



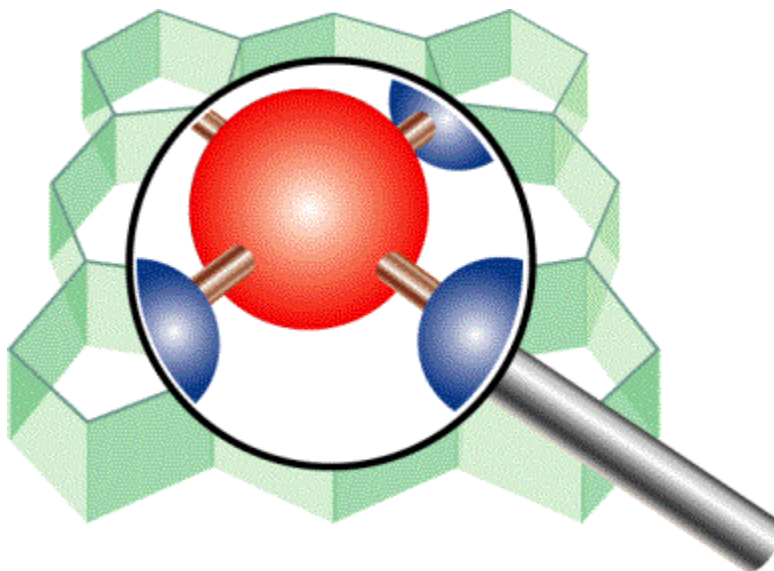
Scientific Computing & Modelling

# ADF-GUI Tutorial

**ADF Program System  
Release 2010**

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# Introduction

This document will provide a hands-on tutorials demonstrating the ADF-GUI. Its purpose is to give a quick tour of the main features of the ADF-GUI.

The first three tutorials provide an overview over all ADF-GUI modules. If you are new to the ADF-GUI, we advise you to study the tutorials in the order presented. The other tutorials are intended to focus on one particular feature of the ADF-GUI, or some particular application.

We estimate that you will need about half an hour for each part of the tutorial, for reading and performing the hands-on activities.

The first three tutorials are also available as videos. The current videos are actually the [tutorial videos](#) for ADF2009, so there will be minor differences with the ADF2010 GUI tutorials.

Additional information may be found in the [ADF-GUI Reference manual](#)

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

- Undo: Ctrl-Z on Linux/Windows, Command-Z on Macintosh
- Save: Ctrl-S on Linux/Windows, Command-S on Macintosh

In general, on Linux and Windows machines use the Control key to access these shortcuts for the menu commands, on a Mac use the Command key.

If you are using a Mac, the ADF-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).

## ADF-GUI modules

The ADF-GUI is the Graphical User Interface for the ADF package. It consists of several modules:

### ADFjobs

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.

### ADFinput

ADFinput (`$ADFBIN/adfinput`) helps ADF 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.

### ADFview

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.

### ADFmovie

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.

#### ADFllevels

ADFllevels (\$ADFBIN/adfllevels) 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.

#### ADFdos

ADFdos (\$ADFBIN/adfdos) shows DOS and GPDOS for ADF 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.

#### ADFspectra

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.

#### ADFTail

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

#### ADFoutput

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.

#### GUIprefs

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.

All ADF-GUI modules have the SCM menu on the left-hand side, on most systems represented by a small SCM logo. Using the SCM menu commands you can easily switch between the different modules of the ADF-GUI.

## Starting the ADF-GUI modules

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

Depending on your platform, you start the ADF-GUI modules in a slightly different way:

### UNIX (such as Linux) users

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

```
$ADFBIN/adfjobs &
```

instead of just

```
adfjobs &
```

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

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

```
xcalc &
```

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

## **Windows users**

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

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

## **Macintosh users**

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

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

# 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 &
```

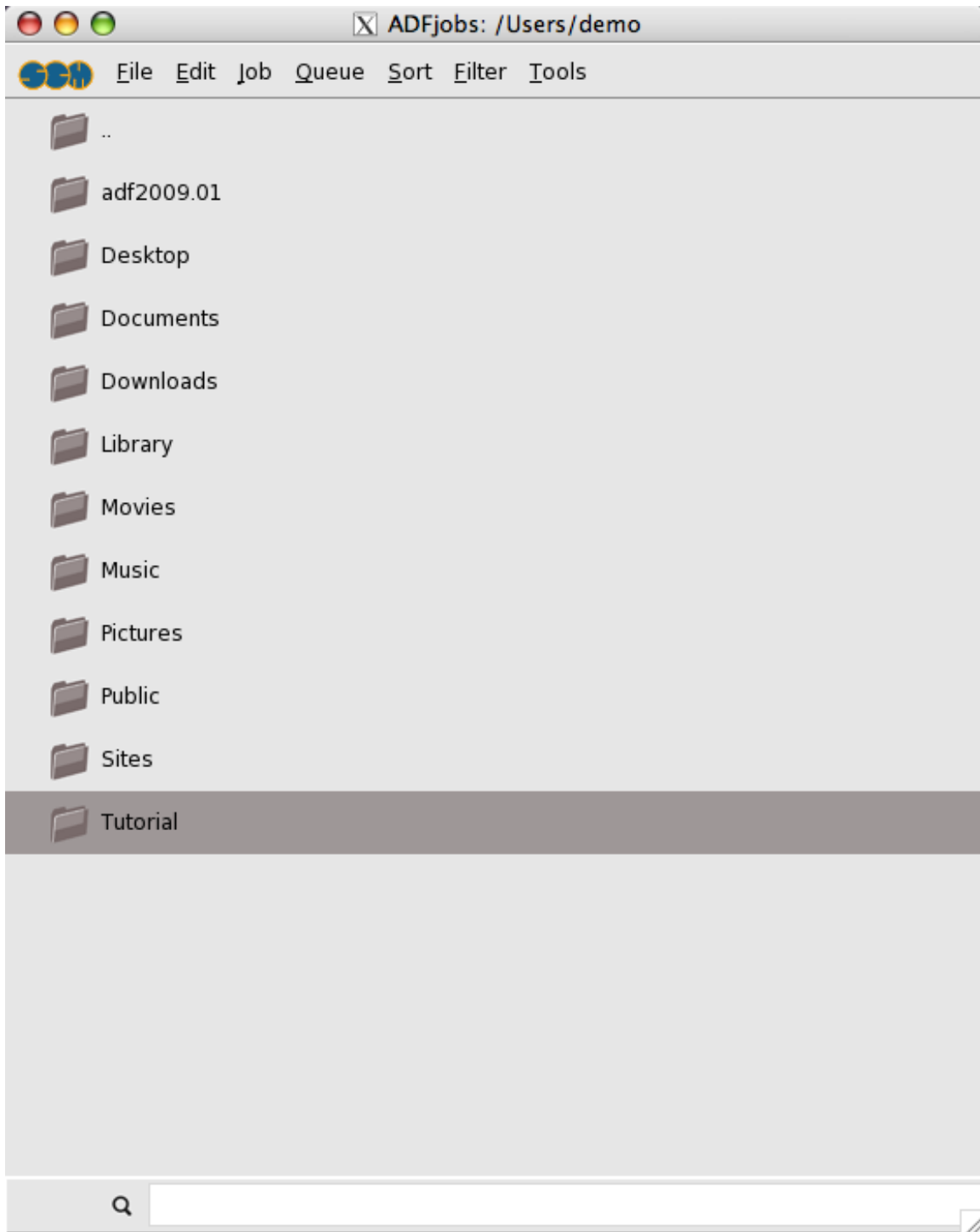
On Windows, one can start ADFjobs by double-clicking on the ADF-GUI icon on the Desktop:

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

On Macintosh, use the ADFLaunch program to start ADFjobs:

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

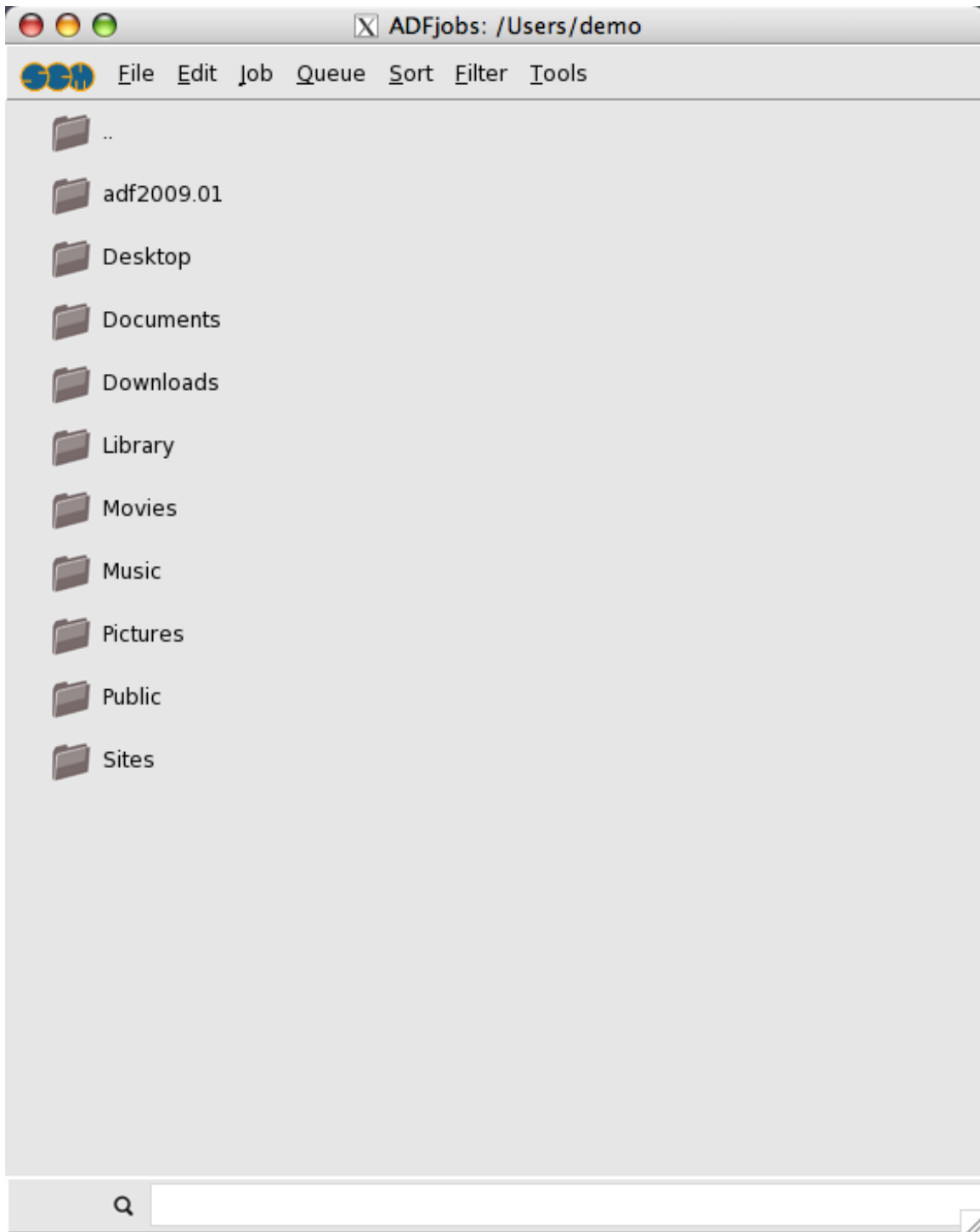




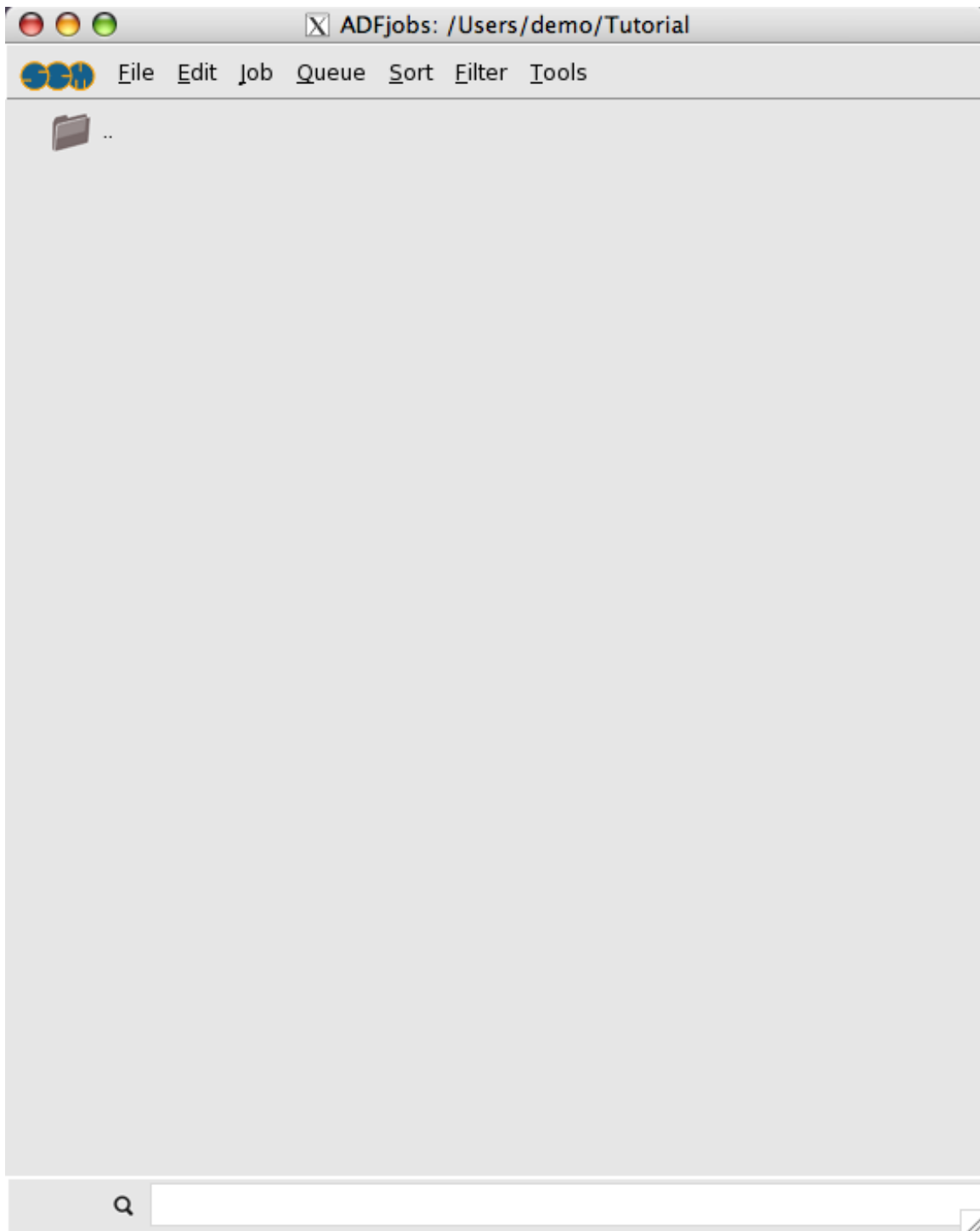
### **Make a directory for the tutorial**

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



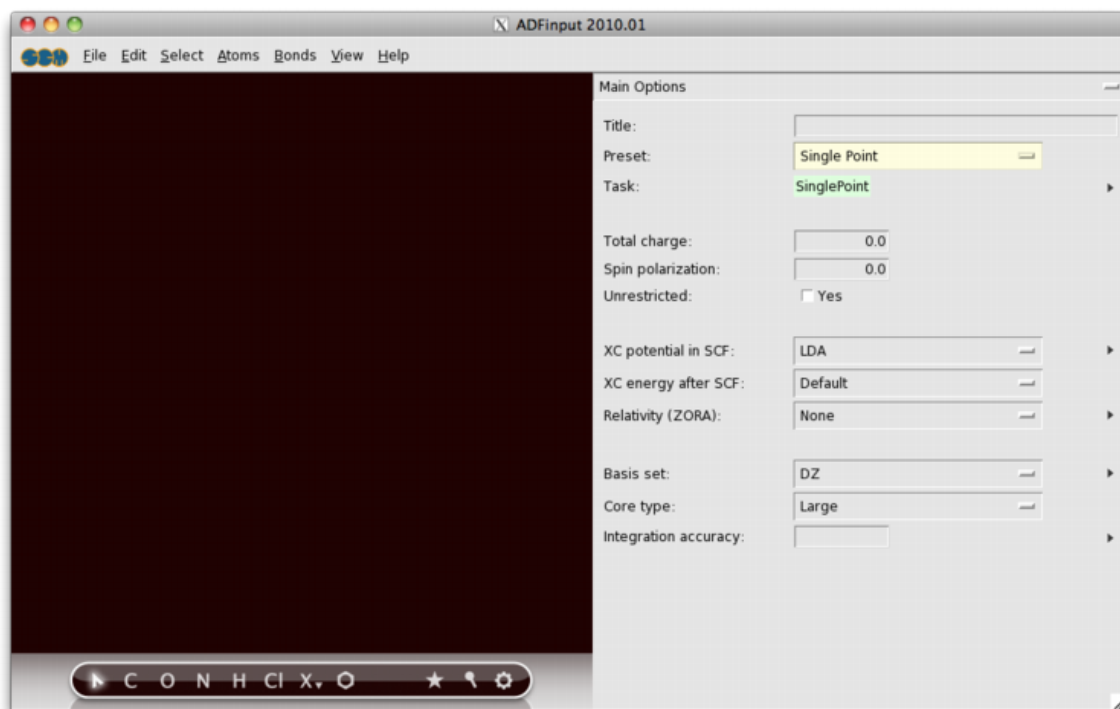
## Start ADFinput

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

Select the **SCM** → **ADFinput** menu command:

use the SCM menu on the top left (the SCM logo on most platforms), next select the ADFinput 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
- 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 'Main Options' panel is visible)

## Undo

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

<u>U</u> ndo	Cmd Z
<u>R</u> edo	Shift Cmd Z
<u>C</u> ut	Cmd X
<u>C</u> opy	Cmd C
<u>P</u> aste	Cmd V
<u>C</u> lear	Cmd B
<u>G</u> roup	Cmd G
<u>U</u> ngroup	Cmd U
Set Origin	
Symmetry	▶
Mirror	▶
Align	▶

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

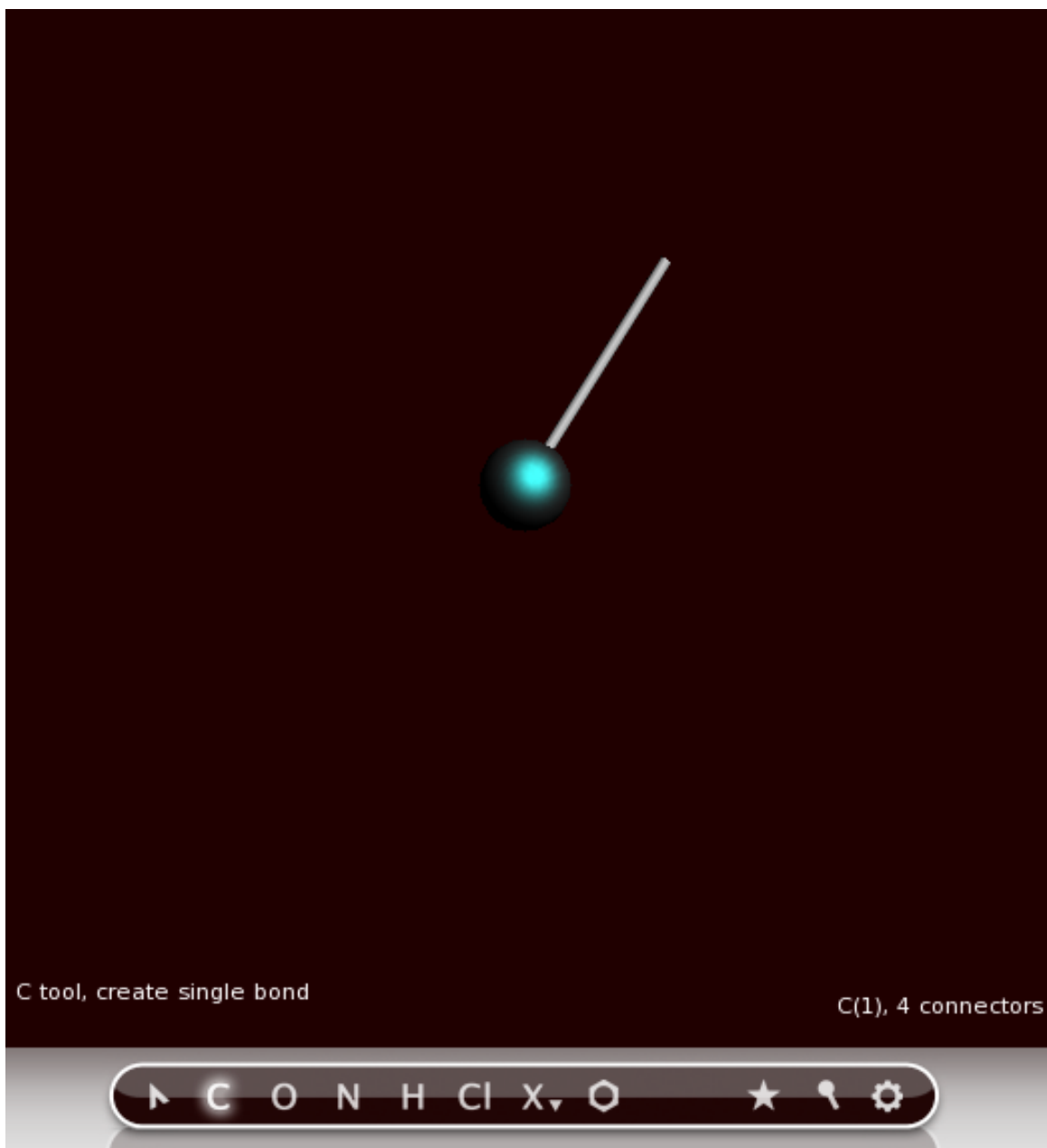
To create an atom, you need to select an atom tool.

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



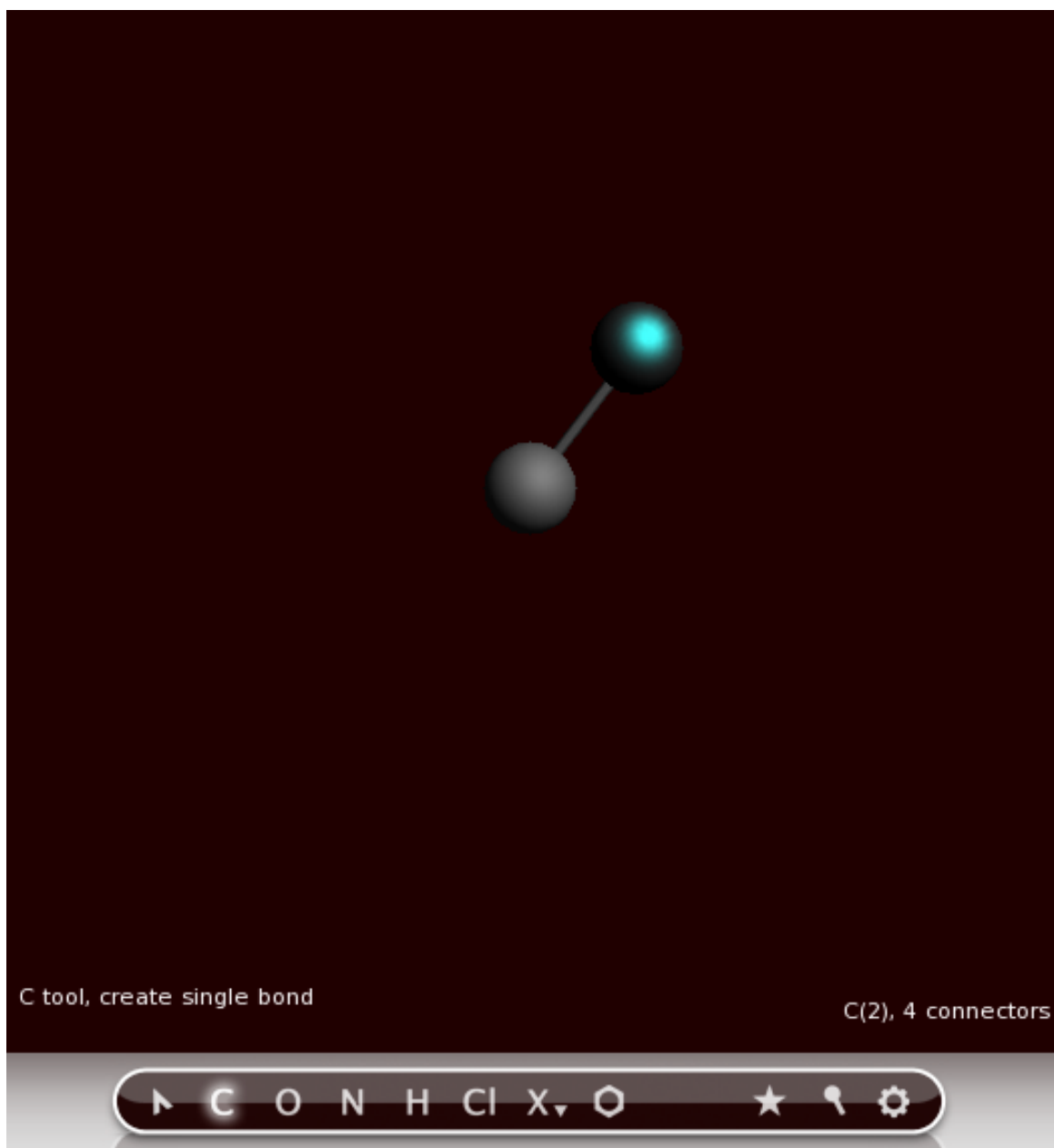
One carbon atom has been created.

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 0, 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.

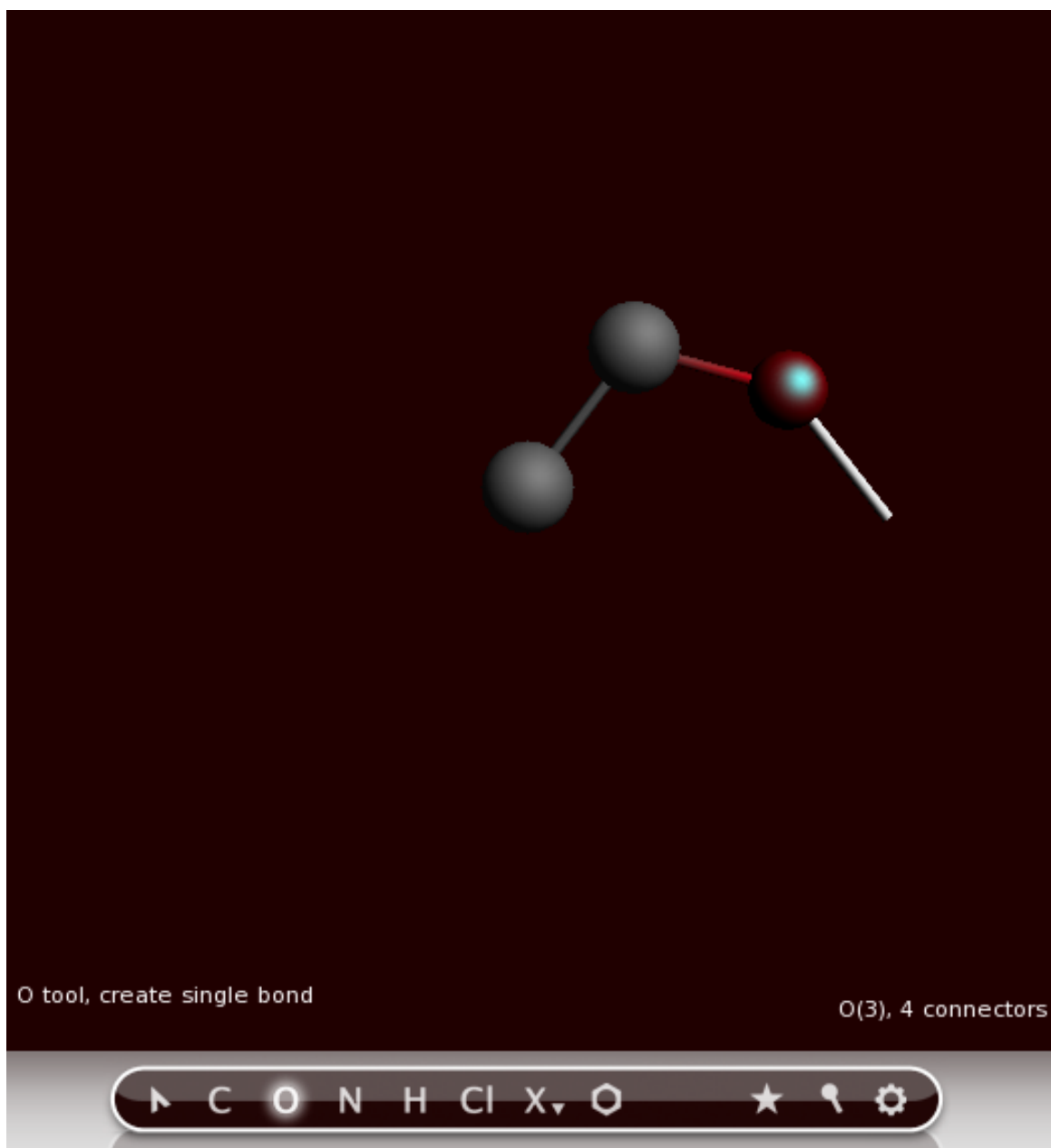
## Create the oxygen atom

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.

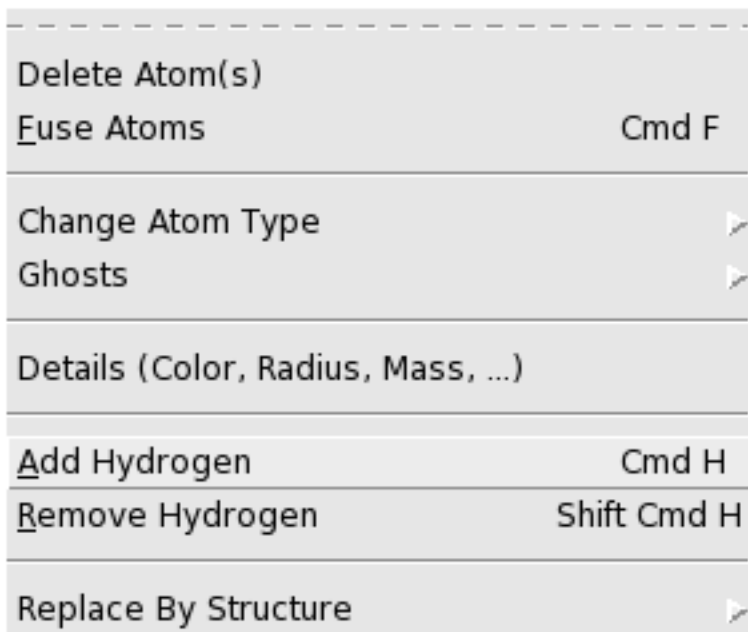
For now, we are done using atom tools, so go back to the select tool:



Select the select-tool by clicking on the button with the arrow

### Add the hydrogens

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



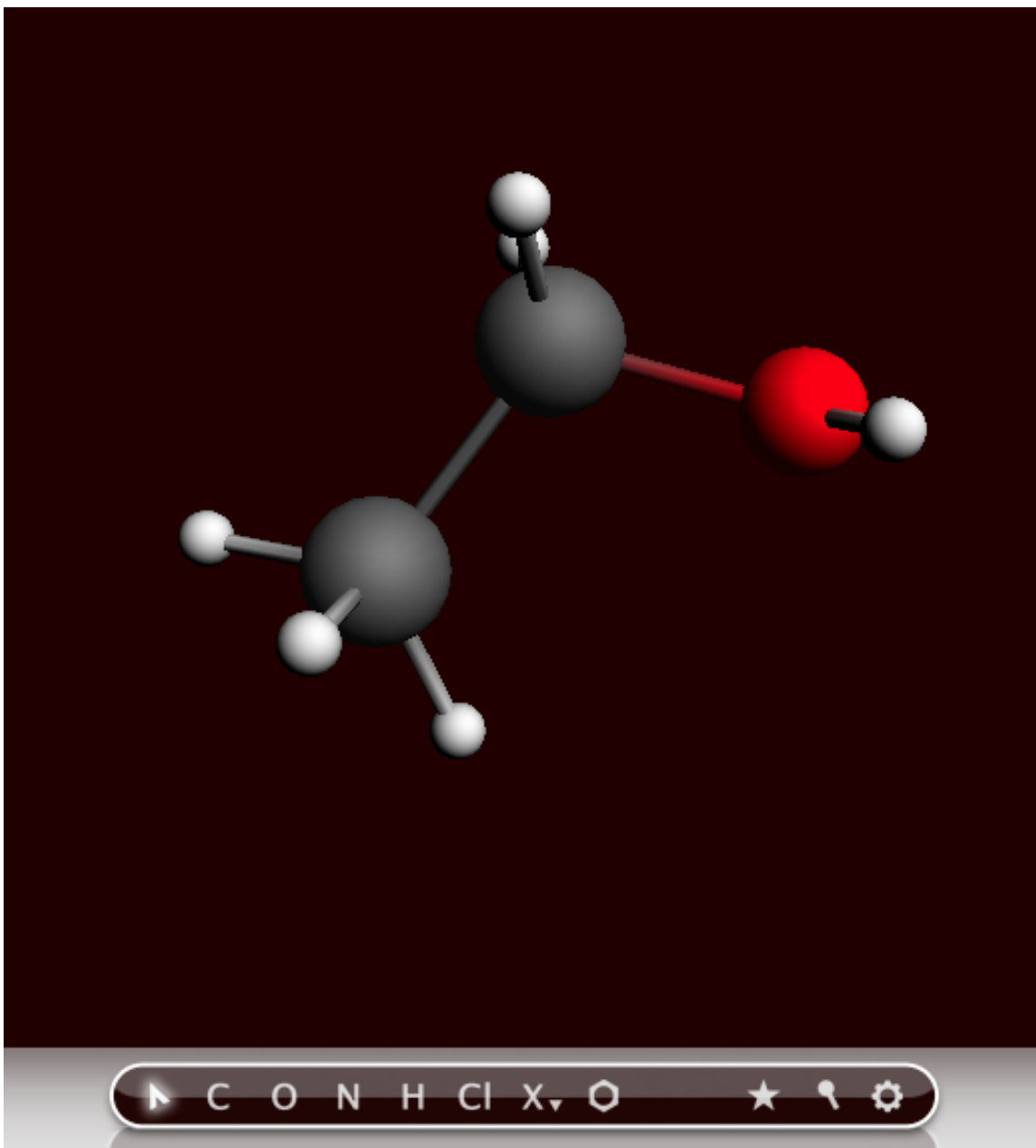
The 'Add Hydrogen' menu command works on the selection only, when present. Thus, only one hydrogen atom would be added to the oxygen atom. This is not what you want. So first we make sure that nothing is selected by clicking in empty space.

Click in empty (drawing) space

Now no atoms are selected any more.

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

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

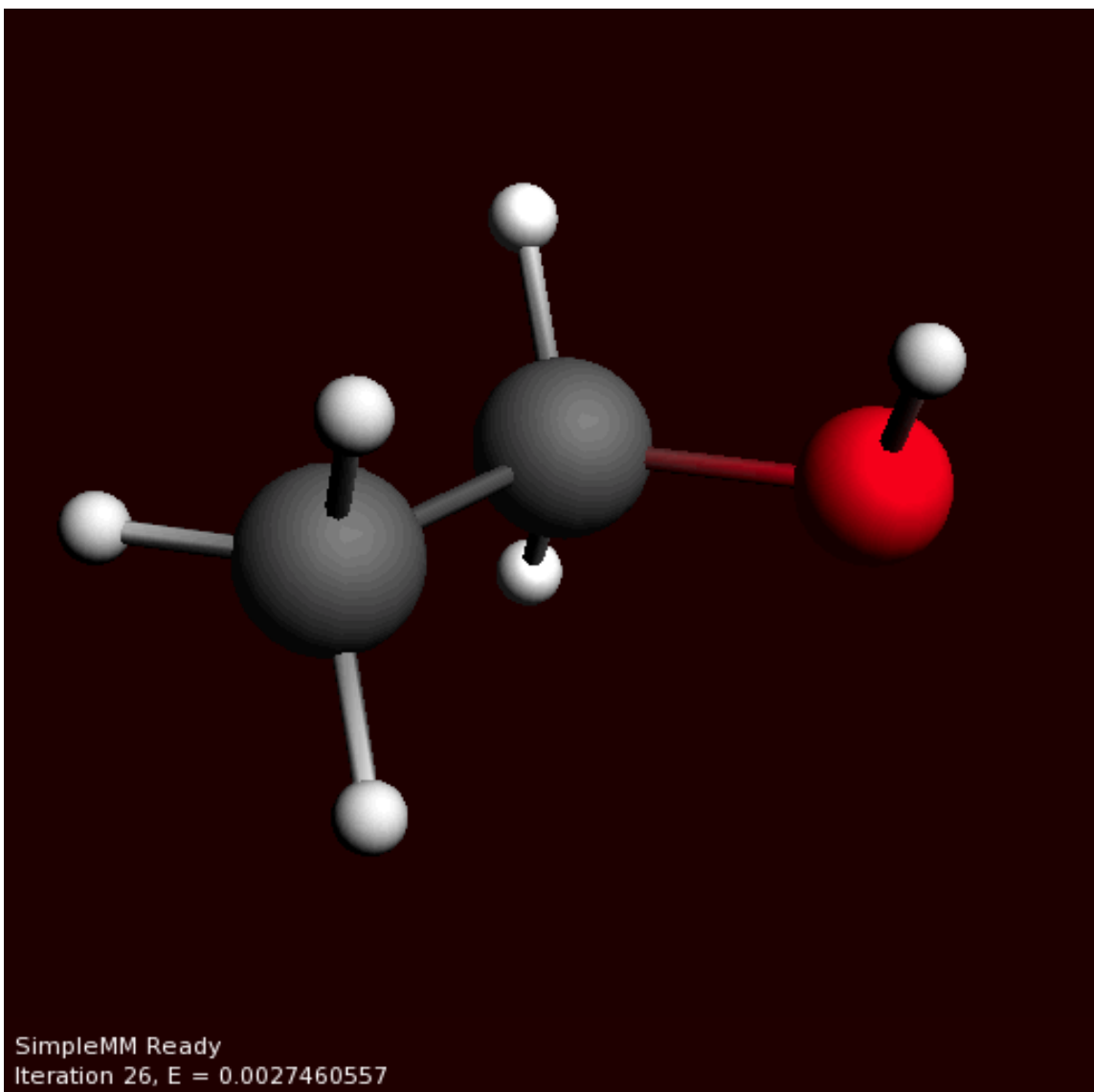


All atoms will be saturated with hydrogen atoms. And you have created an ethanol molecule, though the geometry is still far from perfect.

### **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 'gear wheel' button of the menu bar)



The geometry of the molecule will be pre-optimized very quickly, using a simple (and inaccurate) force field method.

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 Command-Left (drag up or down)

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

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

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

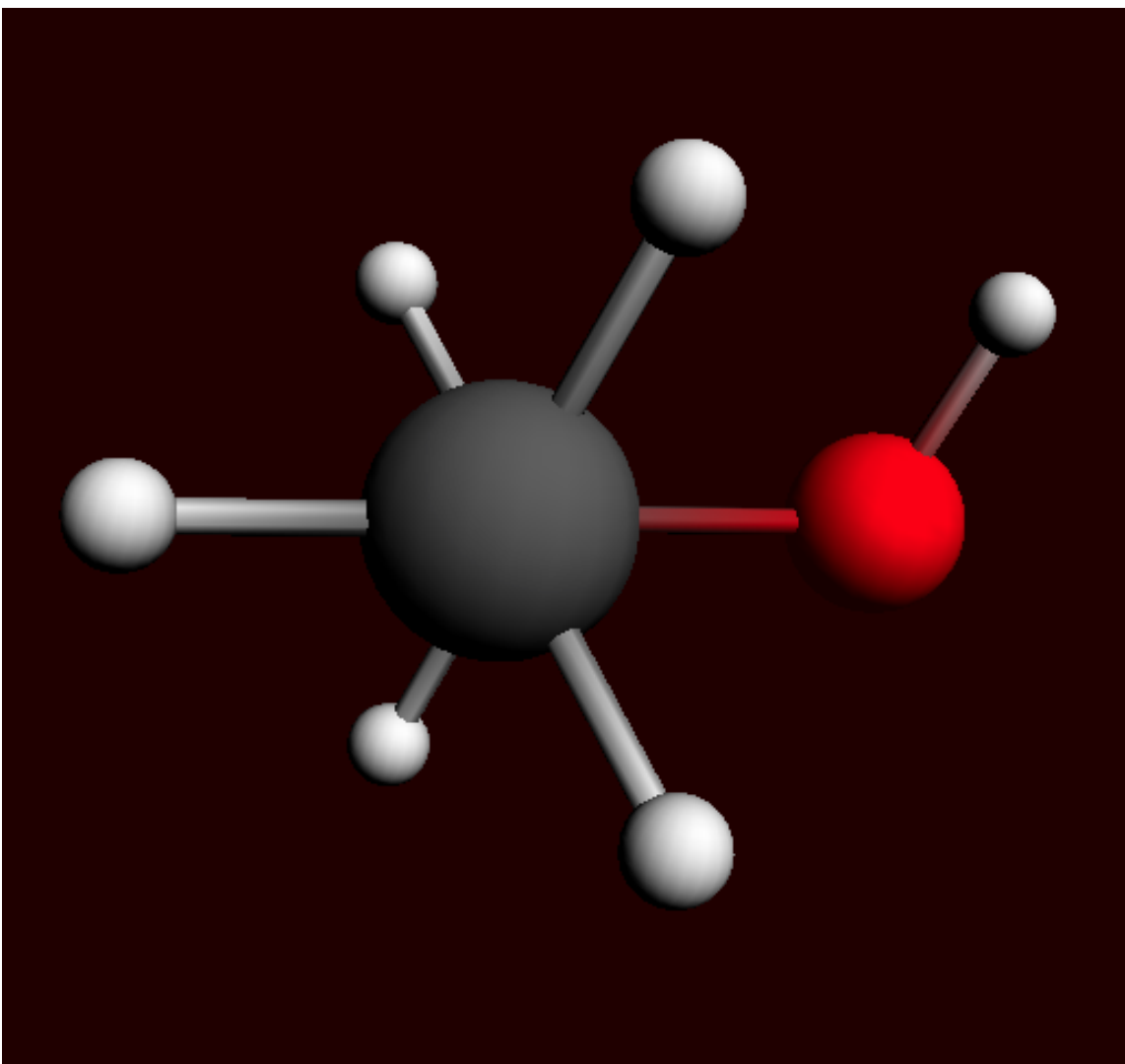
Click with the left mouse button with the ctrl-key, and drag:  
your molecule will rotate in-plane.

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

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

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

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



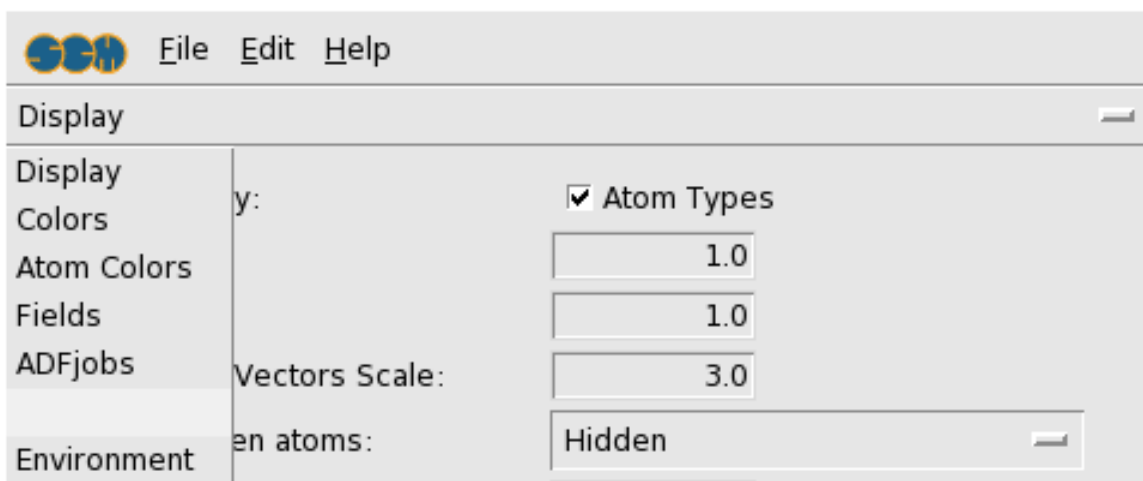
### Atom colors

The atoms of your molecule will have a pre-defined color, as visible in the molecule editor. You can change these colors in two ways: either change the global default color per element, or override the default color for a specific atom. The first method uses the GUIprefs module, 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 GUIprefs module:

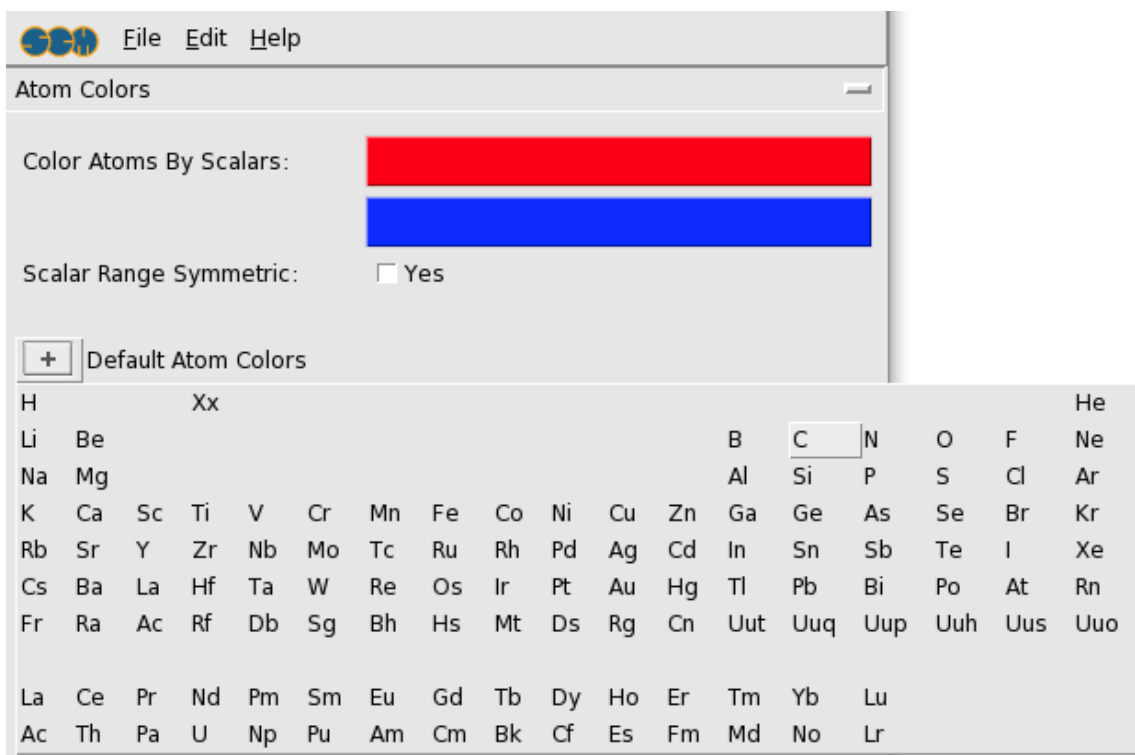
Open the GUIprefs module by using the **SCM** → **Preferences** menu command

ADF Input ADF Levels
COSMO-RS
BAND Input BAND Structure
ReaxFF Input
View Movie Logfile Output Spectra Dos
Close All
Preferences Jobs

In the GUIprefs module, go to the 'Atom Colors' panel (use the pull-down menu on top).



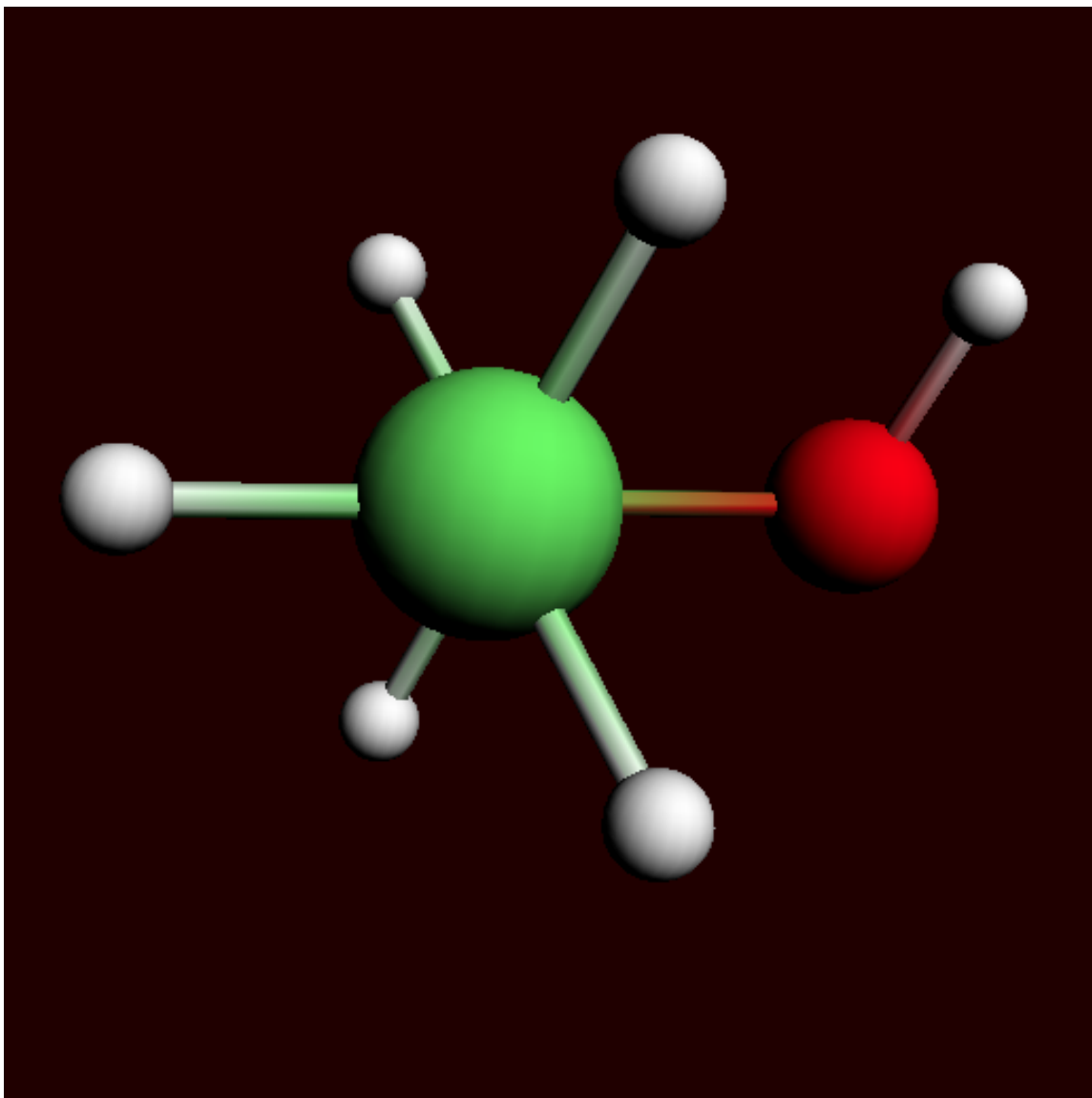
Click on the '+' button, and select C (Carbon) from the periodic table that pops up.



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.

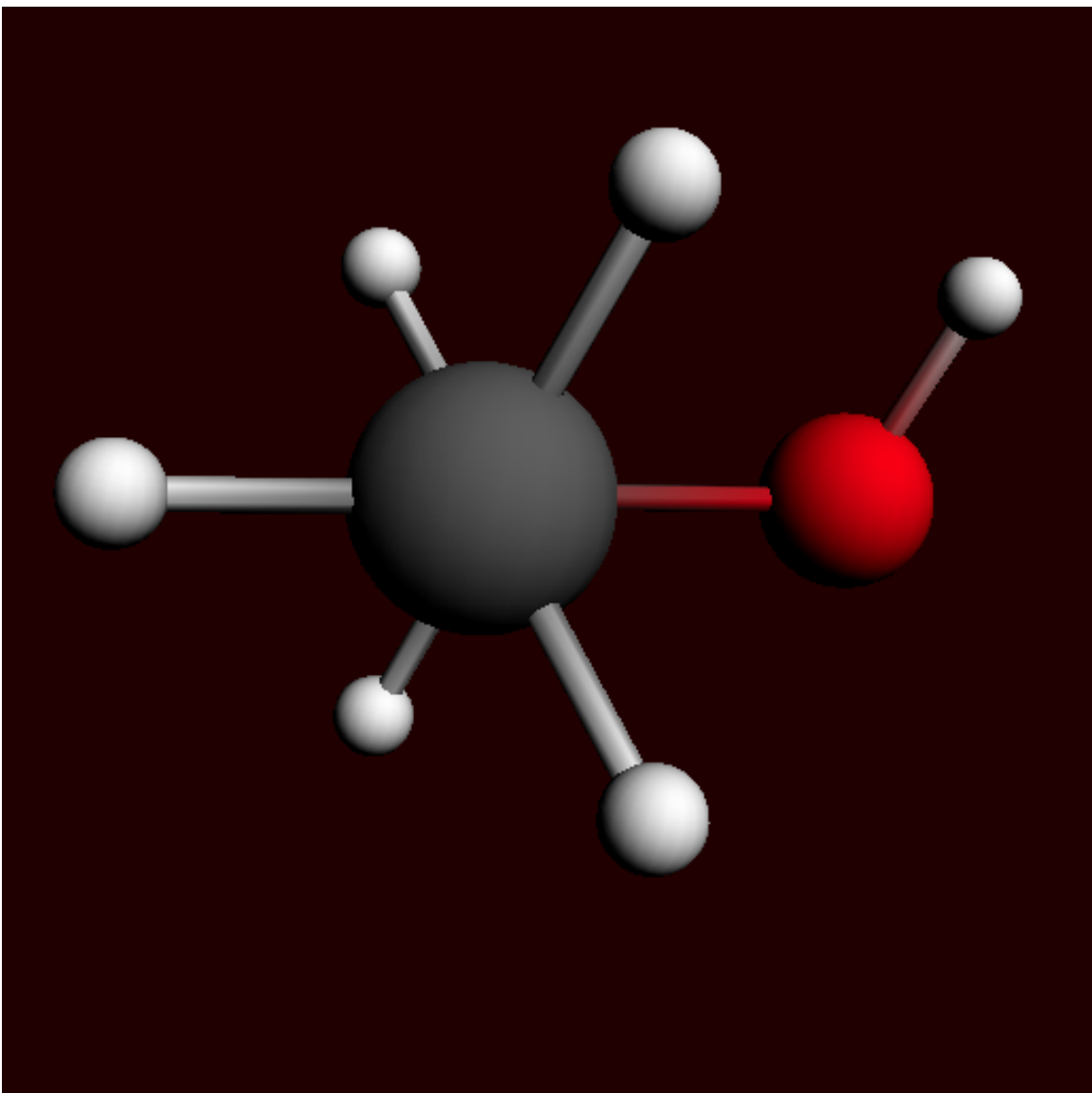
If you quit the GUIprefs module without saving, your original settings will be restored (also in the open modules).

To revert to the default value of carbon, you can remove the carbon color in GUIprefs 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



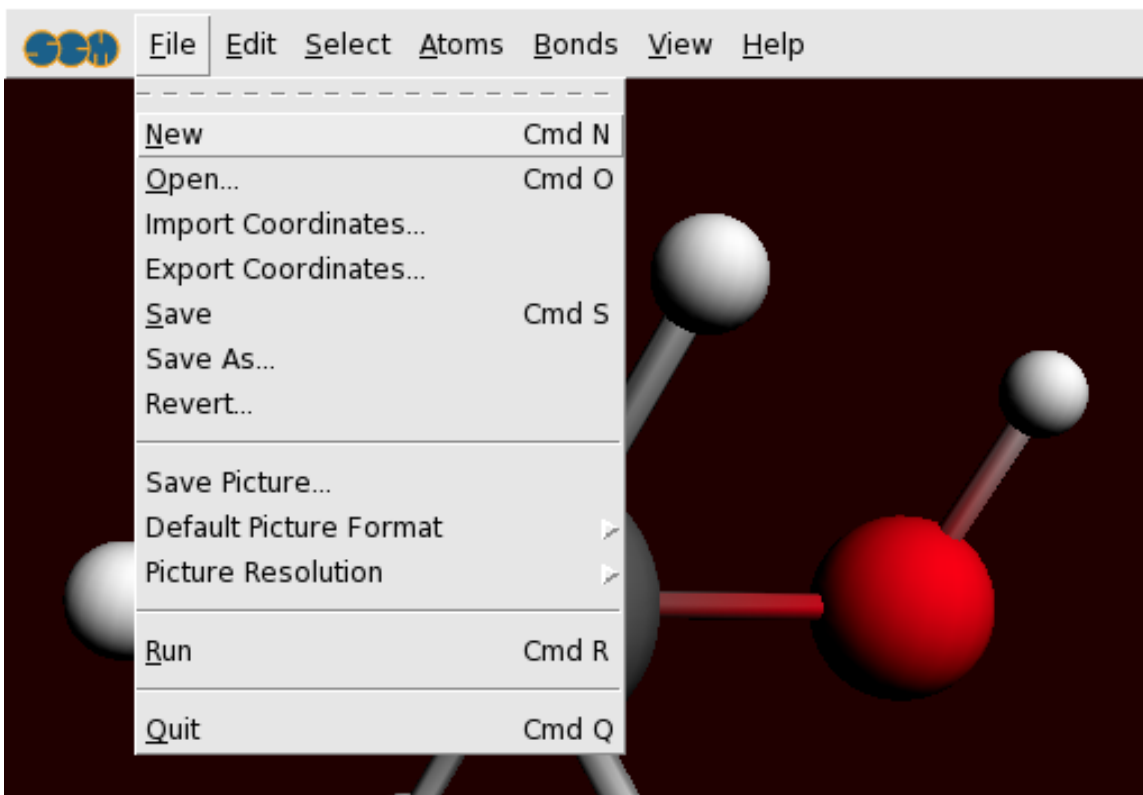


In ADFinput, your carbon atoms now should have their default color again (dark grey).

Use the **File** → **Quit** menu command to close the GUIPrefs module

### **Save picture**

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



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

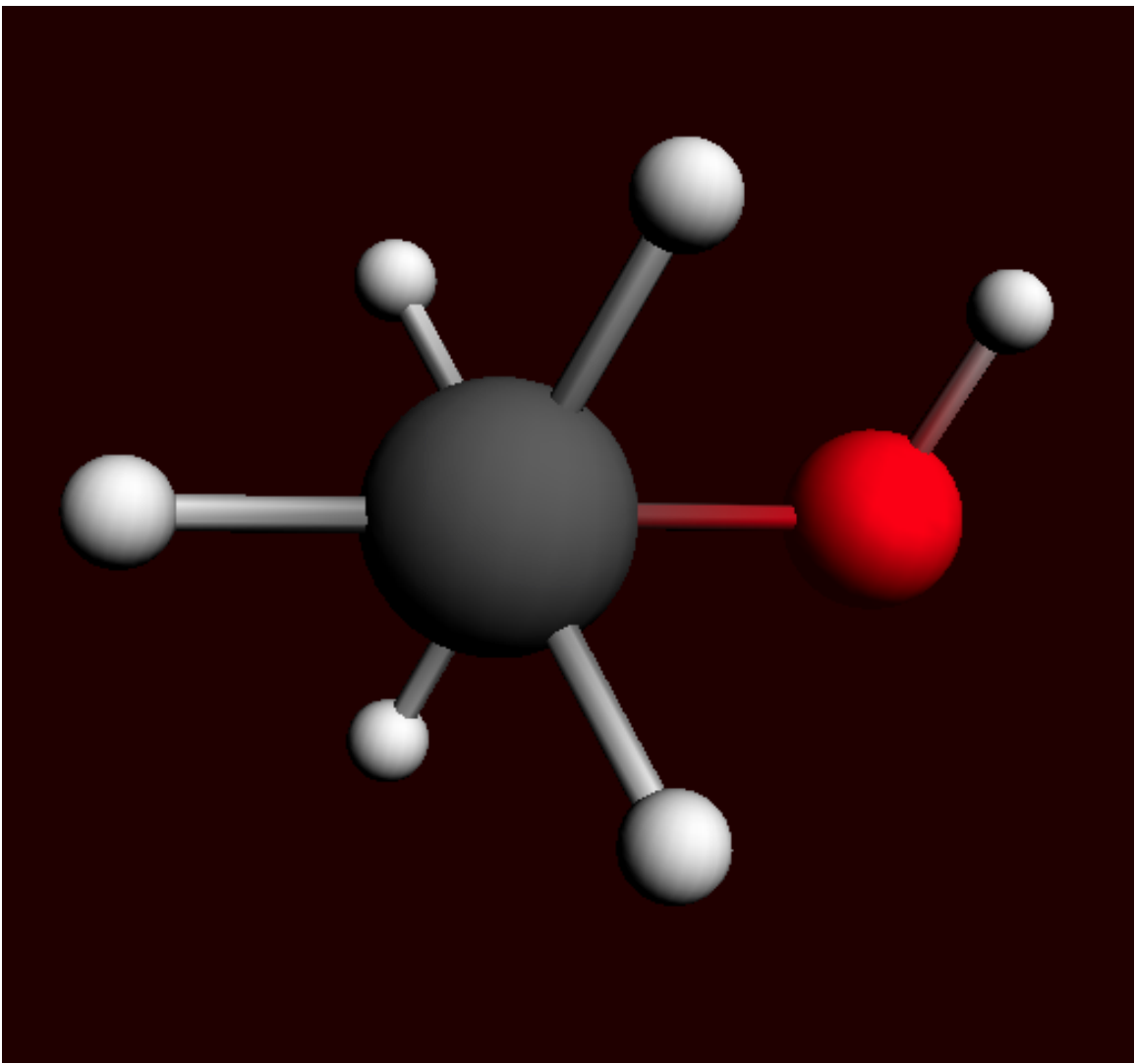
Select the **File** → **Save Picture ...** command  
Enter the name for your picture: ethanol  
Click the 'Save' button

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

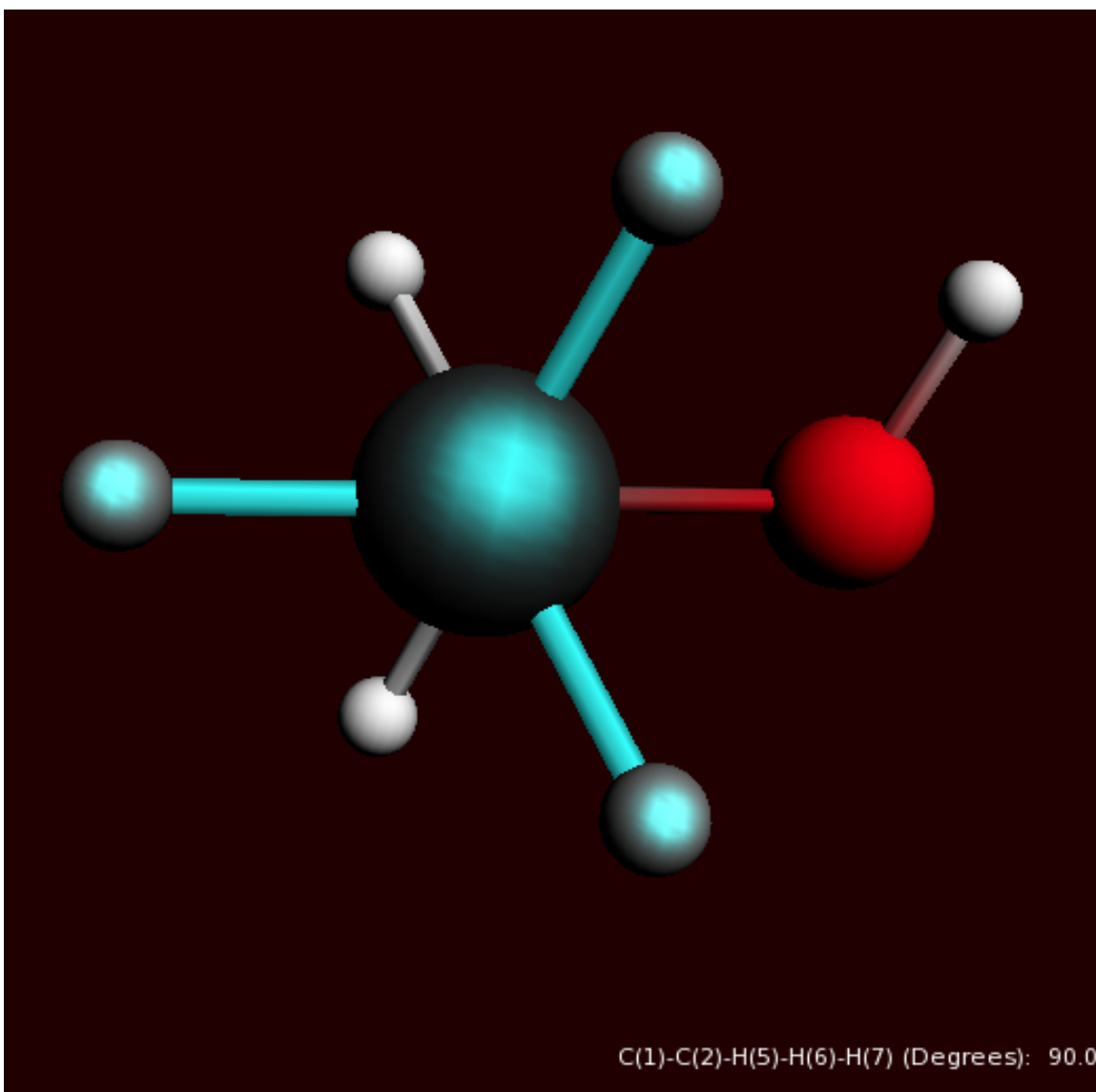
**Rotate such that you look along the C-C axis**

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

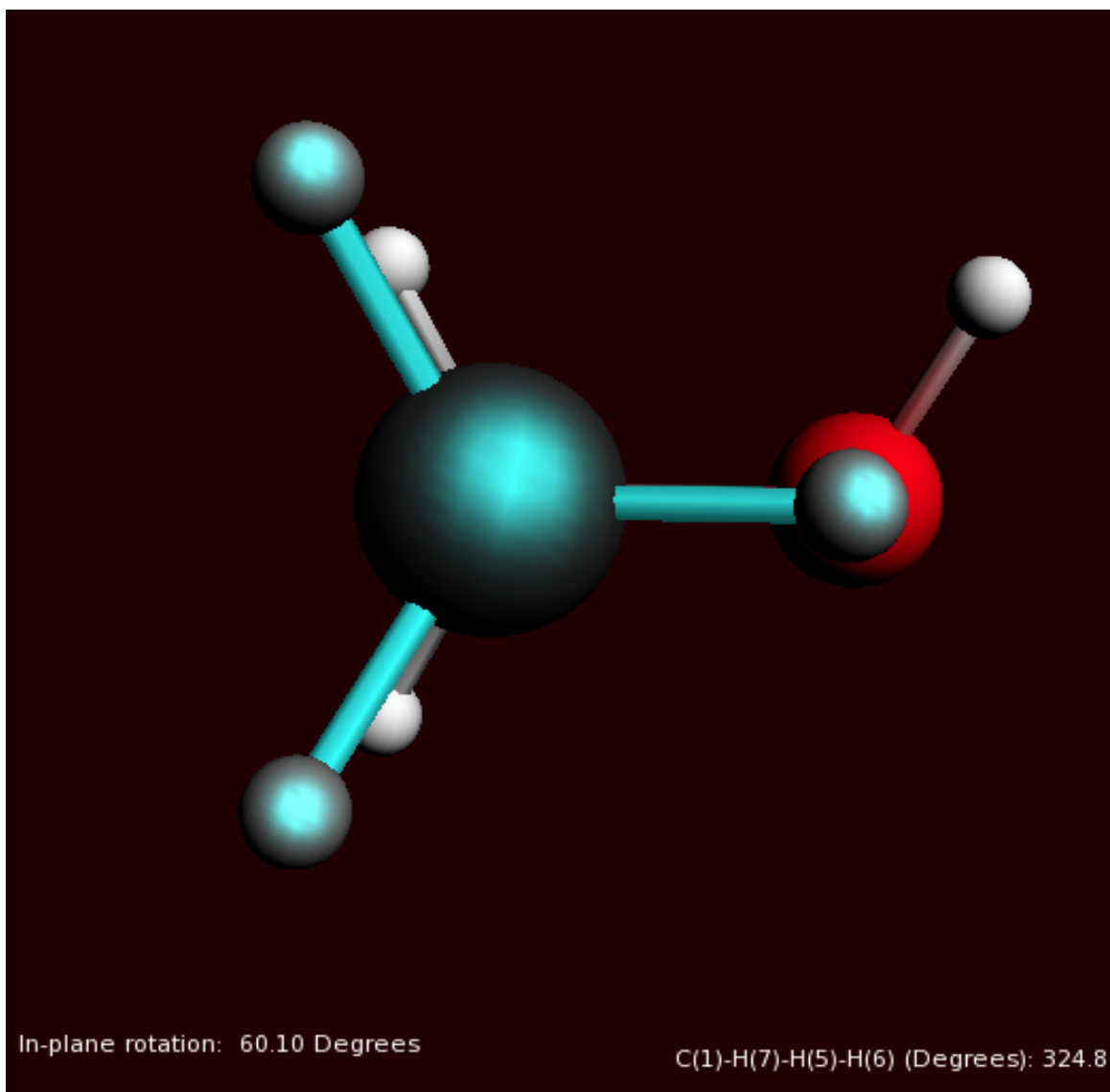
This has almost the same effect (in this case you have not selected the second carbon atom).

### **Rotate the selection**

We are now trying to make an eclipsed geometry.

Ctrl-Click with the left mouse button on 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 on 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 on 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.

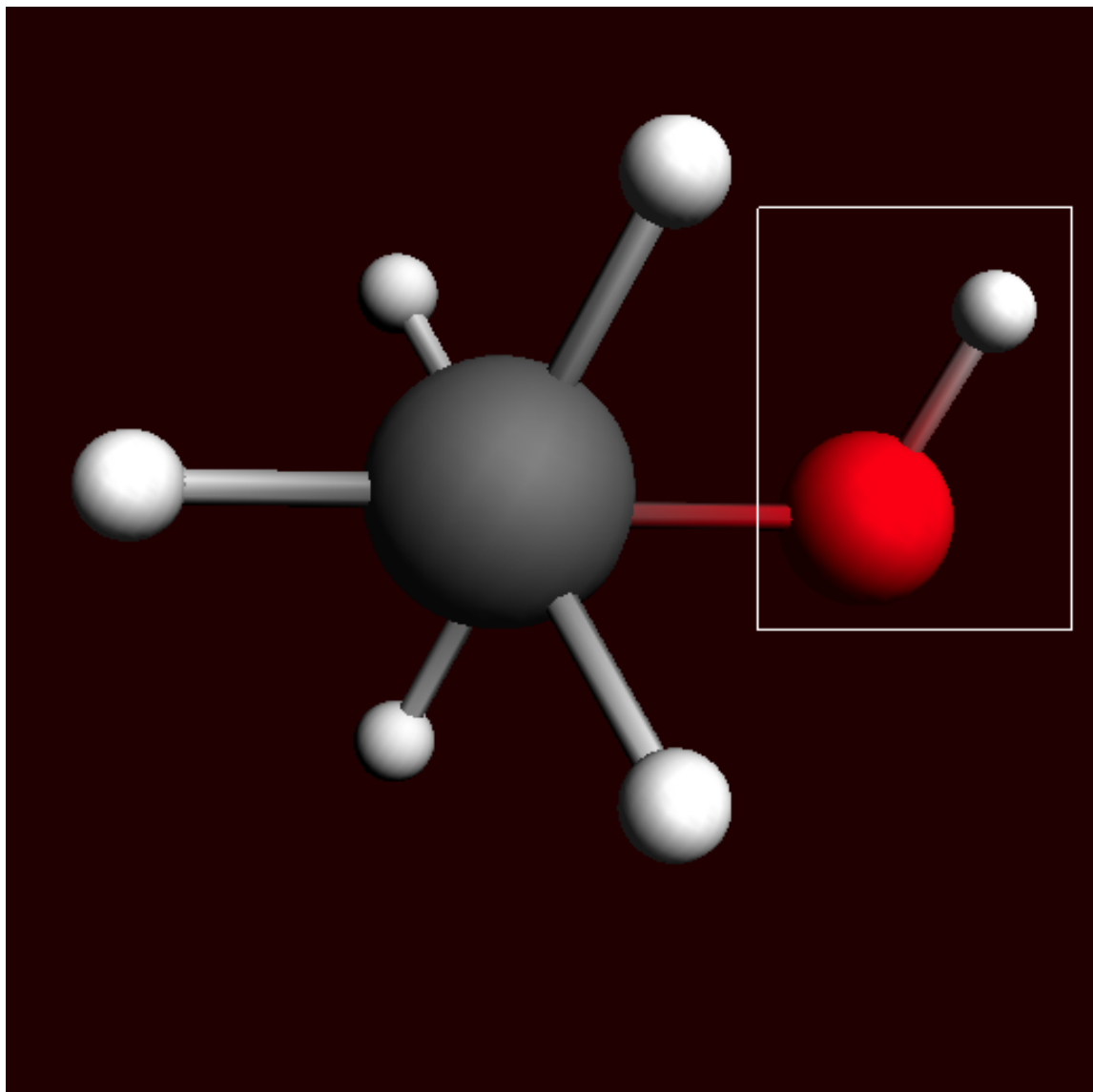
## Getting and setting geometry parameters

### Bond length

First select the oxygen atom and the connected hydrogen atom.

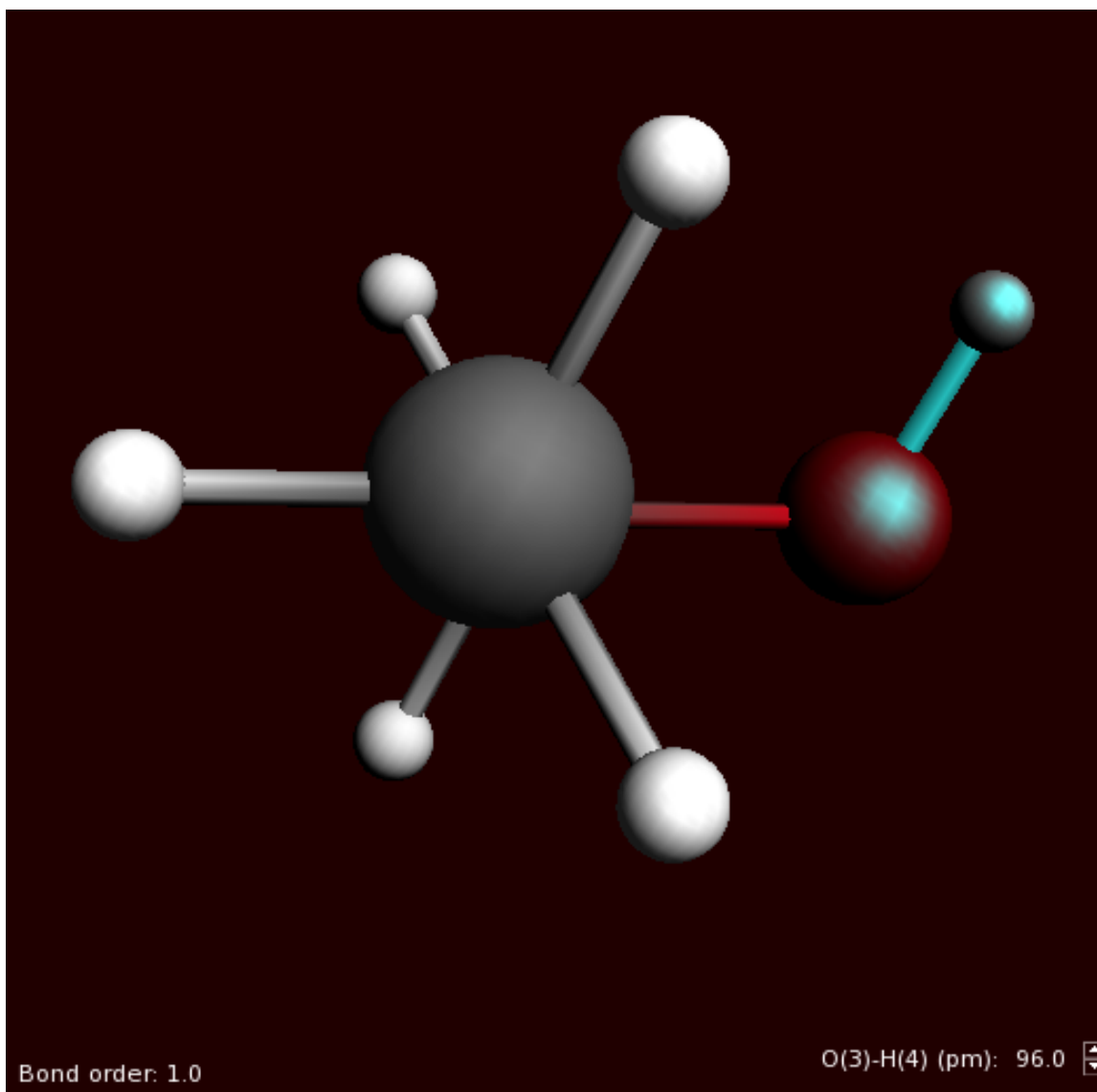
This time we make the selection by dragging a rectangle around all objects that we want to select.

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, and information about the bond.

You can set the distance to any value you wish by editing it, or by pressing the tiny buttons next to the distance.

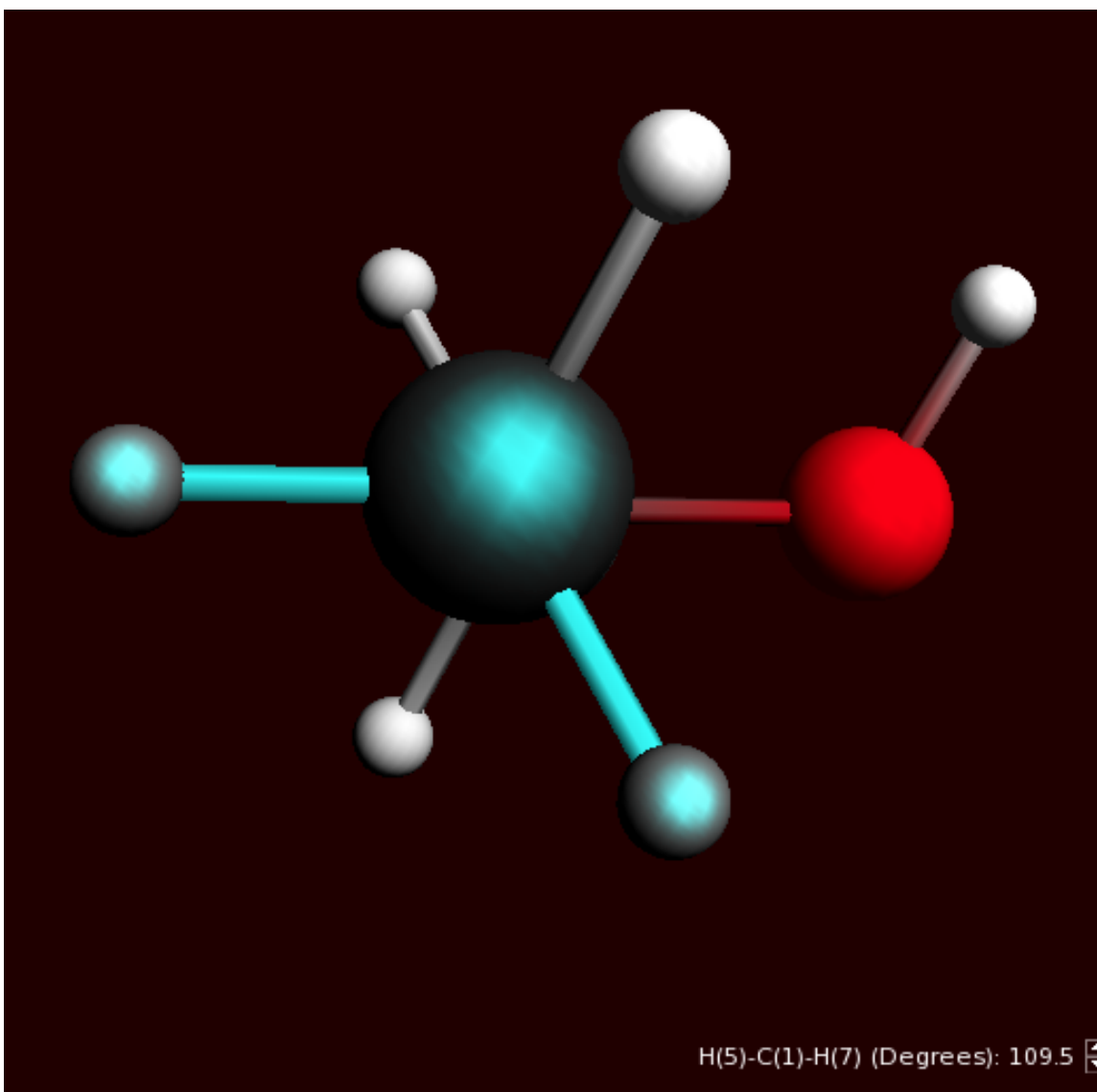
Click and hold a short time on the upper tiny button next to the distance

### **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



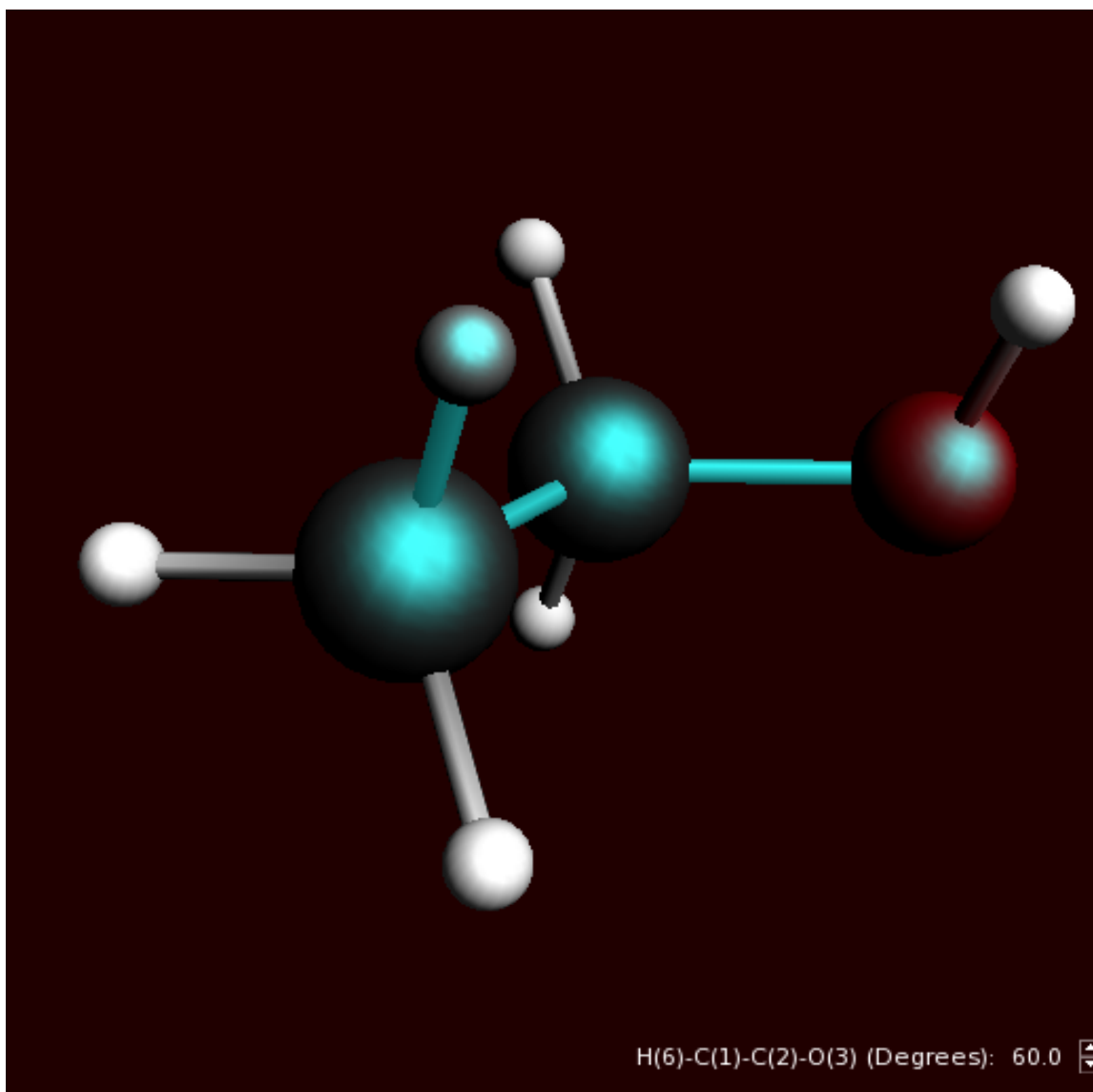
In the status area information about the bond angle of the selected three atoms is given. You can change this value to a value you like.

### Dihedral angle

By selecting four atoms we get information about the dihedral angle. And of course you can also change it.

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 with the pull-down menu on the top of the input panels on the right side.

In the right side of the ADFinput window:  
click and hold on the pull-down menu on the top, currently named 'Main Options'

Select the Coordinates panel (at the top of the right column)

Coordinates

Use: **Cartesian** coordinates

	Move atom(s) up		Move atom(s) down		
C(1)	<input type="checkbox"/>	-0.57088795	<input type="checkbox"/>	-1.10933403	<input type="checkbox"/> 0.08873378
C(2)	<input type="checkbox"/>	0.29815124	<input type="checkbox"/>	0.16102144	<input type="checkbox"/> 0.01329590
O(3)	<input type="checkbox"/>	1.66434034	<input type="checkbox"/>	-0.20715061	<input type="checkbox"/> -0.19944563
H(4)	<input type="checkbox"/>	1.96609834	<input type="checkbox"/>	-0.75728894	<input type="checkbox"/> 0.52746044
H(5)	<input type="checkbox"/>	-0.48577254	<input type="checkbox"/>	-1.65920100	<input type="checkbox"/> -0.83815630
H(6)	<input type="checkbox"/>	-1.60295117	<input type="checkbox"/>	-0.83036732	<input type="checkbox"/> 0.24921781
H(7)	<input type="checkbox"/>	-0.23308431	<input type="checkbox"/>	-1.72863159	<input type="checkbox"/> 0.90792527
H(8)	<input type="checkbox"/>	0.21339419	<input type="checkbox"/>	0.71100773	<input type="checkbox"/> 0.93983967
H(9)	<input type="checkbox"/>	-0.03945056	<input type="checkbox"/>	0.78004741	<input type="checkbox"/> -0.80580511

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 revert to 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 matrix will be recalculated from scratch.

Coordinates

Use:  coordinates

		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"/>	1.54102	<input type="checkbox"/>	0.0	<input type="checkbox"/>	0.0	
3	O(3)	2	1	0	<input type="checkbox"/>	1.43083	<input type="checkbox"/>	109.489	<input type="checkbox"/>	0.0	
4	H(4)	3	2	1	<input type="checkbox"/>	0.960261	<input type="checkbox"/>	109.567	<input type="checkbox"/>	299.979	
5	H(5)	1	2	3	<input type="checkbox"/>	1.08108	<input type="checkbox"/>	109.446	<input type="checkbox"/>	300.01	
6	H(6)	1	2	5	<input type="checkbox"/>	1.08108	<input type="checkbox"/>	109.446	<input type="checkbox"/>	240.005	
7	H(7)	1	2	6	<input type="checkbox"/>	1.08107	<input type="checkbox"/>	109.459	<input type="checkbox"/>	240.0	
8	H(8)	2	1	3	<input type="checkbox"/>	1.08081	<input type="checkbox"/>	109.469	<input type="checkbox"/>	239.994	
9	H(9)	2	1	8	<input type="checkbox"/>	1.08078	<input type="checkbox"/>	109.457	<input type="checkbox"/>	239.978	

Make sure you have Cartesian coordinates selected

## Extending and changing your molecule

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

Select the 'Main Options' panel  
Click on the pre-optimize button

Let's try to change the CH<sub>2</sub>OH group in a COOH group.

Thus, we need to:

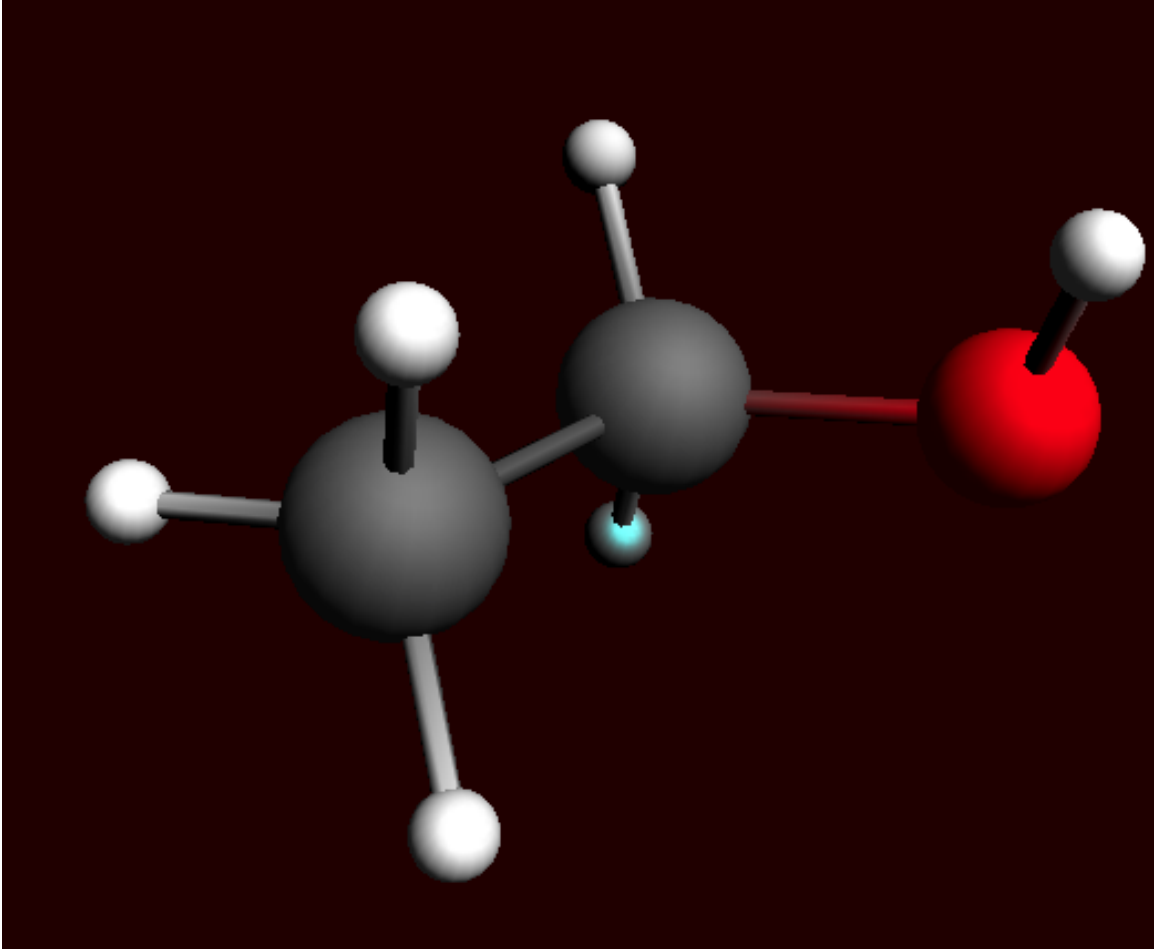
- remove one hydrogen
- change one hydrogen into an oxygen
- change a single bond into a double bond

After this, we will revert to the ethanol molecule.

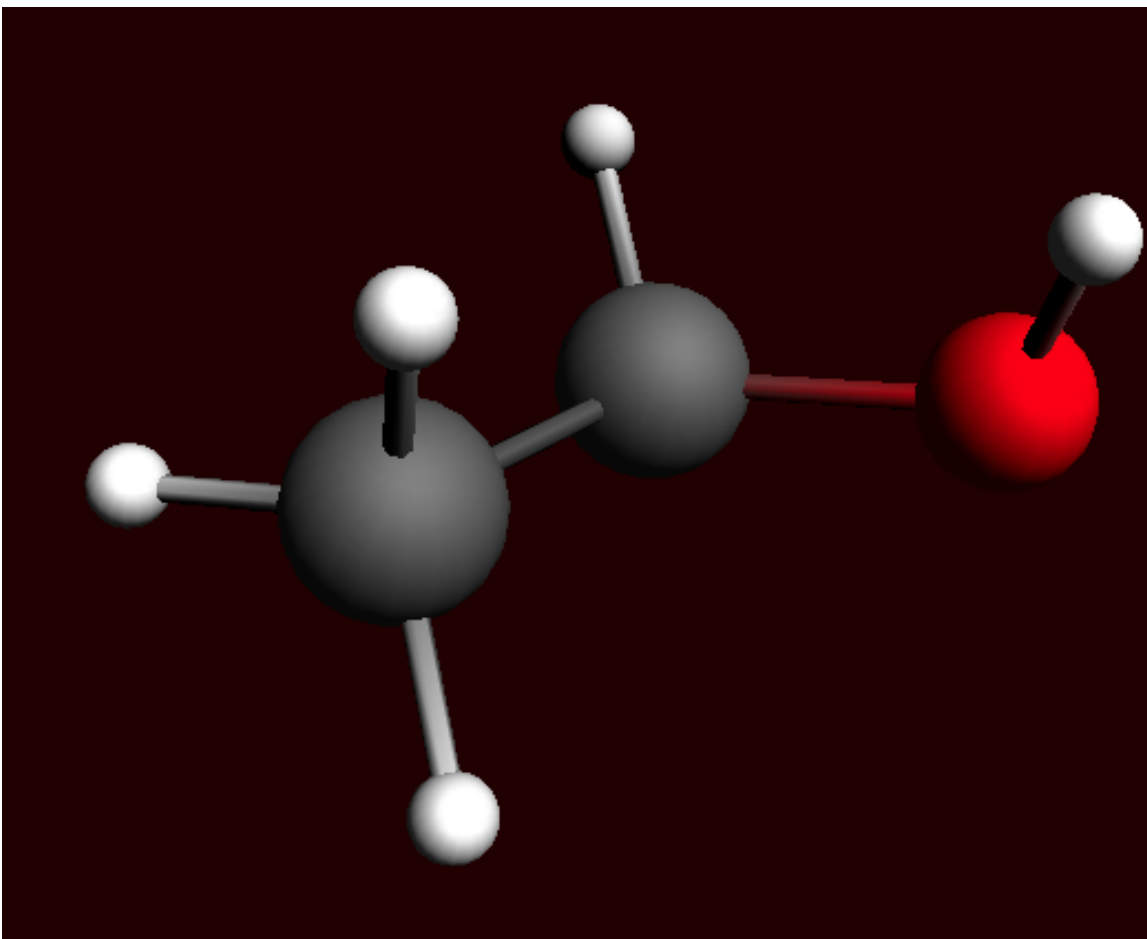
### Delete an atom

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



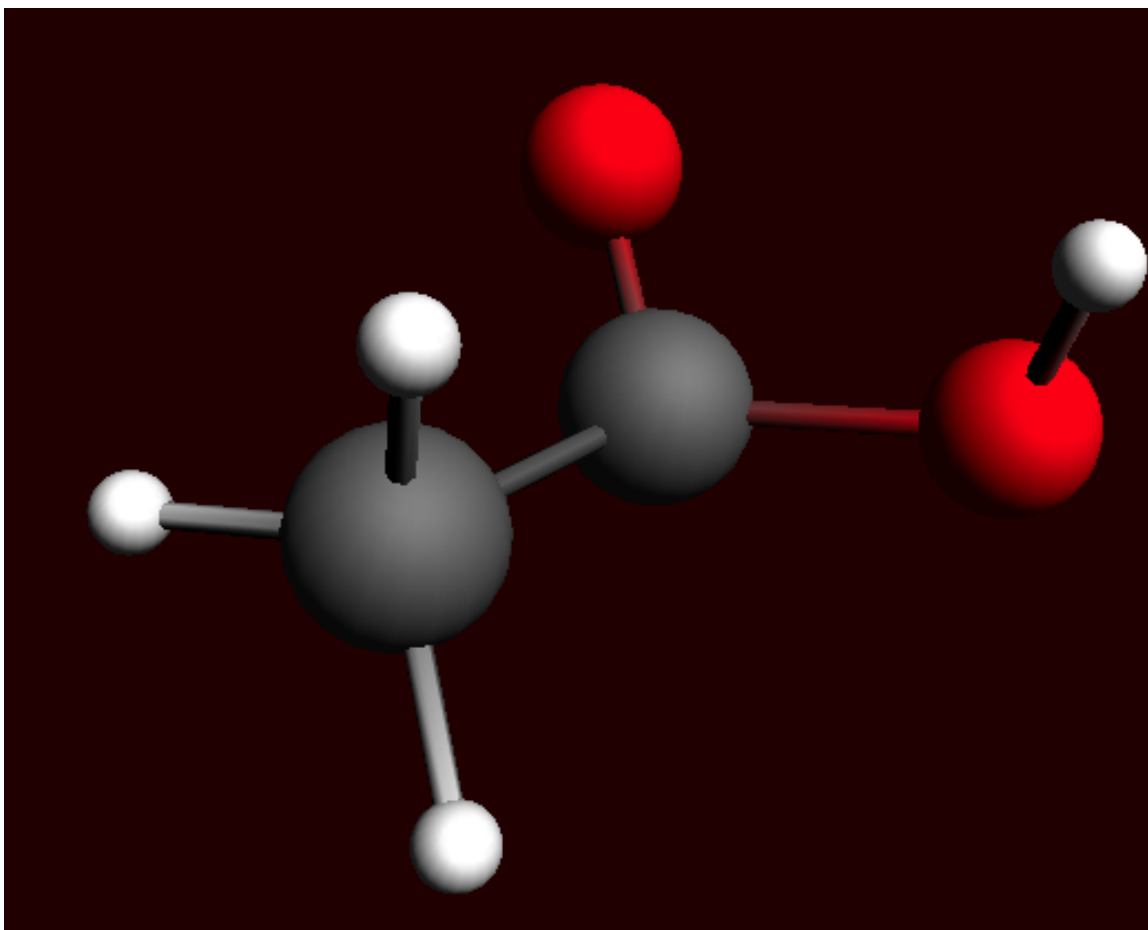
The selected atom is removed.

### **Change the type of an atom**

Next, we will change a hydrogen into an oxygen atom

Select the O-tool

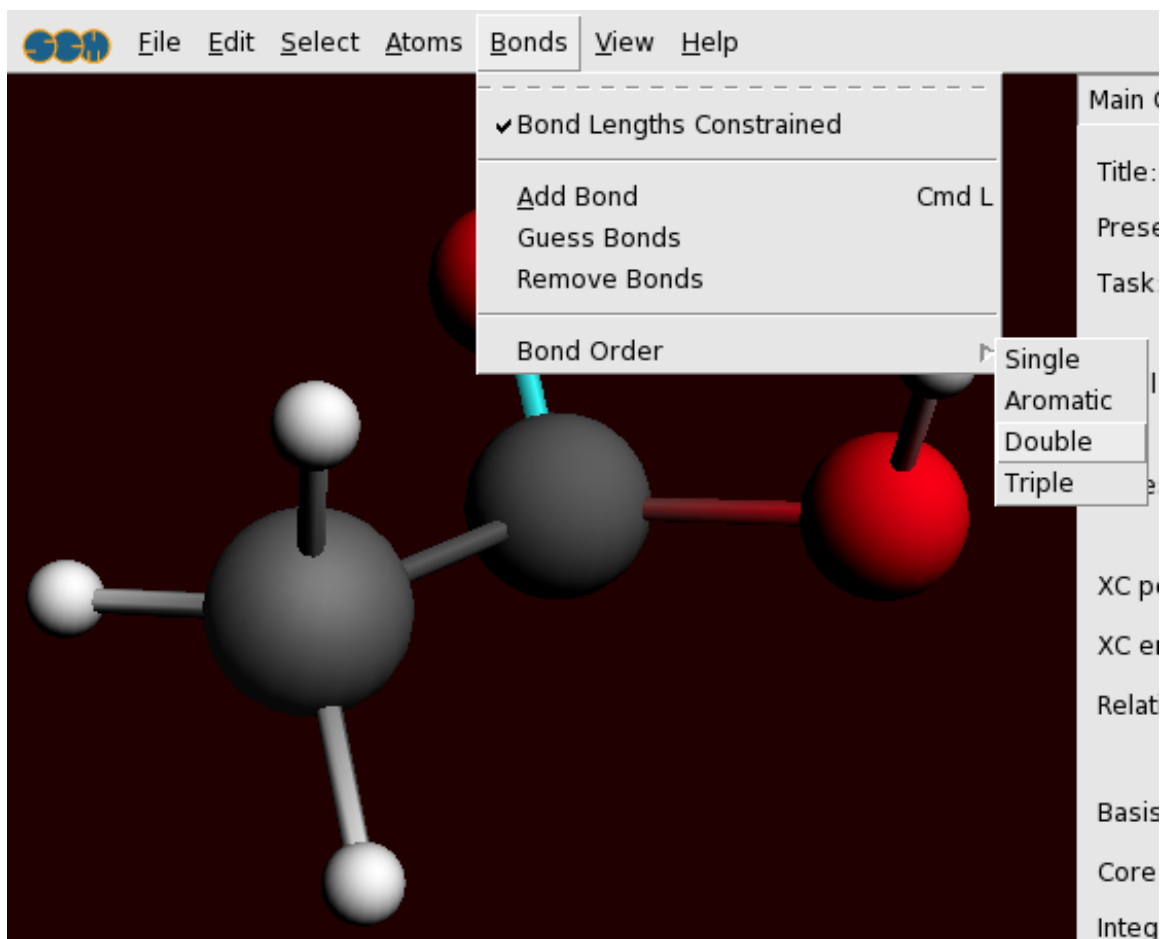
Double-click on the hydrogen that should change into an oxygen



### 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



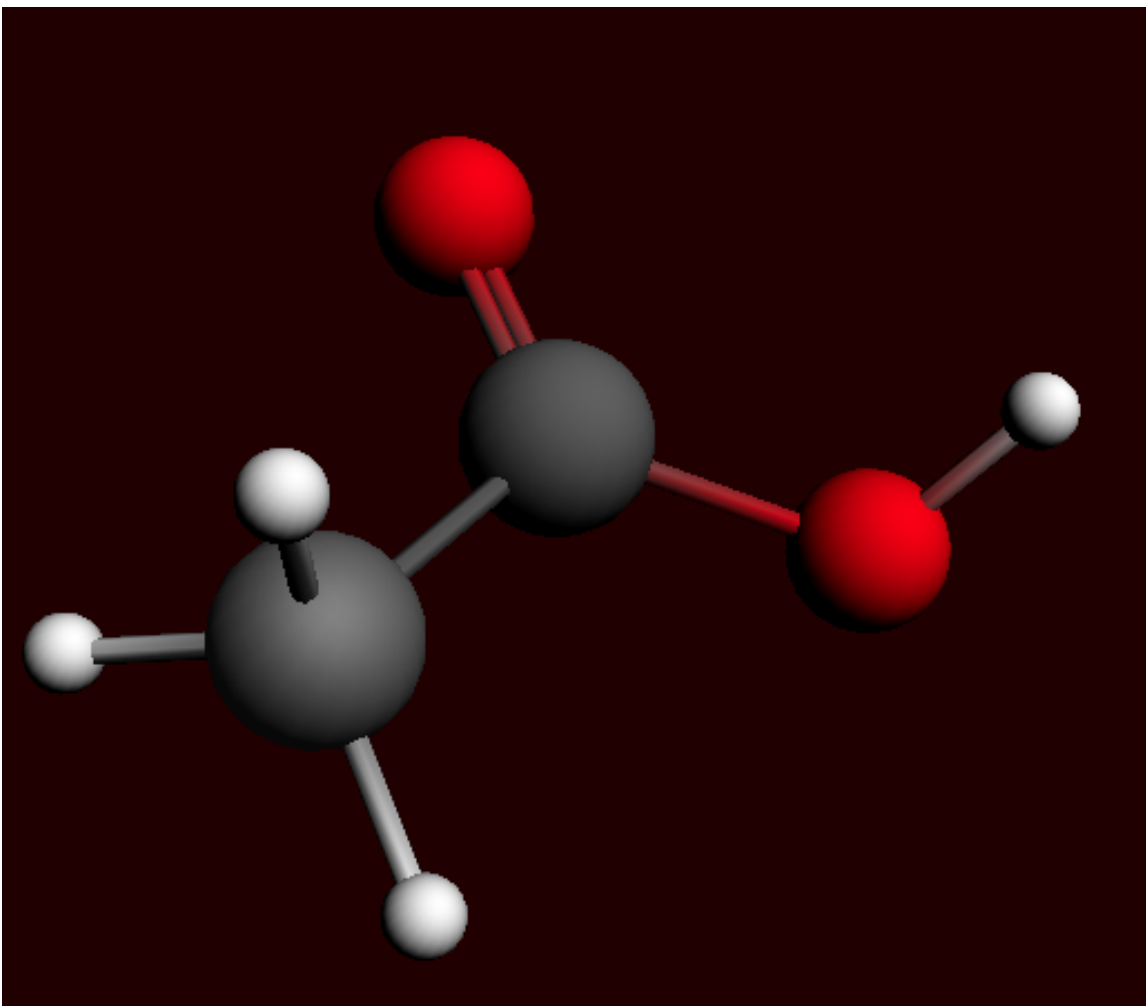
The single bond has changed into a double bond.

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
```



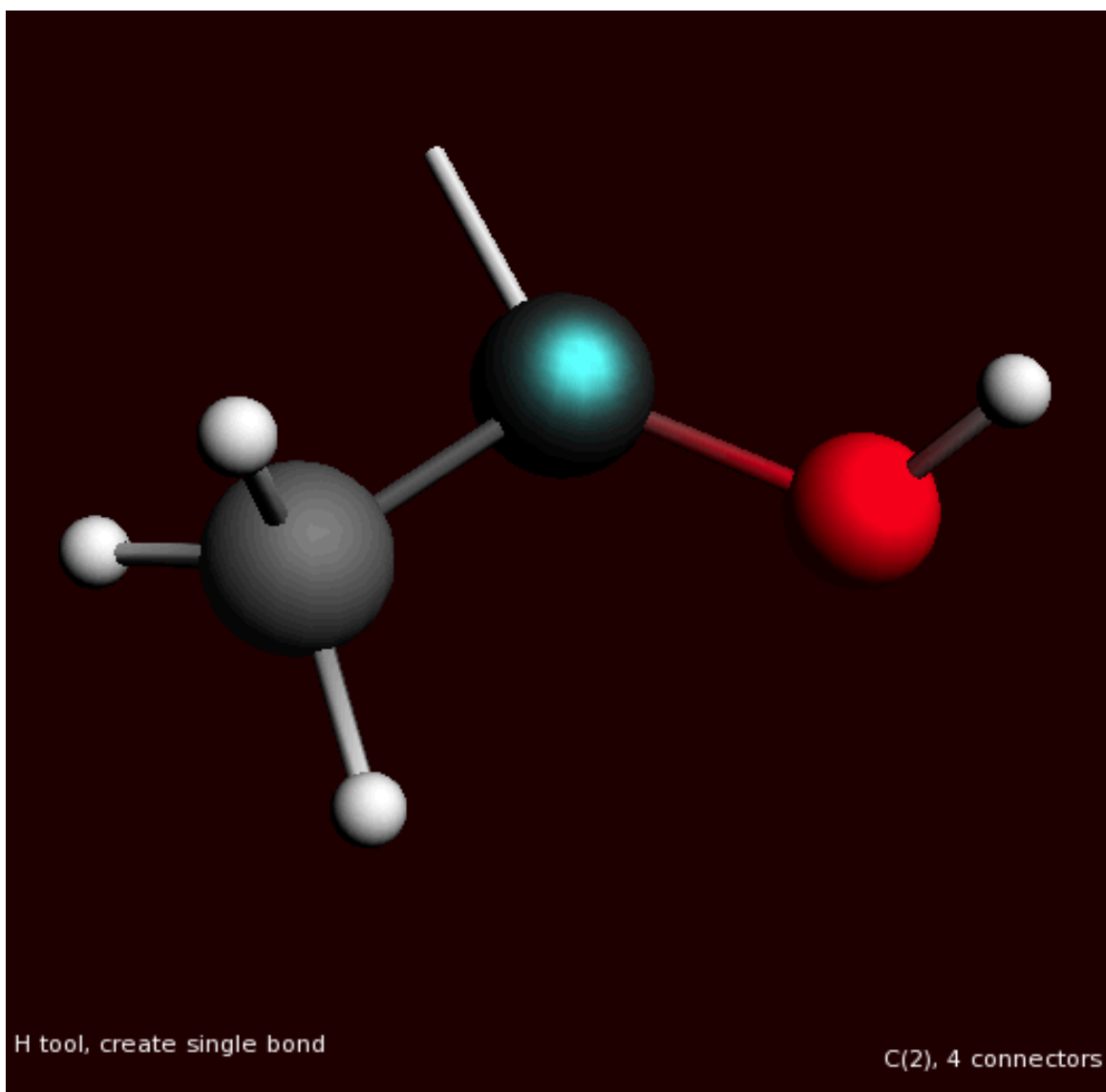
### **Add new (bonded) atoms**

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  
Click once on the carbon atom connected to the oxygen





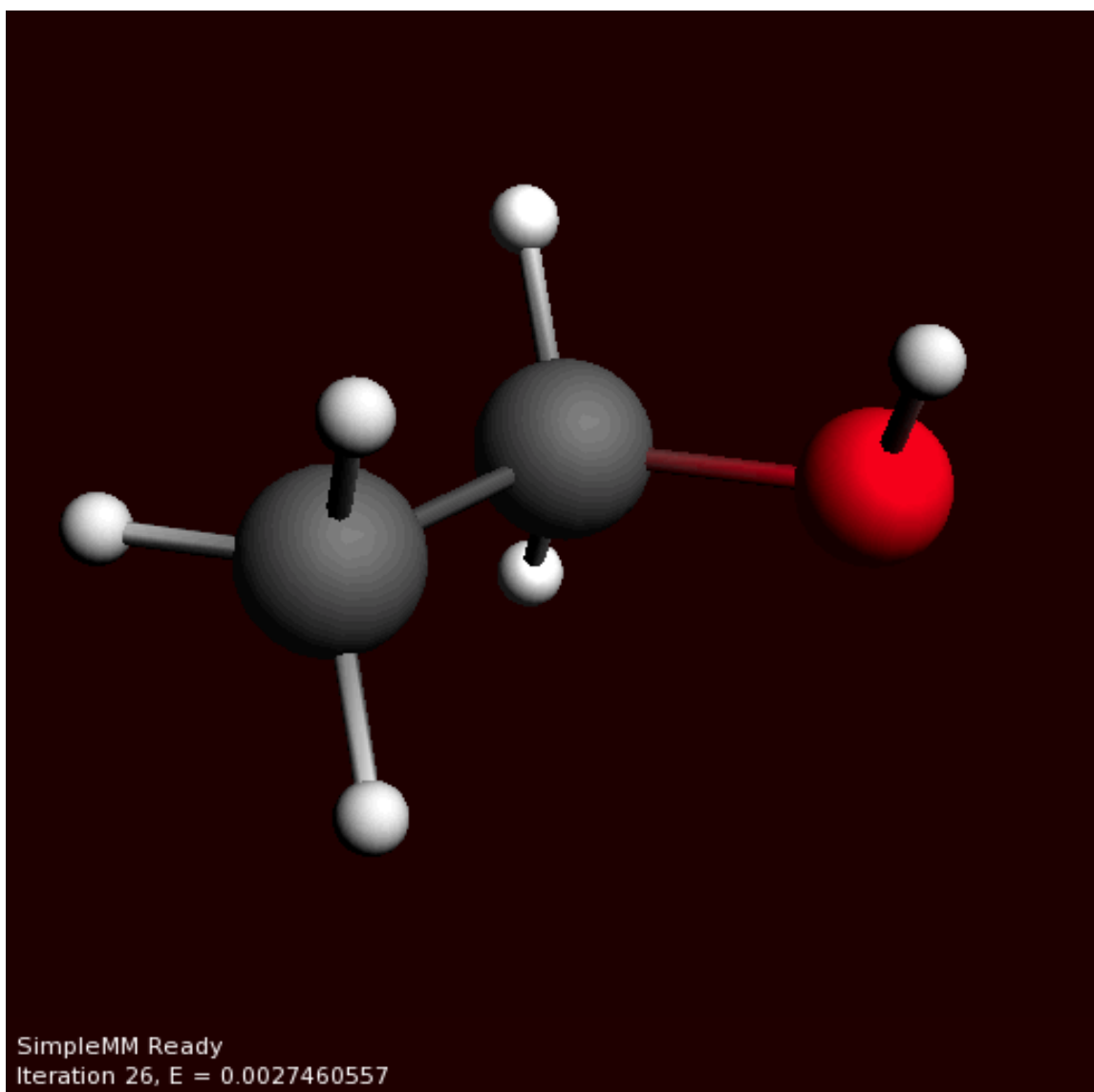
Note that this way you started bonding mode again, as indicated by the bond to the mouse position.

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

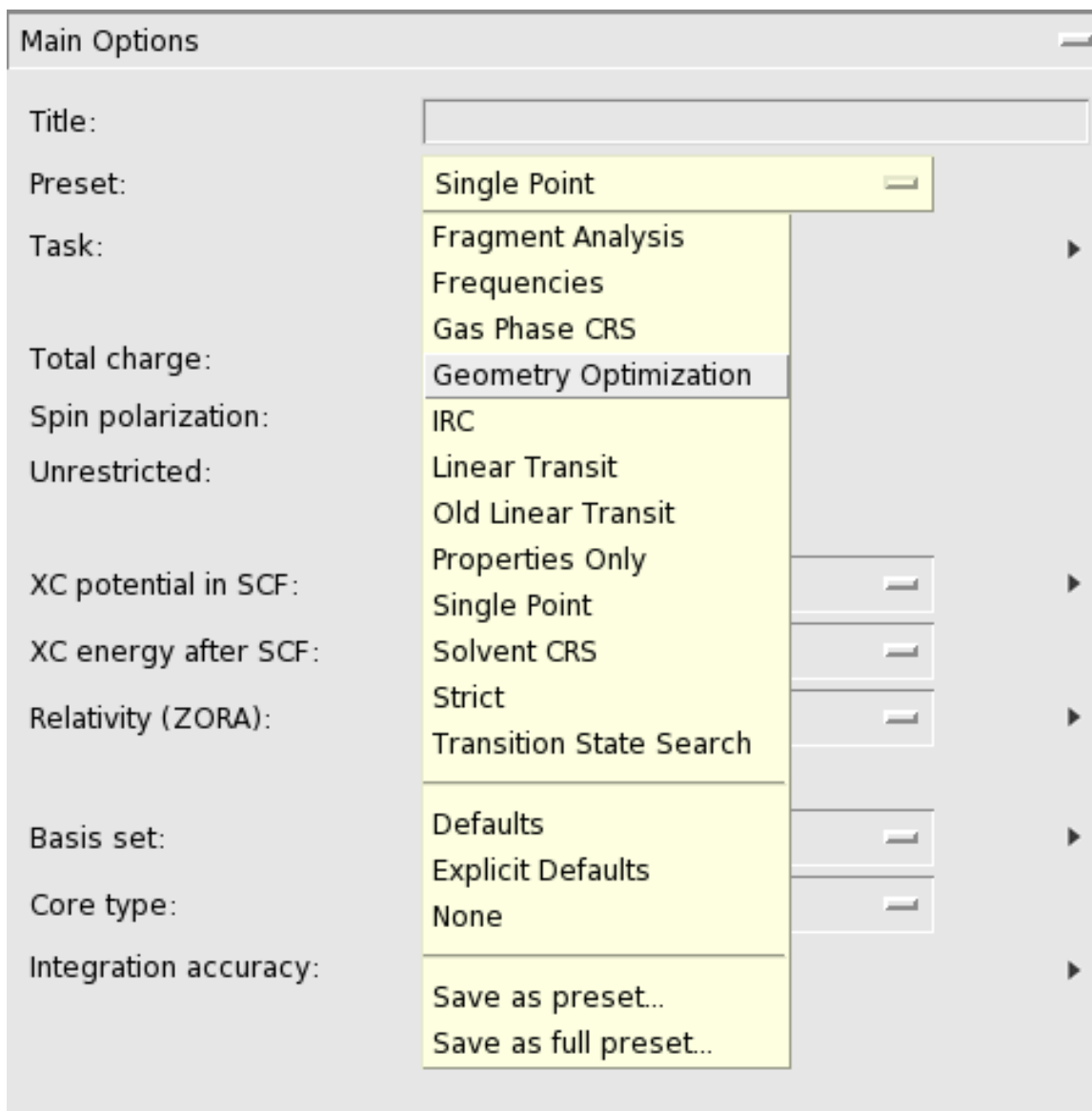
#### Preset

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.

**Main Options**

Title:

Preset:

Task:

Total charge:

Spin polarization:

Unrestricted:  Yes

XC potential in SCF:

XC energy after SCF:

Relativity (ZORA):

Basis set:

Core type:

Integration accuracy:

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

## XC functional

An important input option is the XC functional to use.

For this tutorial the default simple (and fast) LDA potential during the SCF is sufficient. So just leave this at the default value

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

Main Options	
Title:	Ethanol
Preset:	Geometry Optimization
Task:	GeometryOptimization
Total charge:	0.0
Spin polarization:	0.0
Unrestricted:	<input type="checkbox"/> Yes
XC potential in SCF:	LDA
XC energy after SCF:	LDA+GGA+METAGGA
Relativity (ZORA):	None
Basis set:	DZ
Core type:	Large
Integration accuracy:	

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

## Basis set

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

The menu gives access to the basis sets regularly used.

For this tutorial we will choose a very small basis set. This will result in poor results, but the calculation runs much faster. Thus:

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

Main Options	
Title:	Ethanol
Preset:	Geometry Optimization
Task:	GeometryOptimization
Total charge:	0.0
Spin polarization:	0.0
Unrestricted:	<input type="checkbox"/> Yes
XC potential in SCF:	LDA
XC energy after SCF:	LDA+GGA+METAGGA
Relativity (ZORA):	None
Basis set:	SZ
Core type:	Large
Integration accuracy:	

## Integration

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

Increasing the number makes the results more accurate, but will require substantially more computation time. Similarly, decreasing the number will result in less accurate results, but you will get the results faster.

For the tutorial, we will reduce the accuracy in order to speed things up:

```
Set the integration accuracy to 3.0.
```

Main Options

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

Core type: Large

Integration accuracy: 3.0

The color of the field changes to yellow to warn you that you changed a field.

### Other input options

On the right side of the window you will find many more input fields. They are organized in panels. You select a panel with the pull-down menu showing the title of the panel, along the topside.

Main Options	Coordinates
Regions	Electric Field
	Geometry Constraints and Scan
	Solvation
Task: Geometry Optimization	
ESR, EPR, EFG	Accuracy
ETS-NOCV	Basis
Excitations, CD	COSMO
Excited State Geometry	Files (Restart)
Franck-Condon Spectrum	Integration
Hyperpolarizability	Linear Transit (Old)
Localized Orbitals, NBO	NMR Details
Magnetizability, Verdet	Output Details
MCD	Relativity
NMR	SCF
Optical Rotatory Dispersion	SCF Convergence Aids
Other: Etot, Bader, Charge Transport	Spin and Occupation
Polarizability	Symmetry
Raman, VROA	Technical
VanDerWaals	User Input
VCD	XC Details
Thermodynamics	XC SIC
DFTB	FDE
MM	Fragments
Mopac	QMMM
Open Babel	Quild
ORCA	
ReaxFF	

Note that the menu items also 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.



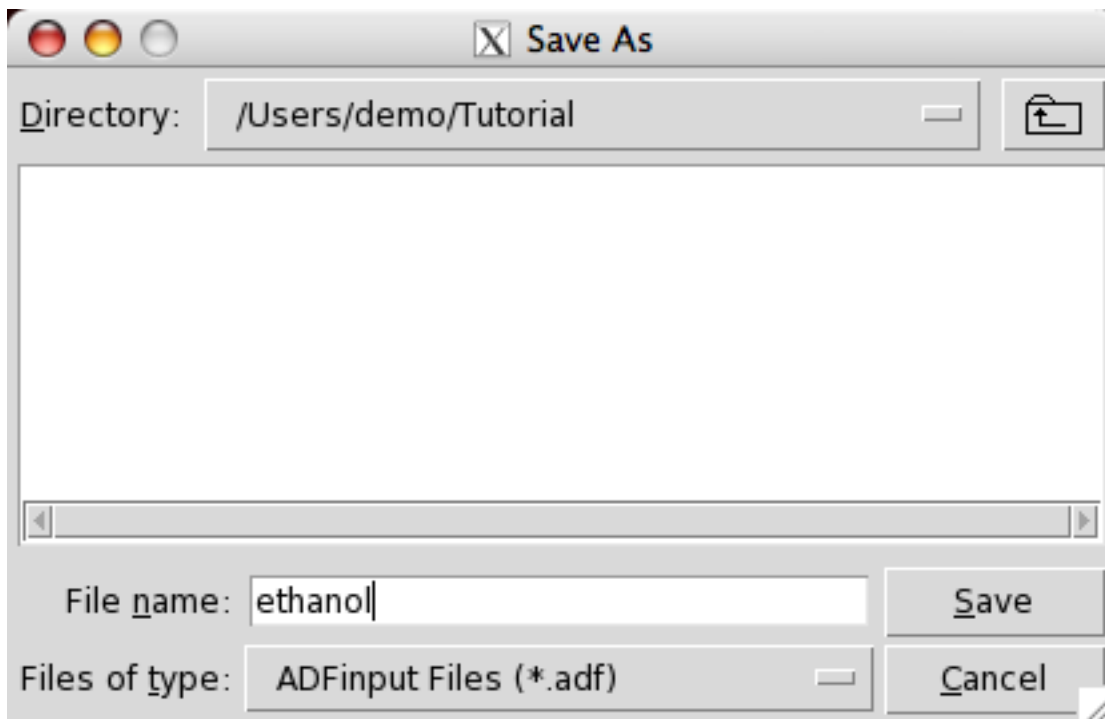
## Step 4: Run your calculation

### Save your input and create a job script

Finally you will want to save your input.

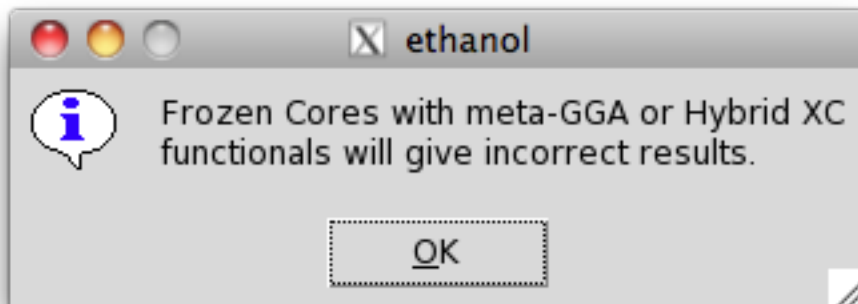
Select the **File** → **Save** command.

Enter the name 'ethanol' in the File name field.



Click on Save

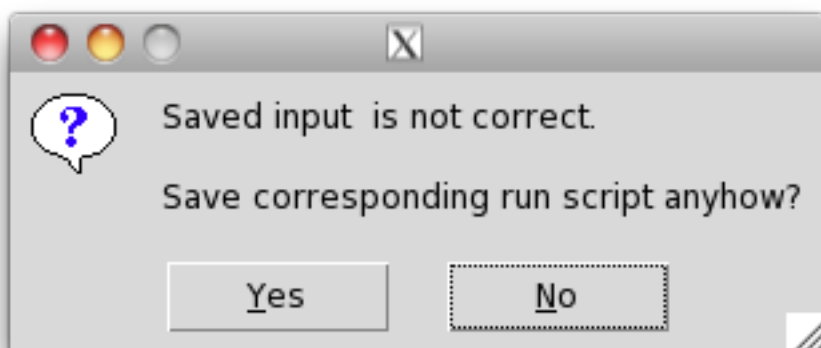
ADFinput will now present a warning dialog:



So the requested option to print meta-GGA results after the final SCF will produce incorrect results when using frozen cores. Normally you will not accept this, for the tutorial lets 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'.

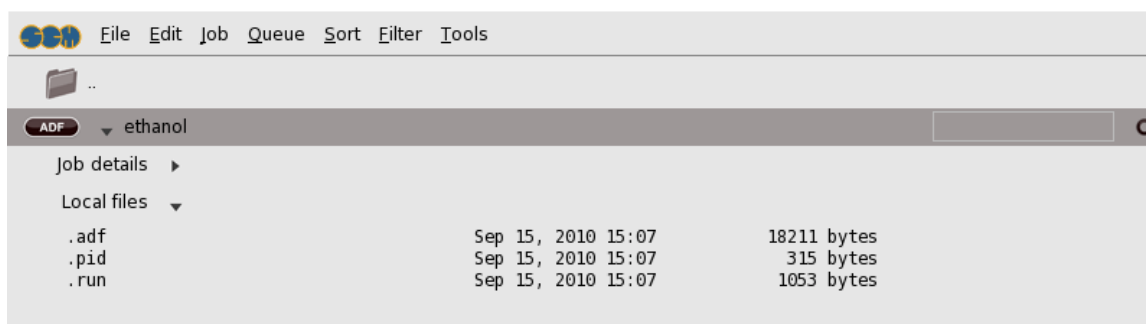
ADFinput has also created a corresponding script file. This script file has the same name, but with an extension '.run' instead of '.adf'.

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 file names 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 open ADFtail to monitor the progress of the calculation (the logfile):

```

ADFtail: ethanol.logfile
File Edit Help
<Sep15-2010> <15:09:35> >>>> PTBAS
<Sep15-2010> <15:09:35> >>>> CYCLE
<Sep15-2010> <15:09:35> 1
<Sep15-2010> <15:09:35> 2 ErrMat 0.00481641 MaxEl 0.00223592
<Sep15-2010> <15:09:35> 3 ErrMat 0.00345014 MaxEl 0.00179030
<Sep15-2010> <15:09:35> 4 ErrMat 0.00169431 MaxEl 0.00082063
<Sep15-2010> <15:09:35> 5 ErrMat 0.00015823 MaxEl -0.00005393
<Sep15-2010> <15:09:35> 6 ErrMat 0.00002157 MaxEl 0.00000634
<Sep15-2010> <15:09:35> SCF converged
<Sep15-2010> <15:09:36> 7 ErrMat 0.00000171 MaxEl 0.00000084
<Sep15-2010> <15:09:36> >>>> TOTEN
<Sep15-2010> <15:09:36> >>>> POPAN
<Sep15-2010> <15:09:36> >>>> DEBYE
<Sep15-2010> <15:09:36> >>>> AMETS
<Sep15-2010> <15:09:36> >>>> ENGRAD
<Sep15-2010> <15:09:36> current energy -2.14941668 Hartree
<Sep15-2010> <15:09:36> energy change 0.00007111 0.00100000 T
<Sep15-2010> <15:09:36> constrained gradient max 0.00075317 0.00100000 T
<Sep15-2010> <15:09:36> constrained gradient rms 0.00026894 0.00066667 T
<Sep15-2010> <15:09:36> gradient max 0.00075317
<Sep15-2010> <15:09:36> gradient rms 0.00026894
<Sep15-2010> <15:09:36> cart. step max 0.00888593 0.01000000 T
<Sep15-2010> <15:09:36> cart. step rms 0.00290821 0.00666667 T
<Sep15-2010> <15:09:36> GEOMETRY CONVERGED
<Sep15-2010> <15:09:36> Calculating Energy Terms for Final Geometry
Coordinates in Geometry Cycle 9
Atom X Y Z (Angstrom)
1.C -1.353018 -1.938591 0.105159
2.C -0.465987 -0.674896 -0.027626
3.O 0.940930 -0.905539 0.236305
4.H 0.890756 -1.334008 1.172532
5.H -1.036047 -2.714742 -0.603232
6.H -2.400876 -1.681177 -0.098352
7.H -1.287049 -2.342666 1.125293
8.H -0.894398 0.117596 0.632437
9.H -0.517911 -0.302545 -1.070119
<Sep15-2010> <15:09:36> >>>> CORORT
<Sep15-2010> <15:09:36> >>>> FITINT
<Sep15-2010> <15:09:36> >>>> CLSMAT
<Sep15-2010> <15:09:36> >>>> ORTHON
<Sep15-2010> <15:09:36> >>>> GENPT
<Sep15-2010> <15:09:36> Acc.Num.Int.= 3.000
<Sep15-2010> <15:09:36> Block Length= 128
<Sep15-2010> <15:09:36> >>>> PTBAS
<Sep15-2010> <15:09:36> >>>> CYCLE
<Sep15-2010> <15:09:37> 1
<Sep15-2010> <15:09:37> 2 ErrMat 0.00000050 MaxEl 0.00000027
<Sep15-2010> <15:09:37> SCF converged
<Sep15-2010> <15:09:44> 3 ErrMat 0.00000029 MaxEl 0.00000015
<Sep15-2010> <15:09:44> >>>> TOTEN
<Sep15-2010> <15:09:45> >>>> POPAN
<Sep15-2010> <15:09:45> >>>> DEBYE
<Sep15-2010> <15:09:45> >>>> AMETS
<Sep15-2010> <15:09:45> >>>> POPUL
<Sep15-2010> <15:09:45> Bond Energy LDA -2.14941668 a.u.
<Sep15-2010> <15:09:45> Bond Energy LDA -58.48860383 eV
<Sep15-2010> <15:09:45> NORMAL TERMINATION
<Sep15-2010> <15:09:45> END
Job ethanol has finished

```

While running the job status symbol in ADFjobs changes:



## Step 5: Results of your calculation

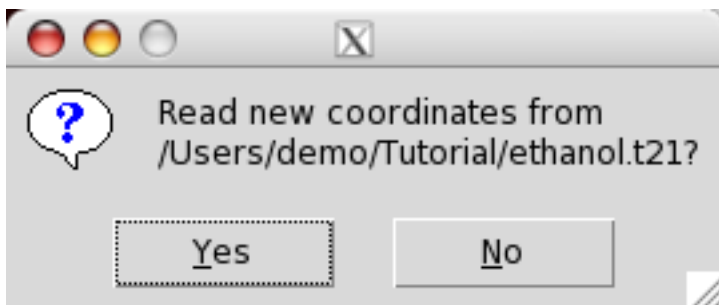
### Logfile: ADFtail

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

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

Now wait for the calculation to finish:

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

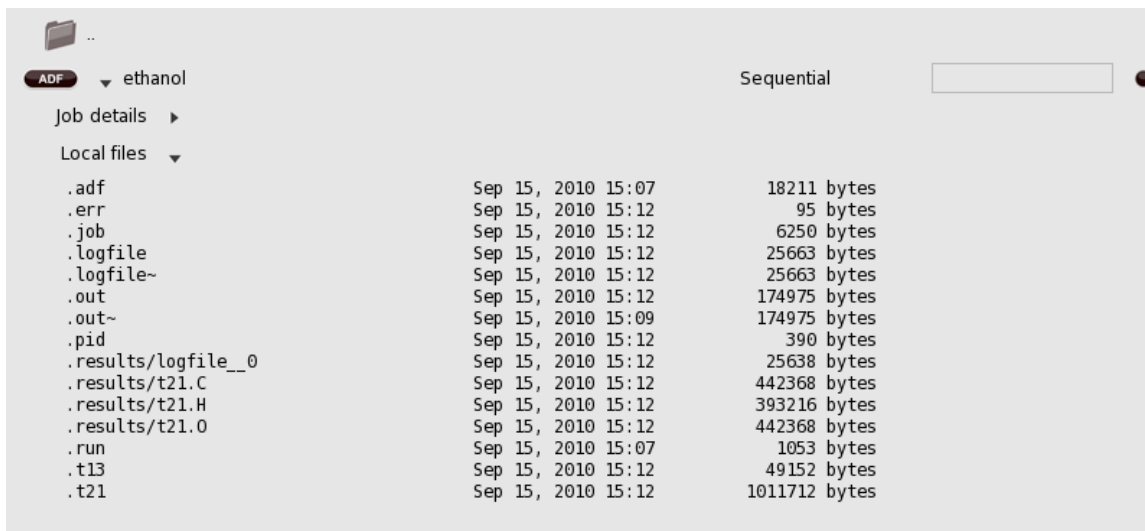


Now close ADFtail by using the **File** → **Quit** menu command:

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

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

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

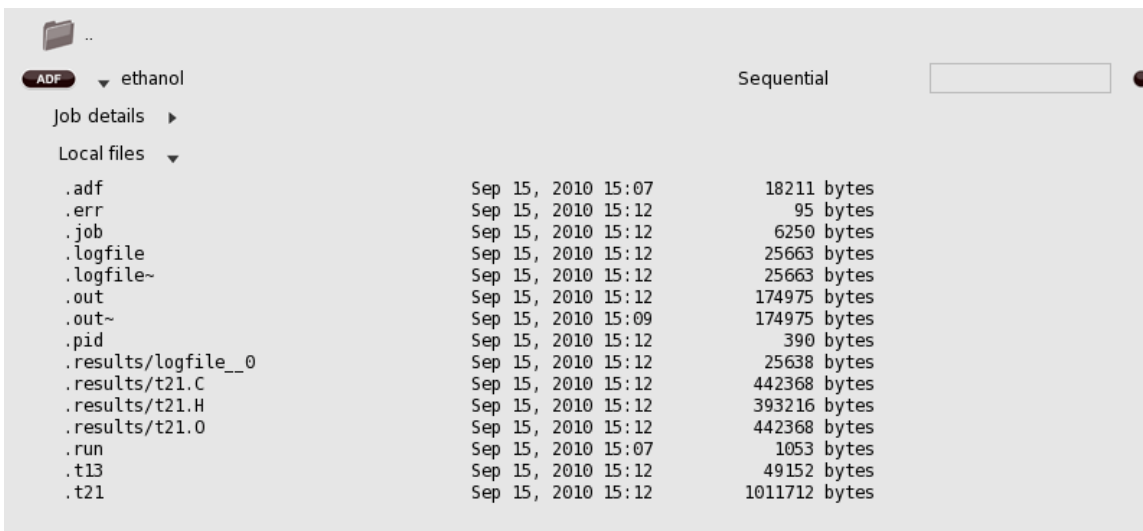
A screenshot of the ADFjobs window. The window title is "ADF ethanol Sequential". Under "Job details", there is a "Local files" section with a list of files and their sizes. The files listed are: .adf (18211 bytes), .err (95 bytes), .job (6250 bytes), .logfile (25663 bytes), .logfile~ (25663 bytes), .out (174975 bytes), .out~ (174975 bytes), .pid (390 bytes), .results/logfile\_\_0 (25638 bytes), .results/t21.C (442368 bytes), .results/t21.H (393216 bytes), .results/t21.0 (442368 bytes), .run (1053 bytes), .t13 (49152 bytes), and .t21 (1011712 bytes).

File	Time	Size
.adf	Sep 15, 2010 15:07	18211 bytes
.err	Sep 15, 2010 15:12	95 bytes
.job	Sep 15, 2010 15:12	6250 bytes
.logfile	Sep 15, 2010 15:12	25663 bytes
.logfile~	Sep 15, 2010 15:12	25663 bytes
.out	Sep 15, 2010 15:12	174975 bytes
.out~	Sep 15, 2010 15:09	174975 bytes
.pid	Sep 15, 2010 15:12	390 bytes
.results/logfile__0	Sep 15, 2010 15:12	25638 bytes
.results/t21.C	Sep 15, 2010 15:12	442368 bytes
.results/t21.H	Sep 15, 2010 15:12	393216 bytes
.results/t21.0	Sep 15, 2010 15:12	442368 bytes
.run	Sep 15, 2010 15:07	1053 bytes
.t13	Sep 15, 2010 15:12	49152 bytes
.t21	Sep 15, 2010 15:12	1011712 bytes

### Files

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

Click on the ADFjobs window



The screenshot shows a window titled 'ADFjobs' with a sub-window for 'ethanol'. The window displays a list of local files with their creation dates and sizes. The files listed are:

File Name	Date and Time	Size
.adf	Sep 15, 2010 15:07	18211 bytes
.err	Sep 15, 2010 15:12	95 bytes
.job	Sep 15, 2010 15:12	6250 bytes
.logfile	Sep 15, 2010 15:12	25663 bytes
.logfile~	Sep 15, 2010 15:12	25663 bytes
.out	Sep 15, 2010 15:12	174975 bytes
.out~	Sep 15, 2010 15:09	174975 bytes
.pid	Sep 15, 2010 15:12	390 bytes
.results/logfile__0	Sep 15, 2010 15:12	25638 bytes
.results/t21.C	Sep 15, 2010 15:12	442368 bytes
.results/t21.H	Sep 15, 2010 15:12	393216 bytes
.results/t21.O	Sep 15, 2010 15:12	442368 bytes
.run	Sep 15, 2010 15:07	1053 bytes
.t13	Sep 15, 2010 15:12	49152 bytes
.t21	Sep 15, 2010 15:12	1011712 bytes

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

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

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

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

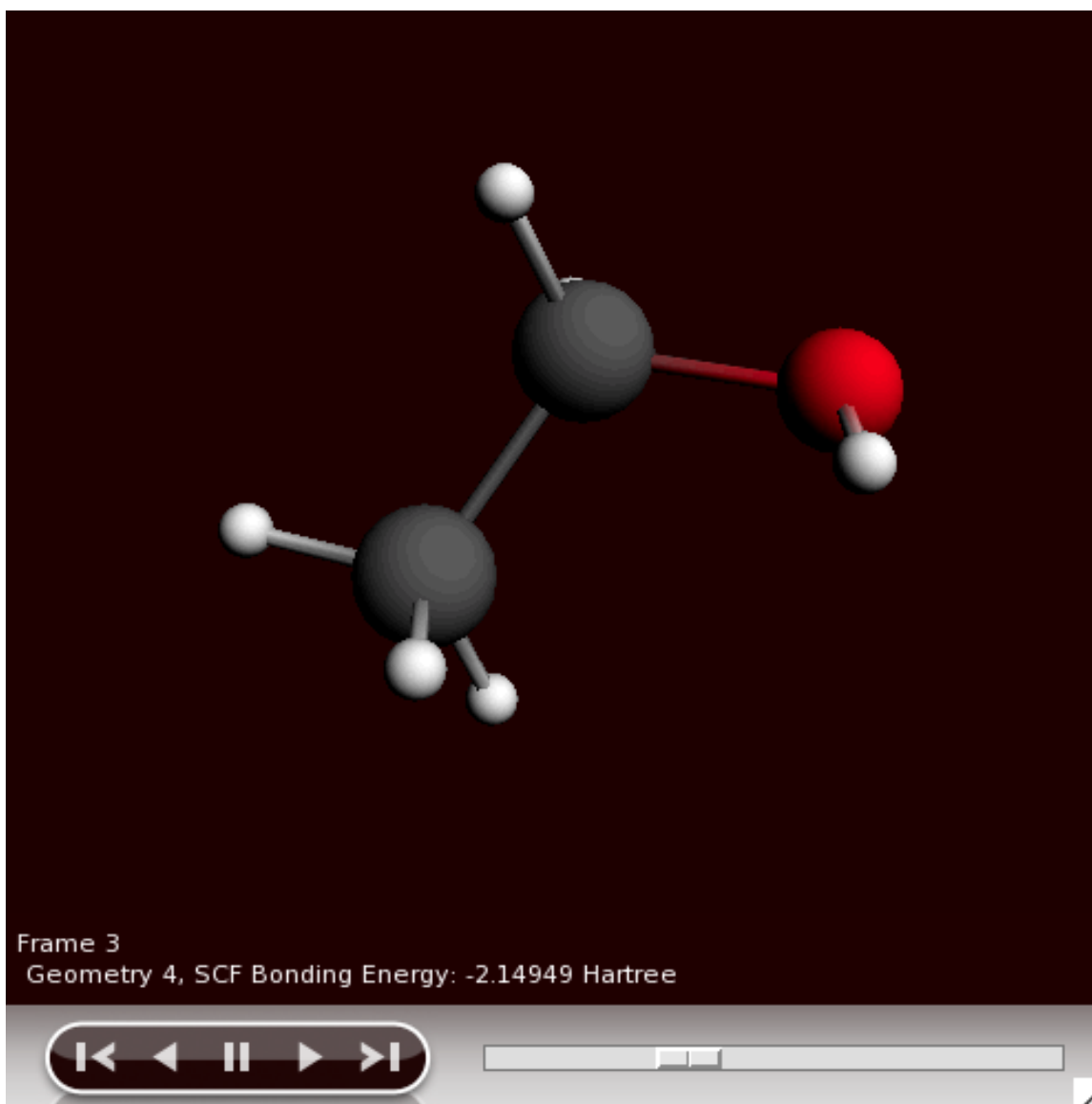
## Geometry changes: ADFmovie

ADF has optimized the geometry, and we can use the ADFmovie module to visualize the progress of the optimization. So let's start ADFmovie:

ADF Input ADF Levels
COSMO-RS
BAND Input BAND Structure
ReaxFF Input
View Movie Logfile Output Spectra Dos
Close All
Preferences Jobs

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

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



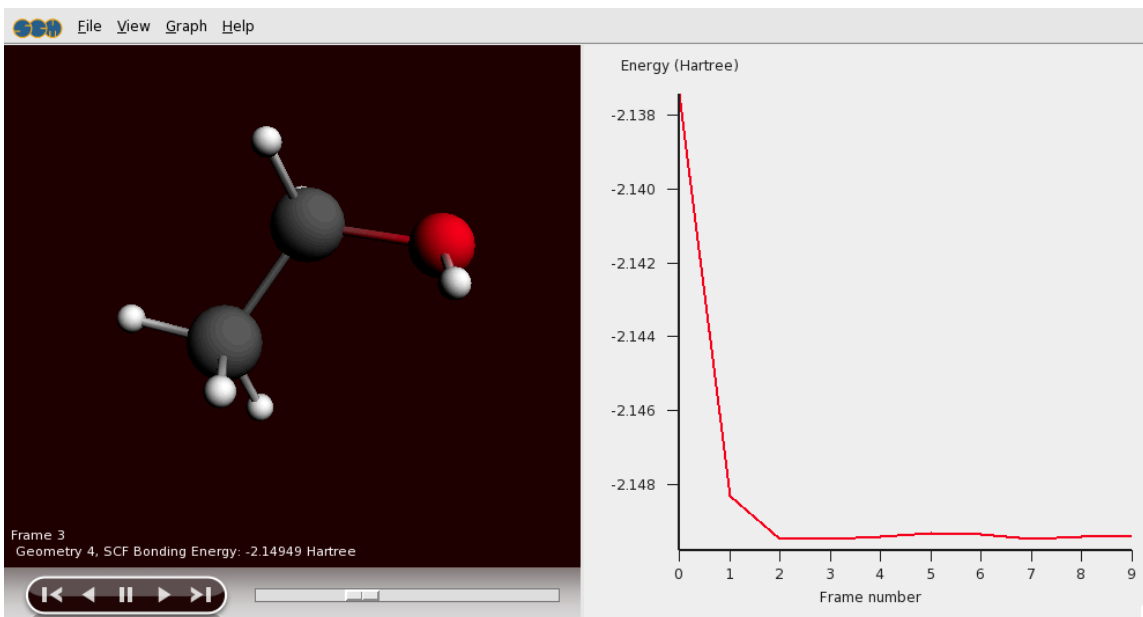
To step through the different geometries, use the slider below the picture. Clicking in the slider will single step through the frames. Or you can grab the slider and move to the frame you wish. Or you can use the left and right arrow keys to single step through the frames.

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

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

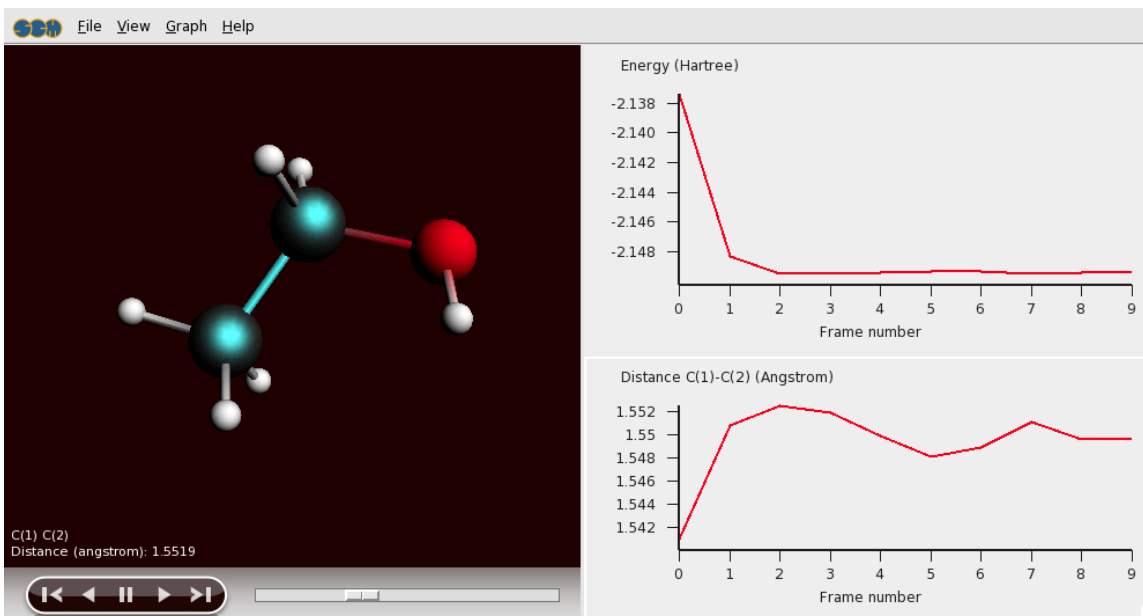
Use the **Graph** → **Energy** menu command





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

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

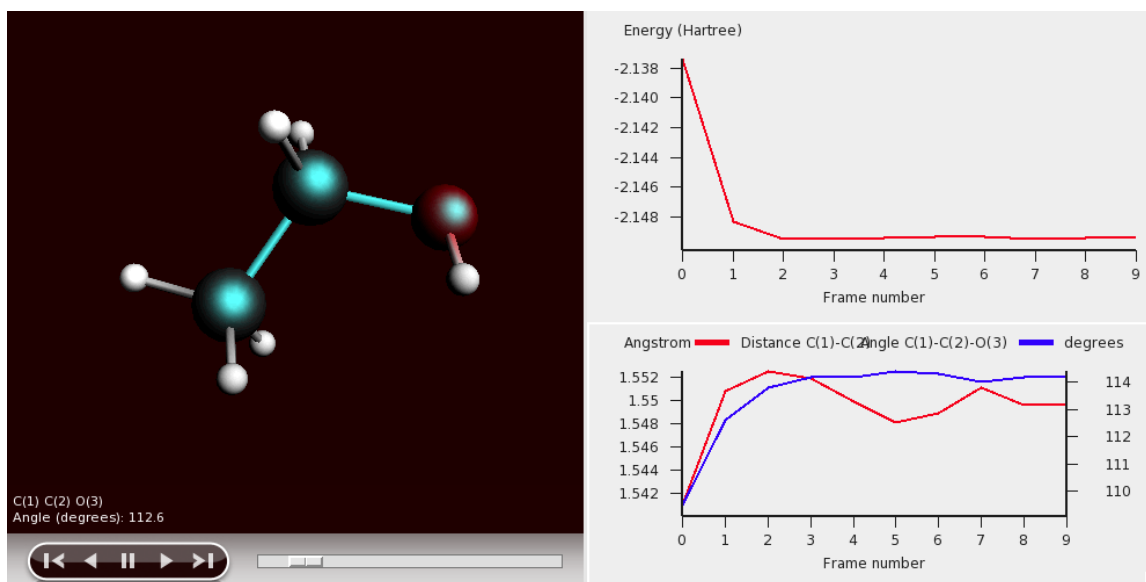


Now you have two graphs. One of them is the 'active' graph. When you make a new graph it will always be the active graph. You can also make a graph active by clicking on it.

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

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

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



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.

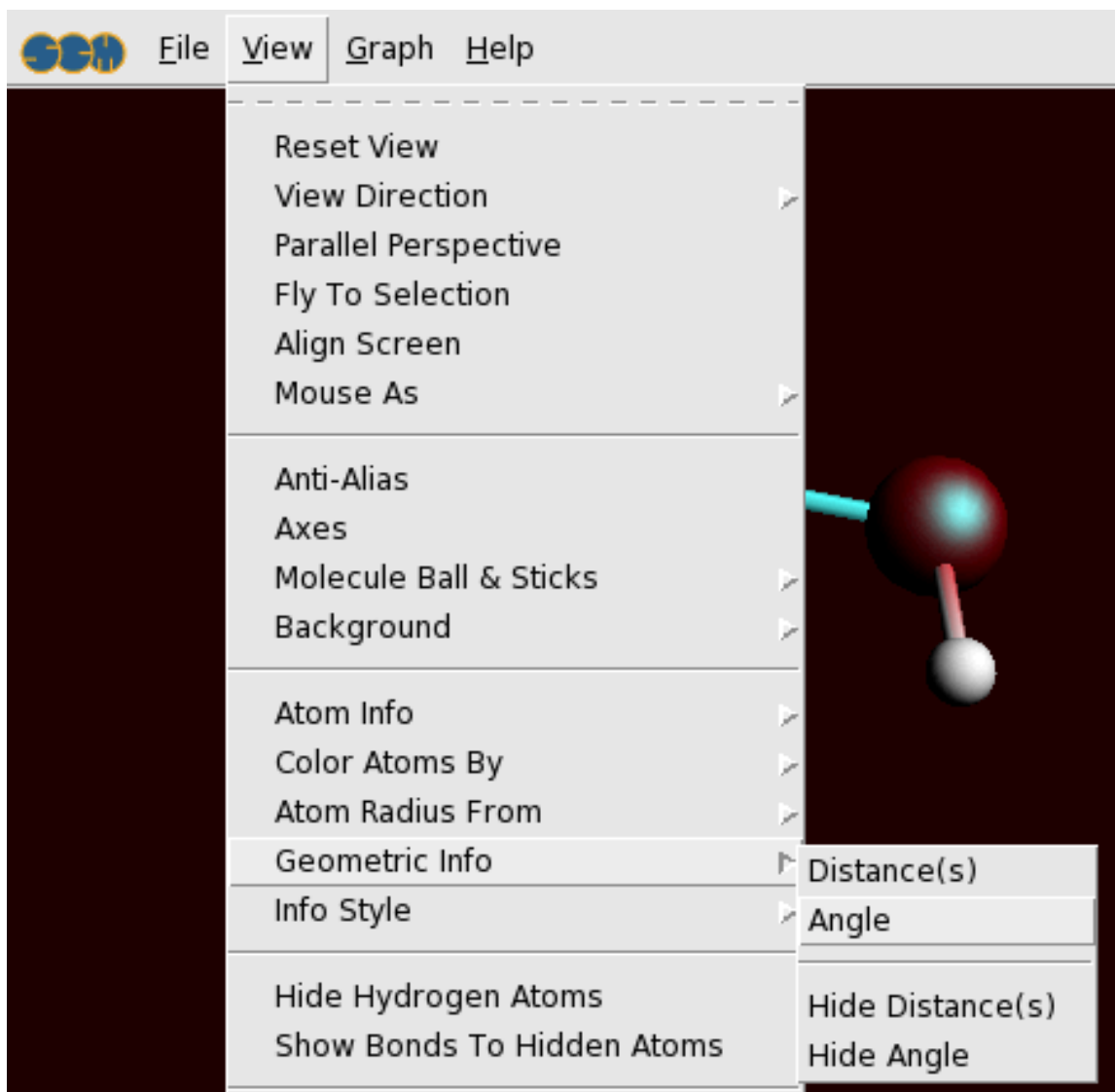
To rotate, translate, or zoom the picture, use your mouse, just as in ADFinput.

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

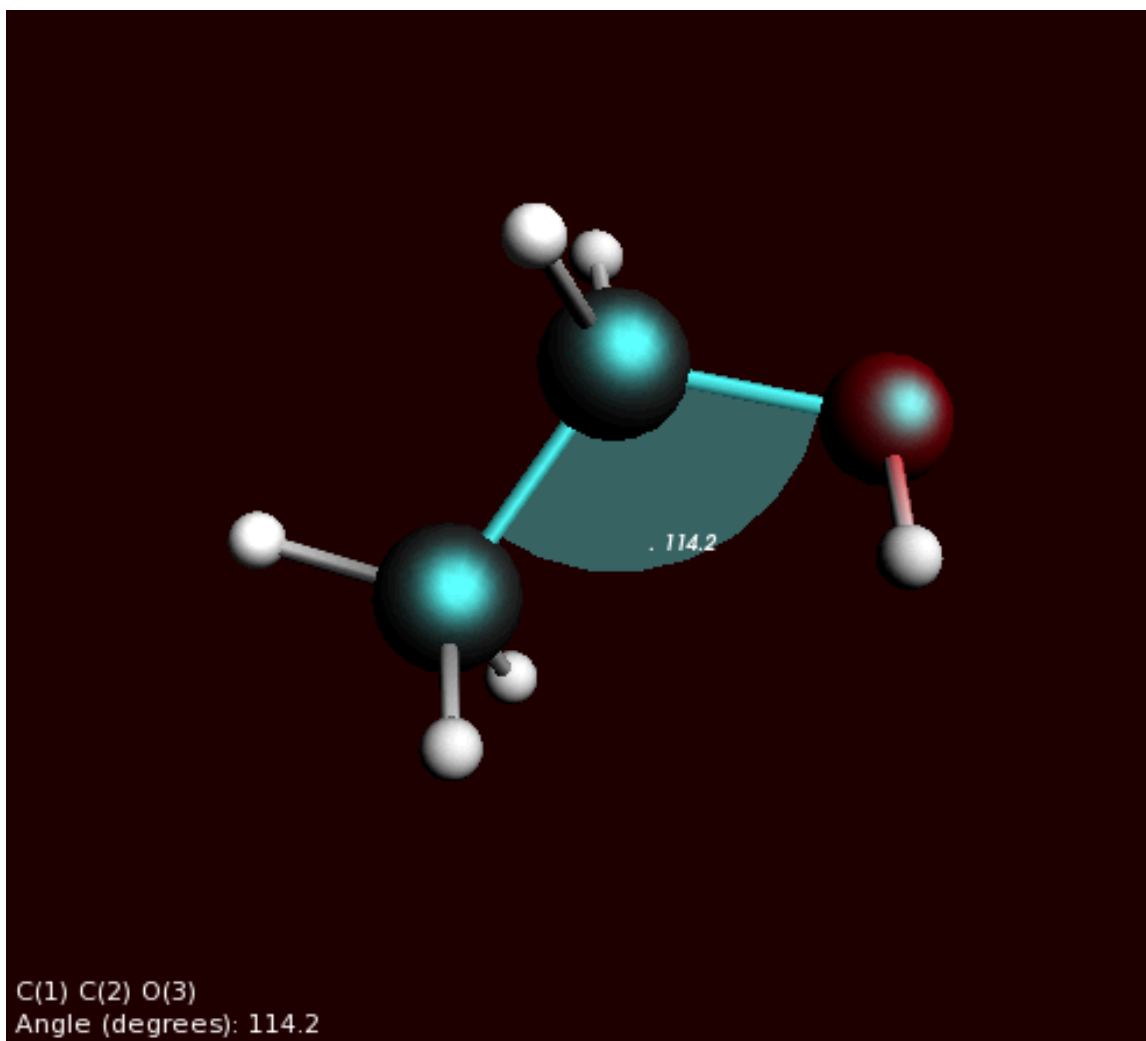
Selecting atoms provides information about atoms, bonds, etc. The information will be updated when you go to another point in the movie (a different geometry). You can see examples of these in the pictures above.

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 :



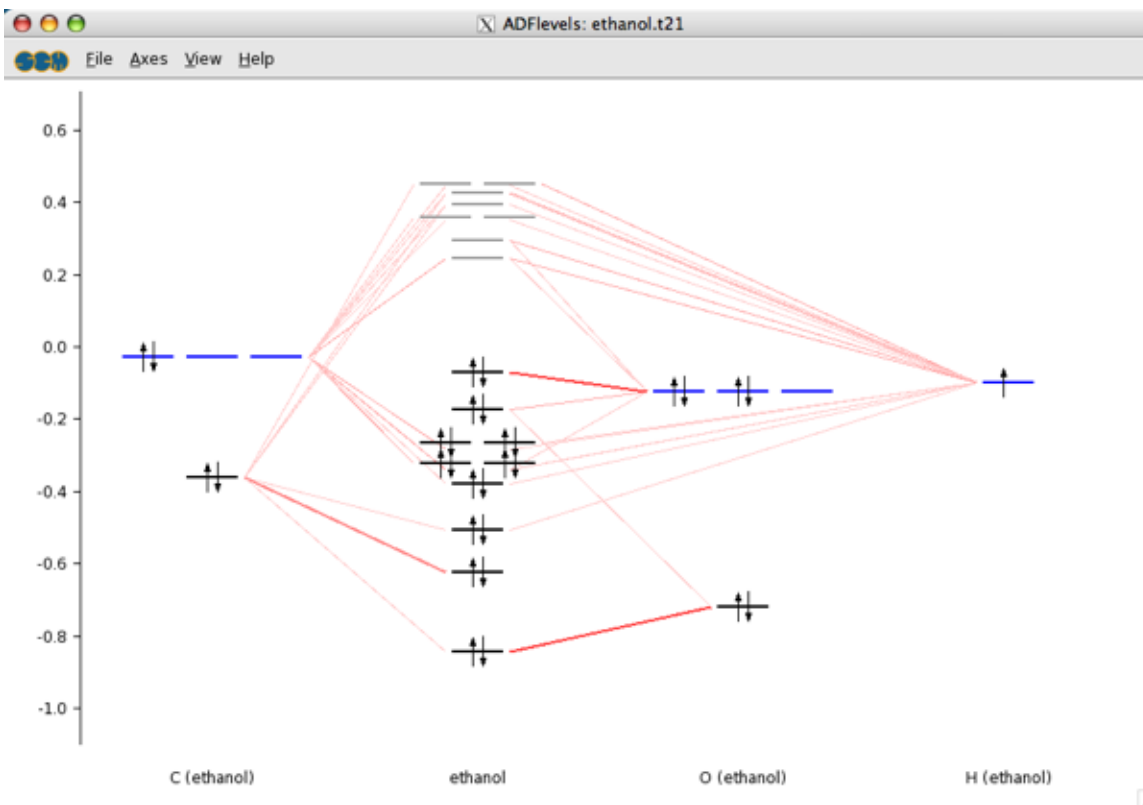
In the ADFmovie window: select **File** → **Quit**

### **Orbital energy levels: ADFlevels**

Select your job in the ADFjobs window by clicking on the job name

Select the **SCM** → **ADF Levels** command

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

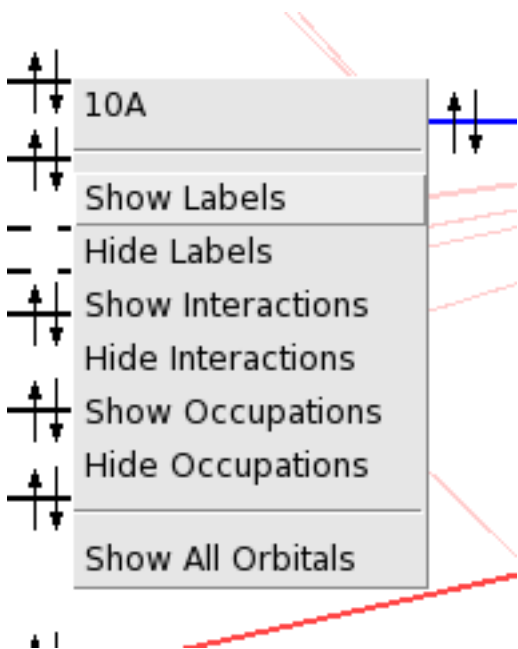


In the diagram you can see from what fragment types the molecular levels are composed.

Move the mouse around, above different levels, without clicking

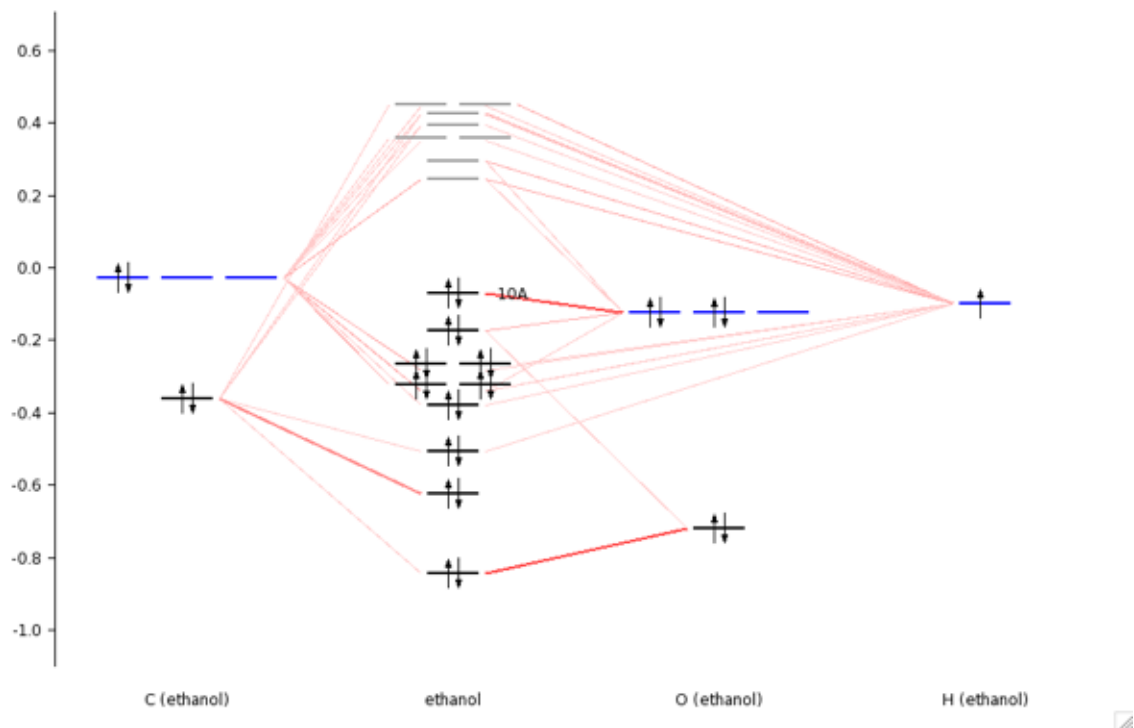
Balloons will pop up with information about the level at the mouse position.

Click and hold on the HOMO level of the molecule



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

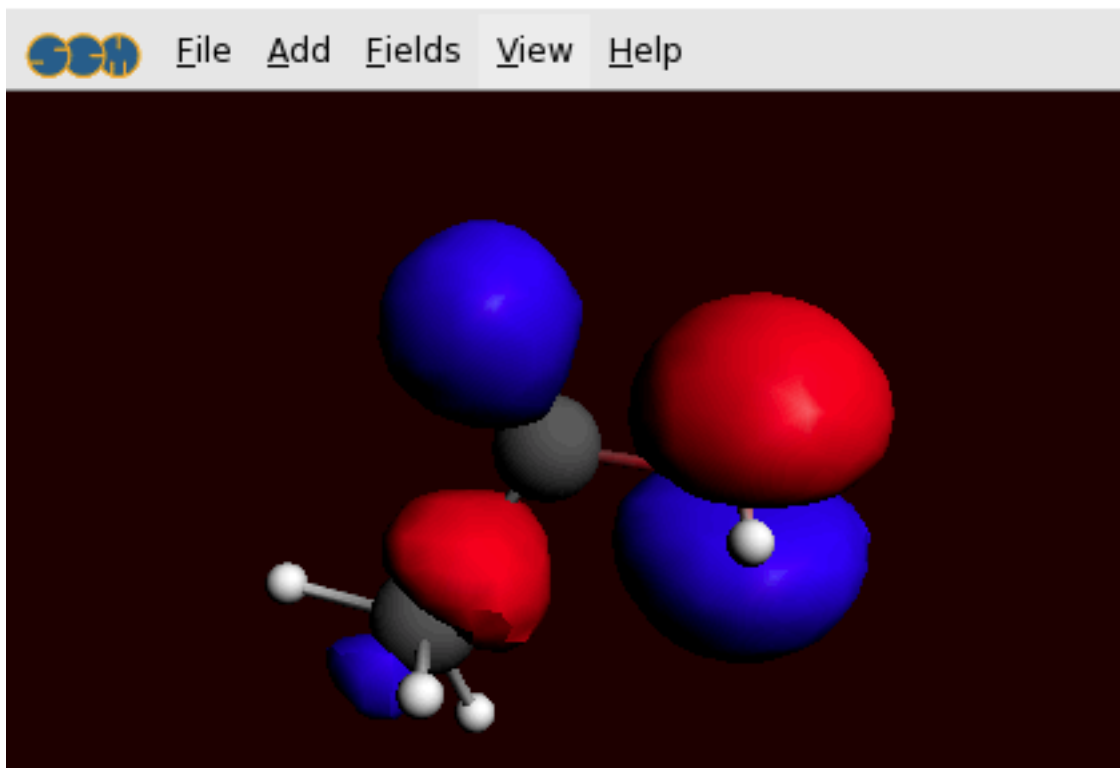
Click and hold on the HOMO of the O fragment type  
In the pop-up, select 'Show Labels'



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

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

A window with a picture of the orbital should appear.



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

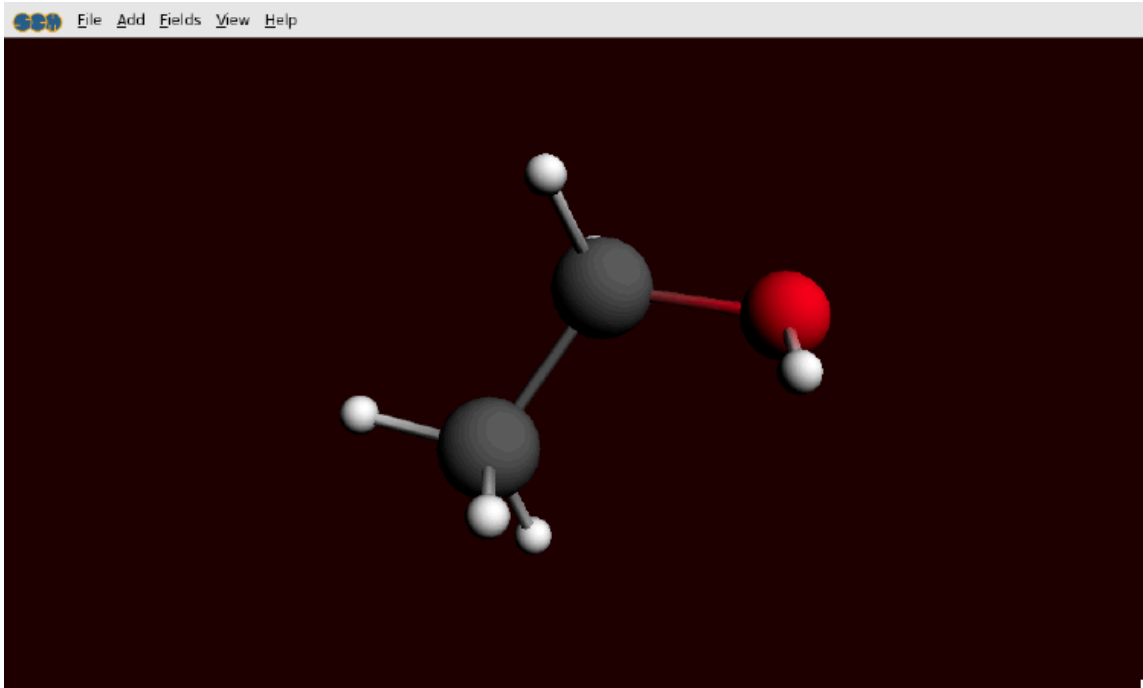
In the window with the orbital: select **File** → **Quit**

In the window with the levels: select **File** → **Quit**

### **Electron density, potential and orbitals: ADFview**

Select **SCM** → **View**

ADFview will startup and show a picture of your molecule:

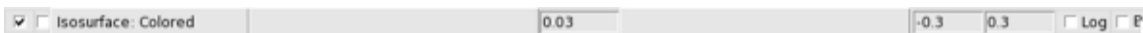


You can use ADFview to visualize all kinds of 'field' related properties: densities, orbitals, potentials, etc. You actually have already used it before: the picture of the orbital that was created using ADFlevels was shown by ADFview.

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

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

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



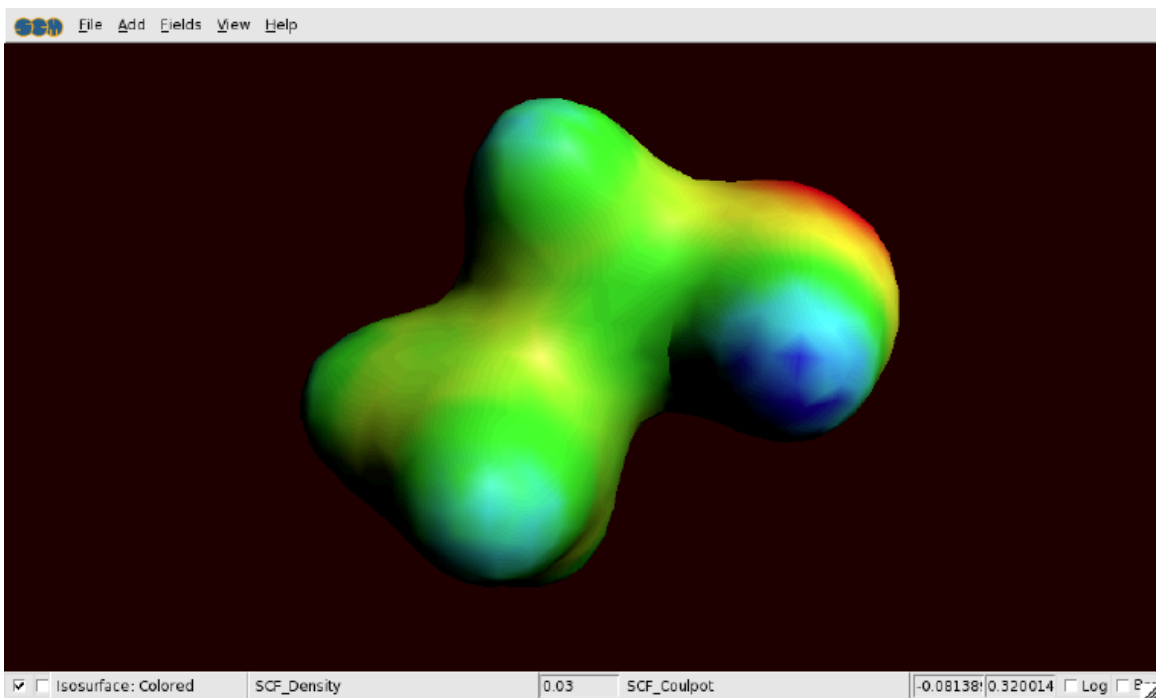
In this particular case the control line contains two pull-down menus that you use to select the fields that you want to visualize.

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



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

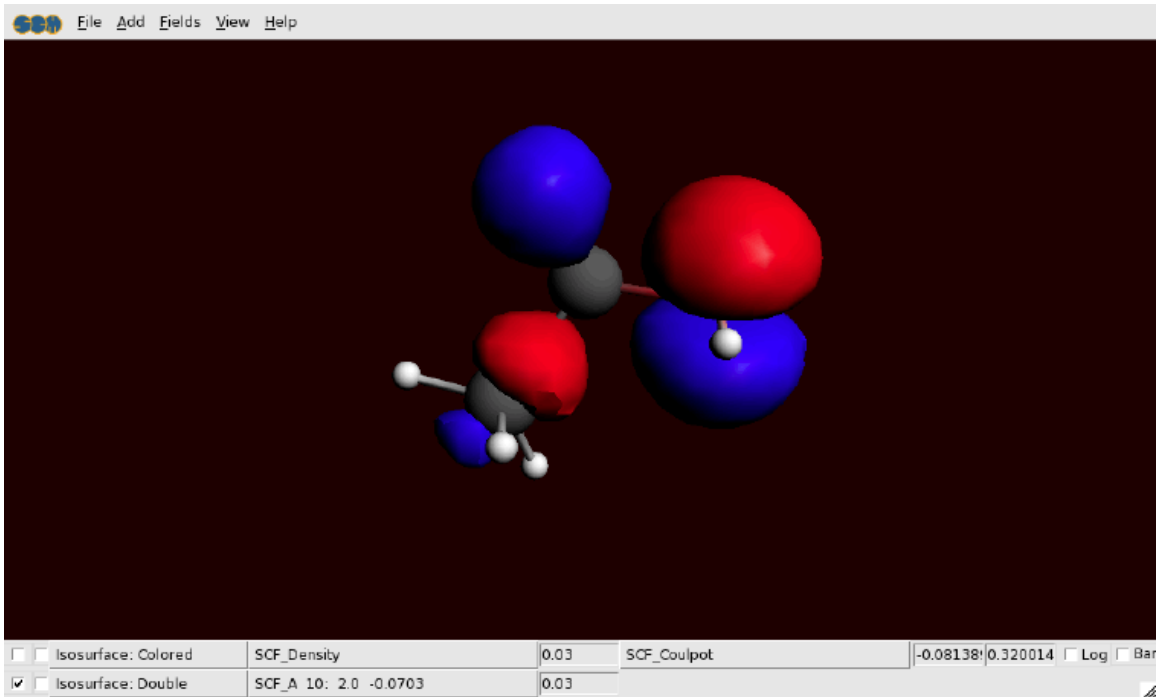




To demonstrate some other possibilities of ADFview, do the following:

Select the **Add** → **HOMO** command

Click on the check box in the FIRST control line to hide the density

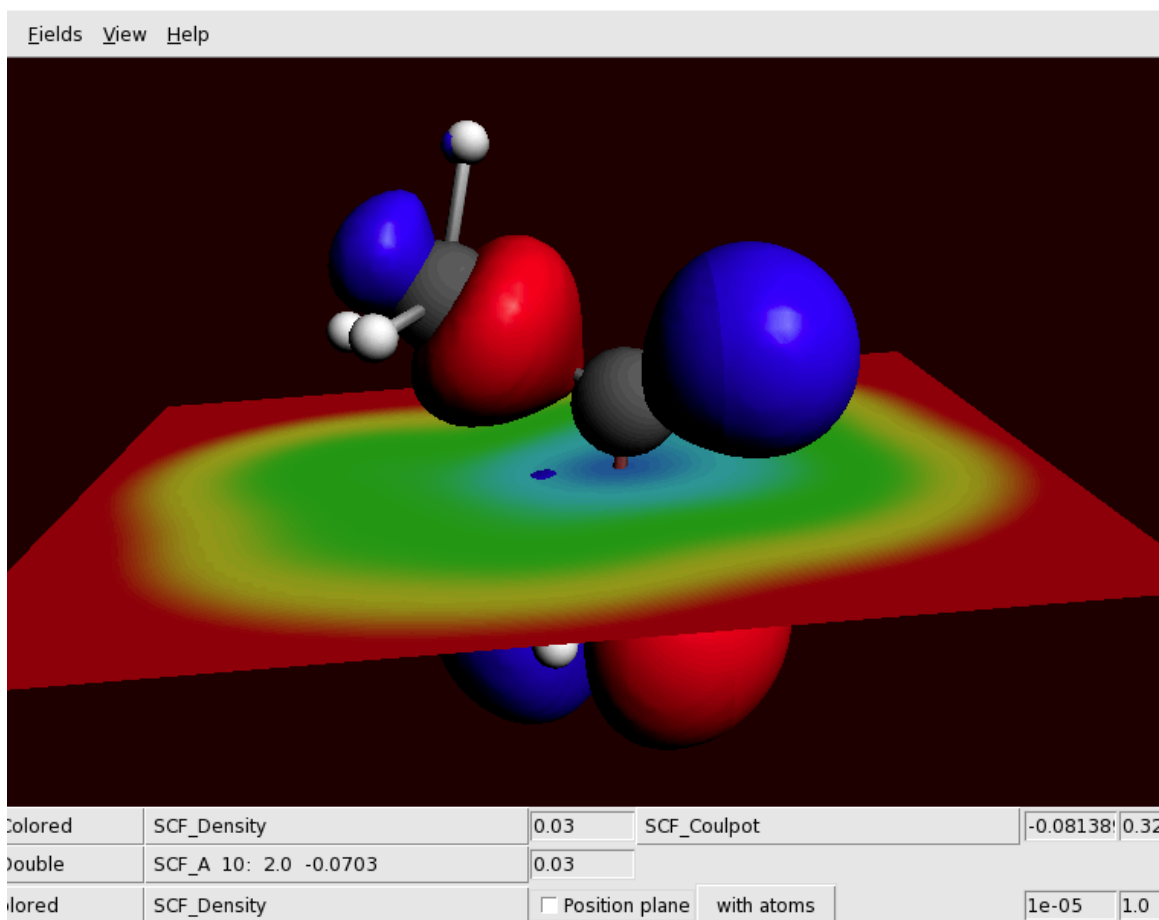


Select the **Add** → **Cut plane: Colored** command

In the new control line, press on the pull-down menu and select **Density** → **SCF**

Rotate your molecule to get a good view

Select the **Fields → Grid → Medium** command  
Click Yes to recalculate the fields



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. Just do not activate Anti-Alias: it makes the pictures even better, but also slows down ADFview very very much.

When you are done, close the ADFview window:

Select **File → Quit**

## 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:

```

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

```

Aton	Cartesian	[a. u./angstrom]		
	X	Y	Z	
1 C	0.006738	-0.023036	0.008017	
2 C	-0.020695	0.063658	-0.058878	
3 O	-0.055232	-0.058310	0.174715	
4 H	0.026593	0.041881	-0.130869	
5 H	-0.007189	0.017312	0.014078	
6 H	0.026076	0.091230	0.003591	
7 H	0.001037	0.010241	-0.022589	
8 H	0.032287	-0.038182	-0.023844	
9 H	-0.009616	-0.014794	0.035778	

```

-----
Geometry Convergence after Step 1
-----
current energy                -2.13741980 Hartree
energy change                 -0.00100000 F
constrained gradient max     0.17471492 0.00100000 F
constrained gradient rms     0.05152199 0.00066667 F
gradient max                  0.17471492
gradient rms                   0.05152199
cart. step max                 0.05924794 0.01000000 F
cart. step rms                 0.02422877 0.00066667 F
-----
Coordinates (Cartesian)
=====

```

Aton	bohr			angstrom			Geometric Variables (0:frozen, *:LT par.)		
	X	Y	Z	X	Y	Z			
1 C	-2.537944	-3.660059	0.198188	-1.342546	-1.936828	0.104877	1	2	3
2 C	-0.881853	-1.255525	-0.055886	-0.466233	-0.664395	-0.029573	4	5	6
3 O	1.747851	-1.739502	0.442316	0.924500	-0.920505	0.234063	7	8	9
4 H	1.764890	-2.382562	2.270100	0.933516	-1.260798	1.201285	10	11	12
5 H	-1.858786	-5.103166	-1.114836	-0.983627	-2.700479	-0.589946	13	14	15
6 H	-4.509885	-3.220946	-0.236755	-2.386529	-1.703975	-0.125285	16	17	18
7 H	-2.419401	-4.385782	2.129718	-1.280292	-2.328856	1.126998	19	20	21
8 H	-1.619009	0.194981	1.260534	-0.856743	0.103179	0.667046	22	23	24
9 H	-1.006937	-0.535202	-2.002007	-0.532848	-0.283217	-1.059417	25	26	27

```

-----
Number of elements of the density matrix on this node (used, total): 126 231
-----
Numerical Integration : Voronoi Polyhedra (Te Velde) *** (parameters, tests) ***
-----
General Accuracy Parameter : 3.00
Symmetry used in the points section: NOSYM
Summary of the Symmetry Unique Points:
-----

```

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. Have a look, and then close the program.

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

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

## Tutorial 2: Excitation energies of ethene

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

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

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

### Step 1: Start ADFinput

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

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

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

Next start ADFinput using the SCM menu. Notice that currently no job is selected. If a job is selected, the SCM menu will open the selected job, which is not what we want at this moment.

You can toggle the selection in ADFjobs using the right mouse button (or control-left).

To clear the selection there are several options:

- press Esc,
- or click anywhere in the search bar on the bottom (except in the input fields),/li>
- or click in empty space,
- or click somewhere on the selected job (but not in an input field or an icon).

Make sure no job is selected in ADFjobs (hit ESC)

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

### 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)

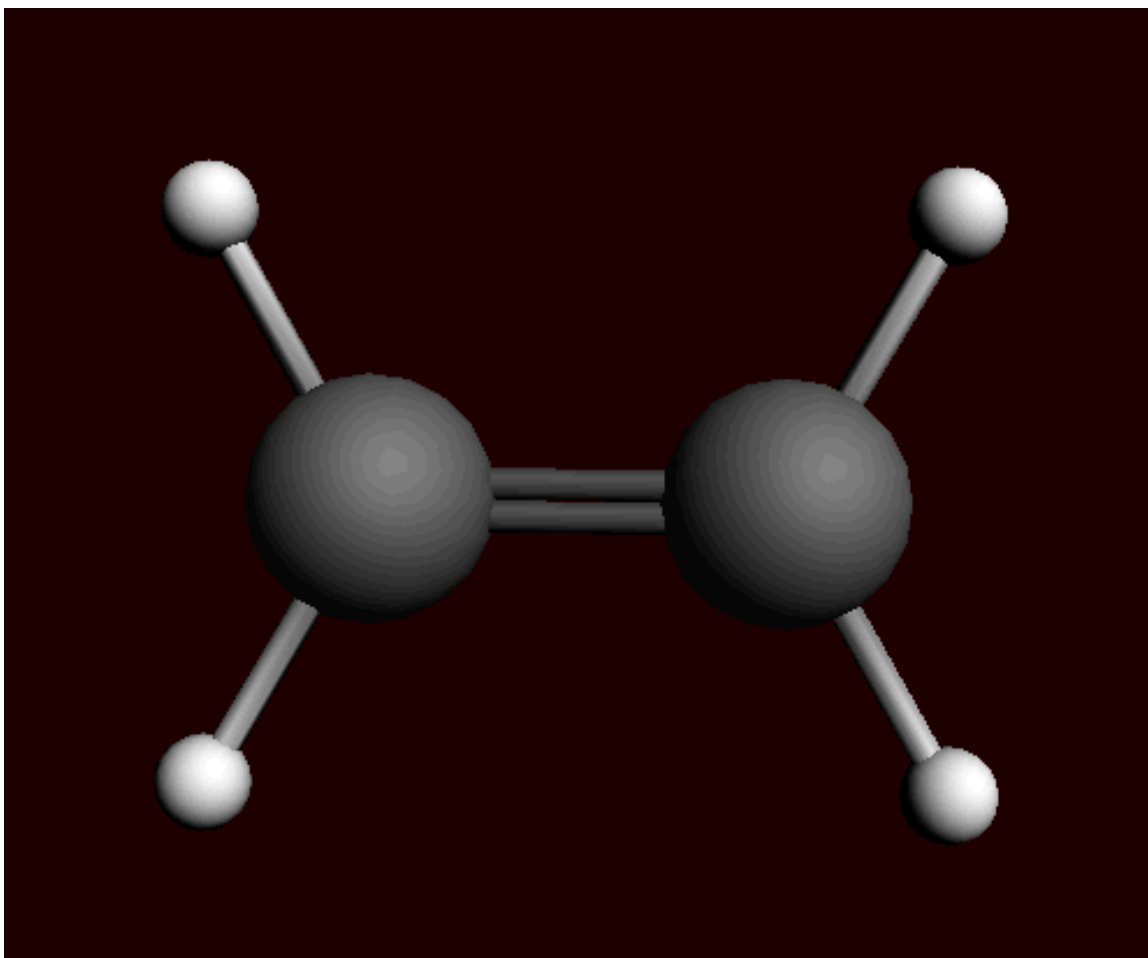
Select the select-tool by clicking on the button with the arrow

Click once in empty space so nothing is selected

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

Click the optimizer button

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 proper title in the Title field (like 'Ethene')  
Select the 'Geometry Optimization' preset

**Main Options**

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

Core type: Large

Integration accuracy:

With the proper options selected, now run ADF:

Select the **File** → **Run** command

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

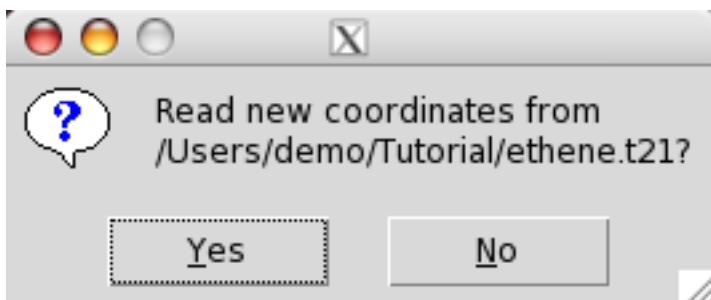
In the file select box, choose a name for your file

(for example 'ethene') and click 'Save'

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

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

The following dialog should appear:



Click 'Yes' to update the coordinates

## Step 4: Calculate the excitation energies

### Select calculations options

To set up the calculation of the excitation spectrum:

Adjust the title to something like 'Ethene excitations'

Select the 'Single Point' template

Select the 'Excitations, CD' panel (use the pull down menu)

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

Excitations, CD

Type of excitations: SingletAndTriplet

Diagonalization method: Davidson

Number of excitations:

Occupied-Virtual energy difference:

From:  Hartree

To:  Hartree

Occupied orbital energies:

From:  Hartree

To:  Hartree

Virtual orbital energies:

From:  Hartree

To:  Hartree

Velocity representation:  Yes

Spin-flip excitations:  Yes

Use ALDA:  Yes

Calculate rotatory strengths (CD):  Yes

### 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

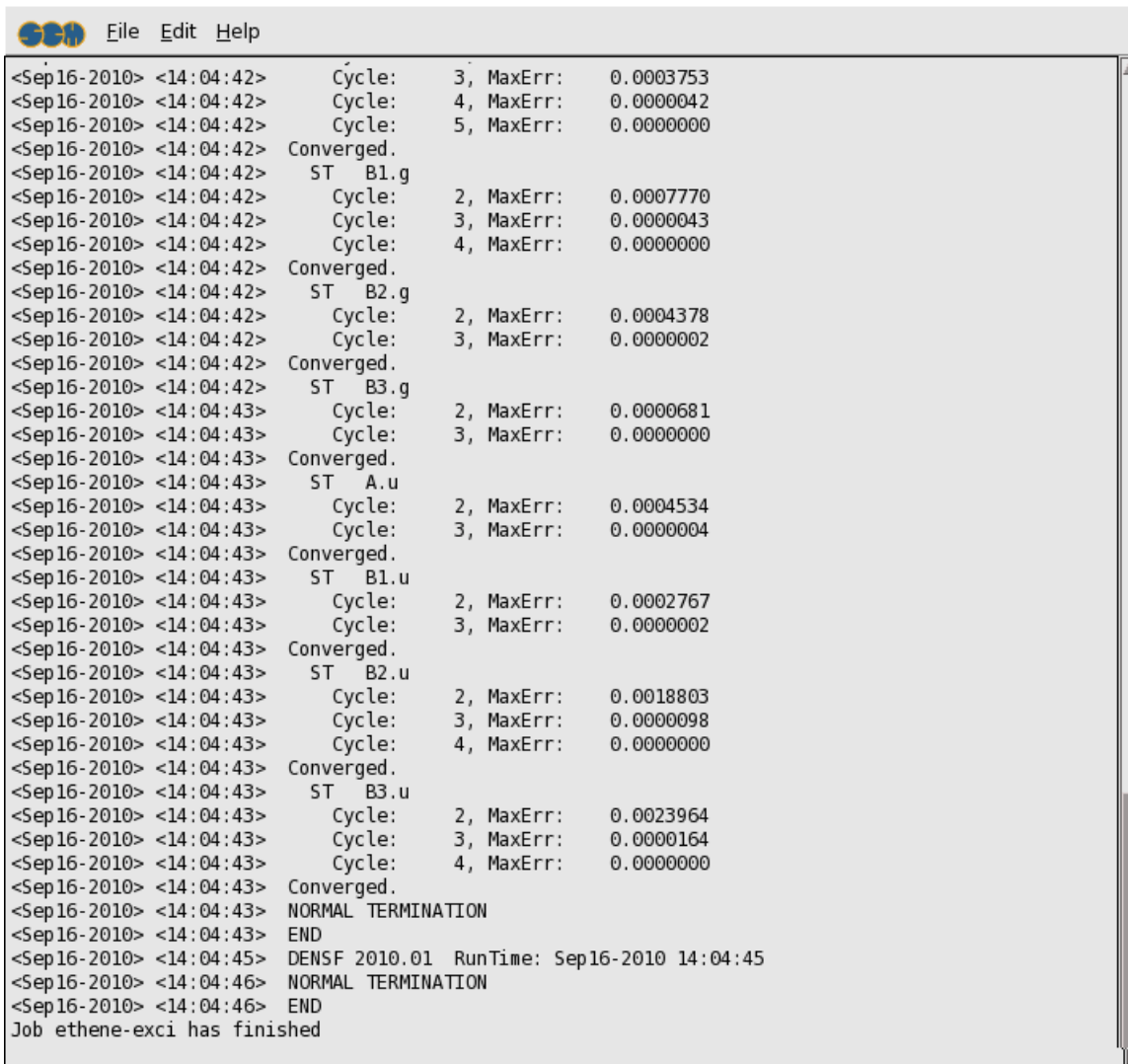
Click 'No' when asked if you wish to update the coordinates



## Step 5: Results of your calculation

### Logfile: ADFtail

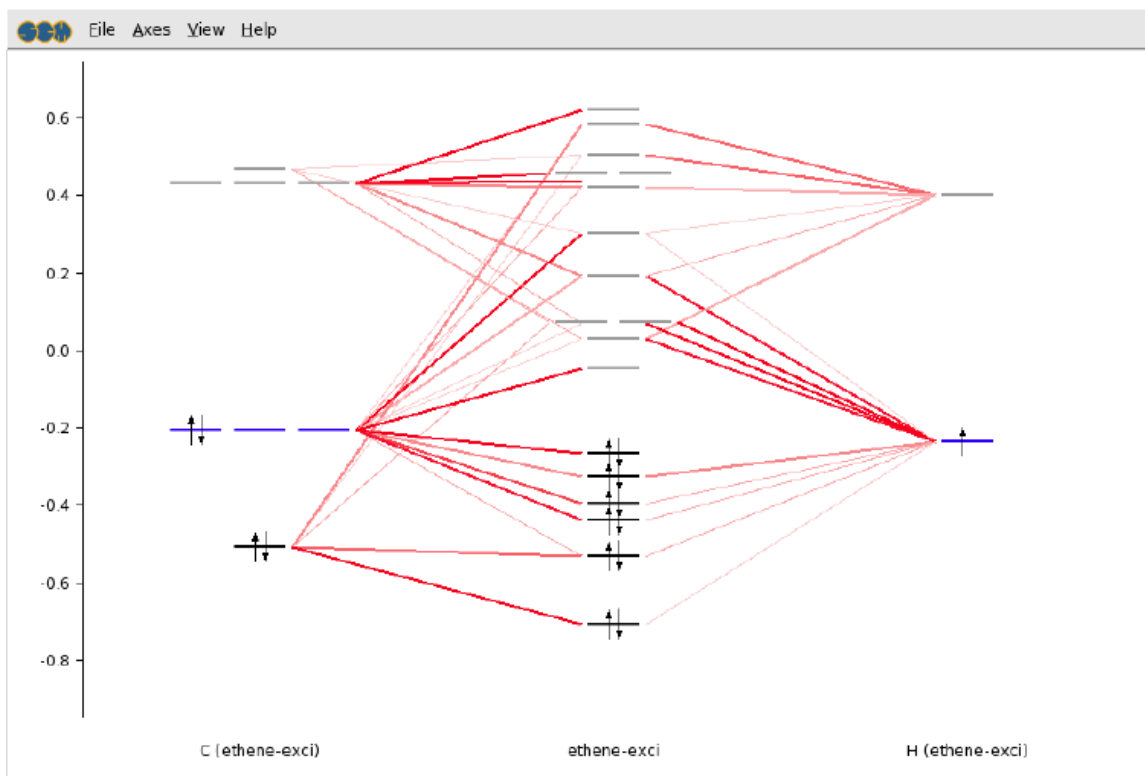
The logfile shows you that the calculation has finished, and that indeed the excitation code has been running:



```
SCM File Edit Help
<Sep16-2010> <14:04:42> Cycle: 3, MaxErr: 0.0003753
<Sep16-2010> <14:04:42> Cycle: 4, MaxErr: 0.0000042
<Sep16-2010> <14:04:42> Cycle: 5, MaxErr: 0.0000000
<Sep16-2010> <14:04:42> Converged.
<Sep16-2010> <14:04:42> ST B1.g
<Sep16-2010> <14:04:42> Cycle: 2, MaxErr: 0.0007770
<Sep16-2010> <14:04:42> Cycle: 3, MaxErr: 0.0000043
<Sep16-2010> <14:04:42> Cycle: 4, MaxErr: 0.0000000
<Sep16-2010> <14:04:42> Converged.
<Sep16-2010> <14:04:42> ST B2.g
<Sep16-2010> <14:04:42> Cycle: 2, MaxErr: 0.0004378
<Sep16-2010> <14:04:42> Cycle: 3, MaxErr: 0.0000002
<Sep16-2010> <14:04:42> Converged.
<Sep16-2010> <14:04:42> ST B3.g
<Sep16-2010> <14:04:43> Cycle: 2, MaxErr: 0.0000681
<Sep16-2010> <14:04:43> Cycle: 3, MaxErr: 0.0000000
<Sep16-2010> <14:04:43> Converged.
<Sep16-2010> <14:04:43> ST A.u
<Sep16-2010> <14:04:43> Cycle: 2, MaxErr: 0.0004534
<Sep16-2010> <14:04:43> Cycle: 3, MaxErr: 0.0000004
<Sep16-2010> <14:04:43> Converged.
<Sep16-2010> <14:04:43> ST B1.u
<Sep16-2010> <14:04:43> Cycle: 2, MaxErr: 0.0002767
<Sep16-2010> <14:04:43> Cycle: 3, MaxErr: 0.0000002
<Sep16-2010> <14:04:43> Converged.
<Sep16-2010> <14:04:43> ST B2.u
<Sep16-2010> <14:04:43> Cycle: 2, MaxErr: 0.0018803
<Sep16-2010> <14:04:43> Cycle: 3, MaxErr: 0.0000098
<Sep16-2010> <14:04:43> Cycle: 4, MaxErr: 0.0000000
<Sep16-2010> <14:04:43> Converged.
<Sep16-2010> <14:04:43> ST B3.u
<Sep16-2010> <14:04:43> Cycle: 2, MaxErr: 0.0023964
<Sep16-2010> <14:04:43> Cycle: 3, MaxErr: 0.0000164
<Sep16-2010> <14:04:43> Cycle: 4, MaxErr: 0.0000000
<Sep16-2010> <14:04:43> Converged.
<Sep16-2010> <14:04:43> NORMAL TERMINATION
<Sep16-2010> <14:04:43> END
<Sep16-2010> <14:04:45> DENSF 2010.01 RunTime: Sep16-2010 14:04:45
<Sep16-2010> <14:04:46> NORMAL TERMINATION
<Sep16-2010> <14:04:46> END
Job ethene-exci has finished
```

### Energy levels: ADFlevels

Select **SCM** → **Levels**



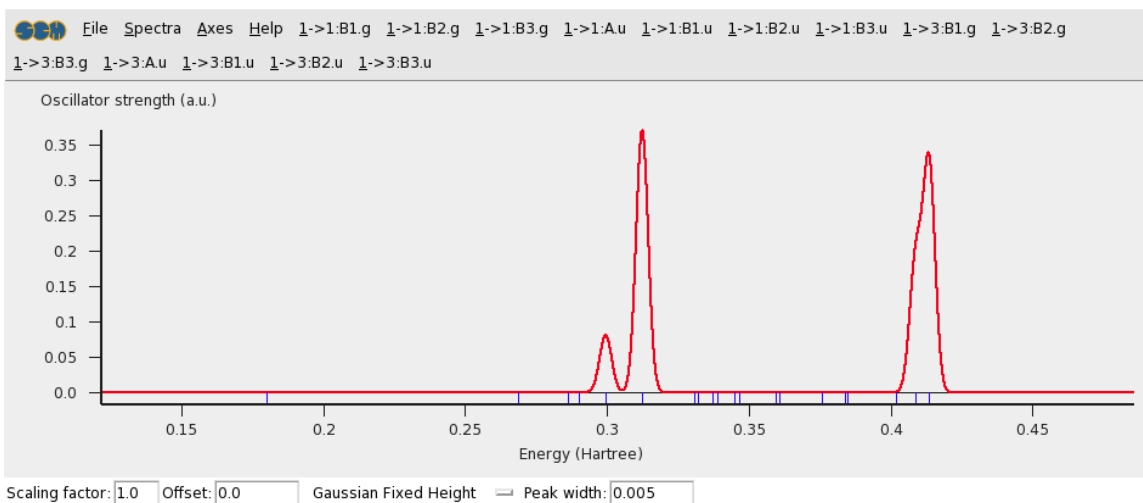
In this level diagram you can see that the HOMO and LUMO consist mainly of carbon p orbitals. It is also easy to see what orbitals the hydrogens take part in.

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.

## 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**

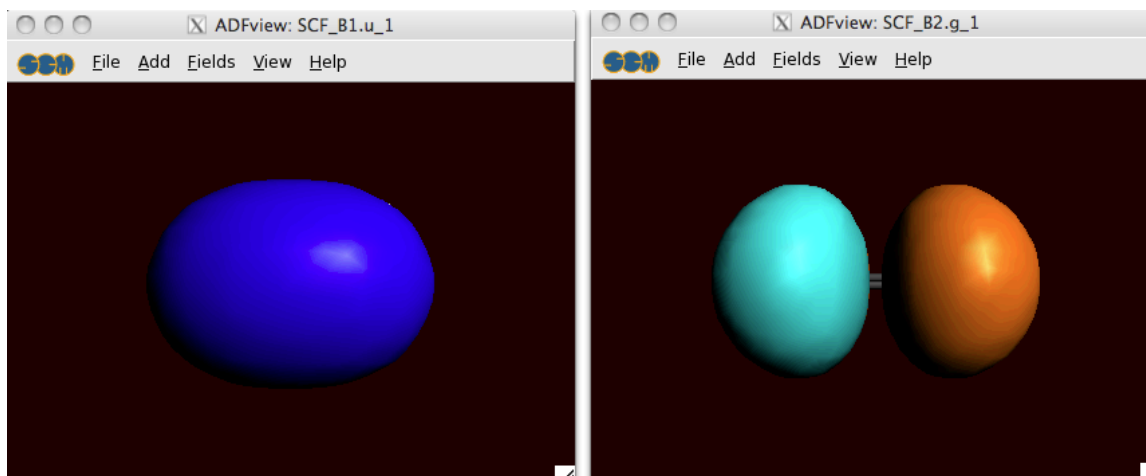
Energy : 0.311957 hartree  
 Oscillator strength : 0.371939  
 Transition dipole moment: -1.33732 0.0 0.0

Composition (major contributions):

96.1%	1b1.u -> 1b2.g, dipole contr:	( -1.65969000 0.00000000 0.00000000)
1.0%	1b3.u -> 3a.g, dipole contr:	( -0.00896519 0.00000000 0.00000000)
0.8%	2a.g -> 3b3.u, dipole contr:	( 0.16178400 -0.00000000 -0.00000000)
0.6%	1b2.u -> 2b1.g, dipole contr:	( -0.03485810 0.00000000 0.00000000)
0.4%	1b1.g -> 3b2.u, dipole contr:	( 0.10452200 0.00000000 0.00000000)
0.3%	2a.g -> 4b3.u, dipole contr:	( 0.05922000 0.00000000 0.00000000)
0.2%	1b1.u -> 2b2.g, dipole contr:	( -0.02820160 -0.00000000 -0.00000000)
0.2%	1a.g -> 2b3.u, dipole contr:	( -0.00279190 0.00000000 0.00000000)
0.1%	1b1.g -> 2b2.u, dipole contr:	( 0.04501950 -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



### 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 transition densities. So we will start ADFview and next load the .t41 file generated by DENSF:

Select **SCM** → **View**

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** → **Double Isosurface**

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

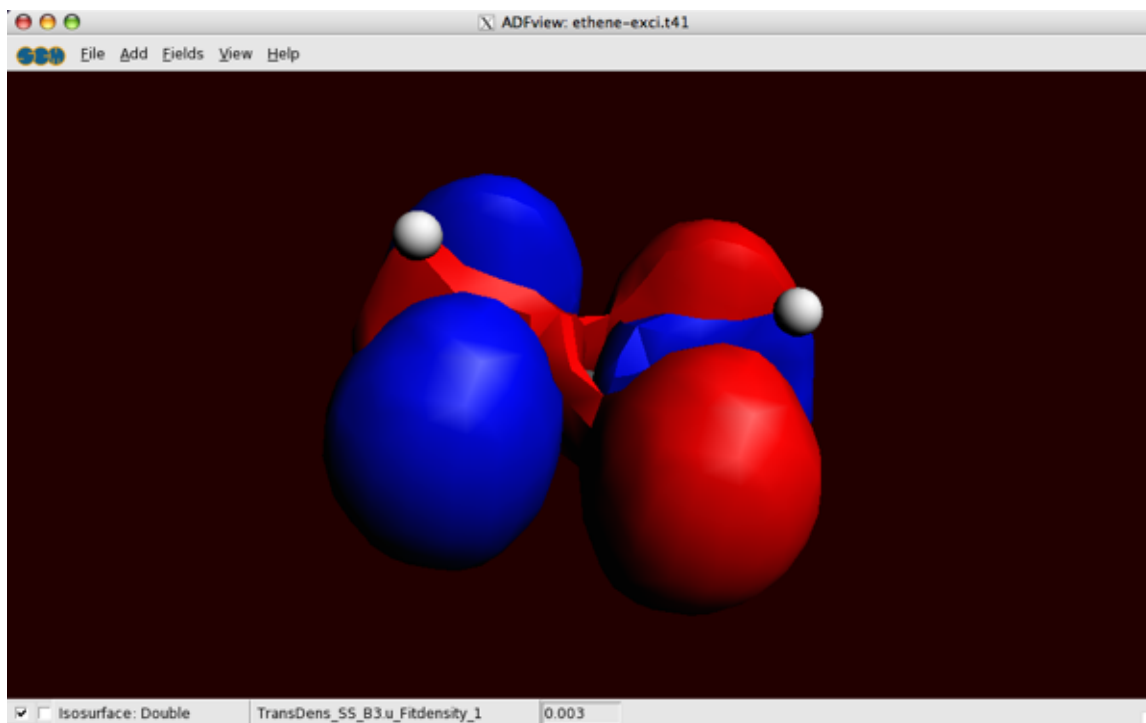


In this case lets select the transition density that belongs to the biggest peak: the Singlet-Singlet 1B3u excitation:

Select the **Transition Density** → **TransDens\_SS\_B3.u\_Fitdensity\_1** field

Change the isovalue to 0.003

Rotate the molecule a little



The resolution is rather coarse, you can use interpolation to get a better picture. Or you can set the default grid to use to Medium (in ADFinput in the 'Densities, Potential, Orbitals' panel).

## 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**

```

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:     0.28639   7.79318  0.000    B3.g
2:     0.29936   8.14591  0.8095E-01 B1.u
3:     0.31222   8.49592  0.3721    B3.u
4:     0.33886   9.22072  0.000    B3.g
5:     0.34647   9.42799  0.000    B2.g
6:     0.35928   9.77657  0.000    B1.g
7:     0.36086   9.81943  0.000    B2.g
8:     0.40193   10.93711 0.000    A.u
9:     0.40862   11.11917 0.1862    B2.u
10:    0.41337   11.24830 0.3226    B3.u

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

Eigenvalues of small (approximate) problem
  i, eigenvalue(i) in dvdson    1    0.3458760990E+00
Eigenvalues of small (approximate) problem
  i, eigenvalue(i) in dvdson    1    0.3447510677E+00
Eigenvalues of small (approximate) problem
  i, eigenvalue(i) in dvdson    1    0.3447447877E+00
Eigenvalues of small (approximate) problem
  i, eigenvalue(i) in dvdson    1    0.3447447783E+00

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

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

```

## Closing the ADF-GUI modules

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

Select **SCM → Close**

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

Select **SCM → Close All**

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

## Tutorial 3: Vibrational frequencies of ethane

### Step 1: Start ADFinput

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

```
cd $HOME
Start adfjobs
Click on the Tutorial folder icon
Start adfinput using the SCM menu
```

### Step 2: Create your ethane molecule

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

```
Select the C-tool
Click once to make a carbon atom
Click again to make a second carbon atom
Select Edit → Add Hydrogen
And do it again: ... add hydrogen
Click the pre-optimize button
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.

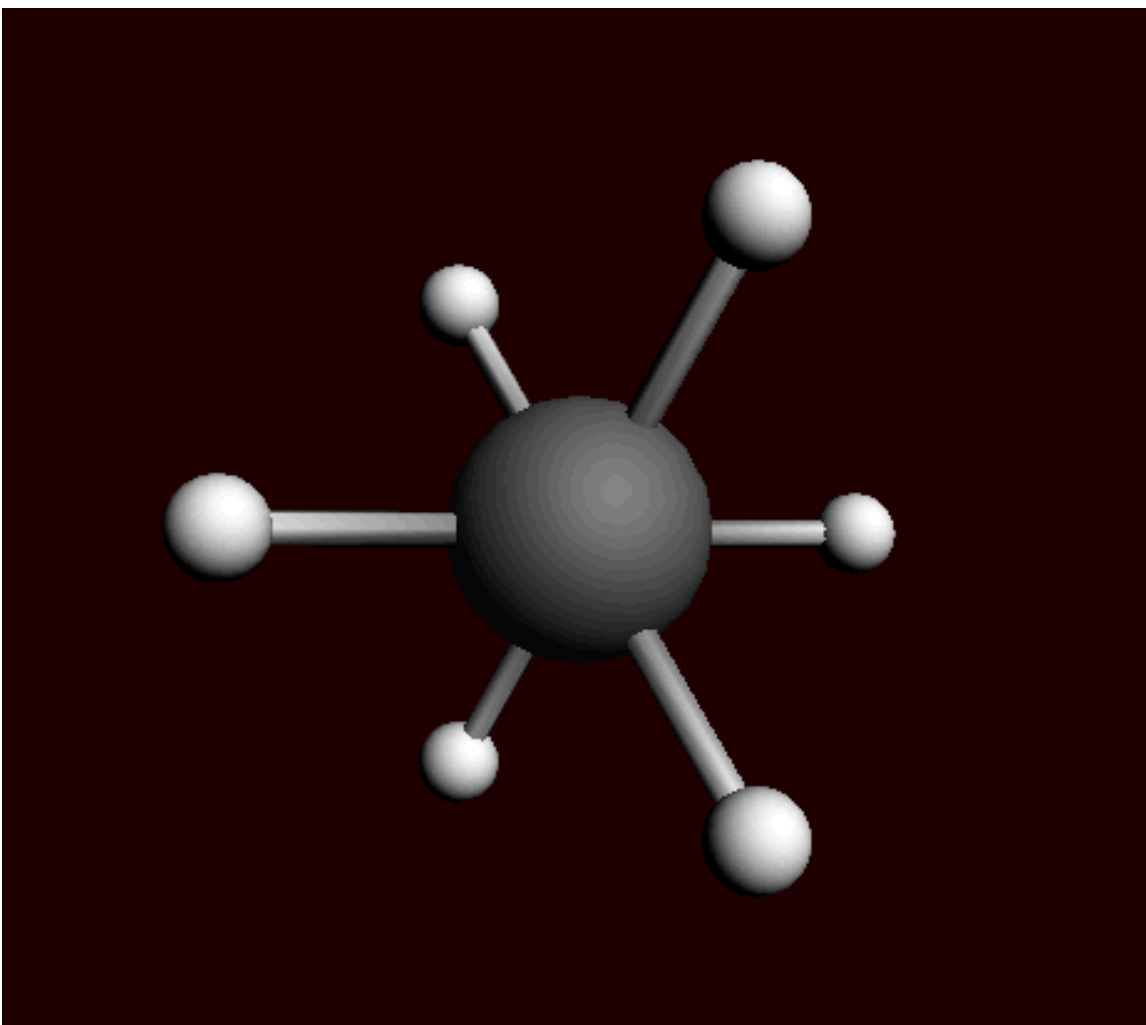
The symmetrization should have enforced perfect D3d symmetry, using the Symmol program. The Symmol program has been developed by Pilati and Forni, see the balloon help on that button for details..

### 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

Main Options

Title: Ethane

Preset: Frequencies

Task: Frequencies

Total charge: 0.0

Spin polarization: 0.0

Unrestricted:  Yes

XC potential in SCF: LDA

XC energy after SCF: Default

Relativity (ZORA): None

Basis set: DZ

Core type: Large

Integration accuracy:

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:

```

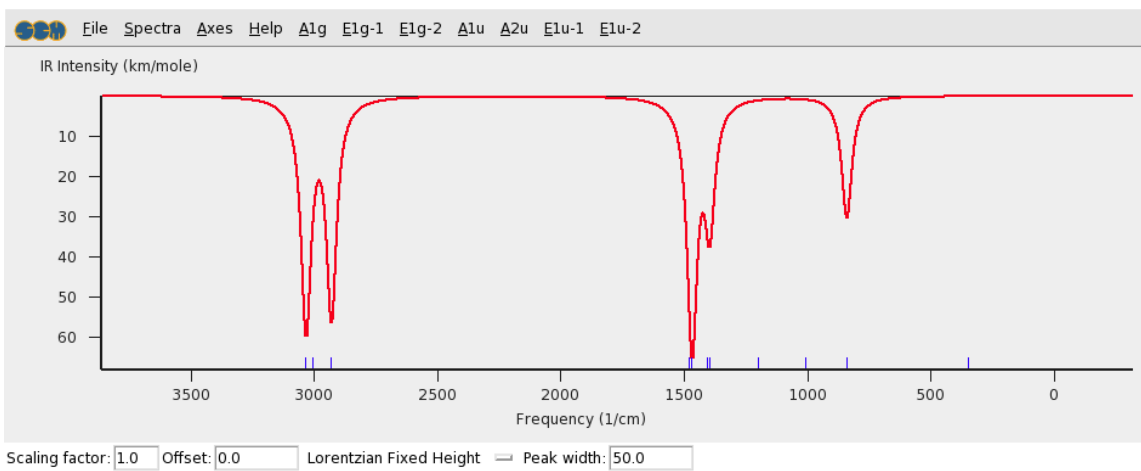
<Sep16-2010> <15:31:11> >>>> AMETS
<Sep16-2010> <15:31:11> Bond Energy LDA -1.51928017 a.u.
<Sep16-2010> <15:31:11> Bond Energy LDA -41.34171689 eV
<Sep16-2010> <15:31:11> >>>> POPUL
<Sep16-2010> <15:31:11> >>>> ENGRAD
<Sep16-2010> <15:31:12> >>>> ENHESS
<Sep16-2010> <15:31:12> >>>> FITINT
<Sep16-2010> <15:31:12> >>>> FIT_A1_COEF01
<Sep16-2010> <15:31:13> >>>> FITINT
<Sep16-2010> <15:31:14> === NUCLEUS: 1
<Sep16-2010> <15:31:18> === NUCLEUS: 3
<Sep16-2010> <15:31:22> >>>> CALC_HESS_PMAT
<Sep16-2010> <15:31:23> >>>> CALC_HESS_WMAT
<Sep16-2010> <15:31:23> NORMAL TERMINATION
<Sep16-2010> <15:31:23> END
Job ethane has finished

```

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

## IR-spectrum (vibrational spectrum): ADFspectra and ADFmovie

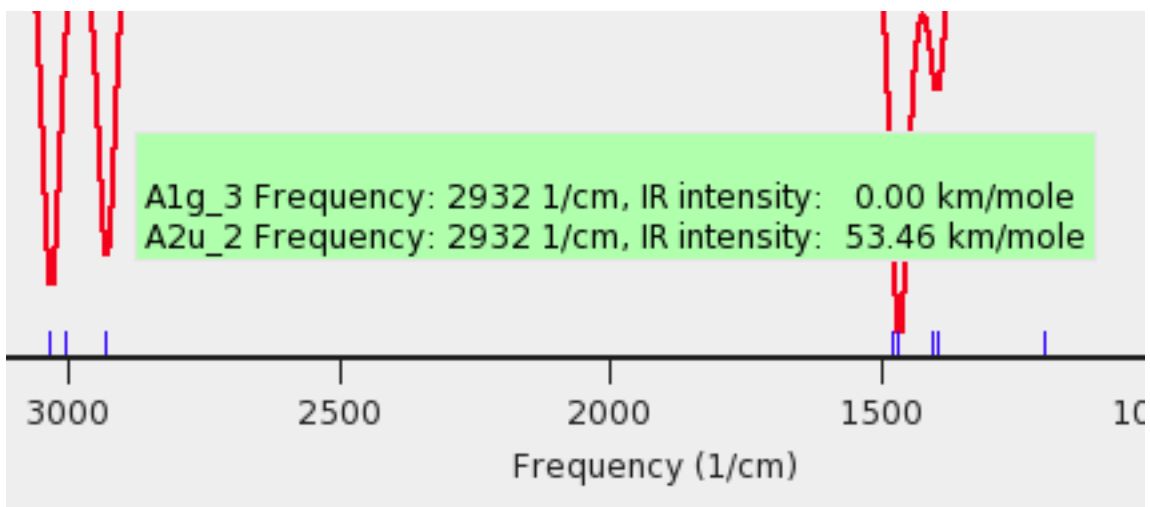
Select **SCM** → **Spectra**



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

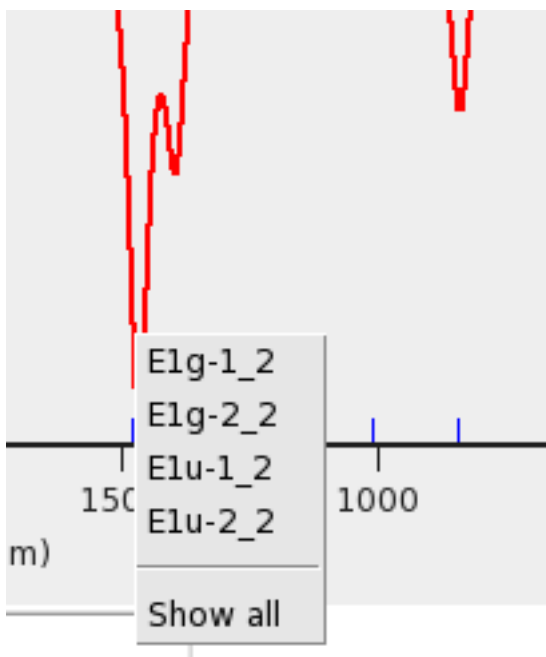
If you move the mouse pointer above the spectrum you will get more information about the peaks in pop-up windows:

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



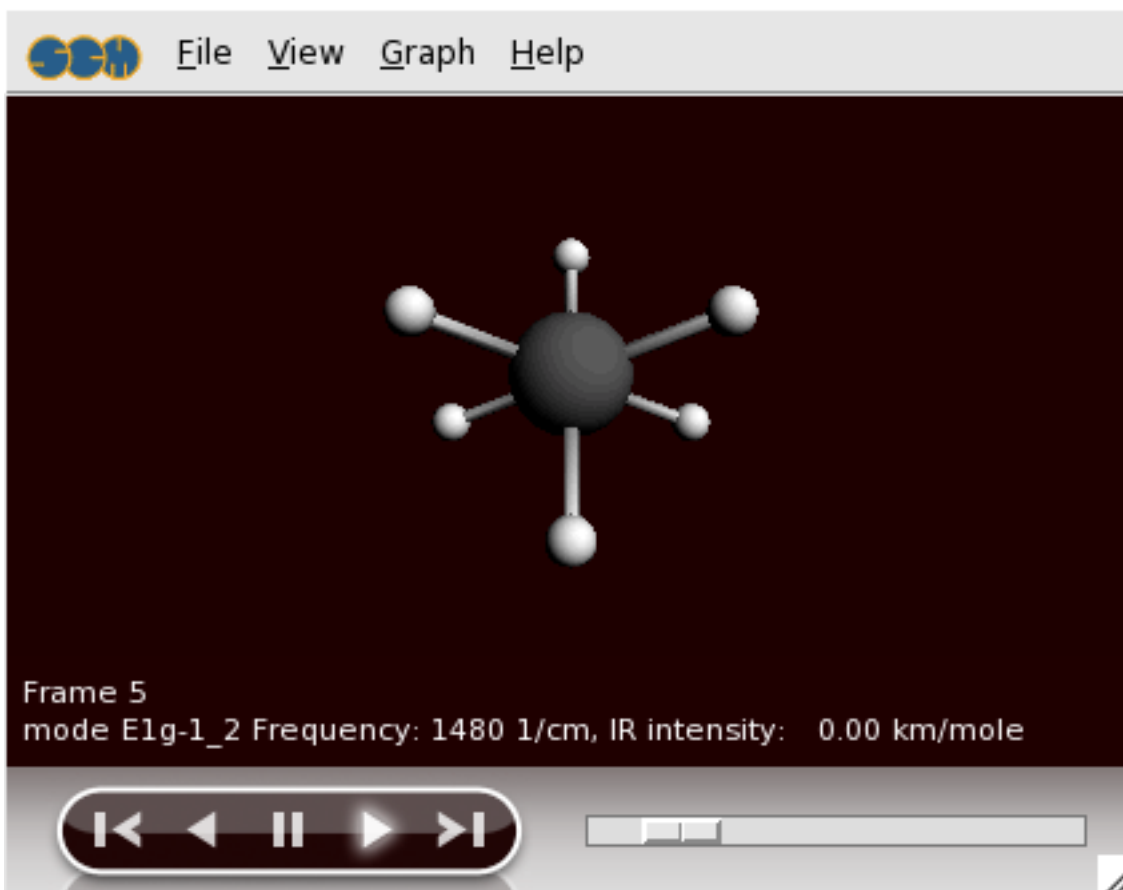
The list of normal modes contributing to the IR peak will show up. By clicking the mouse button at this point, all these modes will be animated, each opened in a separate ADFmovie windows. Alternatively, pressing and holding the mouse button down, a list of these modes with their symmetry labels will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

Press and hold down the mouse on the largest peak



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

Select one of the modes in the pop-up menu



ADFmovie should start and show the corresponding normal mode.

# Advanced ADF-GUI tutorials

## Tutorial 4: Structure Building

First you will build an ethanol molecule again, but this time using structures. As another example, you will build a small peptide chain.

Next, you will learn how to use the predefined metal complex structures.

Finally, you will set up your own structures library.

### Step 1: Start ADFinput

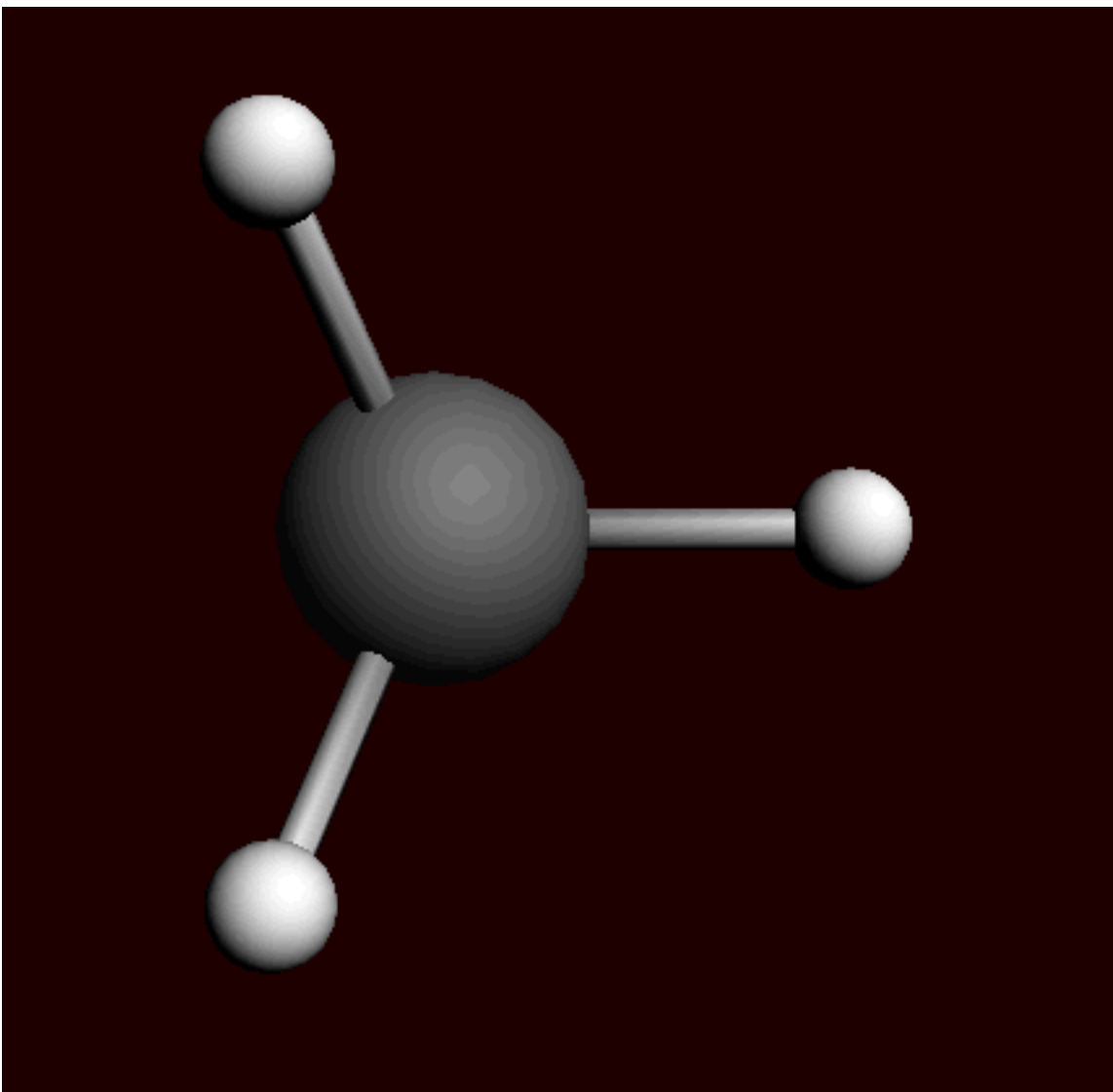
For this tutorial we again prefer to work in the Tutorial directory:

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

### Step 2: Building an ethanol molecule

In the first part of this tutorial you learned how to build an ethanol molecule. Here, we will do this again, but this time using the structures building tool. To start, we first need to build a methane molecule:

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



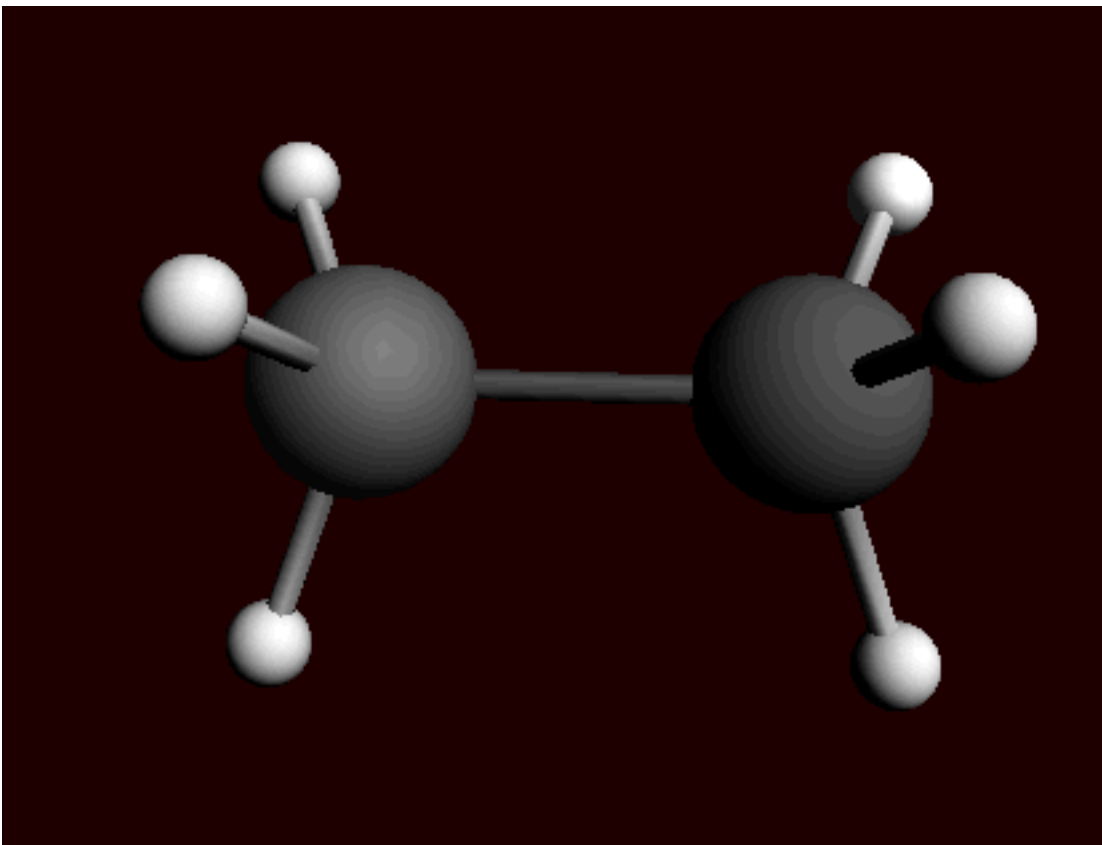
Now, we are ready to start using the structures.

### **Add a methyl group to the methane**

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

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

Double-click on one of the hydrogen atoms



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

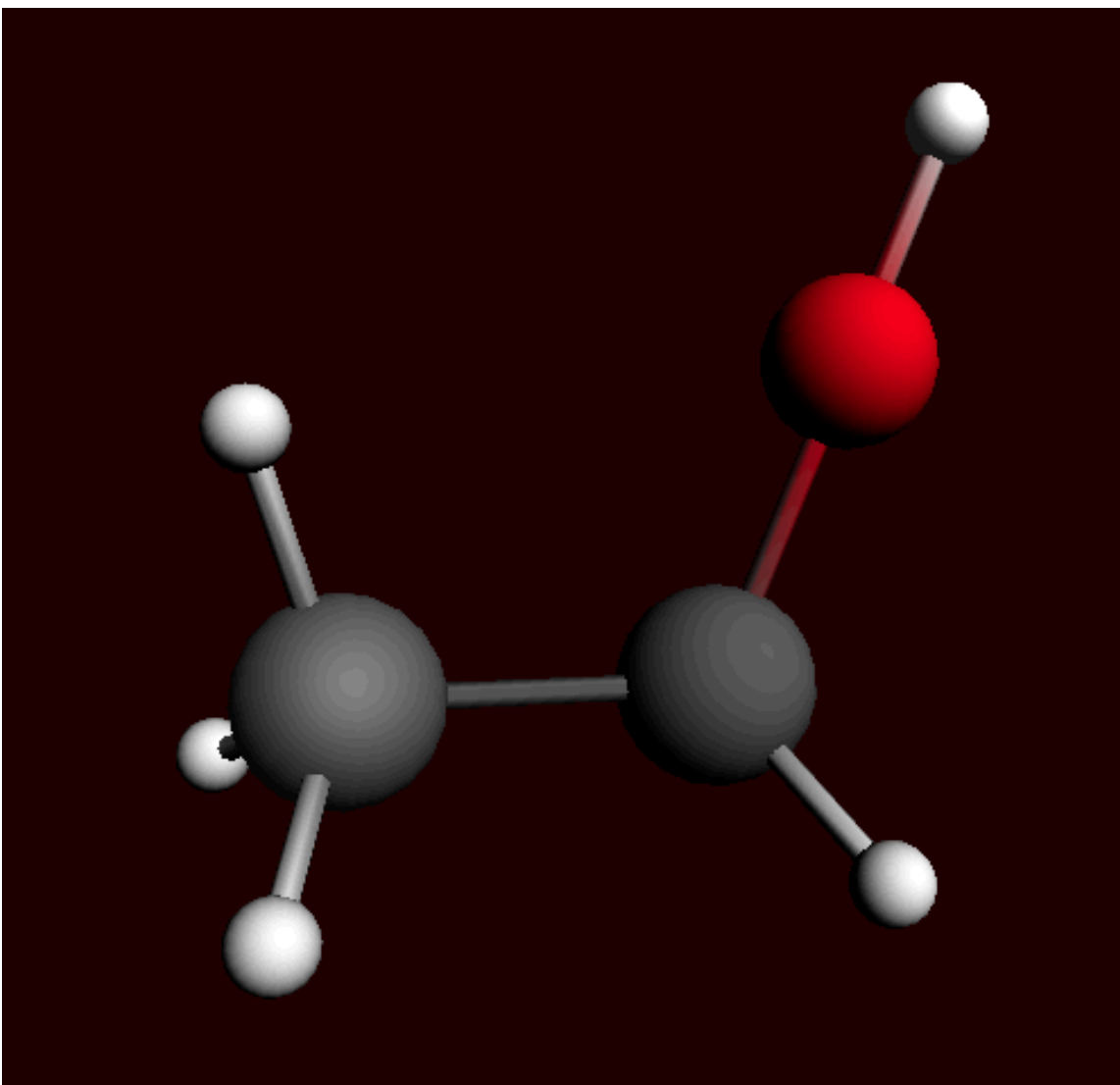
Note that:

- 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.

### Add the 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. Notice that 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:

Click the pre-optimize button

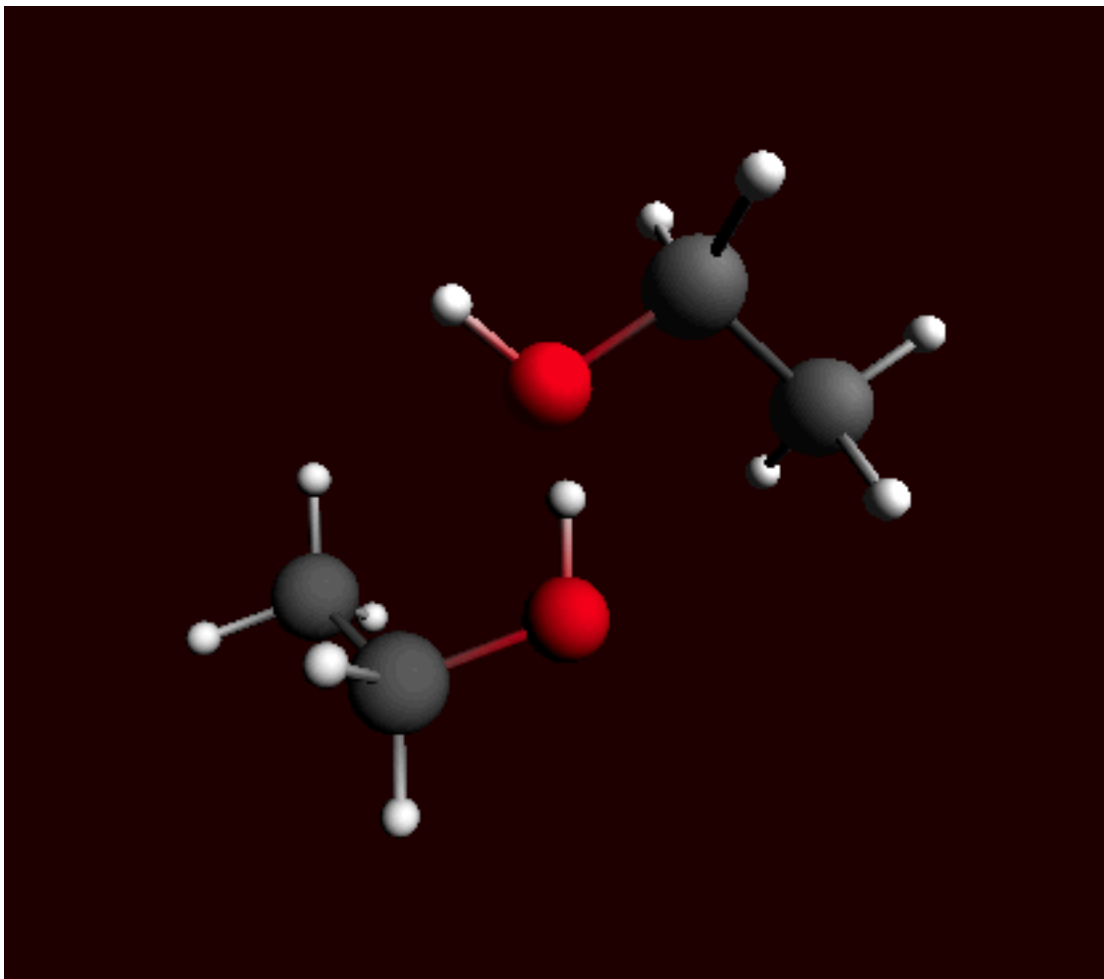
#### **Add another 'solvent' ethanol**

As you might have noticed, ADFinput comes with a number of predefined structures. One of these is the 'Solvent' structure Ethanol. 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  
Use the mouse to rotate the ethanol molecule to your favorite orientation



This way you can easily add explicit solvent molecules.

### Step 3: Building a peptide chain

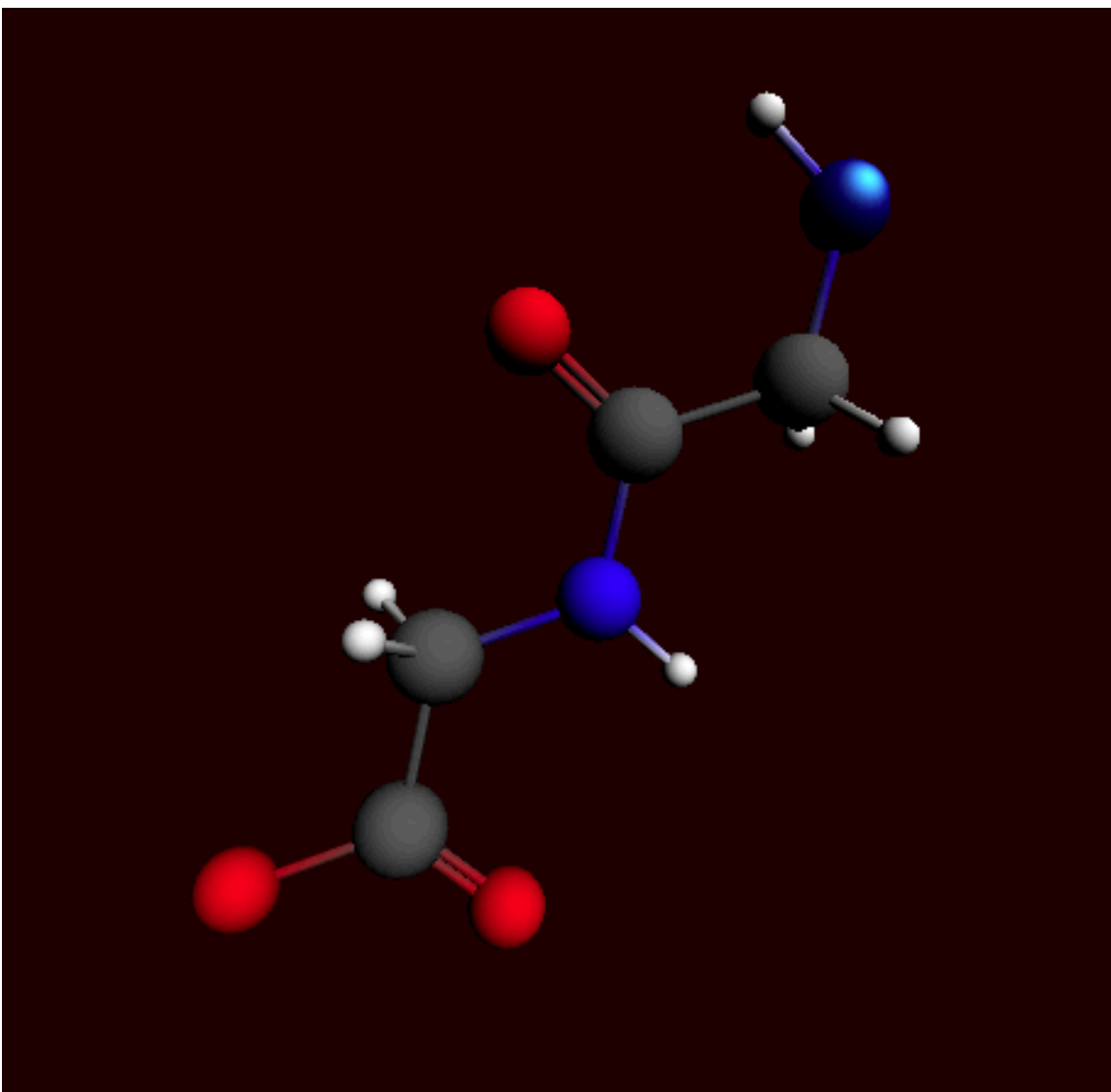
As another example, we will build a small peptide chain.

Select **File** → **New**

Click 'No' as we do not want to save the setup

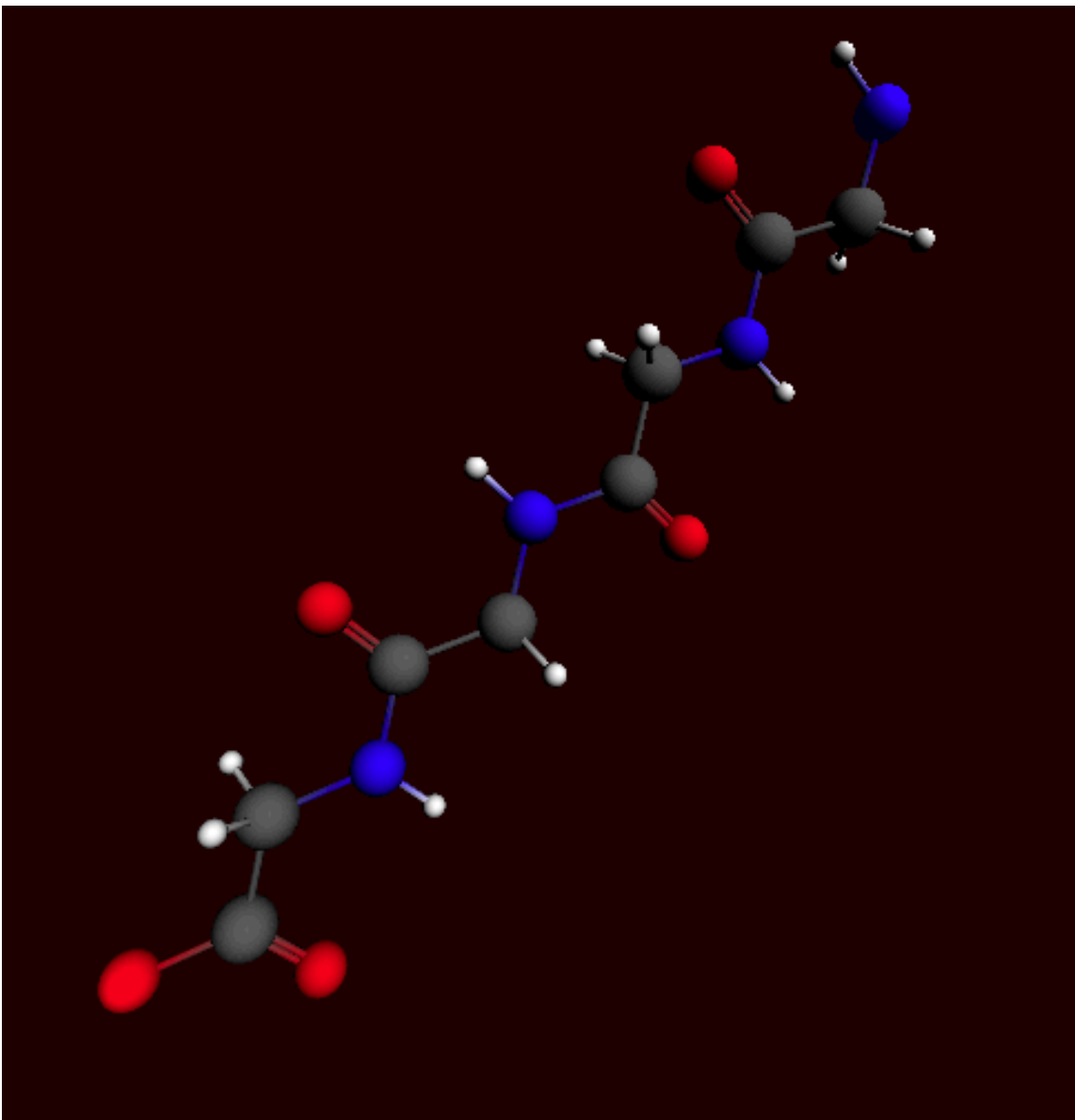
Select the **Structures tool** → **Amino Acids** → **AA Backbone** structure

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.

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**.



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** submenu.

## Step 4: Metal complexes and ligands

In the submenu '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

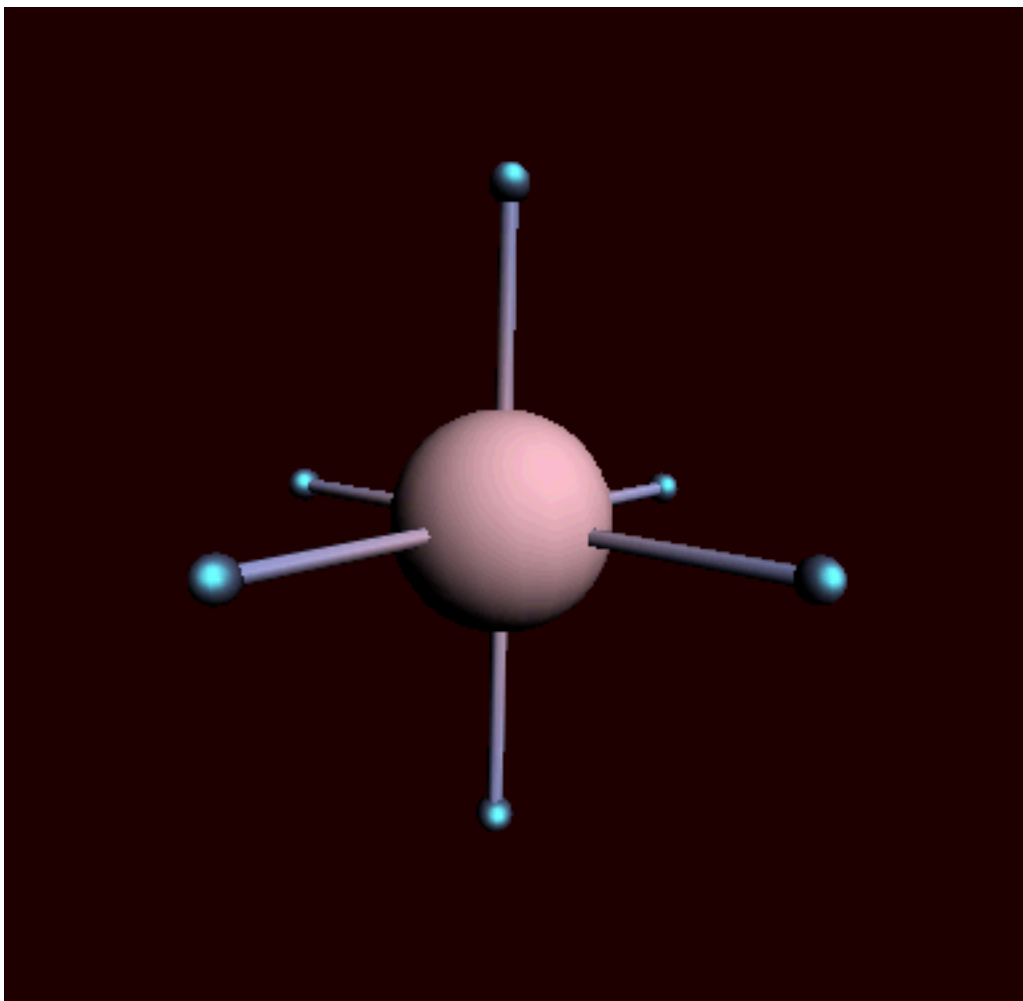
Select the **File** → **New** command  
Click No (do not save changes)

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

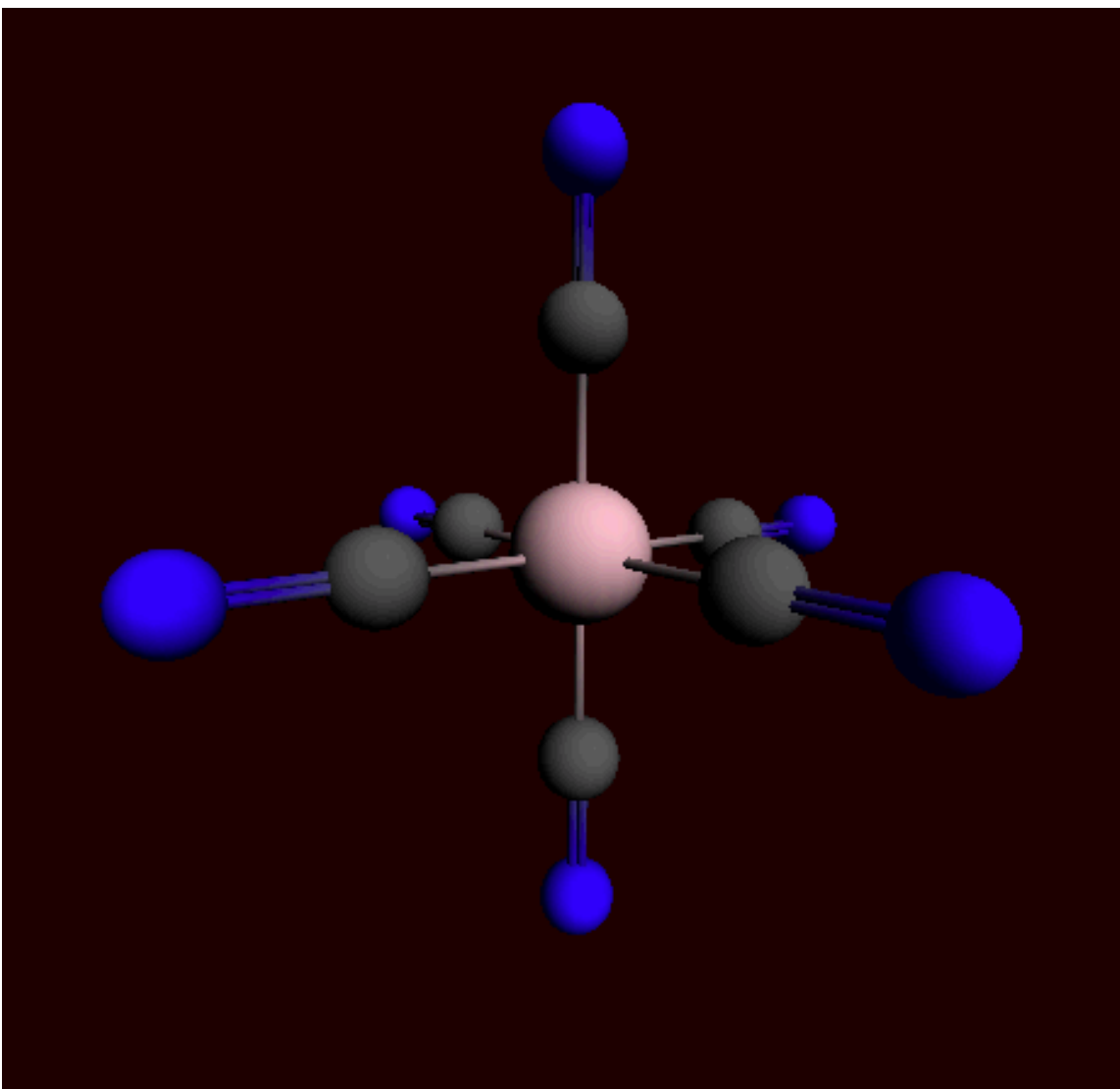
Select **Select** → **Select Atoms Of Same Type** menu command



The Ligands structure submenu 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



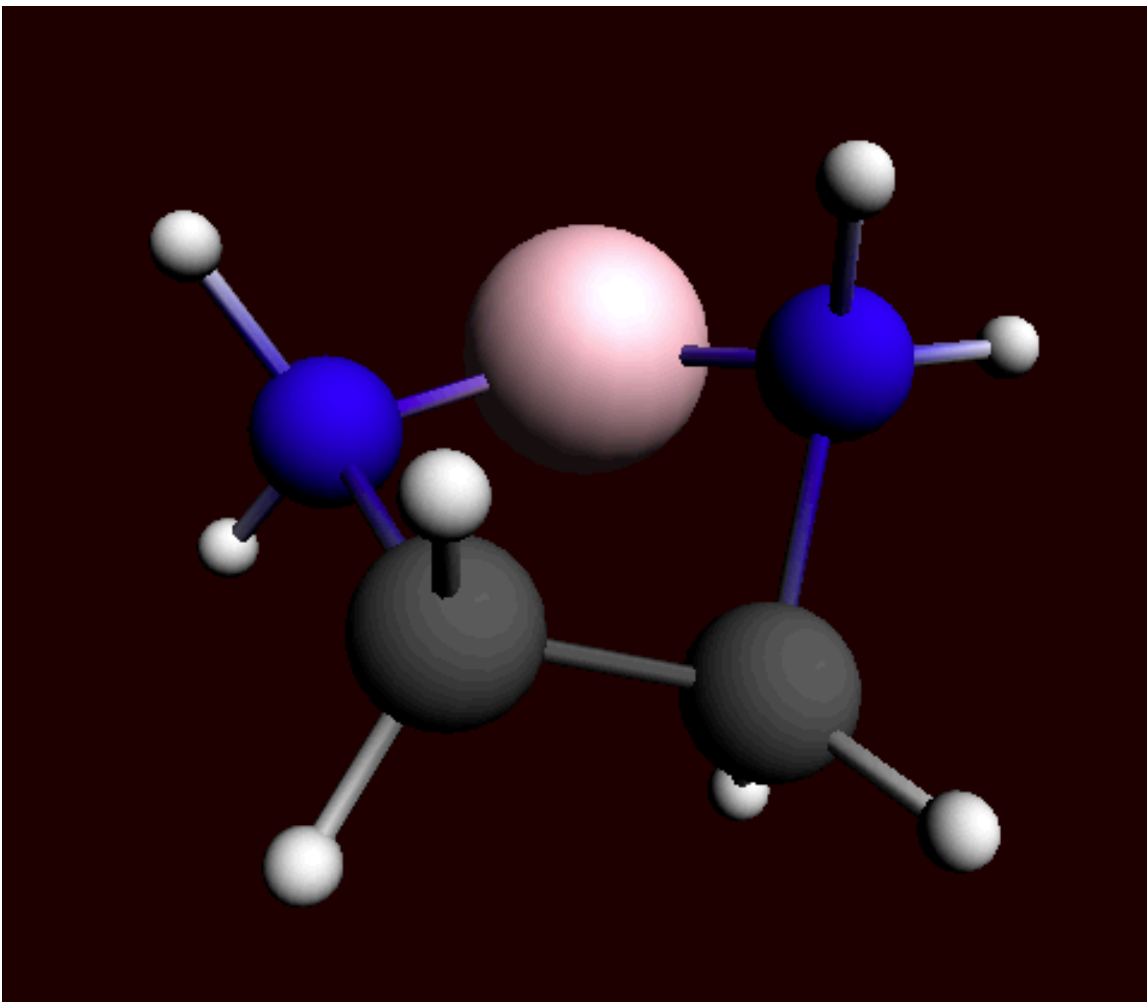
Notice that all dummy atoms in the selection are replaced by CN ligands.

## Bidentate Ligands

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

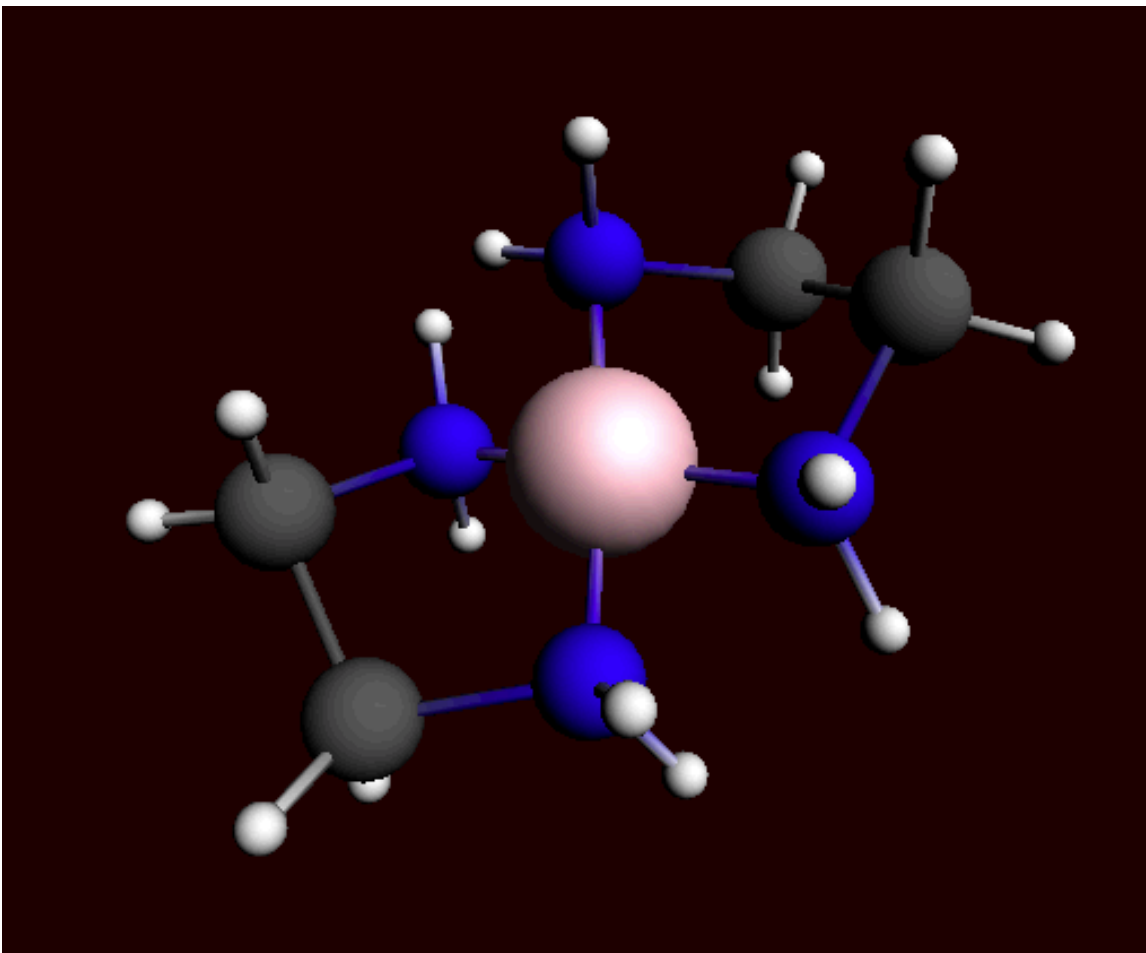
Select the **File** → **New** command  
Click No (do not save changes)

Place an iron atom in the drawing area  
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 spacebar and double-click again on the metal atom



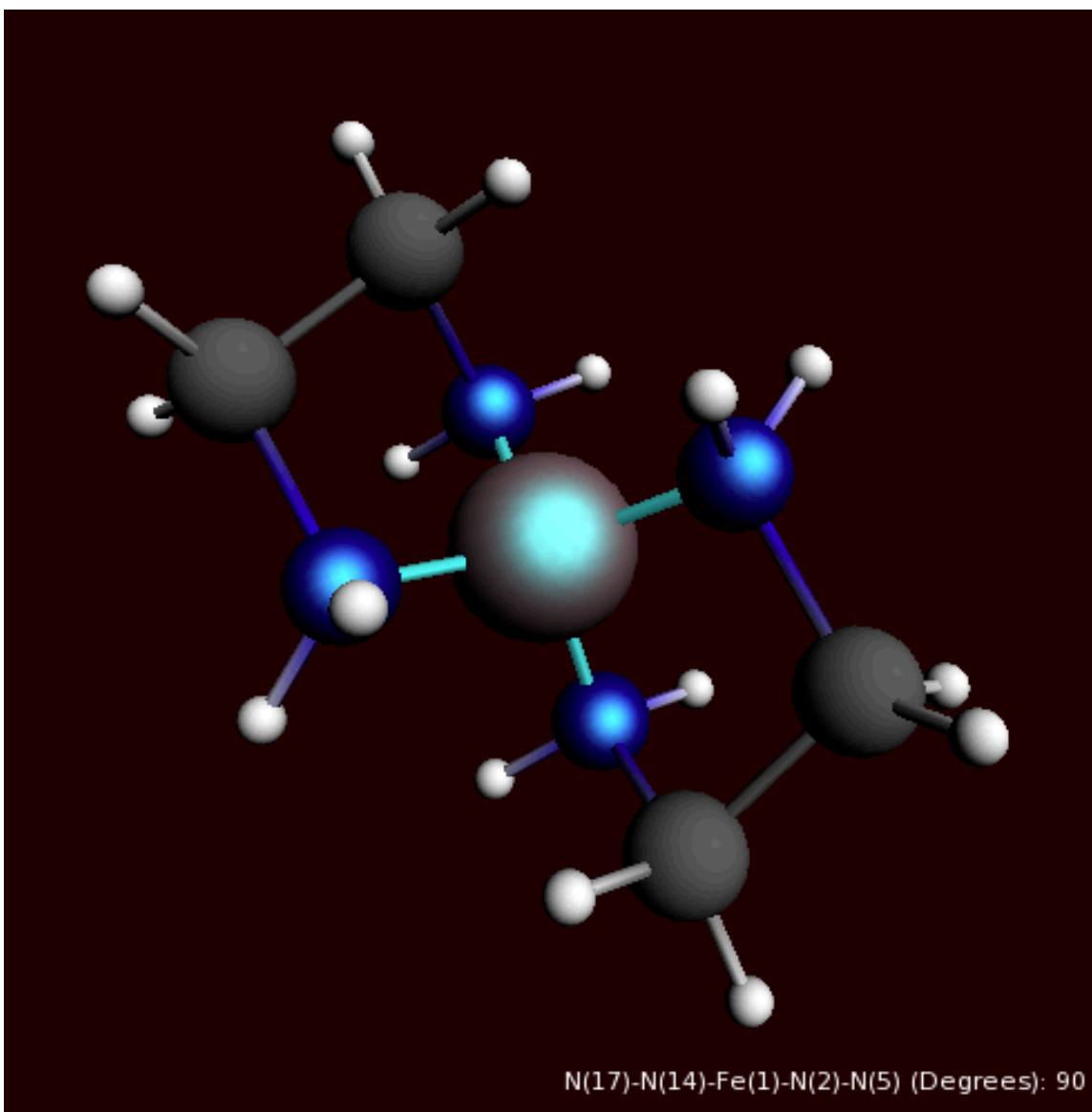
Notice that the second ligand appears opposite the existing one.

### 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





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 5: Your own structures library

You can make your own structure library very easily. First (before starting ADFinput) define an environment variable 'SCM\_STRUCTURES'. It should point to some directory in which to search for possible structures. When you start ADFinput, the \$SCM\_STRUCTURES directory INCLUDING all subdirectories will be searched for structures. A structure is stored in an .adf file, you can just use any .adf file that you have created yourself.

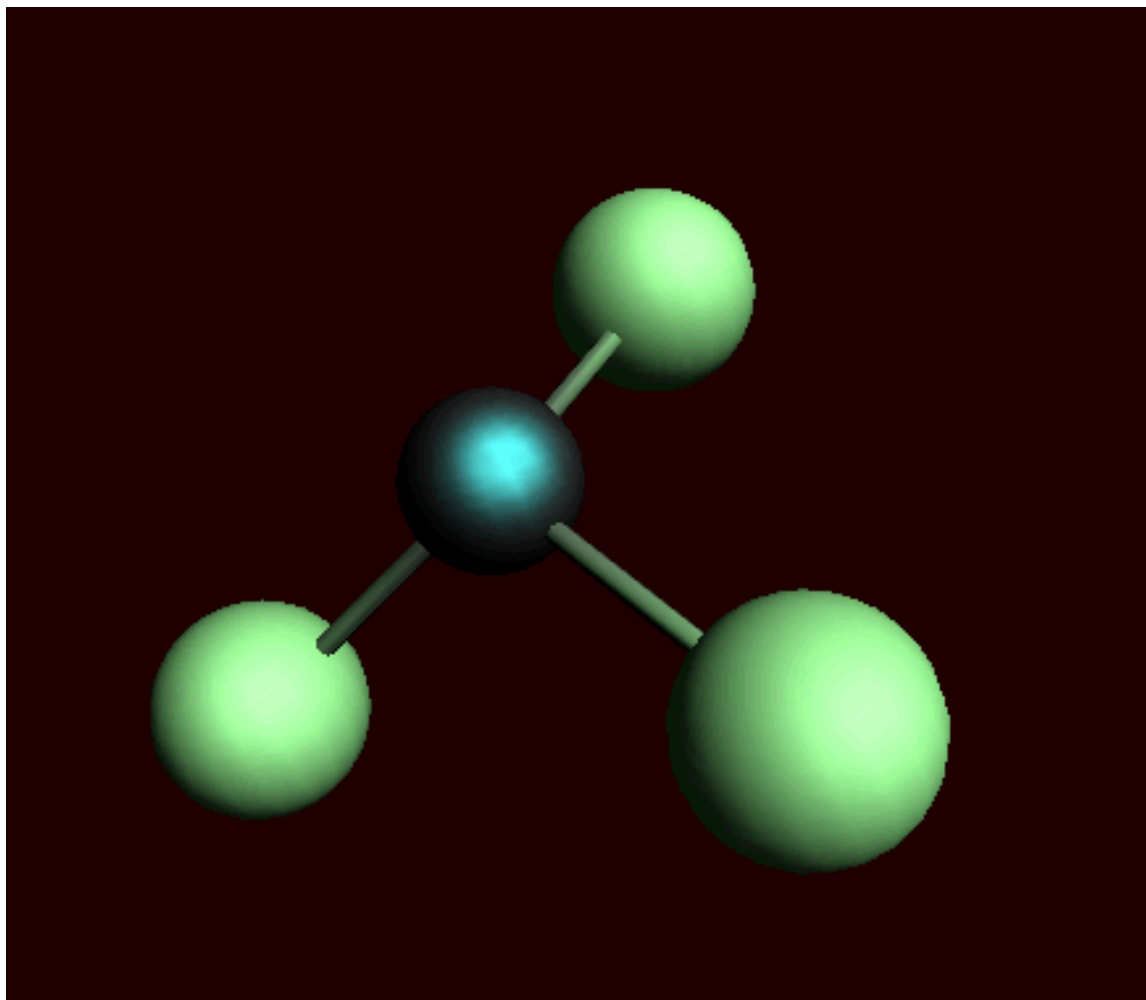
You can define this environment variable in your shell startup scripts, or you can use the Environment panel in the GUIprefs module.

## 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.

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

Place a 'Methyl' structure in the drawing area  
Replace the hydrogen atoms by chloride atoms and pre-optimize  
Select the central carbon atom  
Choose **Edit** → **Set Origin**  
Save the structure in (a subdirectory of) your \$SCM\_STRUCTURES directory



The new structure will 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.

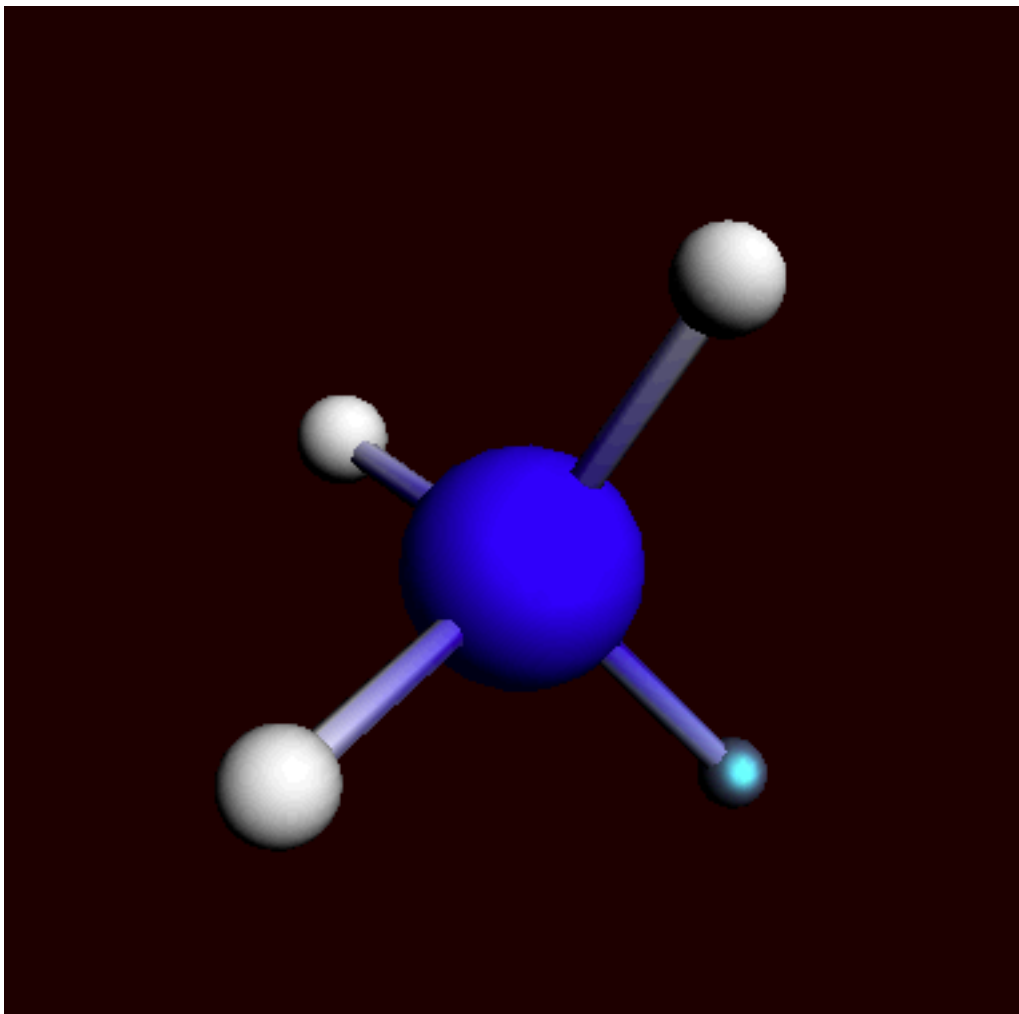
Build a methane molecule

Replace the carbon atom by a nitrogen atom

Select one of the hydrogens and replace it by a dummy atom (the Xx atom type)

Select the dummy atom and choose **Edit** → **Set Origin**

Save the structure in (a subdirectory of) your \$SCM\_STRUCTURES directory



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 NH<sub>3</sub> group is attached to it. Similar behavior has been demonstrated with the bidentate ligands, where the dummy atoms are also used.

## Tutorial 5: HCN Isomerization Reaction

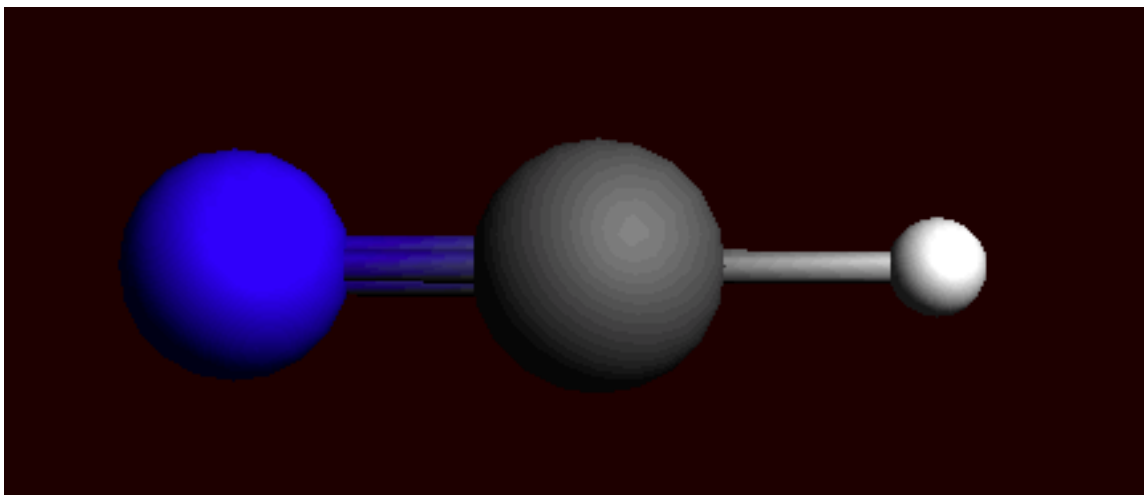
This tutorial consists of several steps to study the isomerization reaction of HCN:

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

### Step 1: Prepare the HCN molecule

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

You should get a linear molecule as shown in Fig 1.



```
Select the "Geometry Optimization" preset
Select the DZP basis set
Save the molecule with the name HCN_GO
Select File → Run
```

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
```

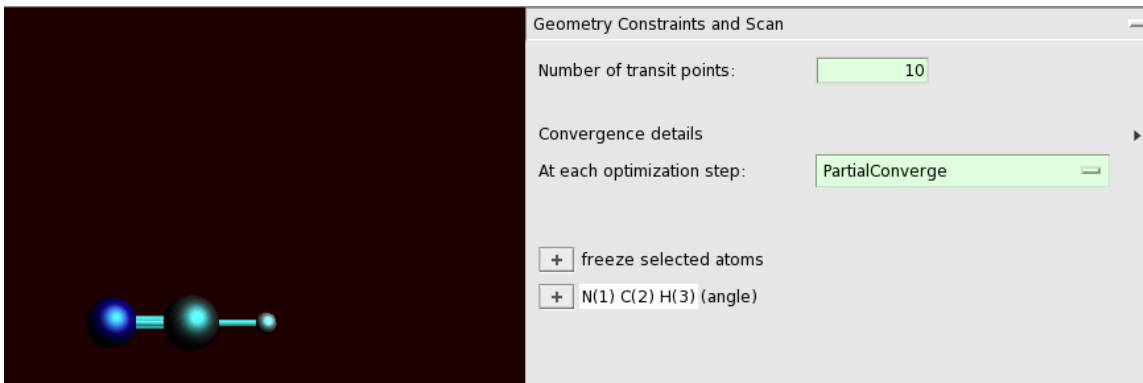
## Step 2: Create a rough approximation for the transition state geometry

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 optimize bond lengths at each angle.

To set up the linear transit calculation:

Select the 'Linear Transit' preset from the 'Main Options' panel  
Now select the 'Geometry Constraints and Scan' panel  
Select all the atoms

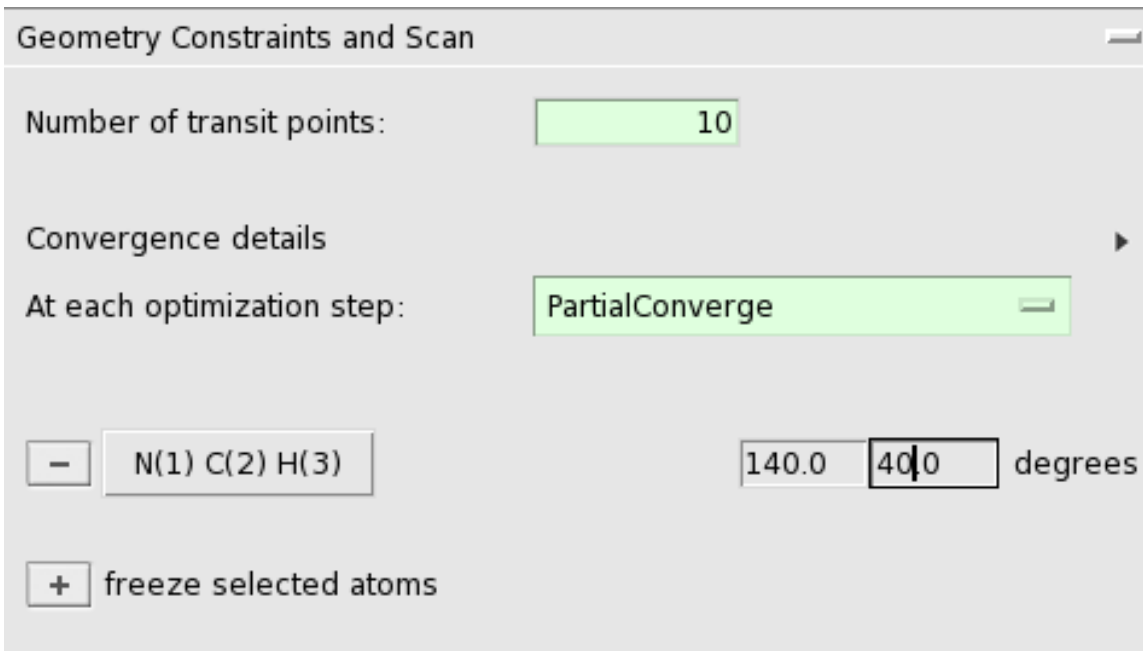
You should see '+ N(1) C(2) H(3) (angle)' note in the right panel now:



Click the '+' sign 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



Before running the calculation, we need to do one more thing: reduce the symmetry. This is necessary because intermediate geometries during the linear transit have lower symmetry than the starting C(lin):

Change the symmetry from AUTO to NOSYM in the 'Symmetry' panel

Symmetry

Molecular symmetry

Symbol: NOSYM

Order of main rotation axis (n): 2

Symmetry tolerance on coordinates:

Symmetric fit for pair distances >:  Angstrom

Use all or symmetry unique points:  All points

Use symmetry in fit:  Yes

The set up is complete. Now we will run the LT calculation:

Save the file with as 'HCN\_LT' (use the **File** → **Save As** command)  
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:

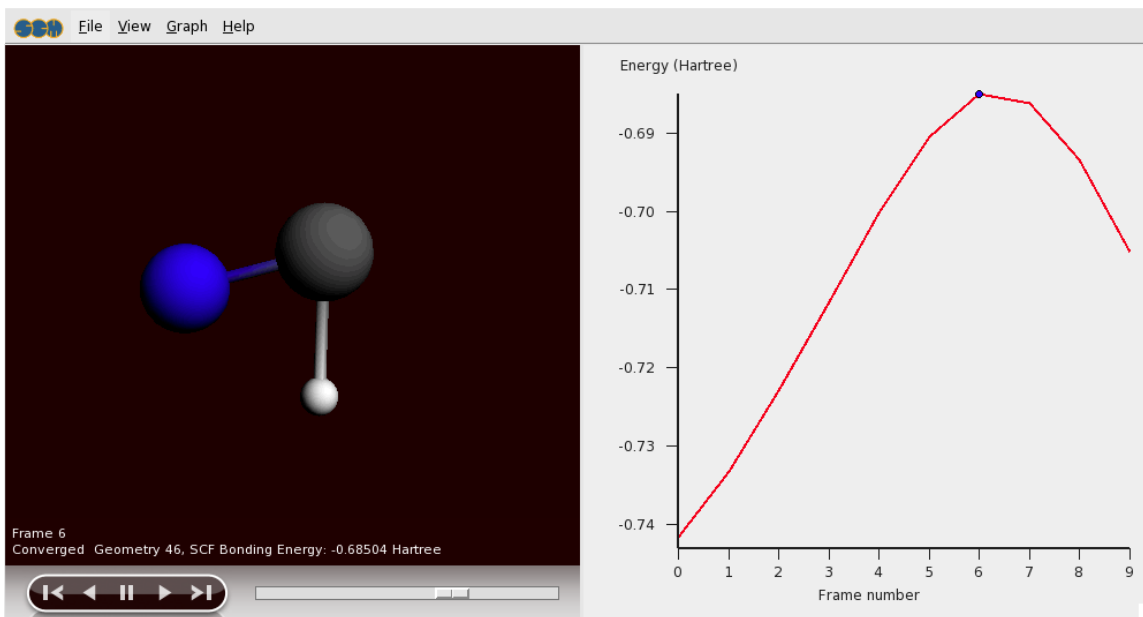
Select the **SCM** → **Movie** command  
Select all atoms (use shift-drag to make a rectangle around the atoms)  
Use the **View** → **Align Screen** command to make sure you can see all atoms  
Click somewhere in empty space to deselect the atoms  
Select the **Graph** → **Energy** command  
Use the **View** → **Converged Geometries Only** command

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. Note 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  
Note which geometry has the maximum energy

You should find that at about 60 degree angle the maximum energy is reached. This is Frame 6 (the 7th LT step), see figure:



You can see it more clearly in the output file:

Select the **SCM** → **Output** menu command

In the ADFoutput window select the **Other Properties** → **'LT Path** command

[Energy \(hartree\) and Dipole \(debye\)](#)

	1	2	3	4	5	6	7	8	9	10
Energy	-0.742	-0.733	-0.723	-0.712	-0.700	-0.690	-0.685	-0.686	-0.693	-0.705
Dipole x	2.684	2.447	2.151	1.804	1.412	0.994	0.600	0.310	0.116	-0.285
y	-0.421	-0.516	-0.598	-0.662	-0.708	-0.746	-0.785	-0.839	-0.975	-1.253
z	0.389	0.490	0.576	0.646	0.699	0.742	0.787	0.846	0.986	1.274
size	2.744	2.548	2.306	2.028	1.727	1.447	1.263	1.232	1.392	1.810

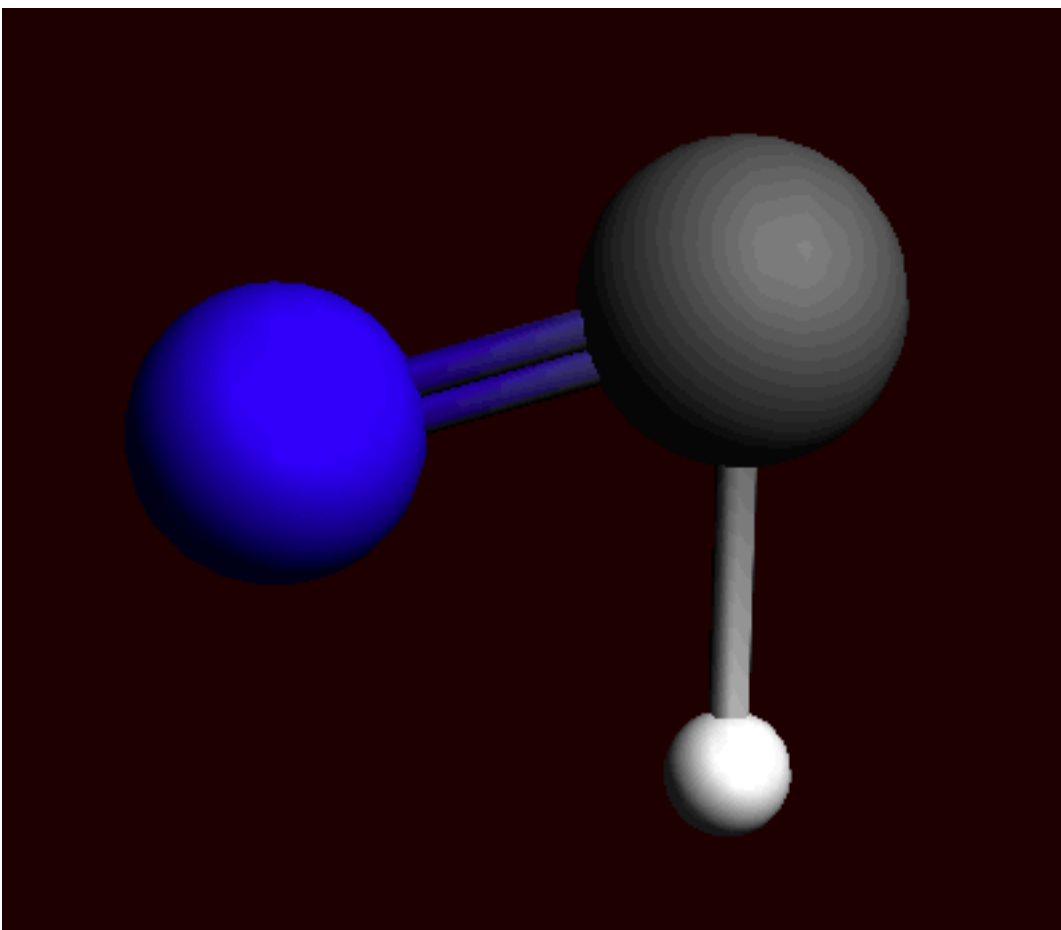
You will see that indeed the geometry number 7 (corresponding to Frame 6 in ADFmovie) has the highest energy. In this particular example the choice of the angle is not very important, but in general you will always want to choose the best approximation for the transition state available.

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

Make sure frame 6 is selected in ADFmovie

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

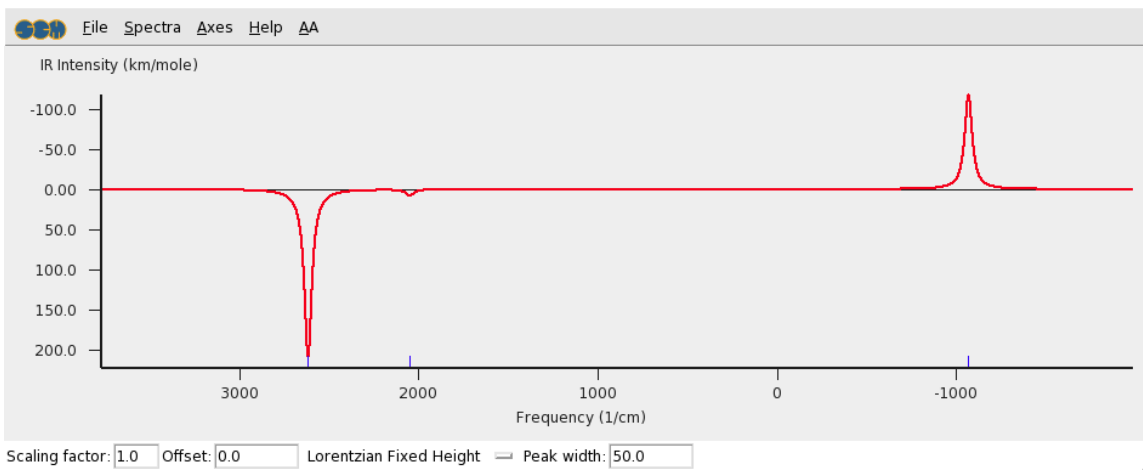
It is important to have a good starting Hessian with one imaginary frequency when performing a TS search. We are going to create such a Hessian by doing a quick frequencies calculation:

```
Select the "Frequencies" preset (from the 'Main' panel)
Set the integration accuracy to 4.0
Change the symmetry back to AUTO
Select the 'Geometry Constraints and Scan' panel
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 1/cm and one peak in the range of negative or very low positive values. A negative frequency value actually means that it is an imaginary frequency.

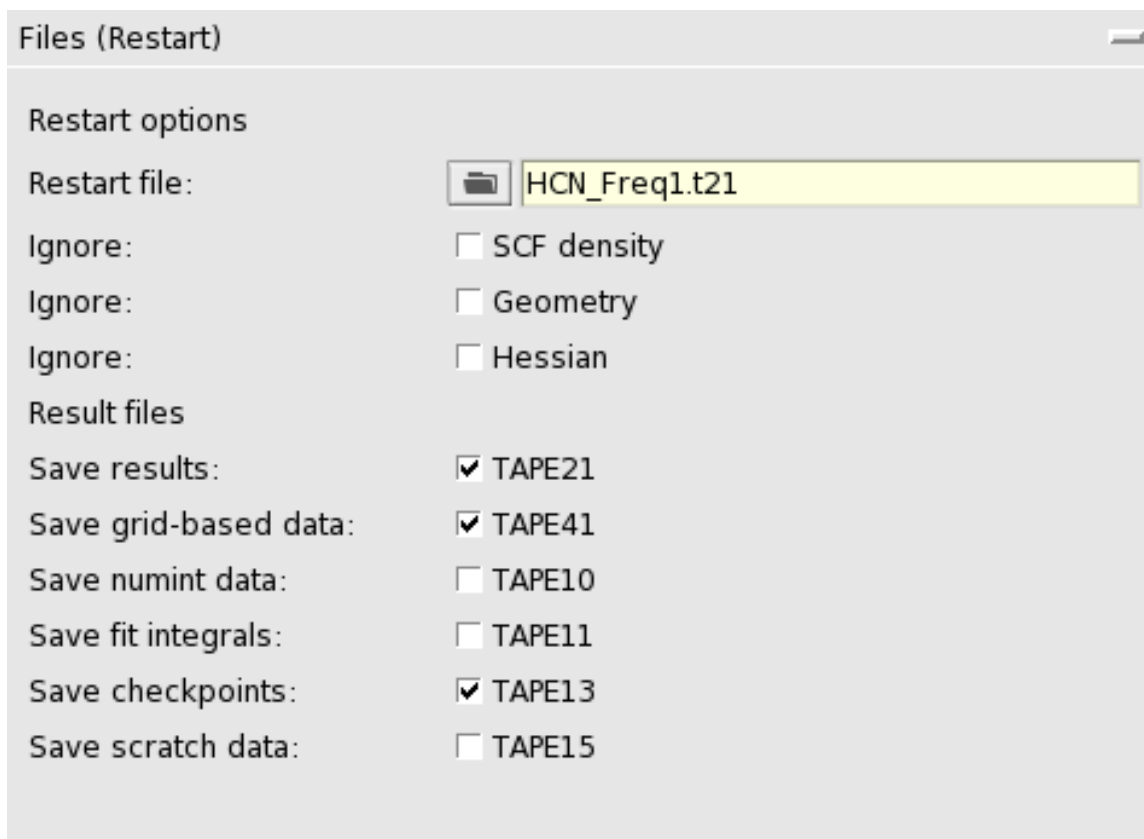
Click with your mouse on the peak corresponding to the imaginary frequency

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

#### Step 4: Search for the transition state

Now you have a result file, HCN\_Freq1.t21, with an initial geometry for a transition state search. This file 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
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 1.18 Angstrom and the H-C-N angle should be about 70 degrees.

## Step 5: Calculating frequencies at the transition state

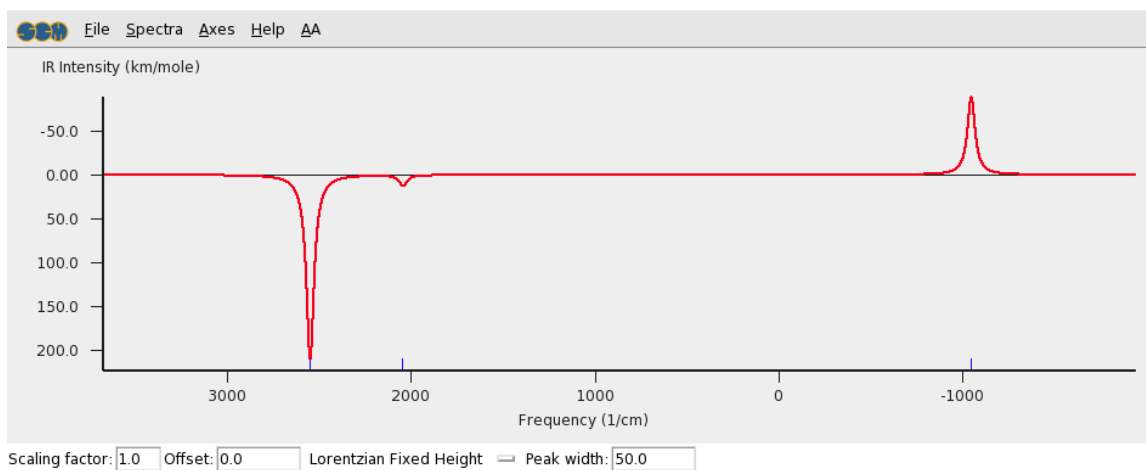
After every transition state search it is wise to verify that you indeed have one and only one imaginary frequency. For this we will repeat the frequency calculation at the TS geometry:

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

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

## Step 6: Following the reaction coordinate

ADF can follow the minimum-energy path from the transition state to one or the other product. The method used in ADF for this is called Intrinsic Reaction Coordinate (IRC). This tutorial step is optional because it might take some time to complete.

```
Bring HCN_Freq2 in ADFinput to the front
Select the "IRC" preset
Go to the 'Task: IRC panel'
```

The 'Task: IRC' panel, on the right-hand side, 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, thus we do not need to change the default.

```
Type 'HCN_IRC' in the 'Title:' field of the 'Main Options' panel
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
```

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

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

Select **SCM** → **Output**

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.

## Tutorial 6: 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

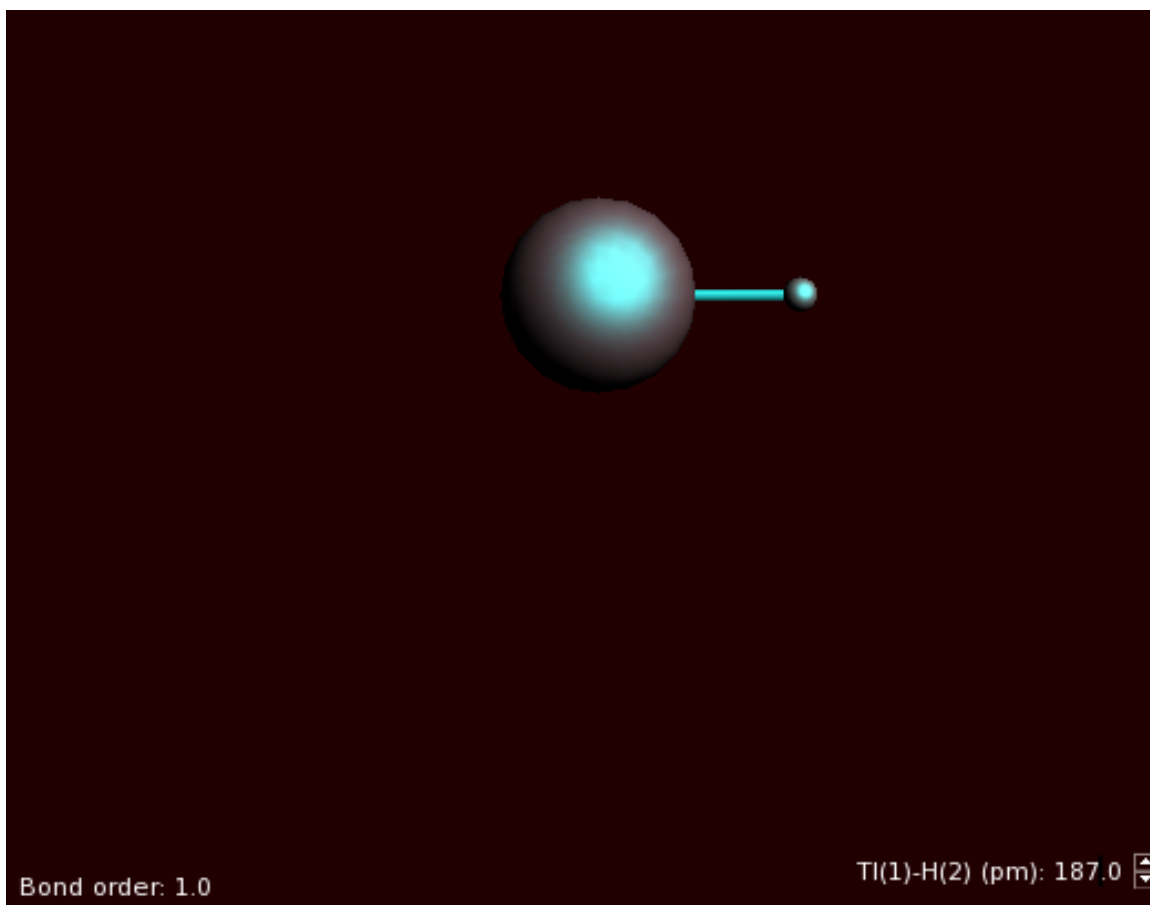
First create a TIH (thallium hydride) molecule with a bond length of 1.87 Angstrom (the experimental bond length):

Open ADFinput and draw a TIH molecule.

Select the Tl and H atoms

Set the distance between the atoms 1.87 Angstrom

(use the distance input field below the molecule)



## Step 2: Set calculation options

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

Set the title to 'TlH spin-orbit coupled'  
Select 'GGA:BP' from the 'xc potential in SCF' menu  
Select 'Spin-Orbit' from 'Level of relativistic theory' menu  
Select the basis set 'TZ2P' from the 'Basis Set' Menu  
Select the core type 'None' from the 'Core Type' menu

The 'Main Options' Menu will now look like:

**Main Options**

Title:

Preset:

Task:

Total charge:

Spin polarization:

Unrestricted:  Yes

XC potential in SCF:

XC energy after SCF:

Relativity (ZORA):

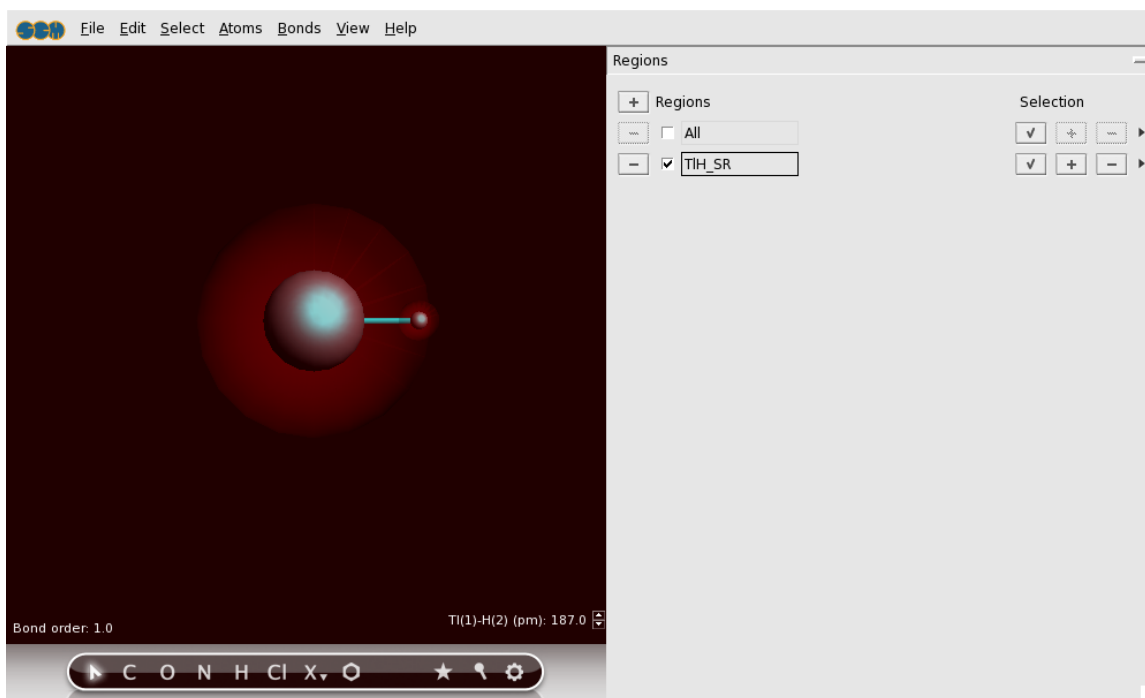
Basis set:

Core type:

Integration accuracy:

We are going to perform a fragment analysis. This will allow us to compare the scalar relativistic results with the spin-orbit results very easily. To do this we will define the whole molecule as one fragment. Just follow the steps, in another tutorial many more details about fragment calculations will be explained.

Select both atoms  
 Select the 'Regions' panel  
 Click the '+' button  
 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.

Select the 'Fragments' panel  
Click the 'Use fragments' check box

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

### Step 3: Run your calculation

Use the **File** → **Save** menu command  
Enter the name 'TlH\_SO' in the 'File name' field  
Click 'Save'

Now you have saved your current options and molecule information. Since we have set up a fragment calculation, also the .adf and .run files for the fragment have been saved. Just to be sure what the fragment will look like, lets check it 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 'TIH\_SO.TIH\_SR.adf'. This is the name of the fragment. You can verify that the fragment has the 'Scalar' relativistic option selected, which is required if the results will be used as a fragment. You could also make changes here, but in this example no changes are required. We will use the fragment as it has been generated by ADFinput automatically, so close this ADFinput window:

Select the ADFinput window with the name 'TlH\_SO.TlH\_SR.adf'.  
Select **File** → **Quit**

Now we want to actually perform the calculation, both for the fragment and the whole molecule.

Select the ADFinput window with the name 'TlH\_SO.adf'.  
Select **File** → **Run**

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

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

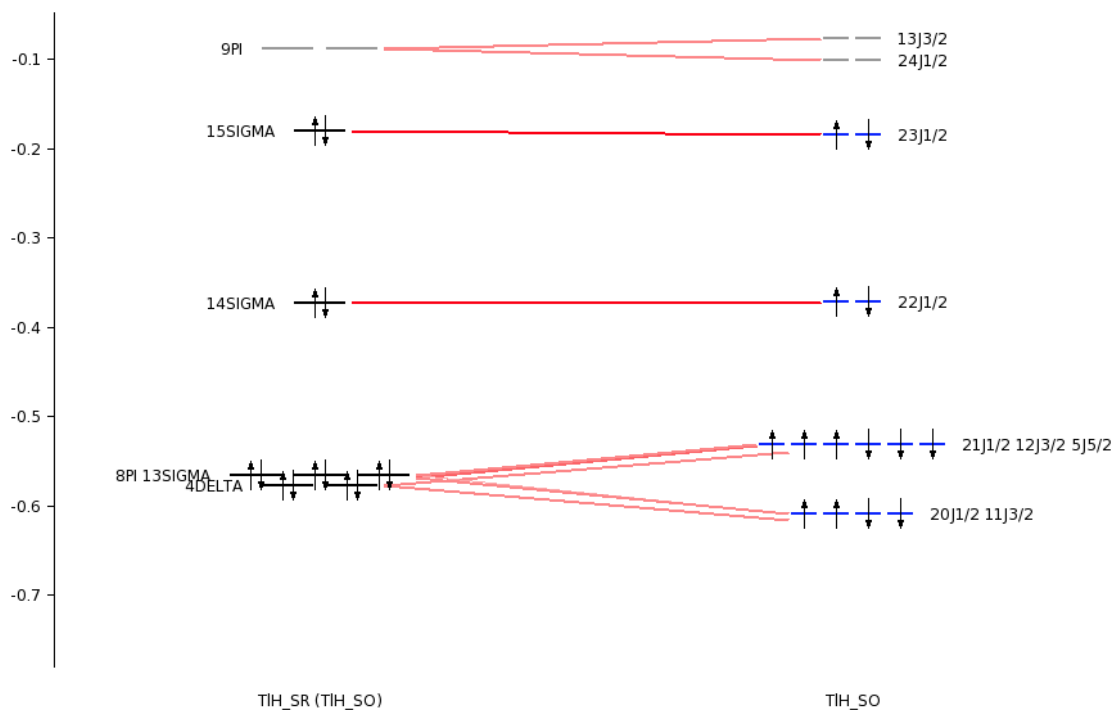
## Step 4: Results of the calculation

### TIH energy diagram

Select the ADFinput window with the name 'TlH\_SO.adf'.  
Select **SCM** → **ADFlevels**  
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.





This Figure shows that the first-order 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 using ADFview, see also the next paragraph. 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)

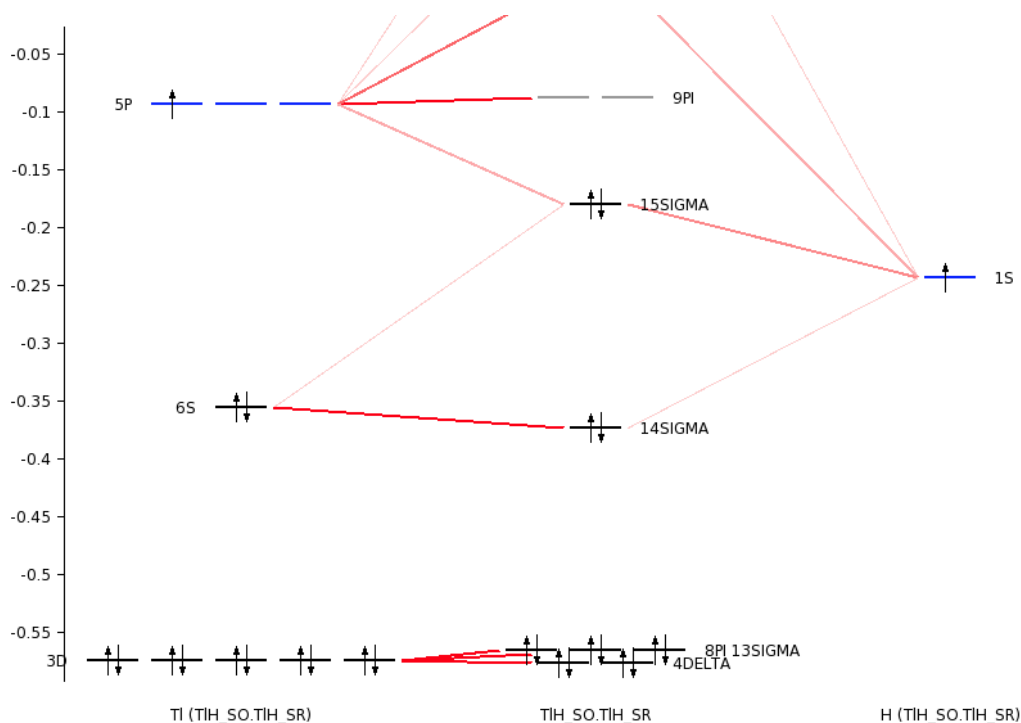
Use the **SCM** → **ADFlevels** command

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 more difficult than visualization of orbitals. A spinor  $\Psi$  is a two-component complex wave function, which can be described with four real functions  $\varphi$ : 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  $\rho$  is:

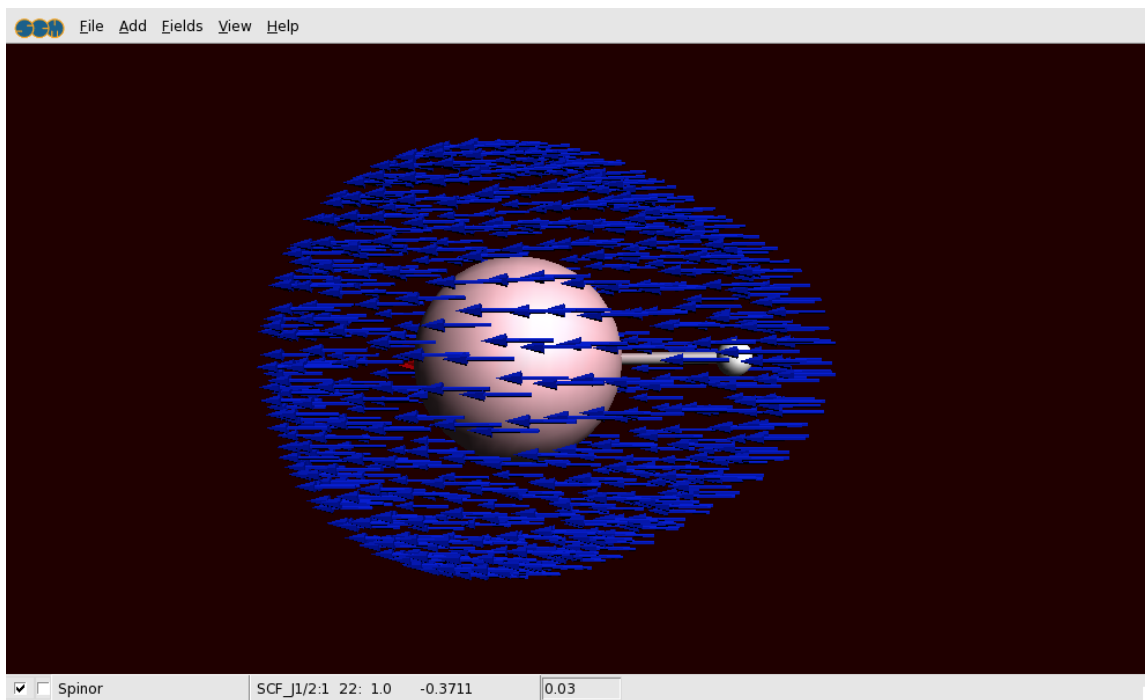
$$\rho = \Psi^\dagger \Psi$$

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 ADF 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 small molecule 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, press on the 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 j1/2 spinor is almost a pure  $\alpha$  orbital. The arrows are drawn starting from points in space where the square root of square root of the density is 0.03. The color of the arrows are default red or blue, indicating minus or plus for the phase factor  $e^{i\theta}$ .

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

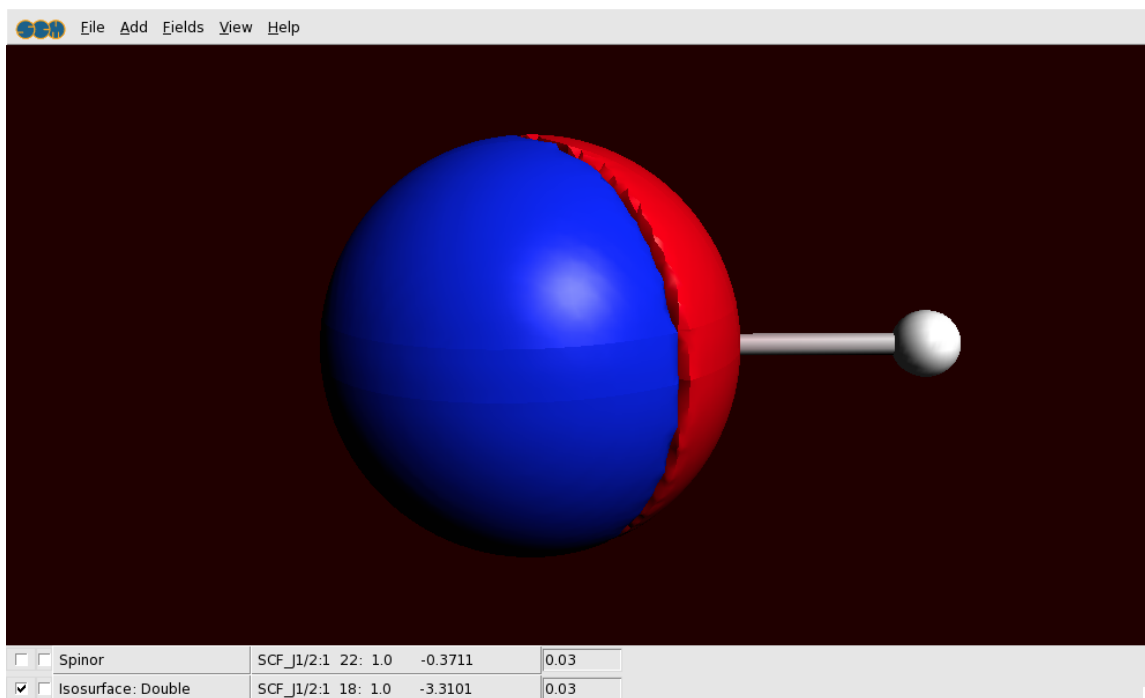
Select **Add** → **'Isosurface: Double (+/-)'**

In the new control line, press on the pull-down menu and

Select **Orbitals (occupied)** → **3** → **'SCF\_J1/2:1 18: 1.0 ..'**

**Deselect View** → **Molecule Ball & Sticks** → **Sticks**

In the control line with 'Spinor' uncheck the check box at the left end of this line



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.

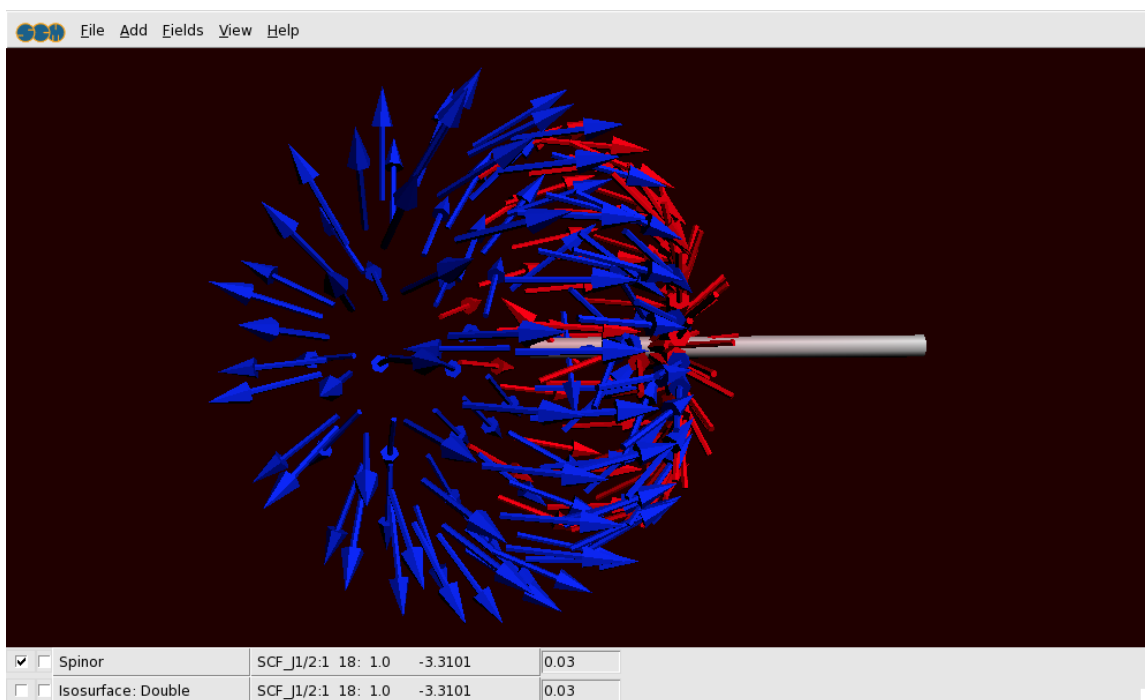
In the control line with 'Spinor', press on the pull-down menu and

Select **Orbitals (occupied)** → **3** → **SCF\_J1/2:1 18: 1.0 ...**

Show the 'Spinor' (check the left checkbox for the spinor line)

Hide the 'Double Isosurface' (uncheck the left check box for the double iso line)

Hide the atoms: **View** → **Molecule Ball&Sticks** → **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 TlH\_SO.adf file and change this to an atomic file.

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

Select the ADFinput window with the name 'TlH\_SO.adf'.  
Delete the H atom (select it and press the backspace key).  
Select the 'Fragments' poanel  
Uncheck the 'Use fragments' option  
Select the 'Regions' panel  
Remove the TlH\_SR region (click on the - button in front of it)  
Select 'Main Options' panel  
Select the preset 'Single Point' in the 'Preset' menu.  
Enter the name 'Tl spin-orbit coupled' in the 'Title' Menu'.  
Check the 'Unrestricted:' box.  
Select the Relativity panel, and then select 'Spin-Orbit' in the 'Relativity:' field there.  
Select 'NonCollinear' from the 'Unrestricted Options' Menu.  
Select **File** → **Save As**  
Enter the name 'Tl\_SO' in the 'File Name' field.  
Click on 'Save'.

Relativity

Relativity (ZORA): Spin-Orbit

Nuclear model: PointCharge

Spin-orbit details

Unrestricted options:  Collinear  NonCollinear

Spin-polarization axis: Z

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

Run the calculation.

Wait until ADFtail shows 'Job ... has finished' as last line

In the window showing the logfile (the ADFtail window Tl\_SO.logfile):

Select **File** → **Quit**

## The H atom

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

Select the ADFinput window with the name 'Tl\_SO.adf'.

Select the 'Main Options' panel.

Enter the name 'H spin-orbit coupled' in the 'Title' Menu'.

Select the Tl atom

Use the **Atoms** → **Change Atom Type** → **H**.

Select **File** → **Save As...**

Enter the name 'H\_SO' in the 'File Name' field.

Click on 'Save'.

Select **File** → **Run**

Wait until ADFtail shows 'Job ... has finished' as last line

In the window showing the logfile (the ADFtail window H\_SO.logfile):

Select **File** → **Quit**

## 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 -1038.60 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 -3.83 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  $-1038.60 - 3.83 + 1039.32 + 0.95 = -2.16$  eV, experimental number is close to  $-2.06$  eV.)

## Tutorial 7: 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 ( $\text{CH}_3\text{COCH}_3$ ) to demonstrate how to use Quild.

### Generate regions

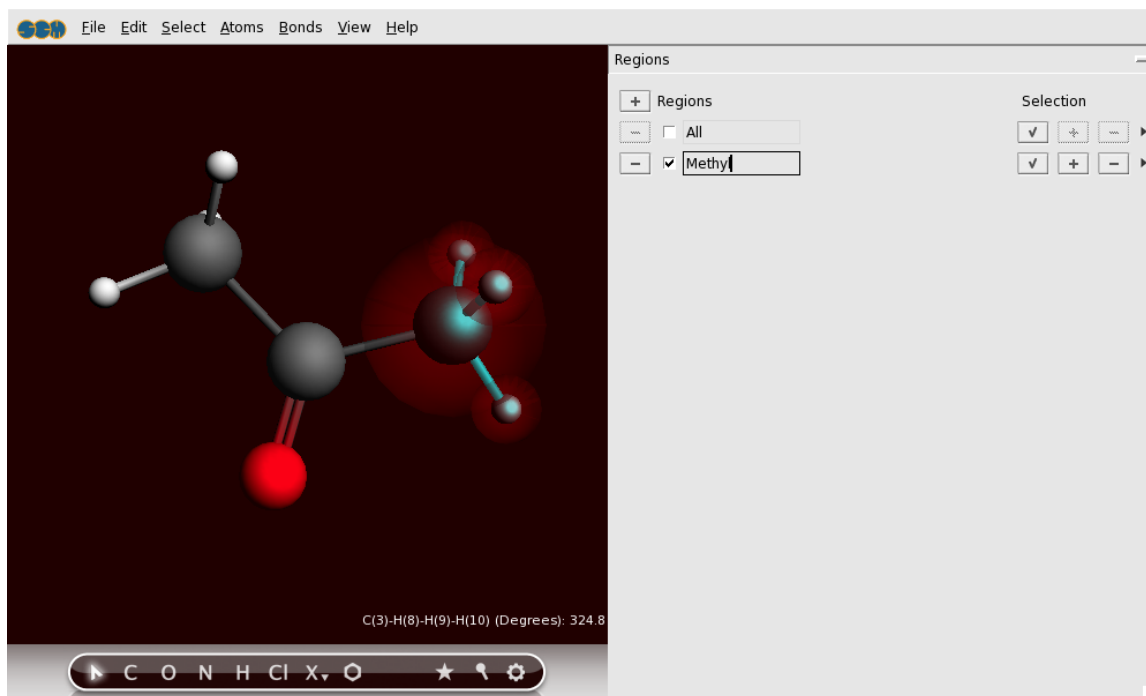
Start ADFinput, and build an Acetone molecule

Select one of the methyl groups

Select the 'Regions' panel

Click on the '+' button to add a new region

Change the name 'Region\_1' into 'Methyl' (the name is editable)



You have just defined a new region, with a name 'Methyl'. In your molecule window you can see what atoms are part of this region: they are enclosed in slightly ghost-like spheres. Note that there are now two regions

define: the region that you defined, and a region called 'All' that is always present. Obviously, the All region includes all atoms.

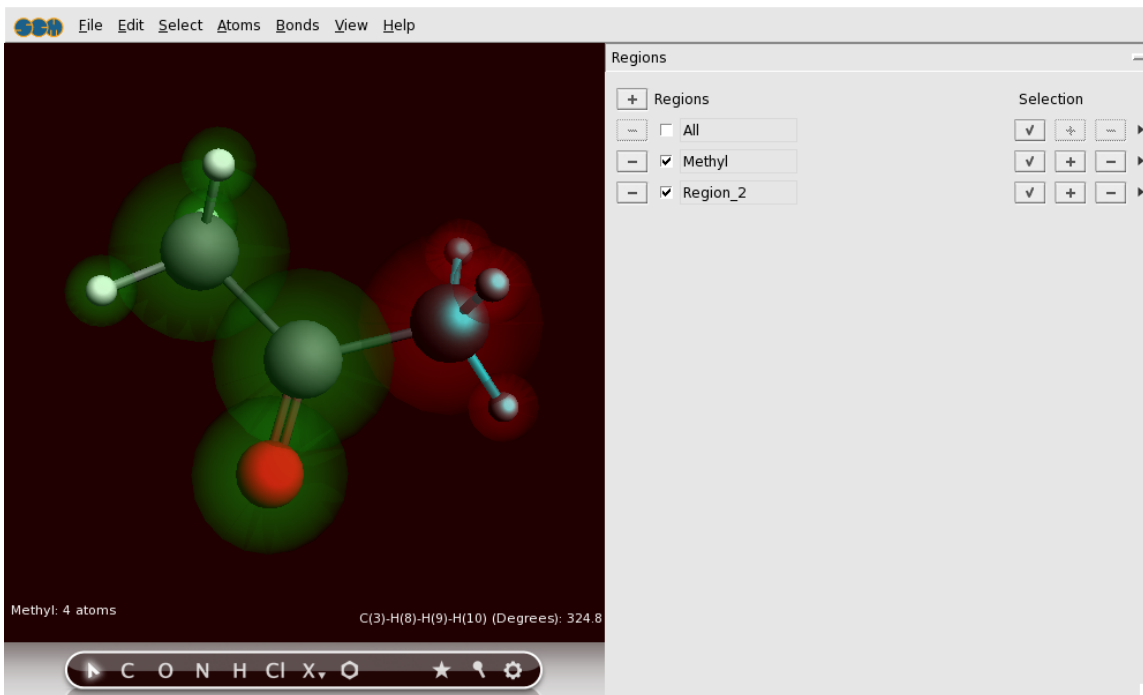
Now we will define yet another region: the rest of the molecule. One way to do this is just to select the atoms that should be part of it, and pressing the '+' button as you did before. However, to demonstrate some of the things you can do with regions we will do it in another way:

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 the check box in front of the 'Methyl' region name to uncheck it

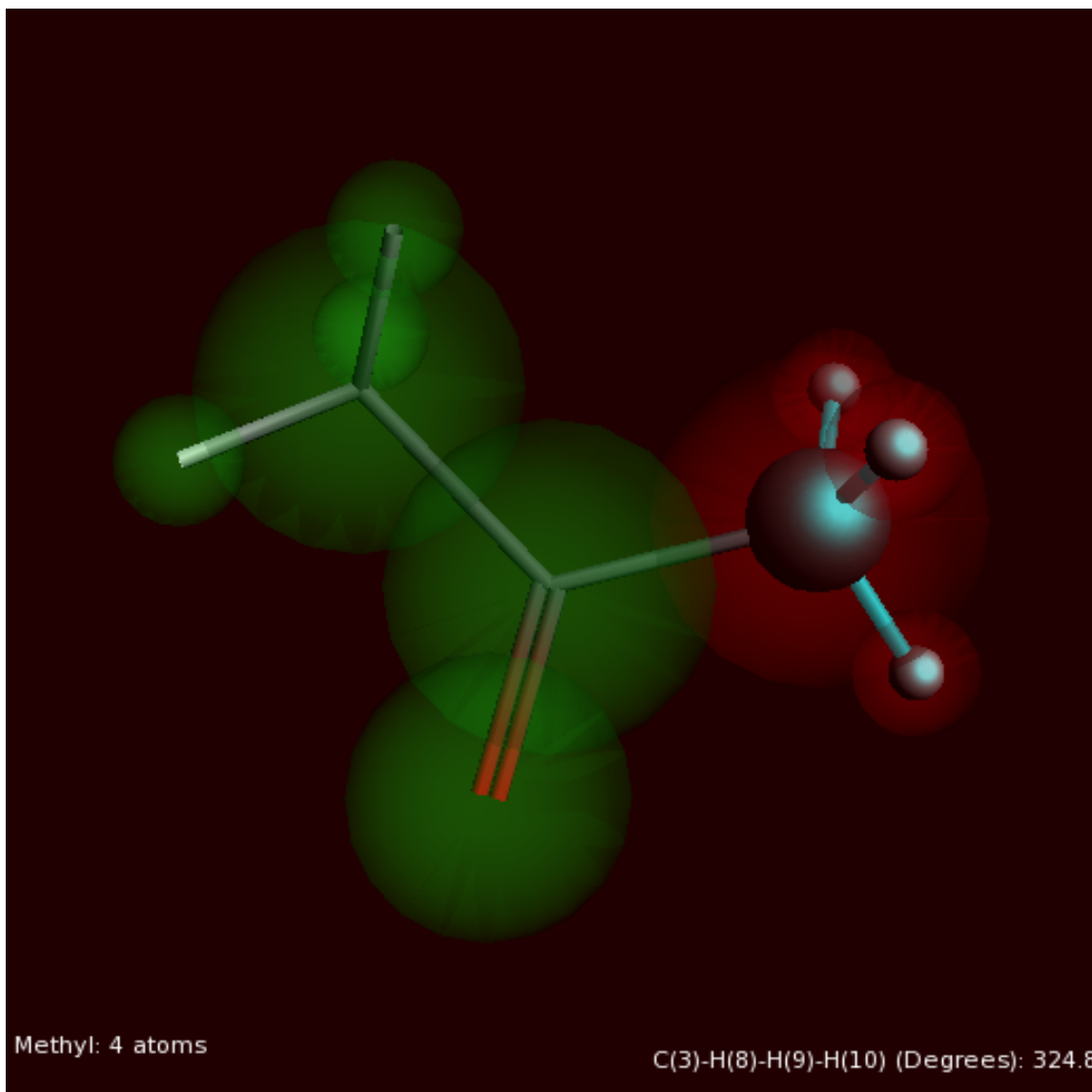
You should observe that the ghost-like region visualization disappears. Please turn it back on:

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:

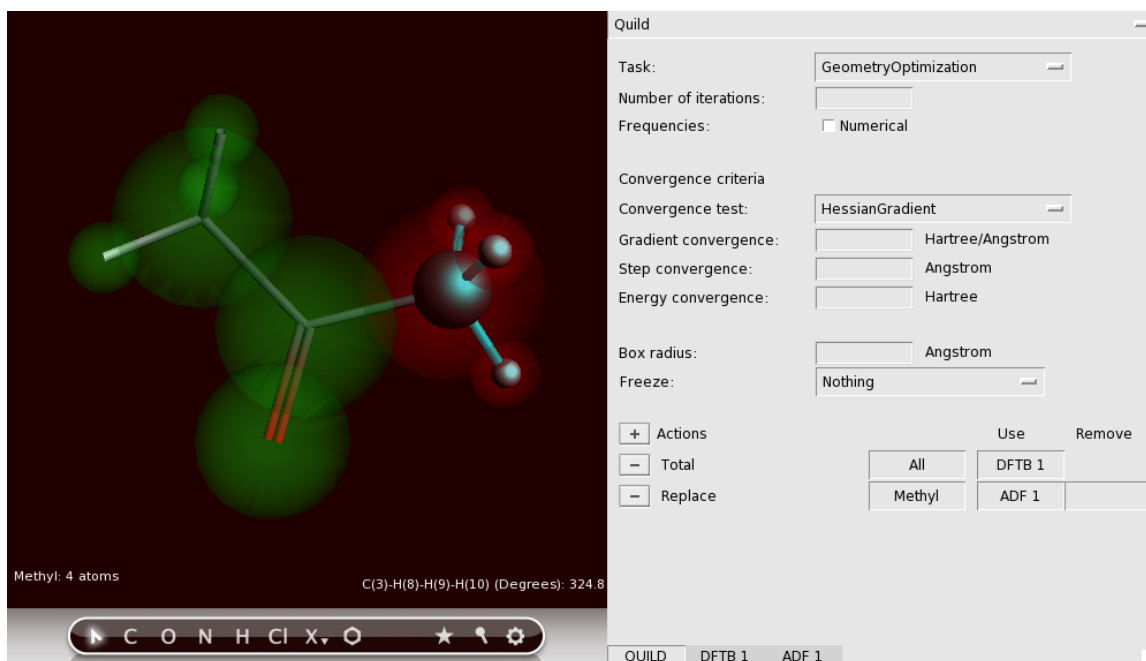
Select the Quild panel

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 whole molecule, and thus the 'All' region is preselected. In the 'Use' field you have specified how to treat the whole molecule: with DFTB.

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

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

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

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

Save your set up

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

Click on the 'ADF 1' tab

Look through the different panels, to see what options ADF will use. Do NOT make changes!

Click on the 'DFTB 1' tab

Click on the 'DFTB 2' tab

Click on the 'Quild' tab

Now let's run this calculation:

Run the calculation

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

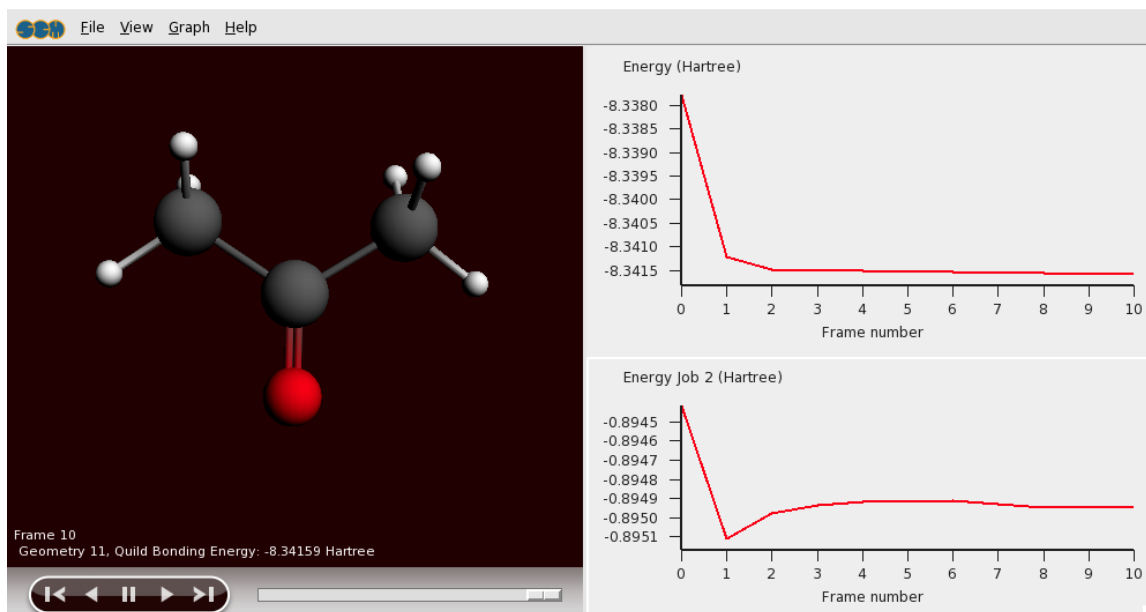
Use the **SCM** → **Movie** command

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

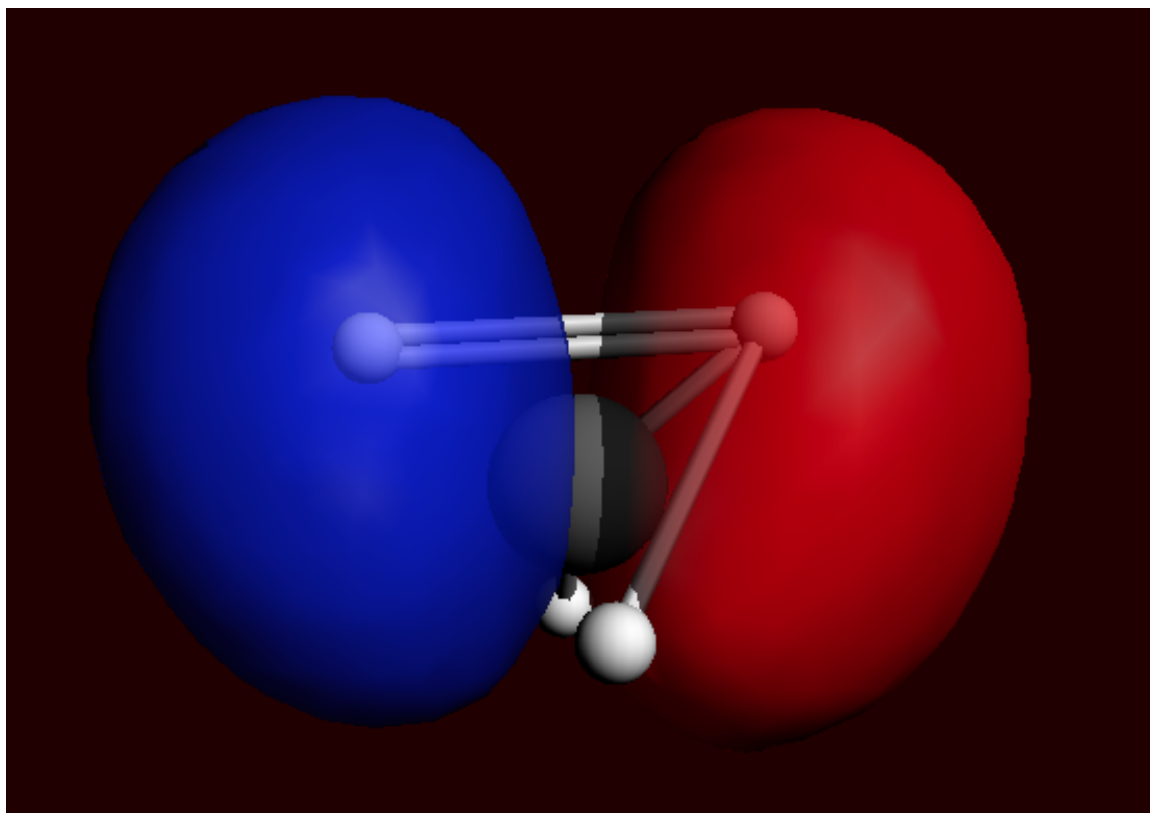
Show the Quild job details (click on the triangle to show the details)

Show the Local files (click on the triangle to show them)

The screenshot shows the ADF software interface with the 'quild' job selected. The 'Job details' section is expanded, and the 'Local files' section is also expanded, showing a list of files and their sizes.

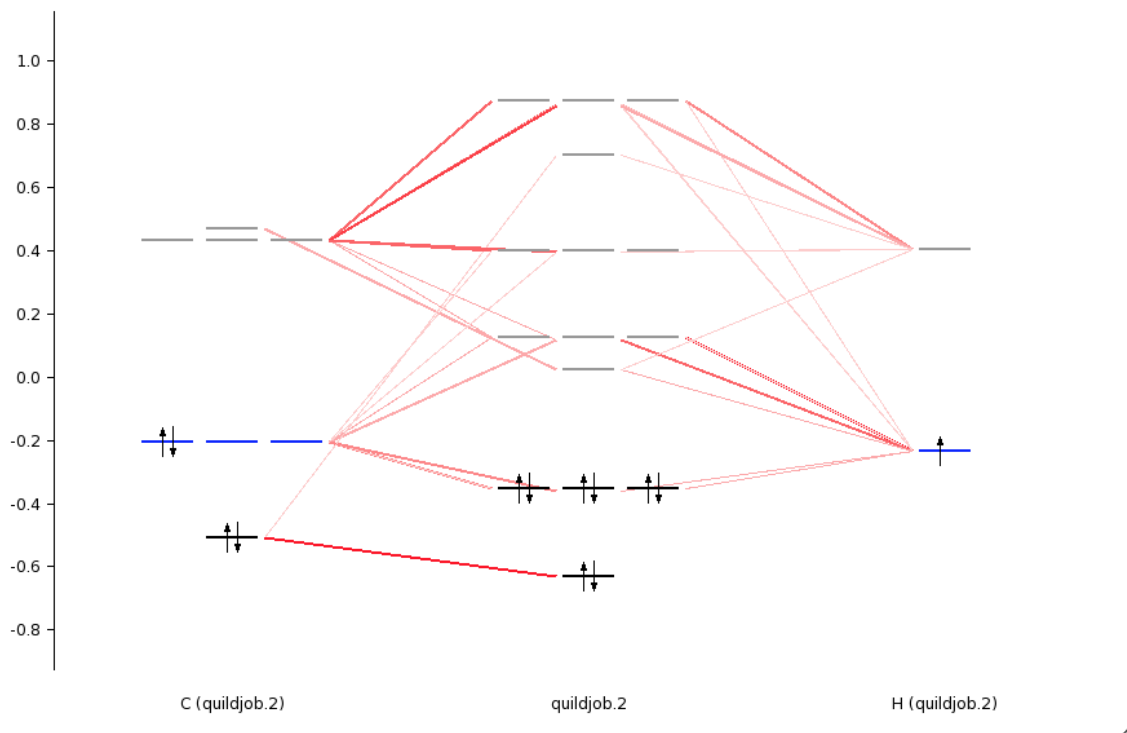
File Name	Date/Time	Size
.adf	Sep 16, 2010 23:36	64735 bytes
.err	Sep 16, 2010 23:37	437 bytes
.job	Sep 16, 2010 23:36	7043 bytes
.logfile	Sep 16, 2010 23:37	46064 bytes
.out	Sep 16, 2010 23:37	247449 bytes
.pid	Sep 16, 2010 23:37	390 bytes
.qkf	Sep 16, 2010 23:37	405504 bytes
.results/logfile_0	Sep 16, 2010 23:37	46041 bytes
.results/quildjob.1.inp	Sep 16, 2010 23:37	683 bytes
.results/quildjob.1.t21	Sep 16, 2010 23:37	12288 bytes
.results/quildjob.2.t21	Sep 16, 2010 23:37	647168 bytes
.results/quildjob.3.inp	Sep 16, 2010 23:37	383 bytes
.results/quildjob.3.t21	Sep 16, 2010 23:37	12288 bytes
.results/quildjob.logfile	Sep 16, 2010 23:37	14 bytes
.run	Sep 16, 2010 23:36	1848 bytes

Double-click on the `.results/quldjob.2.t21` file  
Visualize the HOMO in ADFview  
Click on the Isosource:Double pulldown 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** → **ADF Levels** command



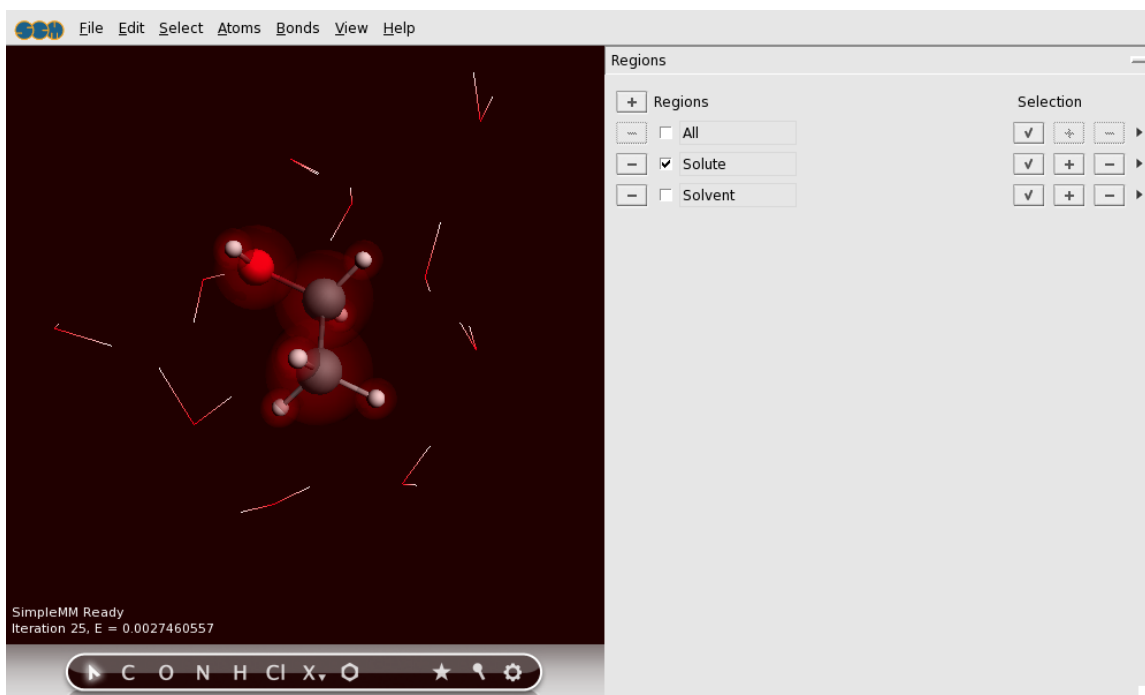
Now you have the ADF result file for the methyl group visible in ADFview and ADFlevels. With ADFview and ADFlevels you can examine the ADF results as usual.

### 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:

```
Build an ethanol molecule
Pre-optimize the structure
Select the 'Solvation' panel
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 Wireframe representation.

## Set up the QM/MM calculation

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

Select the 'QMMM' panel

Select the 'Solute' region in the 'QM Region' pull-down menu

Change the QMMM Task to GeometryOptimization

QMMM

Task: GeometryOptimization

Output level: Normal

Warning level: ReportSevere,StopFatal

Optimization method: ConjugateGradient

Number of steps: 5000

MM gradient convergence: Hartree/Angstrom

Print cycles: 10

Convergence trouble: Continue

Fix MM geometry:  Yes

Electrostatic coupling: None

Capping method: AddRemove

QM Region: Solute

QMMM 1   ADF 1   MM 3

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 3' 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.

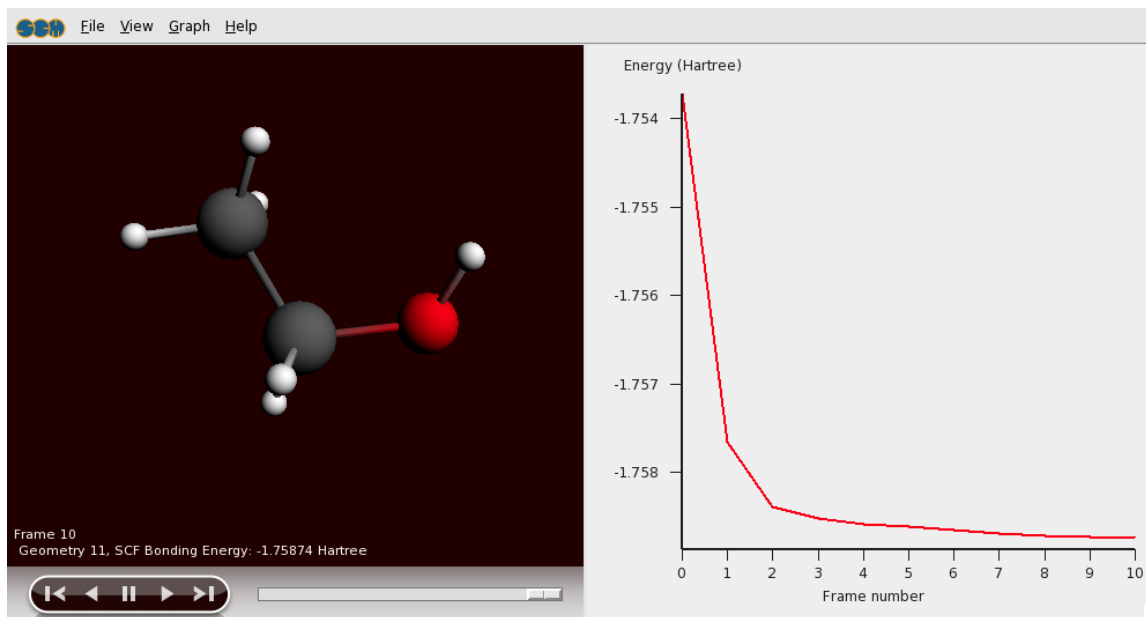
Click on the 'MM 3' tab  
Check the atom types

## Run the QMMM calculation, and see results

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

Show the optimization movie: **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 8: ADF Fragment Analysis

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

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

The tutorial will walk you through two different fragment analysis examples. You will set up the calculation, run it, and visualize the result. 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  $\text{PtCl}_4^{2-}$  fragment, and one  $\text{H}_2$  fragment. It is a good example on how to specify the charges of the fragments.



## Step 1: Build Ni(CO)<sub>4</sub>

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 using the Structures button

(Metal Complexes>ML4 tetrahedral)

Change the central atom into a Ni atom

Select one ligand

Use the **Select** → **Select Atoms Of Same Type** menu command

Change them in CO ligands: **Atoms** → **Replace By Structure** → **Ligands** → **CO**

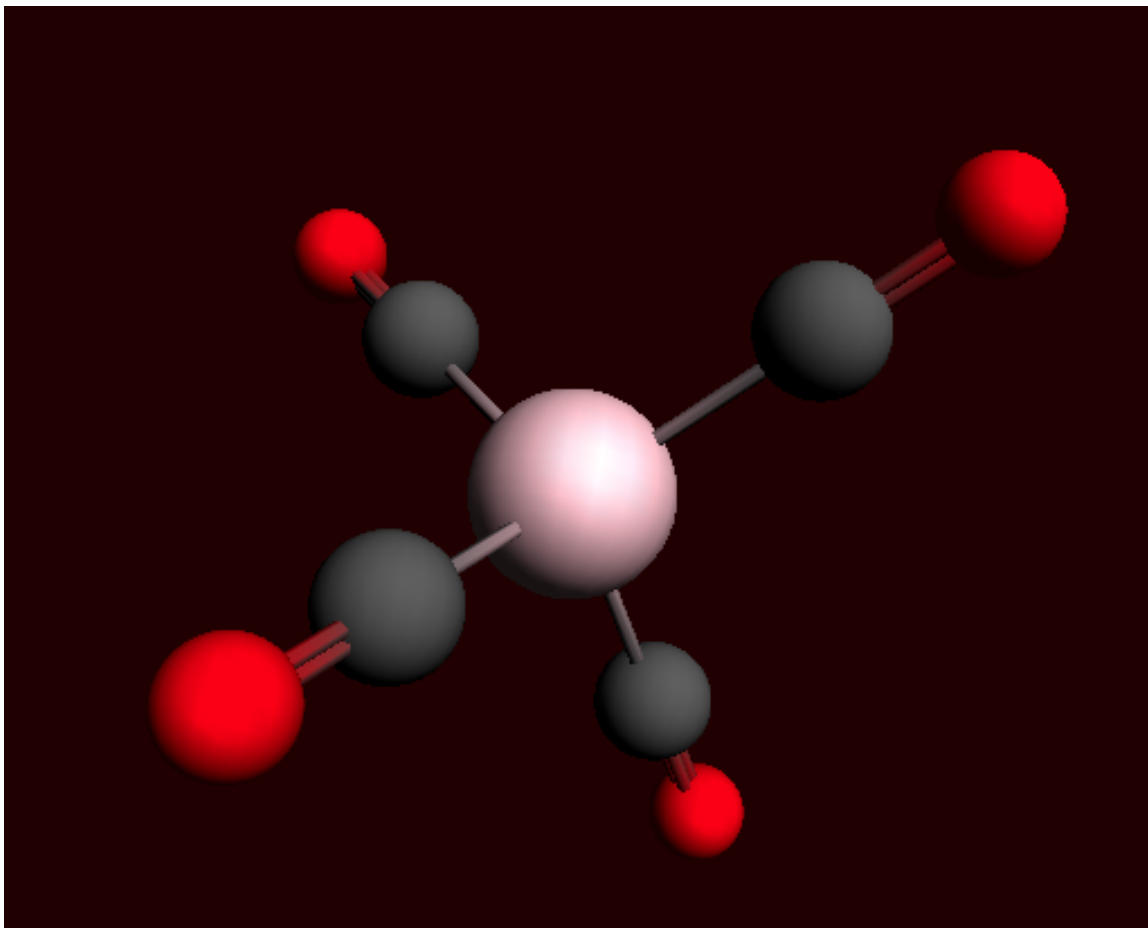
Choose the 'Geometry Optimization' Preset

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 five new regions: one for the Ni atom, and 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.

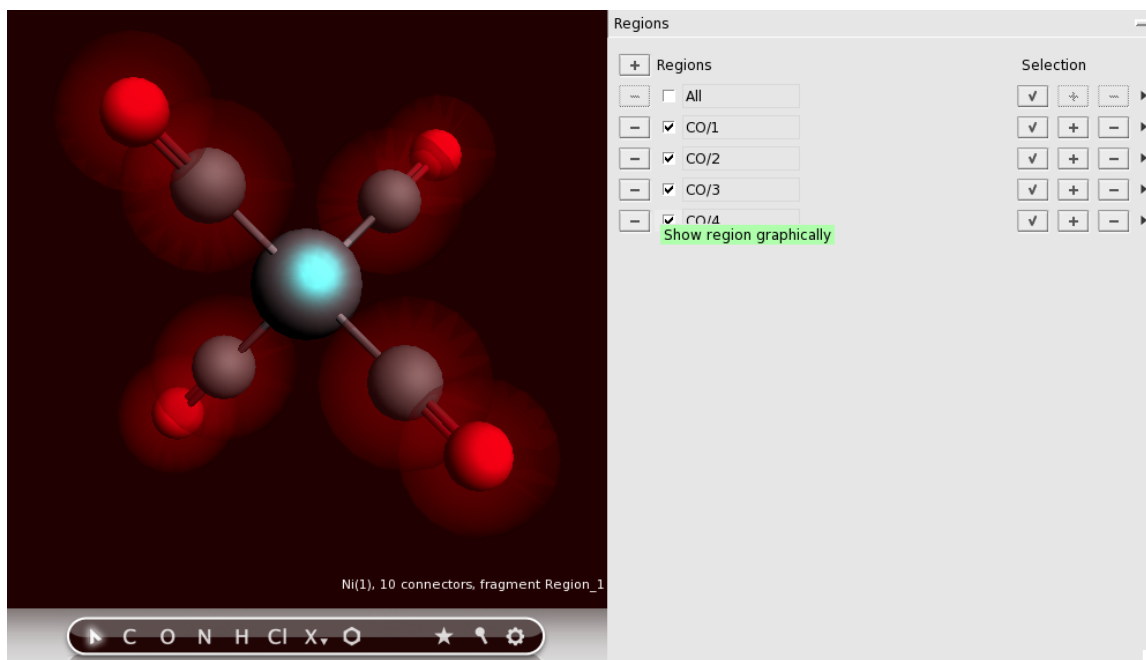
Repeated fragments are indicated with the fragment name followed by '/n', with n the number of the copy. All copies must match such that one fragment can be positioned exactly over another fragment by rotation and translation. ADF checks for this, currently ADFinput does not. In this particular example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

```
Select the 'Regions' panel
Select all atoms
Click the '+' button to add another new region (containing all atoms)
Select the Ni atom
Click the '-' button on the right side of the 'Region_2' line
    to remove the Ni atom from that region
Change the name of 'Region_2' into 'CO'
```

Now two new regions are defined: one for the Ni atom, and one 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
```

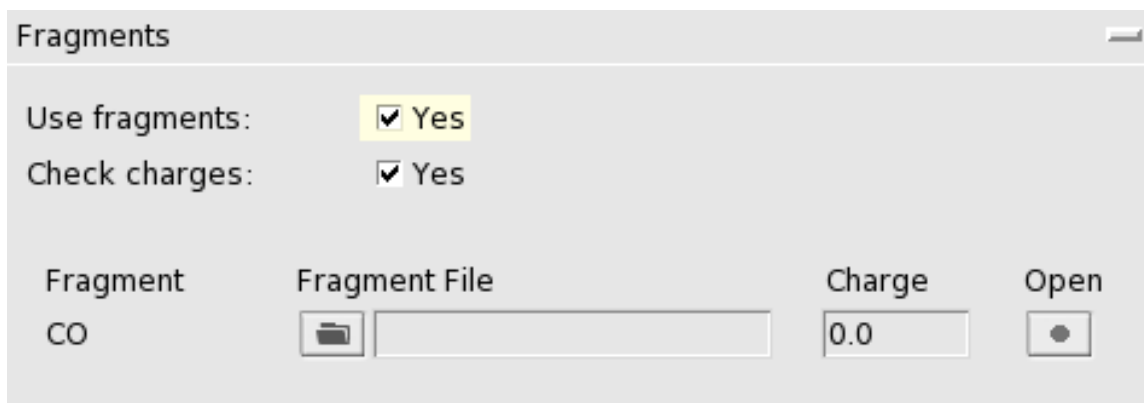
This should result in the following regions:



## 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 Options' panel  
Select the 'Single Point' preset  
Open the 'Fragments' panel  
Check the 'Use fragments' check box



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 3: 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)<sub>4</sub> 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

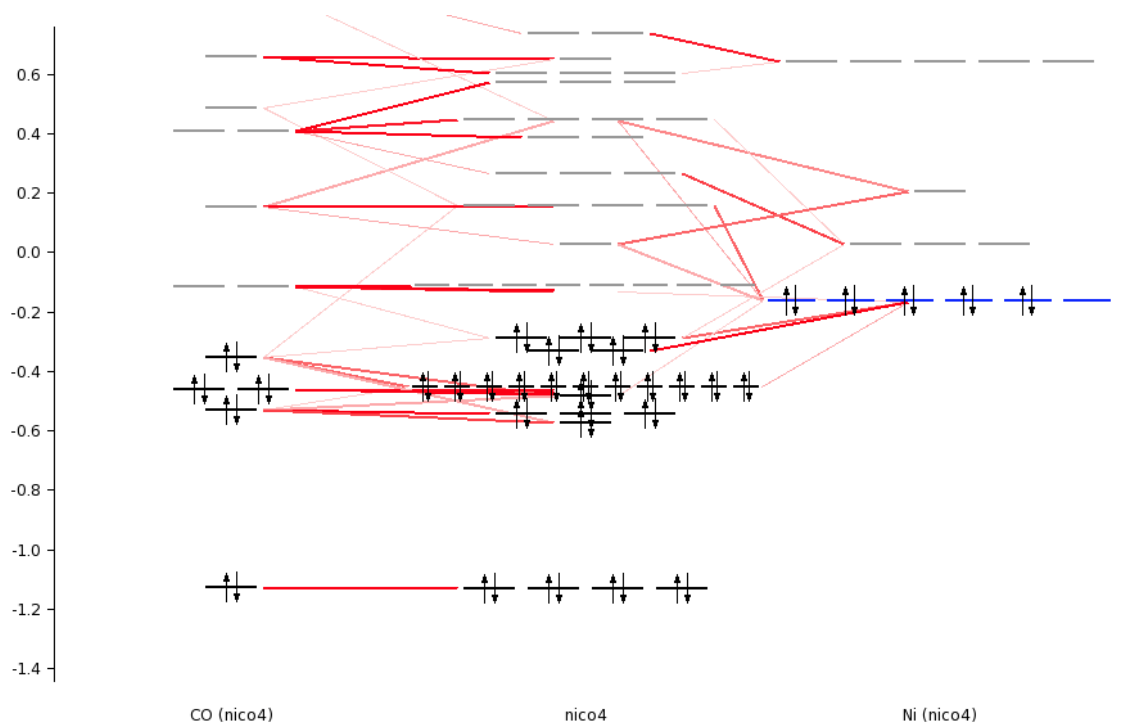
Run

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

The CO-fragment and Ni(CO)<sub>4</sub> 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:

Use the **SCM** → **ADF Levels** command

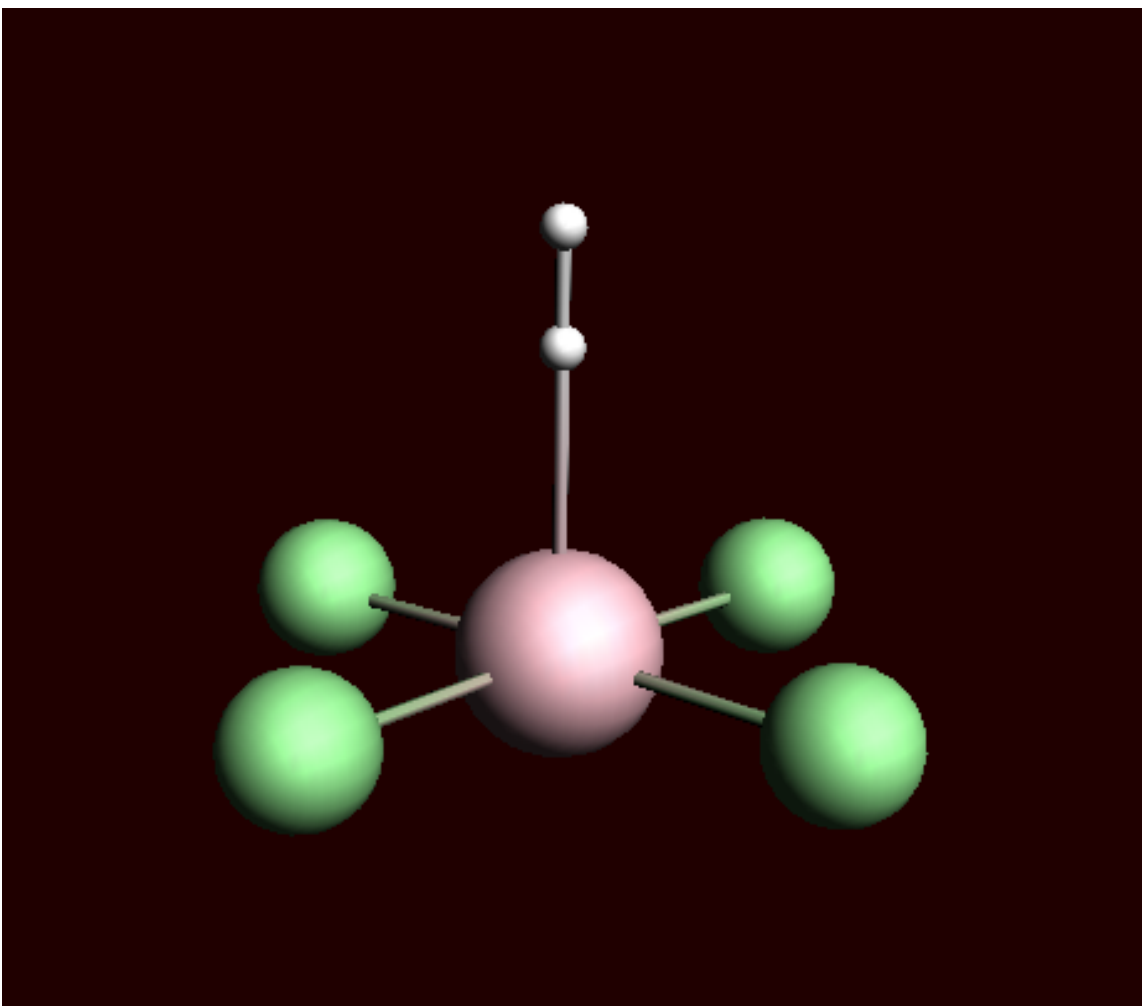


In the center you see the levels of the whole molecule, on the sides you see the CO fragment and the Ni-atom fragment. The interaction lines tell you which molecular orbitals come from which fragment orbitals.

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

### Step 4: Build $\text{PtCl}_4\text{H}_2^{2-}$

The following is a picture of the whole molecule. The colors of the Cl-atoms have been changed for clarity:



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
(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
(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
```

## Step 5: Define fragments

Define the  $\text{PtCl}_4^{2-}$  and  $\text{H}_2$  fragments in the Regions panel:

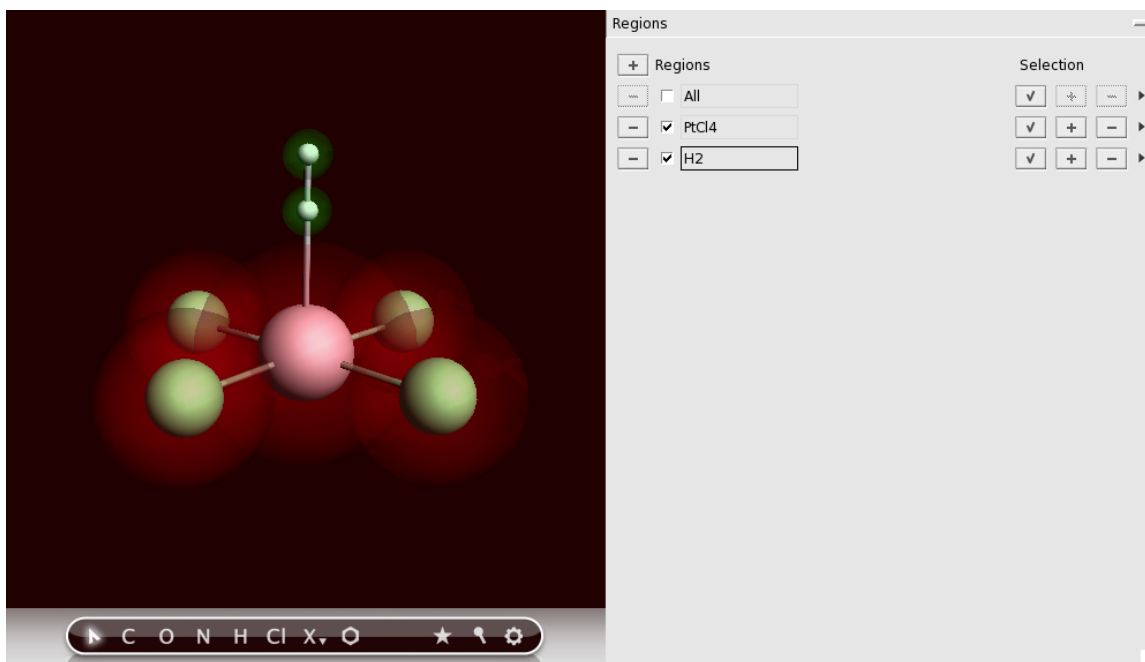
Select the 'Regions' panel

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'



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

Select 'Main Options' panel

Select the 'Single Point' preset

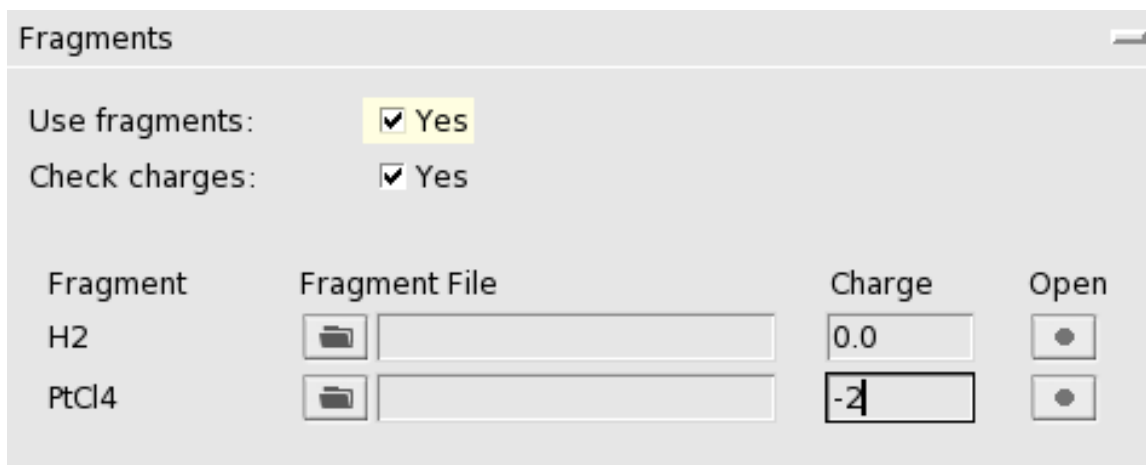
Open the 'Fragments' panel

Check the 'Use fragments' check box

Change the charge of the  $\text{PtCl}_4$  fragment to -2

Save

The other changes (the overall molecule charge, and the scalar ZORA option) have already been set previously. The Single Point 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 'Task: FragmentAnalysis' 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 6: 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 → ADF Levels command
```

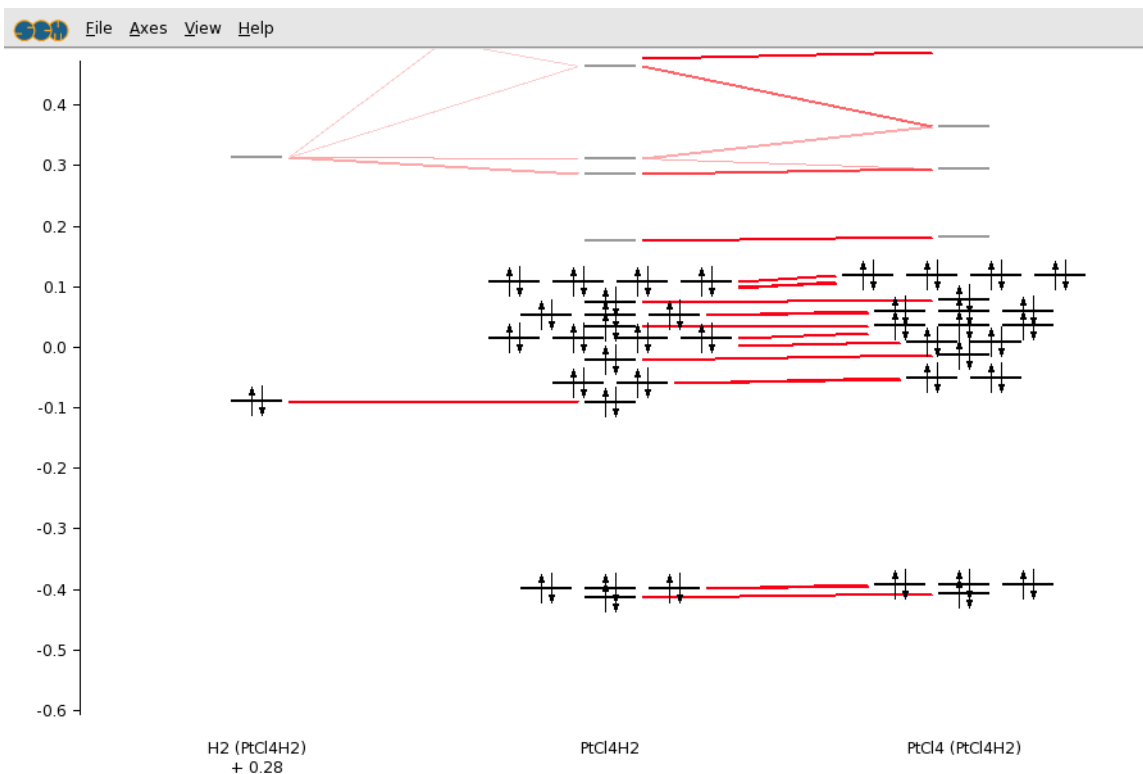
```
Use the mouse (drag with left mouse, scroll wheel, drag with right mouse)
  zoom in on the interesting region (roughly from -0.5 to 0.4)
```

```
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 9: Basis Set Effects for NH<sub>3</sub> (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 (SimpleMM):

```
Click 'Pre-Optimize' gear wheel button
Zoom out to see your atoms ...
```



Using the default pre-optimization algorithm the non-bonded atoms will 'fly away' from each other:



The default pre-optimization will finally stop with 'SimpleMM optimization ready' message. Apparently the result obtained is far away from the well-known anticipated  $\text{NH}_3$  molecule.

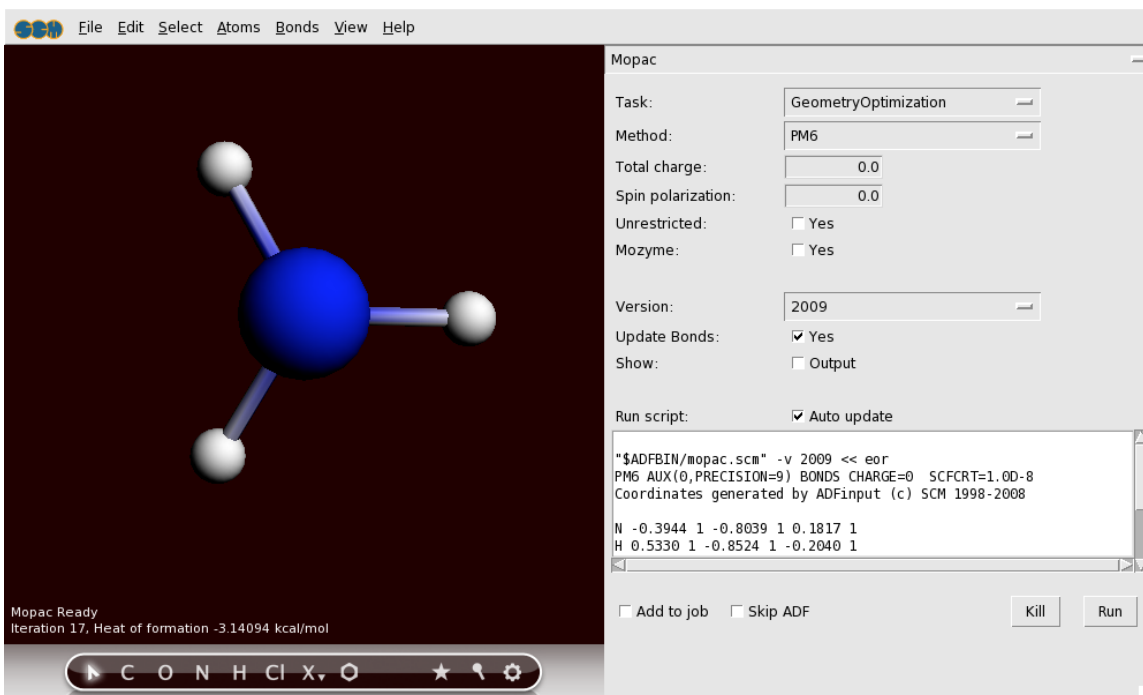
Next we will try to optimize using Mopac. If you do not have Mopac installed, please do exactly the same but use DFTB instead of Mopac.

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

Select the 'Mopac' panel

Click the 'Run' button in the Mopac panel

The message 'MOPAC optimization 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 NH<sub>3</sub> molecule, we will set up a series of calculation: the optimization of NH<sub>3</sub> with ADF, using different basis sets. The first step is to set up a simple geometry optimization:

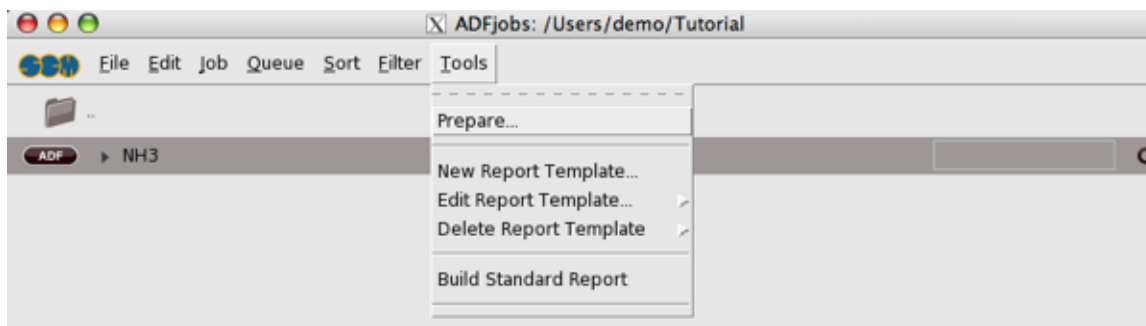
```
Select the 'Main Options' panel
Select the 'Geometry Optimization' preset
Save as NH3
```

We have used all defaults for basis set and so on.

## Step 3: Set up a batch of ADF jobs

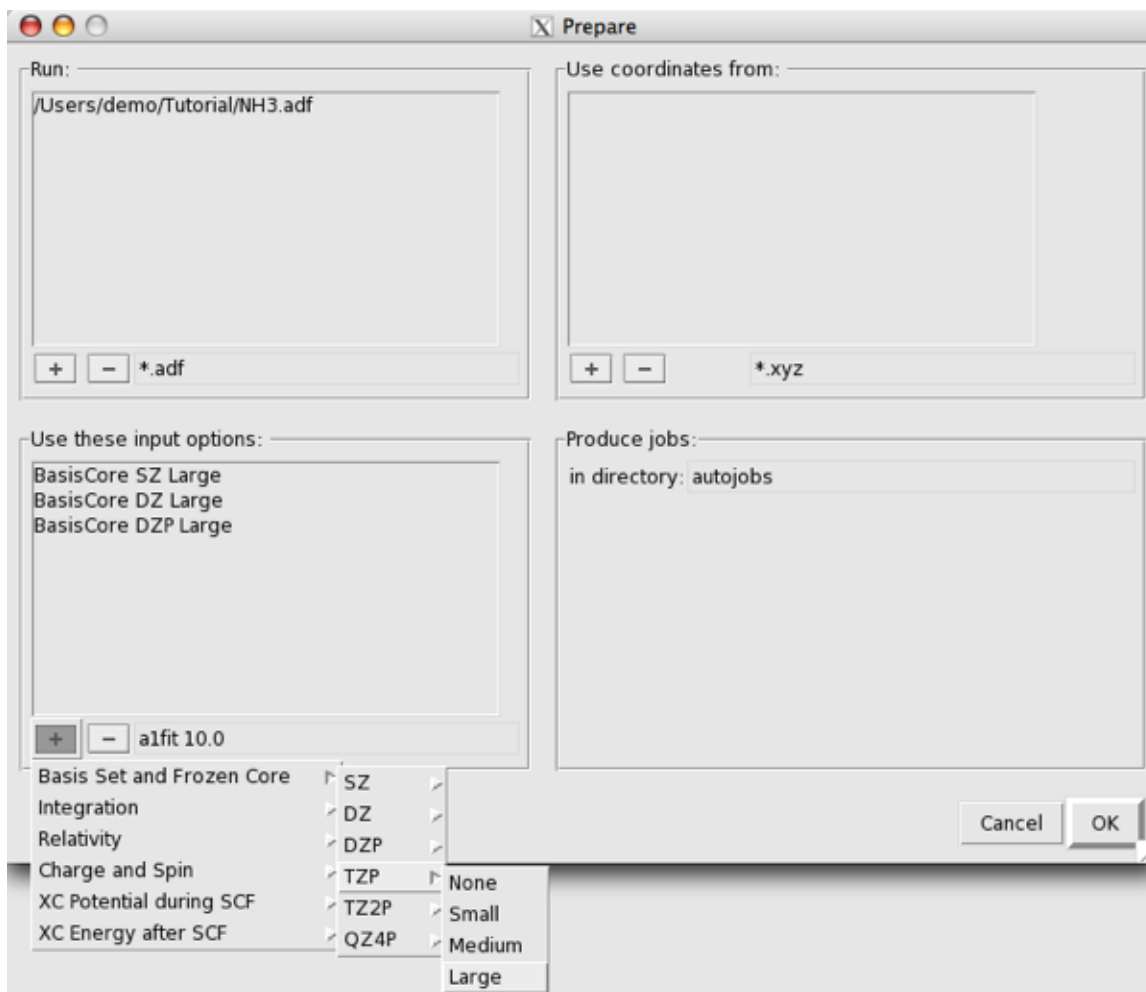
Next we will set up a series of calculations, using the Prepare tool.

```
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 file name (including the path) will show up in the 'Run' field (otherwise, we can select NH3 using '+' button of the 'Run' field).

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 the corresponding ADFtail windows will pop up. Each ammonia optimization job should not take more than a few minutes.

## Step 5: Analyze results of several calculations at once

When all the ammonia optimization jobs are finished, we can compare the results. The main conclusion that you will reach is that DZ (double zeta) basis set optimization, job name 'NH3.DZ.Large', leads to the incorrect planar ammonia molecule. As covered in the preceding tutorials, you can optionally use several GUI modules to observe that:

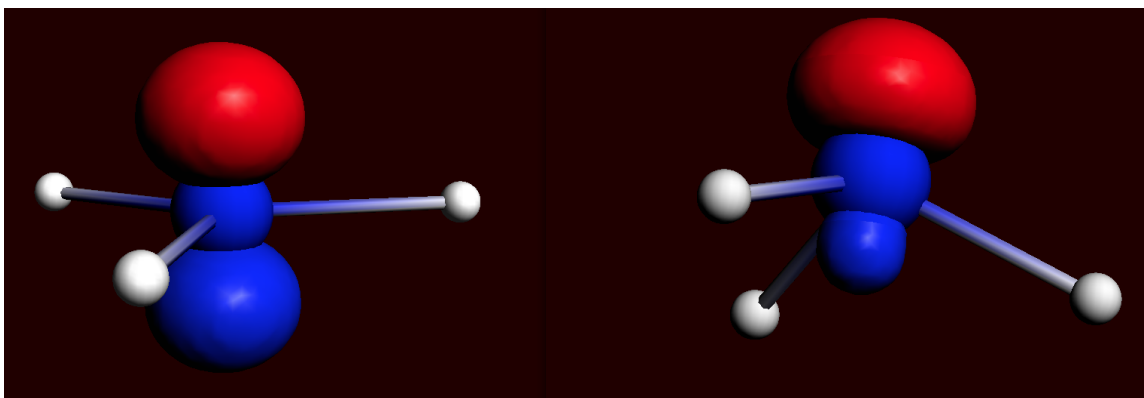
- ADFmovie, which will show the geometry optimization
- ADFinput, which will open the (last) converged geometry
- ADFview, which will open the converged geometry and also would display various density maps in 3D

For example, let us use ADFview to demonstrate the results:

Select job NH3.DZ.Large in the ADFjobs window (should then be highlighted)  
Select **SCM** → **View**  
Select **Fields** → **Grid** → **Fine**  
Select **Add** → **HOMO**  
In the isosurface contour value field which appeared at the bottom,  
change the default '0.03' to '0.3'  
Type 'Ctrl-minus' several times, until the central N atom ball  
does not overlap strongly with the HOMO orbital.

Repeat for the other jobs

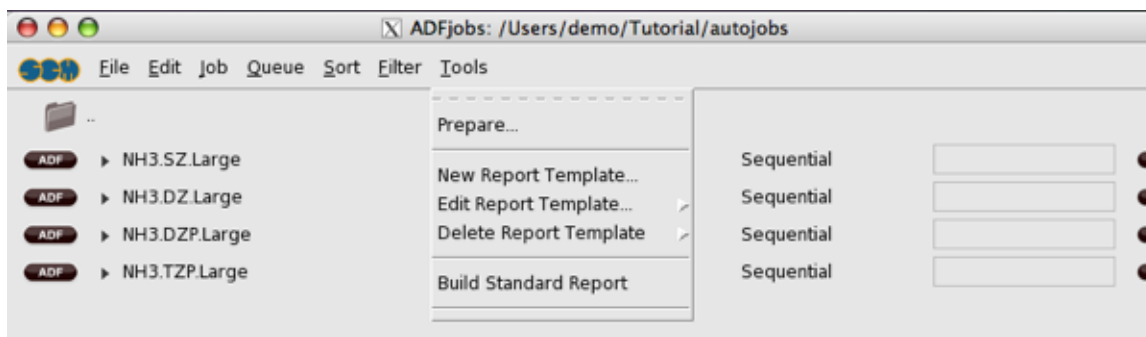
What you will observe is that HOMO of ammonia does not have the anticipated sp<sup>3</sup> hybridization, when DZ basis set is used (first planar ammonia as optimized in DZ, next pyramidal ammonia as optimized in DZP) :



An automated procedure to report results from a list of ADF jobs is available. This task is achieved via using the Report tool within ADFjobs. Below we will demonstrate how to do this for our set of completed NH<sub>3</sub> molecule optimizations.

Go to the ADFjobs window

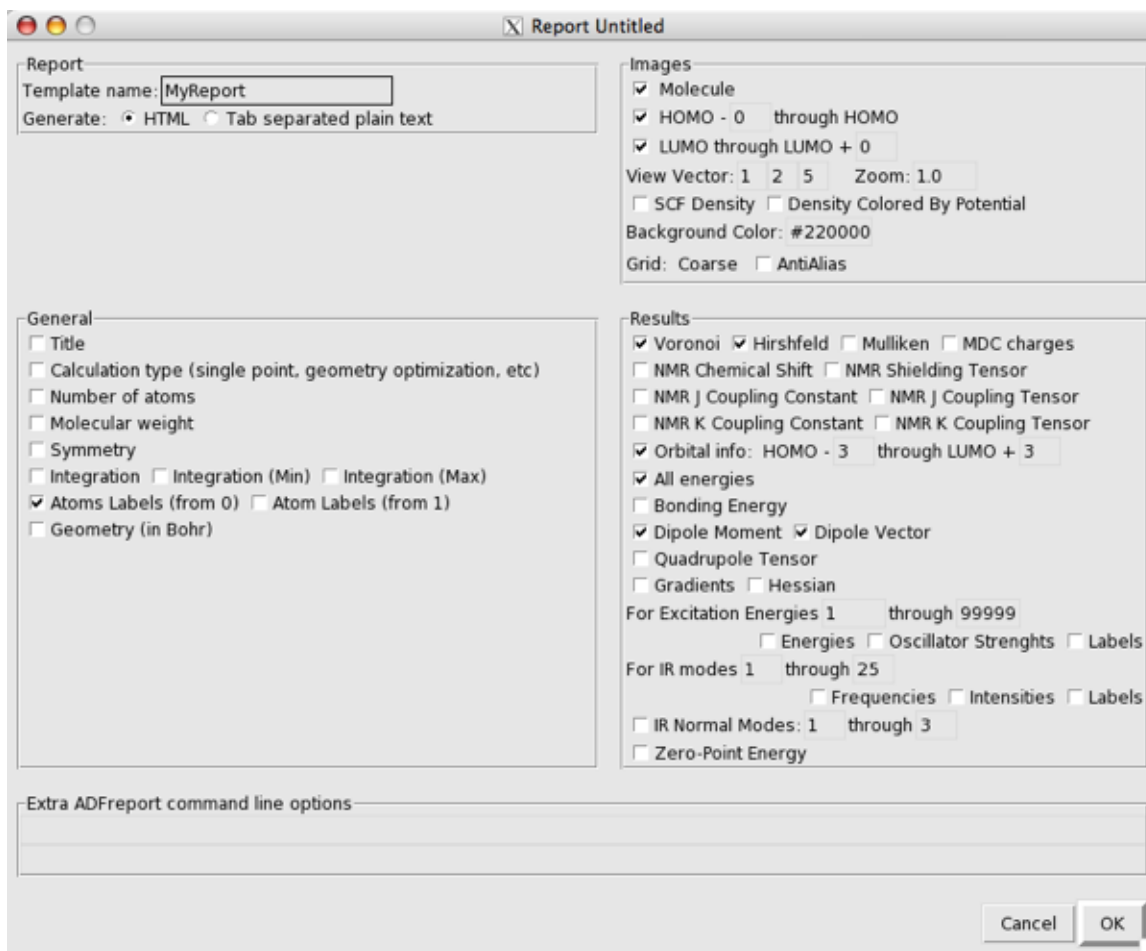
Select **Tools** → **New Report Template...**



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'

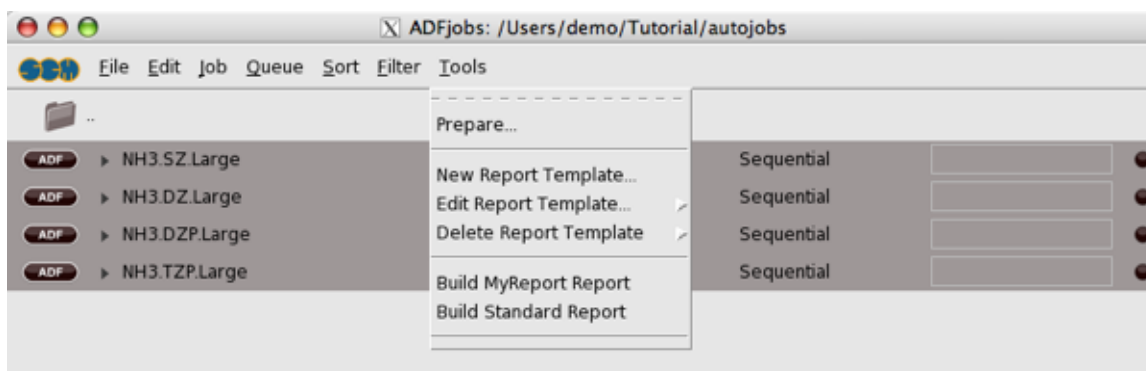
In the 'Results' section check 'Dipole Moment' and 'Dipole Vector'



Click 'OK'

The Report dialog will close, saving our template named 'MyReport'. Now we will generate actual report following the saved template:

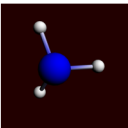
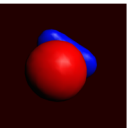
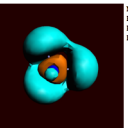
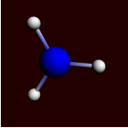
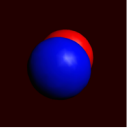
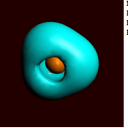
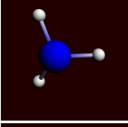
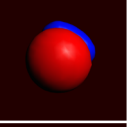
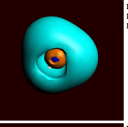
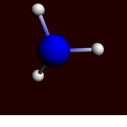
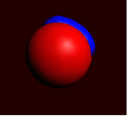
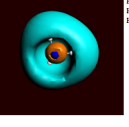
In ADFjobs window, select all the finished jobs from the NH3 set  
 Select **Tools** → **Build MyReport Report**



'Save As' dialog window will pop up, showing the 'report.html' default file name.

Choose your file name and location, then click 'Save'

Now ADF will scan through your job list and prepare the report. Finally the browser will start showing your report file (by default, named 'report.html'):

Calculation	Molecule	HOMO	LUMO	AtomLabels	Voronoi	Hirshfeld	Orbital-Info	HOMO-S:LUMO+3	Energies	Dipole	DipoleVector
/Users/visser/Tutorial/autjobs/NH3.SZ.Large				N(0) H(1) H(2) H(3)	-0.223 0.074 0.075 0.074	-0.264 0.088 0.088 0.088	-0.719753 2.0 A_1 -0.333370 2.0 A_2 -0.331368 2.0 A_3 -0.000468 2.0 A_4 0.305082 0.0 A_5 -0.355370 0.0 A_6 0.355375 0.0 A_7		Bonding Energy: -0.839353 Pauli Repulsion: 1.667536 Electrostatic Interaction: -0.354770 Steric Interaction: 1.362766 Orbital Interaction: -2.202118	0.819	-0.022 -0.055 -0.017
/Users/visser/Tutorial/autjobs/NH3.DZ.Large				N(0) H(1) H(2) H(3)	-0.259 0.121 0.119 0.119	-0.343 0.114 0.114 0.114	-0.750780 2.0 A_1 -0.435364 2.0 A_2 -0.435275 2.0 A_3 -0.189886 2.0 A_4 -0.010291 0.0 A_5 0.110642 0.0 A_6 0.119555 0.0 A_7 0.562272 0.0 A_8		Bonding Energy: -0.716028 Pauli Repulsion: 1.873345 Electrostatic Interaction: -0.312049 Steric Interaction: 1.561296 Orbital Interaction: -2.275315	0.074	0.002 0.074
/Users/visser/Tutorial/autjobs/NH3.DZP.Large				N(0) H(1) H(2) H(3)	-0.259 0.086 0.086 0.087	-0.387 0.102 0.102 0.102	-0.771437 2.0 A_1 -0.418525 2.0 A_2 -0.418502 2.0 A_3 -0.231454 2.0 A_4 -0.051382 0.0 A_5 0.102715 0.0 A_6 0.102722 0.0 A_7 0.337484 0.0 A_8		Bonding Energy: -0.740770 Pauli Repulsion: 1.790996 Electrostatic Interaction: -0.314524 Steric Interaction: 1.476472 Orbital Interaction: -2.217237	0.598	-0.016 -0.040 -0.596
/Users/visser/Tutorial/autjobs/NH3.TZP.Large				N(0) H(1) H(2) H(3)	-0.257 0.086 0.085 0.086	-0.311 0.104 0.104 0.104	-0.770026 2.0 A_1 -0.414518 2.0 A_2 -0.414488 2.0 A_3 -0.228975 2.0 A_4 -0.014621 0.0 A_5 0.058131 0.0 A_6 0.058136 0.0 A_7 0.285636 0.0 A_8		Bonding Energy: -0.744023 Pauli Repulsion: 1.793318 Electrostatic Interaction: -0.325245 Steric Interaction: 1.468073 Orbital Interaction: -2.212091	0.604	-0.017 -0.040 -0.603

The Report tool created a table-like report of the results. Click on the image to see it in detail.

We can clearly see that only for DZ basis optimization our NH<sub>3</sub> molecule is planar, see the last 'row' of the report table. Above, we have selected to report dipole moment and dipole vector; these values show up in the two last columns. Obviously the dipole moment is zero only for the planar NH<sub>3</sub> structure.

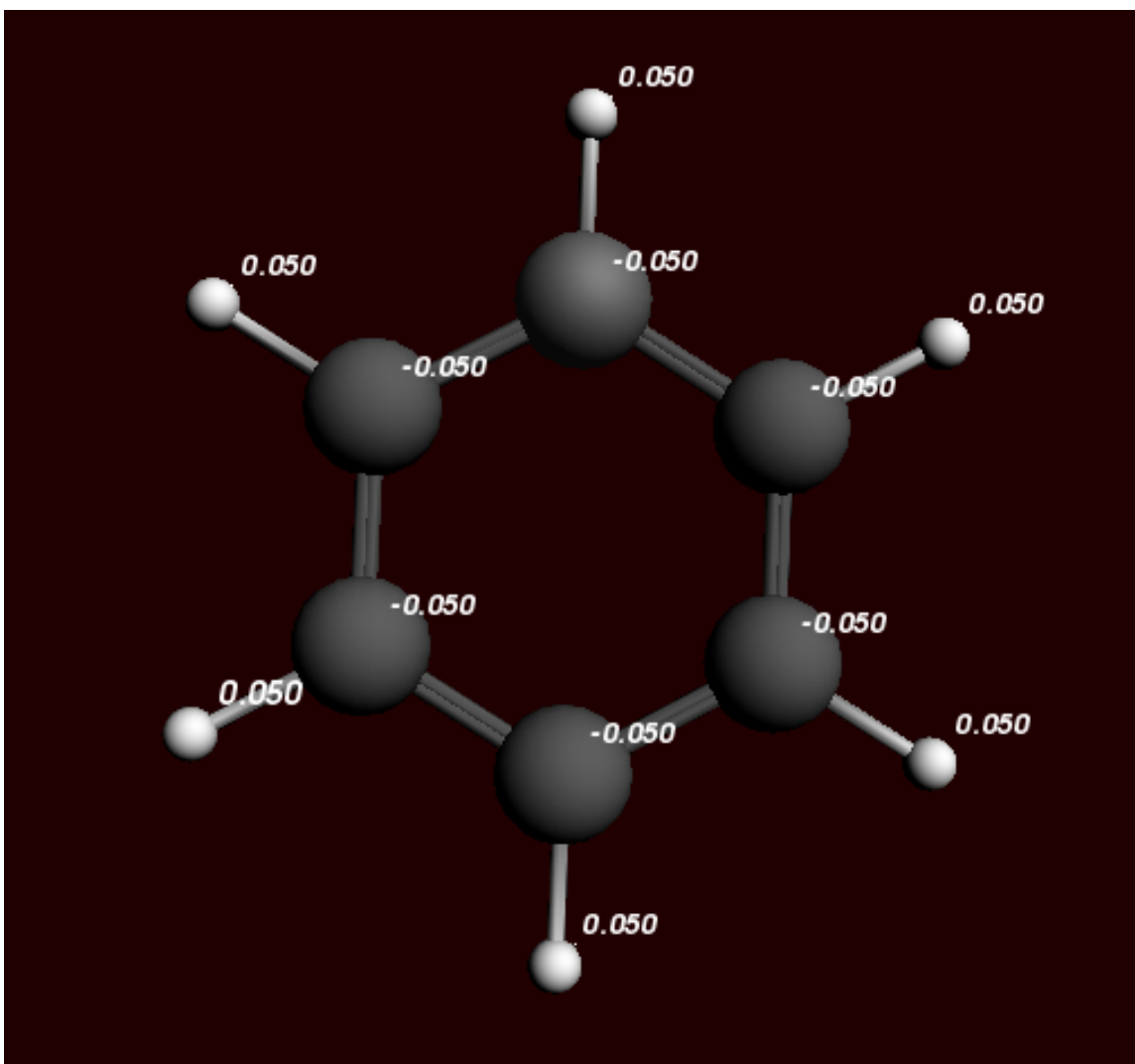
Congratulations, we are done with the ammonia optimization tutorial!

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

## Tutorial 10: DFTB charges, Bader analysis, NBOs, and Occupations

### Step 1: DFTB: Pre-optimize and Charges

Start ADFinput  
 Make benzene  
 Select the DFTB panel  
 Press 'Run' in the DFTB panel to optimize benzene  
 Use the **View** → **Atom Info** → **DFTB Charges** menu command to show the DFTB charges



## Step 2: Bader analysis and NBOs

Next we set up the calculation to show the required properties and run it:

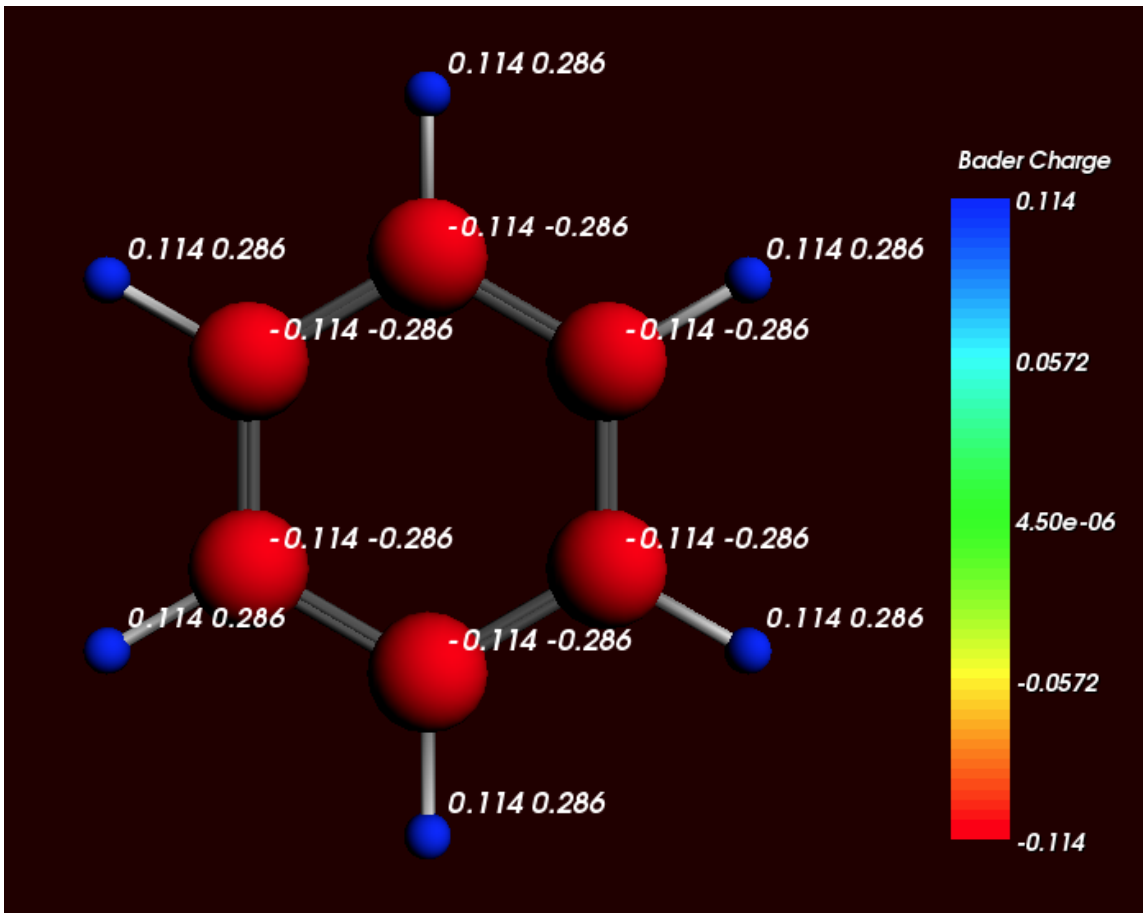
```
Set up a Single Point calculation with no frozen cores
Select the 'Other: Etot, Bader, Charge Transport' panel
Request Bader Atomic Properties
Request Save Bader atomic basins
Select the 'Localized Orbitals, NBO' panel
Request an NBO analysis
Request Boys-Foster localized orbitals
Run this setup
```

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 (View → Atom Info → Bader Charge)
```

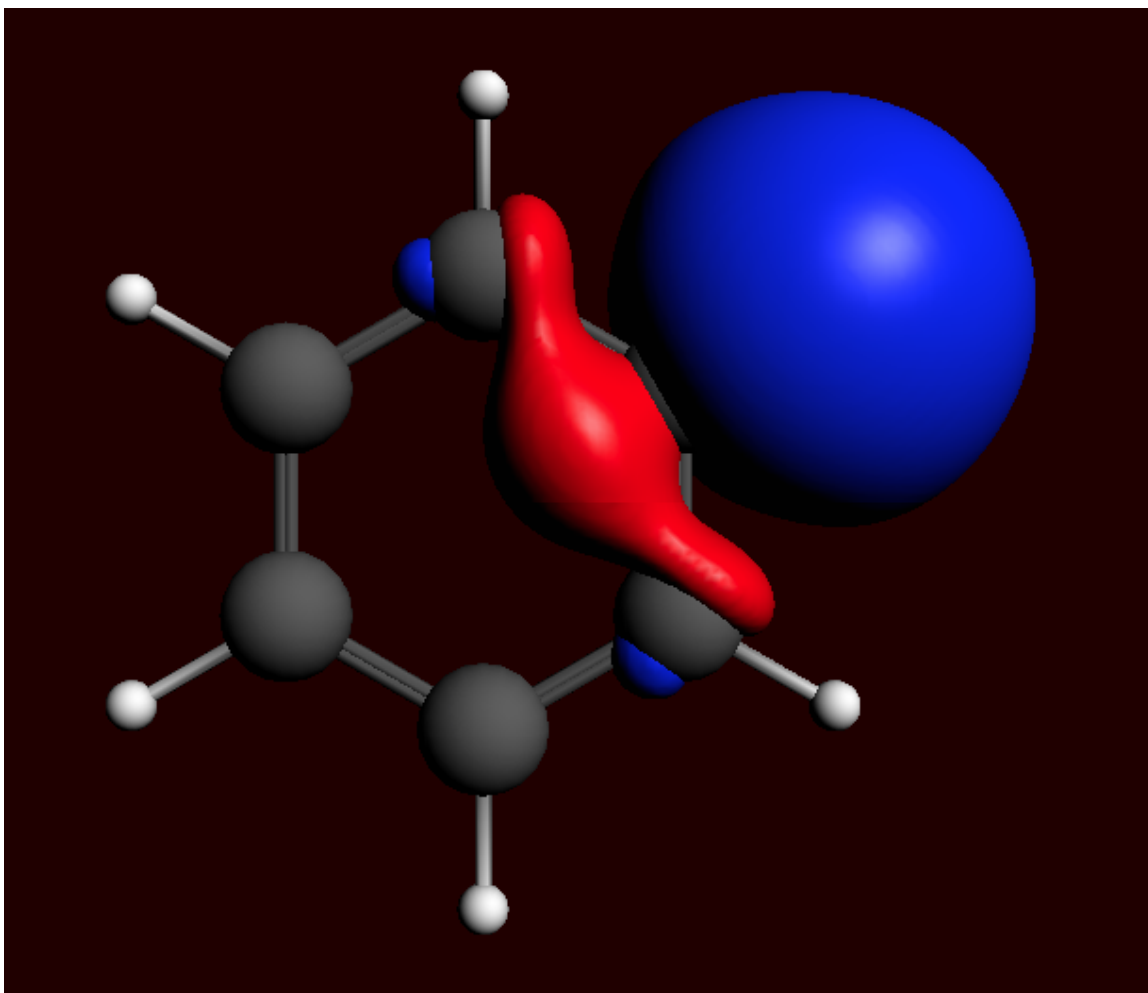


Color the atoms by Bader charges (**View** → **Color Atoms By** → **Bader Charge**)  
Show the Mulliken charges (**View** → **Atom Info** → **Mulliken Charge**)



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 bar, 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**



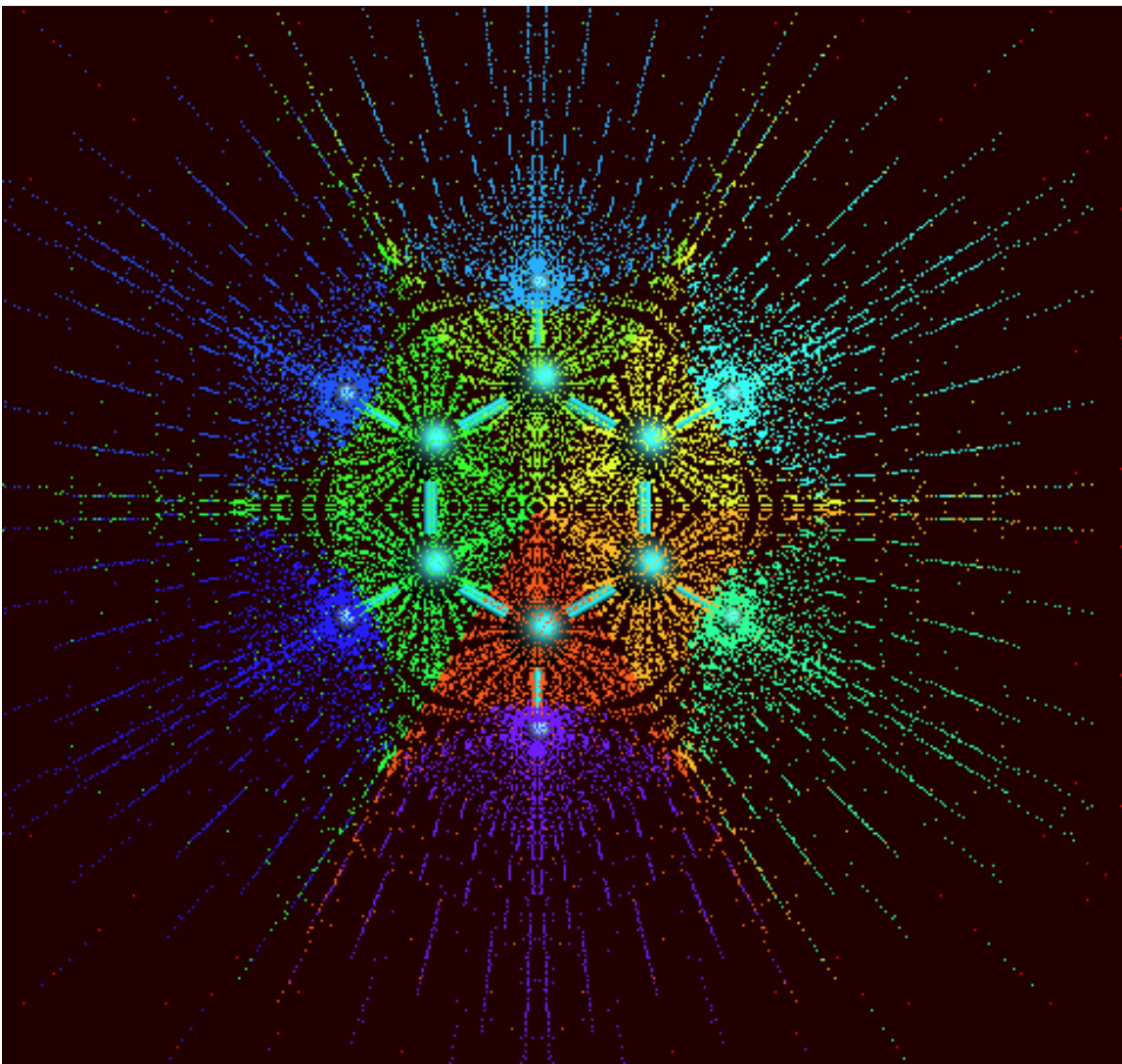
Obviously, you can also visualize the NLMOs or the Boys-Foster localized orbitals (which are just called Localized Orbitals in the fields menu).

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

**Add → Bader Sampling**

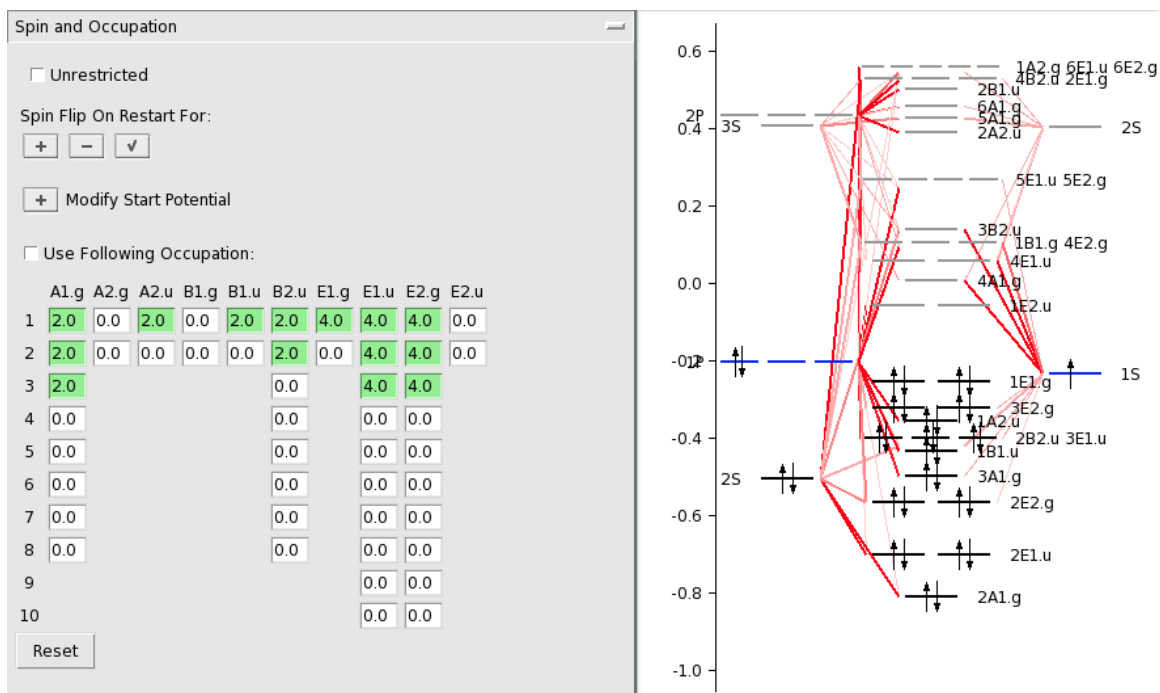


One can also select one or more atoms, to see only the Bader atomic basins of the selected atoms.

### Step 3: Occupations

Now we will remove one electron from a selected orbital (by symmetry) using ADFinput again.

Open your benzene calculation in ADFinput  
Open the spin and occupation panel



In the Spin and Occupation panel you see which orbitals are available (by symmetry, and spin if the current set up is unrestricted). The numbers are the occupations. Next to the ADFinput window ADFlevels will also have opened, and is showing a level diagram of your current molecule. This helps you to select the proper occupation.

The level diagram is based on the existing result file (.t21) found. If none, ADFinput will suggest to do a guess-calculation: a hopefully fast calculation using an inaccurate integration grid, and stopping after a few SCF cycles. The level diagram shown in that case will not be accurate obviously but will still be helpful in selecting the proper occupation.

Now, just as an example, we make a hole in the 3E2.g orbital. Note that this is NOT the HOMO.

Change the 4.0 to 3.0 in the 3 E2.g column (the third row)

Spin and Occupation

Unrestricted

Spin Flip On Restart For:

Modify Start Potential

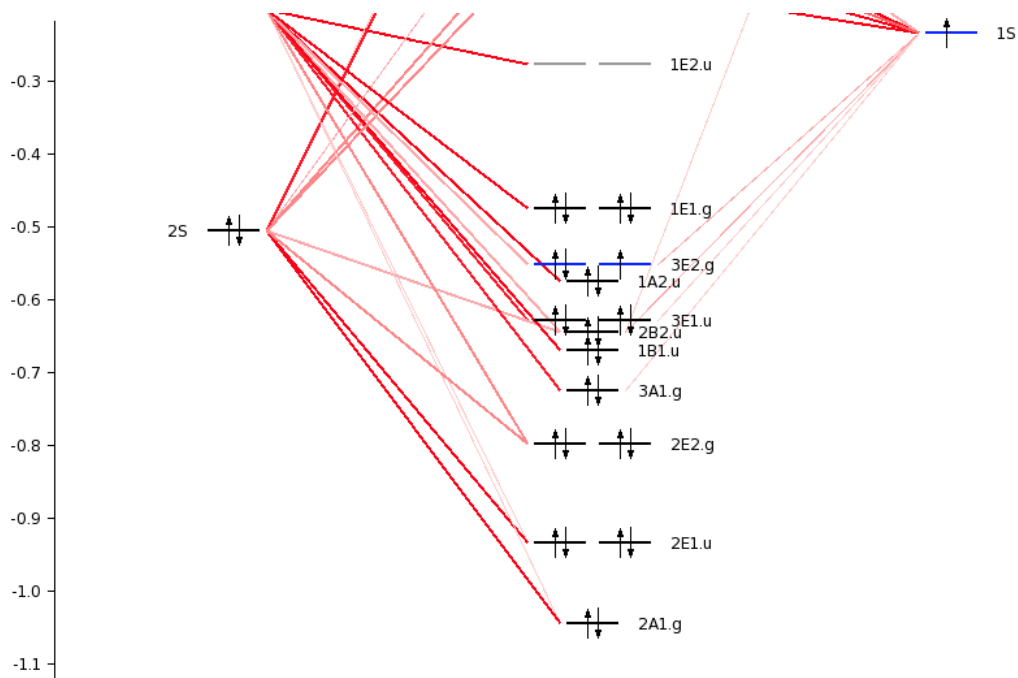
Use Following Occupation:

	A1.g	A2.g	A2.u	B1.g	B1.u	B2.u	E1.g	E1.u	E2.g	E2.u
1	2.0	0.0	2.0	0.0	2.0	2.0	4.0	4.0	4.0	0.0
2	2.0	0.0	0.0	0.0	0.0	2.0	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  
 Close the ADFinpup 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 11: Spin Coupling in Fe<sub>4</sub>S<sub>4</sub> Cluster

This tutorial will help you to:

- build the structure of iron-sulfur cubane,
- control the spin coupling in multicenter radical systems in two different ways (SpinFlip and ModifyStartPotential),
- tweak the SCF convergence in the iron-sulfur cubane case,
- visualize the distribution of spin densities in 3D.

### Step 1: Create and pre-optimize the Fe<sub>4</sub>S<sub>4</sub> cubane model

Embedded into proteins and coordinated by cysteine ligands, iron-sulfur cubanes are often used by nature in electron transfer and catalysis. While their native structures can be extracted from protein data bank (PDB) files, we will use ADFinput module to build a model of the Fe<sub>4</sub>S<sub>4</sub> cubane from scratch in this example.

Start ADFinput

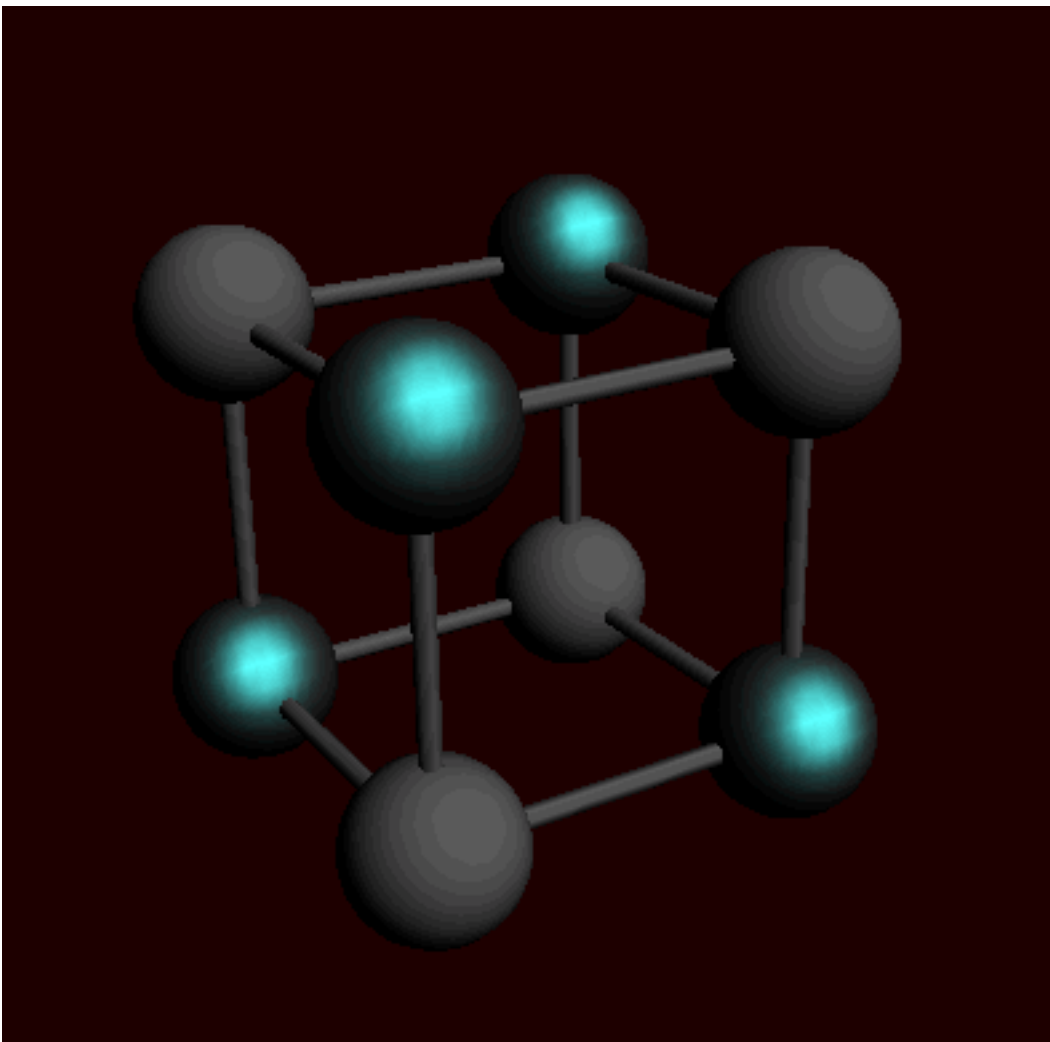
Select the **Structure tool** → **Polyhedra** → **Cube** structure:

Click anywhere in the empty structure drawing area.

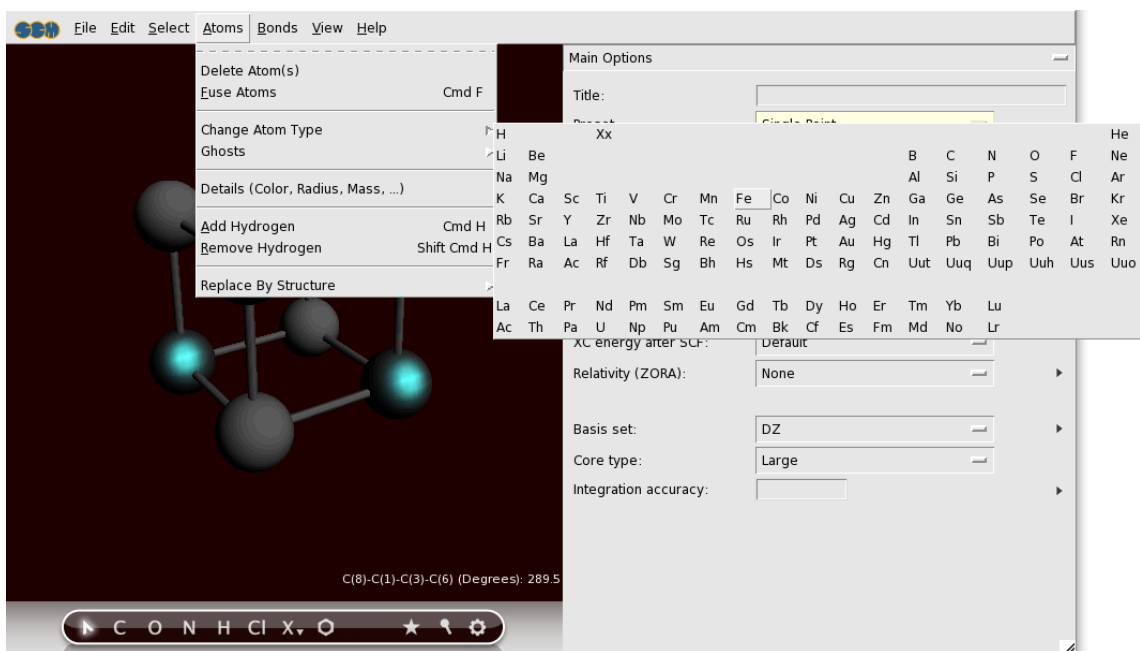
This should place a cube in the building area of ADFinput.

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



Use the **Atoms** → **Change Atom Type** → **Fe** command to change the four atoms into Fe



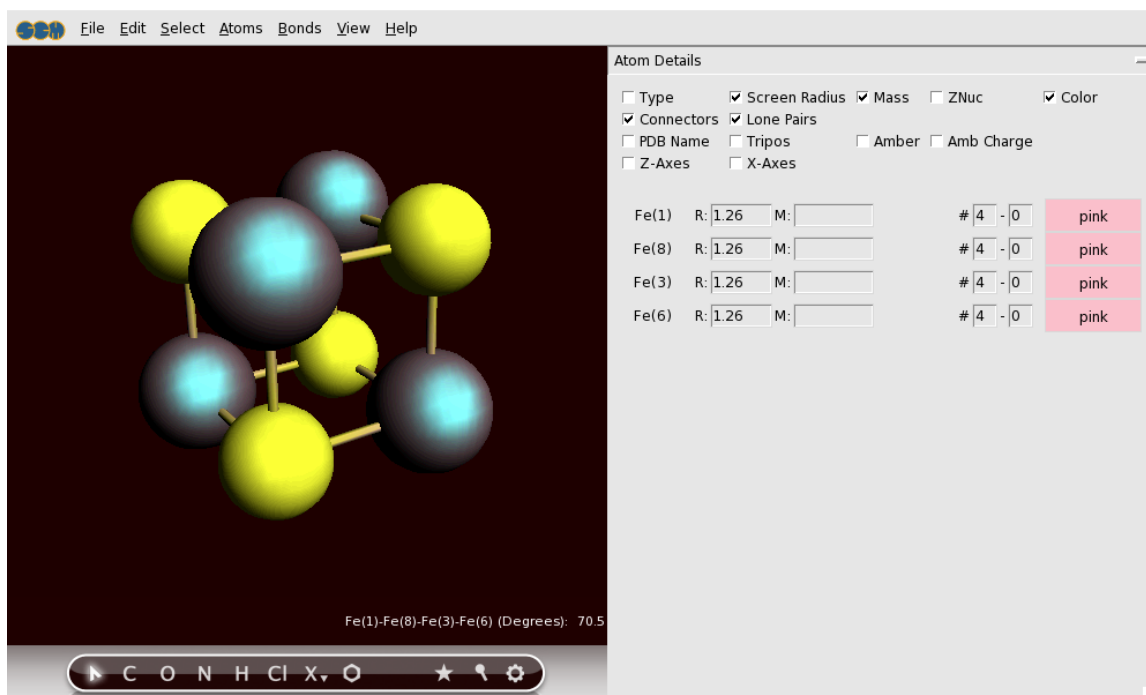
In the same way, change the four remaining carbons into sulfurs.

Now you should see the  $\text{Fe}_4\text{S}_4$  cubane in the structure drawing area of ADFinput. The proper coordination to Fe atoms is important in modeling their electronic structure. In proteins, iron-sulfur cubanes are coordinated by cysteine ligands to the Fe sites. Here, we will model these four cysteines by  $\text{SH}$  ligands. The procedure to add these ligands is described below.

Select all the Fe atoms

Use the **Atoms** → **Details (Color, Radius, Mass, ...)** menu command  
 Change the number of connectors for all Fe atoms to 4





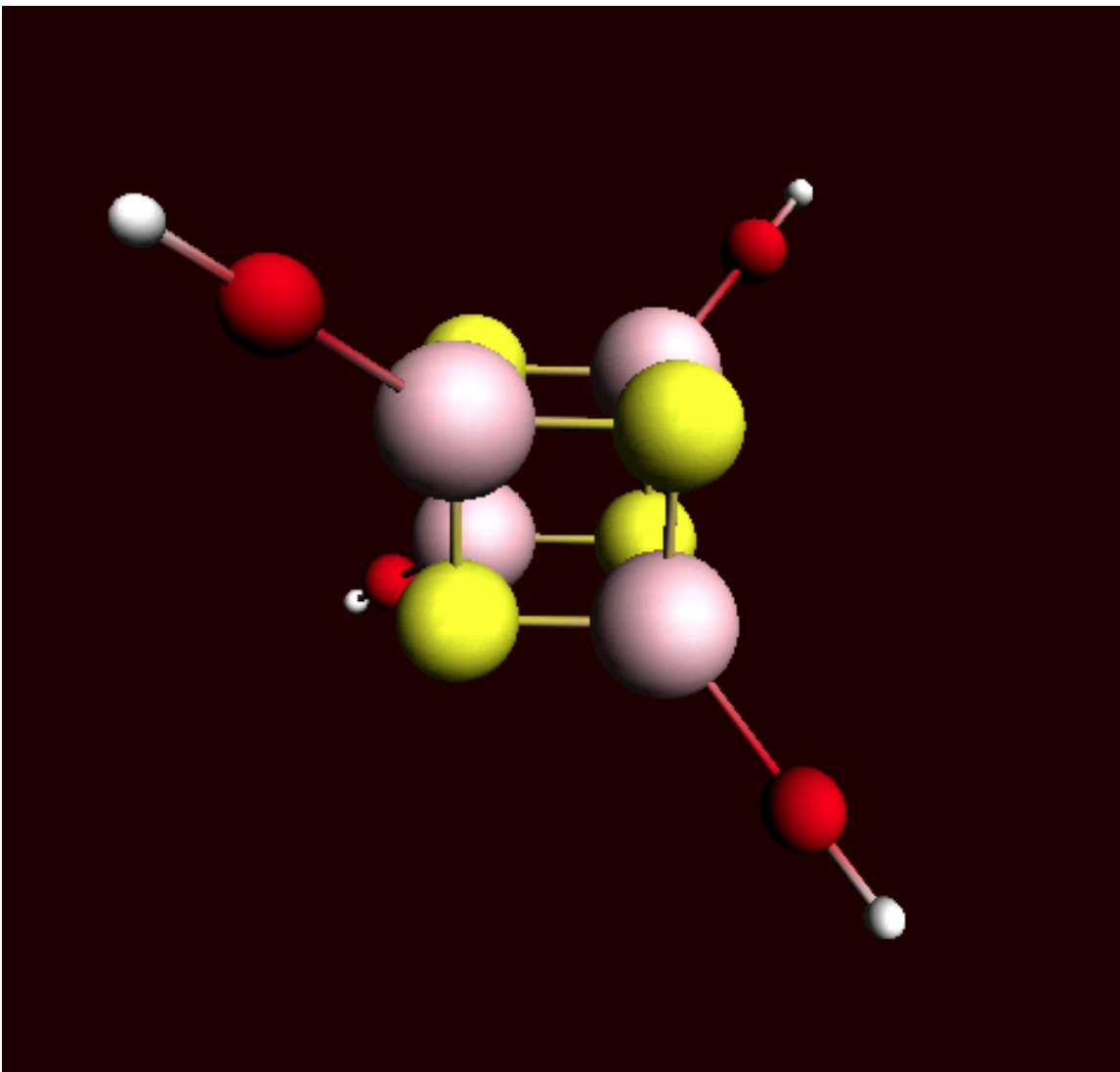
Switch to the Main Options panel

Add hydrogens to them 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

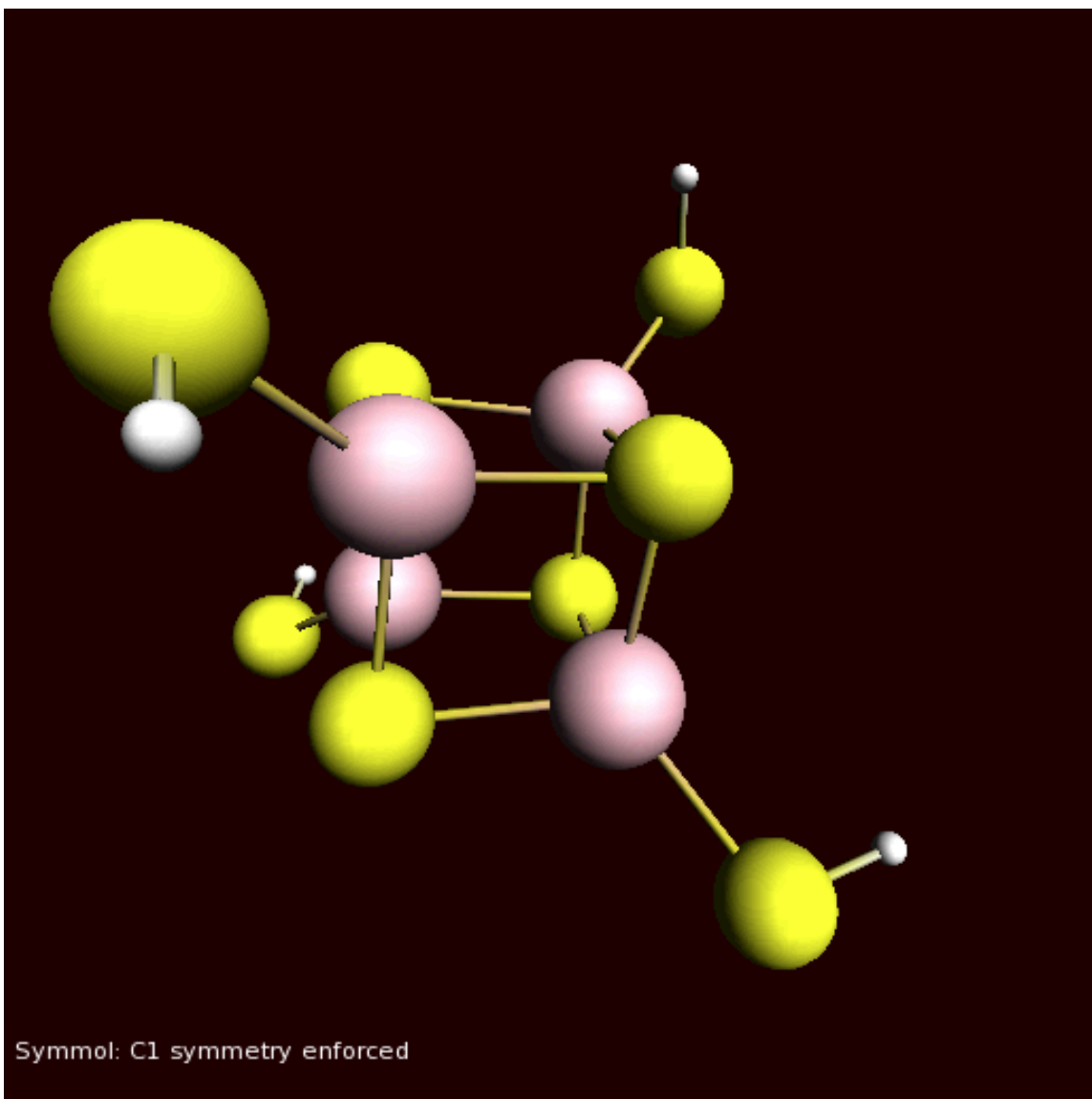
Pre-optimize this structure (the gear wheel tool)

Repeat pre-optimizing until the geometry has converged

(note that the iteration limit is 200 iterations, so if it halts at iteration 200 it normally is not yet converged)

Click the Symmetrize button (the star) to check the symmetry

If the symmetry is not C1, move the hydrogens around, pre-optimize again, etc, until you get a C1 structure.



## Step 2: Obtain the solution for the high-spin (HS) state of the cubane

In  $\text{Fe}_4\text{S}_4$  systems, the iron sites are commonly high-spin ferric ( $\text{Fe}^{3+}$ ,  $S = 2$ ) or ferrous ( $\text{Fe}^{2+}$ ,  $S = 5/2$ ). 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  $\text{Fe}_4\text{S}_4$  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  $\text{Fe}_4\text{S}_4$ , 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 antiparallel. 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 'Main Options' panel

Set the total charge to -2 and spin polarization to 18 (corresponds to  $S = 9$ ).

Check the unrestricted option to 'Yes'.

Run this set-up (use the name FeS\_HS when saving)

ADFtail window will popup showing the progress of the job:

```

SCM File Edit Help
<Sep20-2010> <15:15:27> >>>> POPAN
<Sep20-2010> <15:15:27> >>>> DEBYE
<Sep20-2010> <15:15:27> NORMAL TERMINATION
<Sep20-2010> <15:15:27> END
<Sep20-2010> <15:15:29> ADF 2010.01 RunTime: Sep20-2010 15:15:29
<Sep20-2010> <15:15:29> *** (NO TITLE) ***
<Sep20-2010> <15:15:29> RunType : SINGLE POINT
<Sep20-2010> <15:15:29> Net Charge: -2 (Nuclei minus Electrons)
<Sep20-2010> <15:15:29> Spin polar: 18 (Spin_A minus Spin_B electrons)
<Sep20-2010> <15:15:29> Symmetry : NOSYM
<Sep20-2010> <15:15:29> >>>> FRAGM
<Sep20-2010> <15:15:29> >>>> CORORT
<Sep20-2010> <15:15:29> >>>> FITINT
<Sep20-2010> <15:15:32> >>>> CLSMAT
<Sep20-2010> <15:15:32> >>>> ORTHON
<Sep20-2010> <15:15:32> >>>> GENPT
<Sep20-2010> <15:15:32> Acc.Num.Int.= 4.000
<Sep20-2010> <15:15:33> Block Length= 128
<Sep20-2010> <15:15:33> >>>> PTBAS
<Sep20-2010> <15:15:34> >>>> CYCLE
<Sep20-2010> <15:15:36> 1
<Sep20-2010> <15:15:39> 2 ErrMat 2.52368452 MaxEl 0.32751327
<Sep20-2010> <15:15:41> 3 ErrMat 2.02424258 MaxEl 0.31060821
<Sep20-2010> <15:15:44> 4 ErrMat 1.94804267 MaxEl 0.43365995
<Sep20-2010> <15:15:46> 5 ErrMat 2.95830338 MaxEl -0.48775316
<Sep20-2010> <15:15:48> 6 ErrMat 2.30438831 MaxEl -0.44493490
<Sep20-2010> <15:15:51> 7 ErrMat 1.50415929 MaxEl 0.18480719
<Sep20-2010> <15:15:53> 8 ErrMat 1.31971479 MaxEl 0.26507085
<Sep20-2010> <15:15:56> 9 ErrMat 2.05819300 MaxEl -0.39126883
<Sep20-2010> <15:15:58> 10 ErrMat 1.06816704 MaxEl -0.20561600
<Sep20-2010> <15:16:00> 11 ErrMat 0.37515157 MaxEl -0.06270057
<Sep20-2010> <15:16:03> 12 ErrMat 0.31795025 MaxEl -0.05067647
<Sep20-2010> <15:16:05> 13 ErrMat 0.49433275 MaxEl -0.07828158
<Sep20-2010> <15:16:07> 14 ErrMat 0.13714327 MaxEl 0.02826447
<Sep20-2010> <15:16:09> 15 ErrMat 0.12423769 MaxEl 0.02155456
<Sep20-2010> <15:16:12> 16 ErrMat 0.10857524 MaxEl 0.02113806
<Sep20-2010> <15:16:14> 17 ErrMat 0.02547472 MaxEl -0.00448935
<Sep20-2010> <15:16:17> 18 ErrMat 0.01631663 MaxEl 0.00318341
<Sep20-2010> <15:16:19> 19 ErrMat 0.00260205 MaxEl 0.00046400
<Sep20-2010> <15:16:21> 20 ErrMat 0.00245201 MaxEl 0.00040143
<Sep20-2010> <15:16:24> 21 ErrMat 0.00086766 MaxEl -0.00014596
<Sep20-2010> <15:16:26> 22 ErrMat 0.00047173 MaxEl -0.00008045
<Sep20-2010> <15:16:28> 23 ErrMat 0.00031002 MaxEl -0.00005440
<Sep20-2010> <15:16:31> 24 ErrMat 0.00004548 MaxEl -0.00000849
<Sep20-2010> <15:16:33> 25 ErrMat 0.00004454 MaxEl -0.00000668
<Sep20-2010> <15:16:35> 26 ErrMat 0.00000946 MaxEl 0.00000157
<Sep20-2010> <15:16:38> 27 ErrMat 0.00000320 MaxEl -0.00000069
<Sep20-2010> <15:16:38> SCF converged
<Sep20-2010> <15:16:40> 28 ErrMat 0.00000279 MaxEl -0.00000053
<Sep20-2010> <15:16:41> >>>> TOTEN
<Sep20-2010> <15:16:46> >>>> POPAN
<Sep20-2010> <15:16:46> >>>> DEBYE
<Sep20-2010> <15:16:47> >>>> AMETS
<Sep20-2010> <15:16:47> Bond Energy LDA -3.11113238 a.u.
<Sep20-2010> <15:16:47> Bond Energy LDA -84.65821938 eV
<Sep20-2010> <15:16:47> >>>> POPUL
<Sep20-2010> <15:16:47> NORMAL TERMINATION
<Sep20-2010> <15:16:47> END
Job FeS_HS has finished

```

On modern computers, the SCF solution for our job should be obtained within a few minutes (you should get the 'SCF converged' message). The ADFtail snapshot above shows that the convergence has been obtained in 28 SCF cycles.

### Step 3: Couple the spins in Fe<sub>4</sub>S<sub>4</sub> using the SpinFlip option

While SCF solution for the high-spin (HS) state of a multi-center spin system can often be easily found, this solution does not necessarily correspond to the lowest energy state.

To generate the solution with the desired collinear spin arrangement, one option is to use the 'SpinFlip' concept that has been earlier introduced by L. Noodleman and coworkers. In this two step procedure:

- first the spin-unrestricted HS solution is generated with all the site spins ferromagnetically coupled in one direction (all spins up, ↑).
- Next the  $\alpha$  (↑) and  $\beta$  (↓) electron densities centered at the sites which are expected to be antiferromagnetically coupled (spins down, ↓) to the total spin vector are exchanged for the earlier obtained HS solution, using the SpinFlip option, and the calculation is restarted.

Because this approach often results in lowering the electronic symmetry of the system while retaining its structural symmetry, a solution obtained in such way is often called the broken symmetry (BS) state. In such cases you will need to make sure that your BS calculation is done with lower symmetry. In the current tutorial this is not an issue as we have forced the structure to have no symmetry.

The concept of SpinFlip and BS state can be illustrated considering our iron-sulfur cubane case with two ferric ( $\text{Fe}^{3+}$ ,  $S = 2$ ) and two ferrous ( $\text{Fe}^{2+}$ ,  $S = 5/2$ ) sites. One of the well-characterized BS states for this level of Fe<sub>4</sub>S<sub>4</sub> oxidation corresponds to  $S = (5/2 + 2) - (5/2 + 2) = 0$ , 2↑:2↓.

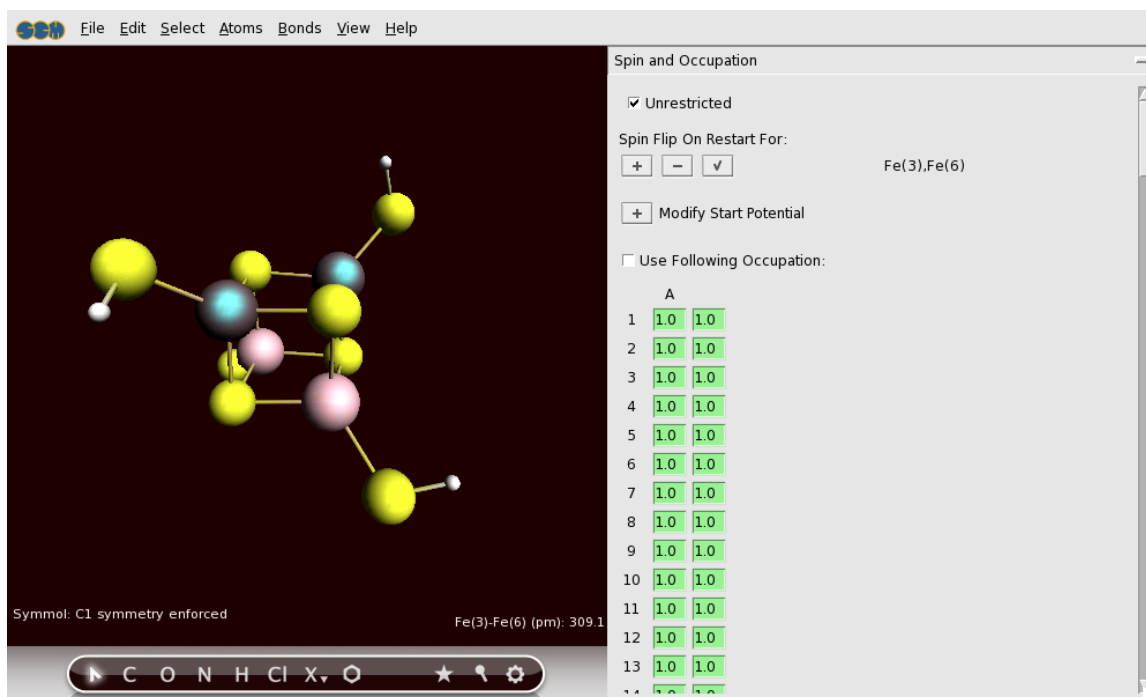
Select the ADFinput window with your FeS\_HS calculation  
Make sure the 'Main Options' panel is visible  
Change the spin polarization from 18 to 0.

This spin polarization setting corresponds to  $S = 0$  zero spin of the BS electronic state.

Select the 'Spin and Occupation' panel

For your information, ADFlevels will show the levels from your previous calculation. As we are not changing the occupations this info is not needed for this tutorial.

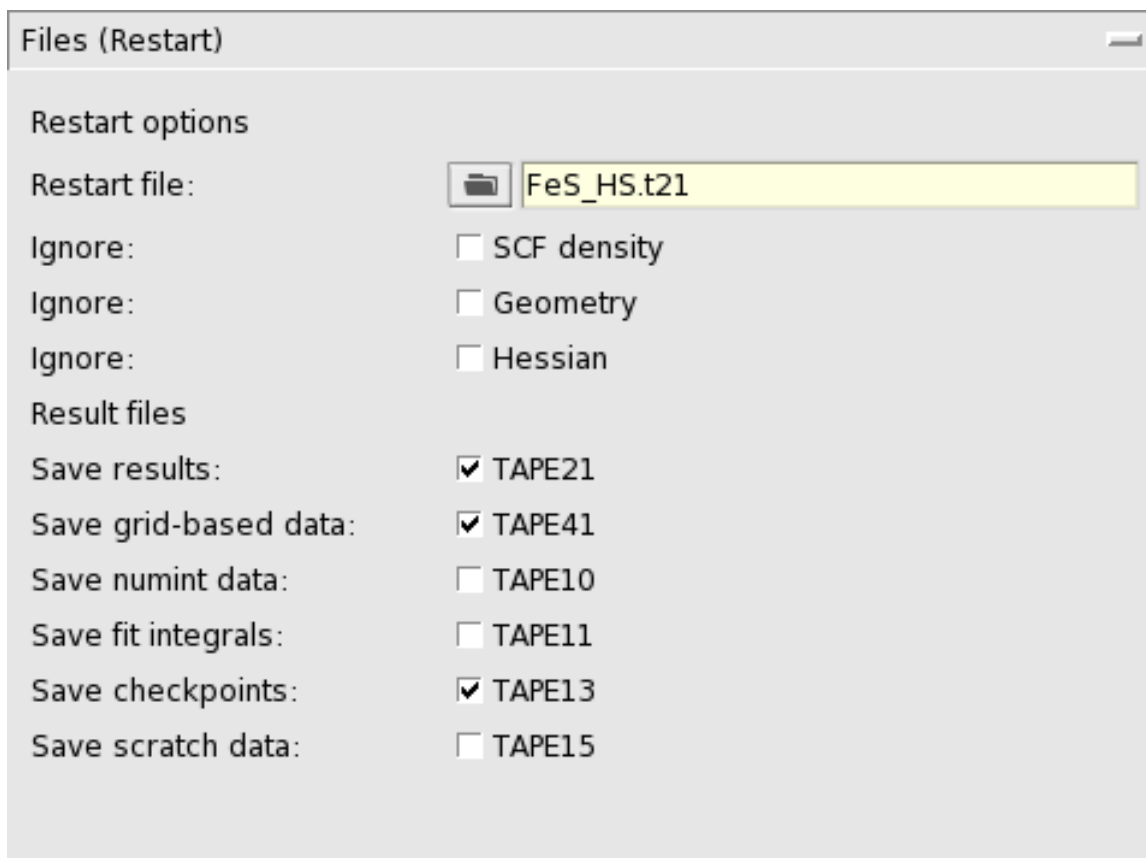
Select the two (out of four) arbitrary Fe sites in the drawing area,  
click **+** next to the **Spin Flip on Restart For:** line.



To achieve the desired BS solution, the SpinFlip procedure should be applied to 2 out of 4 Fe sites of Fe<sub>4</sub>S<sub>4</sub>. In the above example, we selected sites Fe(6) and Fe(8). This will instruct SpinFlip algorithm to interchange  $\alpha$  ( $\uparrow$ ) and  $\beta$  ( $\downarrow$ ) 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:

Select the 'Files (Restart)' panel  
 Close the ADFLevels window  
 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.

Use the **File** → **Save As** command to save the job as FeS\_BS\_SPINFLIP  
Run the calculation



```

<Sep20-2010> <15:27:07> >>>> PTBAS
<Sep20-2010> <15:27:08> >>>> CYCLE
<Sep20-2010> <15:27:10> 1
<Sep20-2010> <15:27:12> 2 ErrMat 0.32490954 MaxEl 0.05169968
<Sep20-2010> <15:27:15> 3 ErrMat 0.58550337 MaxEl 0.08023247
<Sep20-2010> <15:27:17> 4 ErrMat 1.20144200 MaxEl 0.26466420
<Sep20-2010> <15:27:19> 5 ErrMat 0.71799723 MaxEl 0.16782580
<Sep20-2010> <15:27:22> 6 ErrMat 0.20514793 MaxEl -0.02707174
<Sep20-2010> <15:27:24> 7 ErrMat 0.30922344 MaxEl -0.09024768
<Sep20-2010> <15:27:27> 8 ErrMat 0.38808278 MaxEl 0.09015208
<Sep20-2010> <15:27:29> 9 ErrMat 0.10304207 MaxEl 0.03174216
<Sep20-2010> <15:27:32> 10 ErrMat 0.10553319 MaxEl 0.03399937
<Sep20-2010> <15:27:34> 11 ErrMat 0.09158390 MaxEl 0.02804178
<Sep20-2010> <15:27:37> 12 ErrMat 0.07719708 MaxEl 0.02484010
<Sep20-2010> <15:27:39> 13 ErrMat 0.02632009 MaxEl 0.00742002
<Sep20-2010> <15:27:41> 14 ErrMat 0.02348825 MaxEl -0.00514131
<Sep20-2010> <15:27:44> 15 ErrMat 0.00330401 MaxEl 0.00085485
<Sep20-2010> <15:27:46> 16 ErrMat 0.00140216 MaxEl -0.00024730
<Sep20-2010> <15:27:49> 17 ErrMat 0.00170324 MaxEl 0.00031769
<Sep20-2010> <15:27:51> 18 ErrMat 0.00037642 MaxEl 0.00009702
<Sep20-2010> <15:27:53> 19 ErrMat 0.00011027 MaxEl 0.00001877
<Sep20-2010> <15:27:56> 20 ErrMat 0.00017981 MaxEl 0.00004861
<Sep20-2010> <15:27:58> 21 ErrMat 0.00015721 MaxEl -0.00003307
<Sep20-2010> <15:28:00> 22 ErrMat 0.00004894 MaxEl 0.00001310
<Sep20-2010> <15:28:03> 23 ErrMat 0.00005444 MaxEl -0.00001400
<Sep20-2010> <15:28:05> 24 ErrMat 0.00001466 MaxEl 0.00000251
<Sep20-2010> <15:28:07> 25 ErrMat 0.00002369 MaxEl 0.00000654
<Sep20-2010> <15:28:10> 26 ErrMat 0.00000482 MaxEl -0.00000056
<Sep20-2010> <15:28:10> SCF converged
<Sep20-2010> <15:28:12> 27 ErrMat 0.00000242 MaxEl 0.00000063
<Sep20-2010> <15:28:13> >>>> TOTEN
<Sep20-2010> <15:28:18> >>>> POPAN
<Sep20-2010> <15:28:18> >>>> DEBYE
<Sep20-2010> <15:28:19> >>>> AMETS
<Sep20-2010> <15:28:19> Bond Energy LDA -3.17626613 a.u.
<Sep20-2010> <15:28:19> Bond Energy LDA -86.43059906 eV
<Sep20-2010> <15:28:19> >>>> POPUL
<Sep20-2010> <15:28:19> NORMAL TERMINATION
<Sep20-2010> <15:28:19> END
Job FeS_BS_SPINFLIP has finished

```

As displayed in the ADFtail window, our FeS\_BS\_SPINFLIP job converges in 27 cycles.

## Step 4: Coupling the spins using the ModifyStartPotential option

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- $\alpha$  and spin- $\beta$  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- $\alpha$  and spin- $\beta$  electrons, correspondingly, associated with a Fe site.

The practical guide to obtain this BS solution via MODIFYSTARTPOTENTIAL in ADF is given below.

```

Open your FeS_HS calculation in ADFinput
Change the spin polarization from 18 to 0
Open the Spin and Occupations panel
Select the four Fe atoms
Click the '+' in front of 'Modify Start Potential'

```

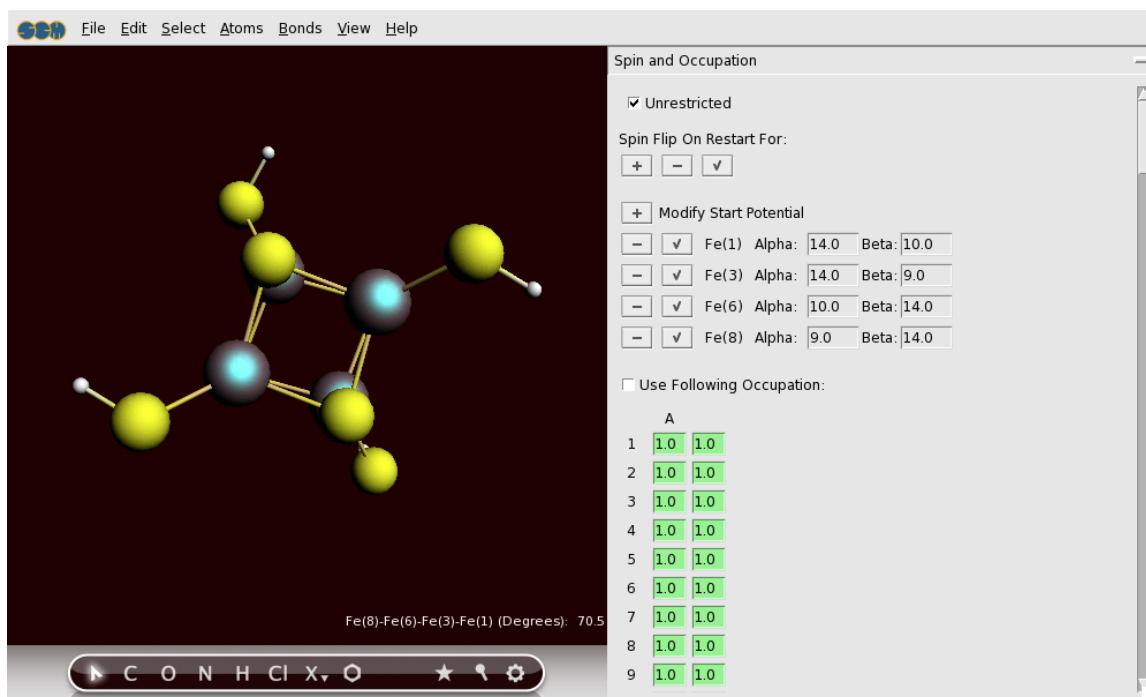
Set the alpha and beta occupations, for the four Fe atoms:

14 alpha and 10 beta

14 alpha and 9 beta

10 alpha and 14 beta

9 alpha and 14 beta



For the spin-up  $\text{Fe}^{3+}$ ,  $S = 2$ , the alpha and beta numbers would be 14 and 9, correspondingly, and for the spin-up  $\text{Fe}^{2+}$ ,  $S = 5/2$ , 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  $\text{Fe}_4\text{S}_4$  oxidation corresponds to  $S = (5/2 + 2) - (5/2 + 2) = 0$ ,  $2\uparrow:2\downarrow$ .

Note that SCF procedure might be problematic in this case. You should experiment how to solve the convergence problems. First you should try with some mixing and level shifting:

Select the 'SCF Convergence Aids' panel

Set **Mixing** value to 0.1

Set **Level Shift** to 0.3 Hartree

Use the **File** → **Save As** command to Save the job as `FeS_BS_MODIFYSTARTPOTENTIAL`

Run your calculation

If your calculation converges, you are ready. If not, try the ARH method:

Select the 'SCF Convergence Aids' panel

Make the Mixing and Level Shift fields empty (that is, undo your previous changes)

Select the 'SCF' panel

Select Yes for the 'Use ARH method' option

Change the maximum number of SCF iterations to 100

Save the job as `FeS_BS_MODIFYSTARTPOTENTIAL` (using the 'File → Save' command)

Run your calculation (this will take some time,  
but normally will converge after many iterations)

```

SCF File Edit Help
<Sep20-2010> <15:57:40> -8222.5636807736
<Sep20-2010> <15:57:46> 121 0.00145697 0.00024445 -8222.5636839701
<Sep20-2010> <15:57:52> 122 0.00628269 0.00083055 -8222.5636801919
<Sep20-2010> <15:57:58> 123 0.00196116 0.00024019 -8222.5636770236
<Sep20-2010> <15:58:04> 124 0.00576716 0.00090416 -8222.5636794114
<Sep20-2010> <15:58:10> 125 0.00274988 0.00040716 -8222.5636743185
<Sep20-2010> <15:58:16> 126 0.00733409 0.00144858 -8222.5636785082
<Sep20-2010> <15:58:22> 127 0.00270189 0.00040705 -8222.5636487377 REDO
<Sep20-2010> <15:58:25> -8222.5636708740
<Sep20-2010> <15:58:31> 128 0.00572331 0.00087884 -8222.5636821657
<Sep20-2010> <15:58:37> 129 0.00453036 0.00076953 -8222.5636652761 REDO
<Sep20-2010> <15:58:40> -8222.5636758545
<Sep20-2010> <15:58:46> 130 0.00285584 0.00031534 -8222.5636777343
<Sep20-2010> <15:58:52> 131 0.00431019 0.00058680 -8222.5636762712
<Sep20-2010> <15:58:58> 132 0.00832472 0.00141499 -8222.5636666780 REDO
<Sep20-2010> <15:59:02> -8222.5636802340
<Sep20-2010> <15:59:08> 133 0.00441828 0.00078298 -8222.5636814799
<Sep20-2010> <15:59:14> 134 0.00206569 0.00026623 -8222.5636553835 REDO
<Sep20-2010> <15:59:18> -8222.5636778794
<Sep20-2010> <15:59:24> 135 0.00155488 0.00018245 -8222.5636805981
<Sep20-2010> <15:59:30> 136 0.00374164 0.00076403 -8222.5636811209
<Sep20-2010> <15:59:36> 137 0.00463595 0.00064105 -8222.5636562424 REDO
<Sep20-2010> <15:59:40> -8222.5636789365
<Sep20-2010> <15:59:45> 138 0.00110608 0.00013020 -8222.5636796972
<Sep20-2010> <15:59:51> 139 0.00112397 0.00016513 -8222.5636756790
<Sep20-2010> <15:59:57> 140 0.00209881 0.00037602 -8222.5636786902
<Sep20-2010> <16:00:03> 141 0.00089181 0.00014646 -8222.5636798678
<Sep20-2010> <16:00:10> 142 0.00125649 0.00015429 -8222.5636790675
<Sep20-2010> <16:00:15> 143 0.00516446 0.00099032 -8222.5636802385
<Sep20-2010> <16:00:22> 144 0.00120300 0.00025424 -8222.5636774060
<Sep20-2010> <16:00:28> 145 0.00096117 0.00009280 -8222.5636803605
<Sep20-2010> <16:00:28> Done Augmented Roothaan-Hall iterations
<Sep20-2010> <16:00:30> 3
<Sep20-2010> <16:00:32> 4 ErrMat 0.04613917 MaxEl 0.00957361
<Sep20-2010> <16:00:35> 5 ErrMat 0.15924073 MaxEl -0.04005460
<Sep20-2010> <16:00:37> 6 ErrMat 0.15802423 MaxEl 0.03737600
<Sep20-2010> <16:00:40> 7 ErrMat 0.04045068 MaxEl -0.00604023
<Sep20-2010> <16:00:42> 8 ErrMat 0.00348183 MaxEl -0.00055829
<Sep20-2010> <16:00:44> 9 ErrMat 0.01022975 MaxEl -0.00302571
<Sep20-2010> <16:00:47> 10 ErrMat 0.00452497 MaxEl 0.00088367
<Sep20-2010> <16:00:49> 11 ErrMat 0.00027810 MaxEl 0.00005423
<Sep20-2010> <16:00:52> 12 ErrMat 0.00019118 MaxEl 0.00006169
<Sep20-2010> <16:00:54> 13 ErrMat 0.00004458 MaxEl -0.00000863
<Sep20-2010> <16:00:57> 14 ErrMat 0.00003189 MaxEl -0.00000799
<Sep20-2010> <16:00:59> 15 ErrMat 0.00000932 MaxEl 0.00000180
<Sep20-2010> <16:01:01> 16 ErrMat 0.00000597 MaxEl 0.00000136
<Sep20-2010> <16:01:04> 17 ErrMat 0.00000201 MaxEl -0.00000044
<Sep20-2010> <16:01:04> SCF converged
<Sep20-2010> <16:01:06> 18 ErrMat 0.00000247 MaxEl -0.00000057
<Sep20-2010> <16:01:07> >>>> TOTEN
<Sep20-2010> <16:01:13> >>>> POPAN
<Sep20-2010> <16:01:13> >>>> DEBYE
<Sep20-2010> <16:01:13> >>>> AMETS
<Sep20-2010> <16:01:13> Bond Energy LDA -3.17733174 a.u.
<Sep20-2010> <16:01:13> Bond Energy LDA -86.45959568 eV
<Sep20-2010> <16:01:13> >>>> POPUL
<Sep20-2010> <16:01:13> NORMAL TERMINATION
<Sep20-2010> <16:01:14> END
Job FeS_BS_MODIFYSTARTPOTENTIAL has finished

```

Hopefully you will be able to converge the job, to the same energy and state as the SpinFlip job.

Thus both the SpinFlip and the ModifyStartPotential option allow you to obtain a desired Fe spin coupling pattern in the Fe<sub>4</sub>S<sub>4</sub> case. While SpinFlip is a two-step approach and ModifyStartPotential works as in a single step, the SpinFlip approach shows a better performance during SCF (much better and faster SCF convergence).

## Step 5: View the spin density of the broken symmetry (BS) solutions

In the two previous steps of this tutorial, we have generated the broken symmetry (BS) solution for the Fe<sub>4</sub>S<sub>4</sub> cubane using alternatively the SpinFlip and ModifyStartPotential options. Here, we will analyze this BS solution viewing the Fe spin densities using ADFview, and confirm that the spin alignment of the iron sites is 2↑:2↓. This type of analysis can also be powerfully used during presentations and for scientific illustrations.

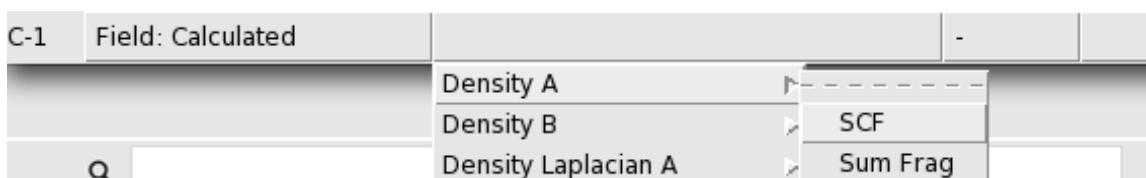
Select your FeS\_BS\_SPINFLIP calculation in ADFjobs  
Use the **SCM** → **View** menu command to activate ADFview

You should see the [Fe<sub>4</sub>S<sub>4</sub>(SH)<sub>4</sub>]<sup>2-</sup> model in the ADFview window now. We have optionally selected FeS\_BS\_SPINFLIP.t21, while FeS\_BS\_MODIFYSTARTPOTENTIAL.t21 could also be used for this purpose.

Use the **Fields** → **Calculated** menu command

Now, you should see the two blank tab fields right to the **Field:Calculated** at the bottom of the ADFview window, separated by the minus '-' sign.

Click the left blank tab menu and select **Density A** → **SCF** check box:



ADFview will take a moment now to calculate the corresponding density for spin- $\alpha$  ('Density A') electrons.

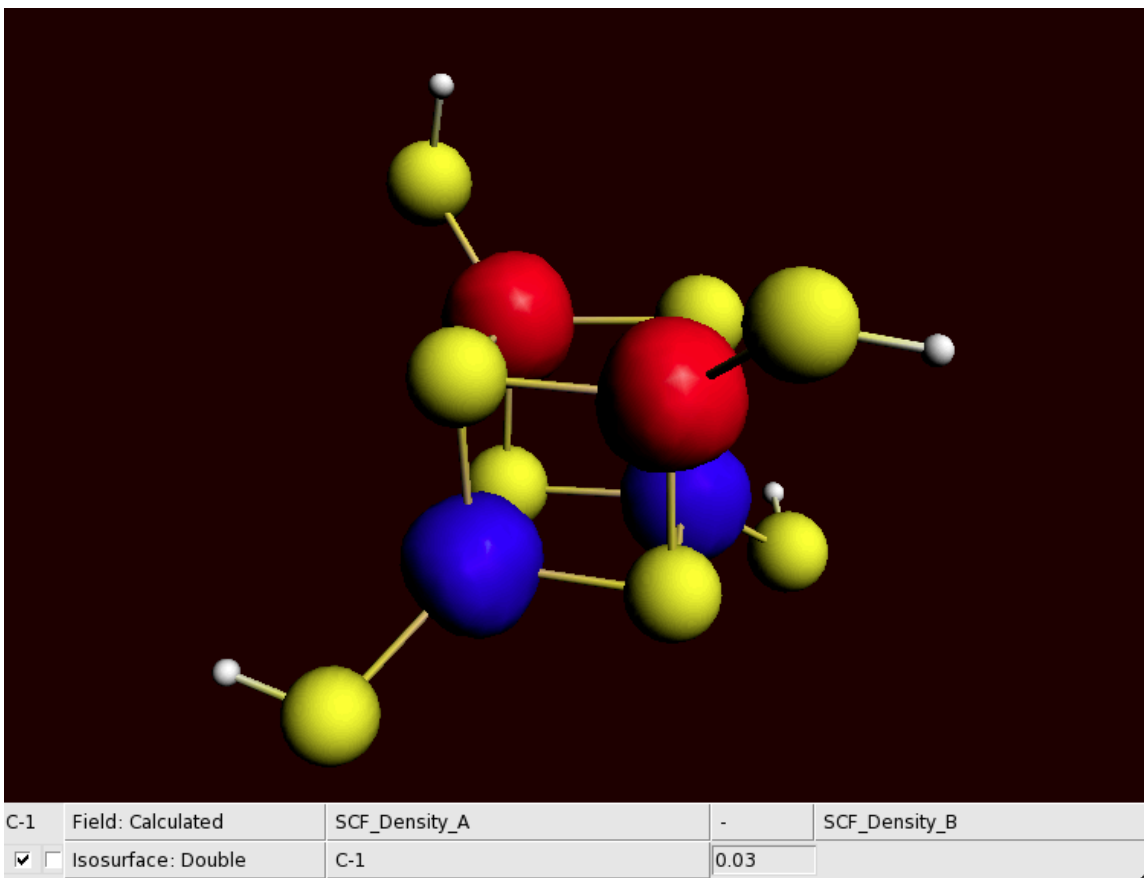
Next, click the right blank tab menu and select **Density B** → **SCF** check box.

Note that the minus '-' sign separating the tabs implies that we have requested ADFview to calculate the 'spin- $\alpha$  - spin- $\beta$ ' density field. ADFview automatically assigns 'C-1' title to this field, see left to the **Field:Calculated**. We will visualize this 'C-1' field using one of the available ADFview options now.

Click the **Add** drop-down menu and select **Isosurface: Double (+/-)**

In the new control line, select the **Other** → **1** → **C-1** field

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



In the same way you can also confirm that for the ferromagnetic HS case (file FeS\_HS.t21), the visualization of the spin densities would display all the four Fe site surrounded by the blobs of the same color.