

Band weights — coherent mixtures

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We will show how to create band weights for coherently mixed orbitals. This is different from adding band weights, since the band weights are already “magnitude-squared”. The example is chosen such that we can have a little tour through the GUI.

The solution will be found in the `solution` directory. You will work in the `task` directory.

The basic converged calculation is already setup in `task`. It is MgB_2 Fig(1). In the following we will refer to boron atoms $B_{0...3}$, which denote the atoms in the right panel. Keep this in mind.

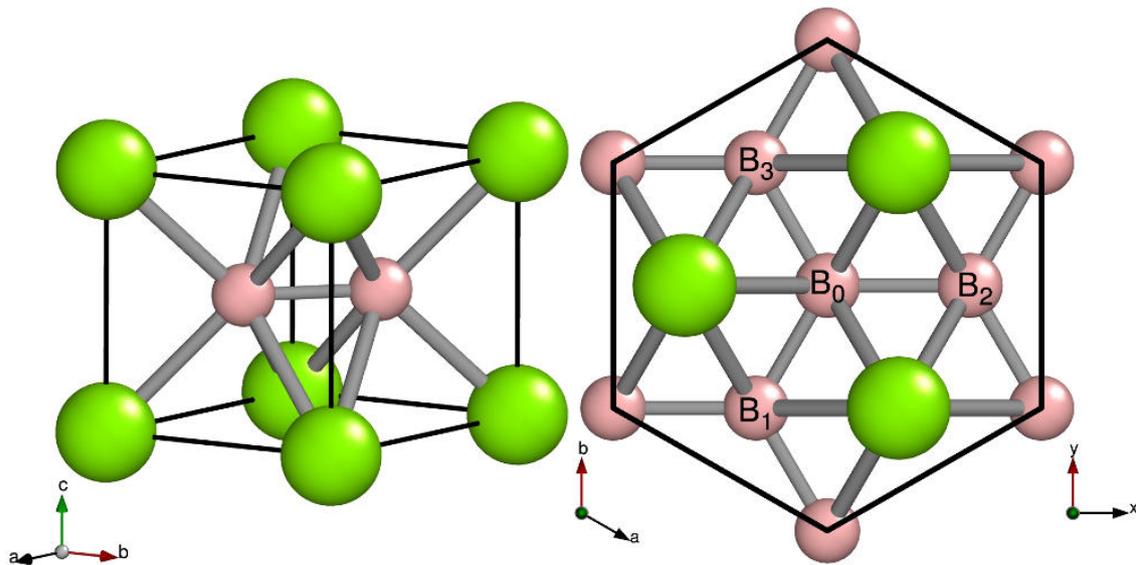


Figure 1: The structure of MgB_2 . Left: unit cell. Right: useful view.

1 The structure view

We need a particular structure representation to continue.

So, we created the right panel of Fig. 1

- First open the structure

```
xfplo =.in
```

- Open the boundary dialog **Input > Boundary**
- In the **Boundary Type** selectbox choose **User defined**.
- Click on the arrow of the **load** button and choose **Hexagonal Faces**.
- At the bottom enter the origin $(\frac{2}{3}, \frac{1}{3}, 0)$. Use fractionals as input: 2/3.
- Hit **enter** (**Accept** button).
- Close the dialog.
- Click on the structure view to make it the current window.

- Switch on the cartesian frame  (hotkey: **a a**) for better orientation.



- Switch to top view  (hotkey: **v t**)
- Hit the **reset** button or **Ctrl-R R** in the structure view (SV) .
- Now, open **Plot > Atom Labels**.
- Check the **visible** checkbox.
- Check out the content of the **Type** combobox.
- Hit the **Load default** button, followed by **enter**.
- Hit the **Set** button and select **Unchecked** from the menu and hit **enter**.
- Now, click on the central atom (B_0) in the SV to select the corresponding label in the **User defined** table.
Check the checkbox in the **first column** and edit the **Label** to read **B\$_0\$**. (use **double click** or **F2** on the label).
- Repeat the last point for the other three atoms according to Fig. 1.
- Edit the **y** line-edit and enter **0.16** and set the **fontscale** to **0.75**.
- Hit **enter** and close the dialog.
- Save the structure setup in **=.xstr**: **Ctrl-S** or **File > Save**
- Close the SV (**Ctrl-W**).

2 The default band weights

First we calculate the default fatbands, since they tell us the first fact about this system.

- Open `fedit` and switch on `bandplot` \triangleright `bandstructure plot` and `bandplot` \triangleright `weights`.

- run

```
fpl022.00-62-x86_64 | tee out
```

- Search “Atom sites” in the output file `out` to establish that the boron sites are 2 and 3.

- run

```
faddwei22.00-62-x86_64
```

- and answer yes to create `=.addwei`

- edit `=.addwei` to look like this

```
weightinfile +bweights
weightoutfile +bwsum

name 'B s'
  atom B sites 2..3 orbitals 2s+0
name 'B p $\tilde{s}$ '
  atom B sites 2..3 orbitals 2p-1 2p+1
name 'B p $\tilde{p}$ '
  atom B sites 2..3 orbitals 2p+0
```

- Now run

```
faddwei22.00-62-x86_64
```

- Run

```
xfbp +bwsum
```

go to the `Edit` \triangleright `Sets` dialog and it's `Weights` tab. In the `Weights` table select all three with the mouse. Then click on the arrow of the button above the `Weights` table and select `Checked`. Hit `enter` or click the `Apply` button. In the main window hit the `autoscale all`

button  or press `Ctrl-A`.

- Print the picture as “`bwei.png`” (`Ctrl-P` or `File` \triangleright `Print`)
- Close `xfbp` (`Ctrl-Q` or `File` \triangleright `Quit`).

You must see Fig. 2.

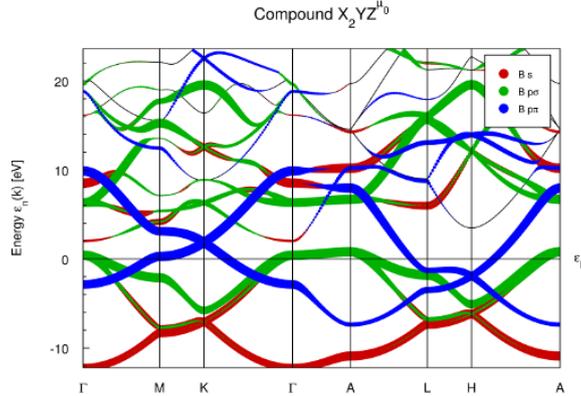


Figure 2: The default B 2s, 2p σ and 2p π fatbands.

We have added all in-plane p orbitals (p_x and p_y) and called them σ (which will become clearer later). The remaining p_z -orbitals form π -bonds along the hexagonal boron ring. Last, the boron s -orbitals are also printed. We see that the s and $p\sigma$ orbitals hybridize while the $p\pi$ bands are mostly criss-crossing the s , $p\sigma$ -bands without much hybridization. This is typical for hexagonally coordinated carbon-ring like structures and indicative of the usefulness of the sp^2 -hybrids. Note further, that the p_x and p_y orbitals are transforming into each other under a fourfold rotation. The threefold rotation present at the boron sites does not have the same symmetry as the $p\sigma$ -orbitals. This is not really an issue for the calculations but it bugs a chemist's mind. The set of three sp^2 -hybrids on the other hand will have manifest C_3 rotational symmetry.

3 sp^2 -hybrids on all B sites

We will construct the sp^2 -hybrids at the central B_0 -atom. At the other inequivalent boron site in the unit cell a similar set of 3 180° rotate sp^2 -hybrids exists.

Now, lets count a bit. We have roughly 3 occupied s - $p\sigma$ bands (red and green in Fig. 2). In total we have 2 boron, which makes 6 such orbitals. Obviously, there must be 3 unoccupied bands of the same orbital character. If we find 3 equivalent orbitals per site, we span the same Hilbert space. The well known answer is the sp^2 -hybrid

$$\begin{aligned}\phi_1 &= \alpha s + \beta p_x \\ \phi_2 &= \alpha s + \beta C_3 p_x \\ \phi_3 &= \alpha s + \beta C_3^2 p_x\end{aligned}$$

where we need to choose the orientation of the p_x lobe to point along the connection of two closest boron atoms. Obviously

$$C_3 \phi_i = \phi_{i+1 \pmod 3}$$

Compare Fig. 3 to Fig. 1.

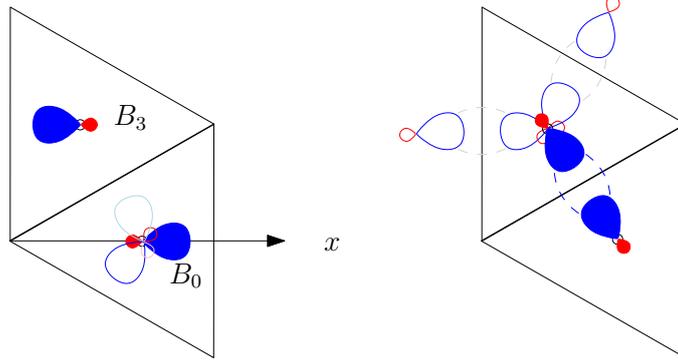


Figure 3: Left: a sketch of the sp^2 hybrids on the B_0 and B_3 sites. The open symbols denote the other two orbitals of site B_0 . Right: two sp^2 hybrids of two closest boron sites can form a bond centered bonding orbital. The remaining two bond centered orbitals are depicted as open symbols.

We still need to chose proper coefficients. There is the matter of sign and magnitude. First we discuss the magnitude. Assuming, that we have orthogonal orbitals (which is true at least for orbitals sitting on the same site.) we can determine the overlap of two orbitals at the same site

$$\begin{aligned}
\langle \phi_1 | \phi_2 \rangle &= \alpha^2 |s|^2 + \alpha\beta \langle s | C_3 p_x \rangle + \alpha\beta \langle p_x | s \rangle + \beta^2 \langle p_x | C_3 p_x \rangle \\
&= \alpha^2 + \beta^2 \langle p_x | C_3 p_x \rangle \\
&= \alpha^2 + \beta^2 \langle p_x | \cos(\gamma) p_x + \sin(\gamma) p_y \rangle, \quad \gamma = 120^\circ \\
&= \alpha^2 + \beta^2 \left\langle p_x \left| -\frac{1}{2} p_x + \frac{\sqrt{3}}{2} p_y \right. \right\rangle \\
&= \alpha^2 - \frac{1}{2} \beta^2
\end{aligned}$$

This must be zero, so $\alpha^2 = \frac{1}{2} \beta^2$. The norm of an orbital should be one

$$\begin{aligned}
|\phi_1|^2 &= \alpha^2 |s|^2 + \alpha\beta \langle s | p_x \rangle + \alpha\beta \langle p_x | s \rangle + \beta^2 |p_x|^2 \\
&= \alpha^2 + \beta^2
\end{aligned}$$

Hence, $1 = \alpha^2 + \beta^2 = \frac{3}{2} \beta^2$, and

$$\begin{aligned}
\alpha &= \sqrt{\frac{1}{3}} \approx 0.577 \\
\beta &= \sqrt{\frac{2}{3}} \approx 0.816
\end{aligned}$$

Another argument would be to request the following identity $\sum_i |\phi_i|^2 = 3\alpha^2 |s|^2 + 3\beta^2 |p|^2 \equiv |s|^2 + 2|p|^2$ in order to obtain a proper density with one s and two p-electrons occupied (according to the band structure). Hence $2|\alpha|^2 = |\beta|^2$. Normalization then gives the known result.

However, we are lazy and use $|\alpha| = |\beta| = \frac{1}{\sqrt{2}}$. In general, one has to make guesses for these pre-factors, since the optimal factors with respect to the final projection outcome usually depend on the hybridizations (on the Hamitonian). We should, however, at least choose coefficients in such a way that the resulting projected DOS is normalized to approximately two/one electrons for non-spinpolarized/spinpolarized calculations, respectively.

Now, if we pick $\phi_1 = \frac{1}{\sqrt{2}}(s + p_x)$ for the sp^2 -hybrid pointing from B_0 to B_2 in Fig. 1 we would expect the outcome to be the blue orbital at B_0 in the left panel Fig. 3 (assuming blue is positive and red negative), right? Well not so fast.

You need to remember this: the orbital is (real) spherical harmonics times radial function. In FPLO the sign of the radial function is determined by the starting condition at the nucleus (all radial functions start positive at the radius 0^+). Then the number of nodes determines the sign of the big bulge of the radial functions in the valence region of the atom. This bulge in turn determines the sign of matrix elements and it affects the sign choice for our hybrid orbitals, since we want the blue blob of Fig. 3.

- Open the `fedit options` menu and check `PLOT BASIS` (hotkey 7). Save and quit `fedit`.
- run

```
fplo22.00-62-x86_64 | tee out
```

(We could interrupt the run after the initial segment, but then it runs fast enough, so let it run.)

- Have a look at the first component (the usual large component) of the radial valence functions for Wyckoff position 2 (boron)

```
xfbp +fval.002.1
```

You will see (Fig. 5) that the 2s radial function is negative around $2 a_B$, while the 2p function is positive. Consequently we will need to use

$$\phi_1 = \frac{1}{\sqrt{2}}(-s + p_x) \quad (1)$$

to obtain the desired sp^2 -orbital. For clarity see Fig. 4.

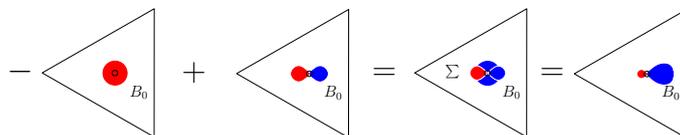


Figure 4: Red: negative. Blue: positive. The orbitals sit at the same site!

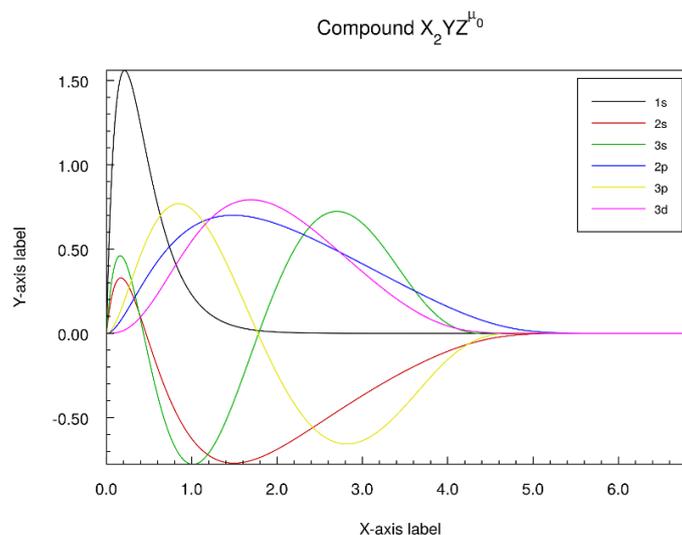


Figure 5: The large component of the radial semi-core and valence functions for boron.

- Ideally, you switch the **PLOT BASIS** option off now.

We are now prepared to create sp^2 -hybrid orbitals on both boron sites. We will create all three $\phi_{1...3}$ at B_0 and then use a trick to get the orbitals at the second site. There are two boron sites per unit cell one of them being B_0 . By looking at the structure you should understand that $B_{1...3}$ are all the second site. By placing one ϕ on each of those atoms we get our three second site orbitals. This example also emphasizes that it does not matter in which unit cell the projector is defined.

We need one more input, which is the connection vectors between the central boron atom and the other three. It is easiest to measure these and use them as local axes of a p_x -orbital, thus defining the p-orbital contribution to the sp^2 .

- Execute

```
xfplo =.xstr
```

- Press **m** or use **Tools > Measure**.
- In the SV first click on the center atom B_0 and then on B_1 to get Fig. 6.

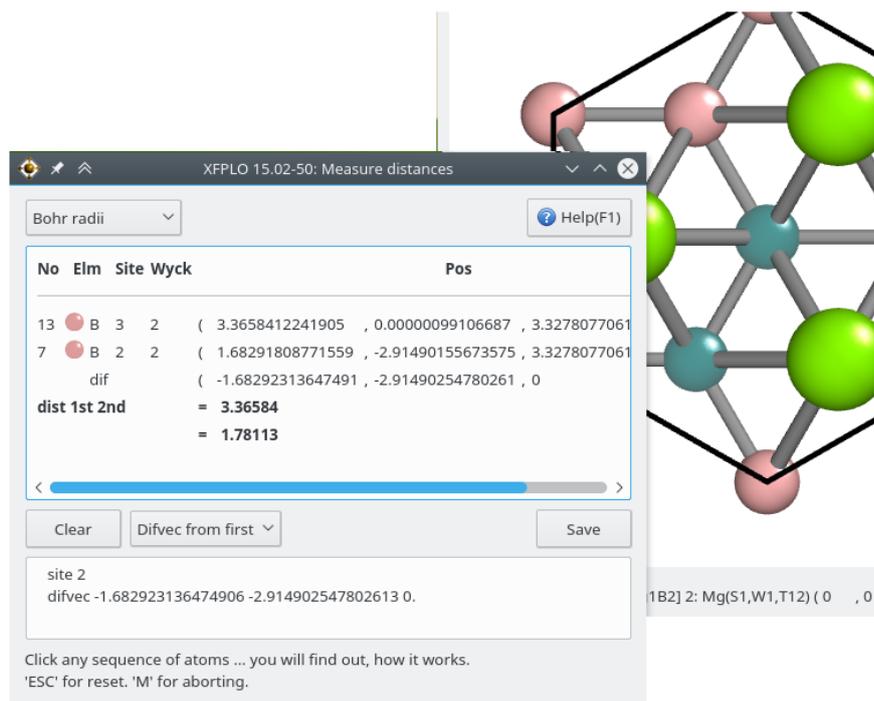


Figure 6: The measurement of the vector $B_1 - B_0$

- You will convince yourself by looking at the table in the measurement tool that **dif** is the vector pointing from the first atom in the table to the second. Write down the difference vector for $B_1 - B_0$ and continue with the other two vectors.
 - Either click on the second atom again to remove it from measurement
 - Or use **escape** to delete the whole list
 - You can click on three atoms to measure angles.

- Press the **m** key to close this tool.
- Also take notice of the box on the bottom of the tool. This is plain text for easy copying.

Well, here is the table. Note, that we are not very precise. For the fatbands that is sufficient. For Wannier functions similar difference vectors must be often much more precise.

i	x	y	z
1	-1.68	-2.91	0
2	3.36	0	0
3	-1.68	2.91	0

Table 1: The difference vectors $B_i - B_0$.

We are finally prepared.

- Close the measurement tool (press **m**)
- Choose menu entry **Activities** \triangleright **FatBands** to open the band weight editor (BWE), Fig. 7. Place the BWE and the SV side by side.

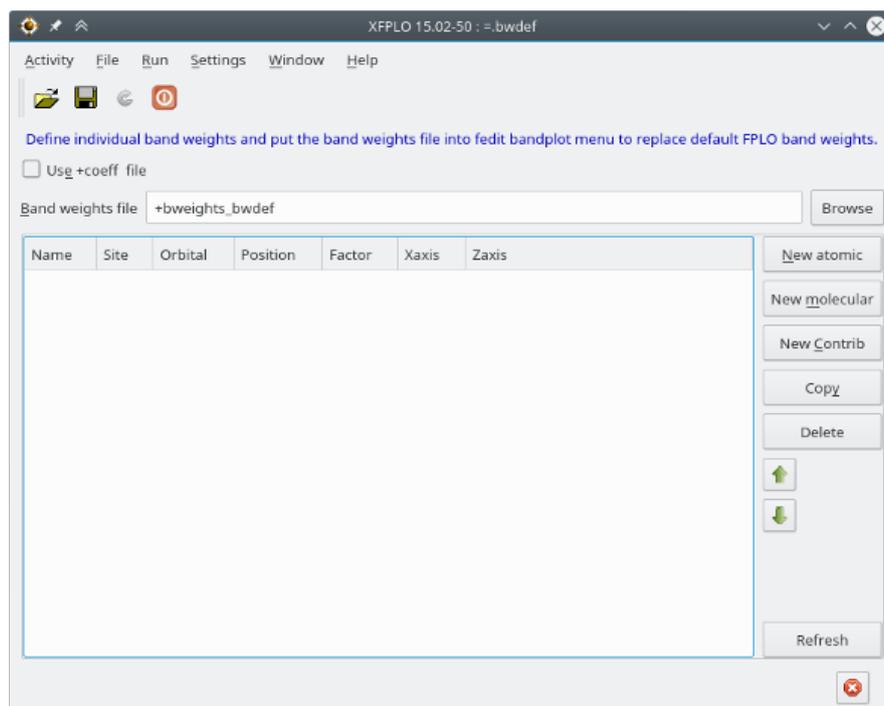


Figure 7: The empty band weight editor

- In the BWE click the **new molecular** button and type **sp2(3,1)**. The first number is the site number which you get by hovering with the mouse pointer over the central atom. In the status bar it will read: **B(S3,W2,T5)**, S=site, W=Wyckoff position, T=type (by default the nuclear charge, but it can be changed in the symmetry dialog). The second number in the name is an index for the orbital.

- Click the **New Contrib** button to open the molecular orbital contribution dialog (MOCD, Fig. 8)

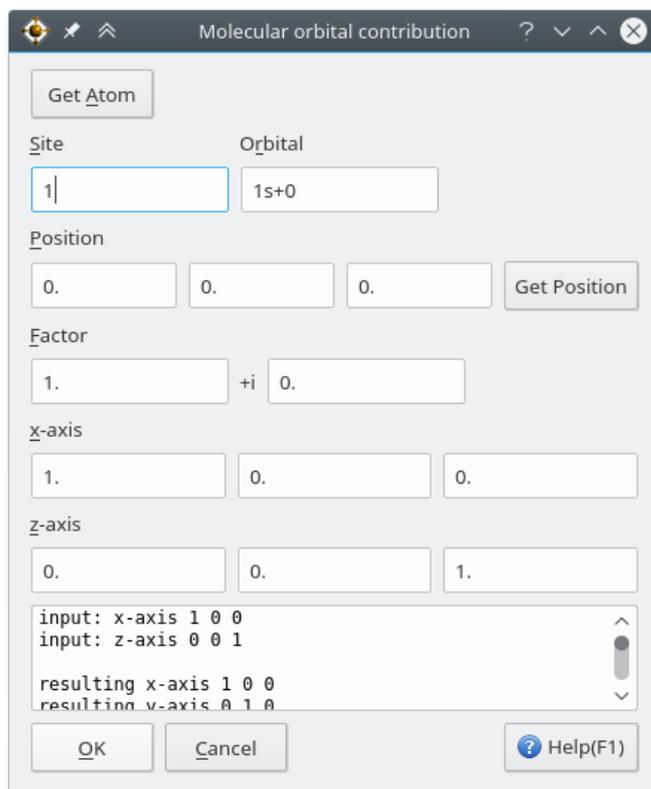


Figure 8: Molecular orbital contribution dialog

- In the MOCD click the **Get Atom** button and click on the central atom B_0 .
- Set **orbital** to $2s+0$ and the **factor** to -0.707 ($\frac{1}{\sqrt{2}}$). We do not need to set **axes**, since an s orbital is spherical.
- Hit **enter** (OK button).

You can always use **space**, **enter** or **double click** on the items in the BWE to re-open the corresponding dialog.

- Now, you have one contrib.
- Copy it by hitting the **Copy** button (or **Alt-y**).
- The copied contrib has the focus, so hit **space** and change the **orbital** into $2p+1$ (p_x) and the **factor** into 0.707 . In the **x-axis** line-edits enter the first difference vector (the one to B_1). See Tab. 1.
- Close the MOCD and compare with Fig. 9

Name	Site	Orbital	Position	Factor	Xaxis	Zaxis
1: sp2(3,1)						
	003	2s+0	3.36584122, 0.00000099, 3.32780771	-0.707	1., 0., 0.	0., 0., 1.
	003	2p+1	3.36584122, 0.00000099, 3.32780771	0.707	-1.68, -2.91, 0.	0., 0., 1.

Figure 9: The first sp^2 orbital projector

Are you convinced that we have defined a projector, which looks like the blue blob of Fig. 3 (just rotated)? Well, then let's add the rest.

- In the BWE single click on the first line for focus and click the **Copy** button.
- Press **space** and change the last number to 2. Then press **enter**.
- Go to the second contrib (last line), hit **space** and change the **x-axis** line-edits to contain the second difference vector of Tab. 1.
- Close the MOCD.
- Click on the second molecular orbital (second green line) and hit the **copy** button.
- Change the name (**space**).
- Go to the last line, press **space** and enter the last difference vector into the **x-axis** line-edits.
- Close the MOCD and in the BWE **File** > **Save** the current table.

We have defined all sp^2 orbitals of the first boron site, Fig 10.

Name	Site	Orbital	Position	Factor	Xaxis	Zaxis
1: sp2(3,1)						
	003	2s+0	3.36584122, 0.00000099, 3.32780771	-0.707	1., 0., 0.	0., 0., 1.
	003	2p+1	3.36584122, 0.00000099, 3.32780771	0.707	-1.68, -2.91, 0.	0., 0., 1.
2: sp2(3,2)						
	003	2s+0	3.36584122, 0.00000099, 3.32780771	-0.707	1., 0., 0.	0., 0., 1.
	003	2p+1	3.36584122, 0.00000099, 3.32780771	0.707	3.36, 0., 0.	0., 0., 1.
3: sp2(3,3)						
	003	2s+0	3.36584122, 0.00000099, 3.32780771	-0.707	1., 0., 0.	0., 0., 1.
	003	2p+1	3.36584122, 0.00000099, 3.32780771	0.707	-1.68, 2.91, 0.	0., 0., 1.

Figure 10: The three sp^2 orbital projector of the first boron site.

Let's define the three MOs of the second boron. All we need to do is to copy each MO, select the proper atom for all contributions and to invert the sign of the coefficient of the p_x -orbital. This is so, since the orbitals at the second site are 180° rotate, which gives a factor of -1 for p but not for s .

- Copy the first molecular orbital and type $2 \times$ **Ctrl-down** or click the **down** button  2 times.
- Rename this orbital into $sp^2(2,1)$ [site number 2 in the structure].

- Select it's first contribution, hit **space**.
- Click the **Get Atom** button and click on B₁ in the structure view. Then in the MOCD press **enter**.
- Select it's second contribution, hit **space**.
- Click the **Get Atom** button and click on B₁ in the structure view. In the MOCD, change the sign of the **factor** and press **enter**.

Now, we copy-modify the second MO.

- Copy the second molecular orbital and type 2× **Ctrl-down** or click the **down** button  2 times.
- Rename this orbital into sp²(2,2) [site number 2 in the structure].
- Select the it's first contribution, hit **space**.
- Click the **Get Atom** button and click on B₂ in the structure view. The in the MOCD press **enter**.
- Select the it's second contribution, hit **space**.
- Click the **Get Atom** button and click on B₂ in the structure view. In the MOCD, change the sign of the **factor** and press **enter**.

And, the last copy-modify action to get the the third MO of the second boron site.

- Copy the third molecular orbital and type 2× **Ctrl-down** or click the **down** button  2 times.
- Rename this orbital into sp²(2,3) [site number 2 in the structure].
- Select the it's first contribution, hit **space**.
- Click the **Get Atom** button and click on B₃ in the structure view. The in the MOCD press **enter**.
- Select the it's second contribution, hit **space**.
- Click the **Get Atom** button and click on B₃ in the structure view. In the MOCD, change the sign of the **factor** and press **enter**.

Fig. 11 shows the table of all six sp²-MO projectors.

Name	Site	Orbital	Position	Factor	Xaxis	Zaxis
1: sp2(3,1)						
	003	2s+0	3.36584122, 0.00000099, 3.32780771	-0.707	1., 0., 0.	0., 0., 1.
	003	2p+1	3.36584122, 0.00000099, 3.32780771	0.707	-1.68, -2.91, 0.	0., 0., 1.
2: sp2(3,2)						
	003	2s+0	3.36584122, 0.00000099, 3.32780771	-0.707	1., 0., 0.	0., 0., 1.
	003	2p+1	3.36584122, 0.00000099, 3.32780771	0.707	3.36, 0., 0.	0., 0., 1.
3: sp2(3,3)						
	003	2s+0	3.36584122, 0.00000099, 3.32780771	-0.707	1., 0., 0.	0., 0., 1.
	003	2p+1	3.36584122, 0.00000099, 3.32780771	0.707	-1.68, 2.91, 0.	0., 0., 1.
4: sp2(2,1)						
	002	2s+0	1.68291809, -2.91490156, 3.32780771	-0.707	1., 0., 0.	0., 0., 1.
	002	2p+1	1.68291809, -2.91490156, 3.32780771	-0.707	-1.68, -2.91, 0.	0., 0., 1.
5: sp2(2,2)						
	002	2s+0	6.7316774, 0.00000099, 3.32780771	-0.707	1., 0., 0.	0., 0., 1.
	002	2p+1	6.7316774, 0.00000099, 3.32780771	-0.707	3.36, 0., 0.	0., 0., 1.
6: sp2(2,3)						
	002	2s+0	1.68291809, 2.91490354, 3.32780771	-0.707	1., 0., 0.	0., 0., 1.
	002	2p+1	1.68291809, 2.91490354, 3.32780771	-0.707	-1.68, 2.91, 0.	0., 0., 1.

Figure 11: All six sp^2 molecular projectors.

Finally,

- in the BWE File ▷ Save the current table and close everything: `Ctrl-Q/Activities ▷ Quit all`.

We are in the position to use these projectors now

- Open fedit and switch on `bandplot ▷ Bandstructure plot, bandplot ▷ Weights` and set `Weights def File` to `=.bwdef`.

- Then run

```
fpl022.00-62-x86_64 | tee out
```

- We got `+bdos/+bdos.b001... +bdos/+bdos.b006` and `+bweights_bwdef`.
- Execute

```
xfbp +bweights_bwdef
```

- Go to the `Edit ▷ Sets` dialog, select the `Weights` tab.
- Select all items in the `Weights` table with the mouse. Click on the arrow of the button above the `Weights` table and select `Checked`.
- In the `properties of all` box increased `factor` to 8 and set the `style` to individual.
- The weights should still be all selected. If not select all: click into the weights table and type `Ctrl-A`.
- In the `individual properties` box uncheck the `fill` checkbox and set `skip` to 5.

- Hit **enter**, close the dialog and autoscale all (**Ctrl-A**) to obtain Fig. 12.

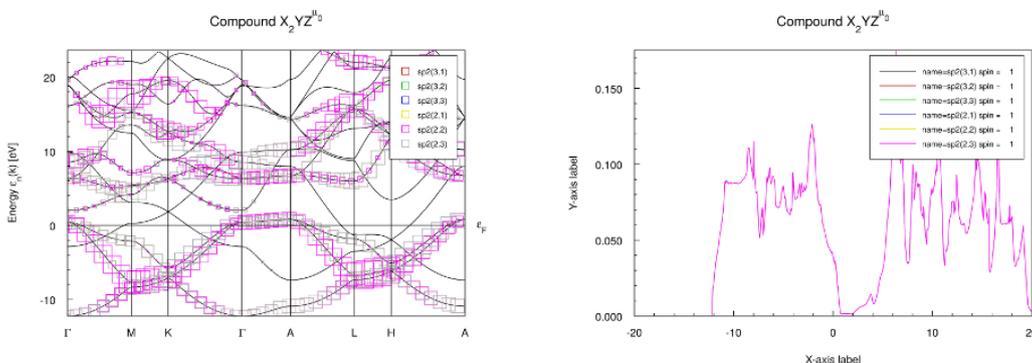


Figure 12: All sp^2 weights. Left: fatbands. Right: DOS.

You might notice that only two colors are visible. This is due to the high symmetry between the two boron sites. However, by switching on one pair of weights at a time you can convince yourself that the first three and the last three weights are different among each other (the last three seem to be identical to the first three, but they differ from the first three by their site number anyhow), which means that we at least are sure that we do not have some identical projectors.

- Let's proceed to show the MO projected dos. Execute

```
xfbp +bdos/*
```

You will realize that all six bdos look the same, which reflects the symmetry of our projector choice.

For some taste

- Open **Edit** \triangleright **Script/Transformations**

- Select **Mode** \triangleright **Python**.

- Write

```
G[1].Gr[1].S[1].integrate()
```

- Hit the **Apply** button. **ONLY ONCE!** Otherwise you integrate the integral.

- Close the dialog **Ctrl-W**

- Press **Ctrl-A**.

You will see that the integrate DOS reaches around 0.949 electrons at the Fermi level ($E = 0$). This makes 5.694 electrons for all sp^2 orbitals. If we add the two occupied $1s$ electrons per boron (makes 4) and the 0.7 occupied p_z electrons per boron (makes 1.4) we get a total of 11.094 electrons or 5.547 per boron, which compares well with the population analysis. Hence, we chose the correct normalization for our projectors. (The 0.7 occupied p_z electrons stem from an LDOS calculation, which we did not perform here.)

- You can close the program: press **Ctrl-W**.

4 Bonding and anti-bonding sp^2 hybrids

Finally, we get to the bonding and anti-bonding combinations of sp^2 -hybrids. Since, we already setup all six hybrids, the final step is a lesson in copy-and-paste. One of the bonding (anti-bonding) combinations are obtained from

$$\phi_B = \frac{1}{\sqrt{2}} (\phi_1(B_0) \pm \phi_1(B_1))$$

where $\phi_1(B_0)$ is the sp^2 -hybrid at B_0 , which points towards B_1 and $\phi_1(B_1)$ sits at B_1 and points towards B_0 .

Please, tightly follow the steps.

- Execute

```
xfplo =.bwdef&
```

- Go to the first MO.
- **Copy** it followed by $5 \times$ **Ctrl-down** to make it the last MO in the table.
- Press **space** to rename it into **sp2 B1**.
- Select the first contribution of the 4-th MO (mouse click or cursor keys) and **copy** it. Press $10 \times$ **Ctrl-down** to make it the last line.
- In the same manner copy the second contribution of the 4-th MO and use **Ctrl-down** to make it the last line.
- Now, for each of the four contributions set the magnitude of the **factor** to 0.5, but **keep the sign**.

We could now apply similar copy past procedure to duplicate MO 2(3) and add the contributions of MO 5(6) to create the other three bonding sp^2 -hybrids as shown in the right panel of Fig. 3. But we skip this part. Instead we construct the anti-bonding combination.

- Go to MO number 7.
- **Copy** it.
- Rename to **sp2 AB1**.
- Invert the sign of the **factor** of the last two contributions of MO 8 to get Fig. 13

7: sp2 B1								
003	2s+0	3.36584122	0.00000099	3.32780771	-0.5	1.	0.	0.
003	2p+1	3.36584122	0.00000099	3.32780771	0.5	-1.68	-2.91	0.
002	2s+0	1.68291809	-2.91490156	3.32780771	-0.5	1.	0.	0.
002	2p+1	1.68291809	-2.91490156	3.32780771	-0.5	-1.68	-2.91	0.
8: sp2 AB1								
003	2s+0	3.36584122	0.00000099	3.32780771	-0.5	1.	0.	0.
003	2p+1	3.36584122	0.00000099	3.32780771	0.5	-1.68	-2.91	0.
002	2s+0	1.68291809	-2.91490156	3.32780771	0.5	1.	0.	0.
002	2p+1	1.68291809	-2.91490156	3.32780771	0.5	-1.68	-2.91	0.

Figure 13: The bonding and anti-bonding MOs.

- in the BWE File \triangleright Save (or Ctrl-S) the current table and close everything: Ctrl-Q/Activities \triangleright Quit all.

- Now, run

```
fplot22.00-62-x86_64 | tee out
```

- We got +bdos/+bdos.b001... +bdos/+bdos.b008 and +bweights_bwdef.

- Execute

```
xfbp +bdos/*
```

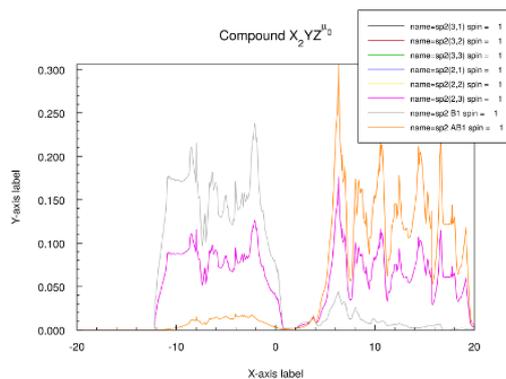


Figure 14: Bonding, anti-bonding and sp^2 DOS.

You will notice that in Fig. 14 the bonding (gray) and anti-bonding (orange) DOS are twice as tall as the sp^2 -DOS. This is due to the fact that only 3 bonding MOs are fully occupied and 6 sp^2 -hybrids are half-occupied. At the end it is the same number of electrons.