

The 2<sup>nd</sup> CMS exercise:  
Maximally localized Wannier functions  
with wien2k & tight-binding analysis

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In this exercise, we will learn more advanced features of wien2k, calculate maximally localized Wannier functions using wien2wannier and wannier90, and use them to construct a simple, yet realistic tight-binding Hamiltonian.

We assume that wien2k version 14.2 is configured for your account and that you already know how to perform standard band-structure calculations. Should it not be the case, please start with the first exercise. A reminder: Chapter 3 of the wien2k documentation available at [www.wien2k.at/reg\\_user/textbooks/usersguide.pdf](http://www.wien2k.at/reg_user/textbooks/usersguide.pdf) provides a step-by-step guide.

Upon completion of all tasks, please send the answers to the numbered questions (in the margins) to O. Janson ([janson@ifp.tuwien.ac.at](mailto:janson@ifp.tuwien.ac.at)) and Prof. K. Held ([held@ifp.tuwien.ac.at](mailto:held@ifp.tuwien.ac.at)).

To log in, please use your existing login name and the password.

A necessary preparatory step includes a GGA calculation for the tetragonal PbVO<sub>3</sub> structure:

Site	Wyckoff position	$x/a$	$y/b$	$z/c$
V	1a	0	0	0
Pb	1b	1/2	1/2	0.5708
O(1)	1a	0	0	0.358
O(2)	2c	1/2	0	-0.1194

Perform a non-spin-polarized calculation using RKMAX = 6.5 on a grid of 200 k-points. For other parameters, use the default values.

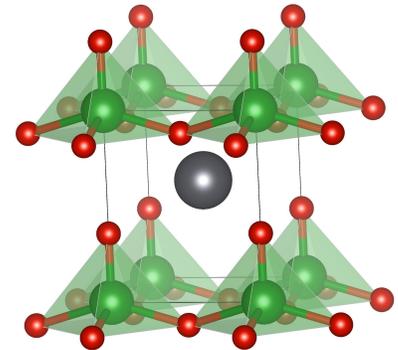


Figure 1: The crystal structure of PbVO<sub>3</sub> featuring VO<sub>5</sub> pyramids.

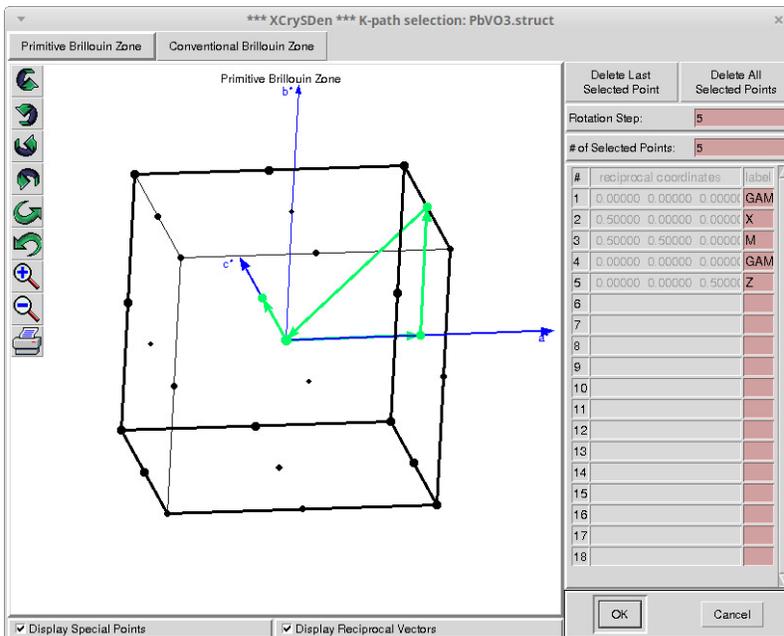
Table 1: The structure of PbVO<sub>3</sub>. The lattice constants are  $a = 3.80 \text{ \AA}$ ,  $c = 4.67 \text{ \AA}$ , the space group is  $P4mm$  (99). Data from R. V. Shpanchenko *et. al*, Chem. Mater. **16**, 3267 (2004).

### Plotting DOS and the band structure

1. You already have a converged density on a very sparse k-mesh. Use a denser k-mesh of 800 points to calculate DOS. Set the parameters in the input file for TETRA such that you get a reasonably good resolution for the energy range of interest ( $\sim \pm 1$  eV around the Fermi energy). You can directly access the DOS values in the files `case.dos1` and `case.dos1ev`.
2. To perform a band structure calculation, we need to prepare a suitable k-path first. To this end, you can open your struct file using the program `xcrysdn` which can be called from a terminal window (here, we assume that your case is named "PbVO<sub>3</sub>" and you are in the home directory):

```
~/../cms00/XCrySDen-1.5.25-bin-semishared/xcrysdn --wien_kpath WIEN2k/PbV03/PbV03.struct
```

Select the  $\Gamma$ -X-M- $\Gamma$ -Z path:



On the next screen, the total number of k-points should be 200. Save the file and copy it to your case directory (e.g., "WIEN2k/PbV03") under the name `(case).klist_band` (e.g., "PbV03.klist\_band"). Then go back to your browser window and proceed with the band structure calculation, but **skip the first step**, as otherwise your `(case).klist_band` file will be overwritten.

**Q1** Report the values for (i) the total DOS and (ii) the  $V d$  contribution at the Fermi energy.

**Q2** How many times do the bands cross the Fermi level? (plot the  $-0.1 \dots 0.1$  eV energy range to check)

3. With a little knowledge of chemistry, we can readily guess that the bands at the Fermi level should be V  $3d$  states (you can however easily check it with wien2k). The next point is to figure out the orbital character of the half-filled band crossing the Fermi level. This can be done by plotting the band characters. The functionality of the web interface is not great for this particular task, so we need to go back to the terminal and inspect the file `<case>.qt1` to figure out the indices of different orbitals:

```
...
JATOM 1 MULT= 1 ISPLIT=-2 tot,0,1,PZ,PX+PY,2,DZ2,DXY,DX2Y2,DXZ+DYZ,3
...
```

Here, V is "JATOM 1" (the same order as in the struct file) and its  $d$  orbitals have column indices 7 to 10 (note that  $xz$  and  $yz$  orbitals are degenerate). Then we go back to the web interface and edit the `<case>.insp` file by adding one more line below the "0 1 0.2" line. For instance, to plot the band characters for the  $x^2 - y^2$  orbital (the 9<sup>th</sup> column), you add

```
1 9 0.2
```

Check the band character accordingly for all the  $d$  orbitals.

Q3 Which V  $3d$  orbital is half-filled?

### *Calculating the maximally localized Wannier functions*

4. We figured out the band character of the half-filled orbital (let's call it  $\mathcal{D}$  orbital), and our next big goal is to construct an effective one-orbital tight-binding model. This model needs to be parameterized and the best way to do it is to calculate the respective maximally localized Wannier function (MLWF). This is done via the wien2wannier interface by the wannier90 program. Both codes are very well documented, so we'll keep the discussion very short here. For a detailed explanation of all steps and the description of the input files please refer to

[www.wien2k.at/reg\\_user/textbooks/wien2wannier\\_userguide.pdf](http://www.wien2k.at/reg_user/textbooks/wien2wannier_userguide.pdf)  
and  
[www.wannier.org/doc/user\\_guide.pdf](http://www.wannier.org/doc/user_guide.pdf).

The calculations are done **in a separate folder** and can not be performed using the web interface. Again, we have to go back to the terminal, `cd` to the case directory and execute there:

```
prepare_w2wdir ../PbV03_wf
cd ../PbV03_wf
export PATH=$PATH:/home/CMS/cms00/wannier90-2.0.0
init_w2w
```

You may add this line to your `.bashrc`.

In the last line, we started an interactive script of wien2wannier. Use 200 k-points without a shift. Next, the program asks for band

indices. wien2k numerates the bands according to their energies at every k-point. Hence, if we have band crossings (which is indeed the case for PbVO<sub>3</sub>), the band with the maximal  $\mathcal{D}$  character can have a different index at different k-points. In other words, we need to perform a disentanglement.

In wien2wannier, we need to specify the range of indices such that the index of the  $\mathcal{D}$ -band **at every k-point** falls into this range. So you should check very carefully by analyzing the band characters (this can be done using the web interface), which indices to feed to wien2wannier.

In the next step, we need to specify projections, i.e. tell the program, which orbitals we are interested in. These are given in the format "site:orbital", where "site" is an integer (should be 1 for V), while for the orbital you should use  $\mathcal{D}$  (dxy, dyz, dz2, dxz, or dx2y2). Since you specified more than one band in the previous step, you will be asked also for other projections. But the rest of the bands represent states that we are not interested in, hence just press Ctrl+D. The program then knows that it needs to do disentanglement.

After finishing the input, execute:

```
x lapw1
x w2w
x wannier90
```

The actual calculation of MLWF was done in the last line. To check, whether the resulting Wannier function reproduces the DFT band dispersion, run gnuplot and execute

```
set yrange[-1:1]; plot 'PbV03_wf.spaghetti_ene' using ($4/0.53):5, 'PbV03_wf_band.dat' with lines}
```

*For perfectionists: To improve the fit, you can play with the disentanglement parameters that are specified in the PbV03\_wf.win file.*

5. We can now use the Wannier functions to compute the  $\langle \vec{0}n | H | \vec{R}m \rangle$  products that can be further used in a tight-binding model. In fact, such products are already computed and stored in the file PbV03\_wf\_hr.dat (columns 6 and 7 for real and imaginary part, respectively; for MLWF the imaginary contributions should be always zero). Open the file and find two most relevant transfer integrals that are symmetrically-inequivalent (all symmetrically equivalent terms are considered as one).

To find out the band indices, go back to the web interface and download the band structure in the agr format. After opening it using xmgrace (If it is not installed, use a copy from /home/CMS/cms15\_30/grace/grace/bin), you can figure out the index of a certain band simply by double-clicking it.

**Q4** Deviations between the Wannier projections and the DFT bands structure are clearly visible, in which parts of the Brillouin zone they are most pronounced? What is the radial spread of the resulting Wannier function? (check the PbV03\_wf.wout file)

**Q5** What are values (in meV)? Taking into account only these two terms, how would you call the resulting model?

### Tight-binding modeling

6. In the final part of the exercise we will perform a tight-binding modeling. From MLWF, we already know the two relevant terms, let's call them  $t_1$  and  $t_2$ . Now we need to evaluate the matrix elements of the tight-binding Hamiltonian matrix, which by virtue of the one-orbital nature of our model, reduces to a simple expression. Matrix elements have this general form:

$$\sum_j t_{ij} e^{-i(\vec{R}_j - \vec{R}_i) \cdot \vec{k}}, \quad (1)$$

where  $t_{ij}$  and  $\vec{R}_j$  are taken from the file `PbV03_wf_hr.dat`,  $\vec{R}_i$  is zero. Note that you should take into account all symmetrically-equivalent  $t_1$  and  $t_2$  and the on-site term  $\epsilon_0$ , which is also listed in `PbV03_wf_hr.dat`. Construct the tight-binding Hamiltonian.

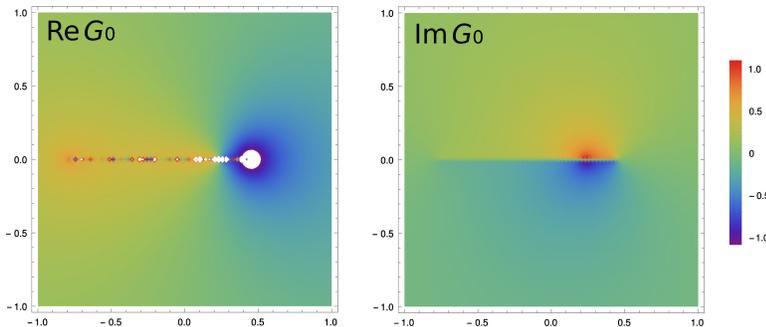
7. Calculate the eigenvalues of the tight-binding Hamiltonian for selected k-points:  $\Gamma = (000)$ ,  $X = (\frac{\pi}{a}00)$ ,  $M = (\frac{\pi}{a}\frac{\pi}{a}0)$ , and  $Z = (00\frac{\pi}{c})$  and compare with the DFT band structure. (Alternatively, you can calculate  $E(\vec{k})$  for the entire  $\vec{k}$ -path, it is even more instructive!)
8. As a final step for today, we will calculate the non-interacting Green's function. For our  $1 \times 1$  problem, it is given by:

$$G_0(\omega) = \frac{1}{N_{\vec{k}}} \sum_{\vec{k} \in \text{BZ}} \frac{1}{\omega - E(\vec{k})}, \quad (2)$$

where  $N_{\vec{k}}$  is the number of  $\vec{k}$  points in the sum and  $\omega$  is a **complex** frequency. By putting  $\omega \rightarrow \omega + i\delta$  ( $\delta$  is a small positive real number), evaluate the spectral function (DOS):

$$A_0(\omega) = -\frac{1}{\pi} \text{Im} G_0(\omega). \quad (3)$$

You can of course evaluate  $G_0$  in the entire complex plane:



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

**Q6** For the tight-binding model with two relevant couplings  $t_1$  and  $t_2$ , write down the final expression for the band dispersion  $E(\vec{k})$ .

**Q7** Write down the energy differences  $E(\text{DFT}) - E(\text{TB})$  for these four points. How would you explain the origin of the deviations?

**Q8** Integrate  $A_0(\omega)$  over all frequencies and report the result. What is the physical meaning of this result?

Figure 2: Real (left) and imaginary (right) parts of the non-interacting Green's function  $G_0(\omega)$  evaluated on the complex plane.