Introduction to MOLCAS

- Ex 1. Basic usage of Molcas (30 min).
- Ex 2. DFT calculations (20 min).
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- Ex 8. Interaction between two molecules (30 min)

Ex. 1. Basic usage of Molcas.

Objective: we will learn how to run Molcas, and use simple graphical interface GV.

Create a simple input file benzene.inp:

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

>>FILE Benzene.xyz
12
 produced by gV
H   0.000000  -2.482348   0.000000
C   0.000000   1.395248   0.000000
```

```
C   1.208320   0.697624   0.000000
C   1.208320  -0.697624   0.000000
C   0.000000  -1.395248   0.000000
C  -1.208320  -0.697624   0.000000
C  -1.208320   0.697624   0.000000
H   0.000000   2.482360   0.000000
H   2.149787   1.241180   0.000000
H   2.149787  -1.241180   0.000000
H  -2.149787  -1.241180   0.000000
H  -2.149787   1.241180   0.000000
>>EOF
```

To submit:
ID: farm

Alternative ways to set up input (inline coordinates):

```
 &GATEWAY
   coord
12
 produced by gV
H   0.000000  -2.482348   0.000000
C   0.000000   1.395248   0.000000
C   1.208320   0.697624   0.000000
....
   basis=ANO-S-VDZ
   group=C1
```

Output files:

- benzene.log - output
- benzene.err - timings, info, etc.
- benzene.grid - grid file
- benzene.dos.grid - grid file in Windows format
- 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:

```
gv.exe benzene.dos.grid
```

Use PageUp/PageDown to scroll orbitals

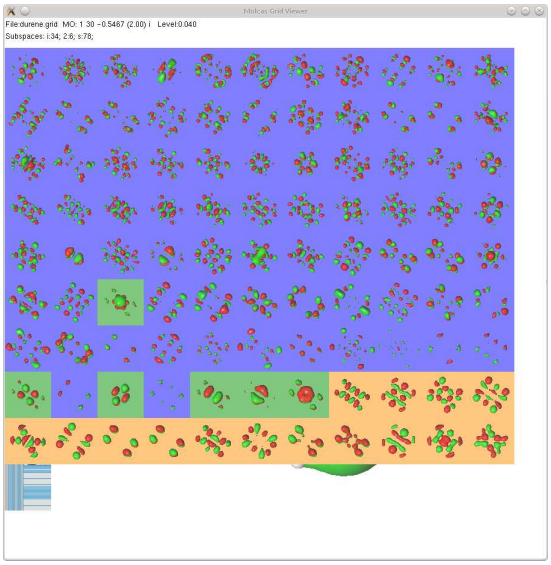
Note the header - Orbital number, orbital energy, occupation, iso-level. Also note the subspaces - number of inactive and virtual (secondary) orbitals.

File:durene.grid MO: 1 36 -0.3277 (2.00) i Level:0.040
Subspaces: i:37; s:81;

Use right mouse button, and 'Show grid' to show a list of orbitals. Finally - the sequence $F4$ # 1 37 jump to the orbital 37 in symmetry 1.

Identify $\pi-$ orbitals and while displaying them press '2' to mark them as RAS2 orbital. (Use 'i' for inactive, 's' for secondary).

Use F3 button to go to multi-view mode (and Esc to go back). Note 6 orbitals with green background.



Save the orbital file using F2 button, and quit by pressing Ctrl-Q.

Observe Benzene.log file, and identify the selected orbitals in the output.

Supplimentary information:
Short description of Molcas input syntax:

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

- Programs started from & symbol
- commands can be written as KEY=VALUE, or in two lines: KEY $< CR >$ VALUE
- Case Insensitive (except for file names)
- Special commands started from $' >'$
- 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: $coord = \$CurrDir/\$Project.xyz$)
- $basis =$. Use 'molcas help basis C' 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

For help:

```
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 B3LYP functional.

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

Repeat the exercise with BLYP functions.

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 IP for N_2 molecule. Using 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 α and β 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

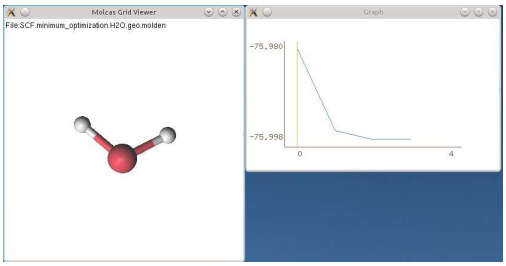
Use the following template to optimize geometry

```
 &GATEWAY
   ..

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

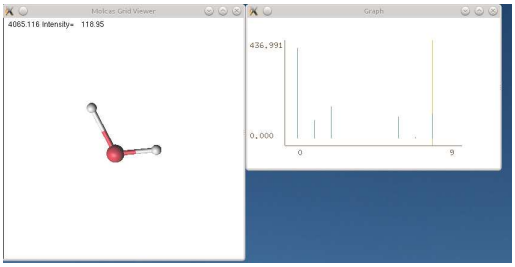
Choose a small molecule and optimize geometry. Optionally observe the difference in bond lengths and angles in between calculations done with different Hamiltomians (HF, DFT, semiempirical (use Mopac).

Observe the convergence of geometries in SLAPAF loops. Use GV to visualize .geo.molden file. Useful keys: Home, End, PgUp, F3.



Ex. 7. Frequency calculation for water molecule

After geometry optimization loop add another module $\&MCKINLEY$, which computes frequencies. The resulting file is .freq.molden. Visualize the vibrations with GV. Useful keys: Home, End, PgUp, F3.



How many freqencies can you see?

Ex. 8. Interaction between two molecules

Using GV construct a complex containing CH_3OH and H_2O molecules. Save the resulting coordinates. Optionally, optimize the geometry (e.g. using MOPAC software).

Now, make two additional copies of XYZ file, and modify them so in one file all atoms from water molecule are changed to X. In another file, in opposite - all atoms from methanol are changed to X.

In the Gateway section add keyword GROUP=C1, and to GRID_IT section add keyword TOTAL (to compute total electron density). Run three calculations, and save resulting grid files.

```
&GATEWAY
coord = complex.xyz
basis = ANO-S-MB
nomove
&seward
&scf
&grid_it
total
name
complex

&GATEWAY
coord = water.xyz
basis = ANO-S-MB
nomove
&seward
&scf
&grid_it
total
name
water

&GATEWAY
coord = methanol.xyz
basis = ANO-S-MB
nomove
&seward
&scf
&grid_it
total
name
methanol
```

Use parameters to run GV (or run GV from a command prompt) in the following way (assuming that grid files have names water and methanol):

```
gv.exe -a 1.0 water.dos.grid methanol.dos.grid --out sum.dos.grid
```

flag '-a 1.0' computes a sum of two grids.

Next command shows the difference between densities $(A+B)-((A)-(B))$.

```
gv.exe -a -1.0 complex.dos.grid sum.dos.grid --out result.dos.grid
```

If the picture is 'void' - press F4 and enter a small number for isovalue, e.g. 0.0001.