



# **POLITECNICO**

## **MILANO 1863**

### **Report of Assigned Projects 1,2,3**

## **Molecular Modeling for Process Engineering**

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*by*

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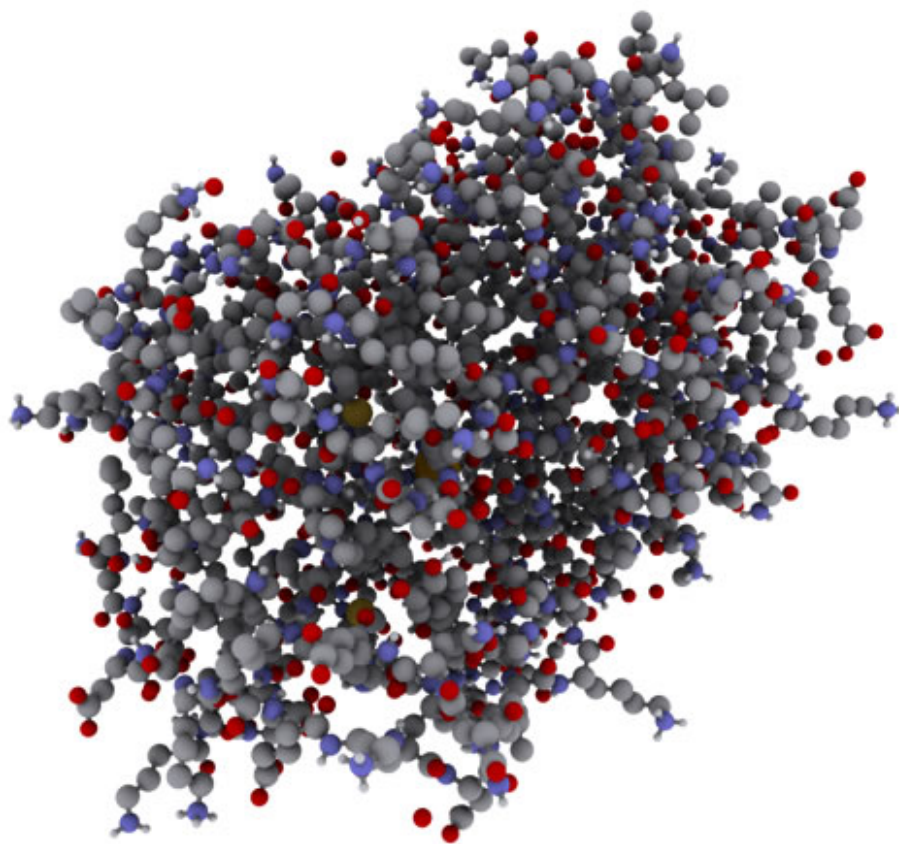
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## 1 Introduction

In this report, I will try to answer to all the questions about practicals of the course of **Molecular Modeling in Process Engineering**. For each practical, I will dedicate a section and I will provide concise answers with the help of any formulas and theoretical annexes.



## 2 Project 1

### Estimation of quantized properties

1. Determine the zero point energy of a methane molecule in a box having the dimension of 1 m. For a particle in a 3D box with sides  $a$ ,  $b$ , and  $c$ , the energy levels are given by the formula:

$$E(n_x, n_y, n_z) = \frac{h^2}{8m} \left( \frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right) \quad (1)$$

where:

- $h$  is the Planck's constant,
- $m$  is the mass of the particle,
- $n_x$ ,  $n_y$  and  $n_z$  are the quantum numbers along the  $x$ ,  $y$ , and  $z$  axes, respectively

In our case  $a = b = c = 1 \text{ m}$ , so the energy levels formula becomes:

$$E(n_x, n_y, n_z) = \frac{h^2}{8m} (n_x^2 + n_y^2 + n_z^2) \quad (2)$$

We aim to find the zero point energy, this corresponds to the ground state energy level, with the quantum numbers  $n_x$ ,  $n_y$  and  $n_z$  all equal to 1:

$$E_{ZPE} = E(1, 1, 1) = \frac{3h^2}{8m} \quad (3)$$

$\text{CH}_4$  has a mass equal to:

$$m_C = 12,011 \text{ u} \quad (4)$$

$$m_H = 1,00784 \text{ u}, \text{ so:} \quad (5)$$

$$m_{\text{CH}_4} = 4 \times m_H + m_C = 4 \times 1,00784 \text{ u} + 12,011 \text{ u} = 16.04236 \text{ u} = 2,66303176 \cdot 10^{-26} \text{ kg} \quad (6)$$

Then:

$$E_{ZPE} = \frac{3h^2}{8m} = 2,1 \cdot 10^{-21} \text{ J} = 0,0131072 \text{ eV} = 0,00048168 \text{ Hartree} \quad (7)$$

2. Determine the energy of the orbitals of atomic hydrogen, and the energy necessary for excitation between different orbitals.

To find the lowest energy levels, we will increment the quantum numbers  $n_x$ ,  $n_y$  and  $n_z$  and find the unique energy levels corresponding to each combination. We will also count the number of different ways each energy level can be reached (i.e., degeneracy of energy level). Let's assume we are in a one-dimensional case ( $a = 1 \text{ m}$ ).

- (a) First Level ( $n_x^2 + n_y^2 + n_z^2 = 6$ )

$$E(1, 2, 1) = E(2, 1, 1) = E(1, 1, 2) = \frac{h^2}{8ma^2} \times 6 \quad (8)$$

- (b) Second Level ( $n_x^2 + n_y^2 + n_z^2 = 9$ )

$$E(1, 3, 1) = E(3, 1, 1) = E(1, 1, 3) = \frac{h^2}{8ma^2} \times 9 \quad (9)$$

- (c) Third Level ( $n_x^2 + n_y^2 + n_z^2 = 12$ )

$$E(2, 3, 1) = E(3, 2, 1) = E(2, 1, 3) = E(3, 1, 2) = E(1, 3, 2) = E(1, 2, 3) = \frac{h^2}{8ma^2} \times 12 \quad (10)$$

And so on. The energy necessary for excitation between different orbitals is computed as the difference between the energy levels. So we can compute the energy excitations for hydrogen keeping in mind that it has a mass equal to  $m_H = 1,00784 u$ . So:

$$E_{1 \rightarrow 2} = E_2 - E_1 = \frac{h^2}{8ma^2} \times 9 - \frac{h^2}{8ma^2} \times 6 = \frac{h^2}{8ma^2} \times (9 - 6) = \frac{h^2}{8ma^2} \times 3 \quad (11)$$

$$E_{2 \rightarrow 3} = E_3 - E_2 = \frac{h^2}{8ma^2} \times 12 - \frac{h^2}{8ma^2} \times 9 = \frac{h^2}{8ma^2} \times (12 - 9) = \frac{h^2}{8ma^2} \times 3 \quad (12)$$

$$E_{1 \rightarrow 3} = E_3 - E_1 = \frac{h^2}{8ma^2} \times 12 - \frac{h^2}{8ma^2} \times 6 = \frac{h^2}{8ma^2} \times (12 - 6) = \frac{h^2}{8ma^2} \times 6 \quad (13)$$

These result in:

$$E_{1 \rightarrow 2} = E_2 - E_1 = 1,33841152 \cdot 10^{-26} J \times 3 = 3,0699 \cdot 10^{-9} \times 3 = 9,209 \cdot 10^{-9} \text{ Hartree} \quad (14)$$

$$E_{2 \rightarrow 3} = E_3 - E_2 = 1,33841152 \cdot 10^{-26} J \times 3 = 3,0699 \cdot 10^{-9} \times 3 = 9,209 \cdot 10^{-9} \text{ Hartree} \quad (15)$$

$$E_{1 \rightarrow 3} = E_3 - E_1 = 3,0699 \cdot 10^{-9} \times 6 = 1,842 \cdot 10^{-8} \text{ Hartree} \quad (16)$$

3. Draw the 1s, 2s, 2p<sub>x</sub>, 2p<sub>y</sub>, and 2p<sub>z</sub> orbitals on a xy plane

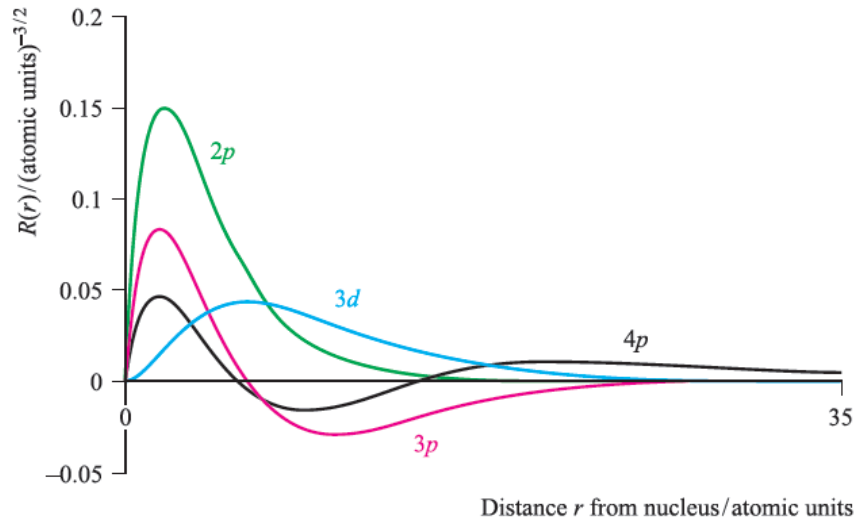


Figure 1: Atomic Orbitals

4. Determine the average distance of an electron in a 1s, 2s, 2p<sub>x</sub>, 2p<sub>y</sub>, and 2p<sub>z</sub> orbital from the nuclei.

Wavefunction of the hydrogen 1s electron is:

$$\psi = \frac{1}{\sqrt{\pi}} \left( \frac{1}{a_0} \right)^{\frac{3}{2}} e^{-\frac{r}{a_0}} \quad (17)$$

Now the probability of finding an electron at a distance  $r$  from the nucleus is  $\psi^2 4\pi r^2 dr$ , this is because  $\psi^2$  is the probability density and  $4\pi r^2 dr$  is the volume in consideration.

$$\psi^2 = \frac{1}{\pi} \left( \frac{1}{a_0} \right)^3 e^{-\frac{2r}{a_0}} \quad (18)$$

$$\psi^2 (4\pi r^2 dr) = 4 \frac{r^2}{a_0^3} e^{-\frac{2r}{a_0}} dr \quad (19)$$

$$dP(r) = 4 \frac{r^2}{a_0^3} e^{-\frac{2r}{a_0}} dr \quad (20)$$



Now mathematically,

$$\bar{r} = \int_0^{\infty} r dP(r) \quad (21)$$

$$\bar{r} = \int_0^{\infty} 4 \frac{r^2}{a_0^3} e^{-\frac{2r}{a_0}} dr \quad (22)$$

Now using integral by parts,

$$\bar{r} = \left[ 2 \frac{r^3}{a_0^2} e^{-\frac{2r}{a_0}} - 3 \frac{r^2}{a_0} e^{-\frac{2r}{a_0}} - 3r e^{-\frac{2r}{a_0}} - \frac{3}{2} a_0 e^{-\frac{2r}{a_0}} \right]_0^{\infty} \quad (23)$$

$$\bar{r} = (0 + 0 + 0 + 0) - \left( 0 + 0 + 0 - \frac{3}{2} a_0 \right) \quad (24)$$

$$\bar{r} = \frac{3}{2} a_0 \approx 79,35 \text{pm} \quad (25)$$

where  $a_0 = 0,53\text{\AA}$  is the Bohr's radius.

Therefore an electron in 1s orbital of an hydrogen atom is at an average distance of 79,35pm from the nucleus.

These type of calculation can be reproduced as well as all the other waverfunctions for each different orbital.



## 3 Project 2

### 3.1 Ethane

#### 3.1.1 Gaussian code

1. Write the input for C<sub>2</sub>H<sub>6</sub> (ethane) and save the file and start the calculations: (**g09 c2h6.com &**)

```
1 %chk=tmp
2 %mem=100MB
3
4 #p B3LYP/6-31+g(d,p) opt pop=full ginput
5
6 Ethane molecule
7
8 0 1
9 C1
10 C2 1 d1
11 H3 1 d2 2 a1
12 H4 2 d2 1 a1 3 t1
13 H5 1 d2 2 a1 4 t2
14 H6 2 d2 1 a1 5 t3
15 H7 1 d2 2 a1 6 t4
16 H8 2 d2 1 a1 7 t5
17
18 d1                1.5
19 d2                1.1
20 a1                109.5
21 t1                180.
22 t2                60.
23 t3               -60.
24 t4                180.
25 t5                60.
```

2. Open the output and examine the result (**emacs c2h6.log**). Correct eventual errors and proceed until you obtain a converged geometry.

```
1          Item                Value      Threshold  Converged?
2  Maximum Force              0.000130      0.000450      YES
3  RMS      Force              0.000037      0.000300      YES
4  Maximum Displacement        0.000366      0.001800      YES
5  RMS      Displacement        0.000211      0.001200      YES
6  Predicted change in Energy=-1.424287D-07
7  Optimization completed.

1  SCF Done:  E(RB3LYP) =  -79.8416412851      A.U. after    5 cycles
2                  Convgt =   0.6007D-08                  -V/T =   2.0110
3  KE=  7.897088919612D+01  PE=-2.679330629561D+02  EE=  6.702166235271D+01
```

3. Visualize the output using Molden, with the command **molden c2h6.log**

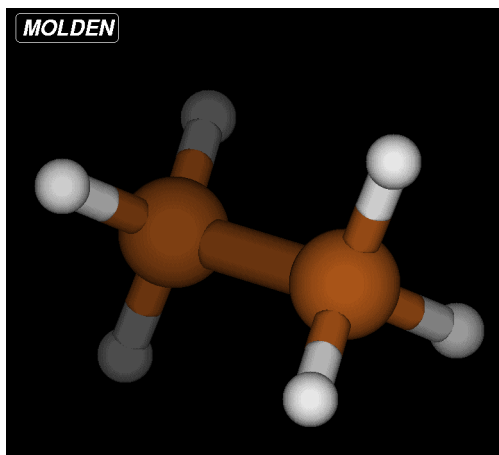


Figure 2: Ethane molecule seen with Molden.

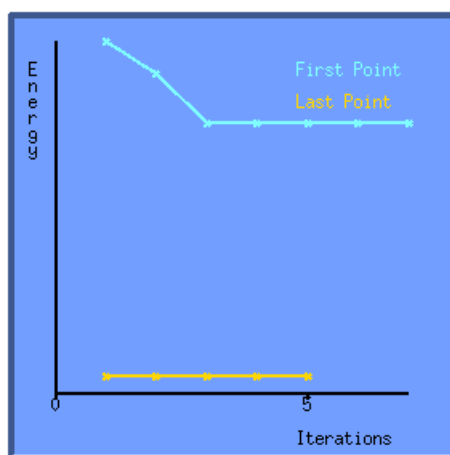


Figure 3: Energy convergence.



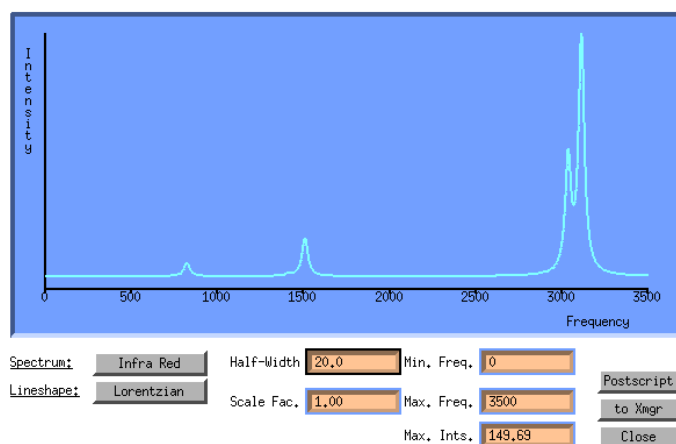


Figure 4: Spectrum of ethane

4. Visualize the orbitals. For this purpose the command lines must be modified as follow: for G09 you have to add in the input line the keyword **pop=full gfnput**.

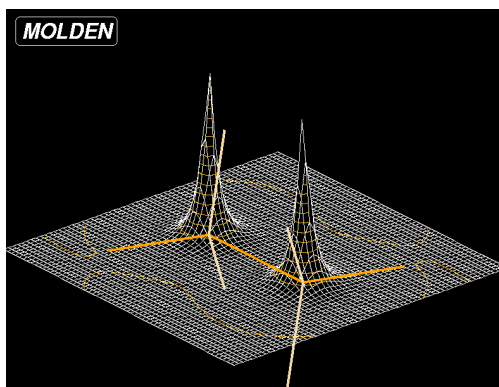


Figure 5: Orbital with lowest energy seen in Molden.

5. Once you have run the calculation, you must: find the energy in the output file and save it. Moreover, examine critically the output file and try to understand what has been done in the calculation.

#### Calculation of the energies of the molecule of ethane

##### Gaussian

Input code:

```

1 %chk=tmp
2 %mem=100MB
3
4 #p B4LYP/6-31+g(d,p) opt freq
5
6 Ethane molecule
7
8 0 1
9 C1
10 C2 1 d1
11 H3 1 d2 2 a1
12 H4 2 d2 1 a1 3 t1

```

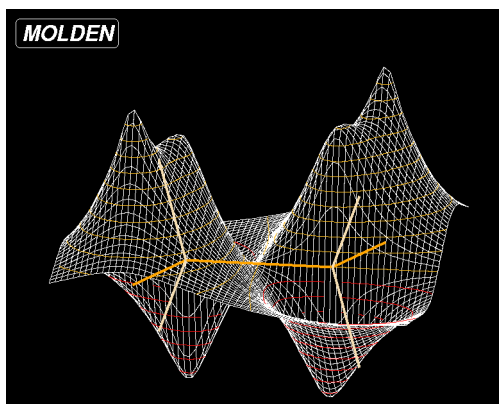


Figure 6: Ethane's HOMO.

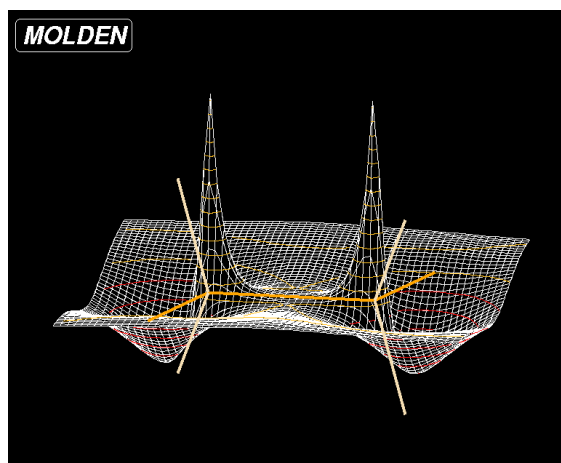


Figure 7: Ethane's LUMO.

```

13 H5 1 d2 2 a1 4 t2
14 H6 2 d2 1 a1 5 t3
15 H7 1 d2 2 a1 6 t4
16 H8 2 d2 1 a1 7 t5
17
18 d1          1.5
19 d2          1.1
20 a1        109.5
21 t1        180.
22 t2         60.
23 t3        -60.
24 t4        180.
25 t5         60.

```

The output file:

```

1 Zero-point correction=          0.074606 (Hartree/
   Particle)
2 Thermal correction to Energy=      0.078093
3 Thermal correction to Enthalpy=    0.079037
4 Thermal correction to Gibbs Free Energy= 0.053177
5 Sum of electronic and zero-point Energies= -79.767035

```



6	Sum of electronic and thermal Energies=	-79.763548		
7	Sum of electronic and thermal Enthalpies=	-79.762604		
8	Sum of electronic and thermal Free Energies=	-79.788465		
9				
10	E (Thermal)	CV	S	
11	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin	
12	Total	49.004	10.096	54.428
13	Electronic	0.000	0.000	0.000
14	Translational	0.889	2.981	36.134
15	Rotational	0.889	2.981	16.296
16	Vibrational	47.227	4.135	1.998
17	Vibration 1	0.698	1.658	1.372

### 3.1.2 Molpro code

Input code:

```
1 memory=50MW
2 nosym
3 geometry={angstrom
4     C1
5     C2 1 d1
6     H3 1 d2 2 a1
7     H4 1 d3 2 a2 3 t1
8     H5 1 d4 2 a3 3 t2
9     H6 2 d5 1 a4 3 t3
10    H7 2 d6 1 a5 3 t4
11    H8 2 d7 1 a6 3 t5
12 }
13
14 d1=1.05
15 a1=110.
16 t1=120.
17 d2=1.03
18 a2=110.
19 t2=-120.
20 d3=1.05
21 d4=1.09
22 d5=1.09
23 d6=1.09
24 d7=1.09
25 t3=60.
26 t4=120.
27 t5=-120.
28 a3=110.
29 a4=110.
30 a5=110.
31 a6=110.
32
33
34 !closed shell input
35 basis=6-31G(d,p)
36
37 hf
```



```
38 !{multi;closed, 10;occ, 16;wf, 26,1,0;state,1 ;maxiter,40}  
39 put,molden,molpro.molden
```

The output report the same results found with Gaussian. Some important results are below reported.

```
1      HF-SCF  
2      -78.77709693
```

This is the Self-Consistent field energy found with the Hartree-Fock theory. We can see that is pretty similar with the one reported in Gaussian (  $E(\text{RB3LYP}) = -79.8416412851$  Hartree ).

Eigenvalues of molecular orbitals listed by Molpro:

```
1  DUMP ORBITAL  1.1 AS ORBITAL    1  occ=    2.0000  eig=   -11.1781  
   GROUP=      2  
2  DUMP ORBITAL  2.1 AS ORBITAL    2  occ=    2.0000  eig=   -11.1623  
   GROUP=      2  
3  DUMP ORBITAL  3.1 AS ORBITAL    3  occ=    2.0000  eig=    -1.1997  
   GROUP=      2  
4  DUMP ORBITAL  4.1 AS ORBITAL    4  occ=    2.0000  eig=    -0.8403  
   GROUP=      2  
5  DUMP ORBITAL  5.1 AS ORBITAL    5  occ=    2.0000  eig=    -0.7355  
   GROUP=      2  
6  DUMP ORBITAL  6.1 AS ORBITAL    6  occ=    2.0000  eig=    -0.6576  
   GROUP=      2  
7  DUMP ORBITAL  7.1 AS ORBITAL    7  occ=    2.0000  eig=    -0.6044  
   GROUP=      2  
8  DUMP ORBITAL  8.1 AS ORBITAL    8  occ=    2.0000  eig=    -0.4521  
   GROUP=      2  
9  DUMP ORBITAL  9.1 AS ORBITAL    9  occ=    2.0000  eig=    -0.3122  
   GROUP=      2
```

We can see that the eigenvalues of molecular orbitals listed above are pretty similar to the one reported by Gaussian:

Nr.	Eigenvalue	Occupation
1	-10.176380	2.00
2	-10.176120	2.00
3	-0.760620	2.00
4	-0.608380	2.00
5	-0.441610	2.00
6	-0.441610	2.00
7	-0.364340	2.00
8	-0.342390	2.00
9	-0.342390	2.00

Figure 8: Eigenvalues of ethane's first molecular orbitals seen by the Molden configuration

The Nuclear Repulsion Energy computed by Molpro:

```
1  NUCLEAR REPULSION ENERGY    51.00511309
```

and the one computed by Gaussian:

```
1  nuclear repulsion energy      41.9922492592 Hartrees
```

We can see that we have a difference of approximately 9 Hartrees between the two energies.

- Determine how the energy changes as a function of the relative orientation of the methyl groups (take 12 points with steps of 10 degrees).

1	Summary of the potential surface scan:		
2	N	t3	SCF
3	1	-90.0000	-78.23171
4	2	-80.0000	-78,27188
5	3	-70.0000	-78,29538
6	4	-60.0000	-78.30312
7	5	-50.0000	-78.29537
8	6	-40.0000	-78.27176
9	7	-30.0000	-78.23130
10	8	-20.0000	-78.17260
11	9	-10.0000	-78.09427
12	10	0.0000	-77.99528
13	11	10.0000	-77.87369
14	12	20.0000	-77.71792
15	13	30.0000	-77.46649
16	14	40.0000	-76.84347
17	15	50.0000	-74.33236

Plot:

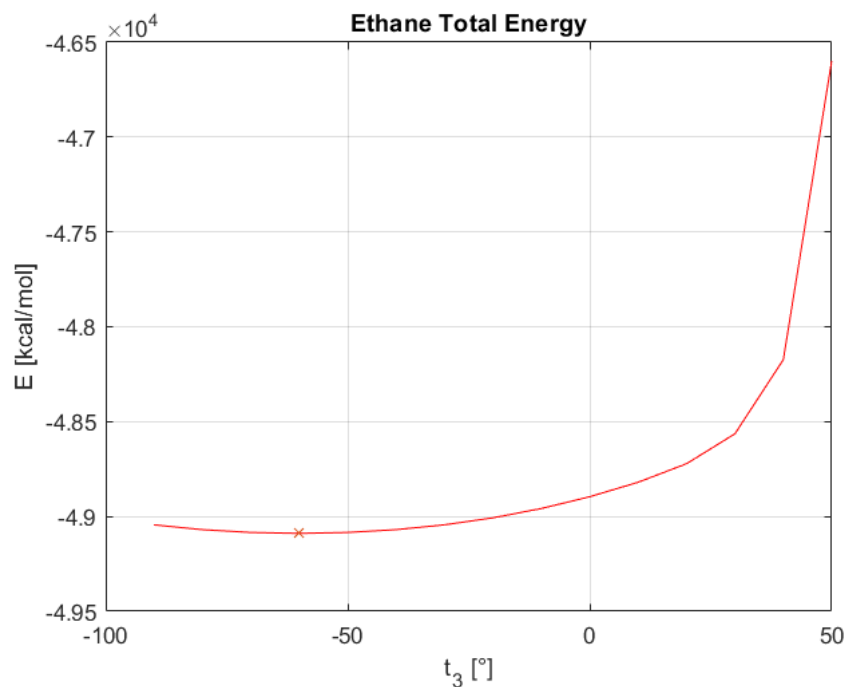


Figure 9: Plot depicting the trend of the total energy of the molecule as the angle  $t_3$  of the dihedral formed by the two C atoms and a reference hydrogen (indeed a methyl group) varies.

We can see, from the plot created with MatLab, a minimum corresponding when the molecule reaches a configuration with the angle  $t_3$  equal to 60 degrees. Every Self-Consistent Field energies found in Gaussian have been converted from Hartree to kcal/mol and subsequently the contribution given by the zero point correction energy ( $ZPE_{ethane} = 0,074606$  Hartree = 46,81598 kcal/mol) was added to each of them obtaining the total energy of the molecule.



## 3.2 Propane

### 3.2.1 Gaussian code

1. Write the input for C<sub>3</sub>H<sub>8</sub> (propane) and save the file and start the calculations: (**g09 c3h8.com &**).

Input code:

```

1 %chk=tmp
2 %mem=100MB
3
4 #p B3LYP/6-31+g(d,p) opt freq pop=full ginput
5
6 Propane
7
8 0 1
9 C1
10 X          1      1.
11 C2          1      rc      2      accx
12 C3          1      rc      2      accx      3      180.
13 H4          1      rh1     2      ahcx      3      90.
14 H5          1      rh1     2      ahcx      3      -90.
15 H6          3      rh2     1      ah2       2      0.
16 H7          4      rh2     1      ah2       2      0.
17 H8          3      rh3     1      ah3       7      dh3
18 H9          3      rh3     1      ah3       7      dh4
19 H10         4      rh3     1      ah3       8      dh3
20 H11         4      rh3     1      ah3       8      dh4
21
22 rc          =          1.5482
23 rh1         =          1.09
24 rh2         =          1.09
25 rh3         =          1.09
26 accx        =          120.
27 ahcx        =          55.
28 ah2         =          111.
29 ah3         =          111.
30 dh3         =          120.
31 dh4         =          -60.

```

2. Open the output and examine the result (**emacs c3h8.log**). Correct eventual errors and proceed until you obtain a converged geometry.

```

1      Item                Value      Threshold  Converged?
2  Maximum Force           0.000015    0.000450    YES
3  RMS Force               0.000007    0.000300    YES
4  Maximum Displacement    0.000243    0.001800    YES
5  RMS Displacement        0.000100    0.001200    YES

1      SCF Done:  E(RB3LYP) = -119.159151901      A.U. after 1 cycles
2      Convrg = 0.1978D-08      -V/T = 2.0108
3  KE= 1.178843168862D+02 PE=-4.389483215940D+02 EE= 1.196680016951D+02

```

3. Visualize the output using Molden, with the command **molden c3h8.log**

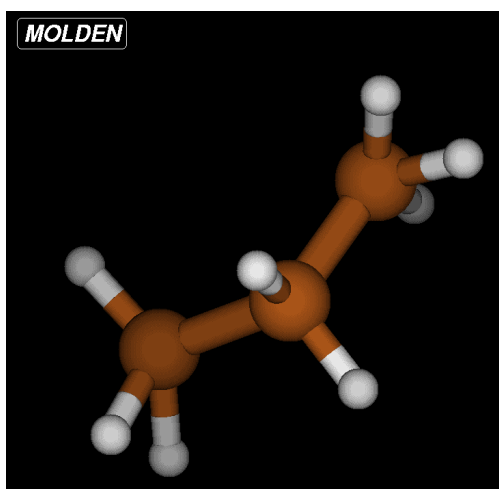


Figure 10: Propane molecule seen with Molden.

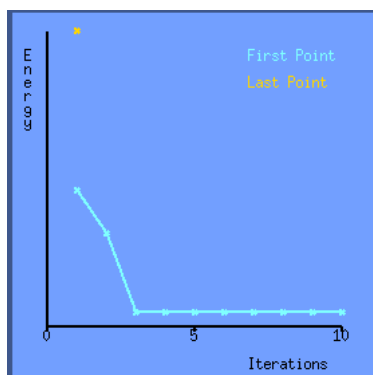


Figure 11: Energy convergence.

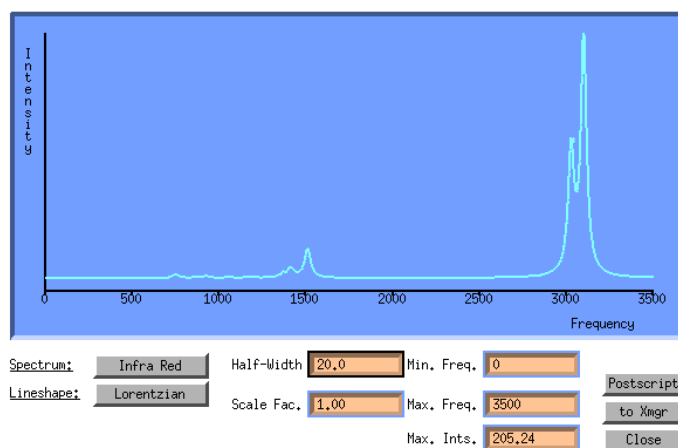


Figure 12: Spectrum of propane.

4. Visualize the orbitals.
5. Once you have run the calculation, you must: find the energy in the output file and save it.

#### **Calculation of the energies of the molecule of propane**

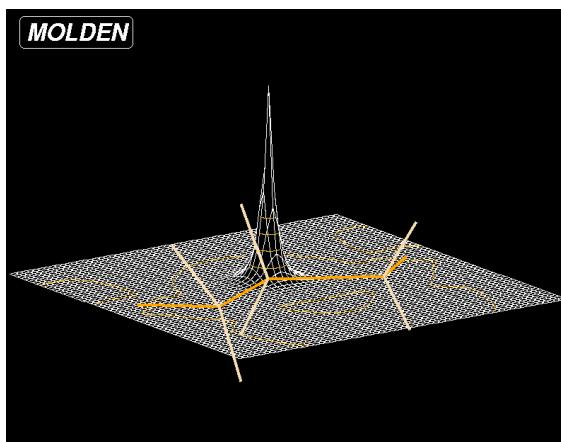


Figure 13: Orbital with lowest energy seen in Molden.

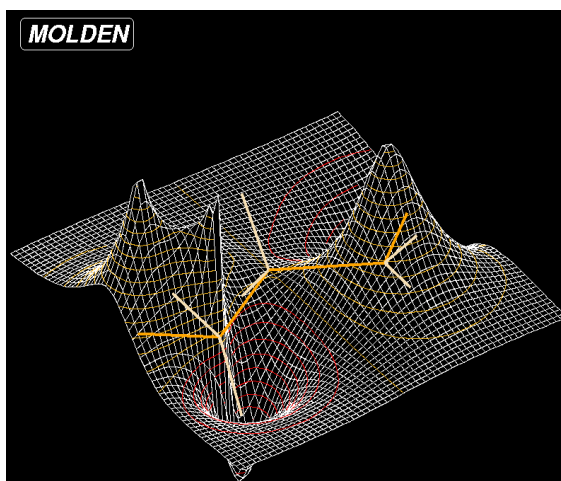


Figure 14: Propane's HOMO

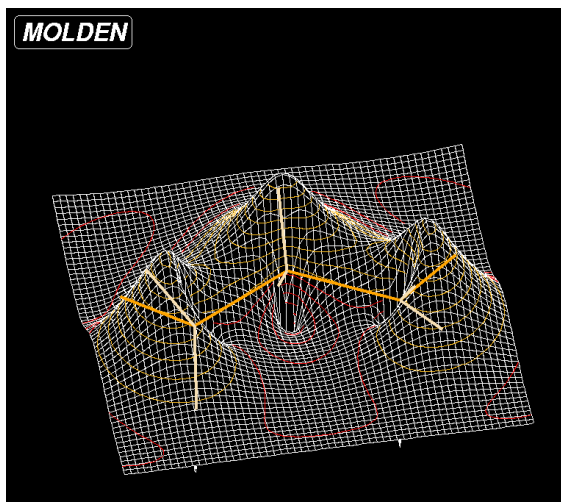


Figure 15: Propane's LUMO





## Gaussian

Input code:

```
1 %chk=tmp
2 %mem=100MB
3
4 #p B3LYP/6-31+g(d,p) opt freq
5
6 Propane
7
8 0 1
9 C1
10 X          1      1.
11 C2          1      rc      2      accx
12 C3          1      rc      2      accx      3      180.
13 H4          1      rh1     2      ahcx      3      90.
14 H5          1      rh1     2      ahcx      3      -90.
15 H6          3      rh2     1      ah2       2      0.
16 H7          4      rh2     1      ah2       2      0.
17 H8          3      rh3     1      ah3       7      dh3
18 H9          3      rh3     1      ah3       7      dh4
19 H10         4      rh3     1      ah3       8      dh3
20 H11         4      rh3     1      ah3       8      dh4
21
22 rc          =          1.5482
23 rh1         =          1.09
24 rh2         =          1.09
25 rh3         =          1.09
26 accx        =          120.
27 ahcx        =          55.
28 ah2         =          111.
29 ah3         =          111.
30 dh3         =          120.
31 dh4         =          -60.
```

The output file:

```
1 Zero-point correction=          0.103276 (Hartree/
   Particle)
2 Thermal correction to Energy=          0.107820
3 Thermal correction to Enthalpy=          0.108765
4 Thermal correction to Gibbs Free Energy=          0.078246
5 Sum of electronic and zero-point Energies=          -119.055876
6 Sum of electronic and thermal Energies=          -119.051332
7 Sum of electronic and thermal Enthalpies=          -119.050387
8 Sum of electronic and thermal Free Energies=          -119.080906
9
10                               E (Thermal)          CV          S
11                               KCal/Mol          Cal/Mol-Kelvin          Cal/Mol-Kelvin
12 Total                          67.658          14.825          64.231
13 Electronic                     0.000          0.000          0.000
14 Translational                   0.889          2.981          37.275
15 Rotational                      0.889          2.981          21.318
16 Vibrational                    65.881          8.863          5.638
17 Vibration      1              0.646          1.815          1.981
```



18	Vibration	2	0.673	1.730	1.602
19	Vibration	3	0.739	1.543	1.097
20			Q	Log10(Q)	Ln(Q)
21	Total Bot		0.102166D-35	-35.990695	-82.871637
22	Total V=0		0.325791D+12	11.512939	26.509523
23	Vib (Bot)		0.873263D-47	-47.058855	-108.357017
24	Vib (Bot)	1	0.910988D+00	-0.040488	-0.093226
25	Vib (Bot)	2	0.718506D+00	-0.143570	-0.330581
26	Vib (Bot)	3	0.499145D+00	-0.301774	-0.694859
27	Vib (V=0)		0.278471D+01	0.444779	1.024142
28	Vib (V=0)	1	0.153918D+01	0.187290	0.431251
29	Vib (V=0)	2	0.137536D+01	0.138416	0.318714
30	Vib (V=0)	3	0.120650D+01	0.081528	0.187725
31	Electronic		0.100000D+01	0.000000	0.000000
32	Translational		0.114964D+08	7.060560	16.257541
33	Rotational		0.101765D+05	4.007600	9.227839

### 3.2.2 Molpro code

Input code:

```

1 memory=500MW
2 nosym
3 geometry={angstrom
4 C1
5 X          1      1.
6 C2          1      rc      2      accx
7 C3          1      rc      2      accx      3      180.
8 H4          1      rh1     2      ahcx      3      90.
9 H5          1      rh1     2      ahcx      3      -90.
10 H6          3      rh2     1      ah2       2      0.
11 H7          4      rh2     1      ah2       2      0.
12 H8          3      rh3     1      ah3       7      dh3
13 H9          3      rh3     1      ah3       7      dh4
14 H10         4      rh3     1      ah3       8      dh3
15 H11         4      rh3     1      ah3       8      dh4
16 }
17
18 rc          =          1.5482
19 rh1         =          1.09
20 rh2         =          1.09
21 rh3         =          1.09
22 accx        =          120.
23 ahcx        =          55.
24 ah2         =          111.
25 ah3         =          111.
26 dh3         =          120.
27 dh4         =          -60.
28
29
30 !closed shell input
31 basis=6-31G(d,p)
32
33 hf

```



```
34    !{multi;closed, 10;occ, 16;wf, 26,1,0;state,1 ;maxiter,40}  
35    put,molden,molpro.molden
```

Some comparisons with Gaussian output:

```
1      HF-SCF  
2      -118.05938129
```

This is the Self-Consistent field energy found with the Hartree-Fock theory. We can see that is quite consistent with the one reported in Gaussian (  $E(\text{RB3LYP}) = -119.159151901$  Hartree )

Eigenvalues of molecular orbitals listed by Molpro:

```
1  DUMP ORBITAL  1.1 AS ORBITAL    1  occ=    2.0000  eig=   -11.2180  
   GROUP=    2  
2  DUMP ORBITAL  2.1 AS ORBITAL    2  occ=    2.0000  eig=   -11.2064  
   GROUP=    2  
3  DUMP ORBITAL  3.1 AS ORBITAL    3  occ=    2.0000  eig=   -11.2064  
   GROUP=    2  
4  DUMP ORBITAL  4.1 AS ORBITAL    4  occ=    2.0000  eig=    -1.0532  
   GROUP=    2  
5  DUMP ORBITAL  5.1 AS ORBITAL    5  occ=    2.0000  eig=    -0.9724  
   GROUP=    2  
6  DUMP ORBITAL  6.1 AS ORBITAL    6  occ=    2.0000  eig=    -0.8248  
   GROUP=    2  
7  DUMP ORBITAL  7.1 AS ORBITAL    7  occ=    2.0000  eig=    -0.6524  
   GROUP=    2  
8  DUMP ORBITAL  8.1 AS ORBITAL    8  occ=    2.0000  eig=    -0.6509  
   GROUP=    2  
9  DUMP ORBITAL  9.1 AS ORBITAL    9  occ=    2.0000  eig=    -0.5343  
   GROUP=    2  
10 DUMP ORBITAL 10.1 AS ORBITAL   10  occ=    2.0000  eig=    -0.5057  
   GROUP=    2  
11 DUMP ORBITAL 11.1 AS ORBITAL   11  occ=    2.0000  eig=    -0.5029  
   GROUP=    2  
12 DUMP ORBITAL 12.1 AS ORBITAL   12  occ=    2.0000  eig=    -0.3681  
   GROUP=    2  
13 DUMP ORBITAL 13.1 AS ORBITAL   13  occ=    2.0000  eig=    -0.3676  
   GROUP=    2
```

As for the ethane molecule, we can see that the eigenvalues of molecular orbitals listed above are pretty similar to the one reported by Gaussian:

Nr.	Eigenvalue	Occupation
1	-10.186790	2.00
2	-10.178480	2.00
3	-10.178470	2.00
4	-0.791890	2.00
5	-0.735720	2.00
6	-0.618680	2.00
7	-0.489940	2.00
8	-0.488380	2.00
9	-0.391640	2.00
10	-0.368550	2.00
11	-0.367910	2.00
12	-0.253510	2.00
13	-0.252030	2.00

Figure 16: Eigenvalues of ethane's first molecular orbitals seen by the Molden configuration



The Nuclear repulsion energy computed in Molpro:

```
1  NUCLEAR REPULSION ENERGY      81.59344361
```

and the one computed by Gaussian

```
1          nuclear repulsion energy      82.2368511117 Hartrees
```

We can see that we have a difference of approximately 0.7 Hartrees between the two energies.

6. Determine how the energy changes as a function of the distances among carbon atoms (take 20 points with steps of 0.05 Å).

Input code:

```
1  %chk=tmp
2  %mem=100MB
3
4  #p scan
5  #pop=full ginput
6
7  Propane
8
9  0 1
10 C1
11 X          1      1.
12 C2          1      rc          2      accx
13 C3          1      rc          2      accx          3      180.
14 H4          1      rh1         2      ahcx          3      90.
15 H5          1      rh1         2      ahcx          3      -90.
16 H6          3      rh2         1      ah2           2      0.
17 H7          4      rh2         1      ah2           2      0.
18 H8          3      rh3         1      ah3           7      dh3
19 H9          3      rh3         1      ah3           7      dh4
20 H10         4      rh3         1      ah3           8      dh3
21 H11         4      rh3         1      ah3           8      dh4
22
23 rc          =          1. 25 0.05
24 rh1         =          1.09
25 rh2         =          1.09
26 rh3         =          1.09
27 accx        =          120.
28 ahcx        =          55.
29 ah2         =          111.
30 ah3         =          111.
31 dh3         =          120.
32 dh4         =          -60.
```

Output code:

```
1  Summary of the potential surface scan:
2      N      rc      SCF
3
4      1      1.0000   -115.46649
5      2      1.0500   -115.75274
6      3      1.1000   -115.97529
7      4      1.1500   -116.14706
8      5      1.2000   -116.27826
```

9	6	1.2500	-116.37704
10	7	1.3000	-116.44985
11	8	1.3500	-116.50183
12	9	1.4000	-116.53706
13	10	1.4500	-116.55881
14	11	1.5000	-116.56967
15	12	1.5500	-116.57172
16	13	1.6000	-116.56663
17	14	1.6500	-116.55576
18	15	1.7000	-116.54021
19	16	1.7500	-116.52088
20	17	1.8000	-116.49854
21	18	1.8500	-116.47382
22	19	1.9000	-116.44728
23	20	1.9500	-116.41939
24	21	2.0000	-116.39055
25	22	2.0500	-116.36113
26	23	2.1000	-116.33143
27	24	2.1500	-116.30173
28	25	2.2000	-116.27225
29	26	2.2500	-116.24319

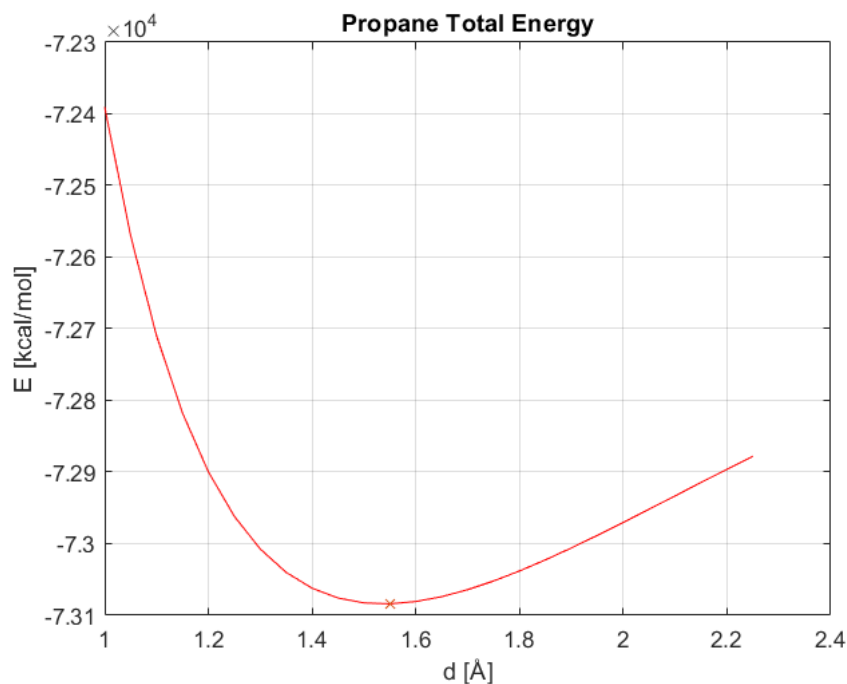


Figure 17: Plot depicting the trend of the total energy of the molecule as the distance  $d$  between carbon atoms varies.

As reported in the MatLab code where I analyzed this plot, the minimum corresponds when  $d = 1,55 \text{ \AA}$ , in line with what is reported by Gaussian ( $d = 1,5332 \text{ \AA}$ ) from the final section of the output reporting the optimized variables. Every Self-Consistent Field energies found in Gaussian have been converted from Hartree to kcal/mol and subsequently the contribution given by the zero point correction energy ( $ZPE_{propane} = 0,103276 \text{ Hartree} = 64,80569 \text{ kcal/mol}$ ) was added to each of them obtaining the total energy of the molecule.



## 4 Project 3

To carry out the project you must: write the input for H and successively H<sub>2</sub>, start the optimization and examine the output file.

### 4.1 Hydrogen atom and molecule

1. Try to understand what has been done in the calculation and which thermodynamic properties have been determined.

#### 4.1.1 Gaussian code

H input code for Gaussian:

```
1 %chk=tmp
2 %mem=100MB
3 #p B3LYP/6-31+g(d,p) opt freq
4
5 Hydrogen Atom
6
7 0 2
8 H
```

H<sub>2</sub> input code for Gaussian:

```
1 %chk=tmp
2 %mem=100MB
3
4 #p B3LYP/6-31+g(d,p) opt freq
5
6 Hydrogen Molecule
7
8 0 1
9 H
10 H 1 d
11
12 d=1.0
```

This calculation is a geometric optimization and frequency calculation for the hydrogen molecule (H<sub>2</sub>). After geometry optimization, the software will calculate the vibrational frequencies of the molecule, which can be used to determine various thermodynamic properties, such as enthalpy, entropy, and specific heat.

In both cases, the thermodynamic properties that could be determined include enthalpy (**H**), entropy (**S**), and Gibbs free energy (**G**), which can be calculated using the vibrational frequencies obtained from the calculation. Furthermore, the total energy obtained from the calculation can be used to calculate the hydrogen binding energy or the ionization energy of hydrogen in the single atom.

2. Find the energy in the output file and save it. (Energies are reported in Hartrees, the conversion to kcal/mol is 1 **Hartree** = 627.5 kcal/mol).

Energy for Hydrogen Atom:

```
1 SCF Done: E(UB3LYP) = -0.500272784191 A.U. after 5 cycles
2 Convrg = 0.1564D-11 -V/T = 1.9742
```

Energy for Hydrogen Molecule H<sub>2</sub>:



```

1 SCF Done: E(RB3LYP) = -1.15099889053 A.U. after 5 cycles
2 Convrg = 0.4542D-08 -V/T = 2.1937

```

In kcal/mol:  $E_H = -313.92 \text{ kcal/mol}$  and  $E_{H_2} = -722.25 \text{ kcal/mol}$

3. Compare the energies of H and  $H_2$  and try to determine the energy of the reaction:  $H_2 \rightarrow 2H$ .

The energy of the reaction can be calculated as the sum of the energies of the products minus the sum of the energies of the reactants. Since the reaction involves the breaking of a hydrogen bond in molecular hydrogen ( $H_2$ ) and the formation of two hydrogen atoms (H), we can represent the reaction equation as:



Now, to calculate the energy of the reaction, we can use the energy values provided by the Gaussian outputs:

$$E_{H_2} = -722.25 \text{ kcal/mol} \quad (27)$$

$$E_H = -313.92 \text{ kcal/mol} \quad (28)$$

The reaction energy will be:

$$\Delta E = \sum E_{products} - \sum E_{reagents} \quad (29)$$

$$\Delta E = 2 \times E_H - E_{H_2} \quad (30)$$

Substituting the values, we get:

$$\Delta E = [2 \times (-313.92) - 722.25] \text{ kcal/mol} \quad (31)$$

$$\Delta E = [-627.84 + 722.25] \text{ kcal/mol} \quad (32)$$

$$\Delta E = 94.41 \text{ kcal/mol} \quad (33)$$

Thus, the reaction energy is  $\Delta E = 94.41 \text{ kcal/mol}$

4. Determine the energy of  $H_2$  at fixed H-H distances (frozen coordinate) and construct a table of  $H_2$  energies as a function of the distance. (You must find out how to do that looking at the gaussian manual)

Input code for scan:

```

1 %chk=tmp
2 %mem=100MB
3
4 #p scan
5
6 Hydrogen Molecule
7
8 0 1
9 H
10 H 1 d
11
12 d 0.5 40 0.025

```

The total energy of the hydrogen molecule depends on the distance between the hydrogen atoms. At smaller distances, the hydrogen atoms are closer together and the potential energy is lower (stabilization). At larger distances, hydrogen atoms move away from each other and the potential energy increases (repulsion).

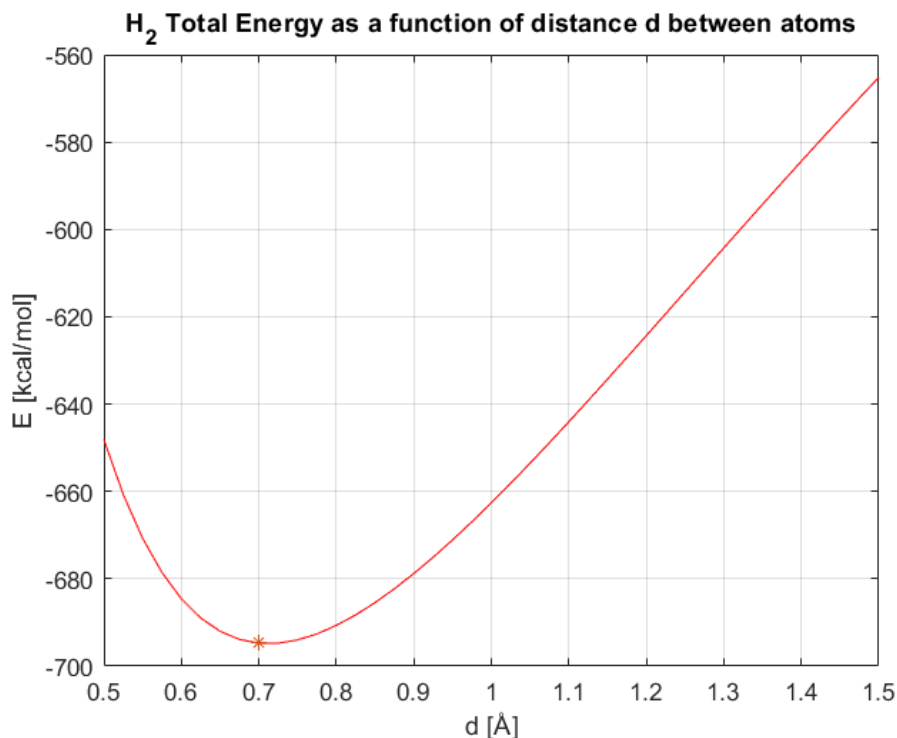


Figure 18:  $E$  as a function of  $d$

The energy term "Zero-point correction" has already been included in the data. This suggests that the energy has been corrected to account for quantum effects known as zero-point energy, which is the minimum energy a particle can have, even at absolute zero temperature, due to quantum uncertainty (from Heisenberg's uncertainty principle).

5. If you are really successful and find this easy, try to do the same using the Molpro code.

#### 4.1.2 Molpro code

Hydrogen Atom:

Input code:

```

1 memory=50MW
2 nosym
3 geometry={
4 H
5 }
6
7
8 !closed shell input
9 basis=6-31G(d,p)
10
11 hf
12 !{multi;closed, 10;occ, 16;wf, 26,1,0;state,1 ;maxiter,40}
13 put,molden,molpro.molden

```

Hartree-Fock approximated energy found by Molpro:





```
1          HF-SCF
2      -0.49823291
```

In agree with the one computed by Gaussian:  $E(\text{UB3LYP}) = -0.500272784191$  Hartree

Hydrogen Molecule  $\text{H}_2$ :

Input code:

```
1  memory=100MW
2  nosym
3  geometry={angstrom
4  H
5  H 1 d
6  }
7
8  d=1.0
9
10
11      !closed shell input
12      basis=6-31G(d,p)
13
14      hf
15      !{multi;closed, 10;occ, 16;wf, 26,1,0;state,1 ;maxiter,40}
16  put,molden,molpro.molden
```

Hartree-Fock approximated energy found by Molpro:

```
1          HF-SCF
2      -1.09947719
```

Approximately near to the one found by Gaussian:  $E(\text{UB3LYP}) = -1.15099889053$  Hartree

Orbital energies of  $\text{H}_2$ :

```
1  Orbital energies:
2
3      1.1      2.1      3.1
4      -0.525626    0.171090    0.878774
```

Nuclear Repulsion Energy:

```
1  NUCLEAR REPULSION ENERGY    0.52917721
```

compared with the Gaussian orbital energies found:

```
1  The electronic state is 1-SGG.
2  Alpha  occ. eigenvalues  --    -0.38581
3  Alpha virt. eigenvalues  --    0.02805    0.67043    0.88099    1.75172
4  Alpha virt. eigenvalues  --    1.91970    2.35480    2.35480    3.37327
```

and the nuclear repulsion energy:

```
1      nuclear repulsion energy    0.5291772086 Hartrees
```

## 4.2 Other molecules

6. If you have mastered all the previous points, you can move forward with the next project by carrying out the optimisation for the following molecules:  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{NO}_2$ .

4.2.1 H<sub>2</sub>O

Input code:

```

1 %chk=tmp
2 %mem=100MB
3
4 #p B3LYP/6-31+g(d,p) opt freq
5
6 Water
7
8 0 1
9 0
10 H1 1 d
11 H2 1 d 2 alpha
12
13 d      = 1.05
14 alpha = 110.

```

Some relevant informations given by the Gaussian output:

```

1 SCF Done: E(RB3LYP) = -76.4340476539 A.U. after 1 cycles
2 Convrg = 0.1608D-09 -V/T = 2.0093

1 Zero-point correction= 0.021280 (Hartree/
  Particle)
2 Thermal correction to Energy= 0.024115
3 Thermal correction to Enthalpy= 0.025060
4 Thermal correction to Gibbs Free Energy= 0.003631
5 Sum of electronic and zero-point Energies= -76.412768
6 Sum of electronic and thermal Energies= -76.409932
7 Sum of electronic and thermal Enthalpies= -76.408988
8 Sum of electronic and thermal Free Energies= -76.430417

```

Since the Self-Consistent Field energy found is:

$$E_{SCF} = -76.4340476539 \text{ Hartree} = -47.962, 3649028 \text{ kcal/mol} \quad (34)$$

and the zero-point correction is:

$$E_{ZPE} = 0.021280 \text{ Hartree} = 13, 3532 \text{ kcal/mol} \quad (35)$$

we can retrieve the total energy of the molecule H<sub>2</sub>O:

$$E_{TOT} = E_{SCF} + E_{ZPE} = [-47.962, 3649028 + 13, 3532] \text{ kcal/mol} = -47.949, 0117 \text{ kcal/mol} \quad (36)$$

```

1 Population analysis using the SCF density.
2
3 *****
4
5 Orbital symmetries:
6   Occupied (A1) (A1) (B2) (A1) (B1)
7   Virtual (A1) (B2) (B1) (A1) (B2) (A1) (B2) (A1) (B2) (B1)
8           (A1) (A1) (A2) (A1) (B1) (A1) (B2) (B2) (A2) (B1)
9           (A1) (A1) (B2) (A1)
10 The electronic state is 1-A1.

```

```
11 Alpha occ. eigenvalues -- -19.16962 -1.02223 -0.54229 -0.39420
    -0.32102
12 Alpha virt. eigenvalues -- 0.02513 0.11448 0.15506 0.15506
    0.20611
13 Alpha virt. eigenvalues -- 0.24188 0.90036 0.98852 1.08848
    1.11265
14 Alpha virt. eigenvalues -- 1.12668 1.23128 1.50290 1.53645
    1.63051
15 Alpha virt. eigenvalues -- 2.23004 2.24126 2.50061 2.63269
    2.64553
16 Alpha virt. eigenvalues -- 3.02392 3.31842 3.50983 3.92159
```

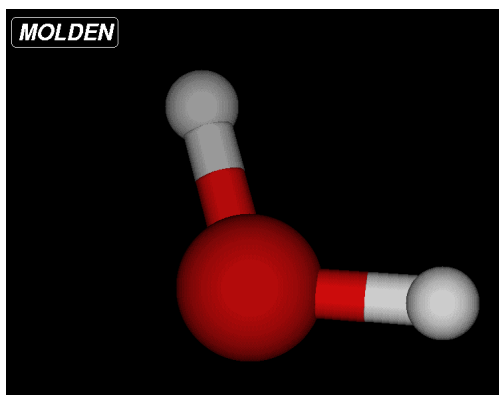


Figure 19: A graphical representation of the water molecule captured with Molden

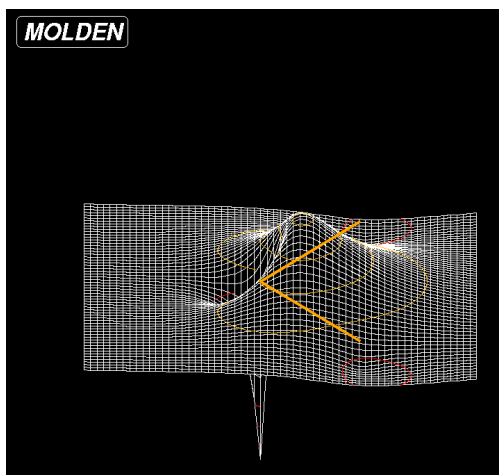


Figure 20: LUMO orbital of water

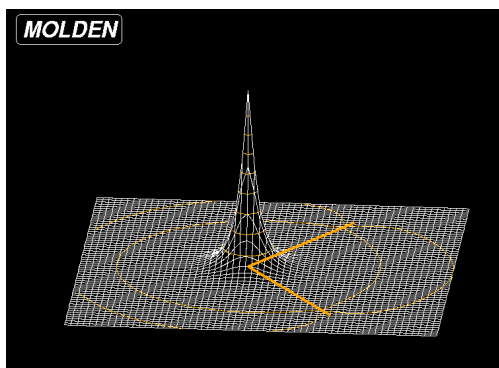


Figure 21: Lowest energy eigenvalue orbital of water

#### 4.2.2 CO

Input code:

```

1 %chk=tmp
2 %mem=100MB
3
4 #p B3LYP/6-31+g(d,p) opt freq pop=full gfinput
5
6 Carbon monoxide
7
8 O 1
9 C
10 O 1 d
11
12 d = 2.20

```

Some relevant informations given by the Gaussian output:

```

1 SCF Done: E(RB3LYP) = -113.317323135 A.U. after 1 cycles
2 Convrg = 0.1500D-09 -V/T = 2.0092

1 Zero-point correction= 0.005017 (Hartree/
Particle)
2 Thermal correction to Energy= 0.007378
3 Thermal correction to Enthalpy= 0.008322
4 Thermal correction to Gibbs Free Energy= -0.014120
5 Sum of electronic and zero-point Energies= -113.312306
6 Sum of electronic and thermal Energies= -113.309945
7 Sum of electronic and thermal Enthalpies= -113.309001
8 Sum of electronic and thermal Free Energies= -113.331443

```

Since the Self-Consistent Field energy found is:

$$E_{SCF} = -113.317323135 \text{ Hartree} = -71.106,620267212 \text{ kcal/mol} \quad (37)$$

and the zero-point correction is:

$$E_{ZPE} = 0.005017 \text{ Hartree} = 3,14816 \text{ kcal/mol} \quad (38)$$

we can retrieve the total energy of the molecule  $\text{H}_2\text{O}$ :

$$E_{TOT} = E_{SCF} + E_{ZPE} = [-71.106,620267212 + 3,14816] \text{ kcal/mol} = -71.103,4721072 \text{ kcal/mol} \quad (39)$$

```

1      Population analysis using the SCF density.
2
3      ****
4
5      Orbital symmetries:
6          Occupied  (SG) (SG) (SG) (SG) (SG) (PI) (PI)
7          Virtual   (PI) (PI) (SG) (SG) (SG) (PI) (PI) (SG) (PI) (PI)
8                   (SG) (PI) (PI) (SG) (SG) (SG) (PI) (PI) (SG) (DLTA)
9                   (DLTA) (PI) (PI) (SG) (DLTA) (DLTA) (PI) (PI)
10                  (SG) (SG) (SG)
11      The electronic state is 1-SG.
12      Alpha occ. eigenvalues --  -19.24971  -10.47699  -0.90083  -0.63484
13                                -0.34699
14      Alpha occ. eigenvalues --  -0.31594  -0.31594
15      Alpha virt. eigenvalues --  -0.22326  -0.22326  -0.16358  0.02137
16                                0.05996
17      Alpha virt. eigenvalues --   0.06217   0.06217   0.17256  0.19789
18                                0.19789
19      Alpha virt. eigenvalues --   0.29161   0.58154   0.58154  0.62682
20                                0.80906
21      Alpha virt. eigenvalues --   1.09832   1.14079   1.14079  1.30657
22                                1.56710
23      Alpha virt. eigenvalues --   1.56737   1.57512   1.57512  1.68378
24                                1.80048
25      Alpha virt. eigenvalues --   1.80051   1.81438   1.81438  2.07853
26                                3.80179
27      Alpha virt. eigenvalues --   3.87267

```

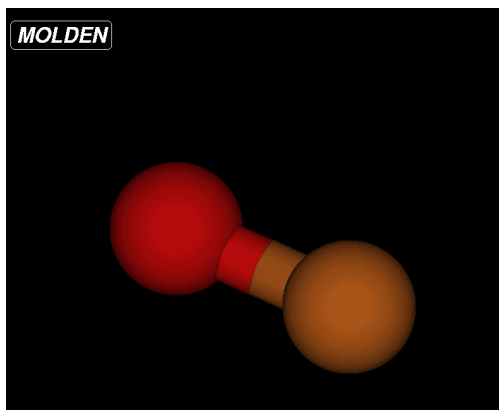


Figure 22: A graphical representation of the carbon monoxide molecule captured with Molden

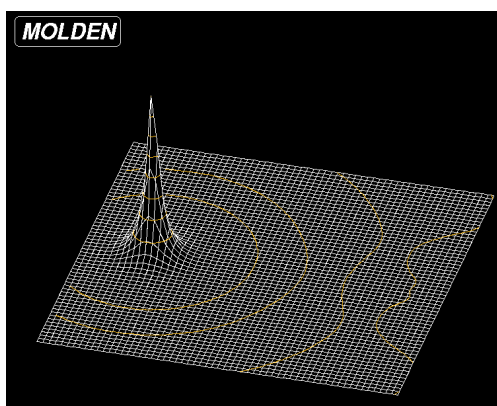


Figure 23: Lowest energy orbital

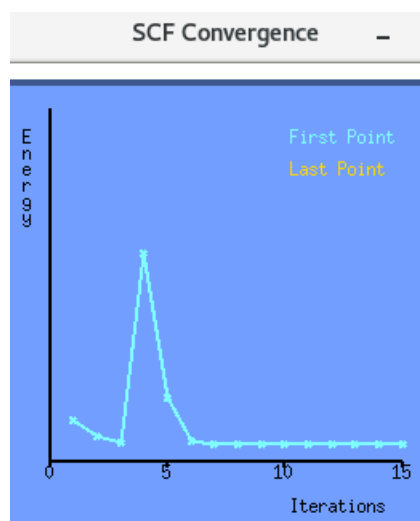


Figure 24: SCF Convergence of CO's energy

### 4.2.3 NO<sub>2</sub>

Input code:

```

1 %chk=tmp
2 %mem=100MB
3
4 #p B3LYP/6-31+g(d,p) opt freq pop=full ginput
5
6 Nitrogen Dioxide
7
8 0 2
9
10 N
11 0 1 d
12 0 1 d 2 alpha
13
14 d      =    1.60
15 alpha =    130.

```

Some relevant informations given by the Gaussian output:



```

1 SCF Done:  E(UB3LYP) = -205.083887112      A.U. after 1 cycles
2              Convrg = 0.2629D-09              -V/T = 2.0089

1 Zero-point correction= 0.008780 (Hartree/
  Particle)
2 Thermal correction to Energy= 0.011717
3 Thermal correction to Enthalpy= 0.012661
4 Thermal correction to Gibbs Free Energy= -0.014600
5 Sum of electronic and zero-point Energies= -205.075107
6 Sum of electronic and thermal Energies= -205.072170
7 Sum of electronic and thermal Enthalpies= -205.071226
8 Sum of electronic and thermal Free Energies= -205.098487

```

Since the Self-Consistent Field energy found is:

$$E_{SCF} = -205.083887112 \text{ Hartree} = -128.690,13916278 \text{ kcal/mol} \quad (40)$$

and the zero-point correction is:

$$E_{ZPE} = 0.008780 \text{ Hartree} = 5,50945 \text{ kcal/mol} \quad (41)$$

we can retrieve the total energy of the molecule  $\text{H}_2\text{O}$ :

$$E_{TOT} = E_{SCF} + E_{ZPE} = [-128.690,13916278 + 5,50945] \text{ kcal/mol} = -128.684,62971278 \text{ kcal/mol} \quad (42)$$

```

1      Population analysis using the SCF density.
2
3      *****
4
5      Orbital symmetries:
6      Alpha Orbitals:
7          Occupied  (B2) (A1) (A1) (A1) (B2) (A1) (A1) (B2) (B1) (B2)
8                   (A2) (A1)
9          Virtual   (B1) (A1) (B2) (A1) (B1) (A1) (B2) (A2) (A1) (B1)
10                  (A1) (B2) (A1) (B2) (B2) (A1) (B1) (B2) (A1) (A1)
11                  (A2) (B2) (A1) (B1) (B2) (A2) (B1) (A1) (A1) (B2)
12                  (B2) (A2) (A1) (B1) (B2) (A1) (B1) (B2) (A2) (A1)
13                  (B2) (A1) (A1) (A1) (B2)
14      Beta  Orbitals:
15          Occupied  (B2) (A1) (A1) (A1) (B2) (A1) (B1) (B2) (A1) (A2)
16                   (B2)
17          Virtual   (A1) (B1) (A1) (B2) (A1) (B1) (A1) (B2) (A2) (A1)
18                   (B1) (B2) (A1) (A1) (B2) (B2) (B1) (A1) (B2) (A1)
19                   (A2) (A1) (B2) (A1) (B1) (B2) (A2) (B1) (A1) (A1)
20                   (B2) (B2) (A2) (A1) (B1) (B2) (A1) (B1) (B2) (A2)
21                   (A1) (B2) (A1) (A1) (A1) (B2)
22      The electronic state is 2-A1.
23      Alpha  occ. eigenvalues --  -19.28467  -19.28466  -14.60224   -1.29998
24                                   -1.15446
25      Alpha  occ. eigenvalues --   -0.69300   -0.59065   -0.58758   -0.58061
26                                   -0.39773
27      Alpha  occ. eigenvalues --   -0.39380   -0.30391
28      Alpha virt. eigenvalues --   -0.10816    0.02984    0.07448    0.08366
29                                   0.08760
30      Alpha virt. eigenvalues --    0.15292    0.17359    0.18865    0.20070
31                                   0.22614

```



28	Alpha virt. eigenvalues --	0.24396	0.25183	0.31104	0.35504
	0.41602				
29	Alpha virt. eigenvalues --	0.75918	0.77525	0.81593	1.02646
	1.09789				
30	Alpha virt. eigenvalues --	1.09795	1.12748	1.14002	1.16963
	1.18692				
31	Alpha virt. eigenvalues --	1.36661	1.38621	1.40287	1.58488
	1.61955				
32	Alpha virt. eigenvalues --	1.70692	1.71784	1.80802	1.82142
	1.84066				
33	Alpha virt. eigenvalues --	2.23445	2.32884	2.67292	2.70857
	2.79171				
34	Alpha virt. eigenvalues --	2.83345	2.96511	3.87618	4.14295
	4.21642				
35	Beta occ. eigenvalues --	-19.27590	-19.27589	-14.59179	-1.28144
	-1.13329				
36	Beta occ. eigenvalues --	-0.66069	-0.56965	-0.56506	-0.54561
	-0.38639				
37	Beta occ. eigenvalues --	-0.35832			
38	Beta virt. eigenvalues --	-0.16500	-0.09201	0.03593	0.07560
	0.08796				
39	Beta virt. eigenvalues --	0.08843	0.15808	0.17517	0.18852
	0.20653				
40	Beta virt. eigenvalues --	0.22754	0.25242	0.25257	0.31493
	0.35928				
41	Beta virt. eigenvalues --	0.44334	0.78353	0.78733	0.82037
	1.03226				
42	Beta virt. eigenvalues --	1.10176	1.11786	1.14950	1.15757
	1.17488				
43	Beta virt. eigenvalues --	1.19557	1.37196	1.40694	1.42472
	1.59332				
44	Beta virt. eigenvalues --	1.62998	1.72351	1.72884	1.82988
	1.84375				
45	Beta virt. eigenvalues --	1.85100	2.25083	2.33876	2.70127
	2.71926				
46	Beta virt. eigenvalues --	2.80779	2.84280	2.98573	3.89857
	4.15458				
47	Beta virt. eigenvalues --	4.22697			

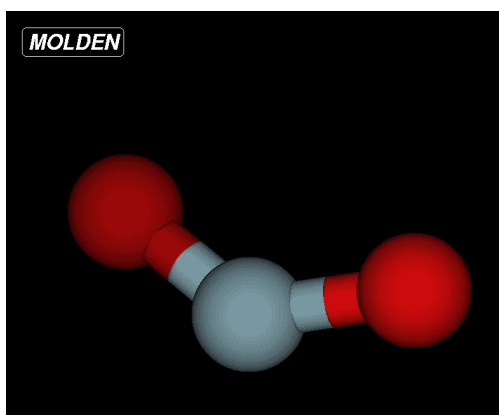


Figure 25: A graphical representation of the carbon monoxide molecule captured with Molden



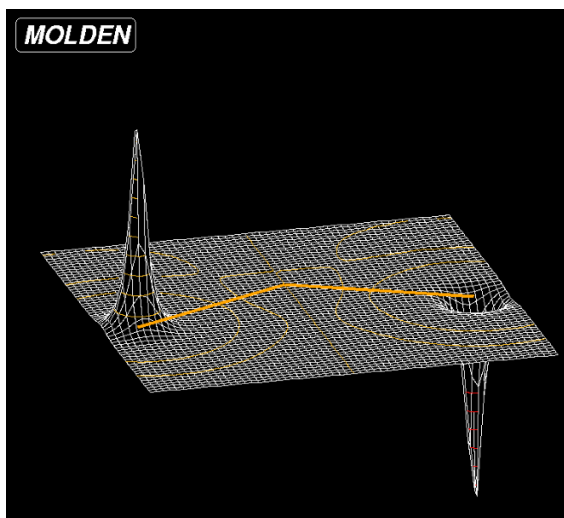


Figure 26: Molecular Orbital  $\alpha$  of minimum energy with  $\sigma$  bond character between nitrogen and one of the oxygen atoms in the  $\text{NO}_2$  molecule

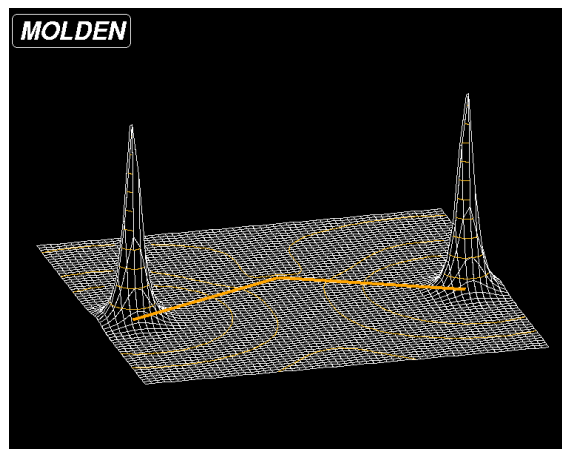


Figure 27: Molecular Orbital  $\alpha$  of minimum energy with  $\pi$  bond character between nitrogen and one of the oxygen atoms in the  $\text{NO}_2$  molecule

Since we obtained two alpha molecular orbitals with minimum energy and different functions for the  $\text{NO}_2$  molecule, it may indicate that the  $\text{NO}_2$  molecule has two molecular orbitals with different symmetry or bonding character. This is due to the fact that this molecule has a resonance structure. This means that the arrangement of electrons can vary between different resonance shapes without changing atomic connectivity. These different resonance shapes can influence the distribution of molecular orbitals.

In the context of molecular orbital theory, the  $\text{NO}_2$  molecule can be treated as a linear combination of different resonance shapes, or resonance contributions. Each resonance contribution can lead to a different distribution of molecular orbitals.

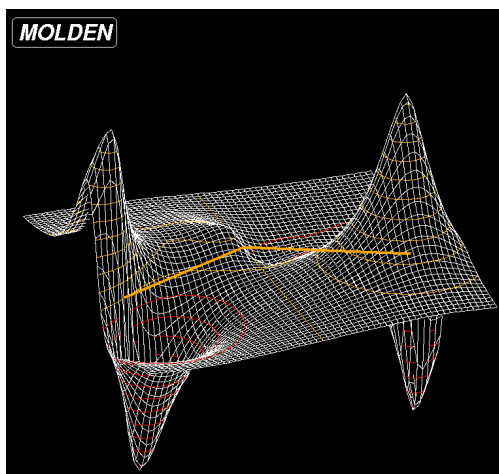


Figure 28: HOMO orbital

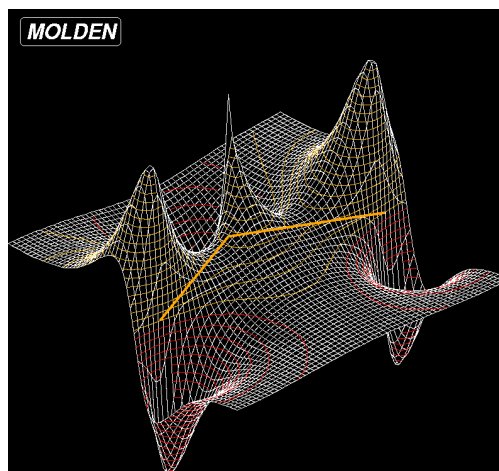


Figure 29: LUMO orbital

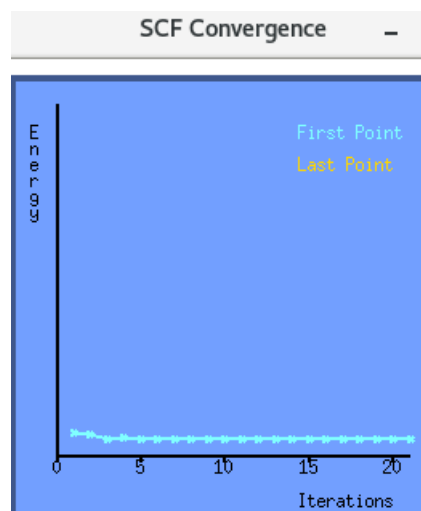


Figure 30: SCF Convergence of NO<sub>2</sub>'s energy



## References

- Course Slides from prof. Antonino Famulari, Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta"
- Course lessons from prof. Carlo Cavallotti, Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta"
- Notes of Applied Chemical Kinetics course by Carlo Cavallotti
- "Introduction to Computational Chemistry", Frank Jensen, II edition, Wiley