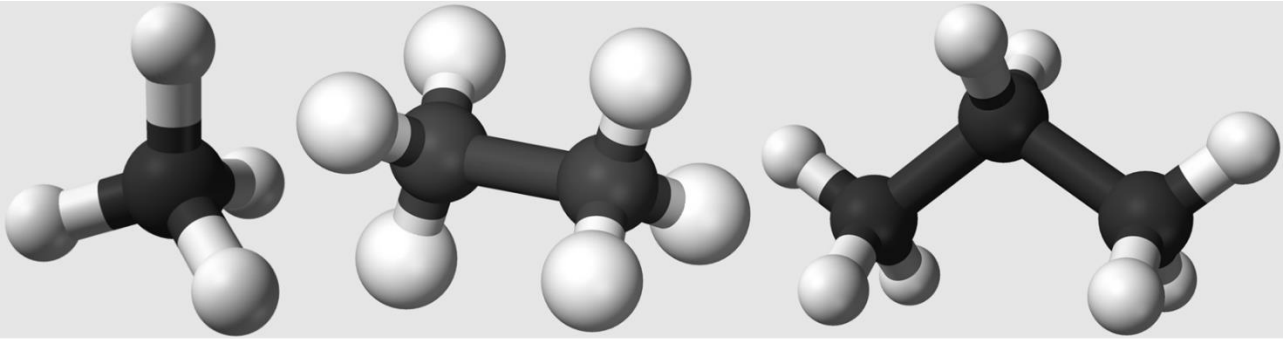
Molecular Modeling in Process Engineering

2023/2024

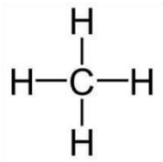
Project 2

Quantum Chemical Calculation of the structures of complex molecules

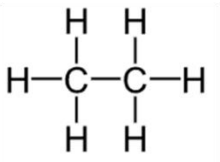
The purpose is to learn how to define the structure of relatively complicated molecules using the Z-Matrix and to determine the energies of ethane and propane solving numerically the Schrodinger equation using the g09 code and/or molpro. A description on how to set up a Z-Matrix is reported at page 575 of the Jensen book.
The first molecule to study is ethane, whose structure is reported below.



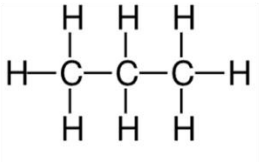
Methane



Ethane



Propane



To carry out the project you must:

- Switch on the virtual machine
- login: the username is ‘ospite’ the password ‘lezione’
- open a command line terminal
- at the prompt, call for the tcsh interpreter (just digit “tcsh” at the command line and give an enter).
- enter in the qm directory (“cd qm”)
- create a subdirectory for the calculation you want to make (“mkdir c2h6”).
- enter in this directory (“cd c2h6”)
- edit an input file for the calculations (“vi c2h6.com”)
- a typical gaussian input for molecule with tethraedral structures(methane) appears as follows (without the comments in parentheses):

```
---
%chk=tmp                          (name of checkpoint file)
%mem=100MB                        (ram memory per core)
                                  (blank line)
#p B3LYP/6-31+g(d,p) opt          (type of calculation)
                                  (blank line)
```

Z-matrix CH_4

```
title
                                                    (blank line)
0 1                                                 (charge and spin multiplicity)
C1
H2  1  d1                                           (d1: distance between atom 1 atom 2)
H3  1  d2  2  a1                                    (a1: angle between atomo 3 and atom 1)
H4  1  d3  2  a2  3  t1                             (t1: dihedral angle between planes 4 1 2 e 1 2 3)
H5  1  d4  2  a3  3  t2

                                                    (blank line)
d1=1.09                                             (distance)
a1=109.                                             (angle)
t1=120.                                             (dihedral angle)
d2=1.03
a2=110.
t2=-120.
d3=1.05
d4=1.1
a3=109.
                                                    (blank line)
----
```

secondo atomo
terzo atomo
quarto atomo

- write the input for C2H6, use the CH4 example as a starting point.
- save the file and start the calculations: ("g09 c2h6.com &)
- open the output and examine the result ("emacs c2h6.log" or "more c2h6.log")
- correct eventual errors and proceed until you obtain a converged geometry.
- visualize the output using molden, with the command "molden c2h6.log"
- visualize the orbitals. For this purpose the command lines must be modified as follow:

G09
- Add in the input line the keyword "pop=full gfinput"
- to visualize the orbitals, open the log file with molden: "molden c2h6.log"
- click on dense mode
- click on orbital
- select an orbital
- under the plot mode, click on the tab at the right bottom.

MOLPRO
- Add the "put,molden,molpro.molden" line at the end of the input
- proceed to visualize using molden

Once you have run the calculation, you must:

1) find the energy in the output file and save it:
2) examine critically the output file and try to understand what has been done in the calculation
3) determine how the energy changes as a function of the relative orientation of the methyl groups (take 6 points with steps of 10 degrees).
4) Try to write and optimize the structure for propane.

Notes on this practical:
- it is important to organize the Z-Matrix so that the modification of one dihedral angle leads to the contextual motion (rotation) of the atoms of the molecular group to which the atom belongs. This is a key concept in order to set up Z-Matrixes able to describe internal motions in molecules.
- write down on a sheet of paper the structural model of the molecule before starting to compile the Z-Matrix.
- make test runs to check that you are positioning properly the atoms.