

Introduction

Below is a brief and likely incomplete manual for using BroadSword to treat calculated XES and XANES spectra so that they better match measured spectra. The BroadSword console is very basic, see Fig. 1, with each step obvious. Below is a stepped our procedure to obtaining Broadened spectra from WIEN2k calculation using monoclinic zirconium oxide as an example.

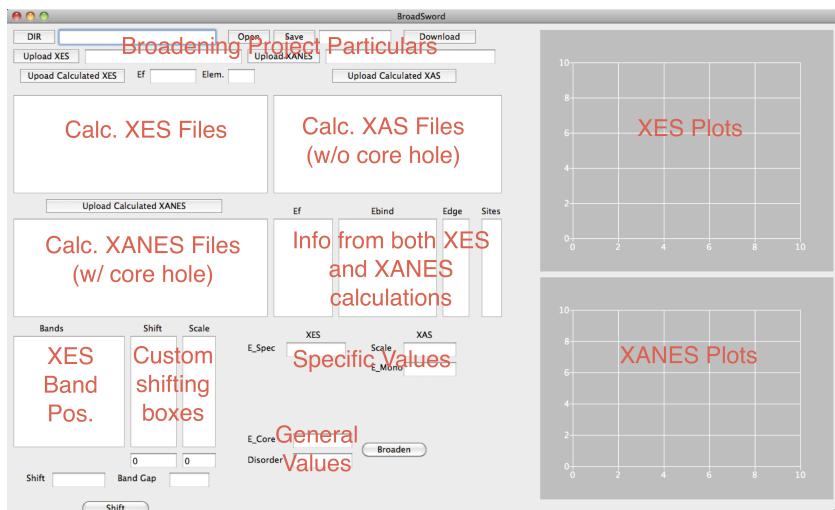


Figure 1: Console

Step One

First, you need to complete calculation for the ground state crystal structure, and an excited state calculation including a core hole on all the atoms on interest. In our case here for ZrO_2 we are interested only in the $\text{O K}\alpha$ XES and $\text{O }1s$ XANES. Since there are two inequivalent O atoms sites we need three calculations total. After this is complete you need to extract the appropriate spectra using the embedded XSPEC program. Please note you should

have increase the energy to 4.5 Ryd in the case.in1(c) file and rerun x-lapw1(c) prior to using x-lapw2(c) -qtl to generate the necessary case.qtl file. Reasonable regions for export are -40 to 20 eV for XES and -10 to 50 eV for XANES; make sure you use the case.txspec file and the case.xspec file.

Step Two

Since broadening is a dynamic procedure require several iterations to fine tune the broadening parameters to match the experiment you must export the spectra you wish to fit the calculated spectra with prior to broadening. Note the code has not been extensively tested with OS dependent delimitation so they may be bugs, please contact me if you have issues. The only requirement on the exported files is that they are ASCII and have no headers, meaning they are a text file with two column vectors only. Now you should have all the files you need, I would suggest you name them in an appropriate manner similar to Fig. 2. It is important you do not have any spaces in the path to your project files!

Step Three

Select you project directory, this will used to store all the files necessary for the broadening and will the location of the outputted broadened spectra. You select you directory using the select directory tab. Fig. 3 shows the important boxes.

Step Four

Next you upload the experimental spectra. Fig. 4 and 5 show the relevant boxes.

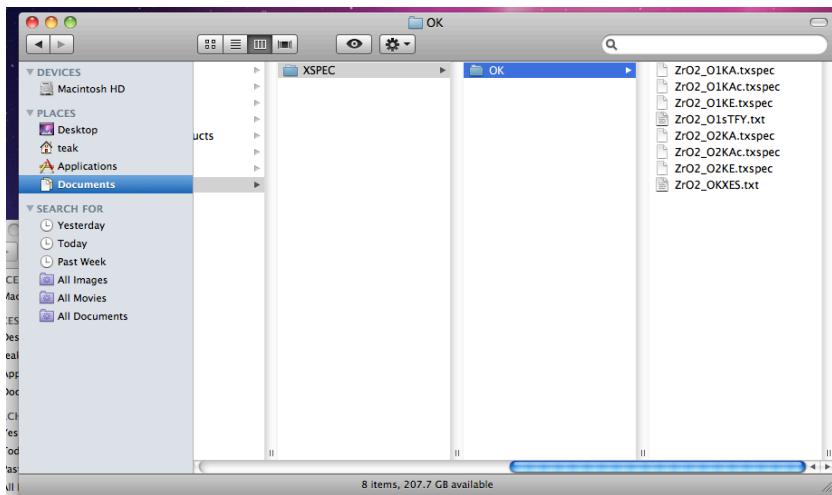


Figure 2: Files

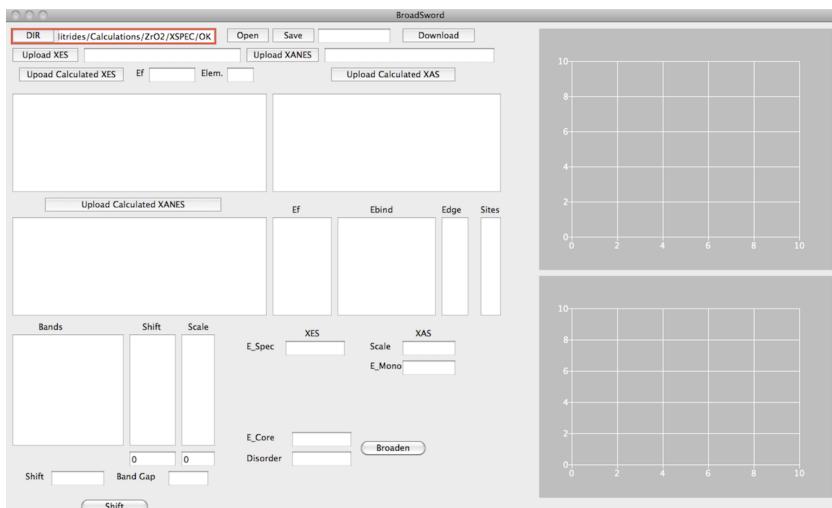


Figure 3:

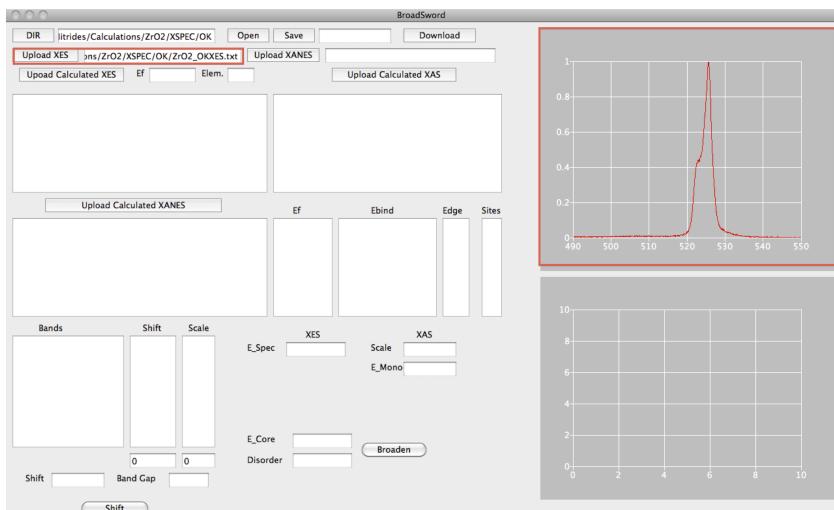


Figure 4:

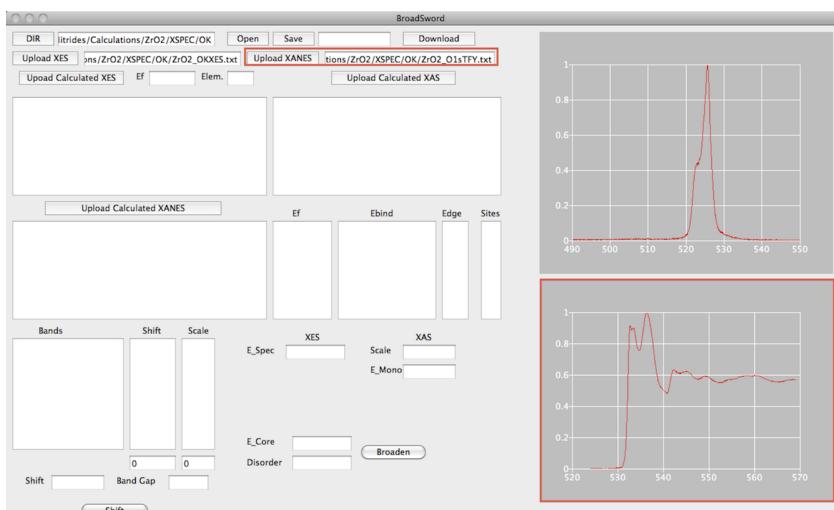


Figure 5:

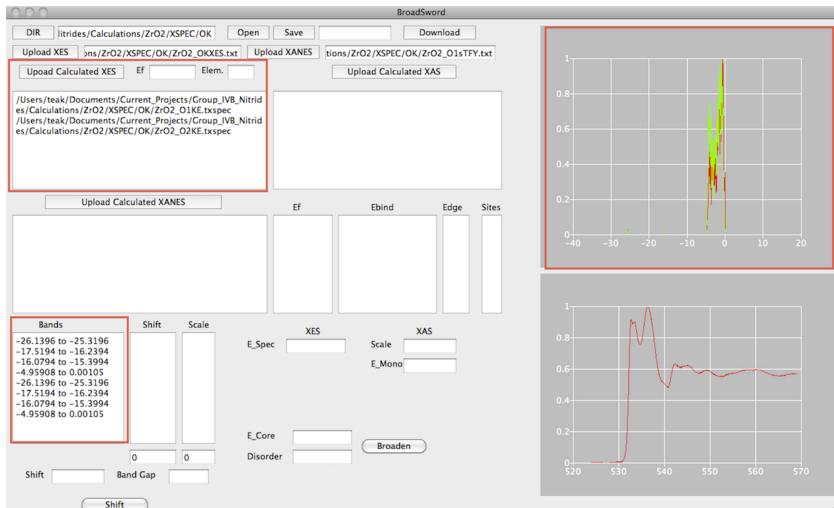


Figure 6:

Step Five

Then you upload the experimental data. The XES is loaded first, see Fig. 6, where the band regions located. This will come up later when specifying the shift required to match the measured spectra. Figs. 7 and 8 show the upload for XAS and XANES, which are the spectra w/o and w/ the core hole included. In all cases do far the different colours represent different spectra with the colours in order: red, green, blue, etc.

Step Six

The remaining information from the calculations is included. There are the the material, Fermi energy from the ground state calculations and element probed (Figs. 9, 10 and 11) along with the binding energy eigenvalues (Figs. 12 and 13). This continues with the Fermi energies from the core calculations as in Figs. 14, 15 and 16. Lastly, the edge (in this case K) and the multiplicity of

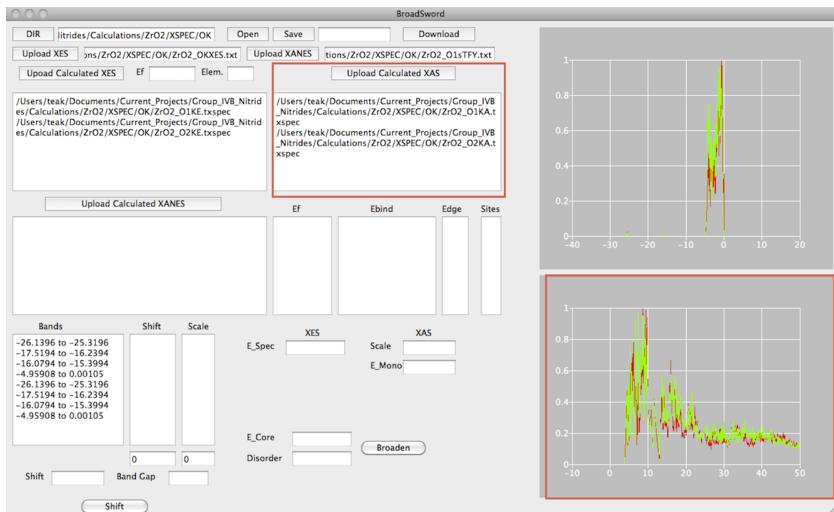


Figure 7:

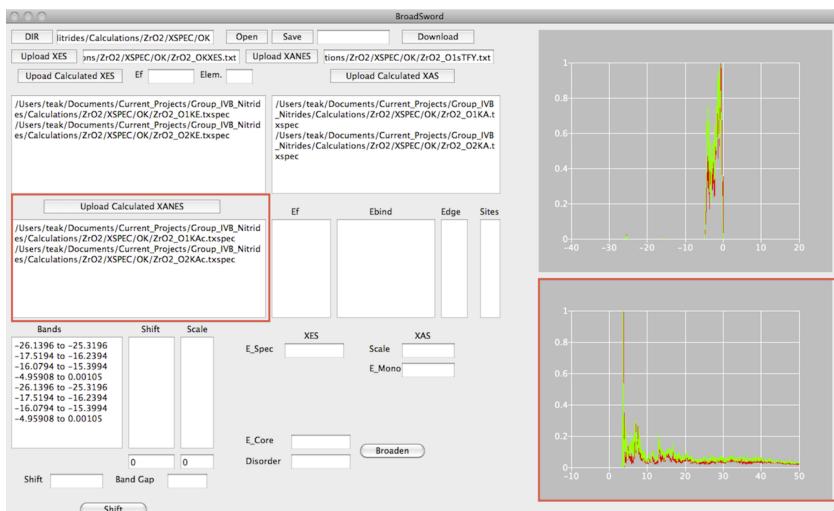


Figure 8:

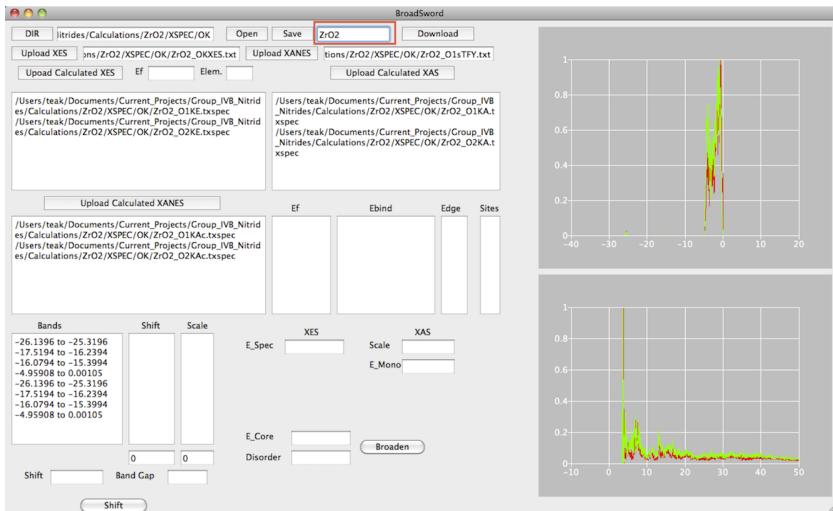


Figure 9:

the crystal sites are added, see Figs. 17 and 18.

Step Seven

Next, you need to shift the spectra to match the experiment. Here you have two options for XES. BroadSword allows for shift of the bands individually. Normally this is not necessary, but since the interaction between bands is underestimated it is at times necessary to shift different band differently. But, if you desire a constant shift across the XES spectra then you specify it as in Fig. 19. Since the XANES spectra is usually always a continuous band, only one shift value is necessary and is applied also in Fig. 19. Depressing the "shift" button will shift the spectra and calculation the electronic band gap from the current separation of the XES and XANES spectra. Alternatively, the shift for each band gap be specified separately as in Fig. 20, but in this case the result is the same. Note that unless the boxes for the single shift are left to zero the list of multiple shifts will be ignored.

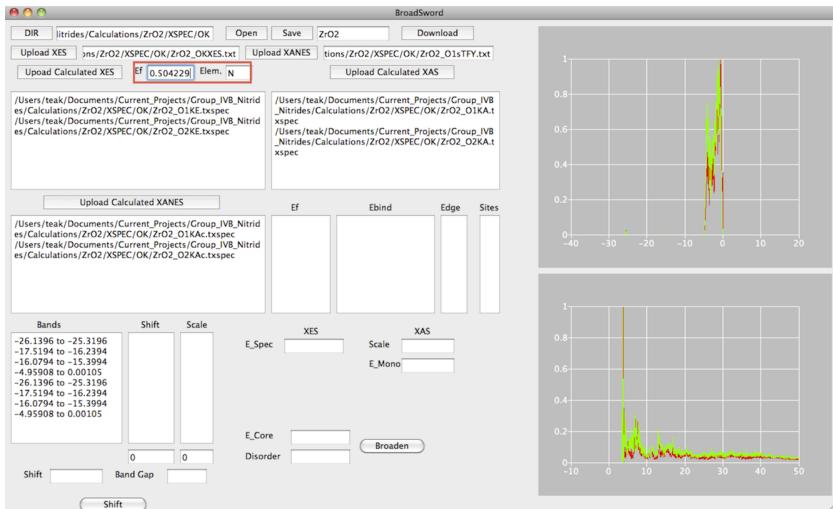


Figure 10:

Step Eight

Will the calculated spectra shifted close to the measured spectra, the criteria for the broadening needs to be applied. These include the core hole lifetime (typically ≈ 0.15 eV for O 1s). The scale for the XES spectra is filled out similar to the shift. The scale dictates the change in the broadening over energy. Refer to the thesis of T.D. Boyko for further information on the effect of the broadening factors. The monochromator and spectrometer resolutions are also applied. The disorder represents the thermal and crystal disorder that causes broadening in the spectra. This is most prevalent in the XANES spectra. Good starting values are represented in Figs.21. Applying the broadening will result in the spectra of Fig. 22. The plotted spectra can be zoomed by dragging a box over the desired region. Buttons appear on the top left corner allowing zoom in and zoom out, see Fig. 23. Tweaking the broadening parameters as in Figs. 24, 25 and 26 results in an adequate fit of the calculated spectra.

File:
/global/scratch/teak/ZrO₂/ZrO₂_Save.scf2

```
:BAN00049: 49  0.775897  0.853854  0.00000000
:BAN00050: 50  0.791871  0.839207  0.00000000
:BAN00051: 51  0.831812  0.868827  0.00000000
:BAN00052: 52  0.843022  0.876756  0.00000000
:BAN00053: 53  0.869036  0.910081  0.00000000
    Energy to separate low and high energystates:  0.08954

:NOE : NUMBER OF ELECTRONS      = 96.000
:FER : F E R M I - ENERGY(TETRAH.M.)= 0.5042292695
:GMA : POTENTIAL AND CHARGE CUT-OFF 12.00 Ry**.5

:POS001: ATOM -1 X,Y,Z = 0.20820 0.77580 0.54110 MULT= 4 ZZ= 40.000 Zr1
LMMAX 49


```

Figure 11:

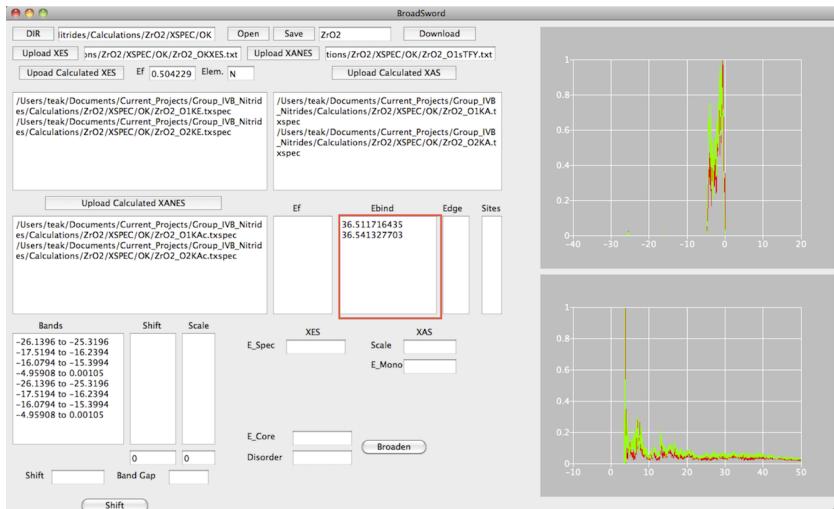


Figure 12:

Step Nine

Save the project using the "Save" button, as in Fig. 27 so that changes can be made a later time. Using the "Open" option will reload the project at any time. However, the full list on shift and scale values for the XES spectra is reloaded. But, as long as the single value shift and scale boxes do not contain zero these will be ignored.

Step Ten

The final spectra can be downloaded into the project folder by simply pressing download. This will result in the spectra files of Fig. 29.

If you have further questions please contact teak.boyko@usask.ca, if you find bugs please report them as well.

File:
/global/scratch/teak/ZrO2/ZrO2.scfc

```
:2PP001: 2P*      -165.047874161 Ry
:2P 001: 2P      -158.737661906 Ry
:3S 001: 3S      -28.713627059 Ry
:3PP001: 3P*      -22.999037133 Ry
:3P 001: 3P      -21.994346090 Ry
:3DD001: 3D*      -11.923602628 Ry
:3D 001: 3D      -11.740054485 Ry

2.ATOM    O 1          1 CORE STATES
CORE-FORCE in mRy/a.u. = |F|   Fx      Fy      Fz
:FC002: 2.ATOM    74.271377282   71.064717623   14.944539916   15.578963997

:1S 002: 1S      -36.511716435 Ry

3.ATOM    O 2          1 CORE STATES
CORE-FORCE in mRy/a.u. = |F|   Fx      Fy      Fz
:FC003: 3.ATOM    93.523874967   -5.318838050   93.327159825   2.909706100

:1S 003: 1S      -36.541327703 Ry
```

Figure 13:

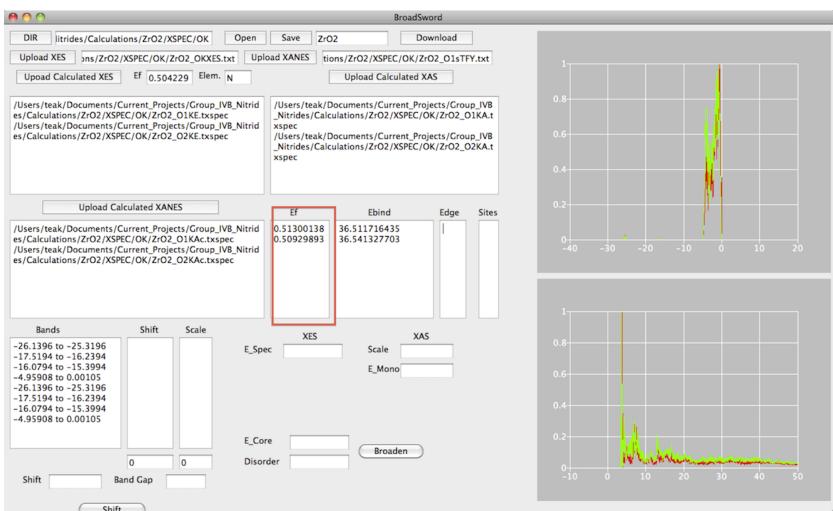


Figure 14:

File:
/global/scratch/teak/ZrO2_O2K/ZrO2_O2K_Save.scf2

```
:BAN00382: 382 0.482133 0.497415 2.00000000
:BAN00383: 383 0.493912 0.506188 2.00000000
:BAN00384: 384 0.497464 0.509299 2.00000000
:BAN00385: 385 0.765810 0.771272 0.00000000
:BAN00386: 386 0.776201 0.783775 0.00000000
:BAN00387: 387 0.790386 0.796748 0.00000000
:BAN00388: 388 0.794224 0.800618 0.00000000
:BAN00389: 389 0.798935 0.806522 0.00000000
    Energy to separate low and high energystates: 0.09622

:NOE : NUMBER OF ELECTRONS      = 768.000
:FER : F E R M I - ENERGY(TETRAH.M.)= 0.5092989362
:GMA : POTENTIAL AND CHARGE CUT-OFF 12.00 Ry**.5

:POS001: ATOM -1 X,Y,Z = 0.00000 0.00000 0.00000 MULT= 1 ZZ= 40.000 Zr1
```

Figure 15:

File:
/global/scratch/teak/ZrO2_O1K/ZrO2_O1K_Save.scf2

```
:BAN00378: 378 0.474861 0.480631 2.00000000
:BAN00379: 379 0.478315 0.483237 2.00000000
:BAN00380: 380 0.479875 0.487435 2.00000000
:BAN00381: 381 0.483155 0.493443 2.00000000
:BAN00382: 382 0.485111 0.499074 2.00000000
:BAN00383: 383 0.491935 0.501967 2.00000000
:BAN00384: 384 0.500915 0.513001 2.00000000
:BAN00385: 385 0.768012 0.775597 0.00000000
:BAN00386: 386 0.782396 0.787296 0.00000000
:BAN00387: 387 0.787790 0.791872 0.00000000
:BAN00388: 388 0.792792 0.798400 0.00000000
:BAN00389: 389 0.796660 0.802455 0.00000000
    Energy to separate low and high energystates: 0.09433

:NOE : NUMBER OF ELECTRONS      = 768.000
:FER : F E R M I - ENERGY(TETRAH.M.)= 0.5130013819
:GMA : POTENTIAL AND CHARGE CUT-OFF 12.00 Ry**.5
```

Figure 16:

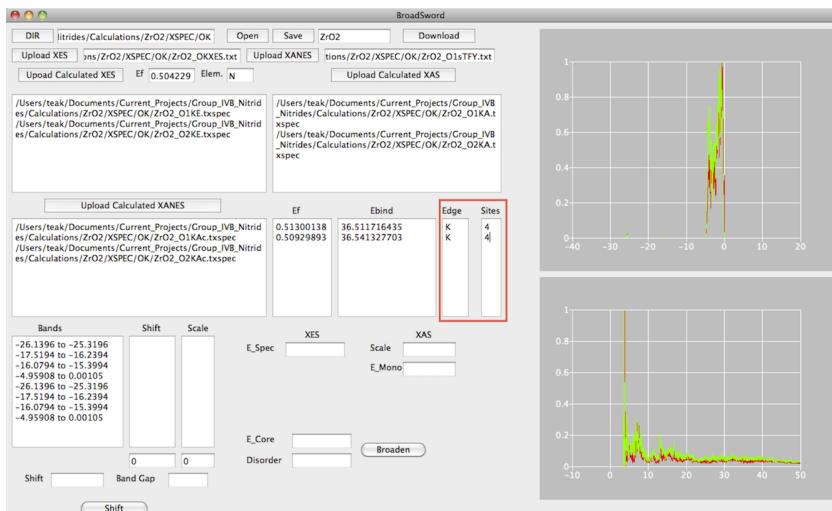


Figure 17:

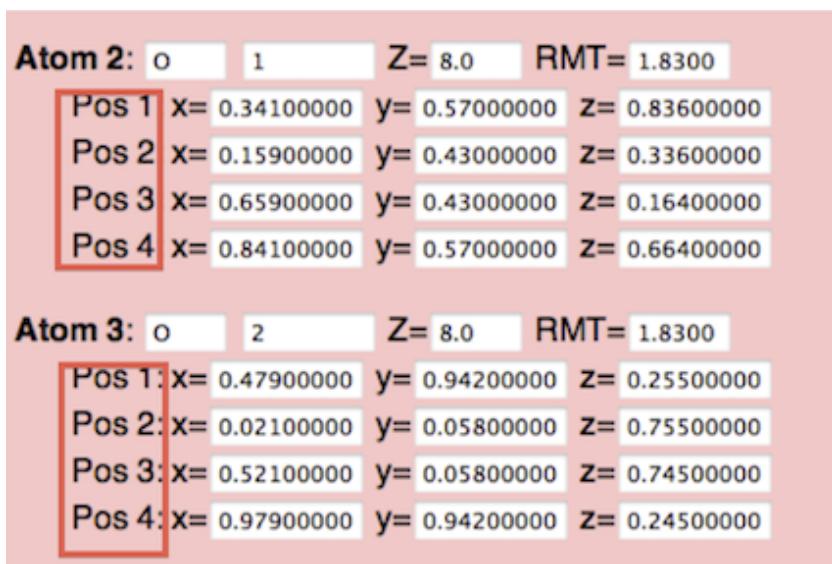


Figure 18:

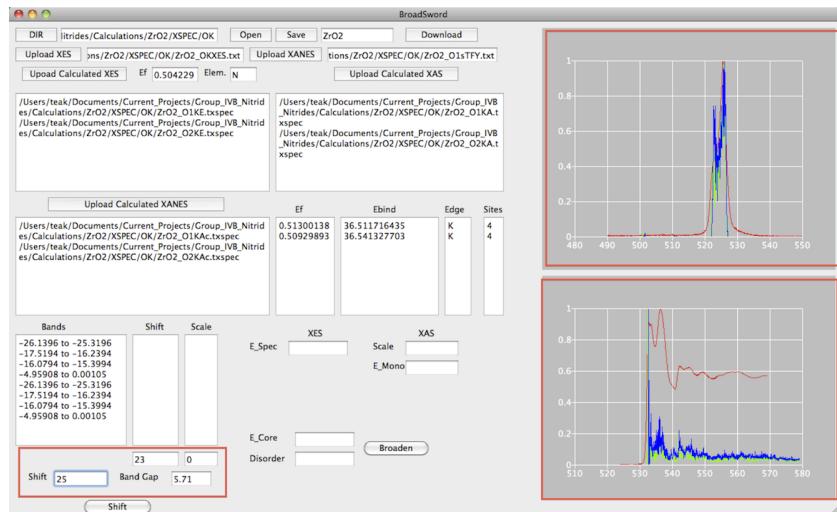


Figure 19:

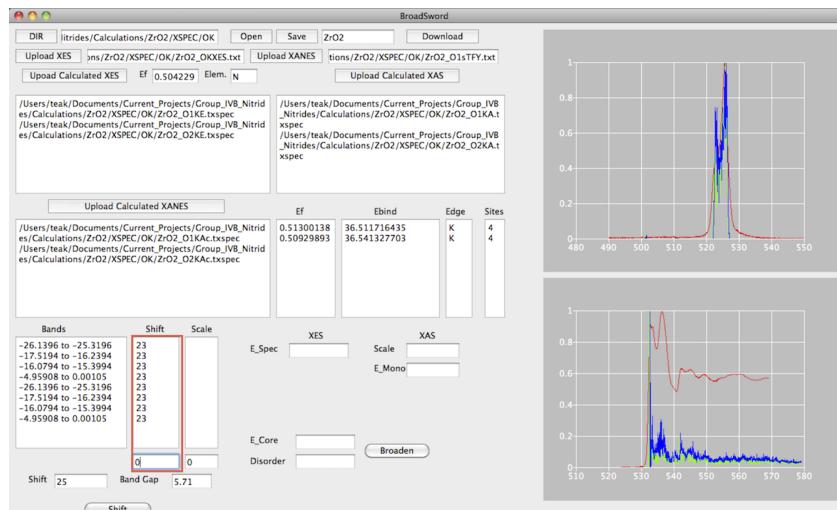


Figure 20:

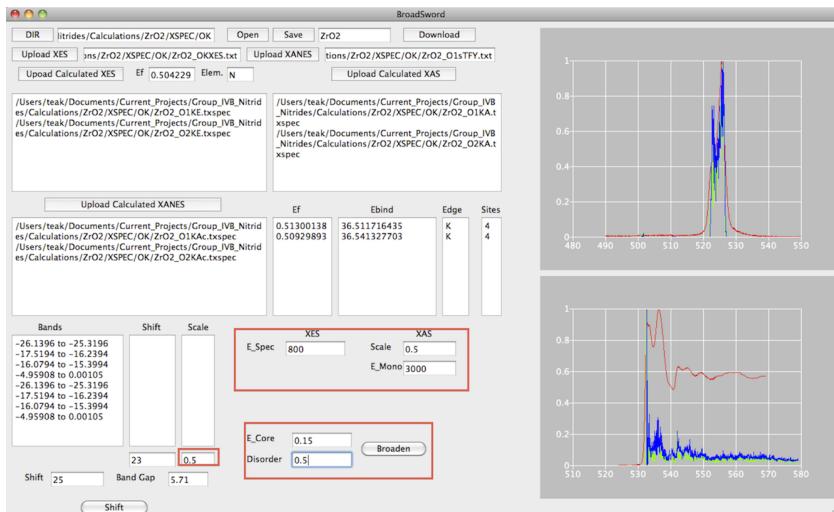


Figure 21:

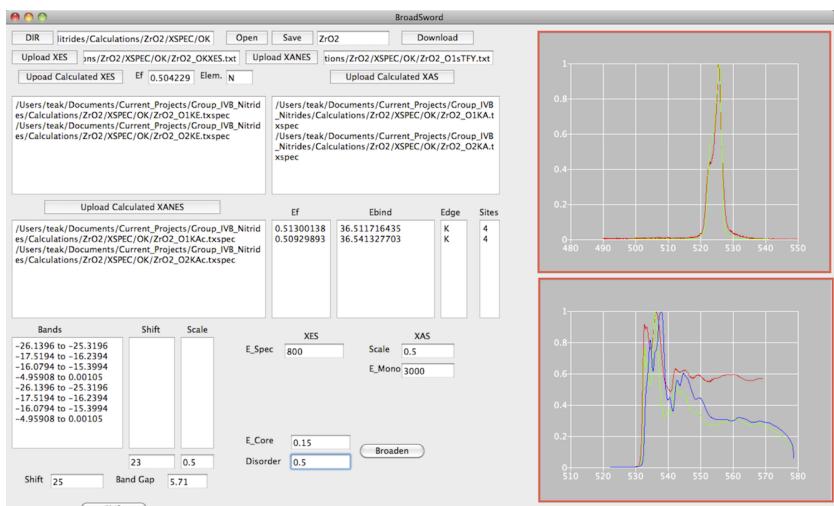


Figure 22:

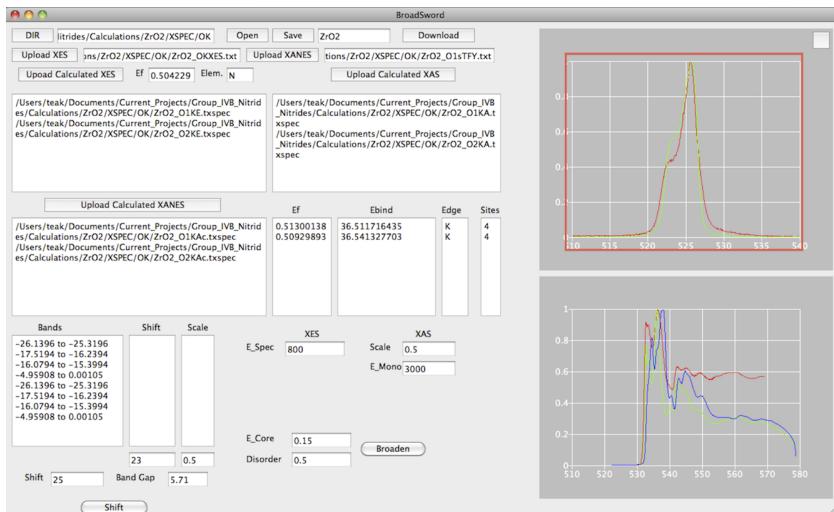


Figure 23:

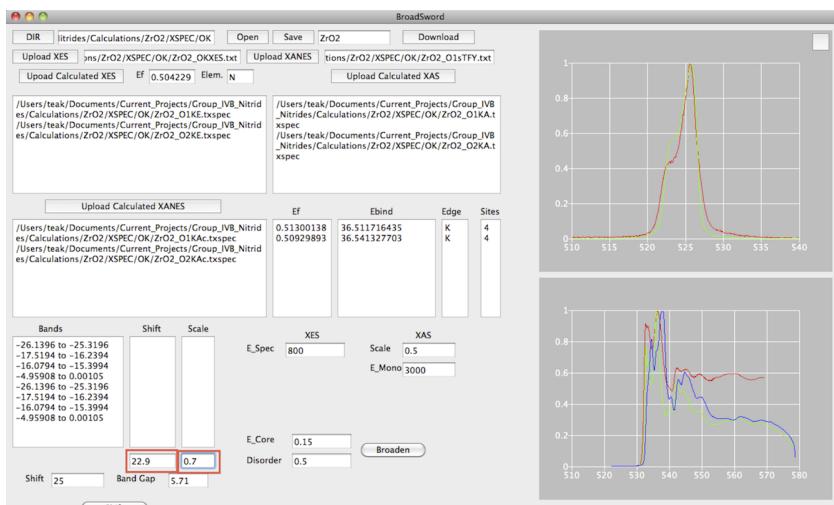


Figure 24:

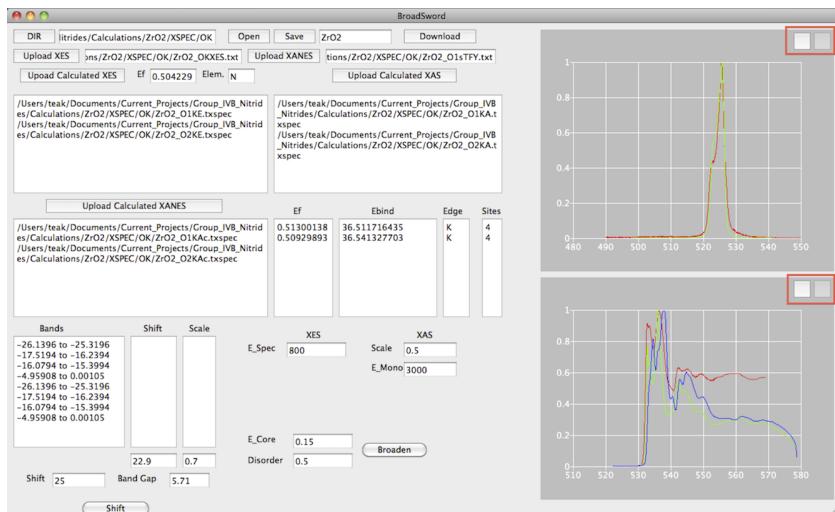


Figure 25:

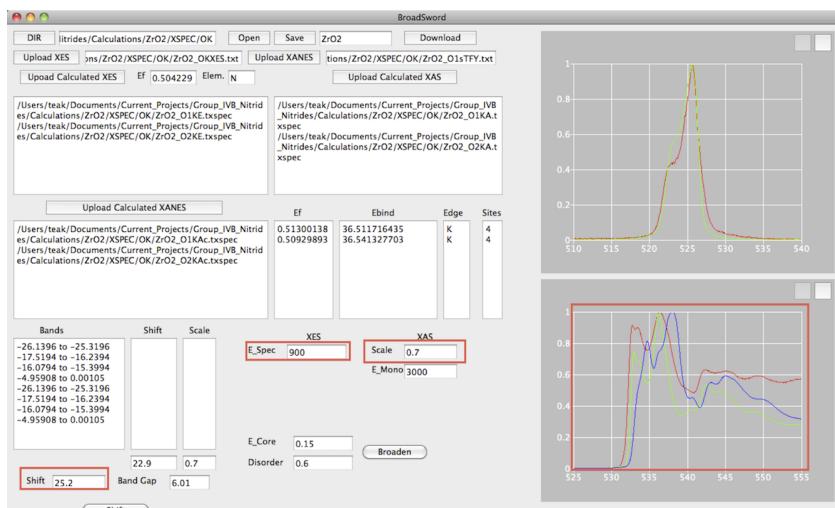


Figure 26:

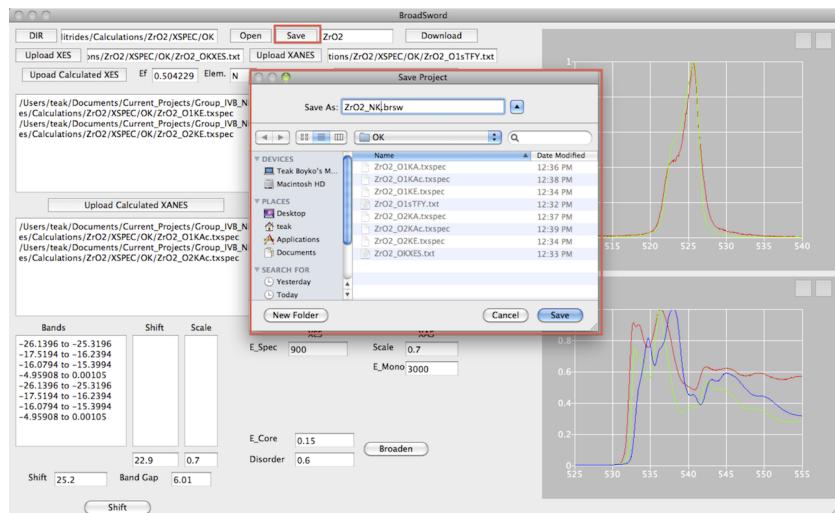


Figure 27:

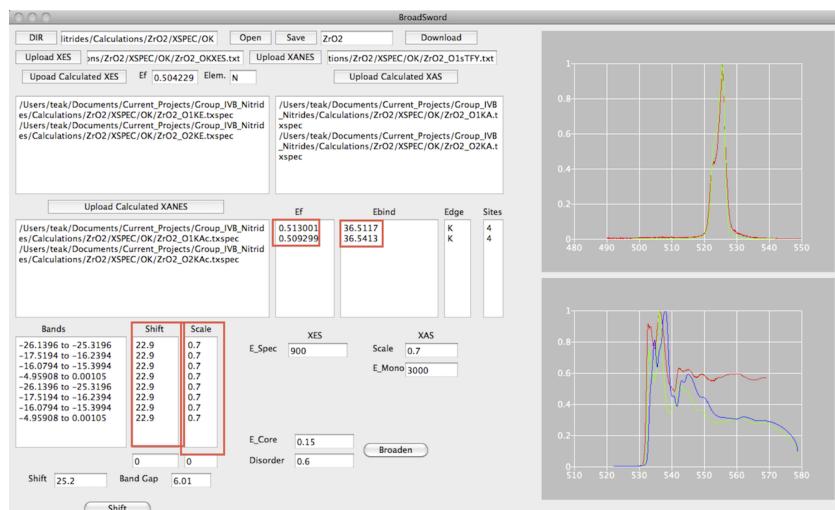


Figure 28:

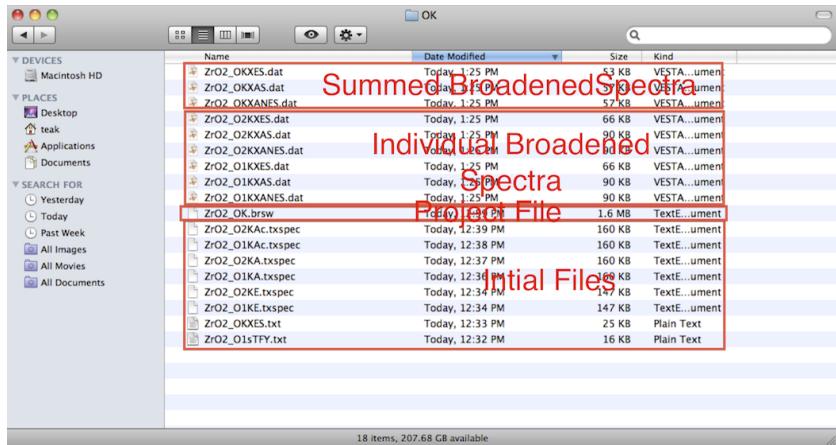


Figure 29: