Scientific Computing & Modelling

BAND-GUI Tutorial

ADF Program System
Release 2010

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Tutorials

Tutorial 1: with a grain of salt

According to any freshmen chemistry textbook, in NaCl one electron is transferred from the Sodium to the Chlorine. The occupied 3p states form the valence band, while the empty sodium states hybridize into a conduction band. We will put these idealized ideas to the test.

This tutorial will teach you how to:

- define the geometry of a NaCl crystal
- run the calculation
- view the band structure
- view an orbital for a particular band and k-point
- view the (partial) density of states
- view the deformation density
- view the atomic charges

The BAND-GUI has been designed to be a lot like the ADF-GUI. This makes it much easier for users to use both programs. To avoid repetition, the BAND-GUI tutorial assumes that you are familiar with some basic usage of the ADF-GUI. If you do not know how to rotate, translate, zoom etc within the ADF-GUI, please read through the first ADF-GUI tutorial before starting with this BAND-GUI tutorial. Even better: try using the ADF-GUI yourself. You can get a demo-license for this purpose if needed.

Step 1: Start BANDinput

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

```
bandinput &
```

On Windows, one can start BANDinput by double-clicking on the BANDinput icon on the Desktop:

```
double click the BANDinput icon on the Desktop
```

On Macintosh, use the ADFLaunch program to start BANDinput:

```
Double click on the ADFLaunch icon
Use the SCM → BANDinput menu command
```
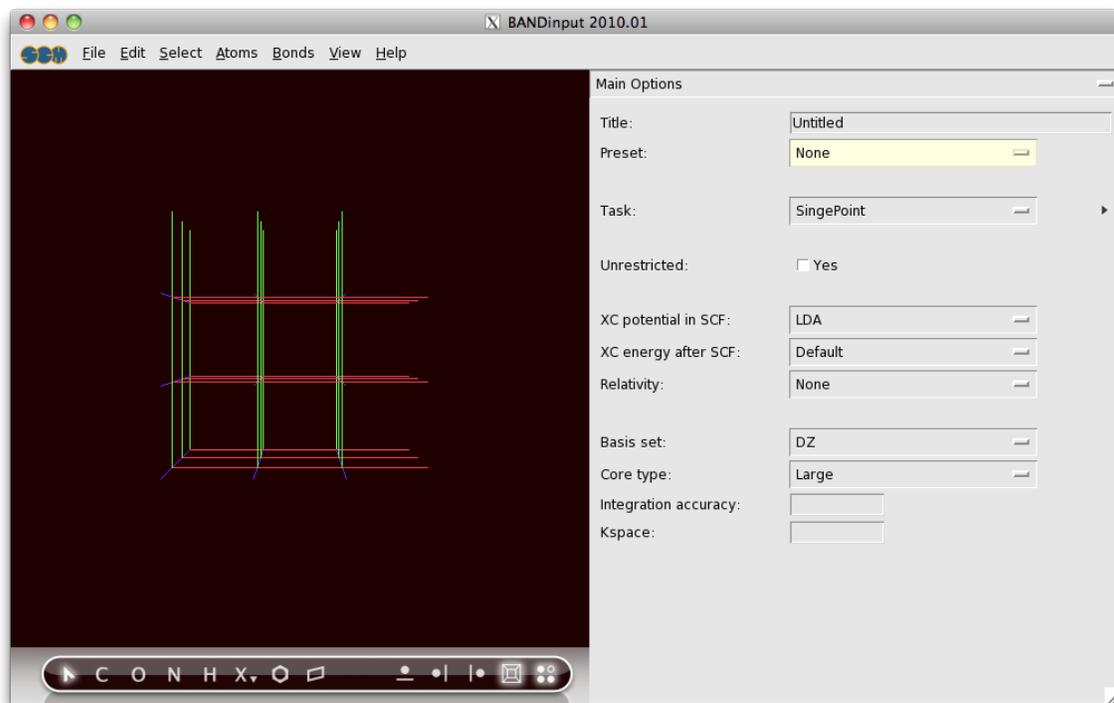
The BANDinput window consists of the following main parts:

1. the menu bar with the menu commands
2. the drawing area of the molecule/crystal editor (the area with the cubes on the middle left side)
3. the status field (on the bottom left of the black area, currently empty)
4. toolbar (at the bottom)
5. a set of selected other options (currently 'Main Options') occupying the right half of the window
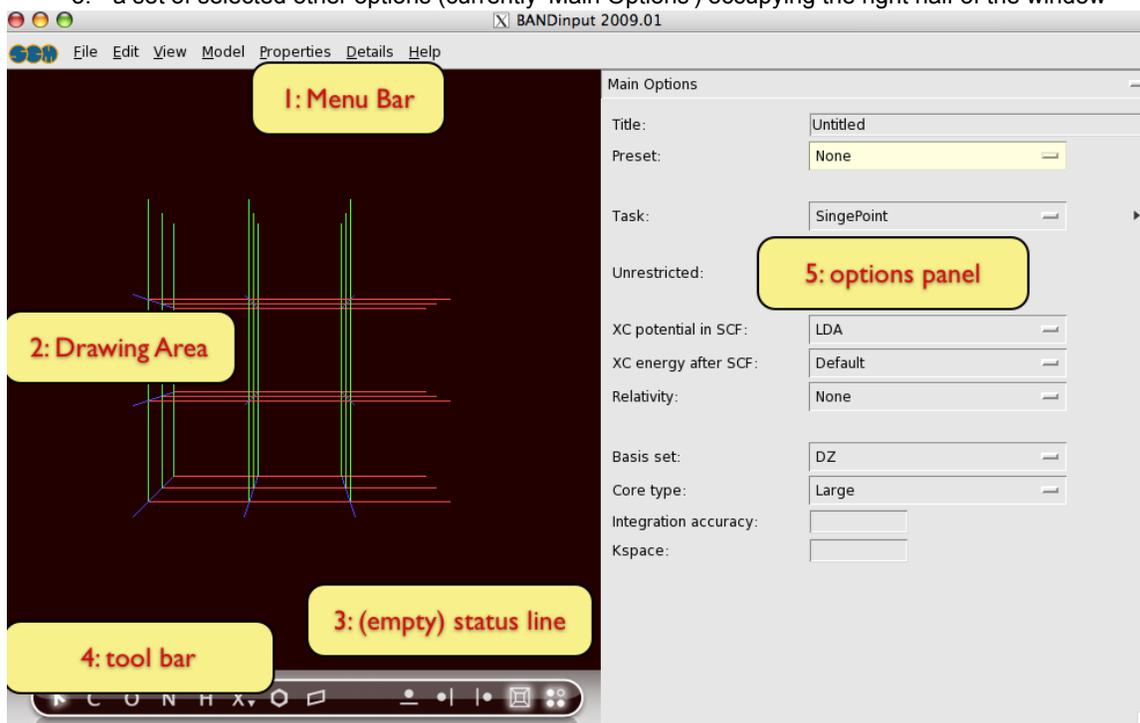
Step 2: Create the unit cell

Select the coordinates tab

```
Choose the 'Coordinates' panel with the pull-down menu
on the right (currently set to 'Main Options')
```
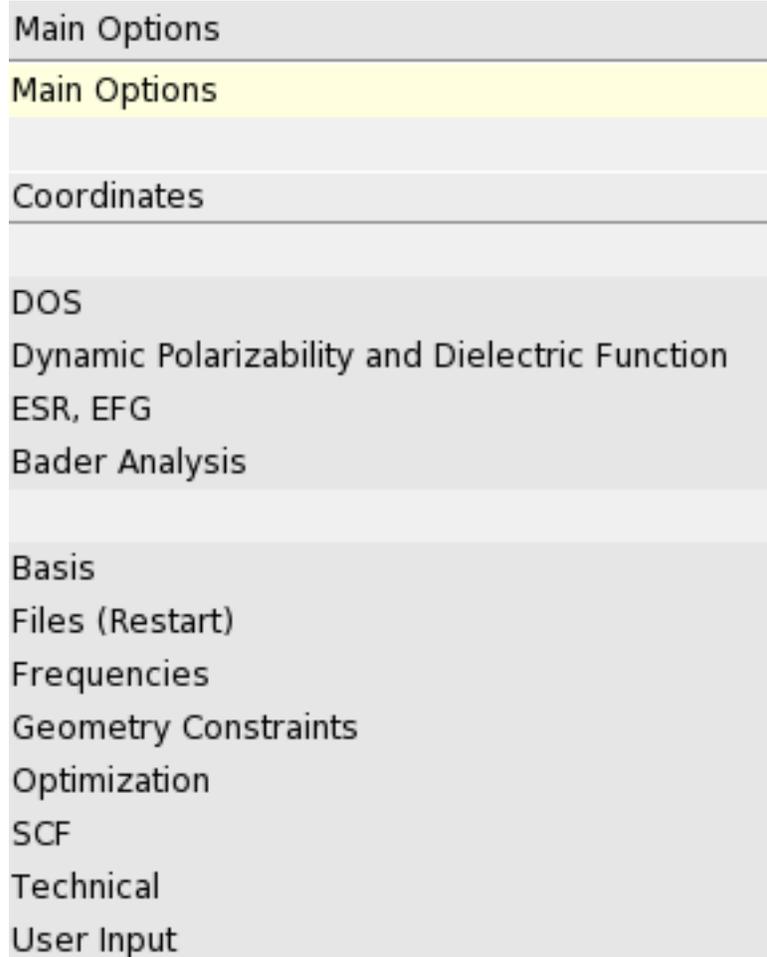

And you will invoke the coordinates panel:

Coordinates

| Periodicity: | Bulk | (lattice) |

Lattice vectors: volume: 27.0

3	0	0
0	3	0
0	0	3

☐ natural   smallest distance: ...... for atom pair: ....

The colored lines that you see in the drawing area are the lattice vectors. The first lattice vector is colored red, the second green, and the third blue. Because a number of neighboring cells are displayed you see a collection of cubes. You can enable/disable this:

Use the **View → Periodic → Repeat Unit Cells** menu command
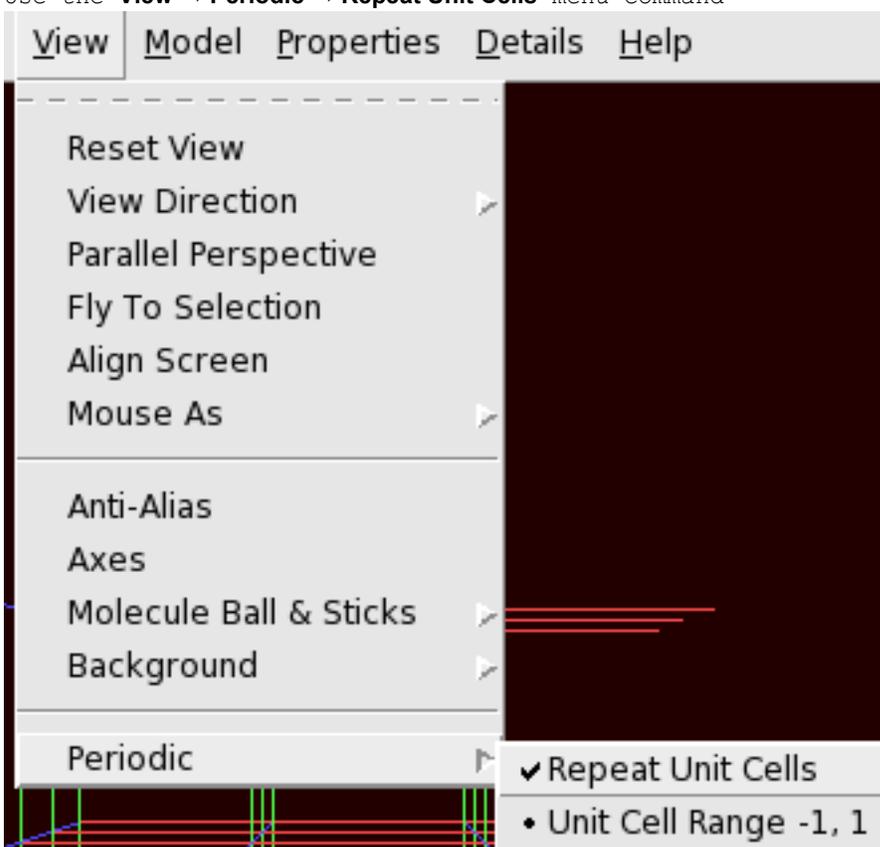
Without the repeated unit cells you see the more clearly the three lattice vectors.
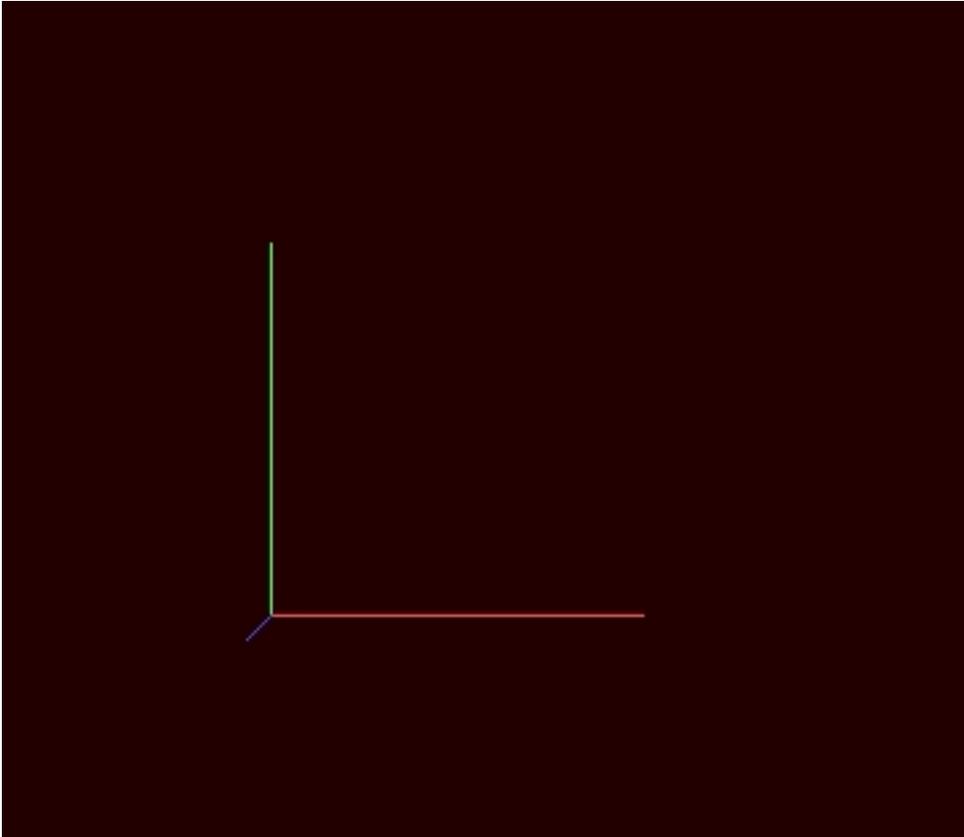
Enter lattice vectors

Salt has an fcc lattice. First we need to set the lattice vectors:

```
Enter the lattice vectors, as shown in the next picture.
To avoid the warning of a singular lattice, set first the off-diagonal
  elements to 2.75 and then the diagonal elements to zero
```

Lattice vectors:		volume: 41.6
0	2.75	2.75
2.75	0	2.75
2.75	2.75	0

Step 3: Add the atoms

Now we will add the Na and Cl atoms:

```
Make sure periodic display is turned off
Select the Sodium (Na) element tool from the periodic system
   that appears when you click the 'X' element on the toolbar
```

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup	Uuh	Uus	Uuo

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
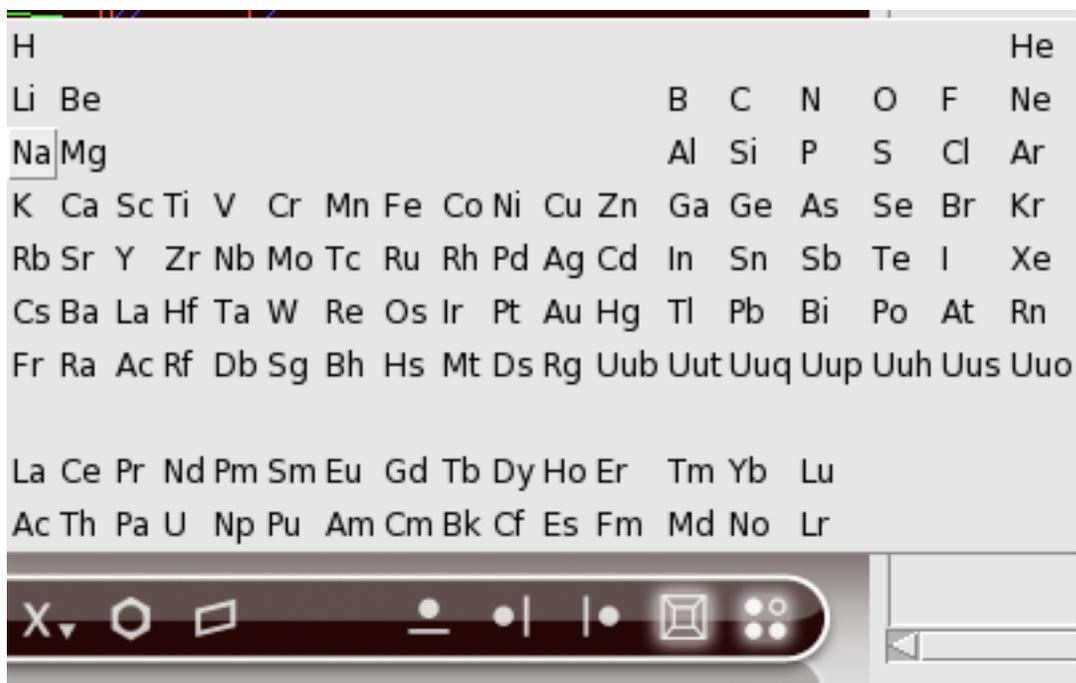
After this you see at the bottom of the screen "Na tool" in the status field:

Na tool
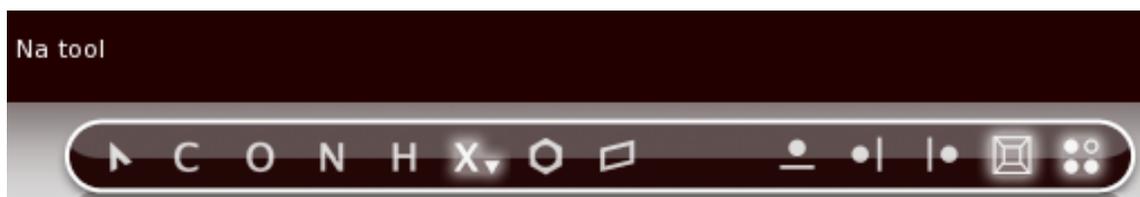
```
Click once in the drawing area, near the origin
Click once on the created atom to stop bonding
```
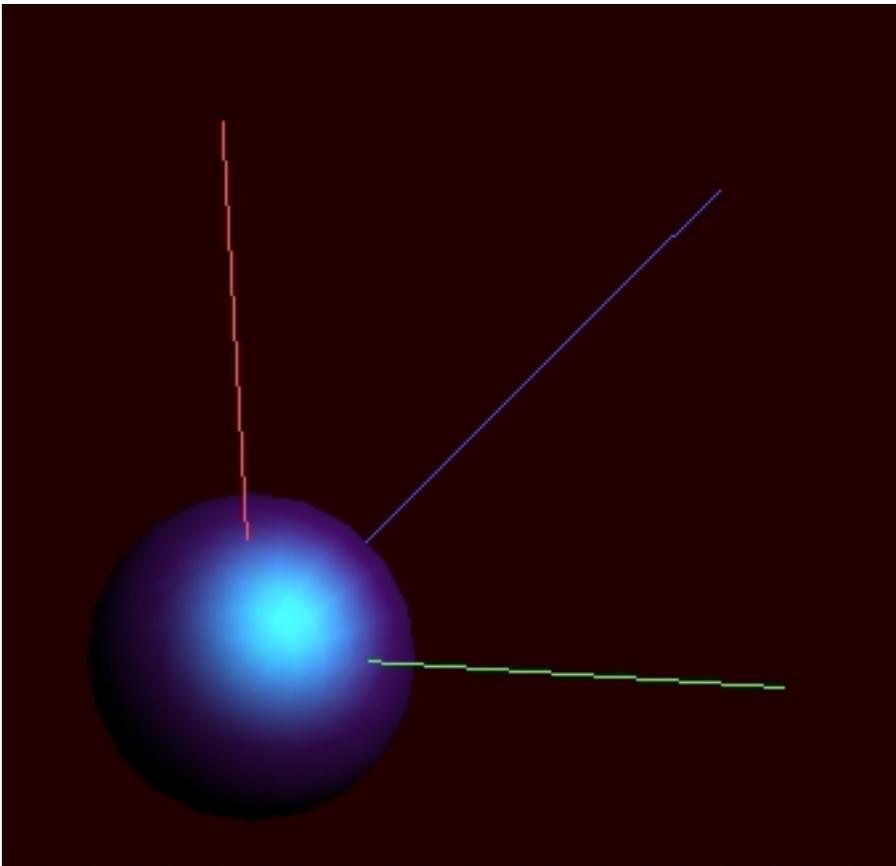
As you can see the atom is not exactly in the origin. This can be fixed if you wish:

Use the 'Set Origin' command from the 'Edit' menu

Edit | View   Model   Properties   Details

Undo   Cmd Z
Redo   Shift Cmd Z

Cut   Cmd X
Copy   Cmd C
Paste   Cmd V
Clear   Cmd B

Group   Cmd G
Ungroup   Cmd U

Set Origin

Define Super Cell...

To add the Cl atom you can proceed the same way.

```
Select the Cl tool
Click once somewhere in the unit cell
Click on the new Cl atom to stop bonding
```
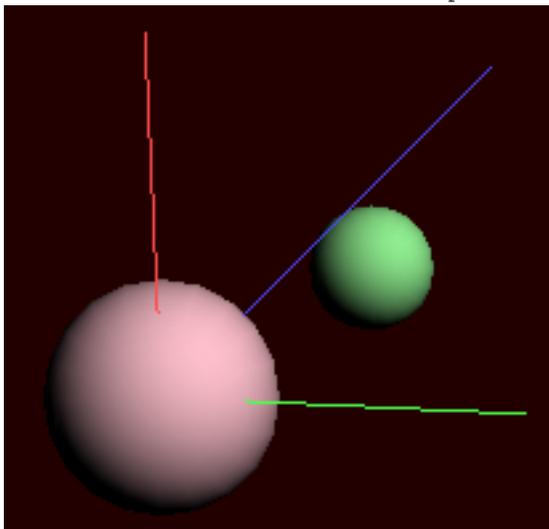
Next you should edit the Cl coordinates and change the Cl color:

```
Change the Cl coordinates to be (2.75,2.75,2.75) in the 'Coordinates' panel
Turn on periodic display (in the 'View' menu)
```

Now your system looks like:
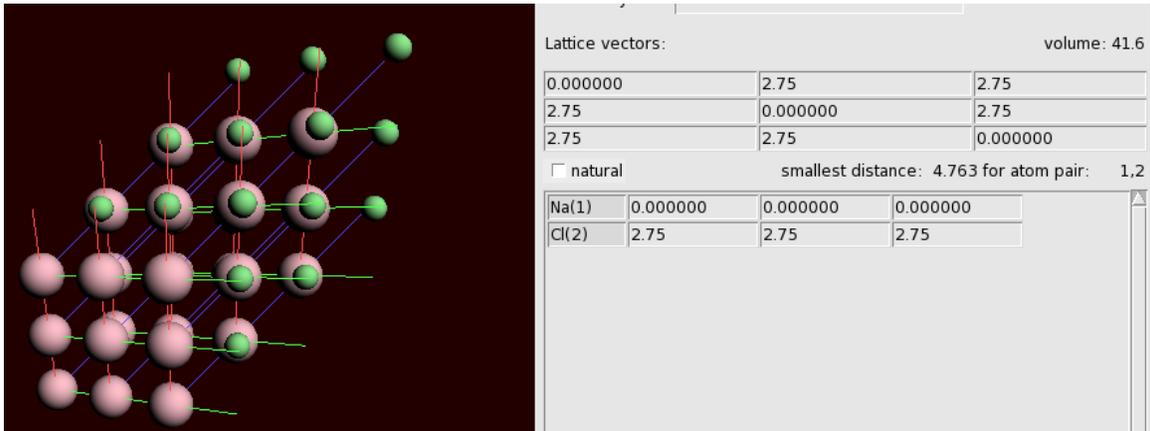
Step 4: Running the calculation

It is a good idea to give your calculation a description.

```
Go back to the "Main options" panel
Enter something appropriate in the "Title" field
Save the result with the File → Save menu command, and name it "NaCl"
Choose File → Run.
```

First, you will be asked to save the file. Name it NaCl.

A window will appear showing the progress of the BAND calculation (the 'logfile'). After a few minutes the calculation has finished, and it looks like:

```
<Sep01-2009> <13:56:50> (  1) Err Cvg T= 7.45E-02    1.00    0 Mix 2.0E-01   8.3E-03
<Sep01-2009> <13:56:50> (  2) Err Cvg T= 4.56E-02    0.78    0 Mix 2.0E-01   1.6E-04
<Sep01-2009> <13:56:50> (  3) Err Cvg T= 3.09E-02    0.71    0 Mix 2.0E-01   2.3E-04
<Sep01-2009> <13:56:50> (  4) Err Cvg T= 2.31E-02    0.69    0 Mix 2.0E-01   2.9E-04
<Sep01-2009> <13:56:50> (  5) Err Cvg T= 1.83E-02    0.70    0 Mix 2.0E-01   3.4E-04
<Sep01-2009> <13:56:51> (  6) Err Cvg T= 1.48E-02    0.72    0 Pal      2    5.0E-04
<Sep01-2009> <13:56:51> HALFWAY
<Sep01-2009> <13:56:51> (  7) Err Cvg T= 4.18E-03    0.72    0 Pal      3    5.5E-04
<Sep01-2009> <13:56:51> (  8) Err Cvg T= 1.44E-04    0.69    0 Pal      3    5.5E-04
<Sep01-2009> <13:56:51> (  9) Err Cvg T= 1.00E-04    0.62    0 Pal      3    5.6E-04
<Sep01-2009> <13:56:51> >>>> ENERGY
<Sep01-2009> <13:56:51> SCF CONVERGENCE
<Sep01-2009> <13:56:51> ( 10) Err Cvg T= 1.29E-05    0.52    0 Pal      3    5.6E-04
<Sep01-2009> <13:56:52> >>>> ENERGY
<Sep01-2009> <13:56:52> ( 11)
<Sep01-2009> <13:56:52>
<Sep01-2009> <13:56:52> Max. cycle time CP:      0.261
<Sep01-2009> <13:56:52>                 IO:      0.012
<Sep01-2009> <13:56:52>
<Sep01-2009> <13:56:52> Mean cycle time CP:      0.148
<Sep01-2009> <13:56:52>                 IO:      0.011
<Sep01-2009> <13:56:52>
<Sep01-2009> <13:56:52> final mix.par.           0.200
<Sep01-2009> <13:56:52> Approx. conv.rate:       0.000
<Sep01-2009> <13:56:52>
<Sep01-2009> <13:56:52> FERMI ENERGY:           -0.4267 A.U.
<Sep01-2009> <13:56:52>                        -11.6098 E.V
<Sep01-2009> <13:56:52> >>>> ENERGY
<Sep01-2009> <13:56:52> ENERGY OF FORMATION:    -0.2635 A.U.
<Sep01-2009> <13:56:52>                         -7.1703 E.V.
<Sep01-2009> <13:56:52>                       -165.3501 KCAL/MOL
<Sep01-2009> <13:56:52> >>>> CHARGE
<Sep01-2009> <13:56:52> >>>> HIRSH
<Sep01-2009> <13:56:52> >>>> DOS
<Sep01-2009> <13:56:52> New DOS!!!
<Sep01-2009> <13:56:52> storing all partial DOS
<Sep01-2009> <13:56:52> integrate over delta E
<Sep01-2009> <13:56:52> >>>> BZSTRUCT
<Sep01-2009> <13:56:52> NOT ALL FILES CLOSED
<Sep01-2009> <13:56:52> NORMAL TERMINATION
<Sep01-2009> <13:56:52> END
Job NaCl has finished
```

```
Wait for the text 'Job ... has finished' in the logfile
   (... will be the name of your run script)
```

The calculation has produced two files: "NaCl.out", which contains the result of the calculation in text format, the second is"NaCl.runkf" which is a binary result file.

Step 5: Examine the band structure

```
Select the SCM → BAND Structure command
```

This will open the bandstructure window:
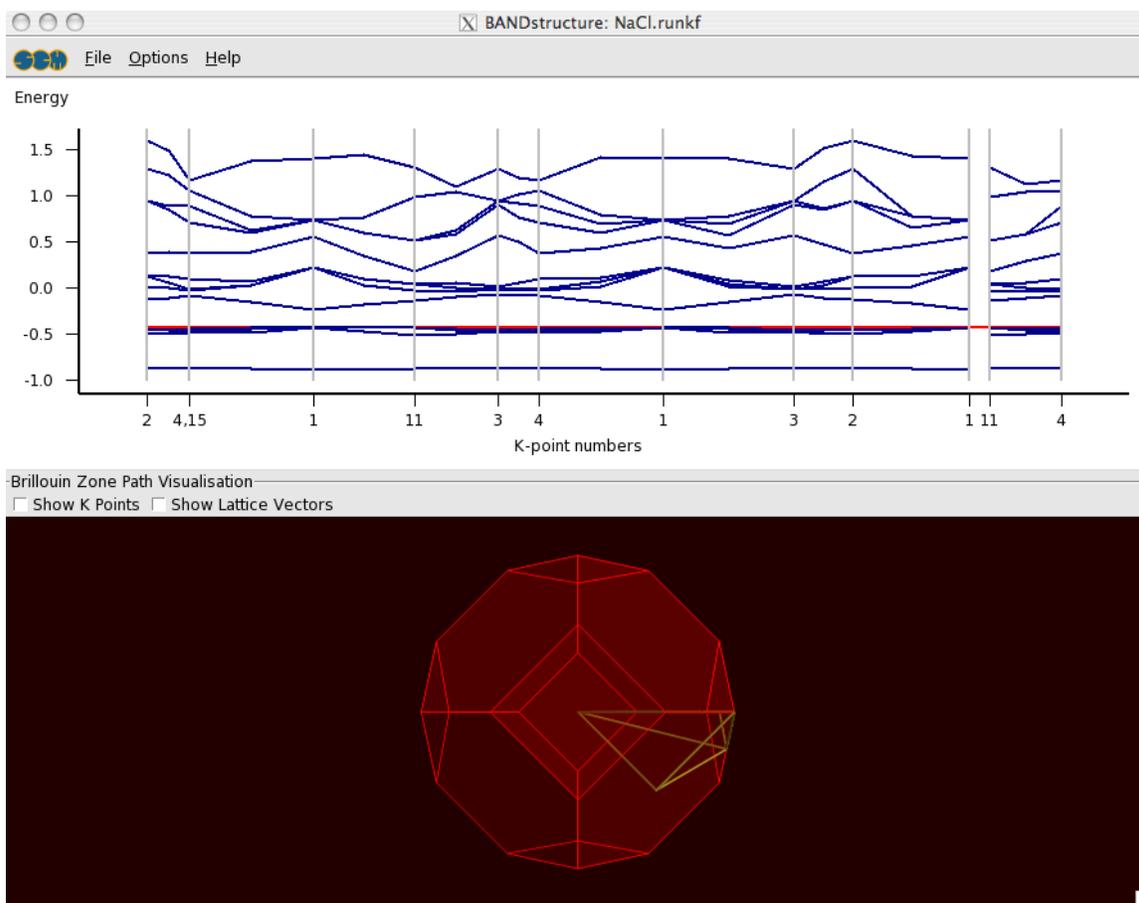
It consists of a plot and a picture of the Brillouin zone. In the plot the red line is the fermi level. Below the Fermi level are four occupied bands. You can see this more clearly by vertical zooming:

```
Click on the right mouse button, and drag the pointer up to zoom vertically
When the region of interest gets out of view,
    drag it into view (with the normal left mouse button)
```

The bottom part of the plot will look like:
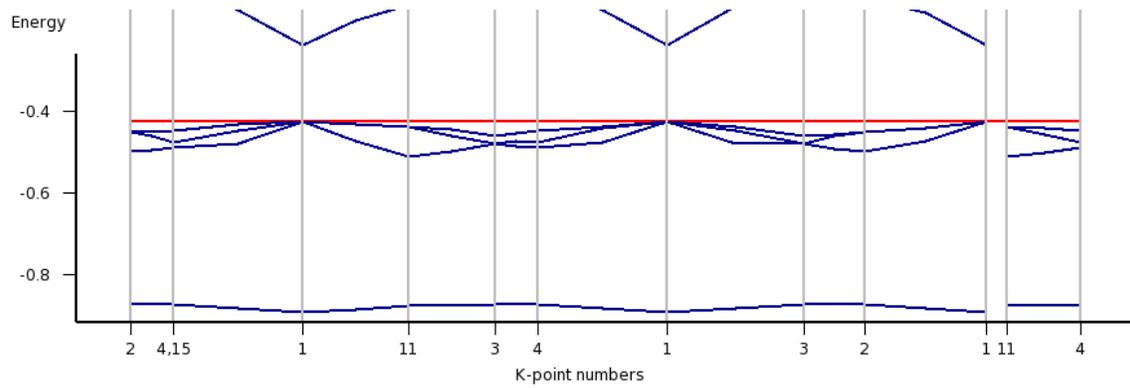
In most k-points you see now four bands below the fermi level. In some k-points you see fewer because they are degenerate.

Now you may wonder about the path taken through the Brillouin zone. This is where the bottom part comes in handy. You can zoom and rotate, just as with molecules in bandinput.

```
Zoom in a bit, by holding the right mouse button and moving upwards
```
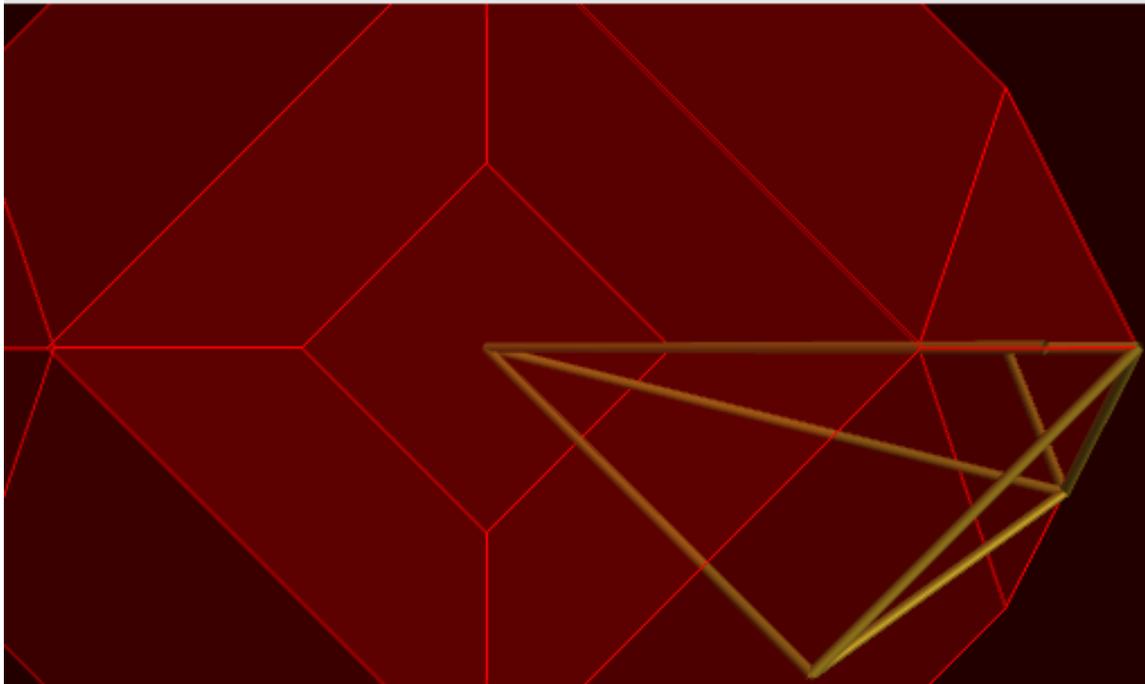


```
Toggle the button to display the k-points
```
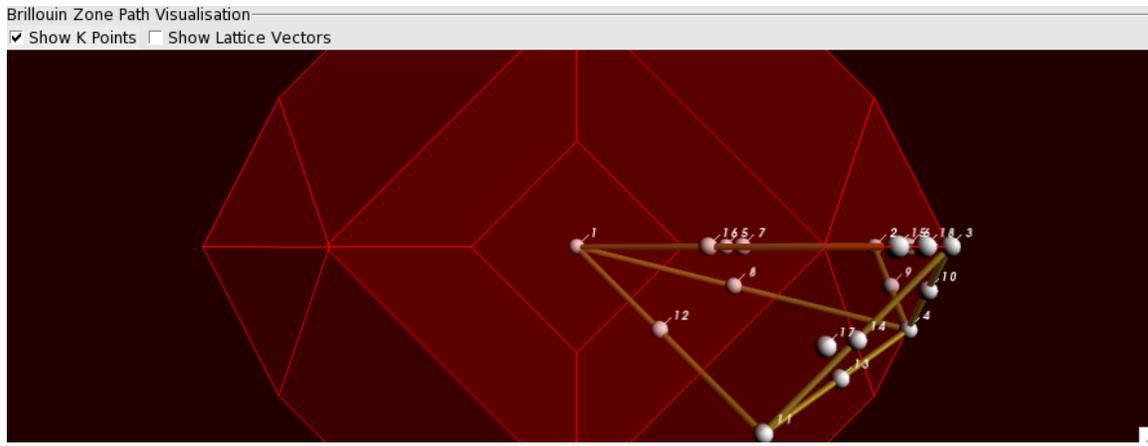
Now click on the line from 11 (via 12) to 1
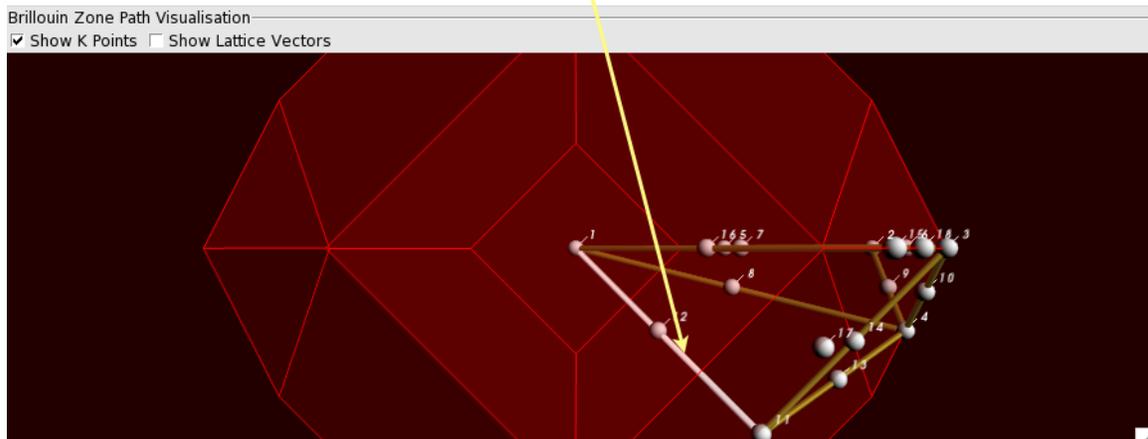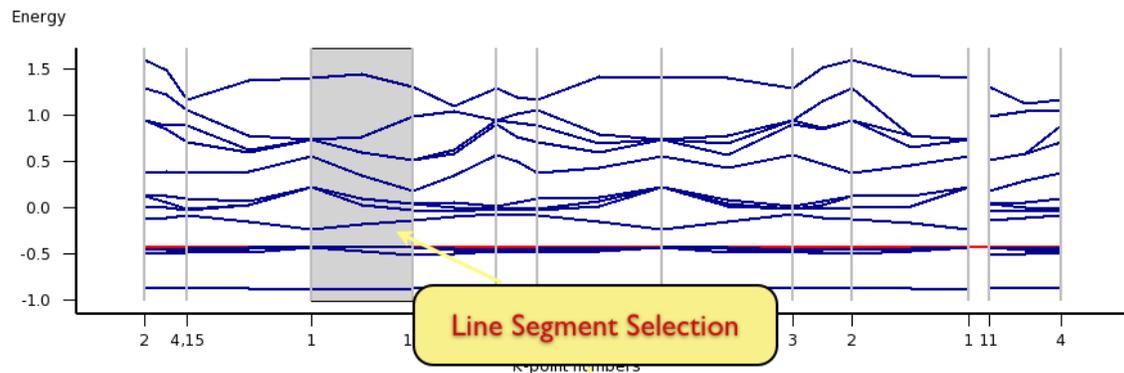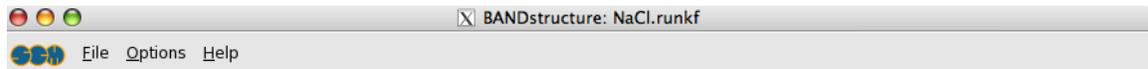
Note how the line lights up, and also how the corresponding segment is indicated in the plot by a gray background. You can also click on the plot to select line segments.

Rotate the Brillouin zone a bit to convince yourself that the line (from k-point 11 to 1) runs from the center to the center of a hexagonal face.

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Step 6: Visualizing the results

Plotting the orbitals

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

```
Open ADFview with the menu SCM → View command
In ADFview: select the Add → Isosurface Double (+/-) command
```
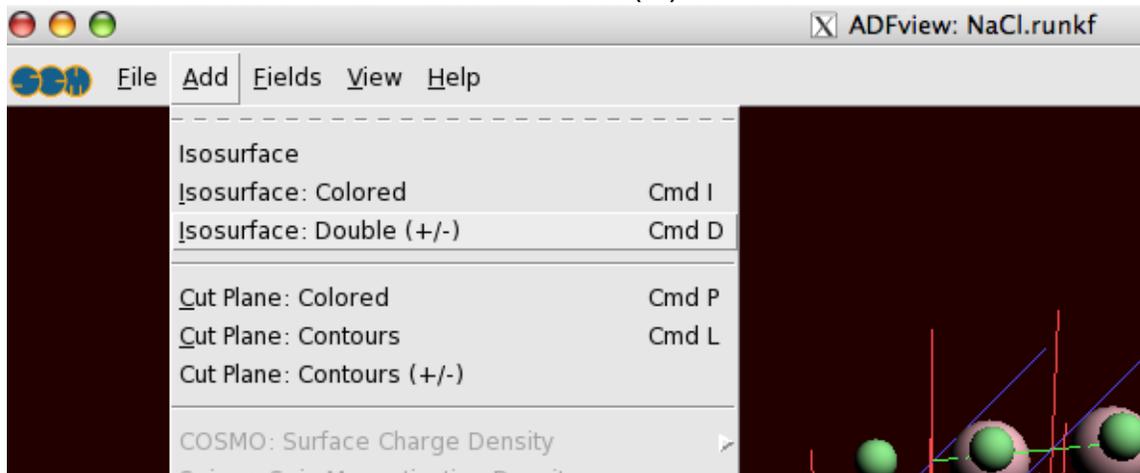

In the bar at the bottom of the window, you can select which field to show.

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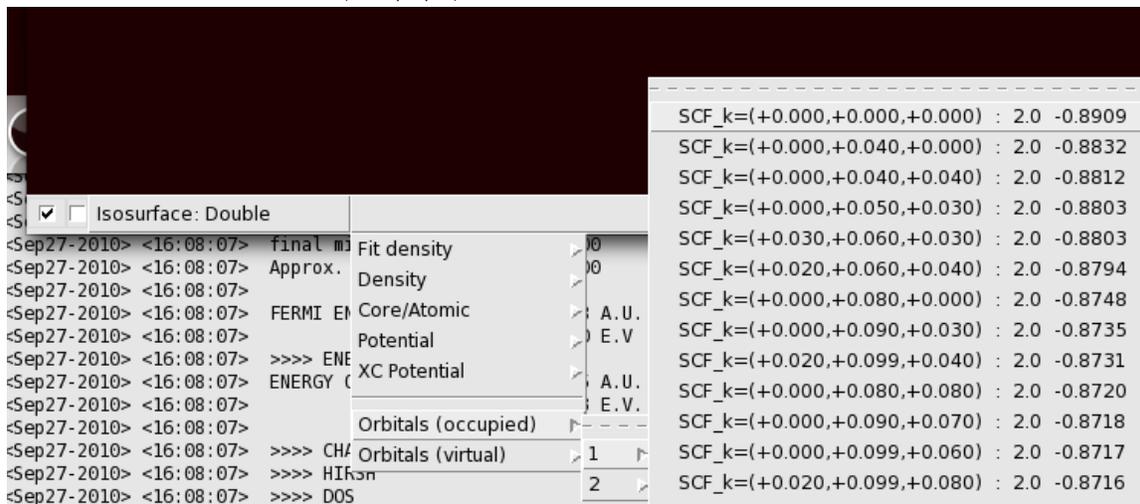

From the label you can see that it has an energy of -0.8909 and the coordinates are (0,0,0). A progress bar will appear, and after a while you will see the orbital:
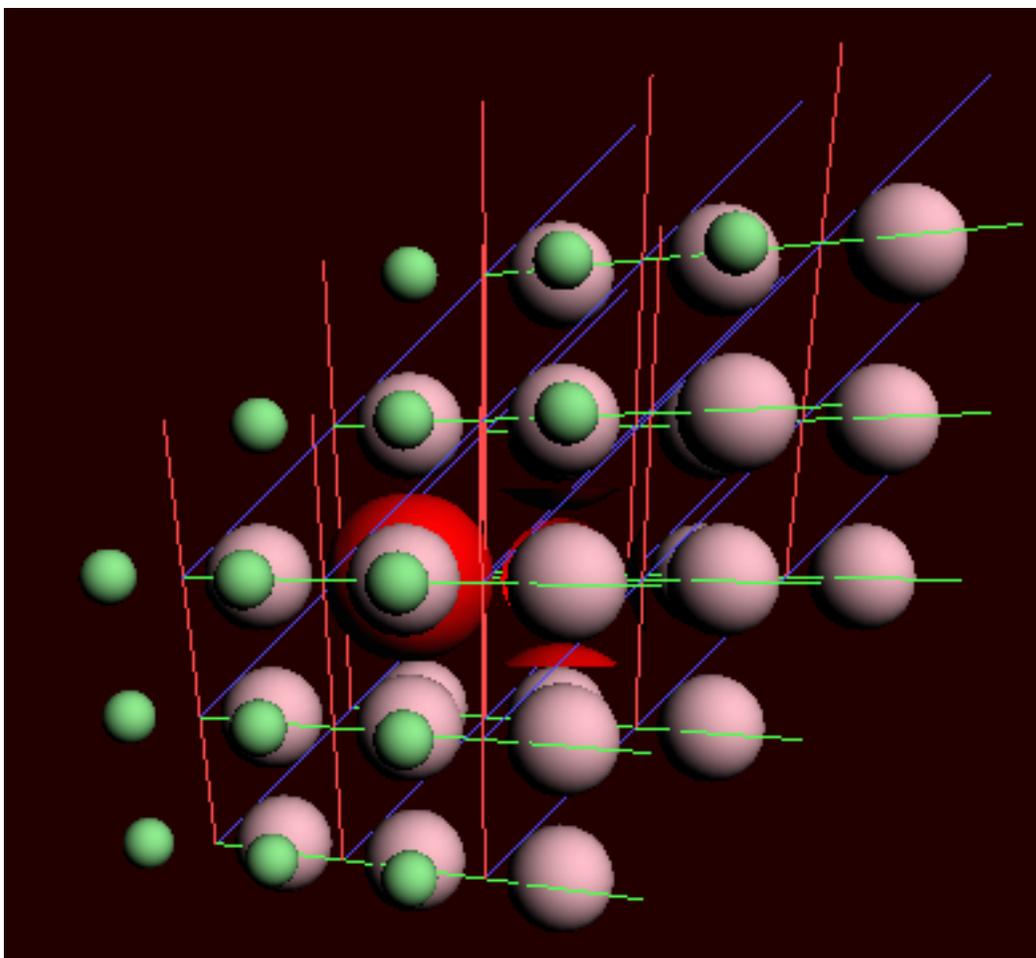
If you rotate it a bit and toggle the isosurface on and off, you can convince yourself that this orbital is located around the small atom, which is the Chlorine.

Toggle the periodic view (the menu **View &rar; Periodic → Show Periodic** command)
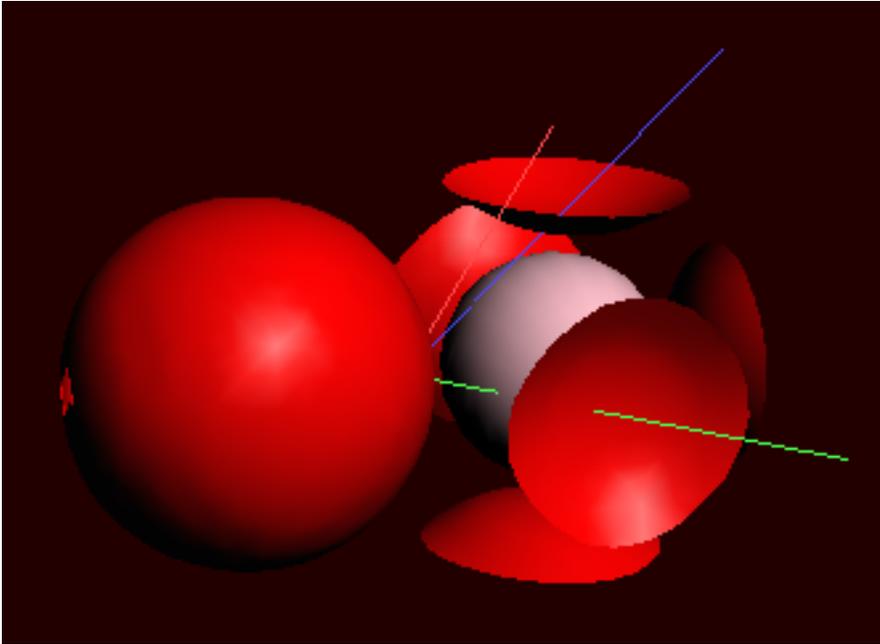
Obviously this is the 3s band of Cl. The strange truncated spheres are due to contributions of neighboring cells.

Let us now take a look at the orbital with the lowest energy of the second band (the first one with an energy **not** around -0.88):

```
Select the lowest orbital of the second band (with energy about -0.05)
```

| SCF_k=(+0.040,+0.119,+0.080) : 2.0 -0.8713 |
| SCF_k=(+0.000,+0.080,+0.000) : 2.0 -0.5103 |
| SCF_k=(+0.000,+0.090,+0.030) : 2.0 -0.5014 |

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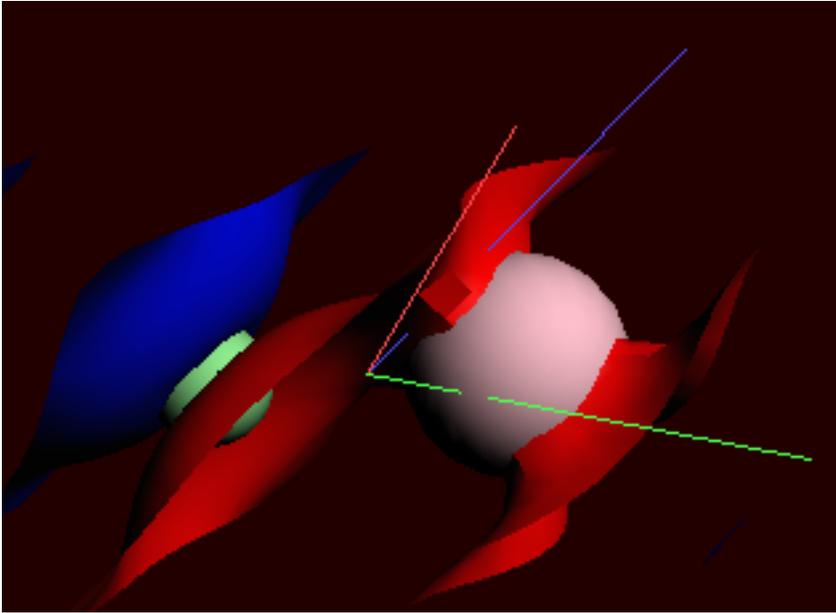
and it clearly consists of a p orbital on the Cl. The part near the Na comes from Chlorine atoms in neighboring cells.

It is generally easier to interpret orbitals at k=(0,0,0). Going up in energy we encounter a degenerate triple at e=-0.49. One of them looks like
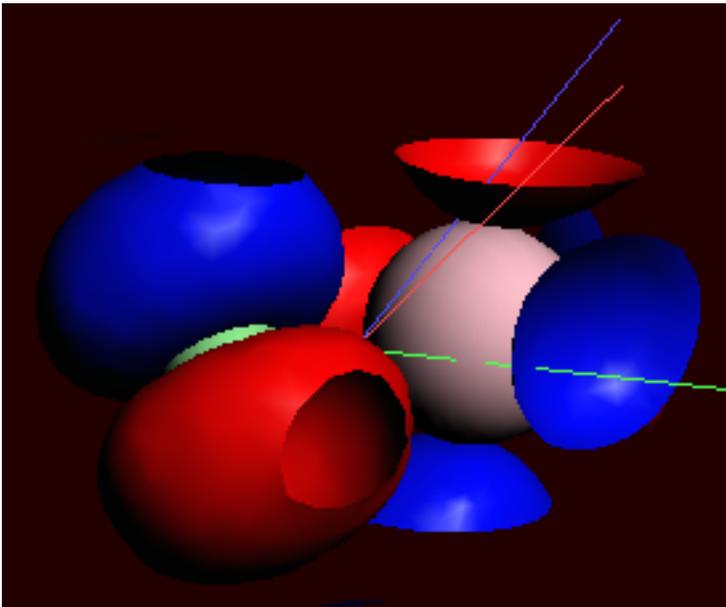
Take a look at all three of them.

From these orbital pictures we can conclude that the valence band is indeed mainly of Chlorine-p character.

You may want to check the lowest orbitals of the (unoccupied) conduction band.

```
Check the lowest orbitals of the conduction band
Do you see a strong Na character in them?
```

Plotting the partial density-of-states

There is in fact a much more easy way to conclude that the valence band is mainly of Chlorine-p character.

`Open the DOS module:` **SCM → Dos**

and a window like this will appear
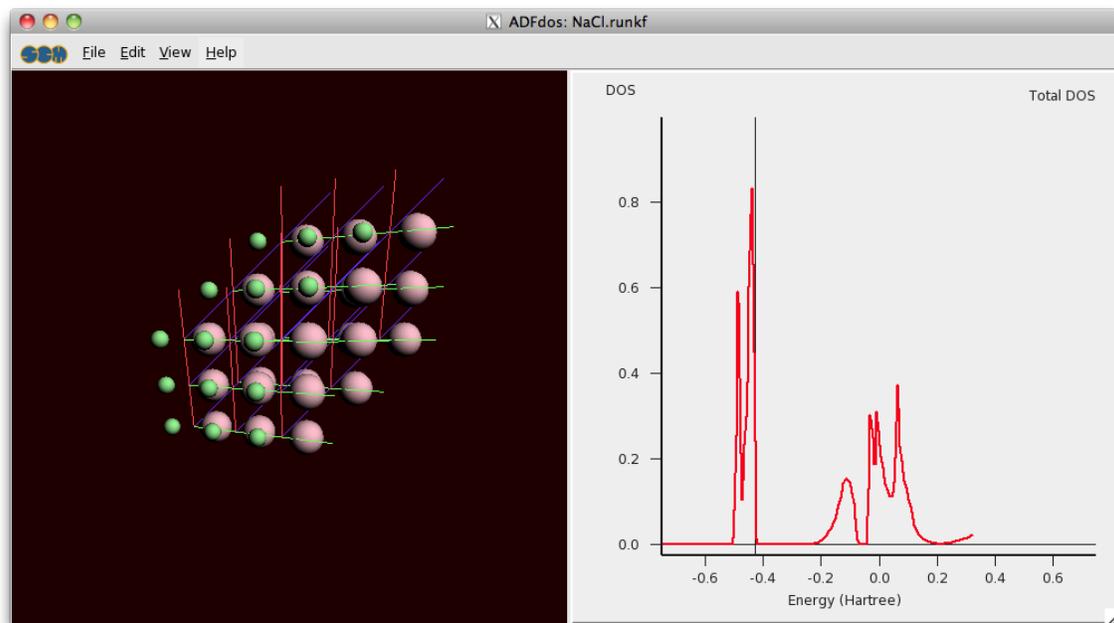
The fermi energy is around -0.43, and there is clearly a gap. Just below it there is a valence band, and at -0.2 Hartree starts the conduction band.

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

(Now you see two plots of the total DOS)

`Select with the mouse the Chlorine atom (the small green one)`
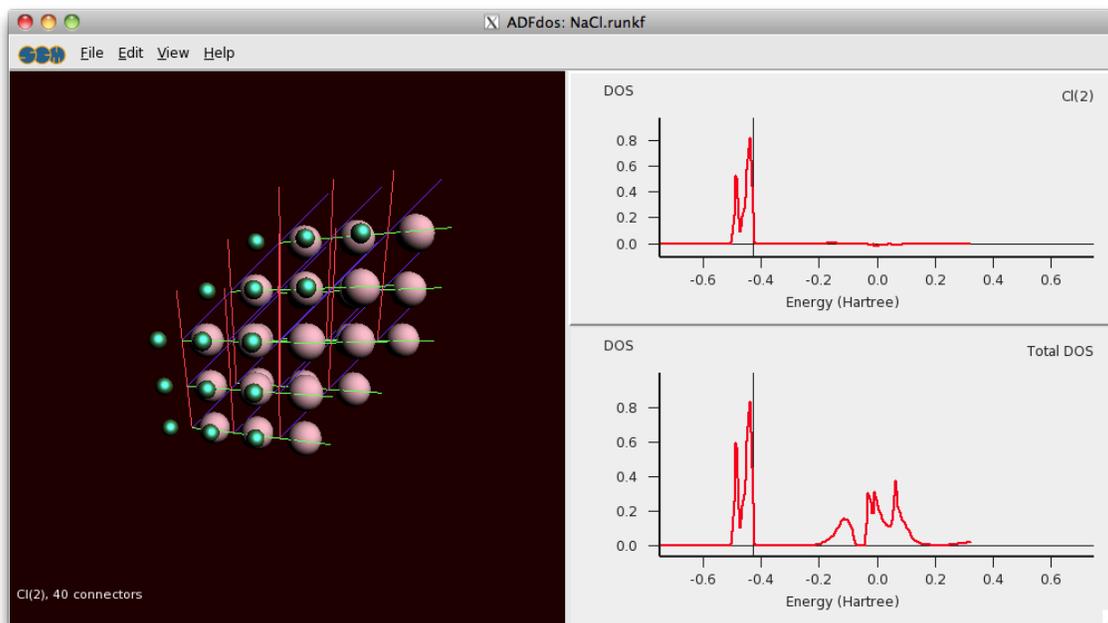
It is already immediately clear that the valence band comes from the Chlorine, and the conduction band from the Sodium.

```
Right-click with the mouse on the selected Cl atom and
   check the 'P-DOS' check box in the pop up menu.
```
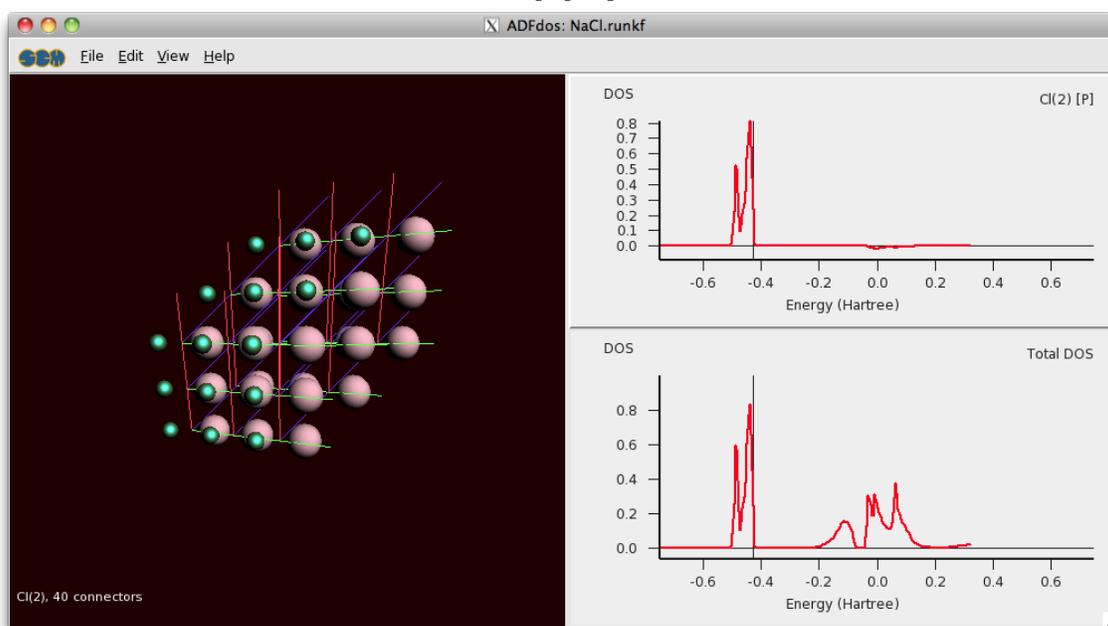

This shows that the valence band is clearly made of Chlorine p-orbitals.

Plotting the deformation density

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

```
Go to ADFview (SCM → View)
Delete the double isosurface with the 'Isosurface: Double'
   pull-down menu in the bar on the bottom
Select the Add → Cutplane: Contours (+/-)  menu command
Select the deformation density in the fields menu
```
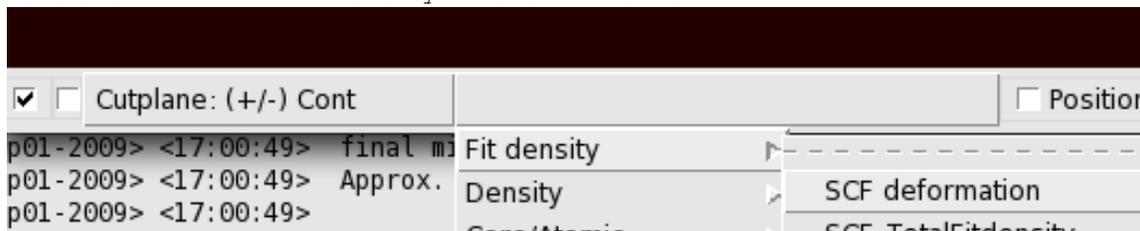

The result is a bit disappointing, because the plane is perpendicular to the atoms
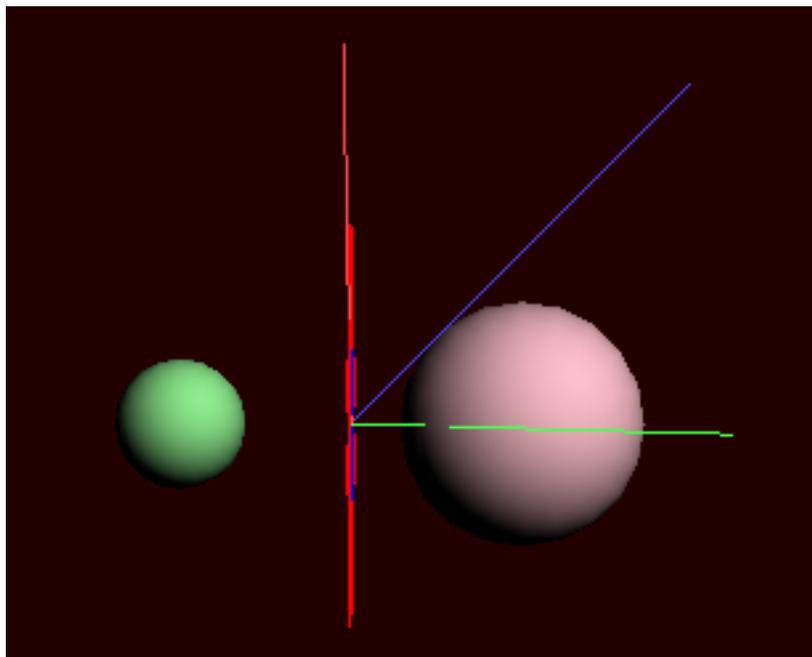
To get it right enable at the bottom the "Position plane" toggle:
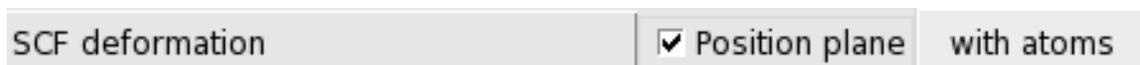
You will now see a white frame. Drag it to the right until you see an arrow in it
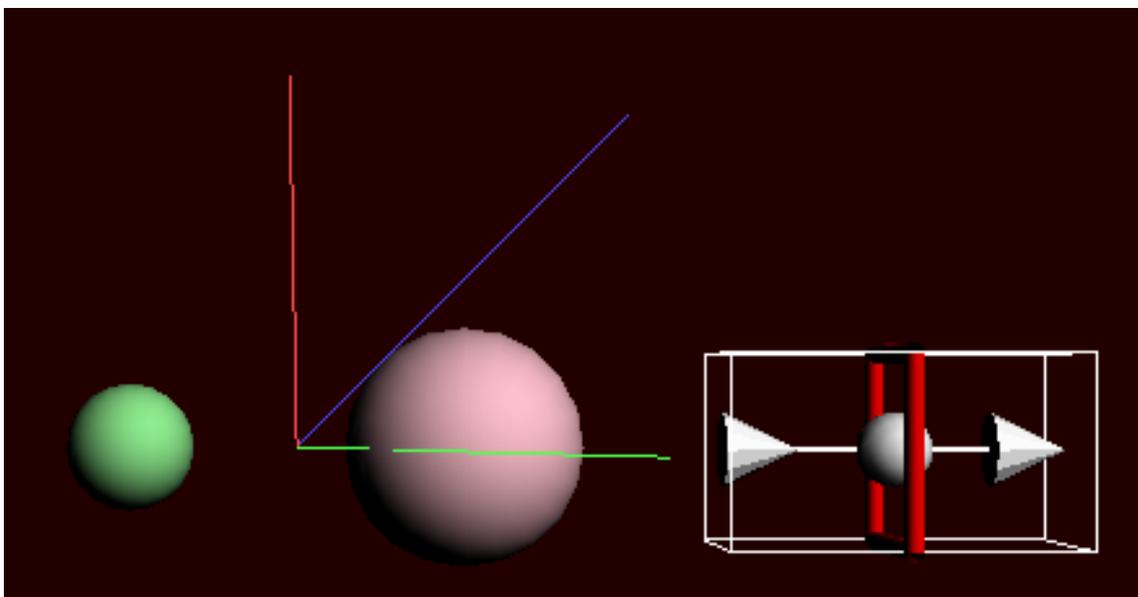
Now you can "grab" the arrow head and turn it to point towards you
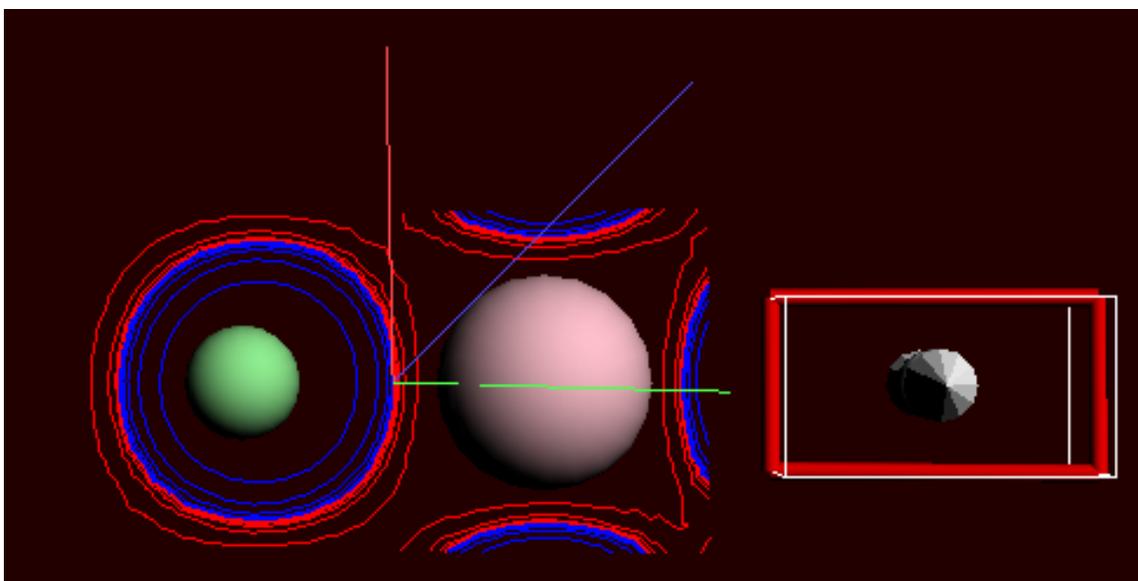
Indeed we see that charge is added (blue) near the Cl and removed (red) from the Na atom. The trend is good, but what is the total amount of charge transferred?

Step 7: Check the charges

```
right click somewhere where there is no atoms

From the popup choose  'Atom Info'  and next 'Hirshfeld Charges'
```
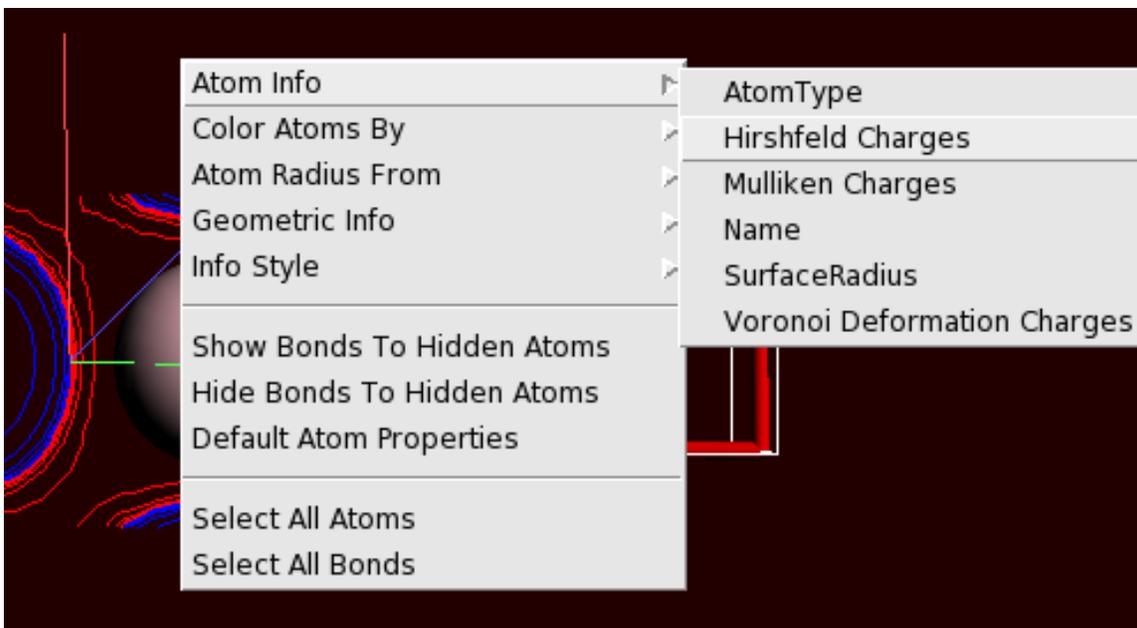
This will show you
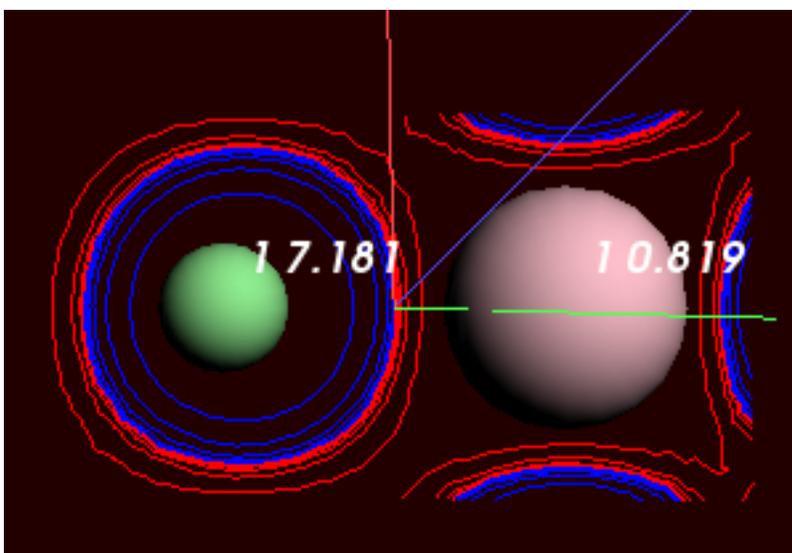
So the amount of charge transferred is only about 0.2. This is of course due to the fact that the Cl p-band overlaps quite significantly with the Na region.

The conclusion of this tutorial: we should take the idea that *one* electron is transferred from Na to Cl with a grain of salt.

Tutorial 2: building structures

In the previous tutorial you learned how to enter the coordinates and lattice vectors directly. In this tutorial we demonstrate the working of several tools that combined give you great flexibility to build structures.

The instruments at your disposal are:

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

The Crystal Structure Database

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

```
Click on the Benzene like pictogram on the toolbar.
Select a "Cubic" lattice and then NaCl
```
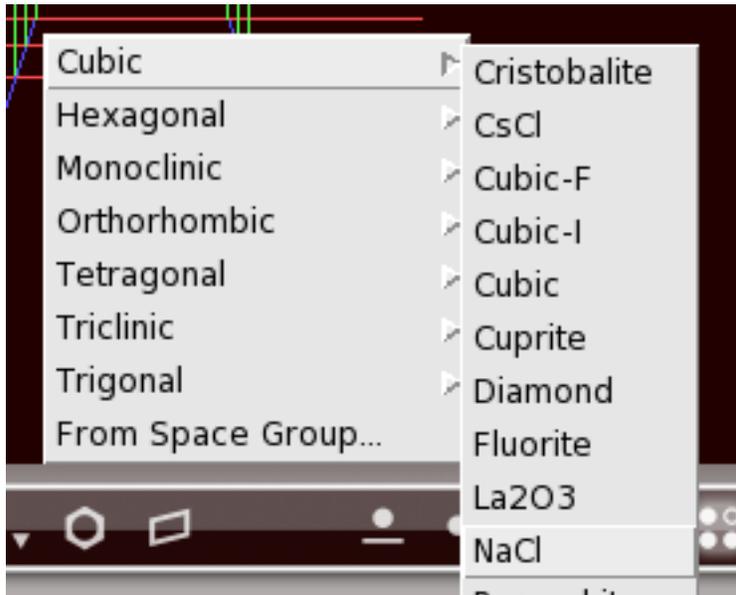

Next a dialog pops up where you can change the parameters of the structure, such as lattice constants
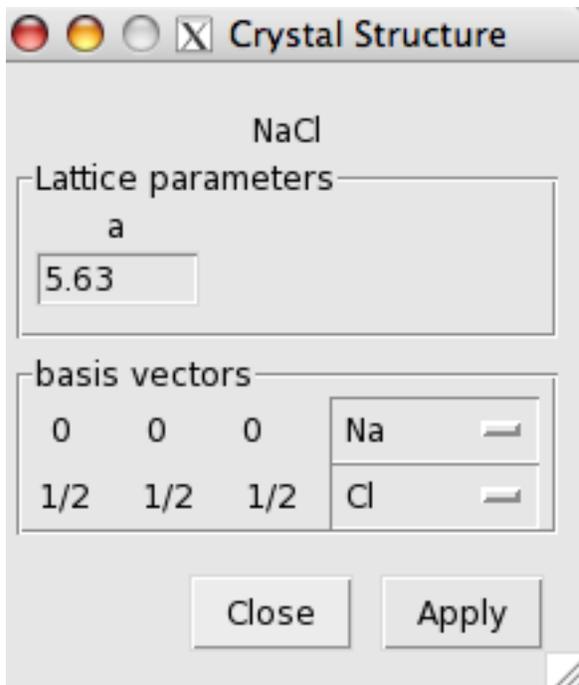
In this case there is no need to change anything.

```
Click Apply.
Click Close
```

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

```
Open again the NaCl dialog
Change the lattice constant and the elements like this
```
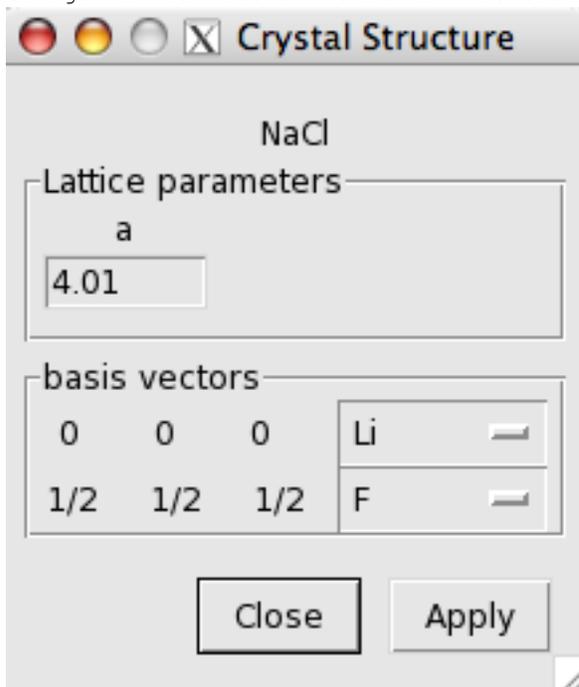
Some crystal structures have more parameters.

```
Select "Tetragonal" and then "rutile"
```
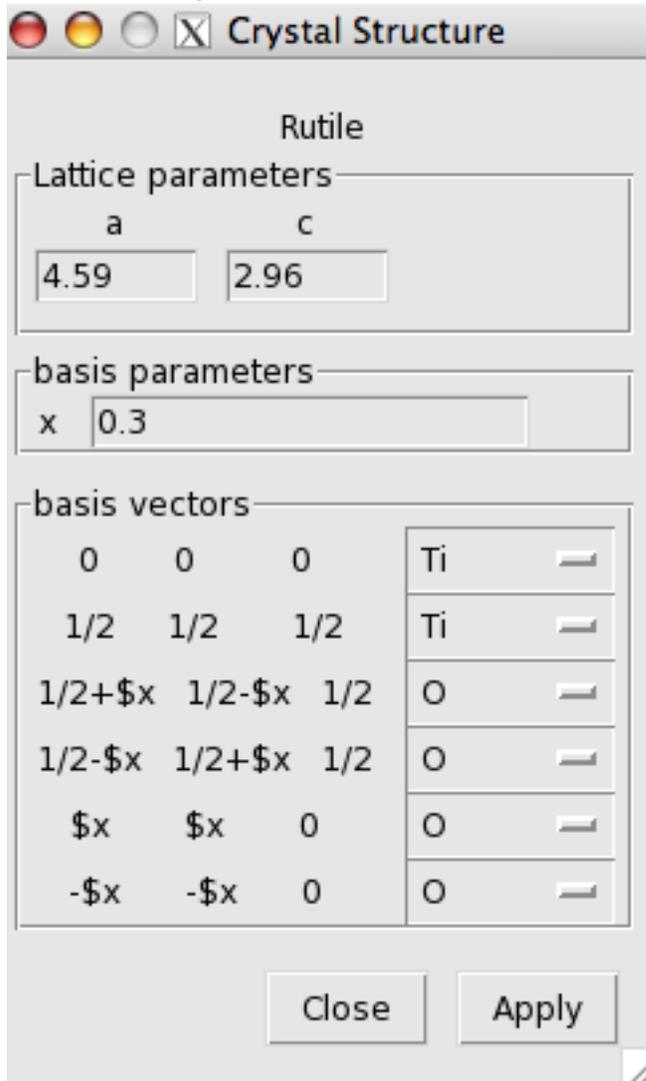

As you can see, it has two lattice parameters that need to be specified. But now also the positions of the oxygens have a parameter "x"

Crystal builder (from space group information)

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

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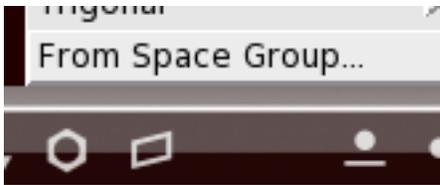
From Space Group...

And the following window pops up

X Crystal Builder

Space Group

Number: 1

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

Name: P 1

Lattice: triclinic

Lattice parameters

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

Coordinates

+

Elem Site Mult. Coords Parameters

Help   Close   Apply
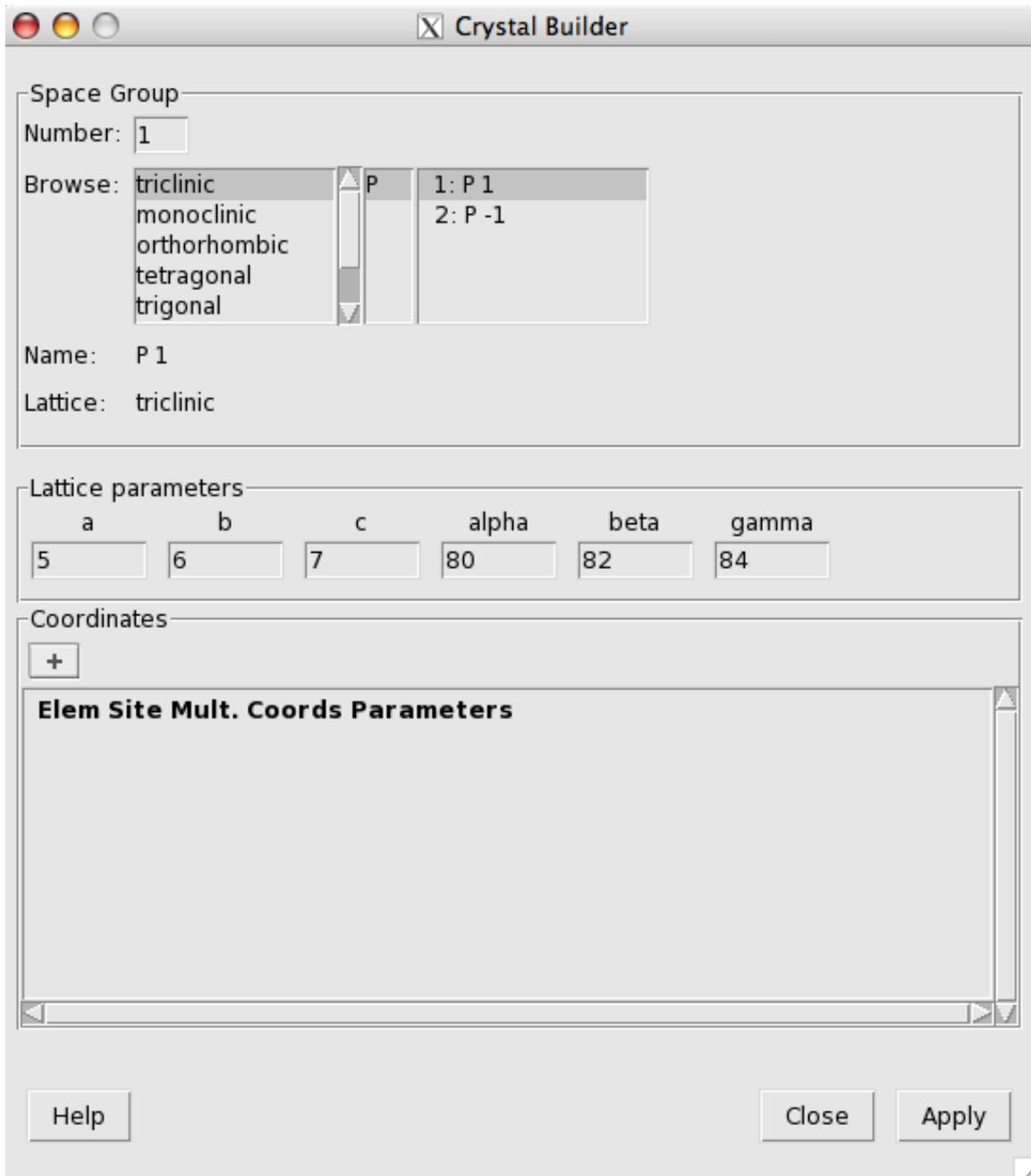
Rutile has the symmetry of space group 136

```
Enter 136 in the "Number" field
```

28

```
┌─Space Group────────────────────────────────────────────────────────────┐
│ Number: │136│                                                            │
│                                                                          │
│ Browse:  triclinic        ▲ P    134: P 42/n n m        ▲                │
│          monoclinic       ▒ I    135: P 42/m b c        ▒                │
│          orthorhombic     ▒      136: P 42/m n m        ▒                │
│          tetragonal       ▒      137: P 42/n m c        ▒                │
│          trigonal         ▼      138: P 42/n c m        ▼                │
│                                                                          │
│ Name:    P 42/m n m                                                      │
│                                                                          │
│ Lattice: tetragonal                                                      │
└──────────────────────────────────────────────────────────────────────────┘
```

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

Now set the two lattice parameters as below

```
┌─Lattice parameters──────────────────────────────────────────┐
│        a              c                                      │
│   │4.59│        │2.96│                                        │
└──────────────────────────────────────────────────────────────┘
```

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

```
┌─Coordinates────────────────────────────────────────────────────────────────┐
│ ┌───┐                                                                        │
│ │ + │                                                                        │
│ └───┘                                                                        │
│    Elem       Site       Mult. Coords Parameters                             │
│  ┌───┐                                                                       │
│  │ — │  Cu  ⊣  k   ⊣  16    x,y,z    x │0.1234│ y │0.1234│ z │0.1234│         │
│  └───┘                                                                       │
│                                                                              │
└────────────────────────────────────────────────────────────────────────────┘
```

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

Select the Ti atom and select the "a" site

```
    Elem       Site       Mult. Coords Parameters
  ┌───┐
  │ — │  Ti  ⊣  a   ⊣  2      0,0,0
  └───┘
```

The oxygens occupy the "f" site.

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

┌─Coordinates───

```
┌───────┐
│   +   │
└───────┘

         Elem        Site       Mult. Coords Parameters

 ┌───┐
 │ – │   Ti    ◁───  a    ◁───  2      0,0,0
 └───┘

 ┌───┐
 │ – │   O     ◁───  f    ◁───  4      x,x,0    x 0.1234
 └───┘
```

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

```
Set "x" to 0.3
```

The final dialog looks like

Crystal Builder

Space Group

Number: 136

Browse:
- triclinic
- monoclinic
- orthorhombic
- tetragonal
- trigonal

P
I

- 134: P 42/n n m
- 135: P 42/m b c
- 136: P 42/m n m
- 137: P 42/n m c
- 138: P 42/n c m

Name: P 42/m n m

Lattice: tetragonal

Lattice parameters

a	c
4.59	2.96

Coordinates

+

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

☐ Conventional Unit Cell

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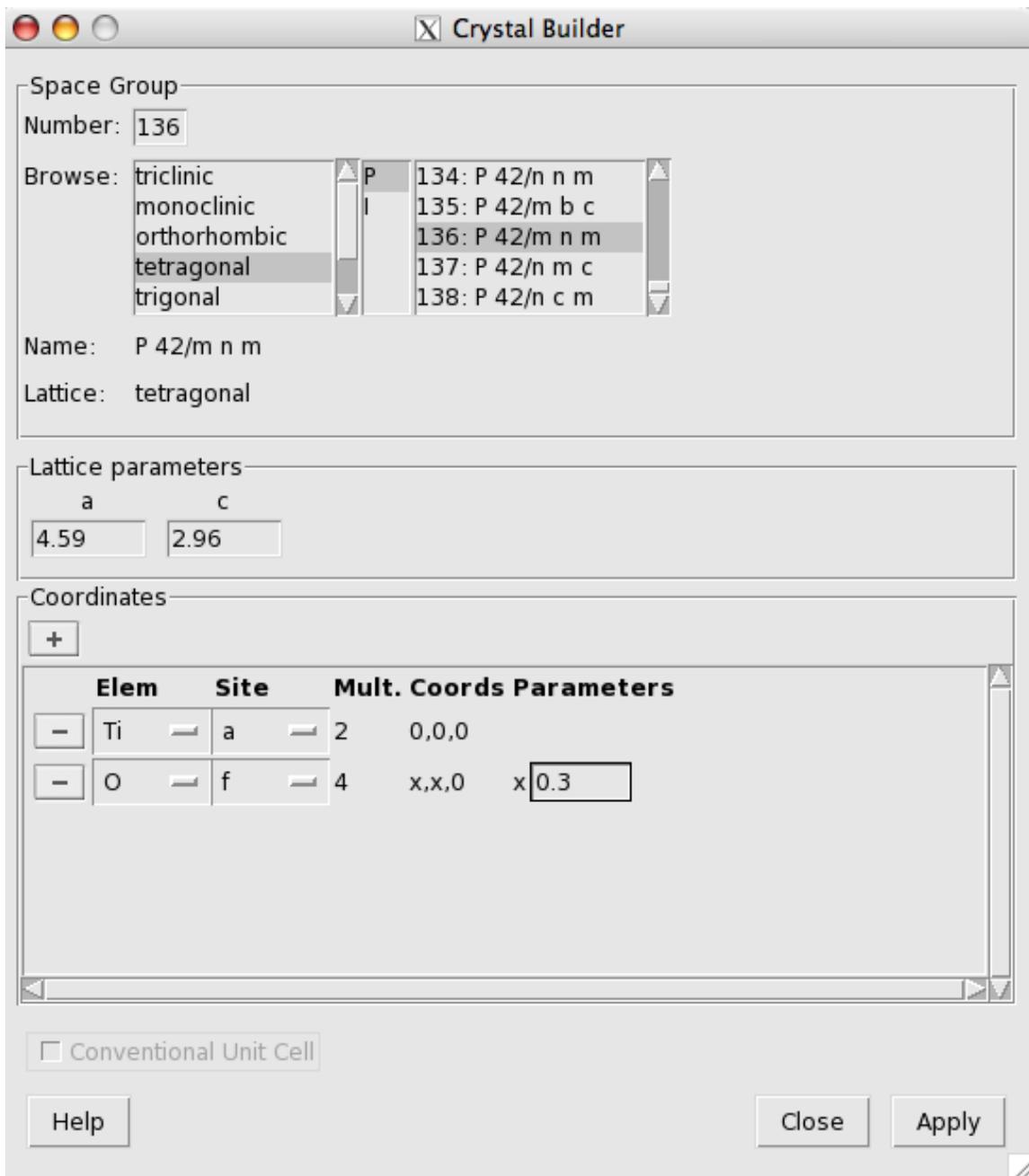
Press "Apply" and if that looks any good press "Close"

31
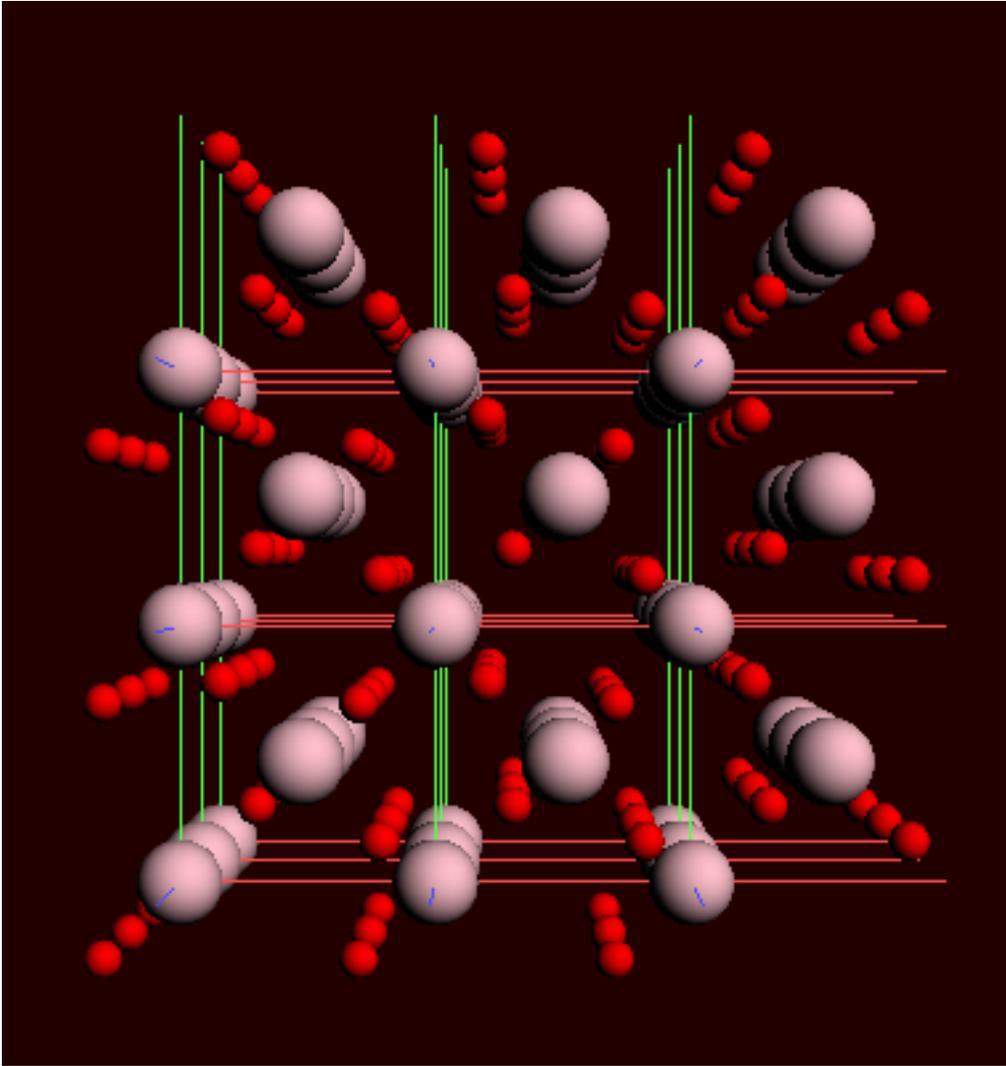
Slicer: building slabs

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

A three layer slab of the Cu(111) surface

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

Cubic	Cristobalite
Hexagonal	CsCl
Monoclinic	Cubic-F
Orthorhombic	Cubic-I
Tetragonal	Cubic
Triclinic	Cuprite
Trigonal	Diamond
From Space Group...	Fluorite
	La2O3
	NaCl
	Perovskite
	Pyrite
	Spinel
	Zincblende
	bcc
	fcc
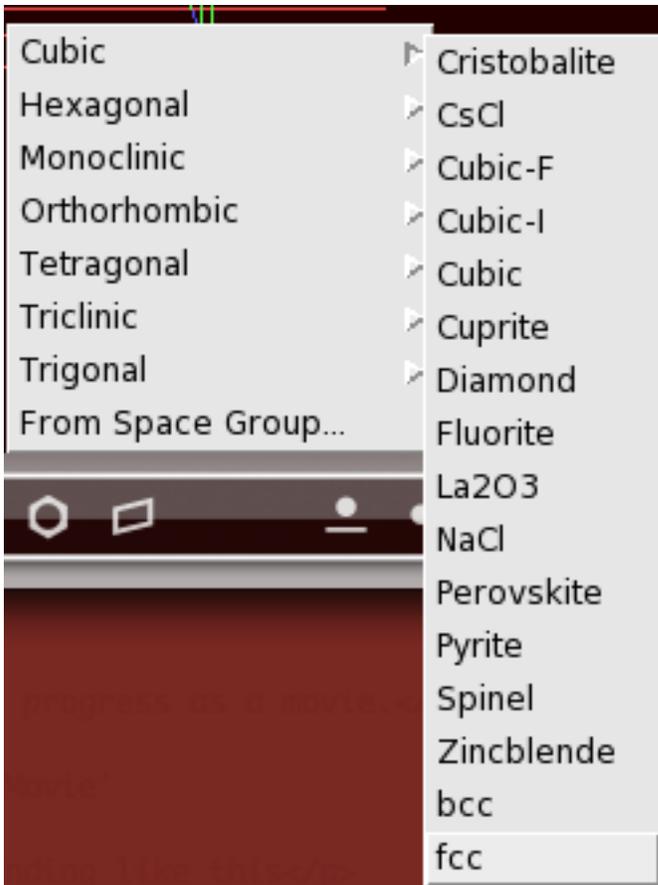
The element and lattice constant are already correct for Cu.
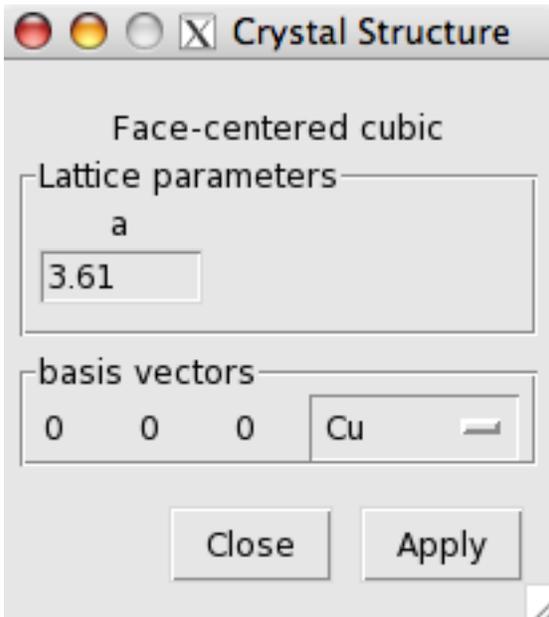
Press "Apply" to generate the Cu lattice

Let us invoke the slicer tool to cut out the slab.

```
Click on the utility knife like icon in the toolbar
```


The following dialog appears
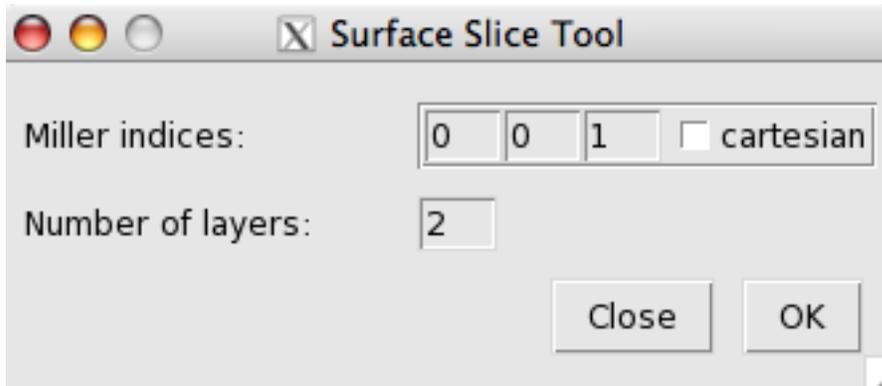

```
Set the Miller indices to (1,1,1)
Select Cartesian
Set the number of layers to 3
```
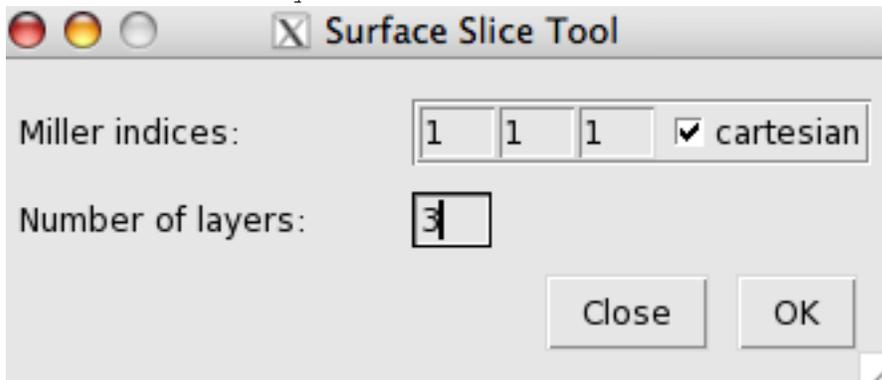

The "Cartesian" option is needed because the Miller indices are usually thought in the conventional unit cell rather than the primitive (minimal) unit cell. After pressing OK you will see (from the top)
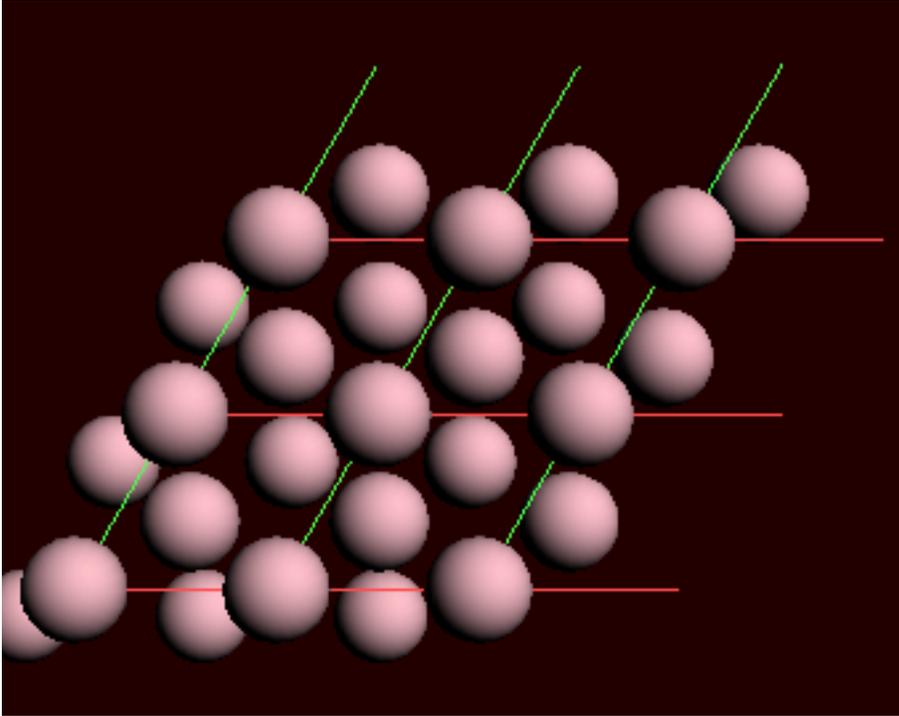
You may want to rotate it or press the side view buttons in the toolbar to convince yourself that it is a three layer slab.

Enlarging the unit cell

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

```
Construct a 3 layer Cu(111) slab (as before)
Select the  Edit → Generate Super Cell...  command
```

Edit	View	Model	Properties	Details

Undo	Cmd Z
Redo	Shift Cmd Z
Cut	Cmd X
Copy	Cmd C
Paste	Cmd V
Clear	Cmd B
Group	Cmd G
Ungroup	Cmd U
Set Origin	
Define Super Cell...	
Map Atoms To Unit Cell...	

Thus invoking the Super Cell Tool

⊖ ⊖ ◯ ☒ Super Cell Tool

┌─Super Cell────────────────────────┐
│ Preset :   ▬ │
│   ┌─────┬─────┐   │
│   │ 1   │ 0   │   │
│   ├─────┼─────┤   │
│   │ 0   │ 1   │   │
│   └─────┴─────┘   │
│   │
│   [Close]   [OK]   │
└────────────────────────────────────┘
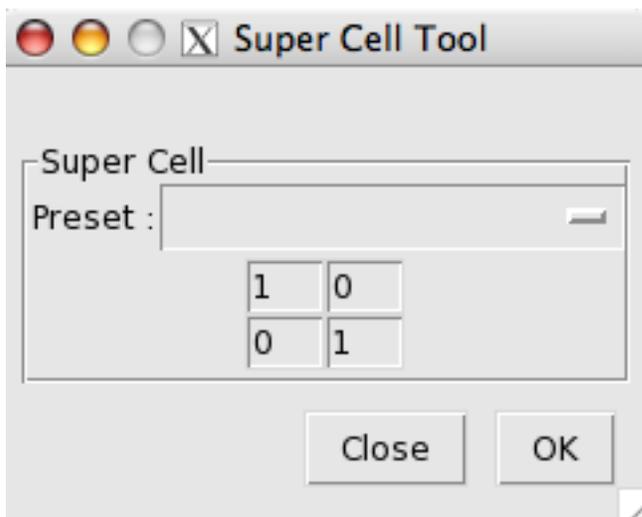
Here you see how new lattice vectors are expressed in terms of old ones. Because we have a slab this is a 2x2 matrix, set initially to the unit matrix.

```
Select the "sqrt(3) x sqrt(3)" option from the "Preset" menu
```
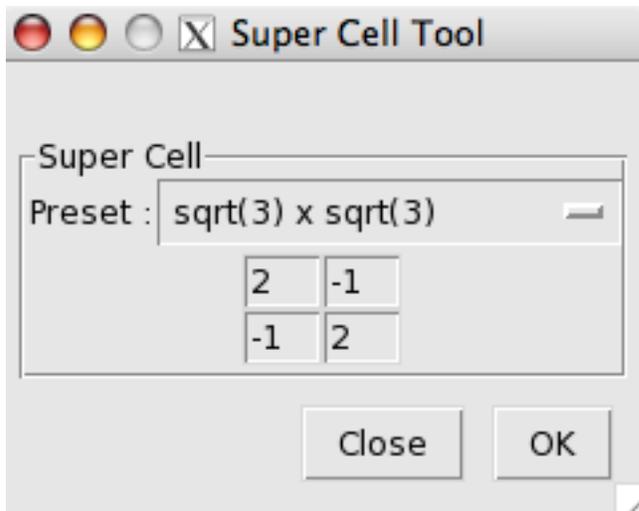
The matrix has now changed into 2,-1,-1,2. Press OK and you get a unit cell with three atoms per layer.

To convince yourself that this is true press the rightmost button in the toolbar (to toggle between periodic repetition), and rotate the system a bit.
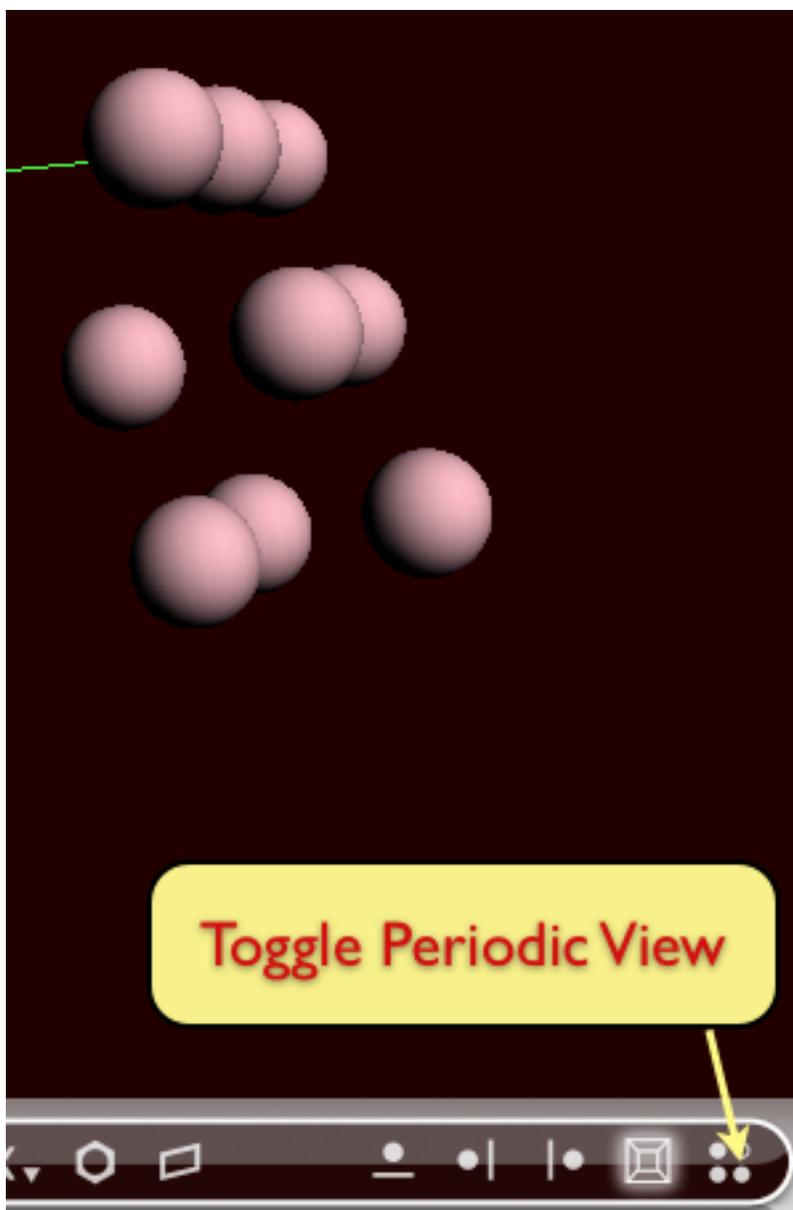
Tutorial 3: a transition state search

This tutorial will teach you how to:

- do a geometry optimization
- watch the geometry optimization as a movie
- do a frequency calculation
- examine the eigen modes
- perform a transition state search
- make a few mistakes and fix them

Throughout we will consider the toy system of a periodic chain with three atoms in the unit cell.

Step 1: Create the H3 toy system

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

```
Select in the 'Coordinates' panel as periodicity 'Chain' and
    make a lattice vector in the x-direction with length 10.
```

Coordinates

Periodicity: Chain   (lattice)

Lattice vectors: volume: 10.0

10	0	0
0	0	0
0	0	0

```
Add with the mouse three hydrogen atoms somewhere in the cell.
Change the coordinates in the table to this
```

☐ natural   smallest distance: 1.000 for atom pair: 1,2

H(1)	0	0	0
H(2)	1	0	0
H(3)	3	0	0

You have now created the cylinder symmetric toy system.

Step 2: Optimize the geometry

```
Go back to the 'Main Options' panel
Choose as task 'GeometryOptimization'.
Save the project as 'H3_geo'
Run it.
```

After it has finished the program asks you

```
Read new coordinates from
/Users/philipse/projects/calc/tutorial/H3_geo.ru
nkf?
```
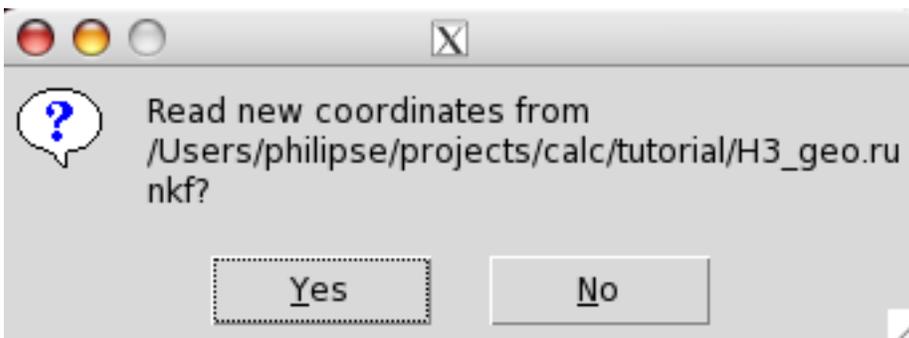
Yes   No

```
Answer 'Yes'.
```

Now let us look at the progress as a movie.

`From the SCM menu select 'Movie'`

A small movie pops up ending like this
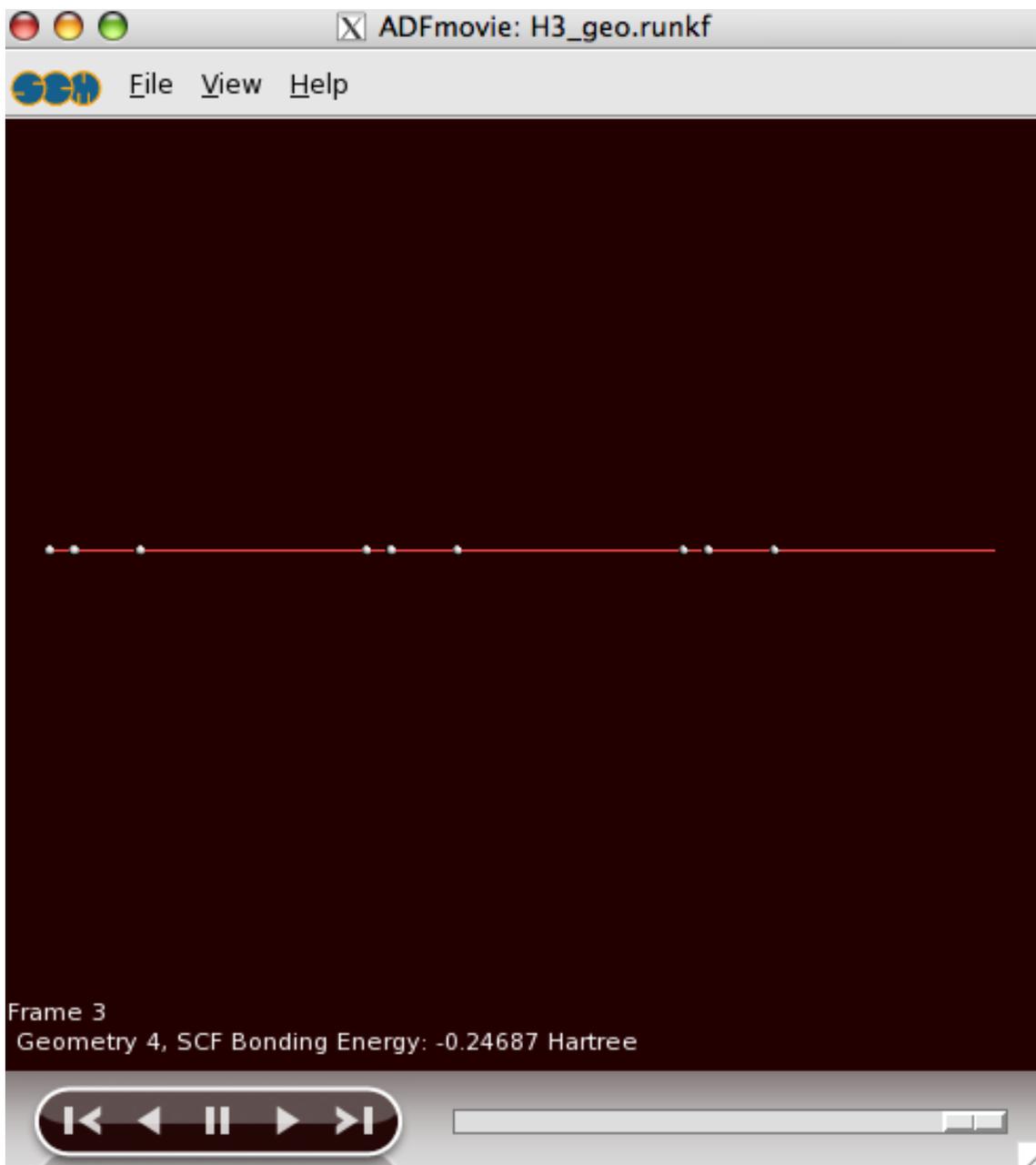
The geometry looks a bit odd. Now take a look how the energy changed during the optimization.

`Choose the` **Graph** → **Energy** `menu command`
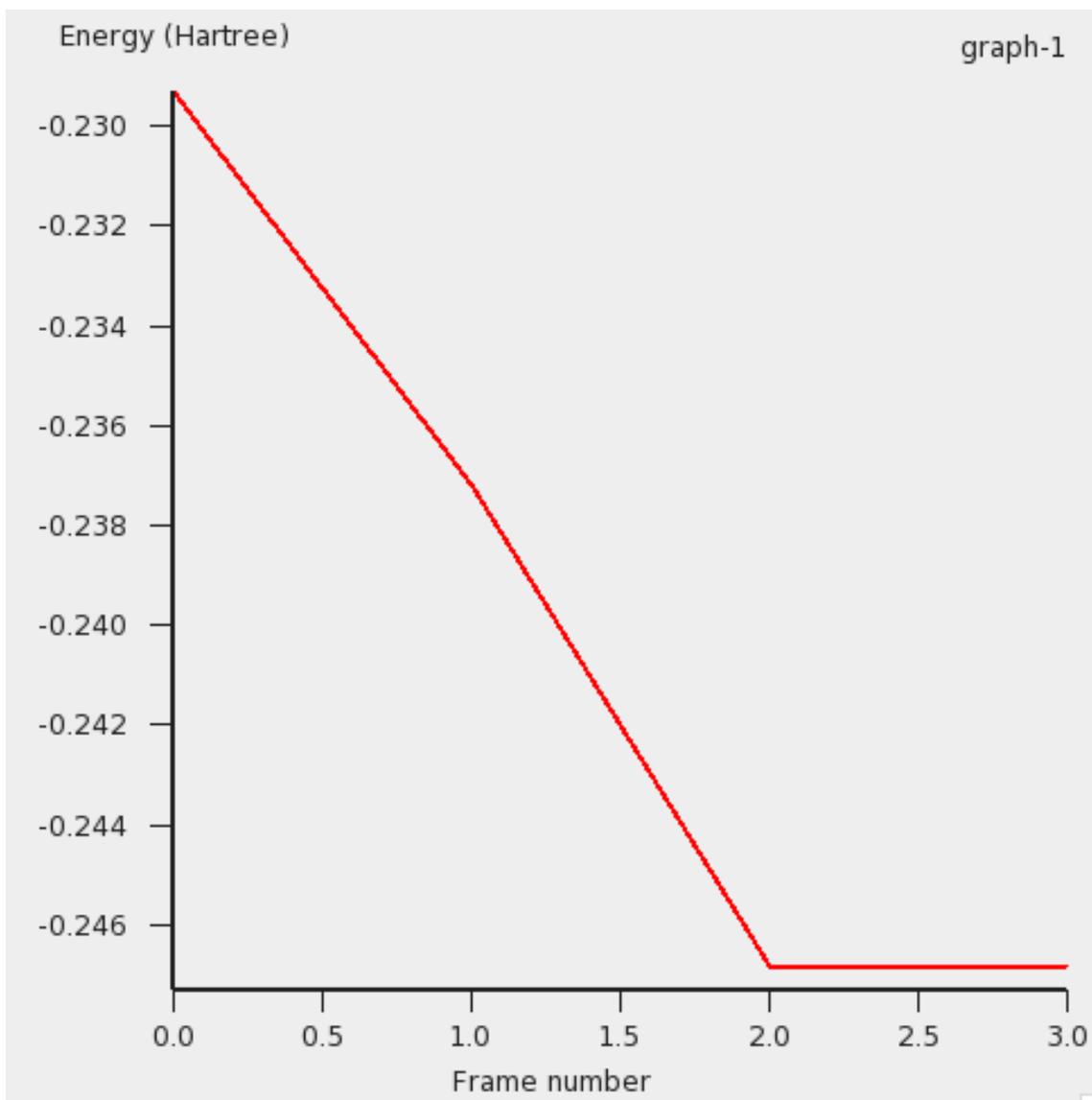
It shows the energy at the four steps: 0, 1, 2, and 3. Since the energy does not change anymore from step 2 to three it should be OK? Well, maybe, but maybe not. Let us check whether we were fully converged.

Open the logfile: **SCM → Logfile**
Scroll from the end a bit upwards and you will see

```
<Sep03-2009> <13:47:06>  >>>> DOS
<Sep03-2009> <13:47:06>  NOT ALL FILES CLOSED
 Coordinates in Geometry Cycle            3
    Atom      X           Y           Z    (Angstrom)
  1.H    0.121365    0.000000    0.000000
  2.H    0.892966    0.000000    0.000000
  3.H    2.985668    0.000000    0.000000
Lattice Vectors
   10.000000    0.000000    0.000000
>>>>
E-test:    -0.246865 hartree
<Sep03-2009> <13:47:06>  current energy                         -0.24686452 Hartree
<Sep03-2009> <13:47:06>  abs of energy change        0.00002981    0.00100000    T
<Sep03-2009> <13:47:06>  constrained gradient max    0.00834195    0.01889726    T
<Sep03-2009> <13:47:06>  constrained gradient rms    0.00352787    0.01259817    T
<Sep03-2009> <13:47:06>  gradient max                0.00834195
<Sep03-2009> <13:47:06>  gradient rms                0.00352787
<Sep03-2009> <13:47:06>  cart. step max              0.00229546    0.01587532    T
<Sep03-2009> <13:47:06>  cart. step rms              0.00095024    0.01058354    T
<Sep03-2009> <13:47:06>  Geometry Converged
<Sep03-2009> <13:47:06>  final calculation
<Sep03-2009> <13:47:06>  >>>> POINTS
```

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

Maybe we are dealing with a shallow minimum. Let us retry with a more strict criterion.

```
Close the logfile and movie windows and go back to 'BANDinput'.
Go to the 'Optimization' panel (click on the triangle next to
GeometryOptimization)
Set the gradient convergence criterion to 0.0001
```

Optimization

Number of iterations:

Initial Hessian from: +

Convergence criteria

Gradient convergence: 0.0001   Hartree/Angstrom

Energy convergence: Hartree

Step convergence: Hartree

```
Save the project and run it
Open adfmovie afterwards and show the energy
```
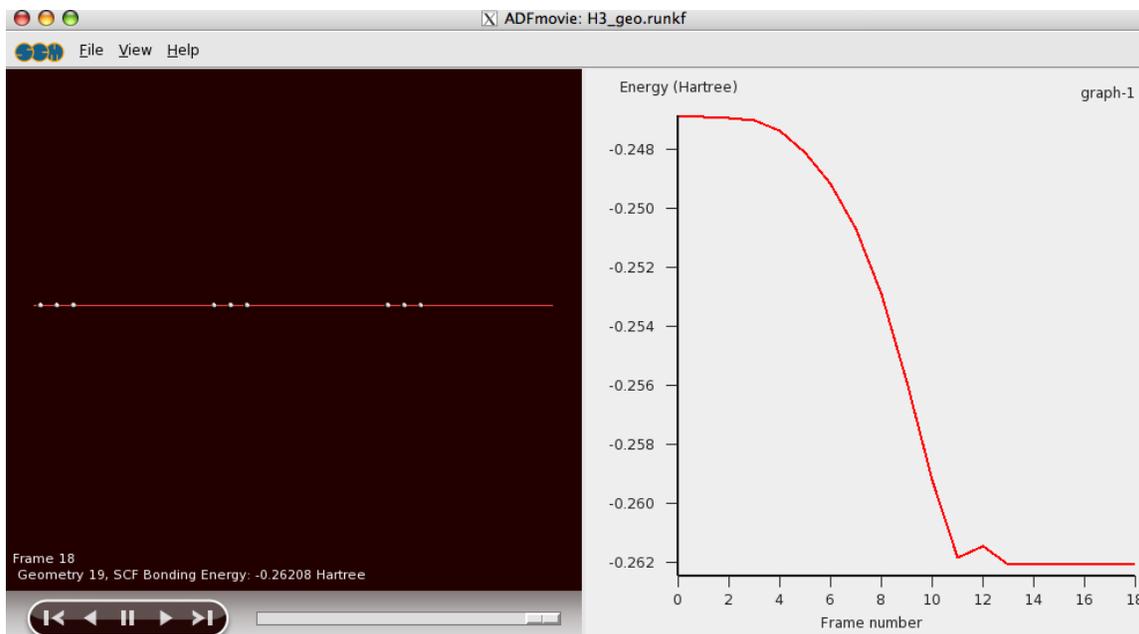
Now that looks more like an optimal geometry!

Step 3: Calculate the Hessian

```
Go to BAND input
Select in the 'Main Options' panel the task 'Frequencies'
```



```
Save the project as H3_freq and run it.
```

After the calculation has finished

```
choose the  SCM → Spectra  command
```
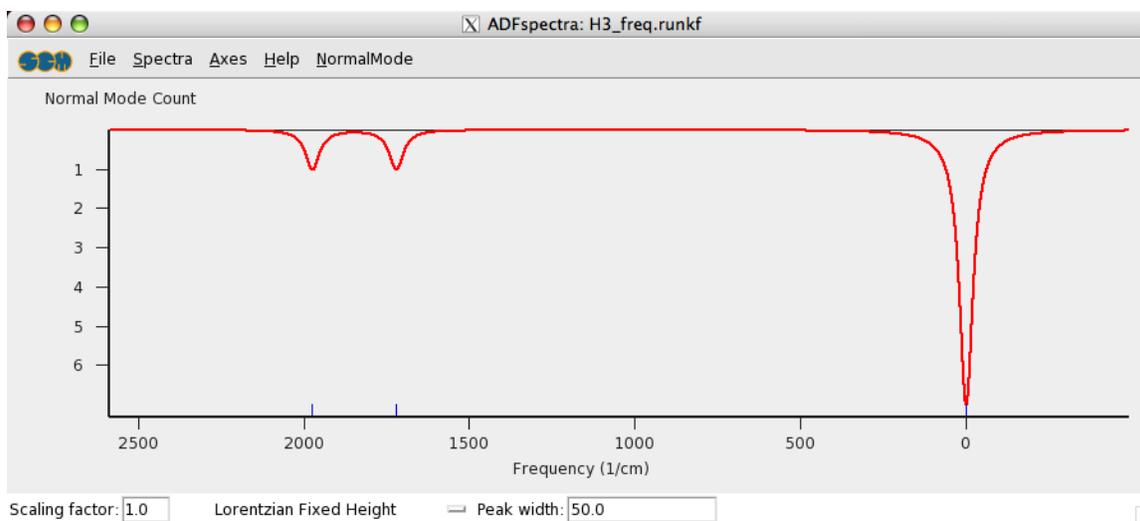
There appear to be three peaks, whereas you would expect 3N degrees of freedom. With three atoms (N=3) we should have nine modes. We can examine this a bit closer

```
click on the 'NormalMode' menu.
```
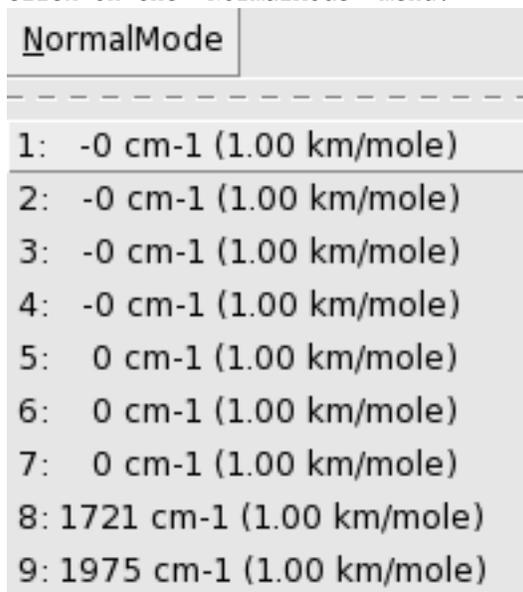

So there are indeed nine vibrational modes. Only two are nonzero because only symmetrical modes are calculated by default. To see what a mode looks like

```
Select the mode at 1700 cm-1, either from the 'NormalMode' menu,
   or by clicking on it directly in the graph.
```

A new movie window pops up visualising the vibrational mode.
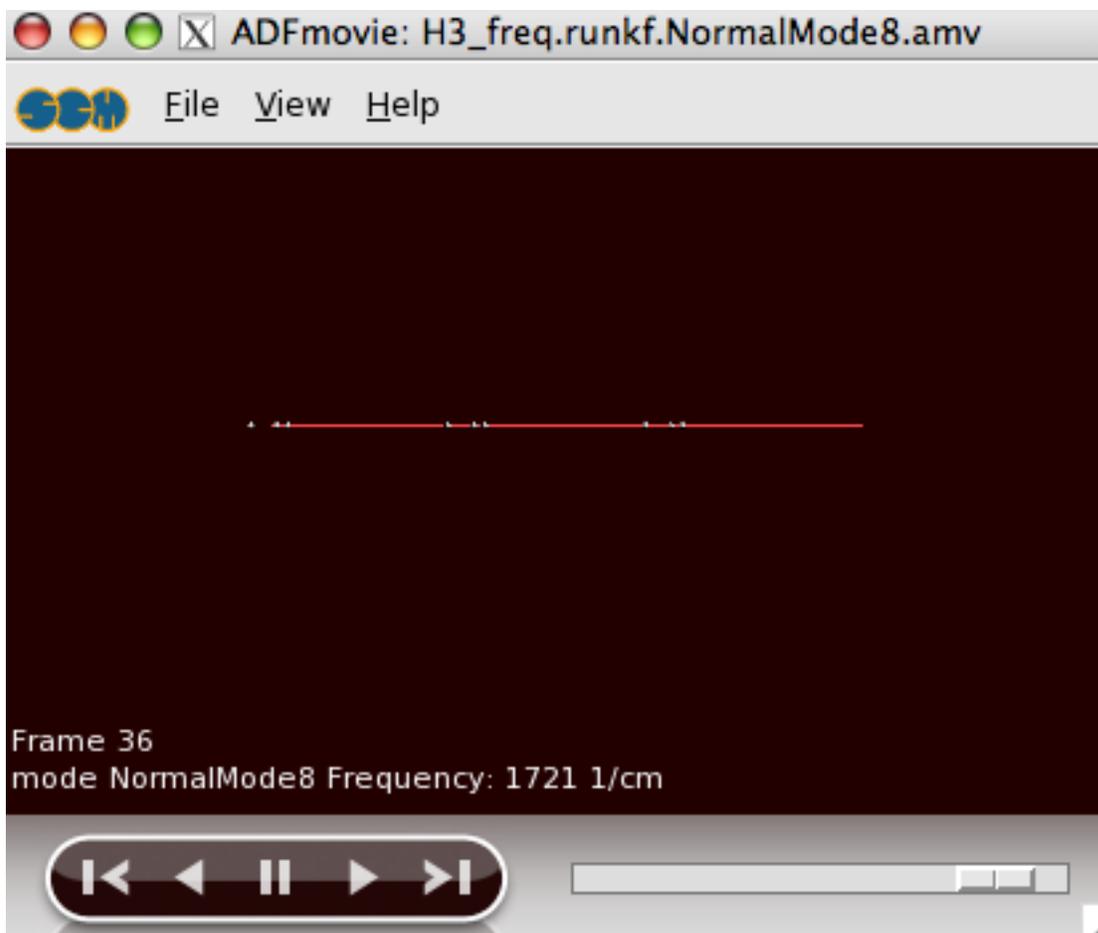
Step 4: Search the transition state

A minimum has vanishing gradients and only positive eigen modes. A (first-order) transition state (saddle point) is characterized by having one negative mode. With a transition state search the optimizer will go uphill in the direction of the lowest (nonzero) eigenmode and downhill in all other degrees of freedom. In our example it would follow mode 8. Let us give it a try from the minimum.

```
Choose in the 'Main Options' panel the task 'TransitionState'
```


We have just calculated a Hessian (with the frequency run) so we'd better use it.

```
Go to the 'Optimization' panel, click on the
   plus button next to 'Initial Hessian From:'
Select with the file dialog 'H3_freq.runkf'.
```
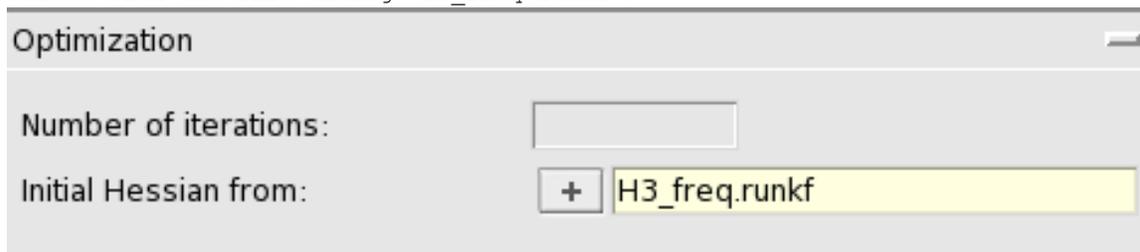
Optimization

Number of iterations:	
Initial Hessian from:	+ H3_freq.runkf

```
Save the  project as 'H3_ts' and run it.
```

The most likely outcome, however, is that the optimizer stops immediately, because the gradients are zero. Therefore, we need to help the optimizer a bit.

```
Move the rightmost atom a tiny bit to the right (increase the x value by 0.01).
```
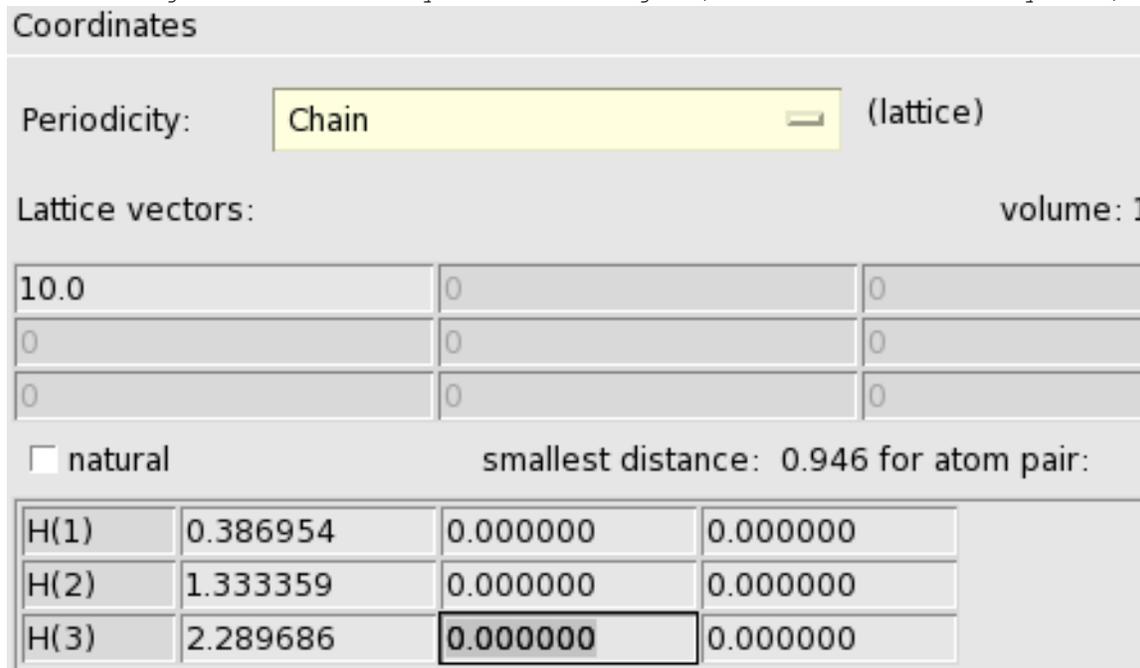
Coordinates

Periodicity: Chain   (lattice)

Lattice vectors: volume: 1

10.0	0	0
0	0	0
0	0	0

☐ natural   smallest distance: 0.946 for atom pair:

H(1)	0.386954	0.000000	0.000000
H(2)	1.333359	0.000000	0.000000
H(3)	2.289686	0.000000	0.000000

(Here I increased the values next to H(3)).

```
Run it again, and now it will run for more cycles.
After it has finished, open adfmovie
```

The last frame looks like
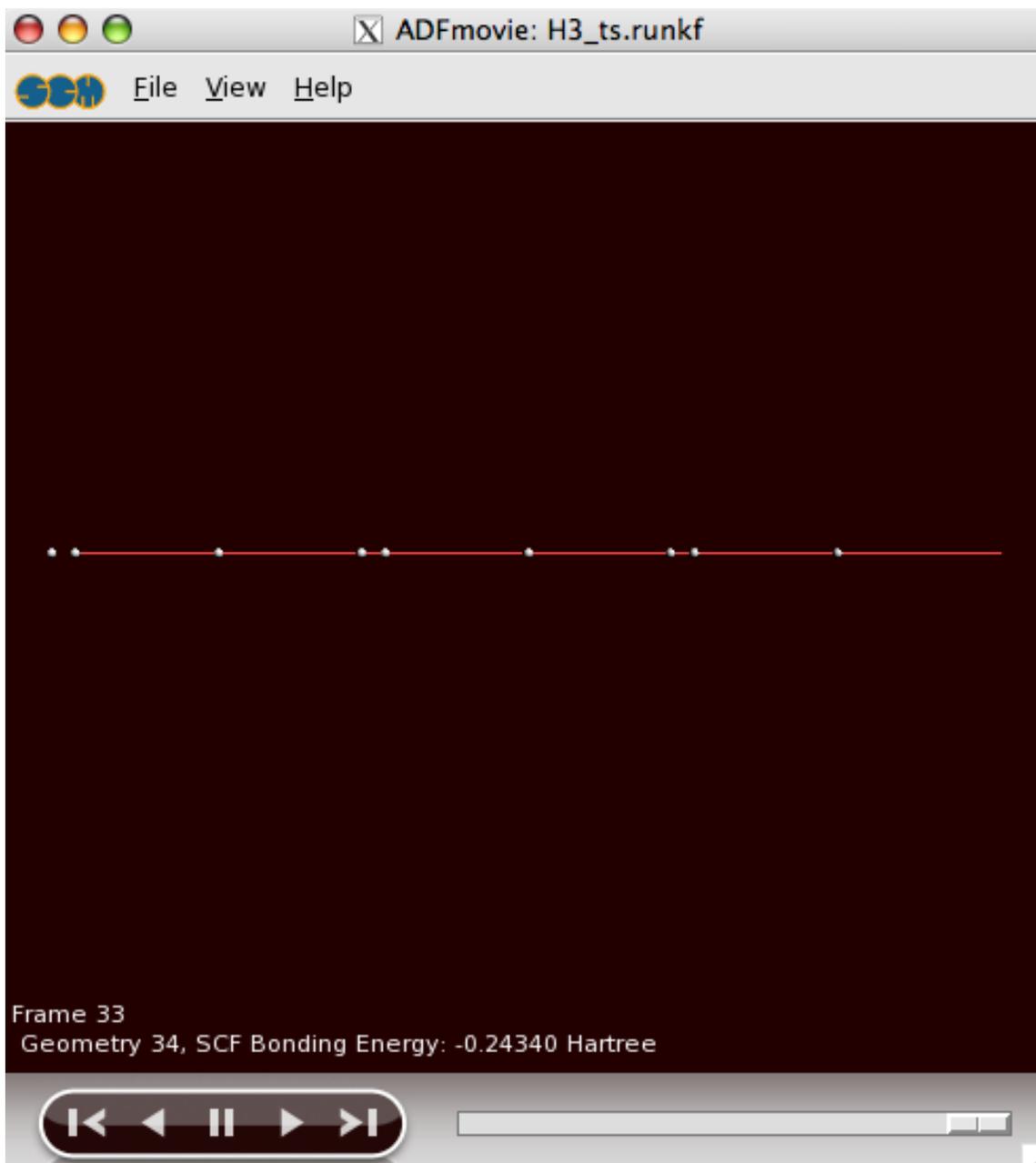
The third H atom ends up exactly in the middle of the (repeated) H1 and H2 atoms. Let us finally check that we are indeed in the transition state.

```
In the 'Main Options' panel select the task 'Frequencies'
Save the project as 'H3_ts_freq' and run it.
Afterwards, open adfspectra and click on the 'NormalModes' menu
```

You should see

```
NormalMode

1:  -44 cm-1 (1.00 km/mole)
2:   -0 cm-1 (1.00 km/mole)
3:   -0 cm-1 (1.00 km/mole)
4:   -0 cm-1 (1.00 km/mole)
5:    0 cm-1 (1.00 km/mole)
6:    0 cm-1 (1.00 km/mole)
7:    0 cm-1 (1.00 km/mole)
8:    0 cm-1 (1.00 km/mole)
9: 4172 cm-1 (1.00 km/mole)
```

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

Tutorial 4: a transition state search with a partial Hessian*

This tutorial will teach you how to:

- calculate a partial Hessian
- do a constrained TS search using the partial Hessian

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

Step 1: Create the system

We are going to make a one layer Li (001) slab with a 2x2 unit cell, assuming familiarity with the build tools

```
From the structure tool select 'Cubic' and 'bcc'
Set 'Element' to Li
Set the lattice parameter to 3.49
Press 'Apply' and 'Close'
Invoke the Slice tool
Set the Miller indices to 001, select 'Cartesian', and enter 1 layer.
Press 'OK'
Use the Edit → Generate Super Cell... command
Select the preset '2x2' and press 'OK'
```

Your screen should look like this (after selecting the 'Coordinates' panel)
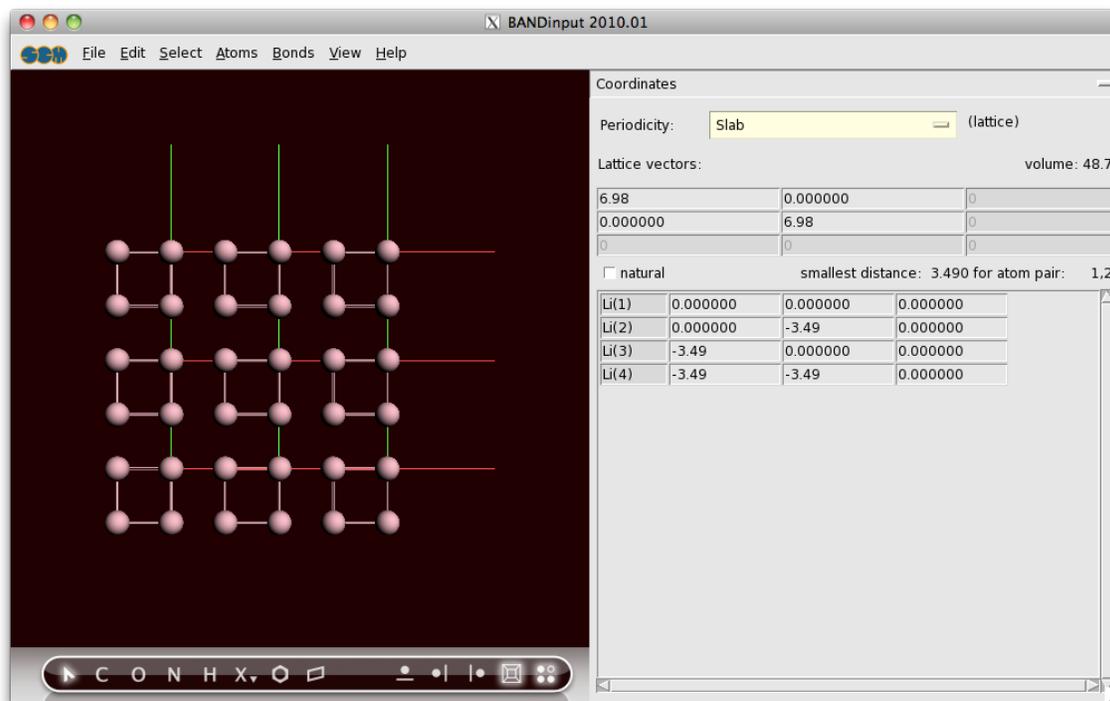
Add with the mouse two hydrogen atoms anywhere in the screen
Select the 'Normal' edit mode
Set in the table the coordinates of the first hydrogen atom to (0, -0.5, 2)
Set the second H atom coordinates to (0, 0.5, 2)

The final geometry looks like this
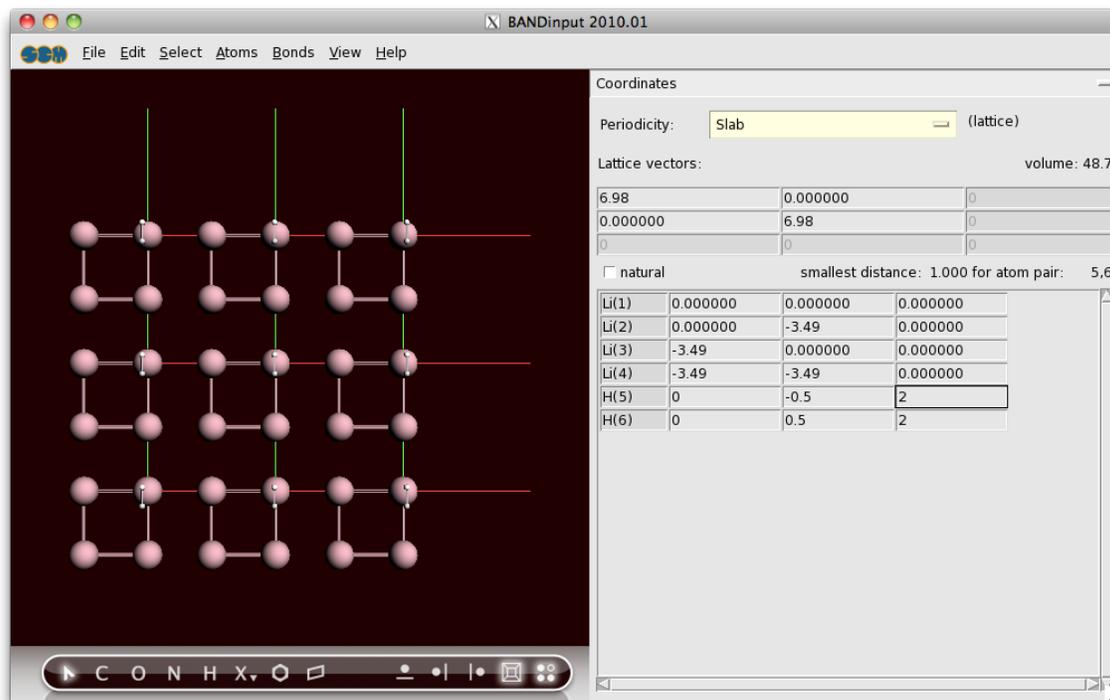
Step 2: Calculate a partial Hessian

```
Select the 'Main Options' panel
Set 'Task' to 'Frequencies'
Set 'Basis Set' to 'SZ'
```



```
Go to the 'Frequencies' panel
Select with the mouse the two tiny Hydrogen atoms
Click on the '+' button next to 'Partial Hessian For:'
```

```
Save the project as 'H2onLi_freq' and run it.
Say 'No' when asked to update the coordinates
```

Let us examine the eigenmodes that we have found for the Hydrogen molecule

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

Now you will see that there is an eigenmode at 448 cm-1 and one at 2164. Convince yourself that the 448 mode moves the H2 perpendicular to the service and that the 2164 more is essentially an H2 stretch mode. The lowest mode looks like a promising start to find the transition state for dissociation over the Li surface.

Step 3: Transition state search with a frozen substrate

We have just found the vibrational modes of the Hydrogen molecule, assuming that the Li substrate remains fixed. Let us now find the transition state under the same assumption.

```
Close the 'Spectra' window and go back to BandInput.
Select the 'Main Options' panel and set 'Task' to 'TransitionState'
```



```
Select the 'Geometry Constraints' panel
I assume that the two hydrogen atoms are still selected.
If not select them again
Use the  Select → Invert Selection  command
Click on the '+' button next to 'freeze selected atoms'
```
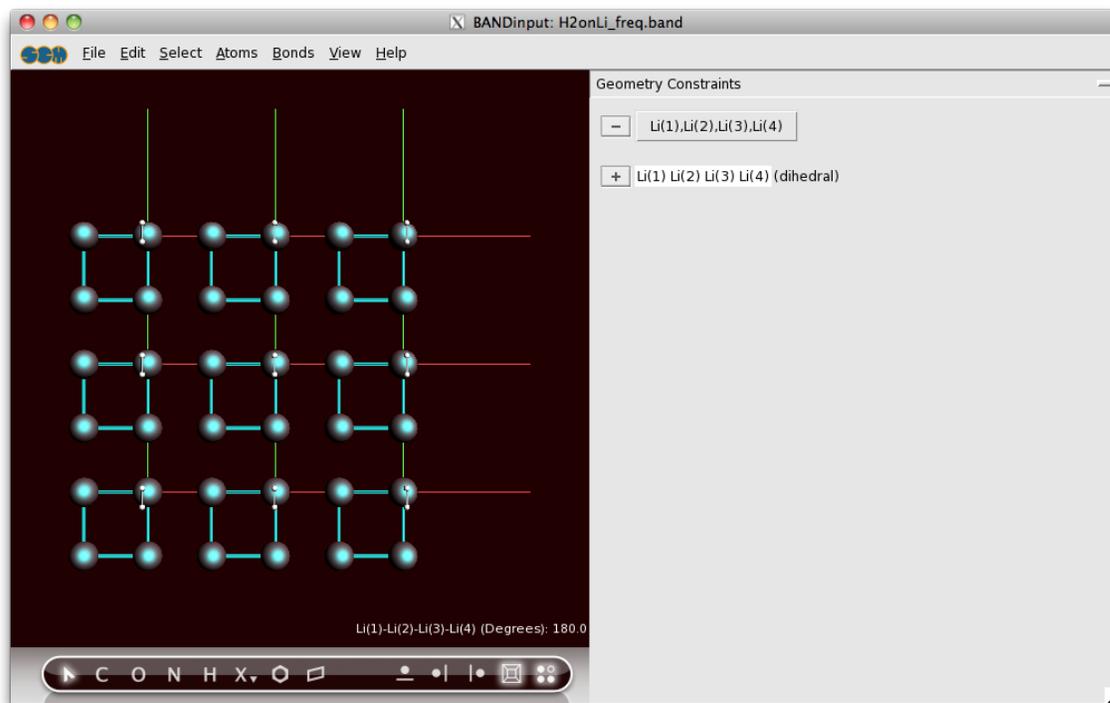
```
Goto the 'Optimization' panel
Set the initial Hessian to 'H2onLi_freq.runkf'
```



```
Save the project as 'H2onLi_ts' and run it.
```

After running it

```
Select SCM → Movie
Show the energy Graph → Energy
Select View → View Direction → Along x axis
```

It should look like
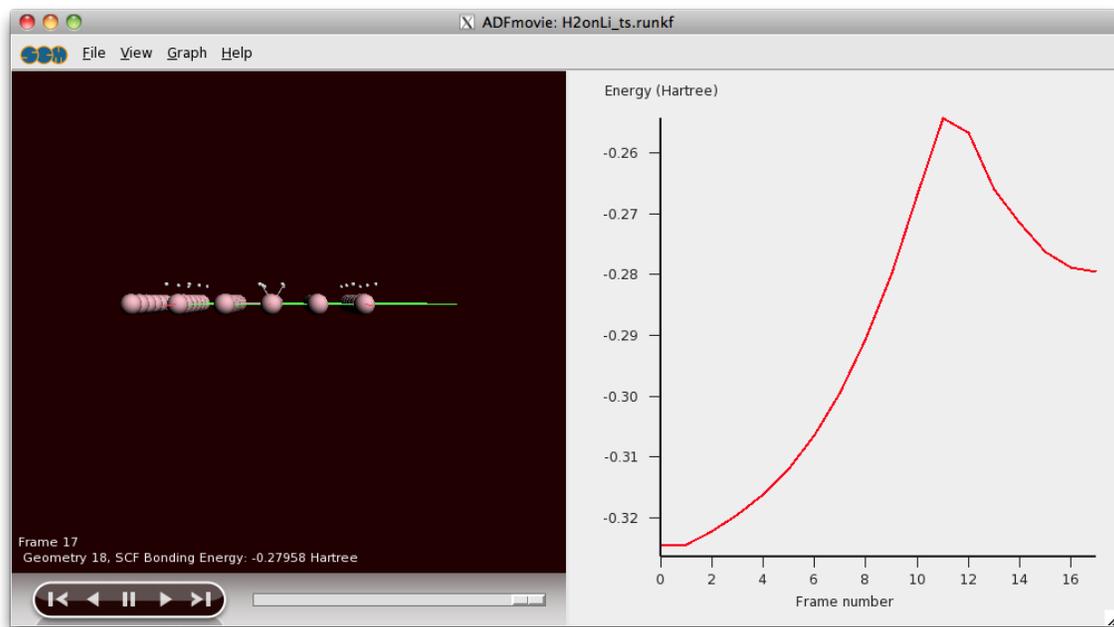
Tutorial Videos

The videos below represent a walk-through of each of the BAND tutorials. The videos contain voice-over commentary.

For readability, we recommend using the ⛶ - button to view the videos in full screen (720p HD).

Subtitles in the videos can be toggled on and off using the CC - button.

Tutorial 1: with a grain of salt

Tutorial 2: building structures

Tutorial 3: a transition state search

Tutorial 4: a transition state search with a partial Hessian