Project 2: Quantum Chemical calculation of the structures of complex molecules

Edoardo Cabiati

To better organize the structure of this work, we will dedicate a separate section for each molecule, whose analysis was requested in the assignment. Please, consider all of the information reported within this paper as associated to a Gaussian-type script and simulation output. If and when we will be discussing a MOLPRO-type of simulation, it will be explicitly noted.
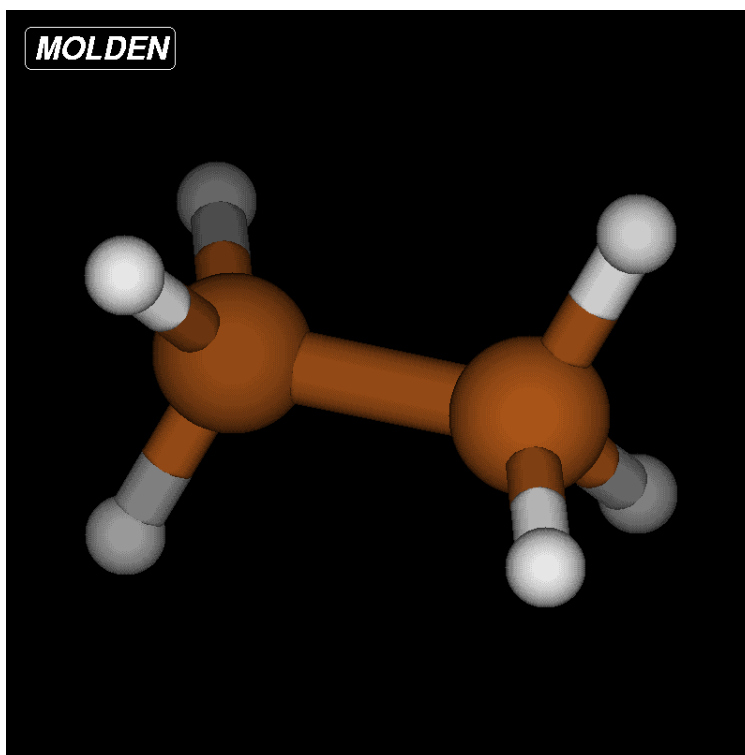
1 Ethane

Figure 1: Ball and Stick representation of ethane as appears in Molden

The script used for the simulation starts by specifying the kind of parameters Gaussian accepts to define the type of analysis that will be carried out. Specifically:

```
#p B3LYP/6-31+g(d,p) opt freq pop=full gfinput
```

where `#p` is the directive used to highlight the Route Section to the Gaussian compiler: it defines the type of calculation (e.g., optimization, frequency) and the method/basis set to be used. One could additionally specify the *Link 0 Commands* that set the system environment, such as the memory and processors to use: for this first simulations, those aren't used. Next up, after the title for the simulation, is the Z-matrix definition:

```
1  0  1
2  C1
3  C2  1  d1
4  H3  1  d2  2  a1
5  H4  1  d3  2  a2  3  t1
6  H5  1  d4  2  a3  3  t2
7  H6  2  d5  1  a4  3  t3
8  H7  2  d6  1  a5  6  t4
9  H8  2  d7  1  a6  6  t5
```
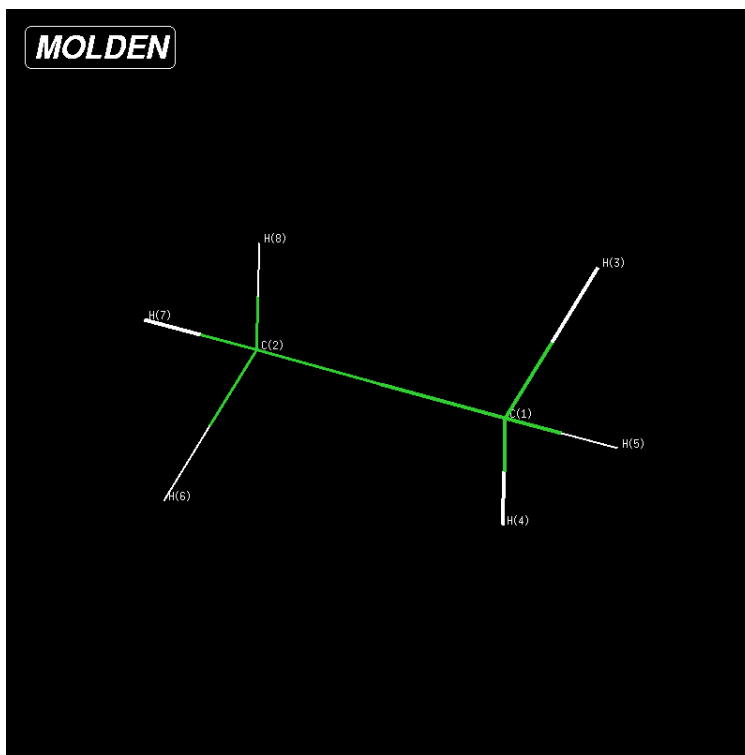

Figure 2: Carbon and Hydrogen labelled configuration for ethane, visualized using Molden

The first row defines the charge and spin multiplicity. Later comes the actual Z-matrix, which specifies the geometry of the system. It is possible to define the Z-matrix using a set of variables, as done in this case. This is useful not only for getting rid of redundant numbers, but also to implicitly enforce symmetry in certain molecules:

```
1  d1 =1.54
2  d2 =1.09
```

```
 3  a1 =111.
 4  d3 =1.09
 5  a2 =111.
 6  t1 =108.
 7  d4 =1.09
 8  a3 =111.
 9  t2 = -108.
10  d5 =1.09
11  a4 =111.
12  t3 =180.
13  d6 =1.09
14  a5 =111.
15  t4 =108.
16  d7 =1.09
17  a6 =111.
18  t5 = -108.
```

This skeletal snippet is enough for Gaussian to perform an optimization and frequency calculation run on ethane using B3LYP as DFT method to solve the system, and 6-31+g(d,p) basis set. In the route section, `pop=full` also requests a detailed output of the molecular orbitals and their populations.

1.1   Find the energy in the output file and save it

The energy (electronic) found by Gaussian for ethane is the following:

```
 1  E(RB3LYP) =   -79.8416407036       A.U.
```

1.2   Examine critically the output file and try to understand what has been done in the calculation

The general outline of any `opt freq` run in Gaussian is the following:

- **Initial Setup Information**: Firstly, the input parameters (method, basis set, charge, multiplicity, initial geometry, type of optimization) are echoed.

- **Optimization Steps**: Gaussian reports energy, gradients, orbital symmetries, atomic displacements and other info for each optimization step. For instance, during energy minimization steps the output is the following:

```
 1      ...
 2
 3      Cycle   1  Pass 1   IDiag   1:
 4      E= -79.8384714843381
 5      DIIS: error= 6.47D-03 at cycle    1 NSaved=   1.
 6      NSaved= 1 IEnMin= 1 EnMin= -79.8384714843381      IErMin= 1
    ErrMin= 6.47D-03
 7      ErrMax= 6.47D-03 EMaxC= 1.00D-01 BMatC= 1.59D-03 BMatP= 1.59D-03
 8      IDIUse=3 WtCom= 9.35D-01 WtEn= 6.47D-02
```

```
 9      Coeff-Com:    0.100D+01
10      Coeff-En:     0.100D+01
11      Coeff:        0.100D+01
12      Gap=      0.359 Goal=   None    Shift=    0.000
13      GapD=     0.359 DampG=1.000 DampE=1.000 DampFc=1.0000 IDamp=-1.
14      RMSDP=9.22D-04 MaxDP=1.04D-02                 OVMax= 1.54D-02
15
16      Cycle   2  Pass 1  IDiag  1:
17      E= -79.8405612646575      Delta-E=        -0.002089780319 Rises=F
     Damp=F
18      DIIS: error= 5.87D-04 at cycle   2 NSaved=   2.
19      NSaved= 2 IEnMin= 2 EnMin= -79.8405612646575      IErMin= 2
     ErrMin= 5.87D-04
20      ErrMax= 5.87D-04 EMaxC= 1.00D-01 BMatC= 1.97D-05 BMatP= 1.59D-03
21      IDIUse=3 WtCom= 9.94D-01 WtEn= 5.87D-03
22      Coeff-Com:   0.191D-02 0.998D+00
23      Coeff-En:    0.000D+00 0.100D+01
24      Coeff:       0.190D-02 0.998D+00
25      Gap=      0.357 Goal=   None    Shift=    0.000
26      RMSDP=9.20D-05 MaxDP=7.12D-04 DE=-2.09D-03 OVMax= 2.35D-03
27
28      ...
29
```
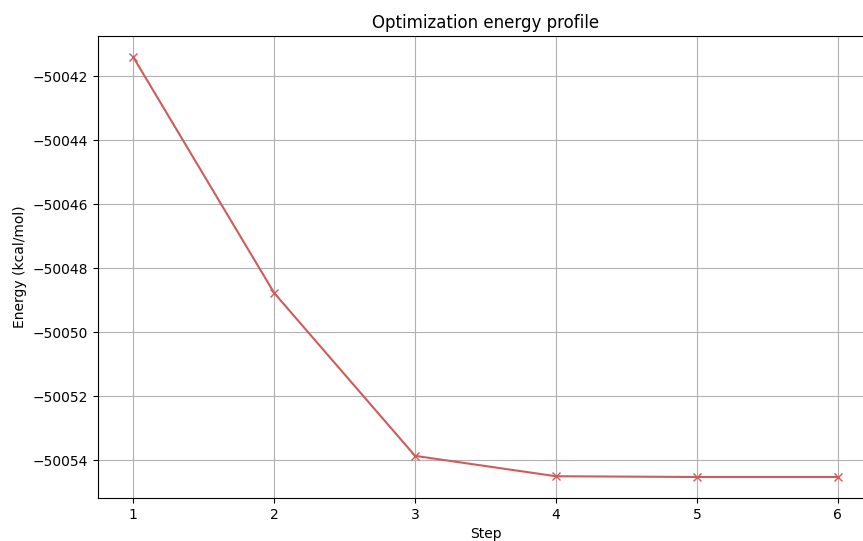

Figure 3: Trend for energy convergence for ethane

- **Convergence Status**: The program checks if the geometry has converged based on the forces and atomic movements.

- **Final Optimized Geometry**:The fully optimized atomic coordinates and final energy of the system are shown

```
                            ----------------------------
                            !    Optimized Parameters    !
                            !  (Angstroms and Degrees)   !

     ! Name   Definition               Value          Derivative Info.
     ! R1     R(1,2)                   1.533          -DE/DX =   -0.0003
                       !
     ! R2     R(1,3)                   1.095          -DE/DX =    0.0004
                       !
     ! R3     R(1,4)                   1.0954         -DE/DX =    0.0001
                       !
     ! R4     R(1,5)                   1.0954         -DE/DX =    0.0001
                       !
     ! R5     R(2,6)                   1.095          -DE/DX =    0.0004
                       !
     ! R6     R(2,7)                   1.0954         -DE/DX =    0.0001
                       !
     ! R7     R(2,8)                   1.0954         -DE/DX =    0.0001
                       !
     ! A1     A(2,1,3)                 111.3188       -DE/DX =    0.0001
                       !
     ! A2     A(2,1,4)                 111.3055       -DE/DX =    0.0001
                       !
     ! A3     A(2,1,5)                 111.3055       -DE/DX =    0.0001
                       !
     ! A4     A(3,1,4)                 107.5692       -DE/DX =   -0.0001
                       !
     ! A5     A(3,1,5)                 107.5692       -DE/DX =   -0.0001
                       !
     ! A6     A(4,1,5)                 107.5762       -DE/DX =   -0.0001
                       !
     ! A7     A(1,2,6)                 111.3188       -DE/DX =    0.0001
                       !
     ! A8     A(1,2,7)                 111.3055       -DE/DX =    0.0001
                       !
     ! A9     A(1,2,8)                 111.3055       -DE/DX =    0.0001
                       !
     ! A10    A(6,2,7)                 107.5692       -DE/DX =   -0.0001
                       !
     ! A11    A(6,2,8)                 107.5692       -DE/DX =   -0.0001
                       !
     ! A12    A(7,2,8)                 107.5762       -DE/DX =   -0.0001
                       !
     ! D1     D(3,1,2,6)               180.0          -DE/DX =    0.0
                       !
     ! D2     D(3,1,2,7)               -60.0          -DE/DX =    0.0
                       !
```

```
28  ! D3      D(3,1,2,8)                    60.0              -DE/DX =      0.0
              !
29  ! D4      D(4,1,2,6)                   -60.0              -DE/DX =      0.0
              !
30  ! D5      D(4,1,2,7)                    60.0              -DE/DX =      0.0
              !
31  ! D6      D(4,1,2,8)                   180.0              -DE/DX =      0.0
              !
32  ! D7      D(5,1,2,6)                    60.0              -DE/DX =      0.0
              !
33  ! D8      D(5,1,2,7)                   180.0              -DE/DX =      0.0
              !
34  ! D9      D(5,1,2,8)                   -60.0              -DE/DX =      0.0
35
```

- **Population Analysis** :information about the distribution of electrons (e.g., Mulliken charges) and orbital populations, if pop=full or a similar option is specified.

- **Frequency Calculation**:

  1. *Vibrational Frequencies*: After the optimization, Gaussian computes vibrational frequencies, showing the normal modes of vibration for the molecule.

  2. *Zero-Point Energy (ZPE)*: The zero-point vibrational energy is provided, which is useful for accurate thermodynamic calculations.

```
1              Zero-point correction=   0.074619 (Hartree/Particle)
2
```

  3. *Thermodynamic Properties*: Enthalpy, entropy, and Gibbs free energy are calculated at the specified temperature (298.15 K by default). Heat capacity, thermal energy and partition functions are also included.

```
1                         E (Thermal)            CV                 S
2                          KCal/Mol        Cal/Mol-Kelvin     Cal/Mol-
       Kelvin
3   Total                   49.015             10.109            56.629
4   Electronic               0.000              0.000             0.000
5   Translational            0.889              2.981            36.134
6   Rotational               0.889              2.981            18.480
7   Vibrational             47.237              4.147             2.015
8   Vibration      1         0.696              1.663             1.387
9
10                            Q              Log10(Q)            Ln(Q)
11  Total Bot         0.103238D-23         -23.986160         -55.230175
12  Total V=0         0.216741D+11          10.335941          23.799385
13  Vib (Bot)         0.653836D-34         -34.184531         -78.712792
14  Vib (Bot)    1    0.620740D+00          -0.207090          -0.476843
15  Vib (V=0)         0.137268D+01           0.137571           0.316768
16  Vib (V=0)    1    0.129707D+01           0.112963           0.260107
```

```
17   Electronic        0.100000D+01              0.000000              0.000000
18   Translational     0.647375D+07              6.811156             15.683266
19   Rotational        0.243902D+04              3.387215              7.799351
20
```

4. *IR spectrum and force constants*

1.3   Output visualization

In this section are presented some images taken from the simulation output using Molden:

Nr.	Eigenvalue	Occupation
1	-10.177440	2.00
2	-10.177240	2.00
3	-0.754980	2.00
4	-0.623700	2.00
5	-0.462200	2.00
6	-0.403890	2.00
7	-0.373720	2.00
8	-0.370740	2.00
9	-0.311310	2.00
10	0.016870	0.00
11	0.029710	0.00
12	0.048540	0.00
13	0.058870	0.00

Figure 4: Eigenvalues and occupation levels as computed by Gaussian

(a)   (b)
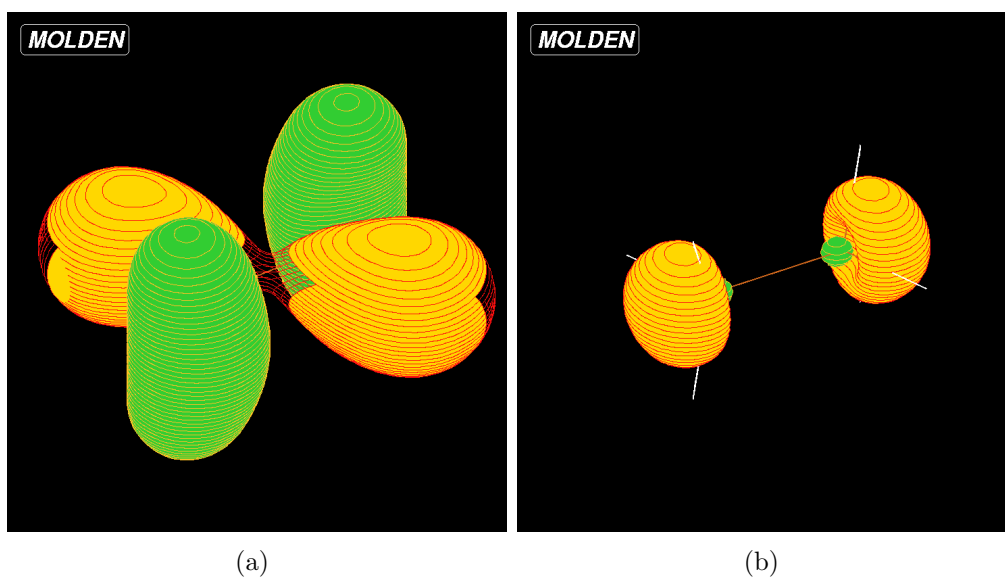
Figure 5: HOMO(a) and LUMO(b) orbitals visualized using isosurfaces (contour value set to 0.05)
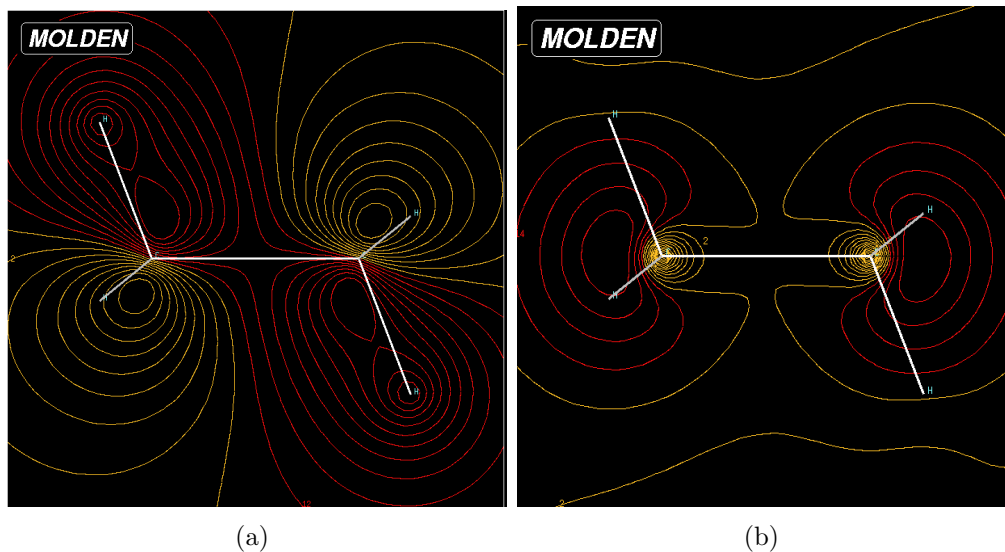
Figure 6: HOMO(a) and LUMO(b) orbitals visualized on euclid plane
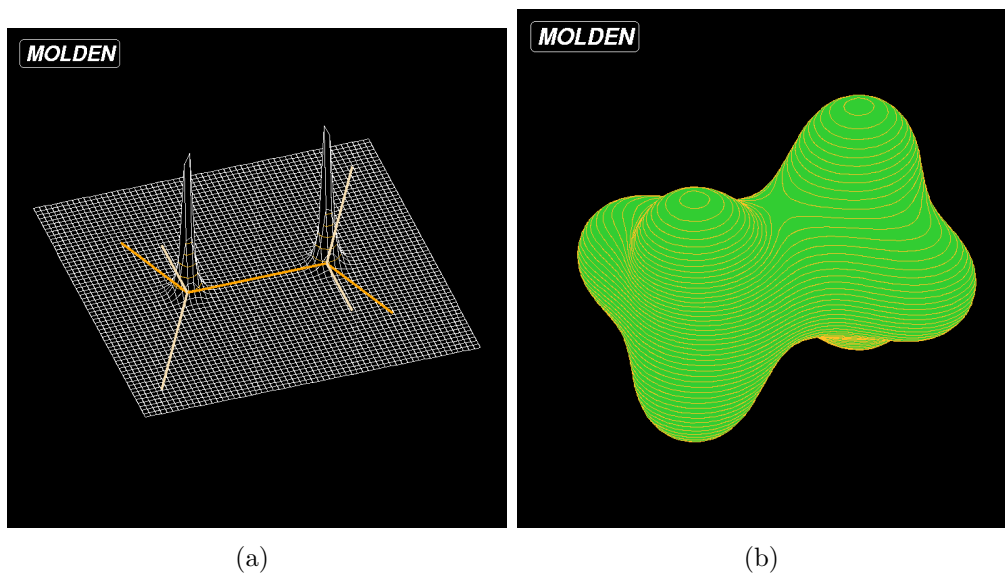
Figure 7: change density as 3D function(a) and using isosurfaces(b)

1.4 Determine how the energy changes as a function of the relative orientation of the methyl groups

A Gaussian-compliant script to compute how the energy of the molecule would change can be found in `/Project2/c2h6/c2h6_scan.com`. It is reported here for convenience:

```
1    #p scan   pop=full gfinput
```

```
 2
 3  ethane
 4
 5  0  1
 6  C1
 7  C2  1  d1
 8  H3  1  d2  2  a1
 9  H4  1  d3  2  a2  3  t1
10  H5  1  d4  2  a3  3  t2
11  H6  2  d5  1  a4  3  t3
12  H7  2  d6  1  a5  6  t4
13  H8  2  d7  1  a6  6  t5
14
15  d1 =1.54
16  d2 =1.09
17  a1 =111.
18  d3 =1.09
19  a2 =111.
20  t1 =108.
21  d4 =1.09
22  a3 =111.
23  t2 = -108.
24  d5 =1.09
25  a4 =111.
26  t3 =180.  36  10.
27  d6 =1.09
28  a5 =111.
29  t4 =108.
30  d7 =1.09
31  a6 =111.
32  t5 = -108.
```

The results of the simulation is then extracted thanks to a Python script and the results are plotted: in particular, a relative rotation of the methyl groups was chosen, considering for each step a 10° difference, for a total of 36 steps (a whole 360° rotation). The results are shown below:
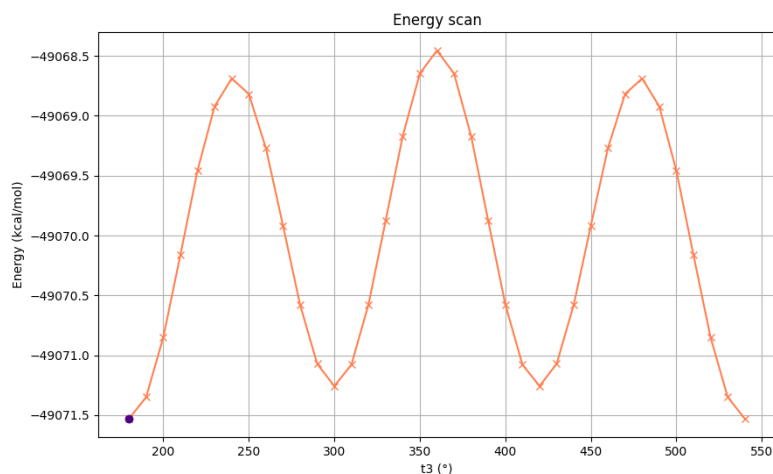
Figure 8: Energy trend for relative rotation of the methyl groups of ethane, starting from the minimum energy configuration. The black dot is the energetic minimum.

The highlighted trend is periodic, as one would expect, with its minimum exactly in the starting/ending point, proof that, at least for the relative-rotational degree of freedom, the optimization process carried out by Gaussian was successful.

2 MOLPRO implementation

An alternative to the use of Gaussian is MOLPRO. Here is the input to reproduce the same kind of computation:

```
***, ethane
print,basis,orbitals
nosym

angstrom
geometry={
C1
C2, C1, d1
H3, C1, d2, C2, a1
H4, C1, d3, C2, a2, H3, t1
H5, C1, d4, C2, a3, H3, t2
H6, C2, d5, C1, a4, H3, t3
H7, C2, d6, C1, a5, H6, t4
H8, C2, d7, C1, a6, H6, t5
}


d1=1.54 Ang
d2=1.09 Ang
```

```
20  a1=111.  Degree
21  d3=1.09  Ang
22  a2=111.  Degree
23  t1=108.  Degree
24  d4=1.09  Ang
25  a3=111.  Degree
26  t2=-108.  Degree
27  d5=1.09  Ang
28  a4=111.  Degree
29  t3=180.  Degree
30  d6=1.09  Ang
31  a5=111.  Degree
32  t4=108.  Degree
33  d7=1.09  Ang
34  a6=111.  Degree
35  t5=-108.  Degree
36
37  basis=6-31G(d,p)
38  hf
39  optg
40  frequencies,analytic
41  put,molden,molpro.molden
42
43  ---
```

3   Propane

We may repeat the same analysis also for propane. The input script for optimization is:

```
1   #p B3LYP/6-31+g(d,p) opt freq pop=full gfinput
2
3   propane
4
5   0  1
6   C1
7   C2  1  dCC
8   C3  1  dCC  2  aCC
9   H4  1  d1  2  a1  3  t1
10  H5  1  d1  2  a1  4  t2
11  H6  2  d2  1  a2  3  t3
12  H7  3  d2  1  a2  2  t3
13  H8  2  d3  1  a3  6  t4
14  H9  2  d3  1  a3  6  t5
15  H10  3  d3  1  a3  7  t4
16  H11  3  d3  1  a3  7  t5
17
18  dCC=1.526
19  aCC=112.4
20  d1=1.096
21  a1=109.56
```
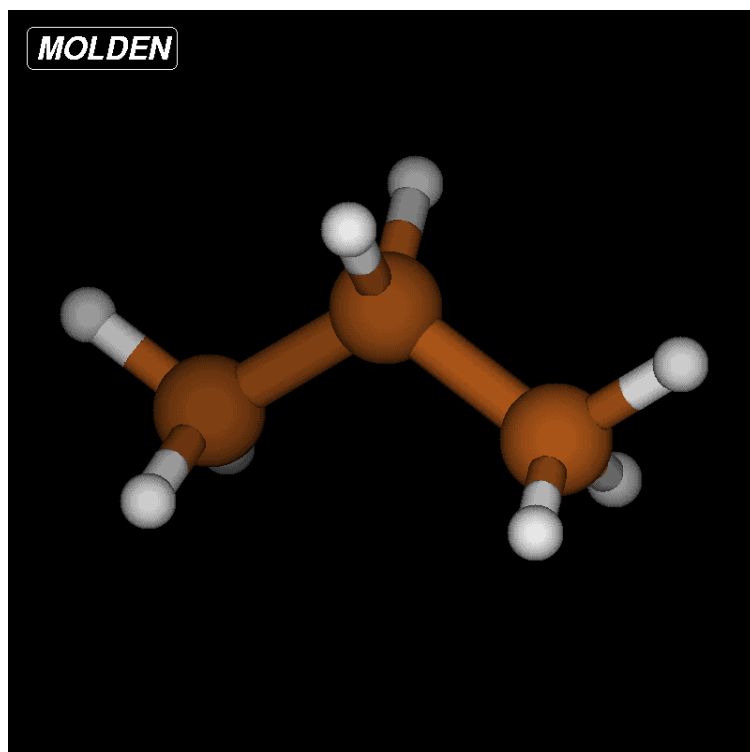
Figure 9: Ball and Stick representation of propane in Molden

```
22  t1 =126.95
23  t2 =106.1
24  d2 =1.089
25  a2 =111.8
26  t3 =180.
27  d3 =1.094
28  a3 =110.6
29  t4 =107.3
30  t5 = -107.3
```
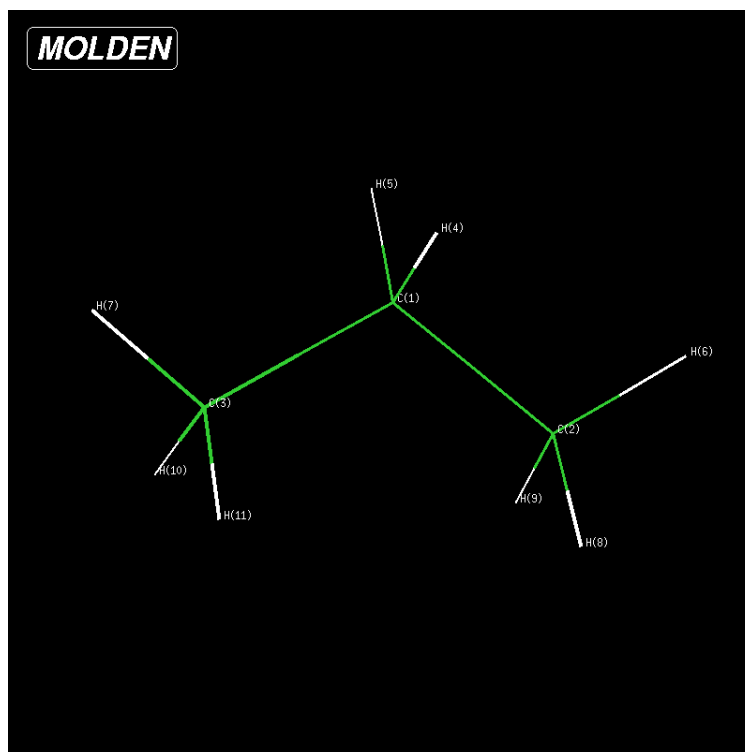
Figure 10: Carbon and Hydrogen labelled configuration for propane, visualized using Molden

3.1 Find the energy in the output file and save it

The final energy for the optimization run using Gaussian is:

```
SCF Done:   E(RB3LYP) =   -119.159151839      A.U.
```

3.2 Output visualization

In this section, some visualizations of the results for propane are shown: as before, HOMO, LUMO, charge density are plotted. The spectrum for propane is also shown.

Nr.	Eigenvalue	Occupation
1	-10.182250	2.00
2	-10.175250	2.00
3	-10.173280	2.00
4	-0.781650	2.00
5	-0.687440	2.00
6	-0.587750	2.00
7	-0.467670	2.00
8	-0.436550	2.00
9	-0.412120	2.00
10	-0.370870	2.00
11	-0.331650	2.00
12	-0.329180	2.00
13	-0.318930	2.00

Figure 11: Eigenvalues and occupation levels as computed by Gaussian

(a)   (b)
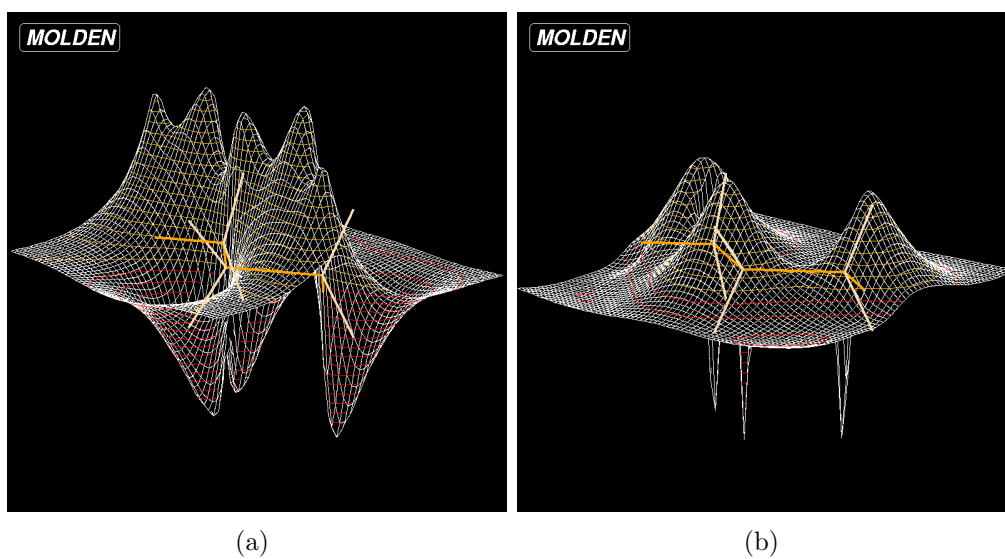
Figure 12: HOMO(a) and LUMO(b) orbitals visualized as 3D functions)
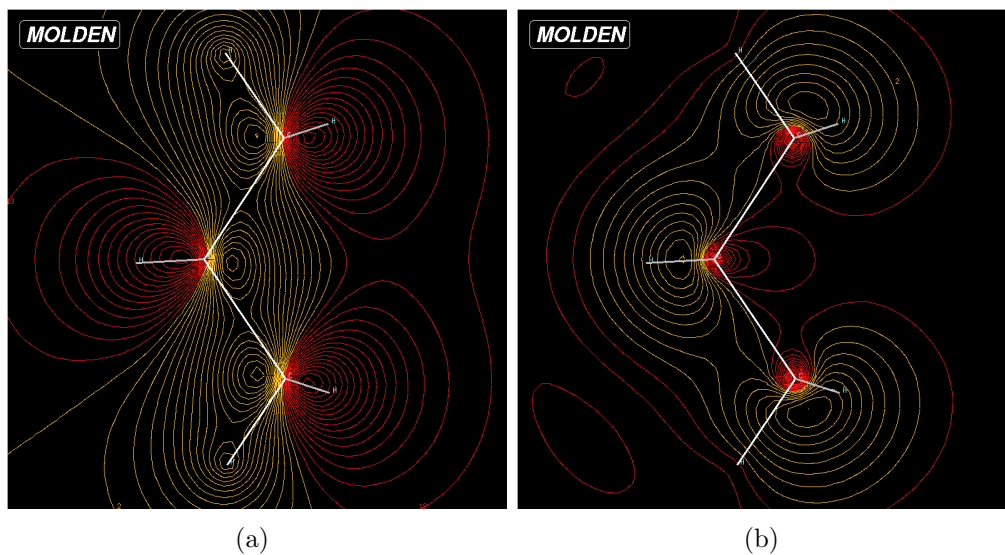
Figure 13: HOMO(a) and LUMO(b) orbitals visualized on euclid plane
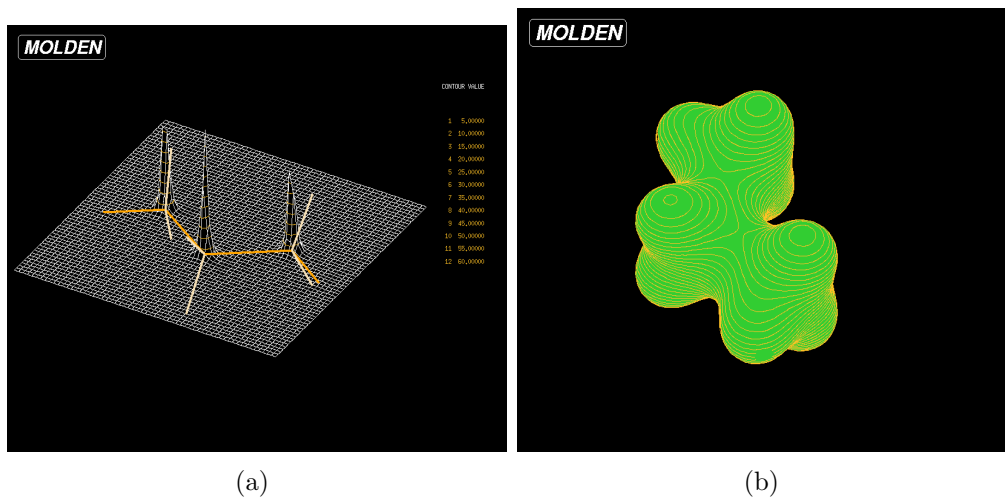

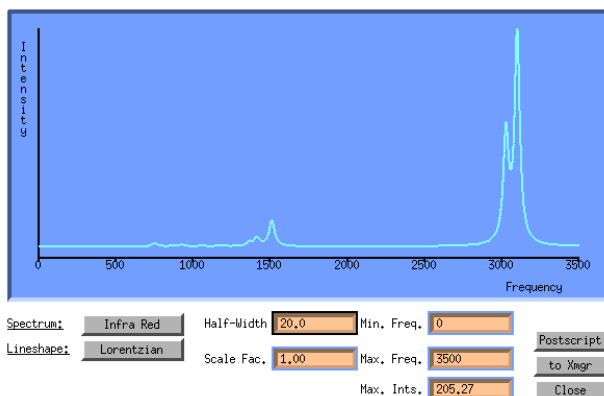Figure 14: change density as 3D function(a) and using isosurfaces(b)

Figure 15: Frequency analysis for propane

3.3 Determine how the energy changes as a function of the relative orientation of the methyl groups

For propane, an analysis, similar to the scan of energies based on relative position carried out for ethane, as also been included. In this case, the group of atoms been rotated with respect to the other ones is the CH_2 at the central position. The used script it the following:

```
1  #p scan pop=full gfinput
2
3  propane
4
5  0 1
6  C1
7  C2 1 dCC
8  C3 1 dCC 2 aCC
9  H4 1 d1 2 a1 3 t1
10 H5 1 d1 2 a1 4 t2
11 H6 2 d2 1 a2 3 t3
12 H7 3 d2 1 a2 2 t3
13 H8 2 d3 1 a3 6 t4
14 H9 2 d3 1 a3 6 t5
15 H10 3 d3 1 a3 7 t4
16 H11 3 d3 1 a3 7 t5
17
18 dCC=1.526
19 aCC=112.4
20 d1=1.096
21 a1=109.56
22 t1=126.95 18 20.
23 t2=106.1
24 d2=1.089
25 a2=111.8
26 t3=180.
27 d3=1.094
```

```
28  a3=110.6
29  t4=107.3
30  t5=-107.3
```

The energy results have been extracted from the `log` file once again and finally plotted, leading to similar results:
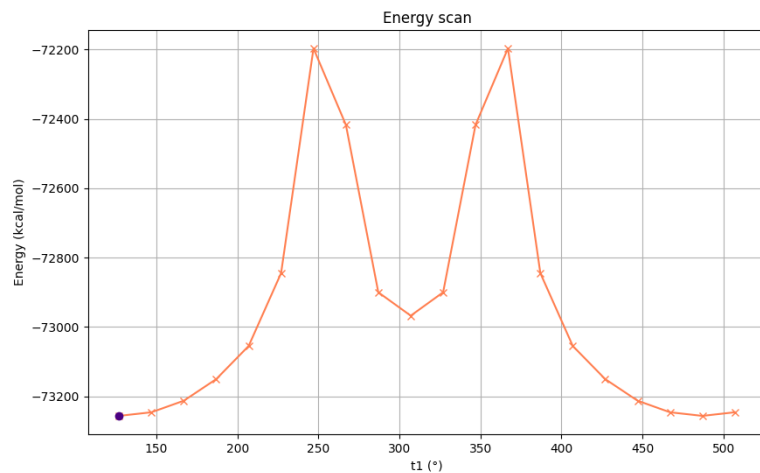

Figure 16: Energy trend for relative rotation of the central CH_2 group, starting from the minimum energy configuration. The black dot is the energetic minimum.