Introduction

In the following, we will learn how to use NEMO package (Leonardo Evaristo de Sousa and Piotr de Silva, Journal of Chemical Theory and Computation 2021 17 (9), 5816-5824 DOI: 10.1021/acs.jctc.1c00476)

This step by step tutorial will use the example of Heptazine (Hz) On a first hand, one will need to compute the frequencies of the optimized structures at the S0, S1, and T1 states using **QChem** au **gaussian** On a second hand, a wigner distribution will be computed using the **NEMO** package.

Finally one will visualize the results using nemoview.

Installation of the NEMO package

First, we need to install the NEMO package on the machine where the calculations will be computed. This can be done by running the following cell.

```
module load SciPy-bundle/2020.03-intel-2020a-Python-3.8.2
git clone https://github.com/LeonardoESousa/NEMO
```

Second, one needs to create the submission script, **~/nemo.sh** . This can be done by copy and paste the following cell.

```
#!/bin/bash
#SBATCH --mem=100GB
#SBATCH --time=1-0
#SBATCH -N 1
#SBATCH -n 24
#SBATCH --partition=xeon24
module purge
module use /home/energy/modules/modules/all
module --ignore-cache load "binutils/2.31.1-GCCcore-8.2.0"
module load iomkl
module load QChem/5.2-multicore
export $QCLOCALSCR=/scratch/lajour
bash $1
rm -rf /scratch/lajour/*
rm slurm*out
```

Ground-state optimization

Nemo is interfaced with Gaussian and QChem only.

Here is an example of optimization and frequencies calculation of the ground state of the molecule using qchem. The inputfile is **Hz_optfreqS0.com** and the outputfile is **Hz_optfreqS0.out**

```
$rem
GEOM_OPT_PRINT  6 !Print all the information of the optimization process
(optional)
JOBTYPE         opt
METHOD  wb97xD
BASIS   cc-pVDZ
MEM_TOTAL       4000
MEM_STATIC      100
$end

$molecule
0 1
N
C  1 1.390948
N  2 1.317471 1 119.100767
C  3 1.315069 2 116.705881 1 -0.004215 0
H  4 1.075573 3 115.805871 2 179.983742 0
N  4 1.315046 3 128.387403 2 0.010584 0
C  6 1.317493 4 116.706392 3 -0.011785 0
N  7 1.317470 6 121.799814 4 179.997928 0
C  8 1.315070 7 116.706019 6 -179.995454 0
H  9 1.075573 8 115.805882 7 -179.990374 0
N  9 1.315045 8 128.387319 7 -0.002529 0
C  11 1.317494 9 116.706427 8 0.006074 0
N  12 1.317470 11 121.799668 9 179.993285 0
C  13 1.315070 12 116.705933 11 -179.996228 0
H  14 1.075572 13 115.805919 12 -179.993637 0
N  14 1.315045 13 128.387316 12 -0.002210 0
$end

@@@

$molecule
read
$end

$rem
JOBTYPE         freq
METHOD  wb97xD
BASIS   cc-pVDZ
MEM_TOTAL       4000
MEM_STATIC      100
$end
```

If a negative frequency is found, the molecule is unstable and the following computations might be erronous. Hence, a strategy is to tighten the convergence criteria and re-run the calculation. Or rerun the optimization from the saddle point.

Once the optimization and the frequencies are computed, it is time to generate the Wigner ensemble.

Wigner ensemble

One needs to create the **EnsembleS0** directory and to paste the file *Hz_optfreqS0.out* in it. Attention, the extension of the file has to be **.out** and not **.log**.

Then, one needs to create the **nemo.sh** file in the **EnsembleS0** directory. This can be done by running the following cell.

```
mkdir EnsembleS0/
cp Hz_optfreqS0.out EnsembleS0/
echo "sbatch ~/nemo.sh \$1" >> EnsembleS0/batch.sh
```

The arborescence should look like the following :

```
EnsembleS0
├── batch.sh
└── Hz_optfreqS0.out
```

Finally, go to the **EnsembleS0** folder then generate the Wigner ensemble with the following steps within the folder **EnsembleS0** To do so, one will select the first option *Generate the inputs for the nuclear ensemble calculation*

```
cd EnsembleS0
nemo
```

```
[EnsembleS0]$ nemo
#     # ####### #     # #######
##    # #        ##   ## #     #
# #   # #        # # # # #     #
#  #  # #####    #  #  # #     #
#   # # #        #     # #     #
#    ## #        #     # #     #
#     # ####### #     # #######
----------Photophysics---------

Choose your option:

ENSEMBLE SETUP:
      1 - Generate the inputs for the nuclear ensemble calculation
      2 - Run the ensemble calculations
      3 - Check the progress of the calculations
      4 - Abort my calculations #(deletes the limit.lx file in the folder
you are. This stops the submission of further jobs. It does not kill jobs
already on the queue)
ABSORPTION:
      5 - Generate the absorption spectrum
EXCITED STATE PROPERTIES (FLUORESCENCE, PHOSPHORESCENCE, ISC):
      6 - Estimate rates and compute emission spectrum
ENSEMBLE DATA:
      7 - Gather ensemble data only
EXCITON ANALYSIS:
      8 - Estimate Förster radius, fluorescence lifetime and exciton
diffusion lengths
1
```

```
Hz_optfreqS0.out #File contains structure and vibrational modes
Is this the frequency file? y ou n? #Press "n" and the program will propose
another file
y

The suggested configurations for you are: #Check the calculation parameters
: method, basis set and so on

$rem
GEOM_OPT_PRINT  6
METHOD   wb97xD
BASIS    cc-pVDZ
MEM_TOTAL        4000
MEM_STATIC       100
$end

Are you satisfied with these parameters? y or n?
y
Solvent's static dielectric constant?
2.38 #For toluene
Solvent's refractive index?
1.4 #For toluene
How many excited states?
10
Prepare input for absorption or fluorescence spectrum only? (y or n)  press
"n" only for excited-state geometries. Allow to compute SOC rates /!\ SOC
not possible with ADC(2) method
Y
Ok, calculations will only be suitable for absorption or fluorescence
spectrum simulations!

How many geometries to be sampled?
500 #To have a representative ensemble, at least 200
Temperature in Kelvin?
300

Generating geometries...

   100.0% of the geometries done.

Done! Ready to run.
```

The folder **Geometries** is generated with all the geometries required. These are generated along the vibrational modes. In addition to the folder **Geometries**, the files Magnitudes*300K*.lx and Opt_Lambda.com are generated. The first one contains the magnitudes of the displacements along the vibrational modes. The second one is a reminescence of older version and are not useful anymore.

Check if the input file **Geometry-01-.com** looks like :

```
[EnsembleS0]$ cat Geometries/Geometry-01-.com

$comment
ABSSPCT
$end
```

```
$rem
cis_n_roots              10
cis_singlets             true
cis_triplets             true
calc_soc                 false
STS_MOM                  true
CIS_RELAXED_DENSITY      TRUE
solvent_method           PCM
GEOM_OPT_PRINT  6
METHOD  wb97xD
BASIS   cc-pVDZ
MEM_TOTAL       4000
MEM_STATIC      100
$end

$pcm
theory                   IEFPCM
ChargeSeparation         Marcus
StateSpecific            Perturb
$end

$solvent
Dielectric               2.38
OpticalDielectric        1.9599999999999997 !Square of 1.4
$end

$molecule
0 1
N   0.03971718136936  -0.04954075376651  -0.09305162034207
C  -0.60242722734286  -1.22998167855624  -0.03840524045065
N   0.08748486595726  -2.26651486282793   0.15508198357482
C   1.39480492258405  -2.21674883250099   0.01480361474069
H   1.99322406536358  -3.10087112748250   0.07320854372390
N   2.14168805921999  -1.02737120411578  -0.09049653528144
C   1.37350101239272   0.01864790878427   0.01099262644877
N   1.97799997771598   1.21738510587816   0.04235194464137
C   1.21101778083085   2.25865379842196   0.02131885328317
H   1.70919782331199   3.18060859112108   0.15211877100936
N  -0.10550847045592   2.36094988141728   0.00161851202900
C  -0.80469867294343   1.19326561222245  -0.04495861619107
N  -2.11861436012403   1.14065212096364   0.06200387308776
C  -2.62996485441531  -0.12475124453871   0.01684246292799
H  -3.79497911209860  -0.08861776682951   0.20606551546139
N  -1.96641949693936  -1.28848651869247  -0.09233838212287
$end
```

Run the ensemble calculation

In this step, one will run the ensemble calculation. This can be done with the second option of nemo with :

```
[EnsembleS0]$ nemo
#     # ####### #      # #######
```

```
##    # #        ##    ## #      #
# #   # #        # # # # #       #
#  #  # #####    #  #  # #       #
#   # # #        #      # #      #
#   ## #         #      # #      #
#     # ####### #       # #######
----------Photophysics---------

Choose your option:

ENSEMBLE SETUP:
        1 - Generate the inputs for the nuclear ensemble calculation
        2 - Run the ensemble calculations
        3 - Check the progress of the calculations
        4 - Abort my calculations (deletes the limit.lx file in the folder
you are. This stops the submission of further jobs. It does not kill jobs
already on the queue)
ABSORPTION:
        5 - Generate the absorption spectrum
EXCITED STATE PROPERTIES (FLUORESCENCE, PHOSPHORESCENCE, ISC):
        6 - Estimate rates and compute emission spectrum
ENSEMBLE DATA:
        7 - Gather ensemble data only
EXCITON ANALYSIS:
        8 - Estimate Förster radius, fluorescence lifetime and exciton
diffusion lengths
2 # Run the ensemble calculations



batch.sh
Is this the batch script? file? y ou n?
y
Maximum number of batches to be submitted simultaneously?
10 # Number of jobs in the queue at one time
Number of processors for each individual job
12 # Depends on the partition uses: The multiplication with the " jobs in
each batch has to be equal to the number of processors in the partition
Number of jobs in each batch. Here, 24 processors were available, so 2 job
were run simultaneously with 12 procs each
2 # Number of jobs in the queue at one time
```

Triplet and singlet state optimization

Here is an example of optimization and frequencies calculation of the ground state of the molecule using qchem. The input files are **Hz_optfreqS1.com** and **Hz_optfreqT1.com** and the output files are **Hz_optfreqS1.out Hz_optfreqT1.out**

```
$rem
GEOM_OPT_PRINT  6
JOBTYPE         opt
METHOD   wb97xD
BASIS    cc-pVDZ
CIS_N_ROOTS      5
```

```
CIS_SINGLETS      true !False for triplet optimization
CIS_TRIPLETS      false !True for triplet optimization
CIS_STATE_DERIV 1
MEM_TOTAL         4000
MEM_STATIC        100
GEOM_OPT_TOL_GRADIENT 150 !Tighened the convergence criteria because
negatives frequencies were first computed.
GEOM_OPT_TOL_DISPLACEMENT       600
GEOM_OPT_TOL_ENERGY      50
$end

$molecule
0 1
N         0.00006        0.00006        0.15645
C        -0.62938        1.26435        0.01273
N         0.11879        2.35949       -0.03235
C         1.45189        2.18957        0.00053
H         2.05506        3.09906        0.00514
N         2.12743        1.02776       -0.03146
C         1.40950       -0.08726        0.01379
N         1.98427       -1.28242       -0.03253
C         1.17057       -2.35197       -0.00089
H         1.65699       -3.32891        0.00264
N        -0.17328       -2.35610       -0.03200
C        -0.78055       -1.17699        0.01450
N        -2.10289       -1.07699       -0.03129
C        -2.62259        0.16238        0.00018
H        -3.71162        0.22968        0.00460
N        -1.95396        1.32817       -0.03288
$end

@@@

$molecule
read
$end

$rem
JOBTYPE           freq
METHOD   wb97xD
BASIS    cc-pVDZ
CIS_STATE_DERIV      1
CIS_N_ROOTS      5
CIS_SINGLETS      true !False for triplet optimization
CIS_TRIPLETS      false !True for triplet optimization
MEM_TOTAL         4000
MEM_STATIC        100
MAX_SCF_CYCLES 200
MAX_CIS_CYCLES 200
$end
```

Wigner ensemble

One needs to create the **EnsembleS1** (**EnsembleT1**) directory and to paste the file *Hz_optfreqS1.out* (*Hz_optfreqT1.out*)in it.

Then, one needs to create the **nemo.sh** file in the **EnsembleS1** (**EnsembleT1**) directory. This can be done by running the following cell.

```
mkdir EnsembleS1/
cp Hz_optfreqS1.out EnsembleS1/
echo "sbatch ~/nemo.sh \$1" >> EnsembleS1/batch.sh
```

or

```
 mkdir EnsembleT1/
cp Hz_optfreqS1.out EnsembleT1/
echo "sbatch ~/nemo.sh \$1" >> EnsembleT1/batch.sh
```

The arborescence should look like the following :

```
EnsembleS1
├── batch.sh
└── Hz_optfreqS1.out
or
EnsembleT1
├── batch.sh
└── Hz_optfreqT1.out
```

Finally, go to the **EnsembleS1** (**EnsembleT1**) folder then generate the Wigner ensemble with the following steps within the folder **EnsembleS1** (**EnsembleT1**) To do so, one will select the first option *Generate the inputs for the nuclear ensemble calculation*

```
cd EnsembleS1
nemo
```

At the difference from the ground-state ensemble, for the question "Prepare input for absorption or fluorescence spectrum only? (y or n)" press "n".

```
[EnsembleS1]$ nemo
#      # ####### #      # #######
##     # #        ##    ## #      #
# #    # #        # # # # #      #
#  #  # # #####   #  #  # #      #
#   # # # #       #      # #      #
#    ## #         #      # #      #
#      # ####### #      # #######
----------Photophysics---------

Choose your option:

ENSEMBLE SETUP:
        1 - Generate the inputs for the nuclear ensemble calculation
        2 - Run the ensemble calculations
        3 - Check the progress of the calculations
```

```
        4 - Abort my calculations
ABSORPTION:
        5 - Generate the absorption spectrum
EXCITED STATE PROPERTIES (FLUORESCENCE, PHOSPHORESCENCE, ISC):
        6 - Estimate rates and compute emission spectrum
ENSEMBLE DATA:
        7 - Gather ensemble data only
EXCITON ANALYSIS:
        8 - Estimate Förster radius, fluorescence lifetime and exciton
diffusion lengths
1

Hz_optfreqT1.out
Is this the frequency file? y ou n?
y

The suggested configurations for you are:

$rem
METHOD   wb97xD
BASIS    cc-pVDZ
MEM_TOTAL       4000
MEM_STATIC      100
$end

Are you satisfied with these parameters? y or n?
y
Solvent's static dielectric constant?
2.38
Solvent's refractive index?
1.4
How many excited states?
5
Prepare input for absorption or fluorescence spectrum only? (y or n)
n #Will compute emission spectra AND SOC constants
Ok, calculations will be suitable for all spectra and ISC rate estimates!

How many geometries to be sampled?
500
Temperature in Kelvin?
300

Generating geometries...

   100.0% of the geometries done.

Done! Ready to run.
```

The folder **Geometries** is generated with all the geometries required. These are generated along the vibrational modes.

Check if the input file **Geometry-01-.com** looks like the following cell, if so run the ensemble calculation as described in the previous section.

```
[EnsembleS1]$ cat Geometries/Geometry-01-.com

$comment
EMISPCT
$end

$rem
cis_n_roots            5
cis_singlets           true
cis_triplets           true
calc_soc               true
STS_MOM                true
CIS_RELAXED_DENSITY    TRUE
solvent_method         PCM
METHOD   wb97xD
BASIS    cc-pVDZ
MEM_TOTAL        4000
MEM_STATIC       100
$end

$pcm
theory                 IEFPCM
ChargeSeparation       Marcus
StateSpecific          Perturb
$end

$solvent
Dielectric             2.38
OpticalDielectric      1.9599999999999997
$end

$molecule
0 1
N   -0.01011961841039   0.01824575984271   0.21051878677385
C    1.24735574010264   0.75023265696078  -0.03288757696271
N    1.09139146015891   2.09709104326643  -0.06542076101527
N    2.37242521442645   0.09379384367060  -0.13265607243157
C    2.37566672791496  -1.14830750383109   0.01744774668435
H    3.31585768898542  -1.87876384180200  -0.01434545362253
C   -0.14462254987935   2.66447437623288  -0.03203222413041
H   -0.16146613685169   3.78870640870462  -0.02704544490080
N    1.28561147502865  -1.99275787331816   0.06349582722178
C    0.06176384120582  -1.38848408496539   0.08939217806750
N   -1.13329317963977  -2.09146318228738  -0.04583829059091
C   -2.22929197379487  -1.45777439689018  -0.17528818348807
H   -3.06464026558267  -2.07798031725186  -0.27846665437763
N   -2.33318945246678  -0.07533322512782   0.00175307139228
C   -1.23970913567289   0.55699589133919   0.05118818767545
N   -1.33974510675090   1.98137815058730   0.06565404616007
$end
```

Visualization of the results

Creation of the visualization environment on your work computer

Download **Visualization code studio** (https://code.visualstudio.com/) and install it on your machine.

Open Visual Studio Code and create a virtual environment

```
python -m venv view and activate this environment : &
".view\Scripts\activate"
```

Note, to deactivate the environment, run the following command: & ".view\Scripts\deactivate"

Import nemoview from github (i.e **Voilà** package) pip install git+https://github.com/LeonardoESousa/NEMO

```
git clone https://github.com/LeonardoESousa/nemoview

cd .\nemoview\

pip install .
```

Import and install labplot pip install git+https://github.com/LeonardoESousa/labplot

to open nemoview : $nemoview

Generation of the results file

The vizualization of the results can be done through the options 5 (Generate the absorption spectrum) and 7 (Gather ensemble data only, used for nemoview) of nemo

```
cd EnsembleS0
nemo
```

choose option 7 and S0 state.

The file Ensemble*S0*.lx is generated Do the same for the S1 and T1 states and the files Ensemble*S1*.lx and Ensemble*T1*.lx are generated.

```
[EnsembleS0]$ nemo
#       # ####### #     # #######
##      # #          ##    ## #      #
# #     # #         # # # # #       #
#  #    # #####    #  #  # #       #
#   # # # #          #      # #       #
#    ## # #          #      # #       #
#       # ####### #     # #######
----------Photophysics---------

Choose your option:
```

```
ENSEMBLE SETUP:
        1 - Generate the inputs for the nuclear ensemble calculation
        2 - Run the ensemble calculations
        3 - Check the progress of the calculations
        4 - Abort my calculations (deletes the limit.lx file in the folder
you are. This stops the submission of further jobs. It does not kill jobs
already on the queue)
ABSORPTION:
        5 - Generate the absorption spectrum
EXCITED STATE PROPERTIES (FLUORESCENCE, PHOSPHORESCENCE, ISC):
        6 - Estimate rates and compute emission spectrum
ENSEMBLE DATA:
        7 - Gather ensemble data only
EXCITON ANALYSIS:
        8 - Estimate Förster radius, fluorescence lifetime and exciton
diffusion lengths
7
What is the initial state (S0, S1, T1, S2 ...)? Accepts comma separated
values Ex: T1,T2
S0 # I visualizs the results obtiained from the ground-state geometry
```

Copy the files **Ensemble*S0*.lx**, **Ensemble*S1*.lx**, **Ensemble*T1*.lx** to your work directory on your computer.

Open *visual studio code* and run a new terminal. Activate the virtual environment and run the following command : nemoview

A google chrome window will open. Click on the button **Open** and select the three ensemble files. In the three widgets "molecule:" right the same thing for the system to understand the same system is studied. Press *Read file*

A window composed of four sections will appear, **Diagram** that depicts the photophysics parameters, **Spectra** represents the absorption or emission spectra of the compound, **Susceptibility** represents the solvent susceptibility of the compound and **Network** represents the initial and final susceptibility of a considered transition.

Diagram

Organization of the energy levels for the S_1 (blue) and T_1 (yellow) ensembles. The arrow represents the direction of the inter-system-crossing. One can modulate this vizualisation through the following parameters : ϵ : variation of the dielectric constant of the solvent n_r : variation of the refractive index of the solvent Cutoff : modulate the number of rows displayed under the diagram. The higher the cutoff, the less row will be displayed. Below the diagram is deplayed a Table : Transition : Transition considered between the two states

```
Rate : Conversion rates between the two states

Error : Error on the rate

Prob : Probability of the transition

AvgDE+L : Average energy difference between the two states
```

```
AvgSOC : Average spin-orbit coupling

AvgSigma : Average broadening

AvgConc : Average of the fraction of the ensemble that contribute to the
ensemble rate.
```

Spectra

Display the absorption, fluorescence and emission spectra of the compound. Once againm the dielectric constant and the refractive index of the solvent can be tuned. To select or deselect a spectrum, click on the corresponding checkbox while pressing "ctrl" key.

Susceptibility

For a better visualization, set the curseur **Bin 10^x (eV)** to -3.

The solvent properties can be extrapolated with the modification of the refractive index and the dielectric constant.

The Figure **a** represents the electronic susceptibility of each electronic state.

The smaller the x value is, the more localized this state is, as can be visualized through the Figure **b** that depicts a strongly Localized excited state for these two states.

Network

represents the initial and final susceptibility of a considered transition.