

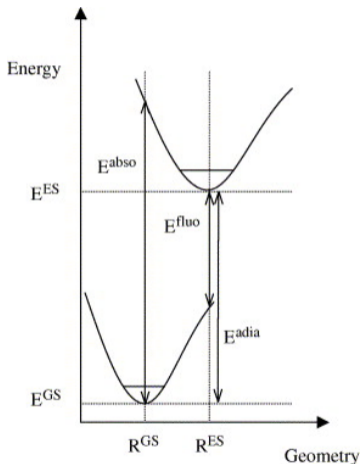


Expertise from Knowledge



Absorbtion and emission spectra of formaldehyde

Background



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

From <http://dx.doi.org/10.1016/j.cpllett.2006.01.068>

Outline

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

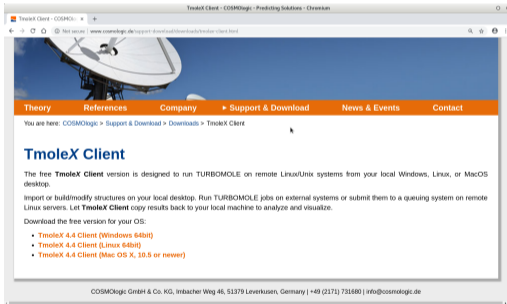
- ▶ Obtain the equilibrium structure of the ground state
- ▶ Calculate the vertical absorption spectrum of the ground state
- ▶ Identify and characterize the first excited state
- ▶ Optimize the structure of the first excited state
- ▶ Calculate the emission spectrum of the first excited state

Download and install TmoleX

Download the TmoleX GUI client from

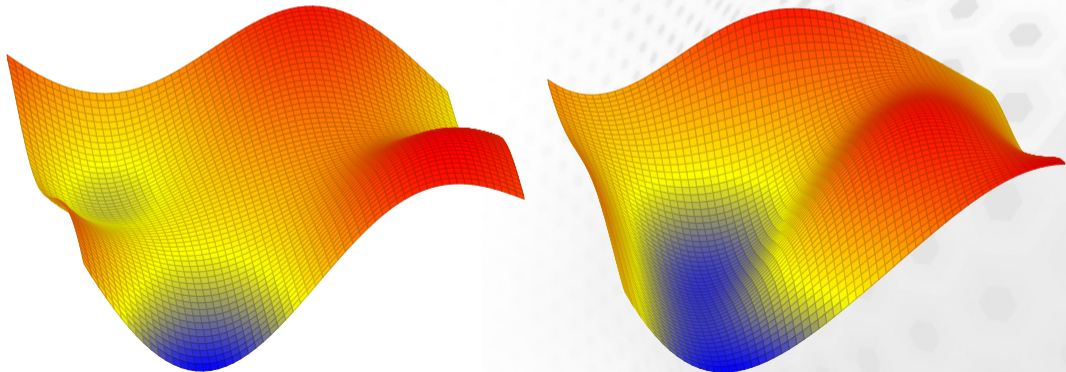
<http://www.cosmologic.de/support-download/downloads/tmolex-client.html>

(Users who feel more comfortable working from the command line are of course free to do so)

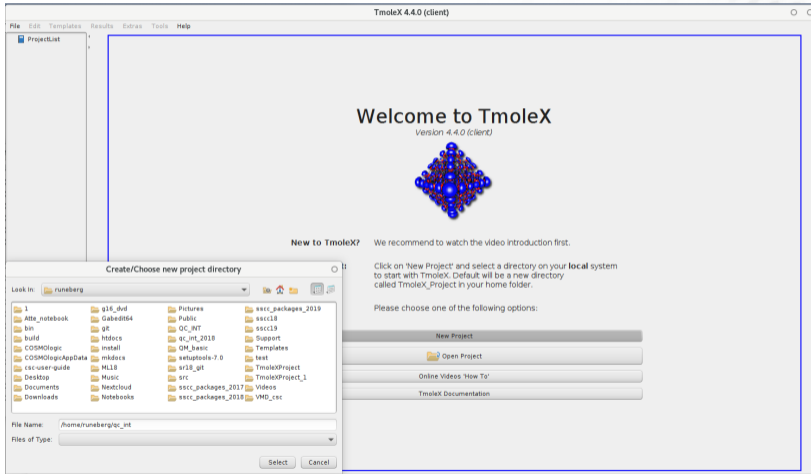


Task 1: Optimize ground state structure of formaldehyde

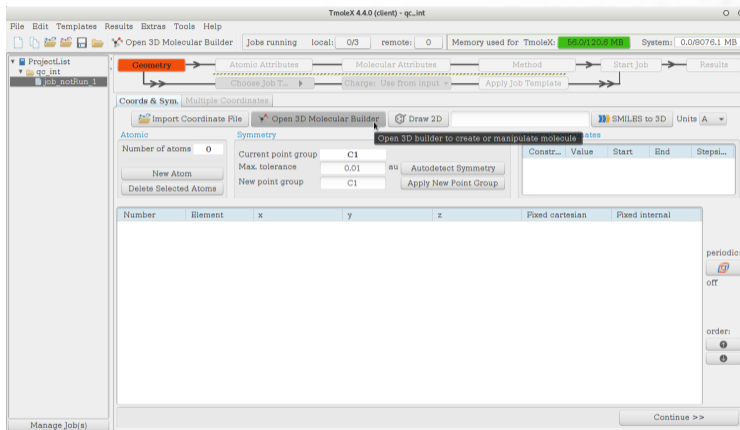
We need an initial guess for the geometry specifying the $3N-6$ internal nuclear coordinates. This initial structure place the system on the energy surface that is uniquely defined by the computational model we are going to use (B-O approx.). The performance of the model often vary at different parts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



Launch TmoleX and create a new project



Define your first Turbomole job

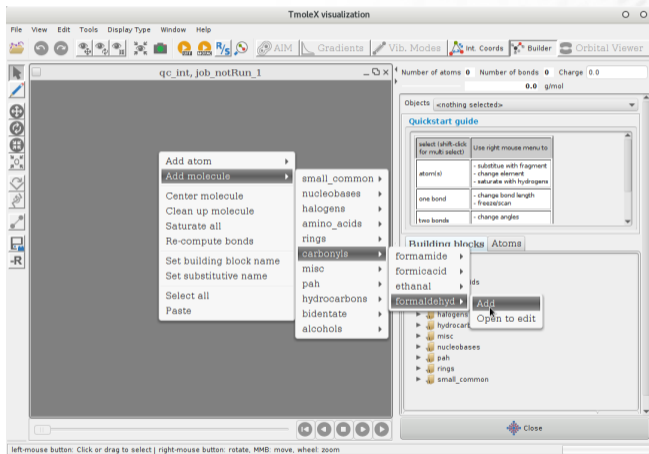


A complete Turbomole job comprises the sequence:

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

Geometry: Build formaldehyde

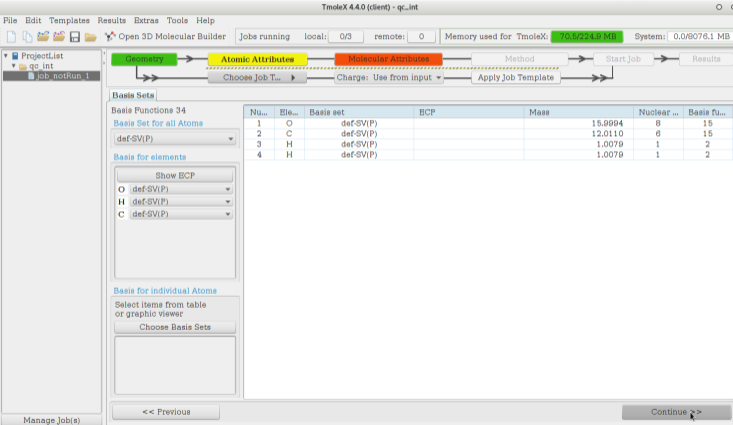
Open the 3D builder, right-click on canvas and load formaldehyde from the library



Close the builder and continue to Atomic Attributes

Atomic Attributes: Select basis set

Select the default def-SV(P) basis set



The screenshot shows the TmoleX 4.4.0 (client) - qc_int interface. The workflow progress bar indicates the current step is 'Atomic Attributes'. The 'Basis Sets' section is active, showing 'Basis Functions 34' and 'Basis Set for all Atoms' set to 'def-SV(P)'. Below this, there are dropdown menus for 'Show BCP' and 'Basis for elements' (O, H, C), all set to 'def-SV(P)'. A table of basis functions is displayed:

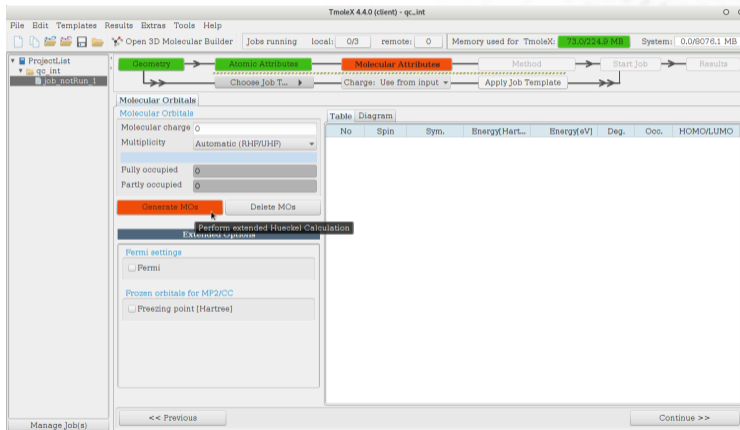
Nu...	Ele...	Basis set	BCP	Mass	Nuclear ...	Basis fu...
1	O	def-SV(P)		15.9994	8	15
2	C	def-SV(P)		12.0110	6	15
3	H	def-SV(P)		1.0079	1	2
4	H	def-SV(P)		1.0079	1	2

At the bottom of the window, there are buttons for '<< Previous' and 'Continue >>'.

Continue to Molecular Attributes

Molecular Attributes: Generate initial guess MOs

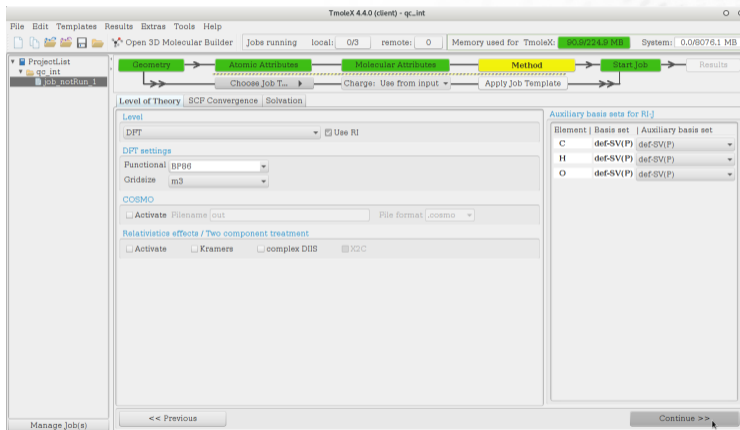
Generate initial MOs by doing an extended Hückel calculation



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

The screenshot shows the TmolX 4.4.0 (client) - qc_int interface. The top menu bar includes File, Edit, Templates, Results, Extras, Tools, and Help. Below the menu bar, there are status indicators for 'Jobs running' (local: 0/3, remote: 0), 'Memory used for TmolX' (95.6/224.9 MB), and 'System' (0.0/9076.1 MB). The main workspace is divided into several sections:

- ProjectList:** Shows a tree view with 'qc_int' and 'job_notRun_1'.
- Workflow:** A sequence of steps: Geometry → Atomic Attributes → Molecular Attributes → Method → Start Job → Results. Below this, there are buttons for 'Choose Job T...' and 'Apply Job Template'.
- Start Calculation:** A section with a 'Job type' dropdown menu and 'Options' for convergence criteria.
- Method:** A section for configuring the computational method.
- Use resources:** A section for setting memory, disk, and CPU usage.
- Save and Run:** A section with buttons for 'Run (local)', 'Save', and 'Run (network)'.

Job type configuration:

- Job type: Geometry Optimization ▶ Ground state
- Spectra & Excited States ▶
- Single Point ▶
- Single Point Properties ▶
- Population Analyses ▶
- Potential Energy Scan(PES) ▶
- Transition State Search ▶
- Templates ▶
- Batch processing ▶

Options:

- Convergence criteria
- Energy: 10^{11} Hartree
- Gradient norm: $|dE/dxyz| = 10^{-11}$ Hartree/Bohr
- Max. no. of cycles:
- Use internal redundant coordinates Include weight derivatives

Method:

- Level: DFT
- Functional: b-p
- RI
- Basis set: def-SV(P) Symmetry C1
- Convergence Parameter
- Energy: Density:

Use resources:

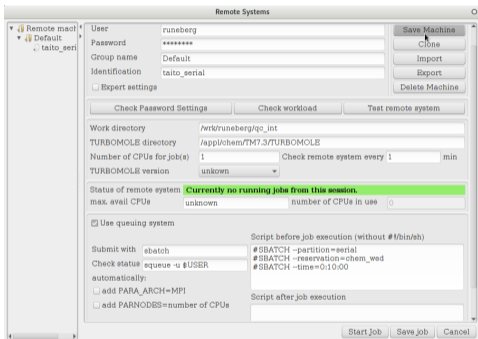
- Memory used for: MB
- Disk: MB for HF
- No. of CPUs:
- Delete scratch files after run

Save and Run:

- Run (local)
- Save
- Run (network)

Continue to Run(network)

Run(network): Setup remote job



Save Settings and Start

Machine/IP: taito.csc.fi

User: trainingXX

Work directory: /wrk/trainingXX/qc_int

TURBOMOLE directory: /appl/chem/TM7.21/TURBOMOLE

Submit with: sbatch

Check status: squeue -u \$USER

Script before job execution:

```
#SBATCH --partition=serial
```

```
#SBATCH --reservation=chem_wed
```

Run(network): Job starts

The screenshot displays the TmoleX 4.4.0 (client) - qc_int interface. The top menu bar includes File, Edit, Templates, Results, Extras, Tools, and Help. Below the menu, there are icons for file operations and a toolbar with 'Open 3D Molecular Builder'. The status bar shows 'Jobs running: local: 0/3 remote: 1', 'Memory used for TmoleX: 146.0/241.2 MB', and 'System: 0.0/9076.1 MB'. The main workspace is divided into several sections:

- ProjectList:** A tree view on the left showing 'ProjectList' expanded to 'qc_int', which contains 'job_GBO_1'.
- Workflow:** A sequence of steps: Geometry → Atomic Attributes → Molecular Attributes → Method → Start Job → Results. Below this, there are buttons for 'Choose Job Te...', 'Charge: Use from input', and 'Apply Job Template'.
- Jobs Table:** A table with columns: ID, Name, Type, Start, Stop, Machine. It contains one entry: ID 1, Name job_GBO_1, Type GBO,DFT/RI,B-P,charge 0,C1,def-SV(P),G..., Start Mar 15, 2019 11:..., Stop Running, Machine taio.csc.fi.
- Energy vs. Geometry cycle:** A graph with a y-axis from 0.0 to 1.0 and an x-axis from 0.0 to 1.0. The graph is currently empty. To the right of the graph are 'Follow' and 'Refresh' buttons.

At the bottom left, there is a 'Manage Job(s)' button.

Results:

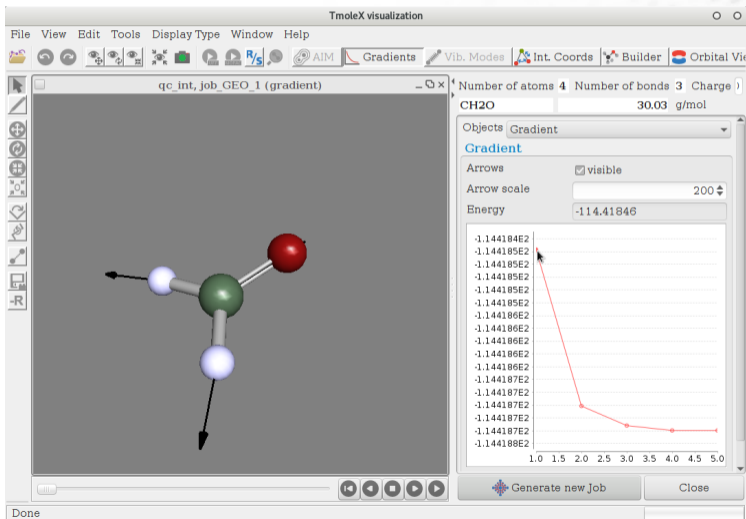
The geometry optimization needed 5 cycles to reach the stationary point on the energy surface

The screenshot displays the TmoleX 4.4.0 (client) - qc_int interface. The top menu bar includes File, Edit, Templates, Results, Extras, Tools, and Help. The main window shows a workflow diagram with steps: Geometry, Atomic Attributes, Molecular Attributes, Method, Start Job, and Results. Below this, the 'Jobs' panel shows the results for a 'Geometry Optimization' job. The job status is 'Converged' for both 'Status mos' and 'Status geometry'. The 'Geometry Convergence Criteria' section shows convergence information: energy change (actual: -0.4453E-06, threshold: 0.1000E-05) and geom. gradient (actual: 0.2802E-04, threshold: 0.1000E-02). The 'Energy' section lists: total energy = -114.41873721126, kinetic energy = 113.44915857782, and potential energy = -227.85788779828. The 'Gradients' section shows a table of results for 5 cycles.

cycle	SCF energy	dE/dxyz
1	-114.4184569894	0.016896
2	-114.4187049913	0.006723
3	-114.4187321500	0.002925
4	-114.4187367567	0.000444
5	-114.4187372820	0.000052

Results: Gradients

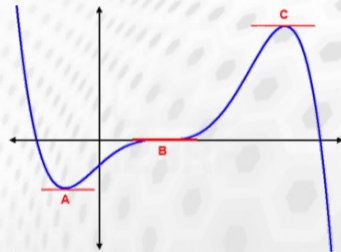
The length of the arrows show how steep the energy surface is in that direction



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")

The screenshot displays the TmoleX 4.4.0 (client) - qc_int interface. The top menu bar includes File, Edit, Templates, Results, Extras, Tools, and Help. The status bar shows 'Jobs running local: 0/3', 'remote: 0', 'Memory used for TmoleX: 66.62793 MB', and 'System: 0.0/9076.1 MB'. The main workspace is divided into several sections:

- Job Results:** Contains convergence information and energy values.

```
convinfo
energy change : actual value = -0.4453E-06 threshold = 8.1008E-05
geom. gradient : actual value = 8.2982E-04 threshold = 8.1098E-02
```

Energy

```
total energy = -114.41873721126
-----
kinetic energy = 113.44915857792
potential energy = -227.86798778628
```
- Gradients:** Shows SCF energy and derivatives over five cycles.

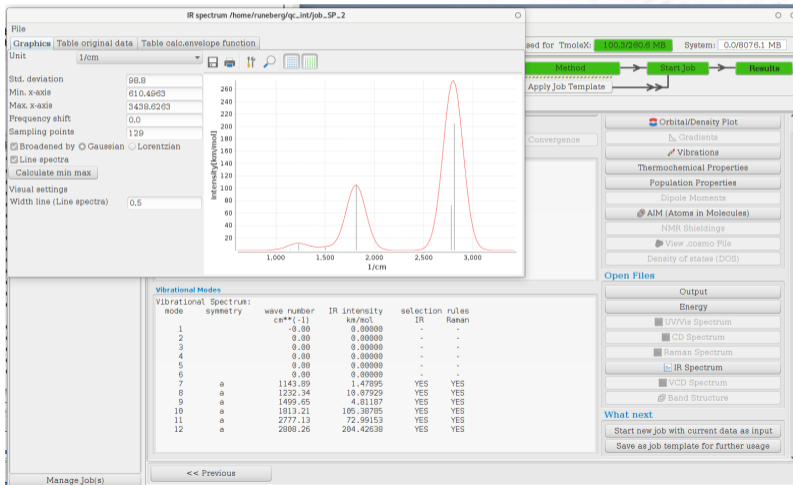
cycle	SCF energy	dE/dxyz
1	-114.4184569894	0.016886
2	-114.4187843913	0.096723
3	-114.4187321588	0.092825
4	-114.4187367567	0.099444
5	-114.4187372828	0.098852
- Thermochemical Properties:** Includes Population Properties, Dipole Moments, AIM (Atoms in Molecules), NMR Shieldings, View .cosmo File, and Density of states (DOS).
- Open Files:** Lists Output, Energy, UV/Vis Spectrum, CD Spectrum, Raman Spectrum, IR Spectrum, VCD Spectrum, and Band Structure.
- What next:** Contains buttons for 'Start new job with current data as input' and 'Save as job template for further usage'.

Vibrational spectrum

The screenshot shows the TmolX 4.4.0 (client) - qc_int interface. The main window displays a workflow diagram with steps: Geometry, Atomic Attributes, Molecular Attributes, Method, Start Job, and Results. The 'Start Calculation' dialog box is open, showing the 'Job typ' section with a tree view. Under 'Spectra & Excited States', 'IR & vibrational frequencies' is selected. The 'Options' section includes convergence criteria for Energy (10^{-6} Hartree), Gradient norm (3×10^{-4} Hartree/Bohr), and Max. no. of cycles (50). The 'Method' section shows Level: DFT, Functional: b-p, Basis set: def-SV(P), and Symmetry: c1. The 'Use resources' section shows Memory used for: 500.0 MB, Disk: 0 MB for HF, and No. of CPUs: 1. The 'Save and Run' section has buttons for Run (local), Save, and Run (network).

Results: Frequency calculation

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



Task 2: Vertical absorption spectrum of the ground state

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

Do for singlet states and 10 excitations

The screenshot displays the TmoleX 4.4.0 (client) - qc_int interface. The main window shows a workflow diagram with steps: Geometry, Atomic Attributes, Molecular Attributes, Method, Start Job, and Results. Below this, the 'Start Calculation' dialog is open, showing various configuration options.

Job typ

- Geometry Optimization
- Spectra & Excited States → UVVis and CD(vertical excitations)
- Single Point
- Single Point Properties
- Population Analyses
- Potential Energy Scan(PBS)
- Transition State Search
- Templates
- Batch processing

Excited states

- Singlet Triplet
- Unrestricted
- Unit: eV
- All IRREPs Number of excited states per IRREP: 10
- Select IRREPs
- for current symmetry: c1

IRREP	A
No. of excitations	5
Needed for	UV ...

Method

- Level: DFT
- Functional: b-p
- RI
- Basis set: def-SV(P) Symmetry: c1
- Convergence Parameter: Energy: 10⁻⁶ Density:

Use resources

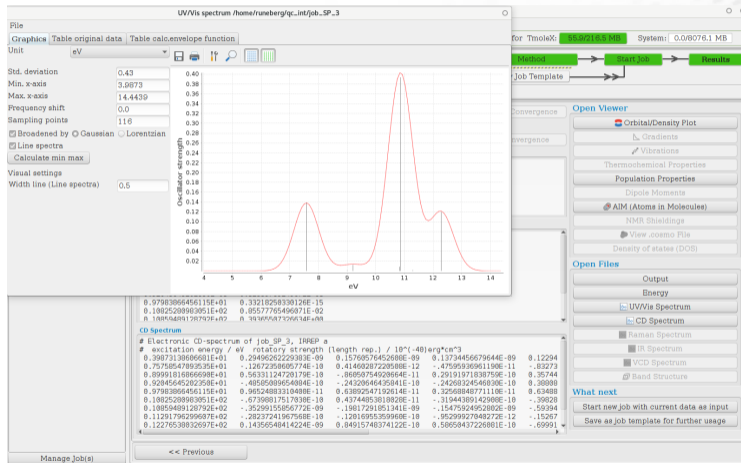
- Memory used for: 100.0 MB
- Disk: 0 MB for HF
- No. of CPUs: 1
- Delete scratch files after run

Save and Run

- Run (local)
- Save
- Run (network)

At the bottom left, there is a 'Manage Job(s)' button and a '<< Previous' button.

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:                0.1465318282411775
Excitation energy:           0.1465318282411775
Excitation energy / eV:      3.987313860668139
Excitation energy / nm:      310.9467885873743
Excitation energy / cm-1:    32159.84338932378

Oscillator strength:
  velocity representation:    0.5214385318188062E-15
  length representation:      0.2185238879746286E-15
  mixed representation:       0.3375573885073748E-15

Rotatory strength:
  velocity representation:    0.5231221861493721E-14
  velocity rep. / 10^(-40)erg*cm3: 0.3379621279421632E-09
  length representation:      0.4565644462775598E-14
  length rep. / 10^(-40)erg*cm3: 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

3D-Visualizer job_SP_3

Choose Molecular Orbital(s)

Sel.	No	Spin	Sym.	Energy[Ha...]	Deg.	Occ.	HOMO/LU...	quick	hig...
<input type="checkbox"/>	12	ab	12a	0.1705	1	0	LUMO + 3		
<input type="checkbox"/>	11	ab	11a	0.1121	1	0	LUMO + 2		
<input type="checkbox"/>	10	ab	10a	0.0463	1	0	LUMO + 1		
<input checked="" type="checkbox"/>	9	ab	9a	-0.0875	1	0	LUMO		
<input checked="" type="checkbox"/>	8	ab	8a	-0.2245	1	2	HOMO		
<input type="checkbox"/>	7	ab	7a	-0.3665	1	2	HOMO - 1		
<input type="checkbox"/>	6	ab	6a	-0.3957	1	2	HOMO - 2		
<input type="checkbox"/>	5	ab	5a	-0.4395	1	2	HOMO - 3		
<input type="checkbox"/>	4	ab	4a	-0.5652	1	2	HOMO - 4		
<input type="checkbox"/>	3	ab	3a	-0.9634	1	2	HOMO - 5		

Choose Density and Electrostatic Properties

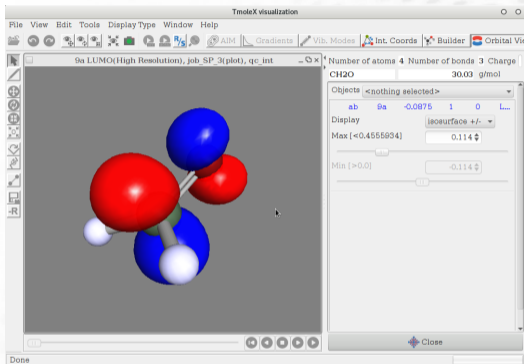
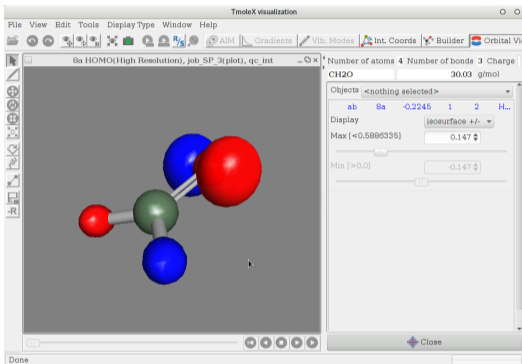
Sel.	Plot-propertyname	Plot-filename	quick	high-res
<input type="checkbox"/>	Excited state, density	td		
<input type="checkbox"/>	Electrostatic potential	tp		
<input type="checkbox"/>	Electric field	tf		
<input type="checkbox"/>	Gradient of electric field	tg		
<input type="checkbox"/>	Electrostatic potential color-c...	tp_td		
<input type="checkbox"/>	ELF (electron localization fun...	te		

File format .plv/plt .dtx

View all in one

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 screenshot shows the Gaussian 4.4.0 GUI with the 'Excited states' section expanded. The 'Geometry Optimization' is set to 'Excited state'. Under 'Spectro & Excited States', 'Single Point' is selected. The 'Excited states' section has 'Diplet' selected, 'RPA: Random Phase Approx.' is chosen, and 'No. of excited state to follow' is set to 1. The 'Options' section shows 'Convergence criteria' set to 5×10^{-11} Hartree, 'Grids/points' set to 3, and 'Max. no. of cycles' set to 50. The 'Method' section shows 'Level' as DFT and 'Functional' as B3P.

The screenshot shows the 'Job Results' section of the Gaussian 4.4.0 GUI. The 'Type of Calculation' is 'Geometry Optimization' and the 'Status' is 'Converged'. The 'SCF Convergence' is also 'Converged'. The 'Geometry Convergence Criteria' table shows the following data:

Iteration	SCF	SCF/3	SCF/2	excitation
1	-114.418732218	113.449178	-227.867987	0.148531959706
2	-114.413770867	113.286712	-227.798484	0.131911395466
3	-114.407766869	113.268112	-227.847862	0.121282656795
4	-114.404202804	113.218742	-227.822826	0.1188175200282
5	-114.402009069	113.221602	-227.812339	0.118025040248
6	-114.403330807	113.218869	-227.822897	0.1188621834237
7	-114.403717648	113.222044	-227.823289	0.118894274248
8	-114.403962578	113.221739	-227.825278	0.118891422143

The 'Gradients' section shows the following data:

Iteration	ex. state energy	(E/Hz)
1	-114.272981618	0.186731
2	-114.261925221	0.878965
3	-114.260663126	0.822269
4	-114.264446215	0.805578
5	-114.264854228	0.805178
6	-114.264570929	0.801282
7	-114.264877491	0.800875
8	-114.264871148	0.800861
9	-114.264873795	0.800865

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.

```
runeberg@vihertikka ~]$ cd qc_int
[runeberg@vihertikka qc_int]$ scp -r job_GEO_4 taito-shell.csc.fi:/wrk/runeberg/qc_int
job.start          100% 764      22.1KB/s  00:00
exspectrum        100% 6030     101.5KB/s 00:00
start-job         100% 968      18.4KB/s  00:00
energy            100% 758      2.3KB/s   00:00
control           100% 2271     49.0KB/s  00:00
Job_Ended         100% 0        0.0KB/s   00:00
start-job.out     100% 29       0.6KB/s   00:00
coord             100% 1419     25.5KB/s  00:00
slurm-41905297.out 100% 206     6.6KB/s   00:00
job.last          100% 50KB     485.8KB/s 00:00
GEO_OPT_CONVERGED 100% 1166     13.5KB/s  00:00
message_output    100% 0        0.0KB/s   00:00
auxbasis          100% 1784     62.7KB/s  00:00
kill-job          100% 1020     27.6KB/s  00:00
gradient          100% 5764     116.3KB/s 00:00
converged         100% 321      7.5KB/s   00:00
mos               100% 23KB     449.3KB/s 00:00
basis             100% 1067     4.3KB/s   00:00
[runeberg@vihertikka qc_int]$ ssh -X taito-shell.csc.fi -l runeberg
```

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

--- Software ---
Available modules can be listed with command: module avail | module spider
--- News ---

2015-05-25: Changed default slurm instance to Taito's. For example
srun now submits jobs to Taito's partitions, like parallel
instead of the oversubscribed.

Your action is required: you are using more storage than your current quota allows. Quota for
$HOME and $USERAPPL is 250.00 GB and your usage is 259.45 GB. You have 1w4d2h57m53s time to
clean your $USERAPPL and $HOME directory.

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
/app1/chem/TM7.3/job-tm73-taito.job
[runeberg@c309 job_GEO_4]$ cpc numforce
```

Copy directory: `scp -r job_GEO_4 taito-shell:/wrk/<username>`

Login: `ssh -X taito-shell -l <username> (-l, letter L)`

Go to directory: `cd /wrk/<username>/job_GEO_4`

NumForce

```
runeberg@c309/nrk/runeberg/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/nrk/runeberg/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
Svibrational 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
Send
[1]+ Done NumForce -ri -ex 1 &>NumForce.out
[runeberg@c309 numforce]$
```

Windows users should issue the command: dos2unix *

Load turbomole environment: module load turbomole/7.3

Copy inputs to a new directory: cpc numforce

Go to new directory: cd numforce

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

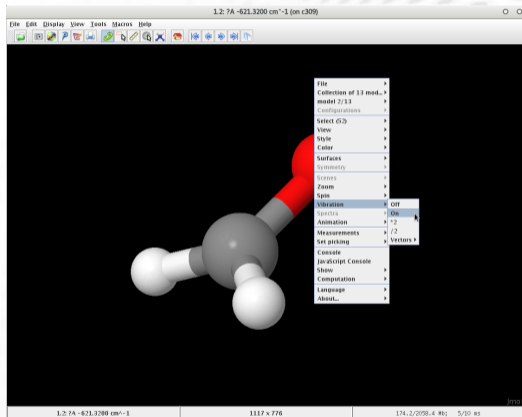
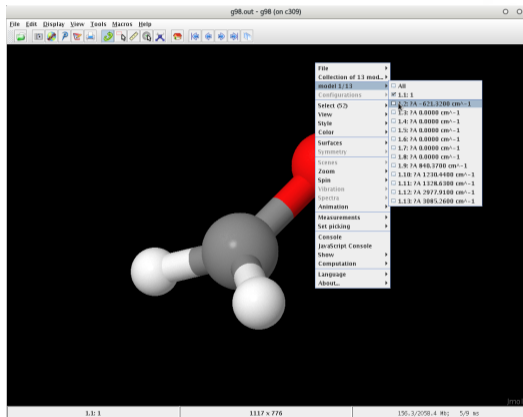
Check results: cat vibspectrum

NumForce

Since there is one imaginary frequency (negative force constant) the stationary structure is not a minimum but a saddle point. Use Jmol to analyze what kind of motion the imaginary frequency corresponds to.

```
runeberg@c309/wrk/runeberg/qc_int/job_GEO_4/numforce
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
$end
[1]+  Done                  NumForce -ri -ex 1 &>NumForce.out
[runeberg@c309 numforce]$ aoforce2g98 numforce/aoforce.out >g98.out
[runeberg@c309 numforce]$ module load jmol
Jmol version 14.2 is now in use
[runeberg@c309 numforce]$ jmol g98.out
```

Launch Jmol using the data in g98.out: `jmol g98.out`

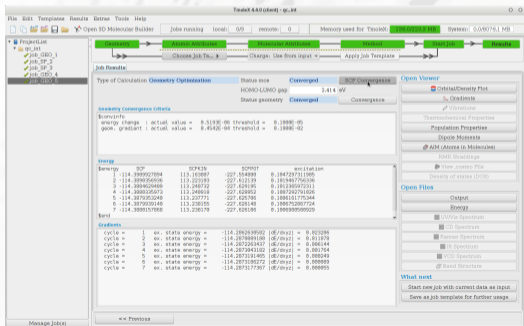
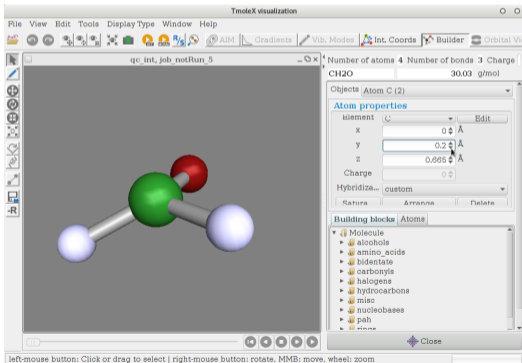


Select the imaginary frequency: `model 2/13`

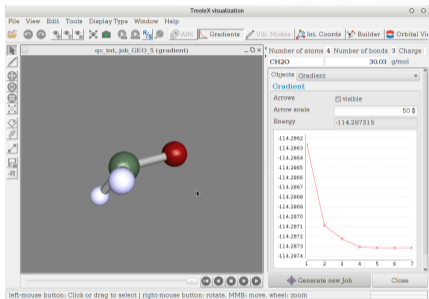
Activate animation: `Vibration: On`

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 to taito-shell and redo the Numforce.

Copy directory: `scp -r job_GEO_5 taito-shell:/wrk/<username>`

Login: `ssh -X taito-shell -l <username>`

Go to directory: `cd /wrk/<username>/job_GEO_5`

NumForce

```
runeberg@vihertikka-ipc_int
[runeberg@vihertikka qc_int]$ scp -r job_GEO_5/ taito-shell.csc.fi:/wrk/runeberg/qc_int
job.start          100% 764      15.2KB/s  00:00
expectrum         100% 4690     101.1KB/s 00:00
start-job         100% 968      34.4KB/s  00:00
energy            100% 608      21.4KB/s  00:00
control           100% 2272     78.5KB/s  00:00
Job Ended         100% 0        0.0KB/s   00:00
slurm-41910540.out 100% 164      5.8KB/s   00:00
start-job.out     100% 29       1.1KB/s   00:00
coord             100% 1505     50.5KB/s  00:00
job_last         100% 50KB     426.5KB/s 00:00
GEO_OPT_CONVERGED 100% 1166     38.1KB/s  00:00
message_output    100% 0        0.0KB/s   00:00
auxbasis         100% 1784     63.6KB/s  00:00
kill-job         100% 1020     36.0KB/s  00:00
gradient         100% 4492     145.4KB/s 00:00
converged        100% 321      11.7KB/s  00:00
mos              100% 23KB     369.5KB/s 00:00
basis            100% 1067     37.4KB/s  00:00
[runeberg@vihertikka qc_int]$ ssh -X taito-shell.csc.fi -l runeberg
```

```
runeberg@c310/wrk/runeberg/qc_int/job_GEO_5/numforce
SHOME and $USERAPPL is 250.00 GB and your usage is 259.45 GB. You have 1w4d1h40m55s time to
clean your $USERAPPL and SHOME directory.

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

[runeberg@c310 ~]$ cd /wrk/runeberg/qc_int/job_GEO_5/
[runeberg@c310 job_GEO_5]$ 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@c310 job_GEO_5]$ 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@c310 job_GEO_5]$ cd numforce/
[runeberg@c310 numforce]$ NumForce -ri -ex 1 &> NumForce.out&
[1] 24182
[runeberg@c310 numforce]$
```

Load turbomole environment: module load turbomole/7.3
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 excited state geometry corresponds to a true minimum. At that geometry, redo the excitation 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: 0.1006980498288955
Excitation energy: 0.1006980498288955
Excitation energy / eV: 2.748134527222786
Excitation energy / nm: 452.4750254949356
Excitation energy / cm^(-1): 22106.66729665125

Oscillator strength:
velocity representation: 0.5177277246839254E-03
length representation: 0.1145399812726133E-02
mixed representation: 0.7700680649872842E-03

Rotatory strength:
velocity representation: 0.1664648129188382E-09
velocity rep. / 10^(-40)erg*cm^3: 0.1875437699281748E-04
length representation: 0.3719325994877944E-18
length rep. / 10^(-40)erg*cm^3: 0.2482863738823989E-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 R^{GS} , R^{ES} , E^{GS} , E^{ES} , as well as E^{abso} , E^{fluo} , E^{adia} and E^{adia}_{ZPVE}
- ▶ Compare your results with experimental data found in the literature
- ▶ Compare your results with computational results obtained at more sophisticated 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 choice of functional?
- ▶ For this particular physical problem is tddft the method of choice?
- ▶ How does the environment interact?
- ▶ Should we be more careful when treating dispersion (intra, inter)?
- ▶ Relativity?
- ▶ Temperature and dynamics?