Users' guide of MakePES

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Contents of Sample Files

Sample files are found in sindo-4.0/doc/MakePES/sample_MakePES

0.harmonic_h2co

1.qff_h2co: Quartic force field for H_2CO
- 1-1.single
- 1-2.parallel
- 1-3.dryrun
- 1-4.generic

2.grid_h2co: Grid PES for H_2CO
- 2-1.1MR
- 2-2.2MR
- 2-3.3MR
- 2-4.1MR_generic

3.mrpes_h2co: Multi-resolution PES for H_2CO

4.water-hexamer

NOTE

MakePES is a command line based program. This manual assumes that you are familiar with basic commands in UNIX. Shell scripts are given for Bourne Shell (bash).

This manual also assumes that an alias is set to invoke RunMakePES,

```
sindo_jar=/path/to/sindo-4.0/jar
alias RunMakePES='java –cp "$sindo_jar/*" RunMakePES'
```

Thus, the command "RunMakePES" in this document is the same as the java command above.

For a theoretical background on PES generation, see Lecture Notes #2 (kougi2.pdf).

0.harmonic_h2co

Proceed to 0.harmoic_h2co and find an input file to perform harmonic vibrational analysis for formaldehyde using Gaussian.

```
> cd 0.harmonic_h2co
> ls
h2co-b3lyp-dz.inp    log/
```

- "log" folder contains sample output files.

h2co-b3lyp-dz.inp is the input file. Run Gaussian by the following command:

```
> runGaussian.sh ./ h2co-b3lyp-dz.inp
```

- review the installation if you cannot run Gaussian with this command.
- the two arguments are (working folder) and (input file), respectively.

You will obtain the following output files when the job ends.

```
> ls h2co-b3lyp-dz.*
h2co-b3lyp-dz.chk   h2co-b3lyp-dz.fchk  h2co-b3lyp-dz.inp
h2co-b3lyp-dz.out
```

.fchk is a formatted check point file, which archives the result of quantum chemistry calculations. Let us convert the fchk file to a minfo file,

```
> java -cp "/path/to/sindo-4.0/jar/*" Fchk2Minfo h2co-b3lyp-dz
```

- The argument after Fchk2Minfo is the basename of output files.

You will find a minfo file,

```
> ls h2co-b3lyp-dz.*
h2co-b3lyp-dz.chk   h2co-b3lyp-dz.fchk  h2co-b3lyp-dz.inp
h2co-b3lyp-dz.out   h2co-b3lyp-dz.minfo
```

Minfo file includes the equilibrium geometry, harmonic frequencies, and vibrational displacement vectors.

The same result can be obatined by JSindo; refer to the usage manual of JSindo. You can find details about the format of minfo file therein, too.

1.qff_h2co

1-1.single

Proceed to 1.qff_h2co/1-1.single to find input files to generate quartic force field (QFF) for formaldehyde,

```
> cd 1.qff_h2co/1-1.single
> ls
GaussianTemplate          makePES.xml          resources.info     log/
```

makePES.xml is the main file, which is structured using tags in xml format. It is divided into sections by, <makePES> … </makePES>, <qchem> … </qchem>, and <qff> … </qff>. The options are specified in each section by <key value="value" />. The value is case insensitive except for filenames. Comment out is possible as usual by <!-- … -->.

makePES

```
<makePES>
  <minfoFile   value="../../0.harmonic_h2co/h2co-b3lyp-dz.minfo" />
                                                  read a minfo file of H2CO
  <MR          value="3" />
                        the order of the mode coupling expansion.
```

makePES

```
<qchem>
    <program   value="gaussian" />          use Gaussian
    <dryrun    value="false"/>              run Gaussian
    <removefiles value="true" />            remove the output of Gauusian
    <title     value="B3LYP/cc-pVDZ" />     set the title
    <template  value="GaussianTemplate" />  the name of template file to
                                            generate Gaussian input
</qchem>
 <qff>
     <stepsize  value="0.5" />              step size of numerical differentiations
     <ndifftype value="hess"/>              numerical differentiations using Hessian
     <mopfile   value="prop_no_1.mop" />    name of a mop file
 </qff>
</makePES>
```

resources.info provides hostname of nodes to run Gaussian. When we run on a single node, it is not important (but still, it should exist). We will later discuss this file in detail for parallel calculations in 1.2-parallel.

GaussianTemplate is a template file to generate input files for Gaussian specified by <template> in <qchem> section. It is the same as the usual input file for Gaussian, except for the red colored text.

GaussianTemplate

```
%chk=#basename#.chk
%NprocShared=2
%mem=1GB
#P B3LYP/CC-PVDZ FREQ  NOSYMMETRY MAXDISK=240GB

Frequency at B3LYP/cc-pVDZ

0  1
#coordinate#
```

MakePES replaces #basename# and #coordinate# by the filename and the coordinates, respectively, to create input files.

”FREQ” keyword is necessary because we use numerical differentiations of the Hessian matrix (i.e., ndifftype = hess).

MakePES is invoked by the following command

```
> RunMakePES >& makePES.out
```

The main input file is set to makePES.xml by default. You can specify a different input file with –f option,

```
> RunMakePES -f makePES.xml >& makePES.out
```

In the output file, the options are first printed, and then the status of electronic structure calculations is printed,

makePES.out

Execute electronic structure calculations.

Thread0> Running minfo.files/mkqff-eq.inp on kyagi-mac3.local at …
Thread0> Running minfo.files/mkqff0-0.inp on kyagi-mac3.local at …
Thread0> Running minfo.files/mkqff0-1.inp on kyagi-mac3.local at …

During this step, Gaussian jobs are carried out in a folder minfo.files. Because we‘ve set <removefiles> to true, the input and output files are removed leaving only minfo files in the folder.

When this step is done, you will see an output like this,

makePES.out

End of electronic structure calculations.
Storing electronic structure data in tempfile ... Done!
Generating prop_no_1.mop... Done!
Removing the tempfiles ... Done!
End of QFF generation.

The QFF coefficients are written to <mopfile>, i.e., prop_no_1.mop.

```
 1.18325736150273080000000e-15    1
 2.70406356551277800000000e-03    1    1
 1.15902498831812420000000e-17    1    1    1
 2.28755761599593520000000e-05    1    1    1    1
-2.10304522036546450000000e-16    2
```

one-body terms:
ci, cii, ciii, ciiii

```
-4.18973572808552500000000e-18    1    2
-6.39823299633265700000000e-14    1    2    2
 1.82212128406061430000000e-13    1    2    2    2
-1.93010983607095930000000e-15    1    1    2
 2.95100635341076400000000e-05    1    1    2    2
 3.22720588413948230000000e-15    1    1    1    2
 9.68702817985278200000000e-19    1    3
 3.12553009698215360000000e-13    1    3    3
```

two-body terms:
cij, cijj, cijjj, ciij, ciijj, ciiij

```
 1.44339506734162400000000e-13    1    2    3
-1.63155216388219100000000e-13    1    2    3    3
-3.08196517760435260000000e-13    1    2    2    3
 6.17123255658516700000000e-14    1    1    2    3
 1.80828304832249210000000e-13    1    2    4
```

three-body terms:
cijk, cijkk, cijjk, ciijk

Note that four-body terms (cijkl) are missing because <MR> was set to 3.

1-2.parallel

The electronic structure calculations are an exclusive bottleneck for generating the PES. In the case of H_2CO, FREQ calculations at 13 grid points are required and they were carried out one by one in one node in the previous section.

MakePES can distribute the grid points to multiple nodes, and process the FREQ calculations in parallel. This function substantially speeds up the calculation. It requires that the nodes have shared disks (via NFS), where the input files as well as sindo/gaussian are located, and are inter-connectable with SSH without being asked for a password.

Proceed to 1-2.parallel to find the same set of input files.

```
> cd 1.qff_h2co/1-1.parallel
> ls
GaussianTemplate          makePES.xml        resources.info     log/
```

Assuming that we use 16 core x 2 nodes, we make the following modification to resources.info and GaussianTemplate

resources.info

beluga01
beluga01
beluga02
beluga02

The hostname of 2 nodes.
We will run 2 processes in each nodes.

GaussianTemplate

%chk=#basename#.chk
%NprocShared=8
%mem=1GB
…

Each Gaussian process uses 8 cores

makePES.xml is the same as before. Set an environment variable SINDO_RSH =ssh, and then invoke MakePES as before,

```
> export SINDO_RSH=ssh
> RunMakePES >& makePES.out
```

You can see in the output that the grid points are distributed to beluga01 and 02, each in 2 processes.

makePES.out

Execute electronic structure calculations.

Thread2@beluga02> Running minfo.files/mkqff0-1.inp on beluga02 at …
Thread3@beluga02> Running minfo.files/mkqff1-0.inp on beluga02 at …
Thread0@beluga01> Running minfo.files/mkqff-eq.inp on beluga01 at …
Thread1@beluga01> Running minfo.files/mkqff0-0.inp on beluga01 at …

When you want to stop the job, a safe way to terminate all Gaussian jobs is to create a file with a name “terminate”.

```
> touch terminate
```

Then, the job stops after Gaussian jobs that are currently running are all finished.

If you want to immediately stop the job, you have to kill the main process, i.e., the java process responsible for RunMakePES. In that case, however, check carefully that all Gaussian child processes are killed as well.

1-3.dryrun

The <dryrun> option generates input files for grid points, and then stops the program without executing Gaussian. Proceed to 1-3.dryrun,

```
> cd 1.qff_h2co/1-3.dryrun
> ls
GaussianTemplate    log1_dryrun_true/   log2_dryrun_false/
makePES.xml         resources.info
```

The only difference is the value of <dryrun> in makePES.xml

makePES.xml

```
<qchem>
    <program  value="gaussian" />
    <dryrun   value="true"/>      stop after generating the input files
```

Running the program creates the input files for Gaussian in the minfo.files folder,

```
> RunMakePES >& makePES.out
> ls minfo.files/
mkqff-eq.inp  mkqff0-1.inp  mkqff1-1.inp  mkqff2-1.inp
mkqff3-1.inp  mkqff4-1.inp  …
```

You may transfer these input files to other computer systems and carry out Gaussian there. Then, convert the formatted checkpoint files to minfo format using Fchk2Minfo.

```
> java -cp "/path/to/sindo-4.0/jar/*" Fchk2Minfo mkqffx-x
```

Bring back the minfo files and locate them in the minfo.files folder,

```
> ls minfo.files/
mkqff-eq.inp     mkqff-eq.minfo   mkqff0-0.inp     mkqff0-0.minfo
mkqff0-1.inp     mkqff0-1.minfo   …
```

Change dryrun to false and run the program again.

makePES.xml

```
<qchem>
   <program  value="gaussian" />
   <dryrun   value="false"/>
```

don't stop after generating the input files

```
> RunMakePES >& makePES.out
> ls
GaussianTemplate  makePES.out       makePES.xml       minfo.files/
prop_no_1.mop     resources.info
```

You will see that the program immideately produces the mopfile.

The two log folders contains the files for the first step (log1_dryrun_true), and the files for the second step (log2_dryrun_false).

Note that, in general, MakePES looks into minfo.files folder for minfo files before starting Gaussian jobs. The job is skipped if a minfo file is found, and starts from the grid point where it ended before. In this example, we provided all minfo files, and thus the electronic structure calculations were all skipped.

1-4.generic

Setting <program> to generic prints the coordinates to a file in xyz format. You have to generate the input files, carry out the electronic structure calculations, and return the information in minfo format by yourself. Nevertheless, this may be useful for users who wish to use programs other than Gaussian.

Proceed to 1-4.generic to find makePES.xml.

```
> cd 1.qff_h2co/1-4.generic
> ls
log1_genxyz/ log2_genmop/ makePES.xml
```

The file is different only in <qchem> section,

makePES

```
<qchem>
    <program   value=”generic" />
    <title     value="B3LYP/cc-pVDZ" />
    <xyzfile   value="makeQFF" />
</qchem>
```

“generic” means no specific program

set the name of xyz file

Running the program creates makeQFF.xyz,

```
> RunMakePES >& makePES.out
> ls
makePES.out   makePES.xml   makeQFF.xyz
```

makeQFF.xyz is written in the usual xyz format,

makeQFF

```
 4                 The number of atoms
mkqff-eq           name of the first point
   C     0.0000000000     0.0000000000    -0.6014736819
   O     0.0000000000    -0.0000000000     0.6027247362
   H     0.0000000000     0.9459644267    -1.2020174143
   H    -0.0000000000    -0.9459644267    -1.2020174143
 4                                  xyz coordinates
mkqff0-0           name of the second point
   C    -0.0125897498    -0.0000000000    -0.6014736819
   O     0.0031430124     0.0000000000     0.6027247362
                                  xyz coordinates
```

The name, colored in red, is the ID of each grid points. We assume you carry out the electronic structure calculations by yourself, and collect the data in a minfo file with a name, ID.minfo.

Locate the minfo files in a minfo.files folder,

```
> ls minfo.files/
mkqff-eq.minfo  mkqff0-1.minfo  mkqff1-1.minfo  mkqff2-1.minfo
mkqff3-1.minfo  mkqff4-1.minfo  mkqff5-1.minfo  mkqff0-0.minfo
mkqff1-0.minfo  mkqff2-0.minfo  mkqff3-0.minfo  mkqff4-0.minfo
mkqff5-0.minfo
```

Run the program again (no need to change anything in makePES.xml).

```
> RunMakePES >& makePES.out
> ls
makePES.out  makePES.xml  makeQFF.xyz   minfo.files/
prop_no_1.mop
```

The program produces the mopfile.

The two log folders contains the files for the first step (log1_genxyz), and the files for the second step (log2_genmop).

2.grid_h2co

2-1.1MR

Proceed to 2.grid_h2co/2-1.1MR to find input files to generate grid PES for formaldehyde,

```
> cd 2.grid_h2co/2-1.1MR
> ls
GaussianTemplate        makePES.xml        resources.info     log/
```

makePES.xml has the same <qchem> section as before. A new section <grid> replaces <qff>.

makePES

```
<makePES>
  <minfoFile   value="../../0.harmonic_h2co/h2co-b3lyp-dz.minfo" />
  <MR          value=”1" />          MR=1 for 1MR-PES
  <dipole      value="true" />       calculate dipole moment surface
  …
  <grid>
    <ngrid  value="11" />            number of grid points for each coordinates
    <fullmc value="true"/>           calculate all modes
  </grid>
</makePES>
```

The generation of a gridPES requires only the energy at grid points, so that FREQ is no longer needed in GaussianTemplate. Don't forget to remove FREQ if you copy the file from QFF. Note that MakePES still works as long as the energy is printed in the output; however, it would be an enormous waste of time! SCF=TIGHT is recommended for HF/DFT calculations.

GaussianTemplate

```
%chk=#basename#.chk
%NprocShared=8        Each Gaussian process uses 8 cores
%mem=1GB
#P B3LYP/CC-PVDZ SCF=TIGHT  NOSYMMETRY MAXDISK=240GB
…                     Don't put a FREQ keyword!
```

Modify resource.info and %NprocShared for your system. In this sample, we run 8 processes of Gaussian with 8 cores (64 cores in total).

resources.info

```
beluga01
beluga01
…          } 4 nodes x 2  = 8 processes
beluga04
beluga04
```

Set an environment variable SINDO_RSH =ssh, and then run MakePES,

```
> export SINDO_RSH=ssh
> RunMakePES >& makePES.out
```

You will find in the output,

makePES.out

Setup MakeGrid module

o ngrid = 11
o 1MR Grid:
1 2 3 4 5 6

} 6 modes x 11 grid = 66 grid points

Enter GridPES generation:

Execute electronic structure calculations.

Thread2@beluga02.local> Running minfo.files/mkg-q1-11-1.inp on beluga02 at …
Thread3@beluga02.local> Running minfo.files/mkg-q1-11-2.inp on beluga02 at …
Thread0@beluga03.local> Running minfo.files/mkg-eq.inp on beluga03 at …

After the energy calculations are done, pot/dipole files are created.

makePES.out

Generating pot files.

o q1.pot [OK]
o q1.dipole [OK]
…
o q6.dipole [OK]

} pot and dipole files are created.

End of GridPES generation:

```
> ls q*
q1.dipole  q2.dipole  q3.dipole  q4.dipole  q5.dipole  q6.dipole
q1.pot     q2.pot     q3.pot     q4.pot     q5.pot     q6.pot
```

q*N*.pot and q*N*.dipole contain the change of the potential energy and dipole moment, respectively, with respect to the equlibrium geomety along mode *N*. The values at the equilibrium geometry are written in eq.pot and eq.dipole.

grid points along Q_5

B3LYP/cc-pVDZ
Number of grids and data
11 1
q5 Energy (V_5)

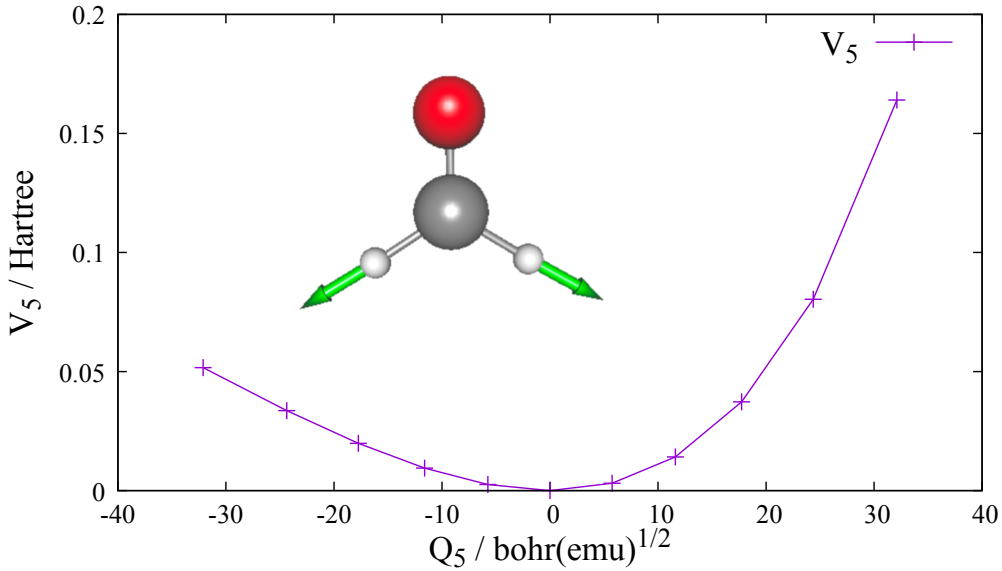
q5	Energy
-32.11897636	5.1637111962e-02
-24.36885358	3.3576631399e-02
-17.73801106	1.9823126834e-02
-11.61455479	9.4296641468e-03
-5.75063885	2.5713497506e-03
-0.00000000	0.0000000000e+00
5.75063885	3.0938756174e-03
11.61455479	1.4162827543e-02
17.73801106	3.7256435616e-02
24.36885358	8.0356295312e-02
32.11897636	1.6406728197e-01

q5.pot (END)

B3LYP/cc-pVDZ
Number of grids and data
11 3

# q5	X (dx)	Y (dy)	Z (dz)
-32.11897636	6.5354419100e-16	-2.1581328800e-14	2.2264673800e-01
-24.36885358	1.5282778610e-15	-3.2503038080e-13	1.6380302600e-01
-17.73801106	-3.5132508090e-15	2.9134816400e-15	1.1545683200e-01
-11.61455479	6.1520087100e-16	-2.6271289280e-13	7.2992832000e-02
-5.75063885	6.2180322100e-16	9.1610204700e-14	3.4762361000e-02
-0.00000000	0.0000000000e+00	0.0000000000e+00	0.0000000000e+00
5.75063885	-5.2036891900e-16	-7.6053530000e-15	-3.1664072000e-02
11.61455479	-4.5814996000e-17	-2.2601766400e-14	-6.0408552000e-02
17.73801106	2.2404410010e-15	1.0871512036e-14	-8.6260919000e-02
24.36885358	3.7191305100e-16	1.0853080599e-14	-1.0913078900e-01
32.11897636	-1.4172511000e-16	1.1229081913e-14	-1.2867327600e-01

q5.dipole (END)



Plots of V_5 at grid points of Q_5. Q_5 (symmetic CH stretching mode) is visualized in the inset. Note that the arrow corresponds to the negative direction of Q_5, that is, the potential becomes flat as the CH bond extends.

2-2.2MR

In this section, we generate 2MR-grid PES for (Q1, Q2) and (Q5, Q6). Proceed to 2.grid_h2co/2-2.2MR,

```
> cd 2.grid_h2co/2-2.2MR
> ls *pot *dipole
eq.dipole  q1.dipole  q2.dipole  q5.dipole  q6.dipole
eq.pot     q1.pot     q2.pot     q5.pot     q6.pot
```

The pot and dipole files obtained in Sec. 2-1 for the equilibrium geometry and along Q1, Q2, Q5, Q6 are placed in the same folder. These files provide the information along the coordinates, and thus reduce the cost.

makePES

```
<makePES>
  <minfoFile   value="../../0.harmonic_h2co/h2co-b3lyp-dz.minfo" />
  <MR          value=”2" />        MR=2 for 2MR-PES
  …
  <grid>
    <ngrid  value=”9" />           number of grid points is reduced to 9
    <mc2 value="1,2, 5,6"/>        (Q1, Q2) and (Q5, Q6)
  </grid>
</makePES>
```

The two-mode terms are specified by <mc2> to (Q1,Q2) and (Q5,Q6). See the appendix on the details of format of mc2.

Calculating these terms with ngrid = 9 would require 9 x 9 x 2 = 162 grid points. In this case, the information along the axis is provided by the files, so that the number of grid points is reduced to 8 x 8 x 2 = 128.

GaussianTemplate and resources.info are the same as before. Run MakePES,

```
> export SINDO_RSH=ssh
> RunMakePES >& makePES.out
```

You may check the settings in the output,

makePES.out

```
Setup MakeGrid module

 o ngrid =    9          number of grid points
 o 1MR Grid:
    1   2   5   6        1-mode terms
 o 2MR Grid:
    (1,2)   (5,6)        2-mode terms

Enter GridPES generation:
```

pot/dipole files are created at the end of the calculation.

makePES.out

Generating pot files.

o q2q1.pot [OK]
o q2q1.dipole [OK]
o q6q5.pot [OK]
o q6q5.dipole [OK]

} 2-mode terms (9x9 grid points) are created.

End of GridPES generation:

In addition to the original files with 11 grid points (q[1-6].pot/dipole), new files for 2MR-PES with 9 grid points (q2q1.pot/dipole and q6q5.pot/dipole) are created.

```
> ls q*
q1.dipole     q2.pot        q5.dipole     q6.pot
q1.pot        q2q1.dipole   q5.pot        q6q5.dipole
q2.dipole     q2q1.pot      q6.dipole     q6q5.pot
```

2-3.3MR

In this section, we generate 3MR-grid PES for (Q4, Q5, Q6). Proceed to 2.grid_h2co/2-3.3MR,

```
> cd 2.grid_h2co/2-3.3MR
> ls *pot *dipole
eq.dipole    q4.dipole    q5.dipole    q6.dipole    q6q5.dipole
eq.pot       q4.pot       q5.pot       q6.pot       q6q5.pot
```

Again, we use the exisiting information (q4, q5, q6, and q6q5) to reduce the cost. By placing these files in the same folder, the grid points are reduced from 729 (=9 x 9 x 9) points to 640 points.

makePES

```
<makePES>
  <minfoFile   value="../../0.harmonic_h2co/h2co-b3lyp-dz.minfo" />
  <MR          value=”3" />        MR=3 for 3MR-PES
  …
  <grid>
    <ngrid  value=”9" />
    <mc3 value=”4,5,6"/>          (Q4, Q5, Q6)
  </grid>
</makePES>
```

GaussianTemplate and resources.info are the same as before. Run MakePES,

```
> export SINDO_RSH=ssh
> RunMakePES >& makePES.out
```

You will find in the output that the 2-mode terms, (Q4, Q5) and (Q4, Q6), are automatically added,

makePES.out

```
Setup MakeGrid module

 o ngrid =    9
 o 1MR Grid:
    4   5   6
 o 2MR Grid:
    (4,5)   (4,6)   (5,6)
 o 3MR Grid:
    (4,5,6)

Enter GridPES generation:
```

1- and 2-mode terms that are subsets of the 3-mode terms are automatically added by the program.

the 3-mode term specified in the input

After iteration over the grid points, we obtain pot and dipole files for (Q4, Q5), (Q4, Q6), and (Q4, Q5, Q6).

makePES.out

Generating pot files.

o q5q4.pot [OK]
o q5q4.dipole [OK]
o q6q4.pot [OK]
o q6q4.dipole [OK]

} Automatically added 2-mode terms

o q6q5q4.pot [OK]
o q6q5q4.dipole [OK]

} The target 3-mode term

End of GridPES generation:

```
> ls q*
q4.dipole       q5q4.dipole     q6q4.dipole     q6q5q4.dipole
q4.pot          q5q4.pot        q6q4.pot        q6q5q4.pot
q5.dipole       q6.dipole       q6q5.dipole
q5.pot          q6.pot          q6q5.pot
```

2-4.1MR_generic

In this section, we illustrate the generic mode for grid PES. Proceed to 2-4. 1MR_generic,

```
> cd 2.grid_h2co/2-4.1MR_generic
> ls
log1_genxyz/ log2_genpot/ makePES.xml
```

makePES.xml has <qchem> section as follow,

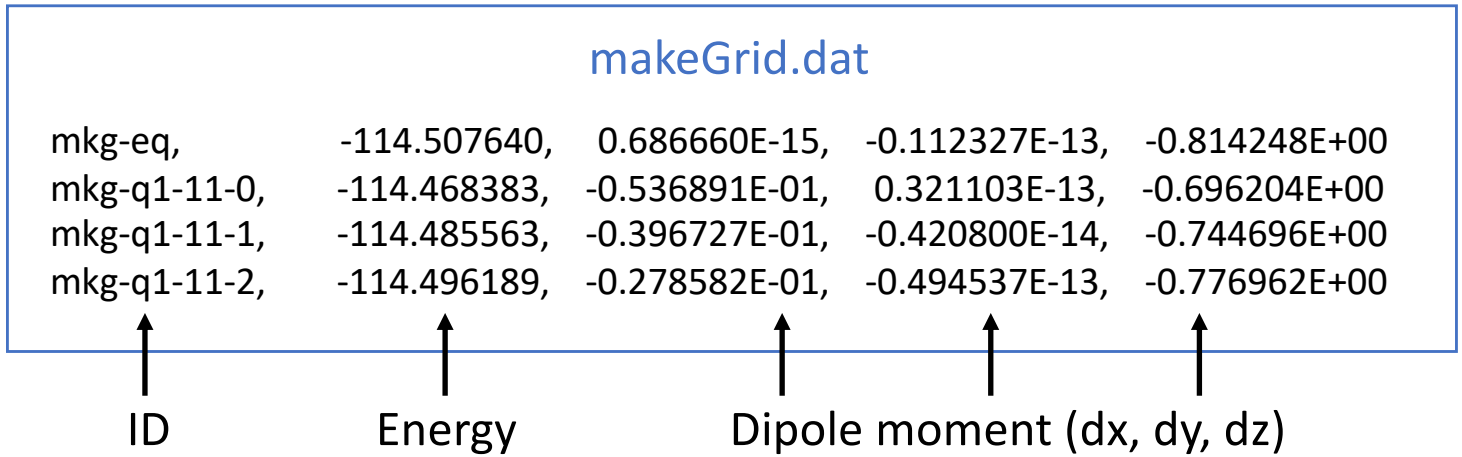
makePES

```
<makePES>
  …
  <qchem>
    <program    value="generic" />        "generic" means no specific program
    <title      value="B3LYP/cc-pVDZ" />
    <xyzfile    value="makeGrid" />       set the name of xyz file
  </qchem>
</makePES>
```

Running the program creates makeGrid.xyz,

```
> RunMakePES >& makePES.out
> ls
makePES.out   makePES.xml   makeGrid.xyz
```

makeGrid.xyz has the same format as in QFF (see Sec. 1.4). For the grid points written in the file, calculate the energy and dipole moments of formaldehyde using your favorate program. Then, compile the information to a file, makeGrid.dat, in a format as follow,



The column must be separated by comma. The length / digit is arbitrary. The order of grid points (i.e., the order of the raw) is also arbitrary. A sample is found in log2_genpot/makeGrid.dat.

Then, run the program again to obtain the pot/dipole files.

```
> RunMakePES >& makePES.out
> ls *pot
eq.pot  q1.pot  q2.pot  q3.pot  q4.pot  q5.pot  q6.pot
```

3.mrpes_h2co

In this section, we calculate a multi-resolution PES, which is a combination of QFF and grid PES. All 1-mode terms are obtained by the grid method using 11 points. Mode coupling strength (MCS) is derived from QFF coefficients, and coupling terms with MCS > 10.0 are generated by the grid method using 9 points.

Proceed to 3.mrpes_h2co to find input files,

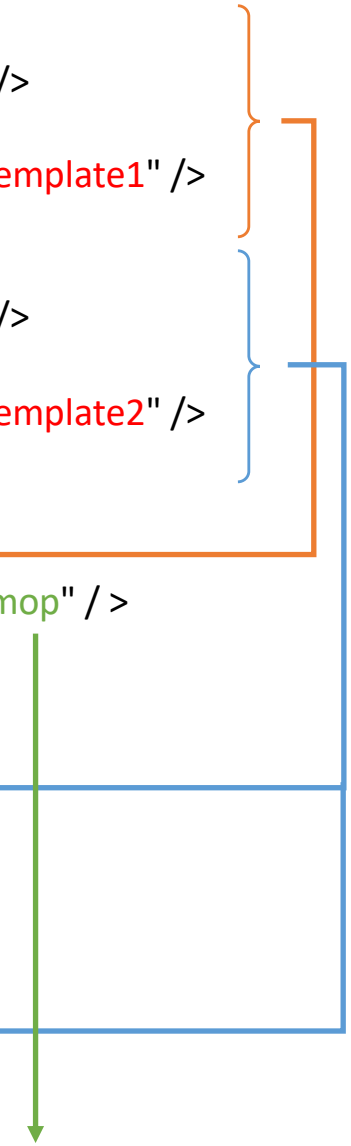
```
> cd 3.mrpes_h2co
> ls
GaussianTemplate1  GaussianTemplate2  log/
makePES.xml        resources.info
```

GaussianTemplate1 and GaussianTemplate2 are the template files to calculate a Hessian matrix (FREQ) and only the energy, respectively.

In makePES.xml, two <qchem> sections are given which specifies GaussianTemplate1 and GaussianTemplate2 attributed to id = “freq” and “ene”, respectively. The ID is associated with QCID of <qff> and <grid>.

makePES.xml

```
<qchem id="freq">
  <program    value="gaussian" />
  …
  <template   value="GaussianTemplate1" />
</qchem>
<qchem id="ene">
  <program    value="gaussian" />
  …
  <template   value="GaussianTemplate2" />
</qchem>
<qff>
  <QCID     value="freq" />
  <mopfile   value="prop_no_1.mop" / >
  …
</qff>
<grid>
  <QCID   value="ene" />
  <ngrid  value="11" />
  <mc1    value="1-6"/>
</grid>
<grid>
  <QCID   value="ene" />
  <ngrid  value=”9" />
  <mcsstrength value="10"/>
  <mopfile    value="prop_no_1.mop"/>
</grid>
```



<qchem> sections are followed by one <qff> and two <grid> sections. MakePES processes these sections in the order they appear in the input file. In the present example,

1. Generate QFF
   prop_no_1.mop is created.
2. Generate 1MR-grid PES with ngrid = 11
   q1 - q6.pot / dipole files are created.
3. Generate 3MR-grid PES with ngrid = 9
   pot/dipole files with MCS > 10 are created.

Step 1 (QFF) must precede Step 3, because prop_no.1.mop is needed to calculate MCS. Step 2 generates 1MR-grid PES, q1 - q6.pot. These files are used in Step 3.

Run the program by typing,

```
> export SINDO_RSH=ssh
> RunMakePES >& makePES.out
```

Find in the makePES.out that the calculation is performed in the above order.

makePES.out

…
Enter QFF generation:
…
Generating prop_no_1.mop... Done!
Removing the tempfiles ... Done!
End of QFF generation.

} QFF generation

Setup MakeGrid module
o ngrid = 11
o 1MR Grid:
1 2 3 4 5 6
Enter GridPES generation:
…
Generating pot files.
o q1.pot [OK]
o q1.dipole [OK]
…
o q6.pot [OK]
o q6.dipole [OK]…
End of GridPES generation:

} 1MR-grid PES generation

makePES.out

Setup MakeGrid module

o Setup MCS: Read QFF Data via prop_no_1.mop ... [OK]
o ngrid = 9
o 1MR Grid:
5 1 2 3 6 4
o 2MR Grid:
(1,5) (2,5) (3,5) (1,6) (2,6) (3,6) (5,6) (2,3) (2,4) (4,6)
o 3MR Grid:
(2,3,6) (2,4,6)

Reads the output of QFF calc.

Coupling terms with MCS > 10.0

Enter GridPES generation:
…
Generating pot files.

o q5q1.pot [OK]
o q5q1.dipole [OK]
…
o q6q4q2.pot [OK]
o q6q4q2.dipole [OK]

} 2, 3MR-grid PES generation

End of 3MR-GridPES generation:

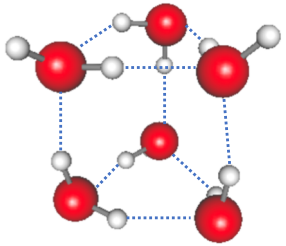
The program detects 10 two-mode terms and 2 three-mode terms where MCS > 10.0. When the calculation is done, you will find the following pot files in the working directory.

```
> ls *pot
eq.pot       q2.pot       q3q2.pot     q4q2.pot     q5q1.pot
q5q3.pot     q6q1.pot     q6q3.pot     q6q4.pot     q6q5.pot
q1.pot       q3.pot       q4.pot       q5.pot       q5q2.pot
q6.pot       q6q2.pot     q6q3q2.pot   q6q4q2.pot
```

4.water-hexamer

4-1.intra

In this section, we generate the PES of water hexamer using the intramolecular modes, i.e., OH stretching and HOH bending modes. There are 18 such modes, and corresponds to mode 31 – 48.



water hexamer (prism)

Proceed to 4.water-haxamer/4-1.intra to find input files,

```
> cd 4.water-hexamer/4-1.intra
> ls
GaussianTemplate    h2o_6-mp2dz.minfo  log/
makePES.xml         resources.info
```

h2o_6-mp2dz.minfo is a minfo file that contains the equlibrium geometry and vibrational modes of water hexamer (prism shape) obtained at the MP2/c—pVDZ level of theory.

GaussianTemplate is a template file to perform FREQ calculations at the MP2/cc-pVDZ level of theory.

In makePES.xml, the active modes are specified by <activemode> to modes 31 – 48. Other sections, <qchem> and <qff>, are the same as before.

makePES.xml

```
<makePES>
  <minfoFile   value="h2o_6-mp2dz.minfo" />
  <MR          value="3" />
  <activemode  value="31-48" />
  <qchem>
    <program     value="gaussian" />
    <dryrun      value="false"/>
    <removefiles value="true" />
    <title       value="MP2/cc-pVDZ" />
    <template    value="GaussianTemplate" />
  </qchem>
  …
```

active modes are set to the intramolecular modes, mode 31 – 48.

Run the program by,

```
> export SINDO_RSH=ssh
> RunMakePES >& makePES.out
```

Find in the output that mode 31-48 are active ,

makePES.out

o Input options read via makePES.xml ... [OK]
- Molecular info via h2o_6-mp2dz.minfo ... [OK]
- InterDomain = false
- ActiveModes:
  * Domain 1
    31 32 33 34 35 36 37 38 39 40
    41 42 43 44 45 46 47 48
- MR = 3
- Dipole = false

} 31 – 48 are active, and 1 – 30 are inactive.

When the calculation ends, you will find that prop_no_1.mop has entry only for modes 31 – 48.

```
DALTON_FOR_MIDAS MP2/cc-pVDZ
 1.2693093572610456000000e-07   31
 3.8331230612195770000000e-03   31   31
 5.2999094588990350000000e-05   31   31   31
-5.3384572915176750000000e-06   31   31   31   31
-3.8778975455244765000000e-06   32
 3.8794005068453160000000e-03   32   32
 1.1584964110841597000000e-04   32   32   32
-6.2778785001575310000000e-06   32   32   32   32
-2.5417319397503540000000e-06   33
 3.8953636442193990000000e-03   33   33
```

Note that it is not easy to tell which modes should be set to active or inactive. The modes can be set to inactive later in the vibrational calculations using sindo. Therefore, I recommend to include as many modes as possible during the PES generation step.

Nevertheless, there are increasing demand to select vibrational modes as the size of system becomes large. For example, a solute in solvent, ligands in a protein, etc. A model that separates the inter- and intra-molecular modes, illustrated in this example, is often used for cluster systems. <activemode> is made to achieve such purposes.

Appendix: List of all keys

General keys

- minfoFile: file name
  The name of minfo file containing the vibrational data. The value is case sensitive.

- MR: 1/2/3
  The order of mode coupling expansion. Can take 1, 2, or 3. (default = 3)

- activemode: string of mode index
  Specifies active modes for PES generation. All modes are active by default. The mode numbers should be separated by camma or space. A hyphen can be used for a sequence of mode number. For example,

  ```
  <entry key="activemode"> 1,2,3,5 </entry>
  ```

  is equivalnet to,

  ```
  <entry key="activemode"> 1-3 5 </entry>
  ```

  which means Q_1,Q_2,Q_3, and Q_5 are active, and Q_4 isn't.

- dipole: true/false
  Generates the dipole moment surface in addition to the PES, when true. (default = false)

QCHEM section

ID: string

- program: string
  gaussian … Interface with Gaussian
  generic … Print the coordinates to a xyz file

- title: string
  A title line that will be printed to PES files.

options for non-generic (=Gaussian)

- removefiles: true/false
  Removes the input/output files of the quantum chemistry program, when true. (default = false)

- dryrun: true/false
  Generates the input files for the quantum chemistry program and exits without execution, when true. (default = false)

- template: file name
  The name of a template file to generate the input files for quantum chemisty jobs.

options for generic

- xyzfile: filename
  Name of a xyz file, where the coordinates are written. (default = makeQFF for QFF and makeGrid for GRID)

QFF section

- QCID: string
  The ID of associated <qchem>

- stepsize: real number
  The step size for numerical differentiations in dimensionless unit ($\sqrt{\omega/\hbar} * Q$). (default = 0.5)

- ndifftype: grad or hess
  The type of numerical differentiations.
  grad : Numerical 3rd-order diff. of gradient.
  hess (default) : Numerical 2nd-order diff. of hessian.

- mopfile: file name
  The name of mop file, in which the QFF coefficients are written. (default = prop_no_1.mop)
  This format is compatible with the MIDAS software developed by Christiansen and coworkers.

- interdomain_hc: true/false
  Prints the harmonic coupling, when true. (default = true)

- gradient and hessian: input/current

  Specifies where the gradient and Hessian are retrieved.

  input (default) : From the input minfo file.

  current : From the current calculation. (mkqff-eq.minfo)

  “input” is useful for combining accurate geometry, gradient, and Hessian, read from the input minfo file, with lower-level cubic and quartic terms, which are calculated by MakePES module.

  On the other hand, one might think of another strategy, where the geometry and coordinates are derived from a low-level of theory, and the QFF at a higher-level of theory. In that case, this option should be set to “current”, which incorporates the gradient and Hessian obtained from the current calculation.

- genhs: true/false

  Generate the 001.hs file, when true. (default = false)

  001.hs is a file which contains the QFF coefficients in the old format; however, this format is deprecated and not recommended to use unless for a debugging purpose to compare the result with the previous version of SINDO.

GRID section

- QCID: string
  The ID of associated <qchem>

- ngrid: integer number
  The number of grid points along each coordinates. (default = 11)

- fullmc: true/false
  All the mode coupling up to the MR-th order is generated, when true. (default = false)

- mc1, mc2, mc3: string of mode index
  The 1, 2, or 3MR terms separated by camma or space.

  Examples:

  - `<mc1 value="1,2,3,5" />` or `<mc1 value="1-3 5" />`

    generates grid points for Q1,Q2,Q3, and Q5.

  - `<mc2 value="1,2, 1,4, 2,4, 3,4" />` or `<mc2 value="1,2, 1-3,4" />`

    generates the grid points for (Q2, Q1),(Q4, Q1),(Q4, Q2), and (Q4, Q3).

  - `<mc3 value="1,2,3, 1,2,4" />`

    generates the grid points for (Q3, Q2, Q1) and (Q4, Q2, Q1).

- mcsstrength: real number
  The threshold value (in cm^{-1}) to select the mode coupling term for generating the grid potential. The coupling terms with MCS larger than this value are generated.

- mopfile: file name
  The name of mop file to obtain MCS.

NOTE: One of fullmc, mc1, mc2, mc3, or mcsstrength must be present to specify the coupling terms.