Users' guide to MakePES

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- In this guide, I will illustrate how to use MakePES to generate QFF, GridPES, and Multiresolution PES. Formaldehyde (H_2CO) is used as an example, but the method is applicable to any molecule.

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

- This guide also assumes that you have installed the program. Change "/path/to" to your installation directory when you see a command like this,

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

- In this guide, we will use Gaussian for the electronic structure calculations. Make sure that you have configured "runGaussian.sh" and the path to it.

```
> export PATH=${PATH}:/path/to/sindo-4.0/script
> runGaussian.sh
USAGE: runGaussian.sh arg[1] arg[2]
arg[1] : current directory
arg[2] : input file
```

- If you don't use Gaussian, you may still use MakePES in generic mode; see 1.4 and 2.4.

Contents

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

0.Harmonic analysis and generation of a minfo file

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/    run.sh
```

- “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   run.sh
```

.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 run.sh
```

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

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

“run.sh” is a script to do this work at once. Change ”/path/to” to your installation directory using an editor,

```
> vi run.sh
#!/bin/bash

sindo_dir=/path/to/sindo-4.0
sindo_jar=$sindo_dir/jar
PATH=$PATH:$sindo_dir/script

runGaussian.sh ./  h2co-b3lyp-dz.inp
java -cp "$sindo_jar/*" Fchk2Minfo h2co-b3lyp-dz
```

Then, run the script.

```
> ./run.sh
> ls
h2co-b3lyp-dz.chk    h2co-b3lyp-dz.fchk  h2co-b3lyp-dz.inp
h2co-b3lyp-dz.minfo  h2co-b3lyp-dz.out   run.sh
```

1.qff_h2co

1-1.single

In this section, we generate a quartic force field (QFF) for formaldehyde [1]. Proceed to 1.qff_h2co/1-1.single to find input files,

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

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 Gaussian
    <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

```
> sindo_jar=/path/to/sindo-4.0/jar
> java -cp "$sindo_jar/*" RunMakePES >& makePES.out
```

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

```
> sindo_jar=/path/to/sindo-4.0/jar
> java -cp $sindo_jar/*" 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 intensive bottleneck for generating the PES. In the case of H_2CO, FREQ calculations at 13 grid points are required. They were carried out one by one in the previous section using one node.

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/1-2.parallel
> ls
GaussianTemplate  log/    makePES.xml  resources.info  run.sh
```

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
> sindo_jar=/path/to/sindo-4.0/jar
> java -cp "$sindo_jar/*" 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 the job is done, you will obtain the same mop file as before, but in a much faster computational time.

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      run.sh
```

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 input files for Gaussian in “minfo.files”,

```
> sindo_jar=/path/to/sindo-4.0/jar
> java -cp "$sindo_jar/*" 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

```
> sindo_jar=/path/to/sindo-4.0/jar
> java -cp "$sindo_jar/*" 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. See the TIPS in 4.2 for more detail.

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,

```
> sindo_jar=/path/to/sindo-4.0/jar
> java -cp "$sindo_jar/*" 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
mkqff0-0          name of the second point
   C    -0.0125897498    -0.0000000000    -0.6014736819
   O     0.0031430124     0.0000000000     0.6027247362
```

xyz coordinates

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.

Run the electronic structure calculations and generete minfo files by yourself. 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).

```
> sindo_jar=/path/to/sindo-4.0/jar
> java -cp "$sindo_jar/*" 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 potential

2.1. 1MR-grid PES

In this section, we generate a grid potential [2]. Proceed to 2.grid_h2co/2-1.1MR to find input files,

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

makePES.xml has the same <qchem> section as before. A new section <grid> replaces <qff>. We also set <dipole> to true to generate dipole memoent surfaces.

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
> sindo_jar=/path/to/sindo-4.0/jar
> java -cp "$sindo_jar/*" 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)

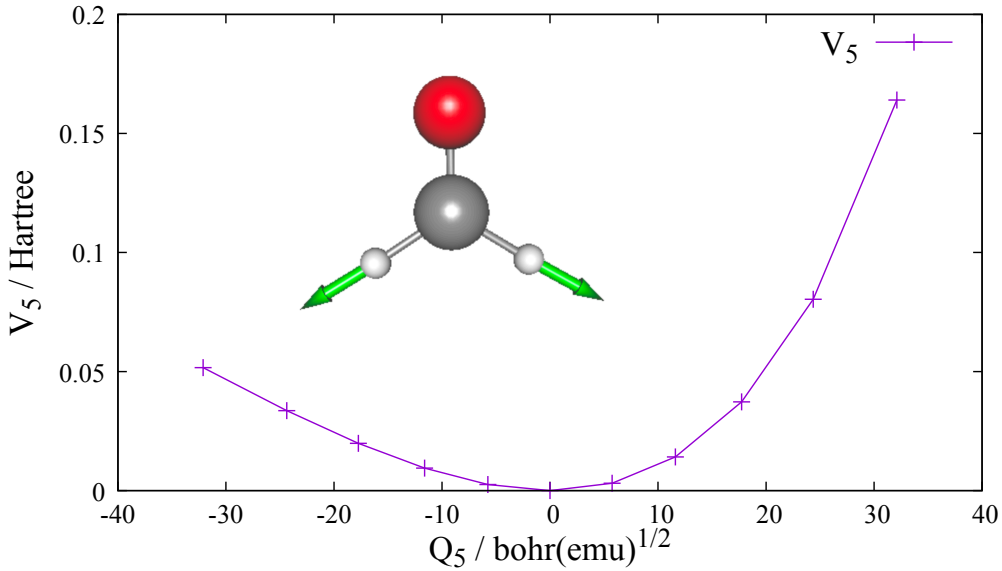
q5	Energy
-32.11897636	5.1637111962e-02
-24.36885358	3.3576631399e-02
-17.73801106	1.9823126834e-02
-11.61455479	9.4296641468e-03
-5.75063885	2.5713497506e-03
-0.00000000	0.0000000000e+00
5.75063885	3.0938756174e-03
11.61455479	1.4162827543e-02
17.73801106	3.7256435616e-02
24.36885358	8.0356295312e-02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

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
GaussianTemplate    makePES.xml    ...
```

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 two 2MR-terms with ngrid = 9 requires 9 x 9 x 2 = 162 grid points. However, we have already calculated the grid points along the axis. In order to re-use them, the pot and dipole files obtained in Sec. 2-1 are placed in the same directory:

```
> ls *pot *dipole
eq.dipole  q1.dipole  q2.dipole  q5.dipole  q6.dipole
eq.pot     q1.pot     q2.pot     q5.pot     q6.pot
```

MakePES make use of the previous calculation whenever possible. In this example, the information along the Q1, Q2, Q5, Q6 axis is provided by the files. Therefore, the number of grid points is reduced from 162 to to 8 x 8 x 2 = 128.

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

```
> export SINDO_RSH=ssh
> sindo_jar=/path/to/sindo-4.0/jar
> java -cp "$sindo_jar/*" 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:
```

and that 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]          } 2-mode terms (9x9 grid points) are created.
  o q6q5.dipole  [OK]
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
```

grid points along Q_5 and Q_6

```
B3LYP/cc-pVDZ
# Number of grids and data                    V65
     9      9      1
#    q5                 q6                 Energy
   -27.93846251    -27.68241971    -6.7200061552e-02
   -19.84484851    -27.68241971    -5.5998358343e-02
   -12.85779017    -27.68241971    -4.1951916512e-02
    -6.33498780    -27.68241971    -2.3826848408e-02
    -0.00000000    -27.68241971     0.0000000000e+00
     6.33498780    -27.68241971     3.2112374522e-02
    12.85779017    -27.68241971     7.6869380577e-02
    19.84484851    -27.68241971     1.4322717035e-01
    27.93846251    -27.68241971     2.5528810814e-01
```

Note that the coupling term V_{65} is

$$V_{65} = V - V_6 - V_5$$

where V is the total energy, and V_5 and V_6 are the 1MR potential along Q_5 and Q_6, respectively. V_{65} is often called an "intrinsic" coupling term.

2.3. 3MR-grid PES

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
> sindo_jar=/path/to/sindo-4.0/jar
> java -cp "$sindo_jar/*" 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)

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

Enter GridPES generation:

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. Generic mode

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
```

makePES.xml has <qchem> section as follow,

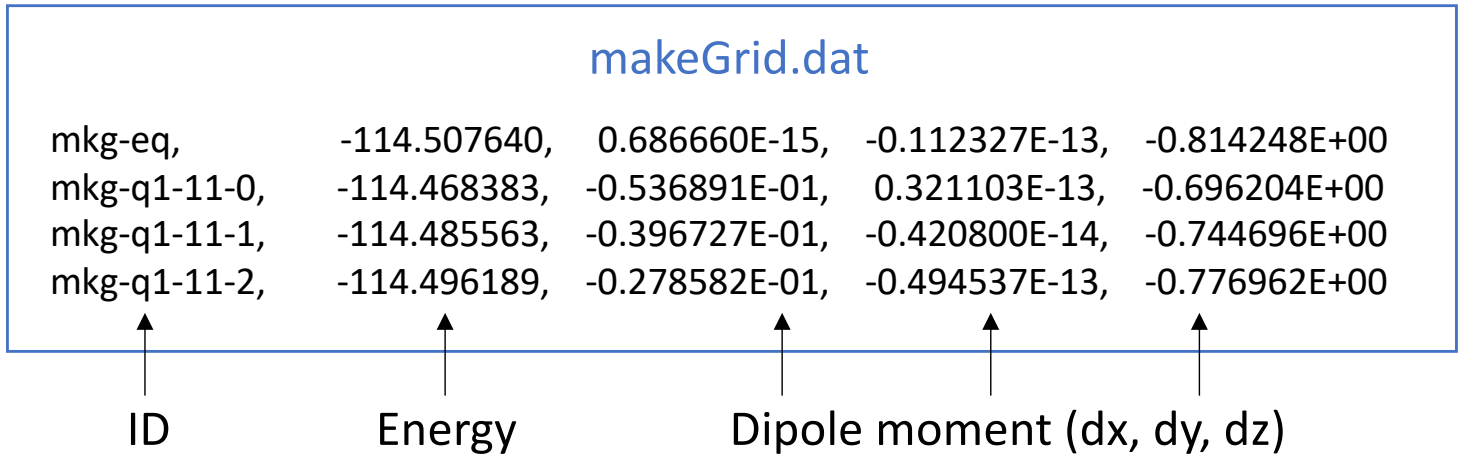
makePES

```
<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,

```
> sindo_jar=/path/to/sindo-4.0/jar
> java -cp "$sindo_jar/*" 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.

```
> sindo_jar=/path/to/sindo-4.0/jar
> java -cp "$sindo_jar/*" RunMakePES >& makePES.out
> ls *pot
eq.pot  q1.pot  q2.pot  q3.pot  q4.pot  q5.pot  q6.pot
```

3. Multiresolution PES

In this section, we generate a multi-resolution PES [3], which combines different levels of electronic structure and functional forms. Here, we will use the following combination:

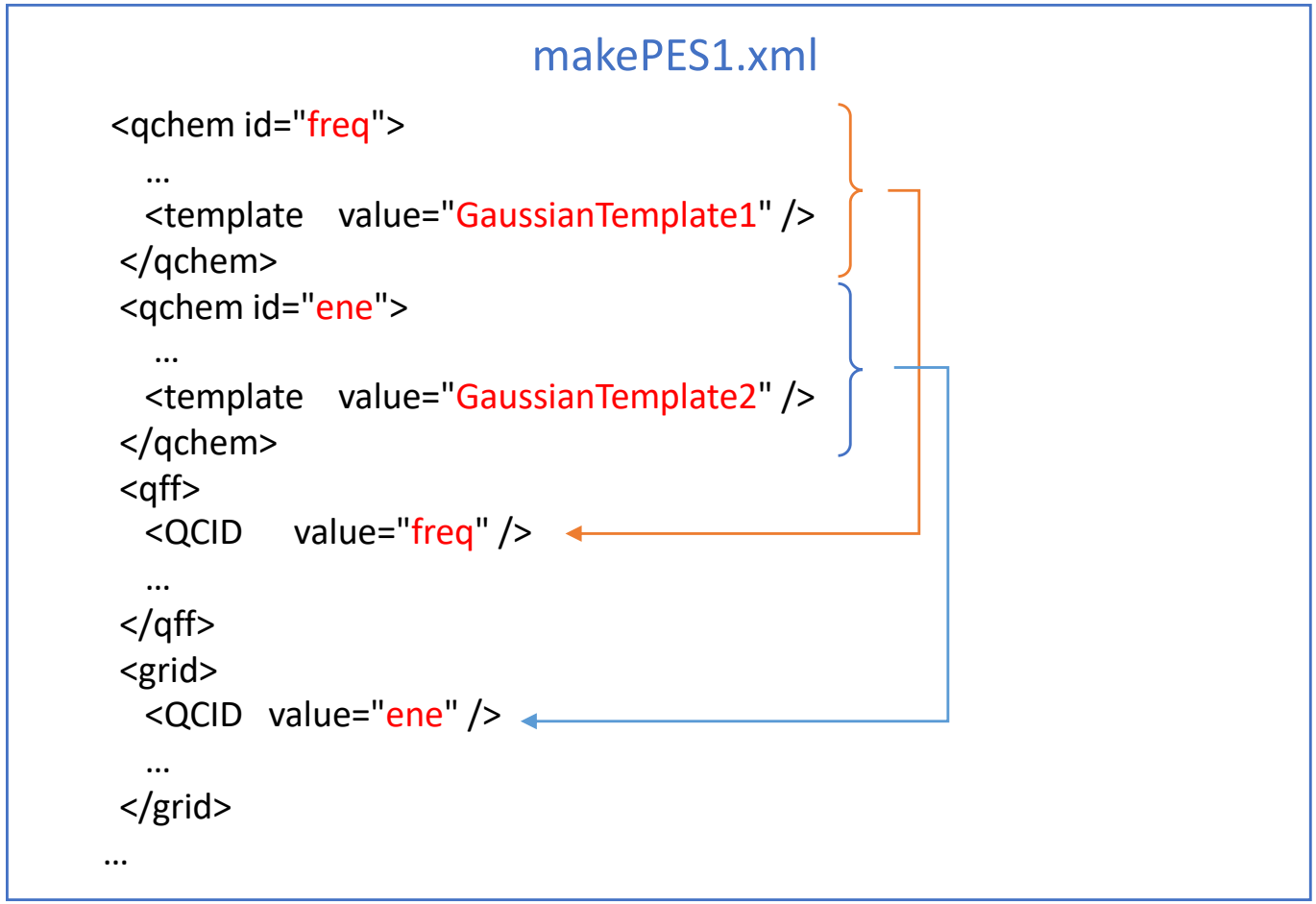
	Electronic Structure	**Functional Form**
1MR	CCSD(T)/cc-pVTZ	Grid-PES (11 points)
Strongly coupled terms (MCS>10)	CCSD(T)/cc-pVTZ	Grid-PES (9 points)
Weakly coupled terms (MCS>1)	B3LYP/cc-pVDZ	Grid-PES (7 points)
Other terms	B3LYP/cc-pVDZ	QFF

Mode coupling strength (MCS) is calculated from QFF coefficients [4].

Proceed to 3.mrpes_h2co to find input files,

```
> cd 3.mrpes_h2co
> ls
GaussianTemplate1  GaussianTemplate2  GaussianTemplate3  log/
makePES1.xml  makePES2.xml  resources.info  run.sh
```

GaussianTemplate1 and GaussianTemplate2 are the template files for Gaussian to calculate the Hessian matrix (FREQ) and only the energy, respectively, at the B3LYP/cc-pVDZ level. In makePES1.xml, these files are associated with <qchem> sections with id="freq" and "ene", and the ID is associated with QCID of <qff> and <grid>.



makePES1.xml

```
<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" />
  <mcstrength value="10"/>
  <mopfile     value="prop_no_1.mop"/>
</grid>
<grid>
  <QCID   value="ene" />
  <ngrid  value="7" />
  <mcstrength value="1"/>
  <mopfile     value="prop_no_1.mop"/>
</grid>
```

1MR-grid PES

Grid PES with MCS > 10

Grid PES with MCS > 1

<qchem> sections are followed by one <qff> and three <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.
4. Generate 3MR-grid PES with ngrid = 7
   pot/dipole files with MCS > 1 are created.

Step 1 (QFF) must precede Step 3 and 4, because prop_no.1.mop is needed to calculate MCS. Note that we only need step4 for the final mrpes; however, we carry out step2 and 3 for a reference.

Modify resource.info and %NprocShared in GaussianTemplate1/2 for your system. In this sample, we run 8 processes of Gaussian with 8 cores (64 cores in total).

GaussianTemplate1/2

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

resources.info

```
beluga01
beluga01
...
beluga04
beluga04
```

4 nodes x 2 = 8 processes

Run the program by typing,

```
> sindo_jar=/path/to/sindo-4.0/jar
> java -cp "$sindo_jar/*" RunMakePES –f makePES1.xml >&
makePES1.out
```

Find in the makePES1.out that the calculation is performed in the above order.

makePES1.out

```
…
Enter QFF generation:
…
Generating prop_no_1.mop... Done!

Setup MakeGrid module
…
Generating pot files.
  o q1.pot  [OK]
  …

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)
```

QFF generation

1MR-grid PES generation

Reads the output of QFF calc.

Coupling terms with MCS > 10.0

When the calculation is done, you will find the following pot files in the current directory.

```
> ls *pot
eq.pot       q3q2.pot     q5q1.pot     q6.pot       q6q4.pot
q1.pot       q4.pot       q5q2.pot     q6q1.pot     q6q4q2.pot
q2.pot       q4q2.pot     q5q3.pot     q6q2.pot     q6q5.pot
q2q1.pot     q4q3.pot     q5q4.pot     q6q3.pot
q3.pot       q5.pot       q5q4q3.pot   q6q3q2.pot
```

Note that the red ones are strongly coupled terms (MCS > 10) generated by 9 grid points, and the blue ones are weakly coupled terms (MCS > 1) generated by 7 grid points.

Before moving on to generate the PES at the CCSD(T)/cc-pVTZ level, we must save the PES@B3LYP data and clean up the current directory,

```
> mkdir pes_b3lyp
> mv minfo.files *pot *dipole pes_b3lyp
```

This is because MakePES looks for pot/dipole files and minfo files in the current directory to restart the job.

The input file for MakePES looks as follow:

makePES2.xml

```
<makePES>
  ...
  <dipole     value="false" />
  <qchem id="ene">
    ...
    <title      value="CCSD(T)/cc-pVTZ" />
    <template   value="GaussianTemplate3" />
  </qchem>
  <grid>
    <QCID   value="ene" />
    <ngrid  value="11" />
    <mc1    value="1-6"/>
  </grid>
  <grid>
    <QCID   value="ene" />
    <ngrid  value="9" />
    <mcstrength value="10"/>
    <mopfile    value="prop_no_1.mop"/>
  </grid>
</makePES>
```

Dipole is turned off because CCSD(T) does not provide a dipole moment.

1MR-grid PES

Grid PES with MCS > 10

use the mop file generated in the last step.

The template input file for CCSD(T)/cc-pVTZ is as follow

GaussianTemplate3

…
#P CCSD(T)/CC-PVTZ NOSYMMETRY MAXDISK=240GB

Run the program by typing,

```
> sindo_jar=/path/to/sindo-4.0/jar
> java -cp "$sindo_jar/*" RunMakePES –f makePES2.xml >&
makePES2.out
```

When the calculation is done, you will find the following pot files in the current directory.

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

Again, we will save all the CCSD(T) data to a directory,

```
> mkdir pes_ccsdt
> mv minfo.files *pot pes_ccsdt
```

We now compile the PES data in one directory,

```
> mkdir pes_mrpes
> mv prop_no_1.mop      pes_mrpes   QFF
> cp $b3lypdir/*pot     pes_mrpes   2MR-, 3MR-Grid PES (MCS > 1)
> cp $ccsdtdir/*pot     pes_mrpes   1MR-grid and 2MR-, 3MR-grid PES (MCS > 10)

> cp $b3lypdir/*dipole pes_mrpes   Dipole moment surface
```

We will use this PES for vibrational calculations. See the Users' guide to FSindo.

4. TIP and FAQ

4.1. How to terminate jobs.

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 the electronic structure 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, you may have to kill all child processes (= electronic structure jobs) manually.

4.2. How to restart a job.

MakePES looks for PES data (pot files and mopfile) and minfo files in a "minfo.files" directory before starting electronic structure jobs. The job is skipped if a minfo file is found, and starts from a point where it ended before.

The same logic applies to a generic mode. MakePES looks for PES data, minfo files, and a grid data file (e.g., makeGrid.dat), and writes to a xyz file the coordinates of grid points that still need to calculate the energy, gradient, etc. Note that the xyz file, if exists, will be saved with an extension of xyz_0. In a generic mode, the PES data (mop/pot files) are generated only when the information of all grid points are provided.

Note that, for this reason, you have to remove the PES data to start a fresh new job.

5. References

QFF

[1] Ab initio vibrational state caluclations with a quartic force field: Applications to H_2CO, C_2H_4, CH_3OH, CH_3CCH, and C_6H_6,
K. Yagi, K. Hirao, T. Taketsugu, M. W. Schmidt, and M. S. Gordon,
J. Chem. Phys. **121**, 1383 (2004).

Grid-PES

[2] Direct vibrational self-consistent field method: Applications to H_2O and H_2CO,
K. Yagi, T. Taketsugu, K. Hirao, and M. S. Gordon,
J. Chem. Phys. **113**, 1005 (2000).

Multiresolution PES

[3] Multiresolution potential energy surfaces for vibrational state calculations,
K. Yagi, S. Hirata, and K. Hirao,
Theor. Chem. Acc. **118**, 681 (2007).

[4] On the coupling strength in potential energy surfaces for vibrational calculations,
P. Seidler, T. Kaga, K. Yagi, O. Christianse, and K. Hirao,
Chem. Phys. Lett. **483**, 138 (2009).

Appendix: List of all keys

General keys

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

- minfo_folder: folder name
  The name of a folder where generated minfo files will be stored. The value is case sensitive. (default = minfo.files)

- MR:
  The order of mode coupling expansion. Each PES type can take its own MR, which precedes the MR here. (default = 3)

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

- 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,

  ```
  <activemode  value="1,2,3,5”>
  ```

  is equivalnet to,

  ```
  <activemode  value=“1-3 5”>
  ```

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

  Note that the modes can be set to inactive later in the vibrational calculations. Therefore, it is recommended to include as many modes as possible during the PES generation step.

  Nevertheless, there are obvious cases where we want to select vibrational modes. For example, a solute in solvent, ligands in a protein, etc. A model that separates the inter- and intra-molecular modes is often used for cluster systems. <activemode> is useful for such purposes.

- interdomain: true / false

  Calculates inter-domain coupling terms, when true. (default = false)

  QFF計算では、実行された量子化学計算の情報から、Gradientで数値微分の場合はtiij, uiiij、Hessianで数値微分の場合は3MRまでドメイン間カップリングが計算可能だが、interdomain = falseではこれらは出力されない。出力したい場合は、interdomain=trueで再計算する。

  Hessianの場合、minfo.filesからデータを読み込めば、追加の量子化学計算なく3MRまで計算できため、実は計算負荷の軽減にはならない。4MRは追加計算が必要となる。

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
  Basename of a xyz file, where the coordinates of grid points are written. ".xyz" is automatically added. The PES data is read from minfo files in QFF and from a dat file, *filename*.dat, in GRID. (default = makeQFF for QFF and makeGrid for GRID)

QFF section

- QCID: string
  The ID of associated <qchem>

- MR:
  The order of mode coupling expansion. Maximum is 4. (default = 3)

- stepsize: real number
  The step size for numerical differentiations in dimensionless unit. (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).

- mcstrength: 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 mcstrength must be present to specify the coupling terms.