connect/setup of w2web environment

- Connect to the Linux machines using mobaXterm as indicated in the instructions.
  - *w2web has already been started automatically and the buttons at the bottom of the screen allow you to connect to w2web (or start new command-windows (xterm)).*
  - *enter user-id/pw and you are connected to w2web. Start with the exercises.*

==================================

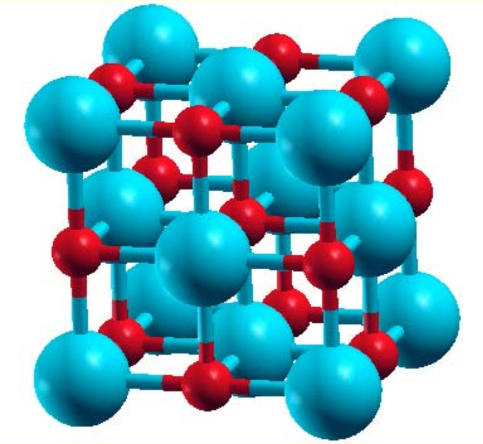
- General instructions for a default installation (at home):
  - *connect to the Linux machine and open a terminal window (usually via ssh (putty, …)*
  - *start w2web (w2web will continue to run until machine reboot or it gets killed explicitly)*
  - `w2web` *(at the **first** time you have to define your*
    - userid/pw,
    - port-number (use and remember a unique xxxx number).
    - Note: it will tell you the address and port to which you should connect via a web-browser
  - *connect to w2web via a webbrowser (firefox, internet explorer). This can also be done from a Windows machine, but xcrysden will not work unless you have a local X-server.*

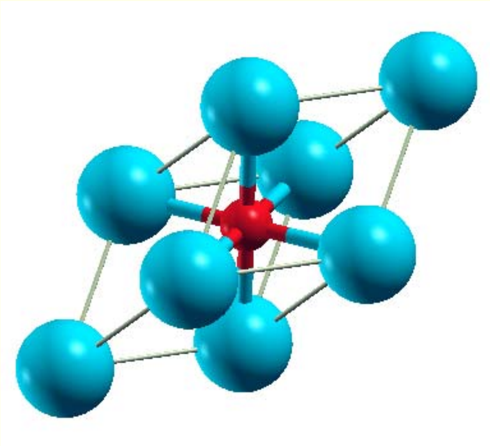
Exercises:

- In the following you find some suggestions for exercises, which teach you various tasks one may perform with WIEN2k.
- New WIEN2k users should start with the first basic exercises (1-4)
- Later on, choose examples of your interest as there are probably more exercises than you can do here.
- Please note, that often "calculational parameters" are set to "minimal cpu-time" instead of "fully converged calculations".
- Do not use such small values for final results and publications without convergence checks !!

Exercise 1: Getting started:

- i) Open a terminal window (skip points i-iii if done before)
- ii) Start w2web (accept all defaults, specify account, port)
- iii) Connect with firefox to w2web as indicated on the screen of ii)
- iv) Try the "quick-start" example for **TiN** (similar to TiC in the UG)
  - *create new session named "TiN", "create" and "select" the suggested directory.*
  - *Generate structure (a=4.235 Ang; reduce RMT by 1%)*
  - *view structure with Xcrysden (switch primitive / conventional cell)*

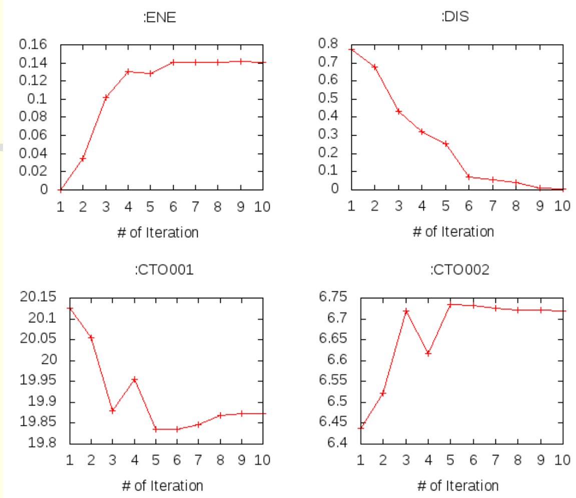




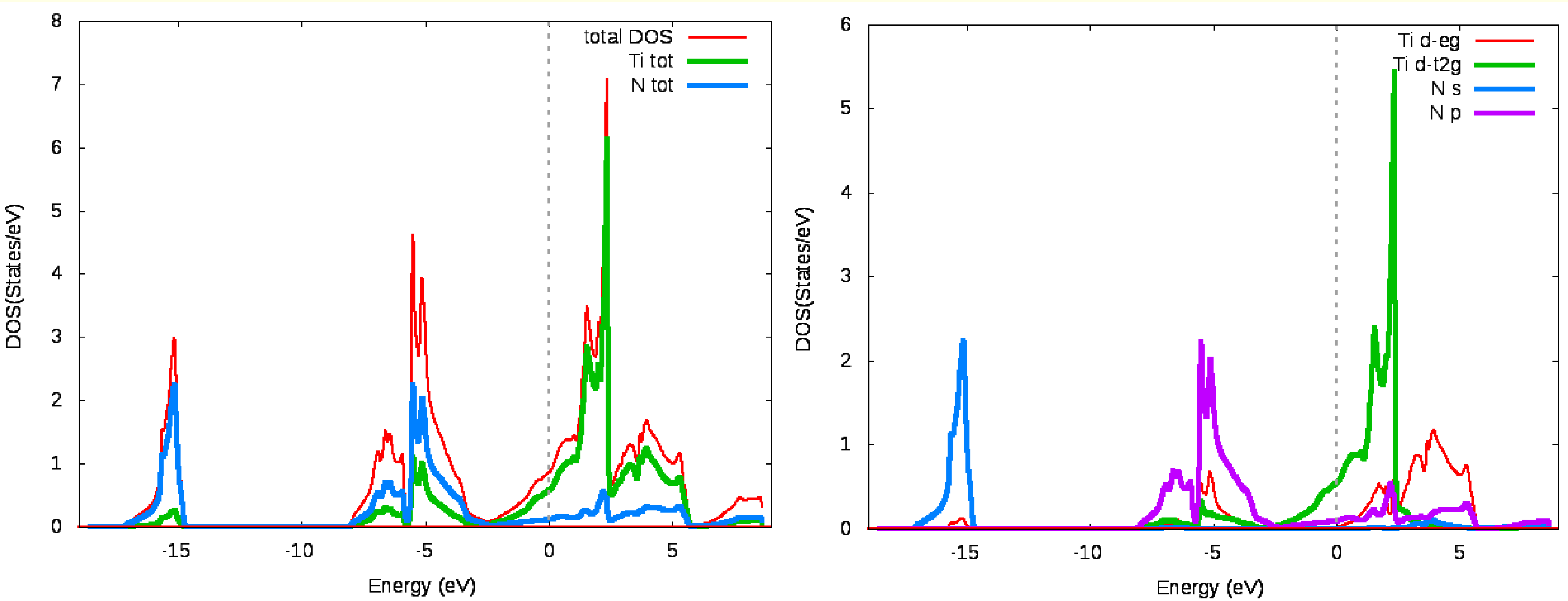
  - *initialize (init_lapw -b); use defaults*
  - *scf-cycle (run_lapw); use defaults; monitor "STDOUT" and "dayfile"*
    - How many iterations did you need ? How long took a single scf-iteration ?

TiN continued

- *utilities: analyse*
  - (:ENE, :DIS, :CTO) graphically



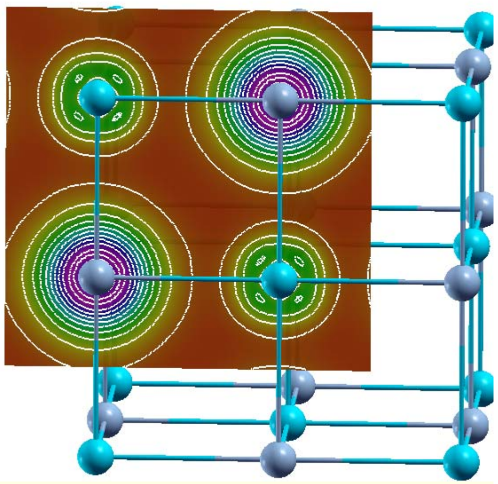
- *utilities: save_lapw (use as save-name: "TiN_exp_pbe_rk7_1000k")*
- *DOS (plot 7 cases: total + Ti-tot + N-tot and Ti-eg + Ti-t2g + N-s + N-p)*



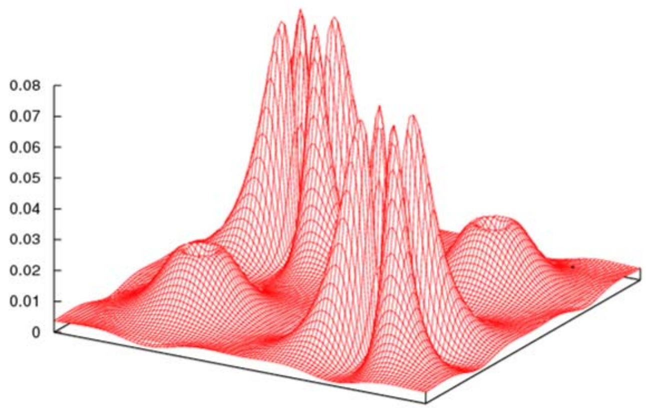
TiN continued …

- *electron density (use xcrysden to select the (100) plane), view it in xcrysden and rhoplot to "understand contour and 3D-plots")*
  - valence density (without semicore, check TiN.scf1 to find a EMIN which truncates the Ti-3s,3p states); compare the density around Ti with TiC (UG)
  - difference density (observe "charge transfer" and "t_{2g}-anisotropy" around Ti)
  - densities of the "N-p" and "occupied Ti-d-band" (get the corresponding E-intervals from DOS-plots (in Ry!) and use these energies in the "x lapw2" step; observe the e_g and t_{2g} asymmetry around Ti and the different N-p "weights", explain the chemical bonding

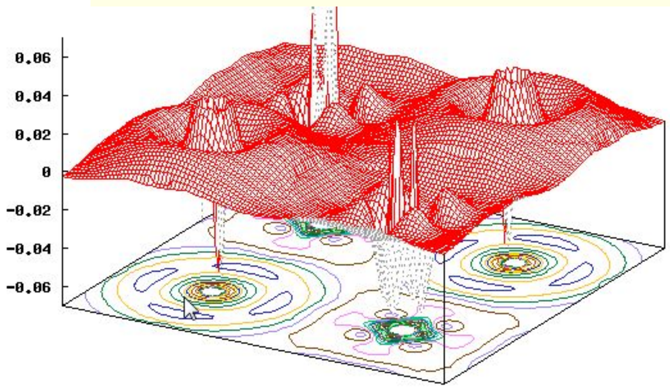
valence ρ



Ti-d band

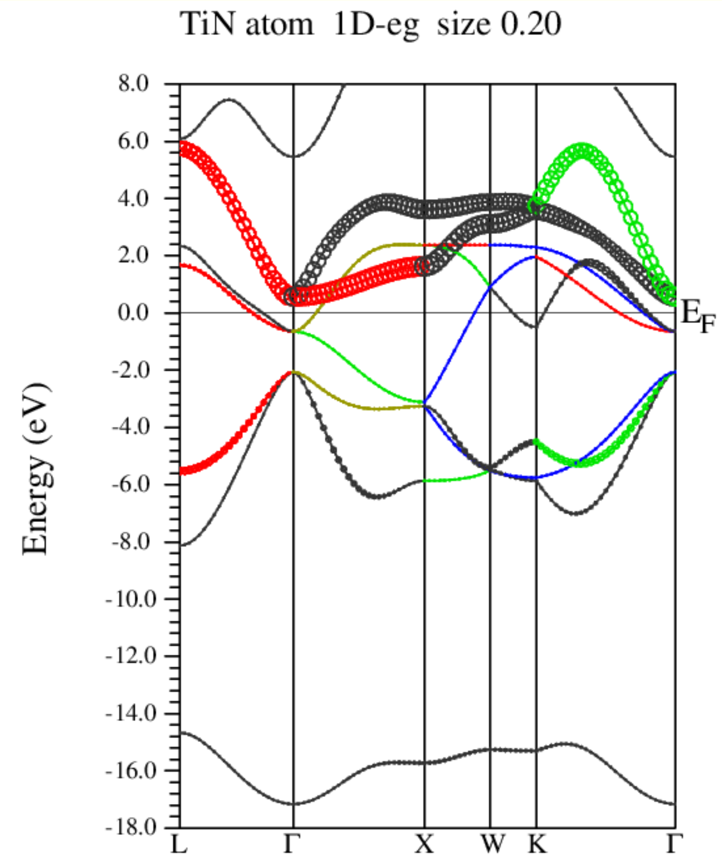


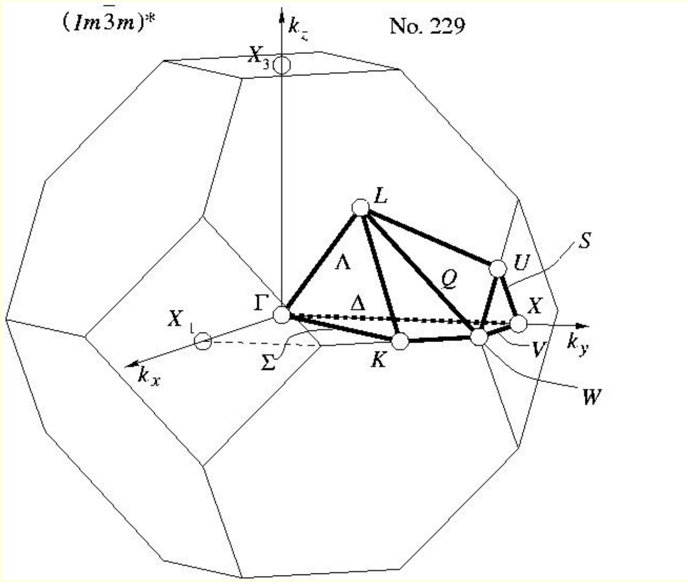
difference density



TiN continued

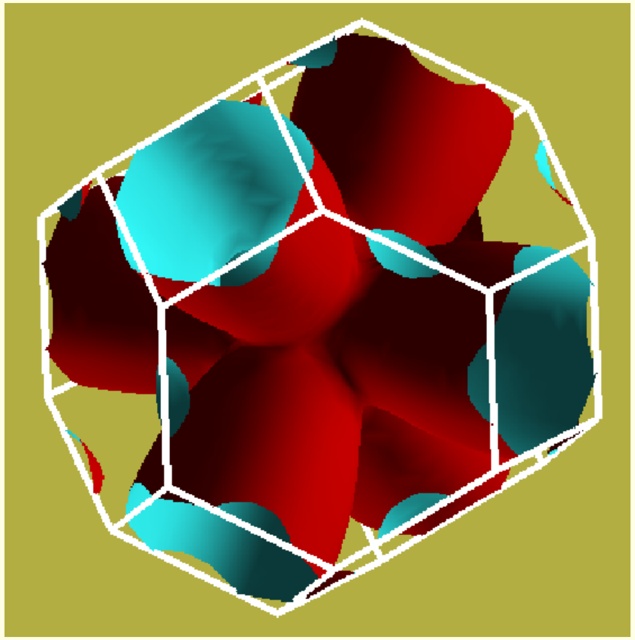
- bandstructure (along L-Gamma-X-W-K-Gamma with "character plotting")
  - *use xcrysden (save as „xcrysden.klist"; select „from xcrysden" in next step and click generate k-mesh)*
  - *identify "t2g-" and "eg-" bands (fat band plots)*





TiN continued …

- *Fermi surfaces*
  - open a terminal, change into the TiN directory and issue:
  - **`xcrysden --wien_fermisurface .`**
    - choose a good k-mesh (eg. 10000 points);
    - plot the FS for all bands (**9**, 10,11) which cross E_F and compare to band structure



Exercises 2: lattice parameter of TiC
Testing accuracy: RKmax and k-points

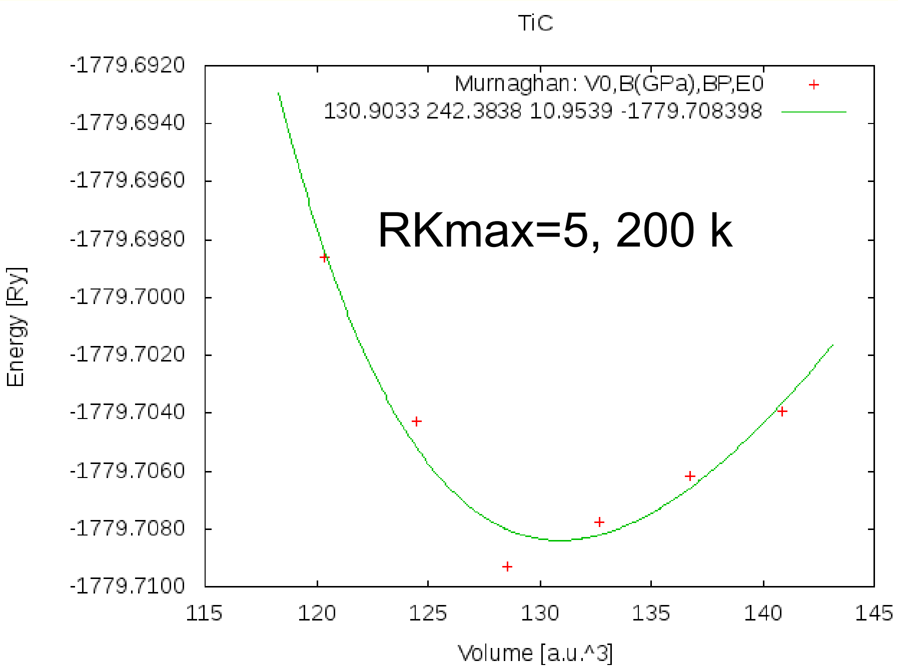
- TiC (fcc, **a=4.328** Ang, **setrmt 4%**)
- a) initialize in expert mode with **LDA, RKmax=5, 200 k-points** (bad values, on purpose !!)
- b) run x optimize and generate 6 structures (-12, -9, -6, -3, 0, 3% volume change)
  - *(because of LDA we expect 1-2% smaller lattice parameter (3-8% in volume) than experiment)*
- c) edit "optimize.job". Modify the “run_lapw” and "save_lapw" commands to:
  - *run_lapw –cc 0.001 –ec 0.00001*
  - *save_lapw ${i}_default_rkm5_200k*
- d) run optimize.job, plot the results (using *rkm5_200k)
- e) set **RKMAX=6.5** in TiC.in1 and x kgen with **1000k**
- f) edit "optimize.job". **Uncomment** the “**cp line”** and **“comment clmextrapol”** modify:
  - *cp ${i}_default_rkm5_200k.clmsum TiC.clmsum # Using previously converged densities saves a lot of CPU time!!*
  - *# clmextrapol ...*
  - *save_lapw ${i}_default_rkm6.5_1000k*
- g) repeat step d) (plot the results for “*_rkm6.5_1000k”)

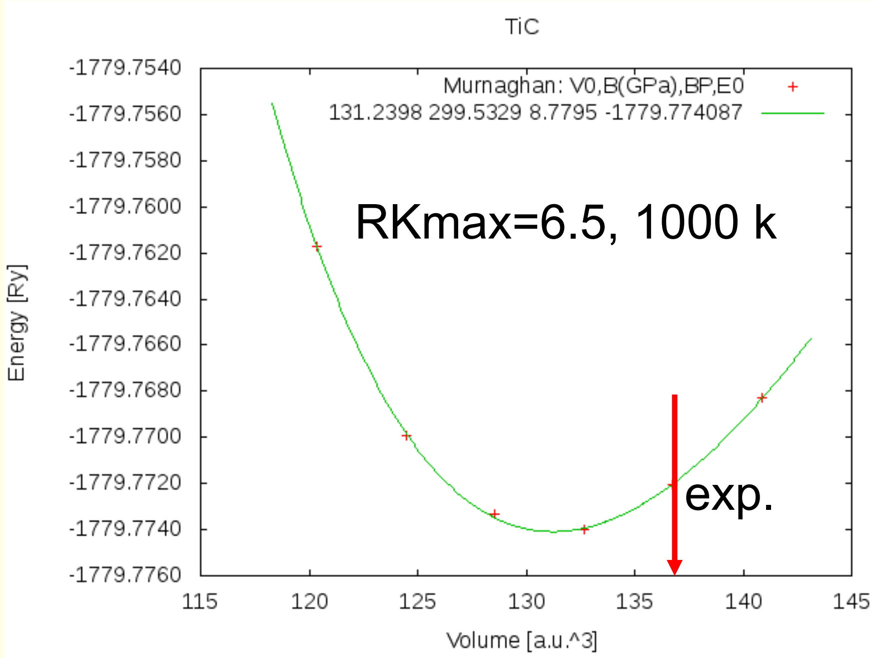
- *Find out how RKmax and k-points lead to smooth/non-smooth curves. Estimate good values and compare in particular B and BP (Bulkmodulus and its volume derivative). Fully converged results would require RKmax=8 - 9 , 10000 k and 10 volumes with ΔV=1%.*
- *You may also do this with another XC-potential (eg. PBEsol) and will see a very large effect …*

- Remember: Depending on the specific property you want to calculate (just a DOS, or Energy-Volume curves, or EFG, or structure optimization with forces,..) and the desired accuracy, the types of atoms, insulator/metal and system size you may need different RKmax and k-point samplings:
  - *H: RKmax > 2.5; sp-elements: RKmax > 5; d-elements: RKmax > 6; f-elements: RKmax > 7; (see our faq-page)*
  - *1 atom/cell, metal: 1000-10000 k-points or more*
  - *1 atom/cell, insulator: 100-1000 k-points or more*
  - *For N atoms/cell you can reduce the k-mesh by a factor N*

- *Remember: Always test your **specific property** for convergence !!*

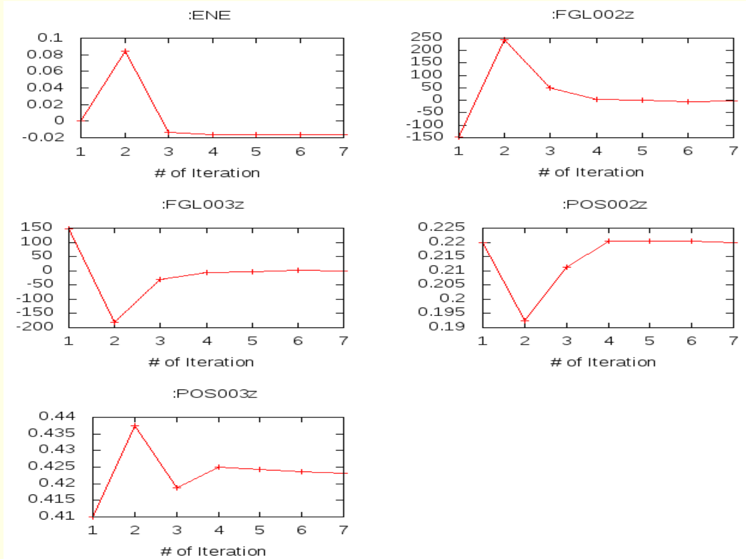
Volume optimization for TiC

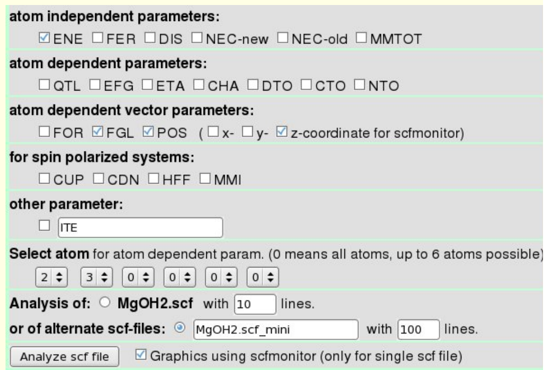




Exercise 3: optimization of positions in $Mg(OH)_2$

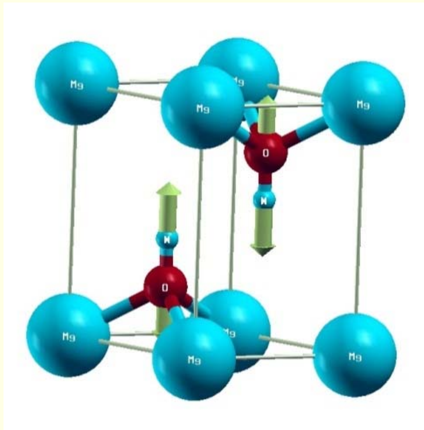
- **create two "cases" (directories) for PORT and MSR1a optimization**
  - *initialize both cases (or copy after init one case to the other and use „rename_files")*
  - *P-3m1 (164), a=b=3.15 c=4.77 Å γ=120º; Mg(0,0,0)   O(1/3,2/3,**0.22**) H(1/3,2/3,**0.41**);   RMT: reduce by 7%*
  - *init_lapw -b –numk 100 –rkmax 3*
- **minimization using PORT:**
  - *min_lapw (or „mini-positions in w2web)*
  - *save_lapw case_relaxed_rkm3*
  - *analyze **case.scf_mini***
    - :ENE :FGL002z :POS002z :FGL003z :POS003z
  - *Find out how many scf cycles you needed*
    - grepline :ITE '*scf' 1   (in terminal)
- **check RKMAX convergence:**
  - *increase RKMAX to 3.5 (case.in1)*
  - *run –fc 1   (and check your forces)*

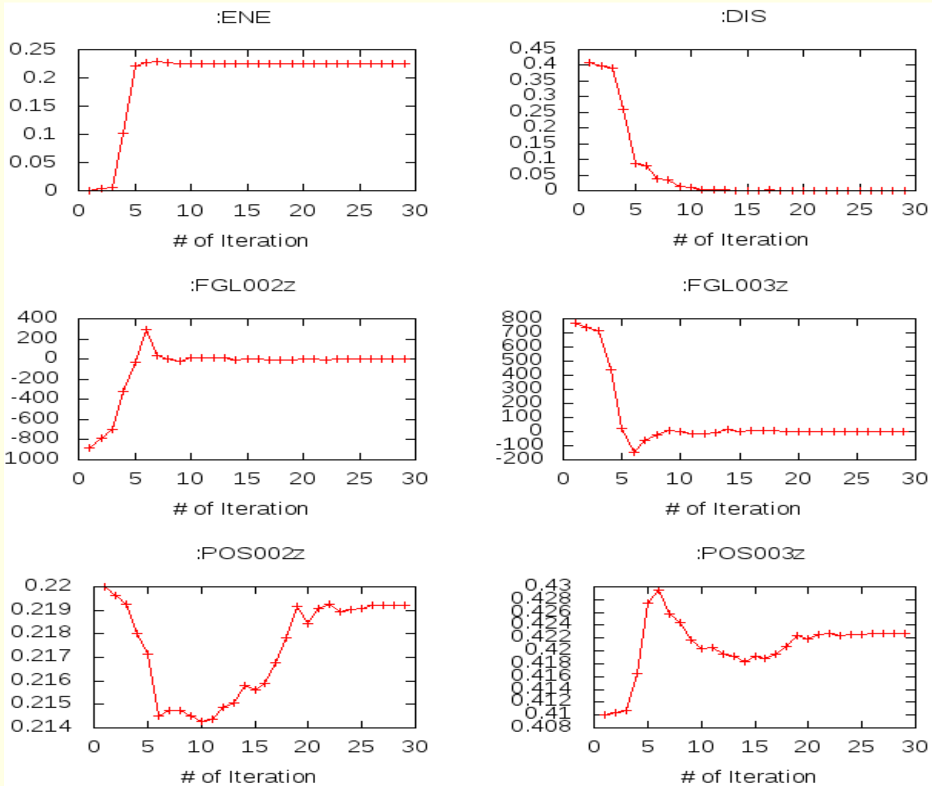




Mg(OH)$_2$ continue

- minimization using MSR1a:
  - ***run -min –fc 1 –cc 0.001 –ec 0.0001***
    - -min sets MSR1a in case.inm, (sometimes a crude scf cycle to come closer to „Born-Oppenheimer“ surface is necessary (run -fc 20)
  - *analyze* ***case.scf*** and find out how many scf cycles you needed
    - :ENE :FGL002z :POS002z :FGL003z :POS003z :ITE
  - *save_lapw case_final*
  - *use the „arrows" utility to display initial forces and final relaxations (see UG p.195)*





Exercise 4: Creation of supercells

- This exercise should be done WITHOUT w2web in a terminal window !
- **creation of basic structure: MgO**
- mkdir super; cd super;
- makestruct (and type in the following information). It creates **init.struct**
  - *MgO: lattice type: F, a= 7.96 bohr*
  - *Mg (0,0,0), O (0.5,0.5, 0.5)*
- cp init.struct super.struct
- view the structure using: xcrysden --wien_struct init.struct

- **16-atom supercell**
- x supercell (use **super.struct**, select **2x2x2** and **F-cell):**
- cp super_super.struct super.struct
- edit super.struct and mark first Mg atom as "**Mg1**"
- x nn and if :WARNINGs appear do the next line:
  - *cp super.struct_nn super.struct; and repeat the "x nn" step above*
- x sgroup and view super.outputsgroup (no errors, but gives you a spacegroup)
  - *how many non-equivalent atoms do you have now ? view the structure with xcrysden. Now you would be ready to run i**nit_lapw -b ....,** but we just save it using **cp super.struct super_16.struct***

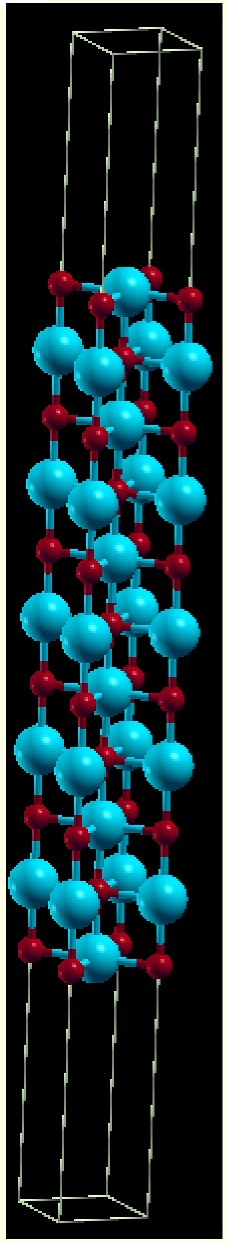
Exercise 4: Creation of supercells (cont.)

- **32, 64 and 128-atom supercells** (as above, but with B, P cell or 4x4x4-F)
- cp init.struct super.struct
- x supercell (use **super.struct**, …**):**
- cp super_super.struct super.struct
- edit super.struct and mark first Mg atom as "**Mg1**"
- x nn and if :WARNINGs appear do the next line:
  - *cp super.struct_nn super.struct; and repeat the "x nn" step above*
- x sgroup and view super.outputsgroup (no errors, but gives you a spacegroup)
  - *how many non-equivalent atoms do you have now ? view the structure with xcrysden. Now you would be ready to run i**nit_lapw -b ….,***
  - *save the structures using **cp super.struct super_32.struct***

- Instead of labelling "Mg1", one could also **remove** an atom (vacancy) or **replace** an atom by another (impurity).
- Replacing atoms is better done in w2web, because this will also update radial meshes. (change **name** of atom AND **remove Z** !!)

Exercise 4: Creation of supercells (cont.)

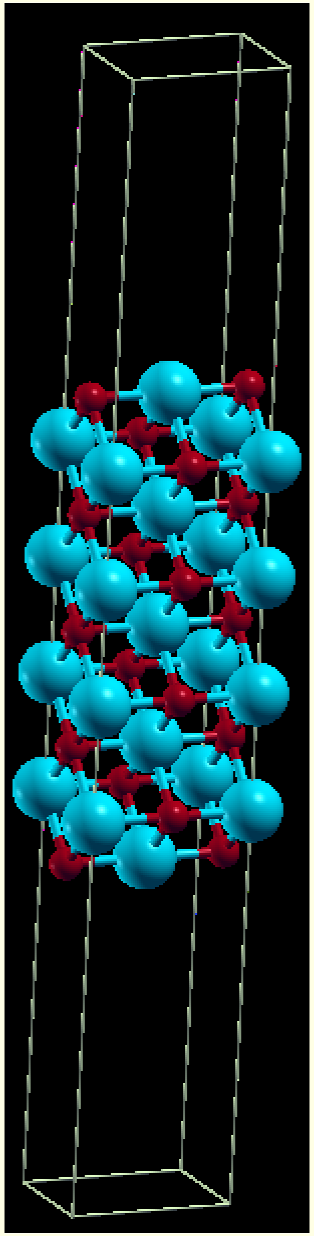
- **(001) surface with 11 layers:**
- cp init.struct super.struct
- x supercell (use **super.struct**, 1x1x5, 30 bohr vacuum in z; repeat atom at 0:y)**:**
- cp super_super.struct super.struct
- xcrysden --wien_struct super_super.struct & (leave it open for comparison)
- x sgroup and view super.outputsgroup (it created a new structure for you)
- cp super.struct_sgroup super.struct
- xcrysden --wien_struct super.struct
  - *what has sgroup done ?? how many total and non-equivalent atoms and how many* ***atoms/layer*** *do you have before/after sgroup ? Do you have inversion symmetry ?*
  - *save the structure using* ***cp super.struct super_surface-001.struct***



- If you now want to study **adsorption** of an atom you could simply add **2 equivalent** atoms manually (w2web !!) at a suitable starting position, eg. (0,0,+/-z) (2 atoms to keep inversion symmetry !!)
- This structure could serve as base for a bigger supercell (for instance 2x2x1) to simulate reduced “coverage”.

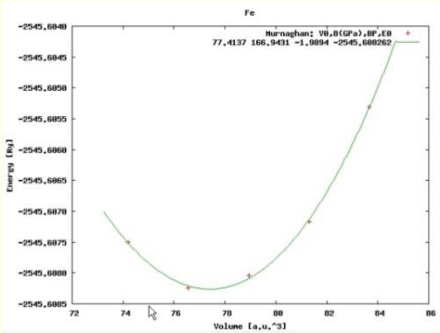
Exercise 4: Creation of supercells (cont.)

- **(110) surface with 9 layers: (**using the **structeditor)**
- octave (use repeat-key arrow-up !)
  - *helpstruct* *# list all possible commands*
  - *a=loadstruct("init.struct");*
  - *ac=makeconventional(a);* *# convert F into P cell*
  - *help makesurface* *# explains the syntax*
  - *sr=makesurface(ac, [1 1 0], 1, 20., 30.);*
  - *showstruct(sr)* *# check out the number of layers and repeat the **sr=makesurface** command with larger thickness until you get 9 layers. How do you get an O-atom at the origin ?*
  - *savestruct(sr,"super.struct")*
  - *quit*
- xcrysden --wien_struct super.struct &
- x sgroup and view super.outputsgroup
- cp super.struct_sgroup super.struct
- xcrysden --wien_struct super.struct
  - *what has sgroup done ?? how many total and non-equivalent atoms and how many **atoms/layer** do you have before/after sgroup ? Do you have inversion symmetry ?*
  - *save the structure using **cp super.struct super_surface-110.struct***



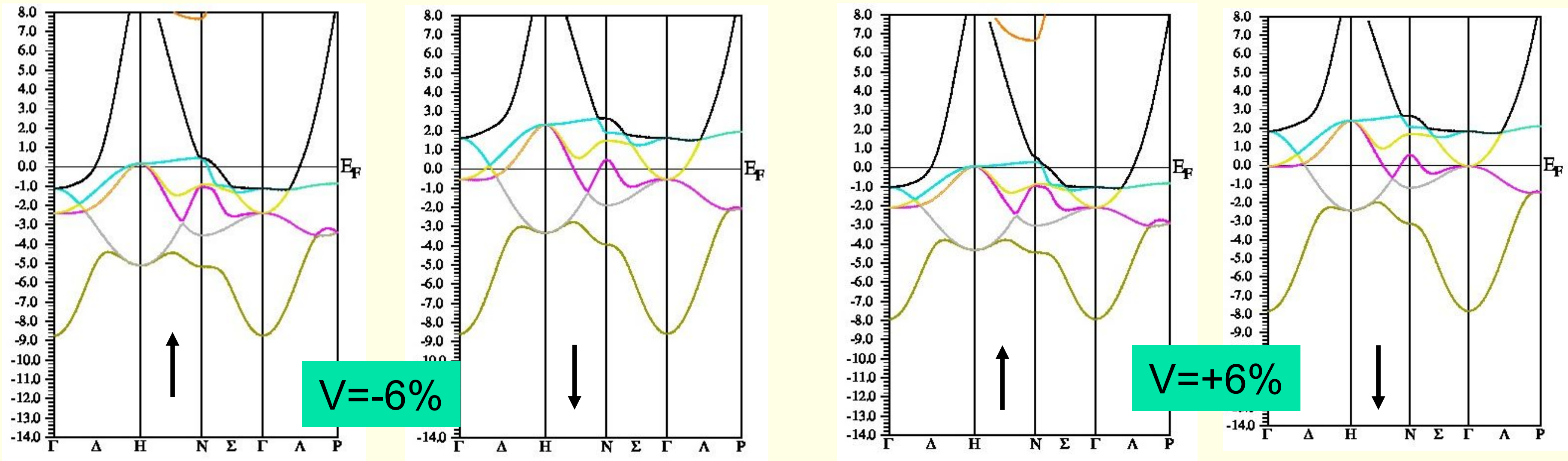
Exercise 5: spin-polarized calculations

- Magnetism: bcc Fe (a_0=2.86 Å)
  - *setrmt: 3%; 5000k; spin-polarization:yes, use RKmax=7, then 8*
  - *do a volume optimization (-6, -3, 0, 3, 6 %) (activate runsp_lapw instead of run_lapw !)*
    - check equilibrium volume, :MMT as function of volume



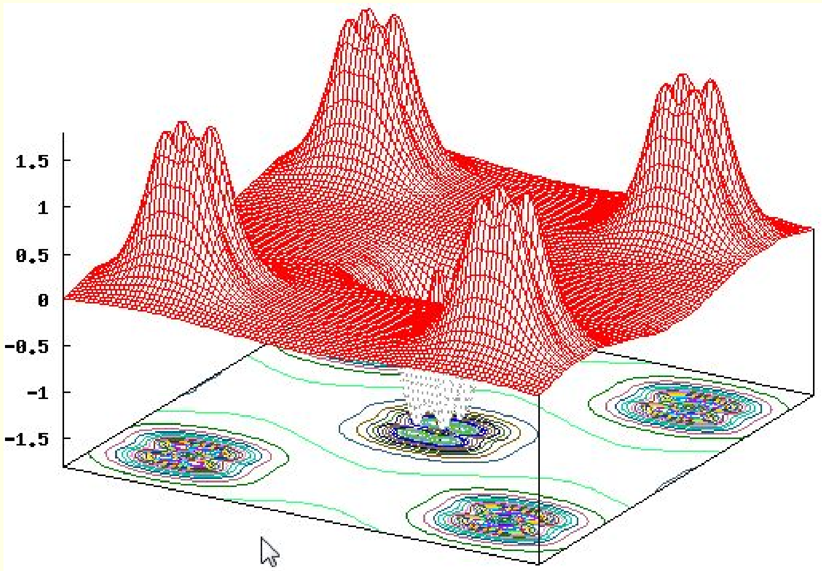
--- MMTOT ----------- in 5 files:
Fe_vol___0.0_rk8_5000k.scf::MMTOT: 2.21
Fe_vol___3.0_rk8_5000k.scf::MMTOT: 2.26
Fe_vol__-3.0_rk8_5000k.scf::MMTOT: 2.16
Fe_vol___6.0_rk8_5000k.scf::MMTOT: 2.31
Fe_vol__-6.0_rk8_5000k.scf::MMTOT: 2.13

- *compare bandstructure and DOS for large/small volumes (restore_lapw for desired volume; x lapw0 "recreates" potentials, adjust EF in case.insp)*



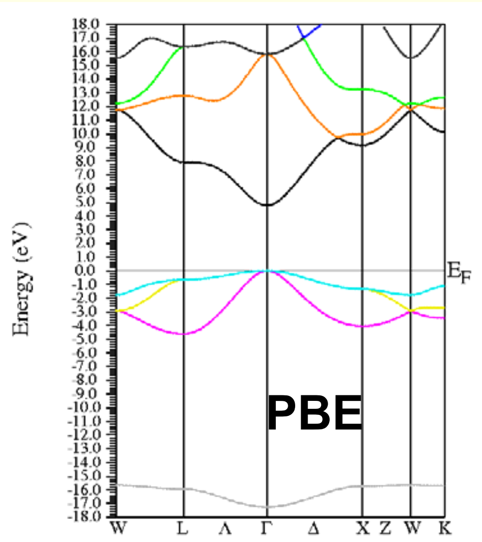
Exercise 6: antiferromagnetic calc.

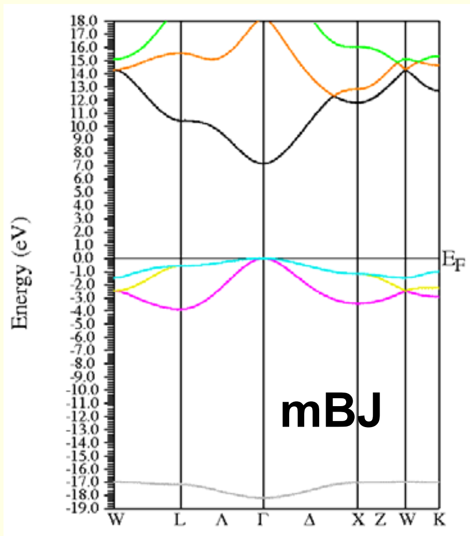
- Antiferromagnetism: bcc Cr (a_0=2.885 Å) (use 5000k, -cc 0.001)
  - *try 2 different calculations:*
  - *ferromagnetic solution (bcc cell with 1 Cr)*
  - *antiferromagnetic calculation (P cell with Cr1 and Cr2 (at 0.5,0.5,0.5))*
    - choose up/dn for the two Cr atoms when creating case.inst
    - for afminput your symmetry operation is "identity+(0.5,0.5,0.5)"
  - *is FM or AFM Cr more stable? (:ENE)*
  - *is FM stable at all ? check moments (MMI001: what "means" 0.000x ???)*
  - *plot spin-densities in the (110) planes*
    - do lapw2 for both spins
    - observe "spatial localization"
    - t_{2g}-asymmetry
    - negative spin-density in interstitial
      - where does it come from ?
      - compare :QTLxxx

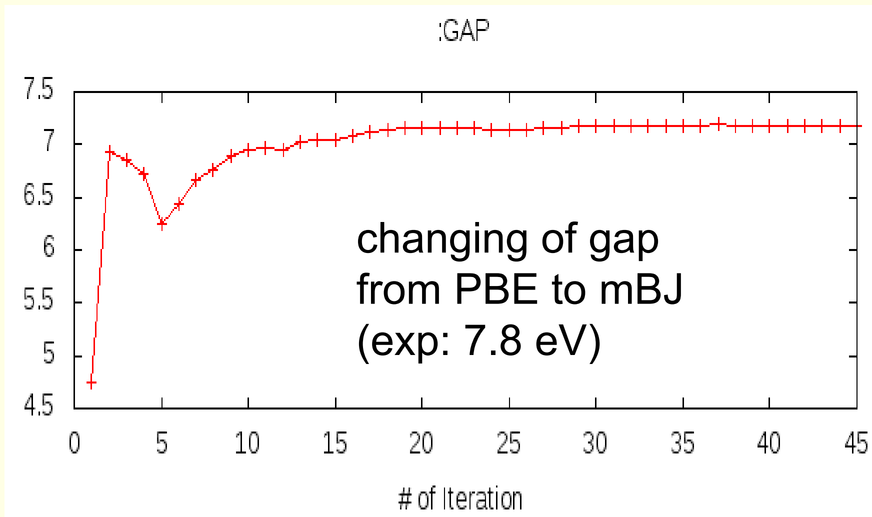


Exercise 7: band gaps of MgO

- MgO (NaCl, a=7.96 bohr; default initialization; scf-cycle)
  - *PBE: check the gap (:GAP from "anaylysis"),*
    - plot a band structure in PBE (E-range from -19 to 18 eV)
  - *TB-mBJ:*
    - save the PBE calculation, execute:
      - init_mbj_lapw (in utils) „phase 1" of the initialization (see also in the UG 4.5.9)
      - run_lapw -NI -i 1
      - rm *.bro*
      - init_mbj_lapw „phase 2", use original mBJ parameters
    - run scf cycle (note, it may not converge in 40 cycles, submit another run with -NI option)
    - monitor the change of the :GAP
    - plot a band structure (fcc) and compare with PBE

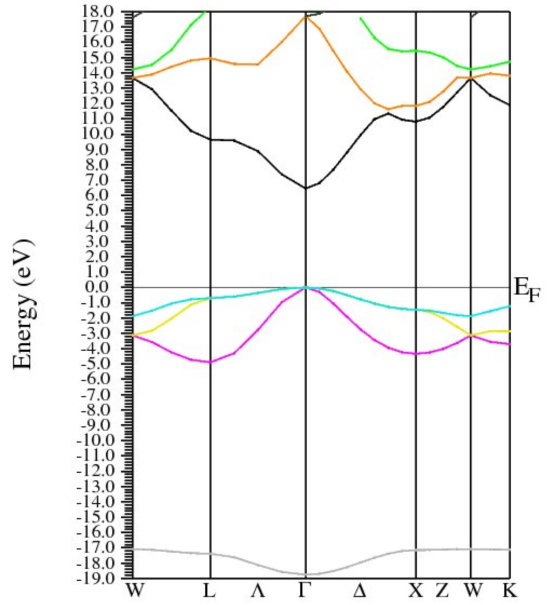






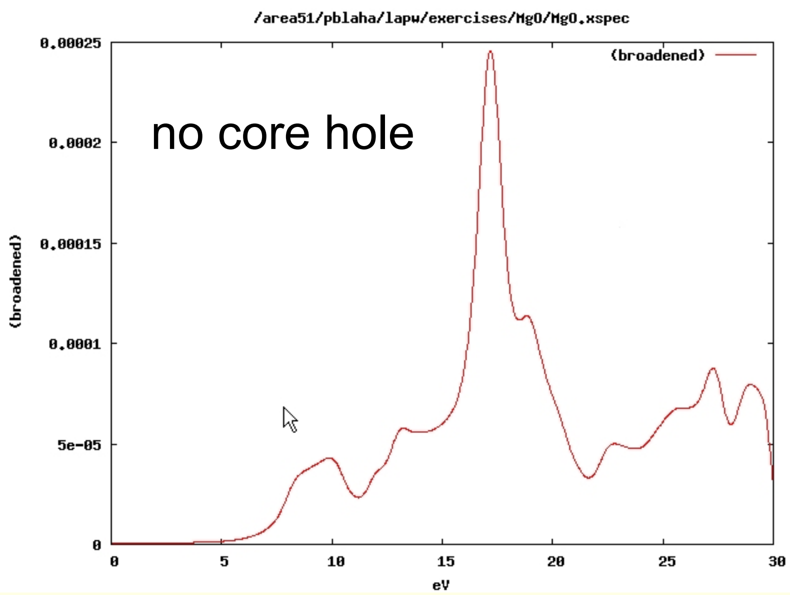
Exercise 7: continued …

- Perform a hybrid-DFT calculation using YS-PBE0
  - create a new case, perform a PBE calculation and save the results.
  - the setup for hybrid-calculations can be made in w2web (Utils/init_hf_lapw), or in a terminal-window using „init_hf_lapw". (More details are given in the UG 4.5.8)
    - Select NBAND=12 (case.inhf)
    - and a 4x4x4 / 4x4x4 k-point mesh (no reduction)
  - scf cycle with **-hf -p -scratch ./** (insert 2 lines with **1:localhost** into **.machines**)
    - we do this in k-parallel since it will take more time, alternatively we could also use a „reduced" hf-k-mesh, see UG
  - monitor the change of the :GAP and compare it with mBJ and exp. gaps (only every 2nd value is from HF !)
  - plot a band structure:
    - only the k-mesh selection can be done in w2web, then open a terminal and change into the proper directory
    - run_bandplothf_lapw -p
    - cp $WIENROOT/SRC_templates/case.insp case.insp (insert E_F and increase the plotting energy range).
    - x spaghetti -hf -p

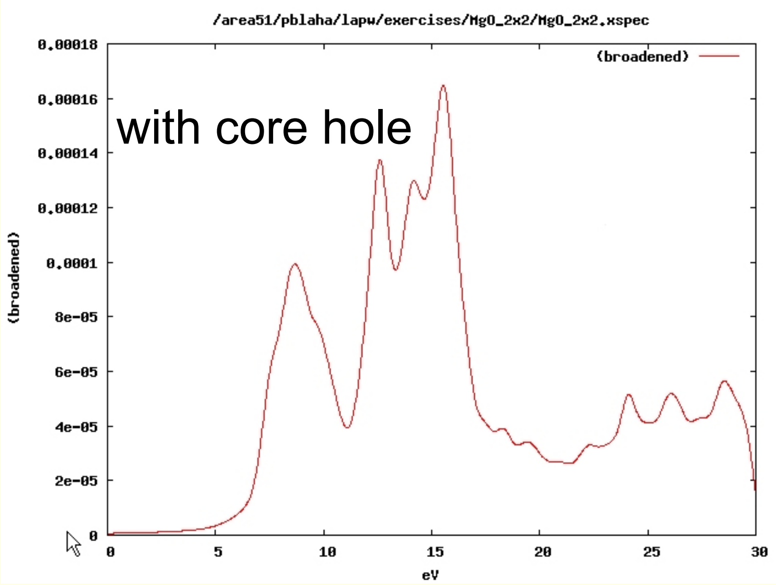


Exercise 8: Mg K-XAS in MgO

- MgO (NaCl structure, a=7.96 bohr; default initialization with 1000 k-points; scf-cycle)
  - *XSPEC task: larger EMAX in MgO.in1; select in MgO.inxs: Mg-K ABS from 0-30 eV, vary broadening)*
- Supercells: MgO 2x2x2 FCC-supercell for core-hole simulation
  - *create new "session", copy MgO.struct into new directory*
  - *x supercell; (specify proper struct-filename, 2x2x2, F-lattice)*
  - *cp supercell-struct file to correct name "case.struct"; "**label**" 1st atom (Mg → Mg1)*
  - *init_lapw (with 200k, RKmax=6.5)*
  - *edit case.inc (remove a core electron from 1st atom)*
  - *edit case.in2 (add one valence electron)*
  - *run_lapw (for bigger calc. use -it and compare timings for 1st and later iterations!)*
  - *edit case.in2 (remove extra valence electron)*
  - *XSPEC task for Mg-K XAS (see above)*



Mg-K XAS



Exercise 9: LDA+U calculations

- NiO: NaCl structure, A-type AFM along [111]
  - *R-cell: 5.605236 5.605236 27.459934 bohr; angles: 90,90,120*
  - *3 non-equivalent atoms: Ni1 (0,0,0), Ni2 (0.5,0.5,0.5), O ±(.25,.25,.25) ("add 2nd position"* ***after*** *first "save_structure"). View and understand the structure (Xcrysden)*
  - *case.inst: flip spin for Ni2, make O "non-magnetic"; use 100k-points*
  - *GGA calculations (save_lapw NiO_gga)*
  - *GGA+U calculations (save_lapw NiO_gga+u)*
    - (use U=7eV, J=0; search the UG to understand case.inorb/indm)
  - *GGA+SO calculations (M=[111], without relativistic LO, Emax=5.0)*
    - after scf: x lapwdm –up –so (for :orb001 in NiO.scfdmup)
  - *GGA+U+SO calculations (cp NiO.indm NiO.indmc)*
  - *compare DOS (total, Ni1, Ni2, O) for GGA and GGA+U*
    - observe the change in gaps (exp: 4eV) and shift of Ni/O weights
    - compare spin moments (GGA: 1.41; GGA+U: 1.76; GGA+U+SO:1.76;GGA+SO: 1.41μB)
    - compare orbital moments for SO and SO+U calculations (0.12 and 0.09μB)
  - *try a TB-mBJ calculation for NiO (start new case, starting from GGA; follow instructions given in P.Blaha's lecture) and compare gap/DOS*

NiO cont…

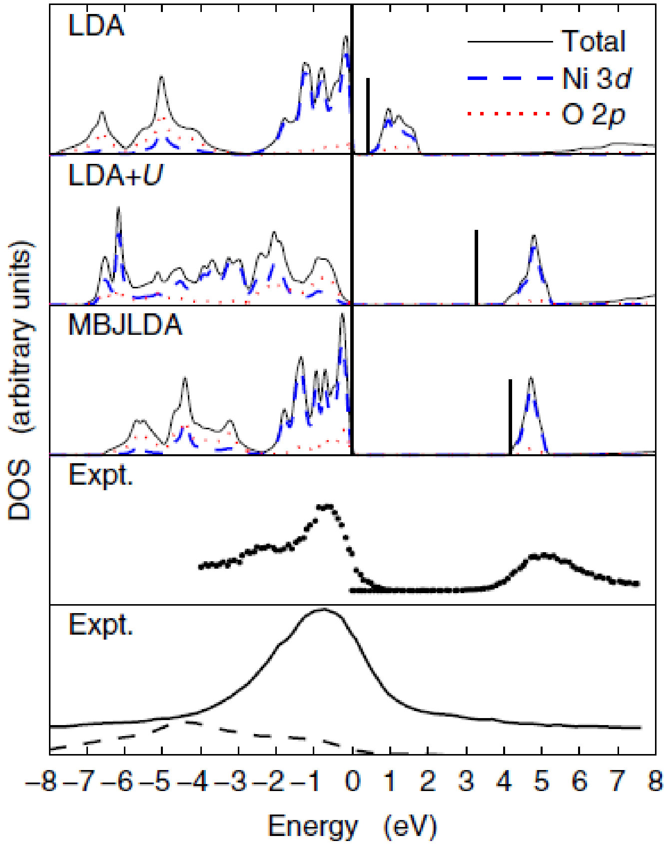
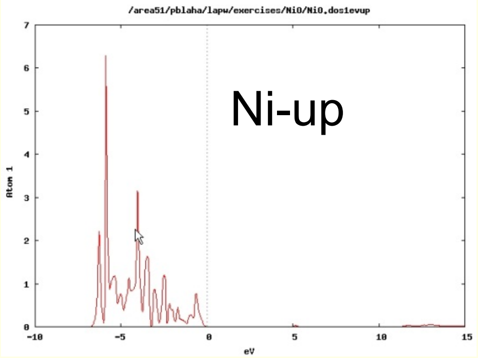
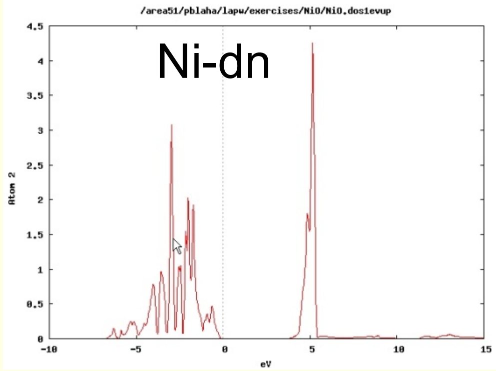


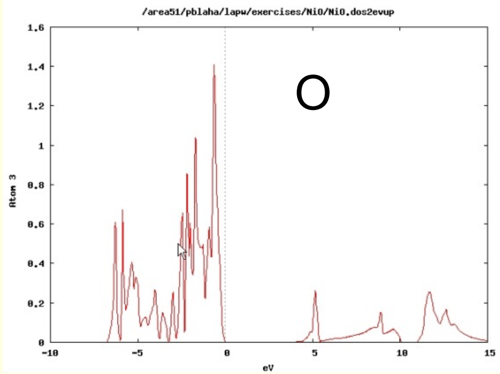
FIG. 2 (color online). DOS of NiO. The vertical bars indicate the end of the fundamental band gap which starts at $E = 0$ eV. The panels labeled "Expt." show photoelectron [25] (upper panel) and XES [33] [lower panel, Ni (solid line) and O (dashed line) spectra] measurements.

from Tran,Blaha, PRL 102, 226401 (2009)

GGA+U



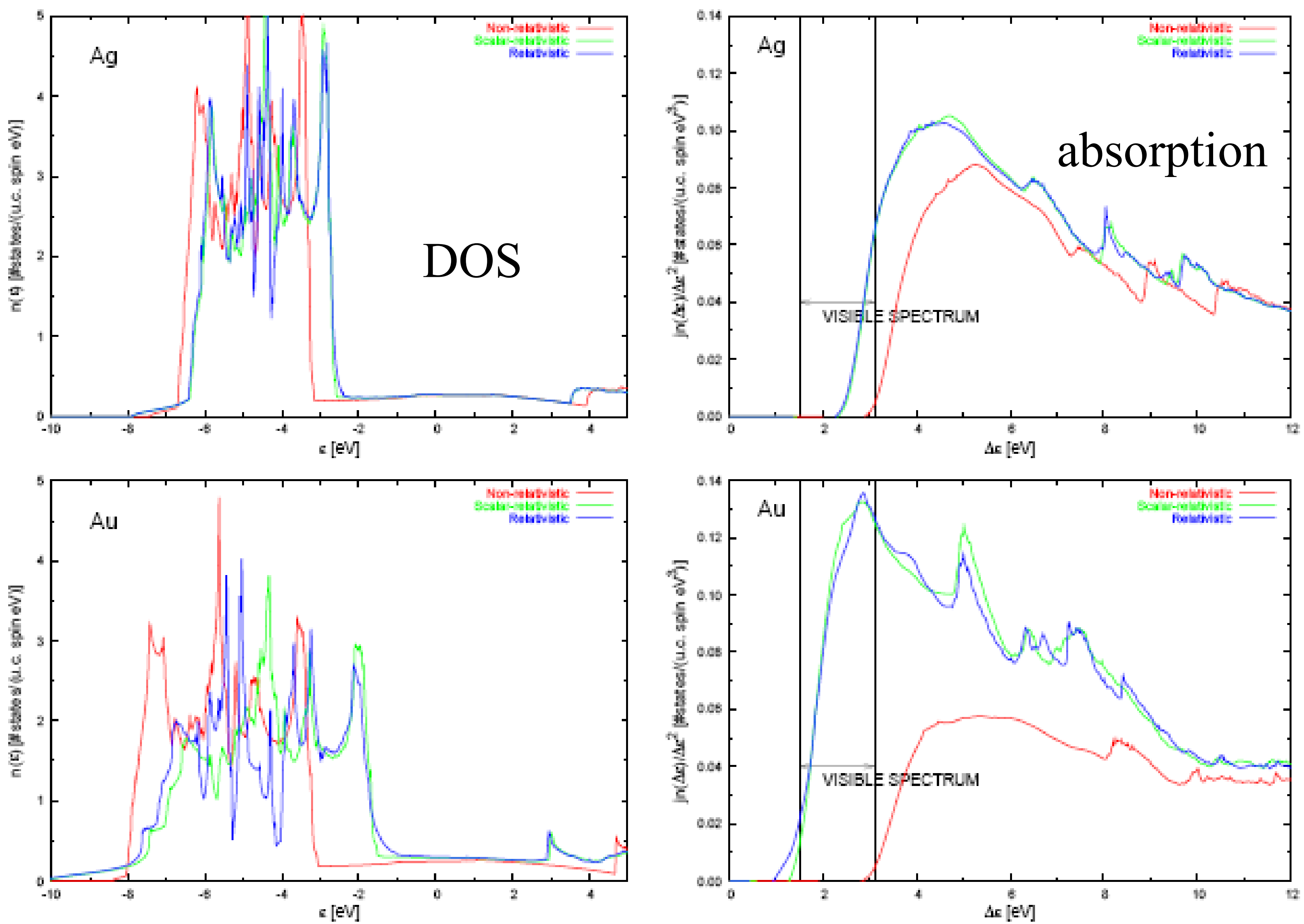




Exercise 10: optical properties

- Optical properties: fcc Al
  - *a_0=4.05 Å*
  - *init_lapw (use 165 **IBZ** k-points only!)*
  - *run_lapw*
  - *calculate optics (as described in the optics lecture, compare with the Al - Fig.)*
    - calculate plasma frequency (case.outputjoint) and dielectric function
    - check your results with respect to k-mesh
      - x kgen (check for about 1000 and 4000 **IBZ**-points)
      - x lapw1
      - x lapw2 –fermi
      - x optic, x joint, x kram
- Optical properties: fcc Ag and Au (both have a_0=4.08 Å)
  - *compare optics without / with spin-orbit coupling (compare with RL)*
    - do NREL (change RELA to NREL in case.struct) first, do the optics
    - do scalar-relativistic calc., do the optics
    - include spin-orbit: run_lapw -so (case.inso **without RLOs** since optic does not support RLOs; put large Emax in case.in1); optics

Ag and Au: a relativistic effect



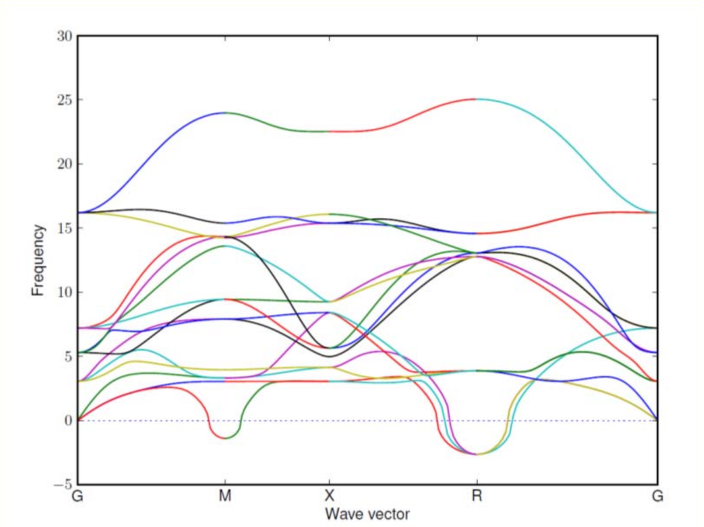
Exercise 11: Phonons of $SrTiO_3$

- This exercise should be done WITHOUT w2web in a terminal window !
- mkdir SrTiO3; cd SrTiO3;
- makestruct
  - *$SrTiO_3$: SG 221(P m-3m), a=b=c=7.38 bohr, α=β=γ=90°*
  - *Sr (0.5, 0.5, 0.5), Ti (0, 0, 0), O (0.5, 0 , 0)*
  - *setrmt 3%*
- cp init.struct SrTiO3.struct
- init_lapw -b -numk 10 -rkmax 6   # (batch mode)
- phonopy --wien2k -c SrTiO3.struct -d --dim="2 2 2"
- mkdir 1; mkdir 2; mkdir 3
- Copy SrTiO3.structS-001, SrTiO3.structS-002 and SrTiO3.structS-003 in 1,2 and 3
- Do the same for directories 1, 2 & 3 (open 3 terminals and do it in parallel):
  - *cd 1*
  - *mv SrTiO3.structS-001 1.struct*
  - *init_lapw -b -numk 10 -rkmax 6   #(batch mode)*
  - *run_lapw -fc 0.1*
  - *cp 1.scf ..*

Phonons continued

- phonopy --wien2k -f 1.scf 2.scf 3.scf
- create band.conf with editor, containing the following information:
  - *ATOM_NAME = Sr Ti O*
  - *DIM = 2 2 2*
  - *PRIMITIVE_AXIS = 1.0 0.0 0.0 0.0 1.0 0.0 0.0 0.0 1.0*
  - *BAND = 0 0 0 1/2 1/2 0 0 1/2 0 1/2 1/2 1/2 0 0 0*
  - *BAND_LABELS = G   M X R G*
  - *BAND_CONNECTION = .TRUE.*
- phonopy --wien2k -c SrTiO3.struct band.conf –p
- save with: phonopy --wien2k -c SrTiO3.struct band.conf –p –s #(pdf format)
- your result should be like:

phonons are unstable because $SrTiO_3$ has distorted, tetragonal structure at low temperatures



Exercise 12: O-NMR of cubic/tetragonal $BaTiO_3$

- This exercise should be done WITHOUT w2web in a terminal window !
- mkdir BaTiO3; cd BaTiO3; mkdir cubic; mkdir tet; cd tet
- makestruct (and type in the following information)
  - *$BaTiO_3$: SG 99 (P 4 m m), a= 3.9926 3.9926 4.0294 Ang*
  - *Ba (0,0, 0.0217), Ti (0.5,0.5, 0.5363), O_1 (0.5,0.5, 0.99805), O_2 (0,0.5, 0.50663)*
- cp init.struct tet.struct
- init_lapw -b -numk 300 -rkmax 6 (batch mode)
- edit .machines (insert 2 lines with 1:localhost)
- run_lapw -p -fc 1 -cc 0.001
- tail *scf and verify that the forces are "small" (no struct opt. necessary)
- x_nmr_lapw -mode in1 -focus O (and view the resulting *in1c_nmr file)
- x_nmr_lapw -p
  - *check tet.outputnmr_integ for σ_{iso} and $\delta_{ax}=1/2(\sigma_{iso}-\sigma_z)$ (σ_z : smallest tensor component)*
  - *grep :EFG003 *scf*
  - *grep :EFG004 *scf*

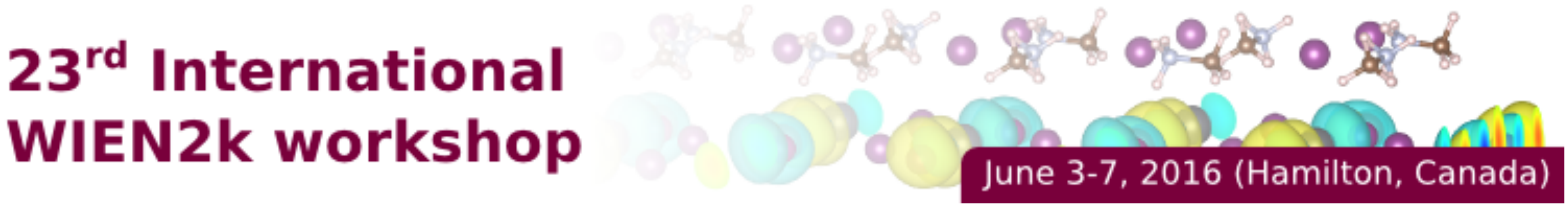
NMR continued ..

- cd ../cubic
- makestruct (and type in the following information)
  - *$BaTiO_3$: SG 221 (P-m3m), a= 4.006 Ang*
  - *Ba (0,0, 0), Ti (0.5,0.5, 0.5), O (0.5,0.5, 0)*
- continue as in the tetragonal case (run_lapw WITHOUT –fc 1, as all positions are fixed).
- *compare with experiment: (R.Blinc et al., J.Phys:Cond.Mat. 20, 085204 (2008))*

case	V_{zz}(exp)	V_{zz}(th)	δ_{iso}(exp)	δ_{iso}(th)	δ_{ax}(exp)	δ_{ax}(th)
cubic	2.46		546		-150	
tet-O1	2.06		520		-142	
tet-O2	2.56		570		-171	

- *Estimate $\delta_{iso}(th)=(\sigma_{iso}(th)-\sigma_{ref}(th))$; estimate $\sigma_{ref}(th)$ to obtain "best" agreement with exp.*
- *$\sigma_{ax} =1/2(\sigma_{iso}- \sigma_z)$*
- *The results are quite sensitive to small structural changes (c/a, positions) and the XC-approximation. You may repeat it using mBJ (with original BJ parameters)*

Exercise IX: Wannier functions and Berry phase



(can be completed in any order)

- **GaAs -- MLWF (~40 mins)**

  Construction of maximally localized Wannier functions for the valence and conduction band

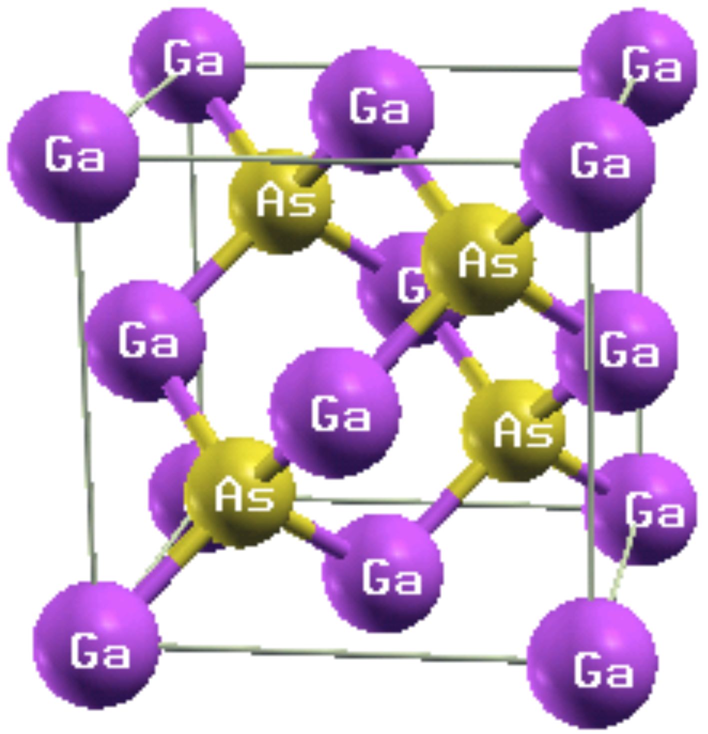
- **Born effective charge of GaN (~30 mins)**

GaAs -- MLWF

+ +

Special thanks to Elias Assmann (TU Graz) for the generous help in preparation of this tutorial

1. Wien2k SCF



Create a tutorial directory, e.g.

$ **`mkdir .../exerciseX/GaAs-MLWF`**

Create the structure file using the following parameters:

2 atoms per primitive unit cell (Ga, As)

Lattice "F" = f.c.c.

Lattice parameters $a_0 = b_0 = c_0 = 10.683$ Bohr

Positions: "0 0 0" for Ga and "1/4 1/4 1/4" for As; RMT's - automatic

You can use `xcrysden` to view the structure

$ **`xcrysden --wien_struct GaAs-MLWF.struct`**

Initialize Wien2k calculation (LDA, ~600 k-points ≡ 8x8x8 mesh)

$ **`init_lapw -b -vxc 5 -numk 600`**

Run regular SCF calculation using default convergence criteria

```
$ run_lapw
```

After SCF cycle is completed (~7 iterations). We proceed with the band structure

Prepare the list of k-point to be used for the band structure plot (`GaAs-MLWF.klist_band` file) using `xcrysden`

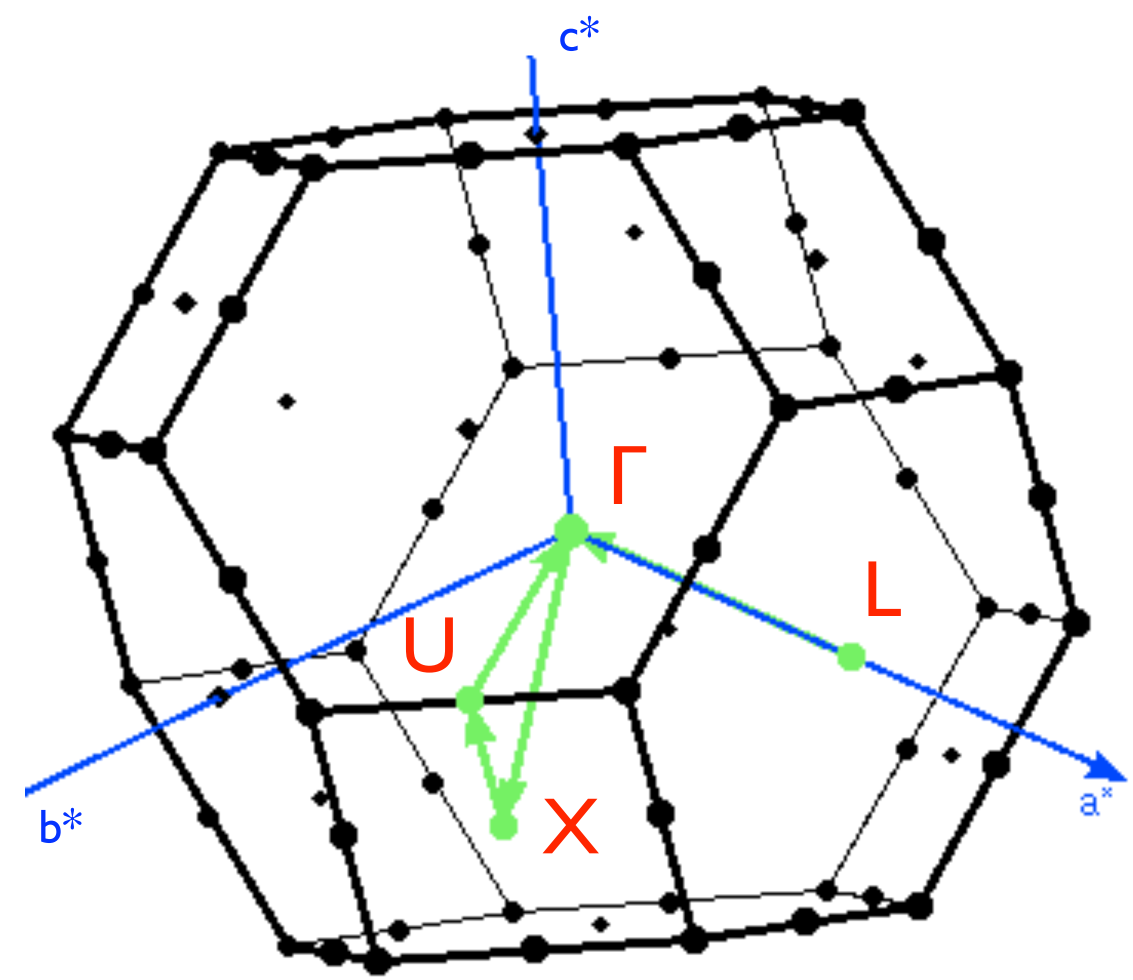
xcrysden File > Open Wien2k > Select k-path

Select points L(1/2 0 0), Γ(0 0 0), X(1/2 1/2 0), U(5/8 5/8 1/4), Γ

Save the list as `GaAs-MLWF.klist_band`

Solve eigenproblem on the k-path

```
$ x lapw1 -band
```



For the band structure plot we will use the web interface (w2web). Create a new session and navigate to the current work directory.

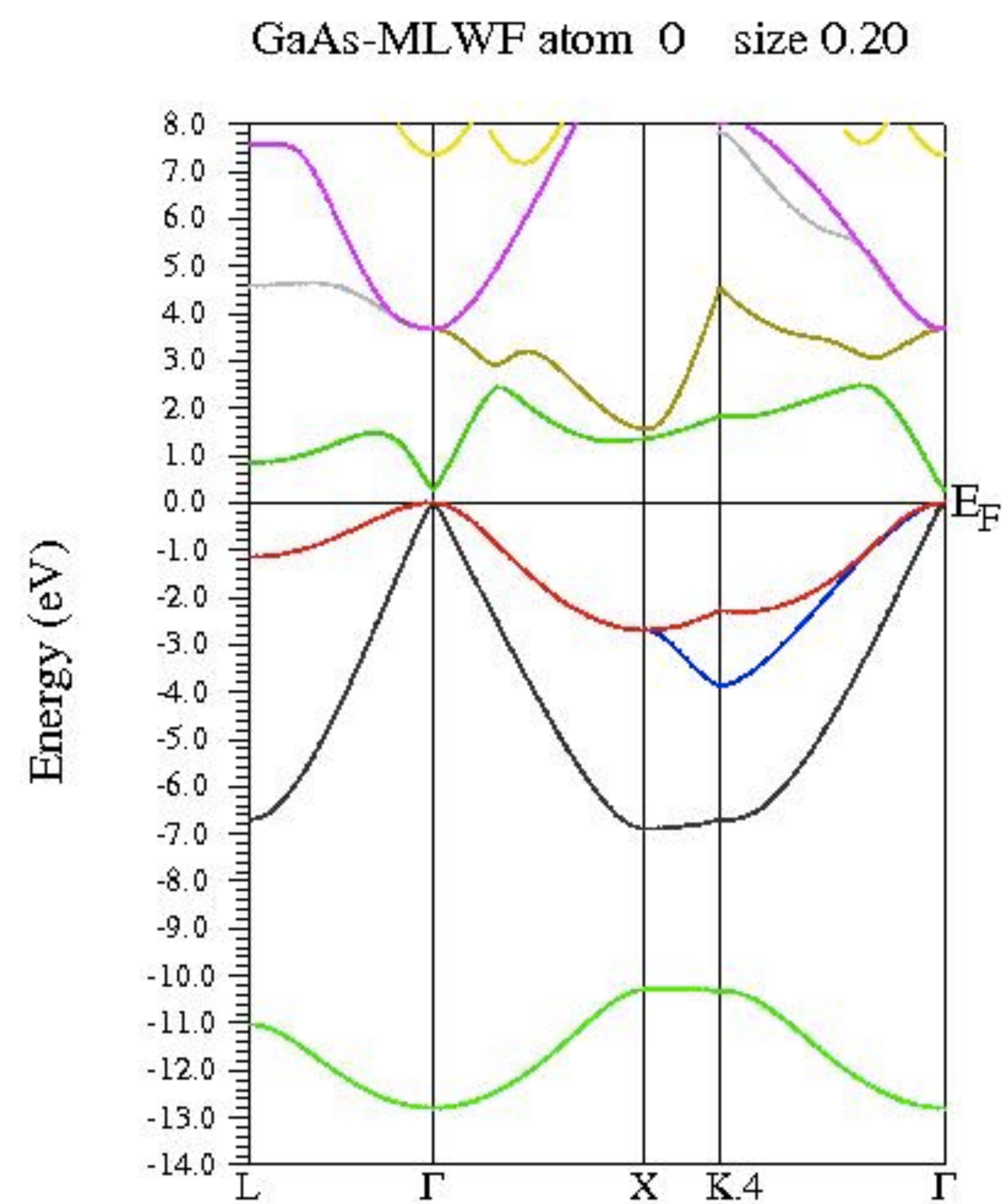
w2web Tasks > Bandstructure

w2web Select "Edit GaAs-MLWF.insp", insert the Fermi energy, save

w2web x spaghetti

w2web plot band structure

Your band structure will be similar to the one shown on the right. Our aim is to construct Wannier functions that reproduce this band structure including valence and some conduction bands.



Before we proceed it is useful to determine the band indices for the region of interest

```
$ grep :BAN *scf2
:BAN00004:   4   -2.243815   -2.243263   2.00000000
:BAN00005:   5   -2.243645   -2.243122   2.00000000
:BAN00006:   6   -0.757612   -0.748891   2.00000000
:BAN00007:   7   -0.748891   -0.745972   2.00000000
:BAN00008:   8   -0.748891   -0.745814   2.00000000
:BAN00009:   9   -0.744948   -0.742764   2.00000000
:BAN00010:  10   -0.743426   -0.742046   2.00000000
:BAN00011:  11   -0.597475   -0.409554   2.00000000
:BAN00012:  12   -0.163606    0.342616   2.00000000
:BAN00013:  13    0.056810    0.342616   2.00000000
:BAN00014:  14    0.094852    0.342616   2.00000000
:BAN00015:  15    0.362856    0.675520   0.00000000
:BAN00016:  16    0.456595    0.748030   0.00000000
:BAN00017:  17    0.612912    1.080595   0.00000000
:BAN00018:  18    0.612912    1.080595   0.00000000
:BAN00019:  19    0.881735    1.145545   0.00000000
```

d-orb. of As and Ga (do not participate in bonding) — bands 4–10

Bands 11–18 (boxed): region of interest

⇧ Emin (Ry) ⇧ Emax ⇧ occupancy

2. Construction of Wannier functions

Prepare a separate directory

```
$ prepare_w2wdir GaAs-MLWF GaAs-WANN
$ cd GaAs-WANN
```

Initialize Wien2Wannier

```
$ init_w2w
```

Select 8x8x8 k-mesh (unshifted);

energy range (eV) -13 10 (this is not very critical);

band indices [Nmin Nmax] 11 18 (see the previous page);

for the projection we choose "1:s,p" and "2:s,p" (1 = Ga, 2 = As)

Get the vector file on the full Brillouin zone mesh

```
$ x lapw1
```

Compute matrix elements needed for Wannier90

$ **x w2w**

Run Wannier90

$ **x wannier90**

Verify the output

spread $\langle \Delta \mathbf{r}^2 \rangle$

⇓

$ **less GaAs-WANN.wout**

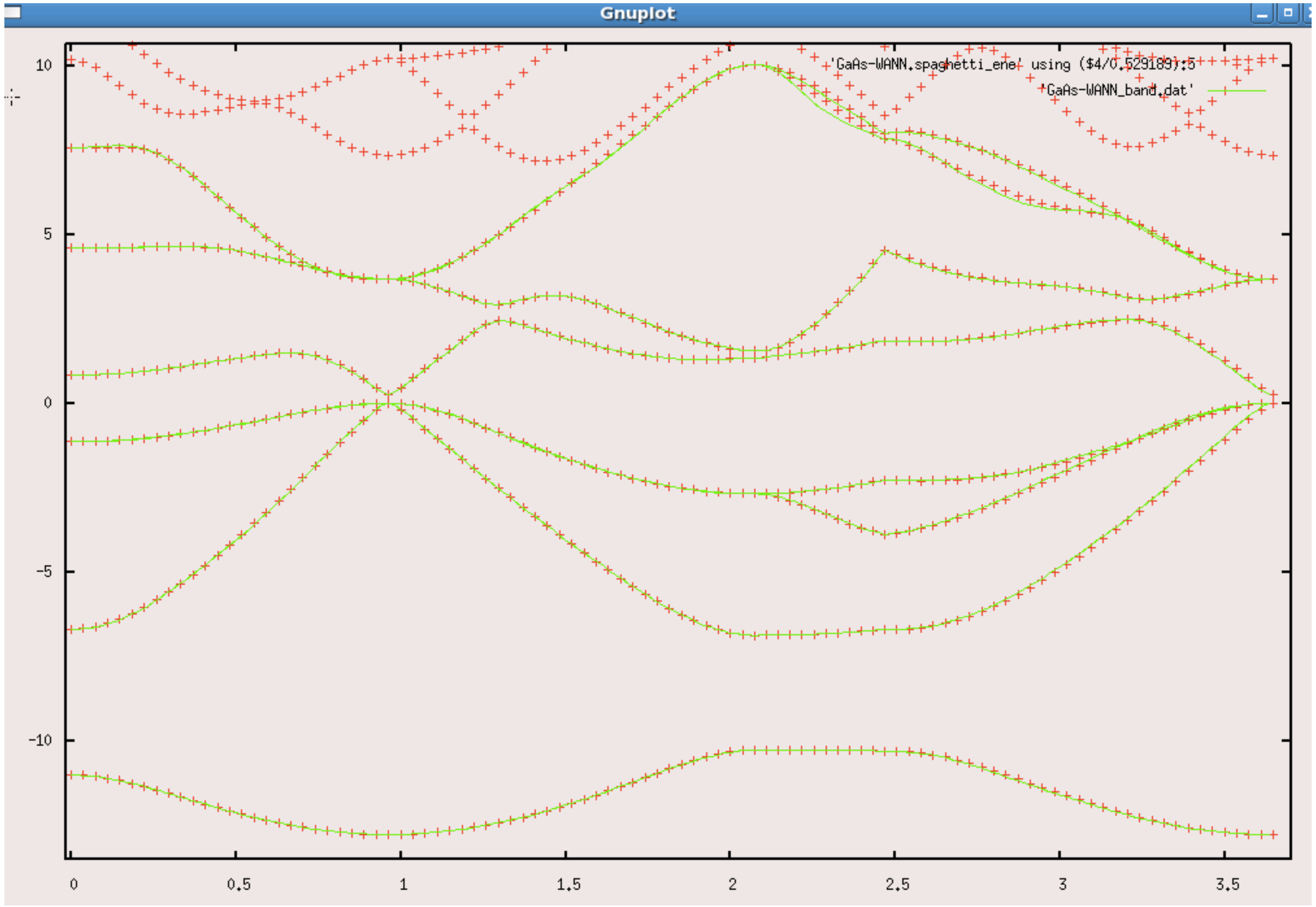
```
...
Final State
  WF centre and spread    1  (  0.000000,  0.000000,  0.000000 )     1.91743858
  WF centre and spread    2  (  0.000000,  0.000000,  0.000000 )     5.85659132
  WF centre and spread    3  (  0.000000,  0.000000,  0.000000 )     5.85659132
  WF centre and spread    4  (  0.000000,  0.000000,  0.000000 )     5.85659105
  WF centre and spread    5  (  1.413312,  1.413312,  1.413312 )     1.61146495
  WF centre and spread    6  (  1.413313,  1.413312,  1.413312 )     3.82142578
  WF centre and spread    7  (  1.413312,  1.413312,  1.413312 )     3.82142578
  WF centre and spread    8  (  1.413312,  1.413312,  1.413313 )     3.82142553
...
```

There you can see the position and spread of the WF's, how they changed in the course of convergence. WF's 1-4 are all positioned at the origin (atom 1), WF's 5-8 are centred at the 2nd atom (please check the coordinates)

3. Post-processing

Plot the band structure

```
$  gnuplot
gnuplot> plot 'GaAs-WANN.spaghetti_ene' using
  ($4/0.529189):5, 'GaAs-WANN_band.dat' with lines
```



+ original Wien2k band structure

– Band structure computed from Wannier functions

Plotting WF's (can take a while)

$ **`write_inwplot GaAs-WANN`**

Select origin "`-1 -1 -1 1`" and axis x, y, z

"` 1 -1 -1 1`"

"`-1  1 -1 1`"

"`-1 -1  1 1`"

mesh: 30 30 30

(Sometimes it is necessary to extend the plotting region beyond the primitive lattice in order to capture WF's centred close to the edges)

Compute the 1st Wannier function on the mesh chosen

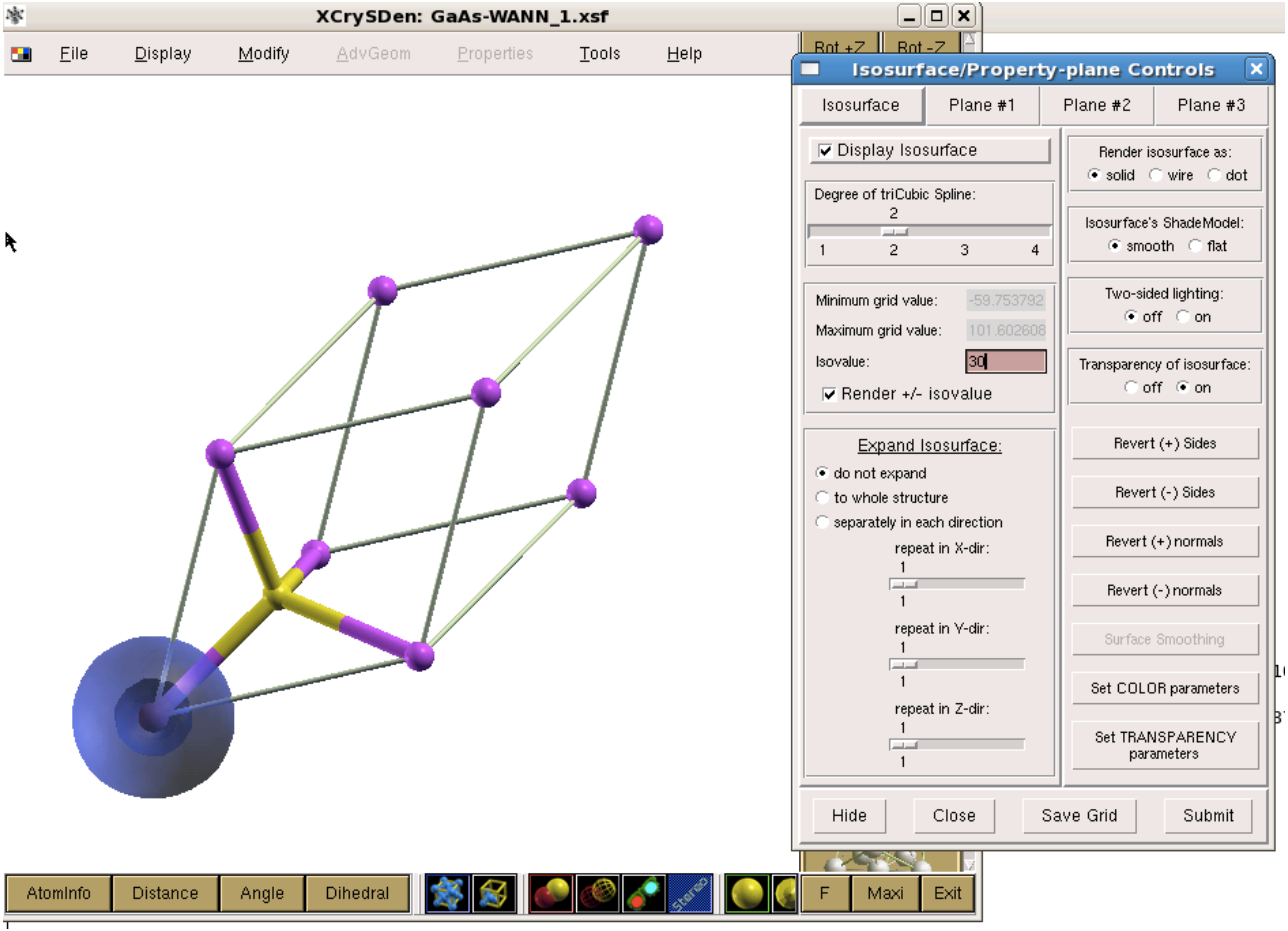
$ **`x wplot -wf 1`**

If you need to plot any other WF's (2, 3, etc), just edit the option.

Convert the output of `wplot` into `xcrysden` format for plotting.

$ **`wplot2xsf`**

Visualize with `xcrysden` (instructions on the next page)



$ xcrysden --xsf GaAs-WANN_1.xsf

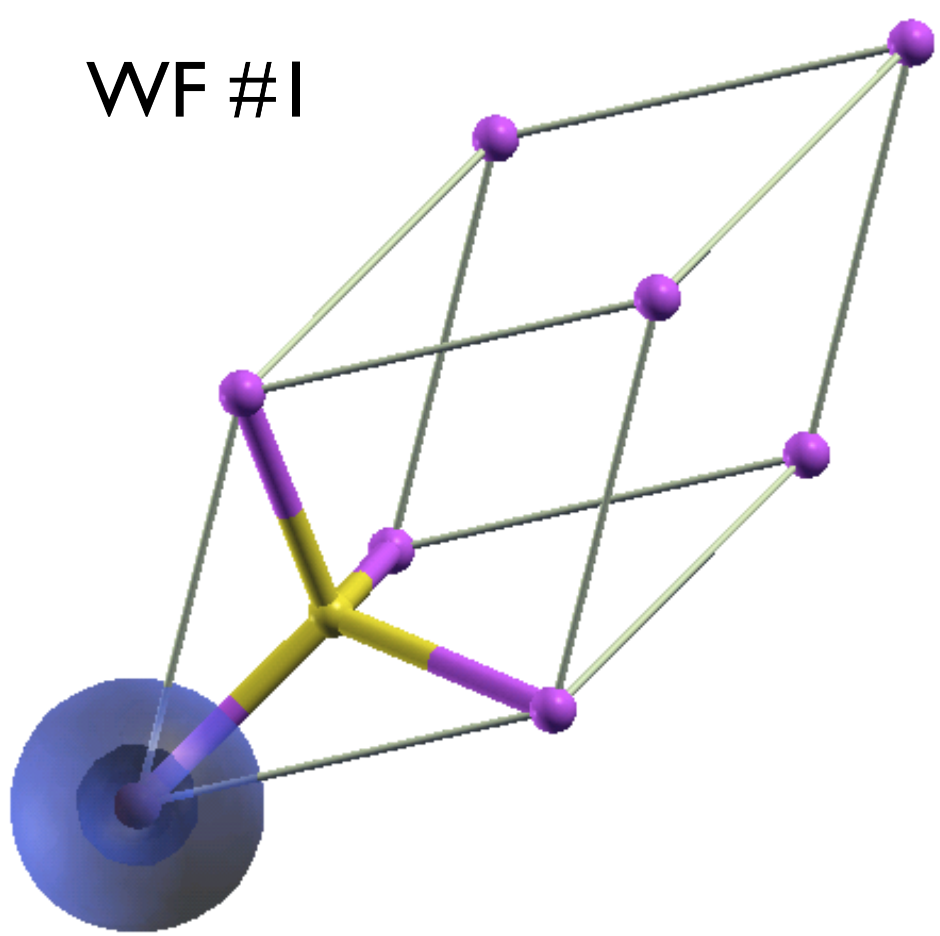
xcrysden Tools > Data Grid > OK

Check “render +/- isovalue”

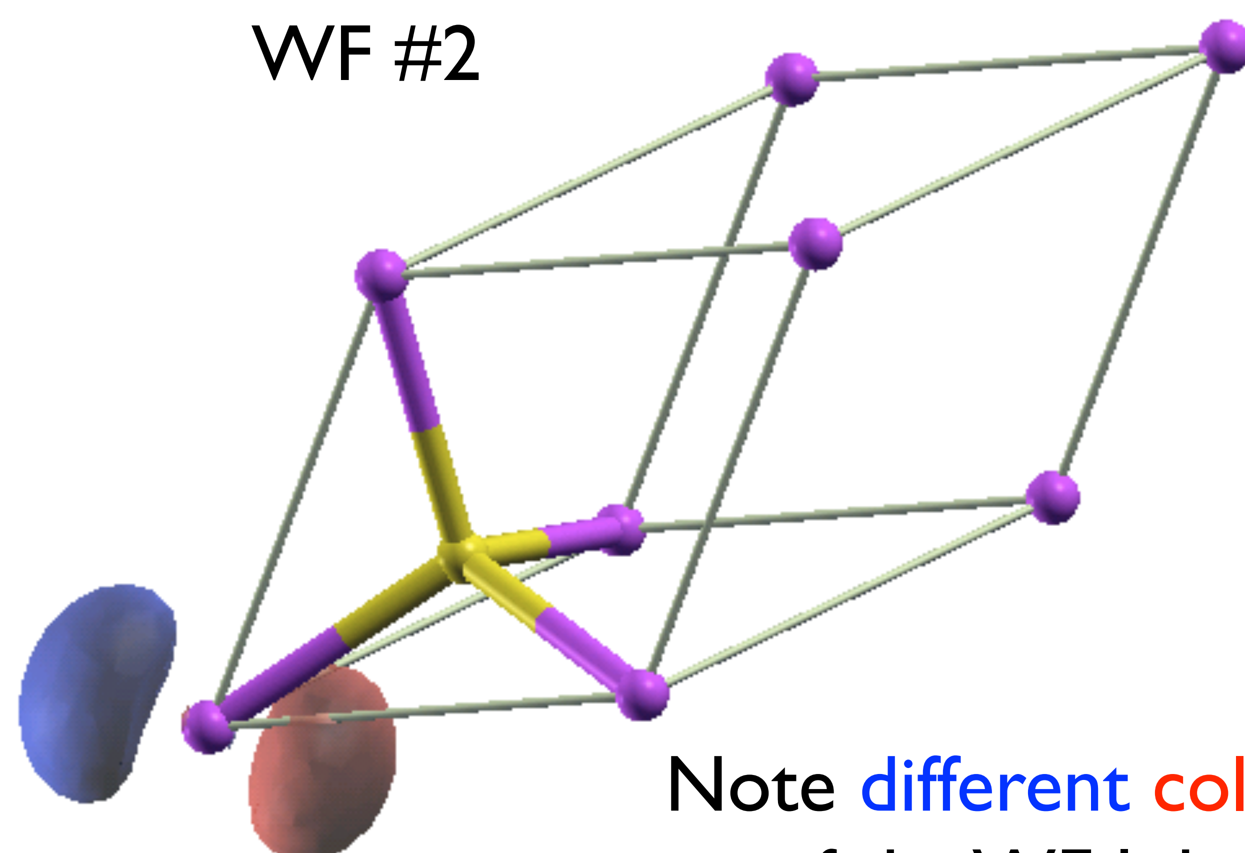
Play with the settings. You will get a spherical (s-like) WF centred at the origin.

The second WF resamples p-orbital (you can get it by editing “GaAs-WANN.inwplot”, re-run “`x wplot`” and “`wplot2xsf`”). The new file should be called **`GaAs-WANN_2.xsf`**

WF #1



WF #2



Note different colours of the WF lobes

Wannier Hamiltonian (similar to LCAO)

```
$  less GaAs-WANN_hr.dat
...
   0     0     0     1     1    -4.335108     0.000000
   0     0     0     2     1    -0.000001     0.000000
   0     0     0     3     1     0.000000     0.000000
   0     0     0     4     1    -0.000001     0.000000
   0     0     0     5     1    -1.472358     0.000000
   0     0     0     6     1    -1.157088     0.000000
   0     0     0     7     1    -1.157088     0.000000
   0     0     0     8     1    -1.157088     0.000000
...
```

Home unit cell

$\langle s_I|$ $|s_I\rangle$

Matrix element (eV) $\langle s_I|H|s_I\rangle = E_{sI}$

no imag. part of the matrix element

no on-site hopping between different orbitals

Determine on site energies E_s and E_p for Ga and As and compare them to those suggested by Harrison (note: only their relative differences are important)

From Harrison's solid state tables:

$E_p(Ga) - E_s(Ga) = 5.9$ eV

$E_p(As) - E_s(As) = 9.9$ eV

$E_p(Ga) - E_p(As) = 3.3$ eV

Wannier Hamiltonian (cont.)

Matrix element (eV)
$\langle s_2|H|s_1\rangle = V_{ss\sigma}$

```
...
      0       0       0       1       1    -4.335108     0.000000
      0       0       0       2       1    -0.000001     0.000000
      0       0       0       3       1     0.000000     0.000000
      0       0       0       4       1    -0.000001     0.000000
      0       0       0       5       1    -1.472358     0.000000
      0       0       0       6       1    -1.157088     0.000000
      0       0       0       7       1    -1.157088     0.000000
      0       0       0       8       1    -1.157088     0.000000
...
      0       0       1       1       1    -0.001219     0.000000
```

$\langle s_2|$

Neighbour unit cell

WF are well localized
⇒ nearest-neighbour suffice

$\langle p_2|H|s_1\rangle = V_{sp}$

Now you have all information required to build your *ab initio* TB sp3 Hamiltonian (Yu & Cardona)

Table 2.25. Matrix for the eight s and p bands in the diamond structure within the tight binding approximation

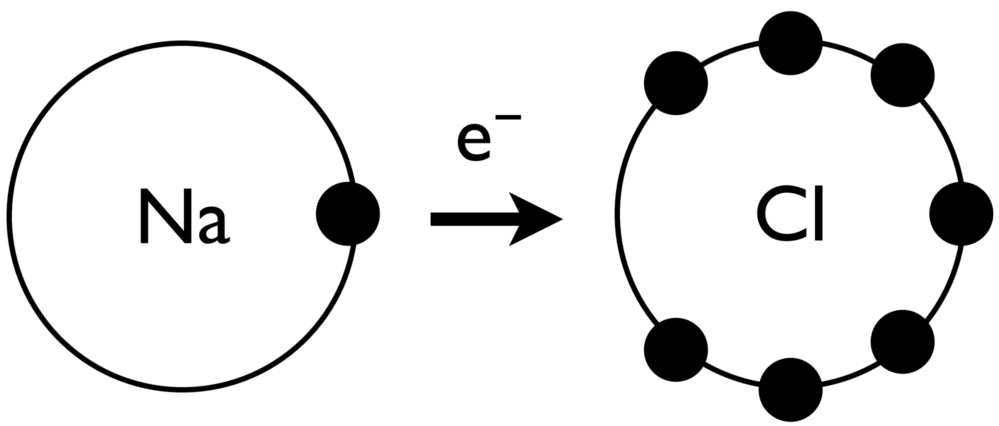
	$S1$	$S2$	$X1$	$Y1$	$Z1$	$X2$	$Y2$	$Z2$
$S1$	$E_s - E_k$	$V_{ss}g_1$	0	0	0	$V_{sp}g_2$	$V_{sp}g_3$	$V_{sp}g_4$
$S2$	$V_{ss}g_1^*$	$E_s - E_k$	$-V_{sp}g_2^*$	$-V_{sp}g_3^*$	$-V_{sp}g_4^*$	0	0	0
$X1$	0	$-V_{sp}g_2$	$E_p - E_k$	0	0	$V_{xx}g_1$	$V_{xy}g_4$	$V_{xy}g_3$
$Y1$	0	$-V_{sp}g_3$	0	$E_p - E_k$	0	$V_{xy}g_4$	$V_{xx}g_1$	$V_{xy}g_2$
$Z1$	0	$-V_{sp}g_4$	0	0	$E_p - E_k$	$V_{xy}g_3$	$V_{xy}g_2$	$V_{xx}g_1$
$X2$	$V_{sp}g_2^*$	0	$V_{xx}g_1^*$	$V_{xy}g_4^*$	$V_{xy}g_3^*$	$E_p - E_k$	0	0
$Y2$	$V_{sp}g_3^*$	0	$V_{xy}g_4^*$	$V_{xx}g_1^*$	$V_{xy}g_2^*$	0	$E_p - E_k$	0
$Z2$	$V_{sp}g_4^*$	0	$V_{xy}g_3^*$	$V_{xy}g_2^*$	$V_{xx}g_1^*$	0	0	$E_p - E_k$

Born effective charge of GaN

\+ + BerryPI

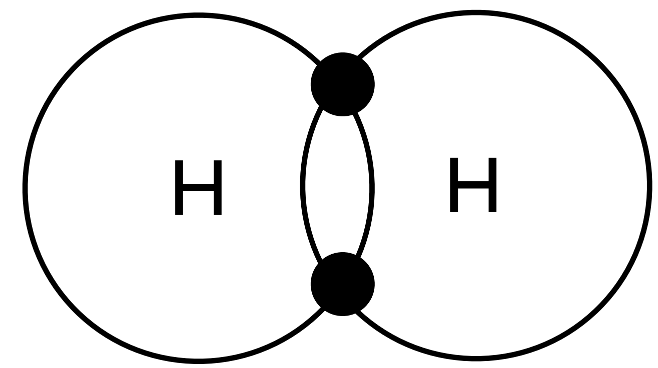
Background

Ionic bond



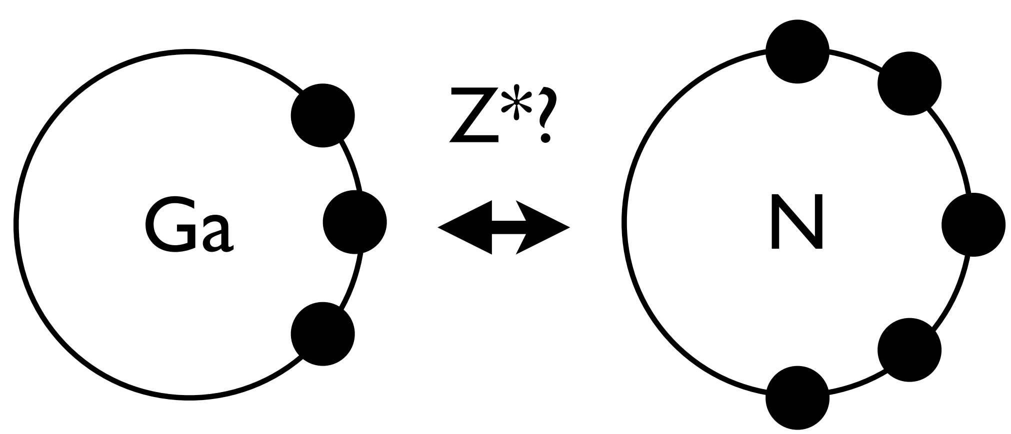
$Z^* = +1$ $Z^* = -1$

Covalent bond



$Z^* = 0$

Mixed



Instructions

w2web Construct a structure file (`../GaN-W/GaN-W.struct`)

4-atoms (2-Ga, 2-N) per unit cell

Hexagonal lattice "H", $\alpha = \beta = 90°$, $\gamma = 120°$

Cell size (Bohr): a = b = 5.963131; c = 9.722374

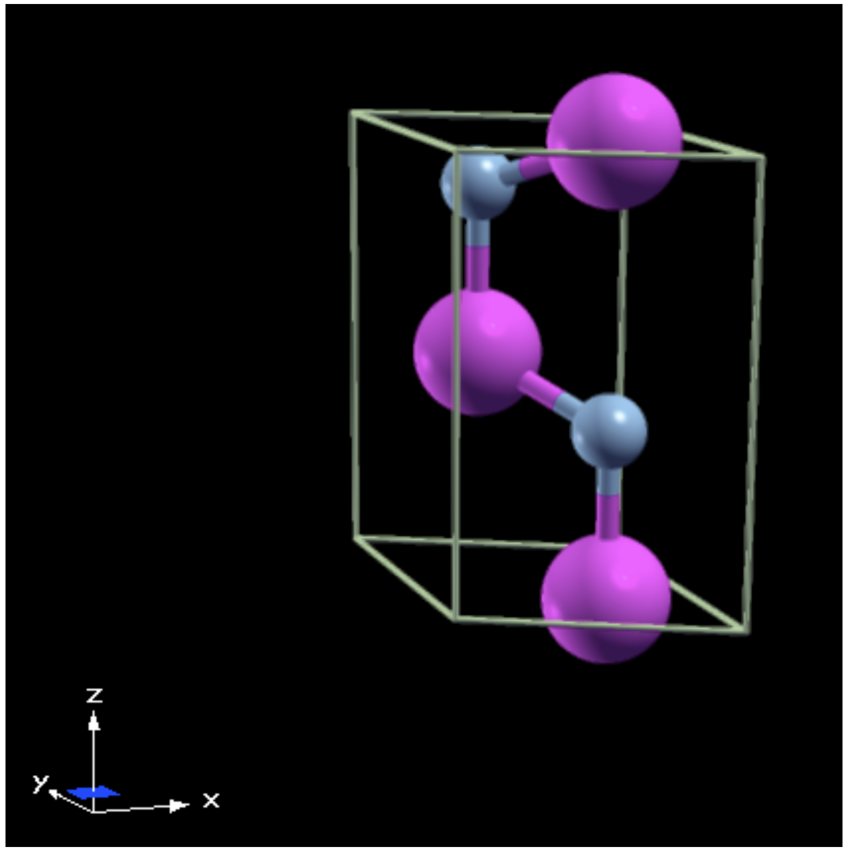
Coordinates:

Ga (2/3 1/3 0)

Ga (1/3 2/3 1/2)

N (2/3 1/3 0.376393)

N (1/3 2/3 0.876393)



Initialize SCF calculation (LDA).

```
$ init_lapw -b -vxc 5 -rkmax 7 -numk 300
```

It is worth to verify the structure with XCrysDen

Perform regular SCF calculation

```
$ run_lapw
```

Run Berry phase calculation

```
$ berrypi -k 8:8:4 | tee log
```

Note the ionic and electronic phases alone Z-axis (wrapped [-π…+π])

Save the calculation

```
$ save_lapw -d Lambda0
```

Introduce small displacement on N-atoms

w2web Edit Z-coordinate of N atoms by adding 0.001 to the equilibrium value of the fractional coordinate u_z. Since nitrogen has 2 equivalent positions, both need to be updated. Think what is the reason for the need to shift both atoms in this case.

Repeat initialization, SCF and Berry phase calculation steps (note "-a" option used in order to update the log file, not overwrite)

```
$ init_lapw -b -vxc 5 -rkmax 7 -numk 300
$ run_lapw
$ berrypi -k 8:8:4 | tee -a log
```

Evaluate the total Berry phase for each of two calculations performed

$$\phi = \phi_{\mathrm{el}} + \phi_{\mathrm{ion}}$$

and its change

$$\Delta\phi = \phi(\mathrm{perturbed}) - \phi(\mathrm{unperturbed})$$

Compute the effective charge Z* of Nitrogen in GaN using a Berry phases and the "shortcut" expression

$$Z^*_{ii} = \frac{\Delta\phi_i}{2\pi\Delta u_i}$$

Here Δ*u* is the displacement in fractional coordinates. The equation applies to the case of one atom displaced. In our case, we need to take into account that 2 N-atoms were shifted.

Compare computed Z* with the literature value of -2.74 [Volume 44D of the series Landolt-Börnstein - Group III Condensed Matter pp 420-423, "GaN: effective charge, dielectric constants" by D. Strauch]

What is the effective change of Ga in this structure?