Scientific Computing & Modelling

GUI Tutorials

ADF Program System
Release 2012

Scientific Computing & Modelling NV
Vrije Universiteit, Theoretical Chemistry
De Boelelaan 1083; 1081 HV Amsterdam; The Netherlands
WWW: www.scm.com
E-mail: support@scm.com

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Introduction

This document will provide a hands-on tutorials demonstrating the ADF-GUI, BAND-GUI and so on. All of these (ADF-GUI, BAND-GUI, DFTB-GUI, ReaxFF-GUI and so on) are very similar and share a lot of options. So collectively these will just be called the GUI.

The first five tutorials provide an overview over all GUI modules, using ADF as computational engine. If you are new to the GUI, we advise you to study the tutorials in the order presented.

The advanced ADF-GUI tutorials focus on particular features of the ADF-GUI, or on some particular application.

Next there are some specialized tutorials that show you how to use the GUI with BAND, DFTB, MOPAC or ReaxFF.

We estimate that you will need about half an hour for each part of the tutorial, for reading and performing the hands-on activities. Typically the calculations should give results that are very close to the results shown in the tutorials. However, in some cases minor changes may occur depending on hardware and software versions.

Many tutorials are also available as videos. The current videos are actually the tutorial videos for ADF2009, so there will be differences with the current tutorials.

Additional information may be found in the GUI manual

Starting the GUI: start ADFjobs

We will assume that you have installed the full ADF package on your machines.

The most convenient way to start the GUI is to first start ADFjobs, one of the GUI modules. Using the SCM menu in ADFjobs (either the text SCM, or the SCM logo) you can next start any other GUI module that you have a license for.

Depending on your platform, you start ADFjobs in a slightly different way:

UNIX (such as Linux) users

In this tutorial we will assume that you have added $ADFBIN to your PATH. We advise you to do this if you have not already done so. If you do not wish to add $ADFBIN to your PATH, you must start the utilities using

```
$ADFBIN/adfjobs &
```

instead of just

```
adfjobs &
```

On all UNIX platforms, including Mac OS X, the GUI modules are XWindow (X11) programs. Your environment should have been set up correctly to run such programs. In particular, you need to make sure that your DISPLAY environment variable has been set properly.

You can test this easily by starting a simple X program from your shell:

```
xcalc &
```

Assuming the xcalc program is in your $PATH, a small window should appear with the image of a calculator. If not, please consult your local system administrator for additional help. Typical problems have to do with your DISPLAY variable, and with security issues when trying to connect to the X server.

Windows users

In this tutorial we will assume that you have installed the ADF package using the Installer with all the options set to default.

You can start the GUI (adfjobs) by double-clicking its icon on the desktop.

Macintosh users

Macintosh users have several easy ways of starting the GUI modules: just like on any other UNIX system (thus, using the command line), or using the ADF2012.01 or ADFLaunch program.

The easiest way is using the ADF2012.01 program (or the older ADFLaunch). When you start it, ADFjobs will be started automatically. Next you can use the SCM menu to start the other ADF-GUI modules.

GUI modules (for the ADF-GUI, BAND-GUI, COSMO-RS GUI, ReaxFF-GUI, and so on)

The ADF-GUI is the Graphical User Interface for the ADF package. It consists of several modules for specific tasks. Those modules work together and exchange information. You should make sure you have no firewall blocking TCP/IP communications inside your machine.

All of the ADF-GUI (and BAND-GUI etc) modules have one common SCM menu on the top left of the window. On most systems it is represented by a small SCM logo. You can use the commands inside the SCM menu to start other GUI modules (or switch to them).

In general when selecting a GUI module from the SCM menu it will start and open the current job. If that module is already open with the current job, it will be activated (brought to the foreground). The current job is the selected job in ADFjobs, or the job open in some other GUI module if you use the SCM menu in that module.

The most important exception is opening an Input module (like ADFinput, BANDinput, ...) or ADFcrs (COSMO-RS) in ADFjobs. In that case the selected job will be ignored, and you can start working on a new calculation. To open the selected job in ADFinput, you need to click the icon in front of the job.

SCM → Preferences

GUIprefs ($ADFBIN/guiprefs) allows you to adjust and save numerous GUI preferences, such as color schemes, environmental variables, etc. The preferences will be used by all ADF-GUI modules.

SCM → ADF Input
SCM → BAND Input
SCM → DFTB Input
SCM → UFF Input
SCM → ReaxFF Input

ADFinput ($ADFBIN/adfinput) helps users to easily create ADF jobs. You can use ADFinput to define your molecule (geometry), pre-optimize it, and to set details of your ADF job using an easy-to-use graphical user interface. ADFinput will generate the basic job script for you. This script takes care of running ADF and property programs as required.

The same module can actually create jobs using different methods: ADF, BAND, DFTB, MM, MOPAC, Open Babel, QMMM, QUILD, ReaxFF and UFF. After starting it, you can simply change the method to use without starting a different module. Alternatively, if you use the **BAND Input** menu command the same module will start up, but will immediately start in BAND-mode (to set up a BAND calculation). Depending on your license, not all options will be available.

SCM → COSMO-RS

ADFcrs ($ADFBIN/adfcrs) enables ADF users to easily select compounds, create COSMO-RS jobs, run the jobs, and visualize the results.

SCM → View

ADFview ($ADFBIN/adfview) displays volume data, such as electron densities, orbitals, electrostatic potentials and more. You can also use it to visualize scalar atomic data like charges, some tensor data, and AIM (Bader) results.

SCM → Movie

ADFmovie ($ADFBIN/adfmovie) follows geometry steps as performed by ADF during geometry optimizations, IRC calculations, etc. It can be used during the calculation to monitor the progress (based on information from the logfile), or it can be used to analyze the geometry changes after a calculation. It is also used to display normal modes calculated with a frequency calculation.

SCM → Levels

ADFlevels ($ADFBIN/adflevels) generates a diagram showing the energy levels of a finished calculation. You can interact with it: show an interaction diagram (how the molecular orbitals are constructed from fragment orbitals), show labels, occupations, orbitals, etc.

SCM → Logfile

ADFtail ($ADFBIN/adftail) shows the contents of a text file, updating when the text file grows (like the UNIX tail -f command). It is typically used to monitor the 'logfile'. The progress of an ADF calculation is always written to this file.

SCM → Output

ADFoutput ($ADFBIN/adfoutput) shows the output of ADF (or any other text file). It will analyze the output and provide quick links to sections of interest.

SCM → Spectra

ADFspectra ($ADFBIN/adfspectra) shows spectra calculated by ADF. It can show IR, Raman, excitation and CD spectra, as well as a DOS plot. For some spectra it can also perform additional tasks (using other ADF-GUI modules), like displaying normal modes or orbitals.

SCM → Band Structure

Bandstructure ($ADFBIN/bandstructure) shows dispersion spectra like the band structure of solids, or phonon spectra, as calculated by for example Band or DFTB.

SCM → Dos

ADFdos ($ADFBIN/adfdos) shows DOS-like results. You can easily select which partial DOS to show by selecting atoms, and you can even select to show the GPDOS for select atoms and L-shells.

SCM → Jobs

This utility ($ADFBIN/adfjobs) manages your ADF jobs: run a job on your local machine or on remote machines. It also serves as a interface to all files belonging to your job, and it serves as a convenient launcher of the other ADF-GUI modules.

Keyboard shortcuts

Some **keyboard shortcuts** for menu commands used in the tutorials are platform specific. For example:

- Undo: ctrl-Z on Linux/Windows, cmd-Z on Macintosh
- Save: ctrl-S on Linux/Windows, cmd-S on Macintosh

In general, on Linux and Windows machines use the ctrl key to access these shortcuts for the menu commands, on a Mac use the cmd key. In the tutorials, these command keys may be mentioned as for example cmd/ctrl-S

If you are using a Mac, the GUI uses the X11 program to run. The X11 program itself may intercept the menu-shortcuts like Cmd-C, Cmd-H, and so on. You can change this using the Preferences command from the X11 menu (Enable key equivalents under X11 should NOT be checked).

A three-button mouse is also very convenient for using the ADF-GUI, and on a Mac you can use a Magic mouse for this purpose. To get three buttons (instead of the standard one or two), download and install the free utility BetterTouchTool, and configure it to add a middle click.

ADF-GUI overview tutorials

Tutorial 1: Geometry optimization of ethanol

This tutorial will help you to:

- create a simple molecule
- view the molecule from all sides and save a picture
- make a couple of changes to the molecule with different tools
- set up your ADF calculation
- perform the actual ADF calculation
- visualize some results: energy levels, geometry, electron density, orbitals, ...

Step 1: Preparations

Start ADFjobs

On a Unix-like system, enter the following command:

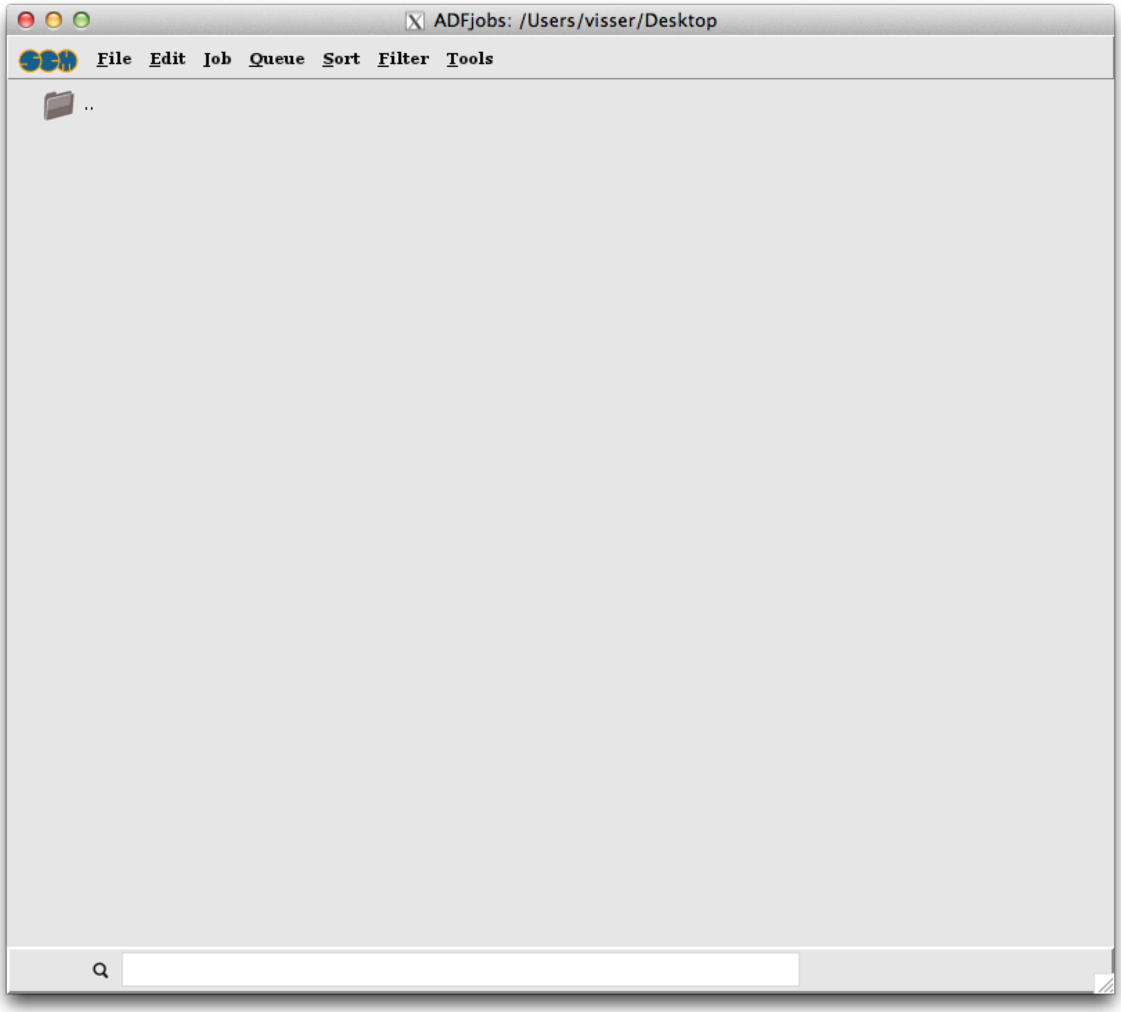
```
cd
adfjobs &
```

On Windows, one can start ADFjobs by double-clicking on the ADF-GUI icon on the Desktop:

```
double click the ADF-GUI icon on the Desktop
```

On Macintosh, use the ADF2012.01 or ADFLaunch program to start ADFjobs:

```
Double click on the ADF2012.01 or ADFLaunch icon
Make sure X11 allows you to use keyboard shortcuts (you only need to do this
once):
    Press Cmd-,
    If nothing happens everything is fine.
    If the X11 Preferences dialog appears:
        uncheck the "Enable key equivalents under X11" check box and close
that dialog.
```

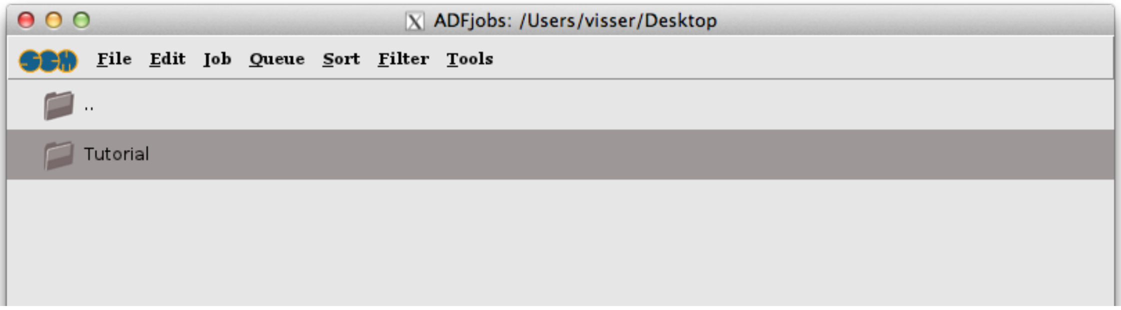


Note that the directory in which ADFjobs depends on how you start ADFjobs, so your screen might look different.

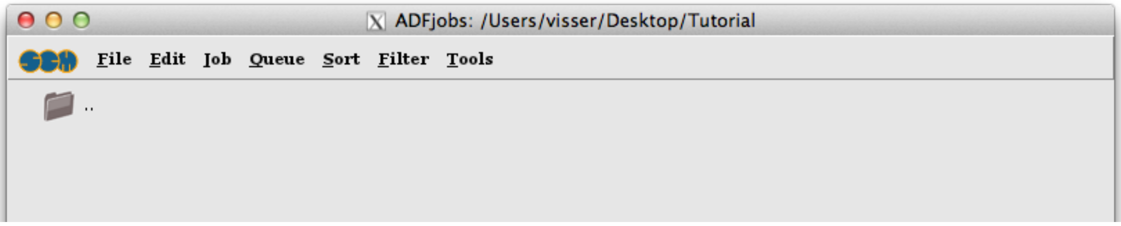
Make a directory for the tutorial

We prefer to run the tutorial in a new, clean, directory. That way we will not interfere with other projects. ADFjobs not only manages your jobs, but also has some file management options. In this case we use ADFjobs to make the new directory:

Select the **File → New Directory** command (thus, the New Directory command from the File menu)
Rename the new directory by typing 'Tutorial' and a Return



Change into that directory by clicking once on the folder icon in front of it



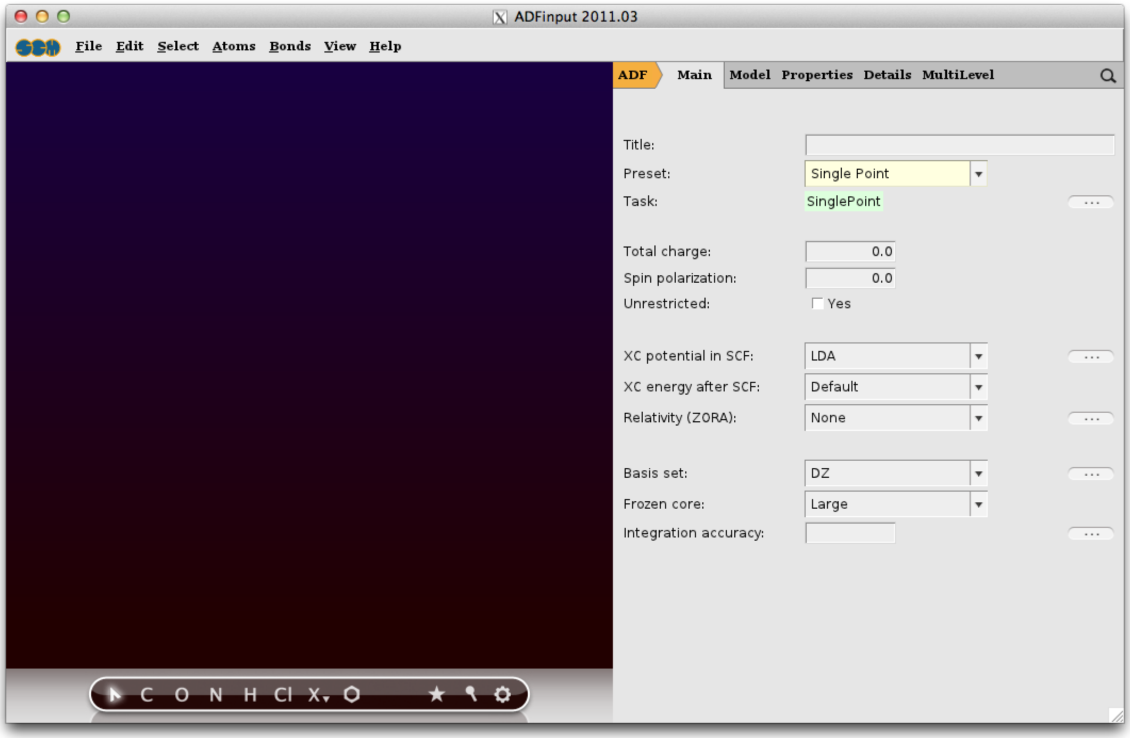
Start ADFinput

Now we will start ADFinput in this directory using the SCM menu:

Select the **SCM → ADF Input** menu command:

> use the SCM menu on the top left (the SCM logo on most platforms), next select the ADF Input command from the menu.

The ADFinput module should start:



Title:
Preset: Single Point
Task: SinglePoint

Total charge: 0.0
Spin polarization: 0.0
Unrestricted: ☐ Yes

XC potential in SCF: LDA
XC energy after SCF: Default
Relativity (ZORA): None

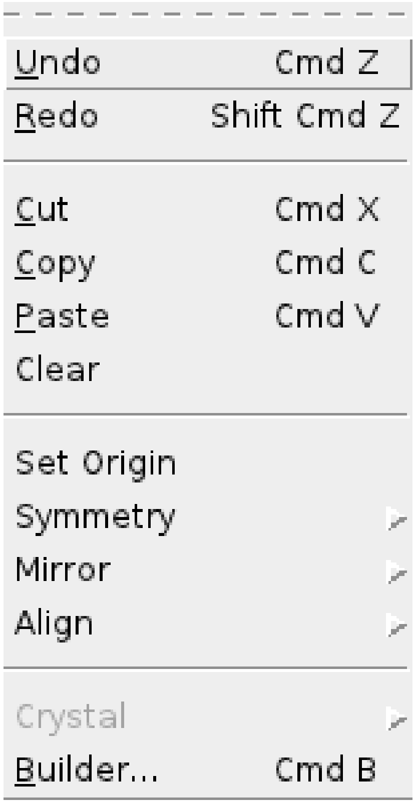
Basis set: DZ
Frozen core: Large
Integration accuracy:

The ADFinput window consists of the following main parts:

- the menu bar with the menu commands (File, Edit, ...)
- the drawing area of the molecule editor (the dark area on the middle left side)
- the status field (lower part of the dark area, blank when the ADFinput is empty as shown above)
- the molecule editor tools
- many panels with several kinds of options (currently the 'ADF Main' panel is visible)
- panel bar with menu commands to activate the panel of choice
- a search tool (at the right of the panel bar)

Undo

ADFinput has an Undo command, which works on your molecule (thus not on your input options).



If you make a mistake while making changes to your molecule, just use the **Edit** → **Undo** menu command to go back in time. You can Undo more than one step, or Redo a step (with **Edit** → **Redo**) if you wish to do so.

Step 2: Create your molecule

Create a molecule

The molecule we are going to create is ethanol.

First we will draw the two carbon atoms, next the oxygen atom, and after that we will add all hydrogen atoms at once. Finally, we will pre-optimize the geometry within ADFinput.

Create the first carbon atom

To create an atom, you need to select an atom tool.

```
Select the C-tool by clicking on the button with the 'C'
```

Back glow is added to the 'C' button to indicate that you are using the C-tool. Also, the status field in the left bottom corner shows 'C tool, create single bond' to indicate that you are using the C-tool.

Now create the first carbon atom:

```
Click somewhere in the drawing area
```

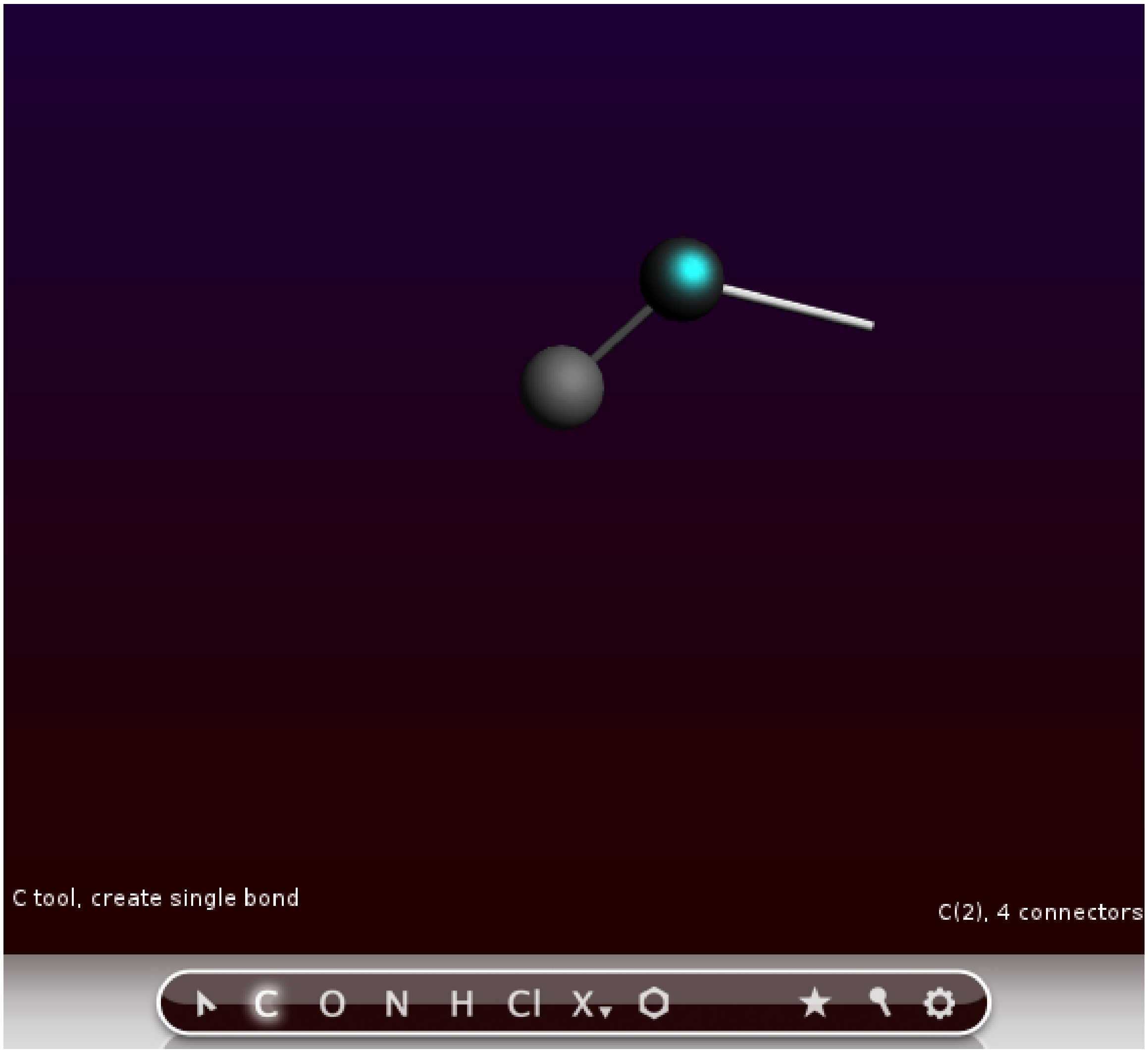
One carbon atom has been created.

Note that:

- If you move the mouse you will see a white line from that carbon atom to the current mouse pointer position: this shows you are in 'bonding' mode, and that the bond will be made to the atom just created.
- The 'C' button has a different color, indicating you are still using the C-tool.
- The carbon atom is selected (the green glow), which indicates that the carbon atom is the current selection.
- The status field contains information about the current selection: it is a Carbon, number 1, with 4 'connectors'
- The status field also shows the current tool (C), and that a single bond will be made.

Create the second carbon atom

`Click somewhere in the drawing area to create the second carbon atom`



A second carbon atom has been created, bonded to the first atom.

The atom will be created along the 'bonding line', at a distance that corresponds to a normal C-C single bond distance. That is, the bond length is constrained while drawing.

The newly created atom becomes the new selection, and you are still in bonding mode. The next bond will be created to the carbon atom just created. And you are still using the C-tool.

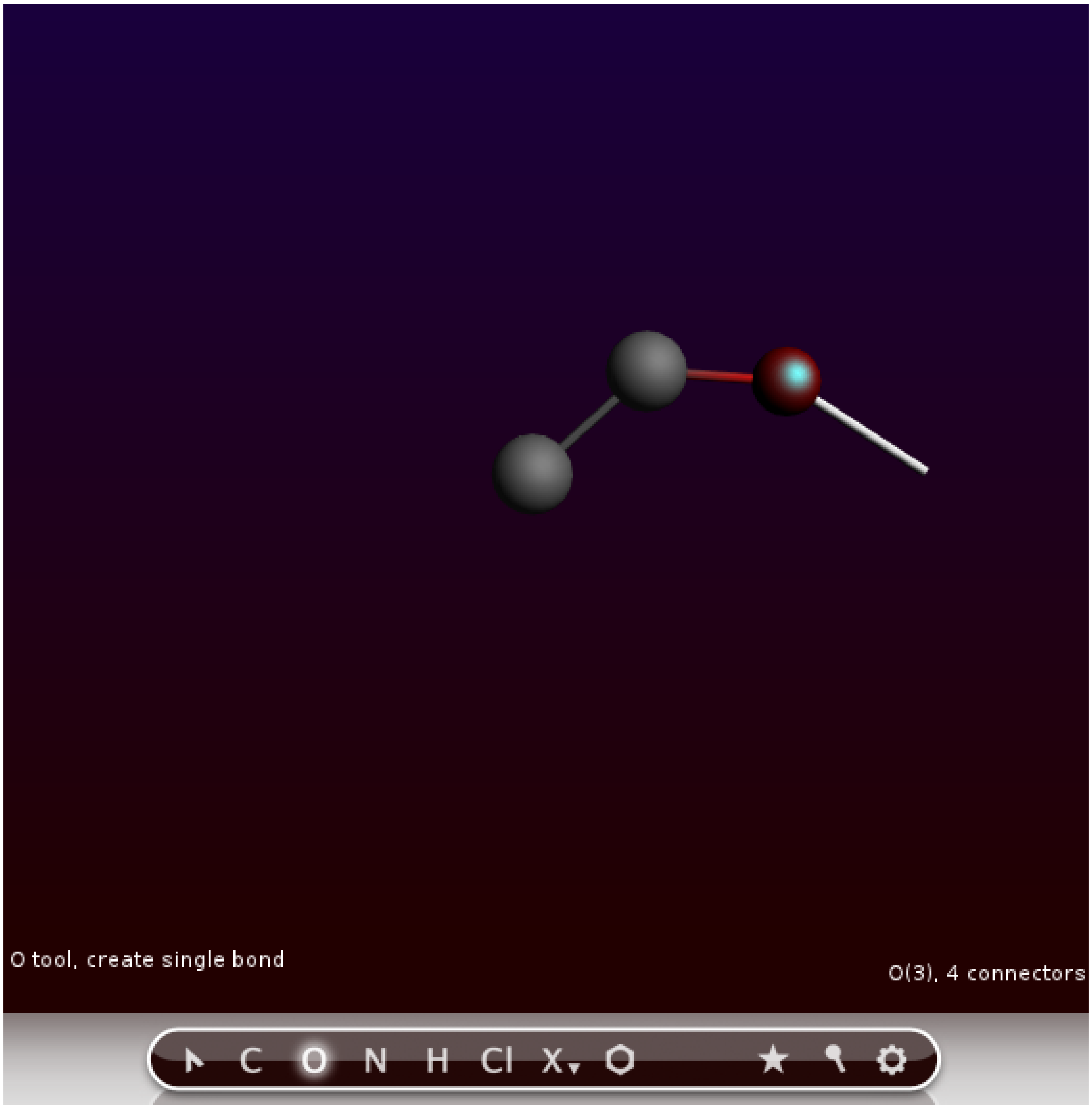
Create the oxygen atom

To create the oxygen atom you need to switch to the O-tool:

`Select the O-tool by clicking on the button with the 'O'`

With the O-tool, create an oxygen atom bonded to the second carbon;

`Click somewhere in the drawing area`



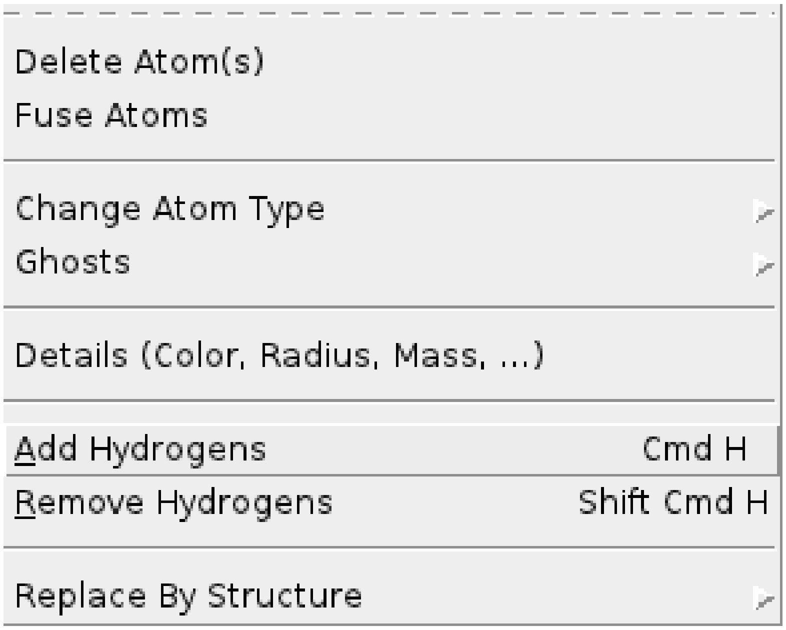
The oxygen atom has been added.

For now, we are done using atom tools, so go back to the select tool:

```
Select the select-tool by clicking on the button with the arrow (or press the
Esc key)
```

Add the hydrogens

Now many hydrogen atoms need to be added. You can do this using the H-tool, but a much easier method is to use the **Atoms** → **Add Hydrogen** menu command:



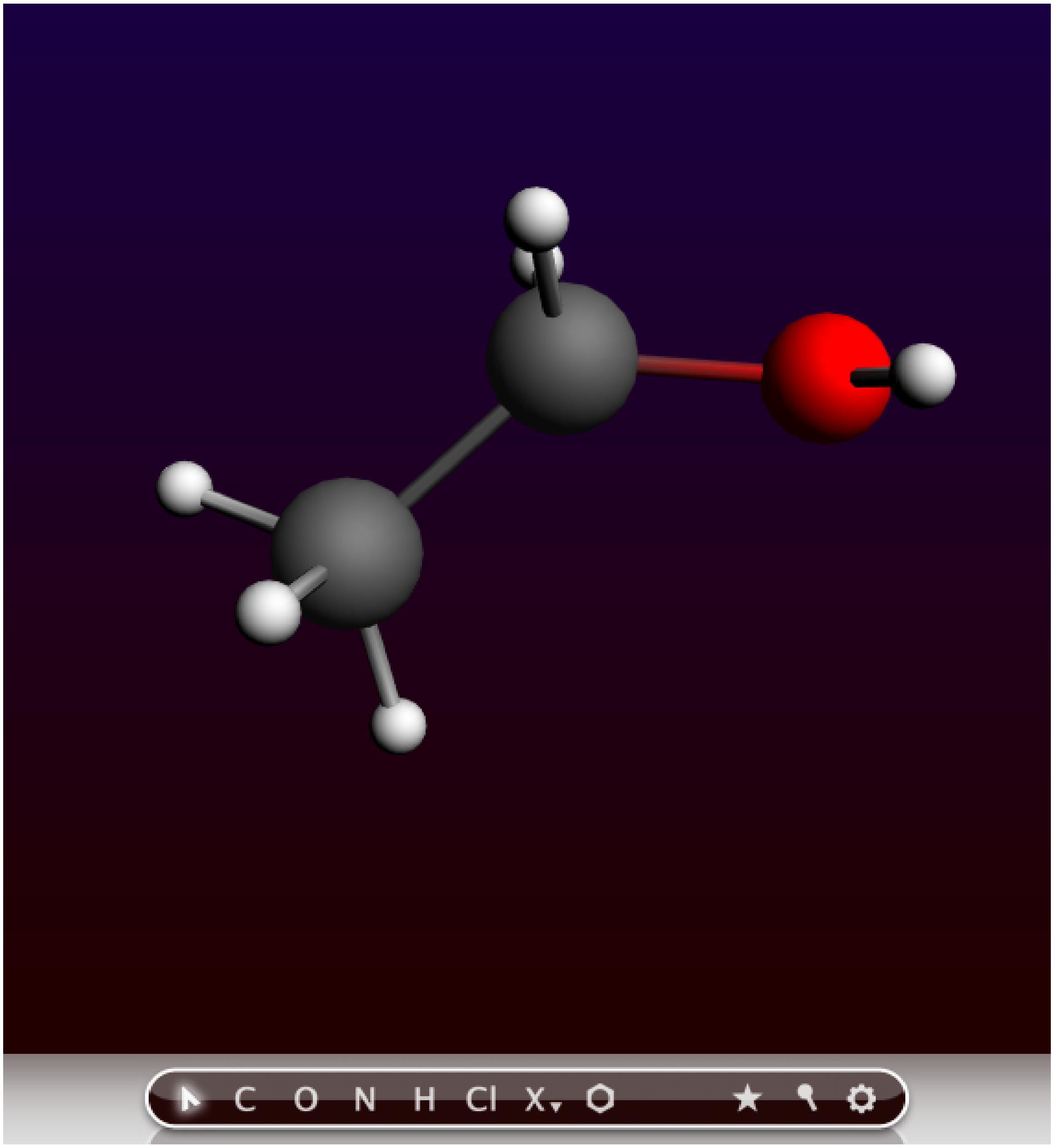
The 'Add Hydrogen' menu command works on the selection only, when present. Thus, only one hydrogen atom would be added to the oxygen atom. This is not what you want. So first we make sure that nothing is selected by clicking in empty space.

`Click in empty (drawing) space`

Now no atoms are selected any more.

`Select the` **Atoms → Add Hydrogen** `command`

Many menu commands have shortcuts. In this case you can also use the shortcut (ctrl-H or cmd-H, depending on your platform) as an alternative. The shortcuts are indicated in the menu commands.

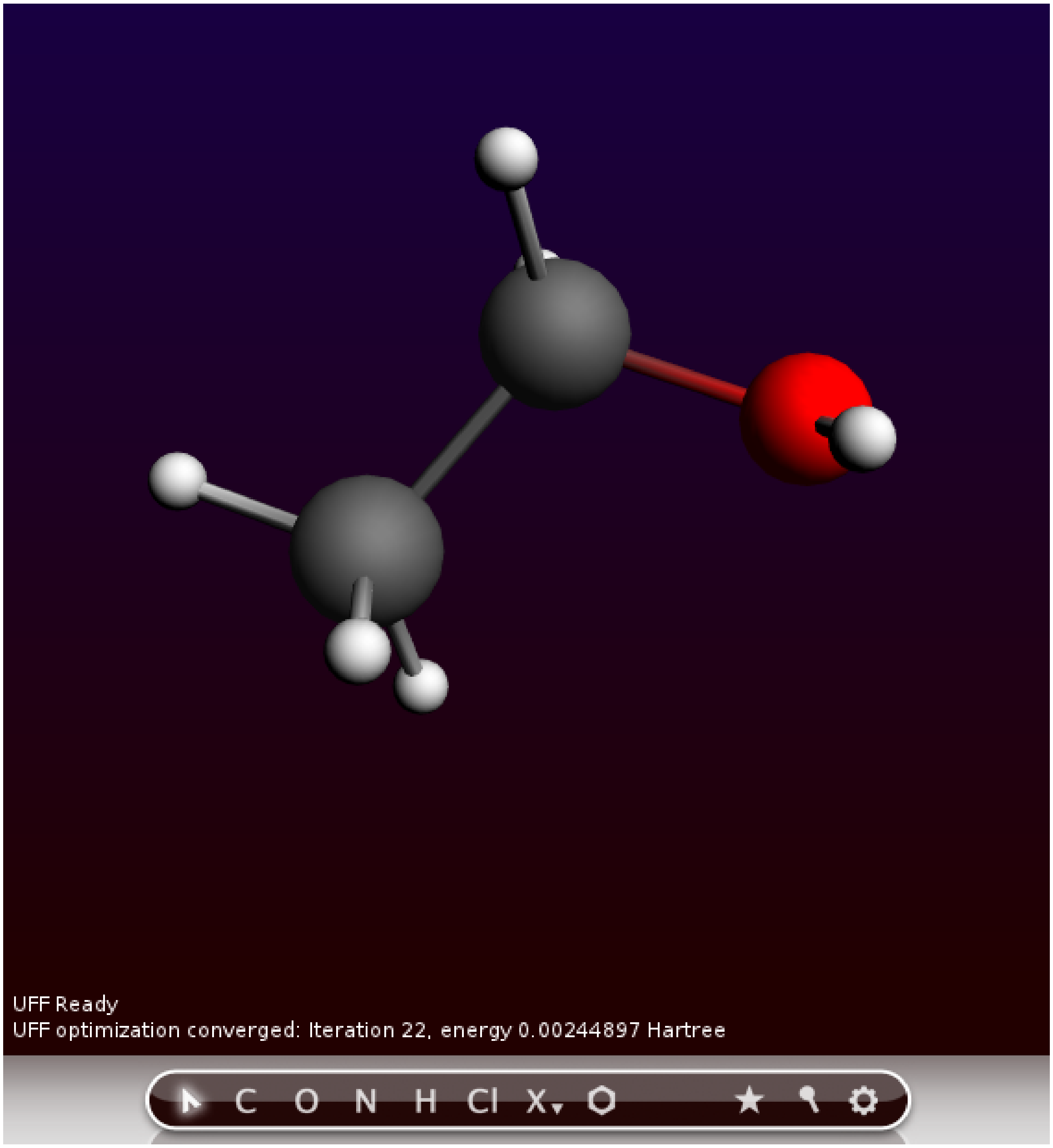


All atoms will be saturated with hydrogen atoms. And you have created an ethanol molecule, though the geometry is still far from perfect.

Pre-optimize the geometry

Now use the optimizer that comes with ADFinput to pre-optimize the geometry.

Click on the pre-optimizer button (the rightmost 'cog wheel' button of the menu bar)



UFF Ready
UFF optimization converged: Iteration 22, energy 0.00244897 Hartree

The geometry of the molecule will be pre-optimized, using UFF by default. Note you can select another pre-optimizer via the Preferences, or use a different pre-optimizer by right-clicking on the cog wheel and selecting the method to use from the pop-up menu.

In the status field below the drawing area you can follow the pre-optimization iteration number and the energy relatively to the starting configuration.

Viewing the molecule

Rotate, translate, or zoom

You can rotate, translate, and zoom your molecule using the mouse.

You need to drag with the mouse: press a mouse button, and while holding it down move it. Which mouse button, and which modifier key you press at the same time, determines what will happen:

Rotate	Left
Rotate in-plane	ctrl-Left
Translate	Middle, or Alt-Left
Zoom	Mouse wheel, Right, or cmd-Left (drag up or down)

The rotate, translate, and zoom operations change how you look at the molecule, they do not change the coordinates.

Click once somewhere in empty space to make sure nothing is selected.

Click with the left mouse button, and drag:
your molecule will rotate.

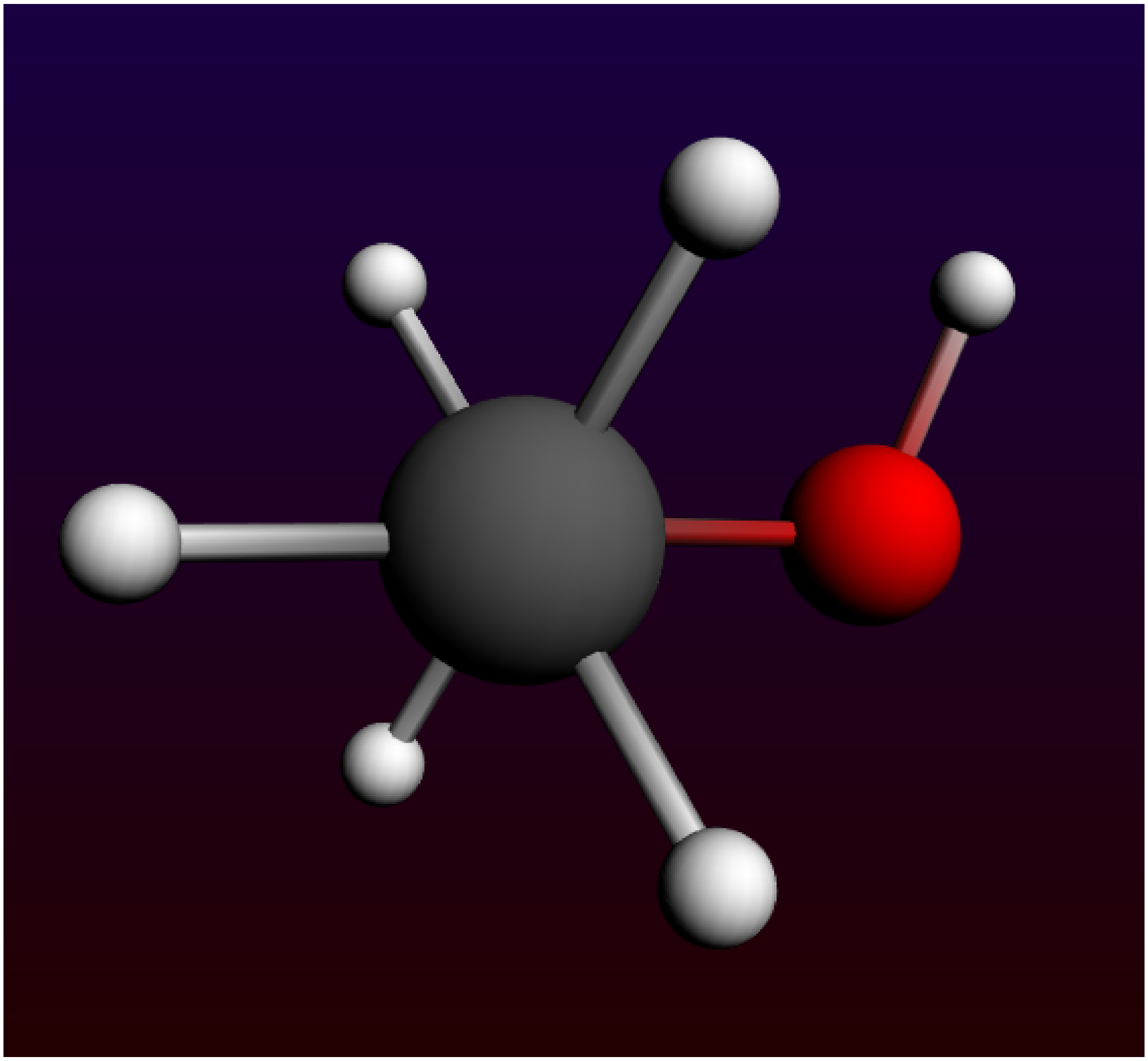
Click with the left mouse button with the ctrl-key, and drag:
your molecule will rotate in-plane.

Click with the middle mouse button (or left with alt-key), and drag:
your molecule will be translated.

Click with the right mouse button (or left with cmd key), and drag up and down:
you will zoom closer to or away from your molecule.

Use the mouse wheel, if you have one:
you will zoom closer to or away from your molecule.

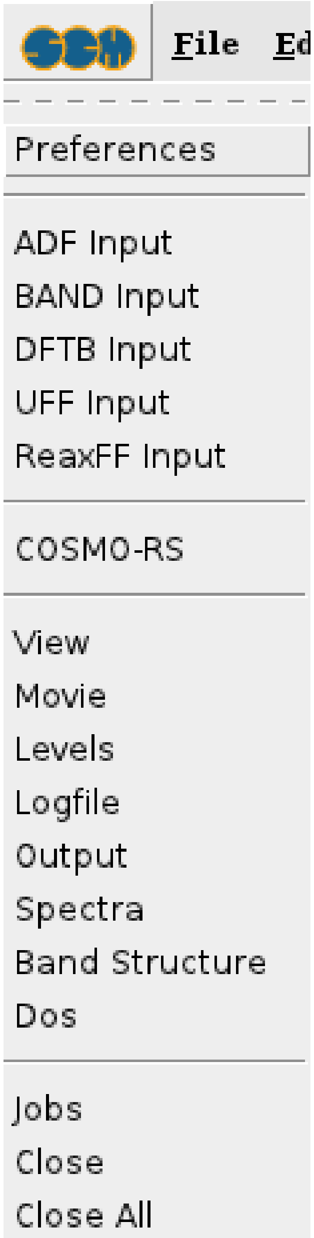
Using all these options, try to position the ethanol as closely as possible as in the following image:



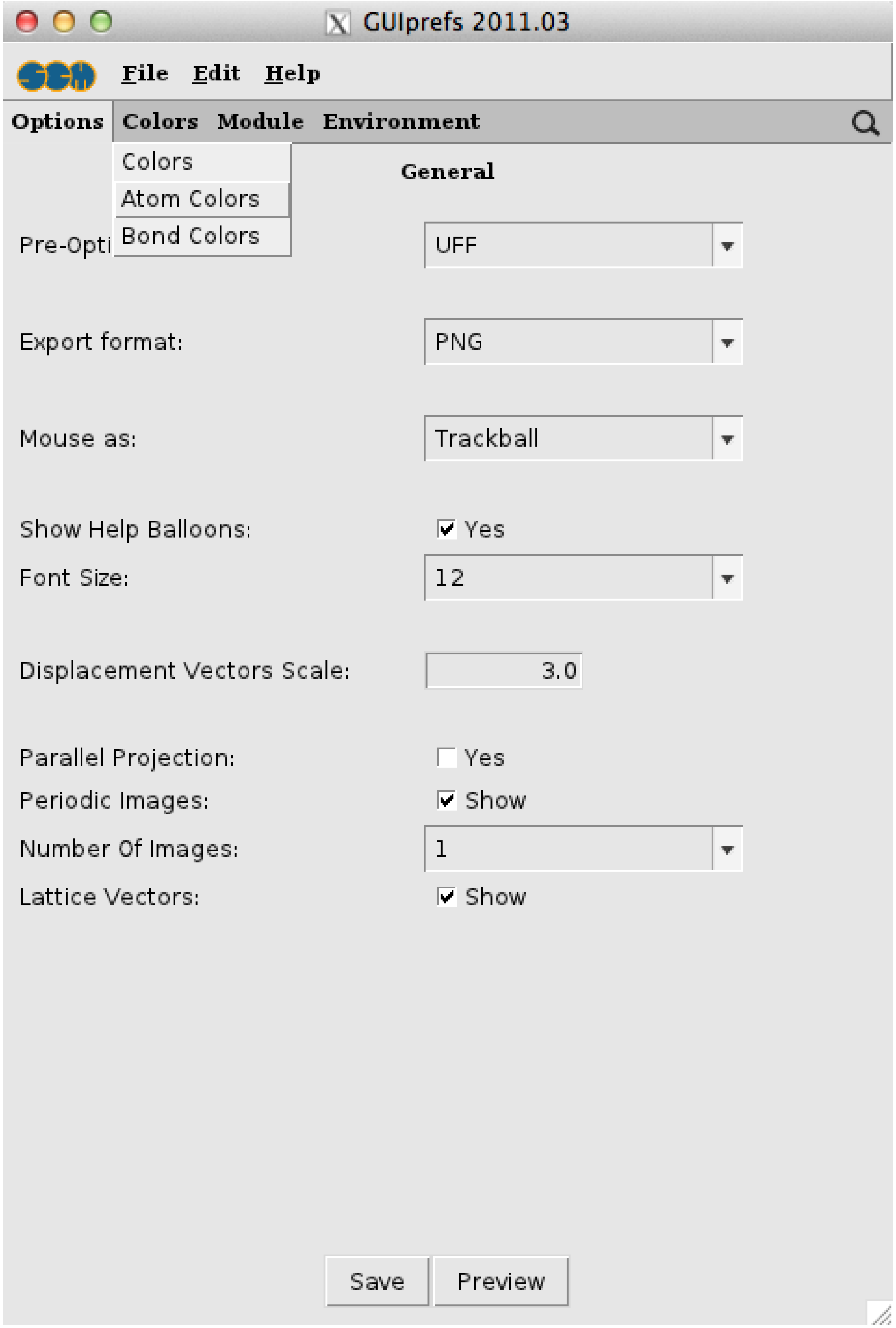
Atom colors

The atoms of your molecule will have a pre-defined color, as visible in the molecule editor. You can change these colors in two ways: either change the global default color per element, or override the default color for a specific atom. The first method uses the Preferences command, the second method uses the 'Atom Details panel' via the **Atoms → Details (Color, Radius, Mass, ...)**. In this tutorial we will change the default color of all Carbon atoms using the Preferences command:

`Use the` **SCM → Preferences** `menu command to start the preferences module`



In the preferences window, go to the 'Atom Colors' panel (use the panel bar Color menu)



Pre-Opti UFF

Export format: PNG

Mouse as: Trackball

Show Help Balloons: ☑ Yes

Font Size: 12

Displacement Vectors Scale: 3.0

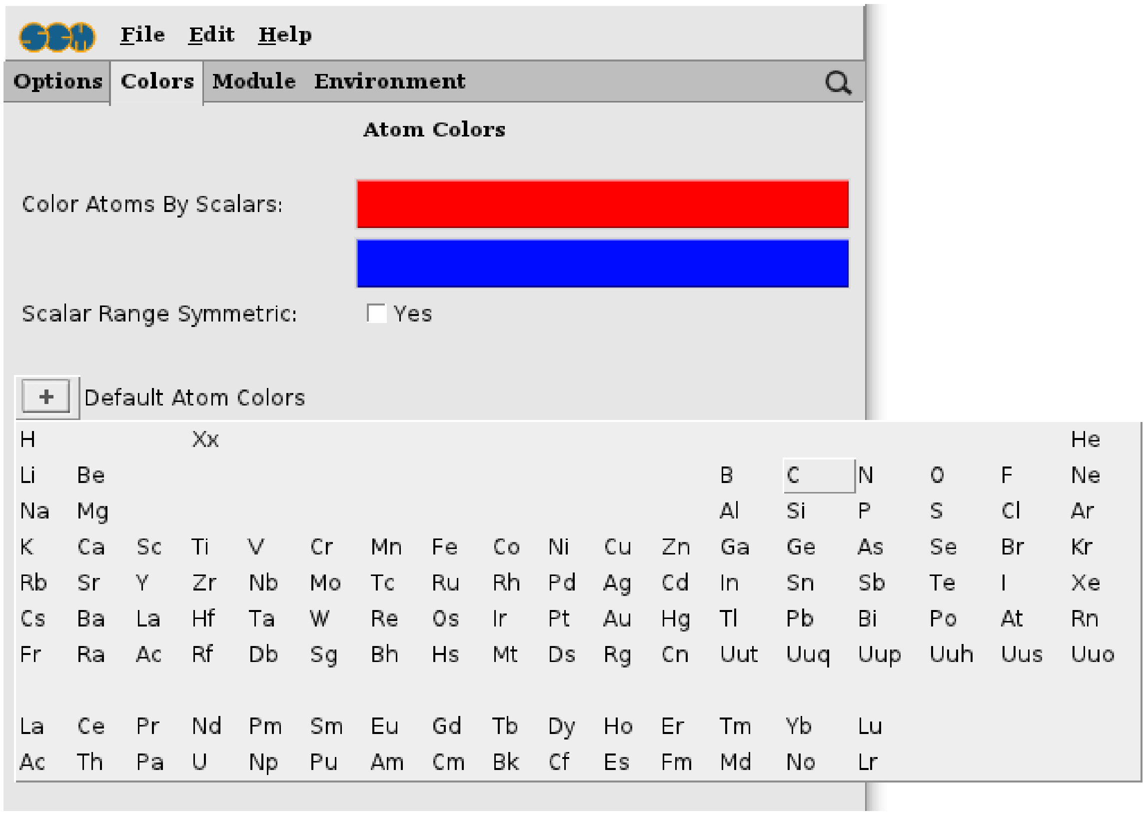
Parallel Projection: ☐ Yes

Periodic Images: ☑ Show

Number Of Images: 1

Lattice Vectors: ☑ Show

Click on the '+' button, and select C (Carbon) from the periodic table that pops up.



Atom Colors

Color Atoms By Scalars:

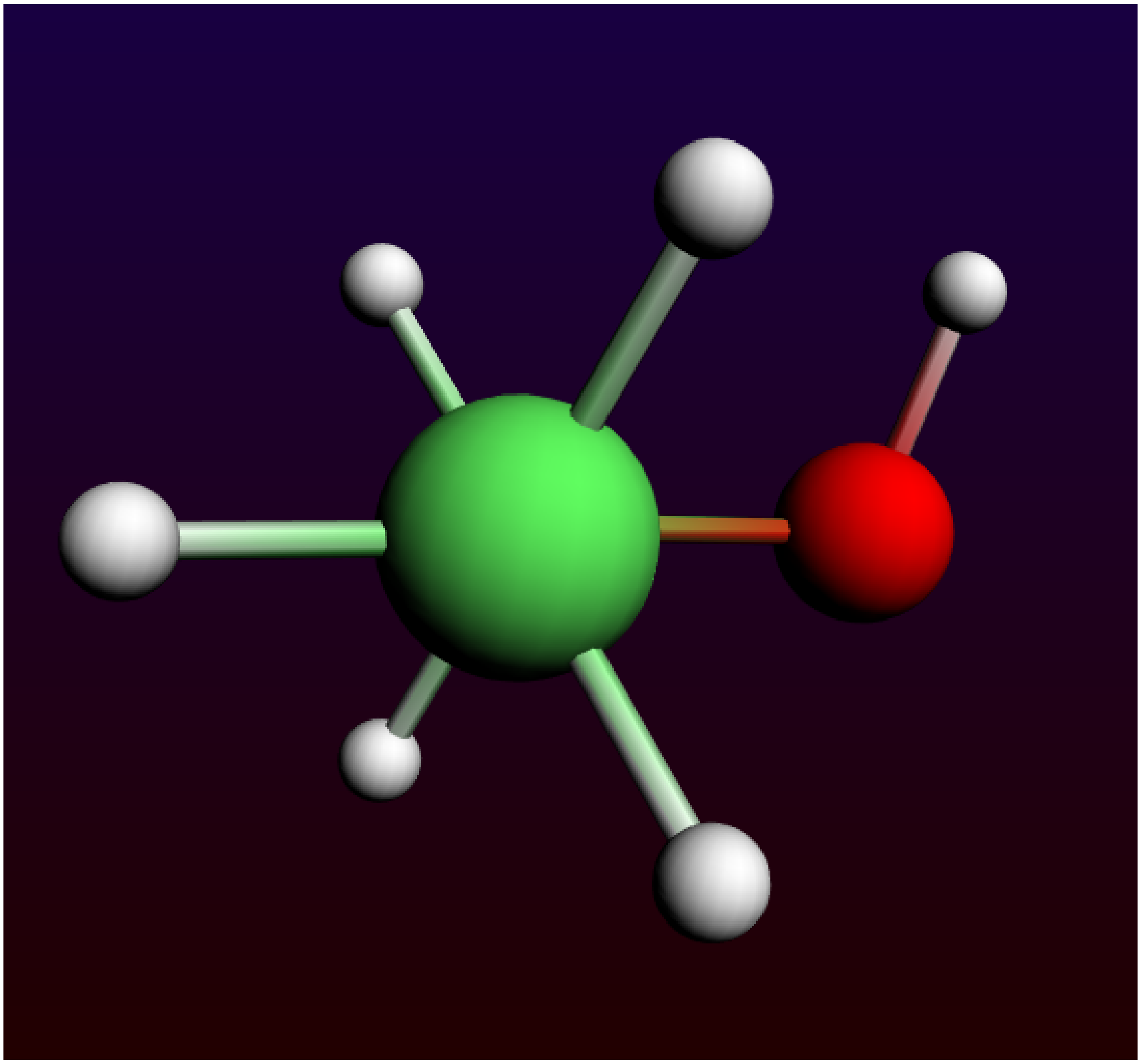
Scalar Range Symmetric: ☐ Yes

Default Atom Colors

H			Xx														He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Uuq	Uup	Uuh	Uus	Uuo
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr			

You can now change the color for the carbon atoms either by clicking on the colored block next to the C label

Click on the colored C-block
Select your favorite color, and dismiss the Color dialog (click the OK button on most platforms)
Click the Preview button in the bottom of the GUIprefs panel.



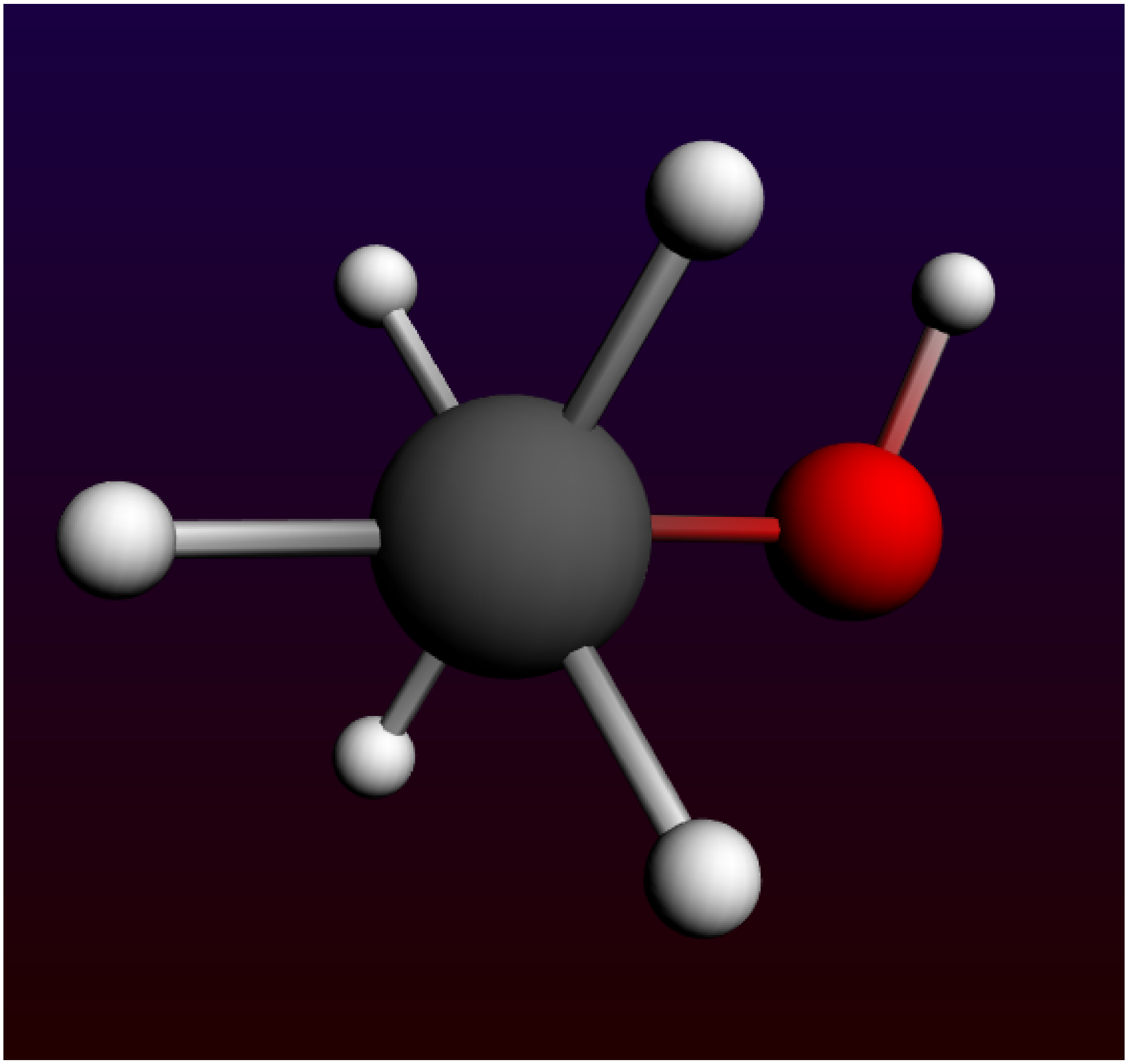
In ADFinput the colors of the carbon atoms will now be adjusted to the color that you have selected.

The 'Preview' button shows the effect of your new preferences in all open GUI modules, but without saving them. Once you are content with your changes, you can use the 'Save' button to store the new defaults.

If you close the Preferences window without saving, your original settings will be restored in the open modules.

To revert to the default value of carbon, you can remove the carbon color in Preferences window by pressing the - button in front of the C color line:

```
Click the '-' button in front of the C color line
Click the 'Preview' button
```



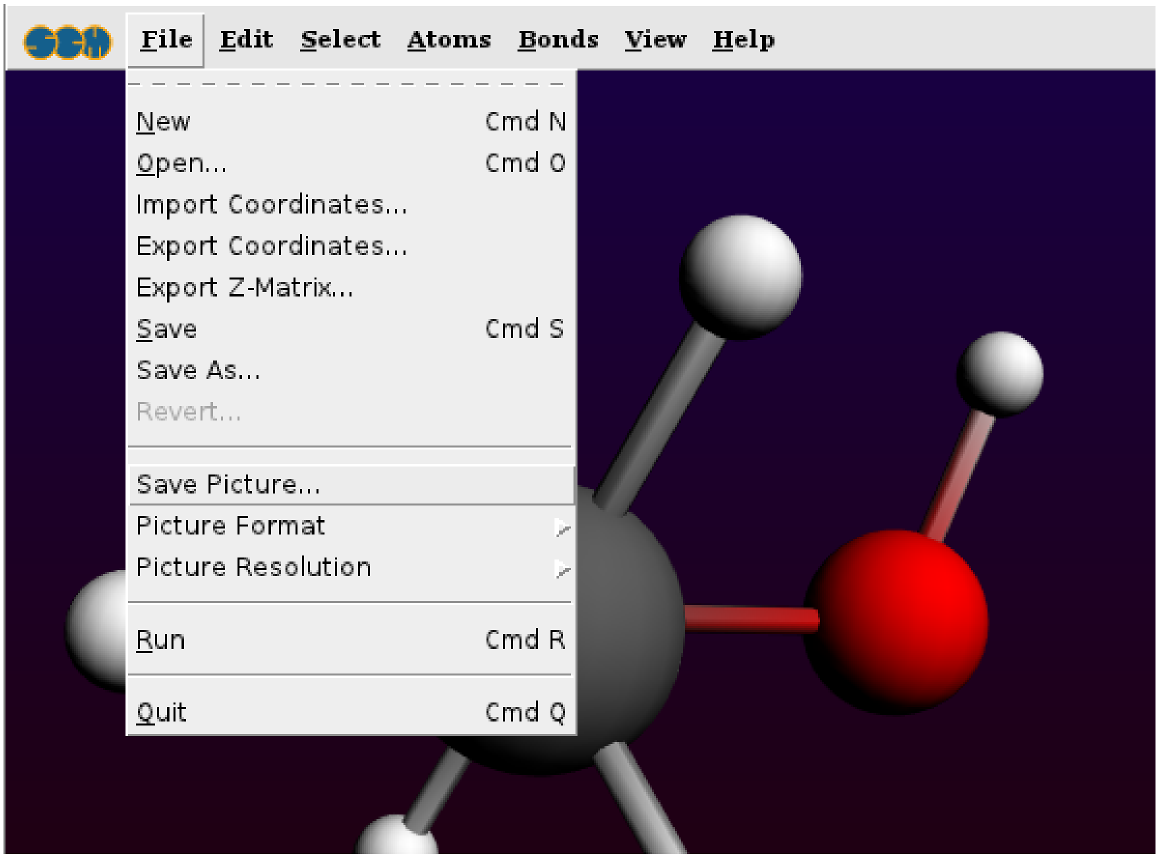
In ADFinput, your carbon atoms now should have their default color again (dark gray).

`Use the` **File → Quit** `menu command to close the GUIprefs module (the Preferences window)`

When quitting the Preferences module without saving, any changes made visible via the Preview button will be undone.

Save picture

You can save a picture of your molecule using the 'Save Picture ...' command from the File menu.



The format used is the PNG format. You can change this using the **File** → **Picture Format** menu command. You can also change the resolution. A smaller resolution will result in a smaller file, but will reduce the quality.

Via the Preferences command it is possible to save your preferred format.

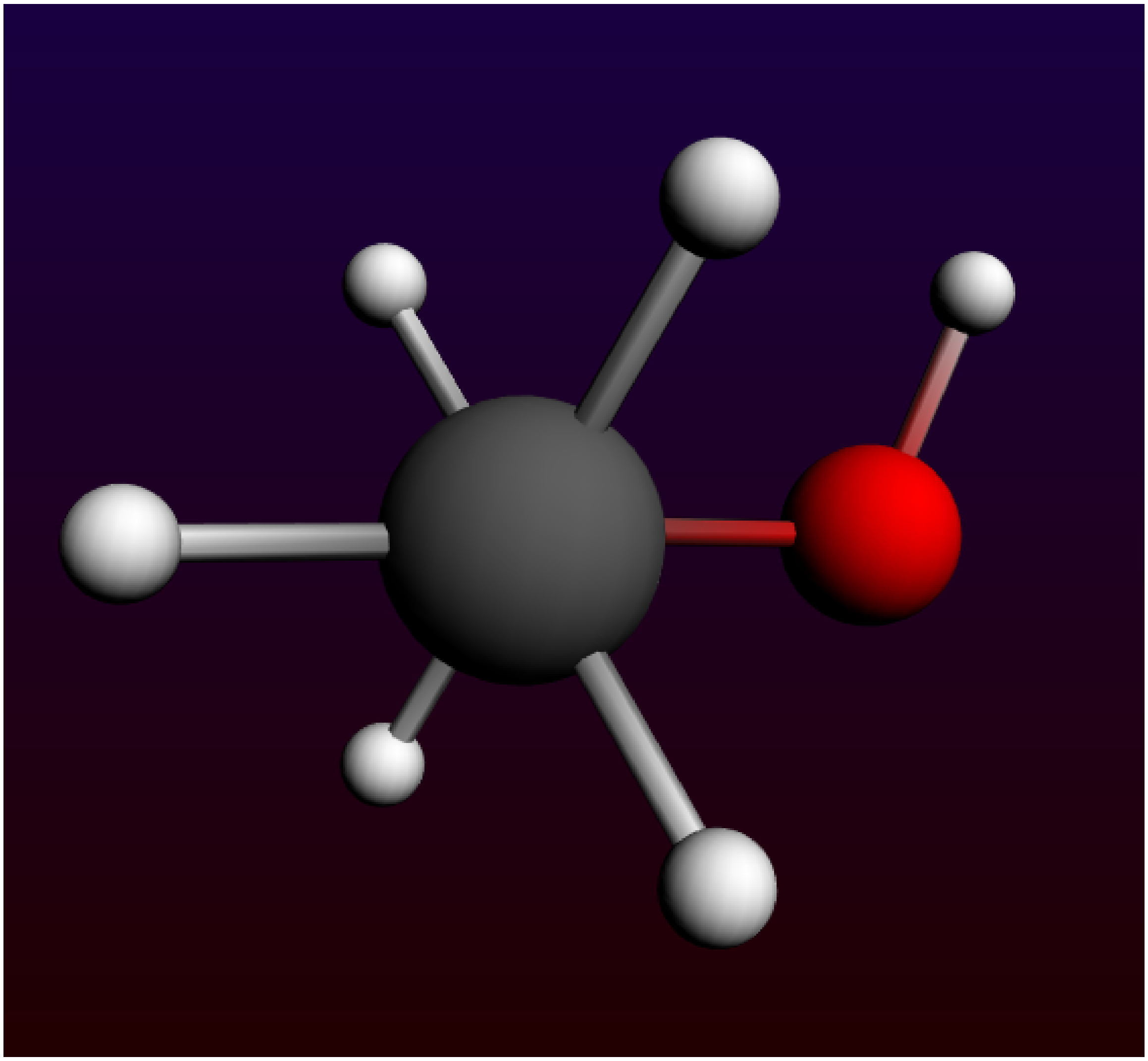
`Select the` **File → Save Picture ...** `command`
`Enter the name for your picture: ethanol`
`Click the 'Save' button`

A picture will be saved to disk containing the image of your molecule. Only the drawing area is saved in the picture, not all the input options.

Molecular conformation

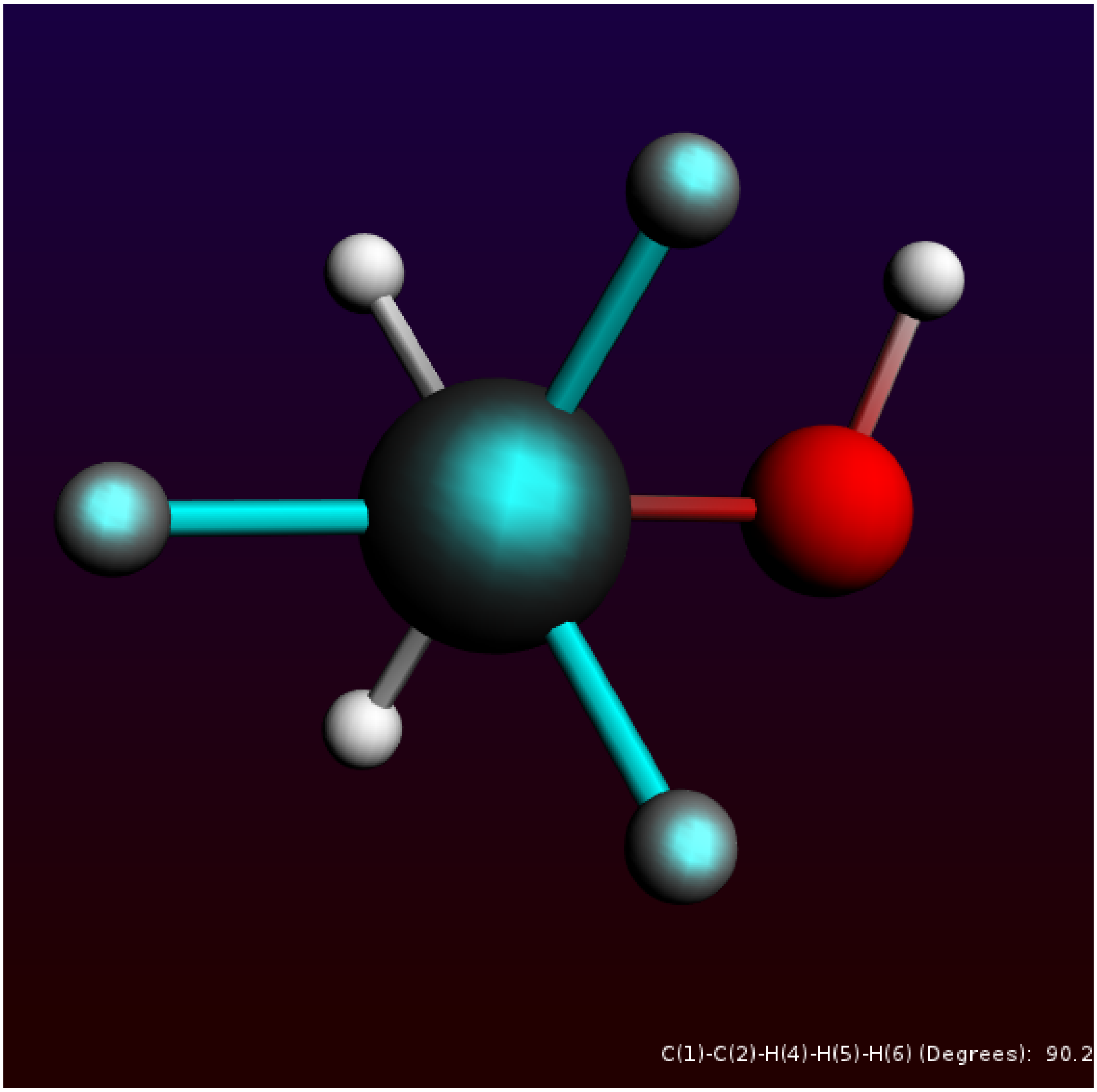
Rotate such that you look along the C-C axis

`Rotate your molecule into the following position:`



Select the top CH3 group

Click once on the top carbon atom
Use the **Select → Select Connected** menu command



As you will notice, all atoms directly connected to the selected atom are added to the selection. Alternatively, you can also make a selection by shift-clicking on the elements you want to select.

```
Click in empty space
Click on the top carbon atom
Shift-Click once (without moving) on each of the top hydrogen atoms
```

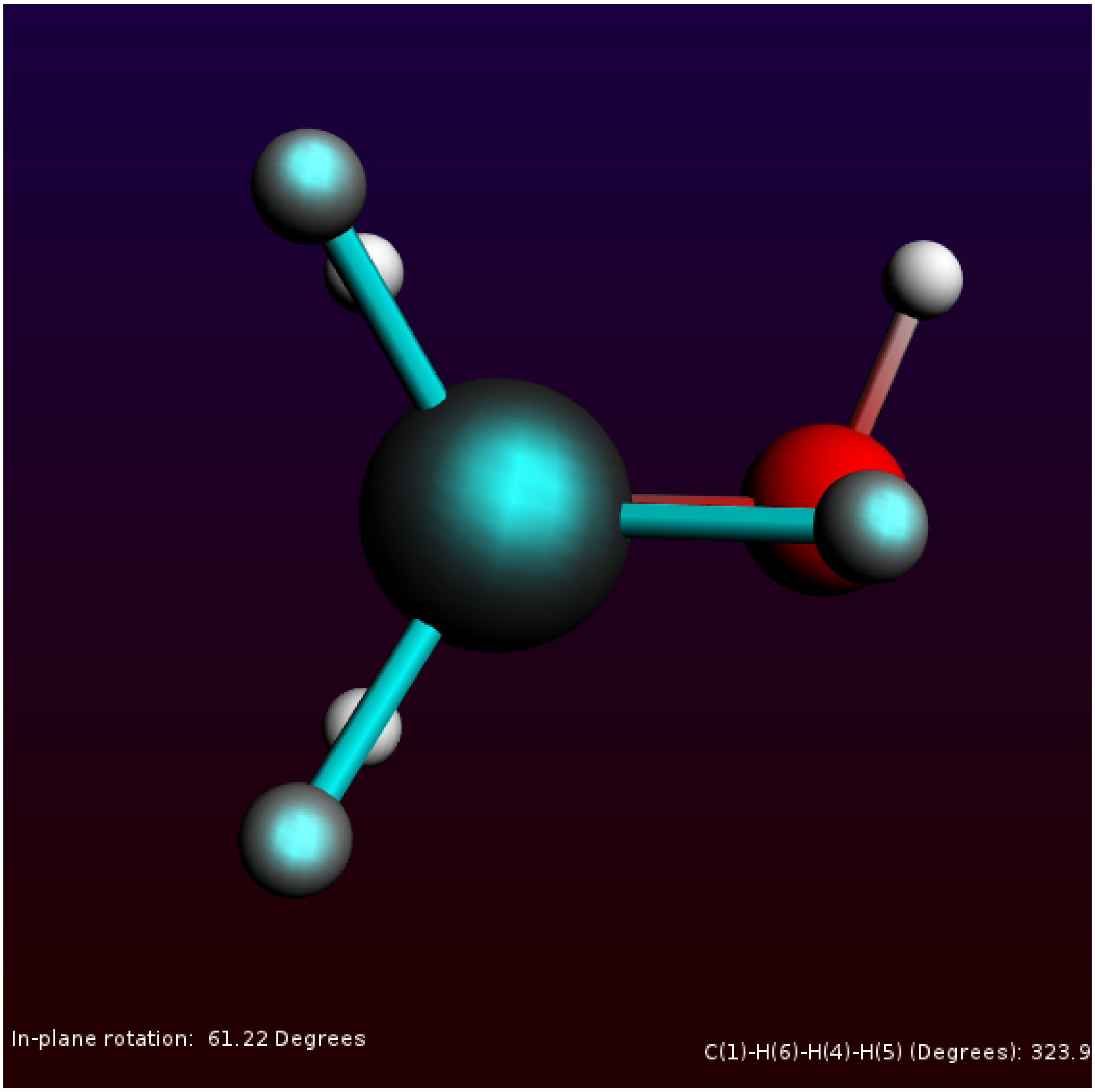
This has almost the same effect (in this case you have not selected the second carbon atom).

Rotate the selection

We are now trying to make an eclipsed geometry.

`ctrl-Click with the left mouse button` **in one of the selected hydrogens**`,`
`and drag around to rotate the selection in-plane.`

Rotate the hydrogen atoms in an almost eclipsed position.



In-plane rotation: 61.22 Degrees

C(1)-H(6)-H(4)-H(5) (Degrees): 323.9

You can move the selection by clicking in a selected object, and dragging with the mouse. All usual operations are possible: rotate, rotate in-plane, translate and zoom. Zoom in this case means moving the selection perpendicular to the screen.

In the status field you see the current rotation angle.

You have to click and start dragging at a selected item. If you click and drag in space you will move the entire molecule.

Back to Staggered Geometry

Click in empty space to clear the selection
Click on the pre-optimize button

The optimizer will bring the structure back to the original staggered geometry. If it does not complete, repeat this step until it does.

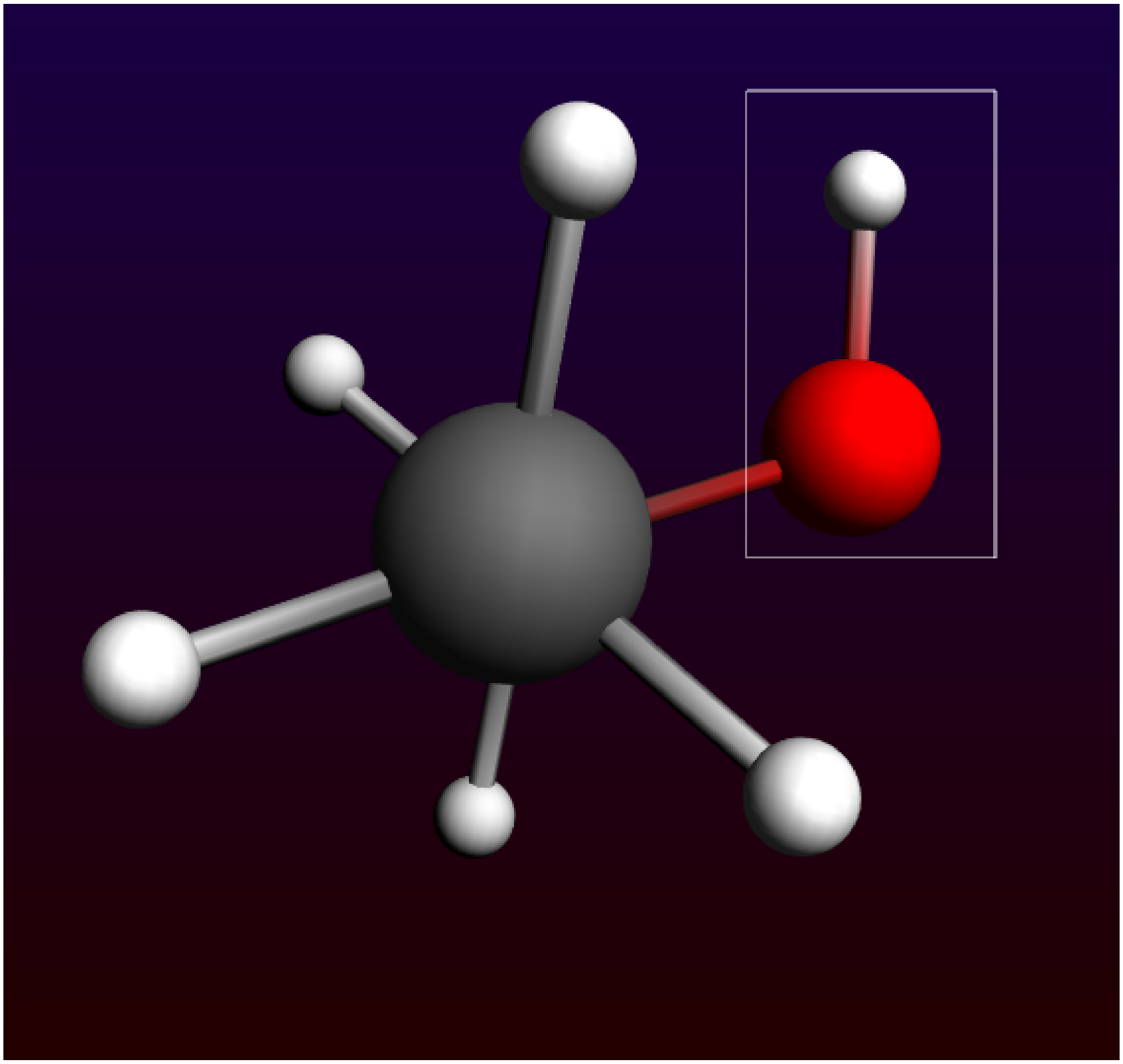
Getting and setting geometry parameters

Bond length

First select the oxygen atom and the connected hydrogen atom.

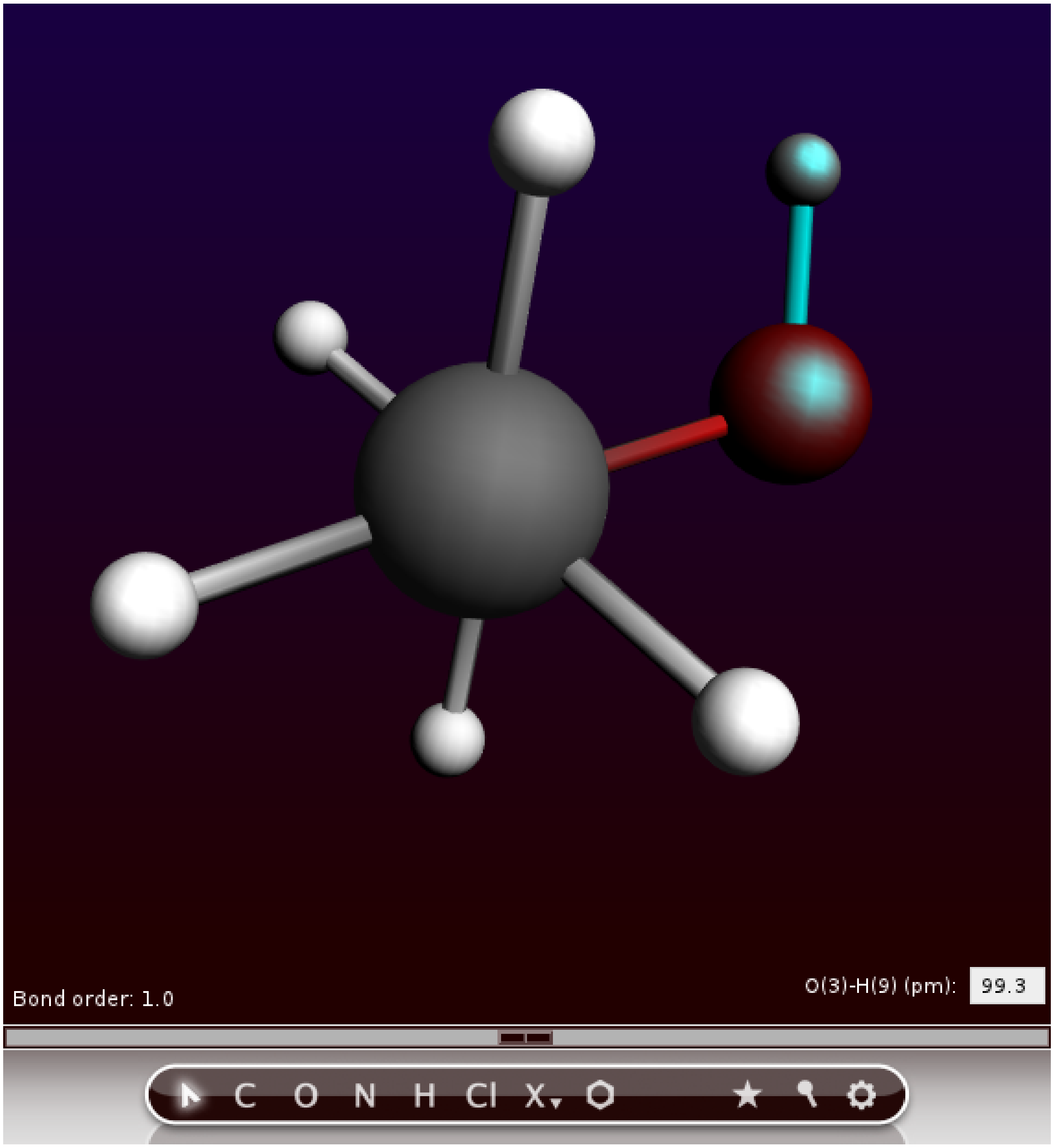
This time we make the selection by dragging a rectangle around all objects that we want to select.

```
Using the left mouse button together with the shift key, drag a rectangle
around the oxygen and hydrogen atom.
```



```
Release the mouse button (and the shift key)
```

The oxygen atom and the hydrogen atom are selected.



Bond order: 1.0

O(3)-H(9) (pm): 99.3

In the status area you see the distance between the selected atoms, information about the bond, and a slider.

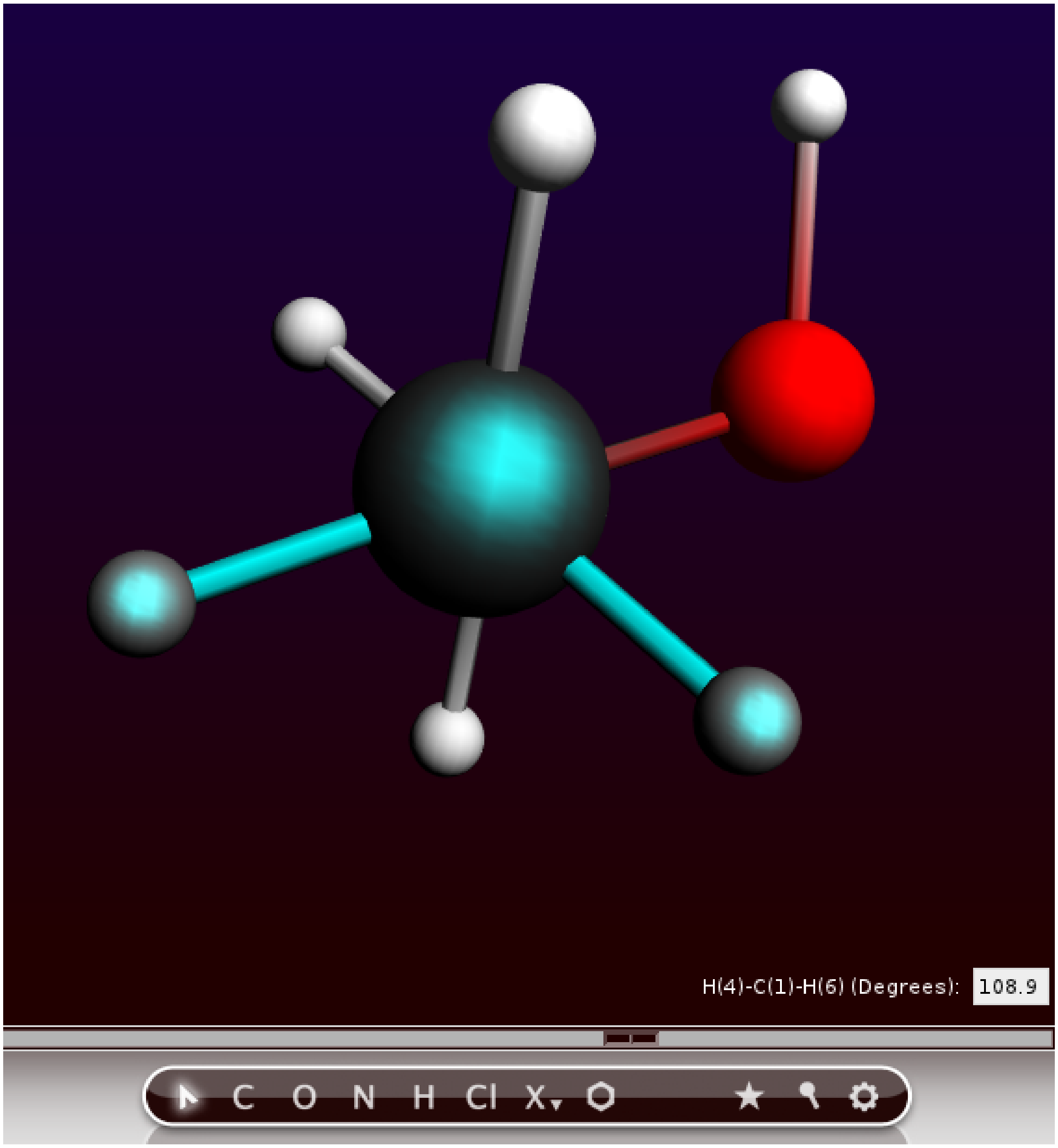
You can set the distance to any value you wish by editing it, or (most conveniently) by using the slider.

Normally the smallest group of atoms will move to create the requested distance. If you press the control key while using the slider the last atom selected will be in the group of atoms to move.

```
Use the slider to move the H atom
```

Bond angle

```
Select first one of the top hydrogens by clicking on it
Next, extend the selection (shift key) by clicking on the top carbon atom
Finally, extend the selection (shift key) by clicking on another top hydrogen
atom
```



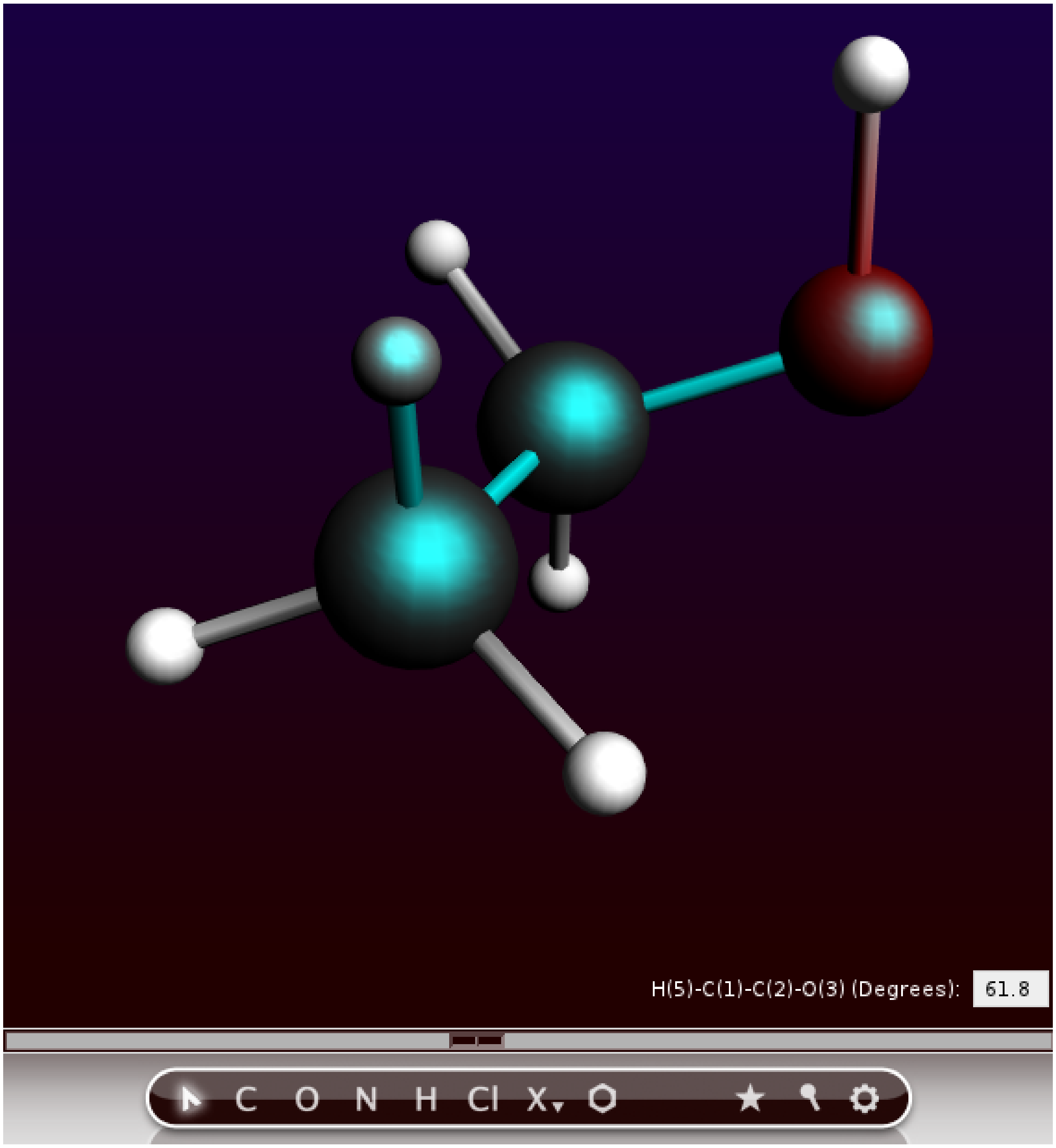
H(4)-C(1)-H(6) (Degrees): 108.9

In the status area information about the bond angle of the selected three atoms is given, and the slider is again visible. You can change this value to a value you like, most conveniently using the slider.

Dihedral angle

By selecting four atoms we get information about the dihedral angle. And of course you can also change it, again most conveniently using the slider.

```
Move the molecule such that you can see all atoms
Select first one of the top hydrogens by clicking on it
Next, extend the selection (shift key) by clicking on the top carbon atom
Next, extend the selection (shift key) by clicking on the next carbon atom
Finally, extend the selection (shift key) by clicking on the oxygen atom
```

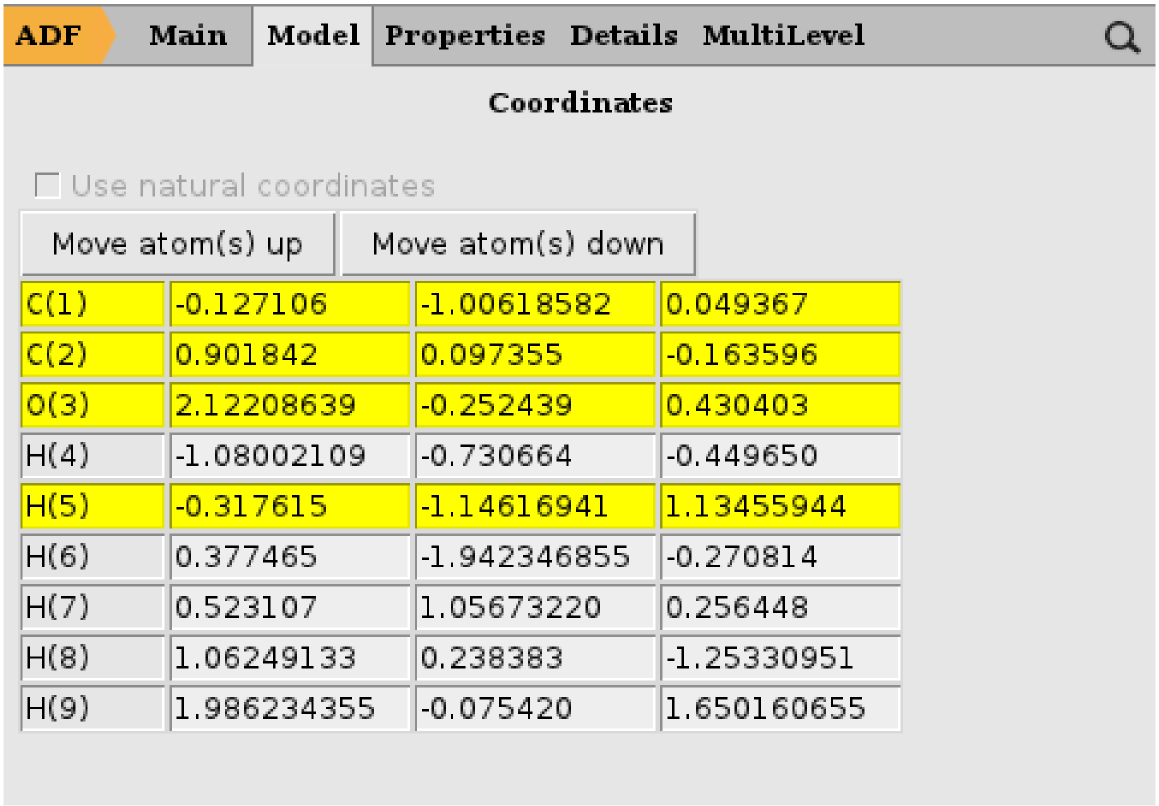


H(5)-C(1)-C(2)-O(3) (Degrees): 61.8

Coordinates

To view the coordinates we have to go to a different input panel. The input panels can be selected using the panel bar on the top of the input panels, the right half of the window.

In the right side of the ADFinput window:
Click on the **Model** tab in the panel bar
Select the **Coordinates** command



C(1)	-0.127106	-1.00618582	0.049367
C(2)	0.901842	0.097355	-0.163596
O(3)	2.12208639	-0.252439	0.430403
H(4)	-1.08002109	-0.730664	-0.449650
H(5)	-0.317615	-1.14616941	1.13455944
H(6)	0.377465	-1.942346855	-0.270814
H(7)	0.523107	1.05673220	0.256448
H(8)	1.06249133	0.238383	-1.25330951
H(9)	1.986234355	-0.075420	1.650160655

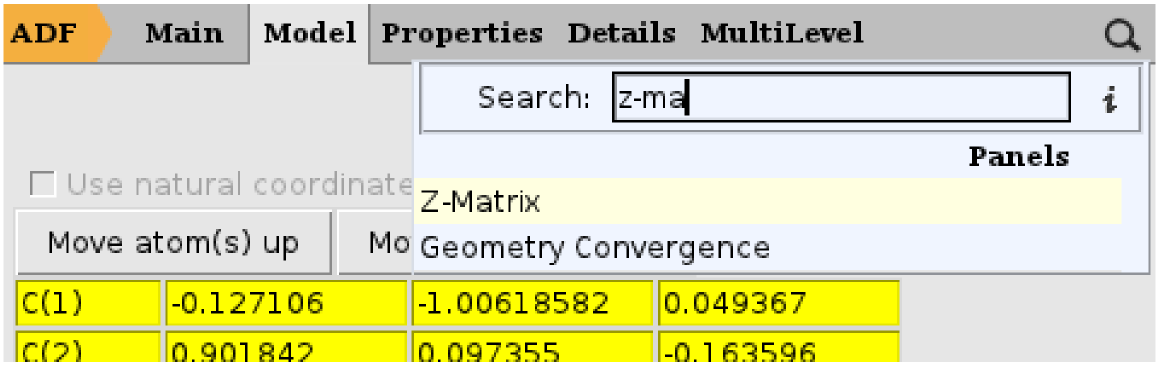
You get a list of all Cartesian coordinates. They will be updated in real time when you make changes to the molecule, and you can also edit the values yourself. In that case, the picture of the molecule will be updated automatically.

Note that some atoms are highlighted. These are the currently selected atoms.

The 'Move Atom(s)' buttons will move the selected atoms up or down. In this way you can re-order the atoms.

You may, in some cases, wish to use Internal coordinates. These will be updated in real time as well, and you can also edit the values yourself. If you re-order the atoms while using the Internal coordinates, the Z-matrix will be recalculated from scratch. The Z-matrix panel is in the Details tab, but we will use the search option to get to it:

```
Click the search icon at the right of the panel bar
Enter the text "z-ma" in the search field
```



Search: z-ma

Panels

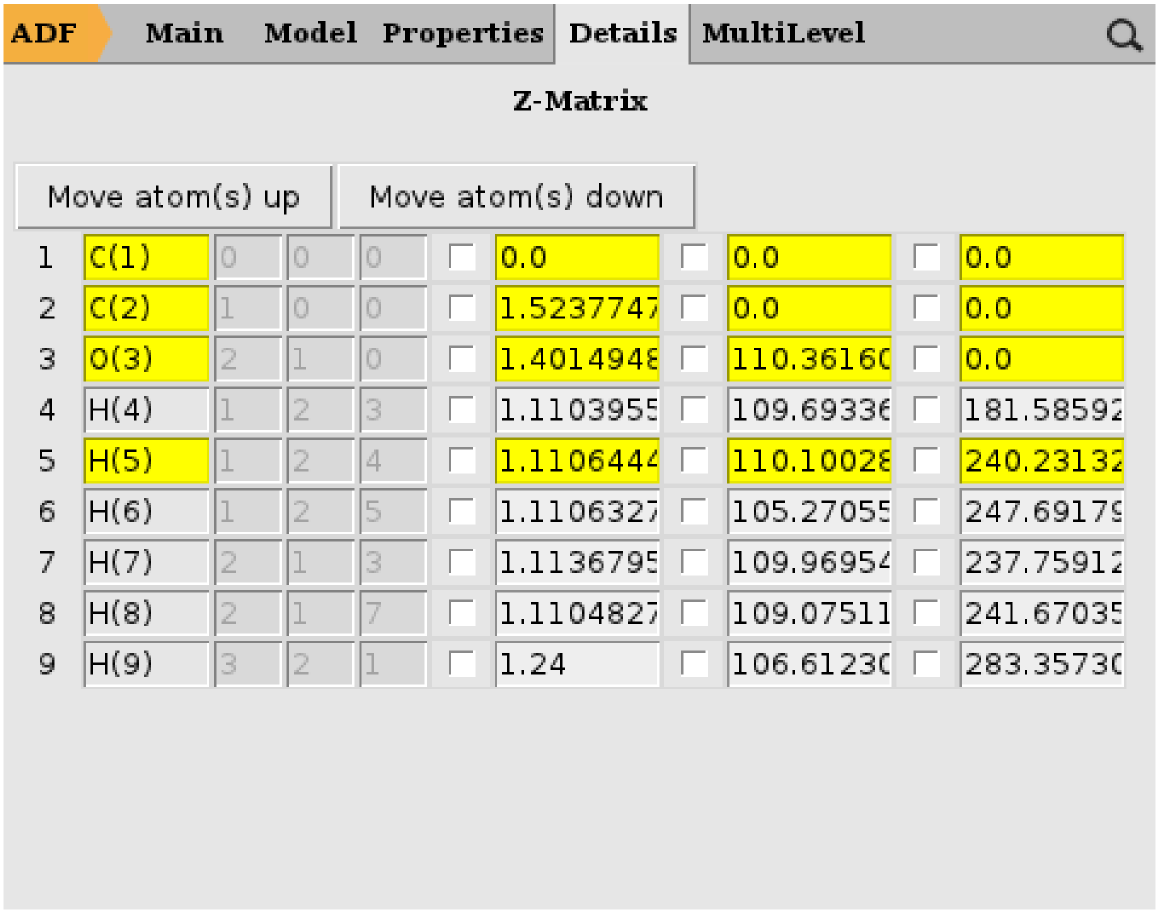
Z-Matrix

Geometry Convergence

C(1)	-0.127106	-1.00618582	0.049367
C(2)	0.901842	0.097355	-0.163596

Note that in the search results the Z-Matrix panel is highlighted, and note that the search is not case sensitive.

```
Click on the selected option (Z-Matrix), or use the return key
```



1	C(1)	0	0	0	☐	0.0	☐	0.0	☐	0.0
2	C(2)	1	0	0	☐	1.523774	☐	0.0	☐	0.0
3	O(3)	2	1	0	☐	1.401494	☐	110.3616	☐	0.0
4	H(4)	1	2	3	☐	1.110395	☐	109.6933	☐	181.5859
5	H(5)	1	2	4	☐	1.110644	☐	110.1002	☐	240.2313
6	H(6)	1	2	5	☐	1.110632	☐	105.2705	☐	247.6917
7	H(7)	2	1	3	☐	1.113679	☐	109.9695	☐	237.7591
8	H(8)	2	1	7	☐	1.110482	☐	109.0751	☐	241.6703
9	H(9)	3	2	1	☐	1.24	☐	106.6123	☐	283.3573

Extending and changing your molecule

Before making some changes, let's re-optimize. We first select the 'Main' panel so the coordinates will not be visible during the pre-optimization. Otherwise this may slow down the pre-optimization.

```
Click on the "Main" tab
Click on the pre-optimize button
```

Let's try to change the CH2OH group in a COOH group.

Thus, we need to:

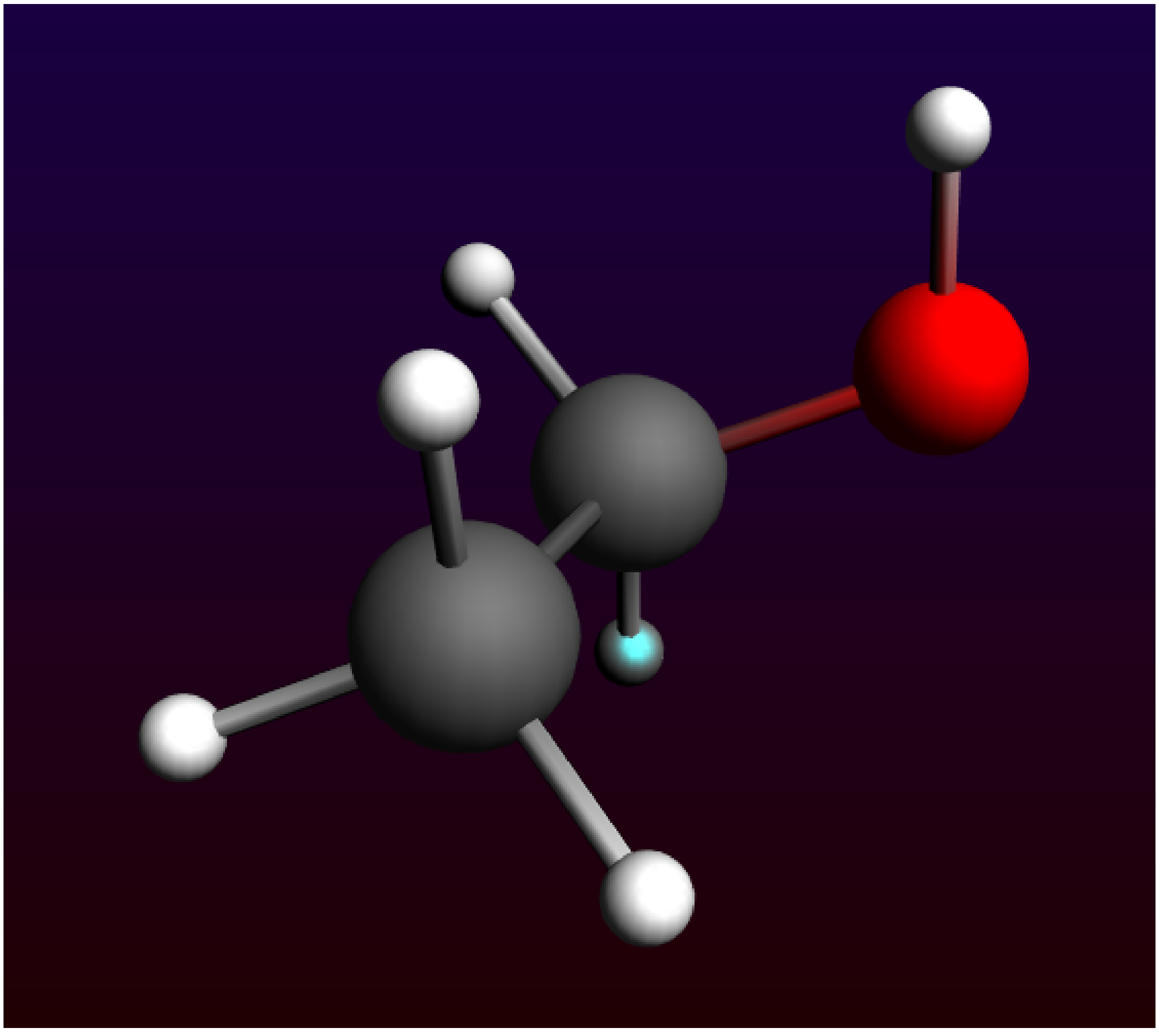
- remove one hydrogen
- change one hydrogen into an oxygen
- change a single bond into a double bond

After this, we will revert to the ethanol molecule.

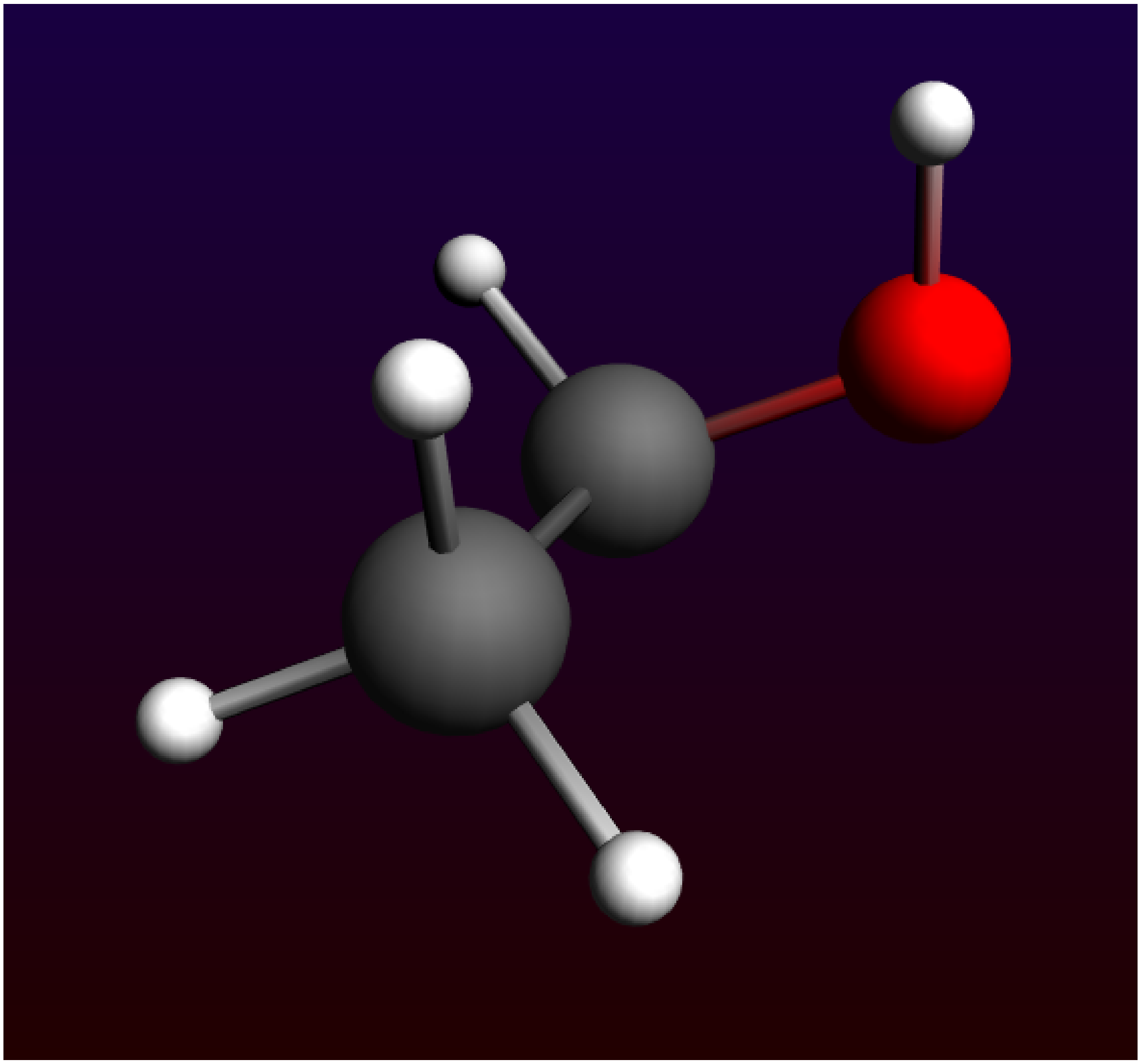
Delete an atom

First: delete one hydrogen

```
Click in empty space to clear the selection
Click once on the hydrogen to delete, it will be selected
```



```
Press the backspace key
```

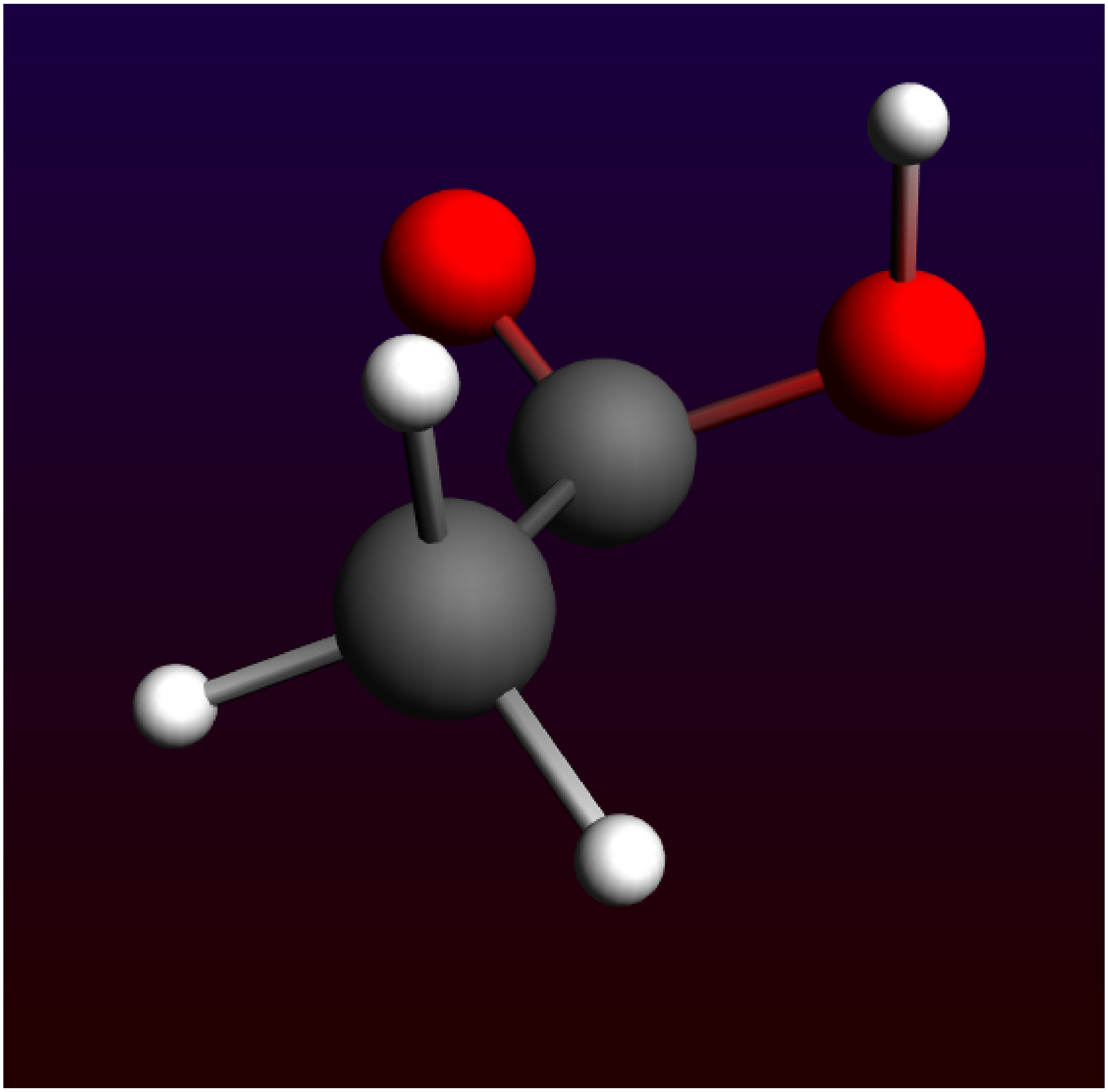


The selected atom is removed.

Change the type of an atom

Next, we will change a hydrogen into an oxygen atom

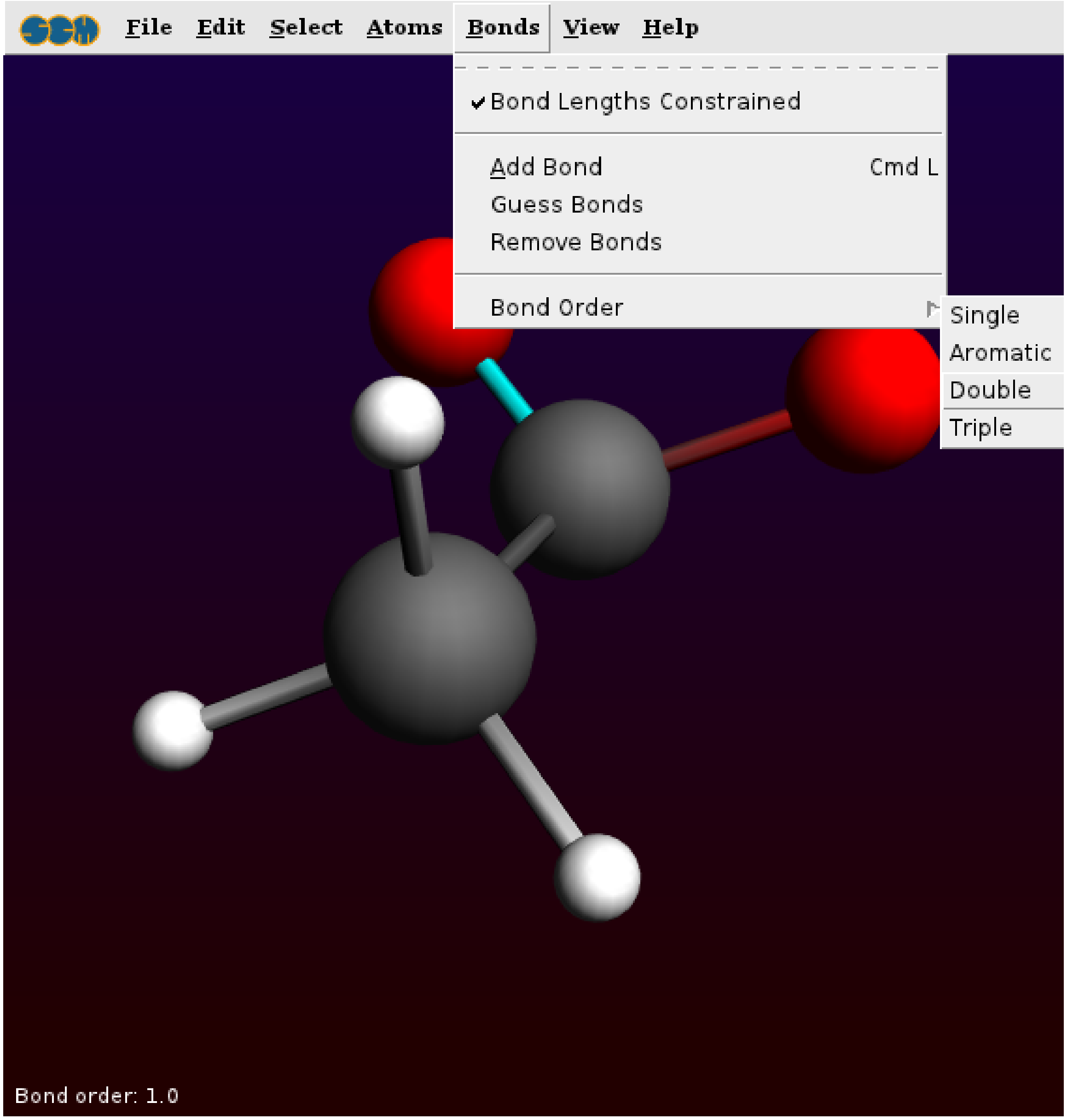
```
Select the O-tool (or press the 'O' key)
Double-click on the hydrogen that should change into an oxygen
```



Change the bond type of an existing bond

Now the oxygen atom is singly bonded to the carbon, we need to change this into a double bond.

`Click on the bond between the carbon and the new oxygen`
`Use the` **Bonds → Bond Order → Double** `menu command (or just press the '2' key)`



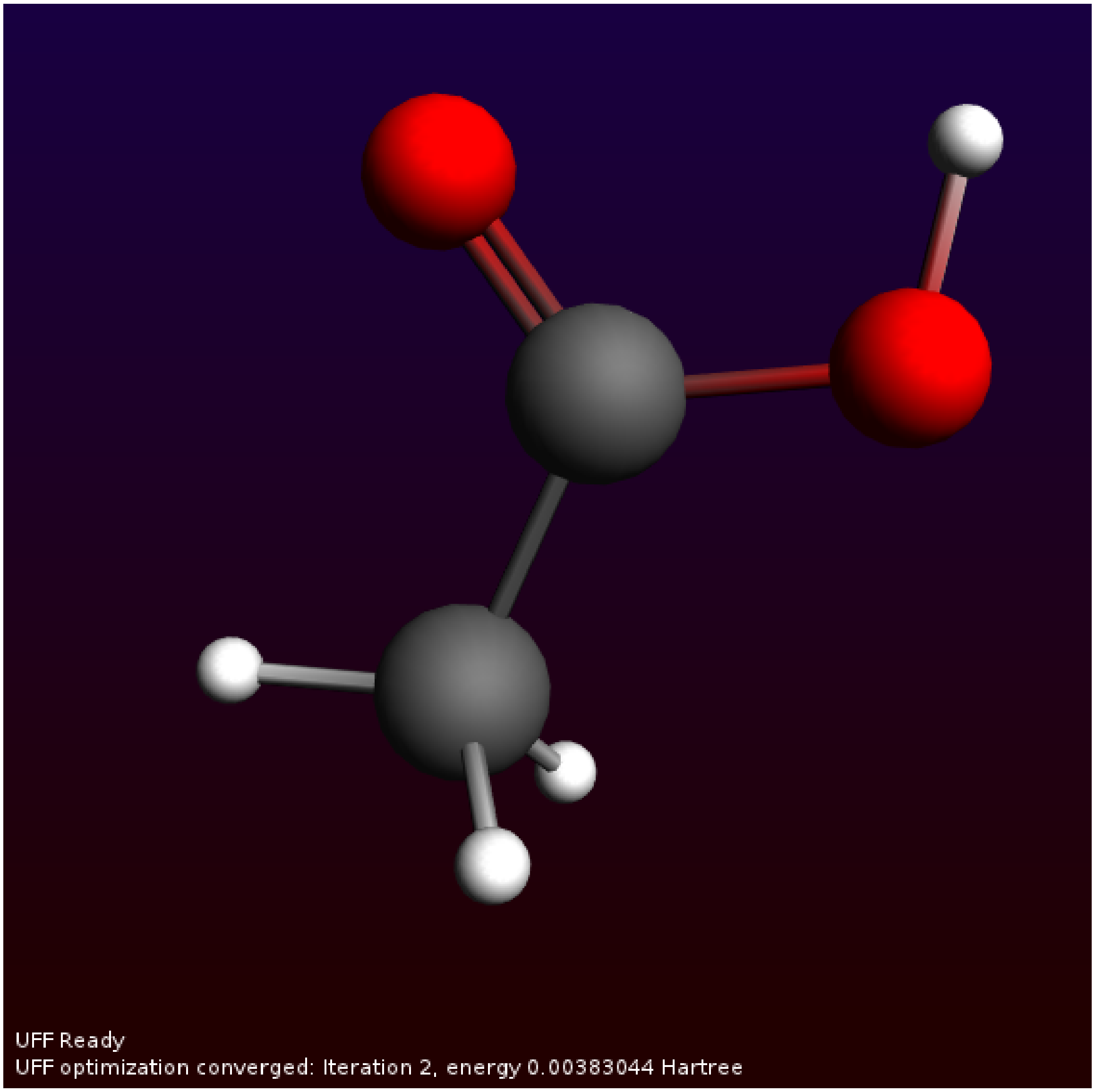
The single bond has changed into a double bond.

Another way to modify a bond type is to click on the bond once which will select this bond. Then click on the bond tool in the menu bar ('ball and stick' logo to the right of the start), and select the proper bond type.

The fastest way to change the bond order is to use the keyboard shortcuts. If you have selected a bond, press 1 for a single bond, 2 for a double bond, 3 for a triple bond and 4 for an aromatic bond.

To get a reasonable geometry optimize the structure:

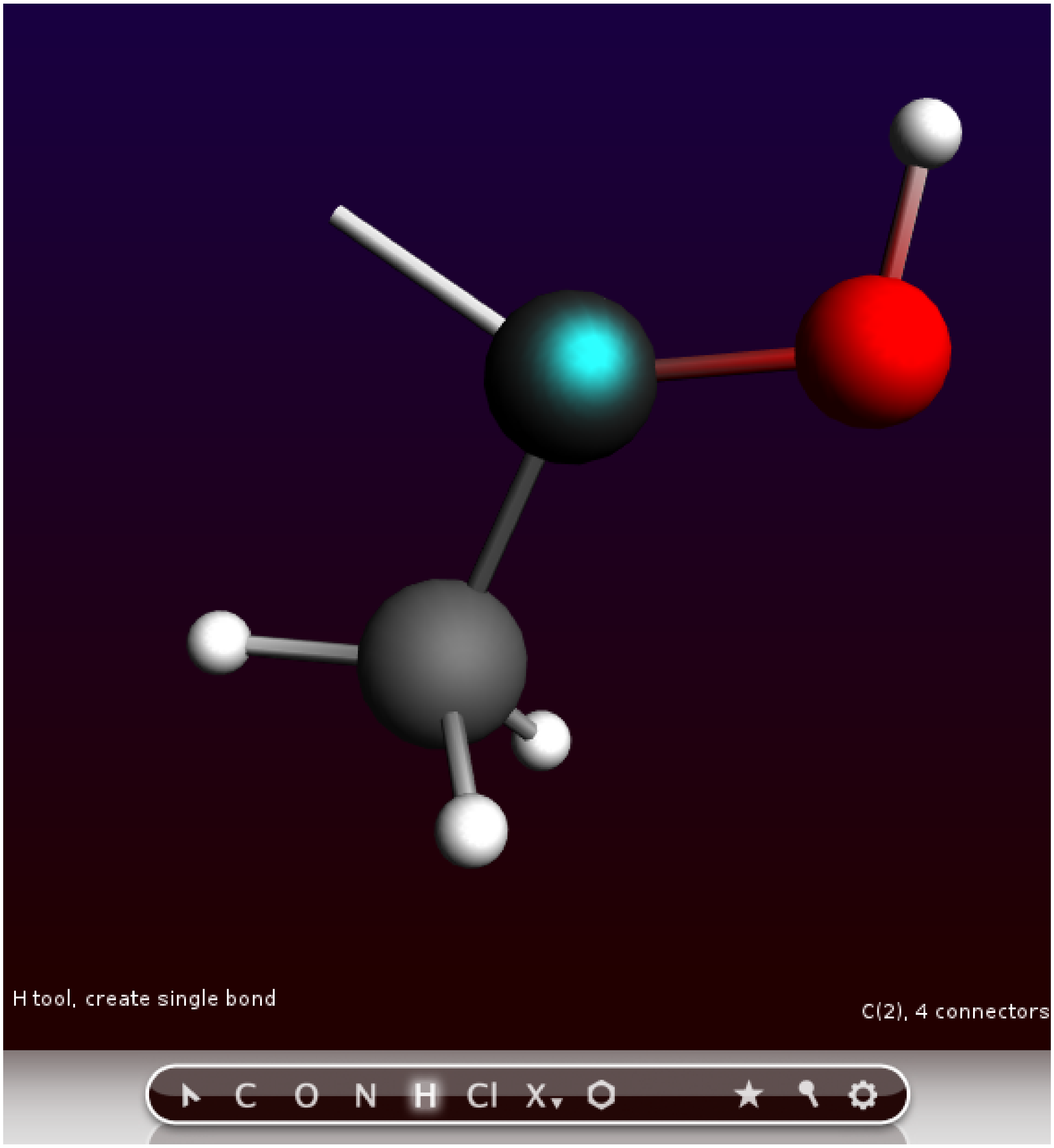
```
Click in empty space to deselect the bond
Press the pre-optimize button
If not converged, press pre-optimize again
```


UFF Ready
UFF optimization converged: Iteration 2, energy 0.00383044 Hartree

Add new (bonded) atoms

Now, to revert to the ethanol molecule, we first remove the new doubly-bonded oxygen atom, and then add one hydrogen atom.

```
Click once on the doubly-bonded oxygen atom to select it
Press the backspace key to delete it

Select the H-tool (or press the 'H' key)
Click once on the carbon atom connected to the oxygen
```

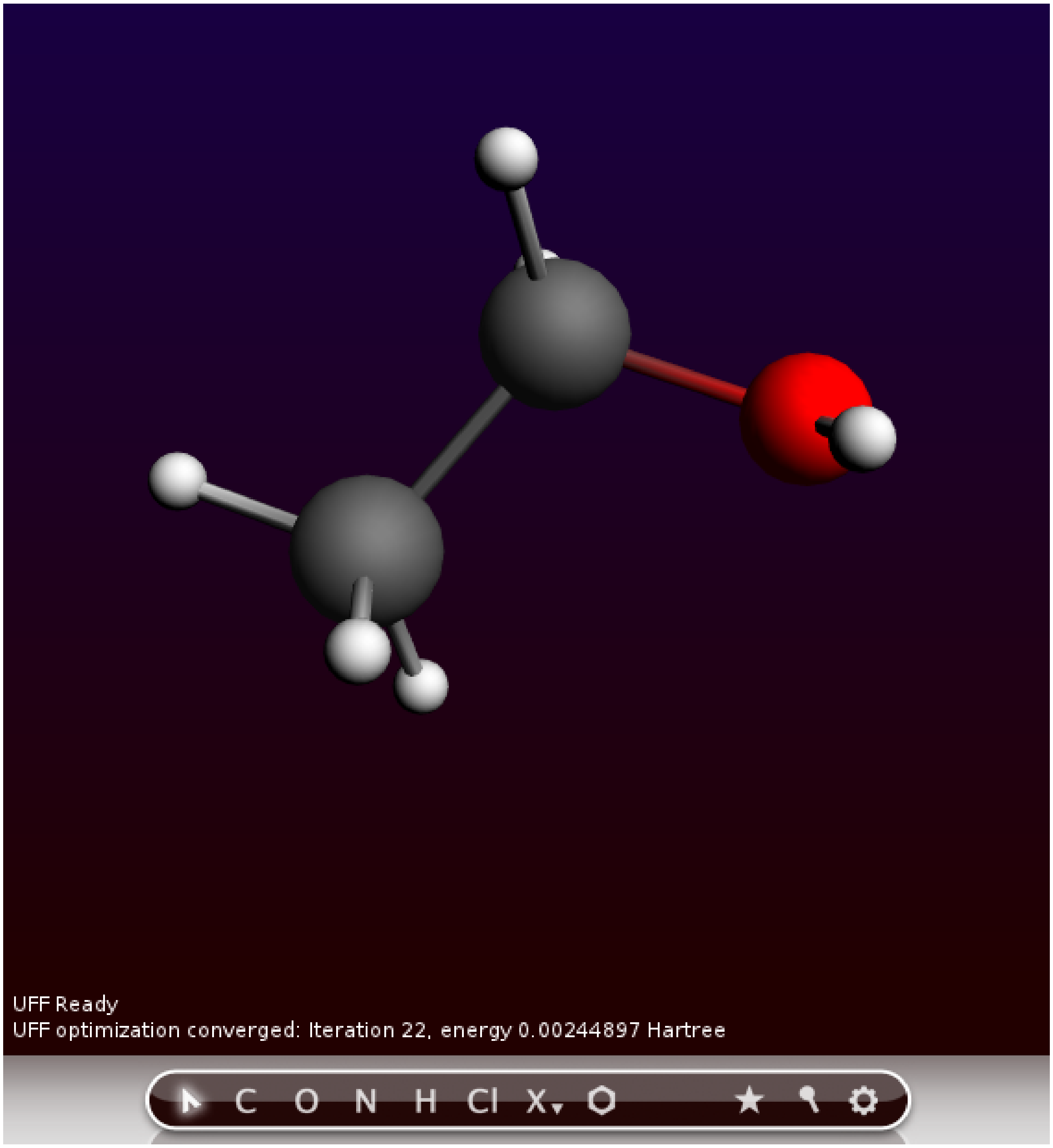


Note that this way you started bonding mode again, as indicated by the bond to the mouse position.

`Click once in empty space to make a hydrogen atom (connected to the carbon!)`
`Click once` **on the just created** `atom to stop bonding`

`Repeat this to add a second hydrogen to the carbon atom`

`Pre-optimize the molecule`


UFF Ready
UFF optimization converged: Iteration 22, energy 0.00244897 Hartree

Once again you have created an ethanol molecule.

Step 3: Select calculation options

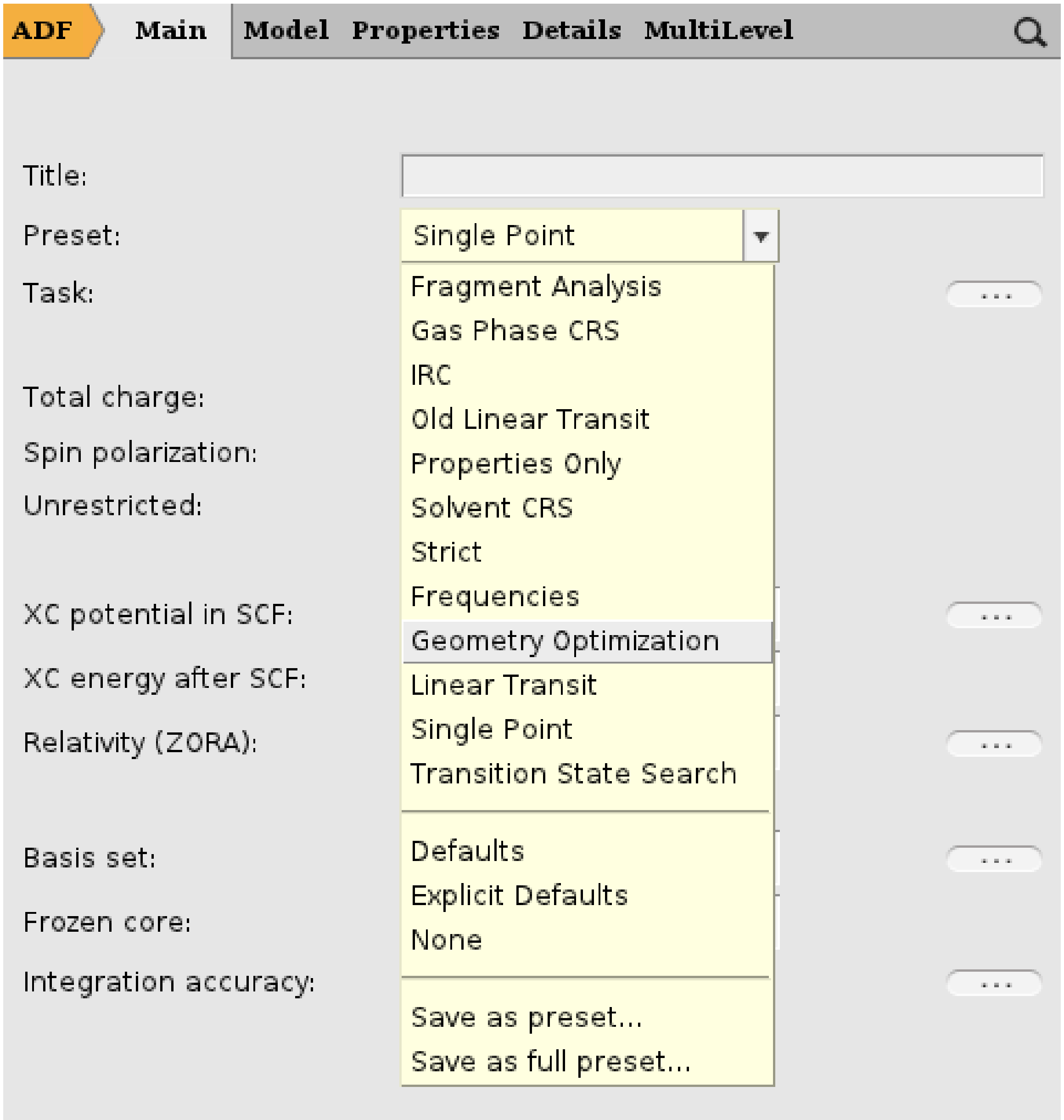
Preset

You should always start by choosing the proper preset.

ADF has many different modes of operation. ADFinput presents the correct settings for some common calculations together as 'presets'.

So to optimize the geometry of the ethanol molecule we choose the proper preset:

`Select the 'Geometry Optimization' preset from the 'Preset' menu.`



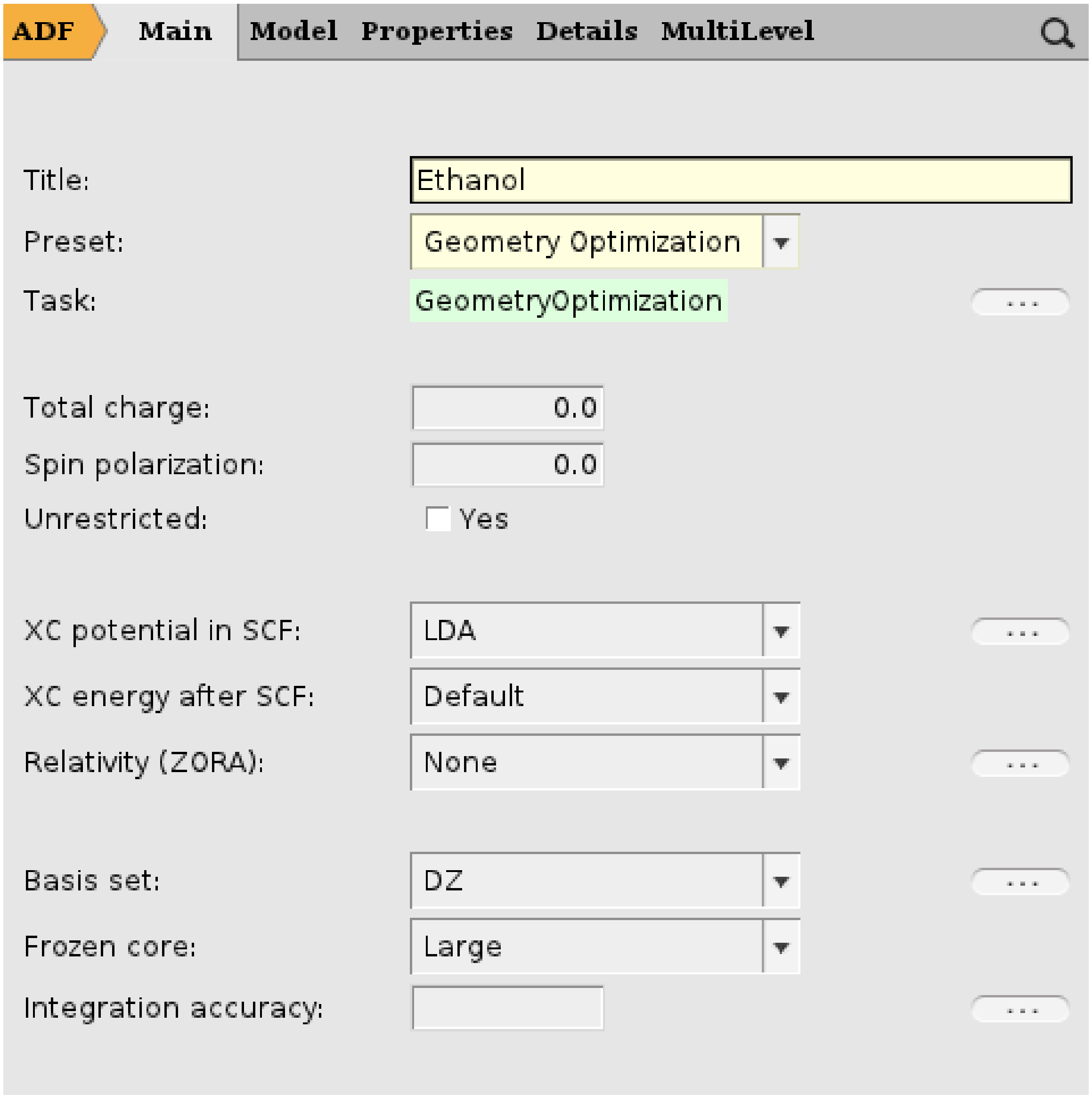
Presets might change any number of input options. In this particular example, the main Task will change from 'Single Point' to 'Geometry Optimization'. You can easily see what fields have been updated by a preset: they are colored green.

If you would use this preset again later, the input values that are set by this preset will revert to the default values. If you made changes to those fields you will lose those changes.

Title

This field, currently empty, has no special meaning for the calculation routine. It will be used as an identifier for your convenience in the result files of the ADF calculation. In this case, let's set the title to the name of the molecule:

`Enter 'Ethanol' without quotes in the 'Title' field.`



Title: Ethanol
Preset: Geometry Optimization
Task: GeometryOptimization
Total charge: 0.0
Spin polarization: 0.0
Unrestricted: ☐ Yes
XC potential in SCF: LDA
XC energy after SCF: Default
Relativity (ZORA): None
Basis set: DZ
Frozen core: Large
Integration accuracy:

Note that as soon as you start typing in the title field, the color of the field changes to yellow. The yellow color here and in other cases indicates that you have made a change with respect to the default value for this field.

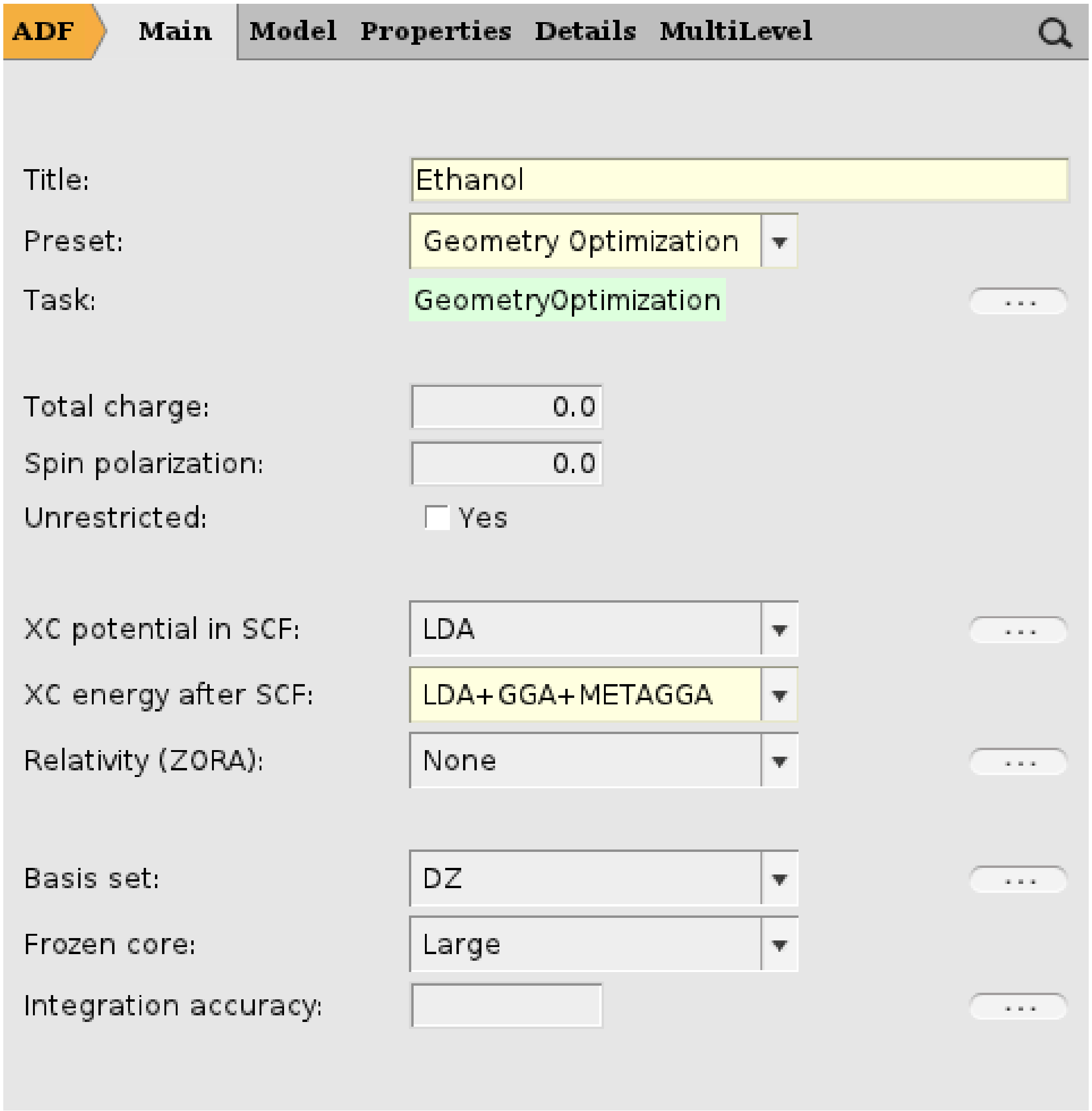
XC functional

An important input option is the XC functional to use.

For this tutorial the default potential during the SCF is sufficient. So just leave this at the default value. For more accurate results you should select a better XC potential.

By selecting the LDA+GGA+METAGGA option for the XC energy ADF will print a table at the end of the calculation showing the energies with many different functionals:

`Select the 'LDA+GGA+METAGGA' option for the XC energy after SCF`



Title: Ethanol
Preset: Geometry Optimization
Task: GeometryOptimization

Total charge: 0.0
Spin polarization: 0.0
Unrestricted: ☐ Yes

XC potential in SCF: LDA
XC energy after SCF: LDA+GGA+METAGGA
Relativity (ZORA): None

Basis set: DZ
Frozen core: Large
Integration accuracy:

Again, since you made a change with respect to the default value the change is highlighted with a yellow color.

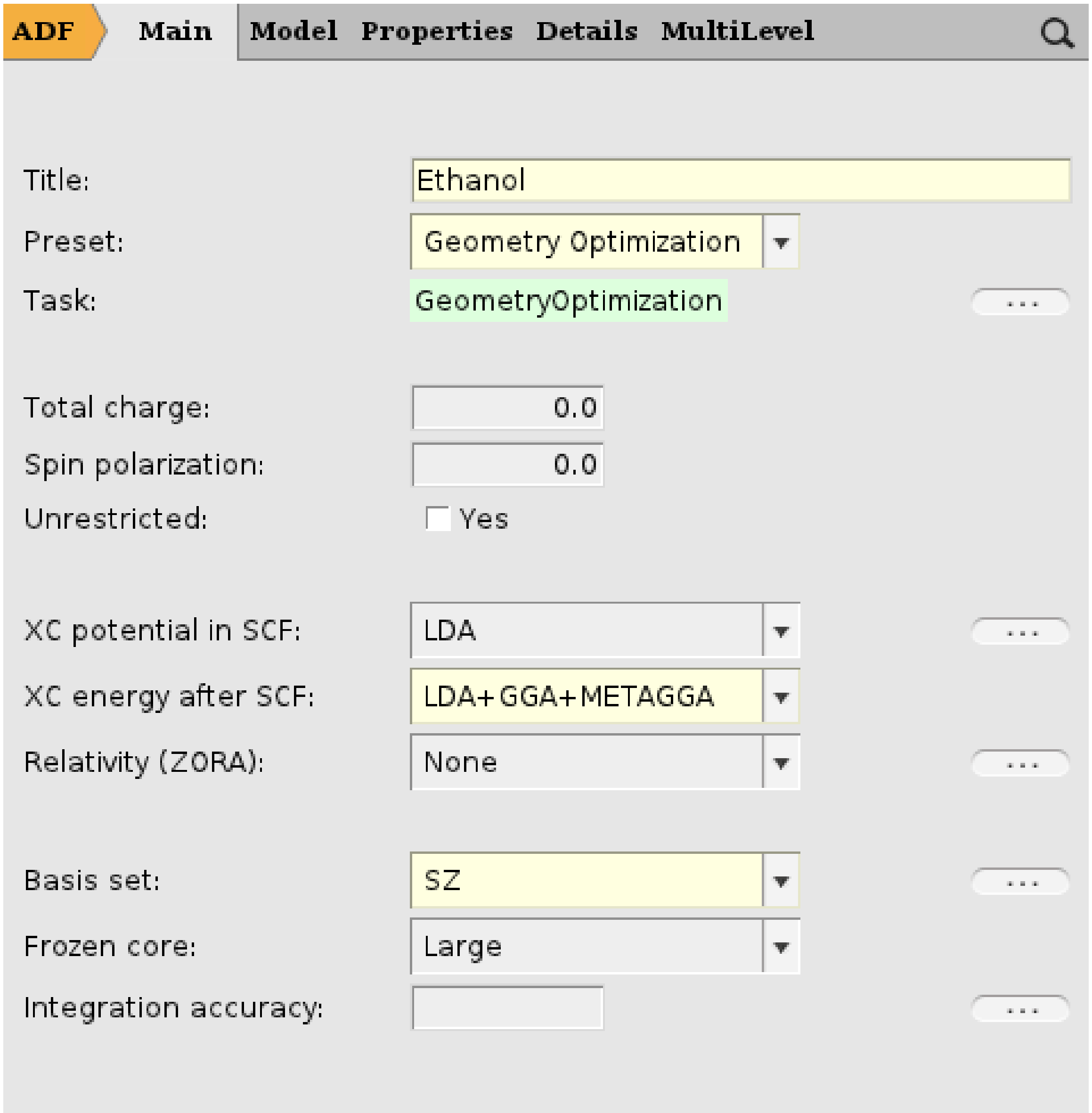
Basis set

With the 'Basis Set' pull-down menu you select the basis set you want to use.

The menu gives access to the basis sets regularly used.

For this tutorial we will choose a very small basis set. This will yield less accurate results, but the calculation runs much faster. Obviously, if you want more accurate results you should use a better quality basis set. Thus:

```
Select 'SZ' from the 'Basis Set' pull-down menu
```



Title: Ethanol

Preset: Geometry Optimization

Task: GeometryOptimization

Total charge: 0.0

Spin polarization: 0.0

Unrestricted: ☐ Yes

XC potential in SCF: LDA

XC energy after SCF: LDA+GGA+METAGGA

Relativity (ZORA): None

Basis set: SZ

Frozen core: Large

Integration accuracy:

Integration

The ADF software package uses a numerical integration scheme for virtually everything it may calculate. The number specified here is roughly the number of significant digits in your results. If you leave the field blank ADF will select a reasonable default value.

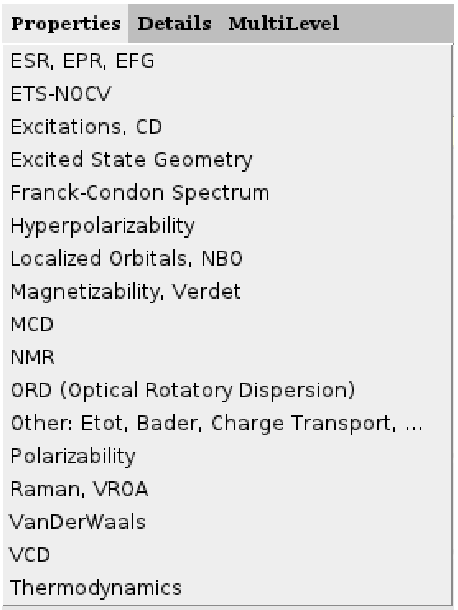
Increasing the number makes the results more accurate, but will require substantially more computation time.

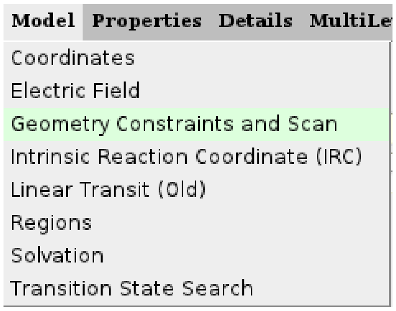
Similarly, decreasing the number will result in less accurate results, but you may get results faster. A too low integration accuracy often leads to convergence problems if the convergence criteria are too strict.

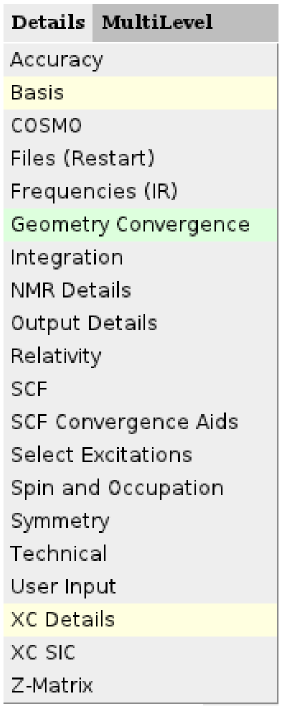
The default value will in most cases be fine, certainly for this tutorial.

Other input options

The panels on the right side contain many more input options. You select a panel with the menus in the panel bar, or by searching for a particular option (as we did to locate the Z-Matrix panel). When searching for an option, any text in the panels will match, as well as from the help balloons. Also the corresponding ADF input keys will match.







The menu items use a color coding to show you which panels have been affected by a preset (green), by the user (yellow), or both (red).

As we will not do anything special right now, you do not need to change anything in other panels.

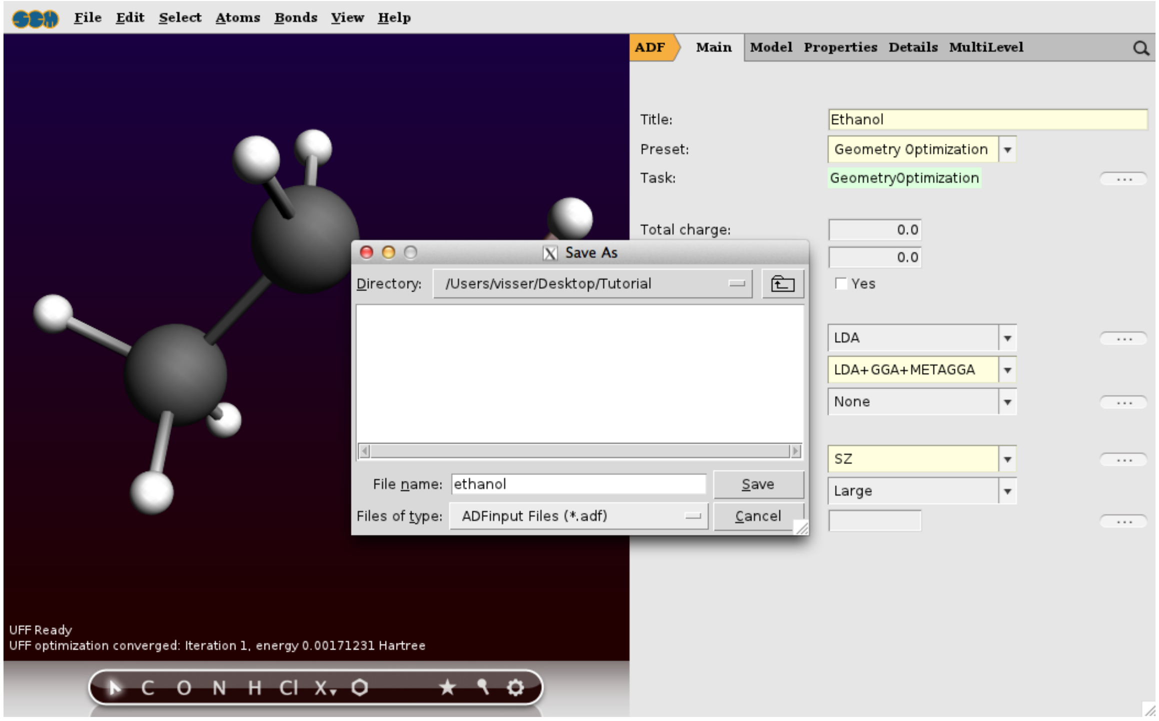
Step 4: Run your calculation

Save your input and create a job script

Finally you will want to save your input.

Select the **File → Save** command.

Enter the name 'ethanol' in the Filename field.



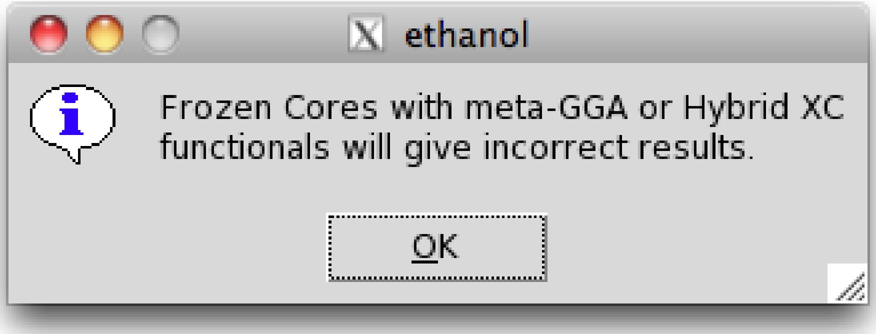
Title: Ethanol
Preset: Geometry Optimization
Task: GeometryOptimization
Total charge: 0.0
0.0
☐ Yes
LDA
LDA+GGA+METAGGA
None
SZ
Large

Directory: /Users/visser/Desktop/Tutorial
File name: ethanol
Files of type: ADFinput Files (*.adf)

UFF Ready
UFF optimization converged: Iteration 1, energy 0.00171231 Hartree

`Click on Save`

ADFinput will now present a warning dialog:

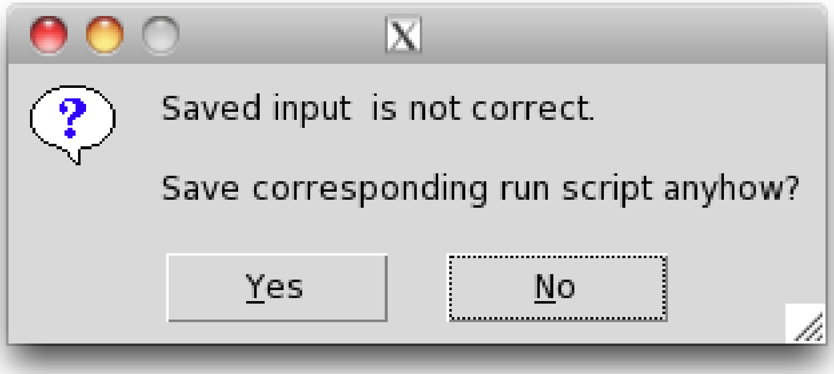


Frozen Cores with meta-GGA or Hybrid XC functionals will give incorrect results.

So the requested option to print meta-GGA results after the final SCF will produce incorrect results when using frozen cores. Normally you would not accept this, but for the tutorial let's just continue with this set-up:

`Click OK to dismiss the warning dialog`

A new dialog pops up asking you if you really want to save the run script even though it will not be correct:



Saved input is not correct.

Save corresponding run script anyhow?

The run script will not be correct because we use the frozen core option together with metaGGA's, as we were told before. Accept this and save it anyhow:

```
Click Yes to save the run script
```

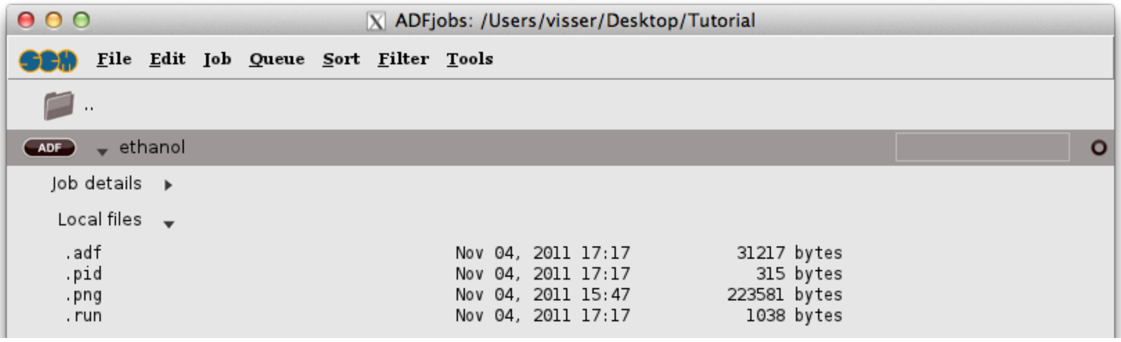
Now you have saved your current options and molecule information. The file will automatically get the extension '.adf'.

ADFinput has also created a corresponding script file. This script file has the same name, but with an extension '.run' instead of '.adf'.

In the ADFjobs module you can see what files have been created:

```
Click once in the ADFjobs window to activate it
Click once on the triangle in front of the name of the job (ethanol)
```

You will see the .adf and .run files, and a .pid file that ADFjobs uses to store information. You might also see the picture that you saved, if you used the name 'ethanol' for it. Only the extensions are listed, so the real filenames are ethanol.adf, ethanol.run and ethanol.pid. Notice the job status icon (the open circle on the right) that ADFjobs uses to indicate a new job.



```
.adf                Nov 04, 2011 17:17     31217 bytes
.pid                Nov 04, 2011 17:17       315 bytes
.png                Nov 04, 2011 15:47    223581 bytes
.run                Nov 04, 2011 17:17      1038 bytes
```

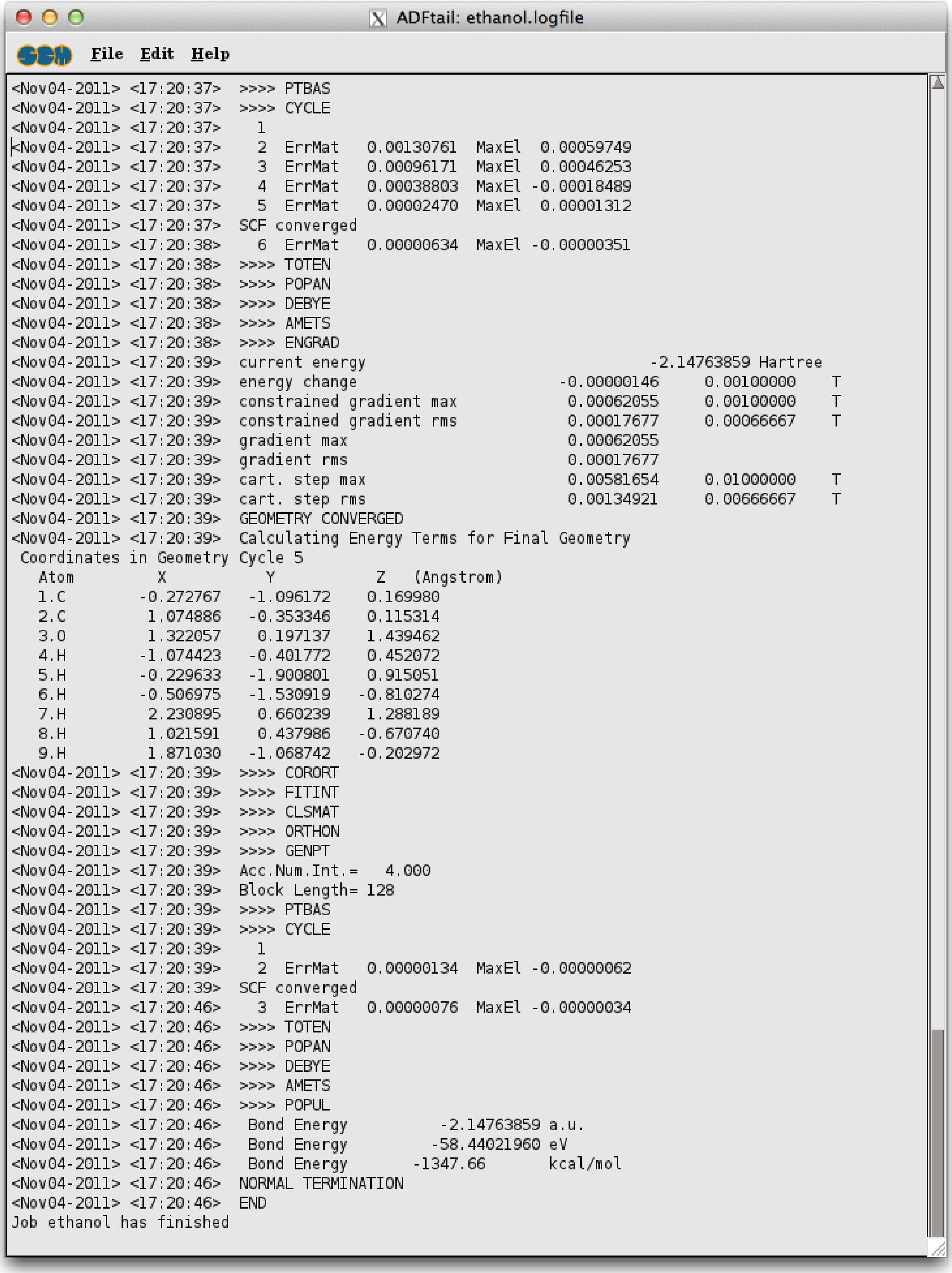
Run your calculation

To actually perform the calculation (the geometry optimization of the ethanol molecule), use the **Job** → **Run** menu command in ADFjobs:

Make sure the ethanol job is selected in ADFjobs (it is if you followed the tutorial)
Select the **Job** → **Run** command

This will execute the run script that has just been created. If you have never made changes in the ADFjobs setup, the default behavior is to run the job in the background on your local computer, using the Sequential queue. This queue will make sure that if you try to run more then one job at the same time, they will be run one after another.

Once your job starts running, ADFjobs will open ADFtail to monitor the progress of the calculation (the logfile):



```
<Nov04-2011> <17:20:37>  >>>> PTBAS
<Nov04-2011> <17:20:37>  >>>> CYCLE
<Nov04-2011> <17:20:37>    1
<Nov04-2011> <17:20:37>    2  ErrMat   0.00130761  MaxEl  0.00059749
<Nov04-2011> <17:20:37>    3  ErrMat   0.00096171  MaxEl  0.00046253
<Nov04-2011> <17:20:37>    4  ErrMat   0.00038803  MaxEl -0.00018489
<Nov04-2011> <17:20:37>    5  ErrMat   0.00002470  MaxEl  0.00001312
<Nov04-2011> <17:20:37>  SCF converged
<Nov04-2011> <17:20:38>    6  ErrMat   0.00000634  MaxEl -0.00000351
<Nov04-2011> <17:20:38>  >>>> TOTEN
<Nov04-2011> <17:20:38>  >>>> POPAN
<Nov04-2011> <17:20:38>  >>>> DEBYE
<Nov04-2011> <17:20:38>  >>>> AMETS
<Nov04-2011> <17:20:38>  >>>> ENGRAD
<Nov04-2011> <17:20:39>  current energy                          -2.14763859 Hartree
<Nov04-2011> <17:20:39>  energy change                 -0.00000146     0.00100000    T
<Nov04-2011> <17:20:39>  constrained gradient max       0.00062055     0.00100000    T
<Nov04-2011> <17:20:39>  constrained gradient rms       0.00017677     0.00066667    T
<Nov04-2011> <17:20:39>  gradient max                   0.00062055
<Nov04-2011> <17:20:39>  gradient rms                   0.00017677
<Nov04-2011> <17:20:39>  cart. step max                 0.00581654     0.01000000    T
<Nov04-2011> <17:20:39>  cart. step rms                 0.00134921     0.00666667    T
<Nov04-2011> <17:20:39>  GEOMETRY CONVERGED
<Nov04-2011> <17:20:39>  Calculating Energy Terms for Final Geometry
 Coordinates in Geometry Cycle 5
   Atom         X            Y            Z   (Angstrom)
   1.C        -0.272767   -1.096172    0.169980
   2.C         1.074886   -0.353346    0.115314
   3.O         1.322057    0.197137    1.439462
   4.H        -1.074423   -0.401772    0.452072
   5.H        -0.229633   -1.900801    0.915051
   6.H        -0.506975   -1.530919   -0.810274
   7.H         2.230895    0.660239    1.288189
   8.H         1.021591    0.437986   -0.670740
   9.H         1.871030   -1.068742   -0.202972
<Nov04-2011> <17:20:39>  >>>> CORORT
<Nov04-2011> <17:20:39>  >>>> FITINT
<Nov04-2011> <17:20:39>  >>>> CLSMAT
<Nov04-2011> <17:20:39>  >>>> ORTHON
<Nov04-2011> <17:20:39>  >>>> GENPT
<Nov04-2011> <17:20:39>  Acc.Num.Int.=    4.000
<Nov04-2011> <17:20:39>  Block Length= 128
<Nov04-2011> <17:20:39>  >>>> PTBAS
<Nov04-2011> <17:20:39>  >>>> CYCLE
<Nov04-2011> <17:20:39>    1
<Nov04-2011> <17:20:39>    2  ErrMat   0.00000134  MaxEl -0.00000062
<Nov04-2011> <17:20:39>  SCF converged
<Nov04-2011> <17:20:46>    3  ErrMat   0.00000076  MaxEl -0.00000034
<Nov04-2011> <17:20:46>  >>>> TOTEN
<Nov04-2011> <17:20:46>  >>>> POPAN
<Nov04-2011> <17:20:46>  >>>> DEBYE
<Nov04-2011> <17:20:46>  >>>> AMETS
<Nov04-2011> <17:20:46>  >>>> POPUL
<Nov04-2011> <17:20:46>   Bond Energy          -2.14763859 a.u.
<Nov04-2011> <17:20:46>   Bond Energy         -58.44021960 eV
<Nov04-2011> <17:20:46>   Bond Energy       -1347.66       kcal/mol
<Nov04-2011> <17:20:46>  NORMAL TERMINATION
<Nov04-2011> <17:20:46>  END
Job ethanol has finished
```

While running the job status symbol in ADFjobs changes:

Step 5: Results of your calculation

Logfile: ADFtail

The logfile is saved and extended by ADF as it is running.

Right now it is already showing in the ADFtail window, but you could have used any text editor.

Now wait for the calculation to finish:

```
Wait until ADFtail shows 'Job ... has finished' as last line
In the dialog that pops up, click 'Yes' to update the geometry
```

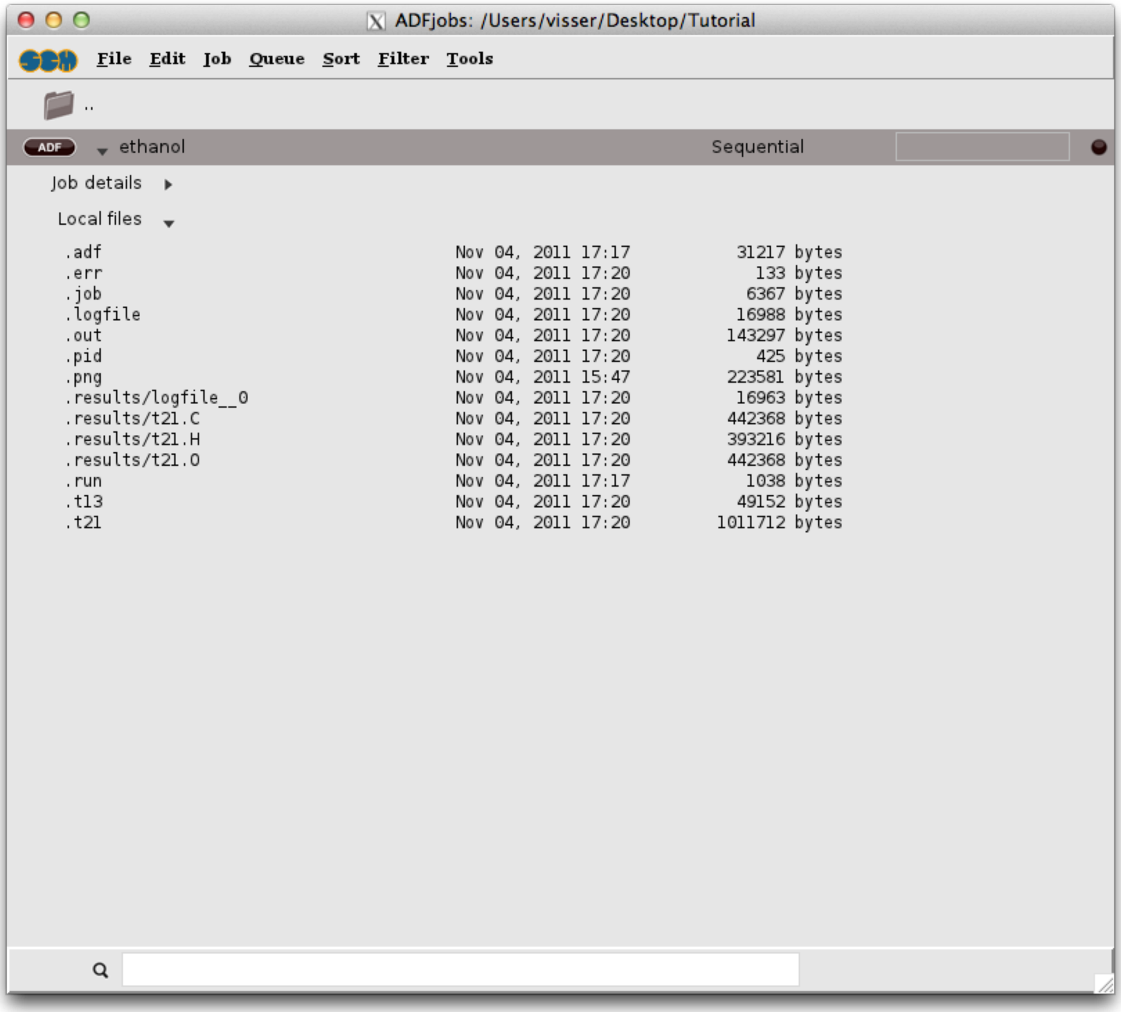
Read new coordinates from /Users/visser/Desktop/Tutorial/ethanol.t21?

Now close ADFtail by using the **File → Quit** menu command:

`In the window showing the logfile (the ADFtail window):`

`Select the` **File → Quit** `command`

In the ADFjobs window, note that the job status icon has changed to indicate that the job is ready:

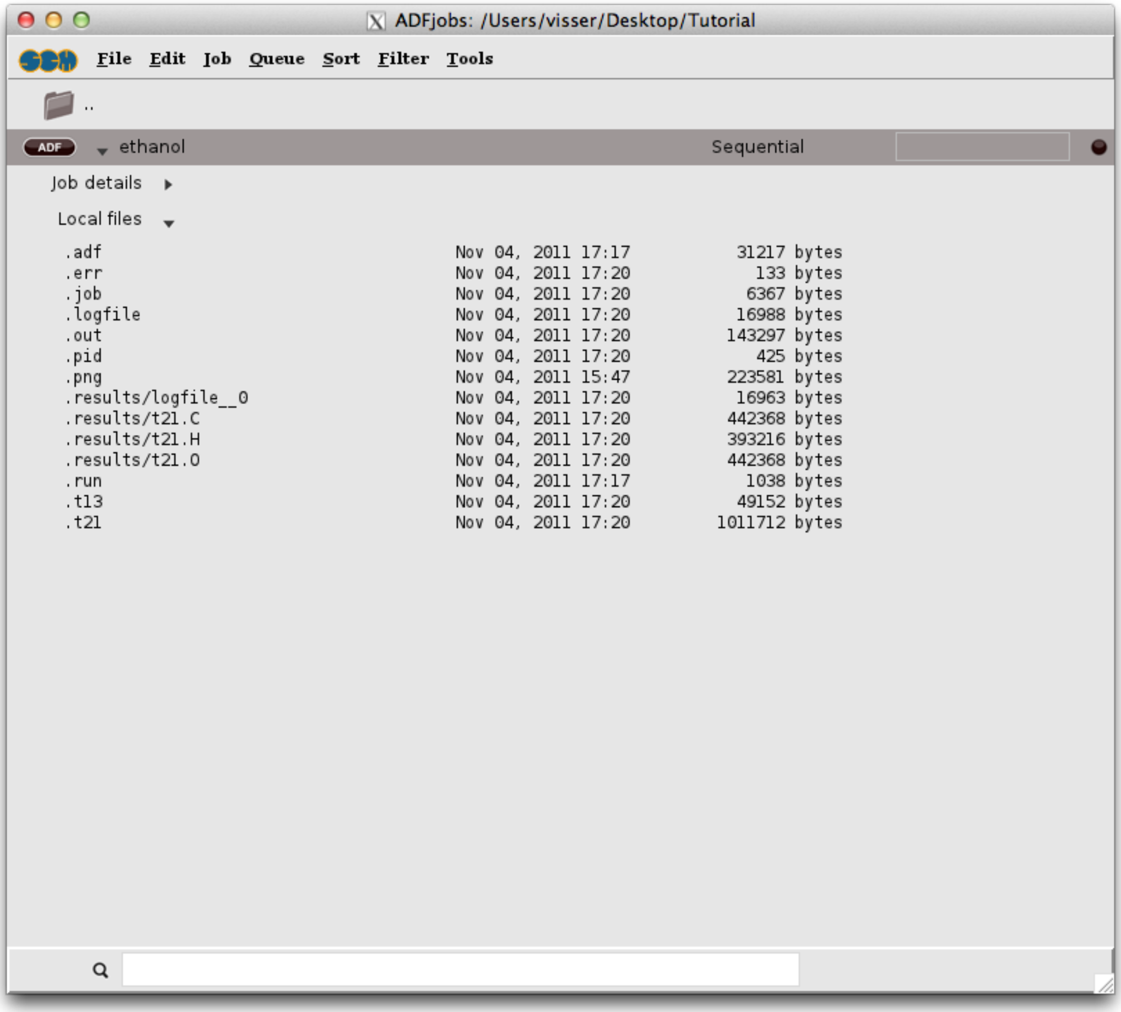


```
.adf                          Nov 04, 2011 17:17      31217 bytes
.err                          Nov 04, 2011 17:20        133 bytes
.job                          Nov 04, 2011 17:20       6367 bytes
.logfile                      Nov 04, 2011 17:20      16988 bytes
.out                          Nov 04, 2011 17:20     143297 bytes
.pid                          Nov 04, 2011 17:20        425 bytes
.png                          Nov 04, 2011 15:47     223581 bytes
.results/logfile__0           Nov 04, 2011 17:20      16963 bytes
.results/t21.C                Nov 04, 2011 17:20     442368 bytes
.results/t21.H                Nov 04, 2011 17:20     393216 bytes
.results/t21.O                Nov 04, 2011 17:20     442368 bytes
.run                          Nov 04, 2011 17:17       1038 bytes
.t13                          Nov 04, 2011 17:20      49152 bytes
.t21                          Nov 04, 2011 17:20    1011712 bytes
```

Files

ADF has created a couple of data files and a couple of text files. You can check this in the ADFjobs window:

`Click on the ADFjobs window`



```
.adf                    Nov 04, 2011 17:17      31217 bytes
.err                    Nov 04, 2011 17:20        133 bytes
.job                    Nov 04, 2011 17:20       6367 bytes
.logfile                Nov 04, 2011 17:20      16988 bytes
.out                    Nov 04, 2011 17:20     143297 bytes
.pid                    Nov 04, 2011 17:20        425 bytes
.png                    Nov 04, 2011 15:47     223581 bytes
.results/logfile__0     Nov 04, 2011 17:20      16963 bytes
.results/t21.C          Nov 04, 2011 17:20     442368 bytes
.results/t21.H          Nov 04, 2011 17:20     393216 bytes
.results/t21.O          Nov 04, 2011 17:20     442368 bytes
.run                    Nov 04, 2011 17:17       1038 bytes
.t13                    Nov 04, 2011 17:20      49152 bytes
.t21                    Nov 04, 2011 17:20    1011712 bytes
```

Note that the Local files are visible because earlier in the tutorial you already clicked on the triangle opening the details for this job.

The .adf file is the input as saved by ADFinput.

The .run file is the run script, also saved by ADFinput.

To enable specific options of your ADF job, changes to the text of the .run script can be made opening it via double-click. A separate text editor window pops up after the double-click (the non-default text editor program can be defined via the $EDITOR variable passed to ADF-GUI). When you run your job, your edited .run file will be used. Note that when you save your input via ADFinput again, your .run file will be overwritten (and thus you loose any changes you made when editing the .run file).

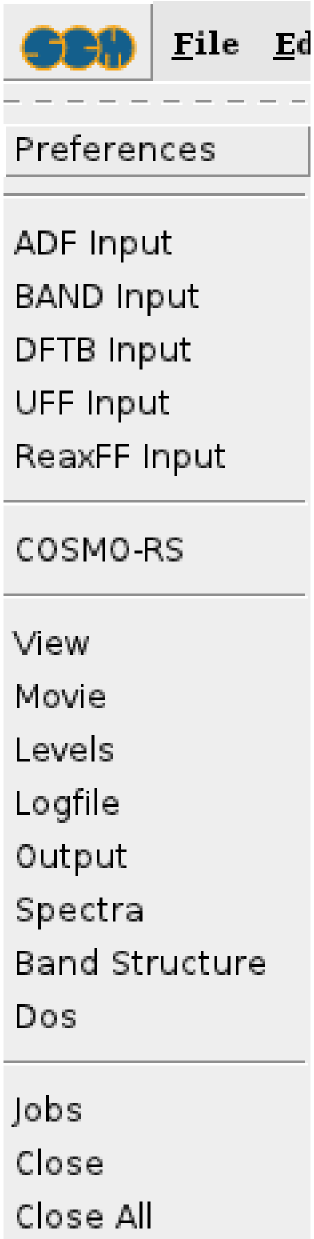
The .job file is a script file based on the .run file, and is created by ADFjobs. It contains all commands required to run your job, and is actually run by ADFjobs when you use the Run command.

The .pid file is a file that contains your job status and configuration. It is used by ADFjobs.

The other files are produced by ADF. The .err file contains error messages, the .logfile shows the progress of the calculation, the .out file is the main (text) output file, and the other files are binary files that store results of the calculation.

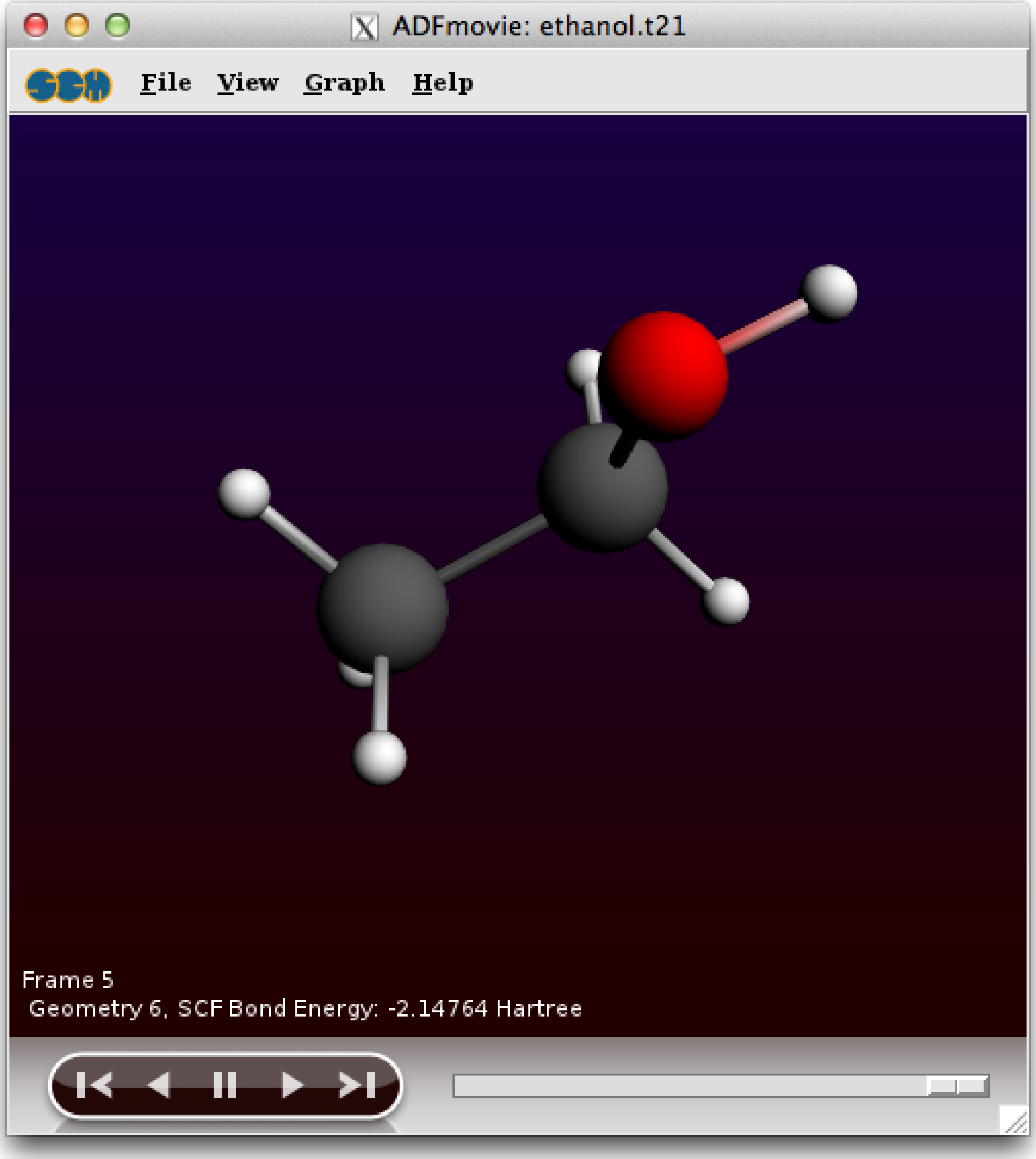
Geometry changes: ADFmovie

ADF has optimized the geometry, and we can use the ADFmovie module to visualize the progress of the optimization. So let's start ADFmovie using the SCM menu in your ADFinput window:



`Select the` **SCM → Movie** `command in ADFinput`

The ADFmovie module will display a movie of the geometry optimization.



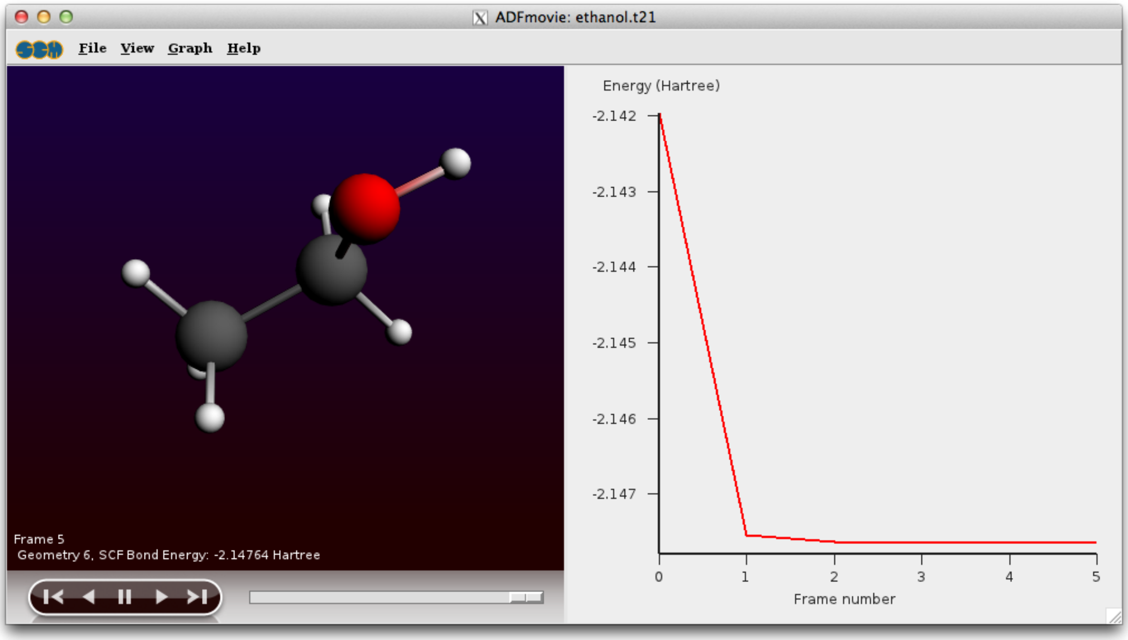
Frame 5
Geometry 6, SCF Bond Energy: -2.14764 Hartree

To step through the different geometries, use the slider below the picture. Clicking in the slider will single step through the frames. Alternatively you can grab the slider and move to the frame you wish, or you can use the left and right arrow keys to single step through the frames.

You control playing with the buttons. When your mouse pointer is above any of the buttons, and not moving, a balloon will pop up showing what that particular button will do.

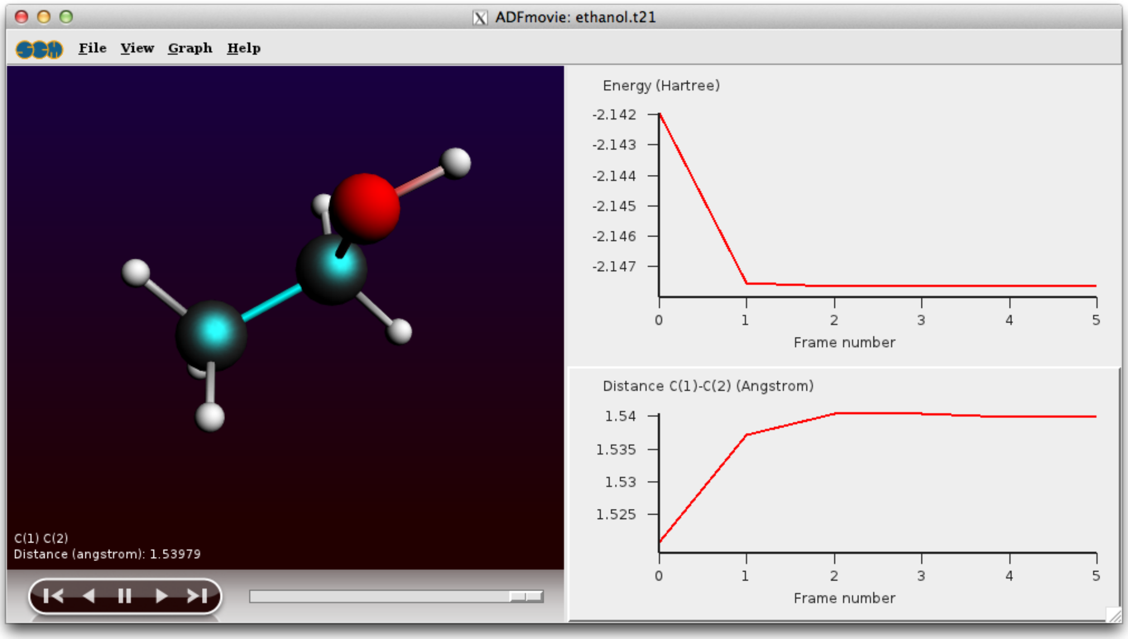
It is often nice to have a graph of the energy as function of the geometry step. ADFmovie can show such graphs easily:

`Use the` **Graph → Energy** `menu command`



You can even show several graphs for different properties at the same time:

Use the **Graph → Add Graph** menu command
Select two carbon atoms by shift-clicking on them
Use the **Graph → Distance, Angle, Dihedral** menu command

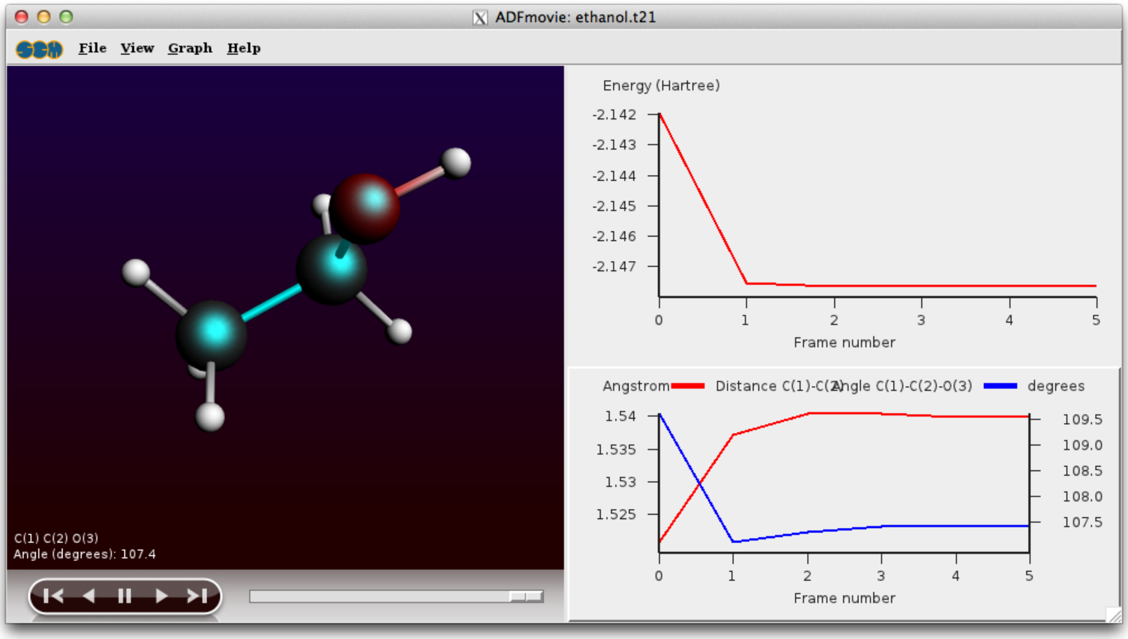


Now you have two graphs. One of them is the 'active' graph. When you make a new graph it will always be the active graph. You can also make a graph active by clicking on it.

When you select a property from the Graph menu (Energy, Distance and so on) that property will be plotted in the active graph.

You can also multiple curves in one graph, if possible: one property per Y axes. You may have several curves on the same Y axes if they are using the same unit (all Angstroms for example):

`Select two carbon atoms and one oxygen atom by shift-clicking on them`
`Use the` **Graph → Distance, Angle, Dihedral** `menu command`



C(1) C(2) O(3)
Angle (degrees): 107.4

Another feature is that you can click on a point in one of the graphs. It will be marked, the movie will jump to that particular step, and if you have more then one graph the corresponding point(s) will also be marked in the other graphs.

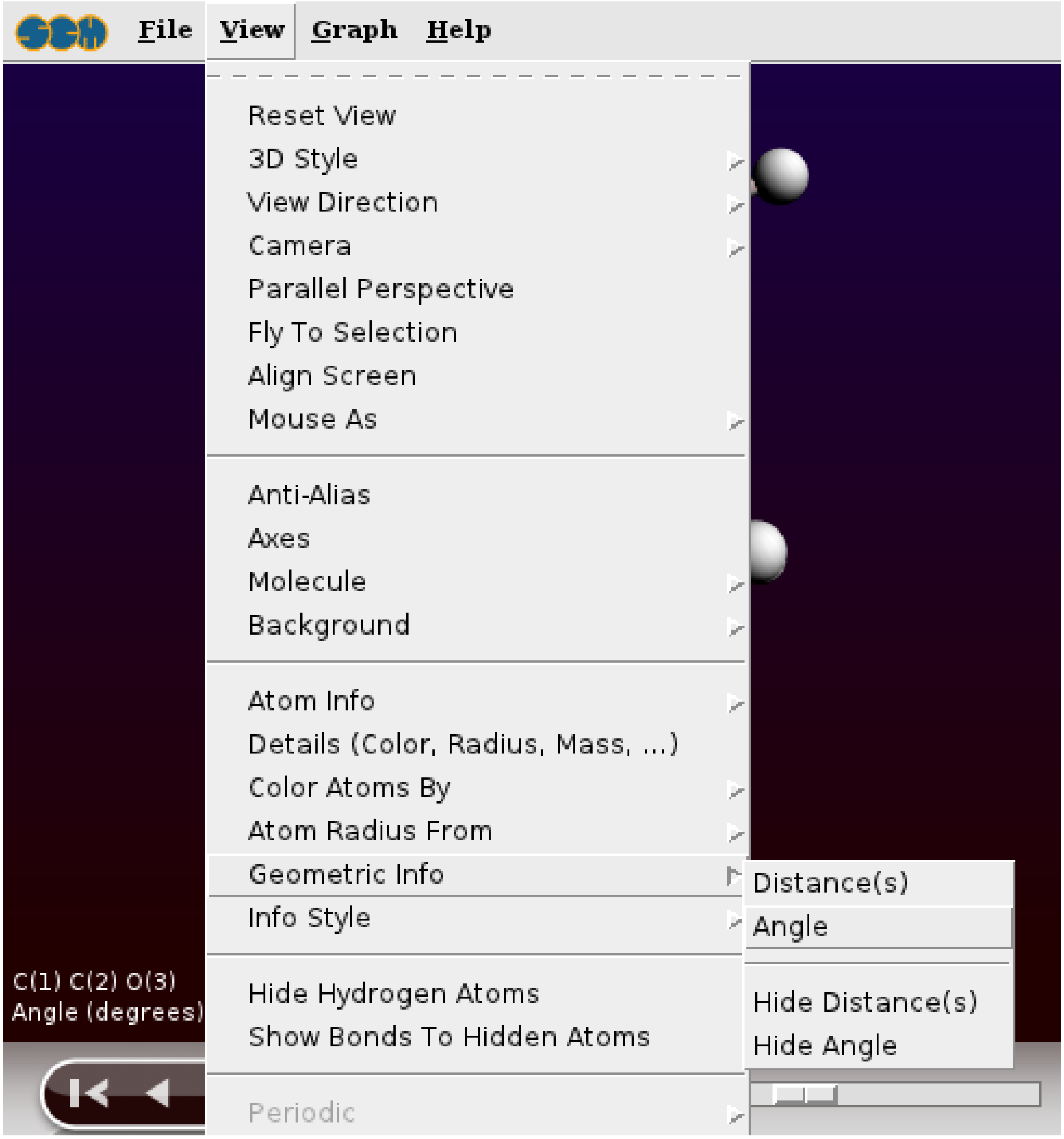
To rotate, translate, or zoom the picture, use your mouse, just as in ADFinput.

`Use the slider to go to a frame in the middle of the optimization`

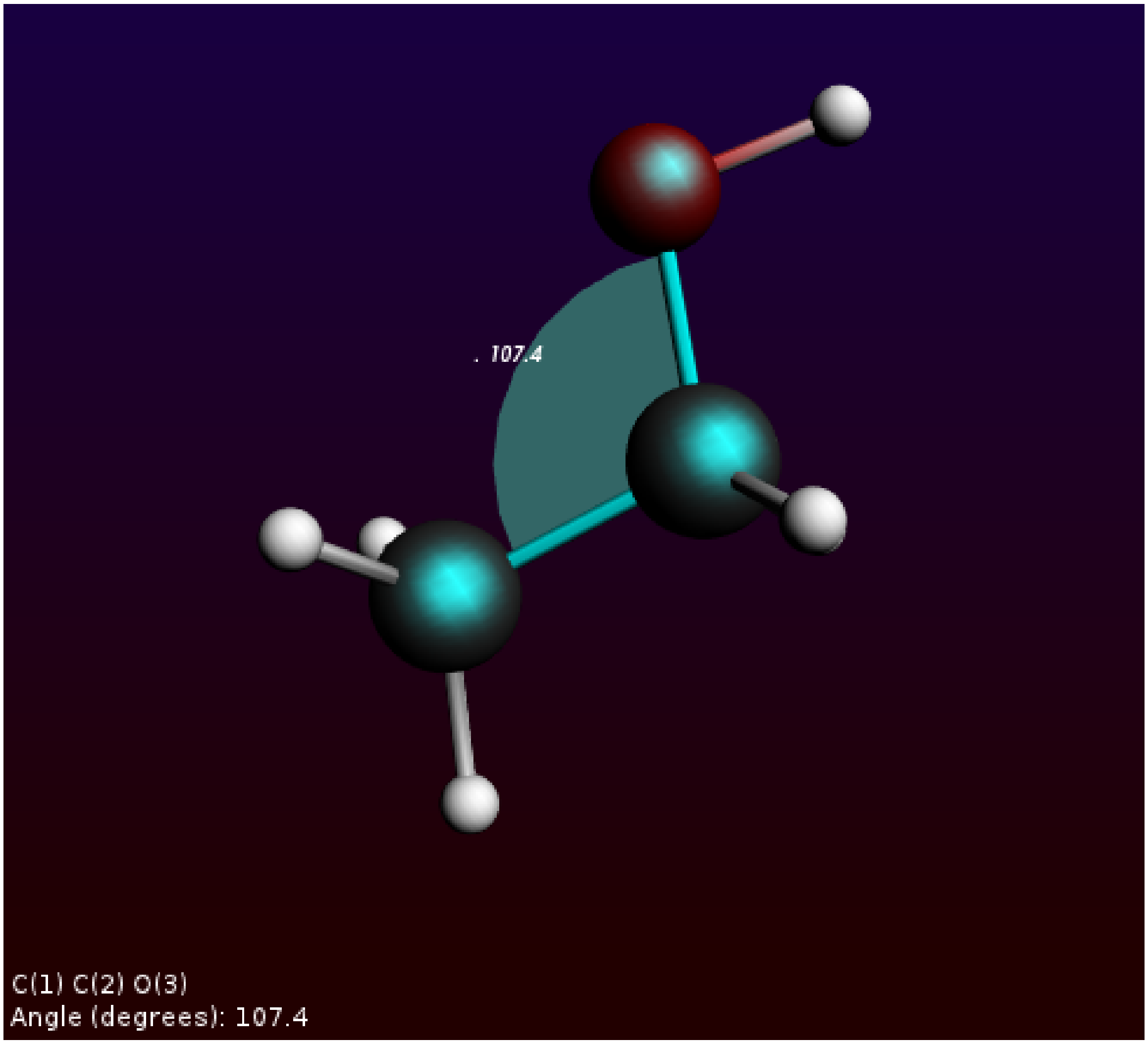
Selecting atoms provides information about atoms, bonds, etc. The information will be updated when you go to another point in the movie (a different geometry). You can see examples of these in the pictures above.

You can also show this information in the 3D window:

`Use the` **View → Geometric Info → Angle** `menu command`



The angle will be visually added to your molecule :

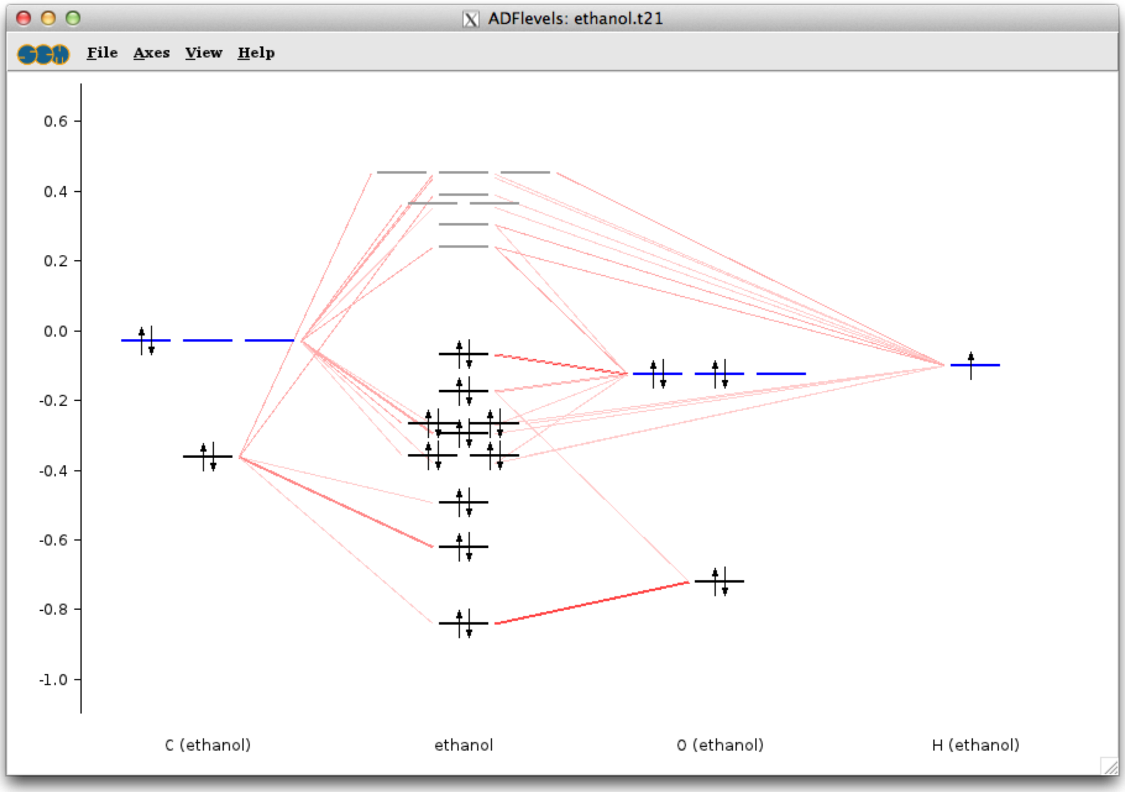


`In the ADFmovie window: select` **File → Quit**

Orbital energy levels: ADFlevels

`Select your job in the ADFjobs window by clicking on the job name`
`Select the` **SCM → Levels** `command`

ADFlevels will start and show a diagram of the energy levels of the ethanol molecule.

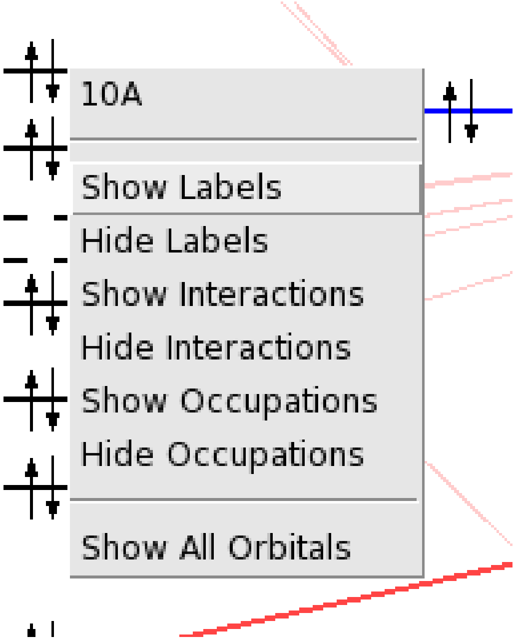


In the diagram you can see from what fragment types the molecular levels are composed.

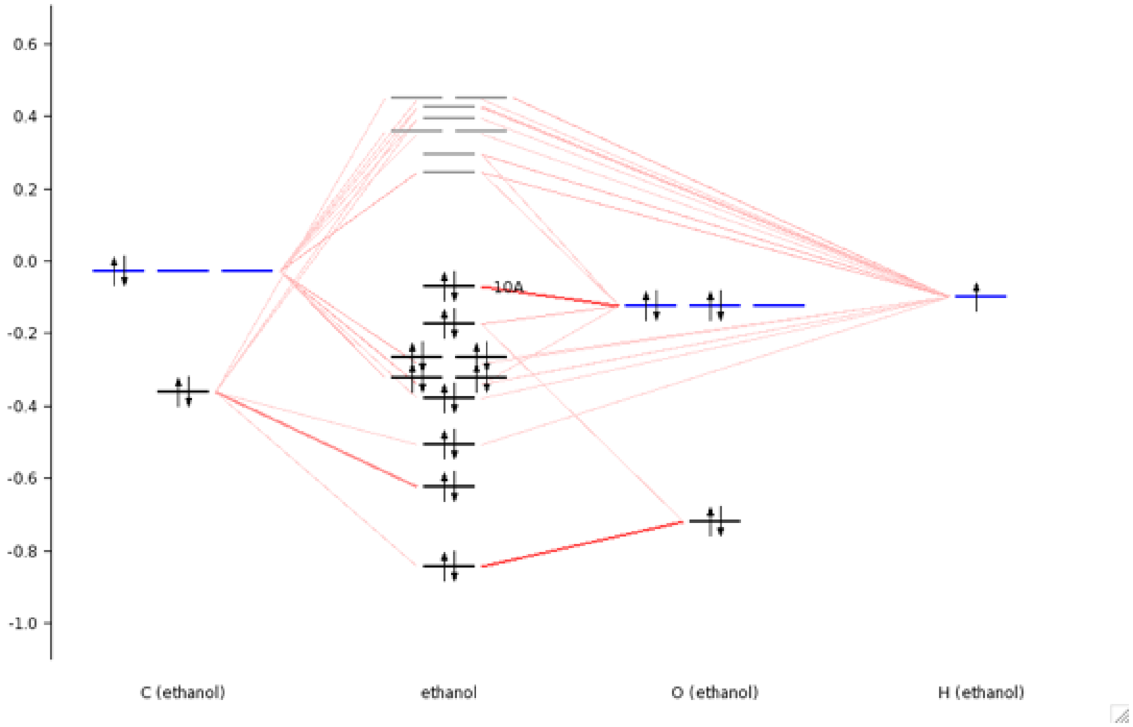
`Move the mouse around, above different levels, without clicking`

Balloons will pop up with information about the level at the mouse position.

`Click and hold on the HOMO level of the molecule`



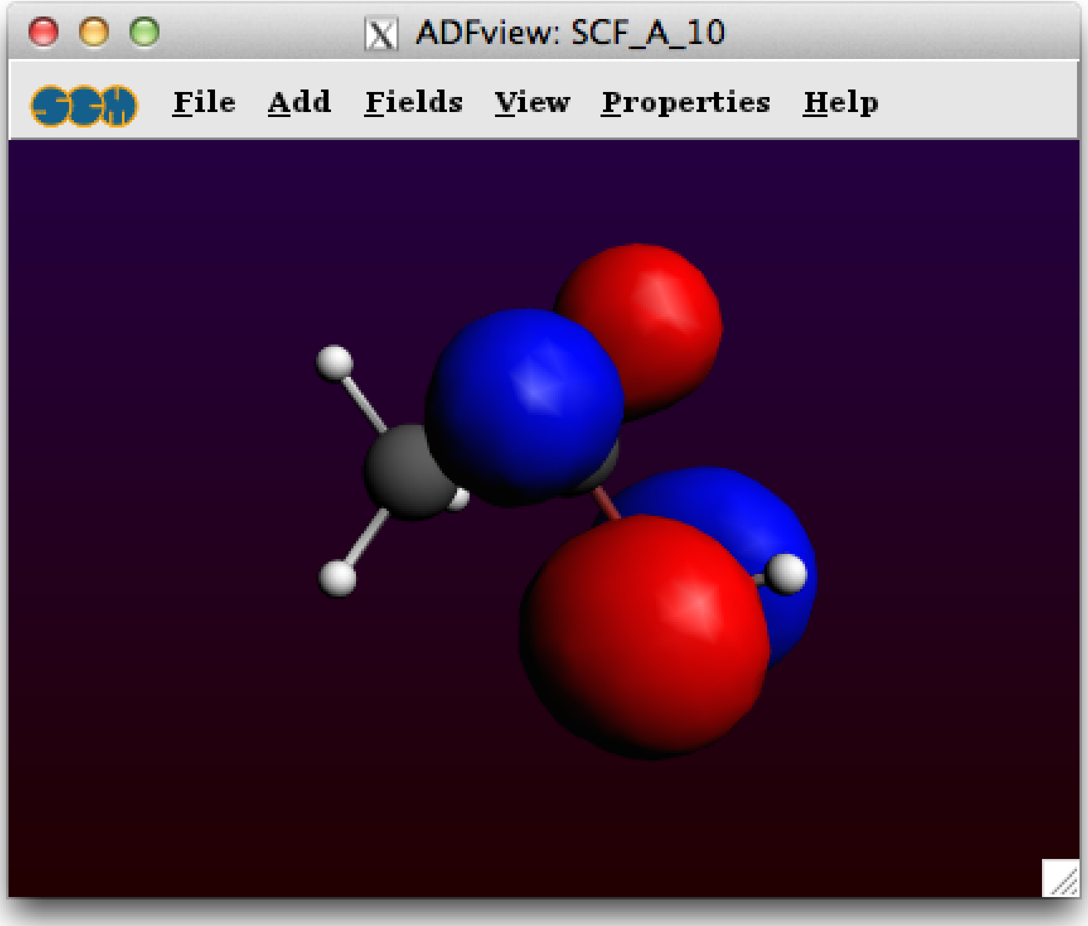
```
In the pop-up that appears, select 'Show Labels'

Click and hold on the HOMO of the O fragment type
In the pop-up, select 'Show Labels'
```



To actually see the orbital, select the orbital from the top of the pop-up menu:

```
Click and hold on the HOMO level of ethanol
Select the '10A' command
```

A window with a picture of the orbital should appear.



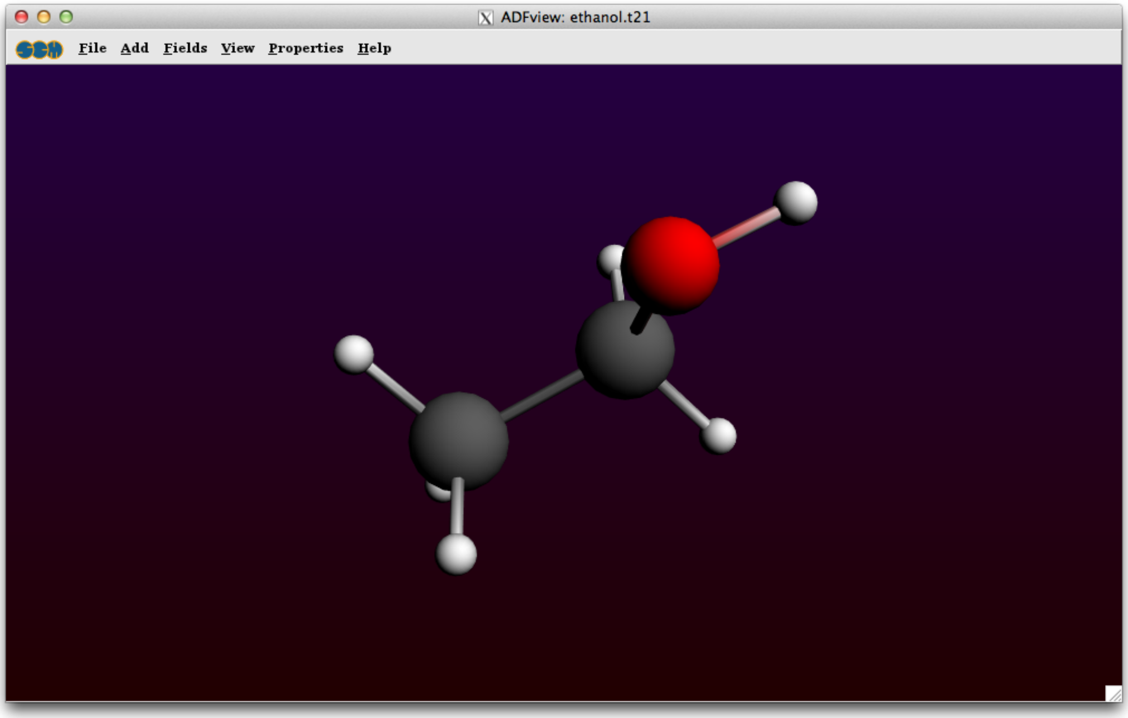
You can move (rotate, translate and zoom) the orbital with your mouse.

Close the window showing the orbital: **File → Quit** (in the window displaying the orbital)

Electron density, potential and orbitals: ADFview

Select **SCM → View**

ADFview will start up and show a picture of your molecule:



You can use ADFview to visualize all kinds of 'field' related properties: densities, orbitals, potentials, etc. You actually have already used it before: the picture of the orbital that was created using ADFlevels was shown by ADFview.

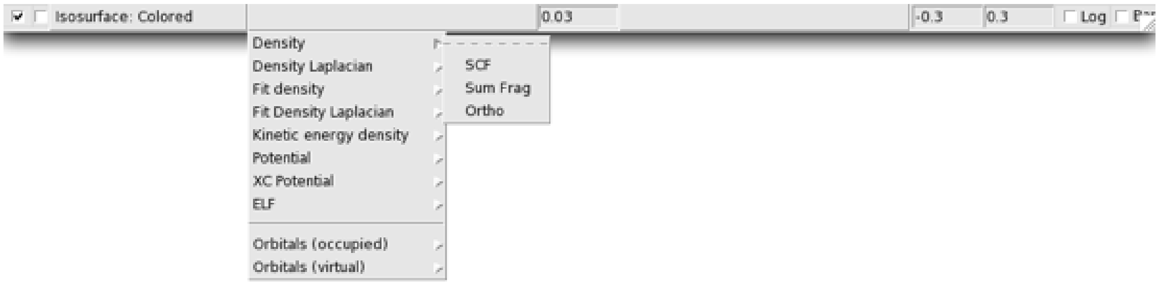
Use the mouse to rotate, translate or zoom, as in ADFinput.

Select the **Add → Isosurface: Colored** command

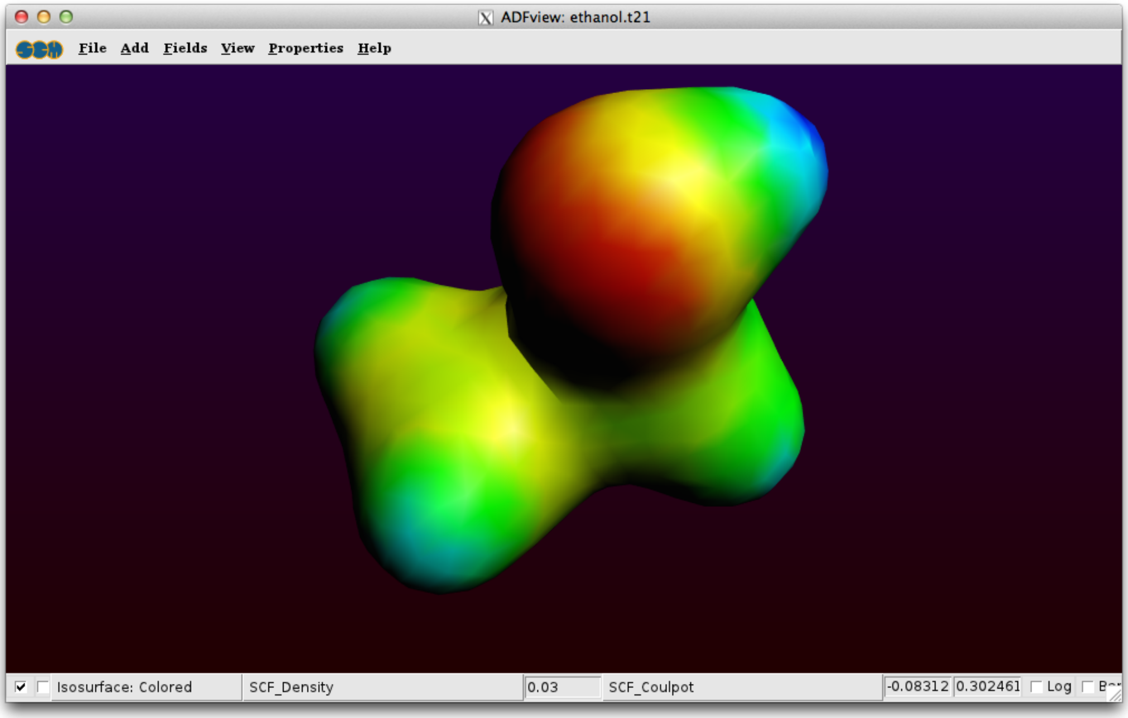
Below the picture a control line will be created. ADFview creates one such line for all visual items and special fields (surfaces, cut planes, calculated fields, etc.) that you add.

In this particular case the control line contains two pull-down menus that you use to select the fields that you want to visualize.

From the first pull-down menu in the control line, select **Density → SCF**



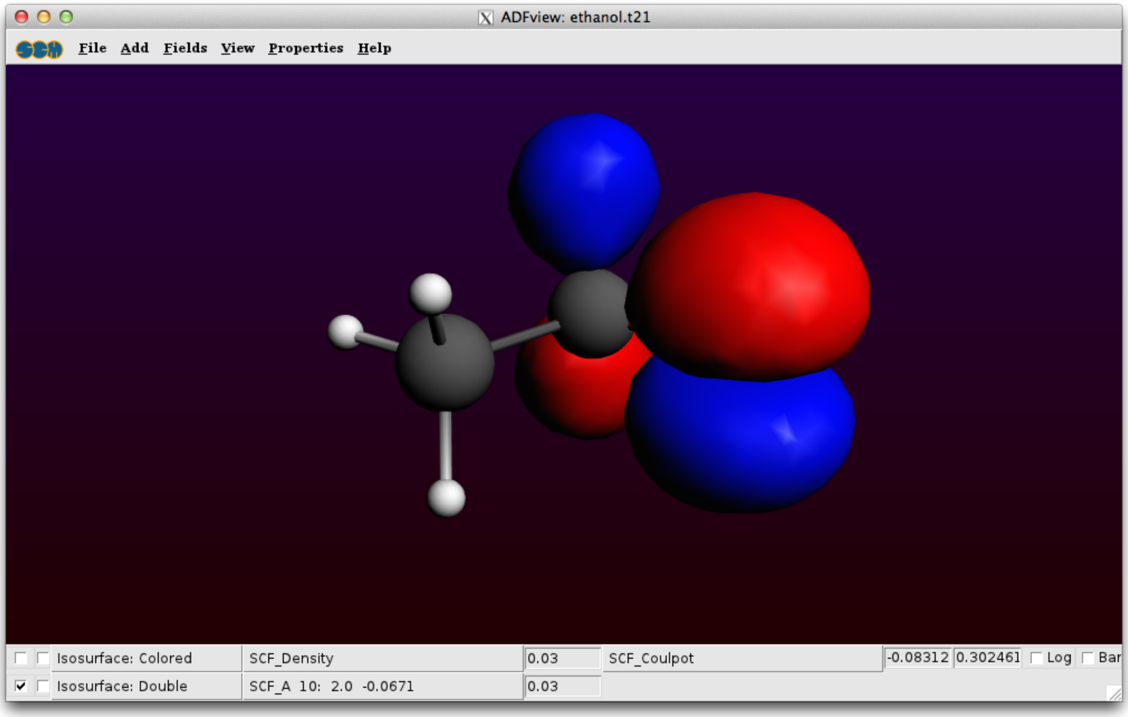
From the second pull-down menu in the control line, select **Potential → SCF**



☑ ☐ Isosurface: Colored | SCF_Density | 0.03 | SCF_Coulpot | -0.08312 | 0.302461 | ☐ Log | ☐ B

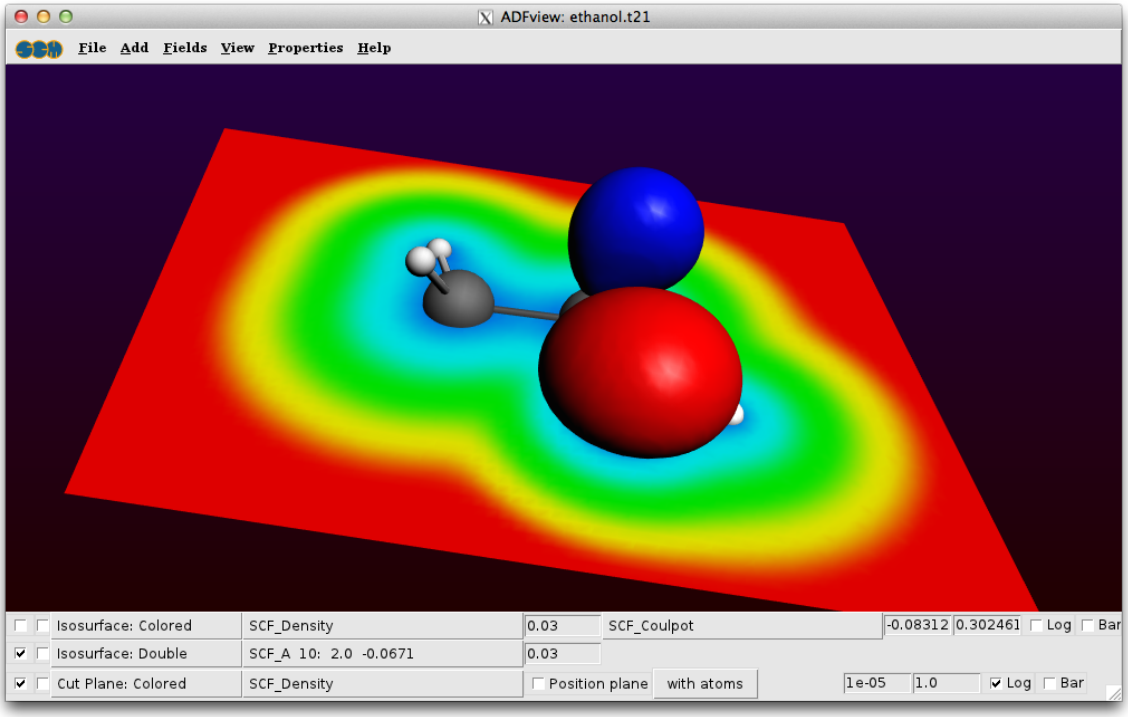
To demonstrate some other possibilities of ADFview, do the following:

Select the **Properties → HOMO** command
Click on the check box in the FIRST control line to hide the density
Rotate the molecule to get a good view



☐ ☐ Isosurface: Colored | SCF_Density | 0.03 | SCF_Coulpot | -0.08312 | 0.302461 | ☐ Log | ☐ Bar
☑ ☐ Isosurface: Double | SCF_A 10: 2.0 -0.0671 | 0.03

Select the **Add → Cut plane: Colored** command
In the new control line, press on the pull-down menu and select **Density → SCF**
Click the check box in front of the 'Isosurface: Double' line to hide the HOMO
Select the Carbon and Oxygen atoms (three atoms)
Click the 'with atoms' button next to the 'Position plane' option (thus the button, not the check box)
Click the check box in front of the 'Isosurface: Double' line to show the HOMO
Select the **Fields → Grid → Medium** command
Click Yes to recalculate the fields
Rotate your molecule to get a good view



☐ ☐ Isosurface: Colored | SCF_Density | 0.03 | SCF_Coulpot | -0.08312 | 0.302461 | ☐ Log | ☐ Bar
☑ ☐ Isosurface: Double | SCF_A 10: 2.0 -0.0671 | 0.03
☑ ☐ Cut Plane: Colored | SCF_Density | ☐ Position plane | with atoms | 1e-05 | 1.0 | ☑ Log | ☐ Bar

You can save the picture you create using the Save Picture menu command:

Select **File → Save Picture ...**
Enter the name (without extension) of the file you want to create
Click Save

A picture with the (file)name you specified has been created.

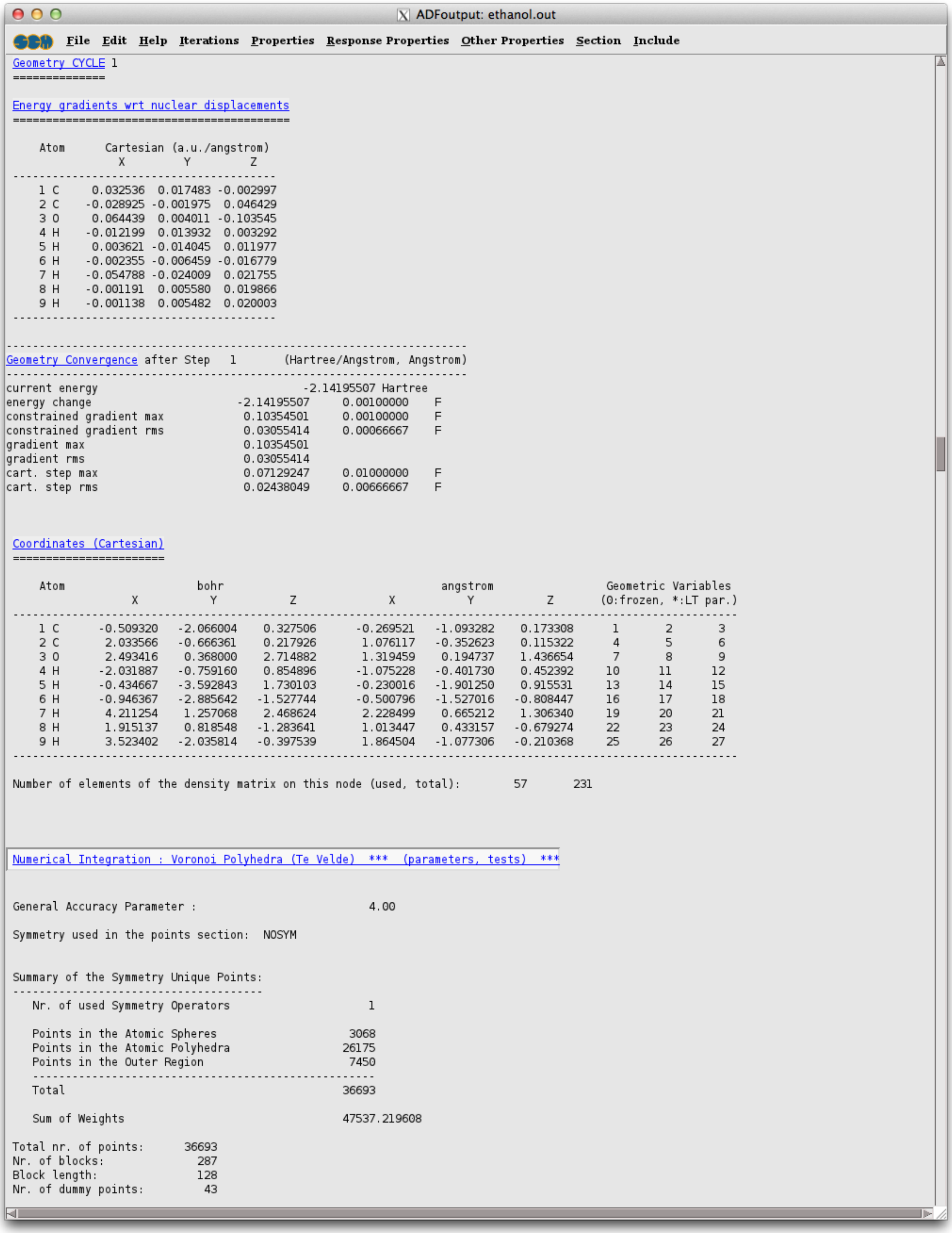
You might want to explore some more of the possibilities of ADFview on your own. Many different properties can be visualized as you probably have noticed in the pull-down menus. Be careful with activating Anti-Alias: it makes the pictures even better, but also slows down ADFview very very much.

Browsing the Output: ADFoutput

The output file (tutorial.out) is a plain text file. You can view it with your favorite text editor (or text viewer). You can also use the ADFoutput GUI module which provides a convenient way to check the results:

Select the **SCM → Output** command
Select the **Iterations → Geometry Cycles** command

The ADFoutput program will start showing the results of your calculation, and via the menu you jumped to the first section with geometry details:



```
 Geometry CYCLE 1
 ==============

 Energy gradients wrt nuclear displacements
 ==========================================

     Atom      Cartesian (a.u./angstrom)
                 X         Y         Z
 ----------------------------------------
     1 C     0.032536  0.017483 -0.002997
     2 C    -0.028925 -0.001975  0.046429
     3 O     0.064439  0.004011 -0.103545
     4 H    -0.012199  0.013932  0.003292
     5 H     0.003621 -0.014045  0.011977
     6 H    -0.002355 -0.006459 -0.016779
     7 H    -0.054788 -0.024009  0.021755
     8 H    -0.001191  0.005580  0.019866
     9 H    -0.001138  0.005482  0.020003
 ----------------------------------------

----------------------------------------------------------------------
Geometry Convergence after Step   1       (Hartree/Angstrom, Angstrom)
----------------------------------------------------------------------
current energy                               -2.14195507 Hartree
energy change                     -2.14195507      0.00100000    F
constrained gradient max           0.10354501      0.00100000    F
constrained gradient rms           0.03055414      0.00066667    F
gradient max                       0.10354501
gradient rms                       0.03055414
cart. step max                     0.07129247      0.01000000    F
cart. step rms                     0.02438049      0.00666667    F


 Coordinates (Cartesian)
 =======================

     Atom                    bohr                                 angstrom                 Geometric Variables
                   X           Y           Z              X           Y           Z       (0:frozen, *:LT par.)
 --------------------------------------------------------------------------------------------------------------
     1 C      -0.509320   -2.066004    0.327506      -0.269521   -1.093282    0.173308      1       2       3
     2 C       2.033566   -0.666361    0.217926       1.076117   -0.352623    0.115322      4       5       6
     3 O       2.493416    0.368000    2.714882       1.319459    0.194737    1.436654      7       8       9
     4 H      -2.031887   -0.759160    0.854896      -1.075228   -0.401730    0.452392     10      11      12
     5 H      -0.434667   -3.592843    1.730103      -0.230016   -1.901250    0.915531     13      14      15
     6 H      -0.946367   -2.885642   -1.527744      -0.500796   -1.527016   -0.808447     16      17      18
     7 H       4.211254    1.257068    2.468624       2.228499    0.665212    1.306340     19      20      21
     8 H       1.915137    0.818548   -1.283641       1.013447    0.433157   -0.679274     22      23      24
     9 H       3.523402   -2.035814   -0.397539       1.864504   -1.077306   -0.210368     25      26      27
 --------------------------------------------------------------------------------------------------------------

 Number of elements of the density matrix on this node (used, total):        57       231



 Numerical Integration : Voronoi Polyhedra (Te Velde)  ***  (parameters, tests)  ***


 General Accuracy Parameter :                          4.00

 Symmetry used in the points section:  NOSYM


 Summary of the Symmetry Unique Points:
 --------------------------------------
    Nr. of used Symmetry Operators                     1

    Points in the Atomic Spheres                    3068
    Points in the Atomic Polyhedra                 26175
    Points in the Outer Region                      7450
    ----------------------------------------------------
    Total                                          36693

    Sum of Weights                                 47537.219608

 Total nr. of points:      36693
 Nr. of blocks:              287
 Block length:               128
 Nr. of dummy points:         43
```

You can use the menus to go to different parts of the output file, or you can just use the scroll bar. If a menu option is shaded, this means that no corresponding section of the output is available.

Clicking an output section title highlighted in blue will skip to the next section with the same title, if present.

As we are now done with tutorial 1, close all windows that belong to this tutorial:

```
Select the SCM → Close All command in any ADF-GUI window
```

All open windows from the ADF-GUI will be closed.

Tutorial 2: Building Molecules

In the first tutorial you have learned how to construct a molecule by building it out of atoms. That may be a complex task for bigger molecules. ADFinput has other ways to build molecules.

The quickest is to search for a molecule inside ADFinput, and use it if it is available.

Another way is to search for the molecule on the Internet, and use either the xyz coordinates or the SMILES string

Or you can build it using the structure tool in ADFinput. As a more realistic example using the structure tool, you will build a small peptide chain. Then you will learn how to use the predefined metal complex structures. You will learn how to set up your own structures library.

Finally, you can combine the crystal tools to cut molecular systems out of crystals. As an example we will make a sphere of Cu atoms.

Step 1: Start ADFinput

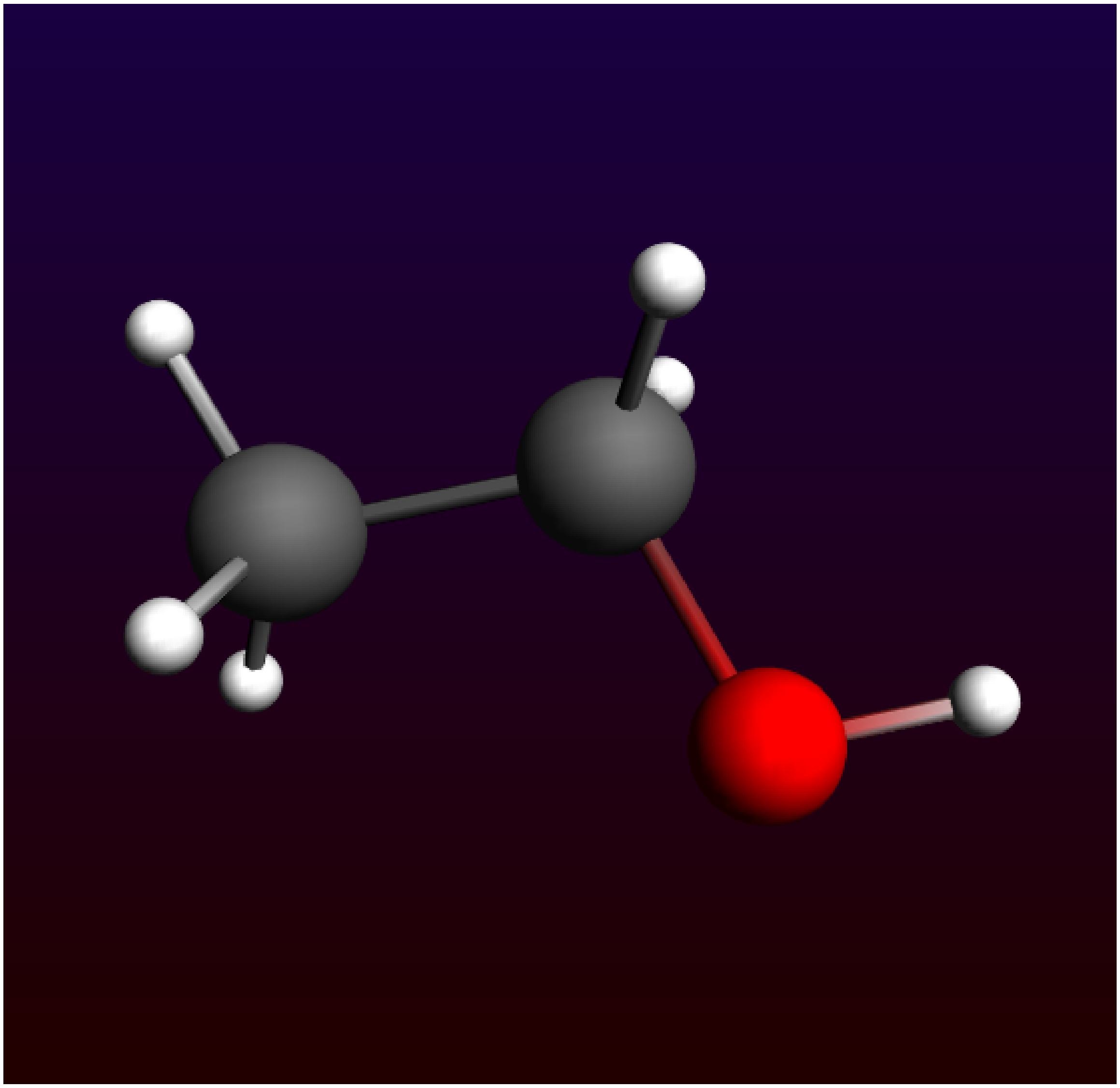
For this tutorial we again prefer to work in the Tutorial directory:

```
cd $HOME
Start ADFjobs
Click on the Tutorial folder icon
Start adfinput via SCM → ADFinput
```

Step 2: Search for ethanol

The quickest solution: search (and find) ethanol.

```
Press ctrl/cmd-F to activate the search box (or click the search icon in the
panel bar)
Enter 'ethanol' as search text (without quotes)
Click on the 'Ethanol (ADF)' match
Rotate to get a good view
```



Your ethanol is ready. The (ADF) in the search results mean that the molecule has already been optimized by ADF, using the BP86 XC potential with a TZP basis set and small core.

For the next demonstration we need a file with the xyz coordinates of ethanol. You can make such a file using the Export Coordinates option:

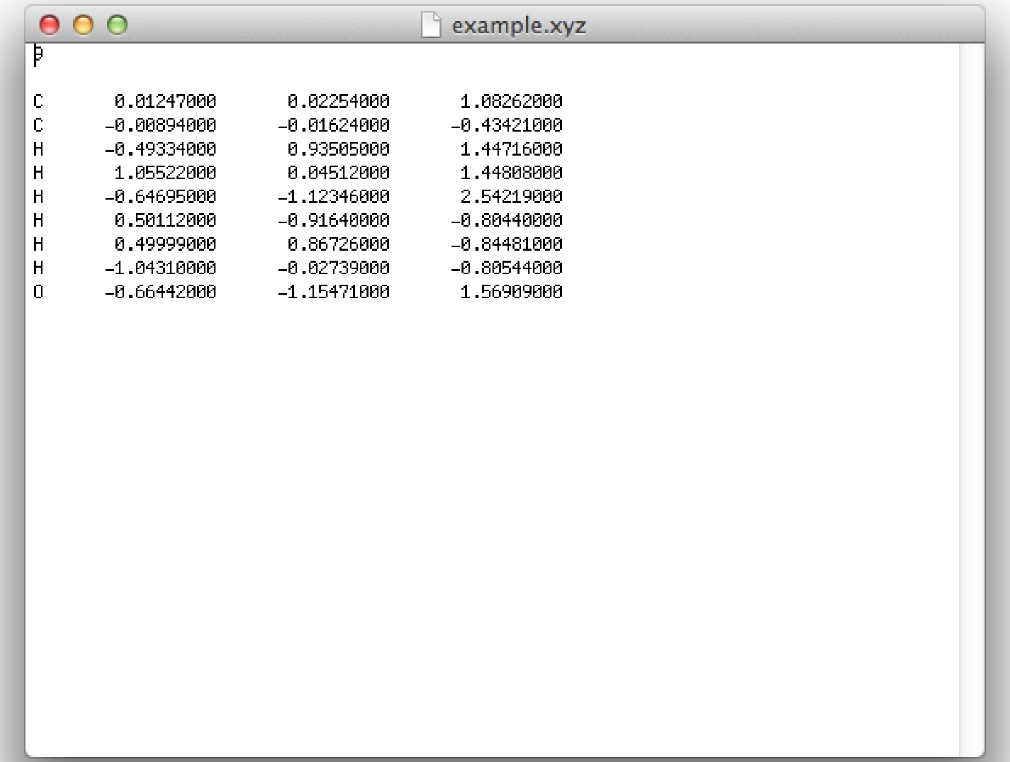
```
Use the File → Export Coordinates... menu command
Enter 'example.xyz' as filename
Click Save
```

Step 3: Import XYZ for ethanol

To import a molecule if you have its structure as xyz file (with element types), you can either use the **File → Import Coordinates...** or the **Edit → Paste** command.

```
Use the File → New menu command in ADFinput
Click 'No' when asked if you want to save your changes
```

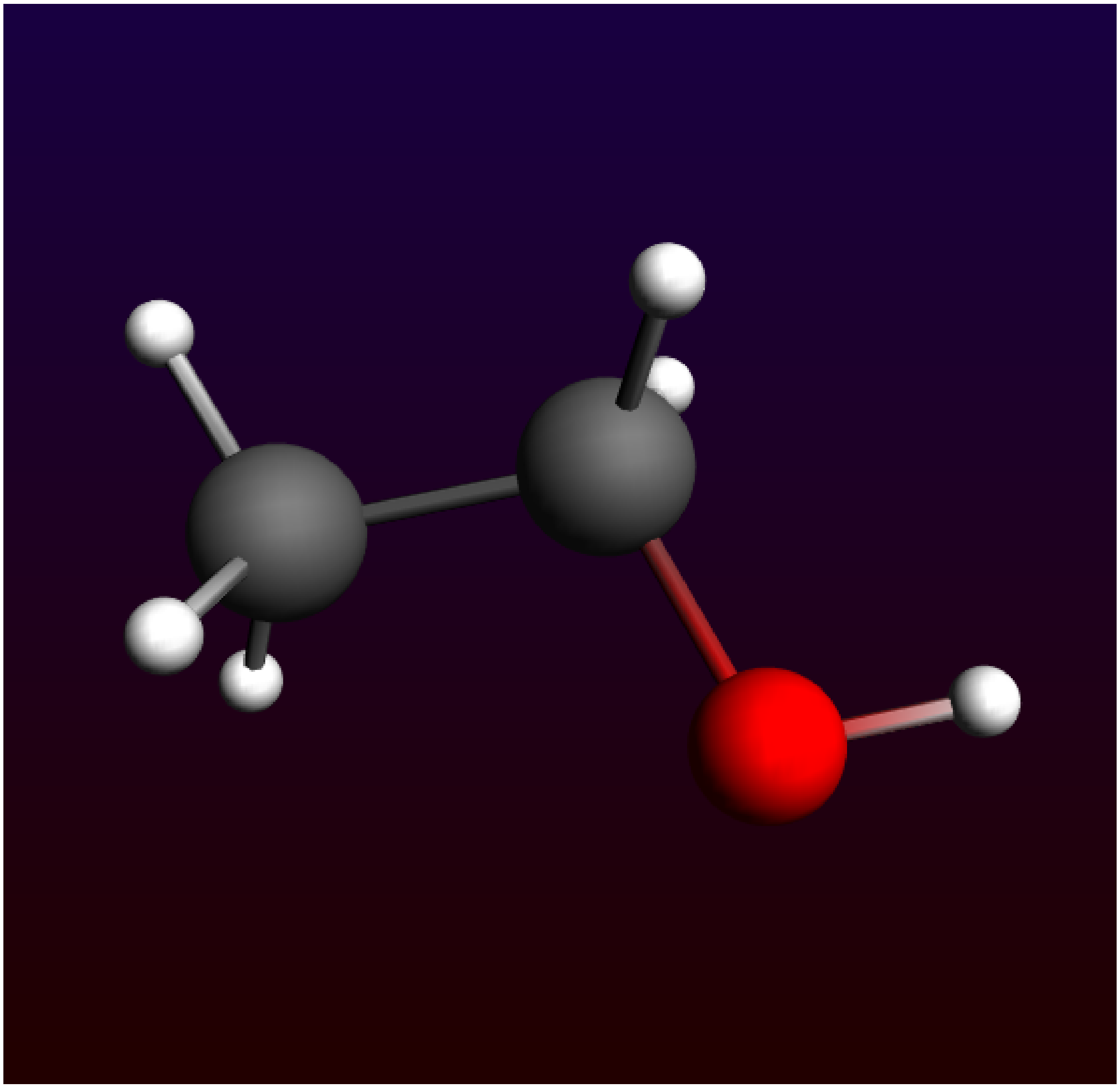
```
Click in the ADFjobs window to activate it
Use the Job → Refresh List menu command (or press F5)
Click the triangle in front of example to show the example.xyz file
ctrl-double click on the .xyz file (listed in Local files)
```



```
9

C      0.01247000      0.02254000      1.08262000
C     -0.00894000     -0.01624000     -0.43421000
H     -0.49334000      0.93505000      1.44716000
H      1.05522000      0.04512000      1.44808000
H     -0.64695000     -1.12346000      2.54219000
H      0.50112000     -0.91640000     -0.80440000
H      0.49999000      0.86726000     -0.84481000
H     -1.04310000     -0.02739000     -0.80544000
O     -0.66442000     -1.15471000      1.56909000
```

This will open a text editor showing the contents of the the example.xyz file. The editor used depends on your operating system, but normally you will be able to select and copy text.

```
Select all text in the ethanol.xyz file
Copy it
Click in the ADFinput window to activate it
Paste the xyz coordinates (ctrl/cmd-V or Edit → Paste)
```



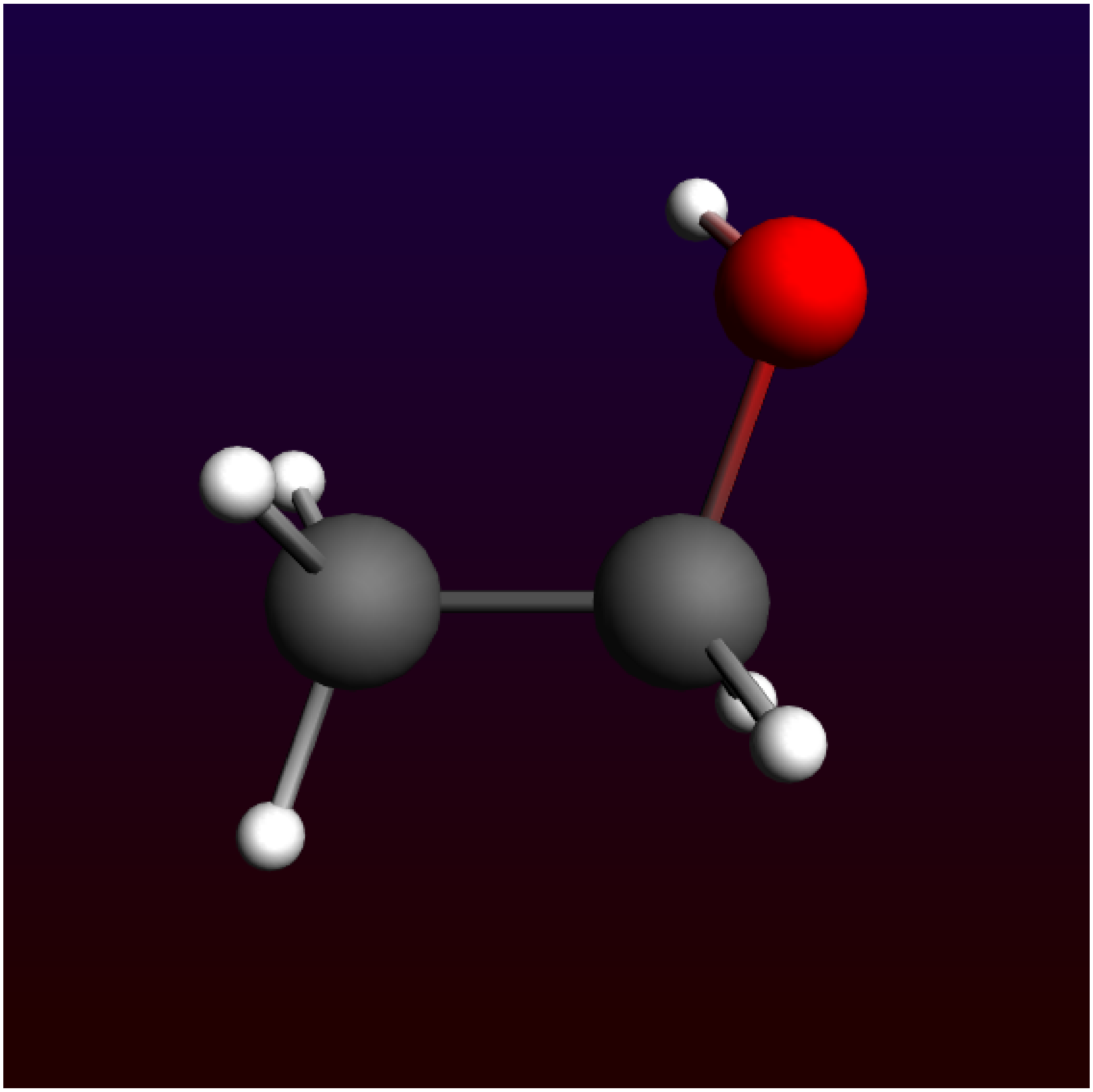
You should again get the ethanol molecule, just as you have saved it.

Step 4: Import SMILES string

ADFinput can also interpret SMILES strings (via OpenBabel). As a demonstration, lets try again with Ethanol:

```
Use the File → New menu command in ADFinput
Click 'No' when asked if you want to save your changes

Open a web browser
Search for ethanol on wikipedia.org
At the right side of the page, click the 'Show' link to show the SMILES
Copy the SMILES string ( CCO )

Click in the ADFinput window to activate it
```

```
Paste the SMILES string (ctrl/cmd-V or Edit → Paste)
Click in empty space in the drawing area to clear the selection
```



Again we have an ethanol molecule. SMILES strings do not contain the 3D structure, it was generated by OpenBabel and is NOT an ADF optimized structure. So normally the next step would be to pre-optimize with UFF (via the cog wheel), and to optimize the geometry with ADF.

SMILES strings work often, but there are also many examples where the resulting structure does not make sense.

Step 5: Build ethanol using the structure tool

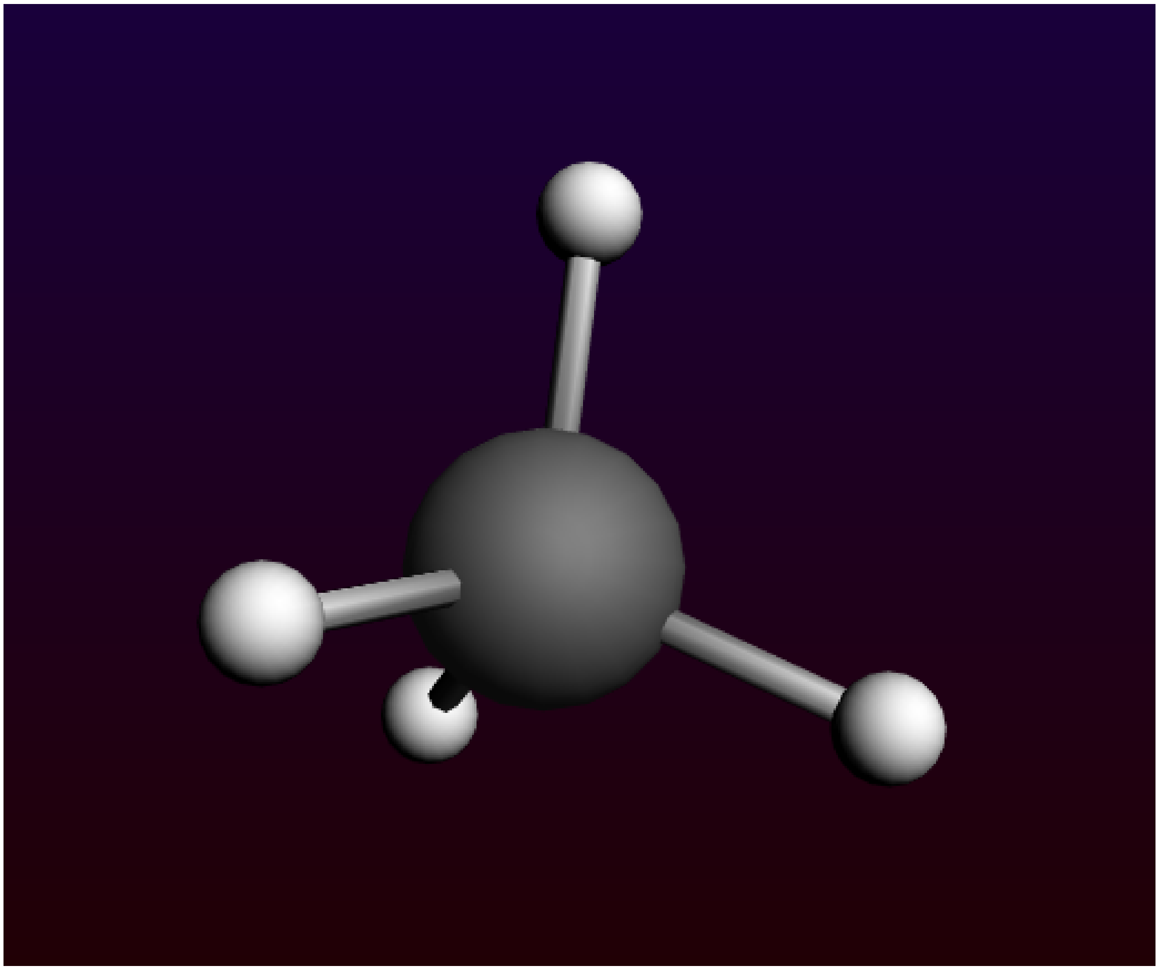
As a demonstration on how to use the structure tool, we start by building a methane molecule:

```
Use the File → New menu command in ADFinput
```

```
Click 'No' when asked if you want to save your changes
```

Select the C-tool
Click somewhere in the drawing area to make a carbon atom
Select **Atoms → Add Hydrogen** , or faster: press the shortcut (ctrl-H or cmd-H)

If your cmd-H shortcut does not work (on a Mac), probably you need to fix your X11 prefereces.

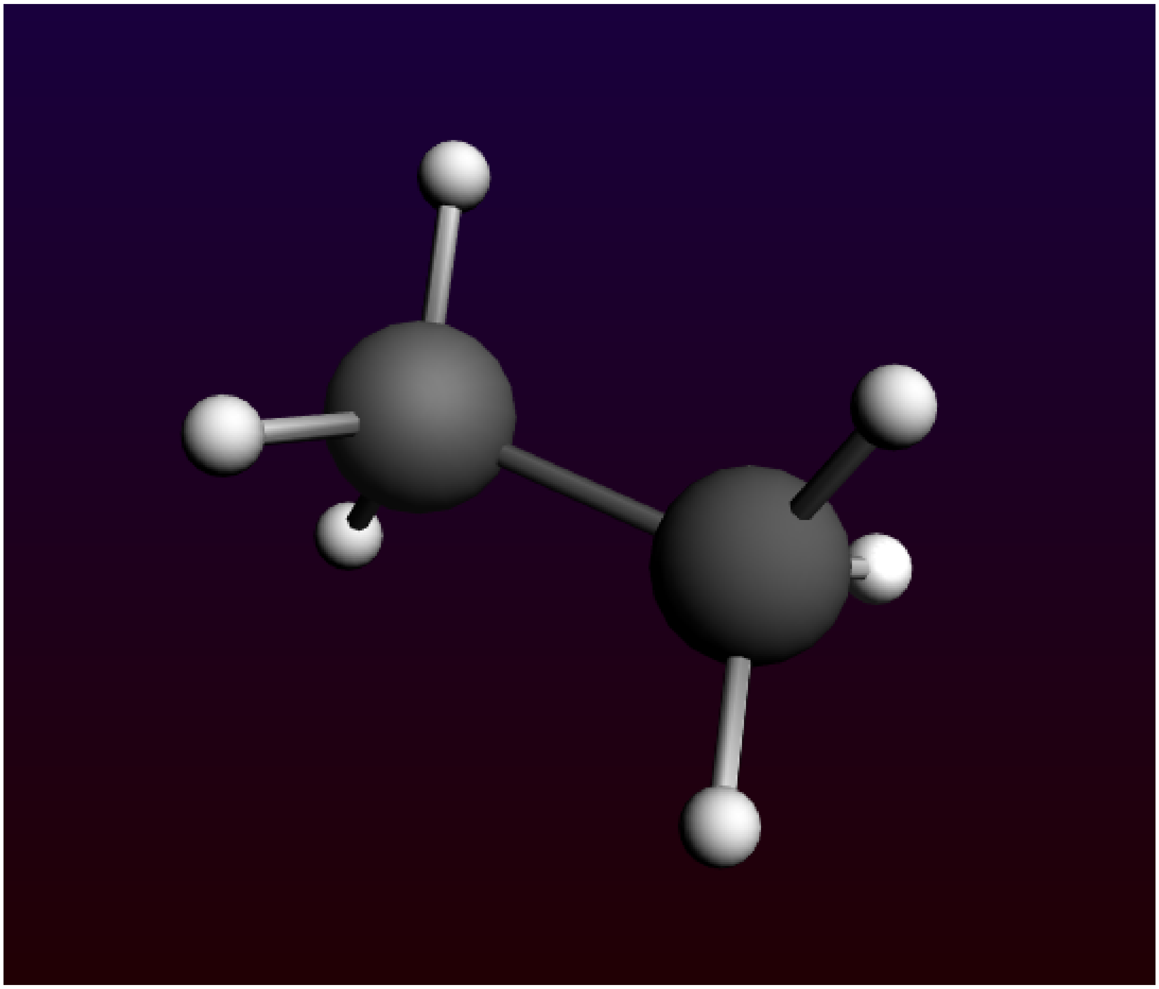


The next step is to add a methyl group, using the structures tool:

Select the **Structures tool → Alkyl Chains → Methyl** structure (the structures tool is the benzene-like logo)

Notice that the button of the structures menu is glowing, which means that the structure-tool is in use.

Double-click on one of the hydrogen atoms
Zoom out if needed (with right mouse button or mouse wheel)



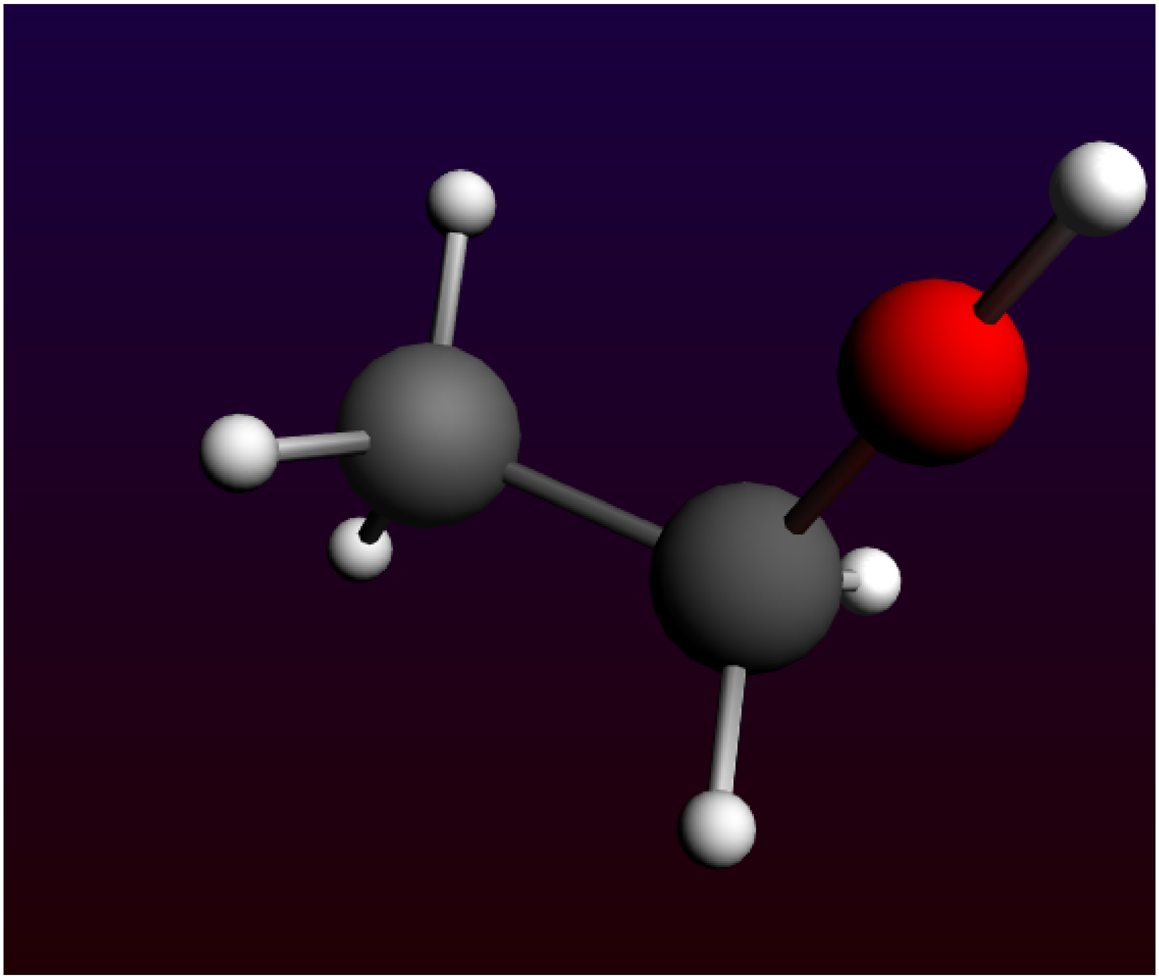
You will see that the hydrogen is replaced by a methyl group.

Note that:

- The methyl is orientated along the newly formed C-C bond and the new hydrogens point away from the existing ones.
- The double-clicked hydrogen is replaced by the carbon atom, since this atom is the 'replacing' atom.
  This atom is defined through having xyz-coordinates (0,0,0).
- The background glow moved from the 'Structures' tool to the 'Pointer' tool button; the 'Pointer' tool is active again.

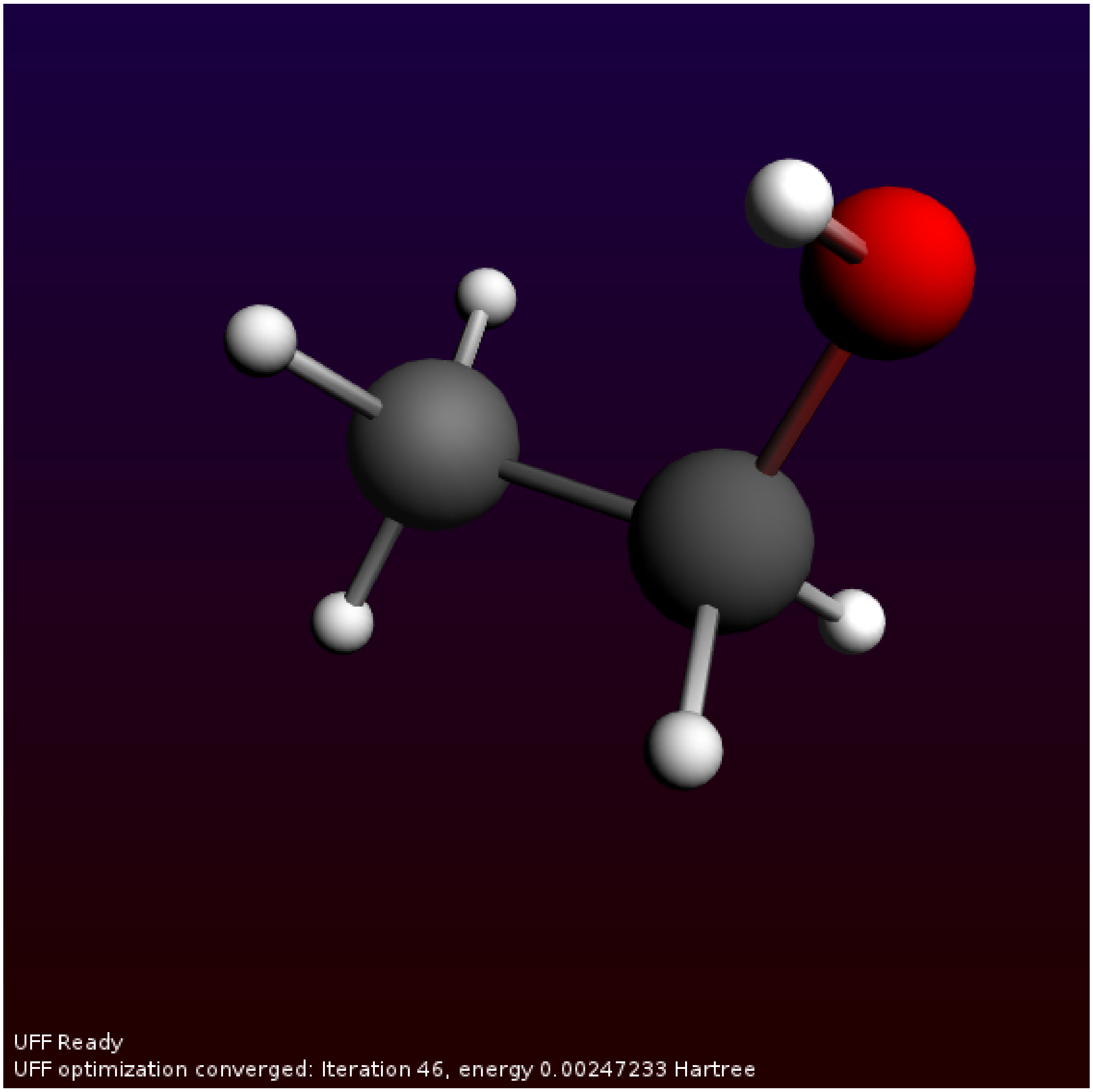
To create ethanol, we need to add a hydroxyl group:

`Select the` **Structures tool → Ligands → OH** `structure`
`Double-click on one of the hydrogen atoms`



Again, the hydrogen is replaced by the structure. In this case, the oxygen replaces the double-clicked atom. The hydrogen is precisely aligned along the C-O bond and points away from the rest of the molecule. This shows you the very general way in which the structures will align according to the bonds in the original molecule and those in the structure. In this case, the hydroxyl group is not immediately orientated as it normally would be in an ethanol molecule:

```
Pre-optimize: click on the cog wheel
```



UFF Ready
UFF optimization converged: Iteration 46, energy 0.00247233 Hartree

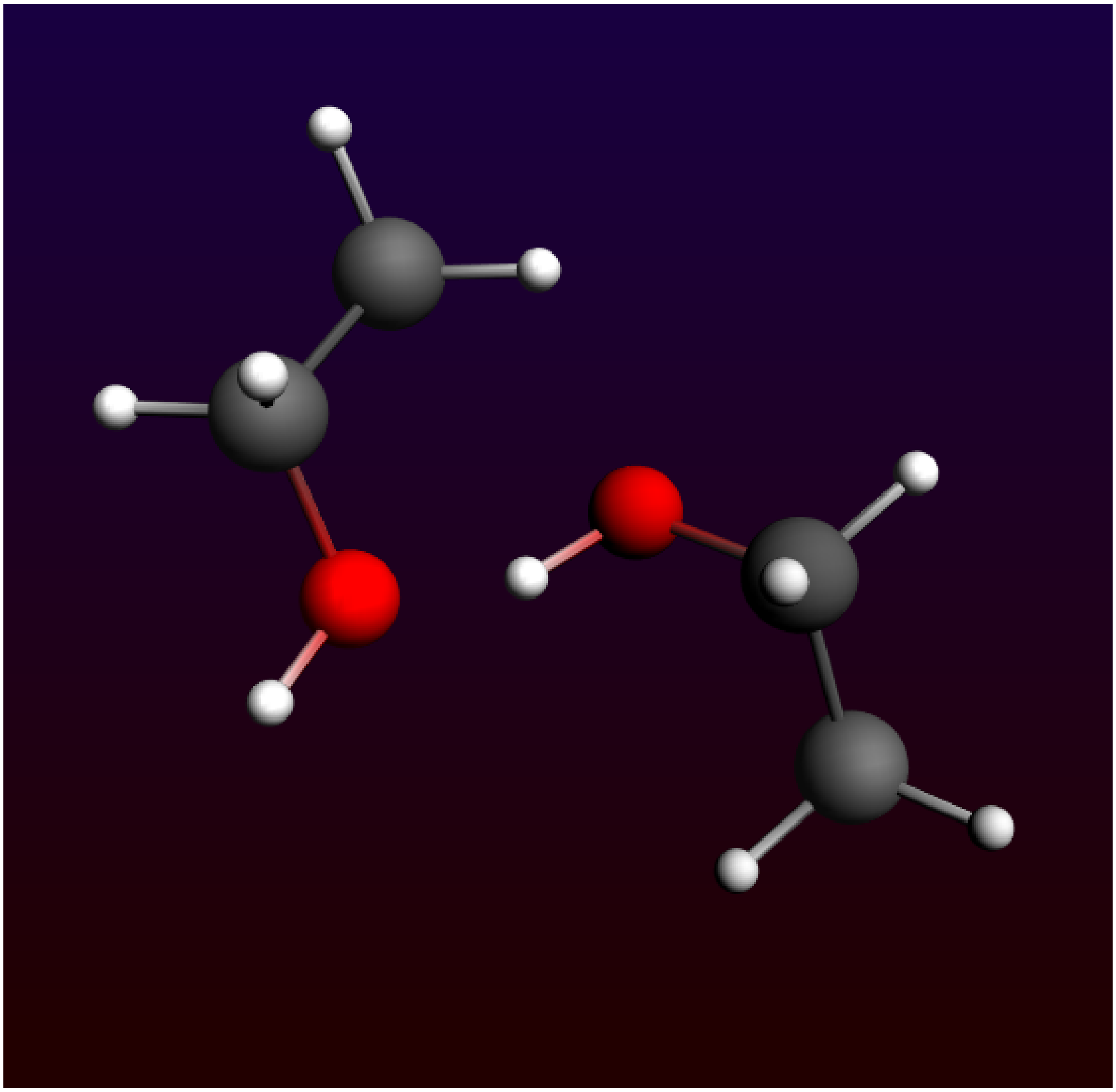
And again we have constructed an ethanol molecule.

ADFinput comes with a many predefined structures. Among them are some typical solvent molecules, so that you can easily add solvent molecules around your system. One of these 'Solvent' structures is Ethanol. Now add this molecule in empty space:

```
Select the Structures tool → Solvents → Ethanol structure
Left-click in empty space near the hydroxyl group
```

Note that the oxygen is selected. Again, this oxygen is defined through having xyz-coordinates (0,0,0). Next we select the new molecule and orient it with the mouse to a reasonable position:

```
Use the Select → Select Molecule menu command (or ctrl/cmd-M)
Use the mouse to rotate and translate the ethanol molecule to your favorite
orientation
```

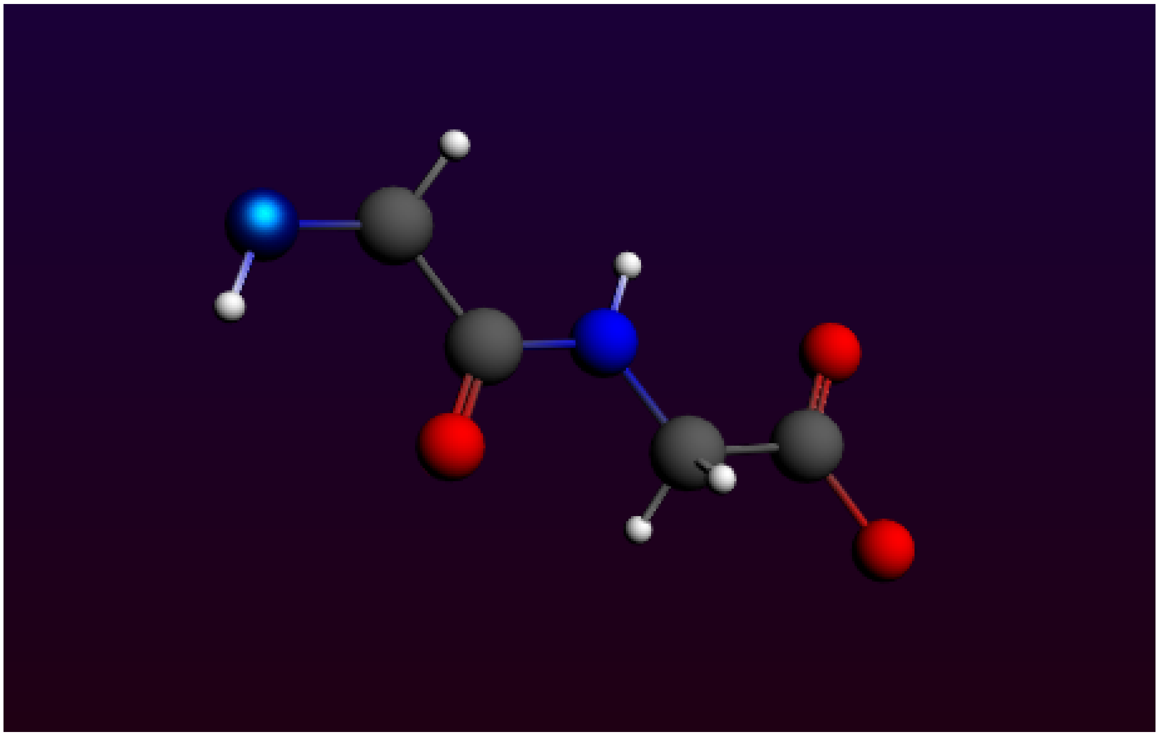


This way you can easily add explicit solvent molecules.

Step 6: Building a peptide chain using the structures tool

Now we will build a small peptide chain as another example using the structures tool.

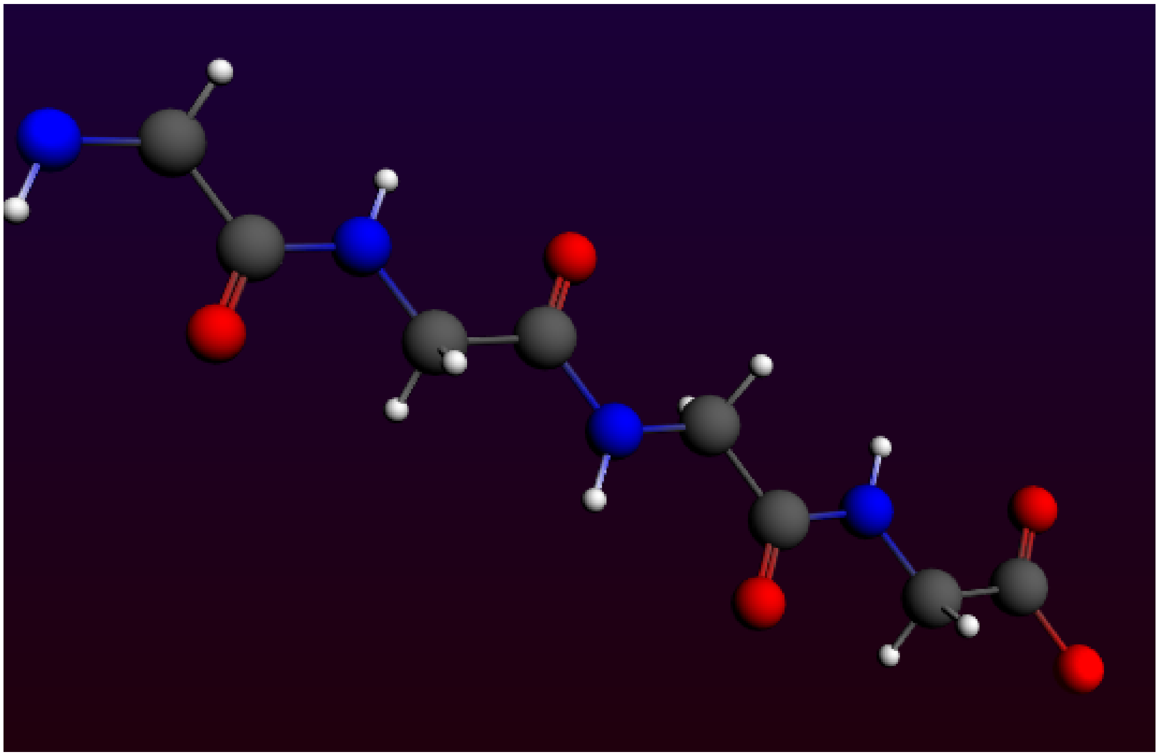
`Select` **File → New**
`Click 'No' as we do not want to save the setup`
`Select the` **Structures tool → Amino Acids → AA Backbone** `structure`
`Place it in the drawing area`



There appears a subunit (or actually two) of a basic peptide chain. Notice that one of the atoms is selected, namely the terminal nitrogen. This atom is, again, the 'replacing' atom. In order to extend the peptide backbone, you now have to choose the right atom to be replaced. The obvious choice is the (non double-bonded) terminal oxygen.

```
Click in empty space to deselect the nitrogen
Press the space bar, which activates the last used option of the 'Structure'
tool ('AA backbone' here).
Double click on the terminal oxygen.
```

`You may want to use` **View → Reset View**.



In a similar fashion, you can now replace the hydrogens on the backbone by amino acid side groups of your choice. These can be found in the **Structures tool → Amino Acid → AA Side Groups** sub-menu.

Step 7: Metal complexes and ligands

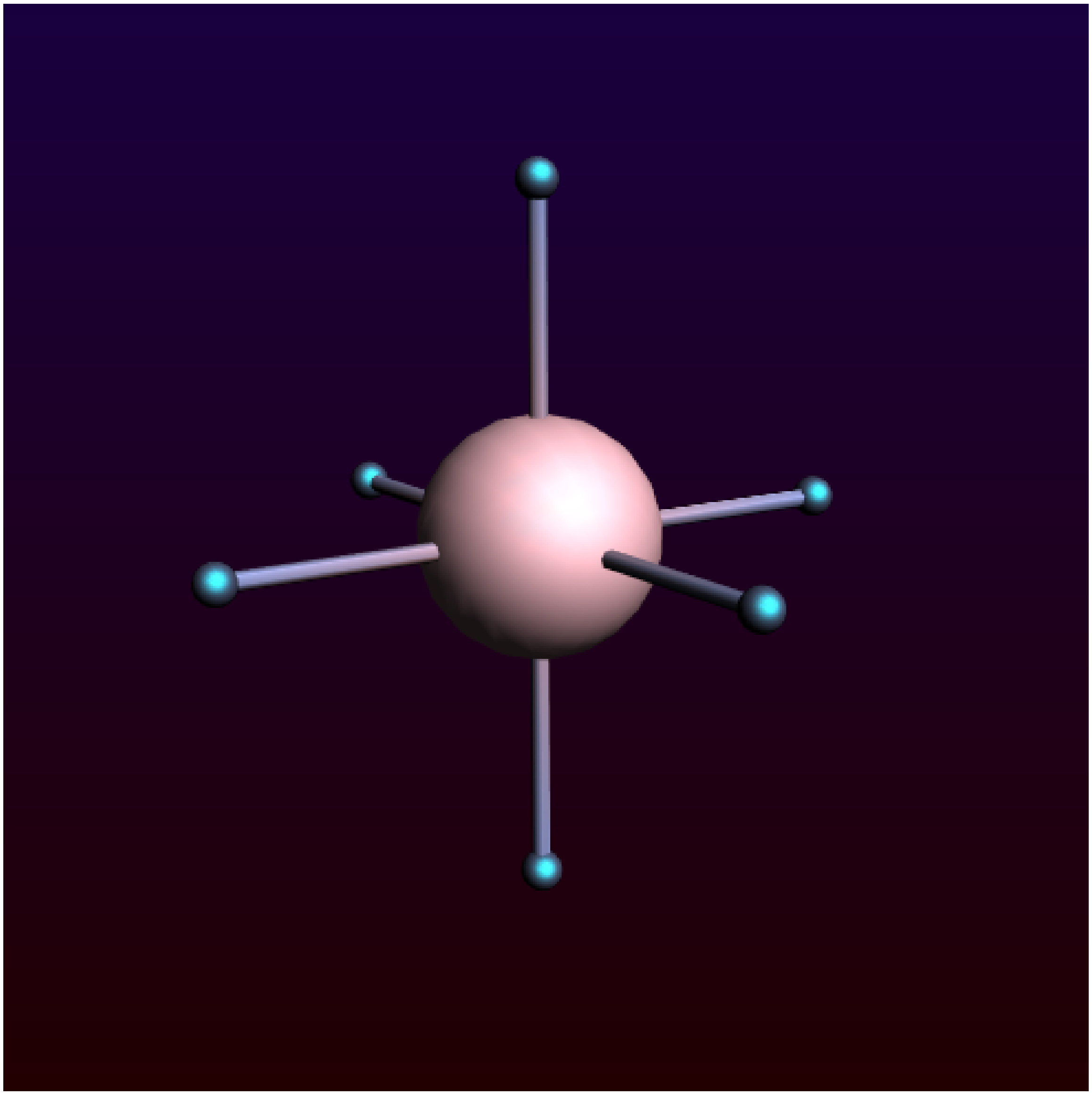
In the sub-menu 'Metal Complexes' you can find a set of predefined complexes corresponding to commonly encountered geometries. Furthermore, there are a number of ligands to be found, which can be easily used with these metal complexes.

Predefined Metal Complex Geometries

Select the **File → New** command
Click No (do not save changes)
Select **Structures tool → Metal Complexes → ML6 Octahedral** tool and place it in the drawing area

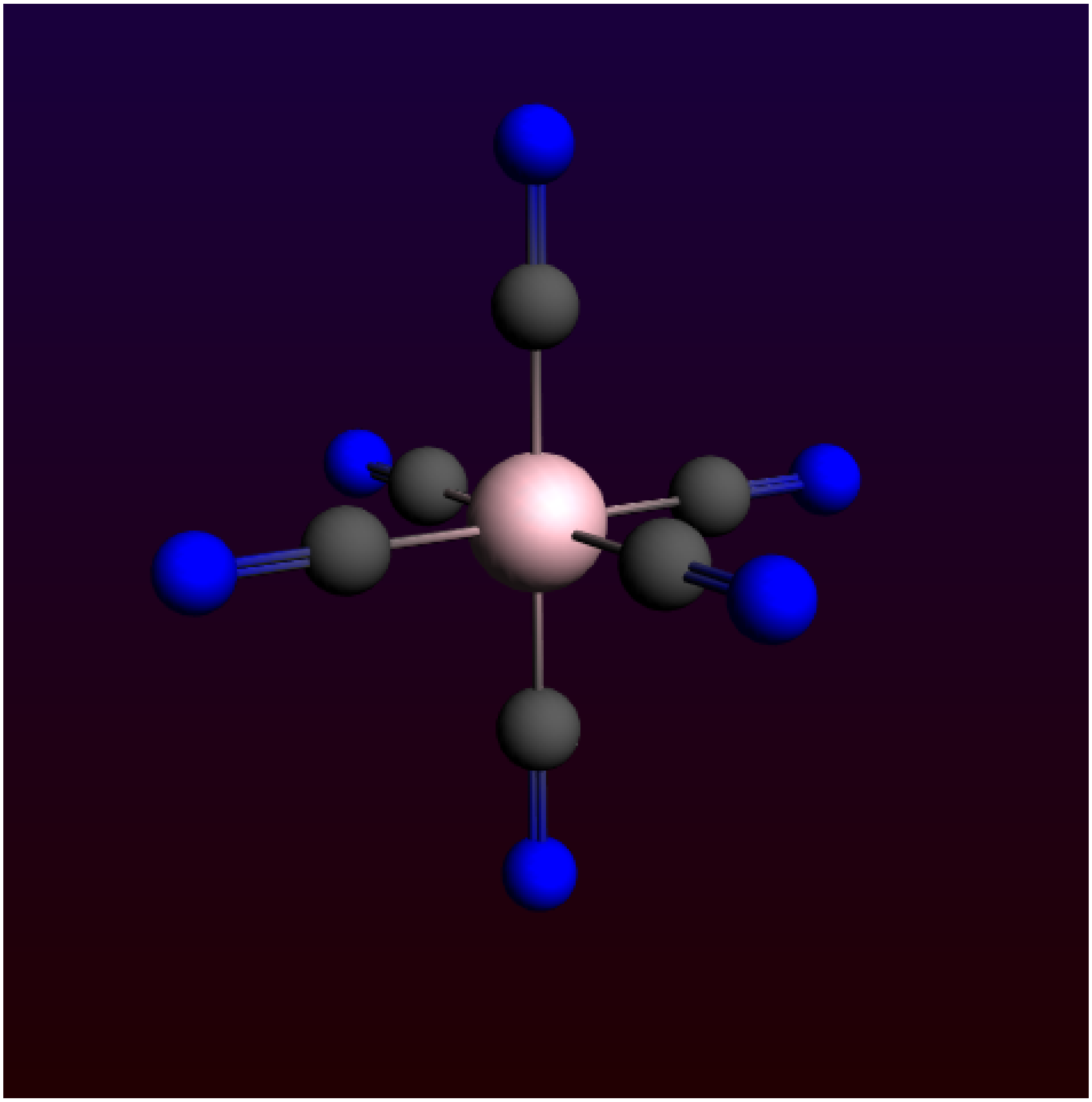
Notice that six dummy ("Xx") atoms have been placed around the metal center in an octahedral fashion.

Select one of the dummy atoms by clicking on it
Select **Select → Select Atoms Of Same Type** menu command



The Ligands structure sub-menu contains a number of ligands which can be used to replace the dummy atoms. The Structure menu can, however, also be reached via the Atoms menu.

Select the **Atoms → Replace By Structure → Ligands → CN** command
Click in empty space to clear the selection
Reset the View if needed

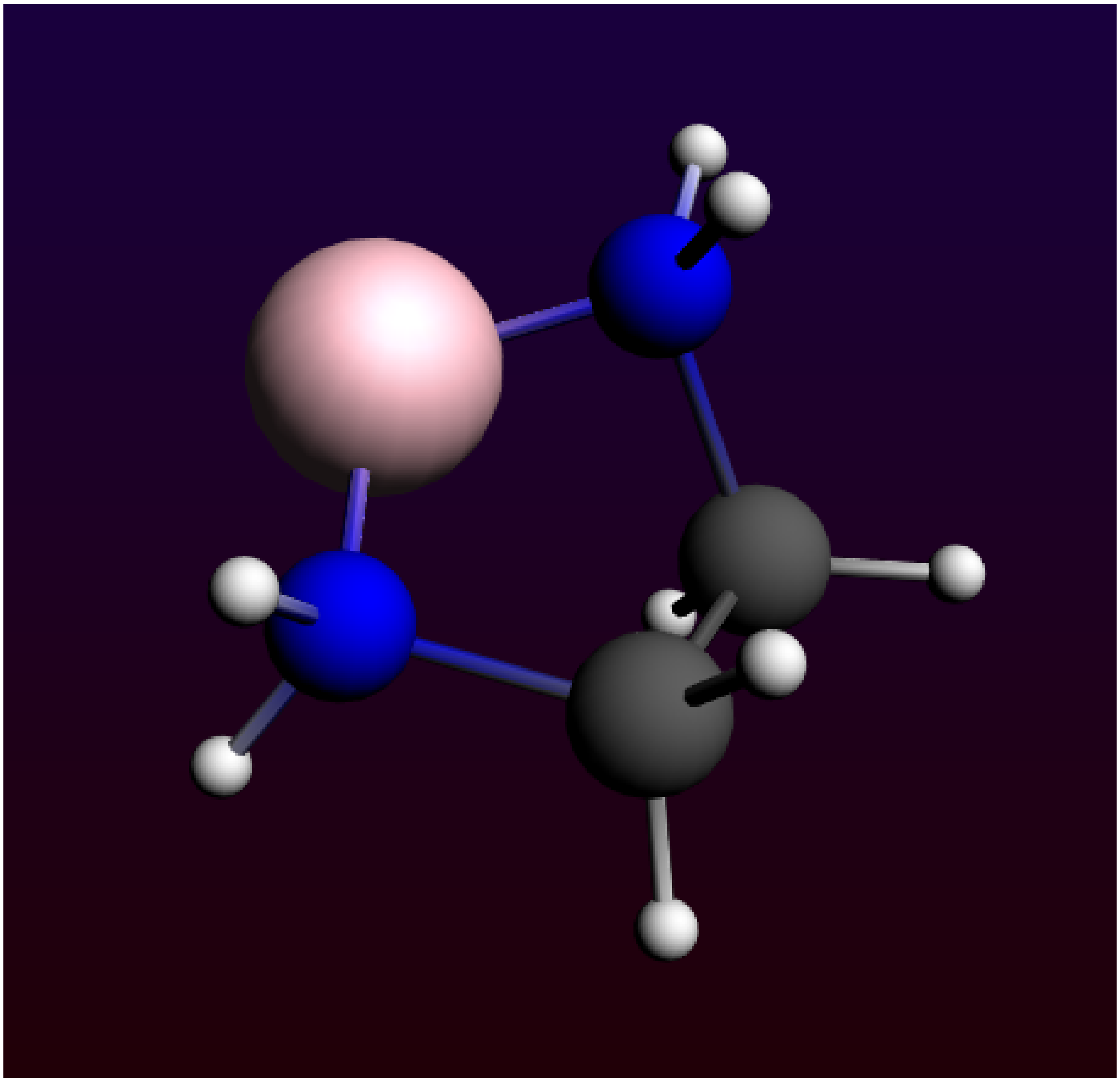


Notice that all dummy atoms in the selection are replaced by CN ligands.

Bidentate Ligands

In order to use the bidentate ligands, we must start with a bare metal center.

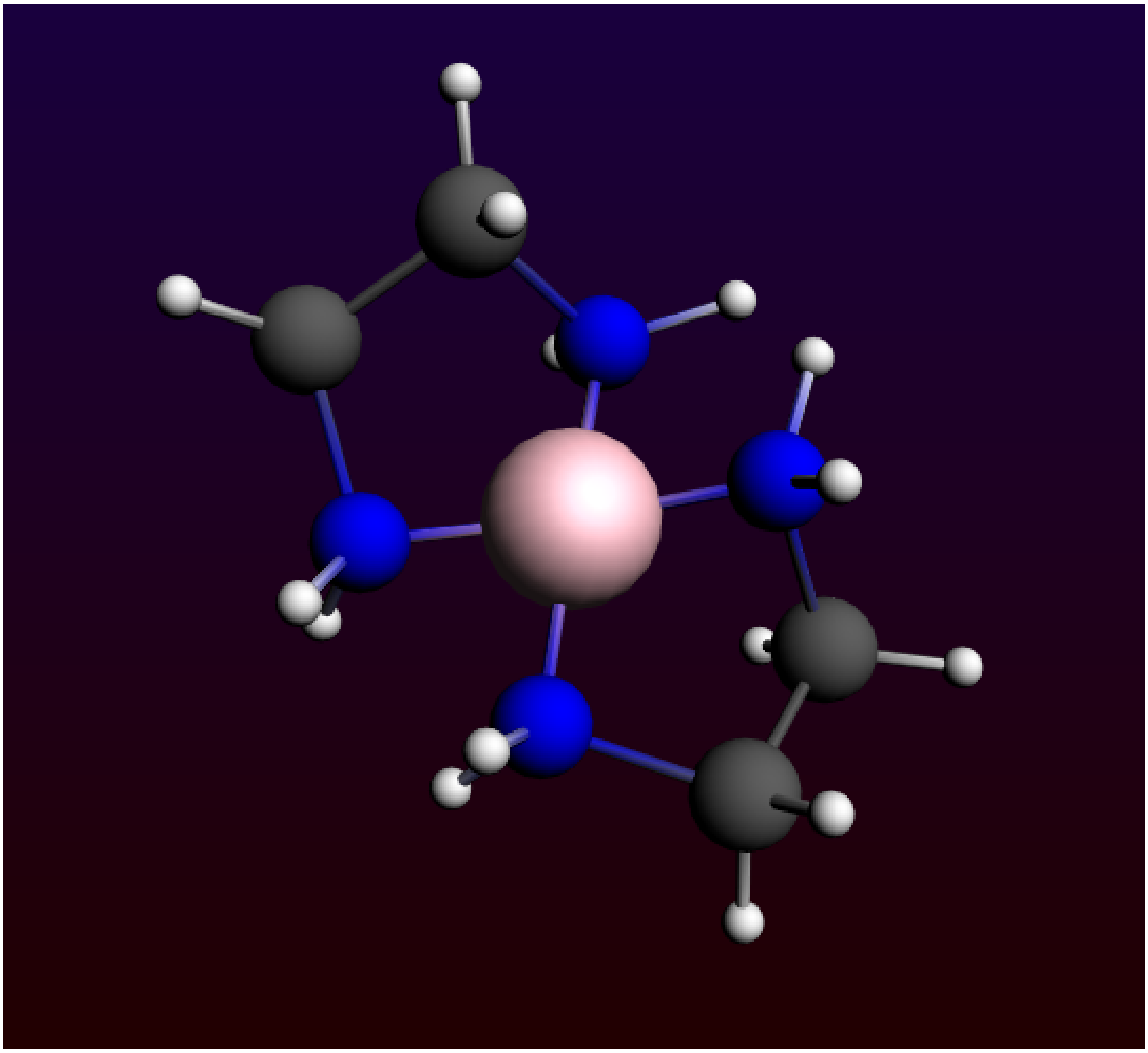
```
Select the File → New command
Click No (do not save changes)

Place an iron atom in the drawing area (click the X button in the toolbar to
get a menu with all elements)
Select the Structures tool → Ligands → Bidentates → Ethylenediamine structure
Double-click on the metal atom
```



You can see that, in this case, the metal atom is not replaced by an atom of the structure, contrary to previous experience, but that the bidentate ligand is simply attached to the central metal atom.

This works because the 'replacing' atom in all bidentate structures is a dummy atom, which has the property that it won't replace an existing atom. The metal atom will simply take over the bonds that existed on the dummy atom in the structure. You can easily verify this when you would place the structure in empty space. Other multidentate ligands are defined in a similar fashion.

`Press space bar and double-click on the metal atom`

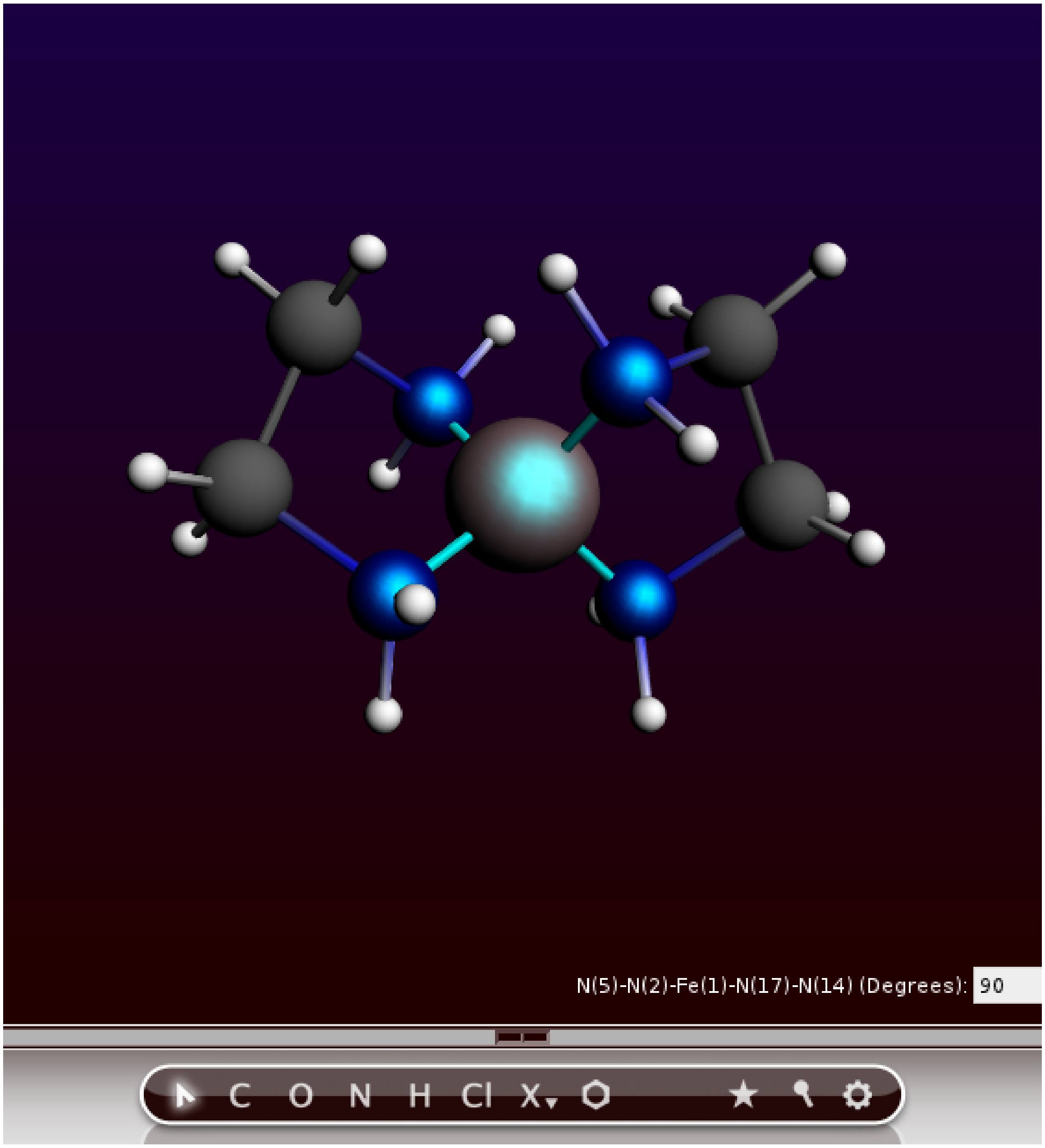


Notice that the second ligand appears opposite the existing one.

Modifying the Plane Angle

To change the relative orientation of two bidentate ligands, we can change the plane angle. The planes are defined by two sets of three atoms, the central one being present in both sets. In this case this will, of course, be the metal atom.

```
Select, in order, the two nitrogens on ligand one, the metal atom, and the
nitrogens on the second ligand.
Change the plane angle to 90 degrees using the slider
```



In this way, you can easily change the environment around the metal from square planer to tetrahedral. This feature works as long as you choose the atoms in right order, and if the defined planes can freely rotate relative to each other.

Step 8: Your own structures library

You can make your own structure library very easily.

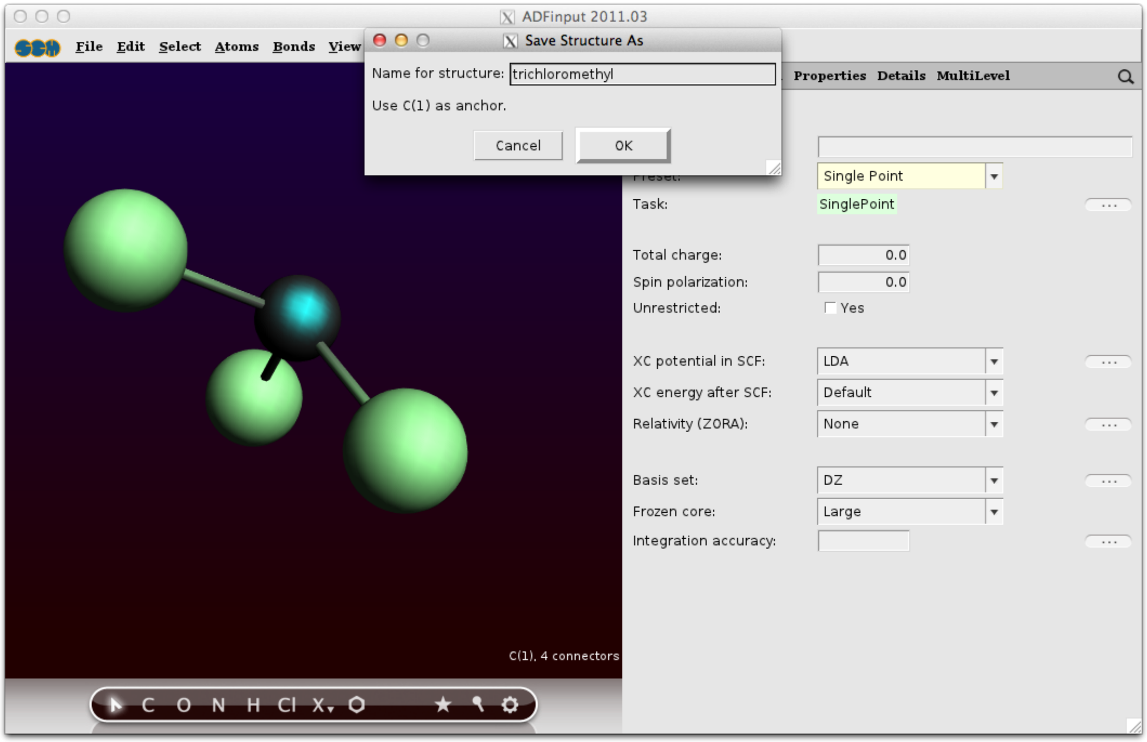
By default, user defined structures will be stored in the .scm_gui/Structures directory.

Defining your structures

To be able to actually use the structures as described earlier, it is necessary to define one of the atoms as having xyz-coordinates (0,0,0). This will then be the atom that will actually appear at the spot of the atom that is replaced by the structure. If you use the Save As Structure command this will be done for you.

Select the **File → New** command
Click No (do not save changes)

Build methane
Replace three of the hydrogens by chloride atoms and pre-optimize
Delete the remaining hydrogen
Select the central carbon atom
Use the **Structures tool → Save As Structure ...** command
Enter a name like trichloromethyl
Note that the selected atom (currently the C atom) will be used as anchor



Name for structure: trichloromethyl
Use C(1) as anchor.
Preset: Single Point
Task: SinglePoint
Total charge: 0.0
Spin polarization: 0.0
Unrestricted: ☐ Yes
XC potential in SCF: LDA
XC energy after SCF: Default
Relativity (ZORA): None
Basis set: DZ
Frozen core: Large
Integration accuracy:
C(1), 4 connectors

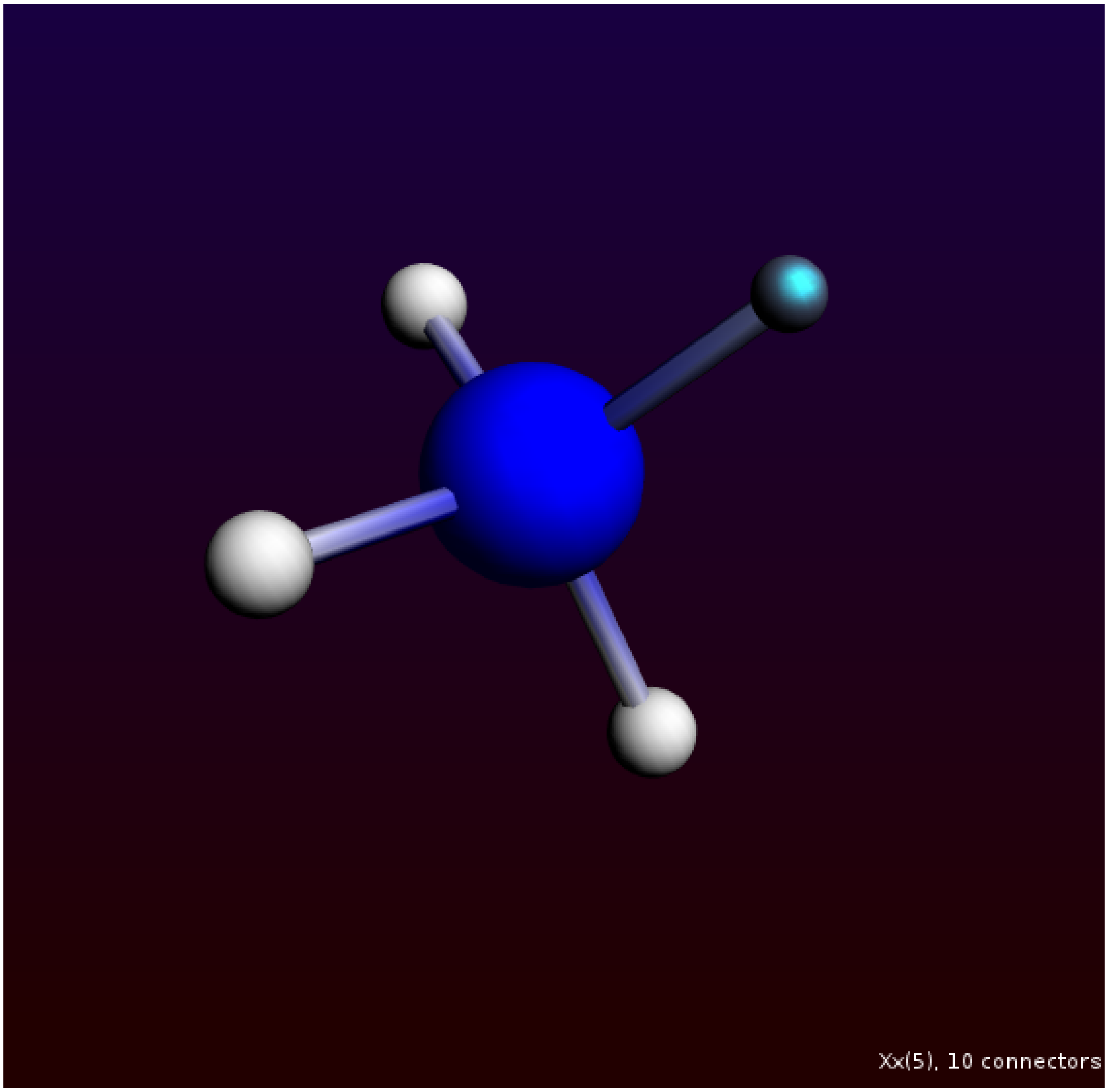
The new structure will appear in the structures menu and can be directly used.

Using dummy atoms

Dummy ("Xx") atoms are treated a little different when used in structures. A dummy atom will not replace an existing atom when it is defined as the 'replacing atom'. Instead, the double-clicked atom will remain and will accept the bonds that the dummy atom had in the structure.

Build a methane molecule
Replace the carbon atom by a nitrogen atom
Select one of the hydrogens and replace it by a dummy atom (the Xx atom type, in the periodic system)

```
Select the dummy atom
Save the structure using the Structures tool → Save Structure As... command
```



Now you can select the structure from the structures menu and directly use it.

```
Select your new structure from the structures menu
Double-click on one of the hydrogens
```

Notice that the hydrogen atom is not removed and that the NH3 group is attached to it. Similar behavior has been demonstrated with the bidentate ligands, where the dummy atoms are also used.

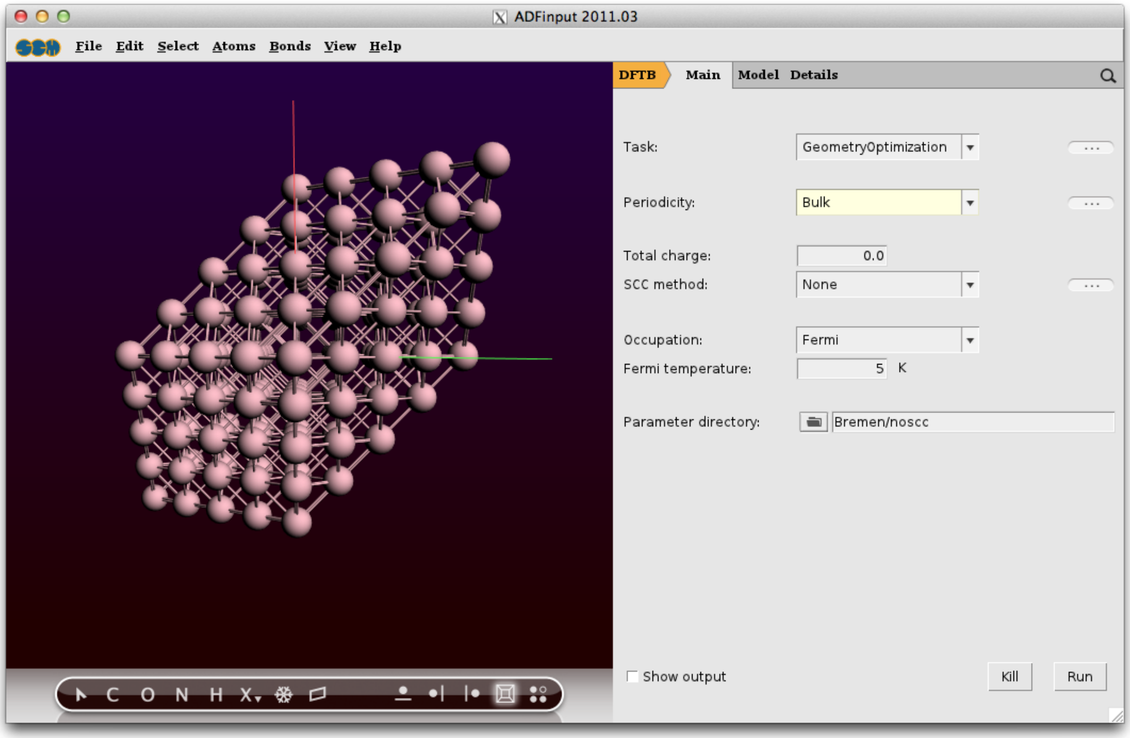
If you want to clean up your structures, you can use the **Structures tool → Manage Structures...** command. If you use it, ADFjobs will open and show the contents of your Structures directory. As the structures are just (simplified) .adf files, you can open them using ADFinput. And using ADFjobs you can rename them or delete them.

Step 9: A sphere of Cu atoms, cut out of the crystal

We start making a Cu crystal, using a super cell so we have many real Cu atoms.

To build the crystal, we need to use the periodic tools. These will work only for programs supporting periodicity, like DFTB.

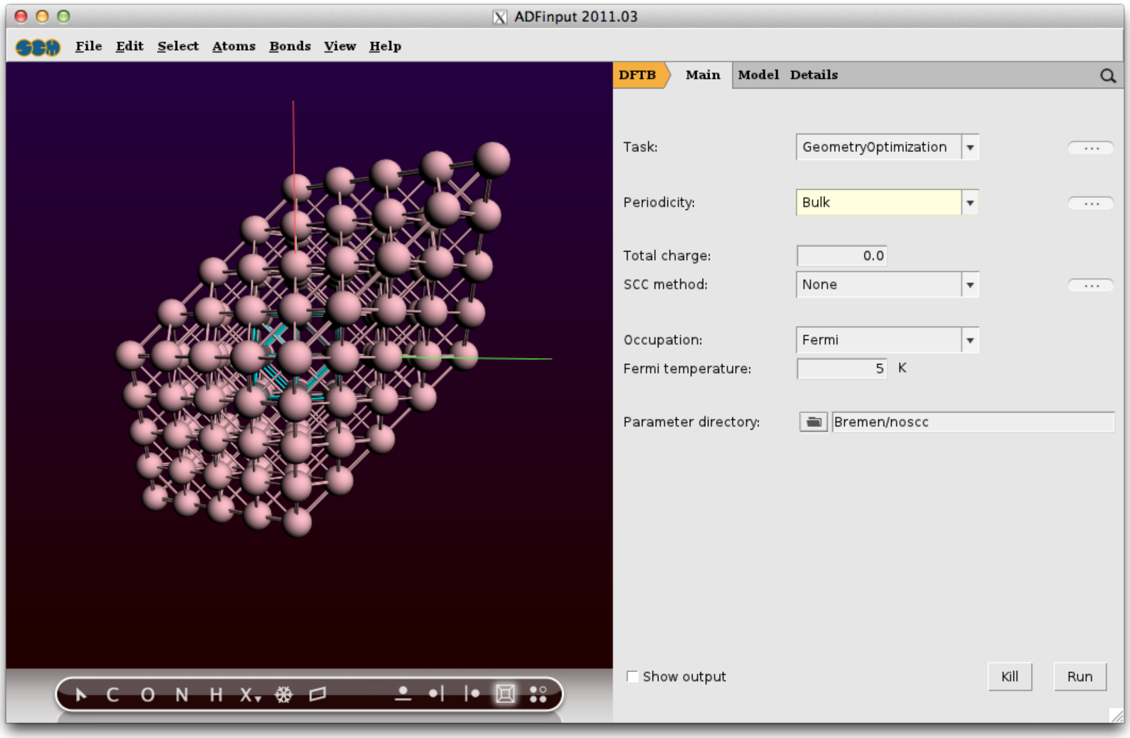
Start ADFinput (or use **File → New** in the currently open ADFinput window)
Switch to DFTB mode (panel bar **ADF → DFTB**)
Select 'Periodicity: Bulk'
Edit → Crystal → Cubic → fcc
Click OK in the pop-up-window
Edit → Crystal → Generate Super Cell...
Click OK in the pop-up-window
Uncheck **View → Periodic → Repeat Unit Cells**, so only one unit cell will be shown



Task: GeometryOptimization
Periodicity: Bulk
Total charge: 0.0
SCC method: None
Occupation: Fermi
Fermi temperature: 5 K
Parameter directory: Bremen/noscc
☐ Show output

Now we have a block of Cu, with explicit Cu atoms (that is using a super cell). Next we will center this block, and select a sphere of atoms around the origin.

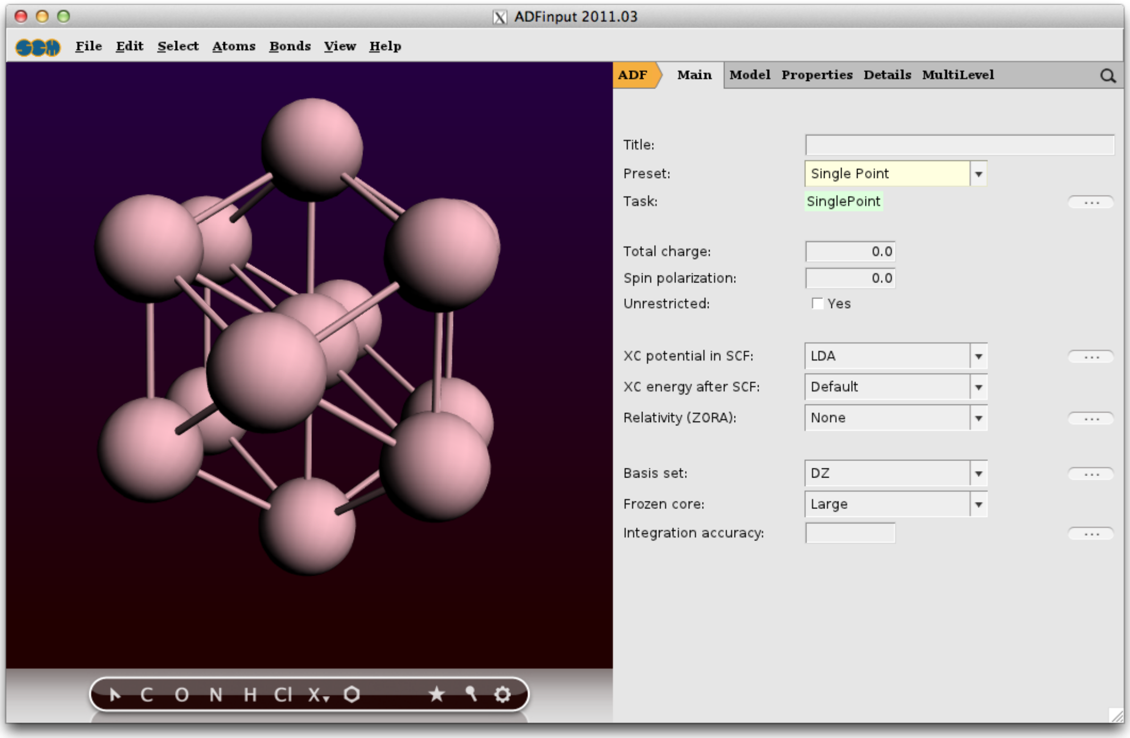
Make sure the origin is in the center of the block: **Edit → Set Origin**
Select → Select Atom Close To Origin
Select → Select Within Radius
Click OK



Task: GeometryOptimization
Periodicity: Bulk
Total charge: 0.0
SCC method: None
Occupation: Fermi
Fermi temperature: 5 K
Parameter directory: Bremen/noscc

Select → Invert Selection
Press the Backspace key to delete the selected atoms
If it does not respond: click once in the drawing area to focus on it, and press the Backspace key again
Switch to ADF: panel bar **DFTB → ADF**
Rotate a little

As you can see, you have a (very small) sphere consisting of Cu atoms in the molecular ADF program:



Title:
Preset: Single Point
Task: SinglePoint
Total charge: 0.0
Spin polarization: 0.0
Unrestricted: ☐ Yes
XC potential in SCF: LDA
XC energy after SCF: Default
Relativity (ZORA): None
Basis set: DZ
Frozen core: Large
Integration accuracy:

Obviously, by making a bigger super-cell and selecting atoms within a larger radius you can make bigger spheres.

Tutorial 3: Building Crystals and Slabs

In this tutorial we demonstrate the working of several tools that combined give you great flexibility to build periodic structures.

If you are not interested in periodic structures (for example, if you only use ADF), you can skip this tutorial.

The instruments at your disposal are:

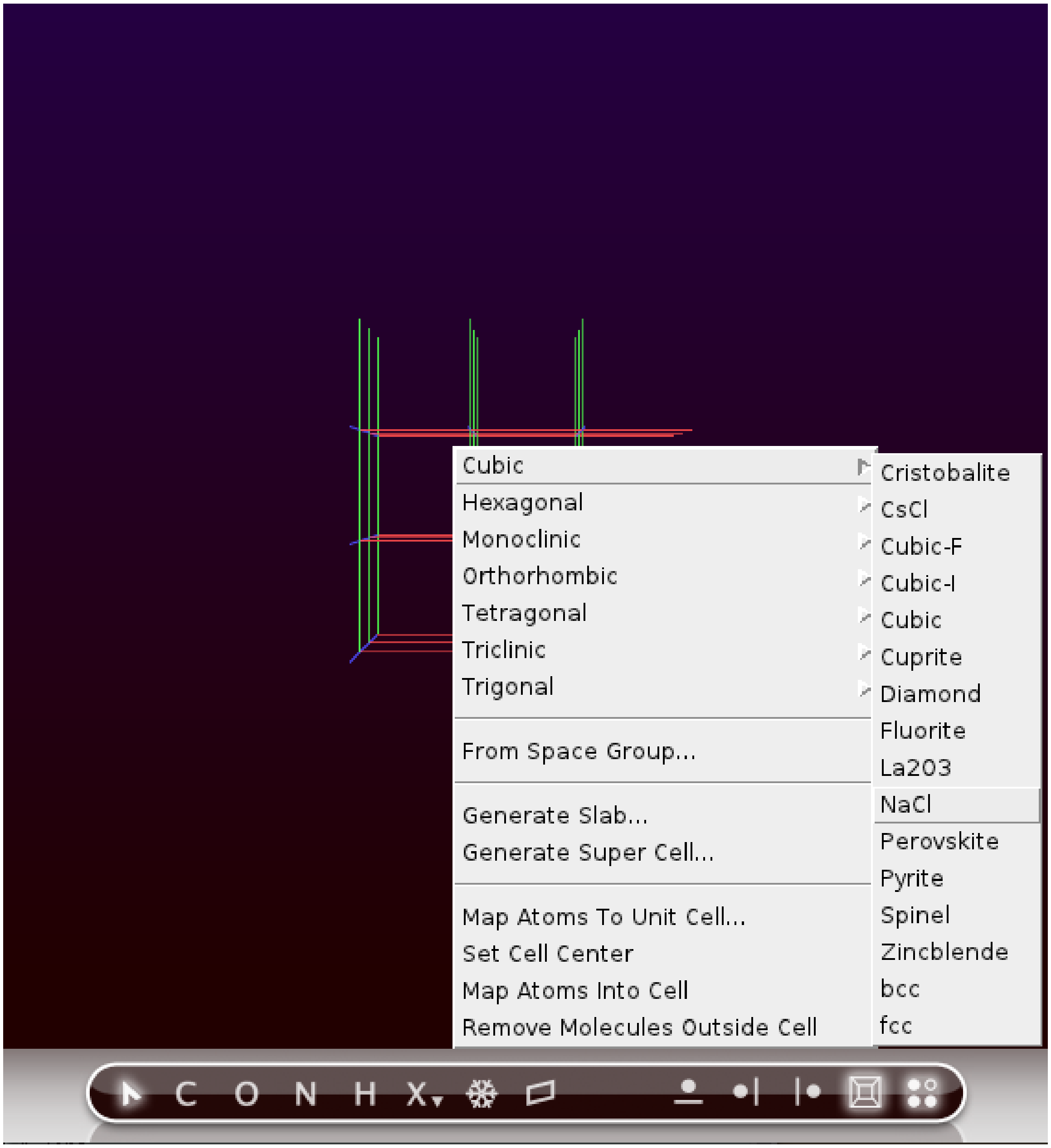
- Small database of predefined crystal structures.
- CIF file importer.
- Crystal builder from space group information.
- Super cell tool to enlarge the unit cell
- Slice tool to cut out slabs from any crystal.

To use these tools you need to use ADFinput in periodic mode. For example, by switching to the BAND mode, or by switching to DFTB or Mopac and next changing the periodicity.

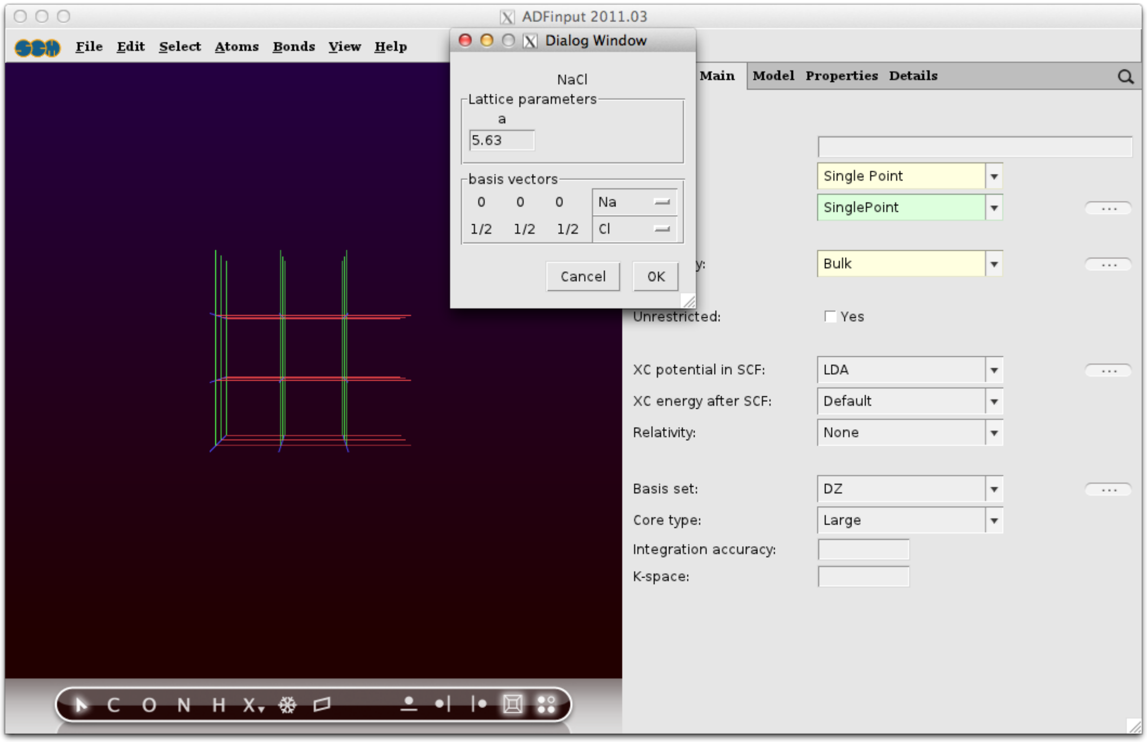
The Crystal Structure Database

If you are lucky your crystal structure is in the database. Of course there are infinitely many possible crystal structures, so the database has to be incomplete. Nevertheless, the most common structures are there. NaCl is one of them.

Start BANDinput (or DFTBinput, and switch the periodicity to 'Bulk')
Click on the snowflake like pictogram on the toolbar.
Select a "Cubic" lattice and then NaCl



Next a dialog pops up where you can change the parameters of the structure, such as lattice constants



NaCl

Lattice parameters

a: 5.63

basis vectors

0	0	0	Na
1/2	1/2	1/2	Cl

Single Point

SinglePoint

Bulk

Unrestricted: ☐ Yes

XC potential in SCF: LDA

XC energy after SCF: Default

Relativity: None

Basis set: DZ

Core type: Large

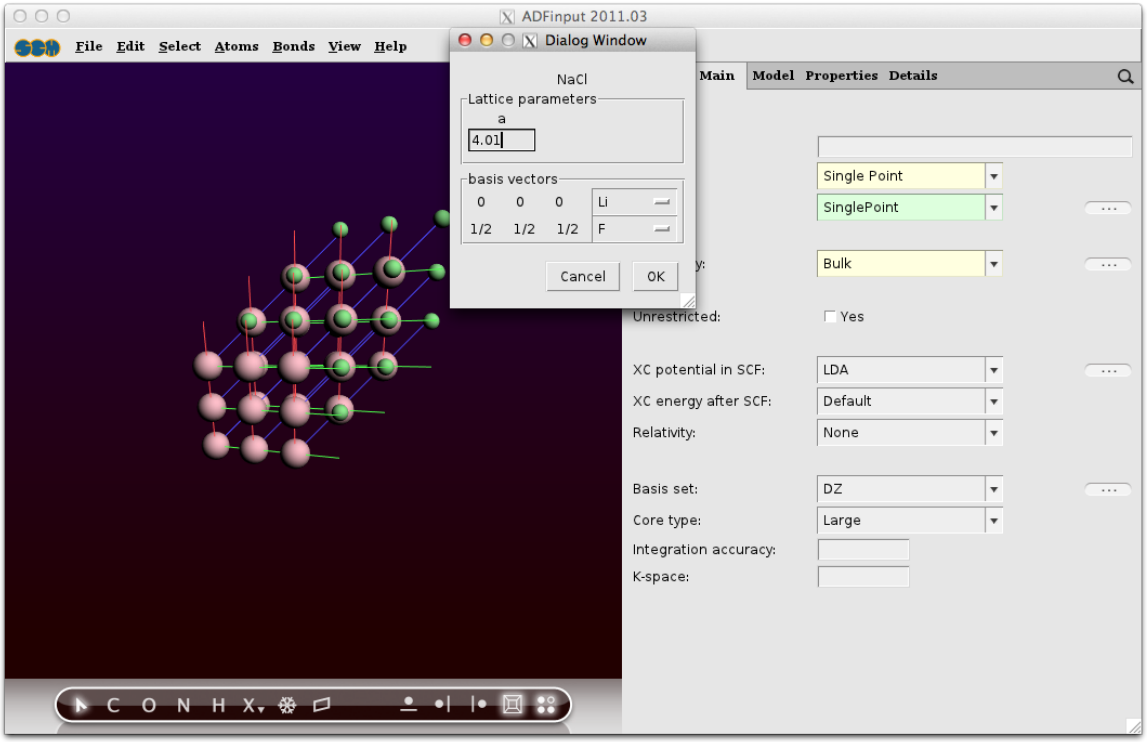
Integration accuracy:

K-space:

In this case there is no need to change anything.

`Click OK`

More often a crystal is not directly in the list. An example is LiF. It has the same crystal structure as NaCl, but other elements and a different lattice constant, namely 4.01:



NaCl

Lattice parameters

a: 4.01

basis vectors

0	0	0	Li
1/2	1/2	1/2	F

Single Point

SinglePoint

y: Bulk

Unrestricted: ☐ Yes

XC potential in SCF: LDA

XC energy after SCF: Default

Relativity: None

Basis set: DZ

Core type: Large

Integration accuracy:

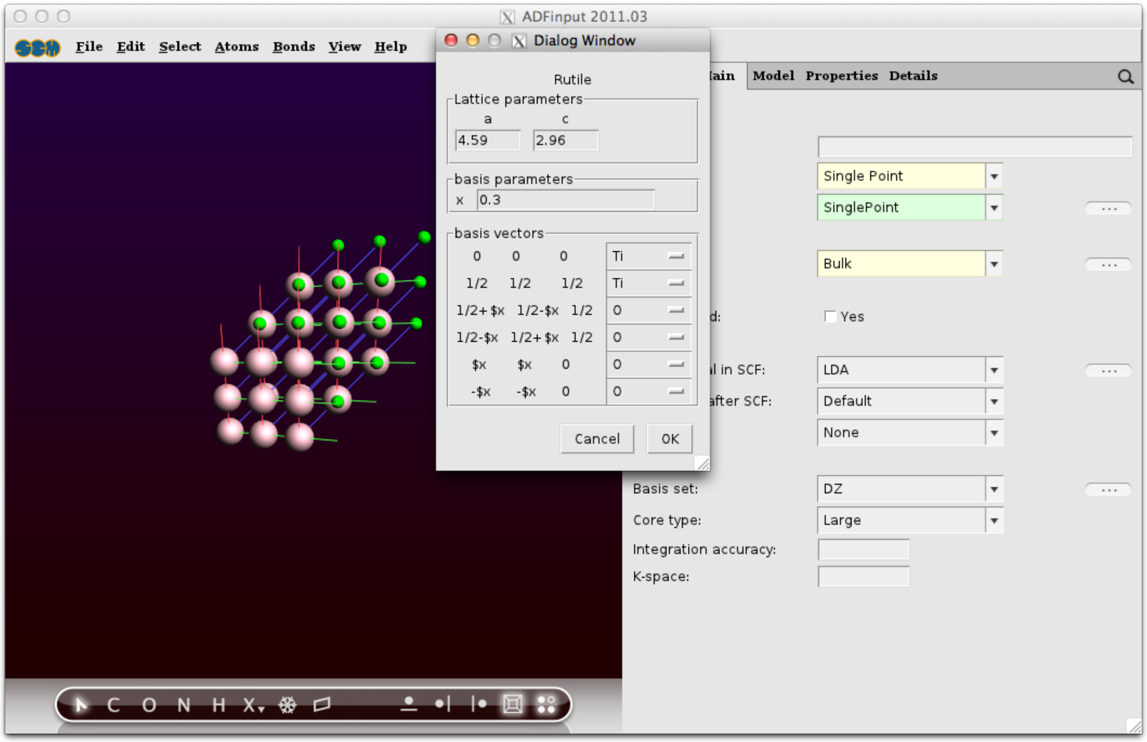
K-space:

Open again the NaCl dialog
Change the lattice constant and the elements as shown
Click OK

The NaCl crystal structure will be replaced by the new LiF crystal structure.

Some crystal structures have more parameters.

Select "Tetragonal" and then "rutile" from the snowflake tool
Click OK



Rutile

Lattice parameters

a 4.59

c 2.96

basis parameters

x 0.3

basis vectors

0	0	0	Ti
1/2	1/2	1/2	Ti
1/2+$x	1/2-$x	1/2	O
1/2-$x	1/2+$x	1/2	O
$x	$x	0	O
-$x	-$x	0	O

Single Point

SinglePoint

Bulk

d: ☐ Yes

l in SCF: LDA

after SCF: Default

None

Basis set: DZ

Core type: Large

Integration accuracy:

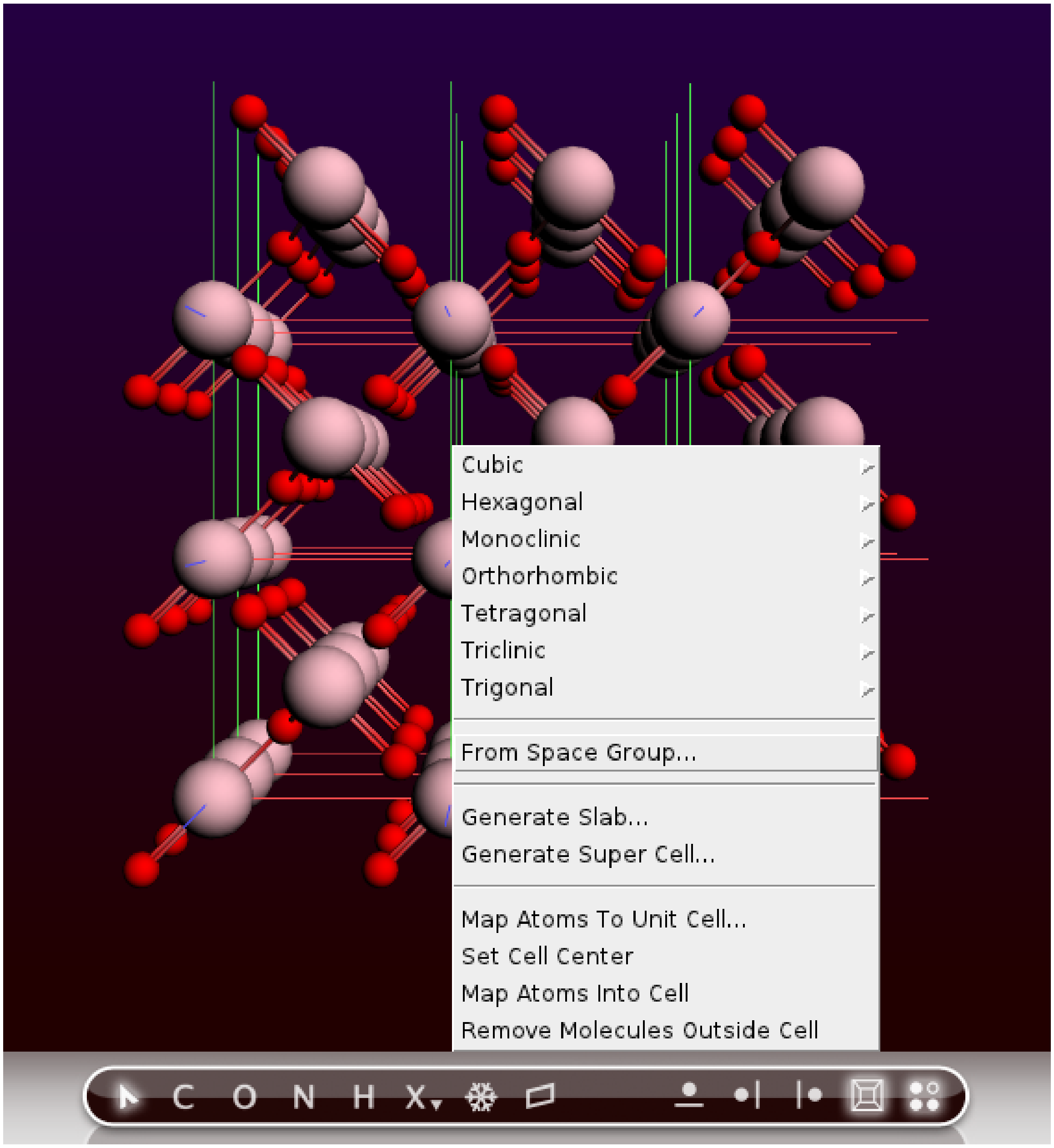
K-space:

As you can see, it has two lattice parameters that need to be specified. But now also the positions of the oxygens have a parameter "x"

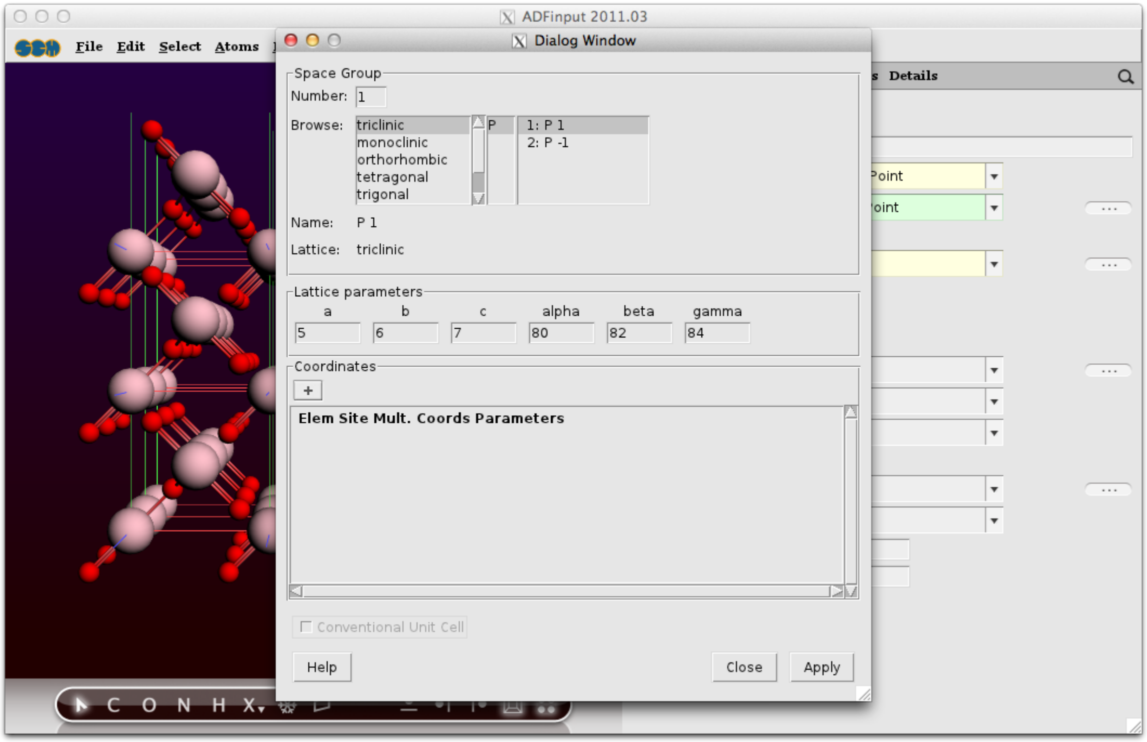
Crystal builder (from space group information)

The structure database is very convenient but by necessity incomplete. A more powerful approach is to build 3D crystals from the space group information. Here we give an example on how to build TiO2, also known as rutile.

```
Open the crystal builder:
Click on the snowflake tool and select "From Space Group"
```



And the following window pops up



Space Group

Number: 1

Browse: triclinic, monoclinic, orthorhombic, tetragonal, trigonal | P | 1: P 1, 2: P -1

Name: P 1

Lattice: triclinic

Lattice parameters

a	b	c	alpha	beta	gamma
5	6	7	80	82	84

Coordinates

+

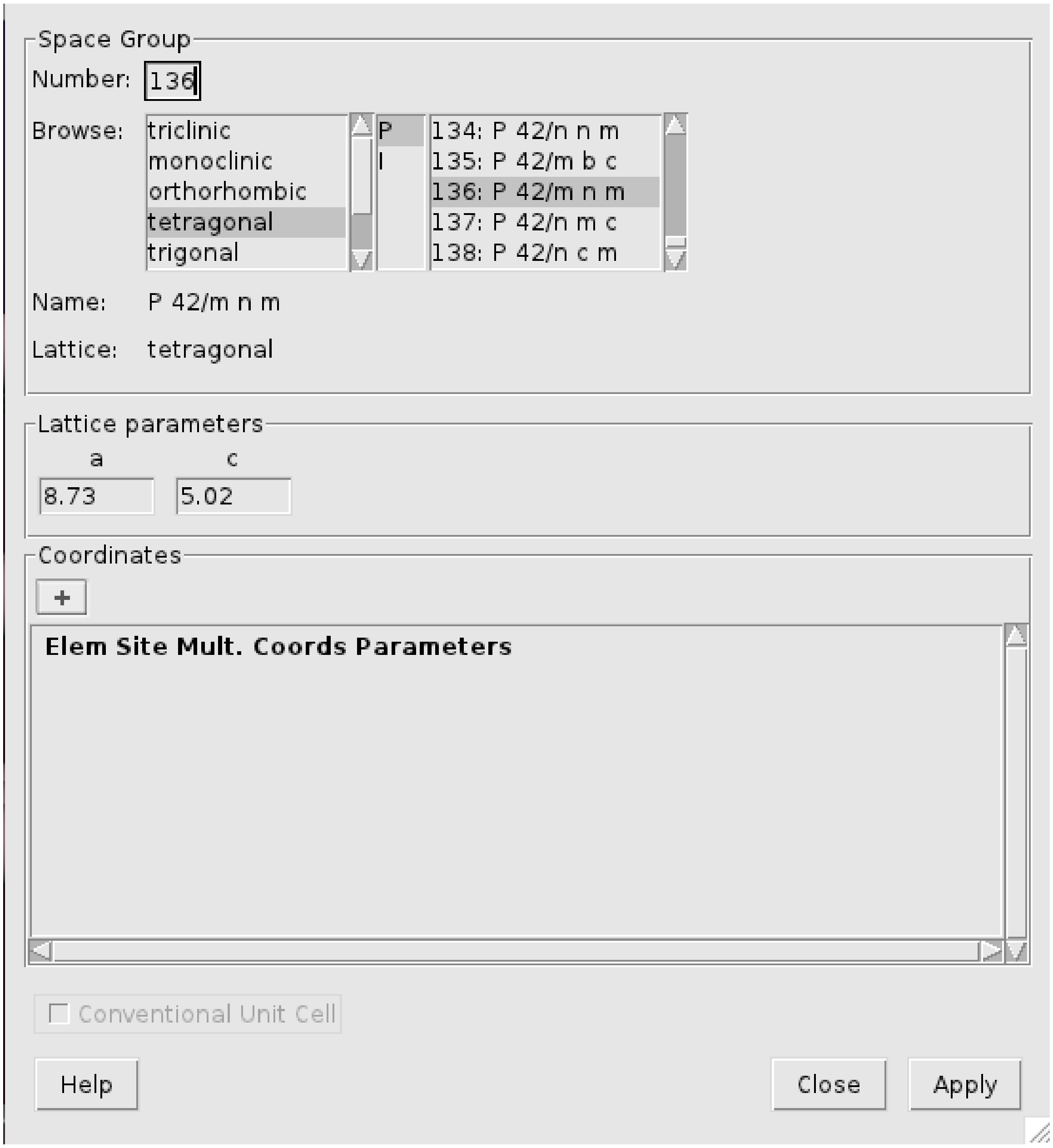
Elem Site Mult. Coords Parameters

☐ Conventional Unit Cell

Help Close Apply

Rutile has the symmetry of space group 136

`Enter 136 in the "Number" field, and a return`



Space Group

Number: 136

Browse: tetragonal — P — 136: P 42/m n m

Name: P 42/m n m

Lattice: tetragonal

Lattice parameters

a	c
8.73	5.02

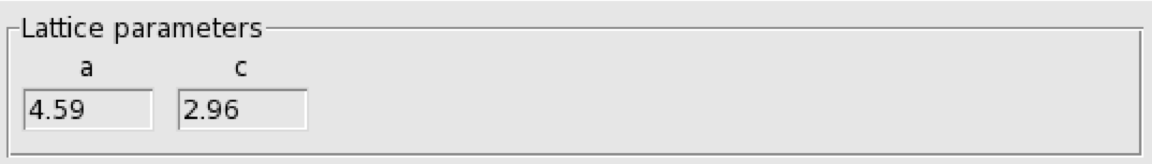
Coordinates

Elem Site Mult. Coords Parameters

☐ Conventional Unit Cell

Note how the Browser reflects the change and also how the "Name" and "Lattice" values change

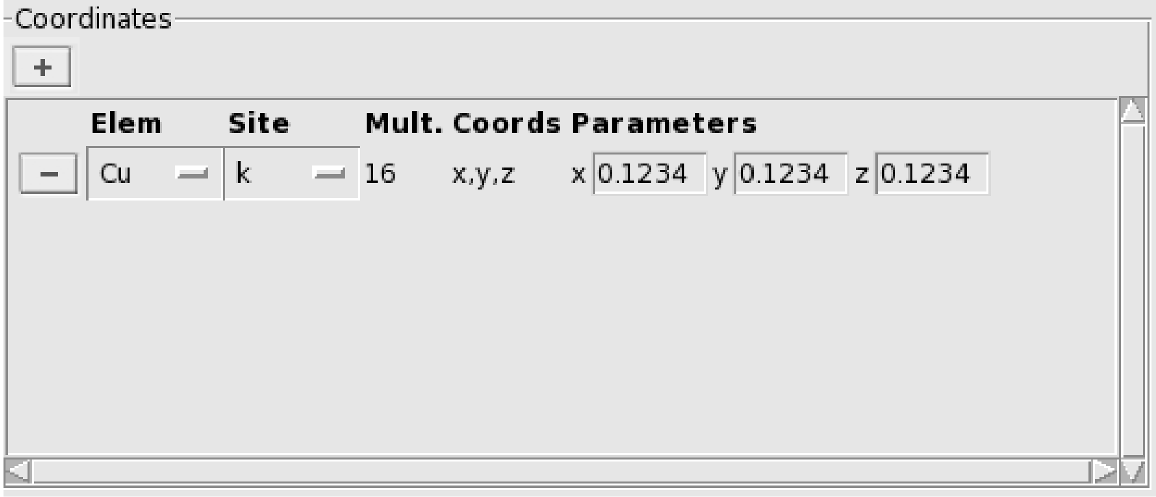
Now set the two lattice parameters as below



Lattice parameters

a	c
4.59	2.96

We still need to define the atomic coordinates. For starters click on the plus below "Coordinates"



Elem	Site	Mult.	Coords	Parameters
Cu	k	16	x,y,z	x 0.1234 y 0.1234 z 0.1234

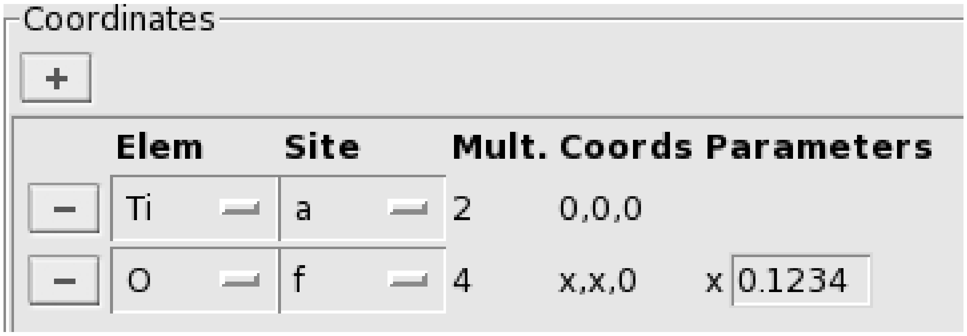
In a book on crystal structures you can find that rutile has two sites occupied. The Ti atom is on the "a" site

Select the Ti atom and select the "a" site

Elem	Site	Mult.	Coords	Parameters
Ti	a	2	0,0,0	

The oxygens occupy the "f" site.

Click on the plus to add a site
Change the atom type to "O" and the site to "f"

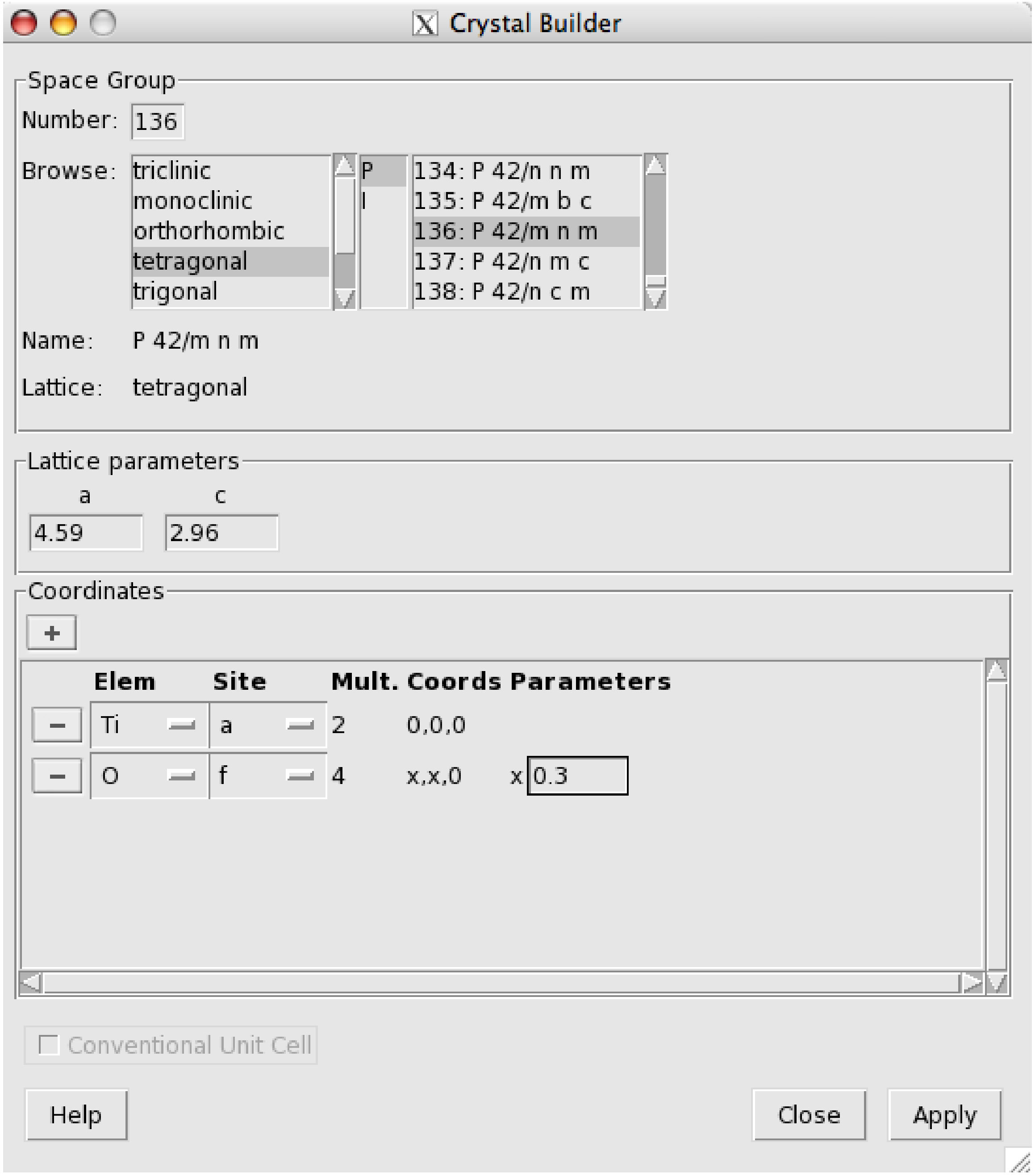


Elem	Site	Mult.	Coords	Parameters
Ti	a	2	0,0,0	
O	f	4	x,x,0	x 0.1234

As you can see in the "Coords" column and the "Parameters" column, this site has an undetermined parameter "x". (It represents a symmetry line for this space group.) In the book you can find that for TiO2 "x=0.3".

Set "x" to 0.3

The final dialog looks like



Number: 136

Name: P 42/m n m

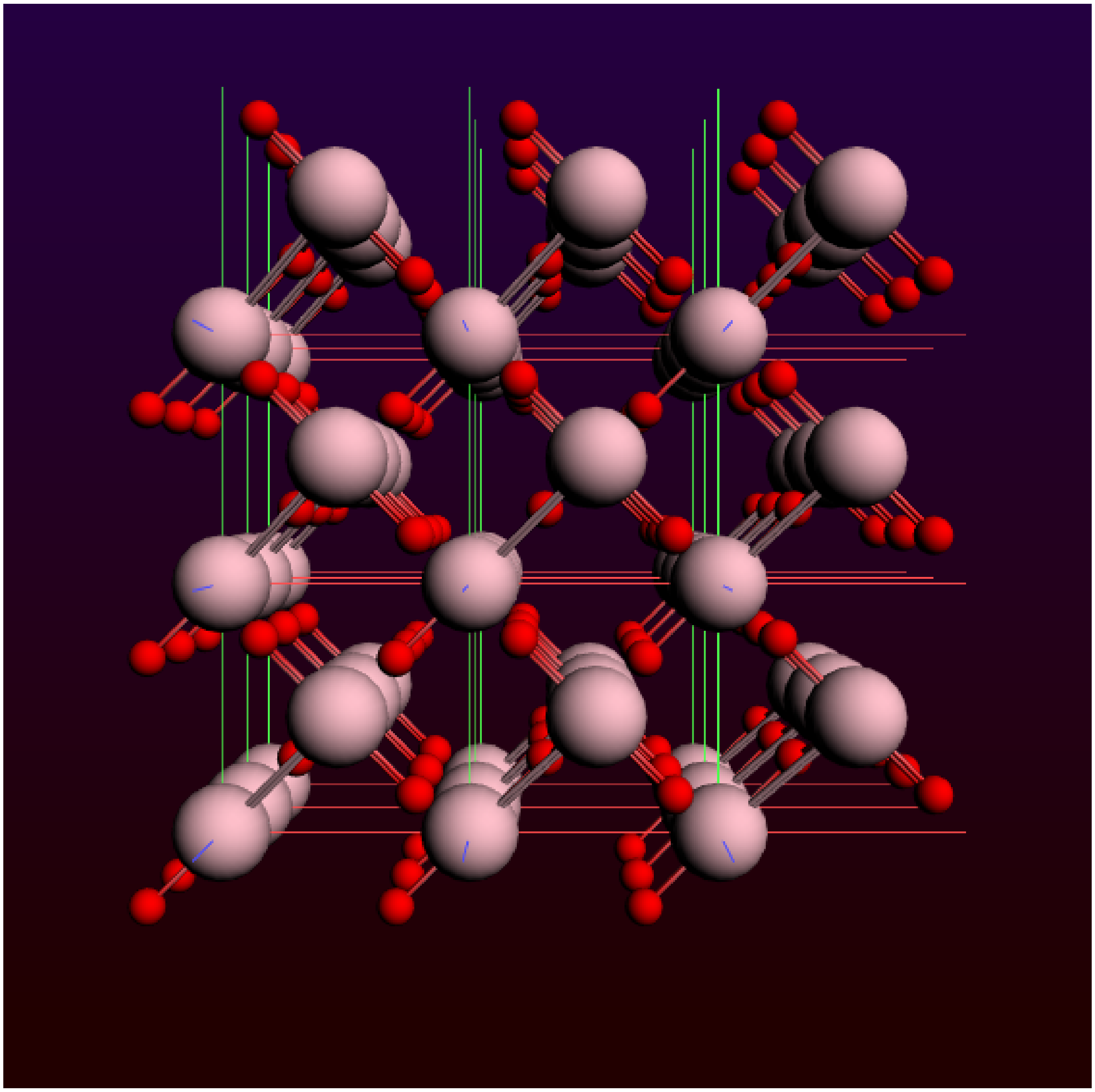
Lattice: tetragonal

a: 4.59

c: 2.96

Elem	Site	Mult.	Coords	Parameters
Ti	a	2	0,0,0	
O	f	4	x,x,0	x 0.3

`Press "Apply" and if that looks any good press "Close"`



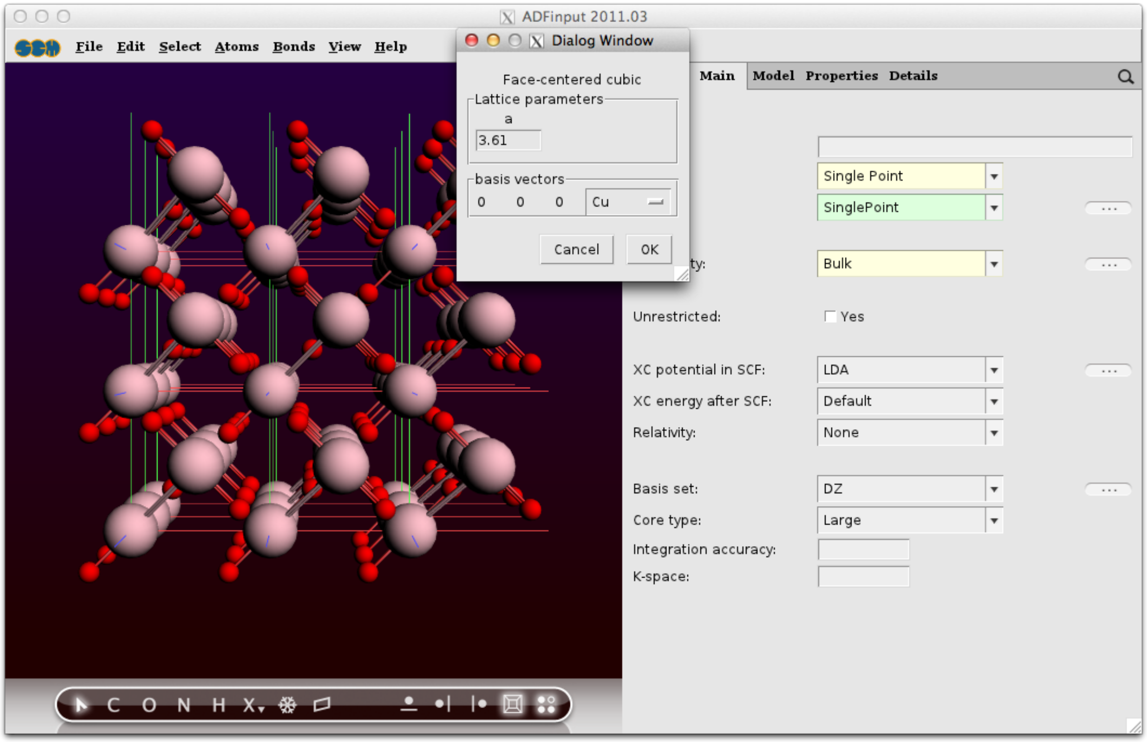
Slicer: building slabs

The slicer is a very easy, yet powerful tool to make slabs from *any* crystal structure.

A three layer slab of the Cu(111) surface

```
Select fcc from the "Cubic" crystals
```

The element and lattice constant are already correct for Cu.



Face-centered cubic
Lattice parameters
a
3.61
basis vectors
0 0 0 Cu
Cancel OK

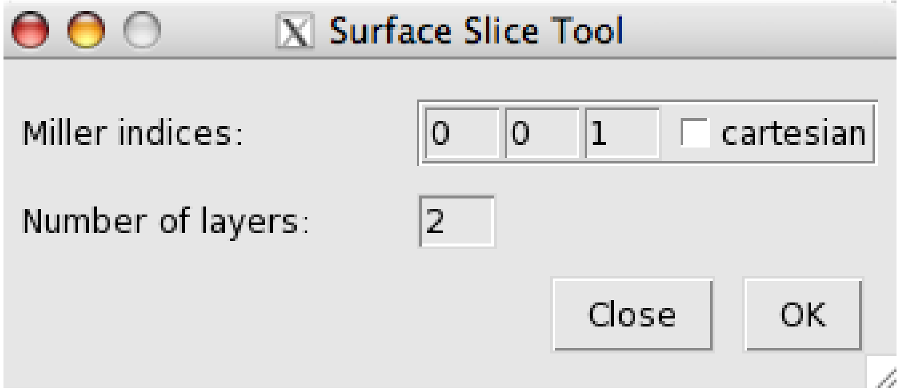
Single Point
SinglePoint
ty: Bulk
Unrestricted: ☐ Yes
XC potential in SCF: LDA
XC energy after SCF: Default
Relativity: None
Basis set: DZ
Core type: Large
Integration accuracy:
K-space:

Press "OK" to generate the Cu lattice

Let us invoke the slicer tool to cut out the slab. The slice tool icon looks like this: ▱

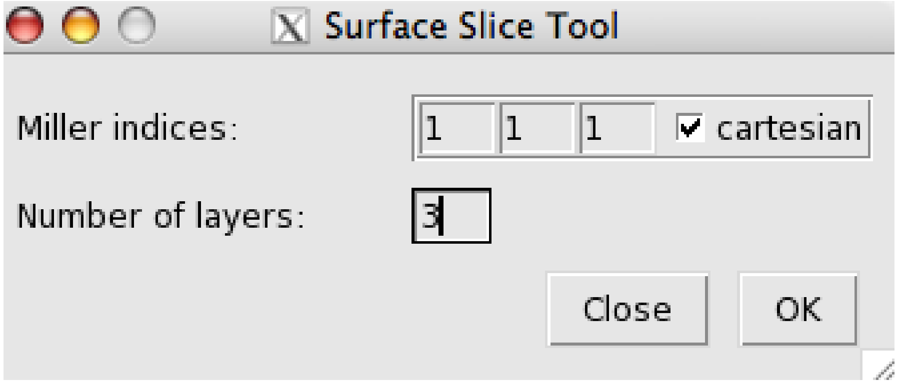
Click on the slicer tool icon in the toolbar

The following dialog appears



Miller indices: 0 0 1 ☐ cartesian
Number of layers: 2
Close OK

Set the Miller indices to (1,1,1)
Select Cartesian
Set the number of layers to 3



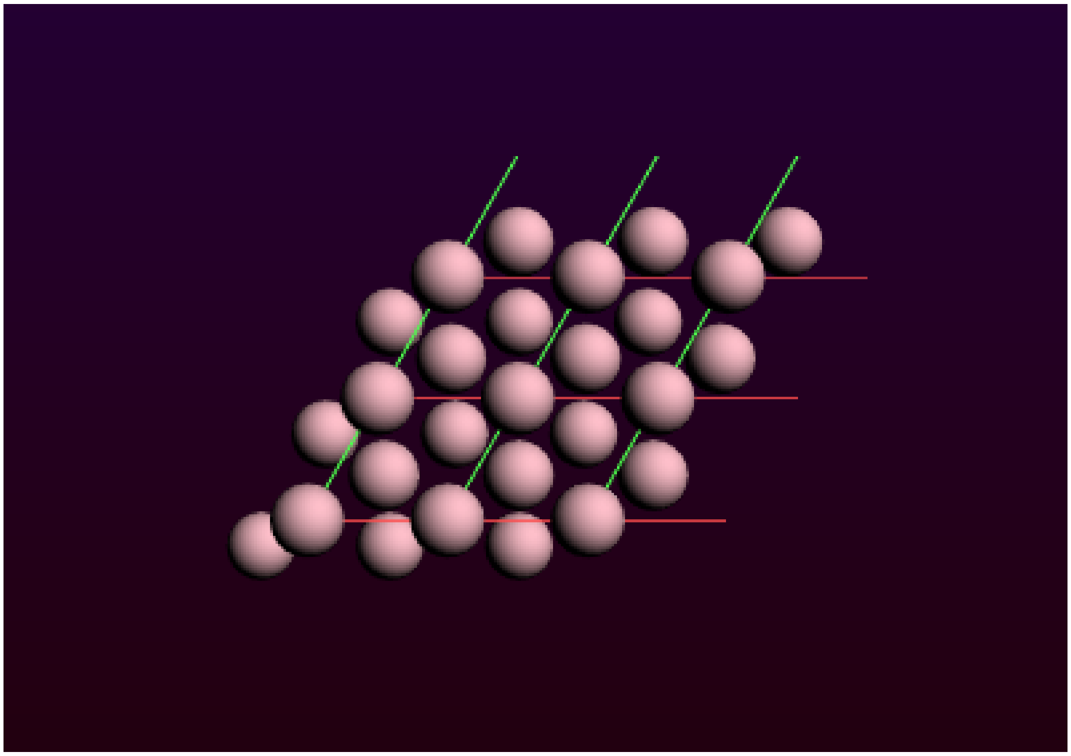
Miller indices: 1 1 1 ☑ cartesian

Number of layers: 3

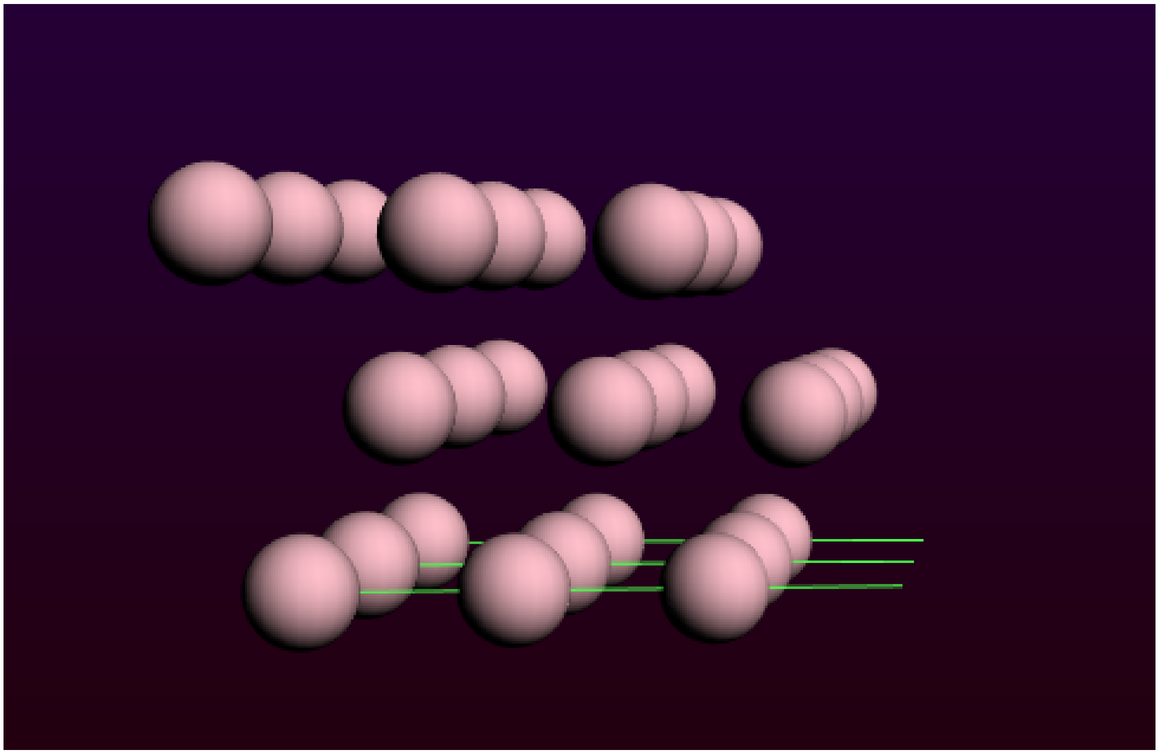
The "Cartesian" option is needed because the Miller indices are usually thought in the conventional unit cell rather than the primitive (minimal) unit cell.

`Press OK`

After pressing OK you will see (from the top)



You may want to rotate it or press the side view buttons in the toolbar to convince yourself that it is a three layer slab.



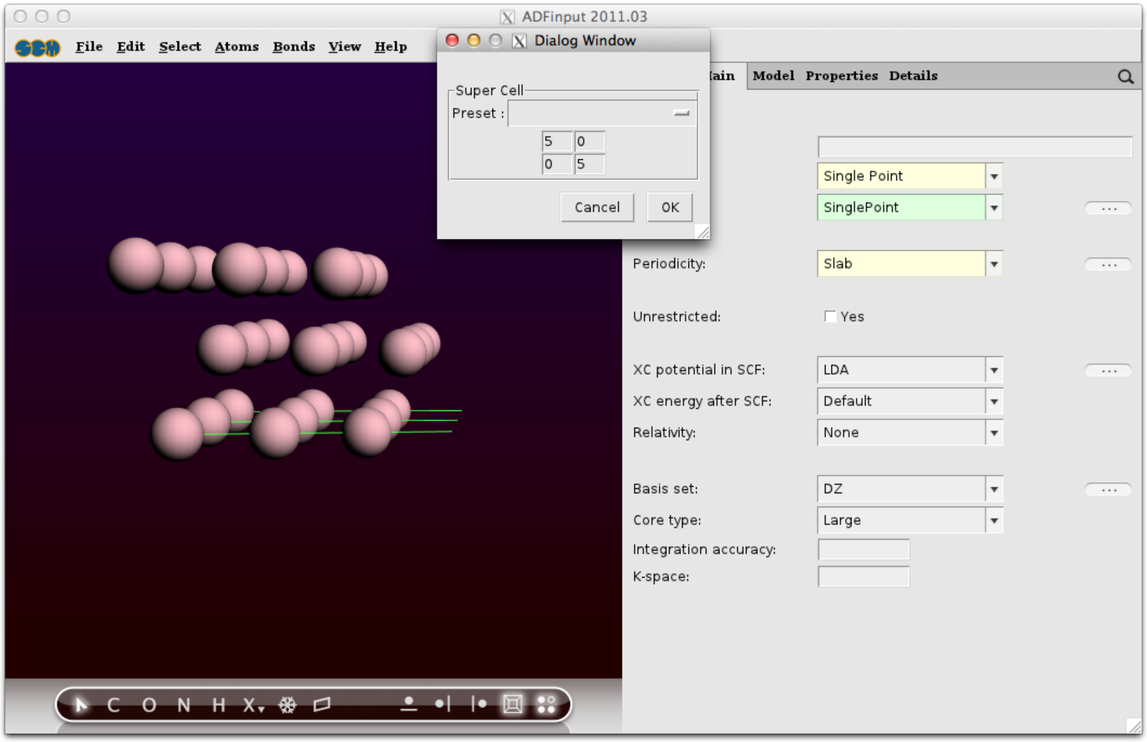
Enlarging the unit cell

Thus far, we have always created primitive unit cells: the smallest possible. Quite often you want to use a larger, less symmetric unit cell. You can do this for chains, slabs, and crystals, but we will demonstrate how it works for a slab.

We will continue to work with the 3-layer Cu slab:

`Select the` **Edit → Crystal → Generate Super Cell...** `command`

Thus invoking the Super Cell Tool



Super Cell

Preset :

5	0
0	5

Cancel OK

Single Point

SinglePoint

Periodicity: Slab

Unrestricted: ☐ Yes

XC potential in SCF: LDA

XC energy after SCF: Default

Relativity: None

Basis set: DZ

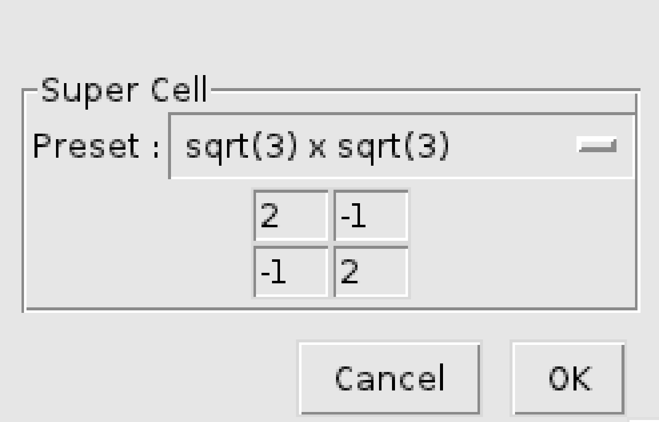
Core type: Large

Integration accuracy:

K-space:

Here you see how new lattice vectors are expressed in terms of old ones. Because we have a slab this is a 2x2 matrix.

```
Select the "sqrt(3) x sqrt(3)" option from the "Preset" menu
```



Super Cell

Preset : sqrt(3) x sqrt(3)

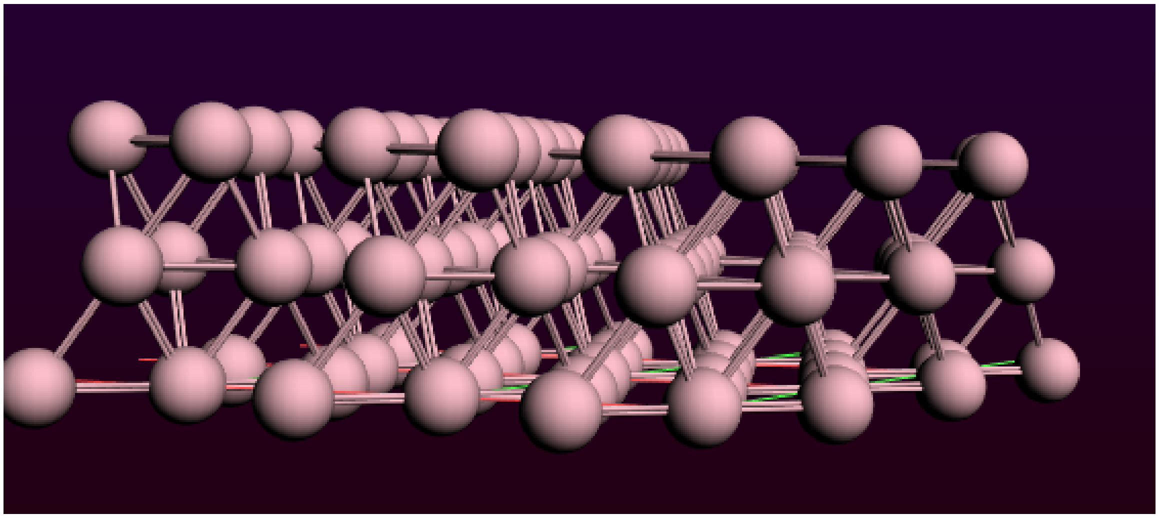
2	-1
-1	2

Cancel OK

The matrix has now changed into 2,-1,-1,2.

```
Press OK
```

and you get a unit cell with three atoms per layer:



```
Close BANDinput
```

Tutorial 4: Excitation energies of ethene

First you will construct an ethene molecule and optimize its geometry. As this is basically the same procedure as in Tutorial 1, only short instructions will be given.

Next you will set up the calculation of excitation energies, and let ADF perform the calculation.

Finally, using ADFlevels, ADFspectra and ADFview, you will examine the results.

Step 1: Start ADFinput

For this tutorial we again prefer to work in the Tutorial directory.

You know how to start ADFjobs (in your home directory), and move to the Tutorial directory:

```
cd $HOME
Start ADFjobs
Click on the Tutorial folder icon
```

Next start ADFinput using the SCM menu:

`Select the` **SCM → ADF Input** `command`

Note that if you start ADFinput via the SCM menu you will start ADFinput without loading a job. If you wish to open ADFinput for a particular job, click on the 'ADF' button in front of it.

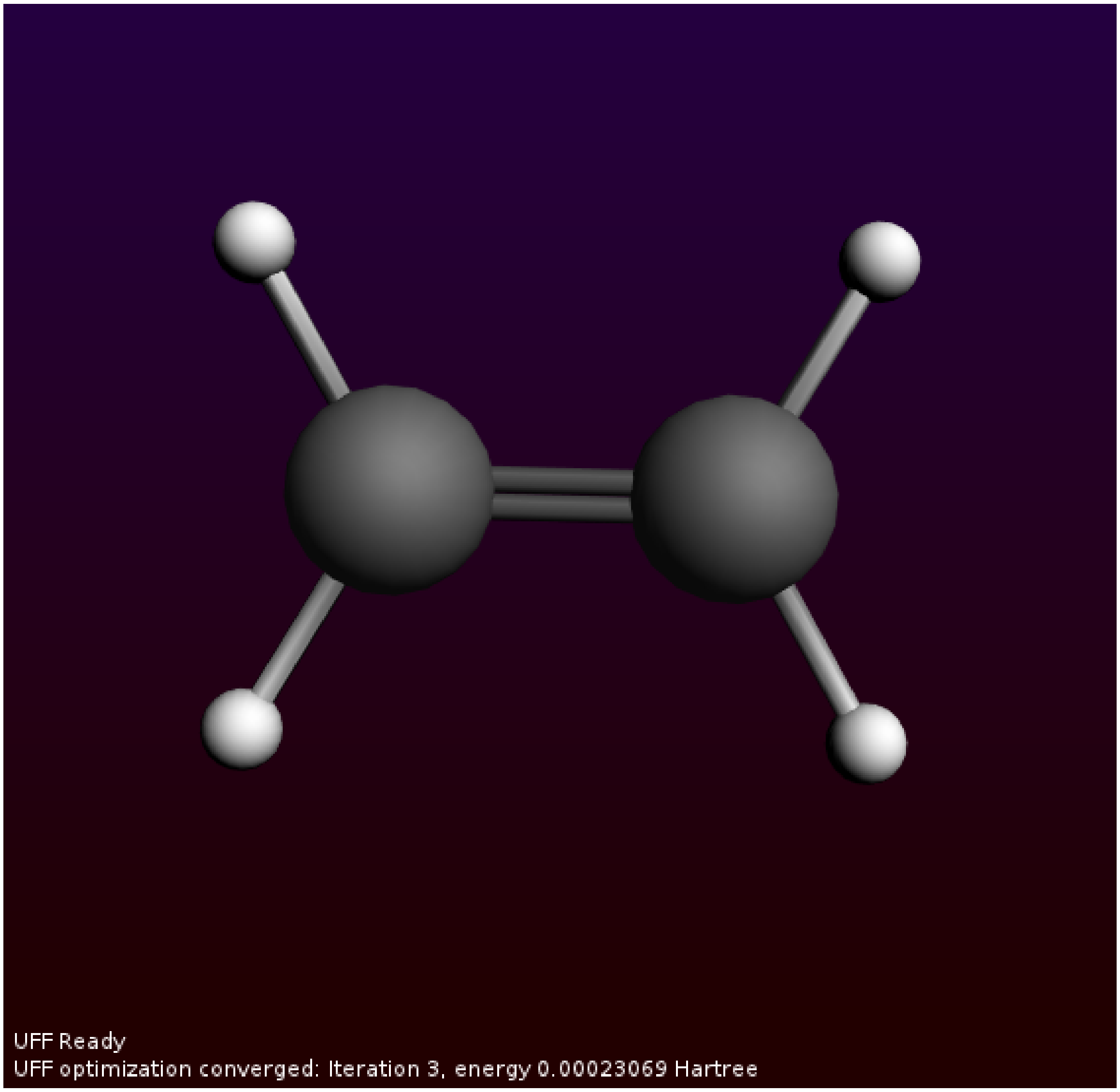
For the View command (and Movie, Levels, and so on) the behavior is different: it will immediately load the job that is selected in ADFjobs.

Step 2: Create your ethene molecule

First we construct an ethene molecule, and pre-optimize its geometry:

Select the C-tool by clicking on the button with the 'C'
Select the Double bond mode **Bond tool → Double**
    (or use the shortcut: press the '2' - key)
Click somewhere in the drawing area to create a carbon atom
Click again to create a second carbon atom (with a double bond)
Click on the just created Carbon atom to stop bonding
Select the **Atoms → Add Hydrogen** command
Click the cog wheel to pre-optimize

Your ethene molecule should look something like this:

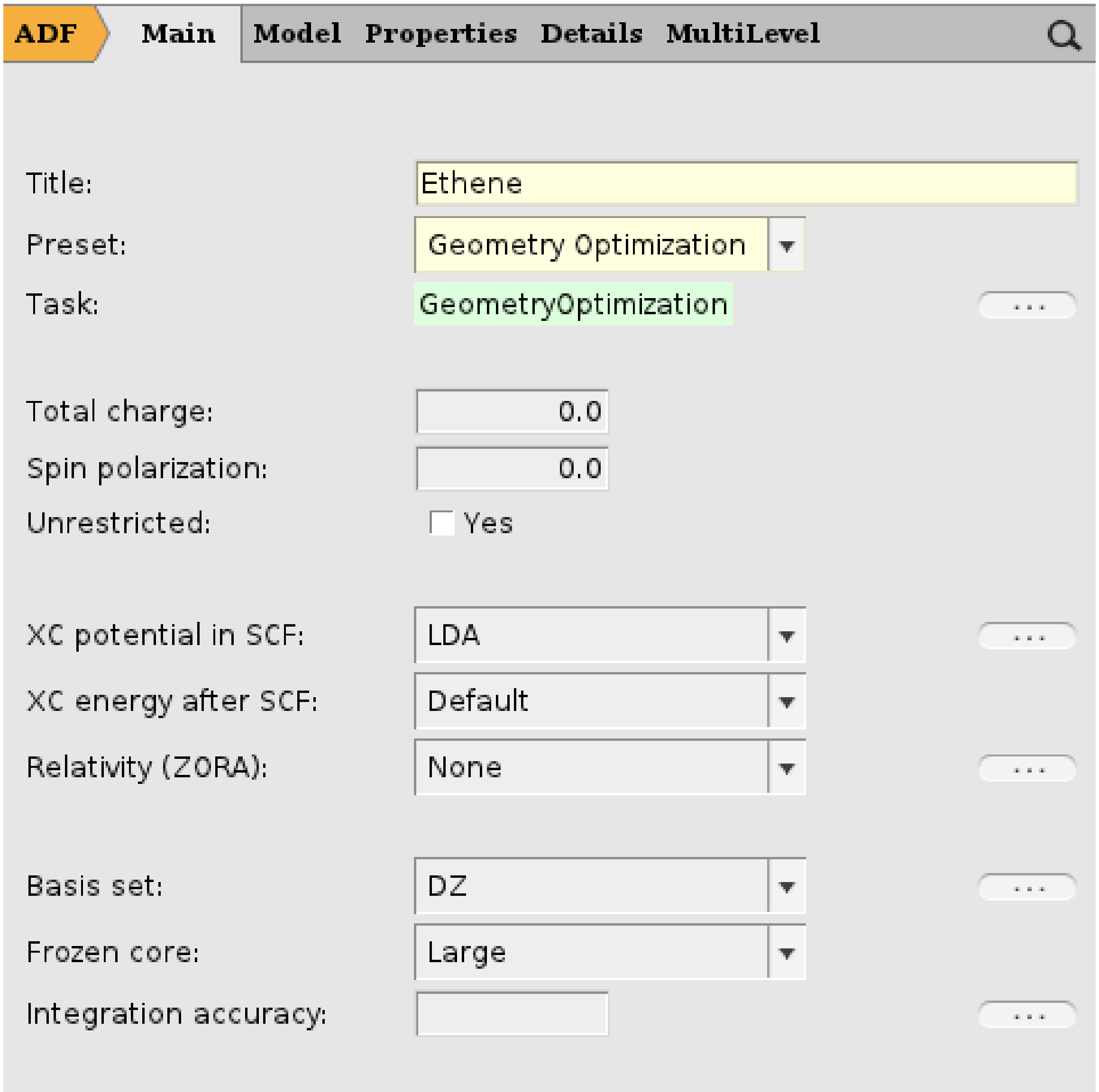


```
UFF Ready
UFF optimization converged: Iteration 3, energy 0.00023069 Hartree
```

Step 3: Optimize the geometry

The next step is to optimize the geometry using ADF:

```
Enter a title in the Title field (like 'Ethene')
Select the 'Geometry Optimization' preset
```



Title: Ethene
Preset: Geometry Optimization
Task: GeometryOptimization
Total charge: 0.0
Spin polarization: 0.0
Unrestricted: ☐ Yes
XC potential in SCF: LDA
XC energy after SCF: Default
Relativity (ZORA): None
Basis set: DZ
Frozen core: Large
Integration accuracy:

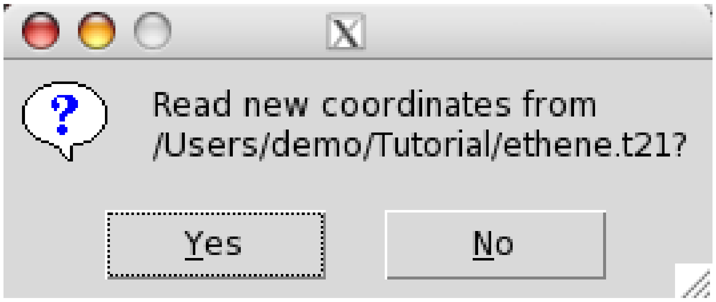
With the proper options selected, now run ADF:

`Select the` **File → Run** `command`
`Click 'Yes' in the pop-up to save the current input`
`In the file select box, choose a name for your file`
`(for example 'ethene') and click 'Save'`

Now ADF will start automatically, and you can follow the calculation using the logfile that is automatically shown.

```
Wait until the optimization is ready (should take very little time)
```

The following dialog should appear:


Read new coordinates from /Users/demo/Tutorial/ethene.t21?

Click 'Yes' to update the coordinates

Step 4: Calculate the excitation energies

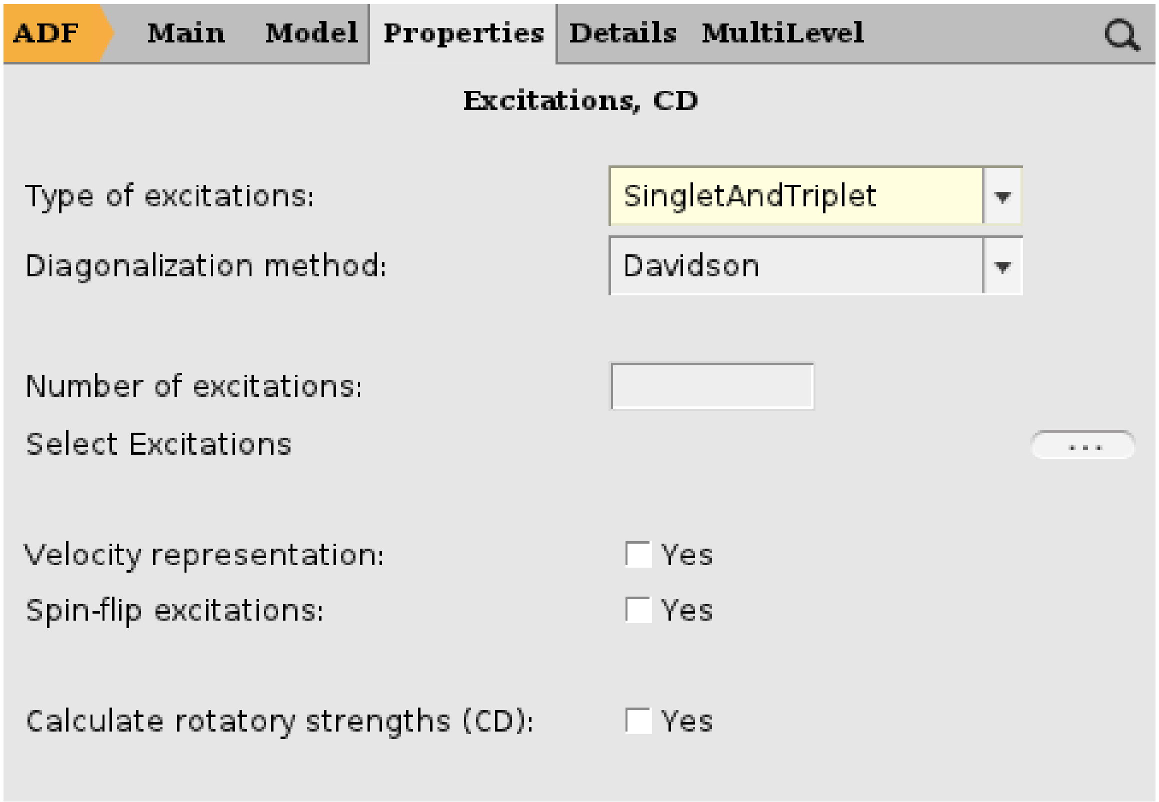
Select calculations options

To set up the calculation of the excitation spectrum:

Adjust the title to something like 'Ethene excitations'

Select the 'Single Point' template

Use the panel bar **Properties → Excitations, CD** command to go to the Excitations panel
For the 'Type of excitations' option, Select 'Singlet and Triplet'



Type of excitations: SingletAndTriplet

Diagonalization method: Davidson

Number of excitations:

Select Excitations ...

Velocity representation: ☐ Yes

Spin-flip excitations: ☐ Yes

Calculate rotatory strengths (CD): ☐ Yes

For the tutorial this set up is fine, normally you would also need to select an XC potential that gives better results, for example SAOP.

Run the calculation

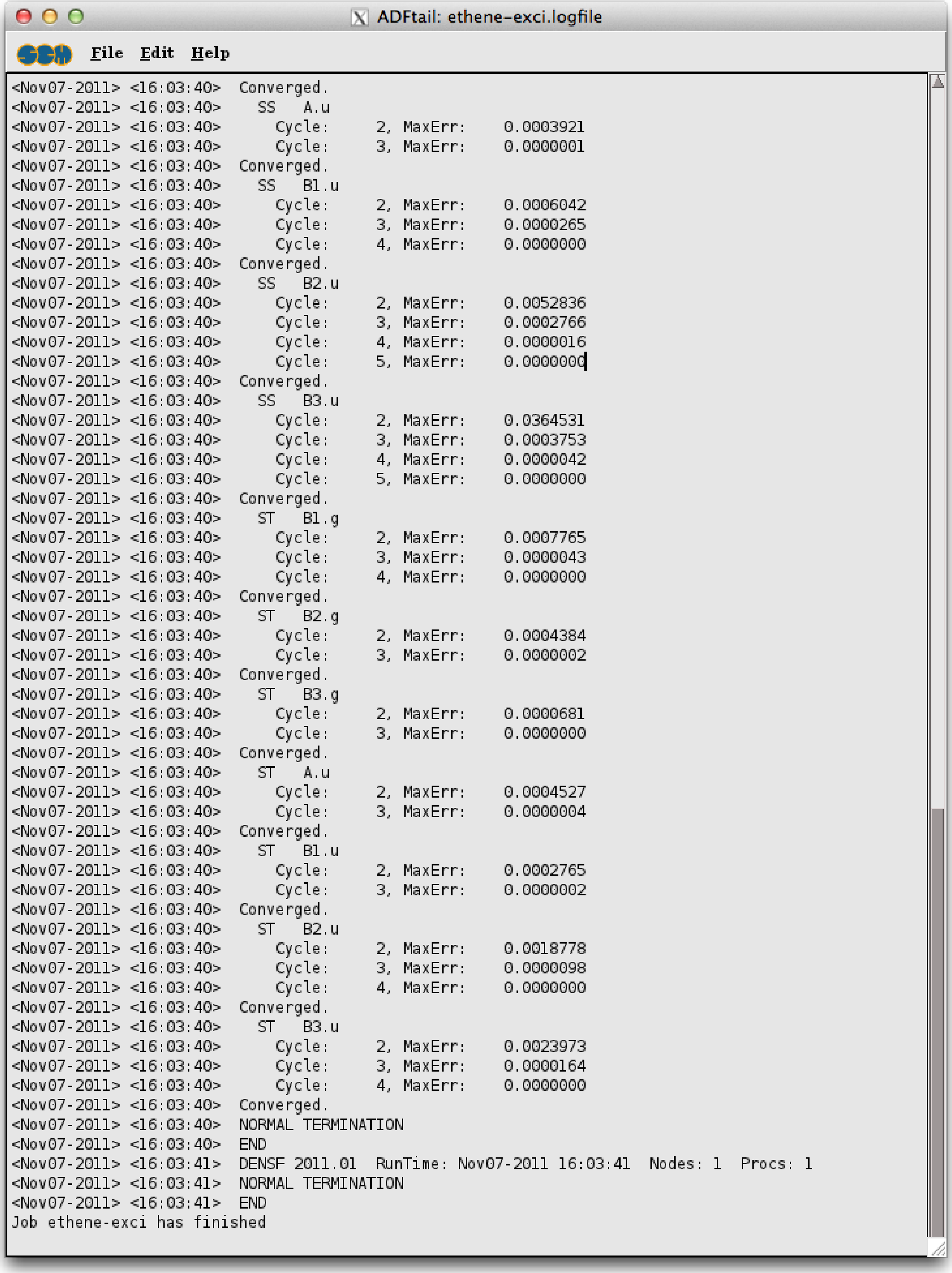
Now everything is ready to actually run ADF. Before running we will save the current input in a different file (though this is not really required):

`Select` **File → Save As...**
`Enter a filename (ethene-exci) and click 'Save'`
`Select` **File → Run**
`Wait for the calculation to finish`

Step 5: Results of your calculation

Logfile: ADFtail

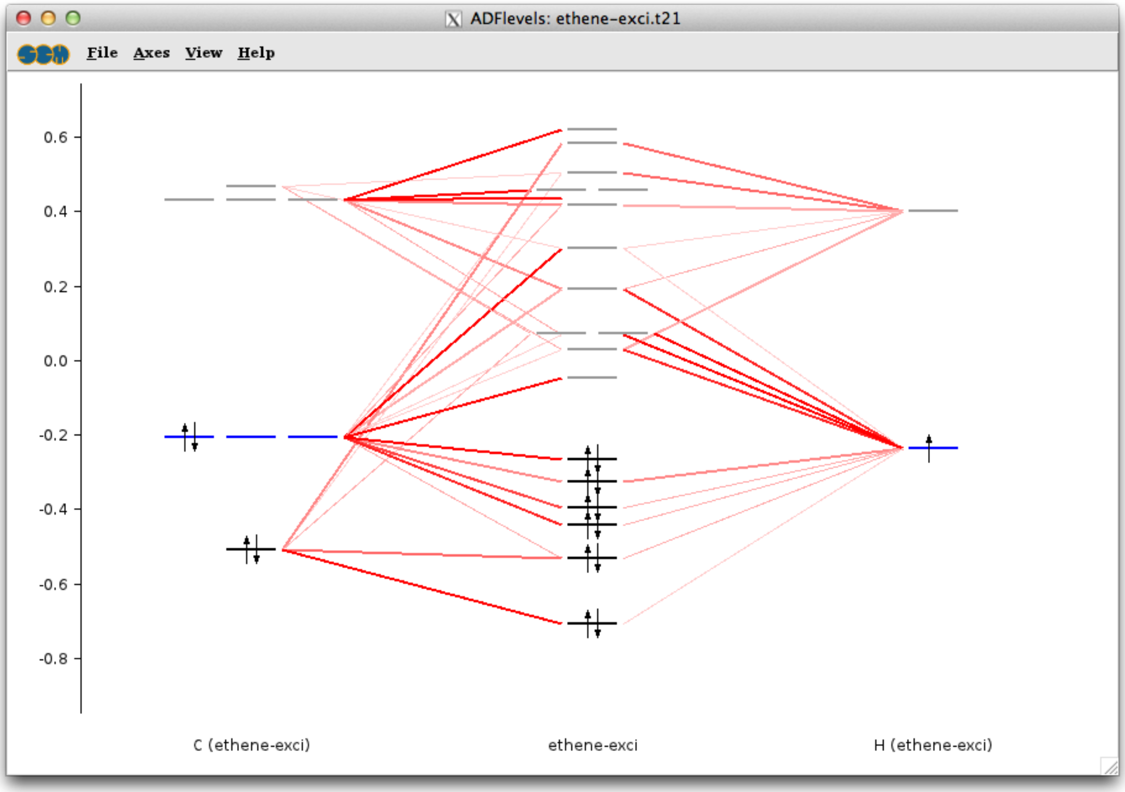
The logfile shows you that the calculation has finished, and that indeed the excitation code has been running:



```
<Nov07-2011> <16:03:40>  Converged.
<Nov07-2011> <16:03:40>    SS   A.u
<Nov07-2011> <16:03:40>      Cycle:     2, MaxErr:    0.0003921
<Nov07-2011> <16:03:40>      Cycle:     3, MaxErr:    0.0000001
<Nov07-2011> <16:03:40>  Converged.
<Nov07-2011> <16:03:40>    SS   B1.u
<Nov07-2011> <16:03:40>      Cycle:     2, MaxErr:    0.0006042
<Nov07-2011> <16:03:40>      Cycle:     3, MaxErr:    0.0000265
<Nov07-2011> <16:03:40>      Cycle:     4, MaxErr:    0.0000000
<Nov07-2011> <16:03:40>  Converged.
<Nov07-2011> <16:03:40>    SS   B2.u
<Nov07-2011> <16:03:40>      Cycle:     2, MaxErr:    0.0052836
<Nov07-2011> <16:03:40>      Cycle:     3, MaxErr:    0.0002766
<Nov07-2011> <16:03:40>      Cycle:     4, MaxErr:    0.0000016
<Nov07-2011> <16:03:40>      Cycle:     5, MaxErr:    0.0000000
<Nov07-2011> <16:03:40>  Converged.
<Nov07-2011> <16:03:40>    SS   B3.u
<Nov07-2011> <16:03:40>      Cycle:     2, MaxErr:    0.0364531
<Nov07-2011> <16:03:40>      Cycle:     3, MaxErr:    0.0003753
<Nov07-2011> <16:03:40>      Cycle:     4, MaxErr:    0.0000042
<Nov07-2011> <16:03:40>      Cycle:     5, MaxErr:    0.0000000
<Nov07-2011> <16:03:40>  Converged.
<Nov07-2011> <16:03:40>    ST   B1.g
<Nov07-2011> <16:03:40>      Cycle:     2, MaxErr:    0.0007765
<Nov07-2011> <16:03:40>      Cycle:     3, MaxErr:    0.0000043
<Nov07-2011> <16:03:40>      Cycle:     4, MaxErr:    0.0000000
<Nov07-2011> <16:03:40>  Converged.
<Nov07-2011> <16:03:40>    ST   B2.g
<Nov07-2011> <16:03:40>      Cycle:     2, MaxErr:    0.0004384
<Nov07-2011> <16:03:40>      Cycle:     3, MaxErr:    0.0000002
<Nov07-2011> <16:03:40>  Converged.
<Nov07-2011> <16:03:40>    ST   B3.g
<Nov07-2011> <16:03:40>      Cycle:     2, MaxErr:    0.0000681
<Nov07-2011> <16:03:40>      Cycle:     3, MaxErr:    0.0000000
<Nov07-2011> <16:03:40>  Converged.
<Nov07-2011> <16:03:40>    ST   A.u
<Nov07-2011> <16:03:40>      Cycle:     2, MaxErr:    0.0004527
<Nov07-2011> <16:03:40>      Cycle:     3, MaxErr:    0.0000004
<Nov07-2011> <16:03:40>  Converged.
<Nov07-2011> <16:03:40>    ST   B1.u
<Nov07-2011> <16:03:40>      Cycle:     2, MaxErr:    0.0002765
<Nov07-2011> <16:03:40>      Cycle:     3, MaxErr:    0.0000002
<Nov07-2011> <16:03:40>  Converged.
<Nov07-2011> <16:03:40>    ST   B2.u
<Nov07-2011> <16:03:40>      Cycle:     2, MaxErr:    0.0018778
<Nov07-2011> <16:03:40>      Cycle:     3, MaxErr:    0.0000098
<Nov07-2011> <16:03:40>      Cycle:     4, MaxErr:    0.0000000
<Nov07-2011> <16:03:40>  Converged.
<Nov07-2011> <16:03:40>    ST   B3.u
<Nov07-2011> <16:03:40>      Cycle:     2, MaxErr:    0.0023973
<Nov07-2011> <16:03:40>      Cycle:     3, MaxErr:    0.0000164
<Nov07-2011> <16:03:40>      Cycle:     4, MaxErr:    0.0000000
<Nov07-2011> <16:03:40>  Converged.
<Nov07-2011> <16:03:40>  NORMAL TERMINATION
<Nov07-2011> <16:03:40>  END
<Nov07-2011> <16:03:41>  DENSF 2011.01  RunTime: Nov07-2011 16:03:41  Nodes: 1  Procs: 1
<Nov07-2011> <16:03:41>  NORMAL TERMINATION
<Nov07-2011> <16:03:41>  END
Job ethene-exci has finished
```

Energy levels: level diagram and DOS

Select **SCM → Levels**

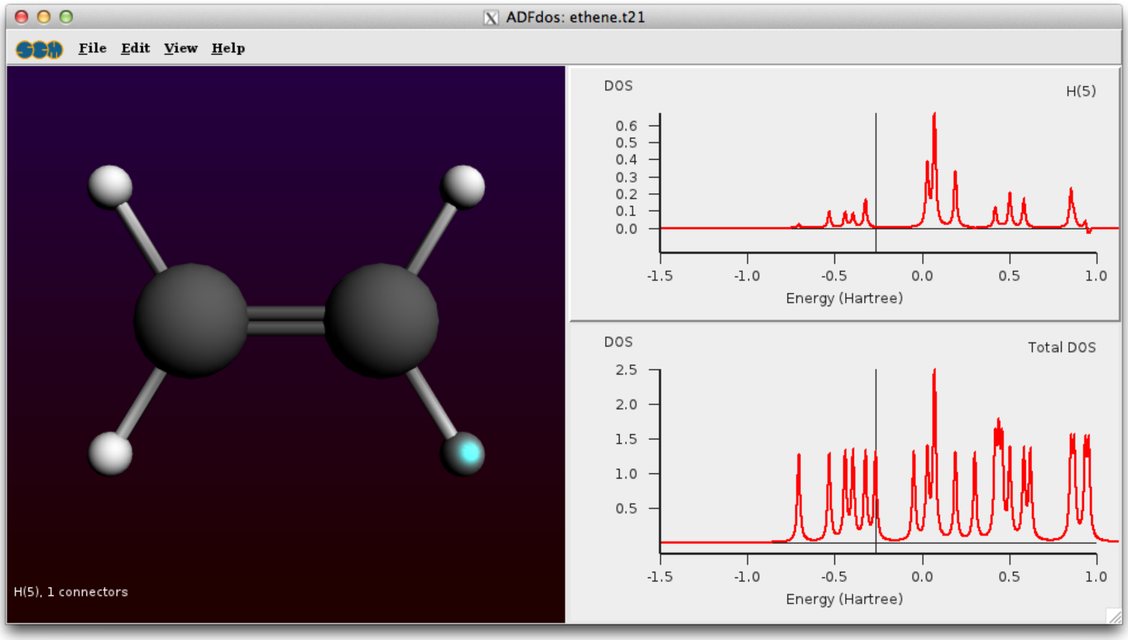


In this level diagram you can see that the HOMO and LUMO consist mainly of carbon p orbitals. It is also easy to see what orbitals the hydrogens take part in.

Note that the carbon and hydrogen stacks show all carbon and hydrogen atoms at once: they show the fragment type. ADFlevels can also show the individual fragments but when using atomic fragments you will get too many fragments. In this particular case symmetry is used, and since there is only one symmetry unique carbon atom and only one symmetry unique hydrogen atom you still would see only one stack per atom type.

`Select` **SCM → DOS**

`In the ADFdos window:`
View → Add Graph
`Select one hydrogen atom`

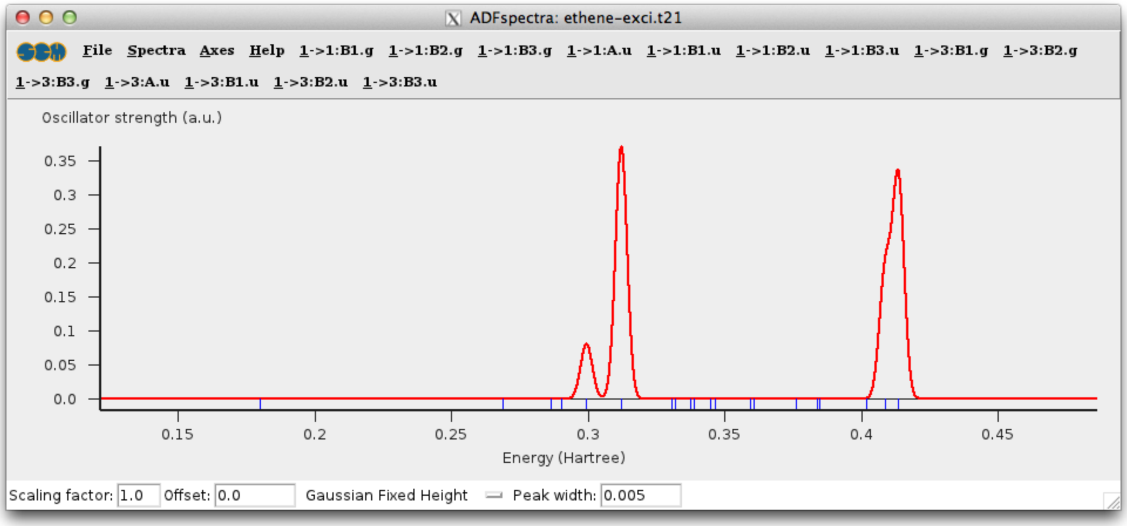


In these plots you can see that the partial DOS for the hydrogen atoms have no contribution to the HOMO. By right clicking on an atom you can also show partial DOS graphs with contribution from selected atoms and selected L-values only.

Excitation spectrum: ADFspectra

Select **SCM → Spectra**

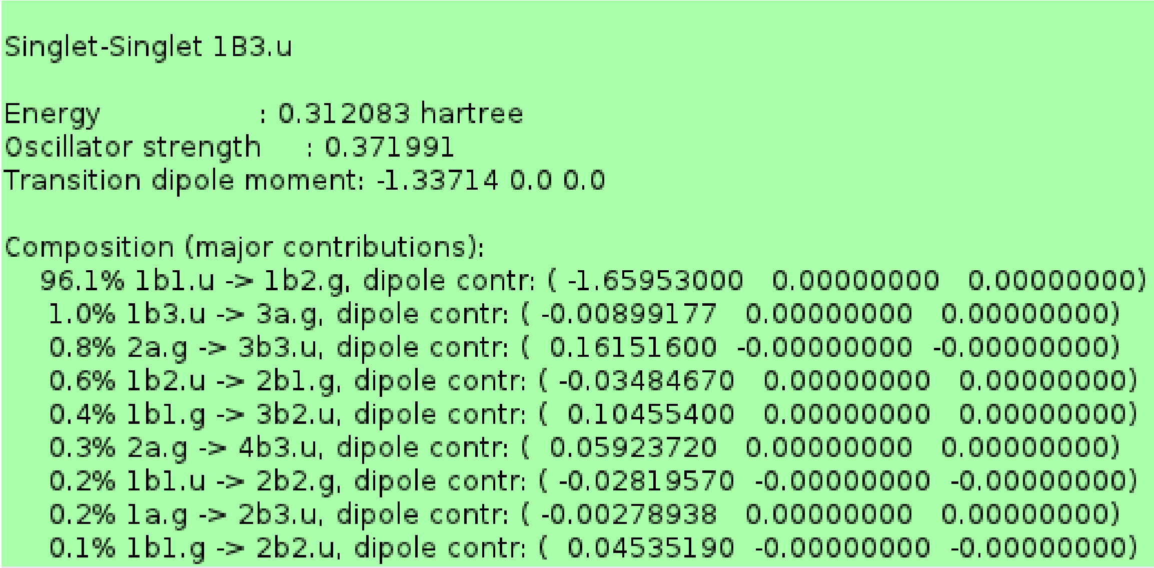
ADFspectra will start and show the calculated excitation spectrum.



Scaling factor: 1.0 Offset: 0.0 Gaussian Fixed Height Peak width: 0.005

When moving the mouse above a peak a pop-up will give you more information about that peak:

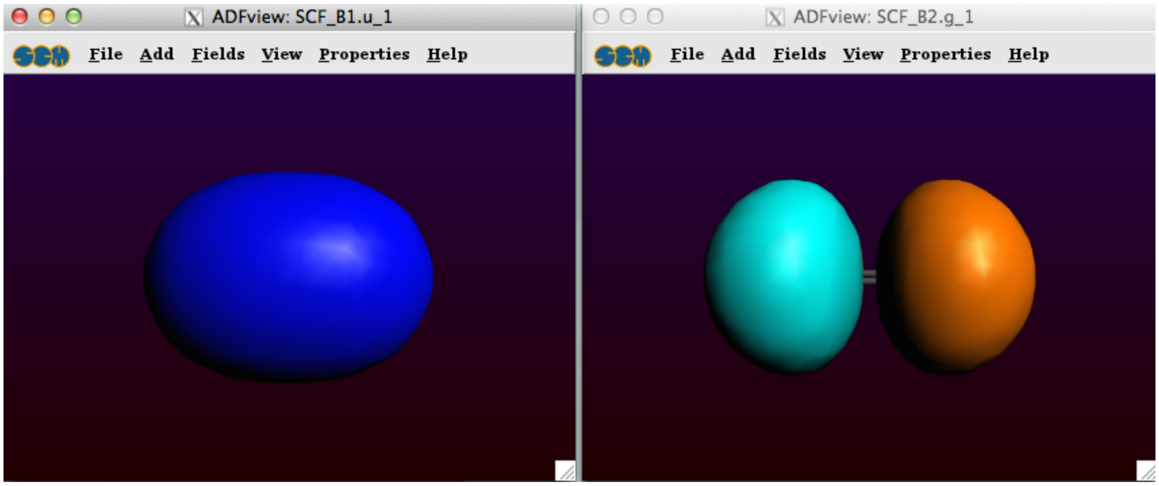
Move the mouse above the largest peak and hold it there



```
Singlet-Singlet 1B3.u

Energy               : 0.312083 hartree
Oscillator strength    : 0.371991
Transition dipole moment: -1.33714 0.0 0.0

Composition (major contributions):
   96.1% 1b1.u -> 1b2.g, dipole contr: ( -1.65953000   0.00000000   0.00000000)
    1.0% 1b3.u -> 3a.g, dipole contr: ( -0.00899177   0.00000000   0.00000000)
    0.8% 2a.g -> 3b3.u, dipole contr: (  0.16151600  -0.00000000  -0.00000000)
    0.6% 1b2.u -> 2b1.g, dipole contr: ( -0.03484670   0.00000000   0.00000000)
    0.4% 1b1.g -> 3b2.u, dipole contr: (  0.10455400   0.00000000   0.00000000)
    0.3% 2a.g -> 4b3.u, dipole contr: (  0.05923720   0.00000000   0.00000000)
    0.2% 1b1.u -> 2b2.g, dipole contr: ( -0.02819570  -0.00000000  -0.00000000)
    0.2% 1a.g -> 2b3.u, dipole contr: ( -0.00278938   0.00000000   0.00000000)
    0.1% 1b1.g -> 2b2.u, dipole contr: (  0.04535190  -0.00000000  -0.00000000)
```

The composition of the excitation in terms of orbital transitions is listed in the pop-up. If you move the mouse inside the pop-up and click on a line the corresponding orbitals will be shown using ADFview:

Move the mouse inside the pop-up and click on the line with the major contribution



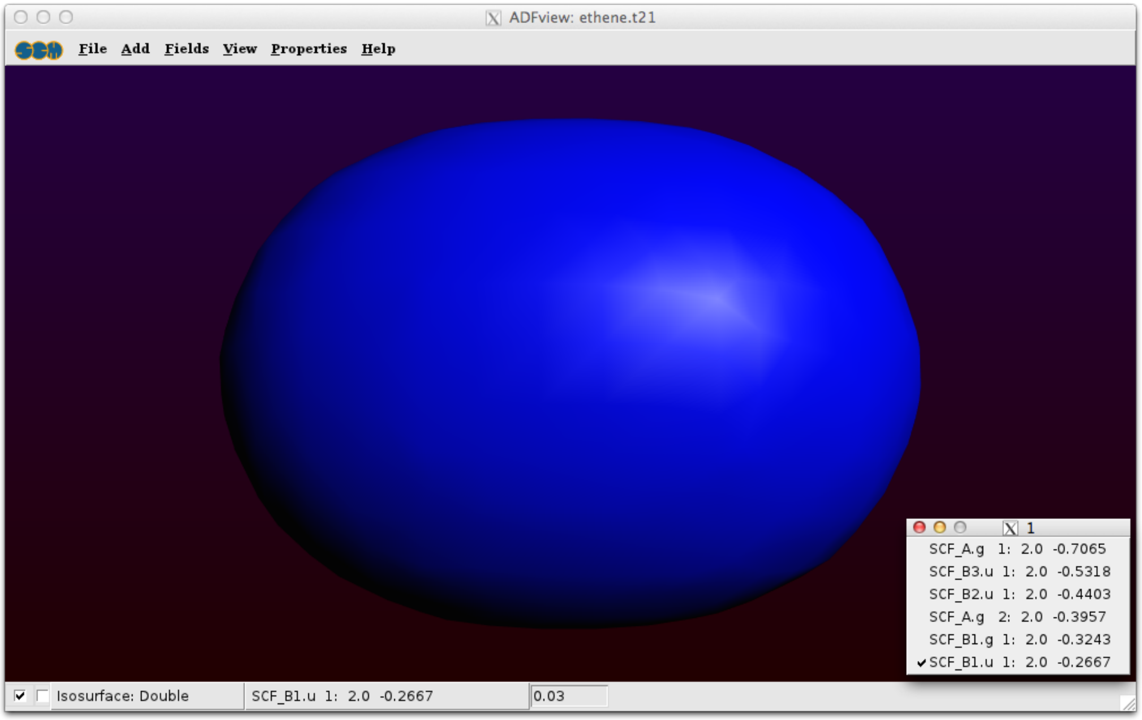
Close the two windows showing the orbitals using **File → Quit** in both windows

Orbitals, orbital selection panel: ADFview

We will now use ADFview to examine the orbitals. Not just one, but have a look at many of them. To do that ADFview has a simple method to make something similar to an 'orbital selection' panel: you can tear off the orbital menus!

Select **SCM → View**
Select **Properties → HOMO**
Click on the field selector pull-down in the control bar for the HOMO (reading SCF_B1.u 1: ...),

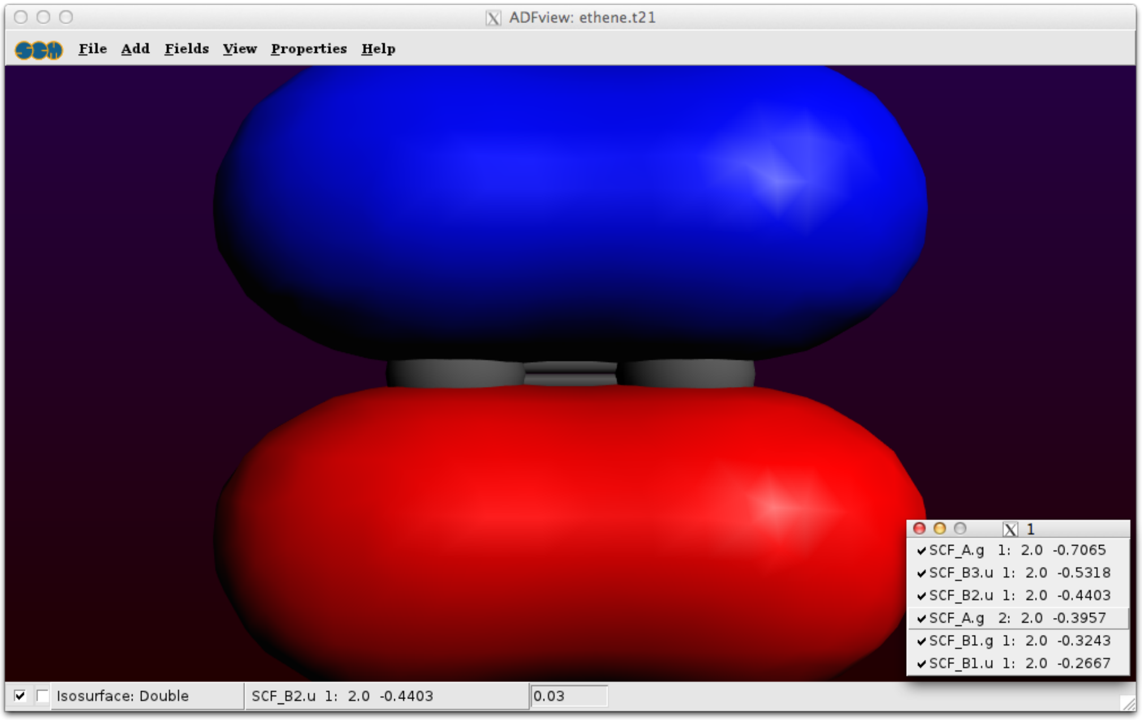
select **Orbitals (occupied)> → 1 → - - - - - - - -** (the dashed line)
The menu will tear off, place it at a convenient location



Now you can just click on the different orbitals in the torn-off menu, and very quickly examine those orbitals:

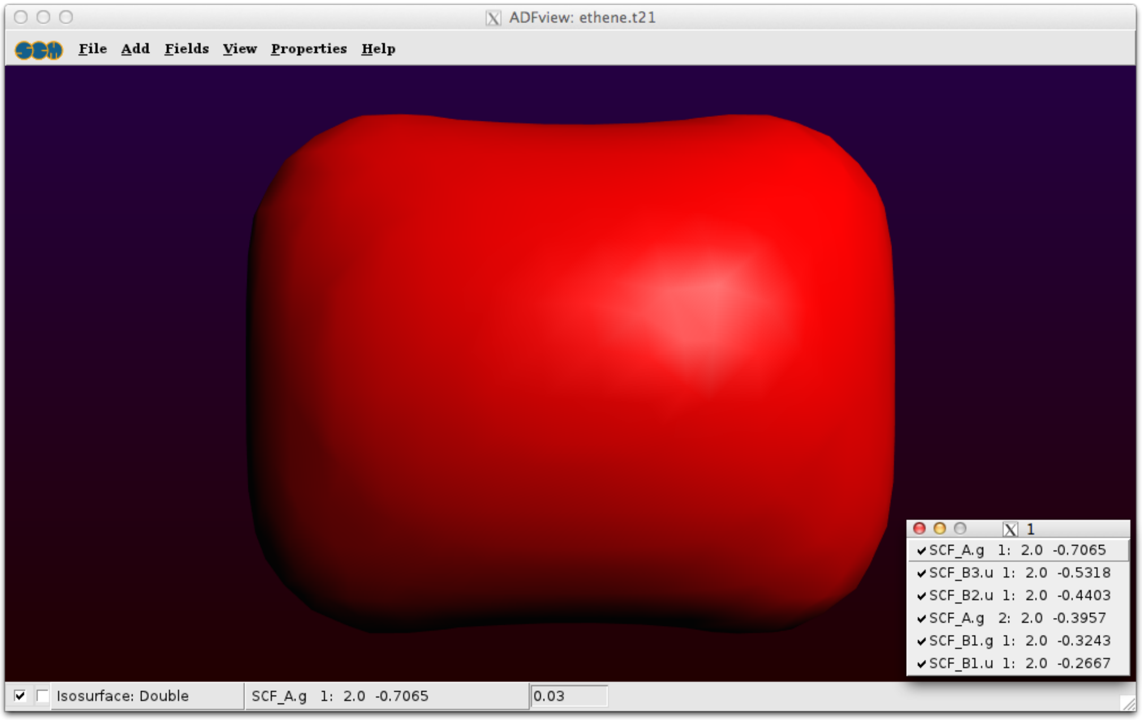
Click on all of the orbitals in the torn-off menu, one by one, and observe the orbitals
Click again on them

When you click the first time on an orbital, its values need to be calculated and then the orbital is shown. When you click for a second time on an orbital in the list, it has already been calculated (indicated by the check mark). And thus it shows immediately.



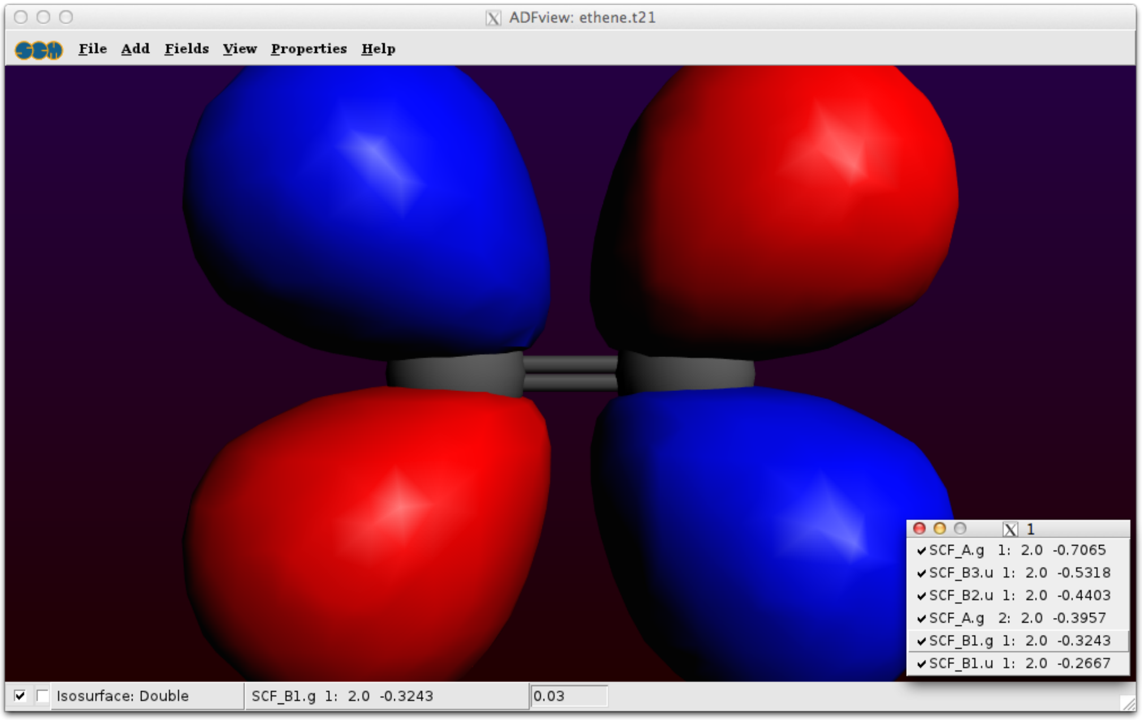
```
✓SCF_A.g  1: 2.0 -0.7065
✓SCF_B3.u 1: 2.0 -0.5318
✓SCF_B2.u 1: 2.0 -0.4403
✓SCF_A.g  2: 2.0 -0.3957
✓SCF_B1.g 1: 2.0 -0.3243
✓SCF_B1.u 1: 2.0 -0.2667
```

```
☑ ☐ Isosurface: Double   SCF_B2.u 1: 2.0 -0.4403   0.03
```



```
✓SCF_A.g  1: 2.0 -0.7065
✓SCF_B3.u 1: 2.0 -0.5318
✓SCF_B2.u 1: 2.0 -0.4403
✓SCF_A.g  2: 2.0 -0.3957
✓SCF_B1.g 1: 2.0 -0.3243
✓SCF_B1.u 1: 2.0 -0.2667
```

```
☑ ☐ Isosurface: Double   SCF_A.g  1: 2.0 -0.7065   0.03
```



Close the torn off menu by clicking in its close box

In the same way you can tear off many menus in the GUI, for example to select virtual orbitals. Not only in the ADFview control bars, but also from the main menu bar. Anywhere you see the dashed menu line.

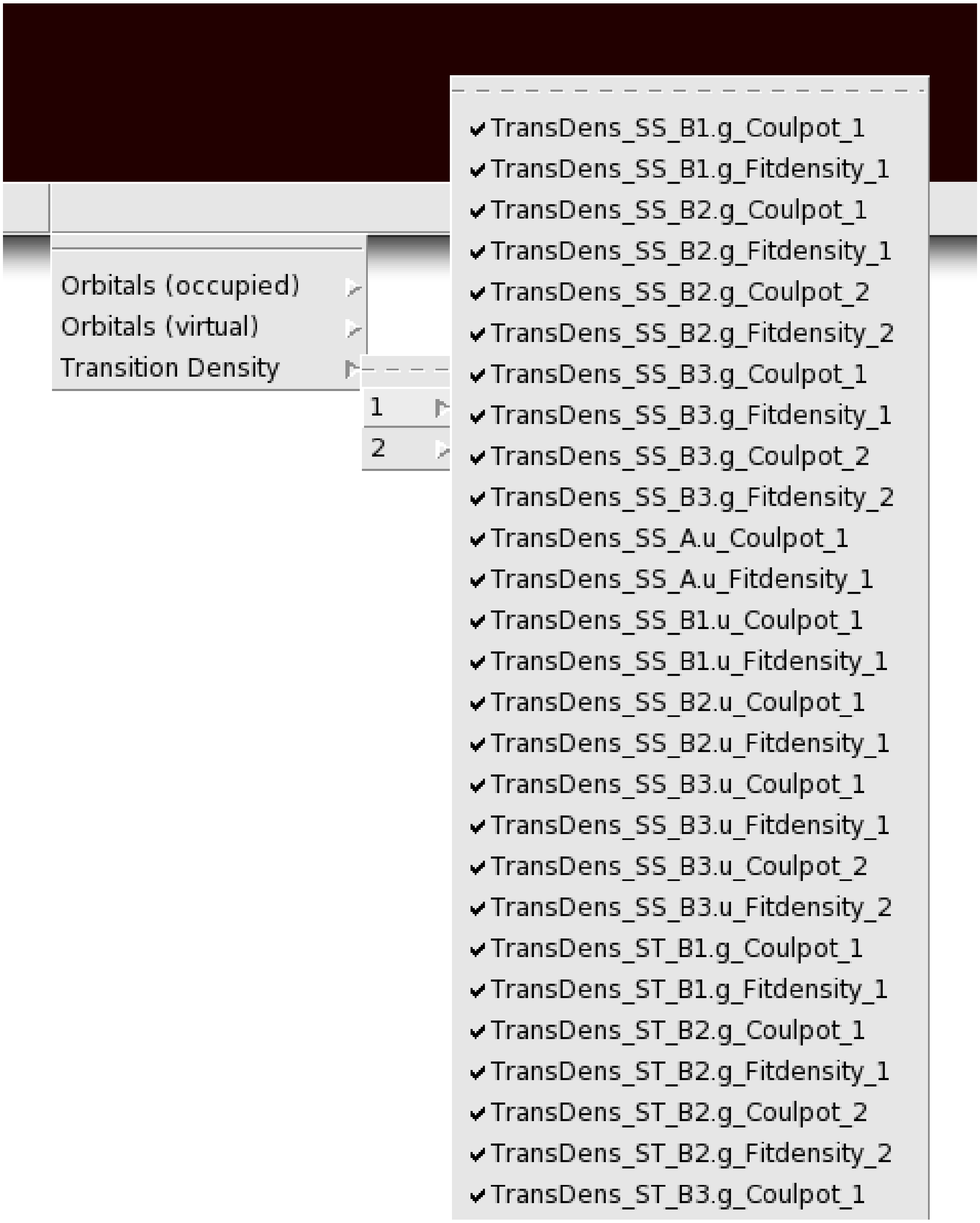
Close ADFview: **File → Quit**

Transition density: ADFview

You can use ADFview to view orbitals etc, but also to have a look at the transition density. At this moment ADFview cannot generate this field automatically, it needs to be calculated first using DENSF. The ADFinput defaults are such that if you perform an excitation calculation, DENSF will automatically calculate the corresponding transitions densities. So we will start ADFview and next load the .t41 file generated by DENSF:

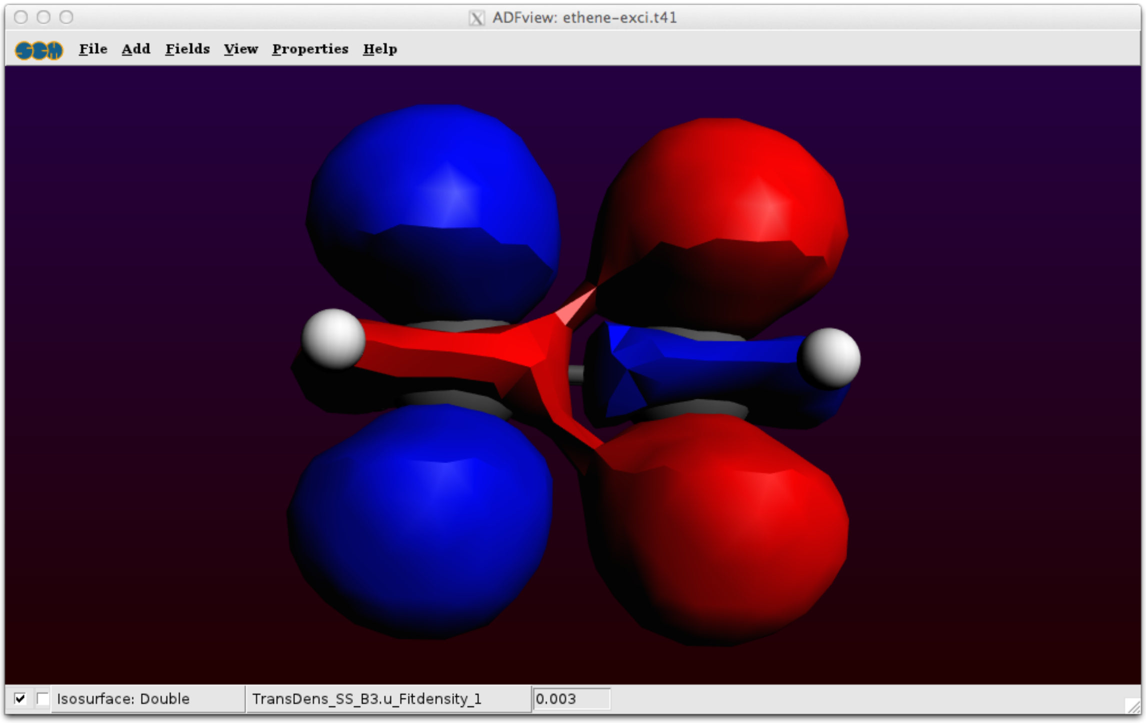
Select **SCM → View**
Select **File → New**
Select **File → Open**
In the file-select pop-up, choose to see all .t41 files using the pop-up menu at the bottom
Select the .t41 file from your calculation (ethene-exci.t41)
Click 'Open'
Select **Add → Isosurface: Double (+/-)**p

In the field pull-down menu (in the control line for the double isosurface) you will now find an entry 'Transition Density', and if you select that you will find all transition densities that are available.



In this case lets select the transition density that belongs to the biggest peak: the Singlet-Singlet 1B3u excitation:

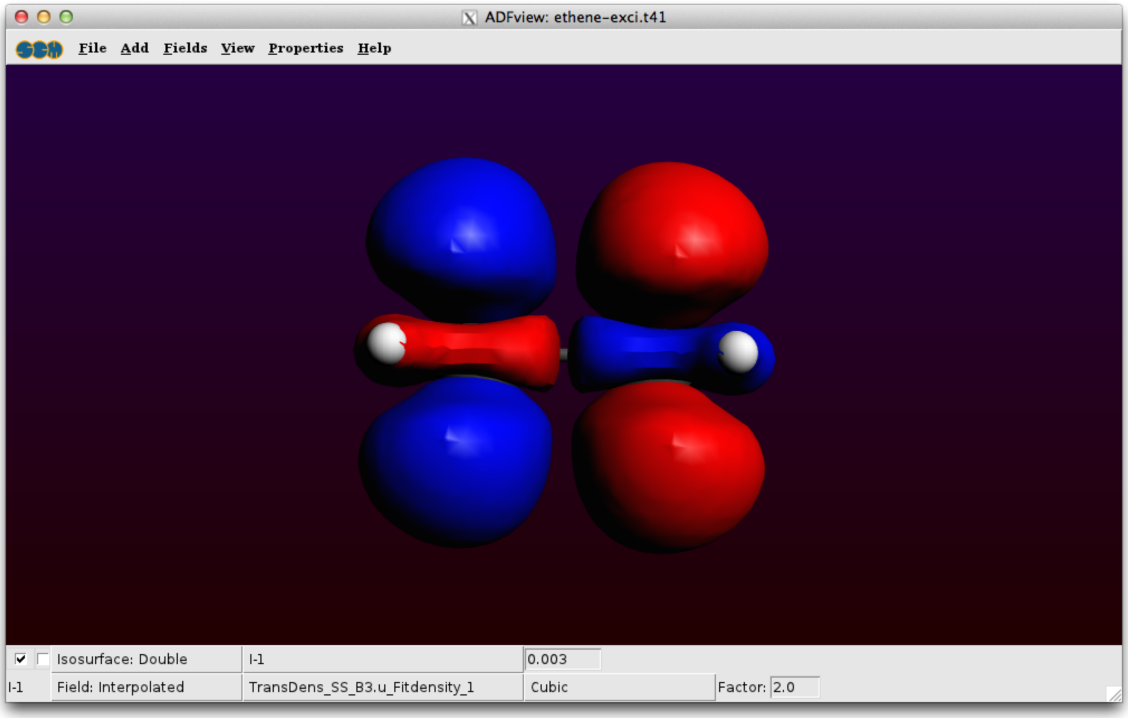
`Select the` **Transition Density → TransDens_SS_B3.u_Fitdensity_1** `field`
`Change the iso value to 0.003`
`Rotate the molecule a little`



☑ ☐ Isosurface: Double TransDens_SS_B3.u_Fitdensity_1 0.003

The resolution is rather coarse, you can use interpolation to get a better picture. Changing the grid has no effect in this case as you are visualizing a .t41 file, which is just data on a grid (in binary form).

Fields → Interpolated
Select the **Transition Density → TransDens_SS_B3.u_Fitdensity_1** field in the I-1 line
In the Isosurface: Double line, change the field to I-1 (in the Other category in the field selector)



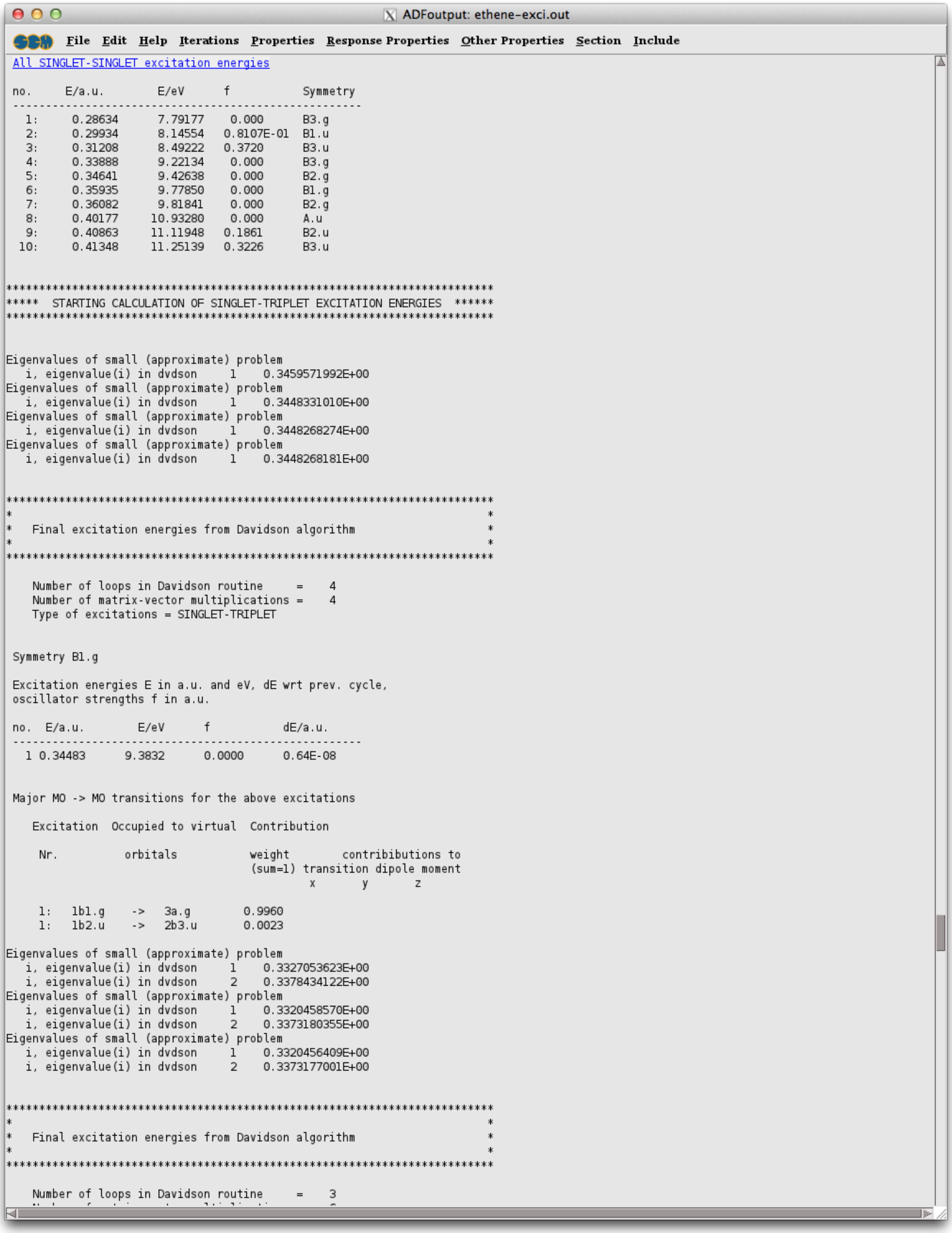
☑ ☐ Isosurface: Double | I-1 | 0.003

I-1 Field: Interpolated | TransDens_SS_B3.u_Fitdensity_1 | Cubic | Factor: 2.0

ADF Output

Using the output browser you can find all details about your excitation calculation. Use the menu to jump to the relevant part of output:

`Select` **SCM → Output**
`Select` **Response Properties → All Singlet-Singlet Excitation Energies**



```
 All SINGLET-SINGLET excitation energies

 no.     E/a.u.        E/eV      f           Symmetry
 -----------------------------------------------------
   1:     0.28634      7.79177    0.000      B3.g
   2:     0.29934      8.14554   0.8107E-01  B1.u
   3:     0.31208      8.49222   0.3720      B3.u
   4:     0.33888      9.22134    0.000      B3.g
   5:     0.34641      9.42638    0.000      B2.g
   6:     0.35935      9.77850    0.000      B1.g
   7:     0.36082      9.81841    0.000      B2.g
   8:     0.40177     10.93280    0.000      A.u
   9:     0.40863     11.11948   0.1861      B2.u
  10:     0.41348     11.25139   0.3226      B3.u


**************************************************************************
*****  STARTING CALCULATION OF SINGLET-TRIPLET EXCITATION ENERGIES  ******
**************************************************************************



Eigenvalues of small (approximate) problem
   i, eigenvalue(i) in dvdson     1    0.3459571992E+00
Eigenvalues of small (approximate) problem
   i, eigenvalue(i) in dvdson     1    0.3448331010E+00
Eigenvalues of small (approximate) problem
   i, eigenvalue(i) in dvdson     1    0.3448268274E+00
Eigenvalues of small (approximate) problem
   i, eigenvalue(i) in dvdson     1    0.3448268181E+00


**************************************************************************
*                                                                        *
*   Final excitation energies from Davidson algorithm                    *
*                                                                        *
**************************************************************************

    Number of loops in Davidson routine     =    4
    Number of matrix-vector multiplications =    4
    Type of excitations = SINGLET-TRIPLET


 Symmetry B1.g

 Excitation energies E in a.u. and eV, dE wrt prev. cycle,
 oscillator strengths f in a.u.

 no.  E/a.u.        E/eV      f           dE/a.u.
 -----------------------------------------------------
   1 0.34483      9.3832      0.0000      0.64E-08


 Major MO -> MO transitions for the above excitations

    Excitation  Occupied to virtual  Contribution

     Nr.          orbitals           weight        contribibutions to
                                     (sum=1) transition dipole moment
                                               x       y       z

     1:   1b1.g    ->   3a.g        0.9960
     1:   1b2.u    ->   2b3.u       0.0023

Eigenvalues of small (approximate) problem
   i, eigenvalue(i) in dvdson     1    0.3327053623E+00
   i, eigenvalue(i) in dvdson     2    0.3378434122E+00
Eigenvalues of small (approximate) problem
   i, eigenvalue(i) in dvdson     1    0.3320458570E+00
   i, eigenvalue(i) in dvdson     2    0.3373180355E+00
Eigenvalues of small (approximate) problem
   i, eigenvalue(i) in dvdson     1    0.3320456409E+00
   i, eigenvalue(i) in dvdson     2    0.3373177001E+00


**************************************************************************
*                                                                        *
*   Final excitation energies from Davidson algorithm                    *
*                                                                        *
**************************************************************************

    Number of loops in Davidson routine     =    3
```

You might get minor differences in the results as the default integration accuracty is only 4.

Closing the ADF-GUI modules

To close all modules for your excitations calculation at once, use the Close command from the SCM menu:

`Select` **SCM → Close**

Close will close all open modules that have your current job loaded, except ADFjobs. The Close All command will close every ADF-GUI module, including ADFjobs:

`Select` **SCM → Close All**

All ADF-GUI modules (and BAND-GUI modules if any) should be closed.

Tutorial 5: Vibrational frequencies of ethane

Step 1: Start ADFinput

For this tutorial we again prefer to work in the Tutorial directory:

```
cd $HOME
Start ADFjobs
Click on the Tutorial folder icon
Start ADFinput using the SCM menu
```

Step 2: Create your ethane molecule

Next we create an ethane molecule. This is almost identical to making ethanol:

```
Select the C-tool
Click once to make a carbon atom
Click again to make a second carbon atom
```
`Select` **Edit → Add Hydrogen**
```
And do it again: ... add hydrogen
Click the pre-optimize button (the cog wheel)
Click the Symmetrize button (the button with the star, on the bottom toolbar)
```

You need to add hydrogen twice: the first time one carbon atom was selected. Thus, the 'Add Hydrogen' command added the hydrogen to that selected atom only. By repeating the 'Add Hydrogen' command the hydrogens are added in all possible places.

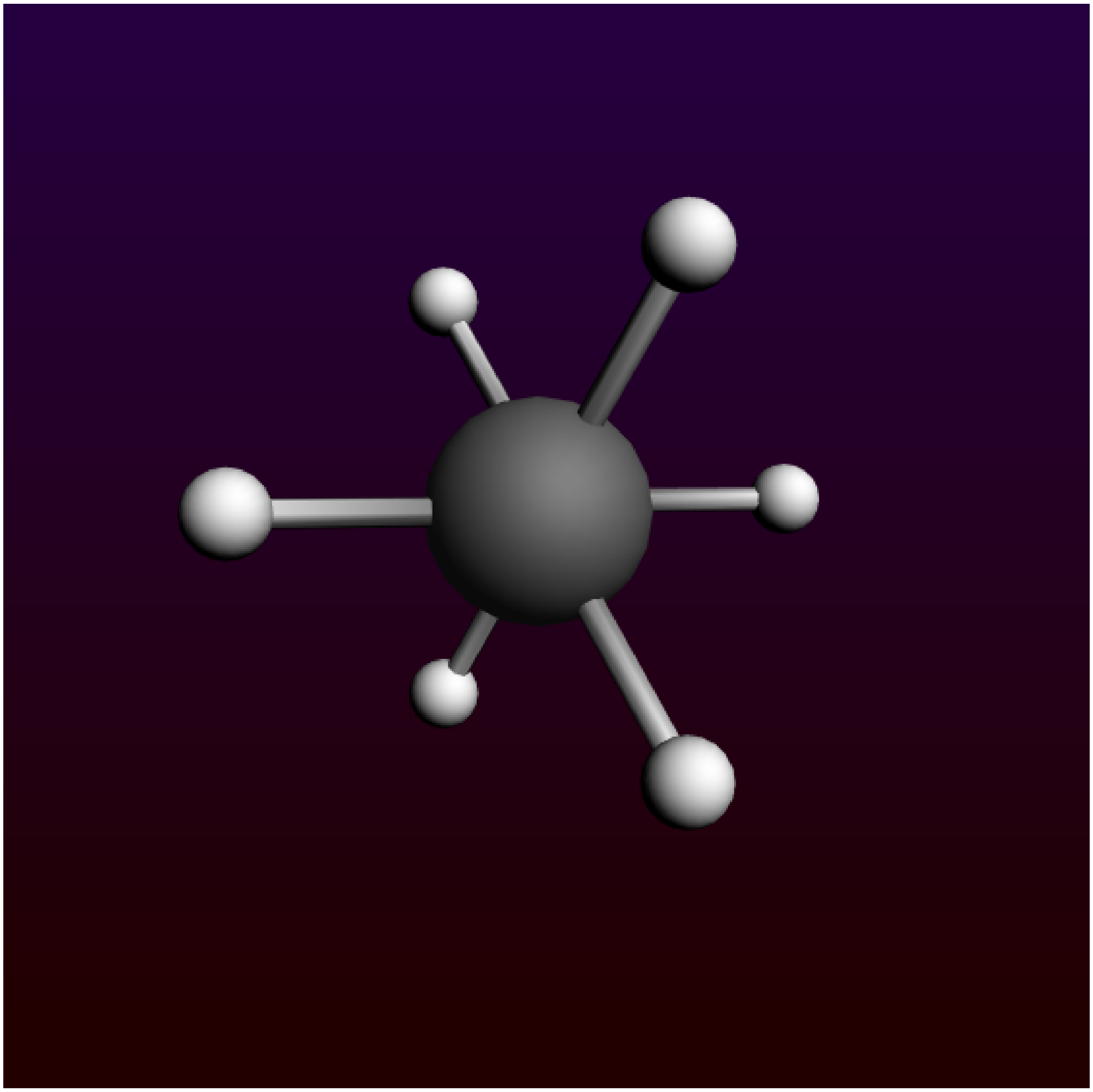
Alternatively, you can, after placing the second atom, click on that atom to finish using the C-tool. In this case none of the carbon atoms will be selected and you can easily add all the hydrogens at the same time.

The symmetrization should have enforced perfect D3d symmetry, using the Symmol program. The Symmol program has been developed by Pilati and Forni, see the balloon help on that button for details..

Step 3: Optimize the geometry

Now optimize the geometry using ADF, as in the second tutorial:

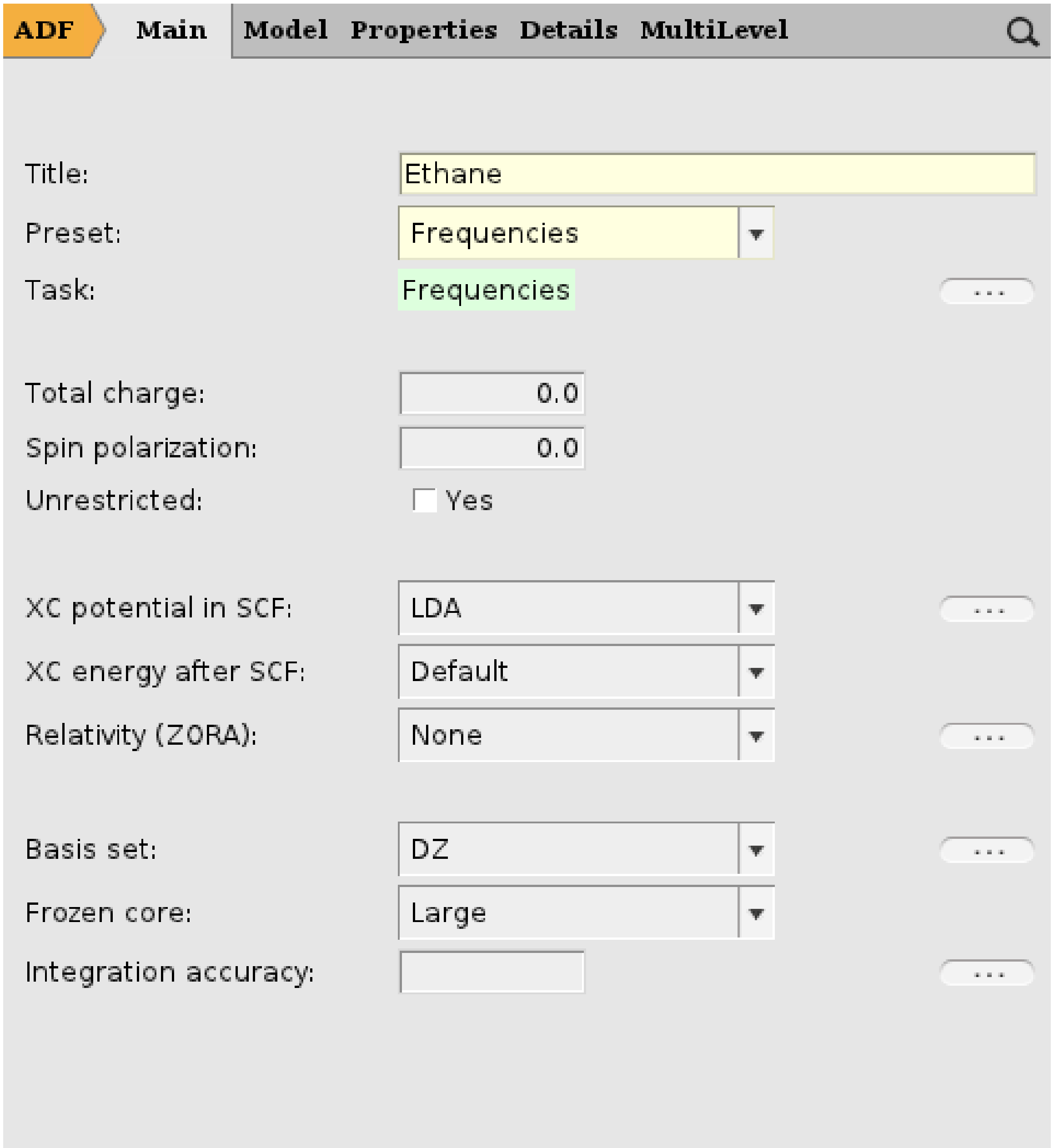
```
Enter a title (like 'Ethane')
Select the 'Geometry Optimization' preset
```
`Select` **File → Run**
```
Save your input with a nice name ('ethane')
Wait for the calculation to finish (check the logfile)
In the dialog that appears, click Yes to import the optimized geometry
```



Step 4: Calculate the vibrational frequencies of ethane

Now we will set up and run the frequencies calculation. It is important to start with the optimized structure, so make sure you did import the optimized coordinates (the last step of the previous instructions).

`Select the 'Frequencies' preset`



Title: Ethane
Preset: Frequencies
Task: Frequencies

Total charge: 0.0
Spin polarization: 0.0
Unrestricted: ☐ Yes

XC potential in SCF: LDA
XC energy after SCF: Default
Relativity (ZORA): None

Basis set: DZ
Frozen core: Large
Integration accuracy:

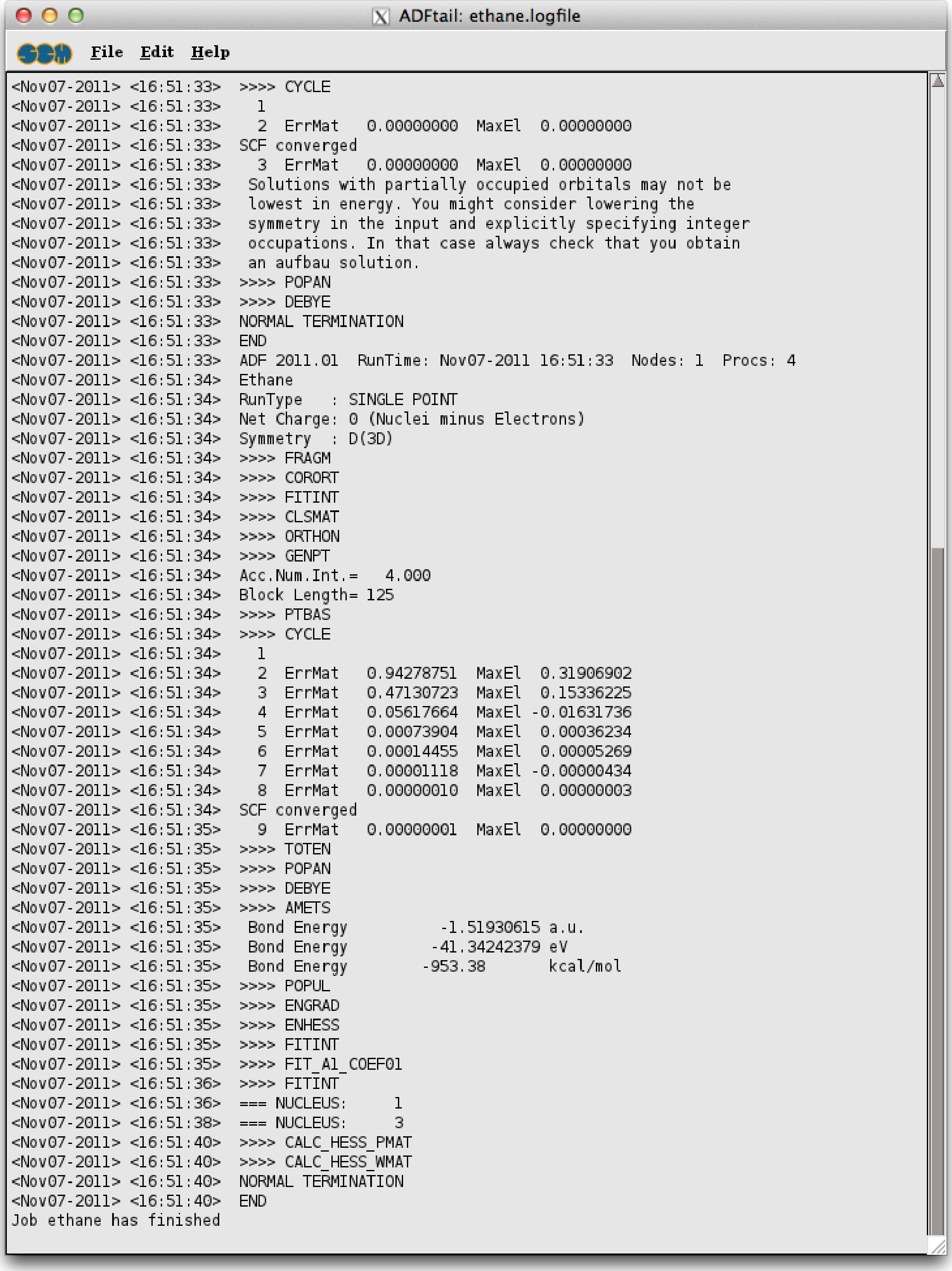
For the tutorial we will use the default XC potential. For better results you should select a better XC potential.

Select **File → Run**
Click 'OK' to save over the previous version
Click 'Yes' when ADFjobs warns that results are already present
Wait for the calculation to finish

Step 5: Results of your calculation

Logfile: ADFtail

When the calculation is finished the end of your logfile will look something like this:

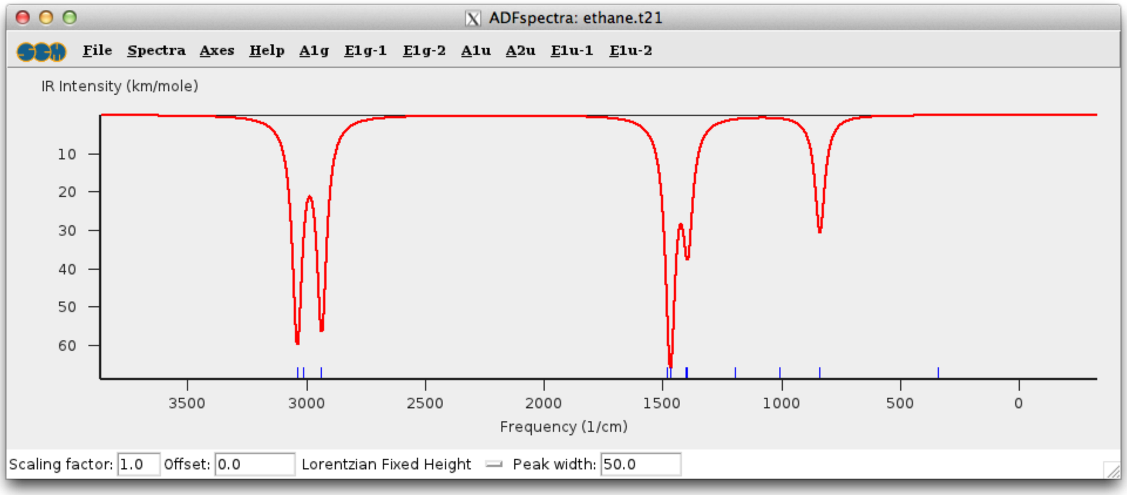


```
<Nov07-2011> <16:51:33>  >>>> CYCLE
<Nov07-2011> <16:51:33>    1
<Nov07-2011> <16:51:33>    2  ErrMat   0.00000000  MaxEl  0.00000000
<Nov07-2011> <16:51:33>  SCF converged
<Nov07-2011> <16:51:33>    3  ErrMat   0.00000000  MaxEl  0.00000000
<Nov07-2011> <16:51:33>   Solutions with partially occupied orbitals may not be
<Nov07-2011> <16:51:33>   lowest in energy. You might consider lowering the
<Nov07-2011> <16:51:33>   symmetry in the input and explicitly specifying integer
<Nov07-2011> <16:51:33>   occupations. In that case always check that you obtain
<Nov07-2011> <16:51:33>   an aufbau solution.
<Nov07-2011> <16:51:33>  >>>> POPAN
<Nov07-2011> <16:51:33>  >>>> DEBYE
<Nov07-2011> <16:51:33>  NORMAL TERMINATION
<Nov07-2011> <16:51:33>  END
<Nov07-2011> <16:51:33>  ADF 2011.01  RunTime: Nov07-2011 16:51:33  Nodes: 1  Procs: 4
<Nov07-2011> <16:51:34>  Ethane
<Nov07-2011> <16:51:34>  RunType   : SINGLE POINT
<Nov07-2011> <16:51:34>  Net Charge: 0 (Nuclei minus Electrons)
<Nov07-2011> <16:51:34>  Symmetry  : D(3D)
<Nov07-2011> <16:51:34>  >>>> FRAGM
<Nov07-2011> <16:51:34>  >>>> CORORT
<Nov07-2011> <16:51:34>  >>>> FITINT
<Nov07-2011> <16:51:34>  >>>> CLSMAT
<Nov07-2011> <16:51:34>  >>>> ORTHON
<Nov07-2011> <16:51:34>  >>>> GENPT
<Nov07-2011> <16:51:34>  Acc.Num.Int.=   4.000
<Nov07-2011> <16:51:34>  Block Length= 125
<Nov07-2011> <16:51:34>  >>>> PTBAS
<Nov07-2011> <16:51:34>  >>>> CYCLE
<Nov07-2011> <16:51:34>    1
<Nov07-2011> <16:51:34>    2  ErrMat   0.94278751  MaxEl  0.31906902
<Nov07-2011> <16:51:34>    3  ErrMat   0.47130723  MaxEl  0.15336225
<Nov07-2011> <16:51:34>    4  ErrMat   0.05617664  MaxEl -0.01631736
<Nov07-2011> <16:51:34>    5  ErrMat   0.00073904  MaxEl  0.00036234
<Nov07-2011> <16:51:34>    6  ErrMat   0.00014455  MaxEl  0.00005269
<Nov07-2011> <16:51:34>    7  ErrMat   0.00001118  MaxEl -0.00000434
<Nov07-2011> <16:51:34>    8  ErrMat   0.00000010  MaxEl  0.00000003
<Nov07-2011> <16:51:34>  SCF converged
<Nov07-2011> <16:51:35>    9  ErrMat   0.00000001  MaxEl  0.00000000
<Nov07-2011> <16:51:35>  >>>> TOTEN
<Nov07-2011> <16:51:35>  >>>> POPAN
<Nov07-2011> <16:51:35>  >>>> DEBYE
<Nov07-2011> <16:51:35>  >>>> AMETS
<Nov07-2011> <16:51:35>   Bond Energy           -1.51930615 a.u.
<Nov07-2011> <16:51:35>   Bond Energy          -41.34242379 eV
<Nov07-2011> <16:51:35>   Bond Energy         -953.38       kcal/mol
<Nov07-2011> <16:51:35>  >>>> POPUL
<Nov07-2011> <16:51:35>  >>>> ENGRAD
<Nov07-2011> <16:51:35>  >>>> ENHESS
<Nov07-2011> <16:51:35>  >>>> FITINT
<Nov07-2011> <16:51:35>  >>>> FIT_A1_COEF01
<Nov07-2011> <16:51:36>  >>>> FITINT
<Nov07-2011> <16:51:36>  === NUCLEUS:      1
<Nov07-2011> <16:51:38>  === NUCLEUS:      3
<Nov07-2011> <16:51:40>  >>>> CALC_HESS_PMAT
<Nov07-2011> <16:51:40>  >>>> CALC_HESS_WMAT
<Nov07-2011> <16:51:40>  NORMAL TERMINATION
<Nov07-2011> <16:51:40>  END
Job ethane has finished
```

At the end ADF calculates the force constants for the vibrations.

IR-spectrum (vibrational spectrum): ADFspectra with normal mode selector and ADFmovie

`Select` **SCM → Spectra**

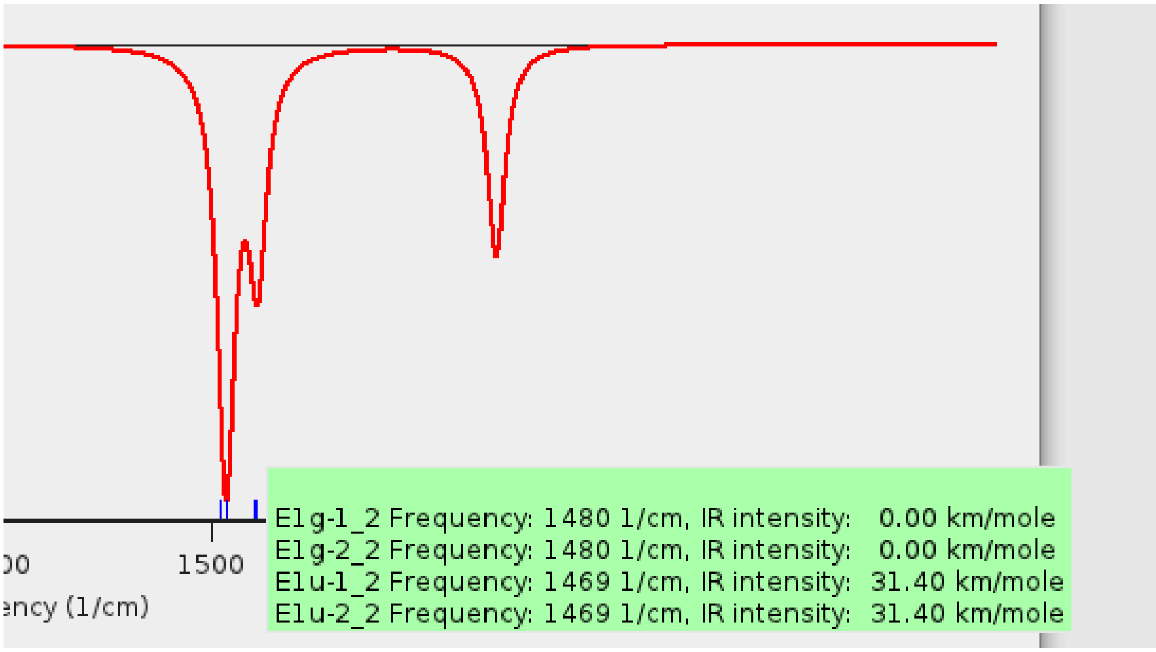


Scaling factor: 1.0 Offset: 0.0 Lorentzian Fixed Height Peak width: 50.0

The IR spectrum is shown. You can save a picture to use in other programs using the 'Save Postscript' command from the 'File' menu. Alternatively, you may export the xy coordinates of the spectrum to a plain text file for you own graphing application.

If you move the mouse pointer above the spectrum you will get more information about the peaks in pop-up windows:

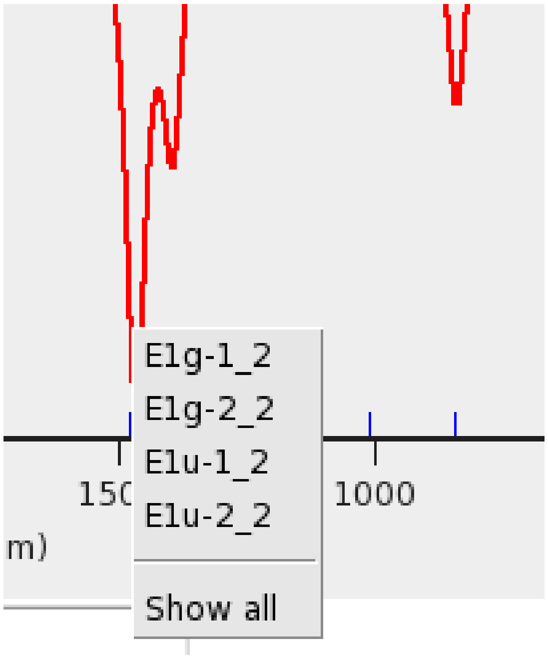
`Move the mouse pointer above the largest peak and keep it there`



```
E1g-1_2 Frequency: 1480 1/cm, IR intensity:   0.00 km/mole
E1g-2_2 Frequency: 1480 1/cm, IR intensity:   0.00 km/mole
E1u-1_2 Frequency: 1469 1/cm, IR intensity:  31.40 km/mole
E1u-2_2 Frequency: 1469 1/cm, IR intensity:  31.40 km/mole
```

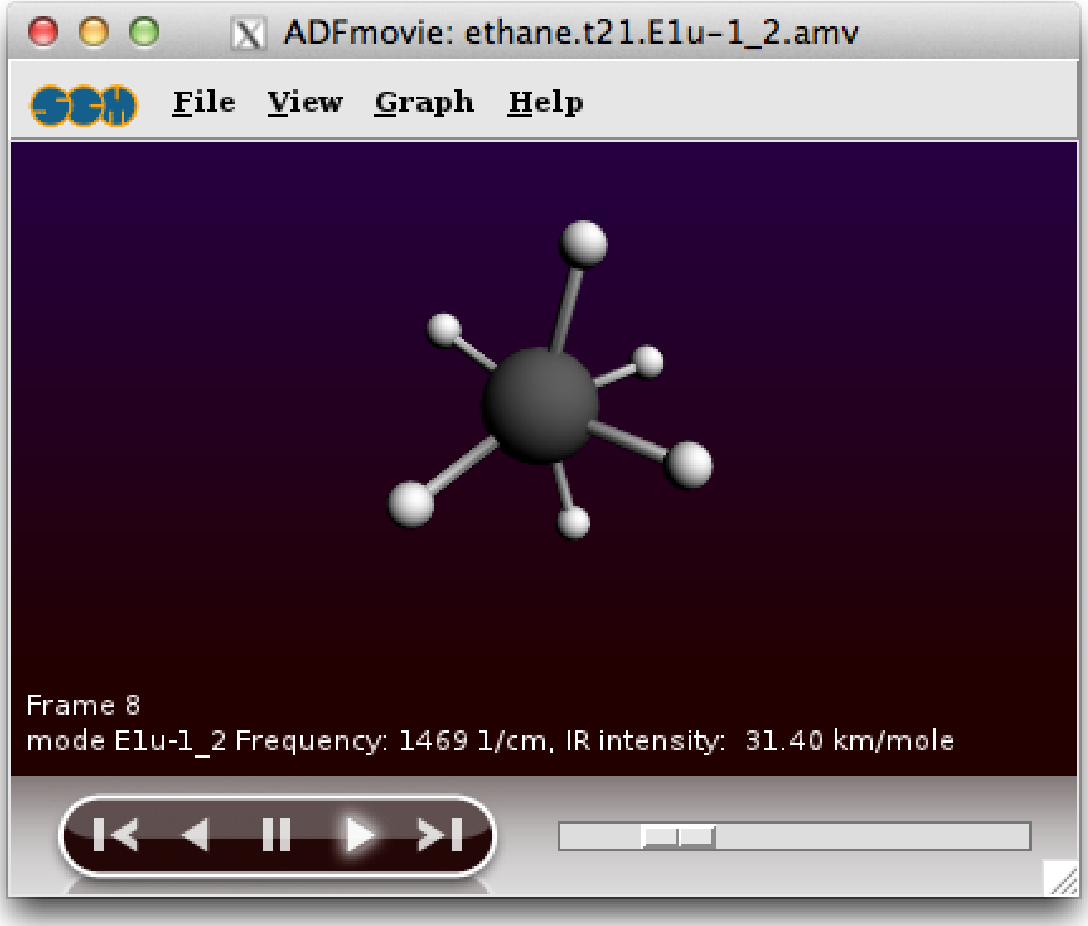
The list of normal modes contributing to the IR peak will show up. By clicking the mouse button at this point, all these modes will be animated, each opened in a separate ADFmovie windows. Alternatively, pressing and holding the mouse button down, a list of these modes with their symmetry labels will show up:

```
Press and hold down the mouse on the largest peak
```



Choosing one of the modes from the the pop-up list, you can visualize only the corresponding mode.

```
Select one of the modes in the pop-up menu
```

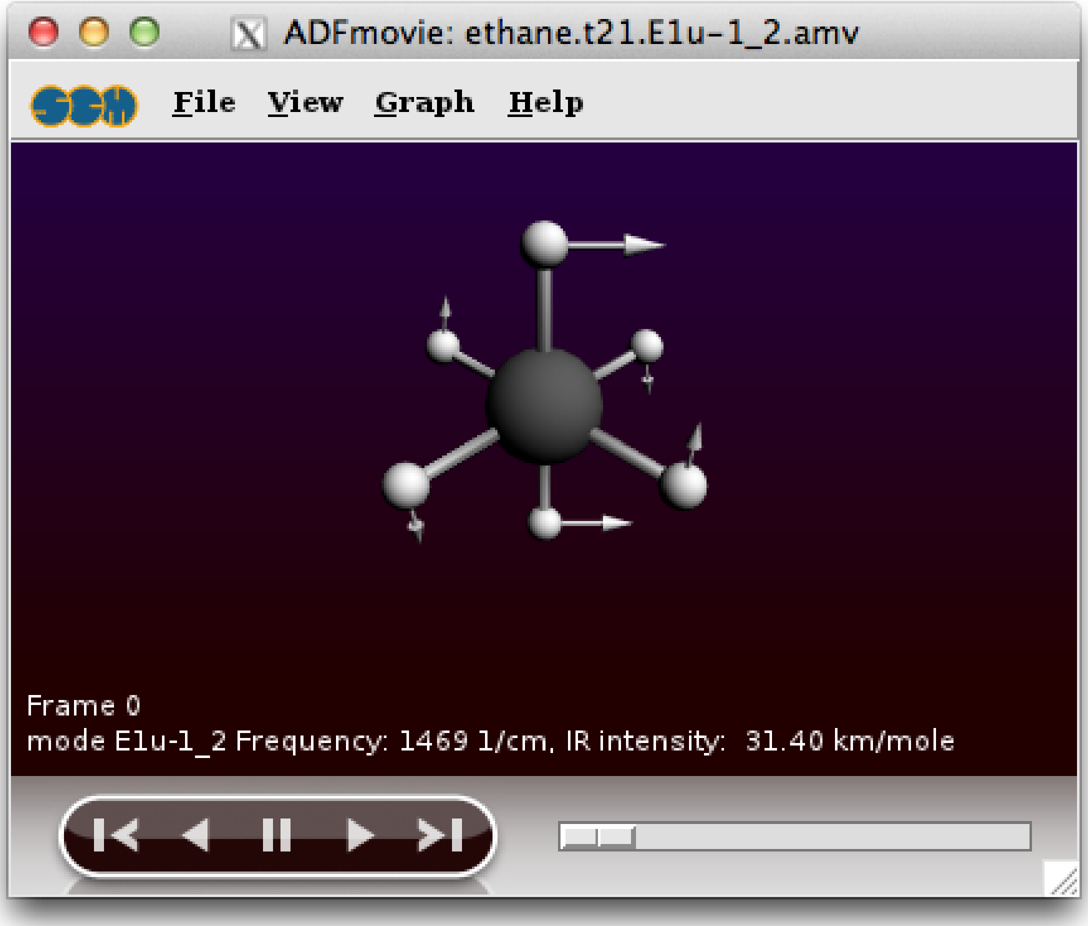


```
Frame 8
mode E1u-1_2 Frequency: 1469 1/cm, IR intensity:  31.40 km/mole
```

ADFmovie should start and show the corresponding normal mode.

You can adjust how the normal mode is visualized. You can make the displacements larger or smaller. The commands are in the Scale Displacements menu located in the View menu, but using keyboard shortcuts is much easier here:

`Use ctrl-L (or cmd-L on a Mac) repeatedly to make the displacements larger`
`Use ctrl-K (or cmd-K on a Mac) repeatedly to make the displacements smaller`
`Use the` **View → Displacement Vectors** `to visualize the normal mode with vectors`

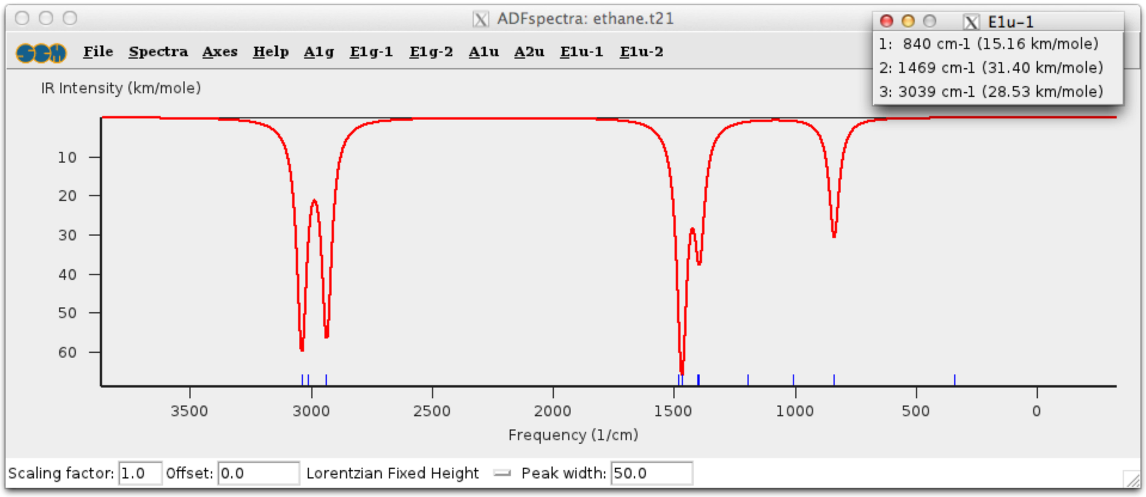


Frame 0
mode E1u-1_2 Frequency: 1469 1/cm, IR intensity: 31.40 km/mole

You can make the vectors larger or smaller using the same ctrl/cmd-L/K

Sometimes you wish to examine many different normal modes. Obviously you can do this as just described, but another way is by selecting the mode of interest from the menu. And to make it more convenient to check many of them, you can tear off these menus, just as you did with the orbital selector menu in ADFview.

`In ADFspectra:` **File → Quit**`, to close all normal modes that might be showing`
`Start ADFspectra again` **SCM → Spectra**
`Click on the E1u-1 menu, and select the dashed bar (- - - -), thus NOT one of the modes`
`Position the torn off menu in a convenient location`



1: 840 cm-1 (15.16 km/mole)
2: 1469 cm-1 (31.40 km/mole)
3: 3039 cm-1 (28.53 km/mole)

Scaling factor: 1.0 Offset: 0.0 Lorentzian Fixed Height Peak width: 50.0

`Click on each of the modes in the torn of menu in turn`
`Observe the movie windows showing the normal modes`

As you will find out, this is an extremely nice and convenient way to examine many different modes.

We are done with this tutorial, so close all open ADF-GUI windows:

SCM → Close All

Advanced ADF-GUI tutorials

Tutorial 6: HCN Isomerization Reaction

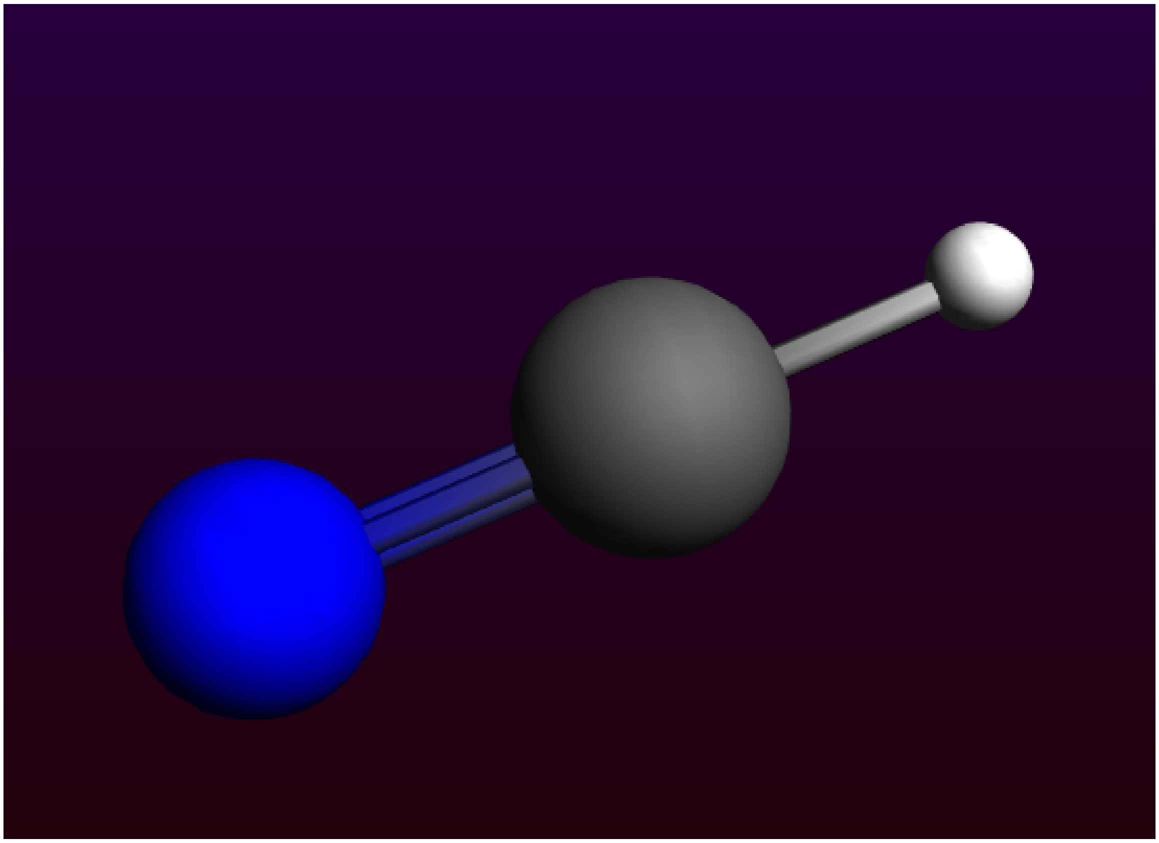
This tutorial consists of several steps to study the isomerization reaction of HCN:

- Geometry optimization
- Linear transit
- Quick frequency calculation
- Transition state search
- Accurate frequency calculation
- IRC

Step 1: Prepare the HCN molecule

```
cd $HOME
Start ADFjobs
Click on the Tutorial folder icon
Start adfinput using the SCM menu
Draw an HCN molecule (first the N, next the C and finally an H atom)
Select the C-N bond and make it a triple-bond
Pre-optimize the geometry
```

You should get a linear molecule:



Select the "Geometry Optimization" preset
Select the DZP basis set
Select **File → Run**, give it the name HCN_GO

The geometry will be optimized, using a DZP basis set.

Click "Yes" when asked to read new coordinates from the HCN_GO.t21 file
Check the C-N and C-H distances

They should be about 115 and 108 pm (1.15 and 1.08 Angstrom), respectively.

Write down the value of the bonding energy printed
at the end of the calculation in the ADFtail window

Step 2: Create a rough approximation for the transition state geometry

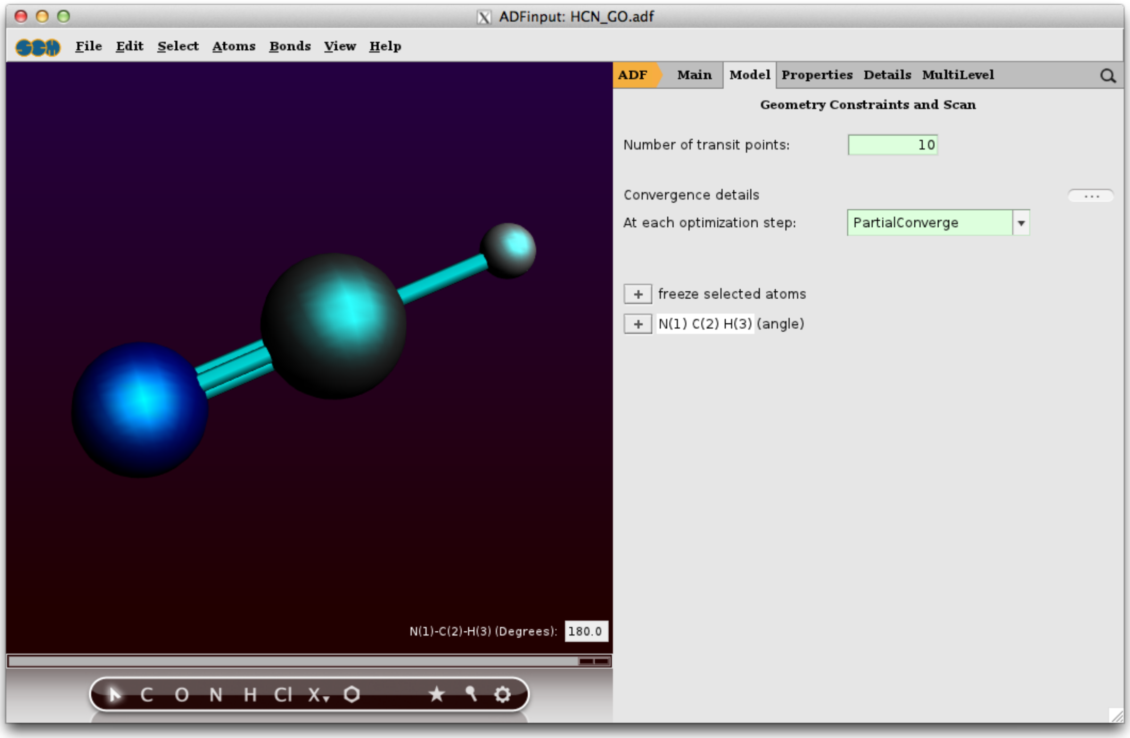
The HCN molecule has an CNH isomer. There is an energy barrier between these two states. We are going to find the transition state and calculate its height.

To find a better starting point for the transition state search we will perform a linear transit calculation as a rough approximation of the reaction path. We will vary the H-C-N angle in steps between 40 and 140 degrees and let ADF optimize bond lengths at each angle.

To set up the linear transit calculation:

Select the 'Linear Transit' preset
Click on the "..." button next to the GeometryOptimization task to go to the 'Geometry Constraints and Scan' panel
Select all the atoms

You should see '+ N(1) C(2) H(3) (angle)' note in the right panel now:



Geometry Constraints and Scan

Number of transit points: 10

Convergence details

At each optimization step: PartialConverge

\+ freeze selected atoms

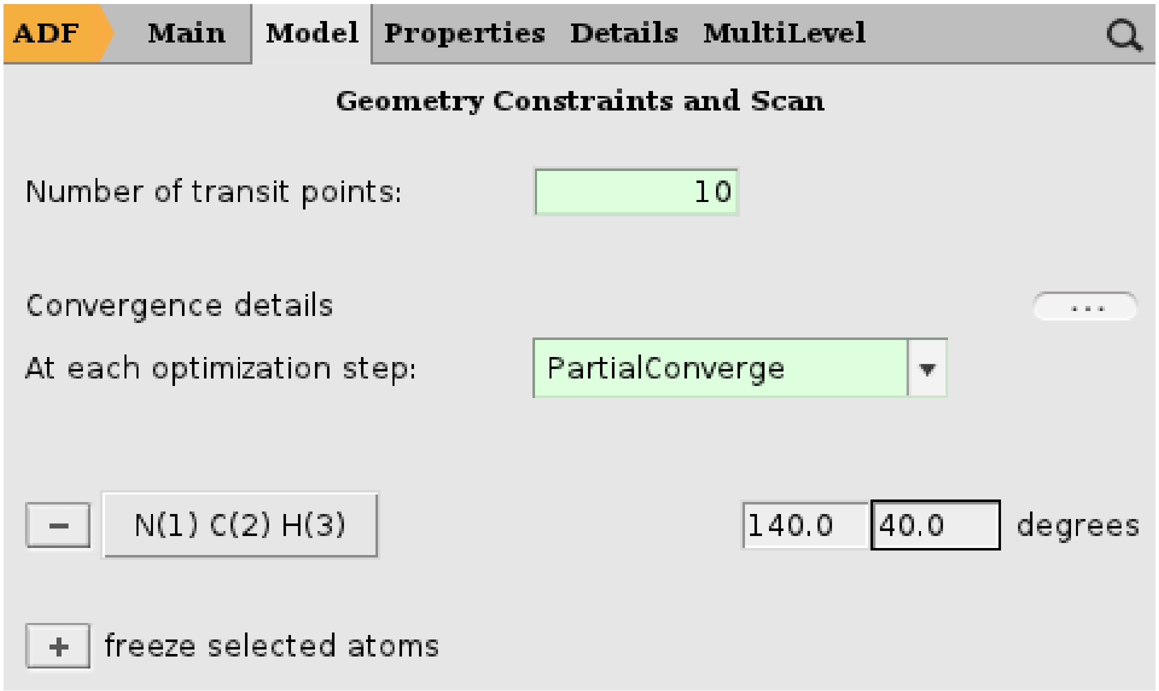
\+ N(1) C(2) H(3) (angle)

N(1)-C(2)-H(3) (Degrees): 180.0

`Click the '+' button to add the angle constraint`

Now '- N(1) C(2) H(3)' and the two fields as limits for the degree parameter appear.

`Enter '140' and '40' in the 'degrees' fields`



Geometry Constraints and Scan

Number of transit points: 10

Convergence details

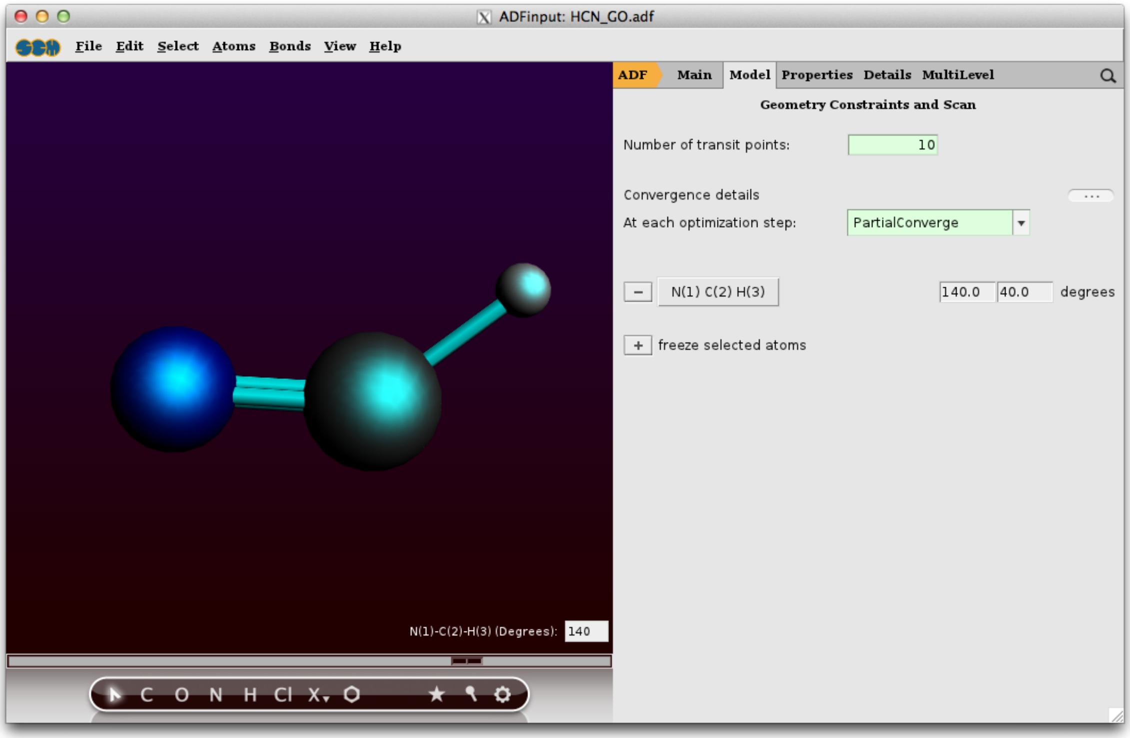
At each optimization step: PartialConverge

− N(1) C(2) H(3) 140.0 40.0 degrees

\+ freeze selected atoms

ADF will have trouble running the current set up because the HCN molecule is perfectly linear. So we will help ADF by changing the angle to 140 degrees, the same as the first point of the LT scan.

Use the slider to change the HCN angle to 140 degrees



Geometry Constraints and Scan

Number of transit points: 10

Convergence details

At each optimization step: PartialConverge

N(1) C(2) H(3) 140.0 40.0 degrees

freeze selected atoms

N(1)-C(2)-H(3) (Degrees): 140

The set up is complete. Now we will run the LT calculation, but we will save it with a new name as we wish to keep the results of the HCN_GO calculation:

Use **File → Save As** to save the file as 'HCN_LT'
Run the calculation

Running might take a few minutes. When the run is finished:

Click "Yes" when asked to read new coordinates

You will see the last geometry, close to CNH. To see how geometry was changing during the LT run, use ADFmovie:

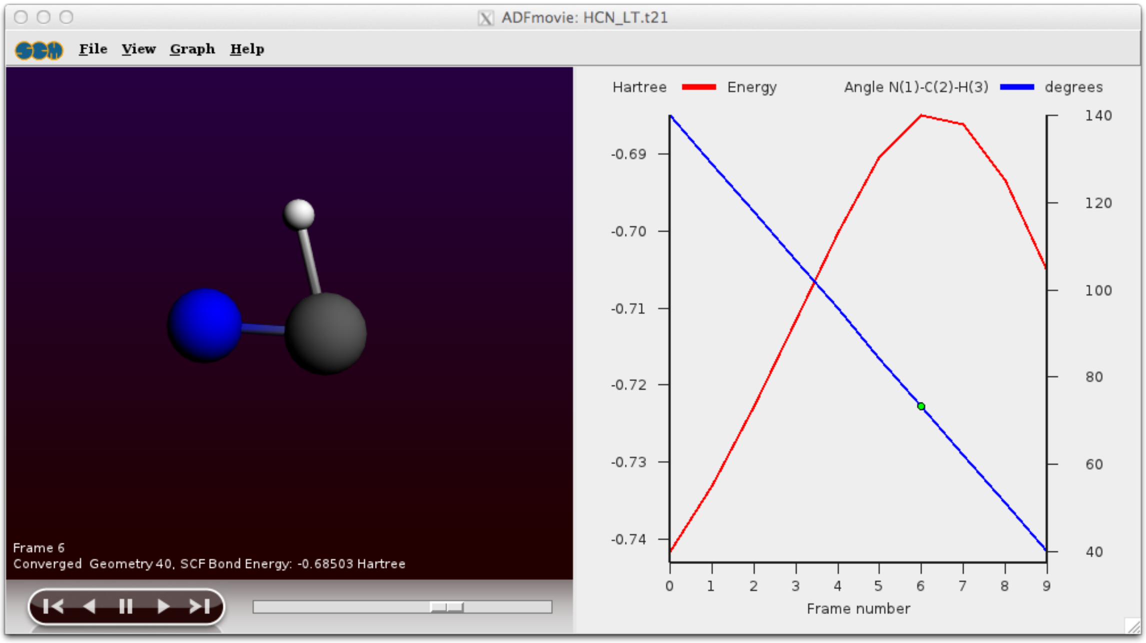
Select the **SCM → Movie** command
Select all atoms (use shift-drag to make a rectangle around the atoms)
Use the **View → Align Screen** command to make sure you can see all atoms
Select the **Graph → Energy** command
Select the **Graph → Distance, Angle, Dihedral** command (to get the angle graph, as three atoms are still selected)
Use the **View → Converged Geometries Only** command
Zoom in to get a better view of the molecule
Press the Play button (the right-pointing triangle in the controls at the left bottom of the ADFmovie window)

You will see the hydrogen atom moving from C to N. You will also see a graph of the energy as function of the LT steps. As the movie is playing a dot shows the corresponding position in the graph.

Somewhere along the path, there is a transition state we are looking for. Remember that you needed to use the 'Optimized Geometries Only' command to filter out all the intermediate geometry step, so that you get only the converged geometries for each LT step.

In the graph, click (without moving!) on the top of the energy graph
Alternatively, use the arrow keys (cursor keys) to move between different steps, or use the slider
Check which geometry has the maximum energy

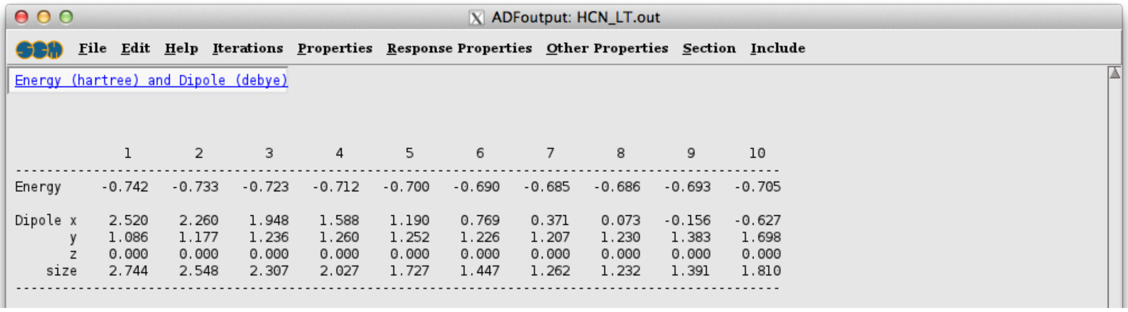
You should find that at around an angle of 60-75 degrees the maximum energy is reached. This is Frame 6 (the 7th LT step):



Frame 6
Converged Geometry 40, SCF Bond Energy: -0.68503 Hartree

You can find this information also in the output file:

Select the **SCM → Output** menu command
In the ADFoutput window select the **Other Properties → 'LT Path** command



Energy (hartree) and Dipole (debye)

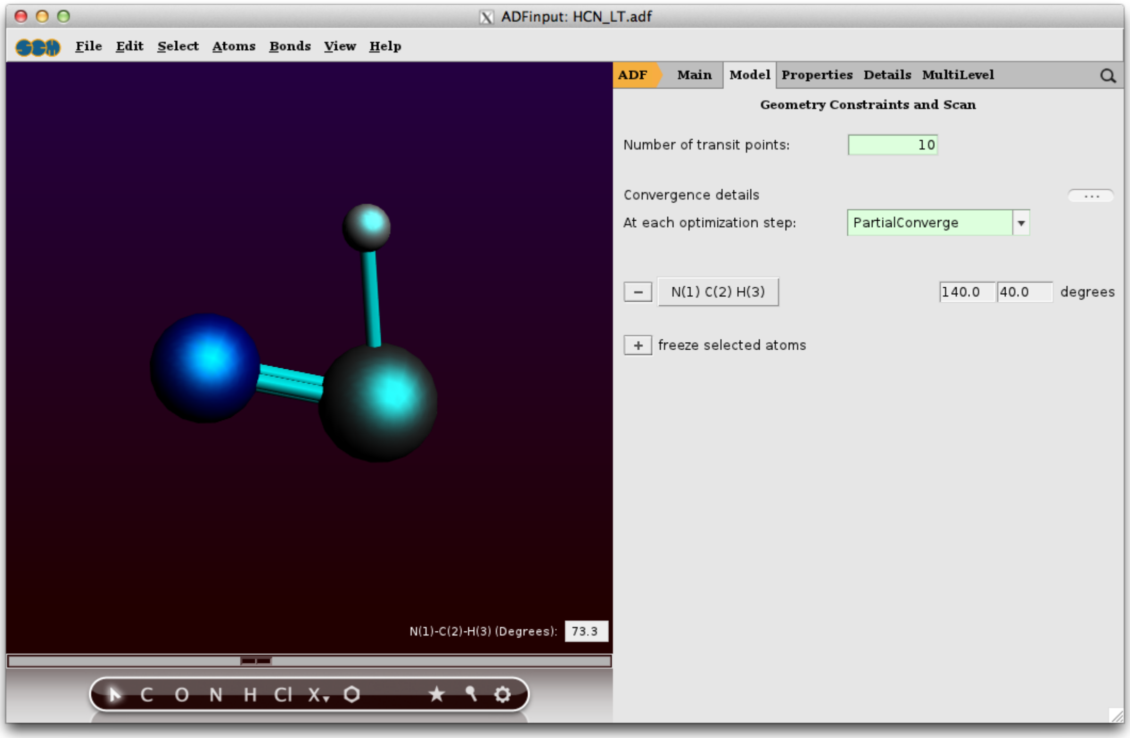
```
              1       2       3       4       5       6       7       8       9      10
 ----------------------------------------------------------------------------------------
 Energy    -0.742  -0.733  -0.723  -0.712  -0.700  -0.690  -0.685  -0.686  -0.693  -0.705

 Dipole x   2.520   2.260   1.948   1.588   1.190   0.769   0.371   0.073  -0.156  -0.627
        y   1.086   1.177   1.236   1.260   1.252   1.226   1.207   1.230   1.383   1.698
        z   0.000   0.000   0.000   0.000   0.000   0.000   0.000   0.000   0.000   0.000
     size   2.744   2.548   2.307   2.027   1.727   1.447   1.262   1.232   1.391   1.810
 ----------------------------------------------------------------------------------------
```

You will see that indeed the geometry number 7 (corresponding to Frame 6 in ADFmovie) has the highest energy. In this particular example the choice of the angle is not very important, but in general you will always want to get the best approximation for the transition state available.

We will now prepare the search for the transition state starting from this geometry:

Click in the ADFmovie window
Make sure frame 6 is selected
Use the **File → Update Geometry In Input** command

The geometry of HCN in your ADFinput window will be updated to match the geometry currently selected in the ADFmovie window:



Geometry Constraints and Scan

Number of transit points: 10

Convergence details
At each optimization step: PartialConverge

− N(1) C(2) H(3) 140.0 40.0 degrees

+ freeze selected atoms

N(1)-C(2)-H(3) (Degrees): 73.3

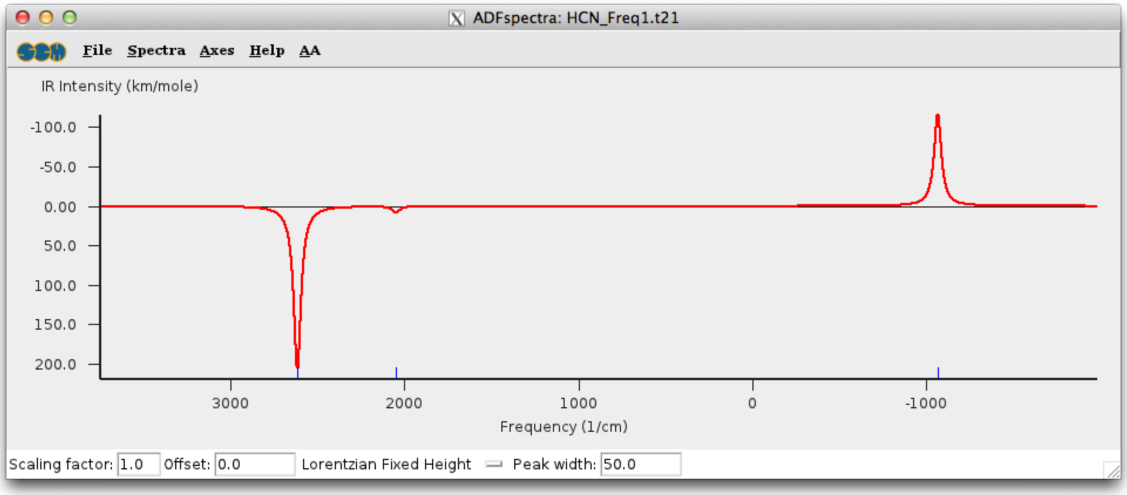
Step 3: Finding the transition state: prepare approximate Hessian

In general, it is important to have a good starting Hessian with one imaginary frequency when performing a TS search. We are going to create such a Hessian by doing a quick frequencies calculation:

Select the "Frequencies" preset (from the Main panel)
Set the integration accuracy to 4
Select the 'Geometry Constraints and Scan' panel (via the ... button or via the panel bar)
Remove the Angle Constraint: click on the '-' in front of the angle constraint
Save the molecule with as 'HCN_Freq1' (Save As)
Run the calculation

The frequency calculation is now in progress and will run very fast. When it has finished:

Select the **SCM → Spectra** command



Scaling factor: 1.0 Offset: 0.0 Lorentzian Fixed Height Peak width: 50.0

If everything was done correctly, you should see a spectrum with three peaks: two in the range of 2000 - 3000 1/cm and one peak in the range of negative or very low positive values. A negative frequency value actually means that it is an imaginary frequency.

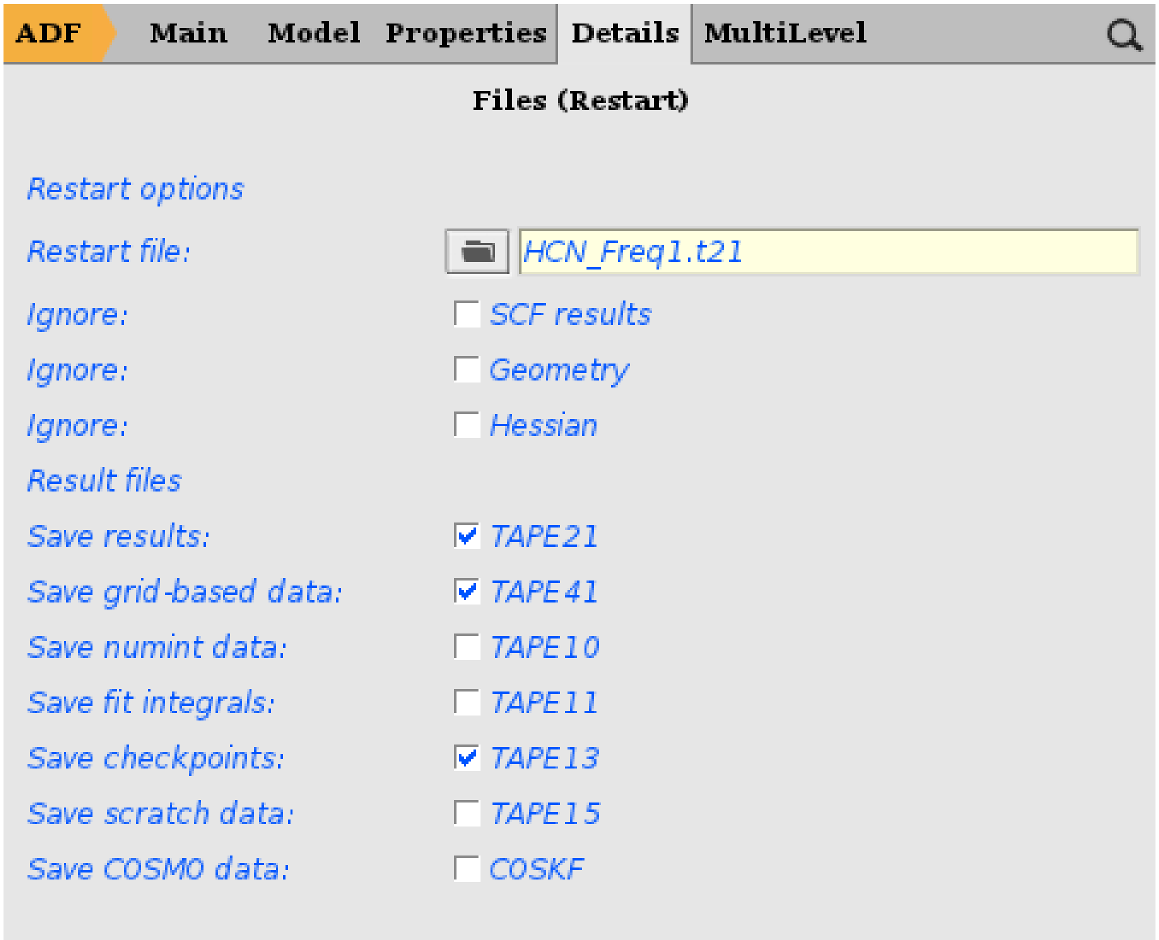
```
Click with your mouse on the peak corresponding to the imaginary frequency
```

The ADFmovie program will start displaying the normal mode corresponding to the frequency. Check that the frequency indeed corresponds to the H atom moving parallel to the C-N bond.

Step 4: Search for the transition state

The result file, HCN_Freq1.t21, has an initial geometry for our transition state search. It also contains a Hessian matrix (produced with the frequencies calculation) that can be used to kick-start the TS procedure.

```
Bring ADFinput with the HCN_Freq1 calculation to the foreground
Select the 'Transition State Search' preset
ctrl/cmd-F and search for 'restart', select the 'Files (Restart)' panel
Click the file select button (looks like a folder) in front of the empty
'Restart file:' field
Select the HCN_Freq1.t21 file and click 'Open':
```



Files (Restart)

Restart options

Restart file: HCN_Freq1.t21

Ignore: ☐ SCF results

Ignore: ☐ Geometry

Ignore: ☐ Hessian

Result files

Save results: ☑ TAPE21

Save grid-based data: ☑ TAPE41

Save numint data: ☐ TAPE10

Save fit integrals: ☐ TAPE11

Save checkpoints: ☑ TAPE13

Save scratch data: ☐ TAPE15

Save COSMO data: ☐ COSKF

```
Save the set up as HCN_TS (Save As)
Run the calculation
```

After the calculation has finished (again very fast), you will be asked to read the new geometry from the results file HCN_TS.t21:

```
Answer "Yes" to import the latest geometry
Make a note of the bond energy for the transition state (visible in the
logfile)
```

ADFinput will now display the transition state geometry.

If you compare the bond energy with the bond energy of the optimized HCN molecule from the first calculation, the difference should be about 1.9 eV. Also check that the geometry makes sense: the C-H and C-N distances should be around 1.20 and 1.19 Angstrom and the H-C-N angle should be about 70 degrees.

Step 5: Calculating frequencies at the transition state

After every transition state search it is good practice to verify that you indeed have one and only one imaginary frequency. For this we will repeat the frequency calculation at the TS geometry:

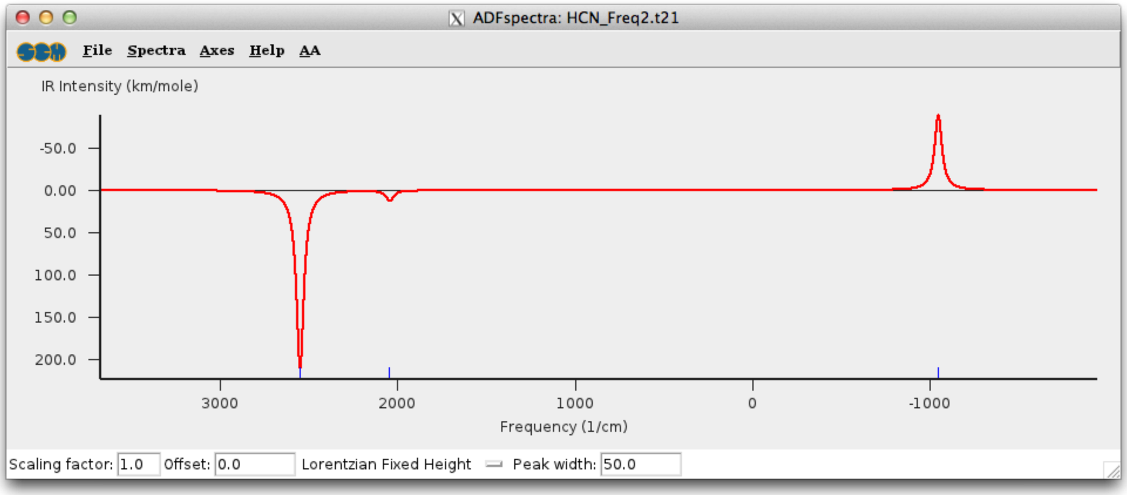
```
Make sure you have HCN_TS open in ADFinput
Select the "Frequencies" preset (from the 'Main' panel)
```

```
Save with name HCN_Freq2
Run
```

The calculation is running, should not take much time. After the calculation has finished:

Select the **SCM → Spectra** command

You will be presented with an IR spectrum of the molecule featuring three bands roughly located at 2550, 2050, and (imaginary) -1040 1/cm.



Scaling factor: 1.0 Offset: 0.0 Lorentzian Fixed Height Peak width: 50.0

```
Click on the band at -1040
```

You should get a movie showing the normal mode corresponding to this frequency, telling us that this is indeed the reaction coordinate we are studying.

Step 6: Following the reaction coordinate

ADF can follow the minimum-energy path from the transition state to one or the other product. The method used in ADF for this is called Intrinsic Reaction Coordinate (IRC). You may want to skip this part as the calculation might take some time to complete.

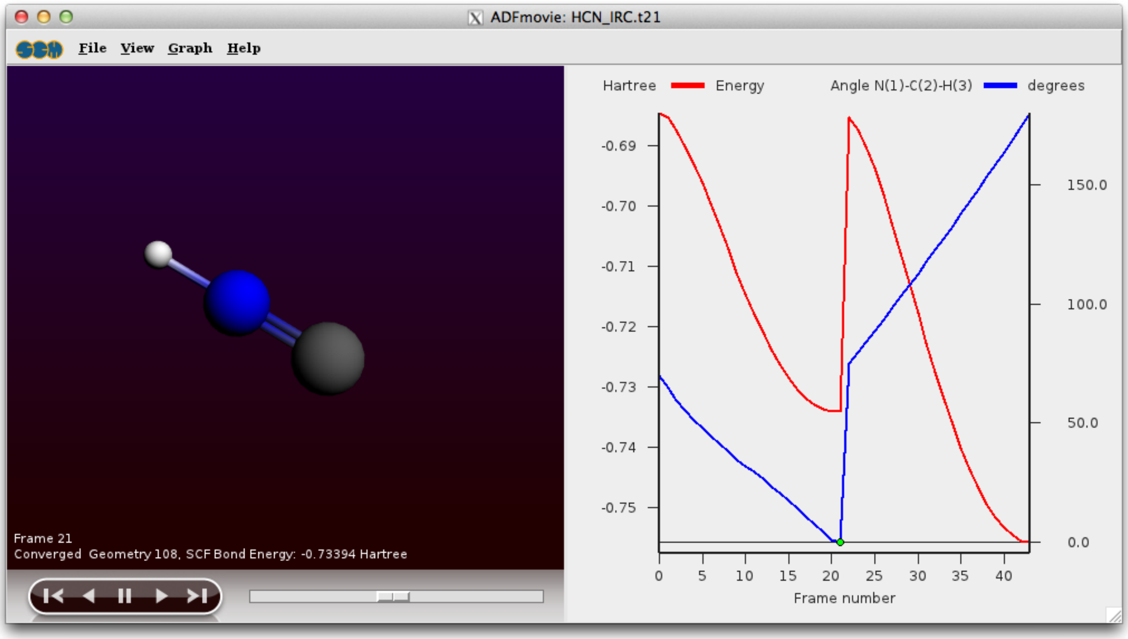
```
Bring HCN_Freq2 in ADFinput to the front
Select the "IRC" preset
Go to the 'Intrinsic Reaction Coordinate (IRC)' panel (in Model, or via the
search, or by clicking on the '...' button)
```

This panel allows you to specify various parameters for the IRC method. The most important parameter is the direction to follow. The choice is more or less arbitrary. By choosing "Forward path" or "Backward path" will lead you to one or the other product but it's hard to tell which of the two in what case. We will calculate both paths at once, so we do not need to change the default.

```
Save as HCN_IRC
Run
```

After some minutes the calculation will finish. You can use ADFmovie to view the IRC path. Of course you need again to make sure to show the converged geometries only:

Select the **SCM → Movie** command
Select the **View → Converged Geometries Only** command
Select the **Graph → Energy** command
Select all atoms
Select the **Graph → Distance, Angle, Dihedral** command



Frame 21
Converged Geometry 108, SCF Bond Energy: -0.73394 Hartree

From this movie you can see the IRC path, and the energies at the most interesting points. As we have calculated the forward and backward path in one run, in the movie you will first see the IRC in one direction (forward), and next resuming in the other direction (backward).

You can also examine some properties along the IRC path by studying the output file:

Select **SCM → Output** (this might take a while, be patient)
Use the **Other Properties → IRC Path** menu command

You will see a table with the properties along the forward path. To get the backwards path:

Click on the blue header 'Dist from TS ...'

The output browser should jump to the next section with that header, which is the table for the backward IRC path.

Finally, at the end of this tutorial you will have many open windows. To close all ADF-GUI related windows at once, you may use the **SCM → Close All** command.

Tutorial 7: TlH (thallium hydride) Spin-Orbit Coupling

This tutorial consists of several steps:

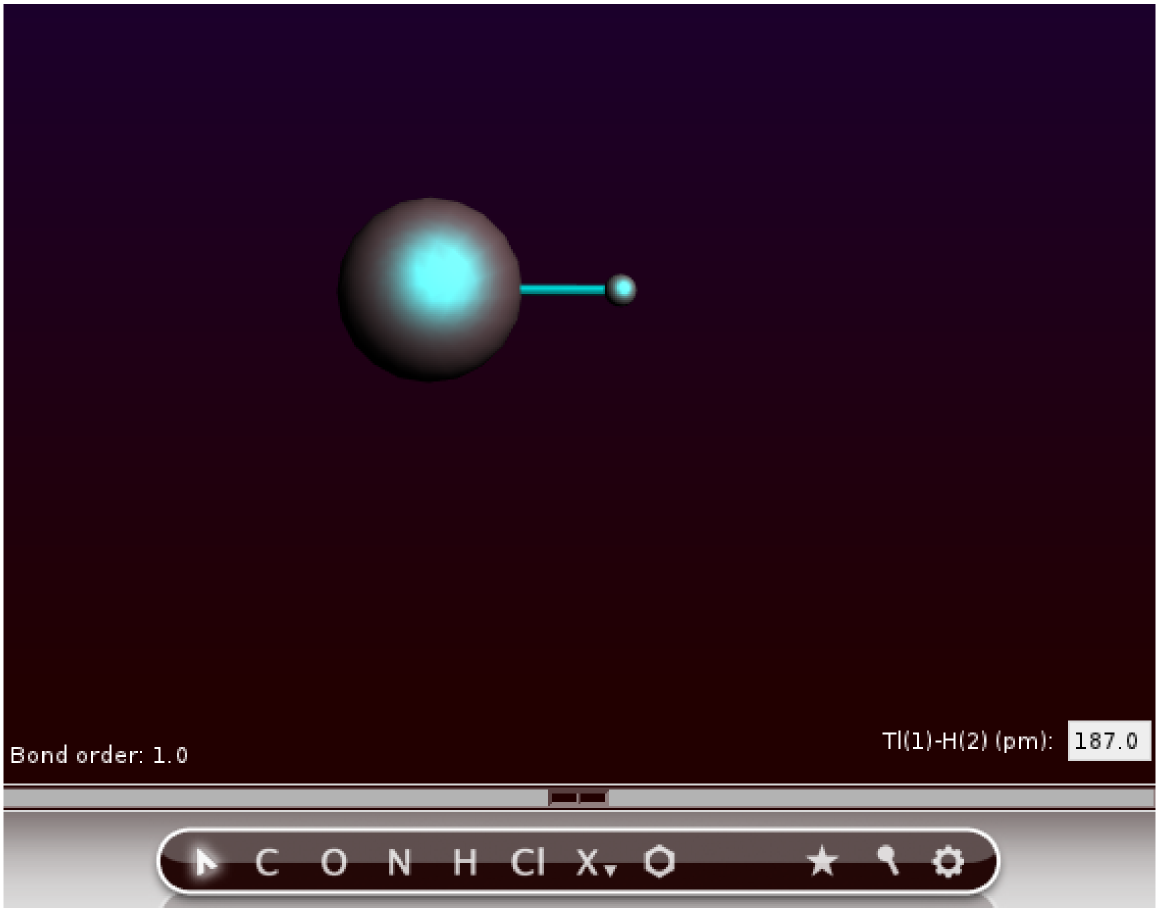
- TlH spin-orbit fragment analysis
- Separate calculations for Tl and H
- Visualization of the energy diagram
- Visualization of spinors

- Calculate the atomization energy

Step 1: Prepare molecule

First create a TlH (thallium hydride) molecule with a bond length of 1.87 Angstrom (the experimental bond length):

```
Open ADFinput and draw a TlH molecule.
Select the Tl and H atoms
Use the slider to set the distance between the atoms 1.87 Angstrom
```



Bond order: 1.0

Tl(1)-H(2) (pm): 187.0

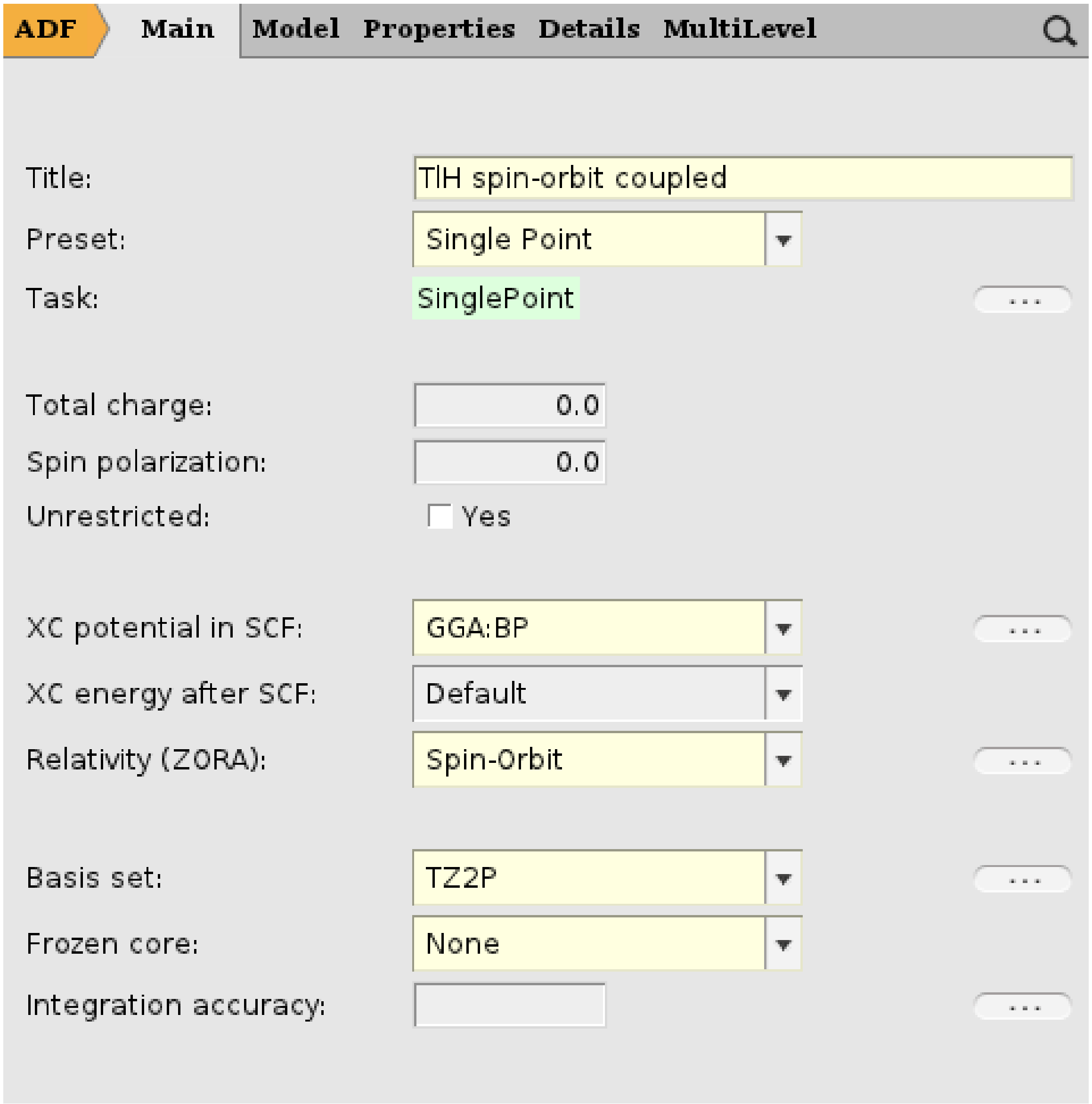
Step 2: Set calculation options

Next we will set up the calculation. The following details need to be set:

```
Clear the selection (click in empty drawing space)

Set the title to 'TlH spin-orbit coupled'

Select the BP GGA as XC potential in SCF
Select the 'Spin-Orbit' relativistic option
```

```
Select the basis set 'TZ2P'
Select the core type 'None'
```

The Main panel will now look like:

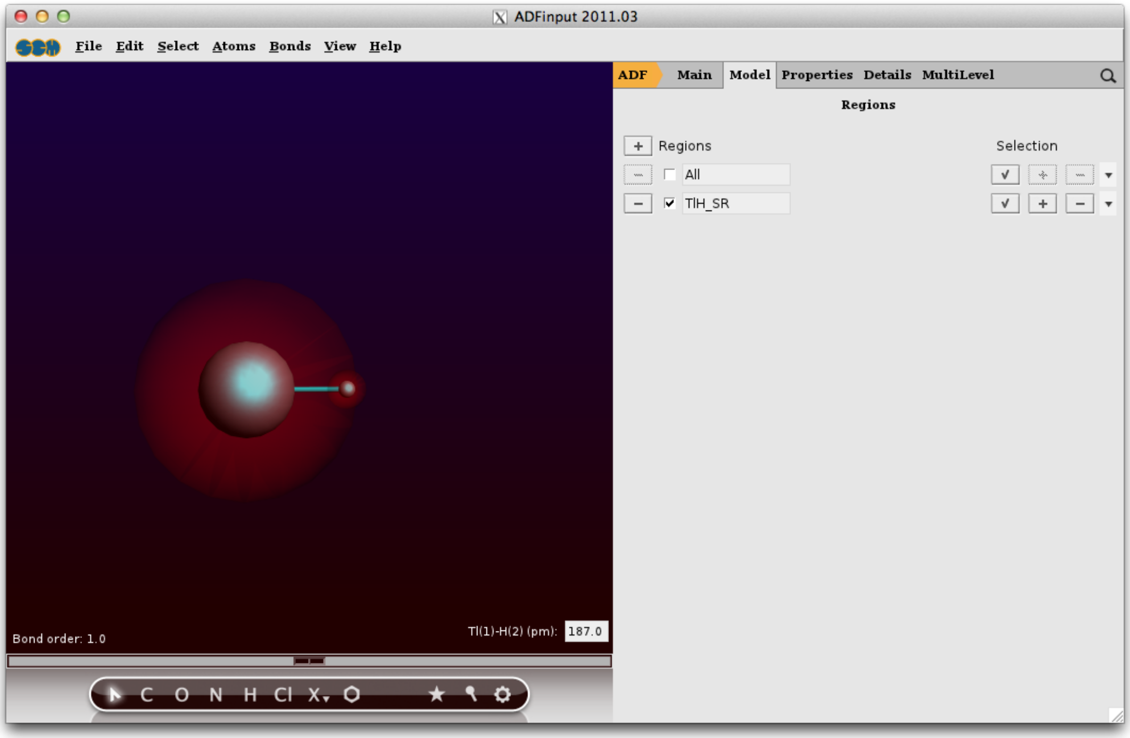


Title: TlH spin-orbit coupled
Preset: Single Point
Task: SinglePoint
Total charge: 0.0
Spin polarization: 0.0
Unrestricted: ☐ Yes
XC potential in SCF: GGA:BP
XC energy after SCF: Default
Relativity (ZORA): Spin-Orbit
Basis set: TZ2P
Frozen core: None
Integration accuracy:

We are going to perform a fragment analysis as a trick to get a diagram that makes it very easy to compare scalar and spin-orbit relativistic results.

Fragment calculations are based on regions, which are just collections of atoms. So we start by making a region:

Select both atoms
Use the panel bar **Model → Regions** command
Click the '+' button to add a new region
Change the name of the new region (Region 1) to TlH_SR



Regions

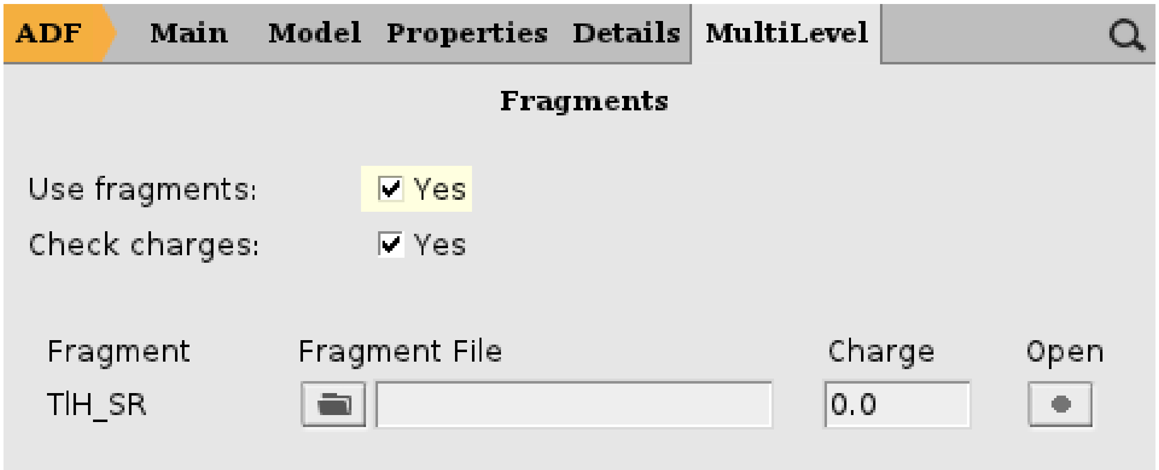
Regions | Selection
☐ All
☑ TlH_SR

Bond order: 1.0

Tl(1)-H(2) (pm): 187.0

You have now defined a region containing all atoms, with name TlH_SR.

Use the panel bar **Multilevel → Fragments** menu command
Click the 'Use fragments' check box



Fragments

Use fragments: ☑ Yes
Check charges: ☑ Yes

Fragment	Fragment File	Charge	Open
TlH_SR		0.0	

Step 3: Run your calculation

Use the **File → Save** menu command
Enter the name 'TlH_SO' in the 'Filename' field
Click 'Save'

Now you have saved your current options and molecule information.

As we have set up a fragment calculation, also the .adf and .run files for the fragment have been saved. Lets study what options are used for the fragment in ADFinput:

`Make sure the 'Fragments' panel is still the current panel`
`Click on the 'Open' button (the dot) for the TlH_SR fragment`

A new ADFinput window will also appear with the name 'ADFinput: TlH_SO.TlH_SR.adf'. This is the name of the molecule, a dot, and the name of the fragment. The fragment should have the 'Scalar' relativistic option selected, as that is required when the results will be used as a fragment. The other options are identical to what you set for the main molecule.

Now close this ADFinput window:

`Select the ADFinput window with the name 'ADFinput: TlH_SO.TlH_SR.adf'`
`Select` **File → Quit**

We are now ready to run the calculation:

`Select the ADFinput window with the name 'TlH_SO.adf.`
`Select` **File → Run**

Now two calculations will run: first the building fragment (using the scalar relativistic option), and next the version including spin-orbit coupling. You will see the two logfiles. Wait until both calculations have finished:

`Wait until ADFtail shows 'Job ... has finished' as last line`
`Select` **File → Quit**
`Repeat for the second ADFtail, thus closing both logfiles`

Step 4: Results of the calculation

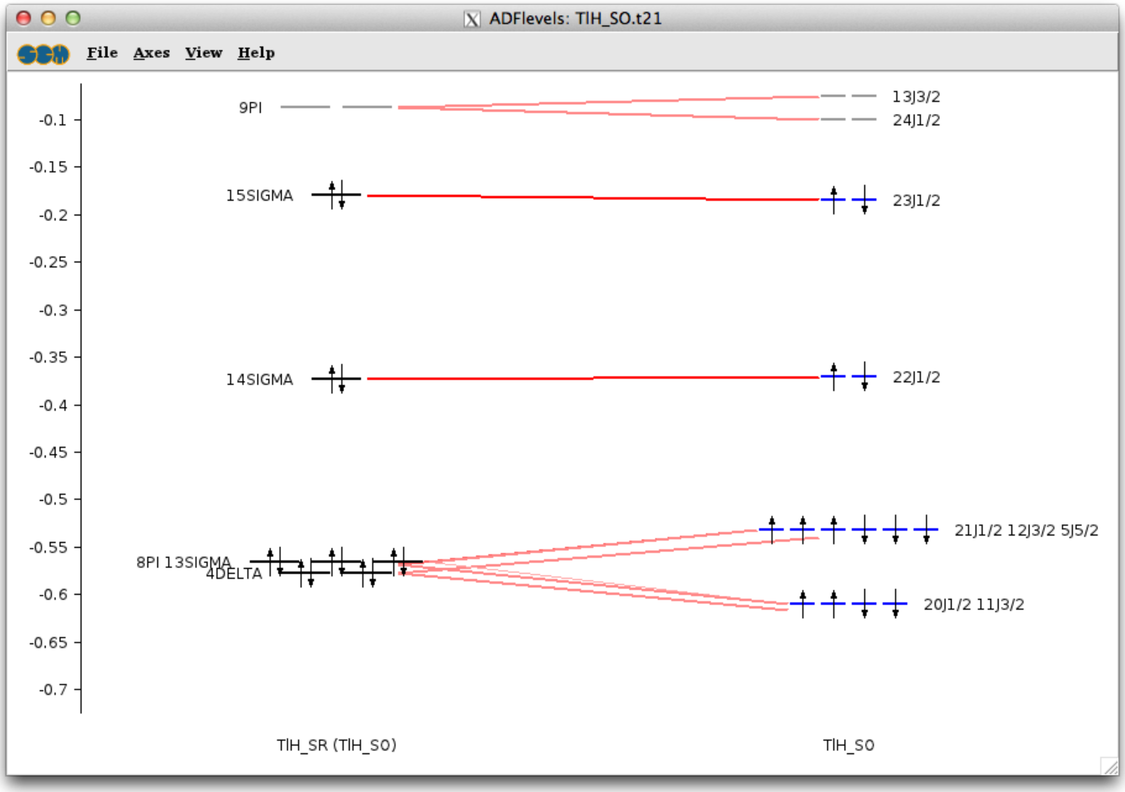
TlH energy diagram

To see the effect of the spin-orbit coupling we will first look at the energy level diagram:

`Select the ADFinput window with the name 'TlH_SO.adf.`
SCM → Levels
`Select` **View → Labels → Show**

`Press and hold the Right mouse button on the stack name 'TlH_SO',`

`Click on 'Zoom HOMO-9 .. LUMO+9'.`
`Next try to zoom using a drag with the right mouse button, or using the scroll wheel.`
`Do this such that only levels between -0.1 and -0.7 eV are shown.`
`You can move the levels vertically by dragging with the left mouse button.`



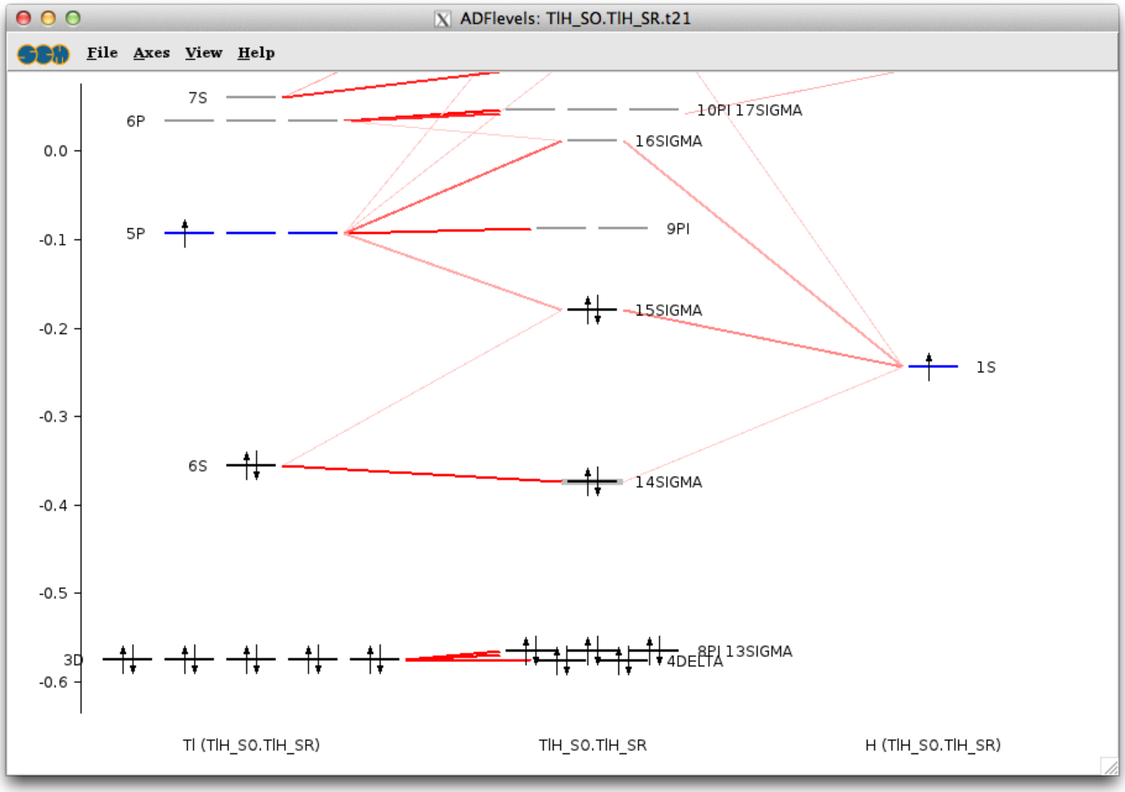
You can see that the spin-orbit coupling is important to split energy levels.

Especially for the Tl core levels the spin-orbit coupling is more important than the ligand field splitting. Compare the 8pi, 13sigma, 4delta orbitals (close to 5d atomic Tl orbitals) with the 11j3/2, 20j1/2 spinors (close to 5d3/2 atomic Tl spinors) and 5j5/2, 12j3/2, and 21j1/2 spinors (close to 5d5/2 atomic Tl spinors).

If you press and hold the right mouse button on one of the levels, you can select a spinor. That spinor will be shown. You can also show all spinors (in the case of a degenerate level) at once.

The energy diagram of the scalar relativistic fragment calculation shows the atomic contributions to the scalar relativistic levels.

```
Bring ADFjobs to the front
Select the TlH_SO.TlH_SR job (the scalar relativistic fragment)
Use the SCM → levels command
Select View → Labels → Show
Press and hold the Right mouse button on the stack name 'TlH_SO.TlH_SR',
Click on 'Zoom HOMO-4 .. LUMO+4'.
Next zoom and move the levels using a right mouse drag and or scroll wheel.
```



Visualization of spinors

Visualization of spinors is conceptually more difficult than visualization of orbitals.

A spinor Ψ is a two-component complex wave function, which can be described with four real functions φ: real part α $\varphi_\alpha{}^R$, imaginary part α $\varphi_\alpha{}^I$, real part β $\varphi_\beta{}^R$, imaginary part β $\varphi_\beta{}^I$:

$$\Psi = \begin{pmatrix} \varphi_\alpha{}^R + i\,\varphi_\alpha{}^I \\ \varphi_\beta{}^R + i\,\varphi_\beta{}^I \end{pmatrix}$$

The density ρ is:

$$\rho = \Psi^\dagger\,\Psi$$

The spin magnetization density **m** is:

$$\mathbf{m} = \Psi^\dagger \boldsymbol{\sigma}\,\Psi$$

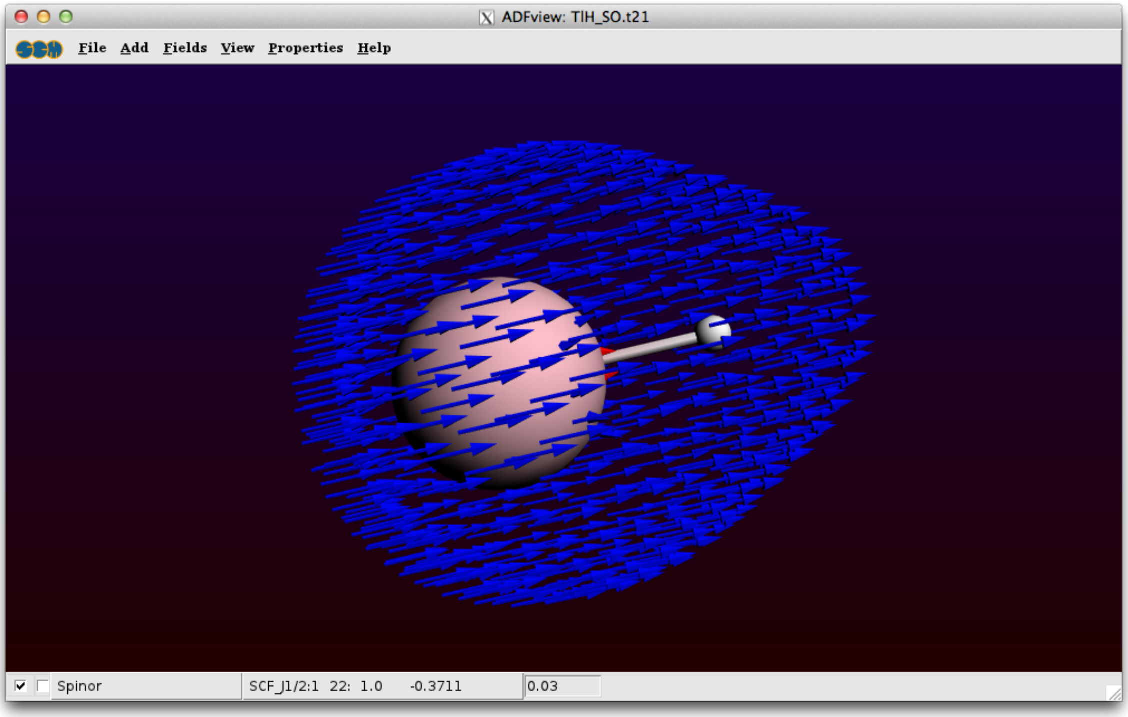
where $\boldsymbol{\sigma}$ is the vector of the Pauli spin matrices. A spinor is fully determined by the spin magnetization density and a phase factor $e^{i\theta}$, which both are functions of spatial coordinates.

In ADFview one can visualize the (square root of the) density and spin magnetization density, however, the phase factor $e^{i\theta}$ is summarized only with a plus or minus sign.

For this tutorial we have a small molecule, and a fine grid is chosen for better visualization.

Select the ADFinput window with the name 'TlH_SO.adf.
Select **SCM → View**
Rotate the molecule, such that one can see both atoms.
Select **Fields → Grid → Fine**
Select **Add → Spinor: Spin Magnetization Density**

In the new control line at the bottom, use the field select pull-down menu and
Select **Orbitals (occupied) → 3 → SCF_J1/2:1 22: 1.0 ... .**

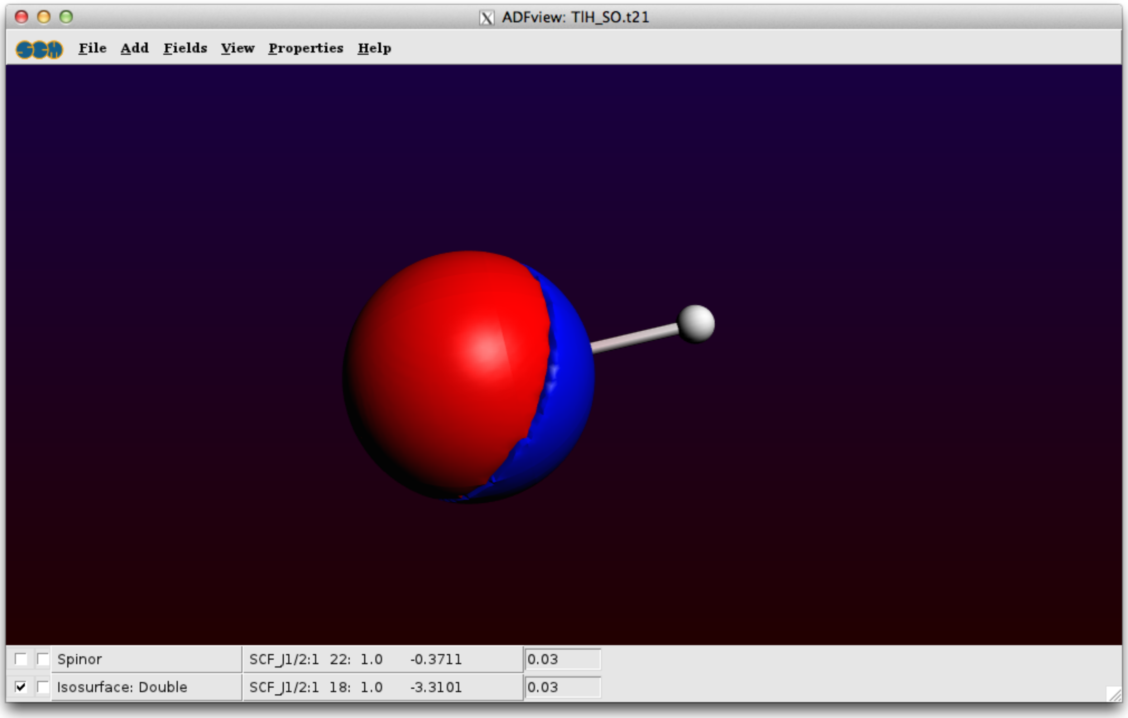


☑ ☐ Spinor | SCF_J1/2:1 22: 1.0 -0.3711 | 0.03

The arrows in this picture are in the direction of the spin magnetization density **m**. All arrows are approximately in the same direction, which means that this spinor is an eigenfunction of spin in this direction of the arrows. In fact this 22 j1/2 spinor is almost a pure α orbital. The arrows are drawn staring from points in space where the square root of square root of the density is 0.03. The color of the arrows are default red or blue, indicating minus or plus for the phase factor $e^{i\theta}$.

The (square root of the) density and the approximate phase vector $e^{i\theta}$ can also be viewed separately:

Select **Add → 'Isosurface: Double (+/-)**
Select **Orbitals (occupied) → 3 → 'SCF_J1/2:1 18: 1.0 ..**
Hide the spinor (uncheck the check box at the left of the Spinor label)

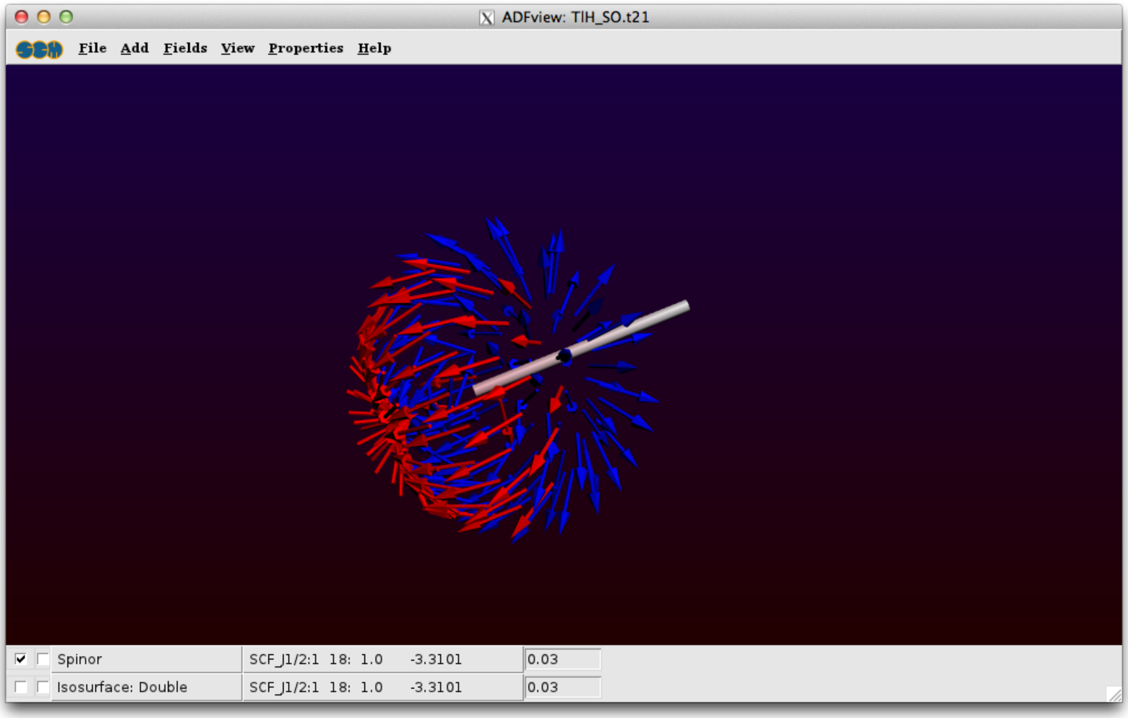


☐ ☐ Spinor — SCF_J1/2:1 22: 1.0 -0.3711 — 0.03

☑ ☐ Isosurface: Double — SCF_J1/2:1 18: 1.0 -3.3101 — 0.03

This spinor 18j1/2 is almost a pure 5p1/2 Tl spinor. A p1/2 atomic orbital has a spherical atomic density, but a spin magnetization density which is not the same in each point in space.

In the control line with 'Spinor', press on the pull-down menu and
Select **Orbitals (occupied) → 3 → SCF_J1/2:1 18: 1.0 ...**
Show the 'Spinor' (check the left check box for the spinor line)
Hide the 'Double Isosurface' (uncheck the left check box for the double iso line)
Hide the atoms: **View → Molecule → Sticks**



☑ ☐ Spinor | SCF_J1/2:1 18: 1.0 -3.3101 | 0.03
☐ ☐ Isosurface: Double | SCF_J1/2:1 18: 1.0 -3.3101 | 0.03

Step 5: Calculate the atomization energy including spin-orbit coupling

The calculation of the atomization energy is not a simple problem in DFT. Spin-orbit coupling is an extra complication. In this paragraph a way is presented how to calculate the atomization energy using spin-polarized calculations in the non-collinear approximation.

If you wish, you can skip the rest of this tutorial.

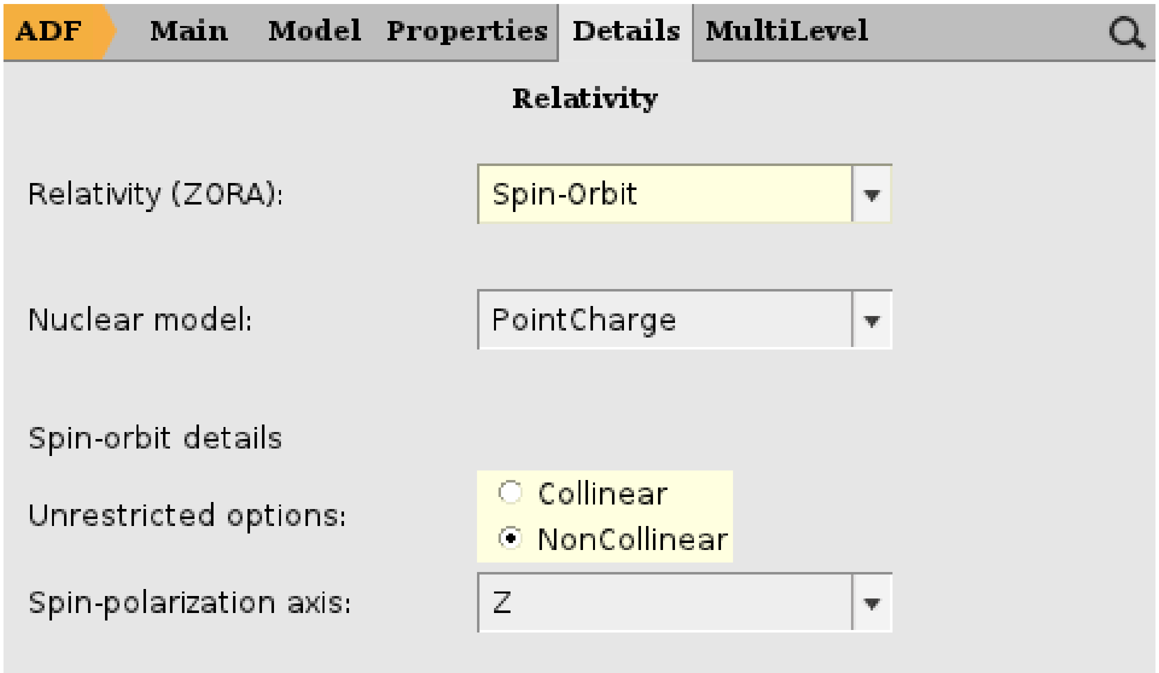
The Tl atom

To calculate an atomization energy we need to calculate the atoms also including spin-orbit coupling. The easiest way is to start with the TlH_SO.adf file and change this to an atomic file.

Since the Tl atom is an open shell atom for an (accurate) atomization energy we need to do an unrestricted calculation. The best theoretical method is the non-collinear method. Note that the 'Spin polarization' field is not used in the non-collinear method.

```
Select the ADFinput window with the name 'TlH_SO.adf
Delete the H atom (select it and press the backspace key)
Use the panel barMultilevel → Fragments command
Uncheck the 'Use fragments' option
Use the panel barModel → Regions command
Remove the TlH_SR region (click on the - button in front of it)
Select 'Main' panel
Enter the name 'Tl spin-orbit coupled' in the 'Title' Menu'
Check the 'Unrestricted:' box

Select the Relativity panel (search for relativity)
Select 'NonCollinear' from the 'Unrestricted Options' Menu
```

Select **File → Save As**
Enter the name 'Tl_SO' in the 'FileName' field
Click on 'Save'
Click OK to acknowledge the warning about fractional occupation numbers



Relativity

Relativity (ZORA): Spin-Orbit
Nuclear model: PointCharge
Spin-orbit details
Unrestricted options: ○ Collinear ● NonCollinear
Spin-polarization axis: Z

Now we want to actually perform the calculation for the Tl atom

Run the calculation: **File → Run**

Wait until ADFtail shows 'Job ... has finished' as last line
In the window showing the logfile (the ADFtail window Tl_SO.logfile):
Select **File → Quit**

The H atom

Basically we can follow the same steps as for the Tl atom, but in this case we will start with Tl_SO.adf file and change this.

Select the ADFinput window with the name 'Tl_SO.adf
Select the 'Main' panel
Enter the name 'H spin-orbit coupled' in the 'Title' field
Select the Tl atom
Use the **Atoms → Change Atom Type → H**
Select **File → Save As...**
Enter the name 'H_SO' in the 'Filename' field
Click on 'Save'
Select **File → Run**
Wait until ADFtail shows 'Job ... has finished' as last line
In the window showing the logfile (the ADFtail window H_SO.logfile):
Select **File → Quit**

TlH atomization energy

The atomization energy including spin-orbit coupling is a combination of several terms.

```
Select the ADFinput window with the name 'TlH_SO.adf.
Select  SCM → Logfile
Write down the value of the bonding energy printed at the end of the
calculation in the
   ADFtail window.  (should be around -1038.62 eV)
Select  File → Open
Select the file 'TlH_SO.TlH_SR.logfile'
Write down the value of the bonding energy printed at the end of the
calculation in the
   ADFtail window.  (should be around -3.84 eV)
Select  File → Open
Select the file 'Tl_SO.logfile'
Write down the value of the bonding energy printed at the end of the
calculation in the
   ADFtail window.  (should be around -1039.32 eV)
Select  File → Open
Select the file 'H_SO.logfile'
Write down the value of the bonding energy printed at the end of the
calculation in the
   ADFtail window.  (should be around -0.95 eV)
```

The atomization energy including spin-orbit coupling is in this case, the bond energy printed in the TlH_SO.logfile plus the the bond energy printed in the TlH_SO.TlH_SR.logfile minus the bond energy printed in the Tl_SO.logfile minus the the bond energy printed in the H_SO.logfile. (approximately -1038.62 - 3.84 + 1039.32 + 0.95 = -2.19 eV, experimental number is close to -2.06 eV.)

Tutorial 8: Multi-Level principles: Regions, QUILD and QMMM

In this tutorial the basic concepts of setting up multi-level calculations in the ADF-GUI will be demonstrated. In most cases one would use a multi-level method for big systems: handle the full system with a fast method, and use ADF to study a particular region of interest with more detail. As big systems will take too much time for a tutorial, the concepts will be shown with very small toy systems that are not typical applications.

Step 1: Regions

For all multi-level calculations you will need to define regions.

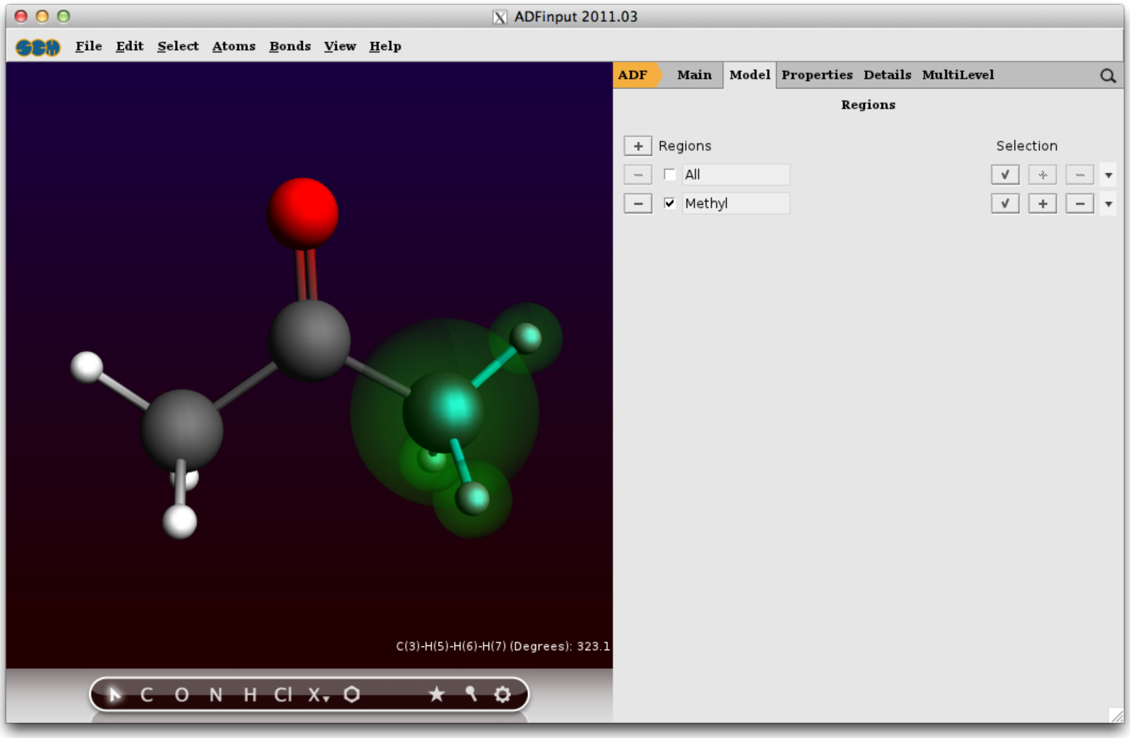
Within ADFinput, **a region is a collection of atoms**. You manage your regions with the 'Regions' panel in ADFinput. It allows you to define new regions, modify existing regions, and to apply some commands on particular regions.

As a first example, we will work with an acetone molecule (CH3COCH3) to demonstrate how to use QUILD.

Generate regions

```
Start ADFinput, and build an Acetone molecule (or search for it ...)
Select one of the methyl groups
```

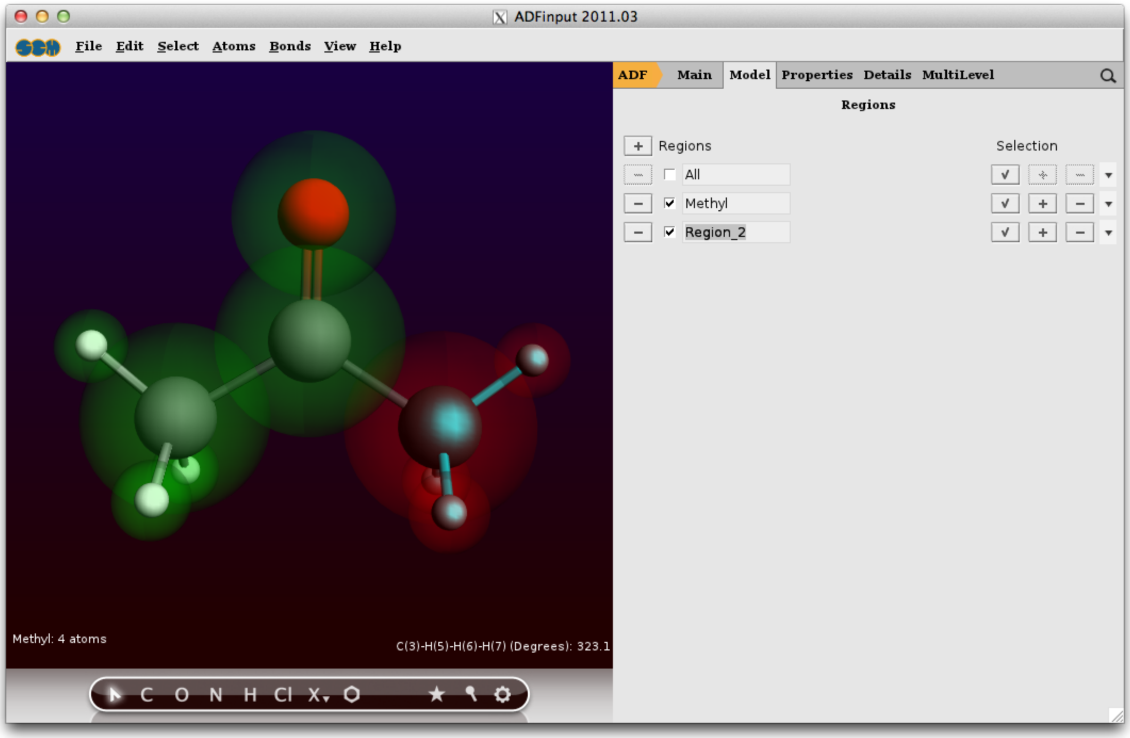
Use the panel bar **Model → Regions** command
Click on the '+' button to add a new region
Change the name 'Region_1' into 'Methyl' (the name is editable)



You have just defined a new region, with a name 'Methyl'. In your molecule window you can see what atoms are part of this region: they are enclosed in slightly ghost-like spheres. Note that there are now (at least) two regions define: the region that you defined, and a region called 'All' that is always present. Obviously, the All region includes all atoms. If you created the acetone molecule via the search command, you may have a third region that was automatically made.

Now we will define yet another region: the rest of the molecule. One way to do this is just to select the atoms that should be part of it, and pressing the '+' button as you did before. However, to demonstrate some of the things you can do with regions we will do it in another way:

Make sure you have only the All and the Methyl region; if you have more, press the '-' button in front of the region
Click the check button in the 'All' region
Click the '+' button to create a new region, as you did before
Click the check button in the 'Methyl' region
Click the '-' button in the 'Region_2' line, on the right-hand side



Basically, what you just did: select all atoms, make a new region containing all atoms, select the atoms in the Methyl region, remove the selected atoms from the new region. By clicking on the select buttons in the regions you can easily verify that your regions are now as they should be.

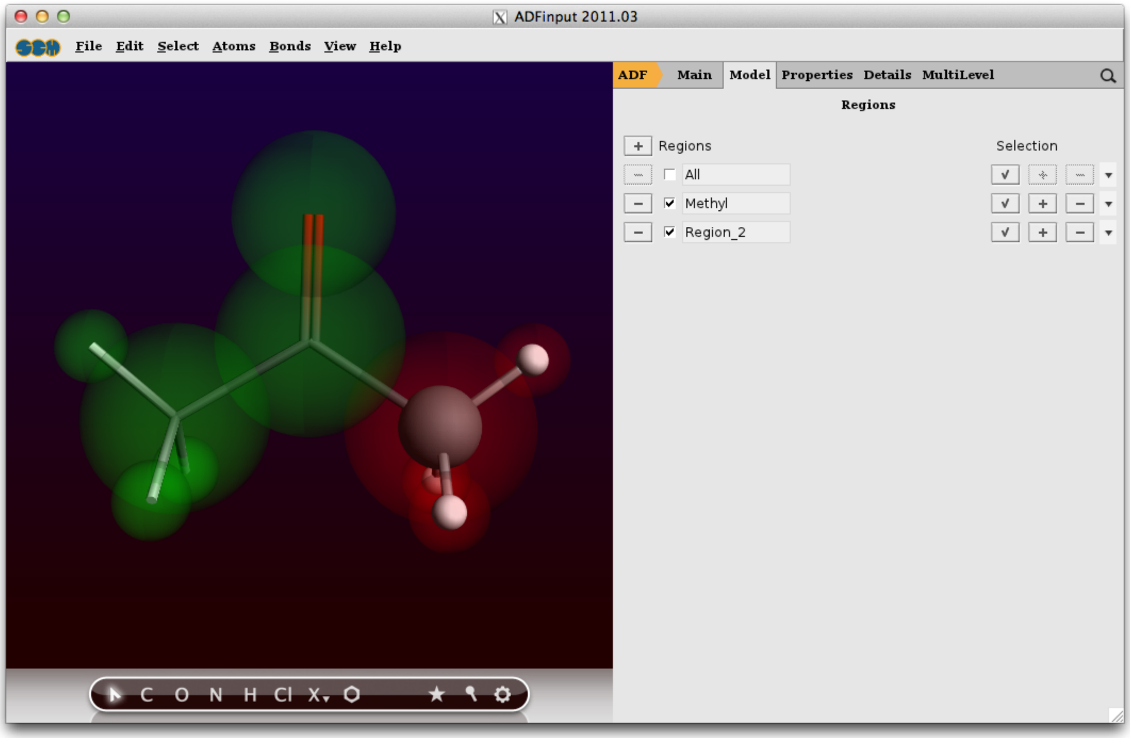
Visualization options per region

You can easily change what regions, and atoms within that region look like:

```
Click in empty (drawing) space to clear the selection
Click in the check box in front of the 'Methyl' region name to uncheck it
```

You should observe that the ghost-like region visualization disappears. Please turn it back on:

```
Click in the check box in front of the 'Methyl' region name to check it
Click on the right arrow at the end of the 'Region_2' line,
  and use the 'Sticks' command from the menu that appears
```



Regions | Selection

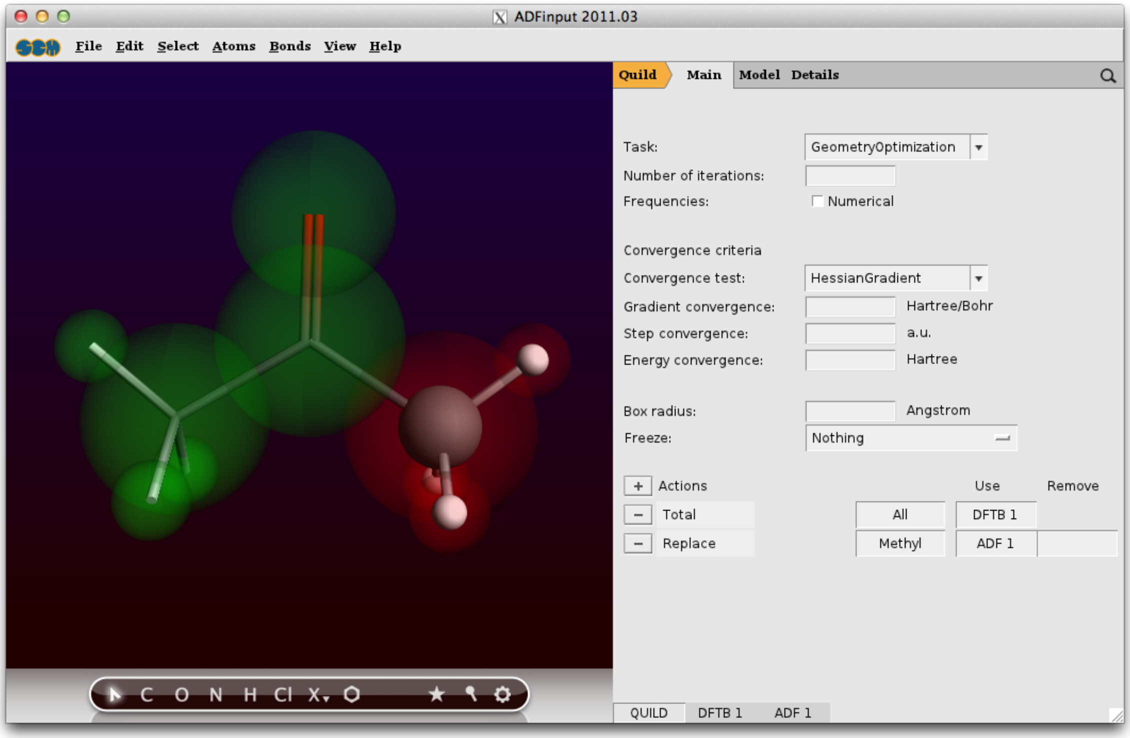
☐ All
☑ Methyl
☑ Region_2

Now anything in 'Region_2' will be visualized as sticks only. Obviously you could also select any of the other display options.

Step 2: QUILD

Once you have defined your regions, it is easy to set up the QUILD calculation:

Use the panel bar **ADF → Quild** menu to select the Quild panel
Click the '+' button to add an action
Click the '+' button to add a second action
In the first action, select DFTB in the 'Use' field
In the second action, select ADF in the 'Use' field



Task: GeometryOptimization
Number of iterations:
Frequencies: ☐ Numerical

Convergence criteria
Convergence test: HessianGradient
Gradient convergence: Hartree/Bohr
Step convergence: a.u.
Energy convergence: Hartree

Box radius: Angstrom
Freeze: Nothing

Actions		Use	Remove
Total	All	DFTB 1	
Replace	Methyl	ADF 1	

The first action ('Total') defines what to do with the full molecule. It normally will apply to the whole molecule, and thus the 'All' region is preselected. In the 'Use' field you have specified how to treat the whole molecule: with DFTB.

The second action ('Replace') tells QUILD to replace the DFTB result for the selected region with results from another method. The region for which we want to do this is the 'Methyl' region, and it happens to be automatically selected. You can use the region pull-down menu will to select another region, and it offers you a short-cut to make a new region.

In the 'Use' field of the second action you have selected what to use as a replacement method: ADF.

In the 'Remove' field it should be specified that you wish to remove the DFTB results for this region. ADFinput will enter this automatically when you save your job. You can also set it manually if you wish.

The Quild panel offers you to set some details for the QUILD calculation. Normally the defaults should work fine.

Save your set up

Below the Quild panel you will now find three tabs: 'Quild', 'DFTB 1', 'ADF 1' and 'DFTB 2'. These tabs allow you to set up the different parts of the calculation. Right now you could make adjustments of the global QUILD settings. If you press on the 'ADF 1' tab, you will have the option to set the details of the ADF calculation (for the 'Methyl' region). And if you click on the 'DFTB 1' tab you can set up details of the DFTB part of the calculation. The 'DFTB 2' tab is the DFTB calculation on the 'Methyl' group that will be removed from the full system. Normally the set up for this calculation is identical to the full system (DFTB 1), but in some special cases you will need to modify it. See the QUILD manual for details.

Click on the 'ADF 1' tab
Look through the different panels, to see what options ADF will use. Do NOT make changes!
Click on the 'DFTB 1' tab

Click on the 'DFTB 2' tab
Click on the 'Quild' tab

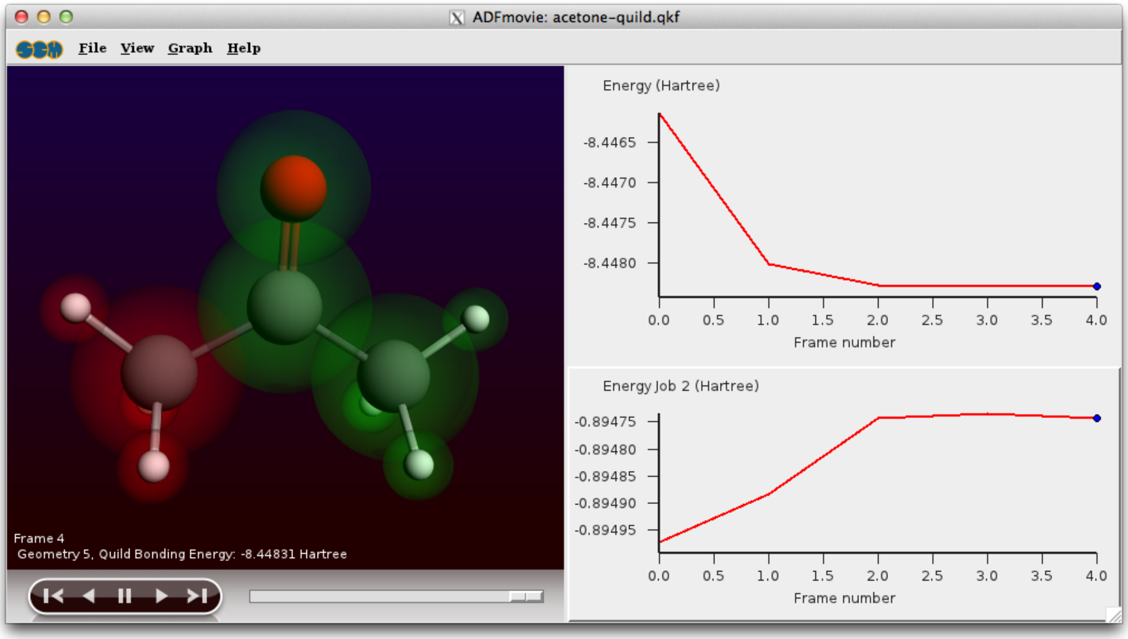
Now let's run this calculation:

File → Run
Click 'No' when asked to update the geometry

When your calculation is finished you can view the resulting optimization using ADFmovie:

Use the **SCM → Movie** command
Add a graph: **Graph → Energy**
Add a second graph: **Graph → Add Graph**

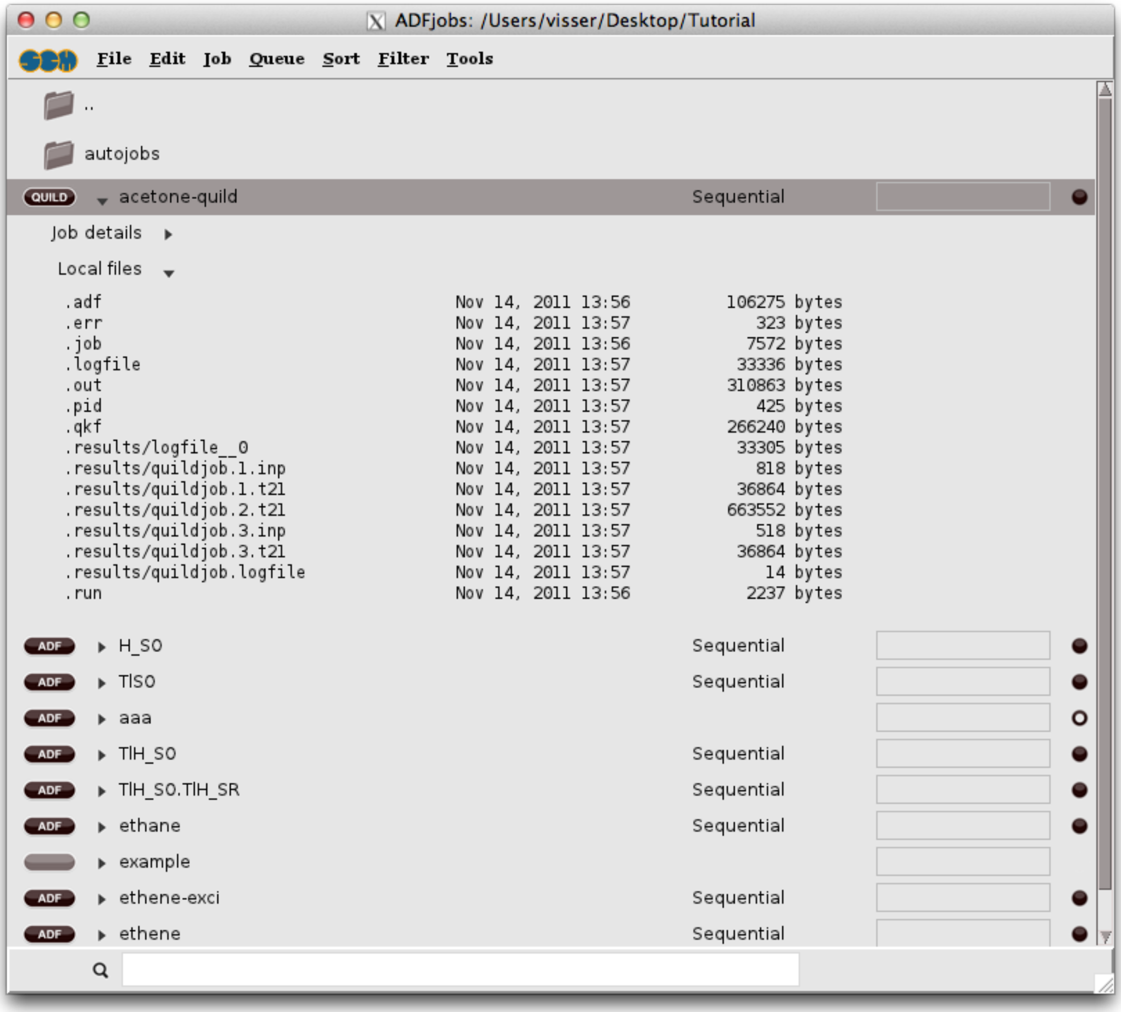
Show the energy of the ADF-subsystem on the second graph:
Graph → Quild Energies → job 2 : ADF ...



Frame 4
Geometry 5, Quild Bonding Energy: -8.44831 Hartree

You can also open the output file using the **SCM → Output** command. The other visualization tools can not be applied to the full QUILD results, but they can be used to examine the result of the ADF calculation (on the Methyl region). This is done in quildjob.2:

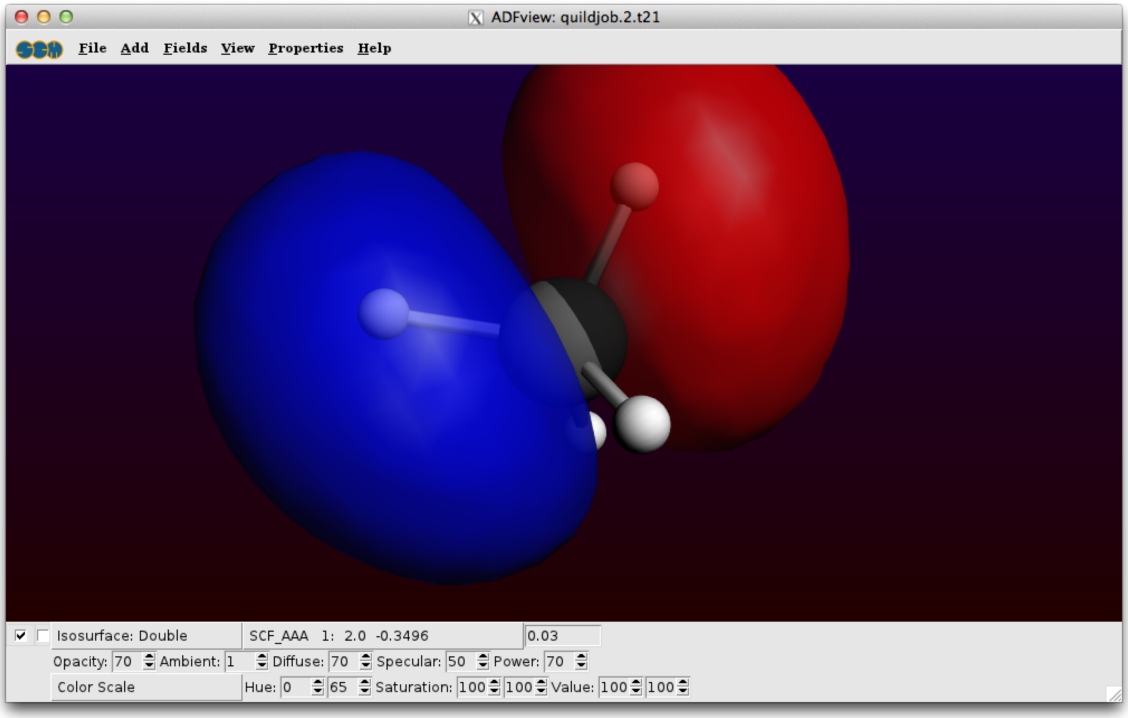
Show the ADFjobs window
Show the QUILD job details (click on the triangle to show the details)



```
acetone-quild                                          Sequential
 Job details
 Local files
 .adf                         Nov 14, 2011 13:56      106275 bytes
 .err                         Nov 14, 2011 13:57         323 bytes
 .job                         Nov 14, 2011 13:56        7572 bytes
 .logfile                     Nov 14, 2011 13:57       33336 bytes
 .out                         Nov 14, 2011 13:57      310863 bytes
 .pid                         Nov 14, 2011 13:57         425 bytes
 .qkf                         Nov 14, 2011 13:57      266240 bytes
 .results/logfile__0          Nov 14, 2011 13:57       33305 bytes
 .results/quildjob.1.inp      Nov 14, 2011 13:57         818 bytes
 .results/quildjob.1.t21      Nov 14, 2011 13:57       36864 bytes
 .results/quildjob.2.t21      Nov 14, 2011 13:57      663552 bytes
 .results/quildjob.3.inp      Nov 14, 2011 13:57         518 bytes
 .results/quildjob.3.t21      Nov 14, 2011 13:57       36864 bytes
 .results/quildjob.logfile    Nov 14, 2011 13:57          14 bytes
 .run                         Nov 14, 2011 13:56        2237 bytes

H_SO                                                   Sequential
TlSO                                                   Sequential
aaa
TlH_SO                                                 Sequential
TlH_SO.TlH_SR                                          Sequential
ethane                                                 Sequential
example
ethene-exci                                            Sequential
ethene                                                 Sequential
```

Using the View menu command you will try to open the .t21 result file for the QUILD job. That will not work, we need to view only the .t21 file of the adf sub-system. To do this, we first open this result file in the KFBrowser. This tool allows you to inspect details of the binary KF files. Next, use the View command in the SCM menu of the KFBrowser to open that specific file in ADFview:

`Double-click on the .results/quildjob.2.t21 file`
`In the KFBrowser window,` **SCM → View**
`In the ADFview window Remove and Guess bonds (this is a work-around a bug that messes up the bond display)`
`Visualize the HOMO in ADFview`
`Click on the Isosurface:Double pull-down menu and use the Show Details command`
`Change the Opacity to 70`



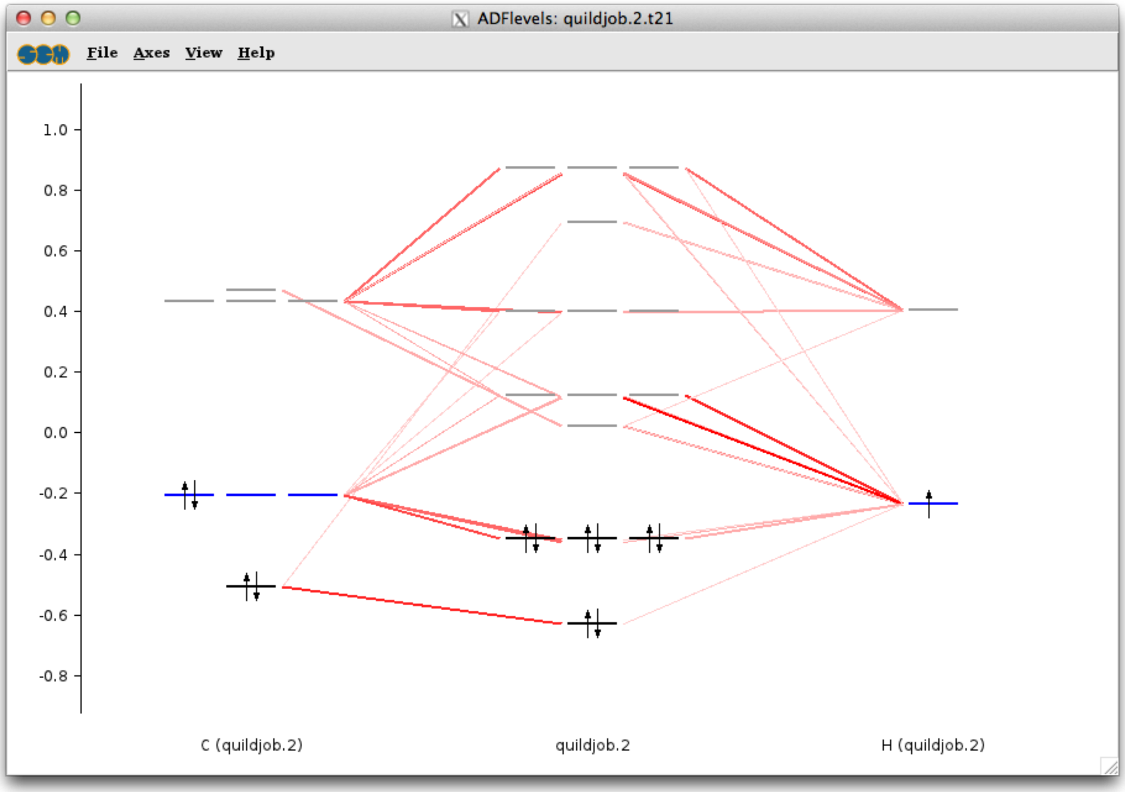
☑ ☐ Isosurface: Double SCF_AAA 1: 2.0 -0.3496 0.03

Opacity: 70 Ambient: 1 Diffuse: 70 Specular: 50 Power: 70

Color Scale Hue: 0 65 Saturation: 100 100 Value: 100 100

Note that QUILD has added a dummy hydrogen to cap the broken bond.

`In the ADFview window, use the` **SCM → Levels** `command`



Now you have the ADF result file for the methyl group visible in ADFview and ADFlevels. With ADFview and ADFlevels you can examine the ADF results as usual.

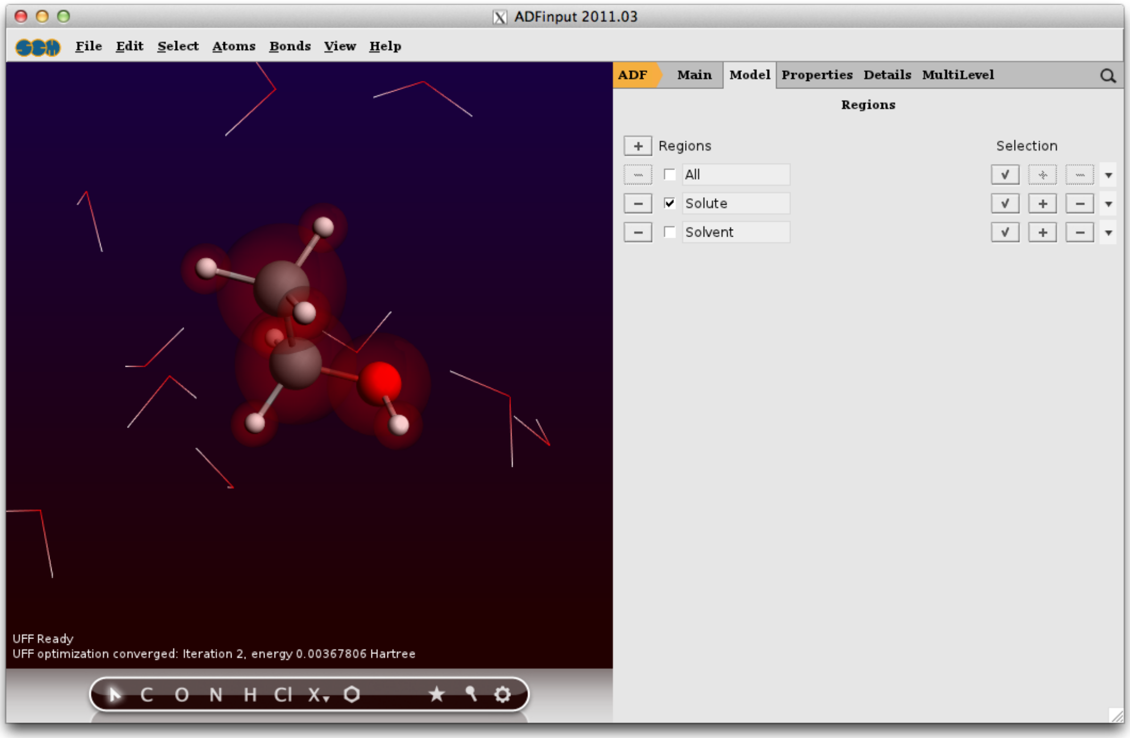
SCM → Close All

Step 3: QMMM

Generate ethanol in water

To demonstrate how to set up a QUILD calculation using ADFinput, we will use ethanol in water as an example. This will also show you how to add explicit solvent molecules to your system:

```
Start ADFinput
Build an ethanol molecule
Pre-optimize the structure
Use the panel bar Model → Solvation command
Click on 'Explicit Solvent Molecules'
Change the radius of the solvent sphere to a small value,
   such that 10 solvent molecules will be generated
Click on 'Add Solvent'
```



Regions

☐ All

☑ Solute

☐ Solvent

UFF Ready

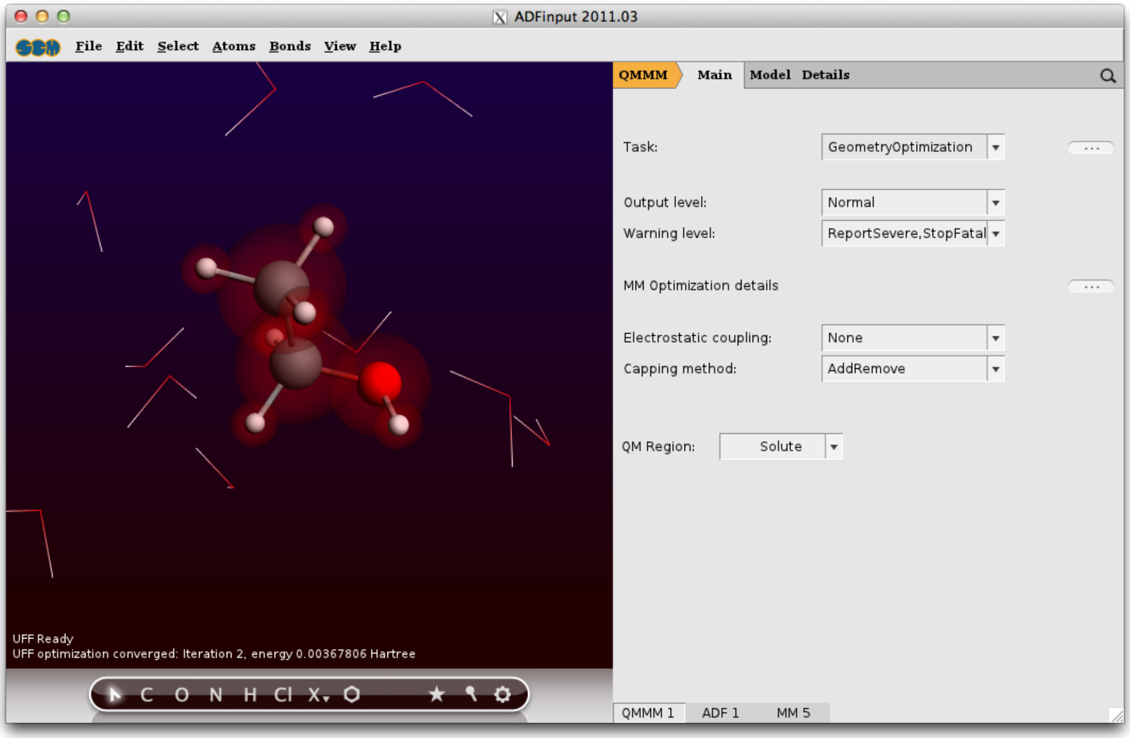
UFF optimization converged: Iteration 2, energy 0.00367806 Hartree

As you can see, ADFinput has generated 10 water molecules around your ethanol molecule. It also has created two regions: a Solute region containing the ethanol molecule, and a Solvent region containing the water molecules. The visualization option for the Solvent region is such that the water molecules will only be shown using a Wire-frame representation.

Set up the QM/MM calculation

The next step is to set up the QM/MM calculation:

ADF → QMMM: select the 'QMMM' panel
Select the 'Solute' region in the 'QM Region' pull-down menu
Change the QMMM Task to GeometryOptimization



Task: GeometryOptimization
Output level: Normal
Warning level: ReportSevere,StopFatal
MM Optimization details
Electrostatic coupling: None
Capping method: AddRemove
QM Region: Solute

UFF Ready
UFF optimization converged: Iteration 2, energy 0.00367806 Hartree

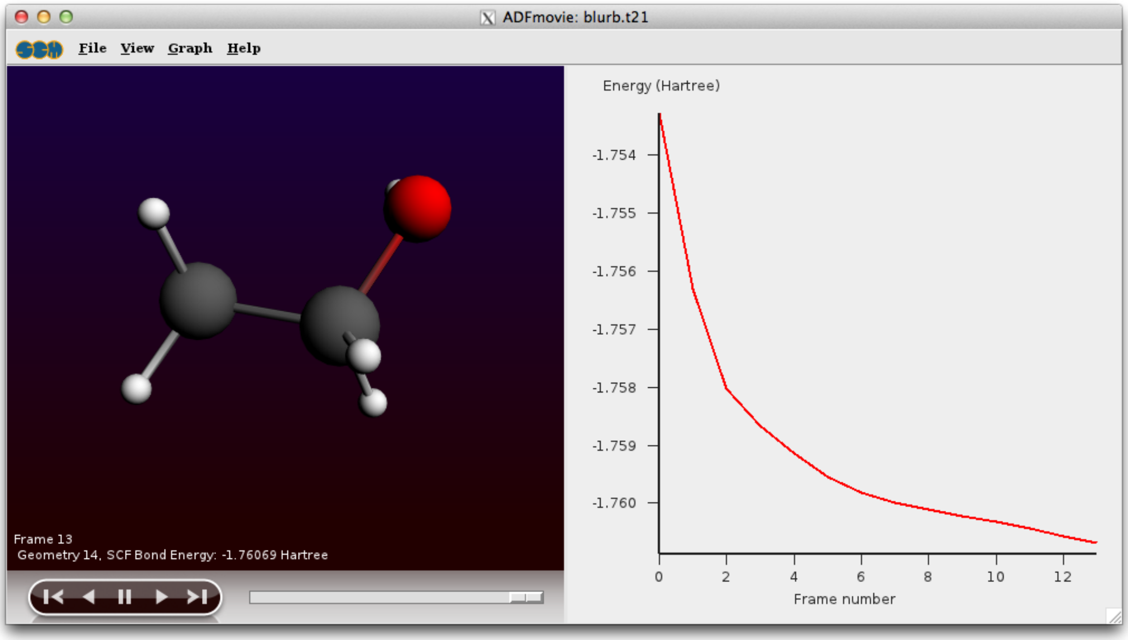
Now you will have three tabs: the main QMMM tab that allows you to set QMMM details, the 'ADF 1' tab that is the setup for the ADF calculation for the Solute subsystem, and the 'MM 5' tab that sets up the MM calculation for the full system.

ADFinput is currently not very smart in setting the proper atom types for a MM calculation. So you will need to examine the atom types as they are generated in the MM input, and fix them if they are not correct. To fix this, if needed, use the Atom Inspector panel to set the Tripos (or Amber) atom types as needed.

Click on the 'MM 5' tab
Activate the 'Run Script' panel (in the panel bar Details)
Check the atom types (in the run script)

Run the QMMM calculation, and see results

Run your calculation **File → Run**
Show the optimization movie:
In the ADFinput window: **SCM → Movie**
Graph → Energy



Frame 13
Geometry 14, SCF Bond Energy: -1.76069 Hartree

Note that ADFmovie (and the other GUI modules) will only show the results for the QM part of your calculation.

To get detailed information on your QMMM calculation, you can check the output file using the **SCM → Output** command.

Tutorial 9: ADF Fragment Analysis

This tutorial will show you how to use the Fragment Analysis within ADF. The two examples used here are:

- $Ni(CO)_4$
- $PtCl_4H_2^{2-}$

You will set up the calculations, run them, and visualize the results.

The resulting ADFinput input file (*.adf) is available in the examples directory included in the ADF distribution. In the examples documentation you can read how to set up a similar calculation without ADFinput.

The first example in this tutorial is $Ni(CO)_4$. It consists of one Ni fragment and once CO fragment that is repeated four times.

The second example is $PtCl_4H_2^{2-}$. It consists of a $PtCl_4^{2-}$ fragment, and one H_2 fragment. It is a good example on how to specify the charges of the fragments.

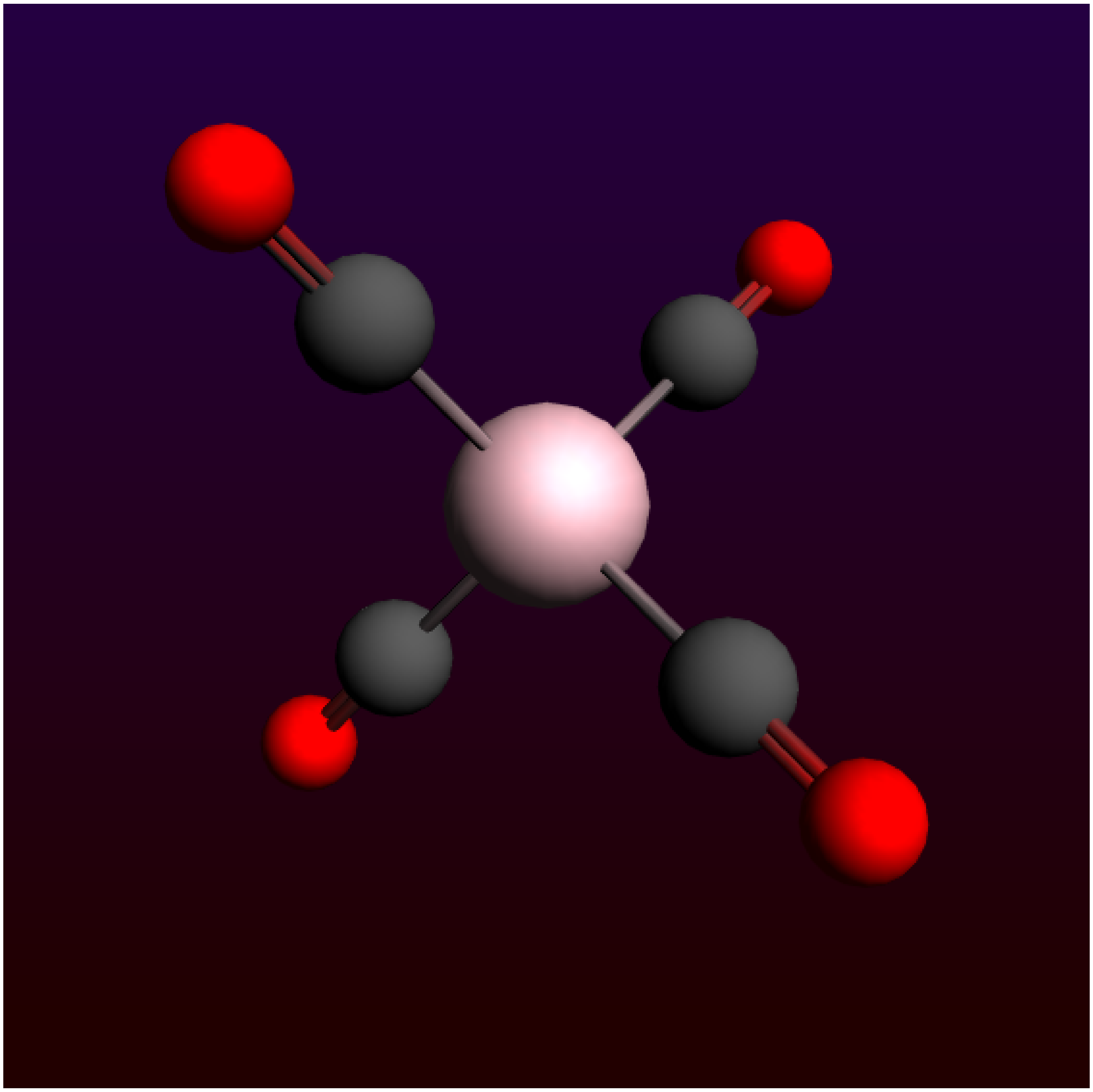
Step 1: Build $Ni(CO)_4$

The structure is perfectly tetrahedral. You should be able to build the molecule yourself, using the techniques described in earlier tutorials. One possible way:

`Start ADFinput`
`Build a tetrahedral metal complex:` **Structure Tool → Metal Complexes → ML4 tetrahedral**

Change the central atom into a Ni atom
Select one ligand
Select all ligands: **Select → Select Atoms Of Same Type** menu command
Change them in CO ligands: **Atoms → Replace By Structure → Ligands → CO**
Choose the 'Geometry Optimization' Preset
Save and Run
When the run has finished, click 'Yes' to import the optimized coordinates
Save

Your molecule should look something like this:



Step 2: Define fragments

The fragments that ADF uses are based on the regions that you define. In this example we will generate four new regions: one for each of the CO ligands. The regions for the CO ligands will get special names to make sure that ADF recognizes them as one fragment repeated four times.

The Ni atom will not be in a region. ADFinput will automatically create atomic fragments for all atoms not in a region.

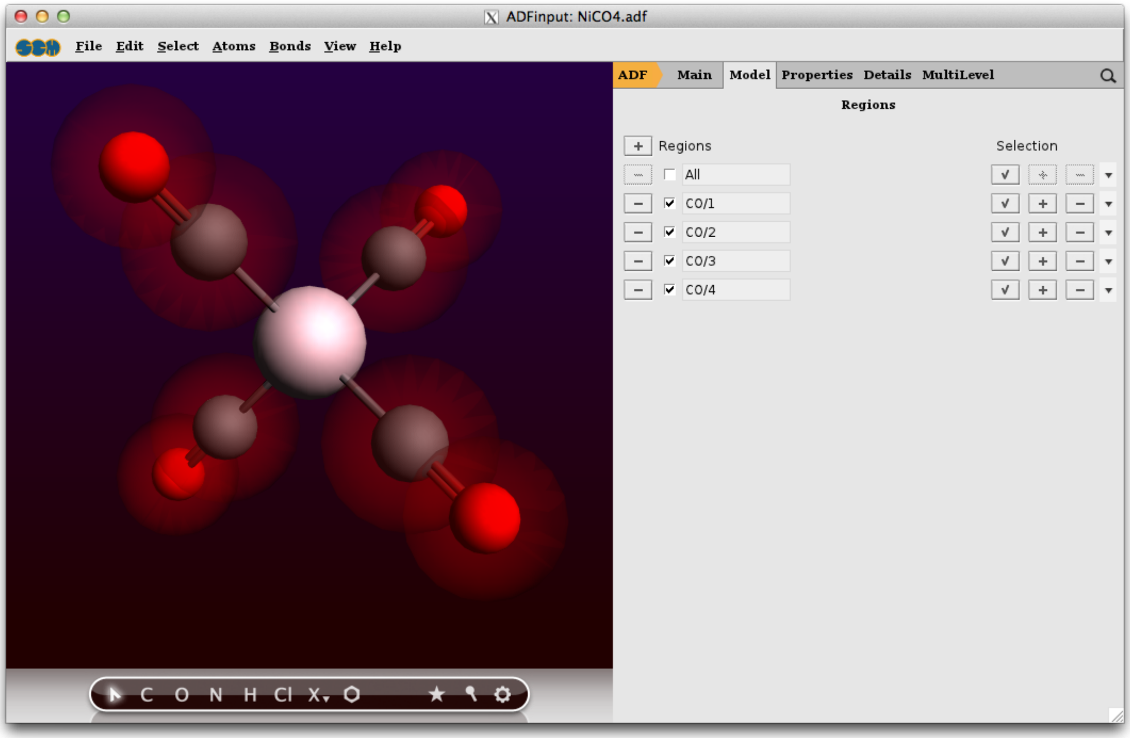
Repeated fragments are indicated with the fragment name followed by '/n', with n the number of the copy. All copies must match such that one fragment can be positioned exactly over another fragment by rotation and translation. ADF checks for this, ADFinput does not. In this particular example all four CO fragments are obviously identical by symmetry.

`Panel bar` **Model → Regions**
`Select all atoms`
`Click the '+' button to add another new region (containing all atoms)`
`Select the Ni atom`
`Remove the Ni atom from Region_1: click the '-' button on the right side of the 'Region_1'`
`Change the name of 'Region_1' into 'CO'`

Now one new region has been defined: the CO region for the ligands. The next step is to split the ligand region into four repeated regions:

`Press the triangle on the right side of the CO region line`
`In the pop-up menu, use the 'Split By Molecule' command`

This should result in the following regions:

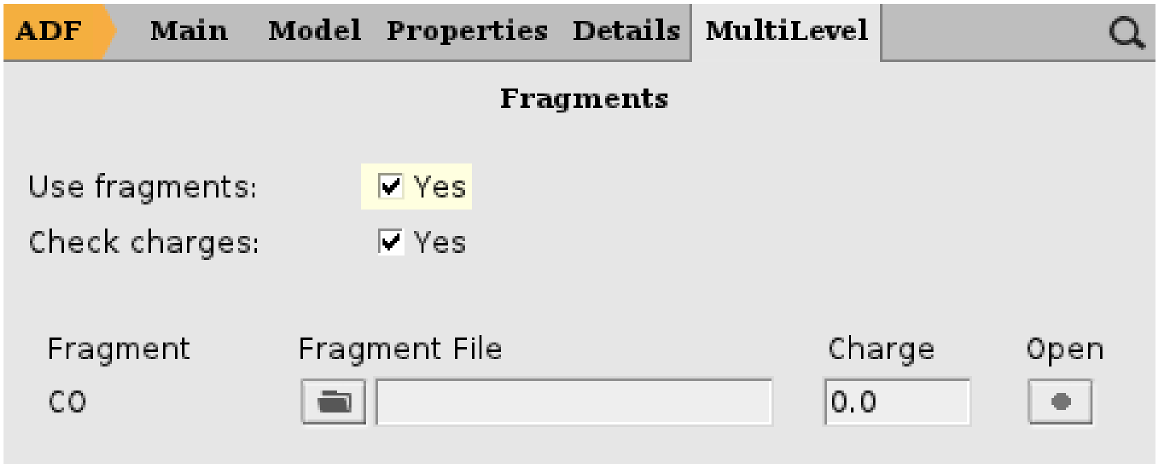


Step 3: set up the fragment analysis run

The next step is very easy: we will tell ADF to perform a Single Point calculation (fragment analysis in ADF only works with a single point calculation), and we tell ADFinput to use the regions that we just defined as fragments:

Open the 'Main' panel
Select the 'Single Point' preset
Panel bar **MultiLevel → Fragments**
Check the 'Use fragments' check box

Instead you could also select the 'Fragment Analysis' preset, which is identical to the Single Point preset but with 'Use fragments' activated.



Fragments

Use fragments: ☑ Yes
Check charges: ☑ Yes

Fragment	Fragment File	Charge	Open
CO		0.0	●

In the Fragments panel you will see that one fragment is present, without charge: the repeated CO fragment. ADF will use basic atomic atoms for any atoms not put in another fragment. Thus, the Ni atom will be an atomic fragment.

Step 4: Run the fragment analysis and view the results

Next you will Save and Run the calculation. When you do this, ADFinput will actually save two different calculations:

- The CO calculation (with matching .adf and .run file)
- The Ni(CO)$_4$ fragment analysis calculation (with matching .adf and .run file)

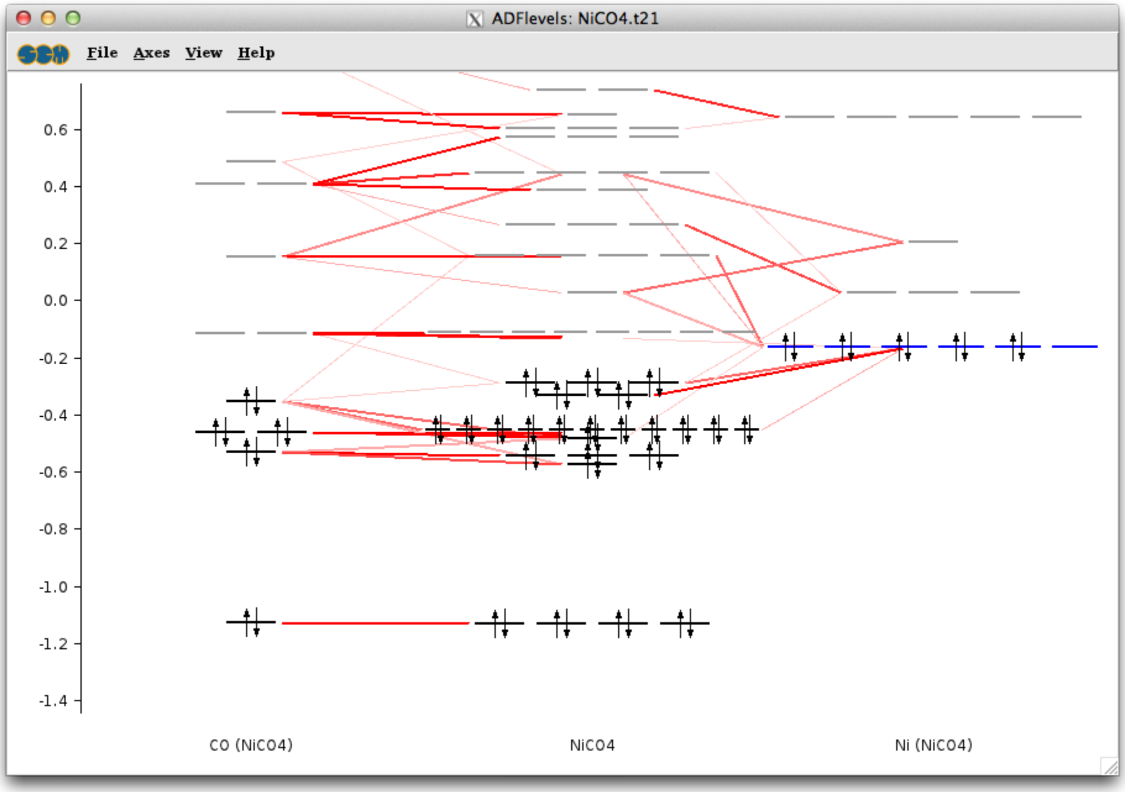
You do not need to set up a separate ADF calculation for the CO fragment: when you run the fragment analysis calculation, the run script will detect that the individual fragments first need to be calculated. It does so automatically. Next, the fragment analysis calculation will run.

Save
Run
Observe the running of the fragment (CO), and the final fragment analysis

The CO-fragment and Ni(CO)$_4$ calculations all have been performed.

This calculation results in the normal .t21 and .out output files. You can view them with the **SCM → View** and **SCM → Output** commands. More interesting in the case of a fragment analysis is the interaction diagram that you can view using ADFlevels:

In the still open ADFinput window: use the **SCM → Levels** command

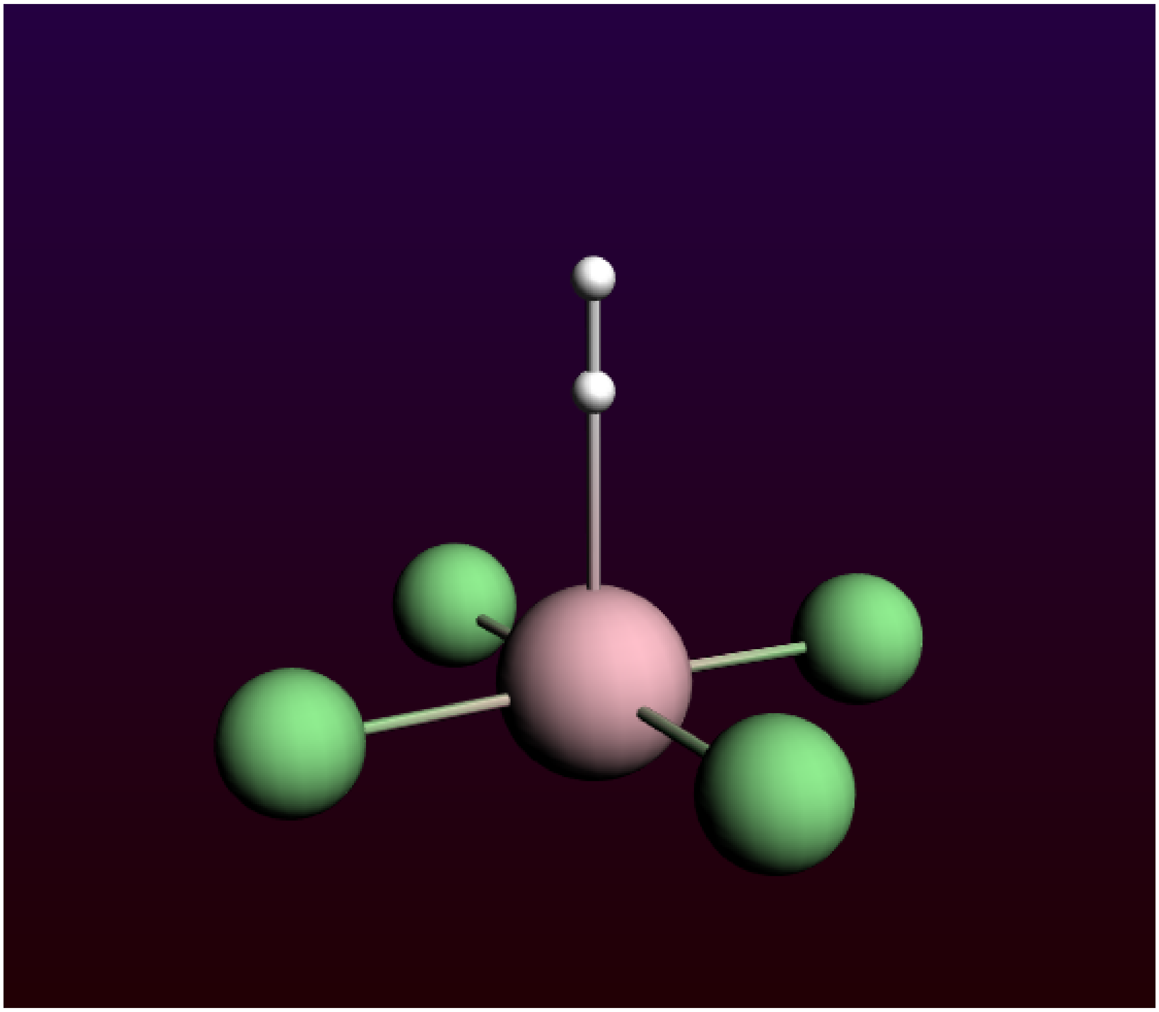


In the center you see the levels of the whole molecule, on the sides you see the CO fragment and the Ni-atom fragment. The interaction lines tell you which molecular orbitals come from which fragment orbitals.

In the output file you can find detailed information about the composition of the molecular levels in terms of the fragment orbitals.

Step 5: Build $PtCl_4H_2^{2-}$

The following is a picture of the $PtCl_4H_2^{2-}$ molecule, after optimization with ADF::



To make this molecule, an easy way is to start with an octahedral complex to ensure symmetry. Next make changes to get this molecule, ending with a geometry optimization with ADF:

Build an octahedral metal complex using the Structures button
  (**Structure Tool → Metal Complexes → ML6 octahedral**)
Change the central atom into a Pt atom
Change four dummies in a plane into Cl atoms
Remove one of the remaining dummies
Change the remaining dummy in OH, via **Structure Tool → Ligands → OH**
  (this will ensure the final two H's do not break symmetry)
Change the O atom into an H atom

Choose the 'Geometry Optimization' Preset
Set the total charge to -2
Select the Scalar ZORA relativistic option

Run

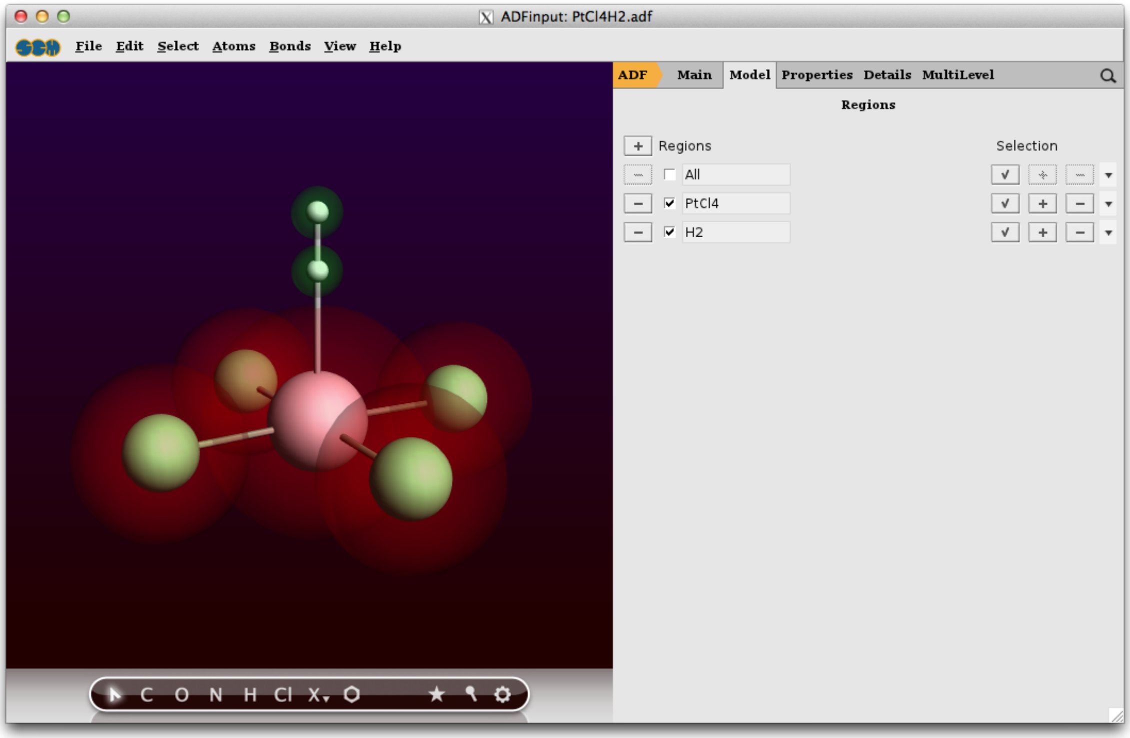
When the run has finished, click 'Yes' to import the optimized coordinates
Save

Note that pre-optimization using UFF will make the geometry worse, if you wish you can pre-optimize using Mopac. But the ADF geometry optimization will also converge without pre-optimization.

Step 6: Define fragments

Define the $PtCl_4^{2-}$ and H_2 fragments in the Regions panel:

Panel bar **Model → Regions**
Select the Pt and Cl atoms
Use the '+' button to add a new region, and name it 'PtCl4'
Select the two H atoms
Use the '+' button to add a new region, and name it 'H2'
Clear the atom selection (click in empty space)



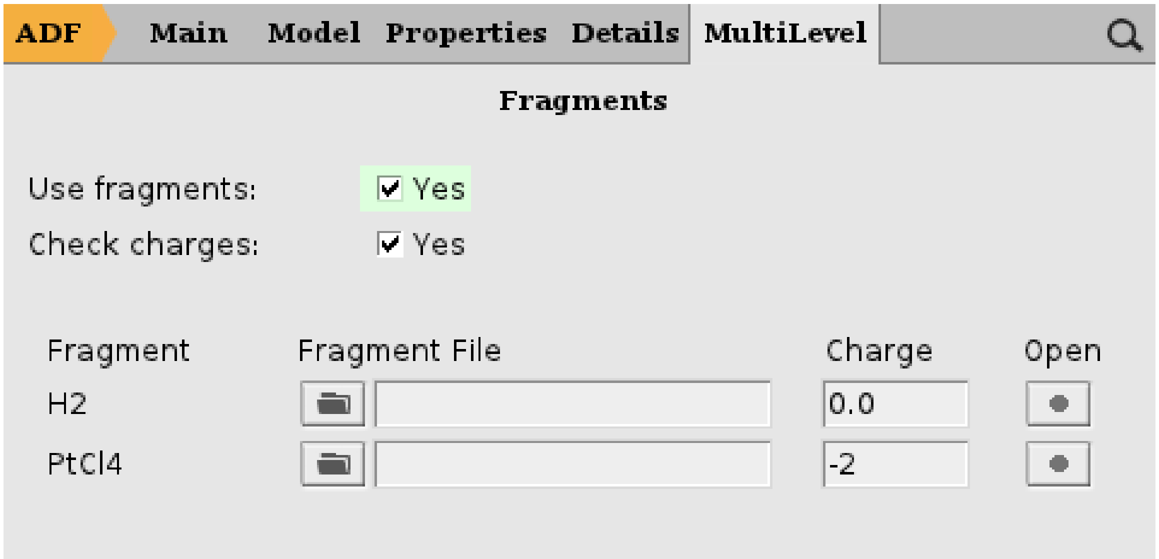
☐ All
☑ PtCl4
☑ H2

Now the fragments are defined. Next, we set up the fragment analysis calculation:

Select 'Main' panel
Select the 'Fragment Analysis' preset
Panel bar **MultiLevel → Fragments**
Change the charge of the PtCl4 fragment to -2

Save

The other changes (the overall molecule charge, and the scalar ZORA option) have already been set previously. The Fragment Analysis preset does not change these.



Fragments

Use fragments: ☑ Yes

Check charges: ☑ Yes

Fragment	Fragment File	Charge	Open
H2		0.0	●
PtCl4		-2	●

When you click on the Open button (the big dot) next to the PtCl4 fragment, you can inspect the PtCl4 fragment setup:

```
Click on the Open button (the big dot next to the PtCl4 fragment) in the
'Fragments' panel
Check the charge of the fragment in the newly opened ADFinput (should be -2)
Close the PtCl4 fragment ADFinput window
```

For more complex calculations, you could make additional changes to your fragment runs. However, normally the set up as created by ADFinput should be fine.

Step 7: Run the fragment analysis and view the results

Next you will Run the calculation:

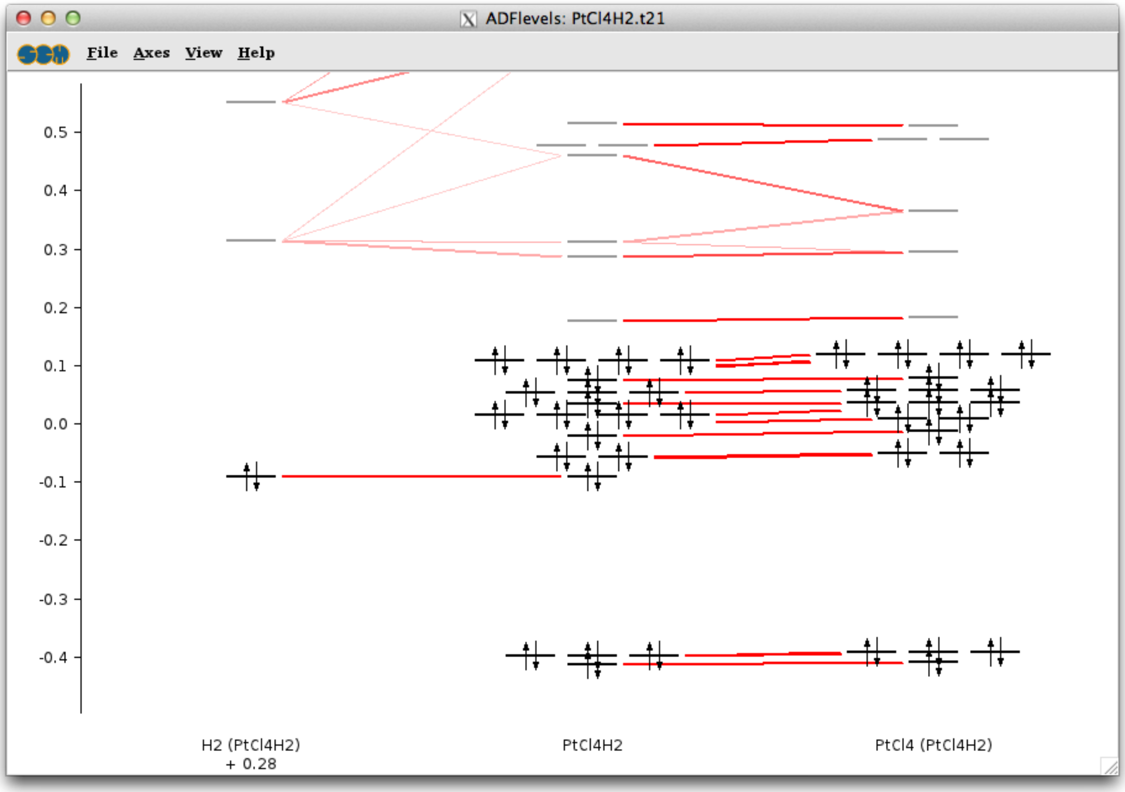
```
Run
```

After the calculation has finished, you can view the resulting interaction diagram:

```
Use the SCM → Levels command

Use the mouse (drag with left mouse, scroll wheel, drag with right mouse)
   zoom in on the interesting region (roughly from -0.5 to 0.4)

Select the PtCl4H2 column (by clicking on the name at the bottom
Use the View → Interactions → Show menu command

With the pop-up menu in the H2 column, shift the H2 levels by +0.28
```

Only interactions between visible levels are shown. So, if you zoom out no interactions will be visible for some of the levels. That is the reason that you will need to use the Show Interactions menu command.

We needed to shift the H2 levels to accommodate that in the final molecule the fragment experiences the -2 charge, but this is absent from the H2 fragment calculation. The interaction diagram should look something like the following:



In the output file you can find detailed information about the composition of the molecular levels in terms of the fragment orbitals.

Tutorial 10: Basis Set Effects for NH_3 (ammonia) Geometry

This tutorial will help you to:

- pre-optimize structures using different methods, including MOPAC
- starting from an existing .adf file, create a batch of similar jobs using the Prepare tool in ADFjobs
- interactively submit a set of jobs using ADFjobs
- using the Report tool in ADFjobs, analyze results of multiple calculations at once

Step 1: Create and pre-optimize your molecule

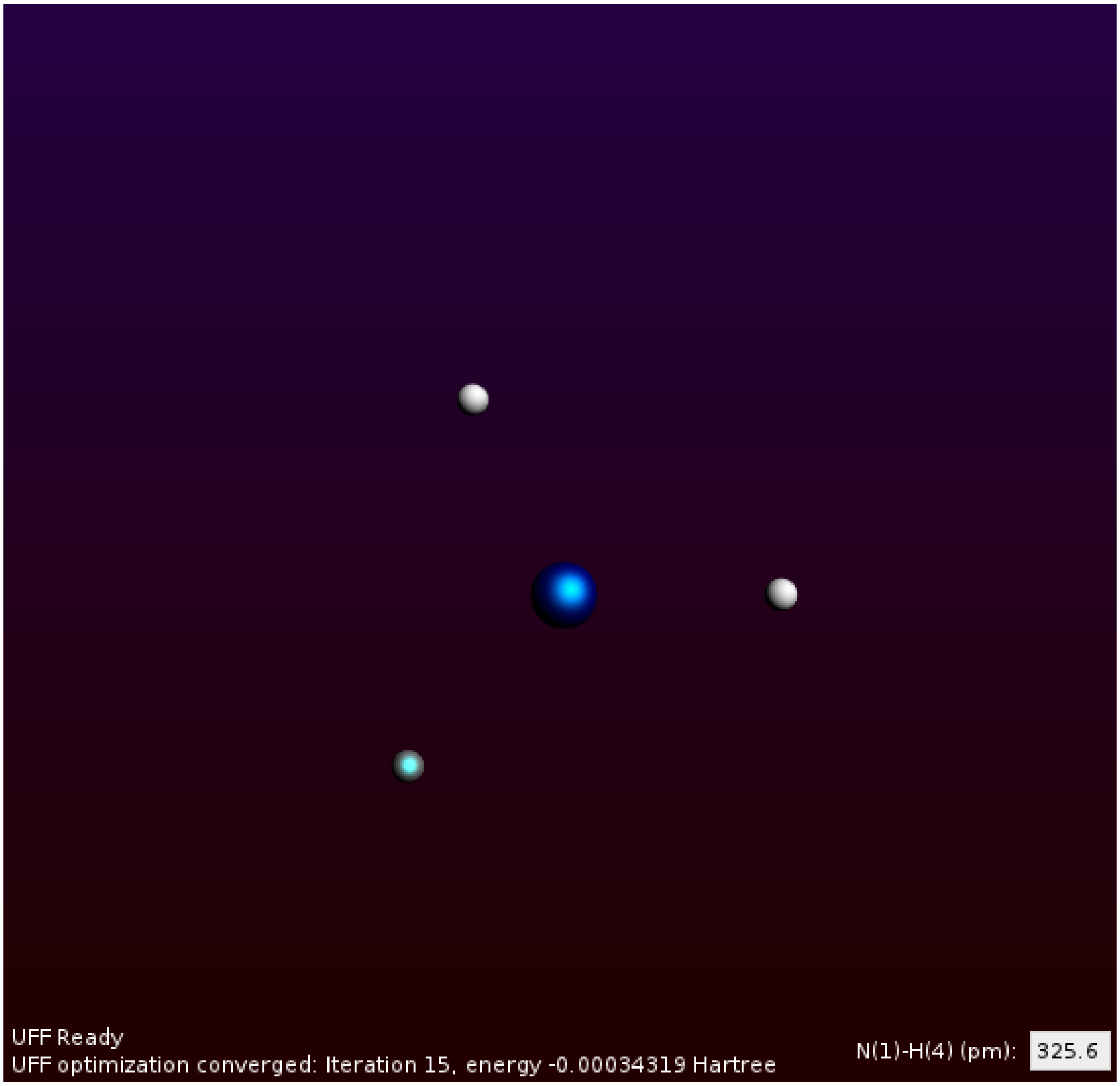
```
Start ADFinput
Create an N atom
Press Esc, and click in empty space so that nothing is selected.
Create an H atom, not too far away
Press Esc, and click in empty space so that nothing is selected.
Add 2 more hydrogen atoms this way.
```

You should see one nitrogen and three hydrogen atoms in the drawing area now. We intentionally did not add bonds between the N and H atoms!

First we will try to optimize this structure using the default pre-optimizer (UFF):

`Click 'Pre-Optimize' cog wheel button`

Using the default pre-optimization algorithm will lead to a structure with way to big N-H distances:



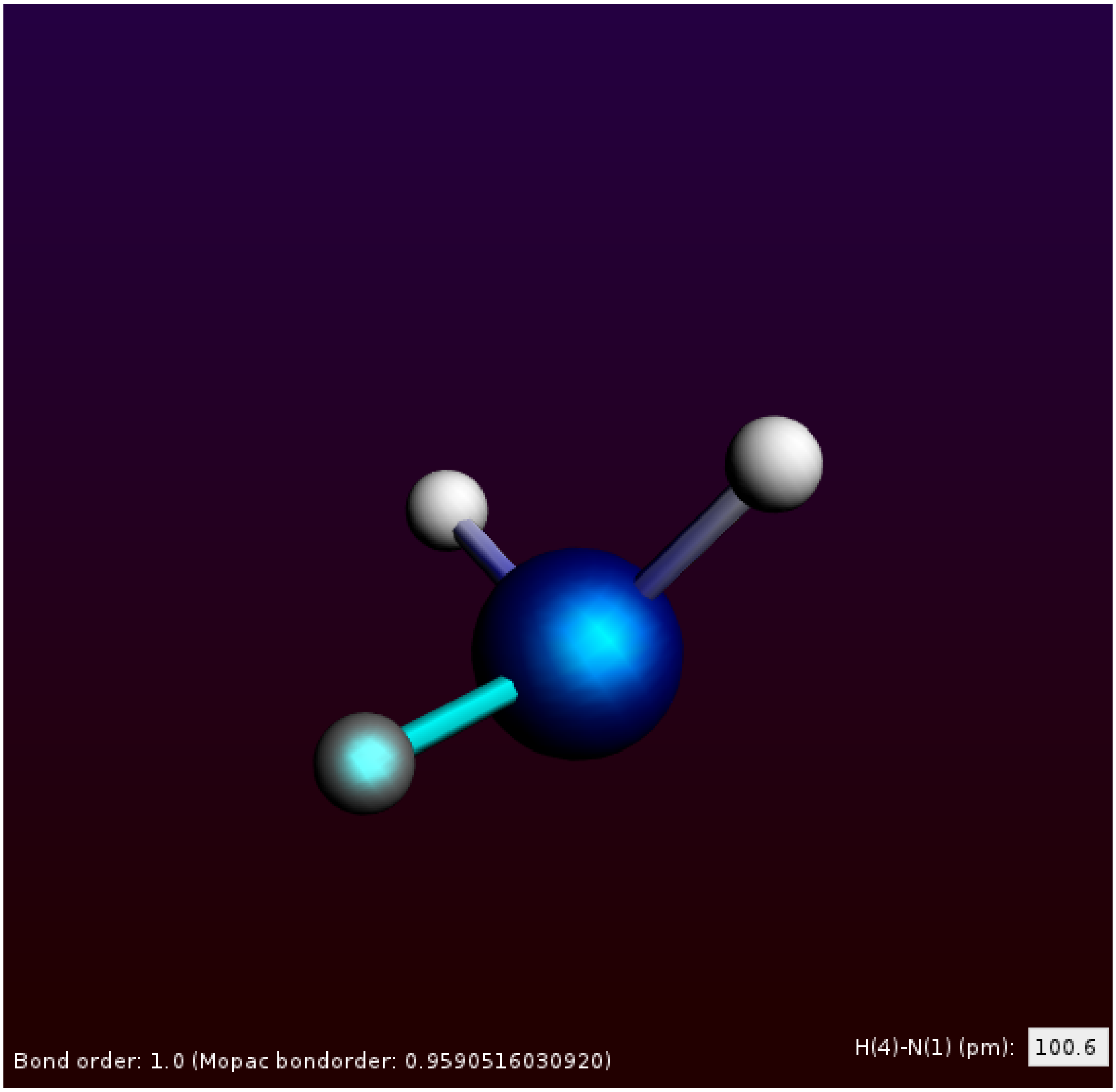
UFF Ready
UFF optimization converged: Iteration 15, energy -0.00034319 Hartree

N(1)-H(4) (pm): 325.6

Next we will try to optimize using Mopac.

`Undo the previous optimization:` **Edit → Undo**
`Right-click on the cog-wheel, select Mopac to pre-optimize`

The message 'MOPAC optimization ready' will be displayed in the ADFinput window:


Bond order: 1.0 (Mopac bondorder: 0.9590516030920)

H(4)-N(1) (pm): 100.6

Mopac will produce a good-looking pyramidal ammonia molecule, with the N-H bond length of about 1.0 Angstrom.

Additionally, it will create proper N-H covalent bonding! These bonds are based on the bond-orders as calculated by Mopac.

Step 2: Set up a single ADF calculation

Now with our pre-optimized NH_3 molecule, we will set up a series of calculation: the optimization of NH3 with ADF, using different basis sets. The first step is to set up a simple geometry optimization:

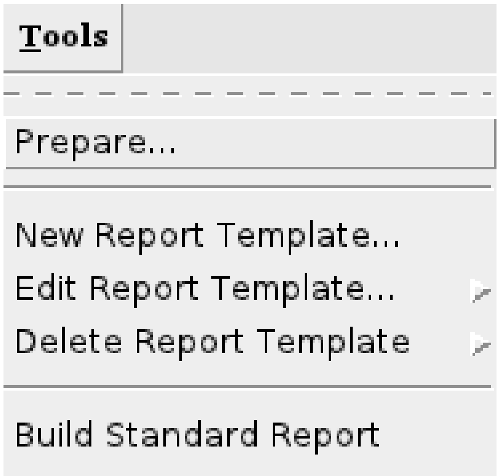
```
Select the 'Main' panel
Select the 'Geometry Optimization' preset
Save as NH3
```

We have used all defaults for basis set and so on.

Step 3: Set up a batch of ADF jobs

Next we will set up a series of calculations, using the Prepare tool.

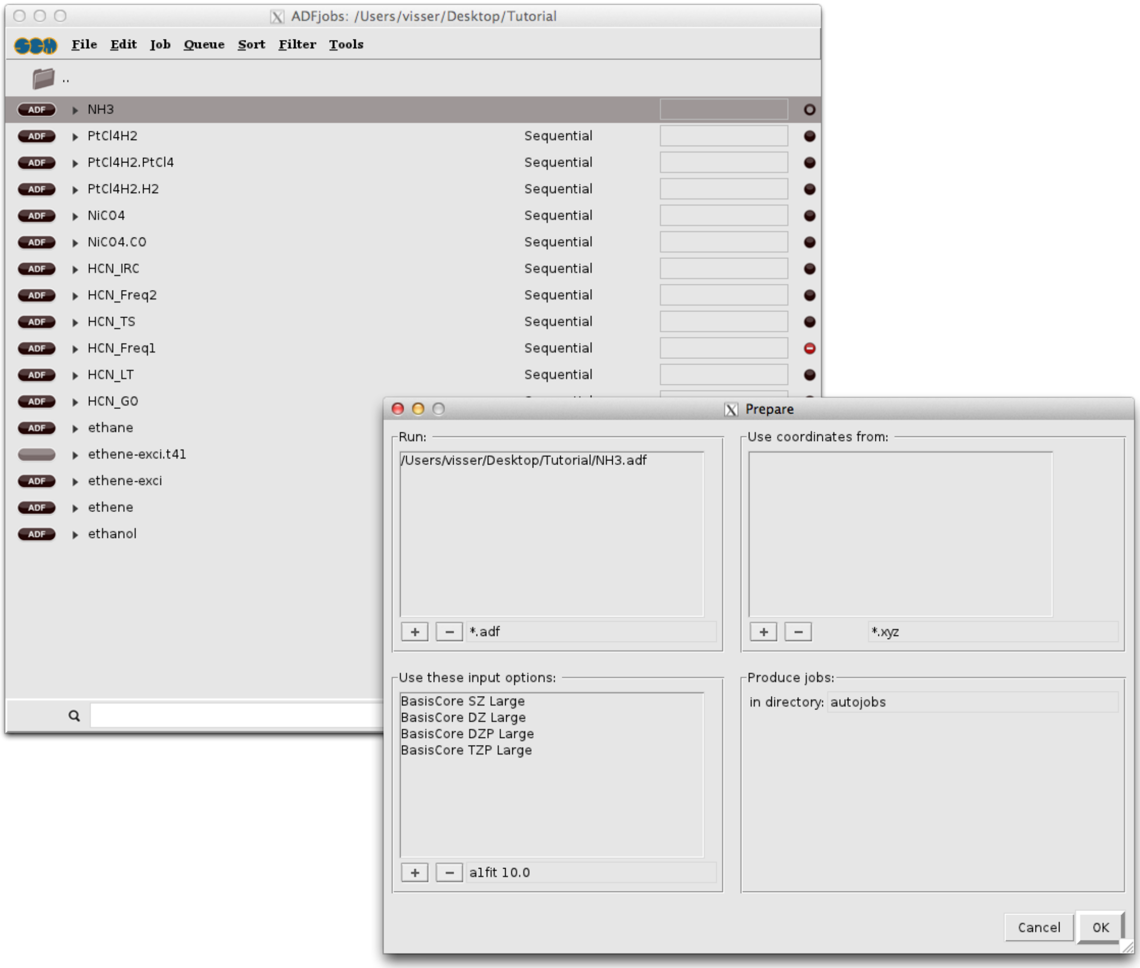
```
Select the ADFjobs window
In ADFjobs window, locate the 'NH3' job saved earlier
Click onto 'NH3' line to select it
Use the Tools → Prepare... command
```



The Prepare dialog window will pop up.

Because we have selected the NH3 job earlier, NH3.adf filename (including the path) will show up in the 'Run' field (otherwise, we can select NH3 using '+' button of the 'Run' field). This means we are going to create jobs that are identical to the NH3 job, but with some details changed (this will next be specified in the Prepare dialog).

```
Go to the 'Use these input options' and click '+'
Choose 'Basis Set and Frozen Core' → 'SZ' → 'Large'
In the similar manner, add basis sets 'DZ', 'DZP', 'TZP',
    .. (optionally 'TZ2P' and 'QZ4P')
Use core 'Large' for all the basis sets
```



NH3
PtCl4H2 Sequential
PtCl4H2.PtCl4 Sequential
PtCl4H2.H2 Sequential
NiCO4 Sequential
NiCO4.CO Sequential
HCN_IRC Sequential
HCN_Freq2 Sequential
HCN_TS Sequential
HCN_Freq1 Sequential
HCN_LT Sequential
HCN_GO
ethane
ethene-exci.t41
ethene-exci
ethene
ethanol

Run: /Users/visser/Desktop/Tutorial/NH3.adf
*.adf

Use coordinates from:
*.xyz

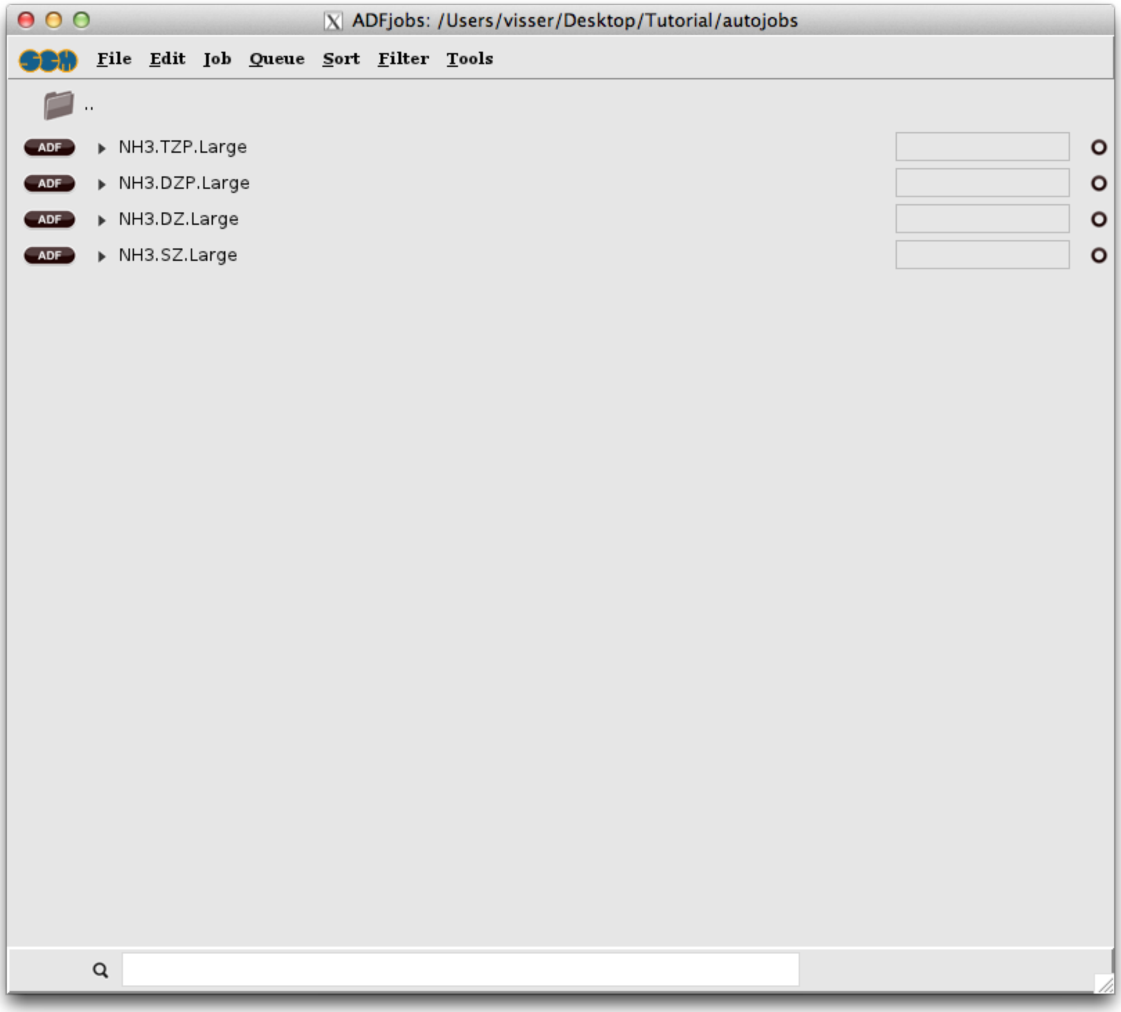
Use these input options:
BasisCore SZ Large
BasisCore DZ Large
BasisCore DZP Large
BasisCore TZP Large
a1fit 10.0

Produce jobs:
in directory: autojobs

The basis set options selected will show up in the 'Use these input options' field. Note that by default the jobs will be created in the 'autojobs' directory, as specified in the 'Produce jobs' section.

`Now click 'OK' in the Prepare window`

The Prepare dialog will close and ADFjobs will open the 'autojobs' directory. Using NH3.adf, the Prepare tool created a set of jobs inside 'autojobs' named as 'NH3.SZ.Large.adf', 'NH3.DZ.Large.adf' etc. The files naming intuitively follows the basis set options which has been used, and the rest of the options of the newly created files are exactly the same as in NH3.adf. The original NH3.adf file has not been altered.



Step 4: Run your set of ADF jobs

Now we are going to run the batch of ADF jobs which has been automatically prepared in the previous Step 3 of the tutorial Using ADFjobs, one can either run this set of jobs one by one, or all at once.

`Click on the first job`
`Shift-Click on the last job`
`Run the jobs` **Job → Run**

This will run the jobs in the default queue. Normally this is the Sequential queue, and the jobs will actually run one after another.

The jobs will start running, and the corresponding ADFtail windows will pop up. Each ammonia optimization job should not take more than a few minutes.

Step 5: Analyze results of several calculations at once

When all the ammonia optimization jobs are finished, we can compare the results. The main conclusion that you will reach is that DZ (double zeta) basis set optimization, job name 'NH3.DZ.Large', leads to the incorrect planar ammonia molecule. As covered in the preceding tutorials, you can optionally use several GUI modules to observe that:

- ADFmovie, which will show the geometry optimization

- ADFinput, which will open the (last) converged geometry

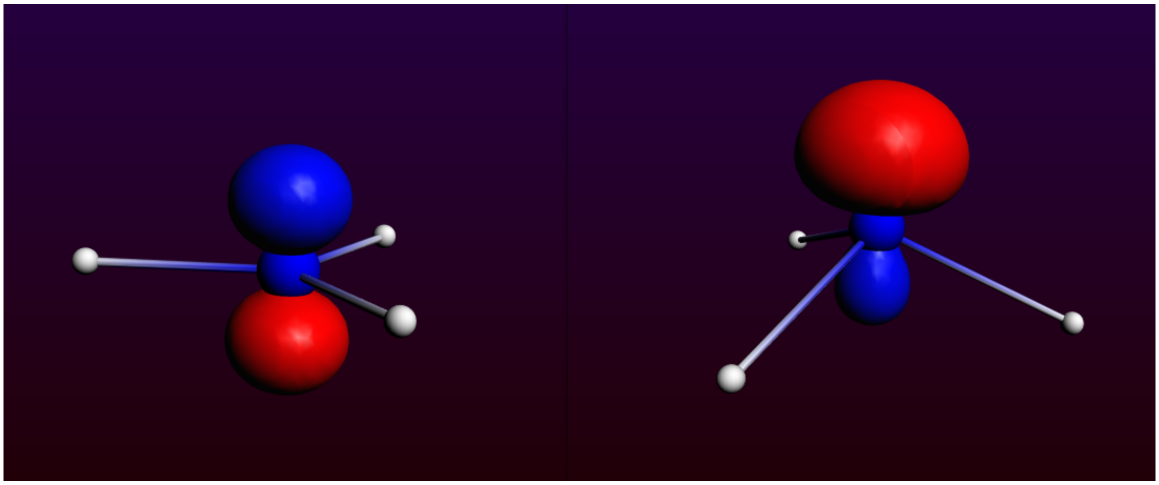
- ADFview, which will open the converged geometry and also would display various density maps in 3D

For example, let us use ADFview to demonstrate the results:

Clear the selection in ADFjobs (press Esc)
Select job NH3.DZ.Large in the ADFjobs window (should then be highlighted)
Select **SCM → View**
Select **Fields → Grid → Fine**
Select **Properties → HOMO**
In the isosurface contour value field which appeared at the bottom,
   change the default '0.03' to '0.3'
Type 'ctrl/cmd-minus' several times, until the central N atom ball
   does not overlap strongly with the HOMO orbital.

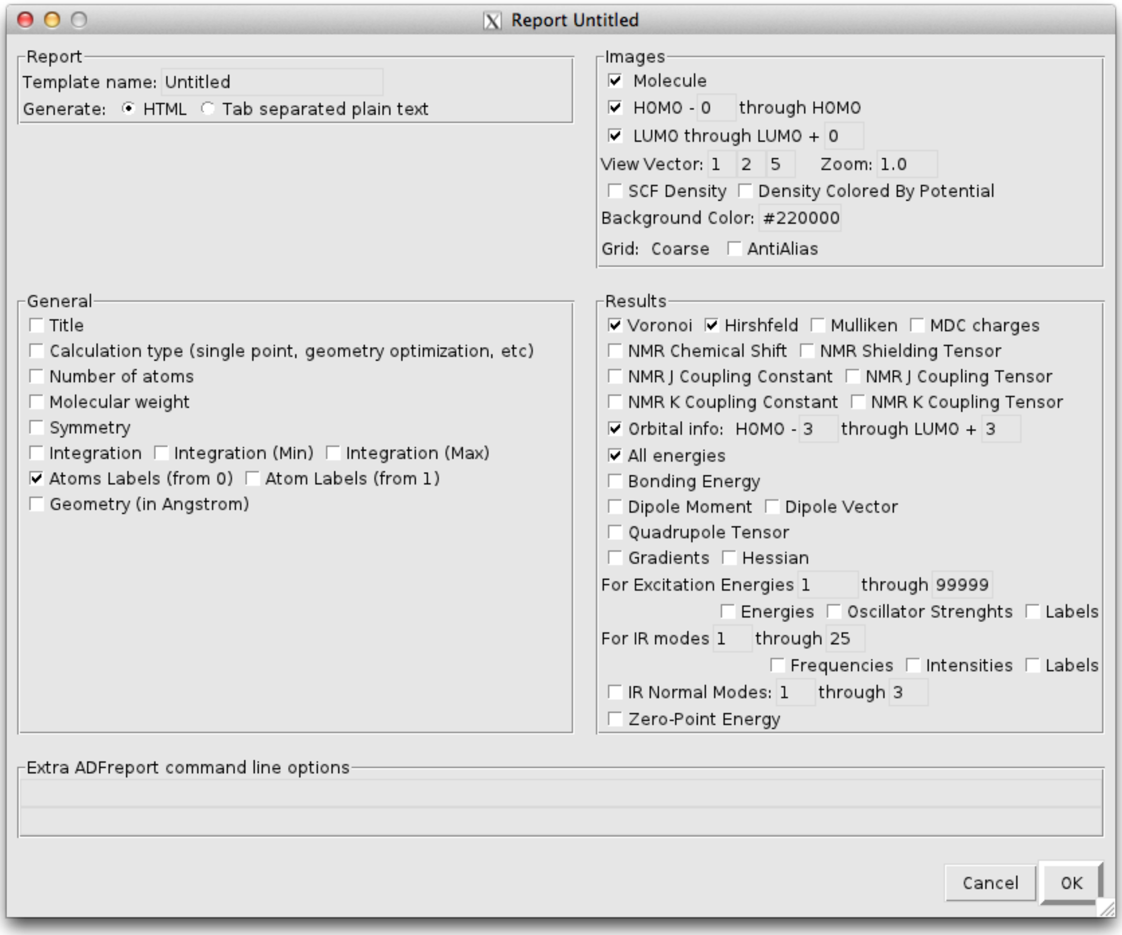
Repeat for this for the DZP calculation

What you will observe is that HOMO of ammonia does not have the anticipated sp3 hybridization, when DZ basis set is used. In the following picture you can see both the DZ and DZP results:



To visualize results from several jobs automatically, you can use the Report tool within ADFjobs:

Go to the ADFjobs window
Select **Tools → New Report Template...**



Report
Template name: Untitled
Generate: ● HTML ○ Tab separated plain text

Images
☑ Molecule
☑ HOMO - 0 through HOMO
☑ LUMO through LUMO + 0
View Vector: 1 2 5 Zoom: 1.0
☐ SCF Density ☐ Density Colored By Potential
Background Color: #220000
Grid: Coarse ☐ AntiAlias

General
☐ Title
☐ Calculation type (single point, geometry optimization, etc)
☐ Number of atoms
☐ Molecular weight
☐ Symmetry
☐ Integration ☐ Integration (Min) ☐ Integration (Max)
☑ Atoms Labels (from 0) ☐ Atom Labels (from 1)
☐ Geometry (in Angstrom)

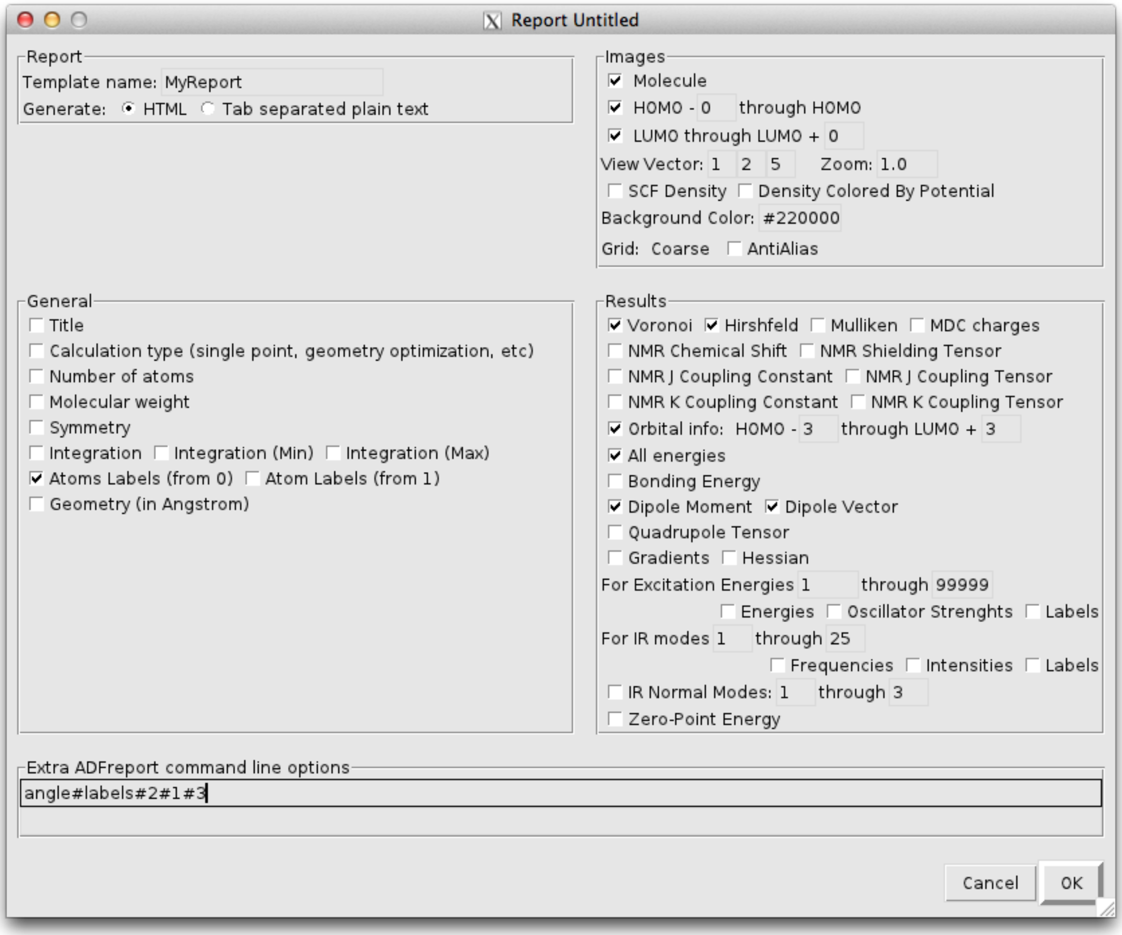
Results
☑ Voronoi ☑ Hirshfeld ☐ Mulliken ☐ MDC charges
☐ NMR Chemical Shift ☐ NMR Shielding Tensor
☐ NMR J Coupling Constant ☐ NMR J Coupling Tensor
☐ NMR K Coupling Constant ☐ NMR K Coupling Tensor
☑ Orbital info: HOMO - 3 through LUMO + 3
☑ All energies
☐ Bonding Energy
☐ Dipole Moment ☐ Dipole Vector
☐ Quadrupole Tensor
☐ Gradients ☐ Hessian
For Excitation Energies 1 through 99999
☐ Energies ☐ Oscillator Strenghts ☐ Labels
For IR modes 1 through 25
☐ Frequencies ☐ Intensities ☐ Labels
☐ IR Normal Modes: 1 through 3
☐ Zero-Point Energy

Extra ADFreport command line options

This will open up Report dialog.

In the 'Report' field, you can choose the name for your report file and its format ('HTML' or 'Tab separated plain text'). The other fields ('General', 'Images', 'Results') contain various relevant options you can choose for preparing your report.

```
In the 'Report'/'Template name' field, type 'MyReport'
In the 'Results' section check 'Dipole Moment' and 'Dipole Vector'
In the 'Extra ADFreport command line options' field: enter 'angle#labels#2#1#3
```



Report

Template name: MyReport

Generate: ● HTML ○ Tab separated plain text

Images

☑ Molecule

☑ HOMO - 0 through HOMO

☑ LUMO through LUMO + 0

View Vector: 1 2 5 Zoom: 1.0

☐ SCF Density ☐ Density Colored By Potential

Background Color: #220000

Grid: Coarse ☐ AntiAlias

General

☐ Title

☐ Calculation type (single point, geometry optimization, etc)

☐ Number of atoms

☐ Molecular weight

☐ Symmetry

☐ Integration ☐ Integration (Min) ☐ Integration (Max)

☑ Atoms Labels (from 0) ☐ Atom Labels (from 1)

☐ Geometry (in Angstrom)

Results

☑ Voronoi ☑ Hirshfeld ☐ Mulliken ☐ MDC charges

☐ NMR Chemical Shift ☐ NMR Shielding Tensor

☐ NMR J Coupling Constant ☐ NMR J Coupling Tensor

☐ NMR K Coupling Constant ☐ NMR K Coupling Tensor

☑ Orbital info: HOMO - 3 through LUMO + 3

☑ All energies

☐ Bonding Energy

☑ Dipole Moment ☑ Dipole Vector

☐ Quadrupole Tensor

☐ Gradients ☐ Hessian

For Excitation Energies 1 through 99999

☐ Energies ☐ Oscillator Strenghts ☐ Labels

For IR modes 1 through 25

☐ Frequencies ☐ Intensities ☐ Labels

☐ IR Normal Modes: 1 through 3

☐ Zero-Point Energy

Extra ADFreport command line options

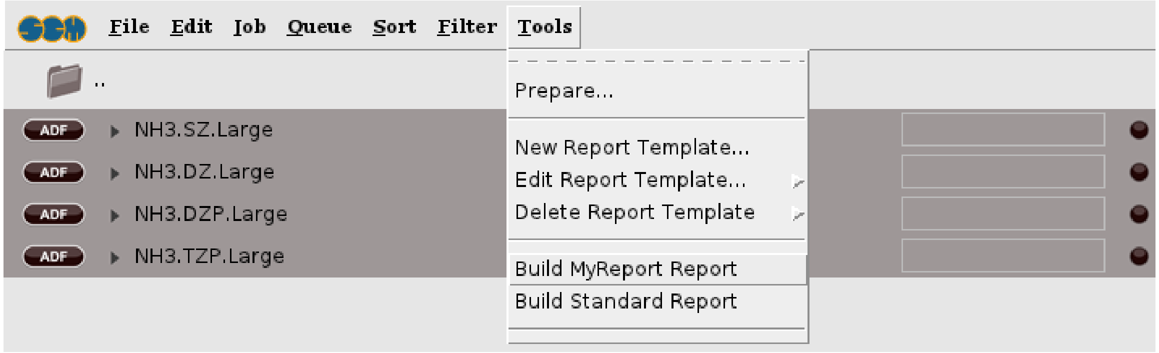
angle#labels#2#1#3

The extra command line options used instruct ADFreport to report the angle between atoms 2, 1 and 3, and include the atom labels for this angle on output. In a similar way more angles could be requested, or distances, or many other properties. For a description of all options please check the adfreport documentation.

```
Click 'OK'
```

The Report dialog will close, saving our template named 'MyReport'. Now we will generate actual report following the saved template:

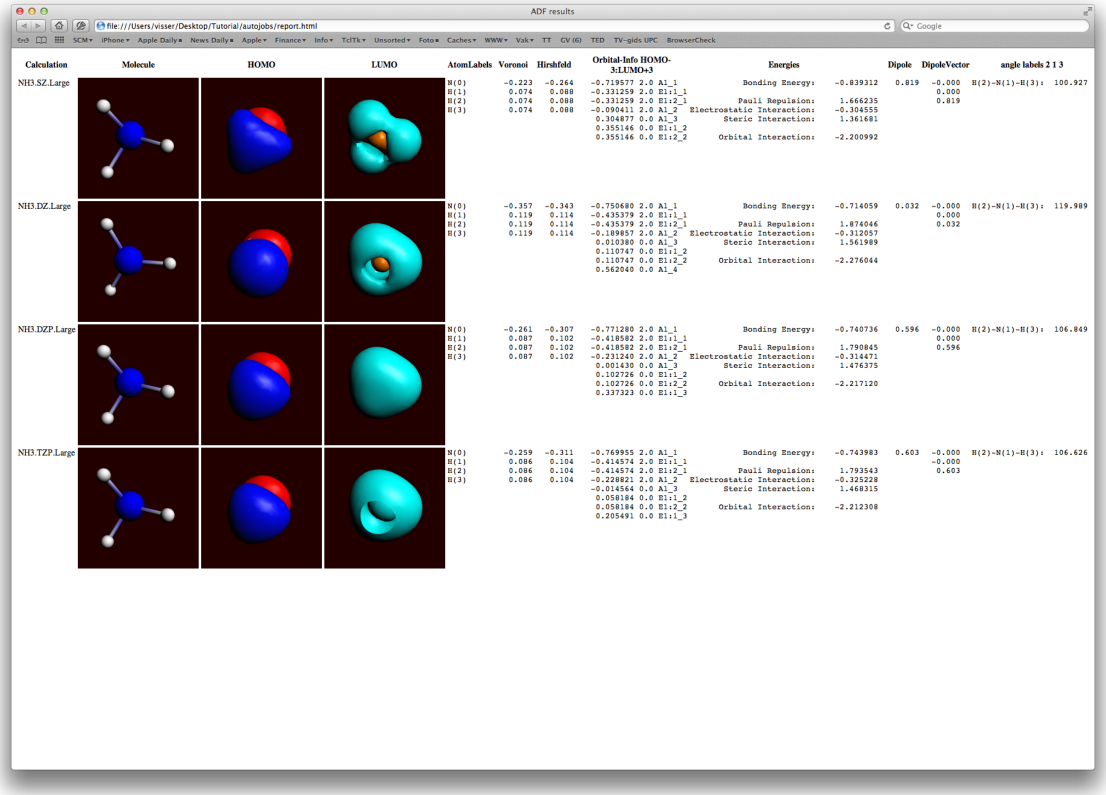
`In ADFjobs window, select all the finished jobs from the NH3 set`
`Select` **Tools → Build MyReport Report**



'Save As' dialog window will pop up, showing the 'report.html' default filename.

`Choose your filename and location, then click 'Save'`

Now ADF will work through all your selected jobs and prepare the report. Finally the browser will start showing your report file (by default, named 'report.html'):



Calculation	Molecule	HOMO	LUMO	AtomLabels	Voronoi	Hirshfeld	Orbital-Info HOMO-3:LUMO+3	Energies	Dipole	DipoleVector	angle labels 2 1 3
NH3.SZ.Large				N(0) H(1) H(2) H(3)	-0.223 0.074 0.074 0.074	-0.264 0.088 0.088 0.088	-0.719577 2.0 A1_1 -0.331259 2.0 E1:1_1 -0.331259 2.0 E1:2_1 -0.090411 2.0 A1_2 0.304877 0.0 A1_3 0.355146 0.0 E1:1_2 0.355146 0.0 E1:2_2	Bonding Energy: -0.839312 Pauli Repulsion: 1.666235 Electrostatic Interaction: -0.304555 Steric Interaction: 1.361681 Orbital Interaction: -2.200992	0.819	-0.000 0.000 0.819	H(2)-N(1)-H(3): 100.927
NH3.DZ.Large				N(0) H(1) H(2) H(3)	-0.357 0.119 0.119 0.119	-0.343 0.114 0.114 0.114	-0.750680 2.0 A1_1 -0.435379 2.0 E1:1_1 -0.435379 2.0 E1:2_1 -0.189857 2.0 A1_2 0.010380 0.0 A1_3 0.110747 0.0 E1:1_2 0.110747 0.0 E1:2_2 0.562040 0.0 A1_4	Bonding Energy: -0.714059 Pauli Repulsion: 1.874046 Electrostatic Interaction: -0.312057 Steric Interaction: 1.561989 Orbital Interaction: -2.276044	0.032	-0.000 0.000 0.032	H(2)-N(1)-H(3): 119.989
NH3.DZP.Large				N(0) H(1) H(2) H(3)	-0.261 0.087 0.087 0.087	-0.307 0.102 0.102 0.102	-0.771280 2.0 A1_1 -0.418582 2.0 E1:1_1 -0.418582 2.0 E1:2_1 -0.231240 2.0 A1_2 0.001430 0.0 A1_3 0.102726 0.0 E1:1_2 0.102726 0.0 E1:2_2 0.337323 0.0 E1:1_3	Bonding Energy: -0.740736 Pauli Repulsion: 1.790845 Electrostatic Interaction: -0.314471 Steric Interaction: 1.476375 Orbital Interaction: -2.217120	0.596	-0.000 0.000 0.596	H(2)-N(1)-H(3): 106.849
NH3.TZP.Large				N(0) H(1) H(2) H(3)	-0.259 0.086 0.086 0.086	-0.311 0.104 0.104 0.104	-0.769955 2.0 A1_1 -0.414574 2.0 E1:1_1 -0.414574 2.0 E1:2_1 -0.228821 2.0 A1_2 -0.014564 0.0 A1_3 0.058184 0.0 E1:1_2 0.058184 0.0 E1:2_2 0.205491 0.0 E1:1_3	Bonding Energy: -0.743983 Pauli Repulsion: 1.793543 Electrostatic Interaction: -0.325228 Steric Interaction: 1.468315 Orbital Interaction: -2.212308	0.603	-0.000 -0.000 0.603	H(2)-N(1)-H(3): 106.626

The Report tool created a table-like report of the results. Click on the image above to see it in detail.

We can clearly see that only for DZ basis optimization our NH_3 molecule is planar (check the last row of the report table). The dipole data are also shown in the report. Obviously the dipole moment is zero only for the planar NH_3 structure.

Congratulations, we are done with the ammonia optimization tutorial!

`If you want to exit all the GUI modules at once: select` **SCM → Close All**

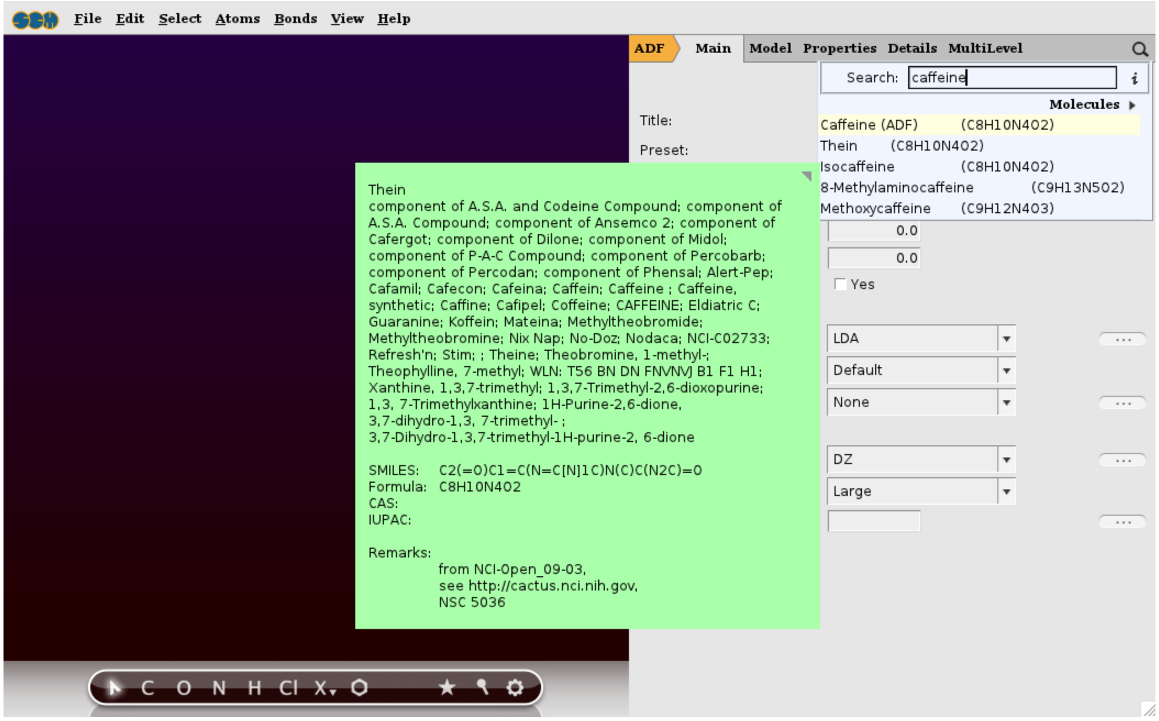
Tutorial 11: Caffeine Bader (AIM) analysis, Benzene NBO visualization and Occupations

Step 1: Setup and optimize Caffeine

`Start ADFinput`

Next we need a reasonable guess for the structure of Caffeine. The quickest way to do this is to search for it in the database of molecules included with the ADF-GUI, and optimize it:

```
Press cmd-F or ctrl-F to activate the search box
Type 'caffeine' in the search box
Move your mouse pointer on top of the 'Thein' search result
```



Search: caffeine

Molecules

Caffeine (ADF) (C8H10N4O2)
Thein (C8H10N4O2)
Isocaffeine (C8H10N4O2)
8-Methylaminocaffeine (C9H13N5O2)
Methoxycaffeine (C9H12N4O3)

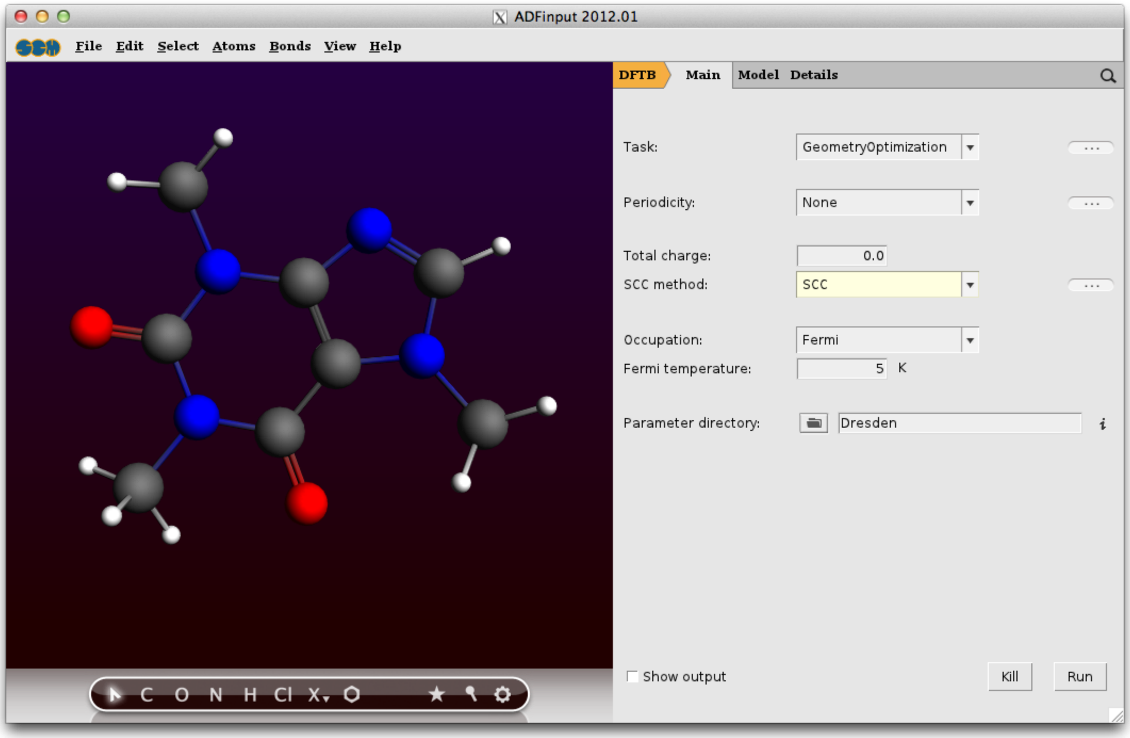
Thein
component of A.S.A. and Codeine Compound; component of A.S.A. Compound; component of Ansemco 2; component of Cafergot; component of Dilone; component of Midol; component of P-A-C Compound; component of Percobarb; component of Percodan; component of Phensal; Alert-Pep; Cafamil; Cafecon; Cafeina; Caffein; Caffeine ; Caffeine, synthetic; Caffine; Cafipel; Coffeine; CAFFEINE; Eldiatric C; Guaranine; Koffein; Mateina; Methyltheobromide; Methyltheobromine; Nix Nap; No-Doz; Nodaca; NCI-C02733; Refresh'n; Stim; ; Theine; Theobromine, 1-methyl-; Theophylline, 7-methyl; WLN: T56 BN DN FNVNVJ B1 F1 H1; Xanthine, 1,3,7-trimethyl; 1,3,7-Trimethyl-2,6-dioxopurine; 1,3, 7-Trimethylxanthine; 1H-Purine-2,6-dione, 3,7-dihydro-1,3, 7-trimethyl- ; 3,7-Dihydro-1,3,7-trimethyl-1H-purine-2, 6-dione

SMILES: C2(=O)C1=C(N=C[N]1C)N(C)C(N2C)=O
Formula: C8H10N4O2
CAS:
IUPAC:

Remarks:
from NCI-Open_09-03,
see http://cactus.nci.nih.gov,
NSC 5036

As you can see, there are several matches. If you position your mouse over the results (without clicking) a balloon will appear showing the details of that match. For this tutorial we use the second match "Thein", from the NCI database. Thein is one of the common names for caffeine (and as you can see there are may alternative names),

```
Click on the 'Thein' search result
Click somewhere in empty space in the molecule drawing area to deselect the
atoms
Switch to DFTB mode (panel bar ADF → DFTB)
Select SCC method SCC
Select the Dresden DFTB parameters:
    click on the parameter folder icon, select Dresden
```



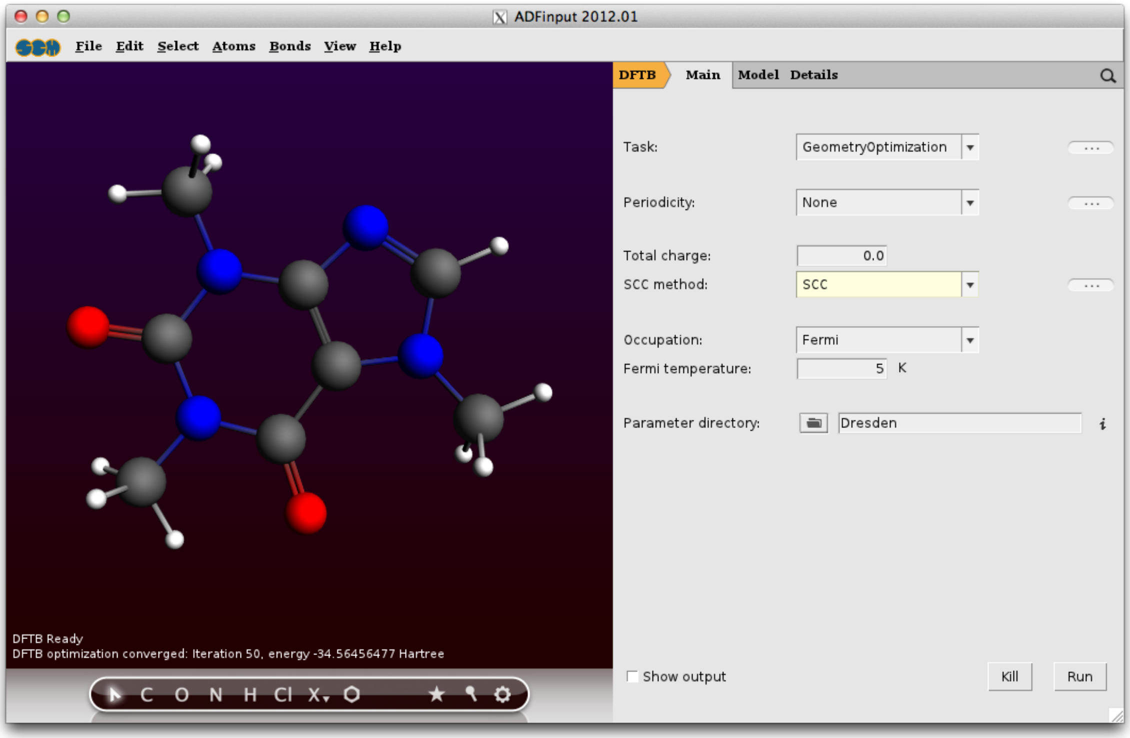
Task: GeometryOptimization
Periodicity: None
Total charge: 0.0
SCC method: SCC
Occupation: Fermi
Fermi temperature: 5 K
Parameter directory: Dresden

Note that only those parameter sets known to be able to handle your system will be shown in the menu.

If you move your mouse over the parameter field, the information balloon will also show references applicable to the selected set of DFTB parameters. More detailed information and references will be displayed if you click on the 'i' button next to the parameter input field.

```
Click the 'Run' button
If the message says 'NOT converged', press 'Run' again.
```

The DFTB program should have created something similar to this structure:



Task: GeometryOptimization
Periodicity: None
Total charge: 0.0
SCC method: SCC
Occupation: Fermi
Fermi temperature: 5 K
Parameter directory: Dresden

DFTB Ready
DFTB optimization converged: Iteration 50, energy -34.56456477 Hartree

Step 2: Calculation setup

Next we will calculate the AIM critical points and paths for the current structure.

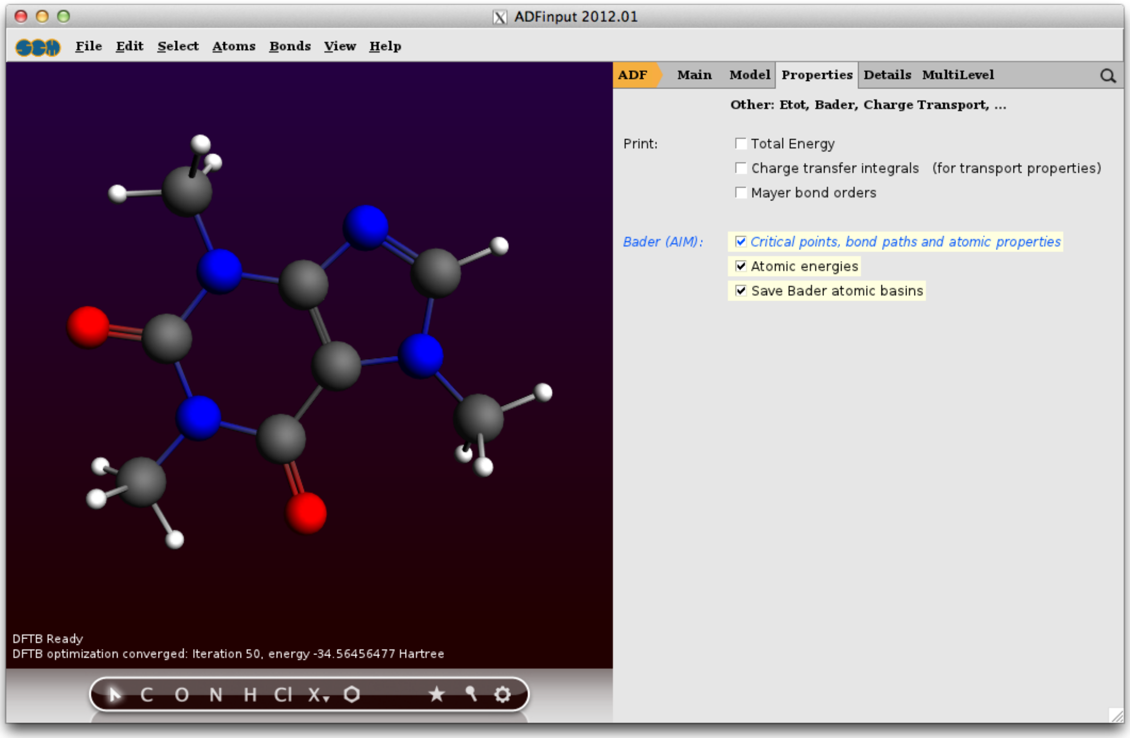
Switch to ADF mode (panel bar **DFTB → ADF**)

Now we want to activate the Bader AIM analysis to find the critical points and bond paths. To find where this option is located, search for it:

Activate the search box (cmd/ctrl-F)
Type 'criti' in the search box
Use the Return key to accept the highlighted match (Other...)

ADFinput will activate the panel that displays the option you are looking for (to calculate the AIM critical points and paths). The matching input options will be marked with blue italic text. Note that we first had to activate the ADF mode, the input option search will restrict the search to panels that belong to the current method (ADF, BAND, DFTB, ...)

Check the box to calculate Bader (AIM) Critical points, bond paths and atomic properties
Check the box to calculate AIM atomic energies
Check the box to save the Bader basins



Other: Etot, Bader, Charge Transport, ...

Print:
☐ Total Energy
☐ Charge transfer integrals (for transport properties)
☐ Mayer bond orders

Bader (AIM):
☑ Critical points, bond paths and atomic properties
☑ Atomic energies
☑ Save Bader atomic basins

```
DFTB Ready
DFTB optimization converged: Iteration 50, energy -34.56456477 Hartree
```

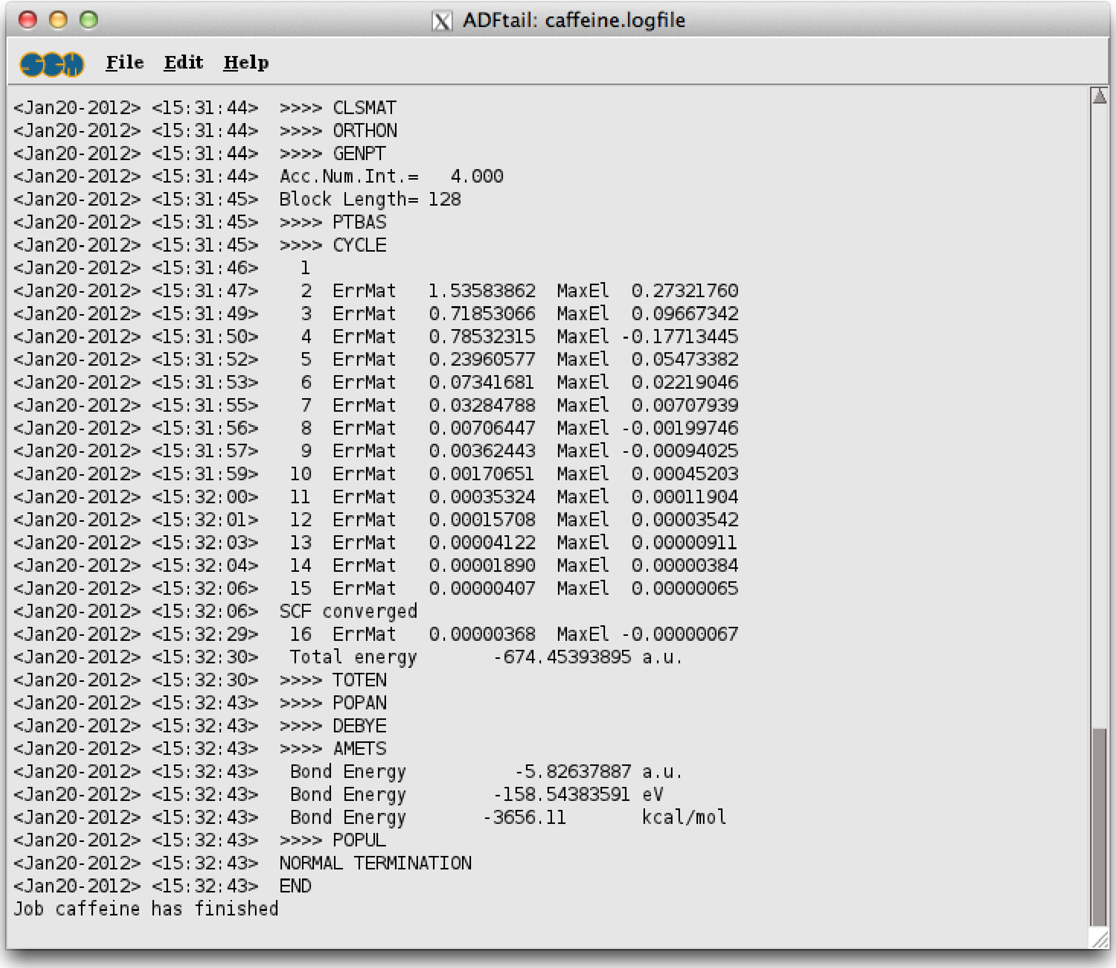
`Run this setup:` **File → Run**

A dialog will pop up in which you must specify a filename to use for your job, for example caffeine:

`Enter 'caffeine' as a Filename, pres the Save button`

After hitting the save button the calculation will start. You will get two extra windows: first a window for ADFjobs that allows you to manage your jobs and keep track of their state (for example, queued or running). You will also get a window showing the ADF log file. This shows you what is going on in the current calculation.

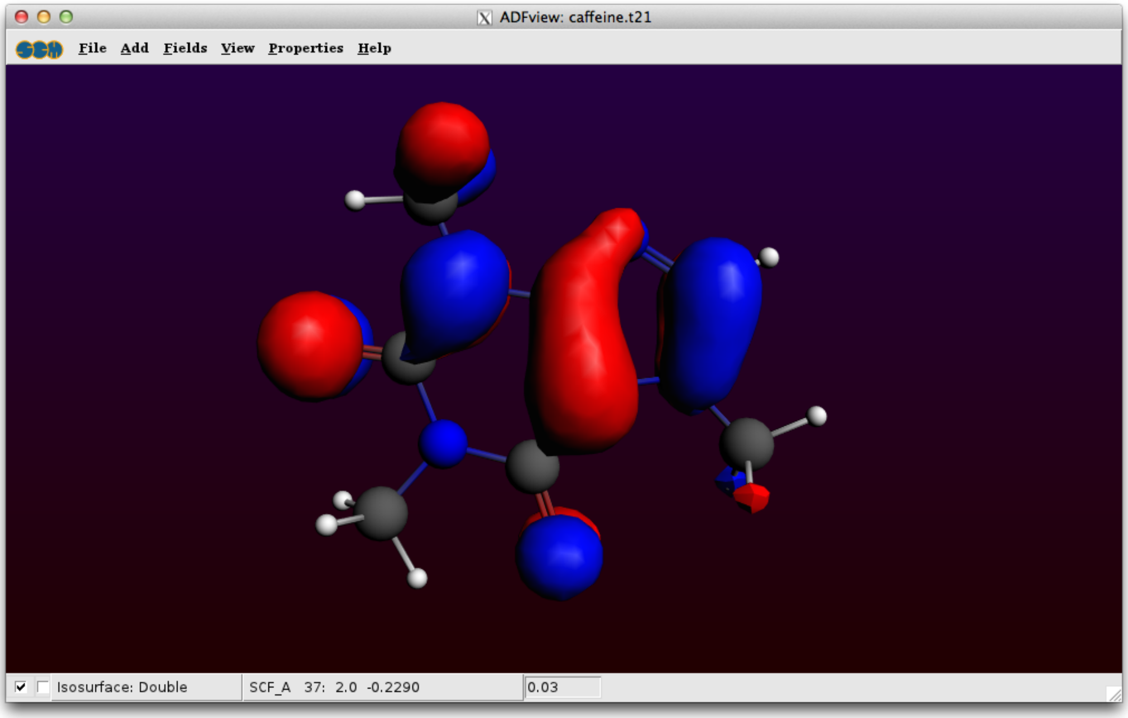
Depending on your computer, the calculation should be ready after a few minutes at most:



```
<Jan20-2012> <15:31:44>  >>>> CLSMAT
<Jan20-2012> <15:31:44>  >>>> ORTHON
<Jan20-2012> <15:31:44>  >>>> GENPT
<Jan20-2012> <15:31:44>  Acc.Num.Int.=   4.000
<Jan20-2012> <15:31:45>  Block Length= 128
<Jan20-2012> <15:31:45>  >>>> PTBAS
<Jan20-2012> <15:31:45>  >>>> CYCLE
<Jan20-2012> <15:31:46>    1
<Jan20-2012> <15:31:47>    2  ErrMat   1.53583862  MaxEl  0.27321760
<Jan20-2012> <15:31:49>    3  ErrMat   0.71853066  MaxEl  0.09667342
<Jan20-2012> <15:31:50>    4  ErrMat   0.78532315  MaxEl -0.17713445
<Jan20-2012> <15:31:52>    5  ErrMat   0.23960577  MaxEl  0.05473382
<Jan20-2012> <15:31:53>    6  ErrMat   0.07341681  MaxEl  0.02219046
<Jan20-2012> <15:31:55>    7  ErrMat   0.03284788  MaxEl  0.00707939
<Jan20-2012> <15:31:56>    8  ErrMat   0.00706447  MaxEl -0.00199746
<Jan20-2012> <15:31:57>    9  ErrMat   0.00362443  MaxEl -0.00094025
<Jan20-2012> <15:31:59>   10  ErrMat   0.00170651  MaxEl  0.00045203
<Jan20-2012> <15:32:00>   11  ErrMat   0.00035324  MaxEl  0.00011904
<Jan20-2012> <15:32:01>   12  ErrMat   0.00015708  MaxEl  0.00003542
<Jan20-2012> <15:32:03>   13  ErrMat   0.00004122  MaxEl  0.00000911
<Jan20-2012> <15:32:04>   14  ErrMat   0.00001890  MaxEl  0.00000384
<Jan20-2012> <15:32:06>   15  ErrMat   0.00000407  MaxEl  0.00000065
<Jan20-2012> <15:32:06>  SCF converged
<Jan20-2012> <15:32:29>   16  ErrMat   0.00000368  MaxEl -0.00000067
<Jan20-2012> <15:32:30>   Total energy       -674.45393895 a.u.
<Jan20-2012> <15:32:30>  >>>> TOTEN
<Jan20-2012> <15:32:43>  >>>> POPAN
<Jan20-2012> <15:32:43>  >>>> DEBYE
<Jan20-2012> <15:32:43>  >>>> AMETS
<Jan20-2012> <15:32:43>   Bond Energy          -5.82637887 a.u.
<Jan20-2012> <15:32:43>   Bond Energy        -158.54383591 eV
<Jan20-2012> <15:32:43>   Bond Energy       -3656.11       kcal/mol
<Jan20-2012> <15:32:43>  >>>> POPUL
<Jan20-2012> <15:32:43>  NORMAL TERMINATION
<Jan20-2012> <15:32:43>  END
Job caffeine has finished
```

Step 3: Orbitals, Potential and AIM results

`Start ADFview` **SCM → View**
`Show the HOMO` **Properties → HOMO**



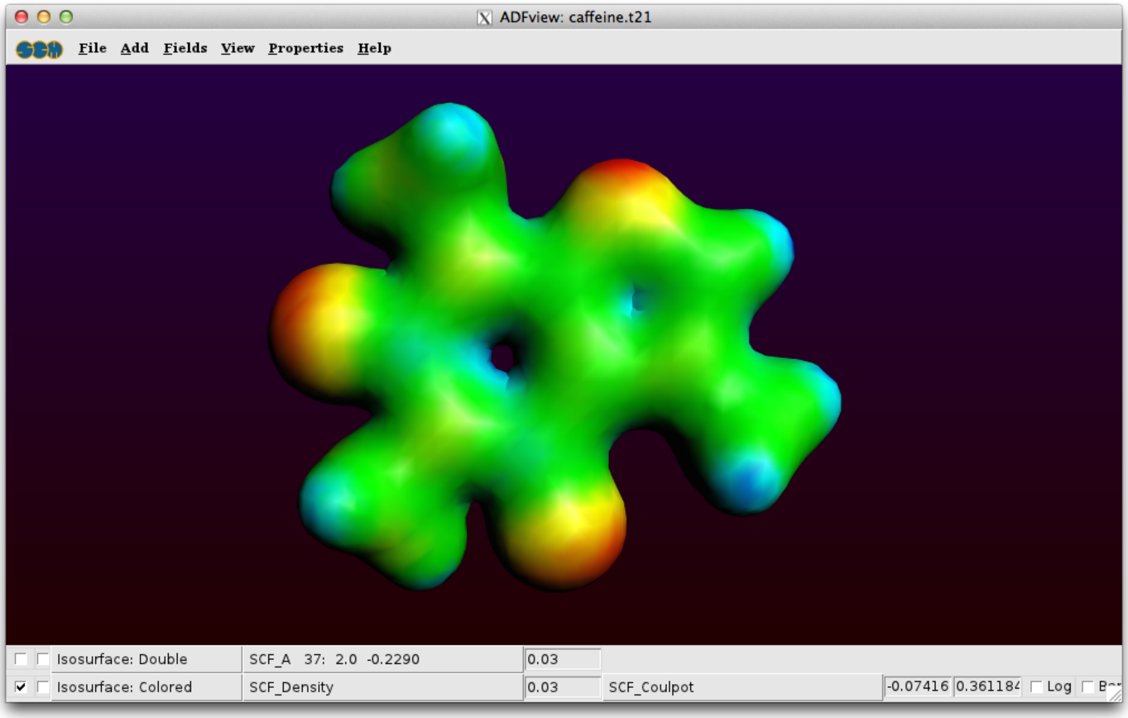
☑ ☐ Isosurface: Double | SCF_A 37: 2.0 -0.2290 | 0.03

Hide the HOMO by unchecking the check box at the lower left corner of the ADFview window

Add → Isosurface: Colored

In the first field selector (to the right of the 'Isosurface: Colored' text at the bottom), select **Density → SCF**

In the second field selector (to the right of the '0.03' text in the same line), select **Potential → SCF**

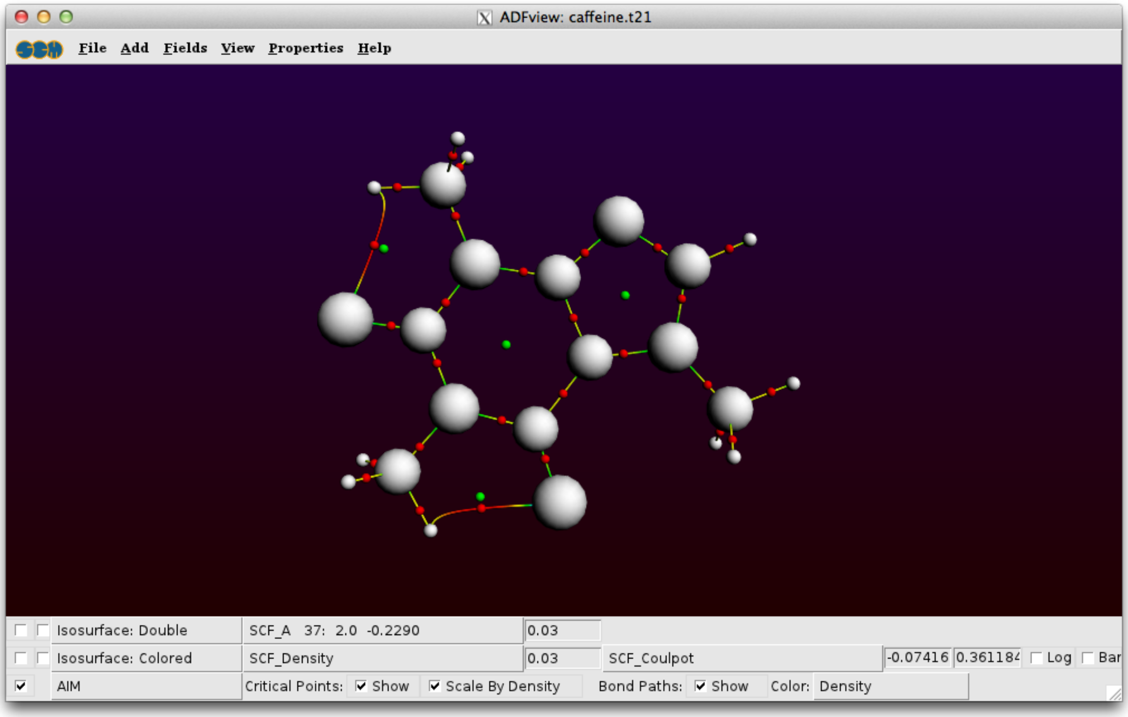


☐ ☐ Isosurface: Double SCF_A 37: 2.0 -0.2290 0.03

☑ ☐ Isosurface: Colored SCF_Density 0.03 SCF_Coulpot -0.07416 0.361184 ☐ Log ☐ B

Hide the surface with the potential energy: uncheck the check box at the lower left corner of the window

Properties → AIM (Bader)



☐ ☐ Isosurface: Double SCF_A 37: 2.0 -0.2290 0.03

☐ ☐ Isosurface: Colored SCF_Density 0.03 SCF_Coulpot -0.07416 0.361184 ☐ Log ☐ Bar

☑ AIM Critical Points: ☑ Show ☑ Scale By Density Bond Paths: ☑ Show Color: Density

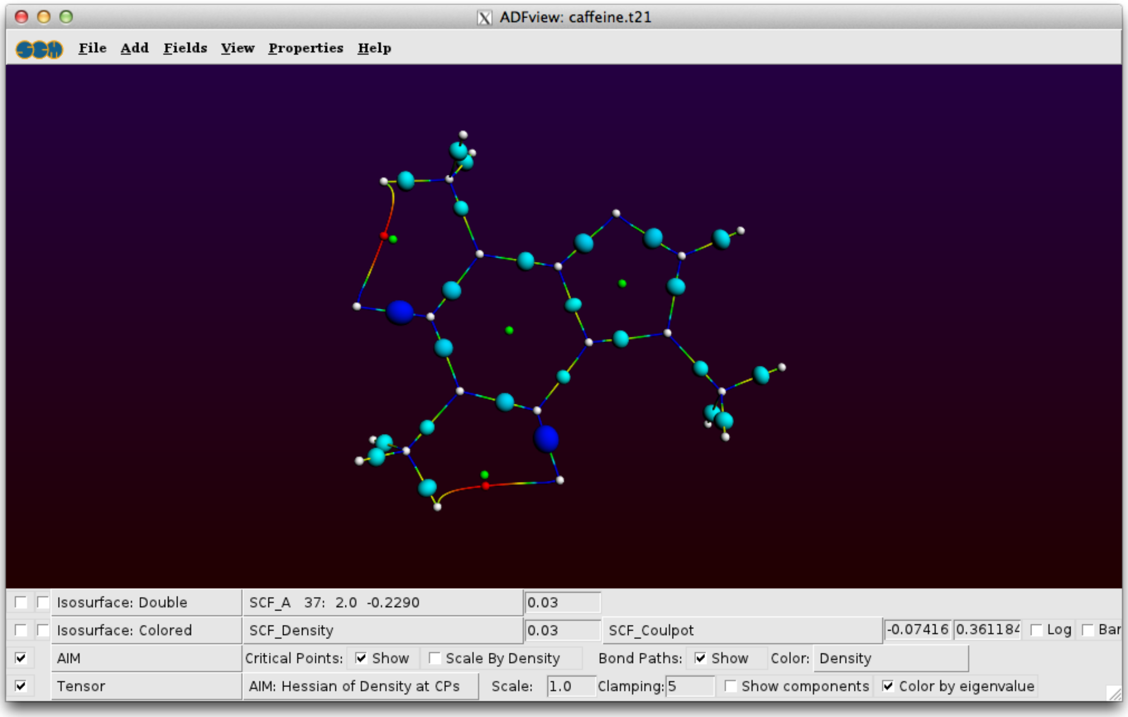
The critical points and bond paths are shown (the molecule balls and sticks representation is hidden). The different types of critical points (atom CP, bond CP, ring CP and cage CP) are indicated by different colors.

The atom CPs are scaled by density by default, which makes them look like atoms. The bond paths are colored by density, by default.

You can also visualize the Hessian of the Density in the critical points:

`Uncheck the 'Scale By Density' check box in the AIM line at the bottom of the window`

Properties → AIM: Hessian of Density at CPs

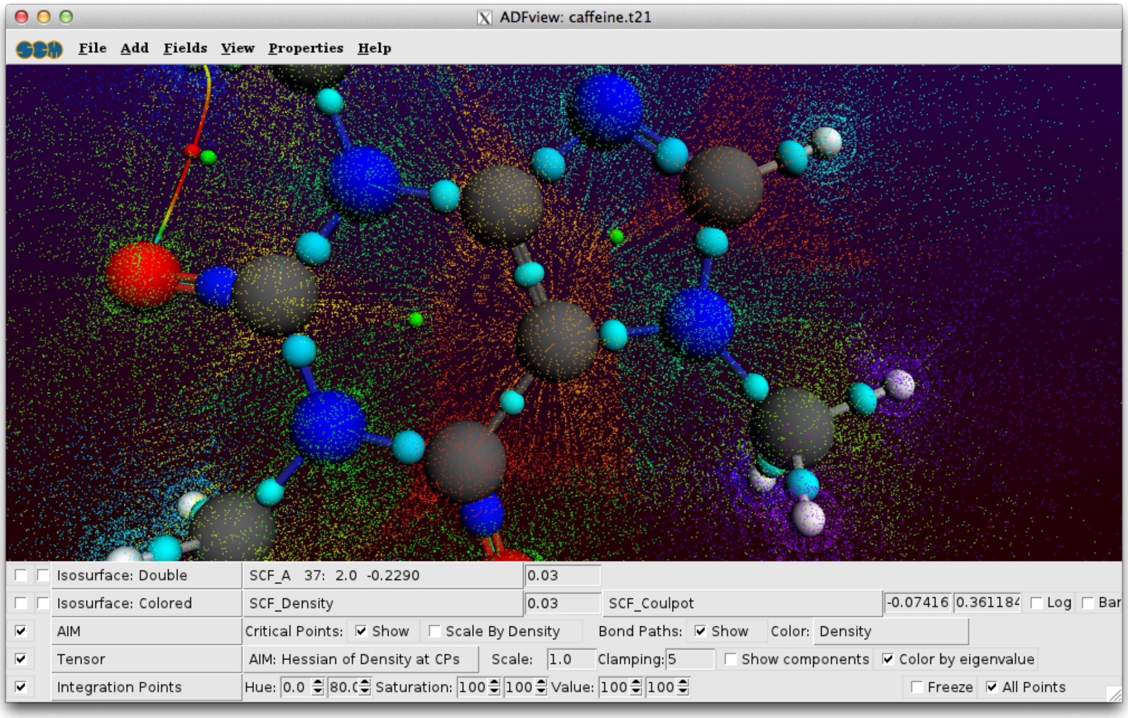


☐ ☐ Isosurface: Double | SCF_A 37: 2.0 -0.2290 | 0.03
☐ ☐ Isosurface: Colored | SCF_Density | 0.03 | SCF_Coulpot | -0.07416 | 0.361184 | ☐ Log | ☐ Bar
☑ AIM | Critical Points: ☑ Show | ☐ Scale By Density | Bond Paths: ☑ Show | Color: Density
☑ Tensor | AIM: Hessian of Density at CPs | Scale: 1.0 | Clamping: 5 | ☐ Show components | ☑ Color by eigenvalue

To get a rough display of the Bader basins, use the Bader sampling option:

Properties → Bader Sampling

`Zoom in`



☐ ☐ Isosurface: Double | SCF_A 37: 2.0 -0.2290 | 0.03
☐ ☐ Isosurface: Colored | SCF_Density | 0.03 | SCF_Coulpot | -0.07416 | 0.361184 | ☐ Log | ☐ Bar
☑ AIM | Critical Points: ☑ Show | ☐ Scale By Density | Bond Paths: ☑ Show | Color: Density
☑ Tensor | AIM: Hessian of Density at CPs | Scale: 1.0 | Clamping: 5 | ☐ Show components | ☑ Color by eigenvalue
☑ Integration Points | Hue: 0.0 | 80.0 | Saturation: 100 | 100 | Value: 100 | 100 | ☐ Freeze | ☑ All Points

The different colored points show the different basins.

ADFview has many options to visualize the results, the options just used are mainly to show off some features. Play around with the different options, for example try out what the check boxes do on the left side. Or try other fields, or colored cut planes, or ...

This finishes the Caffeine Bader (AIM) tutorial, close all its windows:

SCM → Close

Step 4: Benzene Bader charge analysis and NBOs

`Start ADFinput`
`Make a benzene molecule (for example by searching for it with cmd/ctrl-F)`
`Set up a Single Point calculation without frozen cores`

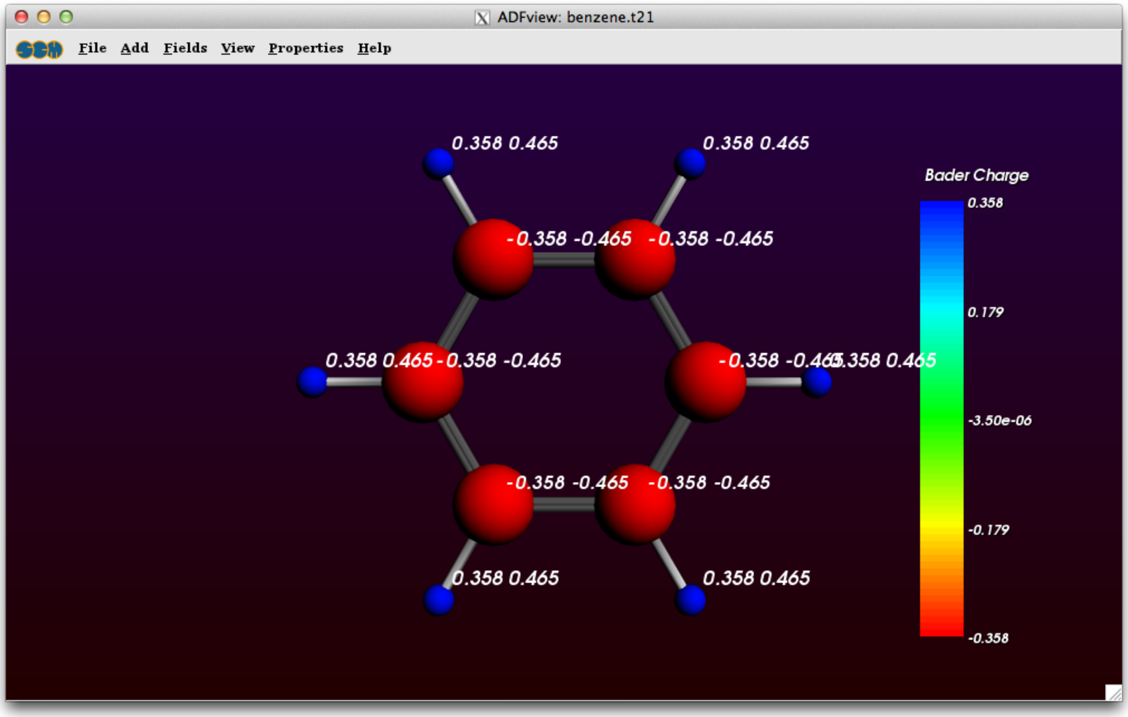
`Panel bar` **Properties → Other: Etot, Bader, Charge Transport**
`Check the 'Bader Atomic energies' option`
`Check the 'Save Bader atomic basins' option`

`Panel bar` **Properties → Localized Orbitals, NBO**
`Check the 'Perform NBO analysis' option`
`Request Boys-Foster localized orbitals`

`Run this setup (`**File → Run**`)`

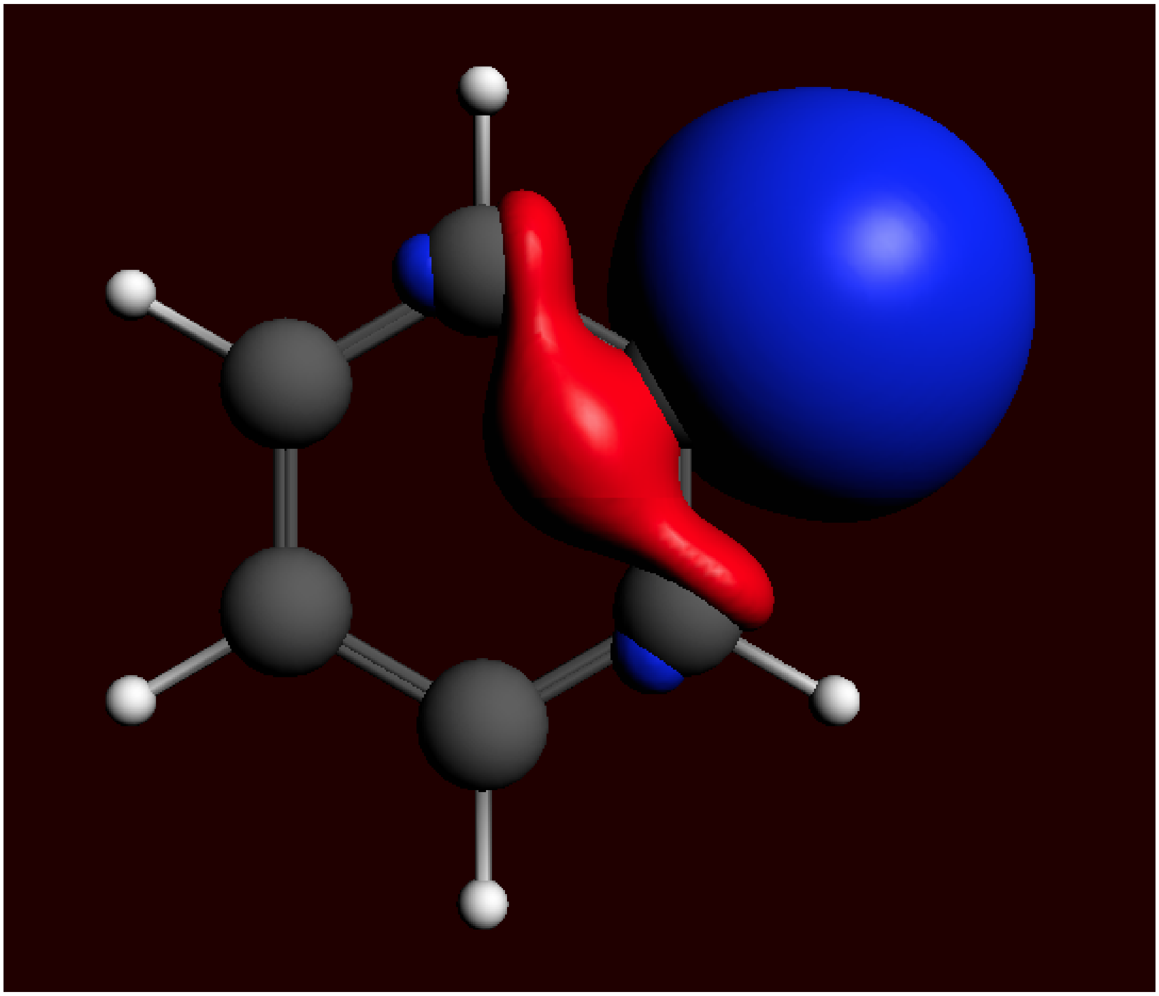
When the calculation is done (it should run very fast), we use ADFview to examine the Bader charges and compare them with Mulliken charges:

Open the results with ADFview
Show the Bader atomic charges (**Properties → Atom Info → Bader Charge → Show**)
Color the atoms by Bader charges (**Properties → Color Atoms By → Bader Charge**)
Show the Mulliken charges (**Properties → Atom Info → Mulliken Charge → Show**)



Next we inspect the NBOs and Boys-Foster localized orbitals. To remove the charge display we close and open ADFview, but you could also have used the View menu to remove them by hand:

Close ADFview
Open the results again with ADFview
Add a Double Isosurface
Use the field menu in the new control line, and
   observe the labels present with the NBOs and NLMOs
Open NBO number 15 (should be similar to C6-H12)
Improve the grid by using **Fields → Grid → Fine**

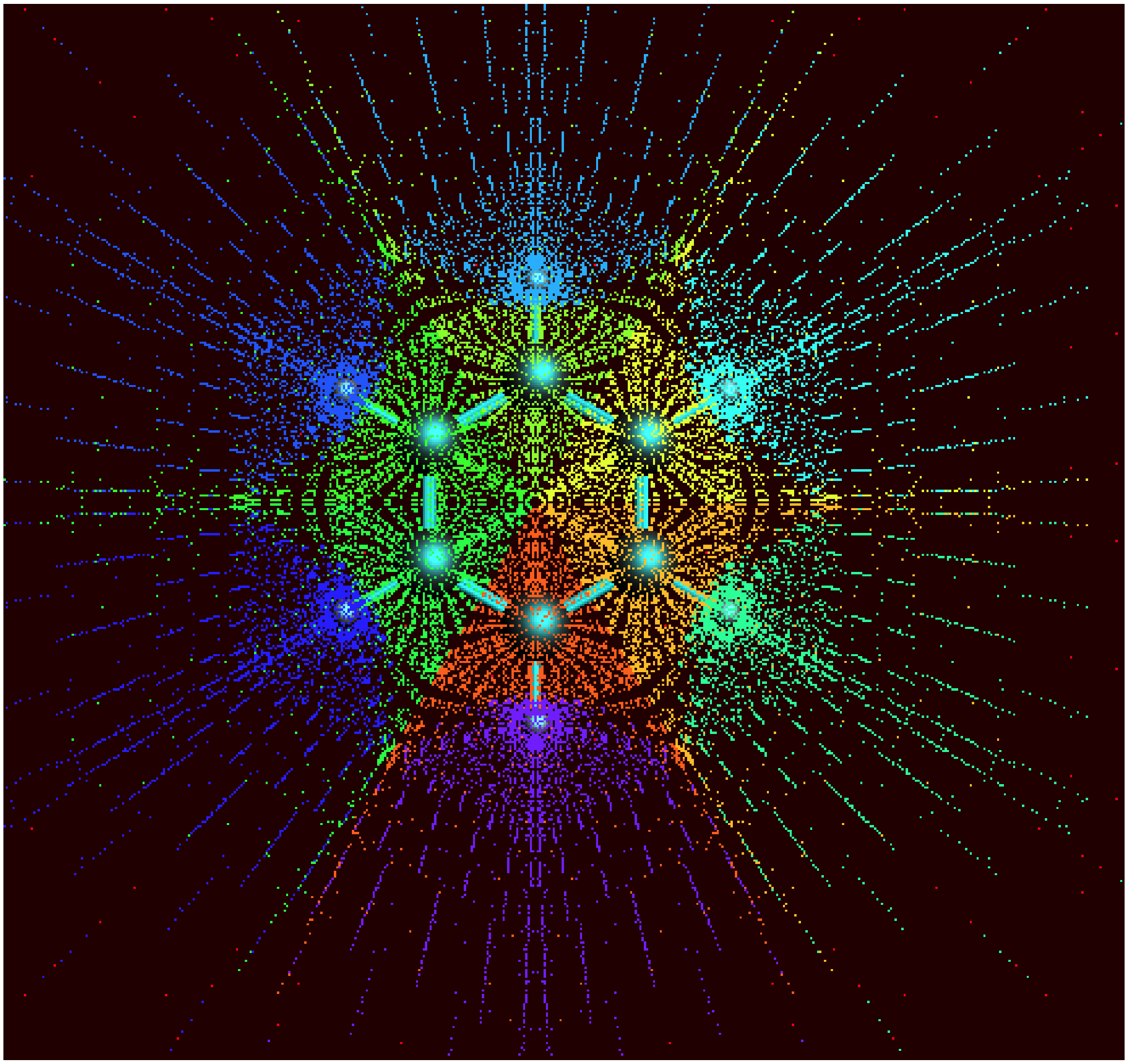


Obviously, you can also visualize the NLMOs or the Boys-Foster localized orbitals (which are just called Localized Orbitals in the fields menu.

Next we inspect the Bader atomic basins. The numerical integration points are used for this purpose. The color indicates to which atomic basin the numerical integration point belongs to.

```
Close ADFview
Open the results again with ADFview
```

Properties → Bader Sampling

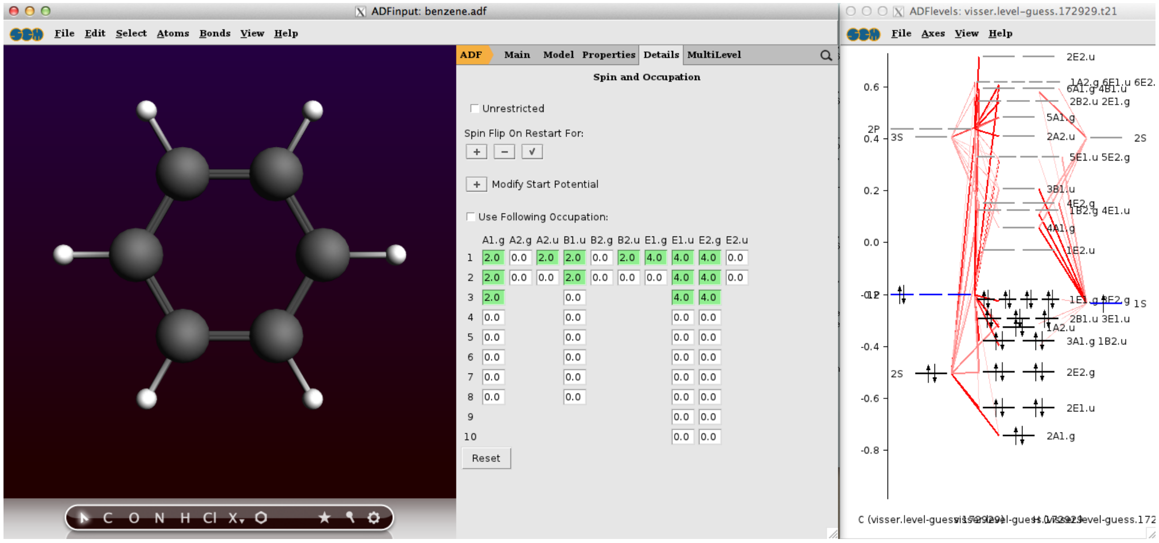


One can also select one or more atoms, to see only the Bader atomic basins of the selected atoms.

Step 5: Occupations

Now we will remove one electron from a selected orbital (by symmetry) using ADFinput again.

`Open your benzene calculation in ADFinput`
Model → Spin and Occupation



Spin and Occupation

☐ Unrestricted

Spin Flip On Restart For:

☐ Modify Start Potential

☐ Use Following Occupation:

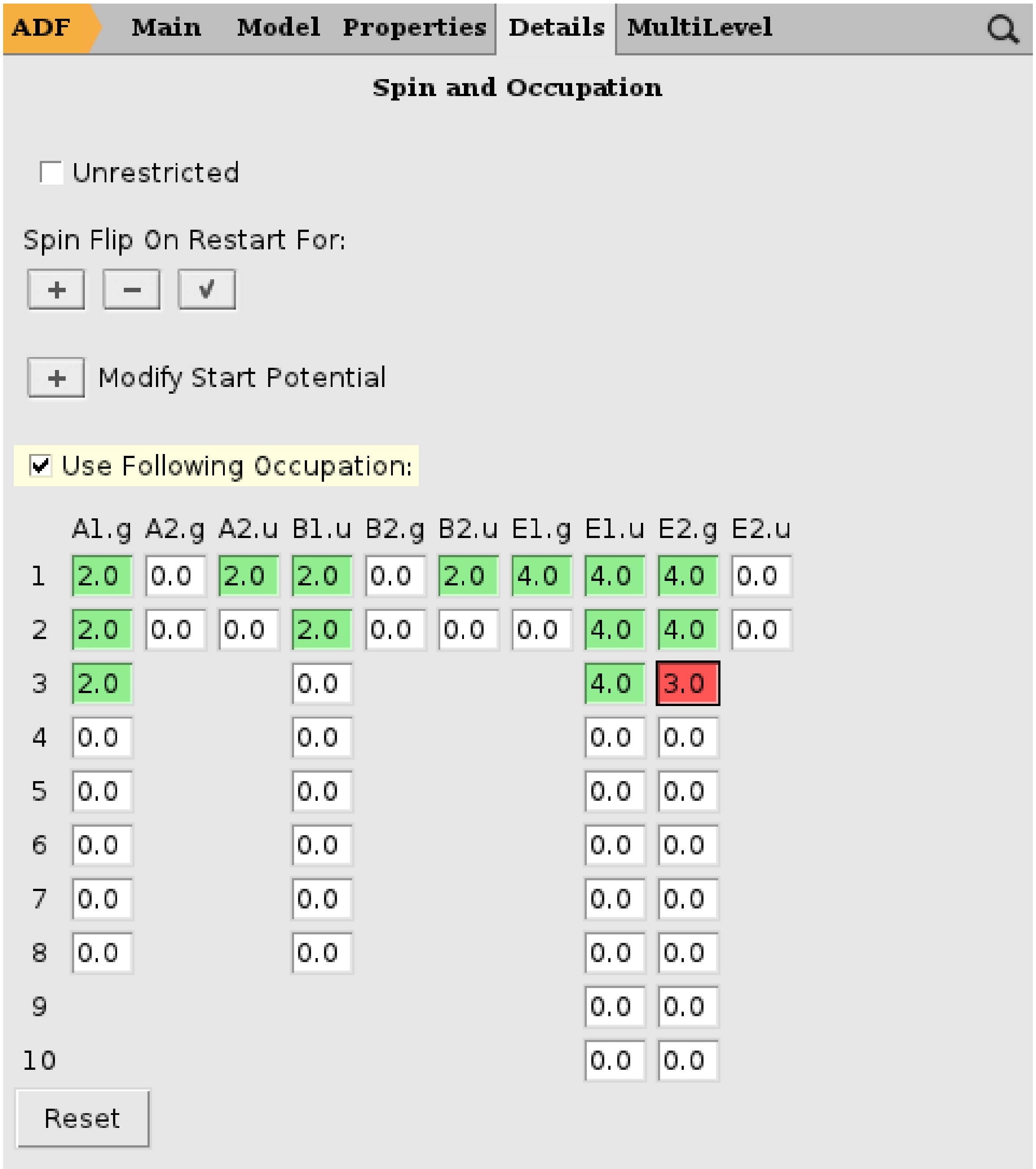
	A1.g	A2.g	A2.u	B1.u	B2.g	B2.u	E1.g	E1.u	E2.g	E2.u
1	2.0	0.0	2.0	2.0	0.0	2.0	4.0	4.0	4.0	0.0
2	2.0	0.0	0.0	2.0	0.0	0.0	0.0	4.0	4.0	0.0
3	2.0			0.0				4.0	4.0	
4	0.0			0.0				0.0	0.0	
5	0.0			0.0				0.0	0.0	
6	0.0			0.0				0.0	0.0	
7	0.0			0.0				0.0	0.0	
8	0.0			0.0				0.0	0.0	
9								0.0	0.0	
10								0.0	0.0	

In the Spin and Occupation panel you see which orbitals are available (by symmetry, and spin if the current set up is unrestricted). The numbers are the occupations. Next to the ADFinput window ADFlevels will also have opened, and is showing a level diagram of your current molecule. This helps you to select the proper occupation.

The level diagram is based on the existing result file (.t21) found. If none, ADFinput will suggest to do a guess-calculation: a hopefully fast calculation using an inaccurate integration grid, and stopping after a few SCF cycles. The level diagram shown in that case will not be accurate obviously but will still be helpful in selecting the proper occupation.

Now, just as an example, we make a hole in the 3E2.g orbital. Note that this is NOT the HOMO.

```
Change the 4.0 to 3.0 in the 3 E2.g column (the third row)
```



Spin and Occupation

☐ Unrestricted

Spin Flip On Restart For:

Modify Start Potential

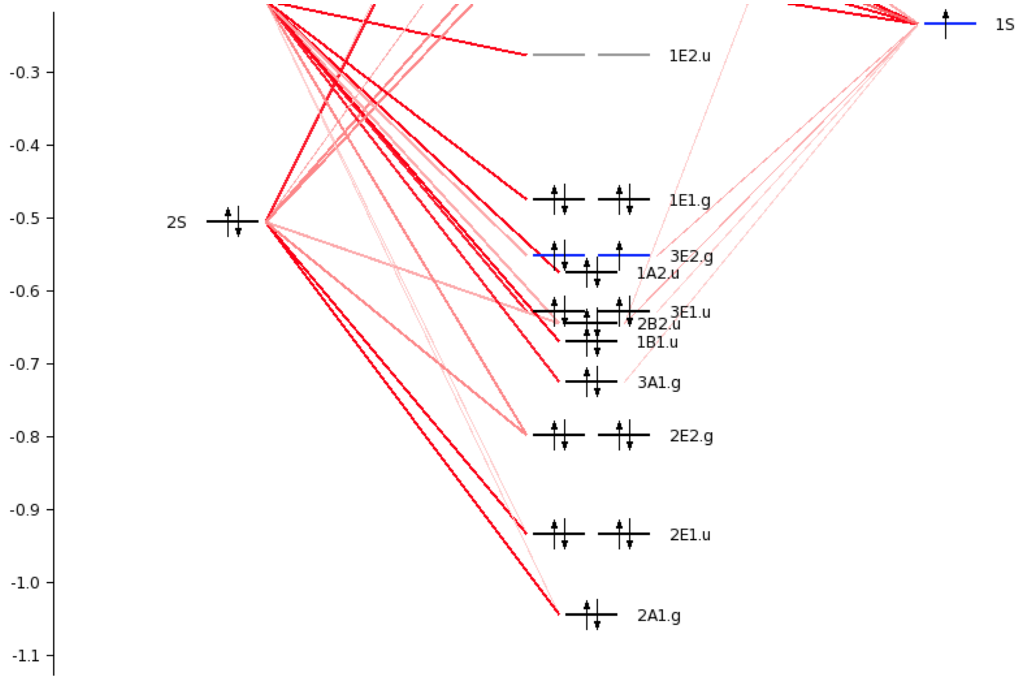
☑ Use Following Occupation:

	A1.g	A2.g	A2.u	B1.u	B2.g	B2.u	E1.g	E1.u	E2.g	E2.u
1	2.0	0.0	2.0	2.0	0.0	2.0	4.0	4.0	4.0	0.0
2	2.0	0.0	0.0	2.0	0.0	0.0	0.0	4.0	4.0	0.0
3	2.0			0.0				4.0	3.0	
4	0.0			0.0				0.0	0.0	
5	0.0			0.0				0.0	0.0	
6	0.0			0.0				0.0	0.0	
7	0.0			0.0				0.0	0.0	
8	0.0			0.0				0.0	0.0	
9								0.0	0.0	
10								0.0	0.0	

Close the guess adflevels
File → Save
Close the ADFinput window
Run (via the **Job → Run** command in ADFjobs

When the run is complete:

Open ADFlevels using the **SCM → Levels** command
In the ADFlevels window, use the **View → Labels → Show** command
Zoom in to the region of interest (for example using your mouse wheel)



In the levels diagram you will observe that the HOMO (the 1E1.g) is completely filled, while the orbital below it has a hole. You can easily see this by the color. Note that we have performed a restricted calculation, so in effect the hole is averaged over the E orbitals.

Tutorial 12: Spin Coupling in Fe_4S_4 Cluster

This tutorial will help you to:

- build the structure of iron-sulfur cubane,
- control the spin coupling in multi-center radical systems in two different ways (SpinFlip and ModifyStartPotential),
- tweak the SCF convergence in the iron-sulfur cubane case,
- visualize the distribution of spin densities in 3D.

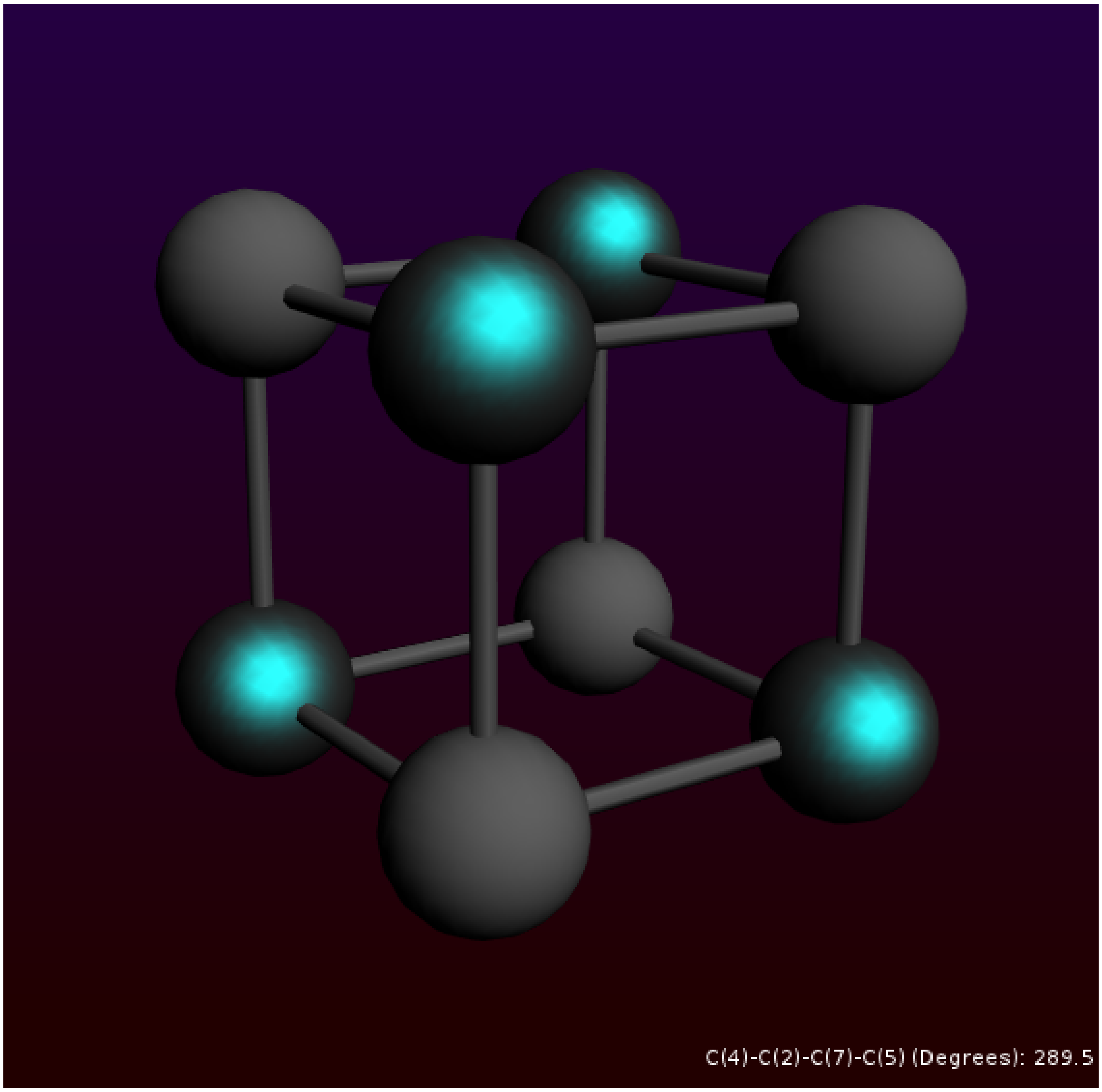
Step 1: Create and pre-optimize the Fe_4S_4 cubane model

Embedded into proteins and coordinated by cysteine ligands, iron-sulfur cubanes are often used by nature in electron transfer and catalysis. While their native structures can be extracted from protein data bank (PDB) files, we will use ADFinput module to build a model of the Fe_4S_4 cubane from scratch in this example.

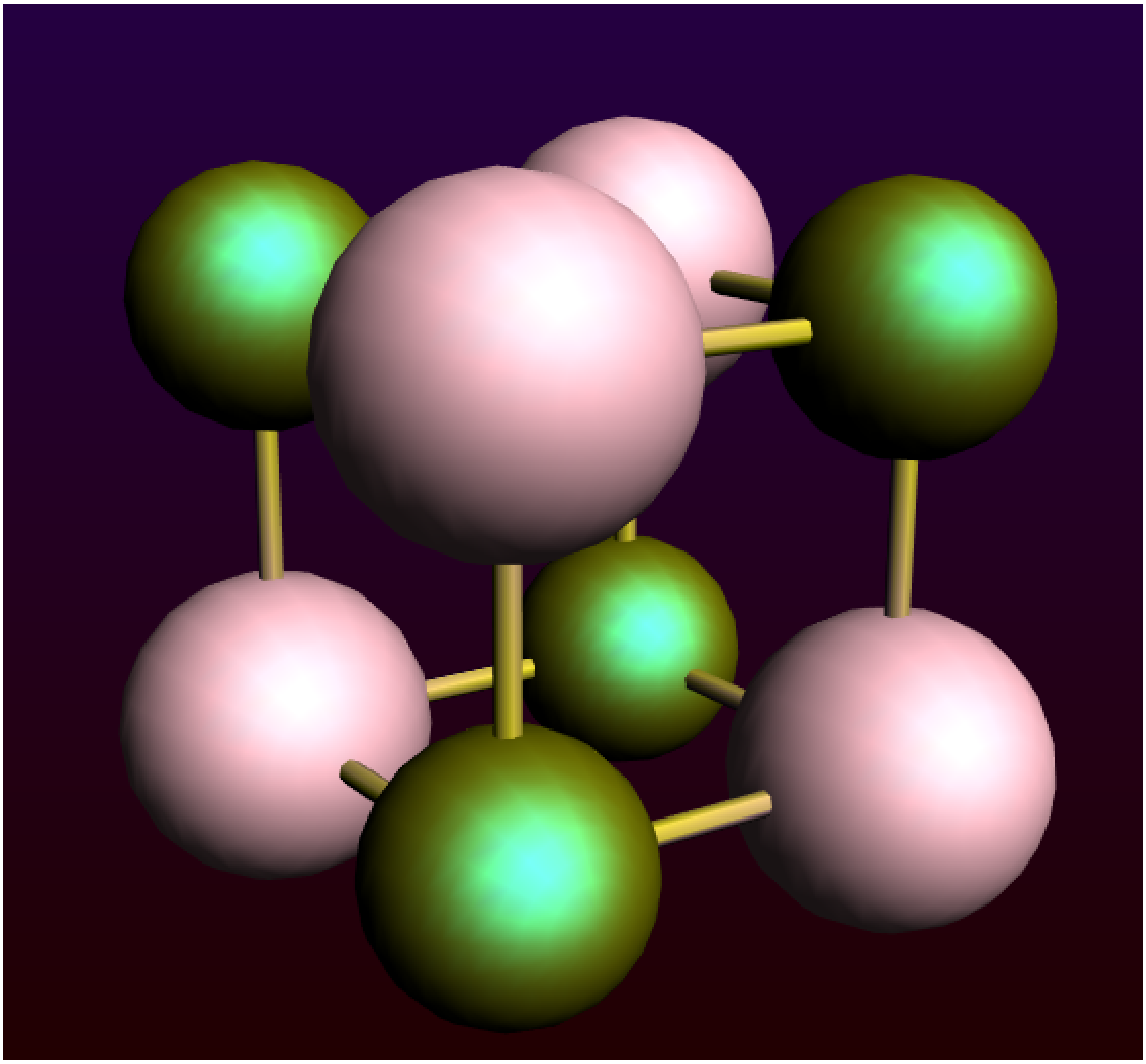
`Start ADFinput`
`Select the` **Structure tool → Polyhedra → Cube** `structure:`
`Click anywhere in the empty structure drawing area.`
`This should place a cube in the building area of ADFinput.`

The cube built is constructed of carbon atoms. We will now change four of these atoms to iron (Fe), and next the remaining four atoms into sulfur (S).

`Via Shift-click, select four carbon atoms in the corners of the cubane`

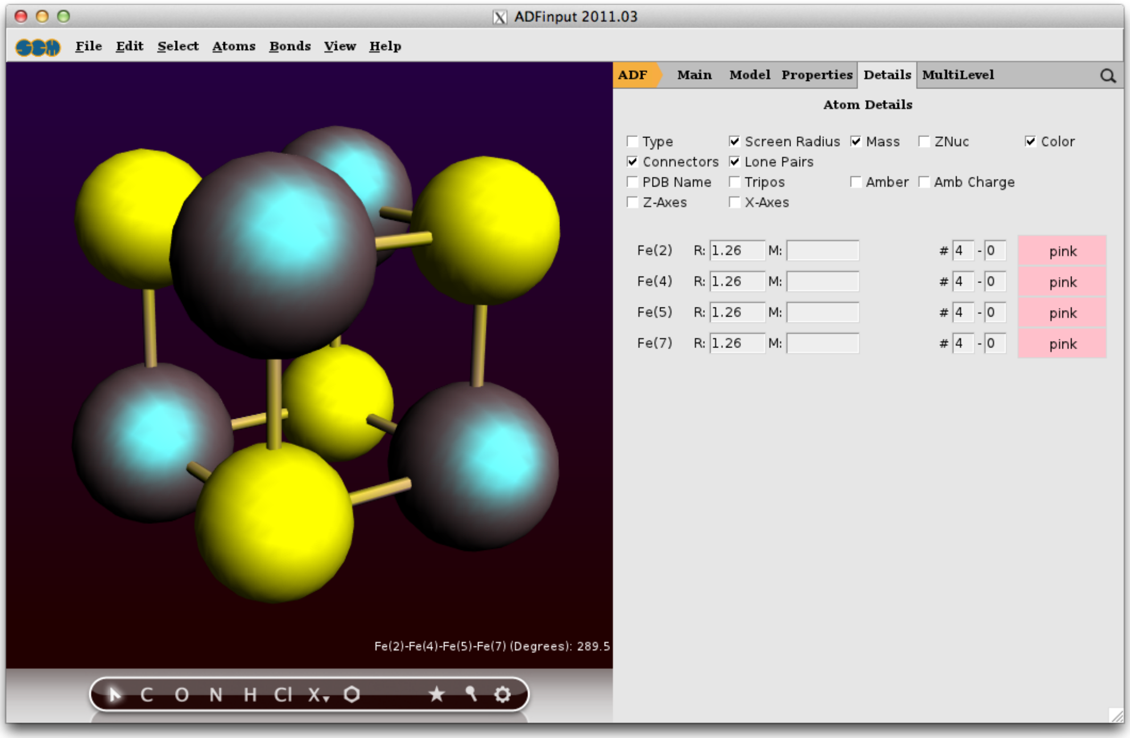


Atoms → Change Atom Type → Fe : `change the four atoms into Fe`
Selection → Invert Selection
Atoms → Change Atom Type → S : `change the other atoms into S`



Now you should see the Fe_4S_4 cubane in the structure drawing area of ADFinput. The proper coordination to Fe atoms is important in modeling their electronic structure. In proteins, iron-sulfur cubanes are coordinated by cysteine ligands to the Fe sites. Here, we will model these four cysteines by $^{-}$SH ligands. The procedure to add these ligands is described below.

Select all Fe atoms (for example by inverting the selection)
Use the **Atoms → Details (Color, Radius, Mass, ...)** menu command
Change the number of connectors for all Fe atoms from 10 into 4



Fe(2)-Fe(4)-Fe(5)-Fe(7) (Degrees): 289.5

Atom Details

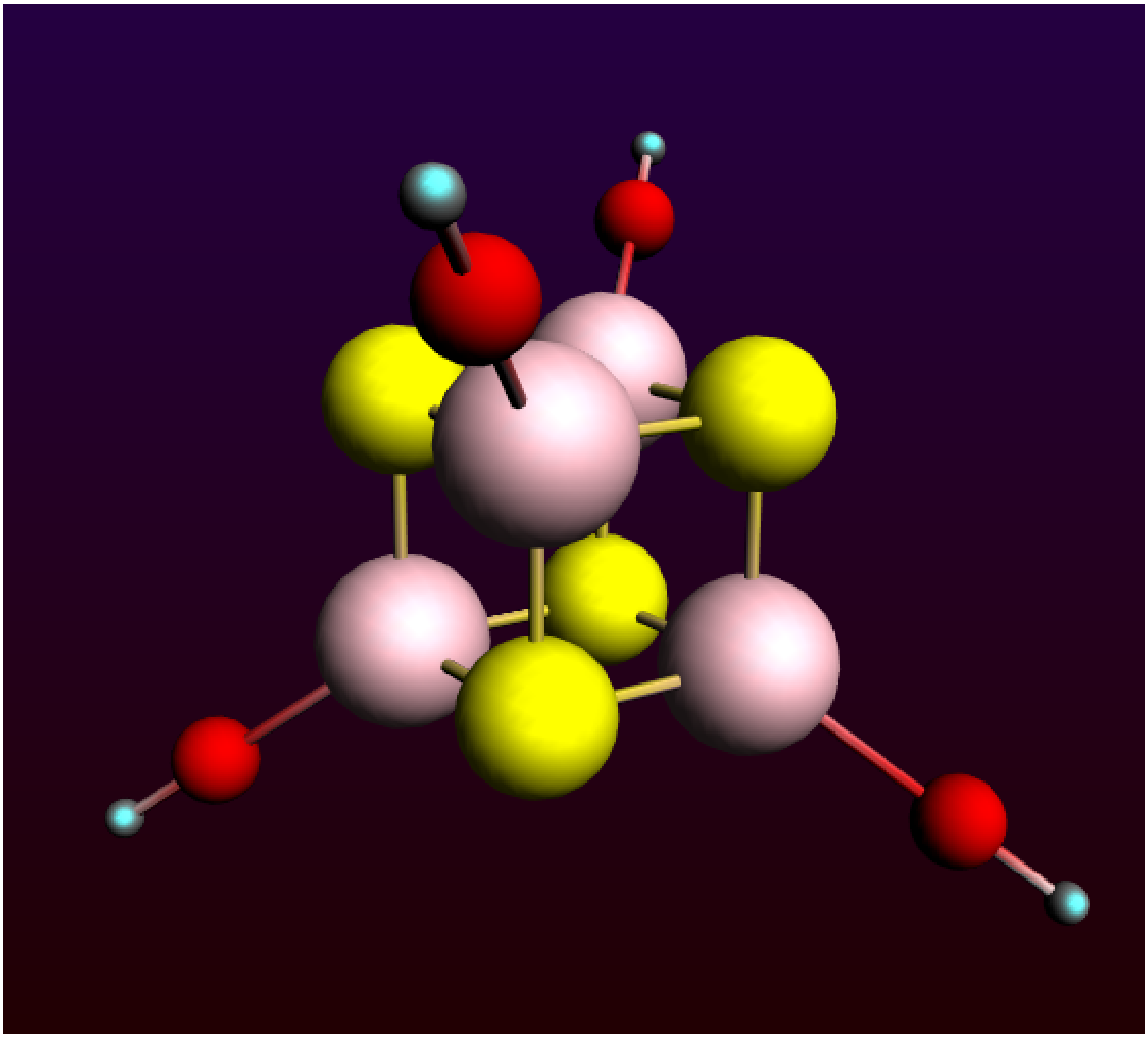
☐ Type ☑ Screen Radius ☑ Mass ☐ ZNuc ☑ Color
☑ Connectors ☑ Lone Pairs
☐ PDB Name ☐ Tripos ☐ Amber ☐ Amb Charge
☐ Z-Axes ☐ X-Axes

Fe(2)	R: 1.26	M:	# 4 - 0	pink
Fe(4)	R: 1.26	M:	# 4 - 0	pink
Fe(5)	R: 1.26	M:	# 4 - 0	pink
Fe(7)	R: 1.26	M:	# 4 - 0	pink

Switch to the Main panel
Add hydrogens to the still selected Fe atoms using the **Atoms → Add Hydrogen** menu command

Select the (newly added) hydrogens
Use the **Atoms → Replace By Structure → Ligands → OH** menu command:

This will replace hydrogen atoms into OH ligands.



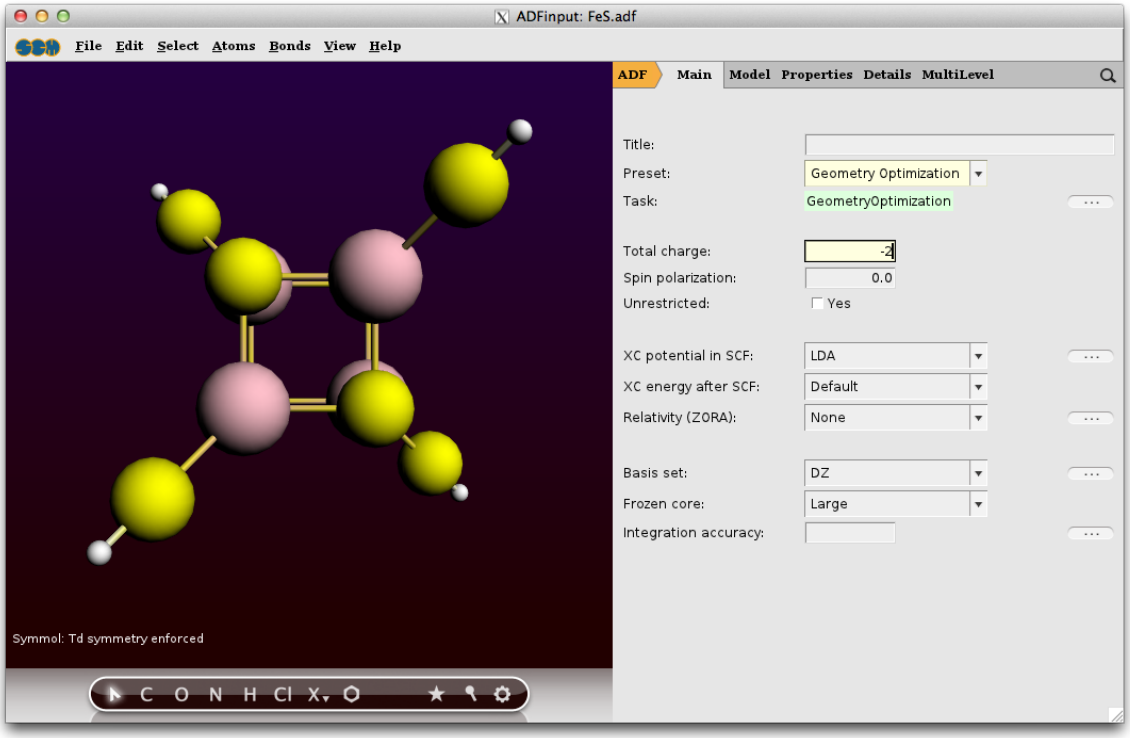
```
Select one of the O atoms
```

Use the **Select → Select Atoms Of Same Type** command to select them all

Use the **Atoms → Change Atom Type → S** to change them into S

The next step is to optimize this structure. It is a difficult system, and the pre-optimizers will fail. So we will use ADF to optimize the geometry.

```
Set the charge to -2
Select the Geometry Optimization preset

Click the Symmetrize button (the star) to check the symmetry (should be Td)
```



Title:
Preset: Geometry Optimization
Task: GeometryOptimization
Total charge: -2
Spin polarization: 0.0
Unrestricted: ☐ Yes
XC potential in SCF: LDA
XC energy after SCF: Default
Relativity (ZORA): None
Basis set: DZ
Frozen core: Large
Integration accuracy:

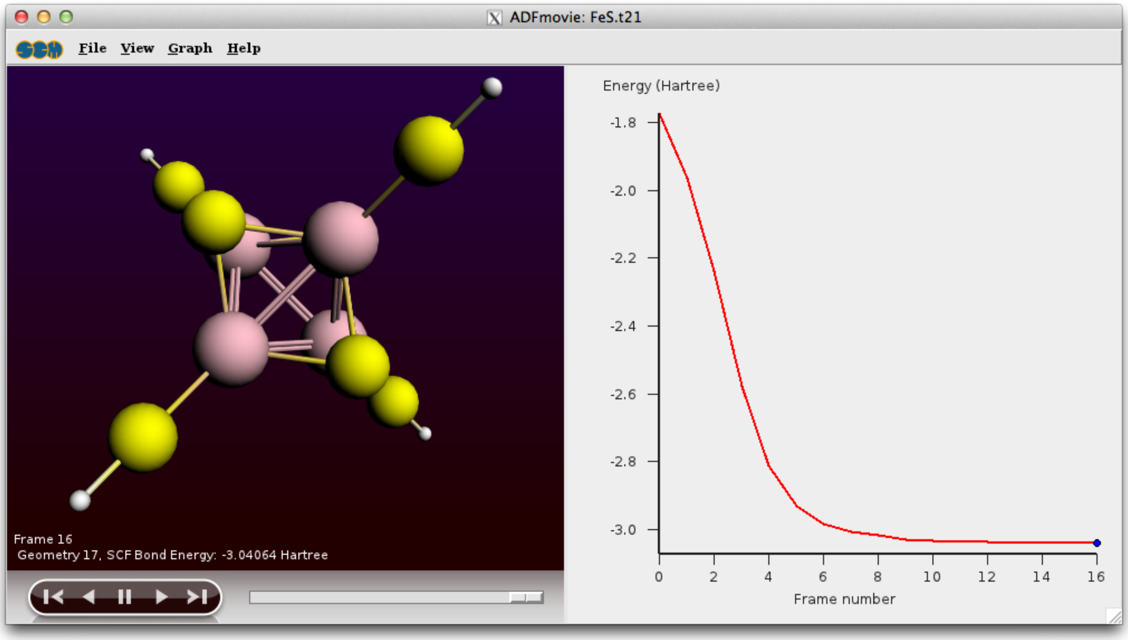
Symmol: Td symmetry enforced

File → Run (enter FeS as name)

When ready, click OK to use the optimized geometry in ADFinput

SCM → Movie

In the Movie window: **Graph → Energy**



Frame 16
Geometry 17, SCF Bond Energy: -3.04064 Hartree

Close the movie window: **File → Quit**

Step 2: Obtain the solution for the high-spin (HS) state of the cubane

In Fe_4S_4 systems, the iron sites are commonly high-spin ferrous (Fe^{3+}, S = 5/2) or ferric (Fe^{2+}, S = 2). For the present example, we will use the iron-sulfur cubane oxidation state where the two sites are ferric and the remaining two are ferrous. This oxidation level of Fe_4S_4 is well-defined and occurs, for example, in rubredoxin and high-potential iron-sulfur proteins (HIPIPs). For our model system, $Fe_4S_4(SH)_4$, this implies the total charge of -2.

The relative directions, or coupling, of the individual site spin vectors is a very important issue in obtaining the desired density functional solution in Fe_4S_4, as well as many other systems which display a multi-center radical character.

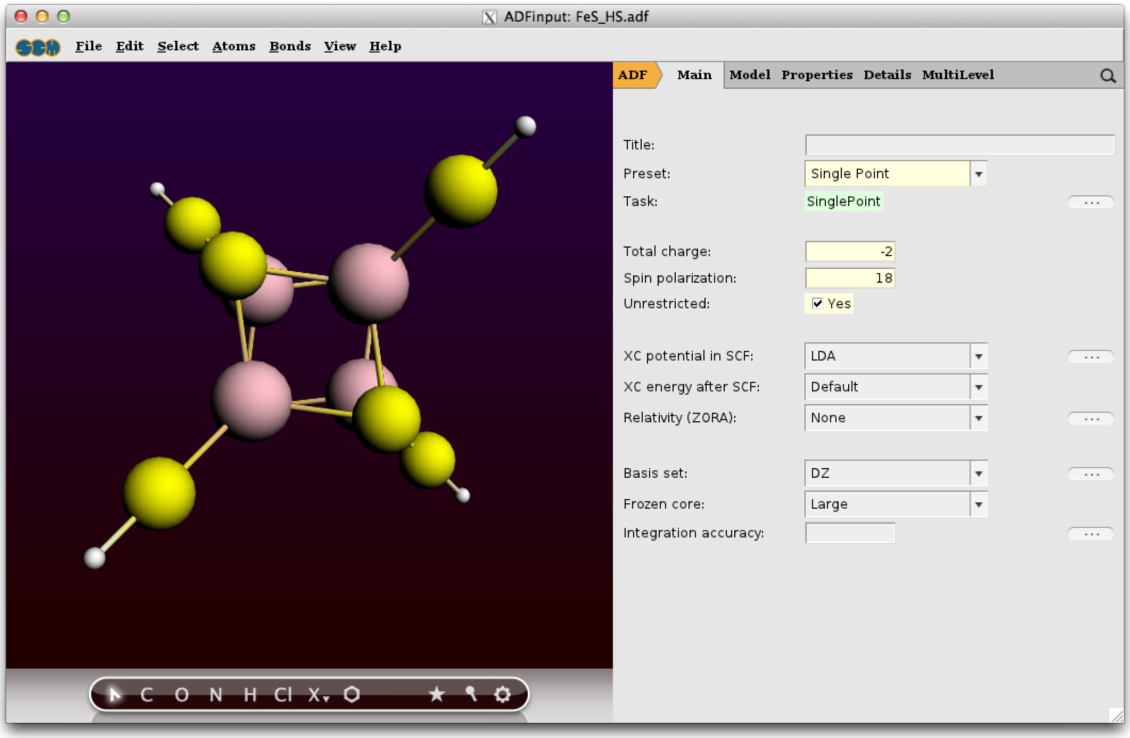
Within the common open-shell approach, the spin vectors are either parallel or anti-parallel. The case when all the spins are parallel is called high-spin (HS). Obtaining self-consisted field (SCF) solution for the HS case is normally simpler because the program does not need to resolve the ambiguity of distribution the sites spin vectors. While the ferromagnetic HS solution commonly does not correspond to the lowest energy electronic state, this solution can be used to obtain the electron density corresponding to the lower energy spin-coupled state. In this step, we will obtain the HS solution for the iron-sulfur cubane, which will be used later in the tutorial. The HS solution for the $[Fe_4S_4(SH)_4]^{2-}$ model corresponds to $S = 2 \times 5/2 + 2 \times 2 = 9$.

```
Select the ADFinput window

Select the Single Point preset
Keep the total charge to -2
Set the spin polarization to 18 (corresponds to S = 9)
Check the unrestricted box
```

File → Save As...

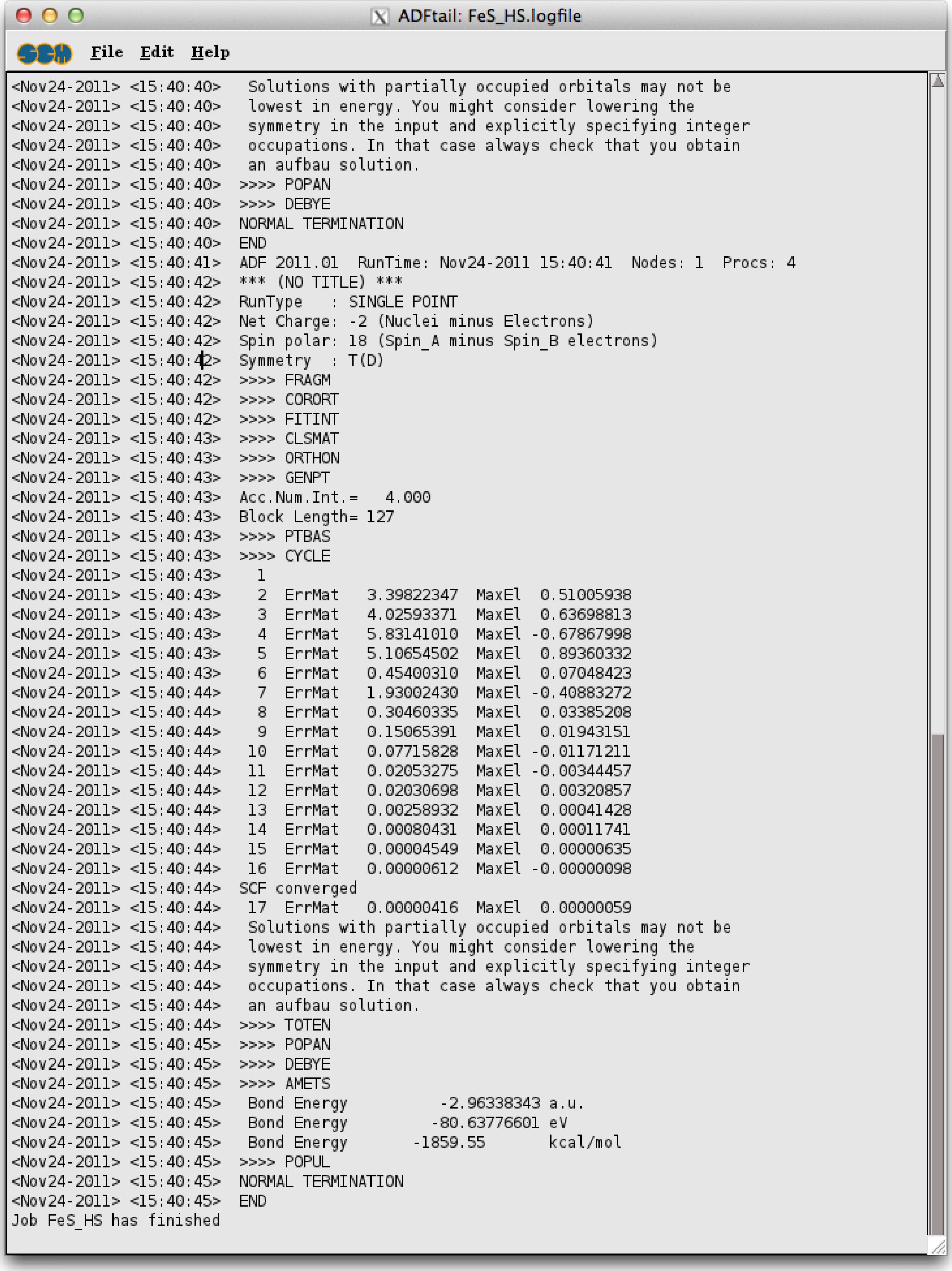
```
Enter FeS_HS as filename and save
```

File → Run



Title:
Preset: Single Point
Task: SinglePoint
Total charge: -2
Spin polarization: 18
Unrestricted: ☑ Yes
XC potential in SCF: LDA
XC energy after SCF: Default
Relativity (ZORA): None
Basis set: DZ
Frozen core: Large
Integration accuracy:

ADFtail window will pop up showing the progress of the job:



```
<Nov24-2011> <15:40:40>   Solutions with partially occupied orbitals may not be
<Nov24-2011> <15:40:40>   lowest in energy. You might consider lowering the
<Nov24-2011> <15:40:40>   symmetry in the input and explicitly specifying integer
<Nov24-2011> <15:40:40>   occupations. In that case always check that you obtain
<Nov24-2011> <15:40:40>   an aufbau solution.
<Nov24-2011> <15:40:40>  >>>> POPAN
<Nov24-2011> <15:40:40>  >>>> DEBYE
<Nov24-2011> <15:40:40>  NORMAL TERMINATION
<Nov24-2011> <15:40:40>  END
<Nov24-2011> <15:40:41>  ADF 2011.01  RunTime: Nov24-2011 15:40:41  Nodes: 1  Procs: 4
<Nov24-2011> <15:40:42>  *** (NO TITLE) ***
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<Nov24-2011> <15:40:42>  Net Charge: -2 (Nuclei minus Electrons)
<Nov24-2011> <15:40:42>  Spin polar: 18 (Spin_A minus Spin_B electrons)
<Nov24-2011> <15:40:42>  Symmetry   : T(D)
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<Nov24-2011> <15:40:42>  >>>> CORORT
<Nov24-2011> <15:40:42>  >>>> FITINT
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<Nov24-2011> <15:40:43>  >>>> ORTHON
<Nov24-2011> <15:40:43>  >>>> GENPT
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<Nov24-2011> <15:40:43>  Block Length= 127
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<Nov24-2011> <15:40:43>    3  ErrMat   4.02593371  MaxEl  0.63698813
<Nov24-2011> <15:40:43>    4  ErrMat   5.83141010  MaxEl -0.67867998
<Nov24-2011> <15:40:43>    5  ErrMat   5.10654502  MaxEl  0.89360332
<Nov24-2011> <15:40:43>    6  ErrMat   0.45400310  MaxEl  0.07048423
<Nov24-2011> <15:40:44>    7  ErrMat   1.93002430  MaxEl -0.40883272
<Nov24-2011> <15:40:44>    8  ErrMat   0.30460335  MaxEl  0.03385208
<Nov24-2011> <15:40:44>    9  ErrMat   0.15065391  MaxEl  0.01943151
<Nov24-2011> <15:40:44>   10  ErrMat   0.07715828  MaxEl -0.01171211
<Nov24-2011> <15:40:44>   11  ErrMat   0.02053275  MaxEl -0.00344457
<Nov24-2011> <15:40:44>   12  ErrMat   0.02030698  MaxEl  0.00320857
<Nov24-2011> <15:40:44>   13  ErrMat   0.00258932  MaxEl  0.00041428
<Nov24-2011> <15:40:44>   14  ErrMat   0.00080431  MaxEl  0.00011741
<Nov24-2011> <15:40:44>   15  ErrMat   0.00004549  MaxEl  0.00000635
<Nov24-2011> <15:40:44>   16  ErrMat   0.00000612  MaxEl -0.00000098
<Nov24-2011> <15:40:44>  SCF converged
<Nov24-2011> <15:40:44>   17  ErrMat   0.00000416  MaxEl  0.00000059
<Nov24-2011> <15:40:44>   Solutions with partially occupied orbitals may not be
<Nov24-2011> <15:40:44>   lowest in energy. You might consider lowering the
<Nov24-2011> <15:40:44>   symmetry in the input and explicitly specifying integer
<Nov24-2011> <15:40:44>   occupations. In that case always check that you obtain
<Nov24-2011> <15:40:44>   an aufbau solution.
<Nov24-2011> <15:40:44>  >>>> TOTEN
<Nov24-2011> <15:40:45>  >>>> POPAN
<Nov24-2011> <15:40:45>  >>>> DEBYE
<Nov24-2011> <15:40:45>  >>>> AMETS
<Nov24-2011> <15:40:45>   Bond Energy          -2.96338343 a.u.
<Nov24-2011> <15:40:45>   Bond Energy         -80.63776601 eV
<Nov24-2011> <15:40:45>   Bond Energy       -1859.55       kcal/mol
<Nov24-2011> <15:40:45>  >>>> POPUL
<Nov24-2011> <15:40:45>  NORMAL TERMINATION
<Nov24-2011> <15:40:45>  END
Job FeS_HS has finished
```

The logfile shows that the convergence has been obtained in 17 SCF cycles.

Step 3: Couple the spins in Fe_4S_4 using the SpinFlip option

While SCF solution for the high-spin (HS) state of a multi-center spin system can often be easily found, this solution does not necessarily correspond to the lowest energy state.

To generate the solution with the desired collinear spin arrangement, one option is to use the 'SpinFlip' concept that has been earlier introduced by L. Noodleman and coworkers. In this two step procedure:

- first the spin-unrestricted HS solution is generated with all the site spins ferromagnetically coupled in one direction (all spins up, ↑).
- Next the α (↑) and β (↓) electron densities centered at the sites which are expected to be antiferromagnetically coupled (spins down, ↓) to the total spin vector are exchanged for the earlier obtained HS solution, using the SpinFlip option, and the calculation is restarted.

Because this approach often results in lowering the electronic symmetry of the system while retaining its structural symmetry, a solution obtained in such way is often called the broken symmetry (BS) state. In such cases you will need to make sure that your BS calculation is done with lower symmetry.

The concept of SpinFlip and BS state can be illustrated considering our iron-sulfur cubane case with two ferrous (Fe^{3+}, $S = 5/2$) and two ferric (Fe^{2+}, $S = 2$) sites. One of the well-characterized BS states for this level of Fe_4S_4 oxidation corresponds to $S = (5/2 + 2) - (5/2 + 2) = 0$, 2↑:2↓.

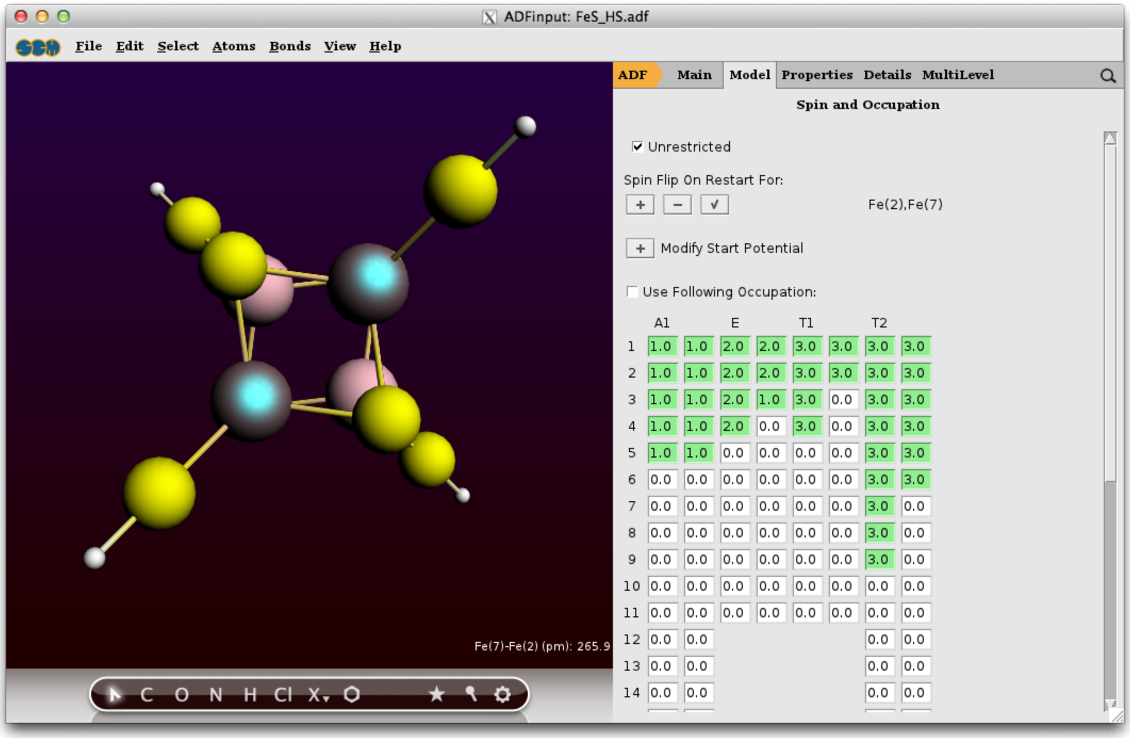
Select the ADFinput window with your FeS_HS calculation
Make sure the 'Main' panel is visible
Change the spin polarization from 18 to 0

This spin polarization setting corresponds to $S = 0$ zero spin of the BS electronic state.

Panel bar **Model → Spin and Occupation**

ADFlevels will show the levels from your previous calculation. As we are not changing the occupations this info is not needed for this tutorial.

Close the window showing the energy level diagram (ADFlevels ...)
Select the two (out of four) arbitrary Fe sites in the drawing area
Click **+** next to the **Spin Flip on Restart For:** line.



Spin and Occupation

☑ Unrestricted

Spin Flip On Restart For: Fe(2),Fe(7)

+ Modify Start Potential

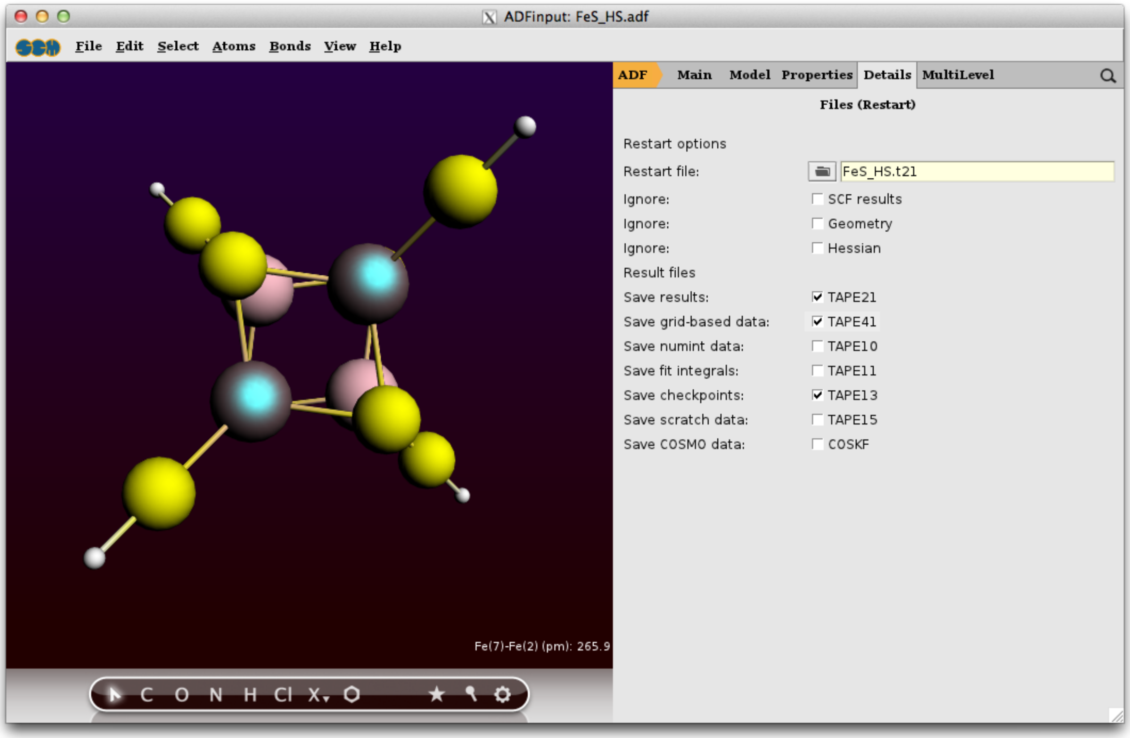
☐ Use Following Occupation:

	A1		E		T1		T2	
1	1.0	1.0	2.0	2.0	3.0	3.0	3.0	3.0
2	1.0	1.0	2.0	2.0	3.0	3.0	3.0	3.0
3	1.0	1.0	2.0	1.0	3.0	0.0	3.0	3.0
4	1.0	1.0	2.0	0.0	3.0	0.0	3.0	3.0
5	1.0	1.0	0.0	0.0	0.0	0.0	3.0	3.0
6	0.0	0.0	0.0	0.0	0.0	0.0	3.0	3.0
7	0.0	0.0	0.0	0.0	0.0	0.0	3.0	0.0
8	0.0	0.0	0.0	0.0	0.0	0.0	3.0	0.0
9	0.0	0.0	0.0	0.0	0.0	0.0	3.0	0.0
10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
11	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
12	0.0	0.0					0.0	0.0
13	0.0	0.0					0.0	0.0
14	0.0	0.0					0.0	0.0

To achieve the desired BS solution, the SpinFlip procedure should be applied to 2 out of 4 Fe sites of Fe_4S_4. In the above example, we selected sites Fe(2) and Fe(7). This will instruct SpinFlip algorithm to interchange α (↑) and β (↓) electron densities associated with these two Fe sites when the job will be restarted, changing the HS 4↑:0↓ spin state to the BS 2↑:2↓ spin state.

The Spin Flip option only works when restarting, so set up the restart calculation from the HS results:

Panel bar **Details → Files (Restart)**
Click folder icon in front of the 'Restart file:' field,
Select the Fe_HS.t21 file (it should already be selected, so just press the Open button)



Files (Restart)

Restart options

Restart file: FeS_HS.t21

Ignore: ☐ SCF results

Ignore: ☐ Geometry

Ignore: ☐ Hessian

Result files

Save results: ☑ TAPE21

Save grid-based data: ☑ TAPE41

Save numint data: ☐ TAPE10

Save fit integrals: ☐ TAPE11

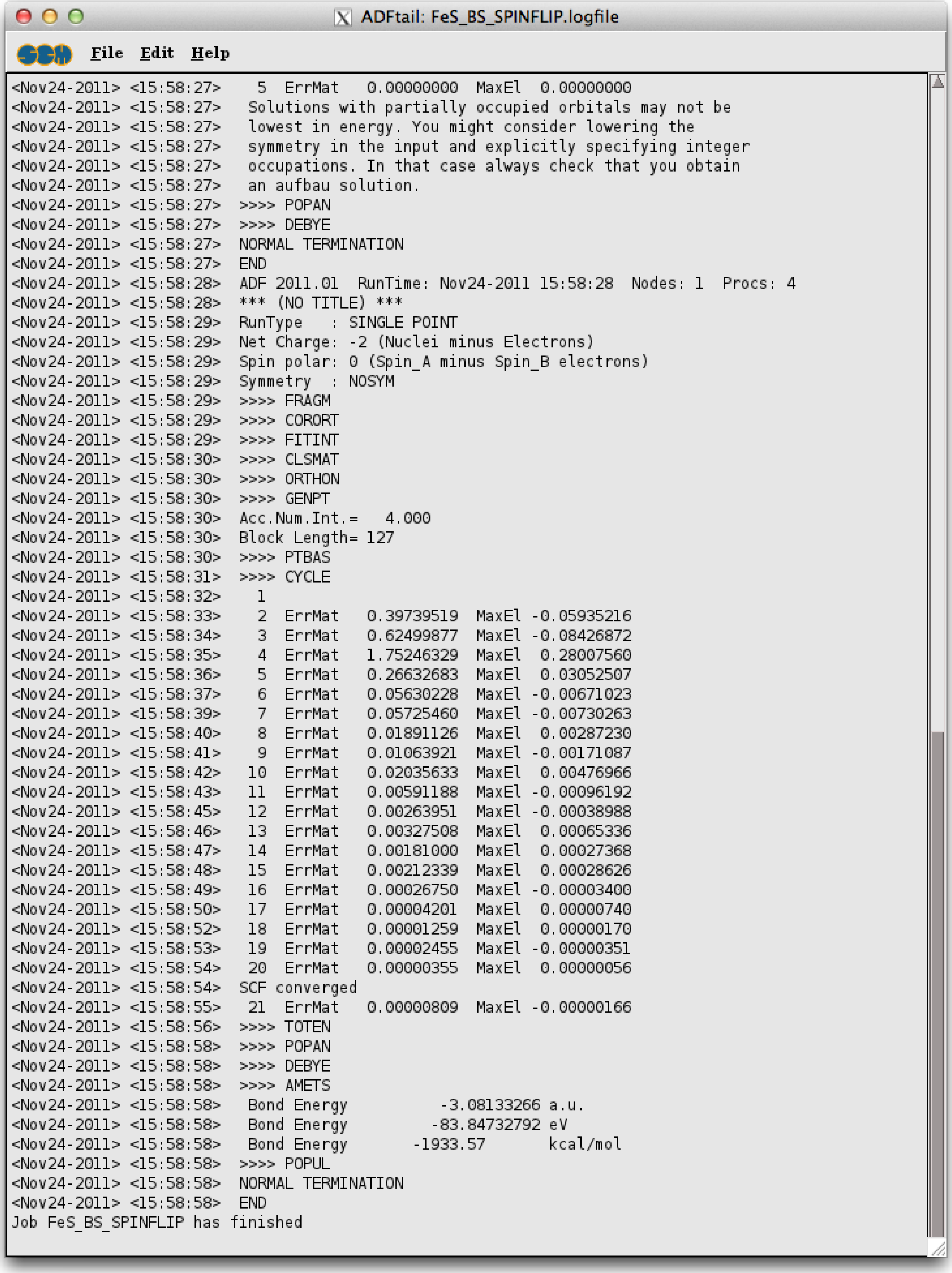
Save checkpoints: ☑ TAPE13

Save scratch data: ☐ TAPE15

Save COSMO data: ☐ COSKF

The above will instruct ADF to read the converged HS solution we obtained in the previous step of the tutorial. This solution has been saved in the Fe_HS.t21.

Panel bar **Details → Symmetry**
Set the symmetry to NOSYM
File → Save As, save the job as FeS_BS_SPINFLIP
File → Run



```
<Nov24-2011> <15:58:27>    5  ErrMat   0.00000000  MaxEl  0.00000000
<Nov24-2011> <15:58:27>   Solutions with partially occupied orbitals may not be
<Nov24-2011> <15:58:27>   lowest in energy. You might consider lowering the
<Nov24-2011> <15:58:27>   symmetry in the input and explicitly specifying integer
<Nov24-2011> <15:58:27>   occupations. In that case always check that you obtain
<Nov24-2011> <15:58:27>   an aufbau solution.
<Nov24-2011> <15:58:27>  >>>> POPAN
<Nov24-2011> <15:58:27>  >>>> DEBYE
<Nov24-2011> <15:58:27>  NORMAL TERMINATION
<Nov24-2011> <15:58:27>  END
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<Nov24-2011> <15:58:28>  *** (NO TITLE) ***
<Nov24-2011> <15:58:29>  RunType   : SINGLE POINT
<Nov24-2011> <15:58:29>  Net Charge: -2 (Nuclei minus Electrons)
<Nov24-2011> <15:58:29>  Spin polar: 0 (Spin_A minus Spin_B electrons)
<Nov24-2011> <15:58:29>  Symmetry  : NOSYM
<Nov24-2011> <15:58:29>  >>>> FRAGM
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<Nov24-2011> <15:58:30>  >>>> CLSMAT
<Nov24-2011> <15:58:30>  >>>> ORTHON
<Nov24-2011> <15:58:30>  >>>> GENPT
<Nov24-2011> <15:58:30>  Acc.Num.Int.=   4.000
<Nov24-2011> <15:58:30>  Block Length= 127
<Nov24-2011> <15:58:30>  >>>> PTBAS
<Nov24-2011> <15:58:31>  >>>> CYCLE
<Nov24-2011> <15:58:32>    1
<Nov24-2011> <15:58:33>    2  ErrMat   0.39739519  MaxEl -0.05935216
<Nov24-2011> <15:58:34>    3  ErrMat   0.62499877  MaxEl -0.08426872
<Nov24-2011> <15:58:35>    4  ErrMat   1.75246329  MaxEl  0.28007560
<Nov24-2011> <15:58:36>    5  ErrMat   0.26632683  MaxEl  0.03052507
<Nov24-2011> <15:58:37>    6  ErrMat   0.05630228  MaxEl -0.00671023
<Nov24-2011> <15:58:39>    7  ErrMat   0.05725460  MaxEl -0.00730263
<Nov24-2011> <15:58:40>    8  ErrMat   0.01891126  MaxEl  0.00287230
<Nov24-2011> <15:58:41>    9  ErrMat   0.01063921  MaxEl -0.00171087
<Nov24-2011> <15:58:42>   10  ErrMat   0.02035633  MaxEl  0.00476966
<Nov24-2011> <15:58:43>   11  ErrMat   0.00591188  MaxEl -0.00096192
<Nov24-2011> <15:58:45>   12  ErrMat   0.00263951  MaxEl -0.00038988
<Nov24-2011> <15:58:46>   13  ErrMat   0.00327508  MaxEl  0.00065336
<Nov24-2011> <15:58:47>   14  ErrMat   0.00181000  MaxEl  0.00027368
<Nov24-2011> <15:58:48>   15  ErrMat   0.00212339  MaxEl  0.00028626
<Nov24-2011> <15:58:49>   16  ErrMat   0.00026750  MaxEl -0.00003400
<Nov24-2011> <15:58:50>   17  ErrMat   0.00004201  MaxEl  0.00000740
<Nov24-2011> <15:58:52>   18  ErrMat   0.00001259  MaxEl  0.00000170
<Nov24-2011> <15:58:53>   19  ErrMat   0.00002455  MaxEl -0.00000351
<Nov24-2011> <15:58:54>   20  ErrMat   0.00000355  MaxEl  0.00000056
<Nov24-2011> <15:58:54>  SCF converged
<Nov24-2011> <15:58:55>   21  ErrMat   0.00000809  MaxEl -0.00000166
<Nov24-2011> <15:58:56>  >>>> TOTEN
<Nov24-2011> <15:58:58>  >>>> POPAN
<Nov24-2011> <15:58:58>  >>>> DEBYE
<Nov24-2011> <15:58:58>  >>>> AMETS
<Nov24-2011> <15:58:58>   Bond Energy          -3.08133266 a.u.
<Nov24-2011> <15:58:58>   Bond Energy         -83.84732792 eV
<Nov24-2011> <15:58:58>   Bond Energy       -1933.57       kcal/mol
<Nov24-2011> <15:58:58>  >>>> POPUL
<Nov24-2011> <15:58:58>  NORMAL TERMINATION
<Nov24-2011> <15:58:58>  END
Job FeS_BS_SPINFLIP has finished
```

As you see, our FeS_BS_SPINFLIP job converges in 21 cycles.

Step 4: Coupling the spins using the ModifyStartPotential option, use ARH SCF convergence method

There is an alternative to SpinFlip available in ADF, which is aimed to achieve a specific spin-coupled solution in a single calculation only. This is done using the MODIFYSTARTPOTENTIAL key in ADF: it allows you to create a spin-polarized potential at the very start of the calculation.

Please read the page of ADF user's guide on MODIFYSTARTPOTENTIAL key prior to proceeding with this step of the tutorial. As follows from the MODIFYSTARTPOTENTIAL description, this key allows to control the ratio of spin-α and spin-β electrons associated with fragments via 'alpha' and 'beta' numbers. For the purpose of the present tutorial, we will consider the four Fe sites as fragments. Apparently, 'alpha' and 'beta' numbers will correspond to the number of spin-α and spin-β electrons, correspondingly, associated with a Fe site.

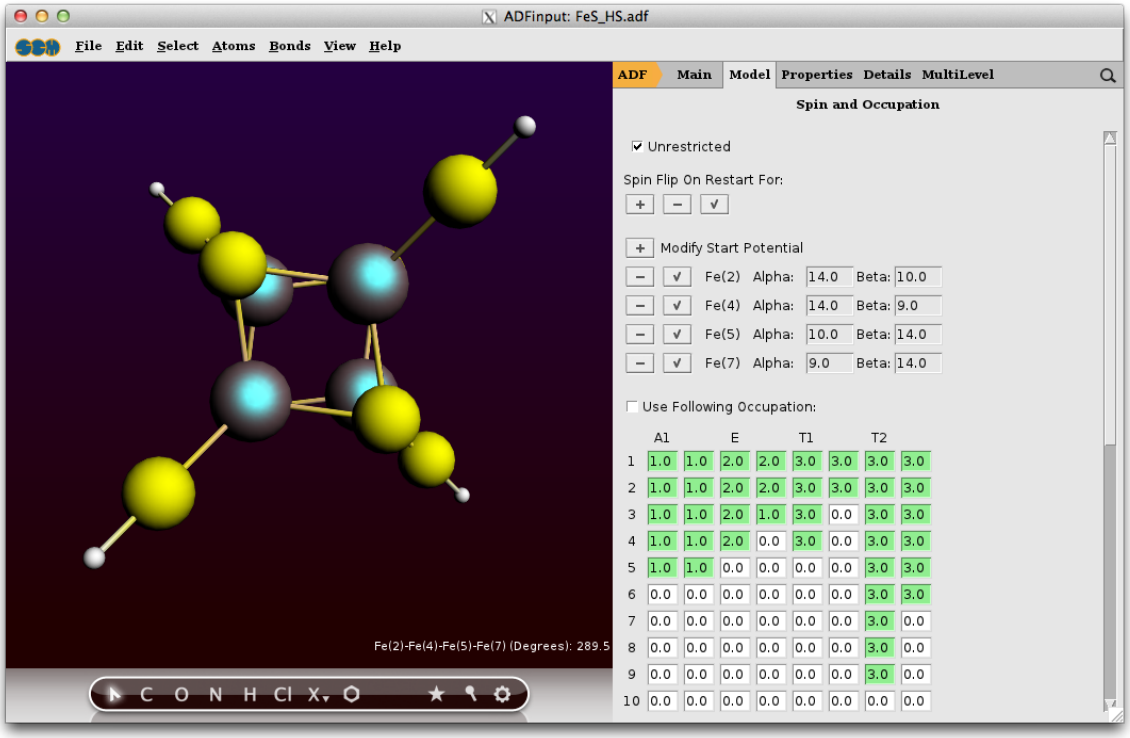
So follow these instructions to obtain the BS solution via the MODIFYSTARTPOPTENTIAL option:

```
Open your FeS_HS calculation in ADFinput
Change the spin polarization from 18 to 0
```

`Panel bar` **Details → Symmetry**
`Set the symmetry to NOSYM`

`Panel bar` **Model → Spin and Occupations**
`Close the ADFlevels window`

```
Select the four Fe atoms
Click the '+' in front of 'Modify Start Potential'
Set the alpha and beta occupations, for the four Fe atoms:
    14 alpha and 10 beta
    14 alpha and  9 beta
    10 alpha and 14 beta
     9 alpha and 14 beta
```



Spin and Occupation

☑ Unrestricted

Spin Flip On Restart For:

+ Modify Start Potential

Fe(2) Alpha: 14.0 Beta: 10.0

Fe(4) Alpha: 14.0 Beta: 9.0

Fe(5) Alpha: 10.0 Beta: 14.0

Fe(7) Alpha: 9.0 Beta: 14.0

☐ Use Following Occupation:

	A1		E		T1		T2	
1	1.0	1.0	2.0	2.0	3.0	3.0	3.0	3.0
2	1.0	1.0	2.0	2.0	3.0	3.0	3.0	3.0
3	1.0	1.0	2.0	1.0	3.0	0.0	3.0	3.0
4	1.0	1.0	2.0	0.0	3.0	0.0	3.0	3.0
5	1.0	1.0	0.0	0.0	0.0	0.0	3.0	3.0
6	0.0	0.0	0.0	0.0	0.0	0.0	3.0	3.0
7	0.0	0.0	0.0	0.0	0.0	0.0	3.0	0.0
8	0.0	0.0	0.0	0.0	0.0	0.0	3.0	0.0
9	0.0	0.0	0.0	0.0	0.0	0.0	3.0	0.0
10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

For the spin-up Fe^{3+}, *S* = 5/2, the alpha and beta numbers would be 14 and 9, correspondingly, and for the spin-up Fe^{2+}, *S* = 2, these numbers are 14 and 10. For the spin-down Fe sites, alpha and beta numbers should be apparently transposed. Also, our desired BS state for this level of Fe_4S_4 oxidation corresponds to *S* = (5/2 + 2) - (5/2 + 2) = 0, 2↑:2↓ .

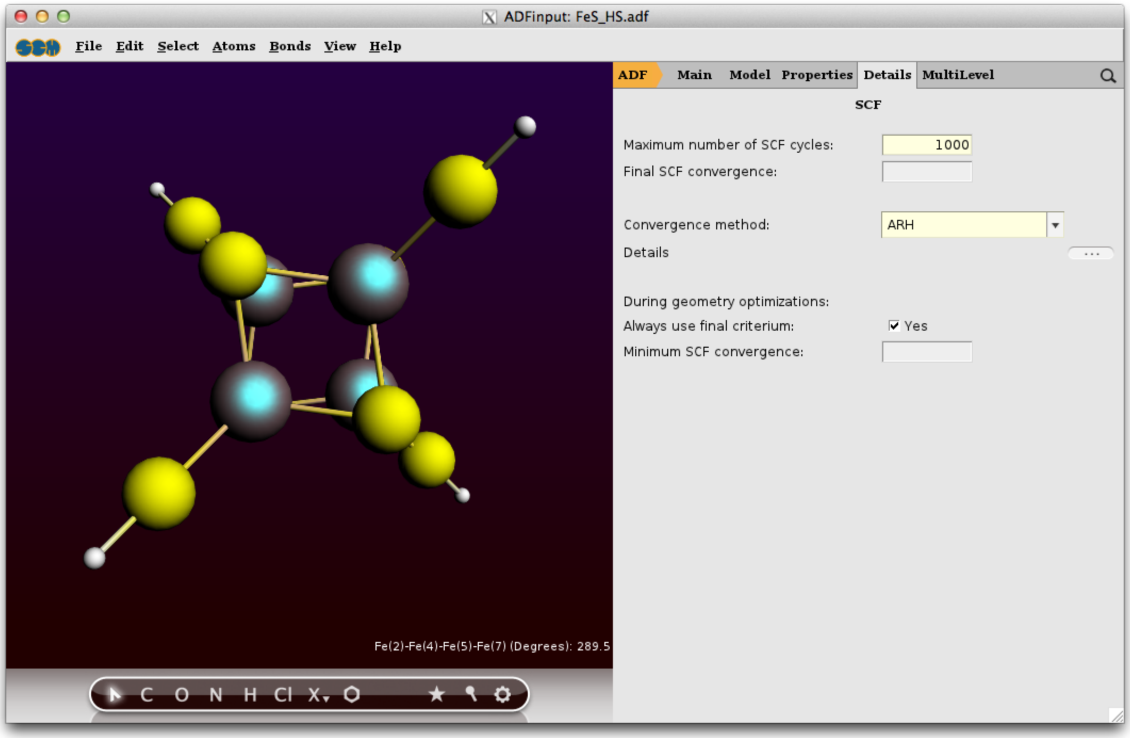
Note that SCF procedure might be problematic.

You can play with several options to help the convergence. In the SCF panel (in Details) you can experiment with several mehods like LISTi, A-DIIS, E-DIIS and ARH. In the SCF convergence details panel further options are available, like mixing, level shifting, orbital freezing and DIIS details.

In this particular case, the ARH method (in the SCF panel) works, although it needs a lot of iterations.

`Panel bar` **Details → SCF**

```
Select the ARH convergence method
Set the maximum number of SCF cycles to 1000
```



Maximum number of SCF cycles: 1000

Final SCF convergence:

Convergence method: ARH

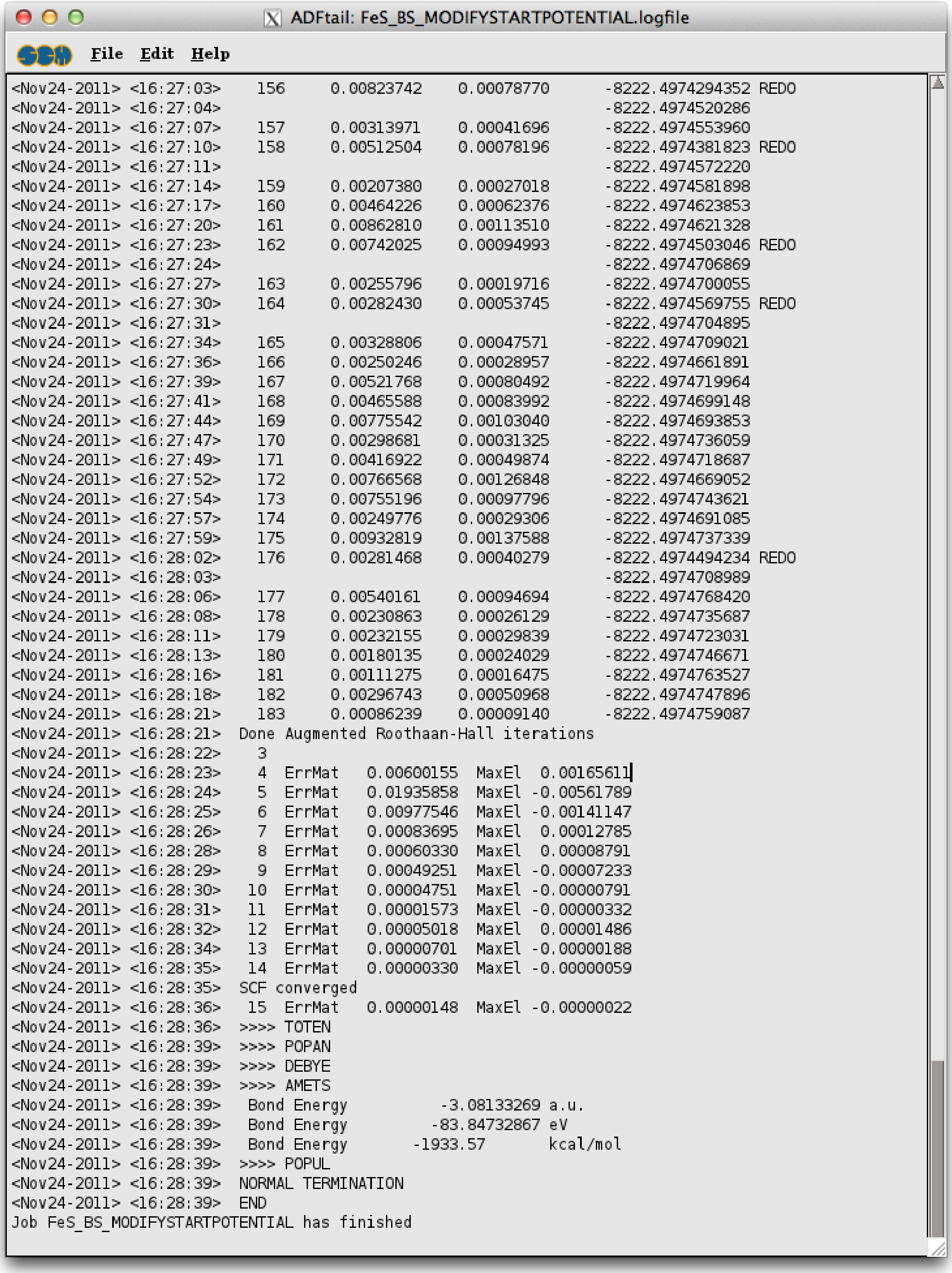
Details

During geometry optimizations:

Always use final criterium: ☑ Yes

Minimum SCF convergence:

File → Save As : `save the job as FeS_BS_MODIFYSTARTPOTENTIAL`
File → Run



```
<Nov24-2011> <16:27:03>   156     0.00823742    0.00078770      -8222.4974294352 REDO
<Nov24-2011> <16:27:04>                                         -8222.4974520286
<Nov24-2011> <16:27:07>   157     0.00313971    0.00041696      -8222.4974553960
<Nov24-2011> <16:27:10>   158     0.00512504    0.00078196      -8222.4974381823 REDO
<Nov24-2011> <16:27:11>                                         -8222.4974572220
<Nov24-2011> <16:27:14>   159     0.00207380    0.00027018      -8222.4974581898
<Nov24-2011> <16:27:17>   160     0.00464226    0.00062376      -8222.4974623853
<Nov24-2011> <16:27:20>   161     0.00862810    0.00113510      -8222.4974621328
<Nov24-2011> <16:27:23>   162     0.00742025    0.00094993      -8222.4974503046 REDO
<Nov24-2011> <16:27:24>                                         -8222.4974706869
<Nov24-2011> <16:27:27>   163     0.00255796    0.00019716      -8222.4974700055
<Nov24-2011> <16:27:30>   164     0.00282430    0.00053745      -8222.4974569755 REDO
<Nov24-2011> <16:27:31>                                         -8222.4974704895
<Nov24-2011> <16:27:34>   165     0.00328806    0.00047571      -8222.4974709021
<Nov24-2011> <16:27:36>   166     0.00250246    0.00028957      -8222.4974661891
<Nov24-2011> <16:27:39>   167     0.00521768    0.00080492      -8222.4974719964
<Nov24-2011> <16:27:41>   168     0.00465588    0.00083992      -8222.4974699148
<Nov24-2011> <16:27:44>   169     0.00775542    0.00103040      -8222.4974693853
<Nov24-2011> <16:27:47>   170     0.00298681    0.00031325      -8222.4974736059
<Nov24-2011> <16:27:49>   171     0.00416922    0.00049874      -8222.4974718687
<Nov24-2011> <16:27:52>   172     0.00766568    0.00126848      -8222.4974669052
<Nov24-2011> <16:27:54>   173     0.00755196    0.00097796      -8222.4974743621
<Nov24-2011> <16:27:57>   174     0.00249776    0.00029306      -8222.4974691085
<Nov24-2011> <16:27:59>   175     0.00932819    0.00137588      -8222.4974737339
<Nov24-2011> <16:28:02>   176     0.00281468    0.00040279      -8222.4974494234 REDO
<Nov24-2011> <16:28:03>                                         -8222.4974708989
<Nov24-2011> <16:28:06>   177     0.00540161    0.00094694      -8222.4974768420
<Nov24-2011> <16:28:08>   178     0.00230863    0.00026129      -8222.4974735687
<Nov24-2011> <16:28:11>   179     0.00232155    0.00029839      -8222.4974723031
<Nov24-2011> <16:28:13>   180     0.00180135    0.00024029      -8222.4974746671
<Nov24-2011> <16:28:16>   181     0.00111275    0.00016475      -8222.4974763527
<Nov24-2011> <16:28:18>   182     0.00296743    0.00050968      -8222.4974747896
<Nov24-2011> <16:28:21>   183     0.00086239    0.00009140      -8222.4974759087
<Nov24-2011> <16:28:21>  Done Augmented Roothaan-Hall iterations
<Nov24-2011> <16:28:22>    3
<Nov24-2011> <16:28:23>    4  ErrMat   0.00600155  MaxEl  0.00165611
<Nov24-2011> <16:28:24>    5  ErrMat   0.01935858  MaxEl -0.00561789
<Nov24-2011> <16:28:25>    6  ErrMat   0.00977546  MaxEl -0.00141147
<Nov24-2011> <16:28:26>    7  ErrMat   0.00083695  MaxEl  0.00012785
<Nov24-2011> <16:28:28>    8  ErrMat   0.00060330  MaxEl  0.00008791
<Nov24-2011> <16:28:29>    9  ErrMat   0.00049251  MaxEl -0.00007233
<Nov24-2011> <16:28:30>   10  ErrMat   0.00004751  MaxEl -0.00000791
<Nov24-2011> <16:28:31>   11  ErrMat   0.00001573  MaxEl -0.00000332
<Nov24-2011> <16:28:32>   12  ErrMat   0.00005018  MaxEl  0.00001486
<Nov24-2011> <16:28:34>   13  ErrMat   0.00000701  MaxEl -0.00000188
<Nov24-2011> <16:28:35>   14  ErrMat   0.00000330  MaxEl -0.00000059
<Nov24-2011> <16:28:35>  SCF converged
<Nov24-2011> <16:28:36>   15  ErrMat   0.00000148  MaxEl -0.00000022
<Nov24-2011> <16:28:36>  >>>> TOTEN
<Nov24-2011> <16:28:39>  >>>> POPAN
<Nov24-2011> <16:28:39>  >>>> DEBYE
<Nov24-2011> <16:28:39>  >>>> AMETS
<Nov24-2011> <16:28:39>   Bond Energy          -3.08133269 a.u.
<Nov24-2011> <16:28:39>   Bond Energy         -83.84732867 eV
<Nov24-2011> <16:28:39>   Bond Energy       -1933.57       kcal/mol
<Nov24-2011> <16:28:39>  >>>> POPUL
<Nov24-2011> <16:28:39>  NORMAL TERMINATION
<Nov24-2011> <16:28:39>  END
Job FeS_BS_MODIFYSTARTPOTENTIAL has finished
```

Hopefully you will be able to converge the job, to the same energy and state as the SpinFlip job.

Thus both the SpinFlip and the ModifyStartPotential option allow you to obtain a desired Fe spin coupling pattern in the Fe_4S_4 case. While SpinFlip is a two-step approach and ModifyStartPotential works as in a single step, the SpinFlip approach shows a better performance during SCF (much better and faster SCF convergence).

Step 5: View the spin density of the broken symmetry (BS) solutions

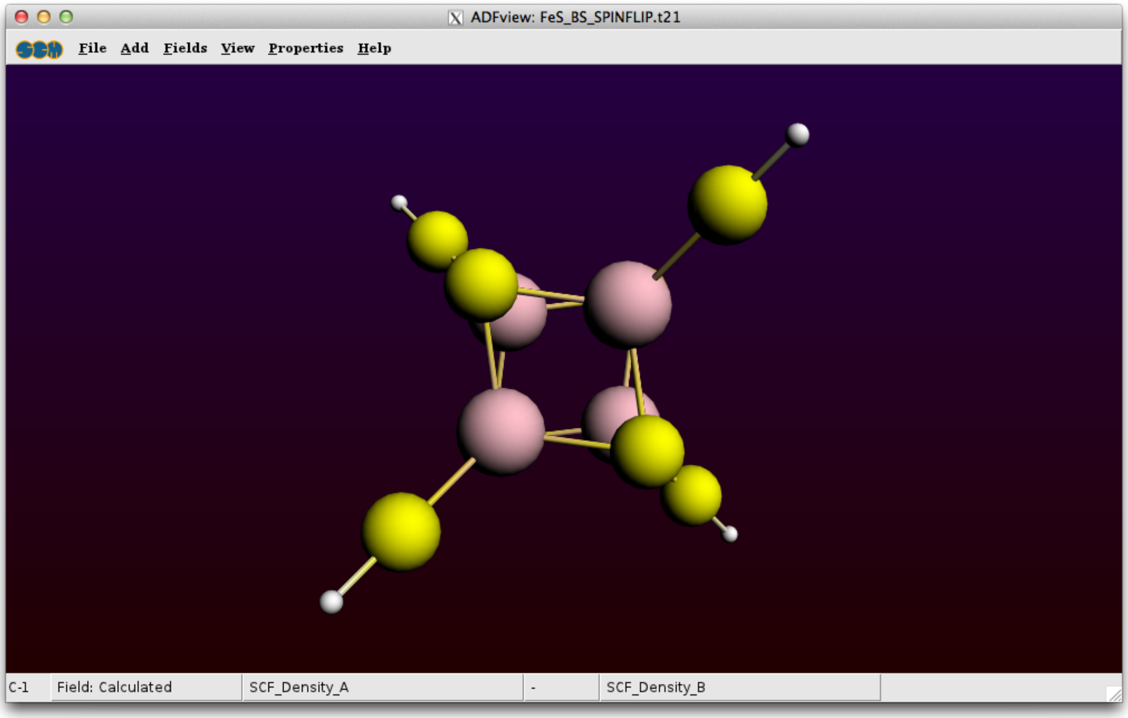
In the two previous steps of this tutorial, we have generated the broken symmetry (BS) solution for the Fe_4S_4 cubane using alternatively the SpinFlip and ModifyStartPotential options. Here, we will analyze this BS solution viewing the Fe spin densities using ADFview, and confirm that the spin alignment of the iron sites is 2↑:2↓ This type of analysis can also be powerfully used during presentations and for scientific illustrations.

Select your FeS_BS_SPINFLIP calculation in ADFjobs
Use the **SCM → View** menu command to activate ADFview

You should see the $[Fe_4S_4(SH)_4]^{2-}$ system in the ADFview window.

The next step is to calculate the spin polarization density:

Fields → Calculated
In the Filed:Calculated line, select the **Density A → SCF** field to the left of the '-'
Next, select the **Density B → SCF** field to the right of the '-'



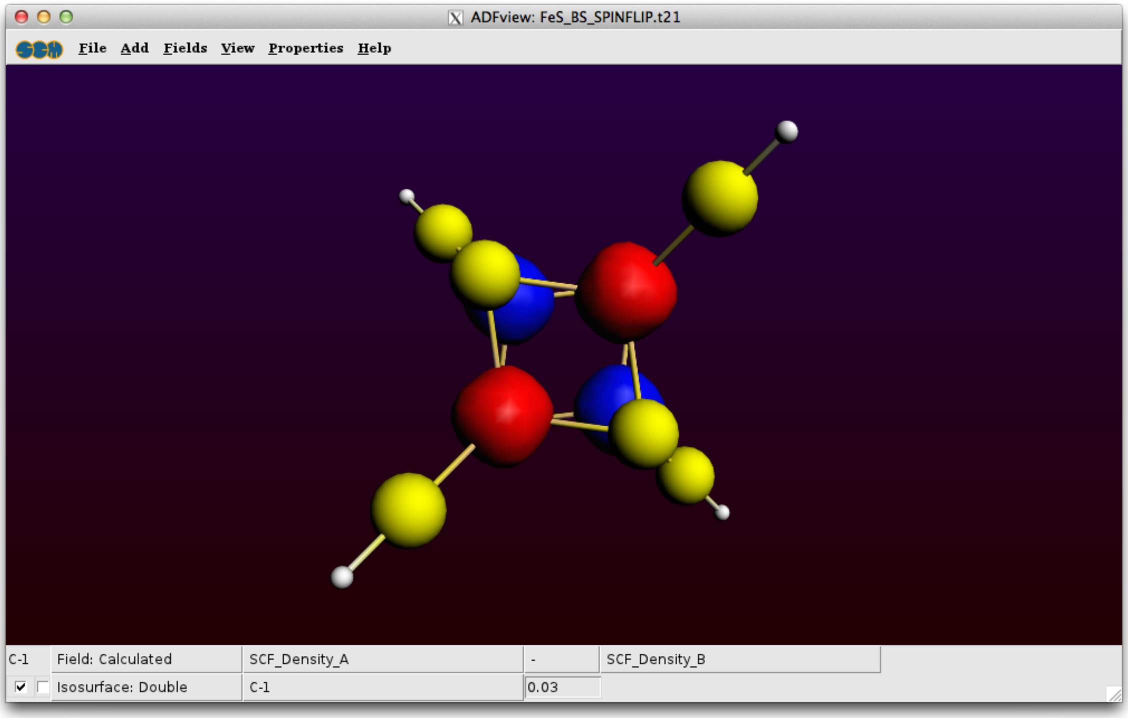
C-1 | Field: Calculated | SCF_Density_A | - | SCF_Density_B

The minus **'-'** sign separating the tabs implies that we have requested ADFview to calculate the 'spin-α - spin-β' density field. ADFview automatically assigns 'C-1' title to this field, see left to the **Field:Calculated**.

We will now visualize this 'C-1' field using one of the available ADFview options:

Add → Isosurface: Double (+/-)
In the new control line, select the **Other → 1 → C-1** field

You should see now the two Fe ions surrounded by blue blobs (spin up,↑) and the other two by red blobs (spin down,↓):



C-1 Field: Calculated SCF_Density_A - SCF_Density_B

☑ ☐ Isosurface: Double C-1 0.03

In the same way you can also check the spin densities for the FeS_HS and FeS_BS_MODIFYSTARTPOTENTIAL results.

BAND-GUI tutorials

This section contains tutorials that show you how to use BAND via the BAND-GUI. As the BAND-GUI is very similar to the ADF-GUI, we will focus here on BAND specific features.

If you are not familiar with the ADF-GUI (or the BAND-GUI), please have a look at the Introduction and ADF-GUI Overview tutorials.

For example, it will show you how to start the BAND-GUI.

The Building Crystals and Slabs tutorial in the overview section is especially important for BAND users.

Tutorial 1: with a grain of salt

According to any freshmen chemistry textbook, in NaCl one electron is transferred from the Sodium to the Chlorine. The occupied 3p states form the valence band, while the empty sodium states hybridize into a conduction band. We will put these idealized ideas to the test.

This tutorial will teach you how to:

- define the geometry of a NaCl crystal
- run the calculation
- view the band structure
- view an orbital for a particular band and k-point
- view the (partial) density of states
- view the deformation density
- view the atomic charges

The BAND-GUI has been designed to be a lot like the ADF-GUI. This makes it much easier for users to use both programs. To avoid repetition, the BAND-GUI tutorial assumes that you are familiar with some basic usage of the ADF-GUI. If you do not know how to rotate, translate, zoom etc within the ADF-GUI, please read through the first ADF-GUI tutorial before starting with this BAND-GUI tutorial. Even better: try using the ADF-GUI yourself. You can get a demo-license for this purpose if needed.

Step 1: Start BANDinput

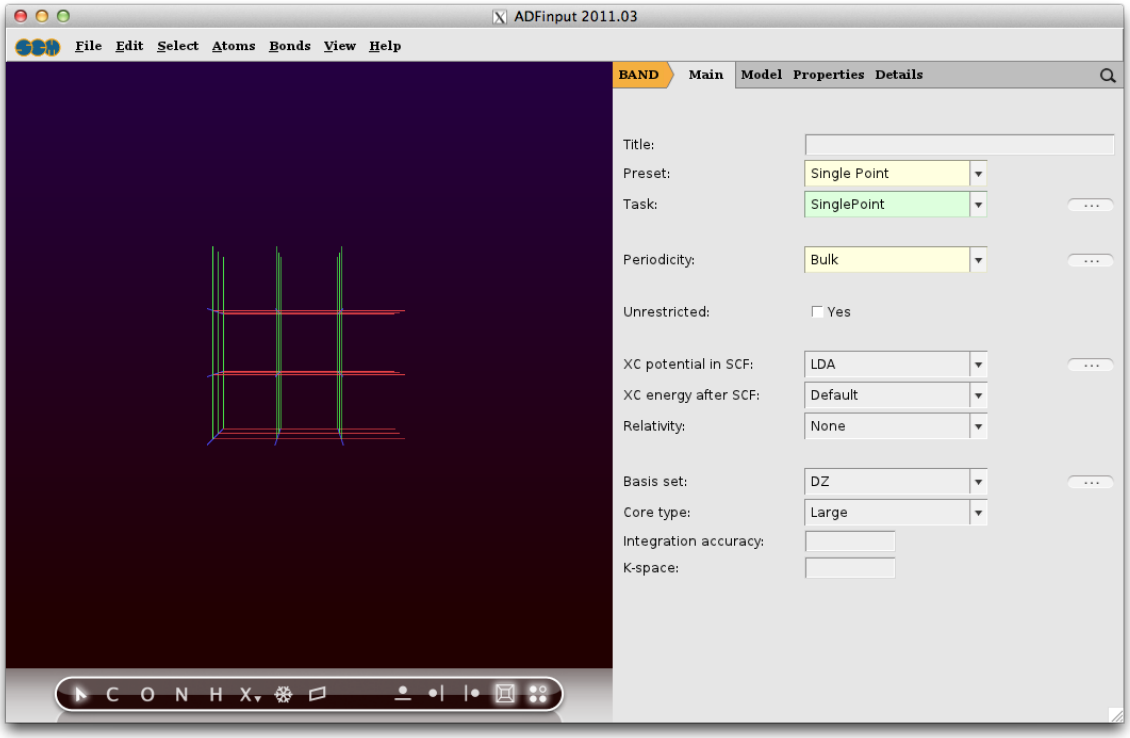
`Start ADFjobs`

We prefer to run the tutorial in a new, clean, directory. That way we will not interfere with other projects. ADFjobs not only manages your jobs, but also has some file management options. In this case we use ADFjobs to make the new directory:

`Select the` **File → New Directory** `command (thus, the New Directory command from the File menu)`
`Rename the new directory by typing 'BandTutorial' and a Return`
`Change into that directory by clicking once on the folder icon in front of it`

Now we can start BANDinput using the SCM menu:

`Use the` **SCM → BANDinput** `menu command`



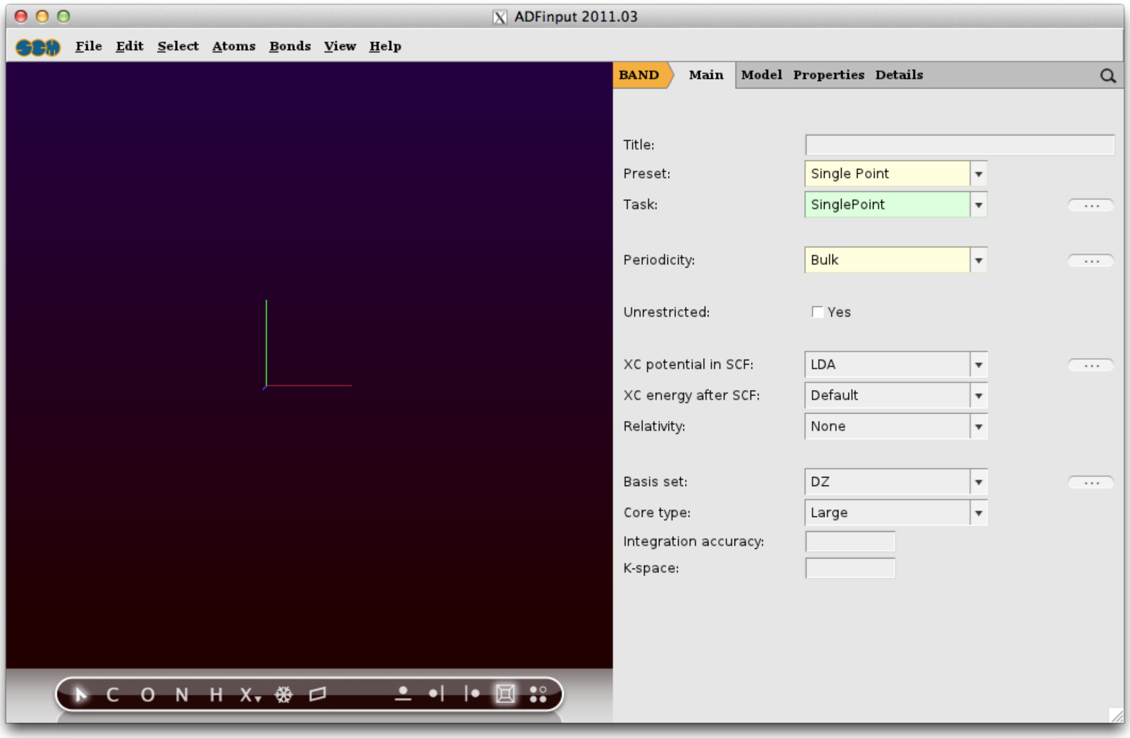
Title:
Preset: Single Point
Task: SinglePoint
Periodicity: Bulk
Unrestricted: ☐ Yes
XC potential in SCF: LDA
XC energy after SCF: Default
Relativity: None
Basis set: DZ
Core type: Large
Integration accuracy:
K-space:

The BANDinput window consists of the following main parts:

- the menu bar with the menu commands (File, Edit, ...)
- the drawing area of the molecule editor (the dark area on the middle left side)
- the status field (lower part of the dark area, blank when the BANDinput is empty as shown above)
- the molecule editor tools
- many panels with several kinds of options (currently the 'BAND Main' panel is visible)
- panel bar with menu commands to activate the panel of choice
- a search tool (at the right of the panel bar)

In the drawing area you see the lattice vectors, with three repetitions of the unit cell along each vector. The first lattice vector is red, the second green, and the third blue. Using the View Periodic menu you can change the display of the periodic images:

View → Periodic → Repeat Unit Cells



Title:
Preset: Single Point
Task: SinglePoint
Periodicity: Bulk
Unrestricted: ☐ Yes
XC potential in SCF: LDA
XC energy after SCF: Default
Relativity: None
Basis set: DZ
Core type: Large
Integration accuracy:
K-space:

If you look in the toolbar with molecular editor tools, you see that the rightmost button is no longer glowing. You can also use this button to toggle the display of the periodic images:

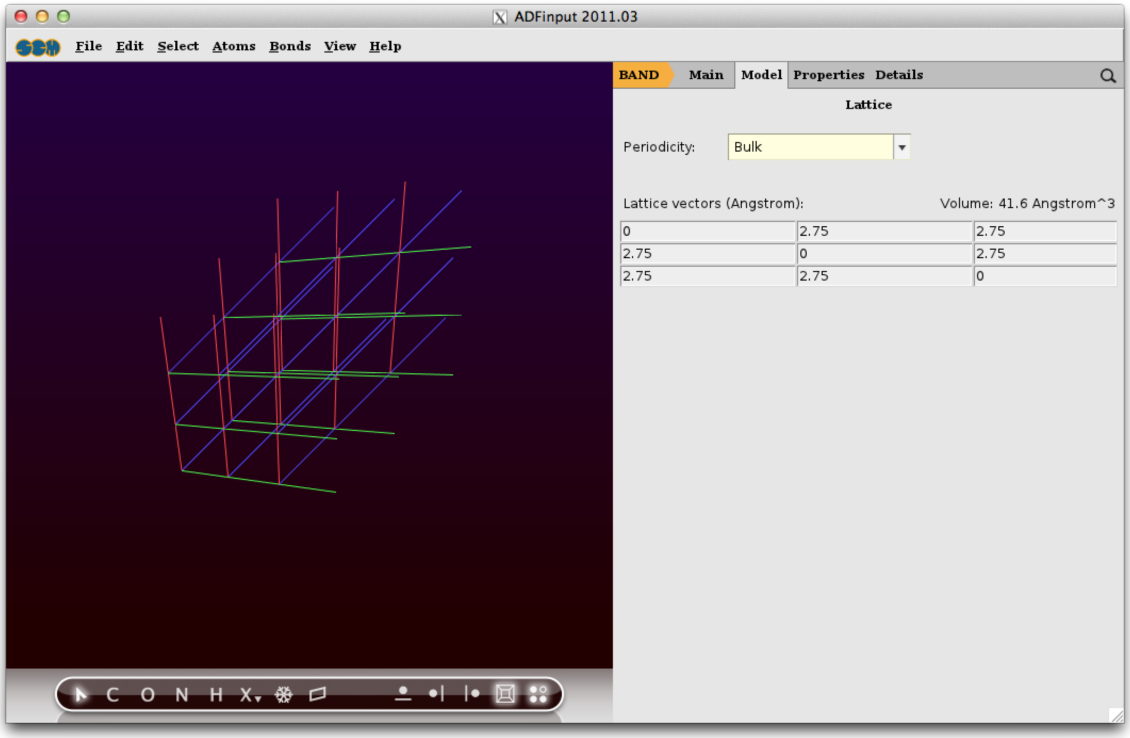
`Click once on the rightmost button in the toolbar (the four dots)`

Now you should see the periodic repetitions again.

Step 2: Set up the unit cell

Salt has an fcc lattice. First we need to set the lattice vectors:

`Panel bar` **Model → Lattice**
`Enter the lattice vectors, as shown below`



Lattice

Periodicity: Bulk

Lattice vectors (Angstrom): Volume: 41.6 Angstrom^3

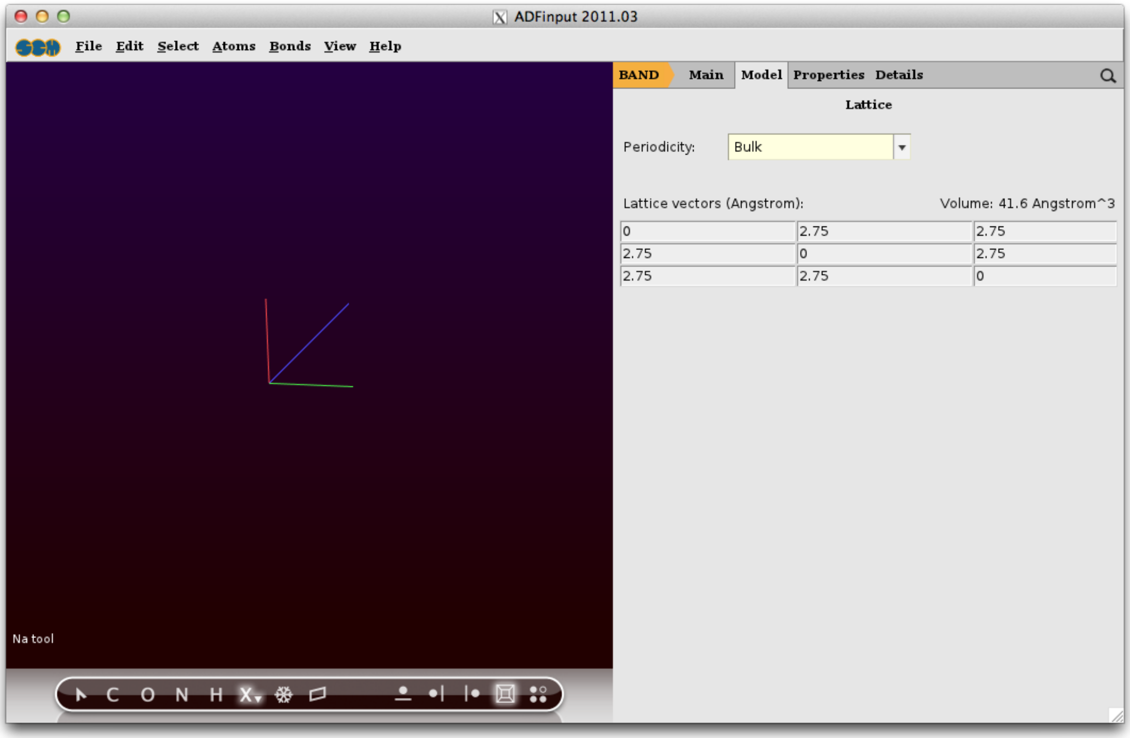
0	2.75	2.75
2.75	0	2.75
2.75	2.75	0

Step 3: Add the atoms

Now we will add the Na and Cl atoms. It is convenient to turn of the periodic display while doing this:

`Uncheck` **View → Periodic → Repeat Unit Cells**
`Click on the X tool, and select Na`

After this you see at the bottom of the screen "Na tool" in the status field:



Lattice

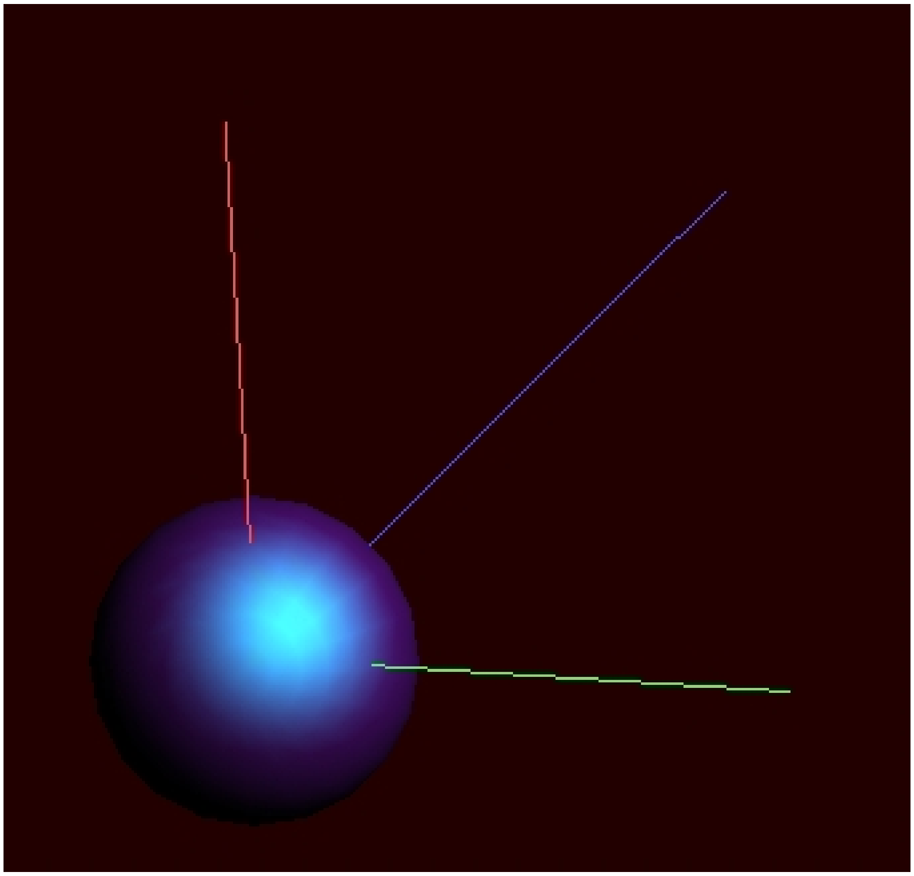
Periodicity: Bulk

Lattice vectors (Angstrom): Volume: 41.6 Angstrom^3

0	2.75	2.75
2.75	0	2.75
2.75	2.75	0

Na tool

```
Click once in the drawing area, near the origin
Click once on the created atom to stop bonding
```

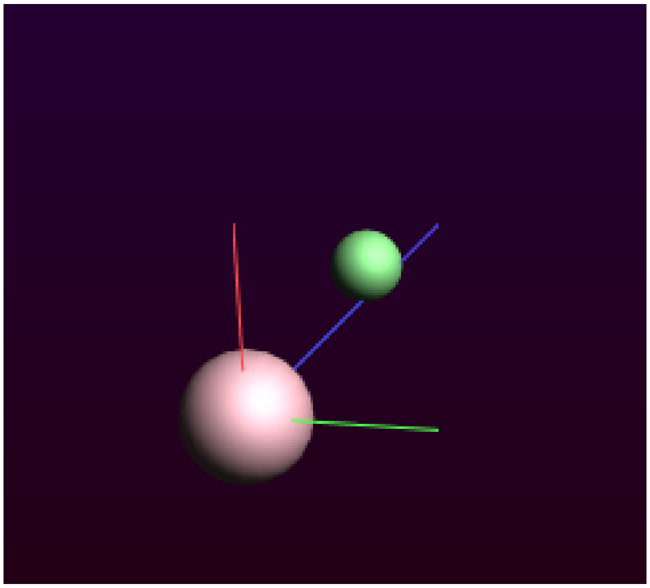


As you can see the atom is not exactly in the origin. This can be fixed if you wish:

Edit → Set Origin

To add the Cl atom you can proceed the same way:

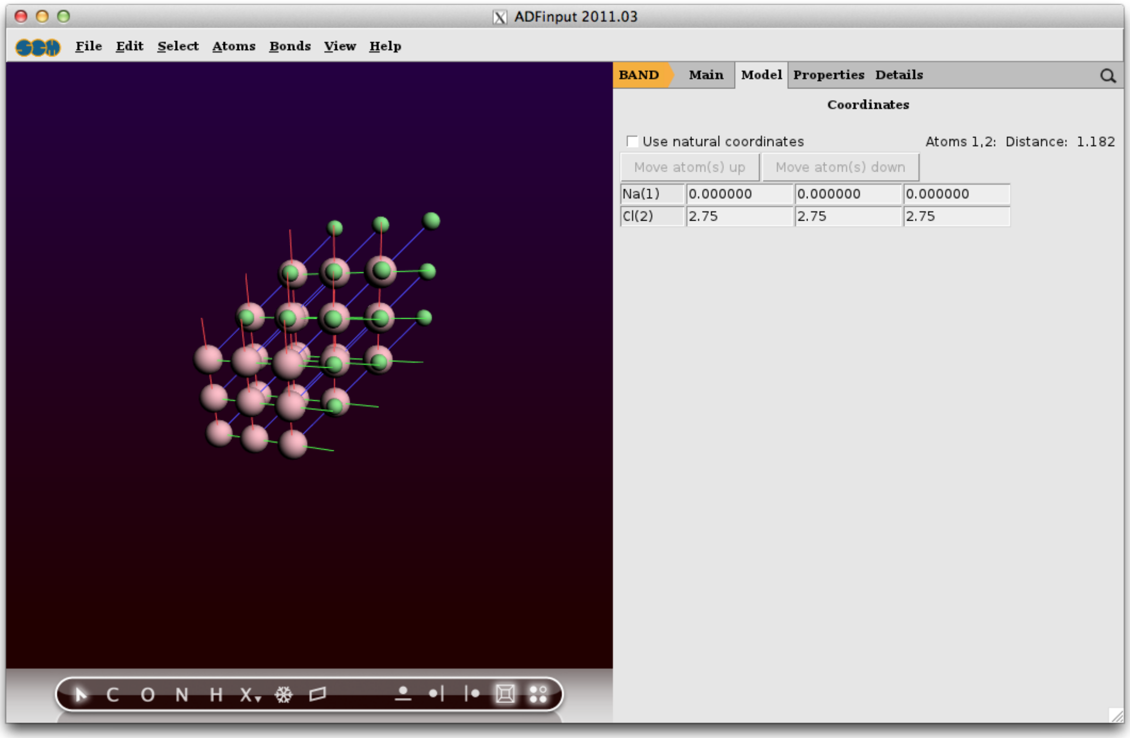
```
Select the Cl tool (via the X button again)
Click once somewhere in the unit cell
Click on the new Cl atom to stop bonding
```



Next you should edit the Cl coordinates and change the Cl color:

Select the coordinates panel: panel bar **Model → Coordinates**
Change the Cl coordinates to be (2.75,2.75,2.75)
Check **View → Periodic → Repeat Unit Cells**

Now your system looks like:



Coordinates

☐ Use natural coordinates

Atoms 1,2: Distance: 1.182

Na(1)	0.000000	0.000000	0.000000
Cl(2)	2.75	2.75	2.75

Step 4: Running the calculation

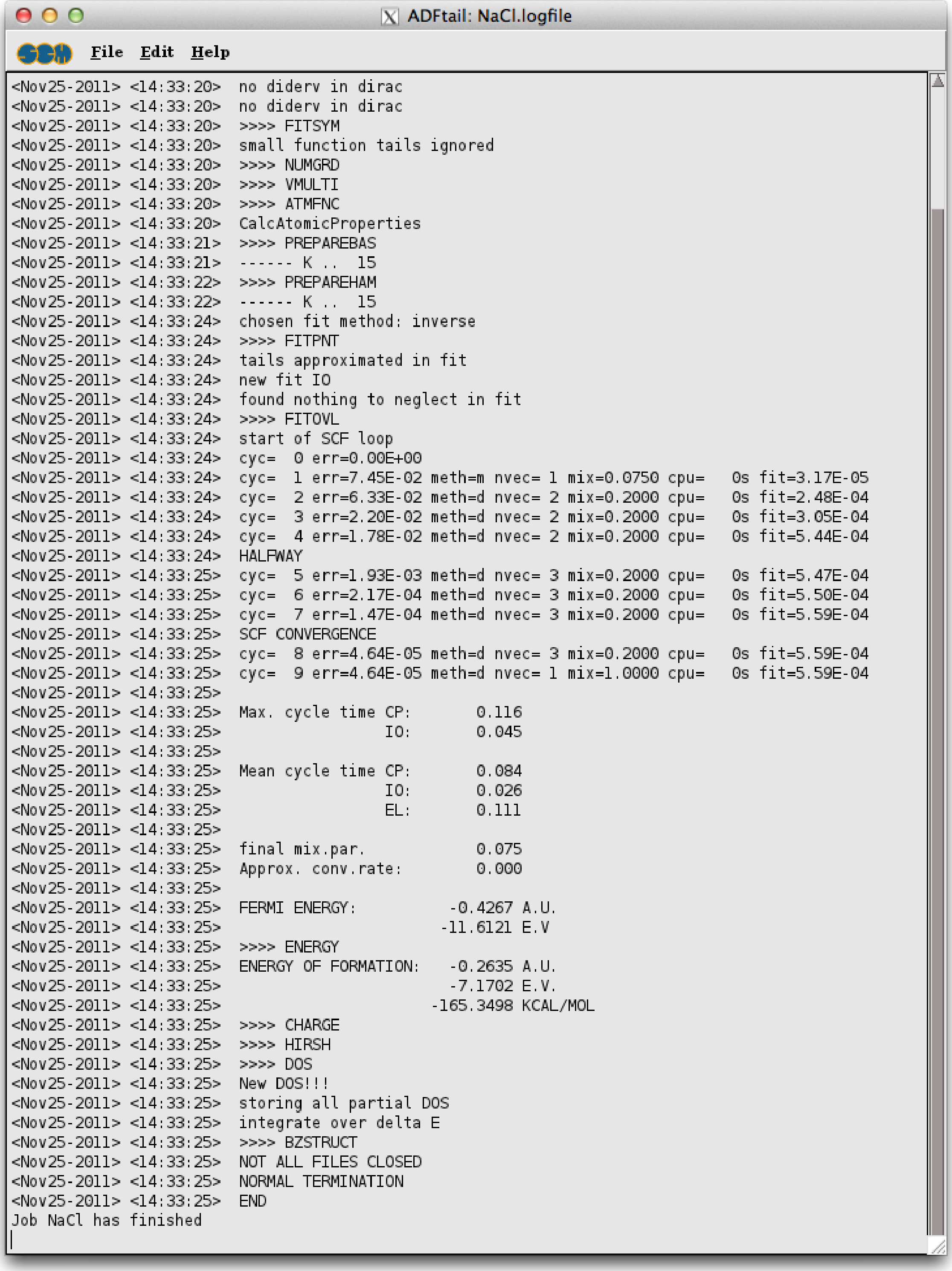
If you wish so, you can give your calculation a title:

`Panel bar` **Main**
`Enter NaCl in the "Title" field`

File → Save`, name it "NaCl" and press Save.`

File → Run

A window will appear showing the progress of the BAND calculation (the 'logfile'). After a few minutes the calculation has finished, and it looks like:



```
<Nov25-2011> <14:33:20>  no diderv in dirac
<Nov25-2011> <14:33:20>  no diderv in dirac
<Nov25-2011> <14:33:20>  >>>> FITSYM
<Nov25-2011> <14:33:20>  small function tails ignored
<Nov25-2011> <14:33:20>  >>>> NUMGRD
<Nov25-2011> <14:33:20>  >>>> VMULTI
<Nov25-2011> <14:33:20>  >>>> ATMFNC
<Nov25-2011> <14:33:20>  CalcAtomicProperties
<Nov25-2011> <14:33:21>  >>>> PREPAREBAS
<Nov25-2011> <14:33:21>  ------ K ..  15
<Nov25-2011> <14:33:22>  >>>> PREPAREHAM
<Nov25-2011> <14:33:22>  ------ K ..  15
<Nov25-2011> <14:33:24>  chosen fit method: inverse
<Nov25-2011> <14:33:24>  >>>> FITPNT
<Nov25-2011> <14:33:24>  tails approximated in fit
<Nov25-2011> <14:33:24>  new fit IO
<Nov25-2011> <14:33:24>  found nothing to neglect in fit
<Nov25-2011> <14:33:24>  >>>> FITOVL
<Nov25-2011> <14:33:24>  start of SCF loop
<Nov25-2011> <14:33:24>  cyc=  0 err=0.00E+00
<Nov25-2011> <14:33:24>  cyc=  1 err=7.45E-02 meth=m nvec= 1 mix=0.0750 cpu=   0s fit=3.17E-05
<Nov25-2011> <14:33:24>  cyc=  2 err=6.33E-02 meth=d nvec= 2 mix=0.2000 cpu=   0s fit=2.48E-04
<Nov25-2011> <14:33:24>  cyc=  3 err=2.20E-02 meth=d nvec= 2 mix=0.2000 cpu=   0s fit=3.05E-04
<Nov25-2011> <14:33:24>  cyc=  4 err=1.78E-02 meth=d nvec= 2 mix=0.2000 cpu=   0s fit=5.44E-04
<Nov25-2011> <14:33:24>  HALFWAY
<Nov25-2011> <14:33:25>  cyc=  5 err=1.93E-03 meth=d nvec= 3 mix=0.2000 cpu=   0s fit=5.47E-04
<Nov25-2011> <14:33:25>  cyc=  6 err=2.17E-04 meth=d nvec= 3 mix=0.2000 cpu=   0s fit=5.50E-04
<Nov25-2011> <14:33:25>  cyc=  7 err=1.47E-04 meth=d nvec= 3 mix=0.2000 cpu=   0s fit=5.59E-04
<Nov25-2011> <14:33:25>  SCF CONVERGENCE
<Nov25-2011> <14:33:25>  cyc=  8 err=4.64E-05 meth=d nvec= 3 mix=0.2000 cpu=   0s fit=5.59E-04
<Nov25-2011> <14:33:25>  cyc=  9 err=4.64E-05 meth=d nvec= 1 mix=1.0000 cpu=   0s fit=5.59E-04
<Nov25-2011> <14:33:25>
<Nov25-2011> <14:33:25>  Max. cycle time CP:       0.116
<Nov25-2011> <14:33:25>                  IO:       0.045
<Nov25-2011> <14:33:25>
<Nov25-2011> <14:33:25>  Mean cycle time CP:       0.084
<Nov25-2011> <14:33:25>                  IO:       0.026
<Nov25-2011> <14:33:25>                  EL:       0.111
<Nov25-2011> <14:33:25>
<Nov25-2011> <14:33:25>  final mix.par.            0.075
<Nov25-2011> <14:33:25>  Approx. conv.rate:        0.000
<Nov25-2011> <14:33:25>
<Nov25-2011> <14:33:25>  FERMI ENERGY:          -0.4267 A.U.
<Nov25-2011> <14:33:25>                        -11.6121 E.V
<Nov25-2011> <14:33:25>  >>>> ENERGY
<Nov25-2011> <14:33:25>  ENERGY OF FORMATION:   -0.2635 A.U.
<Nov25-2011> <14:33:25>                         -7.1702 E.V.
<Nov25-2011> <14:33:25>                       -165.3498 KCAL/MOL
<Nov25-2011> <14:33:25>  >>>> CHARGE
<Nov25-2011> <14:33:25>  >>>> HIRSH
<Nov25-2011> <14:33:25>  >>>> DOS
<Nov25-2011> <14:33:25>  New DOS!!!
<Nov25-2011> <14:33:25>  storing all partial DOS
<Nov25-2011> <14:33:25>  integrate over delta E
<Nov25-2011> <14:33:25>  >>>> BZSTRUCT
<Nov25-2011> <14:33:25>  NOT ALL FILES CLOSED
<Nov25-2011> <14:33:25>  NORMAL TERMINATION
<Nov25-2011> <14:33:25>  END
Job NaCl has finished
```

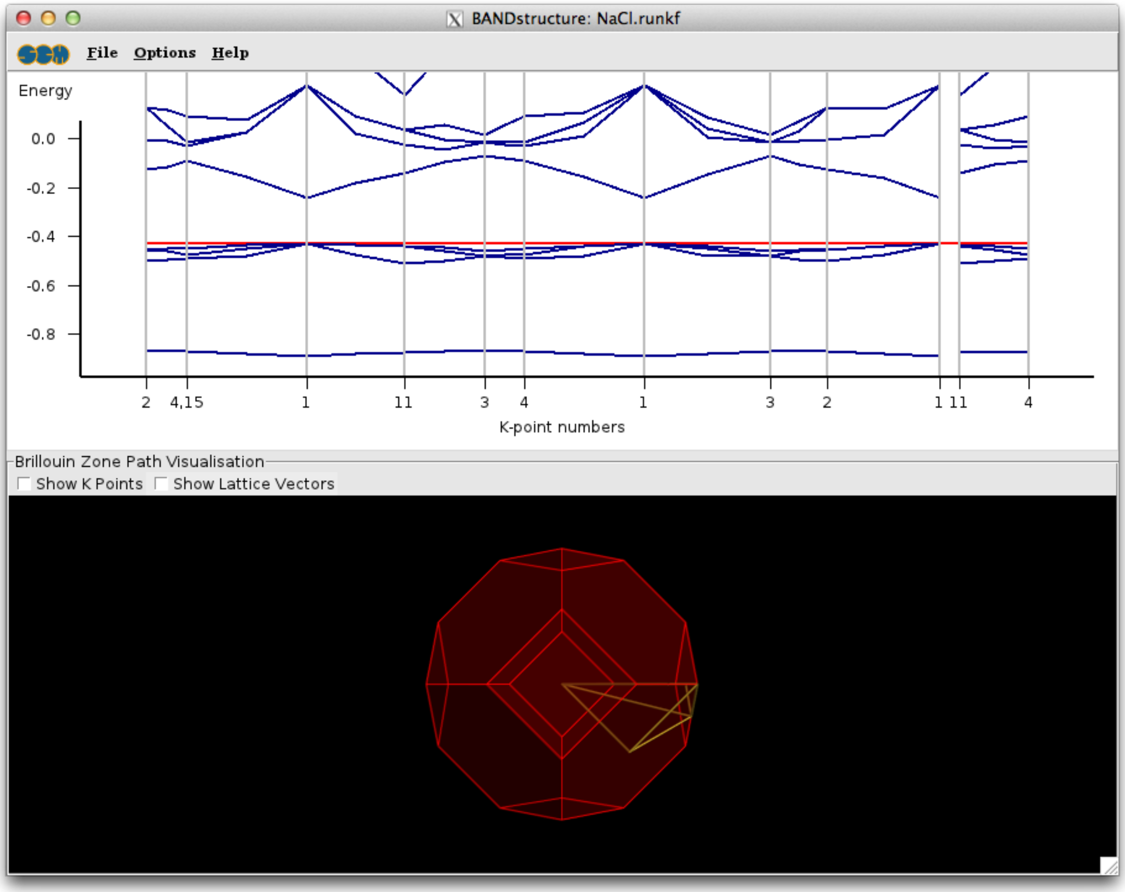
`Wait for the text 'Job NaCl has finished' in the logfile`

The calculation has produced two important result files: "NaCl.out", which contains the result of the calculation in text format, the second is"NaCl.runkf" which is a binary result file.

Step 5: Examine the band structure

SCM → BAND Structure

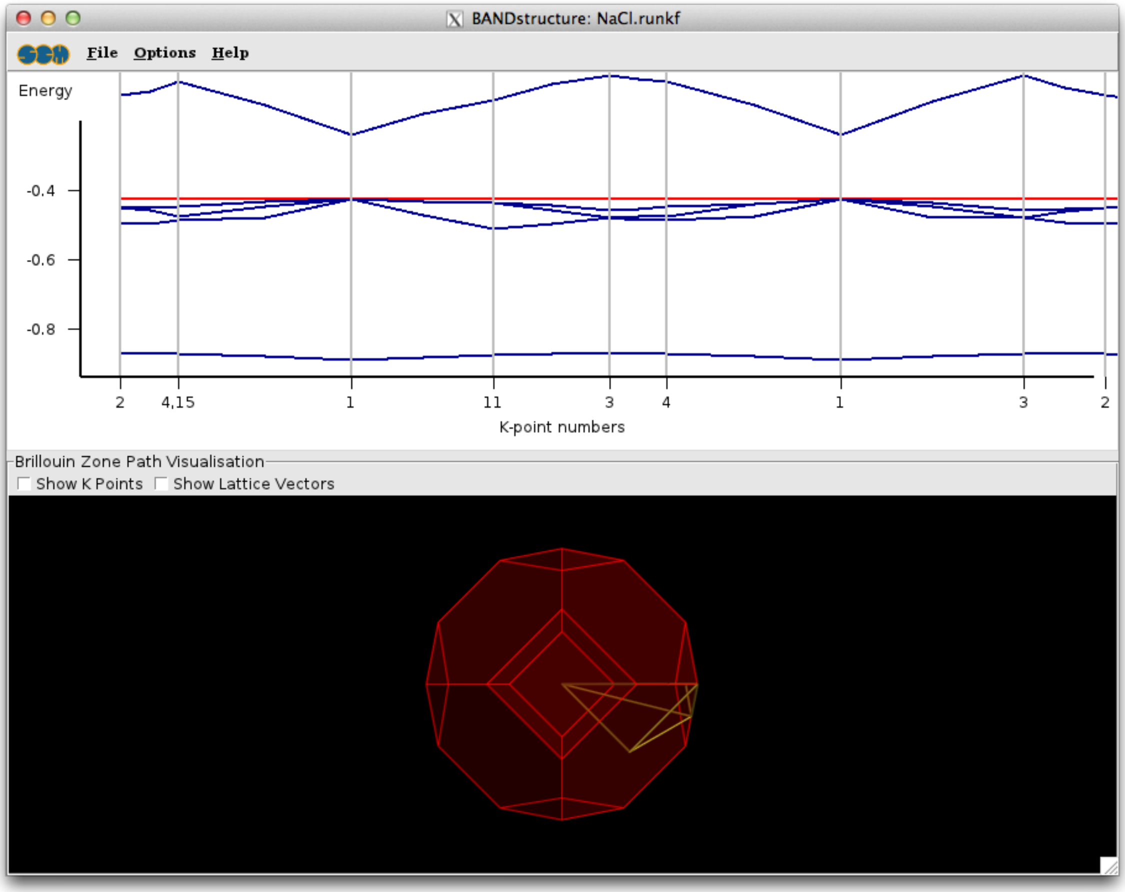
This will open the bandstructure window:



It consists of a plot and a picture of the Brillouin zone. In the plot the red line is the Fermi level. Below the Fermi level are four occupied bands. You can see this more clearly by vertical zooming:

`Click on the right mouse button, and drag the pointer up to zoom vertically`
`When the region of interest gets out of view, drag it into view (with the left mouse button)`

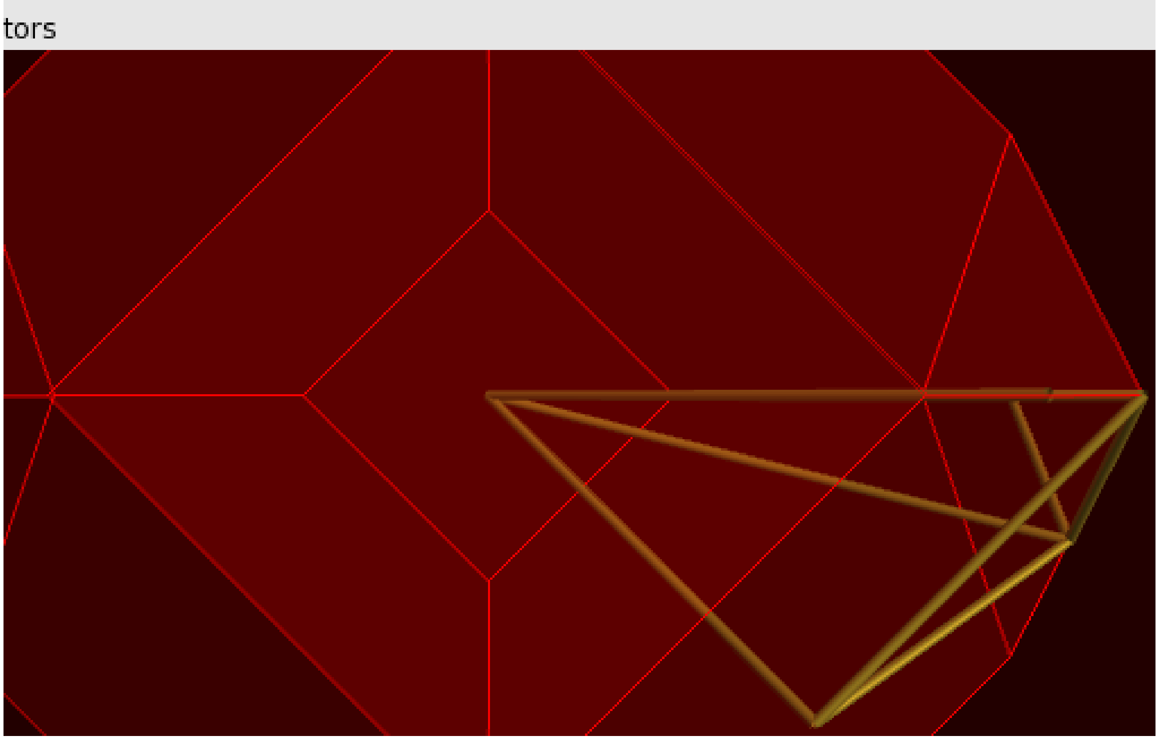
The bottom part of the plot will look like:



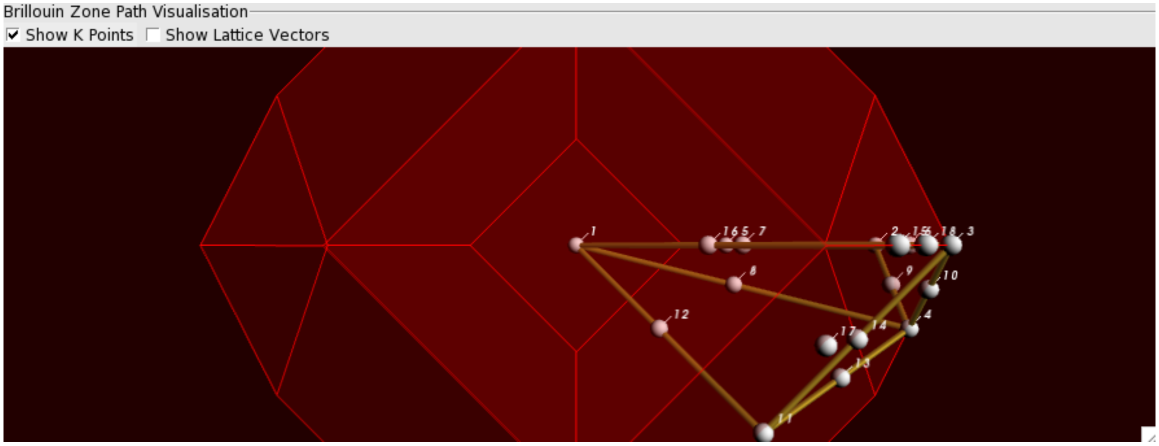
In most k-points you see now four bands below the Fermi level. In some k-points you see fewer because they are degenerate.

Now you may wonder about the path taken through the Brillouin zone. This is where the bottom part comes in handy. You can zoom and rotate, just as with molecules in BANDinput.

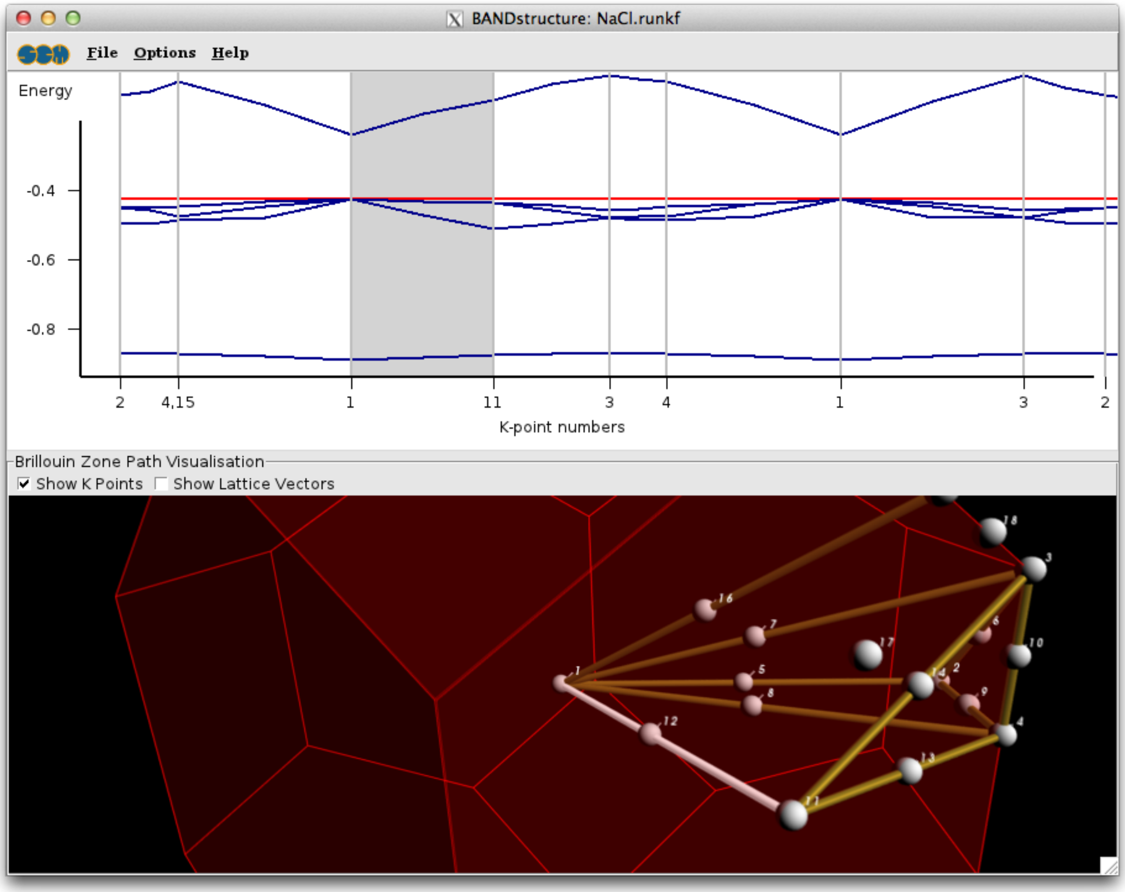
```
Zoom in a bit, by holding the right mouse button and moving upwards
```



Toggle the button to display the k-points



Now click on the line from 11 (via 12) to 1



Note how the line lights up, and also how the corresponding segment is indicated in the plot by a gray background. You can also click on the plot to select line segments.

Rotate the Brillouin zone a bit to convince yourself that the line (from k-point 11 to 1) runs from the center to the center of a hexagonal face.

Step 6: Visualizing the results

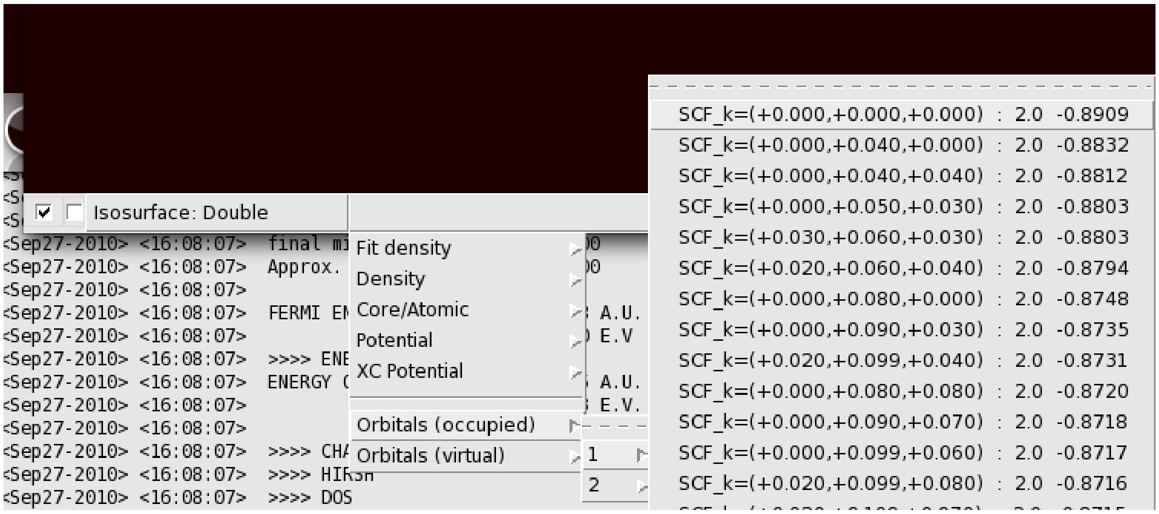
Plotting the orbitals

Now what is the character of the bands? Let us first examine this narrow band at about -0.5 Hartree.

SCM → View
`In ADFview:` **Add → Isosurface Double (+/-)**

In the bar at the bottom of the window, you can select which field to show.

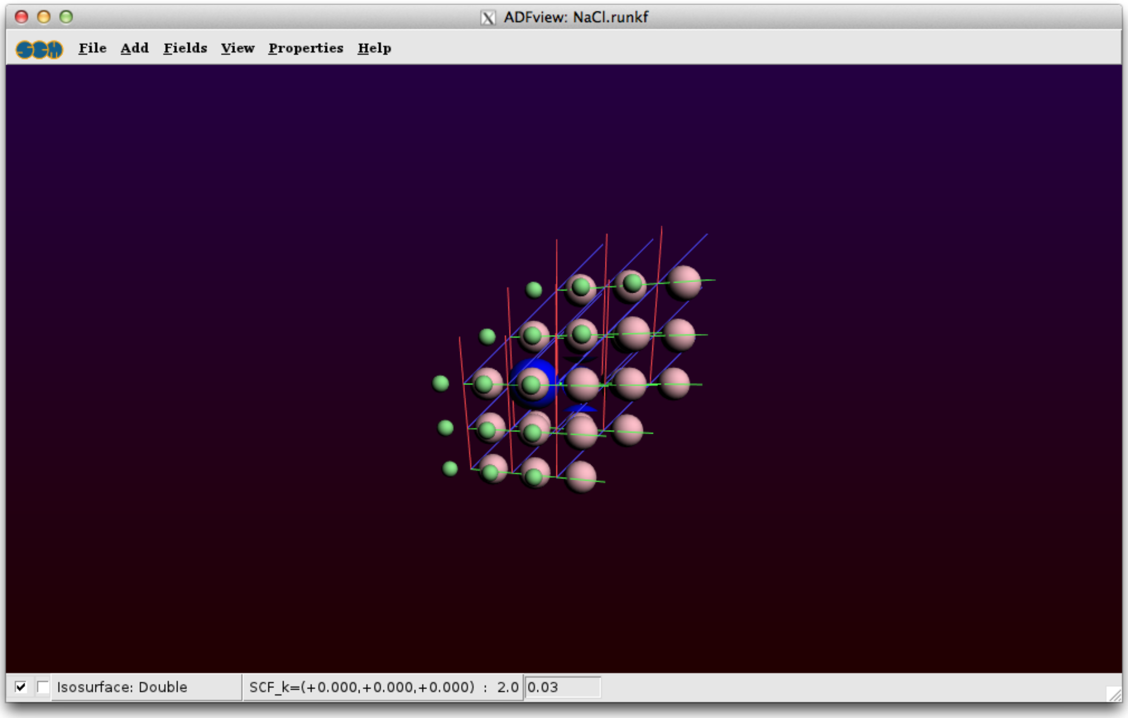
```
Select the lowest band (k=0,0,0)
```



```
<Sep27-2010> <16:08:07>  final mi
<Sep27-2010> <16:08:07>  Approx.
<Sep27-2010> <16:08:07>
<Sep27-2010> <16:08:07>  FERMI EN
<Sep27-2010> <16:08:07>
<Sep27-2010> <16:08:07>  >>>> ENE
<Sep27-2010> <16:08:07>  ENERGY (
<Sep27-2010> <16:08:07>
<Sep27-2010> <16:08:07>
<Sep27-2010> <16:08:07>  >>>> CHA
<Sep27-2010> <16:08:07>  >>>> HIRSH
<Sep27-2010> <16:08:07>  >>>> DOS
```

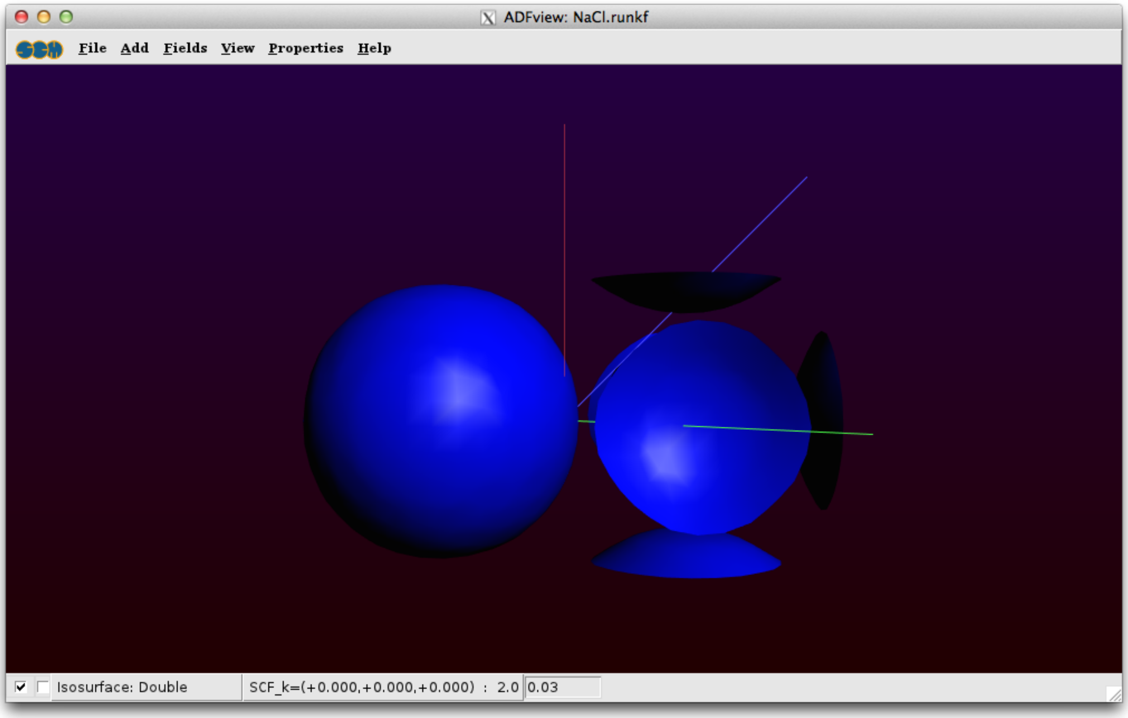
From the label you can see that it has an energy of -0.8909 and the coordinates are (0,0,0).

A progress bar will appear, and after a while you will see the orbital:



If you rotate it a bit and toggle the isosurface on and off (with the check box in front of it), you can convince yourself that this orbital is located around the small atom, which is the Chlorine.

Toggle the periodic view (the menu **View → Periodic → Repeat Unit Cells**)

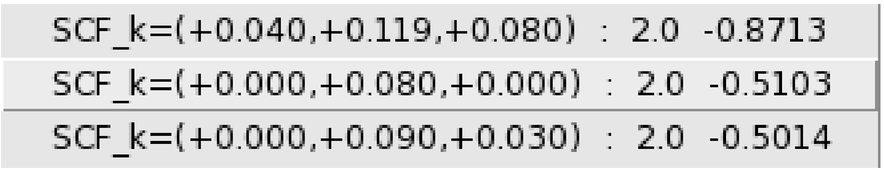


☑ ☐ Isosurface: Double | SCF_k=(+0.000,+0.000,+0.000) : 2.0 | 0.03

Obviously this is the 3s band of Cl. The strange truncated spheres are due to contributions of neighboring cells.

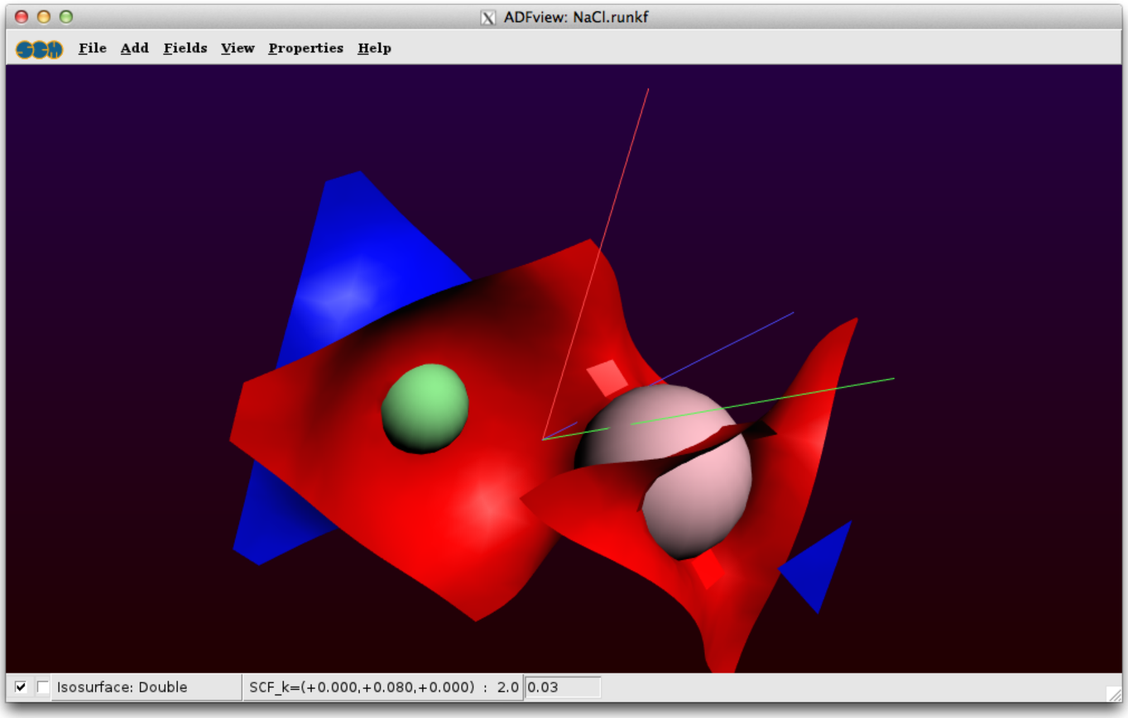
Let us now take a look at the orbital with the lowest energy of the second band (the first one with an energy **not** around -0.88):

```
Select the lowest orbital of the second band (with energy about -0.05)
```



```
SCF_k=(+0.040,+0.119,+0.080) : 2.0 -0.8713
SCF_k=(+0.000,+0.080,+0.000) : 2.0 -0.5103
SCF_k=(+0.000,+0.090,+0.030) : 2.0 -0.5014
```

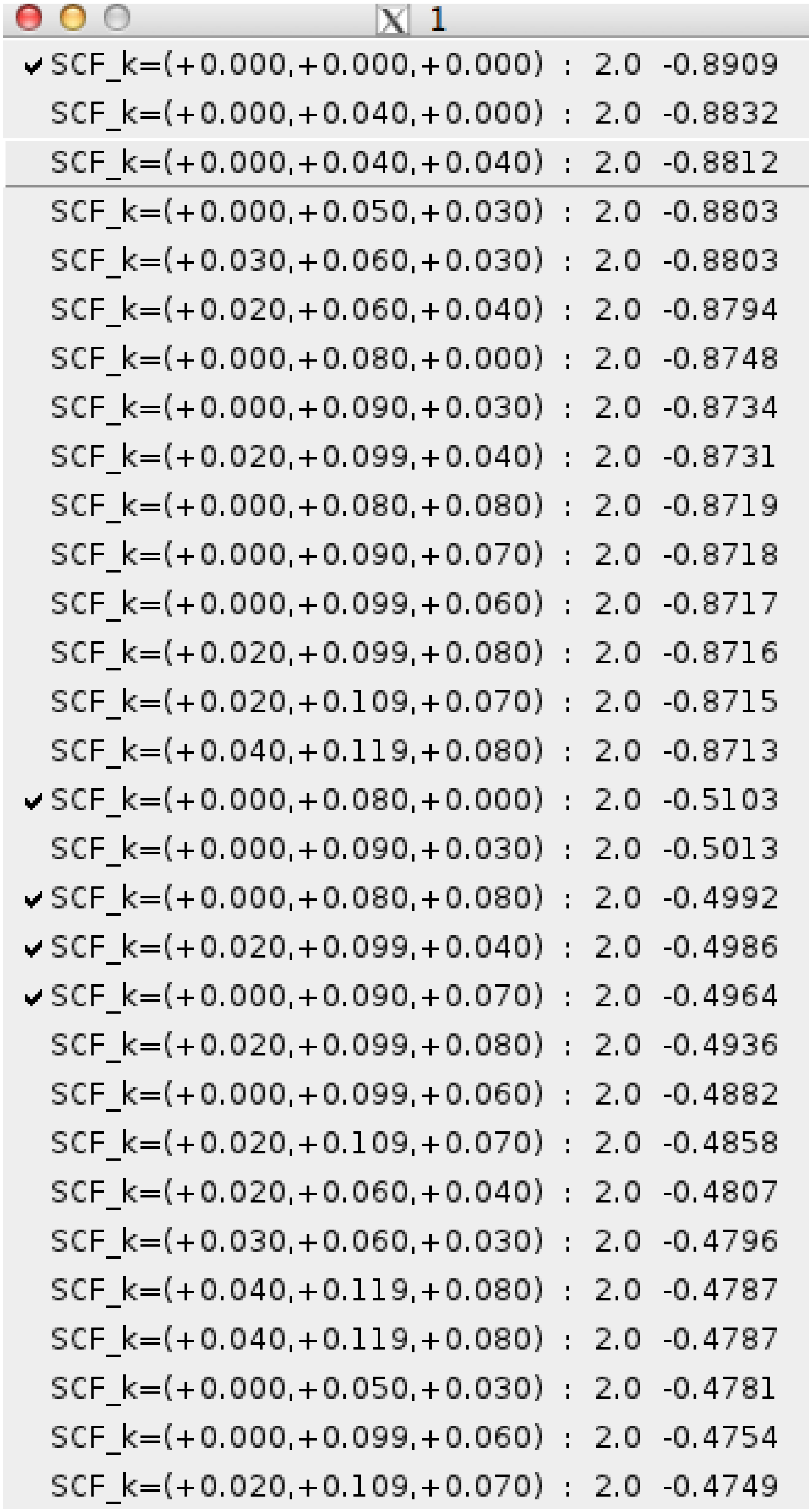
This orbital looks like:



☑ ☐ Isosurface: Double SCF_k=(+0.000,+0.080,+0.000) : 2.0 0.03

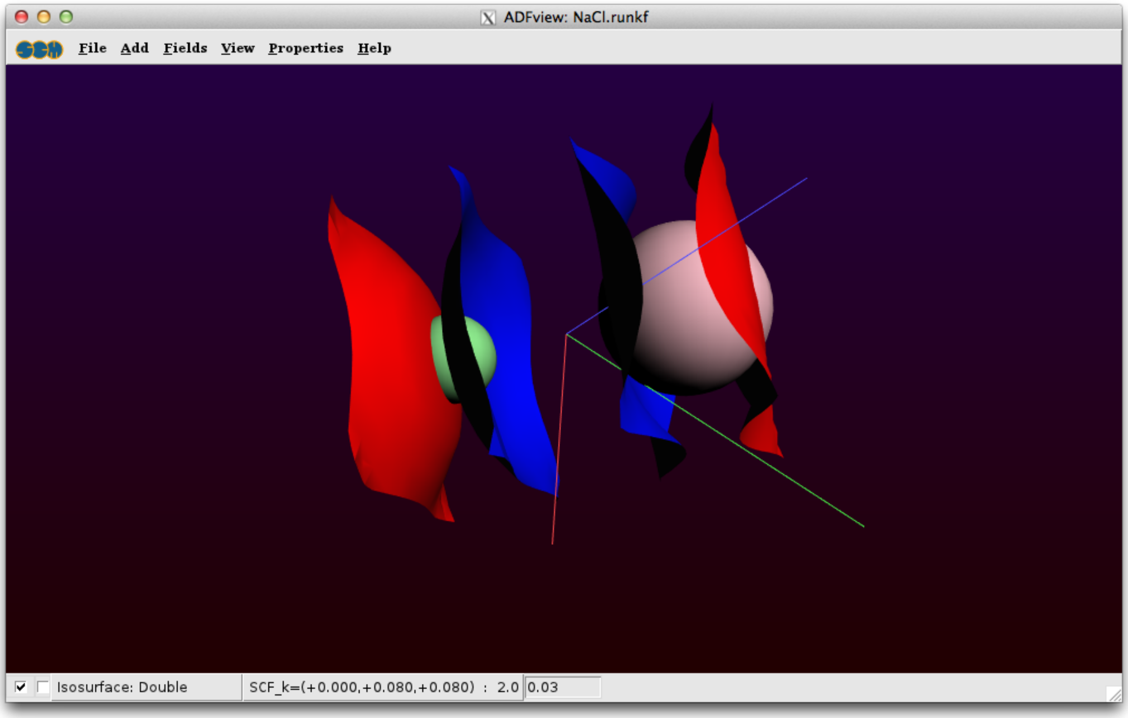
and it clearly consists of a p orbital on the Cl. The part near the Na comes from Chlorine atoms in neighboring cells.

It is generally easier to interpret orbitals at k=(0,0,0). Going up in energy we encounter a degenerate triple at e=-0.49. Note you can tear of the menus to make orbital selection easier:



```
✓ SCF_k=(+0.000,+0.000,+0.000) : 2.0 -0.8909
  SCF_k=(+0.000,+0.040,+0.000) : 2.0 -0.8832
  SCF_k=(+0.000,+0.040,+0.040) : 2.0 -0.8812
  SCF_k=(+0.000,+0.050,+0.030) : 2.0 -0.8803
  SCF_k=(+0.030,+0.060,+0.030) : 2.0 -0.8803
  SCF_k=(+0.020,+0.060,+0.040) : 2.0 -0.8794
  SCF_k=(+0.000,+0.080,+0.000) : 2.0 -0.8748
  SCF_k=(+0.000,+0.090,+0.030) : 2.0 -0.8734
  SCF_k=(+0.020,+0.099,+0.040) : 2.0 -0.8731
  SCF_k=(+0.000,+0.080,+0.080) : 2.0 -0.8719
  SCF_k=(+0.000,+0.090,+0.070) : 2.0 -0.8718
  SCF_k=(+0.000,+0.099,+0.060) : 2.0 -0.8717
  SCF_k=(+0.020,+0.099,+0.080) : 2.0 -0.8716
  SCF_k=(+0.020,+0.109,+0.070) : 2.0 -0.8715
  SCF_k=(+0.040,+0.119,+0.080) : 2.0 -0.8713
✓ SCF_k=(+0.000,+0.080,+0.000) : 2.0 -0.5103
  SCF_k=(+0.000,+0.090,+0.030) : 2.0 -0.5013
✓ SCF_k=(+0.000,+0.080,+0.080) : 2.0 -0.4992
✓ SCF_k=(+0.020,+0.099,+0.040) : 2.0 -0.4986
✓ SCF_k=(+0.000,+0.090,+0.070) : 2.0 -0.4964
  SCF_k=(+0.020,+0.099,+0.080) : 2.0 -0.4936
  SCF_k=(+0.000,+0.099,+0.060) : 2.0 -0.4882
  SCF_k=(+0.020,+0.109,+0.070) : 2.0 -0.4858
  SCF_k=(+0.020,+0.060,+0.040) : 2.0 -0.4807
  SCF_k=(+0.030,+0.060,+0.030) : 2.0 -0.4796
  SCF_k=(+0.040,+0.119,+0.080) : 2.0 -0.4787
  SCF_k=(+0.040,+0.119,+0.080) : 2.0 -0.4787
  SCF_k=(+0.000,+0.050,+0.030) : 2.0 -0.4781
  SCF_k=(+0.000,+0.099,+0.060) : 2.0 -0.4754
  SCF_k=(+0.020,+0.109,+0.070) : 2.0 -0.4749
```

Tear off the 'Occupied orbital menu, group 1
Select the first orbital around e=-0.49



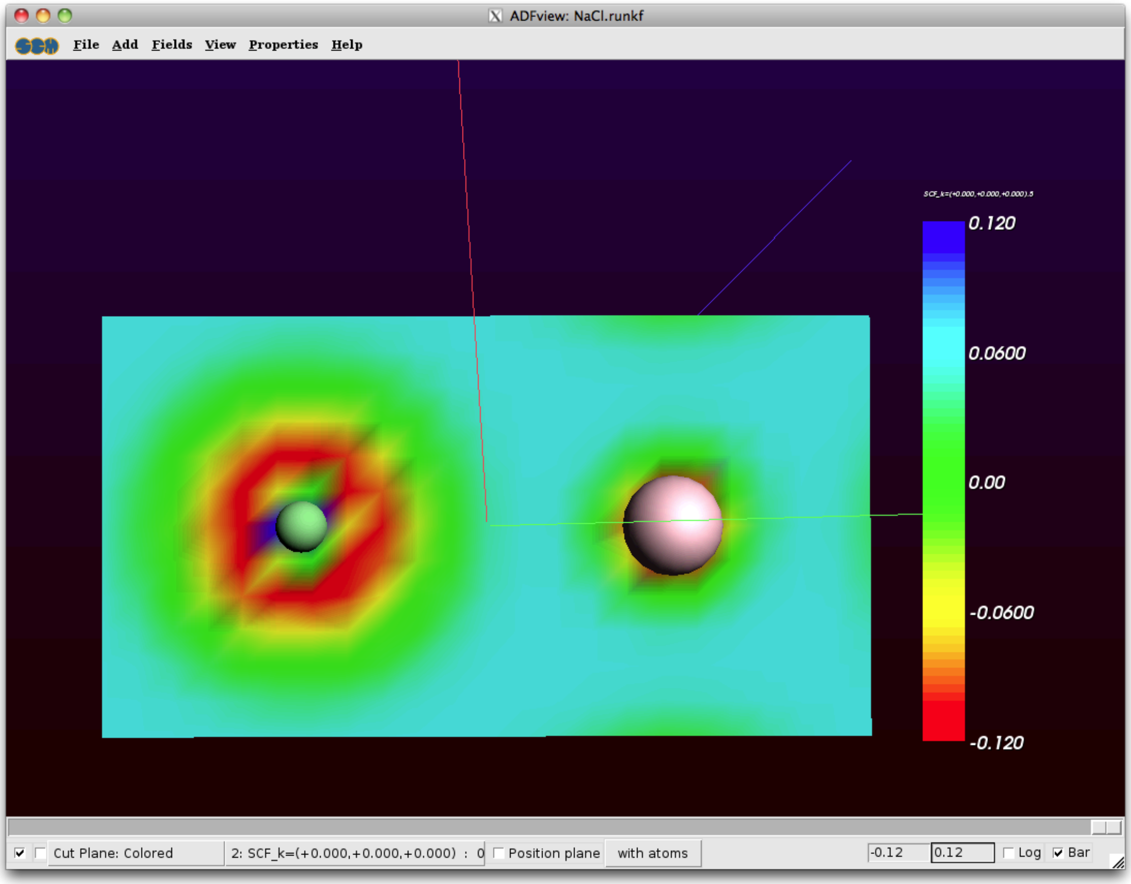
☑ ☐ Isosurface: Double SCF_k=(+0.000,+0.080,+0.080) : 2.0 0.03

Take a look at all three of them.

From these orbital pictures we can conclude that the valence band is indeed mainly of Chlorine-p character.

You may want to check the lowest orbitals of the (unoccupied) conduction band.

Check the lowest orbitals of the conduction band
Do you see a strong Na character in them?
Actually it looks a lot like an *s* function on the Cl atom. However in this case the iso-surface is misleading. With a contour plot you can make it look like this



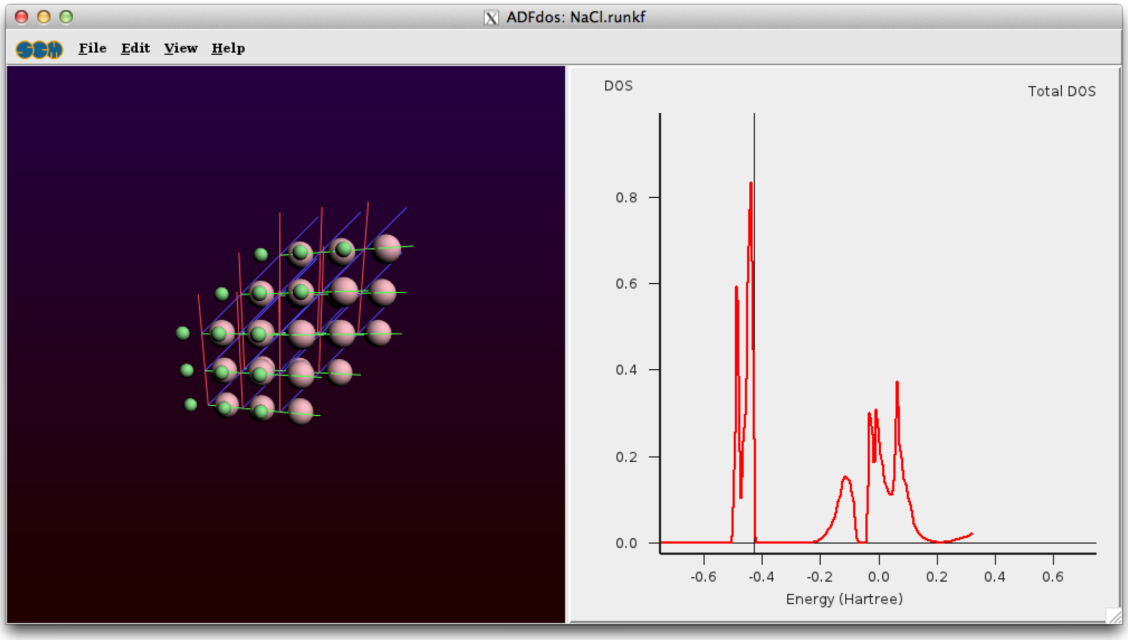
so the orbital has a bit of a muffin-tin shape, the maximum is between the atoms. For such states an iso surface looks misleading. The maximum is closer to the Na atom, so it is really a Na state.

Plotting the partial density-of-states

There is in fact a much more easy way to conclude that the valence band is mainly of Chlorine-p character.

`Open the DOS module:` **SCM → Dos**

and a window like this will appear:

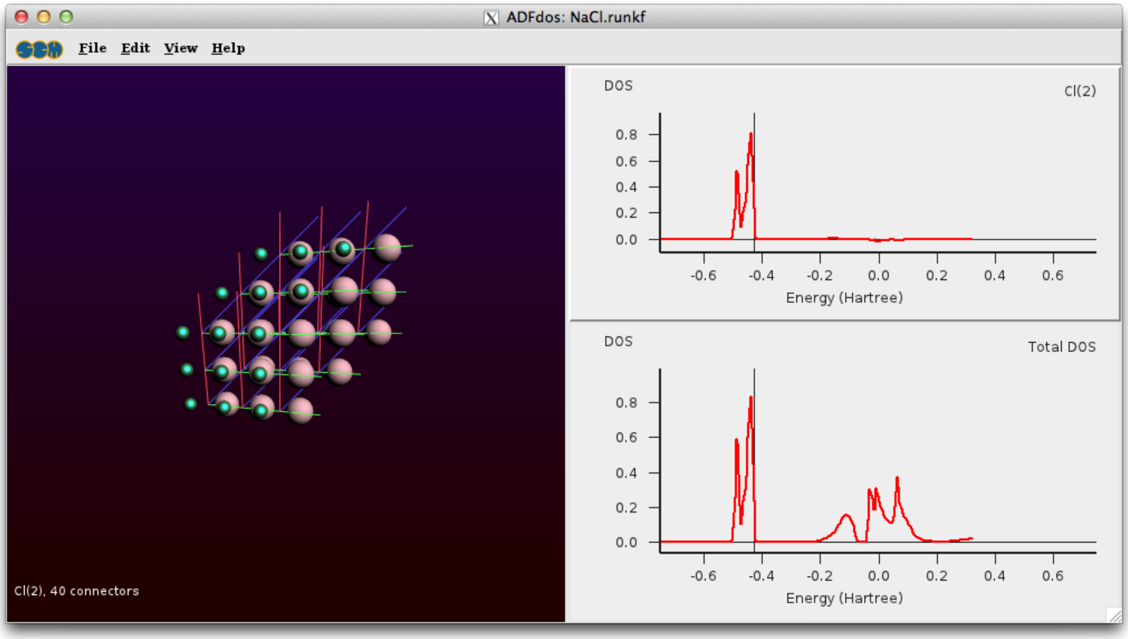


The Fermi energy is around -0.43, and there is clearly a gap. Just below it there is a valence band, and at -0.2 Hartree starts the conduction band.

`Select the` **View → Add Graph** `command`

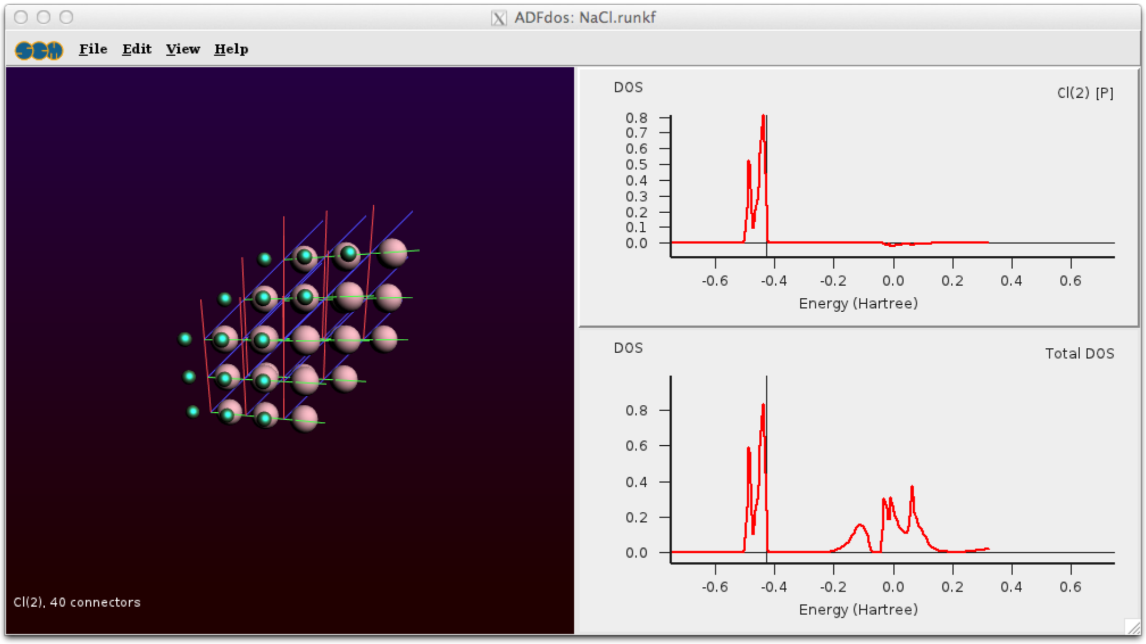
(Now you see two plots of the total DOS)

`Select with the mouse the Chlorine atom (the small green one)`



It is already immediately clear that the valence band comes from the Chlorine, and the conduction band from the Sodium.

Right-click with the mouse on the selected Cl atom and
check the 'P-DOS' check box in the pop up menu.



This shows that the valence band is clearly made of Chlorine p-orbitals.

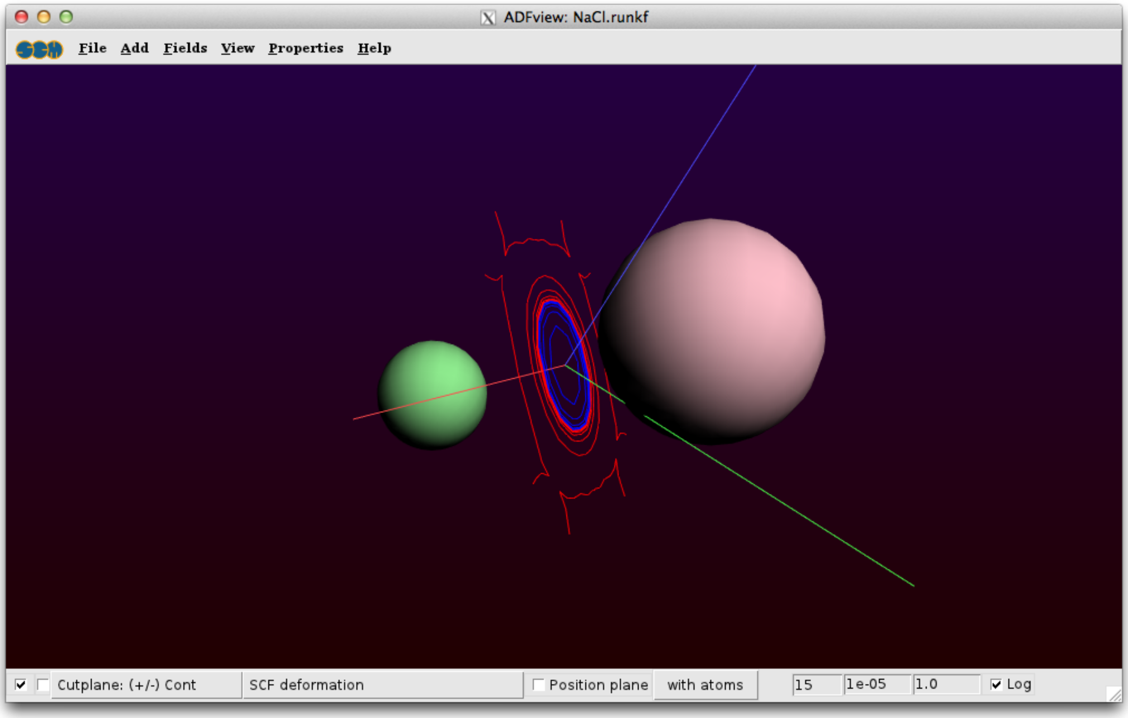
Plotting the deformation density

Naively you might expect that the charge of Na should be +1 and from the Cl -1. This can be best seen by making a cut plane:

Go to ADFview (**SCM → View**)
Delete the double isosurface with the 'Isosurface: Double' pull-down menu in the bar on the bottom and select 'Delete'
Add → Cut Plane: Contours (+/-)
Select the deformation density in the fields menu (in the Fit density sub-menu)

```
p01-2009> <17:00:49>  final mi
p01-2009> <17:00:49>  Approx.
p01-2009> <17:00:49>
```

The result is a bit disappointing, because the plane is perpendicular to the atoms

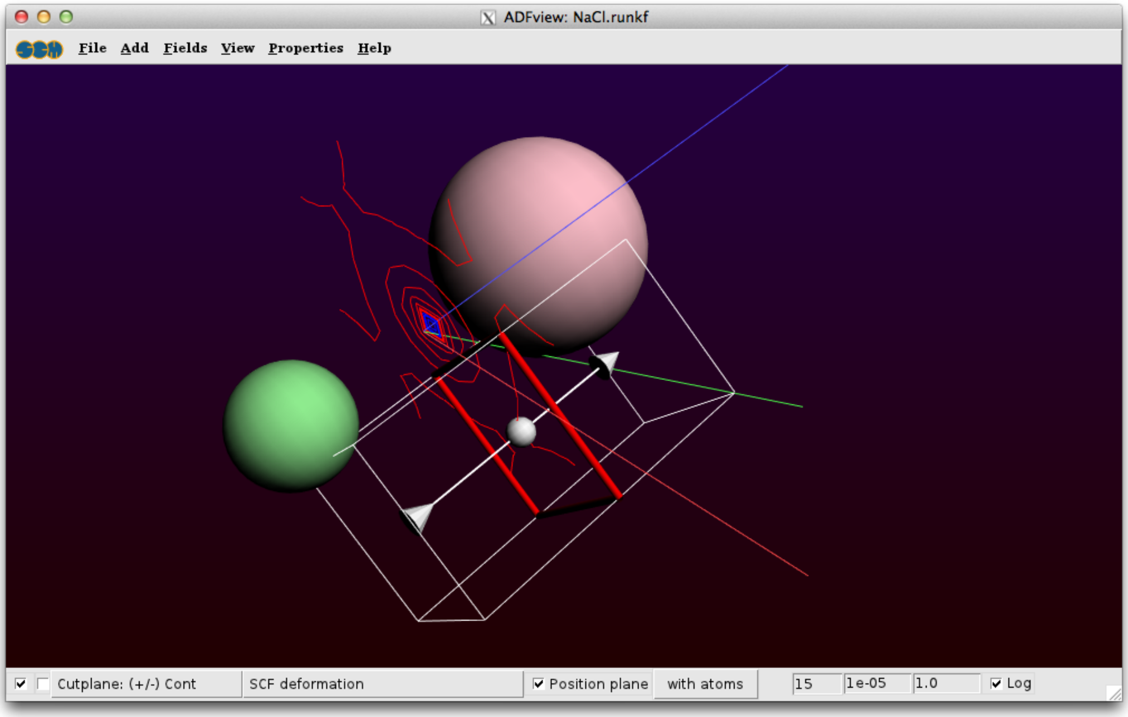


☑ ☐ Cutplane: (+/-) Cont | SCF deformation | ☐ Position plane | with atoms | 15 | 1e-05 | 1.0 | ☑ Log

To get it right enable at the bottom the "Position plane" toggle:

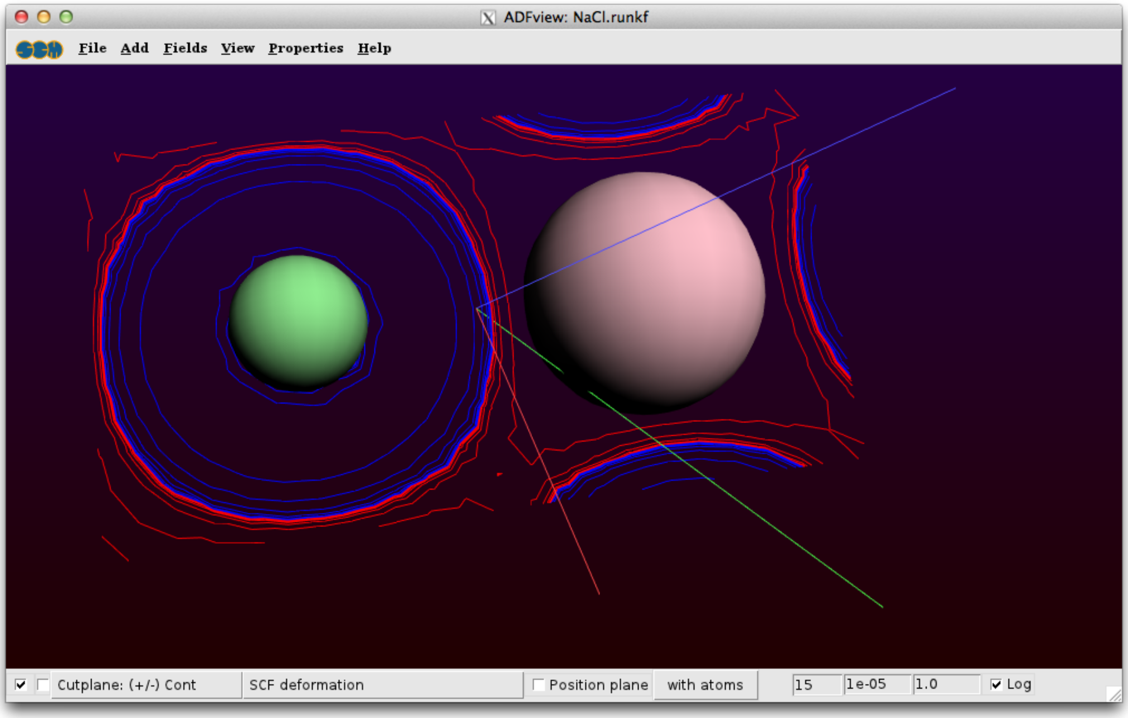
SCF deformation | ☑ Position plane | with atoms

You will now see a white frame. Drag it to the right until you see an arrow in it



☑ ☐ Cutplane: (+/-) Cont | SCF deformation | ☑ Position plane | with atoms | 15 | 1e-05 | 1.0 | ☑ Log

Now you can "grab" the arrow head and turn it to make the plane go through the atoms

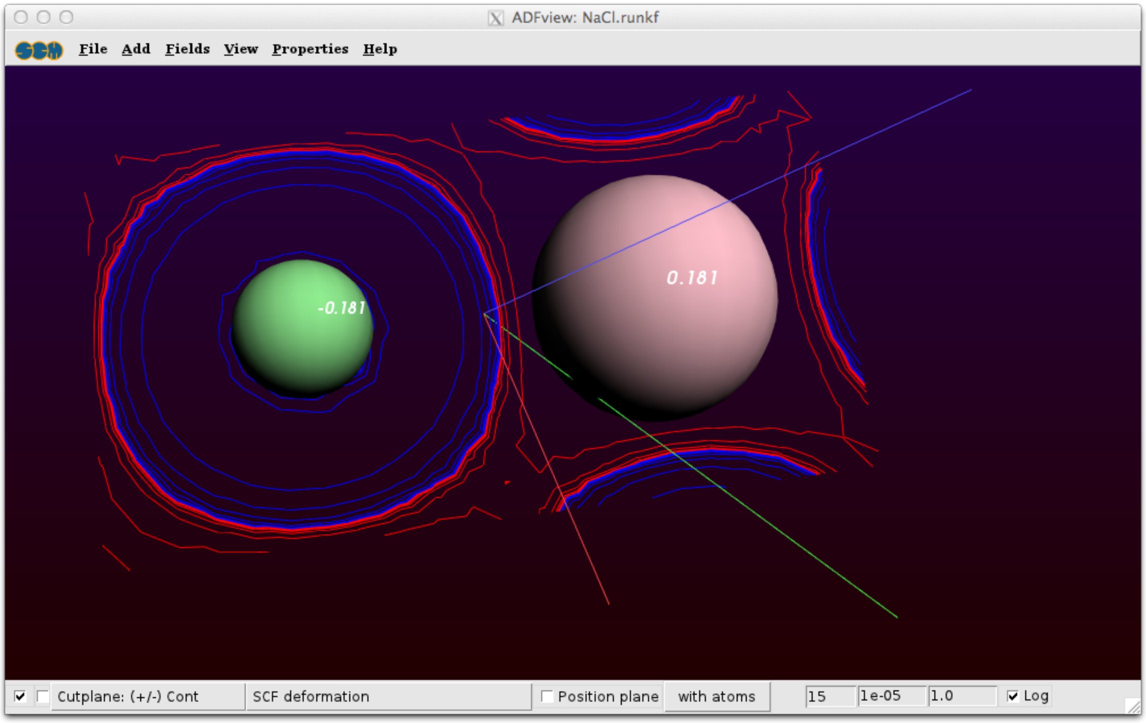


Indeed we see that charge is added (blue) near the Cl and removed (red) from the Na atom. The trend is good, but what is the total amount of charge transferred?

Step 7: Check the charges

Use the "**Properties → Atom Info → Hirshfeld Charges → Show** menu command

This will show you



So the amount of charge transferred is only about 0.2. This is of course due to the fact that the Cl p-band overlaps quite significantly with the Na region.

The conclusion of this tutorial: we should take the idea that *one* electron is transferred from Na to Cl with a grain of salt.

Tutorial 2: a transition state search

This tutorial will teach you how to:

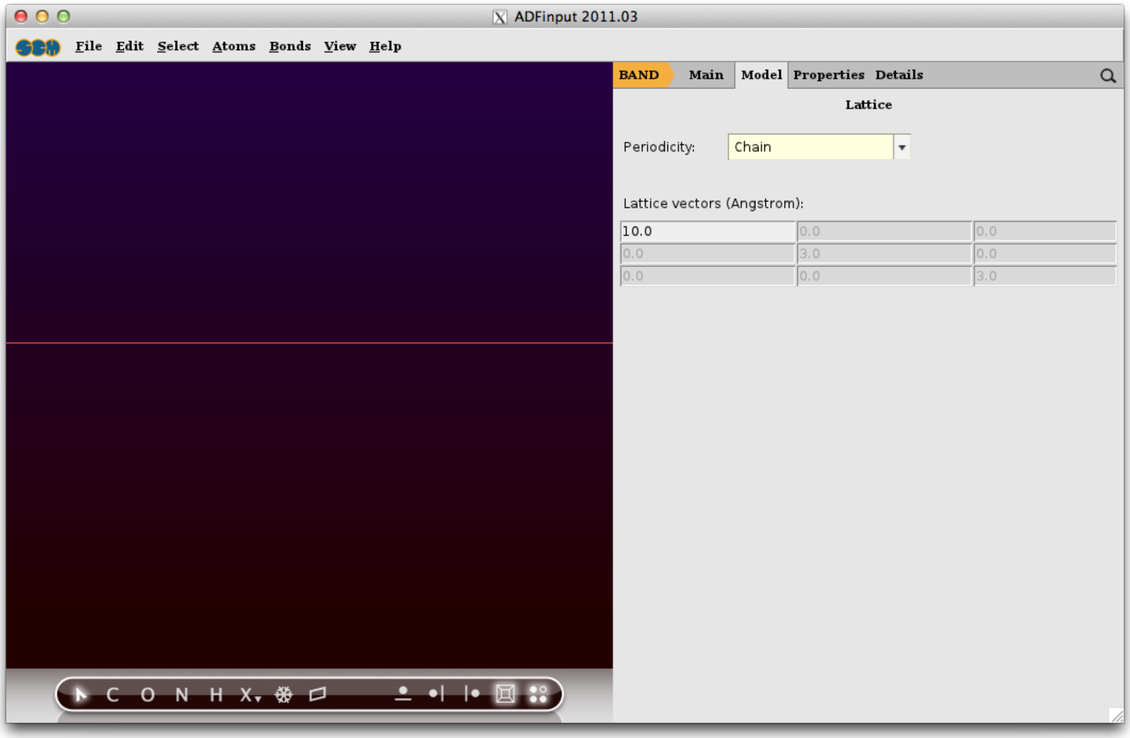
- do a geometry optimization
- watch the geometry optimization as a movie
- do a frequency calculation
- examine the eigen modes
- perform a transition state search
- make a few mistakes and fix them

Throughout we will consider the toy system of a periodic chain with three atoms in the unit cell.

Step 1: Create the H3 toy system

We are going to enter the geometry manually, just as in the first tutorial.

`Start BANDinput`
`Set periodicity to Chain`
`Panel bar` **Model → Lattice**
`Set the lattice constant to 10.0`



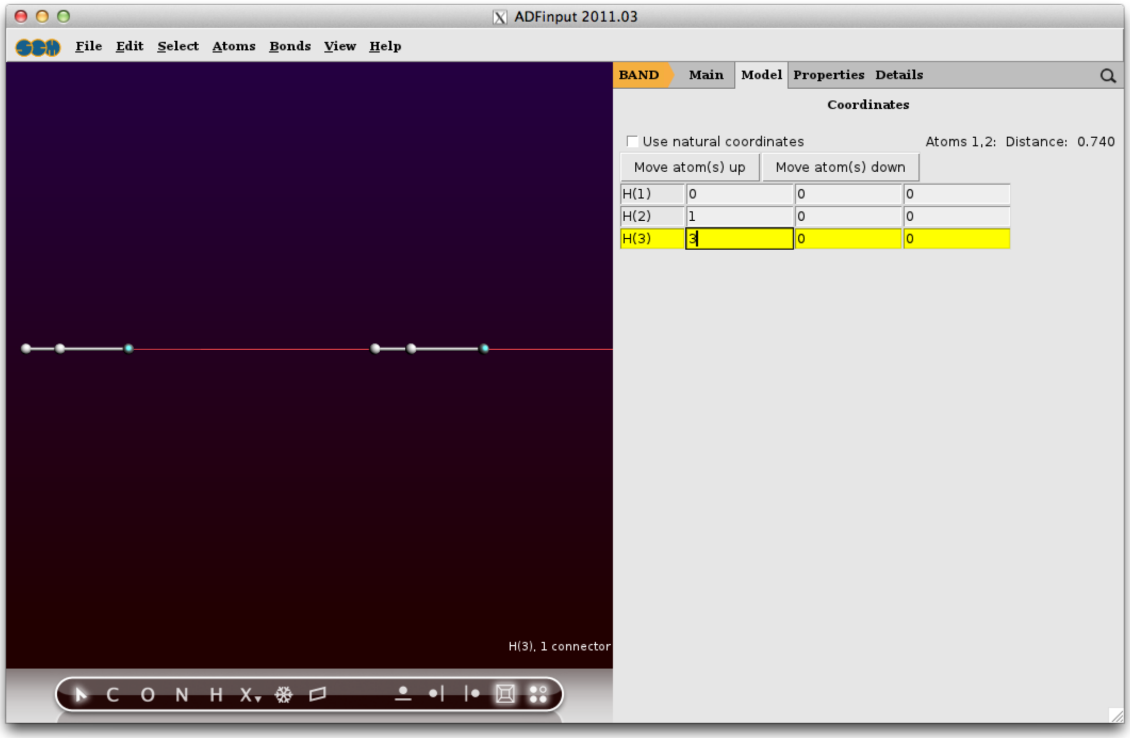
Lattice

Periodicity: Chain

Lattice vectors (Angstrom):

10.0	0.0	0.0
0.0	3.0	0.0
0.0	0.0	3.0

Add with the mouse three hydrogen atoms somewhere in the cell
Panel bar **Model → Coordinates**
Change the coordinates of the H atoms to match the following picture



Coordinates

☐ Use natural coordinates

Atoms 1,2: Distance: 0.740

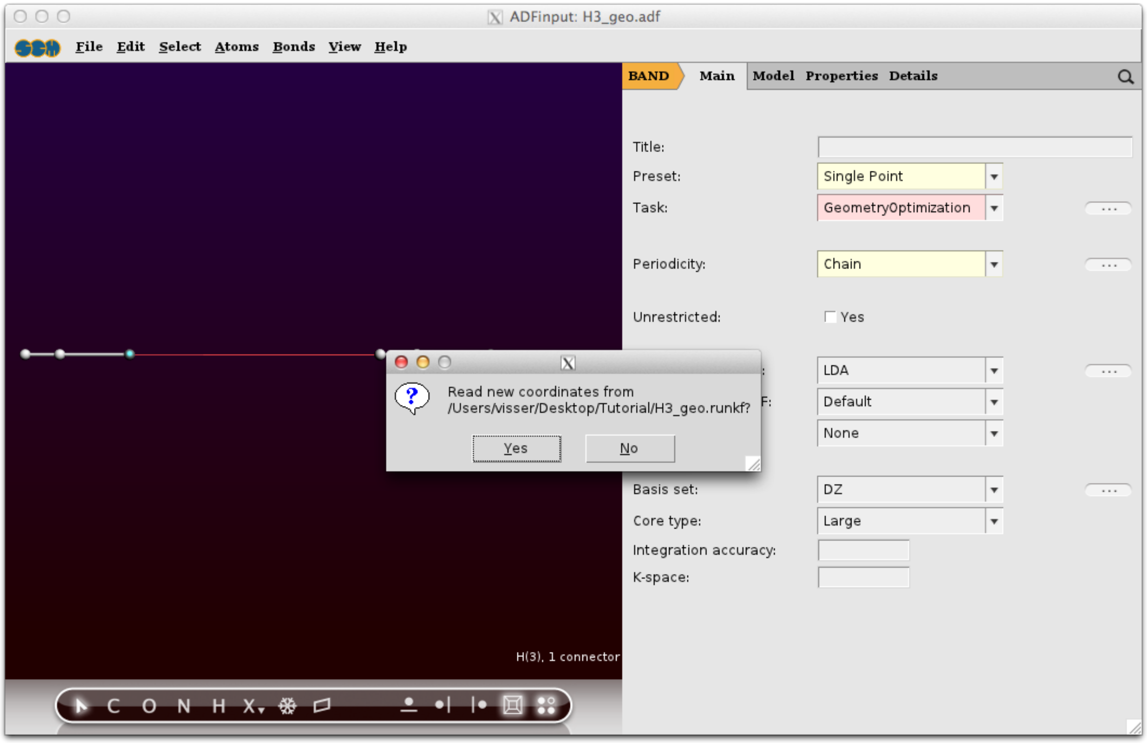
H(1)	0	0	0
H(2)	1	0	0
H(3)	3	0	0

You have now created the cylinder symmetric toy system.

Step 2: Optimize the geometry

```
Go back to the 'BAND Main' panel
Choose as preset 'Geometry Optimization'
```
File → Run, `save the job with name H3_geo`

After it has finished the program asks you



Title:
Preset: Single Point
Task: GeometryOptimization
Periodicity: Chain
Unrestricted: ☐ Yes
LDA
Default
None
Basis set: DZ
Core type: Large
Integration accuracy:
K-space:

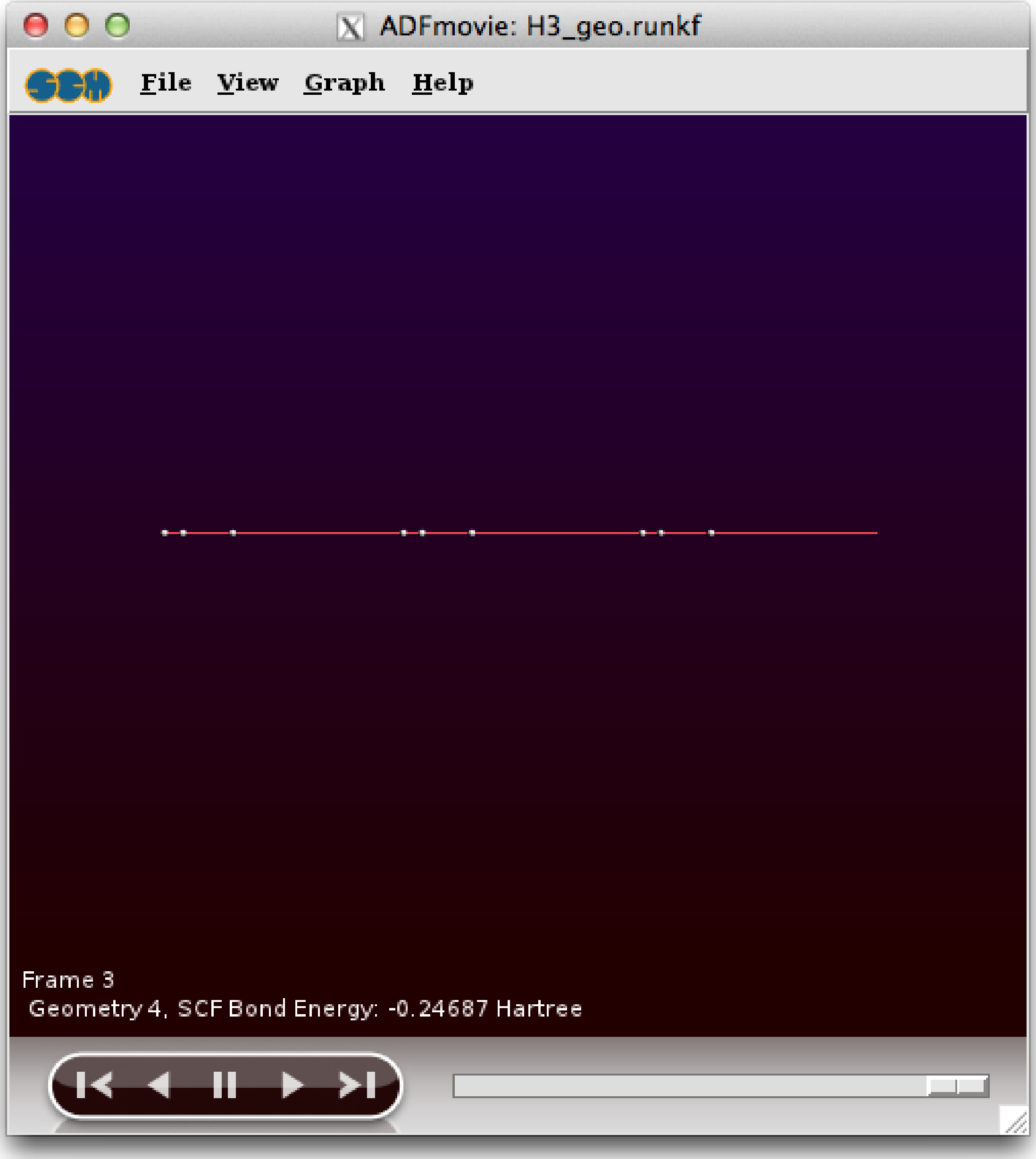
Read new coordinates from /Users/visser/Desktop/Tutorial/H3_geo.runkf?

```
Answer 'Yes'
```

Now let us look at the progress as a movie.

SCM → Movie

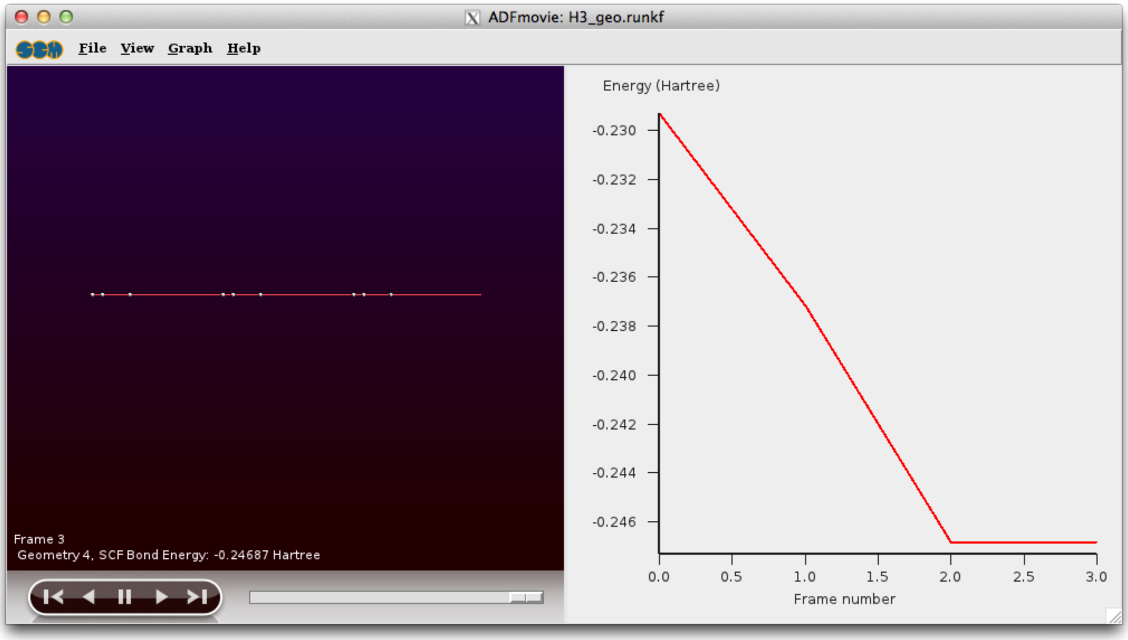
A small movie pops up ending like this



Frame 3
Geometry 4, SCF Bond Energy: -0.24687 Hartree

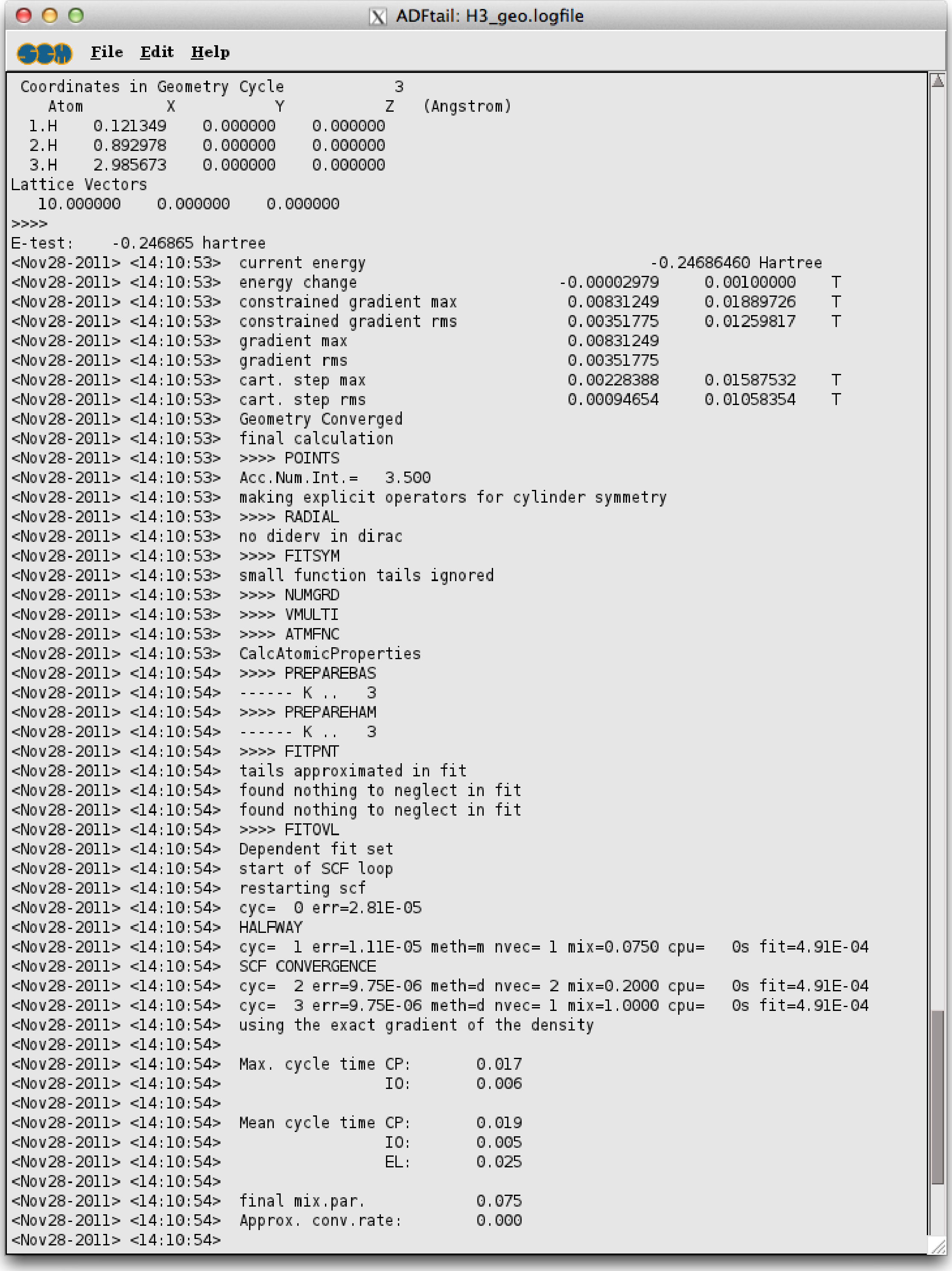
The geometry looks a bit odd. Now take a look how the energy changed during the optimization.

`Choose the` **Graph → Energy** `menu command`



It shows the energy at the four steps: 0, 1, 2, and 3. Since the energy does not change anymore from step 2 to three it should be OK? Well, maybe, but maybe not. Let us check whether we were fully converged.

`Open the logfile:` **SCM → Logfile**
`Scroll from the end a bit upwards and you will see`

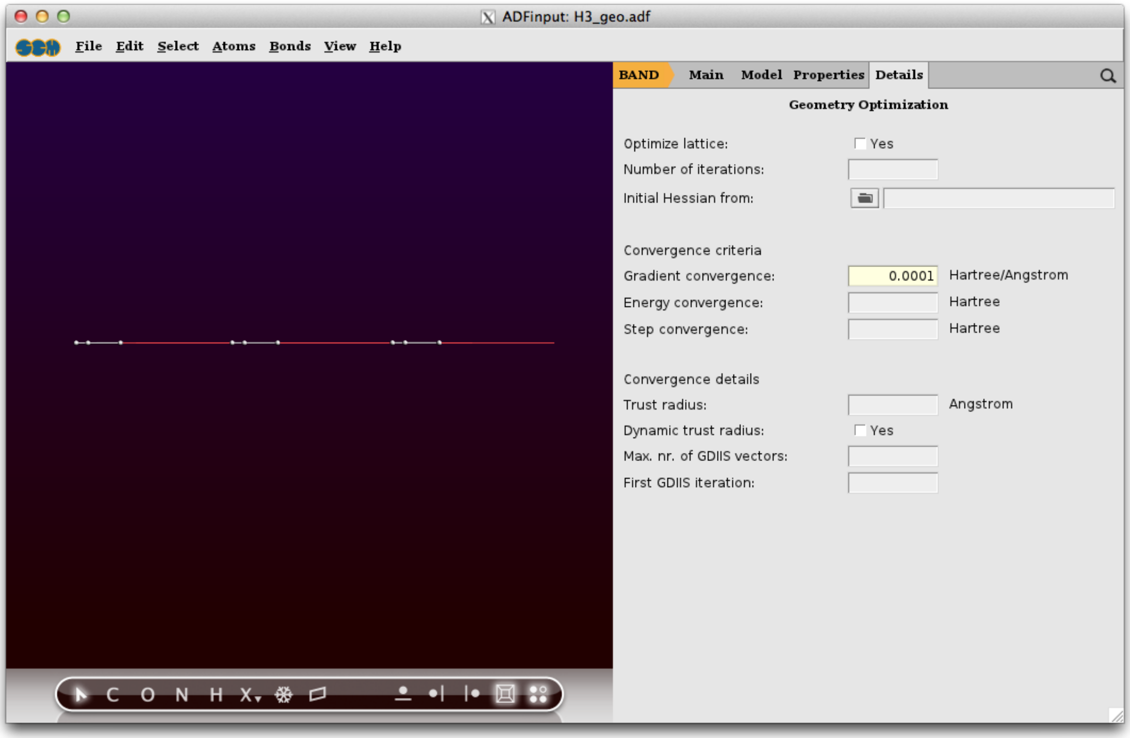


```
 Coordinates in Geometry Cycle          3
    Atom          X           Y           Z    (Angstrom)
  1.H    0.121349    0.000000    0.000000
  2.H    0.892978    0.000000    0.000000
  3.H    2.985673    0.000000    0.000000
Lattice Vectors
   10.000000    0.000000    0.000000
>>>>
E-test:    -0.246865 hartree
<Nov28-2011> <14:10:53>  current energy                               -0.24686460 Hartree
<Nov28-2011> <14:10:53>  energy change                      -0.00002979     0.00100000    T
<Nov28-2011> <14:10:53>  constrained gradient max            0.00831249     0.01889726    T
<Nov28-2011> <14:10:53>  constrained gradient rms            0.00351775     0.01259817    T
<Nov28-2011> <14:10:53>  gradient max                        0.00831249
<Nov28-2011> <14:10:53>  gradient rms                        0.00351775
<Nov28-2011> <14:10:53>  cart. step max                      0.00228388     0.01587532    T
<Nov28-2011> <14:10:53>  cart. step rms                      0.00094654     0.01058354    T
<Nov28-2011> <14:10:53>  Geometry Converged
<Nov28-2011> <14:10:53>  final calculation
<Nov28-2011> <14:10:53>  >>>> POINTS
<Nov28-2011> <14:10:53>  Acc.Num.Int.=    3.500
<Nov28-2011> <14:10:53>  making explicit operators for cylinder symmetry
<Nov28-2011> <14:10:53>  >>>> RADIAL
<Nov28-2011> <14:10:53>  no diderv in dirac
<Nov28-2011> <14:10:53>  >>>> FITSYM
<Nov28-2011> <14:10:53>  small function tails ignored
<Nov28-2011> <14:10:53>  >>>> NUMGRD
<Nov28-2011> <14:10:53>  >>>> VMULTI
<Nov28-2011> <14:10:53>  >>>> ATMFNC
<Nov28-2011> <14:10:53>  CalcAtomicProperties
<Nov28-2011> <14:10:54>  >>>> PREPAREBAS
<Nov28-2011> <14:10:54>  ------ K ..   3
<Nov28-2011> <14:10:54>  >>>> PREPAREHAM
<Nov28-2011> <14:10:54>  ------ K ..   3
<Nov28-2011> <14:10:54>  >>>> FITPNT
<Nov28-2011> <14:10:54>  tails approximated in fit
<Nov28-2011> <14:10:54>  found nothing to neglect in fit
<Nov28-2011> <14:10:54>  found nothing to neglect in fit
<Nov28-2011> <14:10:54>  >>>> FITOVL
<Nov28-2011> <14:10:54>  Dependent fit set
<Nov28-2011> <14:10:54>  start of SCF loop
<Nov28-2011> <14:10:54>  restarting scf
<Nov28-2011> <14:10:54>  cyc=  0 err=2.81E-05
<Nov28-2011> <14:10:54>  HALFWAY
<Nov28-2011> <14:10:54>  cyc=  1 err=1.11E-05 meth=m nvec= 1 mix=0.0750 cpu=   0s fit=4.91E-04
<Nov28-2011> <14:10:54>  SCF CONVERGENCE
<Nov28-2011> <14:10:54>  cyc=  2 err=9.75E-06 meth=d nvec= 2 mix=0.2000 cpu=   0s fit=4.91E-04
<Nov28-2011> <14:10:54>  cyc=  3 err=9.75E-06 meth=d nvec= 1 mix=1.0000 cpu=   0s fit=4.91E-04
<Nov28-2011> <14:10:54>  using the exact gradient of the density
<Nov28-2011> <14:10:54>
<Nov28-2011> <14:10:54>  Max. cycle time CP:       0.017
<Nov28-2011> <14:10:54>                  IO:       0.006
<Nov28-2011> <14:10:54>
<Nov28-2011> <14:10:54>  Mean cycle time CP:       0.019
<Nov28-2011> <14:10:54>                  IO:       0.005
<Nov28-2011> <14:10:54>                  EL:       0.025
<Nov28-2011> <14:10:54>
<Nov28-2011> <14:10:54>  final mix.par.            0.075
<Nov28-2011> <14:10:54>  Approx. conv.rate:        0.000
<Nov28-2011> <14:10:54>
```

You see the final geometry and status of the five convergence criteria. Because they are all satisfied you see the log message 'Geometry Converged'

Maybe we are dealing with a shallow minimum. Let us retry with a more strict criterion.

Close the logfile and movie windows and go back to 'BANDinput'
Go to the 'Geometry Optimization' details panel (click on the "..." button next to GeometryOptimization)
Set the gradient convergence criterion to 0.0001



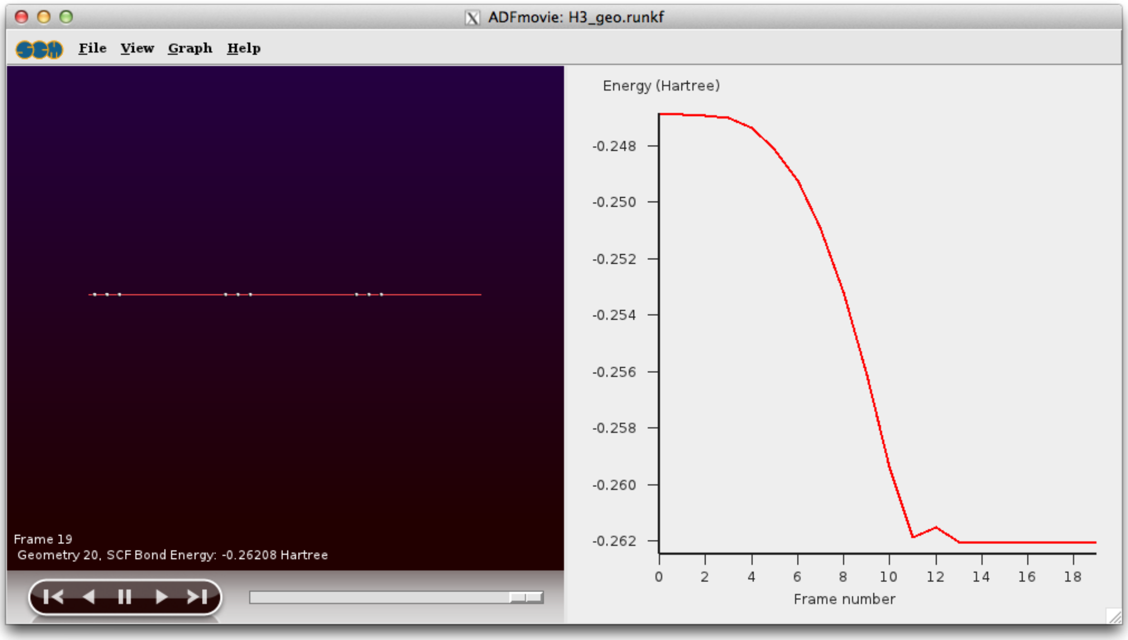
Geometry Optimization

Optimize lattice: ☐ Yes
Number of iterations:
Initial Hessian from:

Convergence criteria
Gradient convergence: 0.0001 Hartree/Angstrom
Energy convergence: Hartree
Step convergence: Hartree

Convergence details
Trust radius: Angstrom
Dynamic trust radius: ☐ Yes
Max. nr. of GDIIS vectors:
First GDIIS iteration:

File → Run (click Yes twice to accept overwriting the previous job
After the optimization, click Yes to accept the new geometry in BANDinput
Open ADFmovie and show the energy

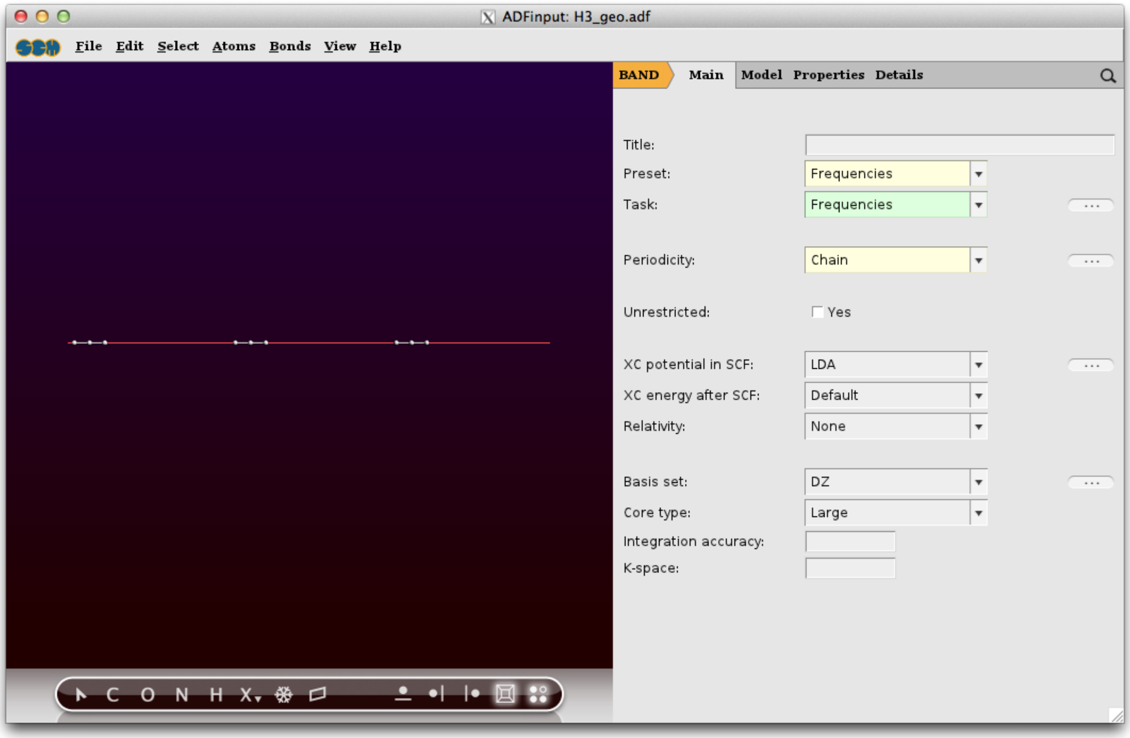


Frame 19
Geometry 20, SCF Bond Energy: -0.26208 Hartree

Now that looks more like an optimal geometry!

Step 3: Calculate the Hessian

```
Go to BANDinput
Select in the 'BAND Main' panel the 'Frequencies' preset
```

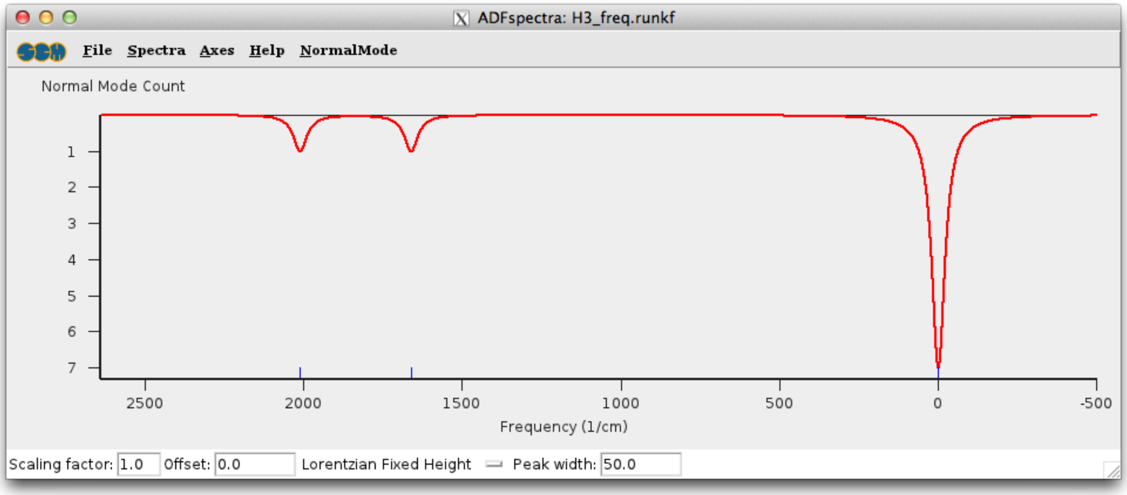


Title:
Preset: Frequencies
Task: Frequencies
Periodicity: Chain
Unrestricted: ☐ Yes
XC potential in SCF: LDA
XC energy after SCF: Default
Relativity: None
Basis set: DZ
Core type: Large
Integration accuracy:
K-space:

File → Save As...
```
Save the project as H3_freq
```
File → Run
```
When it is done, click Yes to accept the new coordinates
```

After the calculation has finished

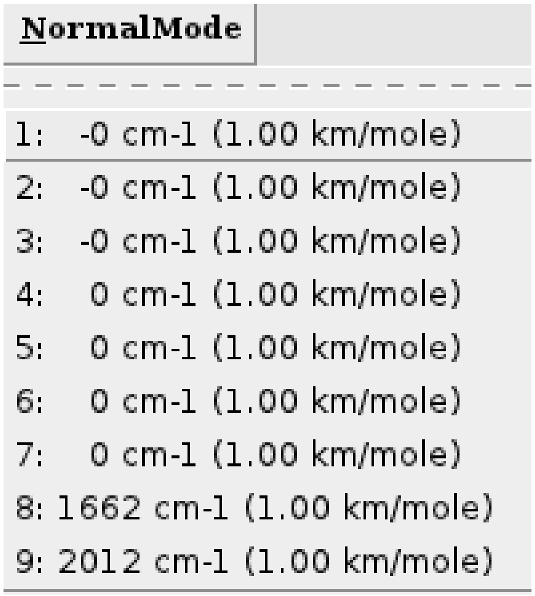
SCM → Spectra



Scaling factor: 1.0 Offset: 0.0 Lorentzian Fixed Height Peak width: 50.0

There appear to be three peaks, whereas you would expect 3N degrees of freedom. With three atoms (N=3) we should have nine modes. We can examine this a bit closer

```
click on the 'NormalMode' menu.
```

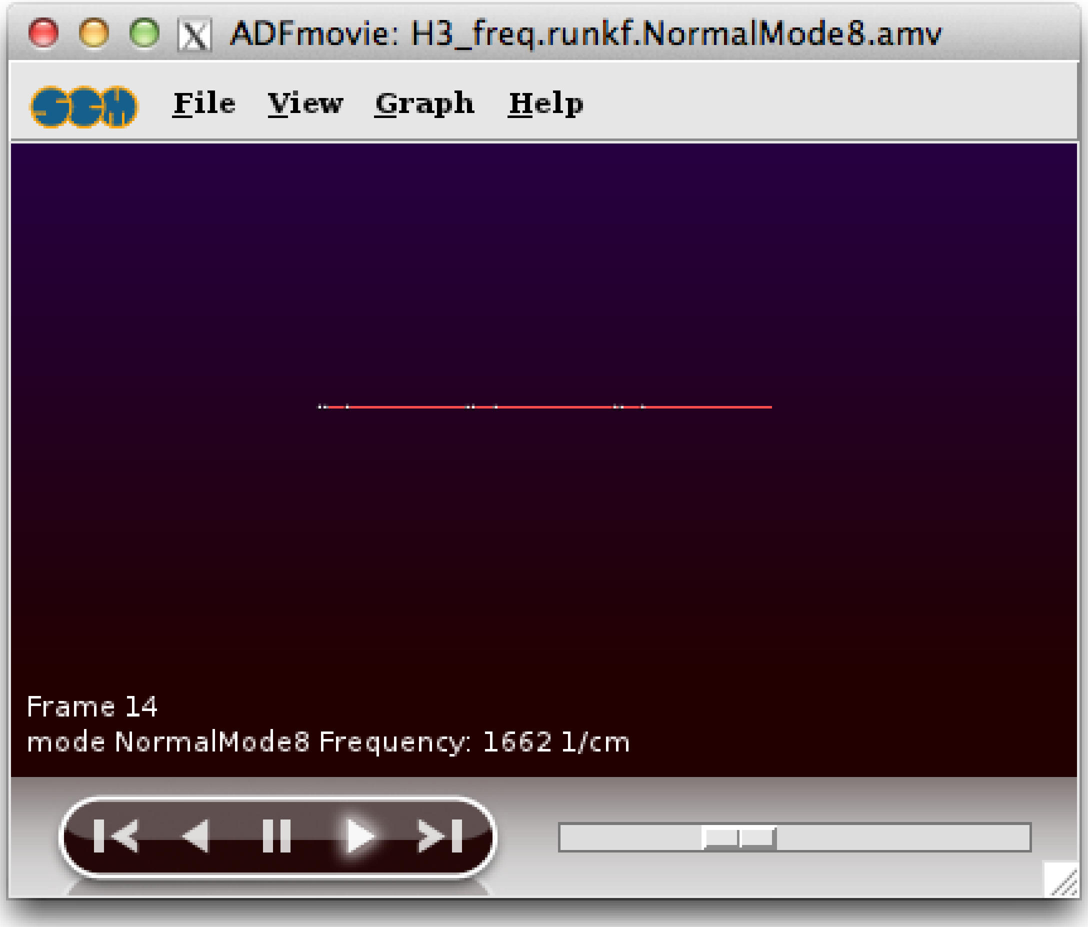


```
1:  -0 cm-1 (1.00 km/mole)
2:  -0 cm-1 (1.00 km/mole)
3:  -0 cm-1 (1.00 km/mole)
4:   0 cm-1 (1.00 km/mole)
5:   0 cm-1 (1.00 km/mole)
6:   0 cm-1 (1.00 km/mole)
7:   0 cm-1 (1.00 km/mole)
8: 1662 cm-1 (1.00 km/mole)
9: 2012 cm-1 (1.00 km/mole)
```

So there are indeed nine vibrational modes. Only two are nonzero because only symmetrical modes are calculated by default. To see what a mode looks like

```
Select the mode at 1662 cm-1, either from the 'NormalMode' menu,
   or by clicking on it directly in the graph.
```

A new movie window pops up visualizing the vibrational mode.

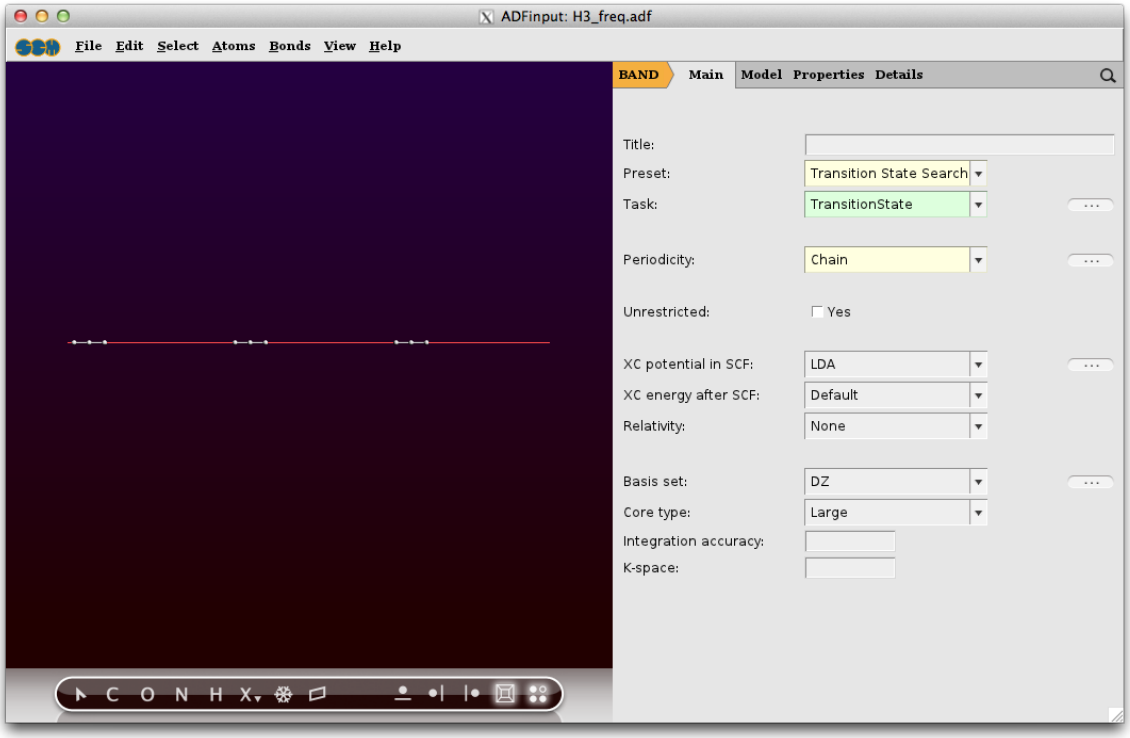


Frame 14
mode NormalMode8 Frequency: 1662 1/cm

Step 4: Search the transition state

A minimum has vanishing gradients and only positive eigen modes. A transition state (first-order saddle point) is characterized by having one negative mode. With a transition state search the optimizer will go uphill in the direction of the lowest (nonzero) eigen-mode and downhill in all other degrees of freedom. In our example it would follow mode 8. Let us give it a try from the minimum.

```
Choose in the 'BAND Main' panel the preset 'Transition State Search'
```

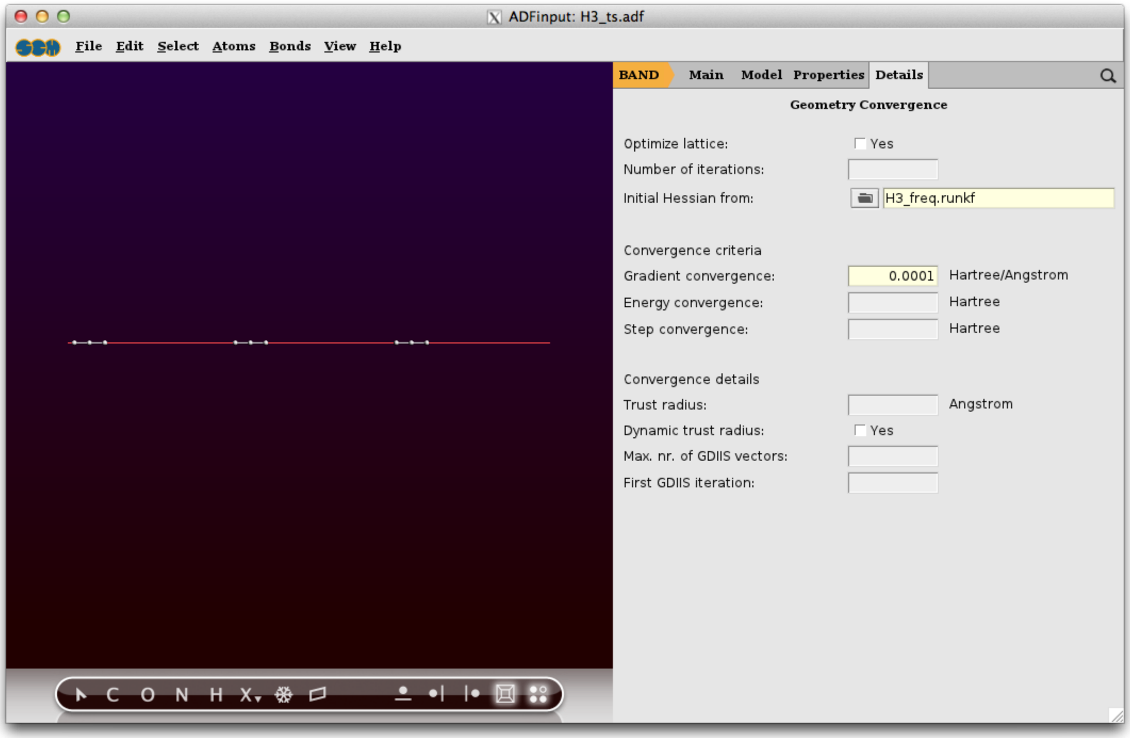


ADFinput: H3_freq.adf

Title:
Preset: Transition State Search
Task: TransitionState
Periodicity: Chain
Unrestricted: ☐ Yes
XC potential in SCF: LDA
XC energy after SCF: Default
Relativity: None
Basis set: DZ
Core type: Large
Integration accuracy:
K-space:

We have just calculated a Hessian (with the frequency run) so we'd better use it.

Use the panel bar **Details → Geometry Convergence** command
Click on the folder button next to 'Initial Hessian From:'
Select with the file dialog 'H3_freq.runkf'



ADFinput: H3_ts.adf

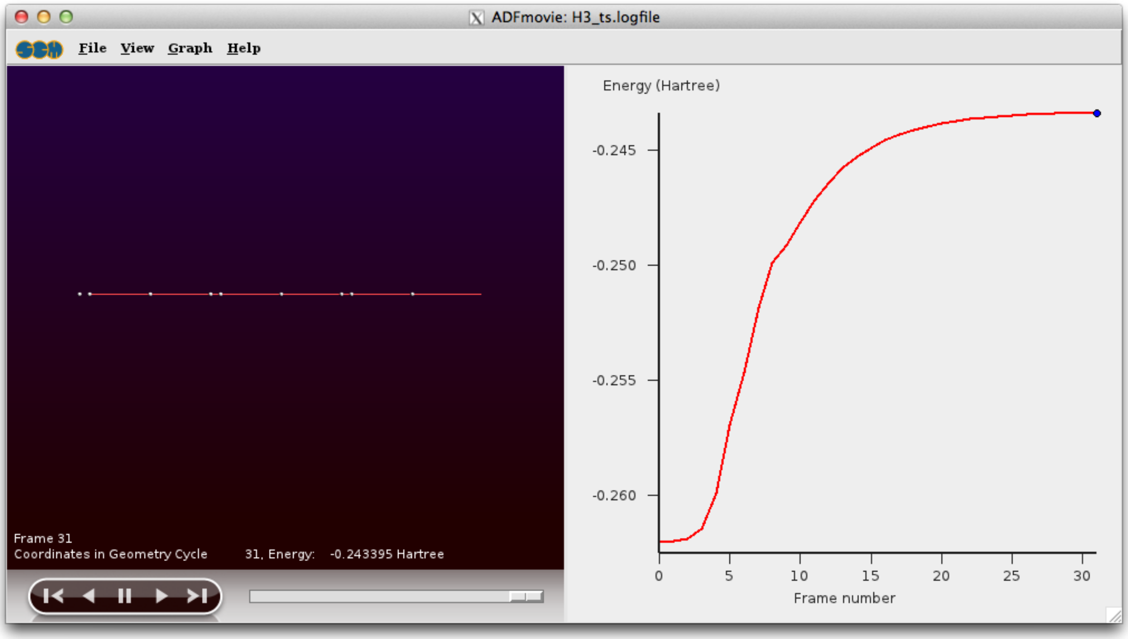
Geometry Convergence

Optimize lattice: ☐ Yes
Number of iterations:
Initial Hessian from: H3_freq.runkf

Convergence criteria
Gradient convergence: 0.0001 Hartree/Angstrom
Energy convergence: Hartree
Step convergence: Hartree

Convergence details
Trust radius: Angstrom
Dynamic trust radius: ☐ Yes
Max. nr. of GDIIS vectors:
First GDIIS iteration:

File → Save As, use name H3_ts
File → Run
After it has finished:
Update the coordinates in BANDinput
SCM → Movie
Graph → Energy

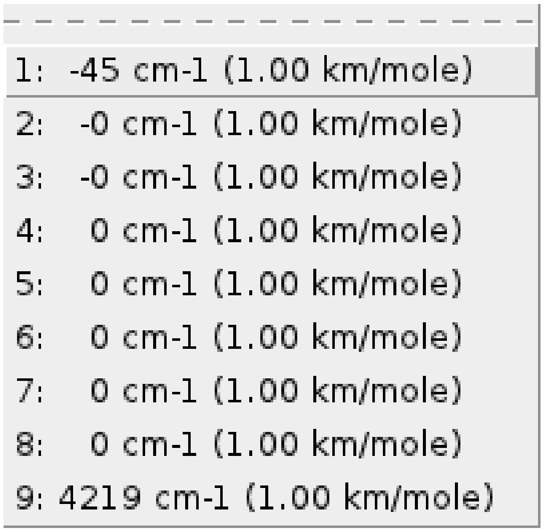


Frame 31
Coordinates in Geometry Cycle 31, Energy: -0.243395 Hartree

The third H atom ends up exactly in the middle of the (repeated) H1 and H2 atoms. Let us finally check that we are indeed in the transition state.

In the 'BAND Main' panel select the task 'Frequencies'
Save the project as 'H3_ts_freq' and run it.
When the calculation is ready:
open ADFspectra and click on the 'NormalModes' menu

You should see:



```
1:  -45 cm-1 (1.00 km/mole)
2:   -0 cm-1 (1.00 km/mole)
3:   -0 cm-1 (1.00 km/mole)
4:    0 cm-1 (1.00 km/mole)
5:    0 cm-1 (1.00 km/mole)
6:    0 cm-1 (1.00 km/mole)
7:    0 cm-1 (1.00 km/mole)
8:    0 cm-1 (1.00 km/mole)
9: 4219 cm-1 (1.00 km/mole)
```

We have found a geometry with vanishing gradients with one weak negative vibrational mode. We have succeeded in finding a transition state.

SCM → Close All

Tutorial 3: a transition state search with a partial Hessian*

This tutorial will teach you how to:

- calculate a partial Hessian
- do a constrained TS search using the partial Hessian

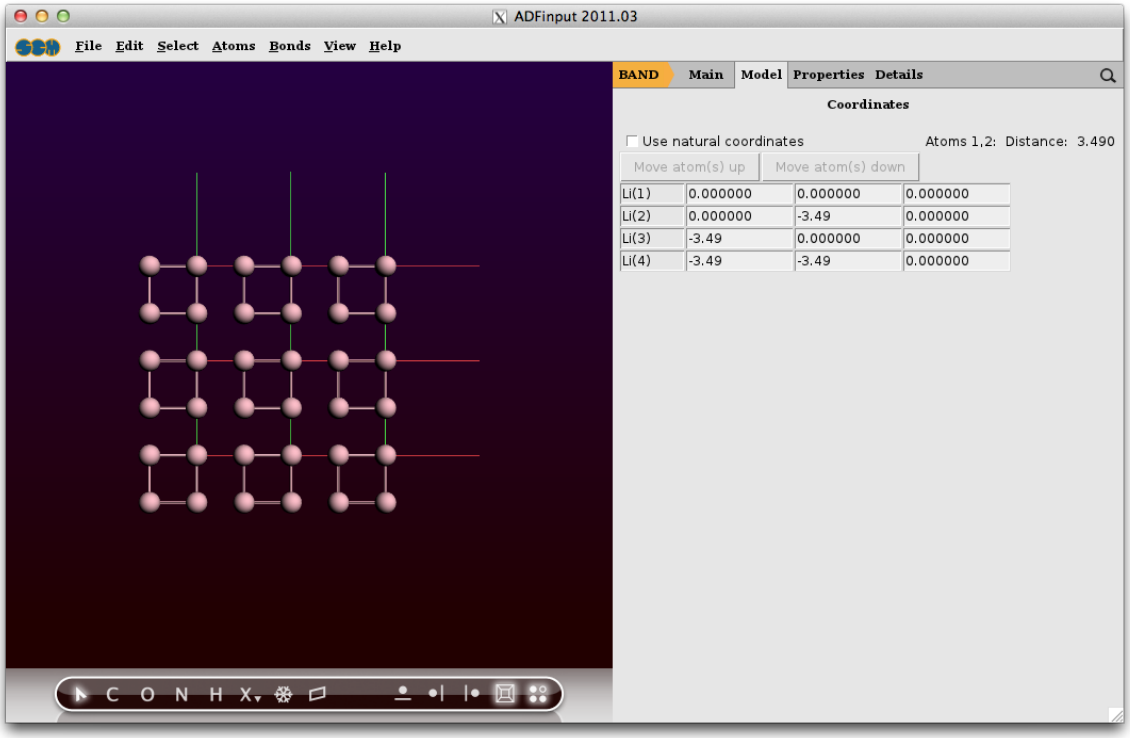
In this "advanced" tutorial we consider a slightly more realistic system. Some of the calculations may require 20 minutes to run on a two core machine.

Step 1: Create the system

We are going to make a one layer Li (001) slab with a 2x2 unit cell, assuming familiarity with the build tools

```
Start BANDinput
From the structure tool select 'Cubic' and 'bcc'
Set 'Element' to Li
Set the lattice parameter to 3.49
Press 'OK'
Invoke the Slice tool
Set the Miller indices to 001, select 'Cartesian', and enter 1 layer.
Press 'OK'
Use the Edit → Crystal → Generate Super Cell... command
Select the preset '2x2' and press 'OK'
Panel bar Model → Coordinates
```

Your screen should look like this:



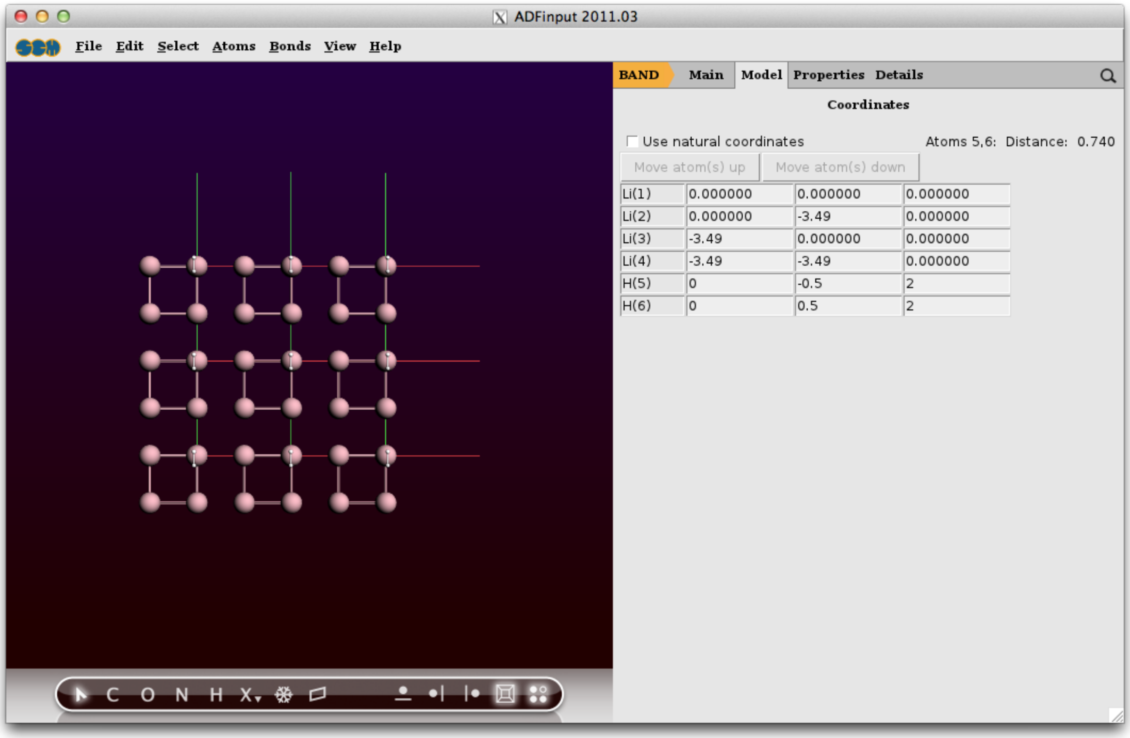
☐ Use natural coordinates

Atoms 1,2: Distance: 3.490

Li(1)	0.000000	0.000000	0.000000
Li(2)	0.000000	-3.49	0.000000
Li(3)	-3.49	0.000000	0.000000
Li(4)	-3.49	-3.49	0.000000

```
Add with the mouse two hydrogen atoms anywhere in the screen
Set in the table the coordinates of the first hydrogen atom to (0, -0.5, 2)
Set the second H atom coordinates to (0, 0.5, 2)
```

The final geometry looks like this



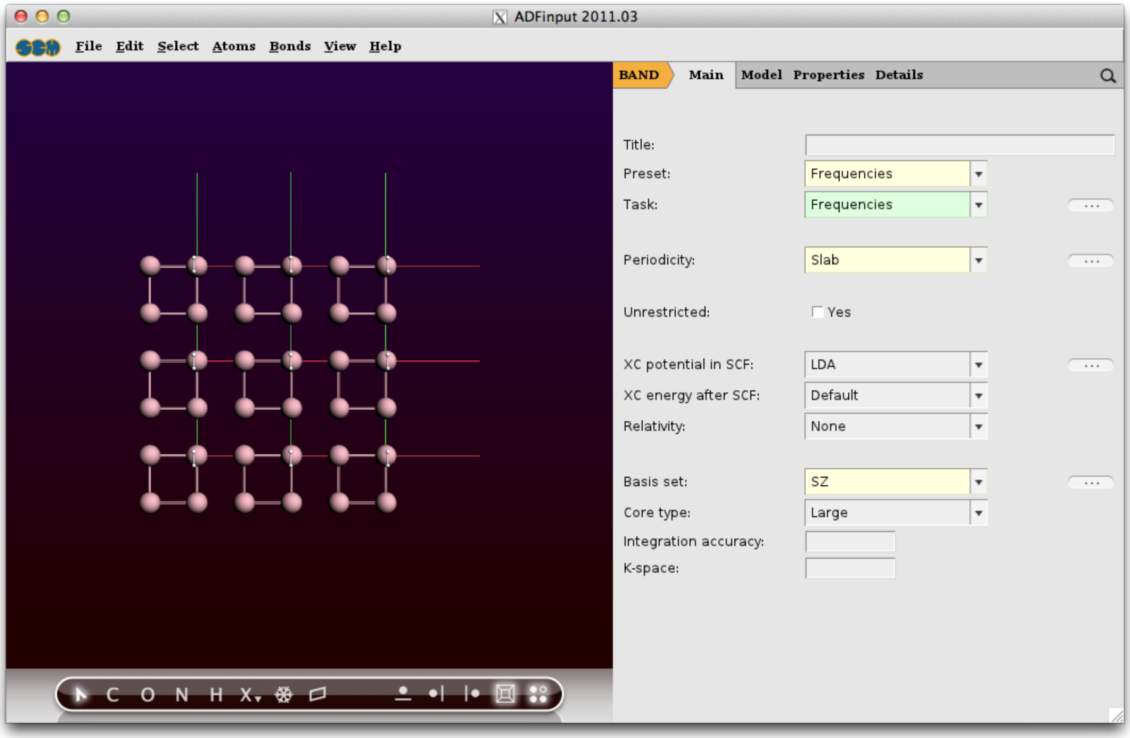
☐ Use natural coordinates

Atoms 5,6: Distance: 0.740

Li(1)	0.000000	0.000000	0.000000
Li(2)	0.000000	-3.49	0.000000
Li(3)	-3.49	0.000000	0.000000
Li(4)	-3.49	-3.49	0.000000
H(5)	0	-0.5	2
H(6)	0	0.5	2

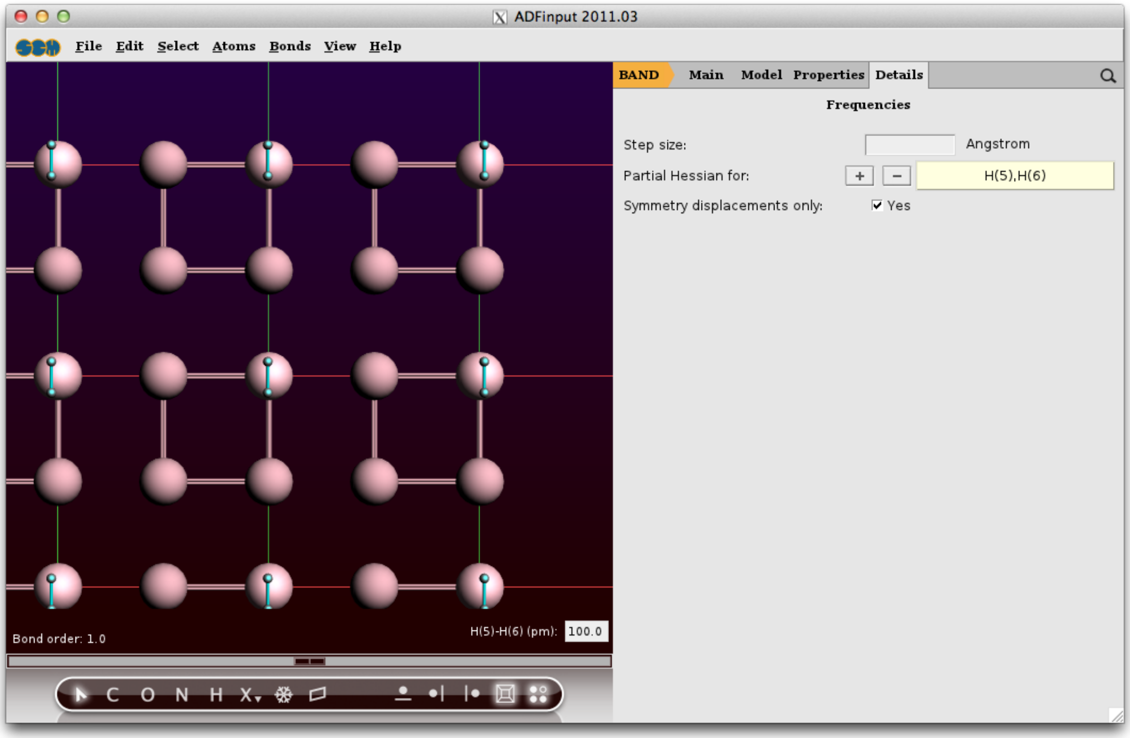
Step 2: Calculate a partial Hessian

Select the 'BAND Main' panel
Select the Frequencies preset
Set 'Basis Set' to 'SZ'



Title:
Preset: Frequencies
Task: Frequencies
Periodicity: Slab
Unrestricted: ☐ Yes
XC potential in SCF: LDA
XC energy after SCF: Default
Relativity: None
Basis set: SZ
Core type: Large
Integration accuracy:
K-space:

Go to the 'Frequencies' details panel (click on the '...' button)
Select with the mouse the two tiny Hydrogen atoms (zoom in to make selecting them easier)
Click on the '+' button next to 'Partial Hessian For:'



Frequencies

Step size: Angstrom
Partial Hessian for: H(5),H(6)
Symmetry displacements only: ☑ Yes

Bond order: 1.0
H(5)-H(6) (pm): 100.0

File → **Run**, name the job H2onLi_freq
Say 'No' when asked to update the coordinates

Let us examine the eigen-modes that we have found for the Hydrogen molecule

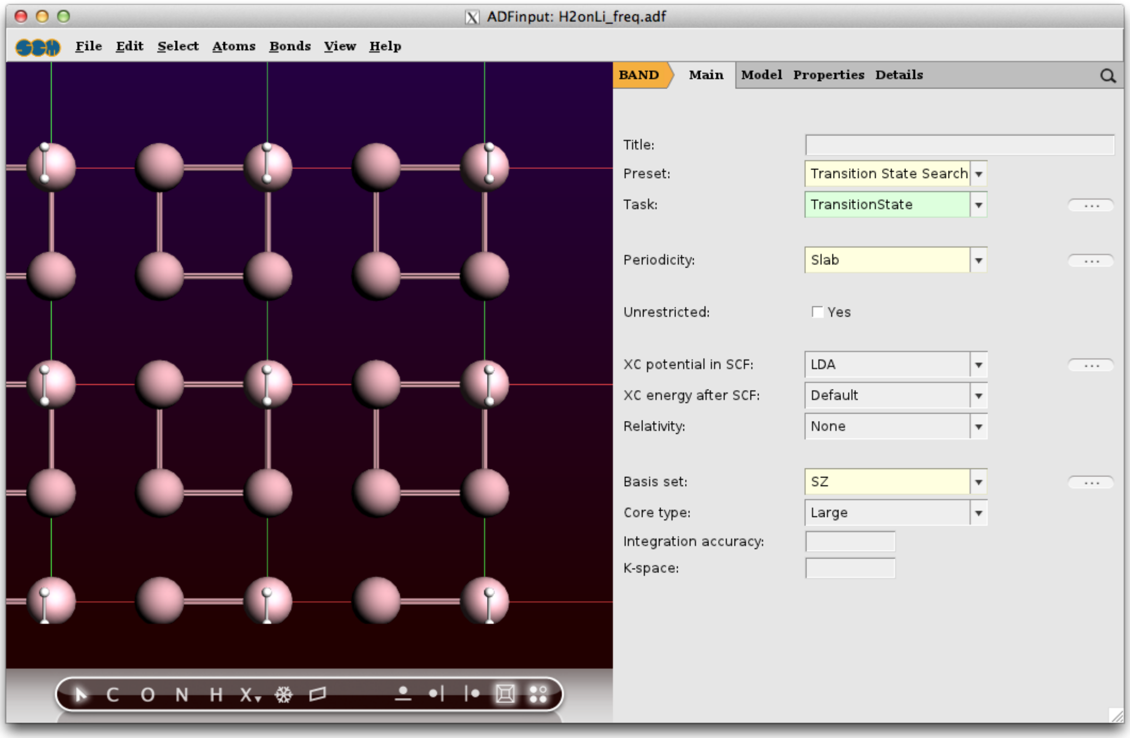
Select the **SCM** → **Spectra** menu command
Open the 'NormalMode' menu

Now you will see that there is an eigen-mode at 452 cm-1 and one at 2422 cm-1. Convince yourself that the 452 mode moves the H2 perpendicular to the service and that the 2422 mode is essentially an H2 stretch mode. The lowest mode looks like a promising start to find the transition state for dissociation over the Li surface.

Step 3: Transition state search with a frozen substrate

We have just found the vibrational modes of the Hydrogen molecule, assuming that the Li substrate remains fixed. Let us now find the transition state under the same assumption.

Close the 'ADFspectra' window and go back to BANDinput.
Select the 'BAND Main' panel and select the 'Transition State Search' preset



Title:

Preset: Transition State Search

Task: TransitionState

Periodicity: Slab

Unrestricted: ☐ Yes

XC potential in SCF: LDA

XC energy after SCF: Default

Relativity: None

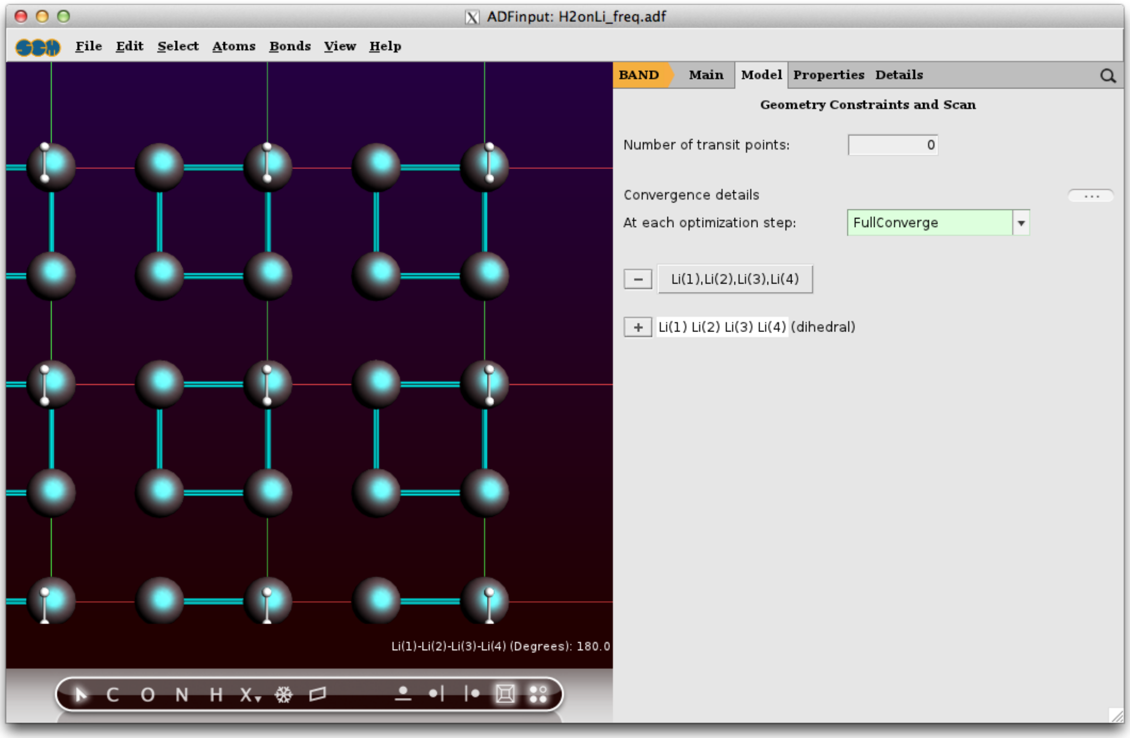
Basis set: SZ

Core type: Large

Integration accuracy:

K-space:

Panel bar **Model** → **Geometry Constraints and Scan**
The two hydrogen atoms are still selected, if not select them again
Use the **Select** → **Invert Selection** command
Click on the '+' button next to 'freeze selected atoms'



Geometry Constraints and Scan

Number of transit points: 0

Convergence details

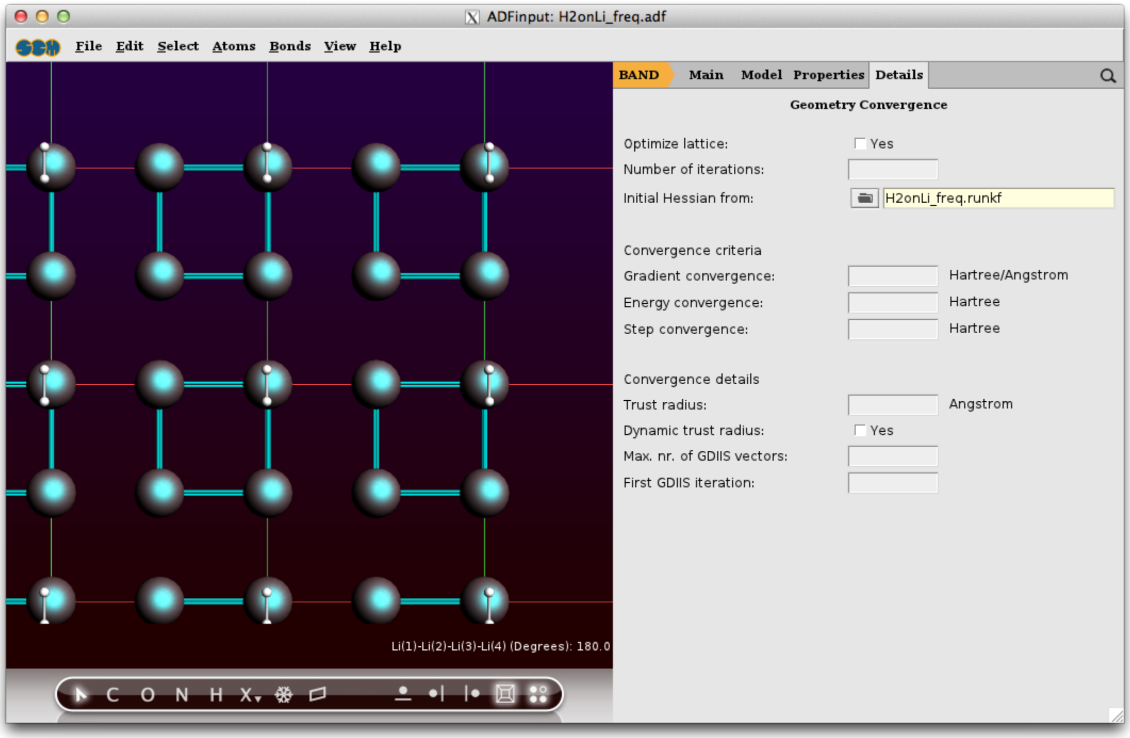
At each optimization step: FullConverge

− Li(1),Li(2),Li(3),Li(4)

\+ Li(1) Li(2) Li(3) Li(4) (dihedral)

Li(1)-Li(2)-Li(3)-Li(4) (Degrees): 180.0

`Panel bar` **Details → Geometry Convergence**
`Set the initial Hessian to 'H2onLi_freq.runkf'`



Geometry Convergence

Optimize lattice: ☐ Yes
Number of iterations:
Initial Hessian from: H2onLi_freq.runkf

Convergence criteria
Gradient convergence: Hartree/Angstrom
Energy convergence: Hartree
Step convergence: Hartree

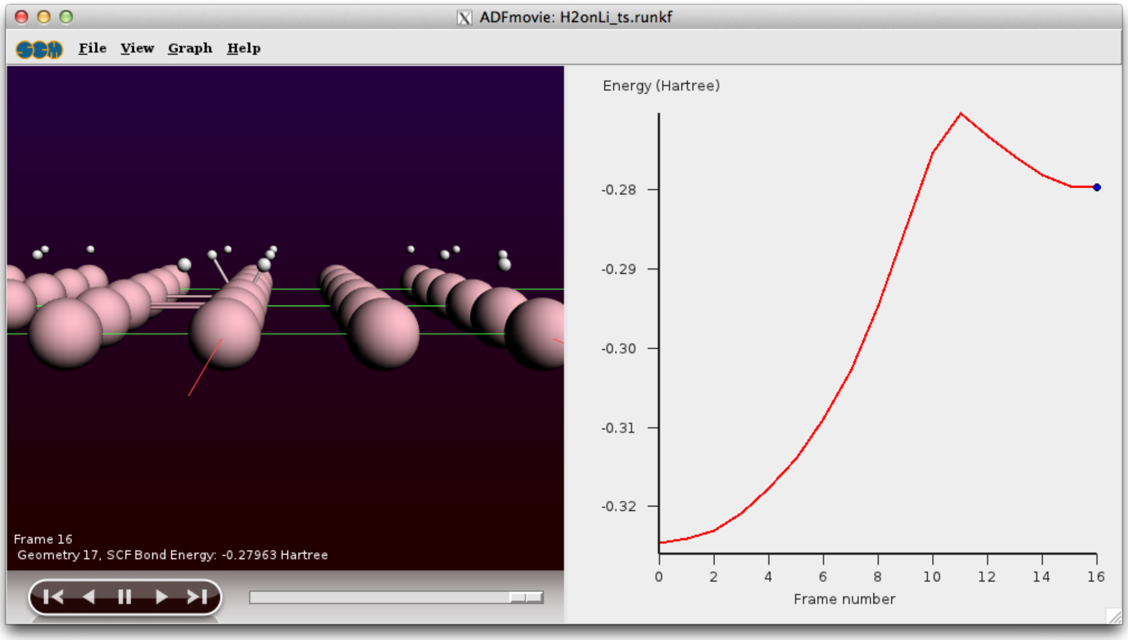
Convergence details
Trust radius: Angstrom
Dynamic trust radius: ☐ Yes
Max. nr. of GDIIS vectors:
First GDIIS iteration:

File → Save As..., `use name H2onLi_ts`
File → Run

After the run has completed:

SCM → Movie
`In the movie window:` **Graph → Energy**
View → View Direction → Along x axis
`Reorient to get a good look`

It should look like


ADFmovie: H2onLi_ts.runkf
File
View
Graph
Help
Frame 16
Geometry 17, SCF Bond Energy: -0.27963 Hartree
Energy (Hartree)
-0.28
-0.29
-0.30
-0.31
-0.32
0
2
4
6
8
10
12
14
16
Frame number

DFTB-GUI tutorials

DFTB provides accurate results at a fraction of the cost of a DFT evaluation. The tutorials in this section show you how to use DFTB via the DFTB-GUI. Since the DFTB-GUI is very similar to the ADF-GUI, we will focus here on DFTB specific features.

If you are not familiar with the ADF-GUI (or the DFTB-GUI), please have a look at the Introduction and ADF-GUI Overview tutorials.

The DFTB-GUI can be launched from ADFJobs or by changing the program from the pull-down menu to DFTB. As such, one can switch seamlessly between different programs, for instance to use DFTB as a pre-optimizer for an ADF or BAND calculations.

Tutorial 1: DFTB charges, frequencies and dynamics (MD)

This tutorial will walk through the main features currently provided by the DFTB engine, using the GUI. DFTB achieves evaluation accuracy at a much lower computational cost than DFT, making it suitable for molecular dynamics evaluations, even on large systems.

We will walk through three different steps in this tutorial. The first step aims at pre-optimizing a simple molecule with DFTB. The second step will evaluate IR frequencies, spectrum and vibrational modes. Finally, the third and last step will perform a simple molecular dynamics evaluation.

Step 1: DFTB: Pre-optimization and Charges

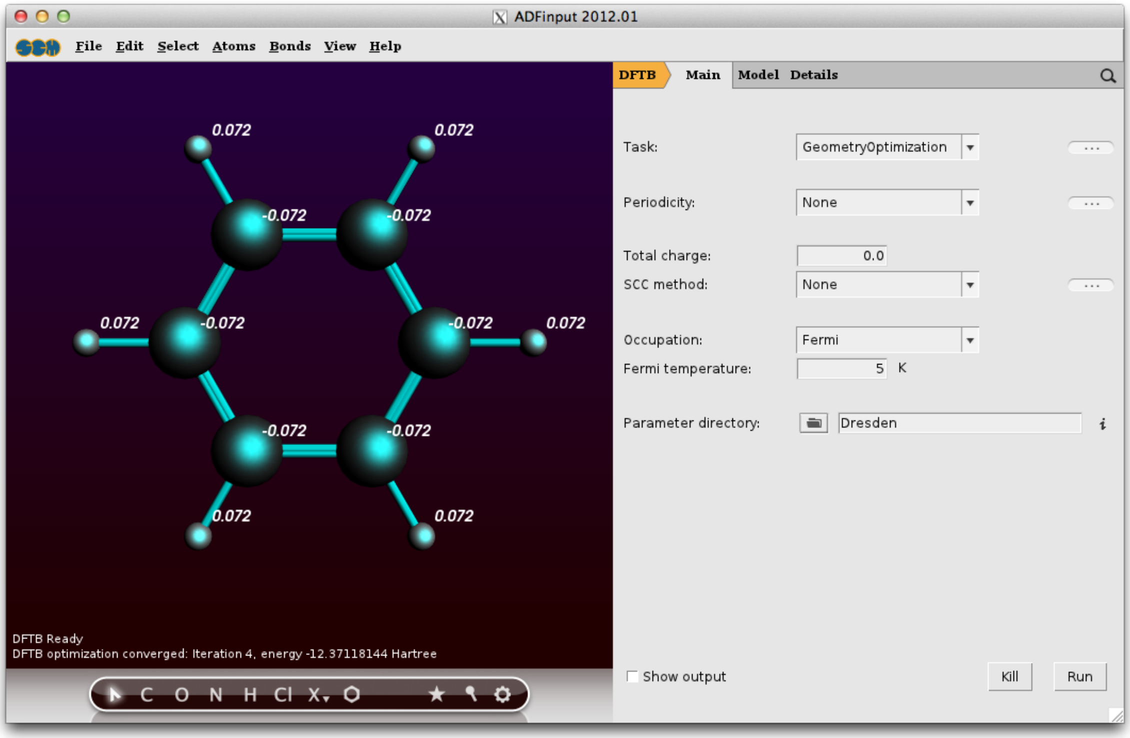
Start ADFjobs
SCM → DFTBinput

Note that DFTBinput and ADFinput are actually identical. By starting DFTBinput from the SCM menu ADFinput will immediately switch to DFTB mode.

In the ADFinput panel:
cmd/ctrl-F, find benzene
Select the entry Benzene(ADF) in the Molecule section of the search result
Select the Main panel
Make sure the **GeometryOptimization** task is selected
Make sure the SCC method is **None**
Make sure the parameter set is "Dresden"
Move your mouse over the parameter set option, and note the references in the help balloon

Click 'Run' in the DFTB panel to optimize the molecule.

When done (DFTB Ready in the lower left corner of the window):
Use the **View → Atom Info → Atomic charge: Net (dftb) → Show** menu command to show the DFTB charges on each atom



DFTB Ready
DFTB optimization converged: Iteration 4, energy -12.37118144 Hartree

Task: GeometryOptimization
Periodicity: None
Total charge: 0.0
SCC method: None
Occupation: Fermi
Fermi temperature: 5 K
Parameter directory: Dresden
☐ Show output

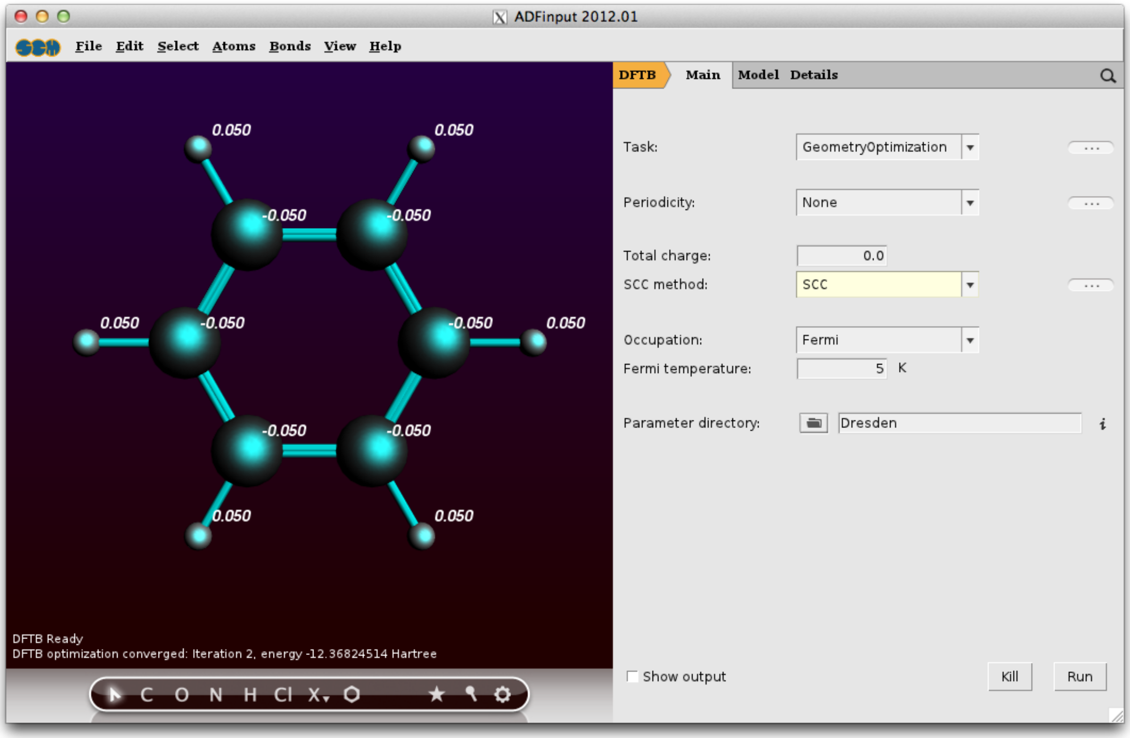
A Self Consistent Charge (SCC) evaluation allows atomic Mulliken charges to vary in an iterative procedure. This influences the DFTB Hamiltonian until self consistence of these charges is reached.

Enabling SCC requires higher computational cost due to the iterative procedure taking place for each energy evaluation, but higher accuracy of the final result. If SCC is disabled, the resulting final charges are not self consistent, thus the procedure will be faster, but less accurate.

`Set the SCC method to` **SCC**

`Click 'Run' again in the DFTB panel to optimize the molecule.`

Note how both equilibrium geometry and atomic charges are affected by the SCC evaluation:



Task: GeometryOptimization

Periodicity: None

Total charge: 0.0

SCC method: SCC

Occupation: Fermi

Fermi temperature: 5 K

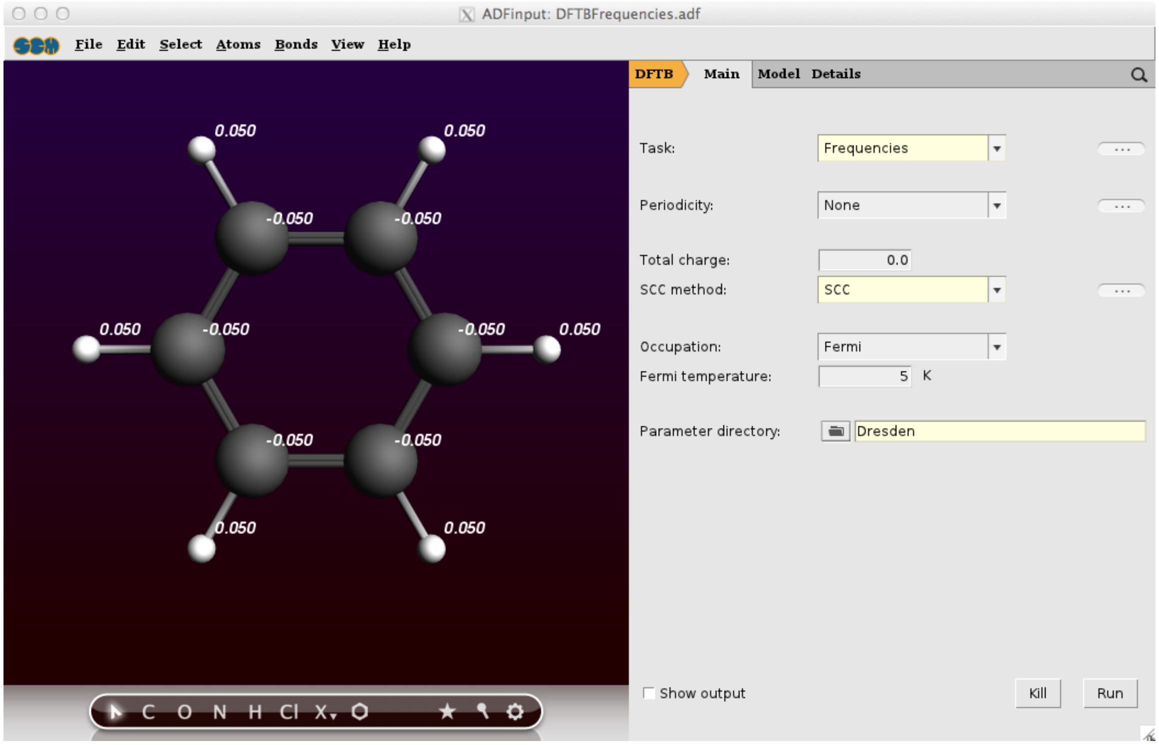
Parameter directory: Dresden

DFTB Ready
DFTB optimization converged: Iteration 2, energy -12.36824514 Hartree

Step 2: Frequency evaluation

This example will show how to compute vibrational frequencies and modes using DFTB.

Choose **Frequencies** as the Task to perform.



Task: Frequencies

Periodicity: None

Total charge: 0.0

SCC method: SCC

Occupation: Fermi

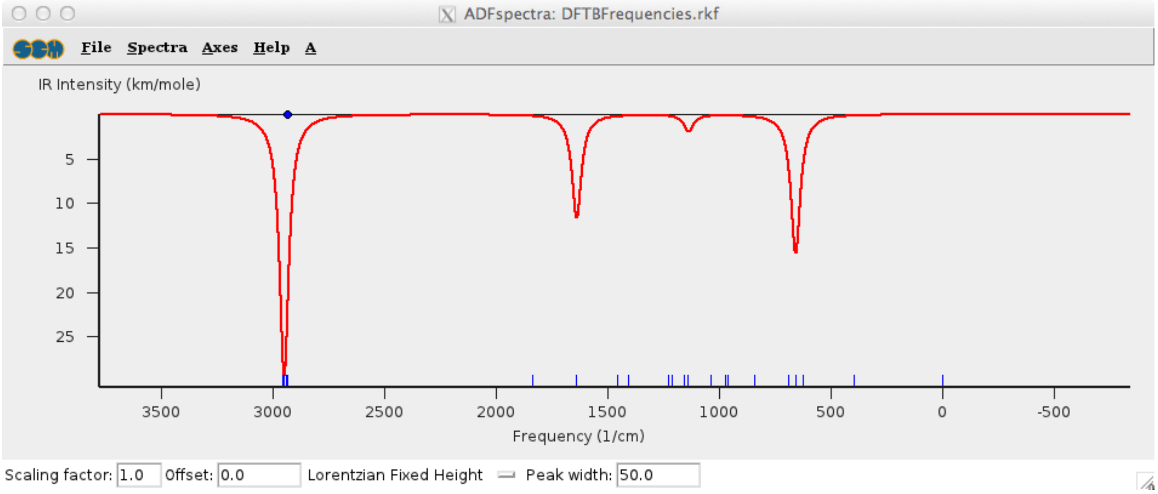
Fermi temperature: 5 K

Parameter directory: Dresden

File → Run, use DFTBFrequencies as name when asked for a name

When the calculation is ready (Job DFTBFrequencies has finished in the logfile):
Close the logfile (**File → Quit**)

In ADFjobs:
Select the "DFTBFrequencies" job
SCM → Spectra
Click on each individual frequency band to show the associated vibrational mode.



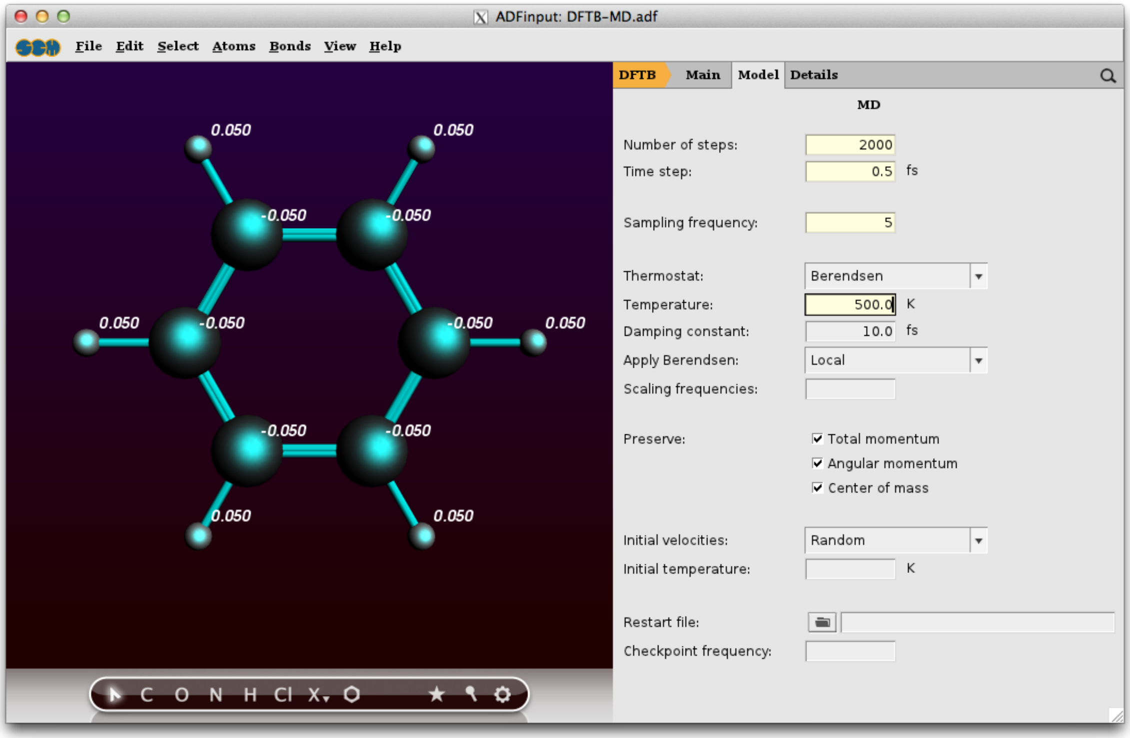
Scaling factor: 1.0 Offset: 0.0 Lorentzian Fixed Height Peak width: 50.0

Step 3: Molecular dynamics

DFTB supports a Velocity Verlet algorithm for Molecular Dynamics. It also supports two types of thermostats. In this example, we will perform a simple molecular dynamics evaluation using DFTB.
In the ADFinput window, choose **MolecularDynamics** as the Task to perform.
Make sure the SCC method **SCC** option is selected, and the parameter set is Dresden

Click on the Details button (...) to the right of the Molecular Dynamics task

Set the **Number of steps** to 2000, the **Time step** to 0.5, and the **Sampling frequency** to 5
Make sure the thermostat is set to Berendsen, and adjust the temperature to 500.0 kelvin.
Save your input choosing **File → Save as ...**, with name "DFTB-MD"



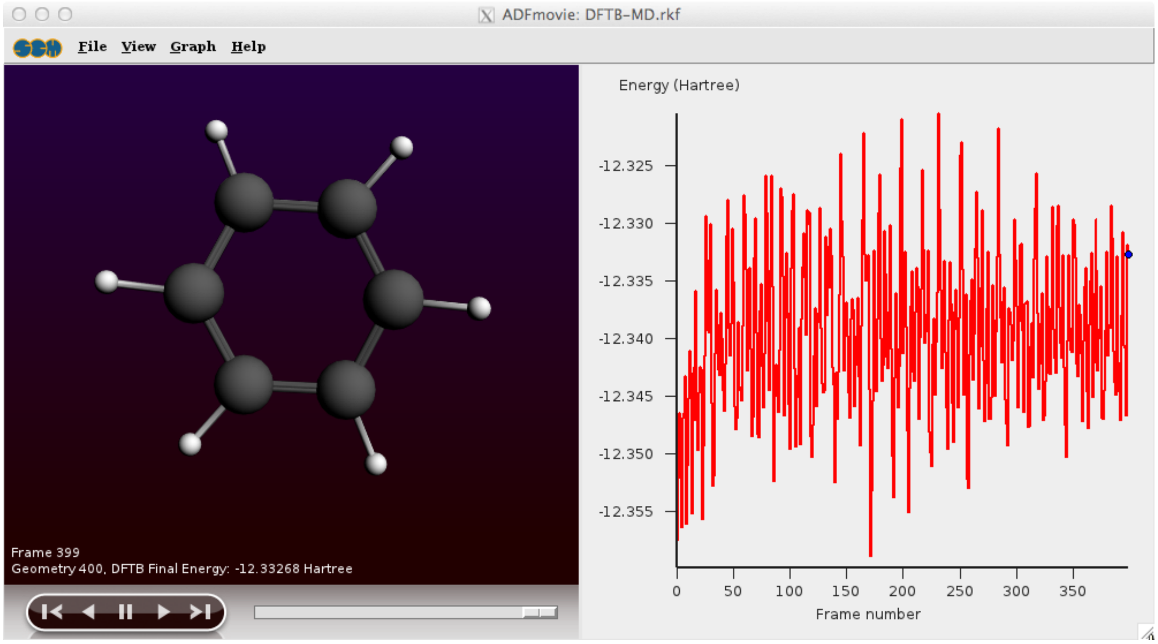
MD

Number of steps: 2000
Time step: 0.5 fs
Sampling frequency: 5
Thermostat: Berendsen
Temperature: 500.0 K
Damping constant: 10.0 fs
Apply Berendsen: Local
Scaling frequencies:
Preserve:
☑ Total momentum
☑ Angular momentum
☑ Center of mass
Initial velocities: Random
Initial temperature: K
Restart file:
Checkpoint frequency:

File → run

You can monitor the calculation in real-time:

While the calculation is running: **SCM → Movie**
In the ADFmovie window: **Graph → Energy**



Frame 399
Geometry 400, DFTB Final Energy: -12.33268 Hartree

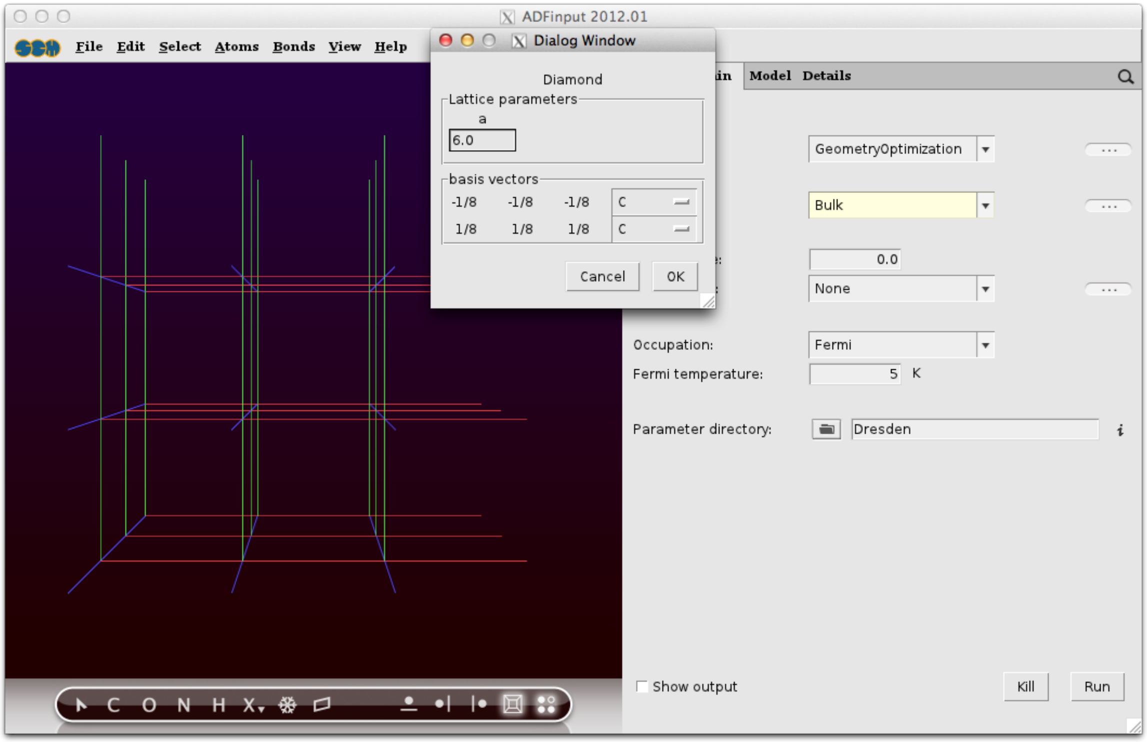
Tutorial 2: Periodic DFTB, Lattice Optimization, DOS, band structure and phonons

This tutorial will walk through the use of periodic DFTB to optimize the lattice parameters. The density of states and band structure of the optimized structures will be displayed.

Step 1: Lattice optimization - input setup

To perform geometry optimization of a lattice, we will start from a diamond crystal with incorrect lattice values, and let DFTB optimize this value. Next, we will proceed to display additional information obtained during the evaluation.

Start ADFinput
Select the DFTB panel: panel bar **ADF → DFTB**
Choose **Bulk** to enable periodicity.
Click the structure tool (the snowflake next to the X tool),
Choose **Cubic → Diamond**
Set the cell parameter **a** to 6.0 and click OK



Diamond

Lattice parameters

a

6.0

basis vectors

-1/8	-1/8	-1/8	C
1/8	1/8	1/8	C

GeometryOptimization

Bulk

0.0

None

Occupation: Fermi

Fermi temperature: 5 K

Parameter directory: Dresden

☐ Show output

Click the Details button (...) for the GeometryOptimization task
Check the **Optimize Lattice** box
Go to the Main panel
Make sure SCC is set to None, and that the Dresden parameter set is selected
Choose **File → Save as...** and save the input as "DFTB-Diamond".

Step 2: Lattice optimization - execution

File → Run.
While the optimization is running, you can watch the progress by clicking **SCM → Movie**

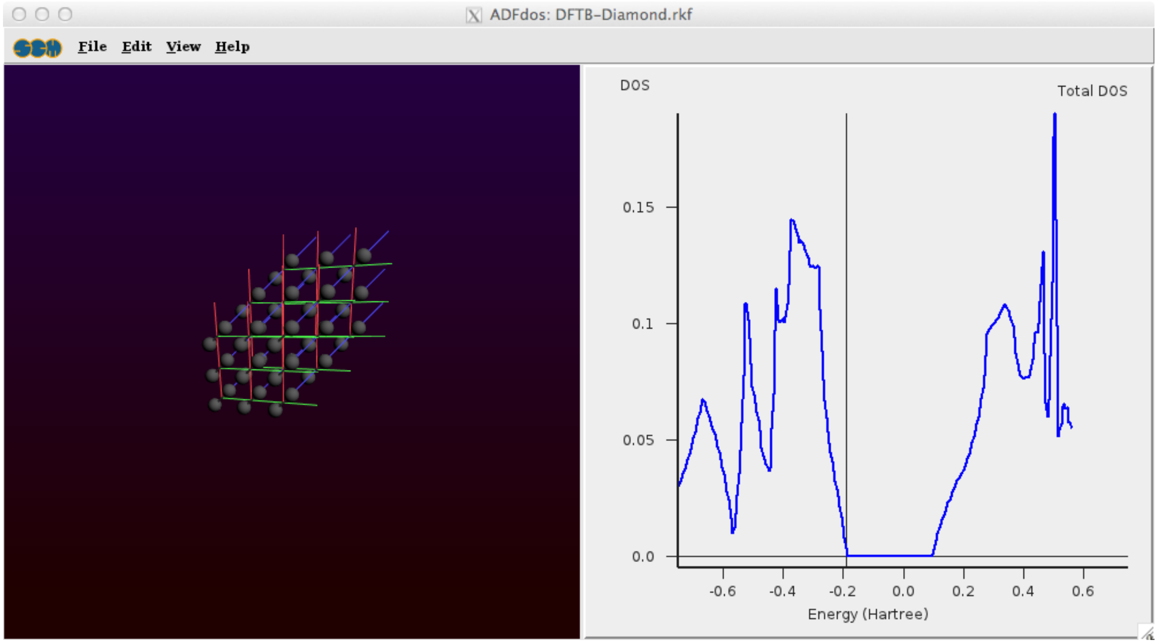
Update the geometry in ADFinput when the job is finished

From the movie, you can observe how the unit cell shrinks as it is optimized.

Step 3: DOS and Band Structure

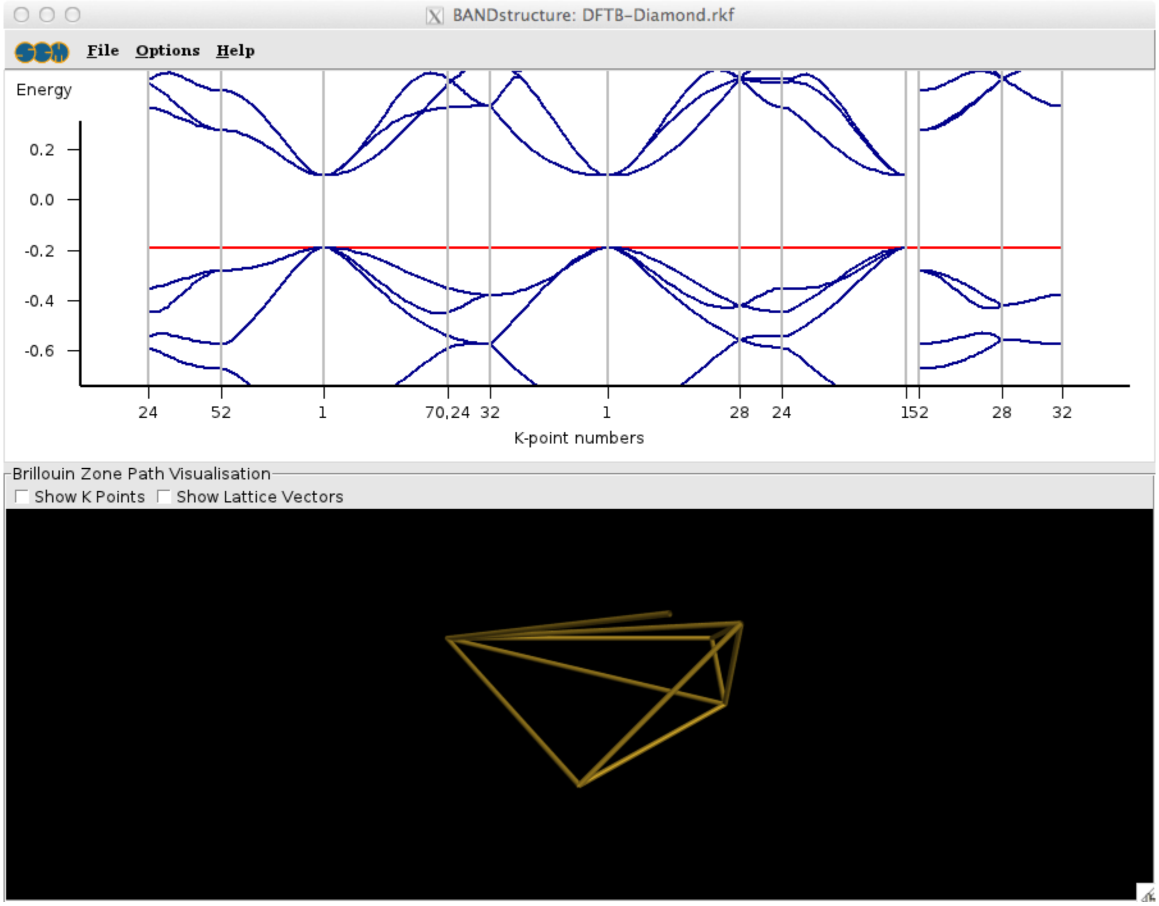
You can visualize the density of states (DOS) directly from the converged optimization.

SCM → DOS (in the ADFmovie or ADFinput window)



Similarly, you can visualize the band structure

SCM → Band Structure



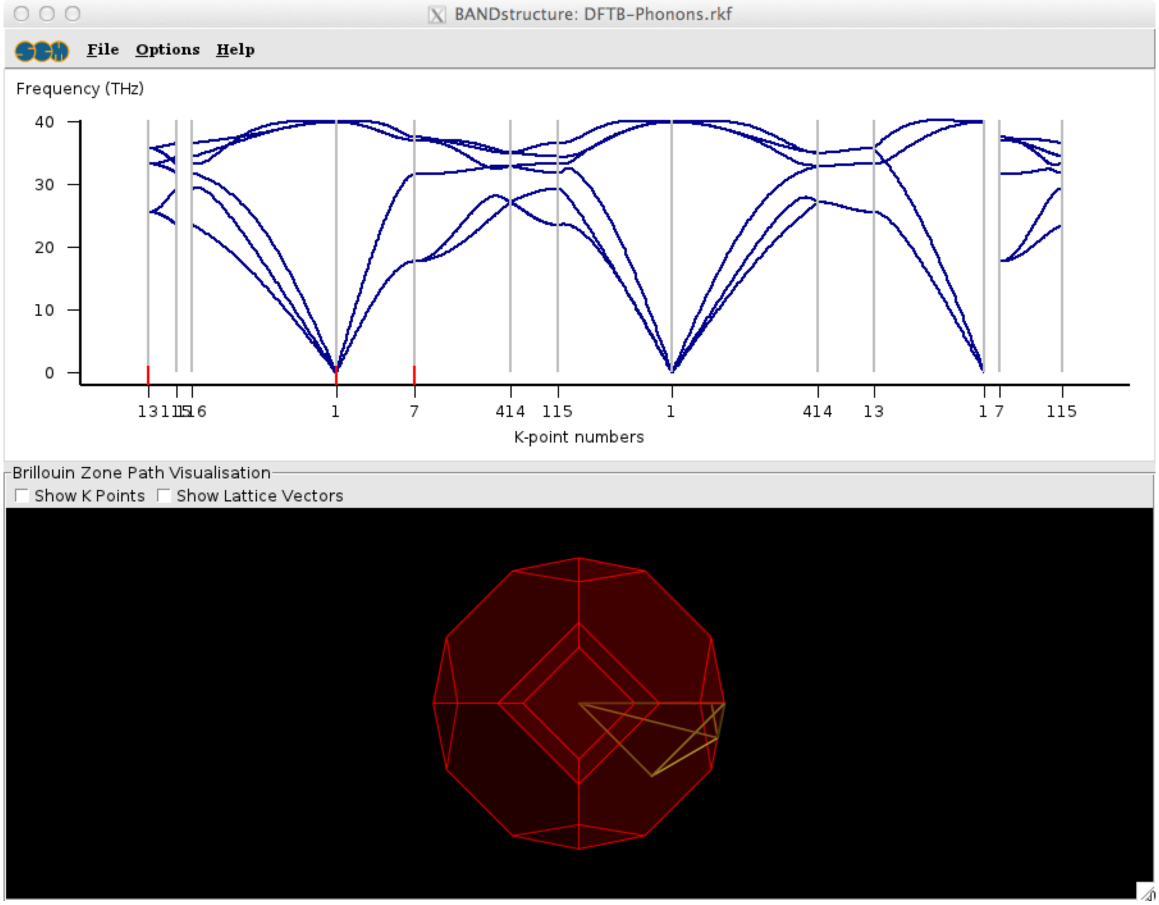
Step 4: Phonons

Activate the ADFinput window with the DFTB-Diamond input
Select "Phonons" as Task
File → Save as..., use "DFTB-Phonons" as filename

File → Run

When completed: use **SCM → Band Structure** in the ADFtail window (showing the logfile)

A window will appear showing the phonons diagram. Clicking on the curves at the location of the vertical red bars will show the actual crystal vibrations.



Tutorial 3: Proton affinities with third order DFTB (DFTB3)

In this tutorial we will calculate a proton affinity, defined as the negative gas phase enthalpy for the protonation reaction $A^- + H^+ \rightarrow AH$. Gaus, Cui and Elstner have shown that third-order terms (DFTB3) generally improve the proton affinities with respect to second order self-consistent charges (SCC).

We will calculate the proton affinity of the acetate anion, CH_3COO^-. In the first step of this tutorial, we will optimize acetic acid at the DFTB3 level. The second step will perform the computation on the anionic species, and compute its proton affinity.

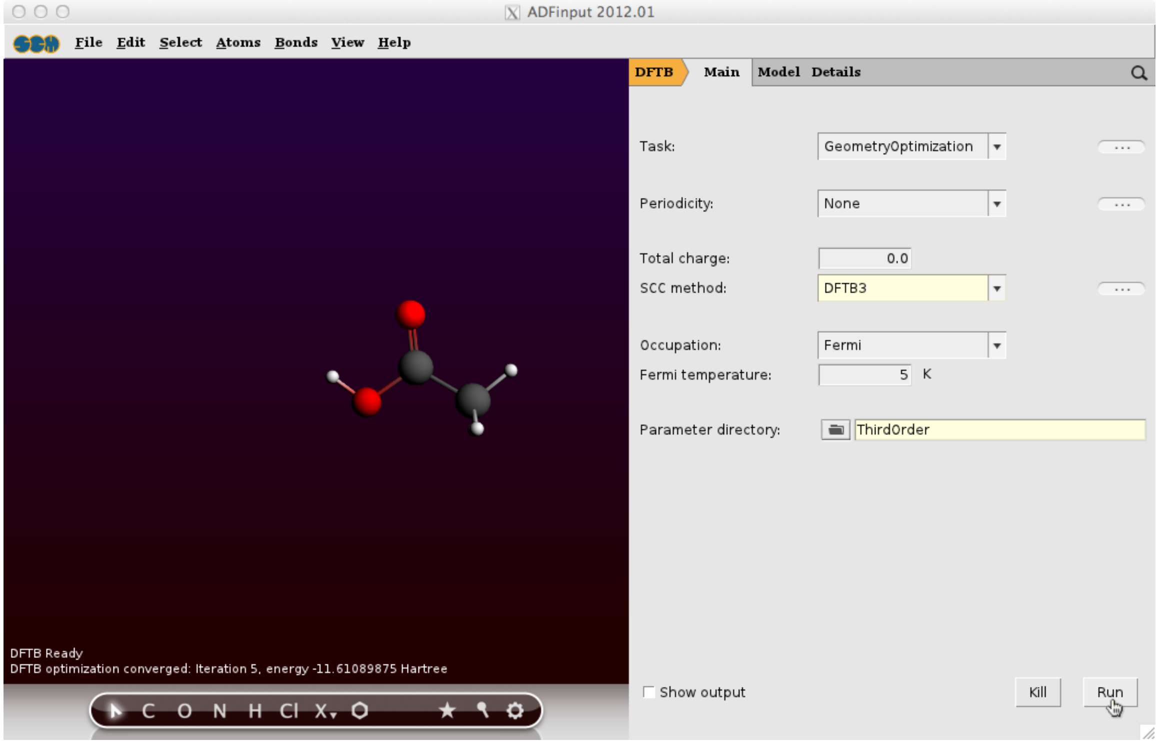
Contact us to enable parameter files from DFTB.org, including the ThirdOrder set for DFTB3, needed to run this tutorial. For non-profit users there is no additional charge for this.

Step 1: Optimization of the neutral molecule

Start ADFjobs
SCM → DFTBinput
Use the **Structure tool**, select **Solvents → Acetic acid**
Click anywhere in the visualization pane. The acetic acid molecule will appear.
Make sure the **GeometryOptimization** task is selected and charge is set to **0.0**
Select **DFTB3** as the SCC method
Select the **ThirdOrder** parameter set.

Click 'Run' in the DFTB panel to optimize the molecule.

When the optimization is complete (DFTB Ready in the lower left corner of the window), note the final energy (for the paramenter set used in this example, E(HAc) = -11.610899 Hartree)



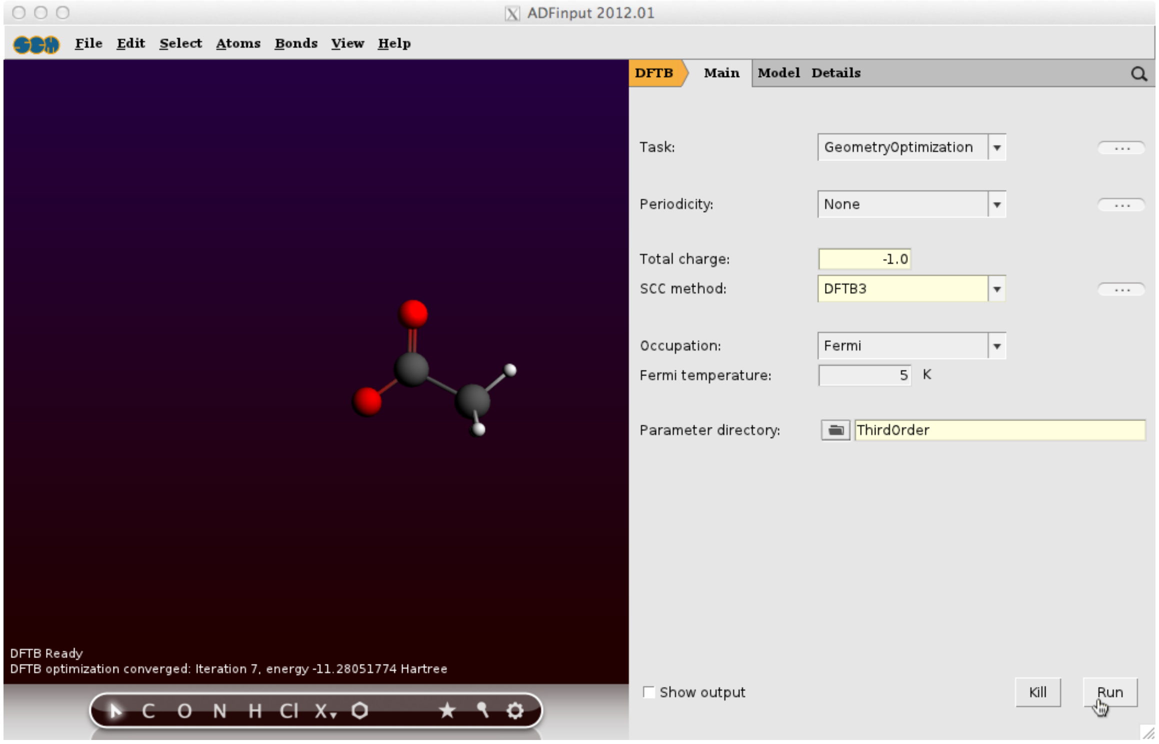
Task: GeometryOptimization
Periodicity: None
Total charge: 0.0
SCC method: DFTB3
Occupation: Fermi
Fermi temperature: 5 K
Parameter directory: ThirdOrder

DFTB Ready
DFTB optimization converged: Iteration 5, energy -11.61089875 Hartree

Step 2: Optimization of the acetate and the hydrogen ions

In order to perform the calculation on the acetate ion, we will remove the hydrogen ion from the previously computed acetic acid molecule.
Select the hydrogen in the COOH group by clicking on it.
Press the Backspace key on your keyboard. This will delete the hydrogen atom.
Select the Main panel
Set the charge to **-1.0**

Click 'Run' in the DFTB panel to optimize the molecule.



Task: GeometryOptimization

Periodicity: None

Total charge: -1.0

SCC method: DFTB3

Occupation: Fermi

Fermi temperature: 5 K

Parameter directory: ThirdOrder

DFTB Ready

DFTB optimization converged: Iteration 7, energy -11.28051774 Hartree

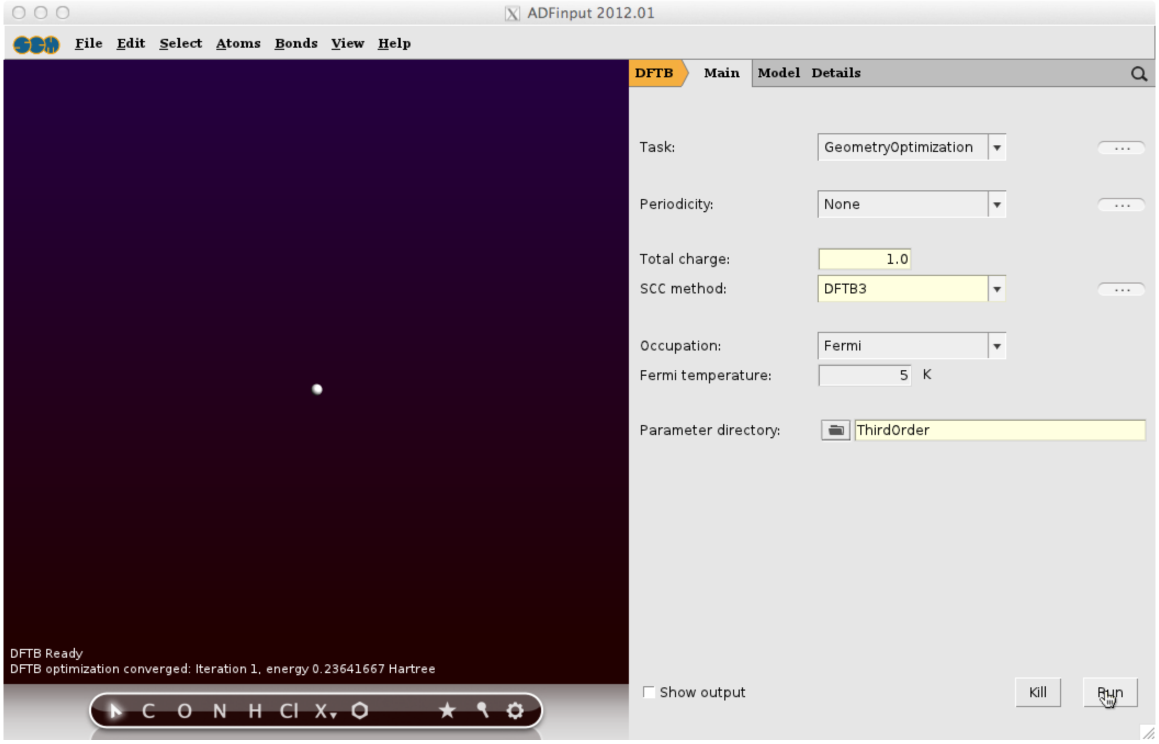
At the end of the procedure, note the final energy (for the parameter set used in this example, $E(Ac^-)$ = -11.280518 Hartree).

Additionally, the energy of the lone proton must be obtained.

Select and delete every atom of the molecule, except one hydrogen atom.
Select the Main panel
Make sure the **GeometryOptimization** task is selected. Although this is effectively a single point calculation, the GeometryOptimization task reports the energy directly in the molecule window, facilitating the read out of the energy.

Set the charge to **1.0**

Click 'Run' in the DFTB panel.



DFTB Ready
DFTB optimization converged: Iteration 1, energy 0.23641667 Hartree

Task: GeometryOptimization
Periodicity: None
Total charge: 1.0
SCC method: DFTB3
Occupation: Fermi
Fermi temperature: 5 K
Parameter directory: ThirdOrder

Finally, annotate the value for E(H^+) = 0.236417 Hartree. The proton affinity is computed as PA = E(Ac^-) + E(H^+) - E(HAc), resulting in a final Proton Affinity of 0.566798 Hartree, or 355.67 kcal/mol.

We leave it as an example to calculate the PA with DFTB2 (SCC), and compare it with the high-level ab initio results that are also quoted in the DFTB3 paper.

MOPAC-GUI tutorial

This section contains tutorials that show you how to use MOPAC via the MOPAC-GUI. As the MOPAC-GUI is very similar to the ADF-GUI, we will focus here on MOPAC specific features.

If you are not familiar with the ADF-GUI (or the MOPAC-GUI), please have a look at the Introduction and ADF-GUI Overview tutorials.

For example, it will show you how to start the MOPAC-GUI.

MOPAC (Molecular Orbital PACkage) is a semiempirical quantum chemistry program based on Dewar and Thiel's NDDO approximation. It is available from OpenMOPAC. The documentation for MOPAC is also available on that site.

MOPAC is included with the ADF distribution. However, it needs to be enabled in your license file. If it is not enabled, please contact SCM to get more information. Note that MOPAC is free for academic users. The MOPAC that is included with the ADF distribution is just the standard MOPAC from OpenMOPAC, and is updated frequently.

If you wish to use a MOPAC version different from the one included with the ADF distribution, you can do this by setting the SCM_MOPAC environment variable, either in your shell startup script or via the **SCM → Preferences** command:

- do not set SCM_MOPAC when you want to run the MOPAC included with the ADF pacakage, in most situations this is the easiest solution
- set SCM_MOPAC to the complete path to the Mopac executable
- set SCM_MOPAC to some command if want to run MOPAC on a different machine, the command must pass the arguments and standard input, and should start the mopac.scm script on the other machine (located in $ADFHOME/bin)

Tutorial 1: Toluene charges, movies, frequencies and normal modes

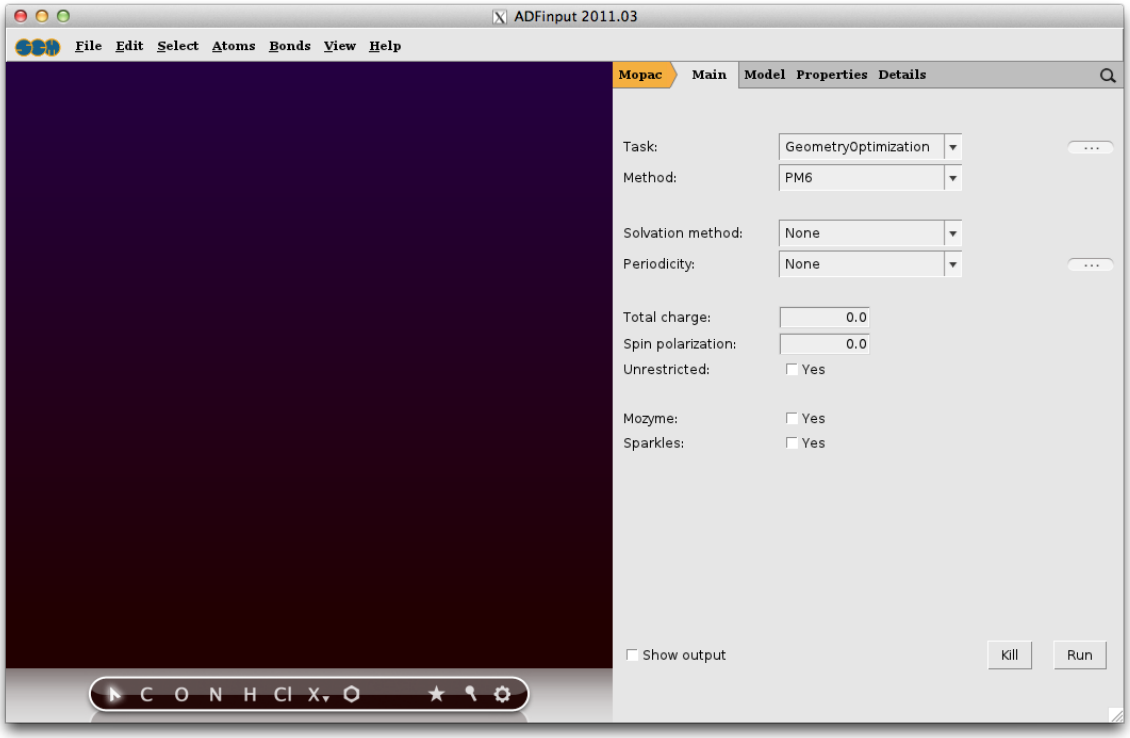
The MOPAC-GUI is basically the same set of programs as the ADF-GUI. we suggest you start with the ADF-GUI tutorials if you are not familiar with the ADF-GUI.

When saving a job and running, MOPAC will be executed. The MOPAC results (output and AUX file) will be converted to a .rkf result file, that allows visualization of the results with the GUI modules like ADFview, ADFmovie and ADFspectra. Results that may be visualized include geometry, optimization changes (with energy), charges, bond orders, frequencies and normal modes. Obviously the MOPAC output file is also available

This tutorial will give you an example how to use MOPAC via the MOPAC-GUI from SCM.

Set up Toluene in MOPACinput

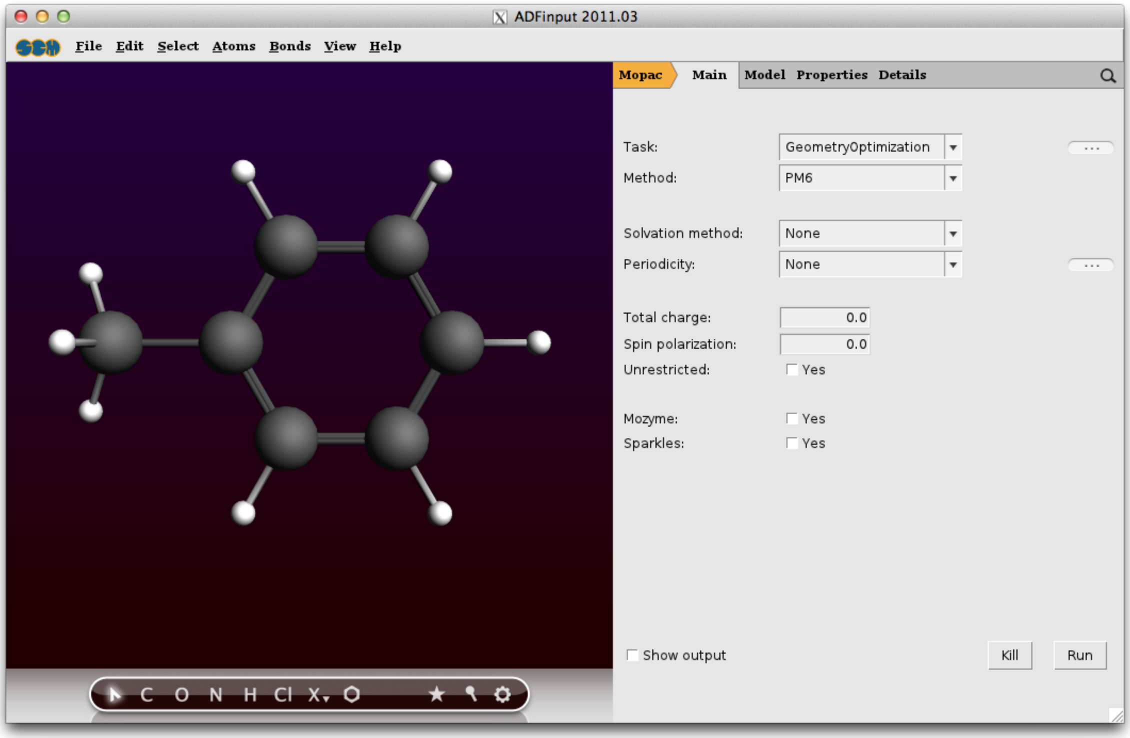
`Start ADFjobs`
SCM → DFTBinput
`In the DFTBinput window:`
`Panel bar` **DFTB → Mopac** `(thus, click on 'DFTB', and select Mopac from the menu)`



Task: GeometryOptimization
Method: PM6
Solvation method: None
Periodicity: None
Total charge: 0.0
Spin polarization: 0.0
Unrestricted: ☐ Yes
Mozyme: ☐ Yes
Sparkles: ☐ Yes

We will now make a Toluene molecule. Most conveniently this is done by simply searching for it within the MOPAC-GUI:

```
Control/Command-F
Enter 'toluene' as search text
Select 'Toluen' (the second match) from the list of matches
Click once in the drawing area in empty space to clear the selection
```

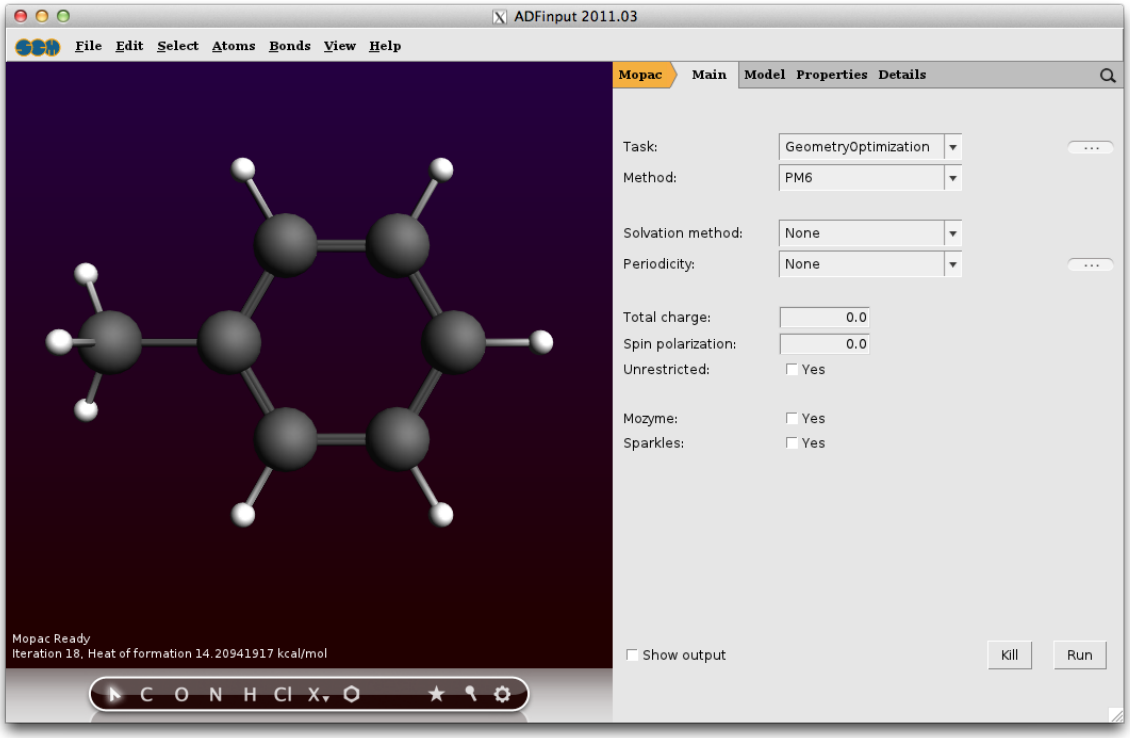


Task: GeometryOptimization
Method: PM6
Solvation method: None
Periodicity: None
Total charge: 0.0
Spin polarization: 0.0
Unrestricted: ☐ Yes
Mozyme: ☐ Yes
Sparkles: ☐ Yes
☐ Show output

Run interactively

In the Mopac Main panel you can see what options for MOPAC have been selected: by default a Geometry optimization will be performed, using the PM6 method. MOPAC will also calculate the bond orders, and the GUI will automatically update the molecular bonds using these calculated bond orders. To show this, we will first remove the bonds and then run MOPAC by pressing the Run button:

Bonds → Remove Bonds
`Press the 'Run' button`



Task: GeometryOptimization

Method: PM6

Solvation method: None

Periodicity: None

Total charge: 0.0

Spin polarization: 0.0

Unrestricted: ☐ Yes

Mozyme: ☐ Yes

Sparkles: ☐ Yes

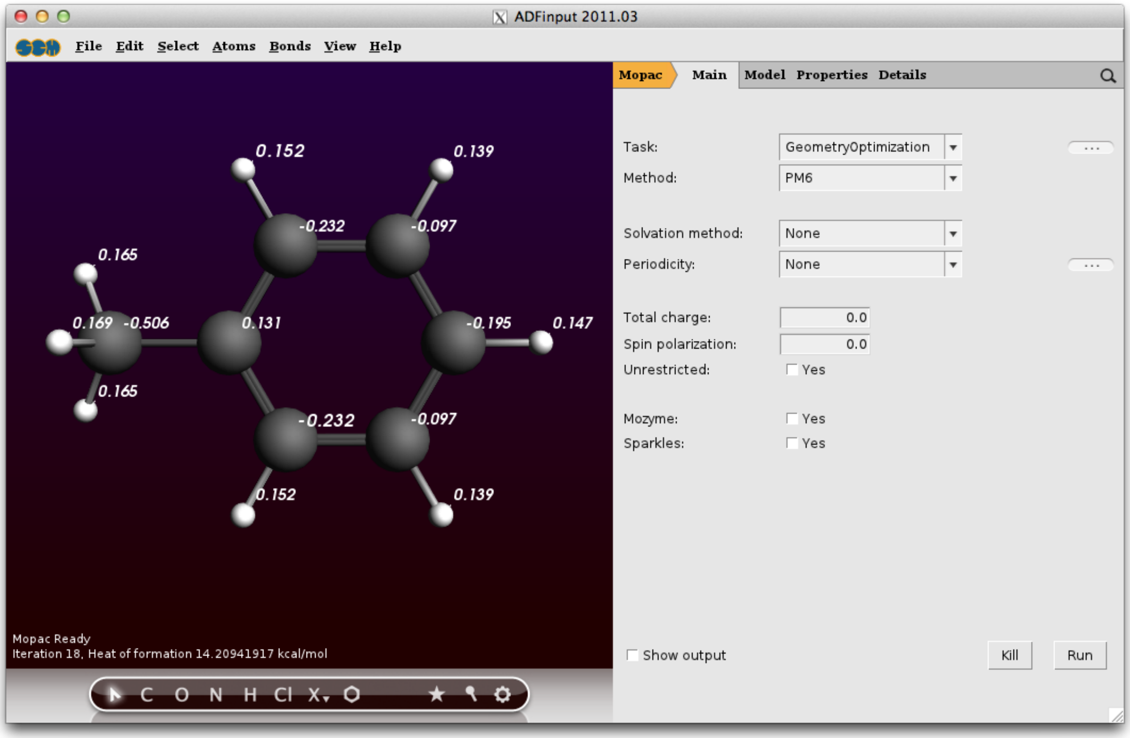
☐ Show output

Mopac Ready
Iteration 18, Heat of formation 14.20941917 kcal/mol

The geometry has been optimized, but as the starting geometry was very reasonable this did not lead to big changes. In the status area you can see that MOPAC used 18 iterations, and you can see the final heat of formation. And obviously the bonds reappeared. These bonds are actually based on the bond orders as calculated by MOPAC.

You can now also show the calculated atomic charges:

View → Atom Info → Mopac Charges → Show



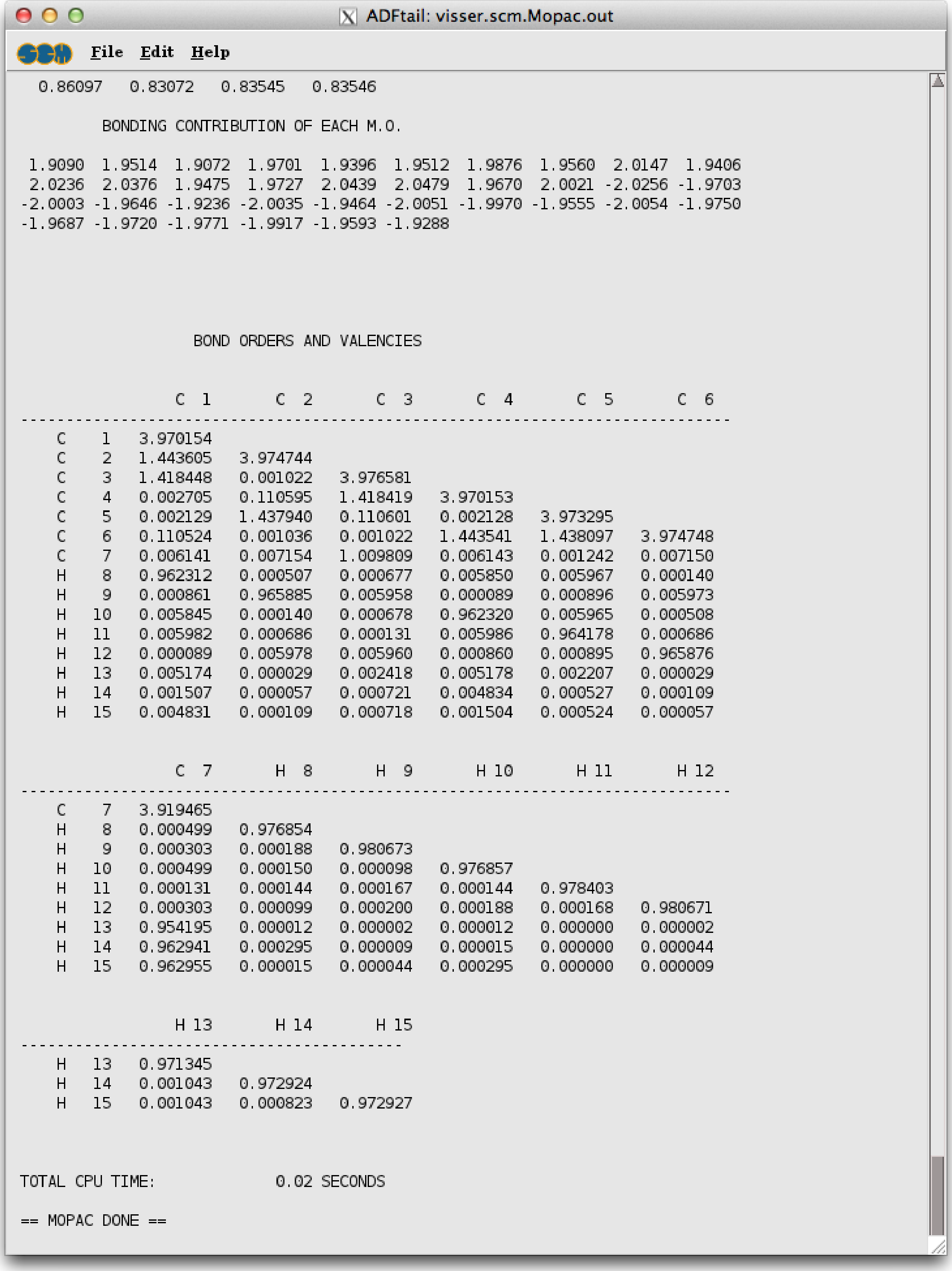
Task: GeometryOptimization
Method: PM6
Solvation method: None
Periodicity: None
Total charge: 0.0
Spin polarization: 0.0
Unrestricted: ☐ Yes
Mozyme: ☐ Yes
Sparkles: ☐ Yes
☐ Show output

Mopac Ready
Iteration 18, Heat of formation 14.20941917 kcal/mol

To see the MOPAC output, check the 'Show output' check box. And there is another way to run MOPAC interactively: use the pre-optimizer button (the cog wheel).

`Check the 'Show output' check box`

`Right-click on the cog-wheel (the pre-optimizer button), and select Mopac from the menu`



```
  0.86097    0.83072    0.83545    0.83546

         BONDING CONTRIBUTION OF EACH M.O.

 1.9090  1.9514  1.9072  1.9701  1.9396  1.9512  1.9876  1.9560  2.0147  1.9406
 2.0236  2.0376  1.9475  1.9727  2.0439  2.0479  1.9670  2.0021 -2.0256 -1.9703
-2.0003 -1.9646 -1.9236 -2.0035 -1.9464 -2.0051 -1.9970 -1.9555 -2.0054 -1.9750
-1.9687 -1.9720 -1.9771 -1.9917 -1.9593 -1.9288





                   BOND ORDERS AND VALENCIES


                 C  1       C  2       C  3       C  4       C  5       C  6
------------------------------------------------------------------------------
    C    1   3.970154
    C    2   1.443605   3.974744
    C    3   1.418448   0.001022   3.976581
    C    4   0.002705   0.110595   1.418419   3.970153
    C    5   0.002129   1.437940   0.110601   0.002128   3.973295
    C    6   0.110524   0.001036   0.001022   1.443541   1.438097   3.974748
    C    7   0.006141   0.007154   1.009809   0.006143   0.001242   0.007150
    H    8   0.962312   0.000507   0.000677   0.005850   0.005967   0.000140
    H    9   0.000861   0.965885   0.005958   0.000089   0.000896   0.005973
    H   10   0.005845   0.000140   0.000678   0.962320   0.005965   0.000508
    H   11   0.005982   0.000686   0.000131   0.005986   0.964178   0.000686
    H   12   0.000089   0.005978   0.005960   0.000860   0.000895   0.965876
    H   13   0.005174   0.000029   0.002418   0.005178   0.002207   0.000029
    H   14   0.001507   0.000057   0.000721   0.004834   0.000527   0.000109
    H   15   0.004831   0.000109   0.000718   0.001504   0.000524   0.000057


                 C  7       H  8       H  9       H 10       H 11       H 12
------------------------------------------------------------------------------
    C    7   3.919465
    H    8   0.000499   0.976854
    H    9   0.000303   0.000188   0.980673
    H   10   0.000499   0.000150   0.000098   0.976857
    H   11   0.000131   0.000144   0.000167   0.000144   0.978403
    H   12   0.000303   0.000099   0.000200   0.000188   0.000168   0.980671
    H   13   0.954195   0.000012   0.000002   0.000012   0.000000   0.000002
    H   14   0.962941   0.000295   0.000009   0.000015   0.000000   0.000044
    H   15   0.962955   0.000015   0.000044   0.000295   0.000000   0.000009


                 H 13       H 14       H 15
------------------------------------------
    H   13   0.971345
    H   14   0.001043   0.972924
    H   15   0.001043   0.000823   0.972927



TOTAL CPU TIME:             0.02 SECONDS

== MOPAC DONE ==
```

As the geometry already had been optimized, nothing much happens. Except the MOPAC output file will be opened and appear in a new window. This file actually starts with the AUX file, followed by the output file.

`Close all windows except ADFjobs (no need to save your setup)`

Save job and results: charges and movies

The previous section showed how to run MOPAC interactively, typically to be used as a pre-optimizer. However, you can also run the MOPAC calculation as a 'real' job. Then the result files will be saved, and you can analyze them with the GUI tools.

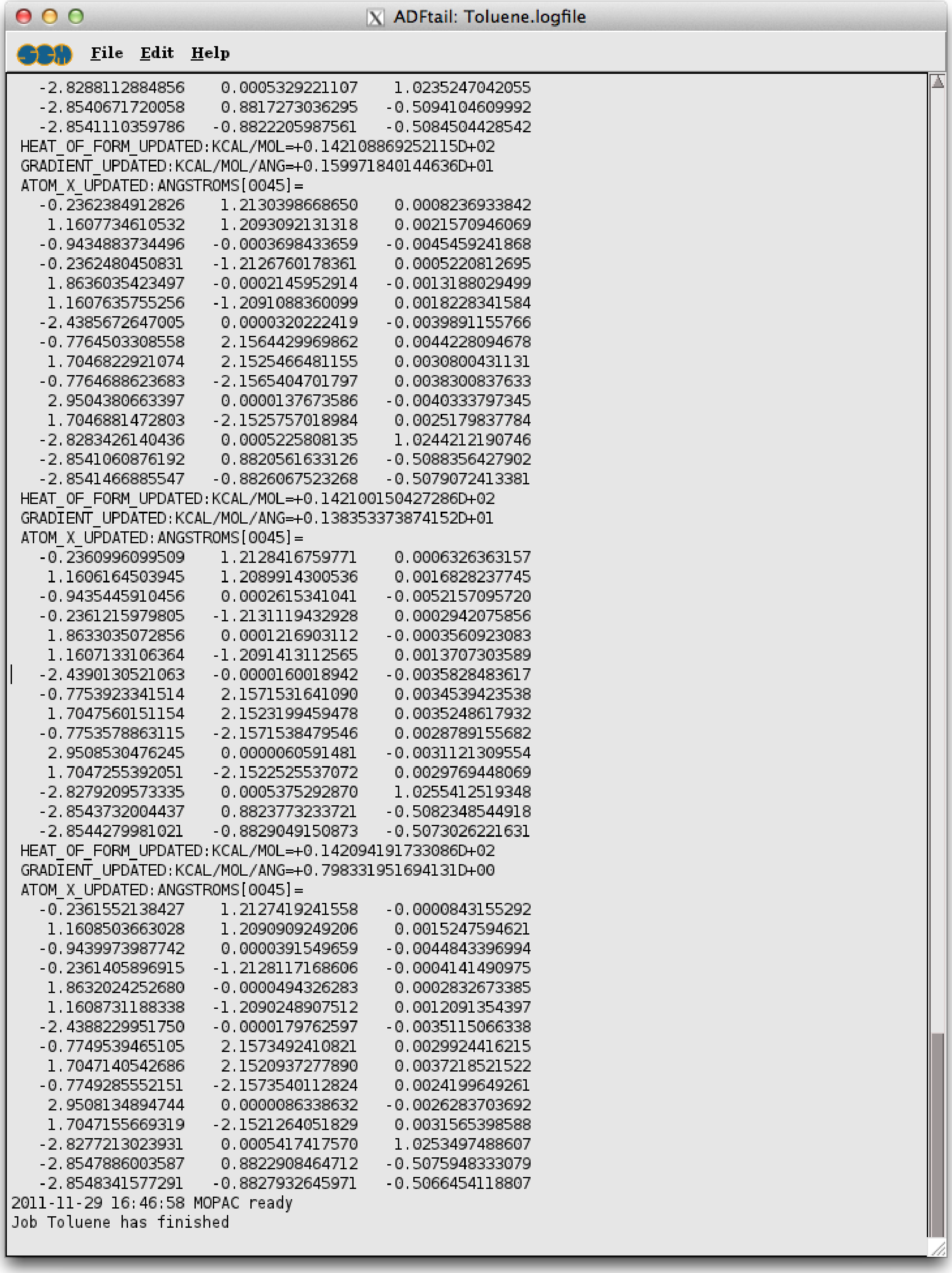
SCM → DFTBinput
`In the DFTBinput window:`

`Panel bar` **DFTB → Mopac** `(thus, click on 'DFTB', and select Mopac from the menu)`
`Control/Command-F`
`Enter 'toluene' as search text`
`Select 'Toluen' (the second match) from the list of matches`
`Click once in the drawing area in empty space to clear the selection`
`Check the 'Show output' check box`

Once again we have our Toluene molecule. Now to run it as a job simply use the Save and Run command from the menu:

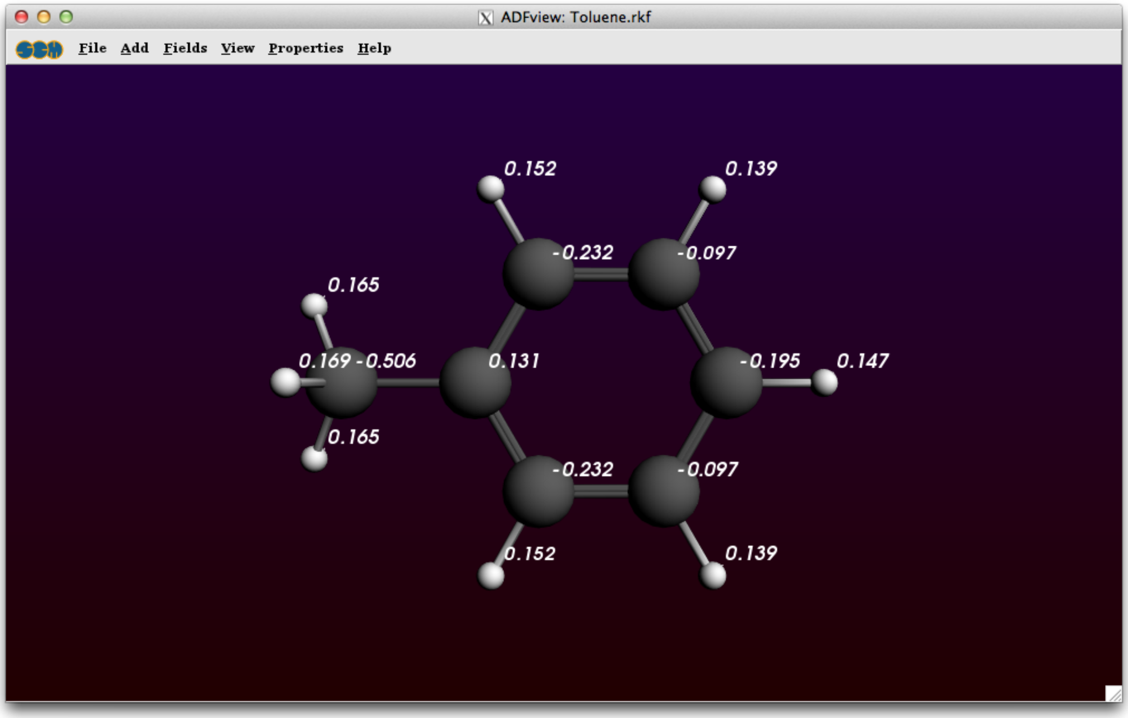
File → Save`, save the job with name 'Toluene'`
File → Run
`When asked to read the new coordinates (when the calculation finishes), click Yes`
SCM → Logfile

The logfile will show the progress of the calculation:



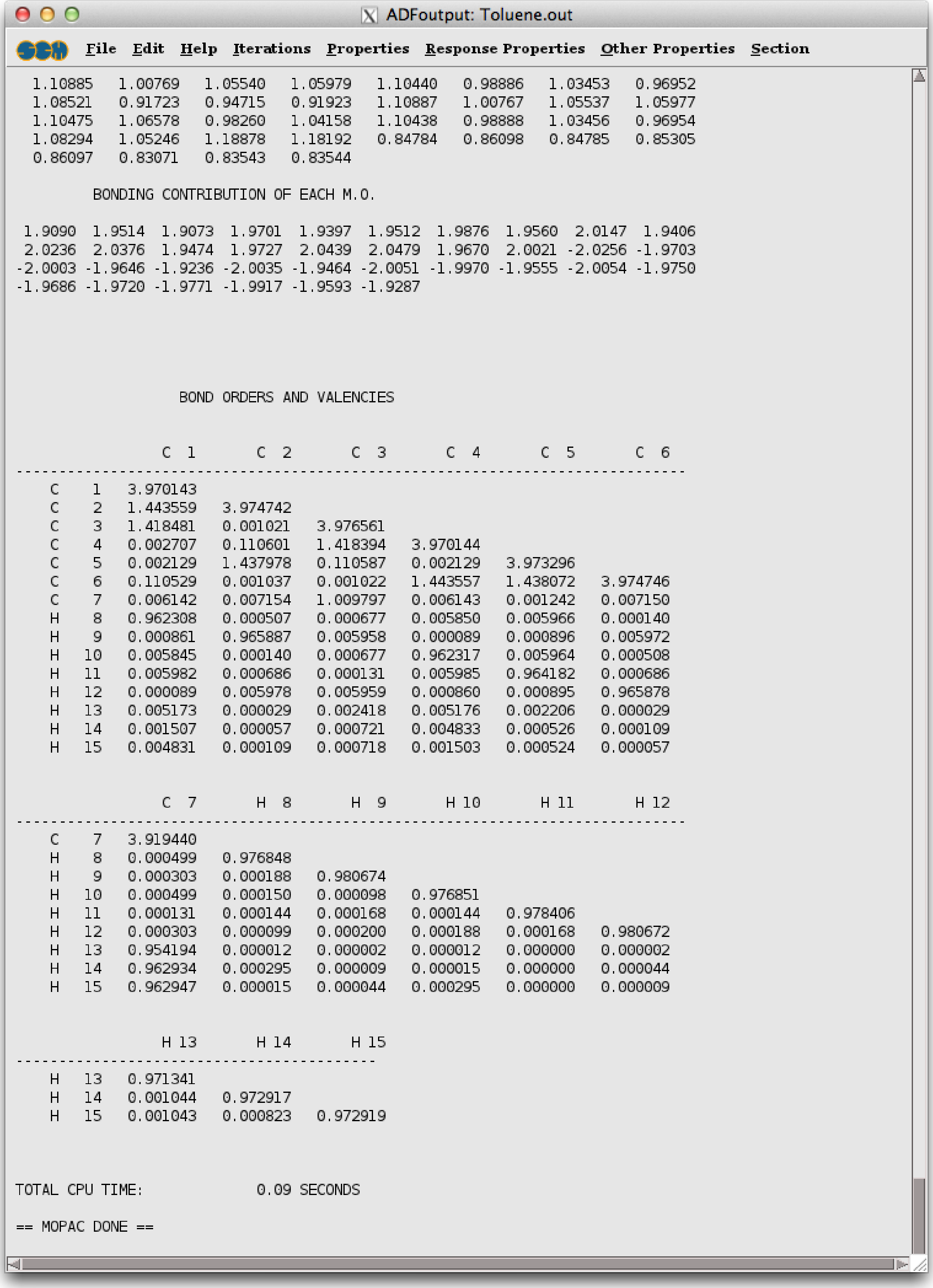
```
   -2.8288112884856    0.0005329221107    1.0235247042055
   -2.8540671720058    0.8817273036295   -0.5094104609992
   -2.8541110359786   -0.8822205987561   -0.5084504428542
 HEAT_OF_FORM_UPDATED:KCAL/MOL=+0.142108869252115D+02
 GRADIENT_UPDATED:KCAL/MOL/ANG=+0.159971840144636D+01
 ATOM_X_UPDATED:ANGSTROMS[0045]=
   -0.2362384912826    1.2130398668650    0.0008236933842
    1.1607734610532    1.2093092131318    0.0021570946069
   -0.9434883734496   -0.0003698433659   -0.0045459241868
   -0.2362480450831   -1.2126760178361    0.0005220812695
    1.8636035423497   -0.0002145952914   -0.0013188029499
    1.1607635755256   -1.2091088360099    0.0018228341584
   -2.4385672647005    0.0000320222419   -0.0039891155766
   -0.7764503308558    2.1564429969862    0.0044228094678
    1.7046822921074    2.1525466481155    0.0030800431131
   -0.7764688623683   -2.1565404701797    0.0038300837633
    2.9504380663397    0.0000137673586   -0.0040333797345
    1.7046881472803   -2.1525757018984    0.0025179837784
   -2.8283426140436    0.0005225808135    1.0244212190746
   -2.8541060876192    0.8820561633126   -0.5088356427902
   -2.8541466885547   -0.8826067523268   -0.5079072413381
 HEAT_OF_FORM_UPDATED:KCAL/MOL=+0.142100150427286D+02
 GRADIENT_UPDATED:KCAL/MOL/ANG=+0.138353373874152D+01
 ATOM_X_UPDATED:ANGSTROMS[0045]=
   -0.2360996099509    1.2128416759771    0.0006326363157
    1.1606164503945    1.2089914300536    0.0016828237745
   -0.9435445910456    0.0002615341041   -0.0052157095720
   -0.2361215979805   -1.2131119432928    0.0002942075856
    1.8633035072856    0.0001216903112   -0.0003560923083
    1.1607133106364   -1.2091413112565    0.0013707303589
   -2.4390130521063   -0.0000160018942   -0.0035828483617
   -0.7753923341514    2.1571531641090    0.0034539423538
    1.7047560151154    2.1523199459478    0.0035248617932
   -0.7753578863115   -2.1571538479546    0.0028789155682
    2.9508530476245    0.0000060591481   -0.0031121309554
    1.7047255392051   -2.1522525537072    0.0029769448069
   -2.8279209573335    0.0005375292870    1.0255412519348
   -2.8543732004437    0.8823773233721   -0.5082348544918
   -2.8544279981021   -0.8829049150873   -0.5073026221631
 HEAT_OF_FORM_UPDATED:KCAL/MOL=+0.142094191733086D+02
 GRADIENT_UPDATED:KCAL/MOL/ANG=+0.798331951694131D+00
 ATOM_X_UPDATED:ANGSTROMS[0045]=
   -0.2361552138427    1.2127419241558   -0.0000843155292
    1.1608503663028    1.2090909249206    0.0015247594621
   -0.9439973987742    0.0000391549659   -0.0044843396994
   -0.2361405896915   -1.2128117168606   -0.0004141490975
    1.8632024252680   -0.0000494326283    0.0002832673385
    1.1608731188338   -1.2090248907512    0.0012091354397
   -2.4388229951750   -0.0000179762597   -0.0035115066338
   -0.7749539465105    2.1573492410821    0.0029924416215
    1.7047140542686    2.1520937277890    0.0037218521522
   -0.7749285552151   -2.1573540112824    0.0024199649261
    2.9508134894744    0.0000086338632   -0.0026283703692
    1.7047155669319   -2.1521264051829    0.0031565398588
   -2.8277213023931    0.0005417417570    1.0253497488607
   -2.8547886003587    0.8822908464712   -0.5075948333079
   -2.8548341577291   -0.8827932645971   -0.5066454118807
2011-11-29 16:46:58 MOPAC ready
Job Toluene has finished
```

SCM → View
Properties → Atom Info → Atom Charge: Net (mopac) → Show



As the 'Show Output' check box has been checked, the Mopac output is available:

`Close the ADFview window`
SCM → Output
`Scroll to the end`



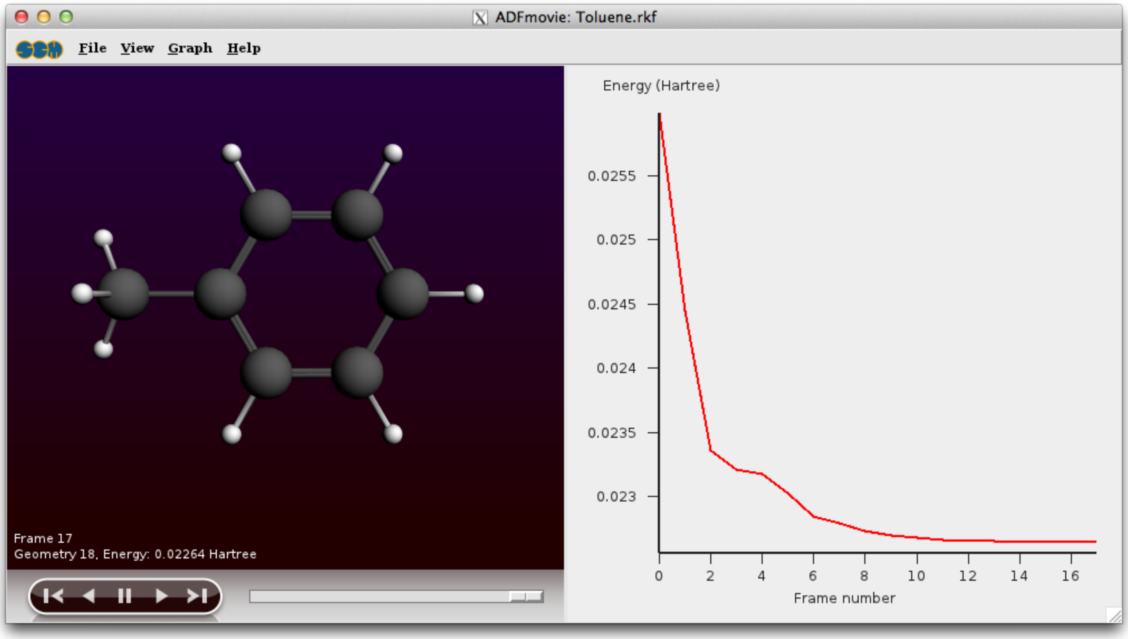
```
  1.10885   1.00769   1.05540   1.05979   1.10440   0.98886   1.03453   0.96952
  1.08521   0.91723   0.94715   0.91923   1.10887   1.00767   1.05537   1.05977
  1.10475   1.06578   0.98260   1.04158   1.10438   0.98888   1.03456   0.96954
  1.08294   1.05246   1.18878   1.18192   0.84784   0.86098   0.84785   0.85305
  0.86097   0.83071   0.83543   0.83544

         BONDING CONTRIBUTION OF EACH M.O.

 1.9090  1.9514  1.9073  1.9701  1.9397  1.9512  1.9876  1.9560  2.0147  1.9406
 2.0236  2.0376  1.9474  1.9727  2.0439  2.0479  1.9670  2.0021 -2.0256 -1.9703
-2.0003 -1.9646 -1.9236 -2.0035 -1.9464 -2.0051 -1.9970 -1.9555 -2.0054 -1.9750
-1.9686 -1.9720 -1.9771 -1.9917 -1.9593 -1.9287




                  BOND ORDERS AND VALENCIES


                C  1       C  2       C  3       C  4       C  5       C  6
--------------------------------------------------------------------------------
   C    1   3.970143
   C    2   1.443559   3.974742
   C    3   1.418481   0.001021   3.976561
   C    4   0.002707   0.110601   1.418394   3.970144
   C    5   0.002129   1.437978   0.110587   0.002129   3.973296
   C    6   0.110529   0.001037   0.001022   1.443557   1.438072   3.974746
   C    7   0.006142   0.007154   1.009797   0.006143   0.001242   0.007150
   H    8   0.962308   0.000507   0.000677   0.005850   0.005966   0.000140
   H    9   0.000861   0.965887   0.005958   0.000089   0.000896   0.005972
   H   10   0.005845   0.000140   0.000677   0.962317   0.005964   0.000508
   H   11   0.005982   0.000686   0.000131   0.005985   0.964182   0.000686
   H   12   0.000089   0.005978   0.005959   0.000860   0.000895   0.965878
   H   13   0.005173   0.000029   0.002418   0.005176   0.002206   0.000029
   H   14   0.001507   0.000057   0.000721   0.004833   0.000526   0.000109
   H   15   0.004831   0.000109   0.000718   0.001503   0.000524   0.000057


                C  7       H  8       H  9       H 10       H 11       H 12
--------------------------------------------------------------------------------
   C    7   3.919440
   H    8   0.000499   0.976848
   H    9   0.000303   0.000188   0.980674
   H   10   0.000499   0.000150   0.000098   0.976851
   H   11   0.000131   0.000144   0.000168   0.000144   0.978406
   H   12   0.000303   0.000099   0.000200   0.000188   0.000168   0.980672
   H   13   0.954194   0.000012   0.000002   0.000012   0.000000   0.000002
   H   14   0.962934   0.000295   0.000009   0.000015   0.000000   0.000044
   H   15   0.962947   0.000015   0.000044   0.000295   0.000000   0.000009


                H 13       H 14       H 15
-------------------------------------------
   H   13   0.971341
   H   14   0.001044   0.972917
   H   15   0.001043   0.000823   0.972919



TOTAL CPU TIME:              0.09 SECONDS

== MOPAC DONE ==
```

Now for a geometry optimization it might be interesting to see a movie of the progress of the optimization:

`Close the ADFoutput window`

SCM → Movie

Graph → Energy



You can also use ADFmovie to get detailed information about the geometry (distances, angles and so on), just as for an ADF geometry optimization. If you don't know how, check the ADF-GUI tutorials.

`Close all windows except ADFjobs and the ADFinput window showing your MOPAC input`

IR spectrum and normal modes

Now we will modify our MOPAC job to perform a frequencies calculation:

```
Activate the ADFinput window (MOPACinput)
In the Mopac Main panel, change the Task to 'Frequencies'
```

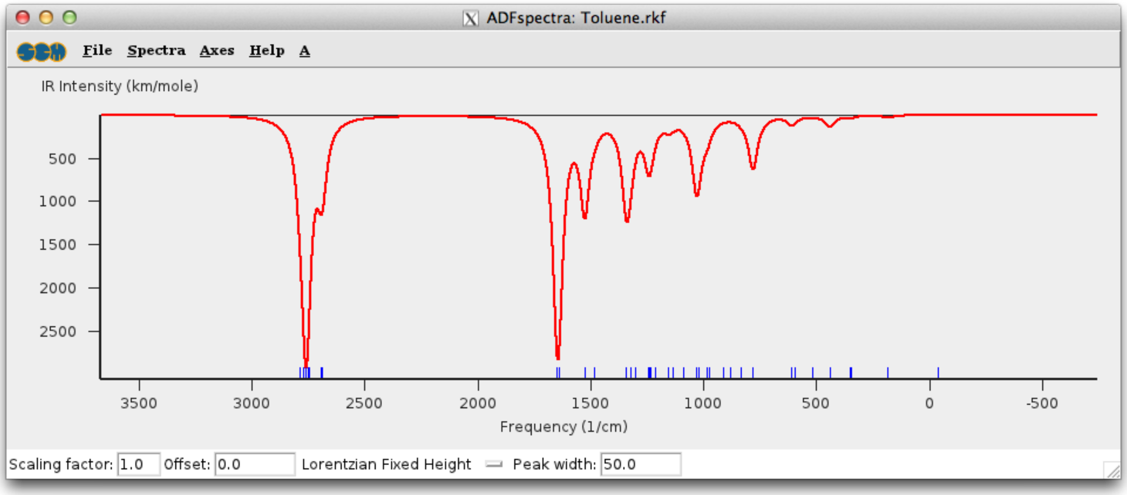
File → Run

```
Answer 'Yes' to save your setup
Answer 'Yes' to acknowledge that you are saving over a previous job
```

The logfile will be shown, and will very soon show the job is ready,

SCM → Spectra

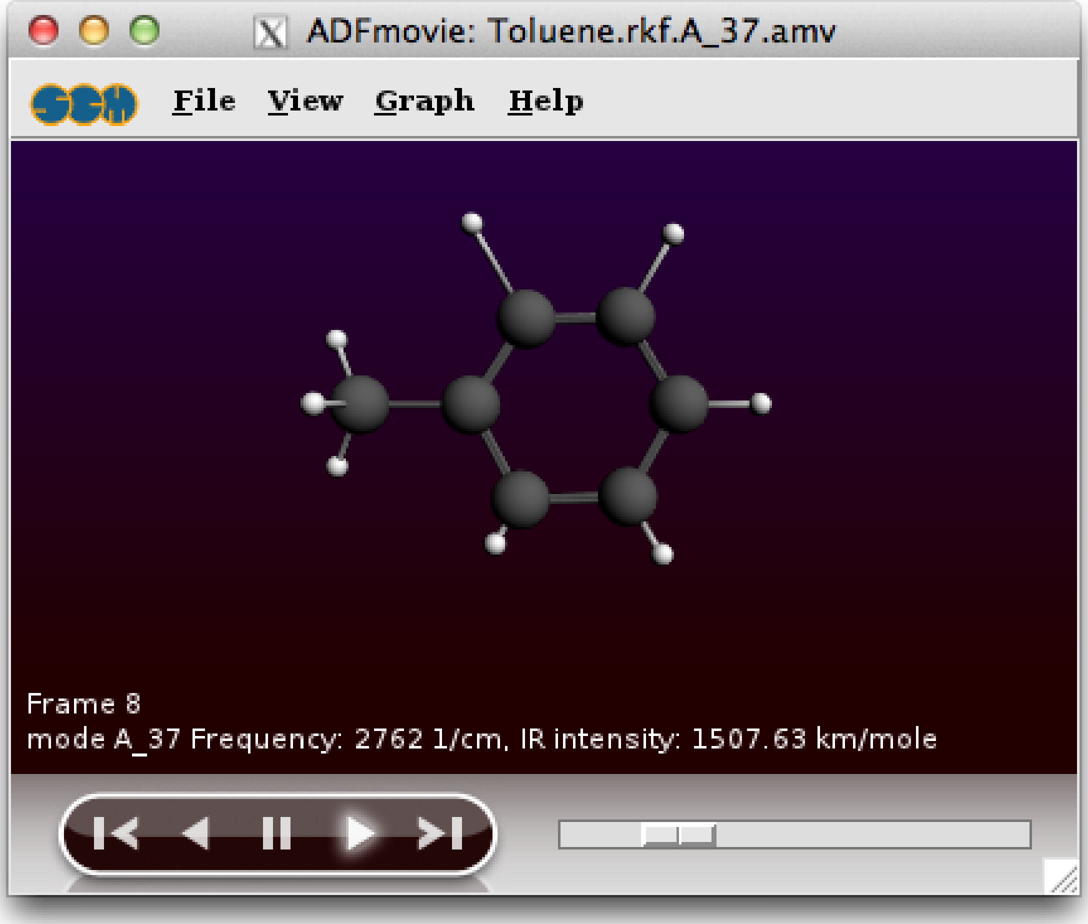
The calculated IR spectrum will be shown:



Scaling factor: 1.0 Offset: 0.0 Lorentzian Fixed Height Peak width: 50.0

```
Right-click on the peak around 2762 cm-1, and select mode A_37 (with the
maximum intensity)
```

The selected mode will be shown:



Frame 8
mode A_37 Frequency: 2762 1/cm, IR intensity: 1507.63 km/mole

In ADFspectra: tear off the A menu by selecting the dashed line (**A → - - - -**)
Use the torn-off menu to examine some more modes
SCM → Close All

ReaxFF-GUI tutorials

This section contains tutorials that show you how to use ReaxFF via the ReaxFF-GUI. As the ReaxFF-GUI is very similar to the ADF-GUI, we will focus here on ReaxFF specific features.

If you are not familiar with the ADF-GUI (or the ReaxFF-GUI), please have a look at the Introduction and ADF-GUI Overview tutorials.

For example, it will show you how to start the ReaxFF-GUI, and how to manually edit molecules.

The first tutorial provides you with an overview over all relevant GUI modules. It will create a mixture of methane and oxygen, and burn it. This will clearly demonstrate that ReaxFF can handle reactions.

The second tutorial will show you how to set up a more complex system and how to use some of the advanced features of ReaxFF. In setting up the system you will also find out how to create an aluminum surface.

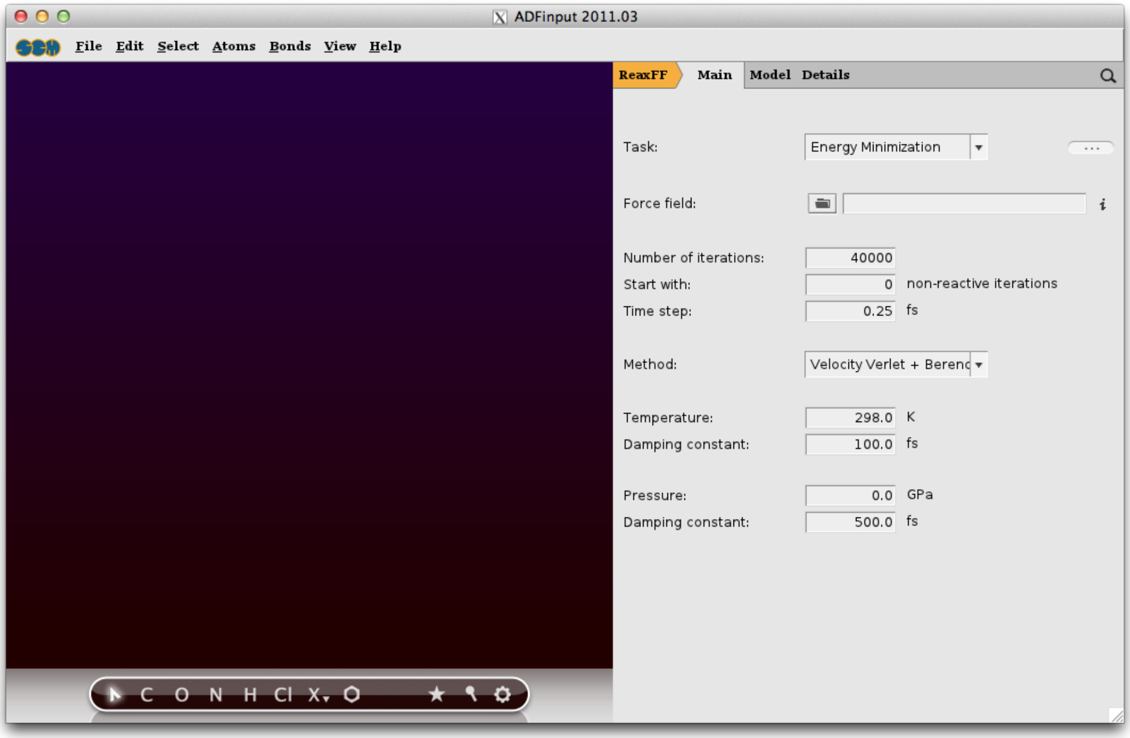
Tutorial 1: Burning methane

This tutorial will help you to:

- create a simple mixture (methane and oxygen)
- set up to burn it quickly (set up your ReaxFF simulation)
- burn it: perform the actual ReaxFF simulation
- visualize what is happening during and after the simulation

Step 1: Start ReaxFFinput

`Start ADFjobs`
SCM → ReaxFF input



Task: Energy Minimization

Force field:

Number of iterations: 40000

Start with: 0 non-reactive iterations

Time step: 0.25 fs

Method: Velocity Verlet + Berend

Temperature: 298.0 K

Damping constant: 100.0 fs

Pressure: 0.0 GPa

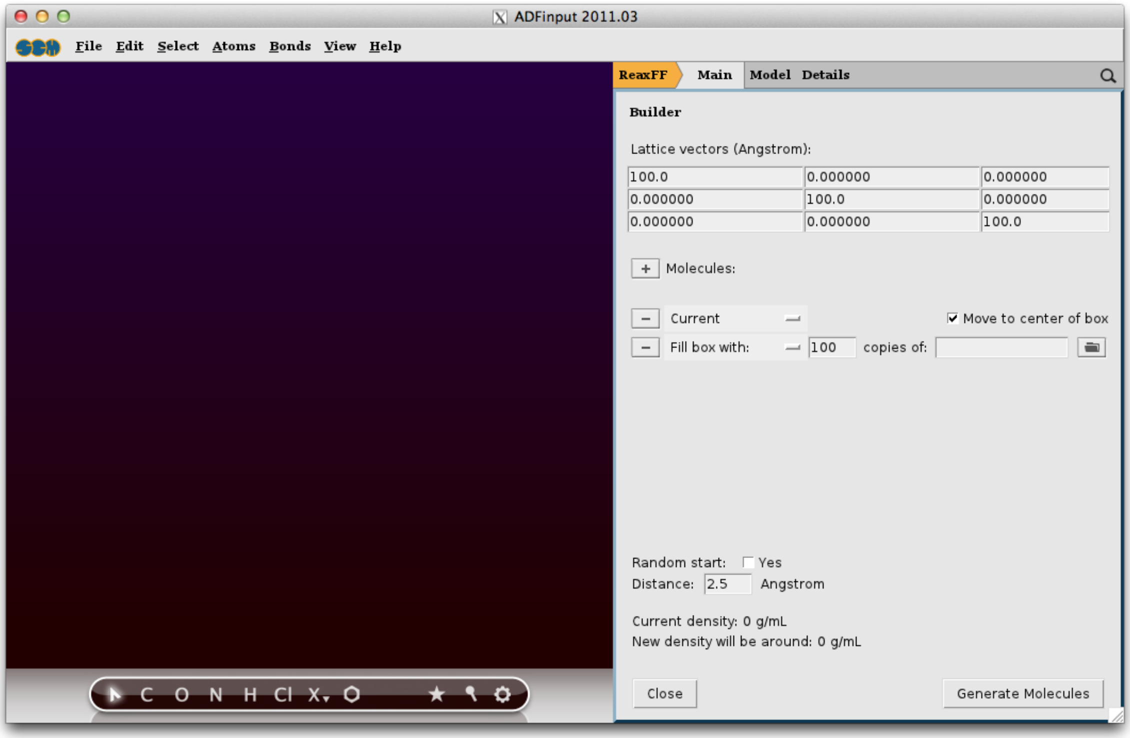
Damping constant: 500.0 fs

Note that ReaxFFinput and ADFinput are actually identical. By starting ReaxFFinput from the SCM menu ADFinput will immediately switch to ReaxFF mode.

Step 2: Create a methane / oxygen mixture

Next we will make the methane - oxygen mixture. For full combustion we need at least 2 oxygen molecules for each methane molecule. So we will use 100 methane molecules and 250 oxygen molecules.

Edit → Builder



Builder

Lattice vectors (Angstrom):

100.0	0.000000	0.000000
0.000000	100.0	0.000000
0.000000	0.000000	100.0

\+ Molecules:

− Current ☑ Move to center of box

− Fill box with: 100 copies of:

Random start: ☐ Yes

Distance: 2.5 Angstrom

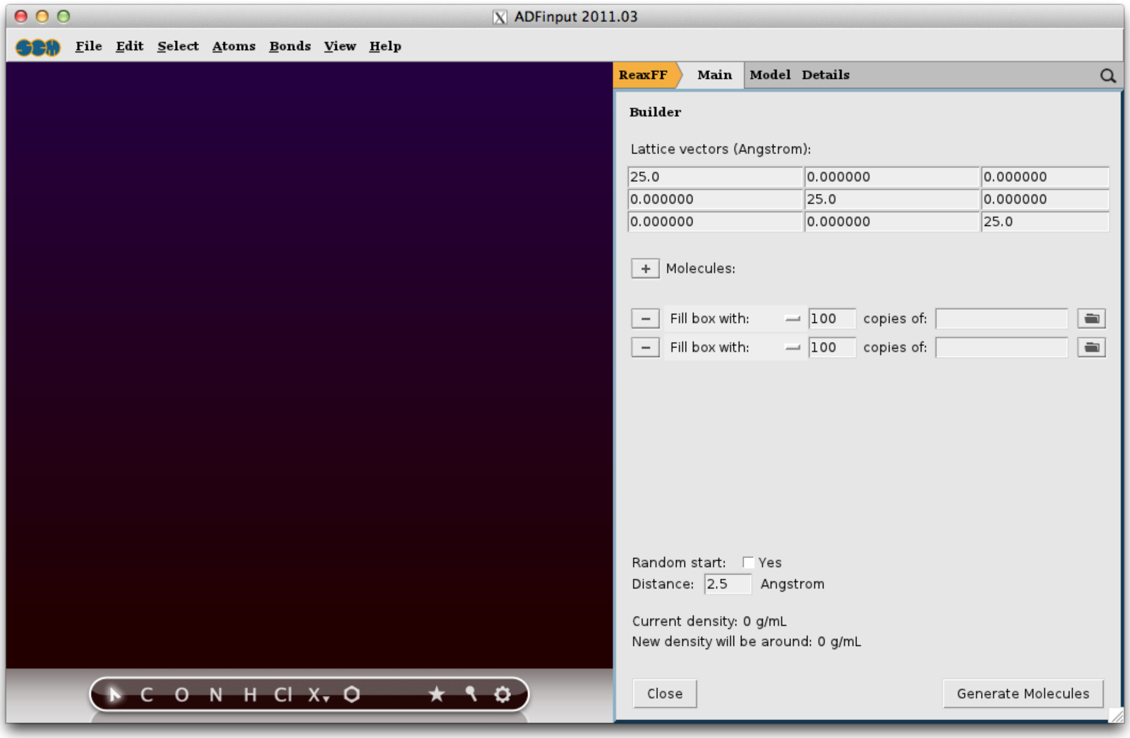
Current density: 0 g/mL

New density will be around: 0 g/mL

The Builder allows you to build your system, and set some things like the cell vectors that define the computation cell. ReaxFF always uses periodic boundary conditions. The default cell is a cube with sides of 100 Angstrom.

You can use the Builder to add many molecules, randomly distributed. In the list of molecules to be added the Current molecule is already present. If you have any molecules already, the new molecules will be added. Right now we have no molecules yet, so we can remove that entry.

```
Click the '-' button in front of 'Current'
Click the + button in front of 'Molecules' once (so now we can specify two
kinds of molecules to add)

Change the box to a cube of 25.0 Angstrom
```



Builder

Lattice vectors (Angstrom):

25.0	0.000000	0.000000
0.000000	25.0	0.000000
0.000000	0.000000	25.0

Molecules:

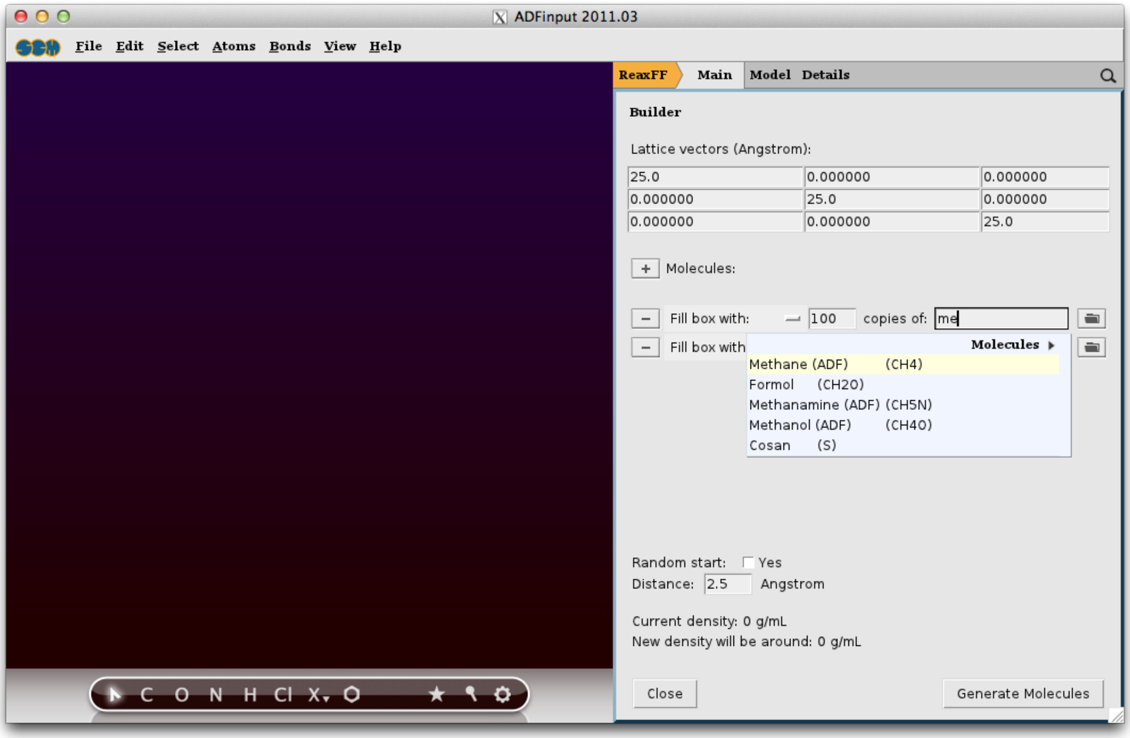
Fill box with: 100 copies of:

Fill box with: 100 copies of:

Random start: ☐ Yes
Distance: 2.5 Angstrom

Current density: 0 g/mL
New density will be around: 0 g/mL

Click in the entry field of the first line
Type 'me' (without the quotes) to search for methane



Builder

Lattice vectors (Angstrom):

25.0	0.000000	0.000000
0.000000	25.0	0.000000
0.000000	0.000000	25.0

Molecules:

Fill box with: 100 copies of: me

Fill box with

Methane (ADF)	(CH4)
Formol	(CH2O)
Methanamine (ADF)	(CH5N)
Methanol (ADF)	(CH4O)
Cosan	(S)

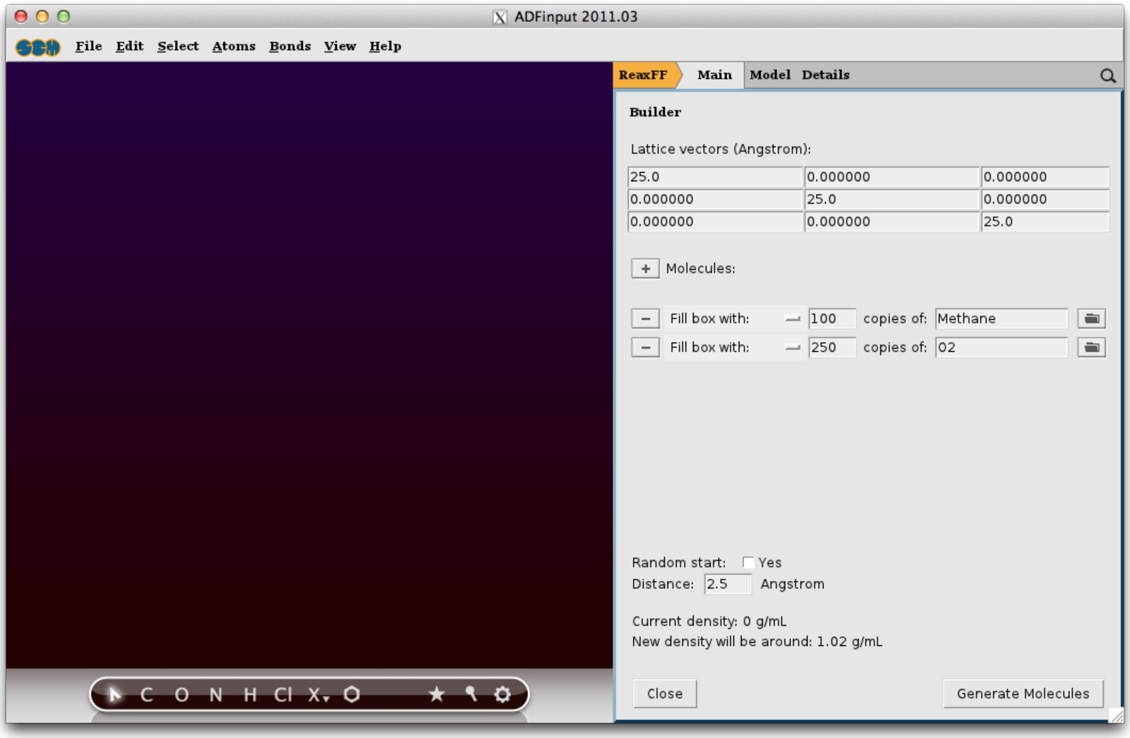
Random start: ☐ Yes
Distance: 2.5 Angstrom

Current density: 0 g/mL
New density will be around: 0 g/mL

As you can see, a search box appears to find your molecule, very similar to the search box in the panel bar.

```
Select the 'Methane (ADF)' match
Click the file select button on the other 'Fill box with' line
Click in the entry field of the second line
Type 'o', to search for O2
Select the 'O2 (ADF)' match
Change the 100 copied of O2 into 250 copies
```

You now have specified how the builder should build your system: 100 methane molecules with 250 oxygen molecules added.



Builder

Lattice vectors (Angstrom):

25.0	0.000000	0.000000
0.000000	25.0	0.000000
0.000000	0.000000	25.0

Molecules:

Fill box with: 100 copies of: Methane
Fill box with: 250 copies of: O2

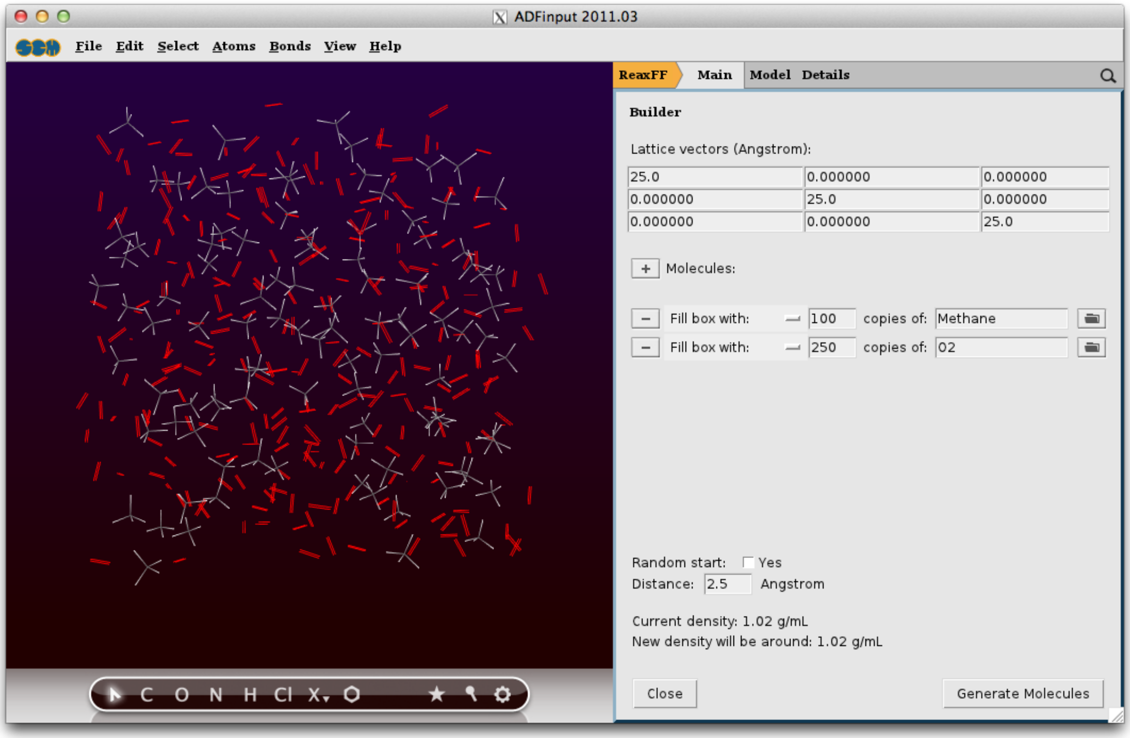
Random start: ☐ Yes
Distance: 2.5 Angstrom

Current density: 0 g/mL
New density will be around: 1.02 g/mL

At the bottom of the Builder panel you can see that the current density is zero. The new density, after adding methane and oxygen, will be around 1 g/mL, which is obviously very high for this mixture. For this tutorial that is fine as it means things will happen faster.

Next we will actually generate the molecules:

```
Click the 'Generate Molecules' button
```



Lattice vectors (Angstrom):

25.0	0.000000	0.000000
0.000000	25.0	0.000000
0.000000	0.000000	25.0

Molecules:

Fill box with: 100 copies of: Methane

Fill box with: 250 copies of: O2

Random start: ☐ Yes

Distance: 2.5 Angstrom

Current density: 1.02 g/mL

New density will be around: 1.02 g/mL

The molecules are generated at random positions and orientations, with constraint that all atoms (between different molecules) are at least the specified distance (2.5 Angstrom) apart.

The system looks good, we can now close the Builder:

```
Click the Close button at the bottom of the Builder window
```

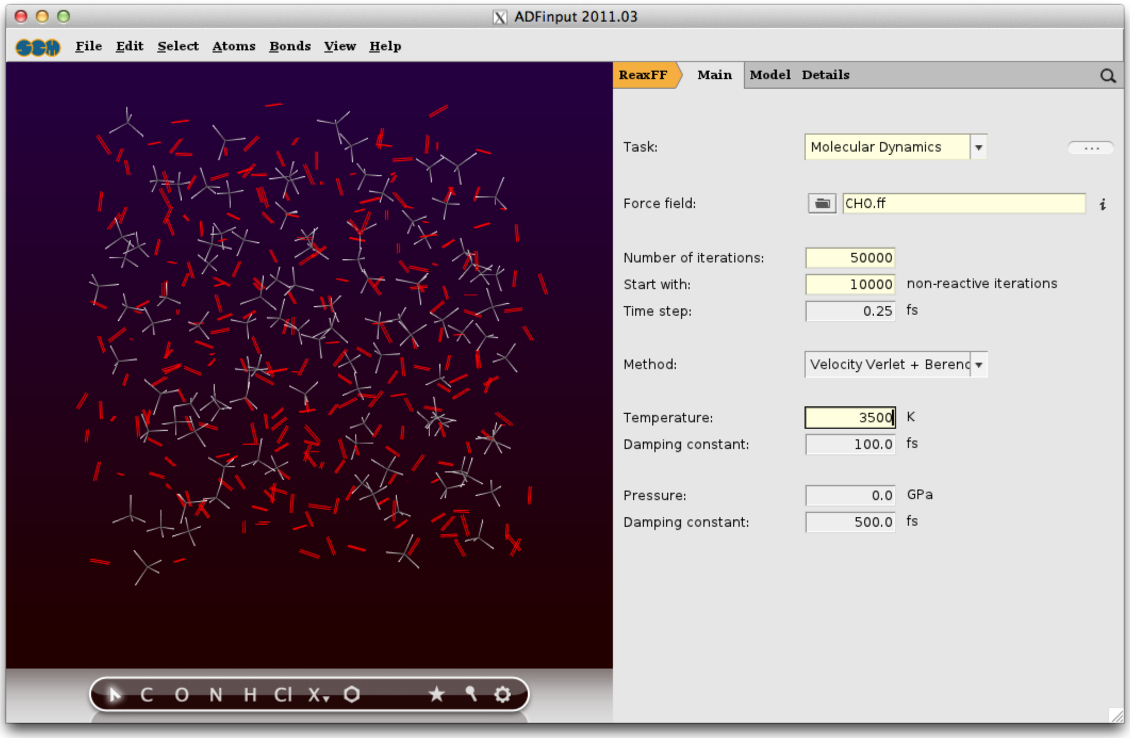
Step 3: Prepare for burning: set up the simulation

The next step is to set up the details of the simulation. For this tutorial we will perform an MD simulation, at very high temperature and density. This is to make things happen quickly. Obviously it is not a realistic system.

```
Select the 'Molecular Dynamics' task
Click the 'i' on the right side of the Force field line
```

A new window should appear describing what force fields are available, including a short description and references. For this particular example we will use the CHO force field for hydrocarbon oxidation.

```
Close the window describing the force fields
Click on the folder-like button in the Force field line
Select the CHO.ff force field

Enter 50000 as number of iterations
Enter 10000 as number of non-reactive iterations

Specify a temperature of 3500 K
```



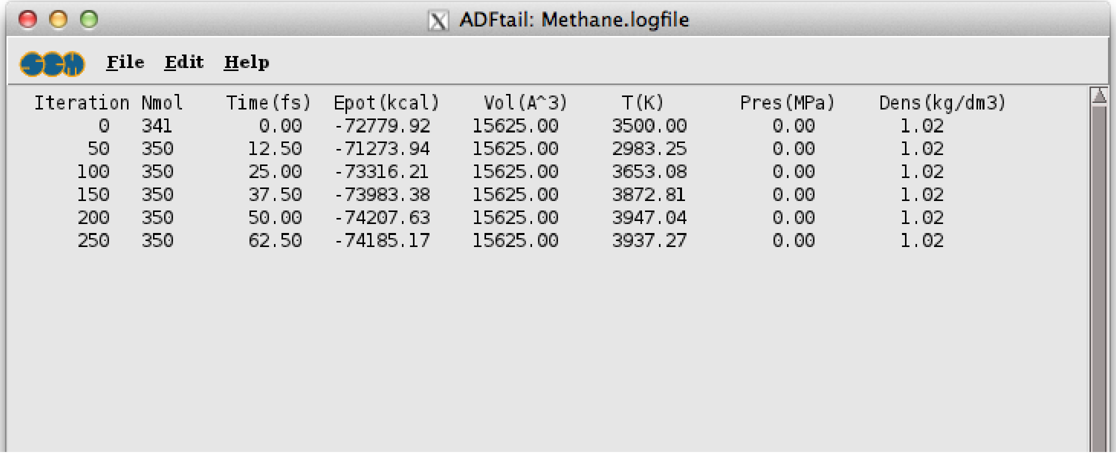
Task: Molecular Dynamics
Force field: CHO.ff
Number of iterations: 50000
Start with: 10000 non-reactive iterations
Time step: 0.25 fs
Method: Velocity Verlet + Berend
Temperature: 3500 K
Damping constant: 100.0 fs
Pressure: 0.0 GPa
Damping constant: 500.0 fs

Step 4: Burn it: run the simulation

Now we will run your set-up:

```
Use the File → Run command
When asked to save your input, save it with the name 'Methane'
```

ADFjobs should come to the foreground, and your job should be visible at the top. On the right side you can see that the job is running (this is indicated by the gear-icon). When running, also a window will appear showing the progress of your simulation (the logfile):

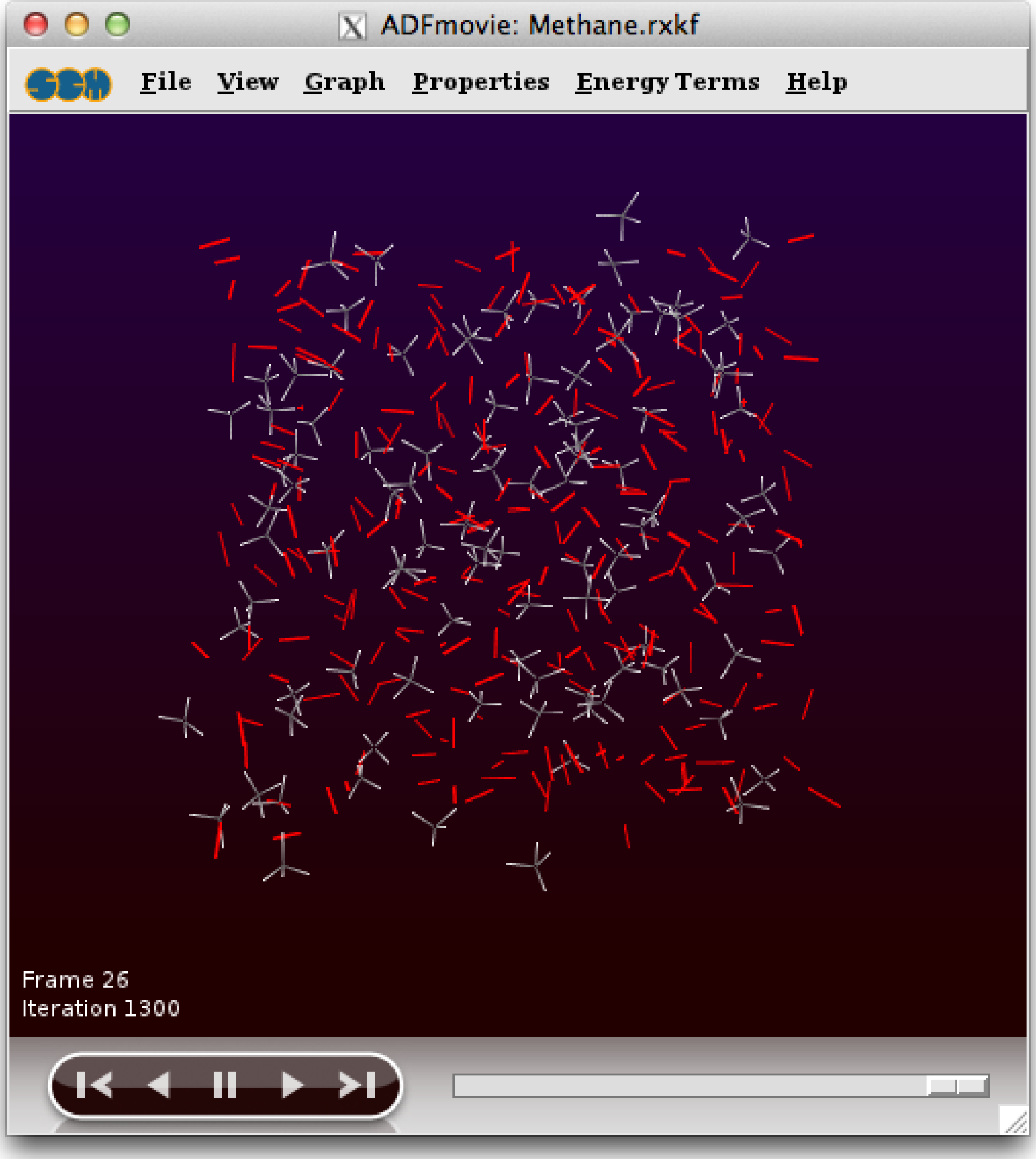


```
Iteration Nmol    Time(fs)  Epot(kcal)   Vol(A^3)     T(K)      Pres(MPa)     Dens(kg/dm3)
        0   341      0.00   -72779.92   15625.00   3500.00        0.00          1.02
       50   350     12.50   -71273.94   15625.00   2983.25        0.00          1.02
      100   350     25.00   -73316.21   15625.00   3653.08        0.00          1.02
      150   350     37.50   -73983.38   15625.00   3872.81        0.00          1.02
      200   350     50.00   -74207.63   15625.00   3947.04        0.00          1.02
      250   350     62.50   -74185.17   15625.00   3937.27        0.00          1.02
```

As you can see in the logfile, the simulation is running.

To see more details, we now will use ADFmovie. Note that you can do this while the simulation is still running!

`Start ADFmovie:` **SCM → Movie** `in the logfile window`

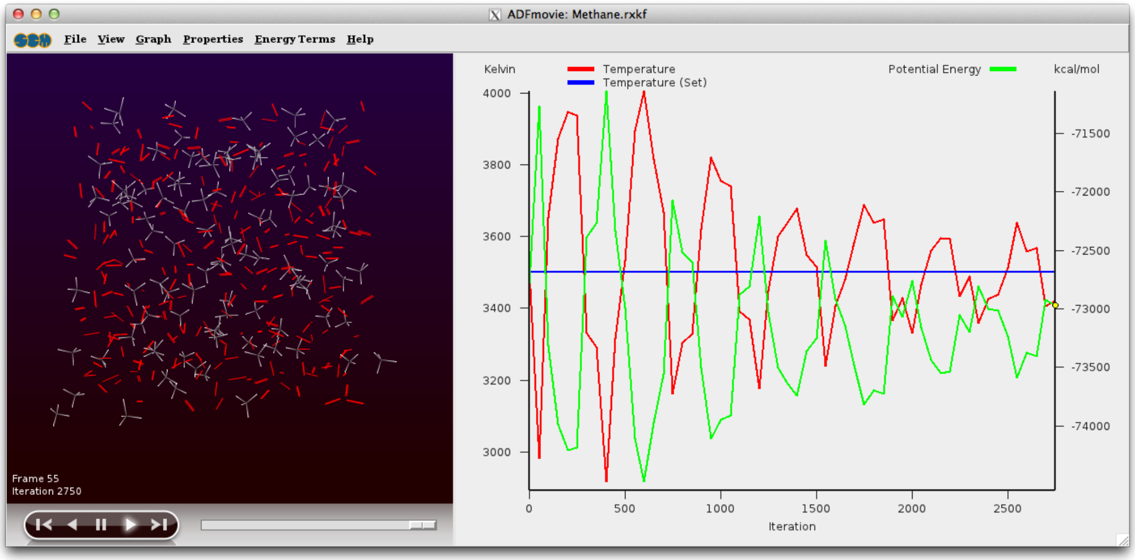


ADFmovie will show you the trajectory of your system. Note that it will automatically read new data as soon as it becomes available.

It can also show graphs of the properties that ReaxFF calculates:

`In the ADFmovie window:`
`Use the` **Properties → Temperature** `command`
`Use the` **Properties → Temperature (Set)** `command`

Use the **Properties → Potential Energy** command
Make the window bigger to make viewing the graph easier



Note that the two temperatures (the actual temperature, and the set temperature) are both plotted on one axes. The other axes is used for the second property (in this case the potential energy).

You can go to a particular point in the simulation using the slider below the window showing your system, or you can click somewhere on one of the curves plotted. You can also use the arrow keys (left and right) to move through the simulation.

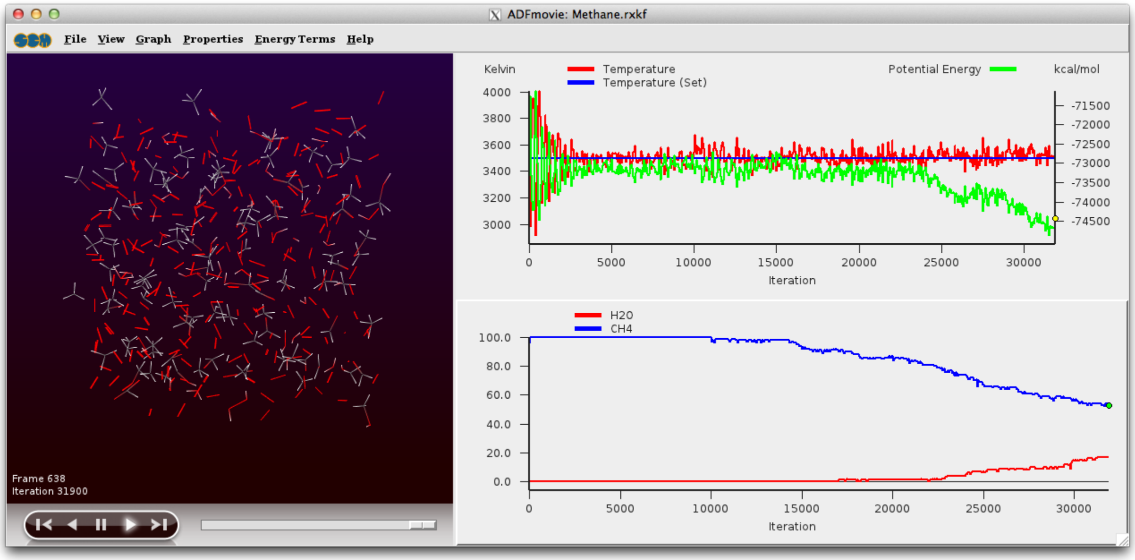
Click on the temperature curve, move around in the movie
Jump to the end of the movie to follow the progress

As ReaxFF is a reactive force field, reactions may take place. In this particular example the methane should react with the oxygen, eventually producing H2O and CO2.

You can make graphs that show how many of the different molecule types are present. The following instructions often work, but it depends on what molecules are present in your simulation. You might try this step again after waiting some time. Remember that we requested 10000 non-reactive iterations, so just leave it running for 30000 iterations or so. Especially the production of H2O and CO2 take some time.

After about 30000 iterations:
Use the **Properties → Molecule Fractions** command
In the window that pop-ups, select H2O
Click Add / Remove

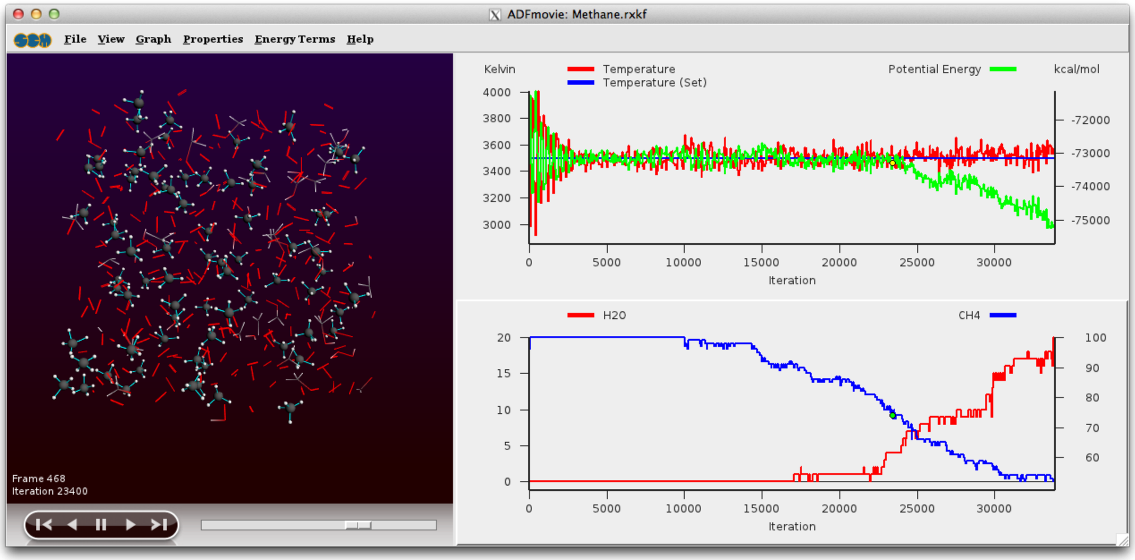
Repeat these three steps for CH4, and for CO2 if any present yet.



Obviously, no reactions take place in the first 10000 iterations.

You can put one of the curves on a different axes if you wish:

Click once on the curve showing the number of CH4 molecules, this makes it the 'active' curve
Use the **Graph → Curve On Right Axes** command

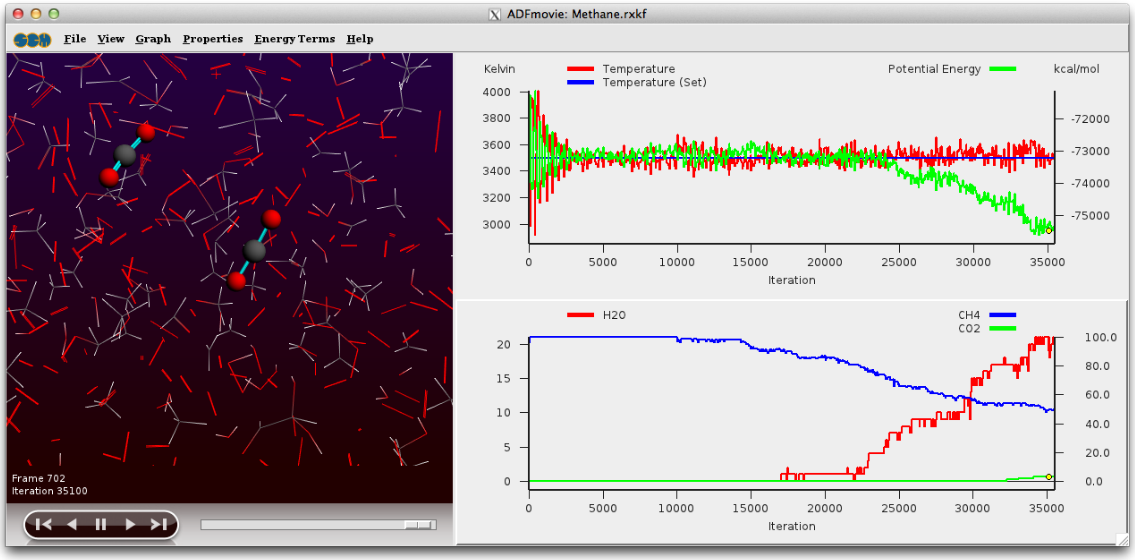


Clicking on the curve also had two other effects (besides making it the active curve): you jumped to the iteration in the movie corresponding to the point where you clicked, and the molecules that belonged to that curve are selected.

The selected molecules are shown with Balls and Sticks, instead of wire-frame only, to make it easier to spot them. Flying to the selection also makes it easier to spot them:

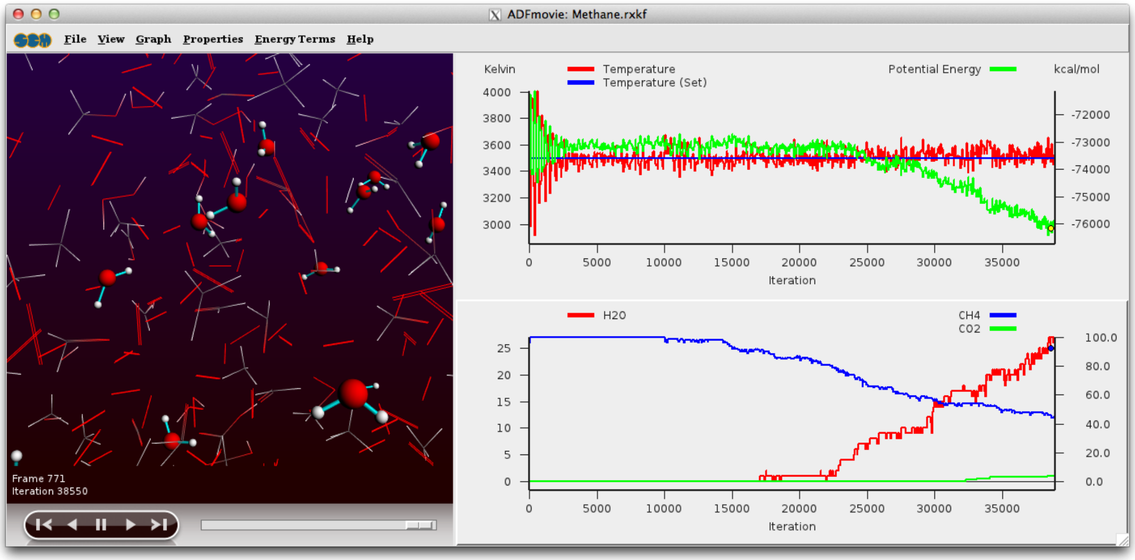
Use the **Properties → Molecule Fractions** command to add a CO2 curve if you have not yet done so

Click on the curve showing the CO2 production
Use the **View → Fly To Selection** command a few times

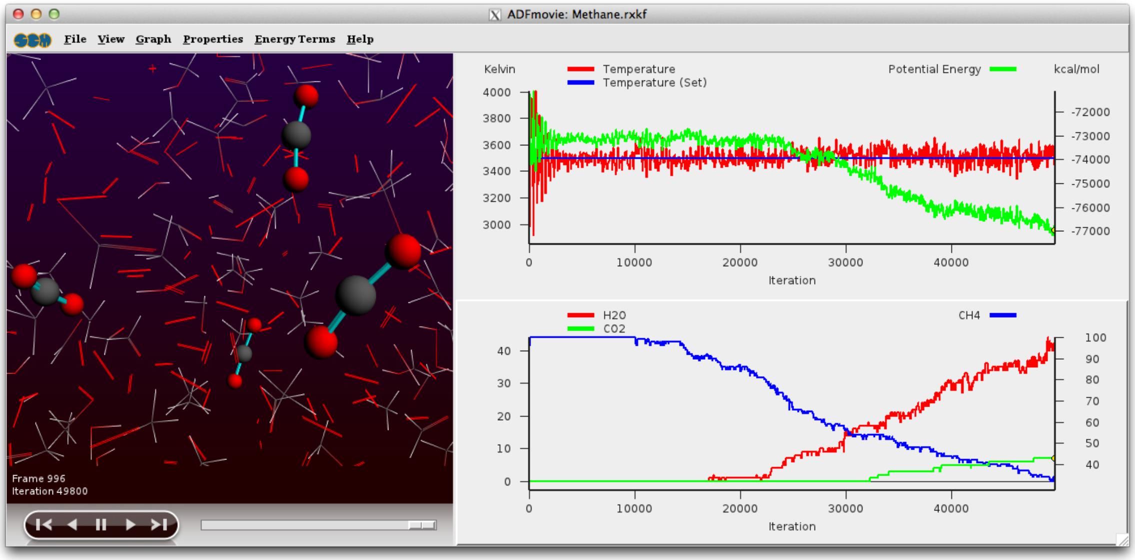


When you now go forward or backwards in time, it is easier to see how the reactions actually take place. Note that the atoms remain selected, even if they are no longer part of a CO2 molecule. In a similar way you can focus on H2O produced:

Click on the curve showing the H2O production
Use the **View → Fly To Selection** command if needed



Wait until the calculation is ready
Select the CO2 curve (click on it)
Move it to the left axes: **Graph → Curve On Left Axes**



To prepare for the next tutorial, quit everything:

Bring the ADFjobs window to the foreground
Use the **SCM → Close** command to close all windows for this job

Tutorial 2: Water on an aluminum surface

This tutorial will help you to:

- create an aluminum slab
- add a solvent (water)
- run the simulation and see what happens

Step 1: Start ReaxFFinput

Start ADFjobs
Use the **SCM → ReaxFF input** menu command

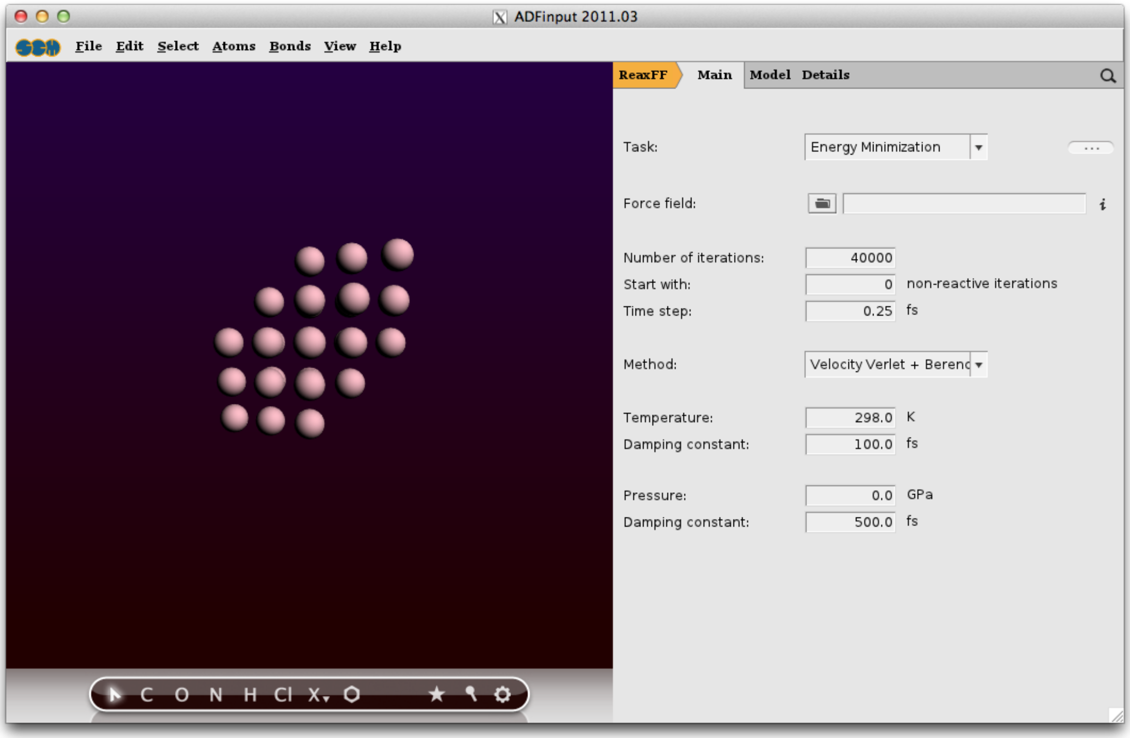
Step 2: Creating the surface

Bulk aluminum has an fcc crystal structure, with a lattice constant of about 4.0 Angstrom.

To create the surface, we first build bulk aluminum:

Edit → Crystal → Cubic → fcc
In the dialog that appears:
    Set the lattice parameter to 4.0
    Set the atom type to Al
    Click the 'OK' button
View → Periodic → Repeat Unit Cells

In your molecule editor screen you should see a picture of the bulk aluminum structure. The unit cell contains one atom. As ReaxFF input by default does not show repeated cells, it had to be turned on explicitly. Otherwise you see only the single atom in the unit cell.



Task: Energy Minimization

Force field:

Number of iterations: 40000

Start with: 0 non-reactive iterations

Time step: 0.25 fs

Method: Velocity Verlet + Berend

Temperature: 298.0 K

Damping constant: 100.0 fs

Pressure: 0.0 GPa

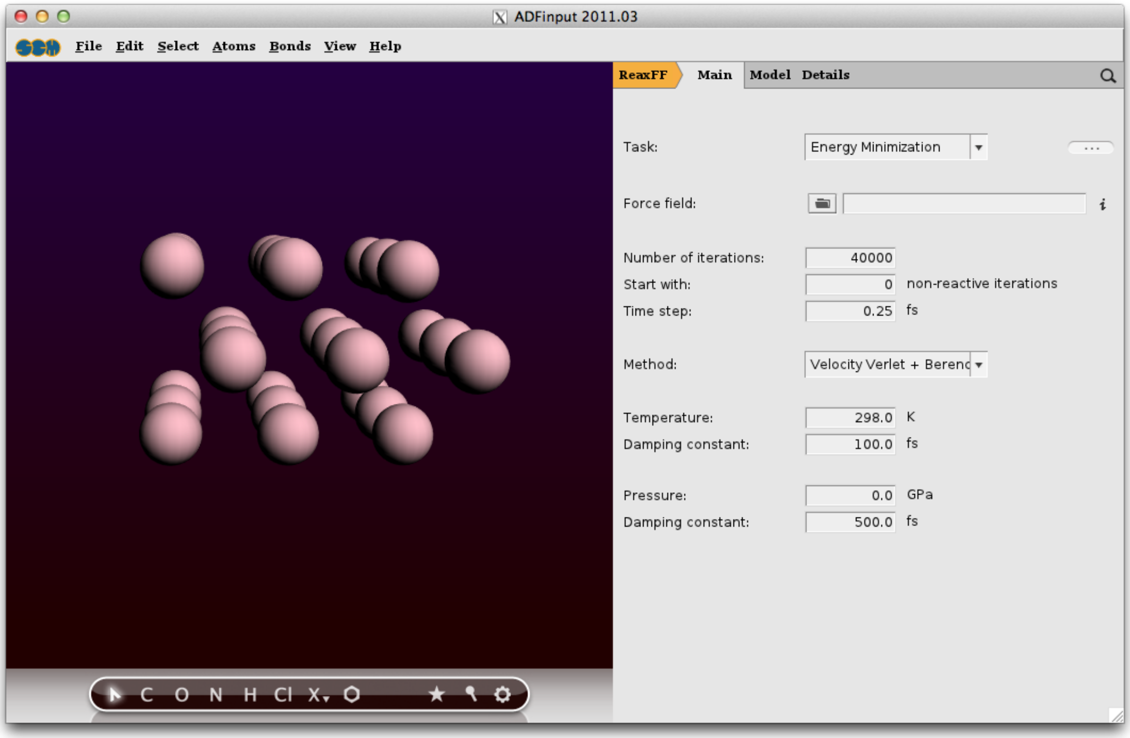
Damping constant: 500.0 fs

Now create the surface:

Edit → Crystal → Generate Slab...

```
In the Dialog window:
    Check the 'cartesian' check box
    Set the number of layers to 3
    Click OK
```

View → Periodic → Repeat Unit Cells



Task: Energy Minimization

Force field:

Number of iterations: 40000

Start with: 0 non-reactive iterations

Time step: 0.25 fs

Method: Velocity Verlet + Berend

Temperature: 298.0 K

Damping constant: 100.0 fs

Pressure: 0.0 GPa

Damping constant: 500.0 fs

You will see three atoms as it is a three-layer slab.

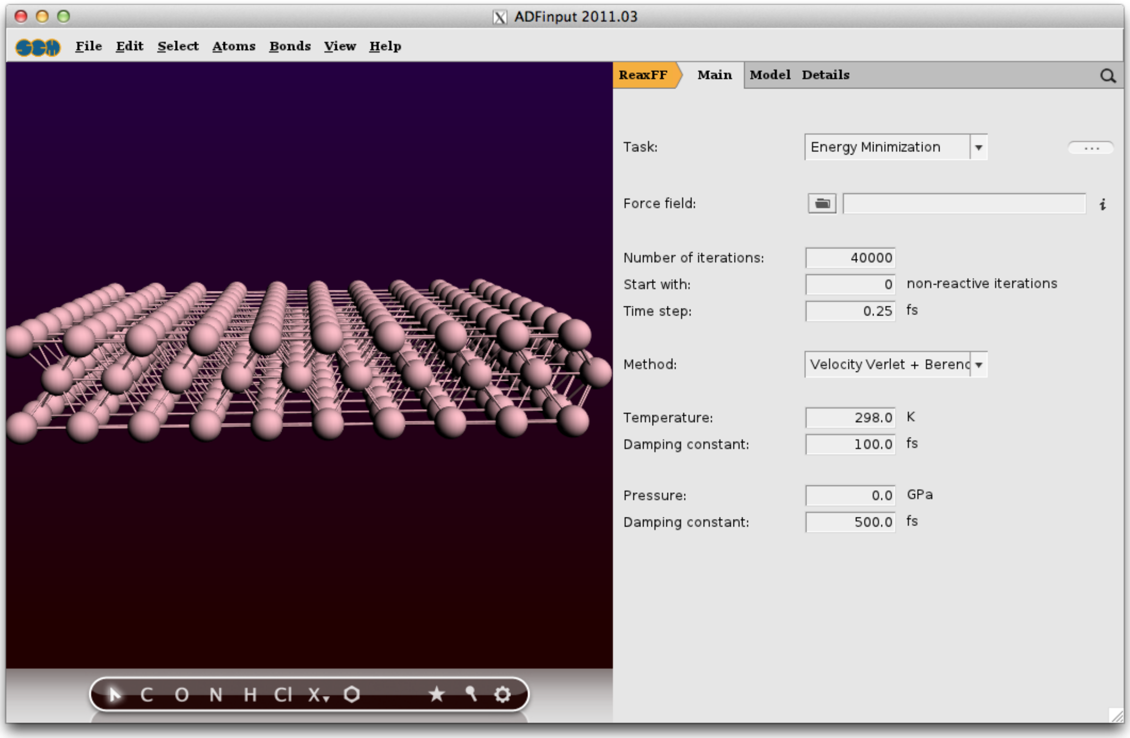
In this case we do not want just one unit cell, but a much bigger piece of the slab:

Edit → Crystal → Generate Super Cell...

`Put 10, 10, 1 on the diagonal`

`Click OK`

`Rotate get a better view`



Task: Energy Minimization

Force field:

Number of iterations: 40000

Start with: 0 non-reactive iterations

Time step: 0.25 fs

Method: Velocity Verlet + Berend

Temperature: 298.0 K

Damping constant: 100.0 fs

Pressure: 0.0 GPa

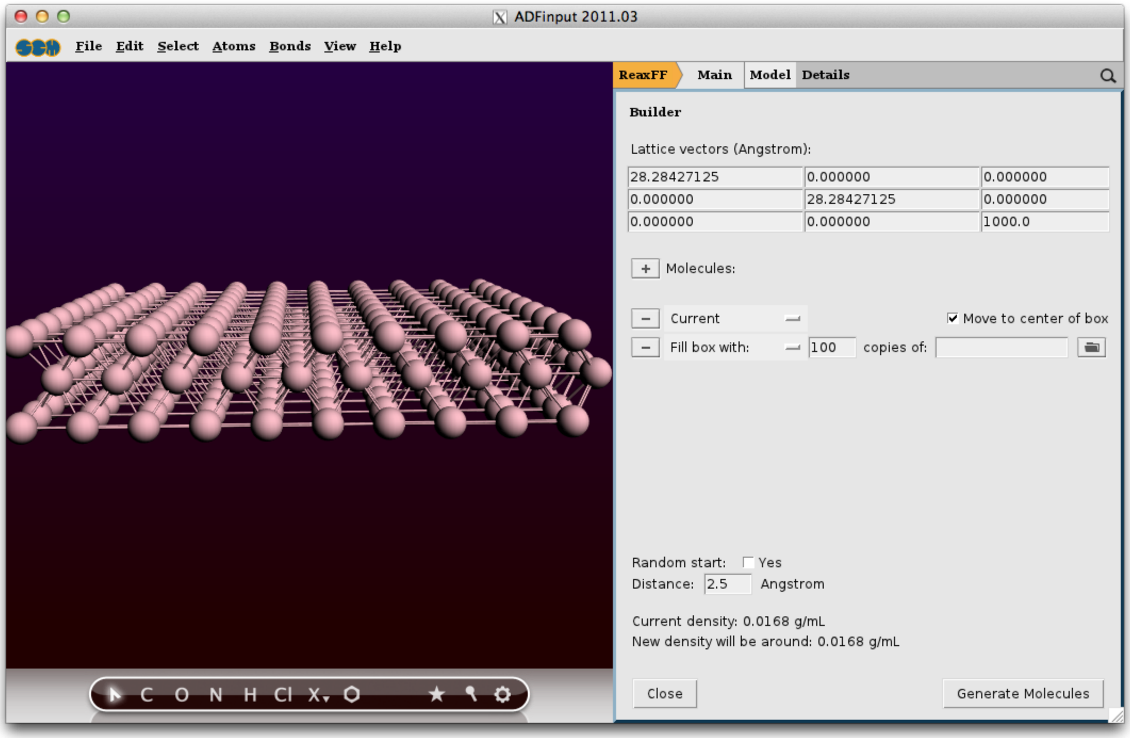
Damping constant: 500.0 fs

Now we have a real slab of aluminum, three layers thick. Note that the Generate Super Cell command adjusted the lattice vectors to match the new unit cell.

Step 3: Add solvent

The next step is to add water to the system, and make sure that the slab is in the center of the simulation box:

Edit → Builder



Builder

Lattice vectors (Angstrom):

28.28427125	0.000000	0.000000
0.000000	28.28427125	0.000000
0.000000	0.000000	1000.0

+ Molecules:

− Current ☑ Move to center of box

− Fill box with: 100 copies of:

Random start: ☐ Yes

Distance: 2.5 Angstrom

Current density: 0.0168 g/mL

New density will be around: 0.0168 g/mL

Change the third dimension of the lattice vectors to 100.0

Check the 'Move to center of box' box on the line for the Current molecule

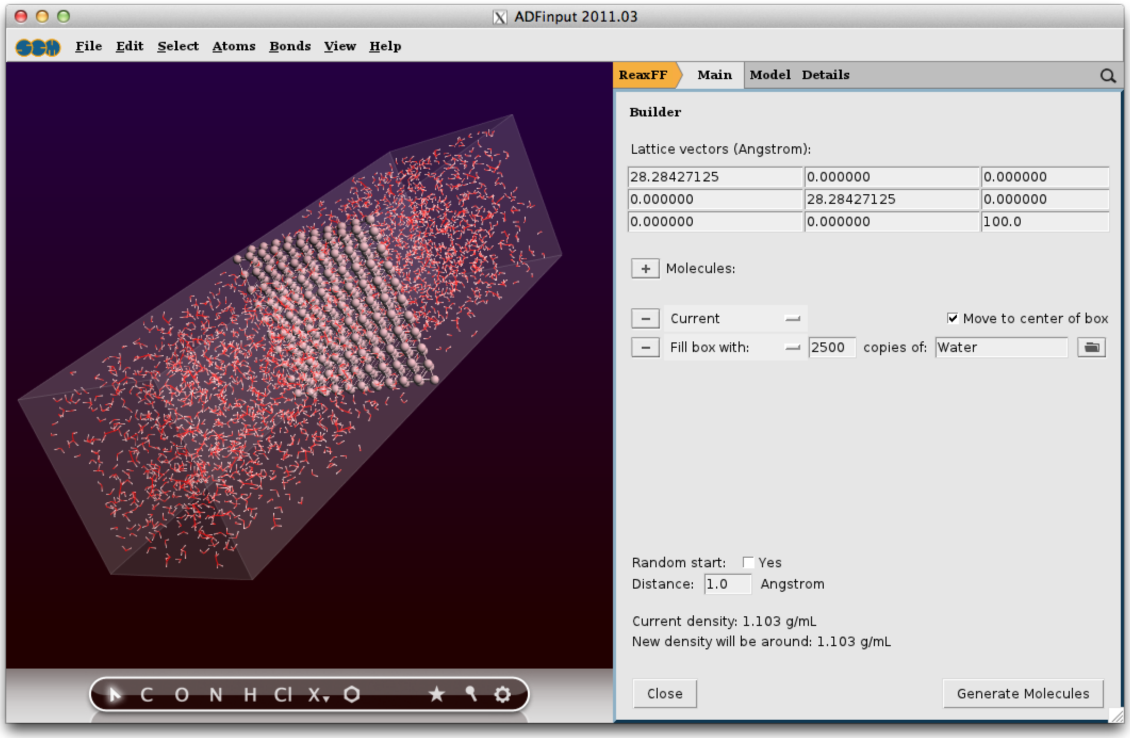
Type 'wa' in the line with 'Fill box with'
Select 'Water (ADF)' from the search results
Specify 2500 copies

Specify a distance of 1.0 Angstrom (this is the minimum distance between the molecules)

Click the 'Generate Molecules' button on the bottom

Use the **View → Periodic → Show Unit Cell** command to visualize the box

Rotate to your favorite view



Builder

Lattice vectors (Angstrom):

28.28427125	0.000000	0.000000
0.000000	28.28427125	0.000000
0.000000	0.000000	100.0

Molecules:

Current ☑ Move to center of box

Fill box with: 2500 copies of: Water

Random start: ☐ Yes

Distance: 1.0 Angstrom

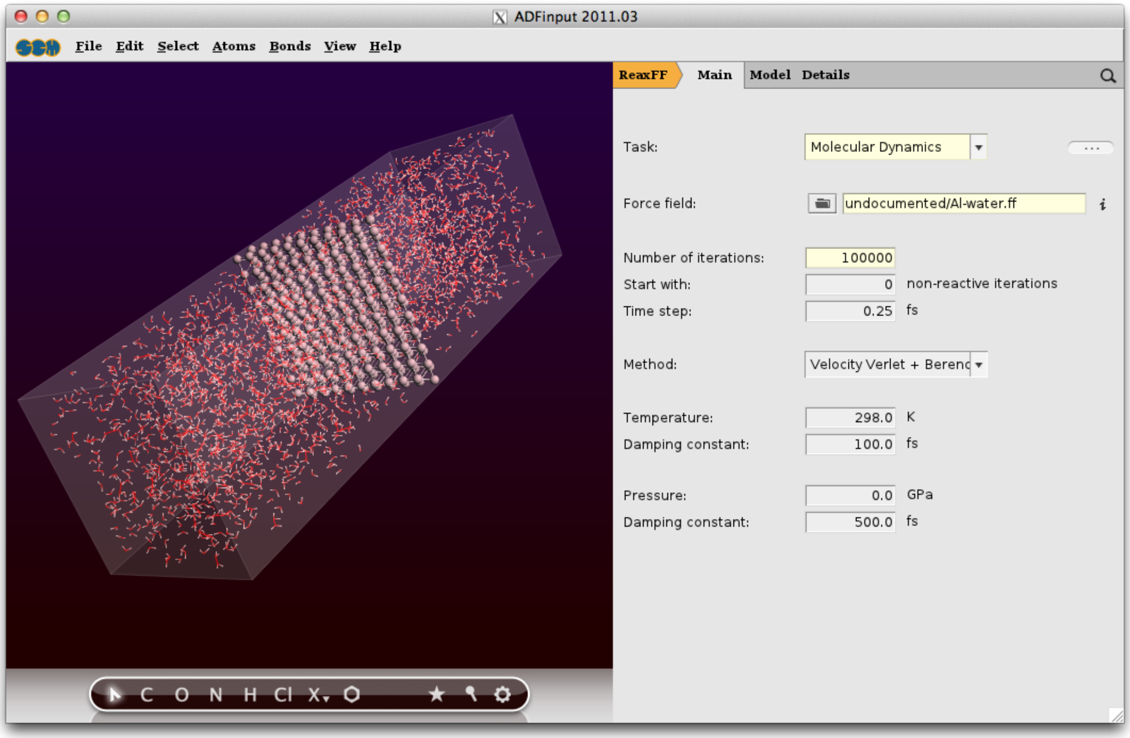
Current density: 1.103 g/mL

New density will be around: 1.103 g/mL

Step 4: Set up the simulation, including a temperature regime

Now we will set up the MD-simulation. We will use the Al-water force field included in the undocumented directory:

```
Close the Builder by clicking the Close button on the bottom

Select the 'Molecular Dynamics' Task

Click on the folder icon to select a force field
Select the undocumented/Al-water.ff

Specify 100000 iterations
```



Task: Molecular Dynamics

Force field: undocumented/Al-water.ff

Number of iterations: 100000

Start with: 0 non-reactive iterations

Time step: 0.25 fs

Method: Velocity Verlet + Berend

Temperature: 298.0 K

Damping constant: 100.0 fs

Pressure: 0.0 GPa

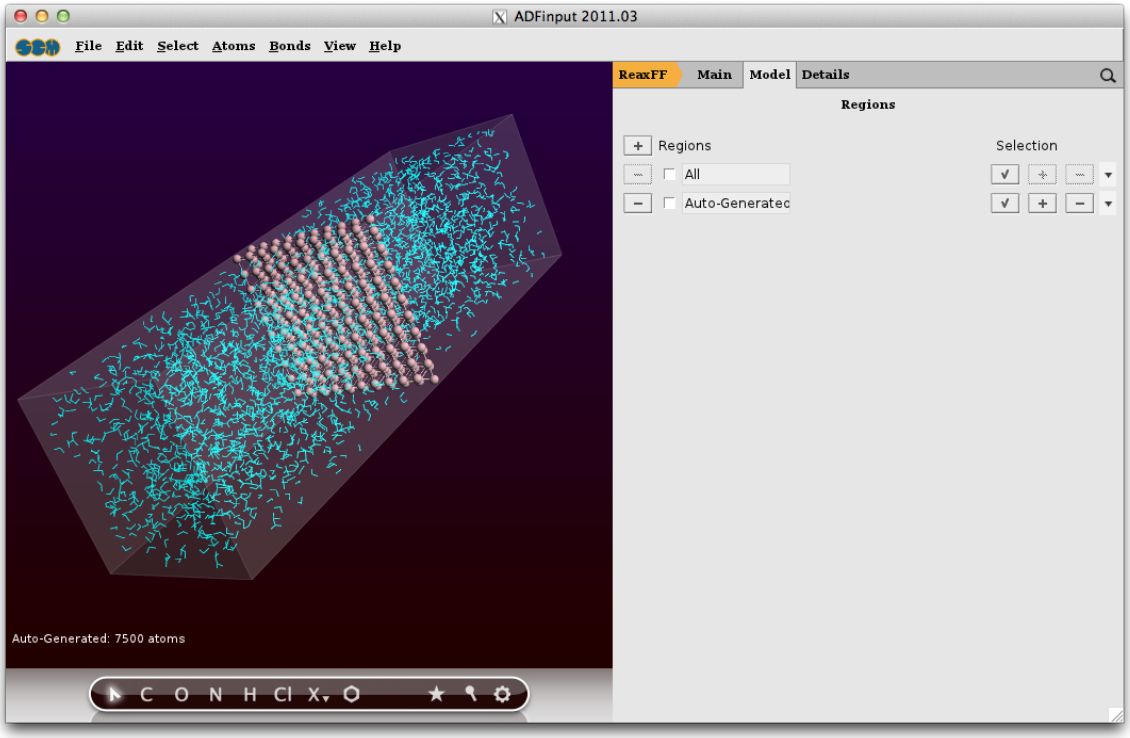
Damping constant: 500.0 fs

In the simulation we would like something to happen. So we will use a high temperature for water, but try to keep the aluminum cool. Also, we will start with a low temperature MD to relax the initial set-up. This can all be accomplished using a temperature regime, specifying different temperatures for different regions.

For this we first need to define two new regions: one for the aluminum slab, and one for the water. Regions in ReaxFFinput are the same as in the ADF-GUI: they are defined as a collection of atoms. Via the Regions panel you can define the regions:

panel bar **Model** → **Regions**

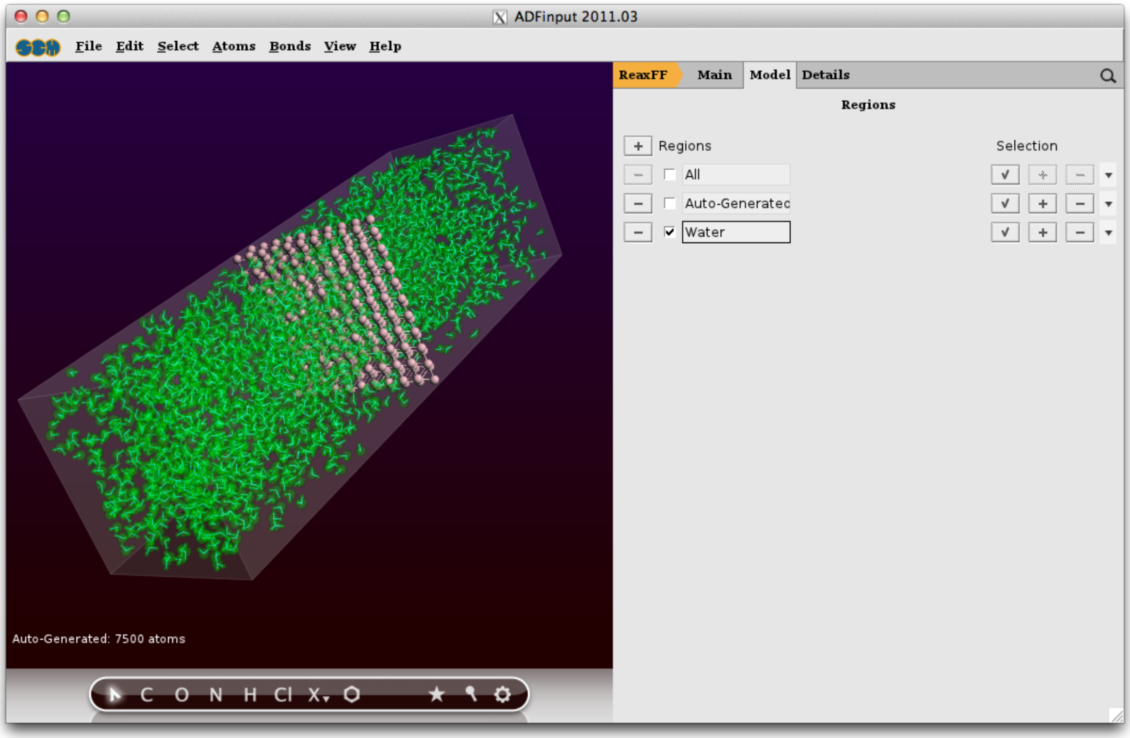
Click once on the select button (the V like button) in the Auto-Generated region



By pressing the select button you have selected all atoms in the 'Auto-Generated' region. This region will always contain the atoms that are added by the Builder. Thus, as you can see, all water molecules are selected.

We are going to set up a region for the water molecules, and a region for the aluminum surface:

```
With the water molecules still selected, press the + button in front of the
Regions label
Click and select the text 'Region_2' and change it into 'Water'
```



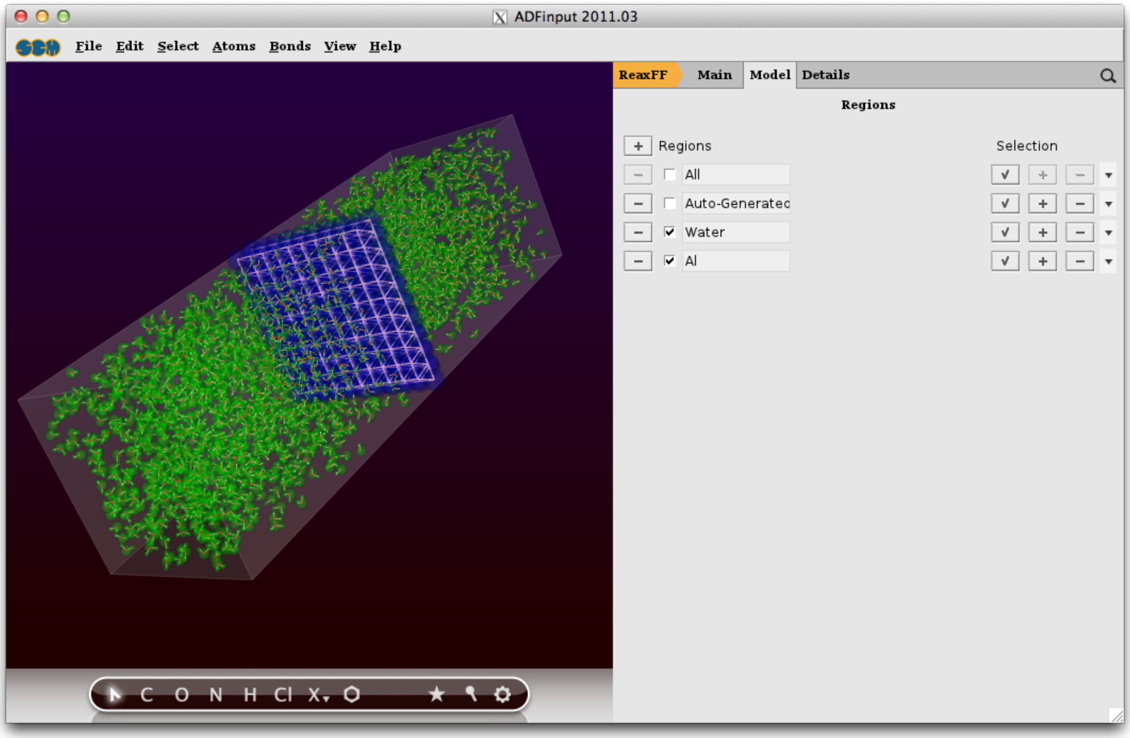
Now we have a region defined that contains all water molecules. Note that the selected atoms (in this case all water molecules) where automatically added to the new region. The + and - buttons add or remove the selected atoms to a region.

Click in the drawing area so it has focus (otherwise the next will select the region name)

Select → Select All

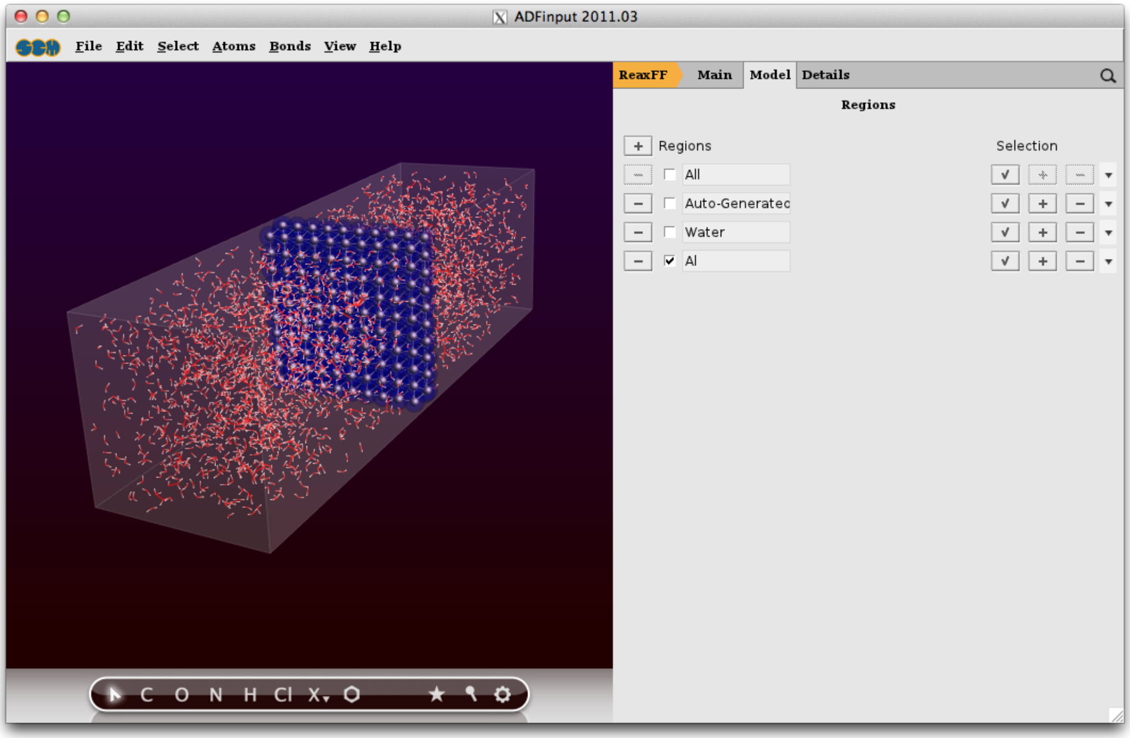
Press the + button in front of the Regions label again to add a new region
(containing everything as everything was selected)
Change the name Region_3 to Al

Click the select button in the Water region to select all water molecules
Click the '-' button in the Al region to remove the water from the Al region
Click in empty space to clear the selection



The different regions are shown with colors. This does make the display a lot slower. You can turn off (or on) this display with the check box in front of the Region names, and you can set visualization style per region:

```
Uncheck the check box at the left of the Water region line
Press the triangle on the right side of the Al region line,
   and choose for the 'Balls And Sticks' visualization option
```

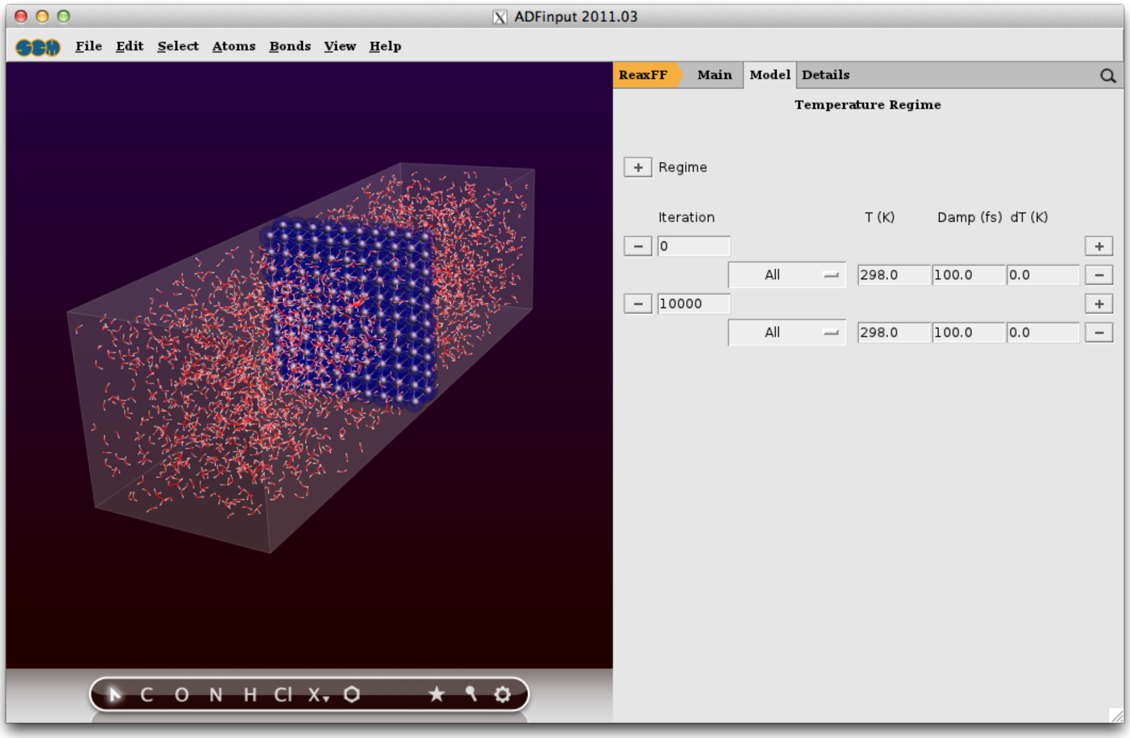


Regions

☐ All
☐ Auto-Generated
☐ Water
☑ Al

Now we have defined the regions that we need, now set up the temperature regime:

`Panel bar` **Model → Temperature Regime**
`Press the '+' button in front of the Regime label twice to add two temperature steps`



Temperature Regime

Iteration		T (K)	Damp (fs)	dT (K)
0				
	All	298.0	100.0	0.0
10000				
	All	298.0	100.0	0.0

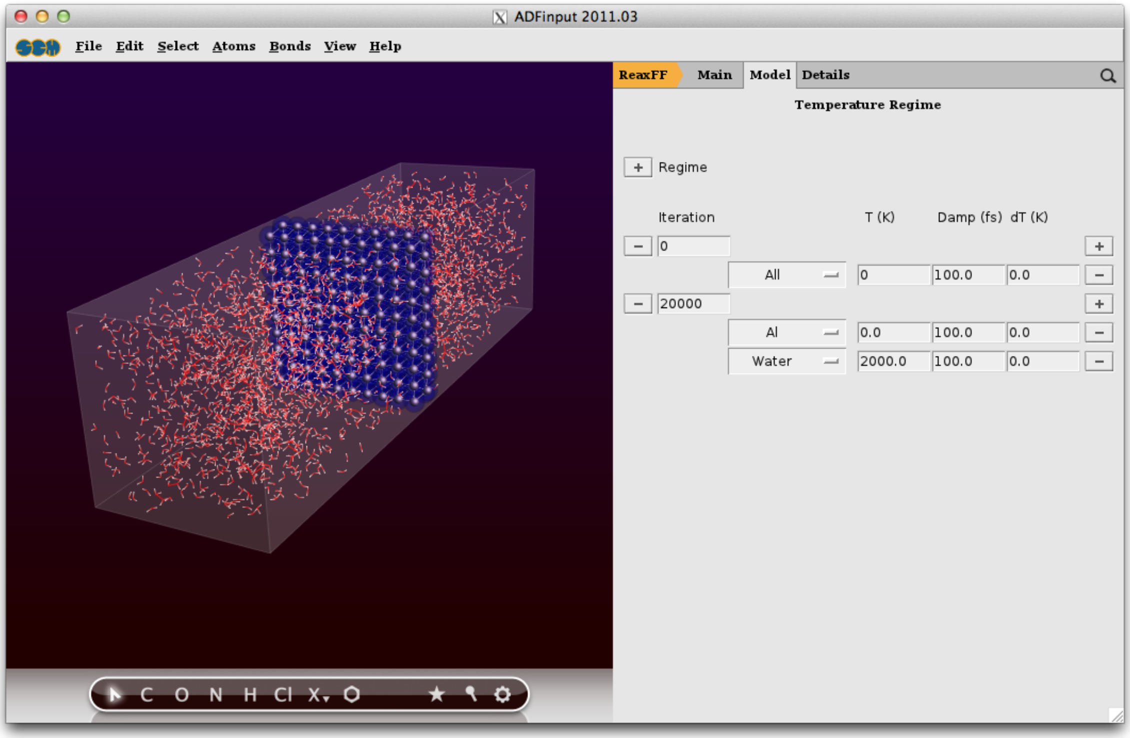
At iteration 0, we start with an MD simulation at T=0 K:

change the first 298 to 0 (note this applies to region All which is everything)

At iteration 20000, we set the water temperature to 2000, while keeping the aluminum temperature at 0:

Change the 10000 to 20000
Press the + button on the right side of the line starting with 20000
Change the first All on the 20000 step to Al, and change its temperature to 0
Change the second All on the 20000 step to Water, and change its temperature to 2000

Your temperature regime setup should look like this:



Temperature Regime

+ Regime

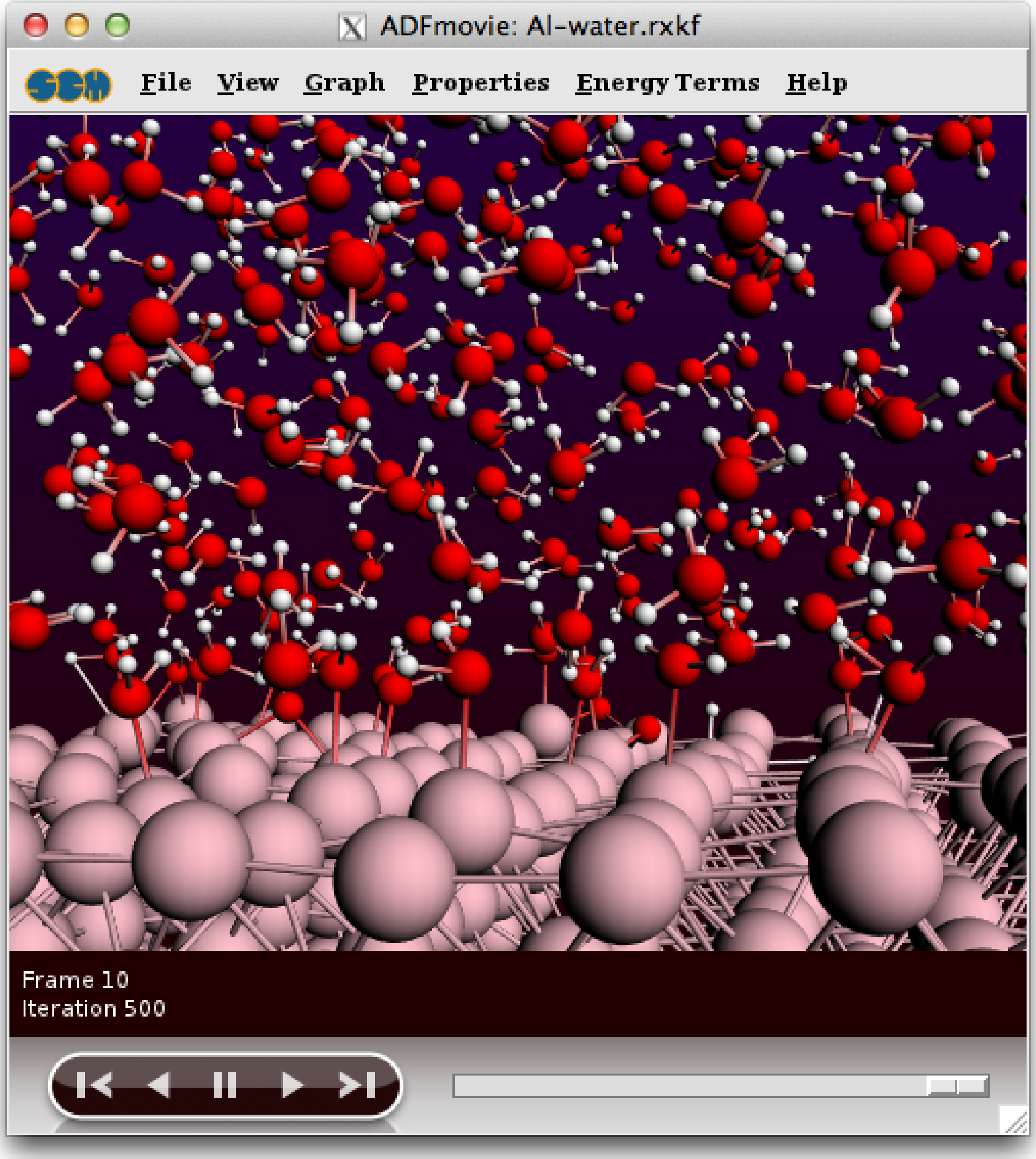
Iteration	Region	T (K)	Damp (fs)	dT (K)
0				
	All	0	100.0	0.0
20000				
	Al	0.0	100.0	0.0
	Water	2000.0	100.0	0.0

Step 5: Run the simulation

Now we can run our set up:

File → Run
When asked to save, specify Al-water as filename

Let it run for some time (until iteration 500 or so)
SCM → Movie
View → Molecule → Balls And Sticks
Rotate and zoom to get a good view of the surface



If you look around, you will most likely see many water molecules attaching to the aluminum surface. After some time, you might also see hydrogen atoms distracted from the water molecules, which are now moving around the surface on their own.

You might leave the simulation running to see what will happen. It will take a lot of time though.

If you do not want to wait for the simulation to finish, kill the job:

`Bring the ADFjobs window to the front`
`Make sure your Al-water job is selected (click once on it if not)`
`Kill it` **Job → Kill**

`Close all GUI modules:` **SCM → Close All**

COSMO-RS GUI Tutorials

This part will provide a hands-on tutorial demonstrating the COSMO-RS GUI. Its purpose is to give a quick tour of the main features of the COSMO-RS GUI.

The first tutorial describes how to create COSMO result files that are needed as input for the COSMO-RS calculation. The second tutorial describes some analysis tools (sigma profile, sigma potential), and shows how to set COSMO-RS parameters. The third tutorial describes how to calculate properties, such as solvent vapor pressures, solvent boiling points, partition coefficients (log P), activity coefficients, solvation free energies, Henry's law coefficients, solubilities, vapor liquid diagrams binary mixture (VLE/LLE), and excess energies. The fourth tutorial describes how to use the COSMO-RS database ADFCRS-2010 of COSMO result files. The fifth tutorial describes how to calculate pK_a values

Additional information may be found in the COSMO-RS part of the GUI Reference manual and COSMO-RS manual

Tutorial 1: COSMO result files

If you already have COSMO result files for all the compounds that you are interested in you can skip this tutorial, without problems of continuity. For example, ADF has a database of COSMO result files, the COSMO-RS database ADFCRS-2010.

The purpose of this tutorial is to teach you how to make data for a compound using the ADF program such that it can be read by COSMO-RS. COSMO-RS expects so called COSMO result files, which are results of quantum mechanical calculation using COSMO. In ADF such a COSMO result file is called a TAPE21 (.t21) file, or a COSKF (.coskf) file. For example the COSMO-RS database ADFCRS-2010 consists of .coskf files. In other programs such a file can be a .cosmo file. For example, at http://www.design.che.vt.edu/VT-Databases.html a database of .cosmo files can be found, which were made with a different program. Note that the optimal COSMO-RS parameters may depend on the program chosen.

Please read through the first ADF-GUI tutorial before starting with this tutorial, see the ADF-GUI tutorials. Even better: try using the ADF-GUI yourself, especially Tutorial 1

In this tutorial an ADF COSMO result file and a MOPAC COSMO result file is made. For ADF COSMO-RS calculations the recommended choice is to use ADF COSMO result files.

Step 1: Start ADFinput

For this tutorial we prefer to work in a separate directory, for example a directory called Tutorial, as was explained in ADF-GUI Tutorial 1.

You know how to start ADFjobs (in your home directory), and move to the Tutorial directory:

```
Start adfjobs
Click on the Tutorial folder icon
```

Next start ADFinput using the SCM menu.

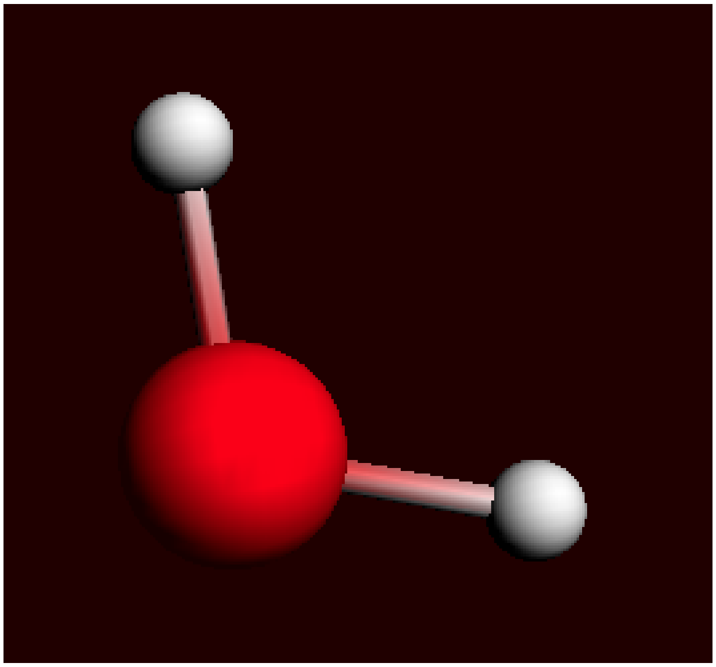
`Select the` **SCM → ADF input** `menu command.`

Step 2: Create the molecule

First we construct a water molecule, and preoptimize its geometry:

`Select the O-tool by clicking on the button with the 'O'`
`Click somewhere in the drawing area to create an oxygen atom`
`Select the select-tool by clicking on the button with the arrow`
`Click once in empty space so nothing is selected`
`Select` **Atoms → Add Hydrogen**
`Click the optimizer button`

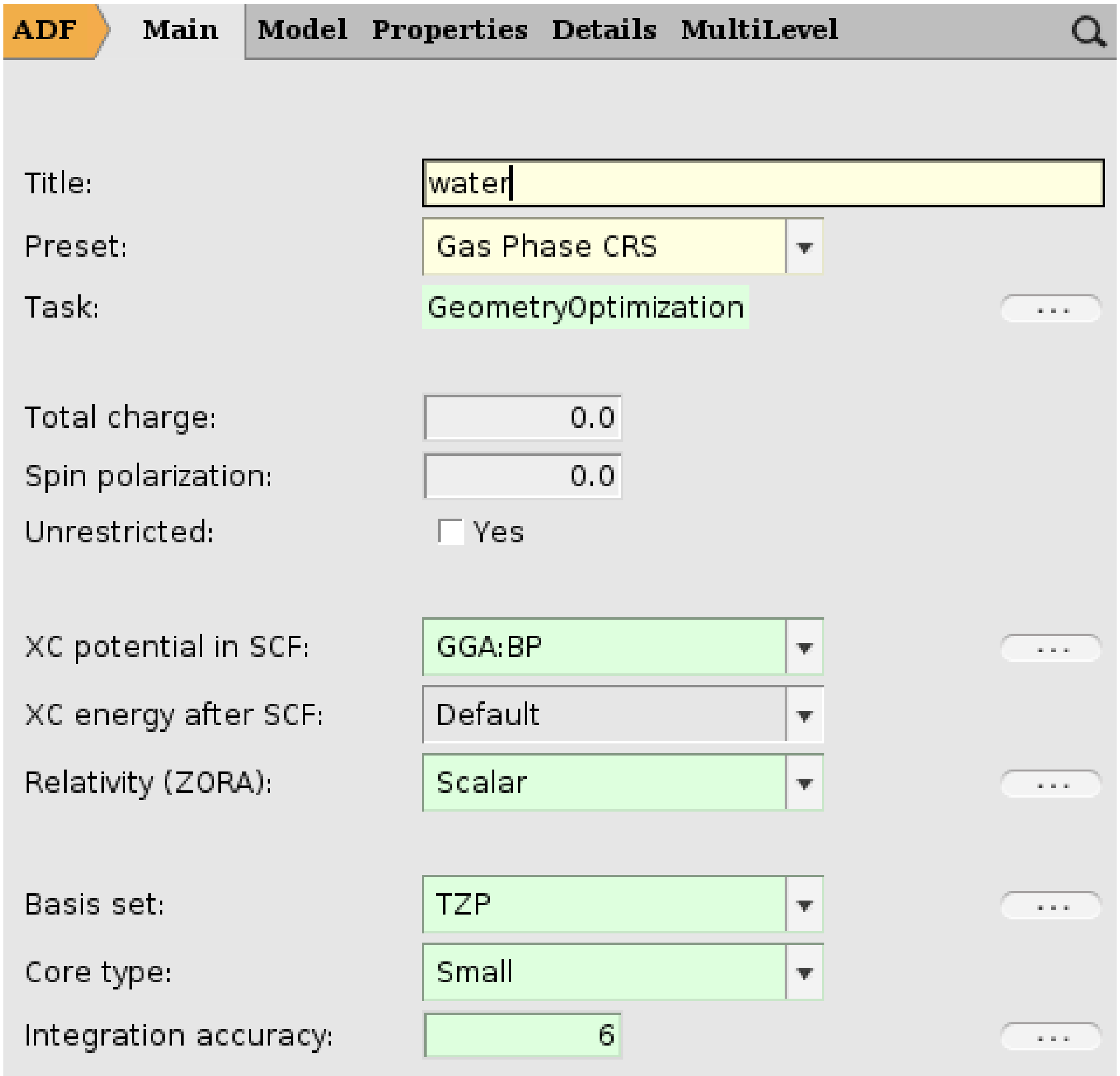
Your water molecule should look something like this:



Step 3: Optimize the gas phase geometry

The next step is to optimize the geometry using ADF. In this case we will use the Becke-Perdew functional and a TZP basis set, since those are used for the optimization of the COSMO-RS parameters.

`Enter a proper title in the Title field (like 'water')`
`Select` **Preset → Gas Phase CRS**



Title: water

Preset: Gas Phase CRS

Task: GeometryOptimization

Total charge: 0.0

Spin polarization: 0.0

Unrestricted: ☐ Yes

XC potential in SCF: GGA:BP

XC energy after SCF: Default

Relativity (ZORA): Scalar

Basis set: TZP

Core type: Small

Integration accuracy: 6

For your information, the proper settings for the gas phase geometry optimization are: The Becke Perdew exchange correlation functional (GGA:BP), use of the scalar relativistic ZORA Hamiltoninan, a TZP small core basis set (for Iodine a TZ2P small core basis set), and an integration accuracy of 6. Like for Iodine for heavier elements than krypton, a TZ2P small core basis set is recommended.

With the proper options selected, now run ADF:

`Select` **File → Run**
```
In the file select box, choose a name for your file
(for example 'water_gasphase' to make a distinction in the
names of the gas phase molecule and the solvated molecule)
and click 'Save'
```

Now ADF will start automatically, and you can follow the calculation using the logfile that is automatically shown.

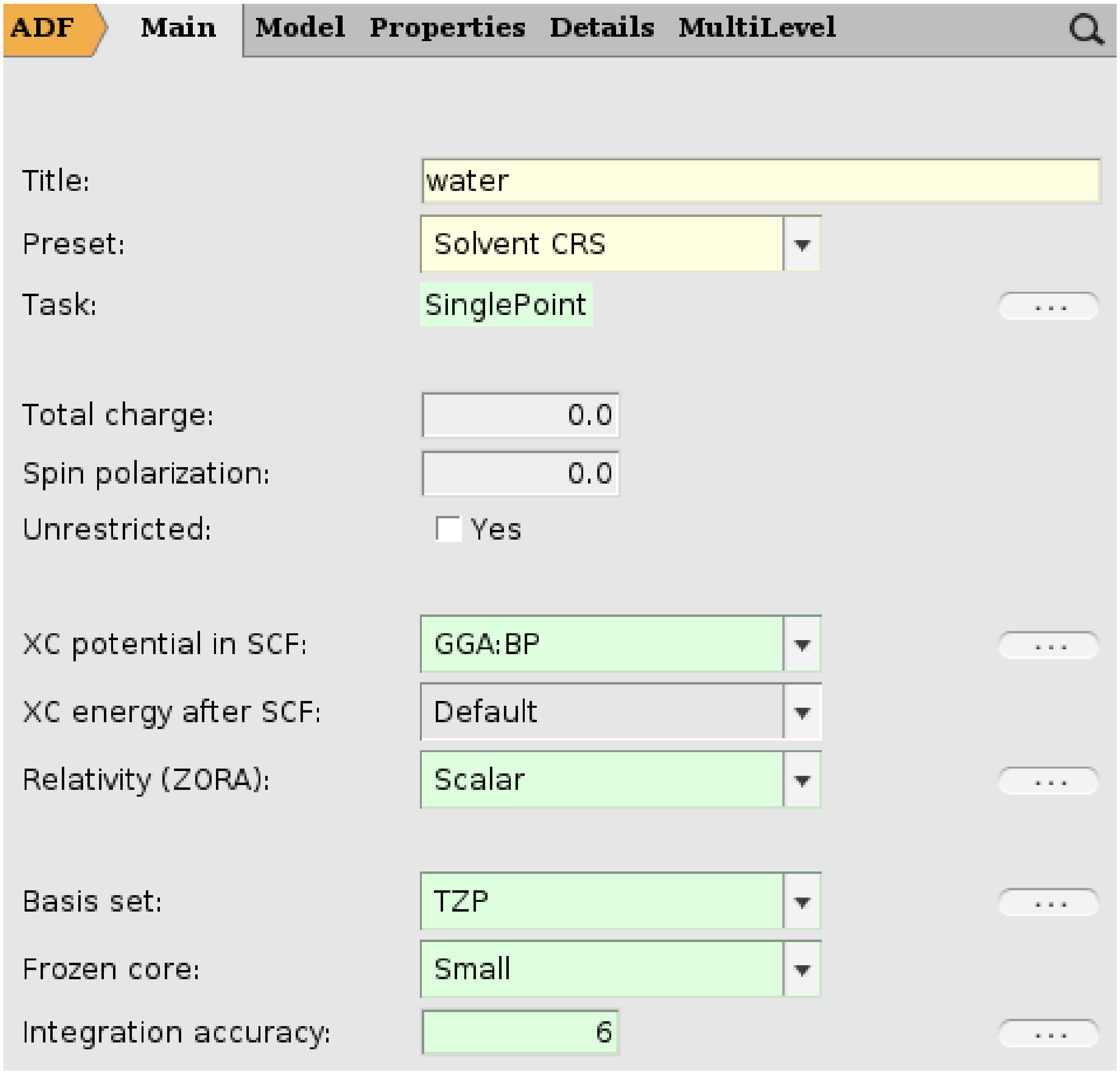
```
Wait until the optimization is ready (should take very little time)
Click 'Yes' in the pop-up to read the coordinates from a .t21 file.
```

Now the geometry of the water molecule is the optimized one.

Step 4: Set up the ADF COSMO parameters

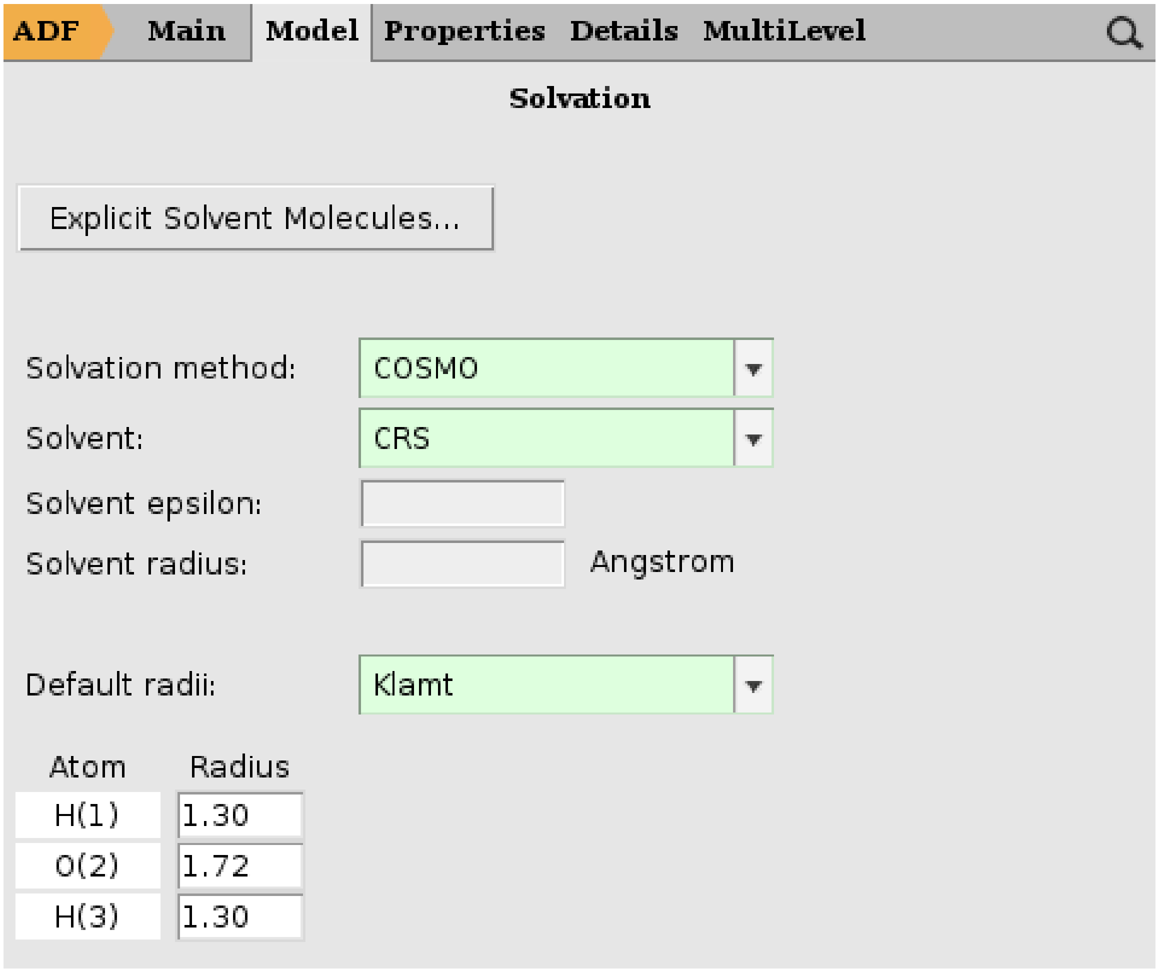
First set up the COSMO calculation with the COSMO parameters as they were used in the ADF parametrization of COSMO-RS. The molecule is in a solvent, represented in the COSMO model by a dielectric medium with a dielectric constant. This dielectric constant is infinite in the COSMO-RS model.

`Select` **Preset** → **Solvent CRS**



Title: water
Preset: Solvent CRS
Task: SinglePoint
Total charge: 0.0
Spin polarization: 0.0
Unrestricted: ☐ Yes
XC potential in SCF: GGA:BP
XC energy after SCF: Default
Relativity (ZORA): Scalar
Basis set: TZP
Frozen core: Small
Integration accuracy: 6

Part of the COSMO parameters that are set can be found if one selects **Model** → **Solvation**. The dielectric constant is infinite if one chooses 'CRS' for the Solvent. The so called 'Klamt' radii are used for the construction of the molecular cavity.



Solvation method: COSMO

Solvent: CRS

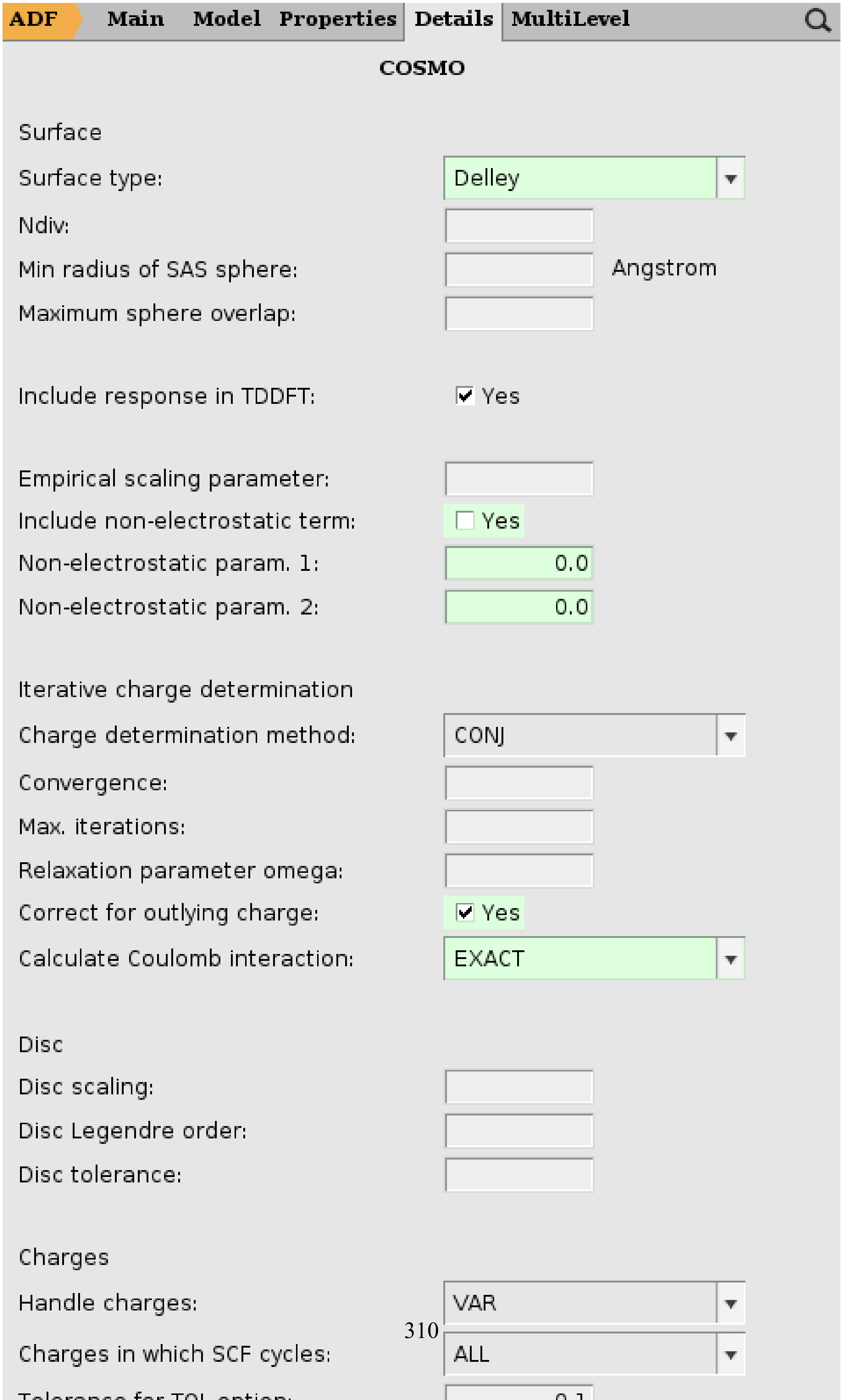
Solvent epsilon:

Solvent radius: Angstrom

Default radii: Klamt

Atom	Radius
H(1)	1.30
O(2)	1.72
H(3)	1.30

Another part of the COSMO parameters that are set can be found if one selects **Details** → **COSMO**:



COSMO

Surface

Surface type: Delley

Ndiv:

Min radius of SAS sphere: Angstrom

Maximum sphere overlap:

Include response in TDDFT: ☑ Yes

Empirical scaling parameter:

Include non-electrostatic term: ☐ Yes

Non-electrostatic param. 1: 0.0

Non-electrostatic param. 2: 0.0

Iterative charge determination

Charge determination method: CONJ

Convergence:

Max. iterations:

Relaxation parameter omega:

Correct for outlying charge: ☑ Yes

Calculate Coulomb interaction: EXACT

Disc

Disc scaling:

Disc Legendre order:

Disc tolerance:

Charges

Handle charges: VAR

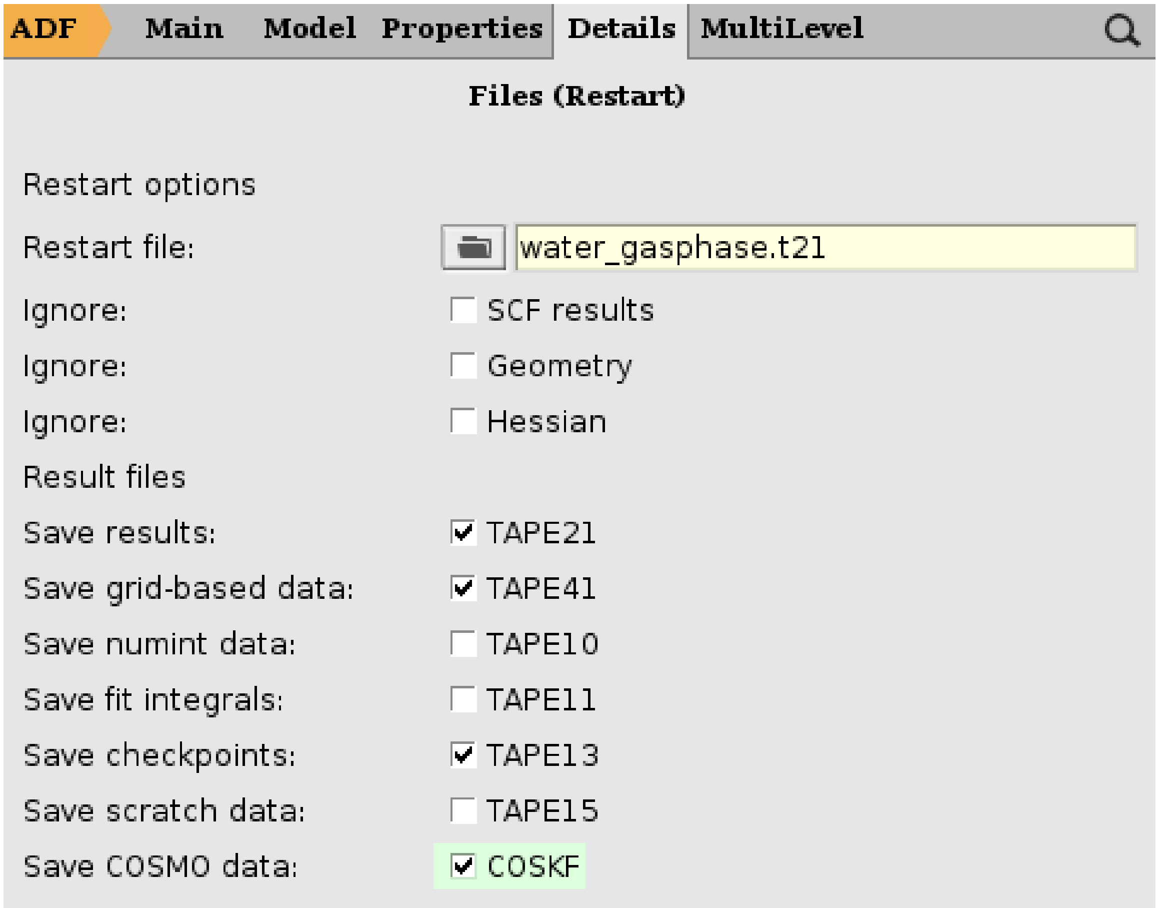
Charges in which SCF cycles: ALL

Tolerance for TOL option: 0.1

Step 5: Perform the ADF COSMO calculation and obtain the ADF COSMO result file

For the COSMO-RS calculation it is important that both the energy of the gas phase molecule and the energy of the solvated molecule are known. Also important is to use the same charge and/or spin-polarization in the gas phase molecule as in the solvated molecule. In order to have both values a restart is required with the .t21 file of the gas phase molecule as restart file for the solvated molecule. Note that this is a different procedure than in the ADF2008.01 tutorial.

Use the panel bar **Details → Files (Restart)** command
Click the file select button next to 'Restart file', a popup window will appear
Select water_gasphase.t21 (the .t21 file of the gas phase molecule)
Click 'Open' in the pop-up



Files (Restart)

Restart options
Restart file: water_gasphase.t21
Ignore: ☐ SCF results
Ignore: ☐ Geometry
Ignore: ☐ Hessian

Result files
Save results: ☑ TAPE21
Save grid-based data: ☑ TAPE41
Save numint data: ☐ TAPE10
Save fit integrals: ☐ TAPE11
Save checkpoints: ☑ TAPE13
Save scratch data: ☐ TAPE15
Save COSMO data: ☑ COSKF

For sake of clarity we will save the COSMO calculation under a different name:

```
Select the 'Save As..' command from the 'File' menu
In the file select box, choose a name for your file
   (for example 'water') and click 'Save'
```

With the proper options selected, now run ADF:

Select **File → Run**

Now ADF will start automatically, and you can follow the calculation using the logfile that is automatically shown.

```
Wait until the COSMO calculation is ready (should take very little time)
Click 'Yes' in the pop-up to read the coordinates from a .t21 file.
```

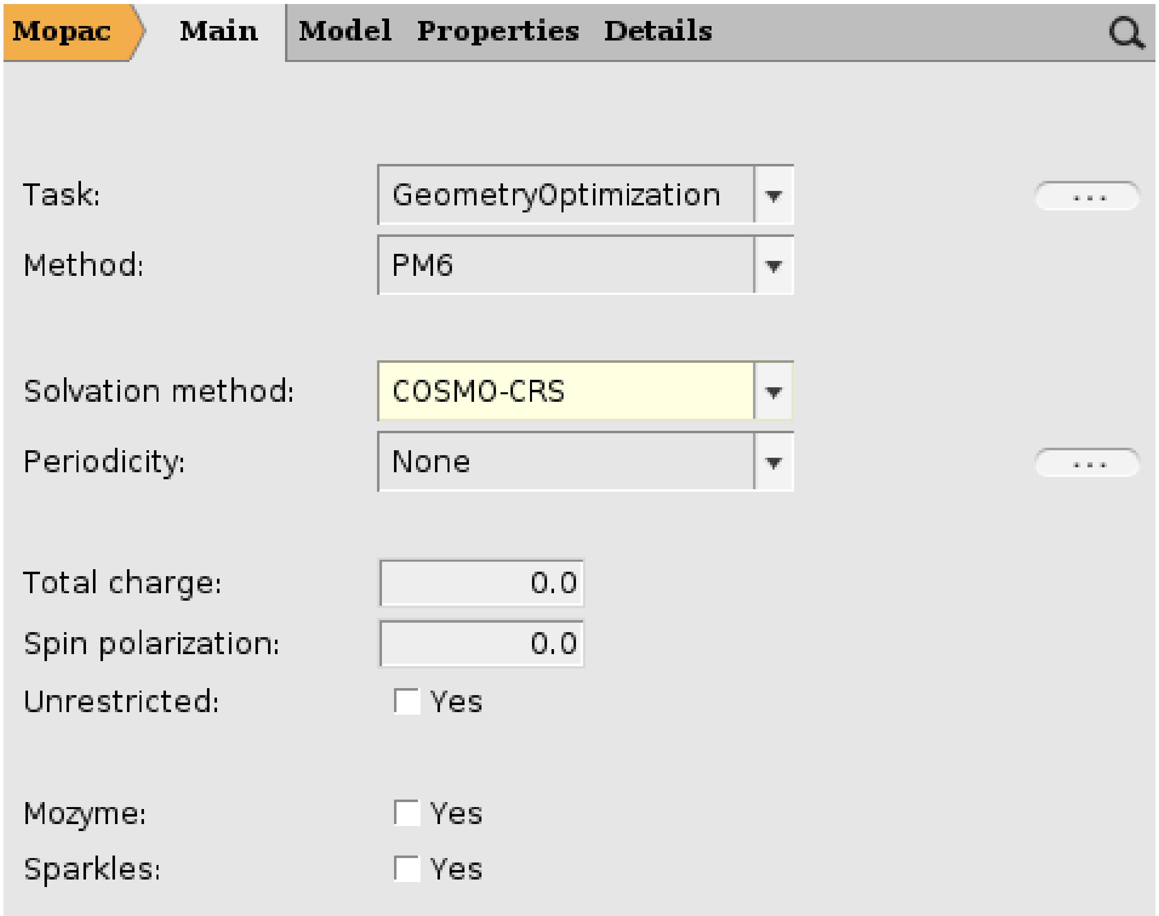
After the calculation has finished the file water.coskf, which is an ADF COSMO result file, can be used as input for a COSMO-RS calculation.

Note that a .coskf file is not a complete .t21 file. For example, if one has such a .coskf file, only the COSMO surface charge density can be viewed with ADFview. Thus a .coskf file is mostly useful for COSMO-RS calculations.

Step 6: MOPAC COSMO result file

A MOPAC COSMO result file can be created in almost the same way as an ADF COSMO result file. In this step we will skip the first steps of creating the water molecule. We will change the program from ADF to MOPAC, and select the COSMO solvation method.

`Select` **ADF → Mopac**
`Select` **Solvation Method → COSMO-CRS**



Task: GeometryOptimization
Method: PM6
Solvation method: COSMO-CRS
Periodicity: None
Total charge: 0.0
Spin polarization: 0.0
Unrestricted: ☐ Yes
Mozyme: ☐ Yes
Sparkles: ☐ Yes

Part of the COSMO parameters that are set can be found if one selects **Details → Run Script**. Technically ADFinput will add some keywords to the input for MOPAC (see also http://www.openmopac.net) in case of a MOPAC COSMO calculation:

```
PM6 EPS=9999.9 RSOLV=1.3 COSWRT NSPA=362
```

For sake of clarity we will save the COSMO calculation under a different name, and run the calculation

```
Select the 'Save As..' command from the 'File' menu
In the file select box, choose 'water_mopac' as name for your file and click
'Save'
```
`Select` **File → Run**
```
Wait until the optimization is ready (should take very little time)
Click 'Yes' in the pop-up to read the coordinates from a .rkf file.
```

After the calculation has finished the file water_mopac.coskf, which is a MOPAC COSMO result file, can be used as input for a COSMO-RS calculation.

Note that MOPAC is a semi-empirical quantum chemistry program, whereas ADF is based on density functional theory (DFT). Thus the MOPAC COSMO result files will not be of the same quality as the ADF COSMO result files.

Tutorial 2: COSMO-RS overview: analysis

Step 1: Copy COSMO result Files

For this tutorial it is convenient to start with an empty directory, for example, with the name Tutorial.

In tutorial 1 it was shown how to make ADF COSMO result files. In this tutorial we will use some ADF COSMO result files that were made before. These files can be found the directory $ADFHOME/examples/crs/Tutorial2. Copy these COSMO result files (water.coskf, methanol.coskf, ethanol.coskf, and benzene.coskf) to the directory Tutorial. As the name suggests these are COSMO result files of water, methanol, ethanol, and benzene, respectively.

Note that these COSKF (.coskf) files contain only the part of an ordinary TAPE21 (.t21) file which is needed in a COSMO-RS calculation. These COSKF files can only partly be used in ADFview, for example.

Step 2: Start ADFcrs

On a Unix-like system, enter the following command:

```
$ADFBIN/adfcrs &
```

On Windows, one can start ADFcrs by double-clicking on the ADFcrs icon on the Desktop:

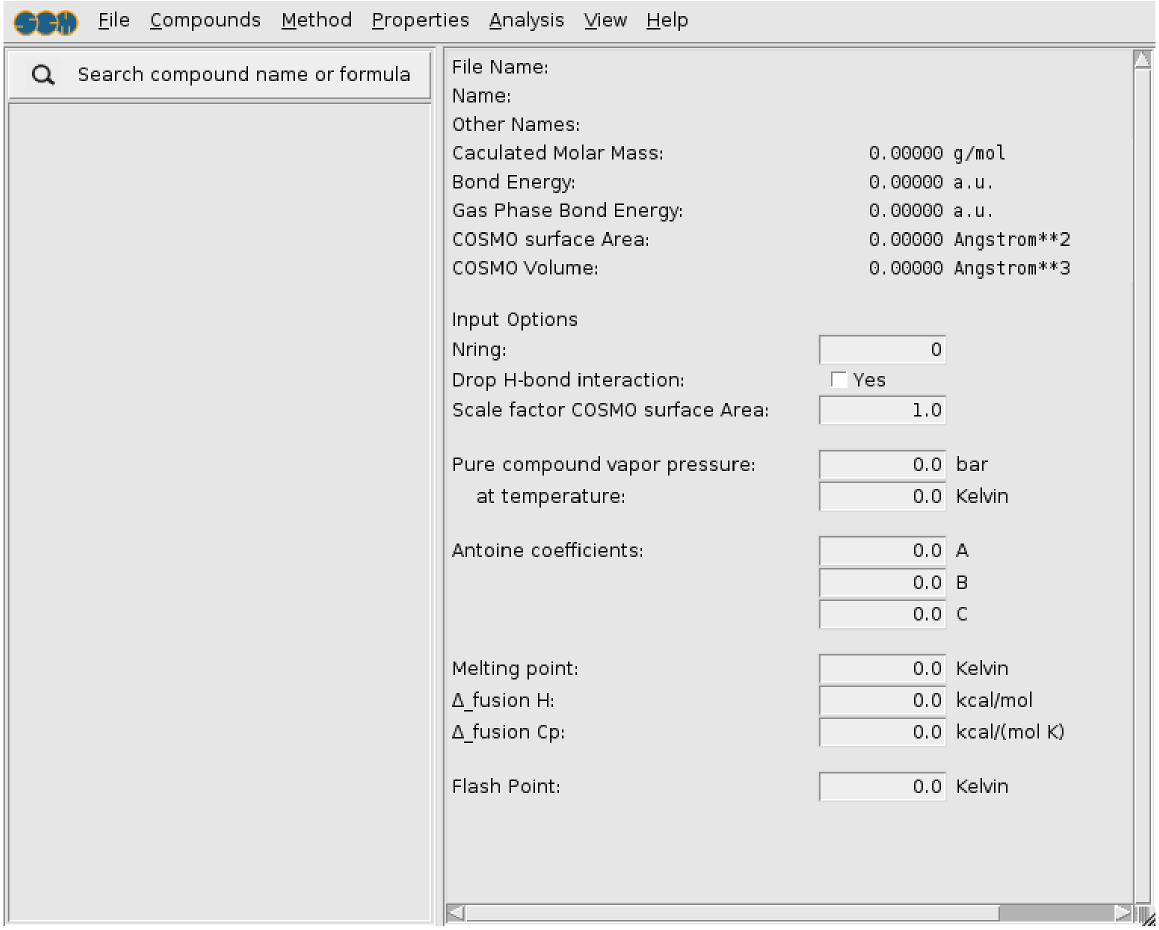
```
double click the ADFcrs icon on the Desktop
```

On Macintosh, use the ADF2012.01 or ADFLaunch program to start ADFcrs:

```
double click on the ADF2012.01 or ADFLaunch icon which will start ADFjobs
```
`Select` **SCM → COSMO-RS**

Alternatively if you know how to start ADFjobs (in your home directory), and move to the Tutorial directory:

```
cd $HOME
Start adfjobs
Click on the Tutorial folder icon
```
`Select` **SCM → COSMO-RS**



File Name:
Name:
Other Names:
Caculated Molar Mass: 0.00000 g/mol
Bond Energy: 0.00000 a.u.
Gas Phase Bond Energy: 0.00000 a.u.
COSMO surface Area: 0.00000 Angstrom**2
COSMO Volume: 0.00000 Angstrom**3

Input Options
Nring: 0
Drop H-bond interaction: ☐ Yes
Scale factor COSMO surface Area: 1.0

Pure compound vapor pressure: 0.0 bar
at temperature: 0.0 Kelvin

Antoine coefficients: 0.0 A
0.0 B
0.0 C

Melting point: 0.0 Kelvin
Δ_fusion H: 0.0 kcal/mol
Δ_fusion Cp: 0.0 kcal/(mol K)

Flash Point: 0.0 Kelvin

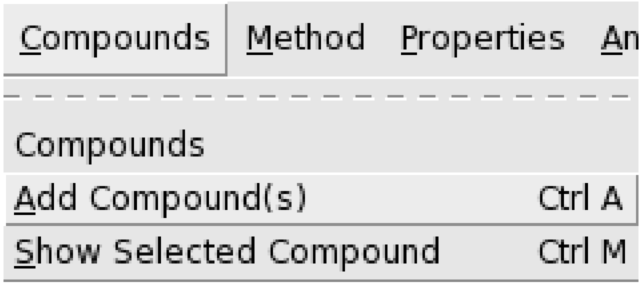
This ADFcrs window consists of the following main parts:

- the menu bar with the menu commands
- on the left: a list of compounds
- on the right: some properties for the selected compound

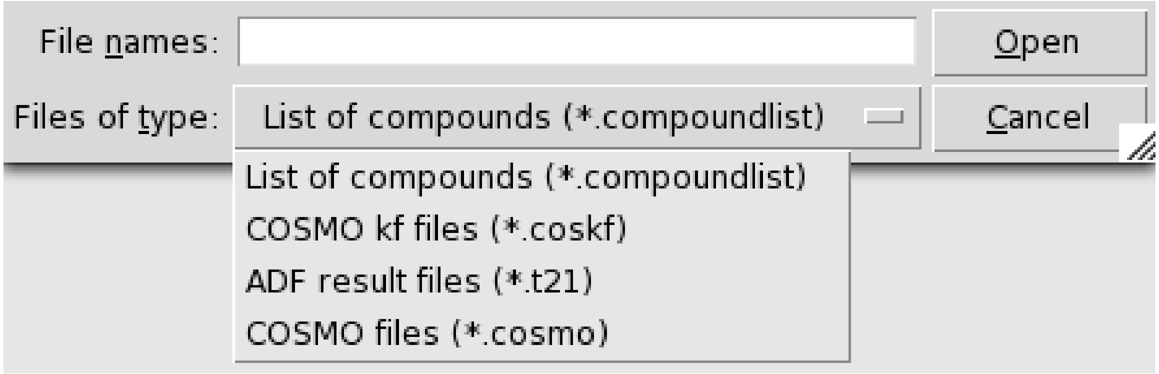
This is the so called 'Compounds' window, which is the window you will get if you select **Compounds** → **Compounds**.

Step 3: Add Compounds

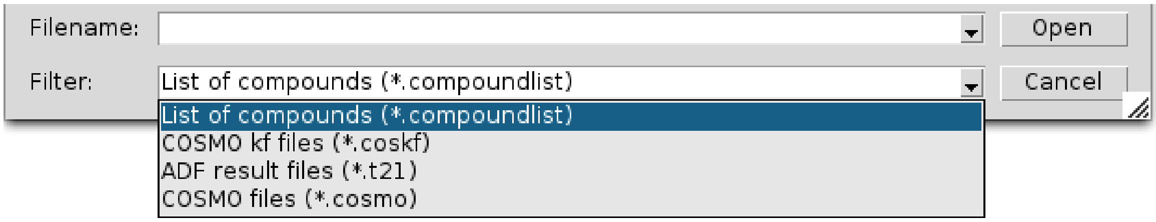
Select **Compounds** → **Add Compound(s)**



A file select box will open , that looks like (may look different on different platforms)

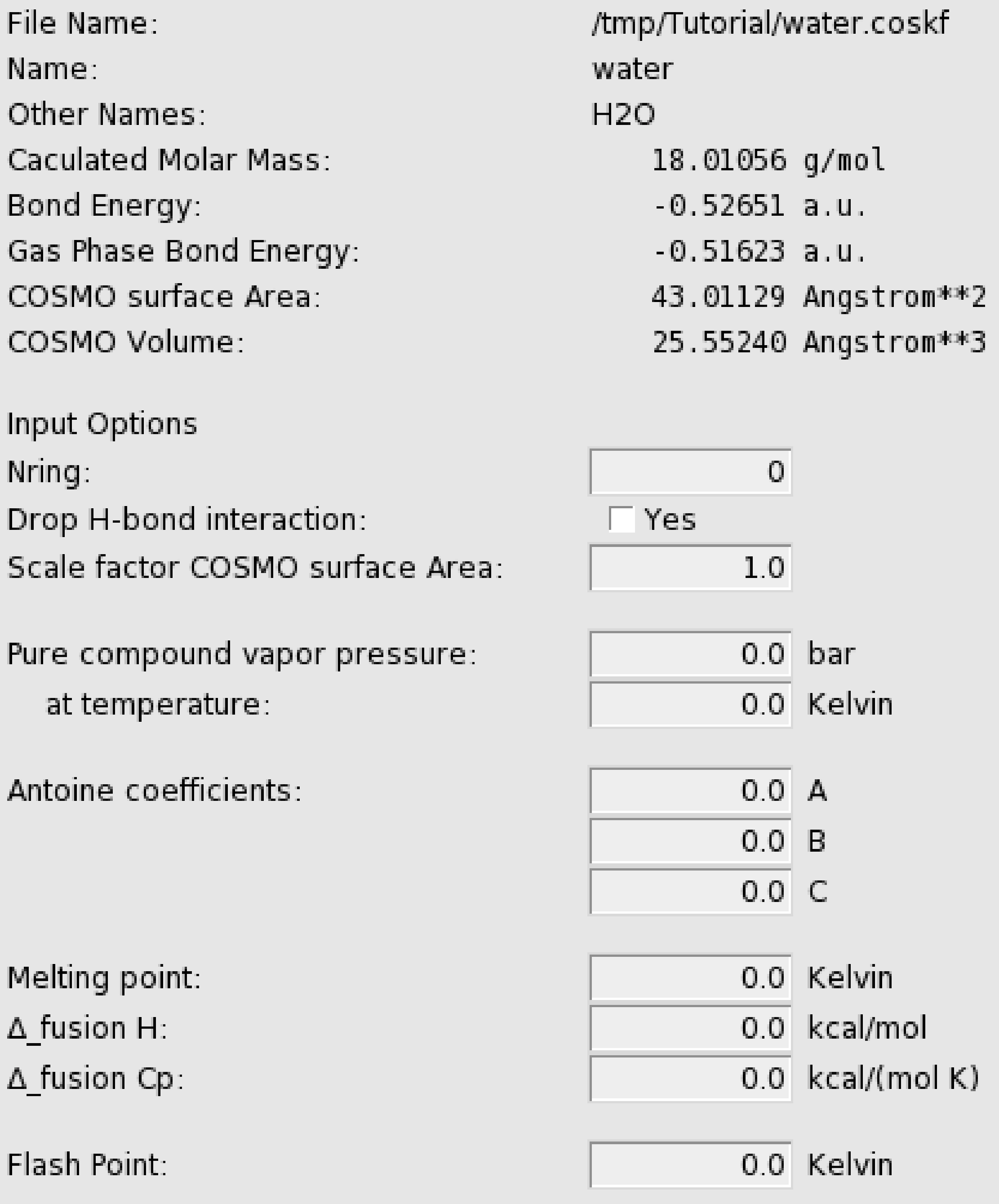


or



`Select` **Files of type** `(or` **Filter**`)` → **COSMO kf file (*.coskf)**
`Select water.coskf`
`Click 'Open'`

On the right side of the 'Compounds' window one finds some data that was written from the file water.coskf. Here it is also possible to add some pure compound input data. We will not do so now since there is no need. For some other types of compounds user input is required at this point, however. We will encounter an example of that in the next step.



File Name: /tmp/Tutorial/water.coskf
Name: water
Other Names: H2O
Caculated Molar Mass: 18.01056 g/mol
Bond Energy: -0.52651 a.u.
Gas Phase Bond Energy: -0.51623 a.u.
COSMO surface Area: 43.01129 Angstrom**2
COSMO Volume: 25.55240 Angstrom**3

Input Options
Nring: 0
Drop H-bond interaction: ☐ Yes
Scale factor COSMO surface Area: 1.0

Pure compound vapor pressure: 0.0 bar
at temperature: 0.0 Kelvin

Antoine coefficients: 0.0 A
0.0 B
0.0 C

Melting point: 0.0 Kelvin
Δ_fusion H: 0.0 kcal/mol
Δ_fusion Cp: 0.0 kcal/(mol K)

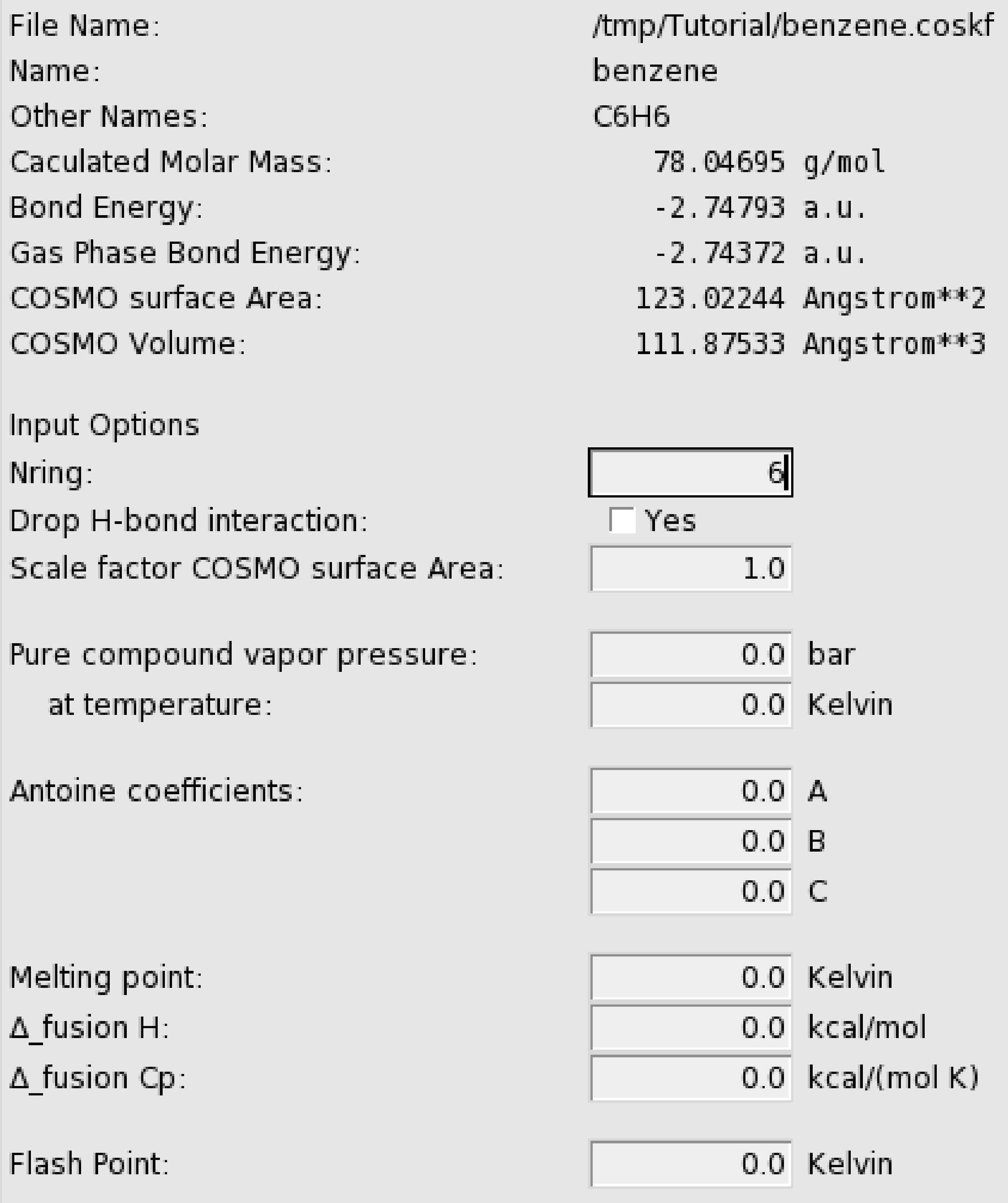
Flash Point: 0.0 Kelvin

Repeat these instructions to add methanol.coskf, ethanol.coskf, and benzene.coskf.

Step 4: Set pure compound parameters

In the COSMO-RS model (see Ref.[2] in the COSMO-RS manual) there is a ring correction term. This is important for, for example, the benzene molecule, which has 6 ring atoms. However, it is really required only when the vapor pressure of the compound is going to be computed (either because that is explicitly requested or because it is used in predicting partial vapor pressures in a mixture or gas/liquid partitioning coefficients).

Click on the left side benzene
Enter '6' without quotes in the 'Nring' field on the right side



File Name: /tmp/Tutorial/benzene.coskf
Name: benzene
Other Names: C6H6
Caculated Molar Mass: 78.04695 g/mol
Bond Energy: -2.74793 a.u.
Gas Phase Bond Energy: -2.74372 a.u.
COSMO surface Area: 123.02244 Angstrom**2
COSMO Volume: 111.87533 Angstrom**3

Input Options
Nring: 6
Drop H-bond interaction: ☐ Yes
Scale factor COSMO surface Area: 1.0

Pure compound vapor pressure: 0.0 bar
at temperature: 0.0 Kelvin

Antoine coefficients: 0.0 A
0.0 B
0.0 C

Melting point: 0.0 Kelvin
Δ_fusion H: 0.0 kcal/mol
Δ_fusion Cp: 0.0 kcal/(mol K)

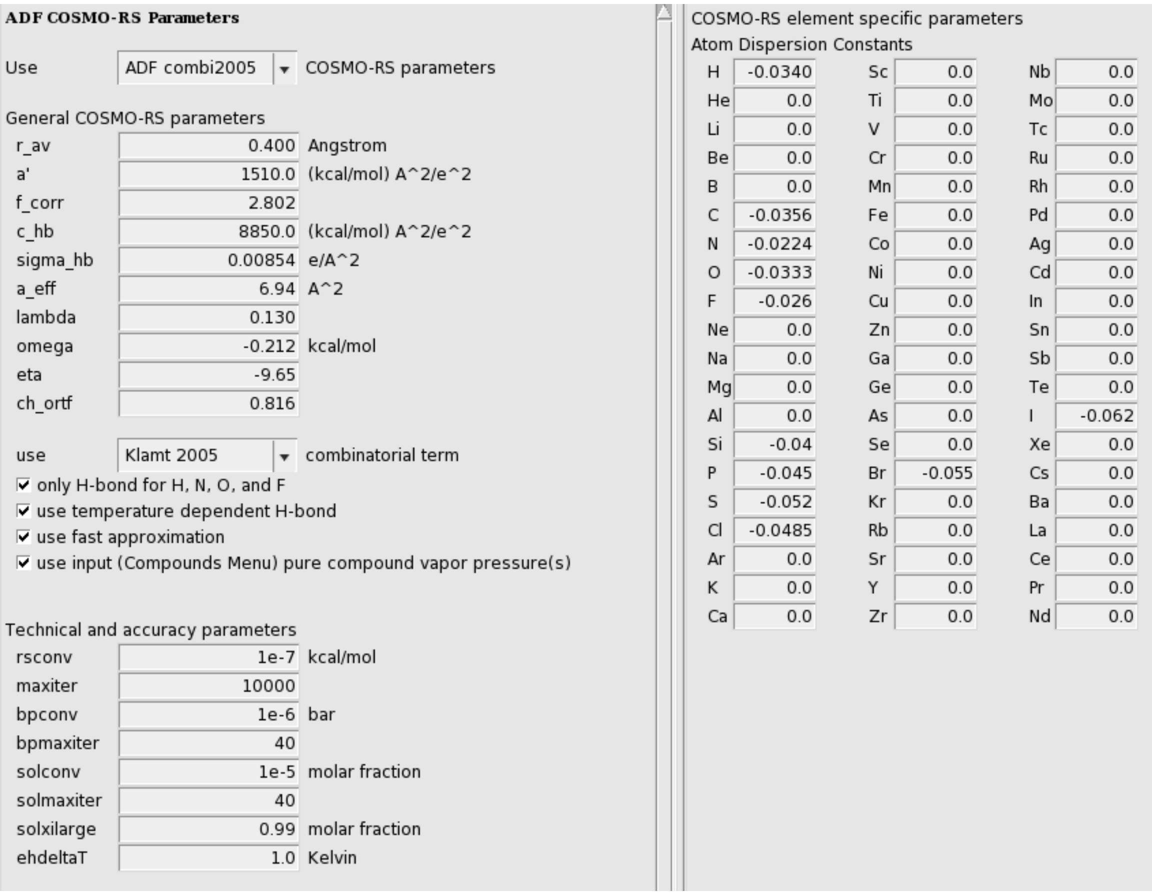
Flash Point: 0.0 Kelvin

For some properties, like solubility of a solid, one can include some pure compound properties in the left window of the 'Compounds' window for a selected compound.

Step 5: Set the COSMO-RS parameters

COSMO-RS

Select **Method → COSMO-RS**
Select **Method → Parameters**



ADF COSMO-RS Parameters

Use: ADF combi2005 ▾ COSMO-RS parameters

General COSMO-RS parameters

r_av	0.400	Angstrom
a'	1510.0	(kcal/mol) A^2/e^2
f_corr	2.802	
c_hb	8850.0	(kcal/mol) A^2/e^2
sigma_hb	0.00854	e/A^2
a_eff	6.94	A^2
lambda	0.130	
omega	-0.212	kcal/mol
eta	-9.65	
ch_ortf	0.816	

use: Klamt 2005 ▾ combinatorial term

- ☑ only H-bond for H, N, O, and F
- ☑ use temperature dependent H-bond
- ☑ use fast approximation
- ☑ use input (Compounds Menu) pure compound vapor pressure(s)

Technical and accuracy parameters

rsconv	1e-7	kcal/mol
maxiter	10000	
bpconv	1e-6	bar
bpmaxiter	40	
solconv	1e-5	molar fraction
solmaxiter	40	
solxilarge	0.99	molar fraction
ehdeltaT	1.0	Kelvin

COSMO-RS element specific parameters

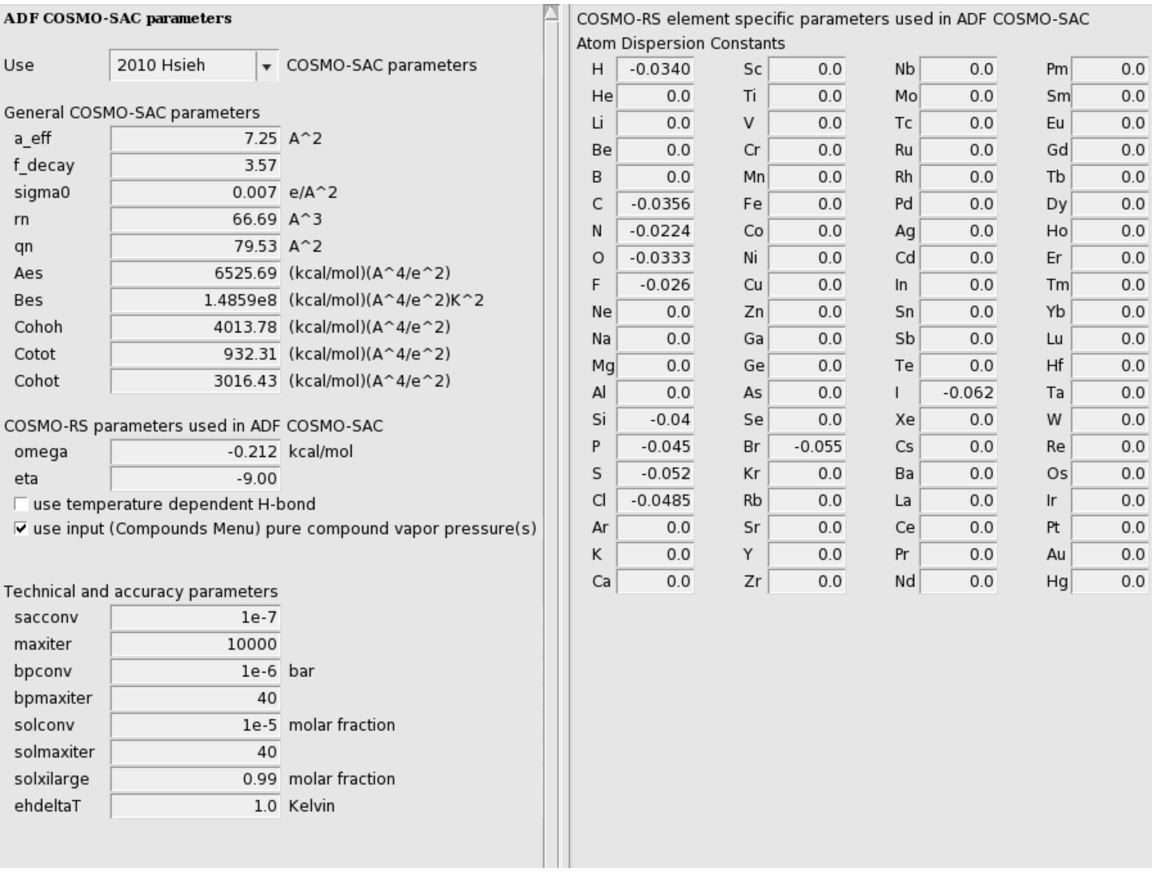
Atom Dispersion Constants

H	-0.0340	Sc	0.0	Nb	0.0
He	0.0	Ti	0.0	Mo	0.0
Li	0.0	V	0.0	Tc	0.0
Be	0.0	Cr	0.0	Ru	0.0
B	0.0	Mn	0.0	Rh	0.0
C	-0.0356	Fe	0.0	Pd	0.0
N	-0.0224	Co	0.0	Ag	0.0
O	-0.0333	Ni	0.0	Cd	0.0
F	-0.026	Cu	0.0	In	0.0
Ne	0.0	Zn	0.0	Sn	0.0
Na	0.0	Ga	0.0	Sb	0.0
Mg	0.0	Ge	0.0	Te	0.0
Al	0.0	As	0.0	I	-0.062
Si	-0.04	Se	0.0	Xe	0.0
P	-0.045	Br	-0.055	Cs	0.0
S	-0.052	Kr	0.0	Ba	0.0
Cl	-0.0485	Rb	0.0	La	0.0
Ar	0.0	Sr	0.0	Ce	0.0
K	0.0	Y	0.0	Pr	0.0
Ca	0.0	Zr	0.0	Nd	0.0

Default 'ADF combi2005' COSMO-RS parameters are selected, which are ADF optimized COSMO-RS parameters. See also a discussion of the COSMO-RS parameters in the COSMO-RS manual. If one selects the 'Klamt' option for 'Use: ... COSMO-RS parameters', the optimized parameters are chosen, which are optimized by Klamt et al., see Ref. [2] in the COSMO-RS manual.

COSMO-SAC

Select **Method → COSMO-SAC**
Select **Method → Parameters**



ADF COSMO-SAC parameters

Use 2010 Hsieh ▾ COSMO-SAC parameters

General COSMO-SAC parameters

a_eff	7.25	A^2
f_decay	3.57	
sigma0	0.007	e/A^2
rn	66.69	A^3
qn	79.53	A^2
Aes	6525.69	(kcal/mol)(A^4/e^2)
Bes	1.4859e8	(kcal/mol)(A^4/e^2)K^2
Cohoh	4013.78	(kcal/mol)(A^4/e^2)
Cotot	932.31	(kcal/mol)(A^4/e^2)
Cohot	3016.43	(kcal/mol)(A^4/e^2)

COSMO-RS parameters used in ADF COSMO-SAC

omega	-0.212	kcal/mol
eta	-9.00	

☐ use temperature dependent H-bond

☑ use input (Compounds Menu) pure compound vapor pressure(s)

Technical and accuracy parameters

sacconv	1e-7	
maxiter	10000	
bpconv	1e-6	bar
bpmaxiter	40	
solconv	1e-5	molar fraction
solmaxiter	40	
solxilarge	0.99	molar fraction
ehdeltaT	1.0	Kelvin

COSMO-RS element specific parameters used in ADF COSMO-SAC

Atom Dispersion Constants

H	-0.0340	Sc	0.0	Nb	0.0	Pm	0.0
He	0.0	Ti	0.0	Mo	0.0	Sm	0.0
Li	0.0	V	0.0	Tc	0.0	Eu	0.0
Be	0.0	Cr	0.0	Ru	0.0	Gd	0.0
B	0.0	Mn	0.0	Rh	0.0	Tb	0.0
C	-0.0356	Fe	0.0	Pd	0.0	Dy	0.0
N	-0.0224	Co	0.0	Ag	0.0	Ho	0.0
O	-0.0333	Ni	0.0	Cd	0.0	Er	0.0
F	-0.026	Cu	0.0	In	0.0	Tm	0.0
Ne	0.0	Zn	0.0	Sn	0.0	Yb	0.0
Na	0.0	Ga	0.0	Sb	0.0	Lu	0.0
Mg	0.0	Ge	0.0	Te	0.0	Hf	0.0
Al	0.0	As	0.0	I	-0.062	Ta	0.0
Si	-0.04	Se	0.0	Xe	0.0	W	0.0
P	-0.045	Br	-0.055	Cs	0.0	Re	0.0
S	-0.052	Kr	0.0	Ba	0.0	Os	0.0
Cl	-0.0485	Rb	0.0	La	0.0	Ir	0.0
Ar	0.0	Sr	0.0	Ce	0.0	Pt	0.0
K	0.0	Y	0.0	Pr	0.0	Au	0.0
Ca	0.0	Zr	0.0	Nd	0.0	Hg	0.0

Only the activity coefficients are calculated according to the COSMO-SAC method. Vapor pressure will be approximated using ideas from the COSMO-RS method, and not using the COSMO-SAC method. In order to do that some COSMO-RS parameters can be set that are used in an ADF COSMO-SAC calculation. See also a discussion of the COSMO-SAC parameters in the COSMO-RS manual.

Step 6: COSMO-RS or COSMO-SAC

One can easily change between the COSMO-RS or COSMO-SAC method that is going to be used in the calculation by selecting **Method → COSMO-RS** or **Method → COSMO-SAC**. Here we will use COSMO-RS, since ADF was parametrized for this method.

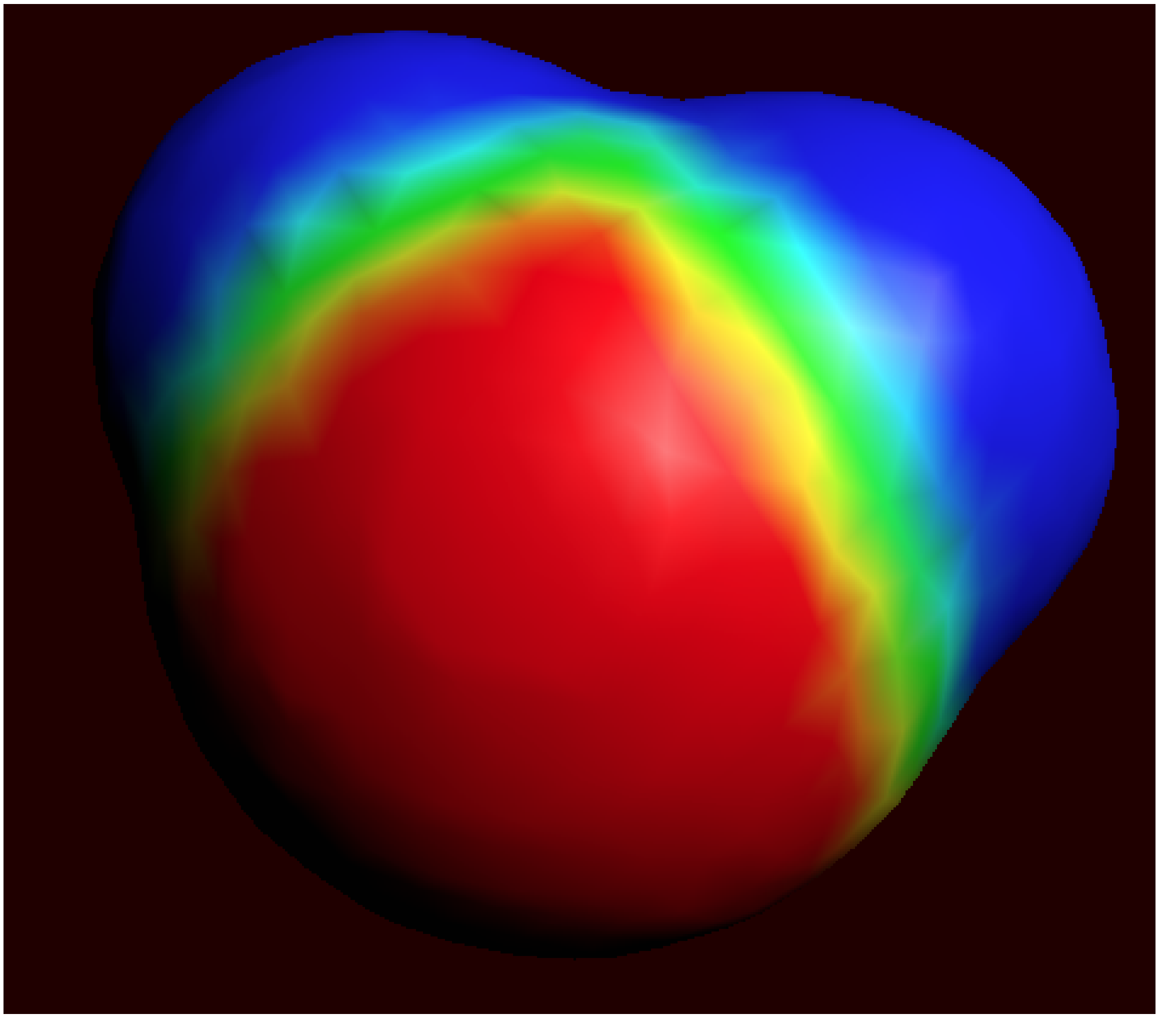
`Select` **Method → COSMO-RS**

Step 7: Visualize the COSMO surface: ADFview

You can use ADFview to have a look at the COSMO surface, and the COSMO surface charge density. This is possible if the COSMO result file of the compound is a .coskf file or a .t21 file.

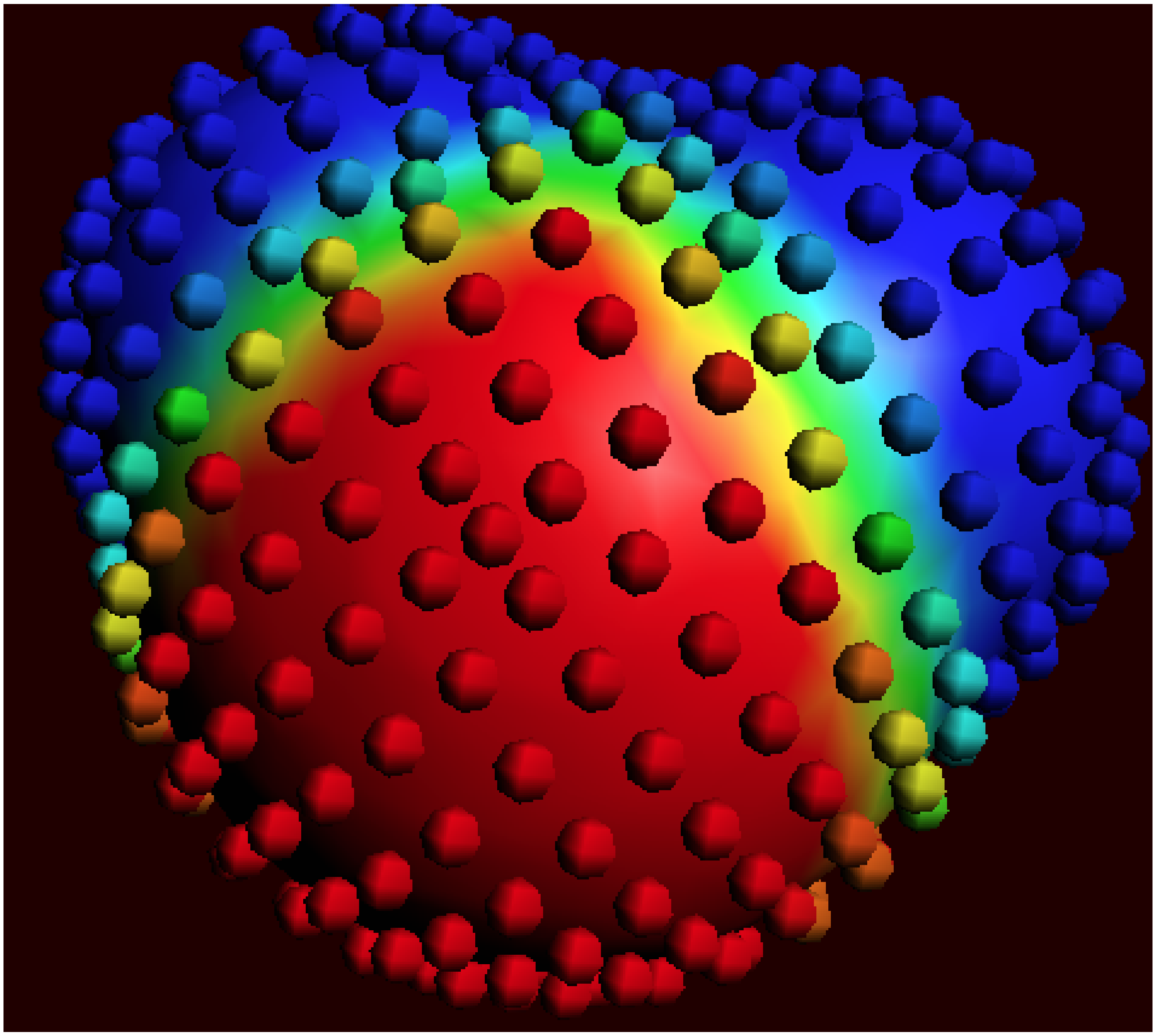
`Select` **Compounds → Compounds**
`Click on the left side water`
`Select` **Compounds → Show Selected Compound**
`Select (in the ADFview window that pop-ups)` **Add →**
COSMO: Surface Charge Density → on COSMO surface (reconstructed)

Then you will see something like:



The red part represents positive COSMO charge density (the underlying molecular charge is negative), the blue part negative COSMO charge density (the underlying molecular charge is positive). You can also look at the COSMO surface points themselves.

`Select` **Add → COSMO: Surface Charge Density → on COSMO surface points**



The small spheres represent the COSMO surface points that are used for the construction of the COSMO surface.

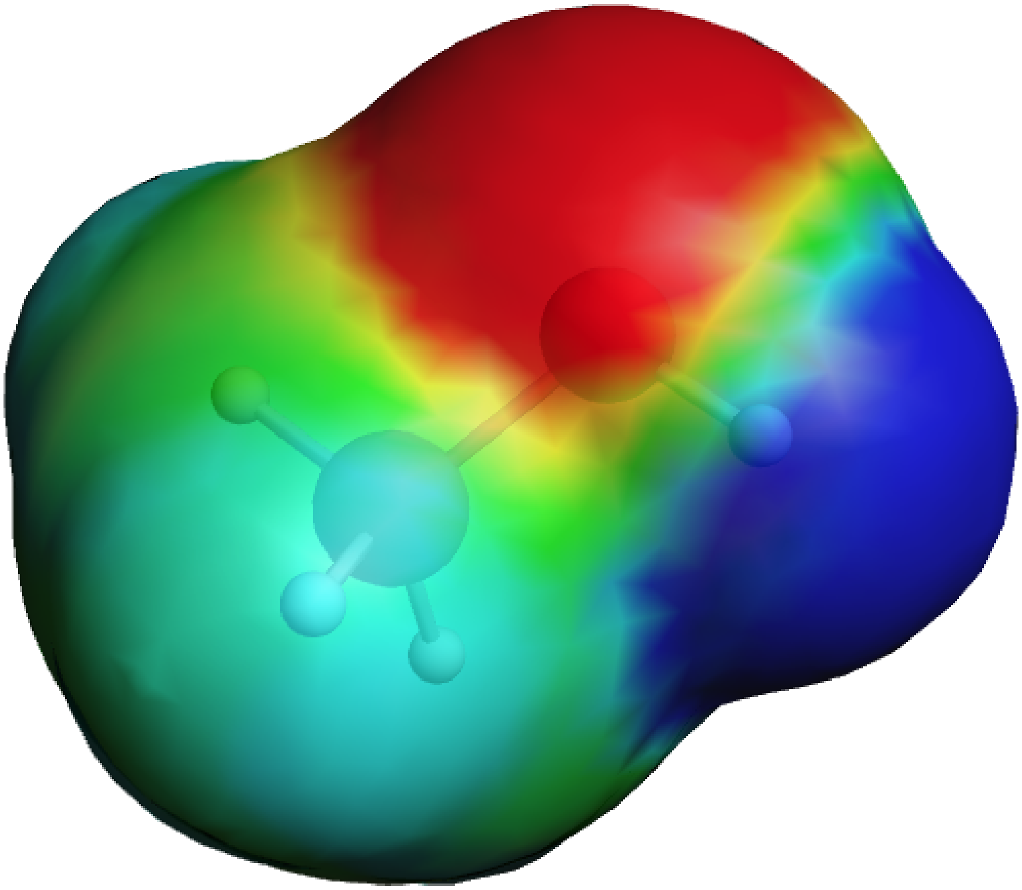
Next we will close this ADFview window.

`Select the ADFView window 'water'`
`Select` **File → Quit**
`Select the COSMO-RS GUI window`

ADFview has many options to change the look of the picture.

`Select` **Compounds → Compounds**
`Click on the left side methanol`
`Select` **Compounds → Show Selected Compound**
`Select (in the ADFview window that pop-ups)` **Add →**
COSMO: Surface Charge Density → on COSMO surface (reconstructed)
`Select` **View → Background → White**
`Check` **View → Anti-Alias**
`Increase the size of the ADFView window, such that a control line`
`at the bottom of the ADFview window is visible`
`In the control line click on the 'Cosmo surface' pull-down menu and`

use the Show Details command
Change the Opacity to 70



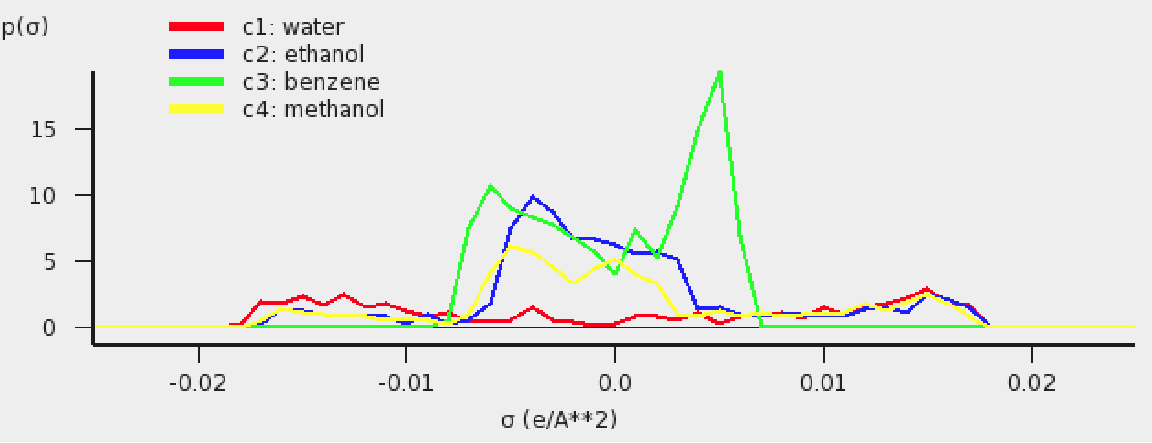
Next we will close this ADFview window.

Select the ADFView window 'methanol'
Select **File → Quit**
Select the COSMO-RS GUI window

Step 8: Analysis: The sigma profile

Select **Analysis → Sigma Profile**
In the left part of the window select 'water' for compound '1'
Select 'ethanol' for compound '2'
Select 'benzene' for compound '3'
Select 'methanol' for compound '4'
Select **File → Run**
Click 'Yes' when asked to 'Save changes (required to run)?'
Enter the name 'tutorial2' in the 'Filename' field

The sigma profiles (σ-profile) of the three pure compounds will be shown in a graph and in a table in the right part of the window. The whole window can be resized. The relative size of the left part of the window compared to the right part can be changed if one moves the sash that is in between these parts. In the right part of the window one can also change the relative size of the upper part compared to the lower part if one moves the sash that is in between these parts.

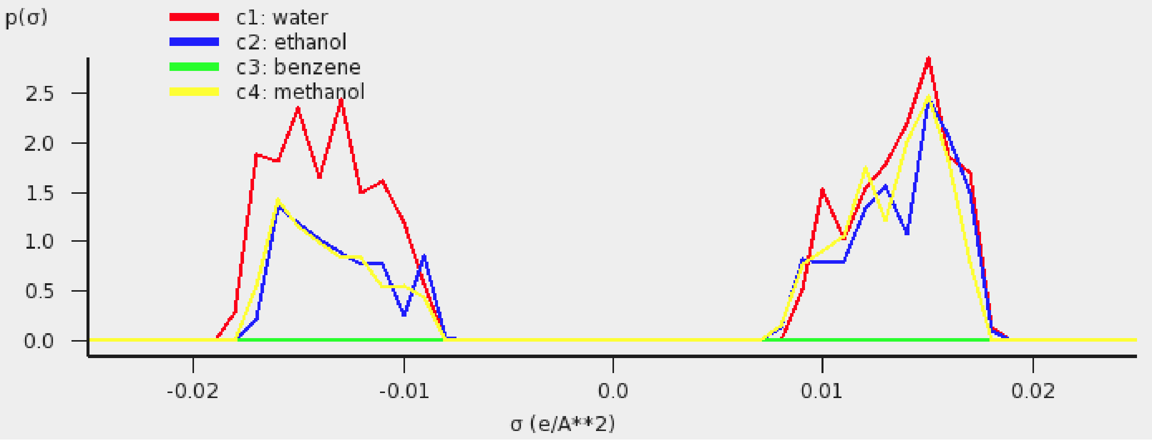


The σ-profile shows the amount of surface area for a given COSMO charge density. If the default settings are used, the red curve is the water σ-profile, the blue curve the methanol σ-profile, the green curve is the benzene σ-profile, and the yellow curve the methanol σ-profile. If one clicks in the graph one can zoom (right mouse, or Command-Left (drag up or down)), or translate (left mouse) the graph. If one clicks in the graph window at the left or below the axes, a popup window will appear in which one can set details for the graph window.

Note that the σ-profile depends on the method (COSMO-RS or COSMO-SAC) that was used in the calculation. Here we have used COSMO-RS. In this case the σ-profile depends on the actual value for r_av (r_{av}), which is one of the COSMO-RS parameters, see one of the previous steps.

One can also look at the hydrogen bonding part of the σ-profile.

```
In the left part of the window select 'Pure: HB' for Solvent
Press 'Run'
```



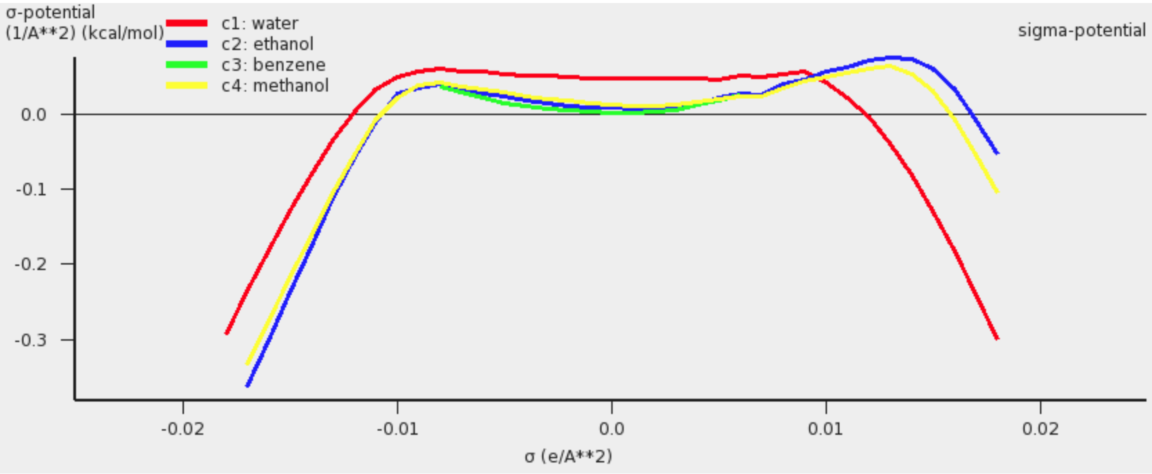
Step 9: Analysis: The sigma potential

Select **Analysis → Sigma Potential**

```
In the left part of the window select 'water' for compound '1'
Select 'ethanol' for compound '2'
Select 'benzene' for compound '3'
```

```
Select 'methanol' for compound '4'
Press 'Run'
```

The sigma potentials (σ-potential) of the three pure compounds will be shown in a graph and in a table in the right part of the window. The σ-potential depends on the temperature of a compound. Here the temperature is set to 25 °C (298.15 K).



If the default settings are used, the red curve is the water σ-potential, the blue curve the methanol σ-potential, the green curve is the benzene σ-potential, and the yellow curve is the methanol σ-potential. In the details for the graph window the line widths for all curves were set to '3'.

Note that the σ-potential is not calculated for values of the COSMO charge density that are non-existent on the COSMO surface of a certain compound.

```
Sigma Potential
Method: COSMO-RS

Temperature:     298.15000 Kelvin
Pure Compounds                    File name
   c1: water                       /tmp/Tutorial/water.coskf
   c2: ethanol                     /tmp/Tutorial/ethanol.coskf
   c3: benzene                     /tmp/Tutorial/benzene.coskf
   c4: methanol                    /tmp/Tutorial/methanol.coskf

σ(e/A**2)              c1             c2             c3             c4
 -0.02500
 -0.02400
 -0.02300
 -0.02200
 -0.02100
 -0.02000
 -0.01900
 -0.01800    -0.29397269
 -0.01700    -0.23690756    -0.36372876                   -0.33340701
 -0.01600    -0.18153786    -0.30097037                   -0.27590320
 -0.01500    -0.12841097    -0.23758220                   -0.21798802
 -0.01400    -0.07897803    -0.17440142                   -0.16028445
 -0.01300    -0.03410305    -0.11309661                   -0.10457933
 -0.01200     0.00328907    -0.05710450                   -0.05337639
 -0.01100     0.03311581    -0.01161227                   -0.00754075
 -0.01000     0.05020093     0.02860749                    0.02232651
 -0.00900     0.05811904     0.03577277                    0.04003047
 -0.00800     0.06143319     0.04158478     0.03787878     0.04246226
 -0.00700     0.05783816     0.03169112     0.02969348     0.03778561
 -0.00600     0.05698220     0.02893939     0.02181825     0.03405602
 -0.00500     0.05403241     0.02388828     0.01508554     0.02941521
 -0.00400     0.05211206     0.01913338     0.01055242     0.02498197
 -0.00300     0.05199226     0.01474734     0.00803712     0.02096977
 -0.00200     0.04980063     0.01204207     0.00571986     0.01826476
 -0.00100     0.04922807     0.01047442     0.00391231     0.01594799
  0.00000     0.04926470     0.00887138     0.00295134     0.01377564
  0.00100     0.04750716     0.00814529     0.00278182     0.01209359
  0.00200     0.04876684     0.00822705     0.00364656     0.01169674
  0.00300     0.04910836     0.00906071     0.00639814     0.01297842
  0.00400     0.04844323     0.01391514     0.01254335     0.01633456
  0.00500     0.04676193     0.02182671     0.01957790     0.02000320
  0.00600     0.05208756     0.02807902     0.02595901     0.02361397
  0.00700     0.05067382     0.02638413                    0.02445748
  0.00800     0.05456122     0.04030095                    0.03516569
  0.00900     0.05734731     0.04713907                    0.04416924
  0.01000     0.04216055     0.05810729                    0.04990077
  0.01100     0.02270744     0.06275628                    0.05488734
  0.01200    -0.00286580     0.07250347                    0.06080846
  0.01300    -0.03827410     0.07610071                    0.06451829
  0.01400    -0.08050303     0.07506712                    0.05328434
  0.01500    -0.12896326     0.06196112                    0.03132241
  0.01600    -0.18213360     0.03330333                   -0.00645187
  0.01700    -0.23950236    -0.00708983                   -0.05380134
  0.01800    -0.30088489    -0.05378152                   -0.10503679
```

Tutorial 3: COSMO-RS overview: properties

How the properties are calculated and definitions used can be found in the section Calculation of properties in the COSMO-RS manual.

Step 1: Start ADFcrs

For this tutorial we assume that you know how start ADFcrs and how to add compounds. Like in tutorial 2 we ask you to add the compounds water, methanol, ethanol, and benzene. One can do this, for example, by opening the .crs file that was created in tutorial 2. Save the file as tutorial3.crs.

`Start ADFcrs`
`Select` **File → Open...**
`Select 'tutorial2.crs' in the 'Filename' field`
`Select` **File → Save As**
`Enter the name 'tutorial3' in the 'Filename' field`

Alternatively on a Unix like system one may copy the COSMO result files (water.coskf, methanol.coskf, ethanol.coskf, and benzene.coskf) in the directory $ADFHOME/examples/crs/Tutorial2 to an empty directory and enter the following command in this directory where the COSMO result files are present:

```
$ADFBIN/adfcrs water.coskf methanol.coskf ethanol.coskf benzene.coskf &
```

Note that one has to set the number of ring atoms for the benzene compound.

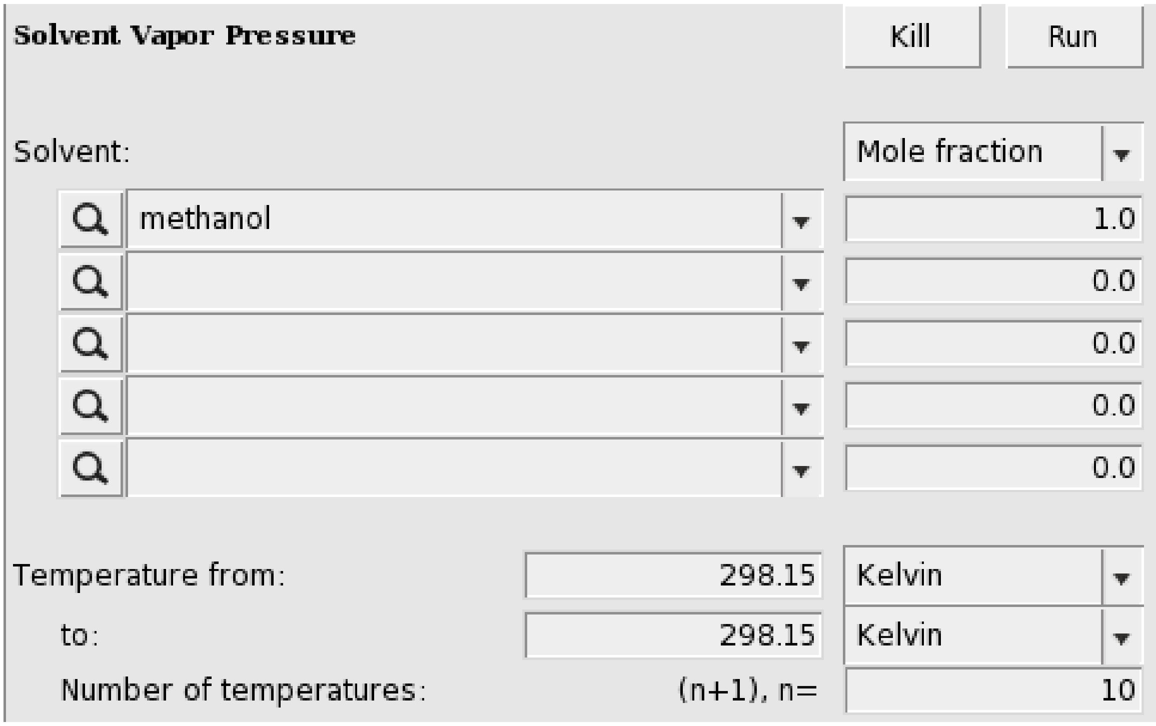
`Select` **Compounds → Compounds**
`Click on the left side benzene`
`Enter '6' without quotes in the 'Nring' field`
`Select` **File → Save As**
`Enter the name 'tutorial3' in the 'Filename' field`

In the compounds window one can also set the vapor pressure of the pure compounds at a given temperature, or set the Antoine parameters. If these values are not specified (if they are zero) then the pure compound vapor pressure will be approximated using the COSMO-RS method. This is relevant, for example, for the calculation of the (partial) vapor pressures of mixtures, calculation of boiling points of mixtures, and calculation of Henry's law constants.

Step 2: Calculate the vapor pressure of a solvent

The vapor pressure of a solvent at different temperatures can be calculated with **Properties → Solvent Vapor Pressure**.

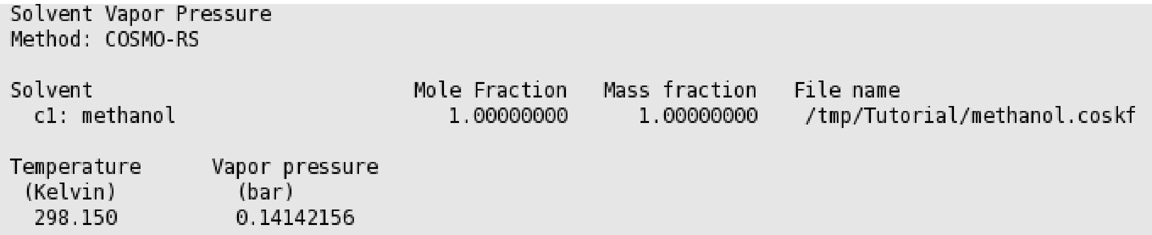
`Select` **Properties → Solvent Vapor Pressure**
`Select 'methanol' for the first component in the Solvent`
`Press 'Run'`



Solvent: Mole fraction
methanol 1.0
0.0
0.0
0.0
0.0

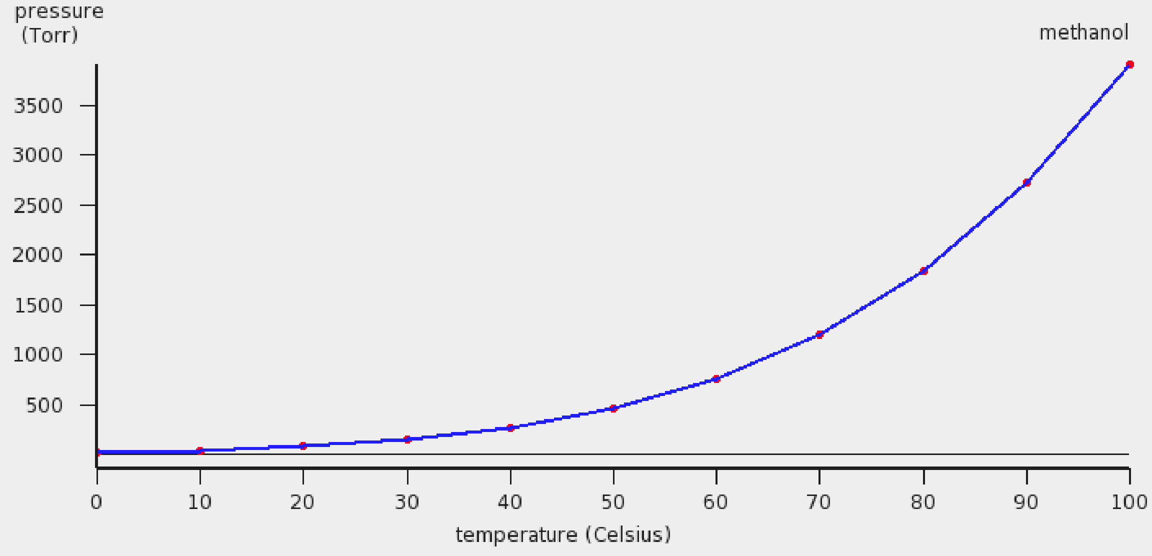
Temperature from: 298.15 Kelvin
to: 298.15 Kelvin
Number of temperatures: (n+1), n= 10

In this case the result is a table with one entry:

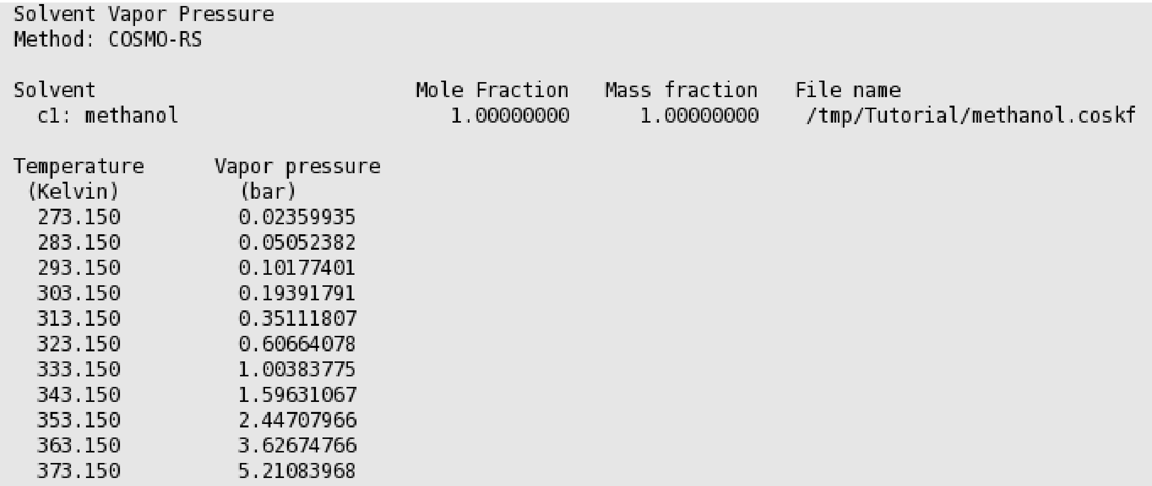

```
Solvent Vapor Pressure
Method: COSMO-RS

Solvent                           Mole Fraction   Mass fraction   File name
  c1: methanol                       1.00000000      1.00000000    /tmp/Tutorial/methanol.coskf

Temperature      Vapor pressure
 (Kelvin)          (bar)
  298.150          0.14142156
```

```
Select Celsius for the unit of temperature
Enter '0.0' without quotes in the 'Temperature from:' field
Enter '100.0' in the 'to:' field
Press 'Run'
```

In this case the result is a graph and a table. If one clicks in the graph window at the left or below the axes, a popup window will appear in which one can set details for the graph window. After some manipulation in the details of the graph, the graph can look like:



In this case COSMO-RS predicts a vapor pressure of about 0.61 bar (around 455 Torr) at 323.15 K (50.0 °C) for the pure liquid methanol.

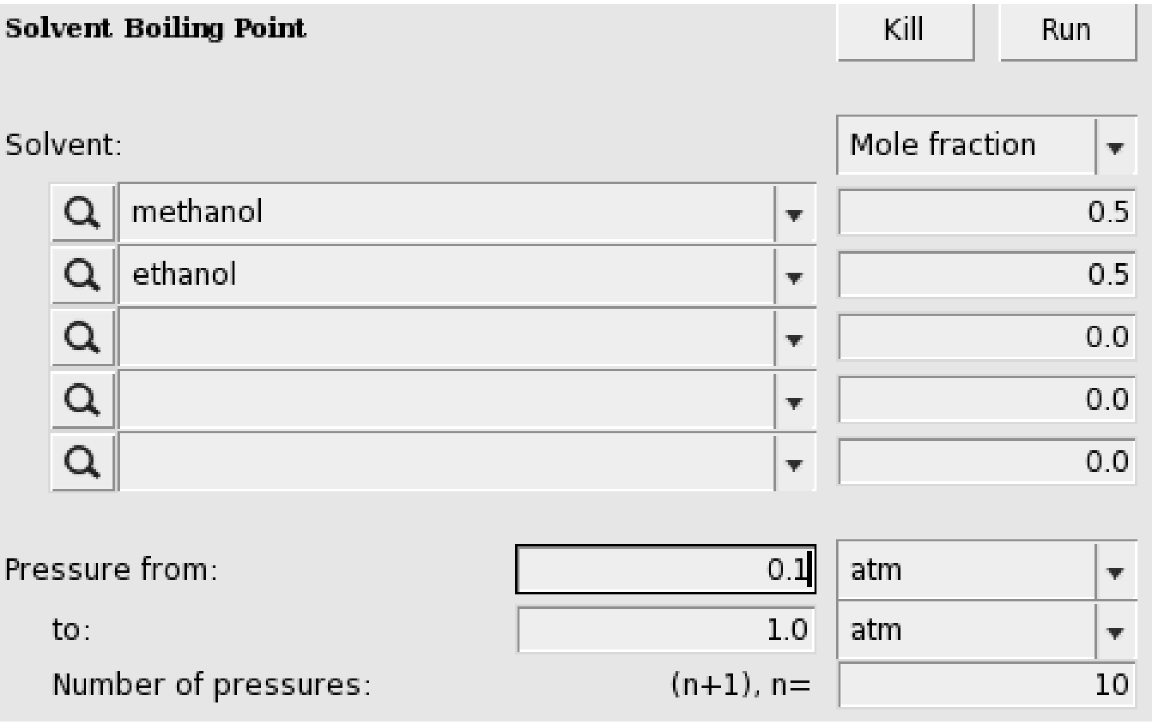


```
Solvent Vapor Pressure
Method: COSMO-RS

Solvent                           Mole Fraction    Mass fraction    File name
  c1: methanol                       1.00000000       1.00000000     /tmp/Tutorial/methanol.coskf

Temperature      Vapor pressure
 (Kelvin)          (bar)
  273.150          0.02359935
  283.150          0.05052382
  293.150          0.10177401
  303.150          0.19391791
  313.150          0.35111807
  323.150          0.60664078
  333.150          1.00383775
  343.150          1.59631067
  353.150          2.44707966
  363.150          3.62674766
  373.150          5.21083968
```

Step 3: Calculate the boiling point of a solvent

The boiling point of a solvent at different pressures can be calculated with **Properties** → **Solvent Boiling Point**.

Select **Properties** → **Solvent Boiling Point**
`Select 'methanol' for the first component in the Solvent`
`Select 'ethanol' for the second component in the Solvent`
`Enter '0.5' for the 'Mole fraction' of methanol`
`Enter '0.5' for the 'Mole fraction' of ethanol`
Select **atm** for the unit of pressure
`Enter '0.1' in the 'Pressure from:' field`
`Enter '1.0' in the 'to:' field`
`Press 'Run'`



Solvent Boiling Point

Solvent: Mole fraction

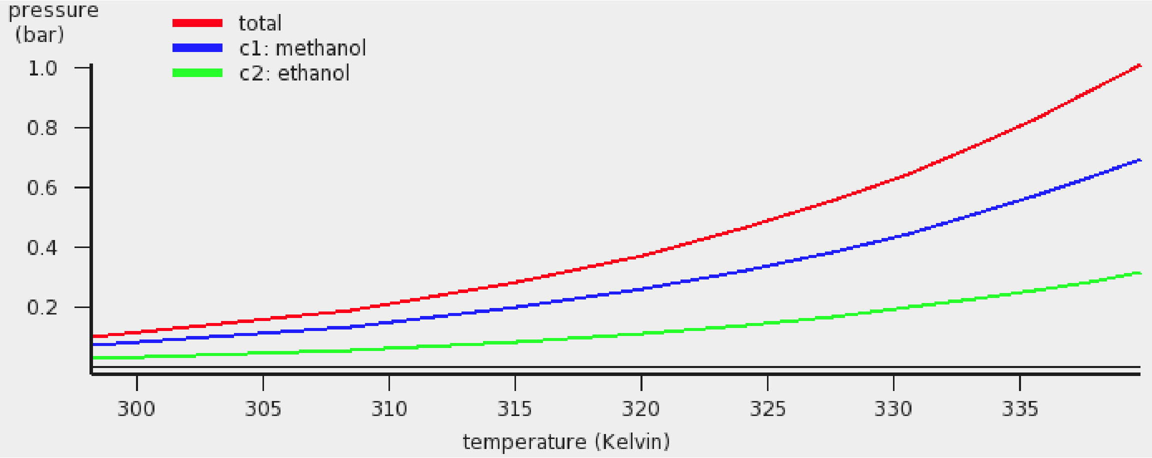
methanol	0.5
ethanol	0.5
	0.0
	0.0
	0.0

Pressure from: 0.1 atm

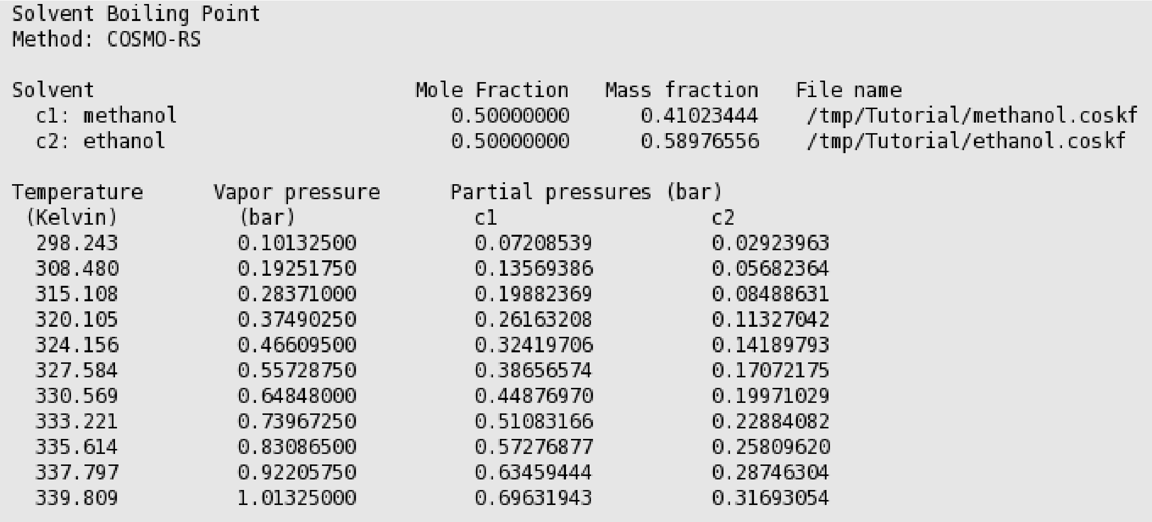
to: 1.0 atm

Number of pressures: (n+1), n= 10

In this case the result (may take several seconds) is a graph and a table.



The red curve is the total vapor pressure, the blue curve the partial methanol vapor pressure, and the green curve is the partial ethanol vapor pressure. The table gives the numerical values.



```
Solvent Boiling Point
Method: COSMO-RS

Solvent                          Mole Fraction   Mass fraction   File name
  c1: methanol                      0.50000000      0.41023444    /tmp/Tutorial/methanol.coskf
  c2: ethanol                       0.50000000      0.58976556    /tmp/Tutorial/ethanol.coskf

Temperature      Vapor pressure      Partial pressures (bar)
 (Kelvin)          (bar)               c1                  c2
  298.243          0.10132500          0.07208539          0.02923963
  308.480          0.19251750          0.13569386          0.05682364
  315.108          0.28371000          0.19882369          0.08488631
  320.105          0.37490250          0.26163208          0.11327042
  324.156          0.46609500          0.32419706          0.14189793
  327.584          0.55728750          0.38656574          0.17072175
  330.569          0.64848000          0.44876970          0.19971029
  333.221          0.73967250          0.51083166          0.22884082
  335.614          0.83086500          0.57276877          0.25809620
  337.797          0.92205750          0.63459444          0.28746304
  339.809          1.01325000          0.69631943          0.31693054
```

Thus in this case COSMO-RS predicts a boiling point of 339.8 K (66.7 °C) at 1 atm. for this mixture of 50% mole fraction methanol and 50% mole fraction ethanol. At this temperature COSMO-RS predicts that the vapor consists about 69% of methanol.

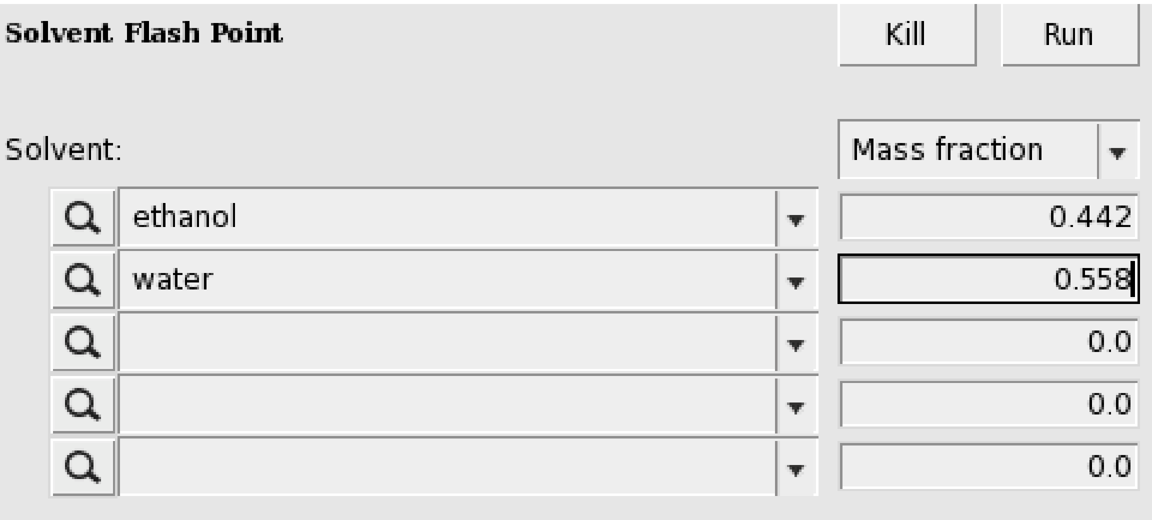
Using **View → Graph Y Axes →** one can view different properties in the graph, like activity coefficients and excess energies.

Step 4: Calculate the flash point of a solvent

The flash point of a mixture can be calculated with **Properties → Solvent Flash Point**, if pure compound flash points are given as input.

Here we mix equal volumes of water (assuming a density of 0.997 kg/L) and ethanol (assuming a density 0.789 kg/L). For a flash point calculation the pure compound flash points are needed as input, since COSMO-RS does not predict pure compound flash points. The ADF COSMO-RS module uses Le Chatelier's mixing rule to calculate the flash point of a mixture.

`Select` **Compounds → Compounds**
`Select 'ethanol'`
`Enter '286' for the 'Flash point' of ethanol`
`Select` **Properties → Solvent Flash Point**
`Change the popup menu 'Mole fraction' in 'Mass fraction'`
`Select 'ethanol' for the first component in the Solvent`
`Select 'water' for the second component in the Solvent`
`Enter '0.442' for the 'Mass fraction' of ethanol`
`Enter '0.558' for the 'Mass fraction' of water`
`Press 'Run'`



Solvent: Mass fraction

ethanol 0.442

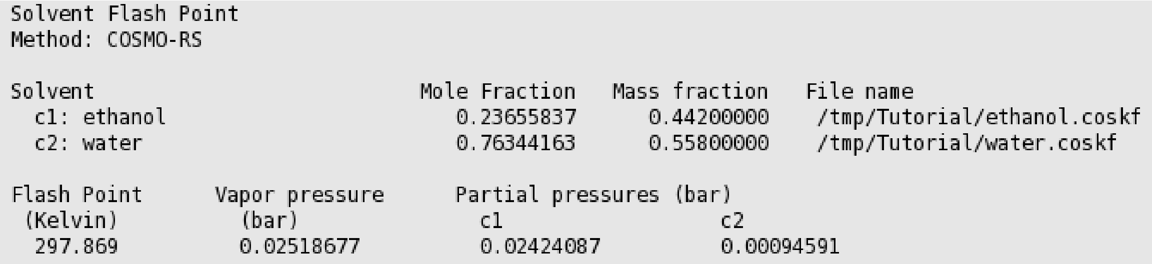
water 0.558

0.0

0.0

0.0

In this case the calculated flash point will be close to 25 °C.



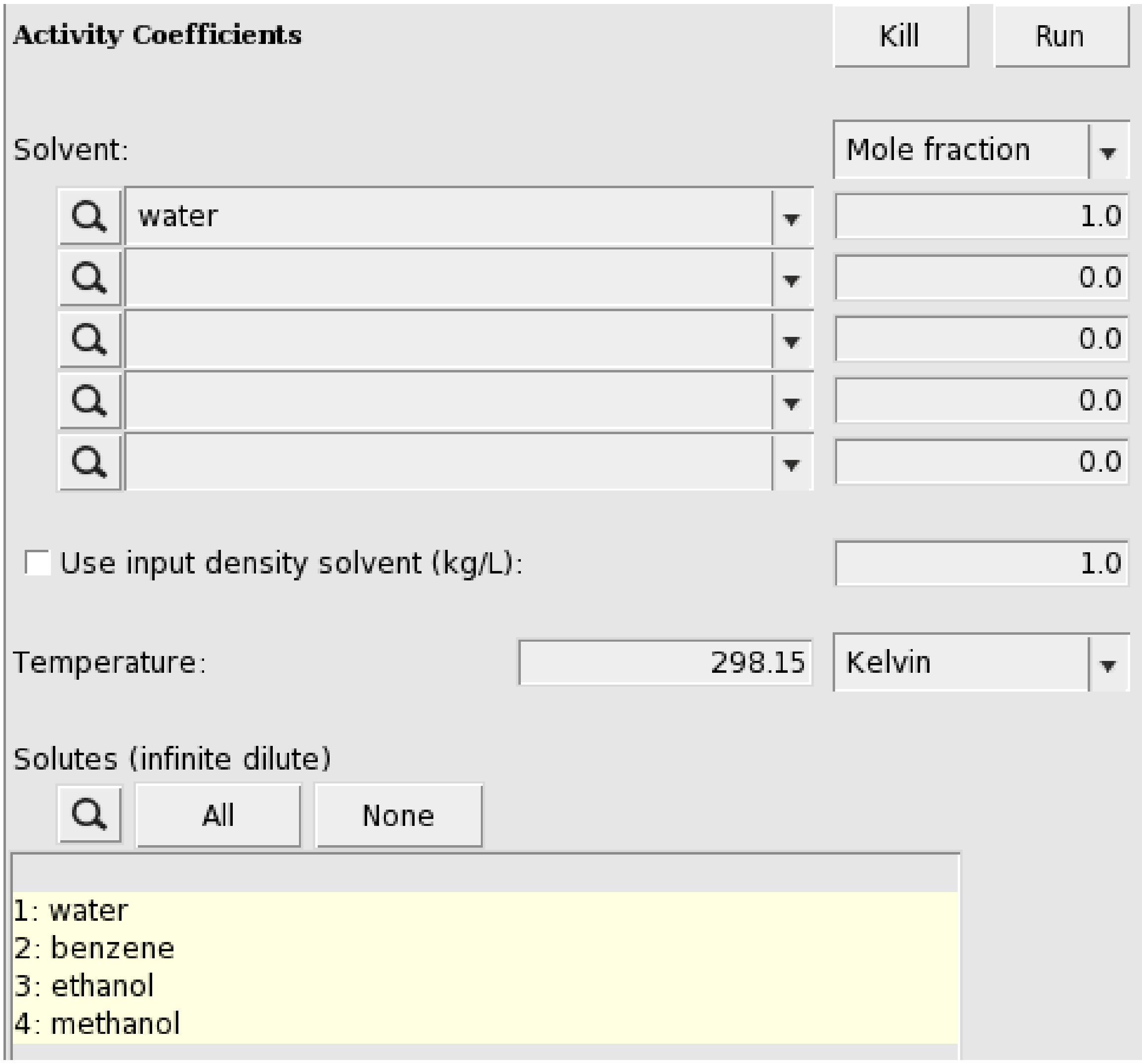
```
Solvent Flash Point
Method: COSMO-RS

Solvent                           Mole Fraction   Mass fraction   File name
  c1: ethanol                        0.23655837      0.44200000    /tmp/Tutorial/ethanol.coskf
  c2: water                          0.76344163      0.55800000    /tmp/Tutorial/water.coskf

Flash Point      Vapor pressure      Partial pressures (bar)
 (Kelvin)          (bar)               c1                  c2
  297.869          0.02518677          0.02424087          0.00094591
```

Step 5: Calculate activity coefficients

The activity coefficients of infinitely diluted solutes in a solvent can be calculated with **Properties → Activity coefficients**.

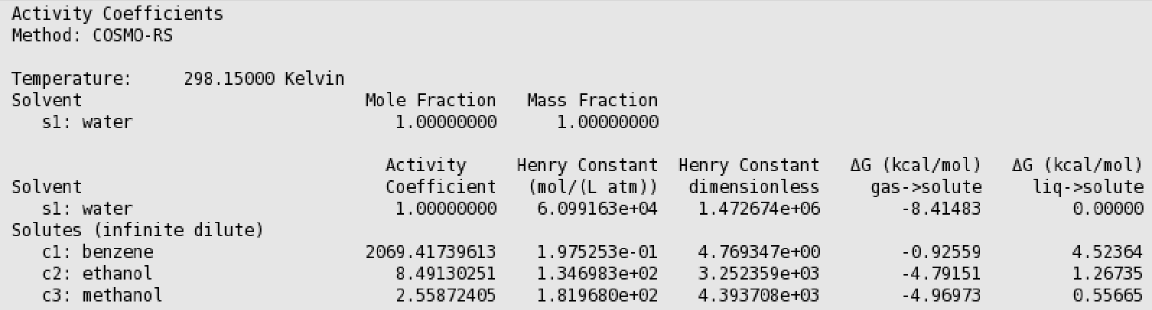
`Select` **Properties → Activity coefficients**

```
Select 'water' for the first component in Solvent
Press 'Run'
```



If one does not supply a density of the solvent in the input the program calculates the density of the solvent by dividing the mass of a molecule with its COSMO volume. Note that the calculated activity coefficients do not depend on this density. One may improve the results for the calculation of the Henry constants, if one includes pure compound vapor pressures in the 'Compounds' window (**Compounds** → **Compounds**).

The result of the calculation is given in the form of a table.



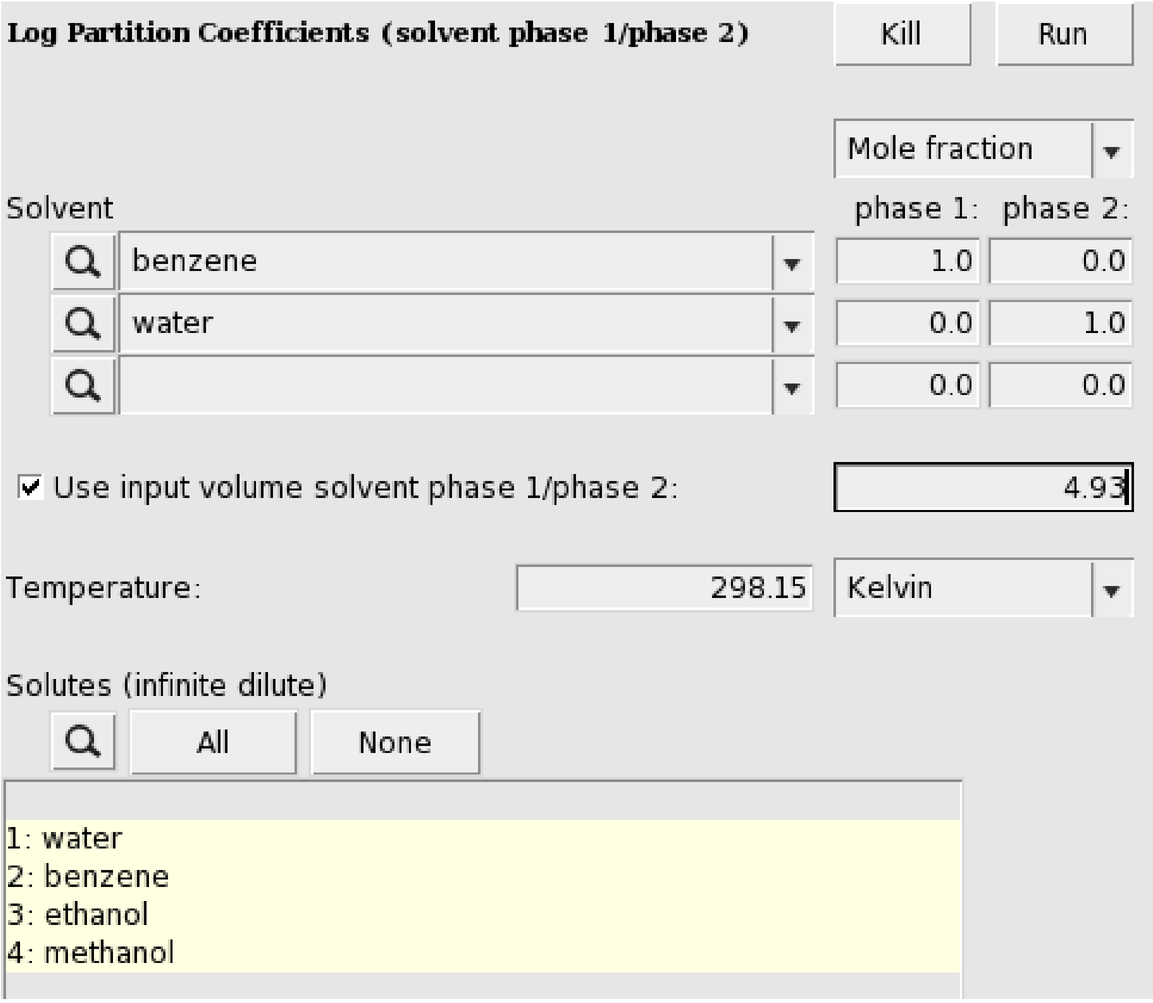
```
Activity Coefficients
Method: COSMO-RS

Temperature:     298.15000 Kelvin
Solvent                            Mole Fraction   Mass Fraction
   s1: water                          1.00000000      1.00000000

                                     Activity     Henry Constant  Henry Constant   ΔG (kcal/mol)   ΔG (kcal/mol)
Solvent                              Coefficient   (mol/(L atm))   dimensionless     gas->solute     liq->solute
   s1: water                          1.00000000    6.099163e+04    1.472674e+06        -8.41483         0.00000
Solutes (infinite dilute)
   c1: benzene                     2069.41739613    1.975253e-01    4.769347e+00        -0.92559         4.52364
   c2: ethanol                        8.49130251    1.346983e+02    3.252359e+03        -4.79151         1.26735
   c3: methanol                       2.55872405    1.819680e+02    4.393708e+03        -4.96973         0.55665
```

Relevant for the calculation of ΔG from the gas phase to the solvated phase is the reference state, used here is 1 mol/L both in both phases.

Step 6: Calculate partition coefficients (log P)

The partition coefficients (log P) of infinitely diluted solutes in a mixture of two immiscible solvents can be calculated with **Properties → Solvent Log Partition Coefficients**.

Select **Properties → Solvent Log Partition Coefficients**
Select 'benzene' for the first component in the solvent
Select 'water' for the second component in the solvent
Click the check box 'Use input volume solvent phase 1/phase 2'
Enter '4.93' in the 'Use input volume solvent phase 1/phase 2' field
Press 'Run'



Log Partition Coefficients (solvent phase 1/phase 2)

Mole fraction

Solvent	phase 1:	phase 2:
benzene	1.0	0.0
water	0.0	1.0
	0.0	0.0

☑ Use input volume solvent phase 1/phase 2: 4.93

Temperature: 298.15 Kelvin

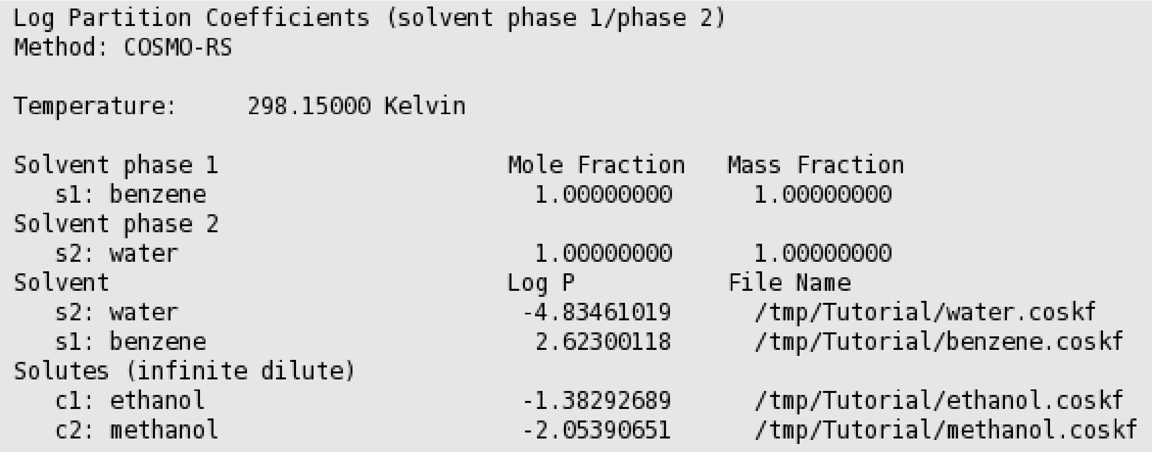
Solutes (infinite dilute)

1: water
2: benzene
3: ethanol
4: methanol

In case of partly miscible liquids, like, for example, the octanol-rich phase of octanol and water, both components have nonzero mole fractions.

Here an input value is used for the volume quotient of the two solvents. If one does not include such value, the program will use the COSMO volumes to calculate the volume quotient. The COSMO volumes can be found in the 'Compounds' window.

The result of the calculation is given in the form of a table.



```
Log Partition Coefficients (solvent phase 1/phase 2)
Method: COSMO-RS

Temperature:     298.15000 Kelvin

Solvent phase 1                    Mole Fraction   Mass Fraction
   s1: benzene                       1.00000000     1.00000000
Solvent phase 2
   s2: water                         1.00000000     1.00000000
Solvent                            Log P           File Name
   s2: water                        -4.83461019     /tmp/Tutorial/water.coskf
   s1: benzene                       2.62300118     /tmp/Tutorial/benzene.coskf
Solutes (infinite dilute)
   c1: ethanol                      -1.38292689     /tmp/Tutorial/ethanol.coskf
   c2: methanol                     -2.05390651     /tmp/Tutorial/methanol.coskf
```

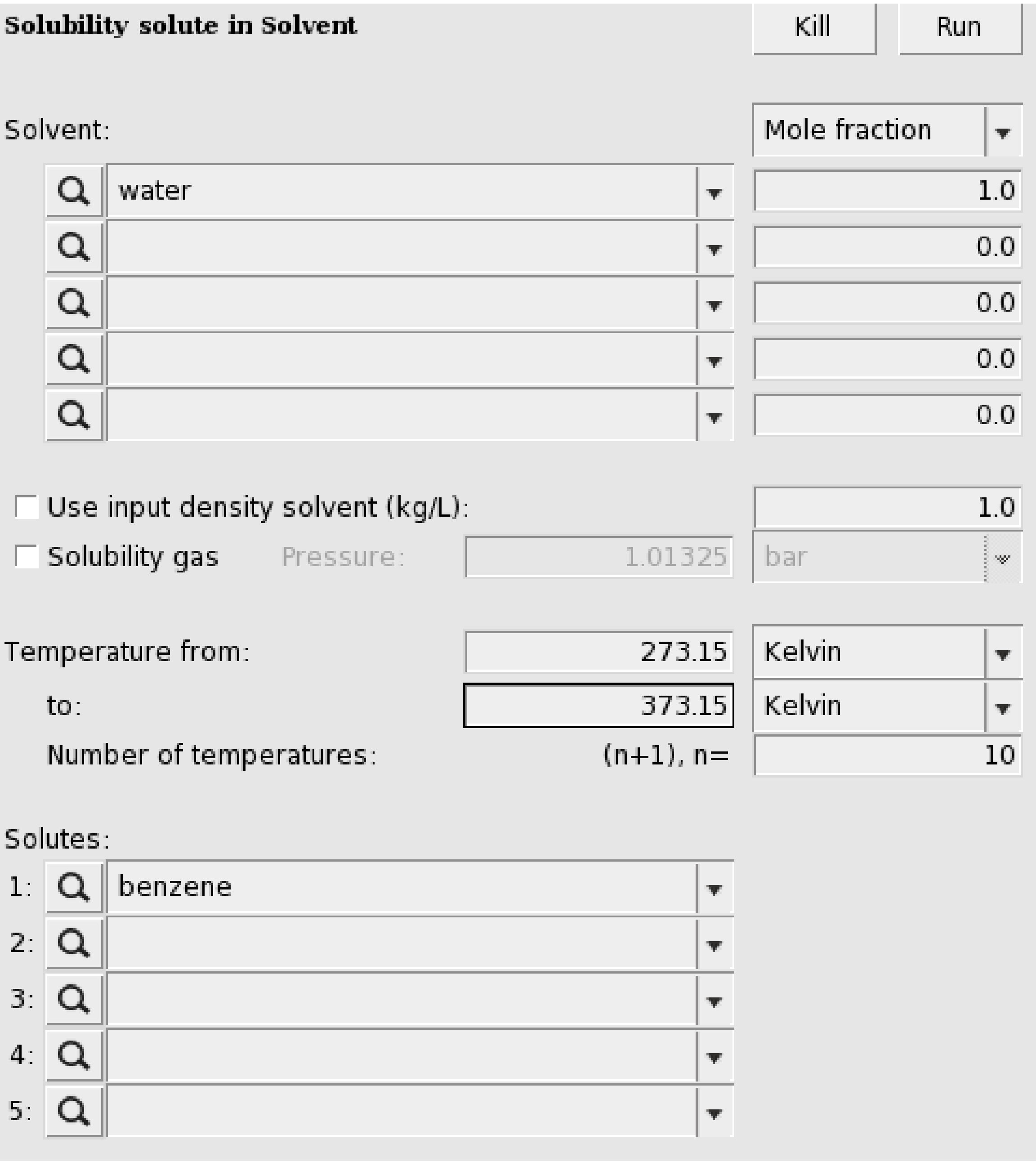
Step 7: Calculate solubility

The solubility of a solute in a solvent can be calculated with **Properties → Solubility**. The solute can either be a liquid, solid, or gas.

Solubility liquid in a solvent

First the solubility of benzene in water for a range of temperatures.

`Select` **Properties → Solubility**
`Select 'water' for the first component in 'Solvent'`
`Select 'benzene' for the first 'Solute'`
`Enter '273.15' without quotes in the 'Temperature from:' field`
`Enter '373.15' in the 'to:' field`
`Press 'Run'`



Solubility solute in Solvent

Solvent: Mole fraction

water 1.0

0.0

0.0

0.0

0.0

☐ Use input density solvent (kg/L): 1.0

☐ Solubility gas Pressure: 1.01325 bar

Temperature from: 273.15 Kelvin

to: 373.15 Kelvin

Number of temperatures: (n+1), n= 10

Solutes:

1: benzene

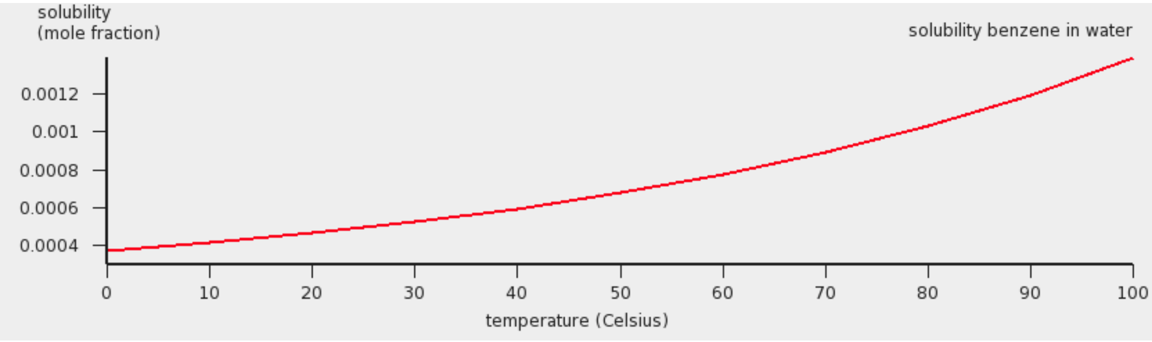
2:

3:

4:

5:

If a range of temperatures is requested a graph is shown.



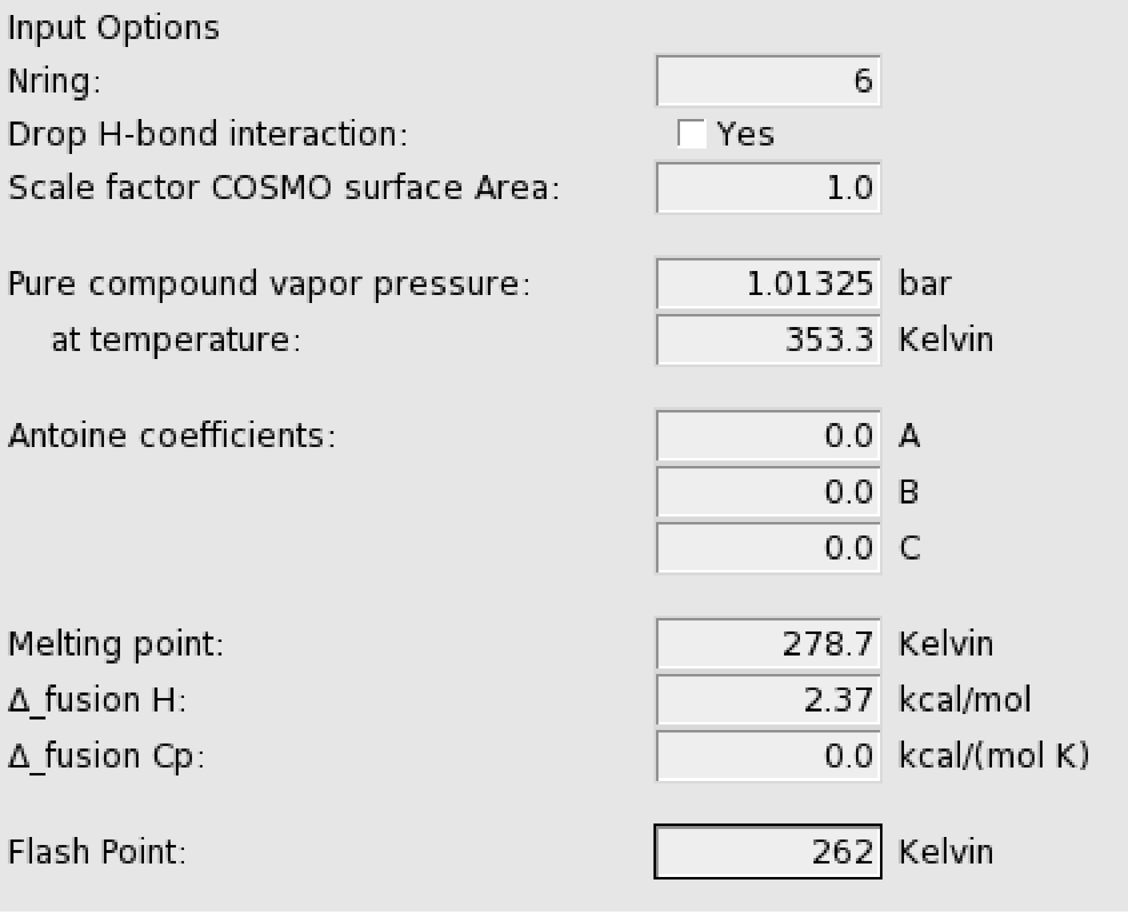
The assumption made in the solubility calculation may be invalid in case of a solubility of a liquid in a solvent, especially if the solubility of the solvent in the liquid is high. For binary systems one may check this by calculating the miscibility gap in the binary mixture of the two liquids. An example is given for the calculation of the miscibility gap in the binary mixture of Methanol and Hexane.

Note that experimentally benzene is a solid below 5.5 °C, and a gas above 80.1 °C. This has not been taken into account yet.

Solubility solid in a solvent

For the solubility of a solid compound it is necessary to include the melting point, the enthalpy of fusion, and optionally, since it is often not so important, the Δ heat capacity of fusion of the pure compound. These values can be given for each compound when 'Compounds' is selected from the 'Compounds' menu. Here, some experimental values will be included for benzene (see, for example, http://en.wikipedia.org/wiki/Benzene).

`Select` **Compounds → Compounds**
`Click on the left side benzene`
`Enter '278.7' in the 'Melting point' field`
`Enter '2.37' in the 'Δ_fusion H' field`

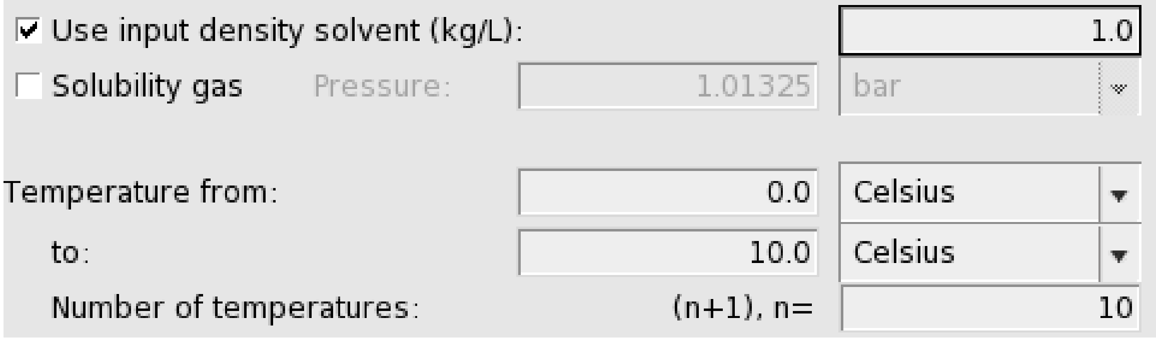


Input Options
Nring: 6
Drop H-bond interaction: ☐ Yes
Scale factor COSMO surface Area: 1.0
Pure compound vapor pressure: 1.01325 bar
at temperature: 353.3 Kelvin
Antoine coefficients: 0.0 A
0.0 B
0.0 C
Melting point: 278.7 Kelvin
Δ_fusion H: 2.37 kcal/mol
Δ_fusion Cp: 0.0 kcal/(mol K)
Flash Point: 262 Kelvin

Also an experimental value for the density of water will be used:

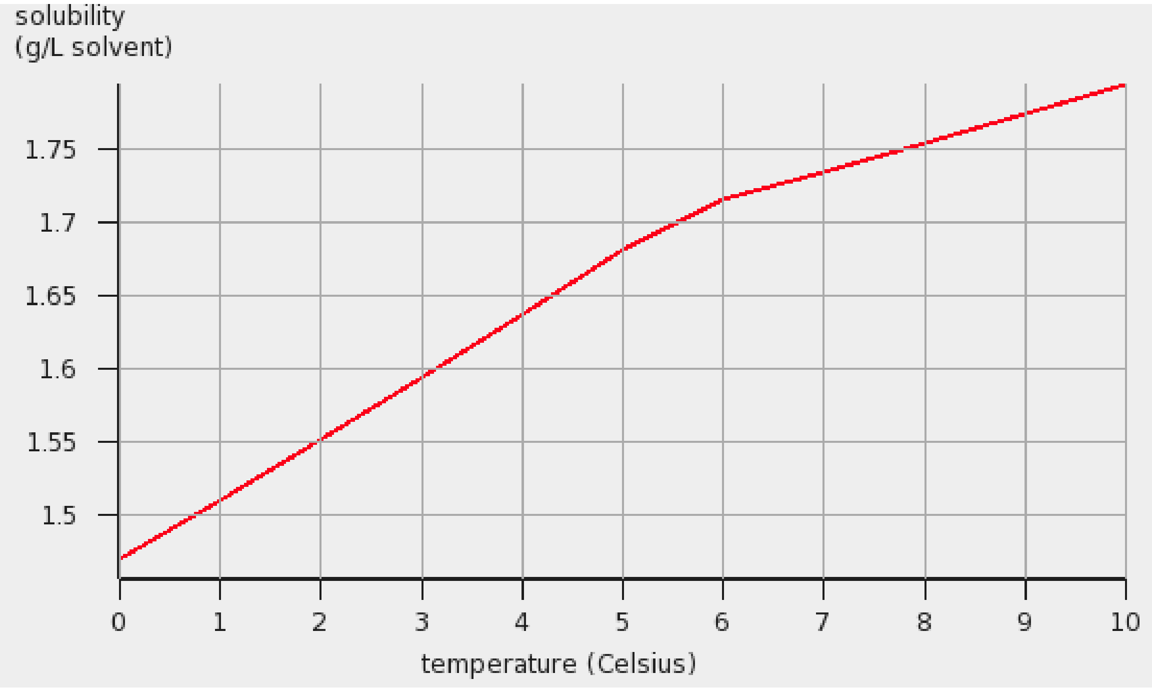
`Select` **Properties → Solubility**
`Select 'water' for the first component in 'Solvent'`
`Select 'benzene' for the first 'Solute'`

Click the check box 'Use input density solvent (kg/L)'
Enter '1.0' in the 'Use input density solvent (kg/L)' field
Change one of the popup menu's 'Kelvin' in 'Celsius'
Enter '0.0' without quotes in the 'Temperature from:' field
Enter '10.0' in the 'to:' field
Select **View → Graph Y Axes → solubility (g/L solvent)**
Press 'Run'



☑ Use input density solvent (kg/L): 1.0
☐ Solubility gas Pressure: 1.01325 bar
Temperature from: 0.0 Celsius
to: 10.0 Celsius
Number of temperatures: (n+1), n= 10

A graph (and table) is shown, which after some manipulations could look like:

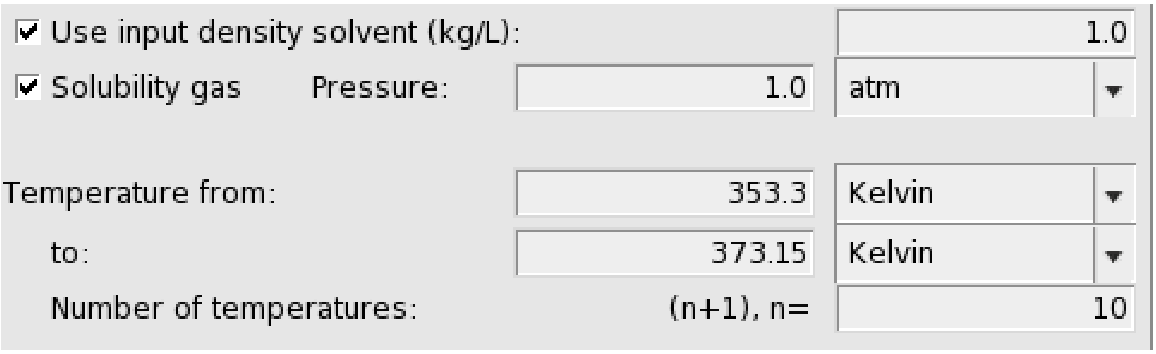


Solubility gas in a solvent

For the solubility of a gas one should click the check box 'Solubility gas' and enter a partial pressure in the 'Pressure' field.

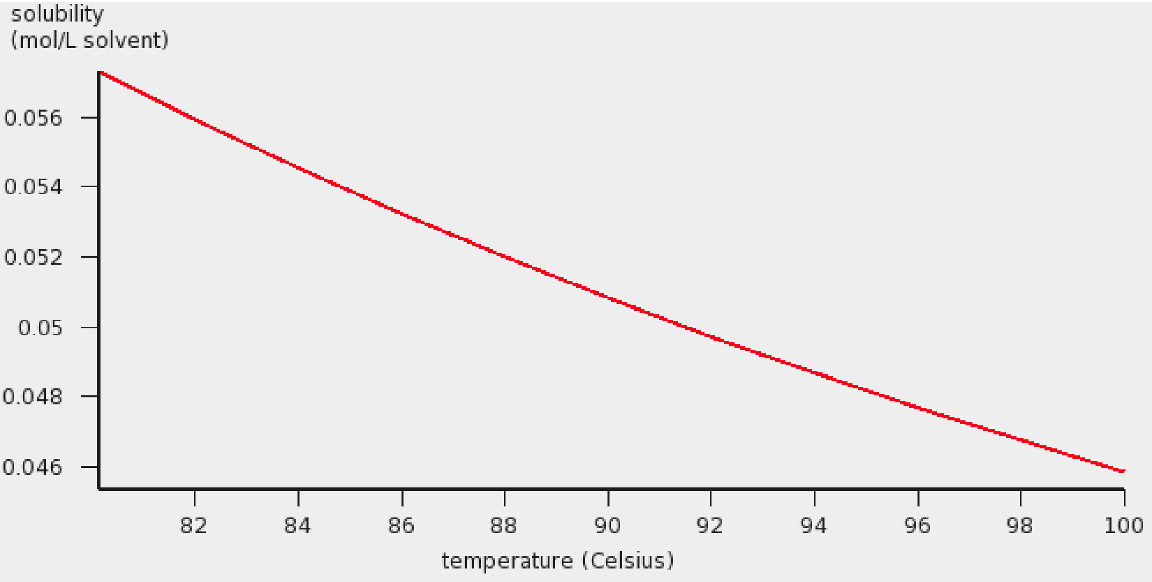
Select **Compounds → Compounds**
Click on the left side benzene
Enter '1.01325' in the 'Pure compound vapor pressure' field
Enter '353.3' in the 'at temperature' field
Select **Properties → Solubility**
Select 'water' for the first component in 'Solvent'

Select 'benzene' for the first 'Solute'
Click the check box 'Use input density solvent (kg/L)'
Enter '1.0' in the 'Use input density solvent (kg/L)' field
Use 'Kelvin' as unit for the temperature
Enter '353.3' without quotes in the 'Temperature from:' field
Enter '373.15' in the 'to:' field
Click the check box 'Solubility gas'
Use 'atm' units for the pressure
Enter '1.0' for the partial vapor pressure of benzene
Select **View → Graph Y Axes → solubility (mol/L solvent)**
Press 'Run'



☑ Use input density solvent (kg/L): 1.0
☑ Solubility gas Pressure: 1.0 atm
Temperature from: 353.3 Kelvin
to: 373.15 Kelvin
Number of temperatures: (n+1), n= 10

A graph (and table) is shown, which after some manipulations could look like:



The solubility of a gas in a solvent can also be calculated using Henry's law, which is valid for ideal dilute solutions,

Select **Properties → Activity coefficients**
Select 'water' for the first component in Solvent
Click the check box 'Use input density solvent (kg/L)'
Enter '1.0' in the 'Use input density solvent (kg/L)' field
Use 'Celsius' as unit for the temperature
Enter '90.0' for 'Temperature'
Select only 'benzene' in the list of 'Solutes (infinite dilute)'
Press 'Run'

The calculated Henry constant for benzene (infinite dilute) in water will be close to 0.049 mol/(L atm) at 90 °C.

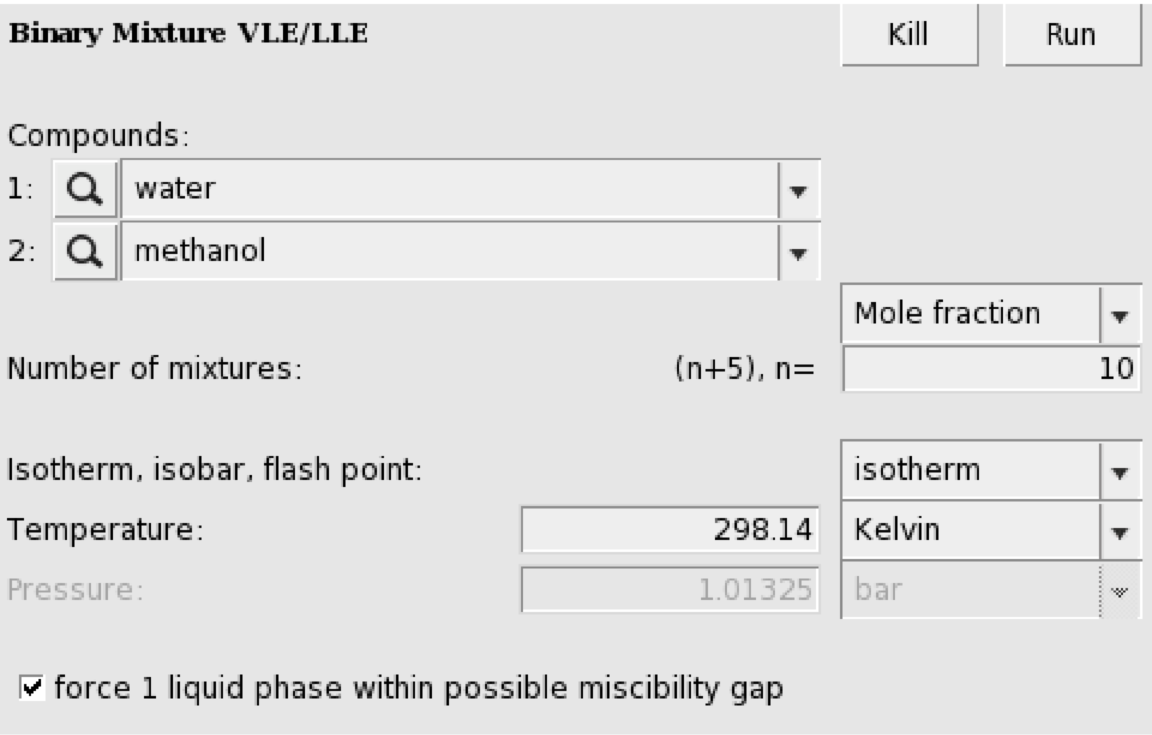
Step 8: Calculate binary mixtures VLE/LLE

A phase diagram of a mixture of two components can be calculated with **Properties → Binary Mixture VLE/LLE**. The binary mixture will be calculated for a list of molar fractions between zero and one. This can be done at constant temperature (isothermal) or at constant vapor pressure (isobaric).

Isothermal

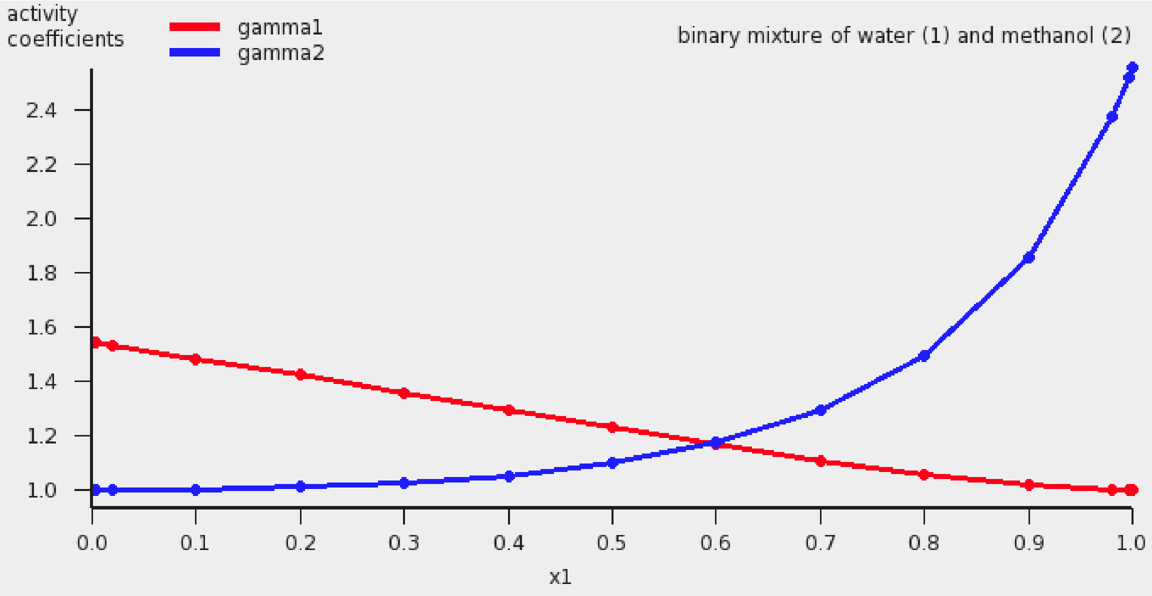
A binary mixture is calculated in which the pure compound vapor pressures are approximated using the COSMO-RS method.

`Select` **Properties → Binary Mixture VLE/LLE**
`Select 'water' for the first compound`
`Select 'methanol' for the second compound`
`Use 'Kelvin' as unit for the temperature`
`Enter '298.14' in the 'Temperature' field`
`Press 'Run'`

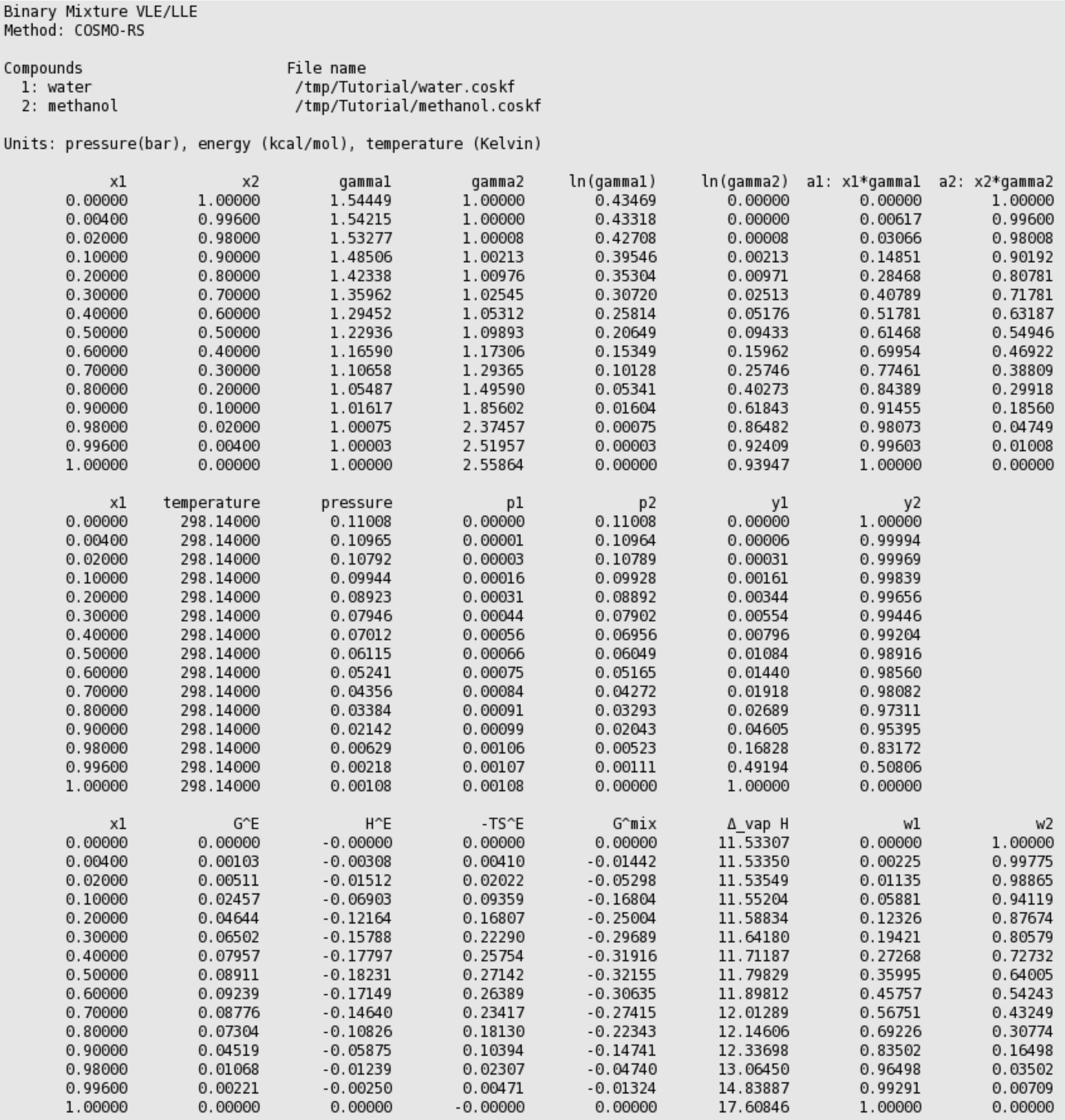


Compounds:
1: water
2: methanol
Mole fraction
Number of mixtures: (n+5), n= 10
Isotherm, isobar, flash point: isotherm
Temperature: 298.14 Kelvin
Pressure: 1.01325 bar
☑ force 1 liquid phase within possible miscibility gap

An activity coefficient plot for water(1) and methanol(2) will be shown.



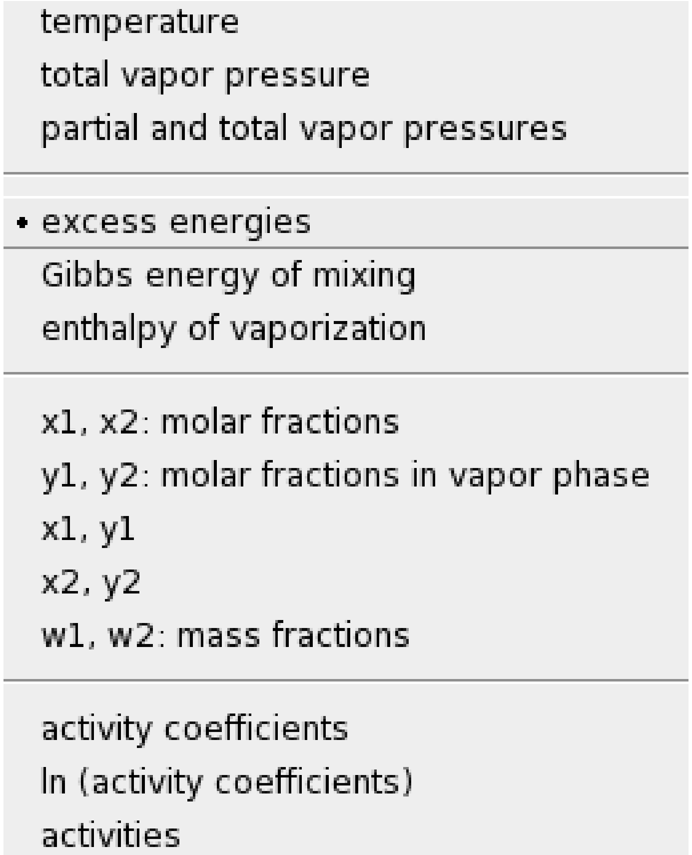
The results of the calculation are also given in the form of a table, which shows the molar (and mass) fraction of each compound in the liquid, the activity coefficients, the activities, the temperature, the total and partial vapor pressures, the molar fraction of each compound in the vapor (Y), the excess Gibbs free energy G^E, the excess enthalpy H^E (calculated with the Gibbs-Helmholtz equation), the excess entropy of mixing -TS^E, the Gibbs free energy of mixing G^{mix}, the enthalpy of vaporization $\Delta_{vap}H$ (calculated with the Clausius-Clapeyron equation).



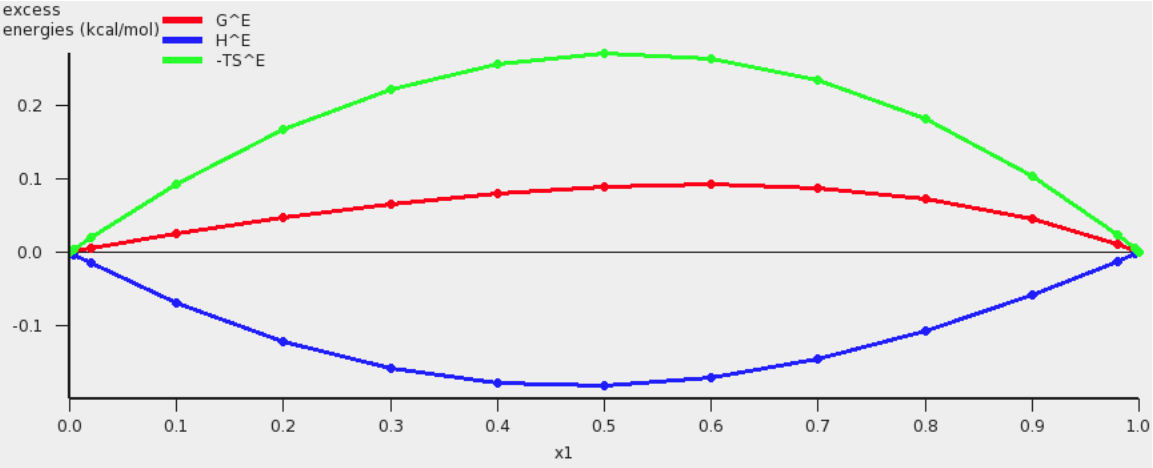
```
Binary Mixture VLE/LLE
Method: COSMO-RS

Compounds                      File name
  1: water                      /tmp/Tutorial/water.coskf
  2: methanol                   /tmp/Tutorial/methanol.coskf

Units: pressure(bar), energy (kcal/mol), temperature (Kelvin)

             x1             x2         gamma1         gamma2     ln(gamma1)     ln(gamma2)  a1: x1*gamma1  a2: x2*gamma2
        0.00000        1.00000        1.54449        1.00000        0.43469        0.00000        0.00000        1.00000
        0.00400        0.99600        1.54215        1.00000        0.43318        0.00000        0.00617        0.99600
        0.02000        0.98000        1.53277        1.00008        0.42708        0.00008        0.03066        0.98008
        0.10000        0.90000        1.48506        1.00213        0.39546        0.00213        0.14851        0.90192
        0.20000        0.80000        1.42338        1.00976        0.35304        0.00971        0.28468        0.80781
        0.30000        0.70000        1.35962        1.02545        0.30720        0.02513        0.40789        0.71781
        0.40000        0.60000        1.29452        1.05312        0.25814        0.05176        0.51781        0.63187
        0.50000        0.50000        1.22936        1.09893        0.20649        0.09433        0.61468        0.54946
        0.60000        0.40000        1.16590        1.17306        0.15349        0.15962        0.69954        0.46922
        0.70000        0.30000        1.10658        1.29365        0.10128        0.25746        0.77461        0.38809
        0.80000        0.20000        1.05487        1.49590        0.05341        0.40273        0.84389        0.29918
        0.90000        0.10000        1.01617        1.85602        0.01604        0.61843        0.91455        0.18560
        0.98000        0.02000        1.00075        2.37457        0.00075        0.86482        0.98073        0.04749
        0.99600        0.00400        1.00003        2.51957        0.00003        0.92409        0.99603        0.01008
        1.00000        0.00000        1.00000        2.55864        0.00000        0.93947        1.00000        0.00000

             x1    temperature       pressure             p1             p2             y1             y2
        0.00000      298.14000        0.11008        0.00000        0.11008        0.00000        1.00000
        0.00400      298.14000        0.10965        0.00001        0.10964        0.00006        0.99994
        0.02000      298.14000        0.10792        0.00003        0.10789        0.00031        0.99969
        0.10000      298.14000        0.09944        0.00016        0.09928        0.00161        0.99839
        0.20000      298.14000        0.08923        0.00031        0.08892        0.00344        0.99656
        0.30000      298.14000        0.07946        0.00044        0.07902        0.00554        0.99446
        0.40000      298.14000        0.07012        0.00056        0.06956        0.00796        0.99204
        0.50000      298.14000        0.06115        0.00066        0.06049        0.01084        0.98916
        0.60000      298.14000        0.05241        0.00075        0.05165        0.01440        0.98560
        0.70000      298.14000        0.04356        0.00084        0.04272        0.01918        0.98082
        0.80000      298.14000        0.03384        0.00091        0.03293        0.02689        0.97311
        0.90000      298.14000        0.02142        0.00099        0.02043        0.04605        0.95395
        0.98000      298.14000        0.00629        0.00106        0.00523        0.16828        0.83172
        0.99600      298.14000        0.00218        0.00107        0.00111        0.49194        0.50806
        1.00000      298.14000        0.00108        0.00108        0.00000        1.00000        0.00000

             x1            G^E            H^E          -TS^E          G^mix        Δ_vap H             w1             w2
        0.00000        0.00000       -0.00000        0.00000        0.00000       11.53307        0.00000        1.00000
        0.00400        0.00103       -0.00308        0.00410       -0.01442       11.53350        0.00225        0.99775
        0.02000        0.00511       -0.01512        0.02022       -0.05298       11.53549        0.01135        0.98865
        0.10000        0.02457       -0.06903        0.09359       -0.16804       11.55204        0.05881        0.94119
        0.20000        0.04644       -0.12164        0.16807       -0.25004       11.58834        0.12326        0.87674
        0.30000        0.06502       -0.15788        0.22290       -0.29689       11.64180        0.19421        0.80579
        0.40000        0.07957       -0.17797        0.25754       -0.31916       11.71187        0.27268        0.72732
        0.50000        0.08911       -0.18231        0.27142       -0.32155       11.79829        0.35995        0.64005
        0.60000        0.09239       -0.17149        0.26389       -0.30635       11.89812        0.45757        0.54243
        0.70000        0.08776       -0.14640        0.23417       -0.27415       12.01289        0.56751        0.43249
        0.80000        0.07304       -0.10826        0.18130       -0.22343       12.14606        0.69226        0.30774
        0.90000        0.04519       -0.05875        0.10394       -0.14741       12.33698        0.83502        0.16498
        0.98000        0.01068       -0.01239        0.02307       -0.04740       13.06450        0.96498        0.03502
        0.99600        0.00221       -0.00250        0.00471       -0.01324       14.83887        0.99291        0.00709
        1.00000        0.00000        0.00000       -0.00000        0.00000       17.60846        1.00000        0.00000
```

These values can also be shown in a graph. The property for the x- and y-axes can be selected from the 'View' Menu. For example, a graph of the excess energies can be shown by:

`Select` **View → Graph Y Axes → excess energies**



A plot of the excess energies will be shown.

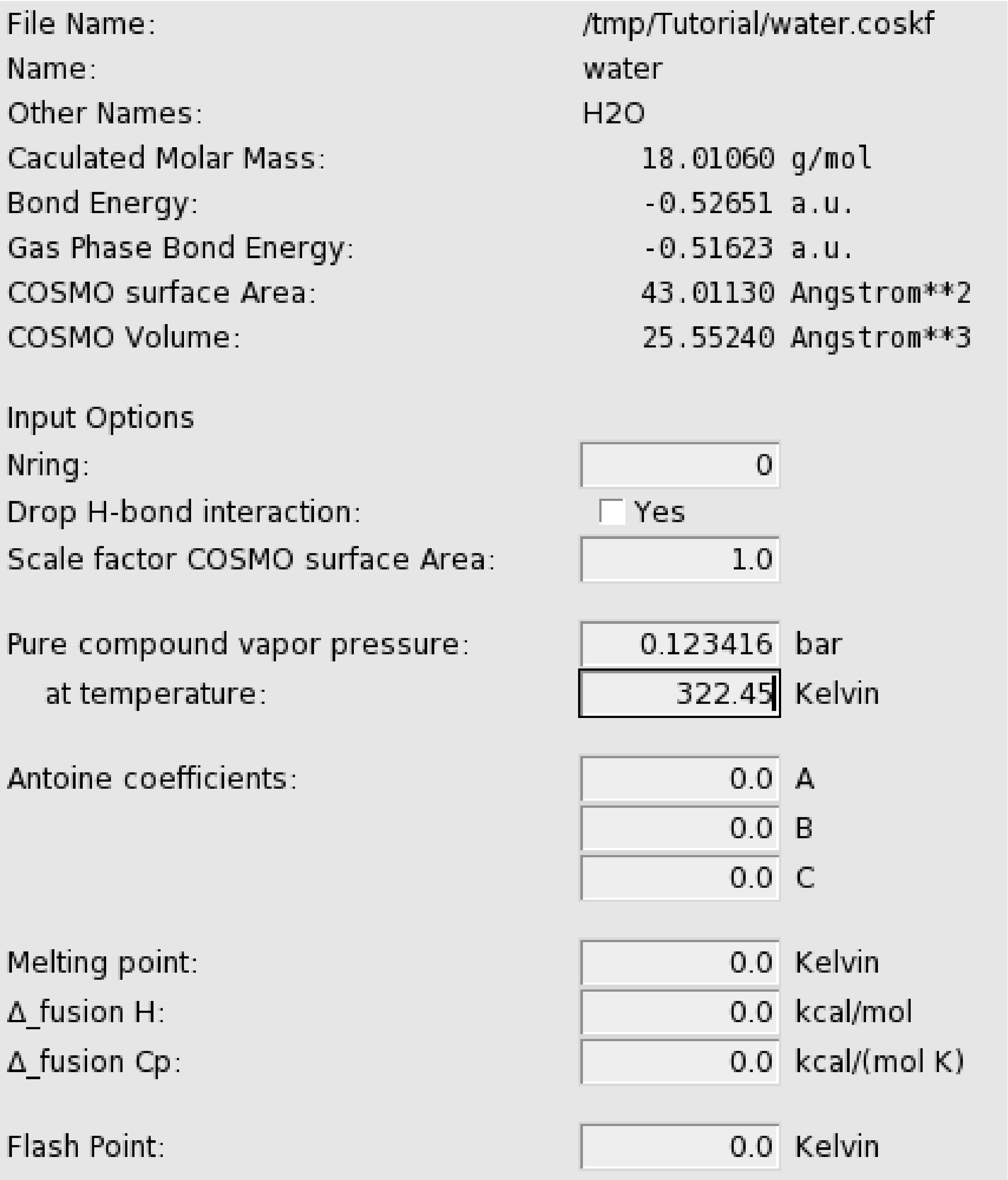


The red curve is the excess Gibbs free energy G^E, the blue curve is the excess enthalpy H^E, and the green curve is -T times the excess entropy S^E.

Isothermal, input pure compound vapor pressure

A binary mixture is calculated with input data for the pure compound vapor pressures. These can be, for example, experimentally observed pure compound vapor pressures. Note that the calculated partial and total vapor pressures will now depend on these input pure compound vapor pressures.

Select **Compounds → Compounds**
Click on the left side water
Enter '0.123416' in the 'Pure compound vapor pressure:' field
Enter '322.45' in the 'at temperature:' field



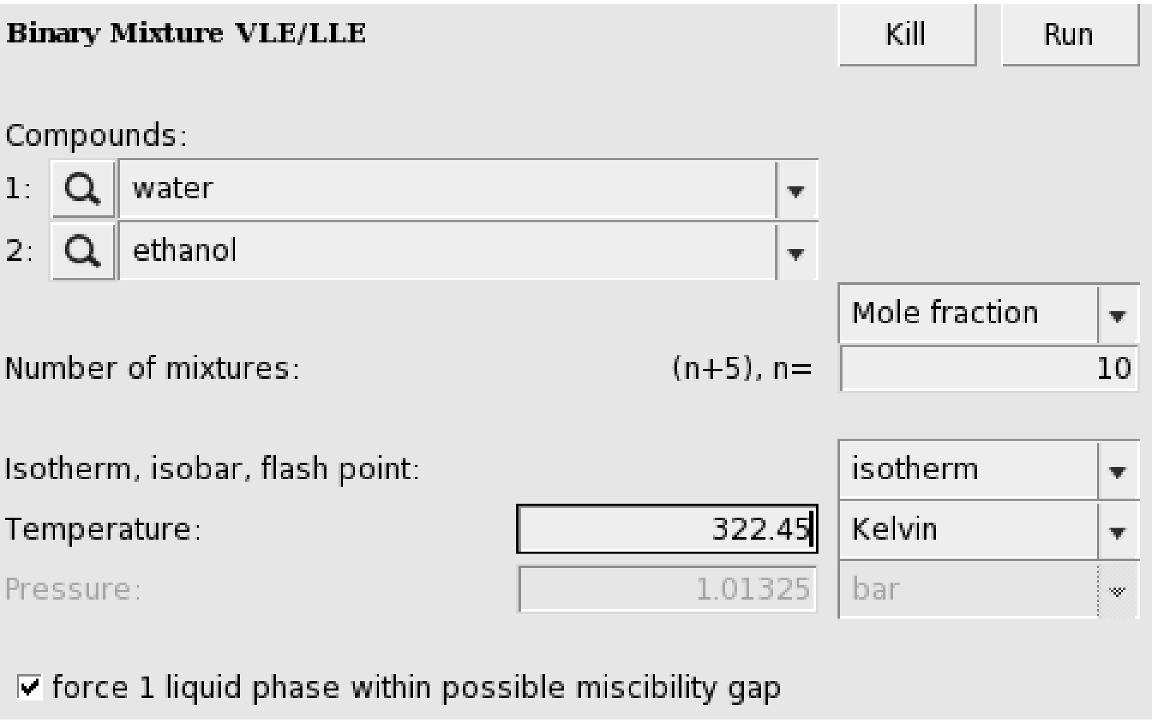
File Name:	/tmp/Tutorial/water.coskf	
Name:	water	
Other Names:	H2O	
Caculated Molar Mass:	18.01060	g/mol
Bond Energy:	-0.52651	a.u.
Gas Phase Bond Energy:	-0.51623	a.u.
COSMO surface Area:	43.01130	Angstrom**2
COSMO Volume:	25.55240	Angstrom**3

Input Options

Nring:	0	
Drop H-bond interaction:	☐ Yes	
Scale factor COSMO surface Area:	1.0	
Pure compound vapor pressure:	0.123416	bar
at temperature:	322.45	Kelvin
Antoine coefficients:	0.0	A
	0.0	B
	0.0	C
Melting point:	0.0	Kelvin
Δ_fusion H:	0.0	kcal/mol
Δ_fusion Cp:	0.0	kcal/(mol K)
Flash Point:	0.0	Kelvin

Click on the left side ethanol
Enter '0.294896' in the 'Pure compound vapor pressure:' field
Enter '322.45' in the 'at temperature:' field
Select **Properties → Binary Mixture VLE/LLE**
Select 'water' for the first compound
Select 'ethanol' for the second compound
Enter '322.45' in the 'Temperature' field
Select **View → Graph X Axes → x2: molar fraction 2**

`Select` **View → Graph Y Axes → partial and total vapor pressures**
`Press 'Run'`


Binary Mixture VLE/LLE

Compounds:
1: water
2: ethanol

Mole fraction

Number of mixtures: (n+5), n= 10

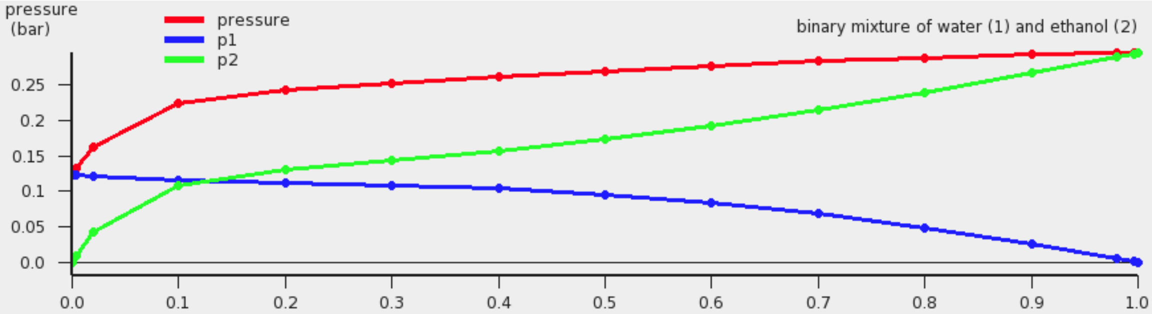
Isotherm, isobar, flash point: isotherm

Temperature: 322.45 Kelvin

Pressure: 1.01325 bar

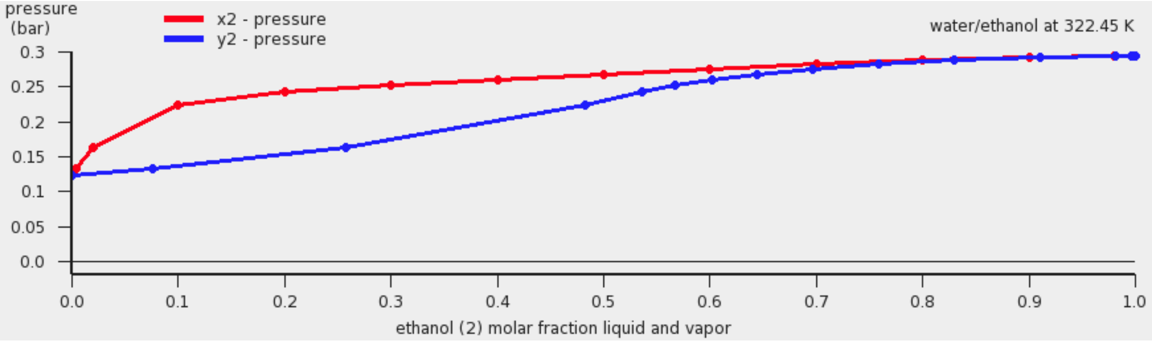
☑ force 1 liquid phase within possible miscibility gap

A vapor liquid equilibrium (VLE) diagram for water(1) and ethanol(2) will be shown.



The red curve is the total vapor pressure, the blue curve is the partial water vapor pressure, and the green curve is the partial ethanol vapor pressure. One can also change the x and y axes, for example:

`Select` **View → Graph X Axes → x2, y2**
`Select` **View → Graph Y Axes → total vapor pressure**

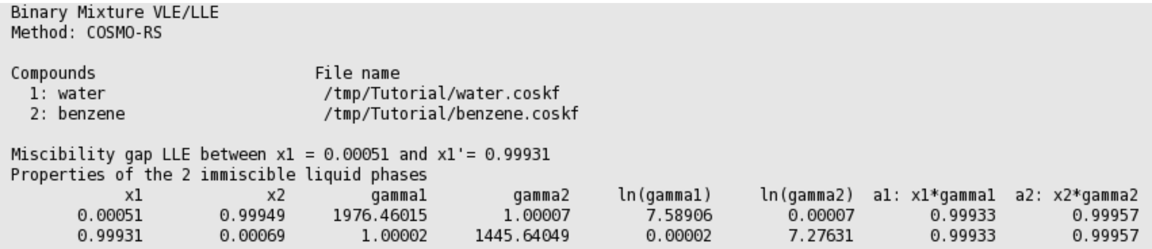


Isothermal, miscibility gap, LLE

Water and benzene do not mix well, thus there will be a miscibility gap.

Select **Properties → Binary Mixture VLE/LLE**
Select 'water' for the first compound
Select 'benzene' for the second compound
Use 'Celsius' as units for the temperature
Enter '50.0' in the 'Temperature' field
Enter '100' for 'Number of mixtures'

In this case a a liquid-liquid equilibrium (LLE) is calculated. The number of mixtures for which the binary mixture is calculated should be not too small, otherwise the properties of the 2 immiscible liquids phases will not be so accurate.



```
Binary Mixture VLE/LLE
Method: COSMO-RS

Compounds                      File name
  1: water                      /tmp/Tutorial/water.coskf
  2: benzene                    /tmp/Tutorial/benzene.coskf

Miscibility gap LLE between x1 = 0.00051 and x1'= 0.99931
Properties of the 2 immiscible liquid phases
             x1            x2        gamma1         gamma2     ln(gamma1)     ln(gamma2)  a1: x1*gamma1  a2: x2*gamma2
        0.00051       0.99949    1976.46015        1.00007        7.58906        0.00007        0.99933        0.99957
        0.99931       0.00069       1.00002     1445.64049        0.00002        7.27631        0.99933        0.99957
```

If the check box 'force 1 liquid phase within possible miscibility gap' is deselected, then results will be shown in the graph and table only for those compositions of the mixture, which are outside of the miscibility gap. If the check box 'force 1 liquid phase within possible miscibility gap' is selected, then results will be shown also within the miscibility gap, with the unphysical conditions that the two liquids are forced to mix.

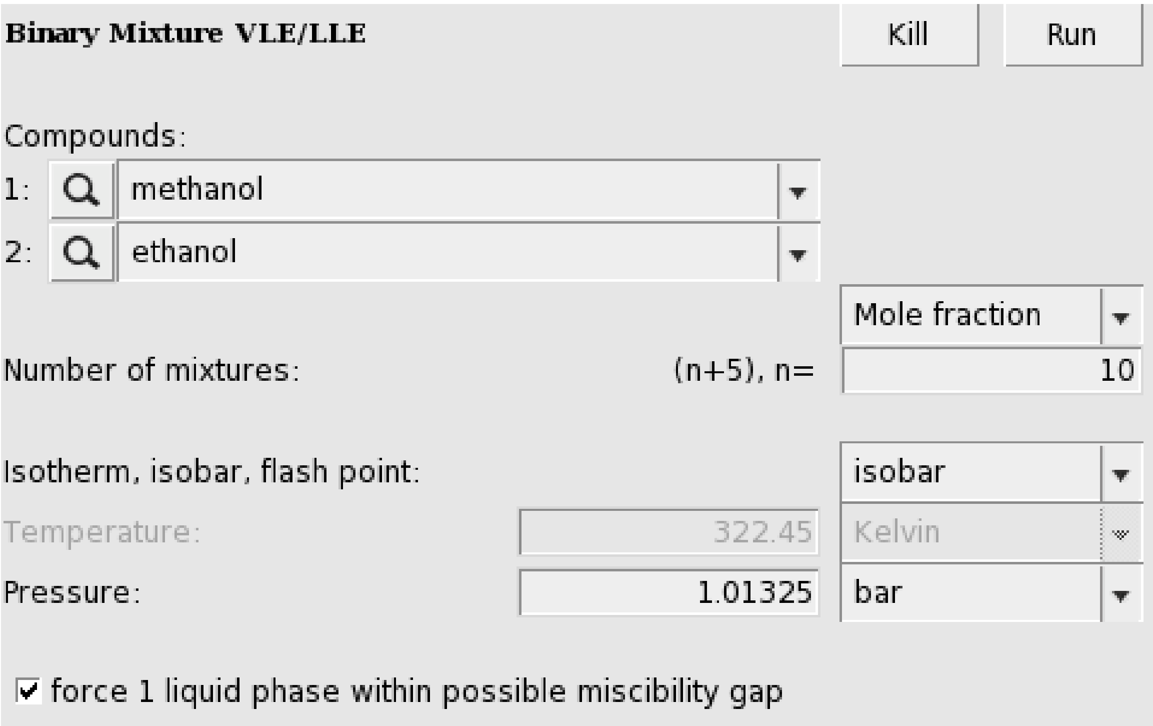
Isobaric

A binary mixture is calculated in which the pure compound vapor pressures are approximated using the COSMO-RS method if the input values for the pure compound vapor pressures are zero. Alternative one can click a check box in the 'Method' Menu.

Select **Method → Parameters**
Click on the check box 'use input (Compounds Menu) pure compound vapor pressures(s)'
to deselect it

☐ use input (Compounds Menu) pure compound vapor pressure(s)

Select **Properties → Binary Mixture VLE/LLE**
Select 'methanol' for the first compound
Select 'ethanol' for the second compound
Enter '10' for 'Number of mixtures'
Select **Isotherm, isobar, flash point → isobar**
Select **View → Graph X Axes → x1: molar fraction 1**
Select **View → Graph Y Axes → Temperature**
Press 'Run'



Binary Mixture VLE/LLE

Compounds:

1: methanol

2: ethanol

Mole fraction

Number of mixtures: (n+5), n= 10

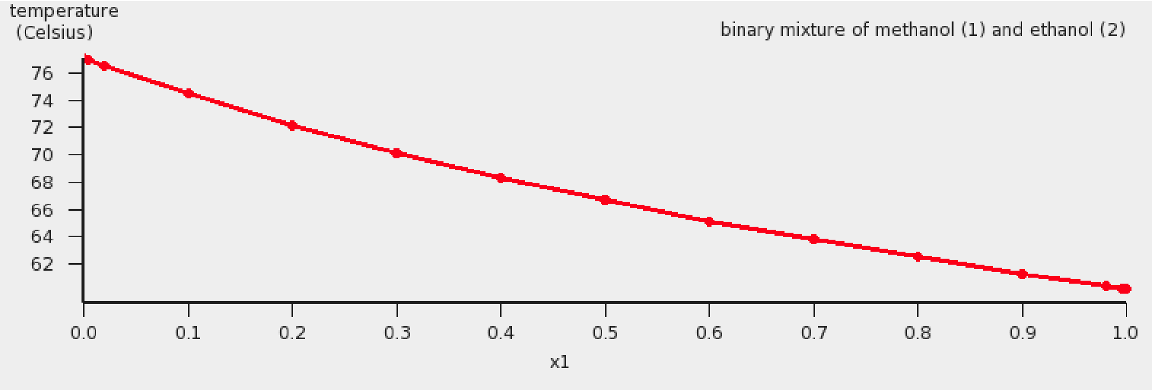
Isotherm, isobar, flash point: isobar

Temperature: 322.45 Kelvin

Pressure: 1.01325 bar

☑ force 1 liquid phase within possible miscibility gap

The calculated boiling points (may take several seconds) for a binary mixture of methanol(1) and ethanol(2) will be shown.



If one clicks in the graph window at the left or below the axes, a popup window will appear in which one can set details for the graph window. In the graph above the 'Units' for the 'Left Y Axes' were chosen to be 'Celsius'.

Next the same binary mixture is calculated in which experimental pure compound vapor pressures are used.

`Select` **Method → Parameters**
`Click on the check box 'use input (Compounds Menu) pure compound vapor pressures(s)'`
`to select it`

☑ use input (Compounds Menu) pure compound vapor pressure(s)

`Select` **Compounds → Compounds**
`Click on the left side methanol`
`Enter '1.01325' in the 'Pure compound vapor pressure:' field`

Enter '338' in the 'at temperature:' field
Click on the left side ethanol
Enter '1.01325' in the 'Pure compound vapor pressure:' field
Enter '351' in the 'at temperature:' field
Select **Properties → Binary Mixture VLE/LLE**
Press 'Run'

The calculated graph will look not very different, but it will be more accurate.

Step 9: Calculate ternary mixtures VLE/LLE

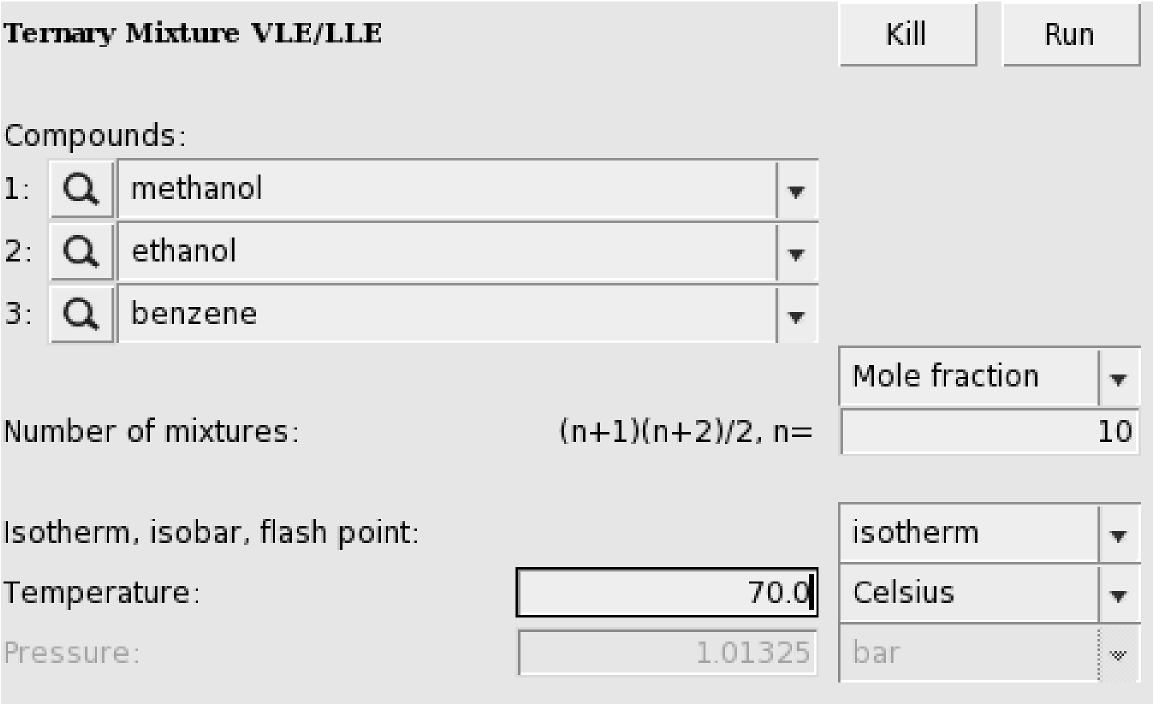
A phase diagram of a mixture of three components can be calculated with **Properties → Ternary Mixture VLE/LLE**. The ternary mixture will be calculated for a list of molar (or mass) fractions between zero and one, for each of the compounds. This can be done at constant temperature (isothermal) or at constant vapor pressure (isobaric).

In this step we will use experimental boiling points as input.

Select **Compounds → Compounds**
Click on the left side water
Enter '1.01325' in the 'Pure compound vapor pressure:' field
Enter '373.15' in the 'at temperature:' field
Click on the left side methanol
Enter '1.01325' in the 'Pure compound vapor pressure:' field
Enter '338' in the 'at temperature:' field
Click on the left side benzene
Enter '1.01325' in the 'Pure compound vapor pressure' field
Enter '353.3' in the 'at temperature' field
Click on the left side ethanol
Enter '1.01325' in the 'Pure compound vapor pressure:' field
Enter '351' in the 'at temperature:' field

Isothermal

Select **Properties → Ternary Mixture VLE/LLE**
Select 'methanol' for the first compound
Select 'ethanol' for the second compound
Select 'benzene' for the third compound
Use 'Mole fraction'
Enter '10' for 'Number of mixtures'
Select **View → Graph X Axes → x1: molar fraction 1**
Select **View → Graph Y Axes → x2: molar fraction 2**
Select **View → Graph Z Colormap → total vapor pressures**
Select **Isotherm, isobar, flash point → isotherm**
Use 'Celsius' as units for the temperature
Enter '70.0' in the 'Temperature' field
Press 'Run'



Ternary Mixture VLE/LLE

Compounds:
1: methanol
2: ethanol
3: benzene

Mole fraction

Number of mixtures: (n+1)(n+2)/2, n= 10

Isotherm, isobar, flash point: isotherm

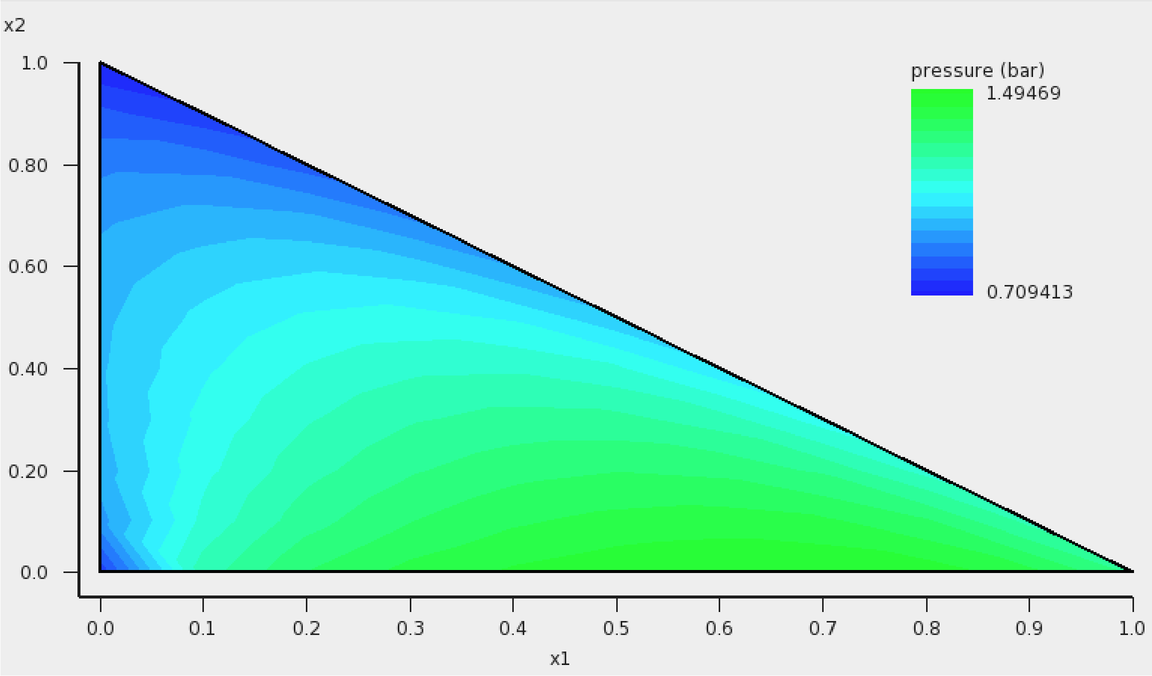
Temperature: 70.0 Celsius

Pressure: 1.01325 bar

The result will be a graph and a table. In the table one can find the results of the calculation at 55 (=(n+1)(n+2)/2, with n=10) different compositions. At those compositions the table shows the molar (and mass) fraction of each compound in the liquid, the activity coefficients, the activities, the temperature, the total and partial vapor pressures, the molar fraction of each compound in the vapor (Y), the excess Gibbs free energy G^E, the excess enthalpy H^E (calculated with the Gibbs-Helmholtz equation), the excess entropy of mixing $-TS^E$, the Gibbs free energy of mixing G^{mix}, the enthalpy of vaporization $\Delta_{vap}H$ (calculated with the Clausius-Clapeyron equation).

These quantities can also be shown in the graph as a colormap, in which the color represents the value of the quantity at a certain composition. On the X axes of the graph one can choose the molar (or mass fraction) of one of the compoumds, on the Y axes one can choos the molar (or mass fraction) of another compoumd. The molar (or mass) fraction of the third compound is then fixed, since the sum of the fractions is 1.

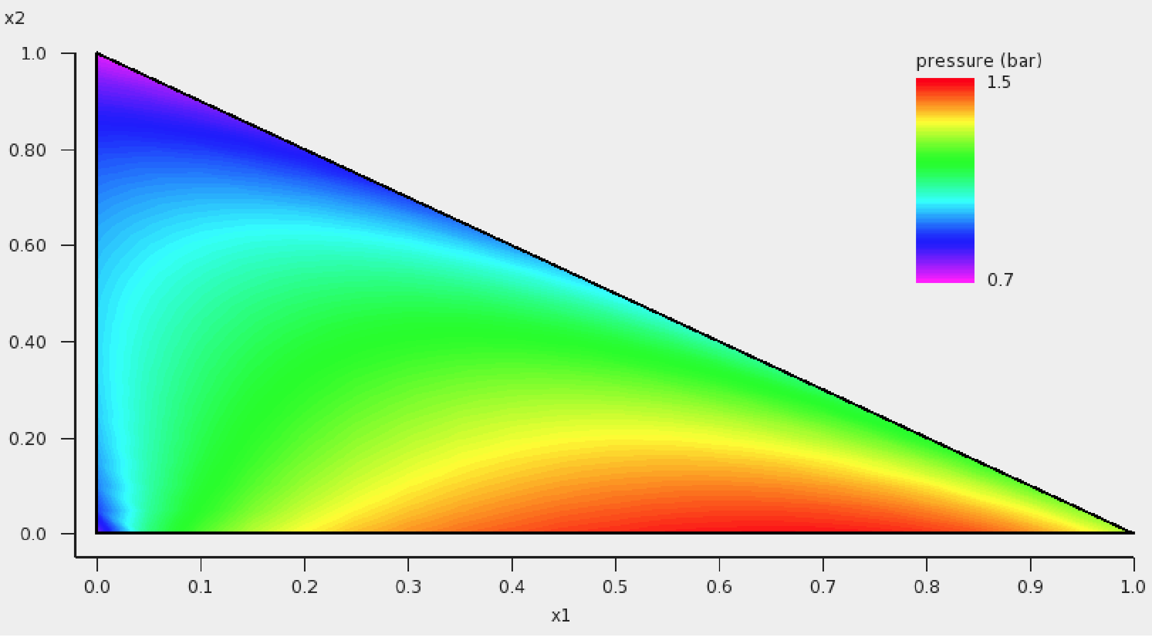
In this case the colormap shows the total vapor pressure:



One can improve the quality of the graph by increasing the number of compositions. Note that the number of different compositions for n=20 is 231 (=(n+1)(n+2)/2).

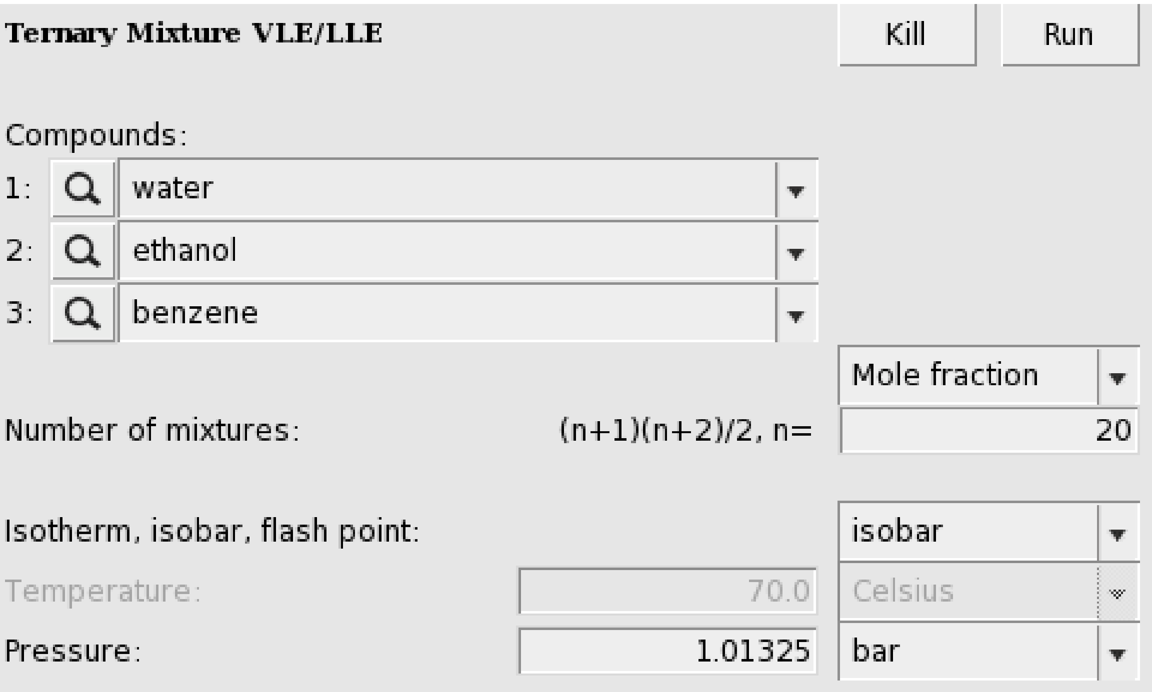
```
Enter '20' for 'Number of mixtures'
Press 'Run'
```

If one clicks in the graph window at the left or below the axes, a popup window 'Graph details' will appear in which one can set details for the graph window. If one chooses in the 'Z Colormap' part of this popup window as the minimum color magenta, as maximum color red, use 100 as number of colors, and change the minimum and maximum values, then the graph could look like this:



Isobaric

Select **Properties → Ternary Mixture VLE/LLE**
Select 'water' for the first compound
Select 'ethanol' for the second compound
Select 'benzene' for the third compound
Use 'Mole fraction'
Enter '20' for 'Number of mixtures'
Select **Isotherm, isobar, flash point → isobar**
Use 'bar' as units for the pressure
Enter '1.01325' in the 'Pressure' field
Select **View → Graph X Axes → x1: molar fraction 1**
Select **View → Graph Y Axes → x2: molar fraction 2**
Select **View → Graph Z Colormap → total vapor pressures**
Press 'Run'



Ternary Mixture VLE/LLE

Compounds:
1: water
2: ethanol
3: benzene

Mole fraction

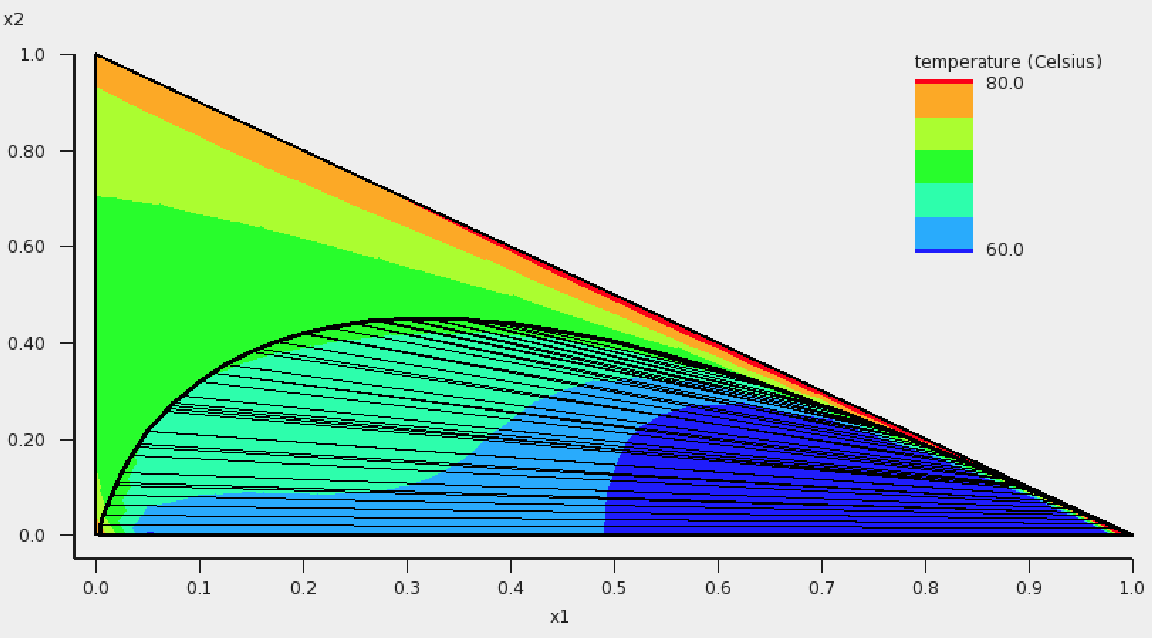
Number of mixtures: (n+1)(n+2)/2, n= 20

Isotherm, isobar, flash point: isobar

Temperature: 70.0 Celsius

Pressure: 1.01325 bar

The result will be a graph and a table. Note that this may take some time, since isobaric calculations are more expensive than isothermal calculations. Click in the graph window at the left or below the axes. If one chooses in the 'Z Zolormap' part of the 'Graph details' as the minimum color blue, as maximum color red, use 5 as number of colors, change the unit to Celsius, and change the minimum and maximum values, then the graph could look like this:

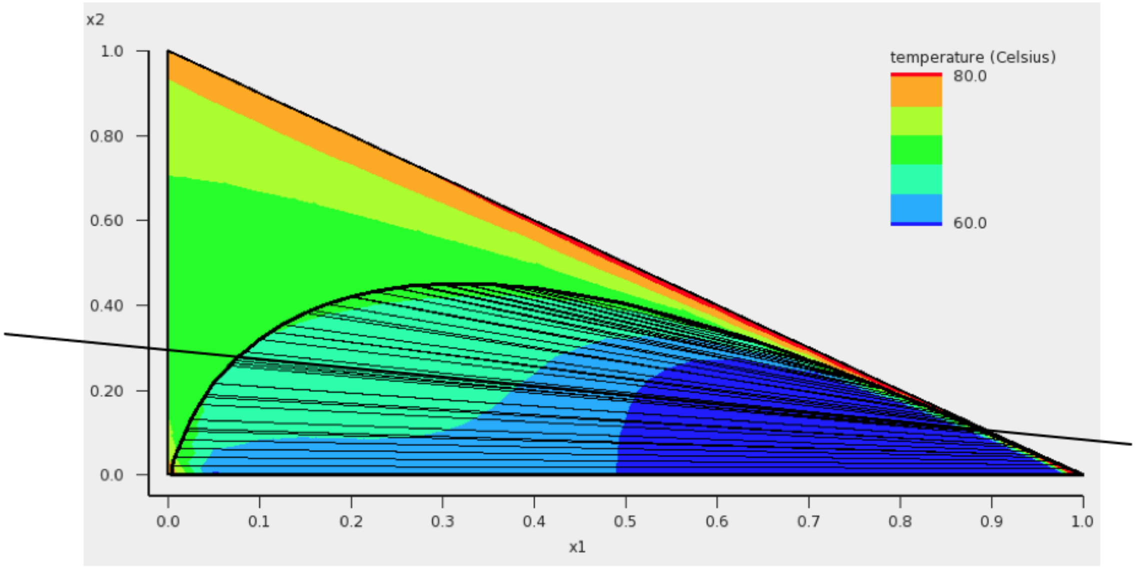


In addition to the colormap of the temperature, an approximate miscibility gap of the ternary mixture is shown in the graph. In this case, within the miscibility gap there are two immiscible phases of the liquid in equilibrium. The composition of the two phases, which are in equilibrium, can be found at the end points of the tie line that are drawn. The calculated temperatures within the miscibility gap are calculated with the unphysical condition that the three liquids are forced to mix, thus these calculated temperatures (and other quantities) within the miscibility gap should not be used. By inspection of the graph, one can observe that the calculated minimum boiling point (azeotrope) is around 68 °C.

Step 10: Calculate a composition line between solvents s1 and s2

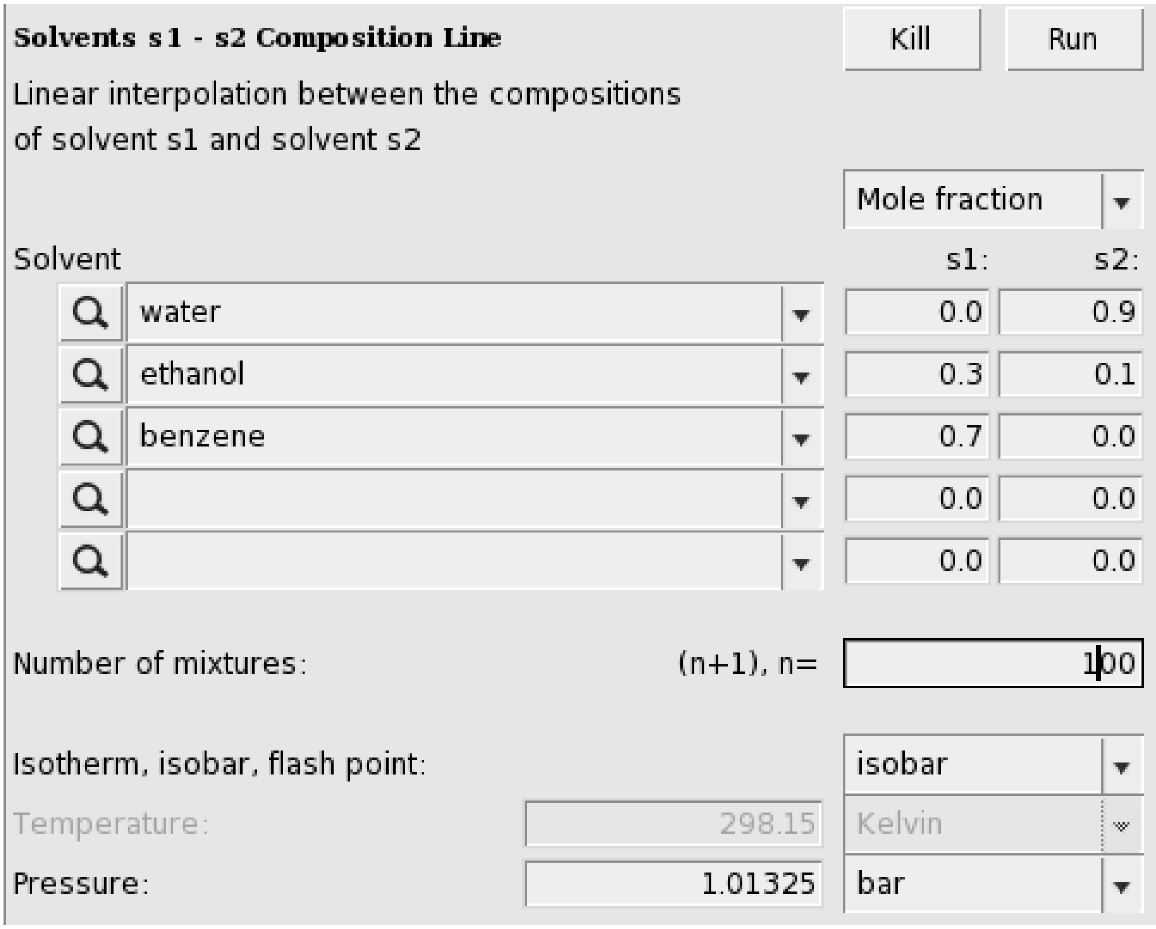
A phase diagram of a mixture of two solvents, which both could be mixtures, can be calculated with **Properties → Solvents s1 - s2 Composition Line**. The mixture will be calculated for a list of molar (or mass) fractions of the solvents between zero and one, and the compositions of solvent 1 and solvent 2 are linearly interpolated. This can be done at constant temperature (isothermal) or at constant vapor pressure (isobaric).

In this step we will try to investigate one of the tie lines of the ternary mixture of water, ethanol, and benzene in more detail. An attempt is made to use the tie line on which ends the calculated minimum boiling point is found, see the tie line which is below the black line in the next picture:



The compositions of solvents s1 and s2 are chosen where the black line in the picture above crosses the boundary of possible compositions. This means that solvent s1 and solvent s2 are mixtures of 2 compounds. Again experimental boiling points are used in the calculation.

`Select` **Properties → Solvents s1 - s2 Composition Line**
`Use 'Mole fraction'`
`Select 'water' for the first compound`
`Select 'ethanol' for the second compound`
`Select 'benzene' for the third compound`
`Enter '0.0' for the mole fraction of compound 1 of solvent s1`
`Enter '0.9' for the mole fraction of compound 1 of solvent s2`
`Enter '0.3' for the mole fraction of compound 2 of solvent s1`
`Enter '0.1' for the mole fraction of compound 2 of solvent s2`
`Enter '0.7' for the mole fraction of compound 3 of solvent s1`
`Enter '0.0' for the mole fraction of compound 3 of solvent s2`
`Enter '100' for 'Number of mixtures'`
`Select` **Isotherm, isobar, flash point → isobar**
`Use 'bar' as units for the pressure`
`Enter '1.01325' in the 'Pressure' field`
`Select` **View → Graph X Axes → s1_x: molar fraction s1**
`Select` **View → Graph Y Axes → pure compound activities**
`Press 'Run'`



Solvents s1 - s2 Composition Line

Linear interpolation between the compositions of solvent s1 and solvent s2

Solvent	s1:	s2:
water	0.0	0.9
ethanol	0.3	0.1
benzene	0.7	0.0
	0.0	0.0
	0.0	0.0

Mole fraction

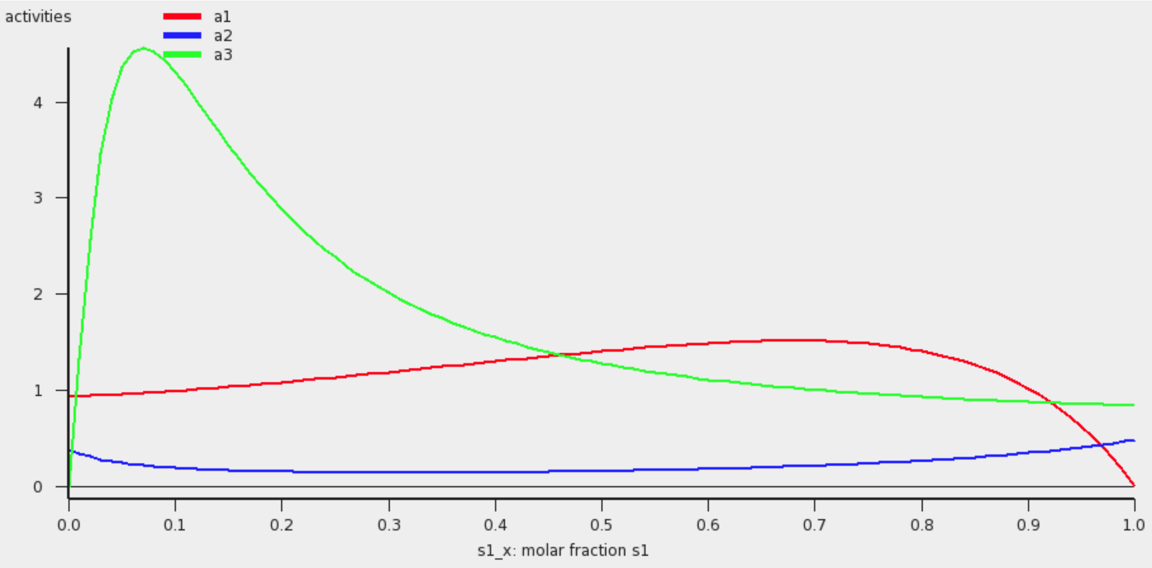
Number of mixtures: (n+1), n= 100

Isotherm, isobar, flash point: isobar

Temperature: 298.15 Kelvin

Pressure: 1.01325 bar

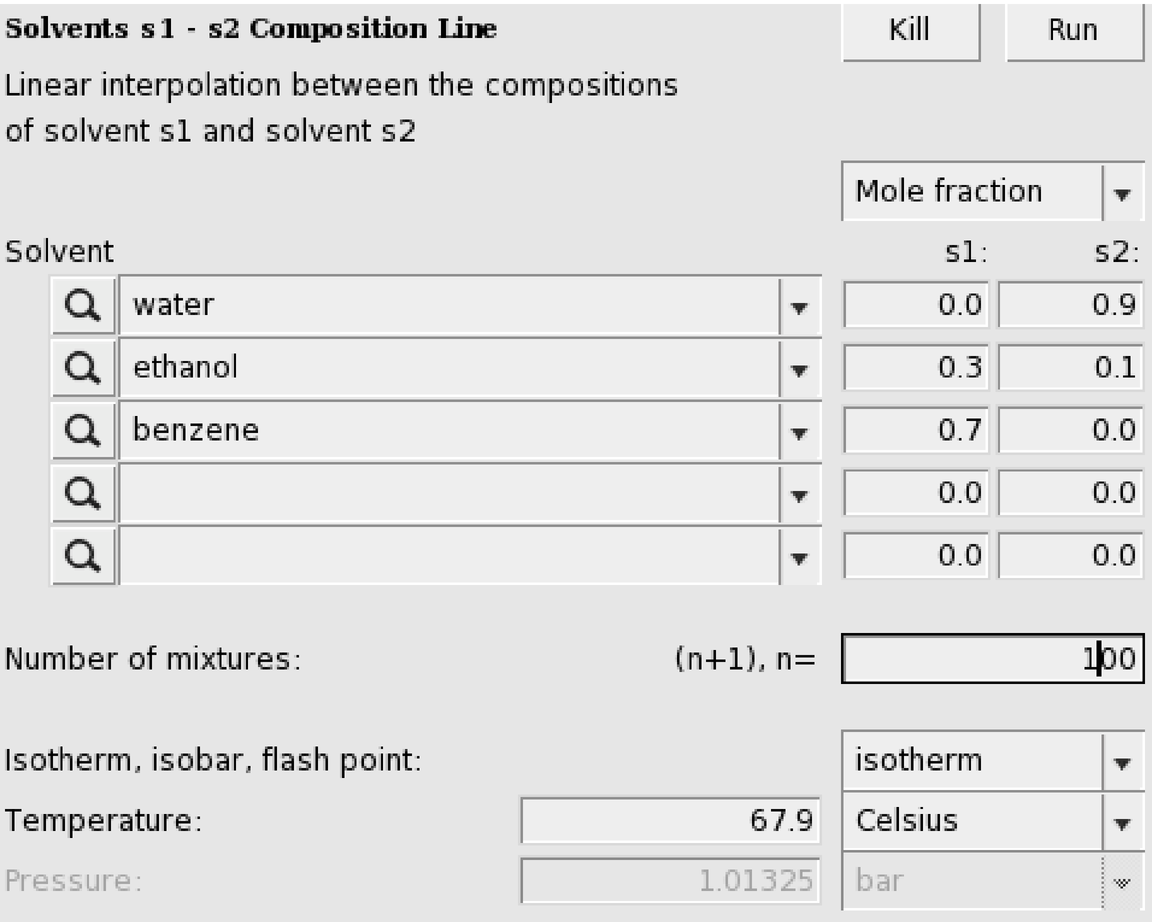
The result will be a table and a graph.



The activities of the pure compounds should be equal at the end point of a tie line $a_1 = a_1'$,$a_2 = a_2'$, and $a_3 = a_3'$. If we look at the graph with close inspection this is approximately true for the molar fraction of solvent s1 with (approximately) s1_x = 0.007 and s1_x' = 0.91. At a molar fraction of 0.91 of solvent s1 the calculated temperature is approximately 67.9 °C.

Next we will use this temperature of 67.9 °C and look at the Gibbs free energy of mixing. This will also give information about the miscibility gap.

`Select` **Isotherm, isobar, flash point → isotherm**
`Use 'Celsius' as units for the temperature`
`Enter '67.9' in the 'Temperature' field`
`Select` **View → Graph X Axes → s1_x: molar fraction s1**
`Select` **View → Graph Y Axes → Gibbs energy of mixing wrt pure compounds**
`Press 'Run'`



Solvents s1 - s2 Composition Line

Linear interpolation between the compositions
of solvent s1 and solvent s2

Mole fraction

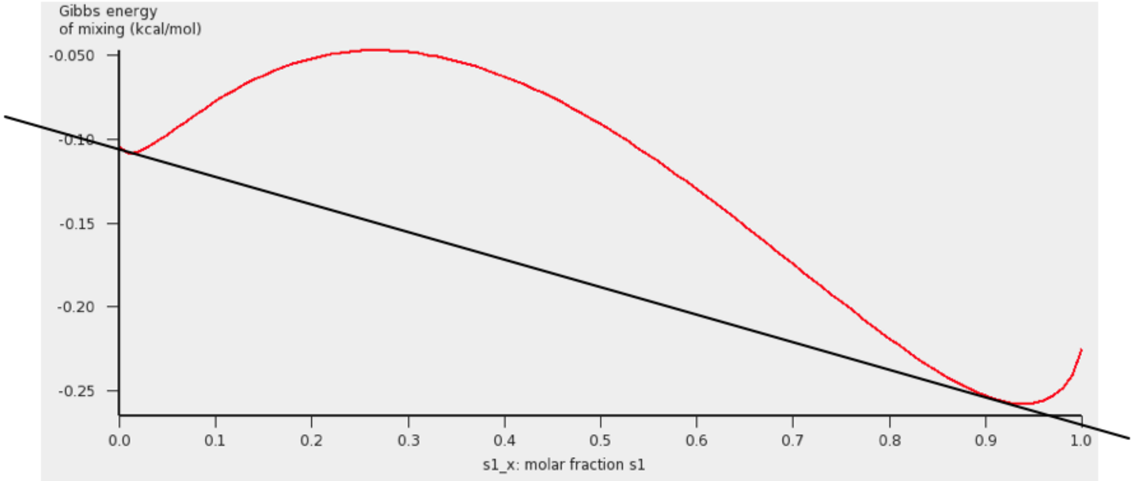
Solvent	s1:	s2:
water	0.0	0.9
ethanol	0.3	0.1
benzene	0.7	0.0
	0.0	0.0
	0.0	0.0

Number of mixtures: (n+1), n= 100

Isotherm, isobar, flash point: isotherm

Temperature: 67.9 Celsius

Pressure: 1.01325 bar



The black line was added to show the miscibility gap more clearly. Indeed at 67.9 °C for molar fractions bewteen s1_x = 0.007 and s1_x' = 0.91, the Gibbs free energy of mixing will be lower if the liquid has 2 phases.

Note, that one should use isothermal conditions, if one wants to use the calculated Gibbs free energy of mixing to determine whether there is a miscibility gap. Note also, that no miscibility gap is calculated if one uses **Properties → Solvents s1 - s2 Composition Line**, even if there is one, like in this case. This is because with the calculated values for only 1 composition line between 2 solvents, that involve more than 2 compounds, in general one does not have enough information to determine the exact miscibility gap.

Tutorial 4: Examples using the COSMO-RS database

ADF has a database of COSMO result files, the COSMO-RS database ADFCRS-2010. Assumed here is that the instruction on this page have been followed to download the database.

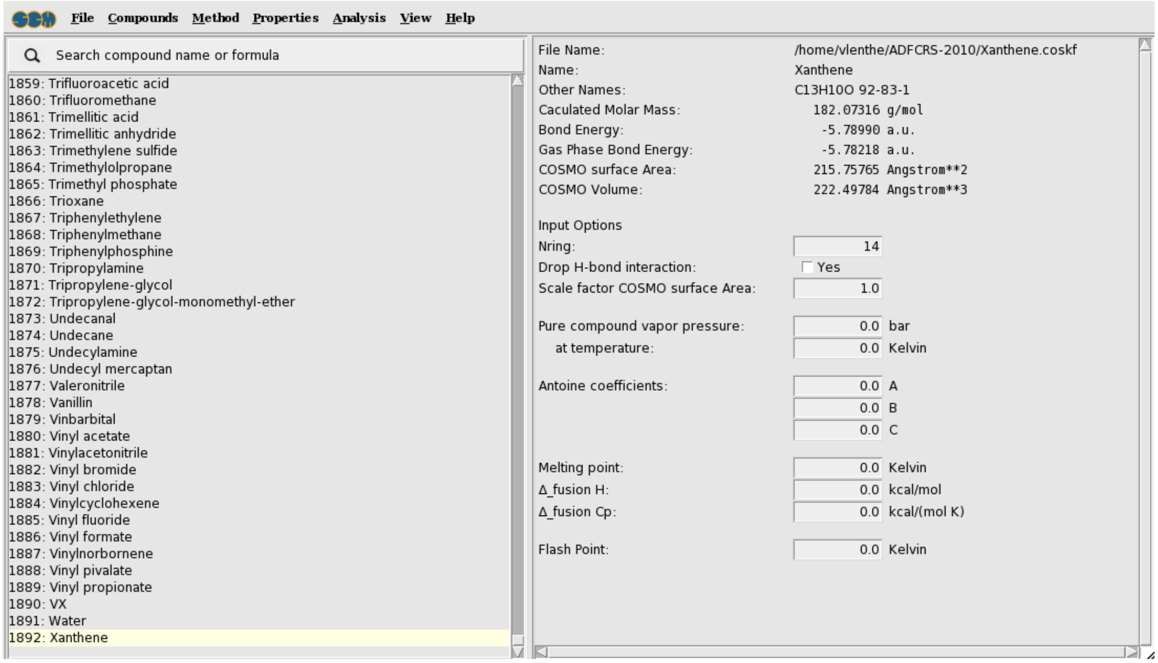
4.1: How to use the COSMO-RS database

Step 1: Add compounds

For this tutorial we assume that you know how start ADFcrs. Next we will add the compounds in the database.

`Select` **Compounds → Add Compound(s)**
`Select` **Directory** `→ the directory of the downloaded COSMO-RS database ADFCRS-2010`
`Select` **Files of type** `(or` **Filter**`)` **→ List of compounds (*.compoundlist)**
`Select all.compoundlist`
`Click 'Open'`

After reading some information about all compounds (may take a minute) the GUI window should look like:



1859: Trifluoroacetic acid
1860: Trifluoromethane
1861: Trimellitic acid
1862: Trimellitic anhydride
1863: Trimethylene sulfide
1864: Trimethylolpropane
1865: Trimethyl phosphate
1866: Trioxane
1867: Triphenylethylene
1868: Triphenylmethane
1869: Triphenylphosphine
1870: Tripropylamine
1871: Tripropylene-glycol
1872: Tripropylene-glycol-monomethyl-ether
1873: Undecanal
1874: Undecane
1875: Undecylamine
1876: Undecyl mercaptan
1877: Valeronitrile
1878: Vanillin
1879: Vinbarbital
1880: Vinyl acetate
1881: Vinylacetonitrile
1882: Vinyl bromide
1883: Vinyl chloride
1884: Vinylcyclohexene
1885: Vinyl fluoride
1886: Vinyl formate
1887: Vinylnorbornene
1888: Vinyl pivalate
1889: Vinyl propionate
1890: VX
1891: Water
1892: Xanthene

File Name: /home/vlenthe/ADFCRS-2010/Xanthene.coskf
Name: Xanthene
Other Names: C13H10O 92-83-1
Caculated Molar Mass: 182.07316 g/mol
Bond Energy: -5.78990 a.u.
Gas Phase Bond Energy: -5.78218 a.u.
COSMO surface Area: 215.75765 Angstrom**2
COSMO Volume: 222.49784 Angstrom**3

Input Options
Nring: 14
Drop H-bond interaction: ☐ Yes
Scale factor COSMO surface Area: 1.0

Pure compound vapor pressure: 0.0 bar
at temperature: 0.0 Kelvin

Antoine coefficients: 0.0 A
0.0 B
0.0 C

Melting point: 0.0 Kelvin
Δ_fusion H: 0.0 kcal/mol
Δ_fusion Cp: 0.0 kcal/(mol K)

Flash Point: 0.0 Kelvin

For the compounds in this database the number of ring atoms (Nring) is provided, which is needed in the COSMO-RS model (see Ref.[2] in the COSMO-RS manual) in order to calculate a ring correction term.

In this 'Compounds' window it is also possible to add some pure compound input data. Pure compound data could be found, for example, at Refs. [411-413].

The file 'all.compoundlist' is a plain text file, in which on each line a filename of a ADF COSMO result file is given. One could make a different .compoundlist file which contains a only a selection of the compounds.

The compounds could also have been added by adding multiple .coskf files, by selecting 'COSMO kf file (*.coskf)' for the popup menu 'Files of type' (or 'Filter'), and selecting all .coskf files. On Windows it may, however, fail to add more than a few hundred .coskf files at a time in this way. If that fails, one should use the .compoundlist file.

References

[411] Wikipedia

[412] NIST Chemistry WebBook

[413] CHERIC. Korea Thermophysical Properties Data Bank: Pure Component Properties

Step 2: Select a compound

There are several ways to select a compound in the list. Here several possibilities are discussed. First browsing:

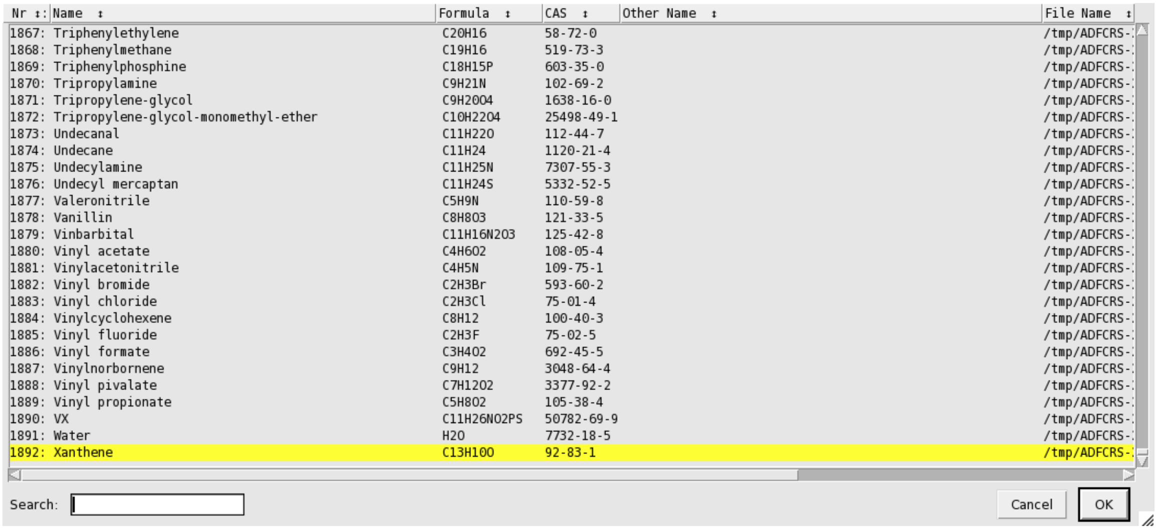
```
Use the scrollbar to quickly scroll
Click on a compound with the mouse, and move the mouse up or down,
     while pressing the mouse
Click on a compound with the mouse, and press the Up or Down key
```

A separate search window will popup if one clicks the search button. In the 'Compounds' window this search button looks like:

In other windows it will look like:

`Select` **Compounds → Compounds**

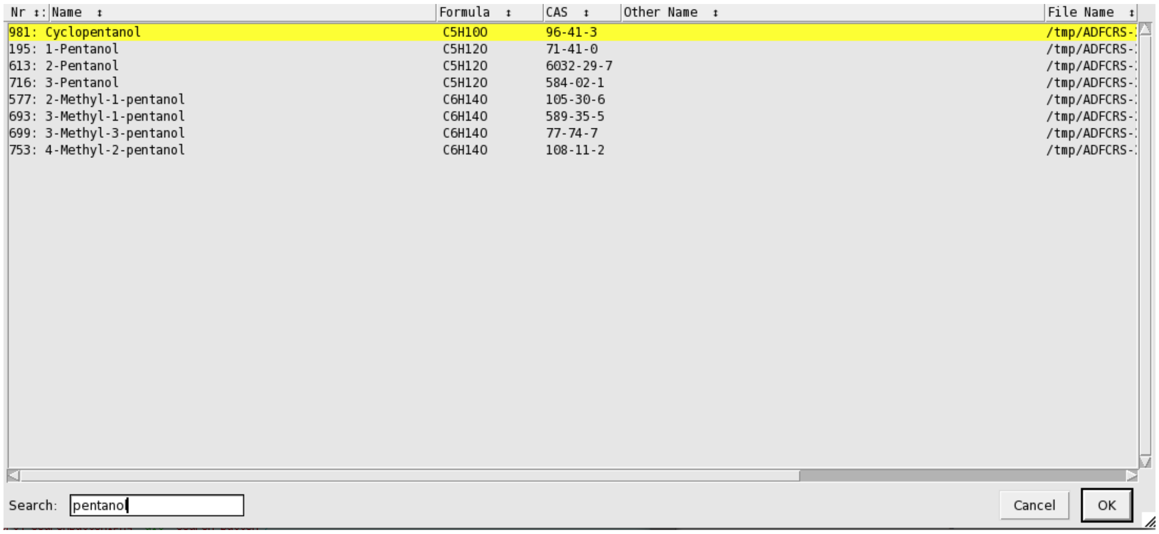
`Click on the search button`



Nr	Name	Formula	CAS	Other Name	File Name
1867:	Triphenylethylene	C20H16	58-72-0		/tmp/ADFCRS-
1868:	Triphenylmethane	C19H16	519-73-3		/tmp/ADFCRS-
1869:	Triphenylphosphine	C18H15P	603-35-0		/tmp/ADFCRS-
1870:	Tripropylamine	C9H21N	102-69-2		/tmp/ADFCRS-
1871:	Tripropylene-glycol	C9H20O4	1638-16-0		/tmp/ADFCRS-
1872:	Tripropylene-glycol-monomethyl-ether	C10H22O4	25498-49-1		/tmp/ADFCRS-
1873:	Undecanal	C11H22O	112-44-7		/tmp/ADFCRS-
1874:	Undecane	C11H24	1120-21-4		/tmp/ADFCRS-
1875:	Undecylamine	C11H25N	7307-55-3		/tmp/ADFCRS-
1876:	Undecyl mercaptan	C11H24S	5332-52-5		/tmp/ADFCRS-
1877:	Valeronitrile	C5H9N	110-59-8		/tmp/ADFCRS-
1878:	Vanillin	C8H8O3	121-33-5		/tmp/ADFCRS-
1879:	Vinbarbital	C11H16N2O3	125-42-8		/tmp/ADFCRS-
1880:	Vinyl acetate	C4H6O2	108-05-4		/tmp/ADFCRS-
1881:	Vinylacetonitrile	C4H5N	109-75-1		/tmp/ADFCRS-
1882:	Vinyl bromide	C2H3Br	593-60-2		/tmp/ADFCRS-
1883:	Vinyl chloride	C2H3Cl	75-01-4		/tmp/ADFCRS-
1884:	Vinylcyclohexene	C8H12	100-40-3		/tmp/ADFCRS-
1885:	Vinyl fluoride	C2H3F	75-02-5		/tmp/ADFCRS-
1886:	Vinyl formate	C3H4O2	692-45-5		/tmp/ADFCRS-
1887:	Vinylnorbornene	C9H12	3048-64-4		/tmp/ADFCRS-
1888:	Vinyl pivalate	C7H12O2	3377-92-2		/tmp/ADFCRS-
1889:	Vinyl propionate	C5H8O2	105-38-4		/tmp/ADFCRS-
1890:	VX	C11H26NO2PS	50782-69-9		/tmp/ADFCRS-
1891:	Water	H2O	7732-18-5		/tmp/ADFCRS-
1892:	Xanthene	C13H10O	92-83-1		/tmp/ADFCRS-

```
Click on 'CAS' to sort by CAS registry number
Click again to reverse the order
Click on 'Nr' to sort by number
```

Click on 'Name' to sort by name
Click on 'Formula' to sort by formula
Enter 'pentanol' in the 'Search' field
Click on 'Cyclopentanol'
Click 'OK'



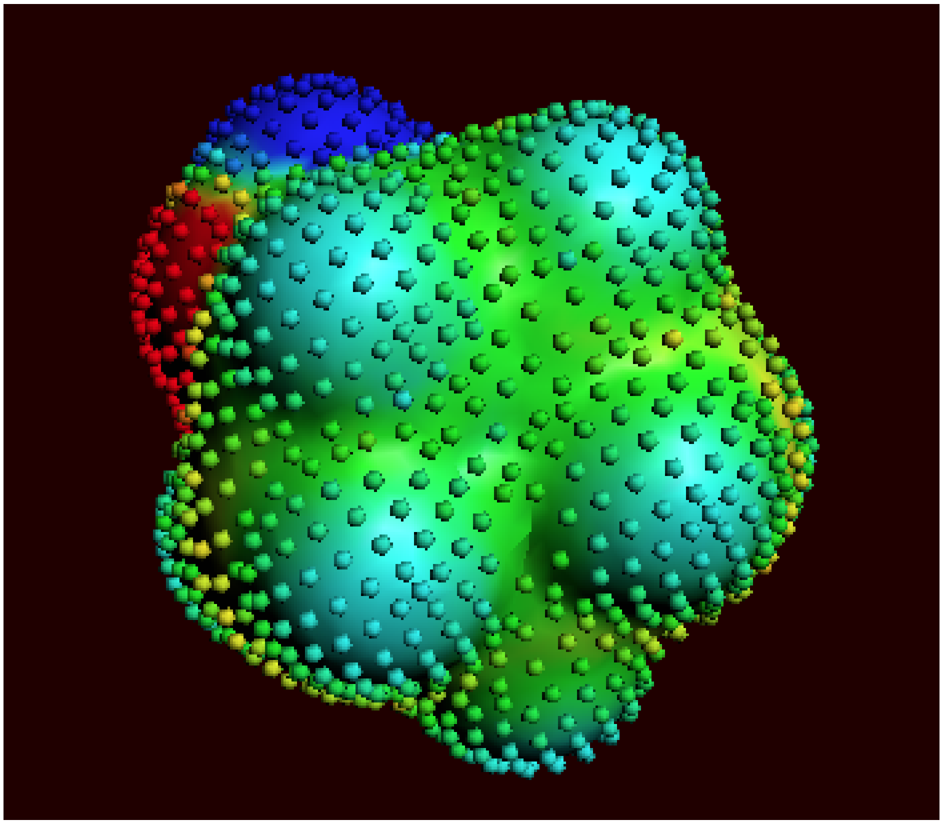
Nr	Name	Formula	CAS	Other Name	File Name
981:	Cyclopentanol	C5H10O	96-41-3		/tmp/ADFCRS-
195:	1-Pentanol	C5H12O	71-41-0		/tmp/ADFCRS-
613:	2-Pentanol	C5H12O	6032-29-7		/tmp/ADFCRS-
716:	3-Pentanol	C5H12O	584-02-1		/tmp/ADFCRS-
577:	2-Methyl-1-pentanol	C6H14O	105-30-6		/tmp/ADFCRS-
693:	3-Methyl-1-pentanol	C6H14O	589-35-5		/tmp/ADFCRS-
699:	3-Methyl-3-pentanol	C6H14O	77-74-7		/tmp/ADFCRS-
753:	4-Methyl-2-pentanol	C6H14O	108-11-2		/tmp/ADFCRS-

Search: pentanol

Step 3: Visualize the COSMO surface: ADFview

You can use ADFview to have a look at the COSMO surface, and the COSMO surface charge density. Here we use the selected cyclopentanol of the previous step.

Select **Compounds → Compounds**
Click on the left side 'Cyclopentanol'
Select **Compounds → Show Selected Compound**
Select **Add → COSMO: Surface Charge Density → on COSMO surface (reconstructed)**
Select **Add → COSMO: Surface Charge Density → on COSMO surface points**



Next we will close this ADFview window:

```
Select the ADFView window 'Cyclopentanol'
Select File → Quit
Select the COSMO-RS GUI window
```

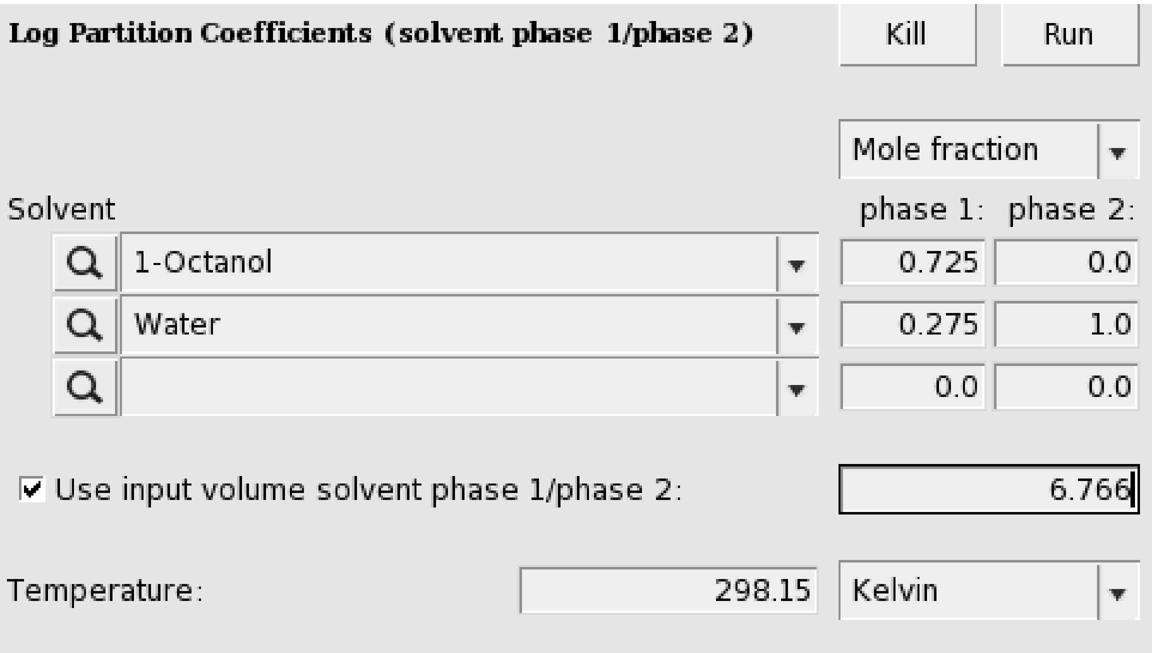
4.2: Octanol-Water partition coefficients (log P_{OW})

In this example the Octanol-Water partition coefficients for 7 different compounds are calculated and compared to experiment.

In case of partly miscible liquids, like the Octanol-rich phase of Octanol and Water, both components have nonzero mole fractions. Next an input value is used for the volume quotient of the two solvents. The values for the nonzero mole fractions in the Octanol-rich phase and the volume quotient of the two solvents were taken from Ref. [421]. If one does not include such value, the program will use the COSMO volumes to calculate the volume quotient. The COSMO volumes can be found in the 'Compound' window.

```
Select Properties → Log Partition Coefficients
Select '1-Octanol' for the first component in the solvent
Select 'Water' for the second component in the solvent
Enter '0.725' for the Mole fraction of 1-Octanol in phase 1
Enter '0.275' for the Mole fraction of Water in phase 1
Enter '1.0' for the Mole fraction of Water in phase 2
Click the check box 'Use input volume solvent phase 1/phase 2'
Enter '6.766' in the 'Use input volume solvent phase 1/phase 2' field
Enter '298.15' for the 'Temperature' in 'Kelvin'
Click the 'None' button below 'Solutes (infinite dilute)'
```

```
Click the search button below 'Solutes (infinite dilute)' to add 'Acetamide',
      'Methanol', 'Formic acid', 'Diethyl ether', p-Dichlorobenzene,
      'Hexamethylbenzene', and '2,2',4,4',5-Pentachlorobiphenyl'
Press 'Run'
Enter the name 'tutorial4' in the 'Filename' field
```



Log Partition Coefficients (solvent phase 1/phase 2)

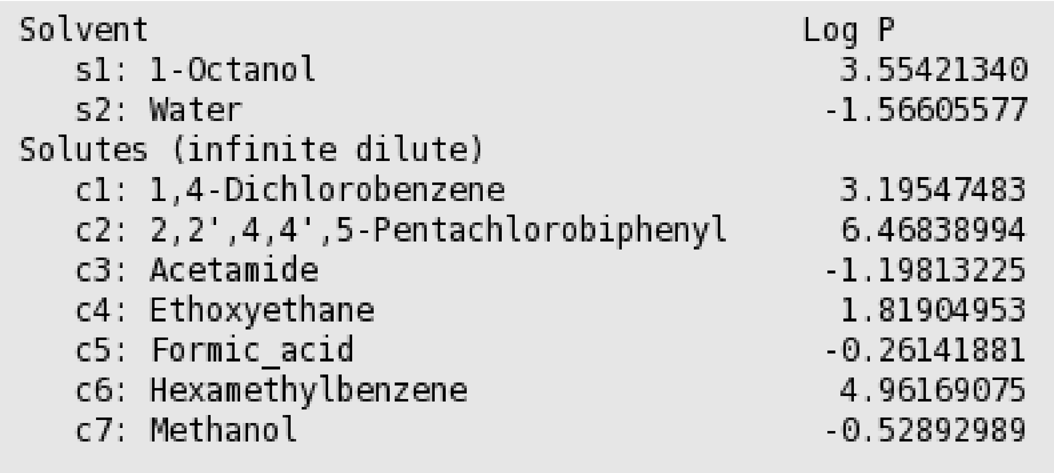
Mole fraction

Solvent	phase 1:	phase 2:
1-Octanol	0.725	0.0
Water	0.275	1.0
	0.0	0.0

☑ Use input volume solvent phase 1/phase 2: 6.766

Temperature: 298.15 Kelvin

The result of the calculation (may take a few seconds) is given in the form of a table. Note that not all compounds were selected as solutes, otherwise the calculation would take much more time.



```
Solvent                                      Log P
   s1: 1-Octanol                              3.55421340
   s2: Water                                 -1.56605577
Solutes (infinite dilute)
   c1: 1,4-Dichlorobenzene                    3.19547483
   c2: 2,2',4,4',5-Pentachlorobiphenyl        6.46838994
   c3: Acetamide                             -1.19813225
   c4: Ethoxyethane                           1.81904953
   c5: Formic_acid                           -0.26141881
   c6: Hexamethylbenzene                      4.96169075
   c7: Methanol                              -0.52892989
```

In the database the name 'Ethoxyethane' is used for 'Diethyl ether', and the name '1,4-Dichlorobenzene' is used for 'p-Dichlorobenzene'. In the search window that popups if the search button is clicked, some alternative names are given for some of the compounds.

Next the calculated Octanol-Water partition coefficients are compared to experiment in the following table.

	Solute	experimental log Pow[422]	calculated log Pow
1	Acetamide	-1.16	-1.20

2	Methanol	-0.82	-0.53
3	Formic acid	-0.41	-0.26
4	Diethyl ether	0.83	1.82
5	p-Dichlorobenzene	3.37	3.20
6	Hexamethylbenzene	4.61	4.96
7	2,2',4,4',5-Pentachlorobiphenyl	6.41	6.47

References

[421] S.-T. Lin and S.I. Sandler, *Prediction of Octanol-Water Partition Coefficients Using a Group Contribution Solvation Model*, Industrial & Engineeering Chemistry research **38** (1999), 4081

[422] Experimental numbers taken from Wikipedia at July 15, 2010, http://en.wikipedia.org/wiki/Partition_coefficient. The experimental numbers may have been determined at a different temperature than 25 °C.

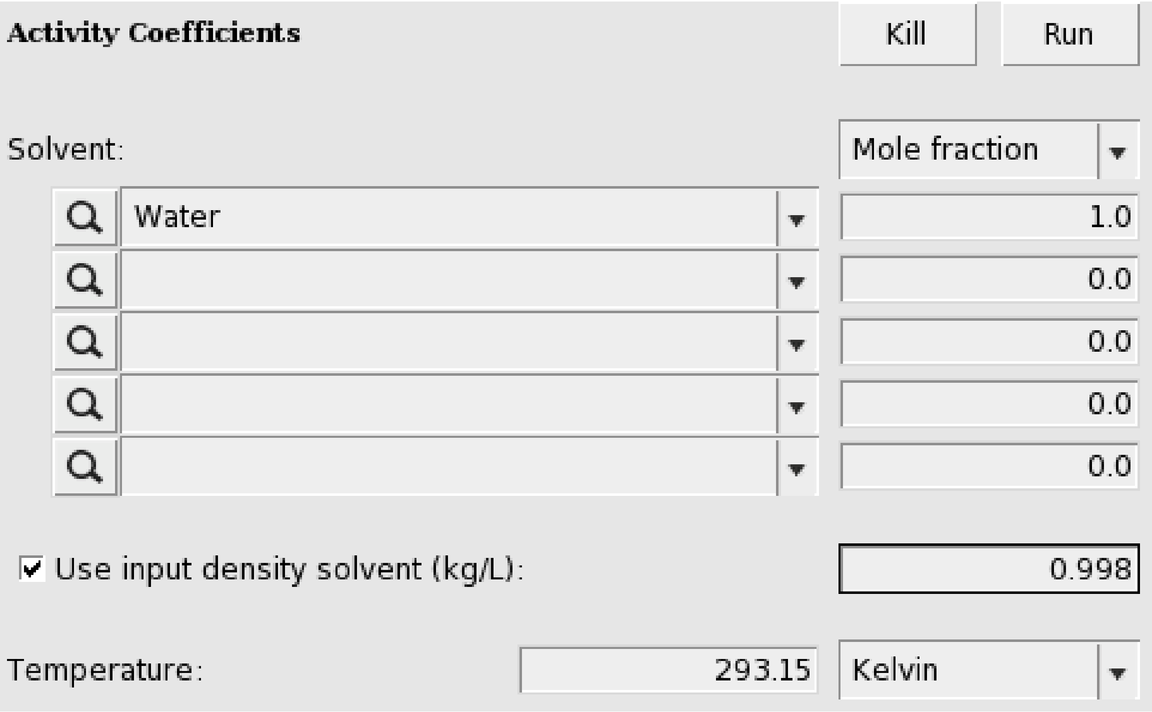
4.3: Henry's law constants

In this example Henry's law constants for 17 different compounds are calculated and compared to experiment.

The Henry's law constants depend on the density of the solvent, Water in this case. If one does not supply a density of the solvent in the input the program calculates the density of the solvent by dividing the mass of a molecule with its COSMO volume. The density of Water at 20 °C (293.15 K) is approximately 0.998 kg/L. Note that the calculated activity coefficients do not depend on the density of Water.

Remark: To only add the compounds needed in this example, one can also open a new COSMO-RS GUI window (**SCM** → **COSMO-RS**), copy the $ADFHOME/examples/crs/Tutorial4/tutorial4.3.compoundlist to the directory where the COSMO-RS database is downloaded, and select this file with **Compounds** → **Add Compound(s)**. This is recommended. The tutorial4.3.compoundlist is a file with a list of compounds that is limited to the coumpounds needed in this example.

```
Select Properties → Activity coefficients
Select 'Water' for the first component in Solvent
Enter '293.15' for the 'Temperature' in 'Kelvin'
Click the check box 'Use input density solvent (kg/L)'
Enter '0.998' in the 'Use input density solvent (kg/L)' field
Click the 'None' button next to 'Compounds'
Click the search button next to 'Compounds' to add some compounds:
'Acetaldehyde', 'Acetone', 'Acetonitrile', 'Benzene', 'Chloromethane',
'Cyclopentane', 'Dimethyl sulfide', 'Ethanol', 'Formaldehyde',
'Methanol', 'Methyl acetate', 'Methyl bromide', 'Methyl fluoride',
'Methyl iodide', 'Pyridine', 'Thiophene', and 'Toluene'
Press 'Run'
```



Solvent: Mole fraction

Water 1.0

0.0

0.0

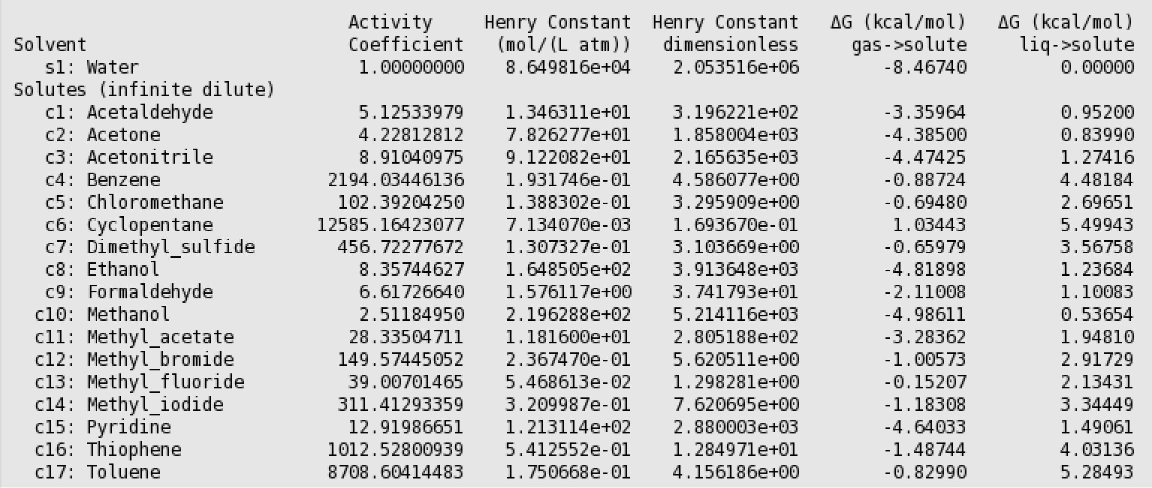
0.0

0.0

☑ Use input density solvent (kg/L): 0.998

Temperature: 293.15 Kelvin

The result of the calculation (may take a few seconds, depending on the number of compounds selected) is given in the form of a table.



```
                                 Activity    Henry Constant  Henry Constant   ΔG (kcal/mol)   ΔG (kcal/mol)
Solvent                         Coefficient   (mol/(L atm))   dimensionless     gas->solute     liq->solute
   s1: Water                     1.00000000    8.649816e+04    2.053516e+06        -8.46740         0.00000
Solutes (infinite dilute)
   c1: Acetaldehyde              5.12533979    1.346311e+01    3.196221e+02        -3.35964         0.95200
   c2: Acetone                   4.22812812    7.826277e+01    1.858004e+03        -4.38500         0.83990
   c3: Acetonitrile              8.91040975    9.122082e+01    2.165635e+03        -4.47425         1.27416
   c4: Benzene                2194.03446136    1.931746e-01    4.586077e+00        -0.88724         4.48184
   c5: Chloromethane           102.39204250    1.388302e-01    3.295909e+00        -0.69480         2.69651
   c6: Cyclopentane          12585.16423077    7.134070e-03    1.693670e-01         1.03443         5.49943
   c7: Dimethyl_sulfide        456.72277672    1.307327e-01    3.103669e+00        -0.65979         3.56758
   c8: Ethanol                   8.35744627    1.648505e+02    3.913648e+03        -4.81898         1.23684
   c9: Formaldehyde              6.61726640    1.576117e+00    3.741793e+01        -2.11008         1.10083
  c10: Methanol                  2.51184950    2.196288e+02    5.214116e+03        -4.98611         0.53654
  c11: Methyl_acetate           28.33504711    1.181600e+01    2.805188e+02        -3.28362         1.94810
  c12: Methyl_bromide          149.57445052    2.367470e-01    5.620511e+00        -1.00573         2.91729
  c13: Methyl_fluoride          39.00701465    5.468613e-02    1.298281e+00        -0.15207         2.13431
  c14: Methyl_iodide           311.41293359    3.209987e-01    7.620695e+00        -1.18308         3.34449
  c15: Pyridine                 12.91986651    1.213114e+02    2.880003e+03        -4.64033         1.49061
  c16: Thiophene              1012.52800939    5.412552e-01    1.284971e+01        -1.48744         4.03136
  c17: Toluene                8708.60414483    1.750668e-01    4.156186e+00        -0.82990         5.28493
```

The Henry's law constants also depend on the vapor pressure of the pure compounds in the gas phase. In the compounds window one can also set these vapor pressures of the pure compounds at a given temperature, or set the Antoine parameters. If these values are not specified (if they are zero) then the pure compound vapor pressure will be approximated using the COSMO-RS method. Best is to include the experimental vapor pressure for a pure compound at the used temperature, thus in this case at 293.15 K.

Select **Compounds → Compounds**
Click on the left side 'Acetaldehyde'
Enter '0.968' in the 'Pure compound vapor pressure:' field
Enter '293.15' in the 'at temperature:' field
Click on the left side 'Acetone'
Enter '0.246' in the 'Pure compound vapor pressure:' field

```
Enter '293.15' in the 'at temperature:' field
Click on the left side 'Acetonitrile'
Enter '0.095' in the 'Pure compound vapor pressure:' field
Enter '293.15' in the 'at temperature:' field
Click on the left side 'Benzene'
Enter '0.100' in the 'Pure compound vapor pressure:' field
Enter '293.15' in the 'at temperature:' field
Click on the left side 'Chloromethane'
Enter '4.94' in the 'Pure compound vapor pressure:' field
Enter '293.15' in the 'at temperature:' field
Click on the left side 'Cyclopentane'
Enter '0.346' in the 'Pure compound vapor pressure:' field
Enter '293.15' in the 'at temperature:' field
Click on the left side 'Dimethyl sulfide'
Enter '0.530' in the 'Pure compound vapor pressure:' field
Enter '293.15' in the 'at temperature:' field
Click on the left side 'Ethanol'
Enter '0.059' in the 'Pure compound vapor pressure:' field
Enter '293.15' in the 'at temperature:' field
Click on the left side 'Formaldehyde'
Enter '4.47' in the 'Pure compound vapor pressure:' field
Enter '293.15' in the 'at temperature:' field
Click on the left side 'Methanol'
Enter '0.129' in the 'Pure compound vapor pressure:' field
Enter '293.15' in the 'at temperature:' field
Click on the left side 'Methyl acetate'
Enter '0.230' in the 'Pure compound vapor pressure:' field
Enter '293.15' in the 'at temperature:' field
Click on the left side 'Methyl bromide'
Enter '1.83' in the 'Pure compound vapor pressure:' field
Enter '293.15' in the 'at temperature:' field
Click on the left side 'Methyl fluoride'
Enter '33.7' in the 'Pure compound vapor pressure:' field
Enter '293.15' in the 'at temperature:' field
Click on the left side 'Methyl iodide'
Enter '0.443' in the 'Pure compound vapor pressure:' field
Enter '293.15' in the 'at temperature:' field
Click on the left side 'Pyridine'
Enter '0.021' in the 'Pure compound vapor pressure:' field
Enter '293.15' in the 'at temperature:' field
Click on the left side 'Thiophene'
Enter '0.082' in the 'Pure compound vapor pressure:' field
Enter '293.15' in the 'at temperature:' field
Click on the left side 'Toluene'
Enter '0.029' in the 'Pure compound vapor pressure:' field
Enter '293.15' in the 'at temperature:' field
Click on the left side 'Water'
Enter '0.02536' in the 'Pure compound vapor pressure:' field
Enter '293.15' in the 'at temperature:' field
Select Properties → Activity coefficients
Press 'Run'
```

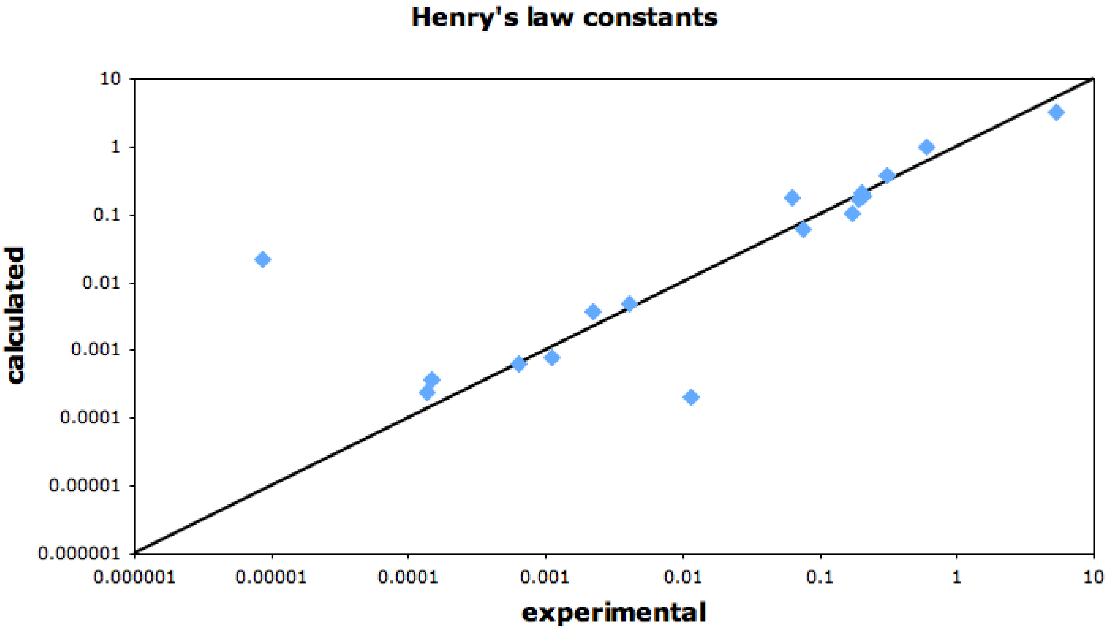
For some of the compounds the Henry's law constants differ quite substantially.

```
                                  Activity     Henry Constant  Henry Constant    ΔG (kcal/mol)    ΔG (kcal/mol)
Solvent                          Coefficient   (mol/(L atm))   dimensionless     gas->solute      liq->solute
   s1: Water                      1.00000000    2.213964e+03    5.256080e+04        -6.33215          0.00000
Solutes (infinite dilute)
   c1: Acetaldehyde               5.12533979    1.131675e+01    2.686663e+02        -3.25847          0.95200
   c2: Acetone                    4.22812812    5.398046e+01    1.281527e+03        -4.16861          0.83990
   c3: Acetonitrile               8.91040975    6.632825e+01    1.574671e+03        -4.28861          1.27416
   c4: Benzene                 2194.03446136    2.559036e-01    6.075300e+00        -1.05105          4.48184
   c5: Chloromethane            102.39204250    1.110009e-01    2.635227e+00        -0.56447          2.69651
   c6: Cyclopentane           12585.16423077    1.289392e-02    3.061091e-01         0.68963          5.49943
   c7: Dimethyl_sulfide         456.72277672    2.319484e-01    5.506589e+00        -0.99380          3.56758
   c8: Ethanol                    8.35744627    1.138660e+02    2.703246e+03        -4.60343          1.23684
   c9: Formaldehyde               6.61726640    1.898164e+00    4.506351e+01        -2.21839          1.10083
  c10: Methanol                   2.51184950    1.732752e+02    4.113655e+03        -4.84802          0.53654
  c11: Methyl_acetate            28.33504711    8.615254e+00    2.045311e+02        -3.09958          1.94810
  c12: Methyl_bromide           149.57445052    2.051216e-01    4.869705e+00        -0.92220          2.91729
  c13: Methyl_fluoride           39.00701465    4.271174e-02    1.014001e+00        -0.00810          2.13431
  c14: Methyl_iodide            311.41293359    4.069860e-01    9.662084e+00        -1.32134          3.34449
  c15: Pyridine                  12.91986651    2.069391e+02    4.912854e+03        -4.95144          1.49061
  c16: Thiophene               1012.52800939    6.762370e-01    1.605426e+01        -1.61714          4.03136
  c17: Toluene                 8708.60414483    2.223173e-01    5.277942e+00        -0.96909          5.28493
```

Experimental determined Henry's law constants might, for example, be found at http://www.henrys-law.org, where a 'compilation of Henry's Law constants for inorganic and organic species of potential importance in environmental chemistry' were listed by R.Sander, and where also an explanation can be found of the many different definitions and units for Henry's law constants.

The calculated Henry's law constants will be compared to experimental values in the next graph and table. The experimental numbers were taken from Ref. [431], where the experimentally determined dimensionless Henry's law constant H^{cc} is the inverse of the dimensionless Henry's law constant $k_H{}^{cc}$, that is used in the COSMO-RS module.

$$H^{cc} = k_{H,\,inv}{}^{cc} = 1/(k_H{}^{cc})$$



	Solute	experimental H^{cc}@20°C [431]	calculated H^{cc}@20°C
1	Methyl_bromide	$2.01\ 10^{-1}$	$2.05\ 10^{-1}$

2	Chloromethane	$3.05\ 10^{-1}$	$3.80\ 10^{-1}$
3	Methyl_fluoride	$6.04\ 10^{-1}$	$9.86\ 10^{-1}$
4	Methyl_iodide	$1.70\ 10^{-1}$	$1.04\ 10^{-1}$
5	Cyclopentane	$5.25\ 10^{0}$	$3.27\ 10^{0}$
6	Benzene	$1.91\ 10^{-1}$	$1.65\ 10^{-1}$
7	Toluene	$2.09\ 10^{-1}$	$1.89\ 10^{-1}$
8	Methanol	$1.37\ 10^{-4}$	$2.43\ 10^{-4}$
9	Ethanol	$1.48\ 10^{-4}$	$3.70\ 10^{-4}$
10	Formaldehyde	$8.61\ 10^{-6}$	$2.22\ 10^{-2}$
11	Acetaldehyde	$2.21\ 10^{-3}$	$3.72\ 10^{-3}$
12	Acetrone	$1.10\ 10^{-3}$	$0.78\ 10^{-3}$
13	Methyl_acetate	$4.02\ 10^{-3}$	$4.89\ 10^{-3}$
14	Acetonitrile	$6.35\ 10^{-4}$	$6.35\ 10^{-4}$
15	Pyridine	$1.14\ 10^{-2}$	$2.03\ 10^{-4}$
16	Dimethyl_sulfide	$6.35\ 10^{-2}$	$1.82\ 10^{-1}$
17	Thiophene	$7.46\ 10^{-2}$	$6.23\ 10^{-2}$

In most cases the calculated Henry's law constants are quite close to the experimental ones, except for Formaldehyde and Pyridine.

The Henry's law constant of Formaldehyde is more than a factor of 10^3 wrong. The origin of this error is that in Water solution the hydration of Formaldehyde leads to Methanediol, and Methanediol is even the dominant form if one dissolves Formaldehyde in Water. This is not taken into account in the calculation. In Ref. [432] a distinction is made between the apparent and intrinsic Henry's law constants, which differ from each other by approximately a factor of 10^3 for Formaldehyde, and a factor of approximately 2.4 for Acetaldehyde. In Ref. [432] the intrinsic Henry's law constant for Formaldehyde was determined to be 2.5 mol/(L atm) at 25 °C, which is close to the value of 1.9 mol/(L atm) which was calculated with COSMO-RS, although at a different temperature of 20 °C.

The calculated Henry's law constant of Pyridine is approximately a factor of 10^2 different than the experimental value in Ref. [431]. However, the experimental values for Pyridine taken from Ref. [433] are $1.1\ 10^2$ mol/(L atm) and $9.0\ 10^1$ mol/(L atm), which are not very different from the calculated value with COSMO-RS of $2.1\ 10^2$ mol/(L atm). Also the experimental values for Pyridine reported in Ref. [434] are in much better agreement with the value calculated with COSMO-RS.

References

[431] J. Staudinger and P.V. Roberts, *A critical compilation of Henry's law constant temperature dependence relations for organic compounds in dilute aqueous solutions*, Chemosphere **44** (2001), 561

[432] E.A. Betterton and M.R. Hoffmann, *Henry's law constants of some environmentally important aldehydes*, Environmental Science & Technology **22** (1988), 1415

[433] R. Sander (1999), *Compilation of Henry's Law Constants for Inorganic and Organic Species of Potential Importance in Environmental Chemistry (Version 3)*, http://www.henrys-law.org

[434] M. Bernauera and V. Dohnal, *Temperature dependences of limiting activity coefficients and Henry's law constants for N-methylpyrrolidone, pyridine, and piperidine in water*, Fluid Phase Equilibria **282** (2009), 100

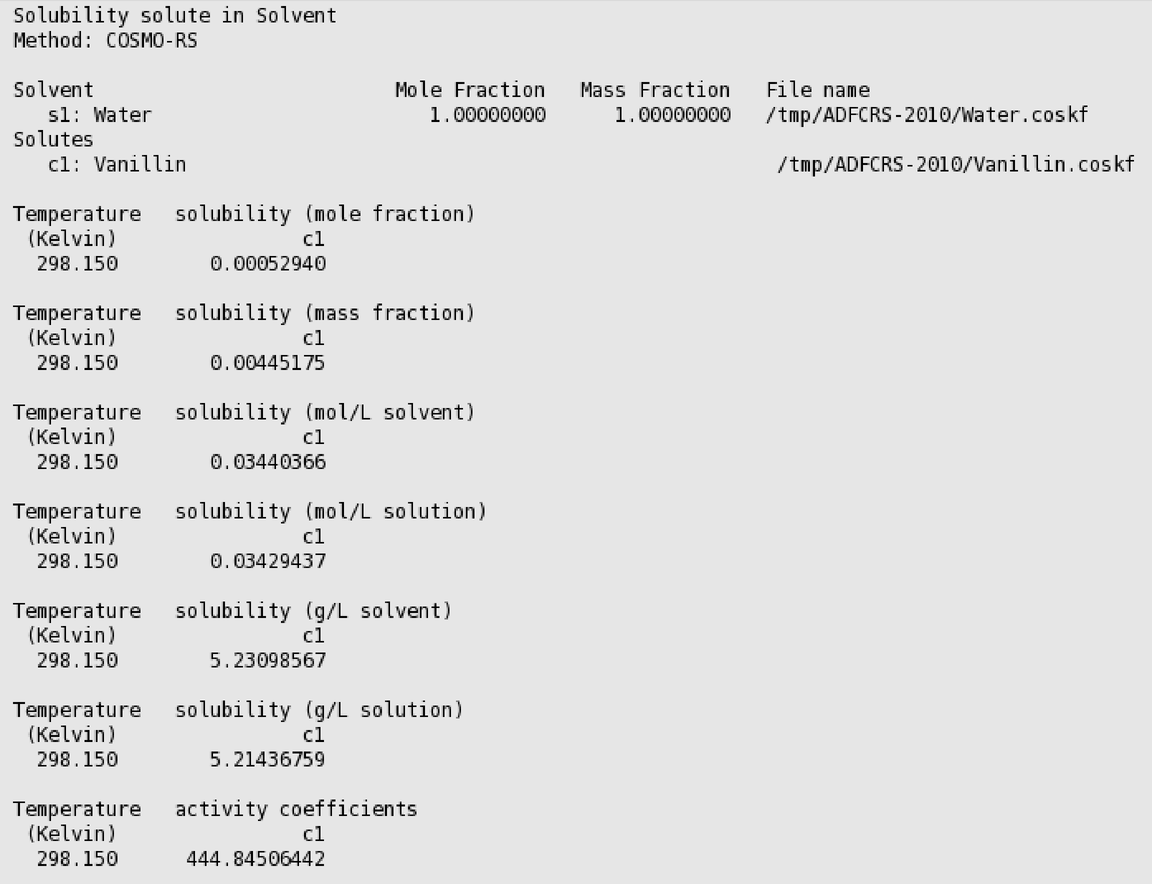
4.4: Solubility of Vanillin in organic solvents

In this example the solubility of Vanillin in 9 different solvents is calculated and compared to experiment.

Vanillin (4-Hydroxy-3-methoxybenzaldehyde) is a solid at room temperature. For the solubility of a solid, one should include the melting point and the enthalpy of fusion of the solid in the right window of the 'Compounds' window for a selected compound. If known the Δ heat capacity of fusion should also be included, although it is often less important.

Remark: To only add the compounds needed in this example, one can also open a new COSMO-RS GUI window (**SCM → COSMO-RS**), copy the $ADFHOME/examples/crs/Tutorial4/tutorial4.4.compoundlist to the directory where the COSMO-RS database is downloaded, and select this file with **Compounds → Add Compound(s)**. The tutorial4.4.compoundlist is a file with a list of compounds that is limited to the coumpounds needed in this example.

`Select` **Compounds → Compounds**
`Click on the left side 'Vanillin'`
`Enter '355' in the 'Melting point:' field`
`Enter '5.35' in the 'Δ_fusion H:' field`
`Select` **Properties → Solubility**
`Select 'Water' for the first component in 'Solvent'`
`Select 'Vanillin' for the first 'Solute'`
`Enter '298.15' without quotes in the 'Temperature from:' field in 'Kelvin'`
`Enter '298.15' in the 'to:' field in 'Kelvin'`
`Press 'Run'`



```
Solubility solute in Solvent
Method: COSMO-RS

Solvent                          Mole Fraction   Mass Fraction   File name
   s1: Water                        1.00000000      1.00000000   /tmp/ADFCRS-2010/Water.coskf
Solutes
   c1: Vanillin                                                   /tmp/ADFCRS-2010/Vanillin.coskf

Temperature   solubility (mole fraction)
 (Kelvin)              c1
  298.150       0.00052940

Temperature   solubility (mass fraction)
 (Kelvin)              c1
  298.150       0.00445175

Temperature   solubility (mol/L solvent)
 (Kelvin)              c1
  298.150       0.03440366

Temperature   solubility (mol/L solution)
 (Kelvin)              c1
  298.150       0.03429437

Temperature   solubility (g/L solvent)
 (Kelvin)              c1
  298.150       5.23098567

Temperature   solubility (g/L solution)
 (Kelvin)              c1
  298.150       5.21436759

Temperature   activity coefficients
 (Kelvin)              c1
  298.150     444.84506442
```

Note that for the calculation of the solubility in units of mol/L and g/L the program uses information of the mass and COSMO volume of the solvent and solute. Especially the COSMO volume may not always be accurate.

In a similar way as we did the solubility calculation of Vanillin in Water, one can now calculate the solubility of Vanillin in several other solvents.

`Select` **Properties → Solubility**
`Select '1,2-Dichloroethane' for the first component in 'Solvent'`
`Press 'Run'`
`Do the same for the solvent '1-Propanol', 'Oxolane' (THF), 'Acetonitrile', '2-Butanone', 'Ethanol', 'Methanol', and 'Toluene'`

These results can be put in a table.

	Solvent	**experimental Solubility Vanillin (mol/L) [441]**	**calculated Solubility Vanillin (mol/L solution)**
1	1,2-Dichloroethane	1.175	2.65
2	1-Propanol	1.820	3.12
3	Oxolane	3.594	4.73
4	Acetonitrile	2.360	3.30
5	2-Butanone	2.138	4.10
6	Ethanol	2.470	3.56
7	Methanol	4.160	4.04
8	Toluene	0.302	0.99
9	Water	0.070	0.034

Compared to experiment there can easily be a factor of 2 deviation.

References

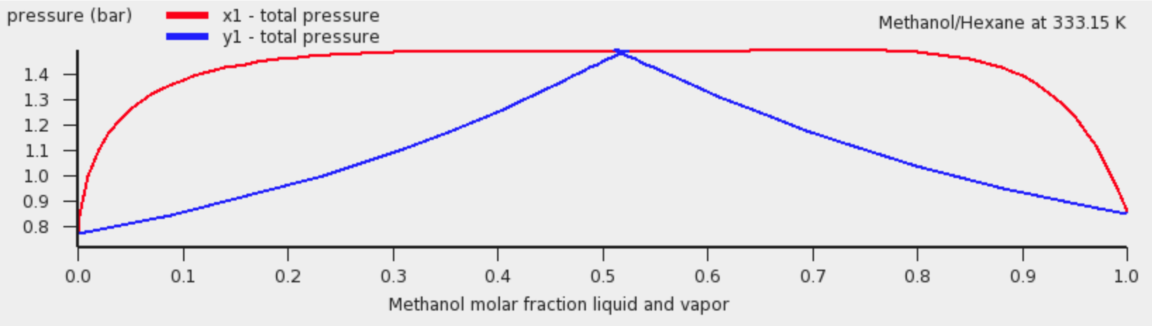
[441] Experimentally determined solubilities of Vanillin in some organic solvents were taken at July 15, 2010, from http://old.oru.edu/cccda/sl/solubility/allsolvents.php?solute=vanillin.

4.5: Binary mixture of Methanol and Hexane

In this example a vapor-liquid diagram of Methanol and Hexane is calculated and compared to experiment.

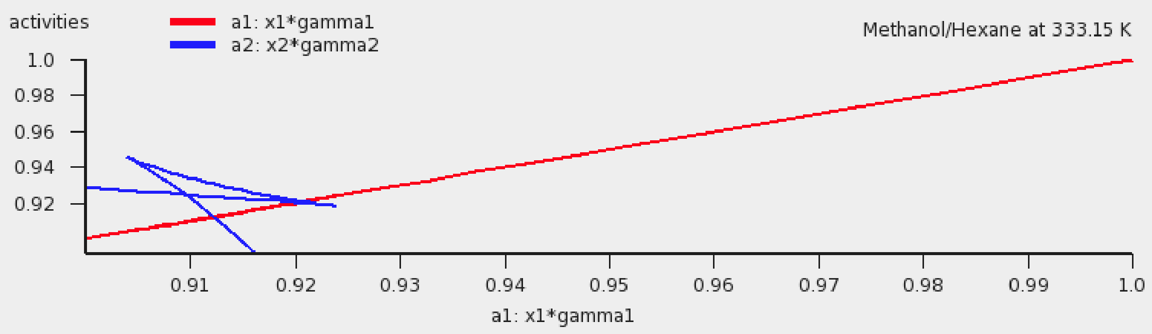
First a binary mixture of Methanol and Hexane is calculated at a constant temperature of 333.15 Kelvin. Next this binary mixture is calculated at a constant pressure of of 1.01325 bar. Experimental pure compound properties are used.

`Select` **Compounds → Compounds**
`Click on the left side 'Methanol'`
`Enter '0.845' in the 'Pure compound vapor pressure:' field`
`Enter '333.15' in the 'at temperature:' field`
`Click on the left side 'Hexane'`
`Enter '0.77' in the 'Pure compound vapor pressure:' field`
`Enter '333.15' in the 'at temperature:' field`
`Select` **Properties → Binary Mixture VLE/LLE**
`Select 'Methanol' for the first compound`
`Select 'Hexane' for the second compound`
`Enter '100' in the 'Number of mixtures' field`
`Select` **Isotherm, isobar, flash point → isotherm**
`Enter '333.15' for the 'Temperature' in 'Kelvin'`
`Press 'Run'`
`Select` **View → Graph X Axes → x1, y1**
`Select` **View → Graph Y Axes → total vapor pressure**



In case of a miscibility gap there are two molar fractions x1 and x1', for which both compounds have the same activities. In the calculation one can plot the activity a1 versus a2. If there is a closed loop, there is a miscibility gap:

`Select` **View → Graph X Axes → a1: x1*gamma**
`Select` **View → Graph Y Axes → activities**

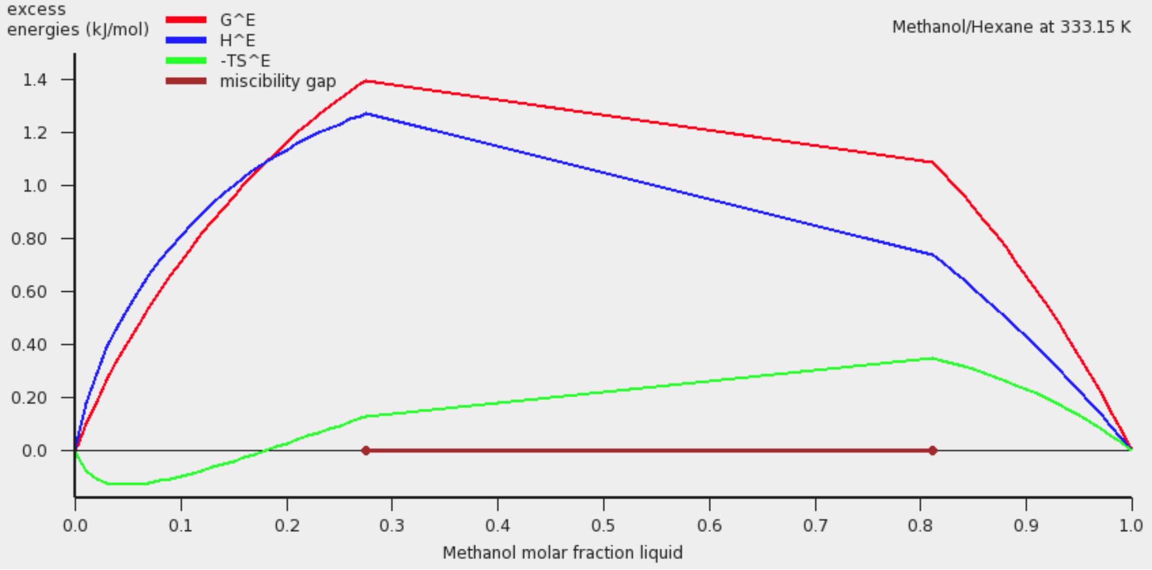


Thus there is a calculated miscibility gap. The properties of the two immiscible liquid phases are given in the table: the calculated miscibility gap is between approximately x1 = 0.275 and x1' = 0.811, with a calculated total vapor pressure of approximately 1.48 bar. Within the miscibility gap, the liquid mixture consists of 2 immiscible liquid phases, one is Methanol-rich, the other Hexane-rich. Note, however, that within the miscibility gap the COSMO-RS calculation further incorrectly uses a forced 1 liquid-phase instead of 2 immiscible liquid phases. Also note that a pressure-maximum azeotrope is in the miscibility gap.

If the check box 'force 1 liquid phase within possible miscibility gap' is selected, then results will be shown also within the miscibility gap, with the unphysical conditions that the two liquids are forced to mix. If the check box 'force 1 liquid phase within possible miscibility gap' is deselected, then results will be shown in the graph and table only for those compositions of the mixture, which are outside of the miscibility gap.

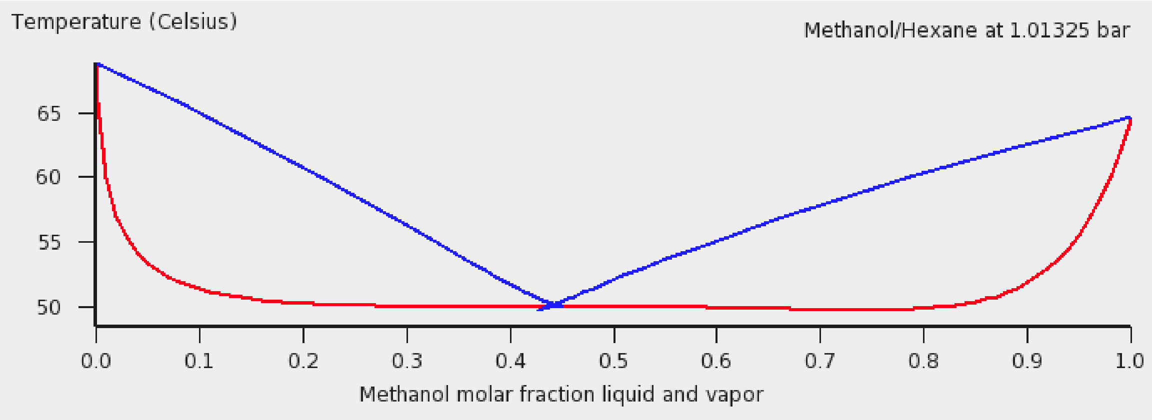

☐ force 1 liquid phase within possible miscibility gap

`Deselect the check box 'force 1 liquid phase within possible miscibility gap'`
`Select` **View → Graph X Axes → x1: molar fraction 1**
`Select` **View → Graph Y Axes → excess energies**

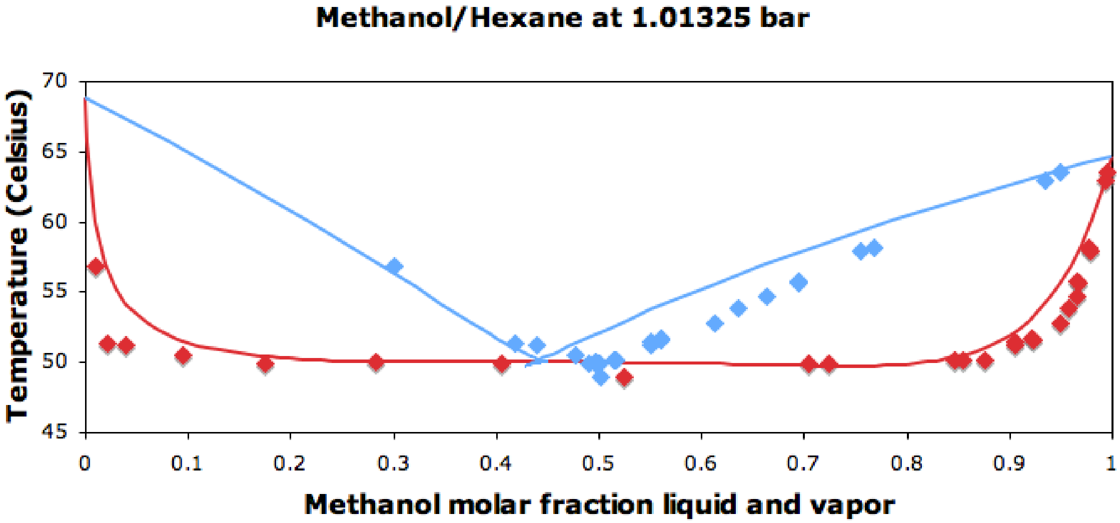


Select **Compounds → Compounds**
Click on the left side 'Methanol'
Enter '1.01325' in the 'Pure compound vapor pressure:' field
Enter '337.8' in the 'at temperature:' field
Click on the left side 'Hexane'
Enter '1.01325' in the 'Pure compound vapor pressure:' field
Enter '342' in the 'at temperature:' field
Select **Properties → Binary Mixture VLE/LLE**
Select 'Methanol' for the first compound
Select 'Hexane' for the second compound
Enter '100' in the 'Number of mixtures' field
Select **Isotherm, isobar, flash point → isobar**
Enter '1.01325' for the 'Pressure' in 'bar'
Press 'Run'
Select **View → Graph X Axes → x1, y1**
Select **View → Graph Y Axes → temperature**
Select the check box 'force 1 liquid phase within possible miscibility gap'

There is a calculated miscibility gap between approximately x1 = 0.221 and x1' = 0.835, with a calculated temperature of approximately 323.3 Kelvin (50.1 °C). Within the miscibility gap, the liquid mixture consists of 2 immiscible liquid phases, one is Methanol-rich, the other Hexane-rich. Note that if the check box 'force 1 liquid phase within possible miscibility gap' is selected, within the miscibility gap the COSMO-RS calculation further incorrectly uses a forced 1 liquid-phase instead of 2 immiscible liquid phases. Also note that a temperature-minimum azeotrope is in the miscibility gap.



Experimental results for the Methanol-Hexane mixture were taken from Ref. [451]. These are compared with the calculated ones in the next graph. More experimental VLE data might also be found at Ref. [452].



References

[451] Wikipedia Hexane data page: http://en.wikipedia.org/wiki/Hexane_(data_page)

[452] CHERIC. Korea Thermophysical Properties Data Bank: Binary Vapor-Liquid Equilibrium Data

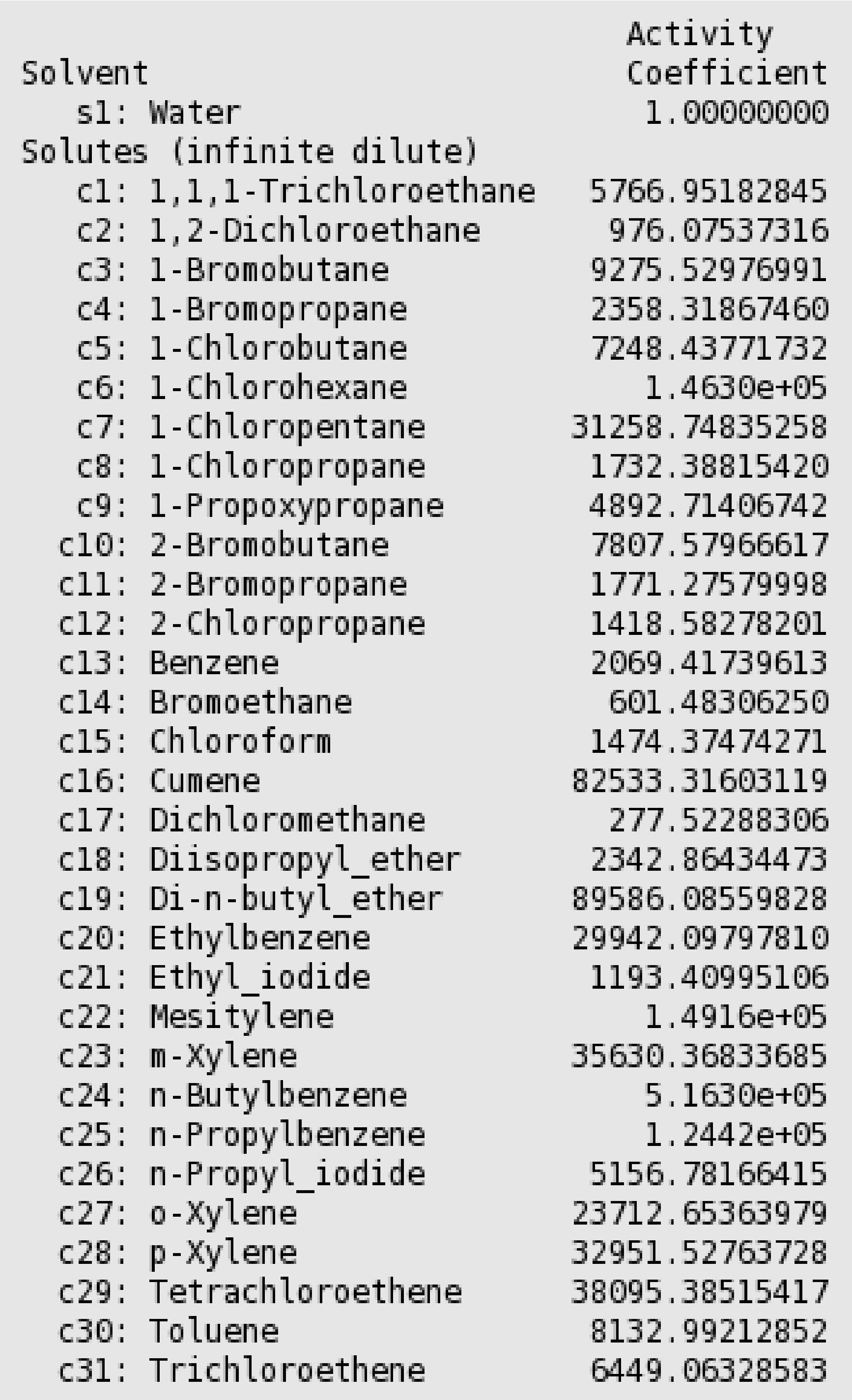
4.6: Large infinite dilution activity coefficients in Water

In this example infinite dilution activity coefficients of 31 organic compounds in Water are calculated and compared to experiment.

Remark: To only add the compounds needed in this example, one can also open a new COSMO-RS GUI window (**SCM** → **COSMO-RS**), copy the $ADFHOME/examples/crs/Tutorial4/tutorial4.6.compoundlist to the directory where the COSMO-RS database is downloaded, and select this file with **Compounds** → **Add Compound(s)**. The tutorial4.6.compoundlist is a file with a list of compounds that is limited to the coumpounds needed in this example.

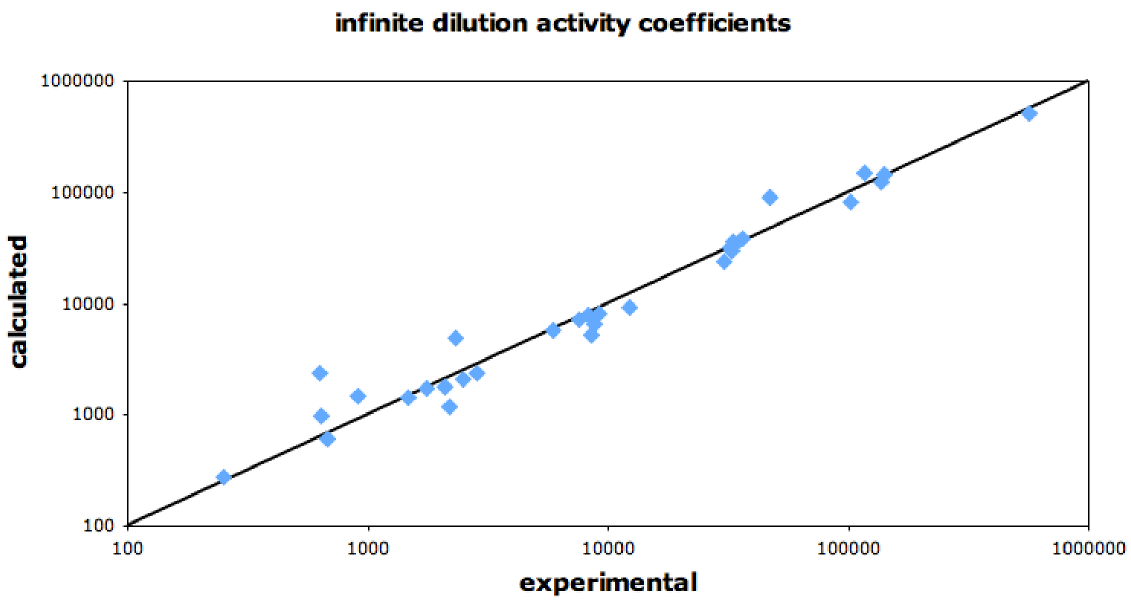
`Select` **Properties → Activity coefficients**
`Select 'Water' for the first component in Solvent`

```
Click the 'None' button next to 'Compounds'
Click the search button below 'Solutes (infinite dilute)' to add some
compounds:
'1,1,1-Trichloroethane', '1,2-Dichloroethane', '1-Bromobutane',
'1-Bromopropane',
'1-Chlorobutane', '1-Chlorohexane', '1-Chloropentane', '1-Chloropropane',
'1-Propoxypropane', '2-Bromobutane', '2-Bromopropane', '2-Chloropropane',
'Benzene', 'Bromoethane', 'Chloroform', 'Cumene', 'Dichloromethane',
'Diisopropyl_ether', 'Di-n-butyl_ether', 'Ethylbenzene', 'Ethyl_iodide',
'Mesitylene', 'm-Xylene', 'n-Butylbenzene', 'n-Propylbenzene',
'n-Propyl_iodide',
'o-Xylene', 'p-Xylene', 'Tetrachloroethene', 'Toluene', and 'Trichloroethene',
Press 'Run'
```



```
                                  Activity
Solvent                           Coefficient
   s1: Water                       1.00000000
Solutes (infinite dilute)
   c1: 1,1,1-Trichloroethane    5766.95182845
   c2: 1,2-Dichloroethane        976.07537316
   c3: 1-Bromobutane            9275.52976991
   c4: 1-Bromopropane           2358.31867460
   c5: 1-Chlorobutane           7248.43771732
   c6: 1-Chlorohexane              1.4630e+05
   c7: 1-Chloropentane         31258.74835258
   c8: 1-Chloropropane          1732.38815420
   c9: 1-Propoxypropane         4892.71406742
  c10: 2-Bromobutane            7807.57966617
  c11: 2-Bromopropane           1771.27579998
  c12: 2-Chloropropane          1418.58278201
  c13: Benzene                  2069.41739613
  c14: Bromoethane               601.48306250
  c15: Chloroform               1474.37474271
  c16: Cumene                  82533.31603119
  c17: Dichloromethane           277.52288306
  c18: Diisopropyl_ether        2342.86434473
  c19: Di-n-butyl_ether        89586.08559828
  c20: Ethylbenzene            29942.09797810
  c21: Ethyl_iodide             1193.40995106
  c22: Mesitylene                  1.4916e+05
  c23: m-Xylene                35630.36833685
  c24: n-Butylbenzene              5.1630e+05
  c25: n-Propylbenzene             1.2442e+05
  c26: n-Propyl_iodide          5156.78166415
  c27: o-Xylene                23712.65363979
  c28: p-Xylene                32951.52763728
  c29: Tetrachloroethene       38095.38515417
  c30: Toluene                  8132.99212852
  c31: Trichloroethene          6449.06328583
```

These results can be put in a graph and a table. Experimental results taken from Ref. [461].



	Solute	experimental γ_2^∞ [461]	calculated γ_2^∞
1	Dichloromethane	253	278
2	Diisopropyl_ether	628	2343
3	1,2-Dichloroethane	641	976
4	Bromoethane	679	601
5	Chloroform	903	1474
6	2-Chloropropane	$1.48\ 10^{3}$	$1.42\ 10^{3}$
7	1-Chloropropane	$1.75\ 10^{3}$	$1.73\ 10^{3}$
8	2-Bromopropane	$2.09\ 10^{3}$	$1.77\ 10^{3}$
9	Ethyl_iodide	$2.19\ 10^{3}$	$1.19\ 10^{3}$
10	1-Propoxypropane	$2.31\ 10^{3}$	$4.89\ 10^{3}$
11	Benzene	$2.48\ 10^{3}$	$2.07\ 10^{3}$
12	1-Bromopropane	$2.86\ 10^{3}$	$2.36\ 10^{3}$
13	1,1,1-Trichloroethane	$5.90\ 10^{3}$	$5.77\ 10^{3}$
14	1-Chlorobutane	$7.61\ 10^{3}$	$7.25\ 10^{3}$
15	2-Bromobutane	$8.32\ 10^{3}$	$7.81\ 10^{3}$
16	n-Propyl_iodide	$8.55\ 10^{3}$	$5.16\ 10^{3}$
17	Trichloroethene	$8.75\ 10^{3}$	$6.45\ 10^{3}$
18	Toluene	$9.19\ 10^{3}$	$8.14\ 10^{3}$
19	1-Bromobutane	$1.22\ 10^{4}$	$0.93\ 10^{4}$
20	o-Xylene	$3.05\ 10^{4}$	$2.37\ 10^{4}$
21	1-Chloropentane	$3.21\ 10^{4}$	$3.13\ 10^{4}$
22	Ethylbenzene	$3.27\ 10^{4}$	$3.00\ 10^{4}$
23	m-Xylene	$3.32\ 10^{4}$	$3.56\ 10^{4}$
24	p-Xylene	$3.33\ 10^{4}$	$3.30\ 10^{4}$
25	Tetrachloroethene	$3.60\ 10^{4}$	$3.81\ 10^{4}$
26	Di-n-butyl_ether	$4.72\ 10^{4}$	$8.95\ 10^{4}$
27	Cumene	$1.02\ 10^{5}$	$0.83\ 10^{5}$
28	Mesitylene	$1.17\ 10^{5}$	$1.49\ 10^{5}$

29	n-Propylbenzene	1.36 10^5	1.24 10^5
30	1-Chlorohexane	1.41 10^5	1.46 10^5
31	n-Butylbenzene	5.66 10^5	5.16 10^5

References

[461] J. Li, A.J. Dallas, D.I. Eikens, P.W. Carr, D.L. Bergmann, M.J. Hait, C.A. Eckert, *Measurement of large infinite dilution activity coefficients of nonelectrolytes in water by inert gas stripping and gas chromatography*, Analytical Chemistry **65** (1993), 3212

4.7: Parametrization of ADF COSMO-RS: ΔG_{hydr}, vapor pressures, partition coefficients

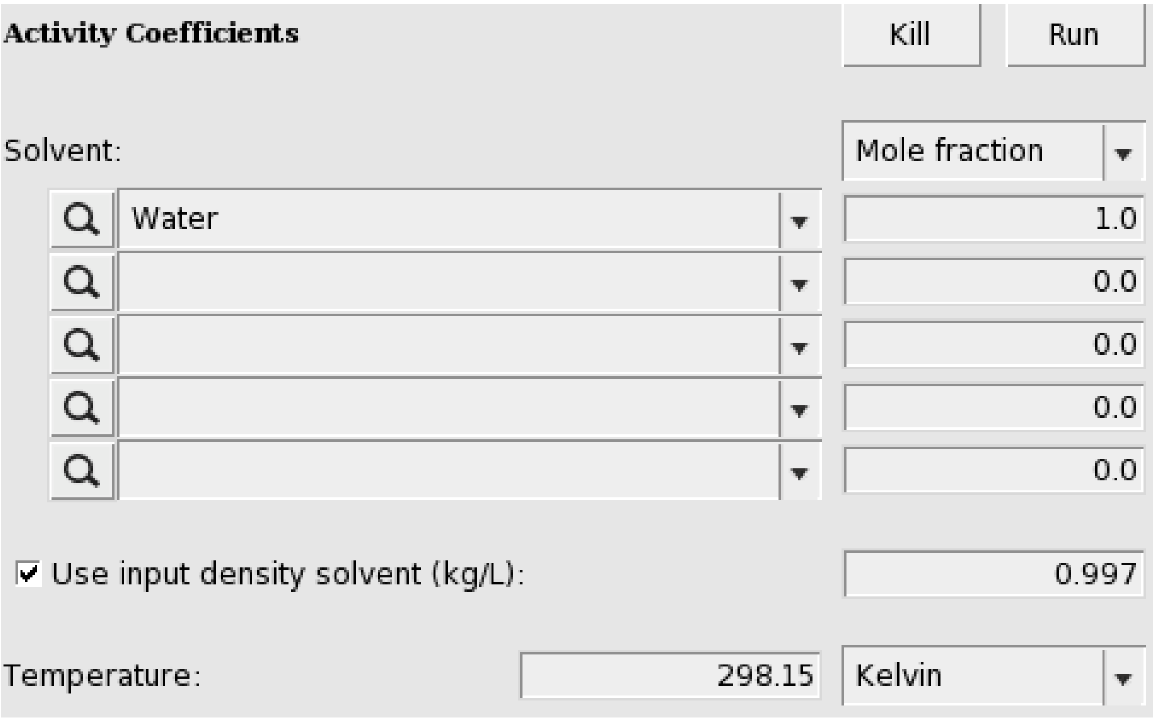
In Ref. [471] the ADF COSMO-RS parameters were fitted to 642 experimental values of properties for the set of 217 molecules from the supplementary material of Klamt et al. [472]. These properties are the ΔG of hydration, the vapor pressure, and the partition coefficients for Octanol/Water, Hexane/Water, Benzene/Water, and Ethoxyethane/Water. In this example all these properties will be calculated for the set of 217 compounds, and the results will be put in this table, and compared to the experimental data collected by Klamt. et al. in Ref. [471].

Open a new COSMO-RS GUI window (**SCM** → **COSMO-RS**). Copy the $ADFHOME/examples/crs/Tutorial4/tutorial4.7.compoundlist to the directory where the COSMO-RS database is downloaded. The tutorial4.7.compoundlist is a file with a list of compounds that is limited to the coumpounds needed in this example.

ΔG of hydration

`Select` **Properties → Activity coefficients**

```
Select 'Water' for the first component in Solvent
Enter '298.15' for 'Temperature Kelvin'
Click the check box 'Use input density solvent (kg/L)'
Enter '0.997' in the 'Use input density solvent (kg/L)' field
Click the 'All' button next to 'Compounds'
Press 'Run'
```



Activity Coefficients

Solvent: Mole fraction

Water 1.0

0.0

0.0

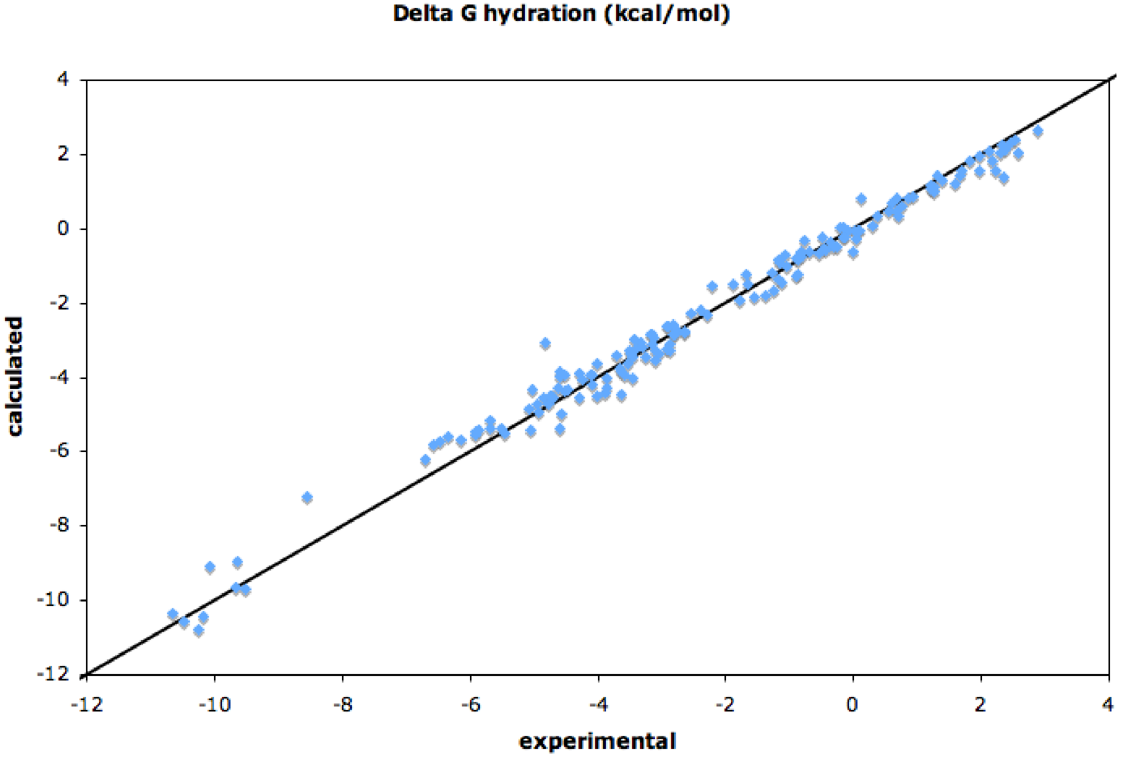
0.0

0.0

☑ Use input density solvent (kg/L): 0.997

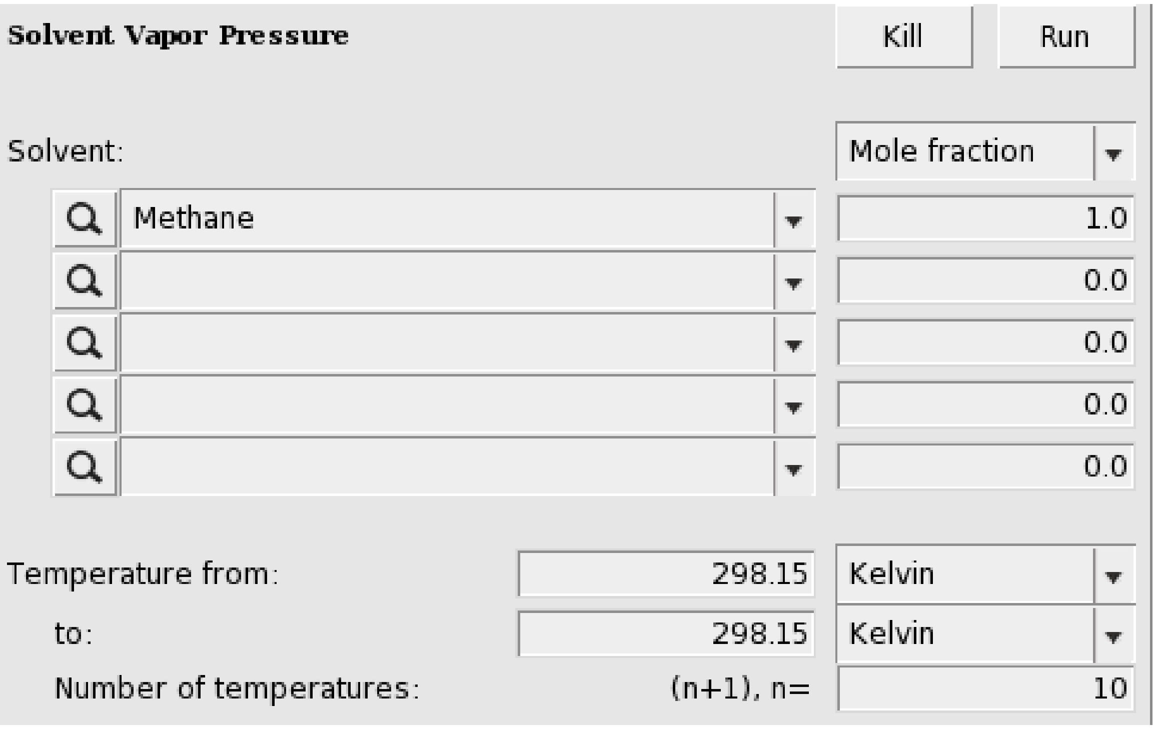
Temperature: 298.15 Kelvin

The results for the free energy of hydration (Δ G (kcal/mol) gas → solute) can be compared with experimental values, see this table and next graph.



Vapor pressure

`Select` **Properties → Solvent Vapor Pressure**
`Select 'Methane' for the first component in the Solvent`
`Enter '298.15' for 'Temperature Kelvin'`
`Press 'Run'`



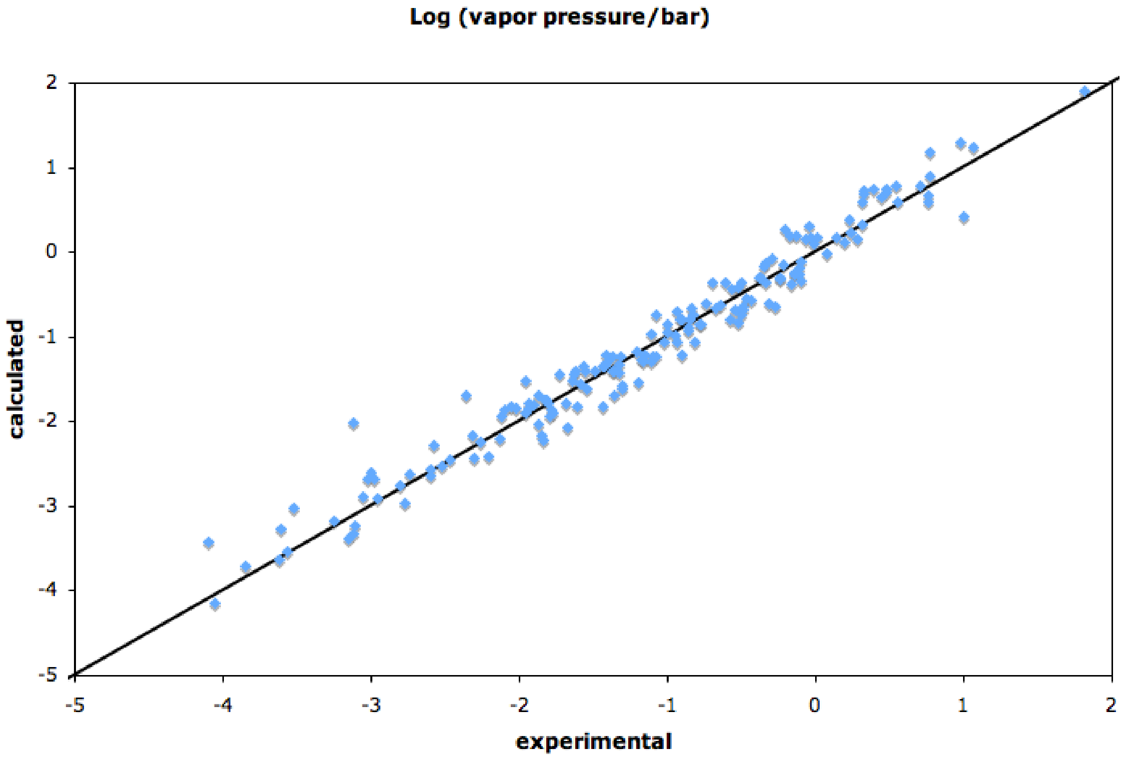
Solvent Vapor Pressure

Solvent: Mole fraction

Methane	1.0
	0.0
	0.0
	0.0
	0.0

Temperature from: 298.15 Kelvin
to: 298.15 Kelvin
Number of temperatures: (n+1), n= 10

One could do this for each of the 217 compounds, and take the $\log_{10}$ of the calculated vapor pressure in bar. The results for the calculated vapor pressures can be compared with experimental values, see this table and next graph. Suggestion is to do this only for a few molecules.



Octanol-Water partition coefficients

Select **Properties → Log Partition Coefficients**

Select '1-Octanol' for the first component in the solvent

Select 'Water' for the second component in the solvent

Enter '0.725' for the Mole fraction of 1-Octanol in phase 1

Enter '0.275' for the Mole fraction of Water in phase 1

Enter '1.0' for the Mole fraction of Water in phase 2

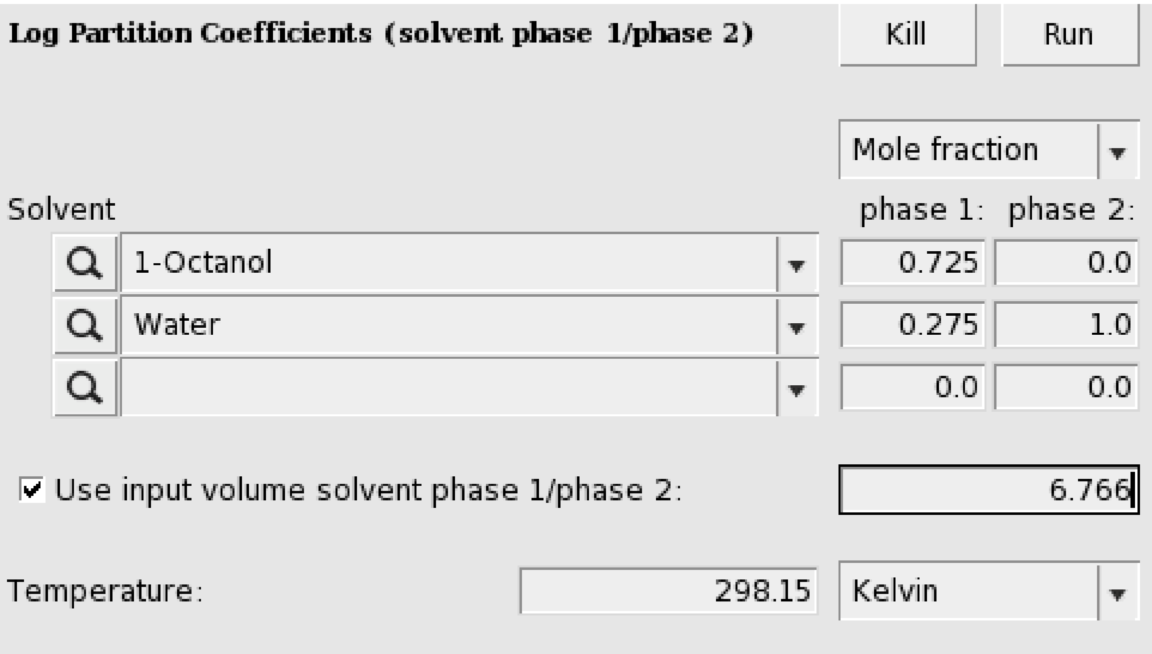
Click the check box 'Use input volume solvent phase 1/phase 2'

Enter '6.766' in the 'Use input volume solvent phase 1/phase 2' field

Enter '298.15' for the 'Temperature' in 'Kelvin'

Click the 'All' button next to 'Solutes'

Press 'Run'



Log Partition Coefficients (solvent phase 1/phase 2)

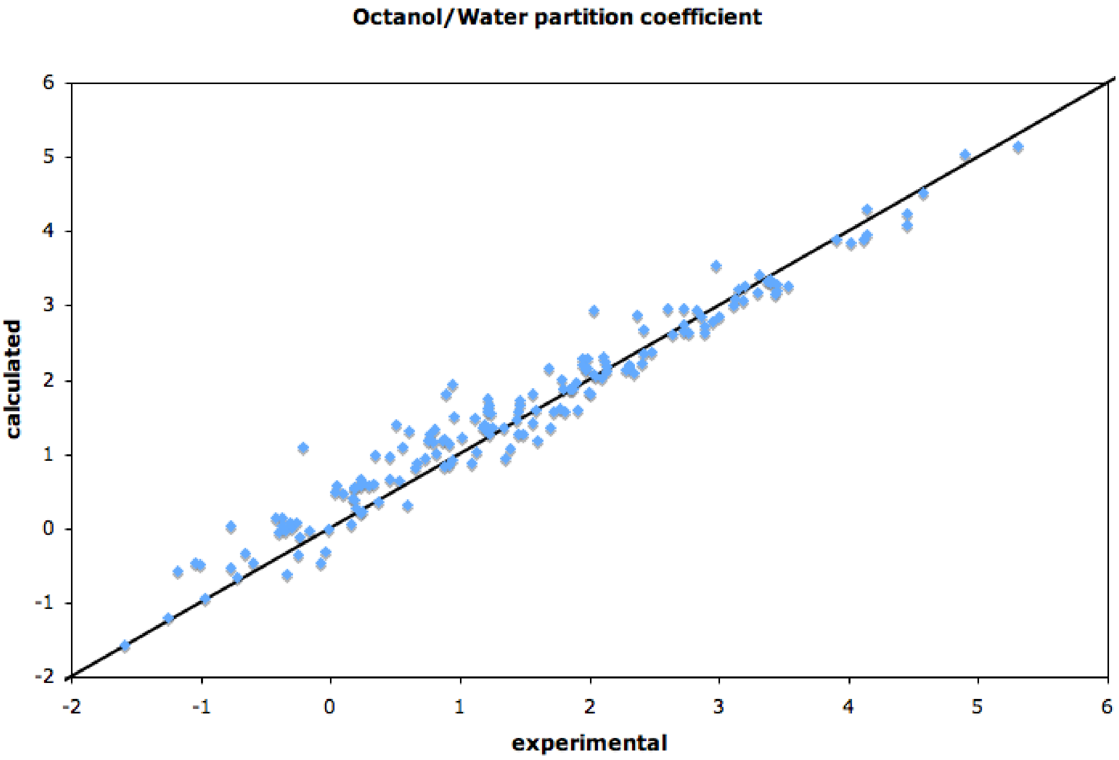
Mole fraction

Solvent	phase 1:	phase 2:
1-Octanol	0.725	0.0
Water	0.275	1.0
	0.0	0.0

☑ Use input volume solvent phase 1/phase 2: 6.766

Temperature: 298.15 Kelvin

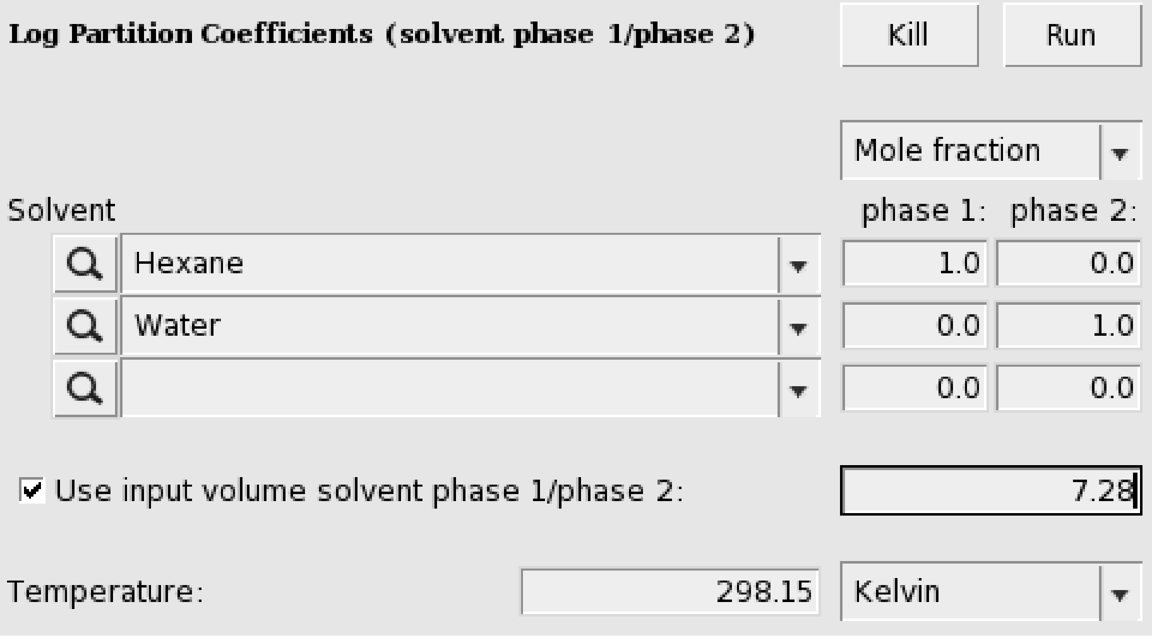
The results for the Octanol-Water partition coefficients can be compared with experimental values, see this table and next graph.



Hexane-Water, Benzene-Water, and Ethoxyethane-Water partition coefficients

`Select` **Properties → Solvent Log Partition Coefficients**
`Select 'Hexane' for the first component in the solvent`

Select 'Water' for the second component in the solvent
Enter '1.0' for the Mole fraction of Hexane in phase 1
Enter '0.0' for the Mole fraction of Water in phase 1
Enter '1.0' for the Mole fraction of Water in phase 2
Click the check box 'Use input volume solvent phase 1/phase 2'
Enter '7.28' in the 'Use input volume solvent phase 1/phase 2' field
Enter '298.15' for the 'Temperature' in 'Kelvin'
Click the 'All' button next to 'Solutes'
Press 'Run'



Log Partition Coefficients (solvent phase 1/phase 2)

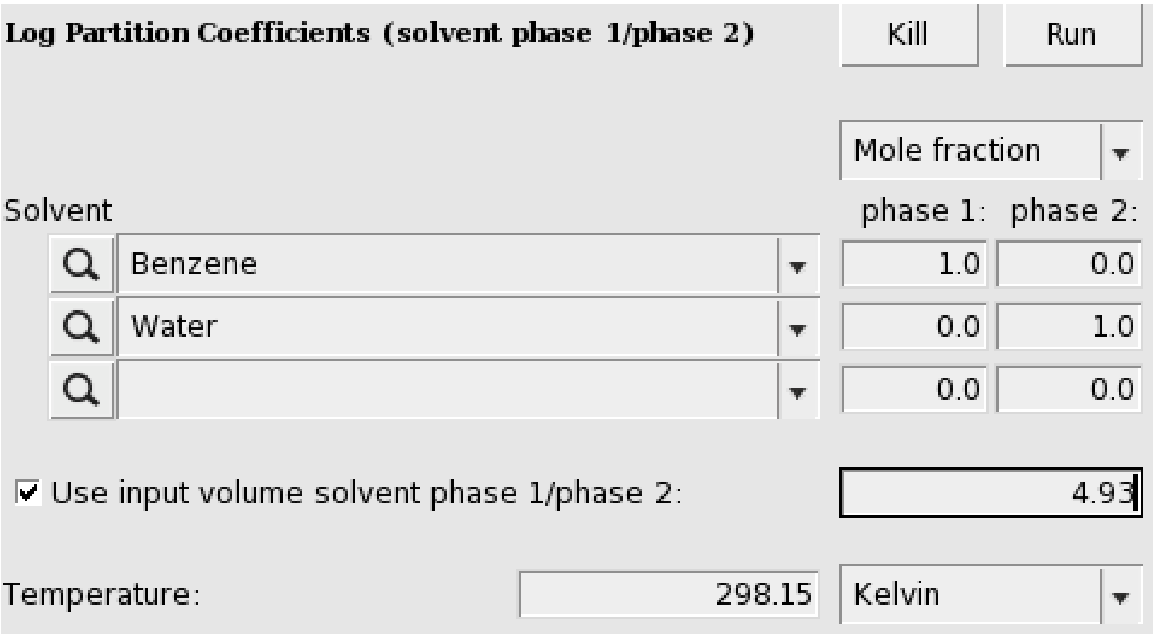
Mole fraction

Solvent	phase 1:	phase 2:
Hexane	1.0	0.0
Water	0.0	1.0
	0.0	0.0

☑ Use input volume solvent phase 1/phase 2: 7.28

Temperature: 298.15 Kelvin

Select **Properties → Solvent Log Partition Coefficients**
Select 'Benzene' for the first component in the solvent
Select 'Water' for the second component in the solvent
Enter '1.0' for the Mole fraction of Benzene in phase 1
Enter '1.0' for the Mole fraction of Water in phase 2
Click the check box 'Use input volume solvent phase 1/phase 2'
Enter '4.93' in the 'Use input volume solvent phase 1/phase 2' field
Enter '298.15' for the 'Temperature' in 'Kelvin'
Click the 'All' button next to 'Solutes'
Press 'Run'



Log Partition Coefficients (solvent phase 1/phase 2)

Mole fraction

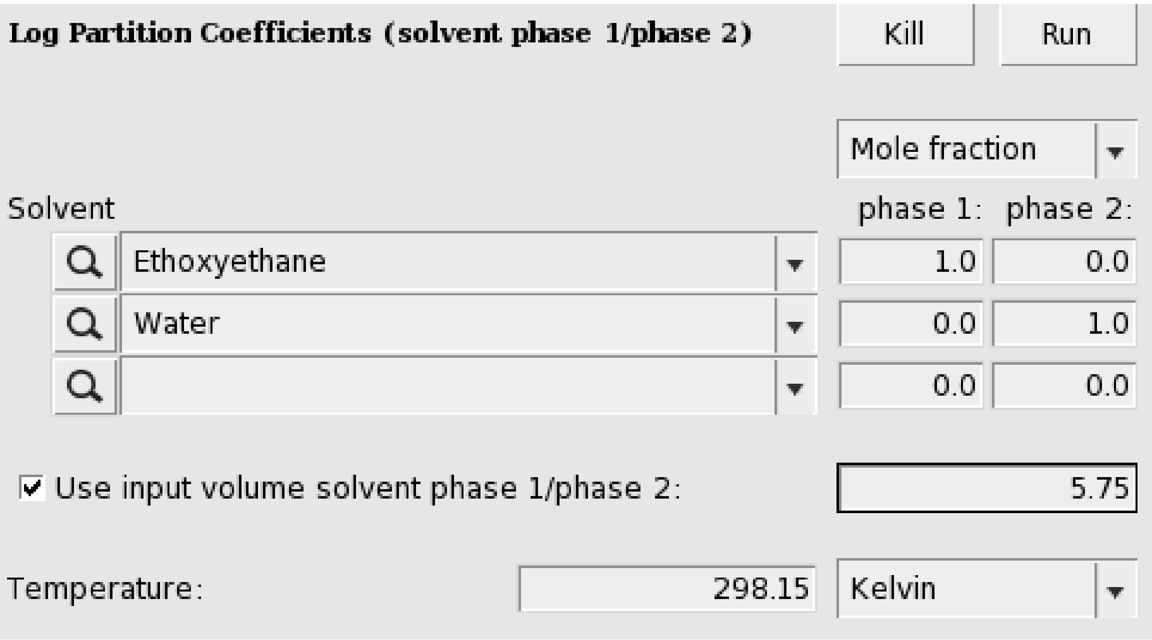
Solvent	phase 1:	phase 2:
Benzene	1.0	0.0
Water	0.0	1.0
	0.0	0.0

☑ Use input volume solvent phase 1/phase 2: 4.93

Temperature: 298.15 Kelvin

`Select` **Properties → Solvent Log Partition Coefficients**

```
Select 'Ethoxyethane' for the first component in the solvent
Select 'Water' for the second component in the solvent
Enter '1.0' for the Mole fraction of Ethoxyethane in phase 1
Enter '1.0' for the Mole fraction of Water in phase 2
Click the check box 'Use input volume solvent phase 1/phase 2'
Enter '5.75' in the 'Use input volume solvent phase 1/phase 2' field
Enter '298.15' for the 'Temperature' in 'Kelvin'
Click the 'All' button next to 'Solutes'
Press 'Run'
```



Log Partition Coefficients (solvent phase 1/phase 2)

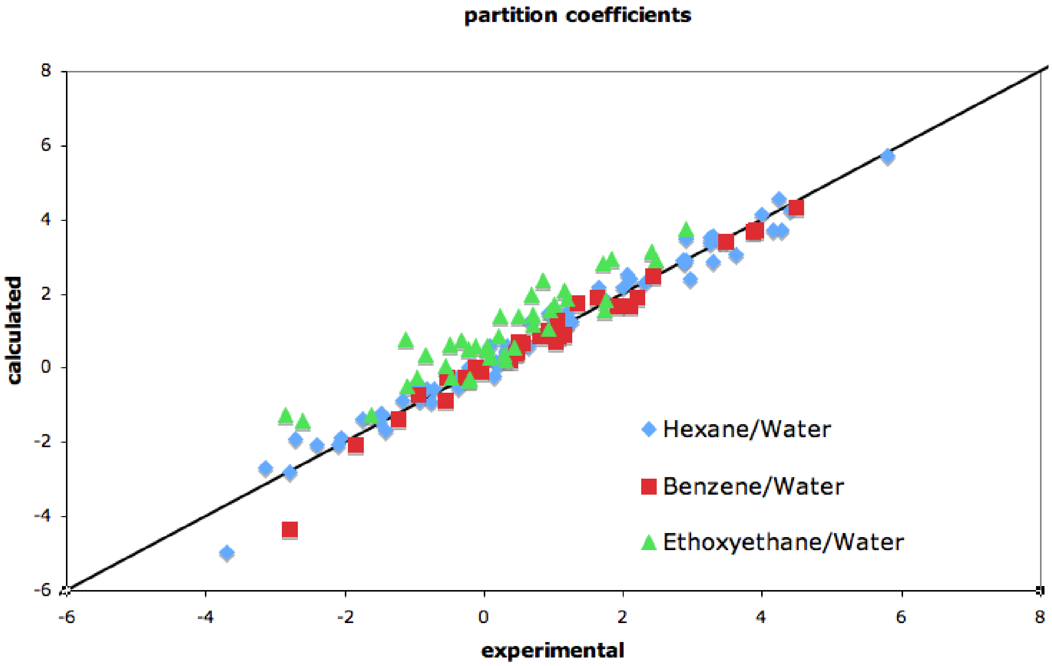
Mole fraction

Solvent	phase 1:	phase 2:
Ethoxyethane	1.0	0.0
Water	0.0	1.0
	0.0	0.0

☑ Use input volume solvent phase 1/phase 2: 5.75

Temperature: 298.15 Kelvin

The results for the Hexane-Water, Benzene-Water, and Ethoxyethane-Water partition coefficients can be compared with experimental values, see this table and next graph.



References

[471] C.C. Pye, T. Ziegler, E. van Lenthe, J.N. Louwen, *An implementation of the conductor-like screening model of solvation within the Amsterdam density functional package. Part II. COSMO for real solvents.* Canadian Journal of Chemistry **87**, 790 (2009)

[472] A. Klamt, V. Jonas, T. Bürger and J.C. Lohrenz, *Refinement and Parametrization of COSMO-RS.* Journal of Physical Chemistry A **102**, 5074 (1998)

Tutorial 5: pK_a values

In the literature one can find several strategies to calculate pK_a values. Some of these strategies involve the inclusion of explicit solvent molecules, in combination with a continuuum model, like COSMO. The strategies described in the next examples do not take into account explicit solvent molecules, only the continuum model is included.

5.1: Empirical pK_a calculation method

In Refs. [511,512] one can find several strategies to calculate pK_a values. The strategy described in this example does not take into account explicit solvent molecules, only the continuum model is included. Like in Ref. [512] an empirical fit is used to correlate calculated values with experimental pK_a values, to account for systematic errors. The largest errors are probably present in the calculation of the solvation energies of the charged species. In these cases one probably should include explicit solvent molecules, however, that may introduce other sources of errors, and this will not be investigated here. The calculation of pK_a values of acids (HA) and bases (B) is based on the following reaction model:

(acids) HA (aq, 1M) + H_2O (l, 1M) → H_3O^+ (aq, 1M) + A^- (aq, 1M) (5.1.1)

(bases) HB^+ (aq, 1M) + H_2O (l, 1M) → H_3O^+ (aq, 1M) + B (aq, 1M) (5.1.2)

The free energy of dissociation for acids and bases is calculated as

$$\text{(acids) } \Delta G^*_{diss} = G(A^-) - G(HA) + G(H_3O^+) - G(H_2O) \qquad (5.1.3)$$

$$\text{(bases) } \Delta G^*_{diss} = G(B) - G(HB^+) + G(H_3O^+) - G(H_2O) \qquad (5.1.4)$$

The * denotes a standard state of 1M (1 mol/L). The pK_a can then be calculated as (see for example Refs. [511,512])

$$pK_a = \Delta G^*_{diss}/(RT \ln(10)) - 1.74 \qquad (5.1.5)$$

At T = 298.15, 1/(RT ln(10)) = 0.733 mol/kcal. The term -1.74 is to correct for the standard state of liquid water, which is 55 mol/L.

Emperical fit

Like in Ref. [512] instead of this equation (5.1.5), a linear fit has been made by correlating the calculated ΔG^*_{diss} values with experimental pK_a values, to account for systematic errors that are present in this method. For acids and bases a different empirical adjusted equation will be used, optimized for the ADF COSMO-RS implementation:

$$\text{(acids) } pK_a = 0.62\ \Delta G^*_{diss}/(RT \ln(10)) + 2.10 \qquad (5.1.6)$$

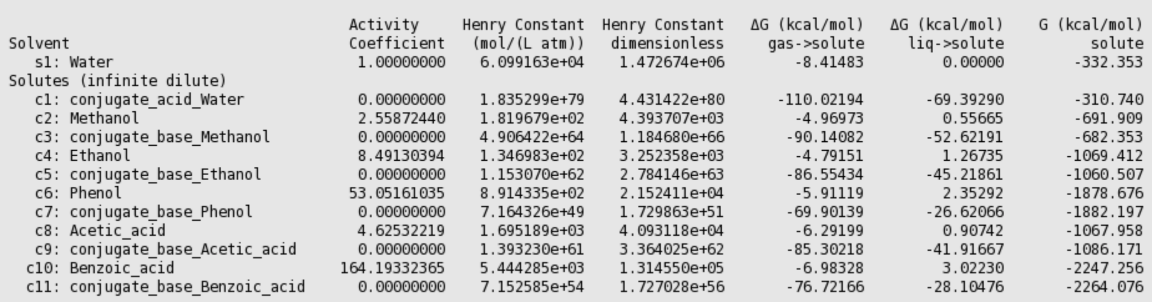
$$\text{(bases) } pK_a = 0.67\ \Delta G^*_{diss}/(RT \ln(10)) - 2.00 \qquad (5.1.7)$$

These fitted parameters are not so far from the fitted parameters in Ref. [512]. Zero-point vibrational energies have not been taken into account in the calculation of the free energy of dissociation. H_3O^+ (Hydronium ion) is the conjugate acid of Water. Molecules can have two or more equivalent sites for protonation or deprotonation are also not taken into account, which can have an effect on the pK_a value. However, such effects are not taken into account here. Like for neutral compounds, one should optimize the anions and cations in the gas phase, and use this geometry also in the COSMO calculation. It is important to choose the lowest energy conformer. In the example below the molecules have a single relevant conformation for the protonated and deprotonated form.

Acids

Copy the .coskf files which are listed in $ADFHOME/examples/crs/Tutorial5/tutorial5.1_acid.compoundlist and the file tutorial5.1_acid.compoundlist the directory Tutorial. The tutorial5.1_acid.compoundlist is a file with a list of acids and their conjugate bases that is limited to the coumpounds needed in this example. In these .coskf files already the correct number of ring atoms is included.

```
Open a new COSMO-RS GUI window
Add the compounds listed in tutorial5.1_acid.compoundlist
Select Properties → Activity coefficients
Select 'Water' for the first component in Solvent
Enter '298.15' for 'Temperature Kelvin'
Click the 'All' button next to 'Compounds'
Press 'Run'
```



```
                                 Activity    Henry Constant  Henry Constant   ΔG (kcal/mol)   ΔG (kcal/mol)    G (kcal/mol)
Solvent                          Coefficient  (mol/(L atm))   dimensionless     gas->solute     liq->solute          solute
   s1: Water                      1.00000000   6.099163e+04    1.472674e+06        -8.41483         0.00000        -332.353
Solutes (infinite dilute)
   c1: conjugate_acid_Water       0.00000000   1.835299e+79    4.431422e+80      -110.02194       -69.39290        -310.740
   c2: Methanol                   2.55872440   1.819679e+02    4.393707e+03        -4.96973         0.55665        -691.909
   c3: conjugate_base_Methanol    0.00000000   4.906422e+64    1.184680e+66       -90.14082       -52.62191        -682.353
   c4: Ethanol                    8.49130394   1.346983e+02    3.252358e+03        -4.79151         1.26735       -1069.412
   c5: conjugate_base_Ethanol     0.00000000   1.153070e+62    2.784146e+63       -86.55434       -45.21861       -1060.507
   c6: Phenol                    53.05161035   8.914335e+02    2.152411e+04        -5.91119         2.35292       -1878.676
   c7: conjugate_base_Phenol      0.00000000   7.164326e+49    1.729863e+51       -69.90139       -26.62066       -1882.197
   c8: Acetic_acid                4.62532219   1.695189e+03    4.093118e+04        -6.29199         0.90742       -1067.958
   c9: conjugate_base_Acetic_acid 0.00000000   1.393230e+61    3.364025e+62       -85.30218       -41.91667       -1086.171
  c10: Benzoic_acid             164.19332365   5.444285e+03    1.314550e+05        -6.98328         3.02230       -2247.256
  c11: conjugate_base_Benzoic_acid 0.00000000  7.152585e+54    1.727028e+56       -76.72166       -28.10476       -2264.076
```

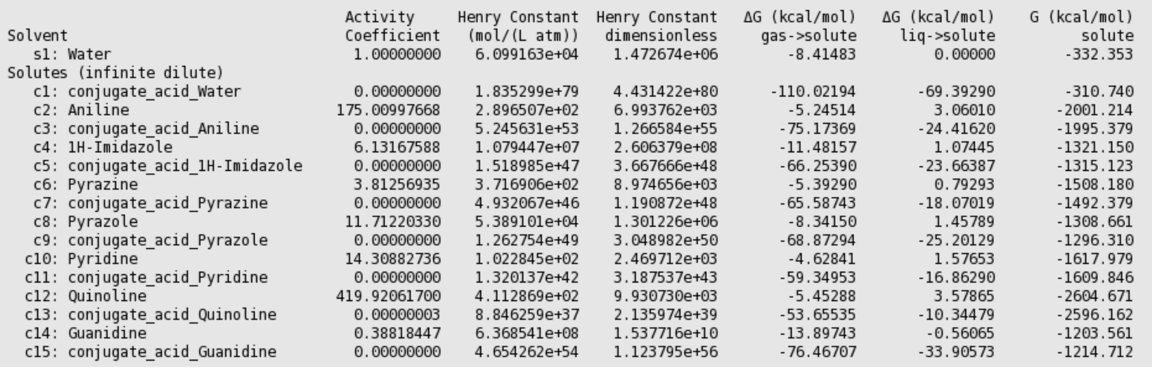
Using equation 5.1.6 (pK_a = 0.62*0.733*ΔG_{diss}+2.10), with ΔG_{diss} = G(conjugate_base_acid) - G(acid) + G(conjugate_acid_Water) - G(Water) in kcal/mol, results can be put in a table.

	Acid	**experimental pK_a [512]**	**calculated pK_a**
1	Methanol	15.5	16.27
2	Ethanol	15.9	15.97
3	Phenol	9.82	10.32
4	Acetic acid	4.75	3.64
5	Benzoic acid	4.27	4.28

Bases

Copy the .coskf files which are listed in $ADFHOME/examples/crs/Tutorial5/tutorial5.1_base.compoundlist and the file tutorial5.1_base.compoundlist the directory Tutorial. The tutorial5.1_base.compoundlist is a file with a list of bases and their conjugate acids that is limited to the coumpounds needed in this example. In these .coskf files already the correct number of ring atoms is included.

```
Open a new COSMO-RS GUI window
Add the compounds listed in tutorial5.1_base.compoundlist
Select Properties → Activity coefficients
Select 'Water' for the first component in Solvent
Enter '298.15' for 'Temperature Kelvin'
Click the 'All' button next to 'Compounds'
Press 'Run'
```



```
                                   Activity    Henry Constant  Henry Constant   ΔG (kcal/mol)   ΔG (kcal/mol)    G (kcal/mol)
Solvent                            Coefficient  (mol/(L atm))   dimensionless     gas->solute     liq->solute          solute
   s1: Water                        1.00000000   6.099163e+04    1.472674e+06        -8.41483         0.00000        -332.353
Solutes (infinite dilute)
   c1: conjugate_acid_Water         0.00000000   1.835299e+79    4.431422e+80      -110.02194       -69.39290        -310.740
   c2: Aniline                    175.00997668   2.896507e+02    6.993762e+03        -5.24514         3.06010       -2001.214
   c3: conjugate_acid_Aniline       0.00000000   5.245631e+53    1.266584e+55       -75.17369       -24.41620       -1995.379
   c4: 1H-Imidazole                 6.13167588   1.079447e+07    2.606379e+08       -11.48157         1.07445       -1321.150
   c5: conjugate_acid_1H-Imidazole  0.00000000   1.518985e+47    3.667666e+48       -66.25390       -23.66387       -1315.123
   c6: Pyrazine                     3.81256935   3.716906e+02    8.974656e+03        -5.39290         0.79293       -1508.180
   c7: conjugate_acid_Pyrazine      0.00000000   4.932067e+46    1.190872e+48       -65.58743       -18.07019       -1492.379
   c8: Pyrazole                    11.71220330   5.389101e+04    1.301226e+06        -8.34150         1.45789       -1308.661
   c9: conjugate_acid_Pyrazole      0.00000000   1.262754e+49    3.048982e+50       -68.87294       -25.20129       -1296.310
  c10: Pyridine                    14.30882736   1.022845e+02    2.469712e+03        -4.62841         1.57653       -1617.979
  c11: conjugate_acid_Pyridine      0.00000000   1.320137e+42    3.187537e+43       -59.34953       -16.86290       -1609.846
  c12: Quinoline                  419.92061700   4.112869e+02    9.930730e+03        -5.45288         3.57865       -2604.671
  c13: conjugate_acid_Quinoline     0.00000003   8.846259e+37    2.135974e+39       -53.65535       -10.34479       -2596.162
  c14: Guanidine                    0.38818447   6.368541e+08    1.537716e+10       -13.89743        -0.56065       -1203.561
  c15: conjugate_acid_Guanidine     0.00000000   4.654262e+54    1.123795e+56       -76.46707       -33.90573       -1214.712
```

Using equation 5.1.7 ((pK_a = 0.67*0.733*ΔG_{diss}-2.00), with ΔG_{diss} = G(base) - G(conjugate_acid_base) + G(conjugate_acid_Water) - G(Water) in kcal/mol, results can be put in a table.

	Base	**experimental pK_a [512]**	**calculated pK_a**
1	Aniline	4.6	5.75
2	1H-Imidazole	7	5.65
3	Pyrazine	0.7	0.85

4	Pyrazole	2.5	2.55
5	Pyridine	5.14	4.62
6	Quinoline	4.80	4.43
7	Guanidine	13.8	14.09

References

[511] J. Ho and M.L. Coote, *A universal approach for continuum solvent pK_a calculations: are we there yet?*, Theoretical Chemistry Accounts **125**, 3 (2010)

[512] F. Eckert, M. Diedenhofen, and A. Klamt, *Towards a first principles prediction of pK_a: COSMO-RS and the cluster-continuum approach*, Molecular Physics **108**, 229 (2010)

5.2: Relative pK_a calculation method

The method described in this example is based on one of the strategies in Ref. [521]. This method uses the experimental pK_a value of a reference compound, experimental gas phase deprotonation energies, and COSMO-RS solvation free energies. A suitable reference compound (HRef) should be chosen, which is similar to the actual compound (HA) one is interested in. For example, the deprotonation reaction could be similar in both compounds. The calculation of pK_a values is based on the following reaction model:

$$\begin{tikzcd}
\text{HA(aq, 1M)} \arrow[d, "-\Delta G^*_{\text{solv}}\ (\text{HA})"] & + & \text{Ref}^-\text{(aq, 1M)} \arrow[d, "-\Delta G^*_{\text{solv}}\ (\text{Ref}^-)"] \arrow[r, "\Delta G^*_{\text{soln}}"] & \text{HRef(aq, 1M)} & + & \text{A}^-\text{(aq, 1M)} \\
\text{HA(g, 1M)} & + & \text{Ref}^-\text{(g, 1M)} \arrow[r, "\Delta G^*_{\text{gas}}"'] & \text{HRef(g, 1M)} \arrow[u, "\Delta G^*_{\text{solv}}\ (\text{HRef})"] & + & \text{A}^-\text{(g, 1M)} \arrow[u, "\Delta G^*_{\text{solv}}\ (\text{A}^-)"]
\end{tikzcd}$$

The * denotes a standard state of 1M (1 mol/L). The free energy of solvation is then calculated as

$$\Delta G^*_{\text{soln}} = \Delta G^*_{\text{gas}} + \Delta G^*_{\text{solv}}(\text{HRef}) + \Delta G^*_{\text{solv}}(\text{A}^-) - \Delta G^*_{\text{solv}}(\text{HA}) - \Delta G^*_{\text{solv}}(\text{Ref}^-)$$

The pK_a can then be calculated as (see for example Ref. [521])

$$\text{p}K_a = \Delta G^*_{\text{soln}}/(RT \ln(10)) + \text{p}K_a(\text{HRef})$$

The success of this method relies on the availability of a suitable reference compound with an accurately known experimental pK_a value. Instead of experimental gas phase deprotonation energies one might calculate the gas phase reaction free energy ΔG^*_{gas}, using DFT or some high level ab initio method.

Example Ethanol

In this example the pK_a value of Ethanol will be calculated. As reference compound Methanol is chosen, which has an experimental pK_a value of 15.5. Experimental deprotonation energies are taken from Ref. [521, supporting information], for Methanol this is $\Delta_r G^0$ = 1569 kJ/mol, and for Ethanol $\Delta_r G^0$ = 1555 kJ/mol, see also, for example, Ref. [522]. The COSMO-RS solvation free energies of Methanol, Methoxide (the conjugate base of Methanol), Ethanol, and Ethoxide (the conjugate base of Ethanol) have already been calculated in the previous tutorial 5.1. At T = 298.15, 1/(RT ln(10)) = 0.733 mol/kcal. The free energy of solvation (kcal/mol) and the pK_a of Ethanol are then calculated as

$$\Delta G^*_{\text{soln}} = (1555-1569)/4.184 - 4.97 - 86.56 + 4.79 + 90.14 = 0.05 \text{ kcal/mol}$$

$$\text{p}K_a\ (\text{Ethanol}) = 0.733 \cdot 0.05 + 15.5 \approx 15.5$$

The calculated pK_a of Ethanol of 15.5 is close to the experimental value of 15.9.

References

[521] J. Ho and M.L. Coote, *A universal approach for continuum solvent pK_a calculations: are we there yet?*, Theoretical Chemistry Accounts **125**, 3 (2010)

[522] NIST Chemistry WebBook