Exercises:

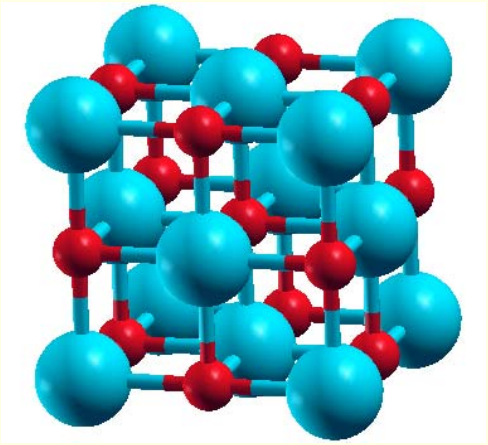
- In the following you find some suggestions for exercises, which teach you various tasks one may perform with WIEN2k.
- Please note, that often “calculational parameters” are set to “minimal cpu-time” instead of “fully converged calculations”.
- Do not use such small values for final results and publications without convergence checks !!

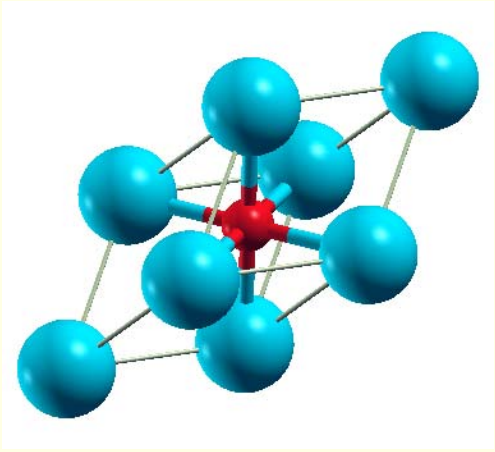
setup of environment

- start **exceed** as indicated on the workshop website
- open a terminal and edit .bashrc (insert: source /gpfs/group/wien2013/rctemplate)
- close this terminal window and reopen another one
- now you are ready to start w2web. Type:
  - w2web
    - at the first time define your userid/pw, port-number (use 8XXX; where XXX refers to your userid uprmiXXX). Note: it will tell you the address and port to connect via a web-browser !
- connect to w2web via a webbrowser (firefox)

Exercise 1: Getting started:

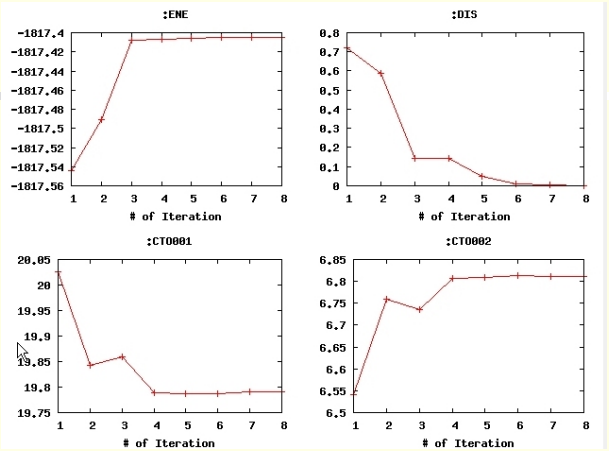
- i) Open a terminal window (skip points i-iii if done before)
- ii) Start w2web (accept all defaults, specify account, port)
- iii) Connect with firefox to w2web as indicated on the screen of ii)
- iv) Try the "quick-start" example for **TiN** (similar to TiC in the UG)
  - *Generate structure (a=4.235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





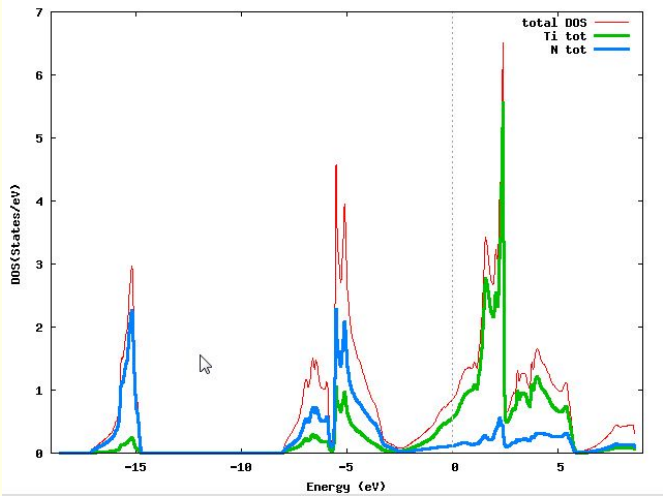
  - *init_lapw (use defaults, 1000 k-points)*
  - *scf-cycle (run_lapw, use defaults; monitor "STDOUT" and "dayfile")*
    - How many iterations did you need ? How long took a single scf-iteration ?

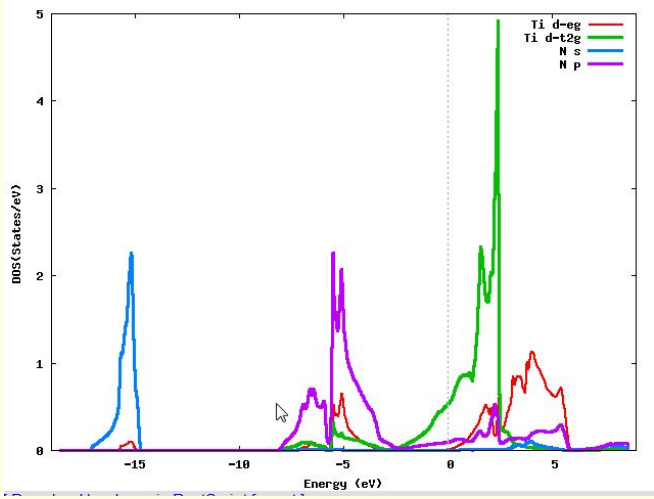
TiN continued



- *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)*

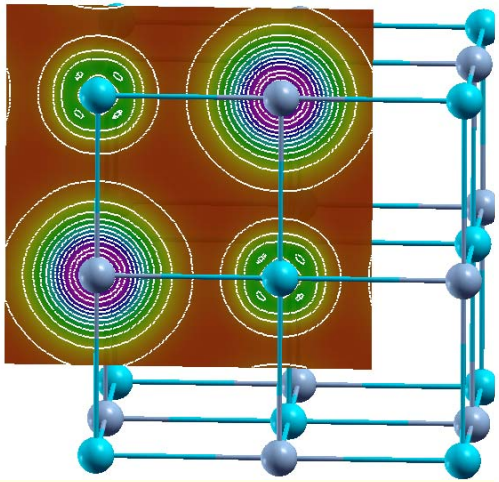




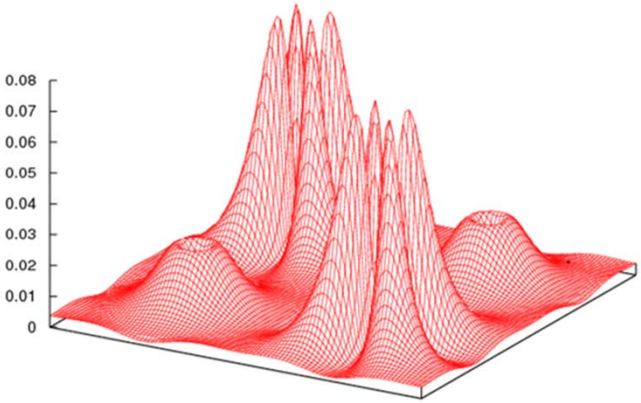
TiN continued ...

- *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

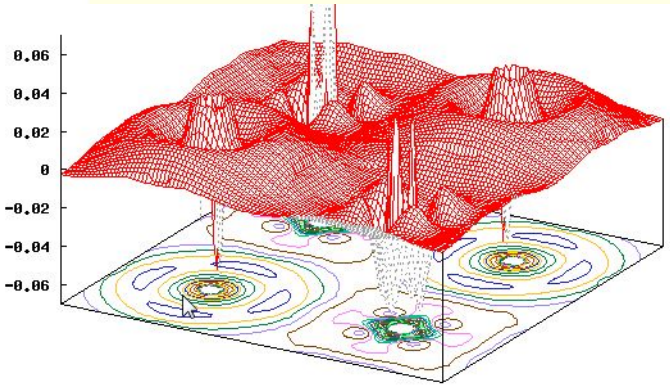
valence ρ



Ti-d band

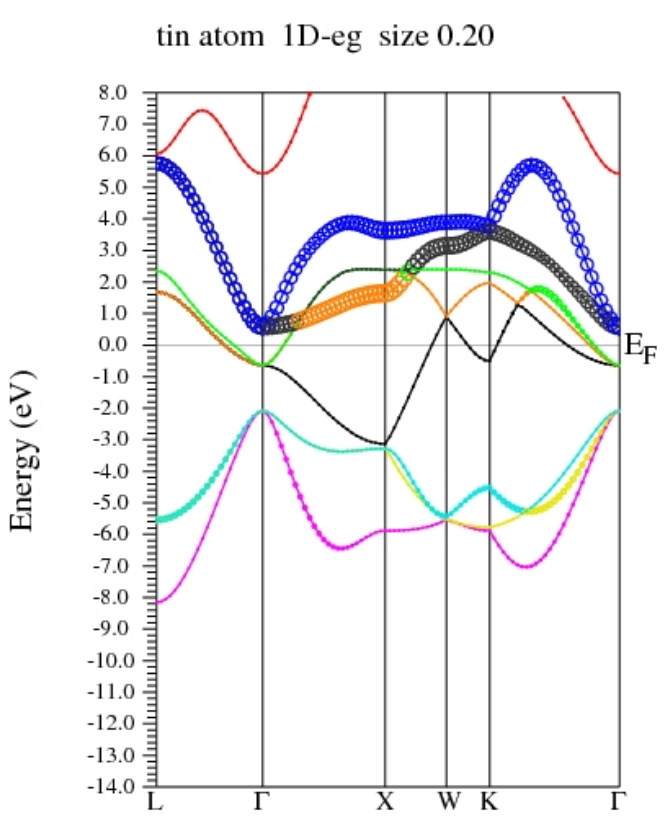


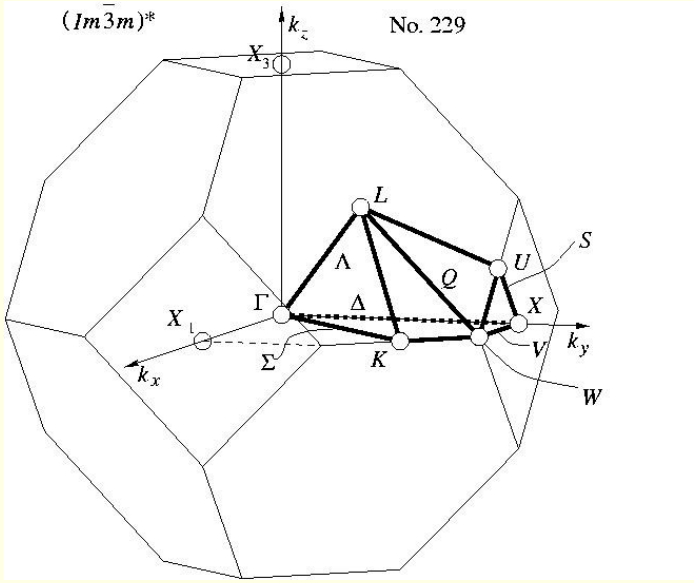
difference density



TiN continued

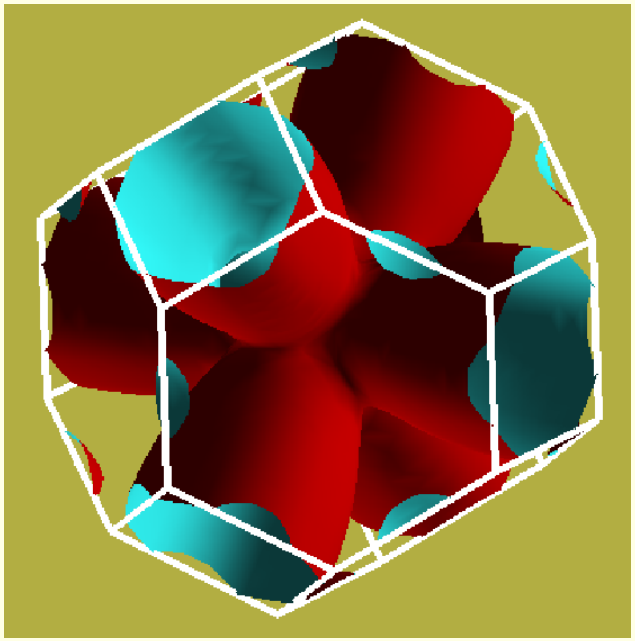
- bandstructure (along L-Gamma-X-W-K-Gamma with “character plotting”)
  - *use xcrysden (save as „xcrysden.klist“; select „from xcrysden“ in next step and click generate k-mesh)*
  - *identify “t2g-” and “eg-” bands (fat band plots)*





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); (DON'T CHANGE to UNIT 5 !!!)
    - 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

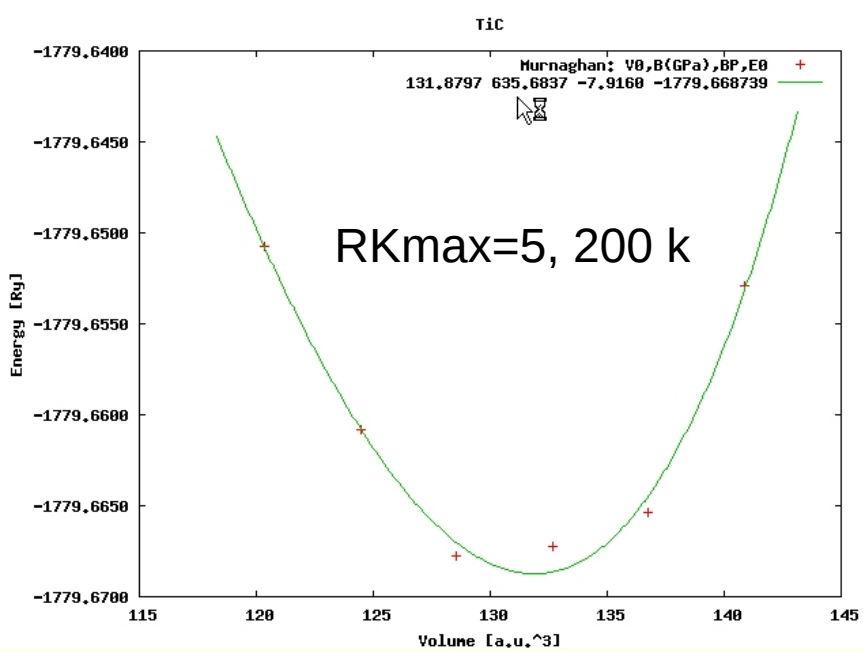
- TiC (fcc, **a=4.328** Ang, **setrmt 4%**)
- a) initialize in expert mode with **LDA, RKmax=5, 200 k-points** (bad values, on purpose !!)
- b) run x optimize and generate 6 structures (-12, -9, -6, -3, 0, 3% volume change)
  - *(because of LDA we expect 1-2% smaller lattice parameter (3-8% in volume) than experiment)*
- c) edit "optimize.job". Modify the “run_lapw” and "save_lapw" commands to:
  - *run_lapw –cc 0.001 –ec 0.0001*
  - *save_lapw ${i}_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 modify:
  - *cp ${i}_rkm5_200k.clmsum TiC.clmsum # Using previously converged densities saves a lot of CPU time!!*
  - *...*
  - *save_lapw ${i}_rkm6.5_1000k*
- g) repeat step d) (plot the results for “*_rkm6.5_1000k”)

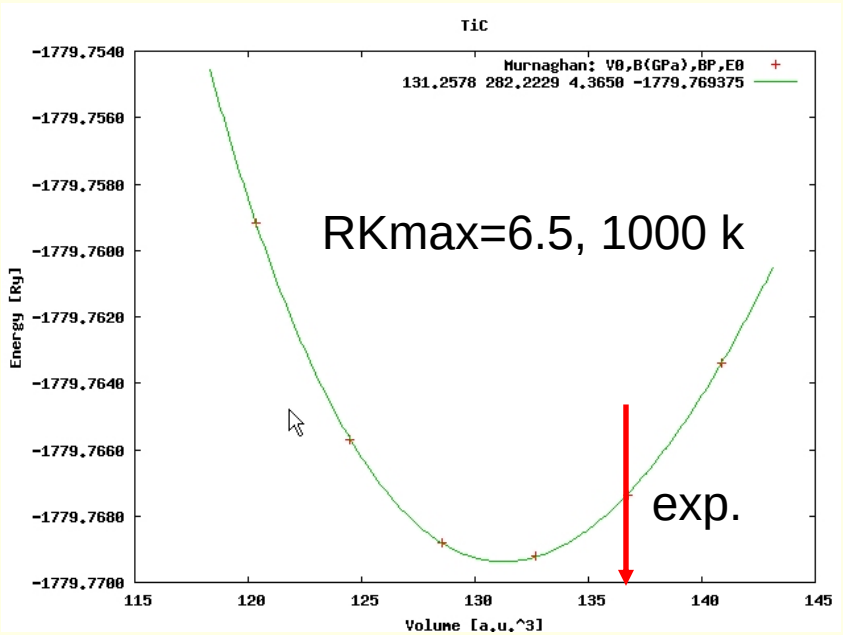
- *Find out how RKmax and k-points lead to smooth/non-smooth curves. Estimate good values and compare in particular B and BP (Bulkmodulus and its volume derivative). Fully converged results would require RKmax=8 - 9 , 10000 k and 10 volumes with ΔV=1%.*
- *You may also do this with another XC-potential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

- 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 !!*

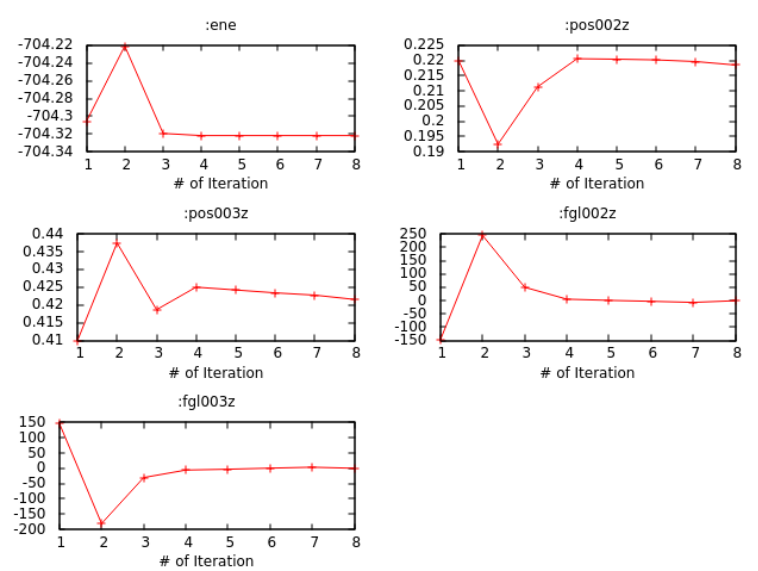
Volume optimization for TiC

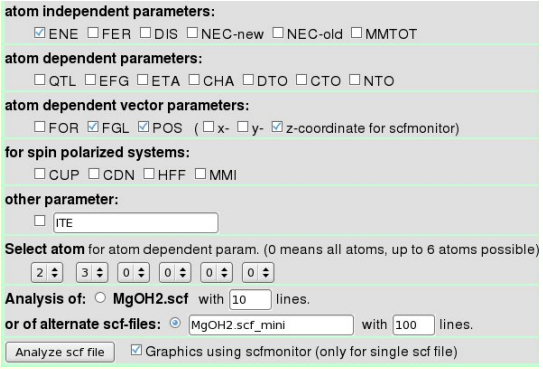




Exercise 3: optimization of positions in $Mg(OH)_2$

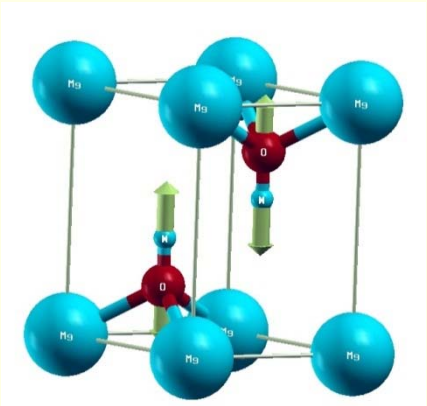
- **create two "cases" (directories) for PORT and MSR1a optimization**
  - *initialize both cases (or copy after init one case to the other and use „rename_files")*
  - *P-3m1 (164), a=b=3.15 c=4.77 Å γ=120°; Mg(0,0,0) O(1/3,2/3,**0.22**) H(1/3,2/3,**0.41**); RMT: reduce by 7%*
  - *init_lapw -b –numk 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)*

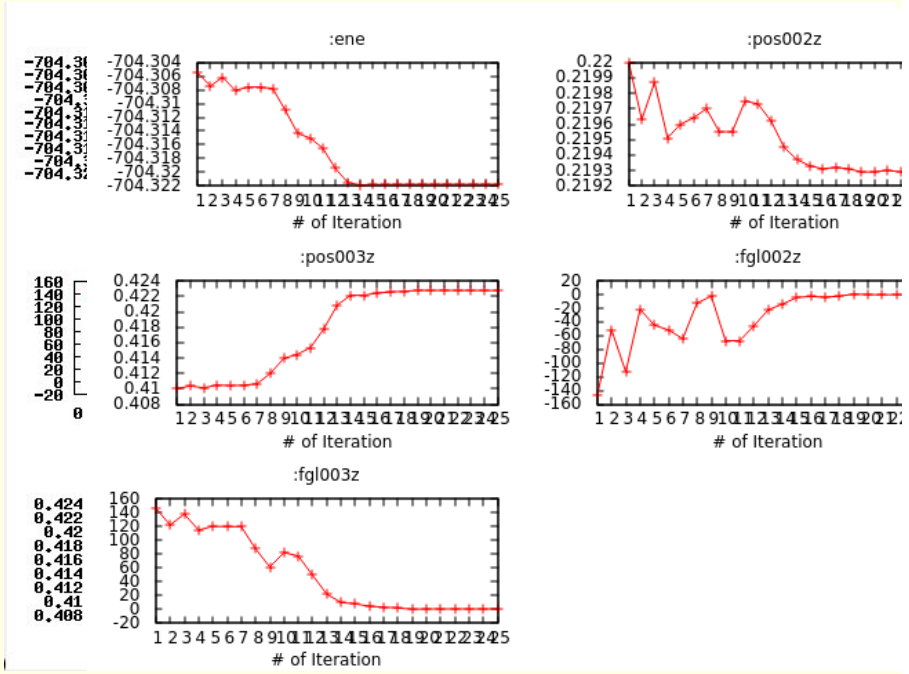




$Mg(OH)_2$ continue

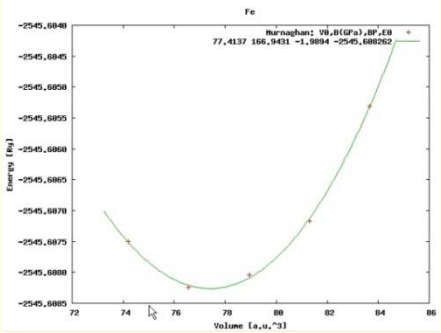
- minimization using MSR1a:
  - *run crude scf cycle to come closer to „Born-Oppenheimer“ surface*
    - run –fc 5; save_lapw case_initial
  - *change MSR1 to MSR1a in case.inm, optimize using:*
    - run –fc 1 –cc 0.0001 –ec 0.00001
  - *analyze **case.scf*** and find out how many scf cycles you needed
    - :ENE :FGL002z :POS002z :FGL003z :POS003z :ITE
  - *save_lapw case_final*
  - *use the „arrows“ utility to display initial forces and final relaxations (see UG p.168)*





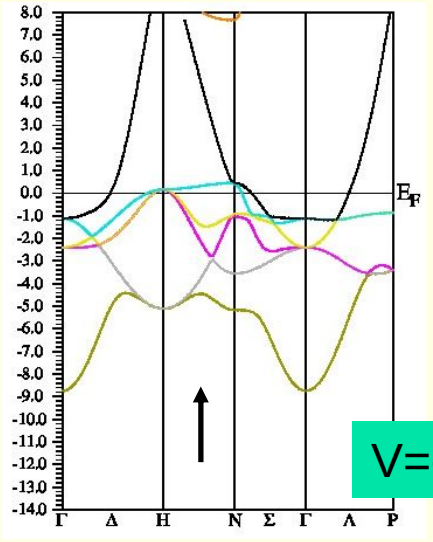
Exercise 4:

- 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

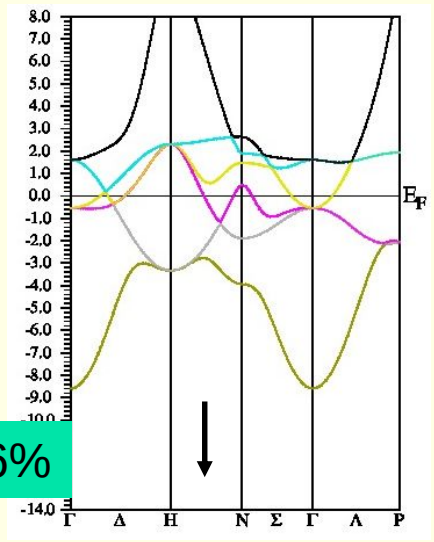


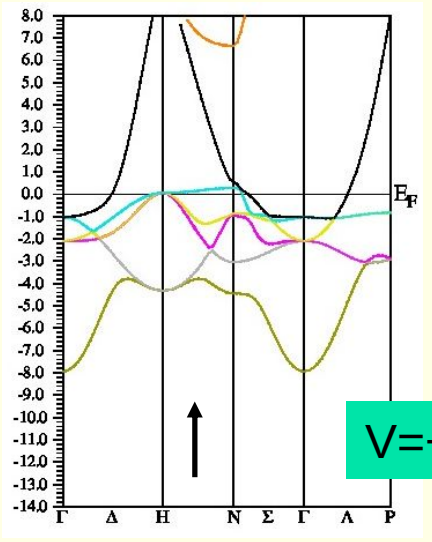
--- MMTOT ---------- in 5 files:
Fe_vol___0.0_rk8_5000k.scf::MMTOT: 2.21
Fe_vol___3.0_rk8_5000k.scf::MMTOT: 2.26
Fe_vol__-3.0_rk8_5000k.scf::MMTOT: 2.16
Fe_vol___6.0_rk8_5000k.scf::MMTOT: 2.31
Fe_vol__-6.0_rk8_5000k.scf::MMTOT: 2.13

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

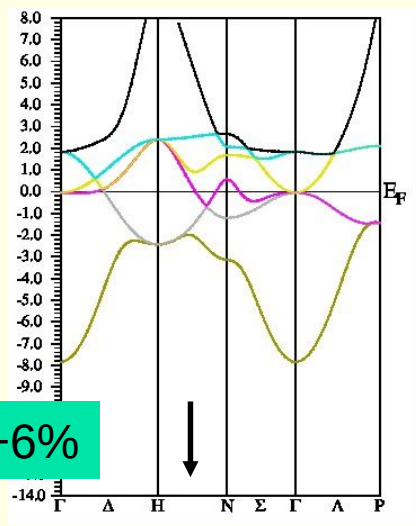


V=-6%



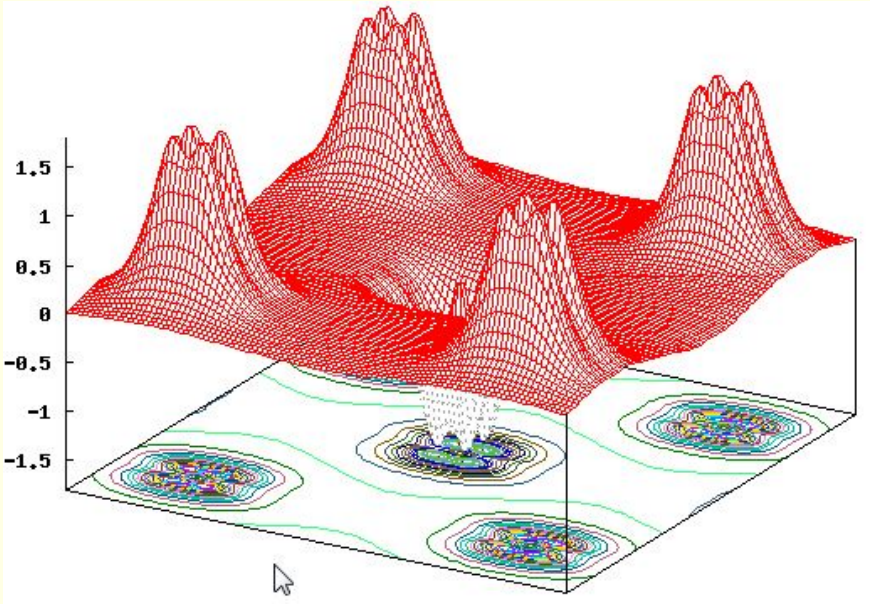


V=+6%



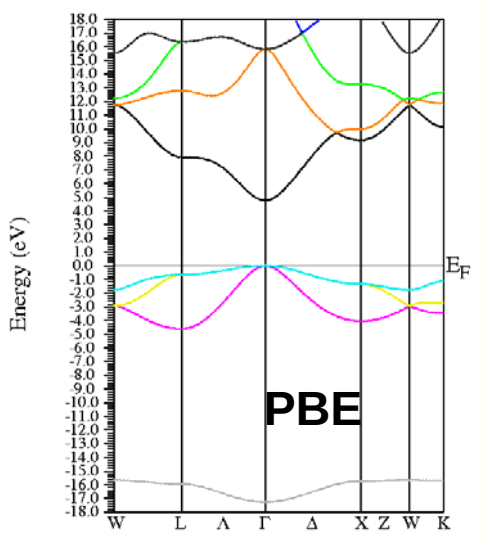
Exercise 4:

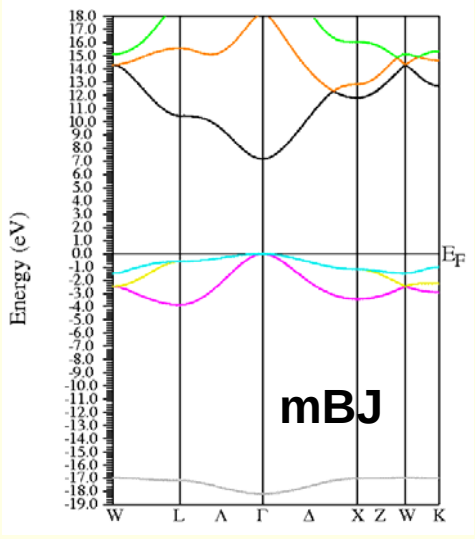
- Antiferromagnetism: bcc Cr (a_0=2.885 Å) (use 5000k, -cc 0.001)
  - *try a ferromagnetic solution (bcc cell with 1 Cr)*
  - *antiferromagnetic calculation (P cell with Cr1 and Cr2 (at 0.5,0.5,0.5))*
    - choose up/dn for the two Fe atoms when creating case.insp
    - for afminput your symmetry operation is “identity+(0.5,0.5,0.5)”
  - *is FM or AFM Cr more stable? (:ENE :-2101.769475 vs. -4203.543208 Ry)*
  - *is FM stable at all ? check moments (MMI001: 0.000 vs. 1.116μ_B; what “means” 0.0 ???)*
  - *plot spin-densities in the (110) planes*
    - observe “spatial localization”
    - t_{2g}-asymmetry
    - negative spin-density in interstitial
      - where does it come from ?
      - compare :QTLxxx

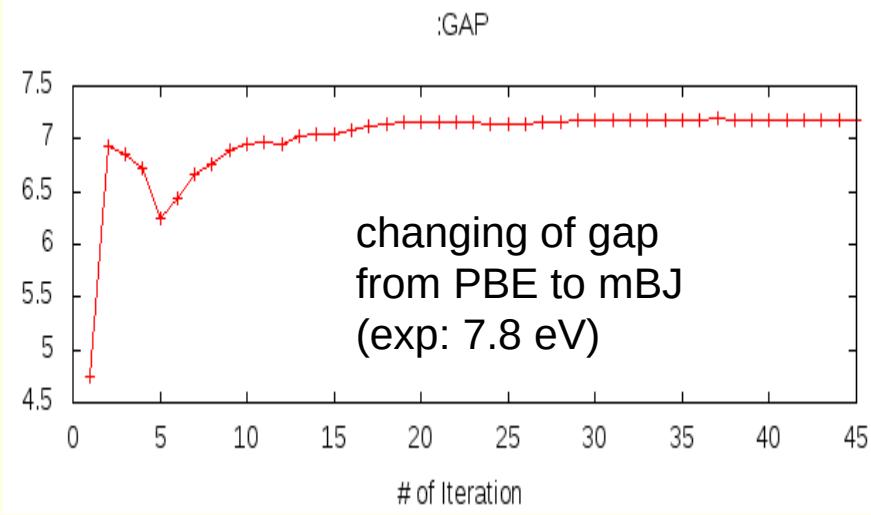


Exercise 5: band gaps of MgO

- 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

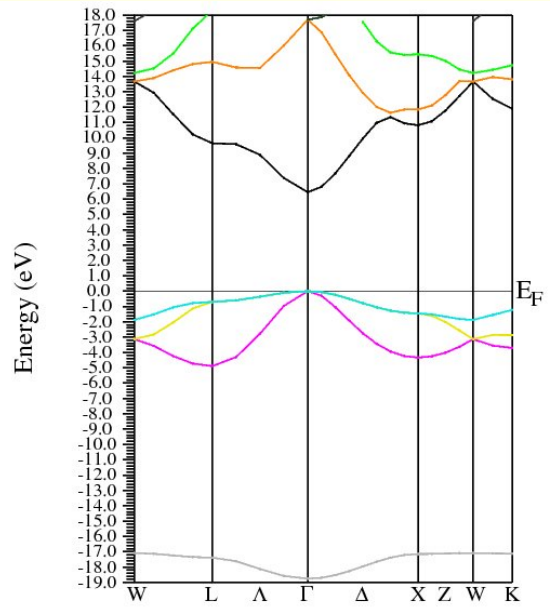






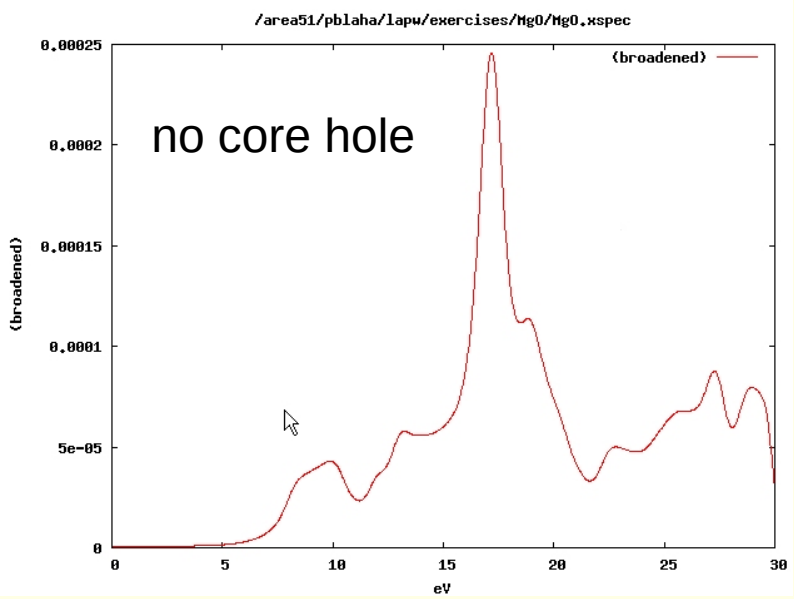
Exercise 5: continued ...

- 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** (insert 4 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

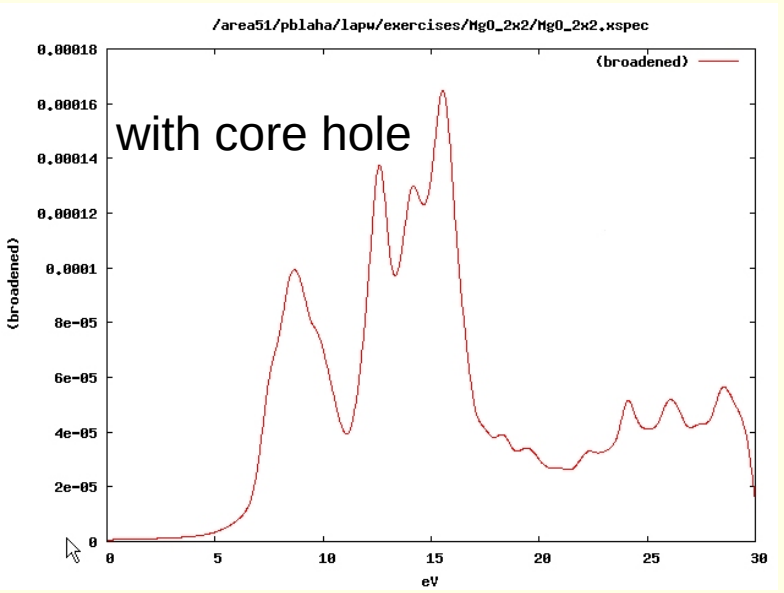


Exercise 6: Mg K-XAS in MgO

- 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 7:

- LDA+U: NiO: NaCl structure, A-type AFM along [111]
  - *R-cell: 5.605236 5.605236 27.459934 bohr*
  - *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...

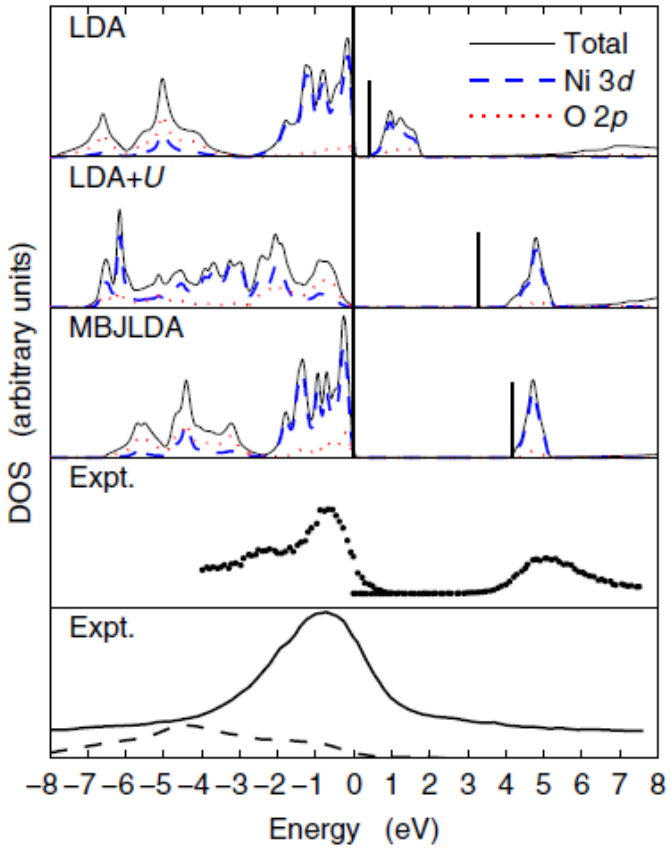
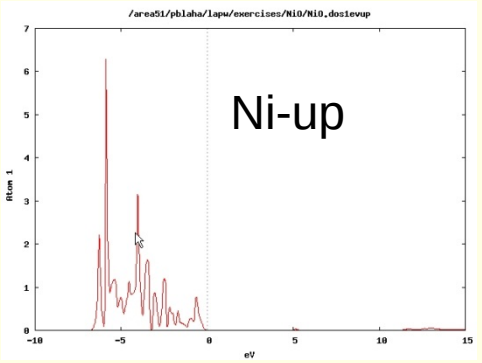
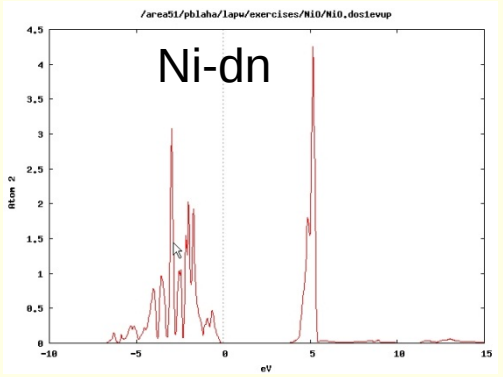


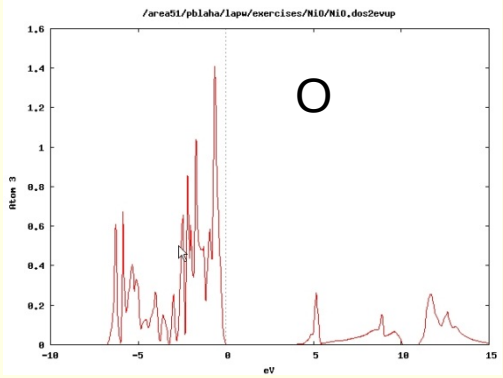
FIG. 2 (color online). DOS of NiO. The vertical bars indicate the end of the fundamental band gap which starts at $E = 0$ eV. The panels labeled "Expt." show photoelectron [25] (upper panel) and XES [33] [lower panel, Ni (solid line) and O (dashed line) spectra] measurements.

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

GGA+U



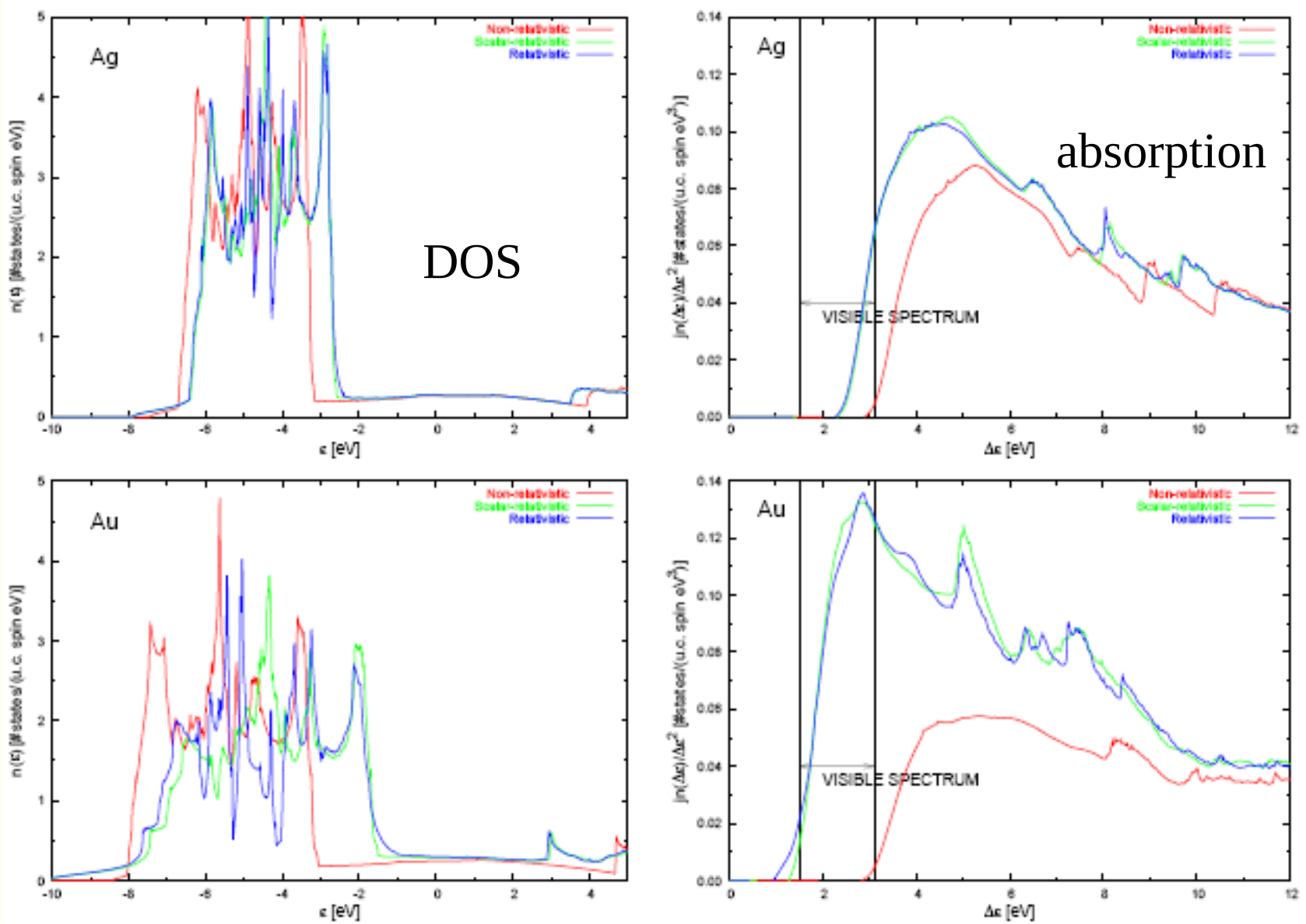




Exercise 7:

- 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 9: O-NMR of tetragonal $BaTiO_3$

- This exercise should be done WITHOUT w2web !
- cd work; mkdir BaTiO3; cd BaTiO3
- 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 BaTiO3.struct
- init_lapw -b (expert mode with defaults)
- edit .machines (insert 4 lines with 1:localhost)
- run_lapw -p -fc 1
- 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
  - *tail BaTiO3.outputnmr_integ*
  - *grep :EFG *scf0*
  - *grep :ETA *scf0*
  - *the exp. shifts are 564 and 523 ppm. Find out, which O-atom corresponds to the large/small shielding. (Unfortunately exp. EFGs are not available)*