

# Introduction

## Reaction Coordinates and Potential Energy Scan, Population Analysis

# Introduction

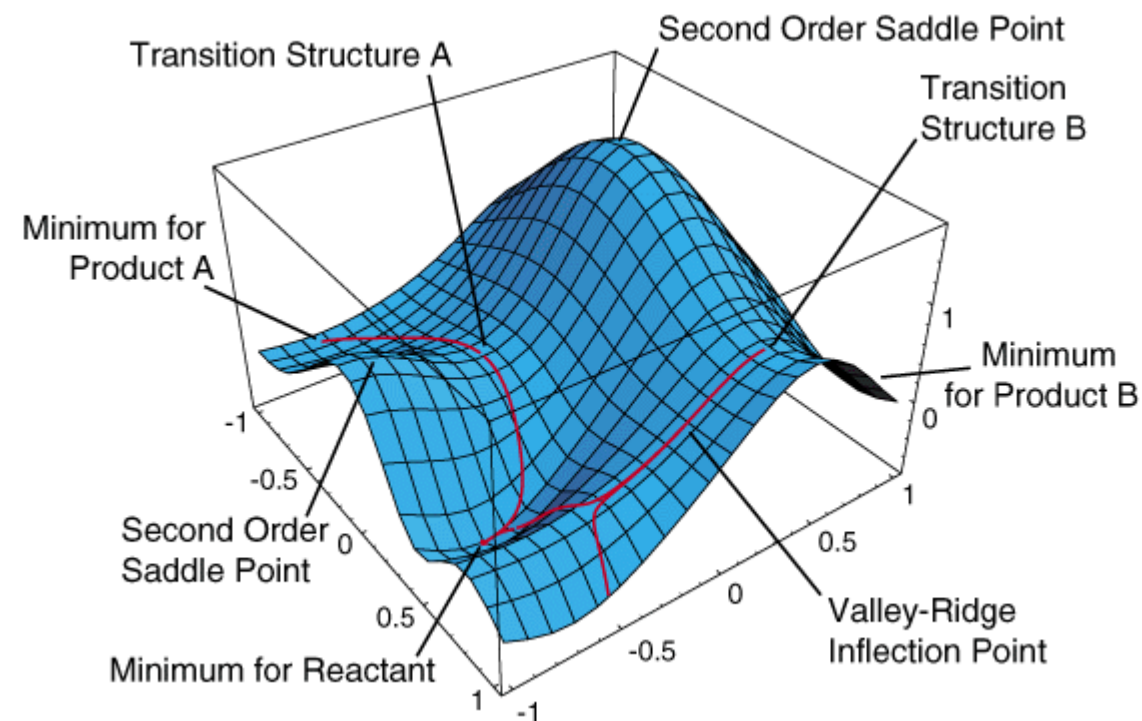
# Reaction Coordinates and Potential Energy Scan

The most important and basic types of calculations in computational chemistry

- the optimization and
- the frequency calculations.

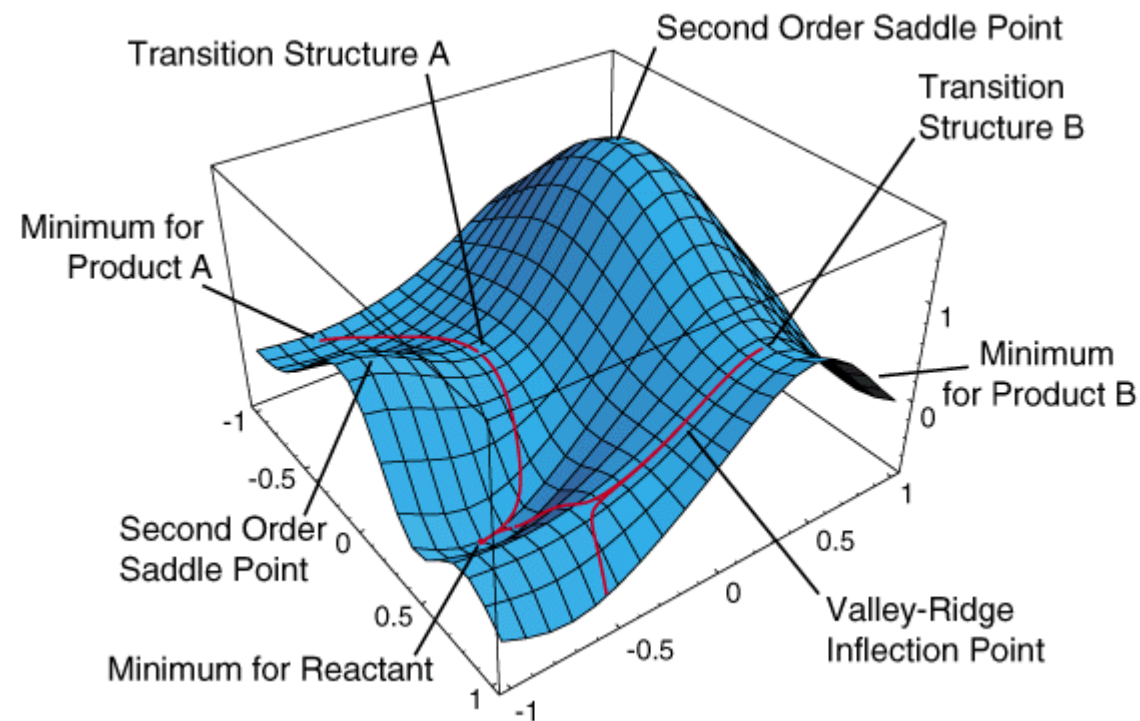
These methods offer the essential factors for thermodynamic and kinetic information to characterize a chemical reaction.

The first step always **choose an appropriate computational method** since the surface of the Potential Energy Surface (right) is highly dependent on the method.



In chemistry, a reaction coordinate is “representation” of progress along a reaction pathway. It is usually a geometric parameter that changes during the conversion of one or more molecular entities.

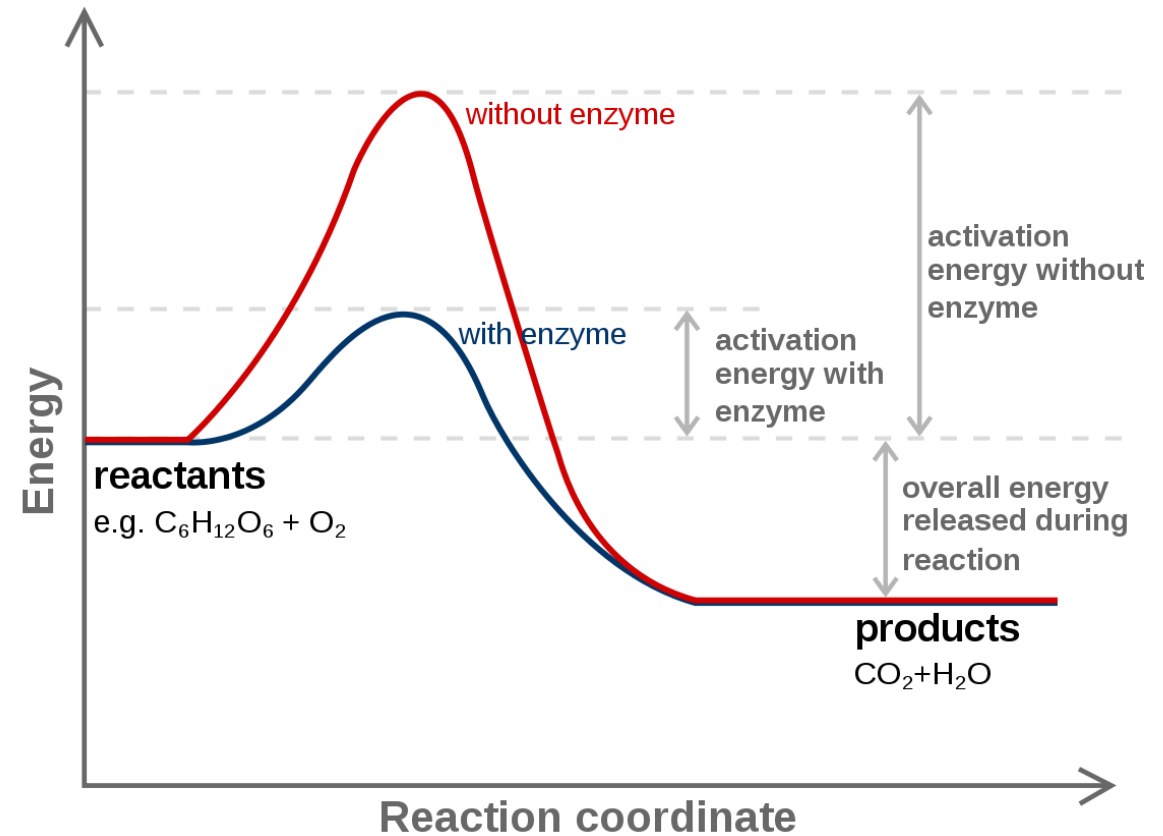
In computational chemistry usually is very complex to study the entire surface, also considering that not all points are interesting. For this reason and for the simplicity of working **on 2D the required points for a reaction are the minima, maxima and saddle points** which will no make our Reaction Coordinates.



In chemistry, a reaction coordinate is an abstract coordinate which represents progress along a reaction pathway. It is usually a geometric parameter that changes during the conversion of one or more molecular entities.

In computational chemistry usually is very complex to study the entire surface, also considering that not all points are interesting. for this reason and for the simplicity of working **on 2D the required points for a reaction are the minima, maxima and saddle points** which will make our Reaction Coordinates.

An important fact to model a chemical reaction is to draw “approximate” PES (2 RC) of the system with the objective to start with better structures.



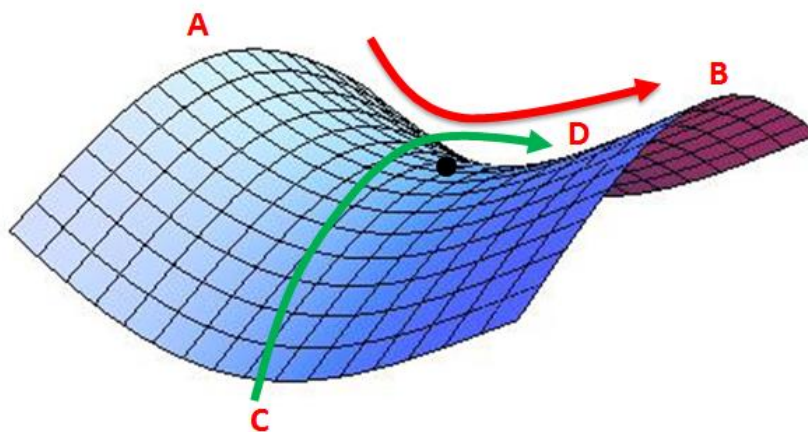
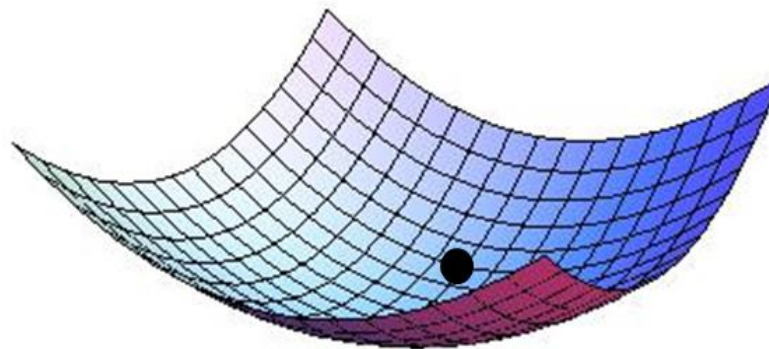
## Characterizing the PES

**Minima** represents stable or quasi-stable species, i.e. reactants and products with finite lifetime.

$$\frac{\partial E}{\partial q_1} = 0 \quad \frac{\partial^2 E}{\partial q_1^2} > 0$$

**Saddle point** represents a maximum along only one direction (that of the reaction coordinate) and is a minimum along all other directions. In other words, a saddle point represents a transition state along the reaction coordinate.

$$\frac{\partial^2 E}{\partial q^2} > 0 \quad \frac{\partial^2 E}{\partial q_1^2} < 0 \quad \frac{d^2 U}{dx^2} = k \quad f = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$



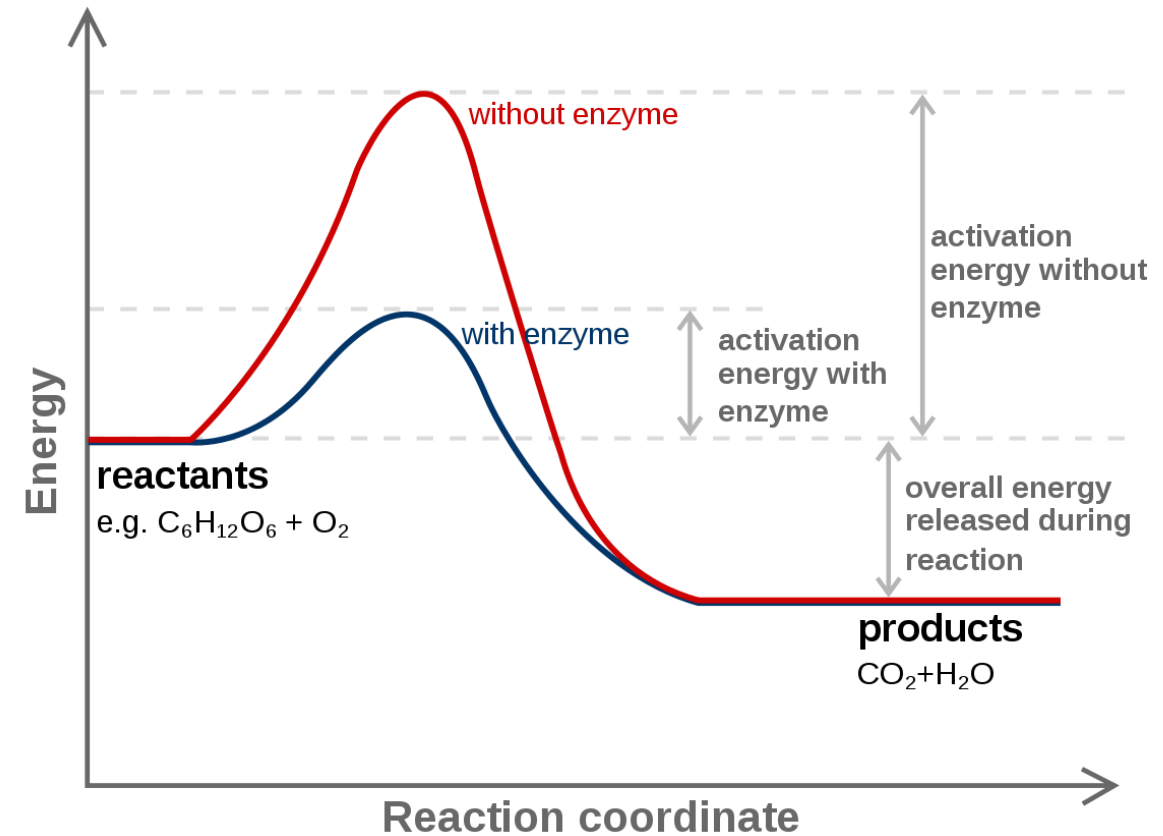
An important fact to model a chemical reaction is to draw “approximate” PES (2 RC) of the system with the objective to start with better structures.

### Step 1: Optimizations of Initial Geometries (i.e. Reactants and Products)

- Frequency Calculation

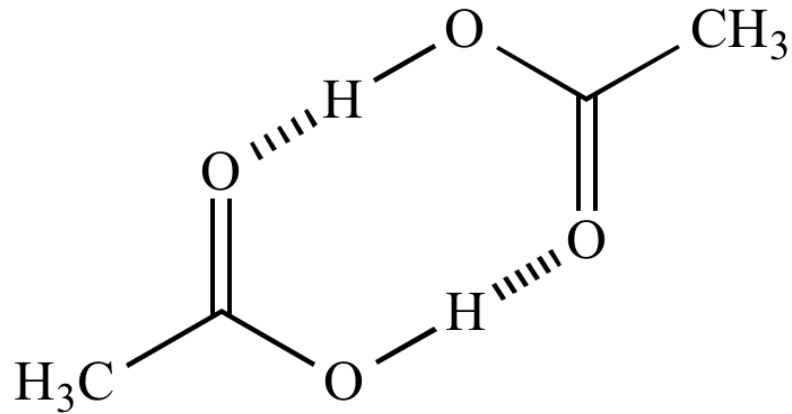
### Step 2: TS Characterization

- Scan
- Frequency Calculation
- Confirmation (IRC, etc)



# Task

➤ model the reaction of this dimerization.



## STEPS:

1. **Optimize Reactants and Products**
2. **Explore PES by performing a Scan**
3. **Performed an Optimization (TS) calculation on the TS**



## STEPS:

### 1. Optimize Reactants and Products

The screenshot shows the Avogadro software interface. On the left, the 'Display Types' panel is visible with 'Ball and Stick' selected. The 'AutoOptimization Settings' panel shows 'Force Field: UFF' and 'Steps per Update: 4'. The 'Algorithm' dropdown is set to 'Steepest Descent'. The 'Extensions' menu is open, showing options like 'Optimize Geometry', 'Molecular Mechanics', 'GAMESS', 'Abinit...', 'Dalton...', 'GAMESS-UK...', 'Gaussian...', 'MOLPRO...', 'MOPAC...', 'NWChem...', 'PSI4...', 'Q-Chem...', 'LAMMPS...', 'Molecular Orbitals...', 'Orca', 'QTAIM', 'GLSL Shaders...', 'Spectra...', and 'Create Surfaces...'. In the center, a 3D ball-and-stick model of acetic acid is shown with atoms numbered 1 through 8. On the right, the 'Gaussian Input' dialog box is open, showing the following settings: Title: Title, Calculation: Geometry Optimization, Processors: 1, Theory: B3LYP, Basis: 6-31G(d), Charge: 0, Multiplicity: 1, Output: Standard, Checkpoint: , Format: Z-matrix. The 'Generate...' button is highlighted.



```
%mem=16gb
%nprocshared=8
%chk=chk.chk
#n RMP6 Opt freq
```

Acetic Acid

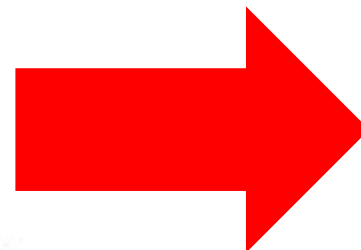
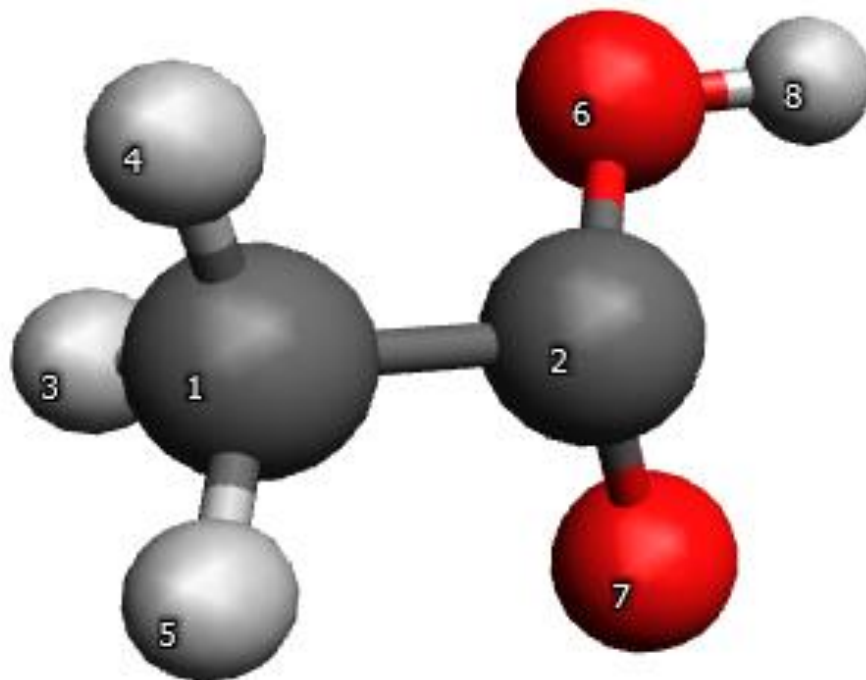
```
0 1
C
C 1 B1
H 1 B2 2 A2
H 1 B3 2 A3 3 D3
H 1 B4 2 A4 3 D4
O 2 B5 1 A5 3 D5
O 2 B6 1 A6 3 D6
H 6 B7 2 A7 1 D7
```

Variables:

```
B1 1.52181
B2 1.11119
A2 110.04177
B3 1.11052
A3 110.10472
D3 239.69912
B4 1.11012
A4 109.83654
D4 119.98736
B5 1.39580
A5 109.87261
D5 57.95628
B6 1.39710
A6 109.59758
D6 297.63524
B7 0.99150
A7 105.22208
D7 163.93769
```

## STEPS:

### 1. Optimize Reactants and Products



```
%mem=16gb  
%nprocshared=8  
%chk=chk.chk  
#n RMP6 Opt freq
```

Acetic Acid

```
0 1  
C  
C 1 B1  
H 1 B2 2 A2  
H 1 B3 2 A3 3 D3  
H 1 B4 2 A4 3 D4  
O 2 B5 1 A5 3 D5  
O 2 B6 1 A6 3 D6  
H 6 B7 2 A7 1 D7
```

Variables:

```
B1 1.52181  
B2 1.11119  
A2 110.04177  
B3 1.11052  
A3 110.10472  
D3 239.69912  
B4 1.11012  
A4 109.83654  
D4 119.98736  
B5 1.39580  
A5 109.87261  
D5 57.95628  
B6 1.39710  
A6 109.59758  
D6 297.63524  
B7 0.99150  
A7 105.22208  
D7 163.93769
```

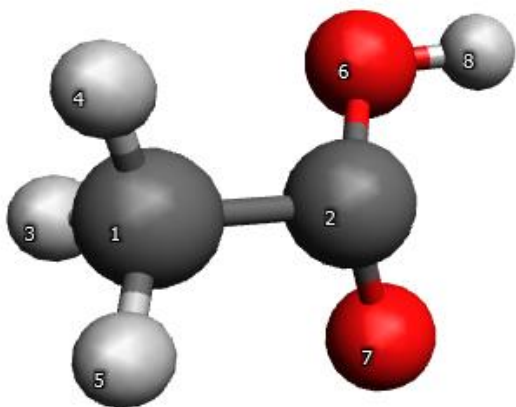
commands:

```
$ module add gaussian:09.E1
```

```
$ g09 input.com > output.log
```

## STEPS:

### 1. Optimize Reactants and Products



A8	2.27508	0.00000	-0.00000	0.00000	0.00000	2.27508
A9	2.08712	0.00000	0.00000	0.00000	0.00000	2.08713
A10	1.96868	-0.00000	-0.00000	-0.00000	-0.00001	1.96867
D1	2.10652	-0.00000	-0.00000	0.00002	0.00002	2.10654
D2	-1.03507	-0.00000	-0.00001	0.00002	0.00001	-1.03506
D3	-0.00002	0.00000	-0.00000	0.00003	0.00002	0.00000
D4	3.14158	-0.00000	-0.00001	0.00002	0.00002	-3.14159
D5	-2.10656	0.00000	0.00000	0.00003	0.00003	-2.10653
D6	1.03504	0.00000	-0.00000	0.00003	0.00003	1.03506
D7	3.14159	0.00000	-0.00000	0.00001	0.00000	3.14159
D8	-0.00001	0.00000	-0.00000	0.00001	0.00001	-0.00000

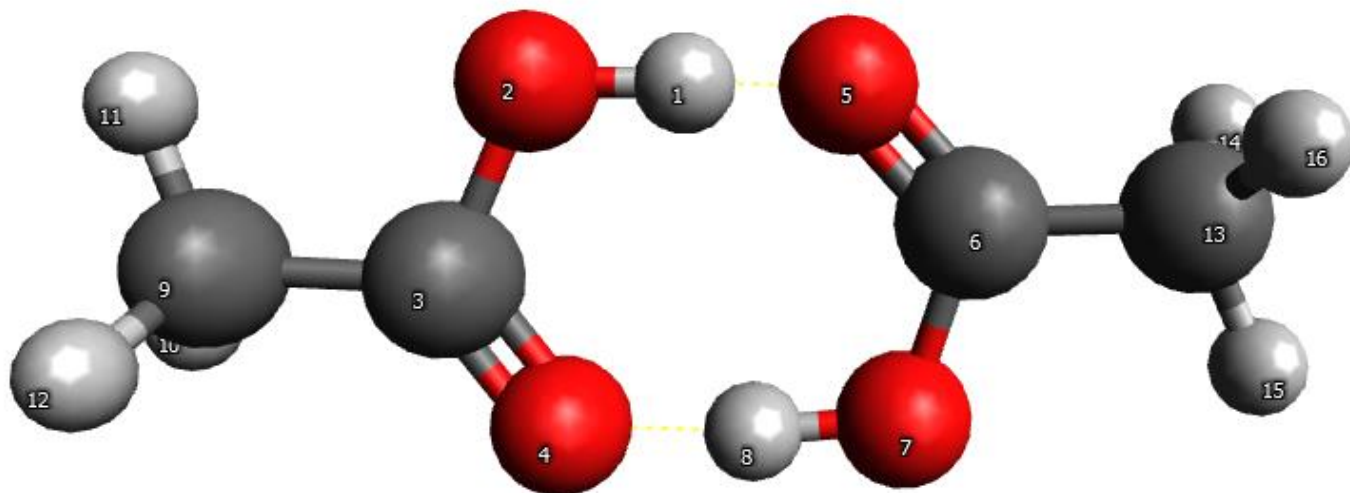
```
Item                Value      Threshold  Converged?
Maximum Force       0.000002   0.000450   YES
RMS Force           0.000001   0.000300   YES
Maximum Displacement 0.000027   0.001800   YES
RMS Displacement    0.000012   0.001200   YES
Predicted change in Energy=-4.752805D-11
Optimization completed.
-- Stationary point found.
```

```
? Optimized Parameters ?
? (Angstroms and Degrees) ?
```

? Name	Definition	Value	Derivative Info.	?
? R1	R(1,2)	1.4842	-DE/DX = 0.0	?
? R2	R(1,3)	1.1024	-DE/DX = 0.0	?
? R3	R(1,4)	1.1028	-DE/DX = 0.0	?
? R4	R(1,5)	1.1024	-DE/DX = 0.0	?
? R5	R(2,6)	1.3795	-DE/DX = 0.0	?
? R6	R(2,7)	1.2076	-DE/DX = 0.0	?
? R7	R(6,8)	0.994	-DE/DX = 0.0	?
? A1	A(2,1,3)	110.8693	-DE/DX = 0.0	?
? A2	A(2,1,4)	112.4394	-DE/DX = 0.0	?
? A3	A(2,1,5)	110.8685	-DE/DX = 0.0	?

## STEPS:

### 2. Explore PES by performing a Scan



### commands:

```
$ module add gaussian:09.E1
```

```
$ g09 input.com > output.log
```

```
%mem=16gb
%nprocshared=3
%chk=chk.chk
#n RPM6 scan

Title

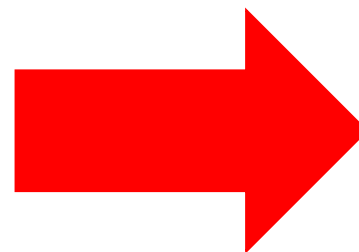
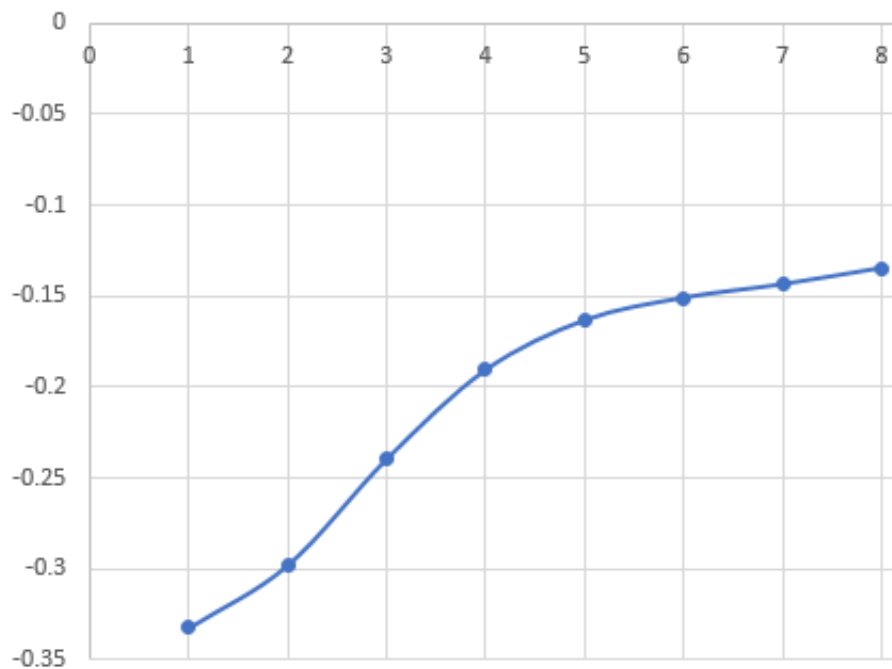
0 1
H
O 1 B1
C 2 B2 1 A2
O 3 B3 2 A3 1 D3
O 3 B4 1 A4 2 D4
C 5 B5 1 A5 2 D5
O 6 B6 5 A6 1 D6
H 7 B7 6 A7 5 D7
C 3 B8 2 A8 1 D8
H 9 B9 3 A9 2 D9
H 9 B10 3 A10 2 D10
H 9 B11 3 A11 2 D11
C 6 B12 5 A12 1 D12
H 13 B13 6 A13 5 D13
H 13 B14 6 A14 5 D14
H 13 B15 6 A15 5 D15

Variables:
B1 0.99403 7 0.3
B2 1.37953
A2 112.79699
B3 1.20766
A3 119.58346
D3 359.99794
B4 3.95017
A4 10.71582
```

## STEPS:

### 2. Explore PES by performing a Scan

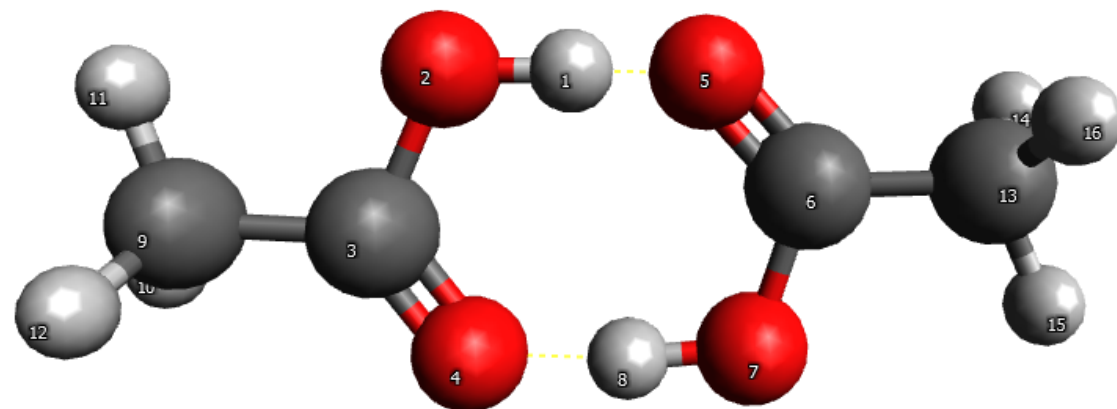
N	B1	SCF
1	0.994	-0.33221
2	1.294	-0.29779
3	1.594	-0.23958
4	1.894	-0.1908
5	2.194	-0.16356
6	2.494	-0.15121
7	2.794	-0.1438
8	3.094	-0.13491
9	3.394	-0.12091
10	3.694	-0.09992
11	3.994	-0.07412



```
Keep J ints in memory in canonical form, NReq=898175.  
Requested convergence on RMS density matrix=1.00D-08 with  
Requested convergence on MAX density matrix=1.00D-06.  
Requested convergence on energy=1.00D-06.  
No special actions if energy rises.  
SCF Done: E(RPM6) = -0.134909126930 A.U. after 15  
NFock= 14 Conv=0.75D-08 -U/T= 0.9948  
Scan completed.
```

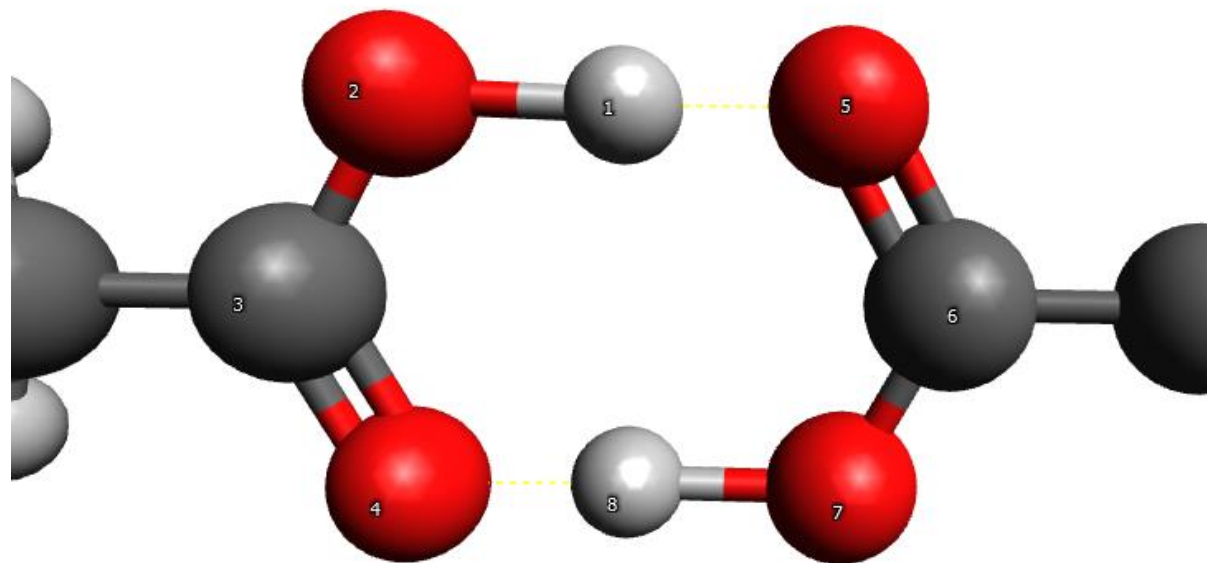
Summary of the potential surface scan:

N	B1	SCF
1	0.9940	-0.33221
2	1.2940	-0.29779
3	1.5940	-0.23958
4	1.8940	-0.19080
5	2.1940	-0.16356
6	2.4940	-0.15121
7	2.7940	-0.14380
8	3.0940	-0.13491



## STEPS:

### 3. Performed an Optimization (TS) calculation on the TS



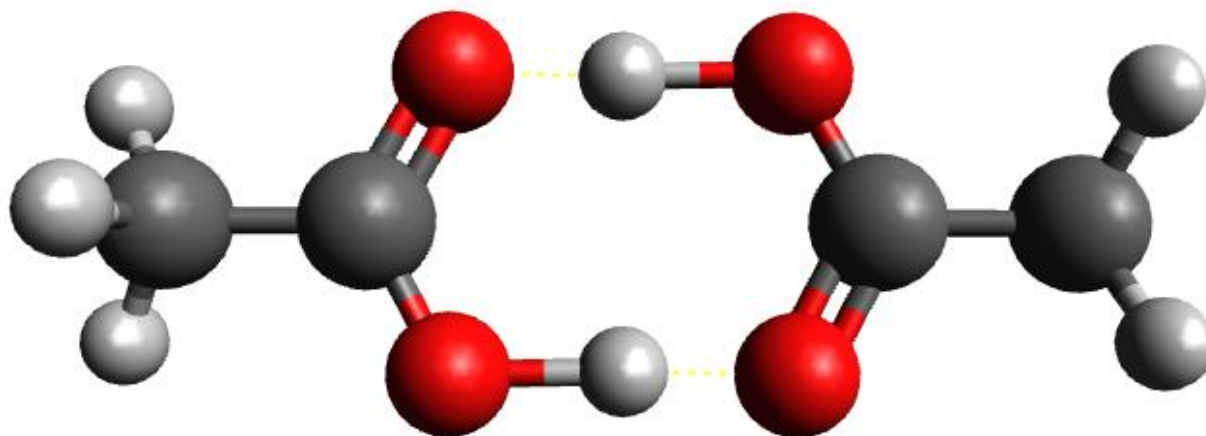
#### commands:

```
$ module add gaussian:09.E1  
$ g09 input.com > output.log
```

```
%mem=16gb  
%nprocshared=3  
%chk=chk.chk  
#n RPM6 opt(CalAll,TS,NoEigenTest,MaxCycle=40) NoSymm freq  
  
Title  
0 1  
H  
O 1 B1  
C 2 B2 1 A2  
O 3 B3 2 A3 1 D3  
O 3 B4 1 A4 2 D4  
C 5 B5 1 A5 2 D5  
O 6 B6 5 A6 1 D6  
H 7 B7 6 A7 5 D7  
C 6 B8 5 A8 1 D8  
H 9 B9 6 A9 5 D9  
H 9 B10 6 A10 5 D10  
H 9 B11 6 A11 5 D11  
C 3 B12 2 A12 1 D12  
H 13 B13 3 A13 2 D13  
H 13 B14 3 A14 2 D14  
H 13 B15 3 A15 2 D15  
Variables:  
B1 1.26210  
B2 1.27210  
A2 117.74556  
B3 1.27943  
A3 122.40418  
D3 359.74398  
B4 3.33521  
A4 10.67782  
D4 180.01226  
B5 1.27941  
A5 117.77423  
D5 180.08064  
B6 1.27971  
A6 122.40488  
D6 359.74533  
B7 1.26211  
A7 117.74340  
D7 0.25340
```

## STEPS:

### 3. Performed an Optimization (TS) calculation on the TS



Filter:  km/mol

$\nu$ (cm <sup>-1</sup> )	I (km/mol)
-811.41	0.000
5.18	0.521
6.30	0.041
56.64	6.774
77.97	0.003
141.89	0.000
214.09	0.000
230.97	4.312
340.10	0.000
479.39	0.000
539.02	0.724
547.38	0.000

Show Spectra...

Animation

Amplitude:

Normalize displacements

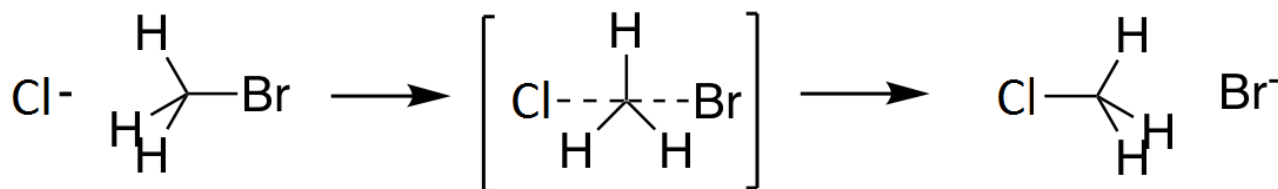
Display force vectors

Animation speed set by frequency

Messages

# Task

> model the reaction of this classic  $\text{S}_{\text{N}}2$  reaction.



## STEPS:

1. Optimize Reactants and Products
2. Explore PES by performing a Scan
3. Performed an Optimization (TS) calculation on the TS



# Population Analysis

Population analysis is the study of charge distribution within molecules.

What does a population analysis deliver

- Determination of the distribution of electrons in a molecule
- Describing the shape of orbitals
- Derivation of atomic charges and dipole ( multiple ) moments

Methods of calculation

- Based on the wave function ( Mulliken, NBO)
- Based on the electron density (Atoms in Molecules)
- Fitted to the electrostatic potential (CHELPG, MK)

# Mulliken Population Analysis

## Advantages

- Available in nearly every software program (most popular method) for molecular modeling.
- Fast and simple method for determination of electron distribution and atomic charged

## Disadvantages

- Strong dependence of the results from the level of theory (basis set or kind of calculation)

Example: Li-charge in LiF

Population	basis set	q(Li,RHF)	q(Li,B3LYP)
Mulliken	STO-3G	+0.227	+0.078
	6-31G	+0.743	+0.593
	6-311G(d)	+0.691	+0.558

# Löwdin population analysis

## Advantages

- Sought to improve upon the Mulliken method
- More stable than Mulliken with changes in basis set.

## Disadvantages

- More computationally expensive

# Natural Bond Orbital Analysis

NBO classifies atomic orbitals into two distinct groups: NAOs, NBOs. NAOs are made up of basis sets of single atoms (core, valence and Rydberg) and the NBOs are a combination of basis set atomic orbitals of two atoms.

Two parts of the methods

- NPA ! Natural population analysis to identify the population numbers
- NBO ! Analysis of the bond order based on the electron population obtained by NPA

# Natural Bond Orbital Analysis

## Advantages

- Smaller dependence on the basis set
- better reproducibility for different molecules
- Orientates itself at the formalism for Lewis formulas

## Disadvantages

- More computationally expensive
- tends to predict larger charges.
- best used for comparing differences rather than absolute atomic charges.

# AIM (Atoms in Molecules)

The population analysis using Atoms in Molecules theory is requested by keyword AIM in a Gaussian input file. Atoms in Molecules theory bases its calculations on the calculated electron density. The existence of critical points defines the existence of a bond between two nuclei in AIM.

## Advantages

- Almost no dependence on the level of basis sets.

## Disadvantages

- For a low level of theory mostly inappropriate
- Instability during calculation runs
- relatively computationally expensive.

## Task

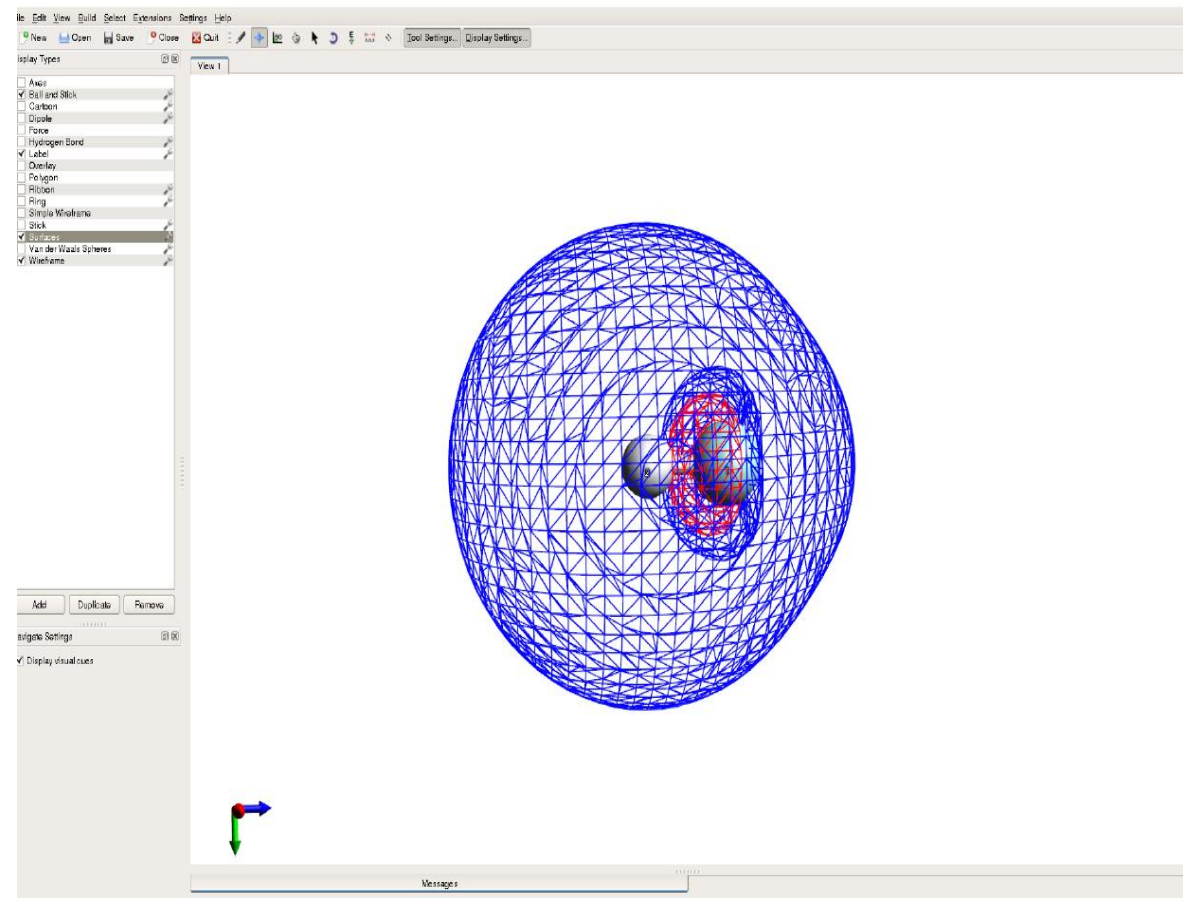
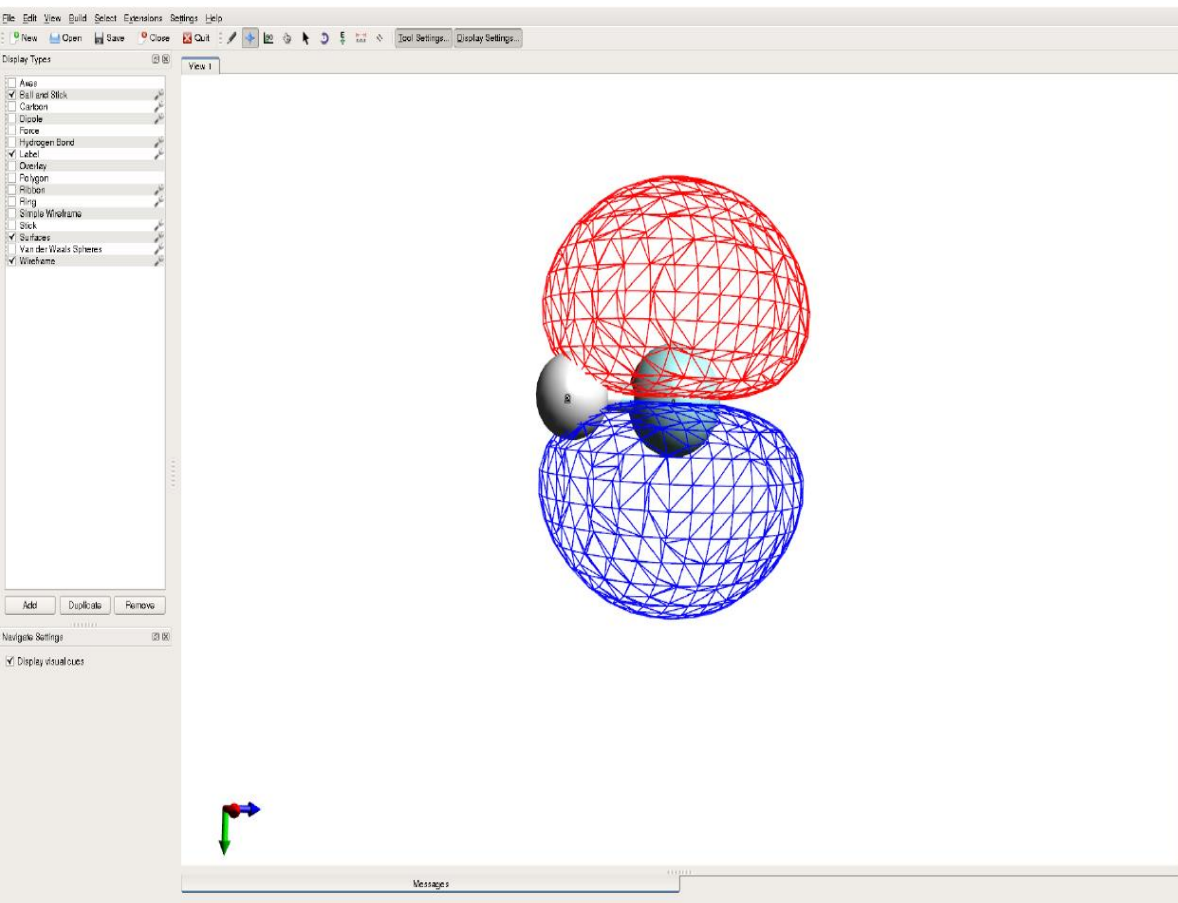
1. Draw HF molecule, optimize the geometry and generate G09 input.
2. Use pop=(full) Pop=Full for Mulliken and Pop=NBO  
After Pop command, add a space and type "FormCheck"
3. Run the calculation

### Visualizing the orbitals

1. Open the \*FChk file in Avogadro
2. Click on Extensions ! Create Surface
3. Select "Molecular Orbital" as surface type
4. Choose the MO you want to visualize and calculate



You should be able to see something like these that shows the HOMO and LUMO of HF molecules



End