

MS@GWEV: An Interface Program of Approximate Spin-Orbit Coupling for Spin-Forbidden Reactions

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The MS@GWEV program is a module of the in-house software GWEV SUITE developed in our group. It was written in Fortran 90 and interfaced to GAUSSIAN 16 (through the keyword `External`) to calculate spin-forbidden reactions involving multiple spin states.

1 Installation

If the `gfortran` compiler has been installed, MS@GWEV may be built by the `make` command in the `MultiState/src` directory,

```
$ cd MultiState/src/
$ make
```

If the `ifort` compiler with the MKL library is preferred, the user may replace `Makefile` by `Makefile-intel` and modify `MKLROOT` therein.

After the installation, the user will see the following contents in the `MultiState` main directory:

```
$ cd ..
$ ls -l
total 464
drwxrwxrwx 1 zouwl zouwl 4096 Nov 1 00:51 doc/
-rwxrwxrwx 1 zouwl zouwl 455143 Nov 1 00:51 multistate.exe
-rwxrwxrwx 1 zouwl zouwl 930 Oct 31 11:05 run-2state.sh
-rwxrwxrwx 1 zouwl zouwl 1130 Oct 31 11:06 run-3state.sh
drwxrwxrwx 1 zouwl zouwl 4096 Oct 31 17:16 src/
-rwxrwxrwx 1 zouwl zouwl 3266 Oct 31 18:19 templet-fes
-rwxrwxrwx 1 zouwl zouwl 2241 Apr 3 2022 templet-o2
drwxrwxrwx 1 zouwl zouwl 4096 Oct 31 18:30 tests/
```

where `run-2state.sh`, `run-3state.sh`, and `multistate.exe` have executable permissions.

2 Script to run MS@GWEV

The following sample script (*i.e.* the script file `MultiState/run-2state.sh`) calculates the mixed-spin ground state from two spin states. The two spin states are computed by GAUSSIAN 16, whereas the other quantum chemistry programs may be supported in the future. For the calculation of three spin states, please refer to the script `MultiState/run-3state.sh`.

```
1  #!/bin/bash
2
3  # Gaussian 16
4  module load chemsoft/g16c-avx
5  export GAUSS_SCRDIR=/tmp/zouwl/GaussianScr
6
7  mkdir -p $GAUSS_SCRDIR
8
9  export gaussian_ein=$2
10 export gaussian_eou=$3
11
12 # MS@GWEV
13 export CurrDir=`pwd`
14 export multistate_dir=$CurrDir/MultiState
15 export ms_scrdir=$CurrDir/JOB001
```

```

16 mkdir -p $ms_scrdir
17 export tem_mstate=$multistate_dir/templet-o2
18 export inp_state1=$ms_scrdir/state1.gjf
19 export inp_state2=$ms_scrdir/state2.gjf
20 export fch_state1=$ms_scrdir/state1.fch
21 export fch_state2=$ms_scrdir/state2.fch
22
23 # generate input files for states 1 and 2
24 $multistate_dir/multistate.exe -gen -gin $gaussian_ein -ctp $tem_mstate \
25   -in1 $inp_state1 -in2 $inp_state2
26
27 rm -f $fch_state1 $fch_state2
28
29 # state 1 calculation
30 g16 -fchk=$fch_state1 $inp_state1
31
32 # state 2 calculation
33 g16 -fchk=$fch_state2 $inp_state2
34
35 # write Gaussian's *.EOu file
36 $multistate_dir/multistate.exe -mix -chi 400 -gin $gaussian_ein -gou $gaussian_eou \
37   -fc1 $fch_state1 -fc2 $fch_state2

```

The script contains five parts:

- Before the line 23, the environment variables of GAUSSIAN and MS@GWEV are loaded.
- Lines 23 to 25, MS@GWEV generates input files of the two spin states according to the *.EIn (from the master calculation) and template (see the next section) files.
- Line 27, delete the old fchk files. If SCF does not converge during geometry optimization or numerical frequency calculations, a new fchk file will not be saved. In this case the old fchk file if not deleted may lead to strange results.
- Lines 29 to 33, the two spin states are calculated by GAUSSIAN, and two fchk files will be saved through the new command line option `-fchk` of GAUSSIAN 16.
- Lines 35 to 37, MS@GWEV calculates energy, gradients, and possible Hessians of the mixed-spin ground state by using the data from *.EIn and two fchk files, and returns them to the GAUSSIAN master calculation through the data file *.EOu. The non-default empirical SOC constant χ may be set by the option `-chi`.

3 Gaussian 16 Template with Two Spin States

This is a GAUSSIAN 16 template to do two-state calculation of O₂ (see MultiState/templet-o2).

```

1  ! templet of G16 input: singlet and triplet state of O2 by DFT/TDDFT
2
3  ! -----
4  ! Single point energy of the first state
5  !
6  ! This step is used to generate a checkpoint file, so you
7  ! must do SP calculation first.

```

```

8  ! -----
9  $sp1
10     *before_geom
11  %mem=8GB
12  %nprocshared=4
13  %chk=o2-s1
14  #p b3lyp/3-21g
15
16  Title: singlet state of O2
17
18  0 1
19     *end_of_input
20
21     *after_geom
22
23     *end_of_input
24
25  ! -----
26  ! Single point energy of the second state
27  !
28  ! This step is used to generate a checkpoint file, so you
29  ! must do SP calculation first.
30  ! -----
31  $sp2
32     *before_geom
33  %mem=8GB
34  %nprocshared=4
35  %chk=o2-s2
36  #p b3lyp/3-21g td(triplets,root=1)
37
38  Title: triplet state of O2
39
40  0 1
41     *end_of_input
42
43     *after_geom
44
45     *end_of_input
46
47  ! -----
48  ! Gradients of the first state
49  ! -----
50  $grad1
51     *before_geom
52  %mem=8GB
53  %nprocshared=4
54  %chk=o2-s1
55  #p b3lyp/3-21g guess=read force

```

```

56
57 Title: singlet state of 02
58
59 0 1
60   *end_of_input
61
62   *after_geom
63
64   *end_of_input
65
66 ! -----
67 ! Gradients of the second state
68 ! -----
69 $grad2
70   *before_geom
71 %mem=8GB
72 %nprocshared=4
73 %chk=o2-s2
74 #p b3lyp/3-21g guess=read td(triplets,root=1) force
75
76 Title: triplet state of 02
77
78 0 1
79   *end_of_input
80
81   *after_geom
82
83   *end_of_input
84
85 ! -----
86 ! Hessians of the first state
87 ! -----
88 $freq1
89   *before_geom
90 %mem=8GB
91 %nprocshared=4
92 %chk=o2-s1
93 #p b3lyp/3-21g guess=read freq
94
95 Title: singlet state of 02
96
97 0 1
98   *end_of_input
99
100   *after_geom
101
102   *end_of_input
103

```

```

104 ! -----
105 ! Hessians of the second state
106 ! -----
107 $freq2
108 *before_geom
109 %mem=8GB
110 %nprocshared=4
111 %chk=o2-s2
112 #p b3lyp/3-21g guess=read td(triplets,root=1) freq
113
114 Title: triplet state of O2
115
116 0 1
117 *end_of_input
118
119 *after_geom
120
121 *end_of_input

```

A few comments on the template:

- A line beginning with an exclamation mark (!) is a comment line, which is ignored by MS@GWEV.
- The template has six parts beginning with the keywords \$sp1, \$sp2, \$grad1, \$grad2, \$freq1, and \$freq2 (case insensitive), indicating the sing-point energy, gradient, and vibrational frequency calculation sections of the first and the second spin states, respectively. Similarly, the keywords like \$sp3 and \$grad4 may be defined for the other states (see MultiState/template-fes).
- In each part of the template, there are two input fields, enclosed in the opening-closing tags *before_geom ... *end_of_input and *after_geom ... *end_of_input, respectively. The text content in the former is the GAUSSIAN input stream for sing-point energy, gradient, or vibrational frequency calculation of a spin state before the molecular geometry, and in the latter is the optional GAUSSIAN input stream after the molecular geometry, such as basis sets and pseudo-potentials.
- In the gradient and vibrational frequency calculations, the keyword **guess=read** is suggested to use, which reads wavefunction of previous step from the chk file (defined via the %chk command; **Don't confuse it with the fchk file in the script!**) as initial guess.
- In this example, the spin state 1 is a closed-shell excited state of O₂ computed by restricted DFT, whereas the spin state 2 is the open-shell triplet ground state of O₂, computed by spin-flip TDDFT (of course unrestricted DFT with the spin multiplicity being 3 is also available).

4 Calling the script in Gaussian master calculation

This is the test input of O₂ (see MultiState/tests/test-2state.inp).

```

1 %nprocshared=1
2 %mem=1gb
3 #p external='MultiState/run-2state.sh'
4 ! opt(nomicro)
5 ! freq
6
7 Two-State calculation (DO SP FIRST.)
8

```

```

9  0  1
10 0
11 0 1 r1
12
13 r1 1.2

```

A few comments on the input:

- The master calculation does not consume too much memory and CPU resources (except the frequency calculation with more than 500 atoms), so one processor with 1 GB of memory is usually enough.
- The keyword **External** is used to call the script.
- Since the charge and spin multiplicity have been set in the template file, here they can be any accepted values.
- The default optimization procedure of **External** is designed for MM calculations but is not suitable for QM calculations, so the option **nomicro** is needed for **opt**.
- Since **guess=read** is specified in the template file for **opt** and **freq** calculations, a single-point calculation has to be performed first to save wavefunctions into the checkpoint files. After the single-point calculation, the user may check electronic configurations, total energies, and populations in the output files of the two spin states; for transition-metal systems with some symmetry, it is highly suggested to check the stabilities of wavefunction since GAUSSIAN may not converge to the lowest solution correctly. Then the user may remove the exclamation mark symbol before **opt** and **freq** and redo the calculation.
- A checkpoint file may be specified by **%chk** in the master calculation to save some important data of the mixed-spin ground state, *e.g.* initial Hessians for subsequent TS and IRC optimization.

5 Options of MS@GWEV

5.1 Options to Control Operating Mode

The following options are case insensitive.

- **-gen**

This mode generates GAUSSIAN input files of spin states, which is the default. The options involved are **-nst**, **-gin**, **-ctp**, **-in1**, ..., **-inN**.

- **-mix**

This mode computes energy, gradient array, and Hessian matrix of the mixed-spin ground state, and returns them to the GAUSSIAN master calculation. The options involved are **-nst**, **-gin**, **-gou**, **-chi** (or **-chs**), **-fc1**, ..., **-fcN**, **-sh1**, ..., **-shN**.

5.2 Other Options

- **-nst N**

This option specifies the number of spin electronic states to be mixed, which is between 1 and 9. The default is 2 if **-nst** is not specified. If $N=1$, GAUSSIAN performs single spin state calculation by calling itself.

- **-gin path/file_name**

This option specifies the path and name of GAUSSIAN's *.EIn file.

- **-gou path/file_name**

This option specifies the path and name of GAUSSIAN's *.EOu file.

- **-ctp path/file_name**

This option specifies the path and name of the template file.

- `-in1 path/file_name`
`-in2 path/file_name`
`...`
`-inN path/file_name`

These options specify the paths and names of the input files for spin states 1, 2, ..., N .

- `-fc1 path/file_name`
`-fc2 path/file_name`
`...`
`-fcN path/file_name`

These options specify the paths and names of the `fchk` files for spin states 1, 2, ..., N .

- `-chi χ`

This option specifies the empirical SO constant (in cm^{-1}). The default is 400 cm^{-1} if `-chi` is not specified. Taking three spin states as an example, the constructed model SO Hamiltonian is

$$\mathbf{H} = \begin{bmatrix} V_1 & -|\chi| & -|\chi| \\ -|\chi| & V_2 & -|\chi| \\ -|\chi| & -|\chi| & V_3 \end{bmatrix} \quad (1)$$

- `-chs $\chi_{1,2}$ $\chi_{1,3}$... $\chi_{2,3}$...`

This option must appear after `-nst N` , which specifies the empirical SO constant (in cm^{-1}) of each pair of spin states, and totally $N(N-1)/2$ values should be provided. Taking three spin states as an example, the constructed model SO Hamiltonian is

$$\mathbf{H} = \begin{bmatrix} V_1 & \chi_{1,2} & \chi_{1,3} \\ \chi_{1,2} & V_2 & \chi_{2,3} \\ \chi_{1,3} & \chi_{2,3} & V_3 \end{bmatrix} \quad (2)$$

- `-sh1 δ_1`
`-sh2 δ_2`
`...`
`-shN δ_N`

These options specify energy shifts (in cm^{-1}) of spin states 1, 2, ..., N . The default values are all 0 cm^{-1} if they are not specified. Taking three spin states as an example, the modified diagonal elements in the model SO Hamiltonian are

$$\mathbf{H} = \begin{bmatrix} V_1 + \delta_1 & & \\ & V_2 + \delta_2 & \\ & & V_3 + \delta_3 \end{bmatrix}. \quad (3)$$

6 Frequently Asked Questions

- **The Gaussian master calculation complains that the basis set is not available for an atom.**

The actual basis set used in the calculation is defined in the template file, whereas in the master GAUSSIAN input file the basis set is usually not needed to specify. In this case GAUSSIAN assumes that the STO-3G basis set is used, which supports the atoms H-Xe. Thus if there are heavier atoms than Xe, GAUSSIAN reports an error.

To solve this problem, one may specify either the SDD or UGBS basis set, which support more atoms, or custom basis functions through the `Gen` keyword (`GenECP` is not necessary).

Please note that, in the case of `External` calculation mode, the non-default basis set in the master input cannot be passed on to the subsequent steps in a multiple-step GAUSSIAN job. Thus `Opt` and `Freq` have to be computed separately; they may also be combined in a single master input through `--Link1--`.

- **How to estimate the SOC constant?**

Please refer to the ESI of **Phys. Chem. Chem. Phys.** 20, 4129, 2018. Some quantum chemistry programs (*e.g.* MOLPRO) can print the first- and the second-order SOC constants separately. For the reaction where the heavy atom has saturated chemical bonds, the results are not sensitive to the SOC constant.

- **Optimization or frequency results by ONIOM with MS@GWEV are totally wrong.**

In the input file of GAUSSIAN, the coordinates of all the atoms belonging to the High layer must be provided first. Next are the Medium layer atoms (if have), and finally the Low layer atoms.