



Scientific Computing & Modelling

GUI Tutorials

**ADF Program System
Release 2013**

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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/adjobs &
```

instead of just

```
adjobs &
```

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.

When you log in to a remote linux UNIX system using `ssh`, make sure you are using X11 forwarding. You can force this by using the `-X` (sometimes with the `-Y`) flag to the `ssh` command. As `ssh` is taking care of setting your `DISPLAY` variable, you should make sure **not** to set it yourself.

Most GUI modules use OpenGL to render the 3D images. With X11 this is done using the GLX X11 extension. You can test if GLX is working properly by running the `glxgears` command:

```
glxgears
```

In case of troubles, the `glxinfo` command might also give useful information.

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 `ADF2013.01` program.

The easiest way is using the `ADF2013.01` program. 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 the New Input module (`ADFinput`) 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 → New 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. Depending on your license, not all options might 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:

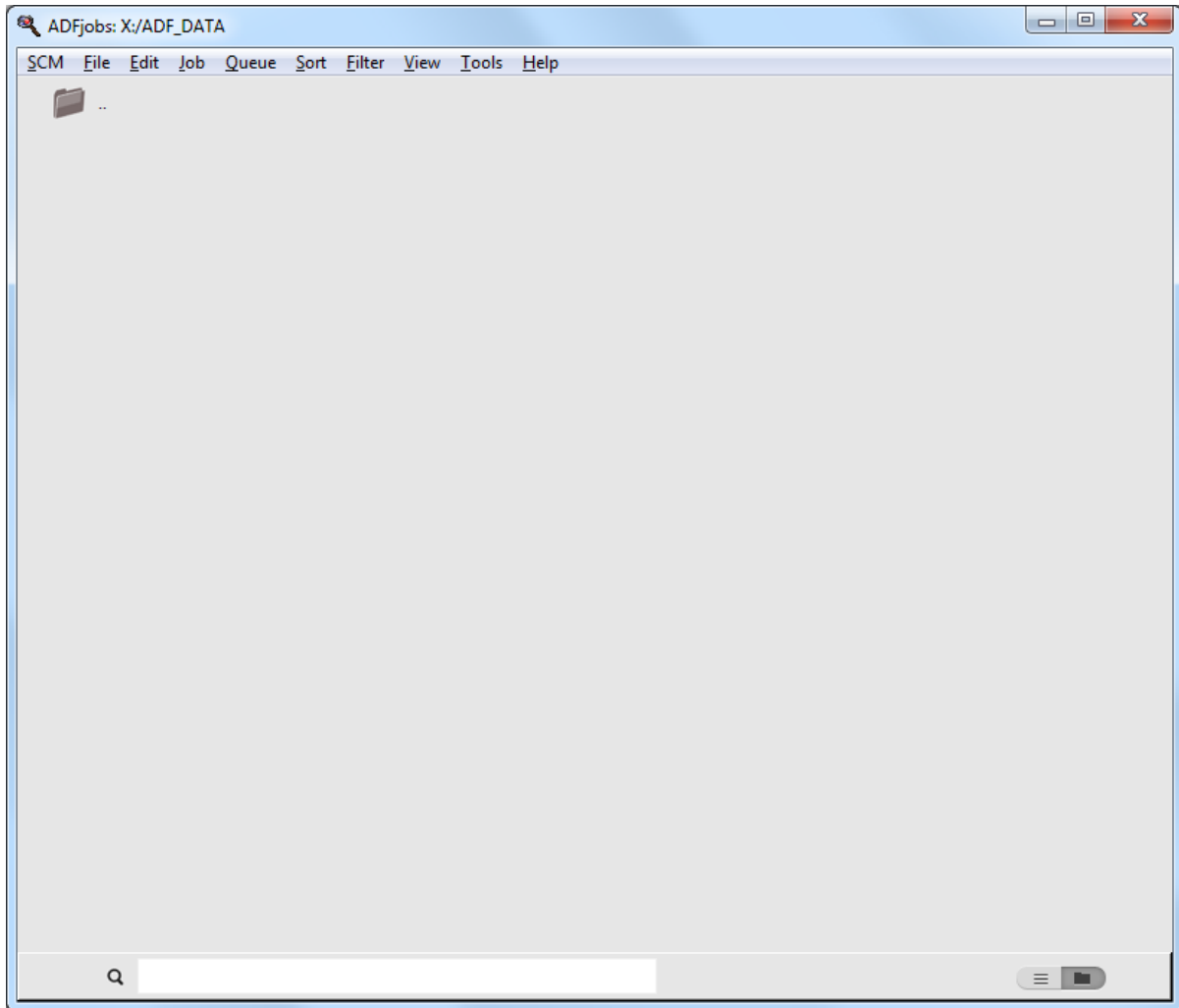
```
cd
adfjobs &
```

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 ADF2013.01 program to start ADFjobs:

```
Double click on the ADF2013.01 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.
```



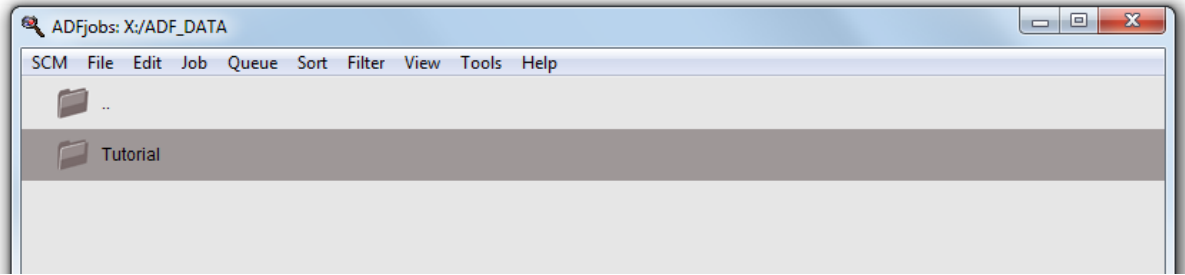
Note that the directory in which ADFjobs depends on how you start ADFjobs, so your screen might look different.

Make a directory for the tutorial

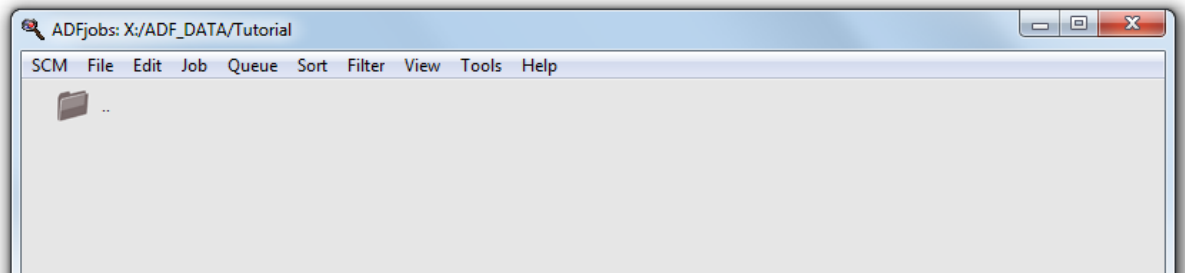
We prefer to run the tutorial in a new, clean, directory. That way we will not interfere with other projects. ADFjobs not only manages your jobs, but also has some file management options. In this case we use ADFjobs to make the new directory:

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



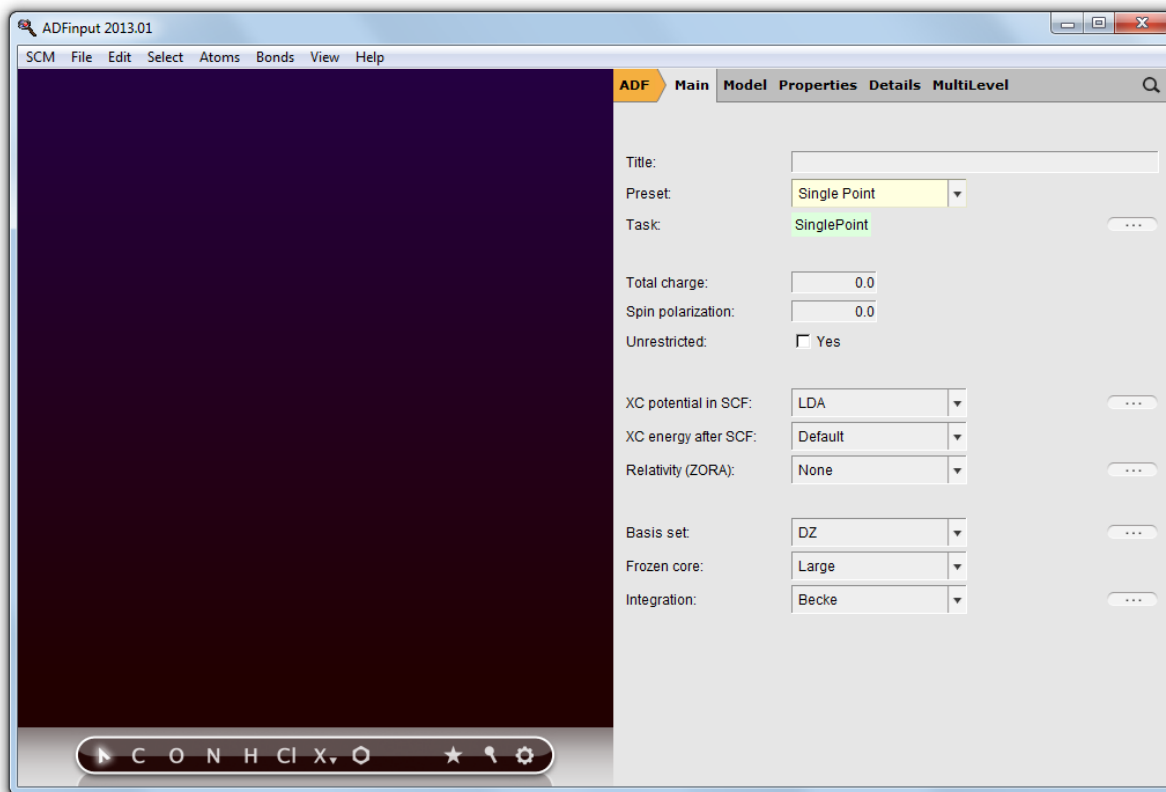
Start ADFinput

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

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

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

The ADFinput module should start:



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).

<u>U</u> ndo	Ctrl Z
<u>R</u> edo	Shift Ctrl Z
<u>C</u> ut	Ctrl X
<u>C</u> opy	Ctrl C
<u>P</u> aste	Ctrl V
Clear	
Set Center Of Mass	
Set Origin	
Symmetry	▶
Mirror	▶
Rotate 90	▶
Align	▶
Crystal	▶
<u>B</u> uilder...	Ctrl B

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

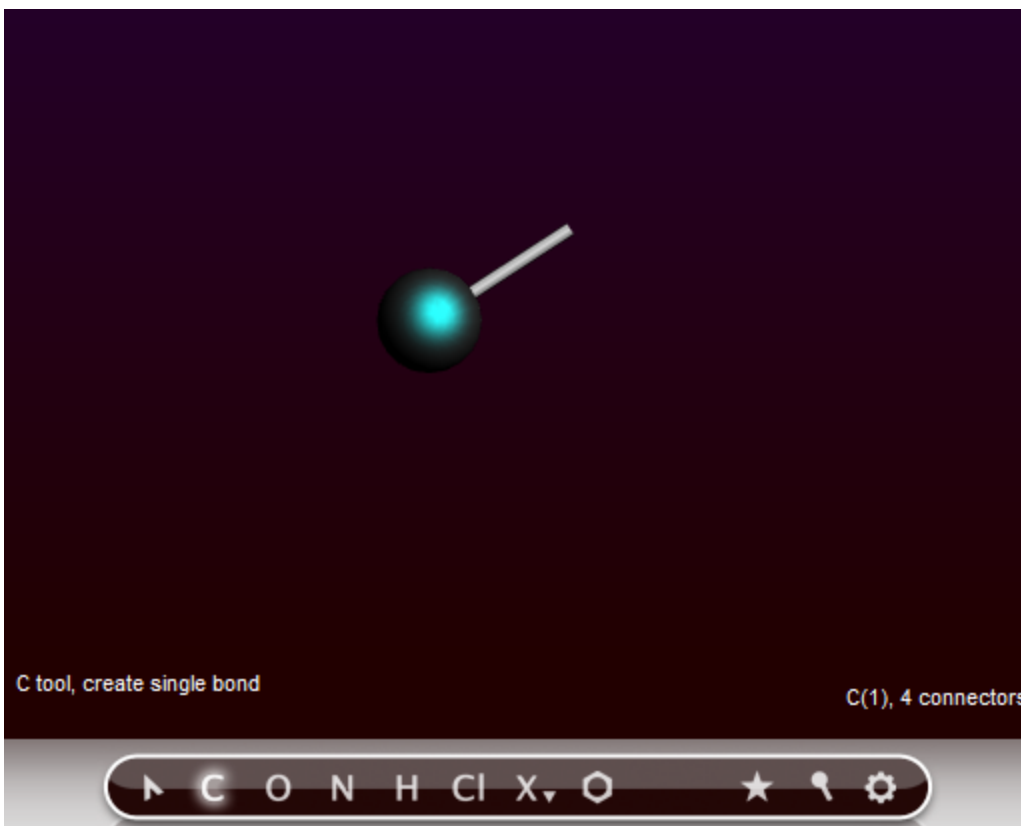
To create an atom, you need to select an atom tool.

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



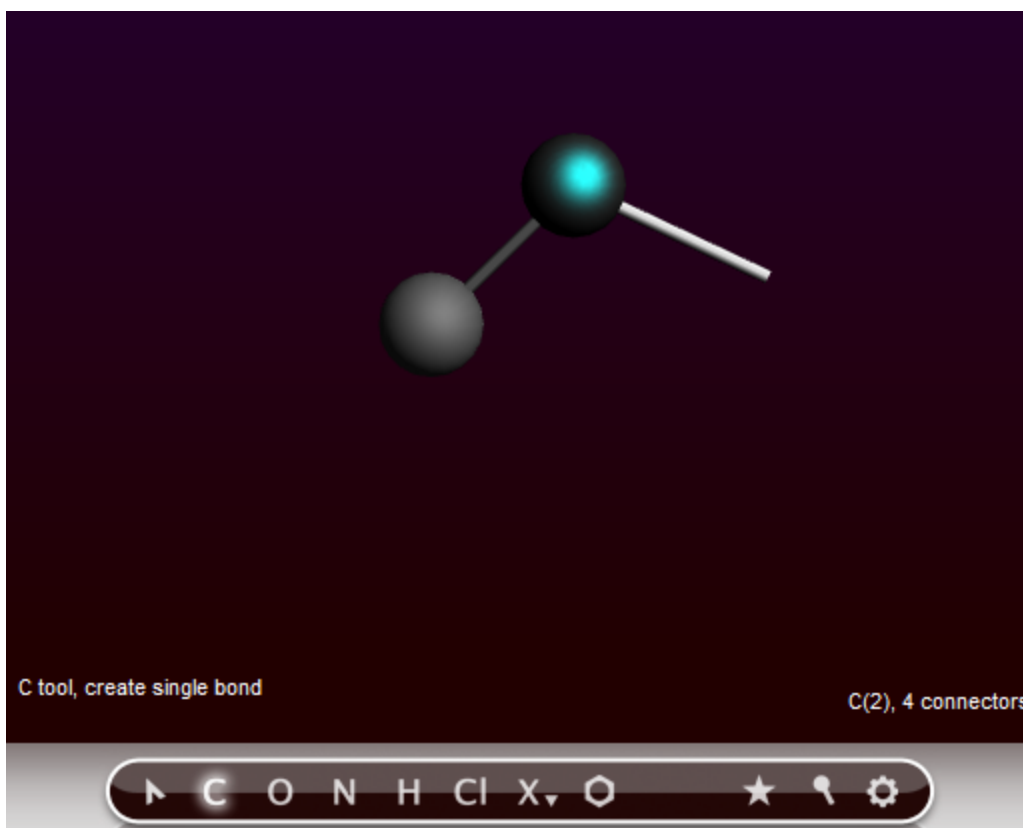
One carbon atom has been created.

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.

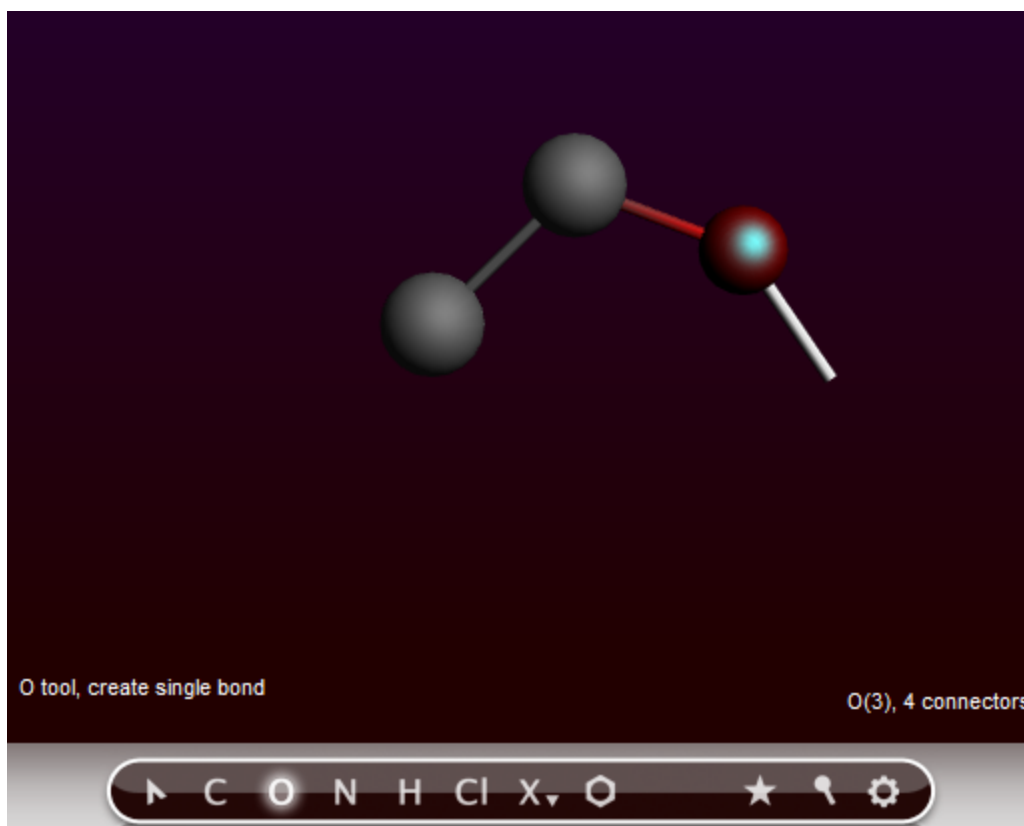
Create the oxygen atom

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:

Delete Atom(s)	
Fuse Atoms	
Change Atom Type	▶
Ghosts	▶
Details (Color, Radius, Mass, ...)	
Add Hydrogens	Ctrl H
Remove Hydrogens	Shift Ctrl H
Replace By Structure	▶

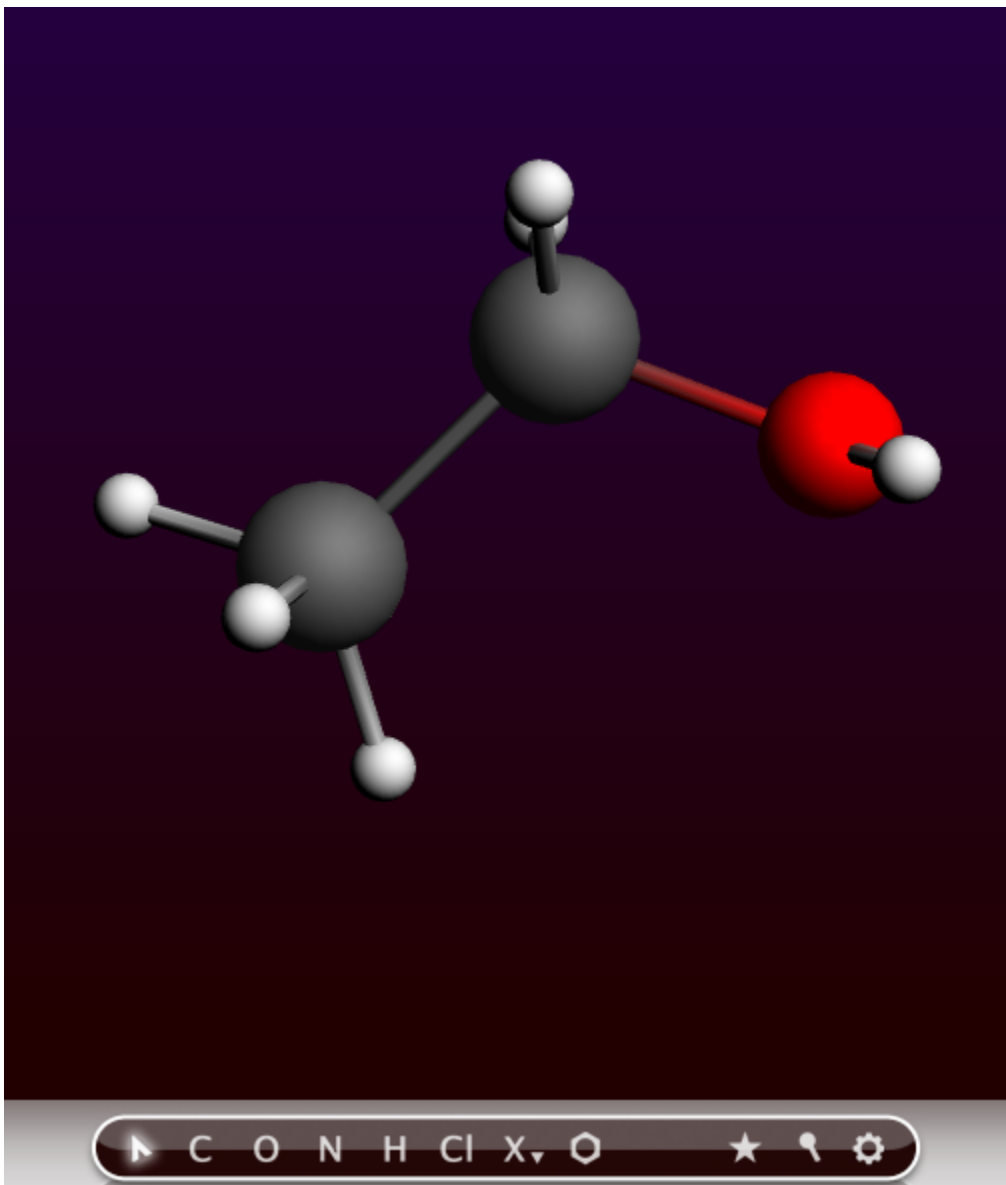
The 'Add Hydrogen' menu command works on the selection only, when present. Thus, only one hydrogen atom would be added to the oxygen atom. This is not what you want. So first we make sure that nothing is selected by clicking in empty space.

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.

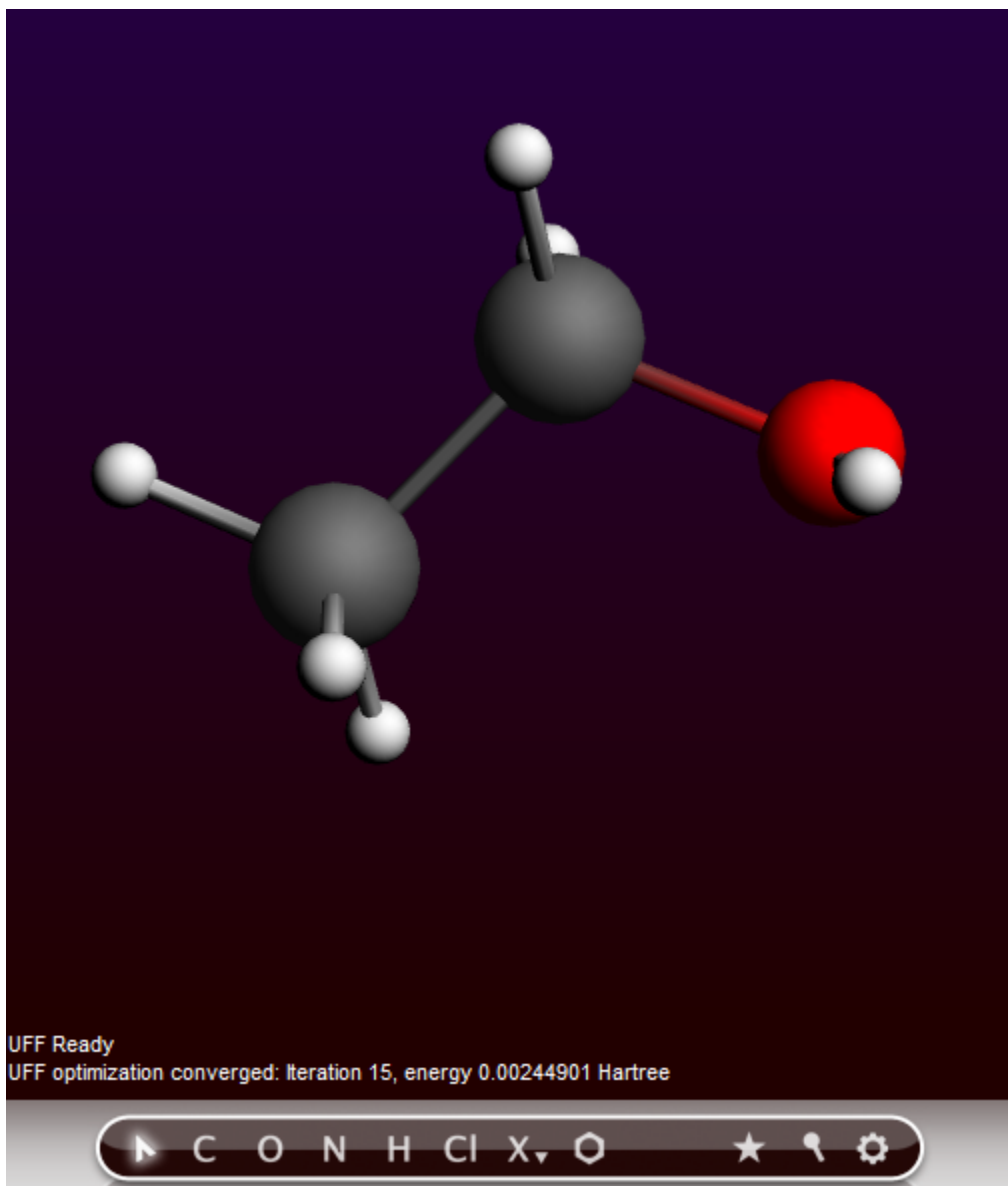


All atoms will be saturated with hydrogen atoms. And you have created an ethanol molecule, though the geometry is still far from perfect.

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)



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.

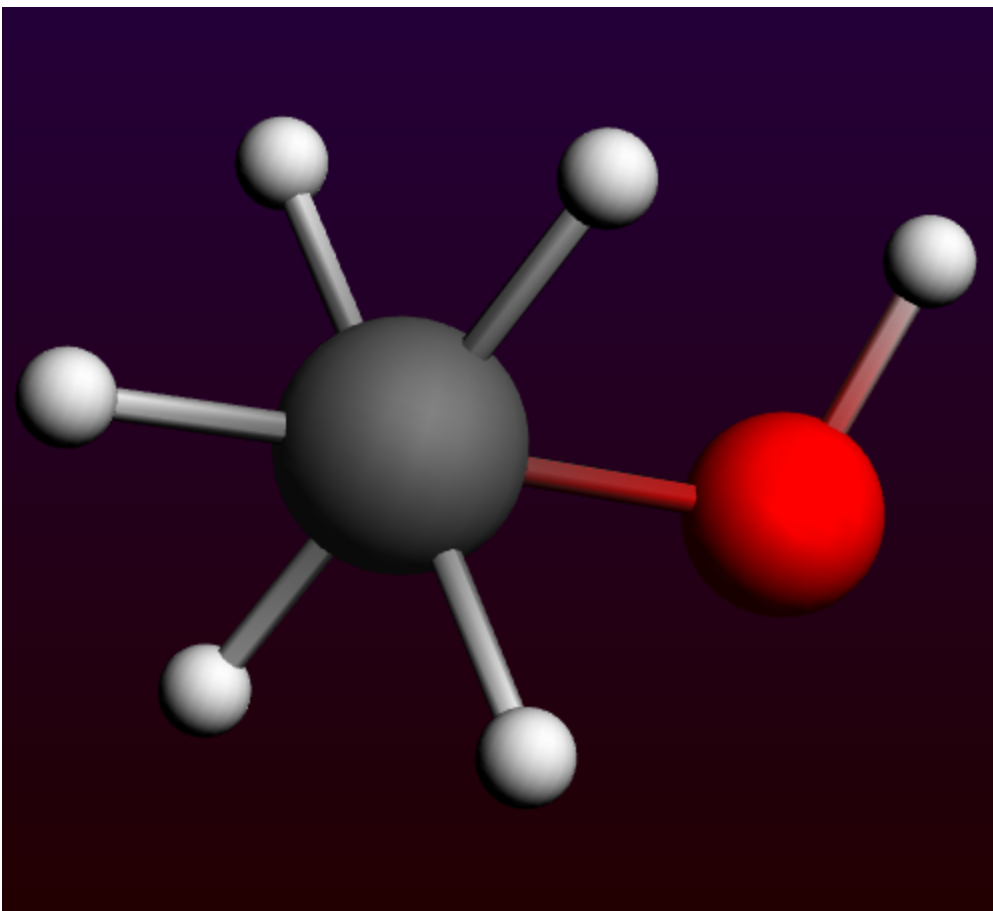
Click with the right mouse button, and drag:
your molecule will be translated.

Click with the right Middle button (if available), and drag up and down:
you will zoom closer to or away from your molecule.

Click with the left mouse button with the alt-key, and drag:
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.

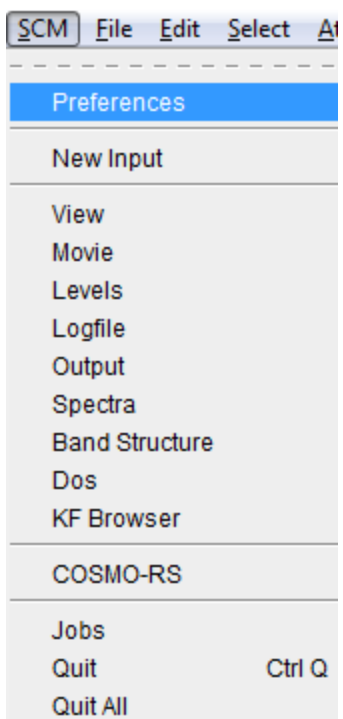
Using all these options, try to position the ethanol as closely as possible as in the following image:



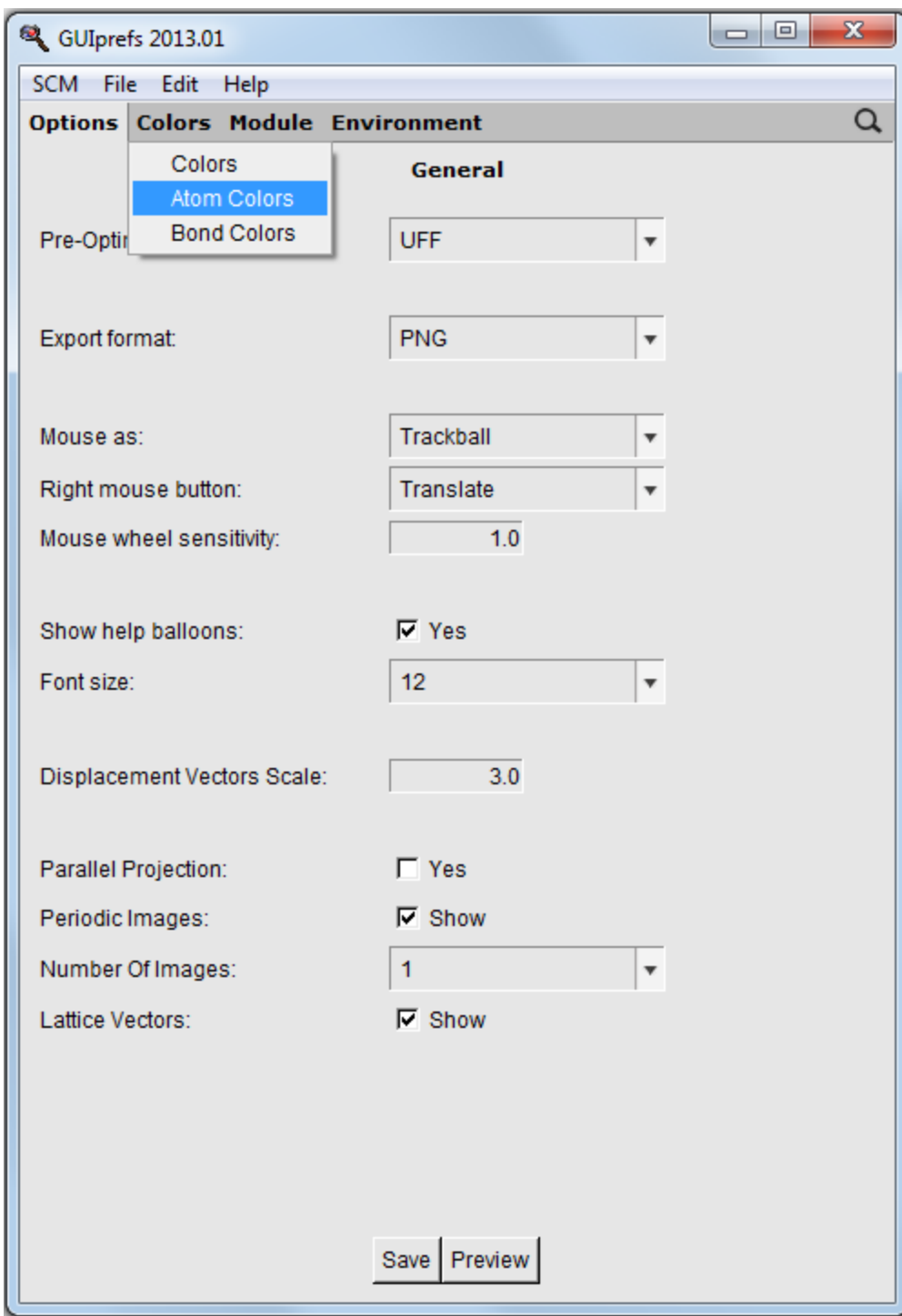
Atom colors

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:

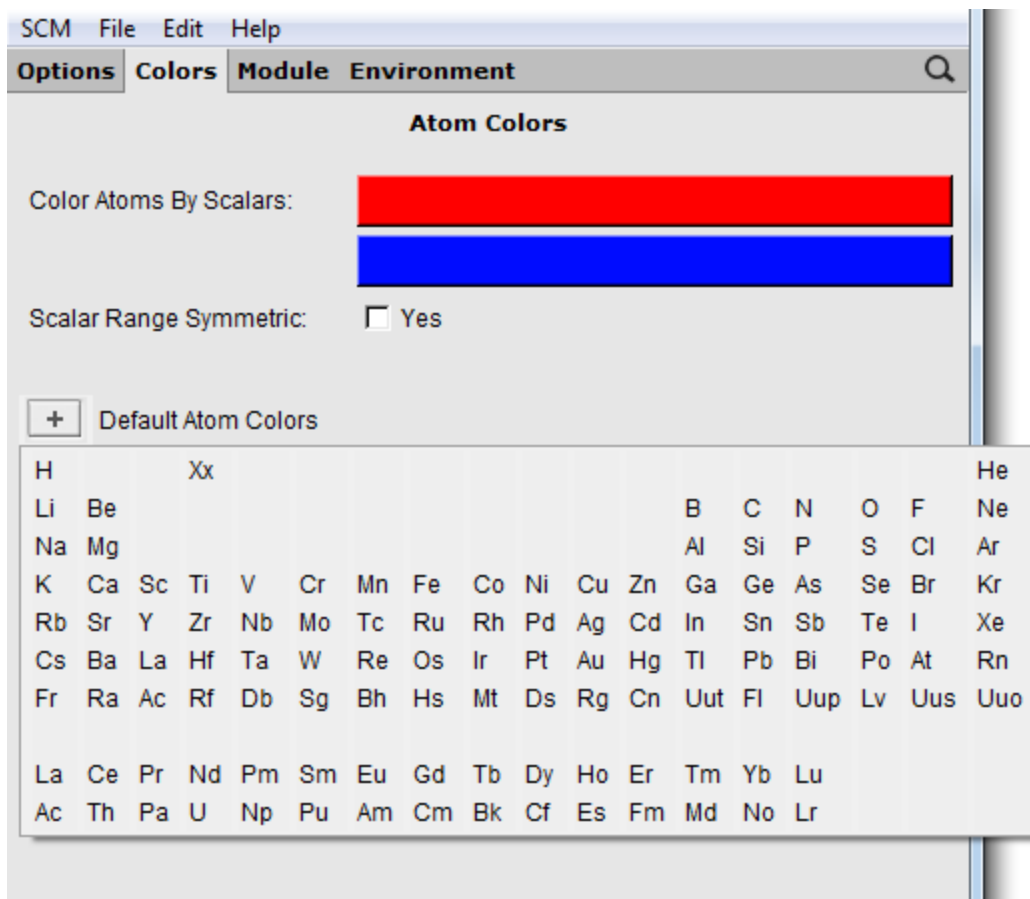
Use the **SCM** → **Preferences** menu command to start the preferences module



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



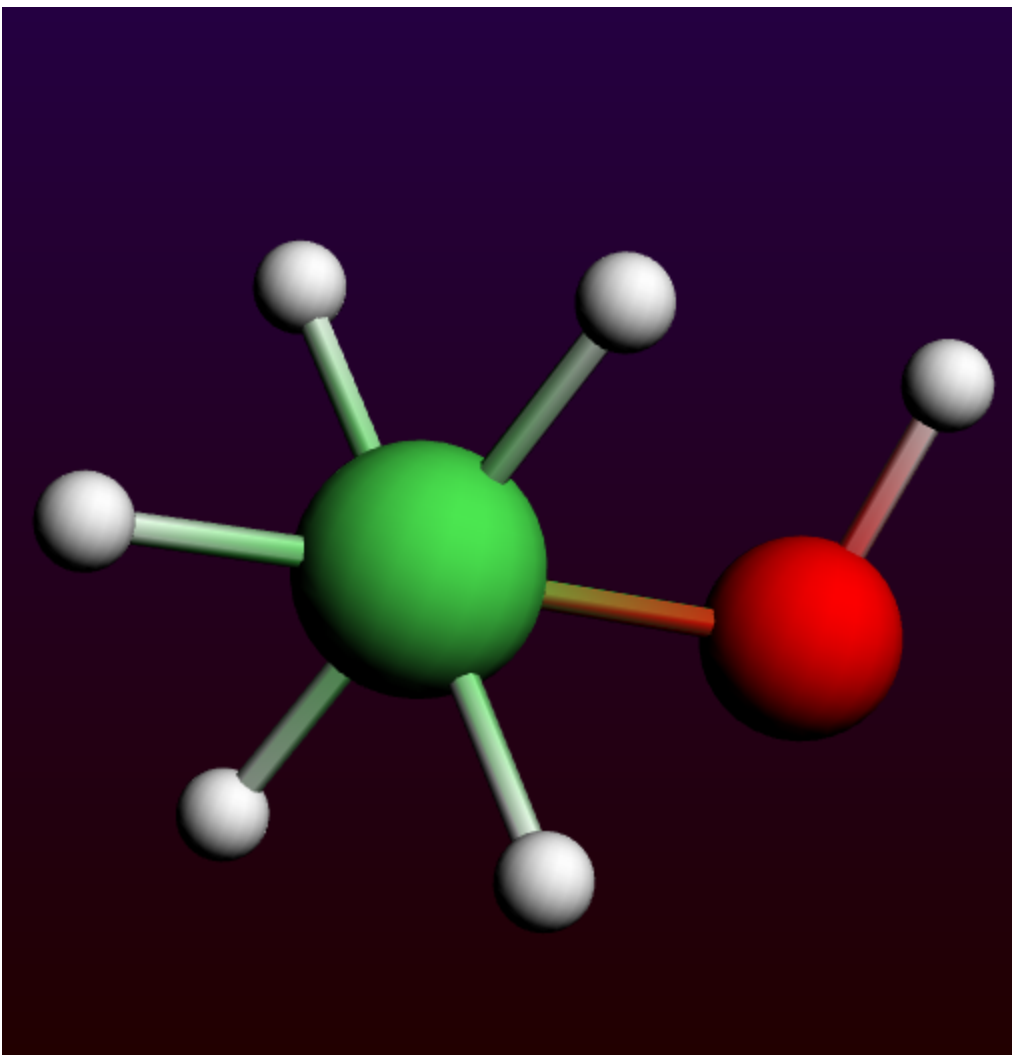
Click on the '+' button, and select C (Carbon) from the periodic table that pops up.



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.



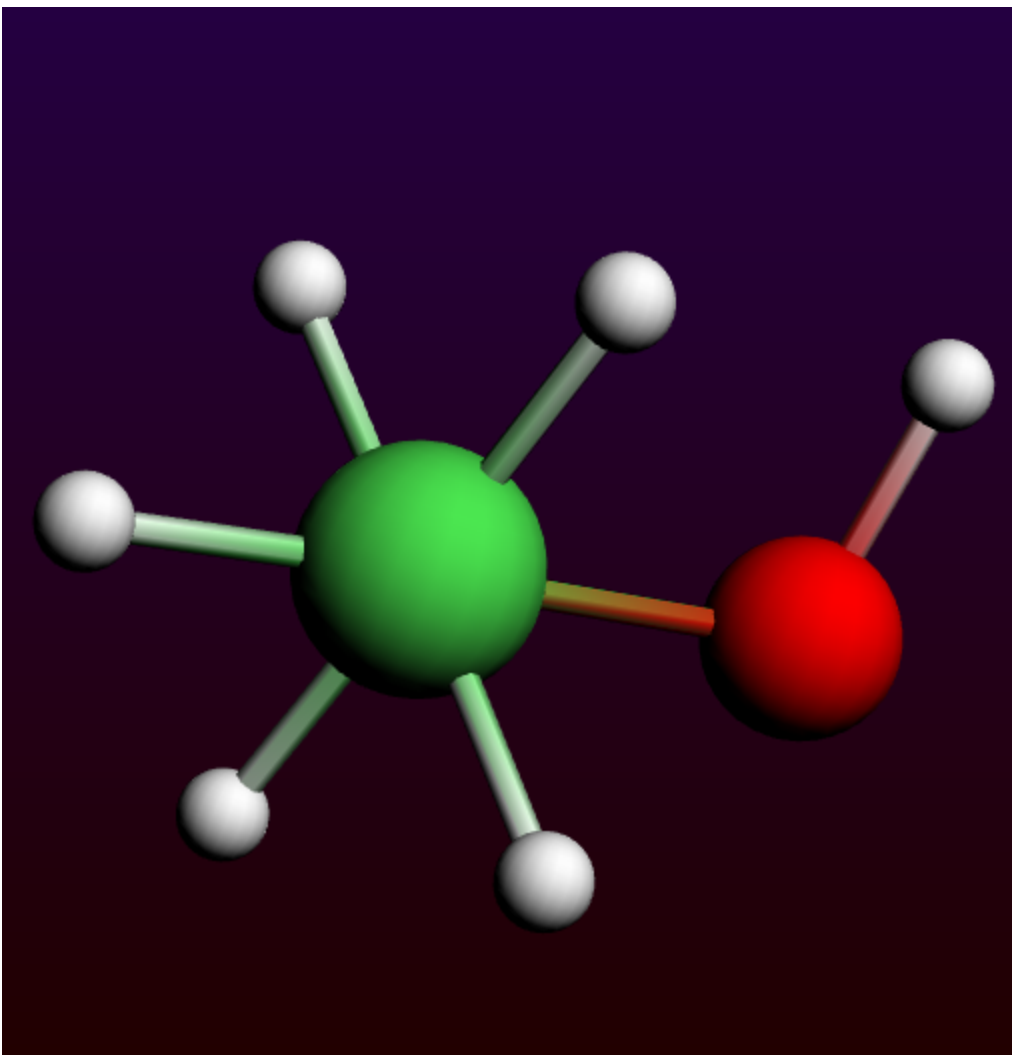
In ADFinput the colors of the carbon atoms will now be adjusted to the color that you have selected.

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



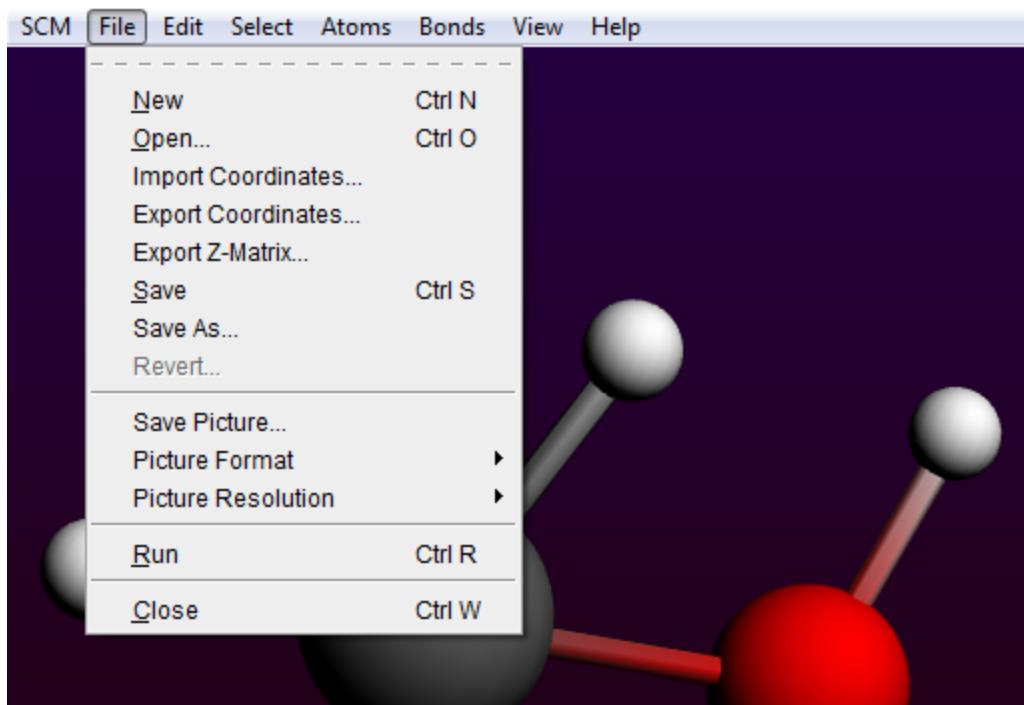
In ADFinput, your carbon atoms now should have their default color again (dark gray).

Use the **File** → **Close** 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.

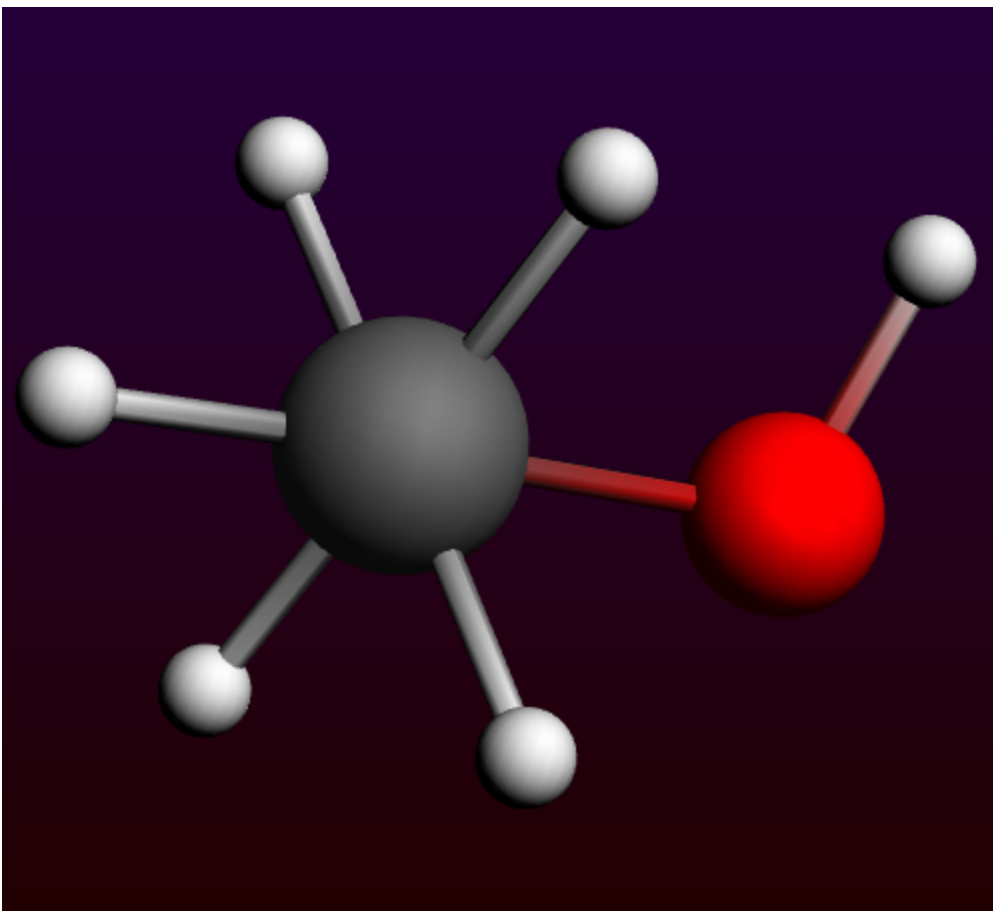
```
Select the File → Save Picture ... command
Enter the name for your picture: ethanol
Click the 'Save' button
```

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

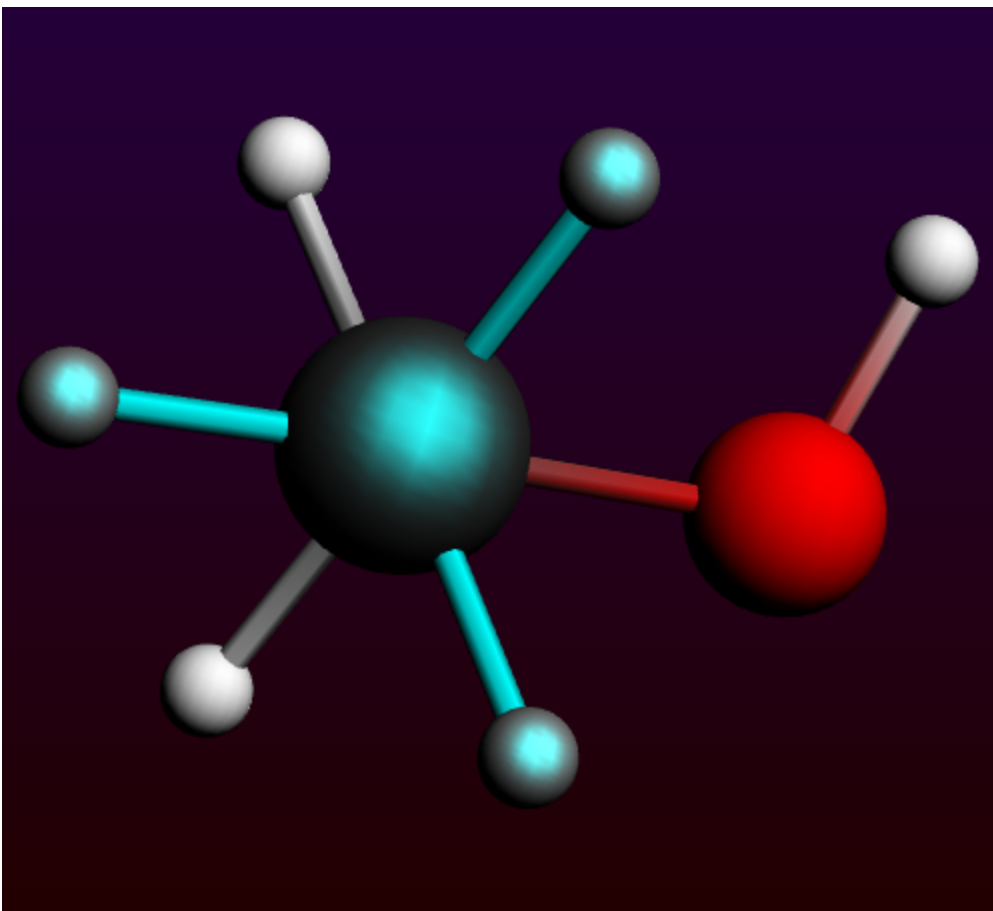
Rotate such that you look along the C-C axis

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

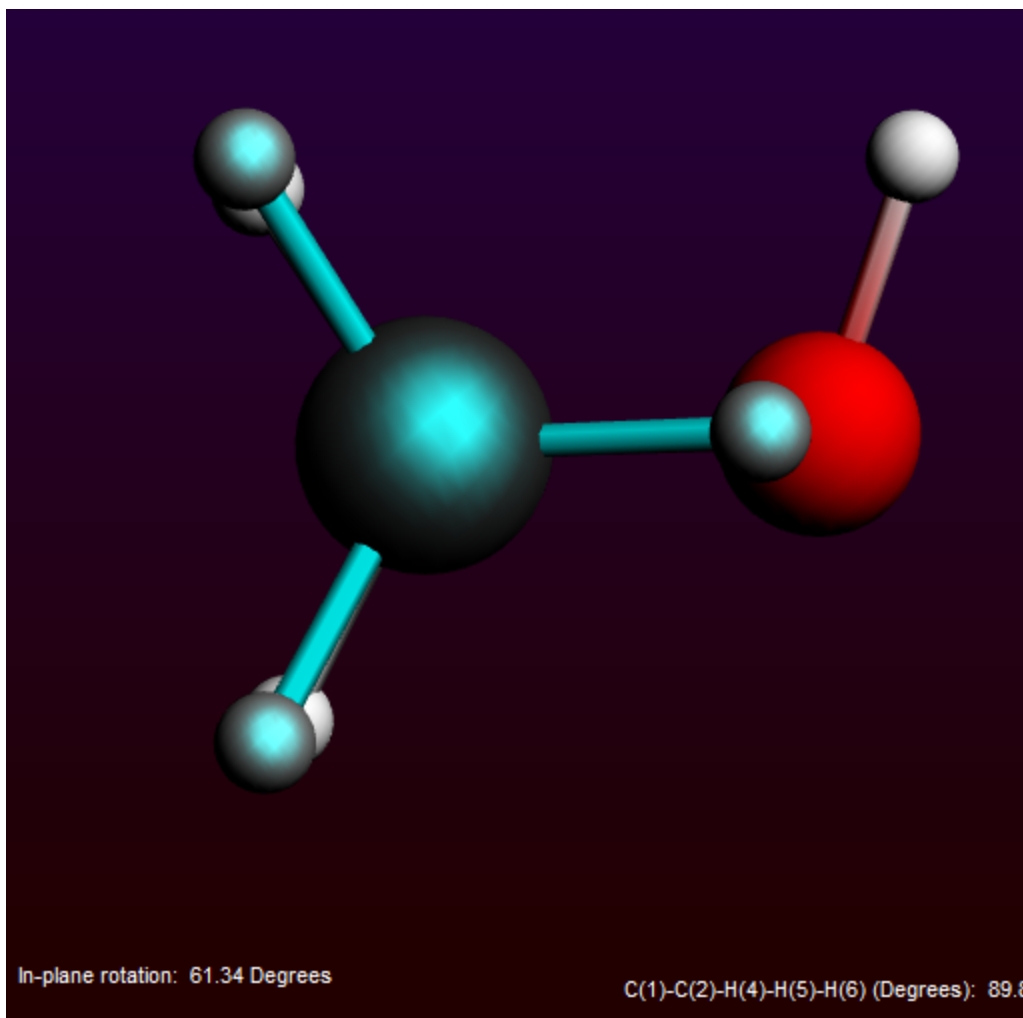
This has almost the same effect (in this case you have not selected the second carbon atom).

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.



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.

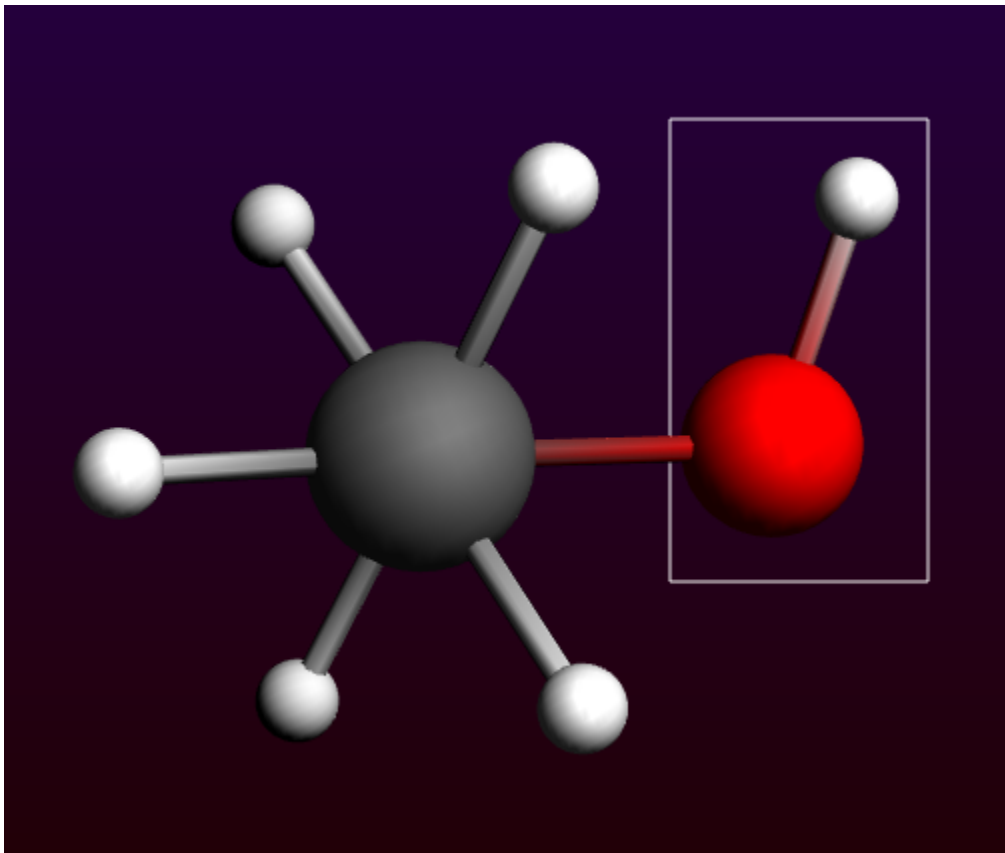
Getting and setting geometry parameters

Bond length

First select the oxygen atom and the connected hydrogen atom.

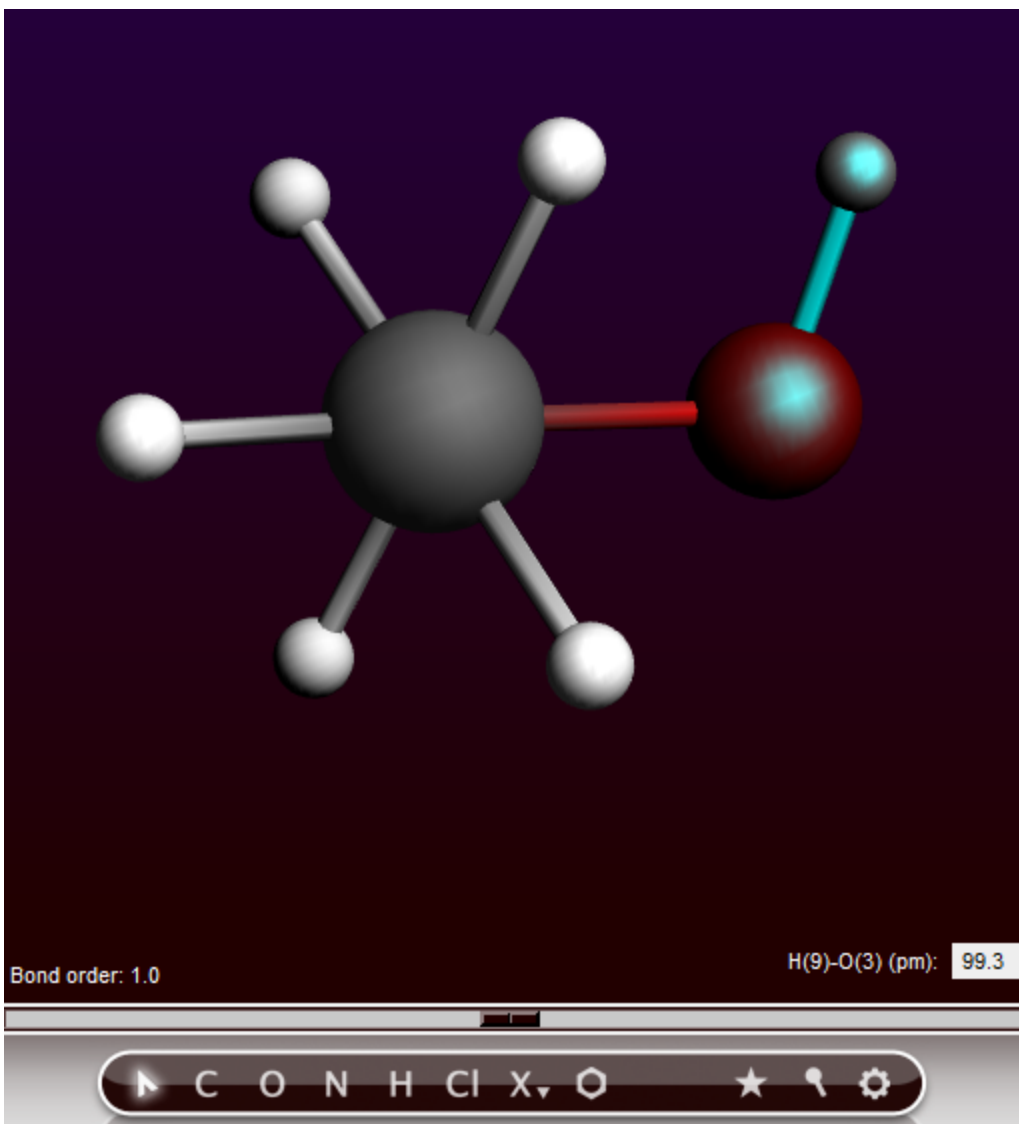
This time we make the selection by dragging a rectangle around all objects that we want to select.

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.



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

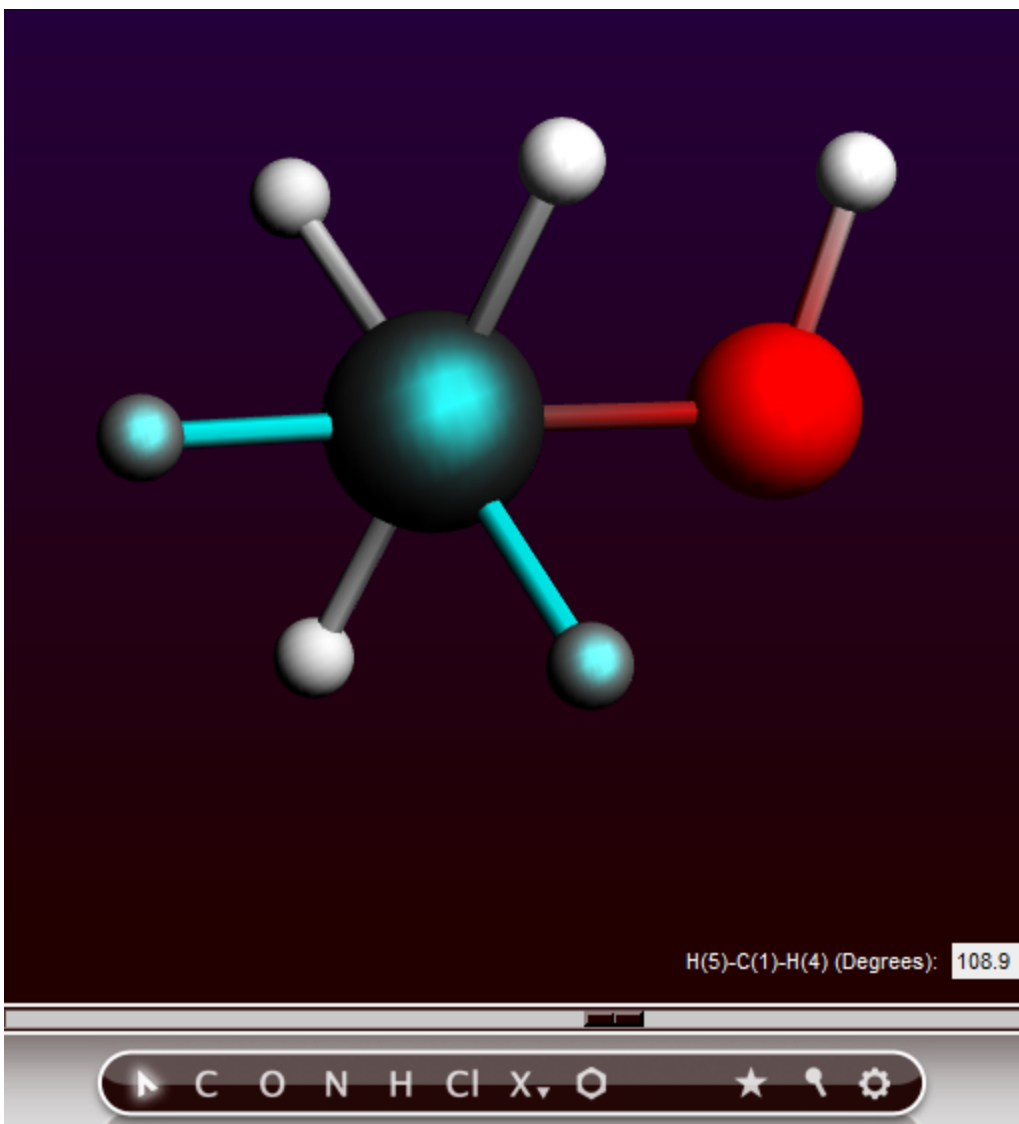
You can set the distance to any value you wish by editing it, or (most conveniently) by using the slider.

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

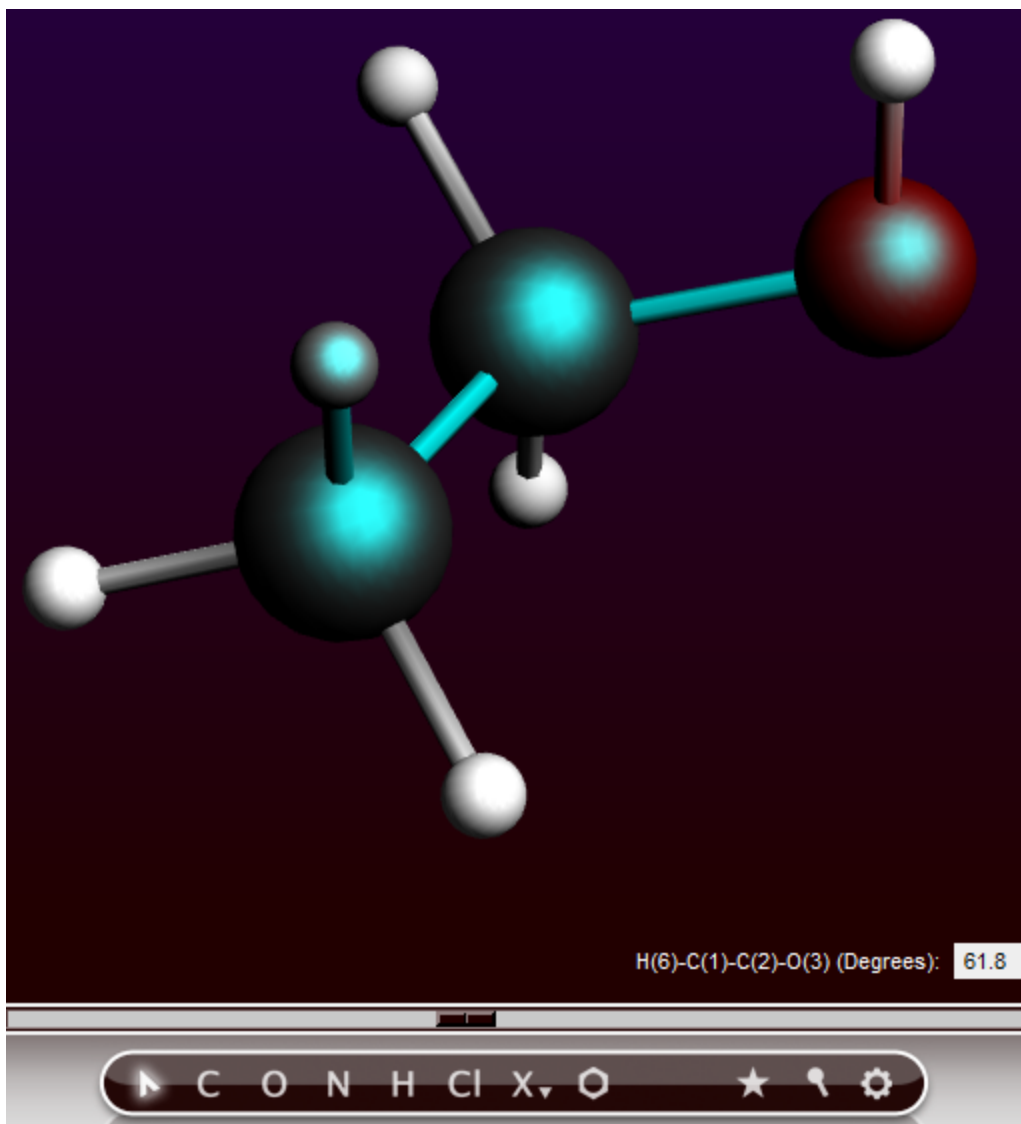


In the status area information about the bond angle of the selected three atoms is given, and the slider is again visible. You can change this value to a value you like, most conveniently using the slider.

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



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

ADF Main Model Properties Details MultiLevel			
Coordinates			
<input type="checkbox"/> Use natural coordinates			
Move atom(s) up		Move atom(s) down	
C(1)	-4.76948522	-5.83845652	0.013345450
C(2)	-3.60359403	-4.88480562	-0.217573000
O(3)	-2.77751330	-4.84082890	0.913772650
H(4)	-4.38832373	-6.85627259	0.242336130
H(5)	-5.40006299	-5.88643887	-0.899437840
H(6)	-5.39190297	-5.48221221	0.861266440
H(7)	-3.98655197	-3.86799645	-0.461856470
H(8)	-3.00640077	-5.24462877	-1.08187842
H(9)	-3.24665744	-4.28130414	1.58647751

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

ADF Main Model Properties Details MultiLevel			
Search: z-ma			
Panels			
Z-Matrix			
Geometry Convergence			
Documentation ▶			
Step 2: Create your molecule			
O(3)	-2.77751330	-4.84082890	0.913772650
H(4)	-4.38832373	-6.85627259	0.242336130

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

ADF Main Model Properties Details MultiLevel										
Z-Matrix										
Move atom(s) up					Move atom(s) down					
1	C(1)	0	0	0	<input type="checkbox"/>	0.0	<input type="checkbox"/>	0.0	<input type="checkbox"/>	0.0
2	C(2)	1	0	0	<input type="checkbox"/>	1.5238358	<input type="checkbox"/>	0.0	<input type="checkbox"/>	0.0
3	O(3)	2	1	0	<input type="checkbox"/>	1.4015299	<input type="checkbox"/>	110.38180	<input type="checkbox"/>	0.0
4	H(4)	1	2	3	<input type="checkbox"/>	1.1107071	<input type="checkbox"/>	110.00883	<input type="checkbox"/>	301.41477
5	H(5)	1	2	4	<input type="checkbox"/>	1.1104521	<input type="checkbox"/>	109.69102	<input type="checkbox"/>	240.17273
6	H(6)	1	2	5	<input type="checkbox"/>	1.1105331	<input type="checkbox"/>	110.10628	<input type="checkbox"/>	240.22672
7	H(7)	2	1	3	<input type="checkbox"/>	1.1136570	<input type="checkbox"/>	109.97070	<input type="checkbox"/>	237.75590
8	H(8)	2	1	7	<input type="checkbox"/>	1.1104667	<input type="checkbox"/>	109.06391	<input type="checkbox"/>	241.66590
9	H(9)	3	2	1	<input type="checkbox"/>	0.9928222	<input type="checkbox"/>	106.62535	<input type="checkbox"/>	283.59740

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

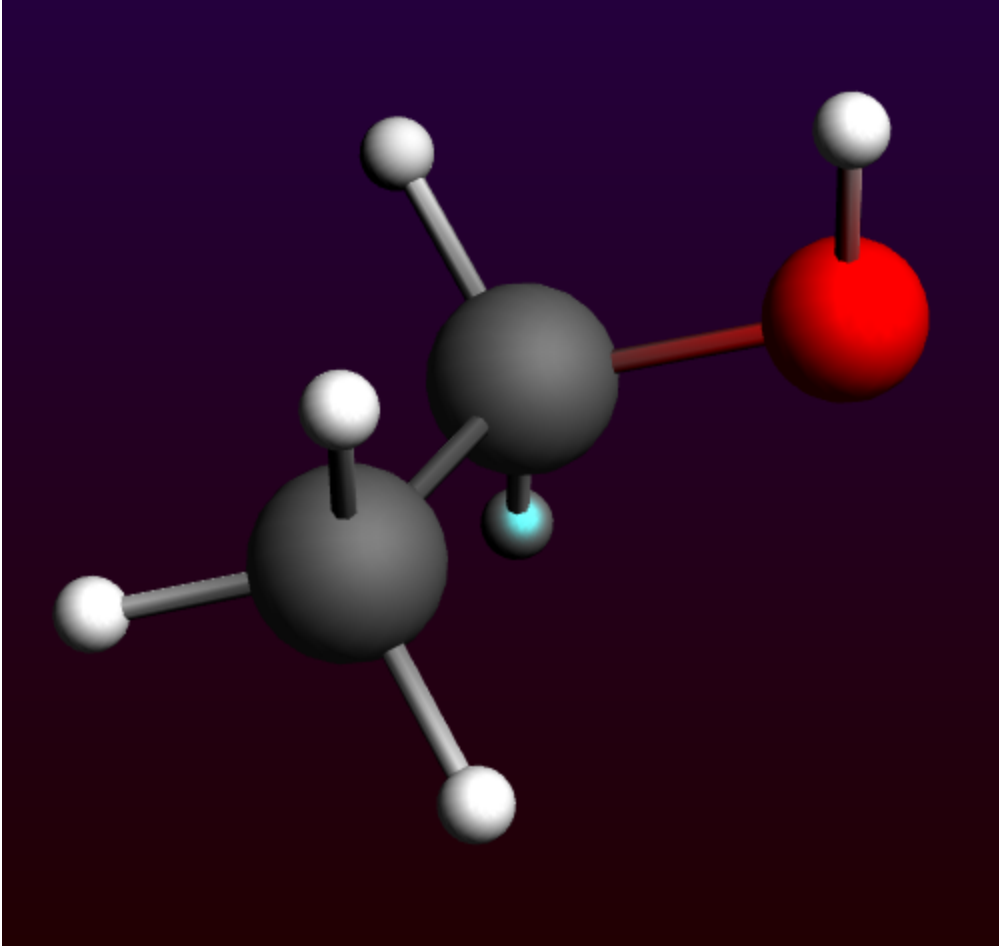
After this, we will revert to the ethanol molecule.

Delete an atom

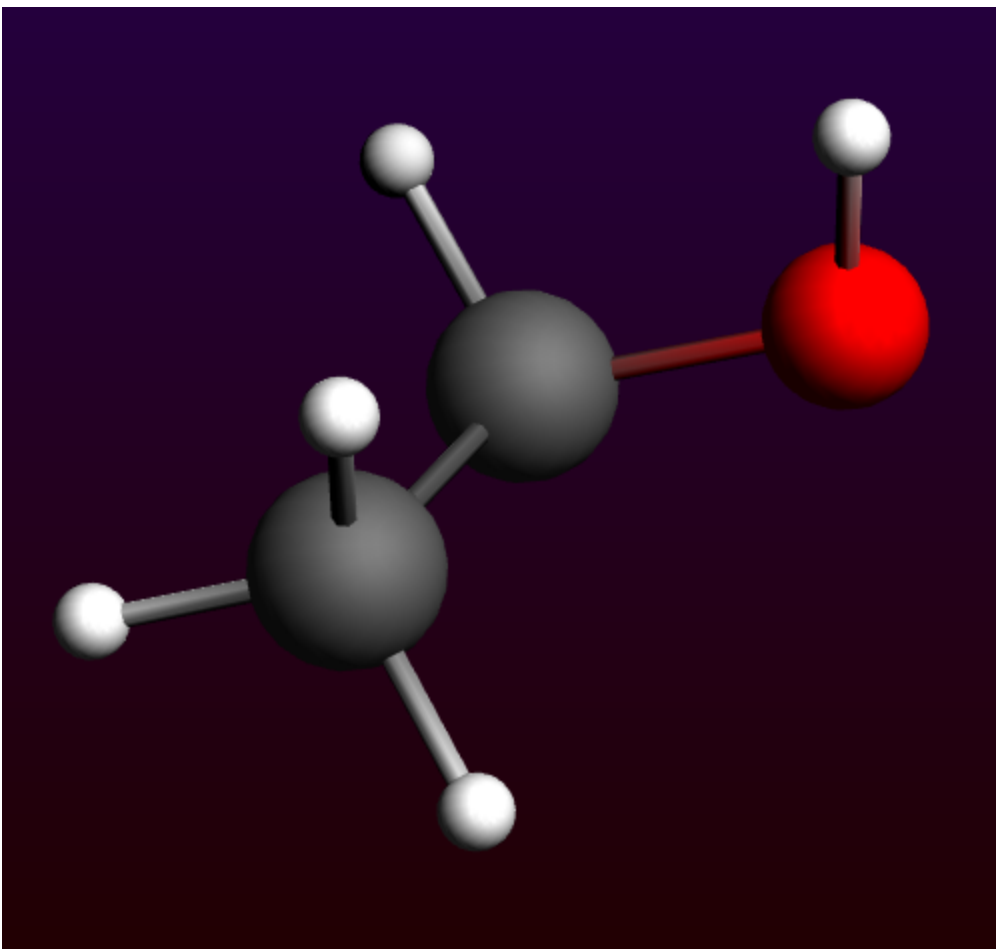
First: delete one hydrogen

Click in empty space to clear the selection

Click once on the hydrogen to delete, it will be selected



Press the backspace key



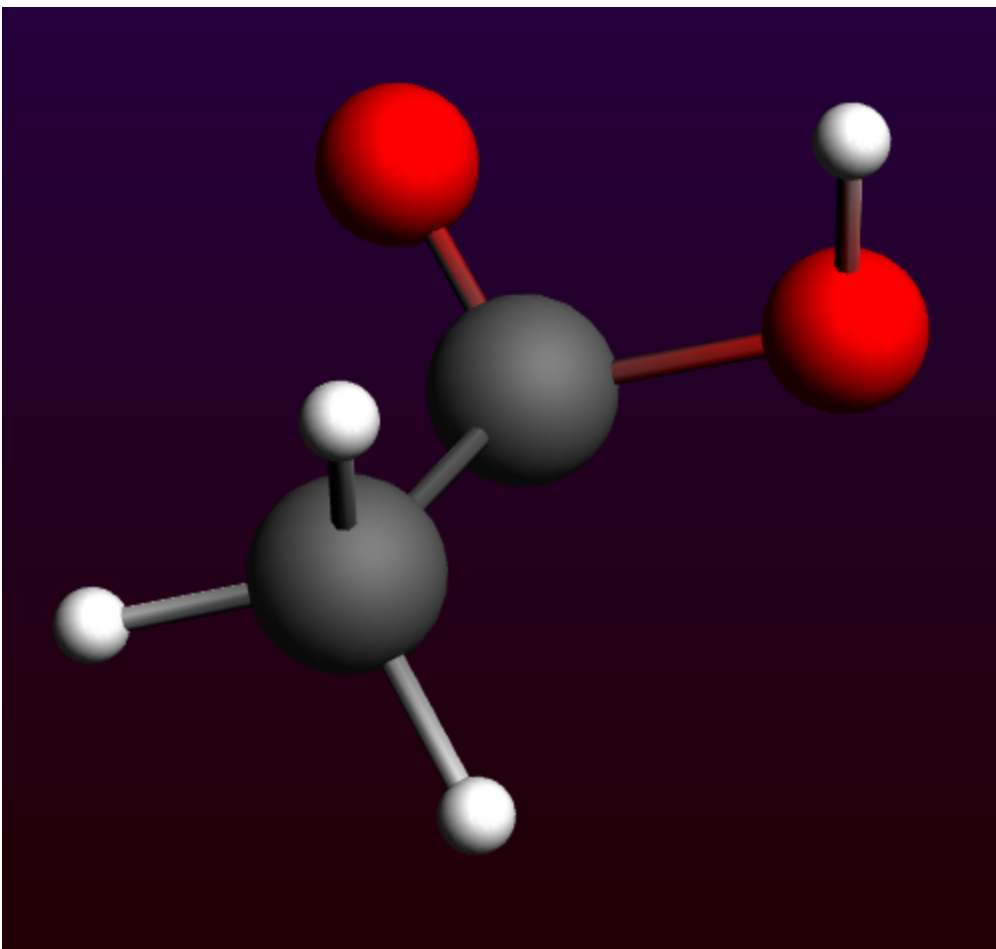
The selected atom is removed.

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

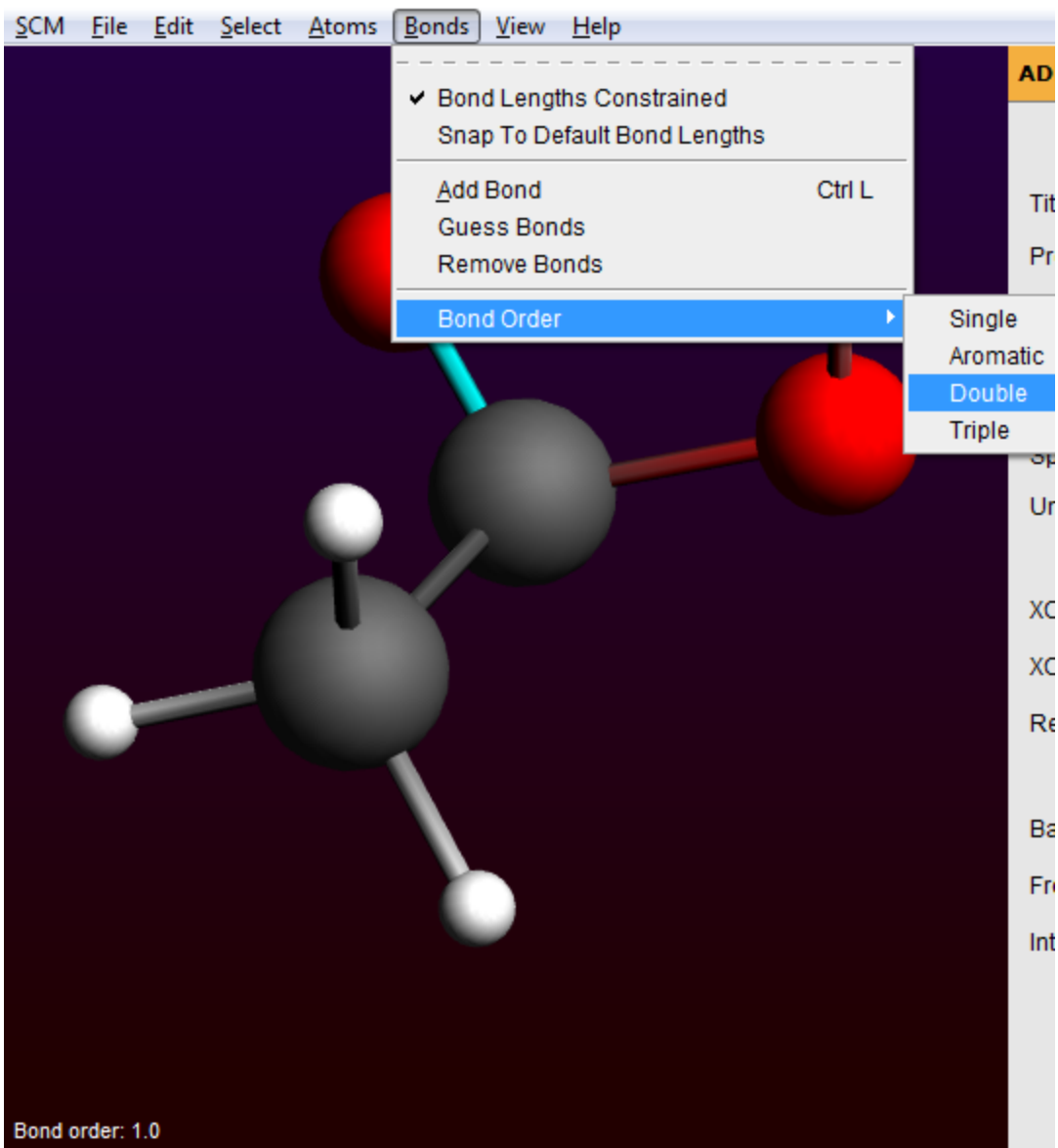


Change the bond type of an existing bond

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)



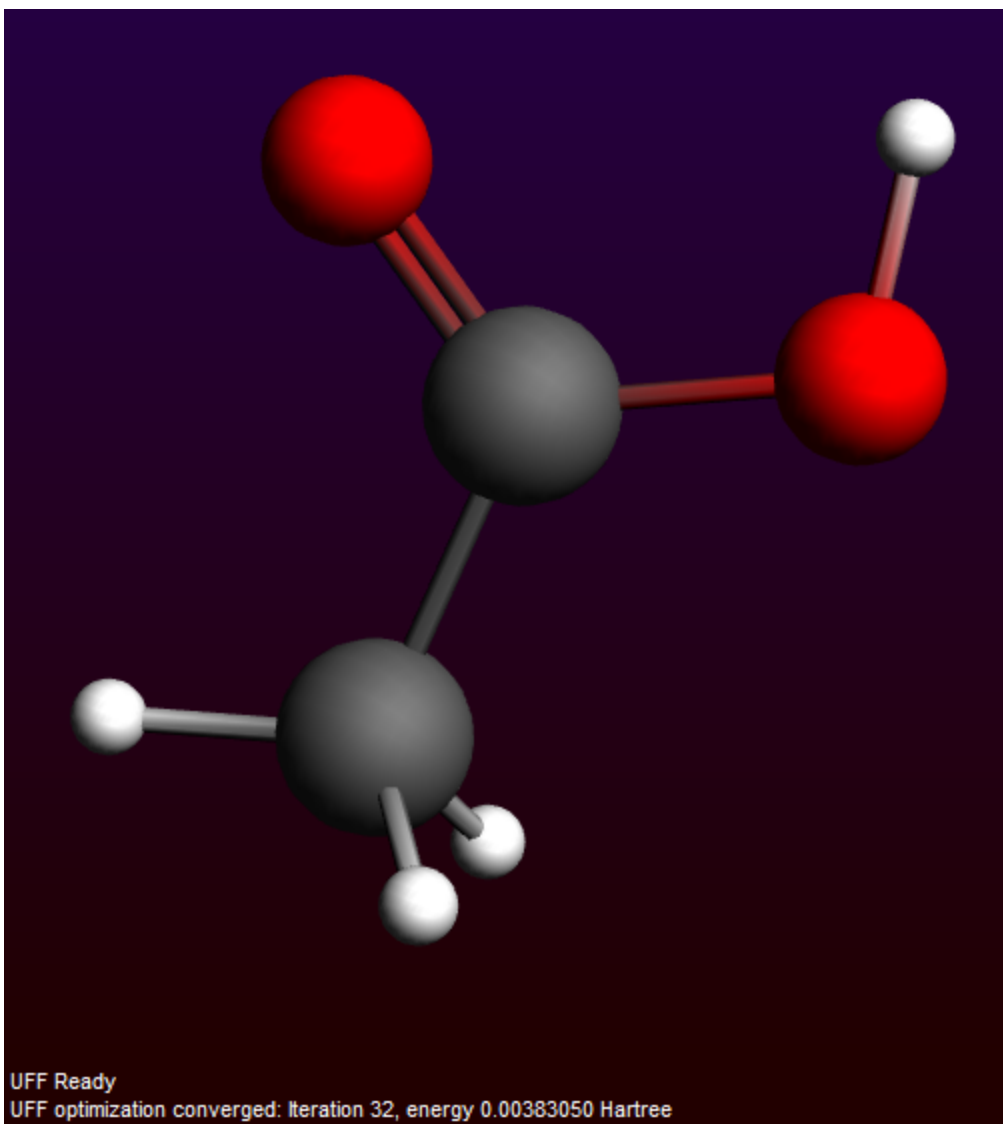
The single bond has changed into a double bond.

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

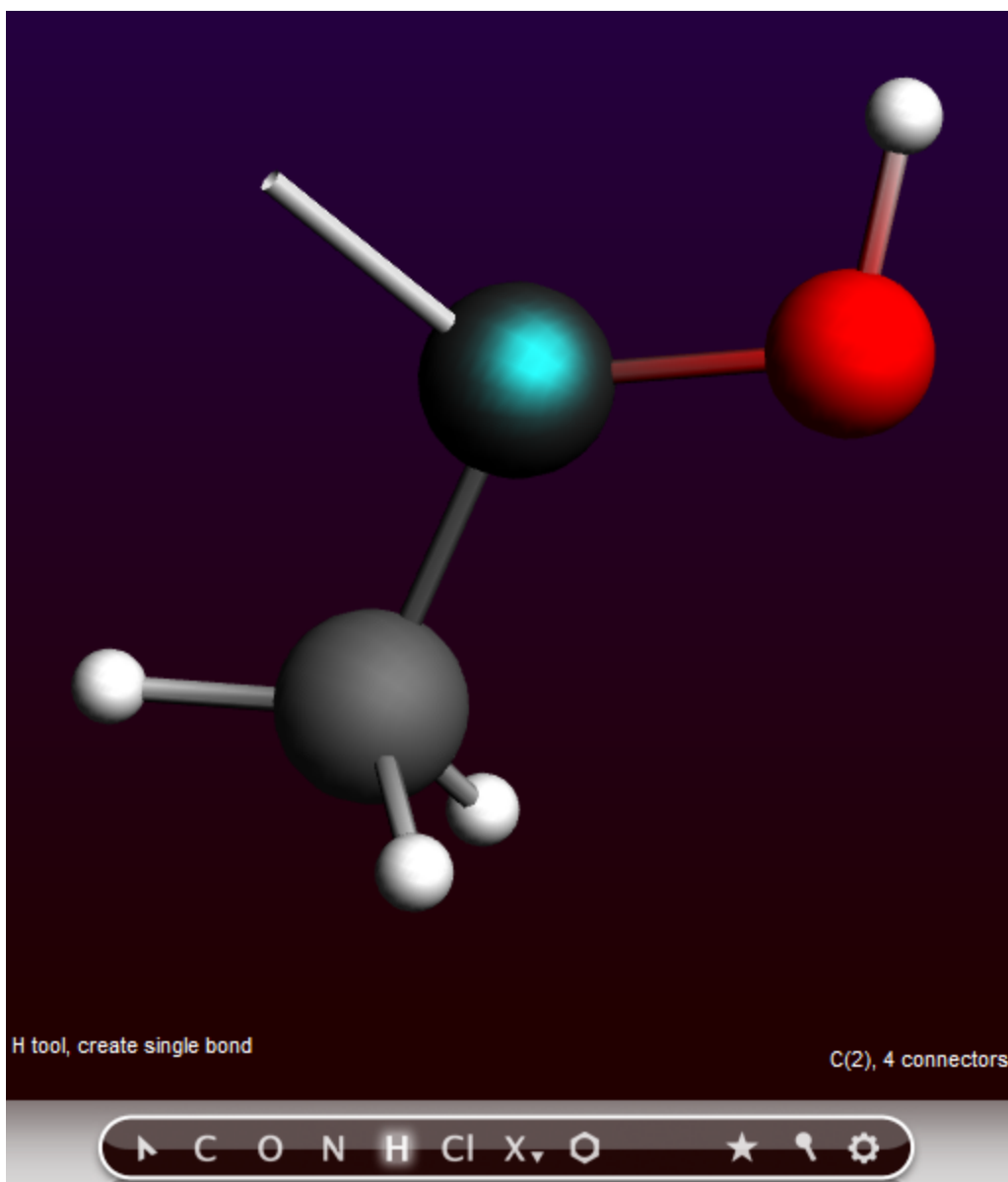


Add new (bonded) atoms

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

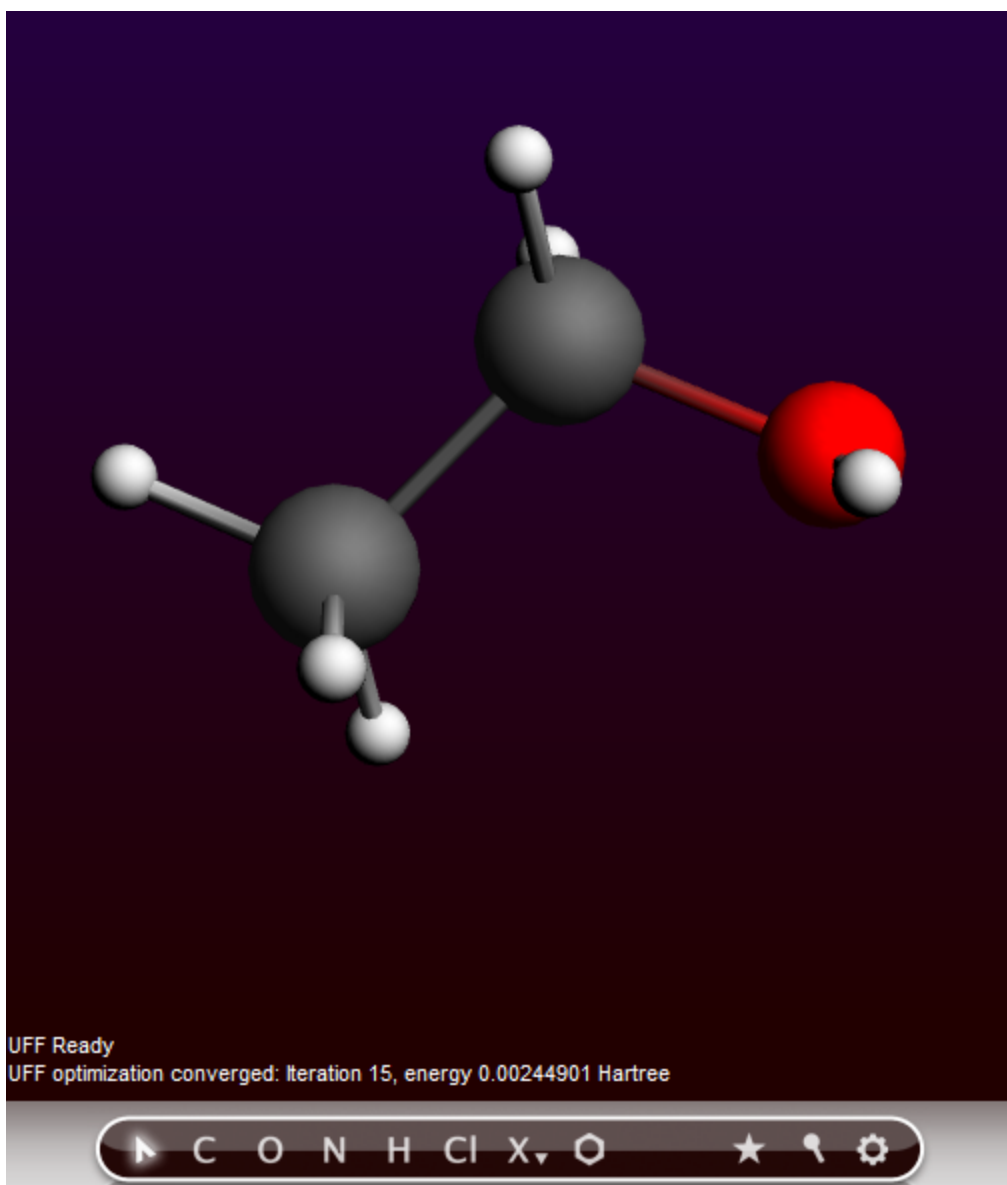


Note that this way you started bonding mode again, as indicated by the bond to the mouse position.

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



Once again you have created an ethanol molecule.

Step 3: Select calculation options

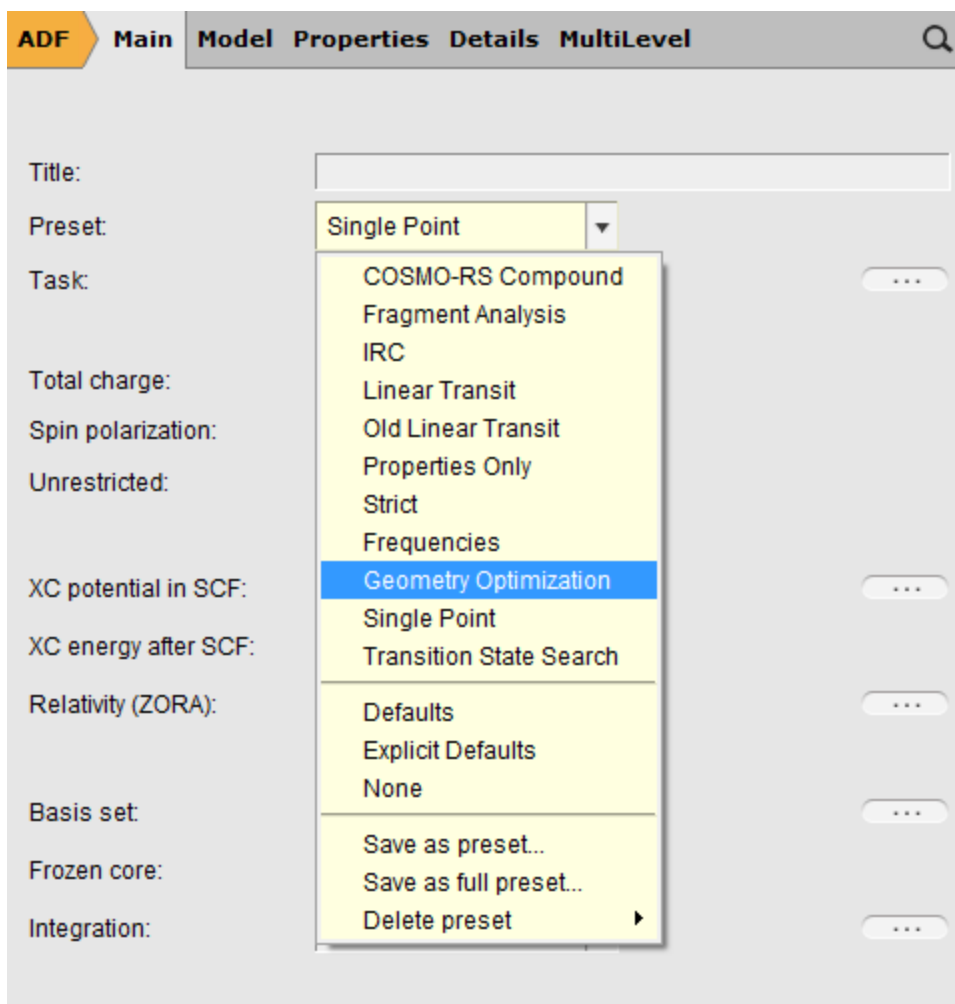
Preset

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.

ADF Main Model Properties Details MultiLevel Q

Title:	<input type="text" value="Ethanol"/>	
Preset:	<input type="text" value="Geometry Optimization"/>	▼
Task:	<input type="text" value="GeometryOptimization"/>	<input type="button" value="..."/>
Total charge:	<input type="text" value="0.0"/>	
Spin polarization:	<input type="text" value="0.0"/>	
Unrestricted:	<input type="checkbox"/> Yes	
XC potential in SCF:	<input type="text" value="LDA"/>	▼ <input type="button" value="..."/>
XC energy after SCF:	<input type="text" value="Default"/>	▼
Relativity (ZORA):	<input type="text" value="None"/>	▼ <input type="button" value="..."/>
Basis set:	<input type="text" value="DZ"/>	▼ <input type="button" value="..."/>
Frozen core:	<input type="text" value="Large"/>	▼
Integration:	<input type="text" value="Becke"/>	▼ <input type="button" value="..."/>

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

ADF Main Model Properties Details MultiLevel Q

Title:	<input type="text" value="Ethanol"/>	
Preset:	<input type="text" value="Geometry Optimization"/>	▼
Task:	<input type="text" value="GeometryOptimization"/>	<input type="button" value="..."/>
Total charge:	<input type="text" value="0.0"/>	
Spin polarization:	<input type="text" value="0.0"/>	
Unrestricted:	<input type="checkbox"/> Yes	
XC potential in SCF:	<input type="text" value="LDA"/>	▼ <input type="button" value="..."/>
XC energy after SCF:	<input type="text" value="LDA+GGA+METAGGA"/>	▼
Relativity (ZORA):	<input type="text" value="None"/>	▼ <input type="button" value="..."/>
Basis set:	<input type="text" value="DZ"/>	▼ <input type="button" value="..."/>
Frozen core:	<input type="text" value="Large"/>	▼
Integration:	<input type="text" value="Becke"/>	▼ <input type="button" value="..."/>

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

ADF Main Model Properties Details MultiLevel Q

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: Becke ▼ ...

Integration

The ADF software package uses a numerical integration scheme for virtually everything it may calculate. A numerical integration scheme generates some kind of grid (and corresponding weights). ADF and BAND have always been using the teVelde (Voronoi) integration scheme. For many calculations the Becke integration grid works better, so in ADF2013 the Becke integration grid method has been added. It now is the default method, and normally you should use the Becke grid option.

In the integration pull-down menu you select what kind of grid to use. For Becke grids you can use the default, or request a specific quality. For teVelde grids you can specify the integration accuracy parameter. That number is roughly the number of significant digits in your results.

Increasing the quality of the grid, or the accuracy parameter makes the results more accurate, but will require substantially more computation time.

Similarly, decreasing the quality 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.

Properties	Details	MultiLevel	Model	Properties	Details	MultiLevel	Details	MultiLevel
ESR, EPR, EFG, ZFS			Coordinates				Accuracy	
ETS-NOCV			Electric Field				ARH Details	
Excitations, CD			Geometry Constraints and Scan				Basis	
Excited State Geometry			Intrinsic Reaction Coordinate (IRC)				COSMO	
Franck-Condon Spectrum			Linear Transit (Old)				Files (Restart)	
Hyperpolarizability			Regions				Frequencies (IR)	
Localized Orbitals, NBO			Solvation				Geometry Convergence	
Magnetizability, Verdet			Spin and Occupation				Integration teVelde	
MCD			Transition State Search				Integration Becke	
NMR							NMR Details	
ORD (Optical Rotatory Dispersion)							Output Details	
Other: Etot, Bader, Charge Transport, ...							Relativity	
Polarizability							SCF	
Raman, VROA							SCF Convergence Details	
VanDerWaals							Select Excitations	
VCD							Symmetry	
Thermodynamics							Technical	
							User Input	
							XC Details	
							Z-Matrix	

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.

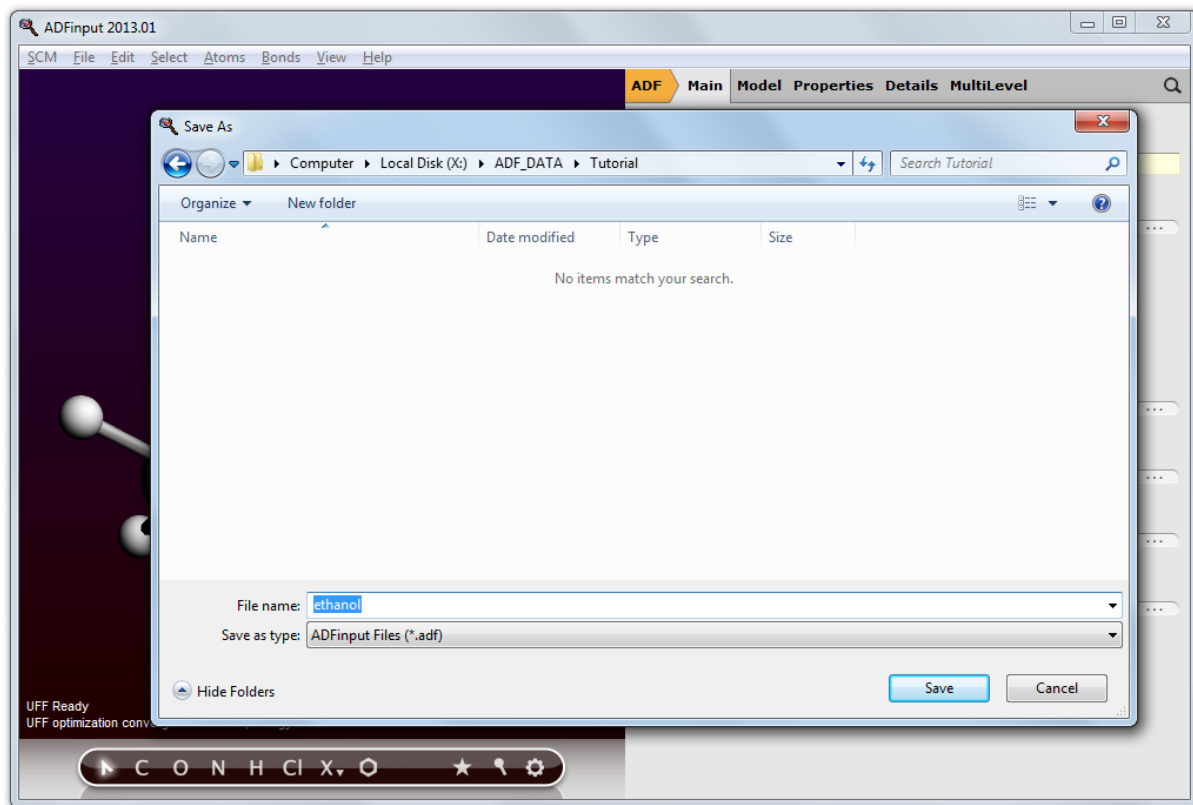
Step 4: Run your calculation

Save your input and create a job script

Finally you will want to save your input.

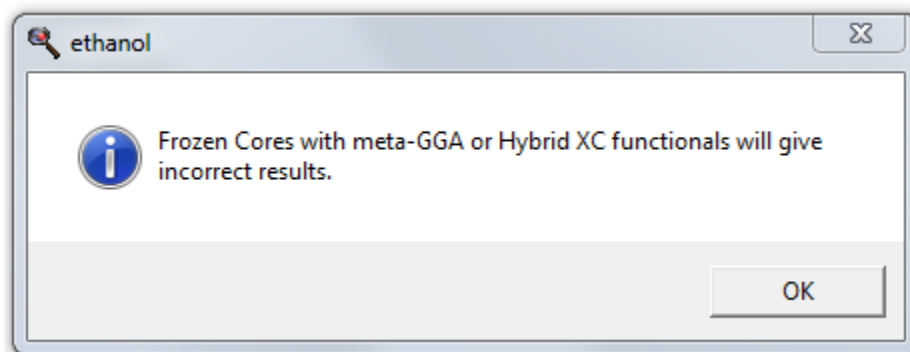
Select the **File** → **Save** command.

Enter the name 'ethanol' in the Filename field.



Click on Save

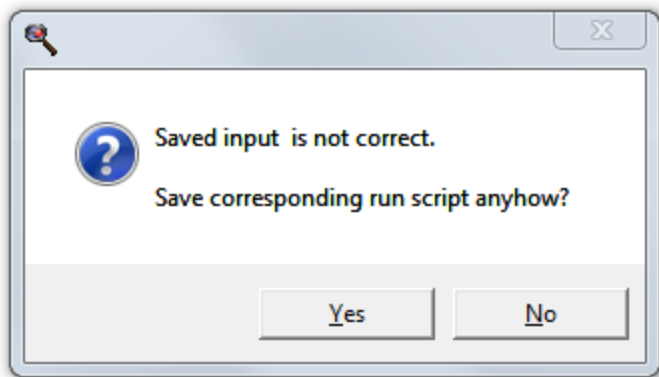
ADFinput will now present a warning dialog:



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:



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'.

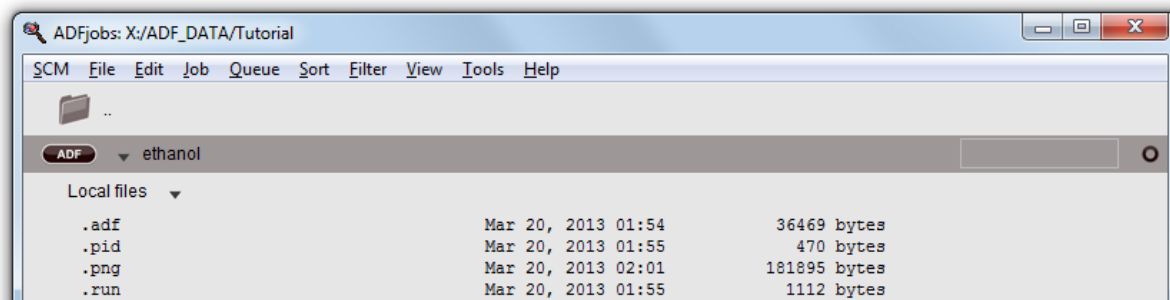
ADFinput has also created a corresponding script file. This script file has the same name, but with an extension '.run' instead of '.adf'.

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.



Run your calculation

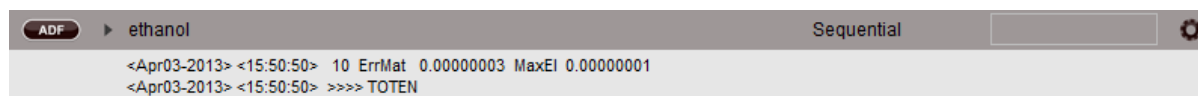
To actually perform the calculation (the geometry optimization of the ethanol molecule), use the **Job** → **Run** menu command in ADFjobs:

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 than one job at the same time, they will be run one after another.

Once your job starts running, ADFjobs will show the progress of the calculation: the last few lines of the logfile:



Note that while running, the job status symbol in ADFjobs changes.

If you wish to see the full logfile while the calculation is running, just click on the logfile lines displayed in the ADFjobs window:

Click on the logfile lines in the ADFjobs window

Now the logfile is showing in the ADFtail window:

```

ADFTail: ethanol.logfile
SCM File Edit Help
<Mar20-2013> <02:03:46>      8 ErrMat  0.00000009 MaxEl  0.00000005
<Mar20-2013> <02:03:46> >>>> TOTEN
<Mar20-2013> <02:03:46> >>>> POPAN
<Mar20-2013> <02:03:46> >>>> DEBYE
<Mar20-2013> <02:03:46> >>>> AMETS
<Mar20-2013> <02:03:46> >>>> ENGRAD
<Mar20-2013> <02:03:46> current energy                -2.14768059 Hartree
<Mar20-2013> <02:03:46> energy change                    -0.00000087  0.00100000  T
<Mar20-2013> <02:03:46> constrained gradient max         0.00013832  0.00100000  T
<Mar20-2013> <02:03:46> constrained gradient rms         0.00005383  0.00066667  T
<Mar20-2013> <02:03:46> gradient max                      0.00013832
<Mar20-2013> <02:03:46> gradient rms                       0.00005383
<Mar20-2013> <02:03:46> cart. step max                    0.00017049  0.01000000  T
<Mar20-2013> <02:03:46> cart. step rms                    0.00006365  0.00666667  T
<Mar20-2013> <02:03:46> GEOMETRY CONVERGED
<Mar20-2013> <02:03:46> Calculating Energy Terms for Final Geometry
Coordinates in Geometry Cycle 5
Atom      X      Y      Z (Angstrom)
1.C      -4.766082  -5.981575  0.000000
2.C      -3.728890  -4.843254  0.000000
3.O      -2.409126  -5.456135  0.000000
4.H      -4.637399  -6.609259  -0.891084
5.H      -5.782776  -5.568039  0.000000
6.H      -4.637399  -6.609259  0.891084
7.H      -1.808532  -4.617844  0.000000
8.H      -3.897792  -4.198620  0.896041
9.H      -3.897792  -4.198620  -0.896041
<Mar20-2013> <02:03:46> >>>> CORORT
<Mar20-2013> <02:03:46> >>>> FITINI
<Mar20-2013> <02:03:46> >>>> CLSMAT
<Mar20-2013> <02:03:46> >>>> ORTHON
<Mar20-2013> <02:03:46> >>>> GENPT
<Mar20-2013> <02:03:46> Block Length= 128
<Mar20-2013> <02:03:46> >>>> PTBAS
<Mar20-2013> <02:03:46> >>>> CYCLE
<Mar20-2013> <02:03:46>      1
<Mar20-2013> <02:03:46>      2 ErrMat  0.00000000 MaxEl  0.00000000
<Mar20-2013> <02:03:46> SCF converged
<Mar20-2013> <02:03:50>      3 ErrMat  0.00000000 MaxEl  0.00000000
<Mar20-2013> <02:03:51> >>>> TOTEN
<Mar20-2013> <02:03:51> >>>> POPAN
<Mar20-2013> <02:03:51> >>>> DEBYE
<Mar20-2013> <02:03:51> >>>> AMETS
<Mar20-2013> <02:03:51> >>>> POPUL
<Mar20-2013> <02:03:53> Bond Energy                -2.14768058 a.u.
<Mar20-2013> <02:03:53> Bond Energy                -58.44136222 eV
<Mar20-2013> <02:03:53> Bond Energy                -1347.69 kcal/mol
<Mar20-2013> <02:03:53> NORMAL TERMINATION
<Mar20-2013> <02:03:53> END
Job ethanol has finished

```

Step 5: Results of your calculation

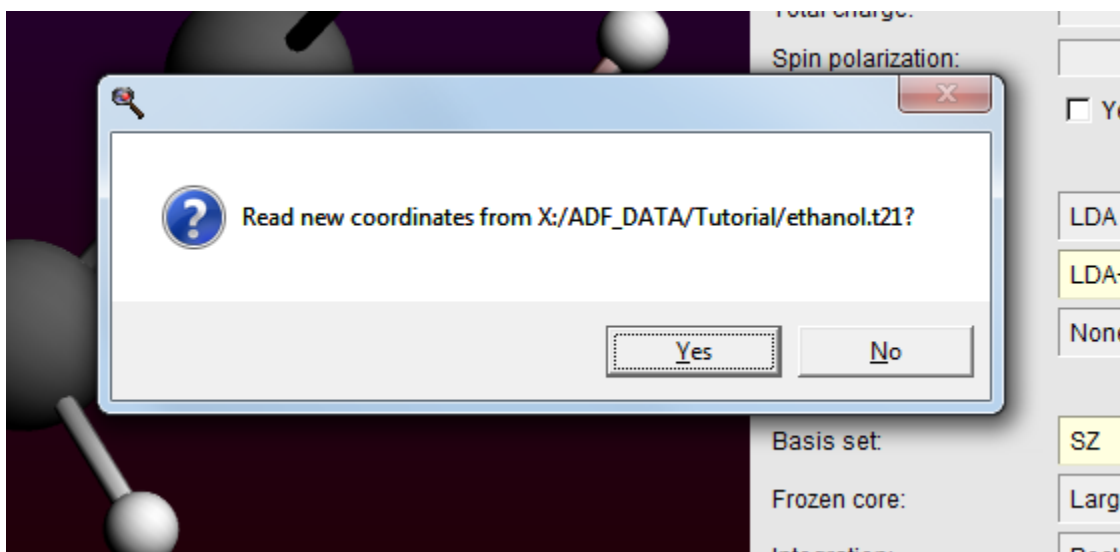
Logfile: ADFTail

The logfile is saved and extended by ADF as it is running. Normally it is most convenient to view it only in the ADFjobs window to prevent screen clutter.

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

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

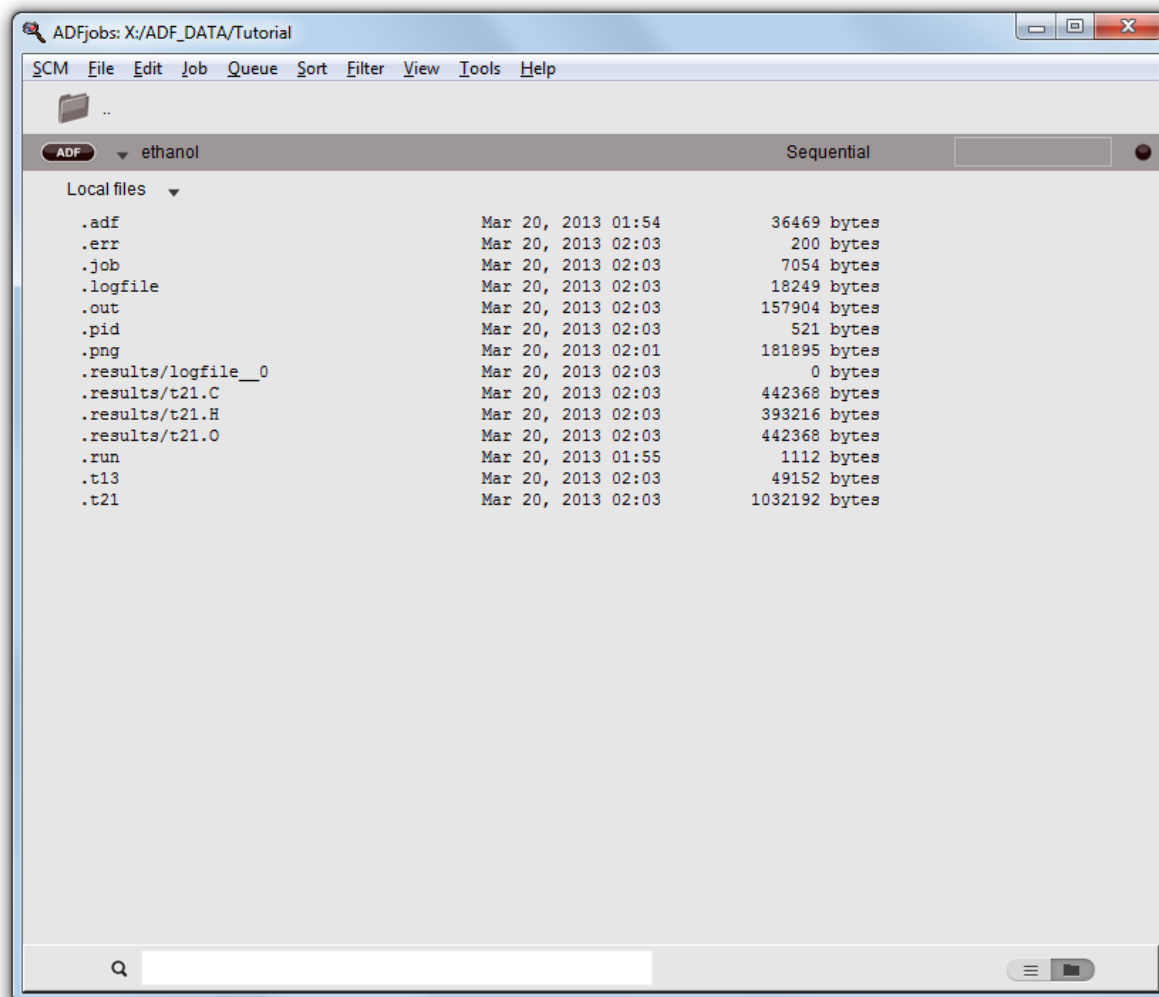


Now close ADFtail by using the **File** → **Close** menu command:

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

Select the **File** → **Close** command

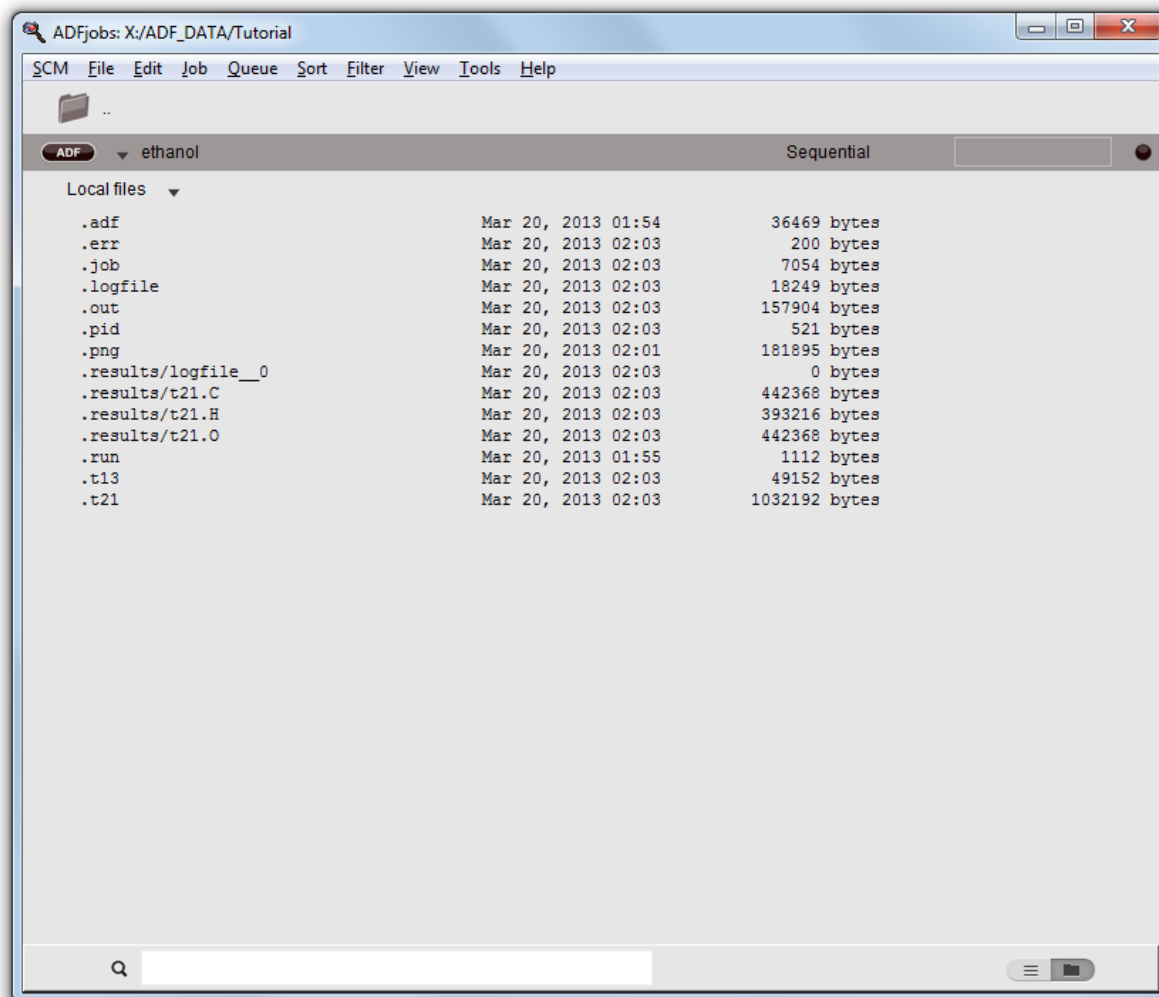
In the ADFjobs window, note that the job status icon has changed to indicate that the job is ready:



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



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 lose any changes you made when editing the .run file).

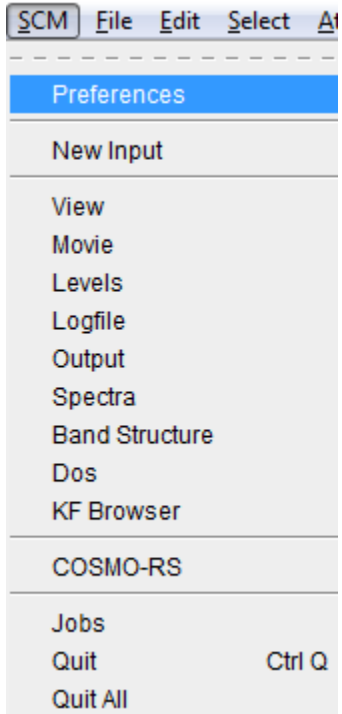
The .job file is a script file based on the .run file, and is created by ADFjobs. It contains all commands required to run your job, and is actually run by ADFjobs when you use the Run command.

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.

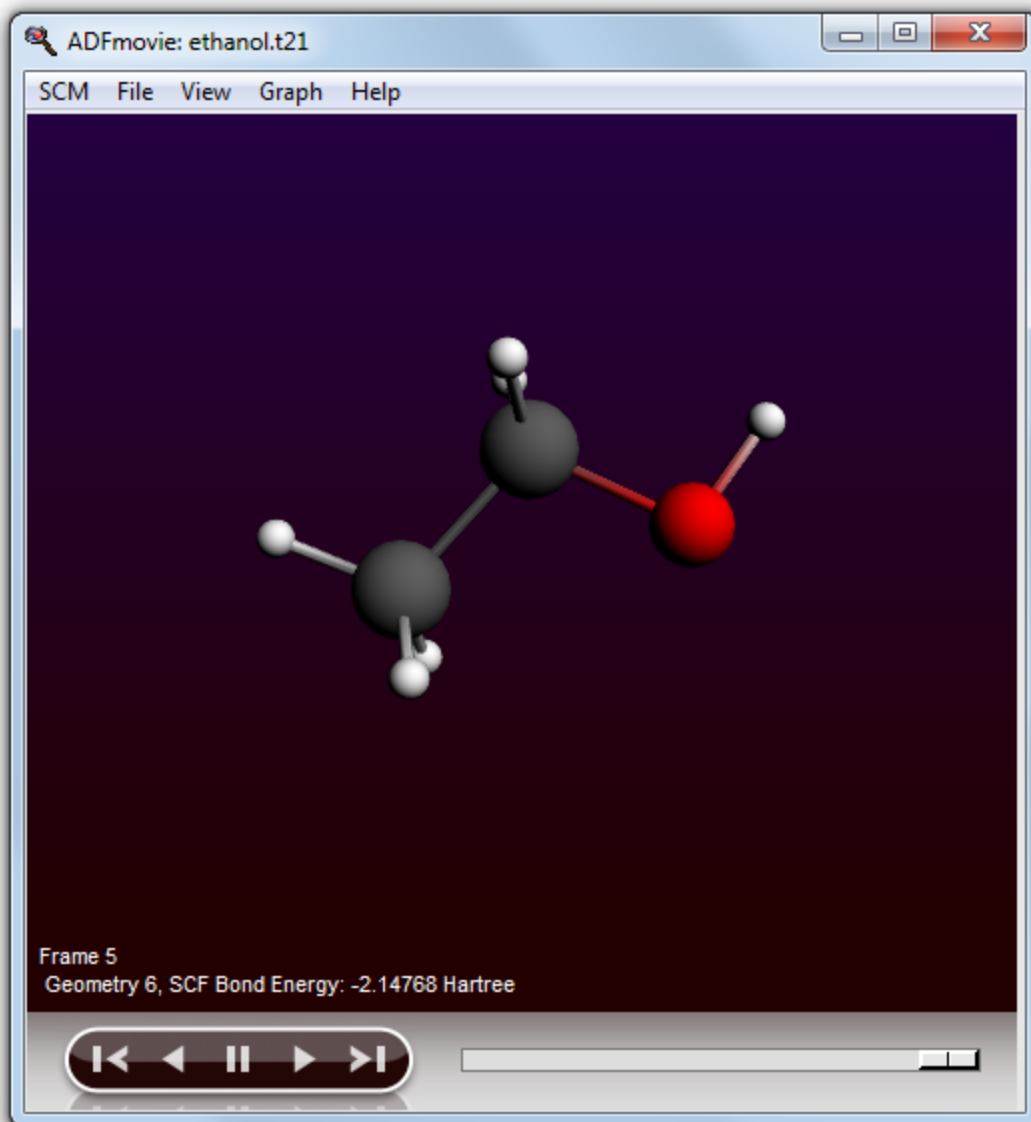
Geometry changes: ADFmovie

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.

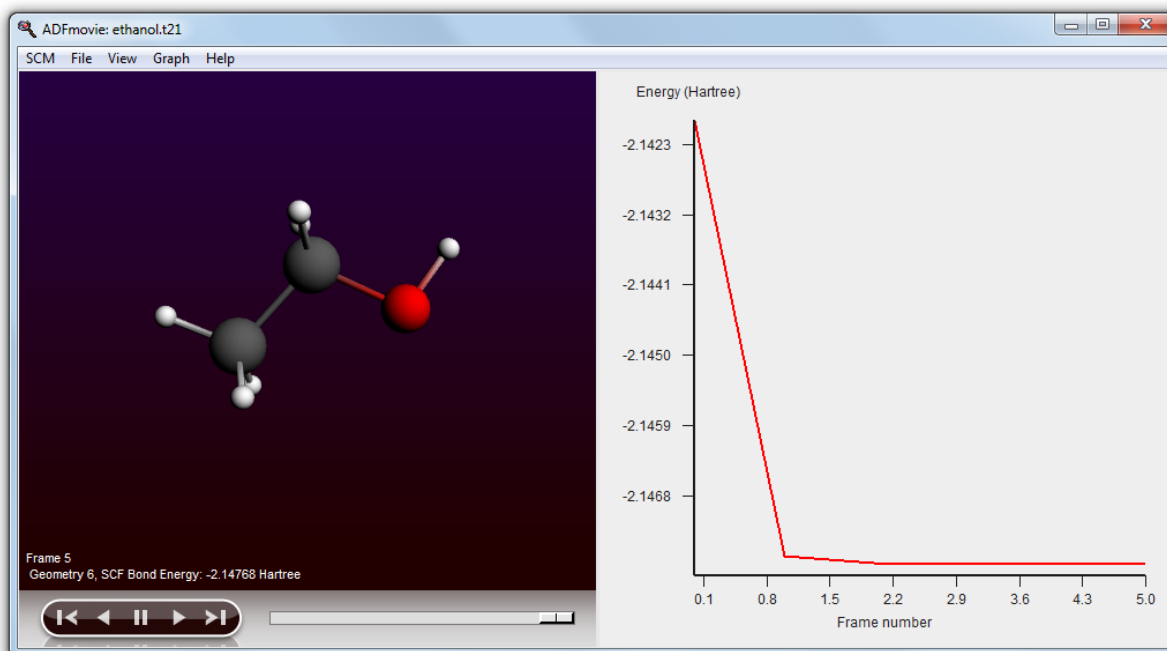


To step through the different geometries, use the slider below the picture. Clicking in the slider will single step through the frames. Alternatively you can grab the slider and move to the frame you wish, or you can use the left and right arrow keys to single step through the frames.

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

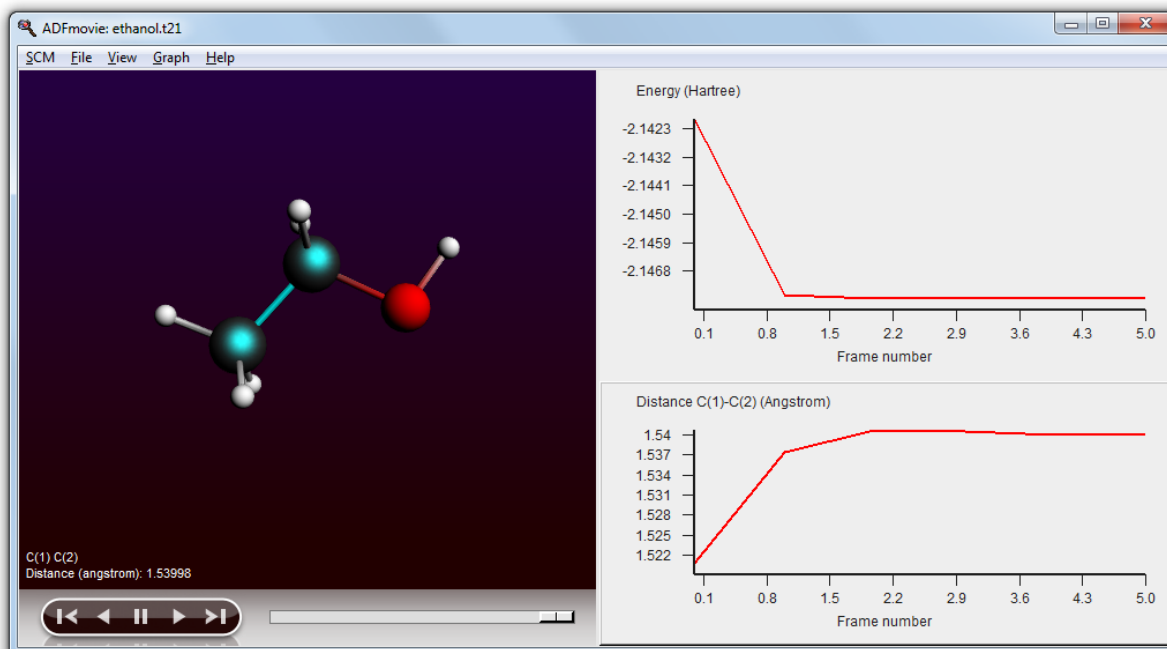


You can even show several graphs for different properties at the same time:

Use the **Graph** → **Add Graph** menu command

Select two carbon atoms by shift-clicking on them

Use the **Graph** → **Distance, Angle, Dihedral** menu command



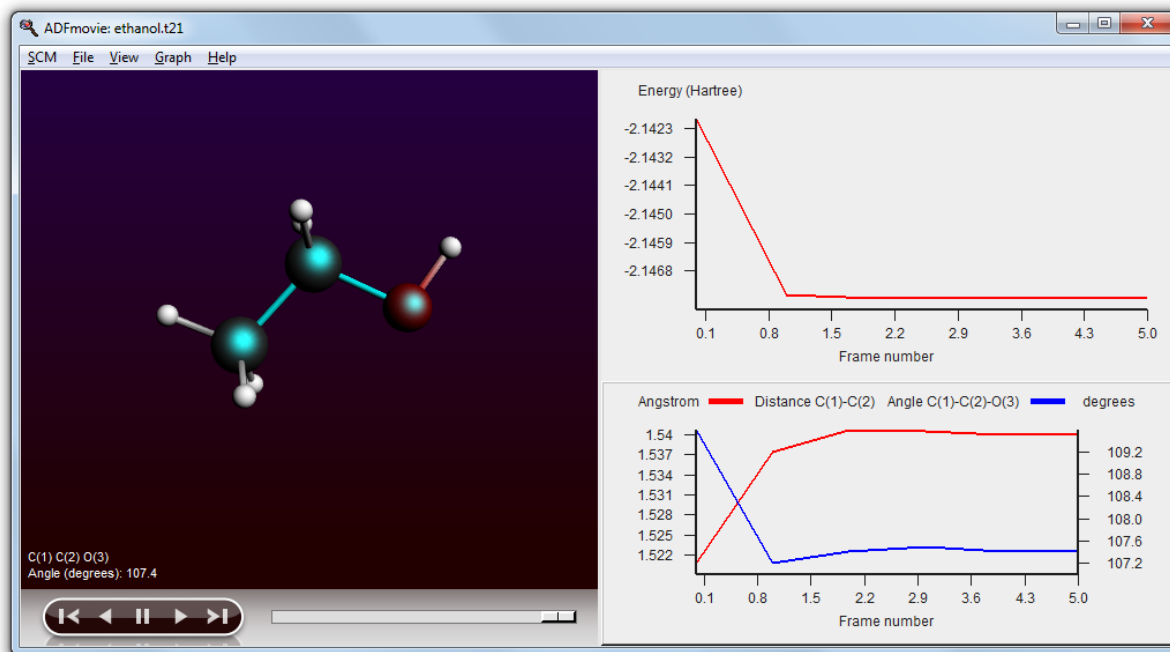
Now you have two graphs. One of them is the 'active' graph. When you make a new graph it will always be the active graph. You can also make a graph active by clicking on it.

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-axis. 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



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 than one graph the corresponding point(s) will also be marked in the other graphs.

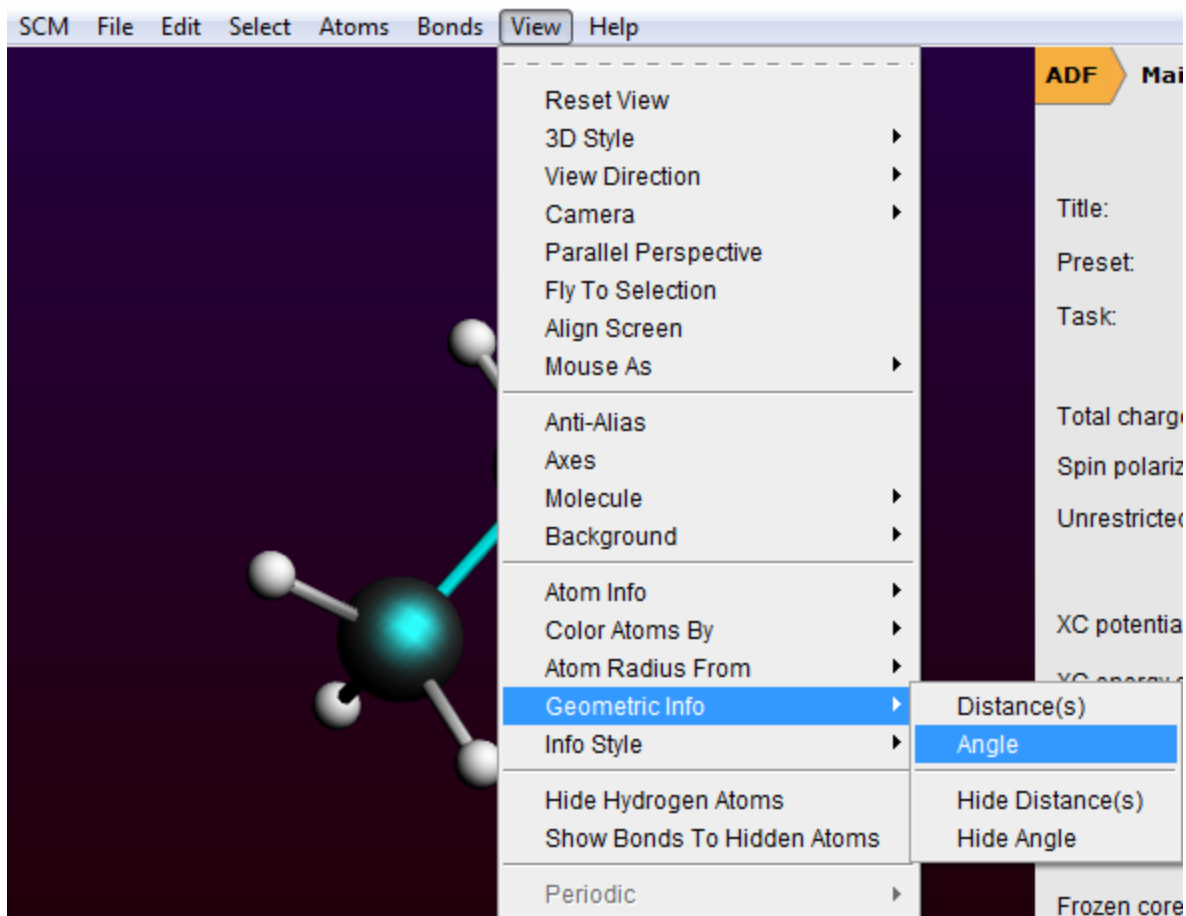
To rotate, translate, or zoom the picture, use your mouse, just as in ADFinput.

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

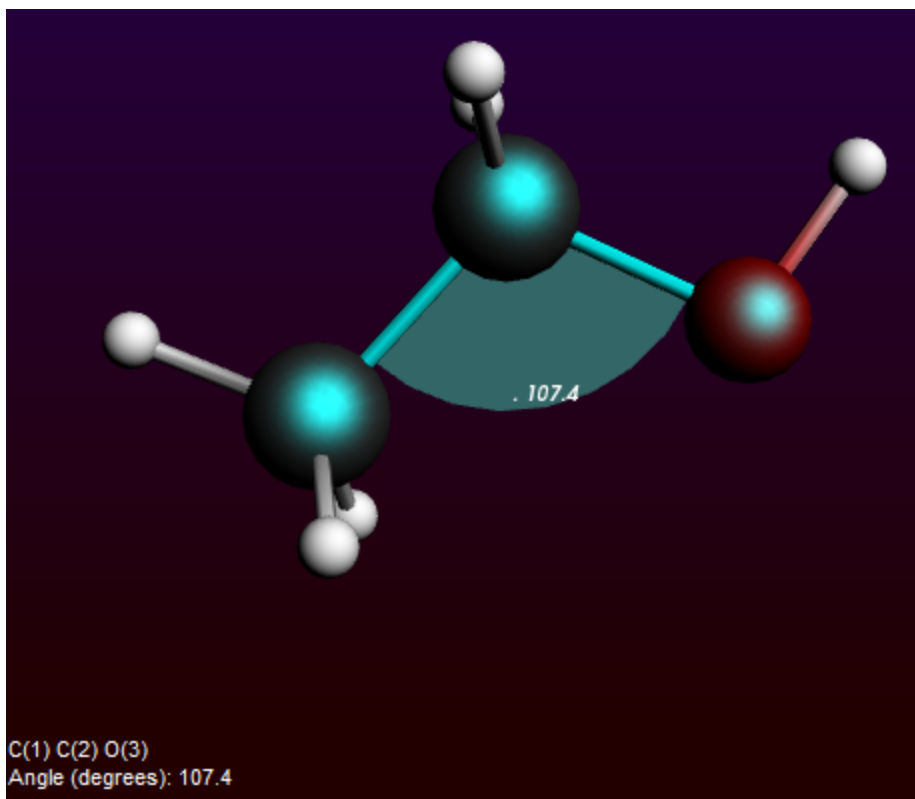
Selecting atoms provides information about atoms, bonds, etc. The information will be updated when you go to another point in the movie (a different geometry). You can see examples of these in the pictures above.

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 :

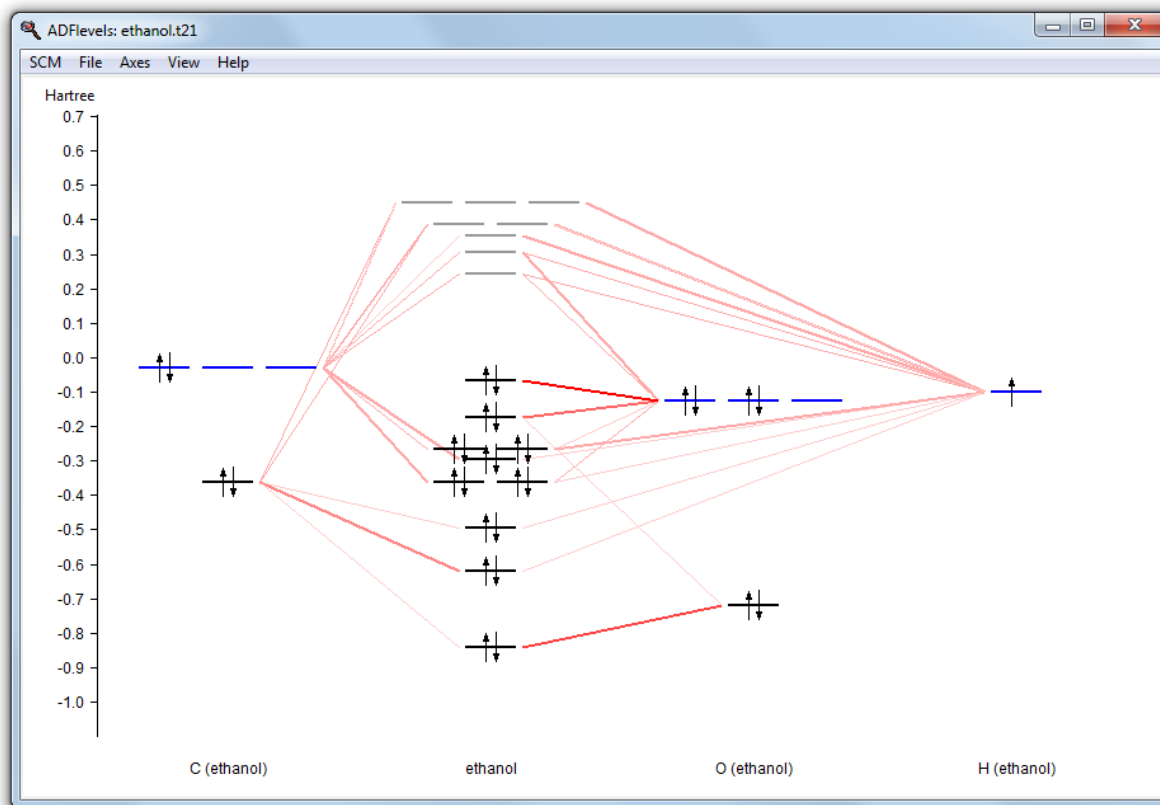


In the ADFmovie window: select **File** → **Close**

Orbital energy levels: ADFlevels

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

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

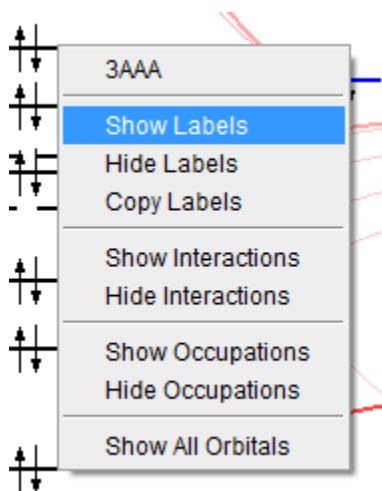


In the diagram you can see from what fragment types the molecular levels are composed.

Move the mouse around, above different levels, without clicking

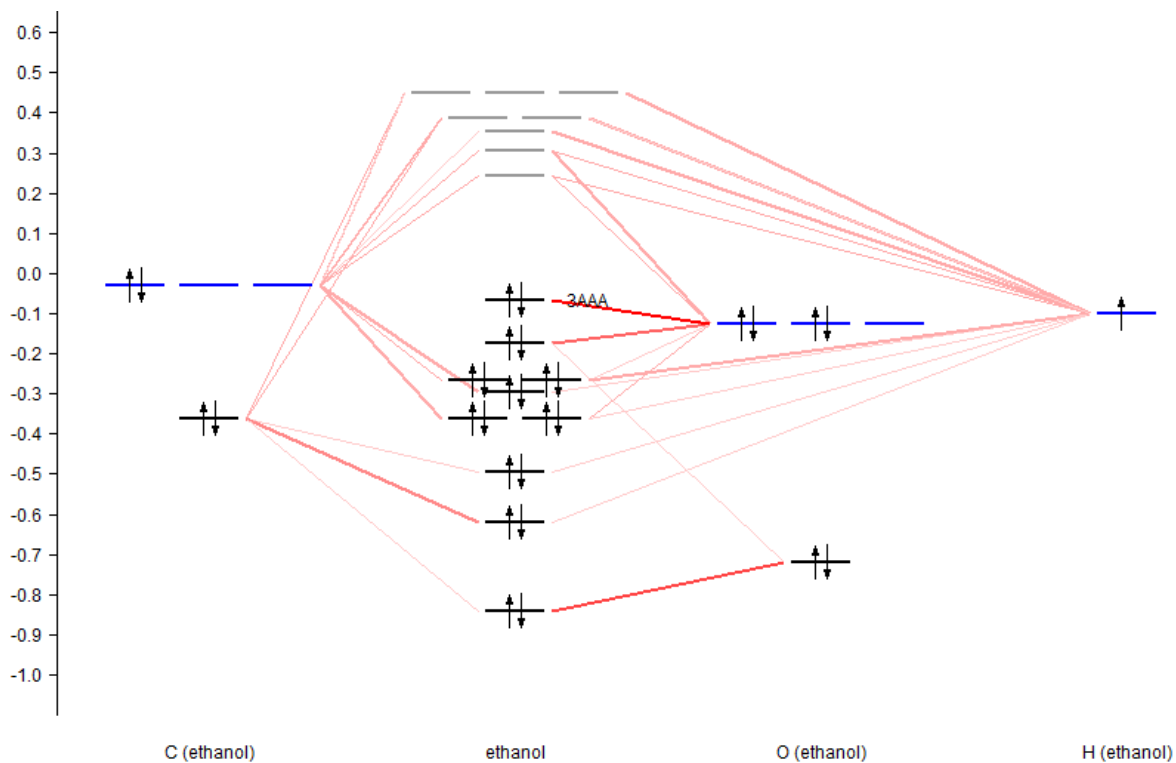
Balloons will pop up with information about the level at the mouse position: The MO number, eigenvalue, occupation, and how it is composed of SFOs (fragment orbitals).

Click and hold on the HOMO level of the molecule



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

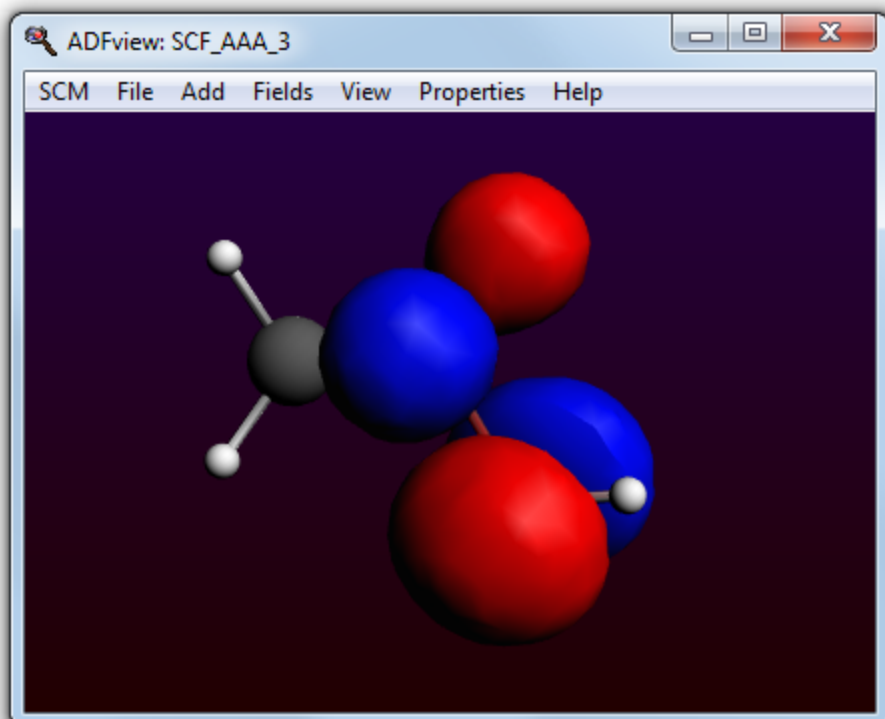
Click and hold on the HOMO of the O fragment type
In the pop-up, select 'Show Labels'



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.



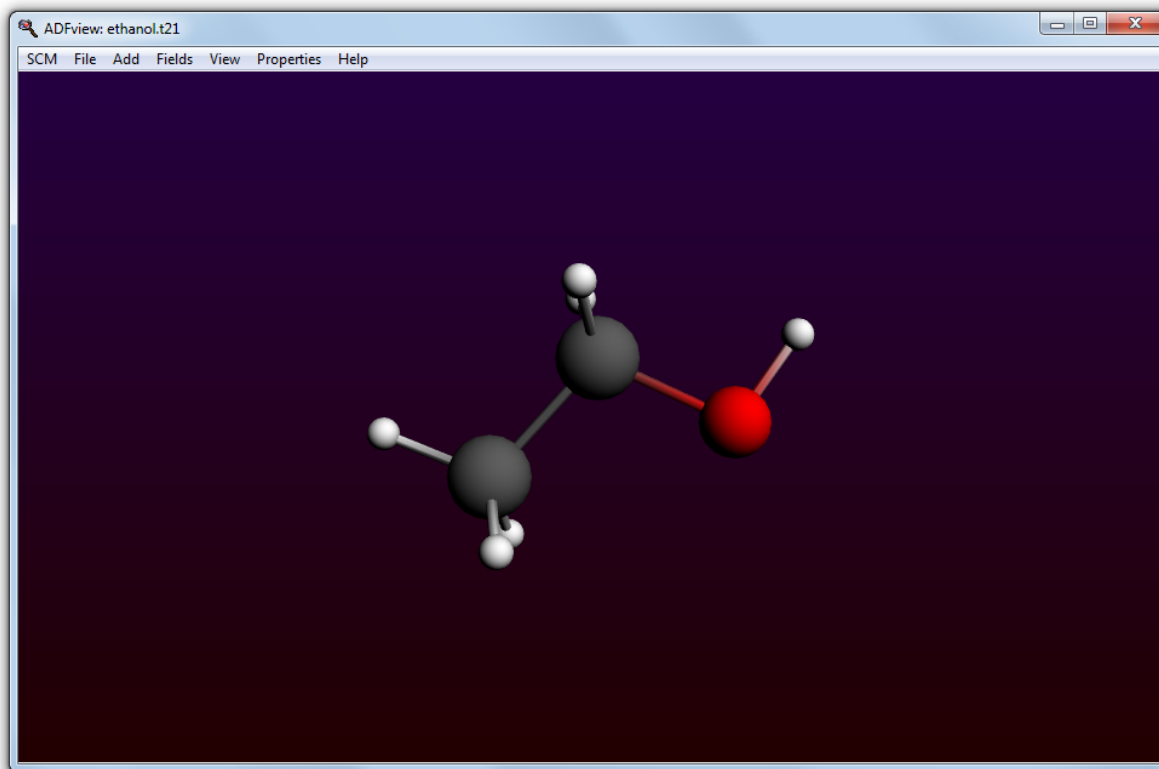
You can move (rotate, translate and zoom) the orbital with your mouse.

Close the window showing the orbital: **File** → **Close** (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.

In the Properties menu there are some pre-defined things to visualize: density, spin-density, HOMO, LUMO and more. If you select one of these, you will see the corresponding item immediately. However, ADFview can do much more and gives you lots of control.

For example, lets show a density isosurface, colored by the electrostatic potential:

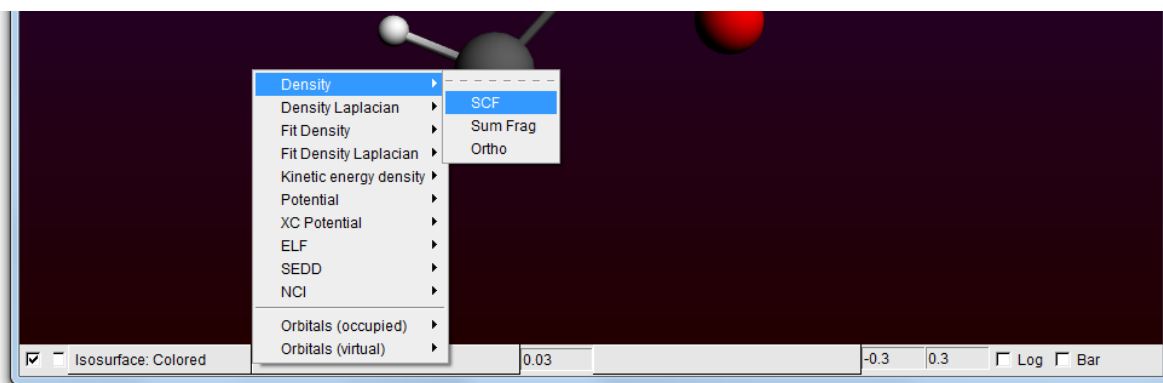
Select the **Add** → **Isosurface: Colored** command

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.

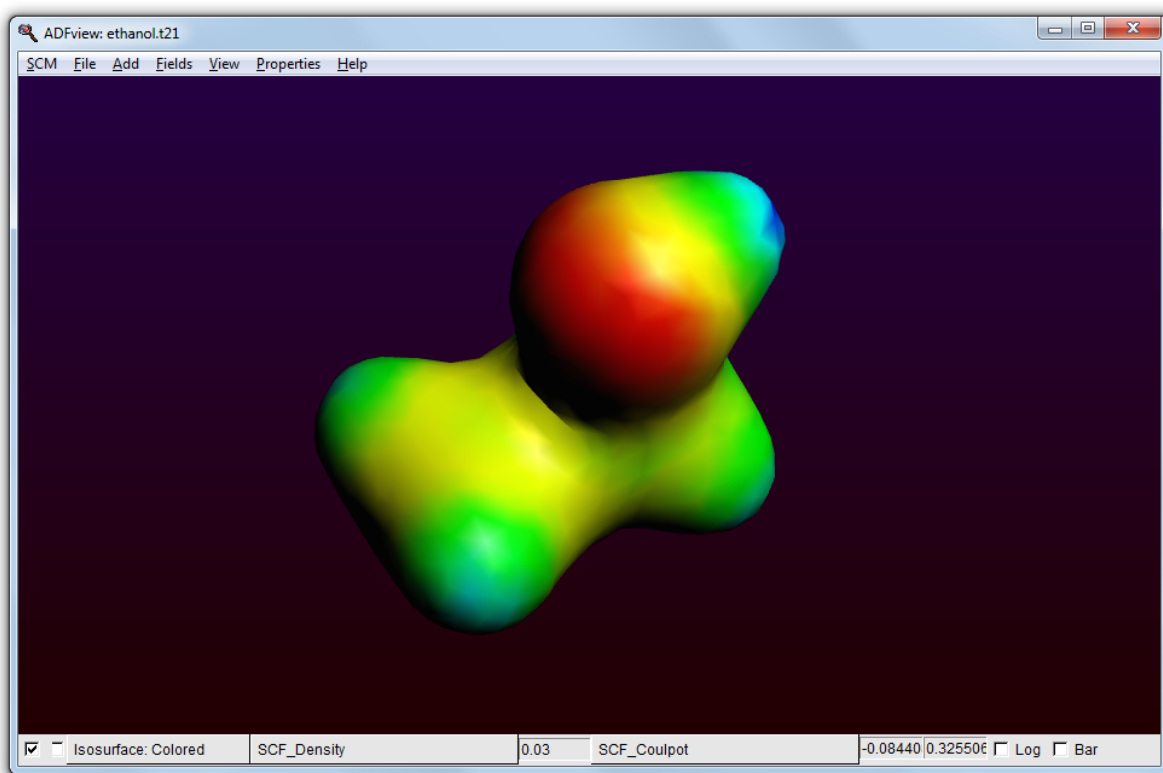


In this particular case the control line contains two pull-down menus that you use to select the fields that you want to visualize.

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**

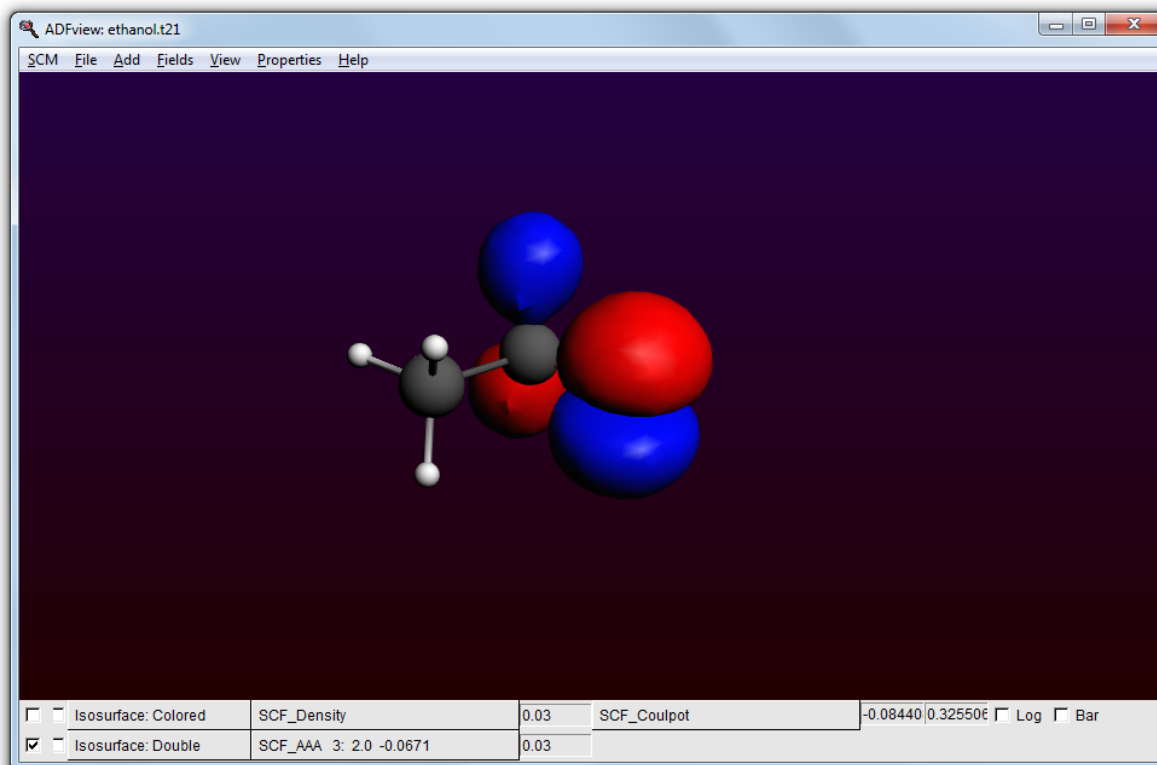


To demonstrate some other possibilities of ADFview, do the following:

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



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)

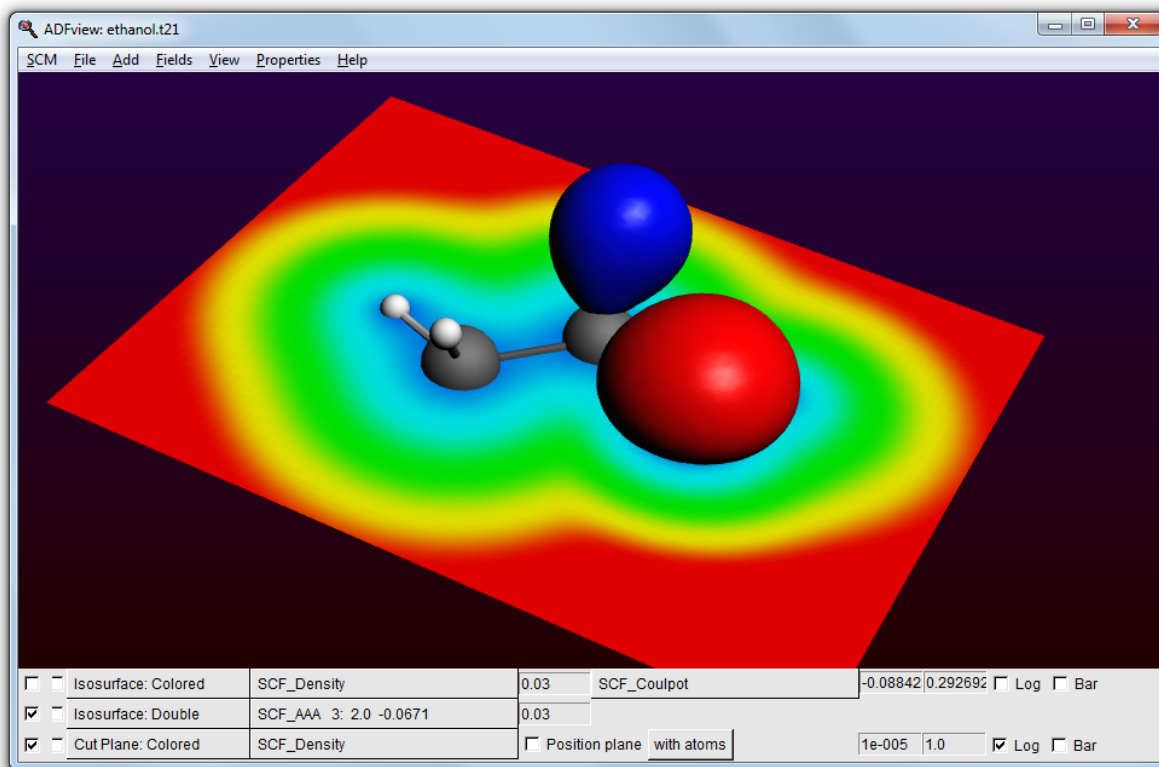
Click the 'with atoms' button next to the 'Position plane' option (thus the button, not the check box)

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



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 ADFview down significantly.

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:

```

ADFoutput: ethanol.out
SCM File Edit Help Iterations Properties Response Properties Other Properties Section Include
Geometry CYCLE 1
=====
Energy gradients wrt nuclear displacements
=====
Atom      Cartesian (a.u./angstrom)
          X      Y      Z
-----
1 C      0.023940  0.028594  0.000000
2 C      0.015784 -0.052219  0.000000
3 O      -0.035558  0.115846  0.000000
4 H      0.003073 -0.008134 -0.016554
5 H      -0.016098  0.008439  0.000000
6 H      0.003073 -0.008134  0.016554
7 H      -0.025776 -0.058148  0.000000
8 H      0.015781 -0.013121  0.000092
9 H      0.015781 -0.013121 -0.000092
-----

Geometry Convergence after Step 1      (Hartree/Angstrom, Angstrom)
-----
current energy                -2.14198838 Hartree
energy change                 -2.14198838      0.00100000  F
constrained gradient max      0.11584569      0.00100000  F
constrained gradient rms      0.03041022      0.00066667  F
gradient max                  0.11584569
gradient rms                   0.03041022
cart. step max                 0.06097344      0.01000000  F
cart. step rms                 0.02429677      0.00666667  F

Primitive Internal Coordinates (atoms in internal order)
-----
index  type  i  j  k  l  value(A,deg)  step
-----
1  bnd  2  9  0  0  1.11924576    0.00646221
2  bnd  2  8  0  0  1.11924576    0.00646221
3  bnd  2  3  0  0  1.45069204    0.05070661
4  bnd  1  6  0  0  1.09791529   -0.01280972
5  bnd  1  5  0  0  1.09784648   -0.01258581
6  bnd  1  4  0  0  1.09791529   -0.01280972
7  bnd  1  2  0  0  1.53744980    0.01663153
8  bnd  3  7  0  0  1.03193650    0.03952034
9  ang  6  1  5  0  108.74035848 -0.18241785
10 ang  6  1  4  0  108.54470376 -0.65345811
11 ang  6  1  2  0  110.41886559  0.39853809
12 ang  5  1  4  0  108.74035847 -0.18241787
13 ang  5  1  2  0  109.93055333  0.20563325
14 ang  4  1  2  0  110.41886558  0.39853808
15 ang  9  2  8  0  106.68290472 -2.33262761
16 ang  9  2  3  0  113.01952247  3.15494515
17 ang  9  2  1  0  108.39367578 -0.78345234

```

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** → **Quit 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 also 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

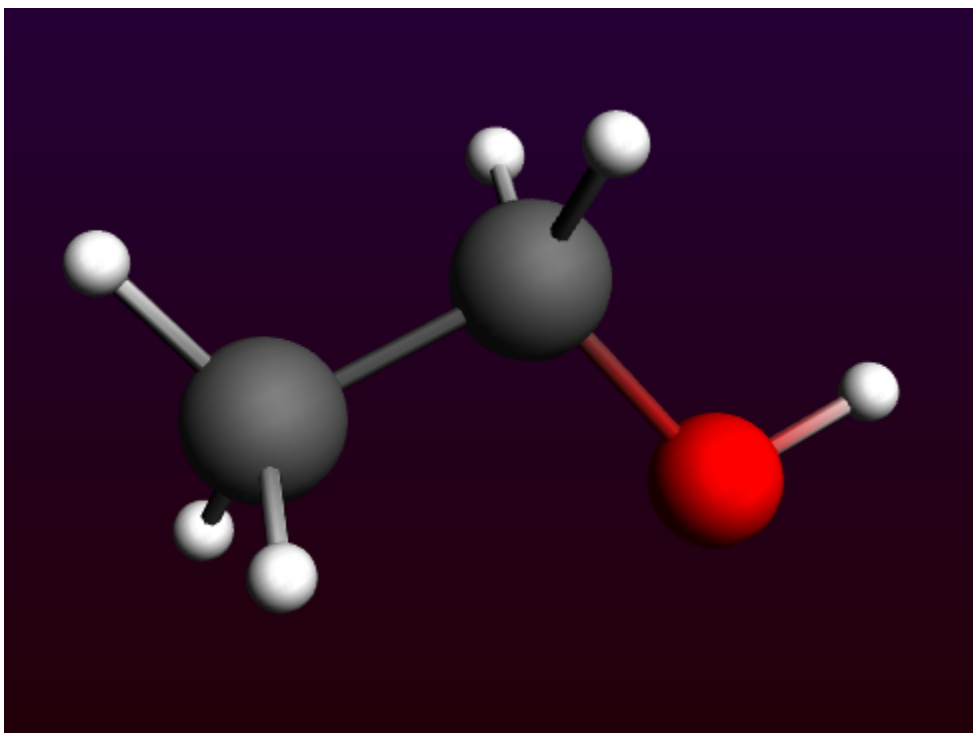
For this tutorial we again prefer to work in the Tutorial directory:

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

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:

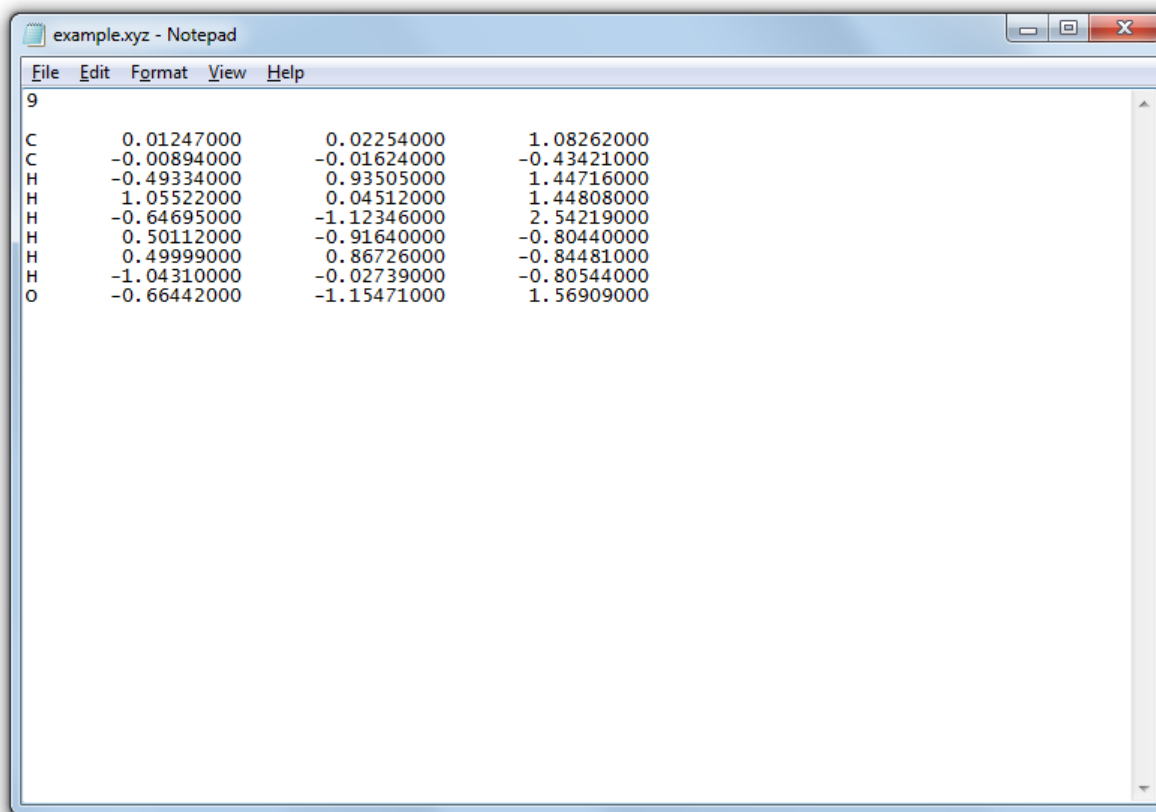
Use the **File** → **Export Coordinates...** menu command
Enter 'example.xyz' as filename
Click Save

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)

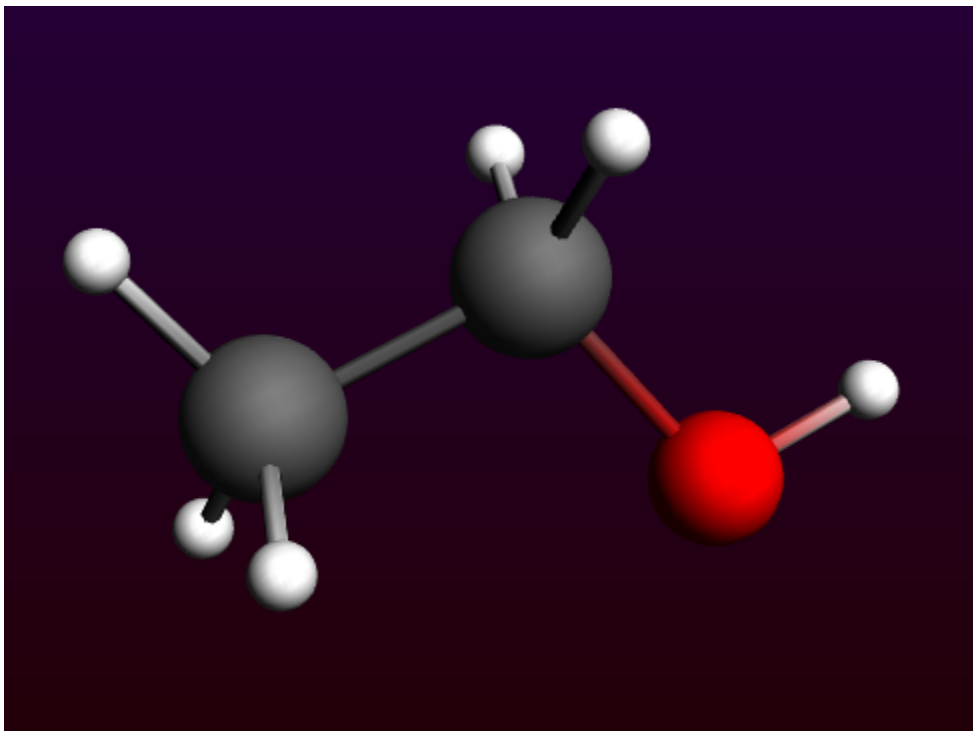


```
example.xyz - Notepad
File Edit Format View Help
9
C      0.01247000      0.02254000      1.08262000
C     -0.00894000     -0.01624000     -0.43421000
H     -0.49334000      0.93505000      1.44716000
H      1.05522000      0.04512000      1.44808000
H     -0.64695000     -1.12346000      2.54219000
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.

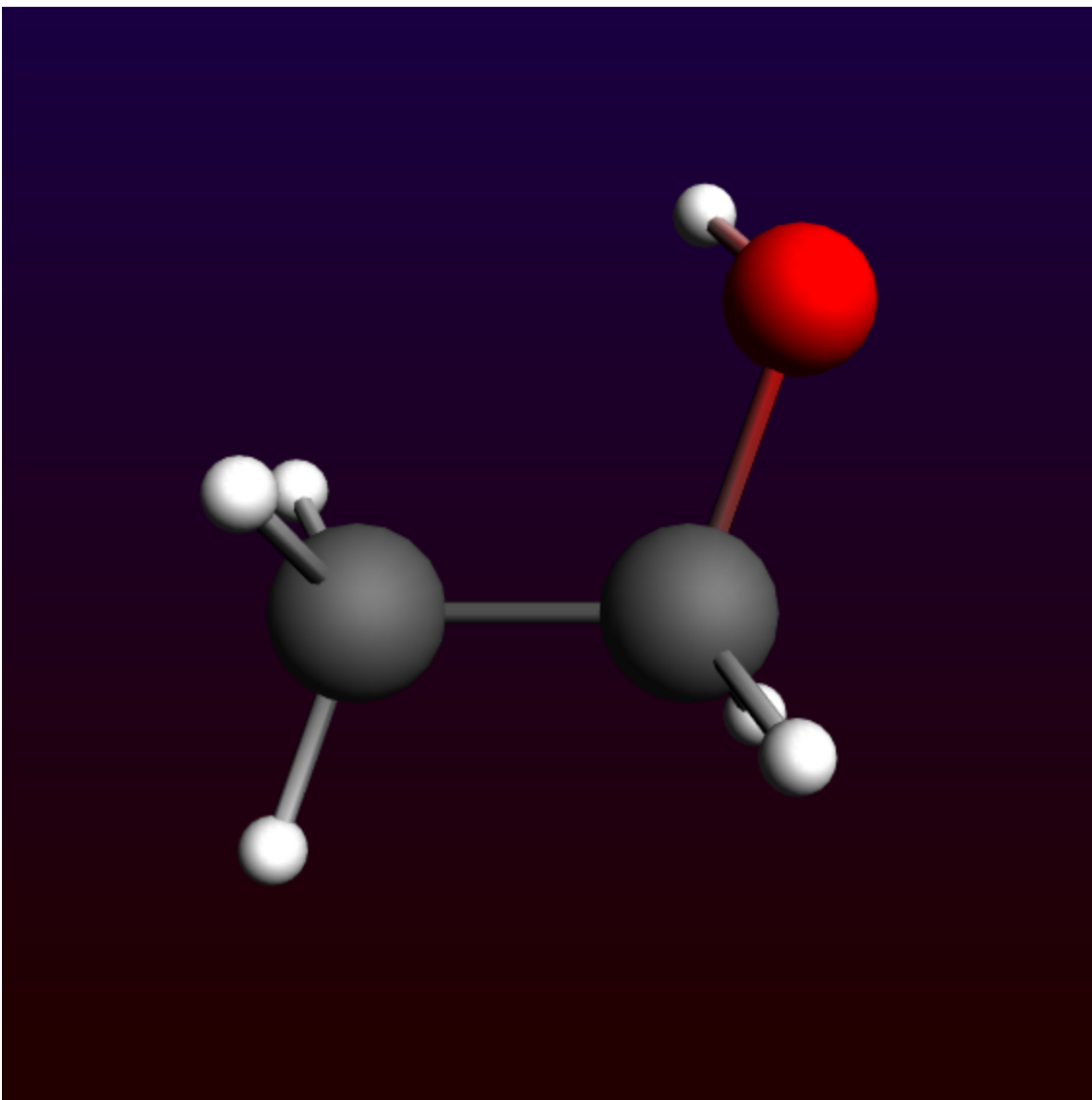
Step 4: Import SMILES string

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

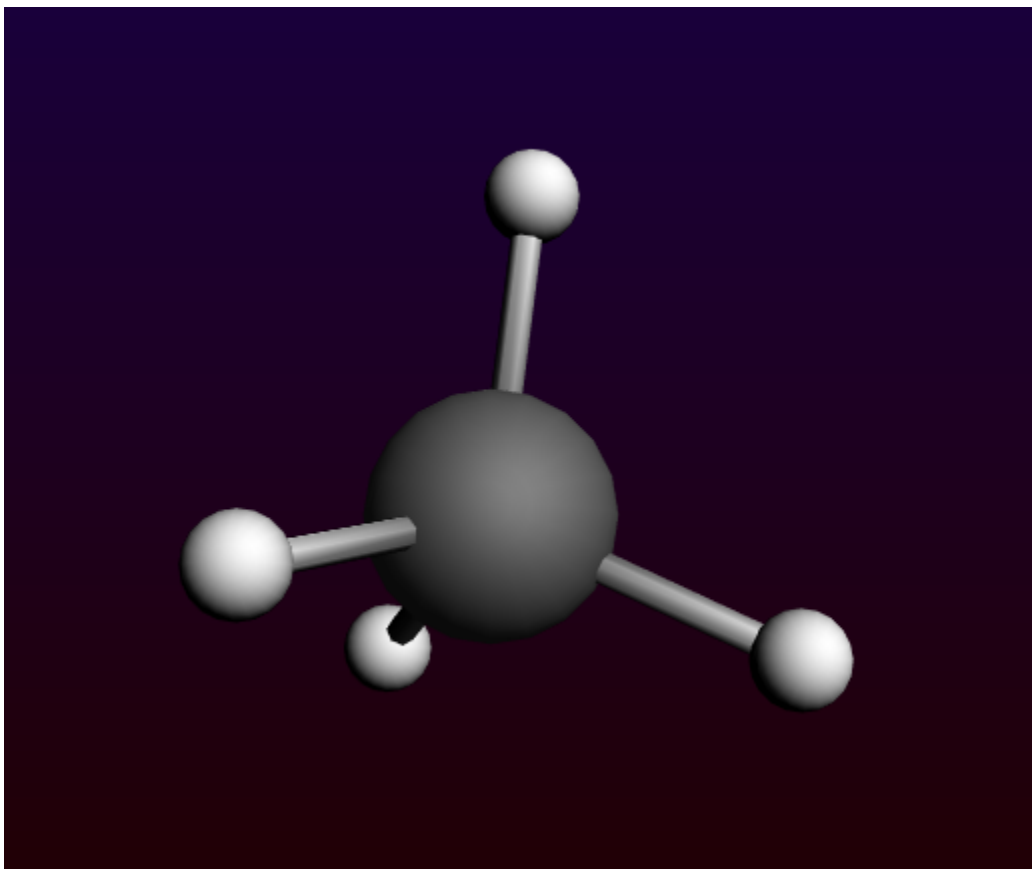
As a demonstration on how to use the structure tool, we start by building a methane molecule:

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 preferences](#).

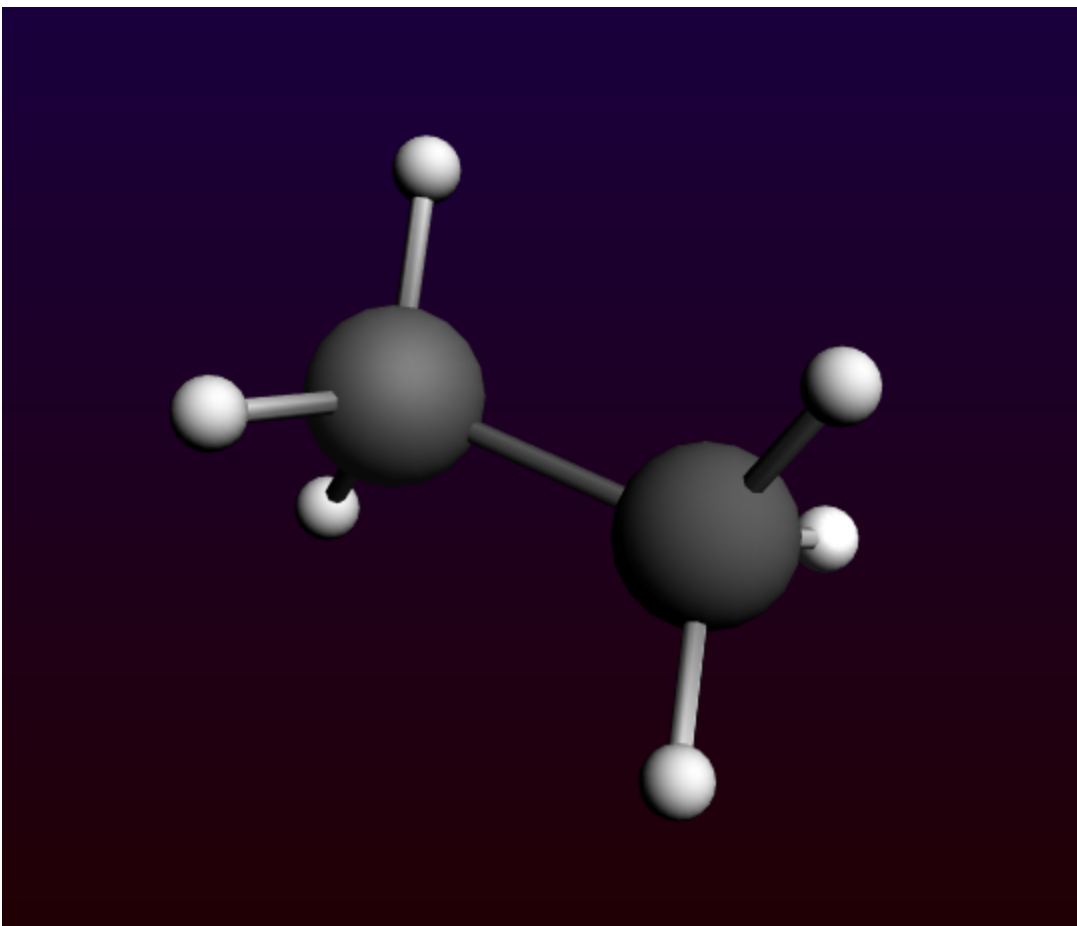


The next step is to add a methyl group, using the structures tool:

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

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)



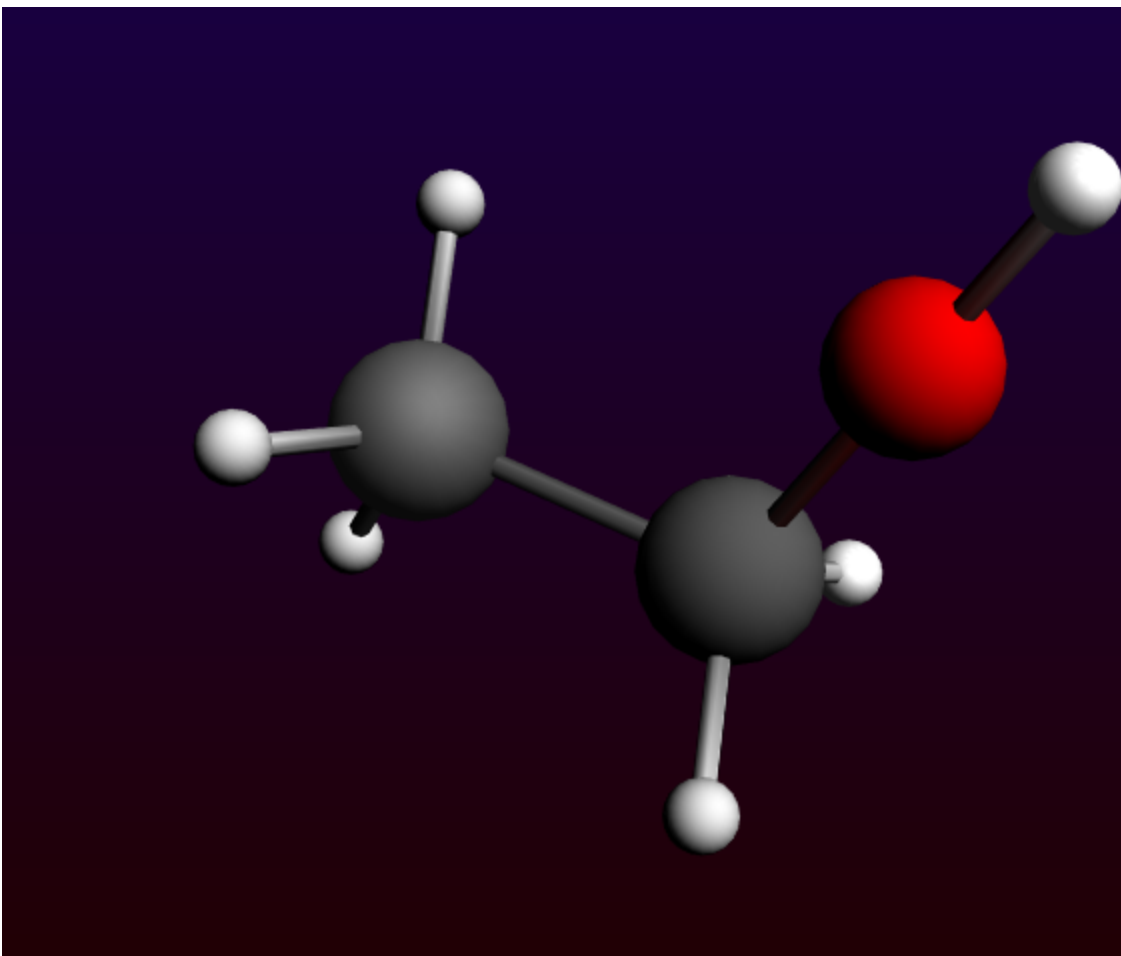
You will see that the hydrogen is replaced by a methyl group.

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.

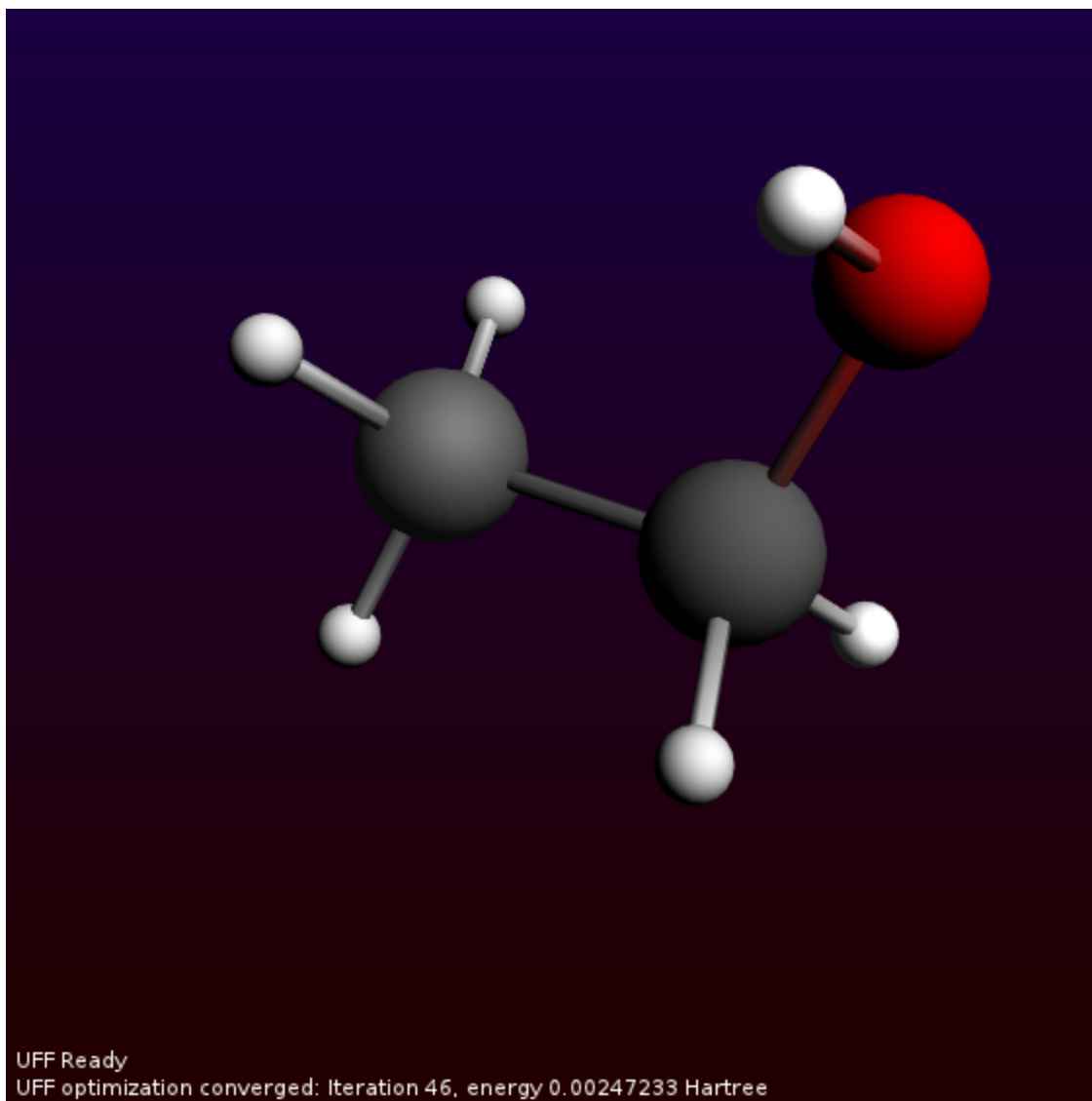
To create ethanol, we need to add a hydroxyl group:

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



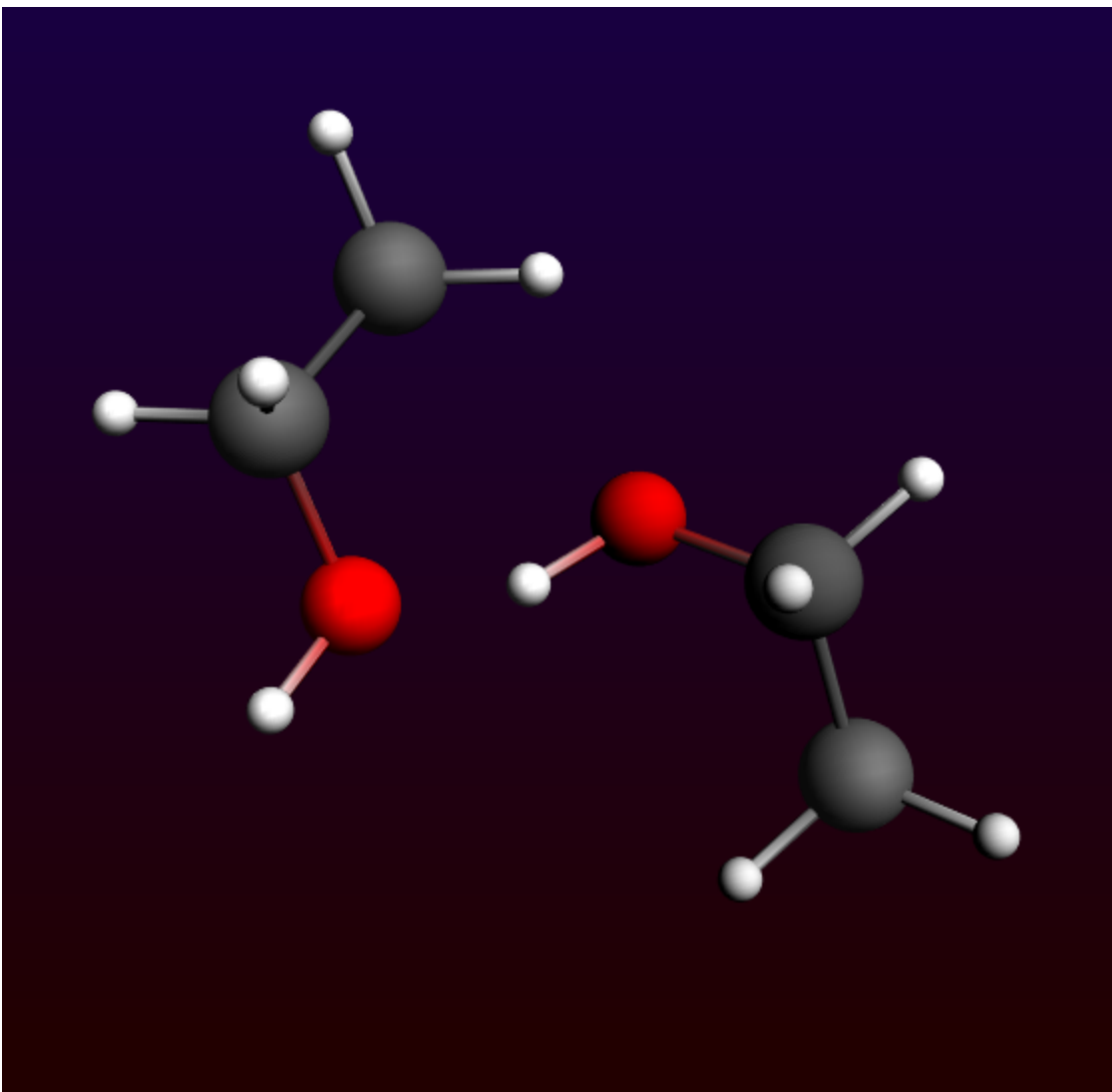
And again we have constructed an ethanol molecule.

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

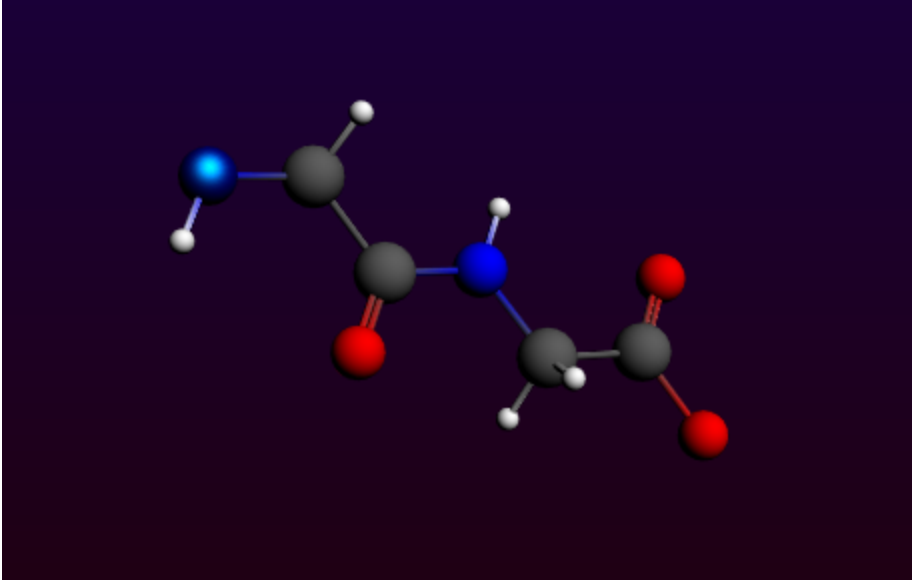
Now we will build a small peptide chain as another example using the structures tool.

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



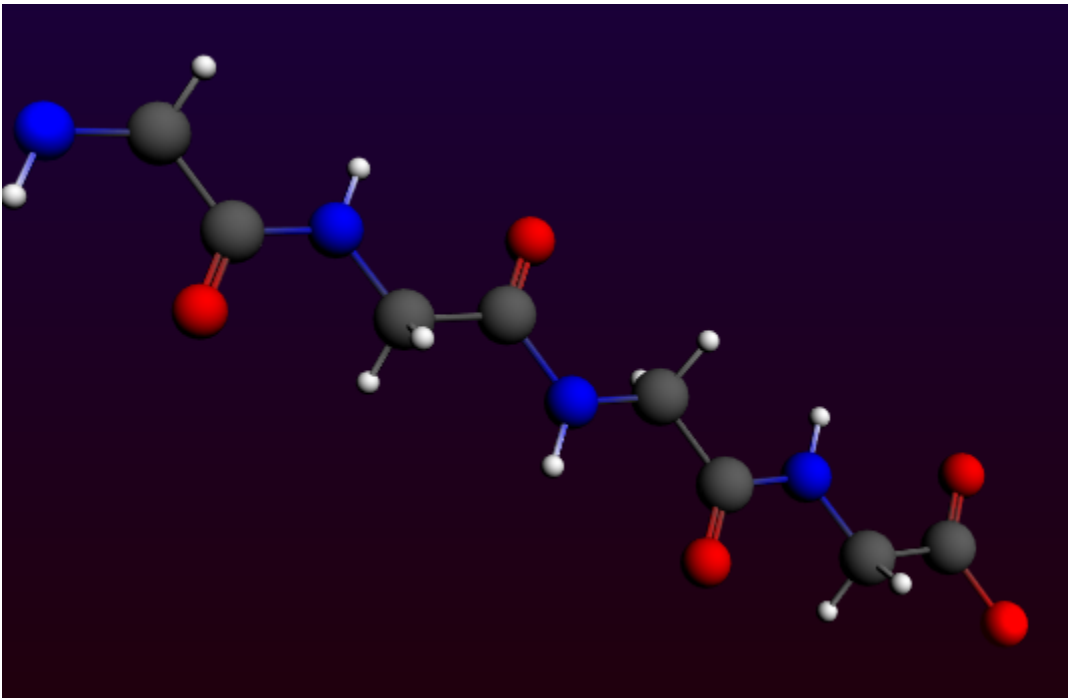
There appears a subunit (or actually two) of a basic peptide chain. Notice that one of the atoms is selected, namely the terminal nitrogen. This atom is, again, the 'replacing' atom. In order to extend the peptide backbone, you now have to choose the right atom to be replaced. The obvious choice is the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

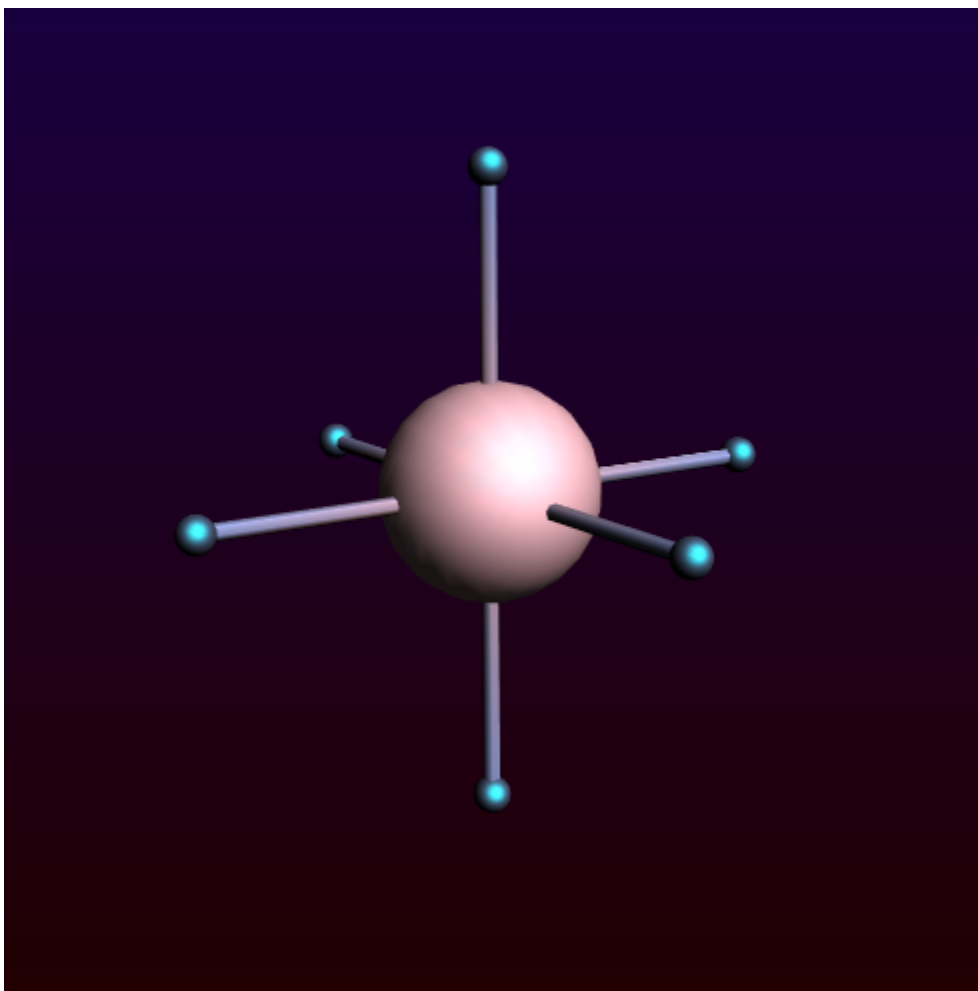
Click No (do not save changes)

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.

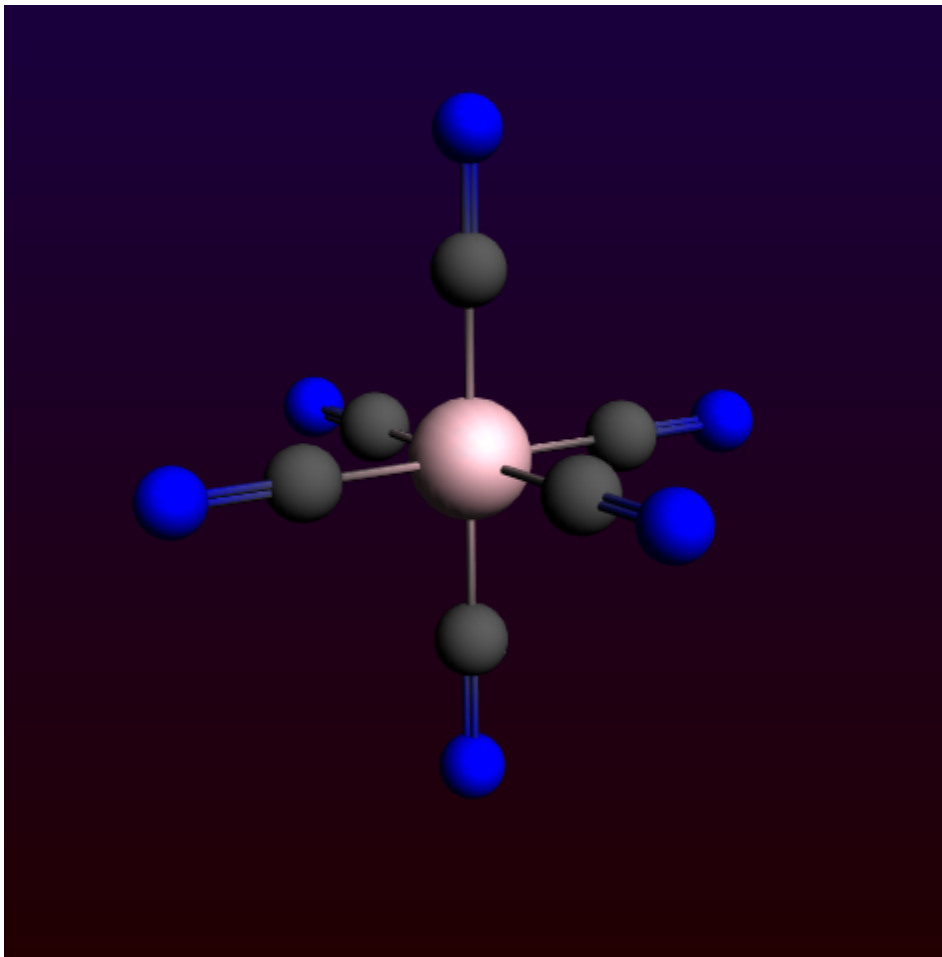
Select one of the dummy atoms by clicking on it

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.

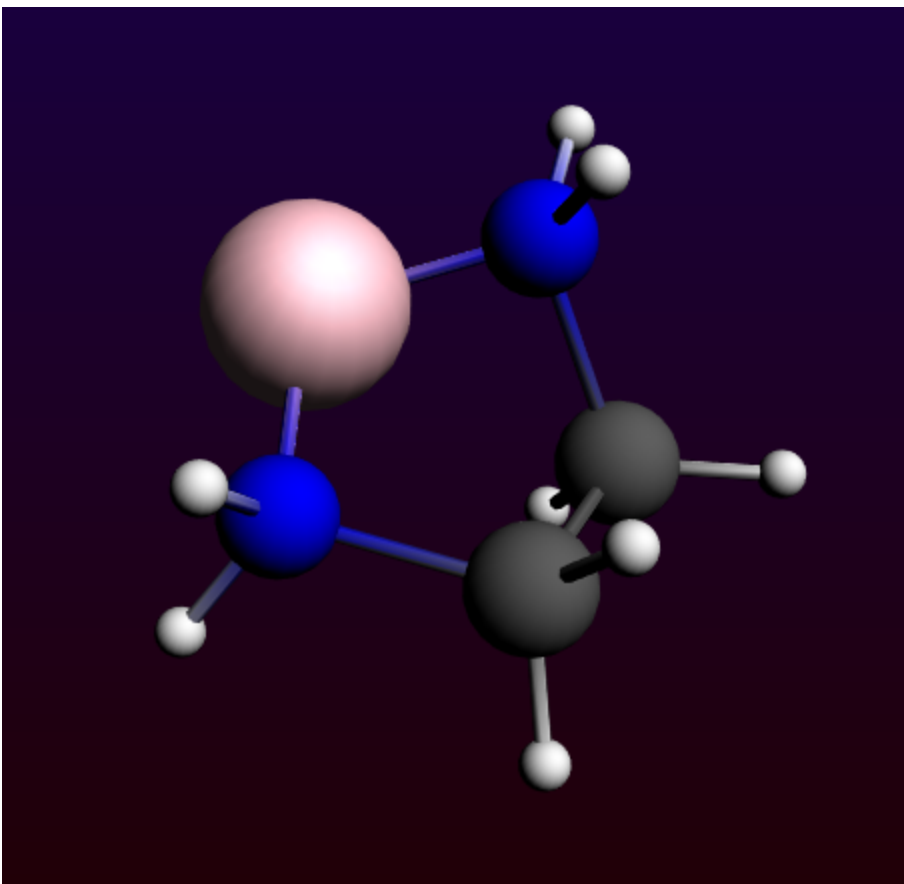
Bidentate Ligands

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)

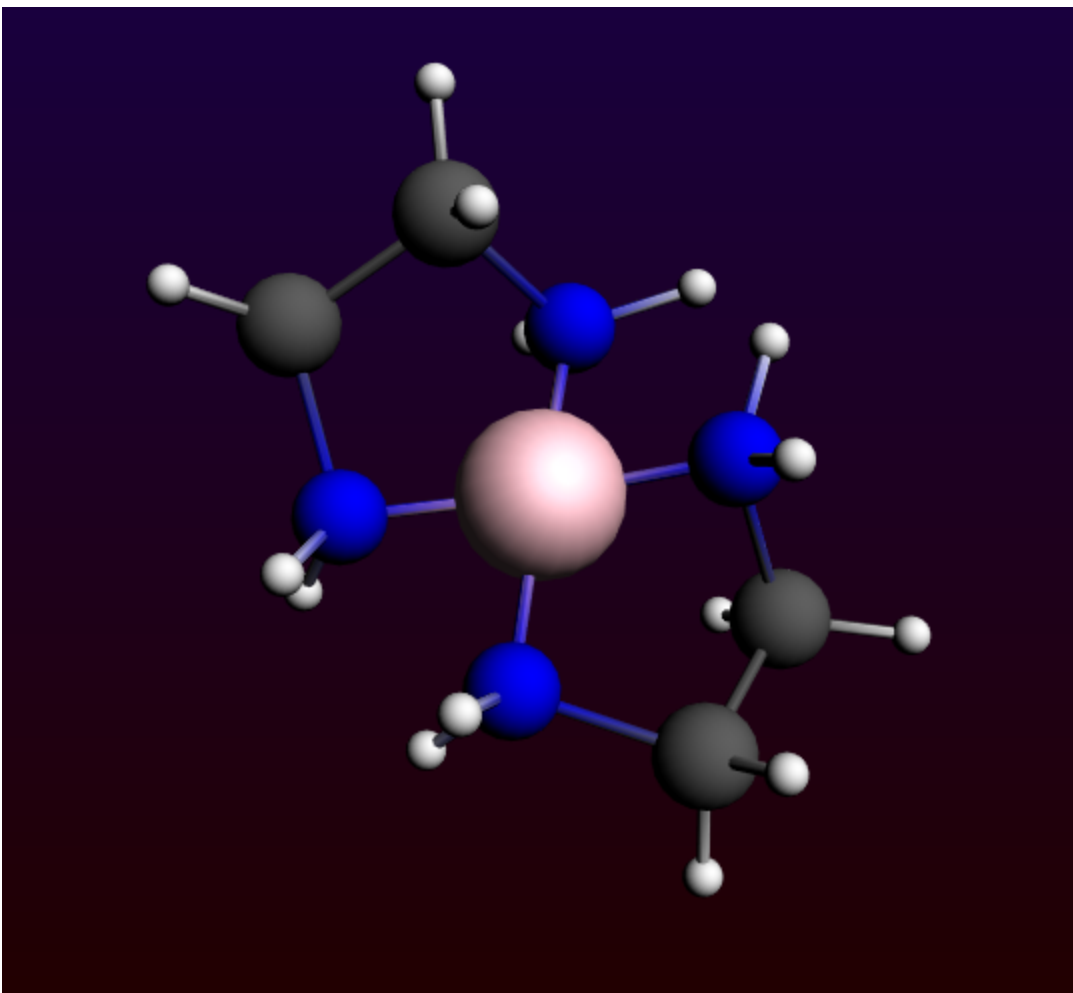
Select the **Structures tool** → **Ligands** → **Bidentates** → **Ethylenediamine** structure
Double-click on the metal atom



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



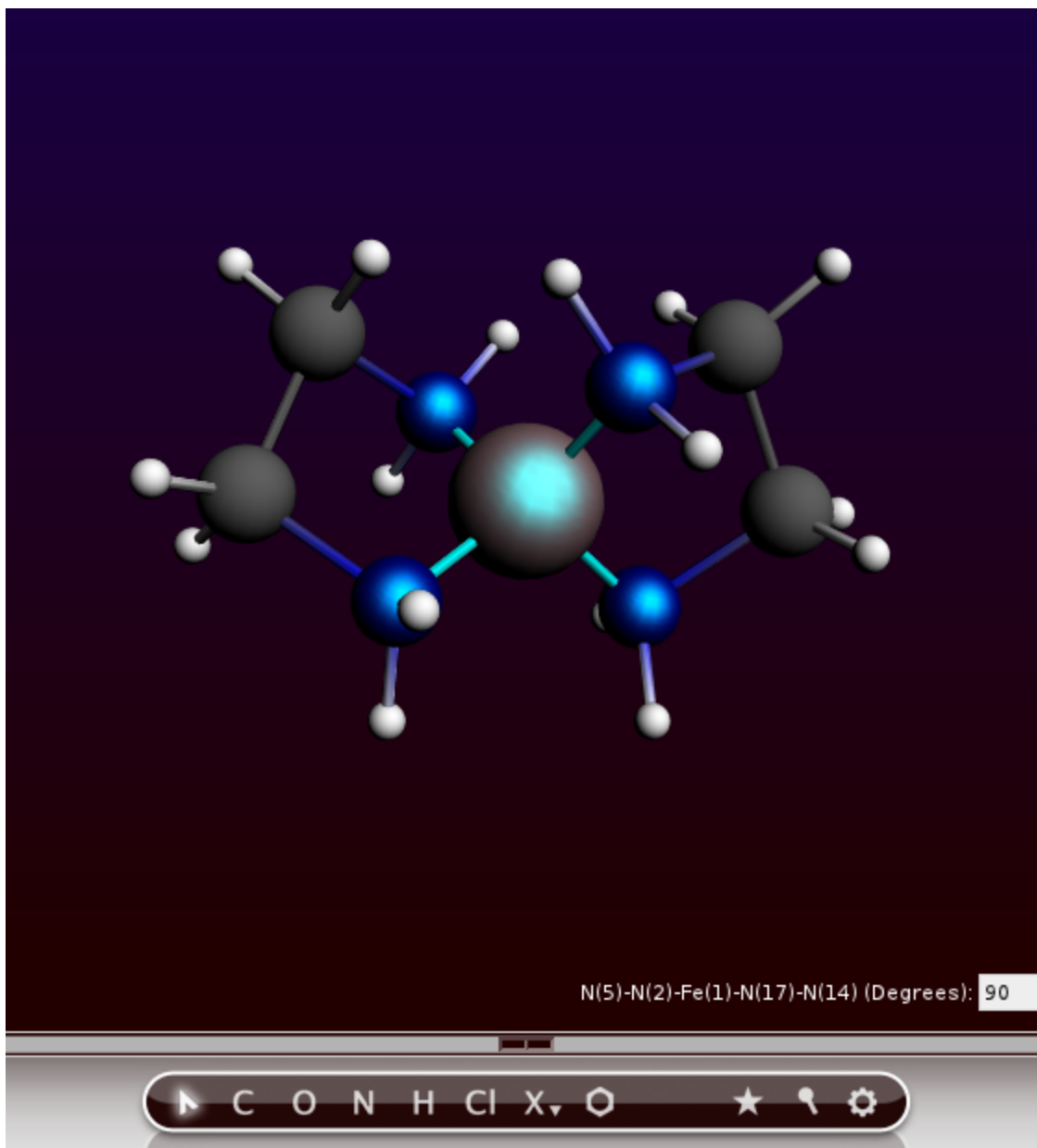
Notice that the second ligand appears opposite the existing one.

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

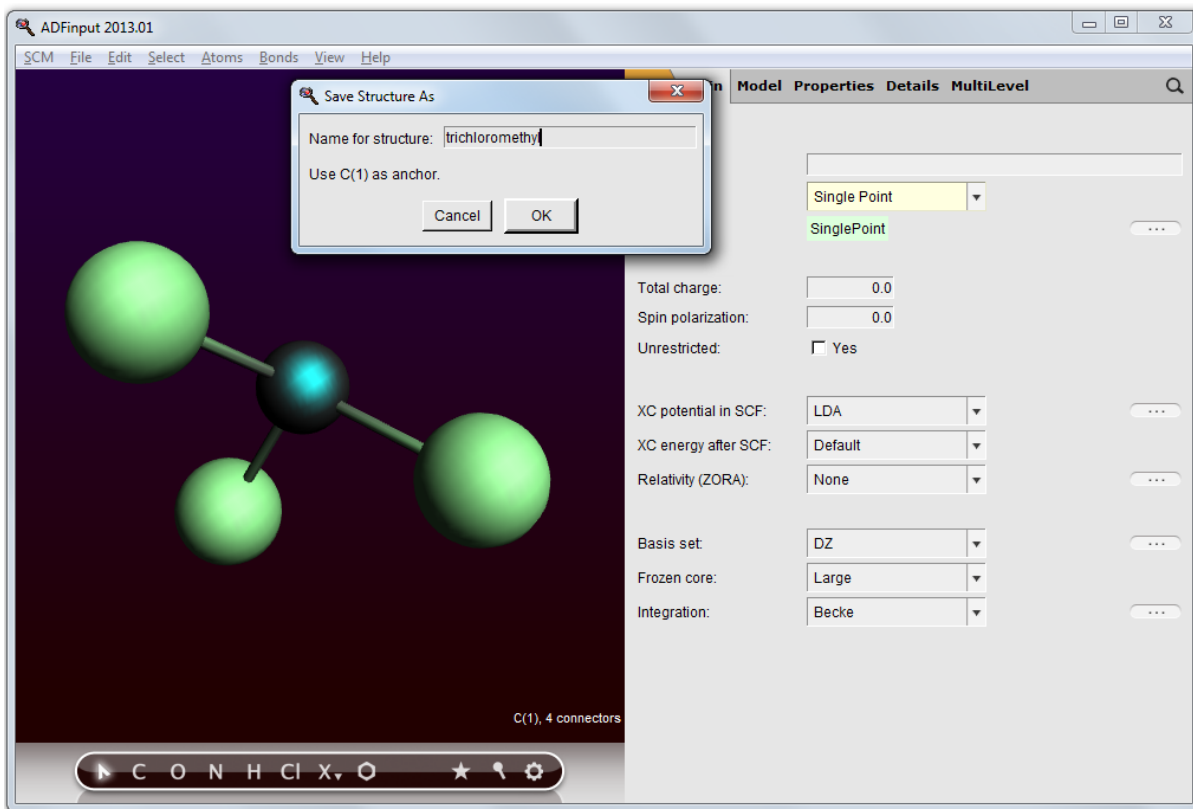
Delete the remaining hydrogen

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



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

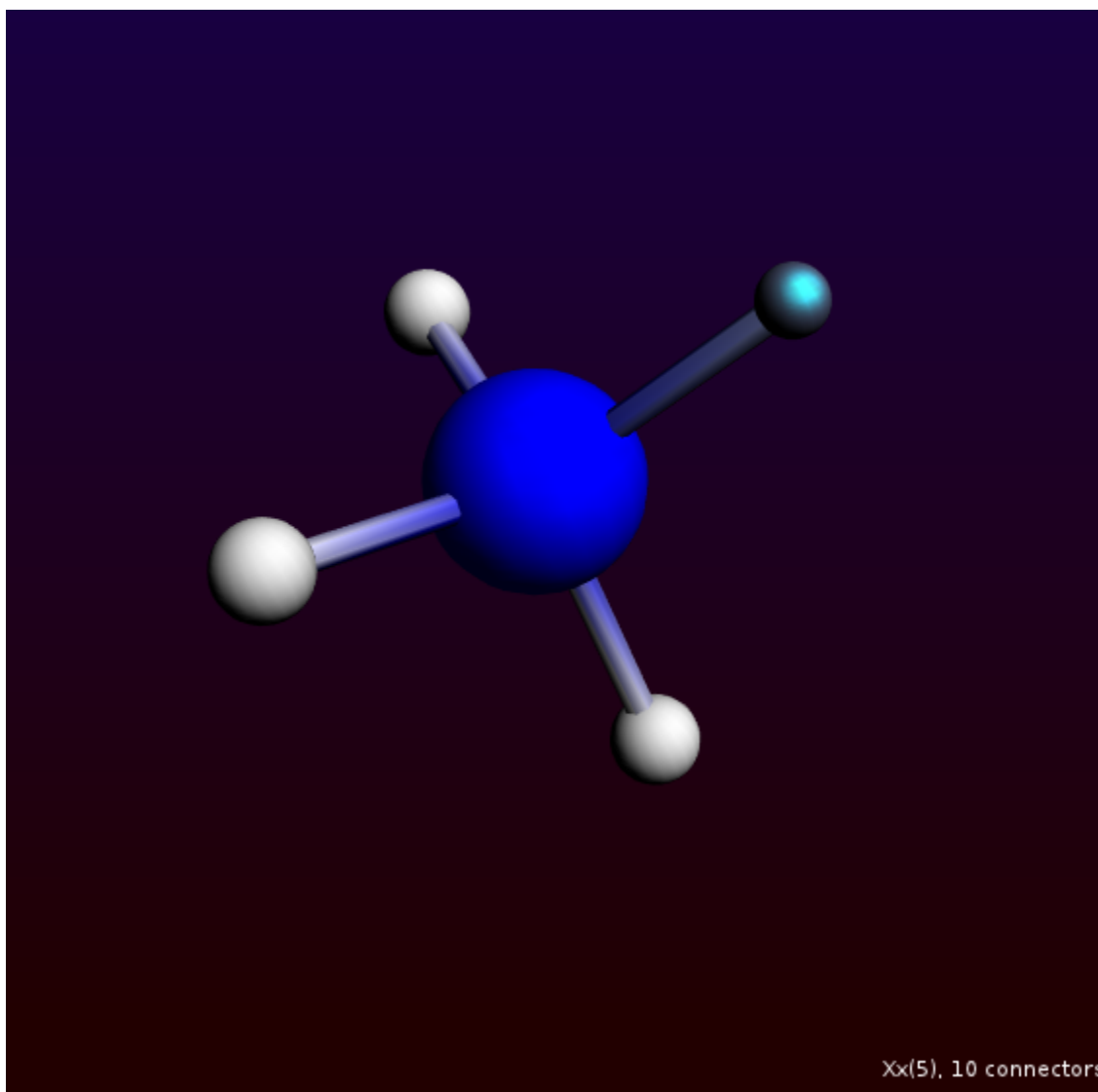
Using dummy atoms

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'

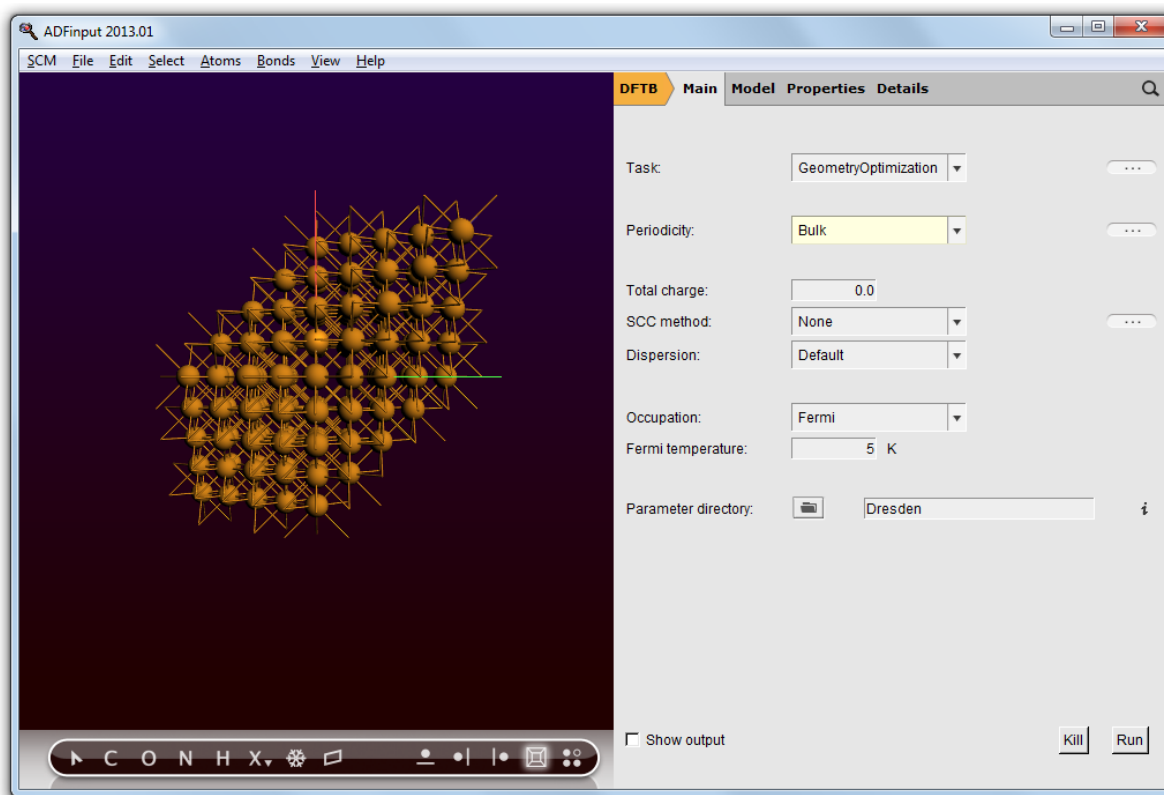
Edit → **Crystal** → **Cubic** → **fcc**

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



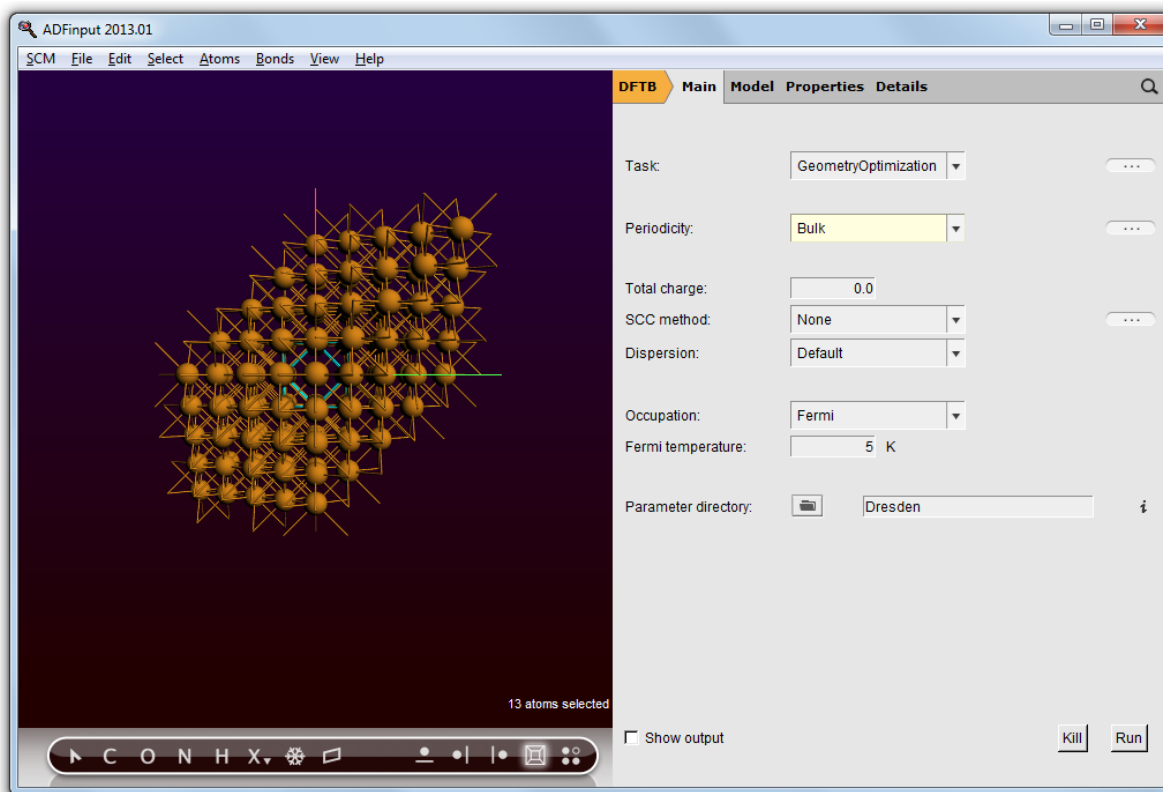
Now we have a block of Cu, with explicit Cu atoms (that is using a super cell). Next we will center this block, and select a sphere of atoms around the origin.

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



Select → Invert Selection

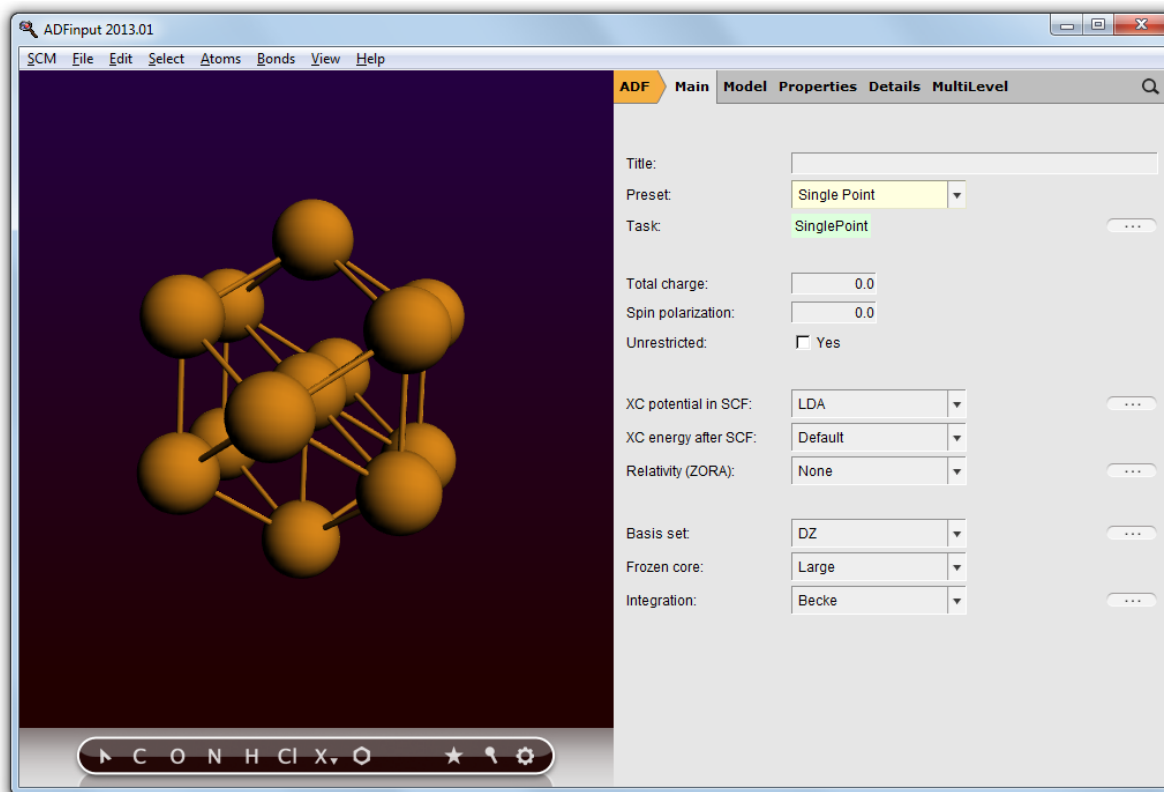
Press the Backspace key to delete the selected atoms

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:



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

Step 10: A carbon nanotube

A small piece of nanotube is included in the molecule database, so you can just search for it and use it. However, typically one wants some specific nanotube structure. And make it infinite (periodic in one dimension). This can conveniently be done by importing the structure as found on the web:

Use a web browser to go to the [TubeGen nanotube structure generator](#)

Request CIF format as output, leave other options at the default values

Click generate

In the browser windows we get the nanotube structure in CIF format, something like the following:

```
data_nanotube

_audit_creation_method      '(3,3) Nanotube -- TubeGen 3.3, J T Frey,
University of Delaware'

_cell_length_a              7.4762
_cell_length_b              7.4762
_cell_length_c              2.4643
_cell_angle_alpha           90.00
_cell_angle_beta            90.00
_cell_angle_gamma           120.00

_symmetry_space_group_name_H-M  'P 1'
```

```
_symmetry_Int_Tables_number      1

loop_
  _atom_site_label
  _atom_site_fract_x
  _atom_site_fract_y
  _atom_site_fract_z
C      0.7762    0.5000    0.0000
C      0.8138    0.7061    0.0000
C      0.7762    0.7762    0.5000
C      0.6077    0.8138    0.5000
C      0.5000    0.7762    0.0000
C      0.2939    0.6077    0.0000
C      0.2238    0.5000    0.5000
C      0.1862    0.2939    0.5000
C      0.2238    0.2238    0.0000
C      0.3923    0.1862    0.0000
C      0.5000    0.2238    0.5000
C      0.7061    0.3923    0.5000
```

Next we want to get this structure into ADFinput:

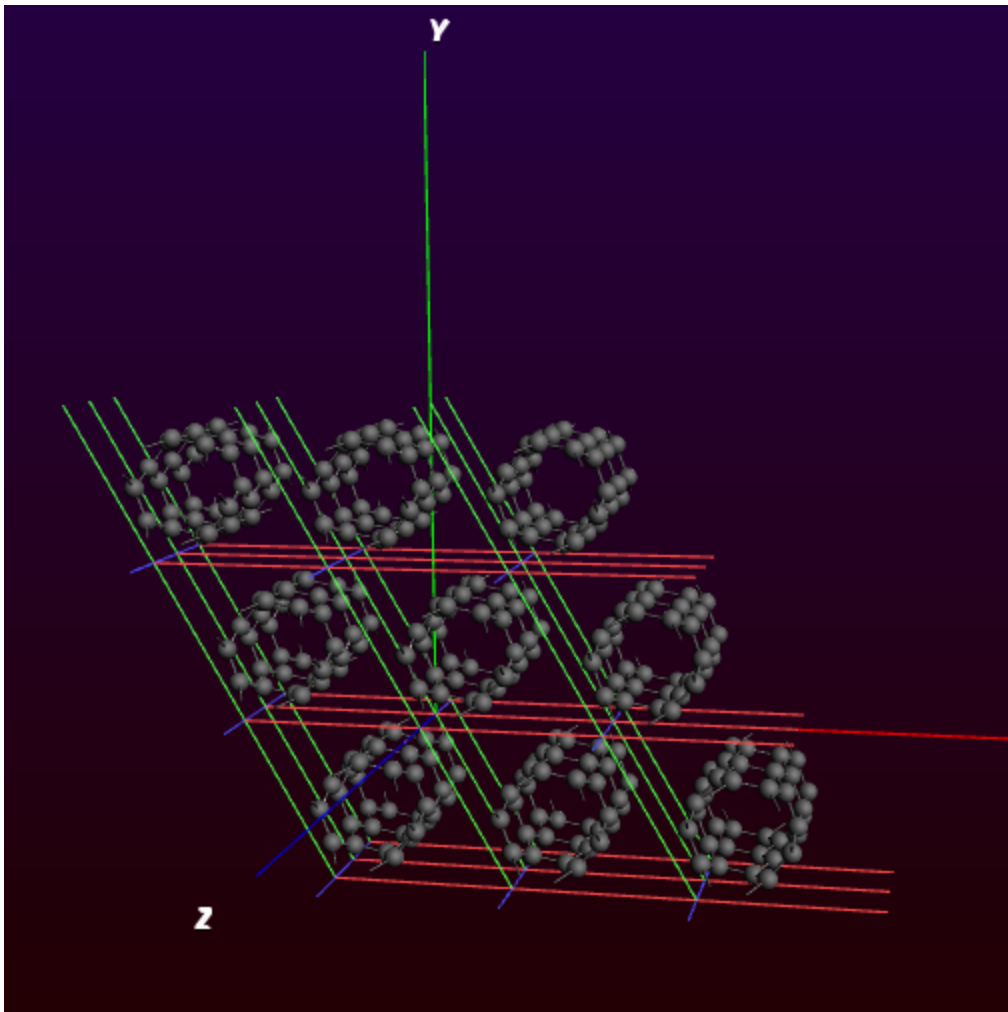
Select the CIF information in your browser
Copy

Start ADFinput

Edit → **Paste**.

View → **Axes**

Rotate to get a good view

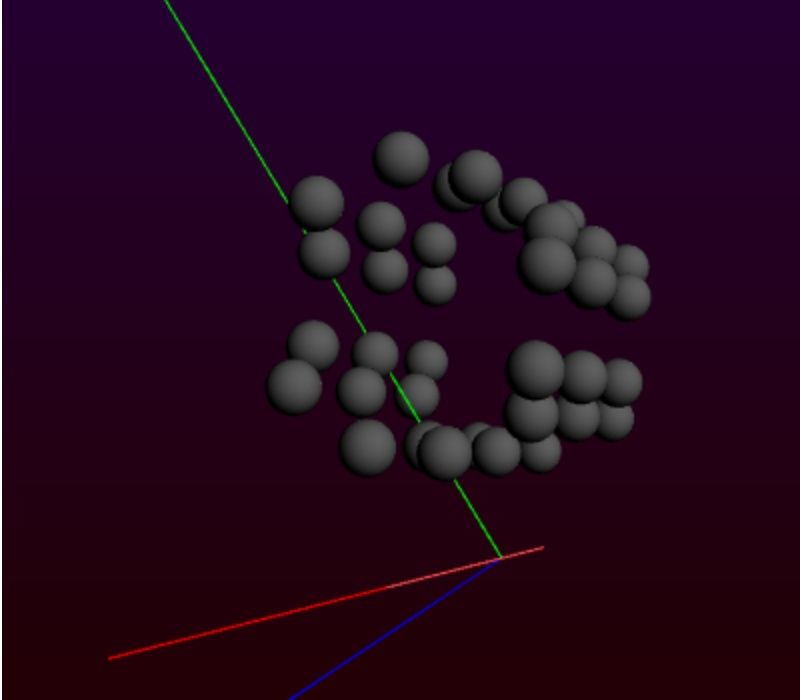


We see a piece of nanotube, repeated in all directions. Actually nine nanotubes are visible.

Notice that the nanotubes are oriented along the Z-axes.

The GUI can handle one-dimensional systems. However, in case of a one dimensional system (a chain) the lattice vector is always along the X direction. So to change our nanotube in a nice periodic one-dimensional structure we need to rotate it (including the lattice vectors) such that the tube is along the X-axes.

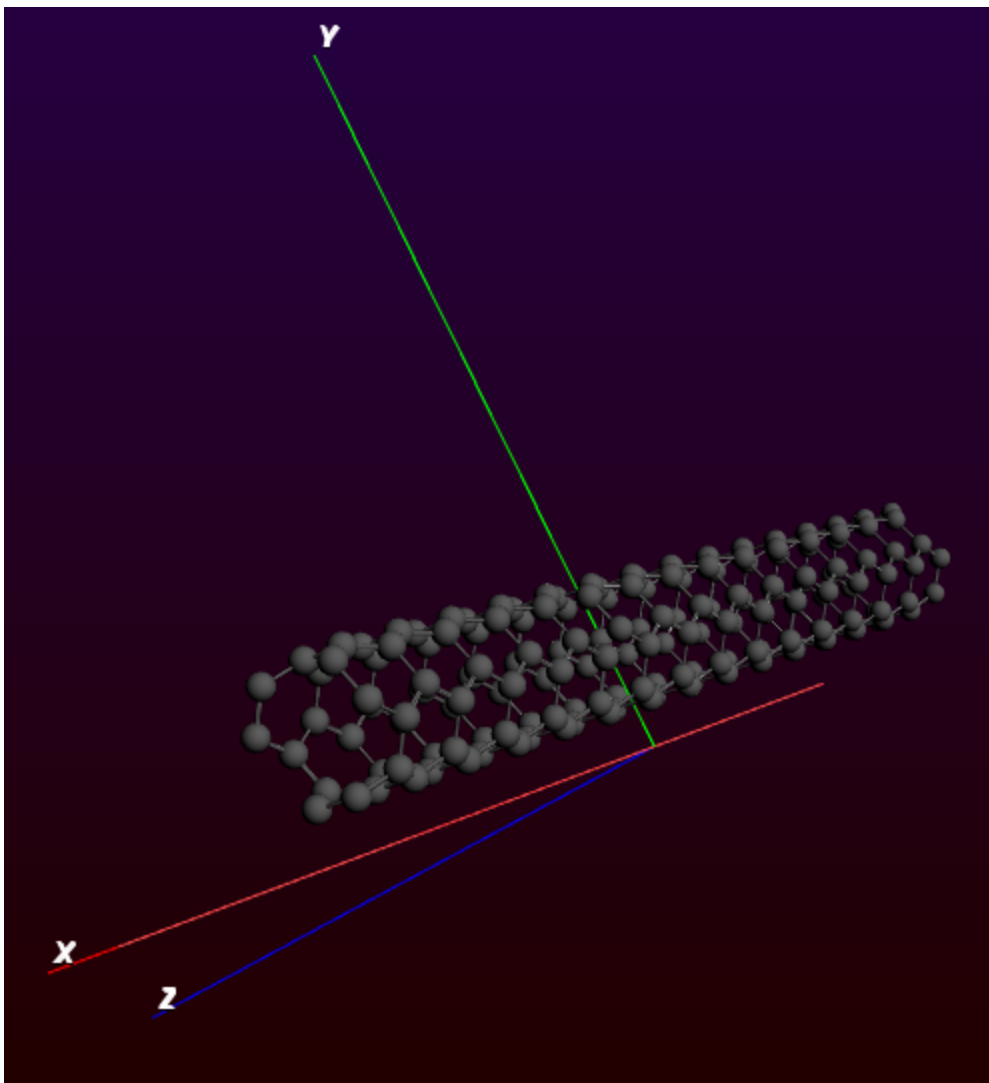
Use the **Edit** → **Rotate 90** menu command to make the nanotube lie along the X-axes
(hint: rotate around the Y-axes)
Switch to a one-dimensional system (chain)



The Rotate 90 command did not only rotate the coordinates of the atoms, but also the lattice vectors. Now we have a small piece of nanotube (remember it already is repeated 3 times for visualization purposes). This might be sufficient for your purposes, but it is easy to make a bigger piece:

Edit → Crystal → Generate Super Cell

Click OK to repeat the unit cell 5 times



Switch to some non-periodic code (like ADF) if you wish to treat this piece of nanotube without infinite symmetry.

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:

- The crystal structures tool.
- The predefined crystal structures in the database (via the search field).
- 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.

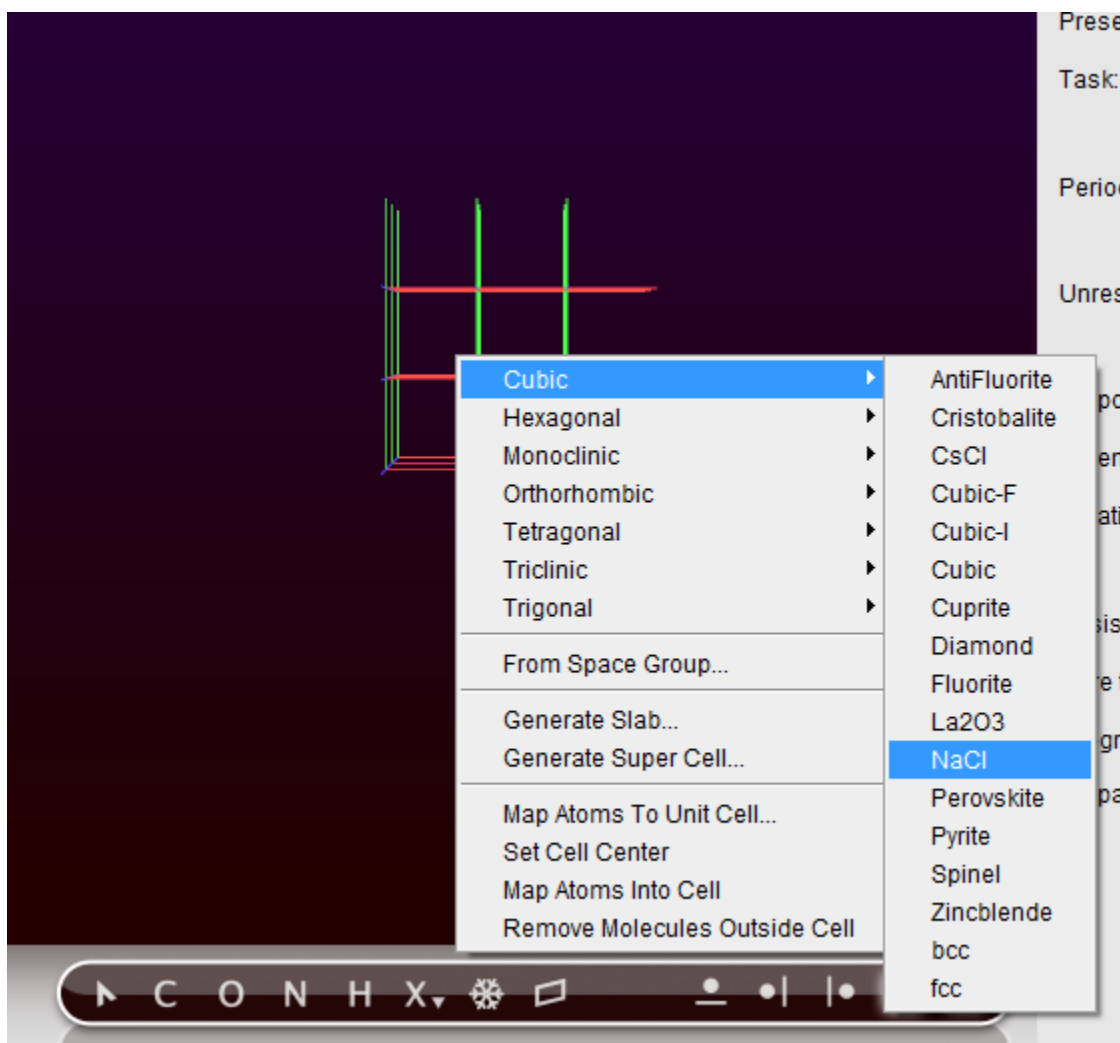
The Crystal Structures Tool

If you are lucky your crystal structure is already included in ADFinput. Most of the common structures are there. NaCl is one of them.

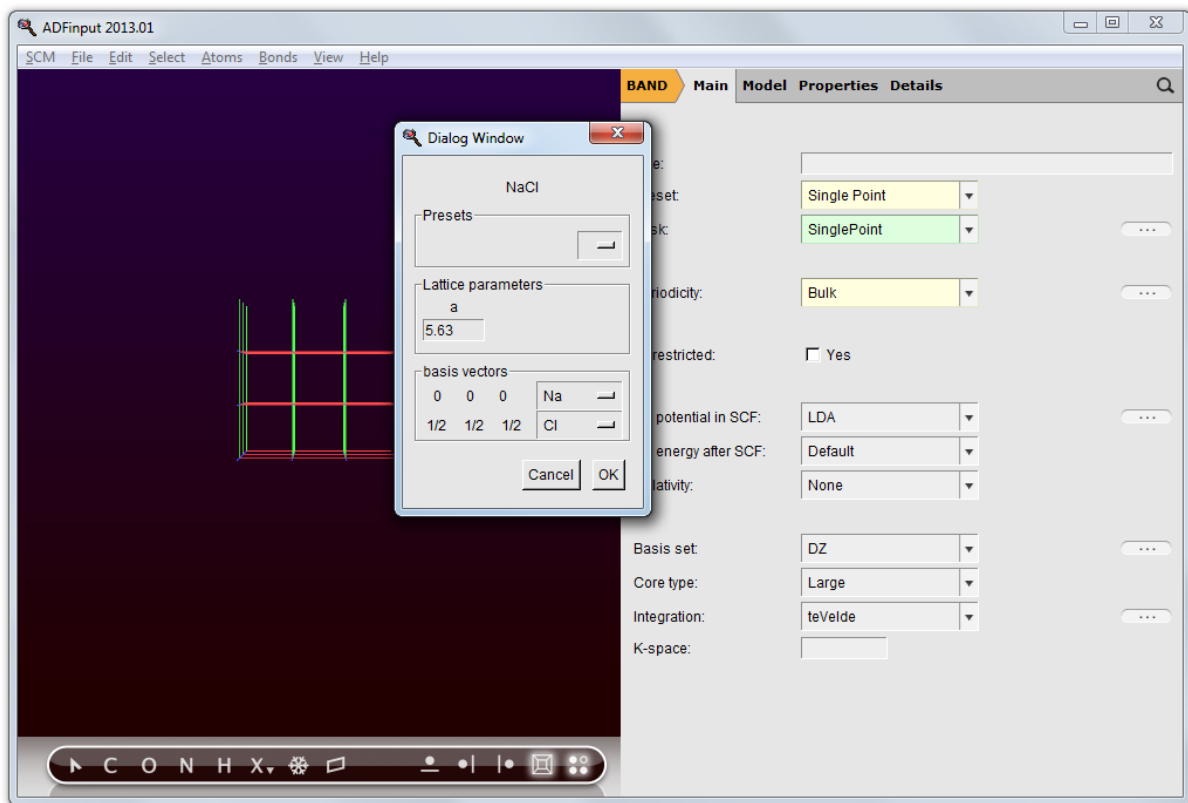
Start ADFinput and switch to BAND (or to DFTB, and switch the periodicity to 'Bulk')

Click on the snowflake like pictogram on the toolbar.

Select a "Cubic" lattice and then NaCl



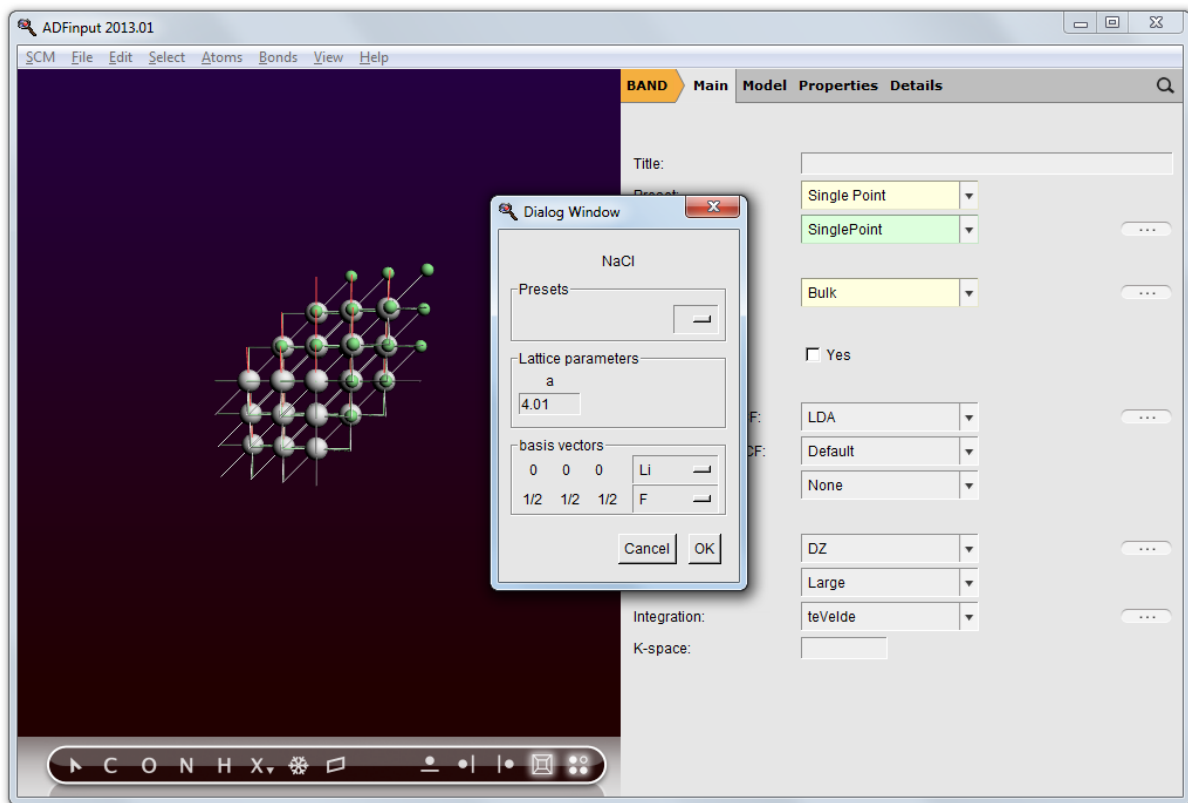
Next a dialog pops up where you can change the parameters of the structure, such as lattice constants



In this case there is no need to change anything.

Click OK

Sometimes 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:

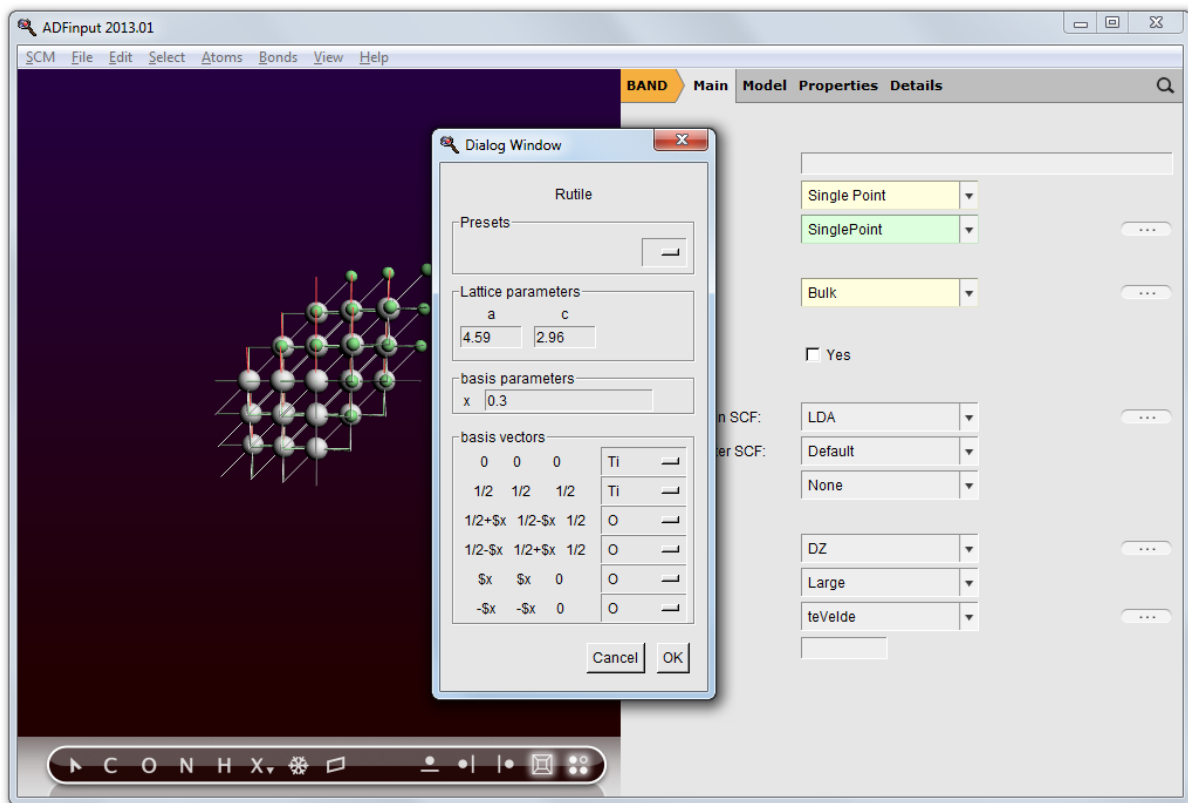


Open again the NaCl dialog
 Change the lattice constant and the elements as shown
 Click OK

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

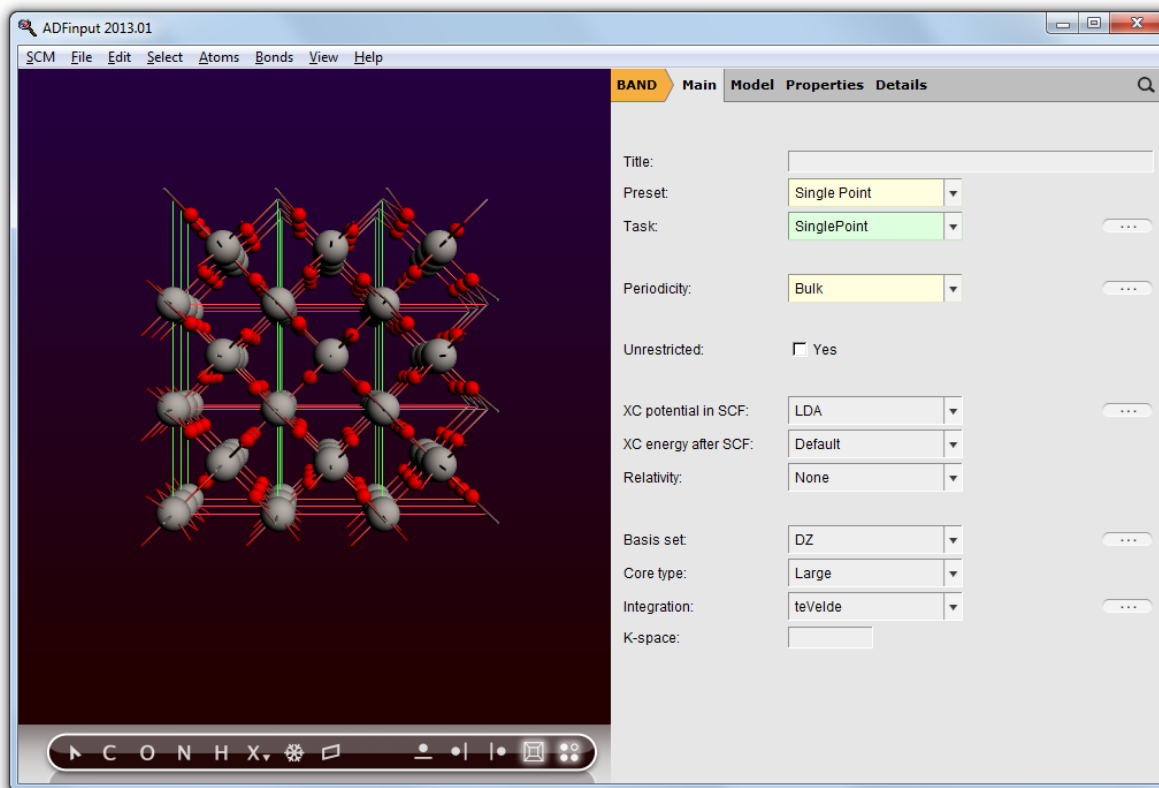
Some crystal structures have more parameters.

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



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"

After clicking 'Ok' your screen will look like this



The Crystal Structures Database

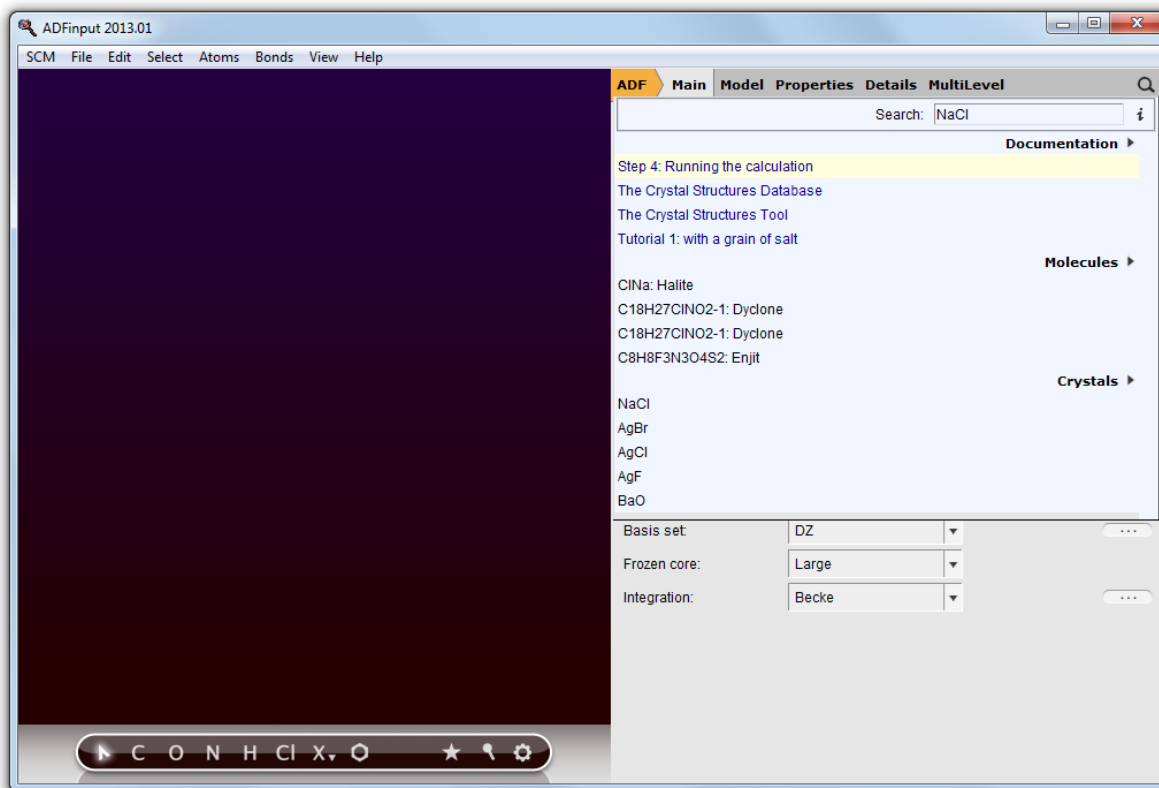
All crystal structures known to the crystal structures tool are also available via the search tool.

Just as you can search for a molecule, you can search for a crystal. So lets make NaCl again:

File → New

Click on the search icon, or press control or command - F
Type 'NaCl' (without the quotes)

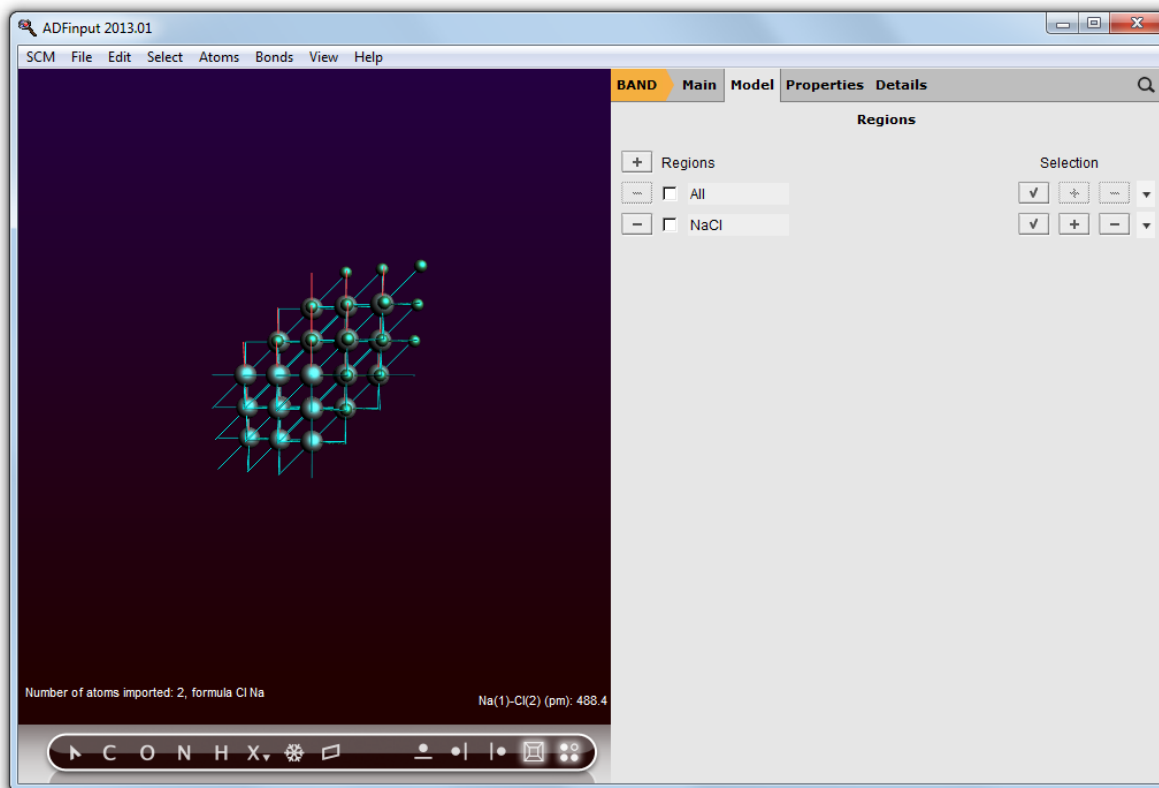
You should get a couple of matches:



Select the NaCl crystal result (not the molecule!):

Click on the 'NaCl' search result (in the Crystals section)

You now should have a NaCl crystal again.



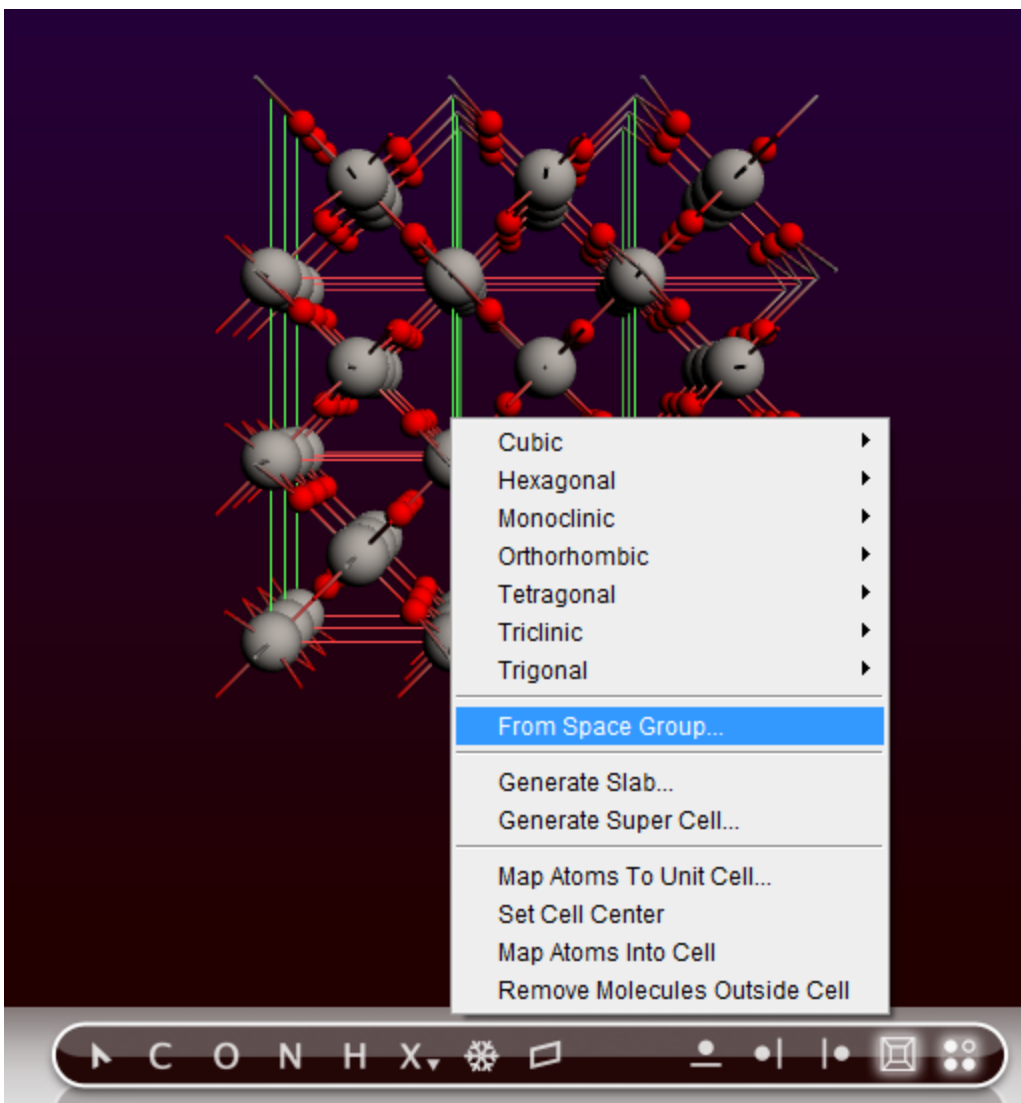
Currently the structures of many simple crystals are included, as well as a few complex structure (optimized by MOPAC). The zeolite frameworks are also included as a starting point to make your zeolite structure.

Crystal builder (from space group information)

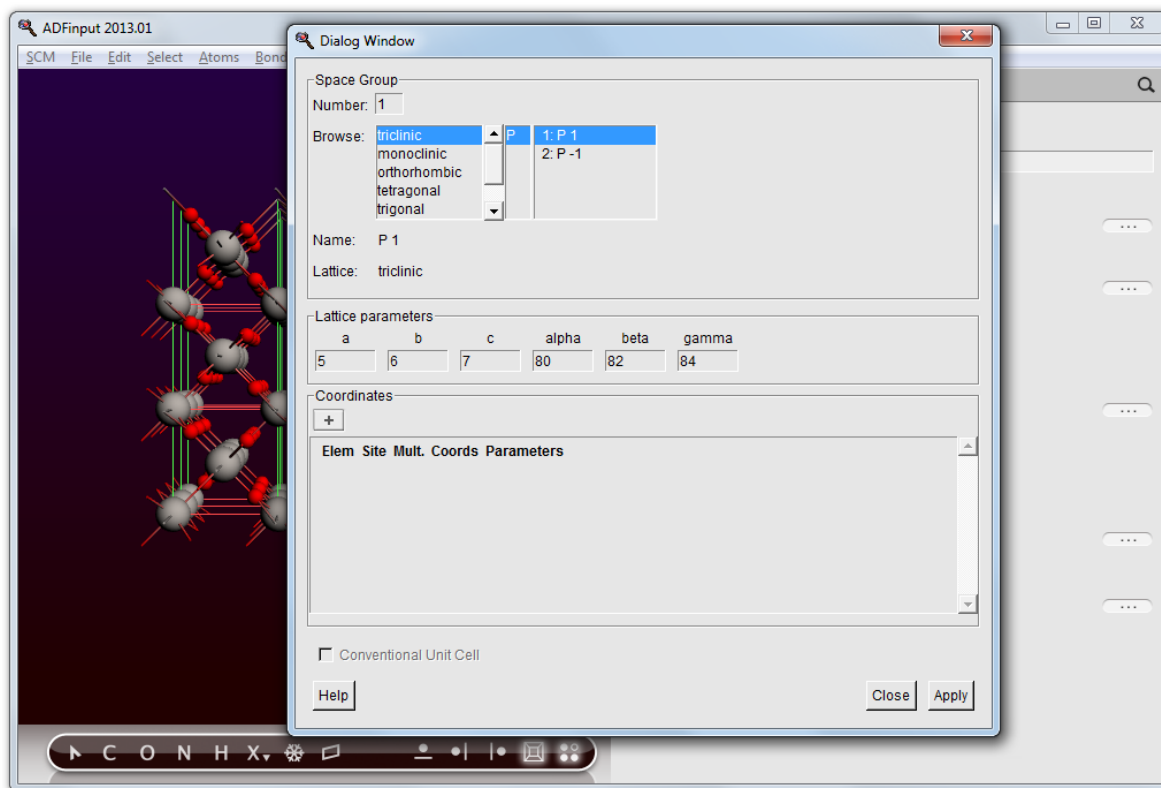
The structure database is very convenient but by necessity incomplete. A more powerful approach is to build 3D crystals from the space group information. Here we give an example on how to build TiO₂ (rutile) again, now from its space group.

Open the crystal builder:

Click on the snowflake tool and select "From Space Group"



And the following window pops up



Rutile has the symmetry of space group 136

in the "Number" field, and press return (enter key on Windows).

Space Group

Number:

Browse:

triclinic	P	134: P 42/n n m
monoclinic	I	135: P 42/m b c
orthorhombic		136: P 42/m n m
tetragonal		137: P 42/n m c
trigonal		138: P 42/n c m

Name: P 42/m n m

Lattice: tetragonal

Lattice parameters

a	c
<input type="text" value="8.73"/>	<input type="text" value="5.02"/>

Coordinates

Elem	Site	Mult.	Coords	Parameters

Conventional Unit Cell

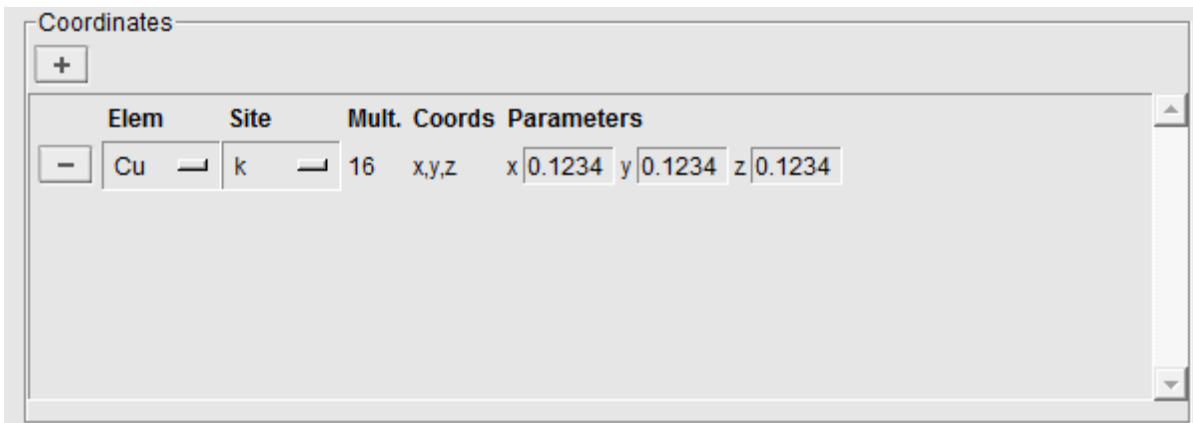
Note how the Browser reflects the change and also how the "Name" and "Lattice" values change

Now set the two lattice parameters as below

Lattice parameters

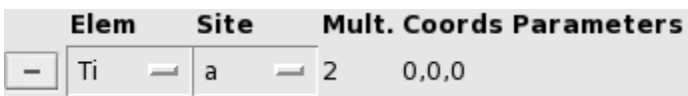
a	c
<input type="text" value="4.59"/>	<input type="text" value="2.96"/>

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



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

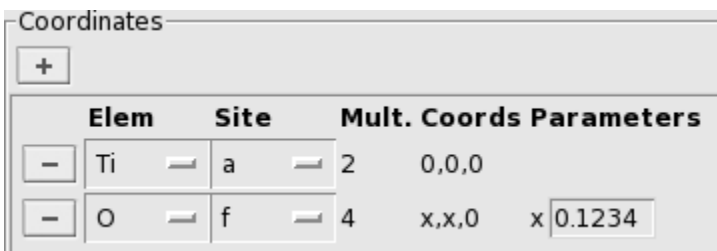
Select the Ti atom and select the "a" site



The oxygens occupy the "f" site.

Click on the plus to add a site

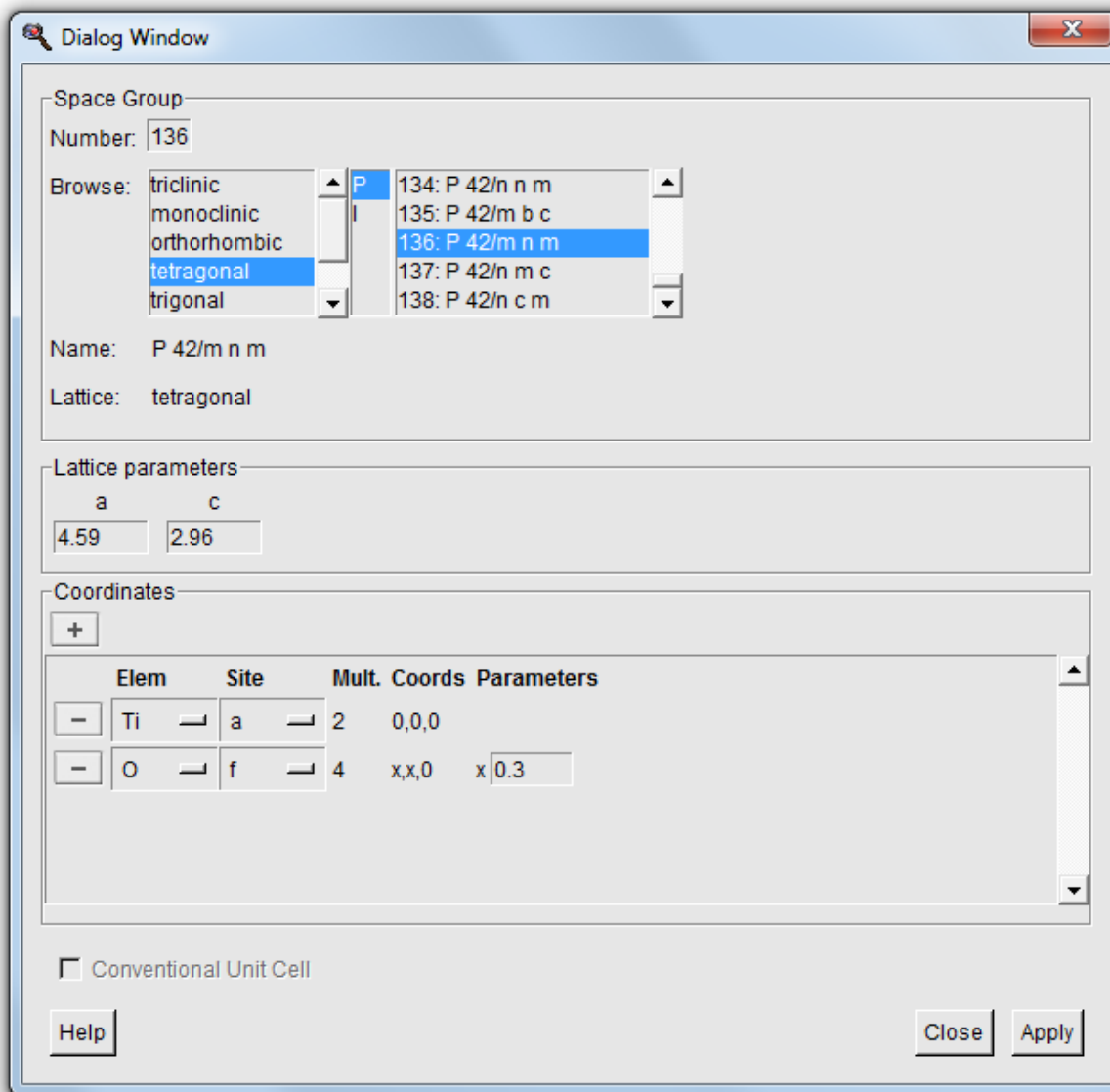
Change the atom type to "O" and the site to "f"



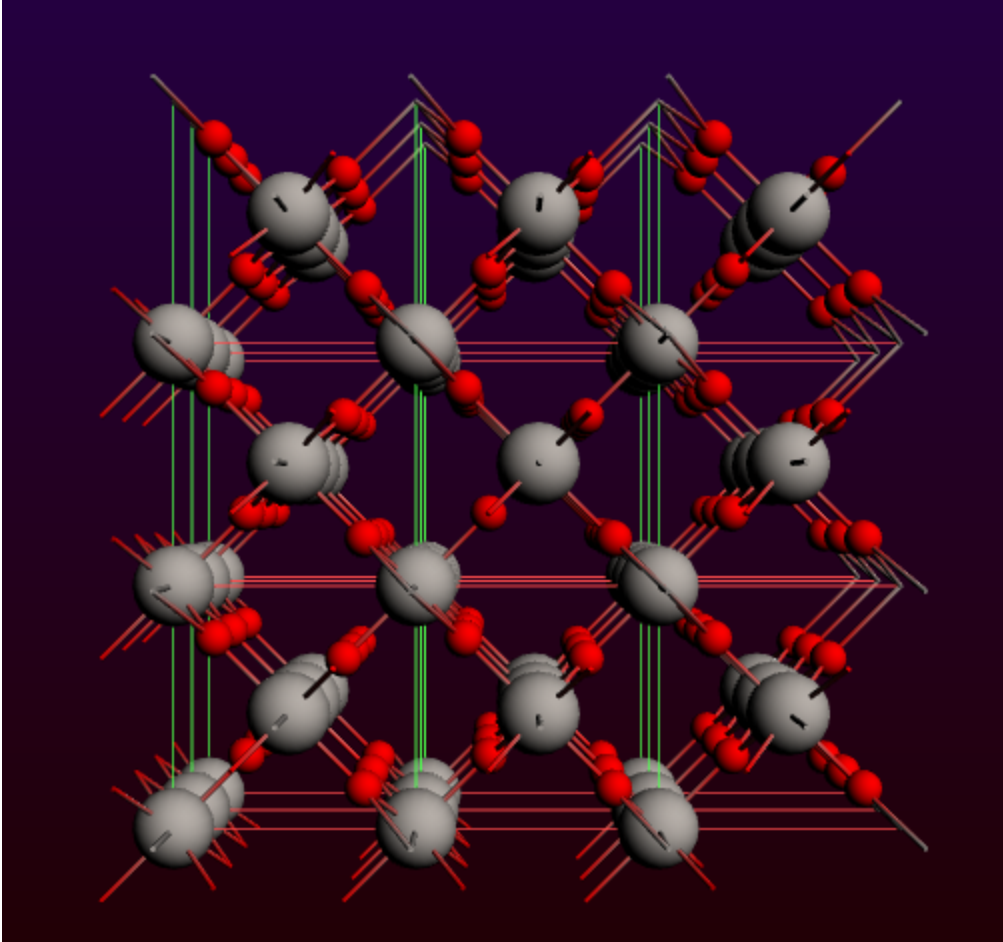
As you can see in the "Coords" column and the "Parameters" column, this site has an undetermined parameter "x". (It represents a symmetry line for this space group.) In the book you can find that for TiO₂ "x=0.3".

Set "x" to 0.3

The final dialog looks like



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



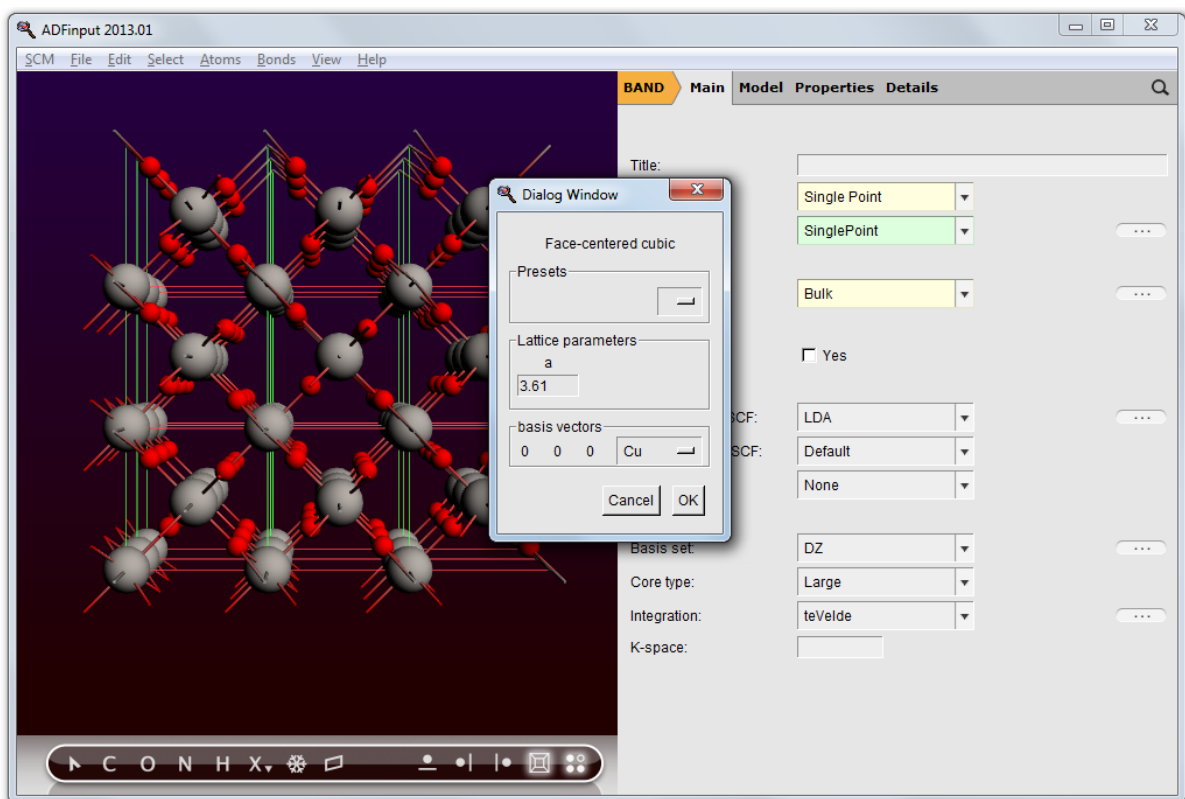
Slicer: building slabs

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

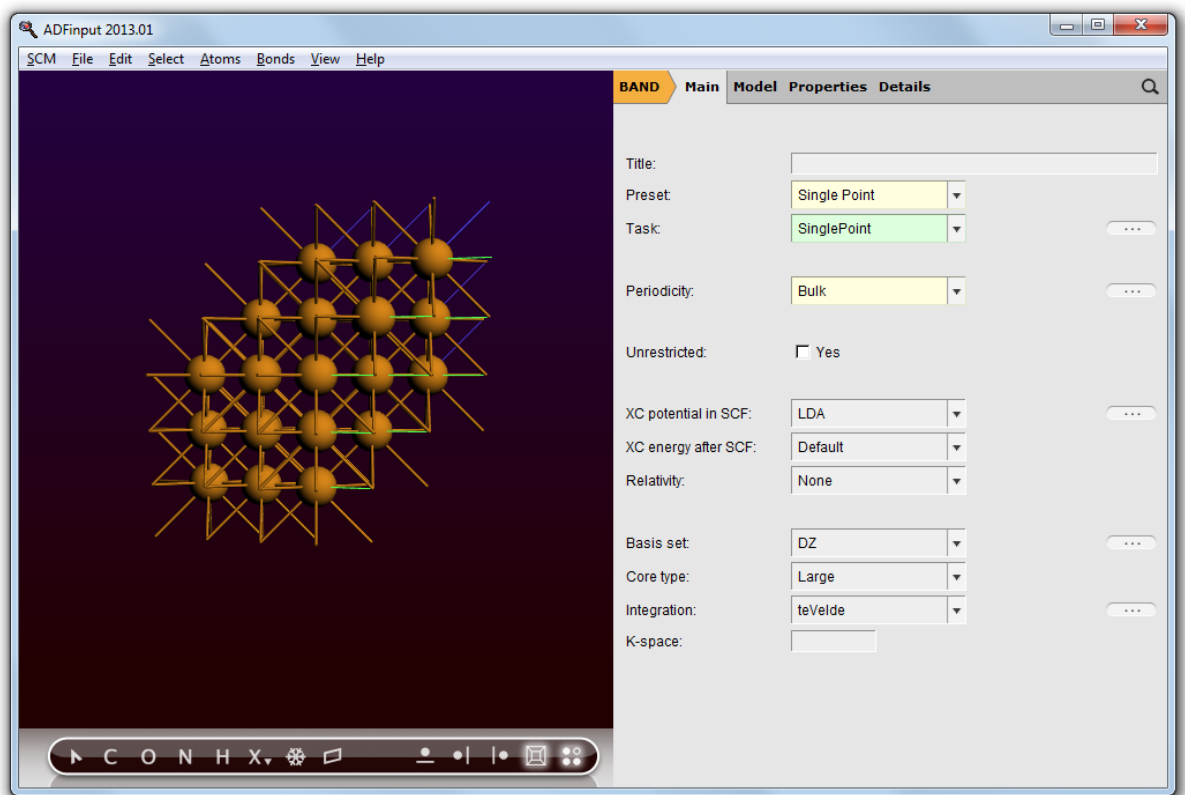
A three layer slab of the Cu(111) surface


Select fcc from the "Cubic" crystals

The element and lattice constant are already correct for Cu.



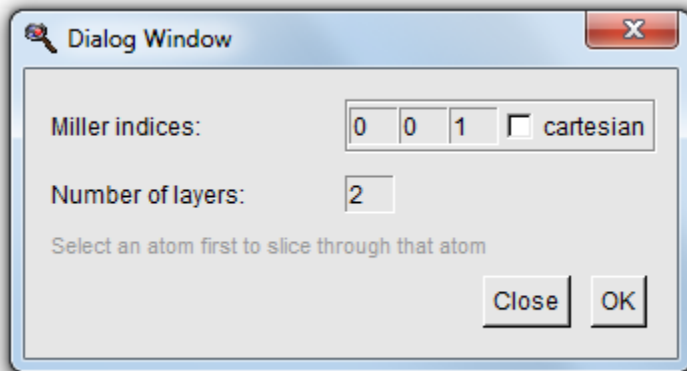
Press "OK" to generate the Cu lattice



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

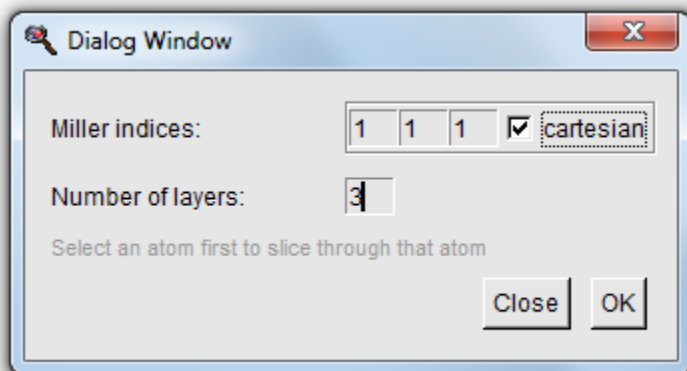
The following dialog appears



Set the Miller indices to (1,1,1)

Select Cartesian

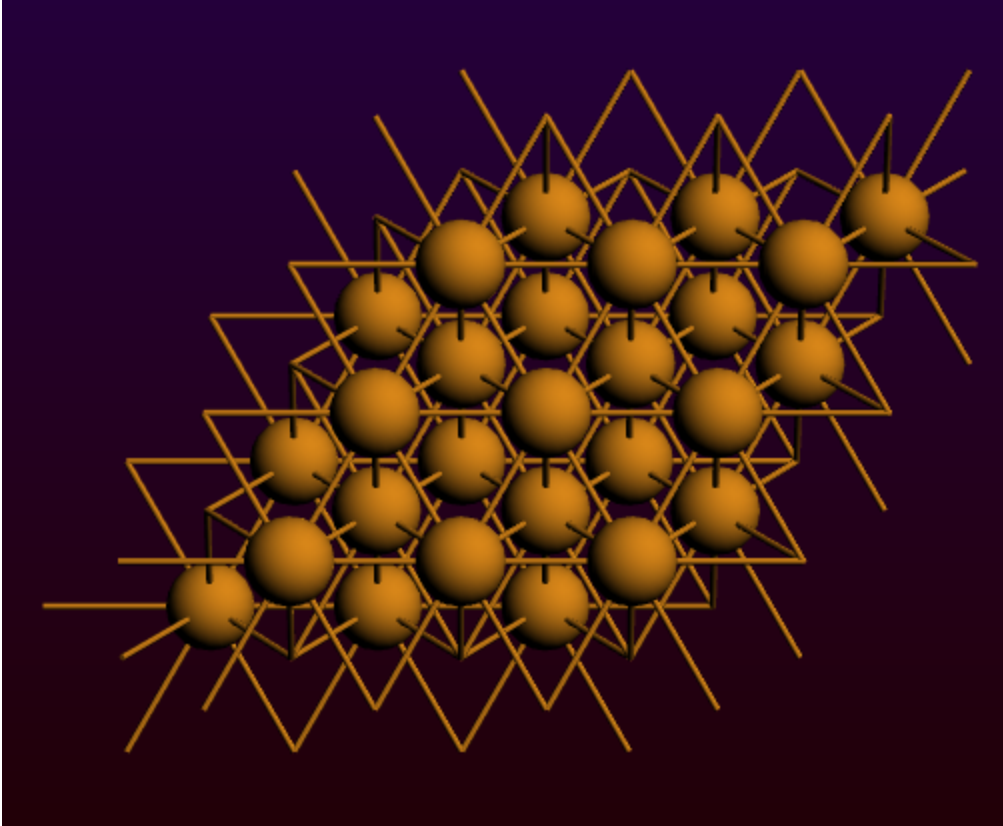
Set the number of layers to 3



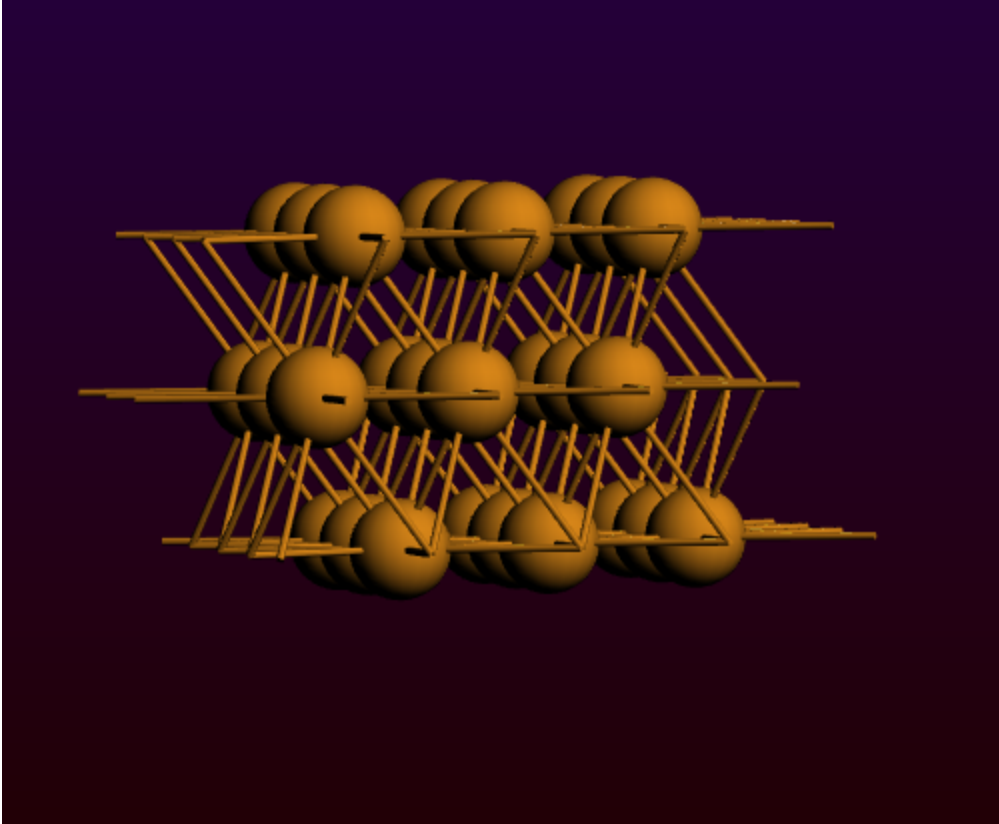
The "Cartesian" option is needed because the Miller indices are usually (with cubic lattices) thought in the conventional unit cell rather than the primitive (minimal) unit cell.

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.



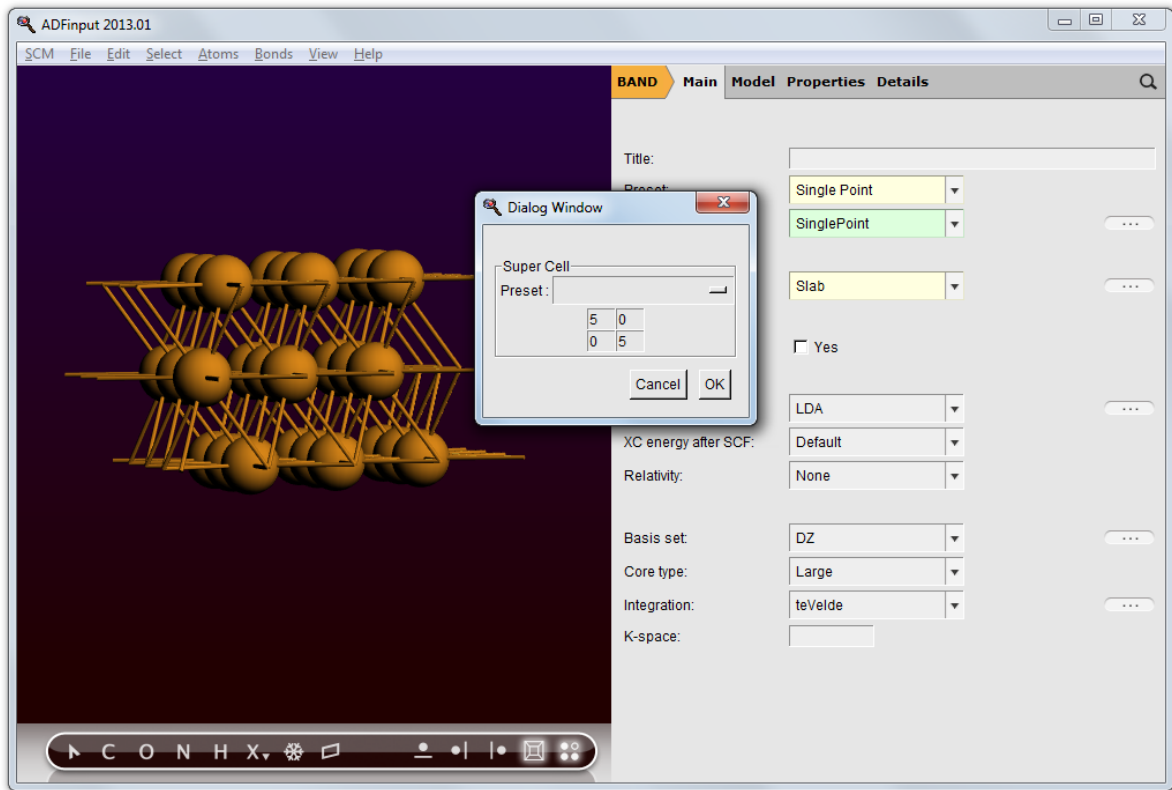
Enlarging the unit cell

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:

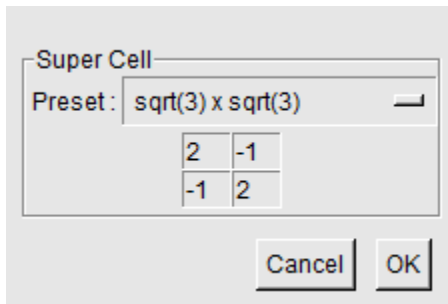
Select the **Edit** → **Crystal** → **Generate Super Cell...** command

Thus invoking the Super Cell Tool



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

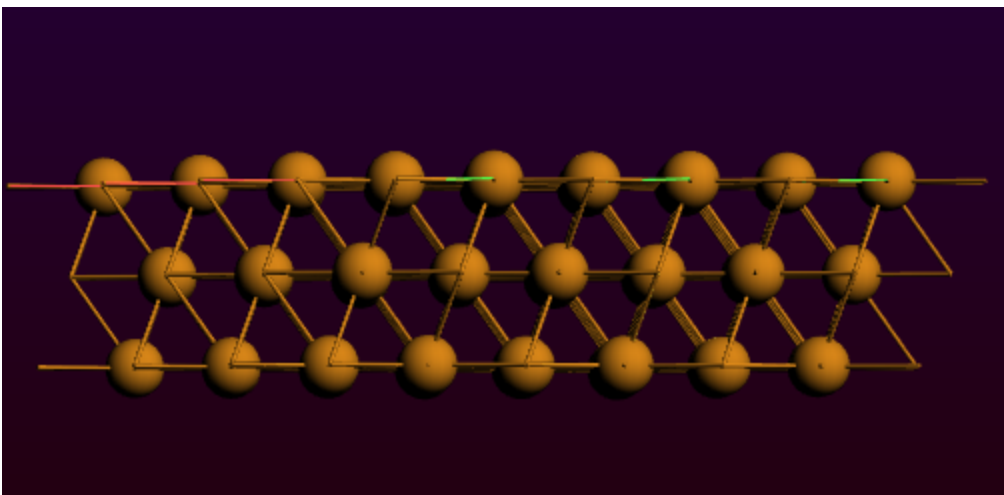
Select the "sqrt(3) x sqrt(3)" option from the "Preset" menu



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

Press OK

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



Close ADFinput

Tutorial 4: Excitation energies and UV/Vis spectrum 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 → New 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.

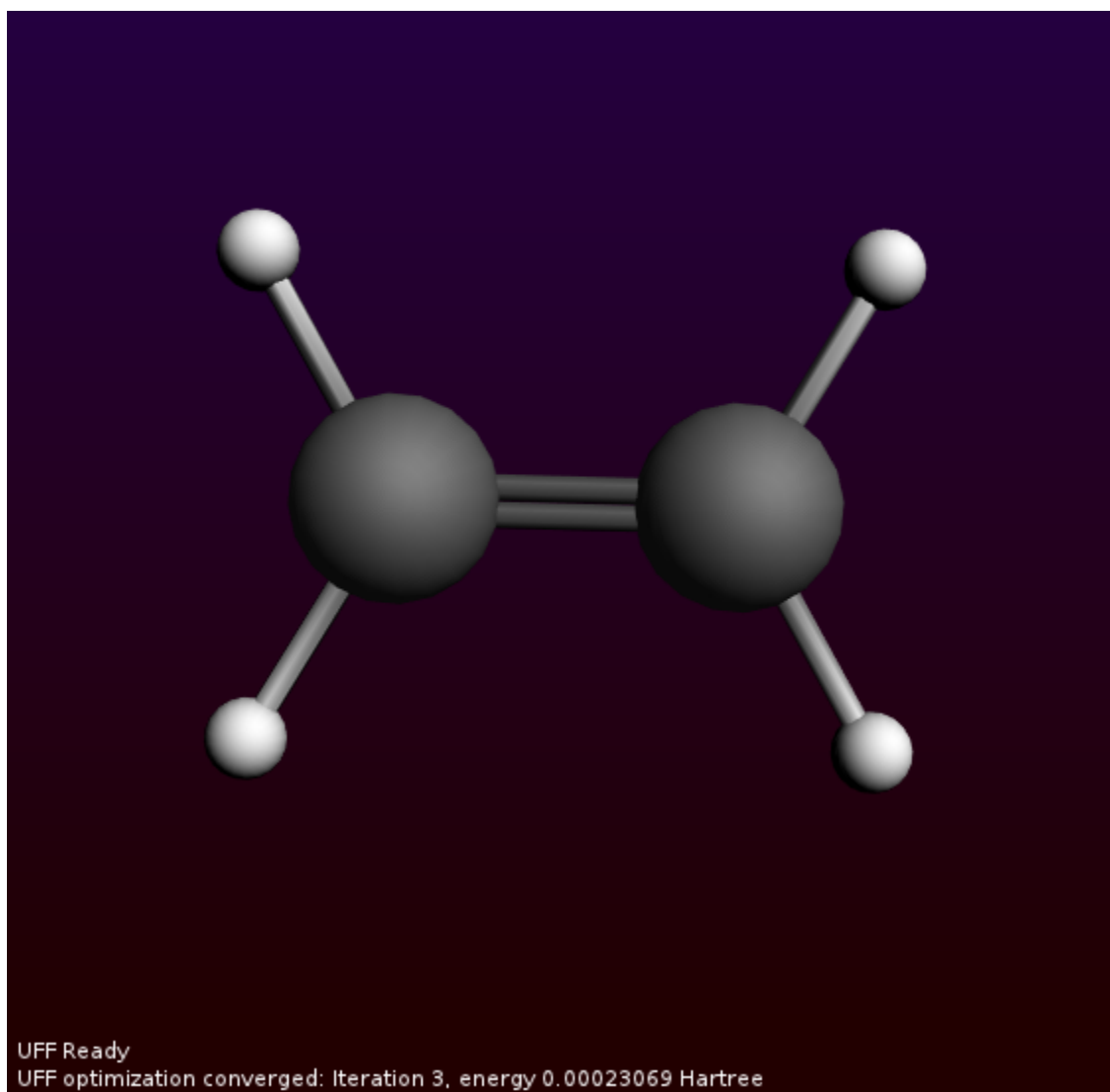
For the View command (and Movie, Levels, and so on) the behavior is different: it will immediately load the job that is selected in ADFjobs.

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:



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

ADF Main Model Properties Details MultiLevel

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: Becke

With the proper options selected, now run ADF:

Select the **File** → **Run** command

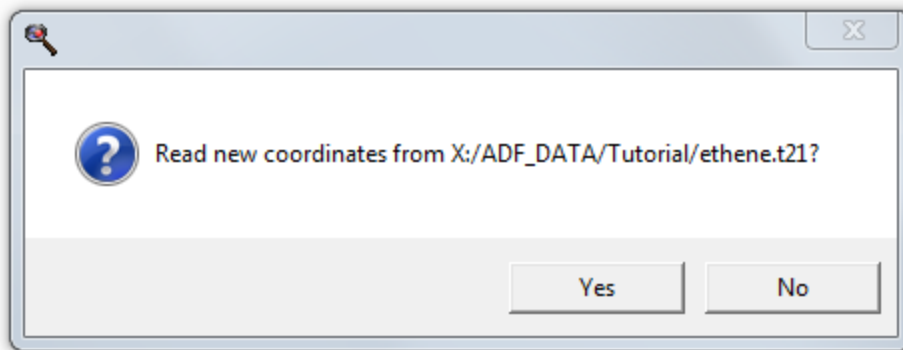
Click 'Yes' in the pop-up to save the current input

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:



Click 'Yes' to update the coordinates

Step 4: Calculate the excitation energies

Select calculations options

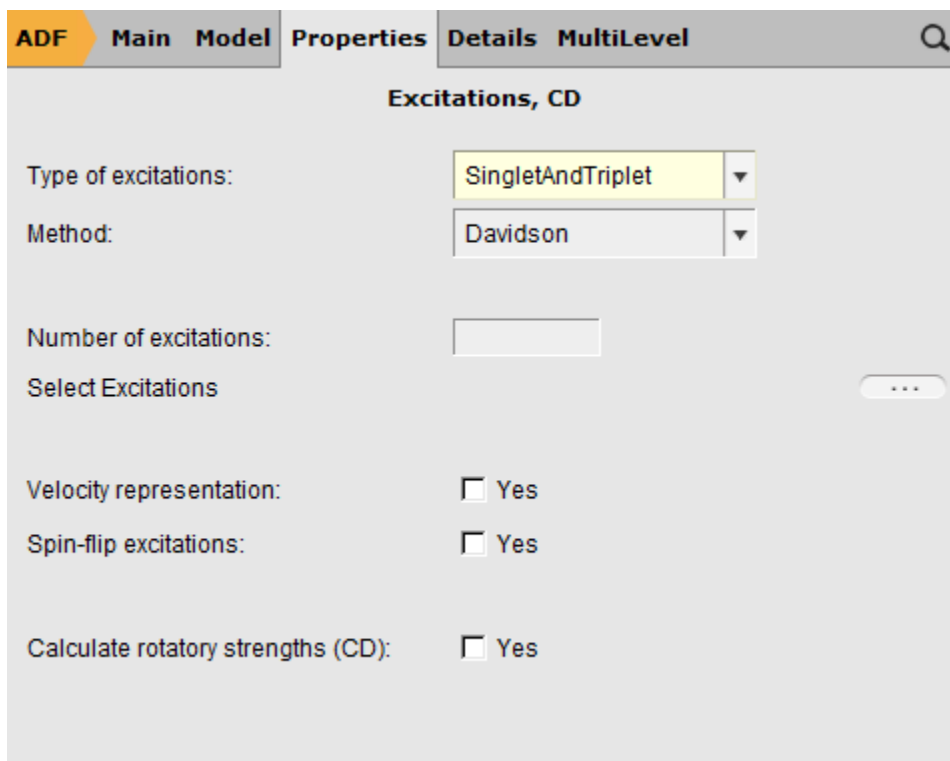
To set up the calculation of the excitation spectrum:

Adjust the title to something like 'Ethene excitations'

Select the 'Single Point' preset

Use the panel bar **Properties** → **Excitations, CD** command to go to the Excitations panel

For the 'Type of excitations' option, Select 'Singlet and Triplet'



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:

```
Select SCM → Logfile
```

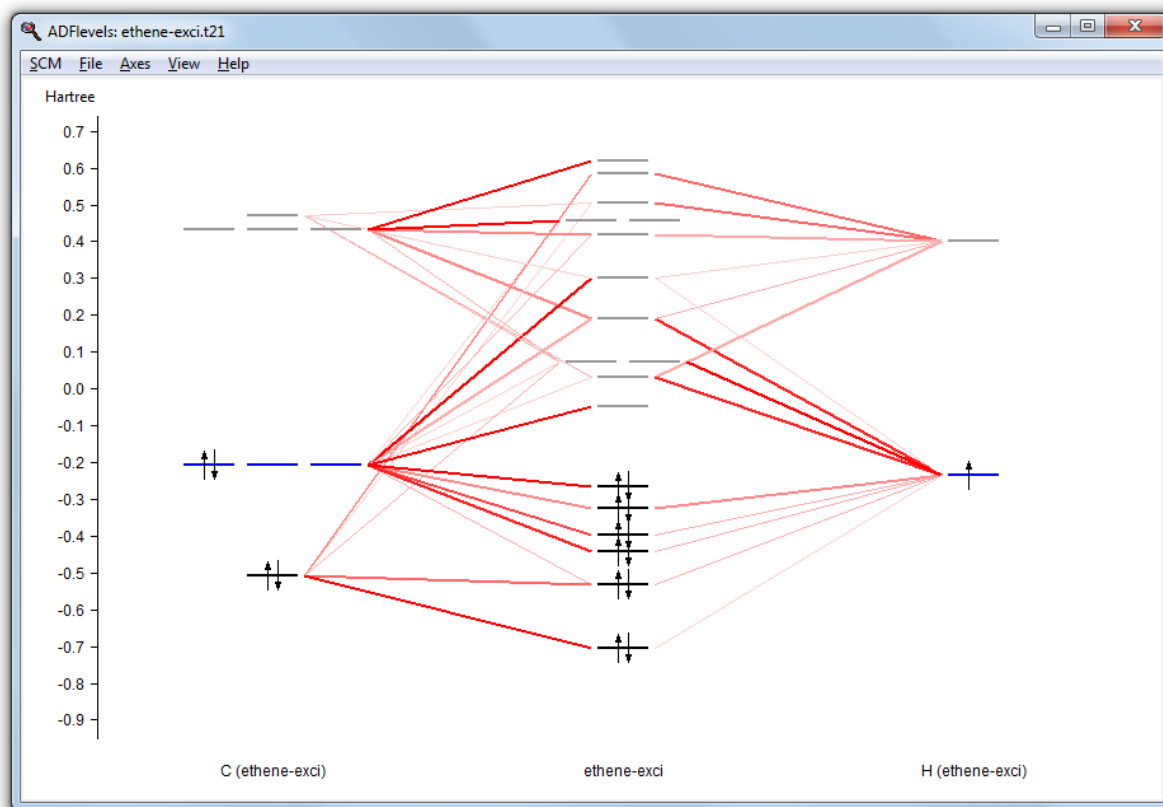
```

ADFTail: ethene-exci.logfile
SCM File Edit Help
<Mar20-2013> <19:02:48>      Cycle:      4, MaxErr:    0.0000000
<Mar20-2013> <19:02:48>      Converged.
<Mar20-2013> <19:02:49>      SS B2.u
<Mar20-2013> <19:02:49>      Cycle:      2, MaxErr:    0.0052761
<Mar20-2013> <19:02:49>      Cycle:      3, MaxErr:    0.0002776
<Mar20-2013> <19:02:49>      Cycle:      4, MaxErr:    0.0000016
<Mar20-2013> <19:02:49>      Cycle:      5, MaxErr:    0.0000000
<Mar20-2013> <19:02:49>      Converged.
<Mar20-2013> <19:02:49>      SS B3.u
<Mar20-2013> <19:02:49>      Cycle:      2, MaxErr:    0.0364425
<Mar20-2013> <19:02:49>      Cycle:      3, MaxErr:    0.0003772
<Mar20-2013> <19:02:49>      Cycle:      4, MaxErr:    0.0000042
<Mar20-2013> <19:02:49>      Cycle:      5, MaxErr:    0.0000000
<Mar20-2013> <19:02:49>      Converged.
<Mar20-2013> <19:02:49>      ST B1.g
<Mar20-2013> <19:02:49>      Cycle:      2, MaxErr:    0.0007760
<Mar20-2013> <19:02:49>      Cycle:      3, MaxErr:    0.0000043
<Mar20-2013> <19:02:49>      Cycle:      4, MaxErr:    0.0000000
<Mar20-2013> <19:02:49>      Converged.
<Mar20-2013> <19:02:49>      ST B2.g
<Mar20-2013> <19:02:49>      Cycle:      2, MaxErr:    0.0004363
<Mar20-2013> <19:02:49>      Cycle:      3, MaxErr:    0.0000002
<Mar20-2013> <19:02:49>      Converged.
<Mar20-2013> <19:02:49>      ST B3.g
<Mar20-2013> <19:02:49>      Cycle:      2, MaxErr:    0.0000681
<Mar20-2013> <19:02:49>      Cycle:      3, MaxErr:    0.0000000
<Mar20-2013> <19:02:49>      Converged.
<Mar20-2013> <19:02:49>      ST A.u
<Mar20-2013> <19:02:49>      Cycle:      2, MaxErr:    0.0004527
<Mar20-2013> <19:02:49>      Cycle:      3, MaxErr:    0.0000004
<Mar20-2013> <19:02:49>      Converged.
<Mar20-2013> <19:02:49>      ST B1.u
<Mar20-2013> <19:02:49>      Cycle:      2, MaxErr:    0.0002766
<Mar20-2013> <19:02:49>      Cycle:      3, MaxErr:    0.0000002
<Mar20-2013> <19:02:49>      Converged.
<Mar20-2013> <19:02:49>      ST B2.u
<Mar20-2013> <19:02:49>      Cycle:      2, MaxErr:    0.0018793
<Mar20-2013> <19:02:49>      Cycle:      3, MaxErr:    0.0000098
<Mar20-2013> <19:02:49>      Cycle:      4, MaxErr:    0.0000000
<Mar20-2013> <19:02:49>      Converged.
<Mar20-2013> <19:02:49>      ST B3.u
<Mar20-2013> <19:02:49>      Cycle:      2, MaxErr:    0.0023976
<Mar20-2013> <19:02:49>      Cycle:      3, MaxErr:    0.0000164
<Mar20-2013> <19:02:49>      Cycle:      4, MaxErr:    0.0000000
<Mar20-2013> <19:02:49>      Converged.
<Mar20-2013> <19:02:49>      NORMAL TERMINATION
<Mar20-2013> <19:02:50>      END
<Mar20-2013> <19:02:50>      DENSEF 2013.01 RunTime: Mar20-2013 19:02:50 Nodes: 1 Procs: 1
<Mar20-2013> <19:02:50>      NORMAL TERMINATION
<Mar20-2013> <19:02:50>      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.

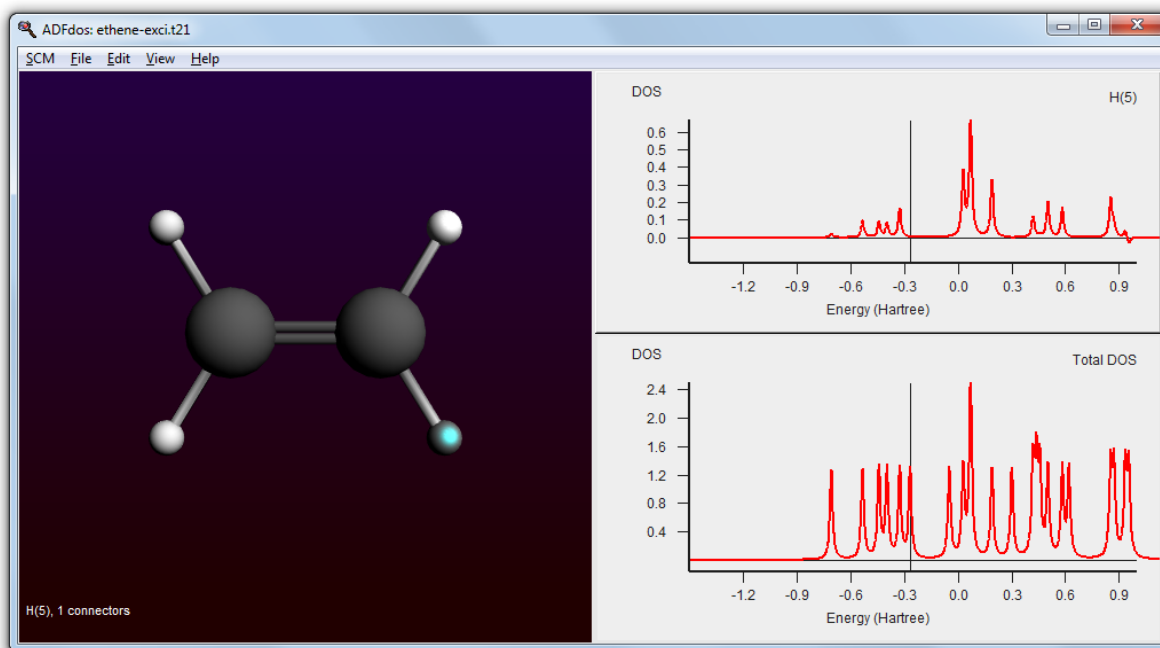
Note that the carbon and hydrogen stacks show all carbon and hydrogen atoms at once: they show the fragment type. ADFlevels can also show the individual fragments but when using atomic fragments you will get too many fragments. In this particular case symmetry is used, and since there is only one symmetry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

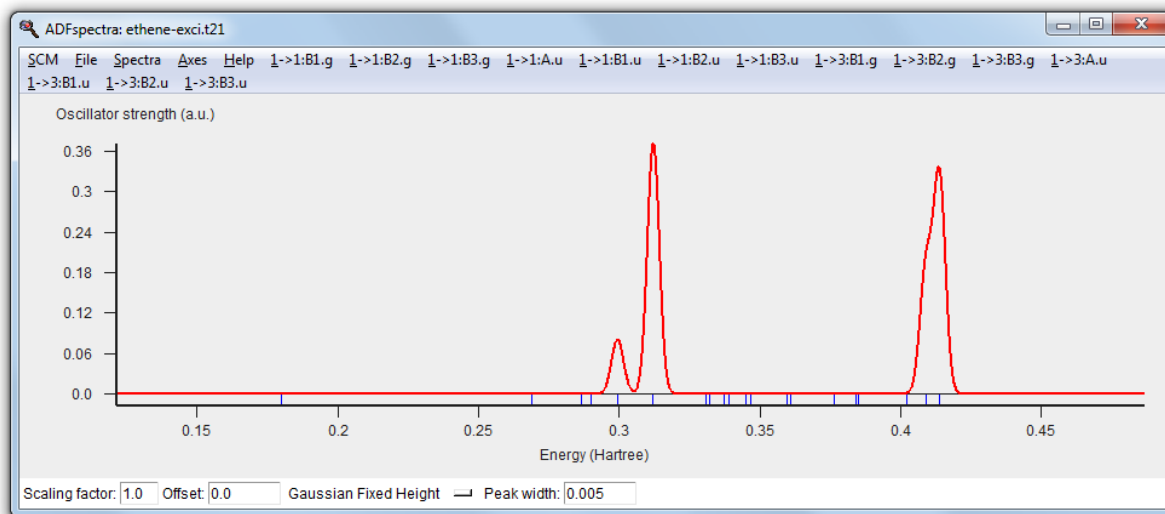


In these plots you can see that the partial DOS for the hydrogen atoms have no contribution to the HOMO. By right clicking on an atom you can also show partial DOS graphs with contribution from selected atoms and selected L-values only.

Excitation spectrum: ADFspectra

Select **SCM** → **Spectra**

ADFspectra will start and show the calculated excitation spectrum.



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

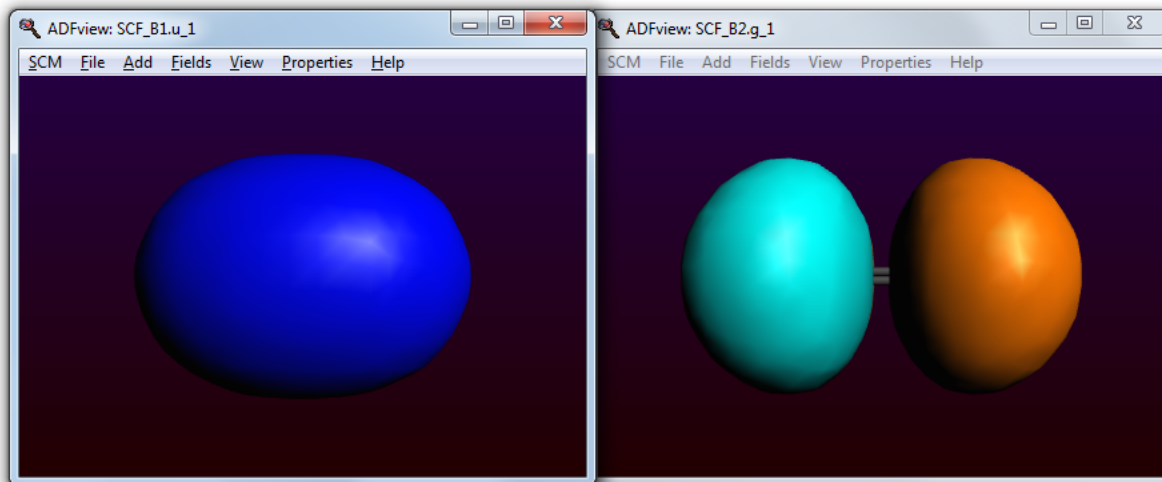
Energy : 0.312121 Hartree
Oscillator strength : 0.372245
Transition dipole moment: -1.33751 0.0 0.0

Composition (major contributions):

```
96.1% 1b1.u -> 1b2.g, dipole contr: (-1.65958000 0.00000000 0.00000000)
1.0% 1b3.u -> 3a.g, dipole contr: (-0.00889203 0.00000000 0.00000000)
0.8% 2a.g -> 3b3.u, dipole contr: ( 0.16153400 0.00000000 0.00000000)
0.6% 1b2.u -> 2b1.g, dipole contr: (-0.03477780 0.00000000 0.00000000)
0.4% 1b1.g -> 3b2.u, dipole contr: ( 0.10460400 0.00000000 0.00000000)
0.3% 2a.g -> 4b3.u, dipole contr: ( 0.05936610 -0.00000000 -0.00000000)
0.2% 1b1.u -> 2b2.g, dipole contr: (-0.02819120 0.00000000 0.00000000)
0.2% 1a.g -> 2b3.u, dipole contr: (-0.00279697 0.00000000 0.00000000)
0.1% 1b1.g -> 2b2.u, dipole contr: ( 0.04469510 -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** → **Close** 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 menu!

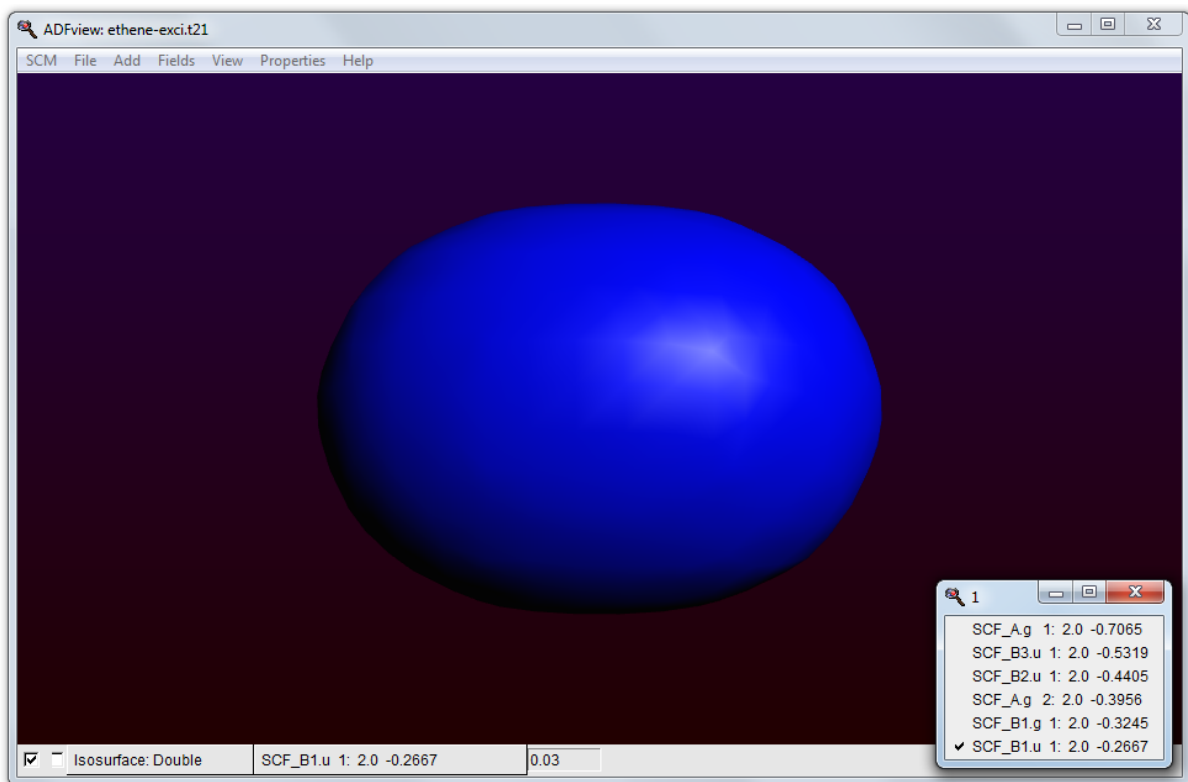
Select **SCM** → **View**

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

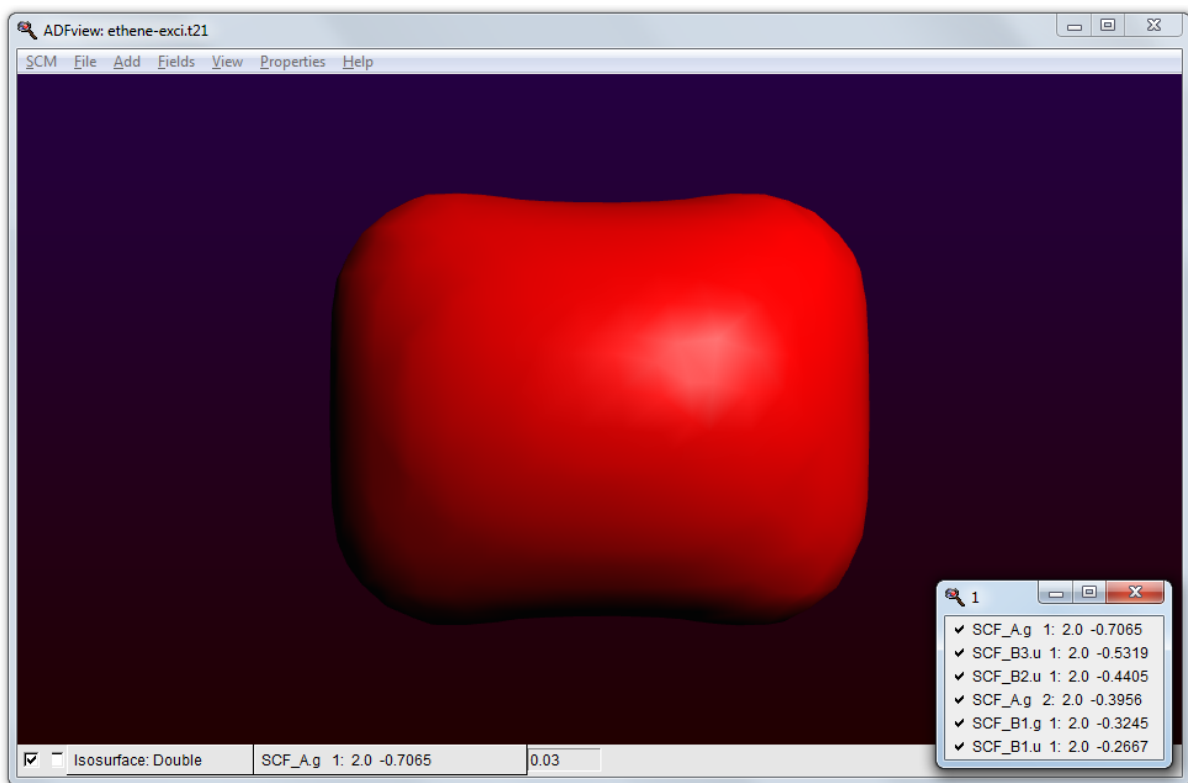
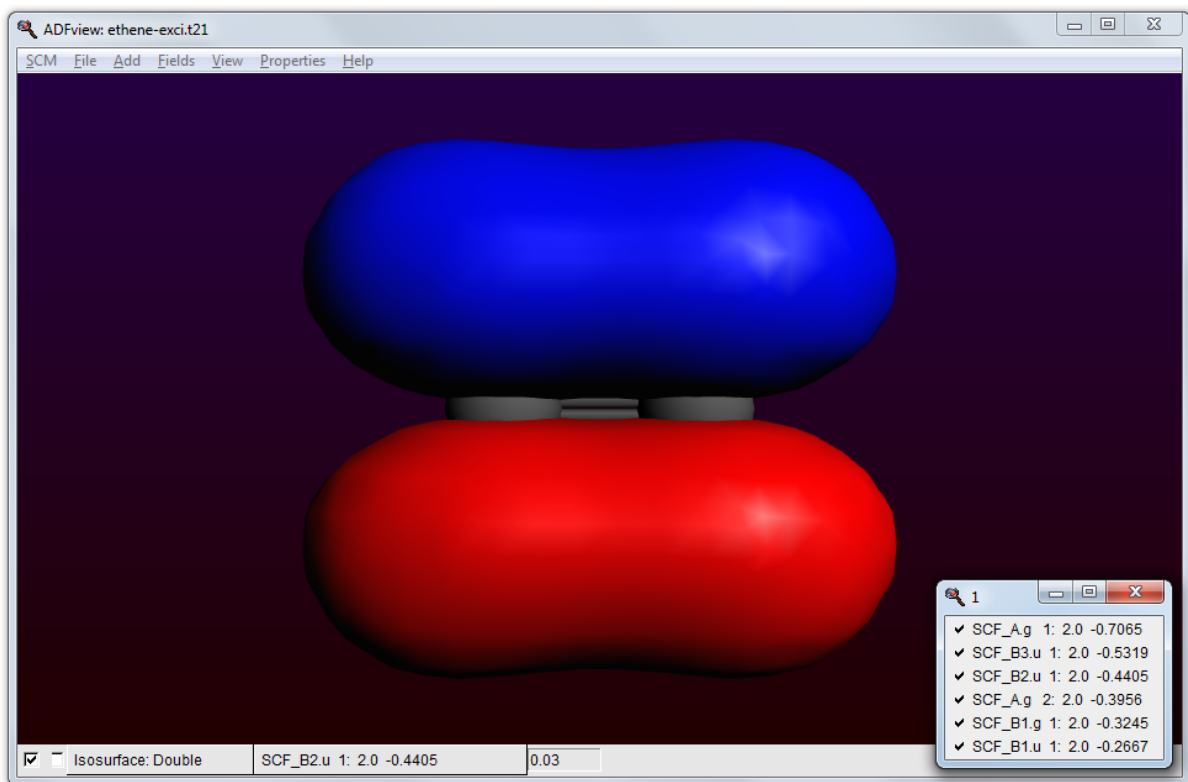


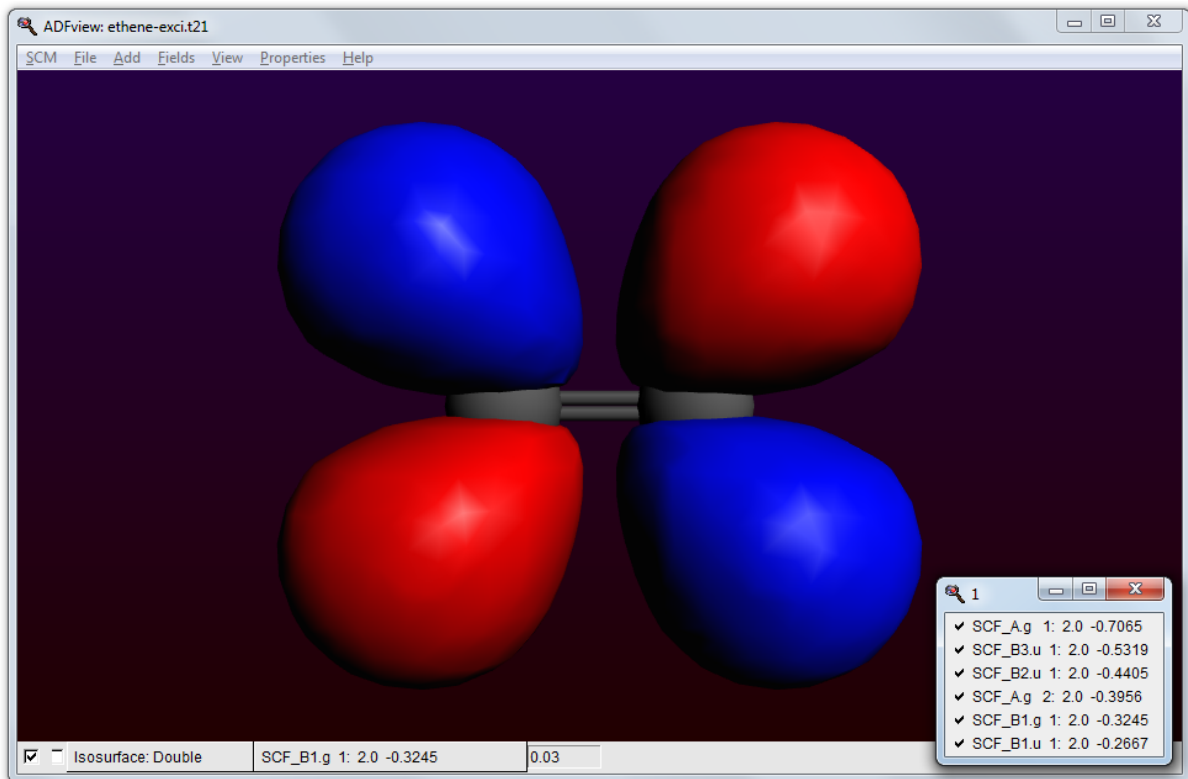
Now you can just click on the different orbitals in the torn-off menu, and very quickly examine those orbitals:

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.





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** → **Close**

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**

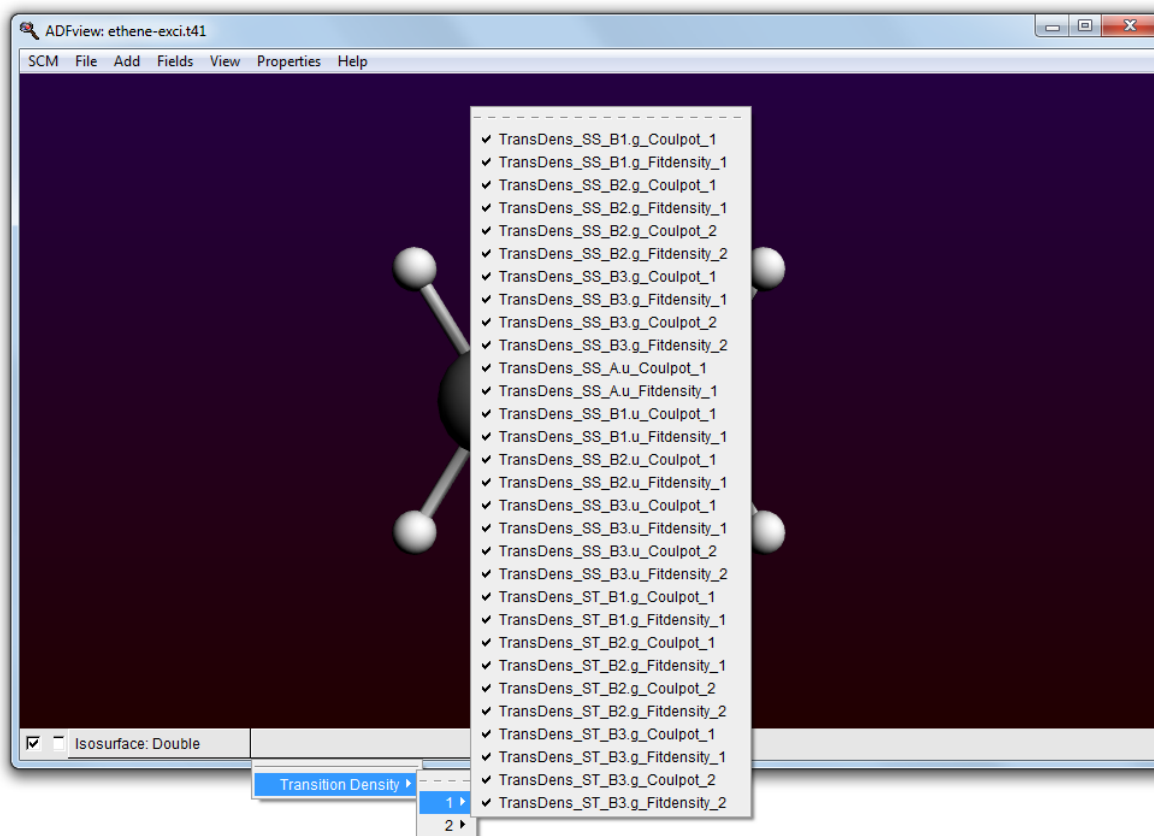
In the file-select pop-up, choose to see all .t41 files using the pop-up menu at the bottom

Select the .t41 file from your calculation (ethene-exci.t41)

Click 'Open'

Select **Add** → **Isosurface: Double (+/-)**

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.

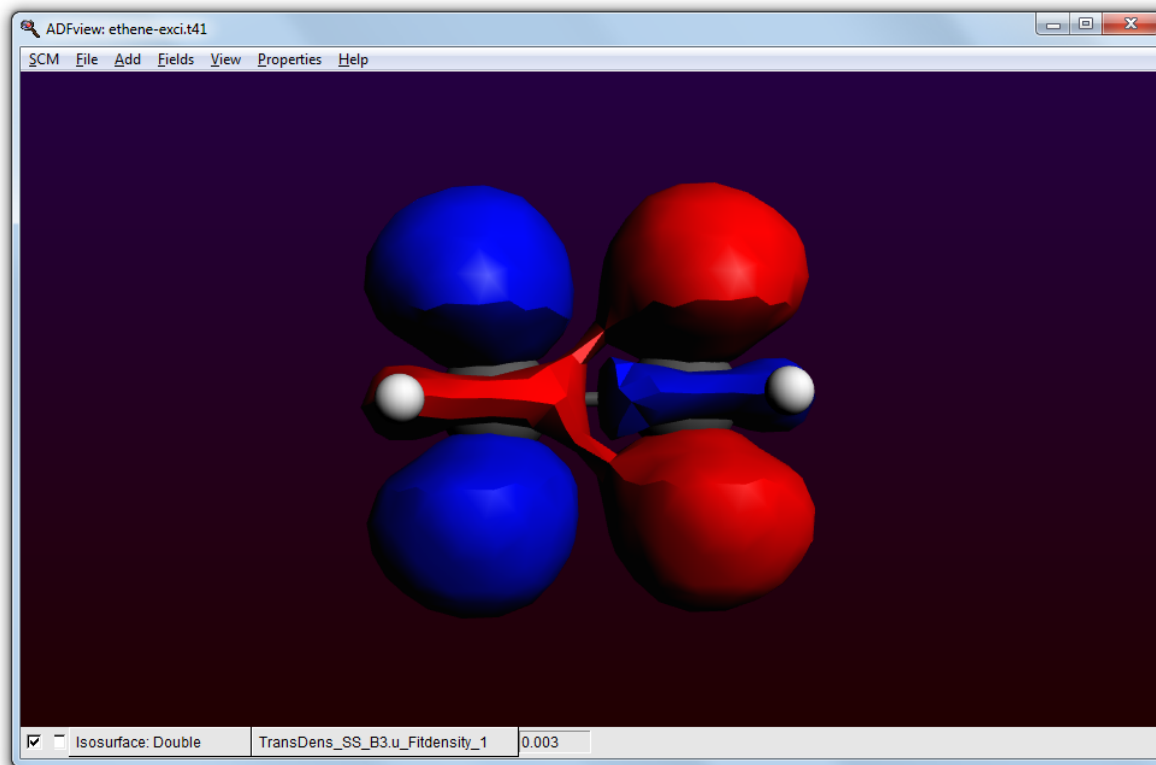


In this case let's select the transition density that belongs to the biggest peak: the Singlet-Singlet 1B3u excitation:

Select the **Transition Density** → **TransDens_SS_B3.u_Fitdensity_1** field

Change the iso value to 0.003

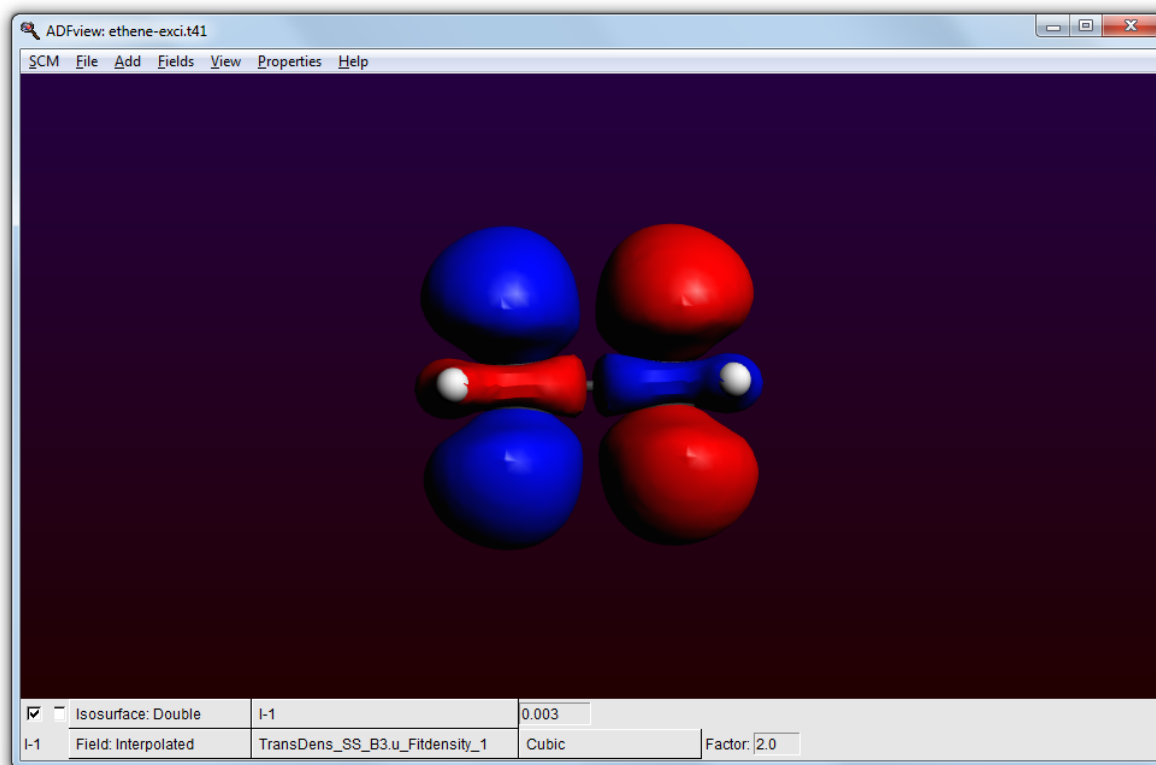
Rotate the molecule a little



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)



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**

```

ADFOutput: ethene-exci.out
SCM File Edit Help Iterations Properties Response Properties Other Properties Section Include
All SINGLET-SINGLET excitation energies
no.      E/a.u.      E/eV      f      Symmetry
-----
1:      0.28640      7.79345    0.000    B1.g
2:      0.29940      8.14720    0.8097E-01 B2.u
3:      0.31222      8.49583    0.3722    B1.u
4:      0.33891      9.22208    0.000    B1.g
5:      0.34651      9.42892    0.000    B3.g
6:      0.35934      9.77819    0.000    B2.g
7:      0.36085      9.81909    0.000    B3.g
8:      0.40193     10.93712    0.000    A.u
9:      0.40867     11.12057    0.1862    B3.u
10:     0.41343     11.25002    0.3225    B1.u

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

Eigenvalues of small (approximate) problem
i, eigenvalue(i) in dvdson  1  0.2689192082E+00
i, eigenvalue(i) in dvdson  2  0.3308996407E+00
Eigenvalues of small (approximate) problem
i, eigenvalue(i) in dvdson  1  0.2688542936E+00
i, eigenvalue(i) in dvdson  2  0.3307967466E+00
Eigenvalues of small (approximate) problem
i, eigenvalue(i) in dvdson  1  0.2688542713E+00
i, eigenvalue(i) in dvdson  2  0.3307967149E+00

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

Number of loops in Davidson routine = 3
Number of matrix-vector multiplications = 6
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.

```

KFBrowser

Most result of the calculation are saved to the KF result file (the .t21 file for an ADF calculation). As of ADF2013 you can inspect the contents of KF files using the KFBrowser. The KFBrowser is a very recent development, feedback and bug reports (there will be bugs ...) are welcome!

The KFBrowser gets the raw data out of the result file, and presents a selection of that might be of interest for users. Over time more results will probably be added to newer versions of the KFBrowser.

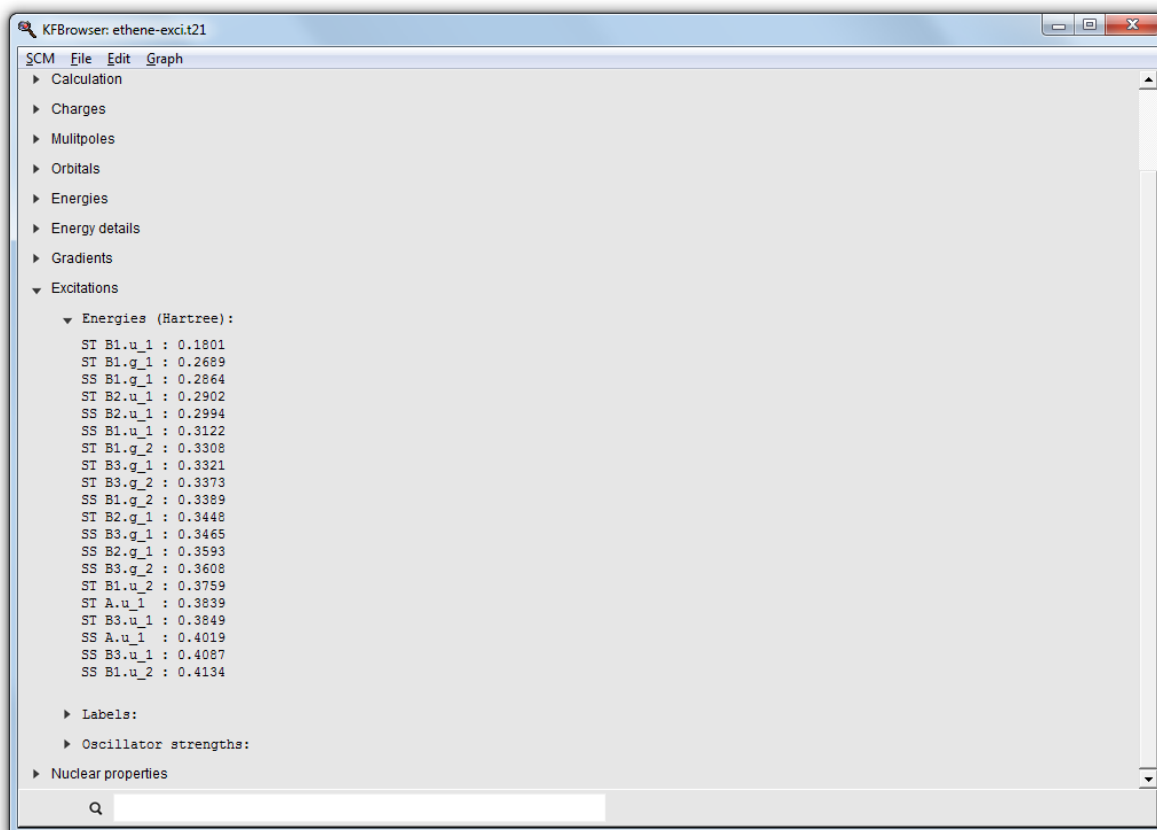
It also gives access to all raw data in the result files. This feature is intended for developers only.

Select **SCM** → **KFBrowser**

In the KFBrowser window that appears:

Click on the arrow in front of Excitations

Click on the arrow in front of Energies (Hartree) (in the Excitations section)



If you click on the name of the property you can select it. Next you can copy it, and paste it for example in Excel:

```
Click on "Energies (Hartree)"
Copy (from the Edit menu or the usual shortcut)
Open Excel or some text editor
Paste
```

After pasting you should have your results nicely formatted in Excel or in some text document. Note that the values are tab-separated, so pasting into Excel will automatically put the data (energies) in cells.

	A	B	C	D	E	F	G	H	I
1	Excitation Energies		Hartree						
2			ST B1.u_1	0.1801					
3			ST B1.g_1	0.2689					
4			SS B1.g_1	0.2864					
5			ST B2.u_1	0.2902					
6			SS B2.u_1	0.2994					
7			SS B1.u_1	0.3122					
8			ST B1.g_2	0.3308					
9			ST B3.g_1	0.3321					
10			ST B3.g_2	0.3373					
11			SS B1.g_2	0.3389					
12			ST B2.g_1	0.3448					
13			SS B3.g_1	0.3465					
14			SS B2.g_1	0.3593					
15			SS B3.g_2	0.3608					
16			ST B1.u_2	0.3759					
17			ST A.u_1	0.3839					
18			ST B3.u_1	0.3849					
19			SS A.u_1	0.4019					
20			SS B3.u_1	0.4087					
21			SS B1.u_2	0.4134					
22									
23									
24									

In a similar way you can copy/paste other results. Or even all results:

In the KFBrowser window:

Edit → **Select All**

Edit → **Copy**

In the Excel or text editor window:

Paste

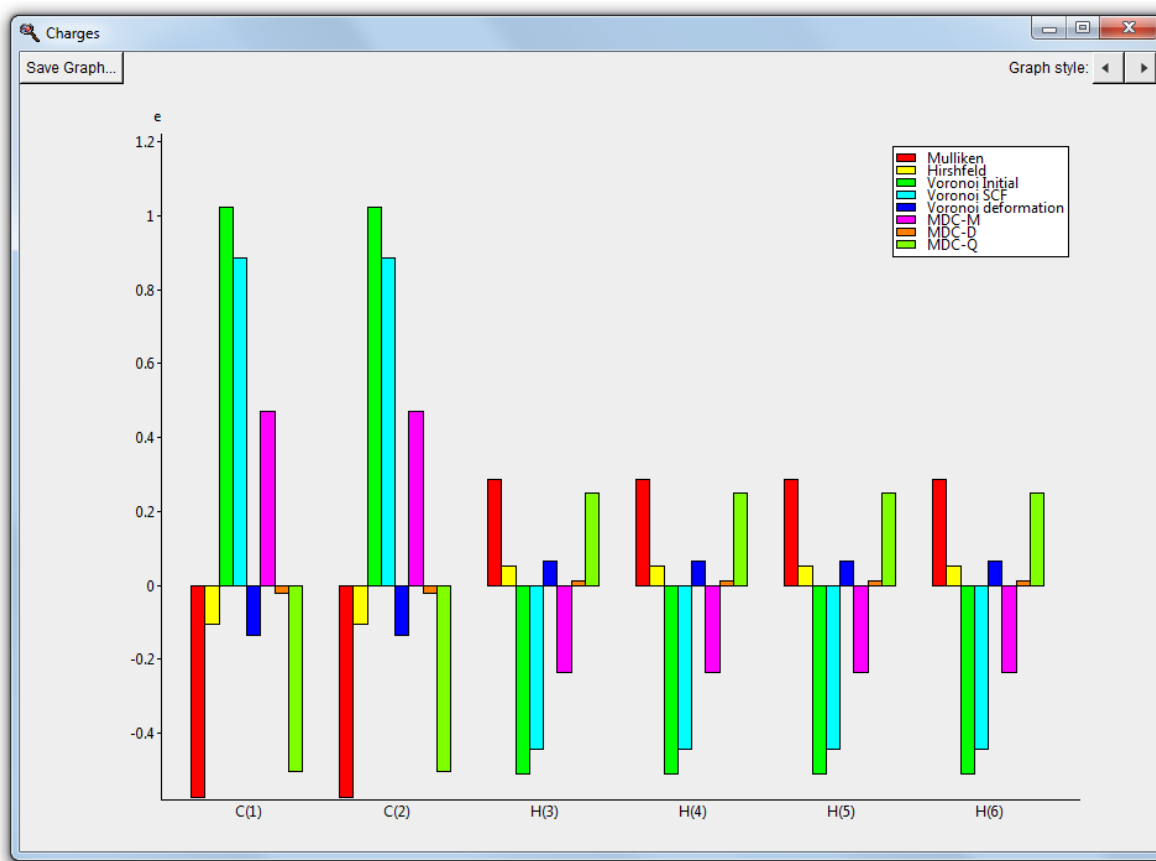
All results should be nicely formatted in your text document or spreadsheet:

	A	B	C	D	E	F	G	H	I
1	General	Title	Ethene excitations						
2	General	Licensed t	SCM Tutorial License /SCM / Amsterdam / NETHERLANDS						
3	General	SCM Userl	u11015						
4	Molecule	Molecular	28.0313	Dalton					
5	Molecule	Number o	6						
6	Molecule	Geometry	Angstrom						
7			C	0	0	0.665181			
8			C	0	0	-0.66518			
9			H	0	-0.93516	-1.2383			
10			H	0	0.935159	-1.2383			
11			H	0	-0.93516	1.238299			
12			H	0	0.935159	1.238299			
13	Molecule	Atom labels							
14			C(1)						
15			C(2)						
16			H(3)						
17			H(4)						
18			H(5)						
19			H(6)						
20	Symmetry	Molecular	D(2H)						
21	Symmetry	Point grou	D(2H)						
22	Symmetry	Irreps	A.g B2.g B3.g B1.u B2.u B3.u						
23	Calculatio	Type	SINGLE POINT						
24	Calculatio	Integratio	4						
25	Calculatio	Integratio	4						
26	Calculatio	Integratio	4						
27	Energy de	Orbital int	Hartree						
28			A.g	-1.08051					
29			B2.g	0.038198					
30			B3.g	-0.78101					
31			B1.u	-1.24558					
32			B2.u	-0.78392					
33			B3.u	-0.40731					
34	Calculatio	Becke inte	NORMAL						
35	Energy de	First-orde	0.001349 Hartree						
36	Calculatio	SCF status	CONVERGED						
37	Gradients	Gradients	Hartree/Bohr						
38			0	0	0				
39			0	0	0				

Another feature of the KFBrowser is that it can show results in simple graphs:

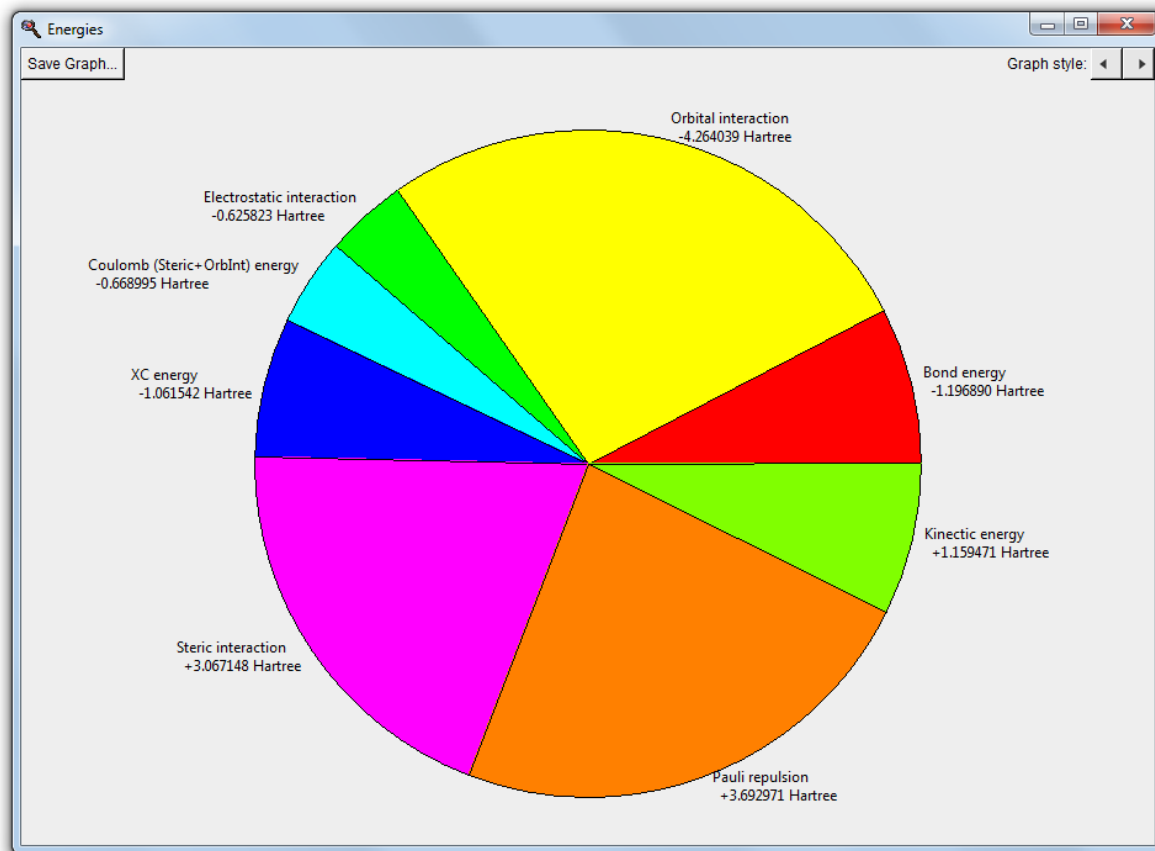
Close the KFBrowser window
 Open it again **SCM** → **KFBrowser**
 Open the Charges section
 Click on Mulliken (e)
 Shift-click on MDC-Q (e)
 Use the **Graph** → **Selection As Graph** command (or double click on the selection)

A window should appear that shows the selected results, charges in this case:



You can use the Graph style buttons to switch to different graph types (XY, Bars or Piechart).

Switch to the KFBrowser window
 Open the Energies section
 Select all energies (click on first, shift-click on last energy)
 Double click on the selection



Finally two features that are intended for developers and expert users: the KFBrowser module can also show the raw data on the result file, and it can dump a KF file as a plain text file. To activate the export mode, use the **File** → **Expert Mode** menu command. To save the contents of the result file as a text file using the **File** → **Save As ASCII...** command.

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** → **Quit**

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** → **Quit All**

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

Tutorial 5: Vibrational frequencies and IR spectrum 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 Atoms → Add Hydrogens
And do it again: ... add hydrogens
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.

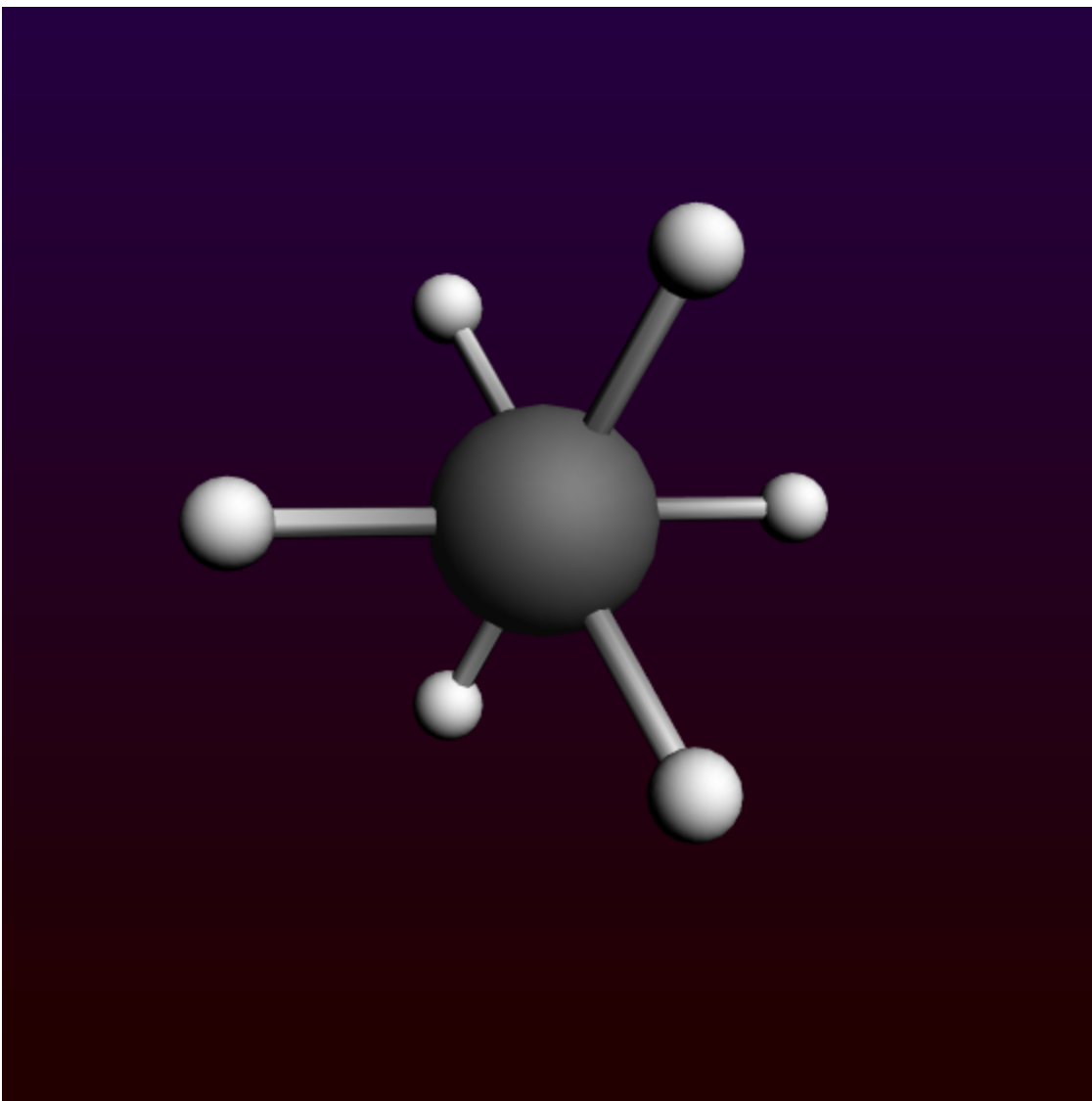
Alternatively, you can, after placing the second atom, click on that atom to finish using the C-tool. In this case none of the carbon atoms will be selected and you can easily add all the hydrogens at the same time.

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

ADF Main Model Properties Details MultiLevel Q

Title:

Preset:

Task: ...

Total charge:

Spin polarization:

Unrestricted: Yes

XC potential in SCF: ...

XC energy after SCF:

Relativity (ZORA): ...

Basis set: ...

Frozen core:

Integration: ...

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:


```

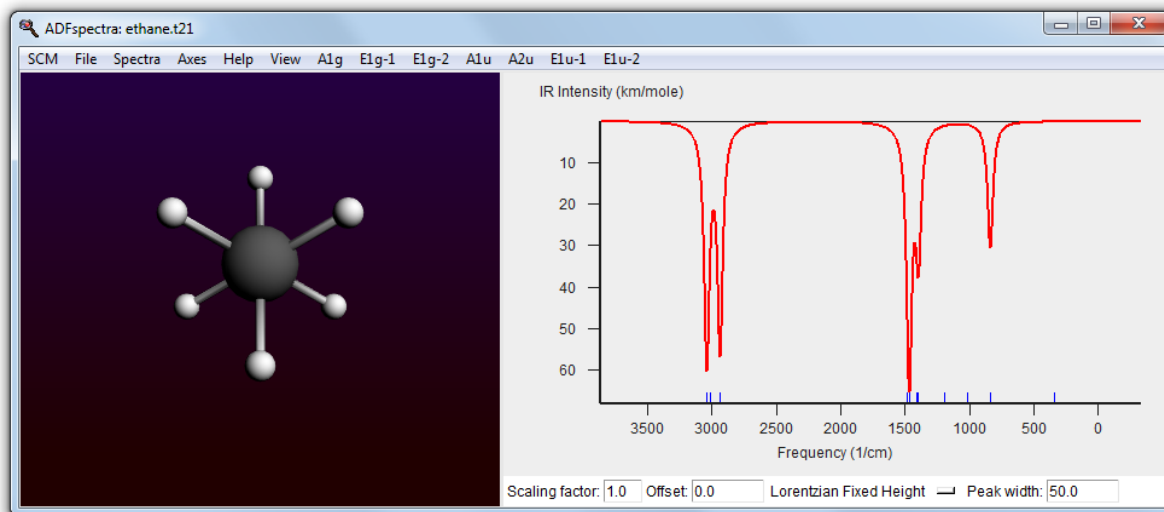
ADFTail: ethane.logfile
SCM File Edit Help
<Mar24-2013> <12:05:28> END
<Mar24-2013> <12:05:29> ADF 2013.01 RunTime: Mar24-2013 12:05:29 Nodes: 1 Procs: 4
<Mar24-2013> <12:05:29> Ethane
<Mar24-2013> <12:05:29> RunType : SINGLE POINT
<Mar24-2013> <12:05:29> Net Charge: 0 (Nuclei minus Electrons)
<Mar24-2013> <12:05:29> Symmetry : D(3D)
<Mar24-2013> <12:05:29> >>>> FRAGM
<Mar24-2013> <12:05:30> >>>> CORORT
<Mar24-2013> <12:05:30> >>>> FITINT
<Mar24-2013> <12:05:30> >>>> CLSMAT
<Mar24-2013> <12:05:30> >>>> ORTHON
<Mar24-2013> <12:05:30> >>>> GENPT
<Mar24-2013> <12:05:30> Block Length= 127
<Mar24-2013> <12:05:30> >>>> PTBAS
<Mar24-2013> <12:05:30> >>>> CYCLE
<Mar24-2013> <12:05:30> 1
<Mar24-2013> <12:05:31> 2 ErrMat 0.94325833 MaxEl 0.31926367
<Mar24-2013> <12:05:31> 3 ErrMat 0.47154314 MaxEl 0.15346110
<Mar24-2013> <12:05:31> 4 ErrMat 0.05641215 MaxEl -0.01640700
<Mar24-2013> <12:05:31> 5 ErrMat 0.00074640 MaxEl -0.00036379
<Mar24-2013> <12:05:31> 6 ErrMat 0.00014850 MaxEl 0.00005417
<Mar24-2013> <12:05:31> 7 ErrMat 0.00001045 MaxEl -0.00000408
<Mar24-2013> <12:05:31> 8 ErrMat 0.00000006 MaxEl 0.00000002
<Mar24-2013> <12:05:31> SCF converged
<Mar24-2013> <12:05:31> 9 ErrMat 0.00000001 MaxEl 0.00000000
<Mar24-2013> <12:05:31> >>>> TOTEN
<Mar24-2013> <12:05:32> >>>> POPAN
<Mar24-2013> <12:05:32> >>>> DEBYE
<Mar24-2013> <12:05:32> >>>> AMETS
<Mar24-2013> <12:05:32> Bond Energy -1.51932911 a.u.
<Mar24-2013> <12:05:32> Bond Energy -41.34304865 eV
<Mar24-2013> <12:05:32> Bond Energy -953.39 kcal/mol
<Mar24-2013> <12:05:32> >>>> POPUL
<Mar24-2013> <12:05:33> >>>> ENGRAD
<Mar24-2013> <12:05:33> >>>> ENHES
<Mar24-2013> <12:05:33> >>>> FITINT
<Mar24-2013> <12:05:33> >>>> FIT_A1_COEF01
<Mar24-2013> <12:05:34> >>>> FITINT
<Mar24-2013> <12:05:35> === NUCLEUS: 1
<Mar24-2013> <12:05:38> === NUCLEUS: 3
<Mar24-2013> <12:05:41> >>>> CALC_HESS_PMAT
<Mar24-2013> <12:05:42> >>>> CALC_HESS_WMAT
<Mar24-2013> <12:05:43> NORMAL TERMINATION
<Mar24-2013> <12:05:43> 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**

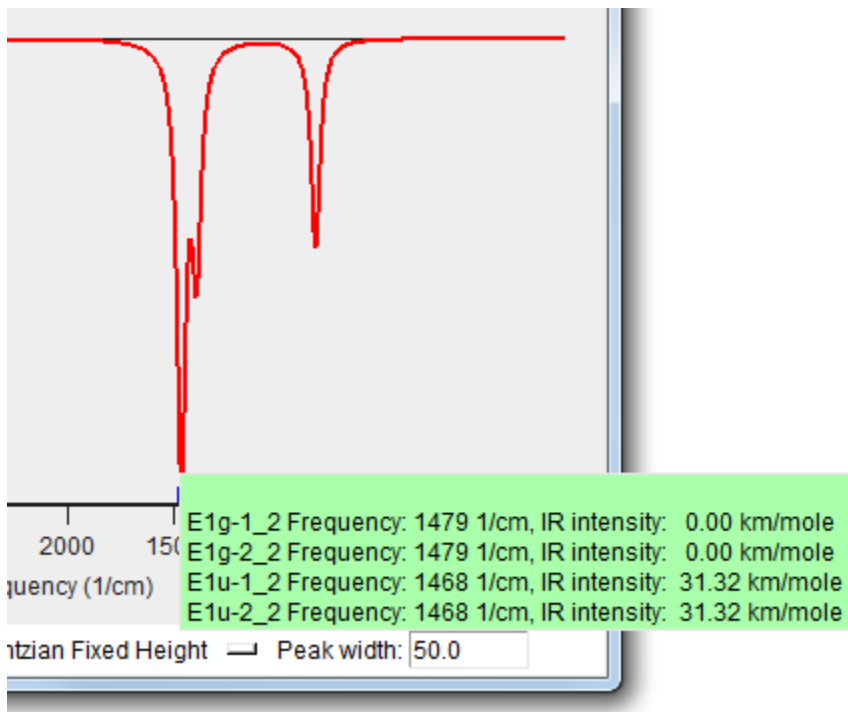


On the left side of the window the molecule (Ethane) is shown.

On the right side the IR spectrum is shown. You can save a picture (of the IR spectrum) 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 your own graphing application.

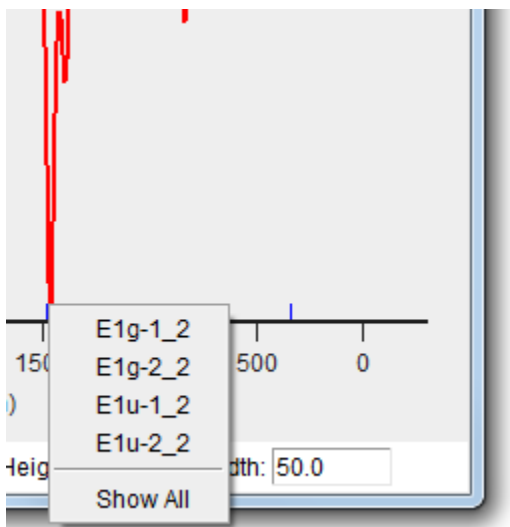
If you move the mouse pointer above the spectrum you will get more information about the peaks in pop-up windows:

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



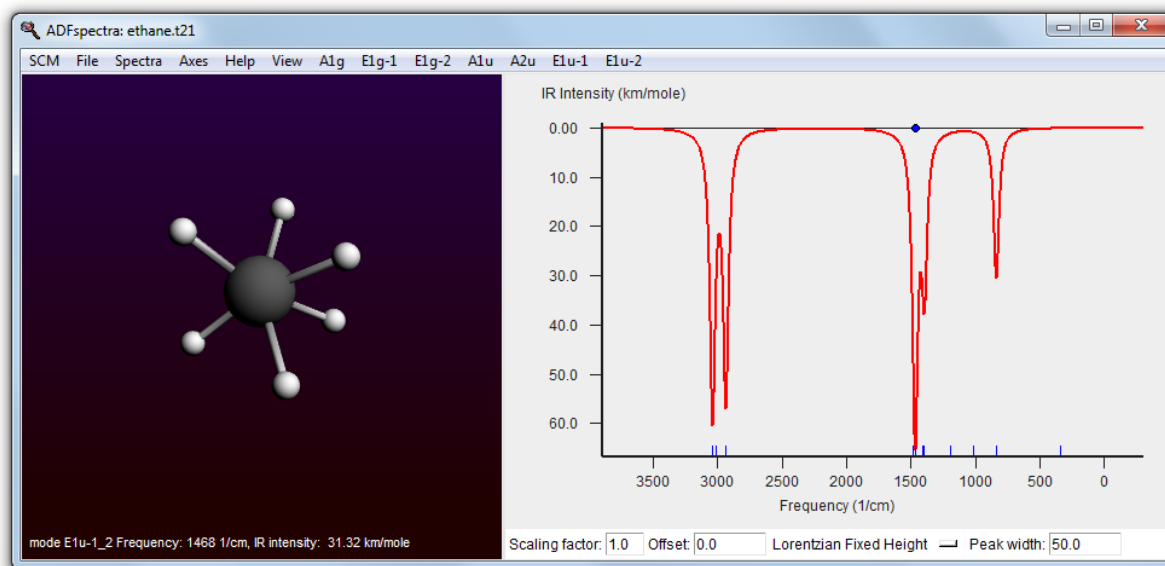
The list of normal modes contributing to the IR peak will show up. By clicking the mouse button at this point, the first of these modes will be shown by animating the ethane molecule on the left. Alternatively, pressing and holding the mouse button down, a list of these modes with their symmetry labels 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 (not the Show All)



The corresponding normal mode should be shown on the left.

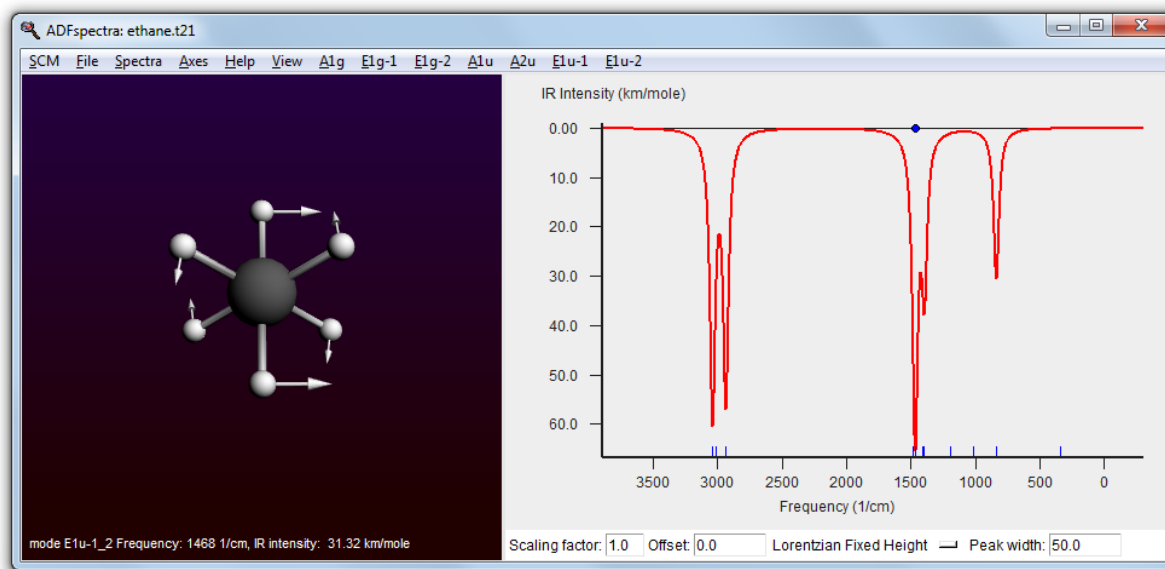
To view another normal mode, most conveniently use the left and right arrow keys to move through them. Alternatively, you can show another mode just as you showed the first mode (click on a peak, or use the pop-up menu).

You can make the displacements larger or smaller via menu commands. Or, more conveniently, use the up and down arrow keys on the keyboard. And you can show the normal mode as vectors:

Use **arrow up** key repeatedly to make the displacements larger
Use **arrow down** key repeatedly to make the displacements smaller

Use the **left** and **right** arrow keys to switch between modes

Use the **View** → **Displacement Vectors** to visualize the normal mode with vectors



You can make the vectors larger or smaller using the same ctrl/cmd-L/K, or arrow up and down.

Another option is to show the normal mode in ADFmovie:

Use the **View** → **Open Mode In ADFmovie**

If you use the 'Show All' command from the pop-up list (instead of one specific mode) all modes in the pop-up list will be shown in ADFmovie windows.

If a mode is visible in ADFmovie you have some extra advanced options. For example, to make a mpg movie showing the mode.

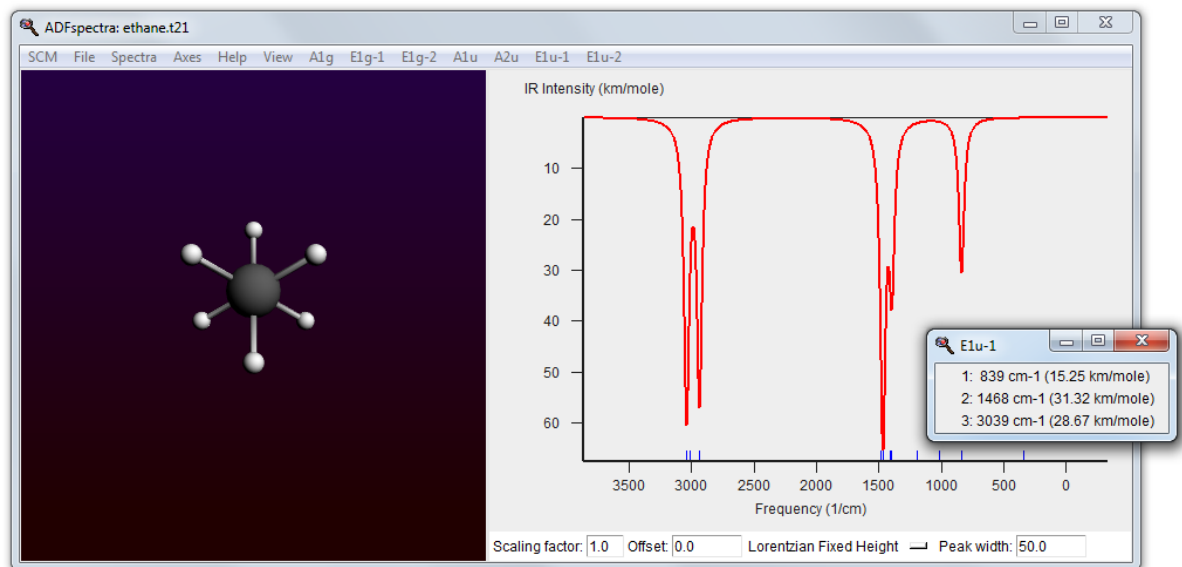
Sometimes you wish to examine many different normal modes. Obviously you can do this as just described, but another way is by selecting the mode of interest from the menu. And to make it more convenient to check many of them, you can tear off these menus, just as you did with the orbital selector menu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

In ADFspectra: **File** → **Close**, 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



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

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

SCM → Quit All

Advanced ADF-GUI tutorials

Tutorial 6: HCN Isomerization Reaction

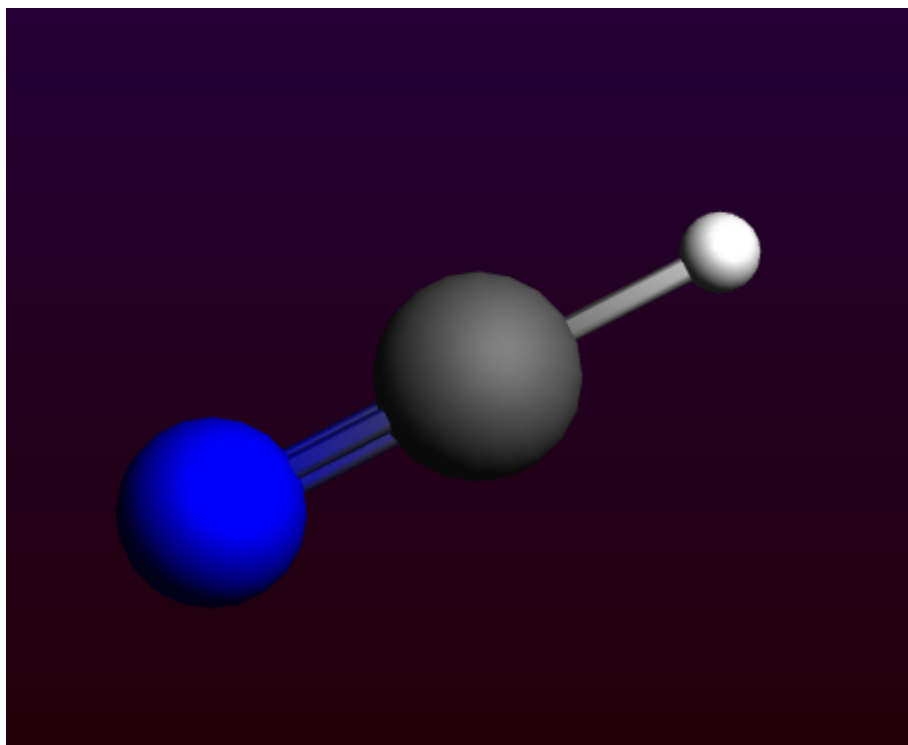
This tutorial consists of several steps to study the isomerization reaction of HCN:

- 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 → New Input menu command
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

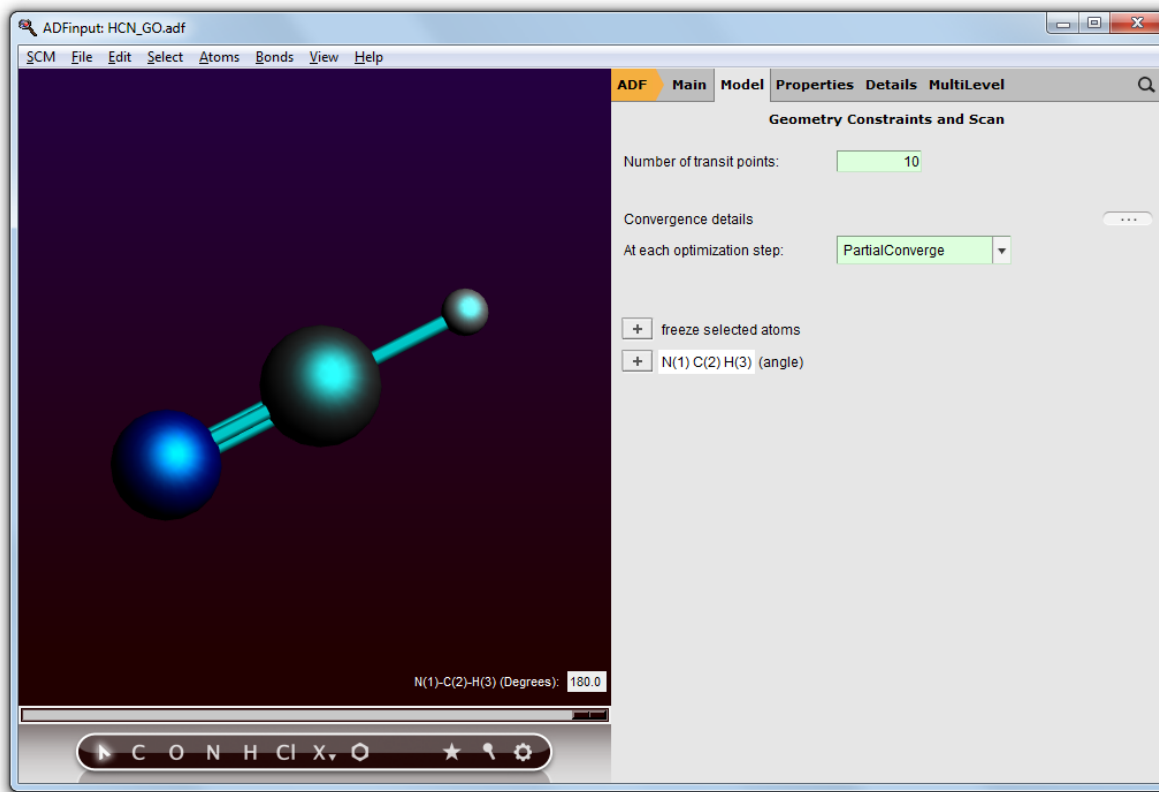
The HCN molecule has an CNH isomer. There is an energy barrier between these two states. We are going to find the transition state and calculate its height.

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

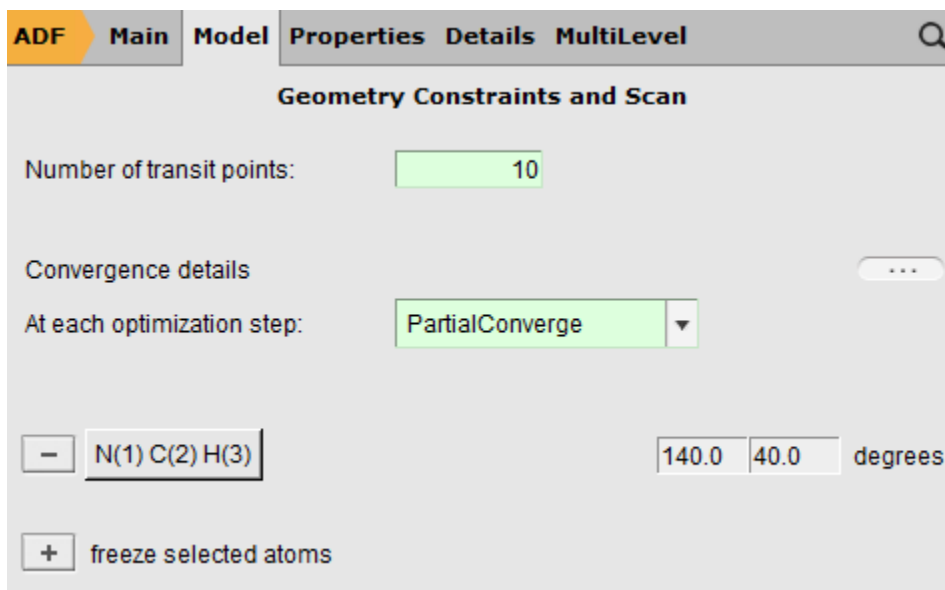
You should see '+ N(1) C(2) H(3) (angle)' note in the right panel now:



Click the '+' button to add the angle constraint

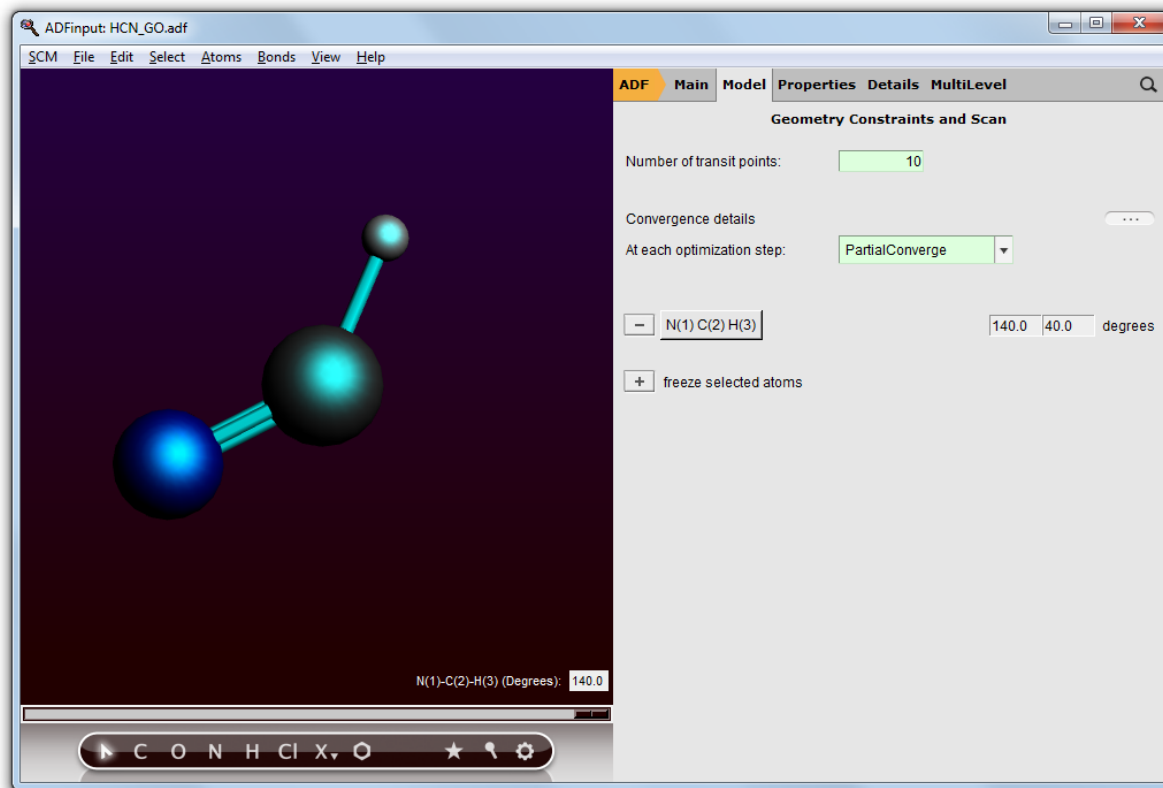
Now '- N(1) C(2) H(3)' and the two fields as limits for the degree parameter appear.

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



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



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)

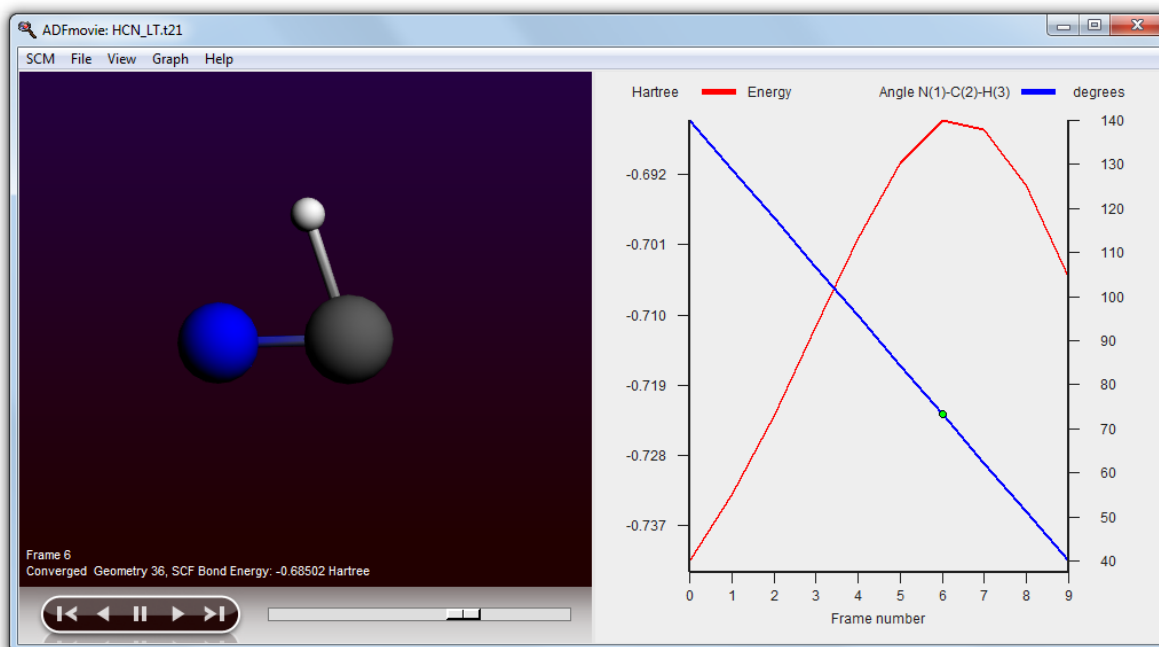
You will see the hydrogen atom moving from C to N. You will also see a graph of the energy as function of the LT steps. As the movie is playing a dot shows the corresponding position in the graph.

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

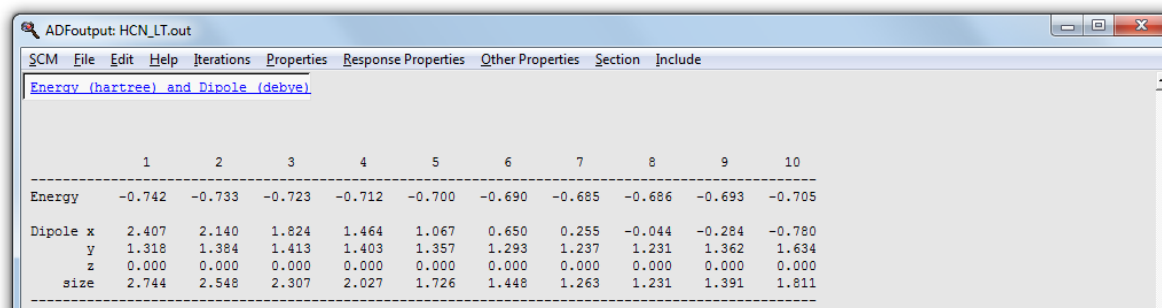
You should find that at around an angle of 60-75 degrees the maximum energy is reached. This is Frame 6 (the 7th LT step):



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

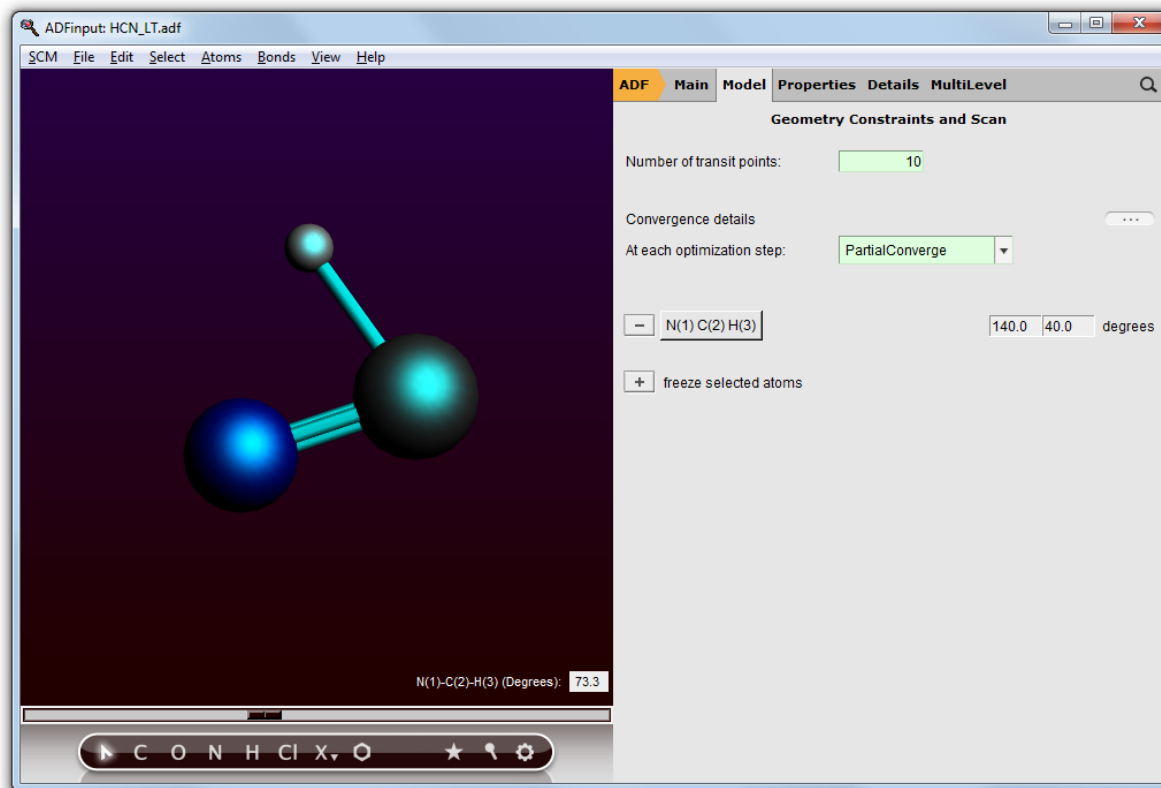


You will see that indeed the geometry number 7 (corresponding to Frame 6 in ADFmovie) has the highest energy. In this particular example the choice of the angle is not very important, but in general you will always want to get the best approximation for the transition state available.

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:



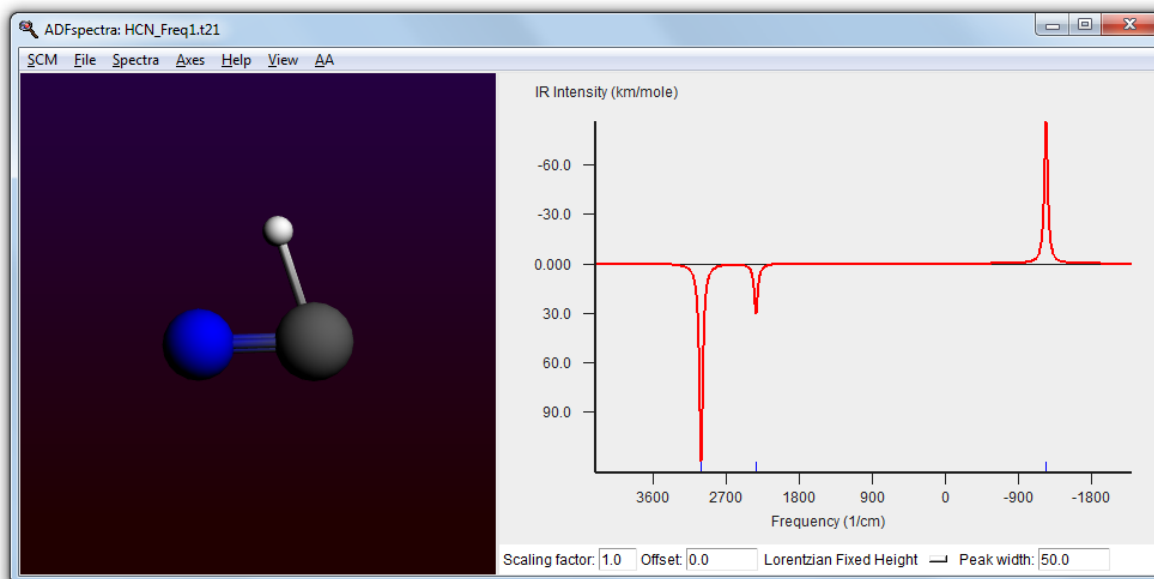
Step 3: Finding the transition state: prepare approximate Hessian

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)
Make sure the integration method is set to 'Becke'
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



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.

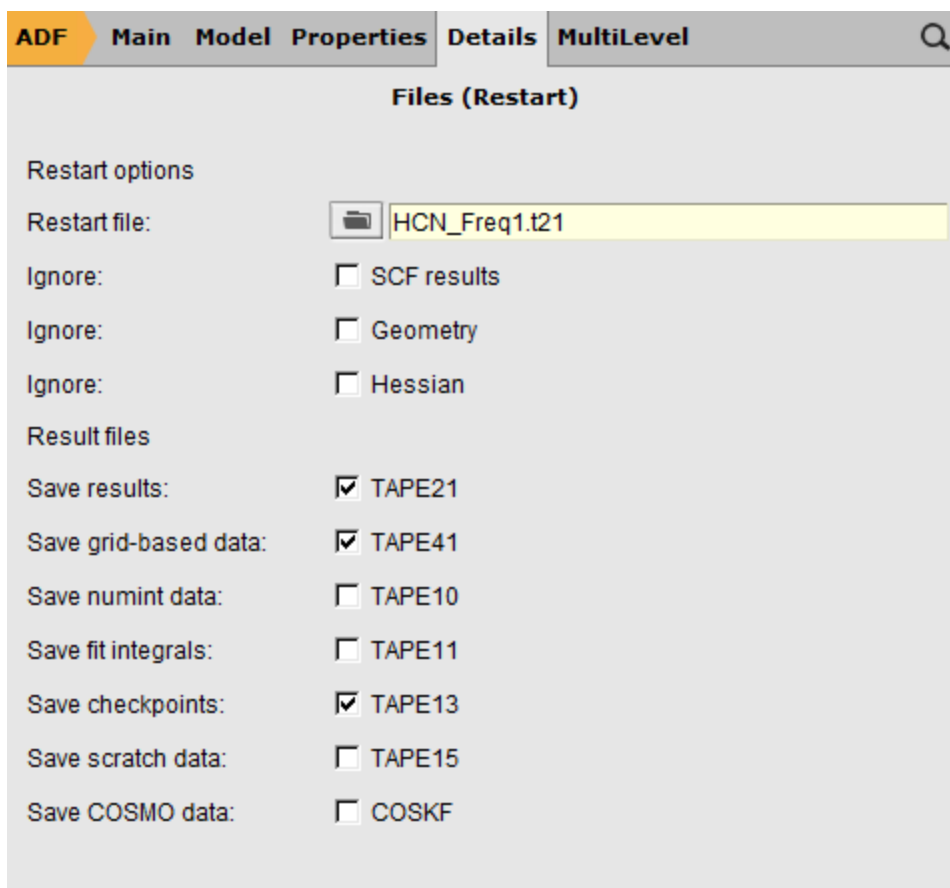
Click with your mouse on the peak corresponding to the imaginary frequency

The normal mode corresponding to that frequency will show on the left side. 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':



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

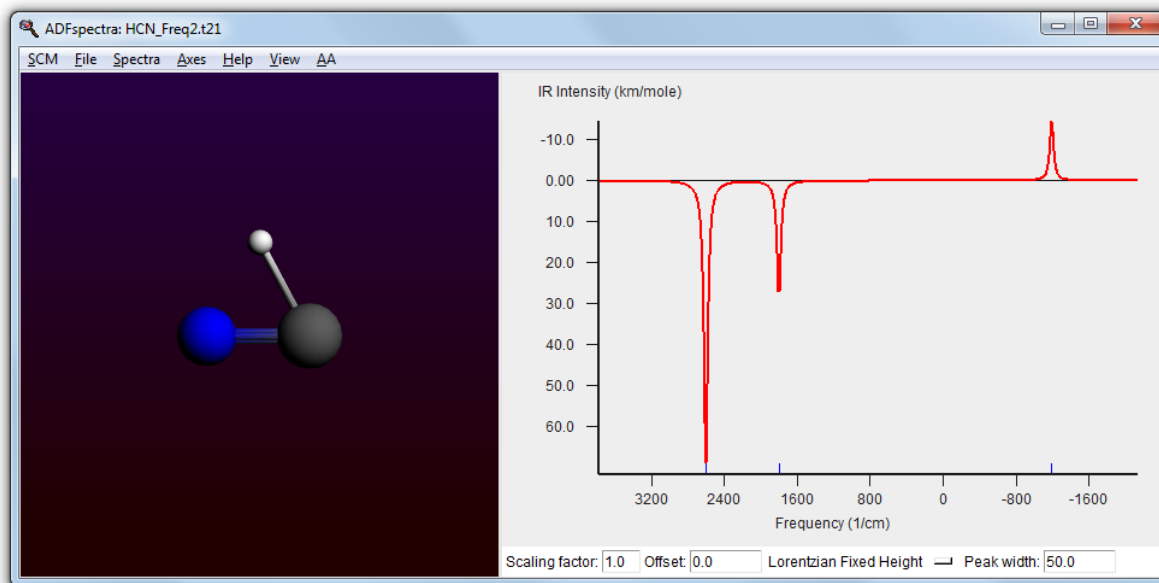
After every transition state search it is good practice to verify that you indeed have one and only one imaginary frequency. For this we will repeat the frequency calculation at the TS geometry:

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.



Click on the band at -1040

The visualization of the normal mode corresponding to this frequency should make it clear 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.

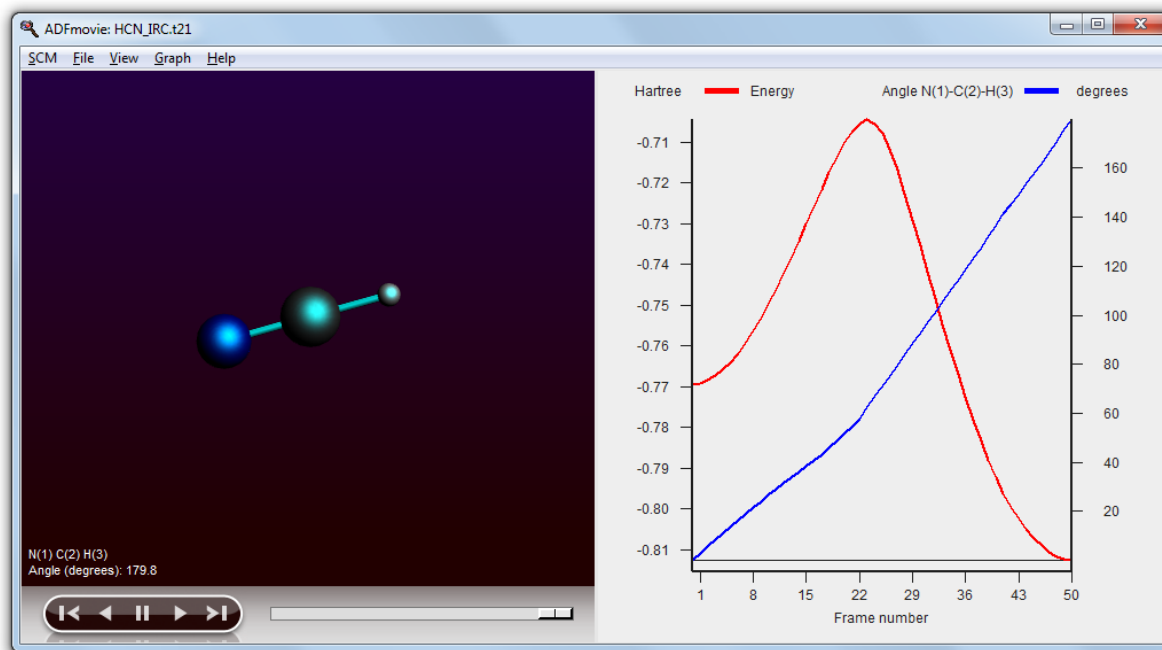
Bring HCN_Freq2 in ADFinput to the front
Select the "IRC" preset
Go to the 'Intrinsic Reaction Coordinate (IRC)' panel (in Model, or via the search, or by clicking on the '...' button)

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
 Click OK when the warning message appears (about the changed order of steps)
 Select the **Graph** → **Energy** command
 Select all atoms
 Select the **Graph** → **Distance, Angle, Dihedral** command



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, the order of the forward path needs to be reversed to get a proper energy graph.

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** → **Quit All** command.

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

This tutorial consists of several steps:

- TIH spin-orbit fragment analysis
- Separate calculations for TI and H

- Visualization of the energy diagram
- Visualization of spinors
- Calculate the atomization energy

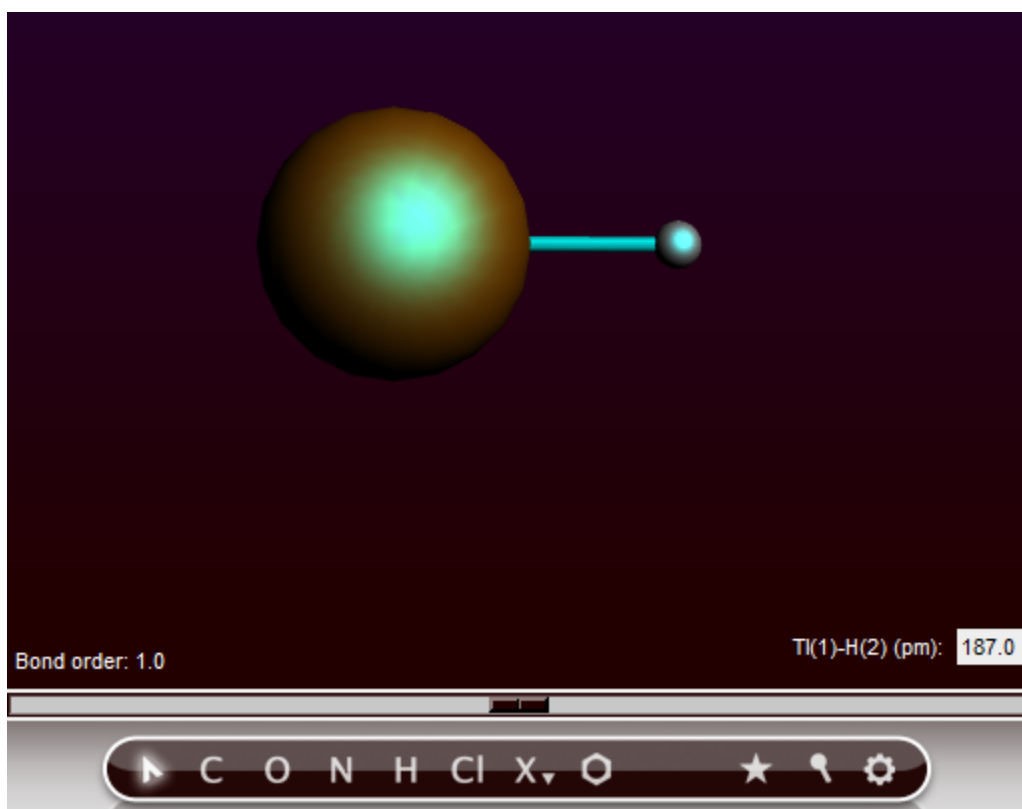
Step 1: Prepare molecule

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

Open ADFinput and draw a TIH molecule.

Select the Tl and H atoms

Use the slider to set the distance between the atoms 1.87 Angstrom



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 'TIH spin-orbit coupled'

Select the GGA → BP as XC potential in SCF

Select the 'Spin-Orbit' relativistic option

Select the basis set 'TZ2P'

Set Frozen core to 'None'

The Main panel will now look like:

The screenshot shows the ADF software interface with the 'Main' panel selected. The panel contains the following configuration options:

- Title: TIH 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: Becke

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.

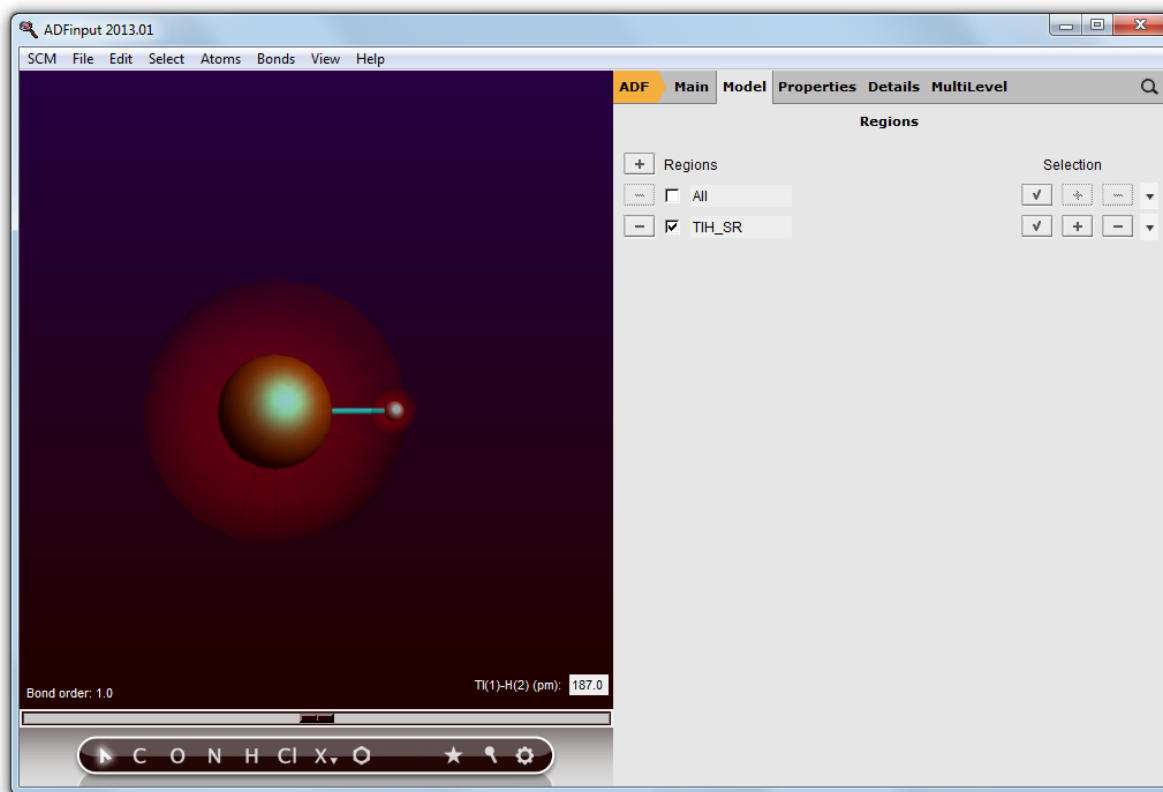
Fragment calculations are based on regions, which are just collections of atoms. So we start by making a region:

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



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

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

Fragment	Fragment File	Charge	Open
TIH_SR	 <input type="text"/>	<input type="text" value="0.0"/>	

Step 3: Run your calculation

Use the **File** → **Save** menu command
Enter the name 'TIH_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: TIH_SO.TIH_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** → **Close**

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** → **Close**
Repeat for the second ADFtail, thus closing both logfiles

Step 4: Results of the calculation

TIH 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**

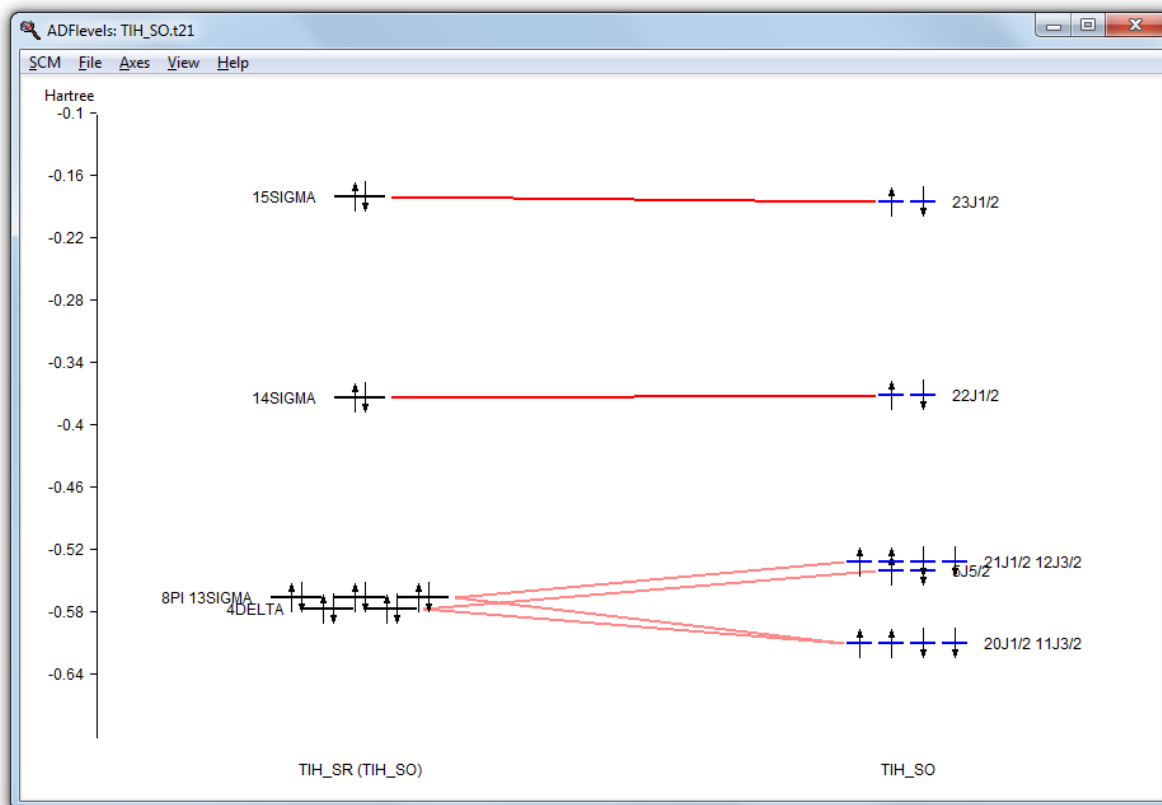
Press and hold the Right mouse button on the stack name 'TlH_SO',

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.



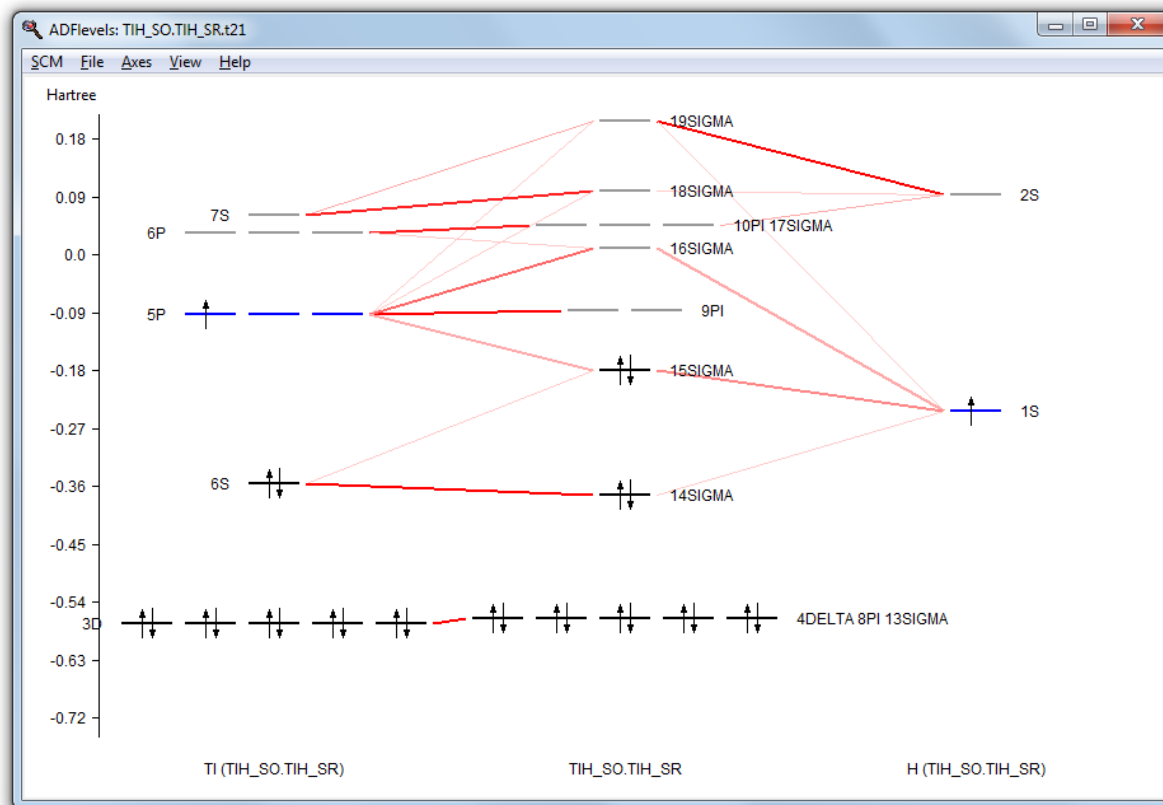
You can see that the spin-orbit coupling is important to split energy levels.

Especially for the TI core levels the spin-orbit coupling is more important than the ligand field splitting. Compare the 8pi, 13sigma, 4delta orbitals (close to 5d atomic TI orbitals) with the 11j3/2, 20j1/2 spinors (close to 5d3/2 atomic TI spinors) and 5j5/2, 12j3/2, and 21j1/2 spinors (close to 5d5/2 atomic TI 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 TIH_SO.TIH_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 'TIH_SO.TIH_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 $\alpha \varphi_\alpha^R$, imaginary part $\alpha \varphi_\alpha^I$, real part $\beta \varphi_\beta^R$, imaginary part $\beta \varphi_\beta^I$:

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

The density ρ is:

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

The spin magnetization density \mathbf{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 'TIH_SO.adf.

Select **SCM** → **View**

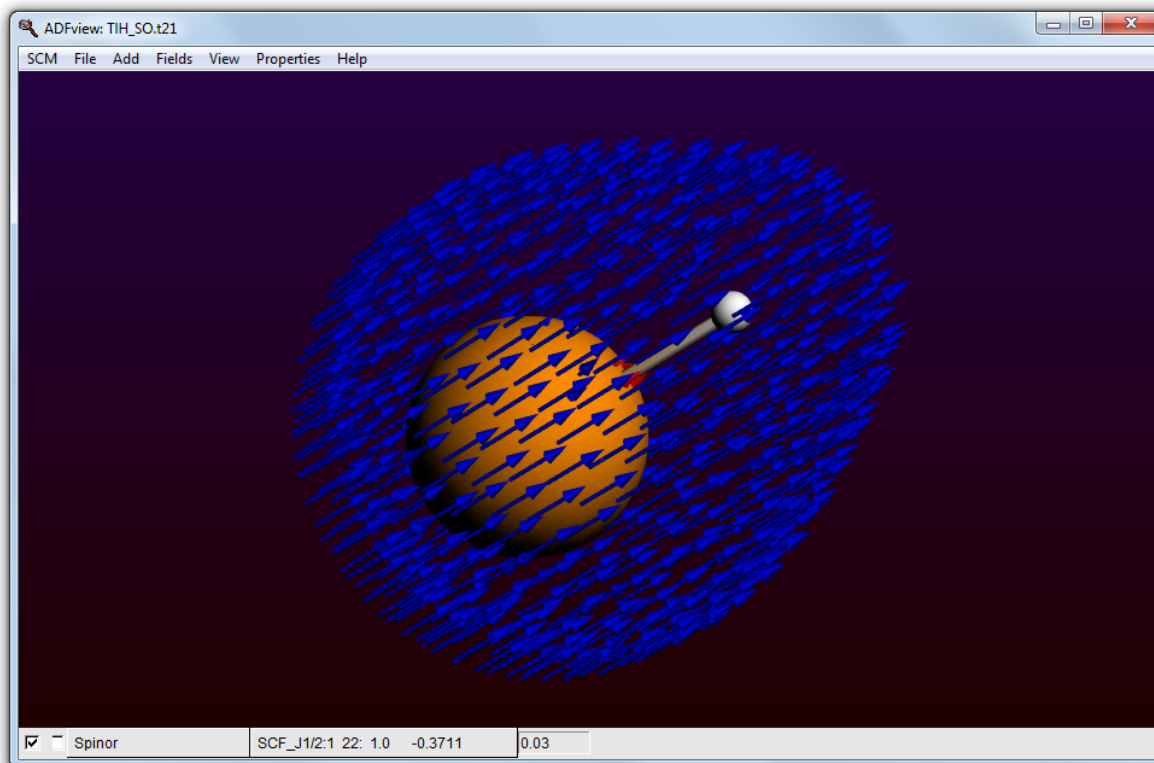
Rotate the molecule, such that one can see both atoms.

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 ...**



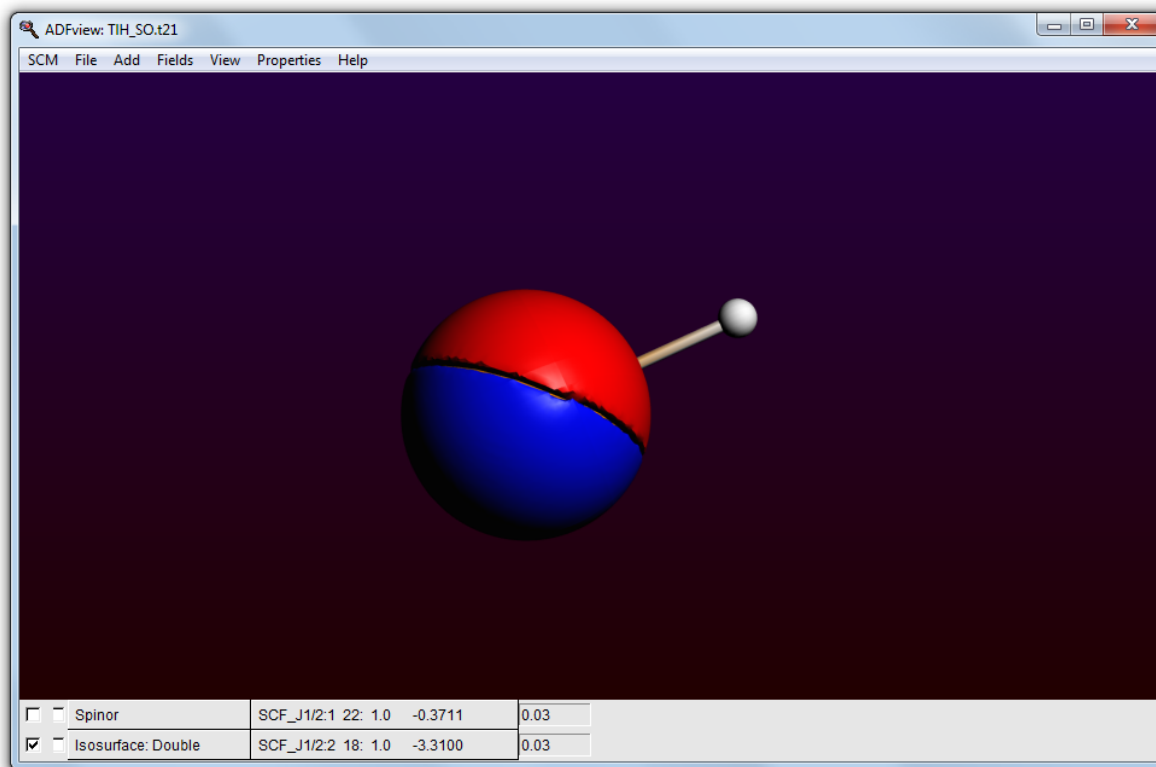
The arrows in this picture are in the direction of the spin magnetization density \mathbf{m} . All arrows are approximately in the same direction, which means that this spinor is an eigenfunction of spin in this direction of the arrows. In fact this 22 $j/2$ spinor is almost a pure α orbital. The arrows are drawn starting from points in space where the square root of the density is 0.03. The color of the arrows is red or blue by default, 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 (+/-)**

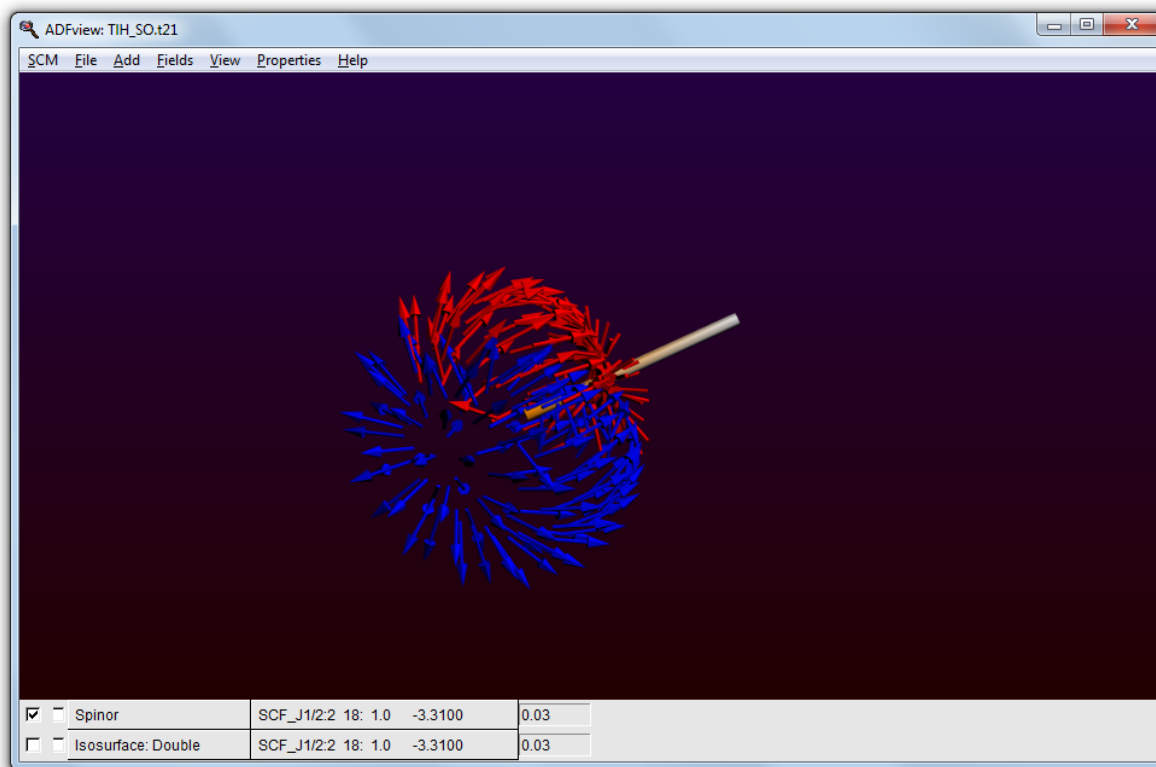
Select **Orbitals (occupied)** → **3** → **'SCF_J1/2:1 18: 1.0 ..**

Hide the spinor (uncheck the check box at the left of the Spinor label)



This spinor $18j_{1/2}$ is almost a pure $5p_{1/2}$ TI spinor. A $p_{1/2}$ 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**



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.

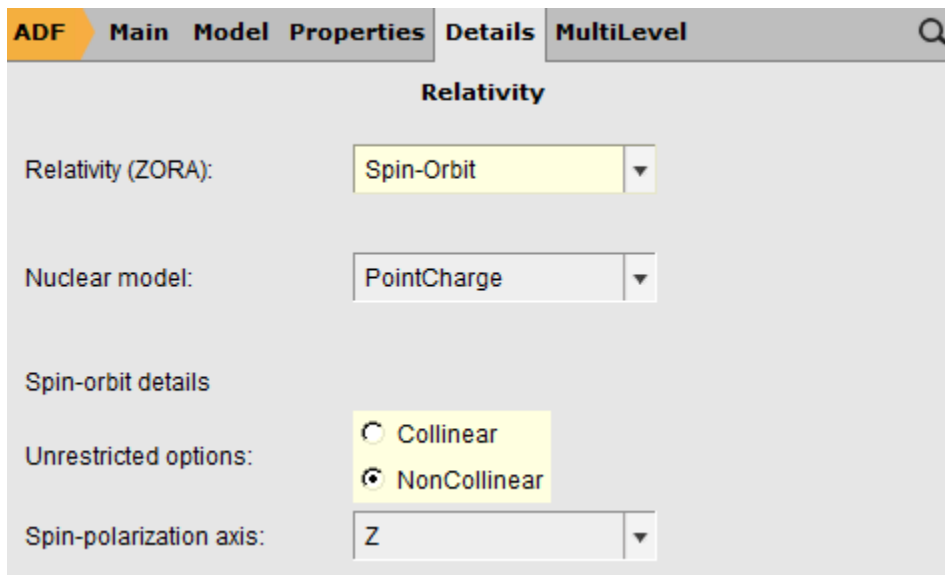
The Tl atom

To calculate an atomization energy we need to calculate the atoms also including spin-orbit coupling. The easiest way is to start with the TIH_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 bar Multilevel → Fragments command
Uncheck the 'Use fragments' option
Use the panel bar Model → 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



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** → **Close**

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** → **Close**

TIH 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 TIH_SO.logfile plus the the bond energy printed in the TIH_SO.TIH_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.

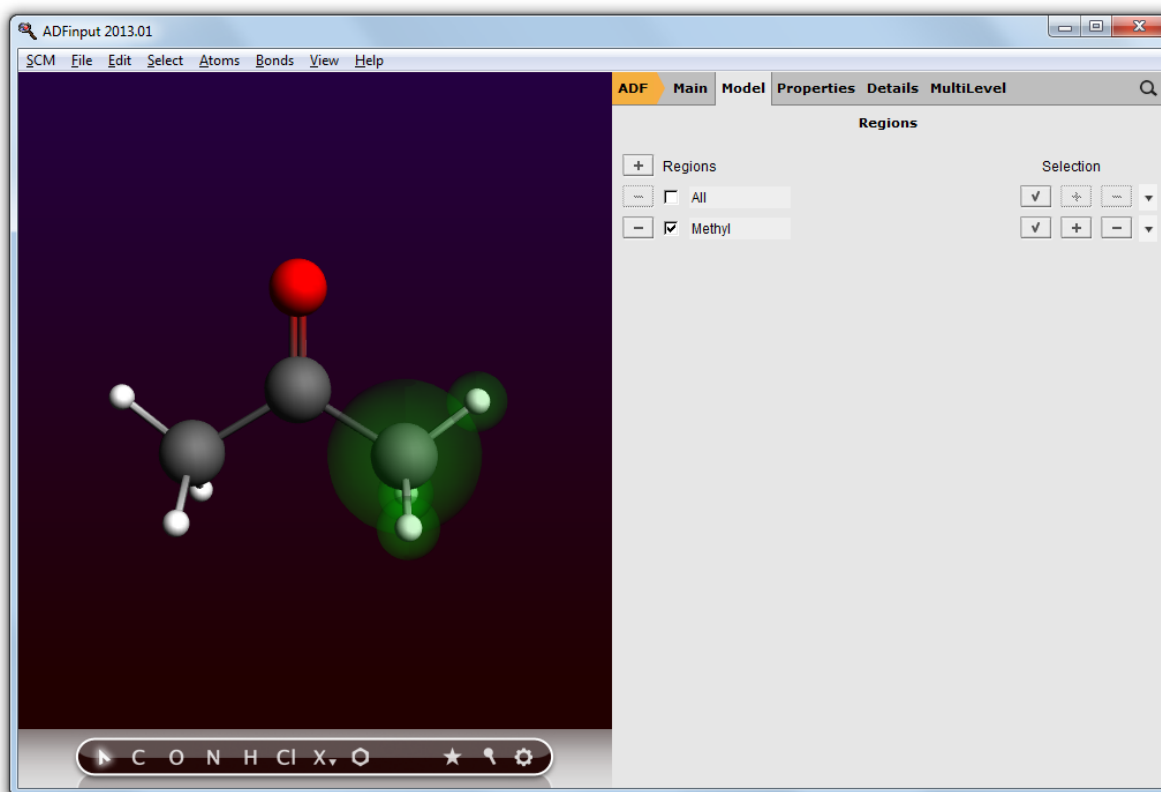
Within ADFinput, **a region is a collection of atoms**. You manage your regions with the 'Regions' panel in ADFinput. It allows you to define new regions, modify existing regions, and to apply some commands on particular regions.

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

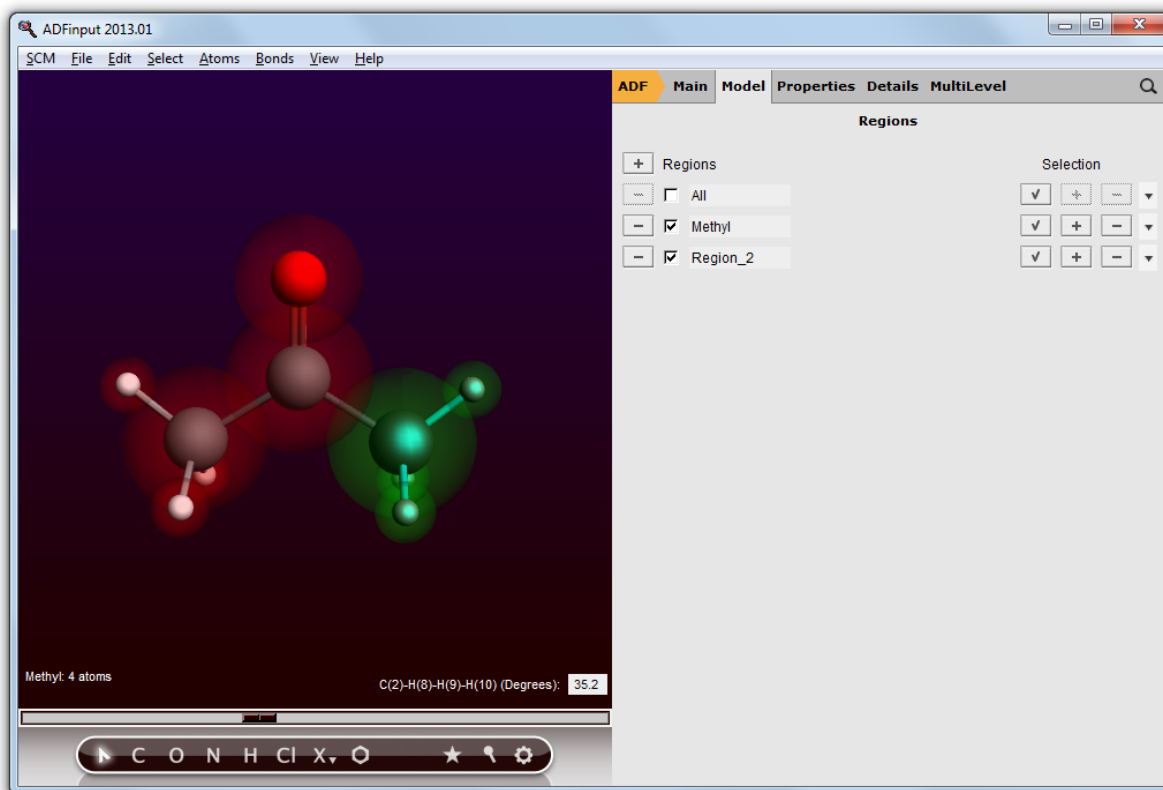
Use the panel bar **Model** → **Regions** command
Click on the '+' button to add a new region
Change the name 'Region_1' into 'Methyl' (the label is editable)



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 highlighted with semi-transparent 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:

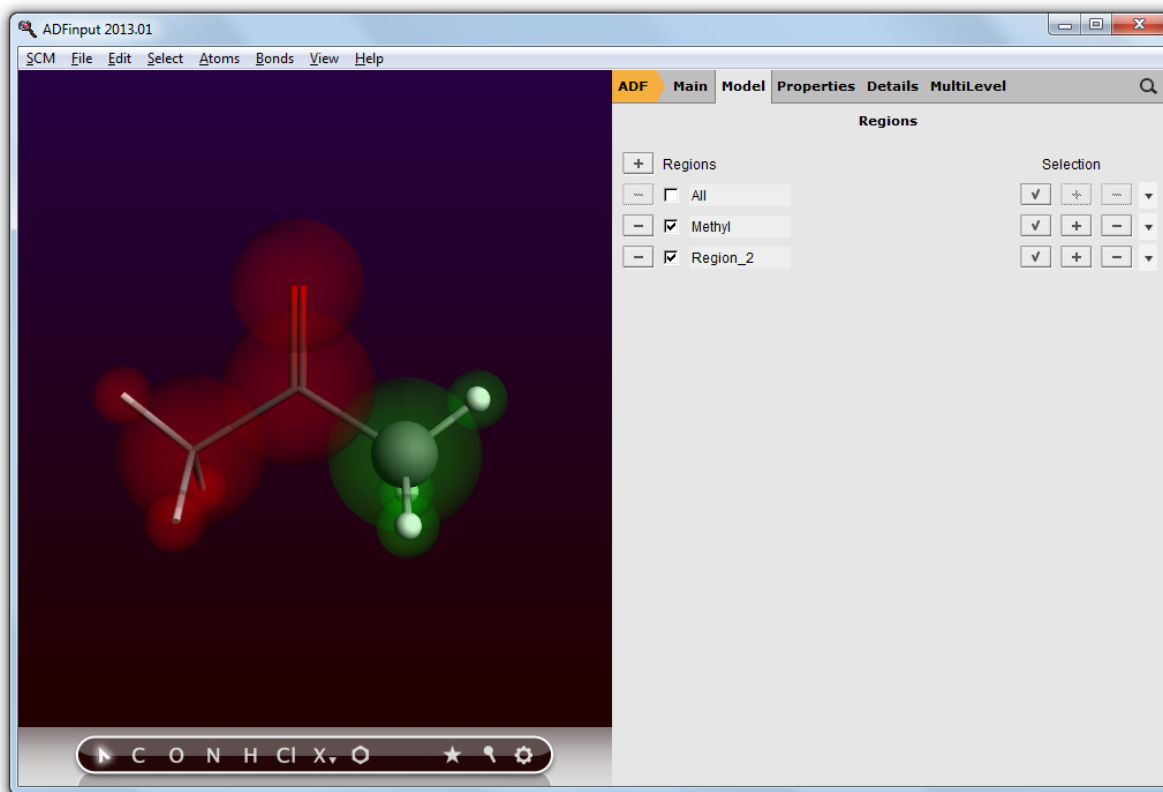
Click in empty (drawing) space to clear the selection

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



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:

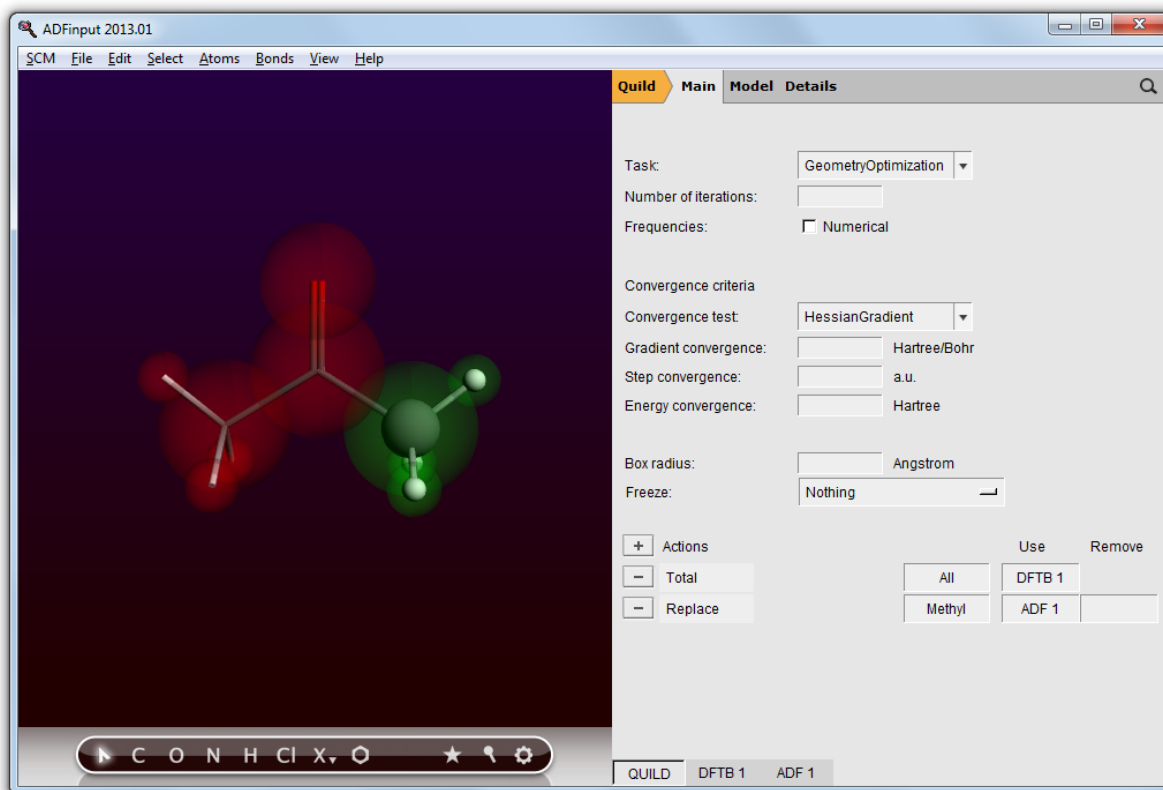
Use the panel bar **ADF** → **Quild** menu to select the Quild panel

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



The first action ('Total') defines what to do with the full molecule. It normally will apply to the entire 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

Four tabs can be found at the bottom of the Quild panel: '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:

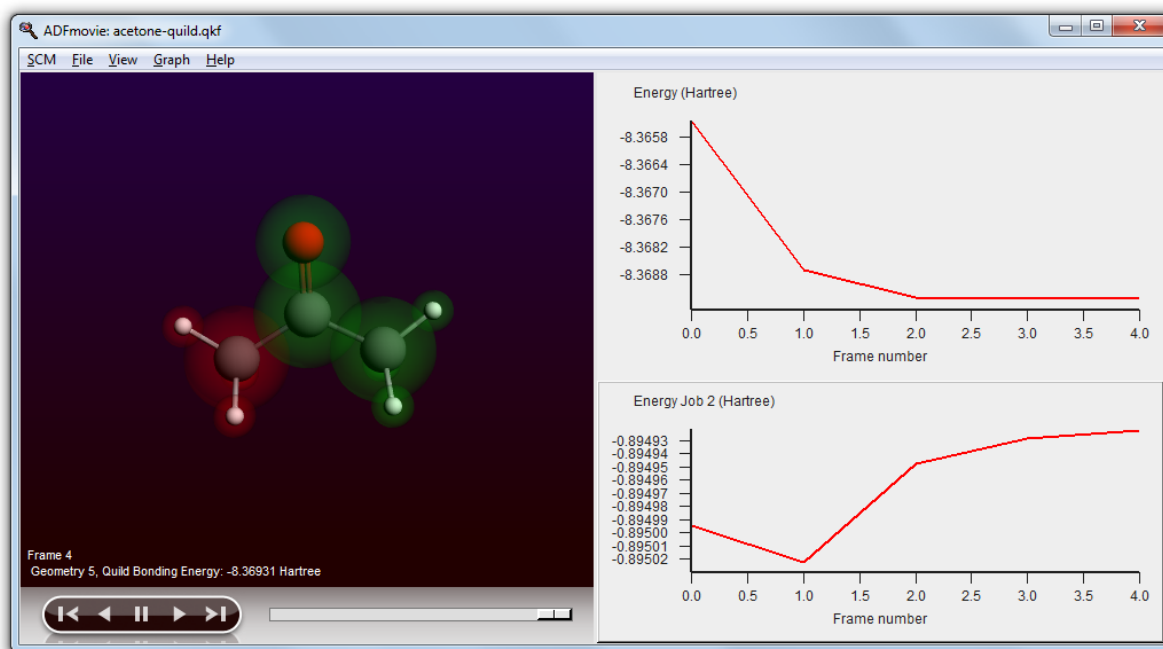
Use the **SCM** → **Movie** command

Add a graph: **Graph** → **Energy**

Add a second graph: **Graph** → **Add Graph**

Show the energy of the ADF-subsystem on the second graph:

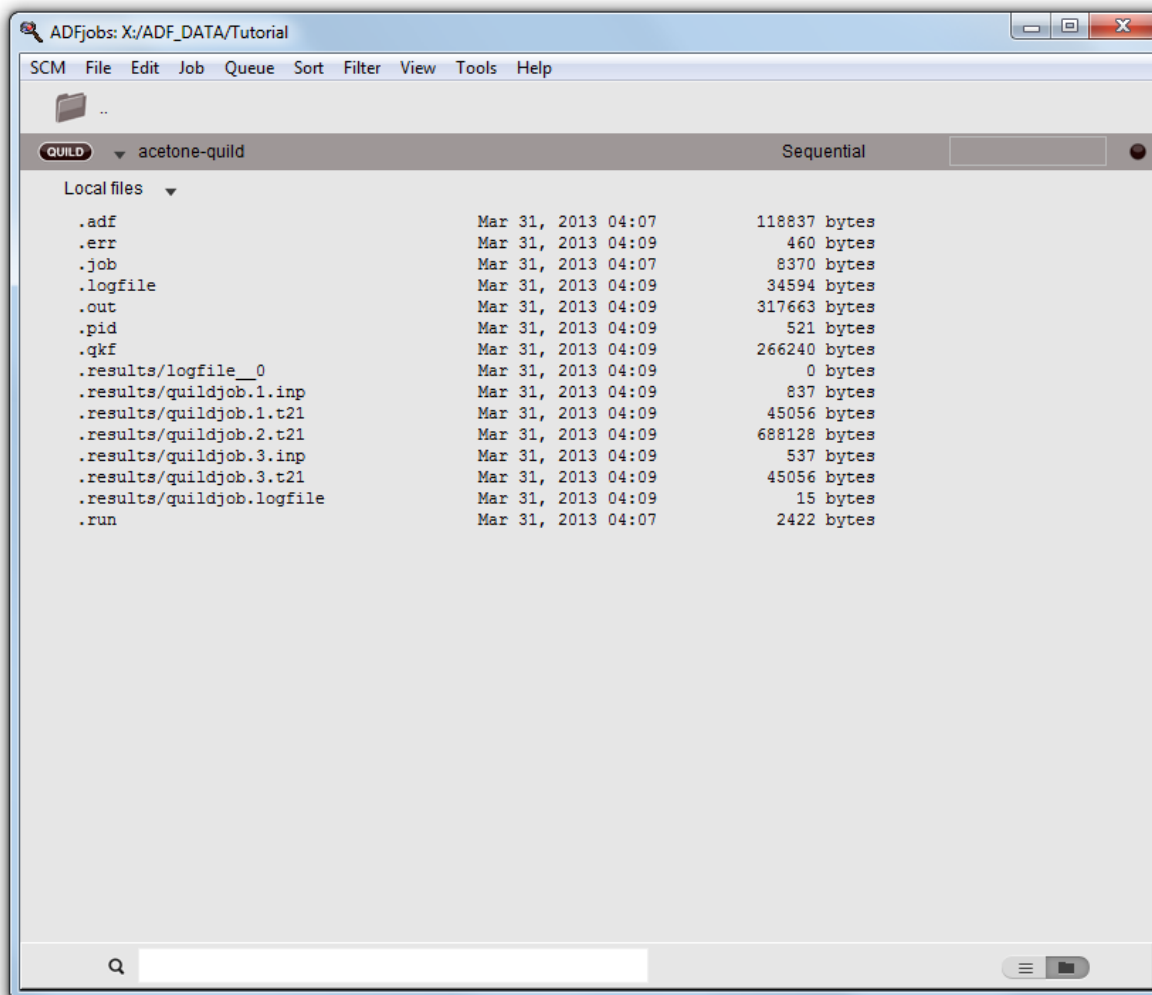
Graph → **Quild Energies** → **job 2 : ADF ...**



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)



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

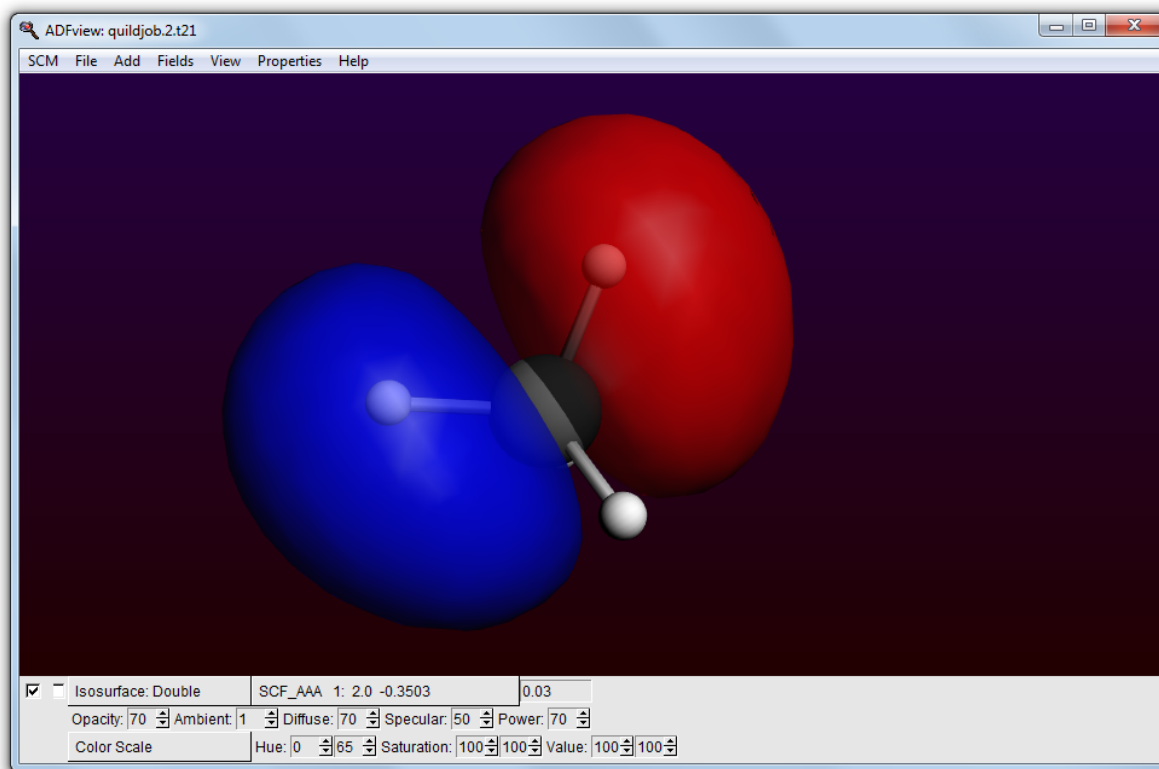
In the KFBrowser window, **SCM** → **View**

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

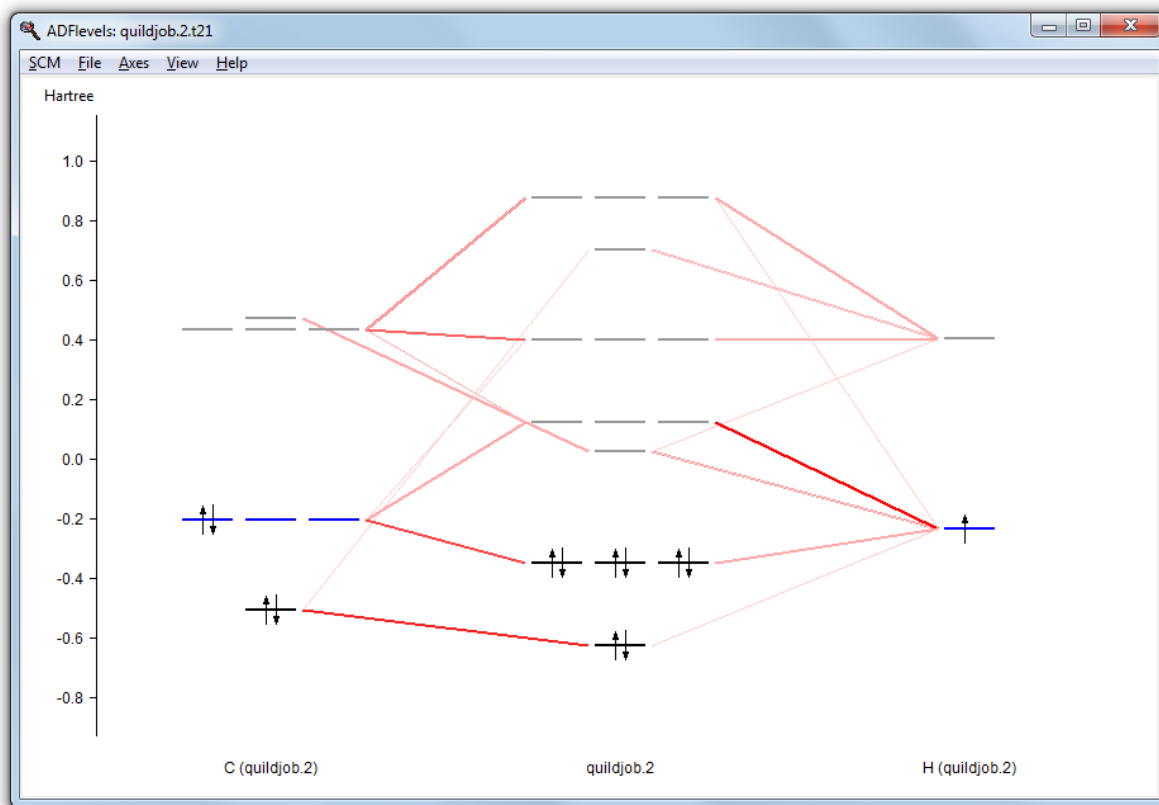
Click on the Isosurface:Double pull-down menu and use the Show Details command

Change the Opacity to 70



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 → **Quit All**

Step 3: QMMM

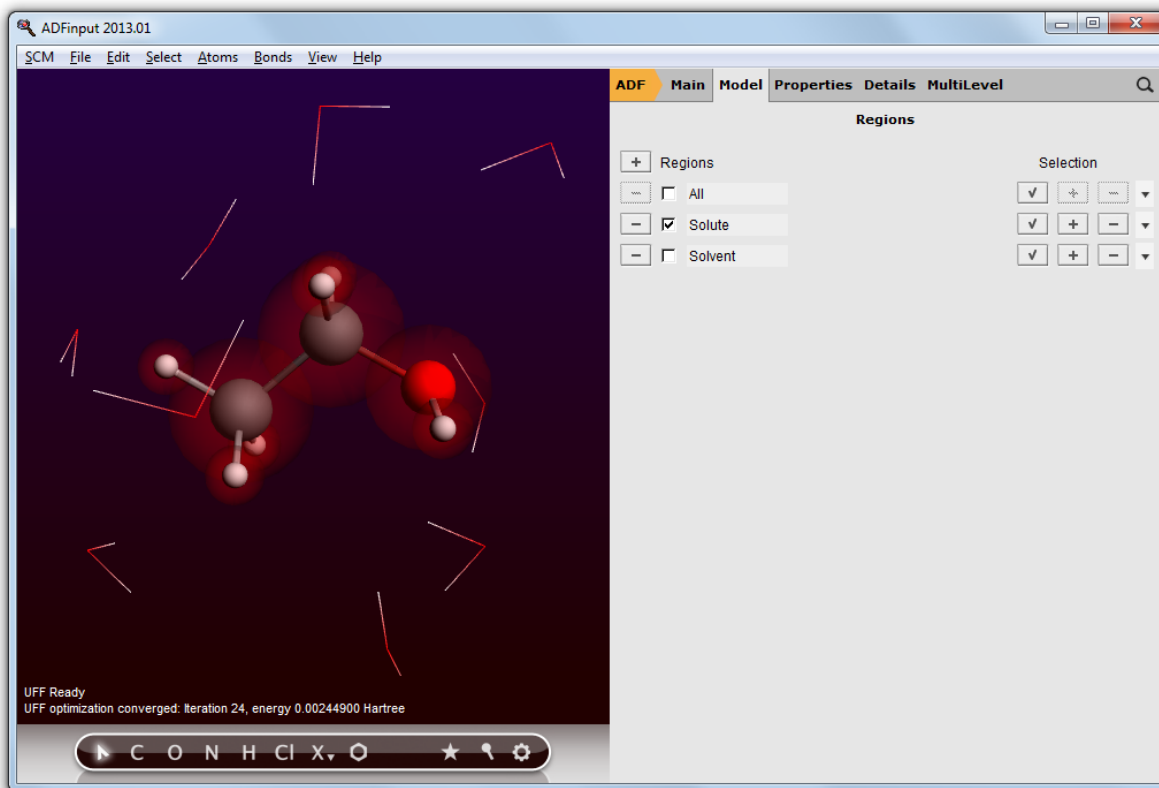
Generate ethanol in water

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'

```



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.

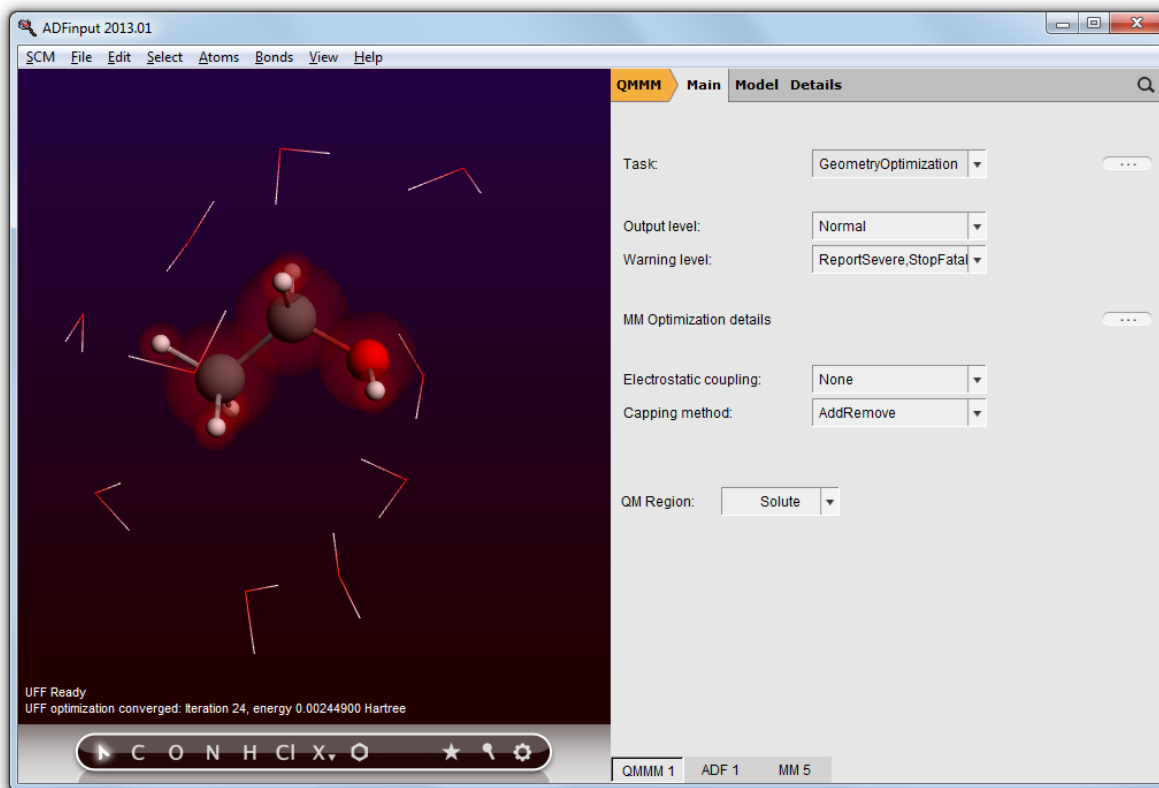
Set up the QM/MM calculation

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



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)

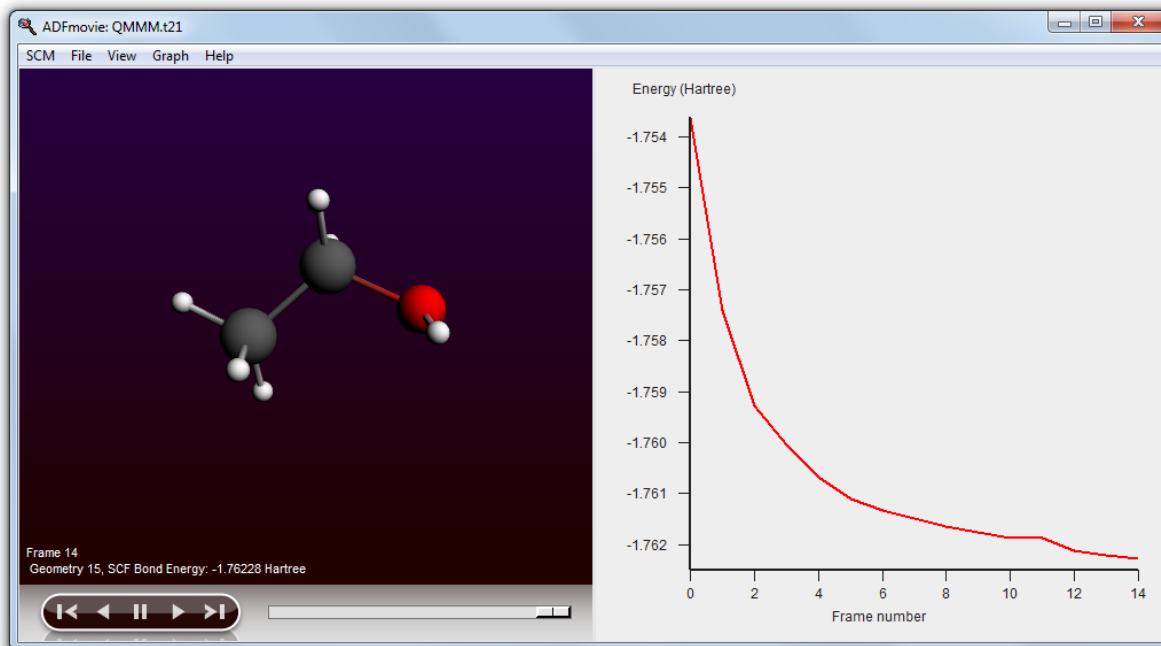
Run the QMMM calculation, and see results

Run your calculation **File** → **Run**

Show the optimization movie:

In the ADFinput window: **SCM** → **Movie**

Graph → **Energy**



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:

- $\text{Ni}(\text{CO})_4$
- $\text{PtCl}_4\text{H}_2^{2-}$

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 $\text{Ni}(\text{CO})_4$. It consists of one Ni fragment and once CO fragment that is repeated four times.

The second example is $\text{PtCl}_4\text{H}_2^{2-}$. 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 $\text{Ni}(\text{CO})_4$

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**

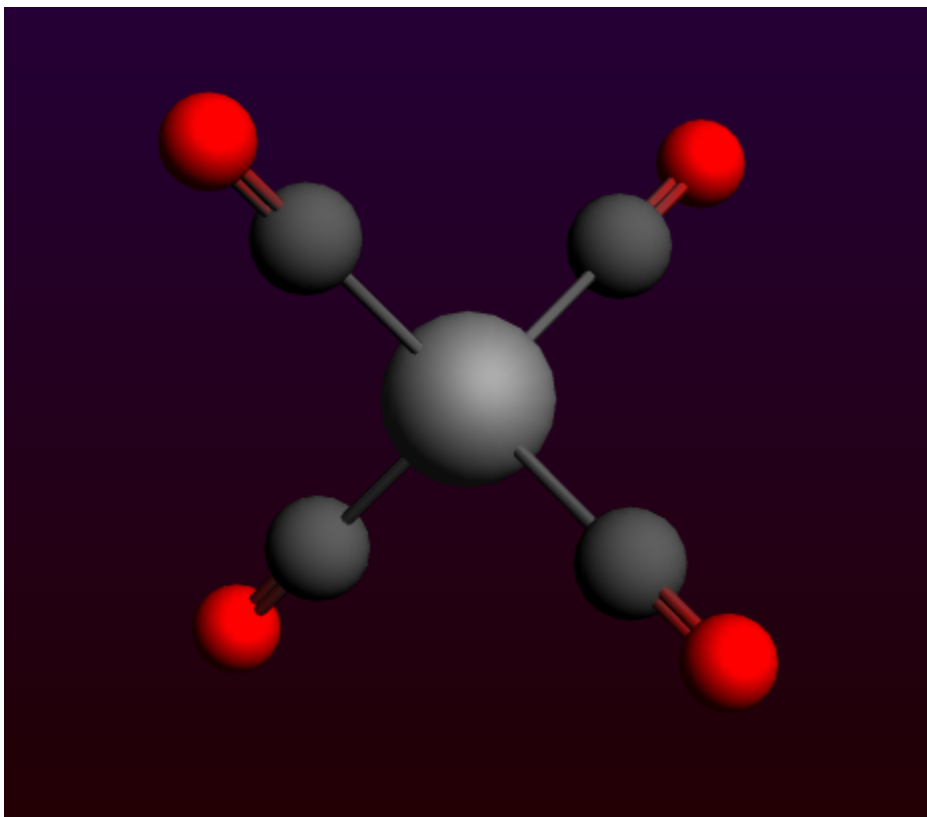
Choose the 'Geometry Optimization' Preset

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'

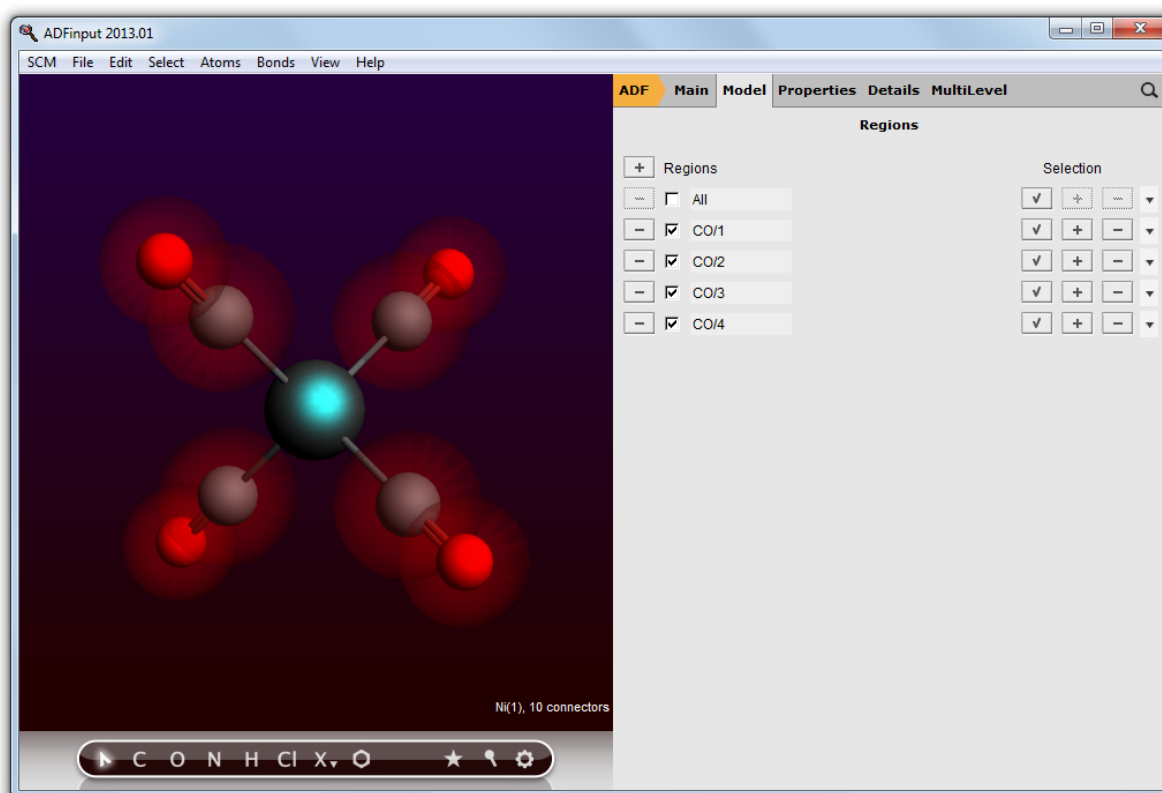
Change the name of 'Region_1' into 'CO'

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:

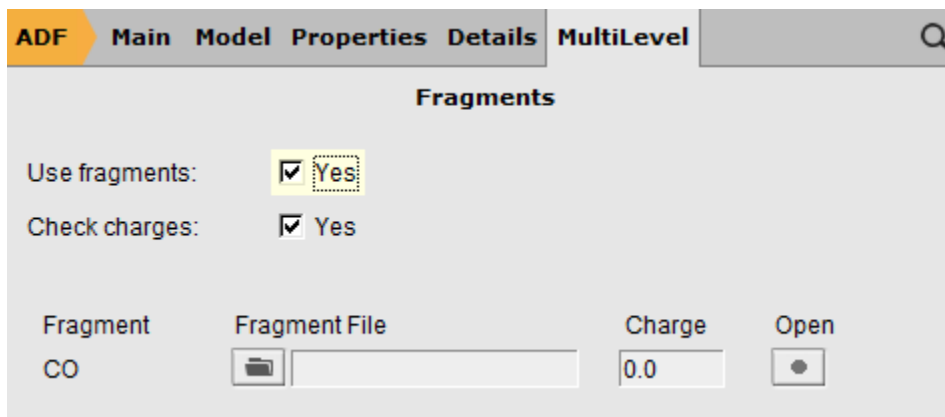
Open the 'Main' panel

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.



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
```

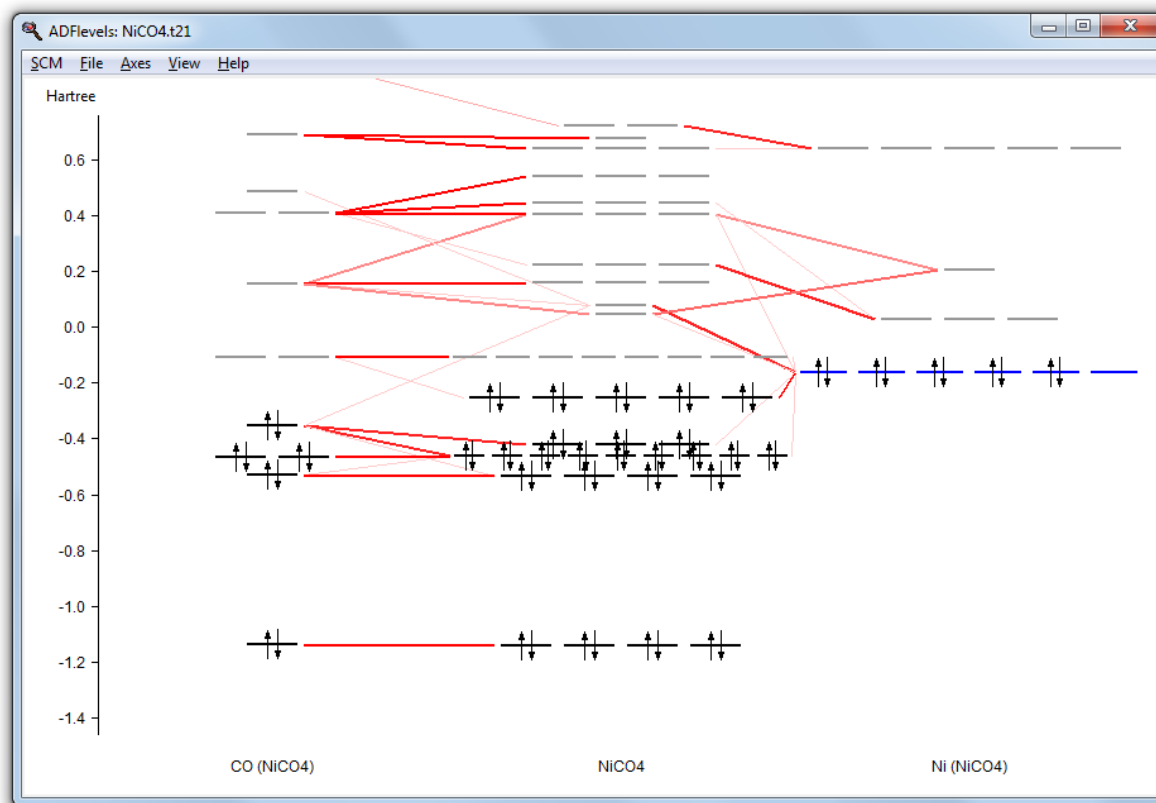
```
Run
```

```
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
```

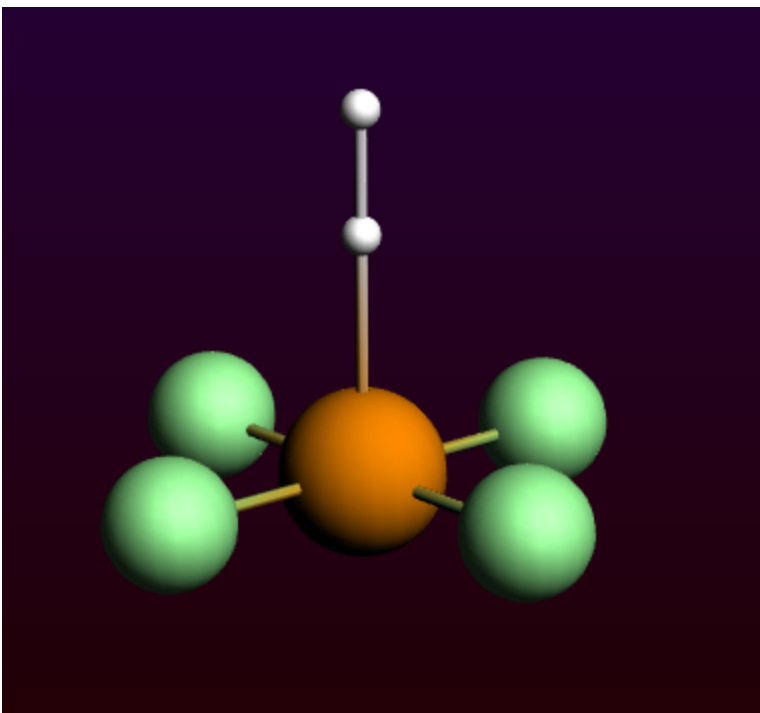



In the center you see the levels of the whole molecule, on the sides you see the CO fragment and the Ni-atom fragment. The interaction lines tell you which molecular orbitals come from which fragment orbitals.

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 $\text{PtCl}_4\text{H}_2^{2-}$

The following is a picture of the $\text{PtCl}_4\text{H}_2^{2-}$ 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.

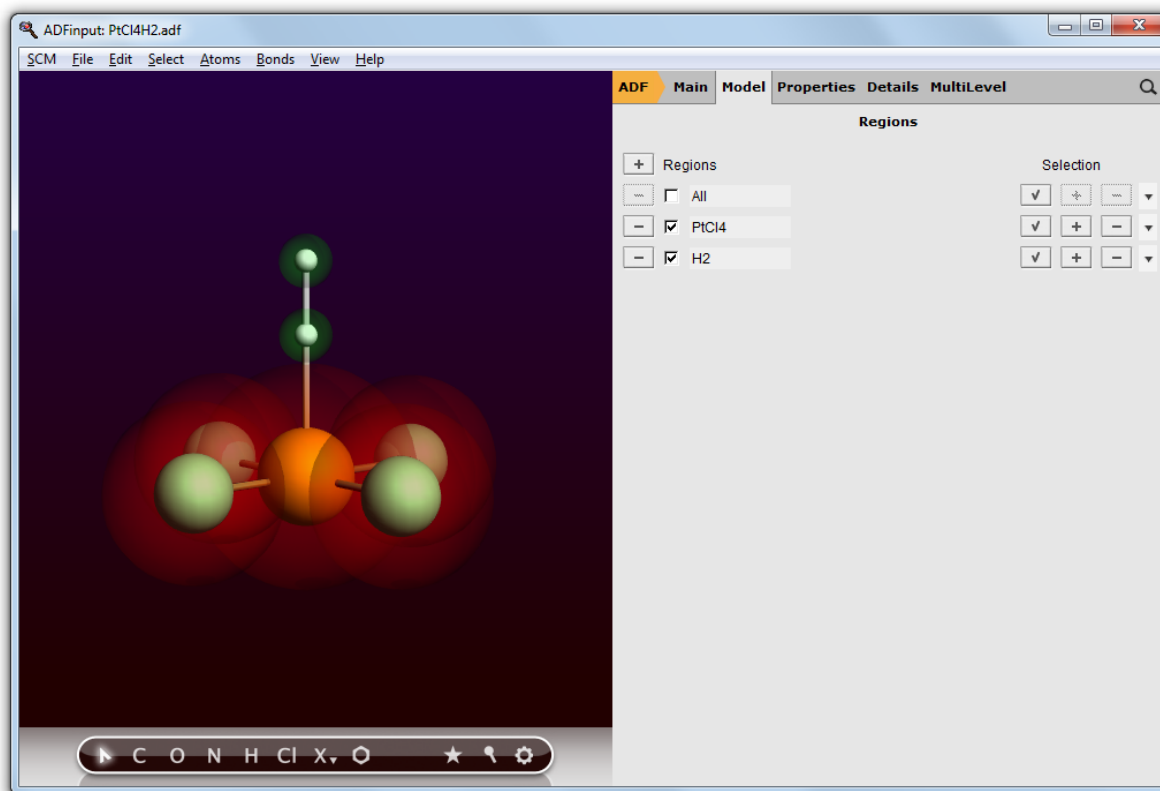
Step 6: Define fragments

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)

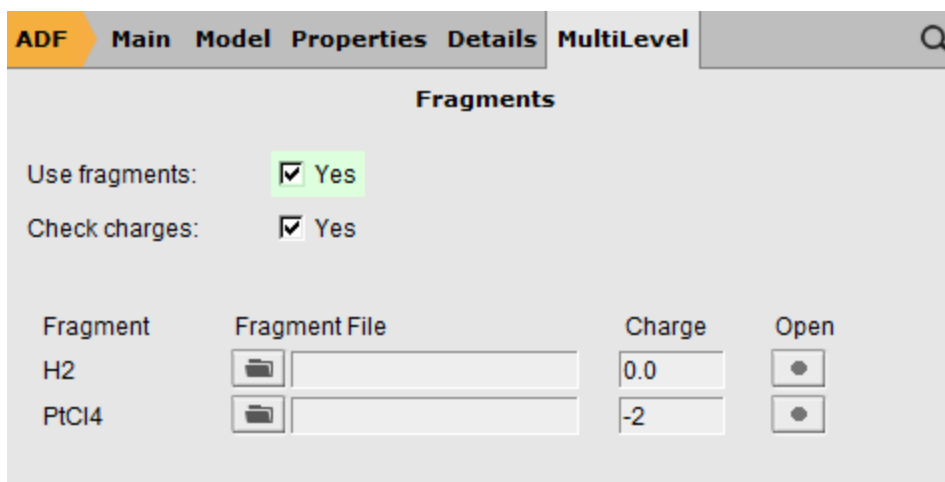


Now the fragments are defined. Next, we set up the fragment analysis calculation:

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.



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

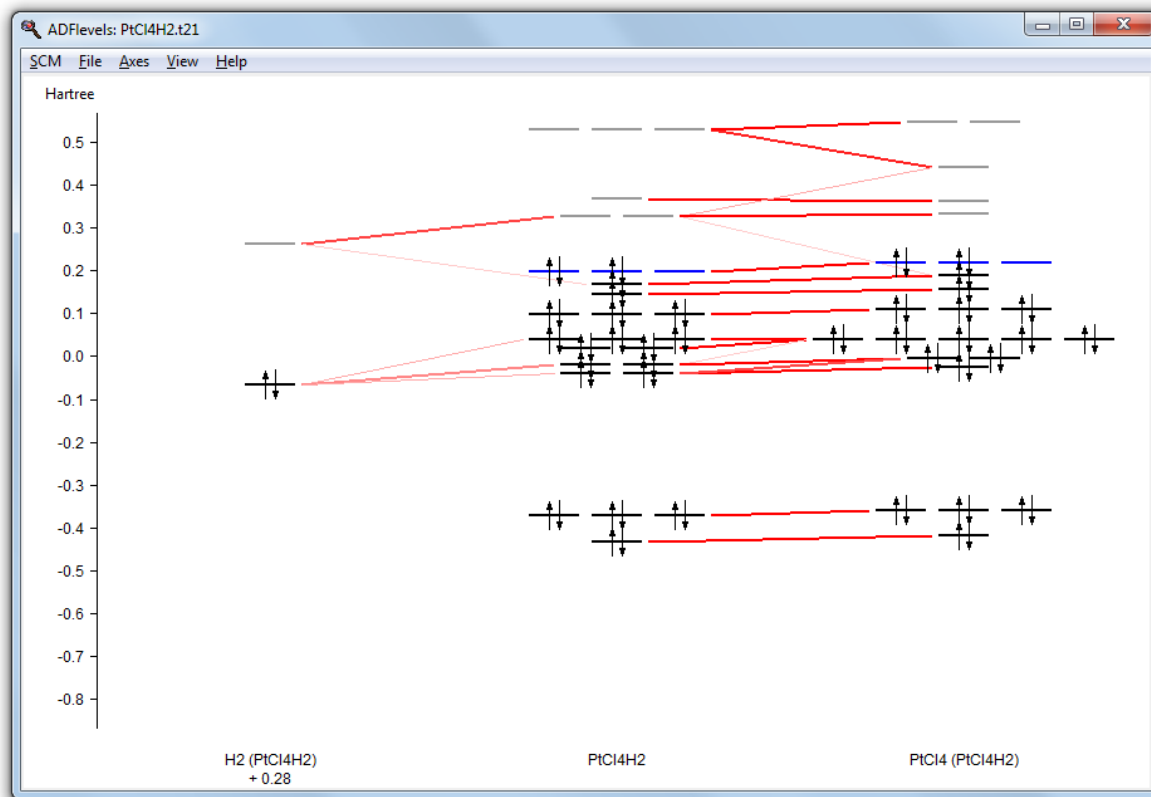
Use the mouse (drag with left mouse, scroll wheel, drag with right mouse)
 zoom in on the interesting region (roughly from -0.5 to 0.4)

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 NH₃ (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:

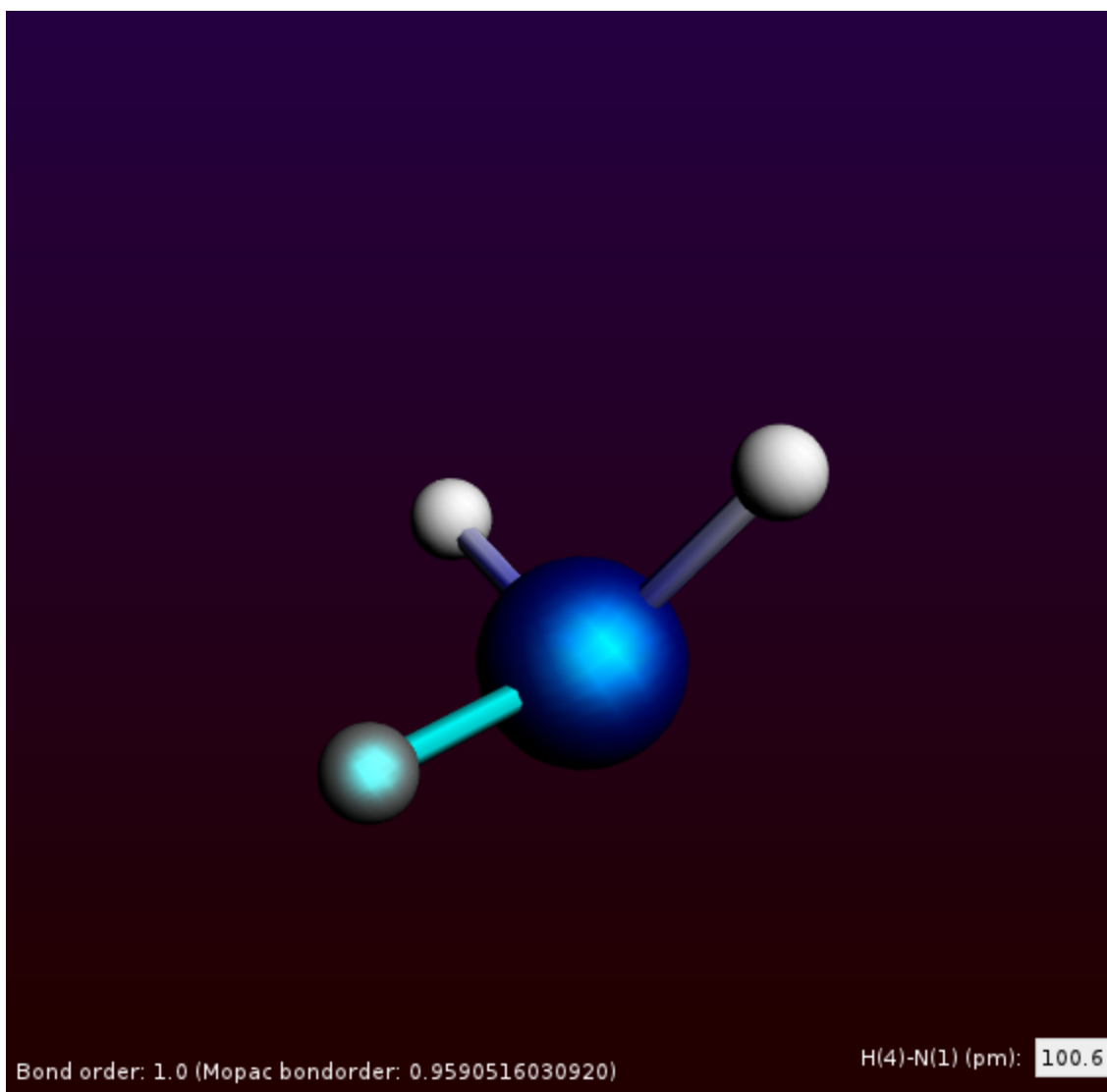


Next we will try to optimize using Mopac.

Undo the previous optimization: **Edit** → **Undo**

Right-click on the cog-wheel, select Mopac to pre-optimize

The message 'MOPAC ready' will be displayed in the ADFinput window:



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 NH₃ 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

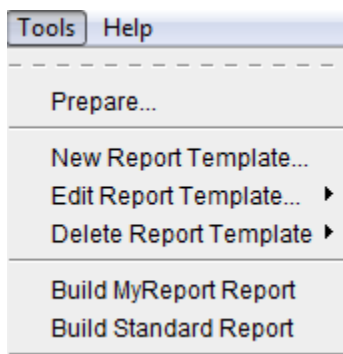
Next we will set up a series of calculations, using the Prepare tool.

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).

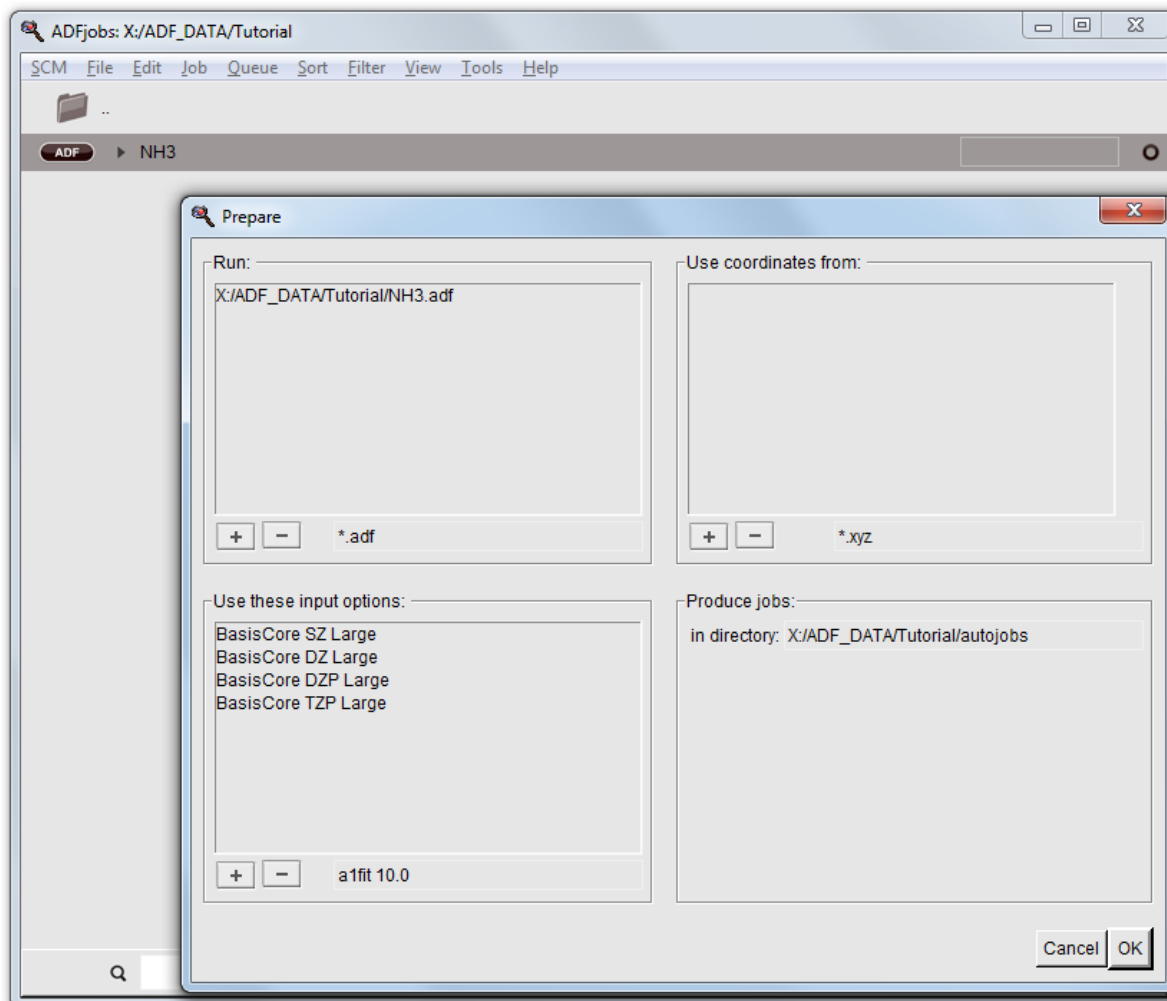
Go to the 'Use these input options' and click '+'

Choose 'Basis Set and Frozen Core' → 'SZ' → 'Large'

In the similar manner, add basis sets 'DZ', 'DZP', 'TZP',

.. (optionally 'TZ2P' and 'QZ4P')

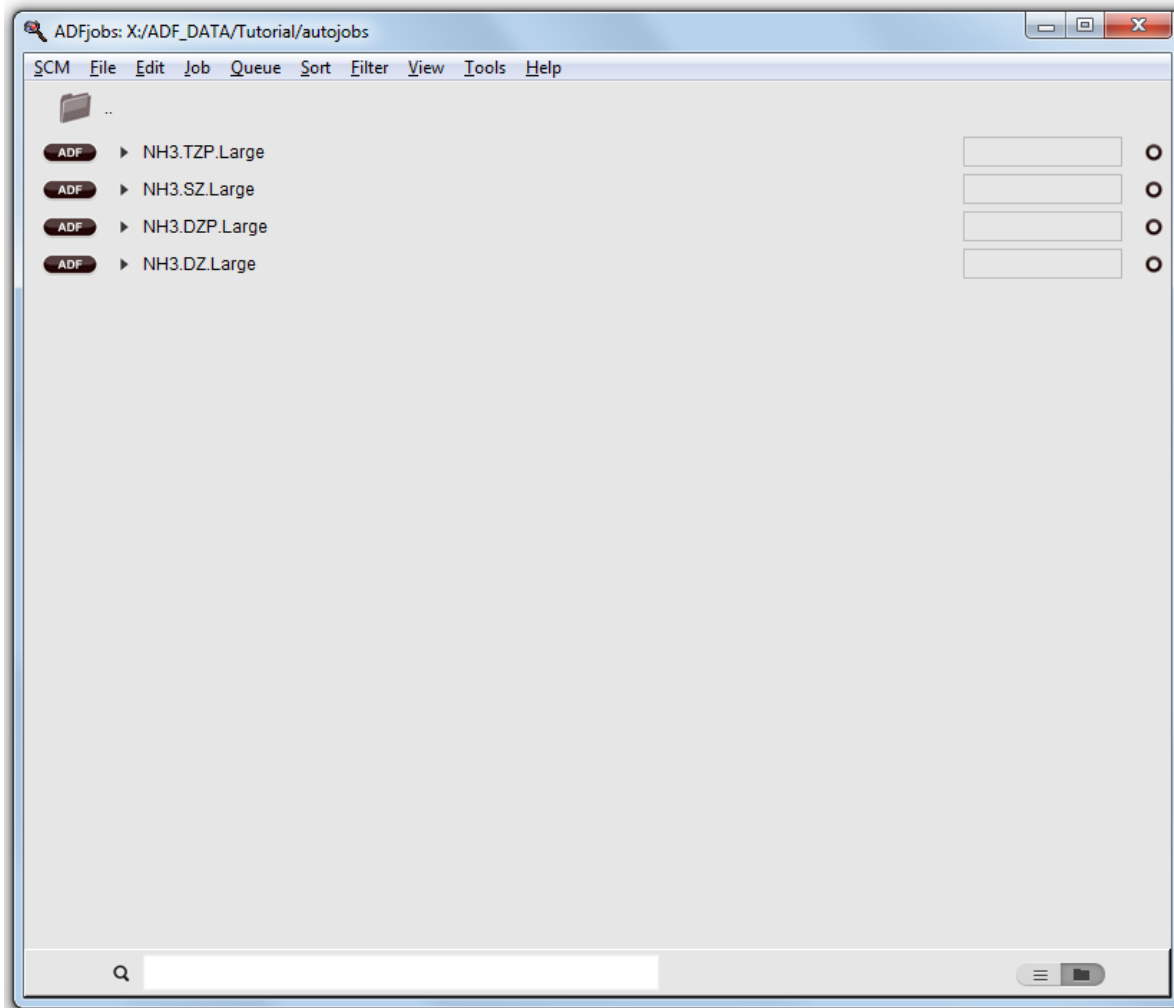
Use core 'Large' for all the basis sets



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 their progress can be tracked in ADFjobs. 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:

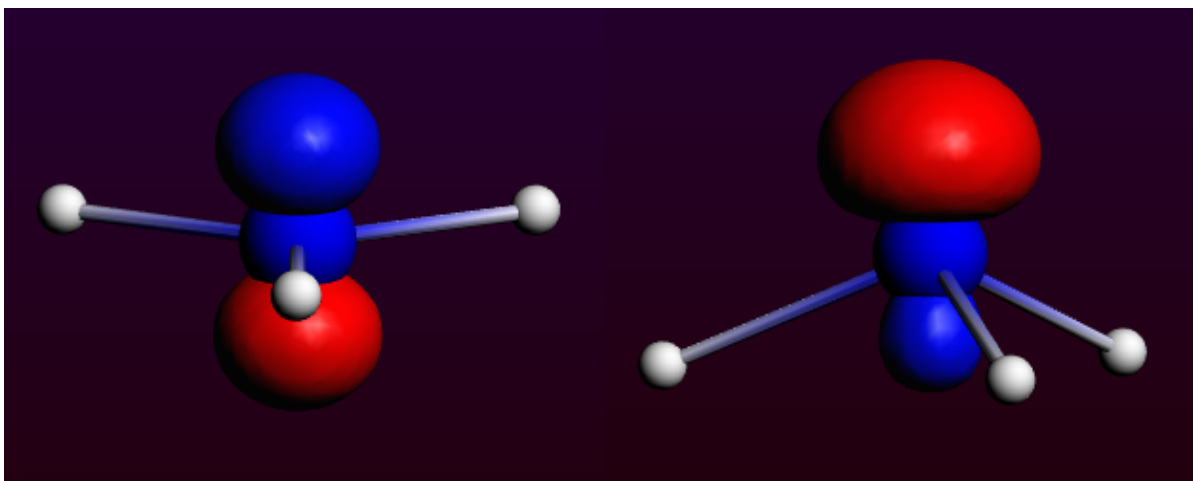
- ADFmovie, which will show the geometry optimization
- ADFinput, which will open the (last) converged geometry
- ADFview, which will open the converged geometry and also would display various density maps in 3D

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.
```

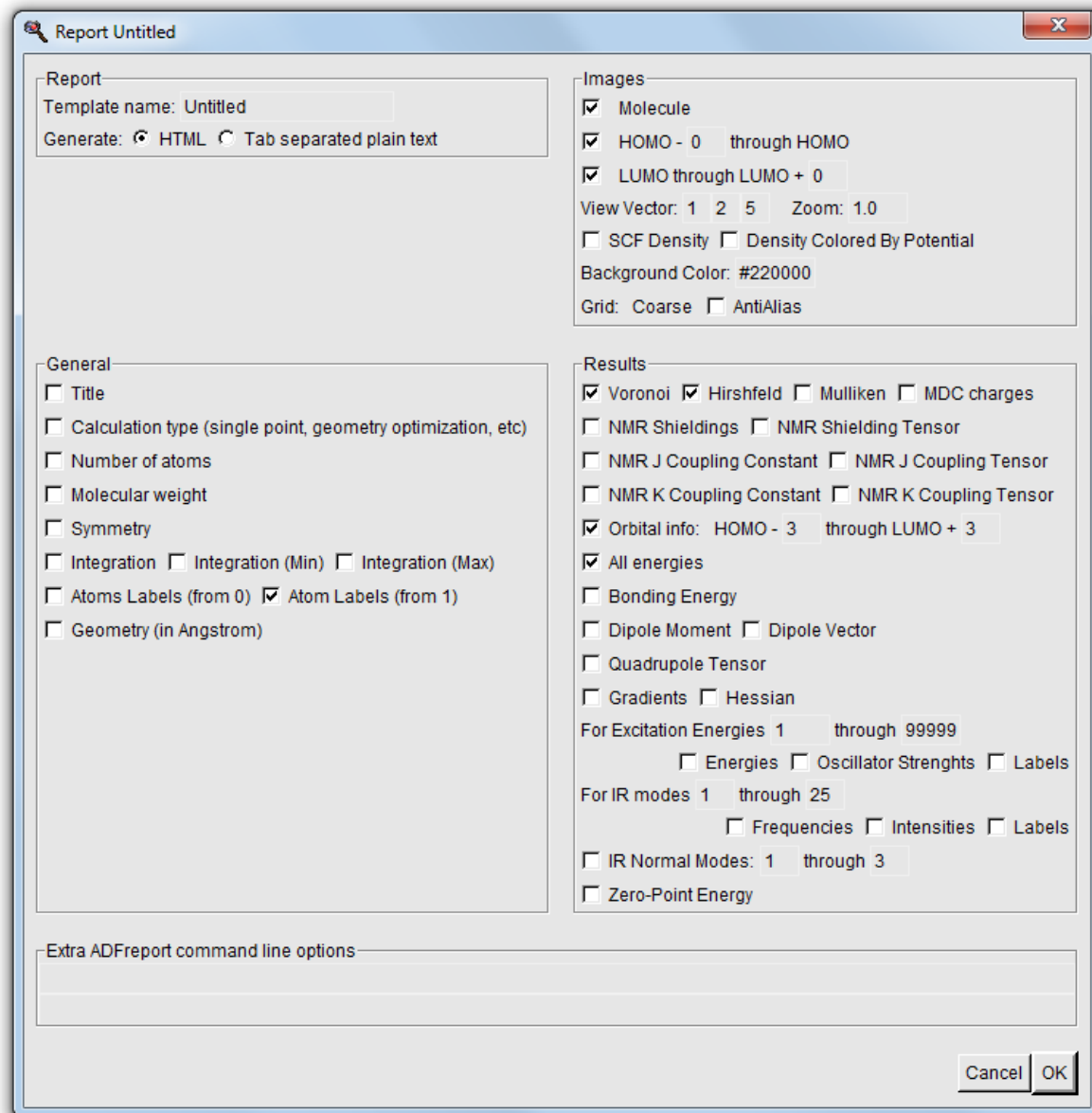
Repeat for this for the DZP calculation

What you will observe is that HOMO of ammonia does not have the anticipated sp^3 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...
```



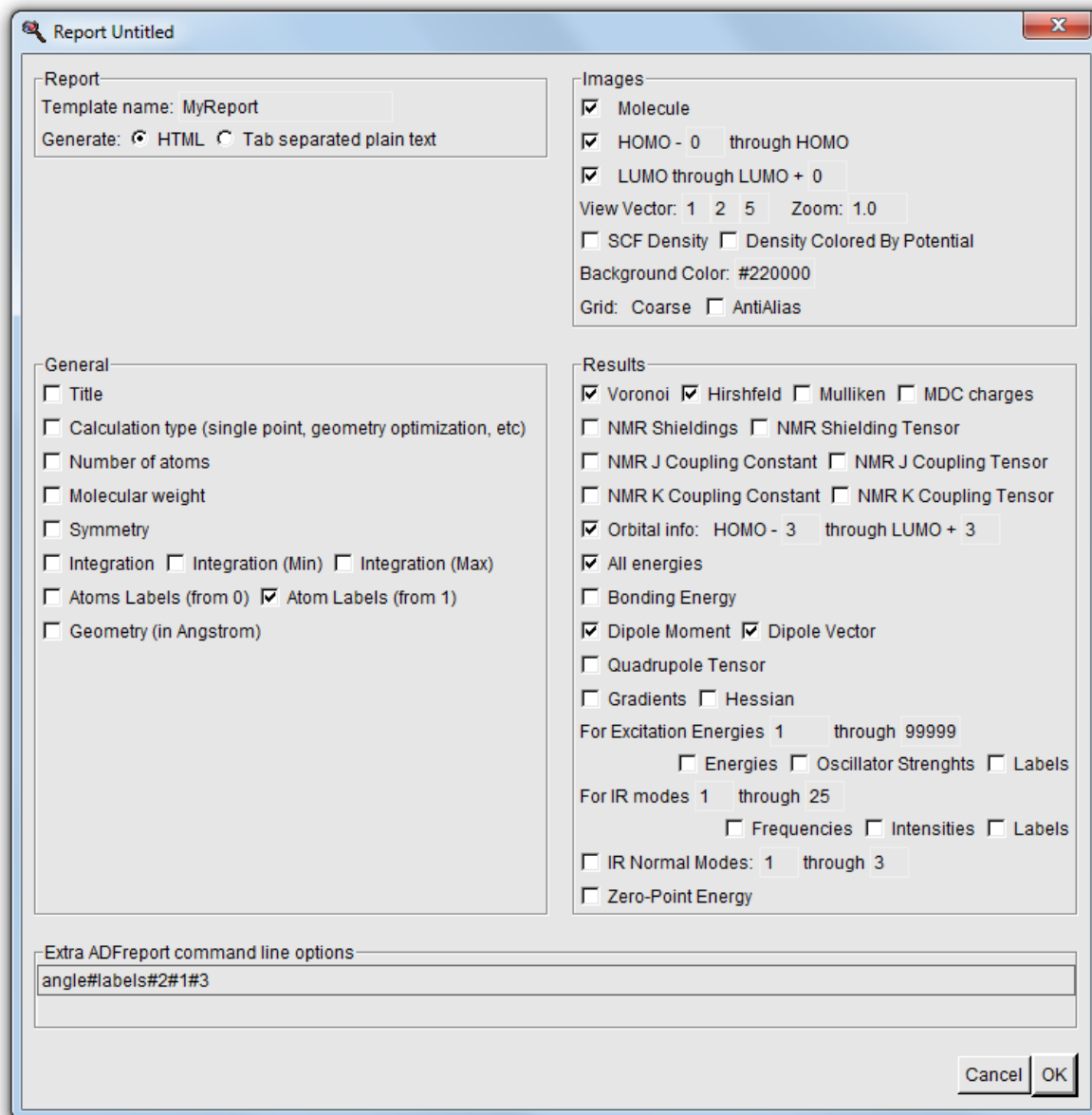
This will open up Report dialog.

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'

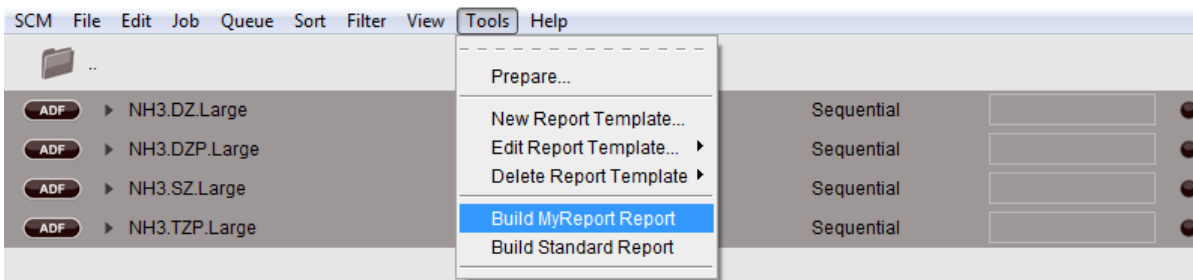


The extra command line options used instruct ADFreport to report the angle between atoms 2, 1 and 3, and include the atom labels for this angle on output. In a similar way more angles could be requested, or distances, or many other properties. For a description of all options please check the adfreport 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	Atom Labels	Voronoi	Hirshfeld	Orbital Info	HOMO-3	LUMO-3	Energies	Dipole	Dipole Vector	angle labels
Tutorial10NH3.SZ.Large				N(1) H(2) H(3) H(4)	-0.292 0.098 0.097 0.096	-0.327 0.109 0.109 0.109	-0.670429 -0.352719 -0.352618 -0.042432	2.0 AA_1 2.0 AA_2 2.0 AA_3 2.0 AAA_1	Electrostatic Interaction: Steric Interaction:	Bonding Energy: Pauli Repulsion: Electrostatic Interaction: Steric Interaction: Orbital Interaction:	-0.825728 1.905941 -0.337504 1.568436 -2.394164	0.000 0.000 -0.000 -0.000	H(2)-H(1)-H(3): 119.996
Tutorial10NH3.DZ.Large				N(1) H(2) H(3) H(4)	-0.358 0.119 0.118 0.121	-0.349 0.114 0.114 0.114	-0.750461 -0.435442 -0.435337 -0.199858	2.0 AA_1 2.0 AA_2 2.0 AA_3 2.0 AAA_1	Electrostatic Interaction: Steric Interaction: Orbital Interaction:	Bonding Energy: Pauli Repulsion: Electrostatic Interaction: Steric Interaction: Orbital Interaction:	-0.714046 1.874142 -0.312058 -1.562104 -2.276150	0.000 0.000 -0.000 -0.000	H(2)-H(1)-H(3): 119.997
Tutorial10NH3.DZP.Large				N(1) H(2) H(3) H(4)	-0.275 0.091 0.091 0.093	-0.323 0.108 0.108 0.108	-0.755472 -0.437369 -0.437250 -0.202126	2.0 AA_1 2.0 AA_2 2.0 AA_3 2.0 AAA_1	Electrostatic Interaction: Steric Interaction: Orbital Interaction:	Bonding Energy: Pauli Repulsion: Electrostatic Interaction: Steric Interaction: Orbital Interaction:	-0.734130 1.887743 -0.312611 1.574802 -2.308933	0.000 0.000 -0.000 -0.000	H(2)-H(1)-H(3): 119.996
Tutorial10NH3.TZP.Large				N(1) H(2) H(3) H(4)	-0.270 0.090 0.089 0.092	-0.325 0.108 0.108 0.108	-0.754012 -0.439342 -0.439228 -0.199858	2.0 AA_1 2.0 AA_2 2.0 AA_3 2.0 AAA_1	Electrostatic Interaction: Steric Interaction: Orbital Interaction:	Bonding Energy: Pauli Repulsion: Electrostatic Interaction: Steric Interaction: Orbital Interaction:	-0.737174 1.888976 -0.325472 1.565503 -2.302678	0.000 0.000 -0.000 -0.000	H(2)-H(1)-H(3): 119.996

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 NH₃ 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 NH₃ structure.

Congratulations, we are done with the ammonia optimization tutorial!

If you want to exit all the GUI modules at once: select **SCM → Quit All**

Tutorial 11: Caffeine Bader (AIM) analysis, Benzene NBO visualization and Occupations

Step 1: Setup and optimize Caffeine

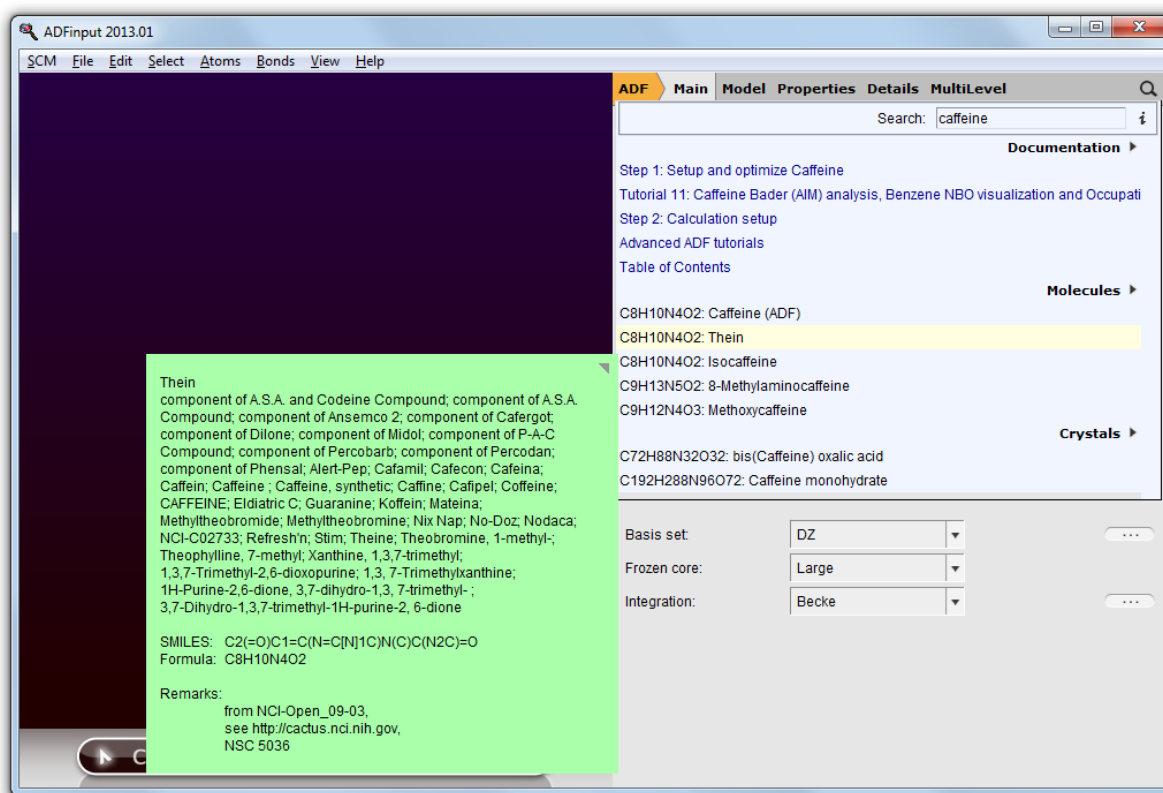
Start ADFinput

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



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 many alternative names),

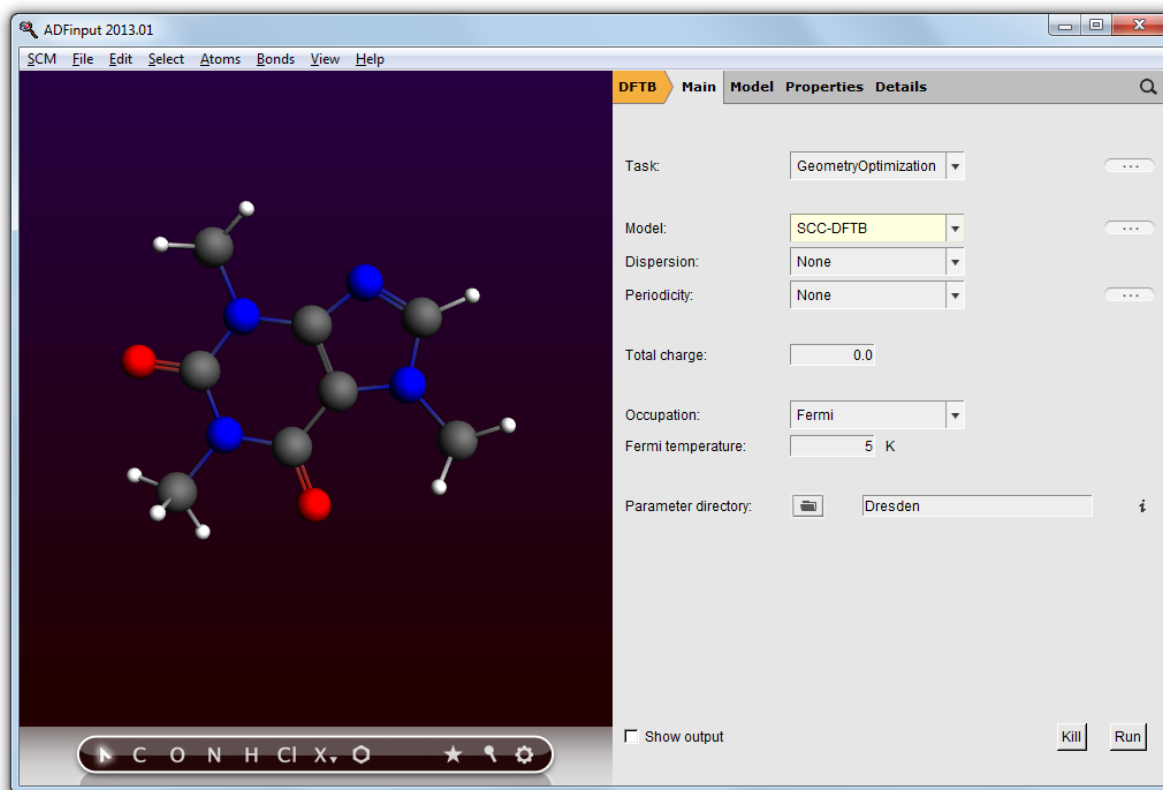
Click on the 'Thein' search result

Click somewhere in empty space in the molecule drawing area to deselect the atoms

Switch to DFTB mode (panel bar **ADF** → **DFTB**)

Select model: SCC-DFTB

Make sure the parameter set is "Dresden" (normally you would want to use better parameters like the included 3OB set)



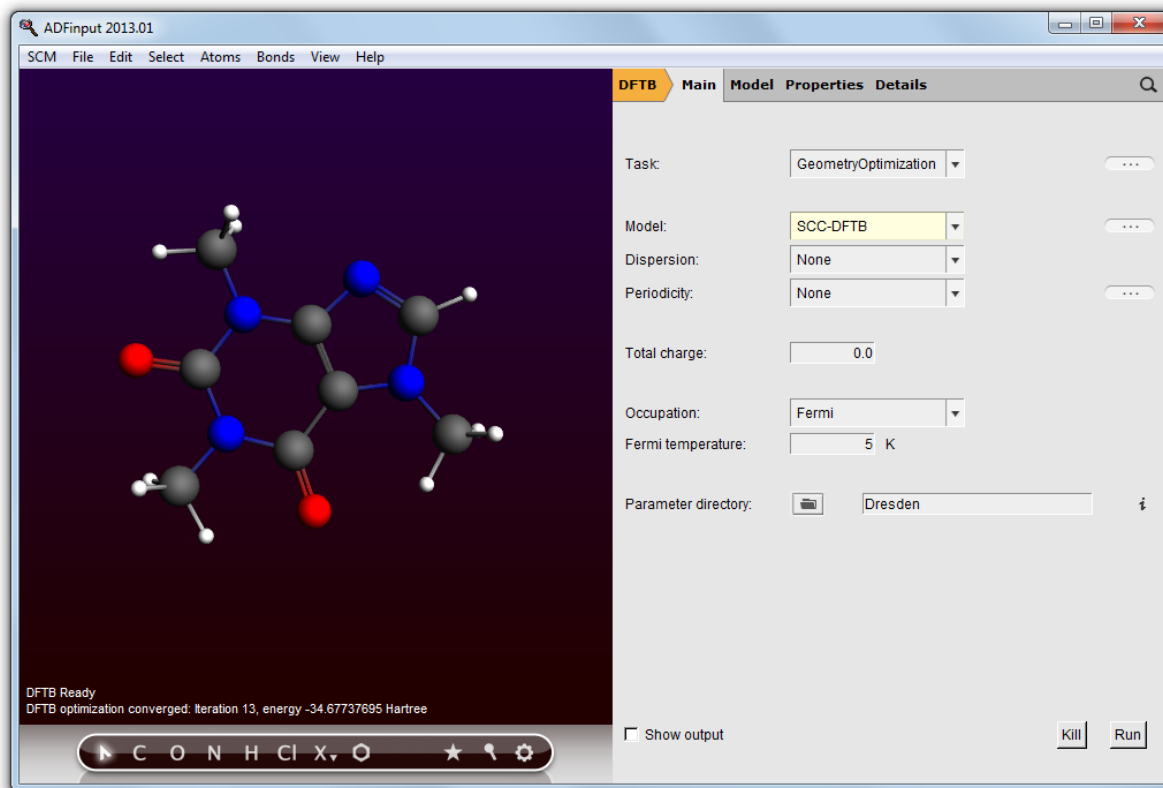
Note that only those parameter sets known to be able to handle your system will be shown in the menu.

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:



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

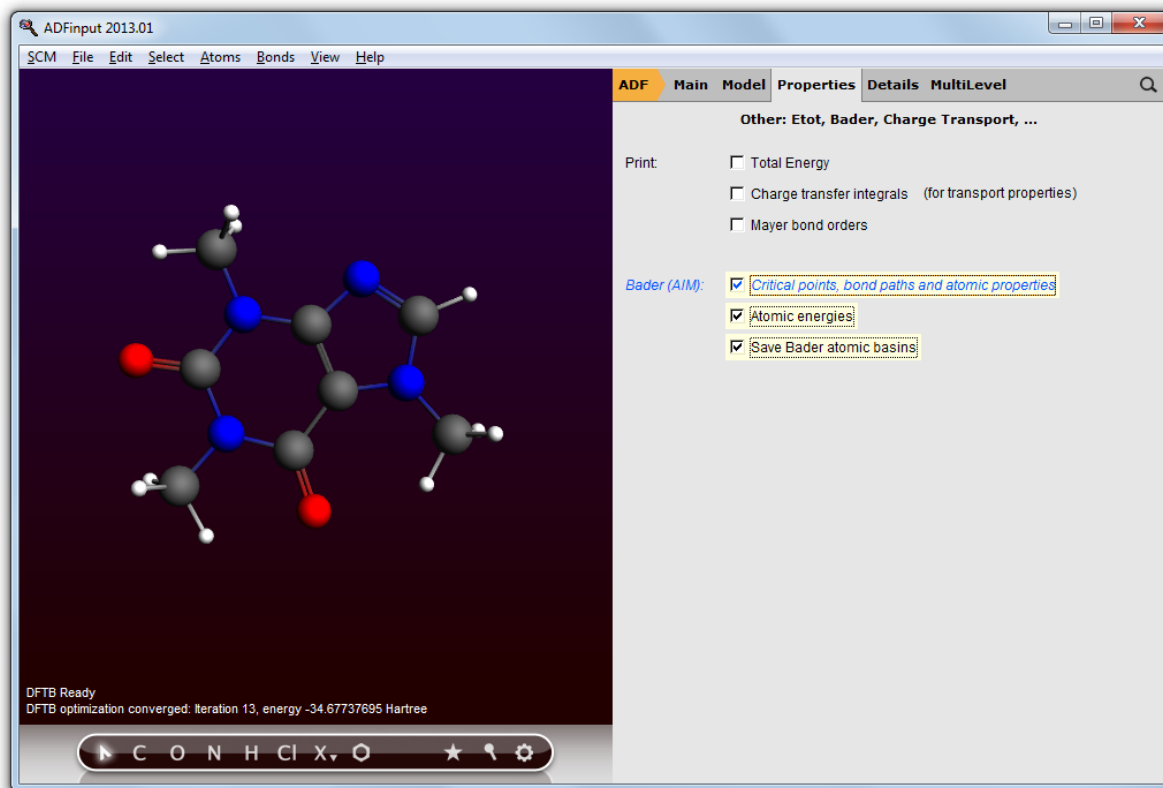
Use the Return key to accept the highlighted match (Other...)

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



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, press 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:

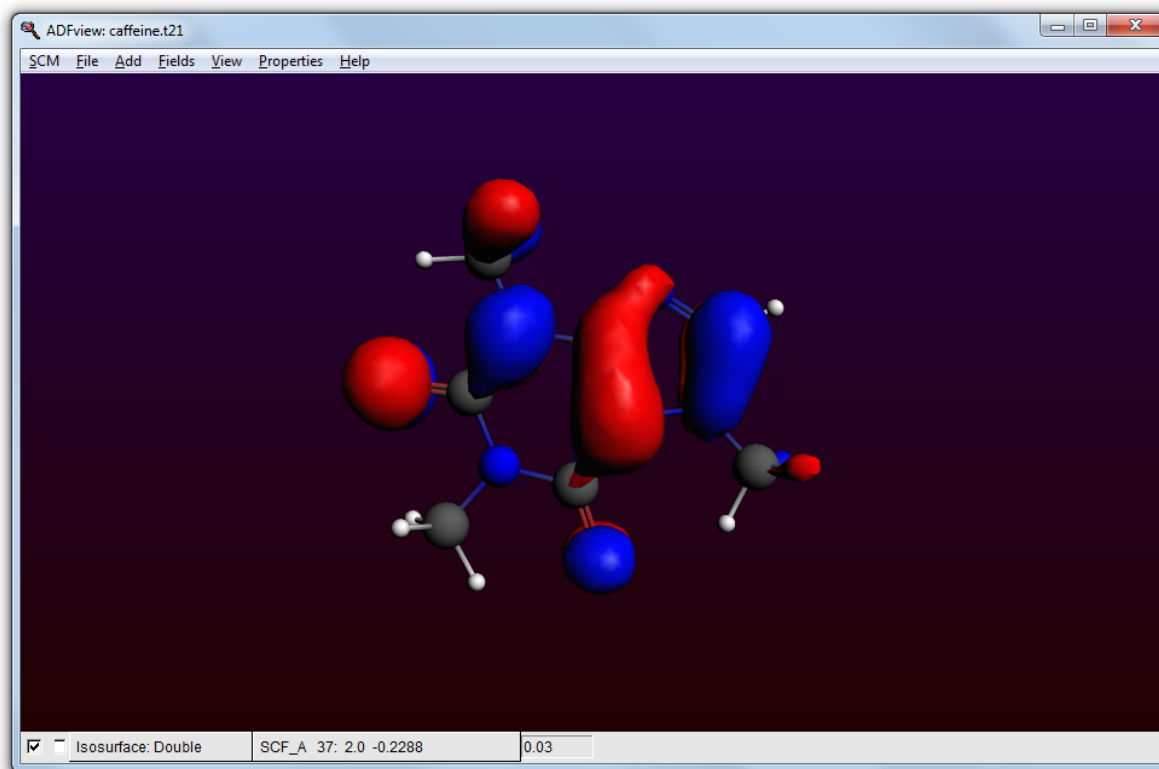
```

ADFtail: caffeine.logfile
SCM File Edit Help
<Apr02-2013> <12:12:30> >>>> POPAN
<Apr02-2013> <12:12:30> >>>> DEBYE
<Apr02-2013> <12:12:30> NORMAL TERMINATION
<Apr02-2013> <12:12:30> END
<Apr02-2013> <12:12:31> ADF 2013.01 RunTime: Apr02-2013 12:12:31 Nodes: 1 Procs: 4
<Apr02-2013> <12:12:32> *** (NO TITLE) ***
<Apr02-2013> <12:12:32> RunType : SINGLE POINT
<Apr02-2013> <12:12:32> Net Charge: 0 (Nuclei minus Electrons)
<Apr02-2013> <12:12:32> Symmetry : NOSYM
<Apr02-2013> <12:12:32> >>>> FRAGM
<Apr02-2013> <12:12:33> >>>> CORORT
<Apr02-2013> <12:12:33> >>>> FITINT
<Apr02-2013> <12:12:34> >>>> CLSMAT
<Apr02-2013> <12:12:34> >>>> ORTHON
<Apr02-2013> <12:12:34> >>>> GENPT
<Apr02-2013> <12:12:35> Block Length= 128
<Apr02-2013> <12:12:35> >>>> PTBAS
<Apr02-2013> <12:12:36> >>>> CYCLE
<Apr02-2013> <12:12:36> 1
<Apr02-2013> <12:12:38> 2 ErrMat 1.53216236 MaxE1 0.27286834
<Apr02-2013> <12:12:39> 3 ErrMat 0.72235627 MaxE1 0.09701125
<Apr02-2013> <12:12:40> 4 ErrMat 0.77948290 MaxE1 -0.17230581
<Apr02-2013> <12:12:41> 5 ErrMat 0.24233443 MaxE1 0.05470156
<Apr02-2013> <12:12:42> 6 ErrMat 0.07326091 MaxE1 0.02209219
<Apr02-2013> <12:12:43> 7 ErrMat 0.03284507 MaxE1 0.00690029
<Apr02-2013> <12:12:45> 8 ErrMat 0.00715308 MaxE1 -0.00201944
<Apr02-2013> <12:12:46> 9 ErrMat 0.00359822 MaxE1 -0.00091574
<Apr02-2013> <12:12:47> 10 ErrMat 0.00166921 MaxE1 0.00043327
<Apr02-2013> <12:12:48> 11 ErrMat 0.00035711 MaxE1 0.00011951
<Apr02-2013> <12:12:49> 12 ErrMat 0.00015831 MaxE1 0.00003595
<Apr02-2013> <12:12:50> 13 ErrMat 0.00004128 MaxE1 0.00000901
<Apr02-2013> <12:12:52> 14 ErrMat 0.00001904 MaxE1 0.00000386
<Apr02-2013> <12:12:53> 15 ErrMat 0.00000434 MaxE1 0.00000073
<Apr02-2013> <12:12:53> SCF converged
<Apr02-2013> <12:13:16> 16 ErrMat 0.00000360 MaxE1 -0.00000068
<Apr02-2013> <12:13:17> Total energy -674.47789416 a.u.
<Apr02-2013> <12:13:17> >>>> TOTEN
<Apr02-2013> <12:13:29> Computing AIM critical points
<Apr02-2013> <12:13:34> >>>> POPAN
<Apr02-2013> <12:13:35> >>>> DEBYE
<Apr02-2013> <12:13:35> >>>> AMETS
<Apr02-2013> <12:13:35> Bond Energy -5.82764289 a.u.
<Apr02-2013> <12:13:35> Bond Energy -158.57823164 eV
<Apr02-2013> <12:13:35> Bond Energy -3656.90 kcal/mol
<Apr02-2013> <12:13:35> >>>> POPUL
<Apr02-2013> <12:13:38> NORMAL TERMINATION
<Apr02-2013> <12:13:39> END
Job caffeine has finished

```

Step 3: Orbitals, Potential and AIM results

Start ADFview **SCM** → **View**
 Show the HOMO **Properties** → **HOMO**

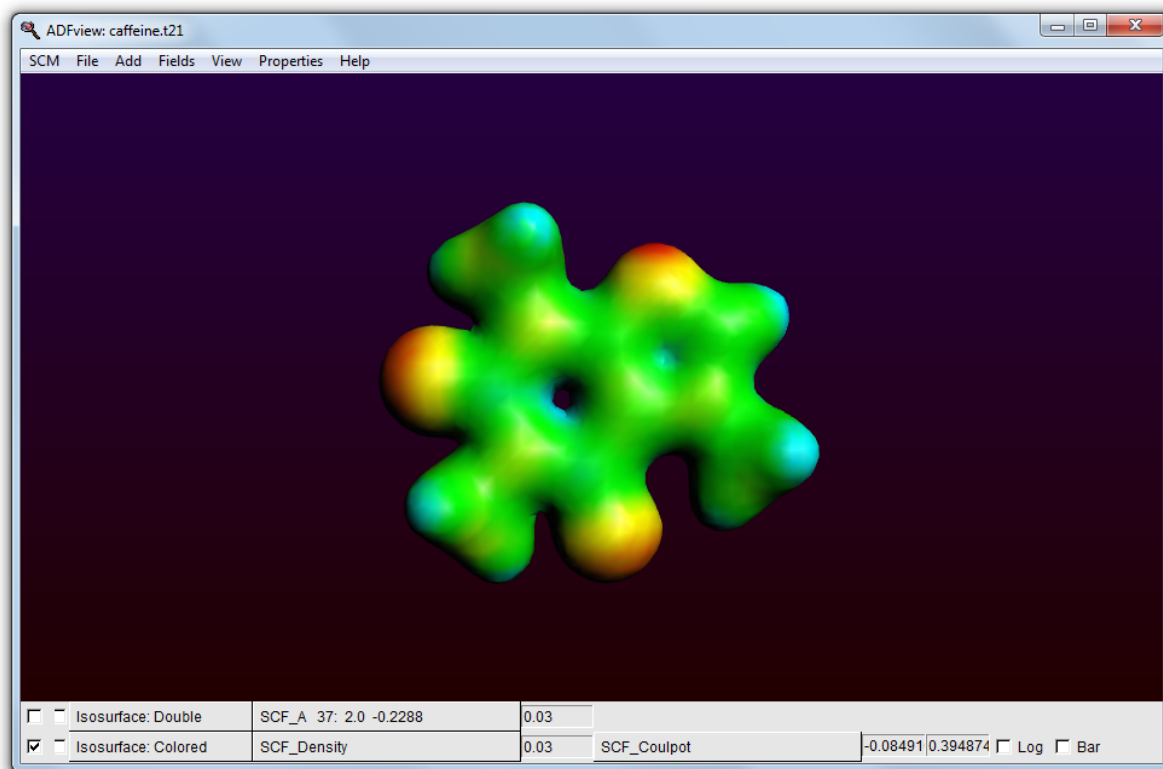


Hide the HOMO by unchecking the check box at the lower left corner of the ADFview window

Add → Isosurface: Colored

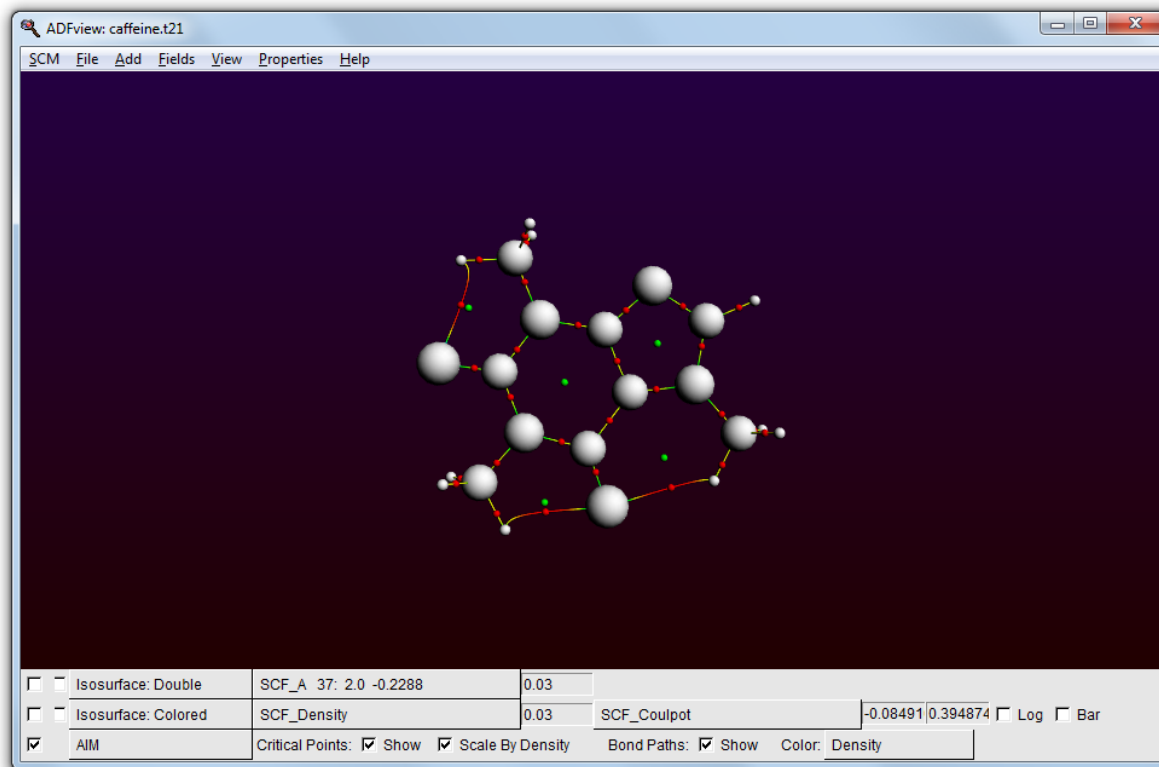
In the first field selector (to the right of the 'Isosurface: Colored' text at the bottom), select **Density** → **SCF**

In the second field selector (to the right of the '0.03' text in the same line), select **Potential** → **SCF**



Hide the surface with the potential energy: uncheck the check box at the lower left corner of the window

Properties → AIM (Bader)

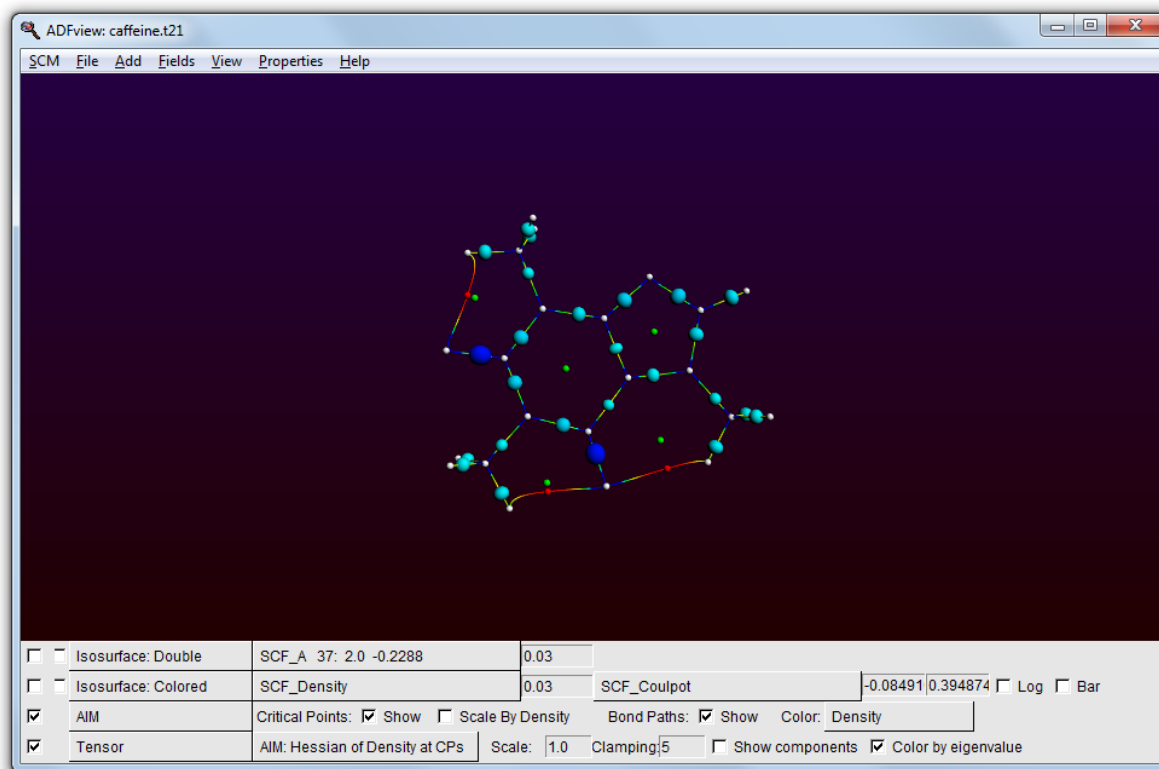


The critical points and bond paths are shown (the molecule balls and sticks representation is hidden). The different types of critical points (atom CP, bond CP, ring CP and cage CP) are indicated by different colors. The atom CPs are scaled by density by default, which makes them look like atoms. The 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

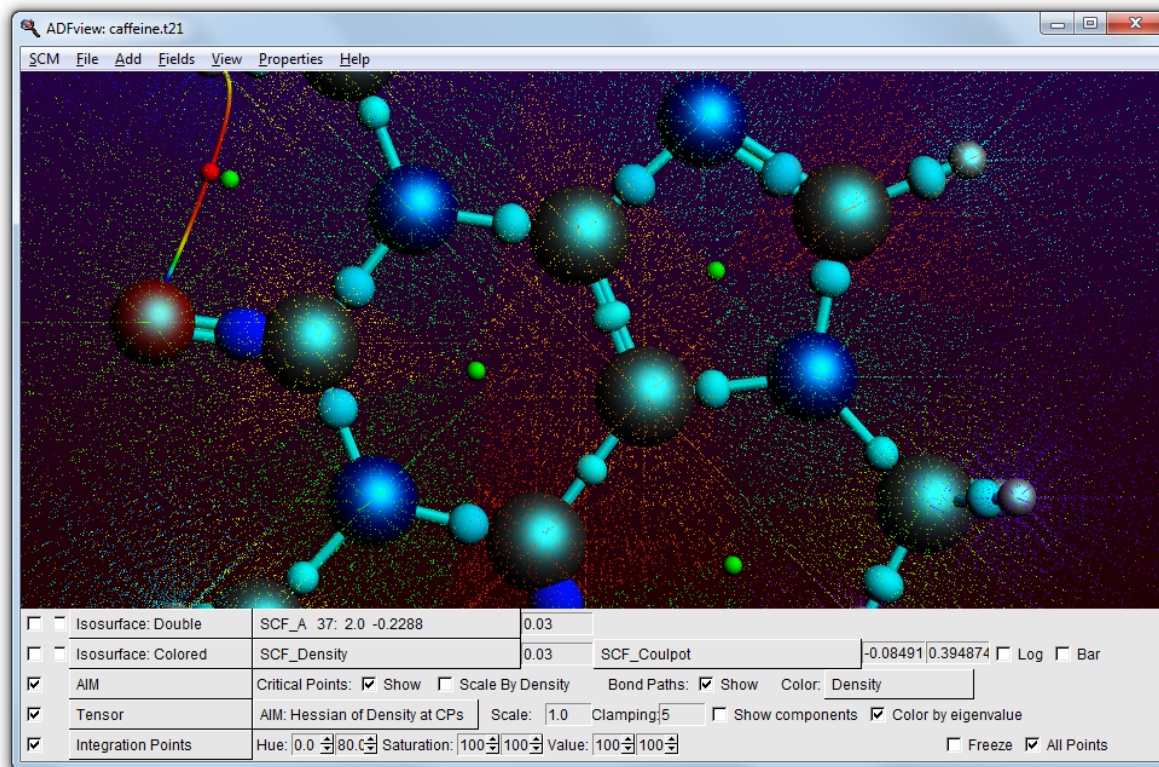
Properties → AIM: Hessian of Density at CPs



To get a rough display of the Bader basins, use the Bader sampling option:

Properties → **Bader Sampling**

Zoom in



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 → Quit

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 '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**)

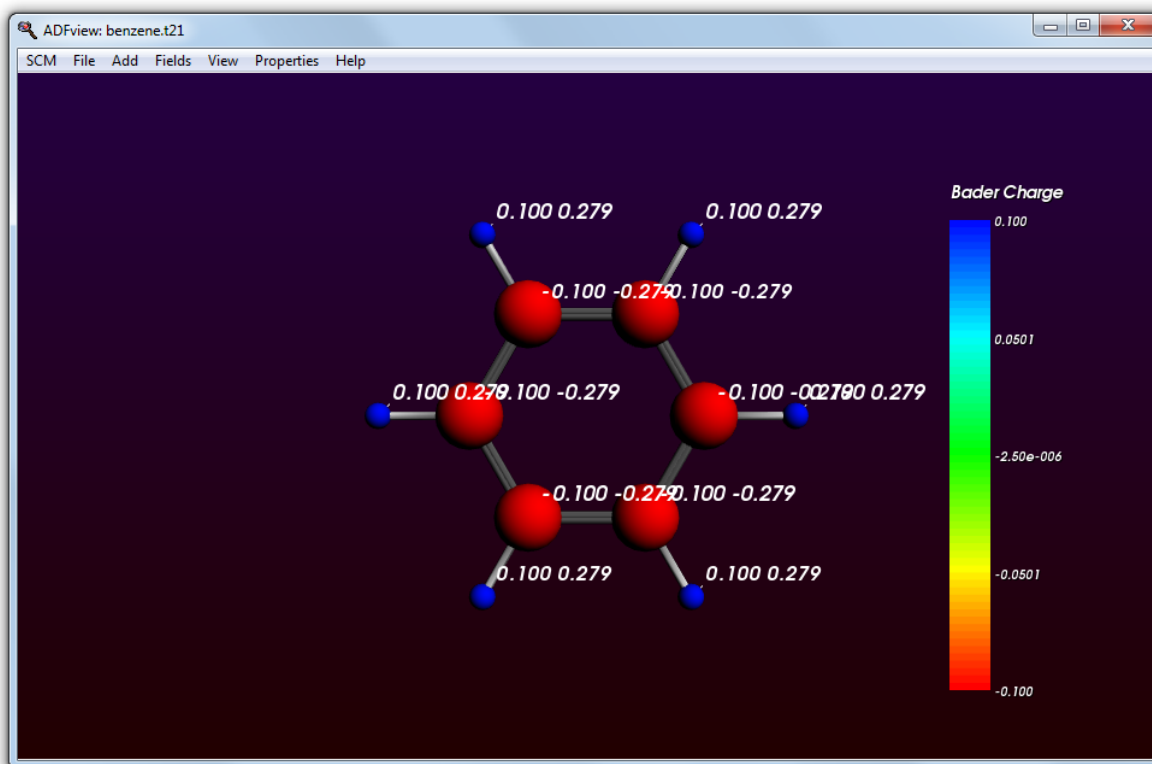
When the calculation is done (it should run very fast), we use ADFview to examine the Bader charges and compare them with Mulliken charges:

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

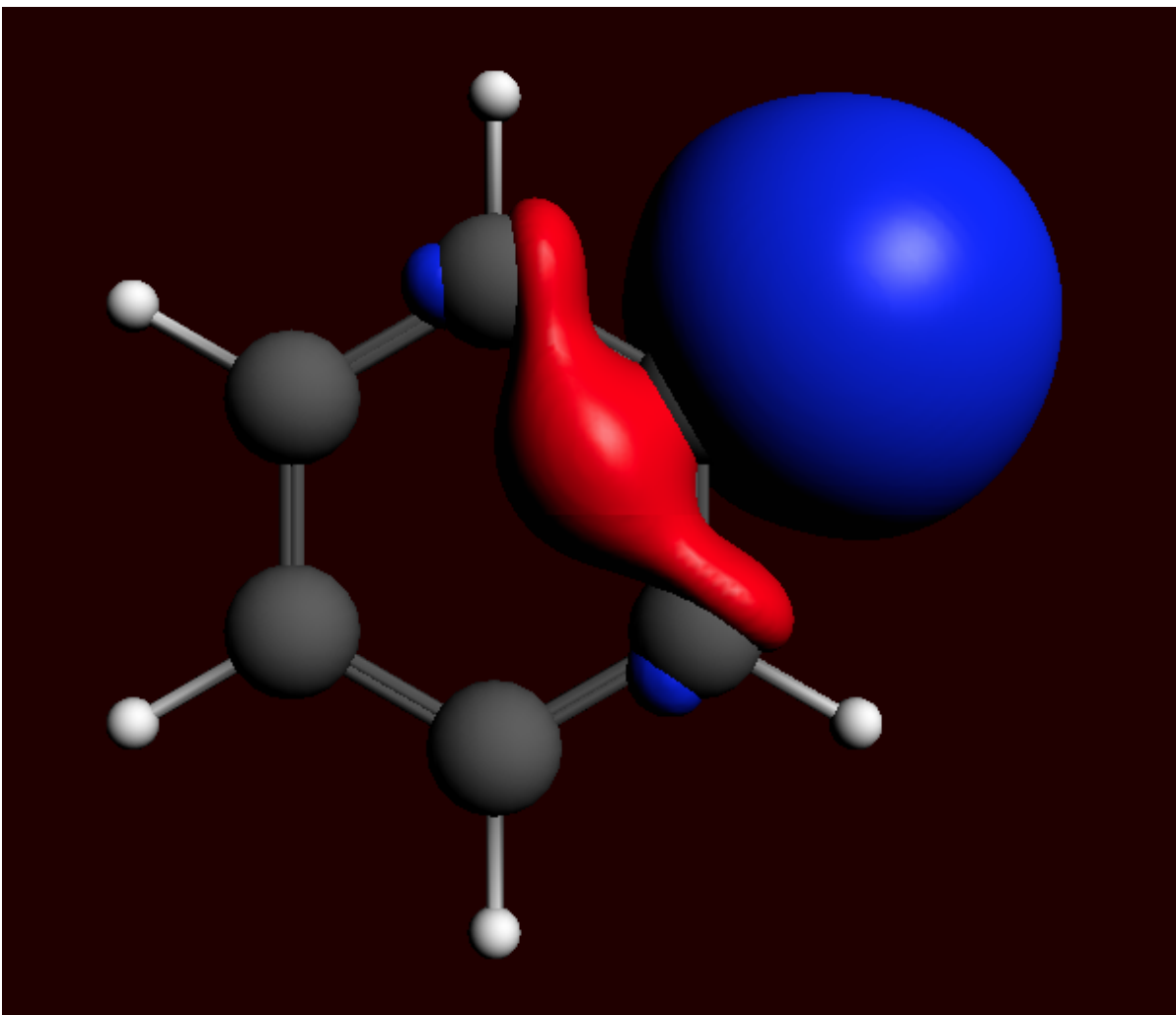
Add a Double Isosurface

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**



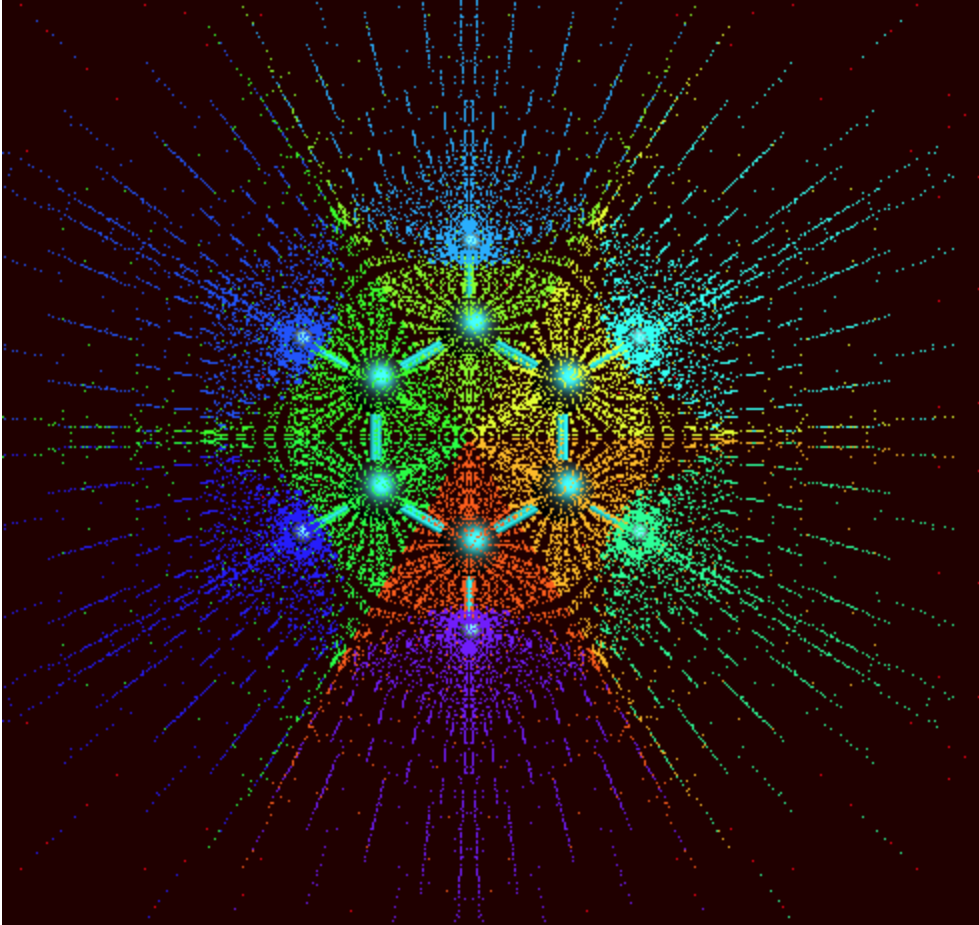
Obviously, you can also visualize the NLMOs or the Boys-Foster localized orbitals (which are just called Localized Orbitals in the fields menu).

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



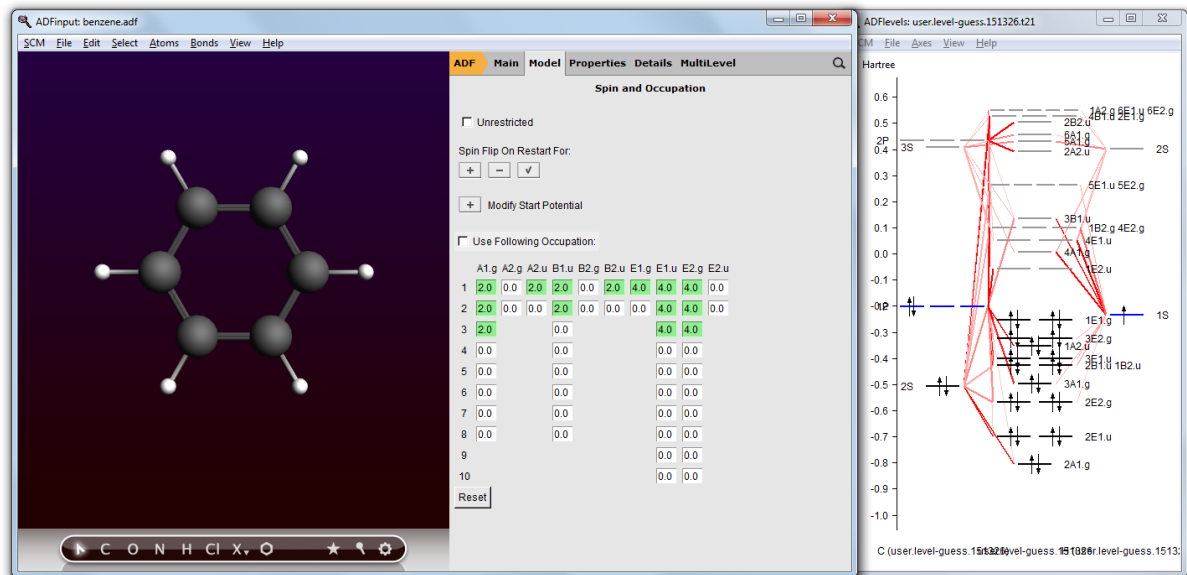
One can also select one or more atoms, to see only the Bader atomic basins of the selected atoms.

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**



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)

ADF Main Model **Properties** Details MultiLevel Q

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

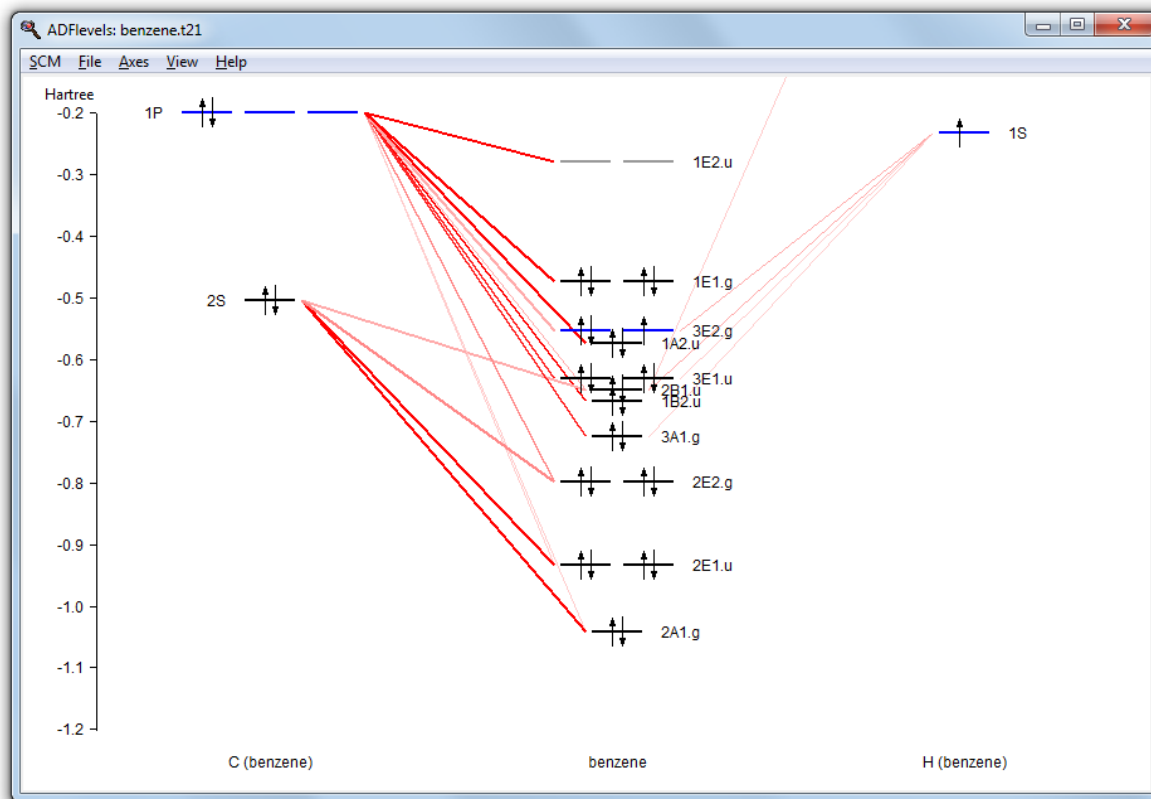
Run (via the **Job** → **Run** command in ADFjobs)

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 Fe₄S₄ 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 Fe₄S₄ 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 Fe₄S₄ cubane from scratch in this example.

Start ADFinput

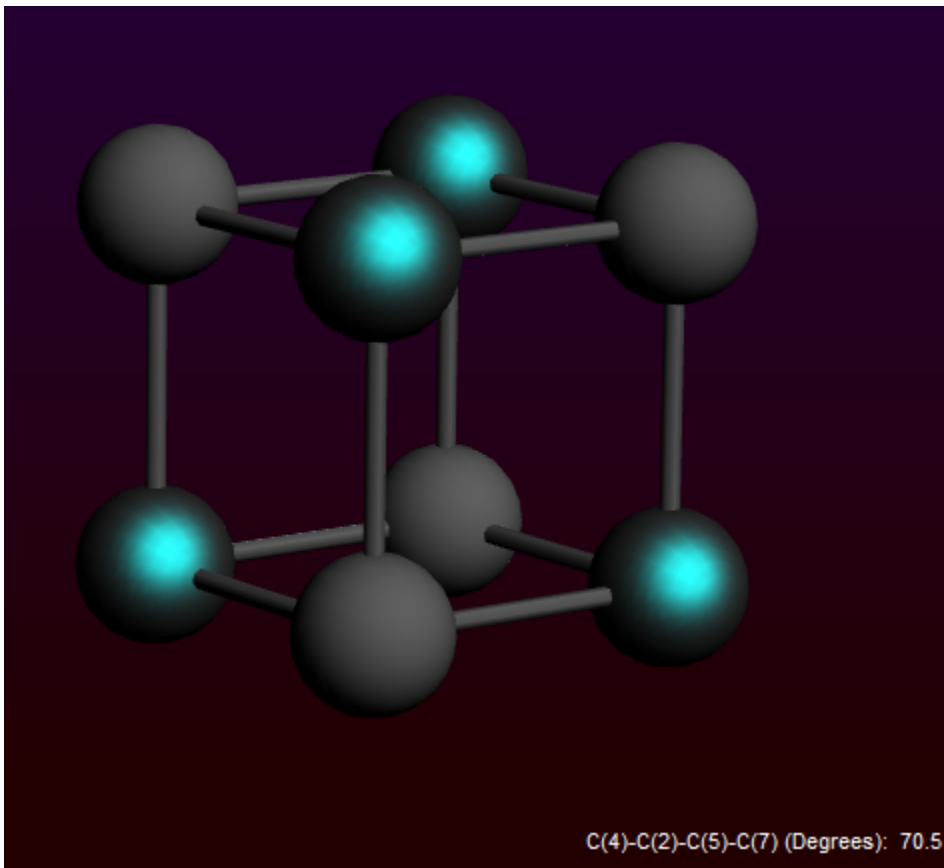
Select the **Structure tool** → **Polyhedra** → **Cube** structure:

Click anywhere in the empty structure drawing area.

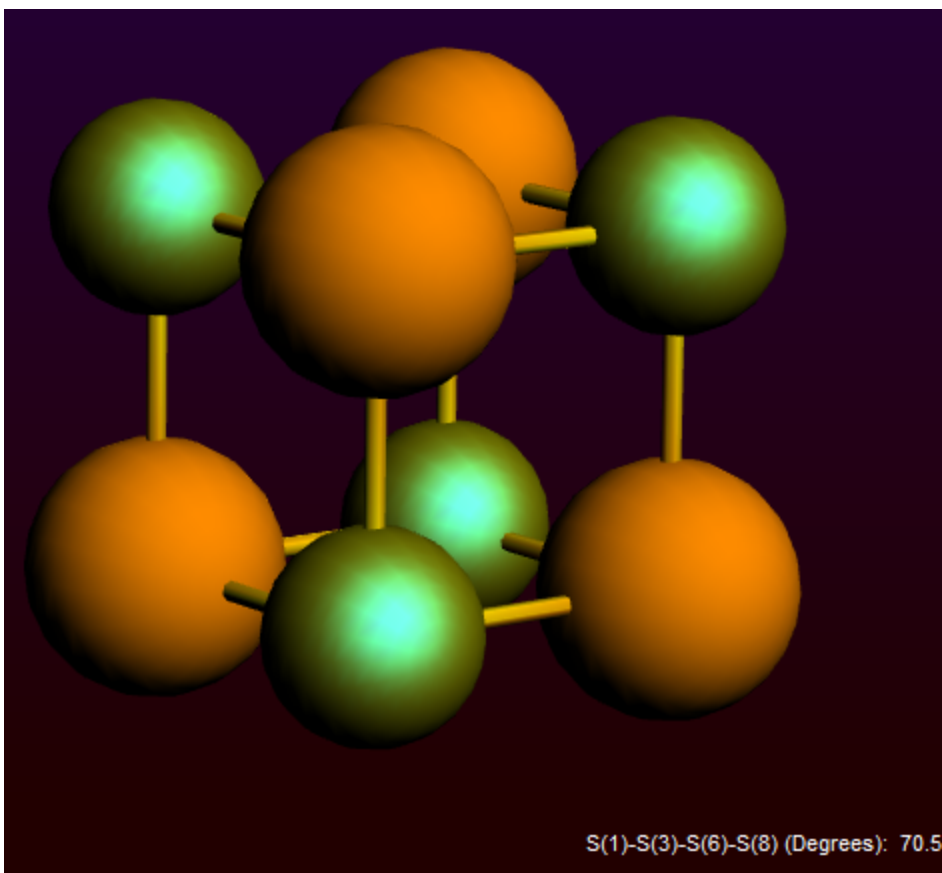
This should place a cube in the building area of ADFinput.

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

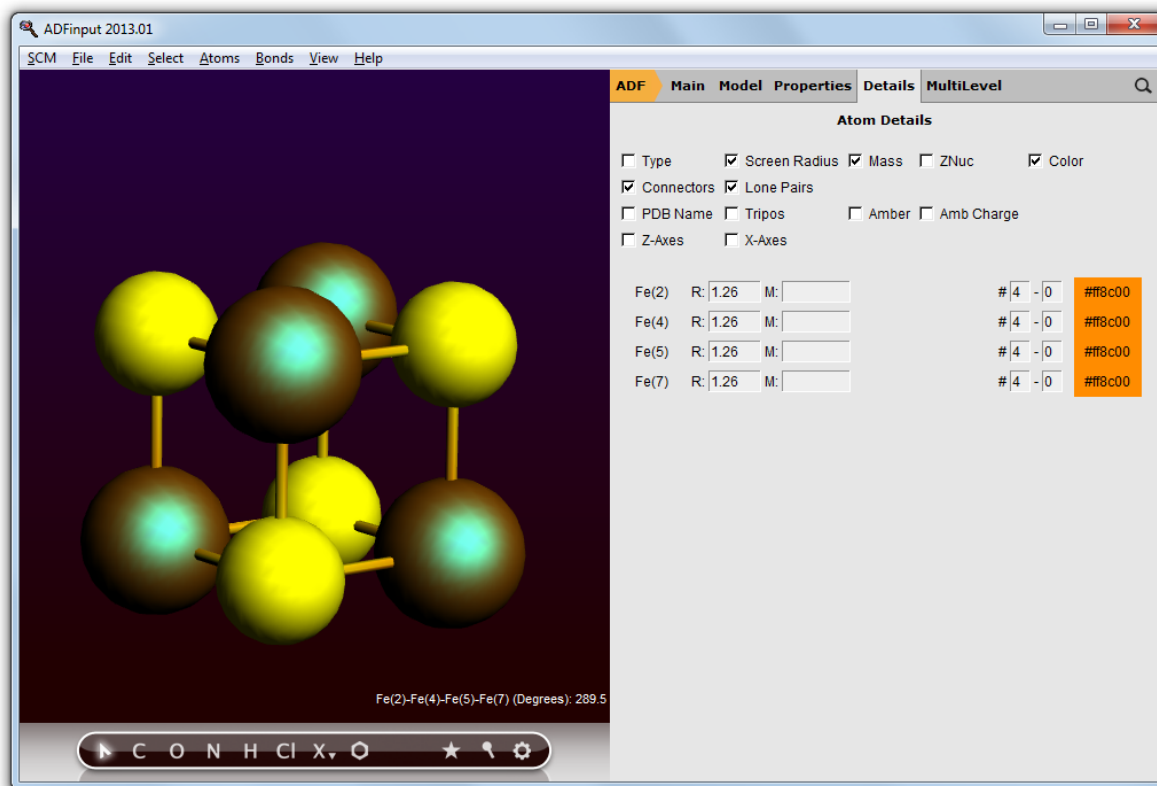


Atoms → **Change Atom Type** → **Fe**: change the four atoms into Fe
Selection → **Invert Selection**
Atoms → **Change Atom Type** → **S**: change the other atoms into S



Now you should see the Fe₄S₄ 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



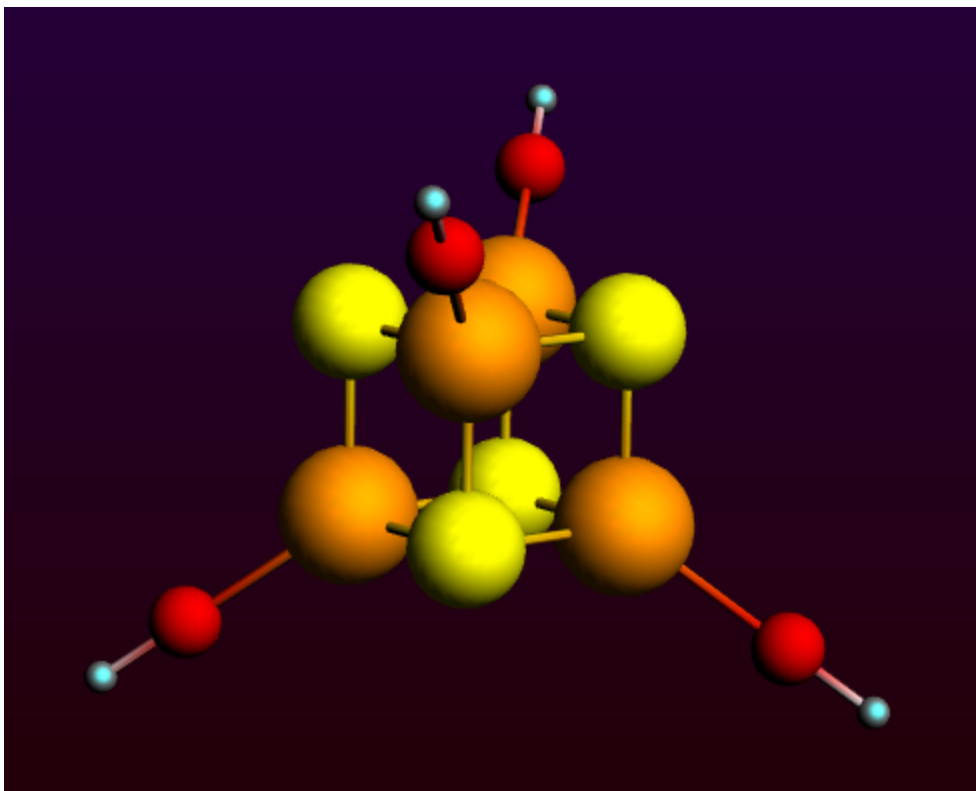
Switch to the Main panel

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

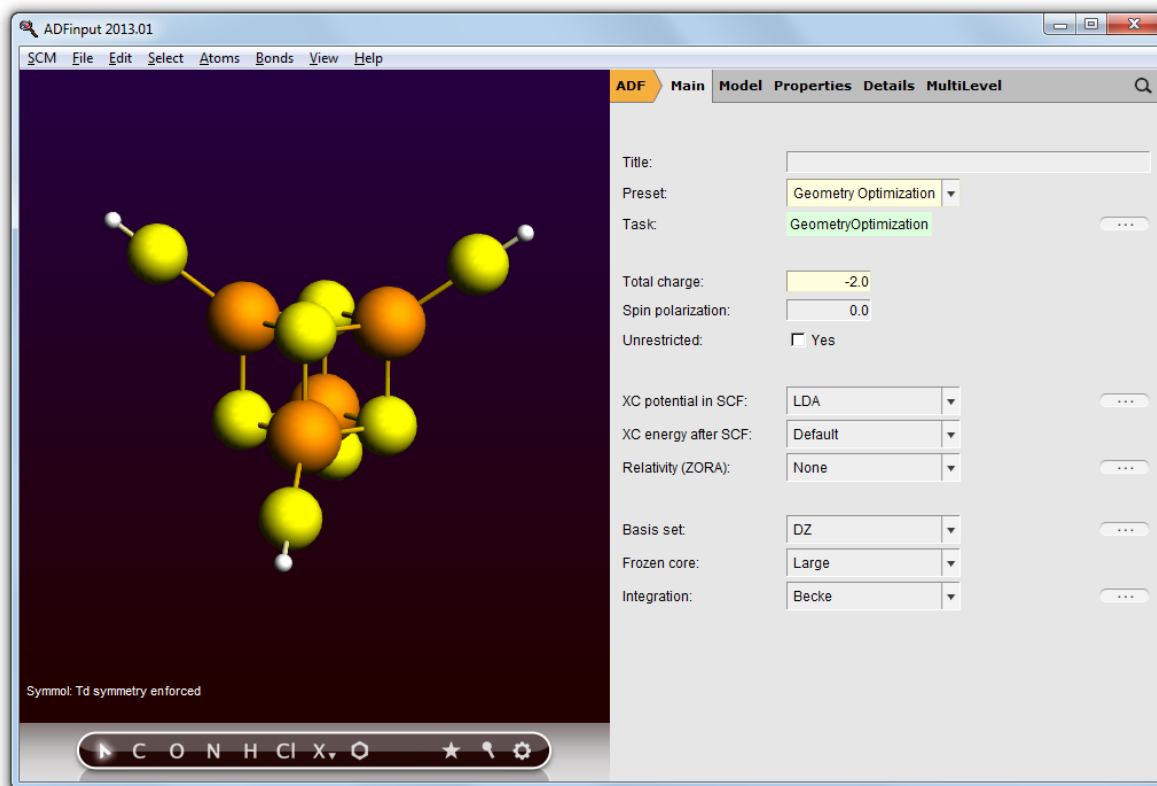
Use the **Atoms** → **Change Atom Type** → **S** to change them into S

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)

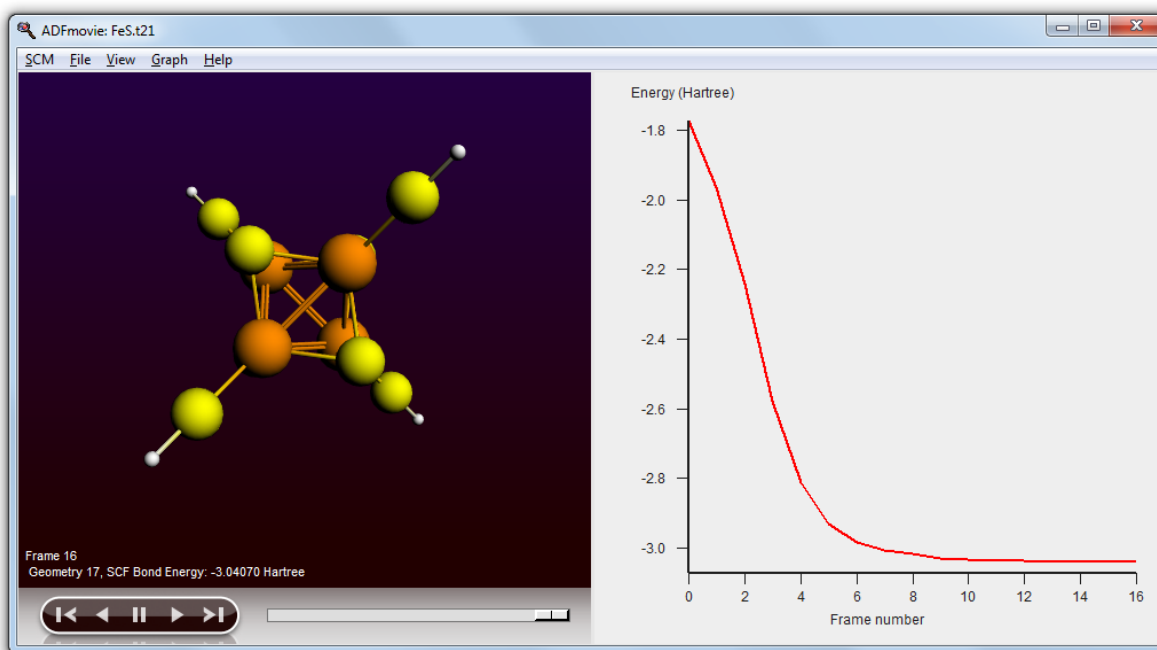


File → **Run** (enter FeS as name)

When ready, click OK to use the optimized geometry in ADFinput

SCM → **Movie**

In the Movie window: **Graph** → **Energy**



Close the movie window: **File** → **Close**

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 (HIPs). For our model system, $\text{Fe}_4\text{S}_4(\text{SH})_4$, 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-consistent 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 $[\text{Fe}_4\text{S}_4(\text{SH})_4]^{2-}$ 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

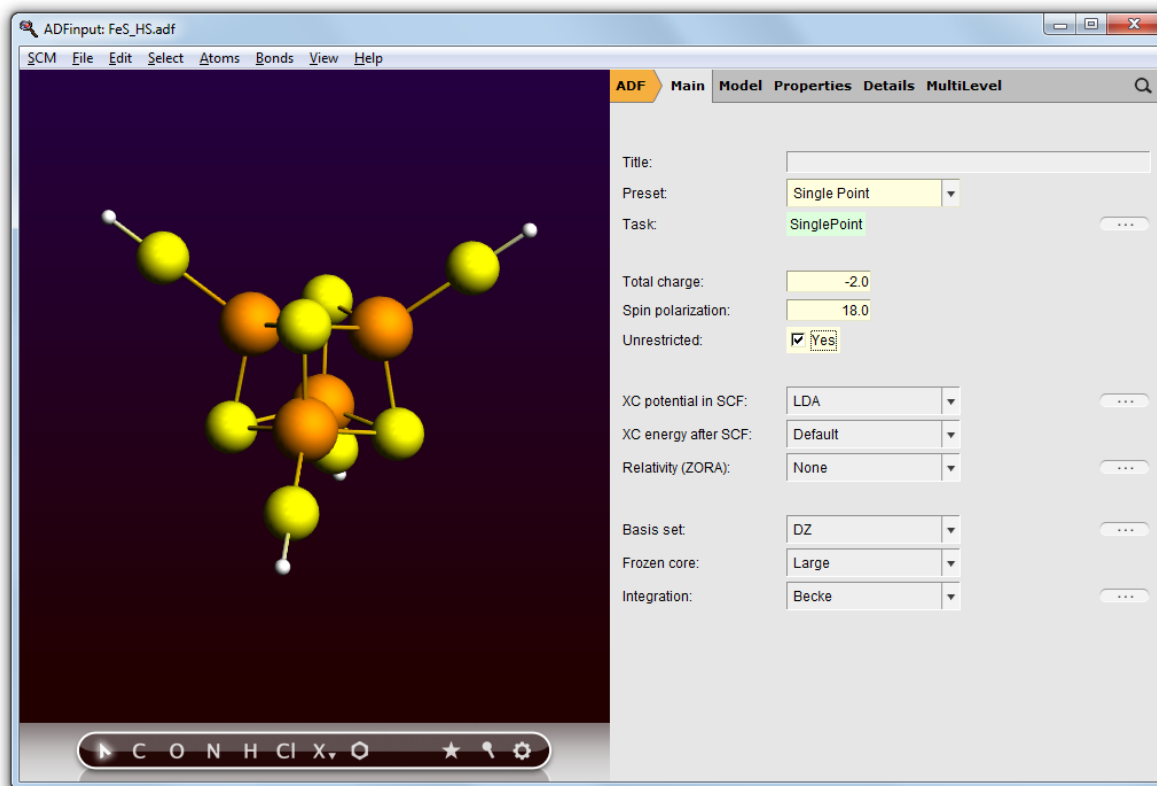
Set the spin polarization to 18 (corresponds to $S = 9$)

Check the unrestricted box

File → **Save As...**

Enter FeS_HS as filename and save

File → **Run**



ADFTail window will pop up showing the progress of the job:

```

ADFTail: FeS_HS logfile
SCM File Edit Help
<Apr02-2013> <01:13:55> RunType : SINGLE POINT
<Apr02-2013> <01:13:55> Net Charge: -2 (Nuclei minus Electrons)
<Apr02-2013> <01:13:55> Spin polar: 18 (Spin_A minus Spin_B electrons)
<Apr02-2013> <01:13:55> Symmetry : T (D)
<Apr02-2013> <01:13:55> >>>> FRAGM
<Apr02-2013> <01:13:59> >>>> CORORT
<Apr02-2013> <01:13:59> >>>> FITINT
<Apr02-2013> <01:14:00> >>>> CLSMAT
<Apr02-2013> <01:14:00> >>>> ORTHON
<Apr02-2013> <01:14:00> >>>> GENPT
<Apr02-2013> <01:14:00> Block Length= 127
<Apr02-2013> <01:14:00> >>>> PTBAS
<Apr02-2013> <01:14:00> >>>> CYCLE
<Apr02-2013> <01:14:00> 1
<Apr02-2013> <01:14:00> 2 ErrMat 3.40074776 MaxEl -0.50984048
<Apr02-2013> <01:14:00> 3 ErrMat 4.02800581 MaxEl 0.63694039
<Apr02-2013> <01:14:00> 4 ErrMat 5.83347121 MaxEl -0.67860896
<Apr02-2013> <01:14:00> 5 ErrMat 5.10877265 MaxEl 0.89310431
<Apr02-2013> <01:14:00> 6 ErrMat 0.45477356 MaxEl 0.07058301
<Apr02-2013> <01:14:00> 7 ErrMat 1.92737621 MaxEl 0.40873106
<Apr02-2013> <01:14:00> 8 ErrMat 0.30436589 MaxEl 0.03397638
<Apr02-2013> <01:14:00> 9 ErrMat 0.15124790 MaxEl 0.01948889
<Apr02-2013> <01:14:01> 10 ErrMat 0.07754150 MaxEl 0.01178686
<Apr02-2013> <01:14:01> 11 ErrMat 0.02022897 MaxEl 0.00340035
<Apr02-2013> <01:14:01> 12 ErrMat 0.02020223 MaxEl -0.00319469
<Apr02-2013> <01:14:01> 13 ErrMat 0.00256652 MaxEl -0.00041046
<Apr02-2013> <01:14:01> 14 ErrMat 0.00080158 MaxEl -0.00011704
<Apr02-2013> <01:14:01> 15 ErrMat 0.00004511 MaxEl -0.00000631
<Apr02-2013> <01:14:01> 16 ErrMat 0.00000611 MaxEl -0.00000098
<Apr02-2013> <01:14:01> SCF converged
<Apr02-2013> <01:14:01> 17 ErrMat 0.00000409 MaxEl 0.00000058
<Apr02-2013> <01:14:01> WARNING: partially occupied orbitals
<Apr02-2013> <01:14:01> Solutions with partially occupied orbitals may not be
<Apr02-2013> <01:14:01> lowest in energy. You might consider lowering the
<Apr02-2013> <01:14:01> symmetry in the input and explicitly specifying integer
<Apr02-2013> <01:14:01> occupations. In that case always check that you obtain
<Apr02-2013> <01:14:01> an aufbau solution.
<Apr02-2013> <01:14:02> >>>> TOTEN
<Apr02-2013> <01:14:02> >>>> POPAN
<Apr02-2013> <01:14:03> >>>> DEBYE
<Apr02-2013> <01:14:03> >>>> AMETS
<Apr02-2013> <01:14:03> Bond Energy -2.96272827 a.u.
<Apr02-2013> <01:14:03> Bond Energy -80.61993814 eV
<Apr02-2013> <01:14:03> Bond Energy -1859.14 kcal/mol
<Apr02-2013> <01:14:03> >>>> POPUL
<Apr02-2013> <01:14:08> NORMAL TERMINATION
<Apr02-2013> <01:14:08> 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 Fe₄S₄ 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, \uparrow).
- Next the α (\uparrow) and β (\downarrow) electron densities centered at the sites which are expected to be antiferromagnetically coupled (spins down, \downarrow) 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 $S = (5/2 + 2) - (5/2 + 2) = 0$, $2\uparrow:2\downarrow$.

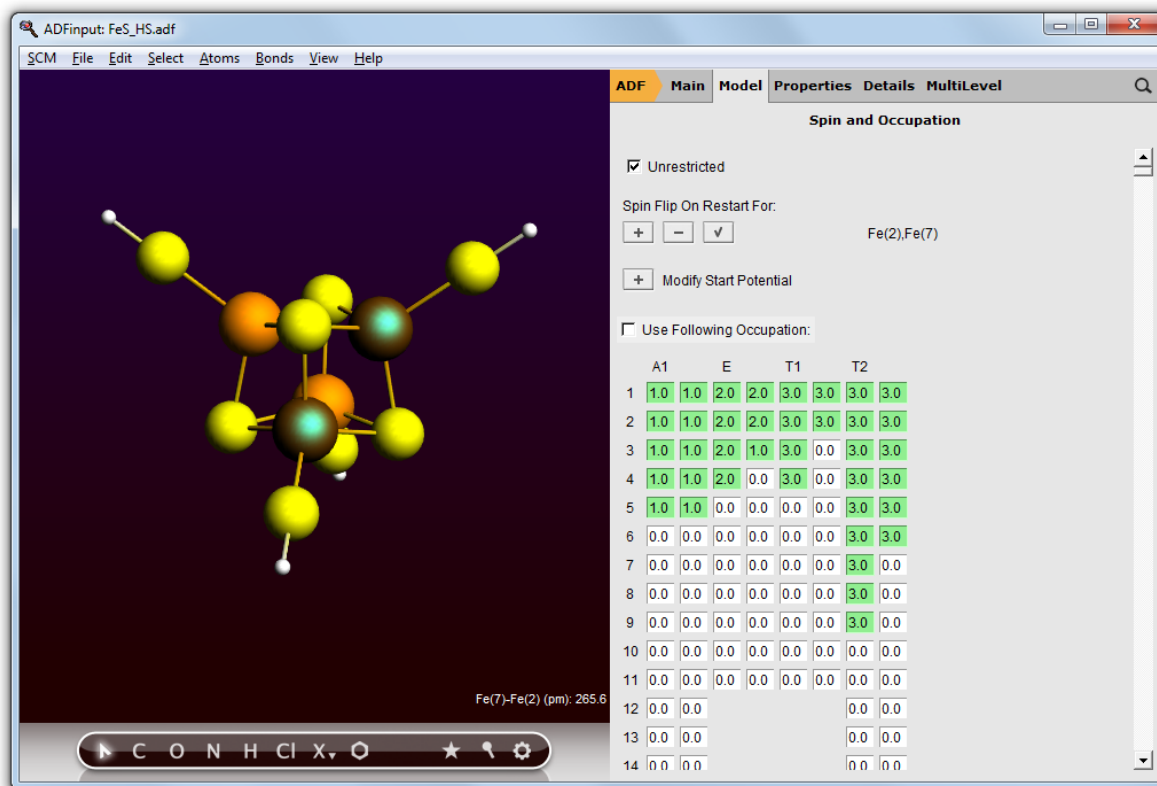
Select the ADFinput window with your FeS_HS calculation
 Make sure the 'Main' panel is visible
 Change the spin polarization from 18 to 0

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.

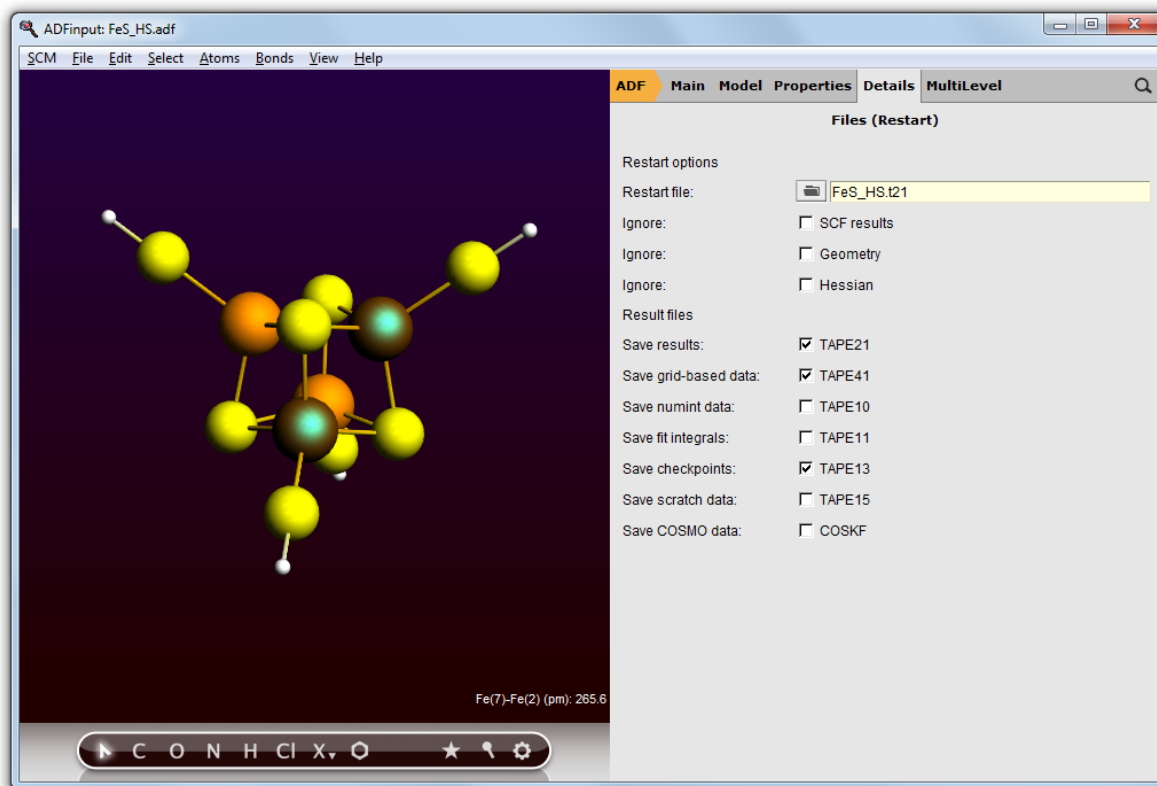


To achieve the desired BS solution, the SpinFlip procedure should be applied to 2 out of 4 Fe sites of Fe₄S₄. In the above example, we selected sites Fe(2) and Fe(7). This will instruct SpinFlip algorithm to interchange α (\uparrow) and β (\downarrow) electron densities associated with these two Fe sites when the job will be restarted, changing the HS 4 \uparrow :0 \downarrow spin state to the BS 2 \uparrow :2 \downarrow 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)



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 symbol to NOSYM

File → **Save As**, save the job as FeS_BS_SPINFLIP

File → **Run**

```

ADFtail: FeS_BS_SPINFLIP.logfile
SCM File Edit Help
<Apr02-2013> <01:34:33> ADF 2013.01 RunTime: Apr02-2013 01:34:33 Nodes: 1 Procs: 4
<Apr02-2013> <01:34:33> *** (NO TITLE) ***
<Apr02-2013> <01:34:33> RunType : SINGLE POINT
<Apr02-2013> <01:34:33> Net Charge: -2 (Nuclei minus Electrons)
<Apr02-2013> <01:34:33> Spin polar: 0 (Spin_A minus Spin_B electrons)
<Apr02-2013> <01:34:33> Symmetry : NOSYM
<Apr02-2013> <01:34:33> >>>> FRAGM
<Apr02-2013> <01:34:35> >>>> CORORT
<Apr02-2013> <01:34:35> >>>> FITINT
<Apr02-2013> <01:34:35> >>>> CLSMAT
<Apr02-2013> <01:34:36> >>>> ORTHON
<Apr02-2013> <01:34:36> >>>> GENPT
<Apr02-2013> <01:34:36> Block Length= 128
<Apr02-2013> <01:34:36> >>>> PTBAS
<Apr02-2013> <01:34:36> >>>> CYCLE
<Apr02-2013> <01:34:37> 1
<Apr02-2013> <01:34:37> 2 ErrMat 0.39670725 MaxEl 0.05917262
<Apr02-2013> <01:34:38> 3 ErrMat 0.62443637 MaxEl -0.08442353
<Apr02-2013> <01:34:38> 4 ErrMat 1.74689977 MaxEl 0.27978924
<Apr02-2013> <01:34:39> 5 ErrMat 0.26854363 MaxEl -0.03079317
<Apr02-2013> <01:34:39> 6 ErrMat 0.05458055 MaxEl 0.00646215
<Apr02-2013> <01:34:40> 7 ErrMat 0.05732161 MaxEl 0.00729052
<Apr02-2013> <01:34:40> 8 ErrMat 0.01905670 MaxEl -0.00289469
<Apr02-2013> <01:34:41> 9 ErrMat 0.01055734 MaxEl 0.00176191
<Apr02-2013> <01:34:41> 10 ErrMat 0.02356708 MaxEl 0.00673121
<Apr02-2013> <01:34:41> 11 ErrMat 0.00559004 MaxEl -0.00094243
<Apr02-2013> <01:34:42> 12 ErrMat 0.00259673 MaxEl -0.00037557
<Apr02-2013> <01:34:42> 13 ErrMat 0.00316780 MaxEl 0.00075655
<Apr02-2013> <01:34:43> 14 ErrMat 0.00178196 MaxEl 0.00029227
<Apr02-2013> <01:34:43> 15 ErrMat 0.00229913 MaxEl 0.00030964
<Apr02-2013> <01:34:44> 16 ErrMat 0.00025905 MaxEl 0.00003443
<Apr02-2013> <01:34:44> 17 ErrMat 0.00004198 MaxEl 0.00000756
<Apr02-2013> <01:34:45> 18 ErrMat 0.00001464 MaxEl -0.00000228
<Apr02-2013> <01:34:45> 19 ErrMat 0.00002337 MaxEl 0.00000355
<Apr02-2013> <01:34:46> 20 ErrMat 0.00000348 MaxEl 0.00000058
<Apr02-2013> <01:34:46> SCF converged
<Apr02-2013> <01:34:46> 21 ErrMat 0.00000577 MaxEl 0.00000148
<Apr02-2013> <01:34:47> >>>> TOTEN
<Apr02-2013> <01:34:49> >>>> POPAN
<Apr02-2013> <01:34:50> >>>> DEBYE
<Apr02-2013> <01:34:50> >>>> AMETS
<Apr02-2013> <01:34:50> Bond Energy -3.08114133 a.u.
<Apr02-2013> <01:34:50> Bond Energy -83.84212155 eV
<Apr02-2013> <01:34:50> Bond Energy -1933.45 kcal/mol
<Apr02-2013> <01:34:50> >>>> POPUL
<Apr02-2013> <01:34:58> NORMAL TERMINATION
<Apr02-2013> <01:34:58> 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

The screenshot shows the ADFinput software interface. The main window title is 'ADFinput: FeS_HS.adf'. The menu bar includes 'SCM', 'File', 'Edit', 'Select', 'Atoms', 'Bonds', 'View', and 'Help'. The 'Model' panel is active, showing 'Spin and Occupation' settings. The 'Unrestricted' checkbox is checked. Under 'Spin Flip On Restart For:', there are buttons for '+', '-', and 'v'. The 'Modify Start Potential' section is expanded, showing a table of alpha and beta occupations for four iron atoms:

Atom	Alpha	Beta
Fe(2)	14.0	10.0
Fe(4)	14.0	9.0
Fe(5)	10.0	14.0
Fe(7)	9.0	14.0

Below this table, there is a section for 'Use Following Occupation:' with a table of occupation numbers for orbitals A1, E, T1, and T2 across 9 atoms:

	A1	E	T1	T2
1	1.0	1.0	2.0	2.0
2	1.0	1.0	2.0	2.0
3	1.0	1.0	2.0	1.0
4	1.0	1.0	2.0	0.0
5	1.0	1.0	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	0.0	0.0

The 3D model on the left shows a cluster of four iron atoms (yellow) and four sulfur atoms (blue). The angle between Fe(2)-Fe(4)-Fe(5)-Fe(7) is 289.5 degrees.

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 $S = (5/2 + 2) - (5/2 + 2) = 0, 2\uparrow:2\downarrow$.

Note that SCF procedure might be problematic.

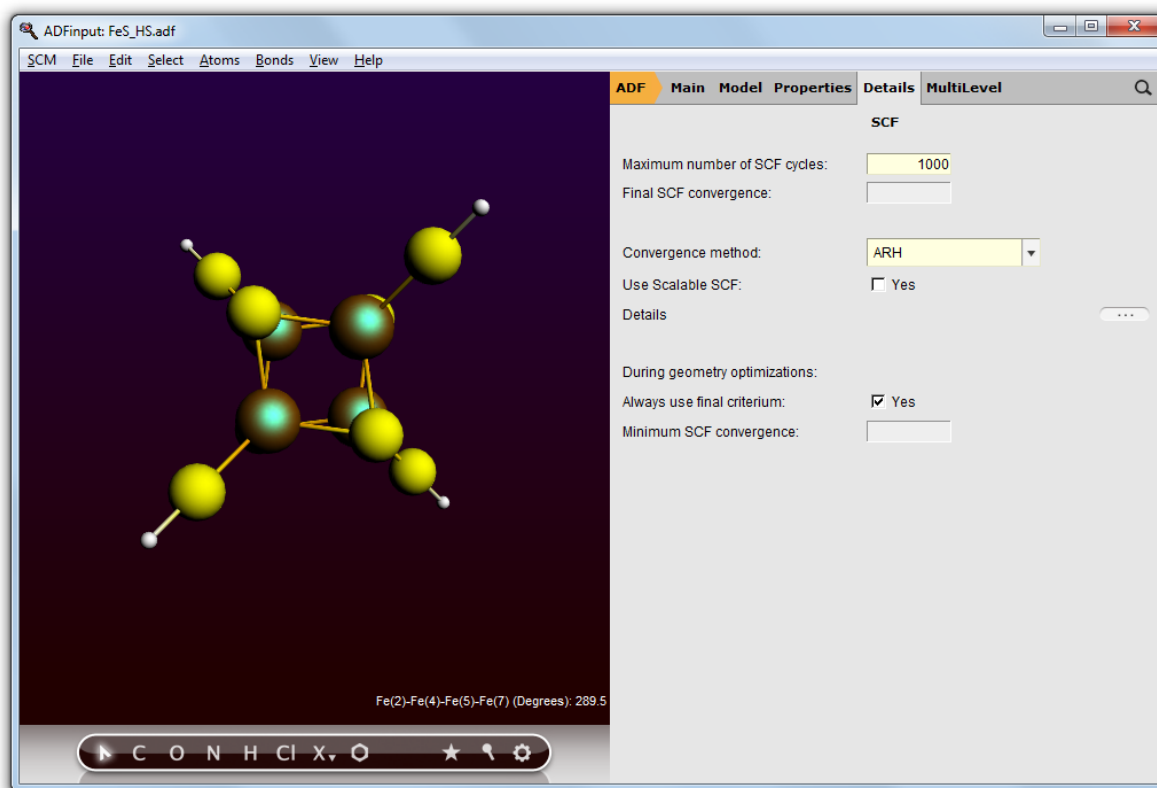
You can play with several options to help the convergence. In the SCF panel (in Details) you can experiment with several methods like LISTi, A-DIIS, E-DIIS and ARH. In the SCF convergence details panel further options are available, like mixing, level shifting, orbital freezing and DIIS details.

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



File → **Save As**: save the job as FeS_BS_MODIFYSTARTPOTENTIAL

File → **Run**

```

ADFtail: FeS_BS_MODIFYSTARTPOTENTIAL.logfile
SCM File Edit Help
<Apr02-2013> <01:55:46> 174 0.00423710 0.00049405 -8222.5362081183 REDO
<Apr02-2013> <01:55:47> -8222.5362726745
<Apr02-2013> <01:55:48> 175 0.00425740 0.00059811 -8222.5362740640
<Apr02-2013> <01:55:50> 176 0.00147065 0.00015603 -8222.5362736087
<Apr02-2013> <01:55:51> 177 0.00299749 0.00040610 -8222.5362764818
<Apr02-2013> <01:55:53> 178 0.00259396 0.00023432 -8222.5362729960
<Apr02-2013> <01:55:55> 179 0.00435022 0.00049972 -8222.5362198055 REDO
<Apr02-2013> <01:55:56> -8222.5362417051 REDO
<Apr02-2013> <01:55:57> -8222.5362767641
<Apr02-2013> <01:55:58> 180 0.00340876 0.00048049 -8222.5362825321
<Apr02-2013> <01:56:00> 181 0.00456025 0.00074108 -8222.5362440855 REDO
<Apr02-2013> <01:56:01> -8222.5362853298
<Apr02-2013> <01:56:02> 182 0.00305806 0.00030728 -8222.5362927883
<Apr02-2013> <01:56:04> 183 0.00357044 0.00047847 -8222.5362915169
<Apr02-2013> <01:56:06> 184 0.00223226 0.00023507 -8222.5362875871
<Apr02-2013> <01:56:08> 185 0.00489825 0.00069699 -8222.5362746384 REDO
<Apr02-2013> <01:56:08> -8222.5362918789
<Apr02-2013> <01:56:10> 186 0.00231919 0.00023150 -8222.5362831983 REDO
<Apr02-2013> <01:56:11> -8222.5362908602
<Apr02-2013> <01:56:12> 187 0.00087568 0.00009499 -8222.5362897284
<Apr02-2013> <01:56:12> Done Augmented Roothaan-Hall iterations
<Apr02-2013> <01:56:13> 3
<Apr02-2013> <01:56:13> 4 ErrMat 0.03396703 MaxE1 -0.01010352
<Apr02-2013> <01:56:14> 5 ErrMat 0.11365611 MaxE1 0.03401585
<Apr02-2013> <01:56:14> 6 ErrMat 0.02197183 MaxE1 -0.00308953
<Apr02-2013> <01:56:14> 7 ErrMat 0.00806834 MaxE1 -0.00133388
<Apr02-2013> <01:56:15> 8 ErrMat 0.00272677 MaxE1 0.00038515
<Apr02-2013> <01:56:15> 9 ErrMat 0.00087105 MaxE1 0.00009456
<Apr02-2013> <01:56:16> 10 ErrMat 0.00211553 MaxE1 -0.00065792
<Apr02-2013> <01:56:16> 11 ErrMat 0.00044257 MaxE1 0.00006929
<Apr02-2013> <01:56:17> 12 ErrMat 0.00013335 MaxE1 0.00002018
<Apr02-2013> <01:56:17> 13 ErrMat 0.00003537 MaxE1 0.00000572
<Apr02-2013> <01:56:18> 14 ErrMat 0.00002478 MaxE1 0.00000446
<Apr02-2013> <01:56:18> 15 ErrMat 0.00001473 MaxE1 0.00000268
<Apr02-2013> <01:56:19> 16 ErrMat 0.00000640 MaxE1 0.00000091
<Apr02-2013> <01:56:19> SCF converged
<Apr02-2013> <01:56:19> 17 ErrMat 0.00001115 MaxE1 -0.00000182
<Apr02-2013> <01:56:20> >>>> TOTEN
<Apr02-2013> <01:56:22> >>>> POPAN
<Apr02-2013> <01:56:23> >>>> DEBYE
<Apr02-2013> <01:56:23> >>>> AMETS
<Apr02-2013> <01:56:23> Bond Energy -3.08114132 a.u.
<Apr02-2013> <01:56:23> Bond Energy -83.84212112 eV
<Apr02-2013> <01:56:23> Bond Energy -1933.45 kcal/mol
<Apr02-2013> <01:56:23> >>>> POPUL
<Apr02-2013> <01:56:31> NORMAL TERMINATION
<Apr02-2013> <01:56:31> 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 Fe₄S₄ 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 Fe₄S₄ 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 $2\uparrow:2\downarrow$. 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

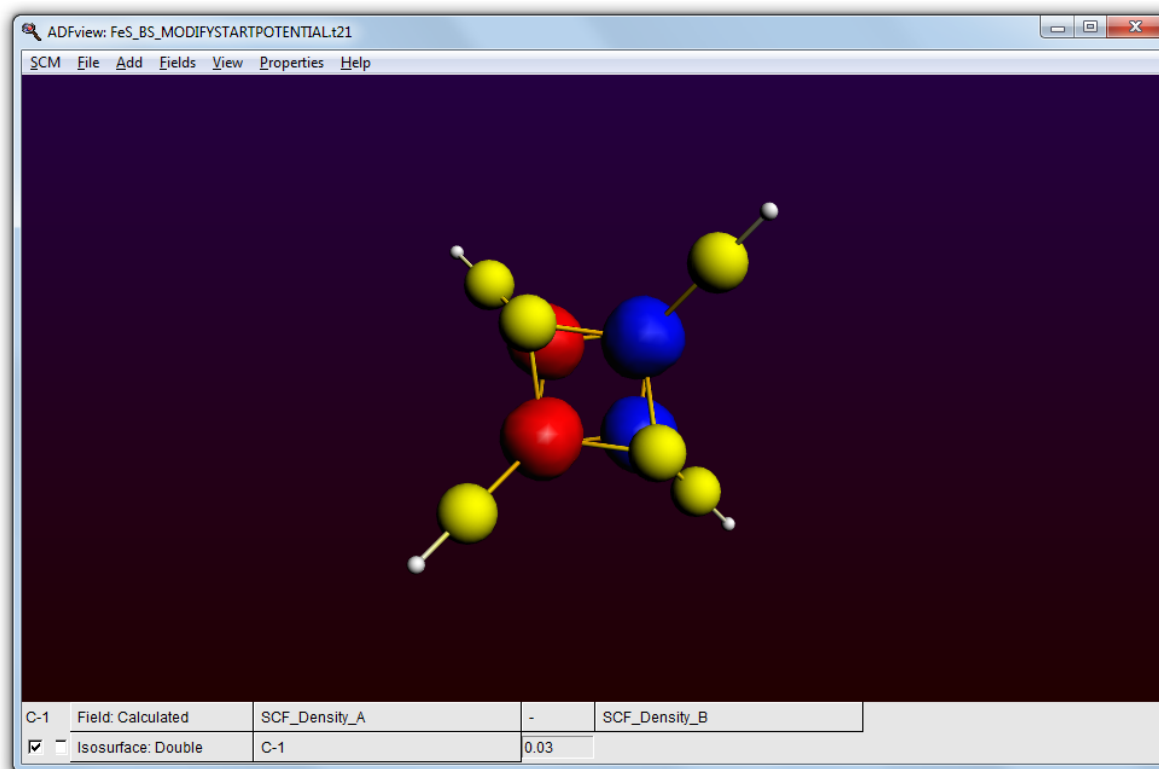
You should see the $[\text{Fe}_4\text{S}_4(\text{SH})_4]^{2-}$ system in the ADFview window.

The spin-density is available as a short-cut in the Properties menu:

Properties → Spin Density

You should see now the two Fe ions surrounded by blue blobs (spin up, \uparrow) and the other two by red blobs (spin down, \downarrow):

Change the iso value to 0.03



Note that you now have two visualization lines: one is a calculated field that actually calculates the difference between the alpha and beta spin density. The other is a double isosurface that visualized the calculated field. You can use these calculated fields for many purposes. For example, by changing the '-' into a '+' you are visualizing the total density instead of the spin difference density.

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 freshman 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 people 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 ADFinput

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)

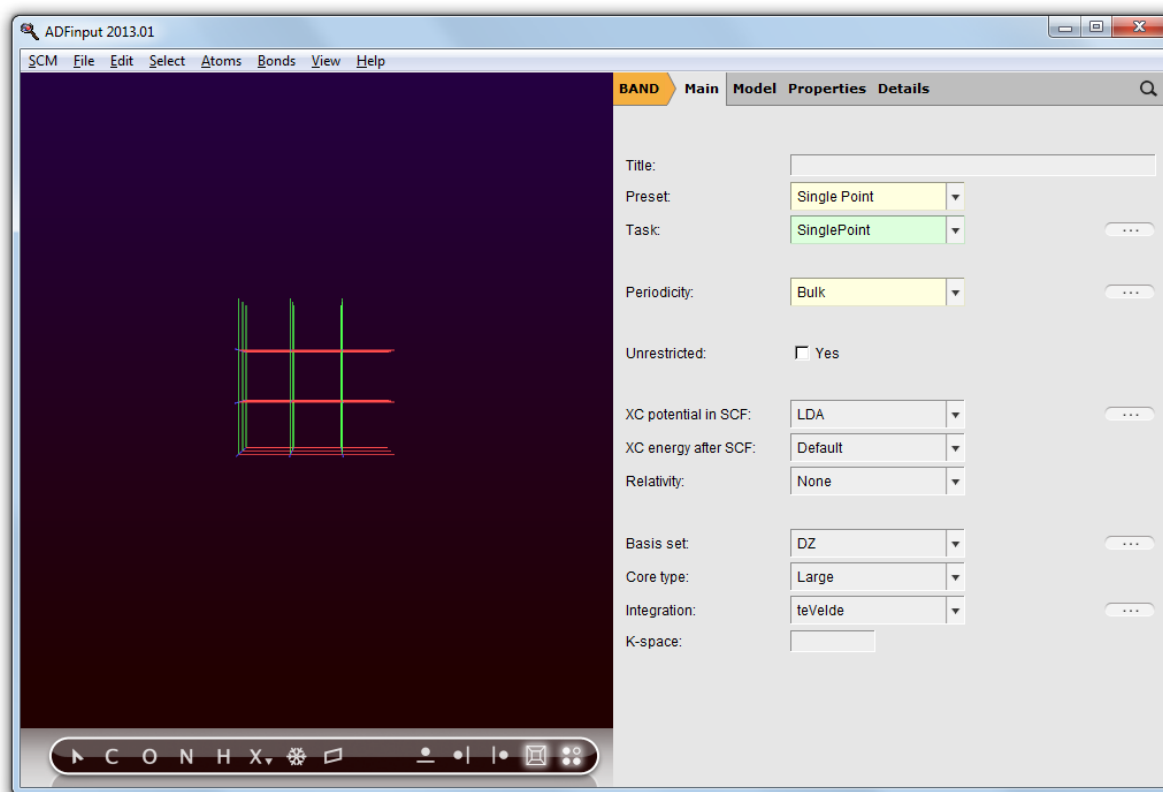
Rename the new directory by typing 'BandTutorial' and a Return

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** → **New Input** menu command

Switch to BAND mode (panel bar **ADF** → **BAND**)

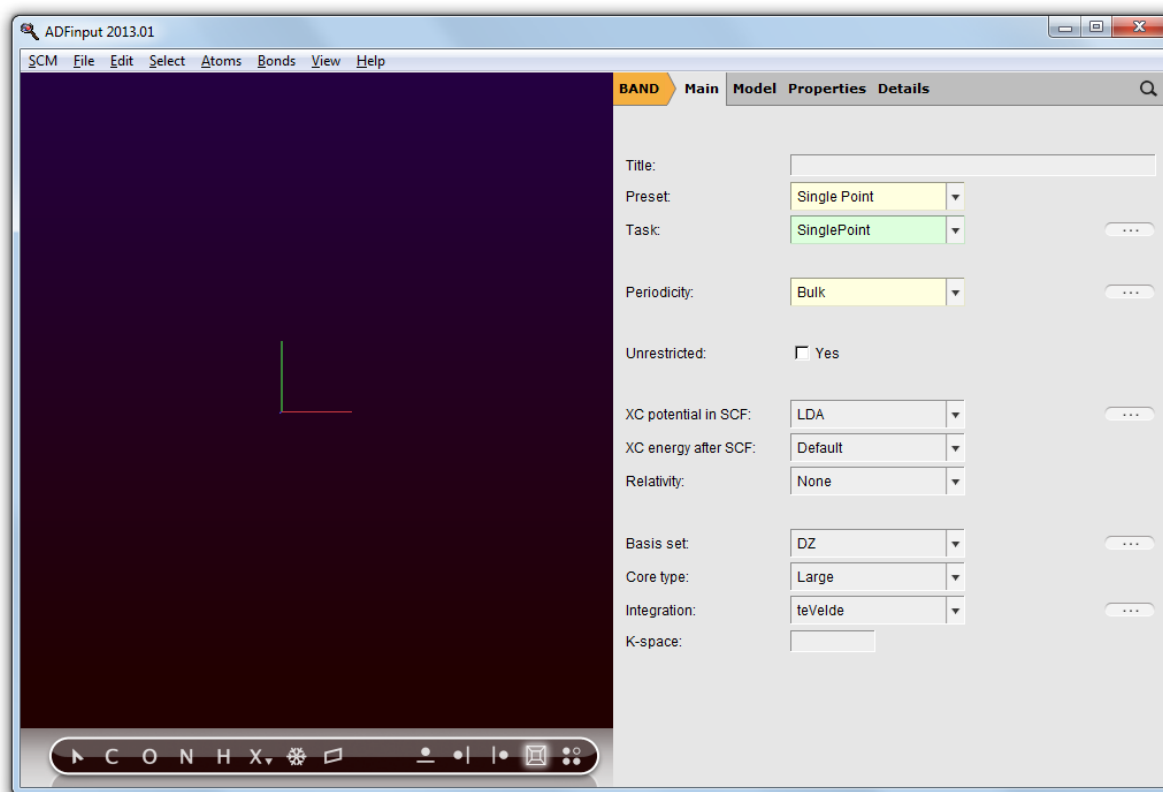


The BANDinput window consists of the following main parts:

- 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 ADFinput 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



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)

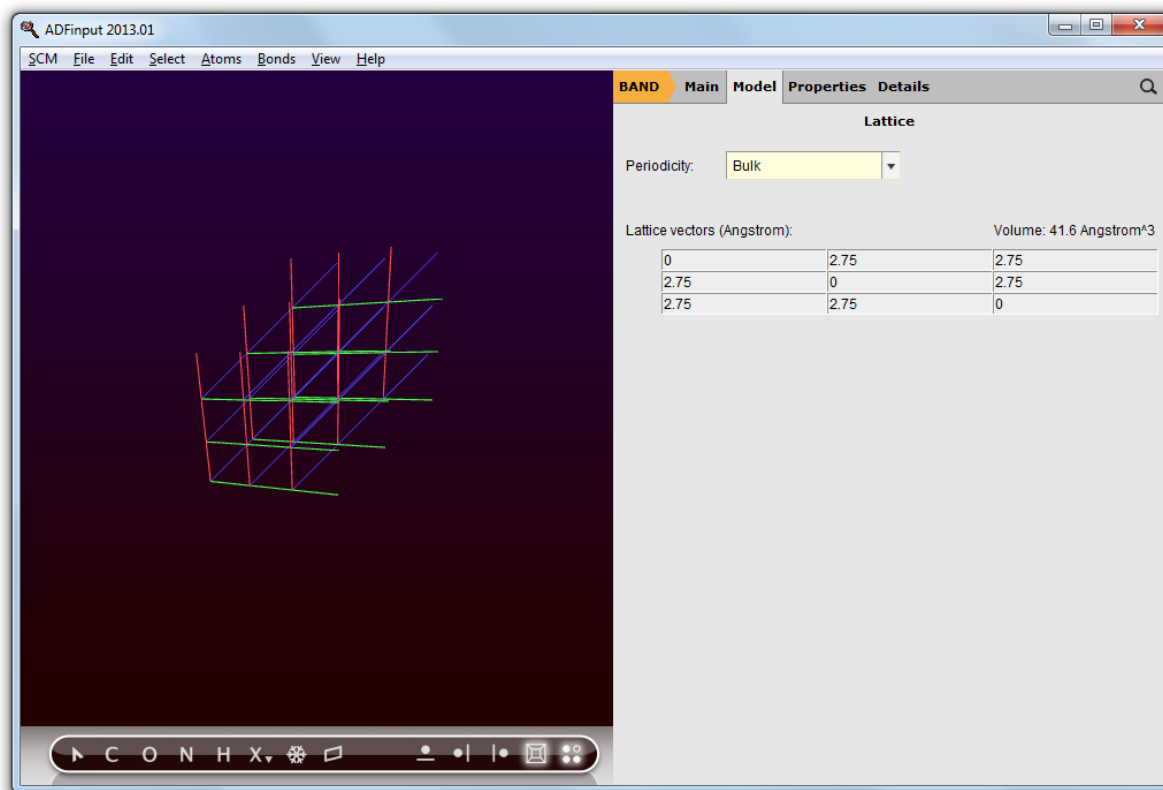
Now you should see the periodic repetitions again.

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



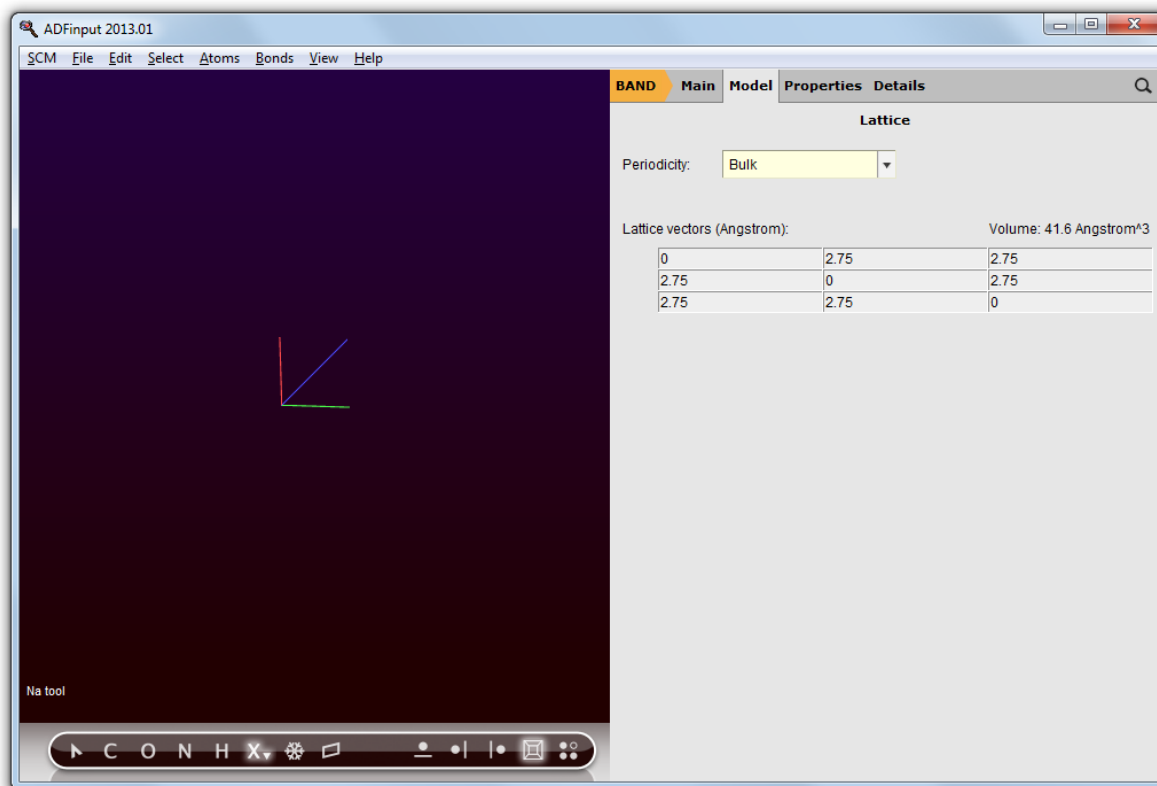
Step 3: Add the atoms

Now we will add the Na and Cl atoms. It is convenient to turn of the periodic display while doing this:

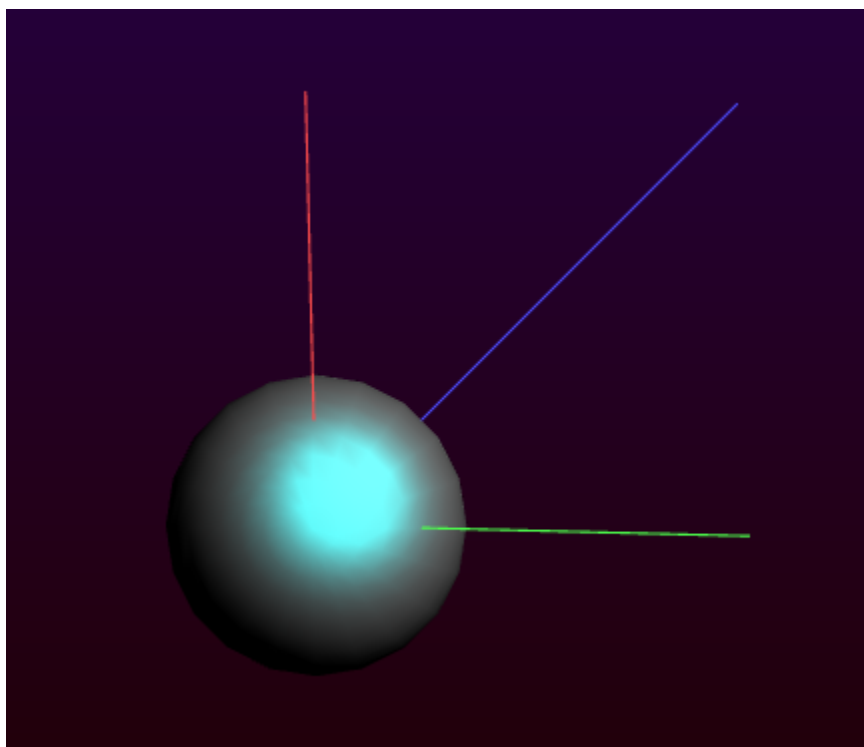
Uncheck **View** → **Periodic** → **Repeat Unit Cells**

Click on the X tool, and select Na

After this you see at the bottom of the screen "Na tool" in the status field:



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:

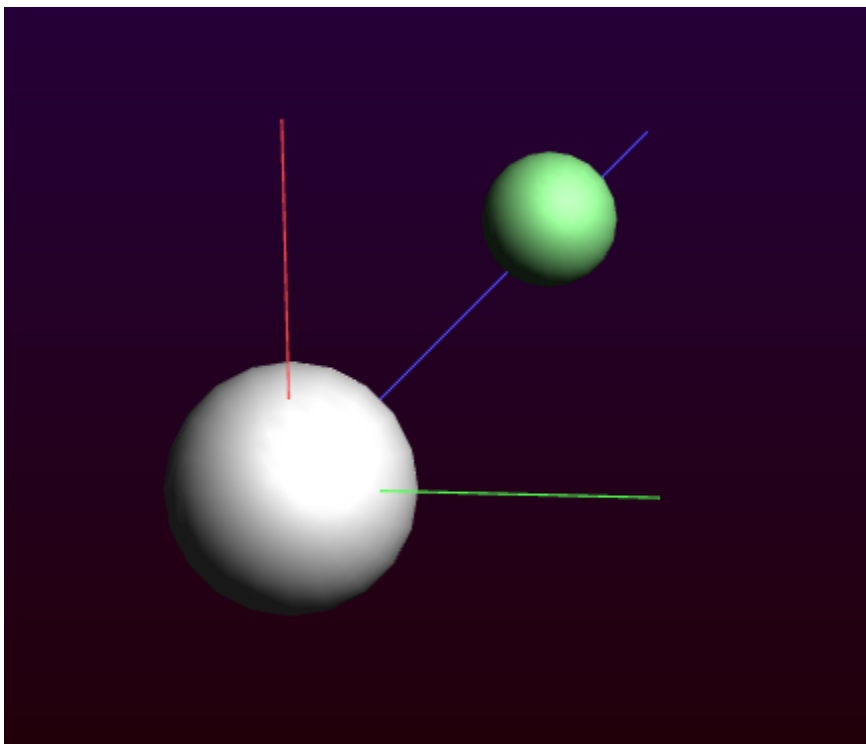
Edit → Set Origin

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



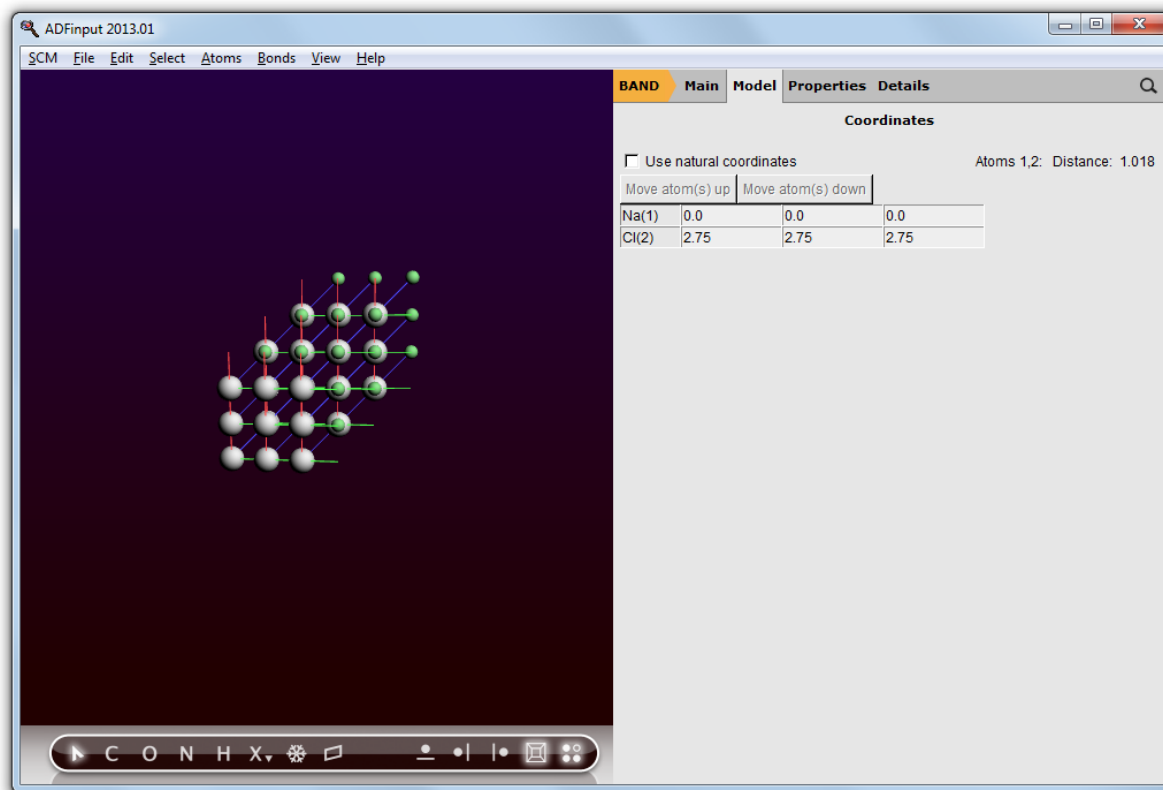
Next you should edit the Cl coordinates and change the Cl color:

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:



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**

The progress of the BAND calculation is visible in the ADFjobs window (a few lines of the 'logfile'). (the 'logfile'). After a few minutes the calculation has finished, and it looks like:

```

ADFTail: NaCl.logfile
SCM File Edit Help
<Mar26-2013> <17:07:52> -
<Mar26-2013> <17:07:52> cyc= 3 err=2.20E-02 meth=d nvec= 2 mix=0.2000 cpu= 0s fit=3.06E-04
<Mar26-2013> <17:07:52> cyc= 4 err=1.78E-02 meth=d nvec= 2 mix=0.2000 cpu= 0s fit=5.43E-04
<Mar26-2013> <17:07:52> cyc= 5 err=1.94E-03 meth=d nvec= 3 mix=0.2000 cpu= 0s fit=5.47E-04
<Mar26-2013> <17:07:52> HALFWAY
<Mar26-2013> <17:07:52> cyc= 6 err=2.17E-04 meth=d nvec= 3 mix=0.2000 cpu= 0s fit=5.50E-04
<Mar26-2013> <17:07:52> cyc= 7 err=1.46E-04 meth=d nvec= 3 mix=0.2000 cpu= 0s fit=5.58E-04
<Mar26-2013> <17:07:52> cyc= 8 err=4.61E-05 meth=d nvec= 3 mix=0.2000 cpu= 0s fit=5.59E-04
<Mar26-2013> <17:07:52> cyc= 9 err=3.70E-05 meth=d nvec= 3 mix=0.2000 cpu= 0s fit=5.59E-04
<Mar26-2013> <17:07:52> cyc= 10 err=2.43E-06 meth=d nvec= 3 mix=0.2000 cpu= 0s fit=5.59E-04
<Mar26-2013> <17:07:52> cyc= 11 err=1.31E-06 meth=d nvec= 3 mix=0.2000 cpu= 0s fit=5.59E-04
<Mar26-2013> <17:07:52> SCF CONVERGENCE
<Mar26-2013> <17:07:52> cyc= 12 err=3.24E-07 meth=d nvec= 3 mix=0.2000 cpu= 0s fit=5.59E-04
<Mar26-2013> <17:07:53> cyc= 13 err=3.24E-07 meth=d nvec= 1 mix=1.0000 cpu= 0s fit=5.59E-04
<Mar26-2013> <17:07:53>
<Mar26-2013> <17:07:53> Max. cycle time CP: 0.156
<Mar26-2013> <17:07:53> IO: 0.016
<Mar26-2013> <17:07:53>
<Mar26-2013> <17:07:53> Mean cycle time CP: 0.087
<Mar26-2013> <17:07:53> IO: 0.003
<Mar26-2013> <17:07:53> EL: 0.140
<Mar26-2013> <17:07:53>
<Mar26-2013> <17:07:53> final mix.par. 0.075
<Mar26-2013> <17:07:53> Approx. conv.rate: 0.000
<Mar26-2013> <17:07:53>
<Mar26-2013> <17:07:53> FERMI ENERGY: -0.4267 A.U.
<Mar26-2013> <17:07:53> -11.6117 E.V
<Mar26-2013> <17:07:53> >>>> ENERGY
<Mar26-2013> <17:07:53> ENERGY OF FORMATION: -0.2635 A.U.
<Mar26-2013> <17:07:53> -7.1707 E.V.
<Mar26-2013> <17:07:53> -165.3593 KCAL/MOL
<Mar26-2013> <17:07:53> >>>> CHARGE
<Mar26-2013> <17:07:53> >>>> HIRSH
<Mar26-2013> <17:07:53> >>>> DOS
<Mar26-2013> <17:07:53> New DOS!!!
<Mar26-2013> <17:07:53> storing all partial DOS
<Mar26-2013> <17:07:53> integrate over delta E
<Mar26-2013> <17:07:53> >>>> BZSTRUCT
<Mar26-2013> <17:07:53> NOT ALL FILES CLOSED
<Mar26-2013> <17:07:53> NORMAL TERMINATION
<Mar26-2013> <17:07:53> END
Job NaCl has finished

```

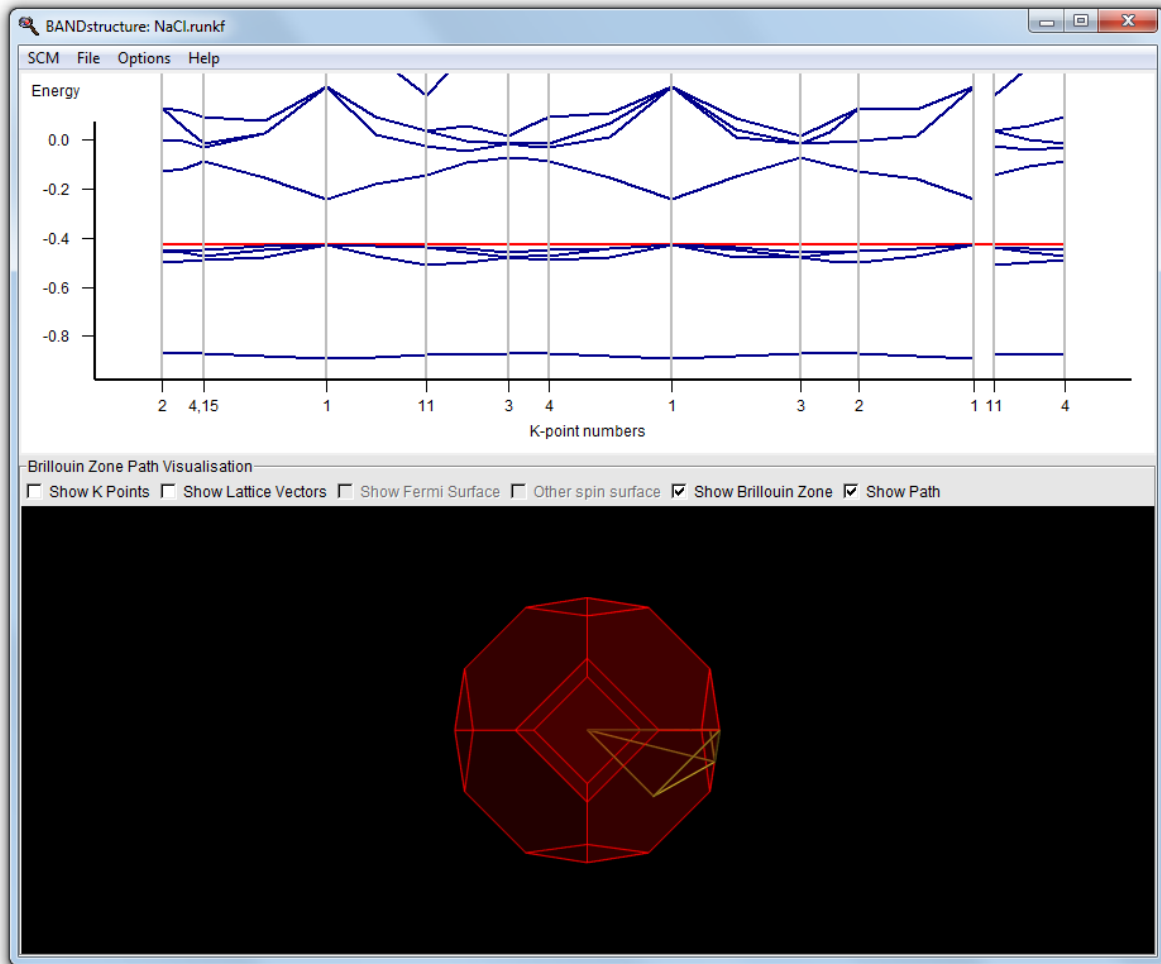
Wait for the text 'Job NaCl has finished'

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

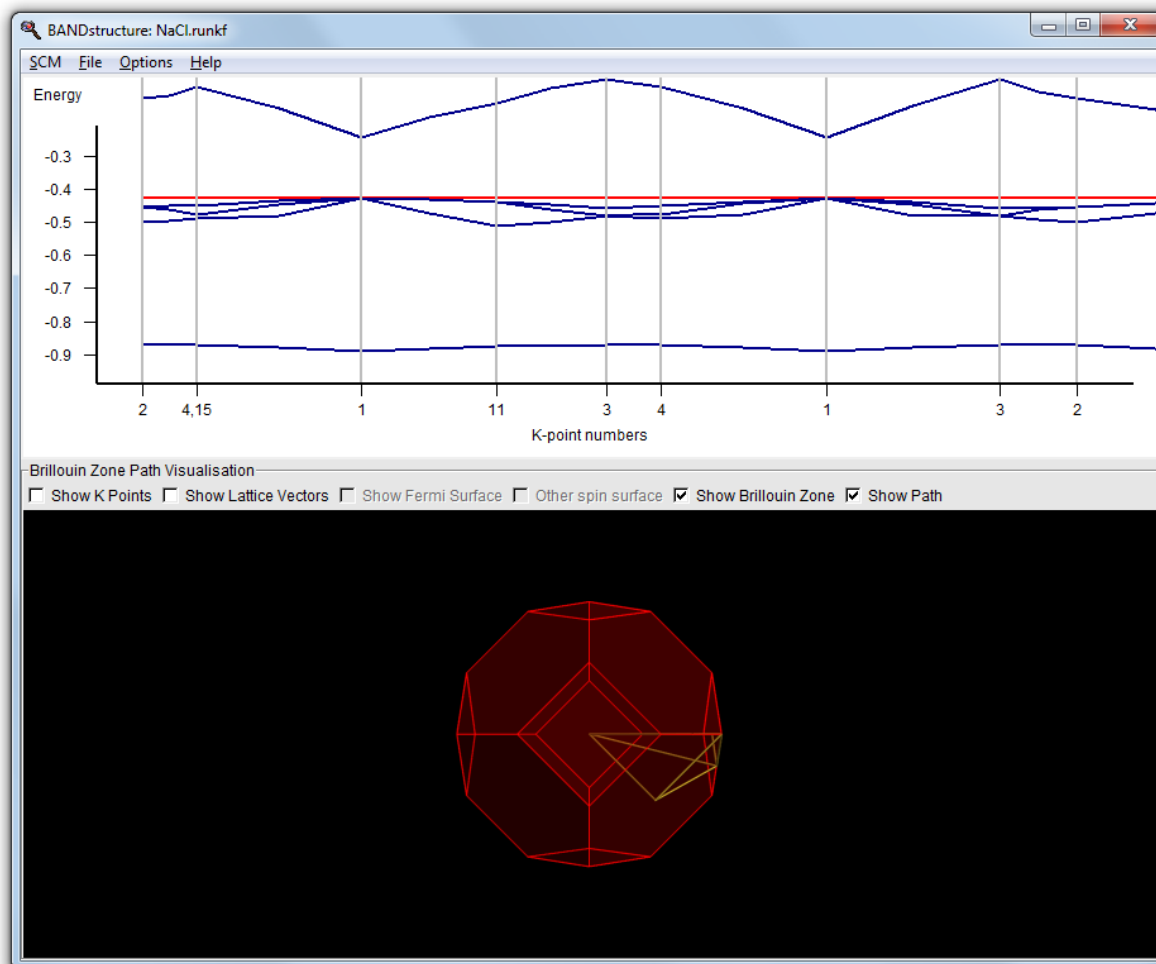
This will open the bandstructure window:



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)

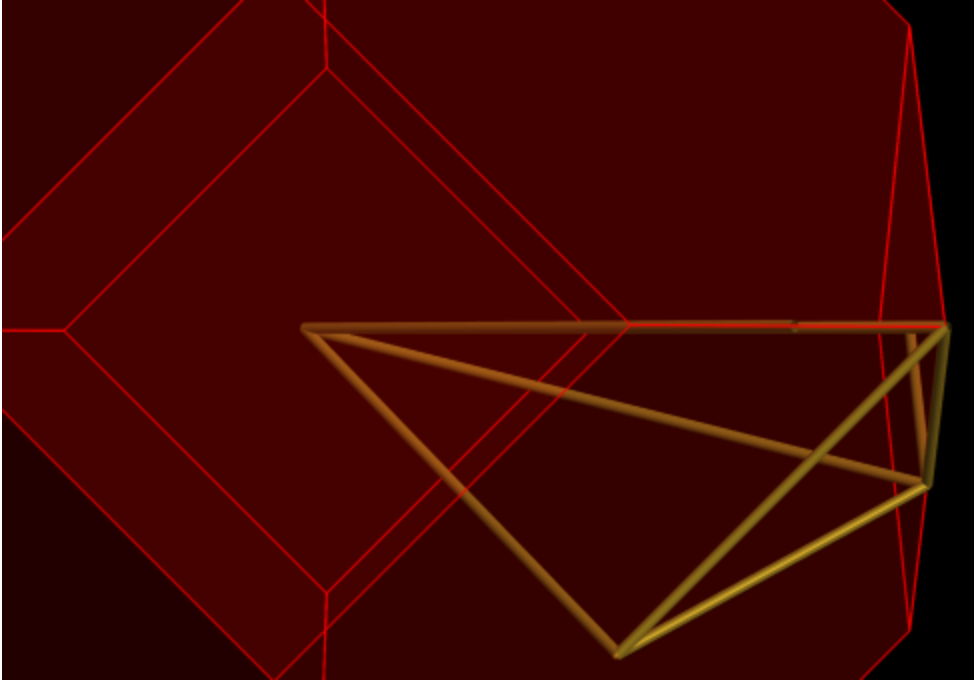
The bottom part of the plot will look like:



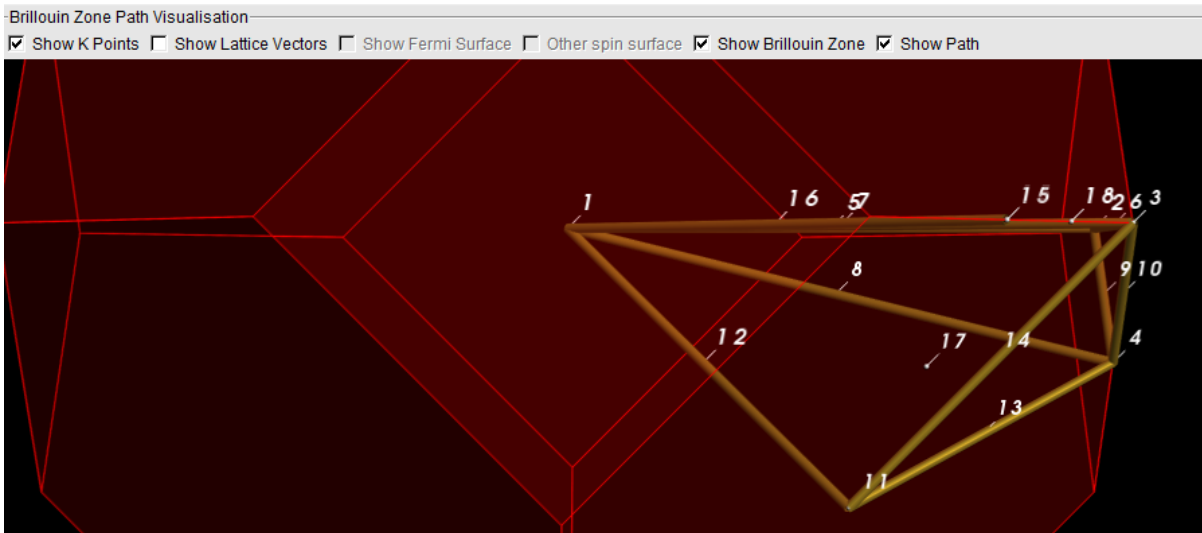
In most k-points you see now four bands below the Fermi level. In some k-points you see fewer because they are degenerate.

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.

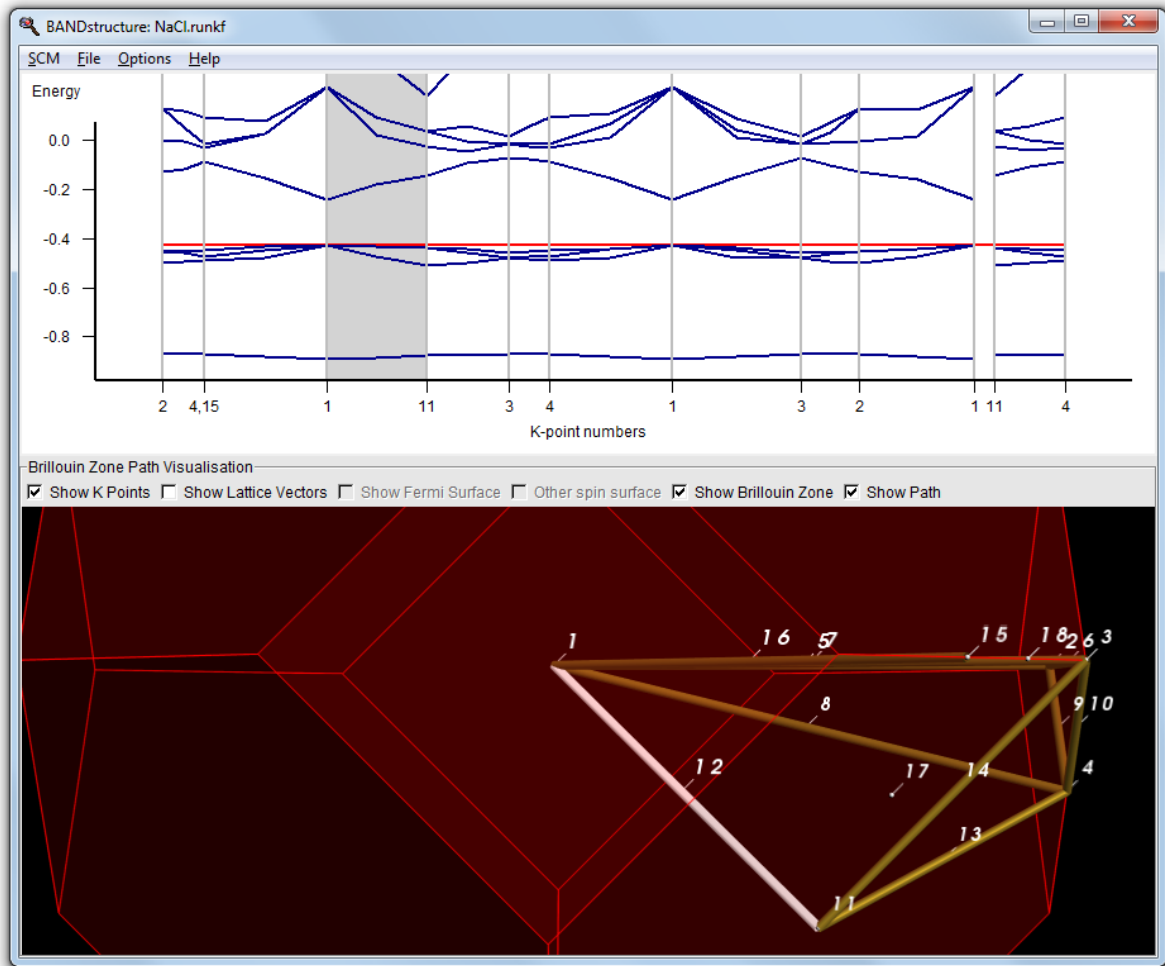
Zoom in a bit, by using the scroll wheel on your mouse or pressing the Middle button and moving upwards



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

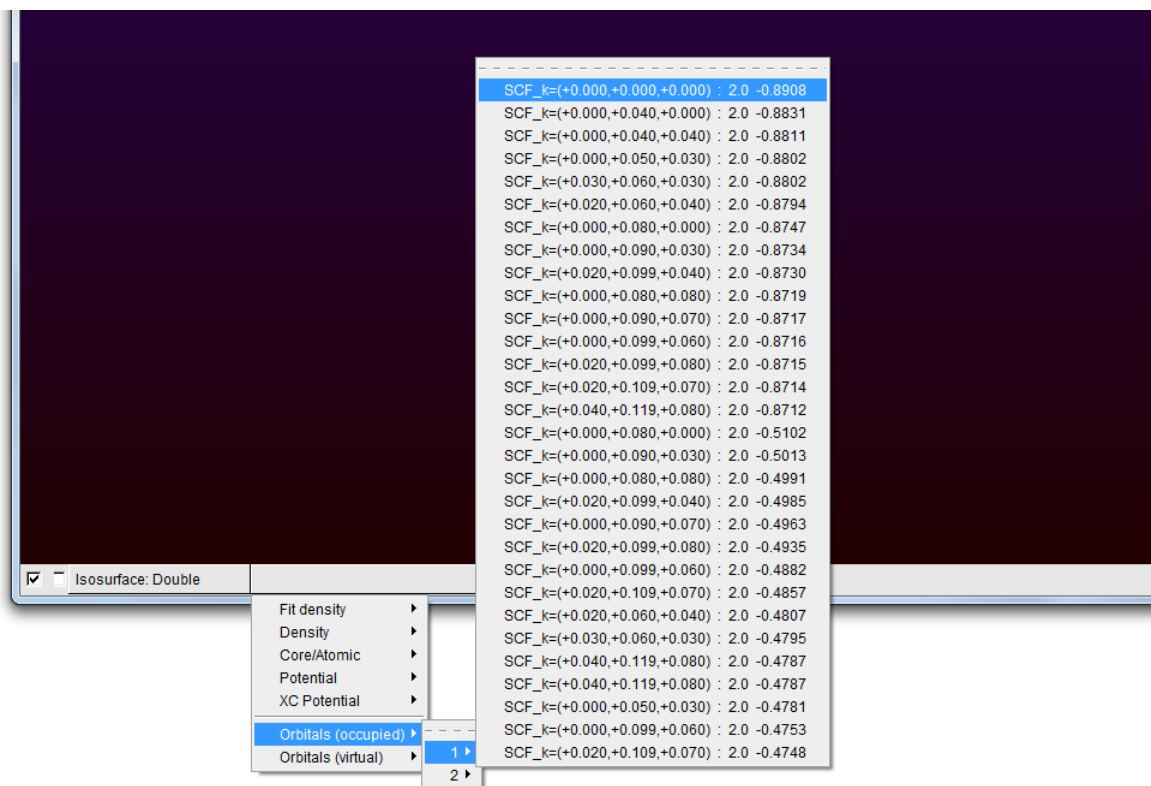
Now what is the character of the bands? Let us first examine this narrow band at about -0.5 Hartree.

SCM → View

In ADFview: **Add** → **Isosurface Double (+/-)**

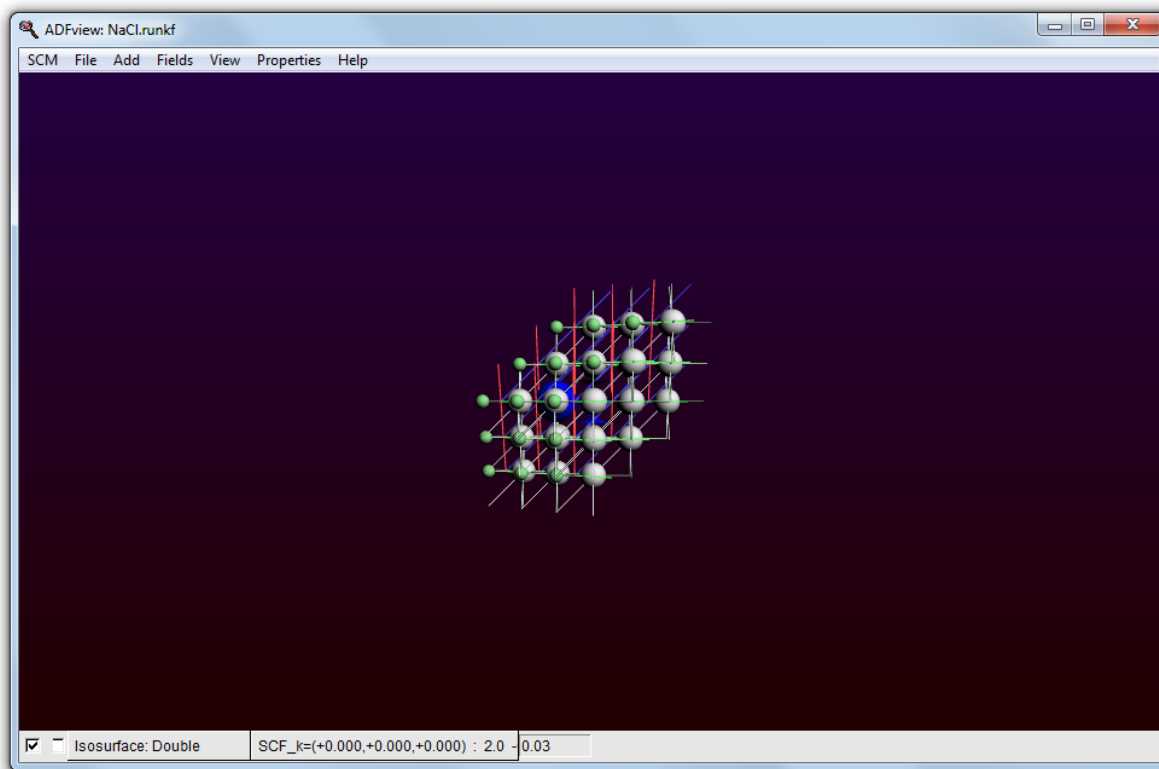
In the bar at the bottom of the window, you can select which field to show.

Select the lowest band ($k=0,0,0$)



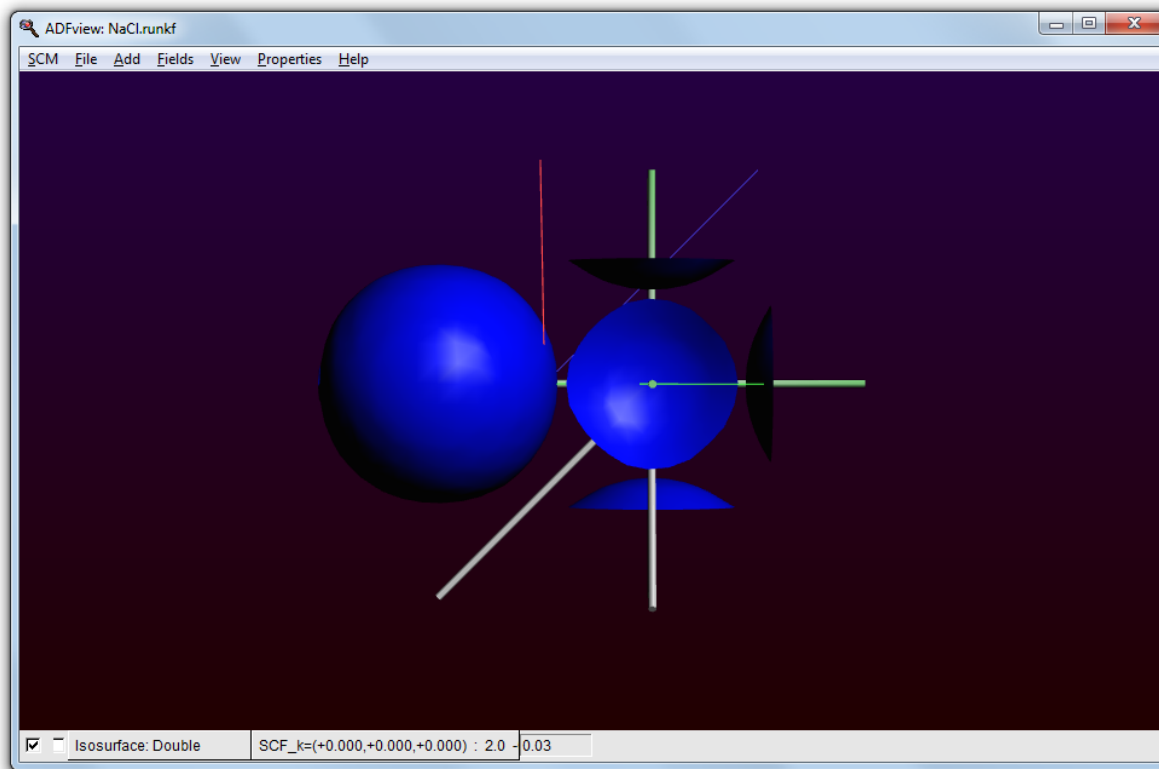
From the label you can see that it has an energy of -0.8908 and the coordinates are (0,0,0).

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**)



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):

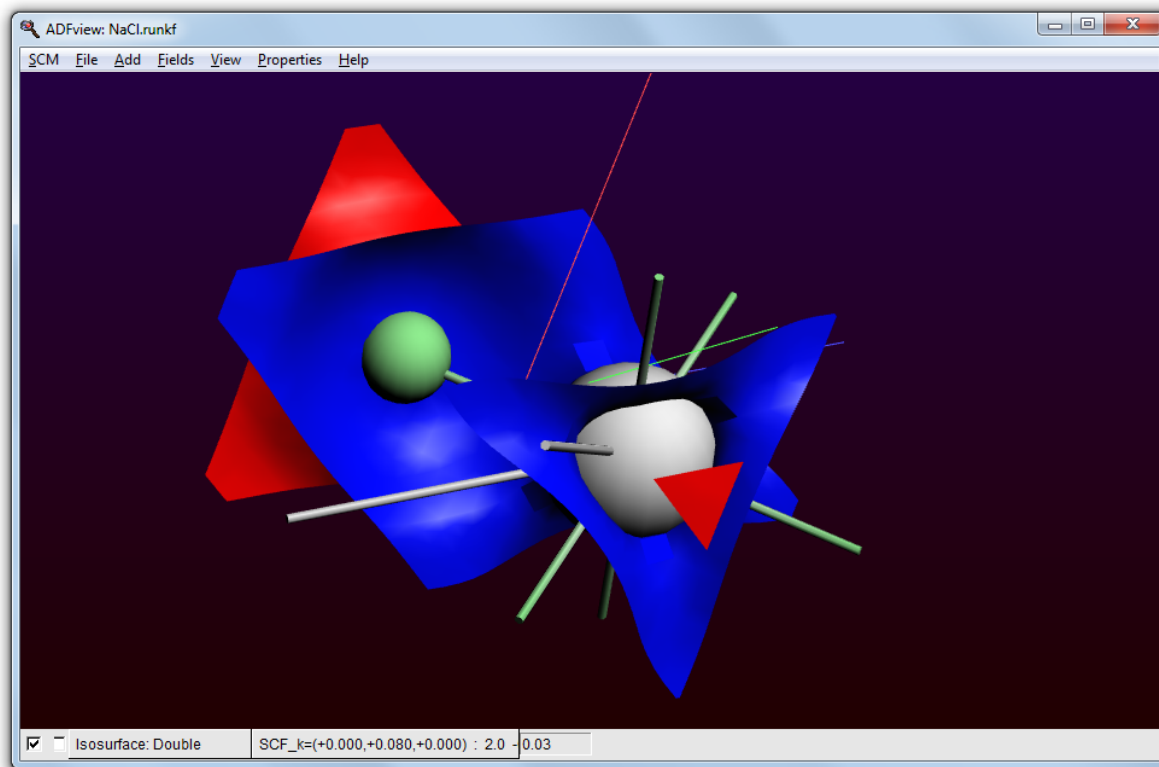
Select the lowest orbital of the second band (with energy about -0.5)

SCF_k=(+0.040,+0.119,+0.080) : 2.0 -0.8712

SCF_k=(+0.000,+0.080,+0.000) : 2.0 -0.5102

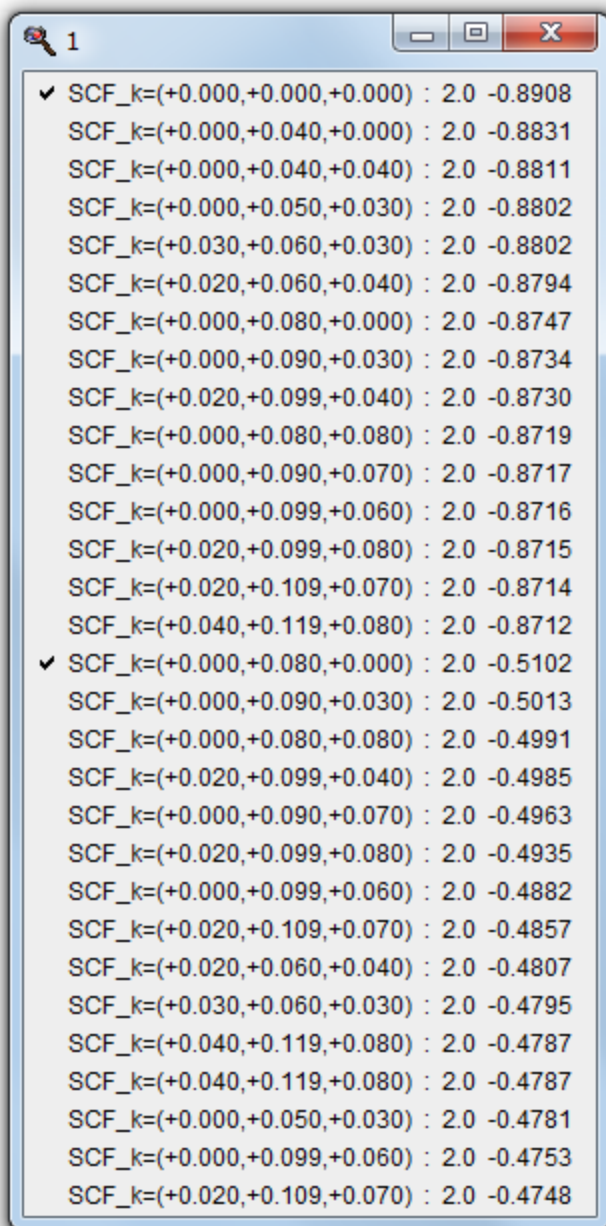
SCF_k=(+0.000,+0.090,+0.030) : 2.0 -0.5013

This orbital looks like:

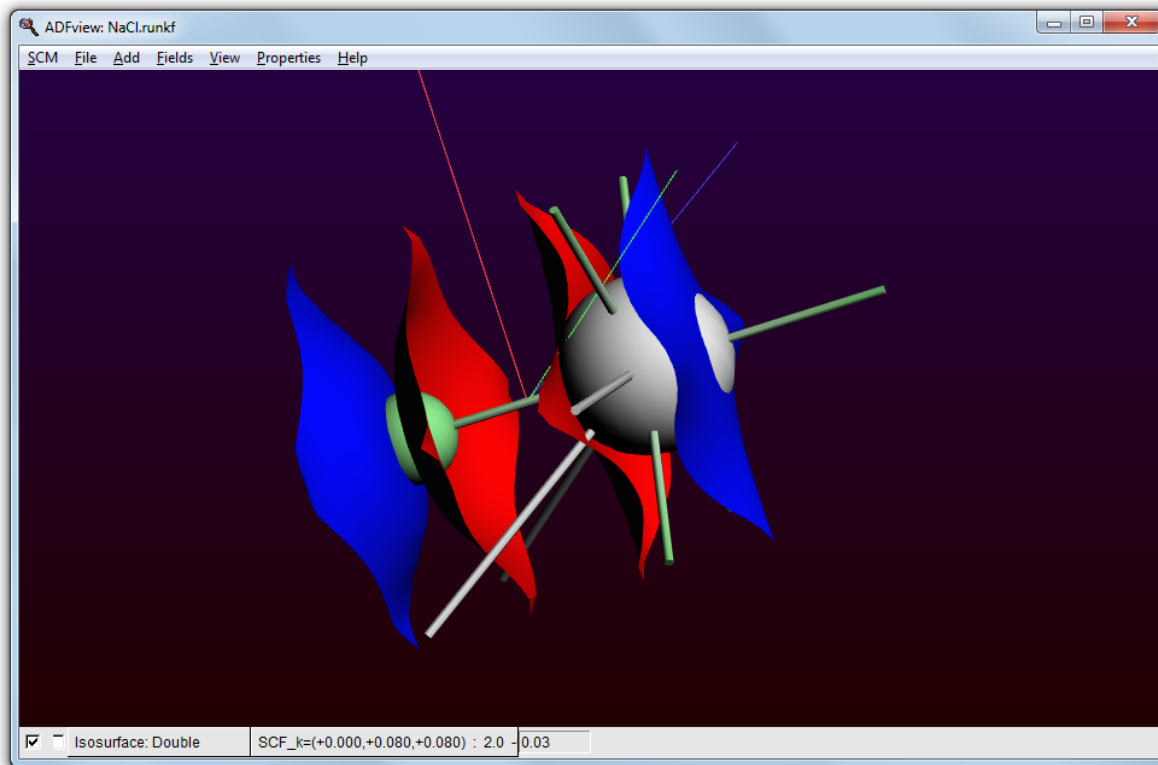


and it clearly consists of a p orbital on the Cl. The part near the Na comes from Chlorine atoms in neighboring cells.

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:



Tear off the 'Occupied orbital menu, group 1
Select the first orbital around $e=-0.49$



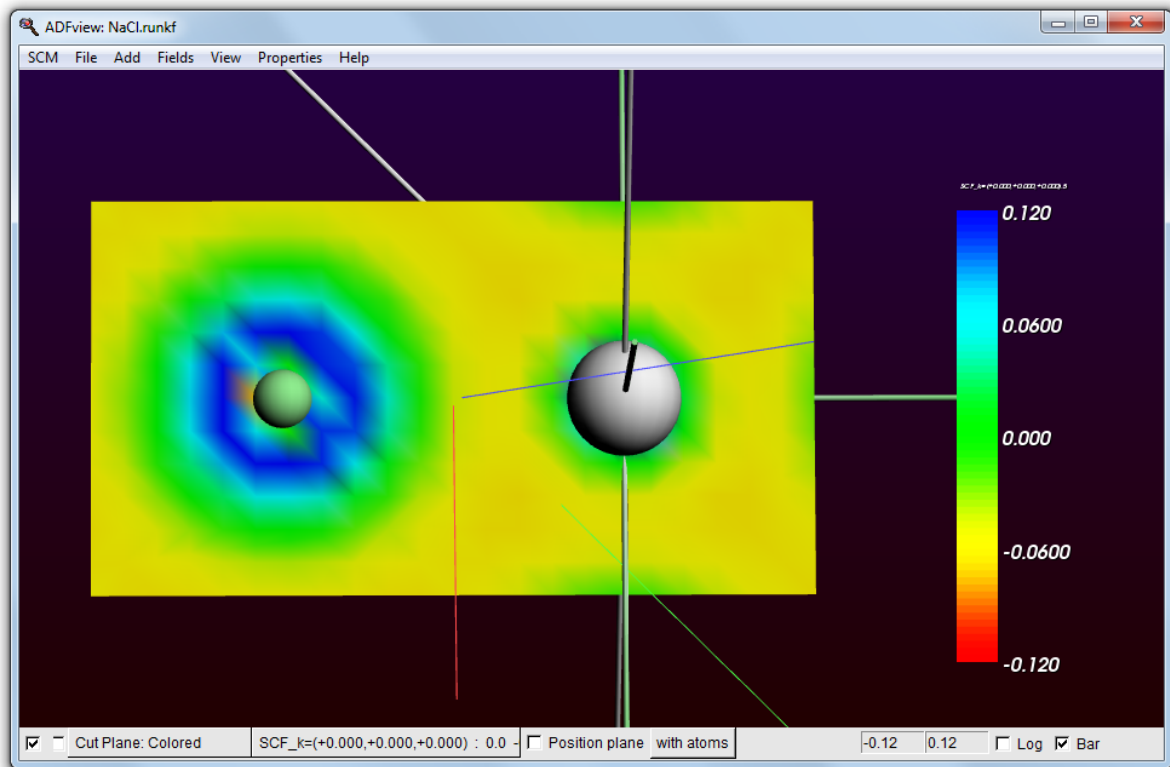
Take a look at all three of them.

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.

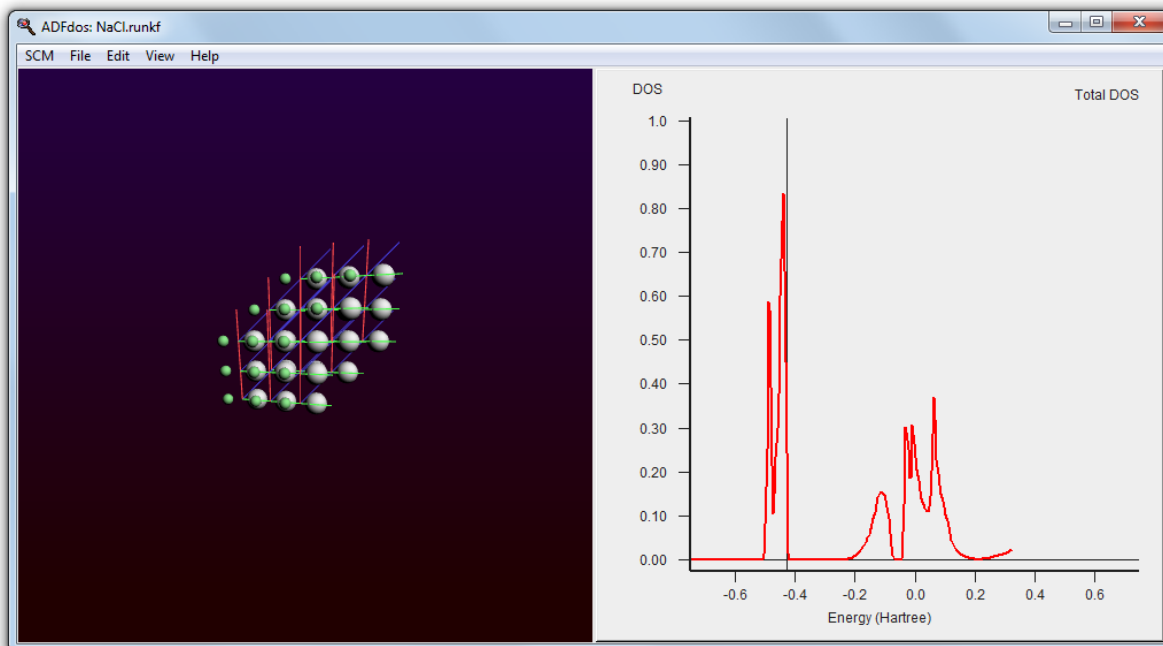
At the end of this step, we will demonstrate how to create such a plot.

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:

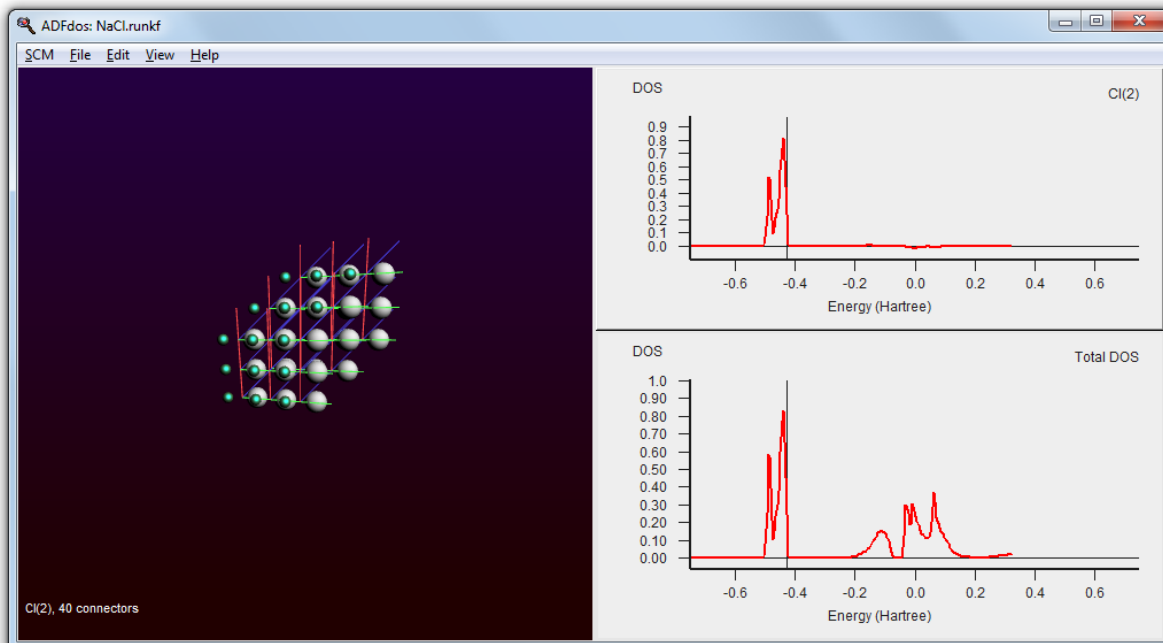


The Fermi energy is around -0.43, and there is clearly a gap. Just below it there is a valence band, and at -0.2 Hartree starts the conduction band.

Select the **View** → **Add Graph** command

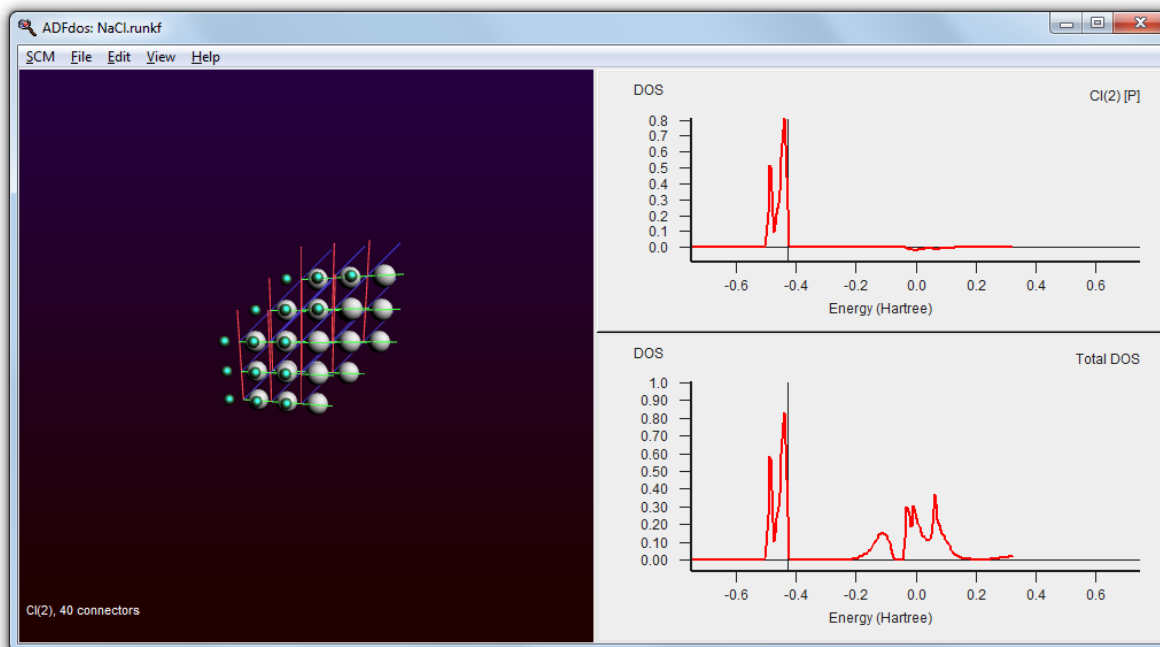
(Now you see two plots of the total DOS)

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

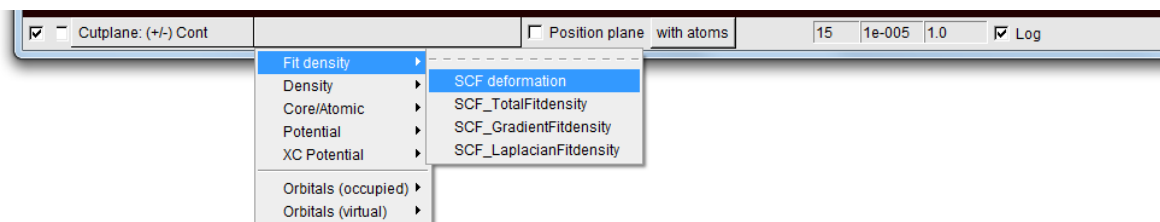
Intuitively you might expect that the charge of Na should be +1 and from the Cl -1. This can be best seen by making a cut plane:

Go to ADFview (**SCM** → **View**)

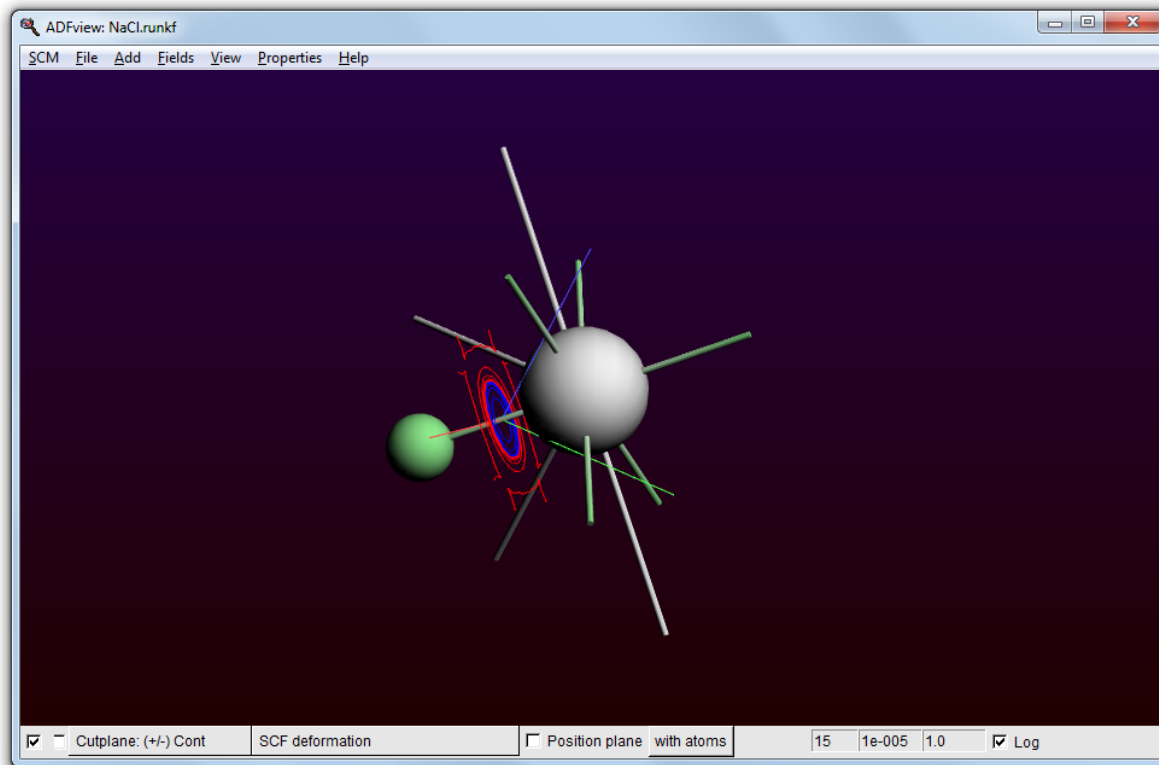
Delete the double isosurface with the 'Isosurface: Double' pull-down menu in the bar on the bottom and select 'Delete'

Add → **Cut Plane: Contours (+/-)**

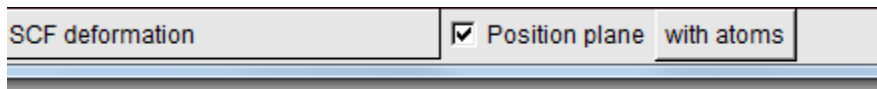
Select the deformation density in the fields menu (in the Fit density sub-menu)



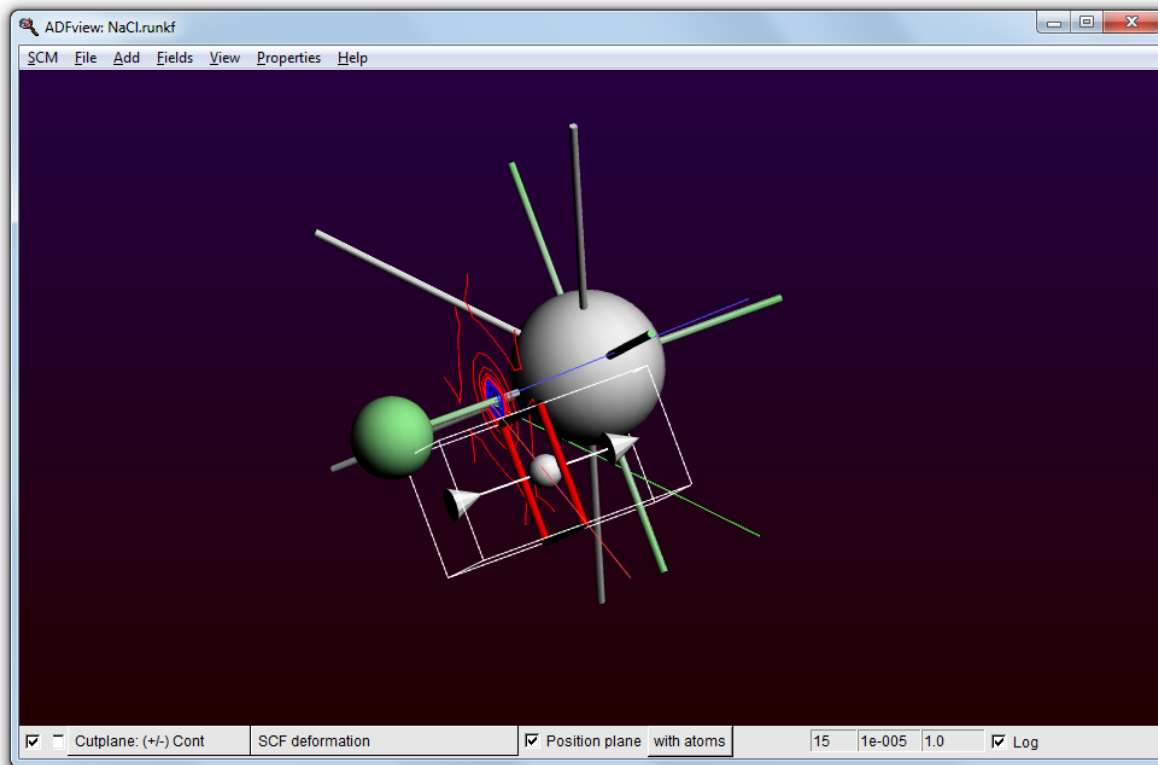
The result is a bit disappointing, because the plane is perpendicular to the atoms



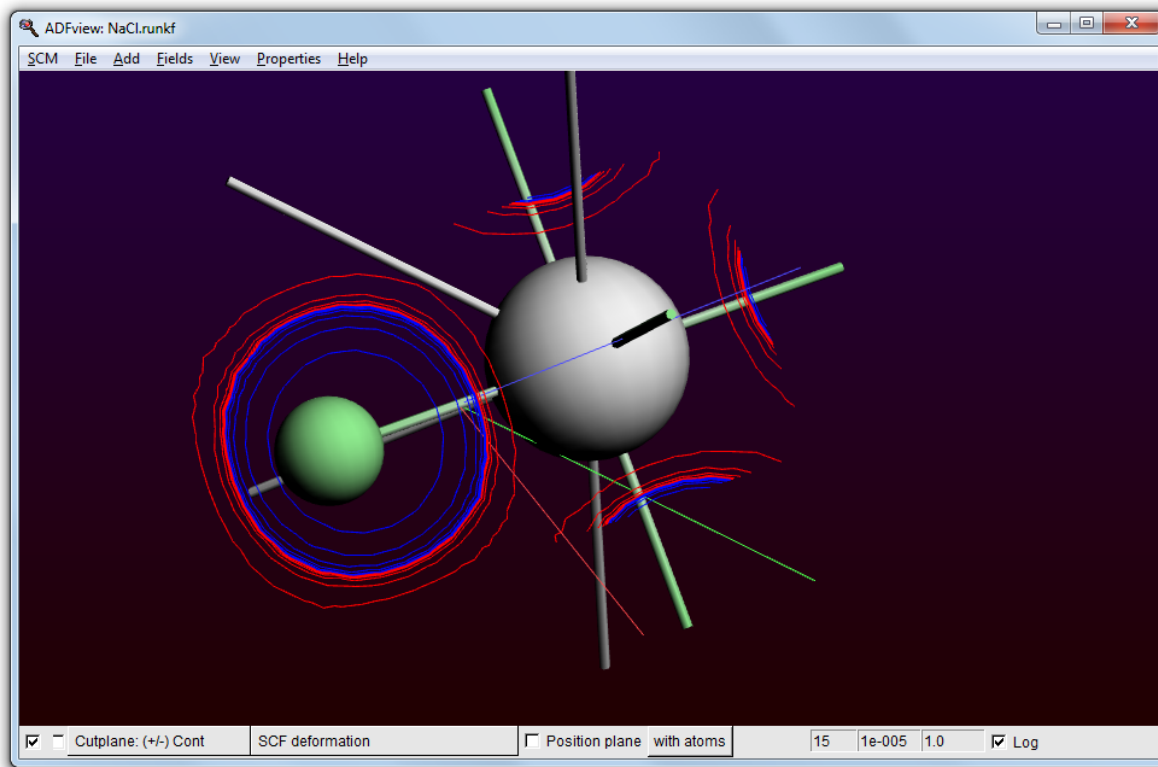
To get it right enable at the bottom the "Position plane" toggle:



You will now see a white frame. Drag it to the right until you see an arrow in it



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?

Creating the density contour plot

Delete the cutplane 'Cutplane: (+/-) Cont'

pull-down menu in the bar on the bottom and select 'Delete'

Add → Cut Plane: colored

Select the unoccupied orbital with the lowest energy, around -0.2413

Uncheck 'log'

Check 'bar'

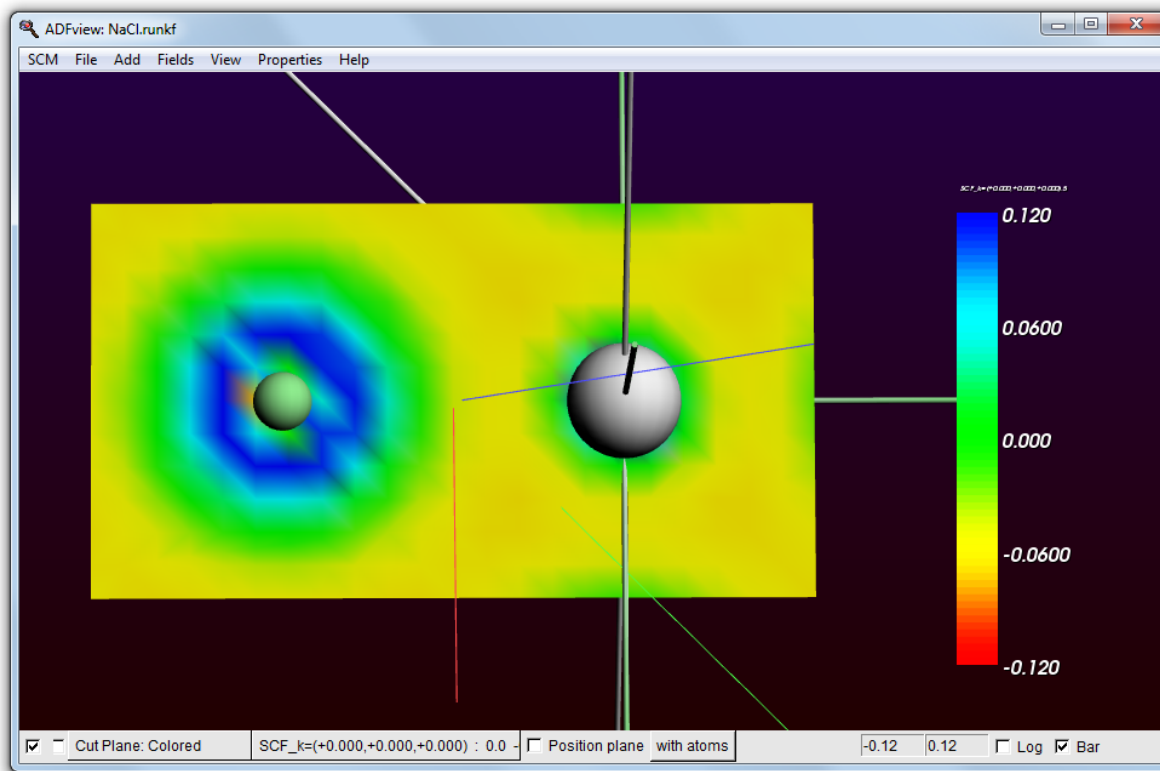
As the plane is perpendicular to the atoms, you need to reposition it.

click the "Position plane" toggle

position the plane through the atoms

turn of the "Position plane" toggle

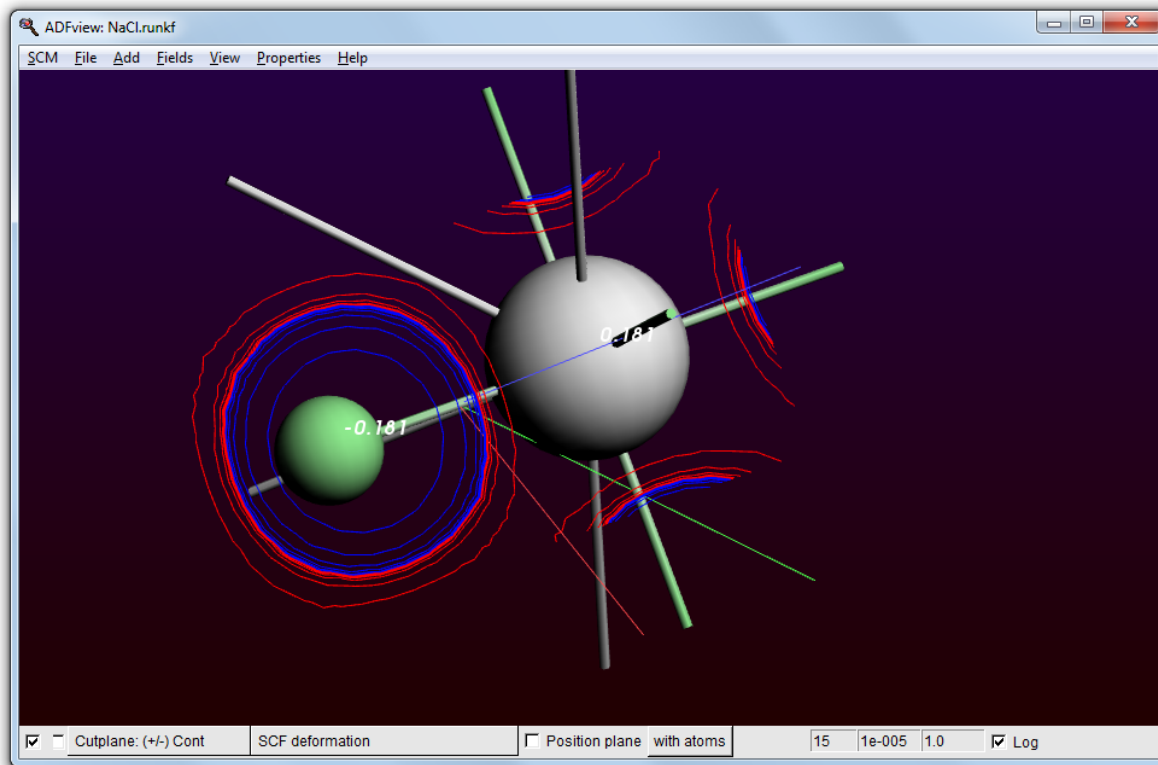
You should now have a picture that looks a lot like this:



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.

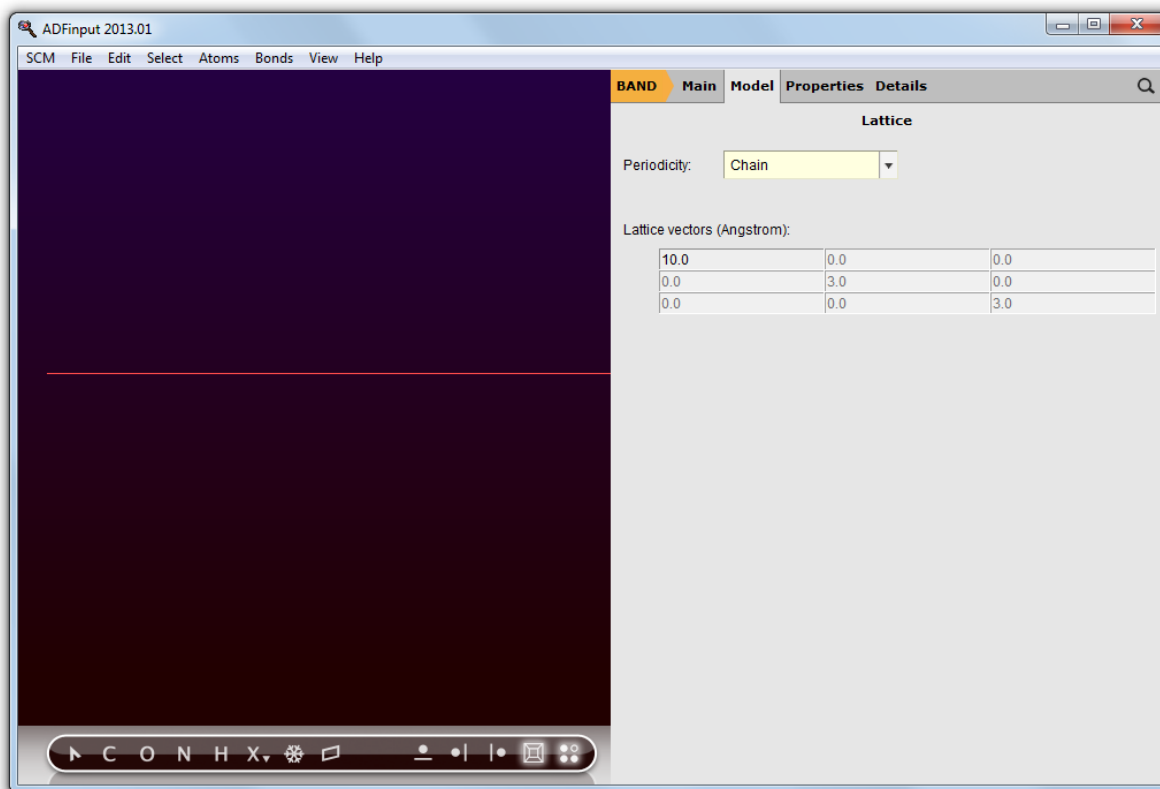
Step 1: Create the H3 toy system

We are going to enter the geometry manually, just as in the first tutorial.

```
Start ADFinput
Switch to BAND mode (panel bar ADF → BAND)
Set periodicity to Chain
```

Panel bar **Model** → **Lattice**

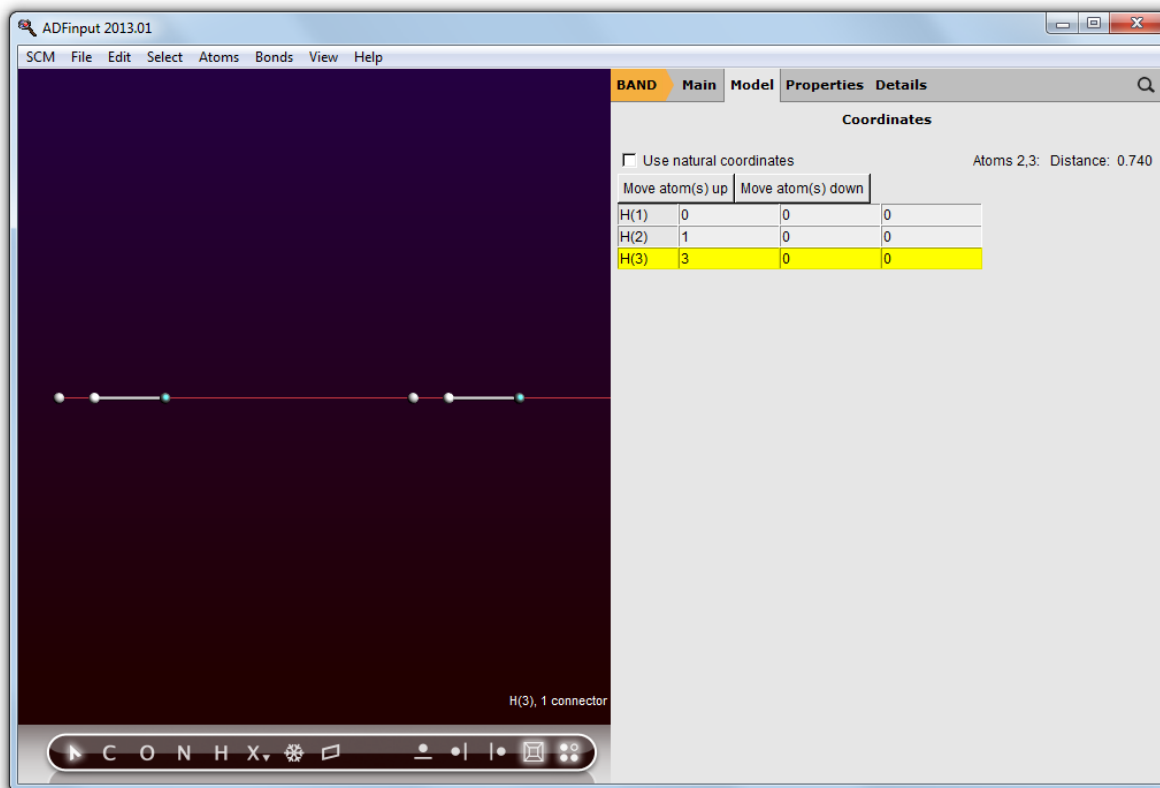
Set the lattice constant to 10.0



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

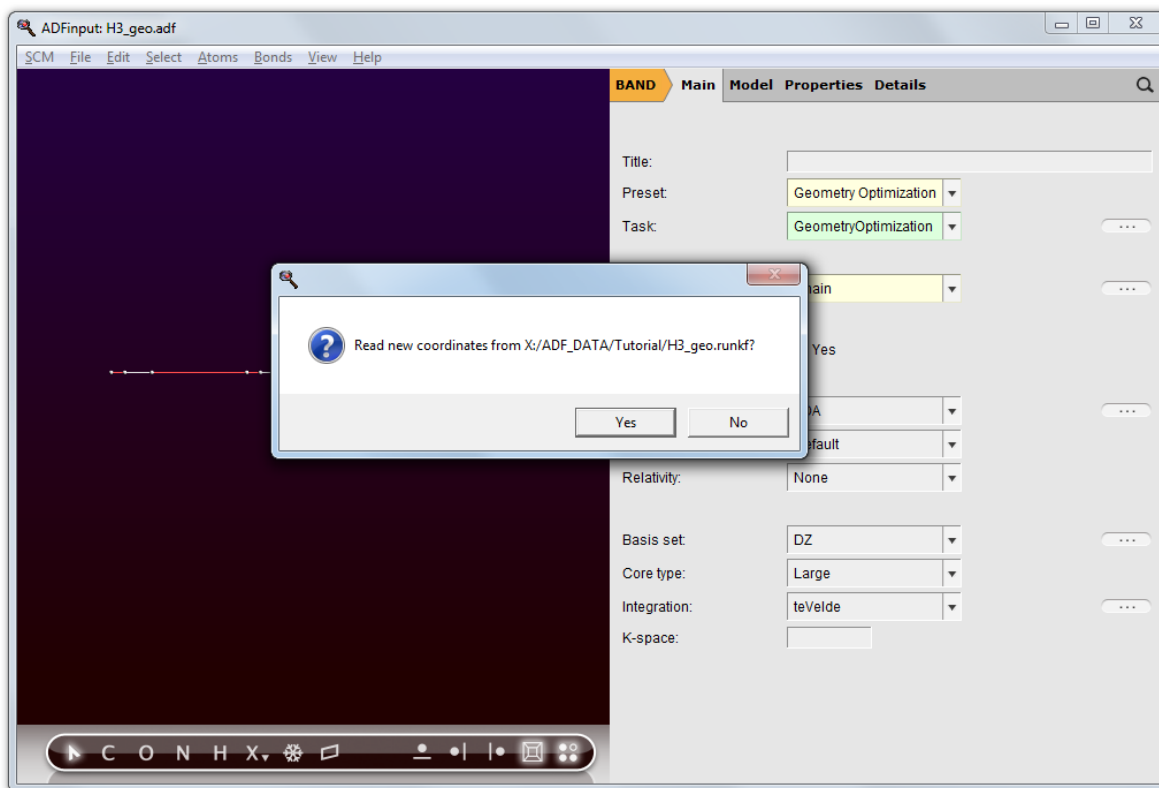


You have now created the cylinder symmetric toy system.

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

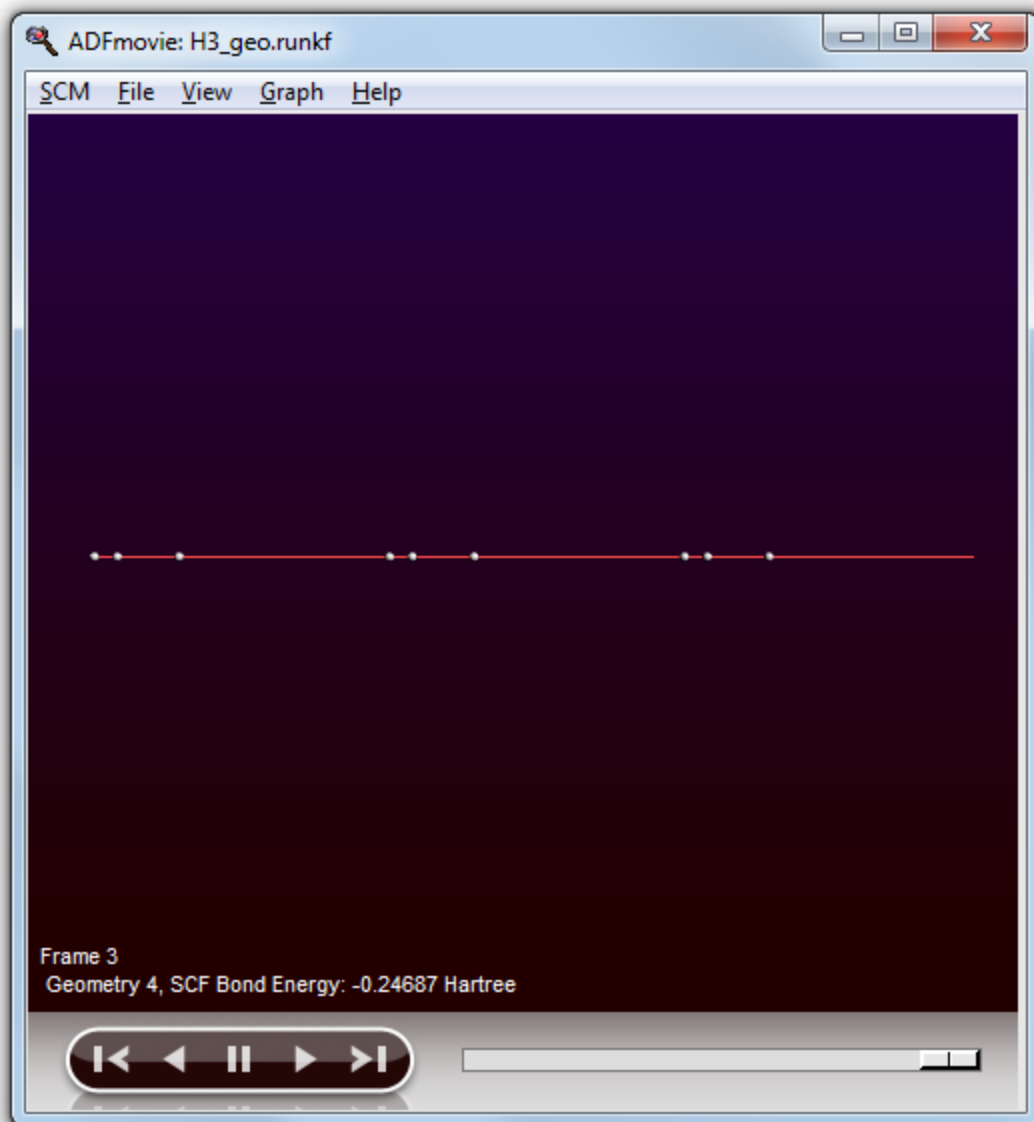


Answer 'Yes'

Now let us look at the progress as a movie.

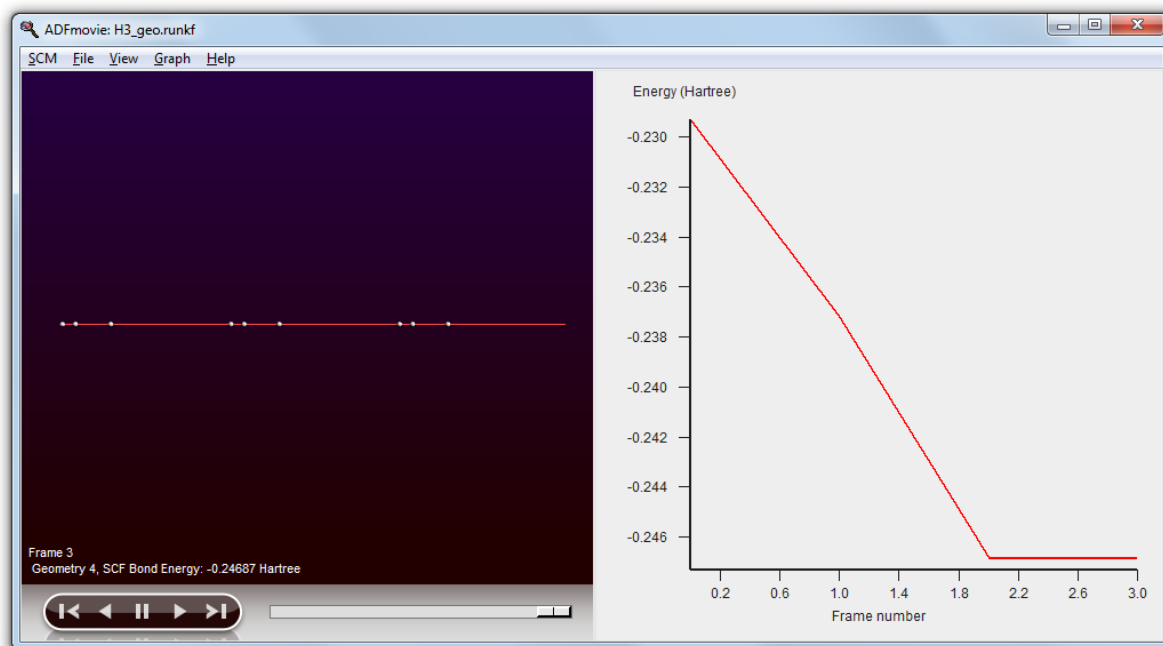
SCM → Movie

A small movie pops up ending like this



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

```

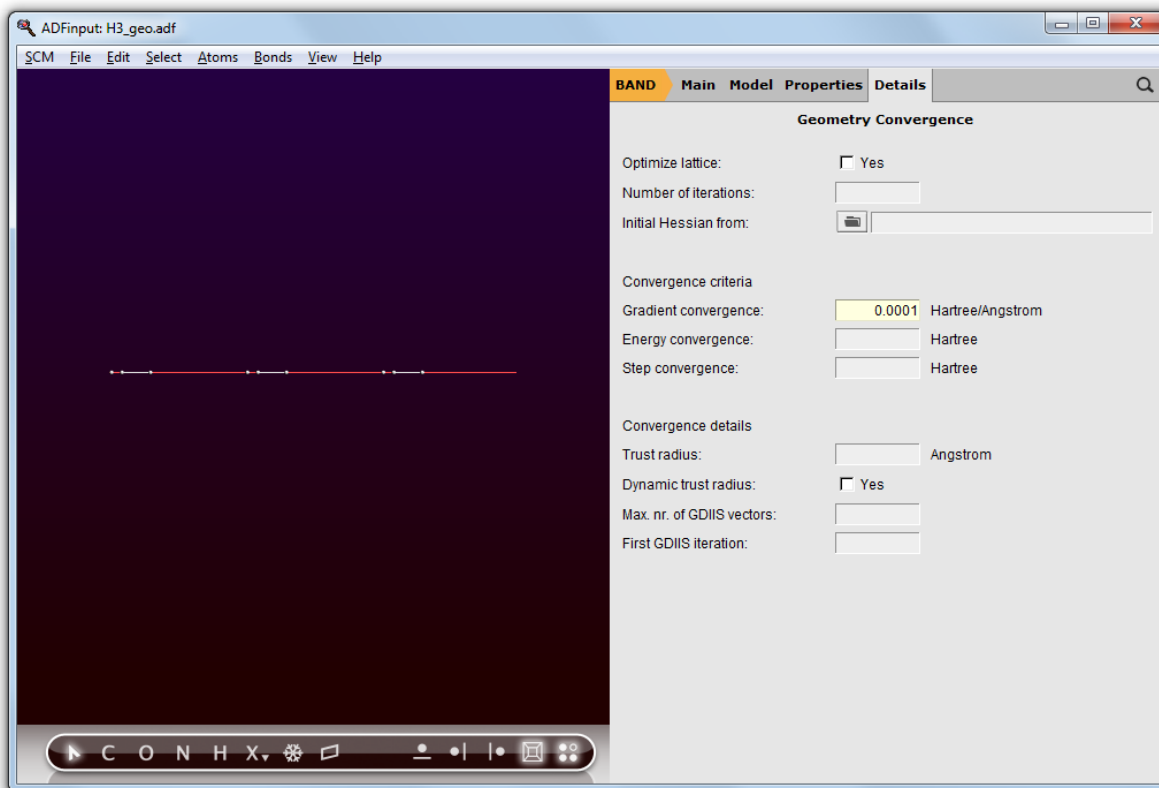
ADFTail: H3_geo.logfile
SCM File Edit Help
<Mar30-2013> <18:20:21> current energy -0.24600433 hartree
<Mar30-2013> <18:26:21> energy change -0.00002980 0.00100000 T
<Mar30-2013> <18:26:21> constrained gradient max 0.00833958 0.01889726 T
<Mar30-2013> <18:26:21> constrained gradient rms 0.00352755 0.01259817 T
<Mar30-2013> <18:26:21> gradient max 0.00833958
<Mar30-2013> <18:26:21> gradient rms 0.00352755
<Mar30-2013> <18:26:21> cart. step max 0.00229381 0.01587532 T
<Mar30-2013> <18:26:21> cart. step rms 0.00094981 0.01058354 T
<Mar30-2013> <18:26:21> Geometry Converged
<Mar30-2013> <18:26:21> final calculation
<Mar30-2013> <18:26:21> >>>> RADIAL
<Mar30-2013> <18:26:21> making explicit operators for cylinder symmetry
<Mar30-2013> <18:26:21> >>>> POINTS
<Mar30-2013> <18:26:21> Acc.Num.Int.= 3.500
<Mar30-2013> <18:26:21> making explicit operators for cylinder symmetry
<Mar30-2013> <18:26:21> >>>> FITSYM
<Mar30-2013> <18:26:21> >>>> NUMGRD
<Mar30-2013> <18:26:21> >>>> VMULTI
<Mar30-2013> <18:26:21> >>>> ATMFNC
<Mar30-2013> <18:26:21> CalcAtomicProperties
<Mar30-2013> <18:26:21> >>>> PREPAREBAS
<Mar30-2013> <18:26:21> ----- K .. 3
<Mar30-2013> <18:26:21> >>>> PREPAREHAM
<Mar30-2013> <18:26:21> ----- K .. 3
<Mar30-2013> <18:26:21> >>>> PREPAREFIT
<Mar30-2013> <18:26:21> Dependent fit set
<Mar30-2013> <18:26:21> start of SCF loop
<Mar30-2013> <18:26:21> restarting scf
<Mar30-2013> <18:26:21> cyc= 0 err=2.75E-07
<Mar30-2013> <18:26:21> HALFWAY
<Mar30-2013> <18:26:21> cyc= 1 err=5.46E-08 meth=m nvec= 1 mix=0.0750 cpu= 0s fit=4.91E-04
<Mar30-2013> <18:26:21> SCF CONVERGENCE
<Mar30-2013> <18:26:22> cyc= 2 err=4.83E-08 meth=d nvec= 2 mix=0.2000 cpu= 0s fit=4.91E-04
<Mar30-2013> <18:26:22> cyc= 3 err=4.83E-08 meth=d nvec= 1 mix=1.0000 cpu= 0s fit=4.91E-04
<Mar30-2013> <18:26:22> using the exact gradient of the density
<Mar30-2013> <18:26:22>
<Mar30-2013> <18:26:22> Max. cycle time CP: 0.031
<Mar30-2013> <18:26:22> IO: 0.016
<Mar30-2013> <18:26:22>
<Mar30-2013> <18:26:22> Mean cycle time CP: 0.012
<Mar30-2013> <18:26:22> IO: 0.012
<Mar30-2013> <18:26:22> EL: 0.023
<Mar30-2013> <18:26:22>
<Mar30-2013> <18:26:22> final mix.par. 0.075
<Mar30-2013> <18:26:22> Approx. conv.rate: 0.000
<Mar30-2013> <18:26:22>
<Mar30-2013> <18:26:22> FERMI ENERGY: -0.2317 A.U.
<Mar30-2013> <18:26:22> -6.3043 E.V
<Mar30-2013> <18:26:22> >>>> ENERGY
<Mar30-2013> <18:26:22> ENERGY OF FORMATION: -0.2469 A.U.
<Mar30-2013> <18:26:22> -6.7175 E.V.
<Mar30-2013> <18:26:22> -154.9099 KCAL/MOL

```

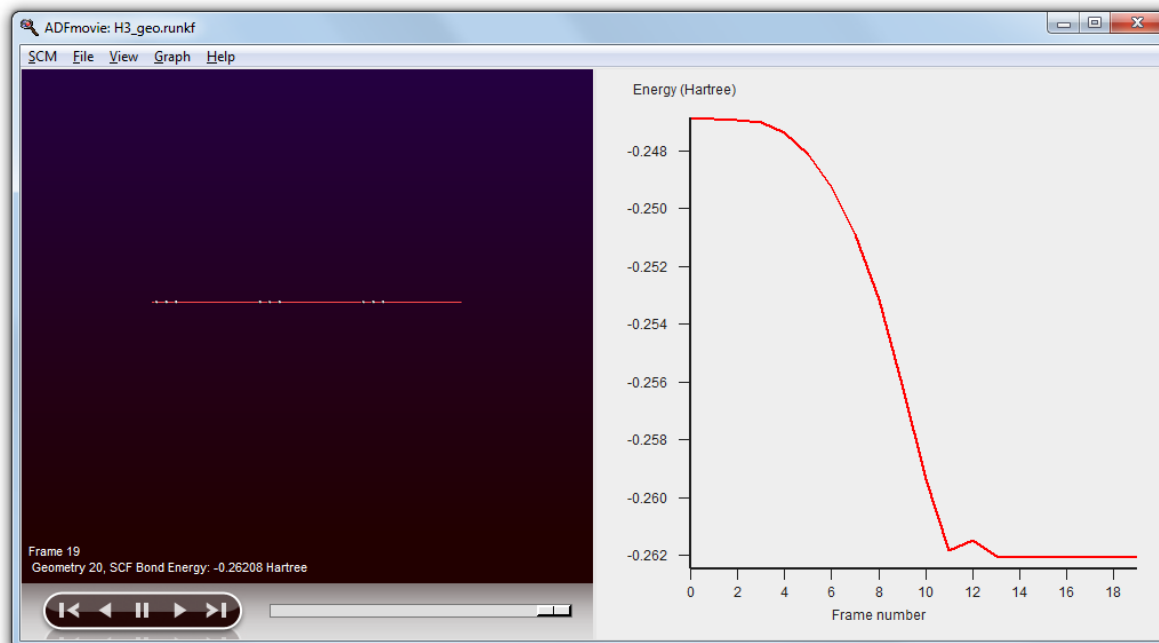
You see the final geometry and status of the five convergence criteria. Because they are all satisfied you see the log message 'Geometry Converged'

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



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

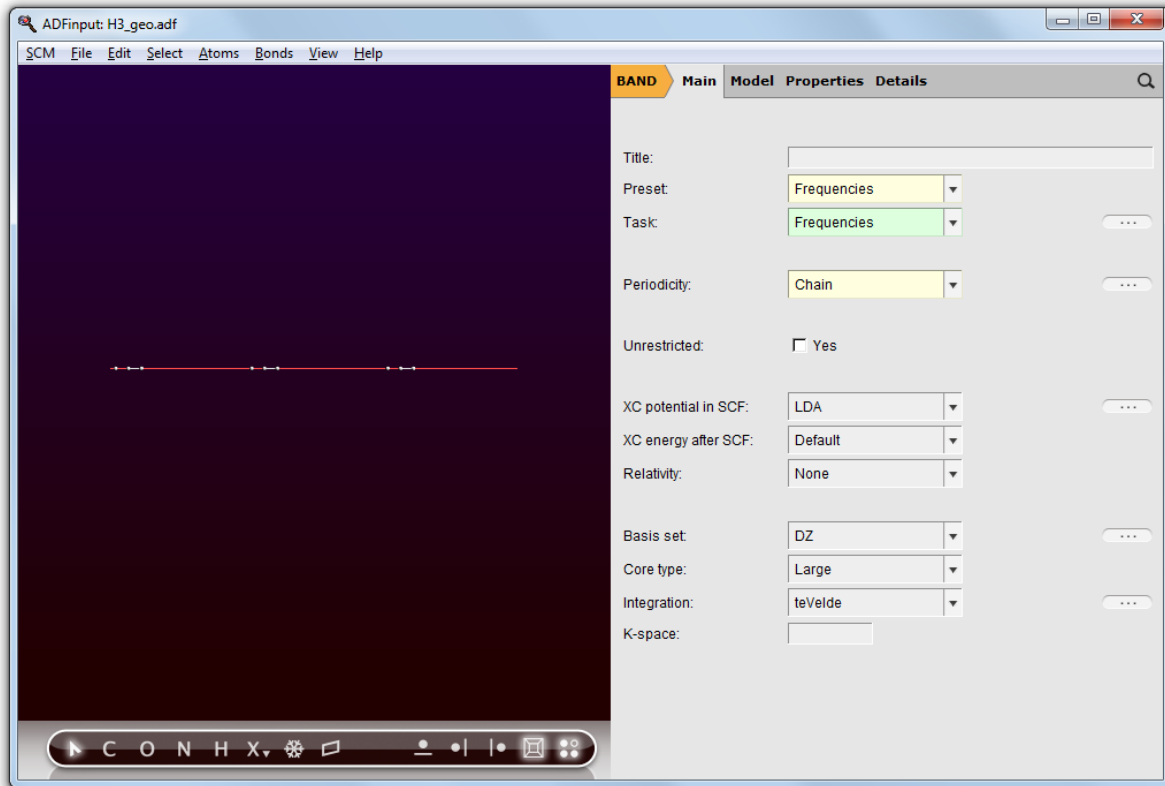


Now that looks more like an optimal geometry!

Step 3: Calculate the Hessian

Go to BANDinput

Select in the 'BAND Main' panel the 'Frequencies' preset



File → **Save As...**

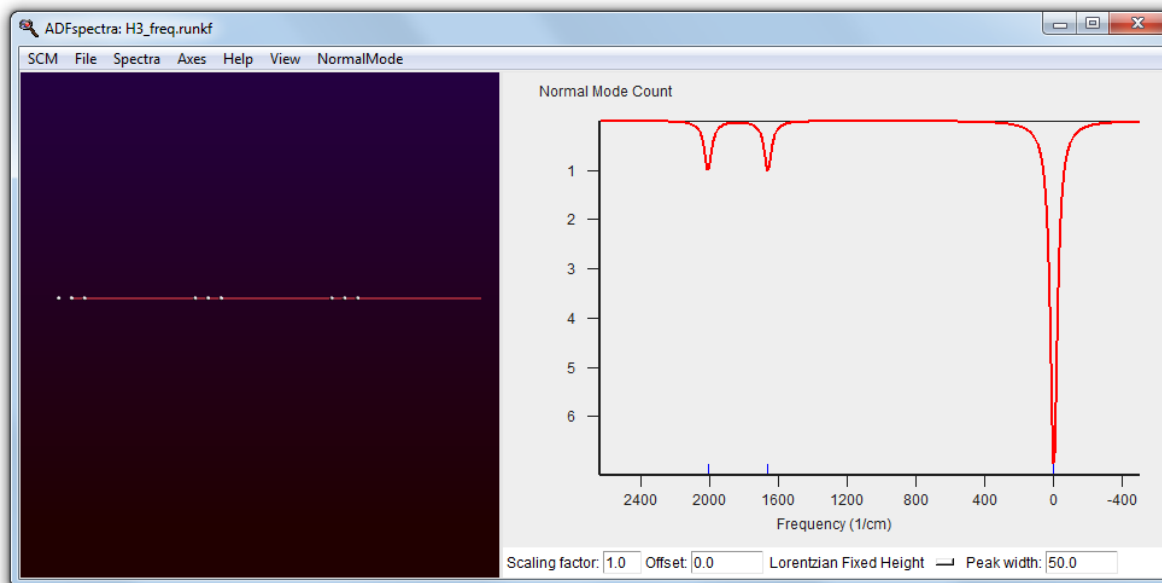
Save the project as H3_freq

File → **Run**

When it is done, click Yes to accept the new coordinates

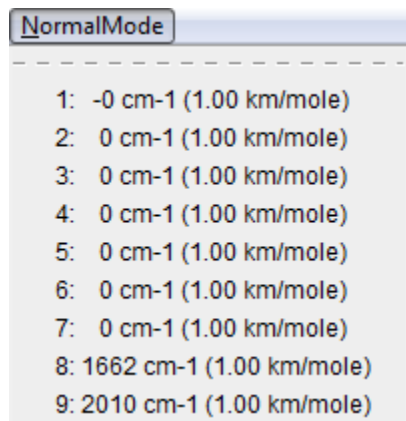
After the calculation has finished

SCM → **Spectra**



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

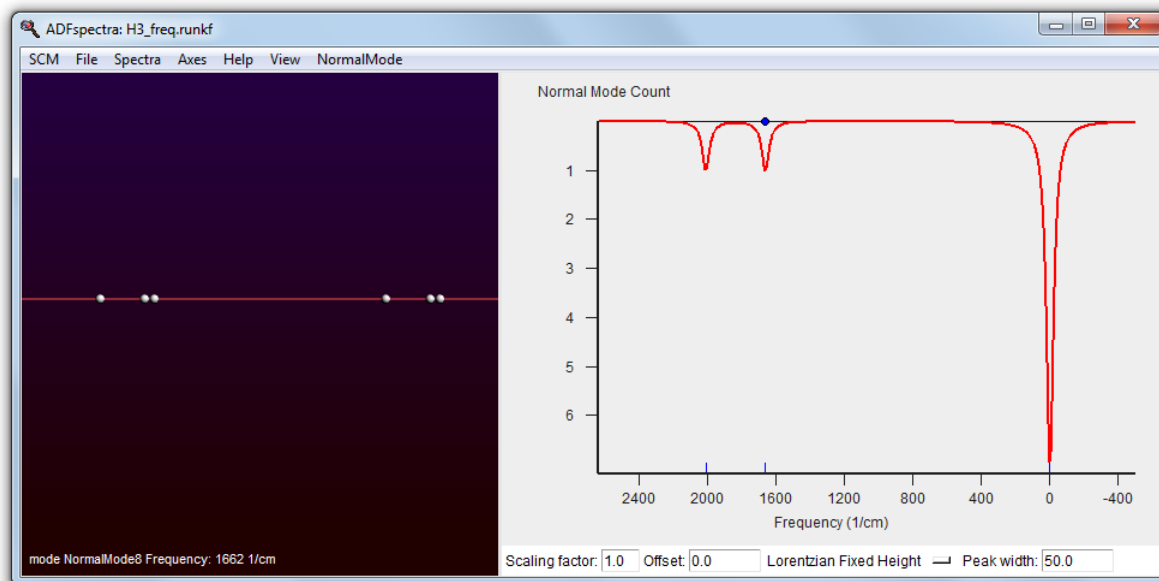
click on the 'NormalMode' menu.



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.

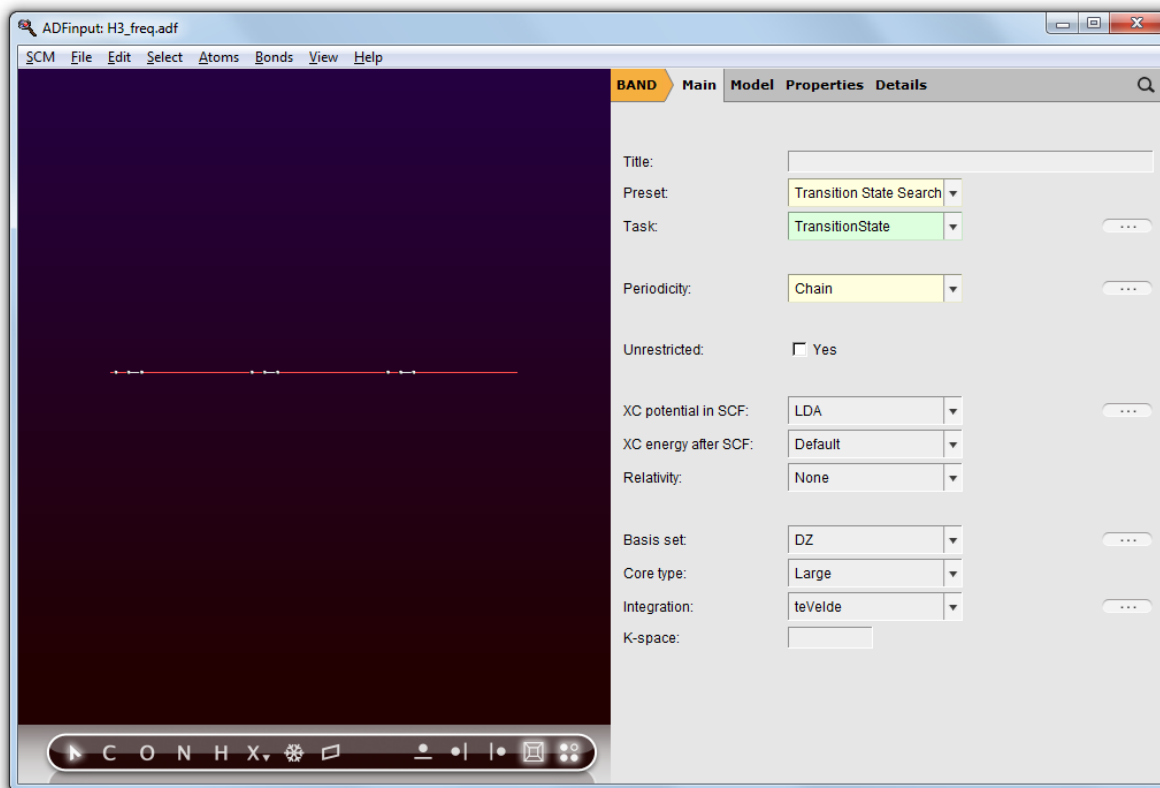
The vibrational mode will be shown on the left:



Step 4: Search the transition state

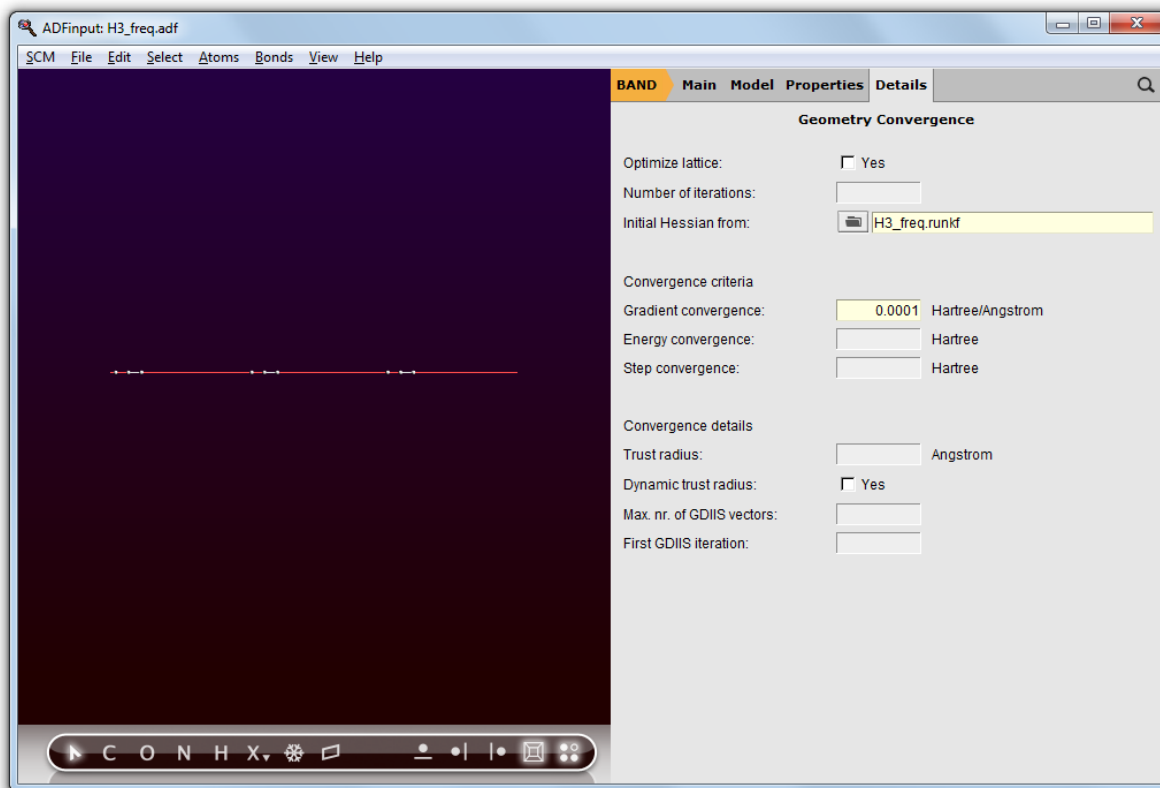
A minimum has vanishing gradients and only positive eigen modes. A transition state (first-order saddle point) is characterized by having one negative mode. With a transition state search the optimizer will go uphill in the direction of the lowest (nonzero) eigen-mode and downhill in all other degrees 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'



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'



File → **Save As**, use name H3_ts

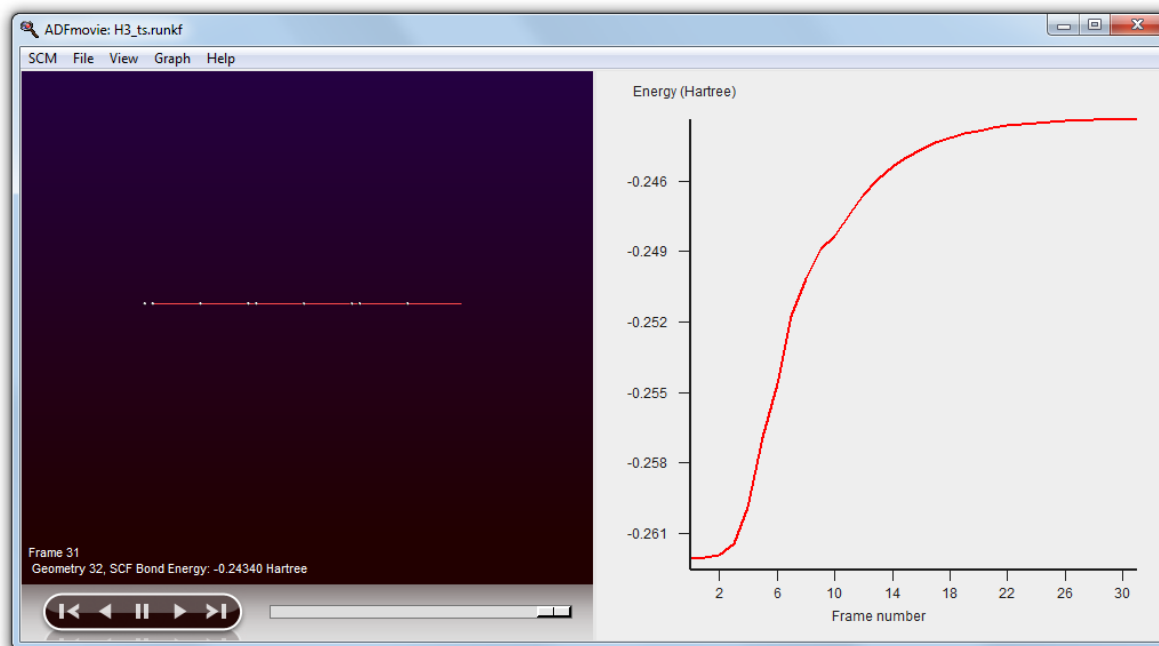
File → **Run**

After it has finished:

Update the coordinates in BANDinput

SCM → **Movie**

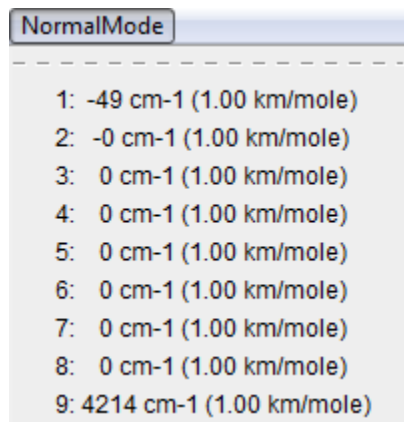
Graph → **Energy**



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:



We have found a geometry with vanishing gradients with one weak negative vibrational mode. We have succeeded in finding a transition state.

SCM → Quit 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

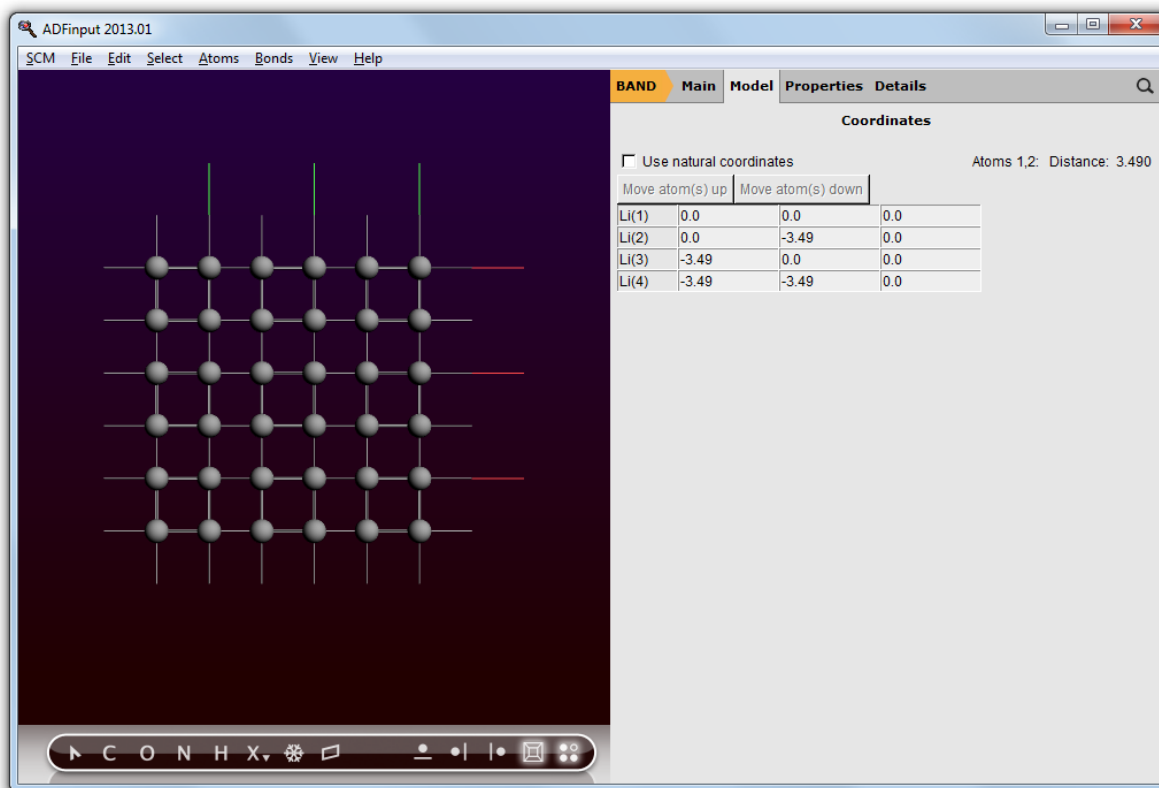
In this "advanced" tutorial we consider a slightly more realistic system. Some of the calculations may require 20 minutes to run on a two core machine.

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

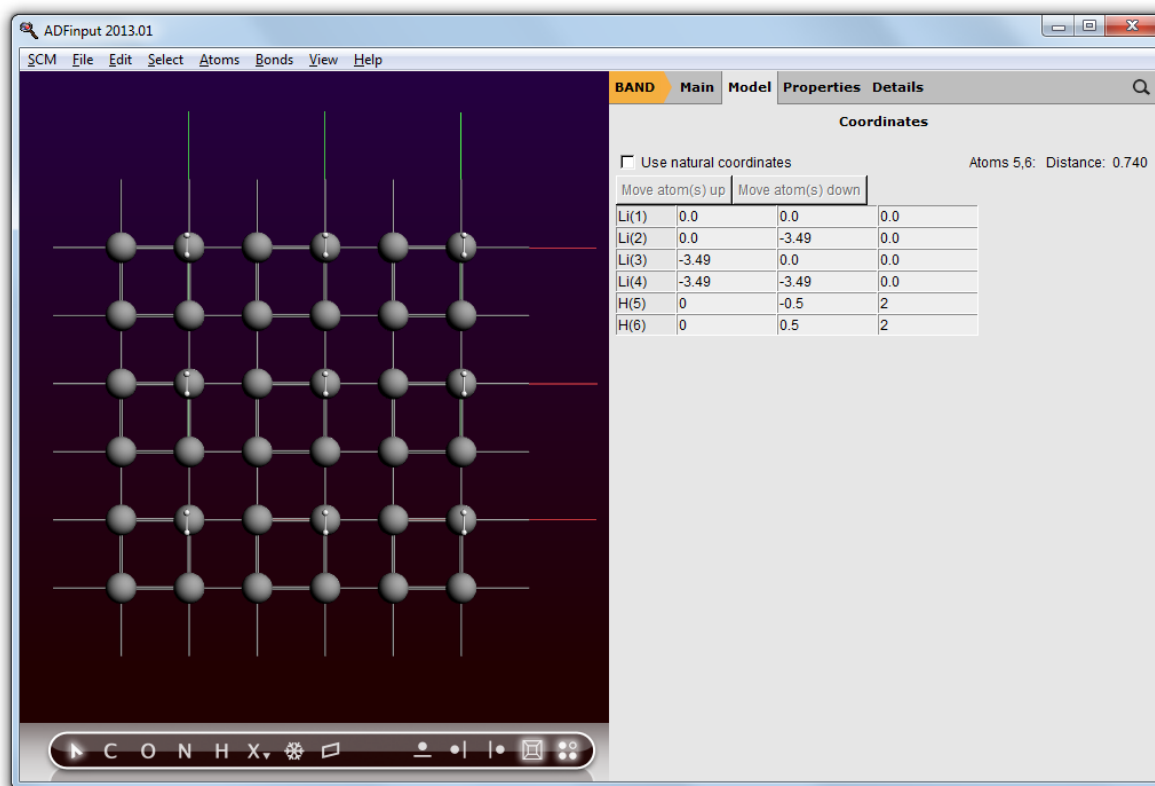
```
Start ADFinput and switch to BAND mode.  
From the structure tool select 'Cubic' and 'bcc'  
Set 'Element' to Li  
Set the lattice parameter to 3.49  
Press 'OK'  
Invoke the Slice tool  
Set the Miller indices to 001, select 'Cartesian', and enter 1 layer.  
Press 'OK'  
Use the Edit → Crystal → Generate Super Cell... command  
Select the preset '2x2' and press 'OK'  
Panel bar Model → Coordinates
```

Your screen should look like this:



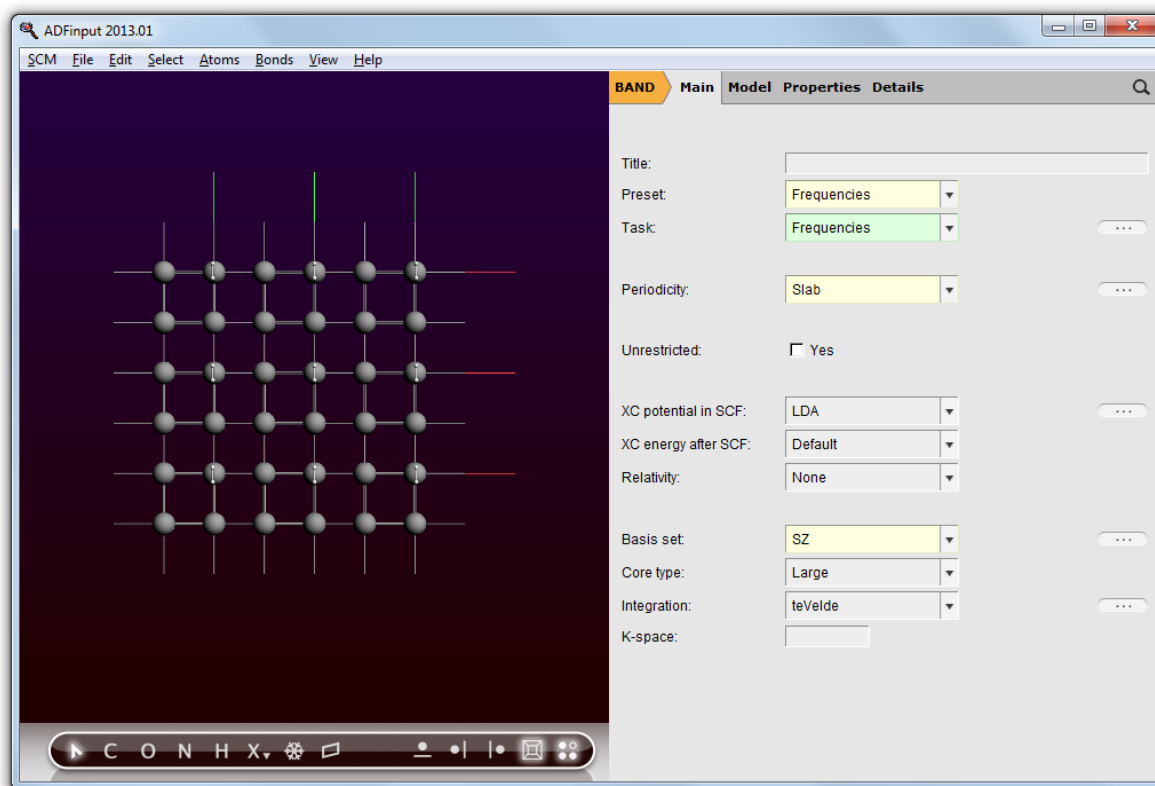
Add with the mouse two hydrogen atoms anywhere in the screen
 Set in the table the coordinates of the first hydrogen atom to (0, -0.5, 2)
 Set the second H atom coordinates to (0, 0.5, 2)

The final geometry looks like this

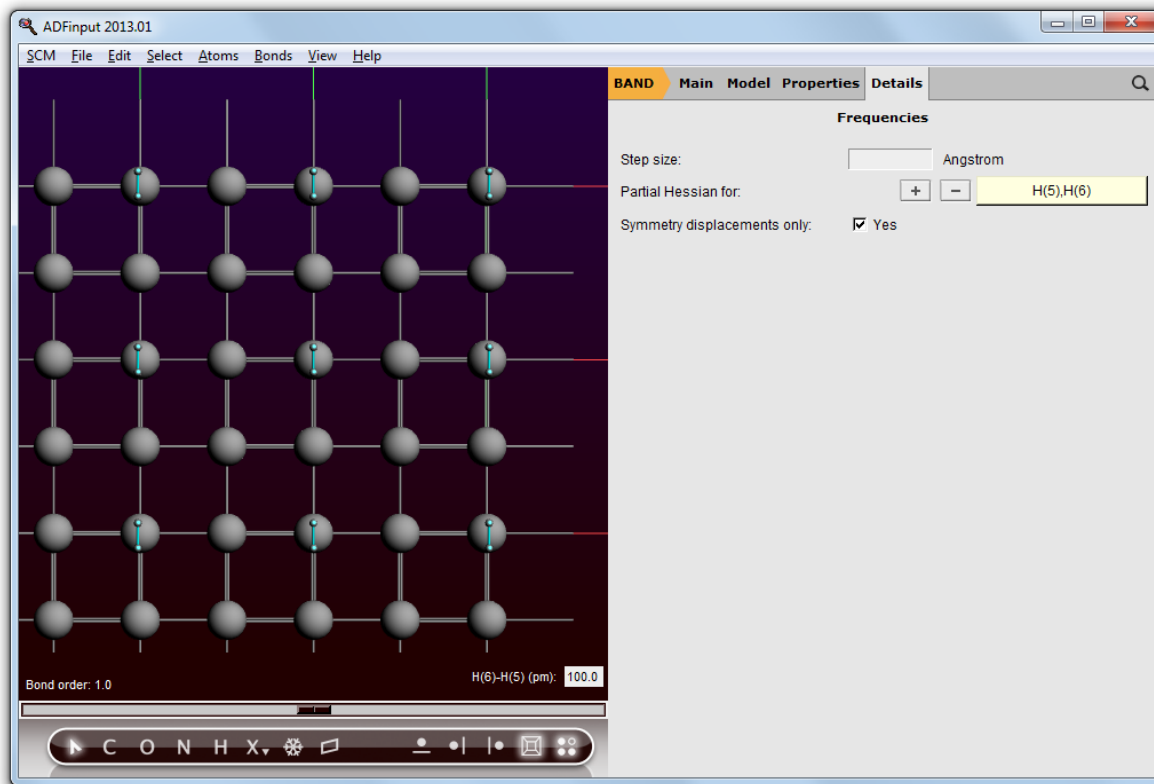


Step 2: Calculate a partial Hessian

Select the 'BAND Main' panel
 Select the Frequencies preset
 Set 'Basis Set' to 'SZ'



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:'



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

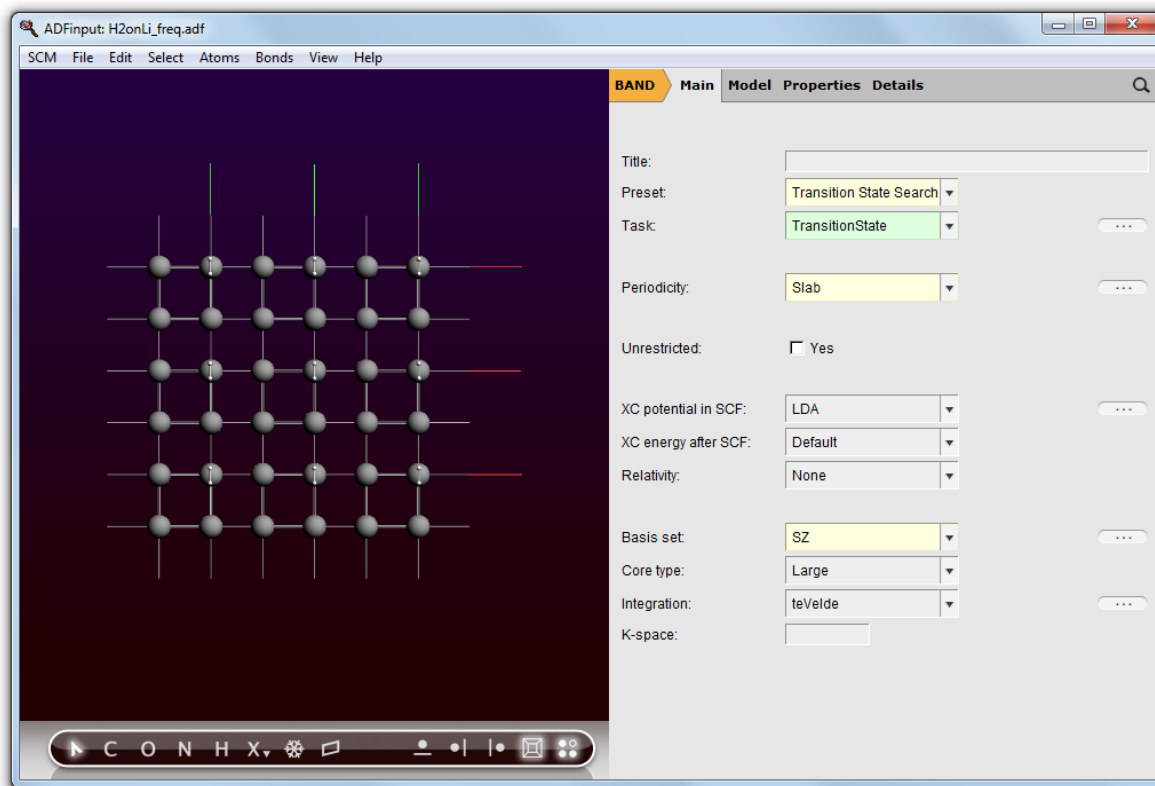
Select the **SCM** → **Spectra** menu command
 Open the 'NormalMode' menu

Now you will see that there is an eigen-mode at 452 cm^{-1} and one at 2428 cm^{-1} . Convince yourself that the 452 mode moves the H_2 perpendicular to the surface and that the 2422 mode is essentially an H_2 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

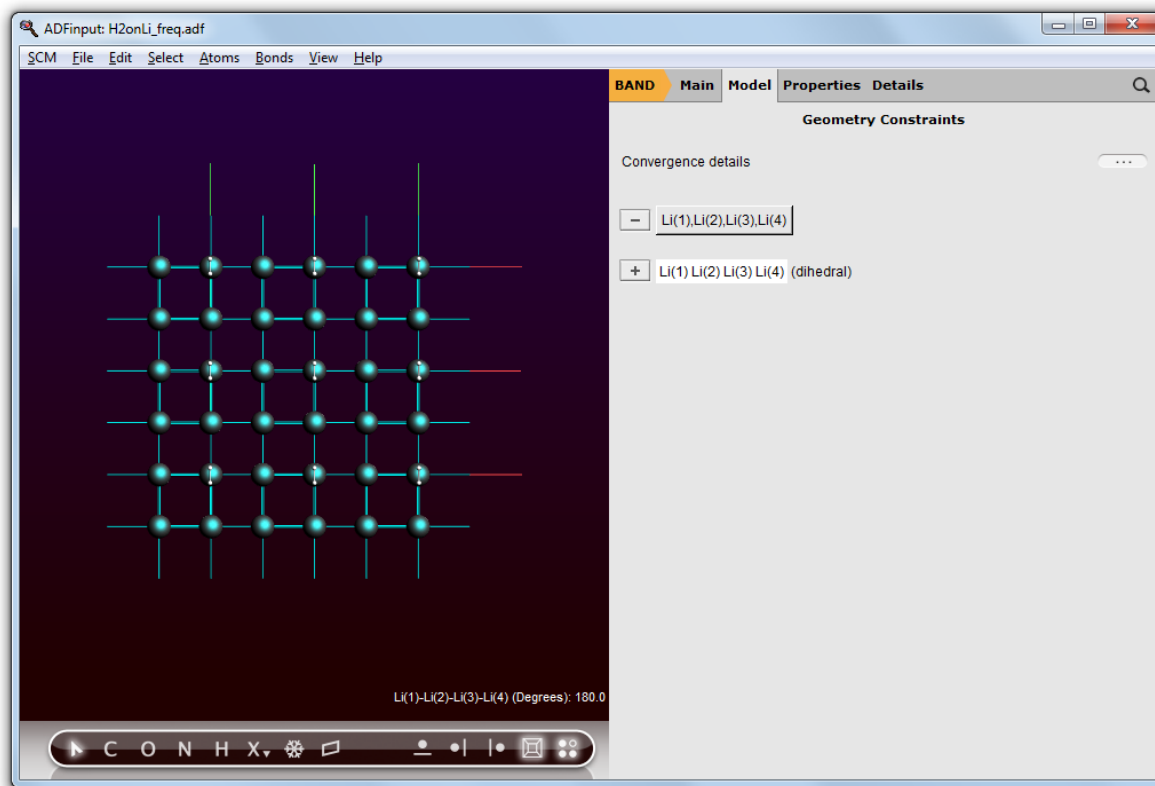


Panel bar **Model** → **Geometry Constraints and Scan**

The two hydrogen atoms are still selected, if not select them again

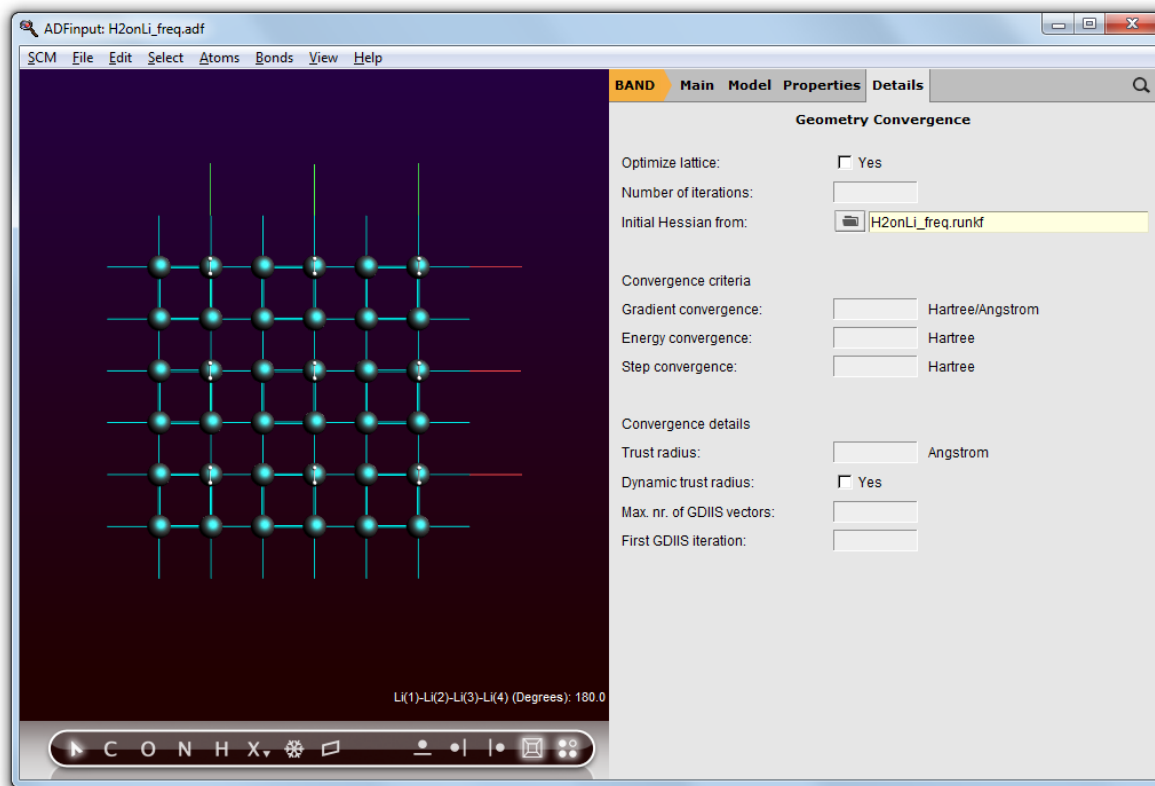
Use the **Select** → **Invert Selection** command

Click on the '+' button next to 'freeze selected atoms'



Panel bar **Details** → **Geometry Convergence**

Set the initial Hessian to 'H2onLi_freq.runkf'



File → **Save As...**, use name H2onLi_ts

File → **Run**

After the run has completed:

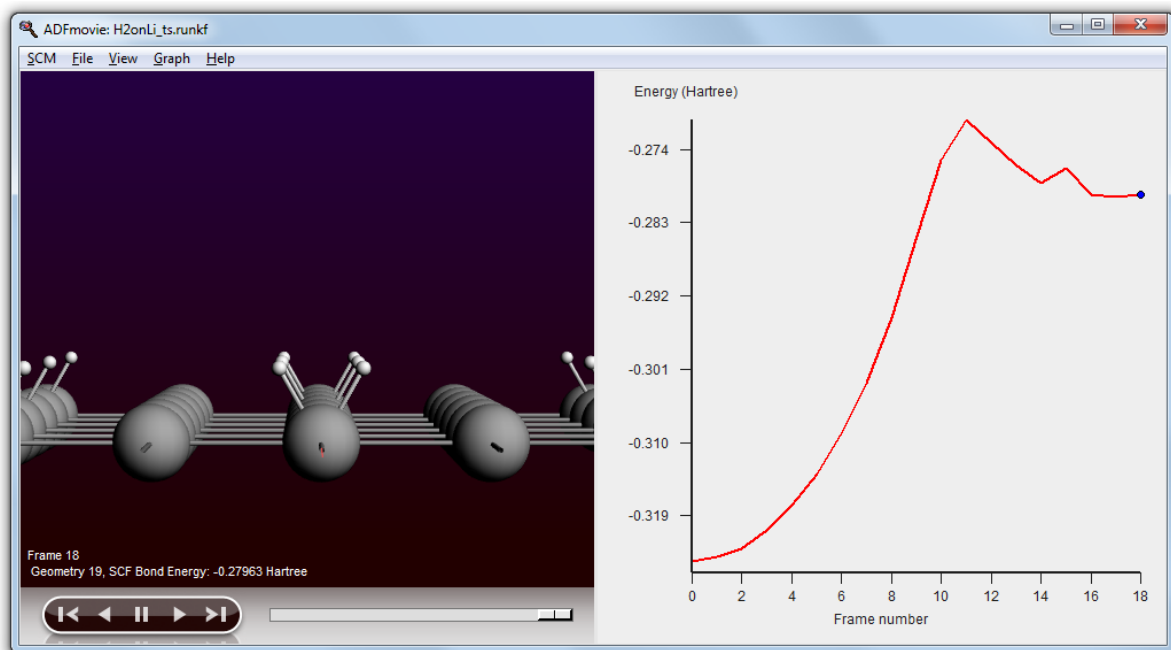
SCM → **Movie**

In the movie window: **Graph** → **Energy**

View → **View Direction** → **Along x axis**

Reorient to get a good look

It should look like



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.

The tutorials use DFTB parameter sets that are available for any user who has a DFTB license. For your convenience also the DFTB parameter sets from DFTB.org have been included. They often give much better results. In general we would advise you use one of the 3OB parameter sets with DFTB3 if possible.

To use the DFTB.org parameters as included with the ADF package you need the option to use them enabled in the license file. For academic users this is free of charge. Please contact us if you want this option enabled. Alternatively, you can download them from the DFTB.org web site (after registration).

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 → **New Input**

Select the DFTB panel: panel bar **ADF** → **DFTB**

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 model is **DFTB**

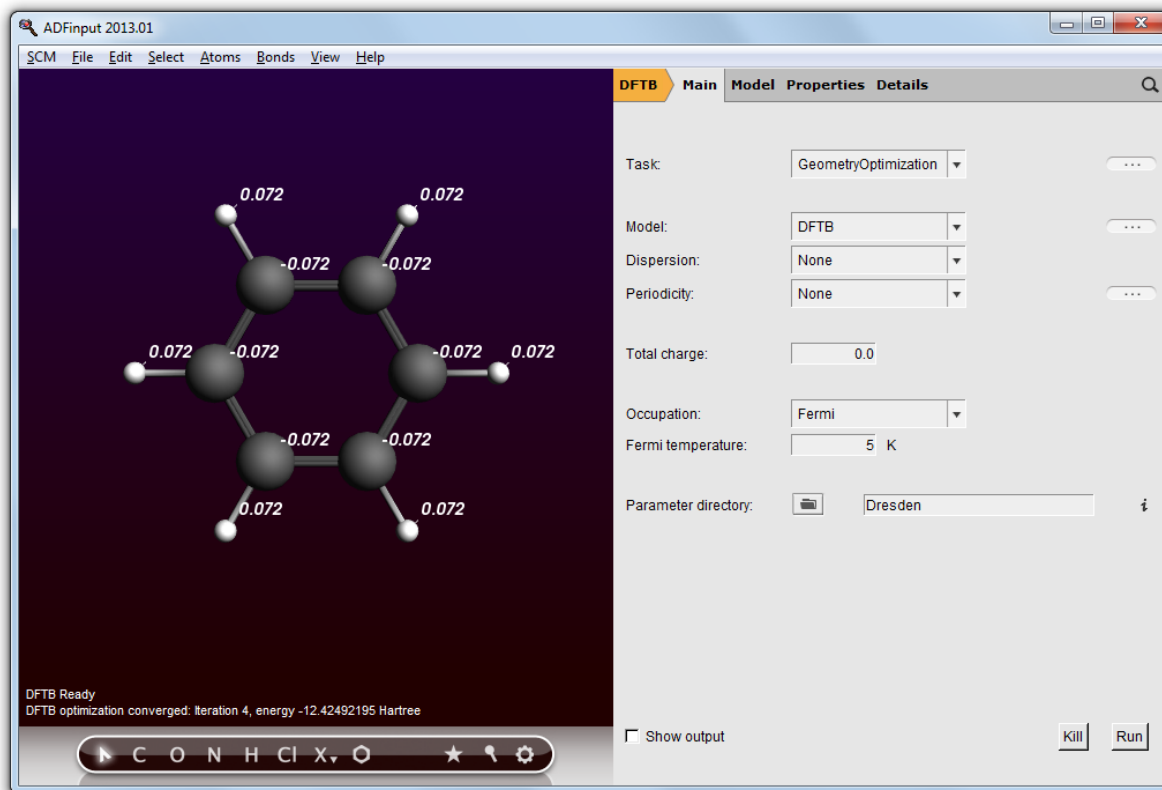
Make sure the parameter set is "Dresden" (normally you would want to use better parameters like the included 3OB set)

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



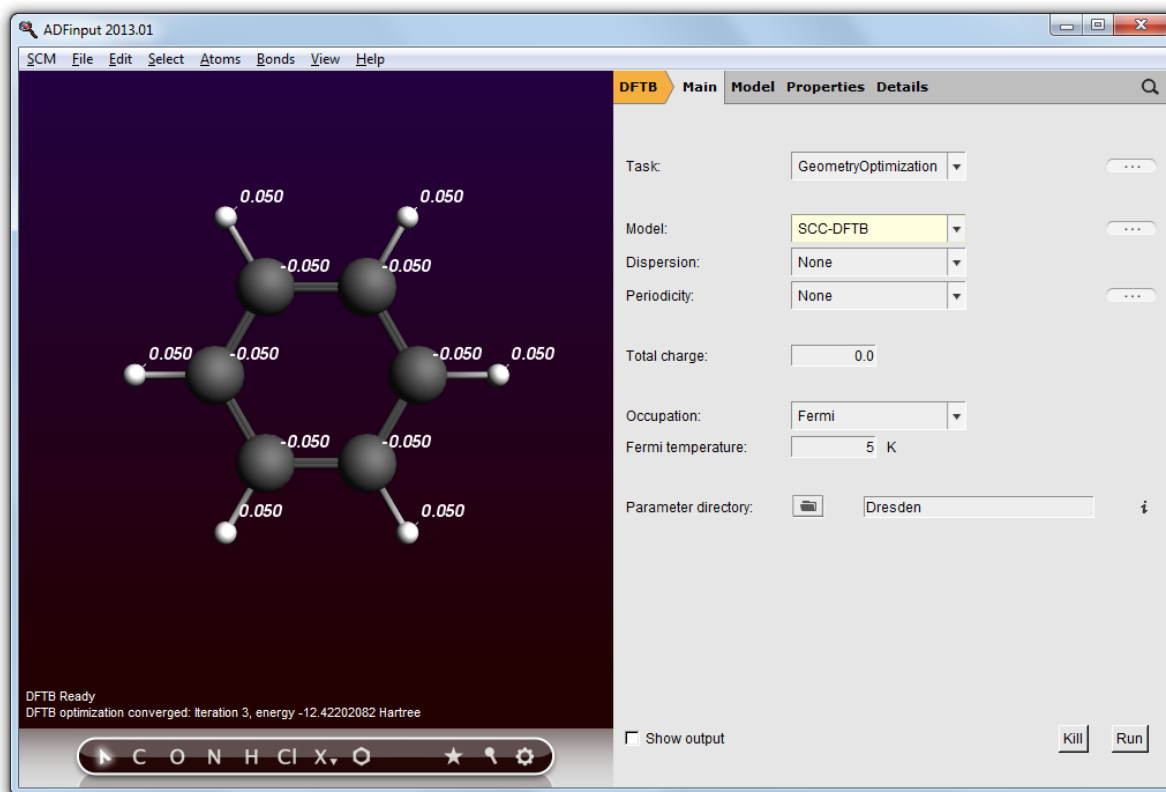
A Self Consistent Charge (SCC) evaluation allows atomic Mulliken charges to vary in an iterative procedure. This influences the DFTB Hamiltonian until self consistency of these charges is reached.

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 model to **SCC-DFTB**

Click 'Run' again in the DFTB panel to optimize the molecule.

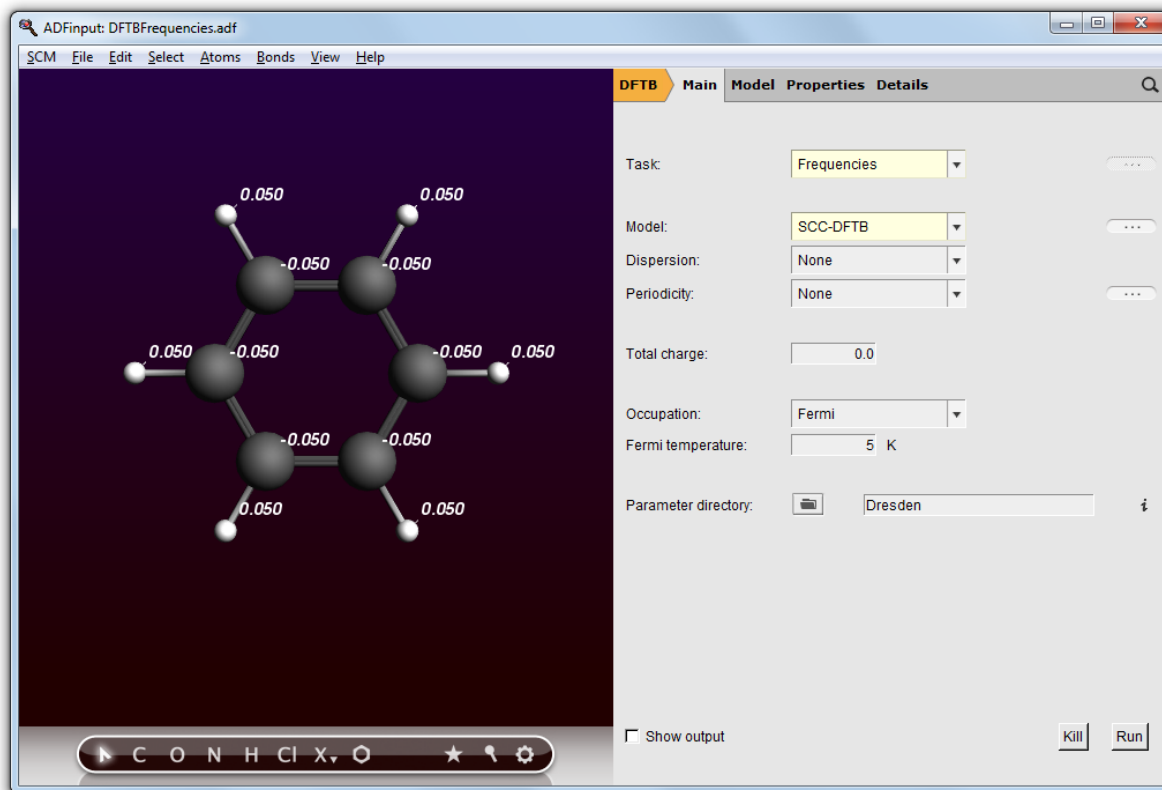
Note how both equilibrium geometry and atomic charges are affected by the SCC evaluation:



Step 2: Frequency evaluation

This example will show how to compute vibrational frequencies and modes using DFTB.

Choose **Frequencies** as the Task to perform.



File → **Run**, use DFTBFrequencies as name when asked for a name

When the calculation is ready (Job DFTBFrequencies has finished in the logfile):

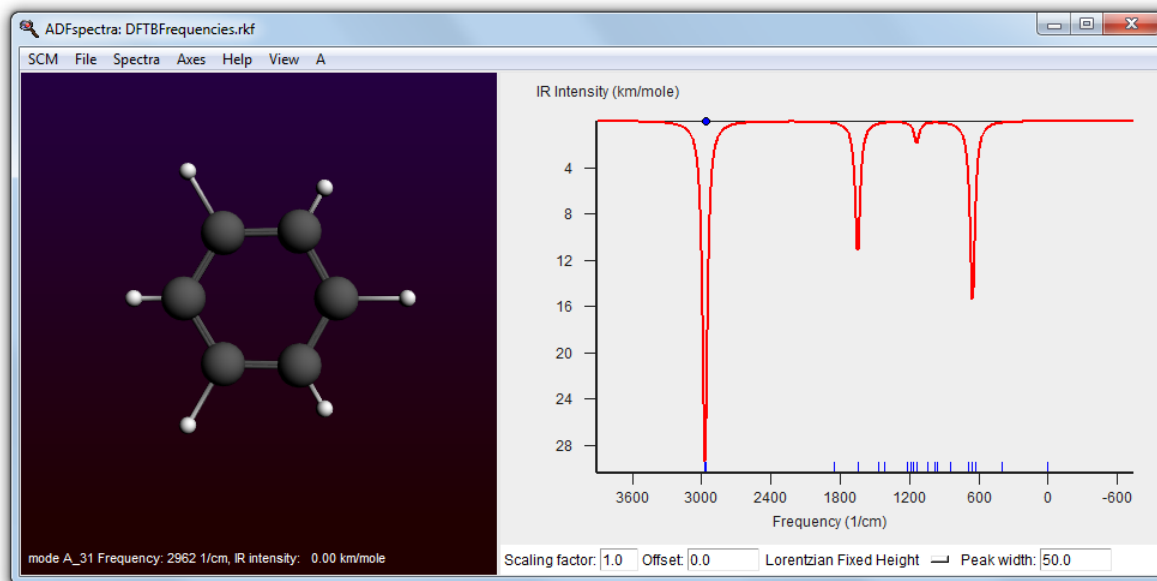
Close the logfile (**File** → **Close**)

In ADFjobs:

Select the "DFTBFrequencies" job

SCM → **Spectra**

Click on each individual frequency band to show the associated vibrational mode.



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.

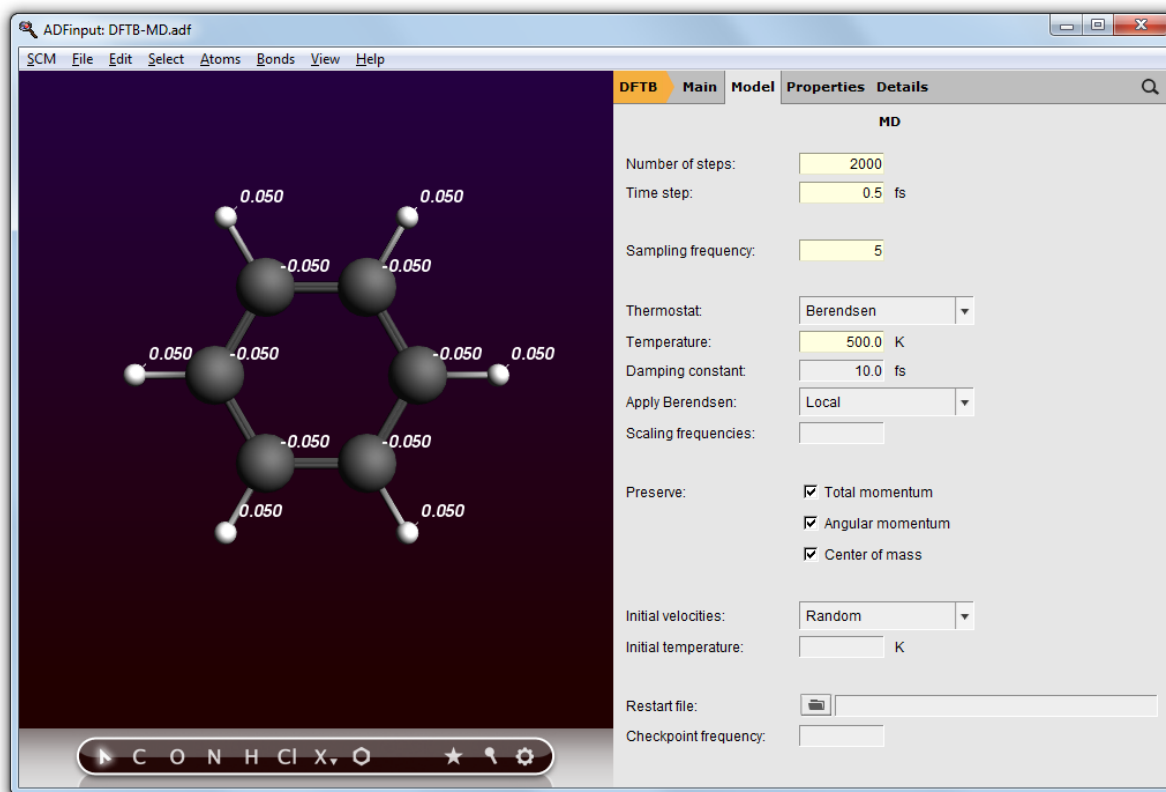
In the ADFinput window, choose **MolecularDynamics** as the Task to perform. Make sure the model **SCC-DFTB** option is selected, and the parameter set is Dresden (normally you want to use better parameters like the included 3OB set)

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"

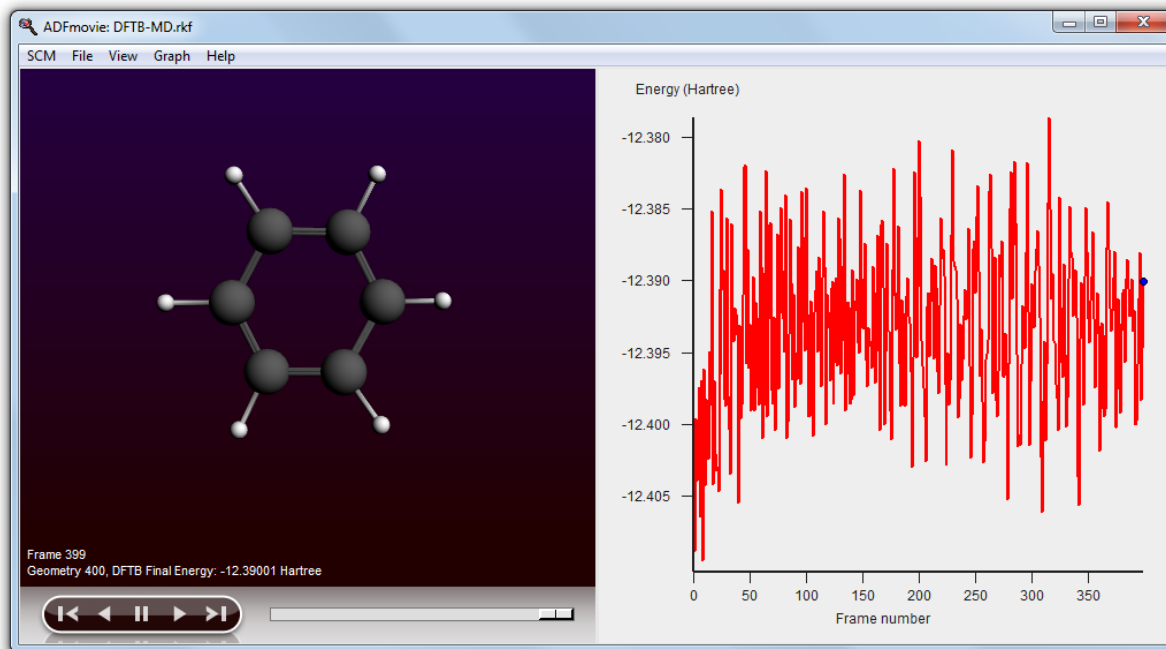


File → **run**

You can monitor the calculation in real-time:

While the calculation is running: **SCM** → **Movie**

In the ADFmovie window: **Graph** → **Energy**



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

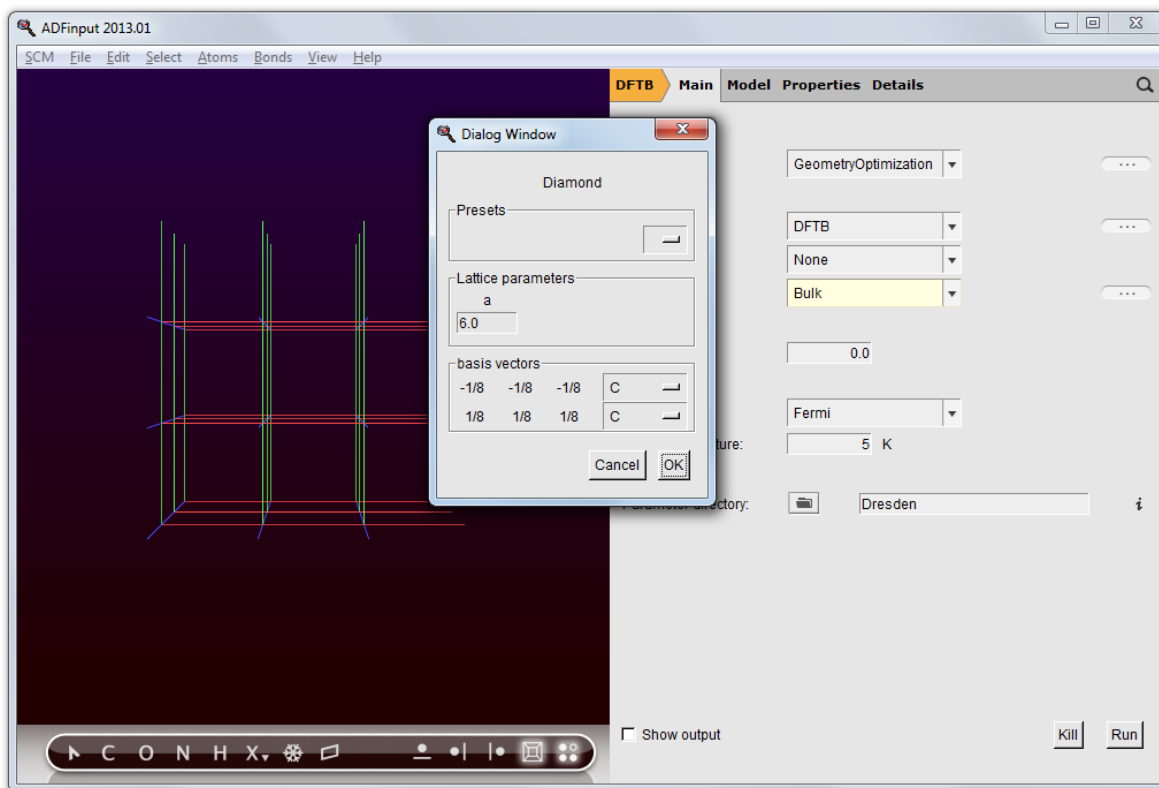
Select the DFTB panel: panel bar **ADF** → **DFTB**

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



Click the Details button (...) for the GeometryOptimization task
 Check the **Optimize Lattice** box
 Go to the Main panel
 Make sure model is set to **DFTB**, and that the Dresden parameter set is selected (normally you would want to use better parameters like the included 3OB set)
 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**

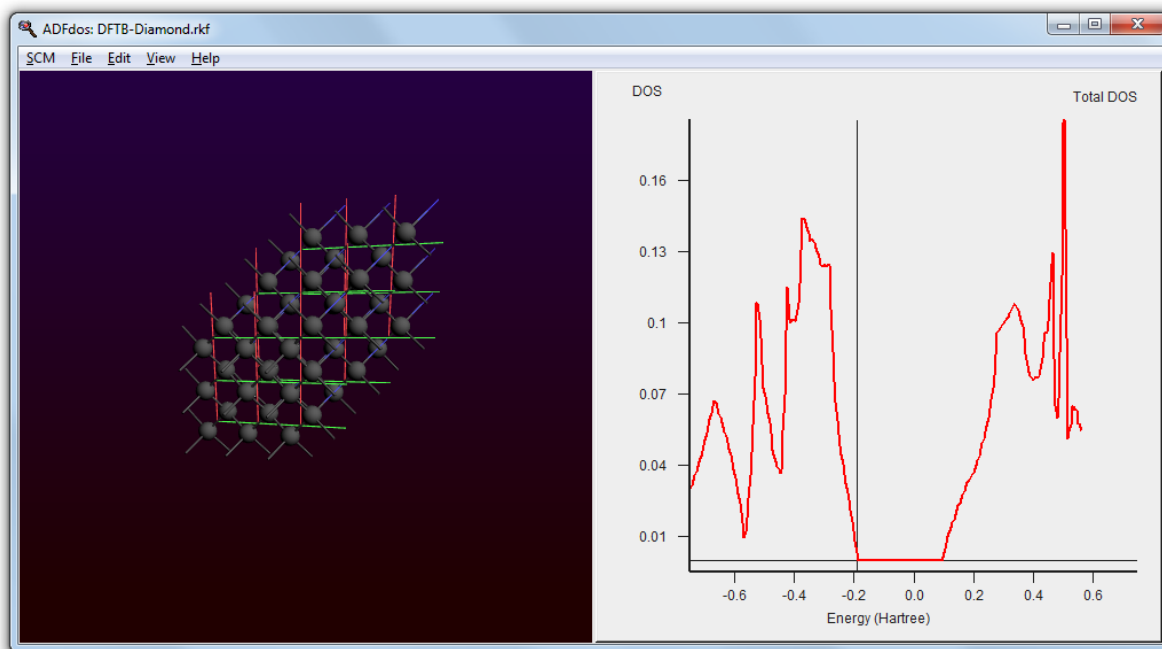
When asked to read the new coordinates (when the calculation finishes), click Yes

From the movie, you can observe how the unit cell shrinks as it is optimized.

Step 3: DOS and Band Structure

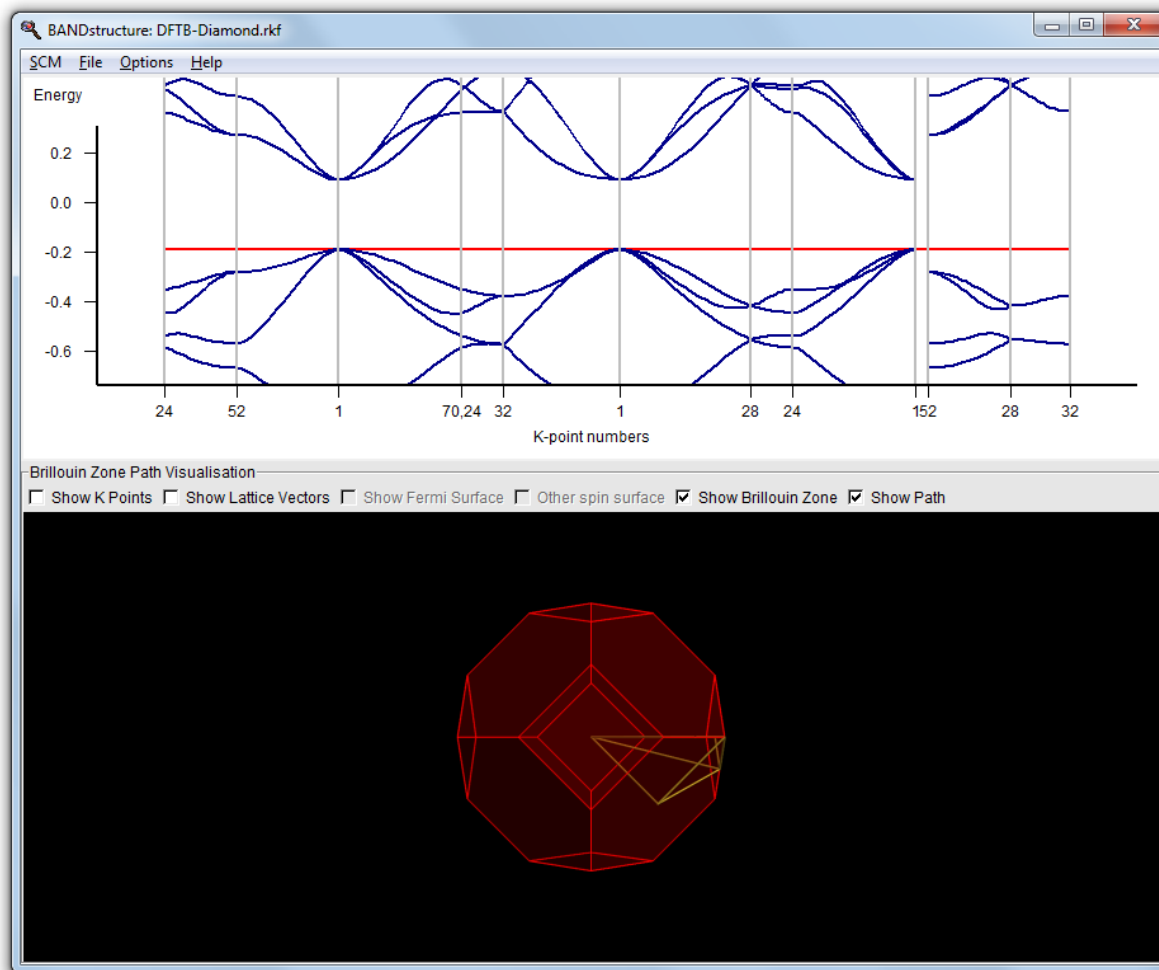
You can visualize the density of states (DOS) directly from the converged optimization.

SCM → **DOS** (in the ADFmovie or ADFinput window)



Similarly, you can visualize the band structure

SCM → Band Structure



Step 4: Phonons

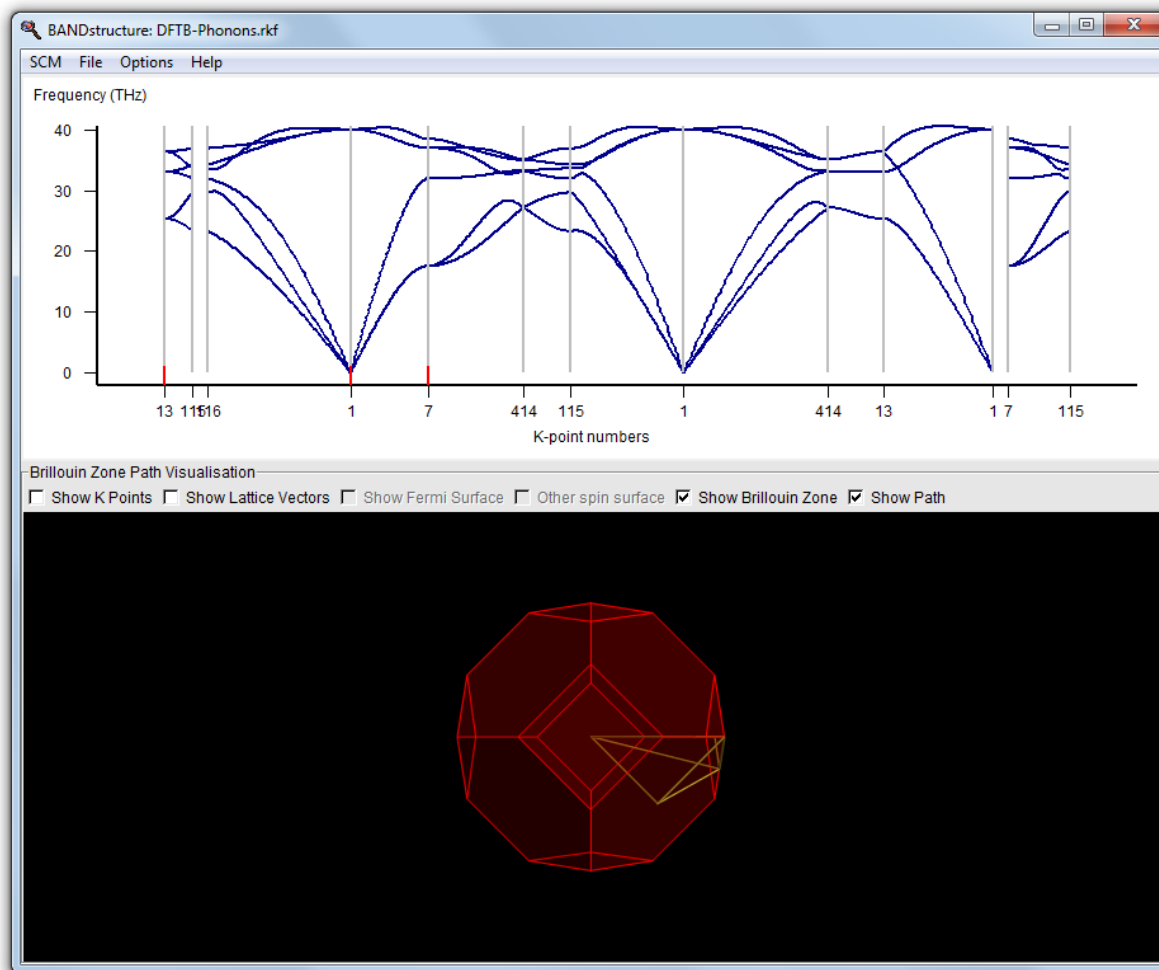
Activate the ADFinput window with the DFTB-Diamond input
 Select "Phonons" as Task

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

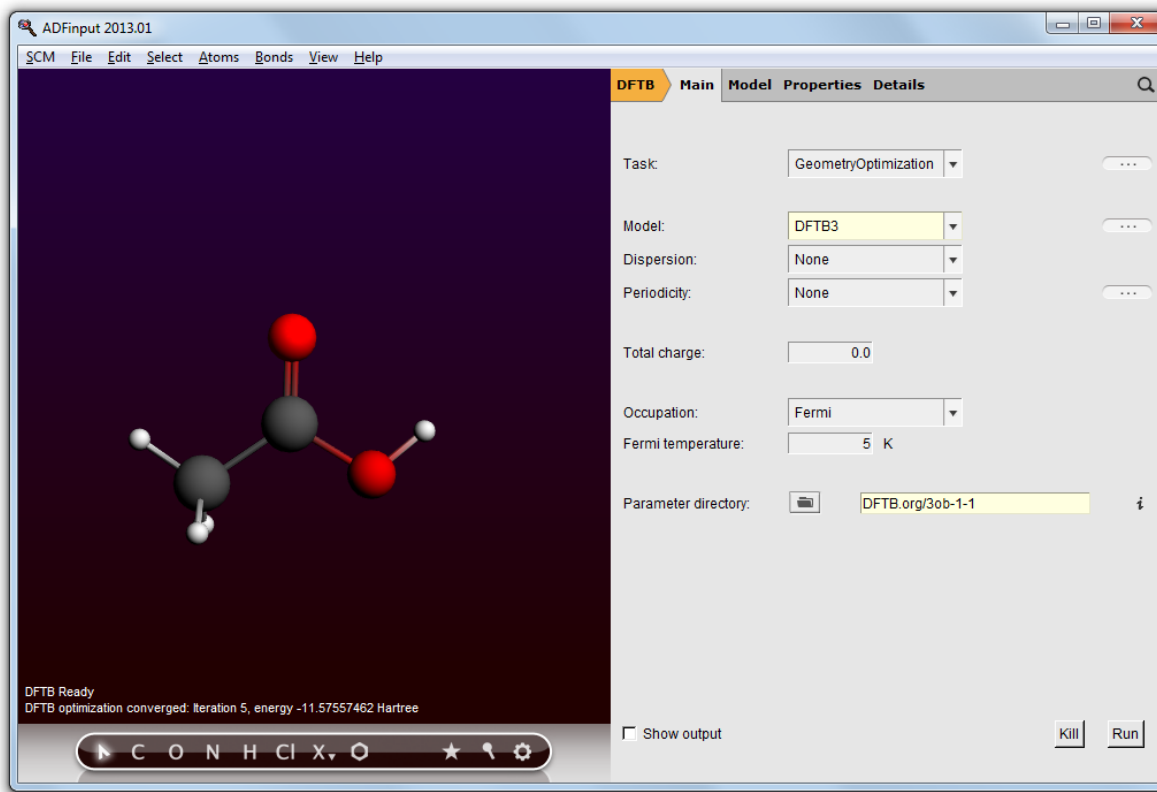
SCM → **New Input**

Switch to DFTB mode (panel bar **ADF** → **DFTB**)

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 model.
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 parameter set used in this example, E(HAc) = -11.57557462 Hartree)

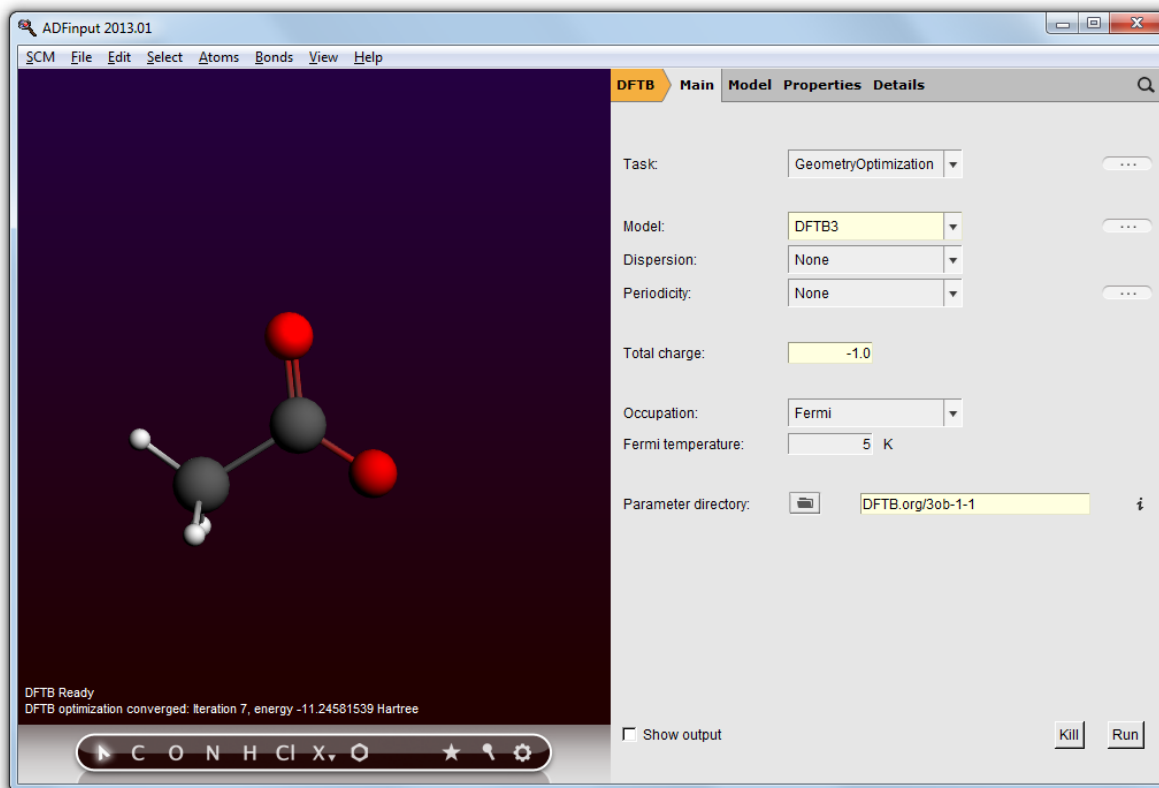


Step 2: Optimization of the acetate and the hydrogen ions

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.



At the end of the procedure, note the final energy (for the parameter set used in this example, $E(\text{Ac}^-) = -11.280518$ Hartree).

Additionally, the energy of the lone proton must be obtained.

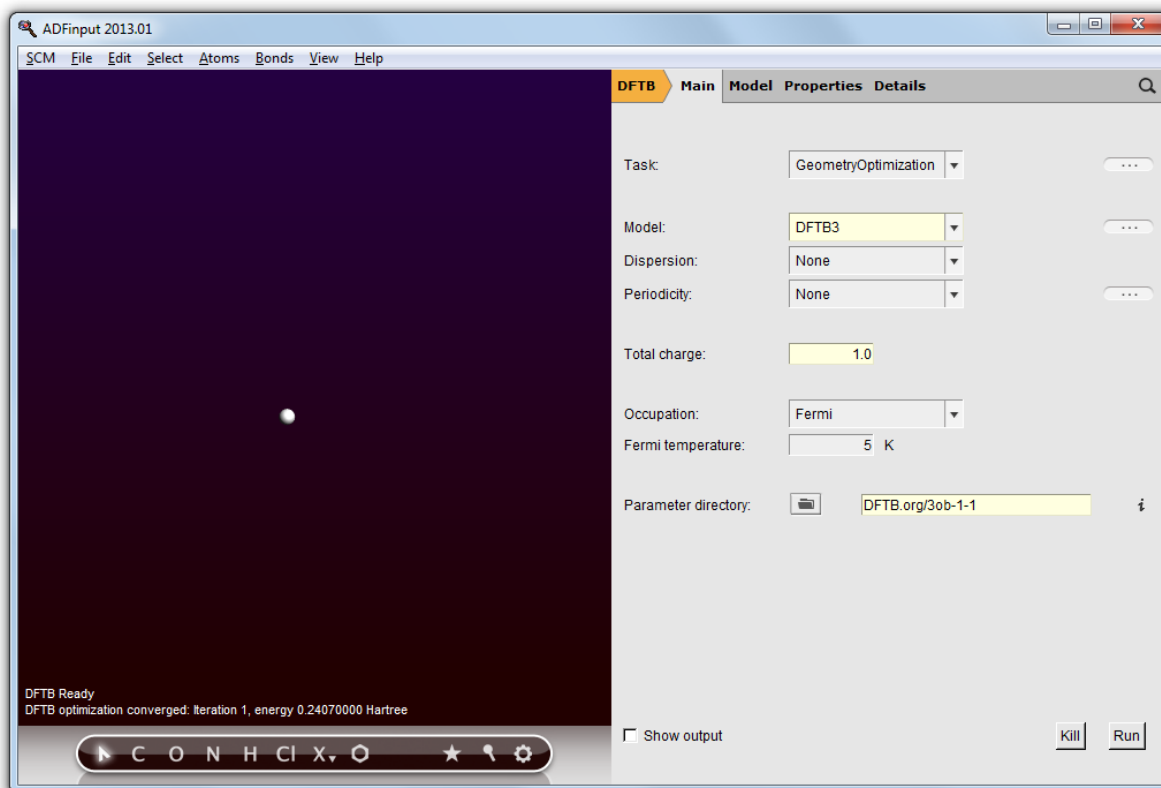
Select and delete every atom of the molecule, except one hydrogen atom.

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.



Finally, annotate the value for $E(\text{H}^+) = 0.236417$ Hartree. The proton affinity is computed as $\text{PA} = E(\text{Ac}^-) + E(\text{H}^+) - E(\text{HAc})$, 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 package, 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 you 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

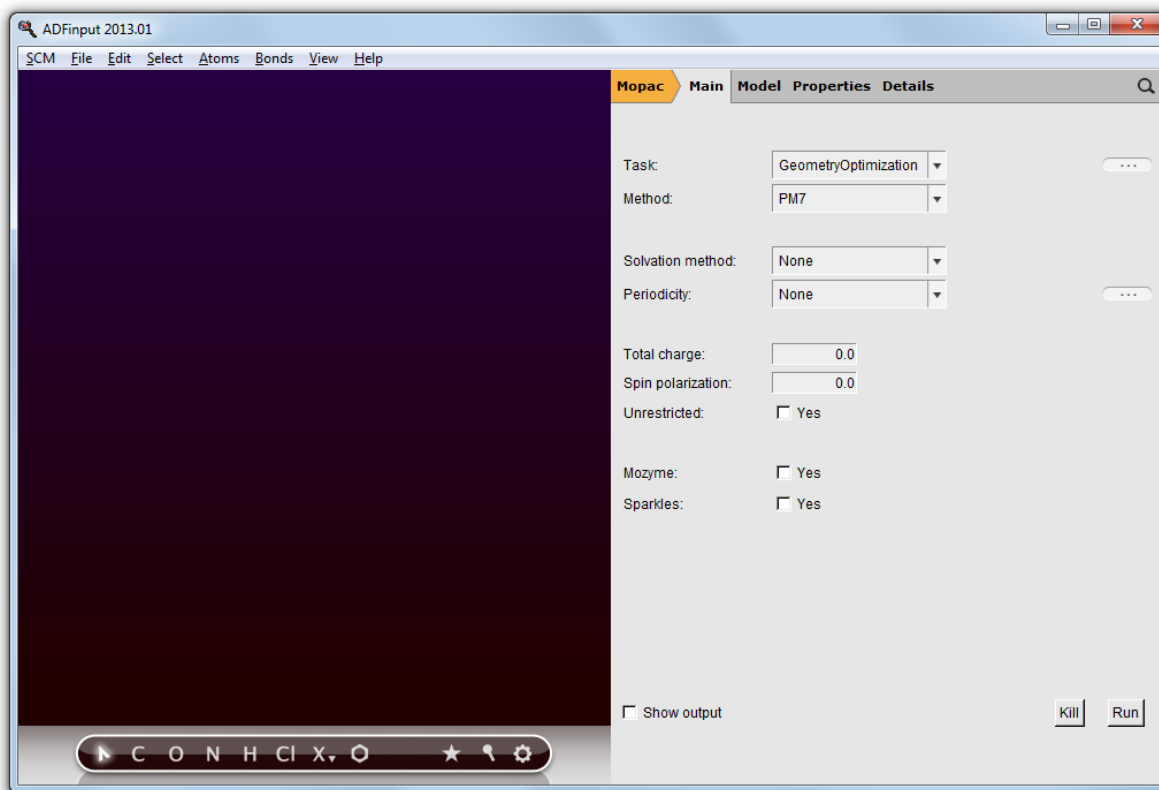
This tutorial will give you an example how to use MOPAC via the MOPAC-GUI from SCM.

Set up Toluene in MOPACinput

Start ADFjobs

SCM → **New Input**

Switch to MOPAC mode (panel bar **ADF** → **Mopac**)



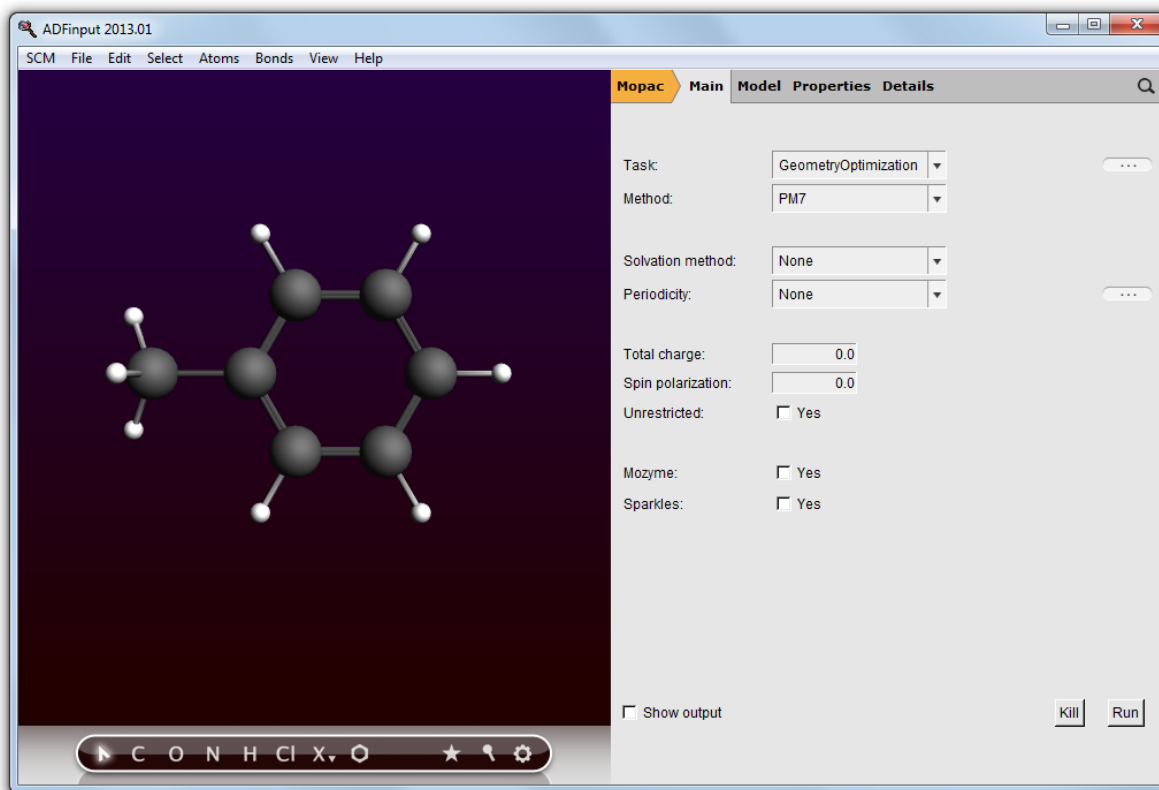
We will now make a Toluene molecule. Most conveniently this is done by simply searching for it within the MOPAC-GUI:

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

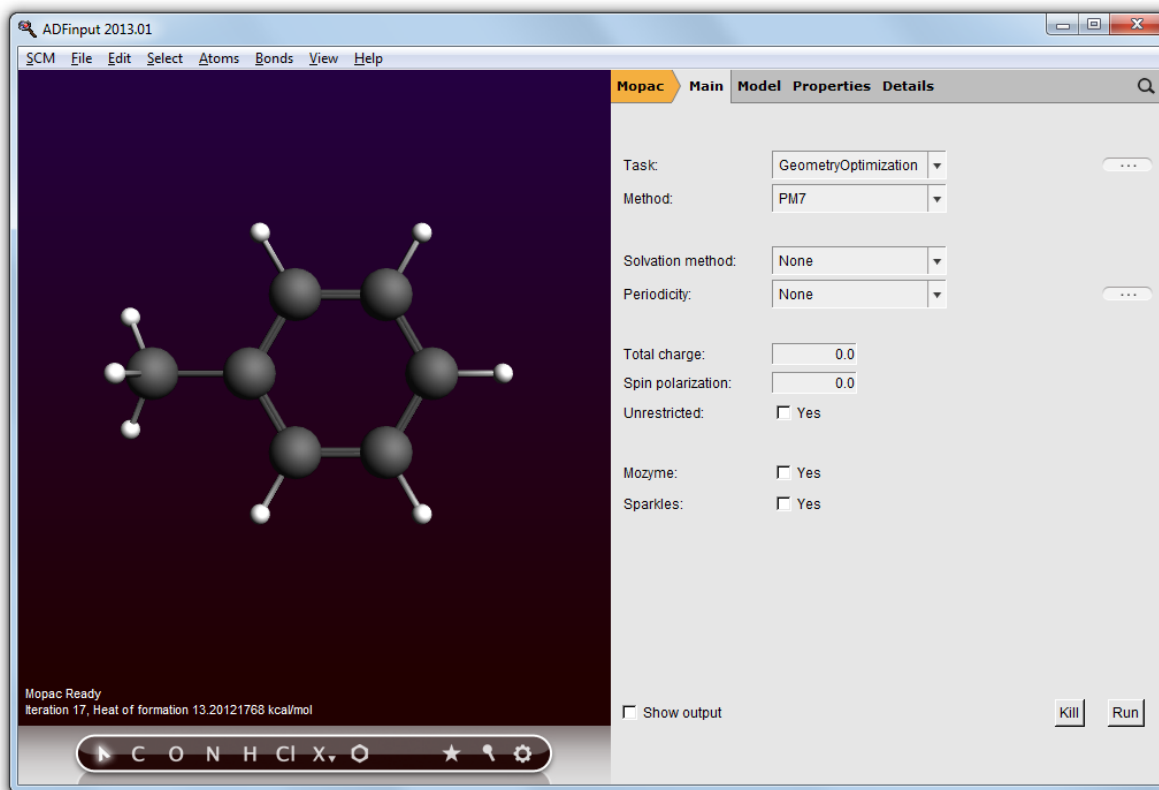


Run interactively

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 PM7 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**

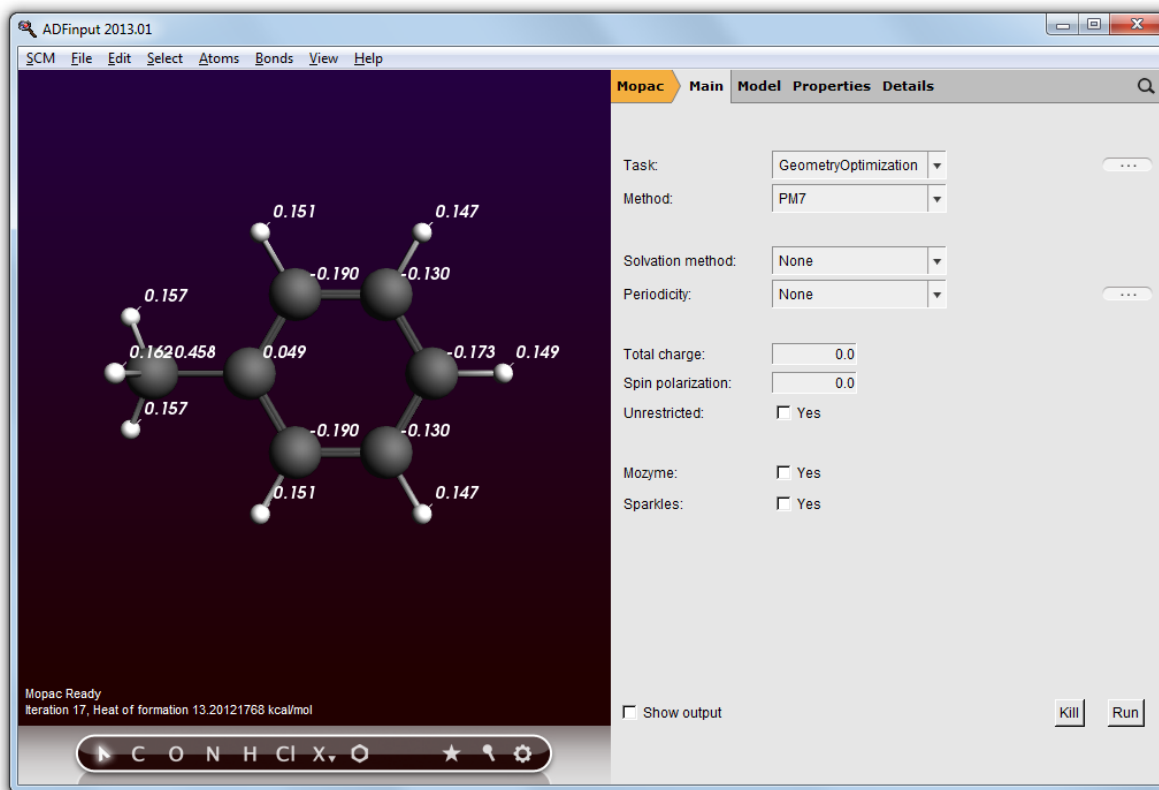
Press the 'Run' button



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 17 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



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


```

ADFTail: user.scm.Mopac.out
SCM File Edit Help

BOND ORDERS AND VALENCIES

-----
      C 1      C 2      C 3      C 4      C 5      C 6
-----
C   1  3.975077
C   2  1.445569  3.976850
C   3  1.423626  0.000592  3.990356
C   4  0.001492  0.111954  1.423363  3.975075
C   5  0.001154  1.440193  0.112143  0.001153  3.976155
C   6  0.111871  0.000617  0.000593  1.445750  1.440128  3.976854
C   7  0.004788  0.006192  1.014831  0.004789  0.001383  0.006187
H   8  0.964047  0.000213  0.000321  0.005095  0.005233  0.000153
H   9  0.000334  0.965666  0.005255  0.000110  0.000352  0.005230
H  10  0.005093  0.000153  0.000321  0.964043  0.005235  0.000214
H  11  0.005214  0.000293  0.000142  0.005216  0.965263  0.000293
H  12  0.000110  0.005237  0.005261  0.000333  0.000351  0.965648
H  13  0.005428  0.000028  0.002465  0.005428  0.002410  0.000028
H  14  0.001860  0.000065  0.000723  0.004493  0.000580  0.000078
H  15  0.004491  0.000078  0.000721  0.001855  0.000577  0.000065

-----
      C 7      H 8      H 9      H 10      H 11      H 12
-----
C   7  3.924652
H   8  0.000970  0.977146
H   9  0.000190  0.000508  0.978380
H  10  0.000970  0.000114  0.000075  0.977143
H  11  0.000097  0.000103  0.000484  0.000103  0.977693
H  12  0.000190  0.000076  0.000129  0.000509  0.000485  0.978375
H  13  0.954893  0.000009  0.000001  0.000009  0.000000  0.000001
H  14  0.964580  0.000285  0.000012  0.000018  0.000000  0.000032
H  15  0.964592  0.000018  0.000032  0.000286  0.000000  0.000012

-----
      H 13      H 14      H 15
-----
H  13  0.973621
H  14  0.001460  0.975383
H  15  0.001460  0.001197  0.975384

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 → New Input

Panel bar **ADF → Mopac**

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

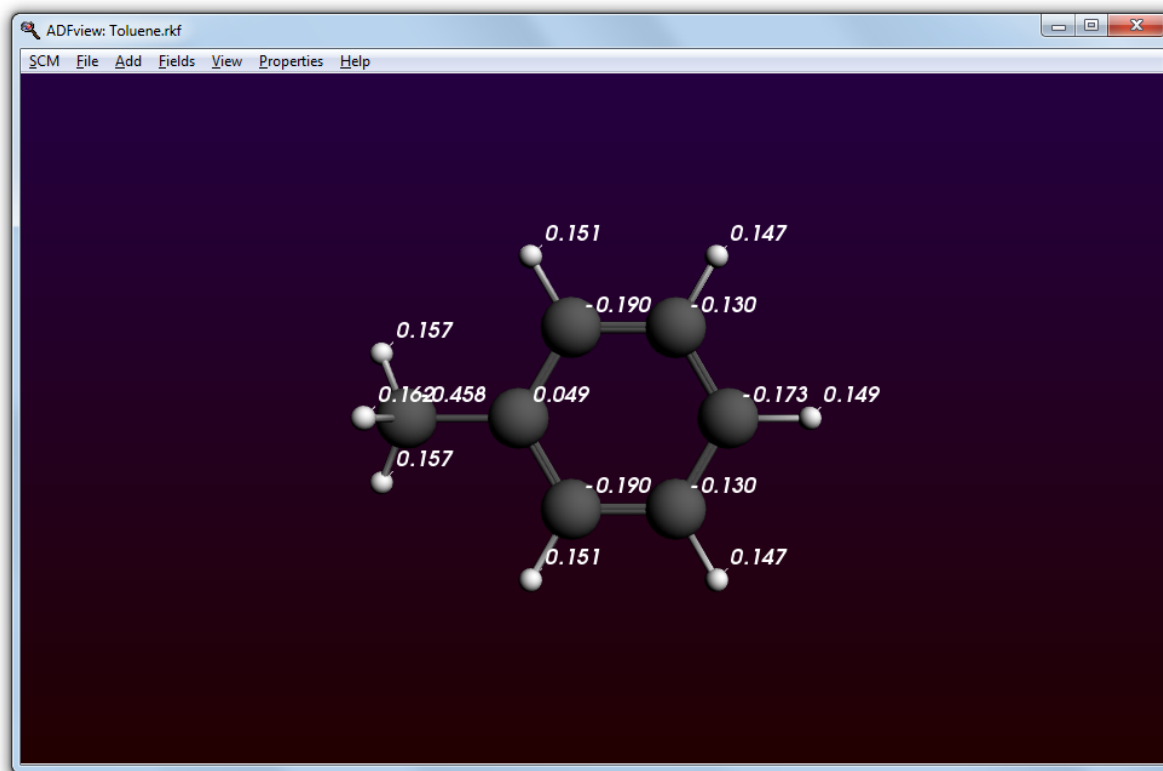
The logfile will show the progress of the calculation:

```

ADFTail: Toluene.logfile
SCM File Edit Help
  1.1569604804490  -1.2059651688366   0.0009513288410
 -2.4292686631073  0.0000286623049  -0.0044670736852
 -0.7791620049250  2.1498338315489   0.0048934817873
  1.7003426280098  2.1489752971448   0.0026038663073
 -0.7791395418895  -2.1498915671944   0.0042611806546
  2.9425976434117  0.0000264002247  -0.0053093403236
  1.7003737553273  -2.1489995735081   0.0020610827510
 -2.8216891698900  0.0005588996158   1.0238967113419
 -2.8457206027442  0.8820484162742  -0.5096486851499
 -2.8457876143642  -0.8825639693947  -0.5087309029206
HEAT_OF_FORM_UPDATED:KCAL/MOL=+0.132030272941774D+02
GRADIENT_UPDATED:KCAL/MOL/ANG=+0.206867212789583D+01
ATOM_X_UPDATED:ANGSTROMS[0045]=
 -0.2362742330428  1.2076860520679   0.0006580242274
  1.1567724743487  1.2061052290361   0.0025073435799
 -0.9379464484841  0.0002254049652  -0.0035336913070
 -0.2360571644866  -1.2079445677694   0.0004487013271
  1.8561014202794  0.0000842479067  -0.0017359703551
  1.1566491888500  -1.2061866670086   0.0020791851935
 -2.4295803989145  -0.0000096339902  -0.0041027546583
 -0.7786495086546  2.1500927645799   0.0045728198213
  1.7004127002822  2.1489946748618   0.0025170468353
 -0.7786154980711  -2.1501296301080   0.0038901321221
  2.9426450952995  0.0000230534883  -0.0045177561891
  1.7004420303895  -2.1490160047802   0.0020358782937
 -2.8213301048241  0.0005623088303   1.0242210580526
 -2.8456588601637  0.8822776298133  -0.5095501761722
 -2.8457291878630  -0.8827669383764  -0.5086038650530
HEAT_OF_FORM_UPDATED:KCAL/MOL=+0.132012176845274D+02
GRADIENT_UPDATED:KCAL/MOL/ANG=+0.910320949274582D+00
ATOM_X_UPDATED:ANGSTROMS[0045]=
 -0.2360865213655  1.2080151493562   0.0011365899251
  1.1567053432487  1.2060017897659   0.0017384885003
 -0.9378991683157  0.0000066067802  -0.0042773974562
 -0.2359641418611  -1.2080658170957   0.0008077190178
  1.8557264188971  -0.0000763116568  -0.0008008697518
  1.1566583478513  -1.2059193555081   0.0014212494373
 -2.4297665924932  -0.0000025520155  -0.0040216844817
 -0.7782589539909  2.1502871637615   0.0041317459683
  1.7003847896161  2.1488126359387   0.0027836340272
 -0.7782332157819  -2.1503183160970   0.0034777376323
  2.9429126105787  0.0000171705623  -0.0042713207304
  1.7004235558820  -2.1488361109650   0.0022871010223
 -2.8211533288455  0.0005604617989   1.0253489105828
 -2.8457457530182  0.8825012000830  -0.5095273788447
 -2.8458079559975  -0.8829844288616  -0.5085718703811
2013-03-24 14:07:26 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

ADFoutput: Toluene.out

SCM File Edit Help Iterations Properties Response Properties Other Properties Section

BOND ORDERS AND VALENCIES

	C 1	C 2	C 3	C 4	C 5	C 6
C 1	3.975087					
C 2	1.445517	3.976853				
C 3	1.423683	0.000591	3.990377			
C 4	0.001492	0.111965	1.423381	3.975087		
C 5	0.001151	1.440240	0.112124	0.001151	3.976162	
C 6	0.111890	0.000617	0.000592	1.445745	1.440118	3.976855
C 7	0.004783	0.006191	1.014806	0.004784	0.001381	0.006187
H 8	0.964050	0.000214	0.000321	0.005095	0.005233	0.000153
H 9	0.000334	0.965665	0.005254	0.000110	0.000351	0.005229
H 10	0.005092	0.000153	0.000321	0.964049	0.005235	0.000214
H 11	0.005214	0.000293	0.000142	0.005216	0.965265	0.000293
H 12	0.000110	0.005235	0.005260	0.000333	0.000350	0.965646
H 13	0.005424	0.000028	0.002460	0.005422	0.002408	0.000028
H 14	0.001858	0.000065	0.000722	0.004491	0.000579	0.000078
H 15	0.004489	0.000078	0.000720	0.001854	0.000576	0.000065

	C 7	H 8	H 9	H 10	H 11	H 12
C 7	3.924655					
H 8	0.000970	0.977148				
H 9	0.000190	0.000508	0.978375			
H 10	0.000969	0.000114	0.000075	0.977147		
H 11	0.000097	0.000103	0.000484	0.000103	0.977696	
H 12	0.000190	0.000076	0.000129	0.000509	0.000485	0.978368
H 13	0.954915	0.000009	0.000001	0.000009	0.000000	0.000001
H 14	0.964588	0.000285	0.000012	0.000018	0.000000	0.000032
H 15	0.964603	0.000018	0.000032	0.000286	0.000000	0.000012

	H 13	H 14	H 15
H 13	0.973624		
H 14	0.001460	0.975386	
H 15	0.001459	0.001197	0.975389

TOTAL CPU TIME: 0.09 SECONDS

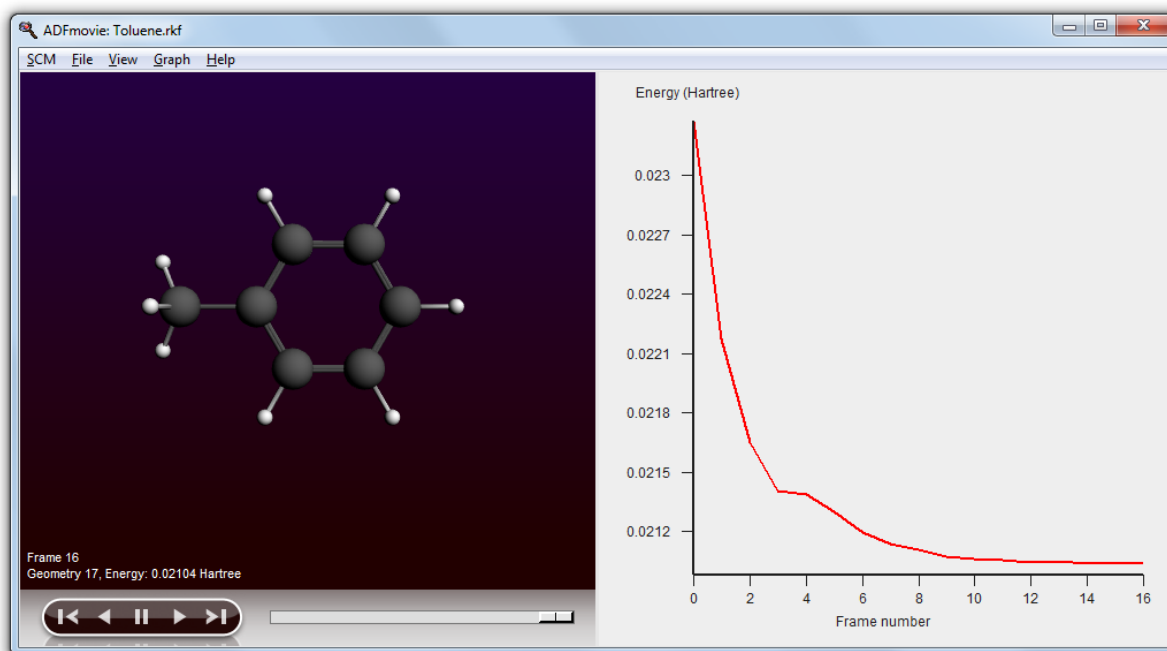
== MOPAC DONE ==

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

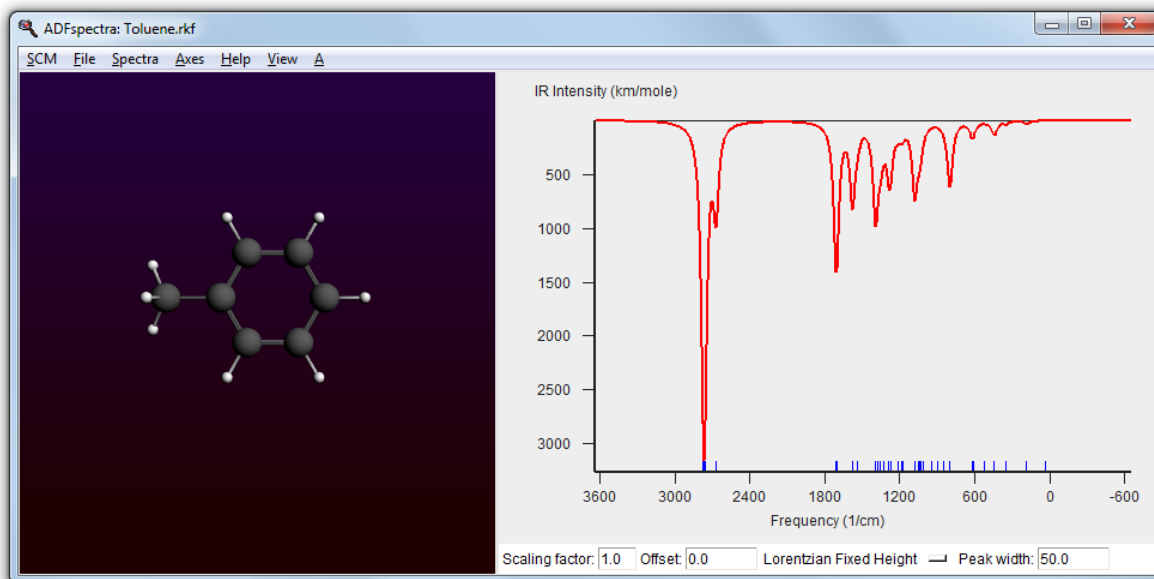
Answer 'Yes' to save your setup

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,

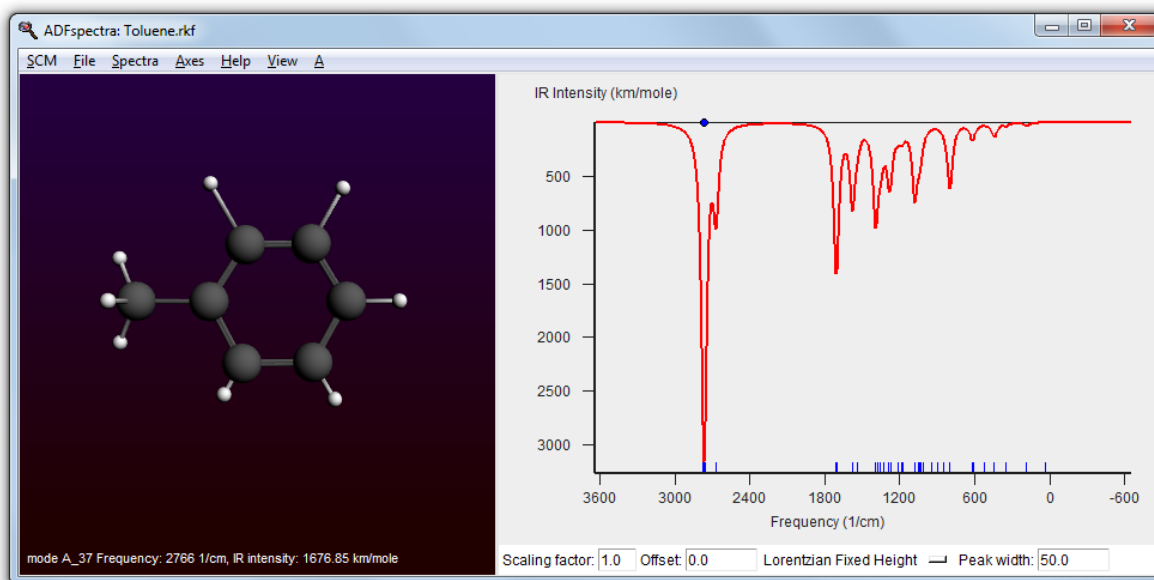
SCM → Spectra

The calculated IR spectrum will be shown:



Right-click on the peak around 2762 cm^{-1} , and select mode A_37 (with the maximum intensity)

The selected mode will be shown:



Browse through the normal modes using the left and right arrow key

Try the alternative method:

In ADFspectra: tear off the A menu by selecting the dashed line (**A** → ----)

Use the torn-off menu to examine some more modes

SCM → Quit 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:

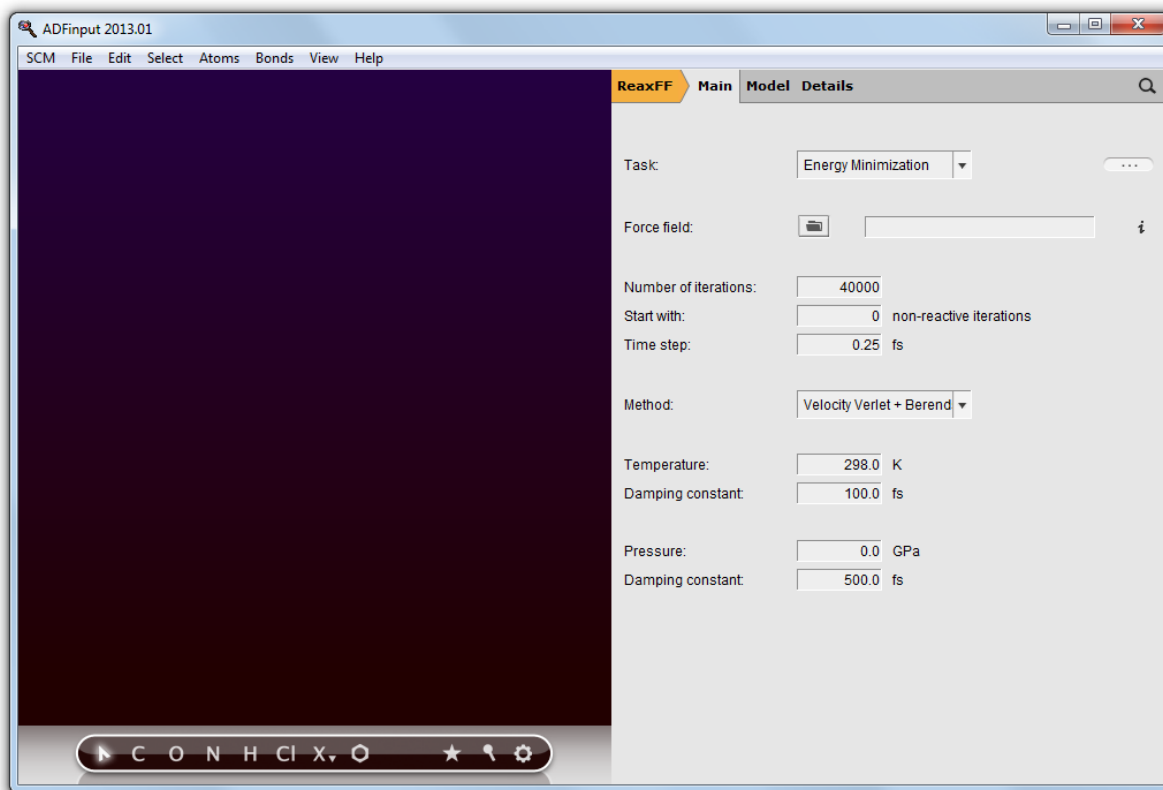
- create a simple mixture (methane and oxygen)
- set up to burn it quickly (set up your ReaxFF simulation)
- burn it: perform the actual ReaxFF simulation
- visualize what is happening during and after the simulation

Step 1: Start ReaxFFinput

Start ADFjobs

SCM → **New input**

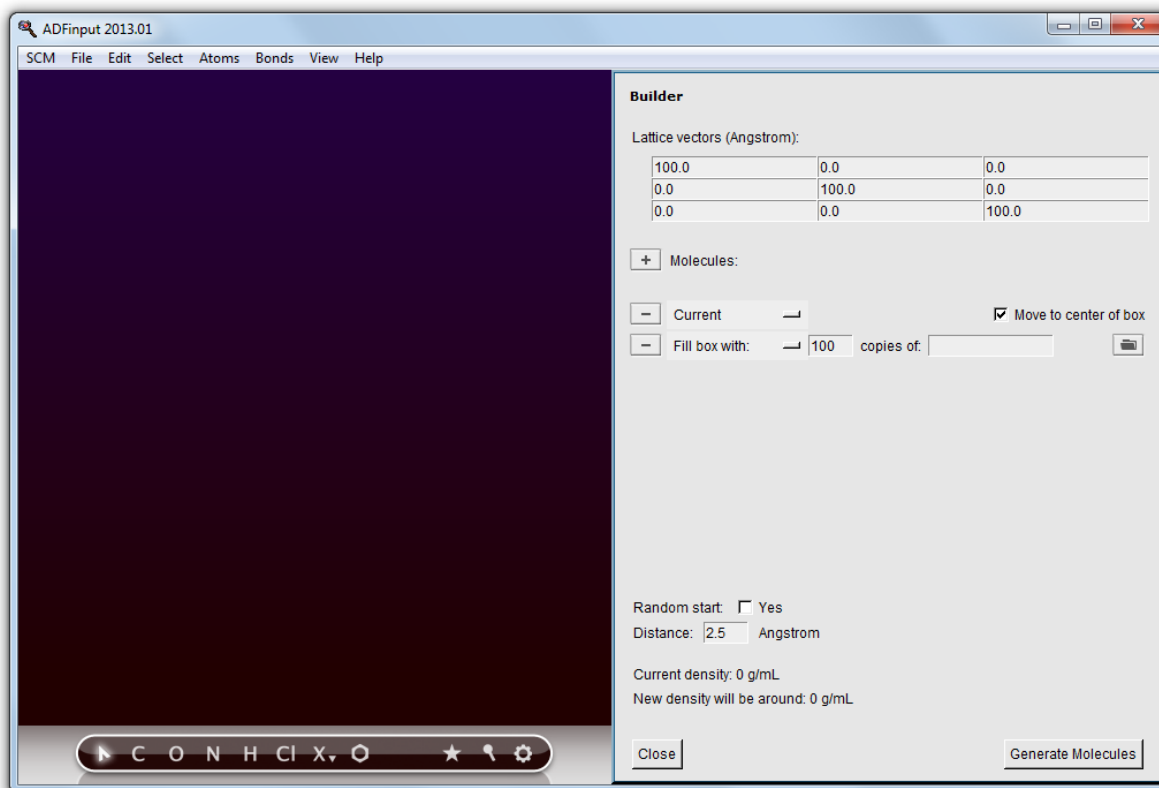
Switch to ReaxFF mode (panel bar **ADF** → **ReaxFF**)



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

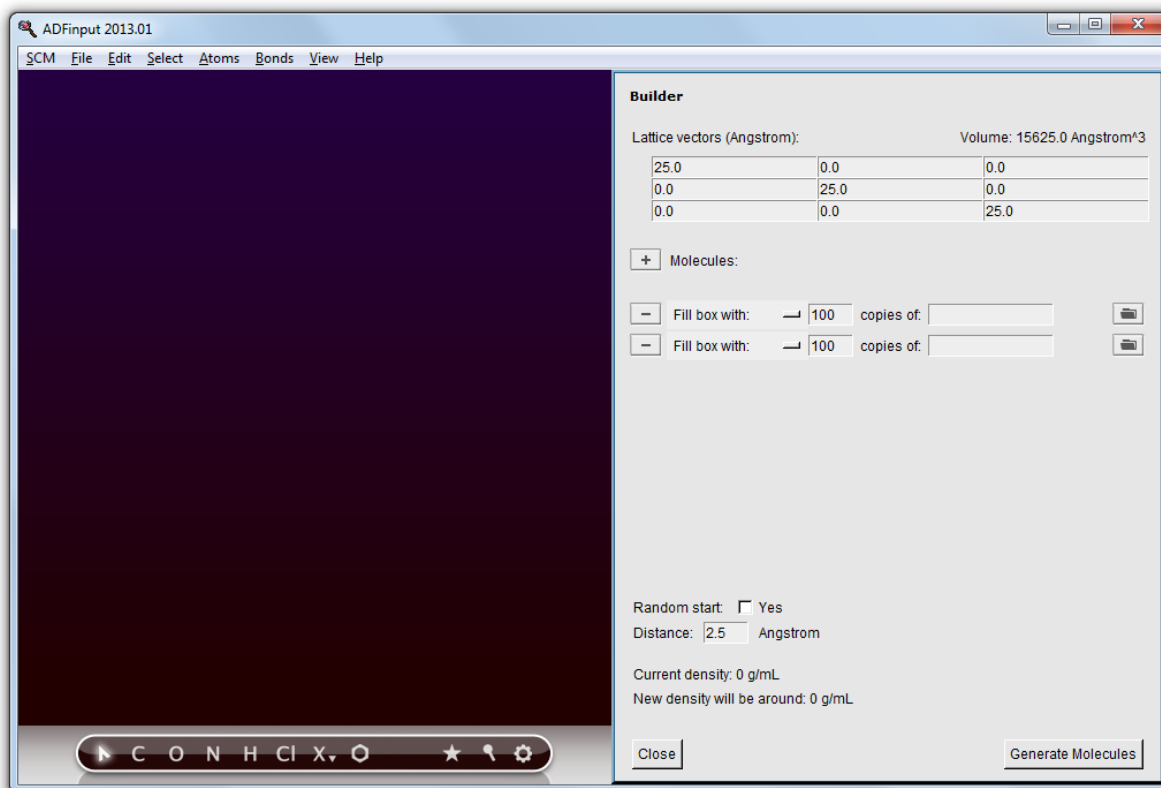


The Builder allows you to build your system, and set some things like the cell vectors that define the computation cell. ReaxFF always uses periodic boundary conditions. The default cell is a cube with sides of 100 Angstrom.

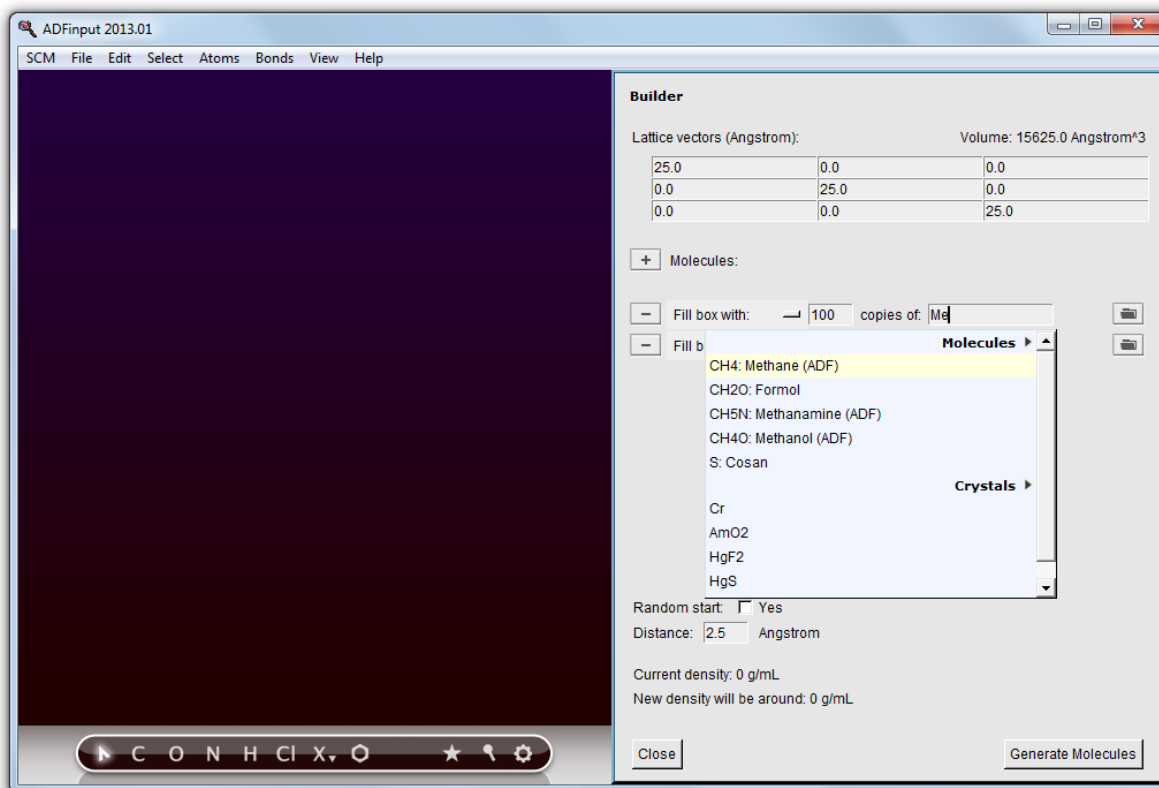
You can use the Builder to add many molecules, randomly distributed. In the list of molecules to be added the Current molecule is already present. If you have any molecules already, the new molecules will be added. Right now we have no molecules yet, so we can remove that entry.

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



Click in the entry field of the first line
Type 'me' (without the quotes) to search for methane



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

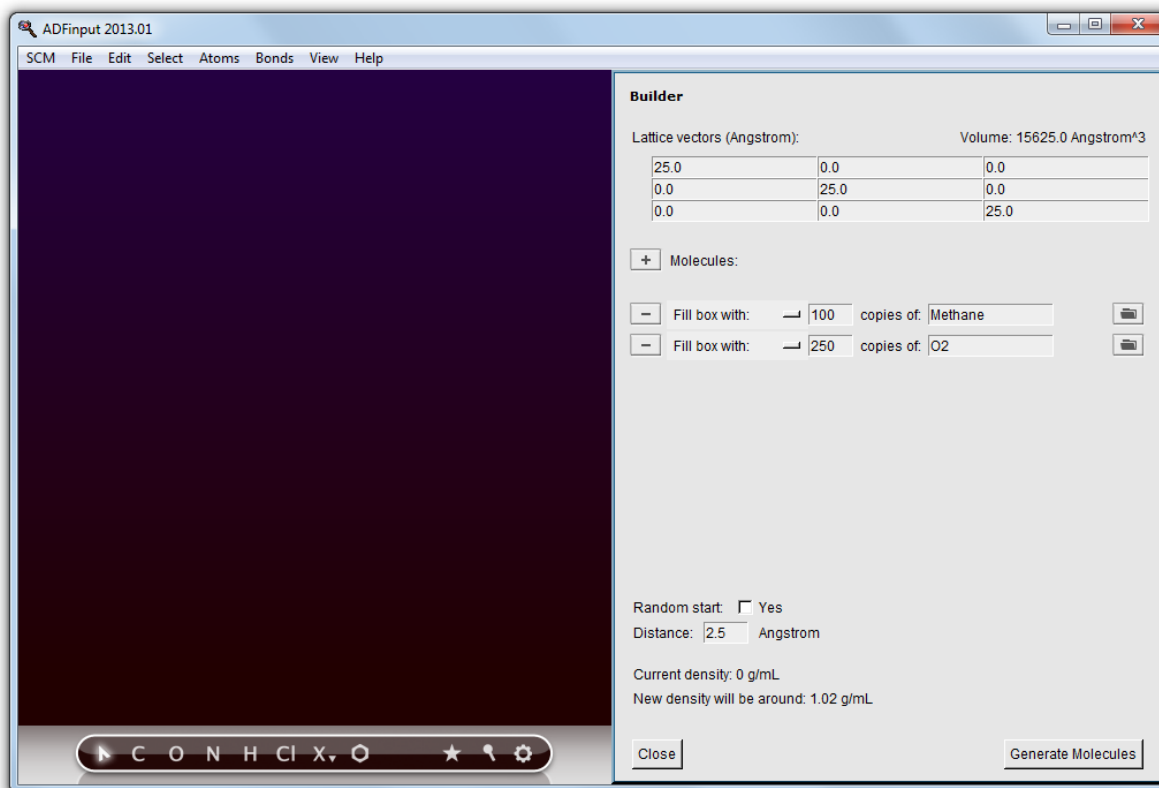
Click in the entry field of the second line

Type 'o', to search for O2

Select the 'O2 (ADF)' match

Change the 100 copied of O2 into 250 copies

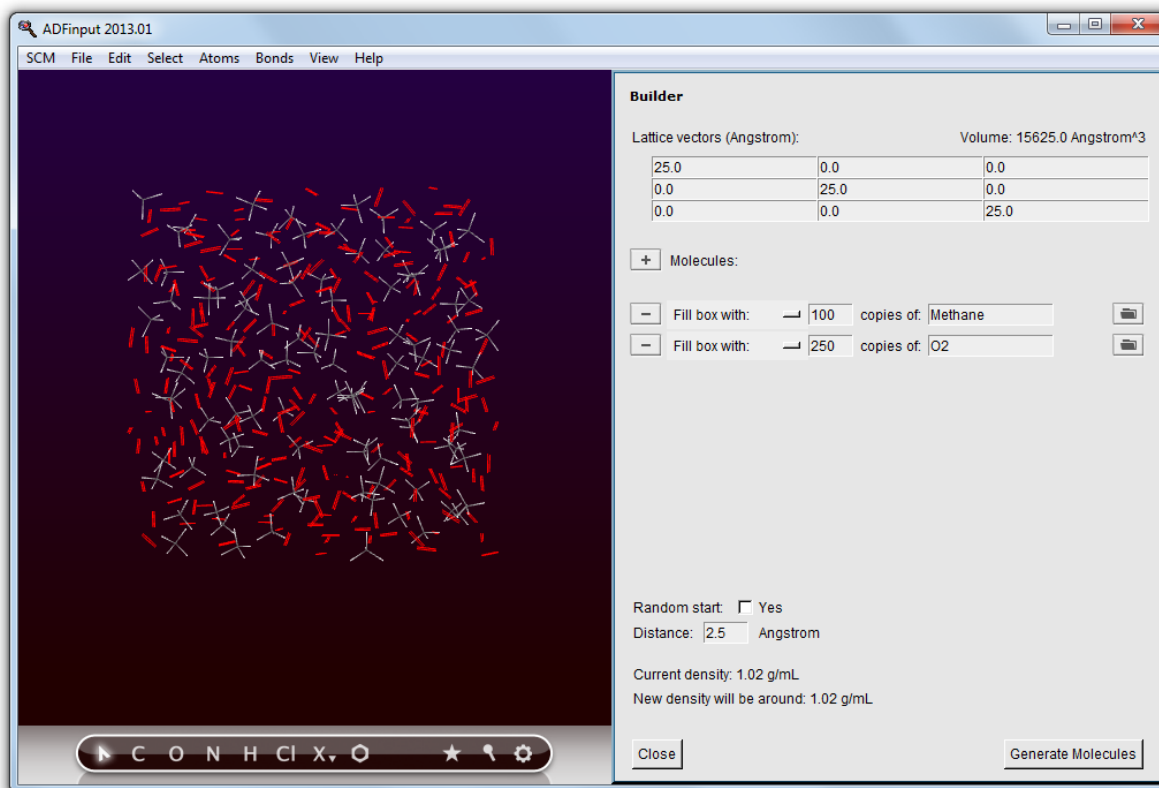
You now have specified how the builder should build your system: 100 methane molecules with 250 oxygen molecules added.



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



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.

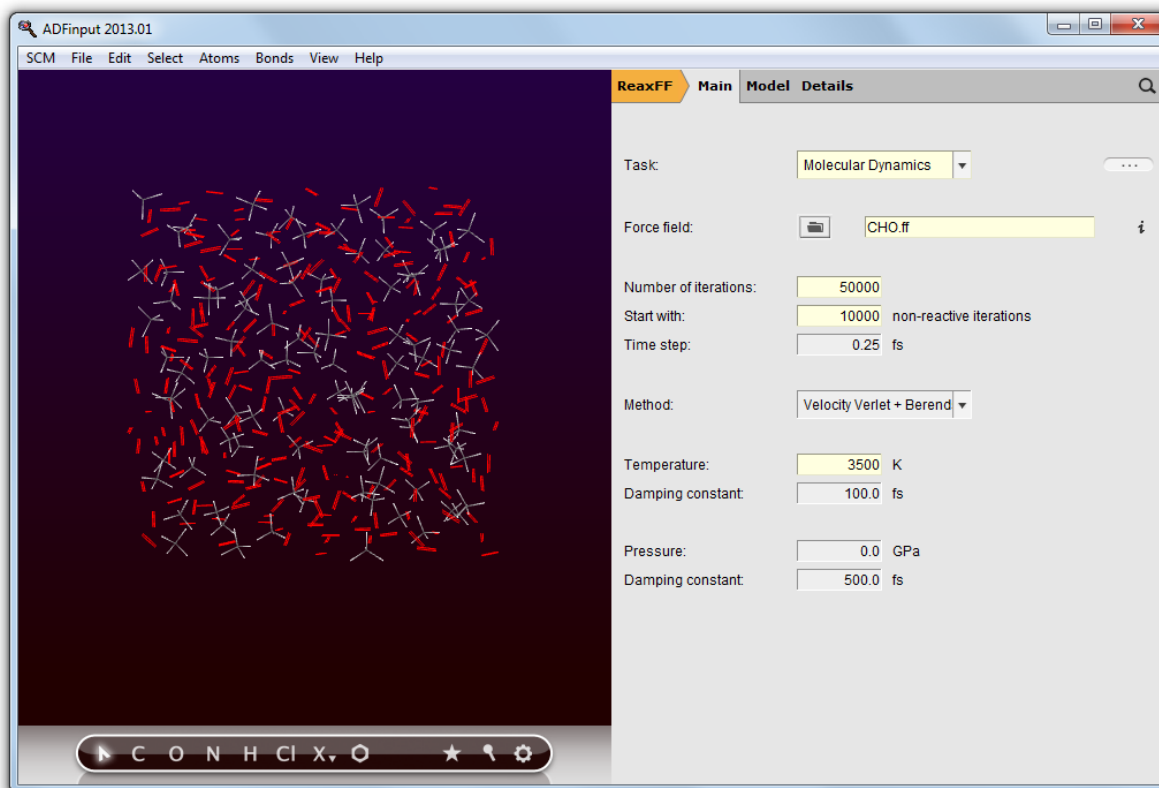
Select the 'Molecular Dynamics' task
Click the 'i' on the right side of the Force field line

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



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'

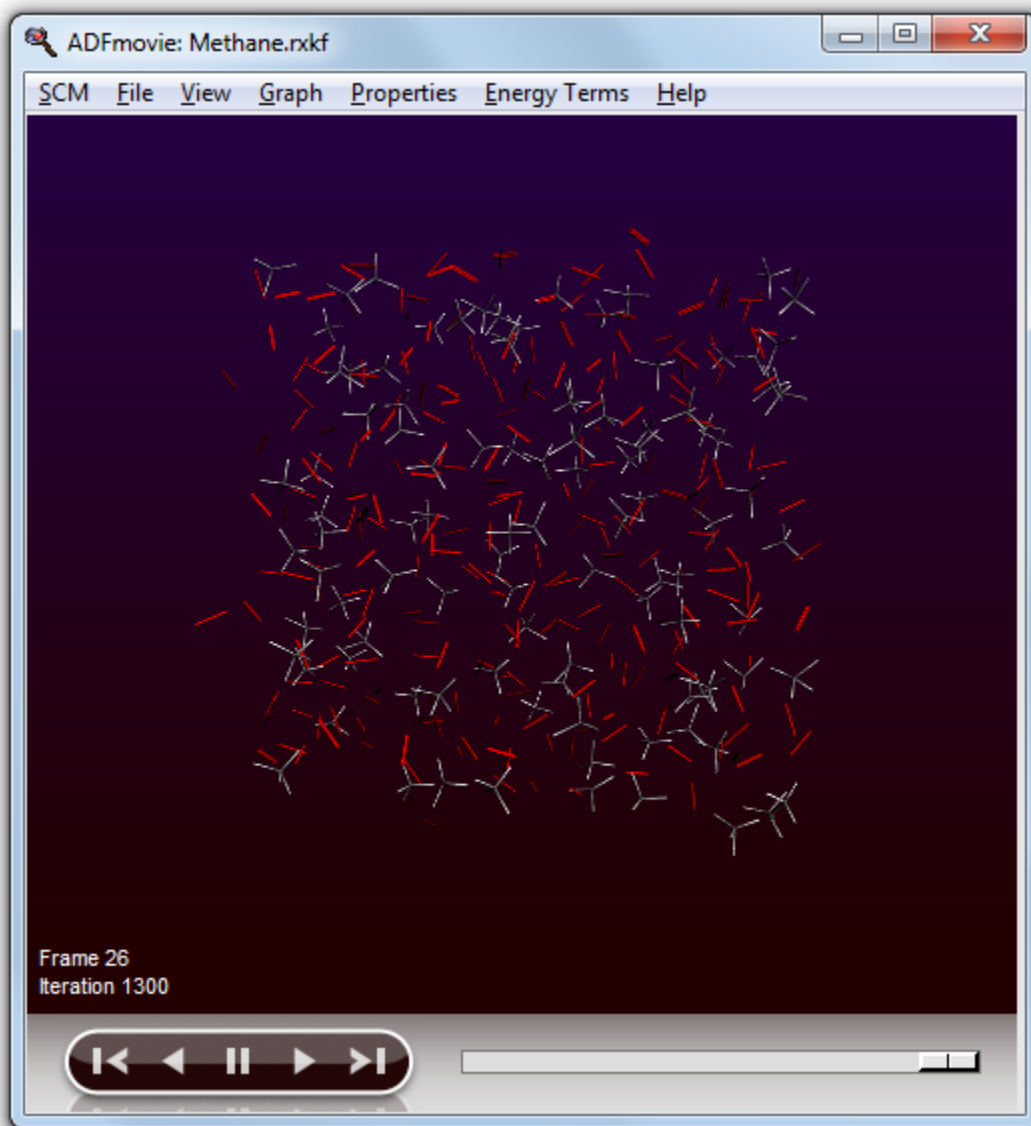
ADFjobs should come to the foreground, and your job should be visible at the top. On the right side you can see that the job is running (this is indicated by the gear-icon). When running, also a window will appear showing the progress of your simulation (the logfile):

Iteration	Nmol	Time (fs)	Epot (kcal)	Vol (A^3)	T (K)	Pres (MPa)	Dens (kg/dm3)
0	350	0.00	-73853.04	15625.00	3500.00	0.00	1.02
50	350	12.50	-71385.09	15625.00	2682.58	0.00	1.02
100	350	25.00	-73141.52	15625.00	3307.45	0.00	1.02
150	350	37.50	-73925.58	15625.00	3611.15	0.00	1.02
200	350	50.00	-74687.56	15625.00	3892.66	0.00	1.02
250	350	62.50	-74030.54	15625.00	3692.65	0.00	1.02
300	350	75.00	-72979.33	15625.00	3350.24	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:

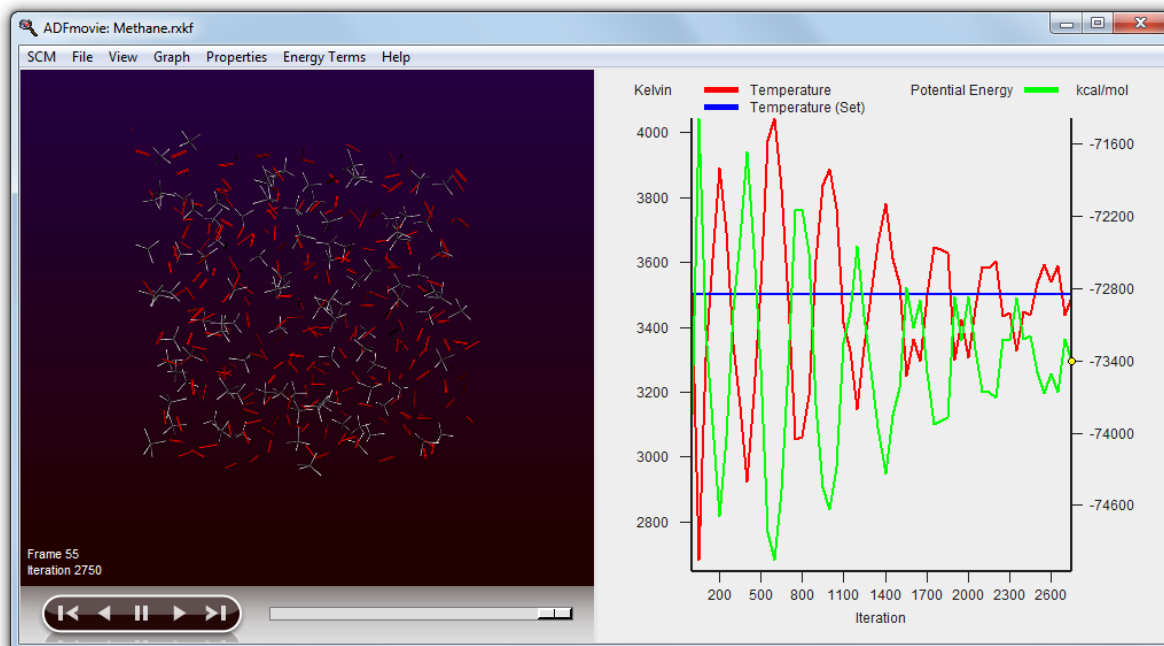
In the ADFmovie window:

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 axis. The other axis 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.

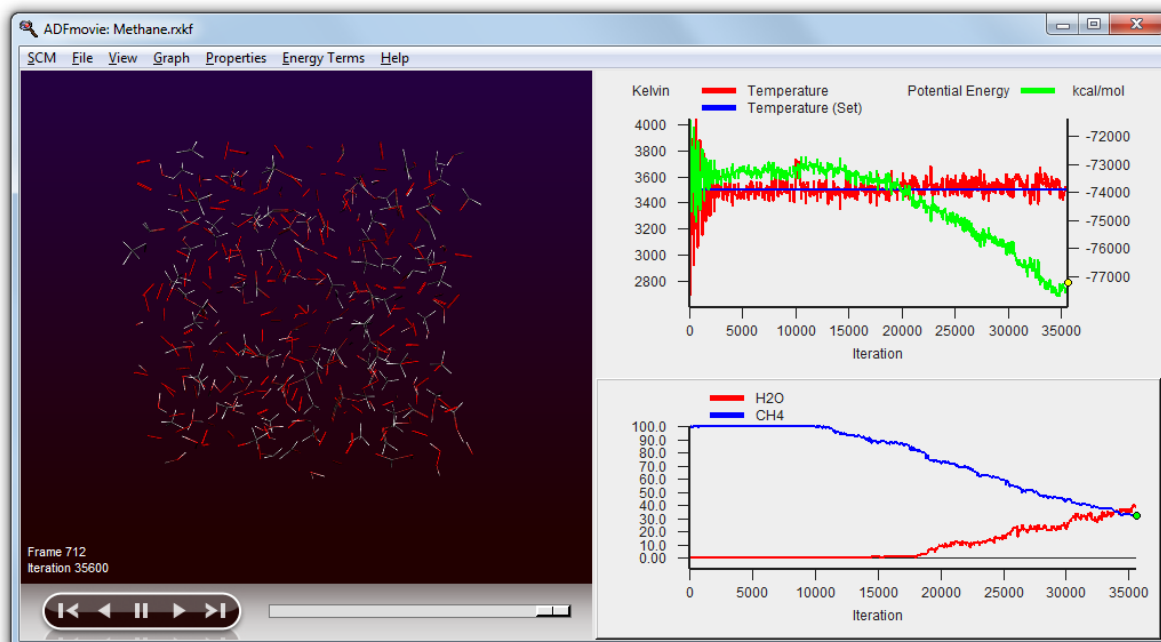
Click on the temperature curve, move around in the movie
 Jump to the end of the movie to follow the progress

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.

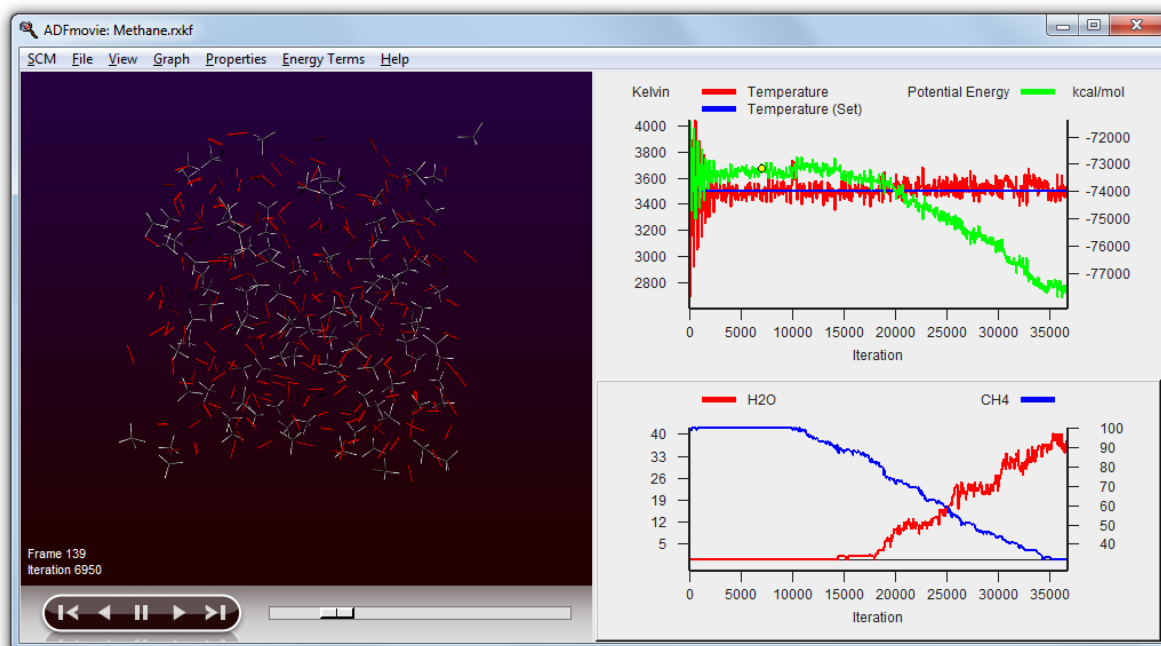


Obviously, no reactions take place in the first 10000 iterations.

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



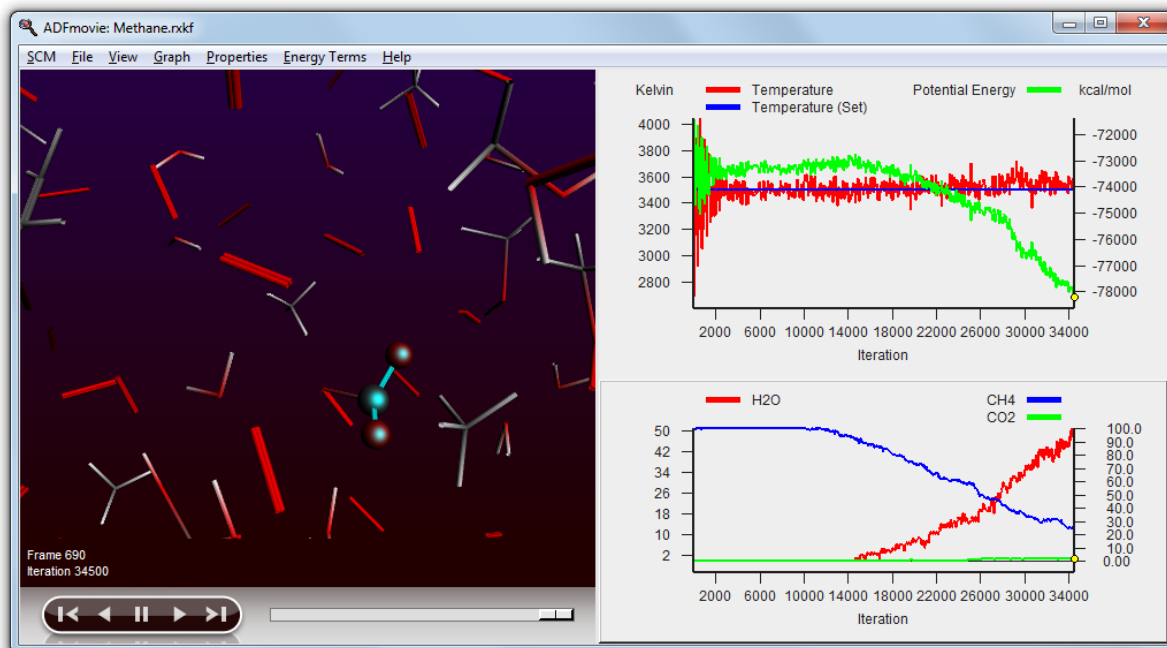
Clicking on the curve also had two other effects (besides making it the active curve): you jumped to the iteration in the movie corresponding to the point where you clicked, and the molecules that belonged to that curve are selected.

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

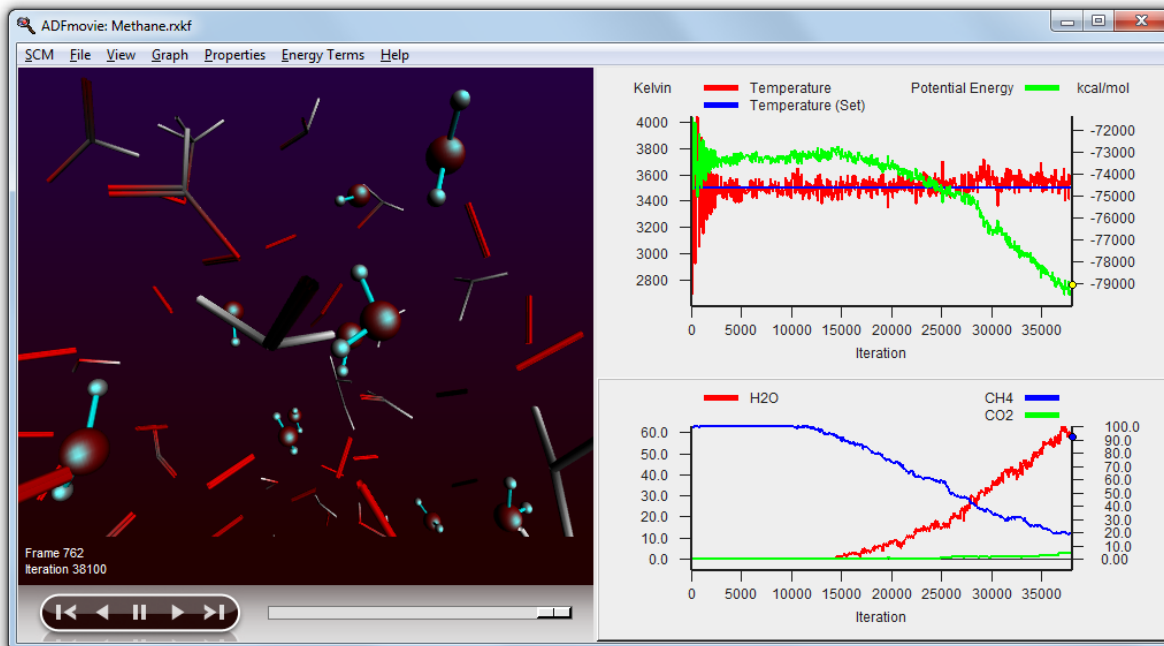
Use the **View** → **Fly To Selection** command a few times



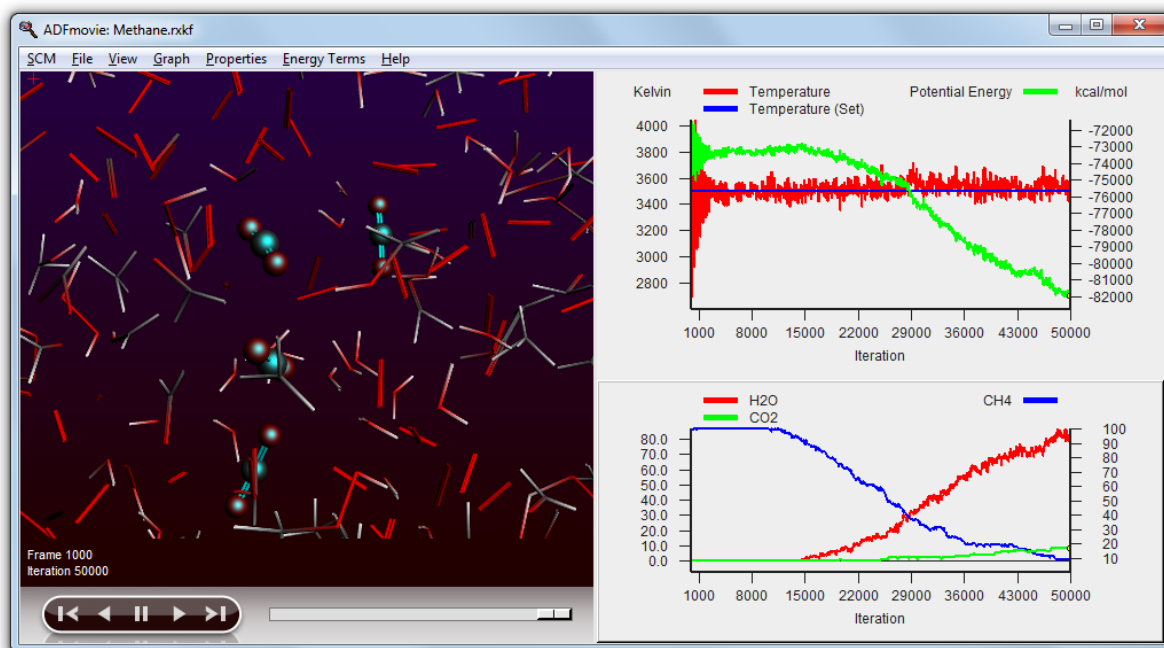
When you now go forward or backwards in time, it is easier to see how the reactions actually take place. Note that the atoms remain selected, even if they are no longer part of a CO2 molecule. In a similar way you can focus on H2O produced:

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 → Quit** 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** → **New input** menu command

Switch to ReaxFF mode (panel bar **ADF** → **ReaxFF**)

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**

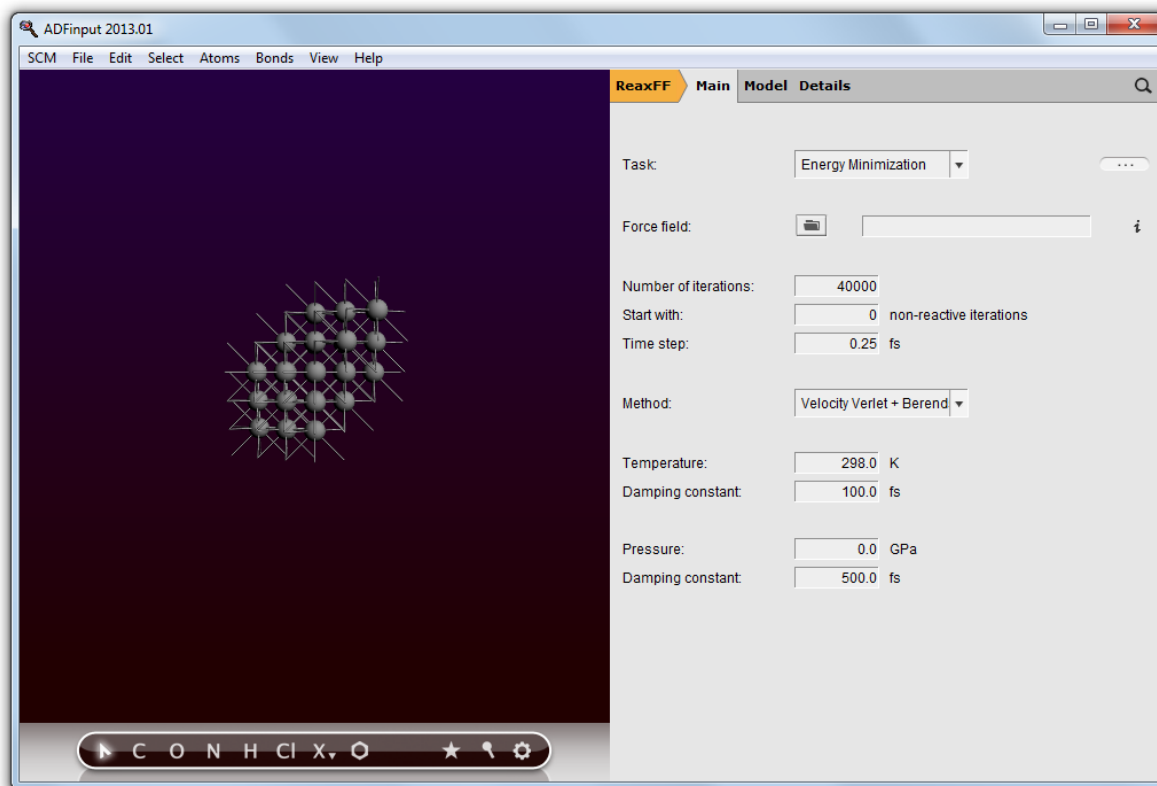
In the dialog that appears:

Select the preset 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.



Now create the surface:

Edit → **Crystal** → **Generate Slab...**

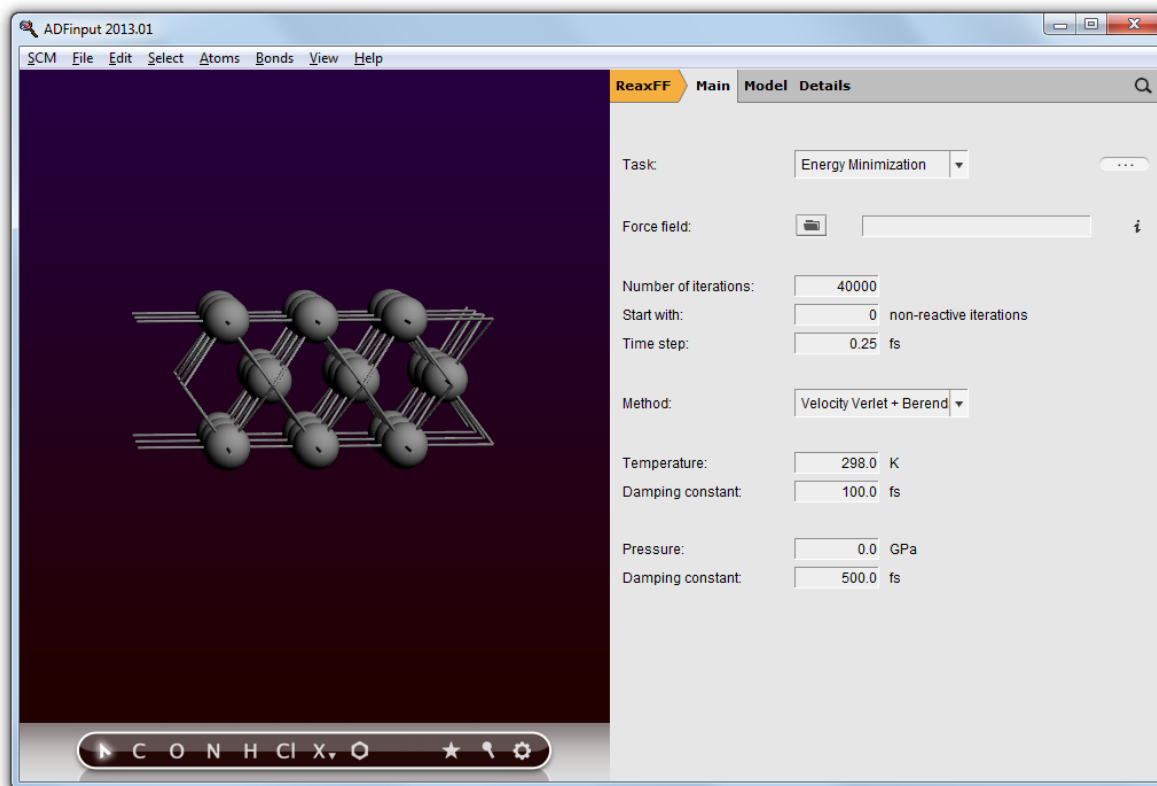
In the Dialog window:

Check the 'cartesian' check box

Set the number of layers to 3

Click OK

View → **Periodic** → **Repeat Unit Cells**



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:

Turn off periodic view:

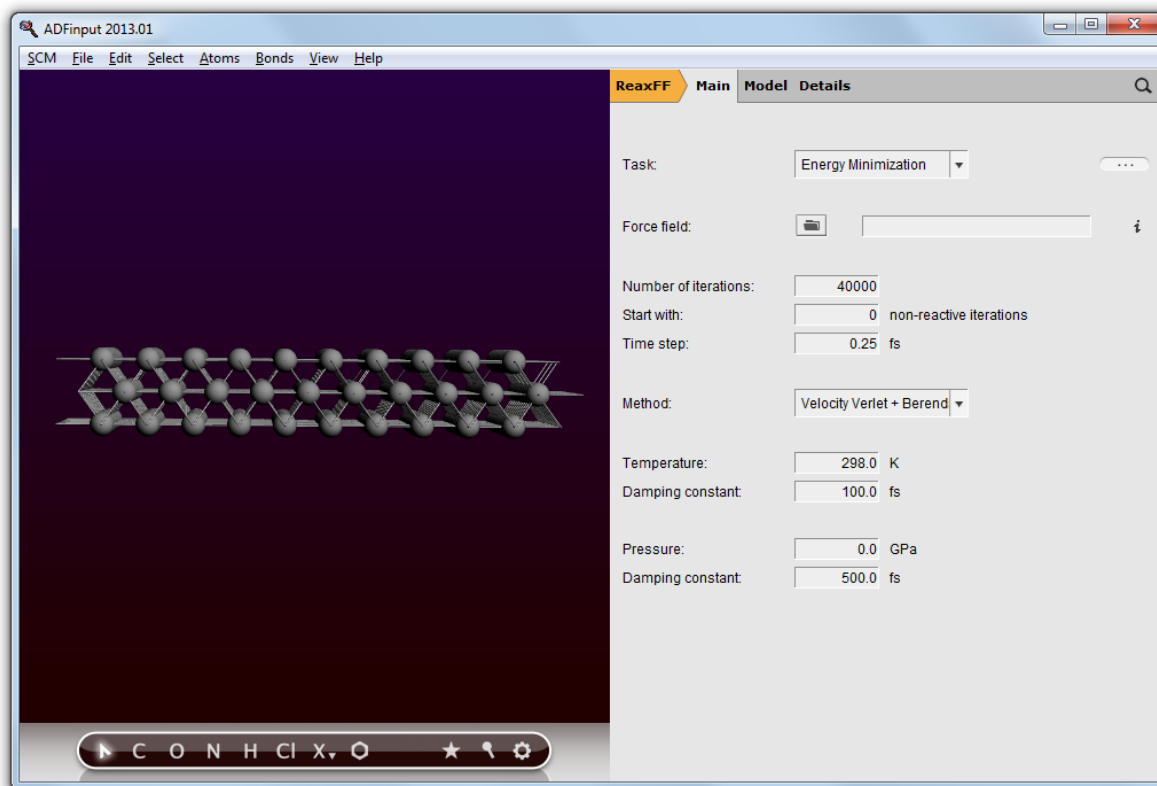
View → **Periodic** → **Repeat Unit Cells**

Edit → **Crystal** → **Generate Super Cell...**

Put 10, 10, 1 on the diagonal

Click OK

Rotate get a better view

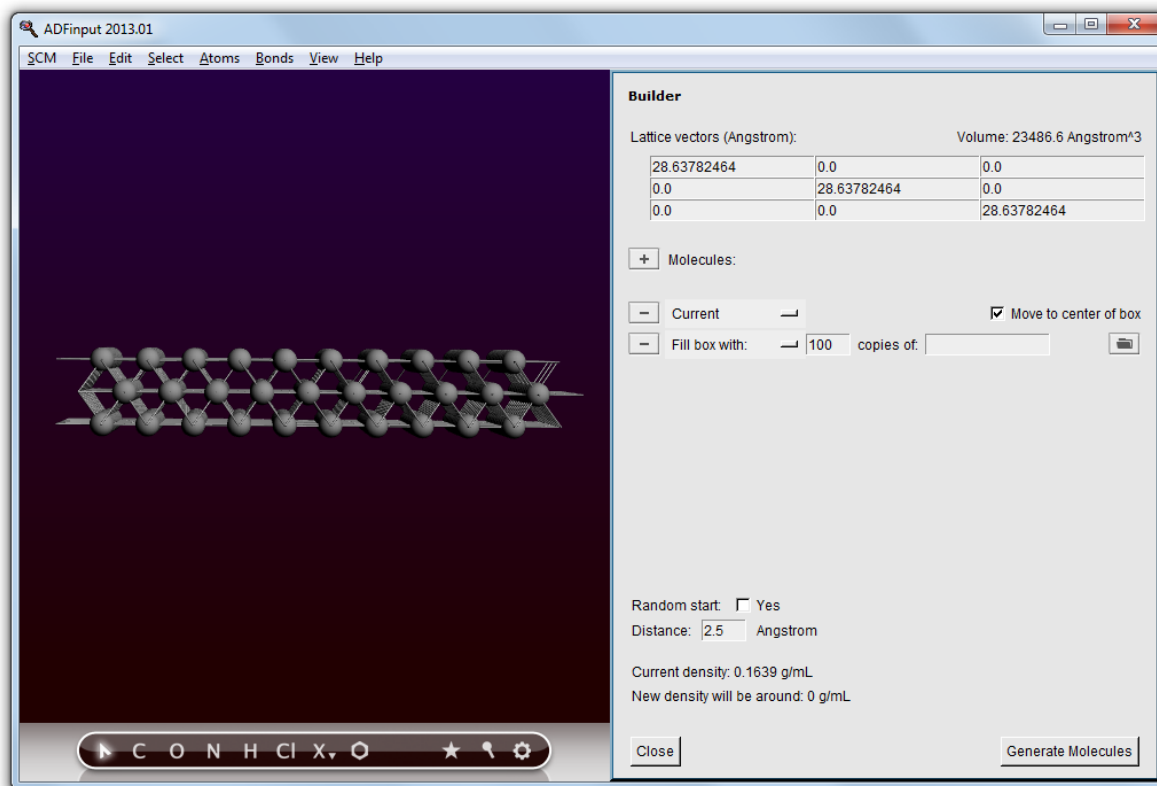


Now we have a real slab of aluminum, three layers thick. Note that the Generate Super Cell command adjusted the lattice vectors to match the new unit cell.

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



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

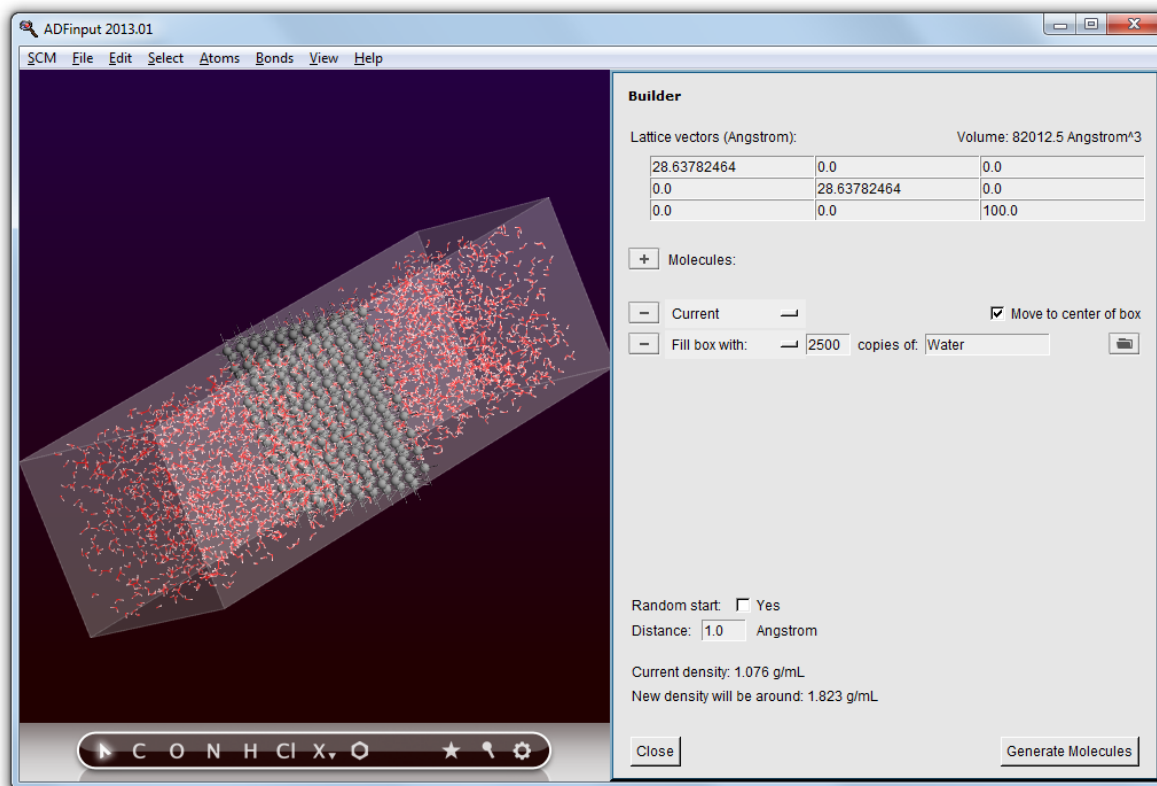
Type 'wa' in the line with 'Fill box with'
 Select 'Water (ADF)' from the search results
 Specify 2500 copies

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



Step 4: Set up the simulation, including a temperature regime

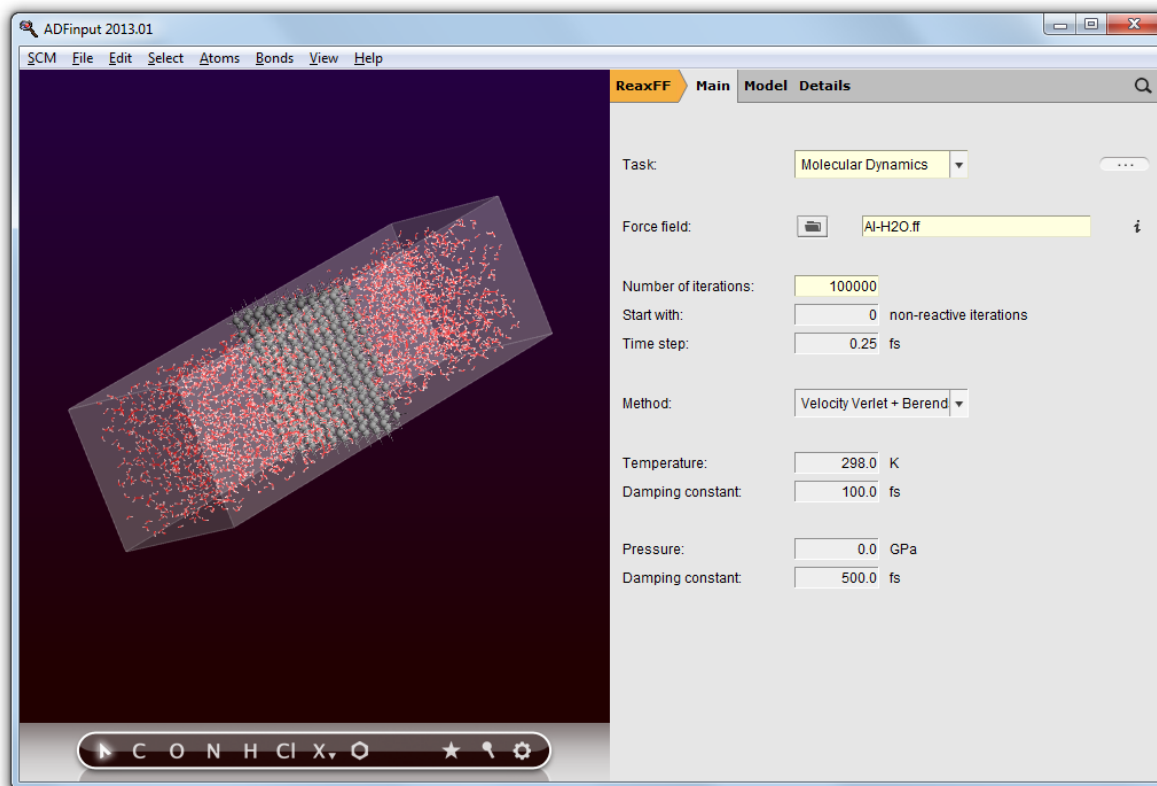
Now we will set up the MD-simulation. We will use the AI-water force field:

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 Other.. -> AI-H2O.ff

Specify 100000 iterations

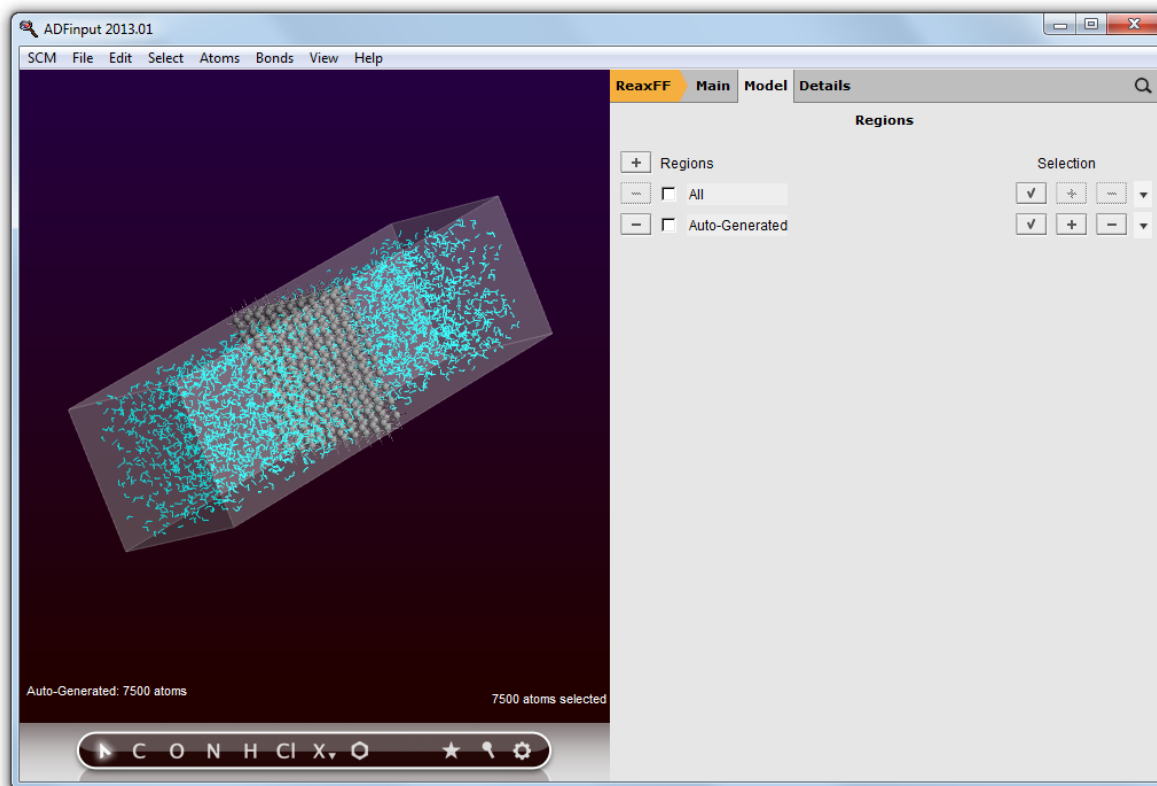


In the simulation we would like something to happen. So we will use a high temperature for water, but try to keep the aluminum cool. Also, we will start with a low temperature MD to relax the initial set-up. This can all be accomplished using a temperature regime, specifying different temperatures for 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**

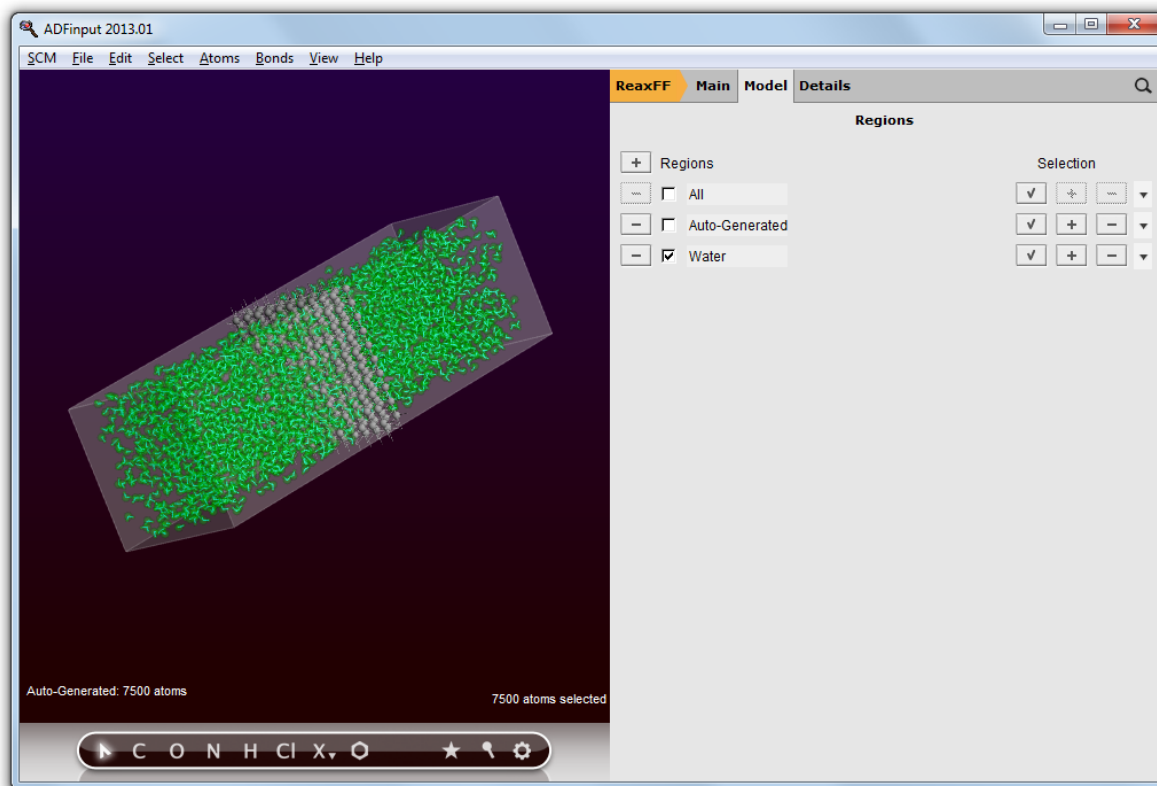
Click once on the select button (the V like button) in the Auto-Generated region



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) were automatically added to the new region. The + and - buttons add or remove the selected atoms to a region.

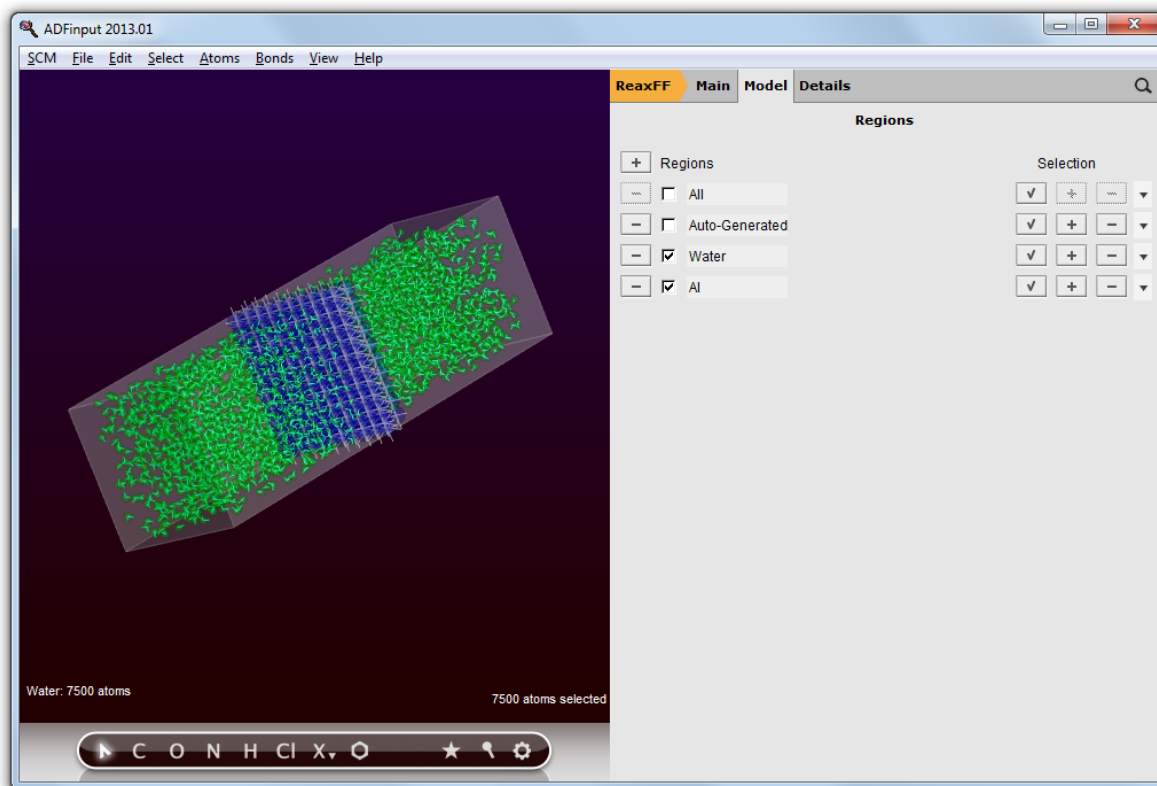
Click in the drawing area so it has focus (otherwise the next will select the region name)

Select → Select All

Press the + button in front of the Regions label again to add a new region (containing everything as everything was selected)

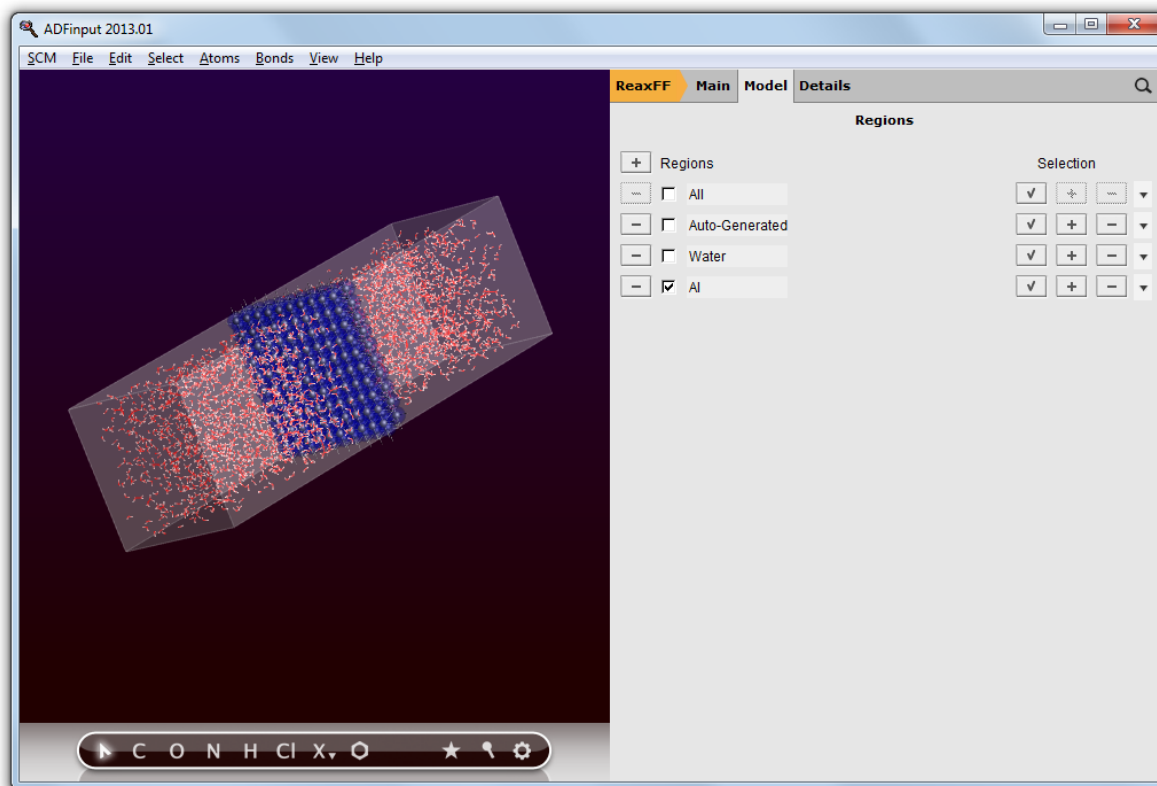
Change the name Region_3 to Al

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:

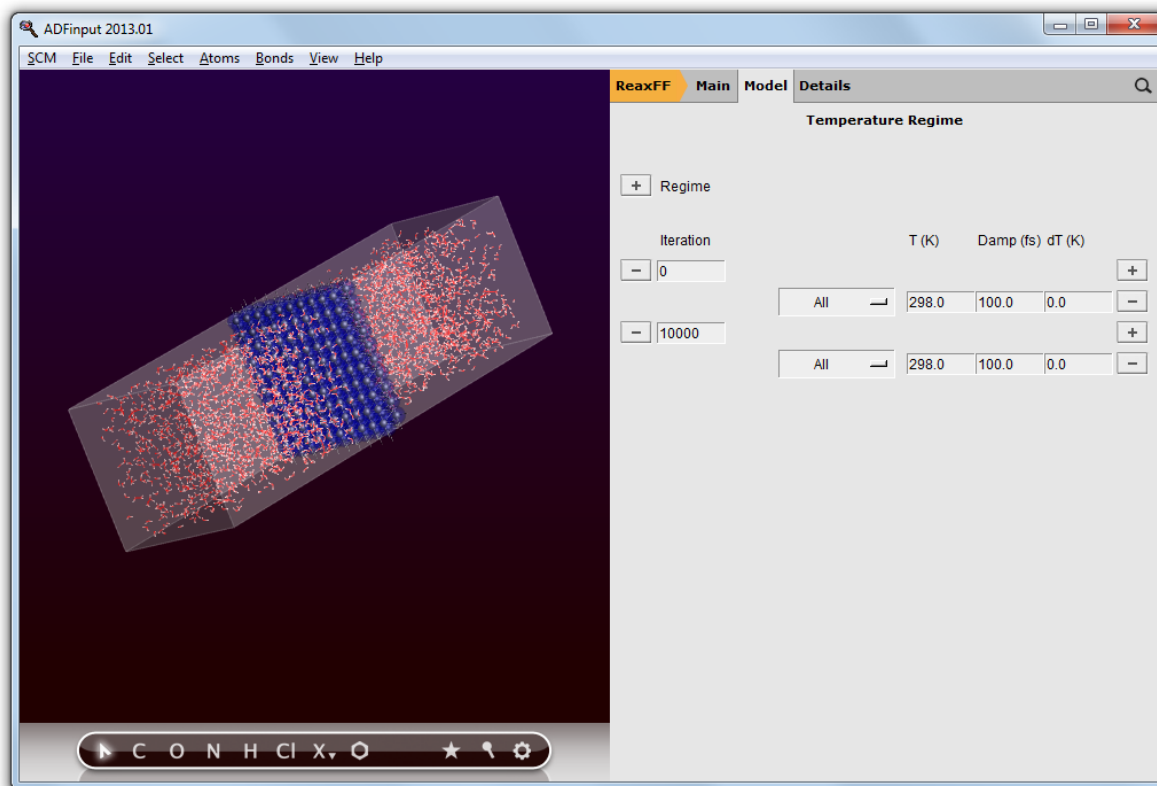
Uncheck the check box at the left of the Water region line
Press the triangle on the right side of the Al region line,
and choose for the 'Balls And Sticks' visualization option



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



At iteration 0, we start with an MD simulation at $T=0$ K:

change the first 298.0 to 0.0 (note this applies to region All which is everything)

At iteration 20000, we set the water temperature to 2000 K, while keeping the aluminum temperature at 0 K:

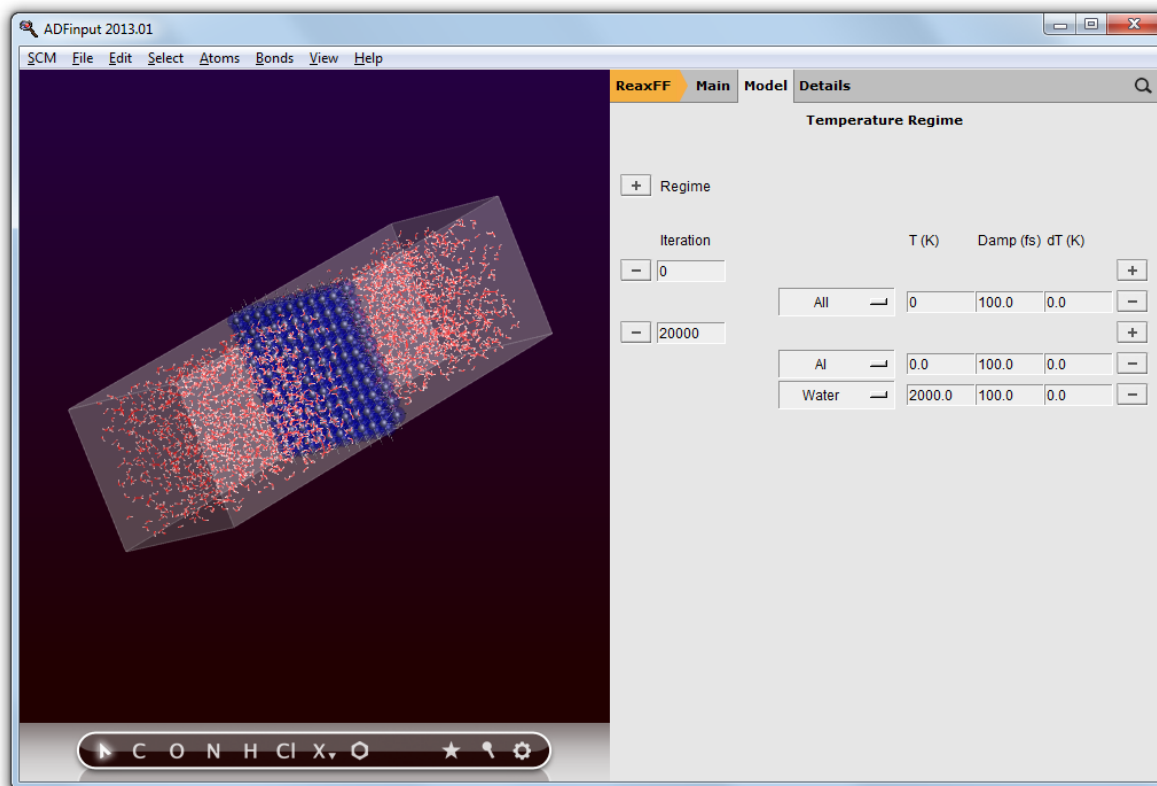
Change the number of iterations from 10000 to 20000

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 0.0 K

Change the second All on the 20000 step to Water, and change its temperature to 2000.0 K

Your temperature regime setup should look like this:



Step 5: Run the simulation

Now we can run our set up:

File → Run

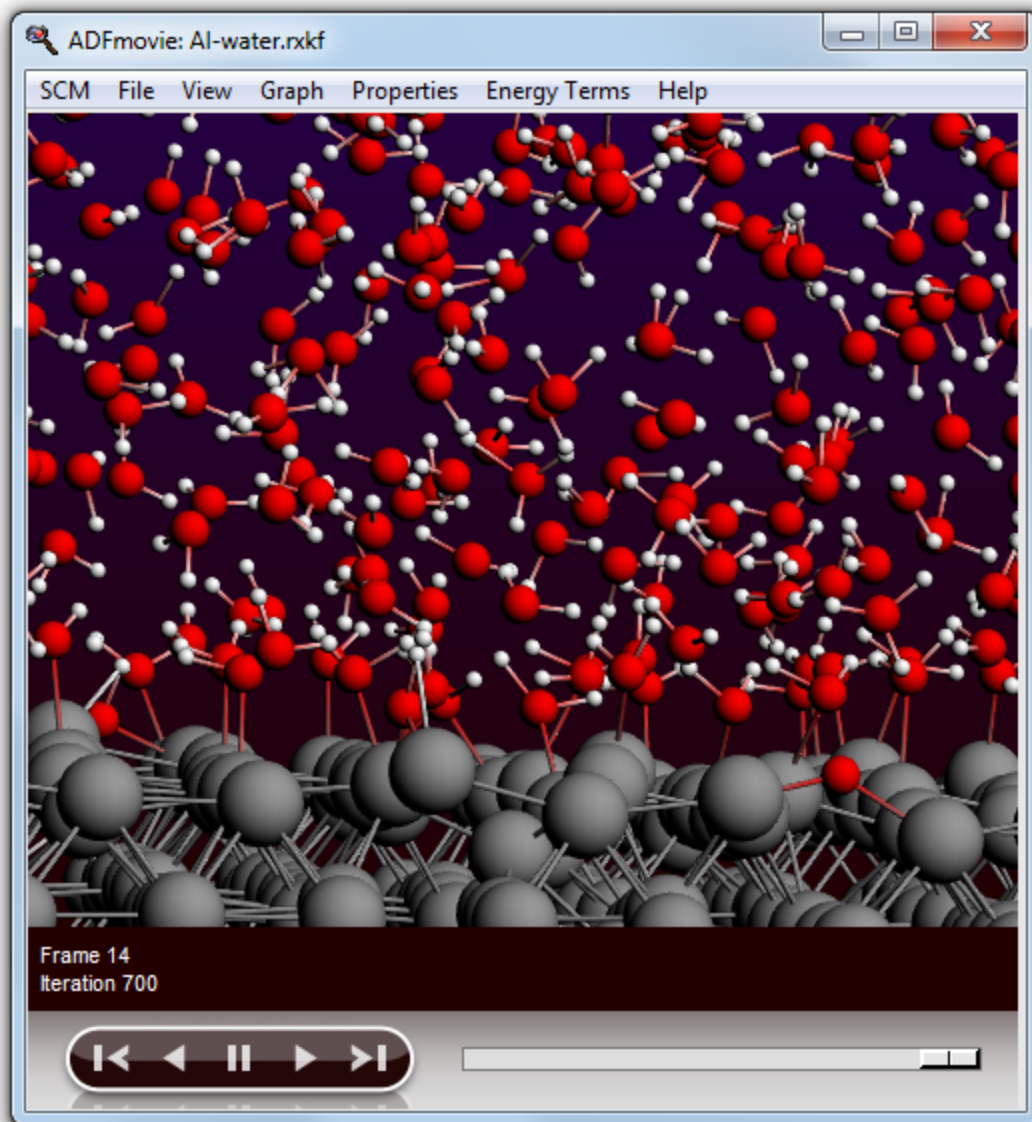
When asked to save, specify Al-water as filename

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 → Quit 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 compound 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 compound 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 compound 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.

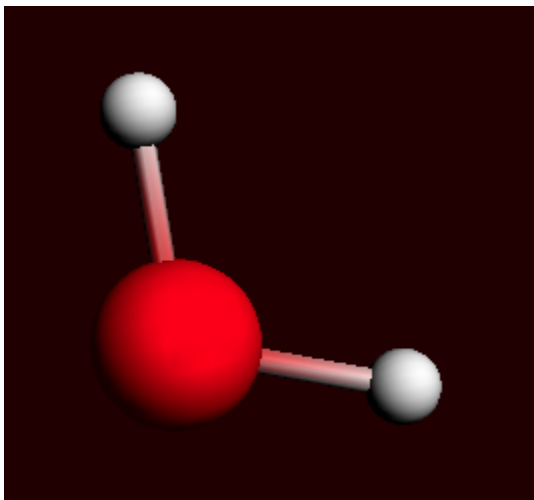
Select the **SCM** → **New input** menu command.

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

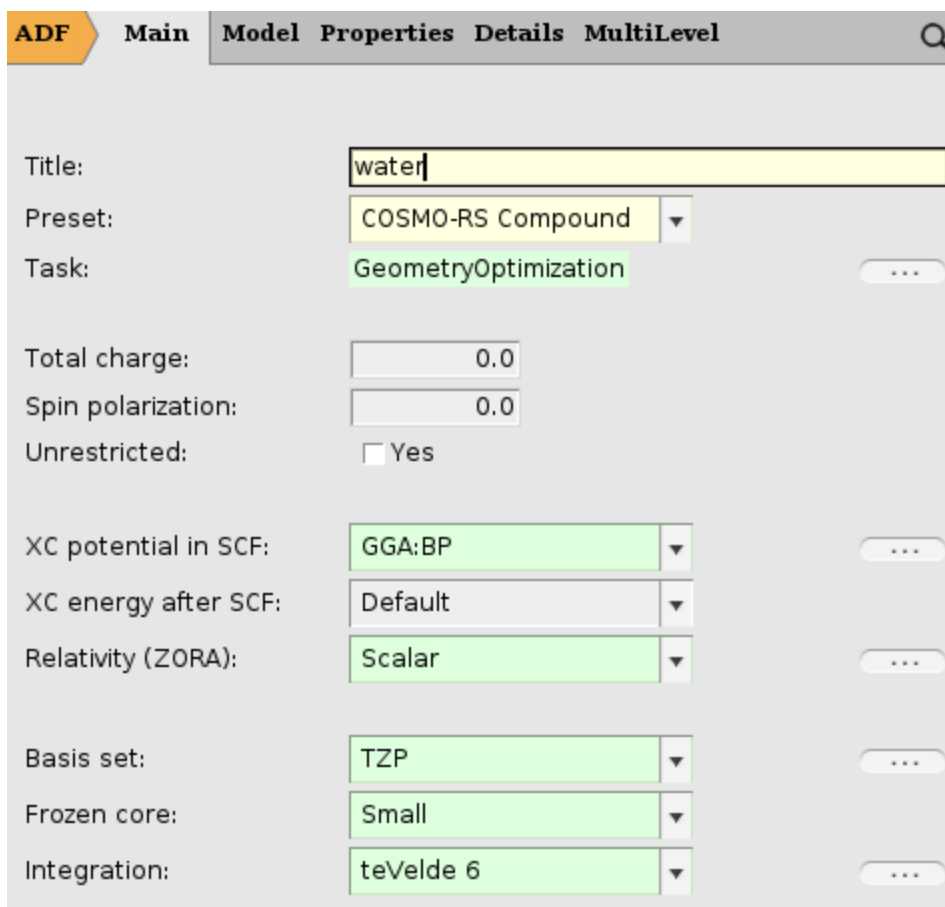
Your water molecule should look something like this:



Step 3: ADF COSMO result file

The next step is to optimize the gas geometry using ADF, and perform the ADF COSMO calculation at the optimized gas phase geometry.

Enter a proper title in the Title field (like 'water')
Select **Preset** → **COSMO-RS Compound**



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 Hamiltonian, 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. Note that these settings were used for the optimization of the COSMO-RS parameters.

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 and ADF-COSMO calculation are 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, and the ADF COSMO calculation has been performed. The result 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.

Expert details

If you do not want to optimize the geometry, set 1 to the number of geometry iterations in **Details** → **Geometry Convergence**. More details on parameters used in the COSMO calculation can be found in **Model** → **Solvation**, and **Details** → **COSMO**. See also [the COSMO-RS manual](#).

Step 4: 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**

The screenshot shows the 'Model Properties Details' window in the MOPAC software. The 'Mopac' tab is selected. The 'Task' dropdown is set to 'GeometryOptimization'. The 'Method' dropdown is set to 'PM7'. The 'Solvation method' dropdown is set to 'COSMO-CRS'. The 'Periodicity' dropdown is set to 'None'. The 'Total charge' and 'Spin polarization' input fields both contain '0.0'. The 'Unrestricted', 'Mozyme', and 'Sparkles' checkboxes are all unchecked.

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.

Expert details

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.

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:

```
PM7 EPS=9999.9 RSOLV=1.3 COSWRT NSPA=362
```

Tutorial 2: COSMO-RS overview: parameters and analysis

Step 1: Start ADFcrs

For this tutorial it is convenient to start with an empty directory, for example, with the name Tutorial.

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:

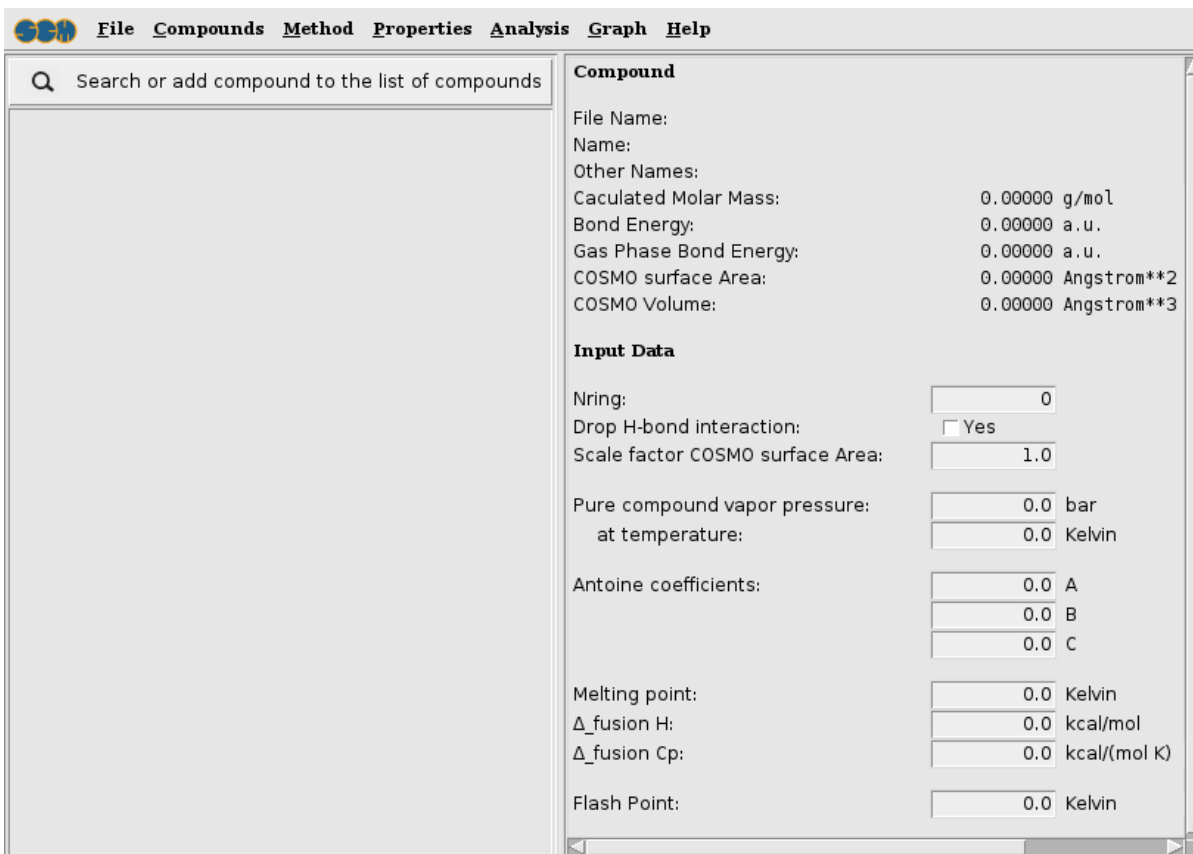
```
double click the ADFcrs icon on the Desktop
```

On Macintosh, use the ADF2013.01 program to start ADFcrs:

```
double click on the ADF2013.01 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
```



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 **List of Added Compounds**, which is the window you will get if you select **Compounds** → **List of Added Compounds**.

If you run the COSMO-RS GUI the first time, you will be asked if you would want to download and install the COSMO-RS compound database:

Download and install the COSMO-RS compound database?

If you have the permission to write such directory (in \$ADFHOME/atomicdata/ADFCRS-2010), it is recommended to download this COSMO-RS compound database. You may need to have administrator privileges to do so. On the other hand, for this tutorial, it is not necessary that the COSMO-RS compound database is downloaded.

Step 2: Add Compounds

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 in the directory \$ADFHOME/examples/crs/Tutorial2. Copy these COSMO result files (water.coskf, methanol.coskf, ethanol.coskf, and

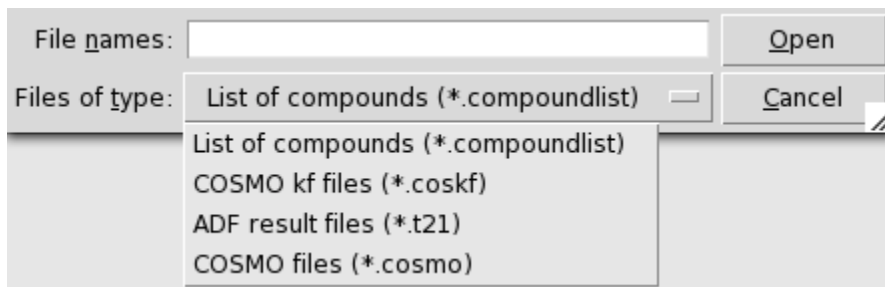
benzene.coskf) to the directory Tutorial. As the name suggests these are COSMO result files of water, methanol, ethanol, and benzene, respectively.

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.

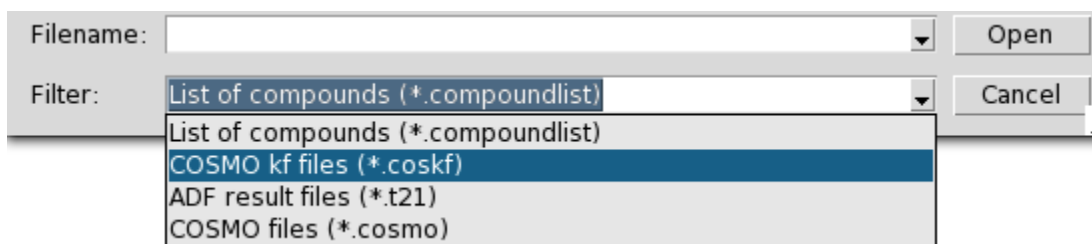
Select **Compounds** → **Add Compound(s)**

List of Added Compounds	
Add Compound(s)	Ctrl A
Install COSMO-RS database...	
Show Selected Compound	Ctrl M
Save Data Selected Compound As	

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 multiple files: benzene.coskf ethanol.coskf methanol.coskf and water.coskf

Click 'Open'

On the right side of the **List of Added Compounds** one finds some data that was written from the last file that was opened, in this case 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.

Compound water

File Name: /tmp/Tutorial/water.coskf
 Name: water
 Other Names: H2O
 Calculated 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 Data

Nring:
 Drop H-bond interaction: Yes
 Scale factor COSMO surface Area:
 Pure compound vapor pressure: bar
 at temperature: Kelvin
 Antoine coefficients: A
 B
 C
 Melting point: Kelvin
 $\Delta_{\text{fusion}} H$: kcal/mol
 $\Delta_{\text{fusion}} C_p$: kcal/(mol K)
 Flash Point: Kelvin

Step 3: 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).

For some properties, like solubility of a solid, one can or one has to include some pure compound properties in the left window of the **List of Added Compounds** for a selected compound.

It is possible to save this pure compound data in as a new COSKF file (or COSMO file).

Click in the left window (in the **List of Added Compounds**) benzene
 Enter '6' without quotes in the 'Nring' field in the right window

Compound benzene

File Name:	/tmp/Tutorial/benzene.coskf
Name:	benzene
Other Names:	C6H6
Calculated 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 Data

Nring:	<input type="text" value="6"/>
Drop H-bond interaction:	<input type="checkbox"/> Yes
Scale factor COSMO surface Area:	<input type="text" value="1.0"/>
Pure compound vapor pressure:	<input type="text" value="0.0"/> bar
at temperature:	<input type="text" value="0.0"/> Kelvin
Antoine coefficients:	<input type="text" value="0.0"/> A
	<input type="text" value="0.0"/> B
	<input type="text" value="0.0"/> C
Melting point:	<input type="text" value="0.0"/> Kelvin
$\Delta_{\text{fusion}} H$:	<input type="text" value="0.0"/> kcal/mol
$\Delta_{\text{fusion}} C_p$:	<input type="text" value="0.0"/> kcal/(mol K)
Flash Point:	<input type="text" value="0.0"/> Kelvin

To save this data in a .coskf file

Click in the left window (in the **List of Added Compounds**) benzene
 Select **Compounds** → **Save Data Selected Compound As**
 Enter the name 'benzene' in the 'Filename' field

If you have followed this tutorial from the start then you will overwrite an existing benzene.coskf file. You will be asked if you want to do that, click 'Yes'. The writing can take some time, especially for larger compounds. During this time the COSMO-RS GUI is not available for other actions.

Step 4: COSMO-RS and COSMO-SAC parameters

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**

Expert option: set COSMO-RS parameters

Select **Method** → **COSMO-RS**

Select **Method** → **Parameters**

ADF COSMO-RS Parameters		COSMO-RS element specific 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			
<input checked="" type="checkbox"/> only H-bond for H, N, O, and F					
<input checked="" type="checkbox"/> use temperature dependent H-bond					
<input checked="" type="checkbox"/> use fast approximation					
<input checked="" type="checkbox"/> 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				
solxlarge	0.99	molar fraction			
ehdeltaT	1.0	Kelvin			
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](#).

Expert option: set COSMO-SAC parameters

Select **Method** → **COSMO-SAC**

Select **Method** → **Parameters**

ADF COSMO-SAC parameters

Use 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	
solxlarge	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](#).

For the rest of the tutorial the COSMO-RS method will be used:

Select **Method** → **COSMO-RS**

Step 5: 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** → **List of Added Compounds**

Click on the left side water

Select **Compounds** → **Show Selected Compound**

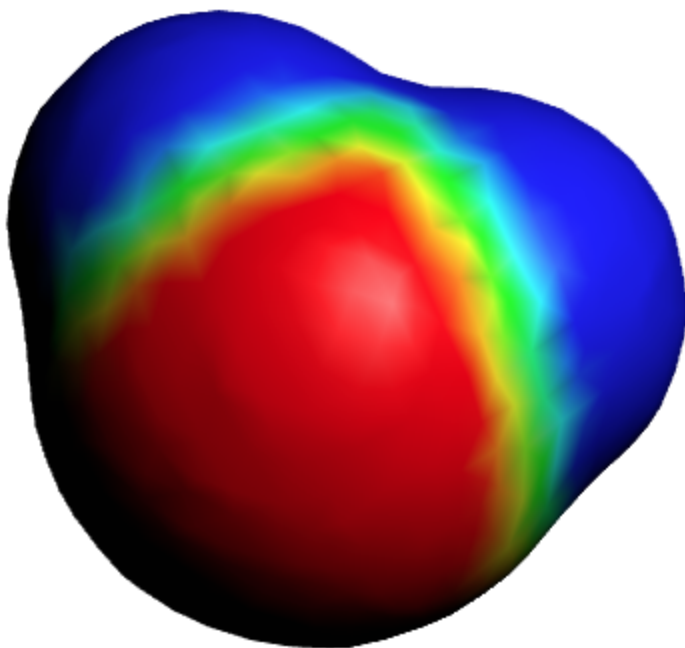
An ADFview window should pop-up

Select **ADFview** → **Add** →

COSMO: Surface Charge Density → **on COSMO surface (reconstructed)**

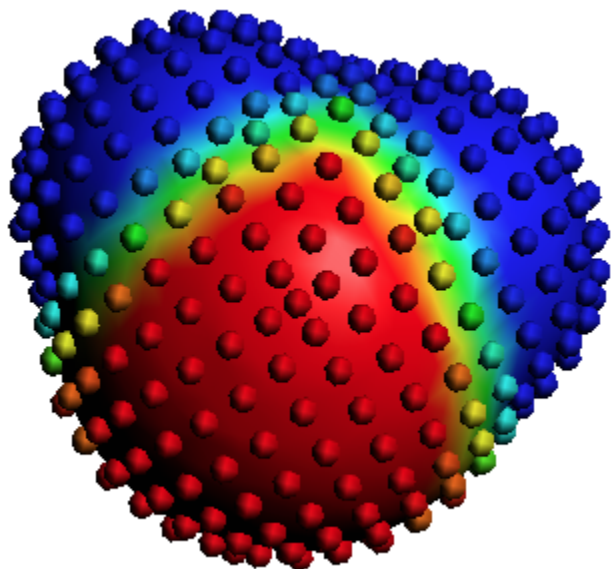
Select **ADFview** → **View** → **Background** → **White**

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** → **Close**

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**

An ADFview window should pop-up

Select **ADFview** → **Add** →

COSMO: Surface Charge Density → on COSMO surface (reconstructed)

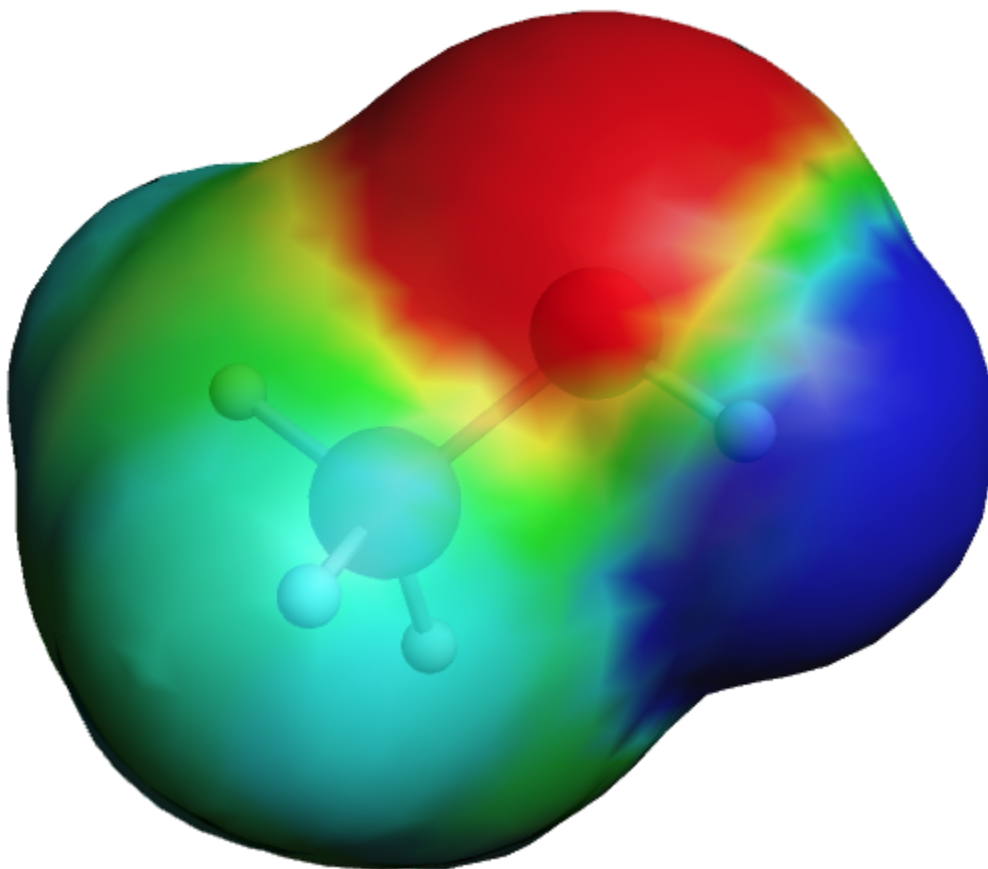
Select **ADFview** → **View** → **Background** → **White**

Check **ADFview** → **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



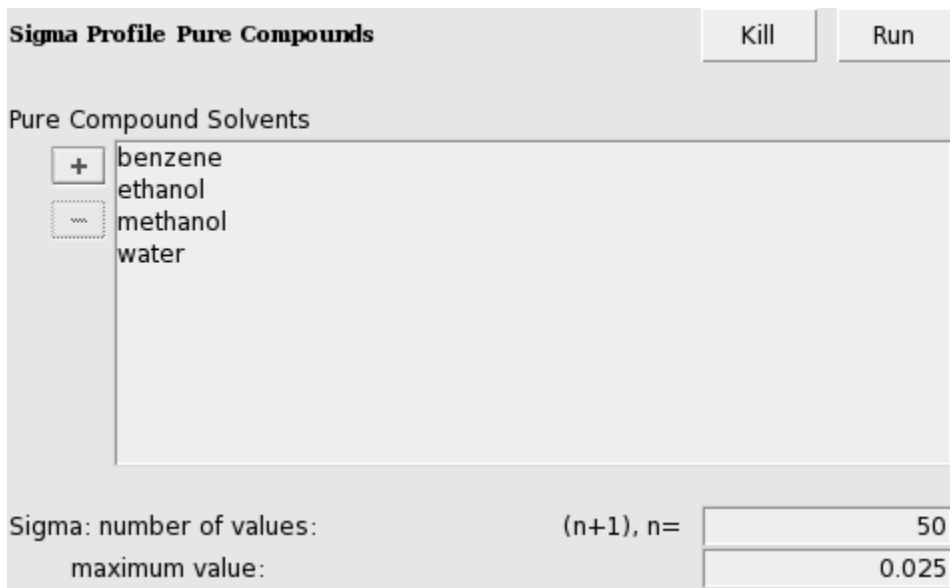
Next we will close this ADFview window.

Select the ADFView window 'methanol'
Select **File** → **Close**
Select the COSMO-RS GUI window

Step 6: Analysis: The sigma profile

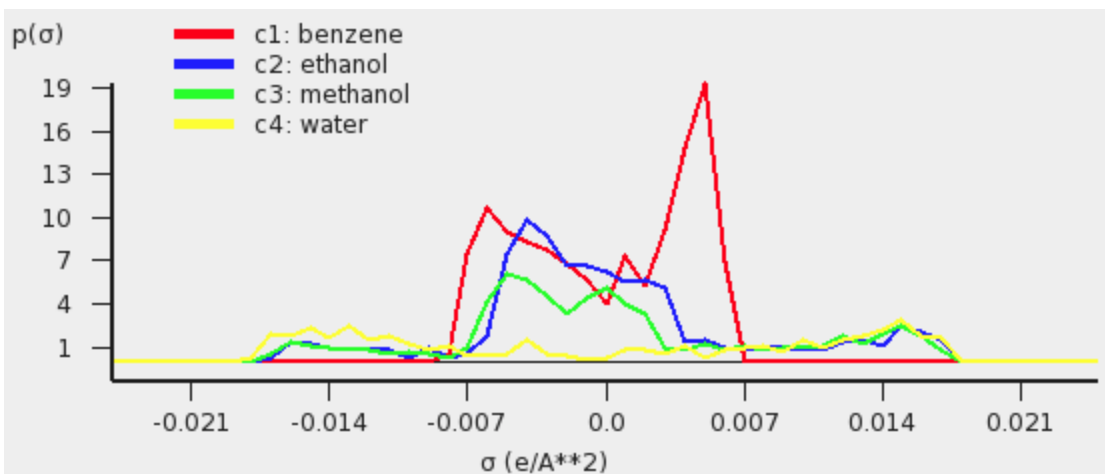
The σ -profile shows the amount of surface area for a given COSMO charge density.

Select **Analysis** → **Sigma Profile Pure Compounds**
Check the '+' button to add 'benzene', 'ethanol', 'methanol', and 'water'



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 four 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.

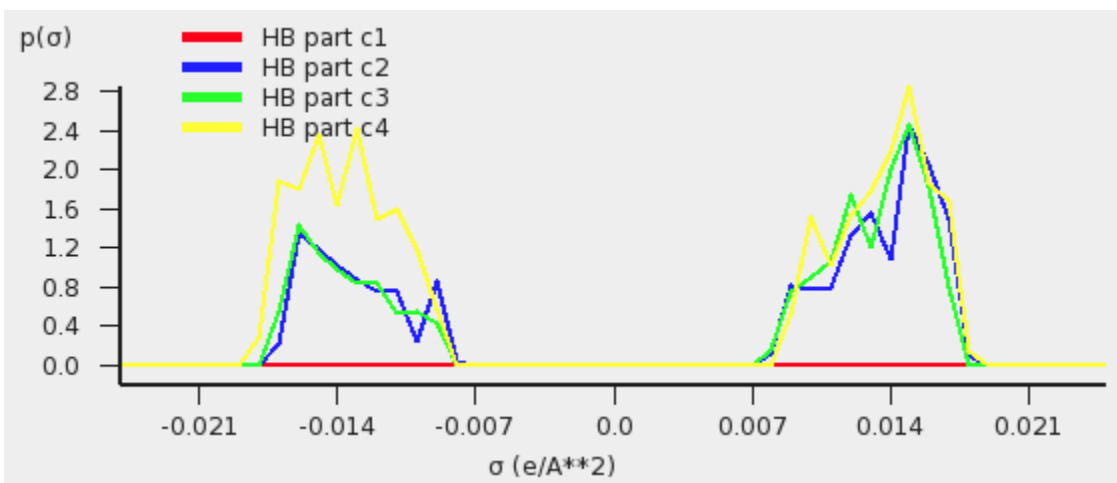


With default settings, if one clicks in the graph one can zoom (right mouse, or Command-Left (drag up or down)), or translate (left mouse) the graph. If one clicks in the graph window at the left or below the axes, a popup window will appear in which one can set details for the graph window.

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.

Select **Graph** → **Y axes** → **hydrogen bonding (HB) part sigma profile**

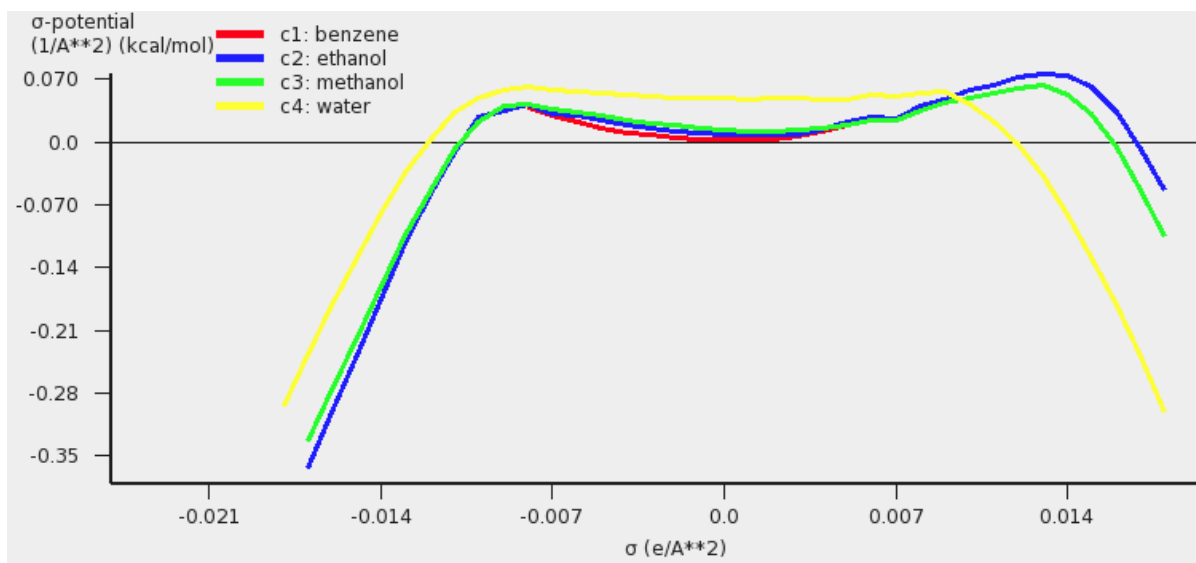


Step 7: Analysis: The sigma potential

Select **Analysis** → **Sigma Potential Pure Compounds**

Check the '+' button to add 'benzene', 'ethanol', 'methanol', and 'water'
Press 'Run'

The sigma potentials (σ -potential) of the four 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).



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 Pure Compounds

Method: COSMO-RS

Temperature: 298.15000 Kelvin

Pure Compounds

File name

c1: benzene	/tmp/Tutorial/benzene.coskf
c2: ethanol	/tmp/Tutorial/ethanol.coskf
c3: methanol	/tmp/Tutorial/methanol.coskf
c4: water	/tmp/Tutorial/water.coskf

$\sigma(e/A^{*2})$	c1	c2	c3	c4
-0.02500				
-0.02400				
-0.02300				
-0.02200				
-0.02100				
-0.02000				
-0.01900				
-0.01800				-0.29397269
-0.01700		-0.36372876	-0.33340701	-0.23690756
-0.01600		-0.30097037	-0.27590320	-0.18153786
-0.01500		-0.23758220	-0.21798802	-0.12841097
-0.01400		-0.17440142	-0.16028445	-0.07897803
-0.01300		-0.11309661	-0.10457933	-0.03410305
-0.01200		-0.05710450	-0.05337639	0.00328907
-0.01100		-0.01161227	-0.00754075	0.03311581
-0.01000		0.02860749	0.02232651	0.05020093
-0.00900		0.03577277	0.04003047	0.05811904
-0.00800	0.03787878	0.04158478	0.04246226	0.06143319
-0.00700	0.02969348	0.03169112	0.03778561	0.05783816
-0.00600	0.02181825	0.02893939	0.03405602	0.05698220
-0.00500	0.01508554	0.02388828	0.02941521	0.05403241
-0.00400	0.01055242	0.01913338	0.02498197	0.05211206
-0.00300	0.00803712	0.01474734	0.02096977	0.05199226
-0.00200	0.00571986	0.01204207	0.01826476	0.04980063
-0.00100	0.00391231	0.01047442	0.01594799	0.04922807
0.00000	0.00295134	0.00887138	0.01377564	0.04926470
0.00100	0.00278182	0.00814529	0.01209359	0.04750716
0.00200	0.00364656	0.00822705	0.01169674	0.04876684
0.00300	0.00639814	0.00906071	0.01297842	0.04910836
0.00400	0.01254335	0.01391514	0.01633456	0.04844323
0.00500	0.01957790	0.02182671	0.02000320	0.04676193
0.00600	0.02595901	0.02807902	0.02361397	0.05208756
0.00700		0.02638413	0.02445748	0.05067382
0.00800		0.04030095	0.03516569	0.05456122
0.00900		0.04713907	0.04416924	0.05734731
0.01000		0.05810729	0.04990077	0.04216055
0.01100		0.06275628	0.05488734	0.02270744
0.01200		0.07250347	0.06080846	-0.00286580
0.01300		0.07610071	0.06451829	-0.03827410
0.01400		0.07506712	0.05328434	-0.08050303
0.01500		0.06196112	0.03132241	-0.12896326
0.01600		0.03330333	-0.00645187	-0.18213360
0.01700		-0.00708983	-0.05380134	-0.23950236
0.01800		-0.05378152	-0.10503679	-0.30088489
0.01900				
0.02000				
0.02100				
0.02200				
0.02300				
0.02400				
0.02500				

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 \$ADFBIN/examples/crs/Tutorial2 to an empty directory and enter the following command in this directory where the COSMO result files are present:

```
$ADFBIN/adfcrs benzene.coskf ethanol.coskf methanol.coskf water.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: Vapor pressure

The vapor pressure of a solvent at different temperatures can be calculated with **Properties** → **Vapor Pressure Pure Solvents** or **Properties** → **Vapor Pressure Mixture**.

```
Select Properties → Vapor Pressure Pure Solvents
Check the '+' button to add 'methanol'
Select unwanted solvents in the the list
Check the '-' button to remove these unwanted solvents
Press 'Run'
```

Solvent Vapor Pressure Kill Run

Pure Compound Solvents

+ methanol

Temperature: number of steps:

from: Kelvin

to: Kelvin

In this case the result is a table with one entry:

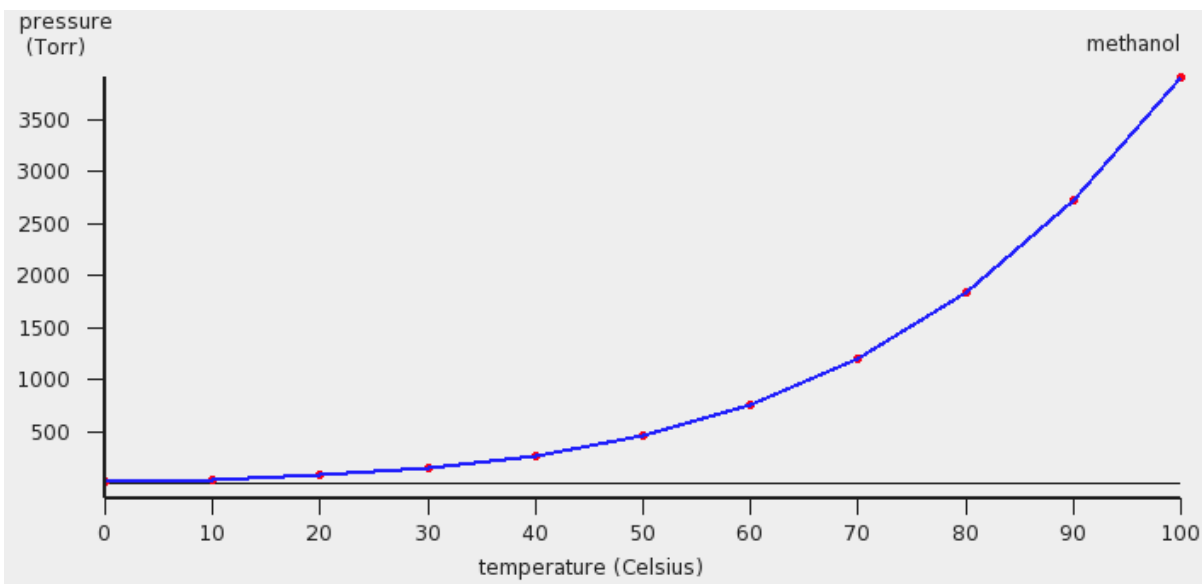
Solvent Vapor Pressure
Method: COSMO-RS

Solvent	File name
c1: methanol	/tmp/Tutorial/methanol.coskf

Temperature (Kelvin)	Vapor pressure (bar)	$\Delta_{\text{vap}} H$ (kcal/mol)
298.150	0.14142156	11.38484886

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	File name
c1: methanol	/tmp/Tutorial/methanol.coskf

Temperature (Kelvin)	Vapor pressure (bar)	$\Delta_{\text{vap}} H$ (kcal/mol)
273.150	0.02359935	11.76707348
283.150	0.05052382	11.62773485
293.150	0.10177401	11.47045660
303.150	0.19391791	11.29454040
313.150	0.35111807	11.09990817
323.150	0.60664078	10.88718616
333.150	1.00383775	10.65773766
343.150	1.59631067	10.41363343
353.150	2.44707966	10.15755774
363.150	3.62674766	9.89265789
373.150	5.21083968	9.62235437

Step 3: Boiling point

The boiling point of a solvent at different pressures can be calculated with **Properties** → **Boiling Point Pure Solvents** or **Properties** → **Boiling Point Mixture**.

Select **Properties** → **Boiling Point Mixture**

Select '2 components' in the popup menu next to Solvent
 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 Kill Run

Solvent 2 components ▼ Mole fraction ▼

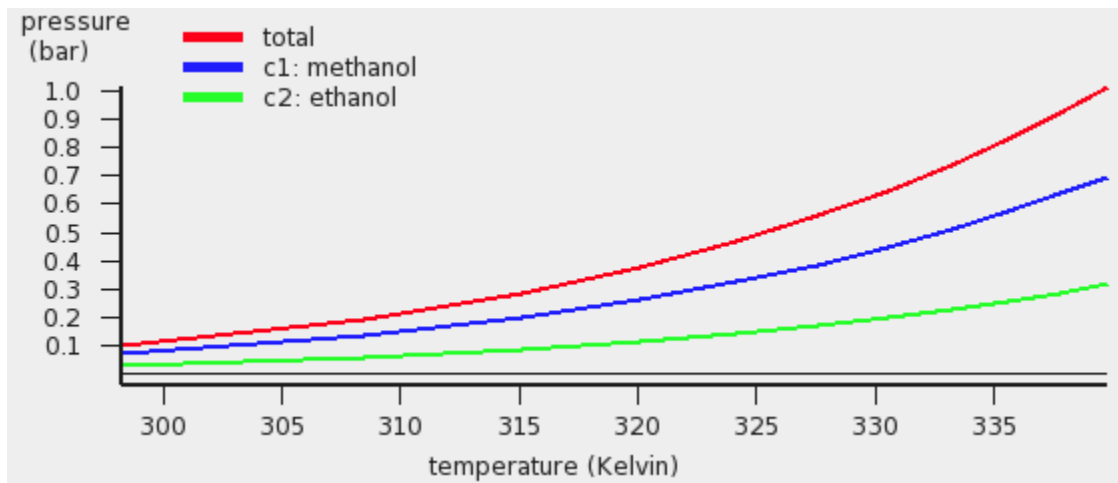
Q	methanol ▼	0.5
Q	ethanol ▼	0.5
Q	▼	
Q	▼	
Q	▼	

Pressure: number of steps: 10

from: 0.1 atm ▼

to: 1.0 atm ▼

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 (Kelvin)	Vapor pressure (bar)	$\Delta_{\text{vap}} H$ (kcal/mol)	excess G^E (kcal/mol)	excess H^E (kcal/mol)	excess $-TS^E$ (kcal/mol)
298.243	0.10132500	11.55487831	0.00671184	-0.00693793	0.01364977
308.480	0.19251750	11.36583106	0.00716689	-0.00613526	0.01330216
315.108	0.28371000	11.23266134	0.00744690	-0.00558597	0.01303287
320.105	0.37490250	11.12684283	0.00765020	-0.00515651	0.01280671
324.156	0.46609500	11.03775287	0.00781002	-0.00479884	0.01260886
327.584	0.55728750	10.96013950	0.00794174	-0.00448968	0.01243142
330.569	0.64848000	10.89096406	0.00805377	-0.00421581	0.01226958
333.221	0.73967250	10.82830388	0.00815123	-0.00396894	0.01212016
335.614	0.83086500	10.77085184	0.00823744	-0.00374349	0.01198093
337.797	0.92205750	10.71767516	0.00831472	-0.00353552	0.01185023
339.809	1.01325000	10.66808232	0.00838472	-0.00334211	0.01172683

Temperature (Kelvin)	Partial pressures (bar)	
	c1	c2
298.243	0.07208539	0.02923963
308.480	0.13569386	0.05682364
315.108	0.19882369	0.08488631
320.105	0.26163208	0.11327042
324.156	0.32419706	0.14189793
327.584	0.38656574	0.17072175
330.569	0.44876970	0.19971029
333.221	0.51083166	0.22884082
335.614	0.57276877	0.25809620
337.797	0.63459444	0.28746304
339.809	0.69631943	0.31693054

Temperature (Kelvin)	Activity coefficients (γ)	
	c1	c2
298.243	1.01335628	1.00942575
308.480	1.01370168	1.00982176
315.108	1.01388857	1.01004205
320.105	1.01401133	1.01019036
324.156	1.01409982	1.01029984
327.584	1.01416723	1.01038518
330.569	1.01422048	1.01045416
333.221	1.01426360	1.01051142
335.614	1.01429920	1.01055986
337.797	1.01432901	1.01060146
339.809	1.01435425	1.01063763

Temperature (Kelvin)	$\ln(\gamma)$	
	c1	c2
298.243	0.01326787	0.00938161
308.480	0.01360866	0.00977384
315.108	0.01379301	0.00999196
320.105	0.01391408	0.01013879
324.156	0.01400135	0.01024716
327.584	0.01406782	0.01033162
330.569	0.01412032	0.01039989
333.221	0.01416283	0.01045656
335.614	0.01419793	0.01050449
337.797	0.01422732	0.01054566
339.809	0.01425220	0.01058145

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 **Graph** → **Y Axes** → one can view different properties in the graph, like activity coefficients and excess energies.

Step 4: Flash point

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** → **List of Added Compounds**

Select 'ethanol'

Enter '286' for the 'Flash point' of ethanol

Select **Properties** → **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'

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 (Kelvin)	Vapor pressure (bar)	$\Delta_{\text{vap}} H$ (kcal/mol)	excess G^E (kcal/mol)	excess H^E (kcal/mol)	excess $-TS^E$ (kcal/mol)	
297.869	0.02518677	12.70401644	0.15830431	-0.13985325	0.29815756	
Flash Point (Kelvin)	Partial pressures (bar)					
297.869	c1	c2				
	0.02424087	0.00094591				
Flash Point (Kelvin)	Activity coefficients (γ)					
297.869	c1	c2				
	1.81417426	1.18027319				
Flash Point (Kelvin)	$\ln(\gamma)$					
297.869	c1	c2				
	0.59563041	0.16574593				

Step 5: Activity coefficients, Henry coefficients, Solvation free energies

The activity coefficients a solvent and the activity coefficients of infinitely diluted solutes in a solvent can be calculated with **Properties** → **Activity coefficients**. At the same time Henry coefficients and solvation free energies will be calculated.

Select **Properties** → **Activity coefficients**

Select 'water' for the first component in Solvent

Add 'benzene', 'ethanol', and 'methanol' to the list of Solutes

Press 'Run'

Activity Coefficients Kill Run

Solvent 1 component Mole fraction

Q	water	1.0
Q		
Q		
Q		
Q		

Use density solvent (kg/L): 1.0

Temperature: 298.15 Kelvin

Solutes (infinite dilute)

- + benzene
- ethanol
- methanol

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, by selecting a compound in the **List of Added Compounds**, and include pure a compound vapor pressure at a given temperature.

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				
Solvent	Activity Coefficient	Henry Constant (mol/(L atm))	Henry Constant dimensionless	ΔG (kcal/mol) gas->solute	ΔG (kcal/mol) 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 the Gibbs free energy of solvation ΔG from the gas phase to the solvated phase is the reference state, used here is 1 mol/L in both phases.

Step 6: Partition coefficients (log P)

Preset Octanol/Water, Benzene/Water, Ether/Water, Hexane/Water

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**. There are presets for the calculation of Octanol/Water, Benzene/Water, Ether/Water, and Hexane/Water partition coefficients. The presets use compounds that are present in \$ADFHOME/atomicdata/ADFCRS. First the preset Octanol/Water is used.

Select **Properties** → **Partition Coefficients (LogP)**

Select 'Preset Octanol-Water' in the popup menu next to Solvent
 Add 'benzene', 'ethanol', and 'methanol' to the list of Solutes
 Press 'Run'

Log Partition Coefficients (solvent phase 1/phase 2) Kill Run

Solvent Mole fraction ▾

Preset Octanol-Water ▾		phase 1:	phase 2:
<input type="text" value="Octanol"/> ▾	<input type="text" value="0.725"/>	<input type="text" value="0.0"/>	
<input type="text" value="Water"/> ▾	<input type="text" value="0.275"/>	<input type="text" value="1.0"/>	
<input type="text" value=""/> ▾	<input type="text" value="0.0"/>	<input type="text" value="0.0"/>	

Use molar volume phase 1/phase 2:

Temperature: Kelvin ▾

Solutes (infinite dilute)

benzene

ethanol

methanol

In case of partly miscible liquids, like the Octanol-rich phase of Octanol and Water, both components have nonzero mole fractions. The preset also gives a value for the molar volume quotient of the two solvents.

The result of the calculation is given in the form of a table.

Solvent	Log P
s1: 1-Octanol	3.55421340
s2: Water	-1.56605577
Solutes (infinite dilute)	
c1: benzene	2.12166806
c2: ethanol	0.08682421
c3: methanol	-0.52892989

User defined

A user can also define 2 phases of a mixture of two (or three) immiscible solvents.

Select **Properties** → **Partition Coefficients (LogP)**

Select 'User Defined 2 components' in the popup menu next to Solvent

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

Add 'ethanol', and 'methanol' to the list of Solutes
 Press 'Run'

Log Partition Coefficients (solvent phase 1/phase 2) Kill Run

Solvent Mole fraction ▼

User Defined 2 components ▼ phase 1: phase 2:

Q benzene ▼	1.0	0.0
Q water ▼	0.0	1.0
Q ▼	0.0	0.0

Use molar volume phase 1/phase 2: 4.93

Temperature: 298.15 Kelvin ▼

Solutes (infinite dilute)

+ ethanol

methanol

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 by selecting a compound in the **List of Added Compounds**.

The result of the calculation is given again 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
s1: benzene          2.62300118         /tmp/Tutorial/benzene.coskf
s2: water            -4.83461019        /tmp/Tutorial/water.coskf
Solutes (infinite dilute)
c1: ethanol          -1.38292689        /tmp/Tutorial/ethanol.coskf
c2: methanol         -2.05390651        /tmp/Tutorial/methanol.coskf
  
```

Step 7: Solubility

The solubility of a solute in a solvent can be calculated with **Properties** → **Solubility in Pure Solvents** or **Properties** → **Solubility in Mixture**. 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 in Pure Solvents**

Check the '+' button to add 'water'

Select 'benzene' for the 'Solute'

Enter '273.15' without quotes for the temperature in the 'from:' field

Enter '373.15' in the 'to:' field

Press 'Run'

Solubility Solute in Pure Solvents Kill Run

Pure Compound Solvents

+ water

Temperature: number of steps: 10

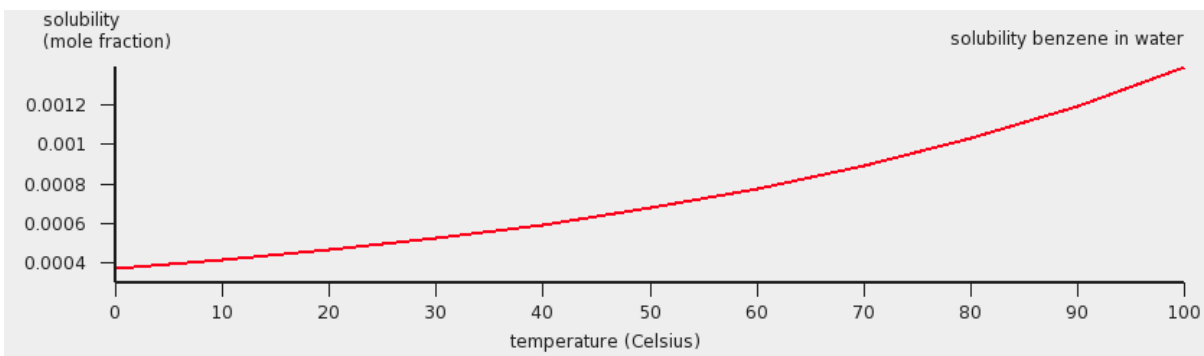
from: 273.15 Kelvin

to: 373.15 Kelvin

Pressure: for solubility of gas: 1.01325 bar

Solute: benzene Liquid

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 in this case. See the next examples.

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 if one selects **Compounds** → **List of Added Compounds**. Here, some experimental values will be included for benzene (see, for example, <http://en.wikipedia.org/wiki/Benzene>).

Select **Compounds** → **List of Added Compounds**

Click on the left side benzene

Enter '278.7' in the 'Melting point' field

Enter '2.37' in the ' $\Delta_{\text{fusion}} H$ ' field

Input Data

Nring:	<input type="text" value="6"/>
Drop H-bond interaction:	<input type="checkbox"/> Yes
Scale factor COSMO surface Area:	<input type="text" value="1.0"/>
Pure compound vapor pressure:	<input type="text" value="1.01325"/> bar
at temperature:	<input type="text" value="353.3"/> Kelvin
Antoine coefficients:	<input type="text" value="0.0"/> A
	<input type="text" value="0.0"/> B
	<input type="text" value="0.0"/> C
Melting point:	<input type="text" value="278.7"/> Kelvin
$\Delta_{\text{fusion}} H$:	<input type="text" value="2.37"/> kcal/mol
$\Delta_{\text{fusion}} C_p$:	<input type="text" value="0.0"/> kcal/(mol K)
Flash Point:	<input type="text" value="262"/> Kelvin

Also an experimental value for the density of water will be used:

Select **Properties** → **Solubility in Mixture**

Select 'water' for the first component in 'Solvent'

Check the '+' button to add 'benzene' in the list of Solutes

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 'from:' field

Enter '10.0' in the 'to:' field

Select **Graph** → **Y Axes** → **solubility (g/L solvent)**

Change the popup menu next to Solutes from 'Liquid' to 'Solid'

Press 'Run'

Solubility Solutes in Solvent Kill Run

Solvent 1 component ▼ Mole fraction ▼

Q	water ▼	1.0
Q	▼	
Q	▼	
Q	▼	
Q	▼	

Use density solvent (kg/L): 1.0

Temperature: number of steps: 10

from: 0.0 Celsius ▼

to: 10.0 Celsius ▼

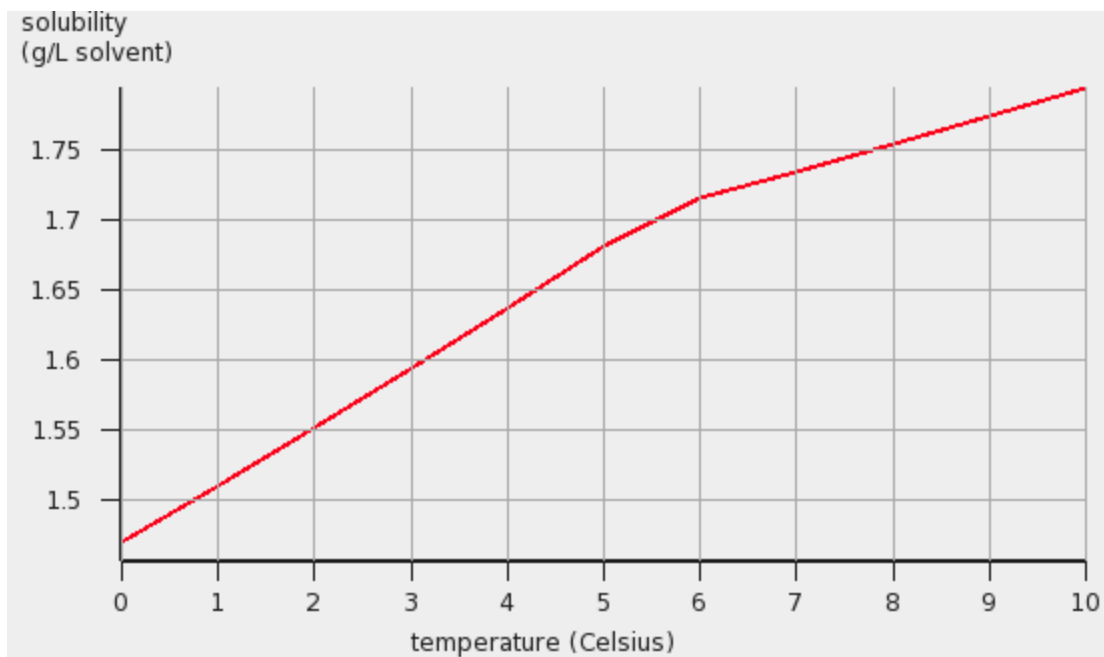
Pressure: for solubility of gas: 1.01325 bar ▼

Solutes Solid ▼

+ benzene

-

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 change the 'Liquid' popup menu in '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 in Mixture**

Select 'water' for the first component in 'Solvent'

Check the '+' button to add 'benzene' in the list of Solutes

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 'from:' field

Enter '373.15' in the 'to:' field

Change the popup menu next to Solutes from 'Solid' to 'Gas'

Use 'atm' units for the pressure

Enter '1.0' for the partial vapor pressure of benzene

Select **Graph** → **Y Axes** → **solubility (mol/L solvent)**

Press 'Run'

Use density solvent (kg/L):

Temperature: number of steps:

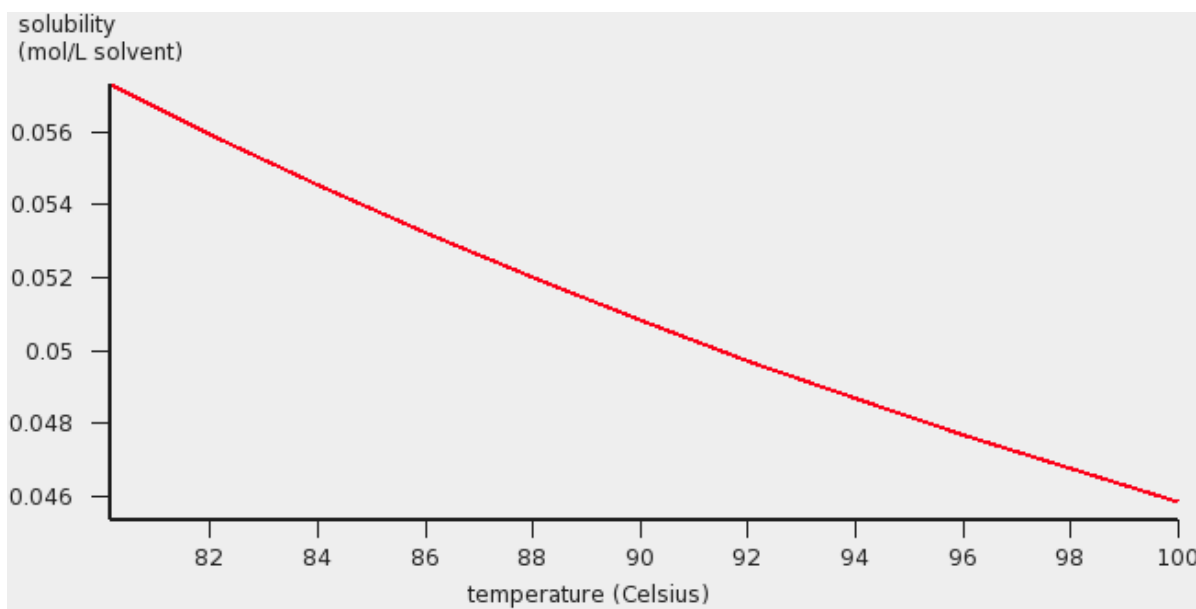
from: Kelvin

to: Kelvin

Pressure: for solubility of gas: atm

Solutes:

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.

Note that for benzene in the compounds window the vapor pressure of benzene at 353.3 Kelvin was entered. If these values are not specified (if they are zero) then the vapor pressure will be approximated using only the COSMO-RS method. This is relevant for all properties where the vapor pressure plays a role, thus it is relevant for the calculation of Henry's law constants and relevant for the calculation of the solubility of a gas in a solvent.

Step 8: 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

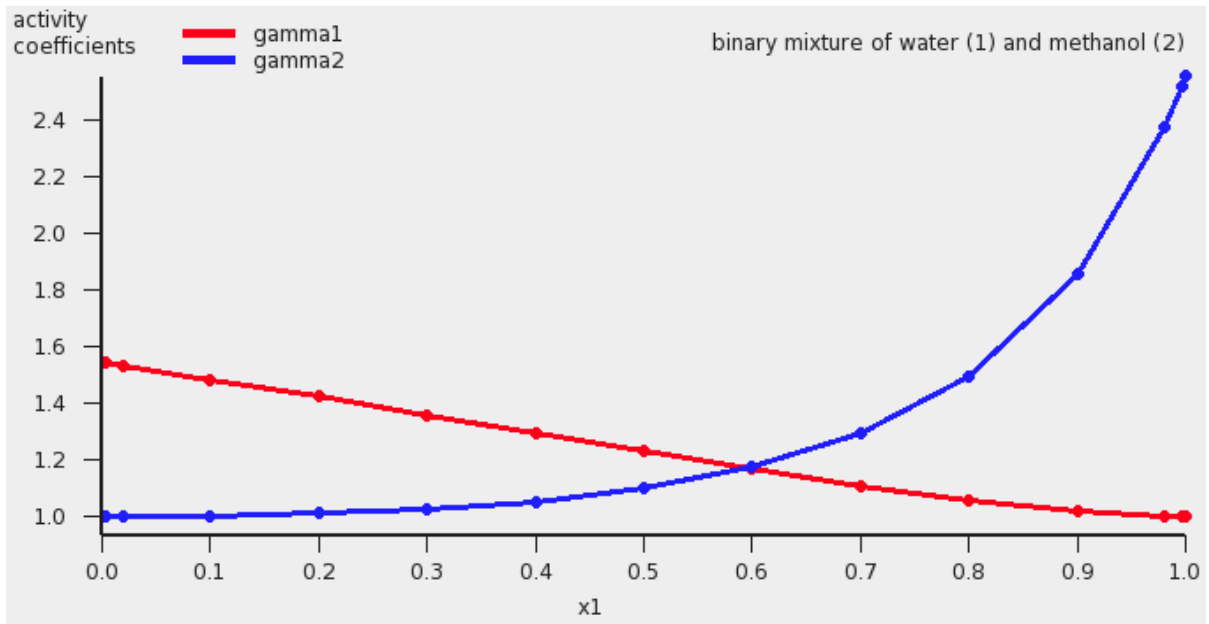
Use 'Kelvin' as unit for the temperature

Enter '298.14' in the 'Temperature' field

Press 'Run'

Binary Mixture VLE/LLE		Kill	Run
Compounds			
1:	<input type="text" value="water"/>		
2:	<input type="text" value="methanol"/>		
Number of mixtures:		(n+5), n=	<input type="text" value="10"/>
Isotherm, isobar, flash point:		isotherm	▼
Temperature:	<input type="text" value="298.14"/>	Kelvin	▼
Pressure:	<input type="text" value="1.01325"/>	bar	▼

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	0.14133	0.00000	0.14133	0.00000	1.00000
0.00400	298.14000	0.14077	0.00001	0.14077	0.00005	0.99995
0.02000	298.14000	0.13855	0.00003	0.13851	0.00024	0.99976
0.10000	298.14000	0.12763	0.00016	0.12747	0.00125	0.99875
0.20000	298.14000	0.11447	0.00031	0.11417	0.00268	0.99732
0.30000	298.14000	0.10189	0.00044	0.10145	0.00432	0.99568
0.40000	298.14000	0.08986	0.00056	0.08930	0.00621	0.99379
0.50000	298.14000	0.07832	0.00066	0.07766	0.00846	0.99154
0.60000	298.14000	0.06707	0.00075	0.06632	0.01125	0.98875
0.70000	298.14000	0.05568	0.00084	0.05485	0.01500	0.98500
0.80000	298.14000	0.04319	0.00091	0.04228	0.02107	0.97893
0.90000	298.14000	0.02722	0.00099	0.02623	0.03624	0.96376
0.98000	298.14000	0.00777	0.00106	0.00671	0.13614	0.86386
0.99600	298.14000	0.00250	0.00107	0.00142	0.42994	0.57006
1.00000	298.14000	0.00108	0.00108	0.00000	1.00000	0.00000

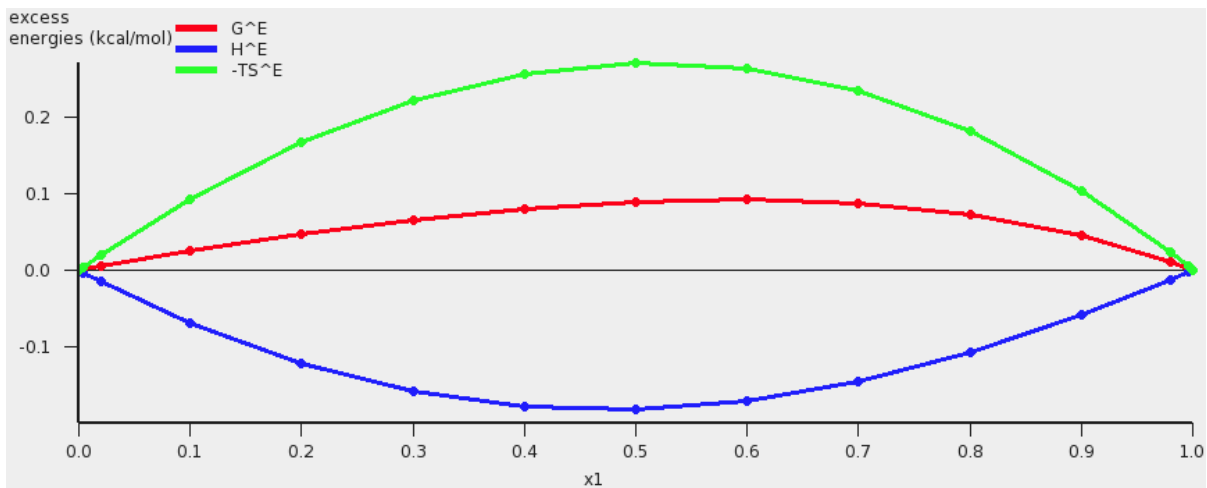
x1	G ^E	H ^E	-TS ^E	G ^{mix}	Δ _{vap} H	w1	w2
0.00000	0.00000	-0.00000	0.00000	0.00000	11.38502	0.00000	1.00000
0.00400	0.00103	-0.00308	0.00410	-0.01442	11.38537	0.00225	0.99775
0.02000	0.00511	-0.01512	0.02022	-0.05298	11.38701	0.01135	0.98865
0.10000	0.02457	-0.06903	0.09359	-0.16804	11.40180	0.05881	0.94119
0.20000	0.04644	-0.12164	0.16807	-0.25004	11.43575	0.12326	0.87674
0.30000	0.06502	-0.15788	0.22290	-0.29689	11.48664	0.19421	0.80579
0.40000	0.07957	-0.17797	0.25754	-0.31916	11.55390	0.27268	0.72732
0.50000	0.08911	-0.18231	0.27142	-0.32155	11.63714	0.35995	0.64005
0.60000	0.09239	-0.17149	0.26389	-0.30635	11.73319	0.45757	0.54243
0.70000	0.08776	-0.14640	0.23417	-0.27415	11.84302	0.56751	0.43249
0.80000	0.07304	-0.10826	0.18130	-0.22343	11.96834	0.69226	0.30774
0.90000	0.04519	-0.05875	0.10394	-0.14741	12.14003	0.83502	0.16498
0.98000	0.01068	-0.01239	0.02307	-0.04740	12.76100	0.96498	0.03502
0.99600	0.00221	-0.00250	0.00471	-0.01324	14.41646	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 'Graph' Menu. For example, a graph of the excess energies can be shown by:

Select **Graph** → **Y Axes** → **excess energies**

temperature
total vapor pressure
partial and total vapor pressures
• excess energies
Gibbs energy of mixing
enthalpy of vaporization
x1, x2: molar fractions
y1, y2: molar fractions in vapor phase
x1, y1
x2, y2
w1, w2: mass fractions
activity coefficients
ln (activity coefficients)
activities

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** → **List of Added 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

Compound water

File Name: /tmp/Tutorial/water.coskf
Name: water
Other Names: H2O
Calculated 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 Data

Nring:
Drop H-bond interaction: Yes
Scale factor COSMO surface Area:
Pure compound vapor pressure: bar
at temperature: Kelvin
Antoine coefficients: A
 B
 C
Melting point: Kelvin
 $\Delta_{\text{fusion}} H$: kcal/mol
 $\Delta_{\text{fusion}} C_p$: kcal/(mol K)
Flash Point: 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 **Graph** → **X Axes** → **x2: molar fraction 2**

Select **Graph** → **Y Axes** → **partial and total vapor pressures**

Press 'Run'

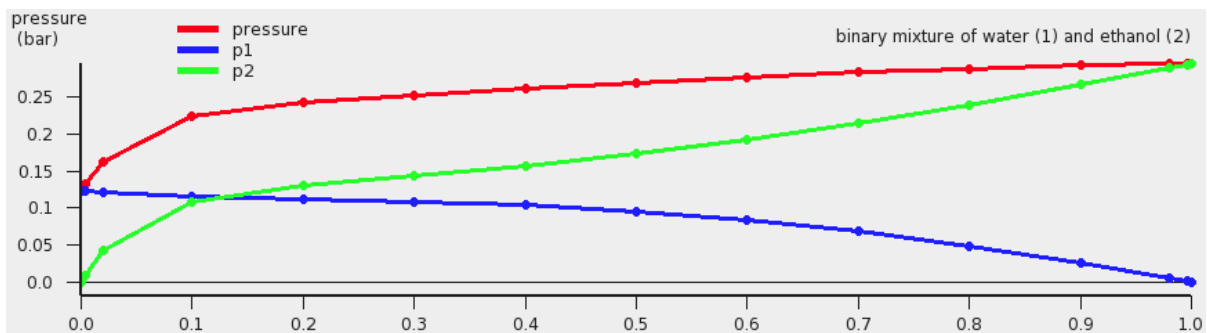
Binary Mixture VLE/LLE Kill Run

Compounds
 1: ▼
 2: ▼

Number of mixtures: (n+5), n= Mole fraction ▼

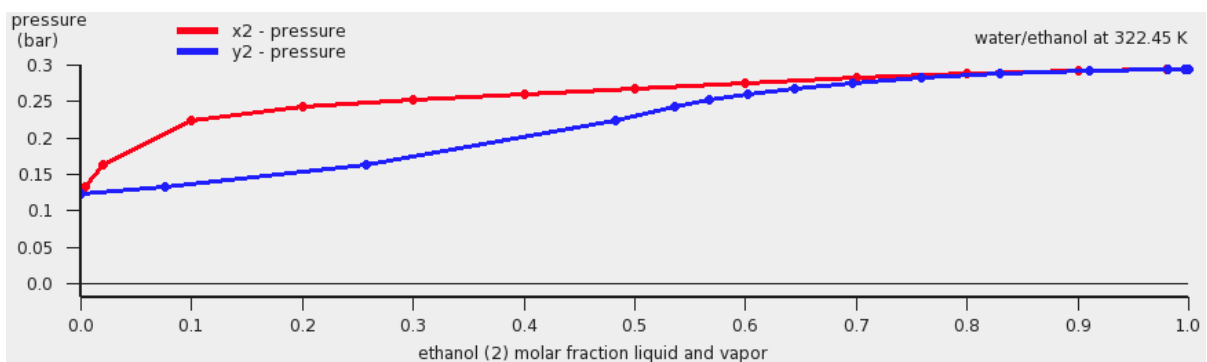
Isotherm, isobar, flash point: isotherm ▼
 Temperature: Kelvin ▼
 Pressure: bar ▼

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 **Graph** → **X Axes** → **x2, y2**
 Select **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 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 $x_1 = 0.00051$ and $x_1' = 0.99931$
 Properties of the 2 immiscible liquid phases

x_1	x_2	γ_{m1}	γ_{m2}	$\ln(\gamma_{m1})$	$\ln(\gamma_{m2})$	$a_1: x_1 \cdot \gamma_{m1}$	$a_2: x_2 \cdot \gamma_{m2}$
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 **Graph** → **X axes** → **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 **Graph** → **X axes** → **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.

Deselect check box

Graph → **X axes** → **force 1 liquid phase within possible miscibility gap**

Select check box

Graph → **X axes** → **force 1 liquid phase within possible miscibility gap**

x1: molar fraction 1
x2: molar fraction 2
y1: molar fraction 1 in vapor phase
y2: molar fraction 2 in vapor phase
x1, y1
• x2, y2
w1: mass fraction 1
w2: mass fraction 2
gamma1: activity coefficient 1
gamma2: activity coefficient 2
a1: $x_1 \cdot \gamma_{m1}$
a2: $x_2 \cdot \gamma_{m2}$
<input checked="" type="checkbox"/> force 1 liquid phase within possible miscibility gap

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**

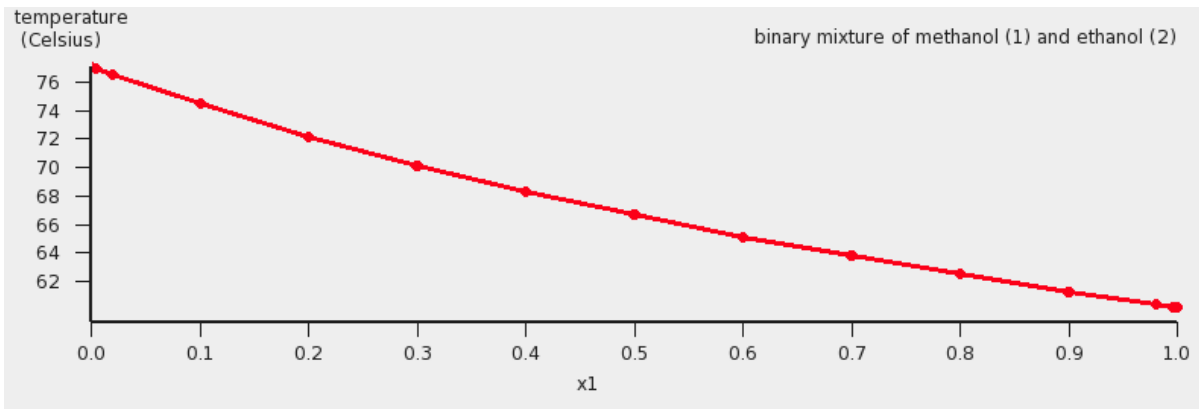
Select **Graph** → **X Axes** → **x1: molar fraction 1**

Select **Graph** → **Y Axes** → **temperature**

Press 'Run'

Binary Mixture VLE/LLE		Kill	Run
Compounds			
1:	<input type="text" value="methanol"/>		
2:	<input type="text" value="ethanol"/>		
		Mole fraction	
Number of mixtures:	(n+5), n=	<input type="text" value="10"/>	
Isotherm, isobar, flash point:		isobar	
Temperature:	<input type="text" value="50"/>	Celsius	
Pressure:	<input type="text" value="1.01325"/>	bar	

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: 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 **Graph** → **X Axes** → **x1: molar fraction 1**
 Select **Graph** → **Y Axes** → **x2: molar fraction 2**
 Select **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'

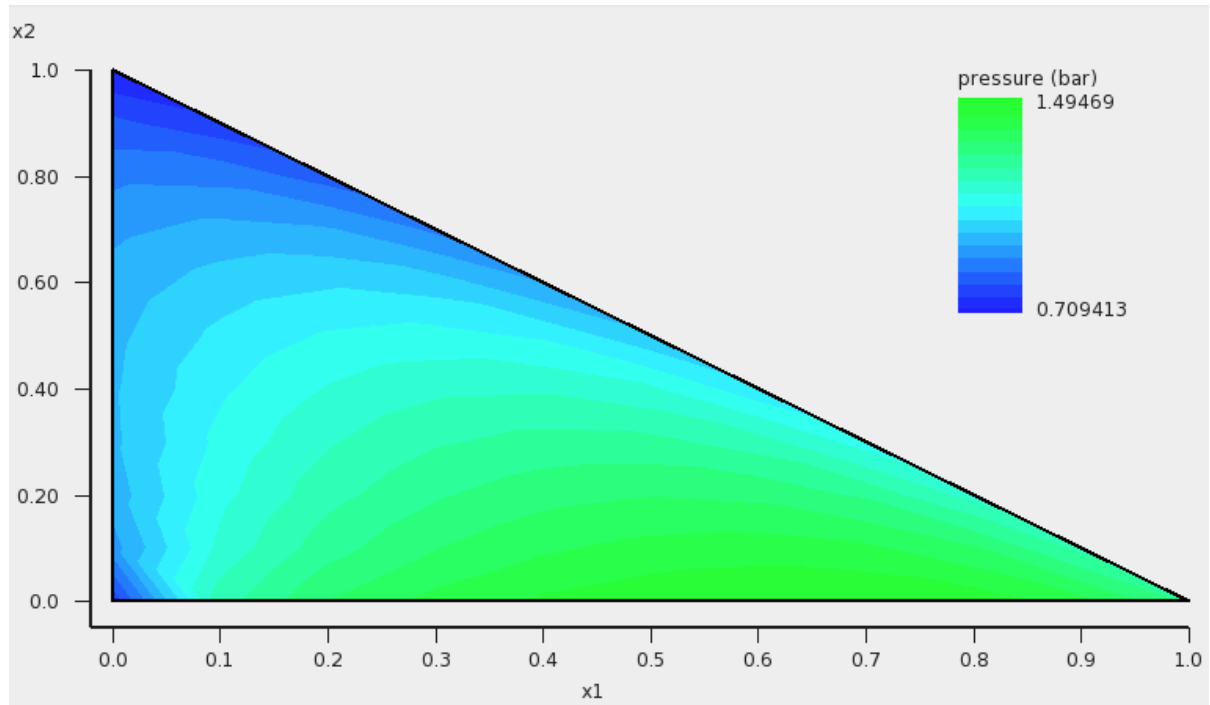
Ternary Mixture VLE/LLE		Kill	Run
Compounds:			
1:	<input type="text" value="methanol"/>	▼	
2:	<input type="text" value="ethanol"/>	▼	
3:	<input type="text" value="benzene"/>	▼	
Number of mixtures:		(n+1)(n+2)/2, n=	<input type="text" value="10"/>
Isotherm, isobar, flash point:		isotherm	▼
Temperature:	<input type="text" value="70.0"/>	Celsius	▼
Pressure:	<input type="text" value="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 compounds, on the Y axes one can choose the molar (or mass fraction) of another

compound. The molar (or mass) fraction of the third compound is then fixed, since the sum of the fractions is 1.

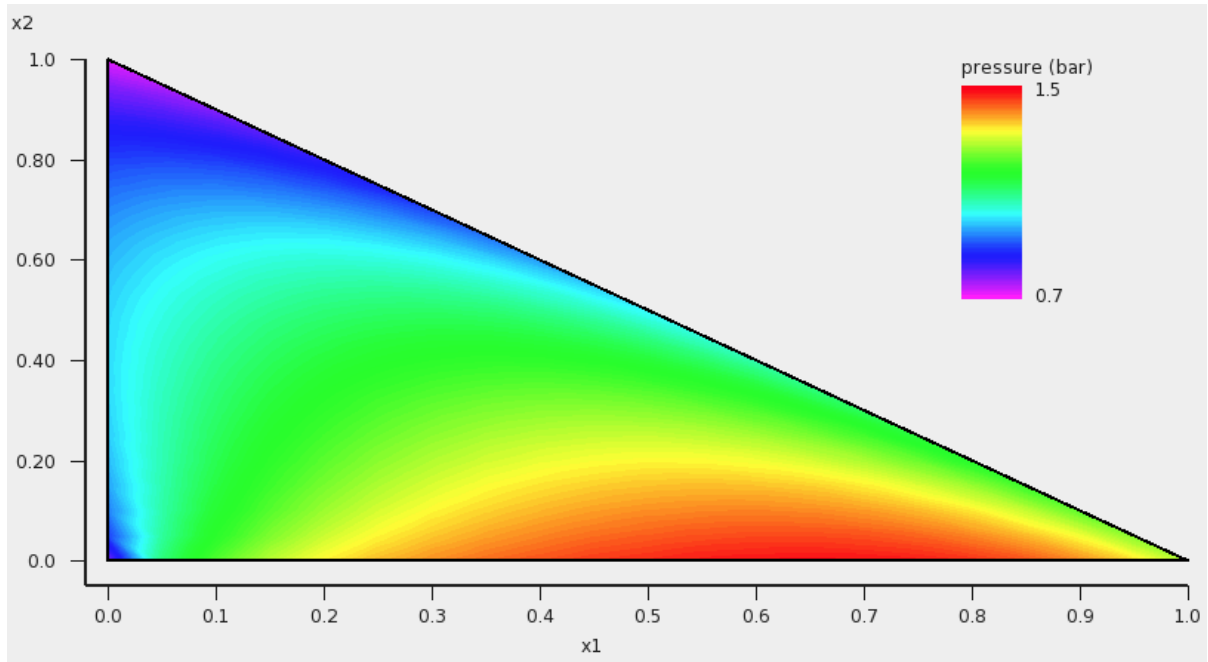
In this case the colormap shows the total vapor pressure:



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 ($=\frac{(n+1)(n+2)}{2}$).

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

Note that isobaric calculations are more expensive than isothermal calculations. Thus the following example takes quite some time, since again for $n=20$ the number of different compositions is 231.

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 **Graph** → **X Axes** → **x1: molar fraction 1**
 Select **Graph** → **Y Axes** → **x2: molar fraction 2**
 Select **Graph** → **Z Colormap** → **temperature**
 Press 'Run'

Ternary Mixture VLE/LLE Kill Run

Compounds:

1: ▼

2: ▼

3: ▼

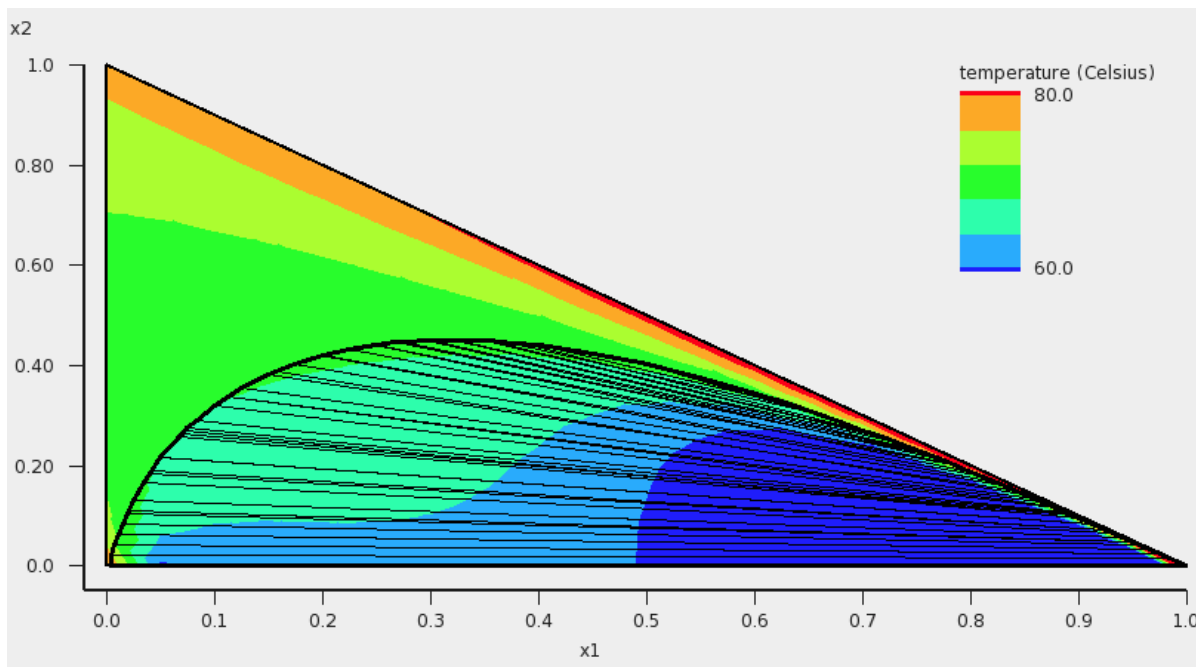
Number of mixtures: $(n+1)(n+2)/2, n=$ Mole fraction ▼

Isotherm, isobar, flash point: isobar ▼

Temperature: Celsius ▼

Pressure: 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 Colormap' 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:

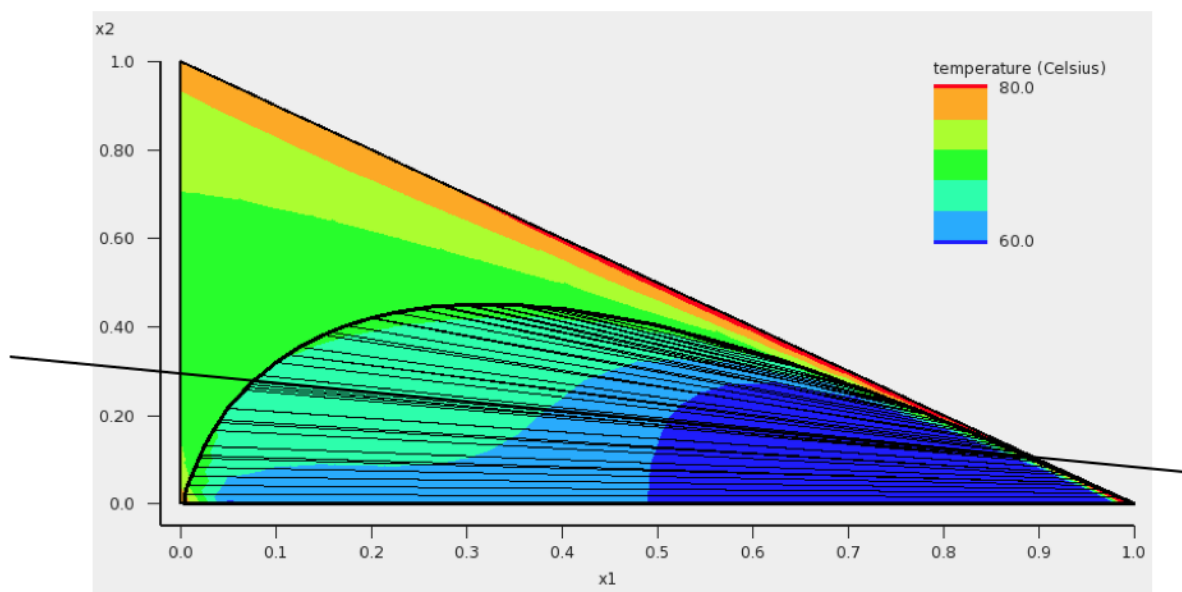


In addition to the colormap of the temperature, an approximate miscibility gap of the ternary mixture is shown in the graph. In this case, within the miscibility gap there are two immiscible phases of the liquid in equilibrium. The composition of the two phases, which are in equilibrium, can be found 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: 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 '3 components' in the popup menu next to Solvent

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 **Graph** → **X Axes** → **s1_x: molar fraction s1**

Select **Graph** → **Y Axes** → **pure compound activities**
 Press 'Run'

Solvents s1 - s2 Composition Line Kill Run

Linear interpolation between the compositions of solvent s1 and solvent s2

Mole fraction ▼

Solvents 3 components ▼

		s1:	s2:
<input type="text" value="Q"/>	water ▼	0.0	0.9
<input type="text" value="Q"/>	ethanol ▼	0.3	0.1
<input type="text" value="Q"/>	benzene ▼	0.7	0.0
<input type="text" value="Q"/>	▼		
<input type="text" value="Q"/>	▼		

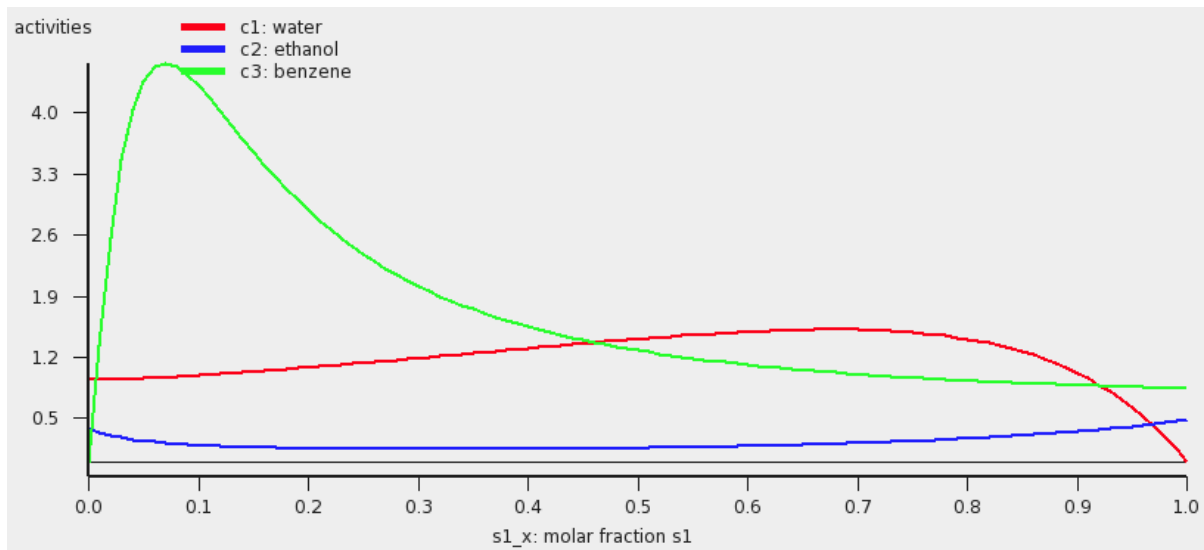
Number of mixtures: (n+1), n=

Isotherm, isobar, flash point: isobar ▼

Temperature: Kelvin ▼

Pressure: 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 **Graph** → **X Axes** → **s1_x: molar fraction s1**

Select **Graph** → **Y Axes** → **Gibbs energy of mixing wrt pure compounds**

Press 'Run'

Solvents s1 - s2 Composition Line Kill Run

Linear interpolation between the compositions of solvent s1 and solvent s2

Solvents 3 components ▼ Mole fraction ▼

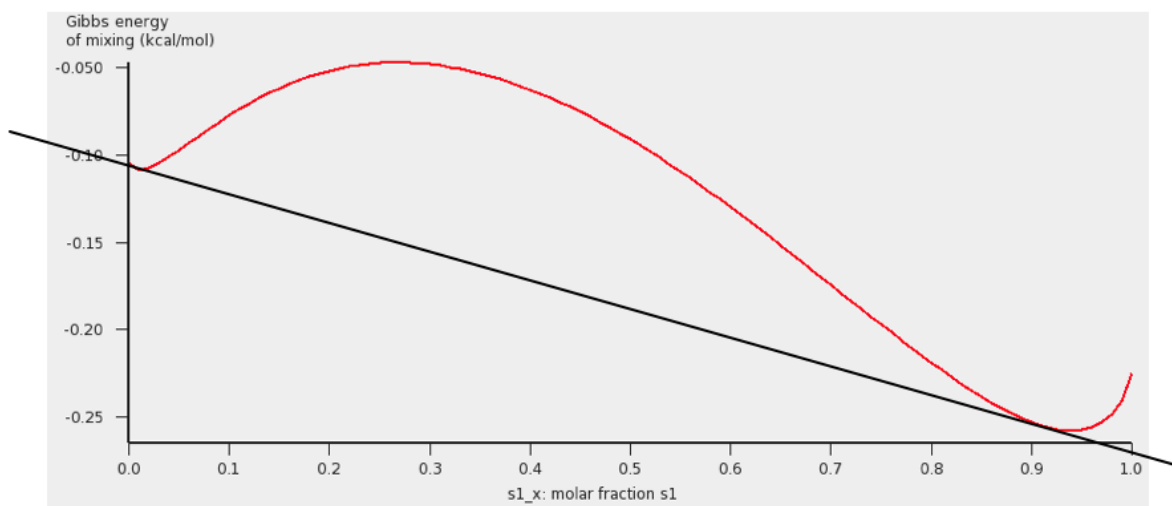
	s1:	s2:
<input type="text" value="water"/>	<input type="text" value="0.0"/>	<input type="text" value="0.9"/>
<input type="text" value="ethanol"/>	<input type="text" value="0.3"/>	<input type="text" value="0.1"/>
<input type="text" value="benzene"/>	<input type="text" value="0.7"/>	<input type="text" value="0.0"/>
<input type="text"/>	<input type="text"/>	<input type="text"/>
<input type="text"/>	<input type="text"/>	<input type="text"/>

Number of mixtures: (n+1), n=

Isotherm, isobar, flash point: isotherm ▼

Temperature: Celsius ▼

Pressure: bar ▼



The black line was added to show the miscibility gap more clearly. Indeed at 67.9 °C for molar fractions between $s1_x = 0.007$ 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 compound database

ADF has a database of COSMO result files, the [COSMO-RS compound database ADFCRS-2010](#).

4.1: Install and use the COSMO-RS compound database

Step 1: Install database

For this tutorial we assume that you know how start ADFcrs. Next we will install the ADFCRS-2010 database.

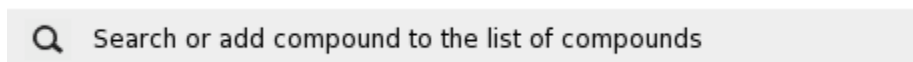
ADFcrs → **Compounds** → **Install COSMO-RS databse...**



Follow the instructions

The downloading and reading of some information about all compounds may take a minute. More information this database can be found on [this page](#). You must have the permission to write this database (in $\$ADFHOMe/atomicdata/ADFCRS-2010$). You may need to have administrator privileges to do so. For this tutorial it is necessary that the COSMO-RS compound database is downloaded in the correct directory $\$ADFHOMe/atomicdata/ADFCRS-2010$.

Step 2: Add or search compounds

There are several ways to select a compound from the database and add it too the **List of Added Compounds**. The easiest way is to use the search button. A separate search window will popup if one clicks the search button. In the **List of Added Compounds** this search button looks like:



In other windows it can look like:  (to select 1 compound) or  (to add multiple compounds).

Select **Compounds** → **Compounds**

Click on the search button

Nr :	dNr :	Name :	Formula :	CAS :	Other Name :	File Name
d1867		Triphenylethylene	C20H16	58-72-0		/home/
d1868		Triphenylmethane	C19H16	519-73-3		/home/
d1869		Triphenylphosphine	C18H15P	603-35-0		/home/
d1870		Tripropylamine	C9H21N	102-69-2		/home/
d1871		Tripropylene-glycol-monomethyl-ether	C10H22O4	25498-49-1		/home/
d1872		Tripropylene-glycol	C9H20O4	1638-16-0		/home/
d1873		Undecanal	C11H22O	112-44-7		/home/
d1874		Undecane	C11H24	1120-21-4		/home/
d1875		Undecyl mercaptan	C11H24S	5332-52-5		/home/
d1876		Undecylamine	C11H25N	7307-55-3		/home/
d1877		Valeronitrile	C5H9N	110-59-8		/home/
d1878		Vanillin	C8H8O3	121-33-5		/home/
d1879		Vinbarbital	C11H16N2O3	125-42-8		/home/
d1880		Vinyl acetate	C4H6O2	108-05-4		/home/
d1881		Vinyl bromide	C2H3Br	593-60-2		/home/
d1882		Vinyl chloride	C2H3Cl	75-01-4		/home/
d1883		Vinyl fluoride	C2H3F	75-02-5		/home/
d1884		Vinyl formate	C3H4O2	692-45-5		/home/
d1885		Vinyl pivalate	C7H12O2	3377-92-2		/home/
d1886		Vinyl propionate	C5H8O2	105-38-4		/home/
d1887		Vinylacetonitrile	C4H5N	109-75-1		/home/
d1888		Vinylcyclohexene	C8H12	100-40-3		/home/
d1889		Vinylnorbornene	C9H12	3048-64-4		/home/
d1890		VX	C11H26N2O2PS	50782-69-9		/home/
d1891		Water	H2O	7732-18-5		/home/
d1892		Xanthene	C13H10O	92-83-1		/home/

Search: Cancel OK

Click on 'CAS' to sort by CAS registry number
Click again to reverse the order
Click on 'Nr' to sort by number
Click on 'dNr' to sort by database 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 :	dNr :	Name :	Formula :	CAS :	Other Name :	File Name
d981		Cyclopentanol	C5H10O	96-41-3		/home/
d194		1-Pentanol	C5H12O	71-41-0		/home/
d613		2-Pentanol	C5H12O	6032-29-7		/home/
d716		3-Pentanol	C5H12O	584-02-1		/home/
d578		2-Methyl-1-pentanol	C6H14O	105-30-6		/home/
d692		3-Methyl-1-pentanol	C6H14O	589-35-5		/home/
d699		3-Methyl-3-pentanol	C6H14O	77-74-7		/home/
d753		4-Methyl-2-pentanol	C6H14O	108-11-2		/home/

Search: Cancel OK

Now Cyclopentanol is added to the **List of Added Compounds**. If the search button is used again Cyclopentanol will have number 1.

Nr :	dNr :	Name :	Formula :	CAS :
1	d981	Cyclopentanol	C5H10O	96-41-3

In the COSMO-RS database there is a file called 'all.compoundlist', which 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. This can be handy if one wants to add compounds to the **List of Added 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.

Step 3: Set pure compound data

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.

After selecting **Compounds** → **List of Added Compounds** and selecting a compound it is also possible to add some pure compound input data. Pure compound data could be found, for example, at Refs. [411-413]. If one wants to save the pure compound input data in a .coskf file Select **Compounds** → **Save Data Selected Compound As**.

References

[411] [Wikipedia](#)

[412] [NIST Chemistry WebBook](#)

[413] [CHERIC. Korea Thermophysical Properties Data Bank: Pure Component Properties](#)

Step 4: 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** → **List of Added Compounds**

Click on the left side 'Cyclopentanol'

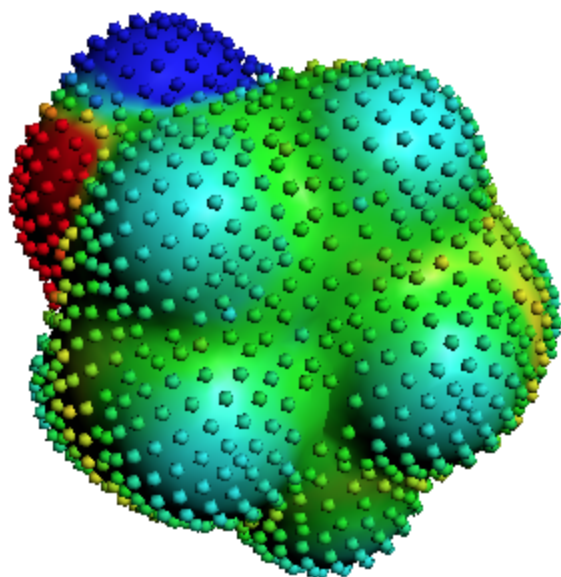
Select **Compounds** → **Show Selected Compound**

Select the ADFView window 'Cyclopentanol'

Select **ADFview** → **Add** → **COSMO: Surface Charge Density** →
on COSMO surface (reconstructed)

Select **ADFview** → **Add** → **COSMO: Surface Charge Density** →
on COSMO surface points

Select **ADFview** → **View** → **Background** → **White**



Next we will close this ADFview window:

```
Select the ADFview window 'Cyclopentanol'  
Select ADFview → File → Close  
Select the COSMO-RS GUI window
```

4.2: Octanol-Water partition coefficients (log Pow)

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 molar 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 by selecting a compound in the **List of Added Compounds**.

```
Select Properties → Log Partition Coefficients  
Select 'Preset Octanol-Water' in the popup menu next to Solvent  
Enter '298.15' for the 'Temperature' in 'Kelvin'  
Check the '+' button 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) Kill Run

Solvent Mole fraction

Preset Octanol-Water phase 1: phase 2:

Octanol	0.725	0.0
Water	0.275	1.0
	0.0	0.0

Use molar volume 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
Solute (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 pops up 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 & Engineering 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**), Select **Compounds** → **Add Compound(s)**, go to the directory where the COSMO-RS compound database is downloaded (\$ADFHOME/atomicdata/ADFCRS-2010), and select tutorial4.3.compoundlist. This is recommended. Then the added compounds are at the top of the list if one uses the '+' button, or search button. The tutorial4.3.compoundlist is a file with a list of compounds that is limited to the compounds 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

Check the '+' button to add

'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'

Activity Coefficients		Kill	Run
Solvent	1 component	Mole fraction	
Q Water		1.0	
Q			
Q			
Q			
Q			
<input checked="" type="checkbox"/> Use 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.

Solvent	Activity Coefficient	Henry Constant (mol/(L atm))	Henry Constant dimensionless	ΔG (kcal/mol) gas->solute	ΔG (kcal/mol) 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.

To include all experimental numbers is rather tedious, thus one could skip the following part, and only look at the results below.

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.

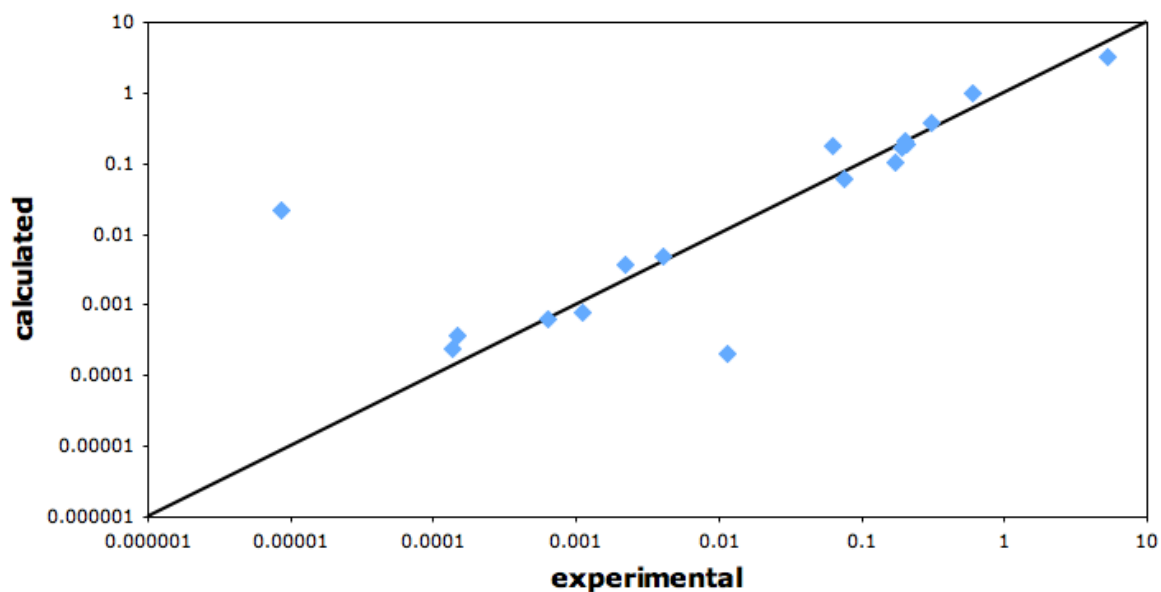
Solvent	Activity Coefficient	Henry Constant (mol/(L atm))	Henry Constant dimensionless	ΔG (kcal/mol) gas->solute	ΔG (kcal/mol) liq->solute
s1: Water	1.00000000	2.213964e+03	5.256080e+04	-6.33215	0.00000
Solutes (infinite dilute)					
c1: Acetaldehyde	5.12533979	1.131675e+01	2.686663e+02	-3.25847	0.95200
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.

$$H^{CC} = k_H, \text{inv}^{CC} = 1/(kH^{CC})$$

Henry's law constants



	Solute	experimental $H^{CC}@20^{\circ}\text{C}$ [431]	calculated $H^{CC}@20^{\circ}\text{C}$
1	Methyl_bromide	$2.01 \cdot 10^{-1}$	$2.05 \cdot 10^{-1}$
2	Chloromethane	$3.05 \cdot 10^{-1}$	$3.80 \cdot 10^{-1}$
3	Methyl_fluoride	$6.04 \cdot 10^{-1}$	$9.86 \cdot 10^{-1}$
4	Methyl_iodide	$1.70 \cdot 10^{-1}$	$1.04 \cdot 10^{-1}$
5	Cyclopentane	$5.25 \cdot 10^0$	$3.27 \cdot 10^0$
6	Benzene	$1.91 \cdot 10^{-1}$	$1.65 \cdot 10^{-1}$
7	Toluene	$2.09 \cdot 10^{-1}$	$1.89 \cdot 10^{-1}$
8	Methanol	$1.37 \cdot 10^{-4}$	$2.43 \cdot 10^{-4}$
9	Ethanol	$1.48 \cdot 10^{-4}$	$3.70 \cdot 10^{-4}$
10	Formaldehyde	$8.61 \cdot 10^{-6}$	$2.22 \cdot 10^{-2}$
11	Acetaldehyde	$2.21 \cdot 10^{-3}$	$3.72 \cdot 10^{-3}$
12	Acetrone	$1.10 \cdot 10^{-3}$	$0.78 \cdot 10^{-3}$
13	Methyl_acetate	$4.02 \cdot 10^{-3}$	$4.89 \cdot 10^{-3}$
14	Acetonitrile	$6.35 \cdot 10^{-4}$	$6.35 \cdot 10^{-4}$
15	Pyridine	$1.14 \cdot 10^{-2}$	$2.03 \cdot 10^{-4}$
16	Dimethyl_sulfide	$6.35 \cdot 10^{-2}$	$1.82 \cdot 10^{-1}$
17	Thiophene	$7.46 \cdot 10^{-2}$	$6.23 \cdot 10^{-2}$

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 $1.1 \cdot 10^2$ mol/(L atm) and $9.0 \cdot 10^1$ mol/(L atm), which are not very different from the calculated value with COSMO-RS of $2.1 \cdot 10^2$ 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. Bernauer 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 **List of Added Compounds** 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**), Select **Compounds** → **Add Compound(s)**, go to the directory where the COSMO-RS compound database is downloaded ($\$ADFHOME/atomicdata/ADFCRS-2010$), and select tutorial4.4.compoundlist. Then the added compounds are at the top of the list if one uses the '+' button, or search button. The tutorial4.4.compoundlist is a file with a list of compounds that is limited to the compounds needed in this example.

Select **Compounds** → **List of Added Compounds**

Click on the 'Search or add compound to the list of compounds'

A search window will pop up

Enter 'Vanillin' in the 'Search' field

Click on 'Vanillin'

Click 'OK'
 The search window will disappear
 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 in Pure Solvents**
 Check the '+' button to add pure compound solvents
 'Water', '1,2-Dichloroethane'
 '1-Propanol', 'Oxolane' (THF), 'Acetonitrile',
 '2-Butanone', 'Ethanol', 'Methanol', and 'Toluene'
 Enter '298.15' without quotes for the temperature in the 'from:' field in
 'Kelvin'
 Enter '298.15' in the 'to:' field in 'Kelvin'
 Select 'Vanillin' for the 'Solute'
 Change the popup menu next to Solute from 'Liquid' to 'Solid'
 Press 'Run'

Temperature (Kelvin)	Solubility (mole fraction)	Solubility (mass fraction)	Solubility (mol/L solvent)	Solubility (mol/L solution)	Solubility (g/L solvent)	Solubility (g/L solution)	Activity coefficient	Pure solvent
298.150	0.18867293	0.26519972	3.01135544	2.64938939	457.86859188	402.83261553	1.24820660	s1: 1,2-Dichloroethane
298.150	0.20728497	0.39831761	3.72965087	3.11947327	567.08350284	474.30762036	1.13613060	s2: 1-Propanol
298.150	0.36932052	0.55270212	6.10510006	4.73201158	928.26423790	719.48978379	0.63766507	s3: Oxolane
298.150	0.16724232	0.42670038	4.27973747	3.30464465	650.72270747	502.46243624	1.40815317	s4: Acetonitrile
298.150	0.32179154	0.50029414	4.99194748	4.10032000	759.01234657	623.44275902	0.73184893	s5: 2-Butanone
298.150	0.19676057	0.44719160	4.63654802	3.55538189	704.97480457	540.58636663	1.19690034	s6: Ethanol
298.150	0.17463534	0.50112797	5.92785943	4.04436234	901.31527134	614.93454561	1.34854036	s7: Methanol
298.150	0.08160121	0.12796592	1.01773318	0.98968810	154.74362549	150.47944554	2.88602101	s8: Toluene
298.150	0.00052940	0.00445175	0.03440366	0.03429437	5.23098567	5.21436759	444.84506442	s9: Water

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.

These results can be put in a table. Compared to experiment there can easily be a factor of 2 deviation.

	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

References

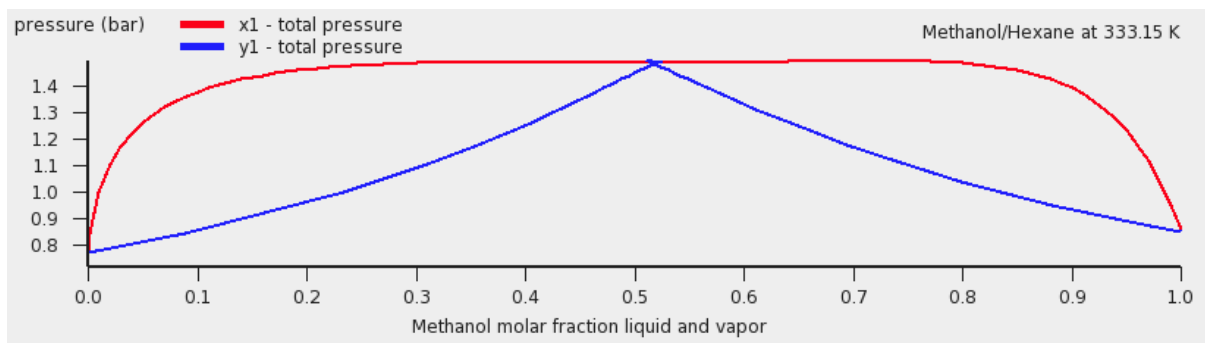
[441] Experimentally determined solubilities of Vanillin in some organic solvents were taken at July 15, 2010, from <http://old.oru.edu/cccd/sl/solubility/allsolvents.php?solute=vanillin>.

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.

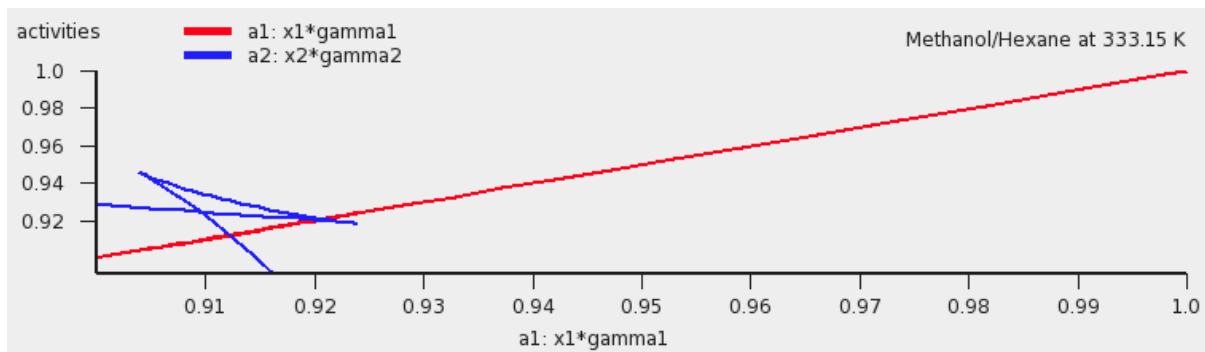
First a binary mixture of Methanol and Hexane is calculated at a constant temperature of 333.15 Kelvin. Next this binary mixture is calculated at a constant pressure of 1.01325 bar. Experimental pure compound properties are used.

Select **Compounds** → **List of Added Compounds**
 Add 'Methanol' and 'Hexane' to this list
 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 **Graph** → **X Axes** → **x1, y1**
 Select **Graph** → **Y Axes** → **total vapor pressure**



In case of a miscibility gap there are two molar fractions x_1 and x_1' , for which both compounds have the same activities. In the calculation one can plot the activity a_1 versus a_2 . If there is a closed loop, there is a miscibility gap:

Select **Graph** → **X Axes** → **a1: $x_1 \cdot \gamma_1$**
 Select **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 $x_1 = 0.275$ and $x_1' = 0.811$, 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.

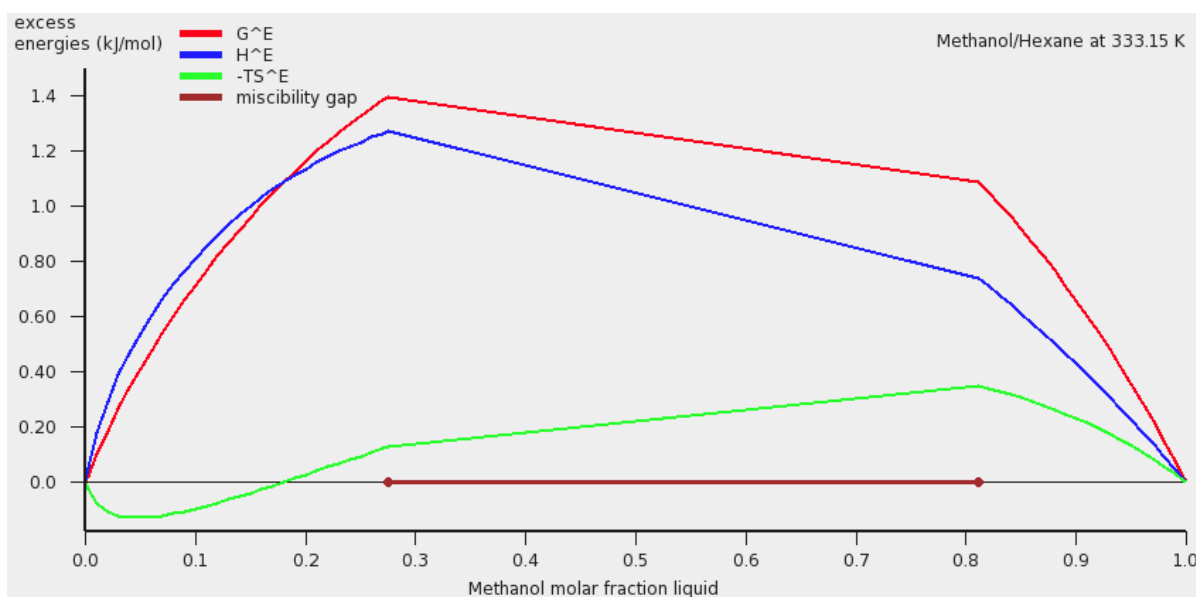
If the check box **Graph → X Axes → force 1 liquid phase within possible miscibility gap** is selected, then results will be shown also within the miscibility gap, with the unphysical conditions that the two liquids are forced to mix. If the check box **Graph → X Axes → force 1 liquid phase within possible 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 **Graph → X Axes → force 1 liquid phase within possible miscibility gap**

Select **Graph → X Axes → x1: molar fraction 1**

Select **Graph → Y Axes → excess energies**



Select **Compounds → List of Added 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'

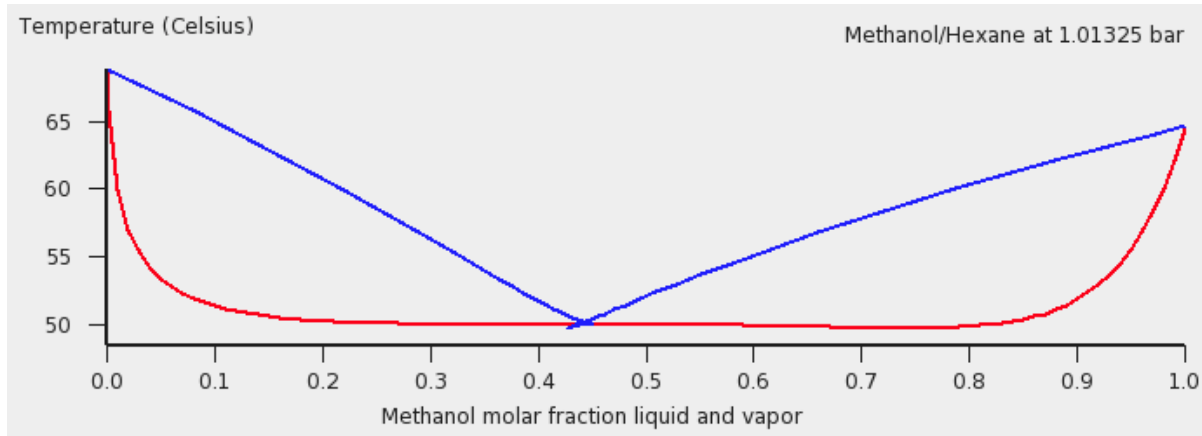
Press 'Run'

Select **Graph → X Axes → x1, y1**

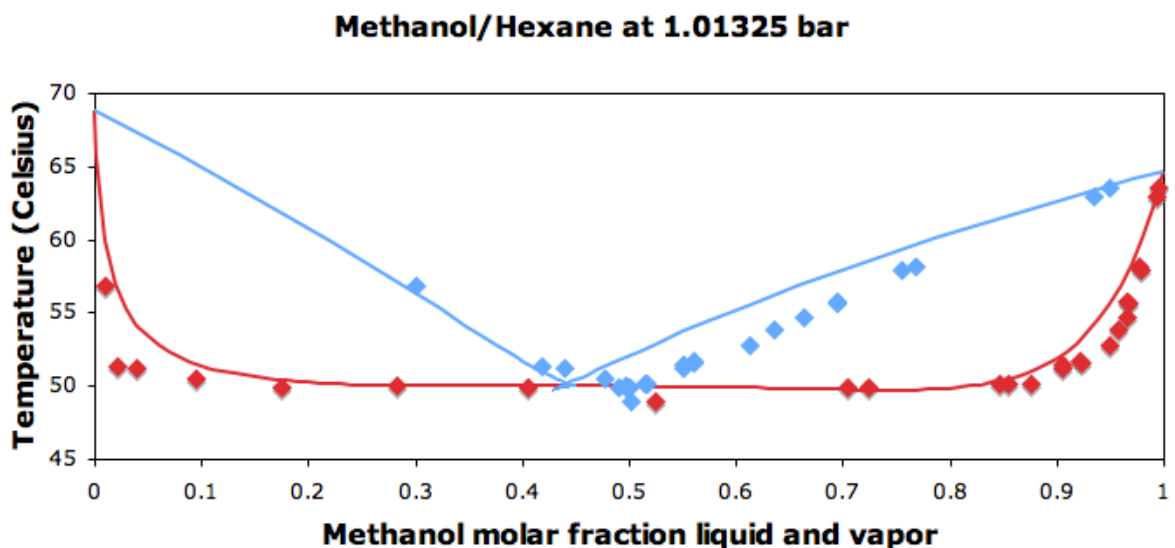
Select **Graph → Y Axes → temperature**

Select the check box **Graph → X Axes → force 1 liquid phase within possible miscibility gap**

There is a calculated miscibility gap between approximately $x_1 = 0.221$ and $x_1' = 0.835$, 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_\(data_page\)](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**), Select **Compounds** → **Add Compound(s)**, go to the directory where the COSMO-RS compound database is downloaded (\$ADFHOME/atomicdata/ADFCRS-2010), and select tutorial4.6.compoundlist. This is recommended. Then the added compounds are at the top of the list if one uses the '+' button, or search button. The tutorial4.6.compoundlist is a file with a list of compounds that is limited to the compounds needed in this example.

Select **Properties** → **Activity coefficients**

Select 'Water' for the first component in Solvent

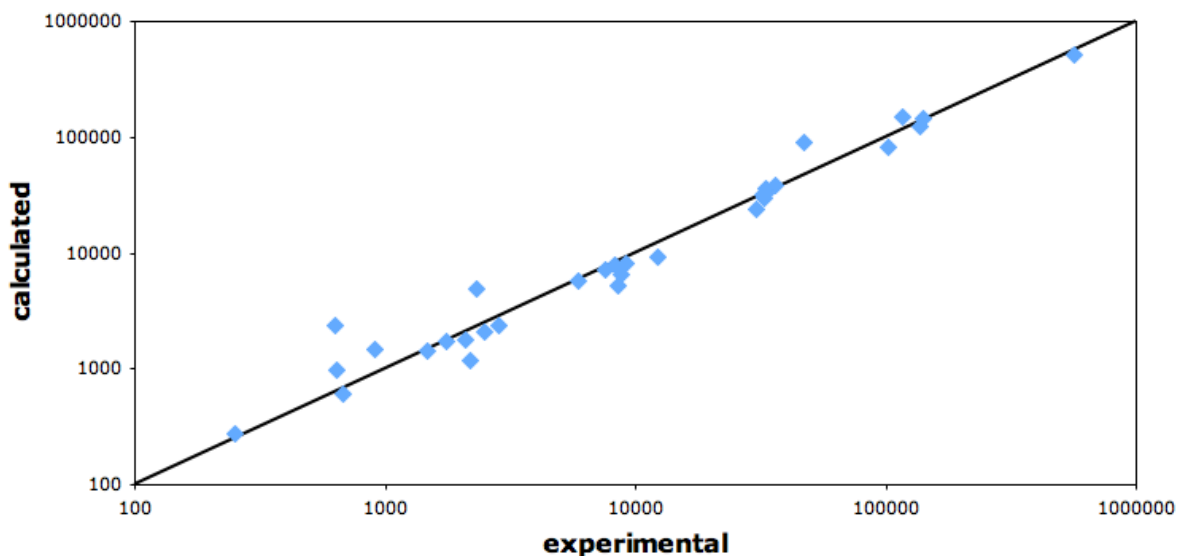
Check the '+' button to add infinite dilute solutes:

'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'

Solvent	Activity Coefficient
s1: Water	1.00000000
Solute (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].

infinite dilution activity coefficients



	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	$1.48 \cdot 10^3$	$1.42 \cdot 10^3$
7	1-Chloropropane	$1.75 \cdot 10^3$	$1.73 \cdot 10^3$
8	2-Bromopropane	$2.09 \cdot 10^3$	$1.77 \cdot 10^3$
9	Ethyl_iodide	$2.19 \cdot 10^3$	$1.19 \cdot 10^3$
10	1-Propoxypropane	$2.31 \cdot 10^3$	$4.89 \cdot 10^3$
11	Benzene	$2.48 \cdot 10^3$	$2.07 \cdot 10^3$
12	1-Bromopropane	$2.86 \cdot 10^3$	$2.36 \cdot 10^3$
13	1,1,1-Trichloroethane	$5.90 \cdot 10^3$	$5.77 \cdot 10^3$
14	1-Chlorobutane	$7.61 \cdot 10^3$	$7.25 \cdot 10^3$
15	2-Bromobutane	$8.32 \cdot 10^3$	$7.81 \cdot 10^3$
16	n-Propyl_iodide	$8.55 \cdot 10^3$	$5.16 \cdot 10^3$
17	Trichloroethene	$8.75 \cdot 10^3$	$6.45 \cdot 10^3$
18	Toluene	$9.19 \cdot 10^3$	$8.14 \cdot 10^3$
19	1-Bromobutane	$1.22 \cdot 10^4$	$0.93 \cdot 10^4$
20	o-Xylene	$3.05 \cdot 10^4$	$2.37 \cdot 10^4$
21	1-Chloropentane	$3.21 \cdot 10^4$	$3.13 \cdot 10^4$

22	Ethylbenzene	$3.27 \cdot 10^4$	$3.00 \cdot 10^4$
23	m-Xylene	$3.32 \cdot 10^4$	$3.56 \cdot 10^4$
24	p-Xylene	$3.33 \cdot 10^4$	$3.30 \cdot 10^4$
25	Tetrachloroethene	$3.60 \cdot 10^4$	$3.81 \cdot 10^4$
26	Di-n-butyl_ether	$4.72 \cdot 10^4$	$8.95 \cdot 10^4$
27	Cumene	$1.02 \cdot 10^5$	$0.83 \cdot 10^5$
28	Mesitylene	$1.17 \cdot 10^5$	$1.49 \cdot 10^5$
29	n-Propylbenzene	$1.36 \cdot 10^5$	$1.24 \cdot 10^5$
30	1-Chlorohexane	$1.41 \cdot 10^5$	$1.46 \cdot 10^5$
31	n-Butylbenzene	$5.66 \cdot 10^5$	$5.16 \cdot 10^5$

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].

- [Table with the calculated and 642 experimental values](#)

Note that these calculations in this section may take a while, because of the many compounds calculated at once.

Open a new COSMO-RS GUI window (**SCM** → **COSMO-RS**). Select **Compounds** → **Add Compound(s)** go to the directory where the COSMO-RS compound database is downloaded ($\$ADFH\text{HOME}/\text{atomicdata}/\text{ADFCRS-2010}$), and select tutorial4.7.compoundlist.

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

Check the '+' button to add infinite dilute solutes, the first 217 from the list

Press 'Run'

Activity Coefficients Kill Run

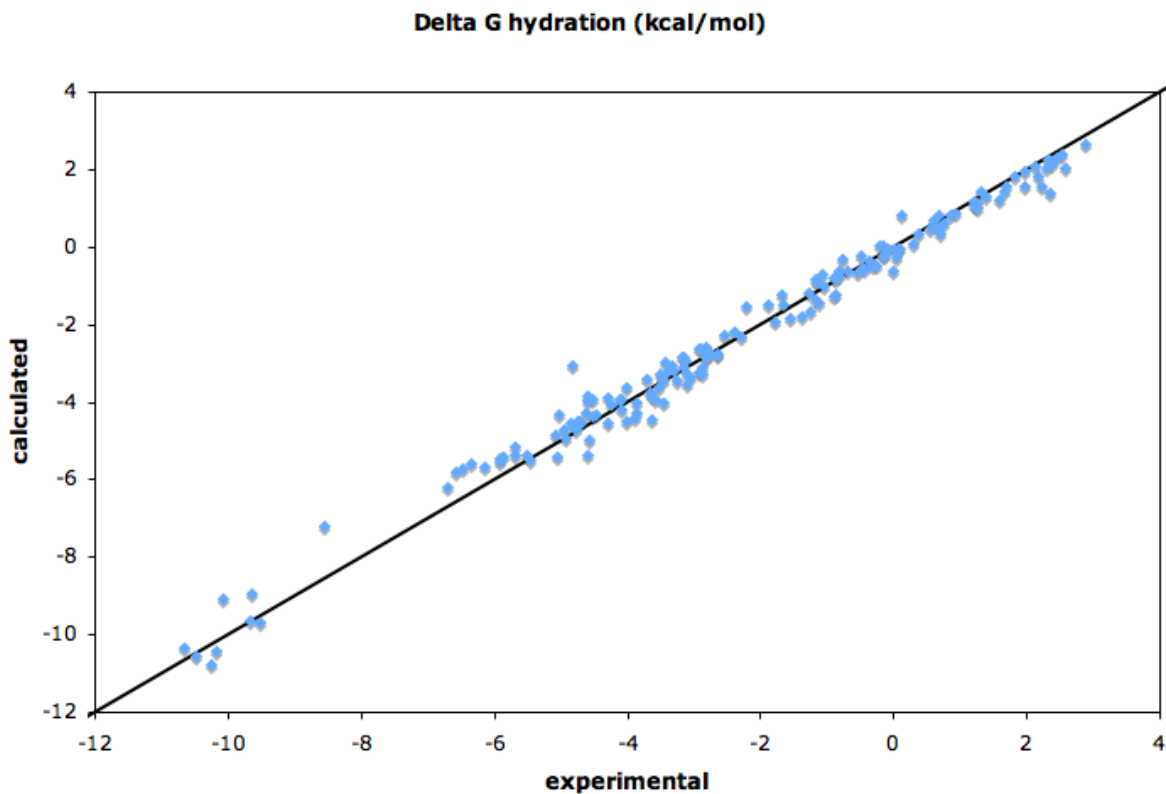
Solvent: 1 component Mole fraction

Q	Water		1.0
Q			
Q			
Q			
Q			

Use density solvent (kg/L): 0.997

Temperature: 298.15 Kelvin

The results for the free energy of hydration (ΔG (kcal/mol) gas \rightarrow solute) can be compared with experimental values, see [this table](#) and next graph.



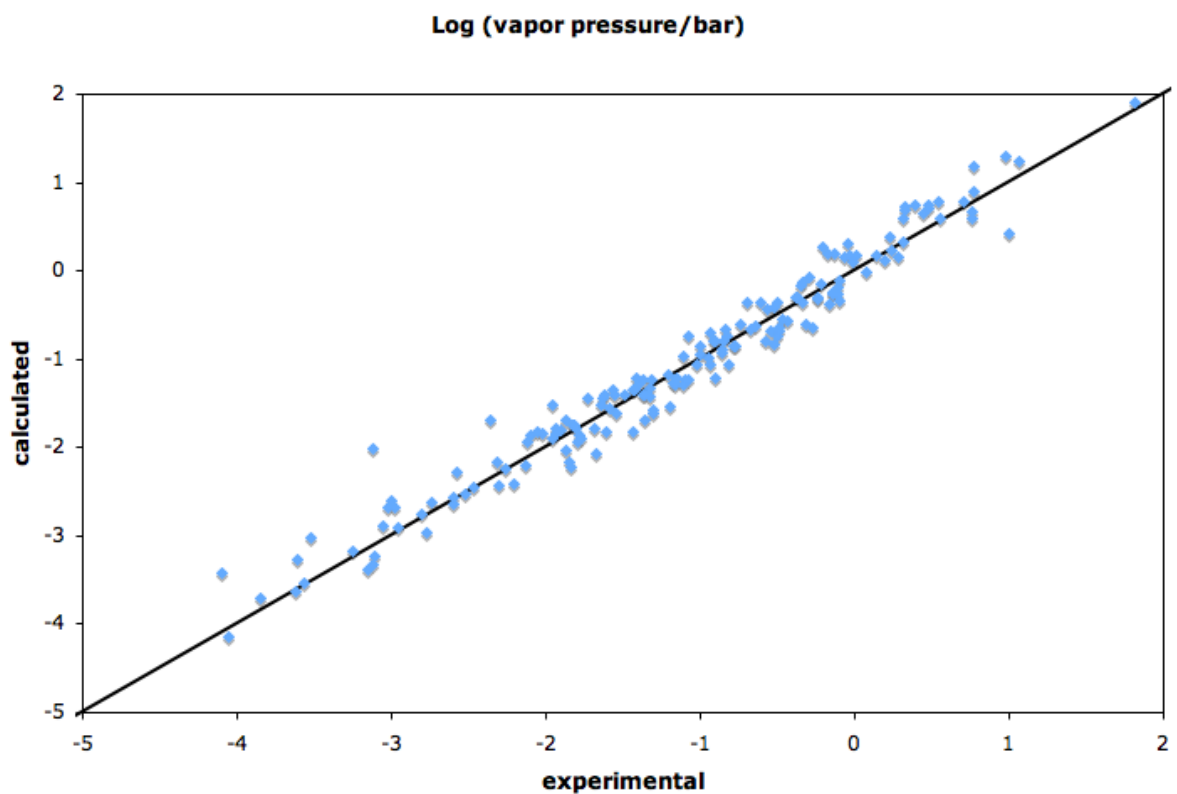
Vapor pressure

Select **Properties** \rightarrow **Vapor Pressure Pure Compounds**
 Enter '298.15' for 'Temperature Kelvin'

Check the '+' button to add the first 217 from the list
Press 'Run'

Solvent Vapor Pressure		Kill	Run
Solvent:		Mole fraction ▼	
Q Methane ▼	▼	1.0	
Q ▼	▼	0.0	
Q ▼	▼	0.0	
Q ▼	▼	0.0	
Q ▼	▼	0.0	
Temperature from:	298.15	Kelvin ▼	
to:	298.15	Kelvin ▼	
Number of temperatures:	(n+1), n=		10

One should 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 'Preset Octanol-Water' in the popup menu next to Solvent

Enter '298.15' for the 'Temperature' in 'Kelvin'

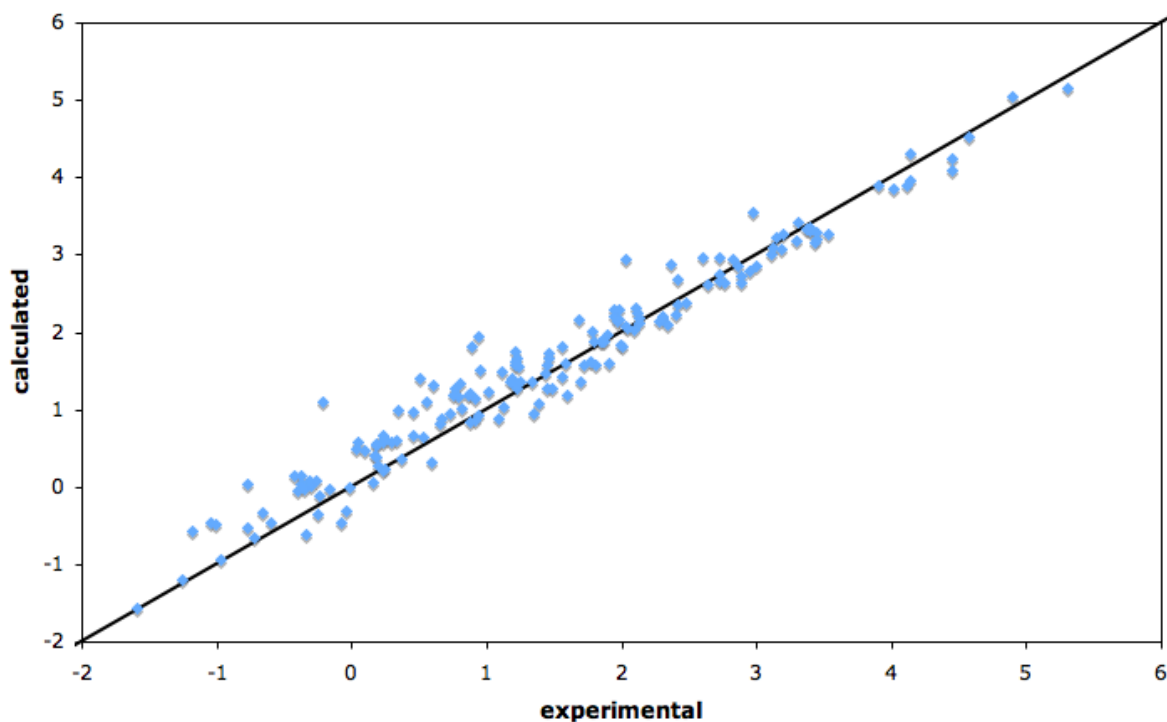
Check the '+' button to add the first 217 from the list
to the list of infinite dilute solutes

Press 'Run'

Log Partition Coefficients (solvent phase 1/phase 2)		Kill	Run
Solvent		Mole fraction ▾	
Preset Octanol-Water ▾		phase 1: phase 2:	
🔍	Octanol ▾	0.725	0.0
🔍	Water ▾	0.275	1.0
🔍	▾	0.0	0.0
<input checked="" type="checkbox"/>	Use molar volume 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.

Octanol/Water partition coefficient



Hexane-Water, Benzene-Water, and Ethoxyethane-Water partition coefficients

Select **Properties** → **Log Partition Coefficients**

Select 'Preset Hexane-Water' in the popup menu next to Solvent

Enter '298.15' for the 'Temperature' in 'Kelvin'

Check the '+' button to add the first 217 from the list
to the list of infinite dilute solutes

Press 'Run'

Log Partition Coefficients (solvent phase 1/phase 2)		Kill	Run
Solvent		Mole fraction	
Preset Hexane-Water		phase 1:	phase 2:
Hexane		1.0	0.0
Water		0.0	1.0
		0.0	0.0
<input checked="" type="checkbox"/> Use molar volume phase 1/phase 2:		7.28	
Temperature:	298.15	Kelvin	

Select **Properties** → **Log Partition Coefficients**

Select 'Preset Benzene-Water' in the popup menu next to Solvent

Enter '298.15' for the 'Temperature' in 'Kelvin'

Check the '+' button to add the first 217 from the list

to the list of infinite dilute solutes

Press 'Run'

Log Partition Coefficients (solvent phase 1/phase 2) Kill Run

Solvent Mole fraction

	phase 1:	phase 2:
Preset Benzene-Water		
Benzene	1.0	0.0
Water	0.0	1.0
	0.0	0.0

Use molar volume phase 1/phase 2: 4.93

Temperature: 298.15 Kelvin

Select **Properties** → **Log Partition Coefficients**

Select 'Preset Ether-Water' in the popup menu next to Solvent

Enter '298.15' for the 'Temperature' in 'Kelvin'

Check the '+' button to add the first 217 from the list

to the list of infinite dilute solutes

Press 'Run'

Log Partition Coefficients (solvent phase 1/phase 2) Kill Run

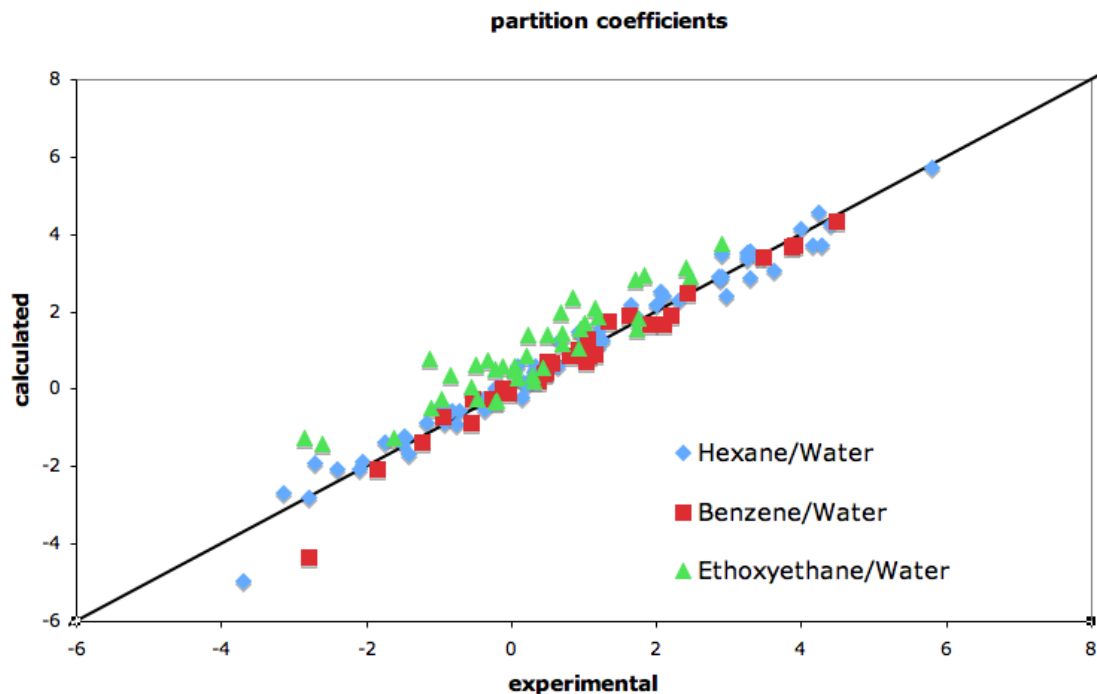
Solvent Mole fraction

	phase 1:	phase 2:
Preset Ether-Water		
Ether	1.0	0.0
Water	0.0	1.0
	0.0	0.0

Use molar volume phase 1/phase 2: 5.75

Temperature: 298.15 Kelvin

The results for the Hexane-Water, Benzene-Water, and Ethoxyethane-Water (Ether-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)

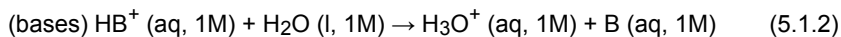
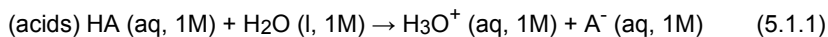
[472] A. Klamt, V. Jonas, T. Bürger and J.C. Lohrenz, *Refinement and Parametrization of COSMO-RS.* *Journal of Physical Chemistry A* **102**, 5074 (1998)

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 continuum 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:



The free energy of dissociation for acids and bases is calculated as

$$\text{(acids) } \Delta G_{\text{diss}}^* = G(\text{A}^-) - G(\text{HA}) + G(\text{H}_3\text{O}^+) - G(\text{H}_2\text{O}) \quad (5.1.3)$$

$$\text{(bases) } \Delta G_{\text{diss}}^* = G(\text{B}) - G(\text{HB}^+) + G(\text{H}_3\text{O}^+) - G(\text{H}_2\text{O}) \quad (5.1.4)$$

The * denotes a standard state of 1M (1 mol/L). The $\text{p}K_{\text{a}}$ can then be calculated as (see for example Refs. [511,512])

$$\text{p}K_{\text{a}} = \Delta G_{\text{diss}}^*/(RT \ln(10)) - 1.74 \quad (5.1.5)$$

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.

Empirical 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 $\text{p}K_{\text{a}}$ 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:

$$\text{(acids) } \text{p}K_{\text{a}} = 0.62 \Delta G_{\text{diss}}^*/(RT \ln(10)) + 2.10 \quad (5.1.6)$$

$$\text{(bases) } \text{p}K_{\text{a}} = 0.67 \Delta G_{\text{diss}}^*/(RT \ln(10)) - 2.00 \quad (5.1.7)$$

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 $\text{p}K_{\text{a}}$ 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 compounds 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'
Check the '+' button to add the first 12 compounds from the list
Press 'Run'
```

	Activity Coefficient	Henry Constant (mol/(L atm))	Henry Constant dimensionless	ΔG (kcal/mol) gas->solute	ΔG (kcal/mol) liq->solute	G (kcal/mol) solute
Solvent						
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 ($pK_a = 0.62 \cdot 0.733 \cdot \Delta G_{diss} + 2.10$), with $\Delta G_{diss} = G(\text{conjugate_base_acid}) - G(\text{acid}) + G(\text{conjugate_acid_Water}) - G(\text{Water})$ 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 compounds 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'

Check the '+' button to add the first 16 compounds from the list

Press 'Run'

	Activity Coefficient	Henry Constant (mol/(L atm))	Henry Constant dimensionless	ΔG (kcal/mol) gas->solute	ΔG (kcal/mol) liq->solute	G (kcal/mol) solute
Solvent						
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 ($pK_a = 0.67 \cdot 0.733 \cdot \Delta G_{diss} - 2.00$), with $\Delta G_{diss} = G(\text{base}) - G(\text{conjugate_acid_base}) + G(\text{conjugate_acid_Water}) - G(\text{Water})$ 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

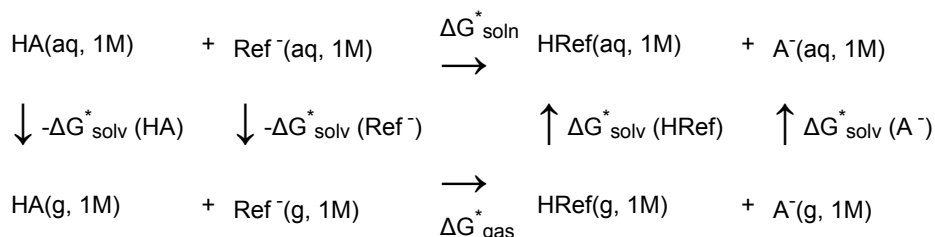
References

[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:



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])

$$\text{pK}_a = \Delta G_{\text{soln}}^*/(RT \ln(10)) + \text{pK}_a(\text{HRef})$$

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

$$\Delta G_{\text{soln}}^* = (1555-1569)/4.184 - 4.97 - 86.56 + 4.79 + 90.14 = 0.05 \text{ kcal/mol}$$

$$pK_a (\text{Ethanol}) = 0.733 \cdot 0.05 + 15.5 \approx 15.5$$

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](#)