MOMAP

Tutorial 02

Phosphorescence Spectrum Calculation

MOMAP

Molecular Material Property Prediction Package
**MOMAP Tutorial**

- Phosphorescence Spectrum Calculation

$\text{Ir(PPy)}_3$ is able to emit light efficiently from the excited triplet state, due to the enhancement of intersystem crossing (ISC) induced by the Ir atom. The ISC efficiency is a result of mixing of singlet and triplet states, so that the normally forbidden singlet-triplet transitions become allowed.

MOMAP is able to simulate the phosphorescence spectrum and calculate the corresponding radiative decay rate constant based on the TVCORF_SPEC and TVSPEC_SPEC subprograms. The TVCORF_SPEC subprogram is used to calculate thermal vibration correlation function (TVCF), while the TVSPEC_SPEC subprogram is used to simulate phosphorescence spectrum.

To begin the TVCORF_SPEC and TVSPEC_SPEC calculations, we need the \texttt{evc} results. The \texttt{evc} calculation can use outputs from other QC programs, such as Gaussian, TURBOMOLE, ChemShell, Dalton, MOLPRO, DFTB and MOPAC etc. It can also read data from the output files, including vibrational frequencies and force constant matrix, and calculate normal mode displacement, Huang-Rhys factor, reorganization energy and Duschinsky rotation matrix between initial and final electronic states under both internal coordinate and Cartesian coordinate.

The basic steps involved in the calculations of Phosphorescence Spectrum are as follows:

1. Gaussian calculations
2. Obtain EDMA, EDME, and Hso (by using Dalton)
3. Vibration analysis \textit{etc}
4. Phosphorescence spectrum calculation

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Gaussian Calculations

Optimization calculation on ground state ($S_0$)

Once the initial geometry is obtained, we have to find the optimized $S_0$ ground state geometry. The route section is set as \texttt{#p opt b3lyp/gen pseudo=read}.

The initial geometry gaussian $S_0$ input file (Irppy-s0-opt.com) is shown as follows:

```
%chk=Irppy3-s0-opt.chk
%mem=32GB
%nprocl=4
%nprocs=16
#p opt b3lyp/gen pseudo=read

Ir Complex No.1 - S0 Opt

0 1
  Ir  -0.00026100  0.00081800  -0.02546400
  C   1.23475200  1.22563100  -1.06555400
  C   3.17477000  2.89735700  -2.32701500
  C   0.92442700  1.99391300  -2.20485100
  C   2.57228300  1.32514600  -0.57850700
  C   3.52102800  2.15413000  -1.20673700
  C   4.16509200  0.43765200  1.21020600
  H   5.33396800 -0.43571700  2.78791400
  H   3.39236400 -1.78733400  3.66167400
  H   1.19605700 -1.58570100  2.48734100
  H   4.98966700  1.01859900  0.81497000

C H N O
6-31G**
****
Ir 0
LANL2DZ
****

Ir 0
LANL2DZ
```

We use g09 or g16 to do the geometry optimization.

Optimization calculation on lowest triplet excited state ($T_1$)

With the optimized $S_0$ geometry at hand, we can start optimizing $T_1$ geometry using the optimized $S_0$ geometry as the initial structure. The route section is set as \texttt{#p opt b3lyp/gen pseudo=read}. 

1
Again, the initial gaussian T1 input file (irppy3-t1-opt.com) is shown as follows:

```plaintext
%chk=Irppy3-t1-opt.chk
%mem=32GB
%nprocl=1
%nprocs=16
#p opt b3lyp/gen pseudo=read

Ir Complex No.1 - T1 opt

0 3
Ir 0.00043600 0.00028600 0.02544800
C 0.20235100 1.72880300 1.06370900
C 0.32555100 4.28900800 2.32011100
C 1.00022100 1.95958100 2.20157500
C -0.54479300 2.84229300 0.57608300

---
H -3.51910800 1.55565400 -3.64762700
H -1.99610700 -0.04366300 -2.47809500
H -2.28620800 4.55115900 -0.81265400

C H N O
6-31G**
****
Ir 0
LANL2DZ
****

Ir 0
LANL2DZ
```

Or

```plaintext
%chk=Irppy3-t1-opt.chk
%mem=32GB
%nprocl=1
%nprocs=16
#p opt td b3lyp/gen pseudo=read

Ir Complex No.1 - T1 opt

0 1
Ir 0.00043600 0.00028600 0.02544800
C 0.20235100 1.72880300 1.06370900

---
```

Again, use g09 or g16 to do the T1 optimization. Here, the first option for T1 optimization is recommended, as it takes much less time.
Fig. 1 Optimized $S_0$ geometry

Fig. 2 Optimized $T_1$ geometry

**TIPS:** To obtain the optimized ground state geometry, use Gaussview to open Irppy3-s0-opt.log file, and save as Irppy3-t1-opt.com. Then, modify the first and last few lines of Irppy3-t1-opt.com.
Frequency calculation on ground state ($S_0$)

The gaussian $S_0$ input file (Irppy3-s0-freq.com) is shown as follows:

```plaintext
%chk=Irppy3-s0-freq.chk
%mem=32GB
%nprocl=1
%nprocs=16
#p freq b3lyp/gen pseudo=read
Ir Complex No.1 - S0 freq
0 1
Ir 0.00043600 0.00028600 0.02544800
C 0.20235100 1.72880300 1.06370900
C 0.32555100 4.28900800 2.32011100
C 1.00022100 1.95958100 2.20157500
C -0.54479300 2.84229300 0.57608300
C -0.47534300 4.10152400 1.20174700
C 1.06299300 3.20800700 2.81873400
H 1.57895800 1.13987100 2.61491300
N -1.33525800 1.32844300 -1.09053800
C -1.39357600 2.59757600 -0.59325500
C -2.23463700 3.54335400 -1.20684000
H -3.65253800 3.91910500 -2.77737000
H -3.51910800 1.55565400 -3.64762700
H -1.99610700 -0.04366300 -2.47809500
H -2.28620800 4.55115900 -0.81265400
C H N O
6-31G**
****
Ir 0
LANL2DZ
****
Ir 0
LANL2DZ
```

We use g09 or g16 to do the $S_0$ frequency calculation.

**TIPS:** Copy Irppy3-t1-opt.com to Irppy3-s0-freq.com, then, modify the first few lines of Irppy3-s0-freq.com to suit for $S_0$ frequency calculation.
Frequency calculation on lowest triplet excited state ($T_1$)

The gaussian $T_1$ input file (Irppy3-t1-freq.com) is as follows:

```
%chk=Irppy3-t1-freq.chk
%mem=32GB
%nprocl=4
%nprocs=16
#p freq b3lyp/gen pseudo=read
Ir Complex No.1 - T1 freq

0 3
Ir   -0.01639400  0.00293500   0.05369300
C    -0.49053500 -1.69965800   1.03808600
C    -1.03578300 -4.22859100   2.22923000
C    -1.33931300 -1.82209600   2.15439300
C    0.08514300  -2.90172200   0.53285900
C   -0.19369100 -4.14580000   1.12866200
C   -1.60735000 -3.05769200   2.74067000
H   -1.78775300 -0.92837100   2.57535000
N     1.13309800 -1.50308700  -1.09078500
C    0.97867800  -2.77250100  -0.62156900
C    1.66682200 -3.82909800  -1.24466900
H    3.03388000 -4.39374900  -2.80336300
H    3.30179200  -2.02181900  -3.61545900
H    2.03081900  -0.22386100  -2.43415800
H    1.54633100  -4.84073100  -0.87668900
```

$ formchk Irppy3-s0-freq.chk
$ formchk Irppy3-t1-freq.chk

Again, we use g09 or g16 to do the $T_1$ frequency calculation.

**TIPS:** To obtain the optimized excited state geometry, use Gaussview to open Irppy3-t1-opt.log file, and save as Irppy3-t1-freq.com. Then, modify the first and last few lines of Irppy3-t1-freq.com.

Now, all the Gaussian related calculations are done.

In the following calculations, the gaussian *.fchk files are needed, we use the Gaussian built-in command formchk to generate the *.fchk file based on output *.chk. The *.fchk file contains readable force constant matrix information that is needed in dushin calculation.

```
```
Vibration Analysis

The evc calculation requires the basic information on initial and final electronic states. Thus, to begin an evc calculation, you need to designate the related file names in MOMAP input file (i.e., momap.inp).

For the Gaussian output files, you have to provide the corresponding .fchk files as well, as done in the last section.

The momap.inp for an evc calculation is straightforward and is shown as follows:

```bash
[evc]$ cat momap.inp

do_evc   = 1     # toggle dushin rotation effect, 1 or 0

&evc
  ffreq(1)  = "Irppy3-s0-freq.log"  # log file of ground state
  ffreq(2)  = "Irppy3-t1-freq.log"  # log file of excited state
/
```

**TIPS:** In each directory, there exists a README file, just follow the instructions in README to carry out the operations. For example, the README in evc is shown as follows:

How to run MOMAP

1) Copy the following gaussian files from upper directory:

```
../gaussian/Irppy3-s0-freq.fchk
../gaussian/Irppy3-s0-freq.log
../gaussian/Irppy3-t1-freq.fchk
../gaussian/Irppy3-t1-freq.log
```

to this directory.

2) Change momap.inp accordingly.

3) Run MOMAP to do the calculation by the following command:

```
./run
```

Copy the following gaussian output files from upper directory:

```
../gaussian/Irppy3-s0-freq.fchk
../gaussian/Irppy3-s0-freq.log
../gaussian/Irppy3-t1-freq.fchk
../gaussian/Irppy3-t1-freq.log
```

to this evc work directory.

A run file is also created, and is shown as follows:
Users may modify the run file, for example, by changing the np option from 4 to 8, and perform the calculation by running the script file:

```
#!/bin/sh
momap -input momap.inp -np 4 &> log &
```

The result files are shown as follows:

```
[evc]$ ls evc.dx.x.com  Irppy3-s0-freq.fchk  momap.inp  run
evccart.dat  evc.dx.x.xyz  Irppy3-s0-freq.log  momap.inp-new
evcdint.abs  evc.out  Irppy3-tl-freq.fchk  nodefile
evcdint.dat  evc.vibl.xyz  Irppy3-tl-freq.log  README
evcdx.v.xyz  evc.vib2.xyz  log  ref
```

- **evc.cart.dat**: Includes frequency, Huang–Rhys factor, and Duschinsky matrix (Cartesian coordinate system).
- **evc.dint.dat**: Includes frequency, Huang–Rhys factor, and Duschinsky matrix (D solved by using internal coordinate system).
- **evc.cart.abs**: Duschinsky matrix file, used to plot 2D Duschinsky figure.
- **evc.cart.nac**: Projection of NACME to normal modes.
- **evc.cart.inp**: Projection of derivatives of transition dipoles to normal modes.
- **evc.dx.x.com**: Molecular overlapping figure of two electron states (viewed by using Gaussview)
- **evc.dx.x.xyz**: Molecular overlapping figure of two electron states (viewed by using Jmol)
- **evc.dx.v.xyz**: Molecular displacement vectors of two electron states (viewed by using Jmol)
- **evc.vib1.xyz**: Molecular vibrational vectors at ground state (viewed by using Jmol)
- **evc.vib2.xyz**: Molecular vibrational vectors at excited state (viewed by using Jmol)
- **evc.out**: evc log file

Except for ffreq(1) and ffreq(2) parameters, the evc program also allows user to project reorganization energy onto the internal coordinate, to take account of isotope effect, and to configure many other advanced settings etc., please refer to the **MOMAP User Guide** for details.

Please check the reorganization energy results between evc.cart.dat and evc.dint.dat. If the energy difference is small (< 1000 cm⁻¹), then use the results in evc.cart.dat to do the next calculations. However, if the energy difference is large, then use evc.dint.dat to do the next calculations.

**Adiabatic Excitation Energy**

Before we can calculate the Fluorescence Spectrum, we need to known the adiabatic excitation energy \( E_{ad} \). The adiabatic excitation energy is the energy difference between the relaxed excited state energy and the ground state energy.

From the S0 Gaussian log file, locate the last line with "SCF Done" in the output Irppy3-s0-freq.log
file in order to find the single point energy at the optimized $S_0$ geometry.

For example, you may use the following commands:

```bash
$ cat Irppy3-a0-freq.log | grep "SCF Done"
```

In this example, the last line with “SCF Done” is like the following:

```
SCF Done:  E(RB3LYP) = -1541.04579988  A.U.
```

Thus, we have the energy $E_{gs}$ at optimized ground state geometry:

$$E_{gs} = -1541.04579990 \text{ a.u.}$$

From the $T_1$ Gaussian log file, locate the last line with “SCF Done” in the output Irppy3-t1-opt.log file in order to find the single point energy at the optimized $S_1$ geometry.

For example, you may use the following commands:

```bash
$ cat Irppy3-t1-opt.log | grep "SCF Done"
```

In this example, the last line with “SCF Done” is like the following:

```
SCF Done:  E(UB3LYP) = -1540.95161701  A.U.
```

Then, we have the single point energy $E_{es}$ at the optimized $S_1$ geometry:

$$E_{es} = -1540.95161701 \text{ a.u.}$$

From the above obtained ground state $S_0$ and excited state $T_1$ energies, we can obtain the adiabatic excitation energy $E_{ad}$:

$$E_{ad} = E_{es} - E_{gs} = [(-1540.95161701) - (-1541.04579988)] \text{ a.u.}$$

$$= 0.0941829 \text{ a.u.}$$

**TIPS:** To find the energies, users may use [Gaussview](#) to open the Gaussian log file, from the menu item **Results** | **Summary** to obtain the value, which is valid for both the ground state and excited state.
Electronic Transition Dipole and Hso Calculation

To calculate the EDMA, EDME and Hso for Irppy3, we need to do the calculations on both the S0 and T1 states. Here, we use DALTON to do the calculations. As we already have had the Gaussian input and output files, we just need to convert the Gaussian files to the DALTON .mol input files, which can be done easily by a MOMAP python script called gjf2mol.py.

Create a directory dalton, enter into that directory, and copy the Irppy3-s0-freq.com and Irppy3-t1-freq.com to the directory.

```
$ mkdir dalton; cd dalton
$ cp ../gaussian/Irppy3-??-freq.com .
$ ./gjf2mol.py Irppy3-s0-freq.com
$ ./gjf2mol.py Irppy3-t1-freq.com
```

From the directory, we can see two mol files are created. The contents of a mol file are shown as follows:

```
[dalton]$ ls
gjf2mol.py  Irppy3-s0-freq.mol  Irppy3-t1-freq.mol
Irppy3-s0-freq.com  Irppy3-t1-freq.com  soc.dal
```

As the DALTON defaults to use Bohr radius as length unit, so we set it to Angstrom in this case. Also remember to make modification to a line related to Ir, that is, change to "Basis=lanl2dz_ecp ECP=lanl2dz_ecp".

In addition to the molecule file, we also need DALTON control files for EDMA, EDME, and SOC calculations, for example:
The contents of DALTON control file for **EDMA** and **EDME** calculation are shown as follows:

```
[dalton]$ cat edma.dal
**DALTON INPUT
.DIRECT
.PARALLEL
.RUN RESPONSE ! Run integrals, wave function, and response
**INTEGRALS ! Calculate SOC 1e, 2e integrals
**WAVE FUNCTIONS
.DFT
B3LYP
*SCF INPUT ! HF input
.MAX DIIS ITERATIONS 300
**RESPONSE ! Input for the response module
*QUADRATIC ! Calculate quadratic response
.ECPHOS ! Specifies a phosphorescence calculation
.APROP
XDIPLLEN
.APROP
YDIPLLEN
.APROP
ZDIPLLEN
.BPROP
X1SPNSCA
.BPROP
Y1SPNSCA
.BPROP
Z1SPNSCA
.ISPABC 0 1 1
.ROOTS 1 ! Triplet
**END OF INPUT
```

**Notes:**

**.APROP, .BPROP** Specify the operators A and B, respectively. The line following this option should be the label of the operator as it appears in the file AOPROPER. These two keywords can be repeated for different properties.

**XDIPLLEN, YDIPLLEN, ZDIPLLEN** Direction of the applied electric field

**.ISPABC** Spin symmetry of excitation operators associated with physical operators A (ISPINA) and B (ISPINB), and the excited states specified with .ROOTS (ISPINC): "0" for singlet and "1" for triplet. Default is "0,0,0", i.e. all of singlet spin symmetry.
The contents of DALTON control file for Hso calculation are shown as follows:

```
[dalton]$ cat soc.dal
**DALTON INPUT
  .DIRECT
  .PARALLEL
  .RUN RESPONSE
**INTEGRALS
  .SPIN-ORBIT
**WAVE FUNCTIONS
  .DFT
  B3LYP
  *SCF INPUT
  .MAX DIIS ITERATIONS
  300
**RESPONSE
  .TRPFLG
  *LINEAR
  .SINGLE RESIDUE
  .PROPRT
  X1SPNSCA
  .PROPRT
  Y1SPNSCA
  .PROPRT
  Z1SPNSCA
  .ISPABC
    0  1  1
  .ROOTS
    1
```

The molecule file for EDMA calculation is \texttt{Irppy3-s0-freq.mol}, while the molecule file for EDME and Hso calculation is \texttt{Irppy3-t1-freq.mol}, as shown below:

```
[dalton]$ cat Irppy3-t1-freq.mol
ATOMBASIS
Generated by MOMAP through gjf2mol.py
Atomtypes=4  Charge=0  \textbf{Angstrom NoSymmetry}
Charge=7.0  Atoms=3  Basis=6-31G**
 N  -1.81693100  -0.04119500  -1.12840500
 N  0.88745100  1.66140100  -1.08084500
 N  1.01965700  -1.58551300  -1.08420700
Charge=77.0  Atoms=1  \textbf{Basis=lanl2dz_ecp ECP=lanl2dz_ecp}
Ir  -0.01622700  0.00540200  0.05635400
Charge=6.0  Atoms=33  Basis=6-31G**
 C  -0.62604700  -1.65690400  1.03633100
 C  -1.37514700  -4.13735100  2.21899300
 C  -1.49005500  -1.71448700  2.14629900
......
Charge=1.0  Atoms=24  Basis=6-31G**
 H  -1.87095200  -0.78930900  2.56583400
 H  -0.14879700  -5.06093700  0.73220700
......
 H  2.01637700  -0.37959700  -2.42547500
 H  1.18202800  -4.94419400  -0.86229500
```
A sample DALTON run file for EDMA calculation is shown as follows:

```
#!/bin/bash
export PATH=/opt/dalton-2018.2:$PATH
export DALTON_TMPDIR=/tmp
module load dalton/2018.2
nohup dalton -mb 120 -noarch -nodelist hosts -N 12 edma Irppy3-s0-freq &> log &
```

The DALTON calculation results for **EDMA** are shown as follows:

<table>
<thead>
<tr>
<th>Transition energy: 2.630 eV</th>
<th>2.630 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>or 471.394 nm</td>
<td>471.394 nm</td>
</tr>
</tbody>
</table>

- **Length gauge / effective charge spin-orbit integrals:**
  - Partial rates (ECSO): X-polarization 6.37282E+05 Transition moment : 0.182
  - Partial rates (ECSO): Y-polarization 6.40145E+05 Transition moment : 0.182
  - Partial rates (ECSO): Z-polarization 5142.6 Transition moment : 1.631E-02

- **Phosphorescence - length gauge / effective charge spin-orbit integrals:**
  - Oscillator strength (/2PI) (ECSO) 6.800284E-04
  - Dipole strength [a.u.] (ECSO) 6.630809E-02
  - Dipole strength E-40 [esu**2 cm**2] 4.283817E+03
  - Total transition rate (ECSO) 4.275233E+05 s⁻¹
  - Total phosphorescence lifetime (ECSO) 2.39054E-06 s

From the above figure, we can obtain the EDMA:

\[
\sqrt{0.182^2 + 0.182^2 + 0.01631^2} \text{ au} \times 2.5417 \text{ debye/au} = 0.655512 \text{ debye}
\]

Similarly, for the EDME calculation, the .dal control file is the same as the that of EDMA, but the .mol molecule file is `Irppy3-t1-freq.mol` instead.

The DALTON calculation results for **EDME** are shown as follows:

<table>
<thead>
<tr>
<th>Transition energy: 2.153 eV</th>
<th>2.153 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>or 575.832 nm</td>
<td>575.832 nm</td>
</tr>
</tbody>
</table>

- **Length gauge / effective charge spin-orbit integrals:**
  - Partial rates (ECSO): X-polarization 1.54617E+05 Transition moment : 0.121
  - Partial rates (ECSO): Y-polarization 21916. Transition moment : 4.544E-02
  - Partial rates (ECSO): Z-polarization 4526.6 Transition moment : 2.065E-02

- **Phosphorescence - length gauge / effective charge spin-orbit integrals:**
  - Oscillator strength (/2PI) (ECSO) 1.432405E-04
  - Dipole strength [a.u.] (ECSO) 1.706244E-02
  - Dipole strength E-40 [esu**2 cm**2] 1.182314E+03
  - Total transition rate (ECSO) 6.035318E+04 s⁻¹
  - Total phosphorescence lifetime (ECSO) 1.656914E-05 s

From the above figure, we can obtain the EDME:

\[
\sqrt{0.121^2 + 0.04544^2 + 0.02065^2} \text{ au} \times 2.5417 \text{ debye/au} = 0.332683 \text{ debye}
\]
The formula for calculating the $\text{Hso}$ is shown as follows:\(^1\)

$$
\langle S_0 \mid \hat{H}^{SO} \mid T_1 \rangle = \sqrt{\left( \langle S_0 \mid \hat{H}^{SO} \mid T_{1,x} \rangle \right)^2 + \left( \langle S_0 \mid \hat{H}^{SO} \mid T_{1,y} \rangle \right)^2 + \left( \langle S_0 \mid \hat{H}^{SO} \mid T_{1,z} \rangle \right)^2} / 3
$$

The DALTON calculation results for Hso are shown as follows:

<table>
<thead>
<tr>
<th>Excited state no:</th>
<th>1 in symmetry 1 (A) - triplet excitation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excitation energy</td>
<td>7.91261834E-02 au</td>
</tr>
<tr>
<td>Energy</td>
<td>2.1531330 eV; 17366.190 cm⁻¹; 207.74576 kJ / mol</td>
</tr>
<tr>
<td>Total energy</td>
<td>-1539.9969 au</td>
</tr>
<tr>
<td>Operator label:</td>
<td>X1SPNCSA; Transition moment: 3.01887547E-04 au</td>
</tr>
<tr>
<td>Operator label:</td>
<td>Y1SPNCSA; Transition moment: -1.28498669E-03 au</td>
</tr>
<tr>
<td>Spin-orbit coupling constant (X1SPNCSA):</td>
<td>66.256658 cm⁻¹; 3.01887547E-04 au</td>
</tr>
<tr>
<td>Spin-orbit coupling constant (Y1SPNCSA):</td>
<td>-282.02198 cm⁻¹; -1.28498669E-03 au</td>
</tr>
<tr>
<td>Spin-orbit coupling constant (Z1SPNCSA):</td>
<td>95.319266 cm⁻¹; 4.34306537E-04 au</td>
</tr>
</tbody>
</table>

From the figure, the Hso is obtained as:

$$
\sqrt{(66.2567^2 + 282.022^2 + 95.3193^2)} / 3 \text{ cm}^{-1} = 176.08 \text{ cm}^{-1}
$$

Once the EDMA, EDME, and Hso are obtained, we can continue to do the Phosphorescence Spectrum Calculation.

**TIPS:** The Gaussian .com file to DALTON .mol file conversion can be done by using the MOMAP python script `gif2mol.py`, while the EDMA, EDME and Hso values can be easily obtained by using the MOMAP python script `dalton_get_info.py` from the DALTON output files.

---

\(^1\) Qian Peng, Qinghua Shi, Yingli Niu, Yuanping Yi,* Shaorui Sun, Wenqiang Li and Zhigang Shuai*, Understanding the efficiency drooping of the deep blue organometallic phosphors: a computational study of radiative and non-radiative decay rates for triplets. J. Mater. Chem. C, 2016, 4,6829-6838.
Phosphorescence Spectrum Calculation

Nonradiative rate $k_{sc}$

Create a directory $k_{sc}$ and go to that directory.

To start the calculation, you need a *.dat file, a MOMAP control file, and an optional parallel control file. The *.dat file is obtained from the previous mentioned evc calculation. A MOMAP control file is used to control how TVCORF_SPEC and TVSPEC_SPEC subprograms behavior. An optional parallel control file is used to control how many computing processes will be used.

Copy the following evc files from upper directory:

```bash
../evc/evc.cart.dat
```

to this $k_{sc}$ work directory.

Create a momap.inp with its contents as follows:

```
[kisc]$ cat momap.inp
do_isc_tvcf_ft = 1          # toggle inter-system crossing correlation function, 1 or 0
do_isc_tvcf_spec = 1        # toggle inter-system crossing spectrum, 1 or 0
&isc_tvcf
DUSHIN   = .t.              # toggle Duschinsky rotation effect, .t. or .f.
Temp     = 298 K            # temperature
tmax     = 1500 fs          # integral interval of correlation function
dt       = 1 fs             # integration timestep of correlation function
Ead      = 0.0941829 au     # adiabatic excitation energy difference between two states
Hso      = 176.08 cm$^{-1}$ # spin-orbital coupling
DSFile   = "evc.cart.dat"   # input dushin file
Emax     = 0.3 au           # upper bound of spectrum frequency
logFile  = "isc.tvcf.log"   # output file for logging
FtFile   = "isc.tvcf.ft.dat"# output file for correlation function info
FoFile   = "isc.tvcf.fo.dat"# output file for spectrum function info
/
```

Also create a run file and change it with execution attribute (e.g., chmod a+rx run), the run file is shown as follows:

```
#!/bin/sh
momap -input momap.inp -np 4 &> log &
```

Users may modify the run file, for example, by changing the np option from 4 to 8, and perform the calculation by running the script file:

```
$ ./run
```

When the calculation finishes, the result files are shown as follows:
The intersystem crossing (ISC) rate constant can be found at the end of `isc.tvcf.log` file. The relationship between ISC rate constant and energy gap can be obtained from `isc.tvcf.fo.dat` file.

<table>
<thead>
<tr>
<th>Filename</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td><code>isc.tvcf.fo.dat</code></td>
<td>Output file for spectrum function</td>
</tr>
<tr>
<td><code>isc.tvcf.ft.dat</code></td>
<td>Output file for correlation function</td>
</tr>
<tr>
<td><code>isc.tvcf.log</code></td>
<td>Output file for logging</td>
</tr>
</tbody>
</table>

Then use the following commands to generate the correlation function plot to check for convergence:

```bash
$ gnuplot *.gnu
$ ps2png *.eps
$ display *.png
```

Fig. 3 Distribution of time vs real part of a converged correlation function

Once the correlation function is known to be converged, we can obtain the nonradiative rate at the end of the `isc.tvcf.log` file. From the file, we can obtain the intersystem crossing radiative rate $k_{isc}$ for Irppy3 molecule is $1.69216792 \times 10^8$ s$^{-1}$. In addition, the reverse intersystem crossing radiative rate is also given in the file.
Radiative rate $k_r$.

Next, we create a directory $kr$ and go to that directory.

Copy the following evc files from upper directory:

```
../evc/evc.cart.dat
```

to this $kr$ work directory.

Create a momap.inp with its contents as follows:

```
[kr]$ cat momap.inp
do_spec_tvcf_ft = 1
# toggle correlation function calculation, 1 or 0

do_spec_tvcf_spec = 1
# toggle fluorescence spectrum calculation, 1 or 0

&spec_tvcf
DUSHIN  = .t.
# toggle Duschinsky rotation effect, t. or f.
Temp    = 298 K
# temperature
tmax    = 1500 fs
# integration time
dt      = 1 fs
# integration timestep
Ead     = 0.0941829 au
# adiabatic excitation energy
EDMA    = 0.655512 debye
# electronic dipole moment of absorption (GS)
EDME    = 0.332683 debye
# electronic dipole moment of emission (ES)
DSFile  = "evc.cart.dat"
# input dushin file
Emax    = 0.3 au
# upper bound of spectrum frequency
dE      = 0.00001 au
# output energy interval
logFile = "spec.tvcf.log"
# output file for logging
FtFile  = "spec.tvcf.ft.dat"
# output file for correlation function info
FoFile  = "spec.tvcf.fo.dat"
# output file for spectrum function info
FoSFile = "spec.tvcf.spec.dat"
# output file for spectrum info

/!
```

Also create a run file and change it with execution attribute (e.g., chmod a+rx run), the run file is shown as follows:

```
#!/bin/sh
momap -input momap.inp -np 4 &> log &
```

Users may modify the run file, for example, by changing the np option from 4 to 8, and perform the calculation by running the script file:

```
$ ./run
```

When the calculation finishes, the result files are shown as follows:

```
[kr]$ ls
evc.cart.dat  README  spec.tvcf.ft.dat  spec.tvcf.spec.gnu
log           ref      spec.tvcf.ft.gnu
momap.inp     run      spec.tvcf.log
nodefile      spec.tvcf.fo.dat  spec.tvcf.spec.dat
```
The radiative decay rate constant can be found at the end of `spec.tvcf.log` file, while the fluorescence spectrum information can be obtained from `spec.tvcf.spec.dat`.

Plot the data from file `spec.tvcf.spec.dat` by using columns 3, 5, and 6, in Linux, we can use `Gnuplot` to do the plotting, and the plot script is shown as follows:

```
[kr]$ cat spec.tvcf.spec.gnu
reset
set nogrid
set lmargin 1.0
set encoding iso_8859_1
set term postscript eps enhanced color 20
set xlabel "Wave number, cm^{-1}" offset 0,0
set ylabel "Intensity, a.u." offset 0,0
set xtics nomirror
set ytics nomirror
set xrange [10000:30000]
set yrange [0:1.15]
set output "spec.tvcf.spec.eps"
plot "spec.tvcf.spec.dat" u 3:5 t "Absorption" w l lw 3 lt 1,
     "" u 3:6 t "Emission" w l lw 3 lt 2
```

Then use the following commands to generate the correlation and spectrum plots:

- `$ gnuplot *.gnu`  
- `$ ps2png *.eps`  
- `$ display *.png`

Fig. 5 Absorption and emission spectrum
The script `ps2png` is used to convert a `.eps` file to `.png` file, with its contents as follows:

```bash
#!/usr/bin/perl -w
#
# ps2png [resolution] file...
#
# Convert a postscript file to PNG, using the gs (GhostScript) command. The resolution defaults to 200, which is a readable compromise for most screens.
# The files should be postscript files. You can omit a .ps suffix and we'll assume it.
#
# Author: John Chambers <jc@trillian.mit.edu>

$ENV{LD_LIBRARY_PATH} = '/usr/X11R6/lib:/usr/eecs/lib:/usr/lib:/usr/lib/aout';

if ( @ARGV == 0 )
{
  print "Usage: ps2png [resolution] file...
"
  exit $?;
}

if (($res = $ARGV[0]) =~ /^d+$/) {shift @ARGV} else {$res = 200}

for $file ( @ARGV )
{
  if ($file =~ /(.*)(w*ps)$/i) {
    $filo = "$1.png";
  } else {
    if ( -f ($fili = "$file.ps") ) {
      $filo = "$file.png";
    } elsif ( -f ($fili = "$file.eps") ) {
      $filo = "$file.png";
    } elsif ( -f ($fili = "$file.PS") ) {
      $filo = "$file.PNG";
    } else {
      print STDERR "Can't find postscript file for $file.
"
      next file;
    }
  }
  system "gs -q -DNOPAUSE -sDEVICE=ppmraw -r$res -sOutputFile='|pnmcrop|pnmtopng > $filo' -- "$fili";
  if ($?) {
    print STDERR "Conversion of "$fili" failed with exit status $?.
"
    exit $?
  }
}
```

**TIPS:** The `ps2png` script needs the `pnmcrop` and `pnmtopng` commands, which can be resolved by installing the `netpbm` packages:

```
$ yum install netpbm netpbm-progs  # provide pnmcrop & pnmtopng etc.
```
Verify Convergence of Correlation Function

Correlation function must be converged before obtaining any calculation results. To verify, plot a graph using the first 2 columns in `spec.tvcf.ft.dat`, which are time and real part of the correlation function (TVCF_RE). TVCF_RE should be very close to zero and stop oscillating before it reaches the integration time limit. Figure 6 shows the distribution of a converged correlation function.

The Gnuplot plot script for the figure is shown as follows:

```
[sumstat]$ cat spec.tvcf.ft.gnu
reset
set nogrid
set lmargin 10
set pointsize 1.0
set encoding iso_8859_1
set term postscript eps enhanced color 20
set xlabel "Time, fs" offset 0,0
set ylabel "TVCF (RE)" offset 0,0
set xtics nomirror
set ytics nomirror
set xrange [-80:80]
set output "spec.tvcf.ft.eps"
plot "spec.tvcf.ft.dat" u 1:2 t "" w l lw 3 lt 1
```

Then use the following commands to generate the graph:

```
$ gnuplot *.gnu
$ ps2png *.eps
$ display *.png
```

Fig. 6 Distribution of time vs real part of a converged correlation function