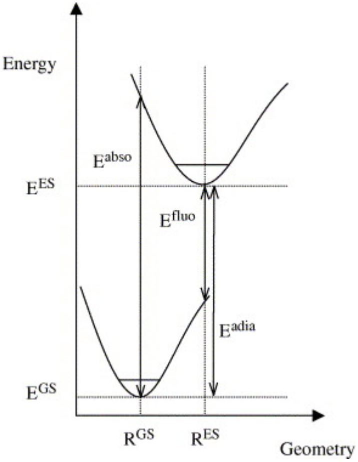
Absorbtion and emission spectra of formaldehyde

Background



From http://dx.doi.org/10.1016/j.cplett.2006.01.068

Fomaldehyde is the prototype molecule for studying the $n \rightarrow \pi^*$ type of excitation chromophores. Here is a scematic presentation of the processes that we are going to study in this session. $\mathbf{R^{GS}}$ and $\mathbf{R^{ES}}$ represent the ground and excited state minimum geometries, respectively. $\mathbf{E^{GS}}$ and $\mathbf{E^{ES}}$ are the corresponding energies. $\mathbf{E^{abso}}$,$\mathbf{E^{fluo}}$ and $\mathbf{E^{adia}}$ are the absorbtion, fluorescence and adiabatic transition energies, respectively.

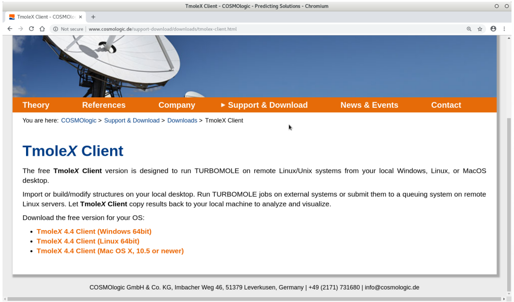
Outline

We are using Turbomole 7.3/TmoleX 4.4/TD-DFT to study formaldehyde in order to:

- Obtain the equilibrium structure of the ground state
- Calculate the vertical absorbtion spectrum of the ground state
- Identify and characterize the first excited state
- Optimize the structure of the first excited state
- Calculate the emission spectrum of the first excited state

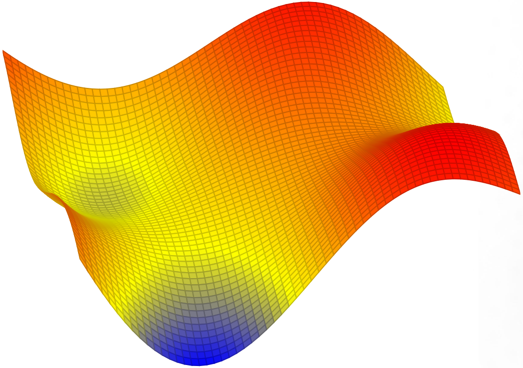
Download and install TmoleX

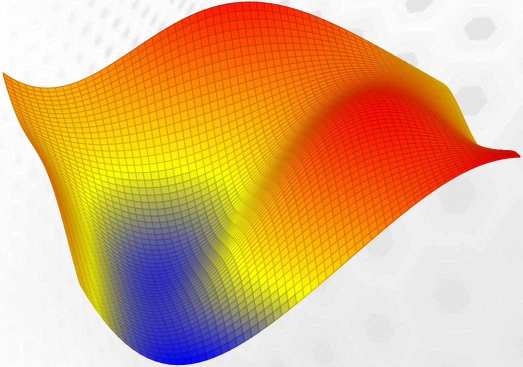
Download the TmoleX GUI client from
`http://www.cosmologic.de/support-download/downloads/tmolex-client.html`
(Users who feel more comfortable working from the command line are of course free to do so)



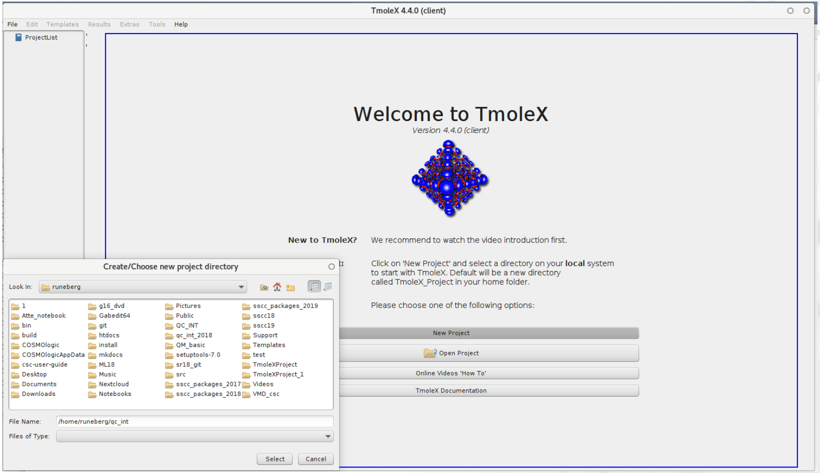
Task 1: Optimize ground state structure of formaldehyde

We need an initial guess for the geometry specifying the 3N-6 internal nuclear coordinates. This initial structure place the system on the energy surface that is uniquely defined by the computational model we are going to use (B-O approx.). The performance of the model often vary at different parts of the surface.

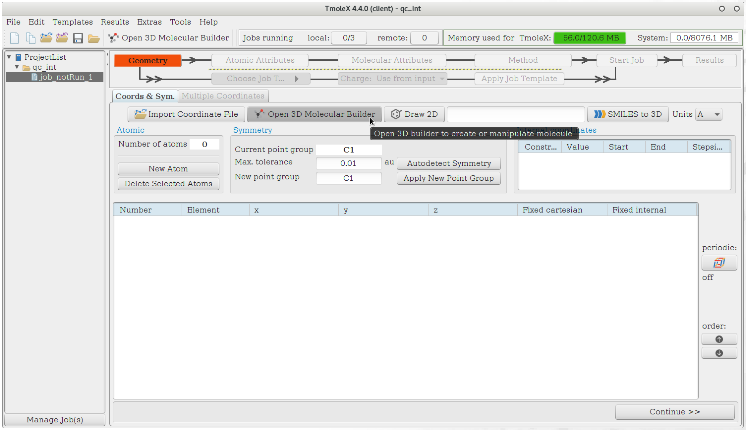




Launch TmoleX and create a new project



Define your first Turbomole job

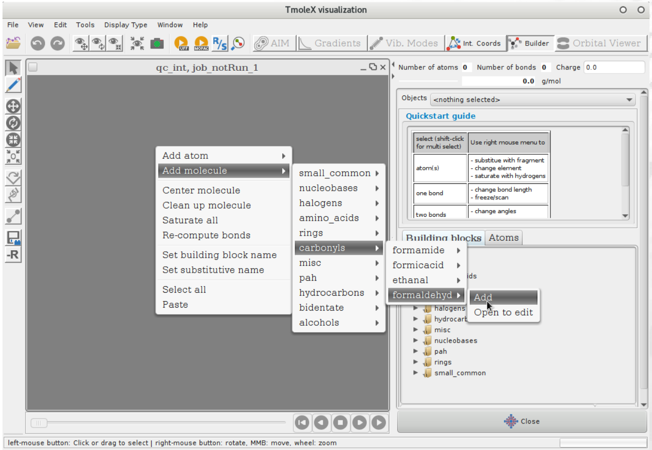


A complete Turbomole job comprises the sequence:

Geometry - Atomic Attributes - Molecular Attributes - Method - Start Job - Results

Geometry: Build formaldehyde

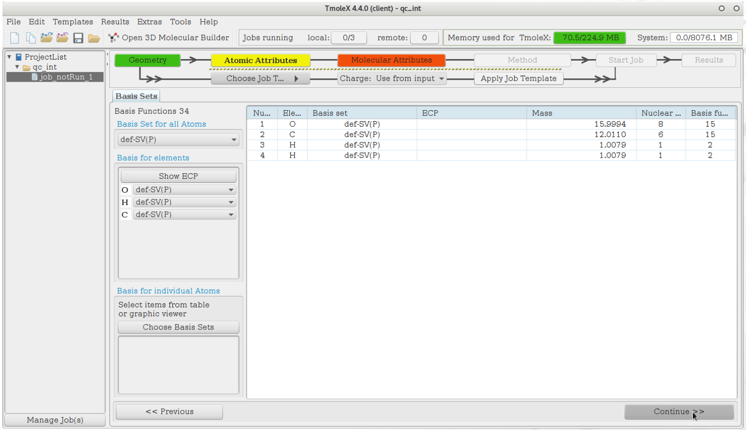
Open the 3D builder, right-click on canvas and load formaldehyde from the library



Close the builder and continue to Atomic Attributes

Atomic Attributes: Select basis set

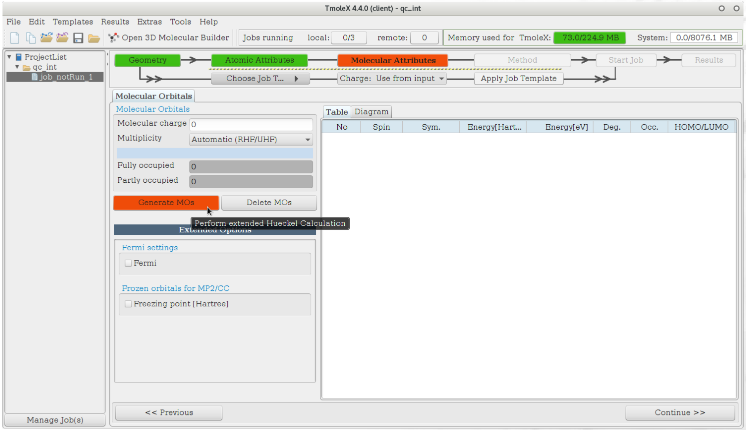
Select the default def-SV(P) basis set



Continue to Molecular Attributes

Molecular Attributes: Generate initial guess MOs

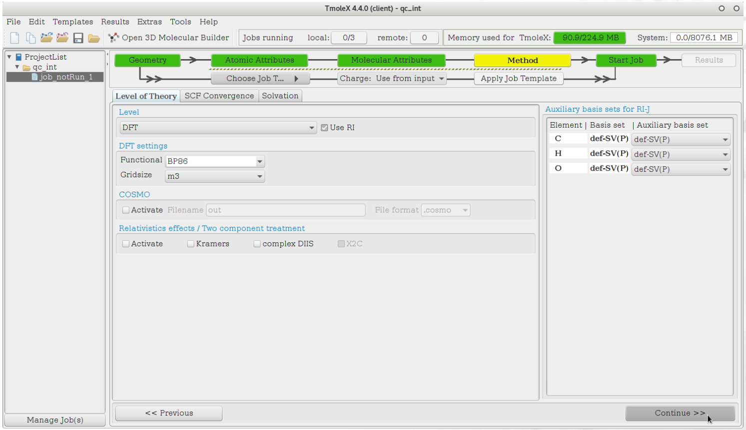
Generate initial MOs by doing an extended Hückel calculation



Continue to Method

Method: Define your method

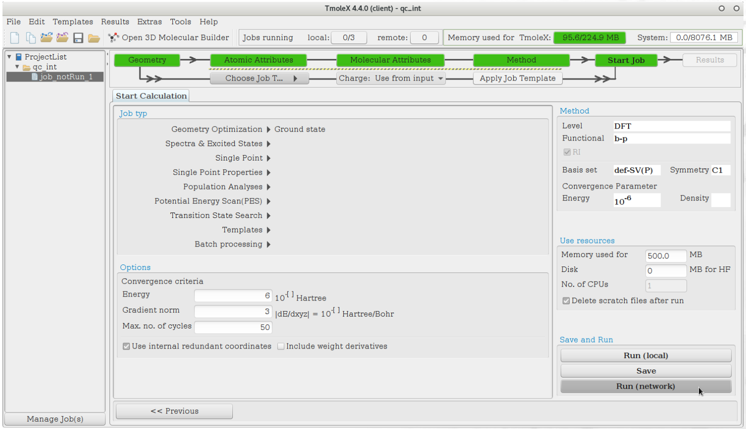
Select the default method (ri-dft BP86/m3)



Continue to Start Job

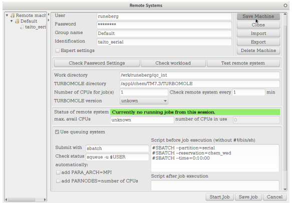
Start Job: Define your job type

We want to do a geometry optimization of the ground state



Continue to Run(network)

Run(network): Setup remote job



Machine/IP: `puhti.csc.fi`

User: `training0XX`

Work directory: `/scratch/project_2002722/training0XX`

TURBOMOLE directory:
`/appl/soft/chem/turbomole/7.4.1/TURBOMOLE`

Submit with: `sbatch`

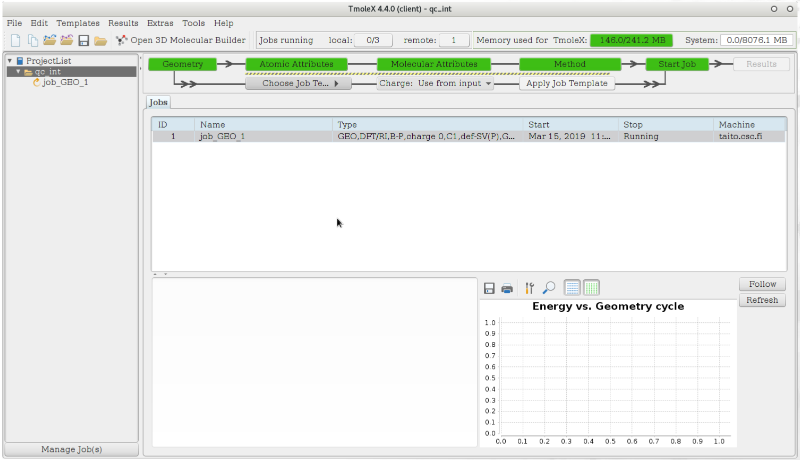
Check status: `squeue -u $USER`

Script before job execution:

```
#SBATCH --partition=small
#SBATCH --account=project_2002722
#SBATCH --time=00:10:00
#SBATCH --reservation=Spring_school_11
```

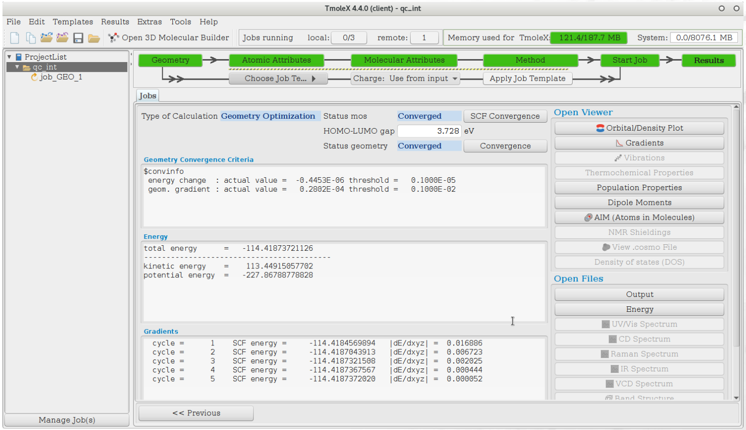
Save Settings and Start

Run(network): Job starts



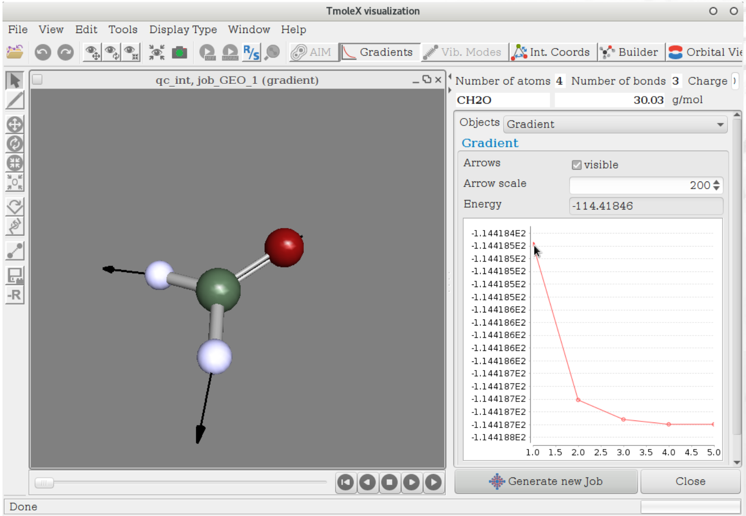
Results:

The geometry optimization needed 5 cycles to reach the stationary point on the energy surface



Results: Gradients

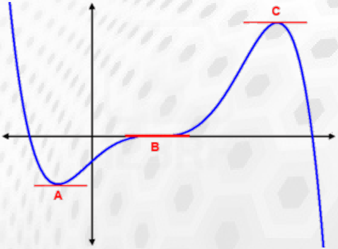
The length of the arrows show how steep the energy surface is in that direction



Results: Gradients

At the end of the geometry optimization we have reached a stationary point (gradient smaller than a given threshold) that could correspond to:

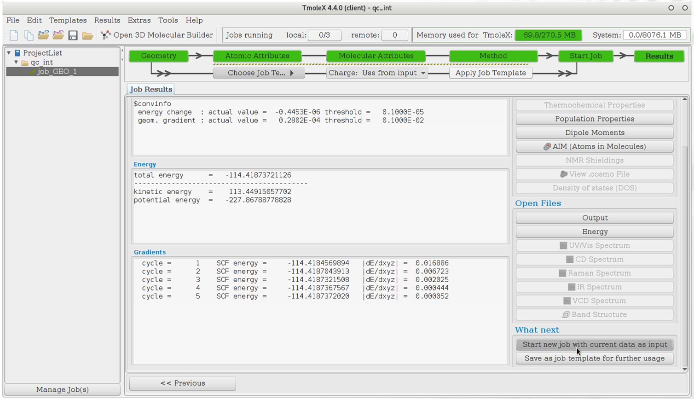
- a minimum **A**
- an inflection point **B**
- a maximum **C**



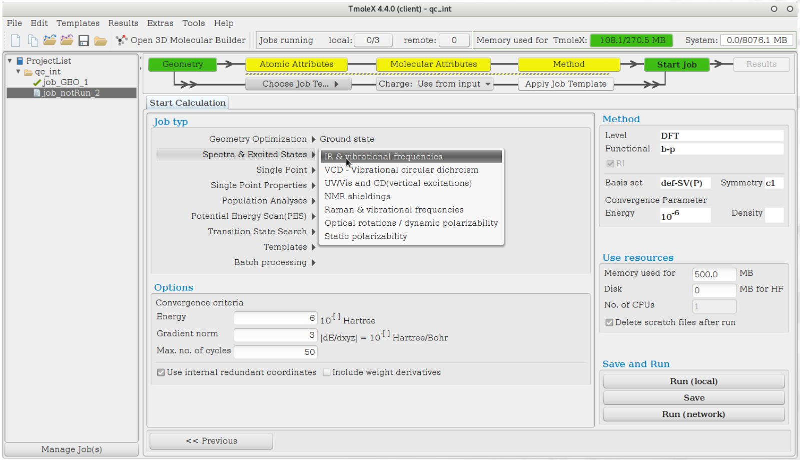
The nature of the stationary point can be deduced from the curvature (Hessian). A positive curvature corresponds to a minimum, a negative to a maximum.

Vibrational spectrum

In order to verify that the stationary point is a true minimum (positive curvature in all directions = positive frequencies) do a frequency calc (Reuse data by just hitting "Start new job by using current data as input")

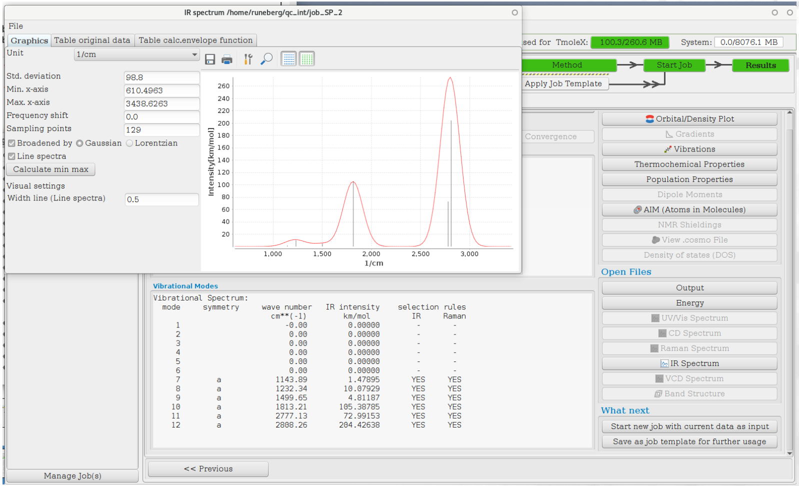


Vibrational spectrum



Results: Frequency calculation

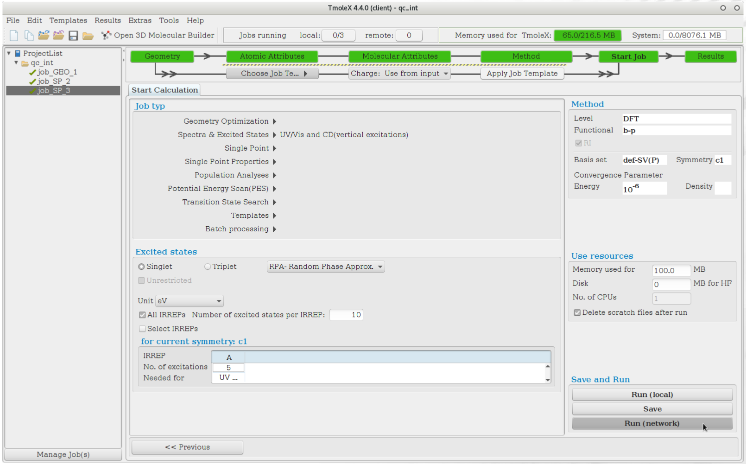
All calculated frequencies are positive indicating that the structure corresponds to a true minimum.



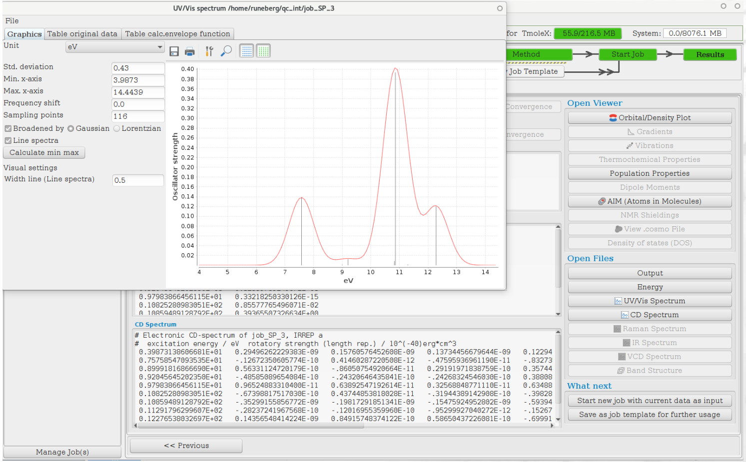
Task 2: Vertical absorbtion spectrum of the ground state

"Start Job" -> "Spectra & Excited states"

Do for singlet states and 10 excitations



Spectra & Excited states

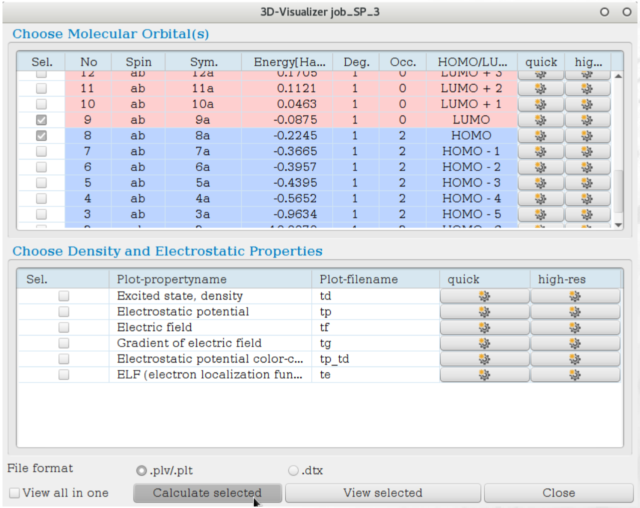


Task 3: Identify and characterize the first excited state

Check output for the lowest excitation E^{abso} and the type of excitation this corresponds to

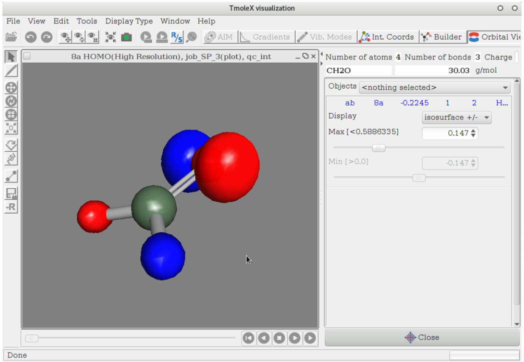
```
TextViewer - escf.out
File  Edit

                         1 singlet a excitation

Total energy:                           0.1465310282411775

Excitation energy:                      0.1465310282411775

Excitation energy / eV:                  3.987313860668139

Excitation energy / nm:                  310.9467885873743

Excitation energy / cm^(-1):             32159.84330932370

Oscillator strength:

   velocity representation:             0.5214305318188062E-15

   length representation:               0.2185238079746286E-15

   mixed representation:                0.3375573805073740E-15

Rotatory strength:

   velocity representation:             0.5231221861493721E-14

   velocity rep. / 10^(-40)erg*cm^3:    0.3379621279421632E-09

   length representation:               0.4565644462775598E-14

   length rep. / 10^(-40)erg*cm^3:      0.2949626222938295E-09

Dominant contributions:

     occ. orbital   energy / eV   virt. orbital     energy / eV   |coeff.|^2*100
       8 a              -6.11         9 a              -2.38         100.0
```

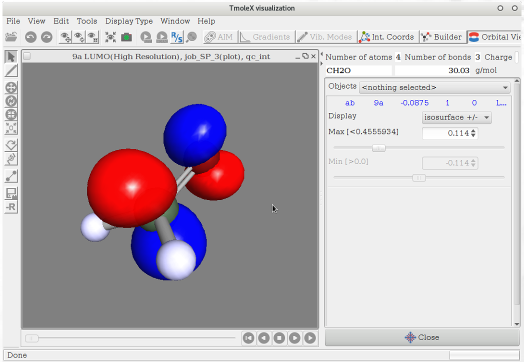
Spectra & Excited states



Select the relevant "8a" and "9a" orbitals

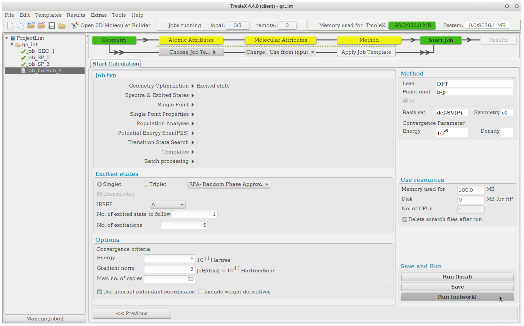
Relevant orbitals

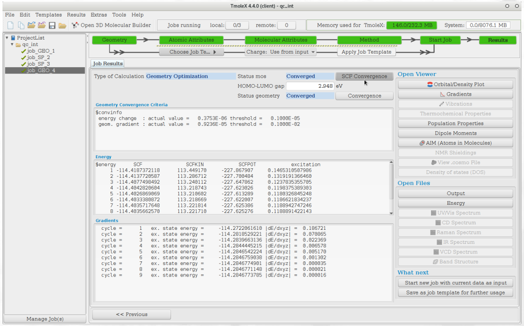




The "8a" HOMO orbital corresponds to a non-bonding (n) electron pair on oxygen. The "9a" LUMO orbital corresponds to an antibonding (π^*) orbital between oxygen and carbon. The lowest vertical excited state is the $n \rightarrow \pi^*$ we are interested in.

Task 4: Optimize the excited state structure





The geometry optimization converged to a stationary point but is it a true minimum?

NumForce

TmoleX is not capable of doing NumForce calc's. Hence we need to copy yhe optimized structure to taito-shell and do the Numforce from command line.

Copy directory: `scp -r job_GEO_4 training050@puhti.csc.fi:/scratch/project_2002722/training050/`

Login: `ssh -X puhti.csc.fi -l training050` (`-l`, letter L)

On Puhti go to directory: `cd /scratch/project_2002722/training050`

NumForce

```
runeberg@c309:/wrk/runeberg/qc_int/job_GEO_4/numforce

https://research.csc.fi/taito-disk-environment

[runeberg@c309 ~]$ cd /wrk/runeberg/qc_int/job_GEO_4/
[runeberg@c309 job_GEO_4]$ ls
auxbasis  converged  exspectrum        Job_Ended  kill-job        slurm-41905297.out
basis     coord      GEO_OPT_CONVERGED job.last   message.output  start-job
control   energy     gradient          job.start  mos             start-job.out
[runeberg@c309 job_GEO_4]$ module load turbomole/7.3
Turbomole version 7.3 environment loaded
For an example jobfile, see
/appl/chem/TM7.3/job-tm73-taito.job
[runeberg@c309 job_GEO_4]$ cpc numforce
File control is copied to numforce
File energy is copied to numforce
File coord is copied to numforce
File auxbasis is copied to numforce
File gradient is copied to numforce
File basis is copied to numforce
File out.cosmo does not exist
File mos is copied to numforce
File coord is copied to numforce
File forceapprox does not exist
File optinfo does not exist
File hessapprox does not exist
[runeberg@c309 job_GEO_4]$ cd numforce/
[runeberg@c309 numforce]$ NumForce -ri -ex 1 &> NumForce.out&
```

```
runeberg@c309:/wrk/runeberg/qc_int/job_GEO_4/numforce
File mos is copied to numforce
File coord is copied to numforce
File forceapprox does not exist
File optinfo does not exist
File hessapprox does not exist
[runeberg@c309 job_GEO_4]$ cd numforce/
[runeberg@c309 numforce]$ NumForce -ri -ex 1 &> NumForce.out&
[1] 35976
[runeberg@c309 numforce]$ cat vibspectrum
$vibrational spectrum
#  mode     symmetry     wave number   IR intensity    selection rules
#                         cm**(-1)        km/mol         IR     RAMAN
     1         a          -621.32         0.00000       YES     YES
     2                      -0.00         0.00000        -       -
     3                       0.00         0.00000        -       -
     4                       0.00         0.00000        -       -
     5                       0.00         0.00000        -       -
     6                       0.00         0.00000        -       -
     7                       0.00         0.00000        -       -
     8         a           840.37         4.28666       YES     YES
     9         a          1230.44        32.87024       YES     YES
    10         a          1328.63         0.11252       YES     YES
    11         a          2977.91        13.33534       YES     YES
    12         a          3085.26         7.52104       YES     YES
$end
[1]+  Done                    NumForce -ri -ex 1 &>NumForce.out
[runeberg@c309 numforce]$
```

Windows users should issue the command: dos2unix *

Load turbomole environment: `module load turbomole/7.4.1`

Copy inputs to a new directory: `cpc numforce`

Go to new directory: `cd numforce`

Start NumForce: `NumForce -ri -ex 1 &> NumForce.out&`

Check results: `cat vibspectrum`

NumForce

Since there is one imaginary frequency (negative force constant) the stationary structure is not a minimum but a saddle point.

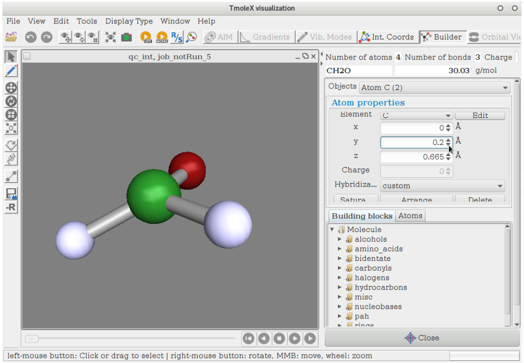
Copy the numforce results bck to your workstation:

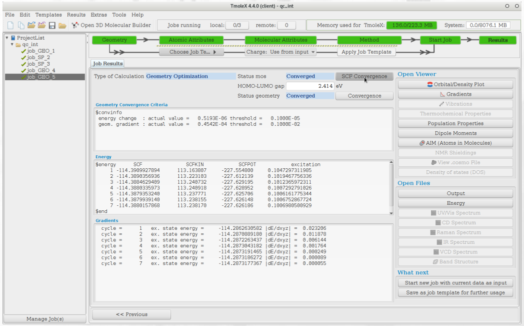
```
scp -r
training050@puhti.csc.fi:/scratch/project_2002722/training050/numforce
.
```

Select the numforce project and animate the imaginary frequency

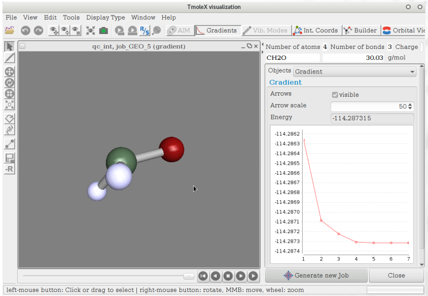
Excited state optimization, new try

Since the mode corresponds to an umbrella motion where the planar structure is balancing on the ridge of folding the umbrella either left or right) we want to distort the new starting structure in that direction. Open the 3D Builder, select the carbon atom and distort it in the y-direction. Then redo the optimization.





From the "Gradients" menu confirm that this is a new stationary point corresponding to a pyramidal structure



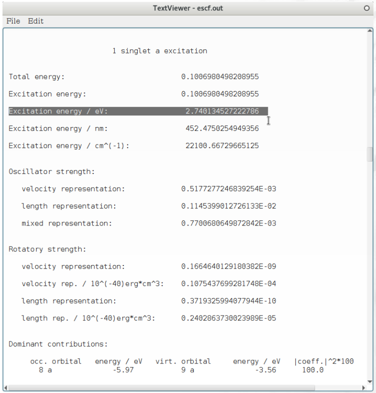
Copy the new optimized structure bach to Puhti and redo the Numforce.

- Copy directory: `scp -r job_GEO_5 training050@puhti.csc.fi:/scratch/project_2002722/training050/`
- Load turbomole environment: `module load turbomole/7.4.1`
- Copy inputs to a new directory: `cpc numforce`
- Go to new directory: `cd numforce`
- Start NumForce: `NumForce -ri -ex 1 &> NumForce.out&`
- Check results: `cat vibspectrum`

Task 5: Calculate the emission spectrum of the first excited state

The optimized exited state geometry corresponds to a true minimum. At that geometry, redo the exitation spectrum `"Start Job" -> "Spectra & Excited states"`

Do it for singlet states and 10 excitations



```
TextViewer - escf.out
File  Edit

                         1 singlet a excitation

Total energy:                              0.1006980498208955
Excitation energy:                         0.1006980498208955
Excitation energy / eV:                     2.740134527222786
Excitation energy / nm:                     452.4750254949356
Excitation energy / cm^(-1):                22100.66729665125

Oscillator strength:
   velocity representation:                0.5177277246839254E-03
   length representation:                  0.1145399012726133E-02
   mixed representation:                   0.7700680649872842E-03

Rotatory strength:
   velocity representation:                0.1664640129180382E-09
   velocity rep. / 10^(-40)erg*cm^3:       0.1075437699281748E-04
   length representation:                  0.3719325994077944E-10
   length rep. / 10^(-40)erg*cm^3:         0.2402863730023989E-05

Dominant contributions:
     occ. orbital   energy / eV   virt. orbital     energy / eV   |coeff.|^2*100
       8 a           -5.97          9 a              -3.56        100.0
```

Results

- Tabulate all relevant data such as $\mathbf{R^{GS}}$, $\mathbf{R^{ES}}$ $\mathbf{E^{GS}}$,$\mathbf{E^{ES}}$, as well as $\mathbf{E^{abso}}$, $\mathbf{E^{fluo}}$ $\mathbf{E^{adia}}$ and $\mathbf{E^{adia}}_{\mathbf{ZPVE}}$
- Compare your results with experimental data found in the literature
- Compare your results with computational results obtained at more sofisticated levels of theories
- If you have time, apply the efficient ricc2 implementation in Turbomole on the system
- If you have time, extend the study to include solvent effects (COSMO)

Possible issues?

- Is the basis set sufficient?
- What is the ultimate choise of functional?
- For this particular physical problem is tddft the method of choise?
- How does the environment interact?
- Should we be more careful when treating dispersion (intra, inter)?
- Relativity?
- Temperature and dynamics?