QUANTICS – How to run a job with local diabatisation – 17 June 2016

Test case: fulvene SA-2-CAS(6,6)/STO-3G

Assuming GAUSSIAN DV, Revision I.04+

```
module load gaussian/devel-modules
module load gdvi04p
```

1 GAUSSIAN data

Data directory: **/work/username/fulv_test/fulv_db**

1.1 Preparing transfile

Input file: **/work/username/fulv_test/fulv_db/start.com**

```
%mem=800mb
%chk=/work/username/fulv_test/fulv_db/start.chk
#P CAS(6,6,NRoot=2)/STO-3G
NoSymm Pop=Full
IOp(5/97=100,10/97=100)
Freq=HPModes IOp(5/17=41000200,10/10=700007)
Guess=Alter

Fulvene FC point

0 1
C                  1.186620       0.000000      -0.119224
H                  2.209989       0.000000       0.225769
C                  0.747975       0.000000      -1.402770
H                  1.353516       0.000000      -2.297938
C                 -1.186620       0.000000      -0.119224
H                 -2.209989       0.000000       0.225769
C                 -0.747975       0.000000      -1.402770
H                 -1.353516       0.000000      -2.297938
C                 -0.000000       0.000000       0.792022
C                 -0.000000       0.000000       2.144452
H                  0.920282       0.000000       2.712245
H                 -0.920282       0.000000       2.712245

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0.5       0.5
```

Job file: **/work/username/fulv_test/fulv_db/jobscript_start**

```
#PBS -l walltime=01:00:00
#PBS -l mem=1600mb
#PBS -joe

module load gaussian/devel-modules
module load gdvi04p

gdv < $WORK/fulv_test/fulv_db/start.com > $WORK/fulv_test/fulv_db/start.log
```

```
qsub jobscript_start
```

N.B.: you may want run the same calculation (changing the name of the file) without "**NoSymm**" in order to get the symmetry species of the normal modes.

1.2 Preparing coinfile

N.B.: this is not a file containing the branching-space (BS) vectors at a conical intersection (CoIn) but BS-like vectors at the Franck-Condon (FC) point, *i.e.*, at the same geometry as in **start.com**. They will serve as a reference for orienting BS-like vectors consistently at other geometries.

Input file: **/work/username/fulv_test/fulv_db/refbs.com**

```
%mem=800mb
%chk=/work/username/fulv_test/fulv_db/refbs.chk
#P CAS(6,6,NRoot=2)/STO-3G
NoSymm Pop=Full
Freq IOp(5/17=41000200,10/10=700007)
Guess=Alter

Fulvene BS point

0 1
C                  1.186620       0.000000      -0.119224
H                  2.209989       0.000000       0.225769
C                  0.747975       0.000000      -1.402770
H                  1.353516       0.000000      -2.297938
C                 -1.186620       0.000000      -0.119224
H                 -2.209989       0.000000       0.225769
C                 -0.747975       0.000000      -1.402770
H                 -1.353516       0.000000      -2.297938
C                 -0.000000       0.000000       0.792022
C                 -0.000000       0.000000       2.144452
H                  0.920282       0.000000       2.712245
H                 -0.920282       0.000000       2.712245

18 19

0.5       0.5
```

Job file: **/work/username/fulv_test/fulv_db/jobscript_refbs**

```
#PBS -l walltime=01:00:00
#PBS -l mem=1600mb
#PBS -joe

module load gaussian/devel-modules
module load gdvi04p

gdv < $WORK/fulv_test/fulv_db/refbs.com > $WORK/fulv_test/fulv_db/refbs.log
```

```
qsub jobscript_refbs
```

1.3 Preparing template

Template file: **/work/username/fulv_test/fulv_db/template.dat**

```
%mem=800mb
%chk=$chk$
#P CAS(6,6,NRoot=$root$)/STO-3G
NoSymm Pop=Full SCF=(MaxCycle=128) IOp(7/33=1)
$Swap:IOp(5/97=100,10/97=100)$
$Freq:Freq IOp(5/17=41000200,10/10=700007)$
$Guess0:Guess=Read$
$Guess:Guess=Cards$

Fulvene

0 1
<geometry>

<mo-coefficients>

0.5       0.5
```

1.4 Preparing DB-reference

DB-reference file: **/work/username/fulv_test/fulv_db/refdb.dat**

```
#New
C             1.186620    0.000000   -0.119224
H             2.209989    0.000000    0.225769
C             0.747975    0.000000   -1.402770
H             1.353516    0.000000   -2.297938
C            -1.186620    0.000000   -0.119224
H            -2.209989    0.000000    0.225769
C            -0.747975    0.000000   -1.402770
H            -1.353516    0.000000   -2.297938
C             0.000000    0.000000    0.792022
C             0.000000    0.000000    2.144452
H             0.920282    0.000000    2.712245
H            -0.920282    0.000000    2.712245
```

N.B.: this is the same geometry (within the same Cartesian frame) as in **start.com**. The content of this file will change once QUANTICS is executed, but the file that will be produced will stay compatible with further calculations.

2 QUANTICS/GAUSSIAN subcommand

Script: **/home/username/bin/gdvi04prun**

```
#!/bin/sh
# script to run GAUSSIAN gdvi04+ during direct dynamics
#
JOB=$1
DIR=$2
#-------------------------------------------------------------------------------
# set Gaussian PATH (no Linda)
module load gaussian/devel-modules
module load gdvi04p
#-------------------------------------------------------------------------------
COM_FILE=${DIR}/${JOB}.com
LOG_FILE=${DIR}/${JOB}.log
CHK_FILE=${DIR}/${JOB}.chk
#-------------------------------------------------------------------------------
# Check wether ${JOB}.com actually exists.
if [[ ! (-a ${COM_FILE}) ]]; then
  echo "File ${COM_FILE} does not exist. Quitting."
  exit 1
fi
#-------------------------------------------------------------------------------
umask a=rw
#-------------------------------------------------------------------------------
# Finally, run job
gdv <${COM_FILE} >${LOG_FILE}
```

3 QUANTICS calculations

3.1 Preparing input

Input file: **/work/username/fulv_test/fulv.inp**

```
################################################################################
###              DD / Propagation in normal modes                        ####
################################################################################

RUN-SECTION
name = fulv
propagation
direct = nmodes       ngwp = 1
title = Fulvene test dynamics local diabatisation
tfinal = 60.0  tout = 0.1  tpsi= 0.1
psi  gridpop  update  steps  auto
```

```
openmp=1
end-run-section

INITIAL-GEOMETRY-SECTION
nstates = 2
init_state = 2
init_basis_dist = shell-diag
cartesian = angst
C             1.186620    0.000000   -0.119224
H             2.209989    0.000000    0.225769
C             0.747975    0.000000   -1.402770
H             1.353516    0.000000   -2.297938
C            -1.186620    0.000000   -0.119224
H            -2.209989    0.000000    0.225769
C            -0.747975    0.000000   -1.402770
H            -1.353516    0.000000   -2.297938
C             0.000000    0.000000    0.792022
C             0.000000    0.000000    2.144452
H             0.920282    0.000000    2.712245
H            -0.920282    0.000000    2.712245
end-cartesian
nmode
1B1  0.0000  216.3578, cm-1 width = 0.7
1B2  0.0000  377.8369, cm-1 width = 0.7
1A2  0.0000  530.7597, cm-1 width = 0.7
2B1  0.0000  628.7249, cm-1 width = 0.7
1A1  0.0000  736.2854, cm-1 width = 0.7
2A2  0.0000  765.4327, cm-1 width = 0.7
3B1  0.0000  809.5737, cm-1 width = 0.7
3A2  0.0000  851.6895, cm-1 width = 0.7
2B2  0.0000  902.5188, cm-1 width = 0.7
4B1  0.0000  917.2892, cm-1 width = 0.7
4A2  0.0000  962.5843, cm-1 width = 0.7
5B1  0.0000  980.0220, cm-1 width = 0.7
2A1  0.0000 1009.5652, cm-1 width = 0.7
3B2  0.0000 1097.1520, cm-1 width = 0.7
3A1  0.0000 1126.0433, cm-1 width = 0.7
4B2  0.0000 1256.6600, cm-1 width = 0.7
4A1  0.0000 1263.8887, cm-1 width = 0.7
5B2  0.0000 1438.5397, cm-1 width = 0.7
6B2  0.0000 1560.4802, cm-1 width = 0.7
5A1  0.0000 1583.1700, cm-1 width = 0.7
6A1  0.0000 1668.5304, cm-1 width = 0.7
7A1  0.0000 1739.8100, cm-1 width = 0.7
7B2  0.0000 1801.8579, cm-1 width = 0.7
8A1  0.0000 1883.0619, cm-1 width = 0.7
9A1  0.0000 3660.1156, cm-1 width = 0.7
8B2  0.0000 3733.8419, cm-1 width = 0.7
10A1 0.0000 3739.7874, cm-1 width = 0.7
9B2  0.0000 3758.8008, cm-1 width = 0.7
11A1 0.0000 3768.5617, cm-1 width = 0.7
10B2 0.0000 3819.8609, cm-1 width = 0.7
end-nmode
end-initial-geometry-section

DIRDYN-SECTION
data = fulv_db
transfile = start.log
coinfile = refbs.log , cas
dreffile = start.log
nbasis = 36
qcprogram = gaussian     method = cas
sacas
ener0 = -227.9461342
ddlog
dbsave
```

```
dd_diab = local
update = tout
db = rdwr     dbmin = 0.  mindv = 0.01
subcmd = ~/bin/gdvi04prun , 2
end-dirdyn-section

end-input
```

Options:

`ngwp = 1` → change 1 for the number of Gaussian basis-functions that you would like to use in the expansion of the wavepacket;

`nstates = 2` → as it stands, local diabatisation works only for a pair of states (however, it should be possible in principle to run calculations involving S_2 and S_1 rather than S_1 and S_0 but this is untested with the current implementation: triggered if you change 2 for a higher number in `init_state`?);

`init_state = 2` → note that we are using adiabatic ordering here, so the second state is, indeed, higher in energy than first one at the FC point (which is not always the case when using the regularised diabatisation);

list between `nmode` and `end-nmode` → normal frequencies must have the same values and appear in the same order as in **start.log**; normal modes can be labelled at your convenience (for example according to their symmetry species if they have been determined as mentioned before);

`data = fulv_db` → same directory as **/work/username/fulv_test/fulv_db**;

`transfile = start.log` → same file as **/work/username/fulv_test/fulv_db/start.log**;

`coinfile = refbs.log , cas` → same file as **/work/username/fulv_test/fulv_db/refbs.log** and CASSCF quantum-chemistry calculations to be specified;

`dreffile = start.log` → same file as **/work/username/fulv_test/fulv_db/start.log** but irrelevant at the moment (not used yet);

`nbasis = 36` → must be equal to the number of orbitals in **start.log**;

`qcprogram = gaussian  method = cas` → local diabatisation requires GAUSSIAN CASSCF quantum-chemistry calculations;

`sacas` → local diabatisation requires state-averaged orbitals in CASSCF quantum-chemistry calculations;

`ener0 = -227.9461342` → energy zero (in hartree): this value can be found in **start.log** (ground-state energy at the FC point);

`ddlog` → extra information printed to **log** file;

`dbsave` → do not change this (other cases may work but are untested);

`dd_diab = local` → local diabatisation;

`update = tout` → compulsory (and make sure that `tout` and `tpsi` have the same value);

`db = rdwr` → do not change this (other cases may work but are untested);

`dbmin = 0.` → compulsory (or you may want to try very small values but this is untested);

`mindv = 0.01` → energy-difference threshold (in hartree) for detecting that a Gaussian basis-function is approaching a conical intersection (can be changed at your convenience);

`subcmd = ~/bin/gdvi04prun , 2` → same script as **/home/username/bin/gdvi04prun**.

3.2 Running job

Job file: **/work/username/fulv_test/fulv.job**

```
#REMINDER: set mem such as > ncpus * mem(template.dat)
#PBS -l select=1:ncpus=1:mem=2400mb
#PBS -l walltime=96:00:00
#PBS -j eo
#PBS -q pqmb

umask 0007

module load intel-suite
module load sqlite/3.10.2
module load gaussian/devel-modules
module load gdvi04p

mkdir -p /work/username/fulv_test/fulv

/xxx/quantics -w /work/username/fulv_test/fulv.inp
```

```
qsub fulv.job
```

Here, **xxx** must be replaced by the actual path of the version of the QUANTICS program that you want to use (provided you have it installed, at least as a user):

```
which quantics
```

N.B.: of course, you may want to use automatic shell scripts with environment variables in order to avoid changing file names every time you want to run a new job, etc. (ask Iakov Polyak for some examples of such scripts).

3.3 New types of results

Usual results will printed to **output** file: **/work/username/fulv_test/fulv/output**

N.B.: the electronic populations are adiabatic.

A few extra checks can be found on **log** file: **/work/username/fulv_test/fulv/log**

- Initialising BS vectors for GWP, mode, time: ...
- Conical intersection approached by GWP, mode, time, states: ...
- Crossing detected for GWP, mode, time: ...
- Swapping detected for GWP, mode, time: ...
- Ambiguity detected for GWP, mode, time: ...
- Diabatisation producing large eigenvalue error for GWP, mode, time, state: ...
- Undefined angle for GWP, mode, time: ...
- Crossing predicted for GWP, mode, time: ...
- Crossing fixed for GWP, mode, time: ...
- Positive Berry phase added for GWP, mode, time: ...
- Negative Berry phase added for GWP, mode, time: ...
- Cumulative angle (in deg.) for GWP, mode, time: ...

→ explanations will be given in the next version of this document... (soon!)