The Beginner MolCAS User Manual

www.teokem.lu.se/molcas/

by Giovanni Ghigo

www.personalweb.unito.it/giovanni.ghigo/MolCAS/molcas-home.html

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The beginner's MolCAS user Manual

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1. Introduction

This manual has been written to help new **MolCAS** users who never used the program and that (like me, I must confess) are a bit too lazy to read the full manual. Note that this manual DOES NOT substitute the official one. The scope of this pages is only to encourage the new users to adopt **MolCAS** as their standard quantum chemical package and to get rid of the idea that **MolCAS** is more difficult to use than other more famous programs. Therefore, in this manual you will not find a description of how to install and run the program (this can be find in Chapter 9 af the official manual) neither a full description of each single programs or keywords (Chapter 3). The only other informations that will be assumed as well know by the users are the basic concept of quantum chemical theory.

Here, the user will be lead through the program starting from very simple examples and guided toward more sofisticated calculations. Every example will be introduced and both the input and piece of output (in the boxes) will be fully explained (hopefully).

Before to start, it is advisable to know a few information about olCAS files and directory, (Chap. **1b**) and about submission script (in Chap. **1c** you can find an example). More details can be found in Section 2 of the manual.

Some new features will be available with the new 7.2 version only.

Every suggestion is, of course, welcome. In case, do not esitate: write me.

1.b The MolCAS MolCAS files and directory

The name of most important **MolCAS** files always start with the name of the job/project **$Project**. Some of them are written (or transferred at the end of a job) in the current directory (**$CurrDir**) but most of them are located in the scratch directory (**$WorkDir**) whose name is **scr_Project** and which should be generated (if not present) by the submission-script.

In the current directory the following files can be found:

- **$Project.input**: input file, the only user-created;
- **$Project.out**: output file;
- **$Project.scf.molden***: input file for molden with HF/SCF MO;
- **$Project.rasscf.molden***: input file for molden with RASSCF MO;
- **$Project.geo.molden***: input file for molden with molecular geometries obtained in an optimization;
- **$Project.freq.molden***: input file for molden with frequencies;
- **$Project.JobIph***: MO from RASSCF (binary)**$Project.RunFile***: Communication (binary).

* These file are originally generated in **$WorkDir** and should be copied in **$CurrDir** at the end of the job by the submission-script. However, sometimes this does not happen. Moreover, during the job, some of them are copied by **MolCAS** in **$WorkDir** with the final extension .autosaved and removed by the submission-script at the endo of the job.

Other useful files that can be find in **$WorkDir** are:

- **$Project.guessorb.molden**: input file for molden with Guess MO;
- **$Project.ScfOrb**: MO from HF/SCF;
- **$Project.OneInt**: One-electron Integrals;
- **$Project.OrdInt**: Two-electron Integrals;
- **$Project.JobMix**: MO from CASPT2 (binary).

1c. The submission script

Here is an example of the simplest shell script that can be used to run MolCAS.

```
01   #!/bin/sh
02   export Project=$1
03   export CurrDir=`pwd`
04   export WorkDir=$CurrDir/scr_$Project
05   export MOLCAS=/progs/Molcas/7.0.dev
06   export MOLCAS_LINK='N'
07   export MOLCASMEM=1024
08   mkdir $WorkDir
09   $MOLCAS/sbin/molcas $Project.input > $Project.log 2>
$WorkDir/$Project.err
```

Note that line 05 must contain the real MolCAS directory. Line 07 must contain the maximun memory allowed: 128 MBytes is enough for the examples but it can be increased for real calculations. Line 08 sometime required to be commented (with #). This will be explained in some examples.

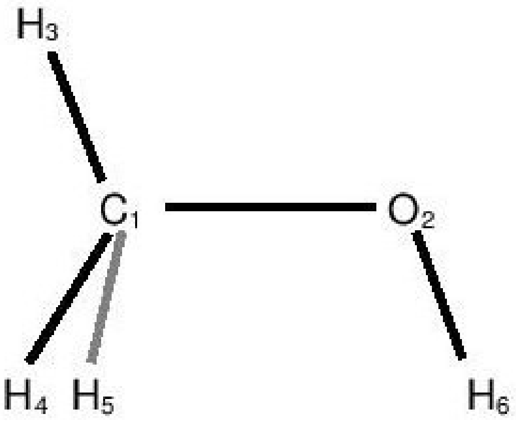
Here is a version a bit more sofisticated. The only difference in the gestion of the files generated by molcas and some nice printouts.

```
 #!/bin/sh
 export CurrDir=`pwd`
 export WorkDir=$CurrDir/scr_$Project
 export MOLCAS=/progs/MolCAS/7.0.dev
 echo
 export Project=$1
 export WorkDir=$CurrDir/scr_$Project
 echo ' ---------------------------------------'
 echo '  Job:' $Project
 echo '  ' `cat $MOLCAS/.molcashome`
 echo '   MolCASMem=' $MOLCASMEM
 echo '   Date:' `date`
 echo ' ---------------------------------------'
 mkdir $WorkDir
$MOLCAS/sbin/molcas $Project.input > $Project.out 2> $WorkDir/$Project.err
 date >> $Project.out
 cat /proc/cpuinfo | grep name >> $Project.out
 rm -f $Project.*Orb.autosaved $Project.*.autosaved
 cp -f $WorkDir/$Project.RunFile $Project.Hessian
 cp -f $WorkDir/$Project.JobIph  $Project.JobIph
 cp -f $WorkDir/$Project.geo.molden  $Project.geo.molden
 cp -f $WorkDir/$Project.freq.molden  $Project.freq.molden
 cp -f $WorkDir/$Project.scf.molden  $Project.scf.molden
 cp -f $WorkDir/$Project.rasscf.molden  $Project.rasscf.molden
 if [ -f $Project.geo.molden ]; then
         if [ -f $Project.rasscf.molden ]; then
                 cat $Project.rasscf.molden >> $Project.geo.molden
         else
                 if [ -f $Project.scf.molden ]; then
                        cat $Project.scf.molden >> $Project.geo.molden
                 fi
         fi
 fi
 if [ -f $Project.freq.molden ]; then
         if [ -f $Project.rasscf.molden ]; then
                 cat $Project.rasscf.molden >> $Project.freq.molden
         else
                 if [ -f $Project.scf.molden ]; then
                       cat $Project.scf.molden >> $Project.freq.molden
                 fi
         fi
 fi
 echo
 echo ' ---------------------------------------'
 echo '  Job:' $Project
 echo '   Date:' `date`
 echo ' ---------------------------------------'
```

2. Your first MolCAS calculation: the HF energy of methanol.

Assuming that the program is correctly installed we can start with the first calculation. In this example we want to calculate the Hartree-Fock energy of the methanol (CH_3OH). The basis set is the well known cc-pVDZ.

First, the sub-program **SEWARD** is called to calculate the mono- and bi-electron integrals. This program will be the first to be called almost in all cases. We use the new keyword ***ZMAT*** which I prefer because more close to the chemists' way of thinking the molecular structures. Details about keyword ***ZMAT*** can be found in the manual, chap. 3.15.3. The molecule is sketched below (grey line means a bond below the molecular plane).



The full input can be find in Appendix.

```
&SEWARD &END
Title
 Your first MolCAS calculation: HF energy of methanol
ZMAT
H.cc-pVDZ.....
C.cc-pVDZ.....
O.cc-pVDZ.....

C1
O2   1  1.400
H3   1  1.089   2  109.471
H4   1  1.089   2  109.471   3 -120.0
H5   1  1.089   2  109.471   3  120.0
H6   2  0.950   1  105.000   3  180.0

```

```
 16    End of Input
 17
 18    &SCF &End
 19    Title
 20     The SCF part
 21    End of Input
```

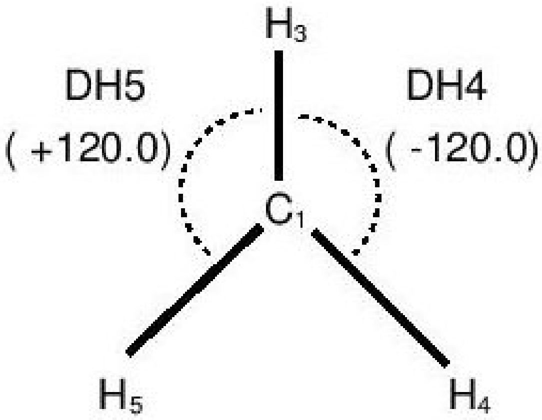
Line 01 declare the program to be executed.

Lines 02 and 03 contain the title. They can be omitted.

Line 04 contains the keyword ***ZMAT*** used to define the molecular structure. But first, the basis sets used for each single atom (one definition for H, one for C, one for O) is listed. Note the dots (details can be found in the manual, chap. 3.15.1). The molecular structure, making reference to the figure above, is defined in linees 09 - 14 as:

- First atom: carbon, *label* **C1**.
- Second atom: oxygen, *label* **O2**, bonded to carbon (*atom-index* **1**) at *distance* **1.400** Å.
- Third atom: hydrogen, label **H3**, bonded to carbon (*atom-index* **1**) at *distance* **1.089** Å and making a planar angle with oxygen (*atom-index* **2**) of **109.471** degrees.
- Fourth atom: hydrogen, label **H4**, bonded to carbon (*atom-index* **1**) at *distance* **1.089** Å, making a planar angle with oxygen (*atom-index* **2**) of **109.471** degrees and a dihedral angle with the first hydrogen (*atom-index* **3**) of **-120.0** degrees.
- Fifth atom: hydrogen, label **H5**, bonded to carbon (*atom-index* **1**) at *distance* **1.089** Å, making a planar angle with oxygen (*atom-index* **2**) of **109.471** degrees and a dihedral angle with the first hydrogen (*atom-index* **3**) of **+120.0** degrees.

  A scketch of these dihedral angles is given below using a Newman's projection (oxygen **O2** is behind carbon **C1**).



- Last atom: hydrogen, label **H6**, bonded to oxygen (*atom-index* **2**) at *distance* **0.950** Å, making a planar angle with carbon (*atom-index* **1**) of **105.000** degrees and a dihedral angle with the first hydrogen (*atom-index* **3**) of **180.0** degrees.

Lines 08 and 15 are blank lines and are used to stop the sections.

In alternative to the Z-Matrix format there is, of course, the Cartesian XYZ format to define the molecular structure (see keyword BASIs in chap. 3.15.2). Line 16 terminates the **SEWARD** input.

Line 17 is used just to separate the sections and can be omitted.

Line 18 starts the **SCF** input.

Lines 19 and 20 contain the title. They can be omitted.

Line 21 terminates the **SCF** input.

By default, **SCF** calculates a molecular wavefunction as singlet (no unpaired electrons) and neutral (no charges).

And now, let see what we can find in the output. The first part contains the **SEWARD** output. Here we can find the Cartesian coordinates both in atomic units and Ångstroms:

```
               ************************************************
               **** Cartesian Coordinates / Bohr, Angstrom ****
               ************************************************

Center  Label           x              y              z                    x              y              z
   1      C1          0.000000       0.000000       0.000000             0.000000       0.000000       0.000000
   2      O2          0.000000       0.000000       2.645617             0.000000       0.000000       1.400000
   3      H3          1.692571       0.000000      -0.598407             0.895670       0.000000      -0.316663
   4      H4         -0.846285       1.465809      -0.598407            -0.447835       0.775673      -0.316663
   5      H5         -0.846285      -1.465809      -0.598407            -0.447835      -0.775673      -0.316663
   6      H6         -1.940220       0.000000       3.331580            -1.026720       0.000000       1.762996
```

then distances and angles. The otput terminates with basis set specifications and the nuclear potential energy:

```
  Basis set specifications :

  Symmetry species           a
  Basis functions             48



                    Nuclear Potential Energy                   41.84412593 au
```

Then we found the **SCF** output. After the details of the calculation and the SCF iterations we find the "**SCF/KS-DFT Program, Final results**" section. Here we can find the converged energy values:

```
      Total SCF energy                             -114.9782183794

      One-electron energy                          -239.8194947236
      Two-electron energy                            82.9971504107
      Nuclear repulsion energy                       41.8441259335
      Kinetic energy (interpolated)                 115.5406117335
      Virial theorem                                  0.9951325050
```

Line "**Total SCF energy**" contains the HF energy (***-114.9782183794*** au.). The coeficients of the molecular orbitals follows. Note that SCF also generates a **$Project.scf.molden** file that can be read with the program molden to see the MO. This file is normally located in the scratch directory but is can be easely copied by the submisio-script.

3. **And your second one:** the DFT(B3LYP) energy of methanol.

With **MolCAS** you can also calculate the energy with the Density Functional Methods (of course). Here an example for methanol. The **SEWARD** section of the output is the same as in the first example. The **SCF** part of the input is the following (the full input can be find in the Appendix):

```
 18    &SCF &End
 19    Title
 20     The DFT part
 21    KSDFT
 22     B3LYP
 23    End of Input
```

Lines 01 - 17 (not shown) are the same as in the previous one.

Line 18 starts the **SCF** input.

Lines 19 and 20 contain the title. They can be omitted.

Line 21 keyword ***KSDFT*** which requires a Kohn-Sham DFT calculation.

Line 22 keyword ***B3LYP*** which specifies the functional to be used.

Line 23 terminates the **SCF** input.

The output of **SEWARD** is the same as before. In the **SCF** output we find again, after the details of the calculation and the SCF iterations, the "**SCF/KS-DFT Program, Final results**" section. Here we can find the converged energy values:

```
      Total KS-DFT energy                          -115.6513810617

      One-electron energy                          -252.6467181463
      Two-electron energy                            95.1512111511
      Nuclear repulsion energy                       41.8441259335
      Kinetic energy (interpolated)                 115.6083888328
      Virial theorem                                  1.0003718781
```

The line "**Total SCF energy**" contains the DFT(B3LYP) energy (***-115.6513810617*** au.). The coeficients of the molecular orbitals follows. Note that SCF also generates a **$Project.scf.molden** file that can be read with the program molden to see the MO.

4. And the third one: an MP2 calculation (methanol, again).

With **MolCAS** you can also calculate several post-SCF energies like MP2 and Coupled Cluster (CC). The input for the first one is very simple. After the **SEWARD** (same as before) and the **SCF** (remember, MP2 is a post SCF method, therefore you need converged Hartree-Fock wavefunction and energy) you just have to add the MP2 part (here named MBPT2 - Many Body Perturbation Theory at 2nd order) **MBPT2**. As usual the full input can be find in the Appendix).

```
 23    &MBPT2 &End
 24    Title
 25     The MP2 calculation.
 26    End of Input
```

Lines 01 - 22 (not shown) are the same as in the first example.

Line 23 starts the **MBPT2** (MP2) input.

Lines 24 and 25 contain the title. They can be omitted.

Line 26 terminates the **MBPT2** input.

The output of **SEWARD** and **SCF** are the same as in the first example. The output on **MBPT2** is very simple. After a few details about the calculations (frozen and active occupied and external orbitals) the results have given. The output is the following:

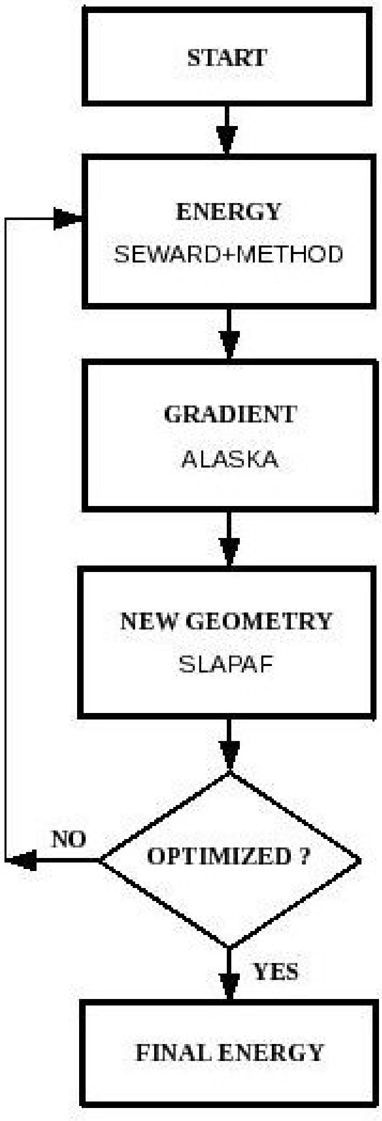
```
 Conventional algorithm used...

       SCF energy                           =     -114.9782183794 a.u.
       Second-order correlation energy      =       -0.3359012163 a.u.

       Total energy                         =     -115.3141195957 a.u.
       Coefficient for the reference state  =        0.9562823661
```

The line "**Total energy**" contains the MP2 energy (***-115.3141195957*** au.).

5. Optimization of geometry: methanol (for the last time).

MolCAS can also optimize structures. Both minima and transition structures (TS) can be localized on the Potential Energy Surface (PES). The module devoted to this operation is **SLAPAF**. This module must be preceded by the module **ALASKA** that yields the Cartesian gradient. When the analytical derivatives are not available **ALASKA** automatically invokes the module **NUMERICAL_GRADIENT**. This happens for MBPT2, CC and CASPT2 optimizations.

The general scheme for any geometry optimization is the following:



Whatever the method (and module) used for the calculation of the energy the first module to be invoked is again **SEWARD**. After the energy the gradient will be evaluated by **ALASKA** and finally, module **SLAPAF** will define the new geometry and, if the gradients and displacement fullfit the required condition, it will invoke the calculation of the energy at the final geometry. Otherwise the cycle will be repeated until optimization or maximum number of steps is reached.

Note that module **ALASKA** is automatically invoked by the **SLAPAF** module. *This is the preferred mode of operation!* In connection with numerical gradients this will ensure that the rotational and translational invariance is fully utilized in order to reduce the number of used displacements.

The full input for the HF optimization of methanol can be find in the Appendix. And these are the most important lines:

```
01    >>> Set MaxIter 5000 <<<
02    >>> Do While <<<
..    ...
26    &SLAPAF &End
27    Iterations
28     20
29    End of Input
30
31    >>> EndDo <<<
```

Lines 01 - 02 and 31 are used to define the cycle.

Lines 03 - 25 (not shown) are the same as in the first example.

Lines 26 - 29 the **SLAPAF** (optimization) input.

Line 27 keyword ***Iterations*** for specifying the maximum number of optimization steps, given in line 28 (***20***).

The output of **SEWARD** and **SCF** are the same as in the first example. The output on **SLAPAF** starts with some details of the optimization algorithms. The section with Energy Statistics follows:

```
*****************************************************************************************************************
********************************** Energy Statistics for Geometry Optimization **********************************
*****************************************************************************************************************

                       Energy     Grad     Grad              Step                 Estimated   Geom     Hessian
Iter      Energy       Change     Norm     Max    Element    Max     Element     Final Energy Update Update Index
  1   -114.97821838  0.00000000 0.333071 0.224740 nrc006   0.233783* nrc006     -115.02052309 RS-RFO  None    0

         Cartesian Displacements           Gradient in internals
       Value      Threshold  Converged?   Value      Threshold  Converged?
    +----------------------------------+----------------------------------+
RMS + 0.1170E+00  0.1200E-02     No    + 0.1178E+00  0.3000E-03     No    +
    +----------------------------------+----------------------------------+
Max + 0.1374E+00  0.1800E-02     No    + 0.2247E+00  0.4500E-03     No    +
    +----------------------------------+----------------------------------+

 Convergence not reached yet!
```

This is the output of the first step. All parameters for the optimization (maximum and RMS of both gradient and displacement) are above the thresholds. In this case, as the maximum number of steps (20) is not reached, an other optimization step is performed. When all condition are fullfitted the output will be like:

```
*****************************************************************************************************************
********************************** Energy Statistics for Geometry Optimization **********************************
*****************************************************************************************************************

                       Energy     Grad     Grad              Step                 Estimated   Geom     Hessian
Iter      Energy       Change     Norm     Max    Element    Max     Element     Final Energy Update Update Index
  1   -114.97821838  0.00000000 0.333071 0.224740 nrc006   0.233783* nrc006     -115.02052309 RS-RFO  None    0
  2   -115.03576486 -0.05754648 0.139585-0.081463 nrc003  -0.166021* nrc003     -115.05309080 RS-RFO  BFGS    0
  3   -115.04887247 -0.01310760 0.033037 0.018068 nrc004  -0.031841  nrc001     -115.04938248 RS-RFO  BFGS    0
  4   -115.04958236 -0.00070990 0.014454-0.007332 nrc001  -0.022427  nrc001     -115.04973174 RS-RFO  BFGS    0
  5   -115.04973289 -0.00015053 0.000532 0.000357 nrc005   0.001421  nrc005     -115.04973331 RS-RFO  BFGS    0

         Cartesian Displacements           Gradient in internals
       Value      Threshold  Converged?   Value      Threshold  Converged?
    +----------------------------------+----------------------------------+
RMS + 0.7962E-03  0.1200E-02     Yes   + 0.1879E-03  0.3000E-03     Yes   +
    +----------------------------------+----------------------------------+
Max + 0.9294E-03  0.1800E-02     Yes   + 0.3570E-03  0.4500E-03     Yes   +
    +----------------------------------+----------------------------------+

 Geometry is converged in   5 iterations to a minimum
```

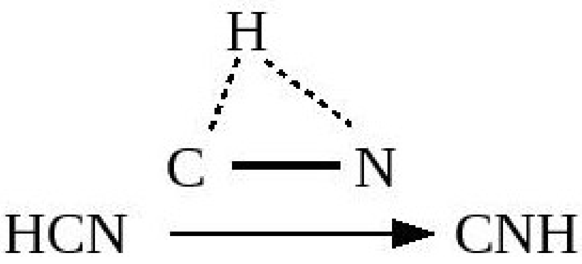
The four condition are fullfitted (`Yes`). The **SLAPAF** output terminates with the final optimized geometry, both in Cartesian coordinates and in Z-Matrix format (if used in **SEWARD** and if the conversion is possible). This one can be used (throughout an easy "cut-and-paste") to prepare a new input.

```
*****************************************************************************************************************
*****************************************************************************************************************

  Geometrical information of the final structure


  NOTE: on convergence the final predicted structure will be printed here.
        This is not identical to the structure printed in the head of the output.


 Nuclear coordinates of the final structure / Bohr, Angstrom

     ATOM               X               Y               Z                    X               Y               Z

     C1            -0.057685        0.000000        0.085315            -0.030526        0.000000        0.045147
     O2            -0.077231        0.000000        2.726828            -0.040869        0.000000        1.442975
     H3             1.909912        0.000000       -0.517301             1.010682        0.000000       -0.273744
     H4            -0.973184        1.679637       -0.705623            -0.514987        0.888826       -0.373400
     H5            -0.973184       -1.679637       -0.705623            -0.514987       -0.888826       -0.373400
     H6            -1.768847        0.000000        3.298381            -0.936034        0.000000        1.745428


 Nuclear coordinates in ZMAT format / Angstrom and Degree

     C1
     O2       1     1.397867
     H3       1     1.088946   2   107.452209
     H4       1     1.095397   2   112.260169   3  -118.745959
     H5       1     1.095397   2   112.260169   3   118.745959
     H6       2     0.944880   1   109.092692   3   180.000000
```

SLAPAF also generates an input file for molden with the geometry changes. Its name is **$Project.geo.molden**. The calculation of the final energy terminates the job.

6. Optimization of a Transition Structure: from HCN to CNH.

The optimization of Transition Structure (TS) with **MolCAS** can be performed in a very easy way adding the keyword ***TS*** in the **SLAPAF** input. In this example we optimize the TS for the reaction



The full input can be find in the appendix. The the most important lines are in the **SLAPAF** section:

```
21    &SLAPAF &End
22    TS
23    Numerical Hessian
24    PRFC
25    Iterations
26     20
27    End of Input
28
29    >>> EndDo <<<
```

Lines 01 - 20 (not shown) are similar to the previous example (a part for the structure).

Line 22 keyword ***TS*** to require the optimization of a transition structure.

Line 23 keyword ***Numerical*** to require the calculation of the numerical Hessian (force constant) matrix.

Line 24 keyword ***PRFC*** (Print Force Constants) to require the print out of the eigenvalues and eigenvectors of the Hessian matrix.

Line 25 keyword ***Iteration*** for specifying the maximum number of optimization steps, given in line 25 (***20***).

The optimization of TS requires a good starting geometry (of course) but also a good Hessian matrix. This is why it is advisable to start the optimization with a numerical estimation of this matrix. 1+2(3N-6) gradients will be estimated before to start the optimization. When the structure is optimized, its geometry is not enough to assure that it is a TS. In order to verify its real nature of the saddle point, it is advisable to check the eigenvalues and eigenvectors of its Hessian.

The output on **SLAPAF** of the last step is the following. First we find the definition of the primitive internal coordinates. These are defined as bonds, and planar and dihedral angles among atoms. The internal coordinates build as linear combinations of the primitive follows. The negative eigenvalue of the Hessian (***-0.027522***) tells us that the structure is a first order saddle point (i.e a Transition Structure) and in its corresponding eigenvector the dominating primitive coordinate is ***a001*** (the N2-C1-H3 angle) which describe the movement of the hydrogen atom.

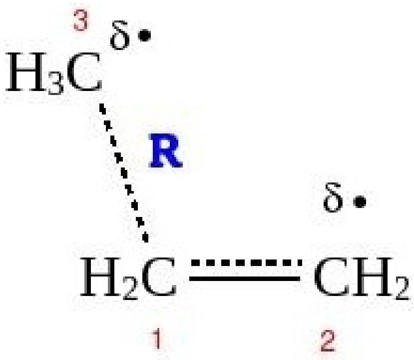
```
********************************************************************************
  Auto-Defined Internal coordinates
********************************************************************************

Primitive Internal Coordinates
b001 = Bond N2 C1
b002 = Bond H3 C1
a001 = Angle N2 C1 H3
Internal Coordinates (Vary)
q001 = 0.98690410 b001 + 0.09649973 b002 + -.12925983 a001
q002 = -.12119354 b001 + 0.97240208 b002 + -.19936477 a001
q003 = 0.10645388 b001 + 0.21241937 b002 + 0.97136275 a001
End Of Internal Coordinates

  Number of redundant coordinates: 3

  Using old reaction mode from disk
  Storing new reaction mode disk

 -------------------------------------------
 Eigenvalues and Eigenvectors of the Hessian

                       1         2         3
 Eigenvalues    -0.027522  0.582963  1.721819

 b001            0.121271 -0.317604  0.940437
 b002            0.405193  0.880738  0.245193
 a001            0.906152 -0.351324 -0.235499

*****************************************************************************************************************
********************************** Energy Statistics for Geometry Optimization **********************************
*****************************************************************************************************************

                       Energy     Grad     Grad              Step                 Estimated   Geom     Hessian
Iter      Energy       Change     Norm     Max    Element    Max     Element     Final Energy Update Update Index
  1    -92.80720679  0.00000000 0.005379-0.003337 nrc002  -0.020106  nrc003      -92.80725311 RSIRFO  None    1
  2    -92.80717119  0.00003559 0.000074 0.000052 nrc002  -0.000199  nrc003      -92.80717120 RSIRFO  MSP     1


         Cartesian Displacements            Gradient in internals
       Value      Threshold  Converged?   Value      Threshold  Converged?
    +----------------------------------+----------------------------------+
RMS + 0.1623E-03  0.1200E-02     Yes   + 0.4279E-04  0.3000E-03     Yes   +
```

```
    +---------------------------------+---------------------------------+
Max + 0.1667E-03  0.1800E-02     Yes   + 0.5203E-04  0.4500E-03     Yes   +
    +---------------------------------+---------------------------------+

 Geometry is converged in   2 iterations to a transition state

*******************************************************************************************************************
*******************************************************************************************************************

  Geometrical information of the final structure


  NOTE: on convergence the final predicted structure will be printed here.
        This is not identical to the structure printed in the head of the output.


 Nuclear coordinates of the final structure / Bohr, Angstrom

     ATOM               X               Y               Z                    X               Y               Z

     C1           -0.006040        0.000000       -0.008402            -0.003196        0.000000       -0.004446
     N2            0.016520        0.000000        2.204310             0.008742        0.000000        1.166471
     H3            2.148300        0.000000        0.395723             1.136831        0.000000        0.209407


 Nuclear coordinates in ZMAT format / Angstrom and Degree

     C1
     N2       1     1.170978
     H3       1     1.159912   2    78.791420
```

After the optimization condition section, the final geometry is printed, both in Cartesian coordinates and in Z-Matrix format (if used in **SEWARD** and if the conversion is possible). **SLAPAF** generates again the input file for molden with the geometry changes (**$Project.geo.molden**) and, due to the numerical Hessian, an input file for molden with the vibrational frequencies and normal modes (**$Project.geo.molden**).

7. Constrained Optimization: building the potential energy curve for CH_3* + $H_2C=CH_2$.

With **MolCAS** it is possible to define the potential energy curve along a single geometrical parameter optimizing the remaining internal coordinates throughout a constrained optimization. In this example we want to define the potential energy curve for the addition of the methyl radical (CH_3*) to ethylene ($H_2C=CH_2$). The **C1-C3** distance **R** will be kept frozen to 2.0 Ångstroms while the remaining internal coordinate will be optimized.



The full input can be find in the Appendix. The **SLAPAF** section of input is:

```
28    &SLAPAF &END
29    Iterations
30     20
31    Constrain
32    R = Bond C1 C3
33    Value
34    R = 2.0 Angstrom
35    End of Constrain
36    End Of Input
```

Lines 01 - 27 (not shown) are similar to the previous examples (a part for the structure).

Lines 29, 30 maximum number of optimization steps.

Lines 31-35 Constrained Optimization sub-section. Starts with keyword ***Constrain*** and finishes with keyword ***End of Constrain***.

Line 32 definition of the internal coordinate (**R**) as bond distance between atoms **C1** and **C3** (remember to use different labels for all atoms). More than one constrained coordinates can be specified here.

Line 33 keyword ***Value*** followed by the values of the constrained coordinates.

Line 34 value (***2.0 Ångstroms***) for the coordinate defined above (**R**).

More details about the definition of the internal coordinate can be find in the manual (3.38.4).

Note that it is not compulsory (but it is advisable) to give an initial geometry where the internal coordinate that has to be kept frozen is already at the required value. As an example, line 13 in the input could be:

```
C3       1     2.500   2   110.0
```

The output on **SLAPAF** of the last step is the following. It starts with the Constrained Optimization Section where we can find the definition and the value of the constrained coordinates and the related gradient (***-0.048157***):

```
ConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraints
ConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraints
Constraints                                                                                        Constraints
Constraints                                  C O N S T R A I N T S                                 Constraints
Constraints                                                                                        Constraints

**************************************************************************************************************
R = BOND C1 C3
VALUE
R = 2.0 ANGSTROM
**************************************************************************************************************


 **********************************
 * Values of primitive constraints *
 **********************************

 R        : Bond Length=  2.000000 / Angstrom  3.779452 / bohr


 **************************************
 * Value of constraints   / au or rad *
 **************************************

   Label        C         C0

 Cns001      3.779452  3.779452
```

```
 ************************************
 * Gradient of primitive constraints *
 ************************************

 R          -0.048157

Constraints                                                                                           Constraints
ConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraints
ConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraints
```

Then we find the optimization condition section and the final geometry as before. The job terminates with the calculation of the final energy.

8. Optimization with User-defined Internal Coordinates: chloroethane.

The optimization of geometry with **MolCAS** can also be performed with a set of "User-defined Internal Coordinates". It must be pointed out that these coordinated, included in the **SLAPAF** input, have nothing to do with the internal coordinates implicitly defined in the Z-matrix used to furnish the geometry in **SEWARD** input. However, for simple cases (as in this example) it can be very easy to define the internal coordinates in the same way for both input sections.

First a set of Primitive Internal Coordinates (PIC) must be given. There are several types of primitive coordinates but here we will see only the most commonly used: bond distances, planar angles, and dihedral angles. More details can be find in the manual, (3.38.4). The PIC must be 3N-6 (N is the number of nuclei) at least, but they can be more (this is what normally happens with the redundant auto-defined coordinates). All make reference to the atomic labels.

The Internal Coordinates (IC) follows. These can correspond to the PIC, and in this case the same label can be used (see example below, case 1) or they can be linear combinations of the PIC defined above (see example below, case 2). In any case, the number of IC must be 3N-6.

CASE 1. the IC corresponds to the PIC:

```
 ...
 CH12 = Bond C7 H12
 ...
 CH12
 ...
```

CASE 2. two ICs are linear combinations of PICs:

```
 ...
 OH4 = Bond O2 H4
 HO5 = Bond H4 O5
 ...
 SumR = 1.0 OH4 + 1.0 HO5
 DifR = 1.0 OH4 - 1.0 HO5
 ...
```

In this example (the full input can be find in the Appendix), the definition of the

Primitive Internal Coordinates is the same used for the Z-matrix input in **SEWARD**. We can find bond distances (lines 28, 29, 31, 34, 37, 40, and 43), planar angles (lines 30, 32, 35, 38, 41, and 44), and dihedral angles (lines 33, 36, 39, 42, and 45). The list of the Internal Coordinates as corresponding PIC follows.

```
 12    C1
 13    Cl2     1   1.75000
 14    C3      1   1.45000   2   109.471
 15    H4      1   1.08900   2   109.471     3   120.000
 16    H5      1   1.08900   2   109.471     3  -120.000
 17    H6      3   1.08900   1   109.471     2    60.000
 18    H7      3   1.08900   1   109.471     6   120.000
 19    H8      3   1.08900   1   109.471     6   240.000
...
 26    &SLAPAF &END
 27    Internal Coordinates
 28    CCl2   = Bond C1 Cl2
 29    CC3    = Bond C1 C3
 30    ClCC3  = Angle Cl2 C1 C3
 31    CH4    = Bond C1 H4
 32    ClCH4  = Angle Cl2 C1 H4
 33    DH4    = Dihedral C3 Cl2 C1 H4
 34    CH5    = Bond C1 H5
 35    ClCH5  = Angle Cl2 C1 H5
 36    DH5    = Dihedral C3 Cl2 C1 H5
 37    CH6    = Bond C3 H6
 38    CCH6   = Angle C1 C3 H6
 39    DH6    = Dihedral Cl2 C1 C3 H6
 40    CH7    = Bond C3 H7
 41    CCH7   = Angle C1 C3 H7
 42    DH7    = Dihedral H6 C1 C3 H7
 43    CH8    = Bond C3 H8
 44    CCH8   = Angle C1 C3 H8
 45    DH8    = Dihedral H6 C1 C3 H8
 46    Vary
 47    CCl2
 48    CC3
 49    ClCC3
 50    CH4
 51    ClCH4
 52    DH4
 53    CH5
 54    ClCH5
 55    DH5
 56    CH6
 57    CCH6
 58    DH6
 59    CH7
 60    CCH7
 61    DH7
 62    CH8
 63    CCH8
 64    DH8
 65    End of Internal
 66    Iterations
```

```
 67      20
 68    End of Input
```

Lines 12 - 19 Z-matrix subsection of **SEWARD** input. Shown here for the identification of the atom labels only.

Lines 27-65 User-defined coordinates sub-section. Starts with keyword ***Internal Coordinates*** and finishes with keyword ***End of Internal***.

Lines 28-45 definition of the PIC. Each label can be 8 characters long.

Line 46 keyword ***Vary*** followed by the list of the ICs to be optimized. Each label can be 8 characters long.

Lines 47-64 list of IC. In these example they correspond to the PIC, therefore they use the same labels.

Lines 66, 67 maximum number of optimization steps.

The output on **SLAPAF** has nothing different than the previous ones.

9. Constrained Optimization with User-defined Internal Coordinates: let's go back to the potential energy curve for CH_3* + $H_2C=CH_2$.

Constrained optimizations of geometries can also be performed with "User-defined Internal Coordinates". In this example (as usual, the full input can be find in the Appendix), we go back to the definition of the potential energy curve for the addition of the methyl radical (CH_3*) to ethylene ($H_2C=CH_2$). The input is the same as for the lesson 7 except for the **SLAPAF** section, obviously. The "frozen" coordinate is again the **C1-C3** that we can define both as Primitive Internal Coordinate and as Internal Coordinate.

The key point of the input is the list of the frozen Internal Coordinates (ICs) in a subsection that follows the keyword ***Fix***. This subsection follows the one with the list of ICs to be optimized (started with the keyword ***Vary***). Note that in this case the frozen coordinate will keep the value originally found in the starting geometry given in **SEWARD** input.

When using IC corresponding to PIC it is advisable to use also the same order for the PICs and the ICs definitions. In this example, the **C1-C3** bond distance (PIC and IC "`CC3`") is the last in both lists (line 54 and 80).

```
 11    C1
 12    C2       1     1.440
 13    C3       1     2.000   2   110.0
 14    H4       1     1.079   2   115.5     3   113.
 15    H5       1     1.079   2   115.5     3  -113.
 16    H6       2     1.075   1   120.5     3    83.
 17    H7       2     1.075   1   120.5     3   -83.
 18    H8       3     1.080   1   105.5     2   180.
 19    H9       3     1.079   1   106.0     8   120.
 20    H10      3     1.079   1   106.0     8  -120.
...
 29    &SLAPAF &END
 30    Internal Coordinates
 31    CC2   = Bond C1 C2
 32    CCC3  = Angle C2 C1 C3
 33    CH4   = Bond C1 H4
 34    CCH4  = Angle C2 C1 H4
 35    DH4   = Dihedral C3 C2 C1 H4
 36    CH5   = Bond C1 H5
```

```
 37    CCH5  = Angle C2 C1 H5
 38    DH5   = Dihedral C3 C2 C1 H5
 39    CH6   = Bond C2 H6
 40    CCH6  = Angle C1 C2 H6
 41    DH6   = Dihedral C3 C1 C2 H6
 42    CH7   = Bond C2 H7
 43    CCH7  = Angle C1 C2 H7
 44    DH7   = Dihedral C3 C1 C2 H7
 45    CH8   = Bond C3 H8
 46    CCH8  = Angle C1 C3 H8
 47    DH8   = Dihedral C2 C1 C3 H8
 48    CH9   = Bond C3 H9
 49    CCH9  = Angle C1 C3 H9
 50    DH9   = Dihedral H8 C1 C3 H9
 51    CH10  = Bond C3 H10
 52    CCH10 = Angle C1 C3 H10
 53    DH10  = Dihedral H8 C1 C3 H10
 54    CC3   = Bond C1 C3
 55    Vary
 56    CC2
 57    CCC3
 58    CH4
 59    CCH4
 60    DH4
 61    CH5
 62    CCH5
 63    DH5
 64    CH6
 65    CCH6
 66    DH6
 67    CH7
 68    CCH7
 69    DH7
 70    CH8
 71    CCH8
 72    DH8
 73    CH9
 74    CCH9
 75    DH9
 76    CH10
 77    CCH10
 78    DH10
 79    Fix
 80    CC3
 81    End of Internal
 82    Iterations
 83     20
 84    End Of Input
```

Lines 11 - 20 Z-matrix subsection of **SEWARD** input. Shown here for the identification of the atom labels only.

Lines 30-81 User-defined coordinates sub-section. Starts with keyword ***Internal Coordinates*** and finishes with keyword ***End of Internal***.

Lines 31-54 definition of the PIC. Each label can be 8 characters long.

Line 55 keyword ***Vary*** followed by the list of the ICs to be optimized. Each label can be 8 characters long.

Lines 56-78 list of IC. In these example they correspond to the PIC, therefore they use the same labels.

Line 79 keyword ***Fix*** followed by the list of the ICs to be kept frozen. Each label can be 8 characters long.

Line 80 IC to be kept frozen. In these example it correspond sto the PIC, therefore it uses the same label.

Lines 82, 83 maximum number of optimization steps.

The output of **SLAPAF**, after the value of the Internal Coordinates, contains the gradient for each frozen IC (***-0.0685*** for `CC3`).

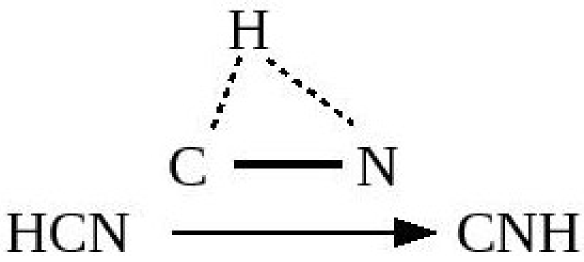
```
 ********************************************
 * Value of internal coordinates / au or rad *
 ********************************************

 CC2          2.7945
 CCC3         1.9414
 CH4          2.0451
 CCH4         1.9630
 DH4         -2.0598
 CH5          2.0451
 CCH5         1.9631
 DH5          2.0600
 CH6          2.0324
 CCH6         2.1014
 DH6         -1.4251
 CH7          2.0324
 CCH7         2.1013
 DH7          1.4255
 CH8          2.0448
 CCH8         1.8889
 DH8          3.1414
 CH9          2.0435
 CCH9         1.8909
 DH9         -2.0952
 CH10         2.0436
 CCH10        1.8907
 DH10         2.0952
 CC3          3.4015

  Following internal coordinates are fixed

CC3      with a gradient of -0.685E-01 is frozen and the gradient is annihilated
```

10. Optimization of a Transition Structure with User-defined Internal Coordinates: from HCN to CNH (again).

The optimization of a Transition Structure (TS) requires a good Hessian matrix. This can be easly obtained with a numerical estimation (see lesson 6) but when the molecular system contains a big number of atoms this can require a very long time: remember that the numerical estimation of the Hessian matrix requires 2(3N-6) gradient calculations!

A new feature implemented in **MolCAS 7.2** allows the numerical estimation of some selected rows (and columns) of the Hessian matrix throughout finite differentiations of the corresponding Internal Coordinates (ICs). This new approach requires the usage of the User-defined Internal Coordinates and of the keyword ***RowH***.

In this example we will optimize again the TS for the Hydrogen migration as in the previous lesson with this new alternative approach (the input file can be find in the Appendix). The initial geometry is the same as in the previous lesson but the number of gradient calculations drops from 8 to 5. Although this is a good result, it does not mean that the new approach is alway more efficient: the reduction of the number of initial gradient estimations (corresponding to the number of ICs for which the selected numerical Hessian is required) can be compensated by the slightly less efficient algorithm for the optimization with User-defined ICs.



The differences in the input are in the **SLAPAF** section only, obviously.

Note that the definition of the geometry given in the **SEWARD** section (lines 12-14) is different than that one used in the **SLAPAF** section: in the former the position of the hydrogen atom (**H3**, line 14) is defined throughout its distance from atom 1 (**N1**) and its planar angle with atom 2 (**N2**) while in the latter the position of **H3** is defined throughout the two distances from **N1** (**CH**, line 31) and **N2** (**NH**, line 32).

Also note that although the migration of the hydrogen atom would require the numerical estimation of the rows (and columns) of the Hessian matrix for both distances **CH** and **NH**, the coupling between the two ICs introduces the necessary information in the matrix about the curvature of the Potential energy Surface (PES) with the differentiation of one IC only.

```
 12    C1
 13    N2      1   1.17000
 14    H3      1   1.16000   2    80.000
...
 21     &SLAPAF &END
 22    TS
 23    PRFC
 24    Iterations
 25     10
 26    Internal Coordinates
 27    CN = Bond C1 N2
 28    CH = Bond C1 H3
 29    NH = Bond N2 H3
 30    Vary
 31    CN
 32    CH
 33    NH
 34    RowH
 35    NH
 36    End of Internal
 37    End Of Input
```

Lines 12 - 14 Z-matrix subsection of **SEWARD** input. Shown here for the identification of the atom labels only.

Line 22 keyword ***TS*** to require the optimization of a transition structure.

Line 23 keyword ***PRFC*** (Print Force Constants) to require the print out of the eigenvalues and eigenvectors of the Hessian matrix.

Lines 24, 25 maximum number of optimization steps.

Lines 26-36 User-defined coordinates sub-section. Starts with keyword ***Internal Coordinates*** and finishes with keyword ***End of Internal***.

Lines 27-29 definition of the Primitive Internal Coordinates (PICs). Each label can be 8 characters long.

Line 30 keyword ***Vary*** followed by the list of the Internal Coordinates (ICs) to be optimized.

Lines 31-33 list of ICs. In these example they correspond to the PIC, therefore they use the same labels.

Line 34 keyword ***RowH*** followed by the list of the ICs for which is required the numerical estimation of row (and column) of the Hessian matrix.

Line 35 IC for which the numerical estimation of row (column) of the Hessian matrix is required.

All defined ICs must be listed below ***Vary*** and ***Fix*** keywords. The ICs listed below the ***RowH*** must correspond to the ones listed as above, i.e. this list is an "extra".

A part for the definition of PICs and ICs, the output of **SLAPAF** is the same as the one in lesson 6.

Most frequent errors in MolCAS

This page contains a set of the most common errors. They are collected from the output message errors and grouped by **MolCAS** module. These are only examples: the possible errors are a number and most of them will give the same messages.

Errors from SEWARD:

The **output** was:

```
 ERROR: Wrong number of basis sets !
        Available= 2  Required= 3
```

This error was generated from the following **input**:

```
ZMAT
H.cc-pVDZ.....
C.cc-pVDZ.....

C1
O2      1   1.40000
H3      1   0.95000   2   109.471
H4      1   0.95000   2   109.471     3  -120.000
H5      1   0.95000   2   109.471     3   120.000
H6      2   1.08900   1   109.471     3   180.000
```

Explanation The molecule contains an Oxygen atom but the basis set was not specified. The following line must be added:

```
O.cc-pVDZ.....
```

Error from SEWARD:

The **output** was:

```
  [BasisConsistency]: Atom NA= 8 requires BS
 ERROR: Basis set inconsistency !
```

This error was generated from the following **input**:

```
...
ZMAT
H.cc-pVDZ.....
C.cc-pVDZ.....
N.cc-pVDZ.....

C1
O2      1   1.40000
H3      1   0.95000   2   109.471
H4      1   0.95000   2   109.471     3  -120.000
...
```

Explanation The molecule also contains an Oxygen atom but the basis set was specified for Nitrogen. The right input is:

```
...
ZMAT
H.cc-pVDZ.....
C.cc-pVDZ.....
O.cc-pVDZ.....

C1
...
```

Error from SEWARD:

The **output** was:

```
 ERROR: Wrong number of basis sets !
        Available= 4  Required= 3
```

This error was generated from the following **input**:

```
...
ZMAT
H.cc-pVDZ.....
C.cc-pVDZ.....
O.cc-pVDZ.....
N.cc-pVDZ.....

C1
O2      1   1.40000
H3      1   0.95000   2   109.471
H4      1   0.95000   2   109.471     3  -120.000
...
```

Explanation The molecule does not contain any Nitrogen atom but its basis set was specified. Just remove (or comment) the corresponding line:

```
...
ZMAT
H.cc-pVDZ.....
C.cc-pVDZ.....
O.cc-pVDZ.....
*N.cc-pVDZ.....

C1
...
```

Error from SEWARD:

The **output** was:

```
 ChkLbl: Duplicate label
Lbl=H
```

This error was generated from the following **input**:

```
...
ZMAT
H.cc-pVDZ.....
C.cc-pVDZ.....
O.cc-pVDZ.....

C
O      1   1.40000
H      1   0.95000   2   109.471
H      1   0.95000   2   109.471     3  -120.000
H      1   0.95000   2   109.471     3   120.000
H      2   1.08900   1   109.471     3   180.000
...
```

Explanation There are more than one Hydrogen atoms, therefore, each one requires a unique label. The input should be (e.g.):

```
...
H1     1   0.95000   2   109.471
H2     1   0.95000   2   109.471     3  -120.000
H3     1   0.95000   2   109.471     3   120.000
H4     2   1.08900   1   109.471     3   180.000
...
```

Error from SEWARD:

The **output** was:

[BasisReader]: Wrong symbol in line C1

This error was generated from the following **input**:

```
...
ZMAT
H.cc-pVDZ.....
C.cc-pVDZ.....
O.cc-pVDZ.....
C1
O2      1   1.40000
H3      1   0.95000   2   109.471
...
```

Explanation The basis set sub-section of the Z-Matrix input must end with a black line before to start the matrix. The correct input is:

```
...
H.cc-pVDZ.....
C.cc-pVDZ.....
O.cc-pVDZ.....

C1
O2      1   1.40000
H3      1   0.95000   2   109.471
...
```

Error from SEWARD:

The **output** was:

EOF reached for file=stdin

This error was generated from the following **input**:

```
...
H4      1   0.95000   2   109.471     3  -120.000
H5      1   0.95000   2   109.471     3   120.000
H6      2   1.08900   1   109.471     3   180.000
End of Input
...
```

Explanation The Z-Matrix section must end with a black line. The correct input is:

```
...
H4      1   0.95000   2   109.471     3  -120.000
H5      1   0.95000   2   109.471     3   120.000
H6      2   1.08900   1   109.471     3   180.000
```

```
End of Input
...
```

Note that this error occurs every time the input is incomplete (e.g. when a keyword must be followed by some number or string).

Error from SEWARD:

The **output** was:

```
  ERROR: Superimposed atoms:  4 5  r=  0.
```

This error was generated from the following **input**:

```
...
O2      1   1.40000
H3      1   0.95000   2   109.471
H4      1   0.95000   2   109.471     3   120.000
H5      1   0.95000   2   109.471     3   120.000
...
```

Explanation Hydrogen atoms **H4** and **H5**, due to the same dihedral angle (**120.**) are superimposed. The correct input is (e.g.):

```
...
O2      1   1.40000
H3      1   0.95000   2   109.471
H4      1   0.95000   2   109.471     3  -120.000
H5      1   0.95000   2   109.471     3   120.000
...
```

Error from SCF:

The **output** was:

```
 VecFind: Error in number of electrons
         An even number of electrons          are required
by RHF, use UHF
```

This error was generated from the following **input**:

```
...
ZMAT
H.cc-pVDZ.....
C.cc-pVDZ.....
```

```
O.cc-pVDZ.....

C1
O2      1   1.40000
H3      1   0.95000   2   109.471
H4      1   0.95000   2   109.471     3  -120.000
H5      1   0.95000   2   109.471     3   120.000

End of Input

&SCF &END
End of Input
```

Explanation This molecule is a radical or an ion but in the **SCF** input it was not specified. The following line must be added:

```
Charge
-1
```

if an anion or:

```
UHF
```

if a radical.

Error from SCF:

The **output** was:

```
 ********************************************************************************
 ********************************************************************************
 ***                                                                          ***
 ***                                                                          ***
 ***    Location: gxRdRun                                                     ***
 ***    Unit    :  -1209758319                                                ***
 ***    RunFile does not exist                                                ***
 ***                                                                          ***
 ***                                                                          ***
 ********************************************************************************
 ********************************************************************************
```

This error was generated from the following **input**:

```
*&SEWARD &END
ZMAT
H.cc-pVDZ.....
C.cc-pVDZ.....
O.cc-pVDZ.....

C1
O2      1   1.40000
H3      1   0.95000   2   109.471
H4      1   0.95000   2   109.471     3  -120.000
H5      1   0.95000   2   109.471     3   120.000
```

```
End of Input

&SCF &END
End of Input
```

Explanation Module **SEWARD** was unactivated! Remove "*****" before ***SEWARD***.

```
&SEWARD &END
ZMAT
H.cc-pVDZ.....
C.cc-pVDZ.....
...
```

Error from SLAPAF:

The **output** was:

```
******************************************
 ERROR: Undefined internal coordinate in
 CO
******************************************
```

This error was generated from the following **input**:

```
...
Internal Coordinates
CO2   = Bond C1 O2
CH3   = Bond C1 H3
OCH3  = Angle O2 C1 H3
CH4   = Bond C1 H4
HCH4  = Angle H3 C1 H4
DH4   = Dihedral O2 H3 C1 H4
CH5   = Bond C1 H5
HCH5  = Angle H4 C1 H5
DH5   = Dihedral H3 H4 C1 H5
Vary
CO
CH3
OCH3
CH4
HCH4
DH4
CH5
HCH5
DH5
End of Internal
...
```

Explanation When using the Primitive Internal Coordinates also as Internal Coordinates (**CO2** in this example) the second ones (specified below the keyword

Vary) must correspond to the first ones (**CO** is a wrong IC, in this case).

```
...
Internal Coordinates
CO2   = Bond C1 O2
...
Vary
CO3
...
```

Error from SLAPAF:

The **output** was:

```
 **********************************************
  ERROR: Undefined internal ROWH coordinate in
  NH
 **********************************************
```

This error was generated from the following **input**:

```
...
C1
N2      1   1.17000
H3      1   1.16000   2    80.000
...
Internal Coordinates
CN  = Bond C1 N2
CH  = Bond C1 H3
NH  = Bond N2 H3
Vary
CN
CH
RowH
NH
End of Internal
...
```

The Internal Coordinates specified for the keyword ***RowH*** must be first listed before below the keyword ***Vary***. The right input is the following:

```
...
Internal Coordinates
CN  = Bond C1 N2
CH  = Bond C1 H3
NH  = Bond N2 H3
Vary
CN
```

```
CH
NH
RowH
NH
End of Internal
...
```

Appendix. Input for lesson 2

```
&SEWARD &END
Title
 Your first MolCAS calculation: HF energy of methanol
ZMAT
H.cc-pVDZ.....
C.cc-pVDZ.....
O.cc-pVDZ.....

C1
O2      1   1.40000
H3      1   0.95000   2   109.471
H4      1   0.95000   2   109.471     3  -120.000
H5      1   0.95000   2   109.471     3   120.000
H6      2   1.08900   1   109.471     3   180.000

End of Input

&SCF &END
Title
 The SCF part
End of Input
```

Appendix. Input for lesson 3

```
&SEWARD &END
Title
 And your second one: the DFT(B3LYP) energy of methanol
ZMAT
H.cc-pVDZ.....
C.cc-pVDZ.....
O.cc-pVDZ.....

C1
O2      1   1.40000
H3      1   0.95000   2   109.471
H4      1   0.95000   2   109.471     3  -120.000
H5      1   0.95000   2   109.471     3   120.000
H6      2   1.08900   1   109.471     3   180.000

End of Input

&SCF &END
Title
 The SCF part
KSDFT
 B3LYP
End of Input
```

Appendix. Input for lesson 4

```
&SEWARD &END
Title
 And the third one:an MP2 calculation (methanol, again).
ZMAT
H.cc-pVDZ.....
C.cc-pVDZ.....
O.cc-pVDZ.....

C1
O2      1   1.40000
H3      1   0.95000   2   109.471
H4      1   0.95000   2   109.471     3  -120.000
H5      1   0.95000   2   109.471     3   120.000
H6      2   1.08900   1   109.471     3   180.000

End of Input

&SCF &END
Title
 The SCF part
End of Input

&MBPT2 &END
Title
 The MP2 calculation.
End of Input
```

Appendix. Input for lesson 5

```
>>>  Set  MaxIter  5000  <<<
>>>  Do  While  <<<

&SEWARD &END
Title
 Optimization of geometry: methanol (for the last time).
ZMAT
H.cc-pVDZ.....
C.cc-pVDZ.....
O.cc-pVDZ.....

C1
O2      1   1.40000
H3      1   0.95000   2   109.471
H4      1   0.95000   2   109.471     3  -120.000
H5      1   0.95000   2   109.471     3   120.000
H6      2   1.08900   1   109.471     3   180.000

End of Input

&SCF &END
Title
 The energy
End of Input

&SLAPAF &END
Iterations
 20
End of Input

>>>  EndDo  <<<
```

Appendix. Input for lesson 6

```
>>> Set MaxIter 5000 <<<
>>> Do While <<<

&SEWARD &END
Title
 Transition Structure  HCN -> CNH
ZMAT
H.cc-pVDZ.....
C.cc-pVDZ.....
N.cc-pVDZ.....

C1
N2      1   1.17000
H3      1   1.16000   2    80.000

End Of Input

&SCF &END
End of input

&SLAPAF &END
TS
Numerical Hessian
PRFC
Iterations
 10
End Of Input

>>> EndDo <<<
```

Appendix. Input for lesson 7

```
>>> Set MaxIter 5000 <<<
>>> Do While <<<

&SEWARD &END
Title
 Energy curve of CH3* + H2C=CH2
ZMAT
H.6-31G*.....
C.6-31G*.....

C1
C2       1     1.440
C3       1     2.000   2   110.0
H4       1     1.079   2   115.5     3   113.
H5       1     1.079   2   115.5     3  -113.
H6       2     1.075   1   120.5     3    83.
H7       2     1.075   1   120.5     3   -83.
H8       3     1.080   1   105.5     2   180.
H9       3     1.079   1   106.0     8   120.
H10      3     1.079   1   106.0     8  -120.

End Of Input

&SCF &END
UHF
End of input

&SLAPAF &END
Iterations
 20
Constrain
R = Bond C1 C3
Value
R = 2.0 Angstrom
End of Constrain
End Of Input

>>> EndDo <<<
```

Appendix. Input for lesson 8

```
>>>  Set  MaxIter  5000  <<<
>>>  Do  While  <<<

&SEWARD &END
Title
 Optimization of geometry with User-defined coordinates: chloroethane.
ZMAT
H.cc-pVDZ.....
C.cc-pVDZ.....
Cl.cc-pVDZ.....

C1
Cl2     1   1.75000
C3      1   1.45000   2   109.471
H4      1   1.08900   2   109.471     3   120.000
H5      1   1.08900   2   109.471     3  -120.000
H6      3   1.08900   1   109.471     2    60.000
H7      3   1.08900   1   109.471     6   120.000
H8      3   1.08900   1   109.471     6   240.000

End of Input

&SCF &END
End of Input

&SLAPAF &END
Internal Coordinates
CCl2   = Bond C1 Cl2
CC3    = Bond C1 C3
ClCC3  = Angle Cl2 C1 C3
CH4    = Bond C1 H4
ClCH4  = Angle Cl2 C1 H4
DH4    = Dihedral C3 Cl2 C1 H4
CH5    = Bond C1 H5
ClCH5  = Angle Cl2 C1 H5
DH5    = Dihedral C3 Cl2 C1 H5
CH6    = Bond C3 H6
CCH6   = Angle C1 C3 H6
DH6    = Dihedral Cl2 C1 C3 H6
CH7    = Bond C3 H7
CCH7   = Angle C1 C3 H7
DH7    = Dihedral H6 C1 C3 H7
CH8    = Bond C3 H8
CCH8   = Angle C1 C3 H8
DH8    = Dihedral H6 C1 C3 H8
Vary
CCl2
CC3
ClCC3
CH4
ClCH4
DH4
CH5
ClCH5
DH5
```

```
CH6
CCH6
DH6
CH7
CCH7
DH7
CH8
CCH8
DH8
End of Internal
Iterations
 20
End of Input

>>>  EndDo  <<<
```

Appendix. Input for lesson 9

```
>>> Set MaxIter 5000 <<<
>>> Do While <<<

&SEWARD &END
Title
 Energy curve of CH3* + H2C=CH2
ZMAT
H.6-31G*.....
C.6-31G*.....

C1
C2       1     1.440
C3       1     1.800   2   110.0
H4       1     1.079   2   115.5     3   113.
H5       1     1.079   2   115.5     3  -113.
H6       2     1.075   1   120.5     3    83.
H7       2     1.075   1   120.5     3   -83.
H8       3     1.080   1   105.5     2   180.
H9       3     1.079   1   106.0     8   120.
H10      3     1.079   1   106.0     8  -120.


End Of Input

&SCF &END
UHF
End of input

&SLAPAF &END
Internal Coordinates
CC2   = Bond C1 C2
CCC3  = Angle C2 C1 C3
CH4   = Bond C1 H4
CCH4  = Angle C2 C1 H4
DH4   = Dihedral C3 C2 C1 H4
CH5   = Bond C1 H5
CCH5  = Angle C2 C1 H5
DH5   = Dihedral C3 C2 C1 H5
CH6   = Bond C2 H6
CCH6  = Angle C1 C2 H6
DH6   = Dihedral C3 C1 C2 H6
CH7   = Bond C2 H7
CCH7  = Angle C1 C2 H7
DH7   = Dihedral C3 C1 C2 H7
CH8   = Bond C3 H8
CCH8  = Angle C1 C3 H8
DH8   = Dihedral C2 C1 C3 H8
CH9   = Bond C3 H9
CCH9  = Angle C1 C3 H9
DH9   = Dihedral H8 C1 C3 H9
CH10  = Bond C3 H10
CCH10 = Angle C1 C3 H10
DH10  = Dihedral H8 C1 C3 H10
CC3   = Bond C1 C3
Vary
```

```
CC2
CCC3
CH4
CCH4
DH4
CH5
CCH5
DH5
CH6
CCH6
DH6
CH7
CCH7
DH7
CH8
CCH8
DH8
CH9
CCH9
DH9
CH10
CCH10
DH10
Fix
CC3
End of Internal
Iterations
 20
End Of Input

>>> EndDo <<<
```

Appendix. Input for lesson 10

```
>>> Set MaxIter 5000 <<<
>>> Do While <<<

&SEWARD &END
Title
 Transition Structure  HCN -> CNH
ZMAT
H.cc-pVDZ.....
C.cc-pVDZ.....
N.cc-pVDZ.....

C1
N2      1   1.17000
H3      1   1.16000   2    80.000

End Of Input

&SCF &END
End of input

&SLAPAF &END
TS
PRFC
Iterations
 10
Internal Coordinates
CN = Bond C1 N2
CH = Bond C1 H3
NH = Bond N2 H3
Vary
CN
CH
NH
RowH
NH
End of Internal
End Of Input

>> EndDo <<<
```