

# Introduction

This document contains a basic tutorial for the *Molcas* code.

- Ex 0. usage of *luscus*
- Ex 1. Basic usage of *Molcas*
- Ex 2. DFT calculation
- Ex 3. Basis Set
- Ex 4. Unrestricted HF and DFT
- Ex 5. Dissociation of H<sub>2</sub>
- Ex 6. Geometry optimization
- Ex 7. Frequencies

## Ex. 0. Basic usage of *luscus*

*Objective:* To learn basic editing of molecules and to learn how to run *luscus*.

### 0.1 Using *luscus*

#### 0.1.1 Building a water molecule from scratch

- Use the "Add" button to add one atom! A hydrogen atom should appear.



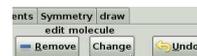
- Repeat the procedure twice again! At this point three hydrogen atoms should appear on the screen.



- Click on the middle atom! The atom should appear surrounded with a blue net. That atom is **selected**. All operations will affect that atom.



- Use the "Change" button to transform this atom into an oxygen! In the periodic system, that appears, select oxygen! (Alternatively, you can use the mouse wheel to change the selected atom.) After changing, you can remove atom selection by pressing the "unselect" button or the middle mouse button.



- Click on one of hydrogen atoms! When the hydrogen atom is selected, click on the oxygen atom. The oxygen atom should appear surrounded with a pink net. This means that all changes will be done on the hydrogen atom with respect to the oxygen atom.



- Please note that selecting two atoms activated the spin button labeled with "bond:". With that spin button, the distance (bond length) between the hydrogen atom and the oxygen atom can be adjusted. Adjust it to 0.96 Å! You can click on the arrows or type

the number in the field and press ENTER.



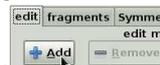
- Unselect atoms and repeat the procedure with the other hydrogen atom!
- Click on atoms in this order: hydrogen, oxygen, hydrogen! At this point, one hydrogen atom is selected for a change with respect to other two atoms. Also the spin button labeled "angle:" is activated.



- Adjust the angle to 104.5°!

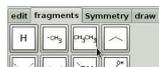


- Optionally, you can draw bonds: select two atoms (hydrogen and oxygen) and press "Add" button. Repeat the procedure with the another bond.

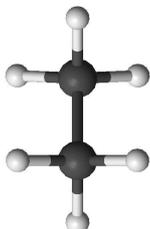


### 0.1.2 Building a methyl-ethyl ether molecule by using fragments.

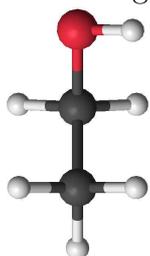
- Select the "fragments" notebook page!



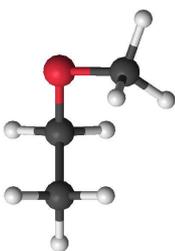
- Click on the "CH<sub>3</sub>CH<sub>3</sub>" button! A molecule of ethane should appear!



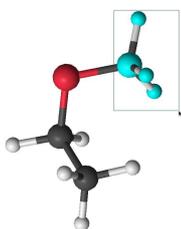
- Select one C-H bond by clicking on a carbon and a hydrogen atom! Carbon atom should be clicked first (it should have a blue net).
- Click on the "-OH" button! At this point, *luscus* should replace the selected C-H bond with the OH group.



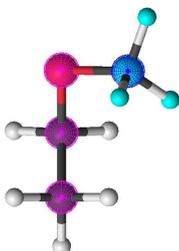
- Using the same procedure, replace the remaining O-H bond with the CH<sub>3</sub> group!



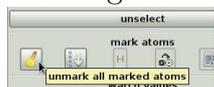
- In order to put the torsional angle C-O-C-C to  $180^\circ$ , all atoms in the methyl group must be rotated at the same time. This is accomplished by **marking** all atoms in the methyl group. Click on all atoms in the methyl group with the opposite mouse button (the order of atoms does not matter at marking). Atoms can also be marked by dragging mouse over the methyl group while pressing the opposite mouse button. Marked atoms should appear in cyan color.



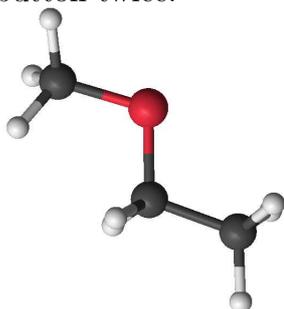
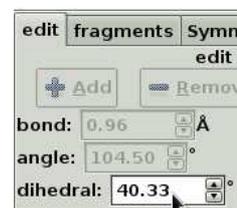
- Select atoms at this order: carbon (in the methyl group), oxygen, carbon (in the ethyl group, connected to the oxygen atom), the remaining carbon!



- In the "edit" notebook page, adjust the dihedral atom to  $180^\circ$ !



Marking can be removed by clicking on the "unmark" button, or in the same way as selection: by pressing the middle mouse button. If atoms in a molecule are marked and selected, marking and selection can be removed by pressing the middle mouse button twice.



### 0.1.3 Building a benzene molecule using symmetry

- We will exploit the  $C_6$  symmetry axis of benzene. *luscus* defines symmetry axis with two atoms (passing through it). Usually for this purpose, dummy atoms are used, but since atoms are easily deleted, any two atoms will suffice. Add two atom to the screen!



- Now, the symmetry unique portion of the molecule must be built around the "axis". In the benzene, that are one carbon and one hydrogen atom. Add one (carbon) atom and place it 1.39 Å from one of the (temporary) atoms in the axis and make sure that it lays at 90° with the respect to the another atom in the axis.



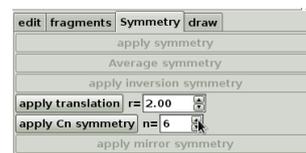
- Add the hydrogen atom at 1.09 Å from the carbon atom. Make sure that it is also at 90° with the respect to the "axis".



- Mark the carbon and the hydrogen atom from benzene (temporary atoms should not be marked)!
- Select atoms in the axis!



- In the "Symmetry" notebook page, adjust  $C_n$  symmetry to 6 and press button "apply  $C_n$  symmetry".



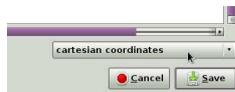
- Delete temporary atoms (select an atom and press the "remove" button)! Optionally, add bonds between atoms!



## Ex. 1. Basic usage of *Molcas*

*Objective:* To learn how to make an input for *Molcas* and how to find results in *Molcas* output.

Use *luscus* to make xyz file of the benzene molecule!



Prepare a simple input file:

```
&GATEWAY
  coord=benzene.xyz
  basis=ANO-S-VDZ
  group=C1
&SEWARD
&SCF
&GRID_IT
  ALL
```

The alternative way is to set up the input with in-line coordinates:

```
&GATEWAY
  coord
  12
File generated by luscus version 0.8.3 beta
H 0.000000000 -2.482348000 0.000000000
C 0.000000000 -1.395248000 0.000000000
C 1.208320000 0.697624000 0.000000000
C 1.208320000 -0.697624000 0.000000000
C 0.000000000 1.395248000 0.000000000
C -1.208320000 -0.697624000 0.000000000
C -1.208320000 0.697624000 0.000000000
H 0.000000000 2.482360000 0.000000000
H 2.149787000 1.241180000 0.000000000
H 2.149787000 -1.241180000 0.000000000
H -2.149787000 -1.241180000 0.000000000
H -2.149787000 1.241180000 0.000000000
  basis=ANO-S-VDZ
  group=C1
&SEWARD
&SCF
&GRID_IT
  ALL
```

Submit calculation to the farm! Upon finishing, several output files should return:

- benzene.log - output
- benzene.err - timings, info, etc.
- benzene.lus - *luscus* file
- benzene.ScfOrb - orbital (restart) file

What to check in the output:

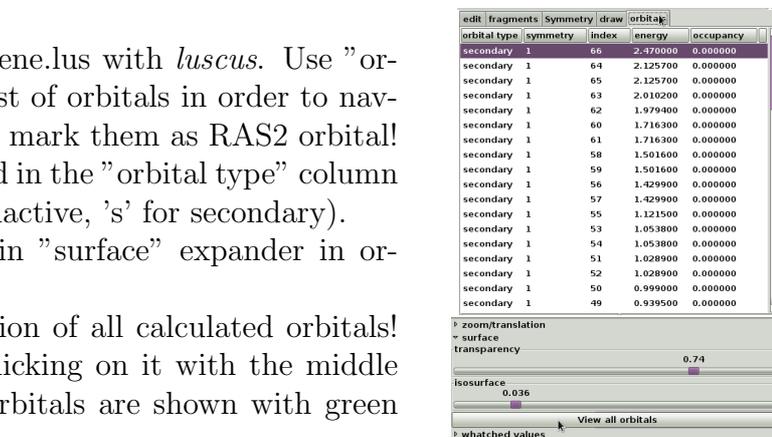
- Header
  - Parameters of calculation
  - Input
- Gateway and Seward
  - Coordinates
  - Symmetry
  - Number of basis functions
- SCF
  - Number of occupied orbitals
  - Hamiltonian
  - SCF-convergence
  - Total energy
  - Orbitals: energy and composition
  - Atomic charges
  - Dipole moment

To visualize orbitals, open benzene.lus with *luscus*. Use "orbitals" notebook page to get the list of orbitals in order to navigate them! Identify  $\pi$  orbitals and mark them as RAS2 orbital! That can be done by selecting a field in the "orbital type" column or pressing number 2 (Use 'i' for inactive, 's' for secondary).

Use "View all orbitals" button in "surface" expander in order to get a multiview representation of all calculated orbitals! Orbital type can be changed by clicking on it with the middle mouse button. Note that RAS2 orbitals are shown with green background.

Save the orbital (GvOrb) file (select "molcas orbital data" in

dropdown menu) and close *luscus*!



## Supplementary information:

Short description of Molcas input syntax:

- Programs names begin with & symbol
- Commands can be written as KEY=VALUE, or in two lines: KEY <CR> VALUE
- Input is case insensitive (except for file names)
- Special commands begin '>'
- Predefined variables:  $\$CurrDir$ ,  $\$WorkDir$ ,  $\$Project$
- To comment, use multi-line comment `/* */`, or single line comment `//`

Explanation of input:

- `&GATEWAY` - first module, collecting information about the system
- `coord` = keyword to specify Cartesian coordinates. (can be also written as: `coord =  $\$CurrDir/\$Project.xyz$` )
- `basis` = definition of a basis set. Select the "Help system" link and type `'molcas help basis C'` command to get the list of available basis sets
- `group` = C1. No symmetry. The alternative is `group = full` (the default)
- `&SEWARD` - Compute integrals and guess starting orbitals
- `&SCF` - Compute Hartree-Fock wavefunction
- `&GRID_IT` - Compute grid for visualization
- `ALL` - keyword to compute all orbitals. Alternative: `SELECT=1:20-40` (select orbitals from 20 to 40 from symmetry 1)

Use online help system, to execute a "molcas help" command:

```
molcas help
molcas help grid_it
molcas help grid_it all
```

## Ex. 2. DFT calculations

Add a line `KSDFT=B3LYP` after `&SCF` in order to use the B3LYP functional!

It is possible to read orbitals as an initial guess, from the previous calculation (`FILEORB=benzene.Scf0rb`).

```
&GATEWAY
  coord=benzene.xyz
  basis=ANO-S-VDZ
  group=C1
&SEWARD
&SCF
  KSDFT=B3LYP
  FILEORB=benzene.Scf0rb
&GRID_IT
  SELECT=1:7-30
```

Observe the differences between the results obtained with the Hartree-Fock Hamiltonian, and the B3LYP Hamiltonian!

Get the list of functionals, using `'molcas help scf ksdft'` command!

## Ex. 3. Basis set

Get the list of basis sets for C atom using `'molcas help basis C'` command!

Consider ANO-S-MB, ANO-S-VDZ, ANO-S-VDZP basis sets! Observe the difference between the results!

## Ex. 4. Unrestricted HF and DFT

Use `UHF` keyword in `&SCF` in order to perform Unrestricted HF calculation!

Compute the ionization potential for  $N_2$  molecule using the Koopman's theorem and the difference between energies for  $N_2$  and  $N_2^+$ !

## Ex. 5. Dissociation of $H_2$ molecule

Use keywords `UHF` and `SCRAMBLE=0.2` (to make permutations in  $\alpha$  and  $\beta$  components of UHF density!

`NODIIS` keyword is used to switch off convergence acceleration.

Compute  $H_2$  molecule at equilibrium distance, and on a large separation!

Compare the results with ones from RHF!

Use the following input to compute the set:

```

>>FOREACH XX in ( 1..40)
>>EVAL DIST=0.5+ $\$XX/10$ 

&GATEWAY
  coord
  2
  h2 molecule
  H 0 0 0
  H  $\$DIST$  0 0
  basis=ANO-S-VDZ
  group=C1
&SEWARD
&SCF
  UHF
  SCRAMBLE=0.2
  NODIIS
>>END DO

```

## Ex. 6. Geometry optimization

Use the following template to optimize geometry:

```

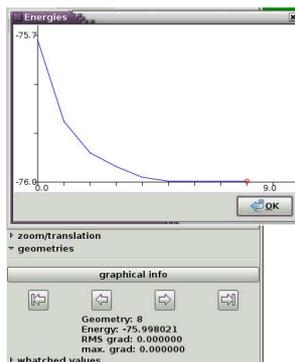
&GATEWAY

...
>>DO WHILE
  &SEWARD
  &SCF
  &SLAPAF
>>END DO

```

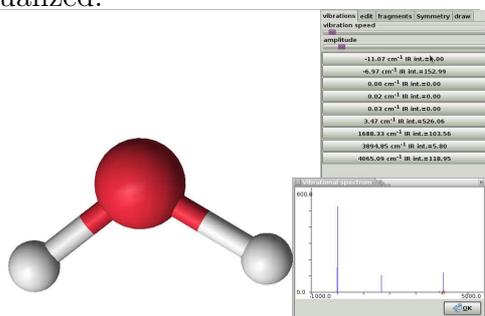
Choose a small molecule and optimize geometry! Optionally, observe the difference in bond lengths and angles in between calculations done with different Hamiltonians (HF, DFT)!

Observe the convergence of geometries in SLAPAF loops! Use *luscus* to visualize .geo.molden file! Use "geometries" expander or mouse wheel to navigate geometries!



## Ex. 7. Frequency calculation

After geometry optimization loop add another module `&MCKINLEY`, which computes frequencies! The resulting file is `.freq.molden`. Visualize the vibrations with *luscus*! Use "vibrations" notebook page to get list of frequencies! Selecting frequencies from the list, normal modes can be visualized.



How many frequencies can you see?