Lithium ELNES with WIEN2k

October 12, 2018

Contents

1 Tools

Here's a list of software I use to run simulations. I've put some installation instructions for linux as needed.

- Wien2k - If you are reading this guide, you either already have it installed somewhere, or should figure out how to do that before buying a license. Otherwise, read the userguide where the installation process is well explained.
- VESTA: `http://jp-minerals.org/vesta/en/download.html`. Download the .rpm file, install it with your package manager in the directory it was downloaded to, eg. "sudo apt-get vesta...rpm"
- Xcrysden: `http://www.xcrysden.org/Download.html`. Download the appropriate tar for your operating system, and make sure to select the semishared version. Unzip it, and just run "$./xcrysden". Add the executable to your path in .bashrc to be able to run it anywhere.
- Critic2: `https://github.com/aoterodelaroza/critic2`. Download the zip from GitHub, unzip where you want to install it (eg ∼/Programs or something), use your package manager (dnf/apt-get) to install autoconf, automake, and your favourite flavour of fortran (if unsure, it is probably gfortran). Then run the 4 commands from the readme: "autoreconf -i", "./configure", "make", and "(sudo) make install". You may or may not need the sudo for the last one.

2 Path

Here is the overall list of things that need to be done to rigorously obtain ELNES spectra with WIEN2k:

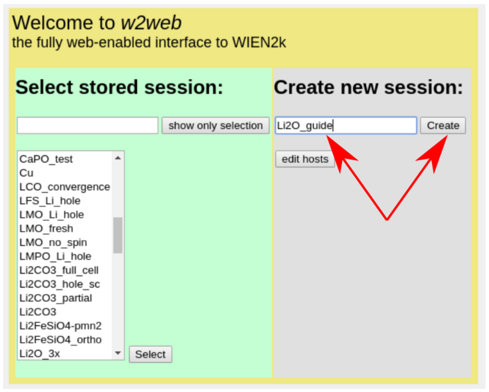
- Load a structure
- Initialize
- Volume convergence/structure optimization
- Set RMT values
- K point/RKmax convergence
- Calculate DOS
- Calculate ELNES
- Include Core Hole, if indicated by DOS, calculate PDOS
- Calculate Screening from density
- Calculate ELNES from partial hole

3 Setup

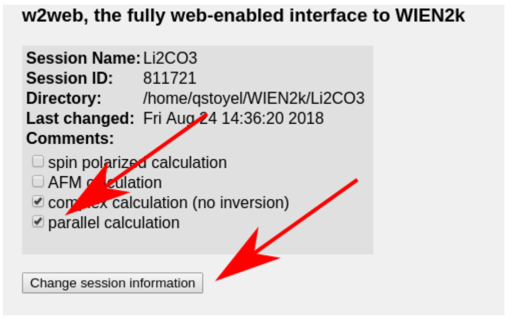
3.1 Load Structure

There a couple things required to start ELNES simulations. Foremost is a crystal structure. This can be obtained from the literature, XRD, or alternatively Materials Project: `https://materialsproject.org/`. Download a cif (the primative cell typically) or enter the coordinates directly into the wien2k struct gen tool, set the rmt and save the file.

Make a new Wien2k session:



Create/change a working directory, and change the session information for parallel calculation.



w2web, the fully web-enabled interface to WIEN2k

Session Name: Li2CO3
Session ID: 811721
Directory: /home/qstoyel/WIEN2k/Li2CO3
Last changed: Fri Aug 24 14:36:20 2018
Comments:

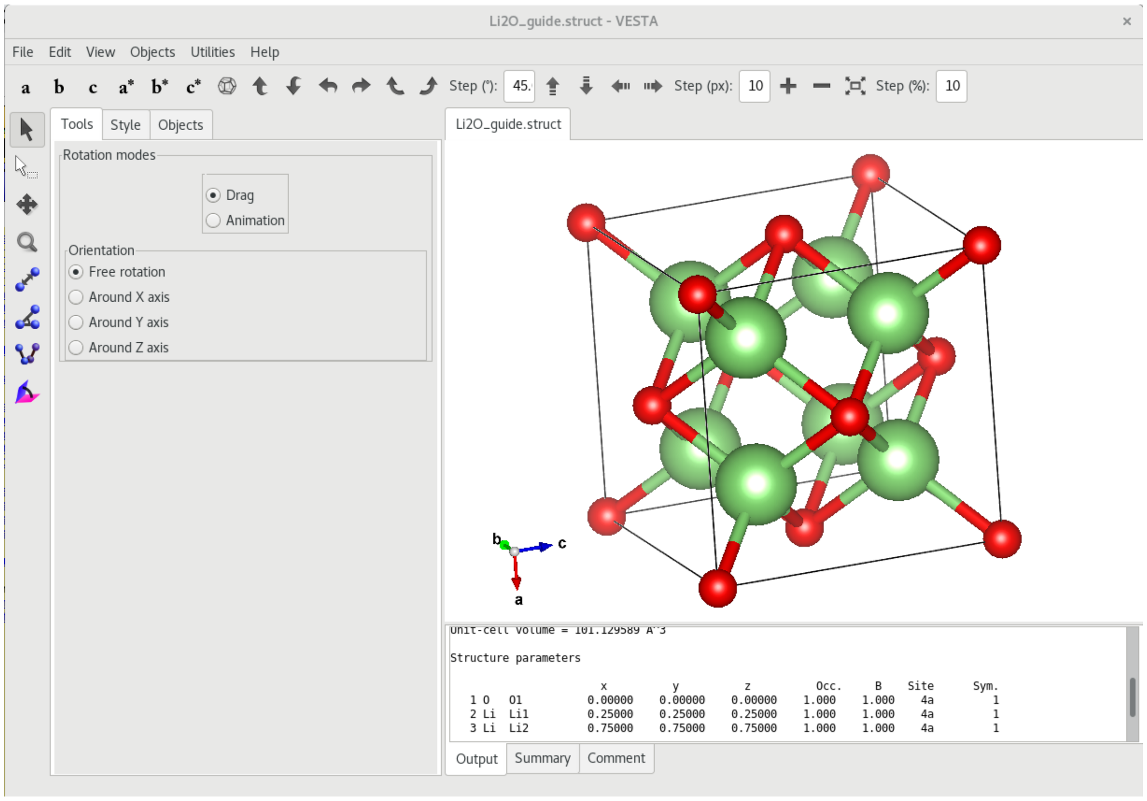
- [ ] spin polarized calculation
- [ ] AFM calculation
- [✓] complex calculation (no inversion)
- [✓] parallel calculation

You will also need to make a ".machines" file which you can either steal from one of my directories, look in the user guide and make your own, cut and paste the one from below, or wait for w2web to automatically generate one at some point after it inevitably crashes on something. Sample .machines file:

```
#==========================================
#This is a valid .machines file
#
granularity:1
1:localhost  #as many of these lines as you want cpu cores running
1:localhost  #ideally pick a multiple of kpoint number
1:localhost  #so something like 5 cores for 10 k points.
```

```
1:localhost
1:localhost
1:localhost
```

Next, go make a struct file, with struct gen, either by importing the cif, or entering the positions manually. Use VESTA (drag n' drop the .struct file) to make sure that the structure is what you'd expect. In the Li2O case this looks like:

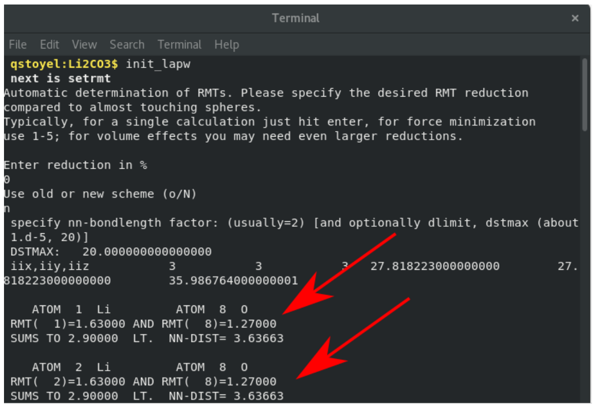


```
Unit-cell volume = 101.129589 A^3

Structure parameters

                      x          y          z          Occ.      B    Site      Sym.
  1 O   O1        0.00000    0.00000    0.00000    1.000    1.000    4a         1
  2 Li  Li1       0.25000    0.25000    0.25000    1.000    1.000    4a         1
  3 Li  Li2       0.75000    0.75000    0.75000    1.000    1.000    4a         1
```

3.2 Initialization

The next step is initialization. This is best done via the command line as it give a little more flexibility and intuition than in w2web, and will need to be run multiple times. The first time will be to set up the calculation for volume optimization, which needs smaller muffin tins. Run **init_lapw** and go through the following steps:

- **setrmt**. Sets the muffin tin size on the atoms. Reduce the sphere size by 5-10% (I used 7%), using either old or new scheme and accept.
- **nn**. Checks for overlapping muffin tins. Enter "2.0", close the first file and use the new NN file if suggested, run **nn** with 2.0 again, look at how much "wiggle room" you have on the spheres, by comparing the "sums to" and the "nn-dist" for every atom, see below:



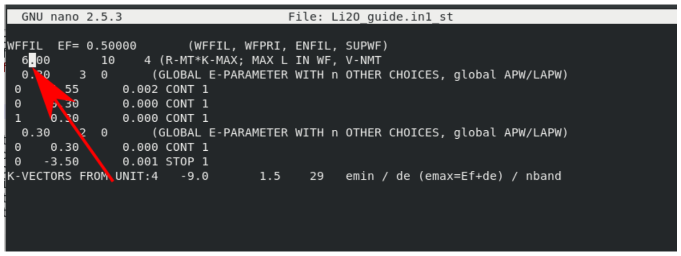
```
qstoyel:Li2CO3$ init_lapw
 next is setrmt
Automatic determination of RMTs. Please specify the desired RMT reduction
compared to almost touching spheres.
Typically, for a single calculation just hit enter, for force minimization
use 1-5; for volume effects you may need even larger reductions.

Enter reduction in %
0
Use old or new scheme (o/N)
n
 specify nn-bondlength factor: (usually=2) [and optionally dlimit, dstmax (about
 1.d-5, 20)]
 DSTMAX:   20.000000000000000
 iix,iiy,iiz           3           3           3   27.818223000000000        27.
818223000000000        35.986764000000001

    ATOM   1  Li         ATOM   8  O
 RMT(  1)=1.63000 AND RMT(  8)=1.27000
 SUMS TO 2.90000  LT.  NN-DIST= 3.63663

    ATOM   2  Li         ATOM   8  O
 RMT(  2)=1.63000 AND RMT(  8)=1.27000
 SUMS TO 2.90000  LT.  NN-DIST= 3.63663
```

- **sgroup**. Verifies the space group. Again, accept any changes the program makes, this first run is all about reducing the cell to the smallest unit cell. Again, the files can be largely ignored at this point, unless there is an indication of a Bravais lattice change, in which case, accept the new struct file. If so, nn and sgroup will run again with "nice" results.

- **symmery**. Generates all the symmetry operations. Run it and continue (enter "c")

- **lstart**. Sets the spin state, selects which XC kernel, and defines cutoff between core and valence states. Accept default spins (up, the no spin case), unless there is a transition metal involved. Select GGA PBE as the XC potential, again, unless there is reason to suspect otherwise. For the purposes of volume optimization, the defualt energy value (-6.0 Ry) works well.

- **kgen** Set the RkMax value in case.in1_st from 7 to the desired value:



```
  GNU nano 2.5.3                       File: Li2O_guide.in1_st

WFFIL  EF= 0.50000       (WFFIL, WFPRI, ENFIL, SUPWF)
  6.00        10    4 (R-MT*K-MAX; MAX L IN WF, V-NMT
  0.30    3  0      (GLOBAL E-PARAMETER WITH n OTHER CHOICES, global APW/LAPW)
 0    [illegible].55      0.002 CONT 1
 0    0.30      0.000 CONT 1
 1    0.30      0.000 CONT 1
  0.30    2  0      (GLOBAL E-PARAMETER WITH n OTHER CHOICES, global APW/LAPW)
 0    0.30      0.000 CONT 1
 0   -3.50      0.001 STOP 1
K-VECTORS FROM UNIT:4   -9.0       1.5    29   emin / de (emax=Ef+de) / nband
```

  and then pick a k_point number. Both of these values should initially be taken for fast convergence, in this case I chose RkMax=6.0, and 16 k points (Li2O is an insulator, for metals 1000 k points is a good starting point).

- **Dstart**: make sure to pick non spin polarized, unless there is reason to believe otherwise (is there a transition metal in the sample?)

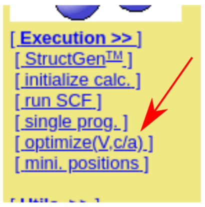
Assuming there were no warnings in the final run through init_lapw, the case can begin to be converged.

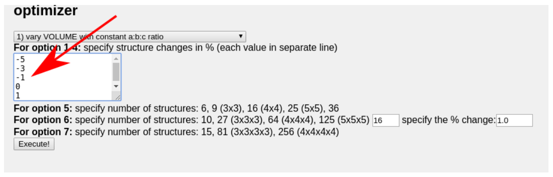
4 Convergence

Ideally, every variable should be converged regarding the simulation. Typically this is cell parameters, k points and Rkmax. The first step is to just make sure the calculation converges, running it with a small RKmax and few kpoints and making sure it finishes without error. Once finished altering parameters in **init_lapw**, run **$ run_lapw -p** to start a calculation. If errors occur, search for them in the userguide, or in the final chapter of this guide. Otherwise proceed with convergence.

4.1 Cell parameters:

This process works best from W2Web, as described in the tutorials and using the muffin tins from **setrmt** reduced by a healthy percentage (∼ 5-10%) to avoid nn errors (you may need to rerun **init_lapw**). As a number (5-11+) of calculations are run in this process, a low number of k points and RKMax values is ideal here. For Li2O, I used 16 kpoints and an RKmax of 6. In the x "optimize" tab, choose what you want to optimize, the first option (volume) works well, unless there are suspicions otherwise. Enter a range of values of test volumes, see picture:




optimizer

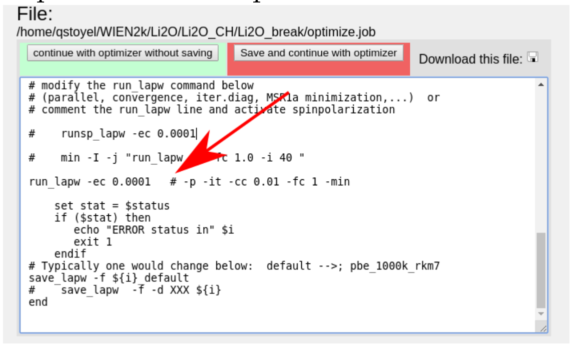
1) vary VOLUME with constant a:b:c ratio

For option 1-4: specify structure changes in % (each value in separate line)

```
-5
-3
-1
0
1
```

For option 5: specify number of structures: 6, 9 (3x3), 16 (4x4), 25 (5x5), 36
For option 6: specify number of structures: 10, 27 (3x3x3), 64 (4x4x4), 125 (5x5x5) 16 specify the % change: 1.0
For option 7: specify number of structures: 15, 81 (3x3x3x3), 256 (4x4x4x4)

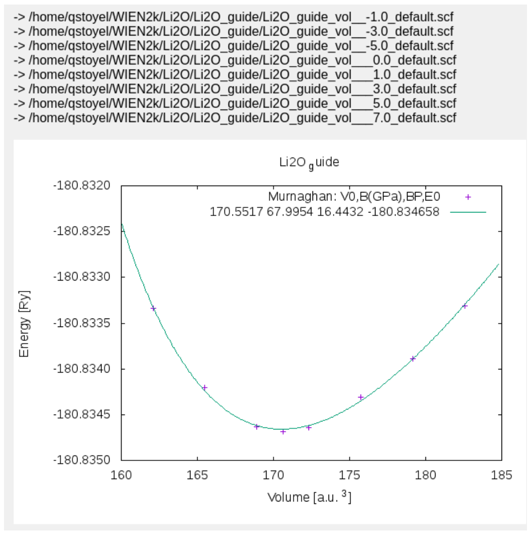
Also make sure to edit "optimize.job" to enable parallization by moving the "#" to after the "-p" in the run_lapw line:


File:
/home/qstoyel/WIEN2k/Li2O/Li2O_CH/Li2O_break/optimize.job

continue with optimizer without saving
Save and continue with optimizer
Download this file:

```
# modify the run_lapw command below
# (parallel, convergence, iter.diag, MSR1a minimization,...)  or
# comment the run_lapw line and activate spinpolarization

#    runsp_lapw -ec 0.0001

#    min -I -j "run_lapw [illegible]fc 1.0 -i 40 "

run_lapw -ec 0.0001   # -p -it -cc 0.01 -fc 1 -min

    set stat = $status
    if ($stat) then
       echo "ERROR status in" $i
       exit 1
    endif
# Typically one would change below:  default -->; pbe_1000k_rkm7
save_lapw -f ${i}_default
#    save_lapw  -f -d XXX ${i}
end
```

You can then "run optimize.job" from w2web. This job is okay to run in the background, which means the browser can be closed without the job stopping. When it is done, plot the "Energy vs Volume," which should look something like this:



```
-> /home/qstoyel/WIEN2k/Li2O/Li2O_guide/Li2O_guide_vol__-1.0_default.scf
-> /home/qstoyel/WIEN2k/Li2O/Li2O_guide/Li2O_guide_vol__-3.0_default.scf
-> /home/qstoyel/WIEN2k/Li2O/Li2O_guide/Li2O_guide_vol__-5.0_default.scf
-> /home/qstoyel/WIEN2k/Li2O/Li2O_guide/Li2O_guide_vol___0.0_default.scf
-> /home/qstoyel/WIEN2k/Li2O/Li2O_guide/Li2O_guide_vol___1.0_default.scf
-> /home/qstoyel/WIEN2k/Li2O/Li2O_guide/Li2O_guide_vol___3.0_default.scf
-> /home/qstoyel/WIEN2k/Li2O/Li2O_guide/Li2O_guide_vol___5.0_default.scf
-> /home/qstoyel/WIEN2k/Li2O/Li2O_guide/Li2O_guide_vol___7.0_default.scf
```

The important feature here is that the overall trend of the curve is clear, if too few k points are chosen, the points will be "noisy." In the case of Li2O, the used lattice parameter of 4.6590Å results in the minimum energy, so no further changes are needed. If we needed a structure with a different lattice parameter, search the case directory for all the struct files and rename the appropriate one to case.struct, eg "Li2O_vol___3.0.struct → Li2O.struct". Alternatively, cut and paste the lattice parameters from this file into the w2web structgen tool.

4.2 Setting the Muffin Tin Size

This is the first step of the process that is specific to calculating the Lithium ELNES. In order to have the ability to insert core holes, the lithium 1S state needs to be treated as a core state. This requires playing with the muffin tin radius and the energy cutoff value in lstart. Rerun **init_lapw** with no reduction in muffin tin size, and during lstart, use a cuutoff energy of -3.5 Ry (The Li 1 S state has an energy of -3.8 Ry). Investigate the case.outputst file (it should pop up) for the following lines for the lithium atom and look at the 1S states:

```
              E-up(Ry)       E-dn(Ry)    Occupancy    q/sphere   core-state
1S        -3.801968      -3.785309   1.00   1.00      0.9904   T
1S        -3.801968      -3.785309   1.00   1.00      0.9904   T
2S        -0.236711      -0.003297   1.00   0.00      0.0595   F
2S        -0.236711      -0.003297   1.00   0.00      0.0595   F
```

These indicate the core states (T/F), their energy levels (in this case ∼ -3.8eV) and how much the electrons in these states are contained in the muffin tins (0.9904). As this is less than 1, it means that some 1S lithium electron is leaking out of the muffin tins, which is why there should now be all kinds of warnings popping up. So go ahead and "ctrl-c" out of init_lapw.

To fix the leakage problem, the Lithium muffin tins need to be bigger. Ideally, they should be just big enough to hold all of the 1S electrons, without making them too different from the other muffin tins, as the larger this difference, the harder things get to calculate/converge. In this case, try Li=2.0, O=1.8 and try init_lapw again making sure to discard the suggested muffin tins from **setrmt**. If that still didn't work (lstart still has leakage errors), keep going until it does. If the RMT values are too different (eg if $\mathrm{RMT}_{\mathrm{Li}} \approx 1.5\mathrm{RMT}_{\mathrm{O}}$) they will cause errors (ghostbands) further along. The solution then is to try and minimize the leakage (and ignore the warnings) and acknowledge that it might be unavoidably causing artifacts. Once the spheres are set in the struct file, rerun **init_lapw**.

4.3 K point and RKMax convergence

To converge these parameters, again start with very low values and then increase them, checking the total energy to determine when they are converged. Generally k points are easier to converge, so start with them and then move on to RKMax. The procedure for converging both of these values is:

- set/increase kpoints or RKMax, either by re-running "x kgen" or editing case.in1 and case.in1_st.
- Run the scf cycle using "run_lapw -p -NI", the NI flag means it will continue from where the previous calculation left off which can save time. The final converged choice should still be run from scratch though (rerun init_lapw, rm *broyd* before running run_lapw)
- Check the energy in case.scf. To do this, find it in "scf files" on w2web and use ctrl+f in your browser to search the file for ":ene" , which should appear in a line that looks like:

  ```
  :ENE  : ********** TOTAL ENERGY IN Ry =          -180.82588608
  ```

  There will be one of these lines for each scf cycle, so find the last one in the document and note the energy.
- loop through the first 3 steps until the energy no longer changes significantly when you increase the kpoints/RKMax. A table is useful here to track these effects eg:

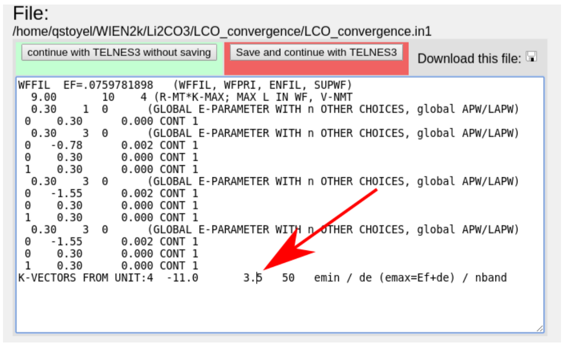
kpoints	RKMax	Energy
16	6.0	-180.82588608
32	6.0	-180.85055185
64	6.0	-180.85166466
32	7.0	-180.85723055
32	8.0	-180.85860820
32*	8.0*	-180.85977640

Depending on the case, the energy will only converge so far. For the above table, I would choose 32 k points and RKMax of 8.0. there were only minimal changes (<0.001Ry) to the energy beyond those. The starred case indicate the calculation being run from scratch.

5 Density of States

In order to determine whether or not a core hole is necessary, the first step is to analyze the DOS. These are best calculated in w2web, clicking the buttons.

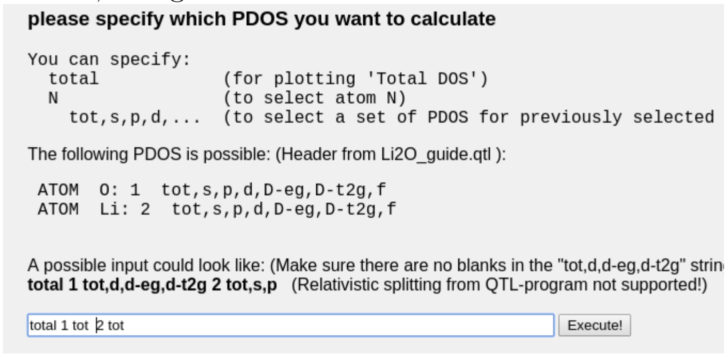
To start, run the optional steps and increase the upper energy limit in case.in1 from 1.5 to ∼ 2-3.5, see picture. This value defines how many higher energy states are included in Ry (1 Ry ≈13.6 eV, 1.5Ry ≈ 20eV). Therefore, to obtain the correct DOS and ELNES for features more than 20eV from the onset, this should be increased to match.


File:
/home/qstoyel/WIEN2k/Li2CO3/LCO_convergence/LCO_convergence.in1

continue with TELNES3 without saving
Save and continue with TELNES3
Download this file:

```
WFFIL  EF=.0759781898   (WFFIL, WFPRI, ENFIL, SUPWF)
  9.00       10    4 (R-MT*K-MAX; MAX L IN WF, V-NMT
  0.30    1  0      (GLOBAL E-PARAMETER WITH n OTHER CHOICES, global APW/LAPW)
 0    0.30      0.000 CONT 1
  0.30    3  0      (GLOBAL E-PARAMETER WITH n OTHER CHOICES, global APW/LAPW)
 0   -0.78      0.002 CONT 1
 0    0.30      0.000 CONT 1
 1    0.30      0.000 CONT 1
  0.30    3  0      (GLOBAL E-PARAMETER WITH n OTHER CHOICES, global APW/LAPW)
 0   -1.55      0.002 CONT 1
 0    0.30      0.000 CONT 1
 1    0.30      0.000 CONT 1
  0.30    3  0      (GLOBAL E-PARAMETER WITH n OTHER CHOICES, global APW/LAPW)
 0   -1.55      0.002 CONT 1
 0    0.30      0.000 CONT 1
 1    0.30      0.000 CONT 1
K-VECTORS FROM UNIT:4  -11.0       3.5   50   emin / de (emax=Ef+de) / nband
```

Then boost the k points value by an order of magnitude to pull out the finer features in the DOS, and run **x lapw -p** and **x lpaw2 -qtl -p**. Then select the total DOS of each atom in case.int, using the w2web interface:


please specify which PDOS you want to calculate

```
You can specify:
  total             (for plotting 'Total DOS')
  N                 (to select atom N)
    tot,s,p,d,...   (to select a set of PDOS for previously selected
```

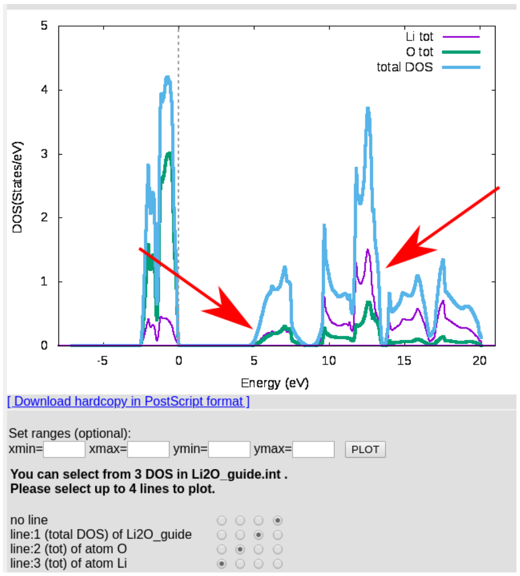
The following PDOS is possible: (Header from Li2O_guide.qtl):

```
 ATOM  O: 1  tot,s,p,d,D-eg,D-t2g,f
 ATOM  Li: 2  tot,s,p,d,D-eg,D-t2g,f
```

A possible input could look like: (Make sure there are no blanks in the "tot,d,d-eg,d-t2g" strin
total 1 tot,d,d-eg,d-t2g 2 tot,s,p (Relativistic splitting from QTL-program not supported!)

```
total 1 tot 2 tot
```

Run **x tetra** and plot the DOS with dosplot, which should give you something like this:



[Download hardcopy in PostScript format]

Set ranges (optional):
xmin= xmax= ymin= ymax= PLOT

You can select from 3 DOS in Li2O_guide.int .
Please select up to 4 lines to plot.

no line ○ ○ ○ ●
line:1 (total DOS) of Li2O_guide ○ ○ ● ○
line:2 (tot) of atom O ○ ● ○ ○
line:3 (tot) of atom Li ● ○ ○ ○

What we are looking for here is whether the conduction band has a large component of unoccupied lithium states, which it does in this case, indicated by the arrows. If the unoccupied states were purely oxygen in nature, no core hole effect would be expected, as there would be no states to alter effecting the ELNES. For more insight on this behavior, the reader is referred to Mauchamp, Jaouen and Schattschneider (2009) "Core-hole effect in the one-particle approximation revisited from density functional theory."

As there is indeed a large component of lithium states in the low conduction band, a core hole is necessary. Before that, we calculate an initial ELNES for comparison later.

6 TELNES3

Once the calculation is converged, ELNES can be calculated. There is a good deal of useful information and a complete description of the input file in the wien2k userguide, which should solve most issues. Again, there is a large list of parameters that must be set for in order to obtain reasonable results. It is also worth converging Kpoints and RKMax against the spectra as well.

The majority of the important parameters need to be set in the **case.innes** file, which is easiest through w2web. Choose the right atom (in this case Li1) for the edge, and the right atomic numbers:

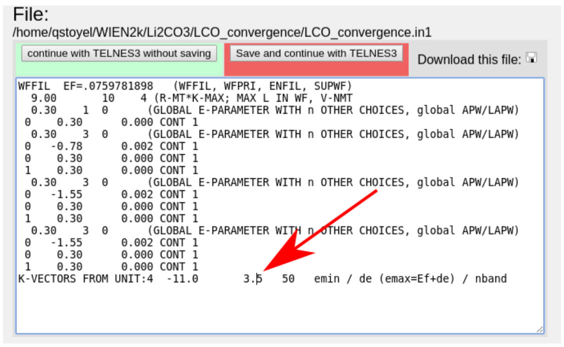
Edge	n	l
K	1	0
L1	2	0
L23	2	1
M45	3	2

Next, set the edge onset, edge values can be found at `http://www.kayelaby.npl.co.uk/atomic_and_nuclear_physics/4_2/4_2_1.html` as well as at a number of other locations. Set the beam energy to it's correct value, same goes for the collection and convergence angles, although TELNES is relatively robust to these: eg 5mrad produces very similar results to 1 mrad.

Set the energy grid to a large range of values, eg -20-50eV so you can see all of the features that might appear. The defaults for the remaining values should be fine.

In addition to the case.innes parameters, increase the number of kpoints, to at least double, or 10×, so that there is less doubt about this being converged, use **x kgen** for this. This should already have been done for calculating the DOS.

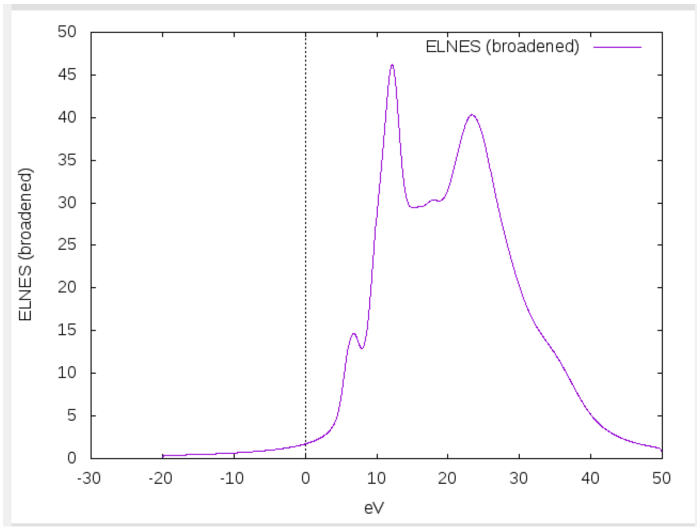
Increase the upper energy limit in case.in1 from 1.5 to ∼ 2-3.5, see picture. This value defines how many higher energy states are included in Ry (1 Ry ≈13.6 eV, 1.5Ry ≈ 20eV). Therefore, to obtain the correct ELNES for features more than 20eV from the onset, this should be increased to match.


File:
/home/qstoyel/WIEN2k/Li2CO3/LCO_convergence/LCO_convergence.in1
continue with TELNES3 without saving
Save and continue with TELNES3
Download this file:

```
WFFIL  EF=.0759781898   (WFFIL, WFPRI, ENFIL, SUPWF)
  9.00       10    4 (R-MT*K-MAX; MAX L IN WF, V-NMT
  0.30    1  0      (GLOBAL E-PARAMETER WITH n OTHER CHOICES, global APW/LAPW)
 0    0.30      0.000 CONT 1
  0.30    3  0      (GLOBAL E-PARAMETER WITH n OTHER CHOICES, global APW/LAPW)
 0   -0.78      0.002 CONT 1
 0    0.30      0.000 CONT 1
 1    0.30      0.000 CONT 1
  0.30    3  0      (GLOBAL E-PARAMETER WITH n OTHER CHOICES, global APW/LAPW)
 0   -1.55      0.002 CONT 1
 0    0.30      0.000 CONT 1
 1    0.30      0.000 CONT 1
  0.30    3  0      (GLOBAL E-PARAMETER WITH n OTHER CHOICES, global APW/LAPW)
 0   -1.55      0.002 CONT 1
 0    0.30      0.000 CONT 1
 1    0.30      0.000 CONT 1
K-VECTORS FROM UNIT:4  -11.0       3.5   50   emin / de (emax=Ef+de) / nband
```

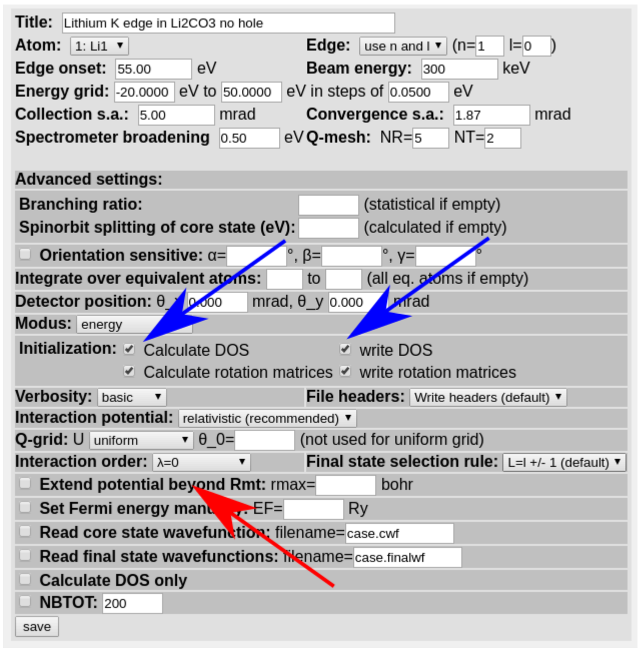
x lapw1 -p, x qtl -telnes -p, and **x telnes3** can then all be run in succession. These are relatively slow commands, so to avoid waiting on them, run all three in sequence from the command line: **$ x lapw1 -p && x qtl -telnes -p && x telnes3.**

Once telnes3 is finished, edit case.inb and play with the spectrometer broadening on the last line, before clicking "x broadening" to generate the final spectra. To experiment with different broadening values, just repeat these steps. Sometimes w2web gets stuck and stops re-broadening the spectra, in which case, just delete the case.broadspec file and run "x broadening" again. Plot the spectrum in a new tab (ctrl+click on "plot") for easy comparison to new spectra without having to save it. Rerun all the TELNES steps, but with a higher/lower number of kpoints to confirm that that is not effecting the spectra. At this point you can also uncheck the "calculate and write DOS" checkboxes in case.innes, which allow you to rerun telnes without needing to rerun **lapw1** each time (unless you change the k points/case.in1 file). If everything went well, the ELNES should look something like (broadening = 0.5):



6.1 Monopole effects

Because the lithium 1S state is quite delocalized, it is susceptible to monopole effects. These cause artifacts in the spectra resulting from non orthogonal states at the muffin tin boundary. Fortunately, it is easy to check for them. Return to the case.innes file and change the interaction order to 0.



Title: Lithium K edge in Li2CO3 no hole
Atom: 1: Li1 ▾ **Edge:** use n and l ▾ (n=1 l=0)
Edge onset: 55.00 eV **Beam energy:** 300 keV
Energy grid: -20.0000 eV to 50.0000 eV in steps of 0.0500 eV
Collection s.a.: 5.00 mrad **Convergence s.a.:** 1.87 mrad
Spectrometer broadening 0.50 eV **Q-mesh:** NR=5 NT=2

Advanced settings:
Branching ratio: (statistical if empty)
Spinorbit splitting of core state (eV): (calculated if empty)
☐ **Orientation sensitive:** α= °, β= °, γ= °
Integrate over equivalent atoms: to (all eq. atoms if empty)
Detector position: θ_x 0.000 mrad, θ_y 0.000 mrad
Modus: energy
Initialization: ✓ Calculate DOS ✓ write DOS
✓ Calculate rotation matrices ✓ write rotation matrices
Verbosity: basic ▾ **File headers:** Write headers (default) ▾
Interaction potential: relativistic (recommended) ▾
Q-grid: U uniform ▾ θ_0= (not used for uniform grid)
Interaction order: λ=0 ▾ **Final state selection rule:** L=l +/- 1 (default) ▾
☐ **Extend potential beyond Rmt:** rmax= bohr
☐ **Set Fermi energy manually:** EF= Ry
☐ **Read core state wavefunction:** filename=case.cwf
☐ **Read final state wavefunctions:** filename=case.finalwf
☐ **Calculate DOS only**
☐ **NBTOT:** 200
save

Telnes now only calculates the monopole component, look in case.outputelnes to confirm this. Compare the monopole contribution to the full spectra, it should be much smaller ($\sim$100$\times$). If it is not, set the interaction order to 1 to enforce dipole selection and use that for all future spectra.

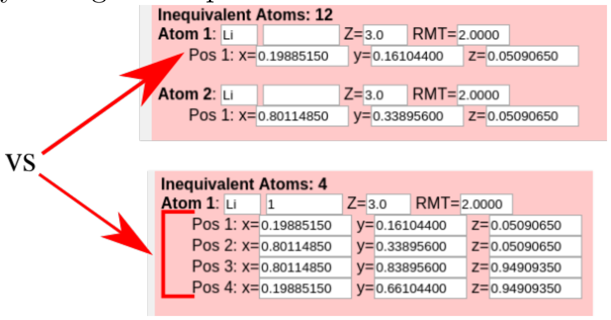
7 Core Hole

To introduce a core hole, start an entirely new case, and copy only the struct and the .machines files. Because of the periodic boundary conditions, it is often necessary to use a supercell to avoid core holes interacting with themselves in neighbouring cells. This depends largely on the size of the original unit cell, for a single atom case (metallic lithium) a 3×3×3 cell is required, for large calcium phosphates, no cell is needed.

Li2O is a small sized cell, so a 2×2×2 supercell is a good starting point, which would need to be compared to a 3×3×3 supercell for full rigorousness.

To generate the supercell, run **x supercell** in the new directory and use the copied struct file, with no shift.

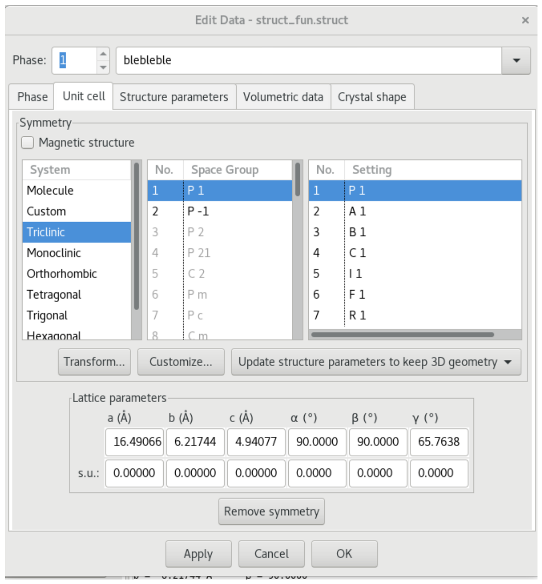
With all core holes, it is essential to remove the symmetry in the unit cell, so there is only a single hole per cell:



```
Inequivalent Atoms: 12
Atom 1: Li              Z=3.0   RMT=2.0000
   Pos 1: x=0.19885150  y=0.16104400  z=0.05090650

Atom 2: Li              Z=3.0   RMT=2.0000
   Pos 1: x=0.80114850  y=0.33895600  z=0.05090650
```

```
Inequivalent Atoms: 4
Atom 1: Li   1          Z=3.0   RMT=2.0000
   Pos 1: x=0.19885150  y=0.16104400  z=0.05090650
   Pos 2: x=0.80114850  y=0.33895600  z=0.05090650
   Pos 3: x=0.80114850  y=0.83895600  z=0.94909350
   Pos 4: x=0.19885150  y=0.66104400  z=0.94909350
```

To achieve this, the cell must be reduced to a P1 space group. This can be done in VESTA. Import the struct file and "remove symmetry", under "Edit → Edit Data → Unit Cell." The spacegroup should switch to P-1, then select "apply"



Phase: 1 blebleble

Symmetry
☐ Magnetic structure

System	No.	Space Group	No.	Setting
Molecule	1	P 1	1	P 1
Custom	2	P -1	2	A 1
Triclinic	3	P 2	3	B 1
Monoclinic	4	P 21	4	C 1
Orthorhombic	5	C 2	5	I 1
Tetragonal	6	P m	6	F 1
Trigonal	7	P c	7	R 1
Hexagonal	8	C m		

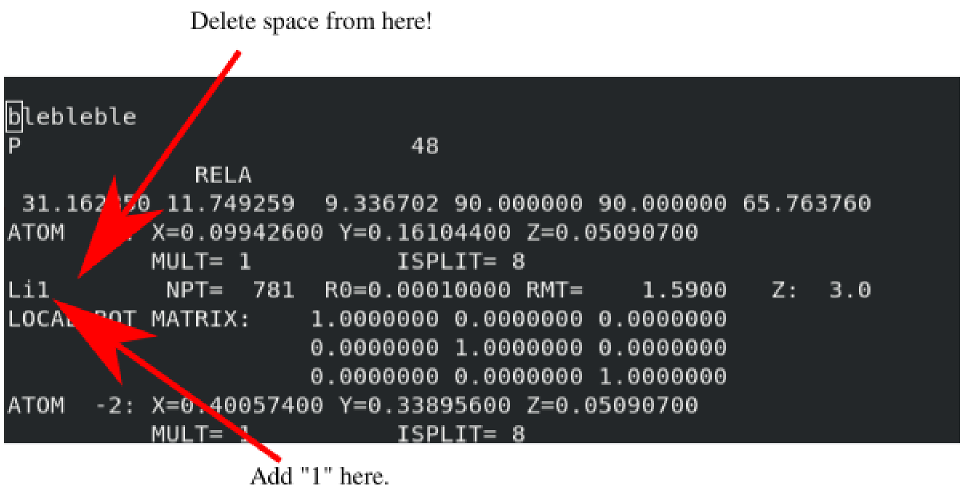
Lattice parameters

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
	16.49066	6.21744	4.94077	90.0000	90.0000	65.7638
s.u.:	0.00000	0.00000	0.00000	0.0000	0.0000	0.0000

To save these changes select "File → Export data" and save the structure as a .cif.

Running **Cif2struct name_of_cif.cif** should then be able to generate a valid struct file, which should be renamed as case.struct. For some reason, I am only able to do this with my local install of wien2k/cif2struct, the remote version complains about " Space group name nor symmetry operations are not given!" I have attached the final struct file that I used to the github directory. It might be necessary to install wien2k after all...

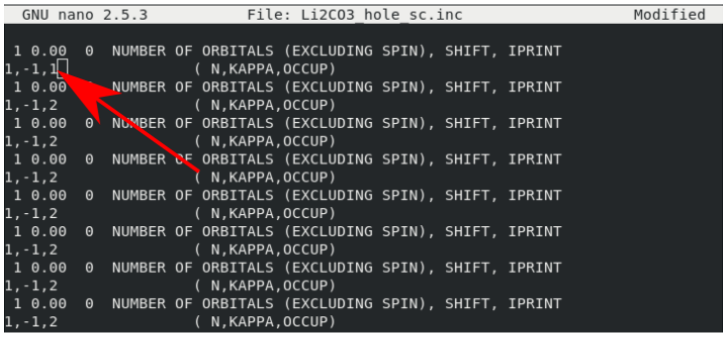
In the new struct file, add a "1" to the end of a lithium atom (AND DELETE A SPACE). The file should look like this:



```
blebleble
P                            48
                RELA
 31.162?50 11.749259  9.336702 90.000000 90.000000 65.763760
ATOM    -1: X=0.09942600 Y=0.16104400 Z=0.05090700
            MULT= 1          ISPLIT= 8
Li1          NPT=  781  R0=0.00010000 RMT=    1.5900   Z:  3.0
LOCAL ROT MATRIX:    1.0000000 0.0000000 0.0000000
                     0.0000000 1.0000000 0.0000000
                     0.0000000 0.0000000 1.0000000
ATOM   -2: X=0.40057400 Y=0.33895600 Z=0.05090700
            MULT= 1          ISPLIT= 8
```

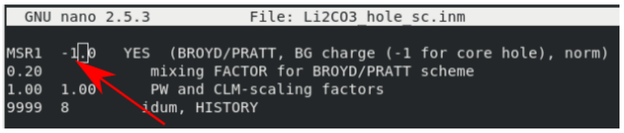
Now run **init_lapw** and accept all of the defaults proposed by **nn**, which may require cycling through **nn** a couple times. **sgroup** should not have any suggestions here, if it does, something has gone wrong and it is trying to restore all of the symmetry. At the end of **init_lapw**, make sure to double check that the struct file is still what it should be in VESTA.

When the struct file is ready, initialize use the converged parameters (RMT, RKMax) from the single cell case. (divide the number of k points appropriately, in this case by 8) After init_lapw, insert a core hole into the cell by editing case.inc and case.inm:



```
  GNU nano 2.5.3           File: Li2CO3_hole_sc.inc                    Modified

 1 0.00   0  NUMBER OF ORBITALS (EXCLUDING SPIN), SHIFT, IPRINT
1,-1,1              ( N,KAPPA,OCCUP)
 1 0.00   0  NUMBER OF ORBITALS (EXCLUDING SPIN), SHIFT, IPRINT
1,-1,2              ( N,KAPPA,OCCUP)
 1 0.00   0  NUMBER OF ORBITALS (EXCLUDING SPIN), SHIFT, IPRINT
1,-1,2              ( N,KAPPA,OCCUP)
 1 0.00   0  NUMBER OF ORBITALS (EXCLUDING SPIN), SHIFT, IPRINT
1,-1,2              ( N,KAPPA,OCCUP)
 1 0.00   0  NUMBER OF ORBITALS (EXCLUDING SPIN), SHIFT, IPRINT
1,-1,2              ( N,KAPPA,OCCUP)
 1 0.00   0  NUMBER OF ORBITALS (EXCLUDING SPIN), SHIFT, IPRINT
1,-1,2              ( N,KAPPA,OCCUP)
 1 0.00   0  NUMBER OF ORBITALS (EXCLUDING SPIN), SHIFT, IPRINT
1,-1,2              ( N,KAPPA,OCCUP)
 1 0.00   0  NUMBER OF ORBITALS (EXCLUDING SPIN), SHIFT, IPRINT
1,-1,2              ( N,KAPPA,OCCUP)
```

In case.inc, a hole is inserted by changing the occupancy of an orbital, the trick in this case is picking out one of the isolated lithium atoms (with mult=1) which depends on where you added the 1 to the struct file. Each set of lines corresponds to the core states of each atom defined in the struct file. This is why it is important to be able to treat the lithium states as core states, otherwise it would not be possible to insert a hole. This is also why it is important to break the symmetry in the unit cell as if not, this would insert holes into multiple atoms. In the case.inm file, the excited electrons need to be added to the background charge:



```
  GNU nano 2.5.3              File: Li2CO3_hole_sc.inm

MSR1   -1.0   YES  (BROYD/PRATT, BG charge (-1 for core hole), norm)
0.20           mixing FACTOR for BROYD/PRATT scheme
1.00   1.00    PW and CLM-scaling factors
9999   8      idum, HISTORY
```

The value is negative as this operation adds charge, not electron number. Once the background charge is added, execute **run_lapw -p** and calculate the ELNES. This might take some time, so you may want to run it remotely using tmux so you can leave it overnight if need be. Once done, calculate the DOS of the Lithium p states and compare to the no hole case:

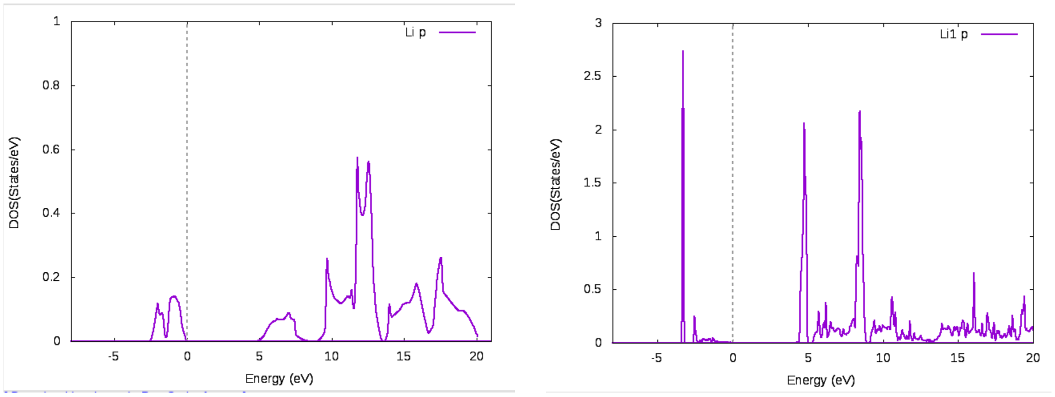
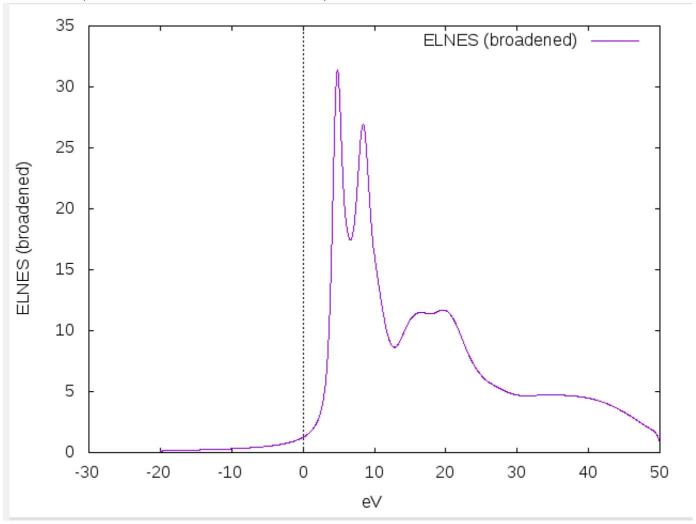


Figure 1: Li P states from no-hole case (left) and hole case (right). Note the dramatic peak growth at 4eV and 7 eV in the hole case, indicating excitonic effects.

The dramatic differences in the unoccupied band when a core hole is introduced, combined with the significant fraction of total unoccupied states represented by the lithium band, indicates core hole effects in the ELNES. Calculating the ELNES, should look something like this (broadening = 0.9), if it all went well:



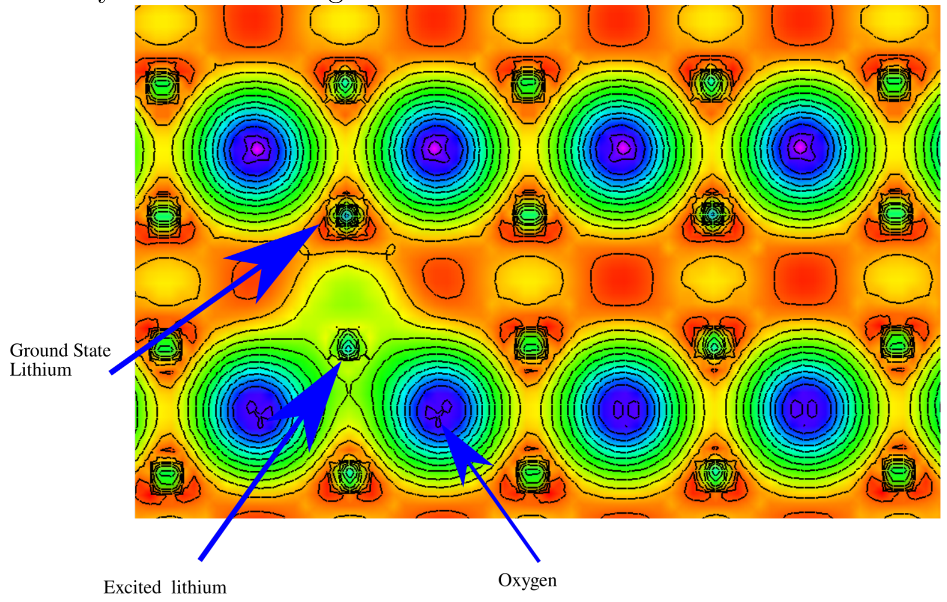
Having determined the need to include a core hole in the calculations, the next step is determining if the hole is shielded, which can be done using density calculations.

8 Density Calculations

Density calculations can be done using either xcrysden (qualitative) or Critic2 (quantitative).

8.1 Xcrysden

Xcyrsden density rendering is well explained in the online wien2k tutorials to which the reader is referred to. Depending on your particular setup, density rendering with xcrysden may need to be performed locally, which will also require install wien2k locally. For Li2O, the density looks something like:



Qualitative investigation of plot shows the excited lithium atom (atom with a hole) distorting the oxygen electron clouds. The atomic basin appears smaller, defined by the ring of yellow surrounding the excited atom, although the entire region around the excited atom has experienced a net gain in electron count (more green than red). These features suggest that there is a non negligible response from the material to the core hole. The regularity of the ground state lithium's appear to indicate that the distance between excited lithium atom is sufficient to isolate the core holes. In this case this distance is more than 9Å which is considered suitable for this purpose.

8.2 Critic2

While Xcrysden is ideal for qualitative analysis, Critic2 is better suited to quantifying electron density features. The documentation for critic, while very complete, is in a giant txt file. The code takes three inputs: the case.struct file, the case.clmsum file, and an input parameters file "more.cri". A sample .cri file is below:

```
crystal ./Li2O.struct
```

```
load ./Li2O.clmsum ./Li2O.struct
auto
integrals gauleg 50 50 cp 2 verbose
sphereintegrals gauleg 50 50 cp 2 R0 1d-1 REND 2.0
```

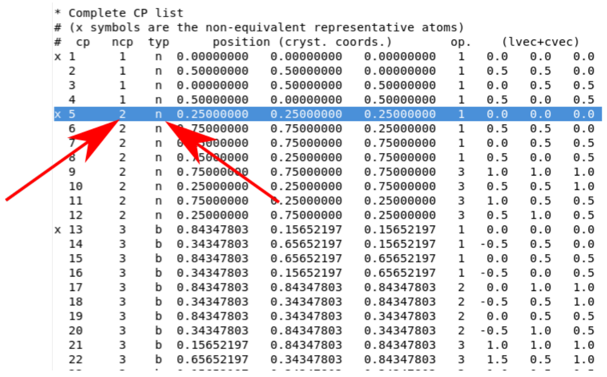
The first line inputs the crystal structure, and the second line tells the code where to find the clmsum/struct files in the second line.

The third line determines the location of all the critical points.

The 4th line calculates the electron population inside the atomic basin surrounding critical point 1. “Gauleg” is an integration option, look in the critic documentation for more options. The two 50’s are sampling parameters, increase/decrease these for more/less accurate calculations.

The 5th line calculates the electron population in spheres surrounding critical point 2. “gualeg 50 50” mean the exact same as on the previous line, R0 is the starting radius, 1d-1 sets the radius step size, REND is the final radius (in bohr).

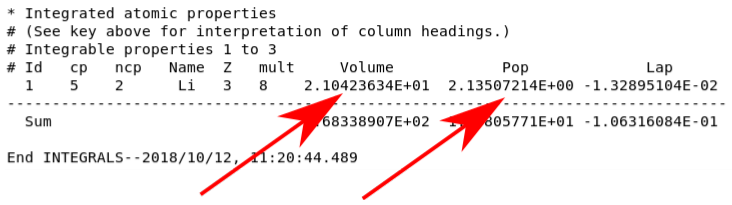
The program is run using **$ critic2 < more.cri > case.cro** in the command line in the case directory. The final file (case.cro) is just where the output is stored and can be called anything. To determine which critical points are needed for the integrals, look at the complete cp list in the output file:



```
* Complete CP list
# (x symbols are the non-equivalent representative atoms)
#  cp   ncp  typ      position (cryst. coords.)        op.    (lvec+cvec)
x 1      1    n  0.00000000   0.00000000   0.00000000   1   0.0   0.0   0.0
  2      1    n  0.50000000   0.50000000   0.00000000   1   0.5   0.5   0.0
  3      1    n  0.00000000   0.50000000   0.50000000   1   0.0   0.5   0.5
  4      1    n  0.50000000   0.00000000   0.50000000   1   0.5   0.0   0.5
x 5      2    n  0.25000000   0.25000000   0.25000000   1   0.0   0.0   0.0
  6      2    n  0.75000000   0.75000000   0.25000000   1   0.5   0.5   0.0
  7      2    n  0.25000000   0.75000000   0.75000000   1   0.0   0.5   0.5
  8      2    n  0.75000000   0.25000000   0.75000000   1   0.5   0.0   0.5
  9      2    n  0.75000000   0.75000000   0.75000000   3   1.0   1.0   1.0
  10     2    n  0.25000000   0.25000000   0.75000000   3   0.5   0.5   1.0
  11     2    n  0.75000000   0.25000000   0.25000000   3   1.0   0.5   0.5
  12     2    n  0.25000000   0.75000000   0.25000000   3   0.5   1.0   0.5
x 13     3    b  0.84347803   0.15652197   0.15652197   1   0.0   0.0   0.0
  14     3    b  0.34347803   0.65652197   0.15652197   1  -0.5   0.5   0.0
  15     3    b  0.84347803   0.65652197   0.65652197   1   0.0   0.5   0.5
  16     3    b  0.34347803   0.15652197   0.65652197   1  -0.5   0.0   0.5
  17     3    b  0.84347803   0.84347803   0.84347803   2   0.0   1.0   1.0
  18     3    b  0.34347803   0.34347803   0.84347803   2  -0.5   0.5   1.0
  19     3    b  0.84347803   0.34347803   0.34347803   2   0.0   0.5   0.5
  20     3    b  0.34347803   0.84347803   0.34347803   2  -0.5   1.0   0.5
  21     3    b  0.15652197   0.84347803   0.84347803   3   1.0   1.0   1.0
  22     3    b  0.65652197   0.34347803   0.84347803   3   1.5   0.5   1.0
```

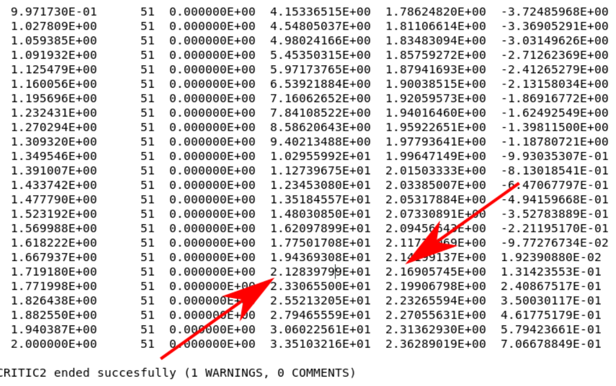
There are a number of similar lists which can be used to identify which atom is of interest. The critical point should be a nuclear critical point (typ = n), and as a double check, the coordinates should match up to those in the struct file. The name should also match, in this case, the ncp 1 corresponds to “Li1.”

The electron populations are located towards the bottom of the document. The first case looks like this:



```
* Integrated atomic properties
# (See key above for interpretation of column headings.)
# Integrable properties 1 to 3
# Id   cp   ncp   Name  Z   mult     Volume            Pop              Lap
  1    5    2      Li   3   8    2.10423634E+01  2.13507214E+00 -1.32895104E-02
------------------------------------------------------------------------------
  Sum                           [illegible].68338907E+02  1.[illegible]805771E+01 -1.06316084E-01

End INTEGRALS--2018/10/12, 11:20:44.489
```

The two values indicated by the arrows are the volume of the basin and how many electrons are inside. The second population is calculated directly below this in a table:



```
  9.971730E-01      51  0.000000E+00  4.15336515E+00  1.78624820E+00  -3.72485968E+00
  1.027809E+00      51  0.000000E+00  4.54805037E+00  1.81106614E+00  -3.36905291E+00
  1.059385E+00      51  0.000000E+00  4.98024166E+00  1.83483094E+00  -3.03149626E+00
  1.091932E+00      51  0.000000E+00  5.45350315E+00  1.85759272E+00  -2.71262369E+00
  1.125479E+00      51  0.000000E+00  5.97173765E+00  1.87941693E+00  -2.41265279E+00
  1.160056E+00      51  0.000000E+00  6.53921884E+00  1.90038515E+00  -2.13158034E+00
  1.195696E+00      51  0.000000E+00  7.16062652E+00  1.92059573E+00  -1.86916772E+00
  1.232431E+00      51  0.000000E+00  7.84108522E+00  1.94016460E+00  -1.62492549E+00
  1.270294E+00      51  0.000000E+00  8.58620643E+00  1.95922651E+00  -1.39811500E+00
  1.309320E+00      51  0.000000E+00  9.40213488E+00  1.97793641E+00  -1.18780721E+00
  1.349546E+00      51  0.000000E+00  1.02955992E+01  1.99647149E+00  -9.93035307E-01
  1.391007E+00      51  0.000000E+00  1.12739675E+01  2.01503333E+00  -8.13018541E-01
  1.433742E+00      51  0.000000E+00  1.23453080E+01  2.03385007E+00  -6.47067797E-01
  1.477790E+00      51  0.000000E+00  1.35184557E+01  2.05317884E+00  -4.94159668E-01
  1.523192E+00      51  0.000000E+00  1.48030850E+01  2.07330891E+00  -3.52783889E-01
  1.569988E+00      51  0.000000E+00  1.62097899E+01  2.09456543E+00  -2.21195170E-01
  1.618222E+00      51  0.000000E+00  1.77501708E+01  2.117[illegible]69E+00  -9.77276734E-02
  1.667937E+00      51  0.000000E+00  1.94369308E+01  2.14[illegible]99137E+00  1.92390880E-02
  1.719180E+00      51  0.000000E+00  2.12839799E+01  2.16905745E+00  1.31423553E-01
  1.771998E+00      51  0.000000E+00  2.33065500E+01  2.19906798E+00  2.40867517E-01
  1.826438E+00      51  0.000000E+00  2.55213205E+01  2.23265594E+00  3.50030117E-01
  1.882550E+00      51  0.000000E+00  2.79465559E+01  2.27055631E+00  4.61775179E-01
  1.940387E+00      51  0.000000E+00  3.06022561E+01  2.31362930E+00  5.79423661E-01
  2.000000E+00      51  0.000000E+00  3.35103216E+01  2.36289019E+00  7.06678849E-01

CRITIC2 ended succesfully (1 WARNINGS, 0 COMMENTS)
```

By matching to the volume value, relatively comparable values should be attainable (2.14 vs 2.17), in the no hole case. The reason for performing two types of population calculation is due to the fact that the atomic basins can become ill defined when a core hole is inserted. This is revealed when the volume of the basin is dramatically larger ($> 20\%$) than the no hole case. In these situations, a comparison of the sphere integrals at the same volume (set by the basin volume in the no hole case) is more appropriate.

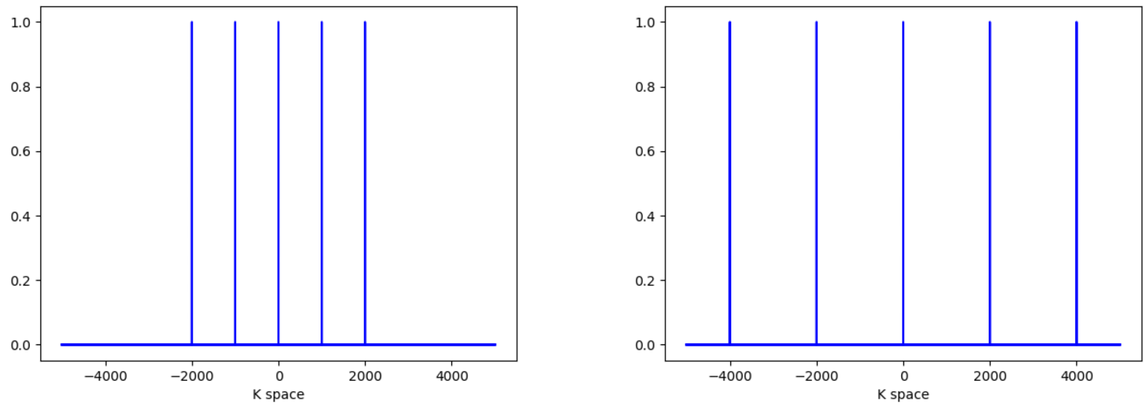
In the case of Li2O, the no hole case had a population of 2.135 and the no hole case had a population of 1.283 (and a smaller basin volume). This indicates that the core hole is slightly screened and has an effective strength of 2.135-1.283 = 0.852. To implement this effect, a third, final supercell calculation is required, with a reduced hole inserted. case.inc would need an occupancy of 1.15 and case.inm would need a background charge of -0.85. This can be rapidly set up by copying the struct file from the full hole calculation and initializing from there.

For this partial hole calculation, the only relevant property is the ELNES calculation as the DOS are somewhat unphysical. This ELNES should represent the best agreement with experiment, if all has gone well and the calculations are converged with all aspects. If all goes well, it should like this:

9 Common Errors/Issues Encountered in Wien2k

9.1 Setting RMT/RKMax

The RKMax value is a little obscure and takes some getting used to. It is defined as the Muffin Tin Radii $\times$ Maximum K point vector. The maximum k point corresponds to the highest frequency plane wave used in the calculation. RKMax defines a cutoff for sampling k space, based on the size of each atom. A visualization of this effect is depicted below:



Two case, both with 5 kpoints and different RKMax's. The plot on the left depicts a smaller RKMax relative to the one on the right.

Increasing RKMax allows for higher frequency (more precise) plane waves to be used in the basis set. These high frequency terms are however more computationally costly (CPU requirements scale as RKMax^3) and less essential for describing large features. This is why the RKMax includes the Muffin Tin radius: large atoms only require lower frequency plane waves. Each atom has an effective RKMax which is relative to the ratio of its radius and that of the smallest atom. Choosing very different muffin tin radii for different elements leads to issues as it becomes more difficult to align the surface features of each atom.

Increasing RKMax arbitrarily does not solve the problem either, as: 1. "approximate numerical linear dependency" occurs at large RKMax values and 2. Calculations become prohibitively expensive. RKMax should at most be between 9-10.

9.2 Ghostbands

Ghostbands are an inevitable consequence of investigating lithium with Wien2k. They manifest as an LAPW2 qtl error during the scf cycles, typically during the first cycle, but sometimes later as well. They are recorded the lapw2(_n).error files as:

```
'l2main' – QTL–B.GT.15., Ghostbands, check scf files
```

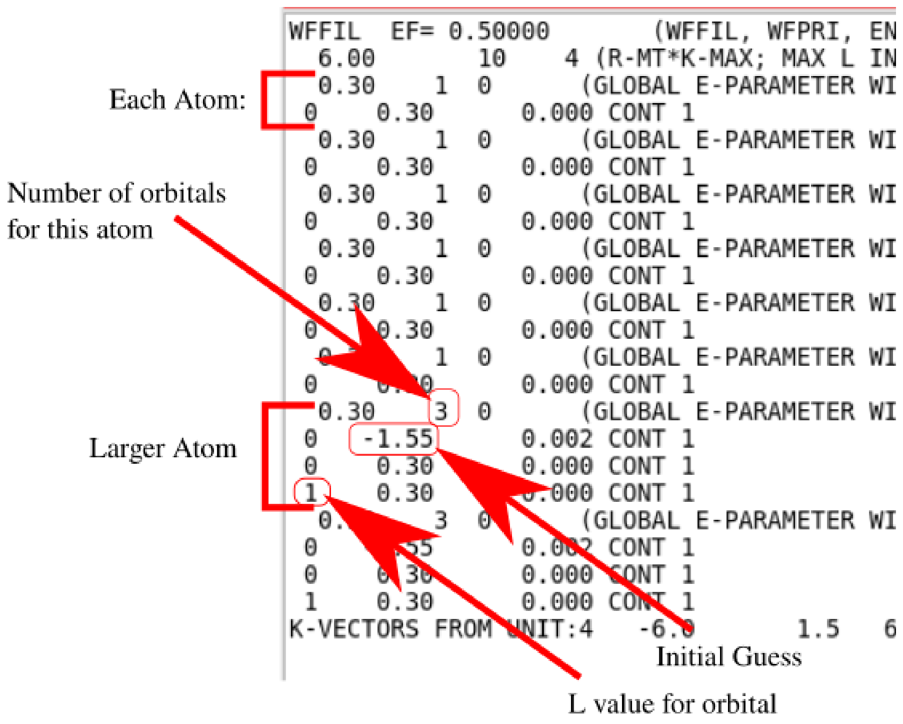
Ghostbands are arise in a number of situations, each of which requires a different solution. Some of these are described below:

- **Muffin Tins badly chosen:** These appear when the muffin tins are too different, or if you ignore everything that **setrmt** does. **Solution:** Diagnose this by running the calculation with the **setrmt** values (might need to remove the core hole) or make the muffin tins more reasonable (might need to allow core leakage).

- **Local Orbitals need better initial guess:** Sometimes the starting points for local orbitals are not close enough to the converged values resulting in divergence. **Solutions:** Figure out which orbitals are causing the issue by looking in case.scf2(_n). The last lines of these files should have a line like this:

  :WARN : QTL-B value eq. 99.95 in Band of energy −0.12674 ATOM= 2 L= 0

  This message also tells us to look in case.in1(_st) and that the problem is with atom 2 and the L=0 orbital. In case.in1(_st), every independent atom is listed, eg:



```
WFFIL  EF= 0.50000       (WFFIL, WFPRI, EN
 6.00        10    4 (R-MT*K-MAX; MAX L IN
 0.30    1  0      (GLOBAL E-PARAMETER WI
0    0.30      0.000 CONT 1
 0.30    1  0      (GLOBAL E-PARAMETER WI
0    0.30      0.000 CONT 1
 0.30    1  0      (GLOBAL E-PARAMETER WI
0    0.30      0.000 CONT 1
 0.30    1  0      (GLOBAL E-PARAMETER WI
0    0.30      0.000 CONT 1
 0.30    1  0      (GLOBAL E-PARAMETER WI
0    0.30      0.000 CONT 1
 0.30    1  0      (GLOBAL E-PARAMETER WI
0    0.30      0.000 CONT 1
 0.30    3  0      (GLOBAL E-PARAMETER WI
0   -1.55      0.002 CONT 1
0    0.30      0.000 CONT 1
1    0.30      0.000 CONT 1
 0.30    3  0      (GLOBAL E-PARAMETER WI
0   -1.55      0.002 CONT 1
0    0.30      0.000 CONT 1
1    0.30      0.000 CONT 1
K-VECTORS FROM UNIT:4   -6.0       1.5    6
```

  To handle ghostbands, either delete the relevant local orbital line (lines that match the atom and orbital number with energy guesses that are not 0.30) and reduce the number of orbitals for that atom correspondingly. A more refined option is to adjust the initial guesses to another value, and rerunning **run_lapw**.

9.3 NN in Optimization

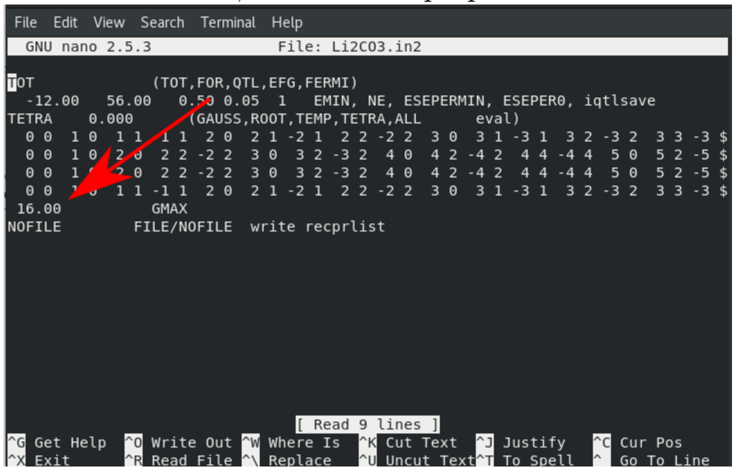
Crashes the first scf cycle almost immediately, due to overlapping muffin tins resulting from a decreased cell size. Solution: decrease all muffin tin sizes before running “x optimize”.

9.4 NR and NT

Before considering a spectra as final, it is important to verify that it is converged with respect to the Q mesh as well. The Q mesh defines which changes in momentum are collectable by the detector. More information on exactly how the mesh is determined can be found in the Telnes section of the userguide. To test convergence, increase these values from NR=5, and NT=2 to larger values, (eg. 7,3), rerun telnes(qtl and telnes3) and make sure that the fine structure does not change.

9.5 GMax Value less than Gmin

Occurs in **dstart**, fix is to bump up the Gmax value in case.in2 from 12.00 to 14.00 or 16.00.



```
  GNU nano 2.5.3                File: Li2CO3.in2

TOT             (TOT,FOR,QTL,EFG,FERMI)
  -12.00   56.00   0.50 0.05  1   EMIN, NE, ESEPERMIN, ESEPER0, iqtlsave
TETRA    0.000       (GAUSS,ROOT,TEMP,TETRA,ALL      eval)
  0 0  1 0  1 1  1 1  2 0  2 1 -2 1  2 2 -2 2  3 0  3 1 -3 1  3 2 -3 2  3 3 -3 $
  0 0  1 0  2 0  2 2 -2 2  3 0  3 2 -3 2  4 0  4 2 -4 2  4 4 -4 4  5 0  5 2 -5 $
  0 0  1 0  2 0  2 2 -2 2  3 0  3 2 -3 2  4 0  4 2 -4 2  4 4 -4 4  5 0  5 2 -5 $
  0 0  1 0  1 1 -1 1  2 0  2 1 -2 1  2 2 -2 2  3 0  3 1 -3 1  3 2 -3 2  3 3 -3 $
 16.00          GMAX
NOFILE        FILE/NOFILE  write recprlist




                          [ Read 9 lines ]
^G Get Help   ^O Write Out  ^W Where Is   ^K Cut Text   ^J Justify    ^C Cur Pos
^X Exit       ^R Read File  ^\ Replace    ^U Uncut Text ^T To Spell   ^  Go To Line
```

9.6 Ordering

If a calculation run apparently unchanged, a possible reason is that all the edits were overwritten by **init_lapw**. The order of a calculation should be:

- Make edits to case.struct file, ie. Muffin Tin Radius
- run **init_lapw**
- Edit .in files. eg. setting RKMax, dealing with ghostbands, inserting core hole, increasing k points...
- **run_lapw**
- Increase Kpoints, run case specific calculations, and/or loop back to and run forwards from there (ie increasing k points/RKMax does not require rerunning **init_lapw**, but changing muffin tin radii does).