

# Controlling the gap with an electric field

## SCM Teaching Exercise

### Introduction

In this workshop you will learn a bit about using *Band*, the program by SCM for periodic DFT. The exercise focusses on a monolayer of Molybdenum disulphide, because this material is of interest for transistors. In particular the switching to and from a conducting state is of crucial importance.

If you have never used the ADF graphical user interface you may want to glance at the tutorials at the SCM website ([http://www.scm.com/Doc/Doc2013/GUI/GUI\\_tutorial/page1.html](http://www.scm.com/Doc/Doc2013/GUI/GUI_tutorial/page1.html)). Unlike the tutorials, not every button click is explained in this exercise, so feel free to ask us.

If you have never heard from 2D-periodic, DFT, etc, do not hesitate to ask us for an explanation...

Enjoy!

## Create the MoS<sub>2</sub> monolayer.

We will first build the crystal from the symmetry information. Open *adfinput*, and select as program *band*. At the bottom click on the snowflake and select *From Space Group*. The MoS<sub>2</sub> crystal is defined by its space group information. The space group is 194, the lattice is defined by **a=3.16** and **c=12.30**. The atomic positions are given by the so-called Wyckoff positions. The Mo atoms are at the twofold **c** site, and the S atoms at the fourfold **f** site, with **z=0.8785**. No matter what, this is what the dialog should look like

Dialog Window

Space Group

Number:

Browse:

orthorhombic	P	190: P -6 2 c
tetragonal		191: P 6/m m m
trigonal		192: P 6/m c c
hexagonal		193: P 63/m c m
cubic		194: P 63/m m c

Name: P 63/m m c

Lattice: hexagonal

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Lattice parameters

a	c
<input type="text" value="3.16"/>	<input type="text" value="10"/>

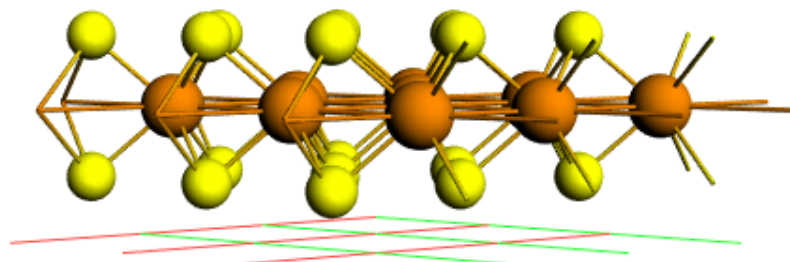
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Coordinates

	Elem	Site	Mult.	Coords	Parameters
<input type="button" value="-"/>	Mo	c	2	1/3,2/3,1/4	
<input type="button" value="-"/>	S	f	4	1/3,2/3,z	z <input type="text" value="0.8785"/>

Conventional Unit Cell

Press apply and close the window. Next go to the *Model* -> *Lattice*, and change the periodicity to *Slab*. Now take a look at the system from the side, like the *x*-direction, and you will see that we have made a double layer. Remove the atoms of the upper layer. Here is the result



## Optimize the geometry

Goto the main panel and select *Geometry Optimization*. Make sure the the lattice is also optimized. Run the calculation (this may take a few minutes) and accept the new coordinates. From the SCM menu you can select *Movie* to watch what happened during the optimization. In particular the energy should have gone down.

## Analyze the DOS

Fire up *Dos* from the SCM menu. You can compare the contribution from the Mo and the S atoms (by clicking on them). The peak on the left is clearly due the the Sulfur ( $3s$ ) states. The rest of the S is from the  $3p$  states. Not surprisingly the Mo also has a big  $d$  contribution (just below and above the fermi level).

## Examine the band structure

If you now open *Band Structure* from the SCM menu, you will see a disappointingly crude picture. Let us make it better. Change the *Run Type* to *Single Point* and goto *Properties -> BandStructure* and set the interpolation to 10. Run the calculation and open again *Band Structure*, now the bands look way better. As you can see we have an indirect band gap from the gamma point to point 2, which is on the edge of the Brillouin zone.

## Electron/hole transport (advanced)

For semiconductors the shape of the bands near the Fermi level tells you something about how easy the electrons (in the bottom of the conduction band) or holes (in top of the valence band) can move. A small curvature is bad, and a big one is good. The inverse of the curvature is called the effective mass of the electron or hole. To calculate it select *Properties -> Band Structure -> Effective Mass*. The result is visible in the raw output in the results section.

## Fix the band gap (advanced)

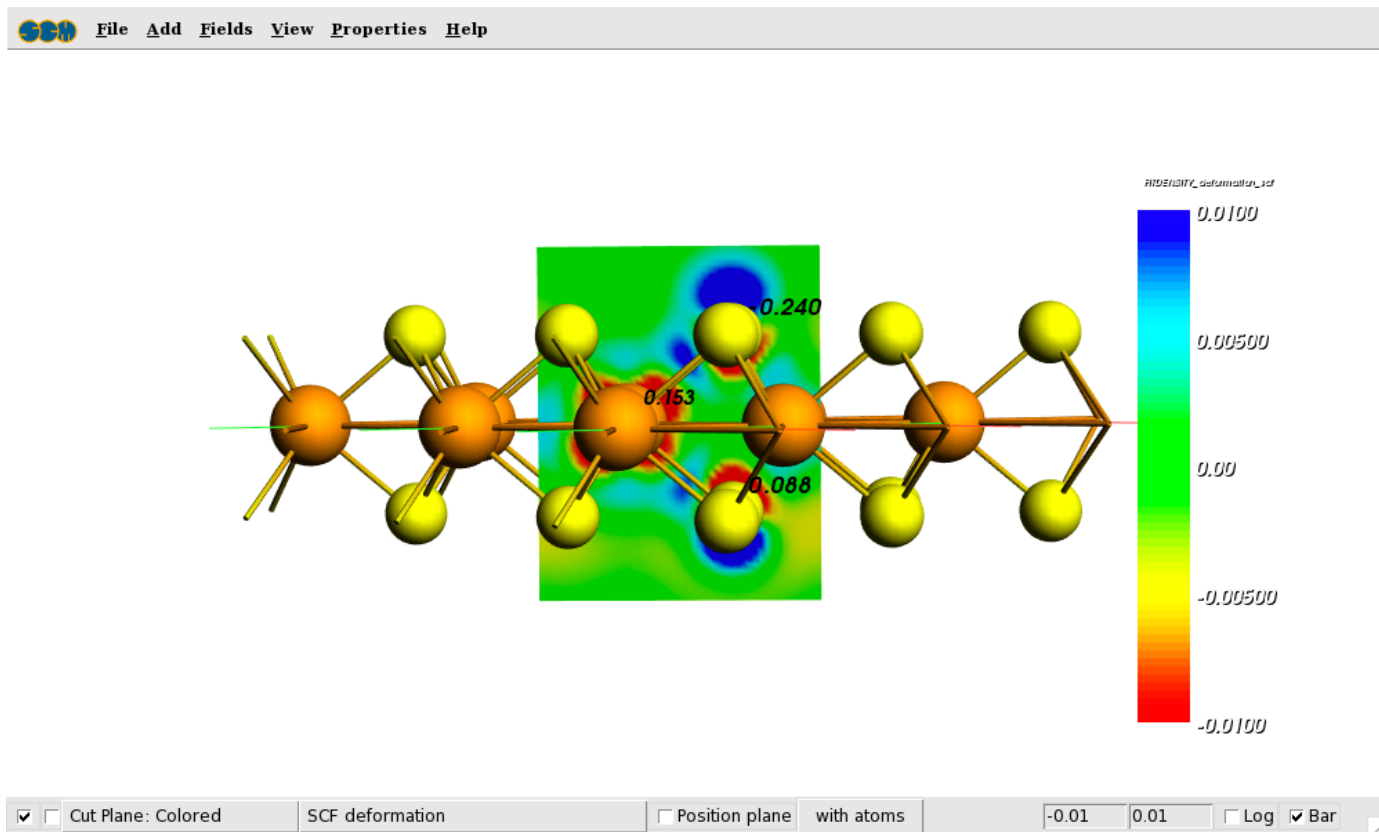
First let us look at the band gap. Fire up *Output* from the SCM menu. Select *Section->Results*, and scroll down to the band gap part. The band gap is 1.2 eV, whereas experimentally it is 1.8. Thus far we have used the LDA functional, which is known to underestimate the gap. There are several so-called model potentials available to specifically solve this problem, although they typically ruin everything else. For systems that are not crystals, the most convenient choice is the GLLB-SC functional. Now the Quasiparticle gap (being a fancy word for band gap) is increased to 1.4 eV.

## Applying an electric field.

Switch back to the normal LDA functional an set in *Model -> Electric Field* the field to 0.1 eV/Å. This has remarkably little effect. Try again with a field of 3.0, now we see the (LDA) gap reduces to 1.0 eV. At what field strength does the material become conducting? Congratulations, you have just switched the device!

## Analyzing the charge

What happens to the charge when you apply an electric field? Open *View* from the SCM menu. Now select *Add* -> *Cut Plane Colored* and select at the bottom *Fit density* -> *SCF deformation*. Select a top and bottom S, right click and select *Atom info* -> *Hirshfeld Charges*. At a field of 3 eV/Å I get after some tweaking this picture



As you can see, the electrons tend to move upwards, as they are (predictably) attracted by the external field.

## Improving the accuracy

Many aspects influence the results of a calculation. Some are technical, such as the choice of basis set, other are theoretical, such as the choice of functional. One thing that is always a good idea is to enable the scalar relativistic Hamiltonian, by selecting *Relativity* -> *Scalar*. This costs you nothing and is always better. (The even better *SpinOrbit* comes with a steep computational burden). The relativistic effect is small for light atoms and grows with the charge of the nucleus. The choice of XC functional is not so straightforward. However, to use a GGA is generally better than using the plain LDA. Among the GGAs the PBE functional is a reasonable choice. Finally, the DZ basis set is usually too small, and one should preferably use a TZP one. For the gap (especially when *p*-electrons are involved) also the spin-orbit might be needed.