PyTDDFT-SO Guide

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1 Overview

PyTDDFT-SO is an open-source Python program that takes output from a Gaussian 16 closed-shell TDDFT calculation and perturbatively includes spin-orbit coupling (SOC) by way of state interaction. This program returns SOC states as a linear combination of the unperturbed states as well as their oscillator strengths, excitation energies, and the spin-orbit Hamiltonian matrix.

2 Gaussian Job Requirements

The Gaussian 16 closed-shell TDDFT calculation must include these parameters in order to properly interface with PyTDDFT-SO.

```
%mem=92GB
%nprocshared=28
%rwf=sr.rwf
#p td(50-50,nstates=10) IOp(3/33=1) pop=full nosymm wb97xd/gen int=dkh IOp(8/10=90) ExtraLinks(L319)

Sr anorcc-vtzp

0 1
 Sr(ZEff=38.0)   0.000000    0.000000    0.000000
```

Figure 1: Example of G16 Input file

Required parameters:

- **%rwf=sr.rwf**: Saves **rwf** file. PyTDDFT-SO reads information from the Gaussian 16 **.rwf** and **.log** files. In this example, the **.rwf** file is saved as **sr.rwf**.
- **td(50-50,nstates=10)**: Performs closed-shell TDDFT calculation solving for 10 singlet and 10 triplet states.
- **IOp(3/33=1) pop=full**: Needed for atomic orbital center and angular momentum information.
- **IOp(8/10=90)**: Use all MOs for TDDFT calculation. All MOs are required for PyTDDFT-SO.

- **ExtraLinks(L319)**: Computes spin-orbit integrals.
- **Sr(ZEff=38.0)**: Geometry of molecule must be in the Gaussian input file. Next to the atomic symbol, **ZEff** should be set to a float equal to the atom's atomic number. This turns off effective nuclear charge scaling when spin-orbit integrals are computed. In this example, the Sr atom has **ZEff** set to 38.0.

3 Running PyTDDFT-SO

After finishing the Gaussian 16 calculation, make sure the rwf and log files are in the same directory as PyTDDFT-SO.

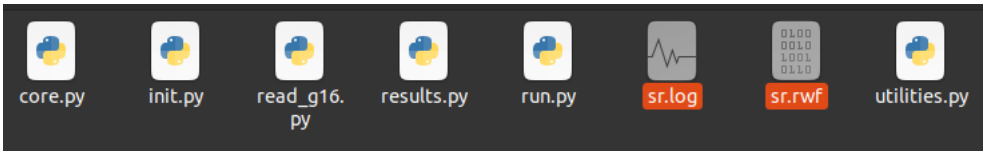

Figure 2: Your PyTDDFT-SO directory should look like this.

The program is initialized by **init.py**. This file should be edited to adjust to the needs of your calculation and computer specifications.

```
import os, sys
from run import Run

# input files
rwf = "sr.rwf"      # name of rwf file
log = "sr.log"      # name of log file
module = False          # True if module load g16
nproc = 6           # number of processes

g16root = ""
if not module:
    g16root = "/home/liaocan8/bin/g16/"

calc = Run(rwf, log, module, nproc, g16root)
calc.start()
calc.clean()
```

Figure 3: init.py

PyTDDFT-SO parameters:

- **rwf**: Name of **.rwf** file
- **log**: Name of **,log** file
- **module**: **True** if you are using modules to load Gaussian 16. If not, set to **False**.
- **nproc**: Set to the number of core you want to use.
- **g16root**: Only set if you are not using modules. Set to your Gaussian 16 directory.

After adjusting your parameters, run **init.py**.

4 Output Files

PyTDDFT-SO produces four output files: **diary.txt**, **indexing_guide.txt**, **Hso.csv**, **soc_energy.txt**.

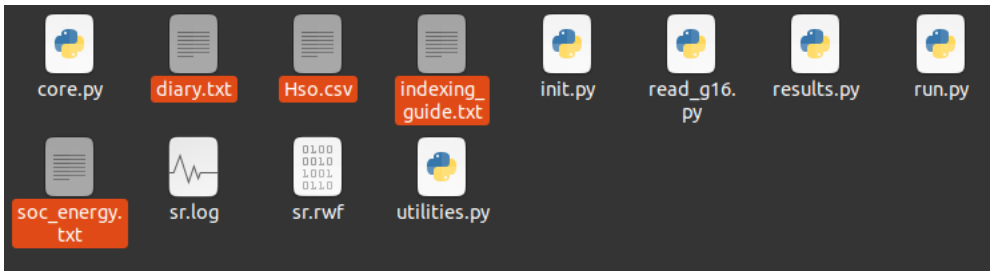

Figure 4: Directory after running PyTDDFT-SO

Output files:

- **diary.txt**: This file contains timing information.
- **indexing_guide.txt**: This helps you convert between PyTDDFT-SO indexing and the Gaussian TDDFT output indexing for the unperturbed states.
- **Hso.csv**: This contains the spin-orbit Hamiltonian matrix
- **soc_energy.txt**: This contains SOC state information. For each SOC state, the contribution of each unperturbed state is given, along with the oscillator strength and excitation energy of the SOC state.

More information about the output files are given below.

4.1 indexing_guide.txt

In the Gaussian 16 input file, if **nstates=N**, then the Gaussian 16 TDDFT output will return 2N states (10 singlets, 10 triplets). These states are indexed 1 through 2N in increasing excitation energy. However, in PyTDDFT-SO, the interaction space is the space of spin microstates along with the ground state. Therefore, the interaction space has a dimension of 4N + 1 and PyTDDFT-SO must have a different index from the Gaussian 16 output.

	Gaussian Index	RTDDFT-SO Index	Excitation Energy	Osc Str	Spin	Ms
0	0	0	0.000000	0.0000	0	0
1	1	1	2.095000	0.0000	1	-1
2	1	2	2.095000	0.0000	1	0
3	1	3	2.095000	0.0000	1	1
4	2	4	2.095000	0.0000	1	-1
5	2	5	2.095000	0.0000	1	0
6	2	6	2.095000	0.0000	1	1
7	3	7	2.095000	0.0000	1	-1
8	3	8	2.095000	0.0000	1	0
9	3	9	2.095000	0.0000	1	1
10	4	10	2.250600	0.0000	1	-1
11	4	11	2.250600	0.0000	1	0
12	4	12	2.250600	0.0000	1	1
13	5	13	2.250600	0.0000	1	-1
14	5	14	2.250600	0.0000	1	0
15	5	15	2.250600	0.0000	1	1
16	6	16	2.250600	0.0000	1	-1
17	6	17	2.250600	0.0000	1	0
18	6	18	2.250600	0.0000	1	1
19	7	19	2.250600	0.0000	1	-1
20	7	20	2.250600	0.0000	1	0
21	7	21	2.250600	0.0000	1	1
22	8	22	2.250600	0.0000	1	-1
23	8	23	2.250600	0.0000	1	0
24	8	24	2.250600	0.0000	1	1
25	9	25	2.574700	0.0000	0	0
26	10	26	2.574700	0.0000	0	0
27	11	27	2.574700	0.0000	0	0
28	12	28	2.574700	0.0000	0	0
29	13	29	2.574700	0.0000	0	0
30	14	30	2.956000	0.6885	0	0
31	15	31	2.956000	0.6885	0	0
32	16	32	2.956000	0.6885	0	0
33	17	33	4.934700	0.0000	1	-1
34	17	34	4.934700	0.0000	1	0
35	17	35	4.934700	0.0000	1	1
36	18	36	5.146399	0.0000	0	0
37	19	37	6.854899	0.0000	1	-1
38	19	38	6.854899	0.0000	1	0
39	19	39	6.854899	0.0000	1	1
40	20	40	7.023999	0.0070	0	0

Figure 5: Example of indexing_gide.txt

The "Gaussian Index" column is the index used by the Gaussian 16 output. The "TDDFT-SO Index" column is the index used by PyTDDFT-SO. The "Excitation Energy" and "Osc Str" column contain the unperturbed excitation energies and oscillator strengths seen in the Gaussian 16 output. The "Spin" column gives the 2S + 1 value (S is the spin quantum number), where singlets are 0 and triplets are 1. This is accompanied by the "Ms" column where the azimuthal spin qunatum number is given, which identifies the spin microstate.

As an example, PyTDDFT-SO state 17 corresponds to state 6 in the Gaussian 16 output. This state is a Ms = 0 triplet.

State zero is always the ground state.

4.2 Hso.csv

This file contains the spin-orbit Hamiltonian. Opening this file on Excel is easier on the eyes.

	0	1	2	3	4	5	6	7	8	9
0	0j	0j	0j	0j	0j	0j	0j	0j	0j	0j
1	0j	(0.07699+0j)	0j	0j	0.00115j	(6e-05+0j)	0j	8e-05j	(-0.00081+3e-05j)	0j
2	0j	0j	(0.07699+0j)	0j	(-6e-05+0j)	0j	(6e-05+0j)	(0.00081+3e-05j)	0j	(-0.00081+3e-05j)
3	0j	0j	0j	(0.07699+0j)	0j	(-6e-05+0j)	-0.00115j	0j	(0.00081+3e-05j)	-8e-05j
4	0j	-0.00115j	(-6e-05-0j)	0j	(0.07699+0j)	0j	0j	1e-05j	(-3e-05-0.00081j)	0j
5	0j	(6e-05-0j)	0j	(-6e-05-0j)	0j	(0.07699+0j)	0j	(3e-05-0.00081j)	0j	(-3e-05-0.00081j)
6	0j	0j	(6e-05-0j)	0.00115j	0j	0j	(0.07699+0j)	0j	(3e-05-0.00081j)	-1e-05j
7	0j	-8e-05j	(0.00081-3e-05j)	0j	-1e-05j	(3e-05+0.00081j)	0j	(0.07699+0j)	0j	0j
8	0j	(-0.00081-3e-05j)	0j	(0.00081-3e-05j)	(-3e-05+0.00081j)	0j	(3e-05+0.00081j)	0j	(0.07699+0j)	0j
9	0j	0j	(-0.00081-3e-05j)	8e-05j	0j	(-3e-05+0.00081j)	1e-05j	0j	0j	(0.07699+0j)
10	0j	0j	0j	0j	0j	0j	0j	0j	0j	0j
11	0j	0j	0j	0j	0j	0j	0j	0j	0j	0j
12	0j	0j	0j	0j	0j	0j	0j	0j	0j	0j
13	0j	0j	0j	0j	0j	0j	0j	0j	0j	0j
14	0j	0j	0j	0j	0j	0j	0j	0j	0j	0j
15	-0j	0j	0j	0j	0j	0j	0j	0j	0j	0j
16	-0j	0j	0j	0j	0j	0j	0j	0j	0j	0j
17	0j	0j	0j	0j	0j	0j	0j	0j	0j	0j
18	0j	0j	0j	0j	0j	0j	0j	0j	0j	0j
19	0j	0j	0j	0j	0j	0j	0j	0j	0j	0j
20	0j	0j	0j	0j	0j	0j	0j	0j	0j	0j
21	-0j	0j	0j	0j	0j	0j	0j	0j	0j	0j
22	0j	0j	0j	0j	0j	0j	0j	0j	0j	0j
23	0j	0j	0j	0j	0j	0j	0j	0j	0j	0j
24	-0j	0j	0j	0j	0j	0j	0j	0j	0j	0j
25	0j	0j	0j	0j	0j	0j	0j	0j	0j	0j
26	0j	0j	0j	0j	0j	0j	0j	0j	0j	0j
27	0j	0j	0j	0j	0j	0j	0j	0j	0j	0j
28	0j	0j	0j	0j	0j	0j	0j	0j	0j	0j
29	0j	0j	0j	0j	0j	0j	0j	0j	0j	0j
30	0j	(-0.00029-1e-05j)	9e-05j	(-0.00029+1e-05j)	(-5e-05+0.0003j)	-0.00071j	(-5e-05-0.0003j)	(0.0005-3e-05j)	-5e-05j	(0.0005+3e-05j)
31	0j	(-0.00049-1e-05j)	-0.00026j	(-0.00049+1e-05j)	0.00047j	0.00037j	-0.00047j	(-0.00027+0.00021j)	3e-05j	(-0.00027-0.00021j)
32	0j	(-0.00013-1e-05j)	0.00078j	(-0.00013+1e-05j)	(1e-05+0.00017j)	0.00021j	(1e-05-0.00017j)	(-0.00013-0.00055j)	1e-05j	(-0.00013+0.00055j)
33	0j	0j	0j	0j	0j	0j	0j	0j	0j	0j
34	0j	0j	0j	0j	0j	0j	0j	0j	0j	0j
35	0j	0j	0j	0j	0j	0j	0j	0j	0j	0j
36	0j	0j	0j	0j	0j	0j	0j	0j	0j	0j
37	0j	-7e-05j	(-0.00078+2e-05j)	0j	-0.00035j	(-4e-05-0.00077j)	0j	-2e-05j	(0.00025-0.00012j)	0j
38	0j	(0.00078+2e-05j)	0j	(-0.00078+2e-05j)	(4e-05-0.00077j)	0j	(-4e-05-0.00077j)	(-0.00025-0.00012j)	0j	(0.00025-0.00012j)
39	0j	0j	(0.00078+2e-05j)	7e-05j	0j	(4e-05-0.00077j)	0.00035j	0j	(-0.00025-0.00012j)	2e-05j
40	0j	(-0.00061-2e-05j)	-8e-05j	(-0.00061+2e-05j)	(3e-05+0.0006j)	0.00087j	(3e-05-0.0006j)	(-0.00062+8e-05j)	6e-05j	(-0.00062-8e-05j)

Figure 6: Part of the spin-orbit Hamiltonian matrix

The first row labels the columns of the matrix and the first column labels the rows. For example, if we want the spin-orbit coupling element between the first excited singlet and the first excited Ms = 0 triplet, we would first identify their Gaussian 16 indices. In the example, this would be Gaussian 16 state 1 and Gaussian state 9. Then we would convert to PyTDDFT-SO indices, that is, PyTDDFT-SO state 2 and 9. Then the spin-orbit coupling element between the two states is on the 2nd row and 9th column, that is, (-8.1E-4) + (3E-5)i.

4.3 soc_energy.txt

This file contains information about the SOC excited states.

```
SOC State: 1    Excitation Energy: 2.0320    Osc Str: 0.0000
State: 1 (Gaussian Index: 1)      16.7002%
State: 2 (Gaussian Index: 1)      0.0009%
State: 3 (Gaussian Index: 1)      16.7002%
State: 4 (Gaussian Index: 2)      16.6263%
State: 5 (Gaussian Index: 2)      0.1716%
State: 6 (Gaussian Index: 2)      16.6263%
State: 7 (Gaussian Index: 3)      0.0888%
State: 8 (Gaussian Index: 3)      32.9914%
State: 9 (Gaussian Index: 3)      0.0888%
State: 37 (Gaussian Index: 19)      0.0003%
State: 38 (Gaussian Index: 19)      0.0052%
State: 39 (Gaussian Index: 19)      0.0003%

SOC State: 2    Excitation Energy: 2.0620    Osc Str: 0.0006
State: 1 (Gaussian Index: 1)      10.1199%
State: 2 (Gaussian Index: 1)      0.1839%
State: 3 (Gaussian Index: 1)      10.1199%
State: 4 (Gaussian Index: 2)      9.8780%
State: 5 (Gaussian Index: 2)      29.7494%
State: 6 (Gaussian Index: 2)      9.8780%
State: 7 (Gaussian Index: 3)      14.8863%
State: 8 (Gaussian Index: 3)      0.1593%
State: 9 (Gaussian Index: 3)      14.8863%
State: 30 (Gaussian Index: 14)      0.0157%
State: 31 (Gaussian Index: 15)      0.1023%
State: 32 (Gaussian Index: 16)      0.0100%
State: 37 (Gaussian Index: 19)      0.0010%
State: 39 (Gaussian Index: 19)      0.0010%
State: 40 (Gaussian Index: 20)      0.0090%

SOC State: 3    Excitation Energy: 2.0624    Osc Str: 0.0006
State: 1 (Gaussian Index: 1)      0.1317%
State: 2 (Gaussian Index: 1)      49.7906%
State: 3 (Gaussian Index: 1)      0.1317%
State: 4 (Gaussian Index: 2)      0.5165%
State: 5 (Gaussian Index: 2)      0.0197%
State: 6 (Gaussian Index: 2)      0.5165%
State: 7 (Gaussian Index: 3)      24.3805%
State: 8 (Gaussian Index: 3)      0.0018%
State: 9 (Gaussian Index: 3)      24.3805%
State: 30 (Gaussian Index: 14)      0.0021%
State: 31 (Gaussian Index: 15)      0.0080%
State: 32 (Gaussian Index: 16)      0.1182%
State: 37 (Gaussian Index: 19)      0.0011%
State: 38 (Gaussian Index: 19)      0.0002%
State: 39 (Gaussian Index: 19)      0.0011%
```

Figure 7: SOC State information in soc_energy.txt

Oscillator strengths and excitation energies of the excited states are given. Additionally, the file contains a percentage of how much of a certain unperturbed state contributes to the SOC state, obtained by the modulus square of the linear combination coefficient.

$$|I>^{SO} = \sum_{J} C_J^{SO} |J>^{noSO} \tag{1}$$

$$\%\text{ of } |J>^{noSO} \text{ in } |I>^{SO} = |C_J^{SO}|^2 \tag{2}$$

For example, unperturbed state 5 constitutes 29.7494% of SOC state 2.