

Lab 3

Conformational energy analysis

Objective

This computational project deals with molecular conformations – the spatial arrangement of atoms of molecules. Conformations are determined by energy, so the essence of the required calculations is to compare energies of different molecular structures. Four classical conformational energy problems are investigated here:

- Problem 1: The inversion barrier of ammonia (planar versus pyramidal)
- Problem 2: The rotation barrier of ethane (staggered & eclipsed conformations)
- Problem 3: The rotational barrier of hydrogen peroxide
- Problem 4: Markovnikov's rule - orientation of electrophilic addition
- Problem 5: Wavefunction-based correlation approaches”

The "umbrella" inversion barrier in ammonia, is the difference in energy between the pyramidal and the planar structures of the ammonia molecule. For both structures, it is important to optimize the geometry. We shall also see that we have to push the calculations to quite a high level to get good agreement with the experimental result. Similarly, rotational barriers can be determined as the difference in energy between two rotational conformations. We will see that ab-initio calculations of the rotational barrier in ethane give good agreement with experiment, even with poor basis sets. Hydrogen peroxide, however, is much less straightforward.

Comparing conformations and the barriers to transitions between them provide important data on molecular structure. Analysis of the same type can be used also to predict the behavior of more complex chemical reactions. This will be demonstrated by a study of the origin of the Markovnikov's rule.

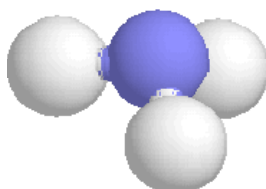
Background

The experimental values of these quantities in several different units are:

| System | KJ/mol | Kcal/mol | mH (milliHartree) |
|---|--------|----------|-------------------|
| Inversion barrier of ammonia | 24.3 | 5.8 | 9.2 |
| Rotational barrier of ethane | 12.1 | 2.9 | 4.6 |
| Rotational barrier of hydrogen peroxide – cis | 29.3 | 7.0 | 11.2 |
| Rotational barrier of hydrogen peroxide – trans | 4.6 | 1.1 | 1.8 |

Note that the experimental structure of hydrogen peroxide is neither planar trans nor planar cis. It is twisted out of plane and there are therefore two barriers to rotation through the two planar structures.

Problem 1: Inversion of ammonia



- 1.1 Use the Hartree-Fock method with the STO-3G, 6-31G, 6-31G(d), and 6-31G(2df, p)¹ basis sets in order to optimize the geometries of pyramidal and planar ammonia molecules.

The calculation is done in the following steps:

- In the Windows version of Gaussian, use the following input for the calculation. In the case of the pyramidal ammonia:

| | |
|-------------------------|--|
| % | |
| Route section | # RHF STO-3G SCF=Tight Opt |
| Title section | Geometry optimization of pyramidal ammonia |
| Charge and multiplicity | 0 1 |
| Molecular specification | N X 1 1.0 H 1 R 2 A H 1 R 2 A 3 120.0 H 1 R 2 A 3 -120.0 R=1.0 A=115.0 |

In the case of the planar ammonia:

| Section | Input |
|-------------------------|---|
| Route section | # RHF STO-3G SCF=Tight Opt |
| Title section | Geometry optimization of planar ammonia |
| Charge and multiplicity | 0 1 |
| Molecular specification | N H 1 R H 1 R 2 120.0 H 1 R 2 120.0 3 180.0 R=1.0 |

¹ You can read more about basis sets in the theoretical background of the computational lab. The last basis set, for example, puts 2 d and 1 f sets of polarization functions on the heavy atoms (nitrogen in this case) and 1 set of p polarization function on each hydrogen atom.

- Submit the Gaussian calculation.
 - Open the output file in Notepad and verify that the run terminated successfully and that convergence was accomplished.
 - Open the output file in GaussView in order to observe the optimized structure.
 - Perform a geometry optimization calculation in GaussView with a larger basis set, 3-21G.
 - Press the Calculate button in the GaussView toolbar and select Gaussian.
 - In the Job Type dialog box, select Optimization to minimum and Calculate Force Constants – never.
 - In the Method dialog box:
Select ground state, Hartree-Fock, Restricted, basis set – 3-21G,
Charge – 0 and Spin – Singlet.
 - Insert a convenient title in the Title section.
 - Deselect 'Write Connectivity' and select 'Ignore Symmetry' in the General dialog box.
Insert SCF=Tight in the Additional Keywords section.
 - Select 'None' in the Solvation dialog box.
 - Submit the calculation.
 - Open the output file optimized structure as calculated using the 3-21G and perform a geometry optimization calculation with a larger basis set, 6-31G(d).
 - Continue this procedure with larger and larger basis sets.
- 1.2 Tabulate the energy difference between the pyramidal and planar optimized structures as calculated using different basis sets. Compare these results with the experimental data.
- 1.3 Tabulate the geometry of each structure.
- 1.4 Use the Hartree-Fock method, the 6-31G(d) to calculate the Mulliken population analysis of the pyramidal and planar ammonia molecules.
- Steps of calculation:
- Open the optimized geometry (output file) of the molecule as calculated using the 6-31G(d) basis set, in GaussView.
 - Perform a Mulliken population analysis of the optimized structure:

Select Energy in the Job Type dialog box.

Select ground State, Restricted Hartree-Fock method, Basis set – 6-31G(d), Charge – 0, Spin – singlet in the Method dialog box.

Deselect any option in the General dialog box.

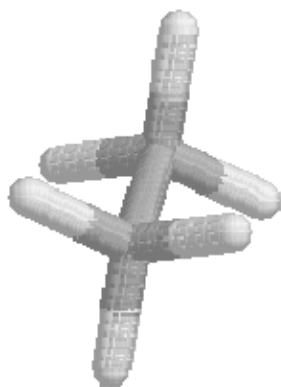
Insert the following line in the Additional Keywords section:

SCF=Tight Pop=full

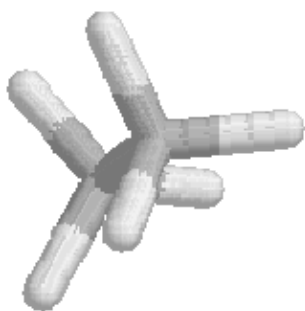
What are the energies of the occupied molecular orbitals of both molecules? What are the orbitals' symmetries? Draw (scheme) the orbitals. What kind of orbitals are them (e.g. bonding /antibonding)?

Problem 2: Rotation barrier of ethane

In the following exercise we would calculate the energy difference between the staggered and eclipsed conformations of ethane. Pictures of these conformations are shown below.



Staggered conformation of ethane



Eclipsed conformation of ethane

- 2.1 Perform geometry optimization calculations of the staggered and the eclipsed conformations of ethane using the Hartree-Fock method and the following basis sets: STO-3G, 3-21G, 6-31G(d) and the 6-31G(d, p).

Steps of calculations:

- Open the Windows version of Gaussian.
- In the case of the staggered conformation, the input file would be the following:

| Section | Input |
|-------------------------|---|
| Route section | # RHF STO-3G SCF=Tight Opt |
| Title section | Geometry optimization of staggered ethane |
| Charge and multiplicity | 0 1 |
| Molecular specification | C C 1 RC H 1 RH 2 T H 2 RH 1 T 3 60.0 H 2 RH 1 T 3 180.0 H 2 RH 1 T 3 300.0 H 1 RH 2 T 5 60.0 H 1 RH 2 T 5 -60.0 |

| | |
|--|-------------------------------|
| | RC=1.54 RH=1.09 T=109.0 |
|--|-------------------------------|

In the case of the eclipsed conformation, the input file would be the following:

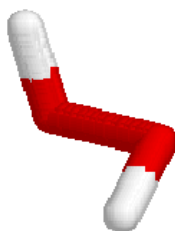
| Section | Input |
|-------------------------|--|
| Route section | # RHF STO-3G SCF=Tight Opt |
| Title section | Geometry optimization of eclipsed ethane |
| Charge and multiplicity | 0 1 |
| Molecular specification | C C 1 RC H 1 RH 2 T H 2 RH 1 T 3 0.0 H 2 RH 1 T 3 120.0 H 2 RH 1 T 3 -120.0 H 1 RH 2 T 4 120.0 H 1 RH 2 T 4 -120.0 RC=1.54 RH=1.09 T=109.0 |

- Submit the Gaussian calculation.
- Open the output file in Notepad and verify that the run terminated successfully and that convergence was accomplished.
- Open the output file in GaussView in order to observe the optimized structure.
- Perform a geometry optimization calculation in GaussView with a larger basis set 3-21G.

- In the Job Type dialog box, select Optimization to minimum and Calculate Force Constants – never.
- In the Method dialog box:
Select ground state, Hartree-Fock, Restricted, basis set – 3-21G, Charge – 0 and Spin – Singlet.
- Insert a convenient title in the title section.
- Deselect any option in the General dialog box.
Insert SCF=Tight in the Additional Keywords section.
- Submit the calculation.
- Open the output file optimized structure as calculated using the 3-21G and perform a geometry optimization calculation with a larger basis set, 6-31G(d).
- Continue this procedure with larger and larger basis sets. In the case of the 6-31G(d) basis set Select Ignore Symmetry in the General dialog box.

2.2 Tabulate the energy, C-C bond length and C-C-H bond angle for each structure, and the energy difference between the staggered and the eclipsed conformations. Compare the results with the experimental data. Is there any significant improvement with the larger basis sets?

Problem 3: Rotation barrier of hydrogen peroxide



3.1 Perform a geometry optimization calculation of hydrogen peroxide at a fixed twist angle using the Hartree-Fock method and 6-31G(d) basis set.

Steps of calculation:

- Open the Windows version of Gaussian.
- The following is an example of input parameters for the geometry optimization calculation of hydrogen peroxide molecule with a fixed twist angle $T=0.0$:

| Section | Input |
|-------------------------|---|
| Route section | #RHF 6-31G(d) SCF=Tight Opt=Z-matrix |
| Title section | Geometry optimization of hydrogen peroxide $T=0.0$ |
| Charge and multiplicity | 0 1 |
| Molecular specification | O O 1 OO H 1 OH 2 A H 2 OH 1 A 3 T OO=1.4 OH=1.0 A=101.0 T=0.0 |

This data set shows a feature of data preparation that we did not yet encounter. The variables OO, OH and A are to be optimized, while T is kept constant. This information is expressed in the input data by putting the value of T in a separate section following a blank line after the variable list. To use this feature we put Opt=Z-matrix on the command line. Note that the twist angle of zero corresponds to the planar cis conformation of the molecule and a twist angle of 180^0 represents the planar trans conformation.

- Submit the Gaussian calculation.

- Open the output file in Notepad and verify that the run terminated successfully and that convergence was accomplished.
- Open the output file in GaussView in order to observe the optimized structure.
- Repeat this procedure with fixed twist angles of 30.0° , 60.0° , 90.0° , 120.0° , 150.0° and 180.0° .

3.2 Tabulate the energy, the O-O bond length, O-H bond length and the O-O-H bond angle as a function of the twist angle, T.

3.3 Plot a graph of the energy of hydrogen peroxide as a function of the twist angle. What can you conclude from the graph?

3.4 Use the RHF method and the 6-31G(d) basis set to calculate the optimized geometry of the cis and trans hydrogen peroxide conformations with the twist angle, T, as a variable not a constant. Use initial values of T that correspond to the cis and to the trans planar conformations. For example, in the case of the cis conformation, an input Gaussian file will be

| | |
|-------------------------|---|
| % | |
| Route section | #RHF 6-31G(d) SCF=Tight Opt |
| Title section | Geometry optimization of hydrogen peroxide T=0.0 |
| Charge and multiplicity | 0 1 |
| Molecular specification | O O 1 OO H 1 OH 2 A H 2 OH 1 A 3 T OO=1.4 OH=1.0 A=101.0 T=0.0 |

- 3.5 Use the RHF method and the 6-31G(d) basis set to calculate the optimized geometry of hydrogen peroxide with T as a variable not a constant. This time, use an initial guess of the twist angle value that is close to the minimum of the graph plotted in 3.3 above. This calculation will give you the actual minimum.
- 3.6 Tabulate the energy and the output twist angle as a function of the input twist angle for the calculations done in 3.4 and 3.5. What can you conclude from the results?
- 3.7 Calculate the energy difference between the cis conformation and the minimum and between the trans conformation and the minimum.
- 3.8 Use the 6-31G(d, p) basis sets and calculate the optimized geometry of the peroxide with $T=0.0^\circ$, $T=180^\circ$ and the T close to the minimal energy geometry which you have found using the 6-31G(d) basis set². Calculate the energy difference between the cis conformation and the minimum and between the trans conformation and the minimum.
- 3.9 Compare the obtained results and the experimental data. How does the size of the basis set effect the results? (Do you obtain convergence?).

Problem 4: Markovnikov's rule - orientation of electrophilic addition

The carbon-carbon double bond is electron-rich and can donate a pair of electrons to an electrophile (Lewis acid). For example, the reaction of two 2-methylpropene with HCl yields 2-chloro-2-methylpropane. Careful study of this and similar reactions by

² In this case use the 'Opt' keyword in the route section of the Gaussian input file rather than the 'Opt=Z-matrix' option.

Ingold and others have led to the following generally accepted mechanism for what is called an electrophilic addition reaction:

The reaction begins with an attack on the electrophile, HCl, by the electrons of the nucleophilic π bond. Two electrons from the π bond form a new σ bond between the entering hydrogen and an alkene carbon. The resulting carbocation intermediate is itself an electrophile, which can accept an electron pair from the nucleophilic chloride ion to form C-Cl bond and yield a neutral addition product.

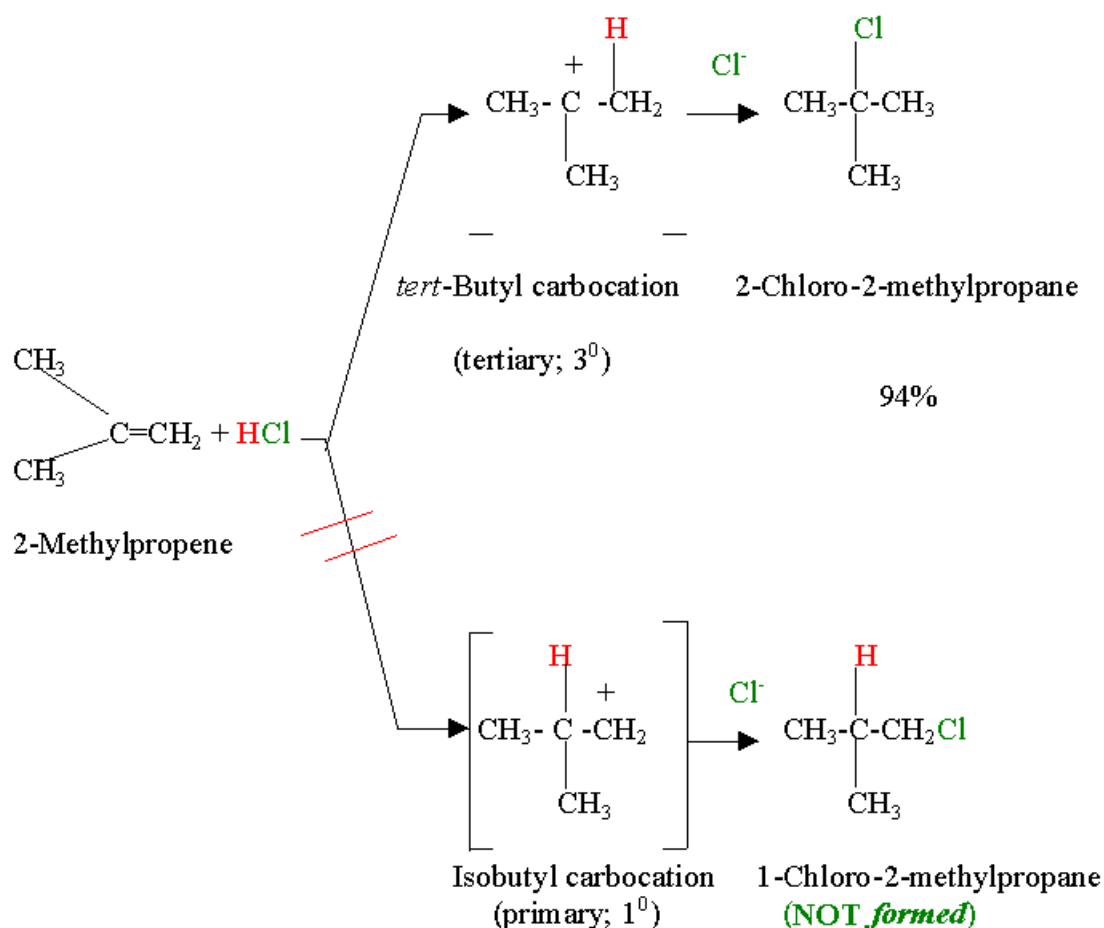
An alternative product could have been formed: the 2-Methylpropene *might* have reacted with the HCl to give 1-chloro-2-methylpropane in addition to 2-chloro-2-methylpropane. This possible route was not taken.

After looking at the results of many such reactions the Russian Chemist Markovnikov proposed what has become known as **Markovnikov's rule**³:

Markovnikov's rule In the addition of HX (where X can be Cl, Br and I atoms) to an alkene, the H attaches to the carbon with the fewer alkyl substituents, and the X attaches to the carbon with more alkyl substituents.

In this part of the laboratory project we will examine the energetic basis for this observation. Using the electrophilic addition of HCl to 2-methylpropene as an example.

³ For more information about Markovnikov's rule you can use:
McMurry, J. Organic Chemistry Fourth Ed. Pacific Grove, CA : Brooks, 1996



The sole product (94%) of this reaction is the 2-Chloro-2-methyl propane.

4.1 Use the RHF method and the 6-31G(d) basis set in order to optimize the geometry of the two intermediate carbocations, reactants and products (pay attention to the total charge of these molecules, make sure that the structure of the 2-Chloro-2-methylpropane is tetrahedral).

Steps of calculation:

- Use the GaussView program to build the molecules.
- Perform an energy optimization calculation with Gaussian⁴.

⁴ Use SCF=Tight in the additional keywords.

- Open the output file in Notepad and verify that the run terminated successfully and that convergence was accomplished.
- Open the output file in GaussView in order to observe the optimized structure. Tabulate the energy of each of the optimized structure, which process is more likely to occur according to the optimized structures and why?

4.2 What are the energy differences between the intermediate state and the reactant of the processes under investigation? Which process is more likely to occur according to these results?

4.3 What are the atomic charges on each carbon atoms on the reactants and intermediate molecules? (Open the output files in GaussView and then press the results button and select Charges to observe the charges or open the output in Notepad and search for Mulliken atomic charges after the geometry optimization convergence).

4.4 Which process is more likely to occur according to the calculated charge distribution? Explain your conclusions.

4.5 Compare the theoretical analysis with Markovnikov's rule.

Problem 5 :

This problem demonstrates the configuration-interaction and many-body perturbative methods taking into account electronic correlations.

The energy, calculated with these methods, is presented at the end of the Gaussian output files.

A. The atomization energy of Phenol.

- 1) Draw the phenol molecule.
- 2) Calculate the energy of atomization (defined as the energy of the molecule minus the sum of the energies of its constituent atoms) of Phenol using the following basis sets:
 - a) 3-21G
 - b) 6-31G
 - c) 6-31G (p,d)
- 3) Tabulate the atomization energy, all the C-C-C angles and the lengths of the C-H and C-O bonds. Compare the results with the experimental data. Is there any improvement with the larger basis sets?
- 4) Now use the 6-31G (p,d) and MP2 method in order to calculate all the quantities. Compare the results with the experimental data. Do you see any significant improvement? Explain!

B. The atomization energy of C_2H_{2x}

Calculate the atomization energy of C_2H_6 , C_2H_4 , C_2H_2 using the HF, MP2 and QCISD methods and the 6-31G(p,d) basis set. Compare your results with the experimental data. Explain.