

The 1st CMS exercise: a DFT calculation with wien2k

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The primary goal of this exercise is to guide you through the main steps of a DFT calculation: the initial setup, a self-consistent calculation, and plotting density of states as well as the band structure.

Calculations will be performed using the code wien2k version 14.2. As a step-by-step guide, please refer to the Chapter 3 of the wien2k documentation available at www.wien2k.at/reg_user/textbooks/usersguide.pdf. Upon completion of all tasks, please send the answers to the numbered questions (in the margins) to O. Janson (janson@ifp.tuwien.ac.at) and Prof. K. Held (held@ifp.tuwien.ac.at).

To log in, please use the login name cms15_□ (mind the underscore symbol) and the password 42cms15. Please change the password (execute "passwd" in a terminal window) immediately after logging in. **Note your new password!**

A few steps to configure wien2k for your account

1. Open a terminal window and execute

```
/home/CMS/cms00/wien2k_14.2/userconfig_lapw''.
```

Use the default settings.

2. Open the file ".bashrc" in your home directory and replace

```
#export LD_LIBRARY_PATH=.....
```

with the following lines:¹

```
export LD_LIBRARY_PATH=\
/opt/intel/composer_xe_2013.4.183/compiler/lib/intel64:\
/opt/intel/mkl/lib/intel64:$LD_LIBRARY_PATH
```

3. open a new terminal window and run "w2web". Choose a port number, e.g. the sum of the default port 7890 and your login number. Copy the URL and paste it into a browser window.

Important: to restart the server, open a terminal window, run "killall w2web" (don't worry about the warnings) and then "w2web".

The cubic modification of MgTi₂O₄ has a spinel structure:

Site	Wyckoff position	x/a	y/b	z/c
Ti	16d	1/2	1/2	1/2
Mg	8a	1/8	1/8	1/8
O	32e	0.25920(2)	0.25920(2)	0.25920(2)



Figure 1: The Black Prince's Ruby of the Imperial State Crown is actually a spinel (MgAl₂O₄).

¹ Backslashes stand for line breaks, you can skip them if you write the command as a single line. You should however keep all forward slashes as well as colons.

Table 1: The structure of MgTi₂O₄ measured at 275 K. The lattice constant $a = 8.509027(5)$ Å, the space group is $Fd\bar{3}m(227)$. Data from M. Schmidt *et. al*, Phys. Rev. Lett. **92**, 056402 (2004).

Basic tasks

Setting up a calculation

1. Create a new session called “MgTi₂O₄” and execute StructGen to create the structure file “MgTi₂O₄.struct”. Follow the instructions and use the suggested muffin-tin radii (if you don’t remember what these radii mean, check the slides of the 2nd DFT lecture) and save the structure. Visualize the crystal structure using either XCrysDen

```
/home/CMS/cms00/XCrysDen-1.5.25-bin-semishared/xcrysden
```

or vesta

```
/home/CMS/cms00/VESTA-x86_64/VESTA
```
2. For the next steps, and use the “**Individual mode**” with default values, except for (i) instgen_lapw, where you should select “**no spin-polarization**”, and (ii) set the value of **RKMAX** to **6.5** (the default is 7.0). Please read all the outputs and try to understand what the program is doing.
3. You will be asked for the number of *k*-points. As we have limited resources at our disposal, choose a very sparse mesh of 100 points, but keep in mind that for an accurate calculation, much denser grids are necessary.
4. After finishing the setup, you are ready to start your first wien2k calculation. Choose a non-spin-polarized calculation (the script on web page may crash, simply ignore it) and run a self-consistent calculation (SCF). You can monitor the progress by refreshing the page (the upper right corner). If the server is not heavily loaded, self-consistency should be reached within ~6 minutes.

The most basic output

5. Most important information on our calculation is written in the file “MgTi₂O₄.scf”. Use the web interface to access this file and examine the output.
6. To plot the density of states (DOS), use the menu “Tasks/DOS” and follow the steps. Make two plots: (i) the total and the atomic-resolved DOS, and (ii) the orbital-resolved DOS for Ti.
7. Plot the band structure (“Tasks/Bandstructure”). Can you say something about the electronic dimensionality of the compound (quasi-1D, quasi-2D, or 3D)?

Important: after you’ve finished all calculations, open a terminal window and run “killall w2web” (don’t worry about the warnings).

Q1 How many atoms does the conventional unit cell comprise? What are the coordination numbers (number of nearest-neighbor oxygen atoms) of Mg and Ti?

Q2 In the output of the symmetry program, check the number of atoms. Why is it different from the number of atoms in the conventional unit cell?

Q3 Check the output of kgen. What is the actual number of points used? What is the meaning of the number indicated in the last column for every point?

Q4 What is the resulting total energy of MgTi₂O₄? Why is this number negative?

Q5 Does GGA yield a metal or an insulator? Describe the structure of the valence band (which atomic states appear at which energy).

Q6 Why some of the Ti *d* orbitals can not be resolved (e.g., *xy* and $x^2 - y^2$)?

Q7 How many bands constitute the manifold (separated by gaps from the other bands) around the Fermi energy? Can you explain it? What are characteristic band widths and the crystal-field splitting for Ti *d* electrons?

More advanced tasks

If you have finished the compulsory part of the exercise and would like to gain more experience in using wien2k, you can perform one or several advanced tasks.

Volume optimization

Calculate the equilibrium GGA volume. You can either use the “optimize (V , c/a)” option, or perform a series of calculations for different volumes. Please keep in mind that such a series of calculations should be done using the same muffin-tin radii, hence you should start a calculation from scratch with reduced (\lesssim 3–5%) radii.

Q* How different is the GGA equilibrium volume from the experimental one?

Dependence on the size of the basis set

For the compulsory part of the exercise, we chose RKMAX=6.5, which is smaller than the default value. Perform additional calculations for RKMAX=7.0 and 7.25 and compare the densities of states.

Q** How large are the basis sets for all three cases (search the output file for “::RKM”)?

Transformation of the local coordinate system

When plotting the orbital-resolved DOS for Ti, we were unable to select the $t_{2g}-e_g$ representation, which is a natural choice for an octahedral environment. Your task is to plot e_g and t_{2g} contributions to the Ti DOS (use the `qt1` program).

Q*** Ti states hybridize with O states. Which of the two channels (t_{2g} or e_g) shows a stronger hybridization? Why?

Electronic density plots

wien2k can be used to visualize electronic density in real space. Plot the electronic density of (110) planes.

Important: after you've finished all calculations, open a terminal window and run “killall w2web” (don't worry about the warnings).