Calculation for XANES and XAFS: Part II. Density Functional Theory

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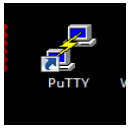
Sham's Group Meeting (Nov. 6, 2013)

WIEN2k

- Density Functional Theory:
  - Computer code (wien2k)
    - Local Density Approximation.
    - Generalized Gradient Approximation.
    - MBJ (Modified Becke-Johnson) exchange potential.
- http://www.wien2k.at/

- Login Workstations: use putty.
  - http://www.uwo.ca/its/sitelicense/putty/index.html



- File transfer: use winscp.
  - http://www.uwo.ca/its/sitelicense/WinSCP/index.html

- View postscript files: use ghostsview.

http://gsview.soft32.com/

Computer Servers

- Workstations:
  - Duxeon.chem.uwo.ca
    - 129.100.60.115
  - xeony.chem.uwo.ca
    - 129.100.60.33
  - Dualo_III.chem.uwo.ca
    - 129.100.61.183

- http://129.100.60.115:1234
- http://129.100.60.33:1234
- http://129.100.61.183:7890
  - **Usersguide**
    html-Version
    pdf-Version

Density Functional Theory

- Kohn-Sham's Equation:

$$E = T[n] + \int v(r)n(r)d^3r + \iint \frac{n(r)n(r')}{|r-r'|}d^3rd^3r' + E_{xc}[n]$$

where

- T[n] is the kinetic energy functional of a system of N electrons,
- v[r] is the potential,
- n[r] is the density,
- and Exc[n] is the exchange and correlation energy functional of an interacting system with density n[r].

Self-consistent Generalized Gradient

- The exchange-correlation energy is given by: $E_{xc}(r) = \int e_{xc}(r) n d^3 r + \int e_{xc}{}^{GGA}(n, \nabla n) d^3 r + \ldots.$
- Energy Minimization $\frac{\delta E(n)}{\delta n} = 0, \forall Z = Const.$
- Where $Z = \int n(r) d^3 r$ and $n = \int \psi^*(r) \psi(r) d^3 r$

Full Potential Augmented Plane Wave Method

$$\varphi_{k_n} = \sum_{lm} [\, A_{lm}\, u_l(r, E_l) + B_{lm} \frac{\partial u_l(r, E_l)}{\partial r}]\, Y_{lm}(r), \forall r \in S$$

$$\varphi_{k_n} = \frac{1}{\sqrt{\omega}} e^{ik_n r}, \forall r \notin S$$

where $k_n = k + K_n$,
k is the wave vector in 1st Brillouin Zone,
K_n is the reciprocal lattice vectors.

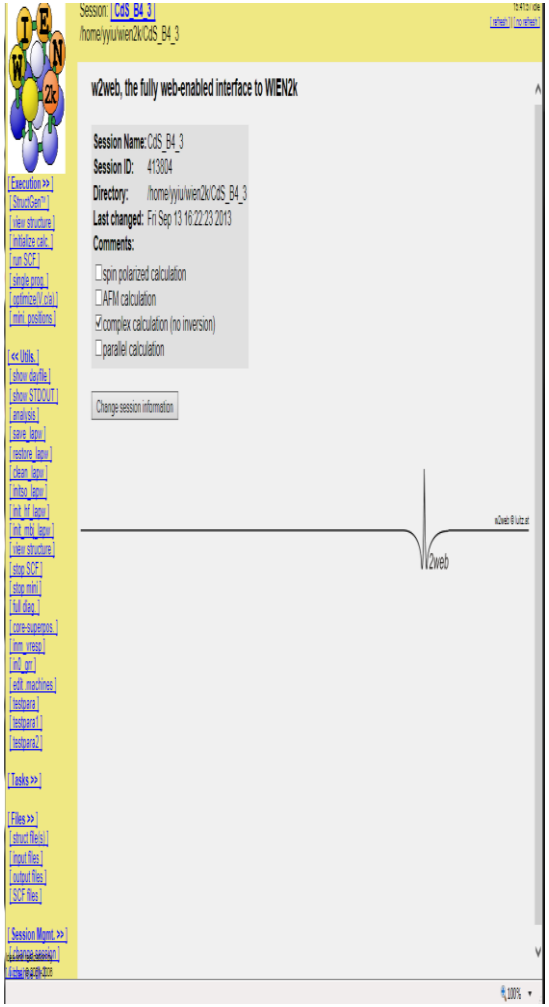
Boundary Conditions:

$$\varphi_{k_n}(S)\big|_{r_s} = \varphi_{k_n}(I)\big|_{r_s}$$ **and**

$$\frac{\partial \varphi_{k_n}(S)}{\partial r}\Big|_{r_s} = \frac{\partial \varphi_{k_n}(I)}{\partial r}\Big|_{r_s}$$

Wien2k: Procedures

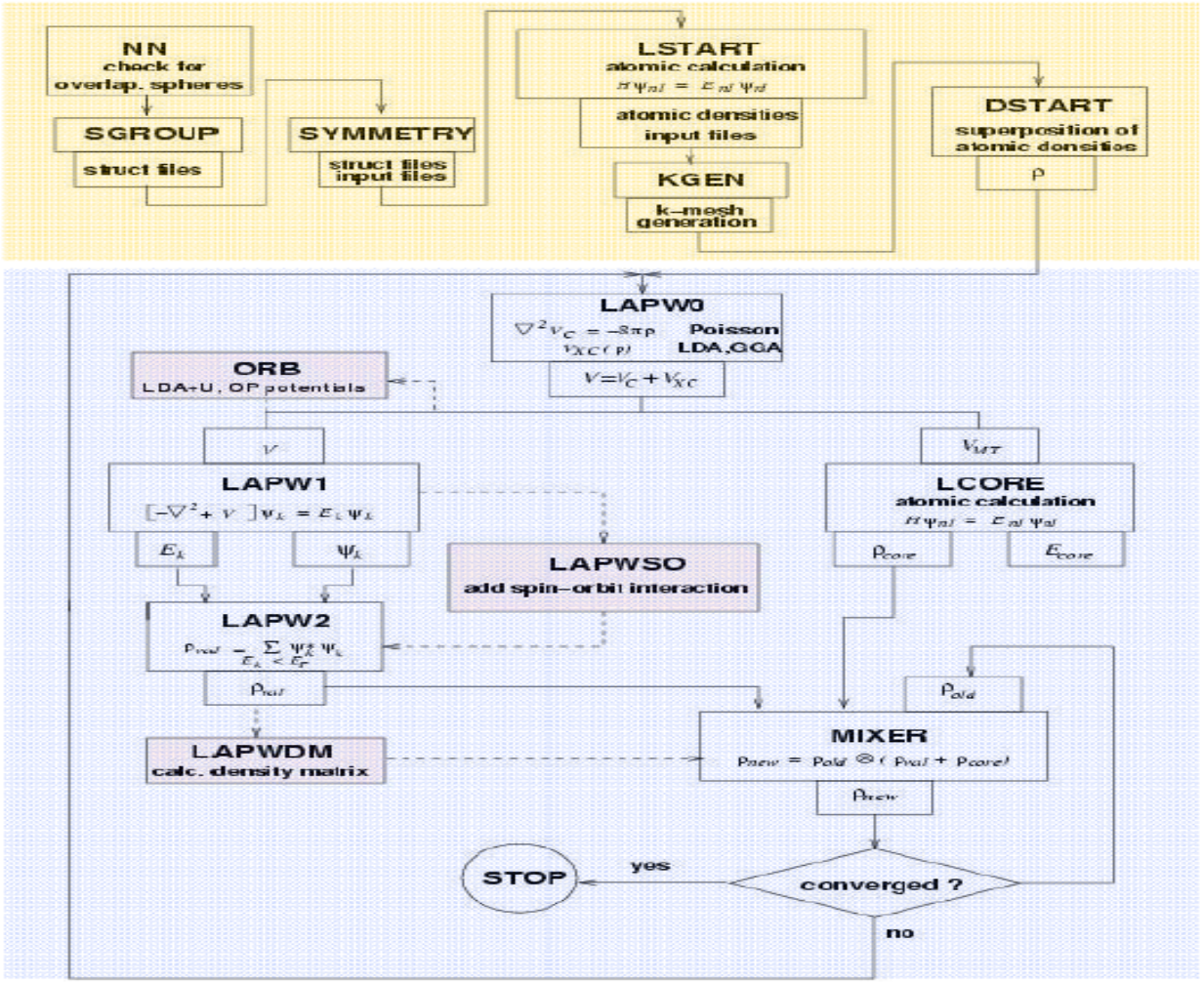
- 1. Structure Generation.
- 2. Initialize Calculation:
  - x nn
  - x sgroup
  - x symmetry
  - x lstart
  - x xkgen (1000 k points)
  - x dstart
- 3. Run scf.
- 4. Calculation of Properties.



Flaw Chart of wien2k

Initialization

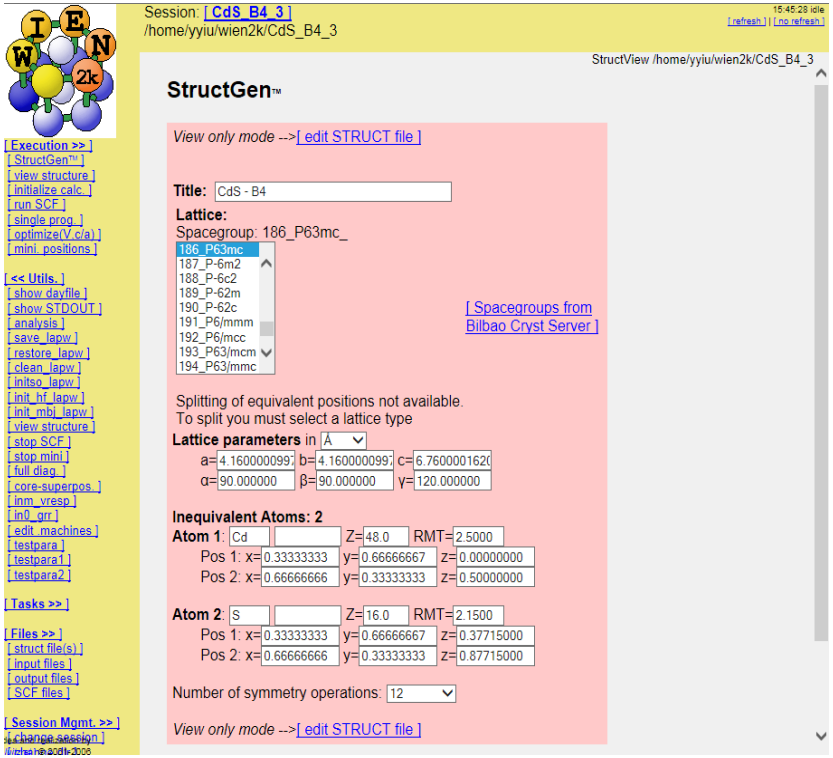
SCF

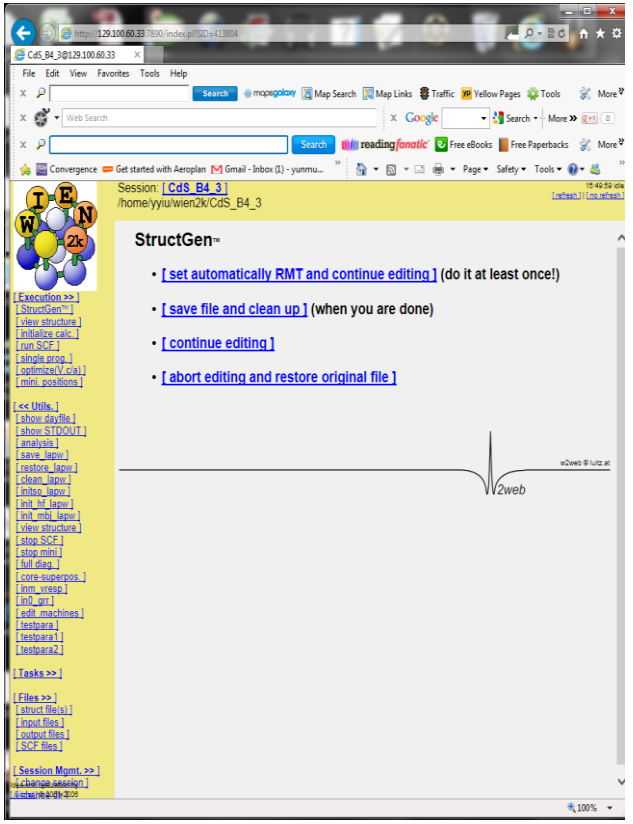


Structure Generation

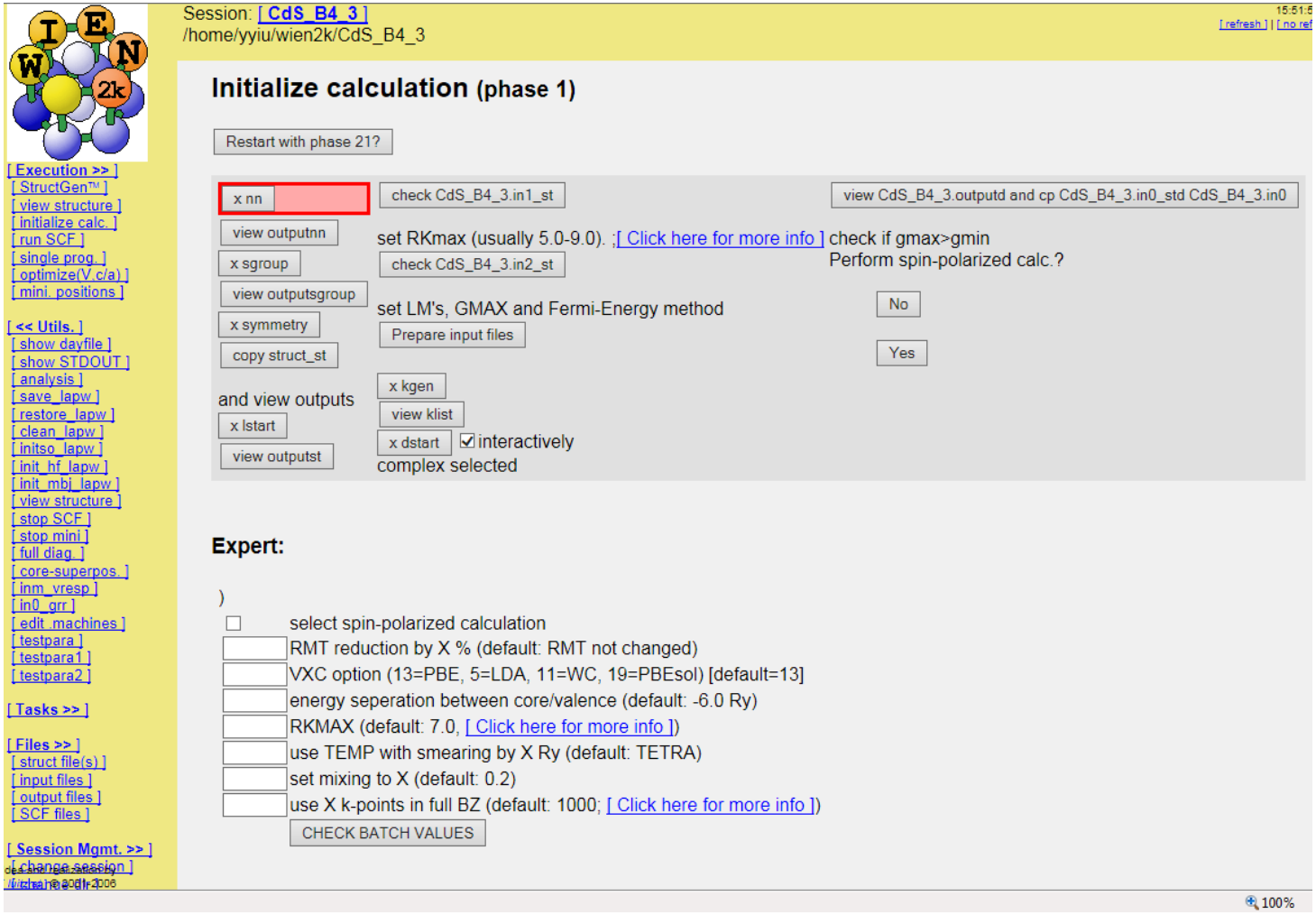
1. Use .cif file to generate case.struct file:
   cif2struct
2. Use case.struct: need space group symmetry.

Save StructGen



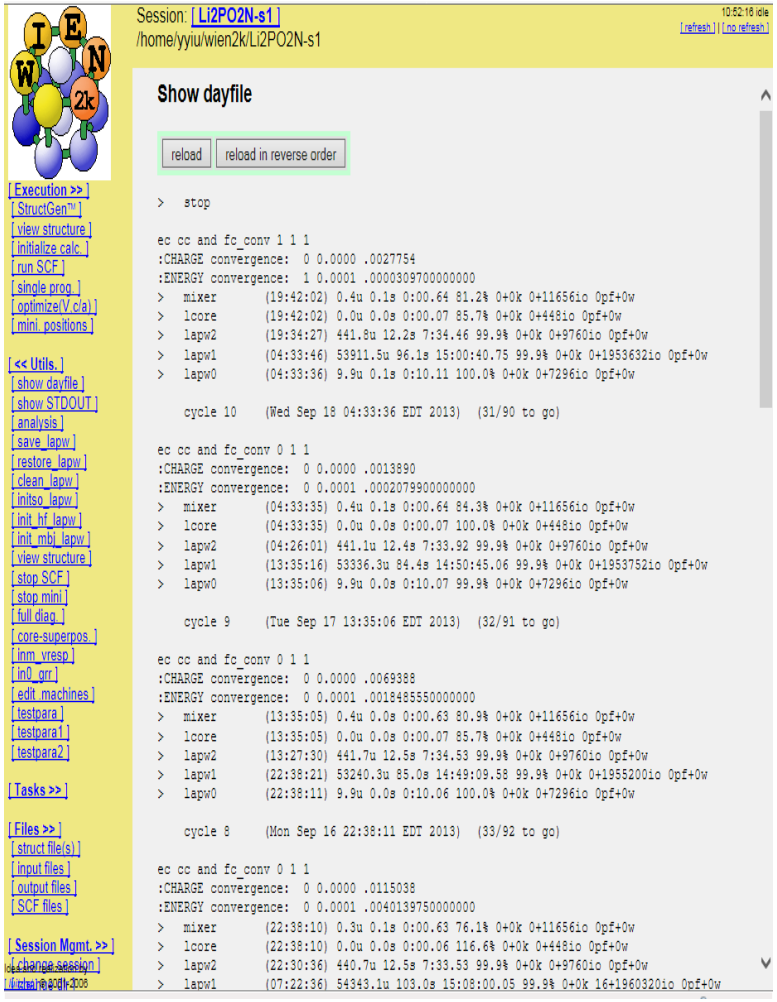


Initialize Calculation

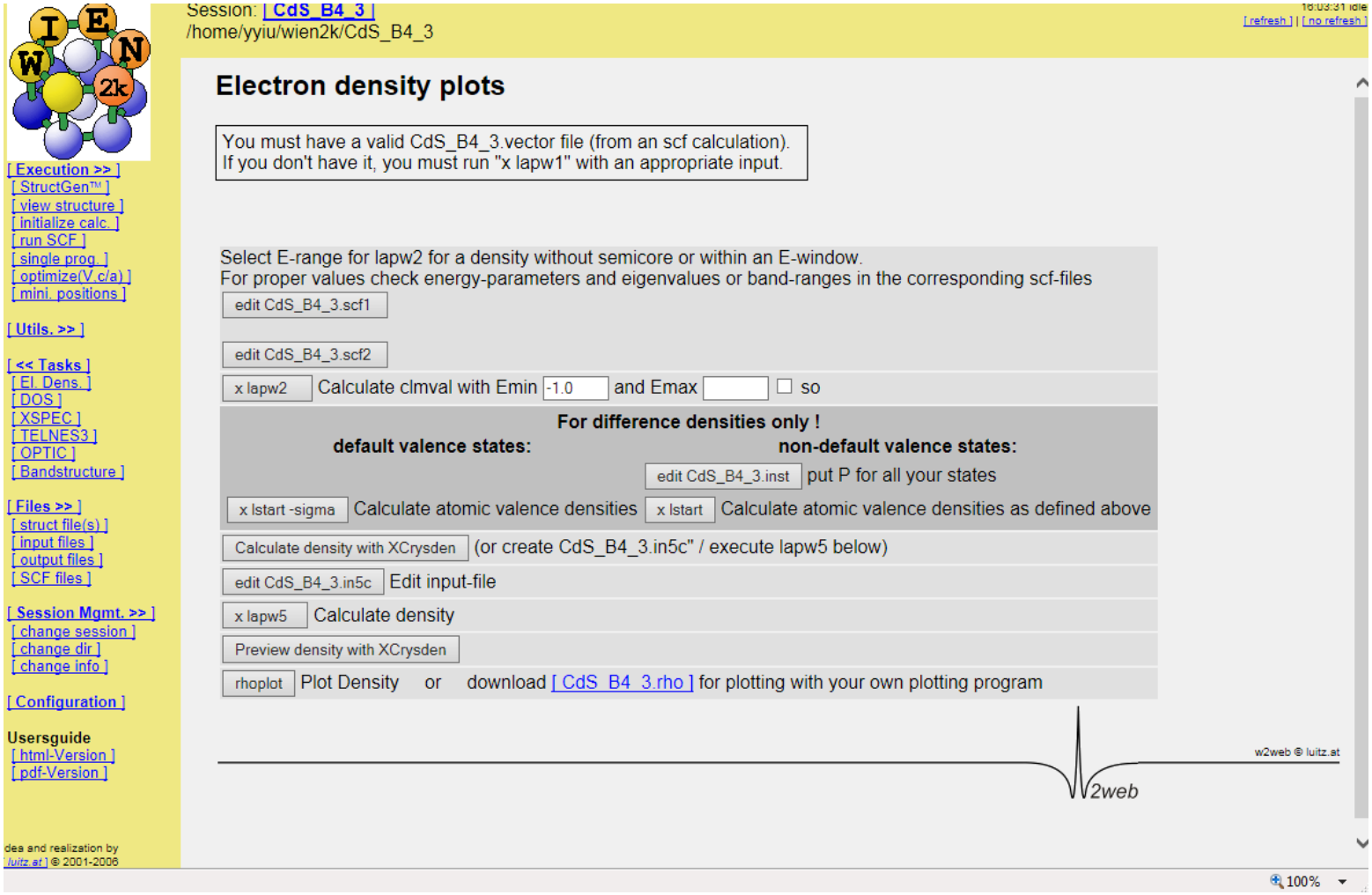


SCF (Self-consistent Field)

- The SCF cycle consists of the following steps:
  - **LAPW0** (POTENTIAL) generates potential from density
  - **LAPW1** (BANDS) calculates valence bands (eigen-values and eigenvectors)
  - **LAPW2** (RHO) computes valence densities from eigenvectors
  - **LCORE** computes core states and densities
  - **MIXER** mixes input and output densities

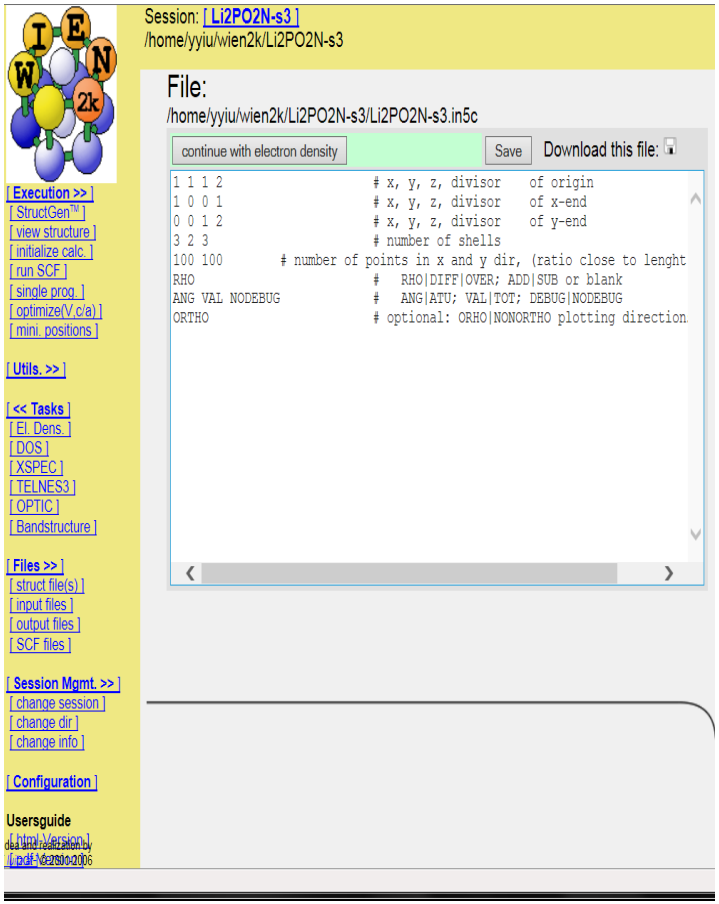


Electron density plots

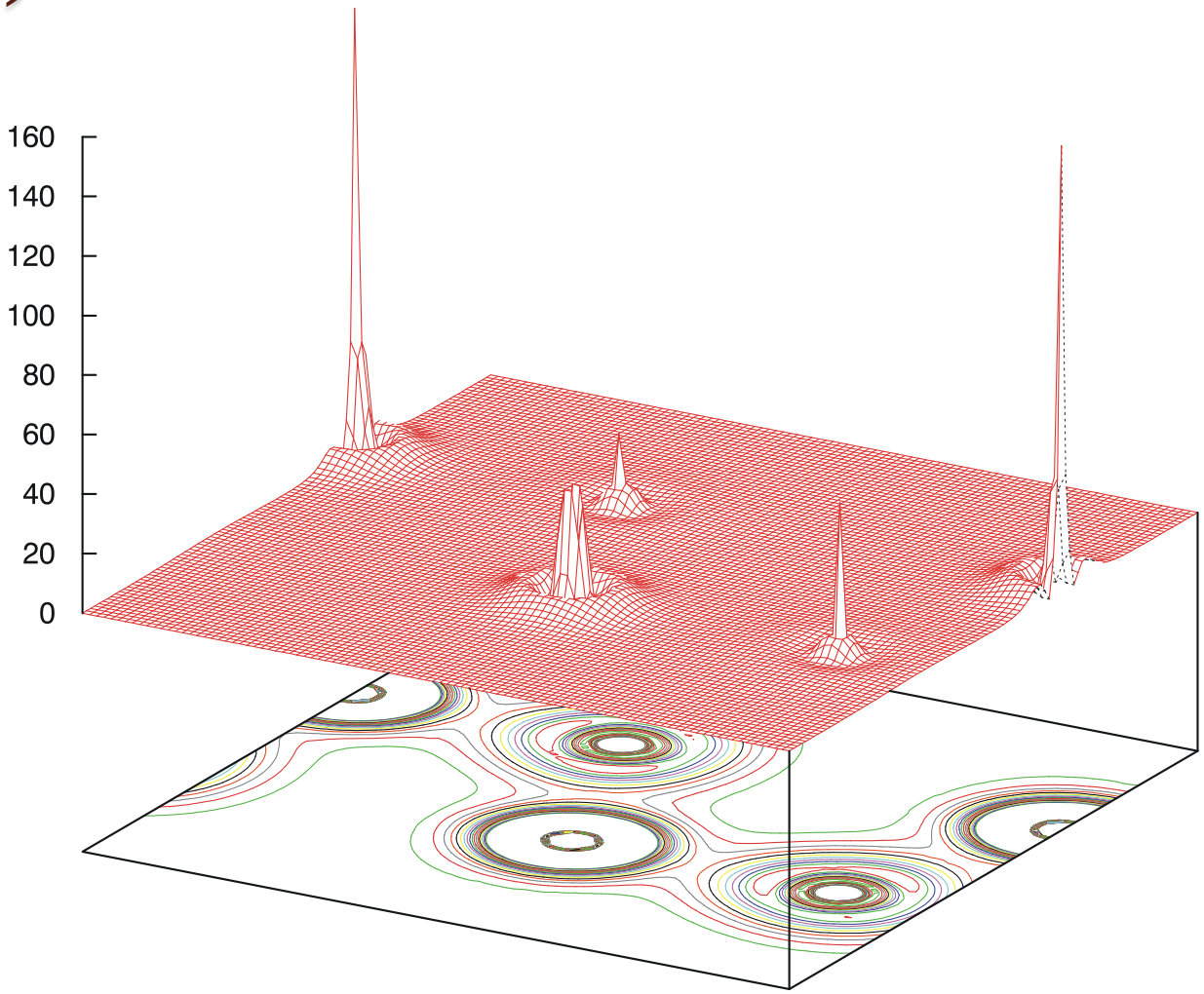


case.in5

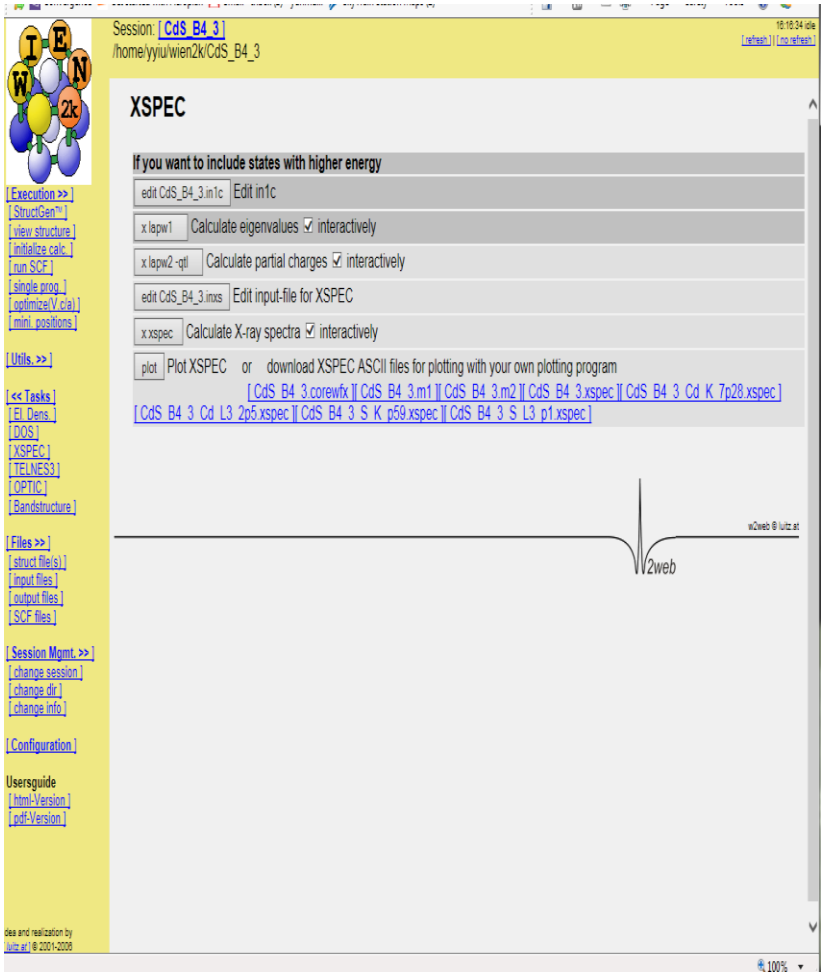
- Direction: [100]
  - 1 0 0 1
  - 1 1 0 1
  - 1 0 1 1
- Direction: [110]
  - 1 0 0 1
  - 0 1 0 1
  - 1 0 1 1
- Direction: [111]
  - 1 1 1 2
  - 1 0 0 1
  - 0 0 1 2



Electron density of CdS_B4 (plane 111)



XSPEC: XANES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/home/yyiu/wien2k/CdS_B4_3
XSPEC
If you want to include states with higher energy
edit CdS_B4_3.in1c Edit in1c
x lapw1 Calculate eigenvalues ☑ interactively
x lapw2 -qtl Calculate partial charges ☑ interactively
edit CdS_B4_3.inxs Edit input-file for XSPEC
x xspec Calculate X-ray spectra ☑ interactively
plot Plot XSPEC or download XSPEC ASCII files for plotting with your own plotting program
[CdS_B4_3.corewfx][CdS_B4_3.m1][CdS_B4_3.m2][CdS_B4_3.xspec][CdS_B4_3_Cd_K_7p28.xspec]
[CdS_B4_3_Cd_L3_2p5.xspec][CdS_B4_3_S_K_p59.xspec][CdS_B4_3_S_L3_p1.xspec]
[Execution >>]
[StructGen™]
[view structure]
[initialize calc.]
[run SCF]
[single prog.]
[optimize(V,c/a)]
[mini. positions]
[Utils. >>]
[<< Tasks]
[El. Dens.]
[DOS]
[XSPEC]
[TELNES3]
[OPTIC]
[Bandstructure]
[Files >>]
[struct file(s)]
[input files]
[output files]
[SCF files]
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[change session]
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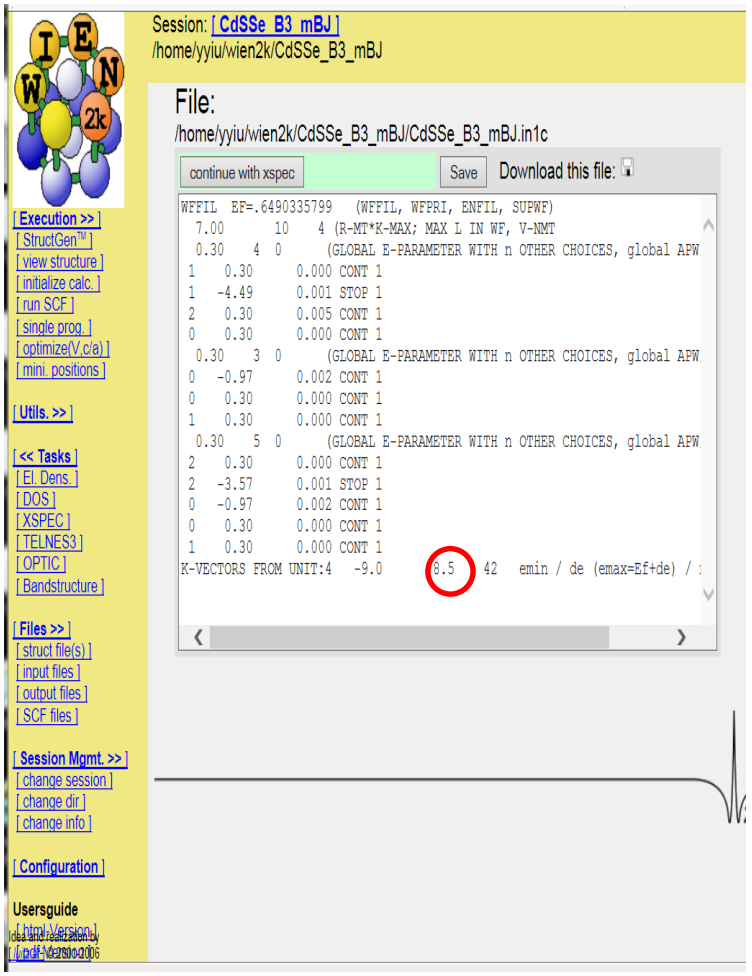
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/home/yyiu/wien2k/CdSSe_B3_mBJ
File:
/home/yyiu/wien2k/CdSSe_B3_mBJ/CdSSe_B3_mBJ.in1c
continue with xspec
Save
Download this file:
WFFIL EF=.6490335799 (WFFIL, WFPRI, ENFIL, SUPWF)
7.00 10 4 (R-MT*K-MAX; MAX L IN WF, V-NMT
0.30 4 0 (GLOBAL E-PARAMETER WITH n OTHER CHOICES, global APW
1 0.30 0.000 CONT 1
1 -4.49 0.001 STOP 1
2 0.30 0.005 CONT 1
0 0.30 0.000 CONT 1
0.30 3 0 (GLOBAL E-PARAMETER WITH n OTHER CHOICES, global APW
0 -0.97 0.002 CONT 1
0 0.30 0.000 CONT 1
1 0.30 0.000 CONT 1
0.30 5 0 (GLOBAL E-PARAMETER WITH n OTHER CHOICES, global APW
2 0.30 0.000 CONT 1
2 -3.57 0.001 STOP 1
0 -0.97 0.002 CONT 1
0 0.30 0.000 CONT 1
1 0.30 0.000 CONT 1
K-VECTORS FROM UNIT:4 -9.0 8.5 42 emin / de (emax=Ef+de) /
[Execution >>]
[StructGen™]
[view structure]
[initialize calc.]
[run SCF]
[single prog.]
[optimize(V,c/a)]
[mini. positions]
[Utils. >>]
[<< Tasks]
[El. Dens.]
[DOS]
[XSPEC]
[TELNES3]
[OPTIC]
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[Files >>]
[struct file(s)]
[input files]
[output files]
[SCF files]
[Session Mgmt. >>]
[change session]
[change dir]
[change info]
[Configuration]
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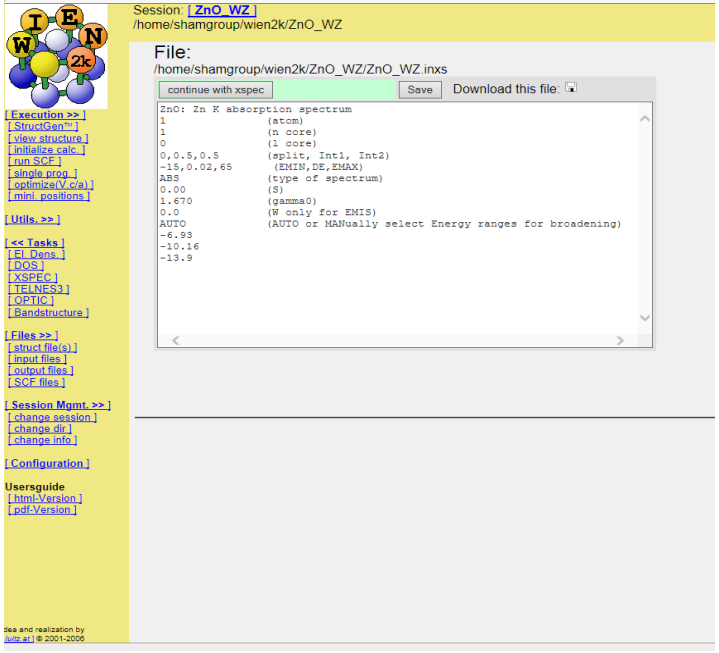
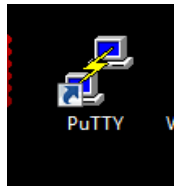
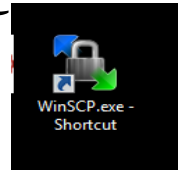
Download XANES Input and Output Files

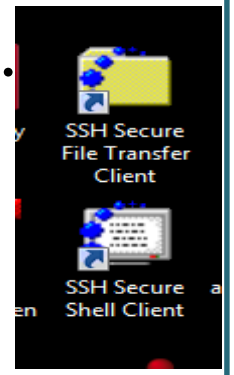
Input file: case.inxs
S (spectrometer broadening FWHM in eV);
gamma0 (broadening parameter for the life-time broadening of the core states);
W (broadening parameter for the life-time broadening of valence states).



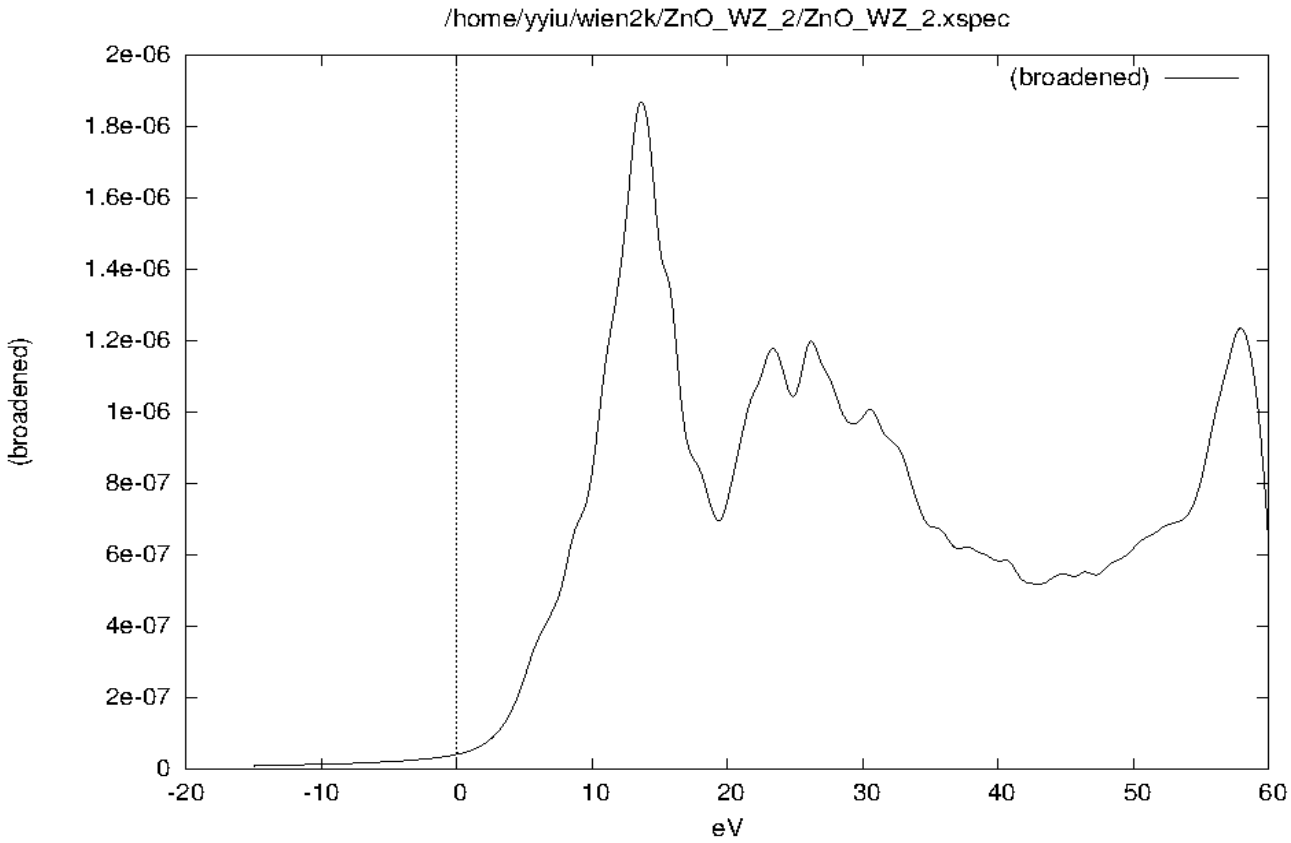
- Use putty to login:
  - cd wien2k/case
  - cp case.xspec case_atom_edge.xspec
- Use winscp for file transfer.
- Old login and file transfer: ssh shell.



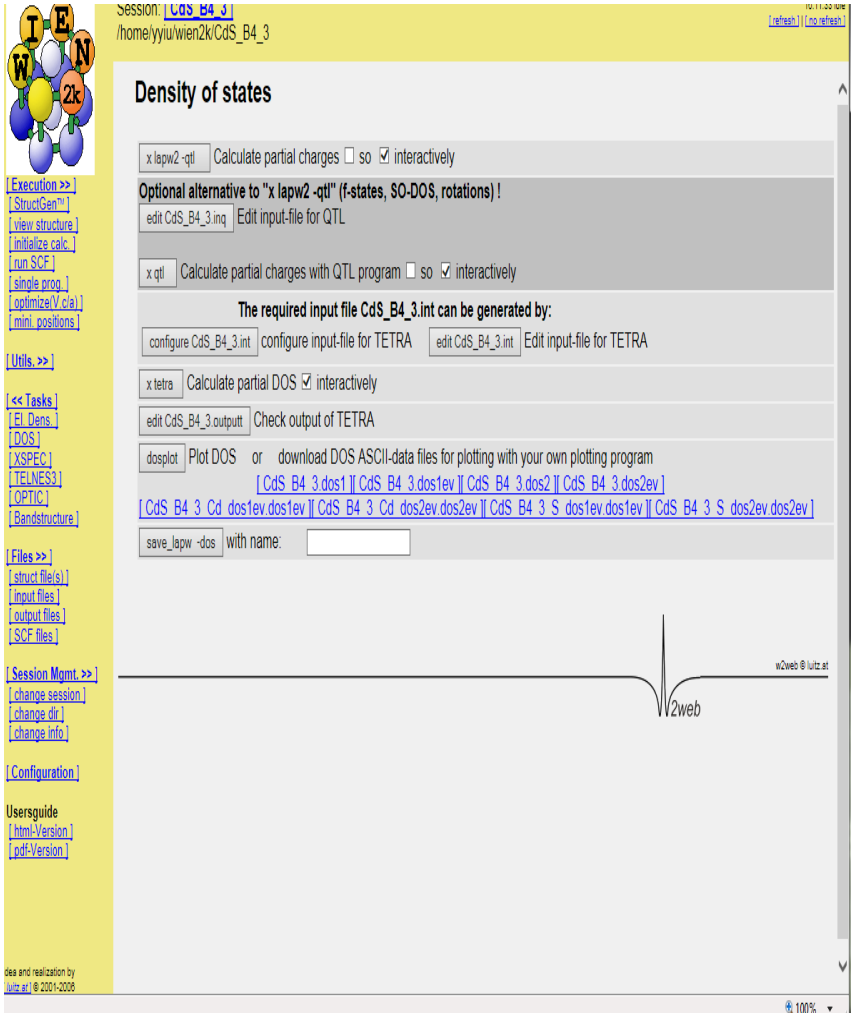


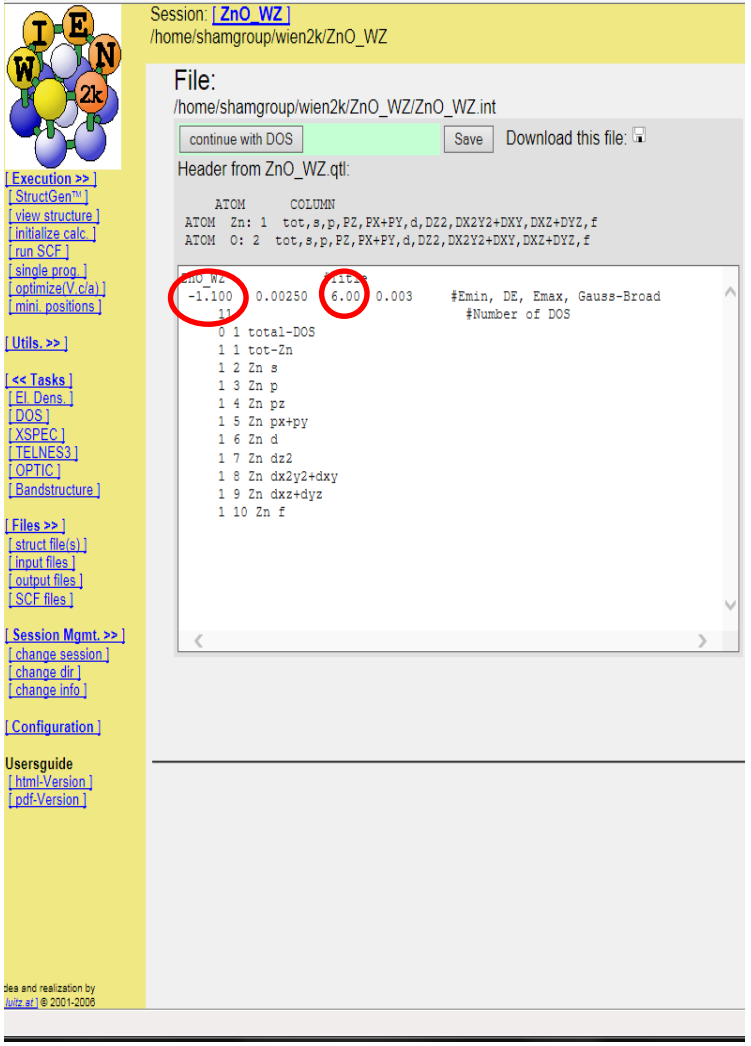


Zn K-edge of ZnO (WZ)

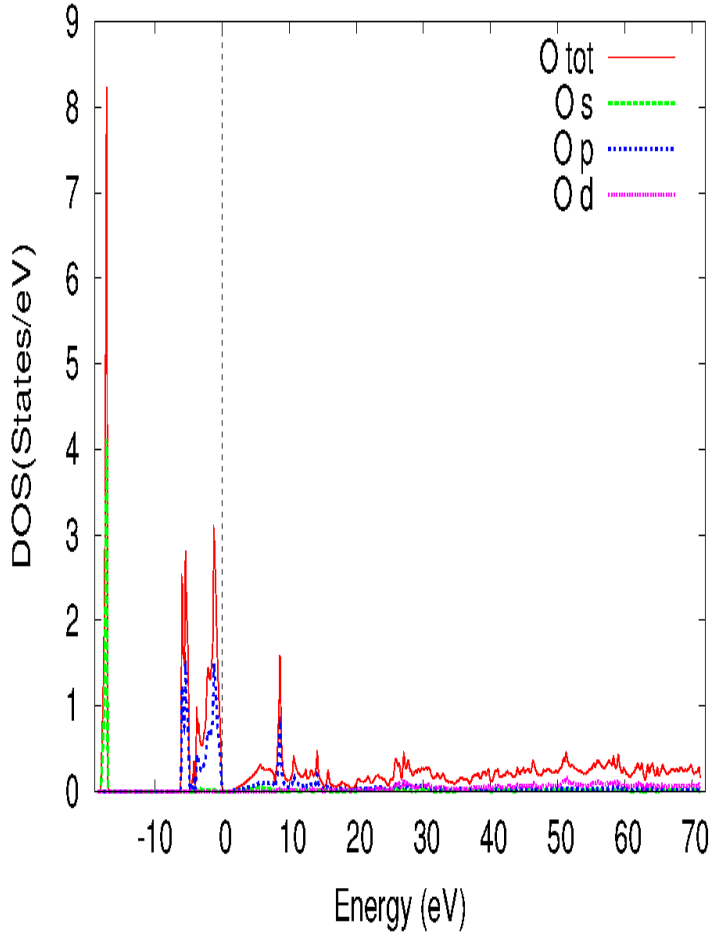


Density of States (DOS)



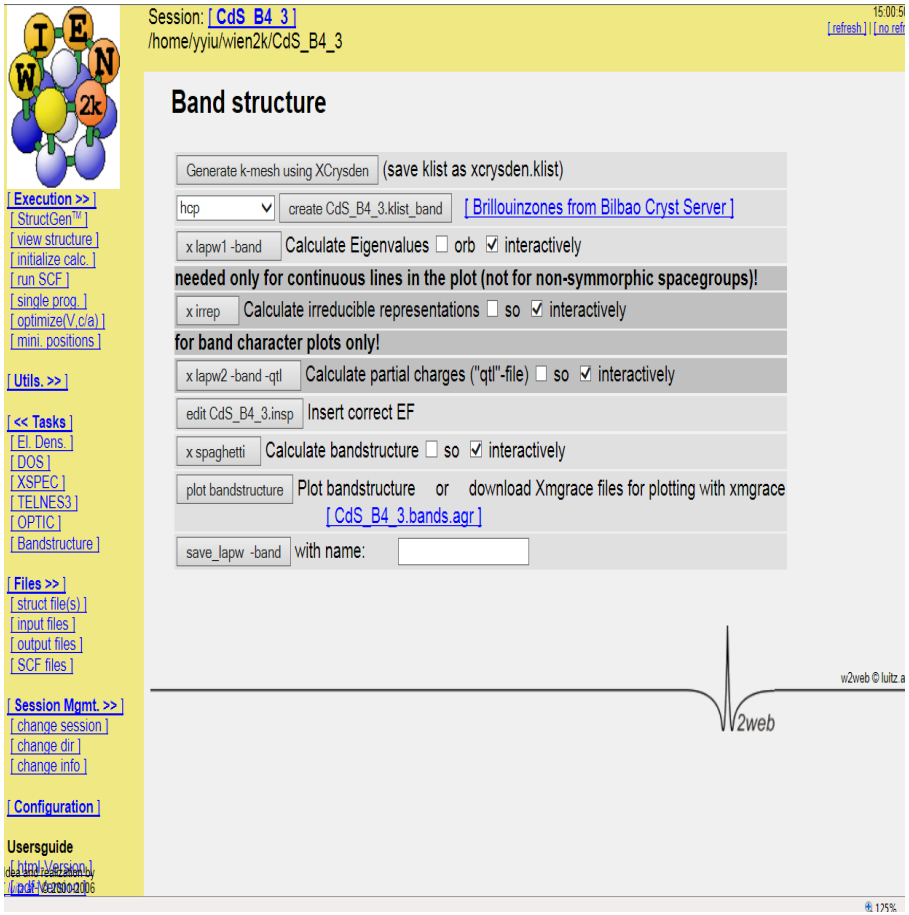


O Partial Density of States of ZnO (WZ)



- Rename DOS Output Files:
  - cd wien2k/case
  - cp case.dos1ev case_atom.dos1ev
  - cp case.dos2ev case_atom.dos2ev
- Download DOS Output Files.

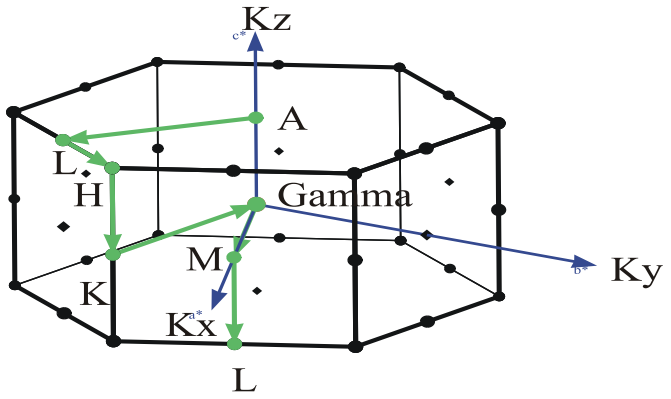
Band structure



- xcrysden plots: choose Brillouin Zone direction, and save as case.lpr.
- View file by ghostview or CorelDraw.

Primitive Brillouin Zone

CdS - B4



Band Structure Plot

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/home/yyiu/wien2k/CdS_B4_3

[Execution >>]
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[view structure]
[initialize calc.]
[run SCF]
[single prog.]
[optimize(V,c/a)]
[mini. positions]

[Utils. >>]

[Tasks >>]

[Files >>]
[struct file(s)]
[input files]
[output files]
[SCF files]

[Session Mgmt. >>]
[change session]
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[change info]

[Configuration]

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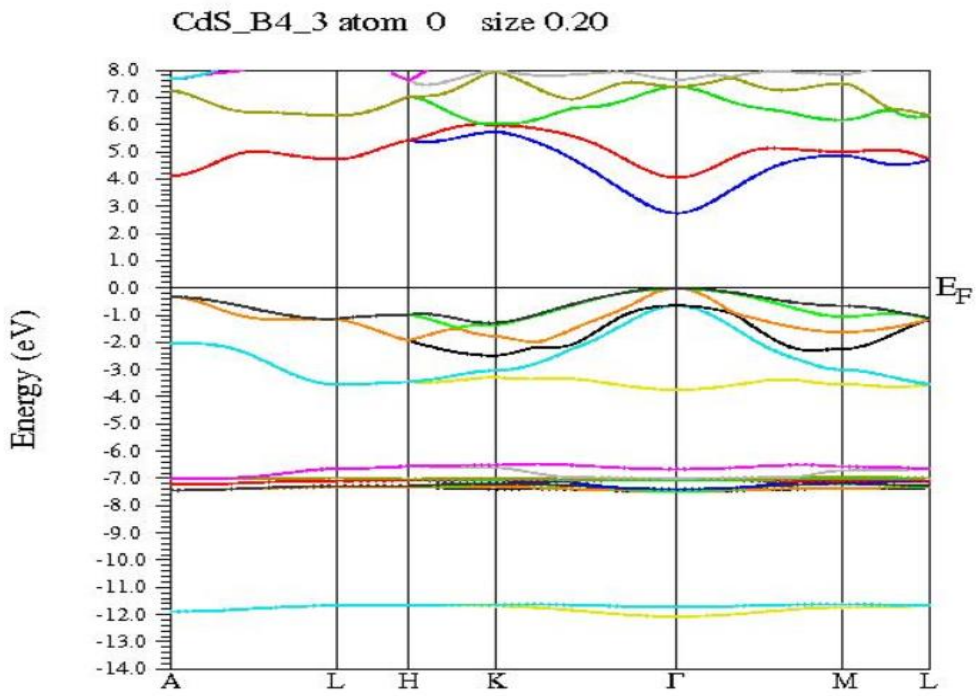
Idea and realization by
[luitz.at] © 2001-2006



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MBJ (Modified Becke-Johnson) exchange potential

- Modified B-J Potential:

$$v_{x,\sigma}^{MBJ}(\vec{r}) = cv_{x,\sigma}^{BR}(\vec{r}) + (3x-2)\frac{1}{\pi}\sqrt{\frac{5}{12}}\sqrt{\frac{2t_\sigma(\vec{r})}{\rho_\sigma(\vec{r})}}$$

$$\frac{xe^{-2x/3}}{x-2} = \frac{2}{3}\pi^{2/3}\rho_\sigma^{5/3}\left\{\frac{1}{6}\left(\nabla^2\rho_\sigma - 2\gamma\left[\sum_{i=1}^{\sigma}|\nabla\psi_i|^2 - \frac{(\nabla\rho_\sigma)^2}{4\rho_\sigma}\right]\right)\right\}^{-1}$$

$\gamma = 1$

- Becke-Roussel Potential

$$v_{x,\sigma}^{BR}(\vec{r}) = -\frac{1}{b_\sigma(\vec{r})}\left[1 - e^{-x_\sigma(\vec{r})} - \frac{1}{2}x_\sigma(\vec{r})e^{-x_\sigma(\vec{r})}\right]$$

  - where

$$b_\sigma = \left[\frac{x_\sigma^3 e^{-x_\sigma}}{8\pi\rho_\sigma}\right]^{1/3}$$

$$\rho_\sigma = \sum_{i=1}^{N_\sigma}|\psi_{i,\sigma}|^2$$

$$t_\sigma = \frac{1}{2}\sum_{i=1}^{N_\sigma}\vec{\nabla}\psi_{i,\sigma}^*\vec{\nabla}\psi_{i,\sigma}$$

$$c = A + B\left(\frac{1}{V_{cell}}\int_{cell}\frac{|\nabla\rho(\vec{r'})|}{\rho(\vec{r'})}d^3r'\right)^{1/2}$$

$A = -0.012$

$B = 1.023\ bohr^{1/2}$

MBJ (Modified Becke-Johnson) exchange potential SCF calculation

- run a regular initialization and SCF calculation using LDA or PBE.
- **init_mbj_lapw**:
  - **cp $WIENROOT/SRC_templates/template.inm_vresp case.inm_vresp**.
  - edit **case.in0** and set "R2V" option (instead of "NR2V") such that the XC potential is written in **case.r2v**.
- **run_lapw -NI -i 1:** to generate the required **case.r2v** and **case.vresp** files.
- "save" the LDA (or PBE) calculation.
- run **init_mbj_lapw** again:
  - edit **case.in0** and change the functional to option indxc=28 (this is mBJ).
  - **cp case.in0 case.in0_grr**
  - choose indxc=50 in **case.in0_grr**. This option will calculate the average of $\nabla\rho/\rho$ over the unit cell.
- edit **case.inm** and choose the PRATT mixing scheme. First use mixing factor (eg. 0.2 or 0.1).
- run the mBJ SCF calculation.
- run DOS properties.

Simple Commands for Unix or Linux

In x-window or use putty:

- top: list of the process, CTRl c to quit.
- cd: change directory.
- cp : copy file.
- vi filename: simple text editor.
  - esc (toggle between commands)
  - x (delete character)
  - dd (delete line)
  - i (insert)
  - ZZ (save file)
  - :q! (exit without saving file)
- emacs: text editor.
- Run command: . /run_lapw –NI –i 1
- When done:
  - cd wien2k
  - cp clean_lapw case/
  - cd case
  - ./clean_lapw
  - logout

Or use http:
Utils
clean_lapw

Summary

- Use wien2k program to calculate self-consistently:
  - Local Density Approximation.
  - Generalized Gradient Approximation.
  - MBJ (Modified Becke-Johnson) exchange potential:
    - Better band gap energy.
- Properties to be calculated:
  - Electron density: lapw5.
  - XANES: xspec.
  - DOS (Densities of States): tetra.
  - Band structure: spaghetti.

References

- N. F. M. Henry and K. Lonsdale: “International Tables For X-ray Crystallography”, Kynoch Press, (Birmingham, England), (1965).
- P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964);
- W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
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