Excited-state dynamics of thiophene using Newton-X

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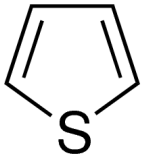
This tutorial will teach you how to perform a trajectory surface hopping (TSH) calculation using the package Newton-X, using the excited-state dynamics of thiophene as an example.



The following is adapted from the official tutorial of Newton-X available online at https://www.univie.ac.at/newtonx/tutorial-2_0.pdf.

The steps that will be required to achieve these calculations are listed here to give you an overview of the tasks (and the software used). They will be detailed in the following.

1. Perform a geometry optimization of thiophene in the ground electronic state (S_0) – Gaussian09.
2. Perform a frequency calculation at the optimized S_0 configuration – Gaussian09.
3. Using the optimized geometry and the frequencies:
    a. Generate an approximate Wigner distribution for uncoupled harmonic oscillators, that will be used to select initial conditions (initial positions and momenta) for our TSH dynamics – Newton-X.
    b. For each selected nuclear geometry, perform a LR-TDDFT calculation to extract the energies and oscillator strengths for a subset of low-lying electronic states – Newton-X.
    c. Plot a photoabsorption cross-section for thiophene based on the previous calculations – Newton-X.
4. Based on the sampled initial conditions, create a series of trajectories and run them one after the other, independently – Newton-X.
5. Collect information about the swarm of trajectories, mimicking the nuclear wavepacket dynamics – Newton-X.

Step 0 – Connect to the cluster

Start by connecting to the machine "*keeper*". To do so, type on the terminal:

```
ssh -Y tp@keeper.lcp.u-psud.fr
```

and use the following password: Tp@!cp!9
You are now on the machine *keeper*, from which you can connect to another machine called *styx* (where you will be able to submit your calculations). To connect to *styx*, type

```
ssh -Y tpX@styx
```

where ***X*** corresponds to your account number. If you have the account *tp1*, then the command line is: `ssh -Y tp1@styx`
The password is the same as for *keeper*.

You are now ready to go!

Create a directory for the tutorial called "*newtonx*" in your home:

```
mkdir ~/newtonx
```

All the directories that we will create during this tutorial should be in this "*newtonx*" directory. In case of doubt, just type

```
cd ~/newtonx
```

and you will find yourself back in the main *newtonx* directory.

Step 1 – Optimize the geometry of thiophene in the ground state

We first need to obtain the optimized geometry of thiophene in the ground electronic state (S_0). To do so, we will simply use Gaussian09 to perform a DFT geometry optimization using the 6-31G* basis set and the exchange/correlation functional ωB97X-D.

In the *newtonx* directory, create a directory called "*1_OPT-DFT*". Go in this directory. We provide below a template input file for Gaussian09 doing this task that you can copy and paste into a file called *go.com* in your "*1_OPT-DFT*" directory.

```
%chk=go.chk
%nproc=1
#P GFINPUT
#wb97xd/6-31g* Opt


 0 1
C       -3.7543238677      2.3595052770     -0.0000000000
C       -2.3558964856      2.4149648795     -0.0000000000
C       -4.2565953604      1.0661546476     -0.0000000000
S       -2.9602486842     -0.0047147667     -0.0000000000
C       -1.7527786637      1.1654528070     -0.0000000000
H       -4.3831800787      3.2397880866      0.0000000000
H       -5.3037983458      0.7957415449     -0.0000000000
H       -1.7987262780      3.3422831663     -0.0000000000
H       -0.6874497461      0.9788211444     -0.0000000000
```

You should respect the precise spacing of the input file (in particular, make sure that you have a blank line as last line of the input).
To gain time, we provide you here with an initial geometry for thiophene that we generated using the software `Avogadro`.

You can submit your Gaussian09 calculation by typing the following command.

```
sub pc mono6 go
```

This command will submit your input file "*go.com*" to a queuing system, asking to run on the queue called *mono6*. To see if your job is running, you can type

```
stu
```

Check carefully your Gaussian09 output file called "*go.log*". You should locate in there a part reading "Optimization completed", attesting to the fact that your geometry optimization was successful.

Step 2 – Perform a frequency calculation at the optimized S_0 configuration

In the *newtonx* directory, create a directory called "*2_FREQ-DFT*". Go in this directory. Copy from the previous directory *1_OPT-DFT* the Gaussian checkpoint file (containing information about the converged geometry).

```
cp ../1_OPT-DFT/go.chk .
```

Use the following template to perform the frequency calculation:

```
%chk=go.chk
%nproc=1
#P GFINPUT
#wb97xd/6-31g* freq=noraman NoSymm guess=read geom=check

 0 1
```

This input file reads information from the checkpoint file (that is why you do not see explicit coordinates for the atoms) and request a frequency calculation. Copy paste the template in a file called "*freq.com*" and submit it to the queue by typing

```
sub pc mono6 freq
```

Once the job is over, you should see in your output file *freq.log* a list of all the vibrational frequencies (you can locate it by looking for "Frequencies" in the output). None of the frequencies should be negative (or to be more precise, imaginary).

Step 3a, 3b, 3c – Generate initial conditions and compute a photoabsorption cross-section s

Using the information generated up to this point, we will create a Wigner distribution for a set of uncoupled harmonic oscillators.

Create a directory called "*3_INITIAL_CONDITION*" in the main directory *newtonx*. Copy in this file the output file from Gaussian09 with the frequencies (*freq.log*). In the file *freq.log*, locate the coordinates of the optimized molecule (search for "Angstrom"), extract them into a new file called "*final.xyz*" (*if you use* `vi`*, you might need to select*

the lines you want to copy, press "y" and copy those lines in the new file pressing "p") and modify the format such that it looks like this:

```
   9
Final geometry
        C          -3.769132    2.375102    0.000000
        C          -2.342370    2.431685    0.000000
        C          -4.242145    1.096773    0.000000
        S          -2.958250   -0.055098    0.000000
        C          -1.769608    1.194830    0.000000
        H          -4.410839    3.248422    0.000000
        H          -5.271629    0.766289    0.000000
        H          -1.771839    3.353082    0.000000
        H          -0.717185    0.946912    0.000000
```

Use Newton-X to convert these coordinates from an xyz format to a Newton-X format:

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

This should generate in your directory a file called "*geom*" containing coordinates in a different format.

In the directory *3_INITIAL_CONDITION*, create a new directory called "*JOB_AD"*. This directory will contain a template input file for Gaussian09 that Newton-X will use every time it needs to collect information about the electronic structure information of the molecule. Move in the directory *JOB_AD* and create a template input file called "*gaussian.com*":

```
%chk=gaussian
%rwf=gaussian
%nproc=4
#TD(NStates=3) 6-31G* wB97XD NoSymm


0 1
        C          -3.769132    2.375102    0.000000
        C          -2.342370    2.431685    0.000000
        C          -4.242145    1.096773    0.000000
        S          -2.958250   -0.055098    0.000000
        C          -1.769608    1.194830    0.000000
        H          -4.410839    3.248422    0.000000
        H          -5.271629    0.766289    0.000000
        H          -1.771839    3.353082    0.000000
        H          -0.717185    0.946912    0.000000
```

The coordinates at the end of this file should be the one in the file *final.xyz* you produced earlier. This template input file requests Gaussian09 to compute the lowest three excited states (S_1, S_2, S_3) using LR-TDDFT.
Create a second file in the directory *JOB_AD* called "*basis*" and containing the simple line:

```
6-31G*
```

This file is just here to inform Newton-X about the type of basis that is used.

Move back to the directory *3_INITIAL_CONDITION*. We will now use the Newton-X input-file generator called "*nxinp*" to request the generation of the initial conditions and the calculation of excitation energies for each nuclear configuration sampled. Run the command

```
$NX/nxinp
```

and you will be required to answer some questions to set up the input file for generating the initial conditions. You shall answer, in the order:

1 for selecting GENERATE INITIAL CONDITIONS
2 for selecting the Wigner distribution
9 for the number of atoms in thiophene
10 for the number of initial conditions you want to generate
geom for the name of the file containing the optimized geometry
4 for GAUSSIAN output
freq.log for the file containing the normal modes
<ENTER> for selecting the default value
<ENTER> for setting the temperature at 0K
n because we do not compute the photoelectron spectrum
1 for checking the energies between NIS and NFS
1 for the initial state (ground state)
4 for the final state (3rd excited state)
<ENTER> for selecting the default value
<ENTER> for selecting the default value
6.5 for selecting the Gaussian09 program and method
<ENTER> for selecting the default value
<ENTER> for selecting the default value
7 to exit

You can as well follow the steps described in the section 4.4.15 (please do not proceed further) of the Newton-X tutorial https://www.univie.ac.at/newtonx/tutorial-2_0.pdf. Caution: please use 10 for the number of points instead of 50. (Setting npoints = 10).

Once you have your file called *initqp_input*, you can submit the generation of initial conditions using the command:

```
sub pc mono6_4 generate_initcond.sh exe
```

IMPORTANT: you have to copy the script `generate_initcond.sh` from another directory in your home to your current directory, by typing the command:

```
cp ~/thiophene/generate_initcond.sh .
```

This calculation will generate 10 initial conditions and, for each of them, a LR-TDDFT calculation will be performed. As such, this will take a bit of time to complete. You can see the progress of the calculation by looking at the output file initcond.log.

Once the calculation is over, we will use *nxinp* to generate the photoabsorption cross-section. Run once again the command

```
$NX/nxinp
```

and give the following answers

5 for selecting GENERATE SPECTRUM
1 for selecting Generate absorption spectrum
1 for selecting the initial state as the ground state
2-4 for selecting the final states
F for the photoabsorption cross-section
1 for using the energy restriction in the final output
-1 for reading the oscillator strength from the final output
<ENTER> for selecting the default value
<ENTER> for selecting the default value
<ENTER> for selecting the default value
<ENTER> for selecting the default value
<ENTER> for setting the temperature at 0K
<ENTER> for setting the refraction index to 1
<ENTER> for selecting the default value
<ENTER> for selecting the default value
7 to exit

The file *cross-section.dat* is thus generated, and you can visualize it with `gnuplot`.

Once more, you can follow the steps described in the 4.7.24 of the Newton-X tutorial if you prefer. Please note that you use 2-4 for the value of nfs instead of 2-11 as described in the tutorial. You can visualize the photoabsorption cross-section (cross-section.dat) using gnuplot.

Step 4 – Generate the different TSH trajectories and run them independently

Finally! We have all the needed ingredients to perform a TSH calculation!

Create a directory called "*4_TSH*" in the main repertory *newtonx*. Go in this directory and copy from the directory *3_INITIAL_CONDITION* the file *geom*, all the files *final_output.**, and the directory JOB_AD. Using *nxinp*, we will do

SET BASIC INPUT & GENERATE TRAJECTORIES

To do this, run

```
$NX/nxinp
```

and give the following answers

2 for selecting SET BASIC INPUT
9 for the number of atoms in thiophene
4 for calculating a total of 4 states (ground + 3 excited states)
3 for starting the dynamics on the 2nd excited state
<ENTER> for selecting the default value

<ENTER> for selecting the default value
6.5 for selecting TDDFT and Gaussian09
100 for performing a nonadiabatic simulation
n for not generating an internal coordinates file
7 to exit

A file called *control.dyn* is generated in the directory *4_TSH*. Copy one of the final_output.* files in final_output with the command

```
cp final_output.1.2 final_output
```

You can now run once again

```
$NX/nxinp
```

and give the following answers

5 for selecting GENERATE TRAJECTORIES
4 for selecting Generate trajectories
<ENTER> for selecting the default value
n for not running the trajectories in a batch system
7 to exit

This last operation will automatically generate a directory called "*TRAJECTORIES*" that will contain 10 different directories "*TRAJX*", where "*X*" will vary from *1* to *10*. Each *TRAJX* directory contains all the required information to perform a TSH dynamics based on a specific set of initial conditions ("*geom*" and "*veloc*").

Once this part done, we will launch a TSH dynamics for one of the trajectories. Move into the directory *TRAJECTORIES* and select one of the trajectories you want to run (i.e., enter one of the *TRAJX* directory). Once there, submit the calculation by typing:

```
sub pc mono6_4 do_dynamics.sh exe
```

IMPORTANT: you have to copy the script `do_dynamics.sh` from another directory in your home to your current directory, by typing the command:

```
cp ~/thiophene/do_dynamics.sh .
```

You can refer to the Newton-X tutorial, section 6.5 for indication on how to perform a statistical analysis of the results after a large number of trajectories have been generated. In fact, we have performed here a single TSH run. You should in principle run way more trajectories to converge the stochastic sampling of initial conditions and hopping algorithm (tens, hundreds, thousands, depending on the quantity you are interested in).

We provide you with a set of trajectories that you can analyze with Newton-X if you want (section 6.6 of the Newton-X tutorial). You can go to the main directory where you have produced your data

```
cd ~/newtonx/
```

and then copy here the results of a 10-trajectory calculation that we performed previously, by typing the command

```
cp -r ~/thiophene/RESULTS .
```

Go to the new directory

```
cd RESULTS/TRAJECTORIES
```

and run the command

```
$NX/nxinp
```

to set the statistical analysis by selecting *6*. You can either analyze the energies (by selecting *1* at the question: Kind of properties to be analysed) or the population of the electronic states (by selecting *2* at the question: Kind of properties to be analysed). Then you can perform the analysis by running

```
$NX/analysis.pl
```

At the end of the statistical analysis, a new directory `ANALYSIS` will be created containing the average quantities that have been computed.

SUGGESTIONS: have a look at the file prop.1 to analyze the energy along single trajectories and at the file mean_value.2 to analyze average electronic populations.

Also, you can go to the directory

```
cd RESULTS/TRAJECTORIES/TRAJ1/RESULTS/
```

and run the command

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

to generate a trajectory-file that can be visualized with VMD (or Molden).

Enjoy!