

Using FireFly in education and research @ home

A short introduction in Computational Chemistry & an overview of strength possibilities of FireFly and how to make calculations more efficient

Part I - Usage





This tutorial was written because computational chemistry applied in the right way has an enormous potential in research.

Due to the lack of helpful introductions and a time consumptive orientation in this issue the appliance of this technology is less than it could/should be.

Nowadays computer technology is able to calculate chemical behaviour of molecules used in research with an adequate accuracy in a manageable time.

In am sure that in 5-10 years every bigger research group will have one scientist who will support current assays.

Computational chemistry has a kind of elitist reputation, because there are several requirements to use this technology in a serious way.

One need good chemical imagination, good computer knowledge, experience in preparing calculations, time to do that and of course an appropriate hardware and software.

I hope this document will help a little bit to enlarge distribution of such technology.

M. Checinski



Used Tools

Till now I tested some QM programs and visualization tools, and think that choosing the free available PC-Gamess/FireFly for calculation and MacMolPlt for visualization is a very good combination. You can also use the combination Gaussian and Gaussian View, but if you want to pay > 1.000 \$ for programs which are not really better than the two mentioned above, please do it.

In the next two chapters I will try to introduce you in these programs.

A. A. Granovsky, PC GAMESS/FireFly version 7.1.C

<http://classic.chem.msu.su/gran/gamess/>

Brett Bode, MacMolPlt version 7.2.1

<http://www.scl.ameslab.gov/~brett/MacMolPlt/>

The PC GAMESS/Firefly is a freely available ab initio and DFT computational chemistry program developed to offer high performance on Intel-compatible x86, AMD64, and EM64T processors. It was initially based on the GAMESS (US) source code of ISU (versions of up to October 25, 1999) extending its functionality in many important areas. The PC GAMESS/Firefly package is developed by the PC GAMESS/Firefly Project Team. The project coordinator and leading developer is Dr. Alex A. Granovsky of the Laboratory of Chemical Cybernetics, Dept. of Chemistry, Moscow State University (MSU).

As of autumn 2008, the PC GAMESS/Firefly Project Team is no longer associated with GAMESS (US) and ISU group, as well as the PC GAMESS/Firefly itself. Therefore, we are glad to announce a one-year transition period starting October 17, 2008. During this period, both PC GAMESS and Firefly names will be valid, and can be used as synonyms. However, starting October 17, 2009, the only valid name for the former PC GAMESS package will be the "Firefly" one.



MacMolPlt is a freely available modern graphics program for plotting 3-D molecular structures and normal modes (vibrations). Modern means Mouse driven interface for real-time rotation and translation, copy and paste functionality for interfacing to other programs such as word processors or other graphics programs, multiple files open at once. It reads a variety of file formats including any GAMESS log or IRC file directly to create animations of IRC's, DRC's, and optimizations.

You may also paste GAMESS and Gaussian-92 style cartesian coordinates directly into the program. Simple Energy Plots (including geometrical parameters). Animation of IRC's, and DRC's including orbitals. Append multiple GAMESS files together to create a single animation.

Build molecules from scratch using cartesian or internal coordinates. 2D orbital, total electron density contour map display. 3D molecular orbital, total electron density display. Simple GAMESS input (.inp) builder. 3D color display with lighting and shading using OpenGL.



Overview

As said PC-Gamess/FireFly is an ab initio program, which reads molecular data and calculations settings and gives results in an output file. It needs no GUI. The “exchange” with this program are the Input/Output files only.

For visualizing calculated molecules one need a tool like MacMolPlt, which at it self can't perform quantum chemistry calculations.

In this chapter we want to see how the exchange with trough ASCII-files works.

We will learn, how an input-file looks like and how to start different runtypes (optimization, single point energy, surface, thermodynamics,) with different basis sets and calculations levels.

Then we looks how pc-gamess “present” us the results, and how we can make further calculations with done runs.

Input file

Ok, lets start with an input-file.

PC-Gamess/FireFly is very flexible, it contains a lot of setting possibilities. Both, system and calculation options. But often you need only some of them. Of course, the amount of input-file depends of calculation type.

The ASCII-file consists of groups (`_$XYZ [...]` `$END`) which contain according settings. Attention should be paid to a space character before every group.

There is also a possibility to insert some comments between groups (! comment).

```
! Short example of a H2O geometry optimization
!  
$CONTRL SCFTYP=RHF RUNTYP=OPTIMIZE $END  
$SYSTEM MWORDS=10 $END  
$BASIS GBASIS=N21 NGAUSS=3 $END  
$DATA  
1st row is reserved for a comment  
C1  
O 8.0 0.0 0.0 0.0  
H 1.0 1.0 1.0 0.0  
H 1.0 -1.0 1.0 0.0  
$END
```

Output file

Output file is often a big file. If calculation was successful we get demanded informations, else we get hints why calculation failed.

Output file contains program version followed by cpu identification, a input copy, computation settings and finally calculation process in a readable form. Short, in a very good documented way.

```
[...]  
      * PC GAMESS version 7.1 (Tornado), build number 4694 *  
      *   Compiled on   Sunday,    27-04-2008, 11:27:46   *  
[...]  
Running on AMD CPU   :   CPU Generation 15, Family 15, Model 72,  
CPU Brand String    :   AMD Turion(tm) 64 X2 Mobile Technology TL-52  
# of cores/package  :   2  
[...]  
INPUT CARD>! This is a short example of a H2O geometry optimization  
INPUT CARD>!  
INPUT CARD> $CONTRL SCFTYP=RHF RUNTYP=OPTIMIZE $END  
[...]  
      $CONTRL OPTIONS  
      -----  
      SCFTYP=RHF           RUNTYP=OPTIMIZE           EXETYP=RUN  
      MLEVEL=              0           LOCAL =NONE           UNITS =ANGS  
      MULT  =              1           ICHARG=              0           MAXIT =           30  
[...]  
      ITER EX DEM  TOTAL ENERGY           E CHANGE  DENSITY CHANGE           ORB. GRAD  
      -----START SECOND ORDER SCF-----  
      1  0  0  -75.529387223  -75.529387223  0.096895582  0.090804473  
      2  1  0  -75.557153257  -0.027766035  0.037335165  0.037766885  
[...]  
                                OVERALL  TIMING  STATISTICS:  
GLOBAL CPU TIME ELAPSED      =           1.1 SECONDS (    0.0 MIN)  
NODE 0 WALL CLOCK TIME      =           0.6 SECONDS (    0.0 MIN)  
JOB CPU UTILIZATION:  TOTAL =          176.80%
```

Punch file

Punch file depends on run-type. For optimization i.e. it contains for every optimization step the coordinates and a \$VEC group which is a kind of conclusion of “orbital settings”.

```
$DATA
1st row is reserved for a comment

C1      0
O       8.0      0.0000000000      0.0000000000      0.0000000000
  N21    3
[...]
```

----- DATA FROM NSERCH= 0 -----				
COORDINATES OF SYMMETRY UNIQUE ATOMS (ANGS)				
ATOM	CHARGE	X	Y	Z
O	8.0	0.0000000000	0.0000000000	0.0000000000

```
[...]
--- RHF ORBITALS --- GENERATED AT 11:25:23 LT 3-JUN-2007
1st row is reserved for a comment

E(RHF)=      -75.4227358108, E(NUC)=      6.2515457668, 11 ITERS
$VEC
  1  1  9.83125434E-01  9.17634027E-02  0.00000000E+00  2.29900845E-03
0.00000000E+00
  1  2 -2.83385141E-02  0.00000000E+00 -3.28544768E-03  0.00000000E+00
7.16051563E-04
  1  3  3.73491962E-03  7.16051563E-04  3.73491962E-03
[...]
```

Later we will see how important this \$VEC group could be.

Run a job

If we wrote an input-file we can start a calculation. The command can be large, so you should use scripts/batch-files to lower complexity. I put some scripts for linux/windows into appendix. Here is a general command line:

Linux

```
<progdir>/pcgamess -i <fav_dir>/test.inp -o <fav_dir>/test.out
```

Windows

```
<progdir>\pcgamess -i <fav_dir>\test.inp -o <fav_dir>\test.out
```

there are other useful parameters which we should use.

- r means to remove all the scratch files which were open using FSF at the end of job.
- f forces PC GAMESS execution even in the presence of the old punch or ircdata files.
- i takes this file as input, use full qualified targets !
- o output to this file.
- p redirects all text files (punch, ircdata, etc...) to the same directory where the output file will be placed.
- ex <ex_dir> means to copy all PC GAMESS runtime extension files from the specified location (Linux specific)
- t <tmp_dir> means to use the specified path to create the temporary directories on all nodes and to put there all the intermediate working files.
- b /home/gran/basifile.lib

a normal command line looks like:

```
[ /home/marek/pcg/pcgamess -r -f -i /data/qm/test.inp -o /data/qm/test.out -t /scratch -  
b /home/marek/pcg/bset/acc-pvtz.lib ] crazy, isn't it ? So use scripts :)
```

How to use MacMolPlt



For a H₂O calculation input- and output-file is manageable, but for bigger molecules our imagination is challenged. So it is useful to work with a visualization tool.

In this chapter we will learn how to use most needed properties of MacMolPlt.

We learned how do write a short input-file for a H₂O optimization, now we try the same with MacMolPlt. There are several way to create an input-file with help of such visualization tool. For those who don't like ASCII-files, Brett Bode has implement a GAMESS-Input-Builder. Other can use MacMolPlt for “optimizing” geometry per hand, before starting a run.

MacMolPlt is a great tool to create/modify molecules and simply to watch calculated results.



How to use MacMolPlt

Ok, at first we have to draw our molecule. Because MacMolPlt is very user-friendly controlling is very intuitive, so if you click through all options you will learn it fast.

Here is just a picture of creating a water molecule.

The screenshot shows the MacMolPlt interface. On the left, the 'Subwindow' menu is open, listing options: Bonds, Coordinates, Energy Plot, Frequencies, Input Builder, Surfaces, Z-Matrix Calculator, and Preferences. The main window displays a 3D ball-and-stick model of a water molecule (H₂O), with two grey spheres representing hydrogen atoms and one red sphere representing an oxygen atom. Below the main window, the 'Coordinates Window' is open, showing a table of atomic coordinates. The table has columns for 'Type', 'X', 'Y', and 'Z'. The 'Type' column is currently empty for the first row, and the 'Coord. Type' is set to 'Cartesian'.

	Type	X	Y	Z
1	O	0.000000	0.000000	0.000000
2	H	1.000000	1.000000	0.000000
3	H	-1.000000	1.000000	0.000000

How to use MacMolPlt

If you want special angles or bond length it is difficult to draw this in cartesian (x,y,z) coordinates. It is easier to work with z-matrices.

For those who don't know what this is the next picture will explain it very fast.

When you work with big molecules you will be very thankful that MacMolPlt exist.

Important is to create a reasonable order of atoms.

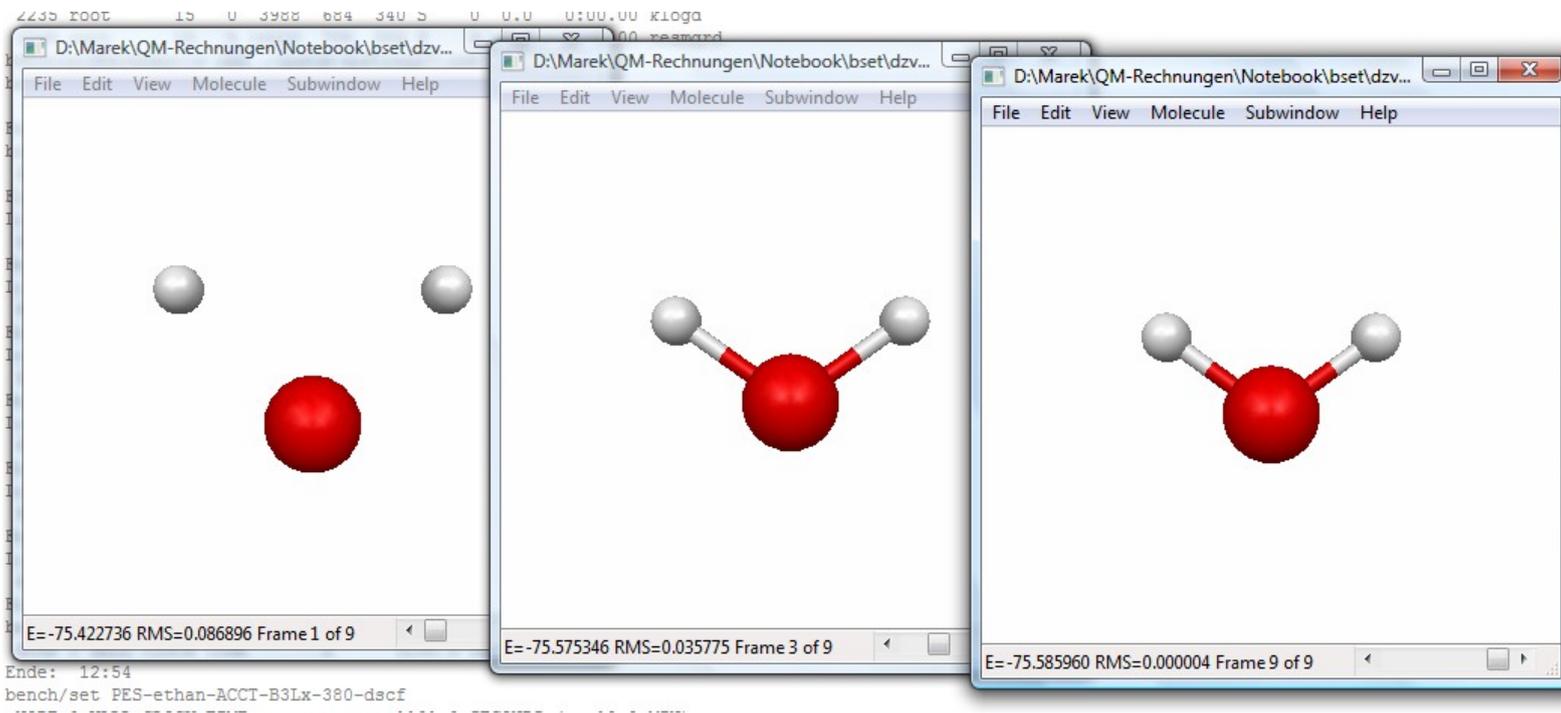
This is very helpful by changing angle of bigger groups.

The screenshot shows the MacMolPlt interface. The main window displays a 3D ball-and-stick model of a bent molecule with two oxygen atoms (grey) and two hydrogen atoms (white). The bonds are shown in red. The 'Coordinates Window' is open, showing a table with columns for Type, atm 1, Length, atm 2, Angle, atm 3, and Dihedral. The table contains the following data:

	Type	atm 1	Length	atm 2	Angle	atm 3	Dihedral
1	O						
2	O	1	1.400000				
3	H	1	0.900000	2	95.00		
4	H	2	0.900000	1	95.00	3	111.00

How to use MacMolPlt

Ok, now if your calculation is finished you can open output file with MacMolPlt.



With the scrollbar at bottom you can see all optimization steps.

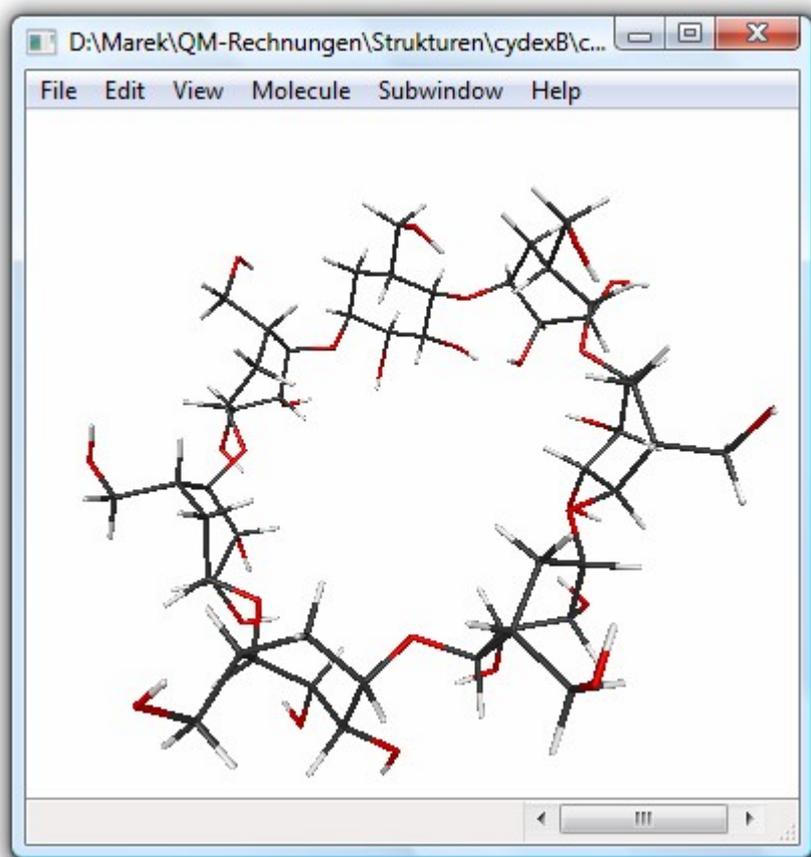
For every step you can see bond length etc. in the coordinates window.

You can choose between cartesian and z-matrix form. If you want, you can now add or delete atoms there and create with input bilder a new input file.

If you use z-matrix format in input file you have to add **COORD=ZMT** in \$CONTROL grp.

How to use MacMolPlt

When you want to calculate bigger molecules drawing could be very boring, so we can be happy about another function of our used visualization program. MacMolPlt have the possibility to import “.mol” files, which we can create with several molecule drawing programs (like acd/chemsketch). After importing such a file, we can copy coordinates in cartesian or in z-matrix form into our input file or use Brett's input builder.



This is an AM1 optimized structure of β -cyclodextrine. At first it was painted with chemsketch and pre-optimized with molecular modelling tool. After importing .mol file z-matrix it was copied into input-file.

Examples



In this chapter i collected some calculations which should give a little insight of possibilities with PC-Gamess and visualizing results with MacMolPlt.

Geometry optimization is a typical run-type in calculations and is origin for many other calculations like vibration modes, exciting states, potential energy surface, transition states etc.

There are several problems you can have by searching “optimal” geometry, one of them is to find a global minimum.

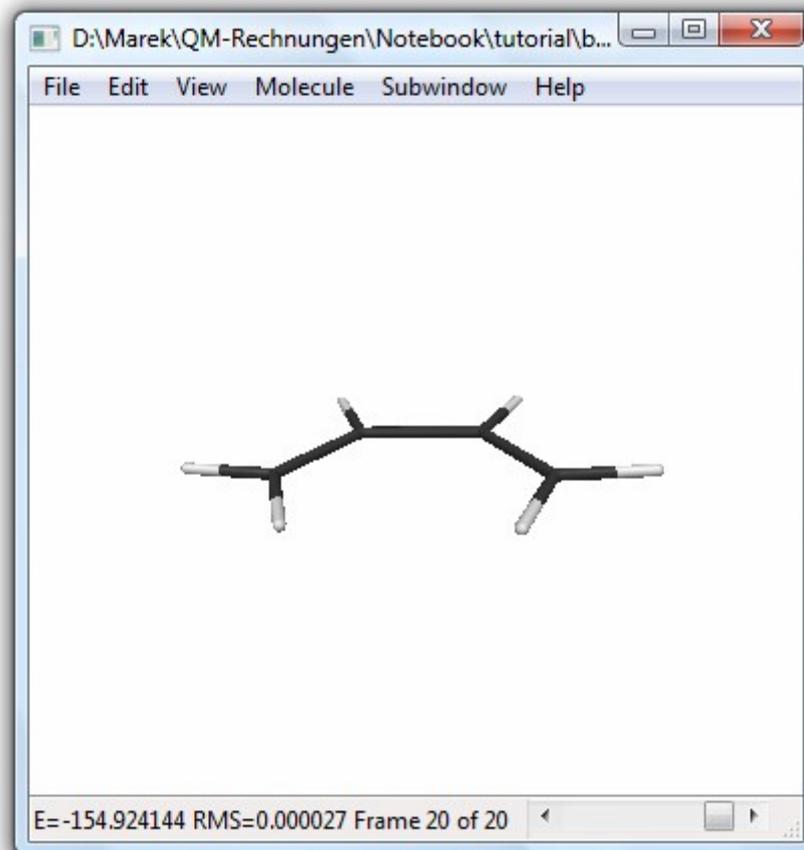


Examples-Geometry

If we want a structure optimization, calculation program search for structures which have lower energy. If program found a structure where small geometry changes don't give lower energy values then it found a minimum. No one can say if this is a global minimum. At that point PC-Gamess helps us to check if there are more stable geometries. We take a minimum geometry and start another runtime called HESSIAN.

Let's check this runtime on cis-butadiene.

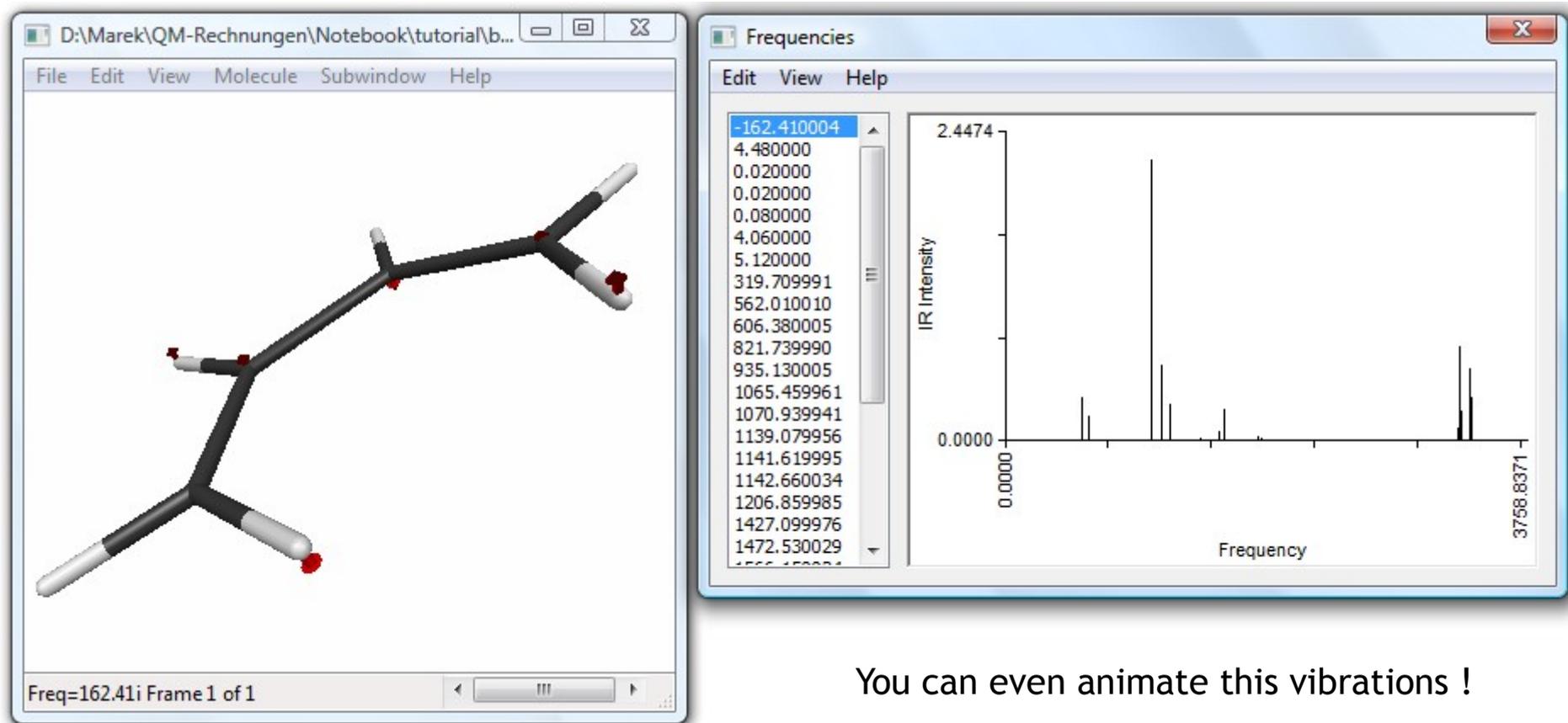
```
$CONTRL SCFTYP=RHF RUNTYP=HESSIAN
        COORD=ZMT MAXIT=100 $END
$SYSTEM TIMLIM=180 MWORDS=80 $END
$BASIS  GBASIS=N31 NGAUSS=6 NDFUNC=1
        NPFUNC=1 $END
$GUESS  GUESS=HUCKEL $END
$DATA
2-Buten
C1
C
C  1  1.32197
H  1  1.07513  2 120.8676
H  1  1.07592  3 116.4375  2 180.0000
C  2  1.47957  1 127.1590  4  0.0000
C  5  1.32194  2 127.1557  1  0.0000
H  6  1.07584  5 122.7014  2  0.0000
H  6  1.07523  5 120.8626  2 180.0000
H  2  1.07816  1 118.0354  5 180.0000
H  5  1.07814  2 114.8040  1 180.0000
$END
```



Examples-Geometry

When we get a minimum, we have to copy the coordinates into a new input file, but now with RUNTYP=HESSIAN in \$CONTRL group.

Results from this run we HAVE to view with MacMolPlt, here we have the great possibility of watching harmonic vibration modes.



You can even animate this vibrations !

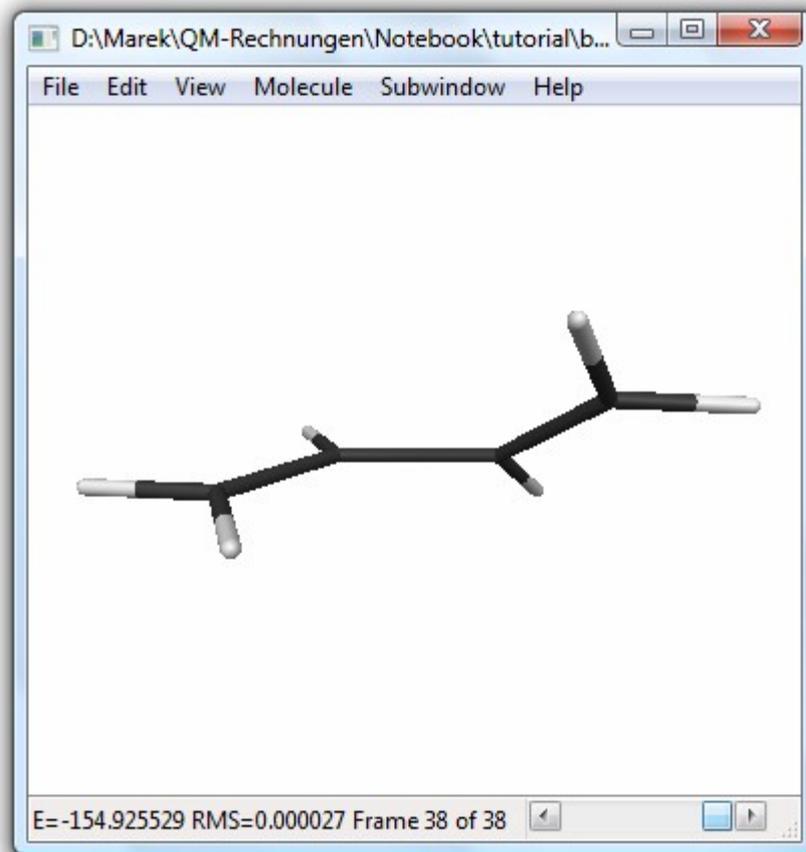
Examples-Geometry

In freq table we saw an imaginary frequency, this is a vibration around a saddle point. Now we have to change geometry like this vib-mode. For that MacMolPlt has again a great tool, with “View/Offset along mode..” you can change geometry in the kind of chosen vibration mode.

If we now copy this new geometry and start another geometry optimization we get the structure beside.

Awesome isn't it ?

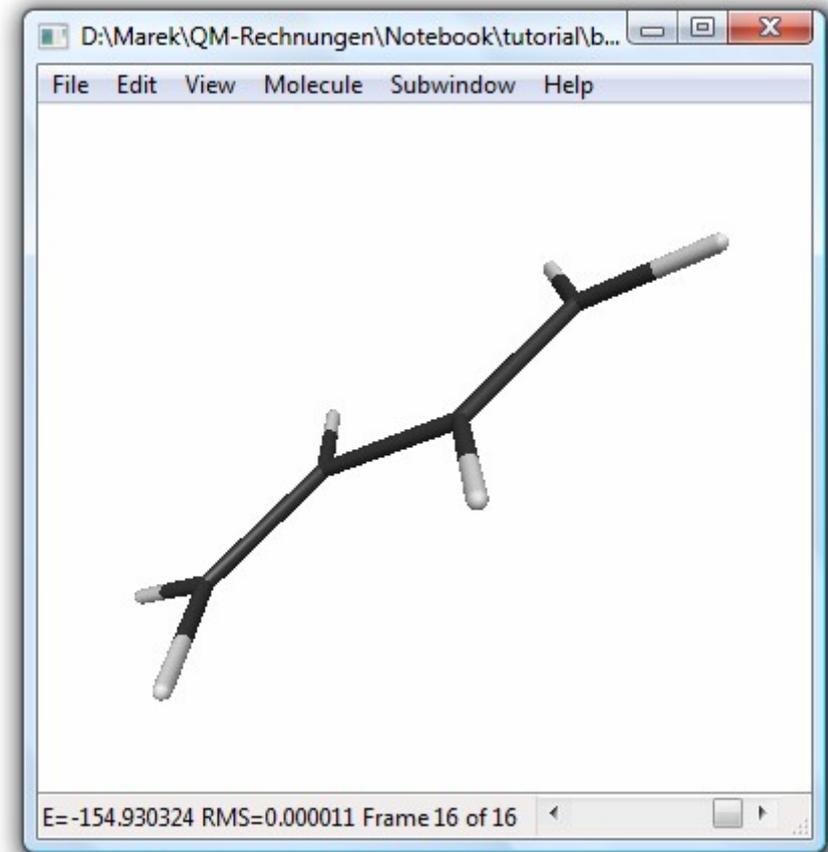
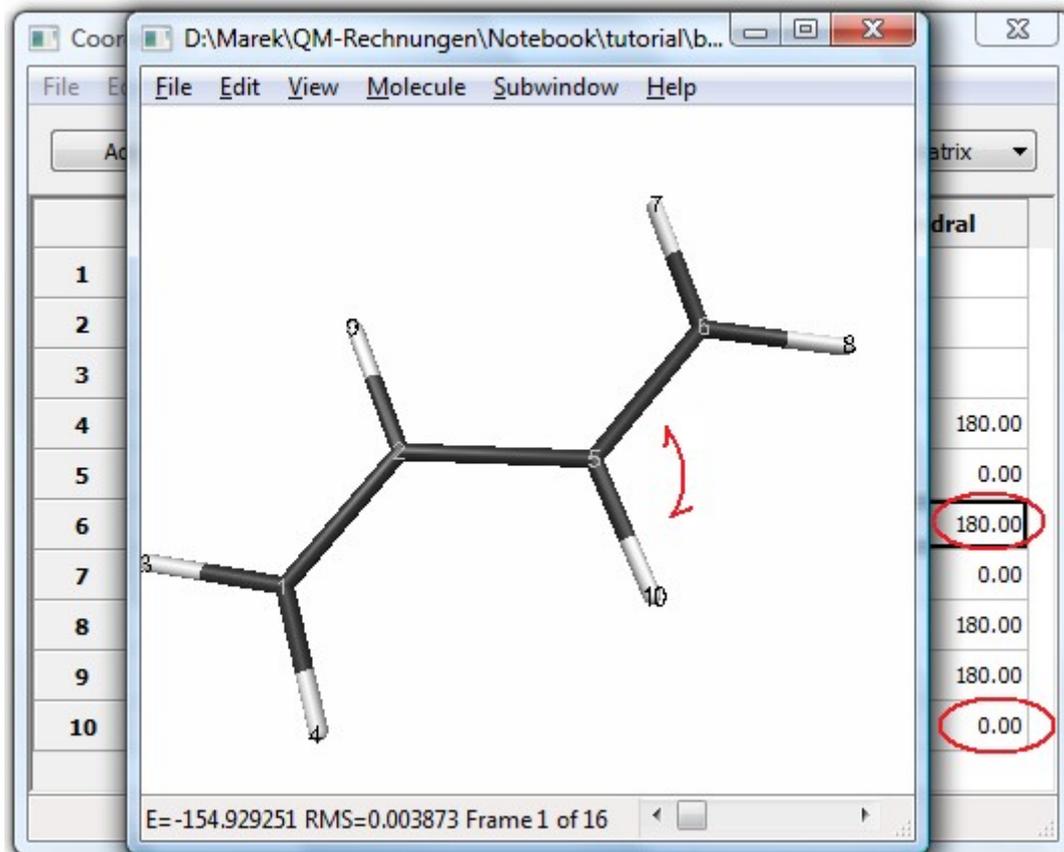
This and not the planar geometry has the lowest energy. The H-H interaction is harder than losing conjugation of pi-system.



Examples-Geometry

O.k. with this new structure we have no imaginary freq, but we can imagine that a trans-butadiene should be more stable as our found cis conformere.

Instead of drawing trans-butadien we can modify our planar-cis-butadien.



Hessian helps you finding a minimum, but there always can be a lower geometry.

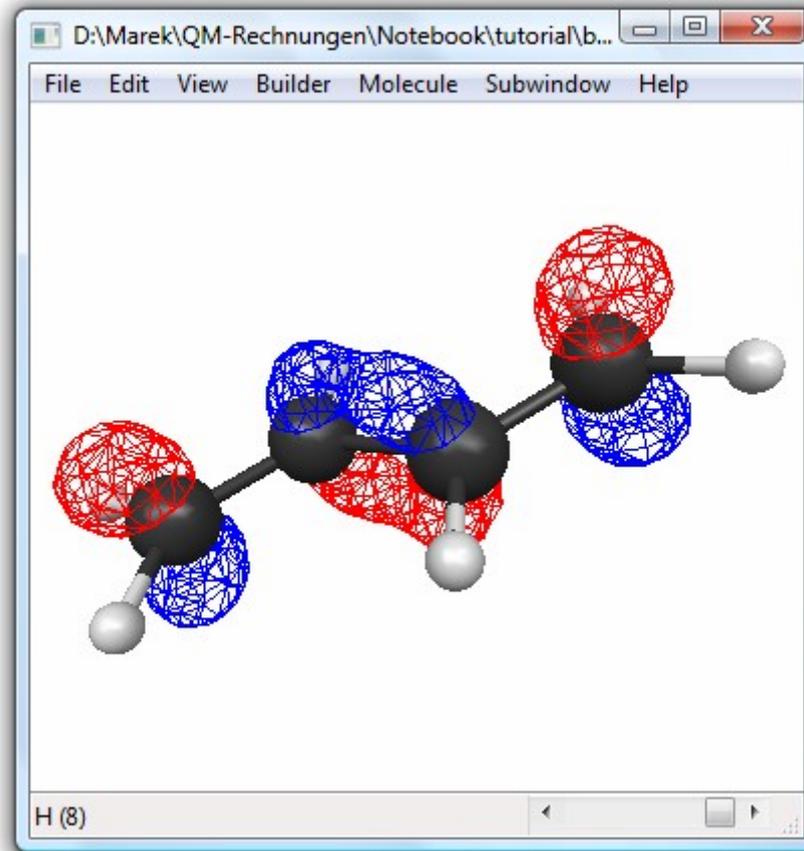
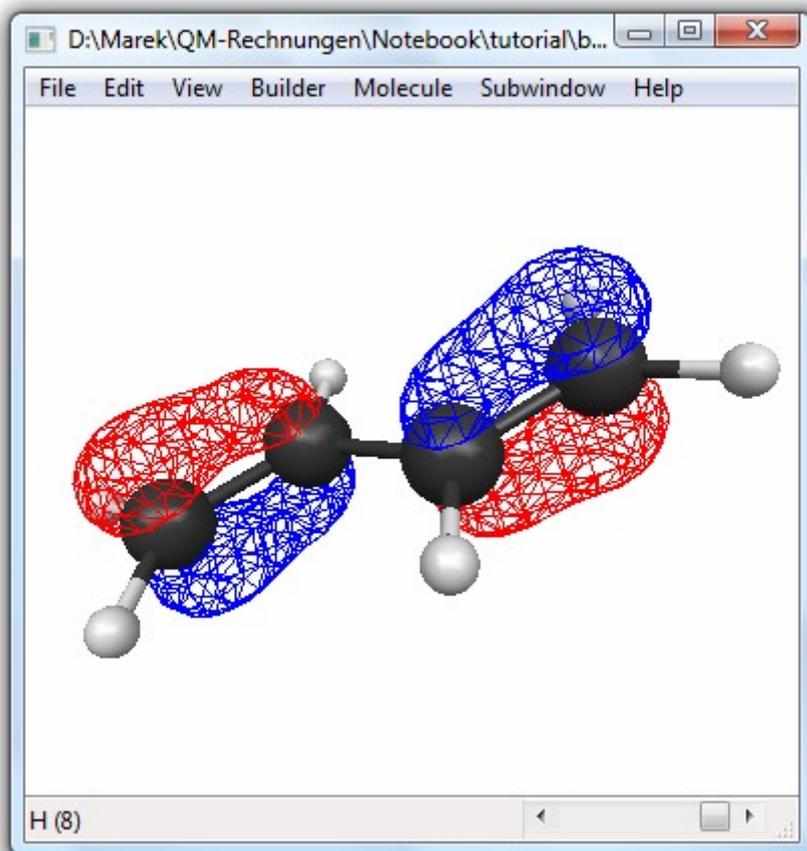
Examples-Geometry

A very nice and useful feature of MacMolPlt is visualization of Orbitals.

We can see how i.e. HOMO/LUMO looks like of trans-butadiene.

In MacMolPlt we find this option under “Subwindow/Surfaces & 3D-Orbitals”

You can find out which of listed MOs are HOMO/LUMO by “Occupation #”



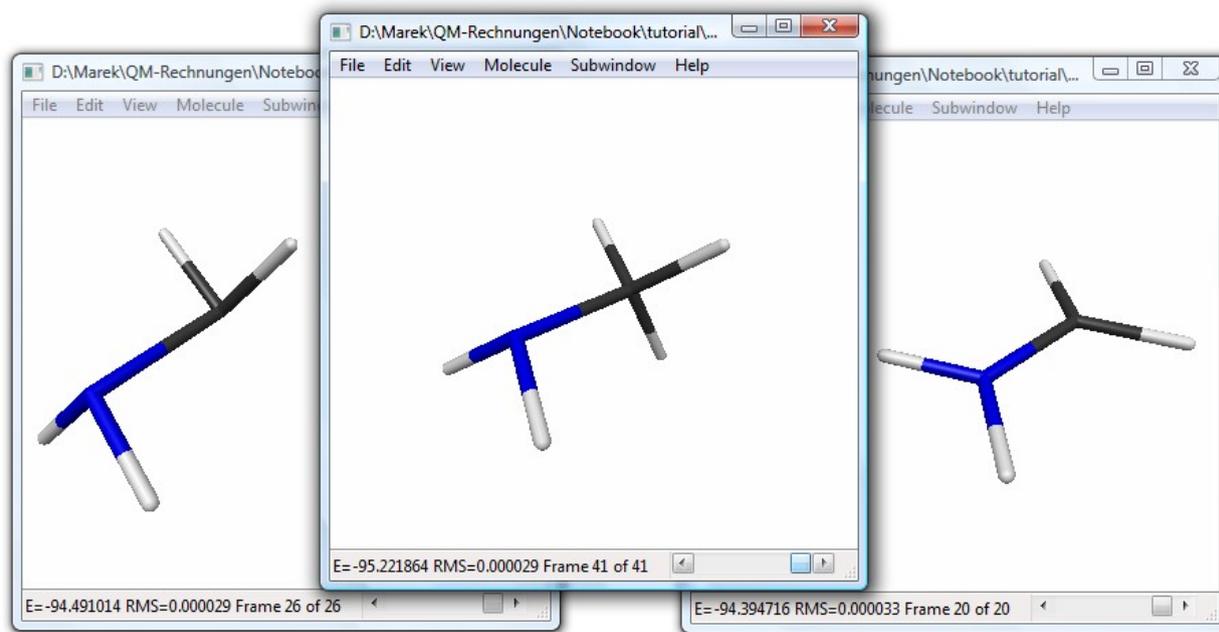
You also can get Electron Density or Electrostatic Potential in 2D/3D.

Examples-Charges

Now we should be able to optimize structures, so we should take the next step and see how to handle charged molecules with PC-Gamess.

To advice program to calculate with pos./neg. charge we have to add ICHARG=x in \$CONTRL grp., where x is a pos./neg. numerical value of demanded charge.

Let's exercise it on methylamine.



This example incredible show the didactical strength of PC-Gamess.

Here we see from theory expecting behaviour.

Anion, maximal repulsion of free electron-pairs. Cation, planar geometry.

Examples-Multiplicity

In the next step we try to calculate structure of a methyl-radical.

To create this structure we could open methylamine file and delete the amine group.

Surly, this is not much faster than creating a new molecule, but if system is bigger it is a comfortable possibility which MacMolPlt gives us.

When we copied new coordinates in input-file, saved as a new file and started a run we get followed message.

```
$CONTRL SCFTYP=RHF RUNTYP=OPTIMIZE
        COORD=ZMT MAXIT=100 $END
$$SYSTEM TIMLIM=180 MWORDS=60 $END
$BASIS  GBASIS=N31 NGAUSS=6 NDFUNC=1 NPFUNC=1 $END
$GUESS  GUESS=HUCKEL $END
$STATPT OPTTOL=0.0001 NSTEP=100 $END
$DATA
Methyl Radikal
C1
C
H  1      1.08452
H  1      1.09153  2 107.8370
H  1      1.08450  2 107.3613  3 -115.9808
$END
```

```
*** CHECK YOUR INPUT CHARGE AND MULTIPLICITY ***
THERE ARE      9 ELECTRONS, WITH CHARGE ICHARG=  0
BUT YOU SELECTED MULTIPLICITY MULT=  1
```

If we have an odd number of electrons resulting spin is $\neq 0$. Because multiplicity is defined by $(2s+1)$ we have to change to **MULT=2** (MULT is by default 1). retry

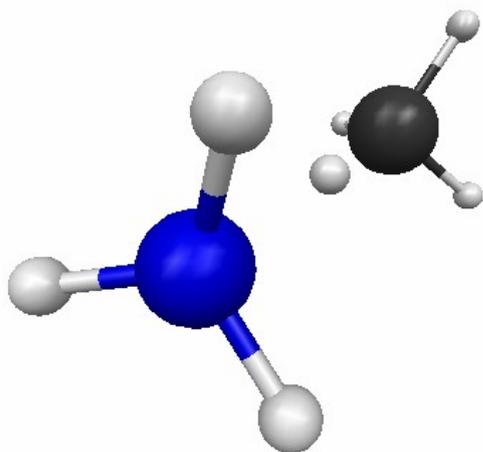
```
*** SCFTYP=RHF MUST HAVE MULT=1 ***
```

Hmm, what's wrong ? The cause is easy we have an odd number of electrons. A restricted Hartree Fock calculation only accept occupation of 0|2. We have to use another RUNTYP. To avoid this restriction we should use an **ROHF** or **UHF** RUNTYPE.

Examples-Freezing Coordinates

In calculations it is sometimes necessary to “freez” some coordinates. I.e. when we will see where a proton will go if it is between NH₃ and PH₃.

To freez coordinates of NH₃ and PH₃ we need to add a \$STATPT group with coordinates which should be freezed.



```
$CONTRL SCFTYP=RHF RUNTYP=OPTIMIZE ICHARG=1 $END
$SYSTEM MWORDS=60 $END
$BASIS GBASIS=N31 NGAUSS=6 $END
$STATPT OPTTOL=0.0001 NSTEP=100
        IFREEZ(1)=1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,
                19,20,21,22,23,24 $END

$DATA
Freezing coordinates
C1
N      7.0      2.00000000      0.00000000      0.00000000
H      1.0      2.40315998      0.00000000      0.92281258
H      1.0      2.09977591      0.85374779     -0.52465492
H      1.0      2.09977591     -0.85374779     -0.52465492
P     15.0     -2.00000000      0.00000000      0.00000000
H      1.0     -3.00332069      0.00000000      1.04042923
H      1.0     -2.62619233      1.06095433     -0.75727904
H      1.0     -2.62619233     -1.06095433     -0.75727904
H      1.0      0.00000000      0.00000000      0.00000000
$END
```

Examples-Freezing Coordinates

Instead of fixing atoms in space you can also fix bond length or angles.

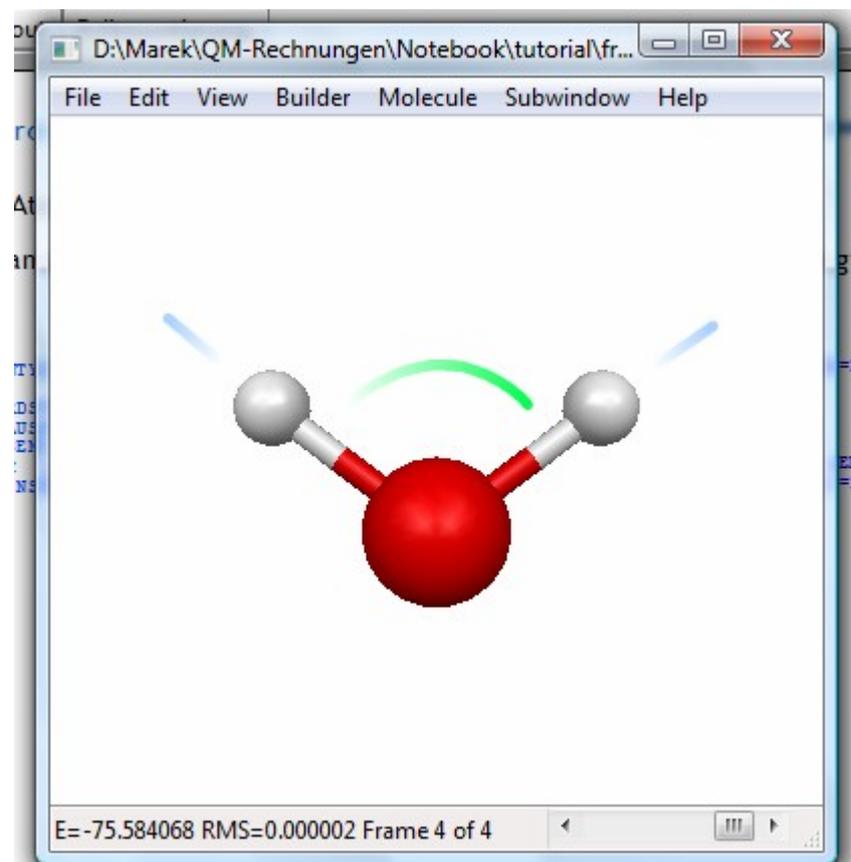
Here are two examples in which we want optimize H2O with a special O-H length or H-O-H angle.

```
$CONTRL SCFTYP=UHF RUNTYP=OPTIMIZE COORD=ZMT
NZVAR=3 $END
$$SYSTEM TIMLIM=10 MWORDS=80 $END
$BASIS GBASIS=N21 NGAUSS=3 $END
$GUESS GUESS=HUCKEL $END
$ZMAT IZMAT(1)=1,1,2 1,1,3 2,2,1,3 $END
$STATPT OPTTOL=0.0001 NSTEP=10 IFREEZ(1)=1,2 $END
$DATA
FreezTest
C1
O
H 1 1.00000
H 1 1.00000 2 90.0000
$END
```

```
$CONTRL SCFTYP=UHF RUNTYP=OPTIMIZE COORD=ZMT
NZVAR=3 $END
$$SYSTEM TIMLIM=10 MWORDS=80 $END
$BASIS GBASIS=N21 NGAUSS=3 $END
$GUESS GUESS=HUCKEL $END
$ZMAT IZMAT(1)=1,1,2 1,1,3 2,2,1,3 $END
$STATPT OPTTOL=0.0001 NSTEP=10 IFREEZ(1)=3 $END
$DATA
FreezTest
C1
O
H 1 1.00000
H 1 1.00000 2 90.0000
$END
```

IFREEZ(1)=3 stands for 3rd variable in IZMAT(1) which is 2,2,1,3. First # stands for angle (1 for length), following # declare atoms.

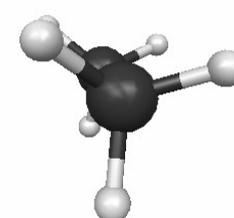
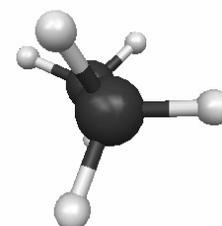
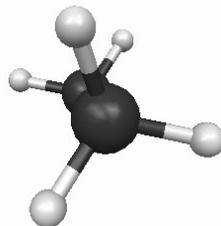
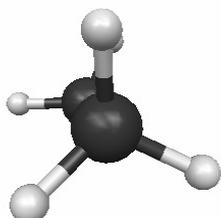
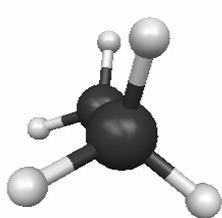
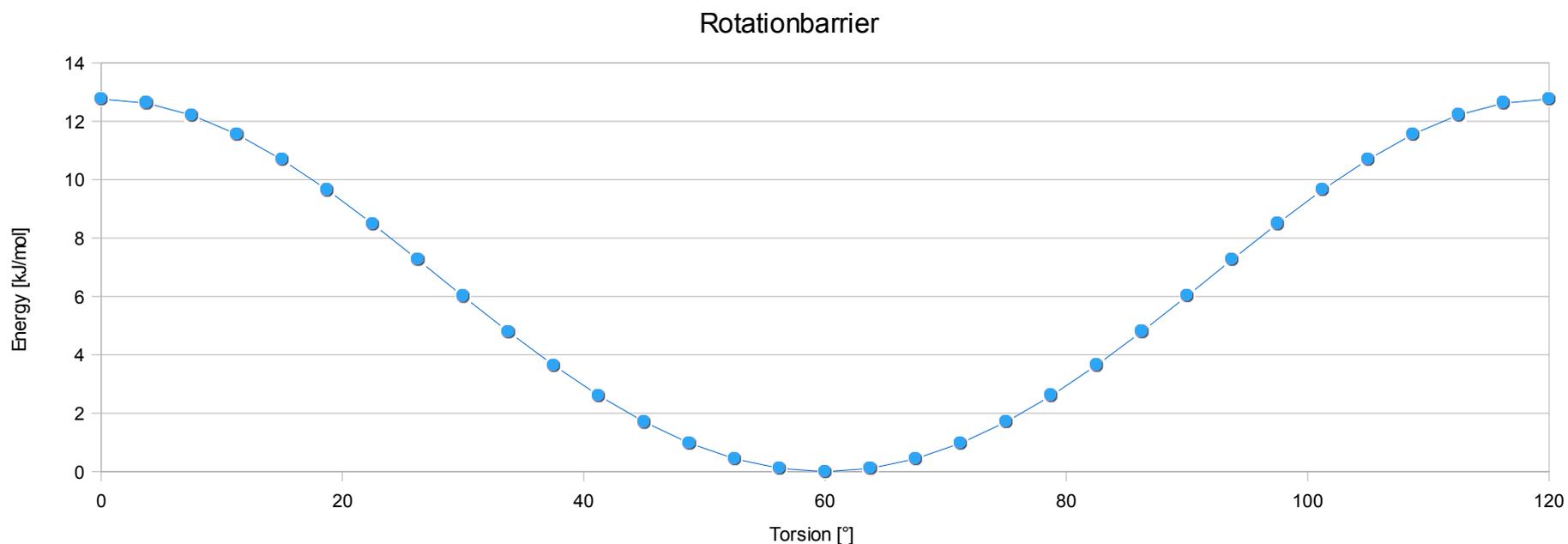
I.e. 2,3,18,88 means angle between atoms 3-18-88 and 1,33,44 bond length between 33-44.



Examples-Relaxed Surface Scan

PC-Gamess has another very interesting feature called Relaxed Surface Scan.

With that tool you have a very useful possibility to study different cases in research and especially in education. You can scan through length, angle, torsion and see how a system react.



Examples-Relaxed Surface Scan

And here is the inputfile:

```
$CONTRL RUNTYP=rsurface NZVAR=18 COORD=ZMT
mplevl=2 $END
$SYSTEM TIMLIM=500 MEMORY=30000000 $END
$BASIS GBASIS=tzv ndfunc=1 $END
! To freeze coord # 12 during constrained
optimization
$statpt opttol=1d-5 nstep=1000 IFREEZ(1)=12 $end
! To scan along coord # 12
$surf ndispl=33 displ=3.75 vect1(12)=1 orig1=0
$end
$DATA
CH3-CH3
C1
C
C 1 r1
h 1 r2 2 a1
h 1 r2 2 a1 3 d1
h 1 r2 2 a1 3 d2
h 2 r2 1 a1 4 dx
h 2 r2 1 a1 6 d1
h 2 r2 1 a1 6 d2
```

```
r1=1.54
r2=1.09
a1=109
d1=120
d2=-120
dx=0
$END
$ZMAT IZMAT(1)=
1, 2, 1,
1, 3, 1,
2, 3, 1, 2,
1, 4, 1,
2, 4, 1, 2,
3, 4, 1, 2, 3,
1, 5, 1,
2, 5, 1, 2,
3, 5, 1, 2, 3,
1, 6, 2,
2, 6, 2, 1,
3, 6, 2, 1, 4,
1, 7, 2,
2, 7, 2, 1,
3, 7, 2, 1, 6,
1, 8, 2,
2, 8, 2, 1,
3, 8, 2, 1, 6,
$END
```

Now its on you how to use this great tool in you research or education lessons.

Examples-Symmetry

Till now in every \$DATA group we had a C1 in 2nd line. This row declare symmetry of following molecule data. Point group symmetry C1 declare no symmetry.

A C2V symmetry would be declared with “CNV 2”.

```
$CONTRL SCFTYP=RHF RUNTYP=OPTIMIZE $END
$SYSTEM MWORDS=10 $END
$BASIS  GBASIS=N21 NGAUSS=3 $END
$DATA
2st row declare point group symmetry
Cnv 2

O  8.0   0.0 0.0 0.0
H  1.0   1.0 0.0 1.0
$END
```

```
$CONTRL SCFTYP=RHF RUNTYP=OPTIMIZE $END
$SYSTEM MWORDS=10 $END
$BASIS  GBASIS=N21 NGAUSS=3 $END
$DATA
2st row declare point group symmetry
Cnv 2
0.0 0.0 0.0 1.0 0.0 0.0
0.0 0.0 1.0
O  8.0   0.0 0.0 0.0
H  1.0   1.0 0.0 1.0
$END
```

Both input-files differs in declaring rotation axis and reflecting surface.

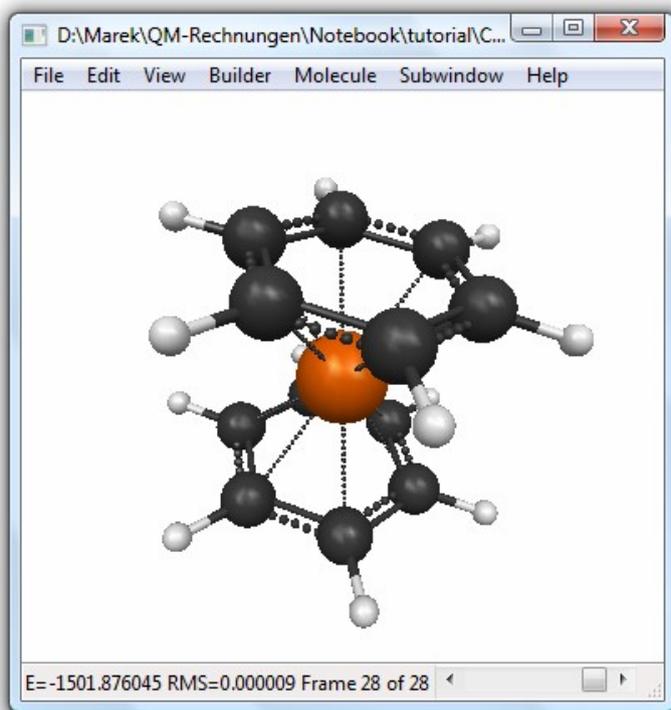
If a blank line follow after point group program will use Z-Axis for rotation and XZ for mirroring. But if you want to declare it by hand we have to define them.

```
0.0 0.0 0.0 1.0 0.0 0.0
0.0 0.0 1.0
```

```
x1 y1 z1 to x2 y2 z2
from path defined before to x3 y3 z3
```

```
-> rotation axis
-> mirroring area
```

To realize why symmetry can be very useful here another example. $\text{Cr}(\text{C}_6\text{H}_6)_2$

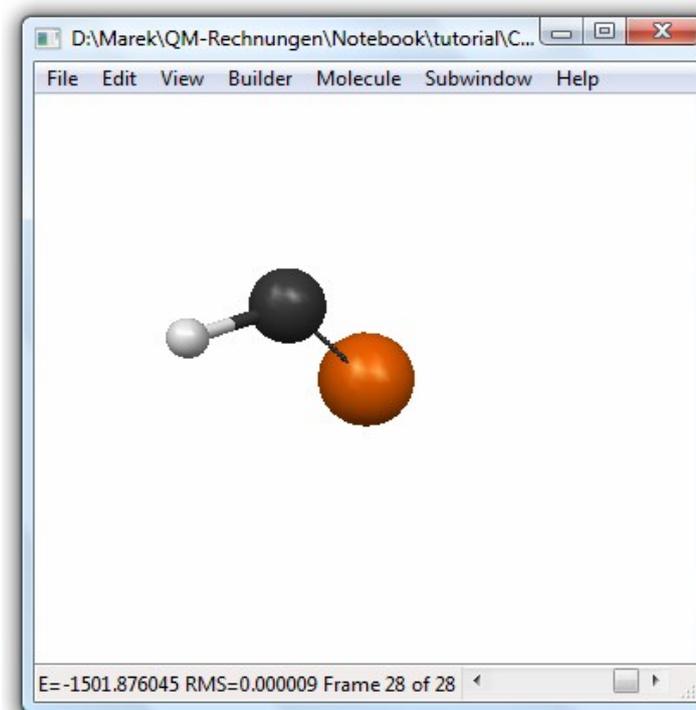


C1 vs C6h

calculation
time

68 : 6
minutes

with same
accuracy



Please realize that defining also force symmetry in optimization, so i.e. you will never get right conformation of cyclohexane by using C6h symmetry. So use this great option with caution.

Examples-Electron correlation

Till now we used HF calculations only. But as we know HF have a lot of disadvantages so, we should use for research methods which contain electron correlation correction.

There are some popular methods which we can use. Møller Plesset Perturbation, Density Functional Theory, Configuration Interaction and Coupled Cluster.

They differs in quality and very much in calculation effort. (see PCG-Tutorial-Basis.pdf)

For education or simple C,H,O calculations MP2 is advisable

For qualitative research with atoms from first 3 rows MP2 is ok.

By using transition metals it is necessary to use at least DFT methods.

CI or CC for usual sized molecules demand high computational capacity, so usage of them is mostly confined to publications.

To instruct PC-Gamess to use Møller-Plesset-Perturbation in Second Order we have to add MPLEVEL=2 in \$CONTRL group.

```
$CONTRL SCFTYP=RHF MPLEVEL=2 RUNTYP=OPTIMIZE $END
$SYSTEM MWORDS=10 $END
$BASIS GBASIS=N21 NGAUSS=3 $END
$DATA
MP2 Calculation
Td
C 6.0 0.0 0.0 0.0
H 1.0 1.0 1.0 1.0
$END
```

Higher MP Level are supported for single-point calculations.

To instruct PC-Gamess to use DFT method like B3LYP we have to change our input file in that way.

```
$CONTRL SCFTYP=RHF DFTTYP=B3LYP RUNTYP=OPTIMIZE $END
$SYSTEM MWORDS=10 $END
$BASIS GBASIS=N21 NGAUSS=3 $END
$DATA
Using B3LYP
Td
C 6.0 0.0 0.0 0.0
H 1.0 1.0 1.0 1.0
$END
```

Examples-Excited States TD-DFT

If you want i.e. to get Energy difference between S0 & exciting state S1, you should optimize structure at first and then calculate exciting states (Frank-Condon).

```

$CONTRL SCFTYP=RHF DFTTYP=B3LYP RUNTYP=OPTIMIZE
      COORD=ZMT MAXIT=100 $END
$SYSTEM TIMLIM=180 MWORDS=380 $END
$BASIS  GBASIS=N31 NGAUSS=6 NDFUNC=1 $END
$GUESS  GUESS=HUCKEL $END
$STATPT OPTTOL=0.0001 NSTEP=200 $END
$DATA
Blub
C1
C
C  1      1.38596
C  1      1.38599  2 120.0009
C  2      1.38591  1 119.9948  3  0.0000
C  3      1.38588  1 119.9986  4 -0.0000
C  4      1.38586  2 120.0061  1 -0.0000
H  1      1.11097  3 119.9978  2 -180.0000
H  2      1.11097  1 120.0014  4 180.0000
H  3      1.11101  1 120.0000  5 -180.0000
H  4      1.11101  2 119.9954  1 180.0000
H  5      1.11109  3 119.9957  1 -180.0000
H  6      1.11101  4 120.0070  2 -180.0000
$end
  
```

```

$CONTRL SCFTYP=RHF DFTTYP=B3LYP CITYP=TDDFT
      RUNTYP=ENERGYCOORD=ZMT MAXIT=100 $END
$TDDFT  NSTATE=3 ISTDY=0 ISTATE=1 $END
$SYSTEM TIMLIM=180 MWORDS=380 $END
$BASIS  GBASIS=N31 NGAUSS=6 NDFUNC=1 $END
$GUESS  GUESS=HUCKEL $END
$STATPT OPTTOL=0.0001 NSTEP=200 $END
$DATA
Blub
C1
C
C  1      1.39754
C  1      1.39758  2 120.0065
C  2      1.39759  1 120.0077  3  0.0000
C  3      1.39761  1 119.9870  4  0.0000
C  5      1.39756  3 120.0063  1  0.0000
H  1      1.08677  2 119.9979  3 180.0000
H  2      1.08679  1 119.9960  4 180.0000
H  3      1.08675  1 120.0094  5 180.0000
H  4      1.08675  2 120.0063  1 180.0000
H  5      1.08676  3 119.9975  1 180.0000
H  6      1.08676  5 119.9973  3 180.0000
$end
  
```

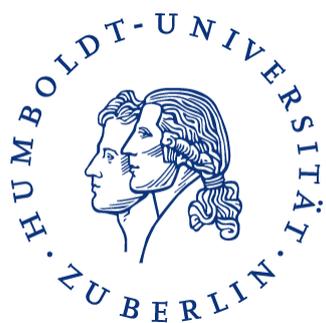
Somewhere at end of output-file you will find the results:

STATE	HARTREE	TDDFT EXCITATION ENERGIES				
		EV	KCAL/MOL	CM-1	NANOMETERS	OSC. STR.
1A	0.2034154902	5.5352	127.6452	44644.54	223.99	0.0000000
1A	0.2314729084	6.2987	145.2515	50802.43	196.84	0.0000000
1A	0.2893291228	7.8730	181.5568	63500.40	157.48	0.0000000

	Lambda [nm]
Benzol	224
Naphthalen	278
Anthracen	380
Phenanthren	309
Chinon	502
Pyridin	252
Bipy	288
Phen	307

.. to be continued

- CASSCF
- and much more



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