EXERCISES

Computational Materials Science

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SHEET 1

Exercise 1: Density functional theory

Goal of this exercise: Use the WIEN2k code to calculate the (1) ground state energy, (2) partial densities of states (DOS) and (3) bandstructure of $SrVO_3$. The steps to this end are given below. You can also follow the *QuickStart* section of the user guide available at `http://www.wien2k.at/reg_user/textbooks`.

Strontium vanadate $SrVO_3$ is a *cubic perovskite* (space group 221, $Pm\bar{3}m$) with a lattice constant of 3.8425 Å and atoms at the positions

Sr	(0, 0, 0)
V	(1/2, 1/2, 1/2)
O1	(0, 1/2, 1/2)
O2	(1/2, 0, 1/2)
O3	(1/2, 1/2, 0)

0. *Preliminaries*: WIEN2k needs to have a few environment variables defined. Go to the directory `~cms00/WIEN2k_12` and execute the script `userconfig`

Then go to `~cms00/XCrySDen-1.5.25-bin-semishared/` (hint: use tab completion) and execute the script `xcConfigure`.

These scripts wrote to your bash init file `~/.bashrc`. To make sure it is reloaded, log out and log back in.

Now start the Wien2web server by executing `w2web`. When asked for a port, please choose **7890 + your account number**. When you are done, you should shut down the server with `killall w2web`. Lastly, start a browser and point it to the w2web URL.

1. Create a *session* for $SrVO_3$. Create a new directory `SrVO3` for your calculation. Now start *StructGen* to create the "master input file" `SrVO3.struct`. (Hint: there are only **3 independent atoms** in the structure, the others are given by symmetry.) When you have entered the relevant information, choose "Save Structure" and "set RMT" (reduce by 0%); then again "Save Structure" and "clean up". Now you can look at the crystal you created with XCrysDen (click "view structure") to make sure it is correct.

Q1. Save a picture of your structure (hint: the little button at the top left of the XCrysDen window allows you to change the background color).

2. Choose *initialize calculation*. Follow the steps. There will be a lot of information to be entered and viewed, but do not worry: you can leave almost everything at its default in this case. Choose **500 k-points**, and **"no" for spin-polarized**.

Q2. After the initialization (specifically, `nn` and `symmetry`), the struct file is now complete. This file is arguably the most important piece of information for any WIEN2k calculation. Look at it: How many atoms are there? How many symmetry operations are there? Consider symmetry operation 29, and explain what it means.

Q3. `kgen` generated a list of *k-points* for your calculation. Look at the `klist` file: How many points are there? Why?

3. You are now ready for your first DFT calculation! Choose *run SCF* ("self-consistent field").

Q4. While the calculation is running, you can monitor its progress via the files `SrVO3.scf` (look for `:ENE` and `:DIS`). It is best to do this from the command line rather than the browser.

You are now in a position to give the answer for our first goal above: What is the ground state energy of $SrVO_3$?[1]

4. When the SCF is done, we can calculate the *density of states*. Choose "Tasks / DOS" and follow the steps (hint: in "configure SrVO3.int", choose the total density of states for each atom, plus the t_{2g} and e_g contributions of V.

Q5. You have now achieved the second goal above: the DOS. This is a very important quantity and can give a lot of information quite concisely.

Also, think about the physics. Which are the most "important" contributions to the DOS? Compare the t_{2g} and e_g contributions of V. Which one is higher in energy? Can you say why?

Can you identify from the DOS which states hybridize with each other? This gives a hint about the bonds in the crystal.

5. Next, we want to view the *bandstructure*. Choose "Tasks / Bandstructure" and follow the steps (hint: the first two points are alternative).

[1] This is a bit of a trick question, because this number by itself means very little, and depends on the details of the calculation. Only a comparison of the energy between different calculations (e.g. with different atomic positions) is really meaningful.

Q6. When you have made it through to "spaghetti", you can answer the third goal: create a bandstructure plot. There are not many options here, but do compare to the DOS. How are DOS and bandstructure related – which one could be derived from which, and how? Can you identify some of the bands? (Which atoms/states they correspond to.)

6. You are done with the compulsory part of the exercise – now it is time to have some fun! Explore your own paths. Here are some suggestions, approximately in increasing order of difficulty:

- Check to see if the various "quality settings" of the calculation (number of k-points, $RK_{\max}$, ...) we used are good enough. (How would you do that? – Hint: what is "good enough" can also depend on what quantity you are interested in.)
- Make a *band character* (or "fat bands") plot. Which band character would you choose?
- Try a different functional. Which one did you use up to now? Which other functionals do you know? Or even: What is a "functional" in this context?
- Plot the optical conductivity. Identify different contributions (hint: compare to the DOS).
- Plot the electron density. There are many options: 2D/3D, SCF density / difference density, valence density / total density, ... – What do "density/difference" and "valence/total" mean?

Hint: before you continue after "spaghetti", you will have to execute "x lapw1" again.

If you need help, ask us, or look in the user guide.