.3646   1.6835e+02         0.0004
...
```

27. Run Gnuplot to visualize the spectrum (Fig. 8).

```
> gnuplot
gnuplot> plot 'spectrum.dat' using 1:2 with lines
```

28. The files final_output* will be also used to initialize the trajectories.

As already observed, the final_output files are used by NEWTON-X to simulate the spectrum and to initialize dynamics trajectories. In this section, they have been generated using a Wigner distribution. Several other options – random velocities, classical distributions, pick-points from a previous dynamics – are included in NEWTON-X. Indeed, for NEWTON-X does not matter how final_output was generated, only that the file with the correct structure exists.

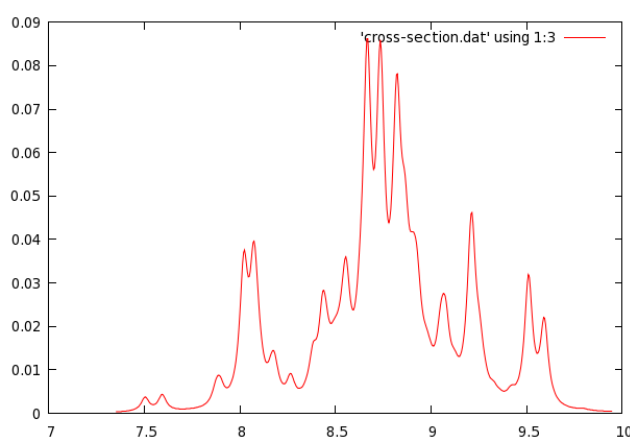


Fig. 8. Spectrum ($\text{\AA}^2 \cdot \text{molecule}^{-1}$) as a function of the excitation energy (eV). Computed with Lorentzian line shape and phenomenological broadening $\delta = 0.05$ eV.

8. Surface hopping dynamics: MCSCF – Columbus

In this section, we will prepare the inputs and run dynamics simulations. The system is methaniminium cation CH_2NH_2^+ and the dynamics will be initiated in the second excited state. The initial conditions were generated in Chapter 0 of this tutorial. The surface hopping¹¹ dynamics will be performed at MCSCF level using COLUMBUS. The trajectory time will be 100 fs with 0.5 fs time step.

The MCSCF level is a complete active space composed by twelve electrons in eight orbitals [CASSCF(12,8)]. Three singlet states will be included in the state-average procedure (SA-3), and the 6-31G* basis set will be used.

8.1 Copying the initial conditions

1. Go to TUTORIAL directory (see section 1.4) create a subdirectory called CNH4_MCSCF_DYN:

```
> mkdir CNH4_MCSCF_DYN
```

2. Move to this directory and copy the initial conditions file for the second excited state there.

```
> cd CNH4_MCSCF_DYN
> cp ../CNH4_MCSCF_IC/IC_MCSCF/final_output.1.3 final_output ! note the new
name
```

3. Create a subdirectory called JOB_NAD.

The directory must be named JOB_NAD since NEWTON-X will search for it.

8.2 Preparing electronic structure input

4. Move to JOB_NAD and create an input for single point non-adiabatic coupling calculation with COLUMBUS at SA-3-CASSCF(12,8)/6-31G*. The orbital occupation and DRT tables are given in the Appendix 12.1 “Methaniminium at CAS(12,8)”. The mocoef file containing the initial molecular orbital coefficients should be provided. Important: even though the simulation will be performed at MCSCF level, the input should be prepared for CI analytical gradient, and full MRCI input must be prepared. In the MRCI input section select “Excitation level = 0”, “NROOT = 3”, and non-adiabatic coupling vectors between the second excited and the ground states and between the second and the first states. Follow the Columbus tutorial (www.univie.ac.at/columbus/tutorial).

Before submitting running any NEWTON-X job is highly advisable to run the job in JOB_NAD directory just to test whether the input and outputs are OK. In the current case, just copy the content of the JOB_NAD into a test directory and run the COLUMBUS job. Check whether the three roots and the non-adiabatic coupling vectors are computed and show reasonable values.

8.3 NEWTON-X input

5. Run nxinp.

```
> $NX/nxinp
```

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

MAIN MENU

1. GENERATE INITIAL CONDITIONS

2. SET BASIC INPUT

3. SET GENERAL OPTIONS

4. SET NONADIABATIC DYNAMICS

5. GENERATE TRAJECTORIES AND SPECTRUM

6. SET STATISTICAL ANALYSIS

7. EXIT
```

```
Select one option (1-7): 2 <ENTER>
```

6. Select option 2: “set basic input” and answer the questions to set the dynamics options.

```
nat: Number of atoms.
The current value of nat is: 6
Enter the new value of nat : <ENTER>
Setting nat = 6

nstat: Number of states.
The current value of nstat is: 2
Enter the new value of nstat : 3 <ENTER>      ! 3 states will be computed
Setting nstat = 3

nstatdyn: Initial state (1 - ground state).
The current value of nstatdyn is: 3
Enter the new value of nstatdyn : <ENTER>      ! dynamics will start in state 3
Setting nstatdyn = 3

dt: Time step for the classical equations.
The current value of dt (fs) is: 0.5
```

```

Enter the new value of dt (fs) : <ENTER>
Setting dt = 0.5

tmax: Total duration of the trajectory.
The current value of tmax (fs) is: 100
Enter the new value of tmax (fs) : <ENTER>
Setting tmax = 100

prog: Quantum chemistry program and method
  0 - ANALYTICAL MODEL
  1 - COLUMBUS
  2.0 - TURBOMOLE RI-CC2
  2.1 - TURBOMOLE TD-DFT
  3 - ACES2 EOM-CCSD (in development)
  4 - MOPAC (in development)
  5 - DFTB
  6 - GAUSSIAN ! NX < 1.2
  6.0 - GAUSSIAN(03) CASSCF ! NX > 1.4
  6.5 - GAUSSIAN(09) TDDFT
  7 - TINKER
  8 - DFTB+
  10.0 - GAMESS
  10.1 - GAMESS ARBITRARY ADIABATIC METHOD
  20 - HYBRID GRADIENT
The current value of prog is: 1
Enter the new value of prog : <ENTER>
Setting prog = 1

thres: Threshold to initiate nonadiabatic coupling calculation.
  0 - Only adiabatic dynamics.
  100 - Only nonadiabatic dynamics
The current value of thres (eV) is: 100
Enter the new value of thres (eV) : <ENTER>
Setting thres = 100

Would you like to generate internal coordinate file? (default=y) n <ENTER>

```

7. In the main nxinp menu, you have the option to set more general options if you select either option 3 or option 4. Normally, this is not necessary, and the default values are good enough.

8. Select option 5: “generate trajectories and spectrum.”

```

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

MAIN MENU

1. GENERATE INITIAL CONDITIONS

2. SET BASIC INPUT

3. SET GENERAL OPTIONS

4. SET NONADIABATIC DYNAMICS

5. GENERATE TRAJECTORIES AND SPECTRUM

```

6. SET STATISTICAL ANALYSIS

7. EXIT

Select one option (1-7): 5 <ENTER>

9. Select the job options.

```
type: What do you want to do?
      1 - Generate spectrum
      2 - Select initial conditions for multiple initial states
      3 - Generate trajectories
      4 - Return to main menu
The current value of type is: 3
Enter the new value of type : <ENTER>
Setting type = 3
```

If for this first option you are asked for “kindjob” instead “type,” this means you are using an old version of NEWTON-X. Contact the distributors to get an updated version of the program.

```
Would you like to apply energy and probability restrictions (y/n)? (default=n)
<ENTER>
```

```
Will the trajectories run in a batch system? n <ENTER>
```

```
Processing data: This may take some minutes. Please, wait...
```

In general, you might want to submit this job to a batch system. In this case, answer “y” to “Will the trajectories run in a batch system?”. You will be asked the name of the submission script and nxinp will look for its existence in the input directory. Files “pmold” and “pmold-ew” in \$NX/./batch/ directory are templates that can be adapted to your batch system.

10. Exit nxinp.

11. Now the input directory should contain a new directory called TRAJECTORIES, which was created by nxinp.

```
> ls
control.dyn  final_output  JOB_NAD  mkdir.log  mkd.inp  TEMP  TRAJECTORIES
```

12. Move to TRAJECTORIES and list the content. You will see that 100 directories named TRAJ1 to TRAJ100 were created. Each one of these directories contains a complete set of input files to run one independent trajectory with different initial conditions (geometry and velocities).

The number of TRAJn directories is controlled by the number of initial conditions in the final_output file. Each initial condition card is split into a geom and veloc files that appear inside TRAJn.

The TRAJn structure of directories (see Fig. 9) is very important in NEWTON-X. Several tools to control the jobs and to perform statistical analysis use it.

Each TRAJn directory can be copied to a different computer or submitted to a different node of a batch system. They should, however, be grouped again after having finished the dynamics calculations.

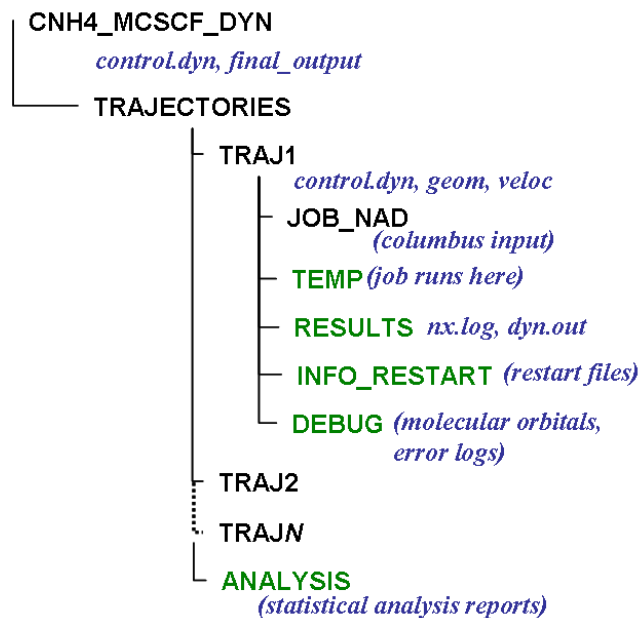


Fig. 9. Directory tree for a complete NEWTON-X surface hopping dynamics job.

8.4 Running NEWTON-X: dynamics simulations

13. Move to TRAJ1 and run this trajectory.

```
> cd TRAJ1
> $NX/moldyn.pl > moldyn.log &
```

14. Move to TRAJ2 and run that trajectory; the same with TRAJ3, TRAJ4, and so on. In the test calculations for this TUTORIAL we have run a total of 60 trajectories, from TRAJ1 to TRAJ60.

If the jobs should be submitted to a batch system you can either go to each TRAJn directory and run

```
> qsub pmold ! pmold is the submission script
```

or in the TRAJECTORIES directory you can run

```
> $NX/submit.pl
```

In this case, you will be asked the initial and final trajectory number that should be submitted, and the submission of all these trajectories will be done automatically.

8.5 Checking the results

15. For each TRAJn, the dynamics output is in three directories:

- RESULTS: the dynamics information;
- INFO_RESTART: stored information to restart the trajectory;
- DEBUG: error messages, convergence information and additional electronic structure files like molecular orbital files.

16. Go to directory TRAJ1/RESULTS.

```
> cd TRAJ1/RESULTS
```

17. If it finished with an error, nx.log should finish like:

```
moldyn.pl:  ::ERROR::  step =      60 time = 30 fs
Trying to save TEMP directory to ../DEBUG/COL.30
```

In this example, the job finished with an error after 60 steps (30 fs). The last COLUMBUS calculation was written into TRAJ1/DEBUG/COL.30/TEMP and you can check what was wrong. More error messages are also written to DEBUG/runnx.error file.

18. Go to directory TRAJ2/RESULTS.

```
> cd ../../TRAJ2/RESULTS
```

19. If the job ended normally, the file nx.log should finish with:

```
moldyn.pl: End of dynamics
===== NEWTON-X ends here =====
```

20. Plot the energies (Fig. 10):

```
> $NX/plot
Number of states: 3
```

The energy information used by plot program is in the file RESULTS/en.dat. It looks like:

<i>!Time (fs)</i>	<i>E0 (au)</i>	<i>E1 (au)</i>	<i>E2 (au)</i>	<i>E(current) (au)</i>	<i>Etot (au)</i>
0.00	-94.412074	-94.081511	-94.016479	-94.016479	-93.971870
0.50	-94.410343	-94.085650	-94.013214	-94.013214	-93.971792
1.00	-94.402481	-94.083425	-94.008725	-94.008725	-93.971517

...

If you give one more state (4, in this example), the total energy is also printed.

You can run the plot program for a sequence of trajectories either to see them on screen or only to generate pictures. To do so, go to TRAJECTORIES directory and run:

```
> $NX/plotall
```

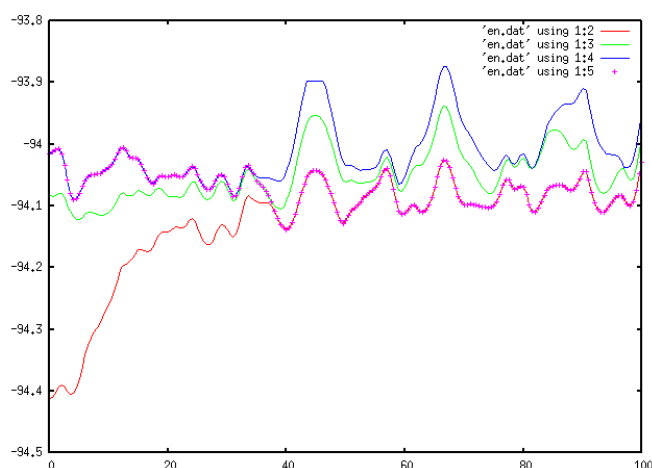


Fig. 10. Potential energies of the three states as a function of time plotted with `$NX/plot`. The crosses indicate the current state of the system at each time step.

21. Visualize the dynamics:

```
> moldern dyn.mld &
```

dyn.mld file is a simple multiple-xyz format file with all geometries along the trajectory. It can be opened by most of the programs for dynamics visualization. One good option is VMD (www.ks.uiuc.edu/Research/vmd), which allow quite complete control of the timeline and excellent rendering quality.

To save disk space, dyn.mld is not automatically created starting from NEWTON-X version 1.2.5. In these new versions, you can get the xyz file by moving to the RESULTS directory and running

```
> $NX/dynout2xyz.pl
```

A file called dyn.xyz (multiple xyz format) is created and can be visualized with programs like Molden or VMD.

22. Geometry, velocities, energies and other quantities are written in a more verbose way in file dyn.out. It looks like:

```
...
STEP          2      Molecular dynamics on state 3      TIME =          1.00 fs
Type of dyn. =    2      N. of hoppings =    0      N. of rejec. hoppings =    0

New geometry:
N      7.0      0.09015243      -0.20946057      1.09319790      14.00307401
C      6.0      0.17542005      -0.09999328      -1.25102014      12.00000000
H      1.0      0.08720540      1.23985176      2.05594456      1.00782504
H      1.0      0.02427253      -1.94636141      2.14504766      1.00782504
H      1.0      -0.26087804      1.97499271      -1.89595326      1.00782504
H      1.0      0.11655483      -1.62034288      -2.62874082      1.00782504

New velocity:
-0.00001223      0.00029810      0.00052112
 0.00012438      0.00027577      -0.00025372
 0.00047115      -0.00279091      -0.00053004
-0.00081528      -0.00210269      0.00076752
-0.00100439      0.00038167      -0.00241802
 0.00003574      -0.00291432      -0.00204379
```

```

Time      Etot      Ekin      Epot E0,      E1, ...
%      1.00      -93.971517      0.037208      -94.402481      -94.083425      -94.008725
Etot variation = 0.000274 au      Worse conservation = 0.000353 au

Wave function state 1:      -0.00027092051898      -0.00017265970290
Wave function state 2:      0.00514996477635      0.00752162117458
Wave function state 3:      0.99995839829598      -0.00003931597926
...

```

“Etot variation” gives $E_{tot}(t) - E_{tot}(t - \Delta t)$. When this quantity is larger than a threshold, the trajectory breaks with “Etot_jump” error message. This threshold can be controlled with the keyword “Etot_jump” in the advanced input.

“Worse conservation” gives $\text{MAX}[E_{tot}(t) - E_{tot}(0)]$ until time t . When this quantity is larger than a threshold, the trajectory breaks with “Etot_drift” error message. This threshold can be controlled with the keyword “Etot_drift” in the advanced input.

In surface hopping approach, the time-dependent wavefunction is written as ¹¹

$$\Psi(t) = \sum_{n=1}^{N_{stat}} \chi_n(t) \psi_i(\mathbf{R}(t)),$$

where ψ_i is the electronic wavefunction (in the adiabatic representation, in this example). The time-dependent coefficients χ_n are complex numbers: The real and imaginary parts of them are given in dyn.out. For example, the line

```
Wave function state 1:      -0.00027092051898      -0.00017265970290
```

means

$$\text{Re}(\chi_0) = -0.00027 \text{ and } \text{Im}(\chi_0) = -0.00017.$$

The normalization of these coefficients is an important check of the quality of the dynamics, and it will be discussed below.

23. Energy information is also written in a different format in file typeofdyn.log. It looks like:

```

...
Time = 37.00 Threshold=** PES= 2 DE_inf = 0.32 DE_sup = 0.78 Type = 4 Next type = 4
Time = 37.50 Threshold=** PES= 2 DE_inf = 0.19 DE_sup = 0.99 Type = 4 Next type = 4
Time = 38.00 Threshold=** PES= 1 DE_inf = ---- DE_sup = 0.23 Type = 4 Next type = 3
...

```

At time 37.5 fs the molecule was on surface 2 (S_1). The energy gap to S_0 was 0.19 eV and to S_2 , 0.99 eV (absolute values). At time 38.0 fs, the molecule was on surface 1 (S_0); therefore a surface hop took place.

24. Gradients, oscillator strengths, and non-adiabatic coupling vectors and log information are written to nx.log (and also in the standard output).

25. The information about the integration of the time-dependent Schrödinger equation is in sh.log file. It looks like:

```

...
substep      step      surf      populations      Total pop
...
|v.h|=      0.000000      0.000145      -0.000015
           4           1           3      0.000000164      1.000000000

```

```
0.000000001
0.999999835
```

...

NEWTON-X keeps two related timelines. The first is composed of the steps used to integrate Newton's equations. For step n , the time is $n \cdot \Delta t$ ($\Delta t = 0.5$ fs in this example). The second timeline is counted in substeps, which are used to integrate the time-dependent Schrödinger equation. The number of substeps per step is defined by keyword "ms," which can be changed in the advance input. The default is $ms = 20$. At the end of a trajectory with N steps, we will have $N \cdot ms$ substeps.

At the substep 4, still during step 1, with the molecule still on surface 3 (S_2), the population of the second excited state (S_2) was:

$$|\chi_2|^2 = 0.999999835.$$

The population is defined as the diagonal terms of the matrix $\chi_i \chi_j^*$. These terms are written in sh.log. Note that

$$\sum_{n=1}^{N_{stat}} |\chi_n|^2 = 1.$$

The normalization factor is also printed there ("Total pop"). When it deviates more than "pop_dev" (a keyword defined in the advance input, whose default is 0.05), the job breaks with an error message.

The inner products of the nuclear velocity and the non-adiabatic coupling vectors, which are proportional to the hopping probability, are also printed:

$$\mathbf{v} \cdot \mathbf{h}_{10} = 0.000000,$$

$$\mathbf{v} \cdot \mathbf{h}_{20} = 0.000145,$$

$$\mathbf{v} \cdot \mathbf{h}_{21} = -0.000015.$$

26. The hopping probability is written in tprob file. It looks like:

random number	substep	step	probabilities			
...						
0.586478467	1386	70	0.000009603	0.013179556	0.000000000	
0.186681612	1387	70	0.000009707	0.013189909	0.000000000	
0.008996025	1388	70	0.000009800	0.013172354	0.000000000	
20.000000000	1389	70	0.000000000	0.000000000	0.000000000	
0.344794082	1390	70	0.000000000	0.000000000	0.000000000	
0.161303038	1391	70	0.000000000	0.000000000	0.000000000	
...						

In the substep 1386 (during step 70), the hopping probabilities were:

$$P_{2 \rightarrow 0} = 0.000009603,$$

$$P_{2 \rightarrow 1} = 0.013179556,$$

$$P_{2 \rightarrow 2} = 0.000000000.$$

These probabilities were compared with the random number 0.586478467 to decide whether a hopping occurs or not. Since the random number was larger than the probabilities, the molecule stays on S_2 surface in the next substep (1387). In the substep 1388, the random number (0.008996) was smaller than $P_{2 \rightarrow 1}$; therefore the molecule hops to surface S_1 . The

surface hopping along the trajectories are marked by a “20.” in the place of the random number.

In the fewest-switches approach under adiabatic representation, the hopping probability from state j to state i is given by:

$$P_{j \rightarrow i}(t) = \begin{cases} -2 \frac{\operatorname{Re}(\chi_i^* \chi_j e^{i\gamma_{ji}})}{|\chi_{ji}|^2} \mathbf{v}(t) \cdot \mathbf{h}_{ji}(t) \delta t, & \text{if } P_{j \rightarrow i} > 0. \\ 0, & \text{if } P_{j \rightarrow i} \leq 0. \end{cases}$$

In this equation, $\delta t = \Delta t / \text{ms}$. Due to this definition, the probability becomes zero for some time intervals (like in substep 1391).

27. Points close to conical intersections (energy gaps smaller than “e_ci”, which is keyword defined in advanced input. The default is 0.2 eV) are written to “report.ci” file.

28. Oscillator strength and transition dipole moments are written to properties.

29. You can generate MOLDEN-format files for any time step including non-adiabatic coupling vectors (as vibrations) and molecular orbitals (if available for that time step). To do so, run:

```
> $NX/arrow
```

COLUMBUS molecular orbital files are stored every “prt_mo” time steps, which is a keyword that can be changed in the advanced input. The MO files are compressed in the DEBUG/COL.t directories with name mocoef_mc.sp.gz.

30. You can check the convergence of the MCSCF and CI calculations during the dynamics in file DEBUG/log.conv.

8.6 Statistical analysis of the trajectories

31. After running your trajectories, you can perform a series of statistical analysis on them.

32. Go to TRAJECTORIES directory, run nxinp, and select option 6: “Set statistical analysis”.

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

MAIN MENU

1. GENERATE INITIAL CONDITIONS

2. SET BASIC INPUT
```

3. SET GENERAL OPTIONS
4. SET NONADIABATIC DYNAMICS
5. GENERATE TRAJECTORIES AND SPECTRUM
6. SET STATISTICAL ANALYSIS
7. EXIT

Select one option (1-7): 6 <ENTER>

33. First, perform a general diagnostic of errors.

```

What do you want to do?
  1 - Generate input for diagnostic (only statistics on errors)
  2 - Generate input for statistical analysis (statistics on wavefunction,
energies, etc.)
  3 - Return to main menu

```

Enter the option (default = 1): 1 <ENTER>

```

ad: Path to the trajectories. The default is the current directory.
The current value of ad is: /home/TUTORIAL/CNH4_MCSCF_DYN_S2/TRAJECTORIES

```

```

Enter the new value of ad : <ENTER>
Setting ad = /home/TUTORIAL/CNH4_MCSCF_DYN_S2/TRAJECTORIES

```

```

itraj: Initial trajectory to be checked.
The current value of itraj is: 1
Enter the new value of itraj : <ENTER>
Setting itraj = 1

```

```

ftraj: Final trajectory to be checked. There is not sensible default value.
The current value of ftraj is:
Enter the new value of ftraj : 60      ! In the test calculations for
Setting ftraj = 60                    this tutorial, we have run 60
                                       trajectories.

```

```

tmin: Initial time. It must be common to all trajectories.
The current value of tmin (fs) is: 0.0
Enter the new value of tmin (fs) : <ENTER>
Setting tmin = 0.0

```

```

Etot_dev: Maximal allowed total energy variation.
The current value of Etot_dev (eV) is: 0.5
Enter the new value of Etot_dev (eV) : <ENTER>
Setting Etot_dev = 0.5

```

```

pop_dev: Maximal allowed variation in the norm of the adiabatic population.
The current value of pop_dev is: 0.1
Enter the new value of pop_dev : 0.05 <ENTER>
Setting pop_dev = 0.05

```

34. Exit nxinp and run:

```
> $NX/diagnostic.pl
```

35. The result is the file diag.log. It contains a summary of what happened to the trajectories. It looks like:

```
Diagnostic of trajectories 1 to 60
```

NEWTON-X tutorial

```

Path to the trajectories: /home/TUTORIAL/CNH4_MCSCF_DYN_S2/TRAJECTORIES
Initial time (fs): 0.0
Max. Energy deviation(eV): 0.5
Max. population deviation: 0.05
Number of states: 3
Normal termination: 36 ! Normal termination
Error termination: 24 ! Error termination

```

```

TRAJECTORY 1:
moldyn.pl: ::ERROR:: step = 60 time = 30 fs
Suggestion: make analysis until time (fs): 30.00

```

```

TRAJECTORY 2:
Normal termination
Suggestion: make analysis until time (fs): 100.00

```

```

...
Distribution of trajectories:
Number of trajs finished between 0.0 and 25 fs: 4
Number of trajs finished between 25 and 50 fs: 8
Number of trajs finished between 50 and 75 fs: 5
Number of trajs finished between 75 and 100 fs: 43
...

```

36 trajectories had normal termination and 43 performed at least 75 fs before finishing.

A trajectory finished in error can still contain relevant information. One of the most often reason for finishing in error is the connection with the adequacy of electronic structure method to compute the energies and gradients for some specific nuclear geometry.

For instance, dynamics trajectories performed with TD-DFT will crash as soon as the molecule enters in a region of strong multireference character. Trajectories performed with CASSCF may crash if the molecule dissociates and the necessary anti-bonding orbitals are not in the active space.

The dynamics information until these critical points, however, usually is correct and can be useful for the global statistical analysis.

For each trajectory, diagnostic.pl program prints until which time the calculation is reliable according to the criteria defined in its input. The log file, for example, says that for TRAJ1, data until 30 fs can be used.

It is not mandatory to run diagnostic.pl before the statistical analysis but it is quite advisable.

If the statistical analysis program finds the diag.log file, it will automatically use the “suggested time” to decide which data to use from each trajectory. You can change these suggested times in diag.log if you want.

36. Run nxinp and select option 6: “Set statistical analysis”.

```

MAIN MENU

1. GENERATE INITIAL CONDITIONS

2. SET BASIC INPUT

3. SET GENERAL OPTIONS

4. SET NONADIABATIC DYNAMICS

```


5. GENERATE TRAJECTORIES AND SPECTRUM

6. SET STATISTICAL ANALYSIS

7. EXIT

Select one option (1-7): 6 <ENTER>

37. Make the input for statistical analysis. Start making the “wave function analysis”.

```

What do you want to do?
  1 - Generate input for diagnostic (only statistics on errors)
  2 - Generate input for statistical analysis (statistics on wavefunction,
energies, etc.)
  3 - Return to main menu

```

Enter the option (default = 2): 2 <ENTER>

```

itrj: Initial trajectory to be analysed.
The current value of itrj is: 1
Enter the new value of itrj : <ENTER>
Setting itrj = 1

```

```

jtrj: Final trajectory to be analysed.
The current value of jtrj is: 10
Enter the new value of jtrj : 60 <ENTER>
Setting jtrj = 60

```

```

tmin: Initial time for the analysis.
The current value of tmin (fs) is: 0
Enter the new value of tmin (fs) : <ENTER>
Setting tmin = 0

```

```

tmax: Final time for the analysis.
The current value of tmax (fs) is: 100
Enter the new value of tmax (fs) : <ENTER>
Setting tmax = 100

```

```

dt: Time step in which outputs are written.
    If TRAJ1/control.dyn is found, default is DT*KT,
    otherwise default is 0.5 fs.
The current value of dt (fs) is: 0.5
Enter the new value of dt (fs) : <ENTER>
Setting dt = 0.5

```

```

proptype: Kind of properties to be analysed.
  1. Energy.
  2. Wave function.
  3. Internal coordinates.
  4. Internal forces (only for COLUMBUS dynamics).
  5. Velocity autocorrelation.
The current value of proptype is: 1
Enter the new value of proptype : 2 <ENTER>

```

```

nstat: Number of states to be analysed.
The current value of nstat is: 2
Enter the new value of nstat : 3 <ENTER>
Setting nstat = 3

```

```

complete_data: Complete data for broken trajectories.
  0. Do not complete data. (default)
  Other positive value. If the last time in the trajectory
  is larger than complete_data, repeat last set of data until
  tmax. Neglect trajectories whose last time is
  smaller than complete_data. (Only for proptype = 2.)
The current value of complete_data is: 0

```

Enter the new value of complete_data : <ENTER>
Setting complete_data = 0

38. Exit nxinp and run:

```
> $NX/analysis.pl > analysis.log &
```

analysis.pl program makes averages over trajectories for several different properties.

39. If everything runs normally, analysis.log ends with:

```
analysis: End of analysis
===== NEWTON-X ends here =====
```

40. Go to the directory ANALYSIS and look at file prop.2. It looks like:

```
!Traj Time/fs SA SB SA.SB a0 a1 a2
  1 0.00 3 3 3.3 0.0000 0.0000 1.0000
  1 0.50 3 3 3.3 0.0000 0.0041 0.9959
  1 1.00 3 3 3.3 0.0000 0.1007 0.8993
...
  1 6.00 3 3 3.3 0.0000 0.4545 0.5455
  1 6.50 3 2 3.2 0.0000 0.6710 0.3290
  1 7.00 2 2 2.2 0.0000 0.8052 0.1948
...
 60 15.00 3 3 3.3 0.0000 0.0388 0.9612
 60 15.50 3 3 3.3 0.0000 0.0628 0.9372
 60 16.00 3 3 3.3 0.0000 0.0927 0.9073
```

Trajectory 1 starts at time 0 fs in surface 3 (given by SA) and ends this time stem still on surface 3 (given by SB). In this step, all population is in surface 3 ($a_2 = |\chi_{22}|^2 = 1$).

At time 6.5 fs, TRAJ1 starts on surface 3 and ends on surface 2, meaning that a hopping took place. Now $|\chi_{22}|^2 = 0.3290$.

This description continues for all trajectories until TRAJ60, for which only data until 16.0 fs was used (because of the instruction in diag.log).

41. Look at mean_value.2.

```
!Time/fs N N0 <a0> da0 N1 <a1> da1 N2 <a2> da2
  0.00 60 0.000 0.000 0.000 0.000 0.000 0.000 1.000 1.000 0.000
  0.50 60 0.000 0.000 0.000 0.000 0.001 0.001 1.000 0.999 0.001
  1.00 60 0.000 0.000 0.000 0.000 0.019 0.080 1.000 0.981 0.080
...
 49.50 48 0.542 0.530 0.483 0.417 0.431 0.475 0.042 0.039 0.183
 50.00 48 0.542 0.528 0.481 0.417 0.435 0.472 0.042 0.036 0.173
 50.50 48 0.521 0.532 0.480 0.438 0.437 0.468 0.042 0.031 0.147
...
 99.00 36 0.722 0.733 0.420 0.222 0.211 0.382 0.056 0.056 0.231
 99.50 36 0.722 0.738 0.419 0.222 0.207 0.381 0.056 0.056 0.232
100.00 36 0.722 0.743 0.415 0.222 0.201 0.376 0.056 0.056 0.232
```

This file contains the average over all trajectories as a function of time.

A time 1 fs, 60 trajectories were used to compute the averages. The fraction of trajectories on state S_2 was $N_2 = 1$, and the average adiabatic population was $\langle |\chi_{22}|^2 \rangle = 0.981$ with standard deviation of 0.080.

At time 100, only 36 trajectories were used to compute the average, most of the trajectories were in the ground state (0.722), and the adiabatic population of the ground state was $\langle |\chi_{22}|^2 \rangle = 0.743$.

42. Plot the fraction of trajectories (occupation) and the average adiabatic population for the second excited state as a function of time (Fig. 11).

```
> gnuplot
gnuplot>plot[x=1:100] 'mean_value.2' using 1:9 with lines,'mean_value.2' using 1:10
```

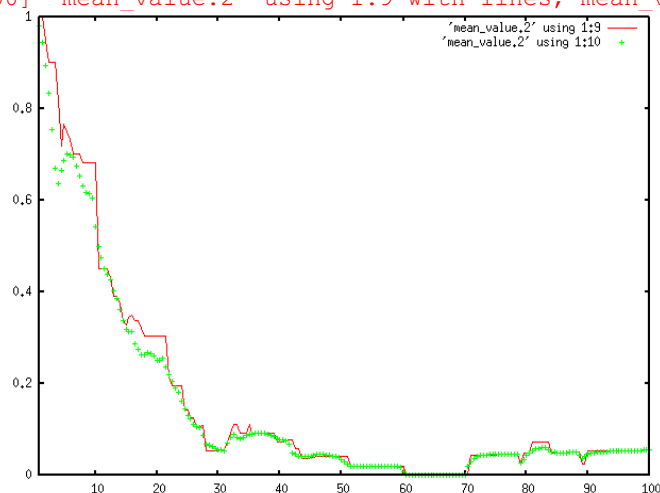


Fig. 11. Fraction of trajectories (solid line) and average adiabatic population (dots) in the second excited state as a function of time.

Fig. 11 shows an exponential decay of the population with a time constant (lifetime) of about 20 fs.

One important test for the quality of the surface hopping dynamics is the comparison between the occupation (fraction of trajectories) and the average adiabatic population.¹⁴ They should be more or less the same.

43. Go to TRAJECTORIES directory, run nxinp again, select Statistical analysis option and choose analysis of “Internal coordinates”.

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

MAIN MENU

1. GENERATE INITIAL CONDITIONS

2. SET BASIC INPUT

3. SET GENERAL OPTIONS
```

4. SET NONADIABATIC DYNAMICS
5. GENERATE TRAJECTORIES AND SPECTRUM
6. SET STATISTICAL ANALYSIS
7. EXIT

Select one option (1-7): 6 <ENTER>

What do you want to do?

- 1 - Generate input for diagnostic (only statistics on errors)
- 2 - Generate input for statistical analysis (statistics on wavefunction, energies, etc.)
- 3 - Return to main menu

Enter the option (default = 2): <ENTER>

Would you like to delete old input files? (prop.inp) y <ENTER>

itrj: Initial trajectory to be analysed.
The current value of itrj is: 1
Enter the new value of itrj : <ENTER>
Setting itrj = 1

jtrj: Final trajectory to be analysed.
The current value of jtrj is: 10
Enter the new value of jtrj : 60 <ENTER>
Setting jtrj = 60

tmin: Initial time for the analysis.
The current value of tmin (fs) is: 0
Enter the new value of tmin (fs) : <ENTER>
Setting tmin = 0

tmax: Final time for the analysis.
The current value of tmax (fs) is: 100
Enter the new value of tmax (fs) : <ENTER>
Setting tmax = 100

dt: Time step in which outputs are written.
If TRAJ1/control.dyn is found, default is DT*KT,
otherwise default is 0.5 fs. The current value of dt (fs) is: 0.5
Enter the new value of dt (fs) : <ENTER>
Setting dt = 0.5

proptype: Kind of properties to be analysed.

1. Energy.
2. Wave function.
3. Internal coordinates.
4. Internal forces (only for COLUMBUS dynamics).
5. Velocity autocorrelation.

The current value of proptype is: 1
Enter the new value of proptype : 3 <ENTER>

nstat: Number of states to be analysed.
The current value of nstat is: 2
Enter the new value of nstat : 3 <ENTER>
Setting nstat = 3

nic: Number of internal coordinates to be analyzed (Maximum = 100).
The current value of nic is: 1
Enter the new value of nic : 1 <ENTER>
Setting nic = 1

The internal coordinates are defined in the intcfl file in the JOB_NAD directory. The coordinate number one in this example corresponds to the CN stretching.

```
iclist: Array with the number of internal coordinates to be analyzed.
        Example: if the stretch corresponds coordinate 1 and the torsion to 12,
        and one wants to analyse both, iclist = 1,12 and nic = 2.
The current value of iclist is: 1
Enter the new value of iclist : <ENTER>
Setting iclist = 1

bmat: Internal coordinates options
      0. Get the internal coord. from output files. COLUMBUS only.
      1. Run cart2int.x program from COLUMBUS to get the internal
coordinates. In this case, an intcfl file with definition
of the internal coordinates is required.
The current value of bmat is: 0
Enter the new value of bmat : <ENTER>
Setting bmat = 0
```

44. Exit nxinp and run:

```
> $NX/analysis.pl > analysis.log &
```

analysis.pl program makes averages over trajectories for several different properties.

45. If everything runs normally, analysis.log ends with:

```
analysis: End of analysis
          ===== NEWTON-X ends here =====
```

46. Go to the directory ANALYSIS and look at file prop.3. It looks like:

```
! Traj Time/fs R_CN (Angstrom)
  1    0.00    1.3237134
  1    0.50    1.3169850
...
 60   16.00    1.6106203
 60   16.50    1.6013954
```

TRAJ1 starts with CN bond length 1.324 Å. In the next step, this distance is 1.317 Å. This information is printed for all trajectories until the last one, TRAJ60, for which only data until 16.5 fs is printed due to the restriction in diag.log.

If you had asked the analysis of more internal coordinates, they would also have appeared in this file as additional columns.

47. Look at mean_value.2.

```
  0.00  60    1.278966  0.037
  0.50  60    1.279945  0.035
  1.00  60    1.286777  0.033
...
 99.50 36    3.586967  2.436
100.00 36    3.597304  2.446
```

At time 0 fs, the average CN distance was 1.279 Å with standard deviation of 0.037. 60 trajectories were used to compute the average. At 100 fs, this average bond length increased to 3.597 Å. The standard deviation, 2.446 Å, is too large to be due only to the smaller number of trajectories included in the computation of the average (36). It may be indicating that more than one reaction channel is present, with somewhat different CN distances.

48. Plot the CN distance for all trajectories as a function of time.

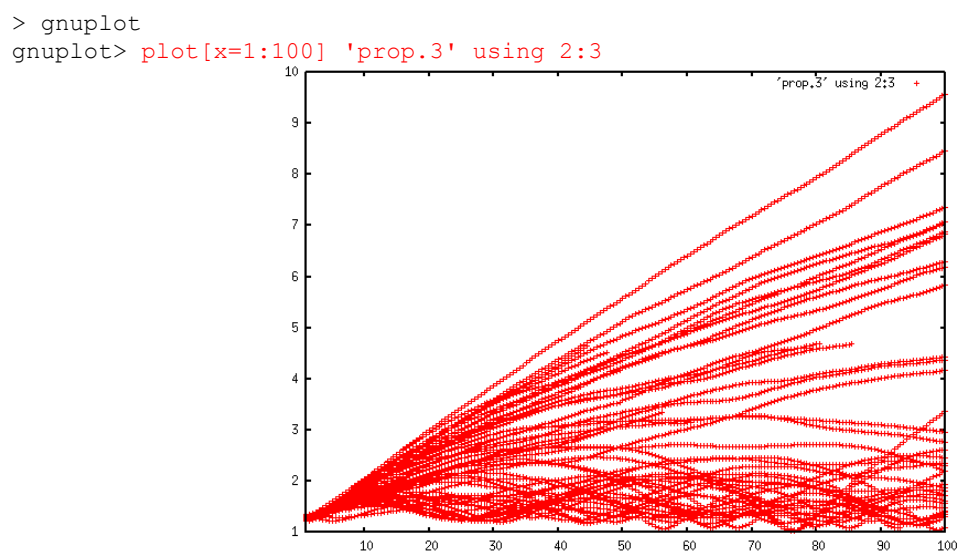


Fig. 12. CN distance (\AA) as a function of time (fs) for all 60 trajectories.

Fig. 12 shows that the trajectories split in two. Part of them keeps the CN distance oscillating below 2 \AA , while other part shows dissociation.

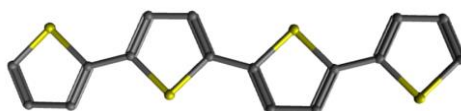
9. Initial conditions and spectrum simulation: TD-DFTB – DFTB+

In this section, we describe the procedure for absorption spectra simulation with the TD-DFTB method implemented in the version 1.3.0 of the DFTB+ code. As a model system, we choose tetrathiophene (4T) molecule. The initial ensemble of molecular geometries will be generated by a Wigner distribution in the ground vibrational state of the ground electronic state. The transition energies and moments to the first ten singlet excited states will be computed at sampled molecular geometries employing the TD-SCC-DFTB method.

Before starting with the spectrum simulations, one should define the following environmental variables: `$NX` pointing to the Newton-X /bin directory, `$DFTBP` pointing to the directory with `dftb+` executable, and `$DP_TOOLS` pointing to the directory with DP-TOOLS binaries. Additionally, one should compile the MODES program for Hessian diagonalization, which is provided within the DFTB+ package.

9.1 Molecular structure optimization

1. Structure of the tetrathiophene molecule:



2. In the TUTORIAL directory (see section 1.4), create a subdirectory called 'OPT-DFTB'.

```
> mkdir OPT-DFTB <ENTER>
```

3. In the directory 'OPT-DFTB' prepare the input, called 'dftb_in.hsd', to run a geometry optimization at DFTB level with DFTB+. To do that, follow the tutorial provided with the DFTB+ source code. An example of 'dftb_in.hsd' file for geometry optimization at SCC-DFTB level with mio-1-1 Slater-Koster set and with applied correction for dispersion interactions is given in subsection 12.5. An example DFTB+ input file for geometry optimization on SCC-DFTB level. An initial structure of the molecule has also to be provided in OPT-DFTB directory in the specific DFTB+ gen format (called 'geom.gen'). This format can be obtained by converting `geom.xyz` file using `xyz2gen` script from `$DP_TOOLS`:

```
> $DP_TOOLS/xyz2gen geom.xyz <ENTER>
```

4. After preparing the input files, geometry optimization should be done by running the dftb+ executable.

```
> $DFTBP/dftb+ <ENTER>
```

5. The optimization produces 'geo_end.gen' file containing the optimized molecular geometry. It should be converted into XYZ format with gen2xyz executable from \$DP_TOOLS.

```
> $DP_TOOLS/gen2xyz geo_end.gen <ENTER>
```

6. In the TUTORIAL directory, create another subdirectory called 4T_TDDFTB_SPEC.

```
> mkdir 4T_TDDFTB_SPEC <ENTER>
```

7. Move to the subdirectory called 4T_TDDFTB_SPEC and copy the optimized molecular structure in XYZ format from OPT-DFTB folder naming it '4T.xyz'.

```
> cd 4T_TDDFTB_SPEC <ENTER>
```

```
> cp ../OPT-DFTB/4T.xyz . <ENTER>
```

8. Convert the optimized geometry (file name '4T.xyz') into NEWTON-X format.

```
> $NX/xyz2nx < 4T.xyz <ENTER>
```

The NEWTON-X geometry file is called 'geom' and looks like

```
S 16.0 11.20712324 -2.20001573 -0.25192415 31.97207180
C 6.0 13.61609551 0.06201520 -0.12725953 12.00000000
C 6.0 12.64588999 2.46987120 -0.07542787 12.00000000
C 6.0 9.95182112 2.54012375 -0.13337266 12.00000000
C 6.0 8.83285060 0.16586502 -0.23016987 12.00000000
C 6.0 6.15850902 -0.46076190 -0.29464519 12.00000000
S 16.0 3.78592384 1.90536030 -0.27037962 31.97207180
C 6.0 1.32112682 -0.36482546 -0.34481897 12.00000000
C 6.0 2.35390828 -2.78436019 -0.39009327 12.00000000
C 6.0 5.03317076 -2.83620067 -0.36429662 12.00000000
H 1.0 1.21660696 -4.49581763 -0.44180331 1.00782504
H 1.0 6.10241244 -4.59191511 -0.39497972 1.00782504
H 1.0 15.59579524 -0.47195449 -0.09619471 1.00782504
H 1.0 13.81675372 4.15502362 0.00513630 1.00782504
H 1.0 8.88412329 4.29684022 -0.09990956 1.00782504
C 6.0 -1.32104394 0.36479169 -0.34479218 12.00000000
C 6.0 -2.35393478 2.78433325 -0.38997763 12.00000000
C 6.0 -5.03320791 2.83624261 -0.36414719 12.00000000
C 6.0 -6.15847396 0.46071841 -0.29455511 12.00000000
S 16.0 -3.78592974 -1.90536348 -0.27039128 31.97207180
C 6.0 -8.83290203 -0.16583303 -0.23006987 12.00000000
C 6.0 -9.95180086 -2.54016698 -0.13333519 12.00000000
C 6.0 -12.64582598 -2.46991739 -0.07535844 12.00000000
C 6.0 -13.61607988 -0.06203125 -0.12710877 12.00000000
S 16.0 -11.20706409 2.20001389 -0.25173369 31.97207180
H 1.0 -1.21655925 4.49586686 -0.44164996 1.00782504
H 1.0 -6.10239188 4.59190532 -0.39476305 1.00782504
H 1.0 -8.88412217 -4.29683243 -0.09993031 1.00782504
H 1.0 -13.81674266 -4.15503583 0.00516462 1.00782504
H 1.0 -15.59581438 0.47194875 -0.09600566 1.00782504
```


The second column contains the atomic number, and the following three columns contain the x, y and z coordinates in atomic units (Bohr). The last column contains the atomic masses, which can be eventually changed to simulate isotopic effects. The file can be freely formatted. The conversion back from NEWTON-X format to xyz can be done with.

> \$NX/nx2xyz

After running this program, the xyz-format geometry is written to file 'geom.xyz'.

9.2 Normal modes computation

9. In the TUTORIAL directory, create another subdirectory called 'FREQ-DFTB' to run a normal mode calculation:

```
> mkdir FREQ-DFTB <ENTER>
```

10. Change to this directory and copy 'geo_end.gen' file from the OPT-DFTB directory renaming it to 'geom.gen':

```
> cd FREQ-DFTB <ENTER>
> cp ../OPT-DFTB/geo-end.gen geom.gen <ENTER>
```

11. Prepare the input and run a Hessian computation at the SCC-DFTB level with DFTB+. To do that, follow the specific DFTB+ documentation. An example of the DFTB+ input for Hessian computation is given in subsection 12.6.

12. Once dftb+ executable is run, 'hessian.out' file containing Hessian matrix will be produced

```
> $DFTBP/dftb+ <ENTER>
```

13. After the 'hessian.out' file is obtained, normal modes should be computed with the MODES program provided within the DFTB+ package. An input called 'modes_in.hsd' should be created in the FREQ-DFTB directory. An example of 'modes_in.hsd' file is given in subsection 12.7. The PlotModes keyword in the 'modes_in.hsd' file should be defined as: PlotModes = -3N :- 1, where N is the number of atoms in the molecule. In the case of tetrathiophene, N equals 30.

14. When the MODES program is run,

```
> $MODES/modes <ENTER>
```

the output file, called 'modes.xyz', containing the 3N normal modes and frequencies is obtained.

9.3 Energy and transition moment input

15. The TUTORIAL directory now looks like:

```
> ls <ENTER>
```

```
FREQ-DFTB OPT-DFTB 4T_TDDFTB_SPEC
```

16. Move to the directory '4T_TDDFTB_SPEC' and create a new subdirectory called JOB_AD.

```
> cd 4T_TDDFTB_SPEC <ENTER>
> mkdir JOB_AD <ENTER>
```

The directory must be named JOB_AD since NEWTON-X will search for it.

17. Move into JOB_AD and prepare two files named, 'geom.gen' and 'dftb_in.hsd' respectively. 'geom.gen' should be copied from the FREQ-DFTB directory:

```
> cd JOB_AD <ENTER>
> cp ../../FREQ-DFTB/geom.gen . <ENTER>
```

In this case, the 'dftb_in.hsd' file is the DFTB+ input file for the computation of excitation energies and oscillator strengths with TD-DFTB. An example of dftb_in.hsd file for the computation with TD-SCC-DFTB method and 3ob-3-1 Slater-Koster set and with dispersion corrections accounted for with the Lennard-Jones potential with the Universal Force Field (UFF) is given below:

```
> vi dftb_in.hsd <ENTER>
Geometry = GenFormat {
  <<< "geom.gen"
}

Driver = {}

Hamiltonian = DFTB {
  SCC = Yes
  Dispersion = LennardJones {
    Parameters = UFFParameters {}
  }
  SlaterKosterFiles = Type2FileNames {
    Prefix = "/path/to/sk/folder/3ob-3-1/"
    Separator = "-"
    Suffix = ".skf"
  }
  MaxAngularMomentum {
    H = "s"
    C = "p"
    S = "d"
  }
  Filling = Fermi {
    Temperature [Kelvin] = 0.0
  }
}

ExcitedState{
  Casida{
    Symmetry = Singlet
    NrOfExcitations = 10
    StateOfInterest = 0
    WriteTransitions = Yes
    WriteTransitionDipole = Yes
  }
}

Analysis{
}

Options {
  WritedetailedOut = Yes
}
```

```

ParserOptions {
ParserVersion = 4
}

Geometry = GenFormat {
  <<< "geom.gen"
}

```

For DFTB+ calculations, it is mandatory that the 'JOB_AD' directory contains the above two files, 'geom.gen' and 'dftb_in.hsd.'

The second order TD-SCC-DFTB computations should, in principle, be performed with mio-1-1 Slater-Koster set. However, this set does not cover the whole range of internuclear distances relevant for nonadiabatic dynamics simulations. Therefore, we recommend using 3ob-3-1 Slater-Koster set, where this problem does not occur. In this case, 3ob-3-1 Slater-Koster set produces the values of excitation energies very close to those obtained with mio-1-1 set.

We recommend running the TD-DFTB computations with the third order corrected DFTB Hamiltonian which should be employed with 3ob-3-1 Slater-Koster set. An example of dftb_in.hsd file for TD-DFTB3 computation is given in subsection 12.8. When TD-DFTB3 method is applied, the geometry optimization and normal modes computation should be performed using DFTB3 Hamiltonian as well.

It is recommended that prior to simulations it should be tested whether the desired number of roots could be computed with TD-DFTB. If the number of roots is relatively small, it could happen that the diagonalization procedure in TD-DFTB is unstable. To circumvent this problem, a sufficiently large number of excitations should be computed (NrOfExcitations variable in 'dftb_in.hsd') independently of the desired number of states in the spectrum simulations.

Before submitting running any NEWTON-X job is highly advisable to run the job in JOB_AD directory just to test whether the input and outputs are OK. In the current case, just copy the content of the JOB_AD into a test directory and run the DFTB+. Check whether the roots and the oscillator strengths are computed and show reasonable values.

From a general point of view, at this stage we have:

- 1) optimized the molecular structure;*
- 2) computed the normal modes;*
- 3) converted the optimized structure file 'name.xyz' into NEWTON-X format 'geom';*
- 4) created the directory (e.g. 4T_TDDFTB_SPEC) in which the spectrum will be computed using the NEWTON-X program interfaced with DFTB+.*

9.4 NEWTON-X input

18. Move to directory TUTORIAL/4T_TDDFTB_SPEC and create a subdirectory called IC-TDDFTB.

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```
> cd TUTORIAL/THIOPHENE_TDDFTB_SPEC <ENTER>
> mkdir IC-TDDFTB <ENTER>
```

19. Move to this directory and copy the optimized DFTB geometry file in NEWTON-X format (geom) there.

```
> cd IC-TDDFTB <ENTER>
> cp ../geom . <ENTER>
```

20. Copy the JOB_AD directory and the normal modes file into IC-TDDFTB.

```
> cp -rf ../JOB_AD .
> cp ../../FREQ-DFTB/modes.xyz .
> ls <ENTER>
```

```
JOB_AD geom modes.xyz
```

```
> ls JOB_AD/ <ENTER>
```

```
dftb_in.hsd geom.gen
```

21. Run the nxinp program and select option 1: Generate initial conditions.

nxinp is the input tool for NEWTON-X. All input procedures, from the initial condition generation, through the dynamics inputs, to the statistical analysis options are performed with it.

```
> $NX/nxinp
```

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

```
MAIN MENU
```

```
1. GENERATE INITIAL CONDITIONS
```

```
2. SET BASIC INPUT
```

```
3. SET GENERAL OPTIONS
```

```
4. SET NONADIABATIC DYNAMICS
```

```
5. GENERATE TRAJECTORIES AND SPECTRUM
```

```
6. SET STATISTICAL ANALYSIS
```

```
7. EXIT
```

```
Select one option (1-7): 1 <ENTER>
```

22. Select the adequate options for the initial condition properties.

nxinp will guide you through a set of questions. Each of them contains a short explanation and the available options. Most of times, the default value is the best option. To accept the default you can just press <ENTER>.

```

...
nact: Distribution:
      1 - Classic harmonic oscillator
      2 - Q/P-uncorrelated quantum harmonic oscillator (Wigner)
      3 - Q/P-correlated quantum harmonic oscillator
      4 - Pick points from previous dynamics
      5 - Random-velocities generation
      6 - Single point on a previous calculation
The current value of nact is: 2
Enter the new value of nact : <ENTER>
Setting nact = 2

numat: Number of atoms.
The current value of numat is: 30
Enter the new value of numat : <ENTER>
Setting numat = 30

npoints: Number of initial conditions to be generated
The current value of npoints is: 1
Enter the new value of npoints : 100 <ENTER>
Setting npoints = 100

```

npoints sets the number of initial conditions that should be generated. This number depends on how many points you want to compute to generate the spectrum and how many trajectories you want to simulate.

In real applications, you will need much more than 100 points. 500 may be a good number. You can also run several short jobs with few points in each one and merge them afterward using the tool "merge_initcond.pl." Thus, with 10 computers running 50 points each, you can quickly have 500 points. See in section 4.5 a note about how to split and merge the jobs.

```

file_geom: File containing the equilibrium geometry.
The current value of file_geom is: 'geom'
Enter the new value of file_geom : <ENTER>
Setting file_geom = 'geom'

ipro: Read vibrational modes from:
      1 - GAMESS output
      2 - TURBOLMOLE output
      3 - COLUMBUS output
      4 - GAUSSIAN output
      5 - MOLDEN file
      6 - DFTB output
      7 - ACES2 output
      8 - BAGEL output
      9 - DFTB+ output
The current value of iprog is: 4
Enter the new value of iprog : 9 <ENTER>
Setting iprog = 9

file_nmodes: File containing the normal modes.
The current value of file_nmodes is: modes.xyz
Enter the new value of file_nmodes : modes.xyz <ENTER>

anh_f: Multiply harmonic frequencies by this factor.
The current value of anh_f is: 1
Enter the new value of anh_f : 1 <ENTER>
Setting anh_f = 1

temp: Temperature.
The current value of temp [K] is: 0.0
Enter the new value of temp [K] : 0.0
Setting temp = 0.0

Are these initial conditions for photoelectron spectrum? (y/n) n

```

```

chk_e: Restrict (or do not) the statistical distribution:
      0 - Do not check the energies.
      1 - Check the energies between states NIS and NFS.
The current value of chk_e is: 0
Enter the new value of chk_e : 1 <ENTER>
Setting chk_e = 1

```

The next keywords define the restriction on the statistical distribution.

```

nis: Initial state (State in which the previous dynamics run. Ground state = 1.).
The current value of nis is: 1
Enter the new value of nis : 1 <ENTER>
Setting nis = 1

```

```

nfs: Final state.
The current value of nfs is: 2
Enter the new value of nfs : 11 <ENTER>
Setting nfs = 11

```

The Wigner distribution will be generated in the ground electronic state (nis = 1), and transition energies between the ground and the tenth excited (nfs = 11) states will be computed. Indeed, with nfs = N, transition information for all states below N will also be computed and collected.

```

kvert: Center of the restriction:
      0 - Provide the energy for center of restriction
      1 - Use the vertical excitation energy of the equilibrium geometry
The current value of kvert is: 1
Enter the new value of kvert : <ENTER>
Setting kvert = 1

```

```

de: Width of restriction (center +/- de/2).
The current value of de (eV) is: 0.5
Enter the new value of de (eV) : 100 <ENTER>
Setting de = 100

```

This large “de” implies that this restriction will not be used. It can be imposed later on.

```

prog: Program and method to compute vertical excitation energies:
      1 - COLUMBUS
      2.0 - TURBOMOLE CC2
      2.1 - TURBOMOLE TDDFT
      2.2 - TURBOMOLE ADC2
      5 - DFTB
      6.5 - GAUSSIAN 09
      8.0 - DFTB+ (Legacy; QM/MM ground state)
      8.5 - DFTB+ (New version; TD-DFTB)
      9 - DFT-MRCI
      10 - GAMESS MCSCF
      12 - BAGEL
      20 - HYBRID ENERGY

```

```

The current value of prog is: 6.5
Enter the new value of prog : 8.5 <ENTER>
Setting prog = 8.5

```

```

iseed: Random number seed.
      0 - default seed value.
     -1 - set random seed.
     >0 - (integer) set specific value for the seed.
The current value of iseed is: 0
Enter the new value of iseed : <ENTER>
Setting iseed = 0

```

```

lvprt: Print level.
      1 - standard level
      2 - debug level
The current value of lvprt is: 1
Enter the new value of lvprt : <ENTER>
Setting lvprt = 1

```

23. Exit nxinp.

9.5 Running NEWTON-X: initial conditions

24. Run the initial condition generation program.

```
> $NX/initcond.pl > initcond.log &
```

In general, with $chk_e = 1$, you might want to submit this job to a batch system. Files “pini” and “pini-ew” in $\$NX/./batch/$ directory are templates that can be adapted to your batch system.

Splitting and merging jobs:

To split the job among several computers, just prepare the input as it was done until here.

Then run

```
> $NX/split_initcond.pl
```

This program will create a directory called INITIAL_CONDITIONS and inside it a sequence of subdirectories called I1, I2, ..., each one containing a complete set of input files.

Copy each directory to a different computer and run the job normally.

To merge the jobs, after the calculations, copy the directories I1, I2, ... back to INITIAL_CONDITIONS directory and from inside this directory run

```
> $NX/merge_initcond.pl
```

This program will ask for the number of jobs to be merged, and it will create a new directory called I_merged with merged results. Move to this directory and proceed with the spectrum simulation as explained below.

9.6 Checking the results

25. Normal job termination is indicated at the end of initcond.log file by:

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

26. The main information is written to the final_output file.

27. Each final_ouput.1.# file (# = 1,11 in this case) contains the same 100 geometries and velocities generated according to the Wigner distribution. For instance, final_output.1.2 contains transition energies and oscillator strengths to excitations into state 2 (first excited state S_1), while final_output.1.3 contains the same information to excitations into state 3 (second excited state S_2) and so on.

9.7 Generating the spectrum

28. Go to directory TUTORIAL/4T_TDDFTB_SPEC and create the directory SPECTRUM.

```
> mkdir SPECTRUM !This name is not compulsory.
```

29. Move to this directory and copy each final_output files there.

```
> cd SPECTRUM <ENTER>
```

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```
> cp ../IC-TDDFTB/final_output* . <ENTER>
```

30. Run nxinp and select option 5: “Generate Trajectories and Spectrum.”

```
> $NX/nxinp
```

1. GENERATE INITIAL CONDITIONS
2. SET BASIC INPUT
3. SET GENERAL OPTIONS
4. SET NONADIABATIC DYNAMICS
5. GENERATE TRAJECTORIES AND SPECTRUM
6. SET STATISTICAL ANALYSIS
7. EXIT

```
Select one option (1-7): 5 <ENTER>
```

31. Go through the next options.

```
type: What do you want to do?
      1 - Generate spectrum
      2 - Select initial conditions for multiple initial states
      3 - Generate trajectories
      4 - Return to main menu
The current value of type is: 3
Enter the new value of type : 1 <ENTER>
Setting type = 1
```

If for this first option you are asked for “kindjob” instead “type,” this means you are using an old version of NEWTON-X. Contact the distributors to get an updated version of the program.

```
nis: Initial state.
The current value of nis is: 1
Enter the new value of nis : <ENTER>
Setting nis = 1
```

```
nfs: Array of final states (comma or dash separated, e.g., 2-4 or 2,3,4).
For trajectories generation only one final state is allowed.
The current value of nfs is: 2
Enter the new value of nfs : 2-11 <ENTER> !Spectrum including each state
Setting nfs = 2-11
```

If nfs should be given as a ‘space separated’ list, this means that you are using an old version of NEWTON-X. Get an updated version at www.newtonx.org.

```
prob_kind: Formula to calculate the transition probabilities:
          A - Einstein-coefficient A (spontaneous emission)
          B - Einstein-coefficient B (induced absorption or induced emission)
          E - Fluorescence (radiative decay rate)
          F - Absorption (photoabsorption cross-section)
          I - Ionization (photoionization cross-section)
The current value of prob_kind is: F
Enter the new value of prob_kind : F
Setting prob_kind = F
```



```

screen: Energy restriction
      0 - don't apply any restriction
      1 - use the original energy restriction written in the final_output files
      2 - apply new energy restriction
The current value of screen is: 0
Enter the new value of screen : 0
Setting screen = 0

```

If the oscillator strength is not available, but the transition energy is, it is still possible to simulate the spectrum by giving a value to the oscillator strength in os_condon option. In this case, all transitions will be computed with the same oscillator strength. For only one final state this option is not bad, but it can be completely inadequate when more than one final state is selected.

```

os_condon: Oscillator strength:
-1- try to read from final_output file.
  x - oscillator strength is always x (Condon approximation).
The current value of os_condon is: -1
Enter the new value of os_condon : -1
Setting os_condon = -1

norm: Normalization of transition intensities:
      local - Use energy-restricted data set
      global - Use complete data set
The current value of norm is: local
Enter the new value of norm : <ENTER> ! with no energy restriction, doesn't
Setting norm = local ! matter.

seed: Seed for the random number generation
      0 - a default random number seed is used
      1 - a randomized seed is used
      Any other positive integer is used as the random number seed
The current value of seed is: 0
Enter the new value of seed : <ENTER>
Setting seed = 0

l_shape: Line shape:
      gauss - Normalized Gaussian function.
      lorentz - Normalized Lorentzian function.
The current value of l_shape is: lorentz
Enter the new value of l_shape : <ENTER>
Setting l_shape = lorentz

delta: Phenomenological broadening of the spectrum.
The current value of delta (eV) is: 0.05
Enter the new value of delta (eV) : <ENTER>
Setting delta = 0.05

```

“delta” is possibly the only option that you need to play with. It controls the width of the Gaussian curve attributed to each one of the 100 transitions (50 initial conditions × 2 final states).

```

temp: Temperature.
The current value of temp (K) is: 0
Enter the new value of temp (K) : <ENTER>

nref: Refraction index.
The current value of nref is: 1
Enter the new value of nref : <ENTER>

eps: Distance between consecutive points in the spectrum.
The current value of eps (eV) is: 0.005
Enter the new value of eps (eV) : <ENTER>
Setting eps = 0.005

```

```

kappa: The range of the spectrum is defined between
Emin-kappa*delta and Emax+kappa*delta, where kappa is an integer.
The current value of kappa is: 3
Enter the new value of kappa : <ENTER>
Setting kappa = 3

```

Processing data: This may take some minutes. Please, wait...

32. Exit nxinp.

33. The simulated cross section using a Lorentzian line shape with phenomenological broadening $\delta = 0.05$ eV is written to cross-section.dat. Looking at this file, we see:

```

!      DE/eV      lambda/nm      sigma/A^2      +/-error/A^2
1.7880  6.9342E+02  0.05927871    0.00784537
1.7930  6.9149E+02  0.06104776    0.00821668
1.7980  6.8957E+02  0.06292593    0.00862500
1.8030  6.8765E+02  0.06492433    0.00907183
1.8080  6.8575E+02  0.06705568    0.00956252
1.8130  6.8386E+02  0.06933466    0.01010346
...

```

```

> gnuplot
gnuplot> plot 'cross-section.dat' using 1:3 with lines

```

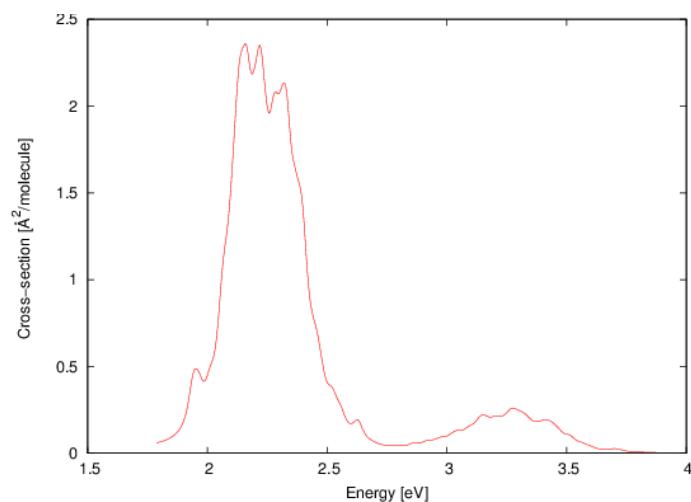


Fig. 13. Photoabsorption cross section ($\text{\AA}^2 \cdot \text{molecule}^{-1}$) of 4T as a function of energy (eV) computed at the TD-SCC-DFTB/3ob-3-1 level.

10. Surface hopping dynamics: TD-DFTB – DFTB+

In this section, we explain how to run surface hopping dynamics simulation with TD-DFTB method using the DFTB+ code. As a model system, we again use tetrathiophene (4T) molecule. The initial conditions generated in Chapter 9 of this tutorial will be used. The trajectory time will be 300 fs with 0.5 fs time step. The electronic structure computations will be run with TD-SCC-DFTB with 3ob-3-1 Slater-Koster set. The dynamics will start in the S_2 state, with initial conditions selected in the interval of 1.75 to 2.75 eV. An energy width of ± 0.5 eV allows to generate trajectories belonging to the whole first absorption band, see Fig. 13. This will generate a large number of trajectories and, for practical reasons, only a few of them will be computed and analyzed in this tutorial).

Before starting with the dynamics simulations, one should define the following environmental variables: \$NX pointing to the Newton-X /bin directory, \$DFTBP pointing to the directory with dftb+ executable, and \$DP_TOOLS pointing to the directory with DP-TOOLS binaries.

10.1 Copying the initial conditions

1. Go to TUTORIAL directory create a subdirectory called 4T_TDDFTB_DYN:

```
> mkdir 4T_TDDFTB_DYN <ENTER>
```

2. Move to this directory and copy the geom file and initial conditions file for the second excited state there.

```
> cd 4T_TDDFTB_DYN
> cp ../4T_TDDFTB_SPEC/geom geom
> cp ../4T_TDDFTB_SPEC/IC_TDDFTB/final_output.1.3 final_output
```

3. Create a subdirectory called JOB_AD.

4. Check the content of the 4T_TDDFTB_DYN directory:

```
> ls <ENTER>
```

```
final_output  geom  JOB_AD
```

The directory must be named JOB_AD since NEWTON-X will search for it.

10.2 Preparing electronic structure input

5. Move to JOB_AD and copy the 'geom.gen' file from the JOB_AD directory created for the spectrum simulations. Create the file 'dftb_in.hsd' input file for the calculation of the excited states. The contents of the JOB_AD directory should be:

```
> ls <ENTER>
dftb_in.hsd geom.gen
```

We here give an example of the 'dftb_in.hsd' file for the computation of excitation energies:

```
> vi dftb_in.hsd

Geometry = GenFormat {
  <<< "geom.gen"
}

Driver = {}

Hamiltonian = DFTB {
  SCC = Yes
  Dispersion = LennardJones {
    Parameters = UFFParameters {}
  }
  SlaterKosterFiles = Type2FileNames {
    Prefix = "/path/to/sk/folder/3ob-3-1/"
    Separator = "-"
    Suffix = ".skf"
  }
  MaxAngularMomentum {
    H = "s"
    C = "p"
    S = "d"
  }
  Filling = Fermi {
    Temperature [Kelvin] = 0.0
  }
}

ExcitedState{
  Casida{
    Symmetry = Singlet
    NrOfExcitations = 10
    StateOfInterest = 0
    WriteTransitions = Yes
    WriteTransitionDipole = Yes
  }
}

Analysis{
}

Options {
  WritedetailedOut = Yes
}

ParserOptions {
  ParserVersion = 4
}
```

The initial DFTB+ input file should contain options for excited states computation, including options for writing the basic outputs as in the given example (WriteTransitions, WriteTransitionDipole, and WriteDetailedOut options should be set to Yes). During dynamics, this file is automatically updated.

Before submitting running any NEWTON-X job is highly advisable to run the job in JOB_AD directory just to test whether the input and outputs are OK. In the current case, just copy the content of the JOB_AD into a test directory and run the DFTB+ job. Check whether the roots are computed and show reasonable values.

10.3 NEWTON-X input

6. Run nxinp.

```
> $NX/nxinp
```

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

MAIN MENU

1. GENERATE INITIAL CONDITIONS

2. SET BASIC INPUT

3. SET GENERAL OPTIONS

4. SET NONADIABATIC DYNAMICS

5. GENERATE TRAJECTORIES AND SPECTRUM

6. SET STATISTICAL ANALYSIS

7. EXIT
```

```
Select one option (1-7): 2 <ENTER>
```

7. Select option 2: “set basic input” and answer the questions to set the dynamics options.

```
nat: Number of atoms.
The current value of nat is: 30
Enter the new value of nat : <ENTER>
Setting nat = 30

nstat: Number of states.
The current value of nstat is: 2
Enter the new value of nstat : 3 <ENTER>
Setting nstat = 3

nstatdyn: Initial state (1 - ground state).
The current value of nstatdyn is: 3
Enter the new value of nstatdyn : <ENTER> ! dynamics will start in state 3 (e.g.
S2)
Setting nstatdyn = 3

dt: Time step for the classical equations.
```

The current value of dt (fs) is: 0.5
 Enter the new value of dt (fs) : <ENTER>
 Setting dt = 0.5

tmax: Total duration of the trajectory.
 The current value of tmax (fs) is: 100
 Enter the new value of tmax (fs) : 300 <ENTER>
 Setting tmax = 300

prog: Quantum chemistry program and method
 0 - ANALYTICAL MODEL
 1 - COLUMBUS
 2.0 - TURBOMOLE CC2
 2.1 - TURBOMOLE TDDFT
 2.2 - TURBOMOLE ADC2
 3 - ACES2 EOM-CCSD (in development)
 4 - MOPAC (in development)
 5 - DFTB
 6.0 - GAUSSIAN CASSCF
 6.5 - GAUSSIAN(09) TDDFT
 7 - TINKER
 8 - DFTB+
 8.5 - DFTB+ (New version; TD-DFTB)
 10.0 - GAMESS
 10.1 - GAMESS ARBITRARY ADIABATIC METHOD
 12.0 - BAGEL
 12.1 - BAGEL ARBITRARY ADIABATIC METHOD
 20 - HYBRID GRADIENT

The current value of prog is: 1
 Enter the new value of prog : 8.5 <ENTER>
 Setting prog = 8.5

thres: Threshold to initiate nonadiabatic coupling calculation.
 0 - Only adiabatic dynamics.
 100 - Only nonadiabatic dynamics
 The current value of thres (eV) is: 100
 Enter the new value of thres (eV) : <ENTER>
 Setting thres = 100

Would you like to generate internal coordinate file? (default=y) y <ENTER>

8. In the main nxinp menu, you have the option to set more general options if you select either option 3 or option 4. Normally, this is not necessary, and the default values are good enough.

9. Select option 5: “generate trajectories and spectrum.”

```

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

```

MAIN MENU

1. GENERATE INITIAL CONDITIONS
2. SET BASIC INPUT
3. SET GENERAL OPTIONS
4. SET NONADIABATIC DYNAMICS

5. GENERATE TRAJECTORIES AND SPECTRUM

6. SET STATISTICAL ANALYSIS

7. EXIT

Select one option (1-7): 5 <ENTER>

10. Select the job options.

```
type: What do you want to do?
      1 - Generate absorption or emission spectrum
      2 - Generate photoelectron spectrum
      3 - Select initial conditions for multiple initial states
      4 - Generate trajectories
      5 - Return to main menu
The current value of type is: 4
Enter the new value of type : 4 <ENTER>
Setting type = 4
```

If for this first option you are asked for "kindjob" instead "type," this means you are using an old version of NEWTON-X. Contact the distributors to get an updated version of the program.

```
Would you like to apply energy and probability restrictions (y/n)? (default=n) y
<ENTER>
```

```
nis: Initial state.
The current value of nis is: 1
Enter the new value of nis : 1 <ENTER>
Setting nis = 1
```

```
nfs: Array of final states (comma or dash separated, e.g., 2-4 or 2,3,4).
For trajectories generation only one final state is allowed.
The current value of nfs is: 2
Enter the new value of nfs : 3 <ENTER>
Setting nfs = 3
```

The next keywords will allow setting the initial condition restrictions between 1.75 and 2.75 eV.

If nfs should be given as a 'space separated' list, this means that you are using an old version of NEWTON-X. Contact the distributors to get an updated version of the program.

```
prob_kind: Formula to calculate the transition probabilities:
          A - Einstein-coefficient A (spontaneous emission)
          B - Einstein-coefficient B (induced absorption or induced emission)
          E - Fluorescence (radiative decay rate)
          F - Absorption (photoabsorption cross-section)
          I - Ionization (photoionization cross-section)
The current value of prob_kind is: F
Enter the new value of prob_kind : F
Setting prob_kind = F
```

```
screen: Energy restriction
        0 - don't apply any restriction
        1 - use the original energy restriction written in the final_output files
        2 - apply new energy restriction
The current value of screen is: 0
```

```

Enter the new value of screen : 2 <ENTER>
Setting screen = 2

e_center: Center of the energy restriction.
    x      - value of the center of restriction
    ref n - use the vertical excitation of final_output.nis.n file
The current value of e_center (eV) is: 0.0
Enter the new value of e_center (eV) : 2.25 <ENTER>
Setting e_center = 2.25

e_var: Width of the energy restriction.
The current value of e_var (eV) is: 0.5
Enter the new value of e_var (eV) : 0.5 <ENTER>
Setting e_var = 0.5

os_condon: Oscillator strength:
-1 - try to read from final_output file.
    x - oscillator strength is always x (Condon approximation).
The current value of os_condon is: -1
Enter the new value of os_condon : -1 <ENTER>
Setting os_condon = -1

norm: Normalization of transition intensities:
    local - Use energy-restricted data set
    global - Use complete data set
The current value of norm is: local
Enter the new value of norm : <ENTER>
Setting norm = local

seed: Seed for the random number generation
    0 - a default random number seed is used
    1 - a randomized seed is used
    Any other positive integer is used as the random number seed
The current value of seed is: 0
Enter the new value of seed : <ENTER>
Setting seed = 0

Will the trajectories run in a batch system? n <ENTER>

Processing data: This may take some minutes. Please, wait...

```

In general, you might want to submit this job to a batch system. In this case, answer “y” to “Will the trajectories run in a batch system?”. You will be asked the name of the submission script and nxinp will look for its existence in the input directory. Files “pmold” and “pmold-ew” in \$NX/./batch/ directory are templates that can be adapted to your batch system.

11. Exit nxinp.

12. Now the input directory should contain a new directory called TRAJECTORIES, which was created by nxinp.

```
> ls
control.dyn  final_output  geom  intcfl  JOB_AD  mkdir.log  mkd.inp  TRAJECTORIES
```

13. Move to TRAJECTORIES and list the content. You will see that only 8 directories named TRAJ1, TRAJ2, ..., TRAJ8 were created. Each one of these directories contains a complete set of input files to run one independent trajectory with different initial conditions (geometry and velocities).

The number of TRAJn directories is controlled by the number of initial conditions in the final_output file and by the energy restrictions imposed.

Each accepted initial condition card is split into a geom and veloc files that appear inside TRAJn. The TRAJn structure of directories (see Fig. 9) is very important in NEWTON-X. Several tools to control the jobs and to perform statistical analysis use it.

Each TRAJn directory can be copied to a different computer or submitted to a different node of a batch system. They should, however, be grouped again after having finished the dynamics calculations.

10.4 Running NEWTON-X: dynamics simulations

14. Move to TRAJ1 and run this trajectory.

```
> cd TRAJ1
> $NX/moldyn.pl > moldyn.log &
```

15. Move to TRAJ2 and run that trajectory; redo the same until TRAJ8.

If the jobs should be submitted to a batch system you can either go to each TRAJn directory and run

```
> qsub pmold      ! pmold is the submission script
```

or in the TRAJECTORIES directory you can run

```
> $NX/submit.pl
```

In this case, you will be asked the initial and final trajectory number that should be submitted, and the submission of all these trajectories will be done automatically.

10.5 Checking the results

16. For each TRAJn, the dynamics output is in three directories:

- a. RESULTS: the dynamics information;
- b. INFO_RESTART: stored information to restart the trajectory;
- c. DEBUG: error messages, convergence information and additional electronic structure files like molecular orbital files.

and the content of each TRAJn directory looks like:

```
> ls TRAJ1/
control.dyn  DEBUG  geom  INFO_RESTART  JOB_AD  moldyn.log  RESULTS  veloc
```

17. Go to directory TRAJ1/RESULTS.

```
> cd TRAJ1/RESULTS
```

18. If it finished with error, nx.log should finish like:

```
moldyn.pl:  ::ERROR::  step =      123 time = 61.5 fs
Trying to save TEMP directory to ../DEBUG
```

In this example, the job finished with an error after 123 steps (61.5 fs). The last GAUSSIAN09 calculation was written into TRAJ1/DEBUG/TEMP and you can check what was wrong. More error messages are also written to DEBUG/runnx.error file.

19. If the job ended normally, the file nx.log should finish with:

```
moldyn.pl: End of dynamics
===== NEWTON-X ends here =====
```

20. Plot the energies (Fig. 14):

```
> $NX/plot
Number of states: 3
```

The energy information used by plot program is in the file RESULTS/en.dat. It looks like:

!Time (fs)	E0 (au)	E1 (au)	E2 (au)	E(current) (au)	Etot (au)
0.00	-40.441290	-40.359339	-40.351548	-40.351548	-40.231344
0.50	-40.455272	-40.373689	-40.366412	-40.366412	-40.232012
1.00	-40.478867	-40.397651	-40.390852	-40.390852	-40.232938
1.50	-40.497562	-40.416751	-40.410319	-40.410319	-40.233126
2.00	-40.506198	-40.425754	-40.419690	-40.419690	-40.233062
2.50	-40.504491	-40.424451	-40.418645	-40.418645	-40.233037
3.00	-40.493040	-40.413368	-40.407782	-40.407782	-40.232816
3.50	-40.474796	-40.395454	-40.390089	-40.390089	-40.232651
4.00	-40.453026	-40.374015	-40.368797	-40.368797	-40.232448
4.50	-40.432195	-40.353514	-40.348333	-40.348333	-40.231913
5.00	-40.420504	-40.342081	-40.336936	-40.336936	-40.231493
...					

If you give one more state (4, in this example), the total energy is also printed.

You can run the plot program for a sequence of trajectories either to see them on screen or only to generate pictures. To do so, go to TRAJECTORIES directory and run:

```
> $NX/plotall
```

In GNU PLOT the basic script (plot.gpi) can be:

```
set terminal postscript enhanced color solid
set xlabel 'time / fs'
set ylabel 'Energy / Hartree'
set xrange [0:200]
set key right bottom

plot\
'en.dat' u 1:2 t 'S_{0}' w p pt 6 ps 2, \
'en.dat' u 1:3 t 'S_{1}' w p pt 6 ps 2, \
'en.dat' u 1:4 t 'S_{2}' w p pt 6 ps 2, \
'en.dat' u 1:5 t 'current' w p pt 7 lt 7 ps 2
```

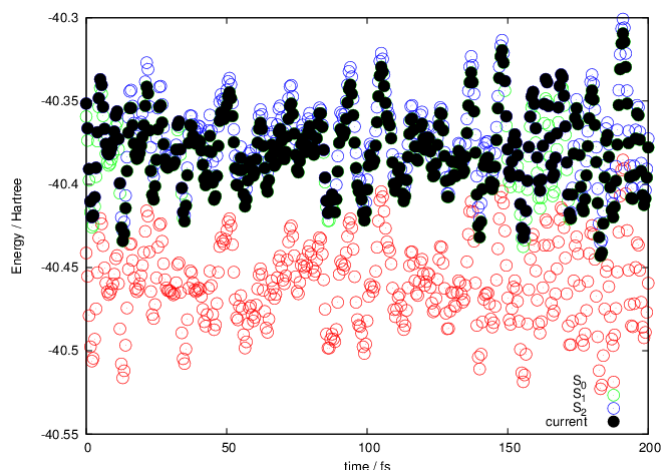


Fig. 14. Potential energies of the three states (S_0 , S_1 , and S_2) for TRAJ1, as a function of time, plotted with GNUPLOT. The black circles indicate the current state of the system at each time step.

21. Visualize the dynamics:

```
> molder dyn.mld &
```

dyn.mld file is a simple multiple-xyz format file with all geometries along the trajectory. It can be opened by most of the programs for dynamics visualization. One good option is VMD (www.ks.uiuc.edu/Research/vmd), which allow quite complete control of the timeline and excellent rendering quality.

To save disk space, dyn.mld is not automatically created starting from NEWTON-X version 1.2.5. In these new versions, you can get the xyz file by moving to the RESULTS directory and running

```
> $NX/dynout2xyz.pl
```

A file called dyn.xyz (multiple xyz format) is created and can be visualized with programs like Molden or VMD.

22. Geometry, velocities, energies and other quantities are written in a more verbose way in file dyn.out.

The first time-step looks like:

```
*** Molecular Dynamics ***

Output printed at each kt= 1 steps ( 0.50 fs).

STEP          0      Molecular dynamics on state 3      TIME =          0.00 fs
Type of dyn. =  2      N. of hoppings =  0      N. of rejec. hoppings =  0

  Initial geometry:
S   16.0   11.11957280   -2.12119841   -0.28374050   31.97207180
C    6.0   13.61627460    0.13945509   -0.13197526   12.00000000
C    6.0   12.54200800    2.55973916   -0.14698730   12.00000000
...

  Initial velocity:
  0.00003306  -0.00005273    0.00002912
  0.00011503   0.00032972   -0.00011814
 -0.00010832  -0.00012902    0.00016772
```

```

...
      Time      Etot      Ekin      Epot E0,      E1, ...
%      0.0      -40.231344      0.120205      -40.441290      -40.359339      -40.351548
Etot variation = 0.000000 au      Worse conservation = 0.000000 au

Wave function state 1:      0.0000000000000000      0.0000000000000000
Wave function state 2:      0.0000000000000000      0.0000000000000000
Wave function state 3:      1.0000000000000000      0.0000000000000000
...

```

The last time-step looks like:

```

STEP      600      Molecular dynamics on state 2      TIME =      300.00 fs
Type of dyn. = 4      N. of hoppings = 9      N. of rejec. hoppings = 0

```

```

New geometry:
S      16.0      11.24794953      -2.22980526      -0.27345268      31.97207180
C      6.0      13.40114809      0.06087430      0.00408292      12.00000000
C      6.0      12.50873875      2.54730083      -0.24891648      12.00000000
...

```

```

New velocity:
-0.00003984      0.00005159      -0.00006712
0.00021068      -0.00014223      0.00009530
0.00027127      0.00003428      -0.00028440
...

```

```

      Time      Etot      Ekin      Epot E0,      E1, ...
%      300.00      -40.232104      0.145495      -40.456390      -40.377599      -40.368816
Etot variation = 0.000086 au      Worse conservation = -0.002297 au

Wave function state 1:      0.0000000000000000      0.0000000000000000
Wave function state 2:      -0.31551315165131      -0.92278596278823
Wave function state 3:      0.01799916326745      -0.22043944324402

```

“Etot variation” gives $E_{tot}(t)-E_{tot}(t-\Delta t)$. When this quantity is larger than a threshold, the trajectory breaks with “Etot_jump” error message. This threshold can be controlled with the keyword “Etot_jump” in the advanced input.

“Worse conservation” gives $\text{MAX}[E_{tot}(t)-E_{tot}(0)]$ until time t . When this quantity is larger than a threshold, the trajectory breaks with “Etot_drift” error message. This threshold can be controlled with the keyword “Etot_drift” in the advanced input.

In surface hopping approach, the time-dependent wavefunction is written as ¹¹

$$\Psi(t) = \sum_{n=1}^{N_{stat}} \chi_n(t) \psi_i(\mathbf{R}(t)),$$

where ψ_i is the electronic wavefunction (in the adiabatic representation, in this example). The time-dependent coefficients χ_n are complex numbers: The real and imaginary parts of them are given in dyn.out. For example, the line in the last time-step means

```
Wave function state 2:      -0.3155135165131      -0.92278596278823
```

$$\text{Re}(\chi_0) = -0.315514 \text{ and } \text{Im}(\chi_0) = -0.922786$$

The normalization of these coefficients is an important check of the quality of the dynamics, and it will be discussed below.

23. Energy information is also written in a different format in file typeofdyn.log. It looks like:

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```

...
Time = 33.50 Threshold=**** PES = 3 DE_inf = 0.09 DE_sup = ----- Type = 2
Next type = 2
Time = 34.00 Threshold=**** PES = 3 DE_inf = 0.09 DE_sup = ----- Type = 2
Next type = 2
Time = 34.50 Threshold=**** PES = 3 DE_inf = 0.09 DE_sup = ----- Type = 2
Next type = 2
Time = 35.00 Threshold=**** PES = 2 DE_inf = 2.33 DE_sup = 0.10 Type = 2
Next type = 4
Time = 35.50 Threshold=**** PES = 2 DE_inf = 2.34 DE_sup = 0.11 Type = 4
Next type = 4
Time = 36.00 Threshold=**** PES = 2 DE_inf = 2.36 DE_sup = 0.12 Type = 4
Next type = 4
...

```

At time 34.50 fs the molecule was on surface 3 (S_2). The energy gap to S_1 DE_{inf} was 0.09 eV. At time 35.00 fs, the molecule was on surface 2 (S_1); therefore a surface hop took place. The energy gap with S_0 was 2.33 eV.

24. Gradients, oscillator strengths and non-adiabatic coupling vectors and log information are written to nx.log (and also in the standard output).

25. The information about the integration of the time-dependent Schrödinger equation is in sh.out file. It looks like:

```

...
substep      step  surf  populations      Total pop
|v.h|=      0.000000  0.000000  -0.003483
      1381      70    3    0.0000000000    1.0000000000
                0.657086922
                0.342913078
...

```

NEWTON-X keeps two related timelines. The first is composed by the steps used to integrate Newton's equations. For step n , the time is $n \cdot \Delta t$ ($\Delta t = 0.5$ fs in this example). The second timeline is counted in substeps, which are used to integrate the time-dependent Schrödinger equation. The number of substeps per step is defined by keyword "ms," which can be changed in the advance input. The default is $ms = 20$. At the end of a trajectory with N steps, we will have $N \cdot ms$ substeps.

At the substep 1381, still during step 70 with the molecule still on surface 3 (S_2), the population of the second excited state (S_2) was:

$$|\chi_2|^2 = 0.342913078.$$

The population is defined as the diagonal terms of the matrix $\chi_i \chi_j^$. These terms are written in sh.out. Note that*

$$\sum_{n=1}^{N_{stat}} |\chi_n|^2 = 1.$$

The normalization factor is also printed there ("Total pop"). When it deviates more than "pop_dev" (a keyword defined in the advance input, whose default is 0.05), the job breaks with an error message.

The inner products of the nuclear velocity and the non-adiabatic coupling vectors, which are proportional to the hopping probability, are also printed:

$$\begin{aligned}\mathbf{v} \cdot \mathbf{h}_{10} &= 0.000000, \\ \mathbf{v} \cdot \mathbf{h}_{20} &= 0.000000, \\ \mathbf{v} \cdot \mathbf{h}_{21} &= -0.003483.\end{aligned}$$

26. The hopping probability is written in tprob file. It looks like:

random number	substep	step	probabilities		
...					
0.092029851	1386	70	0.000000000	0.008861272	0.000000000
0.586478467	1387	70	0.000000000	0.008917638	0.000000000
0.186681612	1388	70	0.000000000	0.008973452	0.000000000
0.008996025	1389	70	0.000000000	0.009028650	0.000000000
...					

In the substep 1389 (during step 70), the hopping probabilities were:

$$\begin{aligned}P_{2 \rightarrow 0} &= 0.000000000, \\ P_{2 \rightarrow 1} &= 0.009028650, \\ P_{2 \rightarrow 2} &= 0.000000000.\end{aligned}$$

These probabilities were compared with the random number 0.008996025 to decide whether a hopping occurs or not. Since the random number was larger than the probabilities, the molecule hops to surface S_1 .

In the fewest-switches approach under adiabatic representation, the hopping probability from state j to state i is given by:

$$P_{j \rightarrow i}(t) = \begin{cases} -2 \frac{\text{Re}(\chi_i^* \chi_j e^{i\gamma_{ji}})}{|\chi_{ij}|^2} \mathbf{v}(t) \cdot \mathbf{h}_{ji}(t) \delta t, & \text{if } P_{j \rightarrow i} > 0. \\ 0, & \text{if } P_{j \rightarrow i} \leq 0. \end{cases}$$

In this equation, $\delta t = \Delta t / m_s$. Due to this definition, the probability becomes zero for some time intervals (not reported in the above example... have a look by yourself in the tprob file!).

27. Points close to conical intersections (energy gaps smaller than “e_ci”, which is keyword defined in advanced input. The default is 0.2 eV) are written to “report.ci” file.

28. The statistical analysis of the dynamics results is described in section 6.6.

11. Hybrid dynamics: QM/MM – Columbus/Tinker

11.1 General explanations of hybrid calculations

The most popular hybrid method is the QM/MM approach, in which a reactive primary system is treated quantum mechanically (QM), while the remaining (secondary) system is treated by molecular mechanics (MM). There is a vast literature reviewing the QM/MM approach, and we can specially refer to Refs.¹⁵⁻¹⁷.

The NEWTON-X implementation the energies and gradients are for subsets of atoms are treated with different programs, and the partial results are joint into a resulting total (hence 'hybrid') energy and gradient.

For that purpose, the complete set of atoms of the whole system is split in disjoint regions. These regions need not to follow physical reasoning (they often will, but they can also pick, e.g. single atoms out of molecules), but are logical entities for the definition of the single partial calculations.

The whole calculation is split into jobs. Each of these jobs can treat one or more regions of atoms, and the result enters the total multiplied by a user-defined factor. One region can be treated by multiple jobs and to care about 'double counting' of atoms is left to the user completely.

A hybrid setup (which is done in the JOB_AD or JOB_NAD directory) consists of some general information about the hybrid setup ('control' parameters), the definition of the atoms, some of their properties and membership to the regions and the definition of the partial jobs, which regions they are concerned with and how they shall be put together to the overall result.

The exact file-structure of a hybrid setup is explained in the NEWTON-X documentation.

11.2 Formamide with water using hybrid gradients

In this Chapter, we will set up a calculation with hybrid gradients for a formamide molecule with one water molecule as solvent (which is physically not very meaningful but keeps the input files short). We will start from standard XYZ files and set up QM/MM non-adiabatic surface-hopping dynamics trajectories. Ground and two excited states will be computed, and the dynamics will start in the second excited state.

Formamide (QM part) will be treated with COLUMBUS at the SA-3-CASSCF(6,4)/6-31G* level, while the water (MM part) will be introduced using electrostatic embedding and OPLSAA/TIP3P-parameters¹⁸ with TINKER for the intramolecular water-forces and the van der Waals interaction.

The initial conditions will be created with random velocities.

This kind of initial conditions is not without problems. The quantum mechanical core should, in reality, have a much higher kinetic energy to overcome the zero point energy while the environment should only get the thermal energy. There are tools and extended explanations available for the creation of hybrid initial conditions with NX.

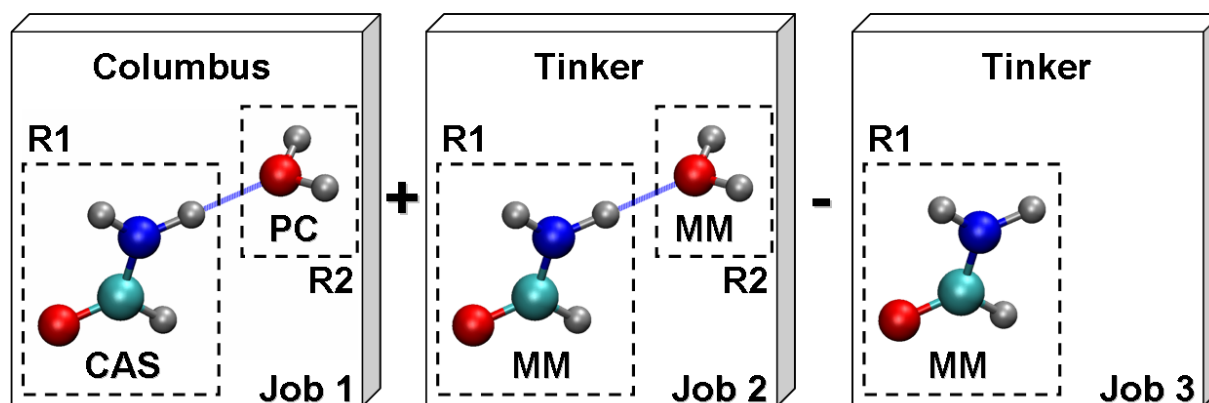


Fig. 15. QM/MM scheme for formamide (QM) and one water molecule (MM) within the electrostatic embedding.

11.3 Before starting

For NEWTON-X everything has to be setup as usual, especially the \$NX- and \$COLUMBUS-environment variables have to be set and the TINKER-executable 'testgrad.x' has to be in the standard path or available somewhere. See the NEWTON-X documentation on the usage of TINKER on the last topic.

Before beginning to set up, a hybrid calculation one needs some additional information at hand. In the documentation for NEWTON-X (\$NX/./docs/) a file 'hybrid_setup_sheet.pdf' is provided. It is an aid for having the essential information necessary in the setup of a hybrid dynamics together. For example in this tutorial, a pre-filled sheet is in Appendix 12.2. Print this sheet or display it on your screen. It contains the information to be entered in the setup.

The whole system will consist of one formamide- and one water-molecule (see Fig. 15). The formamide will be the QM-region, treated with Columbus at the SA-3-CASSCF(6,4)/6-31G* level and the water will be the second region, included via electrostatic embedding using OPLSAA/TIP3P-parameters. This means, that we will need 3 jobs

1. QM-calculation using COLUMBUS with the formamide in the geom file and the water integrated as point-charges (thus region 1+2). The value for the point-charges will be taken from the OPLSAA/TIP3P force field. The result of this job will be added to the total result. This job will give the non-adiabatic couplings and oscillator strengths.
2. MM-calculation using TINKER applying the OPLSAA/TIP3P parameters for all atoms in the system (region 1+2). It is important to make sure, that the electrostatic QM-MM interactions are **not** computed by TINKER (this will be done with special parameters for the formamide in the .key file for the tinker job). The result of this job will be added to the total result.
3. MM-calculation using TINKER with OPLSAA/TIP3P for only the formamide atoms. Again the electrostatic QM-MM interactions must not be computed. The result of this job will be subtracted from the total result.

In principle, if we used only zero force constants for the formamide intramolecular parameters the third job would not be necessary. On the one side it is easier to use the present parameters (with the exception of the electrostatics), and on the other side for bigger molecules the intramolecular 1,5 and above vdW interactions cannot be excluded from a Tinker calculation (in job 2) and have to be subtracted.

11.4 Hybrid input set up

1. In the tutorial directory (see section 1.4) create a subdirectory called MD-OCNH3_H2O-NAD-QMMM:

```
> mkdir MD-OCNH3_H2O-NAD-QMMM
```

2. Move to this directory and create a directory JOB_NAD

```
> cd MD-OCNH3_H2O-NAD-QMMM
> mkdir JOB_NAD
```

3. Move to JOB_NAD and create two standard XYZ format files, one containing the coordinates of the formamide (formamide.xyz) and another containing the coordinates of water (water.xyz):

```
> cd JOB_NAD
> vi formamide.xyz
```

6

```
C    -0.3106169684    -0.0533771829    0.0674384499
O     0.8916220270     0.0010327193     0.2950091787
N    -0.9169204320    -1.2047342003    -0.1861665224
H    -0.9363365876     0.8391191694     0.0627462758
H    -1.9262814755    -1.2273336136    -0.3743612135
H    -0.3679476519    -2.0465508730    -0.1892965762
```

If COLUMBUS is one of the programs that will be used in the calculation, the hydrogen atoms should appear at the end of the file. This is the case of formamide in our example. If you have multiple regions entering the geom. file they will be appended in ascending order of the number of the regions, so your hydrogen atoms should all be at the end of the last region.

The regions, which enter the Columbus-calculation only as point charges (and thus will not be in the geom file, but in the potential.xyz file) need not be reordered. This is the case of the water molecule in our example.

```
> vi water.xyz

3

OW    -3.6514305598   -1.2731920247   -0.6968800390
HW    -4.1044098748   -1.1659898886   -1.5379231182
HW    -4.3744584769   -1.3471341056   -0.0677564351
```

The setup-script will use the names given in these files to distinguish between different kinds of atoms, e.g., atoms of the same atom type, but with different point charges. It is, before all, necessary to give different names to atoms that will have different point charge atoms. In this example, the oxygen atom in formamide is labeled O, while the oxygen atom in water is labeled OW.

The values used in these files are the equilibrium structure of the two molecules. They will be used only to generate the input values. The initial conditions for the dynamics are prepared separately (see section 11.6).

4. Run `hybrid_input_fromxyz.pl`. It will ask you a series of questions. The data to be entered are on the setup sheet (Appendix 12.2).

```
> $NX/hybrid_input_fromxyz.pl

Of how many regions consist your system?
? 2<Enter>          ! QM and MM

.xyz for region 1?
? formamide.xyz<Enter>

.xyz for region 2?
? water.xyz<Enter>

How many jobs will be in the calculation?
? 3<Enter>          ! 1- Columbus: [formamide (CAS) + water (point charge)]
                   ! 2- Tinker:  +[formamide + water (MM)]
                   ! 3- Tinker:  -[formamide (MM)]

! The following sections always appear on a cleared screen
Regions chosen for job 1:
Choose regions for job 1.
   region  1 ( formamide.xyz) .. [ 1]
   region  2 (      water.xyz) .. [ 2]
clear choice ..... [D]
finished choosing .....[X]
? 1<Enter>

! clear screen
Regions chosen for job 1: 1
Choose regions for job 1.
```

```

        region  1 ( formamide.xyz) .. [ 1]
        region  2 (      water.xyz) .. [ 2]
        clear choice ..... [D]
        finished choosing .....[X]
? 2<Enter>

! clear screen
Regions chosen for job 1: 1,2
Choose regions for job 1.
        region  1 ( formamide.xyz) .. [ 1]
        region  2 (      water.xyz) .. [ 2]
        clear choice ..... [D]
        finished choosing .....[X]
? x<Enter>

! clear screen
Which method should be used in job #1
        COLUMBUS           [1]
        TINKER              [2]
        TURBOMOLE           [3]
        ANALYTICAL MODEL    [4]
? 1<Enter>

Should some region(s) be treated as pointcharges?(y/n)
? y<Enter>

! clear screen
Chosen for pointcharges in job #1:
Choose pointcharge-regions for job #1.
        region  1 ( formamide.xyz) .. [ 1]
        region  2 (      water.xyz) .. [ 2]
        clear choice ..... [D]
        finished choosing .....[X]
? 2<Enter>

! clear screen
Chosen for pointcharges in job #1:2
Choose pointcharge-regions for job #1.
        region  1 ( formamide.xyz) .. [ 1]
        region  2 (      water.xyz) .. [ 2]
        clear choice ..... [D]
        finished choosing .....[X]
? x<Enter>

With which factor shall the $method-job #1 enter the result?
? 1<Enter>

```

The most common factors will be +1 and -1 for addition or subtraction of energies and gradients of a job to or from the total result. Other values are absolutely valid and allowed, though, even if they may not be physically sensible.

```

! clear screen
Regions chosen for job 2:
Choose regions for job 2.
        region  1 ( formamide.xyz) .. [ 1]
        region  2 (      water.xyz) .. [ 2]
        clear choice ..... [D]
        finished choosing .....[X]
? 1<Enter>

! clear screen
Regions chosen for job 2: 1
Choose regions for job 2.
        region  1 ( formamide.xyz) .. [ 1]
        region  2 (      water.xyz) .. [ 2]
        clear choice ..... [D]
        finished choosing .....[X]
? 2<Enter>

```

```

! clear screen
Regions chosen for job 1: 1,2
Choose regions for job 1.
    region  1 ( formamide.xyz) .. [ 1]
    region  2 (      water.xyz) .. [ 2]
clear choice ..... [D]
finished choosing .....[X]
? x<Enter>

! clear screen
Which method should be used in job #2
    COLUMBUS           [1]
    TINKER              [2]
    TURBOMOLE          [3]
    ANALYTICAL MODEL   [4]
? 2<Enter>

With which factor shall the $method-job #2 enter the result?
? 1<Enter>

! clear screen
Regions chosen for job 3:
Choose regions for job 3.
    region  1 ( formamide.xyz) .. [ 1]
    region  2 (      water.xyz) .. [ 2]
clear choice ..... [D]
finished choosing .....[X]
? 1<Enter>

! clear screen
Regions chosen for job 3: 1
Choose regions for job 3.
    region  1 ( formamide.xyz) .. [ 1]
    region  2 (      water.xyz) .. [ 2]
clear choice ..... [D]
finished choosing .....[X]
? x<Enter>

! clear screen
Which method should be used in job #2
    COLUMBUS           [1]
    TINKER              [2]
    TURBOMOLE          [3]
    ANALYTICAL MODEL   [4]
? 2<Enter>

With which factor shall the $method-job #1 enter the result?
? -1<Enter>

! clear screen
Which job will give the properties
(nonadiabatic couplings, oscillator strengths, ...)?
Choose 0 for none.
? 1<Enter>

Restrict nonadiabatic couplings to some regions?(y/n)
? y<Enter>

```

It is possible (and probably wise) to restrict the computation of the hopping-related effects to the nonadiabatic couplings of the core region. The electrostatic embedding in Columbus in principle also computes nonadiabatic coupling vectors for the point charges. In many cases (e.g. when a thermostat is acting on the MM-environment) this could give artificial results.

```

! clear screen
Chosen for nadregions:

Choose nadregions.

```

```

region 1 ( formamide.xyz) .. [ 1]
region 2 (      water.xyz) .. [ 2]
clear choice ..... [D]
finished choosing ..... [X]
? 1<Enter>

Chosen for nadregions: 1

Choose nadregions.
region 1 ( formamide.xyz) .. [ 1]
region 2 (      water.xyz) .. [ 2]
clear choice ..... [D]
finished choosing ..... [X]
? x<Enter>

```

Properties that cannot be linearly combined are all given by only one of the jobs for the whole system. This affects mainly non-adiabatic coupling vectors and oscillator strengths. The user has to take care that he selects a job which can provide them.

Now the script will ask you for each kind of atom it found in the XYZ-files for the point charge and, if the name of the atom is not an atomic symbol, for the atom-type. It knows only atom types in the periodic system of elements up to Krypton, which is the same limitation as in COLUMBUS.

The default value for charges is 0.0000, and for all atoms that are not treated as point charges by Columbus or Turbomole you can accept this value by just hitting <Enter>.

```

! clear screen
Point charge for symbol C?[0.0000]
? <Enter>

! clear screen
Point charge for symbol O?[0.0000]
? <Enter>

! clear screen
Point charge for symbol N?[0.0000]
? <Enter>

! clear screen
Point charge for symbol H?[0.0000]
? <Enter>

! clear screen
Atom type for symbol OW?
? O<Enter>

Point charge for symbol HC?[0.0000]
? -0.834<Enter>
! this value is taken from the OPLSAA-parameters for Oxygen in Water (TIP3P)

! clear screen
Atom type for symbol HW?
? H<Enter>

Point charge for symbol HW?[0.0000]
? 0.417<Enter>

```

5. At this point, several input files and directories will have been generated.

```
> ls -t
```

```

JOB_3.tinker  job_2.tinker.data  hybrid.coords      hybrid.nuclear_charges  job_1.columbus.data
JOB_2.tinker  job_3.tinker.data  hybrid.geom        hybrid.pointcharges     water.xyz
JOB_1.columbus  hybrid.add_data    hybrid_gradients.inp  hybrid.xyz              formamide.xyz

```

```
hybrid.control hybrid.atoms hybrid.masses job_1.columbus.control
```

From the user point of view, the most important file is `hybrid_gradients.inp`. It contains the complete set of information about the job.

```
> vi hybrid_gradient.inp
```

```
$job ID = 1 regions = 1,2 program = columbus pointcharges = 2 factor = 1 $end
$job ID = 2 regions = 1,2 program = tinker factor = 1 $end
$job ID = 3 regions = 1 program = tinker factor = -1 $end
$control properties = 1 natoms = 9 $end
$atoms
  C  6.0  -0.58698100  -0.10086826  0.12744020  12.00000000  0.0000  1
  O  8.0  1.68492145  0.00195156  0.55748655  15.99491464  0.0000  1
  N  7.0  -1.73272850  -2.27661770  -0.35180374  14.00307401  0.0000  1
  H  1.0  -1.76941972  1.58570542  0.11857328  1.00782504  0.0000  1
  H  1.0  -3.64014444  -2.31932440  -0.70744017  1.00782504  0.0000  1
  H  1.0  -0.69532029  -3.86742067  -0.35771869  1.00782504  0.0000  1
  OW 8.0  -6.90020375  -2.40598424  -1.31691242  15.99491464  -0.8340  2
  HW 1.0  -7.75621060  -2.20340156  -2.90625351  1.00782504  0.4170  2
  HW 1.0  -8.26652850  -2.54571452  -0.12804111  1.00782504  0.4170  2
$end
```

Refer to the NEWTON-X documentation for an explanation of the groups, keywords, and formats in this file. It is, however, trivial to see that, for example, the line:

```
$job ID = 3 regions = 1 program = tinker factor = -1 $end
```

is telling that JOB 3 should apply for region 1, using TINKER and that the result should be subtracted (factor = -1). The geometry is written with an extended format:

```
! Symbol At.Number x/bohr y/bohr z/bohr Mass/amu charge/au region
  C  6.0  -0.58698100  -0.10086826  0.12744020  12.00000000  0.0000  1
```

The usage of the program `hybrid_input_fromxyz.pl` to prepare the input is optional. Indeed, the user needs only to create the `hybrid_gradient.inp` file by any means. The remaining files can then be generated by simply executing:

```
> $NX/hybrid_read_onefile.pl
```

The same is true if the user wants to modify the job inputs. This may be done either by running `hybrid_input_fromxyz.pl` or by directly changing `hybrid_gradient.inp` file and updating the remaining files with the `hybrid_read_onefile.pl`.

11.5 Preparation of the third-party jobs

The subdirectories for the single jobs (JOB_1.columbus, JOB_2.tinker, and JOB_3.tinker) have now been created. The next step in the input procedure is to create the third-party inputs for each one of the three jobs.

11.5.a) COLUMBUS

6. Change to the directory of the COLUMBUS job.

```
> cd JOB_1.columbus
```

Use the `geom` file there to create an input for single point non-adiabatic coupling calculation with COLUMBUS at SA-3-CASSCF(6,4)/6-31G*. The same remarks as in section 8.2 apply. The electronic structure setup-sheet can be found in Appendix 12.4. Don't forget to add a line to the

'control.run' file (any position) containing the keyword 'potmat'. Refer to the COLUMBUS documentation, section 'Properties' → Solvent Effects on this topic.

You need to add the keyword potmat to the control.run only for the generation of the initial mocoef file. During runtime, NEWTON-X will add the keyword automatically if you have point charges in your COLUMBUS-job.

11.5.b) TINKER

7. Here we will begin creating the tinkin.key file. This file will contain not only the usual keywords (parameters, archive, digits 8) but also the forged electrostatic parameters for formaldehyde.

Change now to the directory of the second job (JOB_2.tinker). Copy the oplsa.prm-file from the 'params' directory of your TINKER-installation into this directory.

```
> cd ../JOB_2.tinker
> cp <tinker_install_dir>/params/oplsaa.prm ./
```

Look up in oplsa.prm the parameter numbers that would suite formaldehyde. In the file provided with Tinker Ver. 4 these are

atom	82	21	C	"NC=O Amide"	6	12.000	3
atom	83	22	O	"NC=O Amide"	8	15.999	1
atom	84	23	N	"H2NC=O Amide"	7	14.007	3
atom	87	24	H	"H2NC=O Amide"	1	1.008	1
atom	119	29	HC	"HC=O Formyl Aldehyde"	1	1.008	1

Copy these lines to the tinkin.key file and edit the parameter number (second column) giving numbers that do not occur yet in the parameter file (>3000 should be a safe choice). Keep the group numbers (which are used by Tinker for the identification when calculating vdW-, and intramolecular parameters). Add for each of the new atom types a “charge ### 0.000” line.

Your finished file should look like this:

```
parameters oplsa
archive
digits 8

atom 3001 21 C "NC=O Amide" 6 12.000 3
atom 3002 22 O "NC=O Amide" 8 15.999 1
atom 3003 23 N "H2NC=O Amide" 7 14.007 3
atom 3004 24 H "H2NC=O Amide" 1 1.008 1
atom 3005 29 HC "HC=O Formyl Aldehyde" 1 1.008 1

charge 3001 0.0000
charge 3002 0.0000
charge 3003 0.0000
charge 3004 0.0000
charge 3005 0.0000
```

This will affect the formamide atoms to behave exactly as if they had gotten the original parameters with exception of the electrostatic interaction which is switched off.

Use either the geom file or the file geometry.xyz (standard XYZ in Angstrom) to create a TINKER input for a NEWTON-X dynamics with OPLSAA-parameters. Force field numbers are (for the file provided with Tinker Ver. 4):

formamide	C	3001
	O	3002
	N	3003
	H-C	3004
	H-N	3005
water	O (OW)	186
	H (HW)	187

```
> vi tinkin.xyz
```

```
9 Tinker input
 1  C   -0.31061700   -0.05337700    0.06743800   3001   2   3   4
 2  O    0.89162200    0.00103300    0.29500900   3002   1
 3  N   -0.91692000   -1.20473400   -0.18616700   3003   1   5   6
 4  H   -0.93633700    0.83911900    0.06274600   3005   1
 5  H   -1.92628100   -1.22733400   -0.37436100   3004   3
 6  H   -0.36794800   -2.04655100   -0.18929700   3004   3
 7  O   -3.65143100   -1.27319200   -0.69688000   186    8   9
 8  H   -4.10441000   -1.16599000   -1.53792300   187    7
 9  H   -4.37445800   -1.34713400   -0.06775600   187    7
```

You can use MOLDEN for the conversion of the XYZ file to a TINKER input. This will write MM3 parameters, though. The script \$NX/hybrid_tinker_paramconv.pl can help you to convert this file easier. Edit a file 'paramconv.dat' and write on each line the parameter numbers (comma separated) which should be substituted (it is assumed here that the TINKER input with MM3 parameters has been saved to a file called geometry_tinker_mm3.xyz).

```
> vi paramconv.dat
```

```
3,3001
7,3002
5,3003
28,3004
9,3005
6,186
21,187
```

Execute the script – it will substitute every occurrence of the first parameter stated in each line with the second one and write a file with the ending .paramconv

```
> $NX/hybrid_tinker_paramconv.pl geometry_tinker_mm3.xyz
```

```
> cp geometry_tinker_mm3.xyz.paramconv tinkin.xyz
```


If you do not have the TINKER executables in your \$PATH you can copy the binary testgrad.x to your job-directory. It will then be executed from there. Refer to the TINKER section of the NEWTON-X documentation on this topic.

You can test, whether your job is set up is correct by manually executing the command line NEWTON-X is calling.

```
> testgrad.x tinkin.xyz -k tinkin.key y n n
```

The last output lines should be

Total Gradient Norm and RMS Gradient per Atom :

Anlyt	Total Gradient Norm Value	28.92022947
Anlyt	RMS Gradient over All Atoms	9.64007649

8. Change now to the directory of the third job (JOB_3.tinker). Copy the oplsa.prm-file and the tinkin.key from the JOB_2.tinker directory.

```
> cd ../JOB_3.tinker
> cp ../JOB_2.tinker/oplsaa.prm ./
> cp ../JOB_2.tinker/tinkin.key ./
```

Use either the geom. file or the file geometry.xyz (standard XYZ in Angstrom) to create a TINKER input for a NEWTON-X dynamics with the forged OPLSAA-parameters of the .key-file.

```
> vi tinkin.key
```

```
6 Tinker input
 1  C  -0.31061700  -0.05337700   0.06743800  3001  2  3  4
 2  O   0.89162200   0.00103300   0.29500900  3002  1
 3  N  -0.91692000  -1.20473400  -0.18616700  3003  1  5  6
 4  H  -0.93633700   0.83911900   0.06274600  3005  1
 5  H  -1.92628100  -1.22733400  -0.37436100  3004  3
 6  H  -0.36794800  -2.04655100  -0.18929700  3004  3
```

11.6 Initial conditions generation

There are several possible ways to set up the initial conditions for a QM/MM job. In this example, this will be done by setting the initial geometry constant at the equilibrium structure and generating random velocities. Other possible ways to generate initial conditions is to perform dynamics in the ground state and then picking random points along the trajectory to initiate the excited state dynamics. In this latter case, special care should be taken to avoid correlated points and to have a representative sample of the phase space.

The preferable and soundest way to create hybrid initial conditions is to use a Wigner distribution of the quantum harmonic oscillator for the QM-core, pick q/p points from a thermalized trajectory for the MM-environment and merge these two sets of initial conditions. This procedure is subject of a separate HOWTO.

For this example simply create initial conditions with random velocities giving a kinetic energy of 1eV.

One tool to improve the hybrid initial conditions is already included in NEWTON-X, \$NX/hybrid_mixed initcond. It will let you set the kinetic energy of the two molecules to half of their respective zero point energy, as expected from the Virial theorem. For formamide the zero point energy is $ZPE = 1.232$ eV; therefore, the initial kinetic energy will be assumed to be $E_{kin} = 0.616$ eV. For water, $ZPE = 0.559$ eV and $E_{kin} = 0.280$ eV. In a more realistic example when hundreds of water molecules are included, the kinetic energy of the water could be set to $3/2k_B T$.

In the appendix, there is a short description how to use this script for our example.

Change to the main directory (one directory above JOB_NAD) and copy the hybrid.geom file there as “geom”. Run nxinp to create the initial conditions.

```
> cd ../../
> ls
JOB_NAD
> cp JOB_NAD/hybrid.geom ./geom
> $NX/nxinp
```

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

```
MAIN MENU

1. GENERATE INITIAL CONDITIONS

2. SET BASIC INPUT

3. SET GENERAL OPTIONS

4. SET NONADIABATIC DYNAMICS

5. GENERATE TRAJECTORIES AND SPECTRUM

6. SET STATISTICAL ANALYSIS

7. EXIT
```

```
Select one option (1-7):1
```

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

```
GENERATE INITIAL CONDITIONS

nact: Distribution:
      1 - Classic harmonic oscillator
```

```

    2 - Q/P-uncorrelated quantum harmonic oscillator (Wigner)
    3 - Q/P-correlated quantum harmonic oscillator
    4 - Pick points from previous dynamics
    5 - Random-velocities generation
    6 - Single point on a previous calculation
The current value of nact is: 2
Enter the new value of nact : 5

numat: Number of atoms.
The current value of numat is: 9
Enter the new value of numat : <Enter>
Setting numat = 9

npoints: Number of initial conditions to be generated
The current value of npoints is: 1
Enter the new value of npoints : 10
Setting npoints = 10

file_geom: File containing the equilibrium geometry.
The current value of file_geom is: geom
Enter the new value of file_geom : <Enter>
Setting file_geom = geom

ekin: Kinetic energy (eV).
The current value of ekin (eV) is: 0
Enter the new value of ekin (eV) : 1
Setting ekin = 1

temp: Temperature
The current value of temp (K) is: 0
Enter the new value of temp (K) : <Enter>
Setting temp = 0

iseed: Random number seed.
    0 - default seed value.
   -1 - set random seed.
   >0 - (integer) set specific value for the seed.
The current value of iseed is: 0
Enter the new value of iseed : <Enter>
Setting iseed = 0

lvprt: Print level.
    1 - standard level
    2 - debug level
The current value of lvprt is: 1
Enter the new value of lvprt : <Enter>

```

```

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

```

MAIN MENU

1. GENERATE INITIAL CONDITIONS
2. SET BASIC INPUT
3. SET GENERAL OPTIONS
4. SET NONADIABATIC DYNAMICS
5. GENERATE TRAJECTORIES AND SPECTRUM

6. SET STATISTICAL ANALYSIS

7. EXIT

Select one option (1-7): 7

NEWTON-X INPUT DONE

> ls

geom initqp_input JOB_NAD

> \$NX/initcond.pl

```
=====
                          NEWTON-X
Newtonian dynamics close to the crossing seam
=====
```

...

Starting Initial Condition generation

initcond.pl: paths:

Base: /cellar/matruc/NX-devel/nx-tutorial/hybrid

Temp: /cellar/matruc/NX-devel/nx-tutorial/hybrid/TEMP

Debug: /cellar/matruc/NX-devel/nx-tutorial/hybrid/DEBUG

NACT = 5: initial conditions will be generated by
generating random velocities

initcond.pl:

```
NACT      = 5
FILE_GEOM = geom
NUMAT     = 9
NPOINTS  = 10
EKIN     = 1
TEMP     = 0
ISEED    = 1234
LVPRT    = 1
```

Checking geometry lines

== Calling RANINCON program by B. Sellner, 2007 ==

Starting raninicon at Wed Mar 16 10:13:49 CET 2011

Job done

Finished raninicon successfully at Wed Mar 16 10:13:50 CET 2011

End of initial conditions generation.

===== NEWTON-X ends here =====

> ls

DEBUG final_output geom initqp_input JOB_NAD TEMP

11.7 NEWTON-X input

- Run again nxinp and create an input for non-adiabatic simulations with 3 states, starting in state 3 with 0.5 fs timestep and 10 fs total duration. As method choose 'HYBRID GRADIENT' with COLUMBUS and TINKER as programs.

> \$NX/nxinp

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

MAIN MENU

1. GENERATE INITIAL CONDITIONS
2. SET BASIC INPUT
3. SET GENERAL OPTIONS
4. SET NONADIABATIC DYNAMICS
5. GENERATE TRAJECTORIES AND SPECTRUM
6. SET STATISTICAL ANALYSIS
7. EXIT

Select one option (1-7): 2 <ENTER>

nat: Number of atoms.
The current value of nat is: 9
Enter the new value of nat : <ENTER>
Setting nat = 9

nstat: Number of states.
The current value of nstat is: 2
Enter the new value of nstat : 3 <ENTER> ! 3 states will be computed
Setting nstat = 3

nstatdyn: Initial state (1 - ground state).
The current value of nstatdyn is: 3
Enter the new value of nstatdyn : <ENTER> ! dynamics will start in state 3
Setting nstatdyn = 3

dt: Time step for the classical equations.
The current value of dt (fs) is: 0.5
Enter the new value of dt (fs) : <ENTER>
Setting dt = 0.5

tmax: Total duration of the trajectory.
The current value of tmax (fs) is: 100
Enter the new value of tmax (fs) : <ENTER>
Setting tmax = 100

prog: Quantum chemistry program and method

- 0 - ANALYTICAL MODEL
- 1 - COLUMBUS
- 2.0 - TURBOMOLE RI-CC2
- 2.1 - TURBOMOLE TD-DFT
- 2.2 - TURBOMOLE ADC2 ! NX > 1.4
- 3 - ACES2 EOM-CCSD (in development)
- 4 - MOPAC (in development)
- 5 - DFTB
- 6 - GAUSSIAN
- 6.0 - GAUSSIAN(03) CASSCF

NEWTON-X tutorial

```

6.5 - GAUSSIAN(09) TDDFT
7 - TINKER
8 - DFTB+
10.0 - GAMESS
10.1 - GAMESS ARBITRARY ADIABATIC METHOD
20 - HYBRID GRADIENT
The current value of prog is: 1
Enter the new value of prog : 20<ENTER>
Setting prog = 20

Programs used for hybrid gradient
1 - COLUMBUS
2 - TINKER
3 - TURBOMOLE
99 - finished
(default=99) 1<Enter>

Programs used for hybrid gradient
1 - COLUMBUS
2 - TINKER
3 - TURBOMOLE
99 - finished
(default=99) 2<Enter>

Programs used for hybrid gradient
1 - COLUMBUS
2 - TINKER
3 - TURBOMOLE
99 - finished
(default=99) <Enter>

thres: Threshold to initiate nonadiabatic coupling calculation.
0 - Only adiabatic dynamics.
100 - Only nonadiabatic dynamics
The current value of thres (eV) is: 100
Enter the new value of thres (eV) : <ENTER>
Setting thres = 100

Would you like to generate internal coordinate file? (default=y) n <ENTER>

```

10. At this point, the main NEWTON-X input file control.dyn has been created. You may proceed through the other options in the main menu to advanced settings. In our example, the default options will be used. We proceed directly to the trajectory directories generation (option 5).

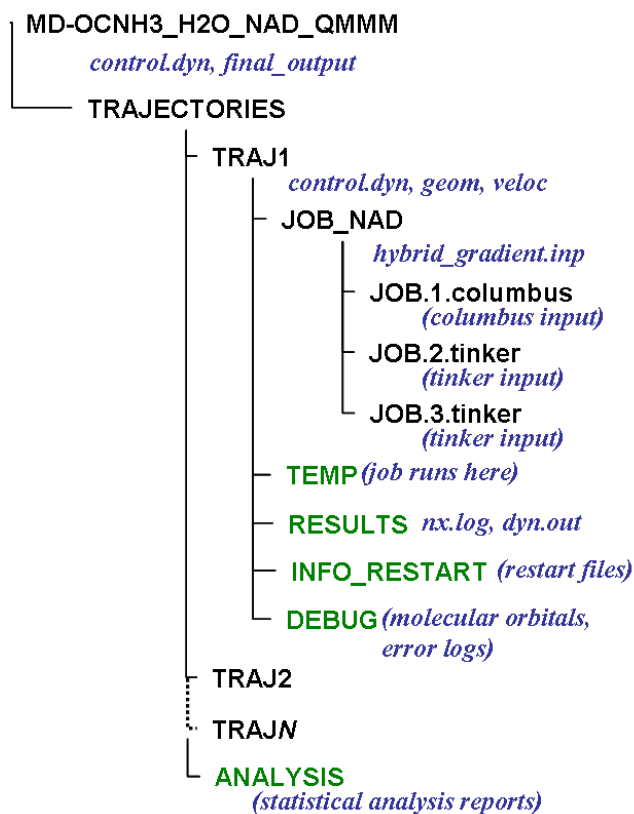


Fig. 16. Directory tree for a complete QM/MM surface hopping dynamics job with NEWTON-X.
Compare to the conventional case in Fig. 9.

```

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

MAIN MENU

1. GENERATE INITIAL CONDITIONS

2. SET BASIC INPUT

3. SET GENERAL OPTIONS

4. SET NONADIABATIC DYNAMICS

5. GENERATE TRAJECTORIES AND SPECTRUM

6. SET STATISTICAL ANALYSIS

7. EXIT
  
```

Select one option (1-7): 5 <ENTER>

11. Select the job options.

```

type: What do you want to do?
      1 - Generate spectrum
      2 - Select initial conditions for multiple initial states
      3 - Generate trajectories
      4 - Return to main menu
The current value of type is: 3
Enter the new value of type : <ENTER>
Setting type = 3

Would you like to apply energy and probability restrictions (y/n)? (default=n)
<ENTER>

Will the trajectories run in a batch system? n <ENTER>

Processing data: This may take some minutes. Please, wait...

```

In general, you might want to submit this job to a batch system. In this case, answer “y” to “Will the trajectories run in a batch system?”. You will be asked the name of the submission script and `nxinp` will look for its existence in the input directory. Files “`pmold`” and “`pmold-ew`” in `$NX/./batch/` directory are templates that can be adapted to your batch system.

12. Select option 7 to exit `nxinp`.

13. The trajectories have been created in the `TRAJECTORIES` directory from where you can run them as usual. The final directory structure is shown in Fig. 16, including the results directory.

```

> ls
control.dyn  final_output  JOB_NAD  mkdir.log  mkd.inp  TRAJECTORIES

> ls TRAJECTORIES
TRAJ1  TRAJ10  TRAJ2  TRAJ3  TRAJ4  TRAJ5  TRAJ6  TRAJ7  TRAJ8  TRAJ9

> ls TRAJECTORIES/TRAJ1
control.dyn  geom  JOB_NAD  veloc

```

14. Move to the first trajectory to execute it.

```

> cd TRAJECTORIES/TRAJ1
> $NX/moldyn.pl > moldyn.log &

```

29. After finishing the calculation, move to the `RESULTS`. If the job ended normally, the file `nx.log` should finish with:

```

moldyn.pl: End of dynamics
===== NEWTON-X ends here =====

```

15. Plot the energies (Fig. 17).

```

> cd RESULTS
> $NX/plot
Number of states:3<ENTER>

```

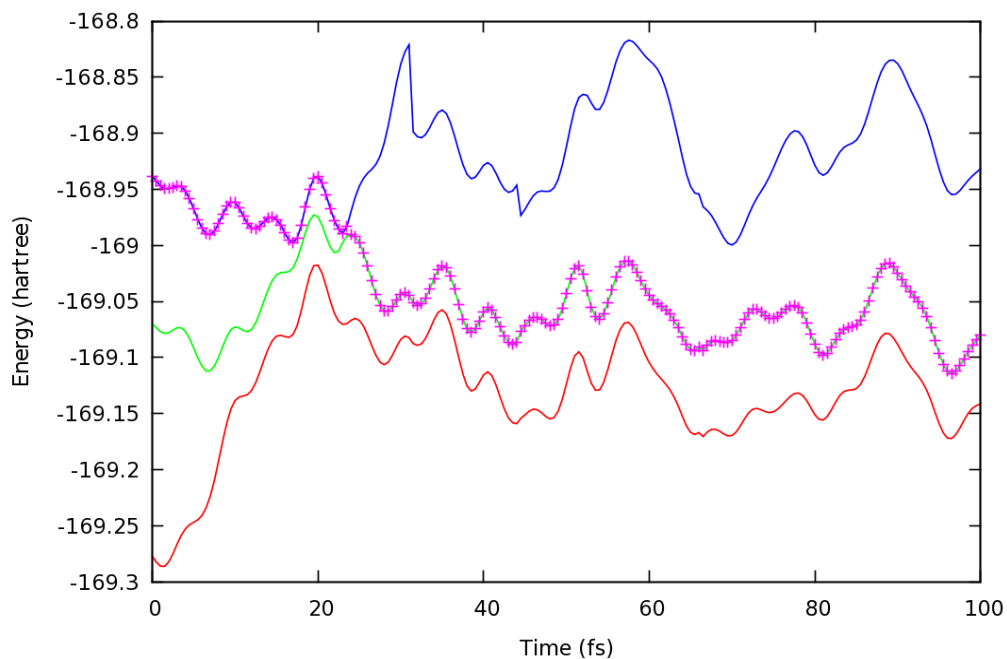



Fig. 17. Potential energy as a function of time for the first trajectory. Crosses indicate the current state. A surface hopping from S_2 to S_1 occurs at 23.5 fs.

To know more about how to make the analysis of individual trajectories and statistical analysis of several trajectories you should study Chapter 8.

12. Appendices

12.1 Methaniminium at CASSCF(12,8)

System: CH_2NH_2^+ Point Group: C_1

N. Electrons: 16

Multiplicity:

Level: SA-3-CASSCF(12,8)

		IRREP							
		a							
SCF	DOCC	8							
	OPSH	0							
MCSCF	DOCC	2							
	RAS	0							
	CAS	8							
	AUX	0							
MRCI	FC	2							
	FV	0							
		DOCC	0						
		ACT	8						
		AUX	0						
		INT	8						

State	Multiplicity	N. electrons	Symmetry
1	1	16	A
1	1	16	A
1	1	16	A

 Number of distinct rows (DRTs): **1**

	1	2	3	4	5	6	7	8
D_{2h}	a_g	b_{3u}	b_{2u}	b_{1g}	b_{1u}	b_{2g}	b_{3g}	a_u
D_2	a	b_2	b_1	b_3				
C_{2h}	a_g	b_u	a_u	b_g				
C_{2v}	a_1	b_1	b_2	a_2				
C_i	a_g	a_u						
C_s	a'	a''						
C_2	a	b						
C_1	a							

12.2 Generation of mixed random velocities

Change back to the parent directory and call the script \$NX/hybrid_mixed_initcond.pl

This script spares you the work to split the geom file manually, generate the initial conditions for the different regions separately, and then merge the final_output files.

Note, that in this example we won't equilibrate the structure of the system. The original coordinates are optimized with OPLSAA/TIP3P-parameters, but usually one will have to equilibrate the structure to the method used in the dynamics. A damped dynamics, beginning with zero velocities is a good choice of method for doing that.

```
> cd ../
> $NX/hybrid_mixed_initcond.pl
```

16. Answer the questions to generate 5 initial conditions with 2 methods. Region one (the formamide) gets halve the zero point energy, the water gets kinetic energy for 298 K.

```
XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
X                               MIXED INITIAL CONDITIONS GENERATOR                               X
XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
```

This script allows generating initial conditions for NEWTON-X simulations using different methods for different parts of the system. The regions for the hybrid gradients must have been defined (hybrid.atoms) beforehand.

How many simulation starting points do you want to generate?

```
10<Enter>          ! 10 trajectories
```

How many different initial condition generation methods will be used?

```
2<Enter>          ! Separated init. cond. for formamide and water
```

Which regions should be treated by method 1 (separated by spaces)?

Available regions: 1 2

```
1                ! First, formamide
```

*** Initial velocities generation for method 1 ***

For random velocities, type in two positive real numbers, the kinetic energy energy (in eV) and the temperature (in K) in that order, with blanks in between.

If you want to generate the velocities with a different method, type anything else (enter is enough) to open the Newton-X input program.

```
0.566 0           ! ZPE/2 ( $\pm 0$  K standard deviation)
```

calling nxinp...

Generating initial conditions with method 1...

Which regions should be treated by method 2 (separated by spaces)?

Available regions: 2

```
2                ! Now, water
```

*** Initial velocities generation for method 1 ***

For random velocities, type in two positive real numbers, the kinetic energy energy (in eV) and the temperature (in K) in that order, with blanks in between.

If you want to generate the velocities with a different method, type anything else (enter is enough) to open the Newton-X input program.

```
0.028 0           ! ZPE/2 ( $\pm 0$  K standard deviation)
```

calling nxinp...

Generating initial conditions with method 2...

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```
Merging into final_output  
Done! Initial conditions succesfully generated in final_output
```

The initial conditions are written to the `final_output` file. It contains ten cards, each one with the same geometry but with different random velocities for the whole system formamide + water.

12.3 Datasheet for hybrid setup

System: **HCONH-H2O**

Date:

Number of regions: **2**

XYZ-files for regions

region	1	2	3	4	5
filenam e	formamide.xyz	water.xyz	/		

Number of jobs: **3**

Job-definitions:

ID	1	2	3	4	5	6	7	8
regions	1,2	1,2	1	/				
program	Col	Tinker	Tinker	/				
(pointcharges)	2	---	---	/				
factor	1	1	-1	/				

Job to give properties: **1**

Atom type definitions

name	atomic symbol	point charge
C	C	---
O	O	---
H	H	---
N	N	---
Ow	O	-0.834
Hw	H	0.417

12.4 Formamide at CASSCF(6,4)

System: HCONH_2

Point Group: C_1

N. Electrons: 24

Multiplicity:

Level: SA-3-CASSCF(6,4)

		IRREP							
		a							
SCF	DOCC	12							
	OPSH	0							
MCSCF	DOCC	9							
	RAS	0							
	CAS	4							
	AUX	0							
MRCI	FC	9							
	FV	0							
	DOCC	0							
	ACT	4							
	AUX	0							
	INT	4							

State	Multiplicity	N. electrons	Symmetry
1	1	24	A
1	1	24	A
1	1	24	A

Number of distinct rows (DRTs):	1
---------------------------------	---

12.5 An example DFTB+ input file for geometry optimization on SCC-DFTB level

```
Geometry = GenFormat {
  <<<< "geom.gen"
}

Driver = ConjugateGradient{ }

Hamiltonian = DFTB {
  SCC = Yes
  Dispersion = LennardJones {
    Parameters = UFFParameters { }
  }
  SlaterKosterFiles = Type2FileNames {
    Prefix = "/path/to/sk/folder/3ob-3-1/"
    Suffix = ".skf"
  }
  MaxAngularMomentum {
    H = "s"
    C = "p"
    S = "d"
  }
  Filling = Fermi {
    Temperature [Kelvin] = 0.0
  }
}
Analysis{
}
Options {
  WritedetailedOut = Yes
}

ParserOptions {
  ParserVersion = 4
}
```

12.6 An example DFTB+ input for hessian computation on SCC-DFTB level

```
Geometry = GenFormat {
  <<<< "geom.gen"
}

Driver = SecondDerivatives{}

Hamiltonian = DFTB {
  SCC = Yes
  Dispersion = LennardJones {
    Parameters = UFFParameters {}
  }
  SlaterKosterFiles = Type2FileNames {
    Prefix = "/path/to/sk/folder/3ob-3-1/"
    Suffix = ".skf"
  }
  MaxAngularMomentum {
    H = "s"
    C = "p"
    S = "d"
  }
  Filling = Fermi {
    Temperature [Kelvin] = 0.0
  }
}
Analysis{
}
Options {
  WritedetailedOut = Yes
}

ParserOptions {
  ParserVersion = 4
}
```


12.7 An example of MODES input for normal modes computation

```
Geometry = GenFormat {  
  <<< "geom.gen"  
}  
  
SlaterKosterFiles = Type2FileNames {  
  Prefix = "/path/to/sk/folder/3ob-3-1/"  
  Separator = "-"  
  Suffix = ".skf"  
}  
  
Hessian = {  
  <<< "hessian.out"  
}  
  
DisplayModes {  
  PlotModes = -90:-1  
  Animate = No  
  XMakeMol = No  
}
```

12.8 An example of DFTB+ input for spectrum simulation on TD-DFTB3 level

```

Geometry = GenFormat {
  <<<< "geom.gen"
}
Driver = {}
Hamiltonian = DFTB {
  SCC = Yes
  Dispersion = LennardJones {
    Parameters = UFFParameters {}
  }
  ThirdOrderFull = Yes
  HubbardDerivs = {
    C = -0.1492
    H = -0.1857
    S = -0.11
  }
  DampXH = Yes
  DampXHExponent = 4.00
  SlaterKosterFiles = Type2FileNames {
    Prefix = "/home/ljlj/jana/sk/3ob-3-1/"
    Separator = "-"
    Suffix = ".skf"
  }
}
MaxAngularMomentum {
  S = "d"
  H = "s"
  C = "p"
}
Filling = Fermi {
  Temperature [Kelvin] = 0.0
}
}
ExcitedState{
  Casida{
    Symmetry = Singlet
    NrOfExcitations = 10
    StateOfInterest = 0
    WriteTransitions = Yes
  }
  WriteTransitionDipole = Yes
}
}
Options {
  WritedetailedOut = Yes
}
ParserOptions {
  ParserVersion = 4
}
}

```

13. References

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