



Exercises:



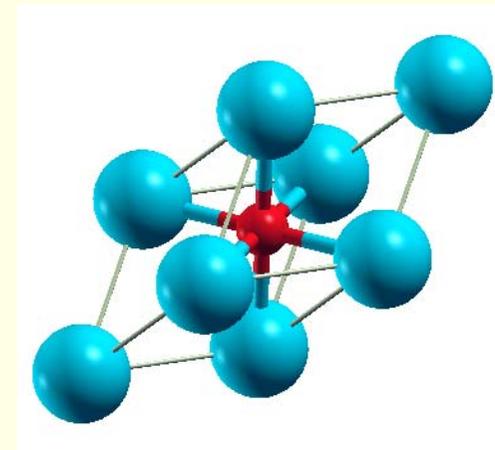
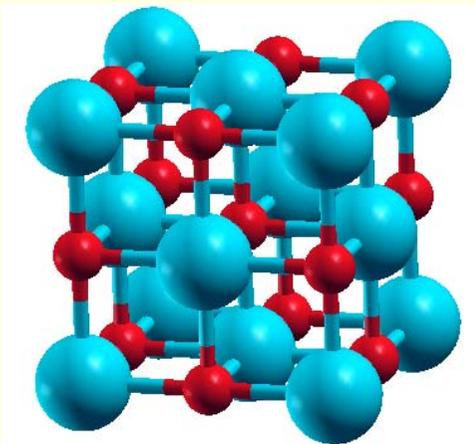
- In the following you find some suggestions for exercises, which teach you various tasks one may perform with WIEN2k.
- Please note, that often “computational parameters” are set to “minimal cpu-time” instead of “fully converged calculations”.
- Do not use such small values for final results and publications 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)
 - *Generate structure (a=4.235 Ang; reduce RMT by 1%)*
 - *view structure with Xcrysden (switch from primitive to conventional cell)*



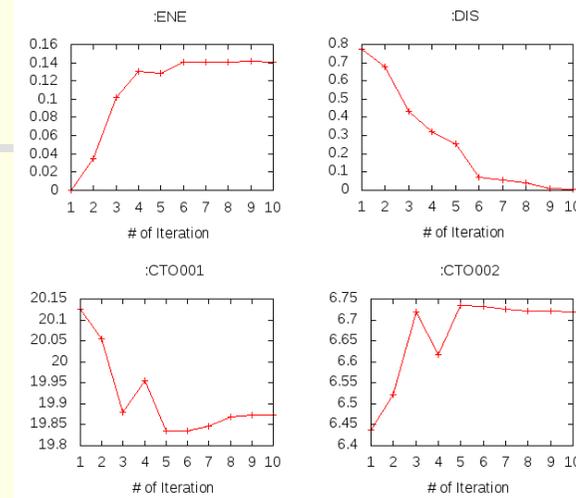
- *init_lapw (use defaults, 1000 k-points)*
- *scf-cycle (run_lapw, use defaults; monitor "STDOUT" and "dayfile")*
 - How many iterations did you need ? How long took a single scf-iteration ?



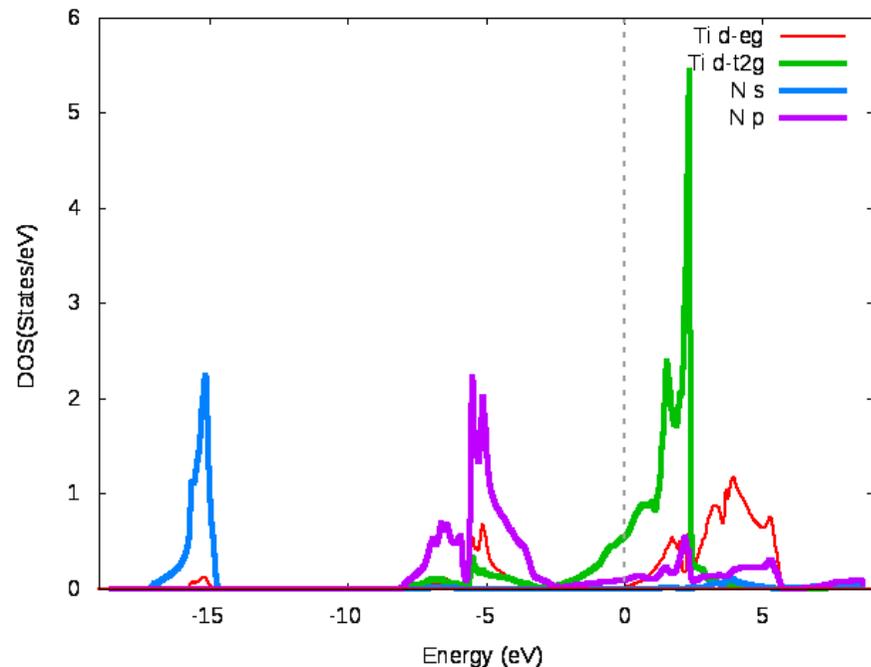
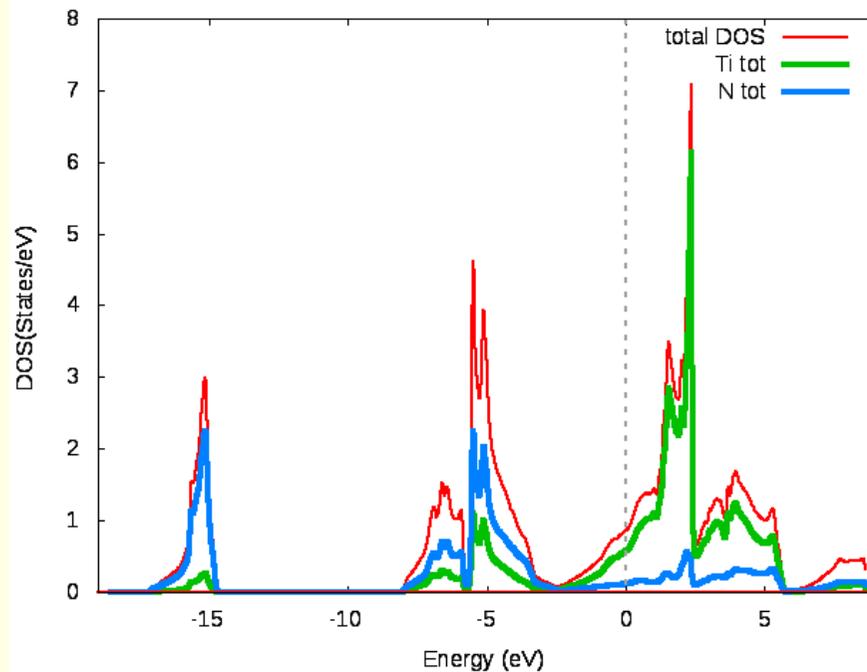
TiN continued



- *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)*



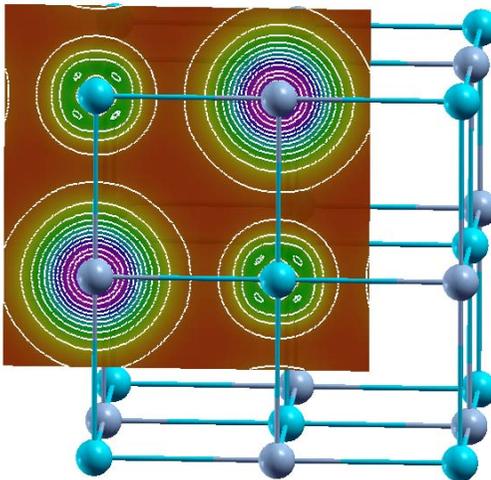


TiN continued ...

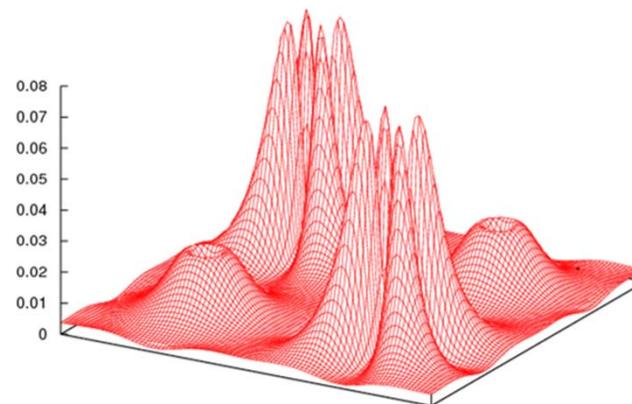


- *electron density* (use *xcrysden* to select the (100) plane), view it in *xcrysden* and *rhoplot* to “understand contour and 3D-plots”)
 - valence density (without semicore, check TiN.scf1 to find a EMIN which truncates the Ti-3s,3p states); compare the density around Ti with TiC (UG)
 - difference 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)

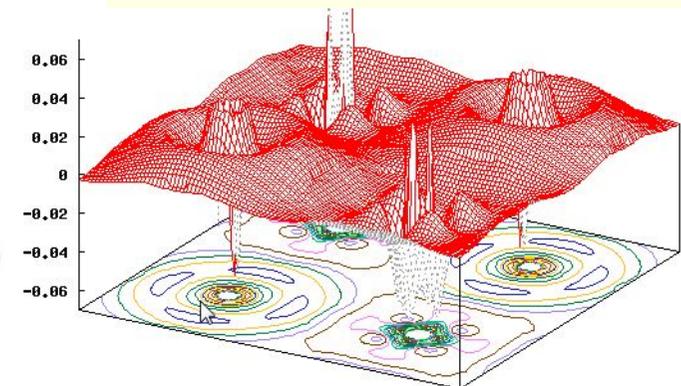
valence ρ



Ti-d band



difference density

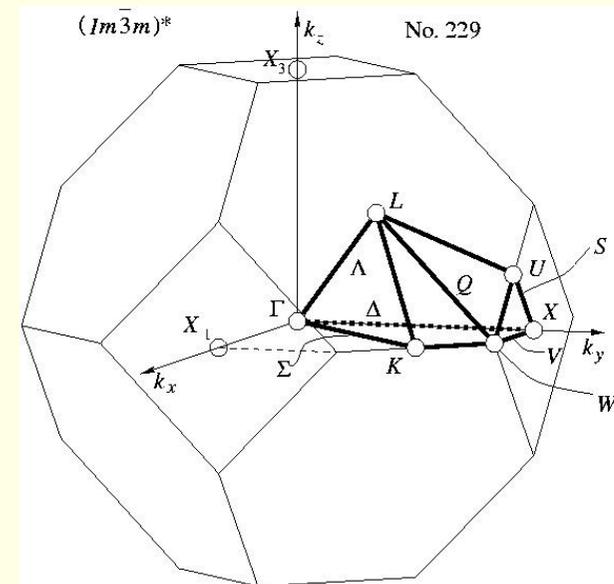
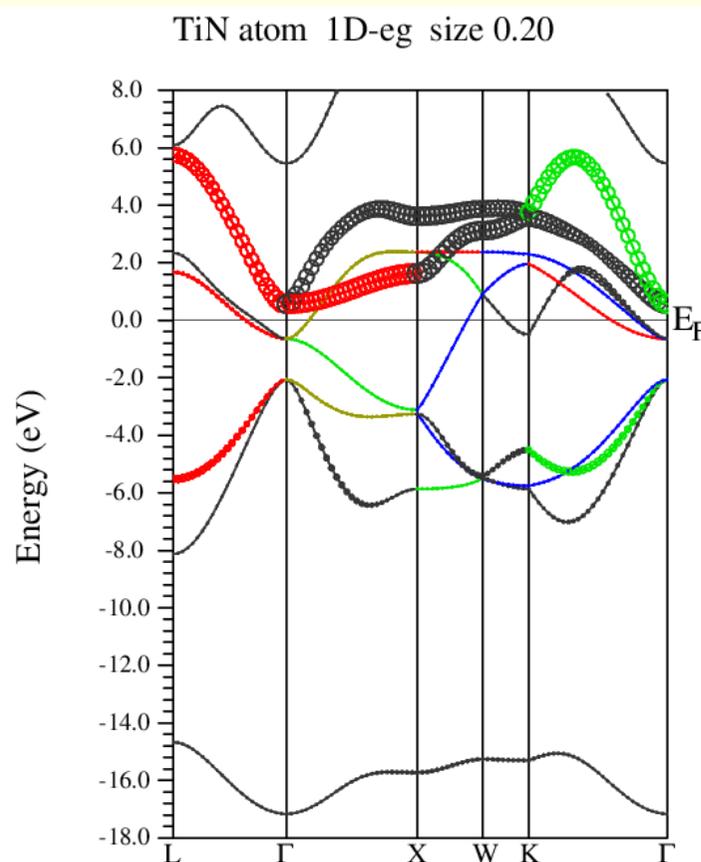




TiN continued



- 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)



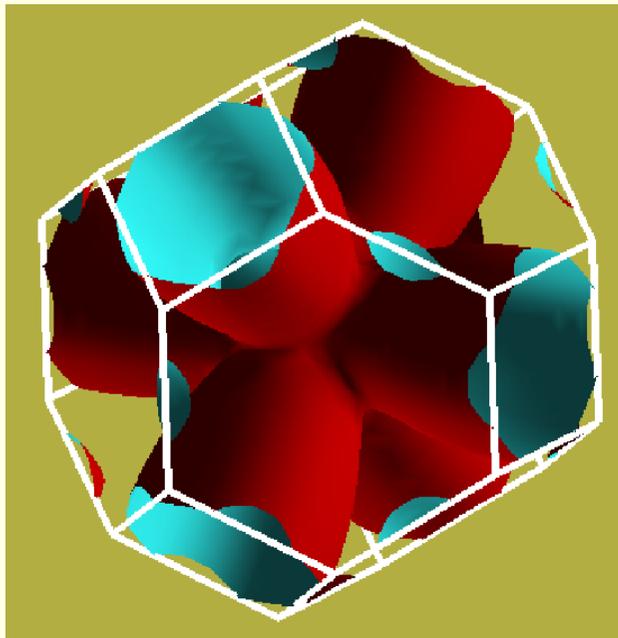


TiN continued ...



■ *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 0.00001`
 - `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")

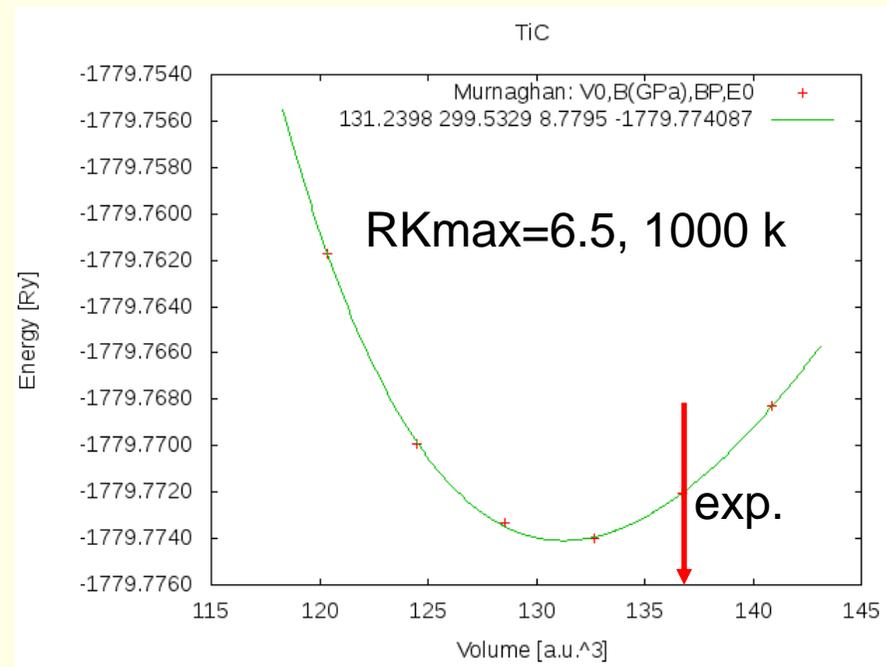
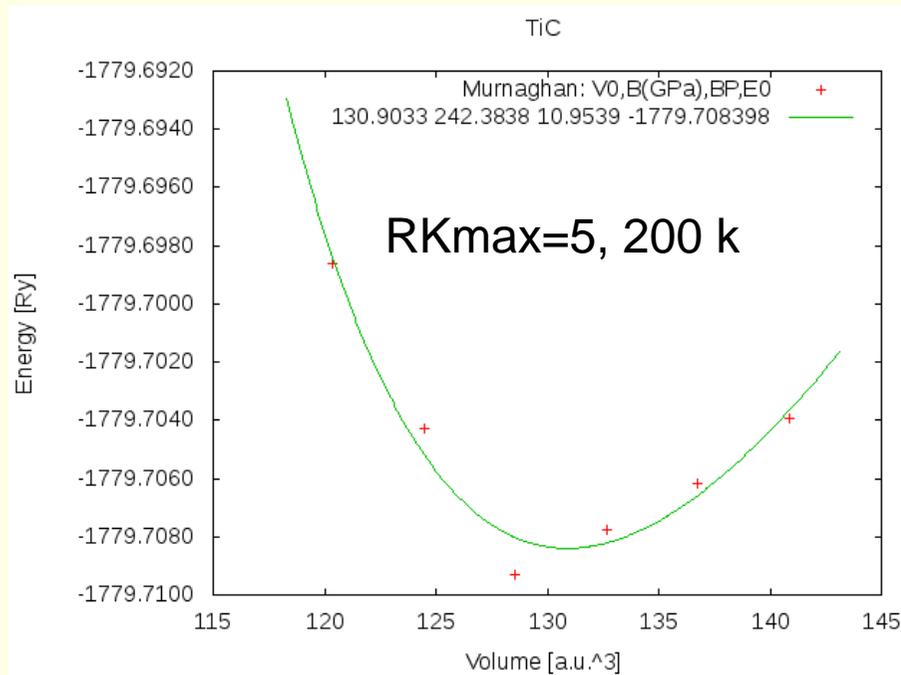
- Find out how RKmax and k-points lead to smooth/non-smooth curves. Estimate good values and compare in particular B and BP (Bulkmodulus and its volume derivative). Fully converged results would require RKmax=8 - 9 , 10000 k and 10 volumes with $\Delta V=1\%$.
- You may also do this with another XC-potential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

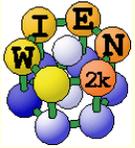
- Remember: Depending on the specific property you want to calculate (just a DOS, or Energy-Volume curves, or EFG, or structure optimization with forces,..) and the desired accuracy, the types of atoms, insulator/metal and system size you may need different RKmax and k-point samplings:
 - H: RKmax > 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 $\text{Mg}(\text{OH})_2$



■ 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 $\gamma=120^\circ$; $\text{Mg}(0,0,0)$ $\text{O}(1/3,2/3,0.22)$
 $\text{H}(1/3,2/3,0.41)$; 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`

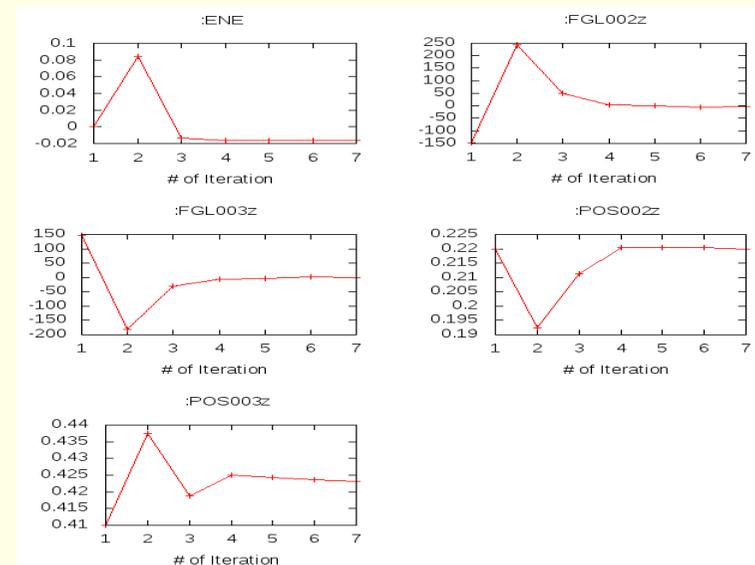
- Find out how many scf cycles you needed

- `grep line :ITE '*scf' 1` (in terminal)

■ check RKMAX convergence:

- increase RKMAX to 3.5 (`case.in1`)

- run `-fc 1` (and check your forces)



atom independent parameters:
 ENE FER DIS NEC-new NEC-old MMTOT

atom dependent parameters:
 QTL EFG ETA CHA DTO CTO NTO

atom dependent vector parameters:
 FOR FGL POS (x- y- z-coordinate for scfmonitor)

for spin polarized systems:
 CUP CDN HFF MMI

other parameter:
 ITE

Select atom for atom dependent param. (0 means all atoms, up to 6 atoms possible)
2 3 0 0 0 0

Analysis of: MgOH2.scf with 10 lines.
or of alternate scf-files: MgOH2.scf_mini with 100 lines.

Analyze scf file Graphics using scfmonitor (only for single scf file)



Mg(OH)₂ continue



■ minimization using MSR1a:

■ ***run -min -fc 1 -cc 0.001 -ec 0.0001***

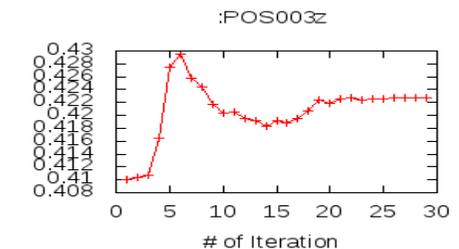
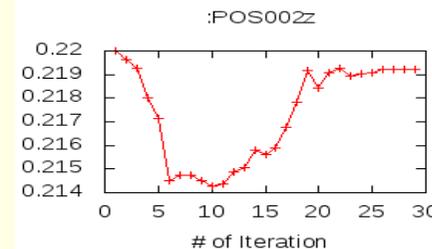
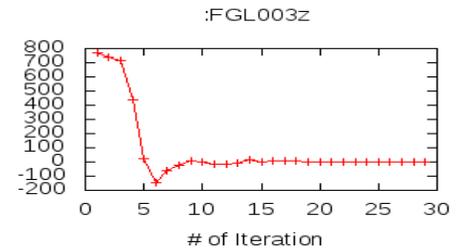
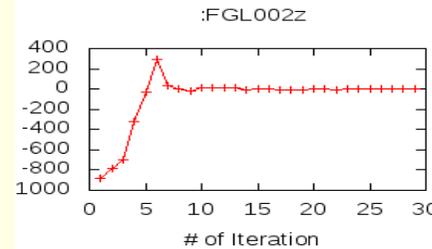
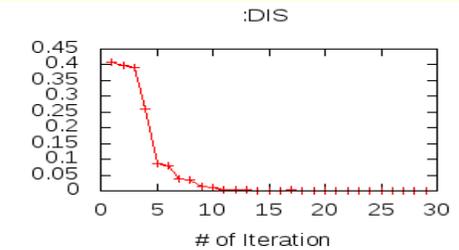
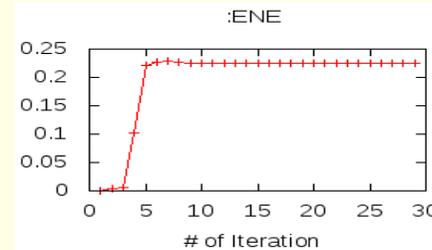
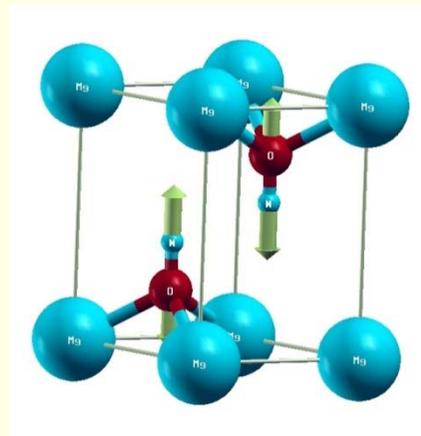
■ -min sets MSR1a in case.inm, (sometimes a crude scf cycle to come closer to „Born-Oppenheimer“ surface is necessary (run -fc 20)

■ ***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.168)***



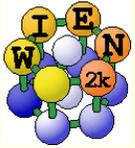


Exercise 4: Creation of supercells



- 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`
- `cp super.struct_nn super.struct`; repeat the `nn` and `cp` steps until errors disappear
- `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 `init_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`
- `cp super.struct_nn super.struct`; repeat the `nn` and `cp` steps until errors disappear
- `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 `init_lapw -b`*
 - *save the structures using `cp super.struct super_32.struct`*

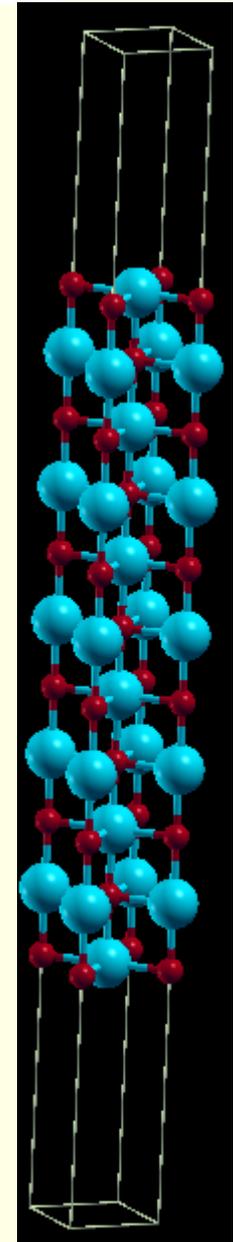
- Instead of labelling "Mg1", one could also **remove** an atom (vacancy) or **replace** an atom by another (impurity).
- Replacing atoms is better done in `w2web`, because this will also update radial meshes. (change **name** of atom AND **remove Z** !!)



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".

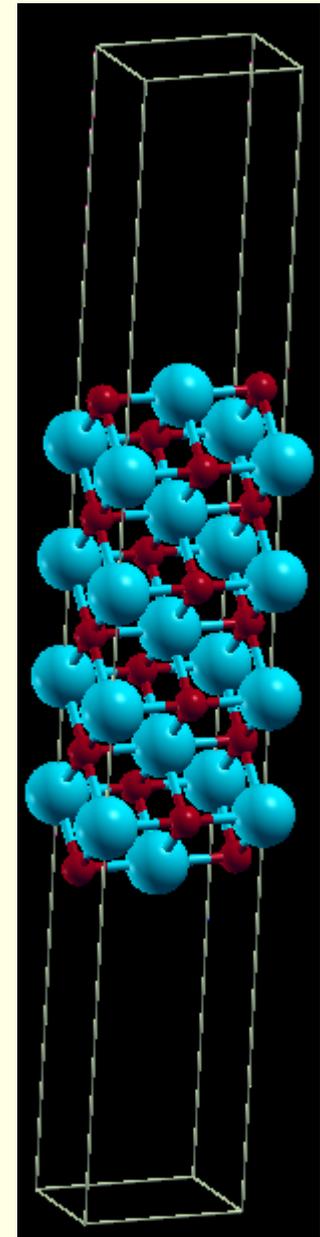




Exercise 4: Creation of supercells (cont.)



- **(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*
- **xcrystden --wien_struct super_super.struct &**
- **x sgroup** and view *super.outputsgroup*
- **cp super.struct_sgroup super.struct**
- **xcrystden --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: Phonons in Si:

■ Calculate the optical Γ phonon in Si:

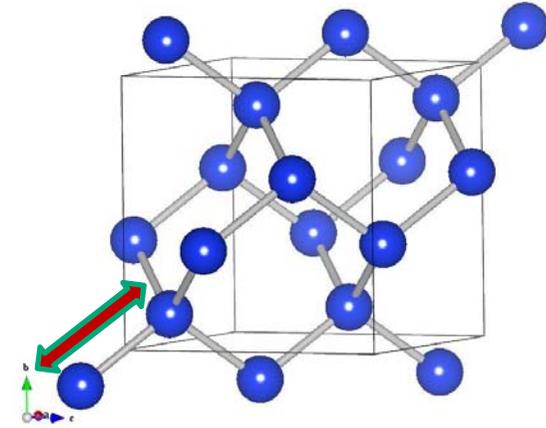
- FCC, $a_0=5.43 \text{ \AA}$; Si at $\pm(.125+x, .125+x, .125+x)$
- use PBE, 500k, -fc 1 -cc 0.001
- Perform calculations with $x=-.005, 0, +.005$
 - (initialization with x.ne.0 to break symmetry !!)
- due to the anharmonicity of the vibration determine the force constant k from the forces (convert them into Ry/bohr) using:

$$\Delta E = \frac{k}{2}u^2 + 4k_{xyz}\left(\frac{u}{\sqrt{3}}\right)^3, \quad F = ku + \frac{4}{\sqrt{3}}k_{xyz}u^2, \quad u = \sqrt{3}xa_0$$

- from k calculate the frequency (exp: 15.53 THz)

$$\omega[\text{THz}] = 108.9 \sqrt{\frac{k}{M}} \quad \text{with } k[\text{Ry / bohr}^2] \text{ and the atomic mass } M (28.0855)$$

$$\text{conversion : } \sqrt{\frac{13.6\text{eV} * 1.6 * 10^{-19} \text{ J / eV}}{1.66 * 10^{-27} \text{ kg}}} / .529177 * 10^{-10} \text{ m} * 241.8\text{THz}$$



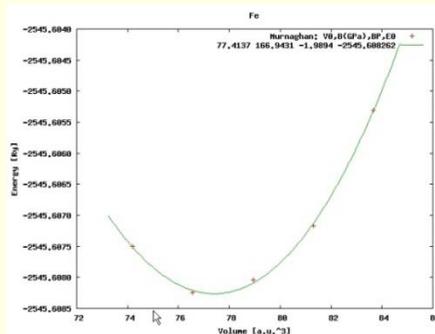


Exercise 6:



■ Magnetism: bcc Fe ($a_0=2.86 \text{ \AA}$)

- *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, :MMTOT as function of volume*



--- MMTOT ----- in 5 files:

Fe_vol__0.0_rk8_5000k.scf::MMTOT: 2.21

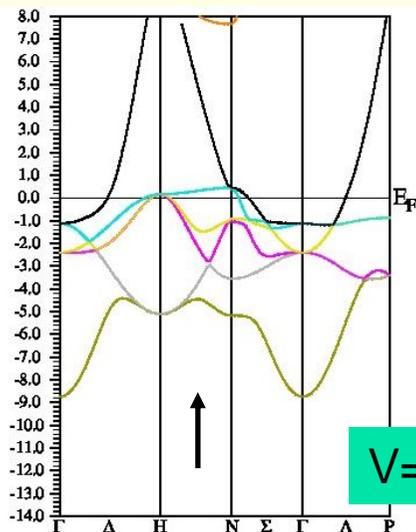
Fe_vol__3.0_rk8_5000k.scf::MMTOT: 2.26

Fe_vol__-3.0_rk8_5000k.scf::MMTOT: 2.16

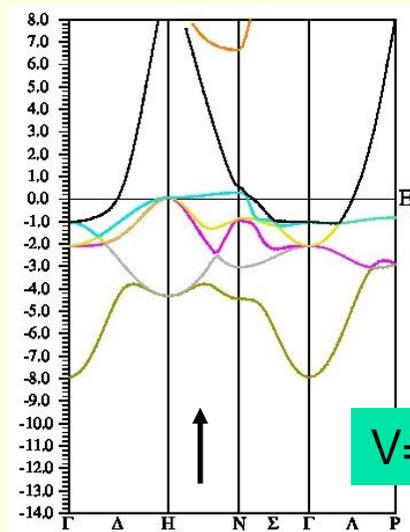
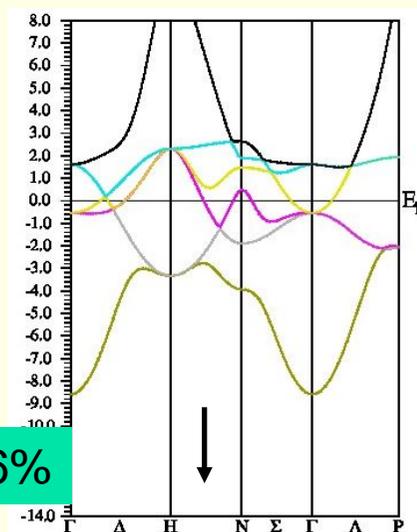
Fe_vol__6.0_rk8_5000k.scf::MMTOT: 2.31

Fe_vol__-6.0_rk8_5000k.scf::MMTOT: 2.13

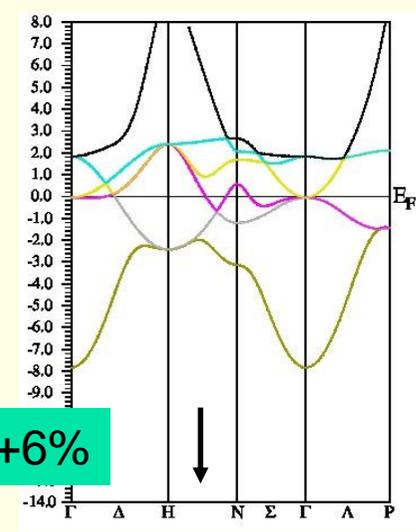
- *compare bandstructure and DOS for large/small volumes (restore_lapw for desired volume; x lapw0 "recreates" potentials, adjust EF in case.insp)*



V=-6%



V=+6%

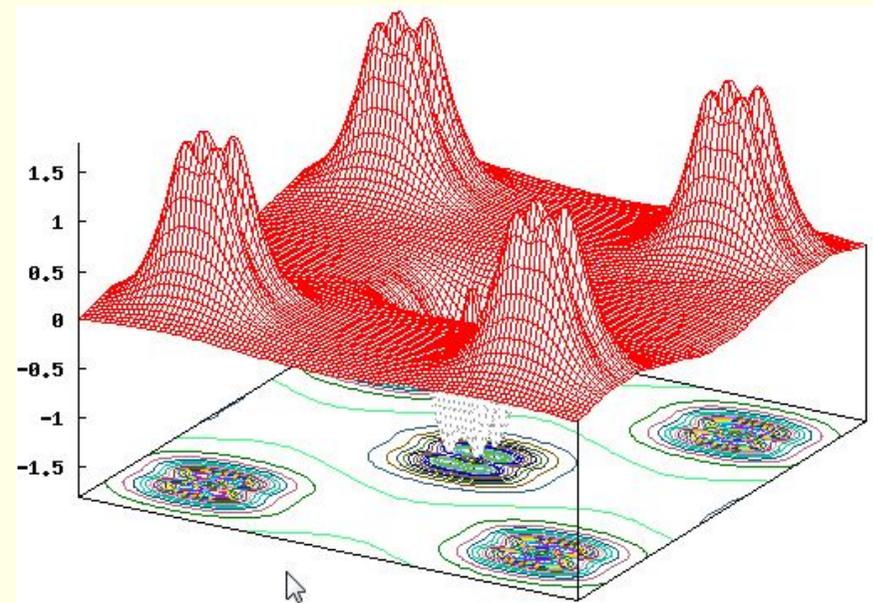


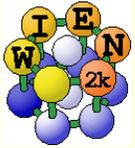


Exercise 7:



- **Antiferromagnetism: bcc Cr ($a_0=2.885 \text{ \AA}$)** (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 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 :-2101.769475 vs. -4203.543208 Ry)*
 - *is FM stable at all ? check moments (MMI001: 0.000 vs. $1.226\mu_B$; 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

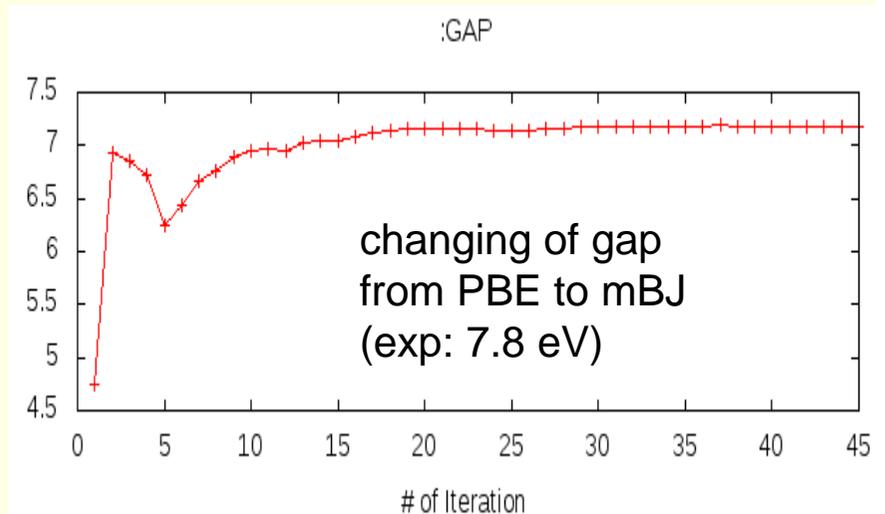
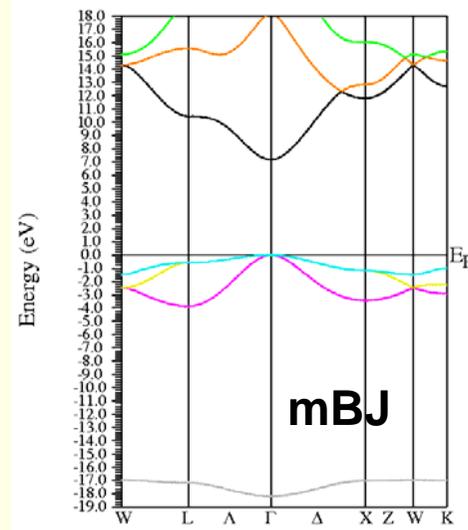
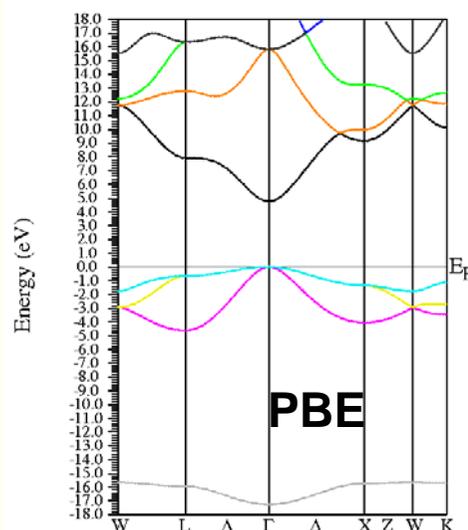




Exercise 8: band gaps of MgO



- **MgO** (NaCl, $a=7.96$ bohr; default initialization; scf-cycle)
 - **PBE**: check the gap (:GAP from "analysis"),
 - 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

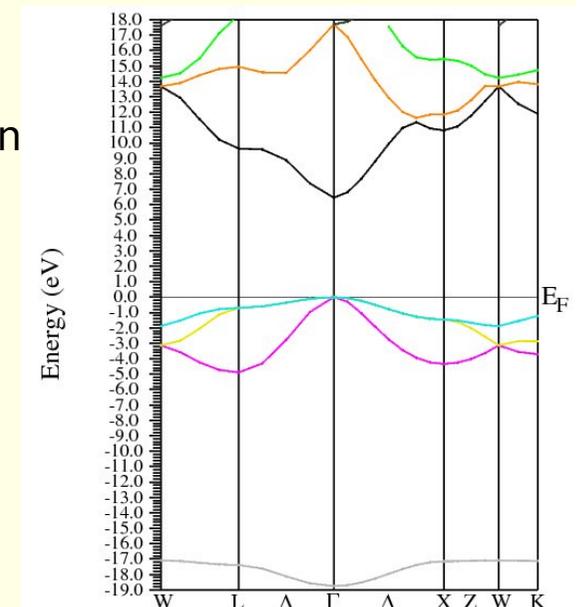




Exercise 8: continued ...



- 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 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 `bandplot_hf_lapw -p`
 - `cp $WIENROOT/SRC_templates/case.insp case.insp` (insert E_F and increase the plotting energy range).
 - `x spaghetti -hf -p`

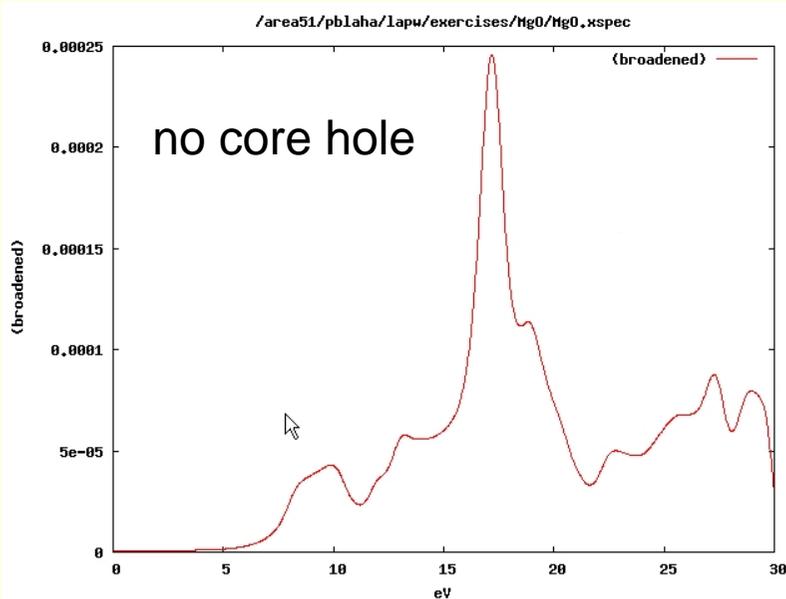




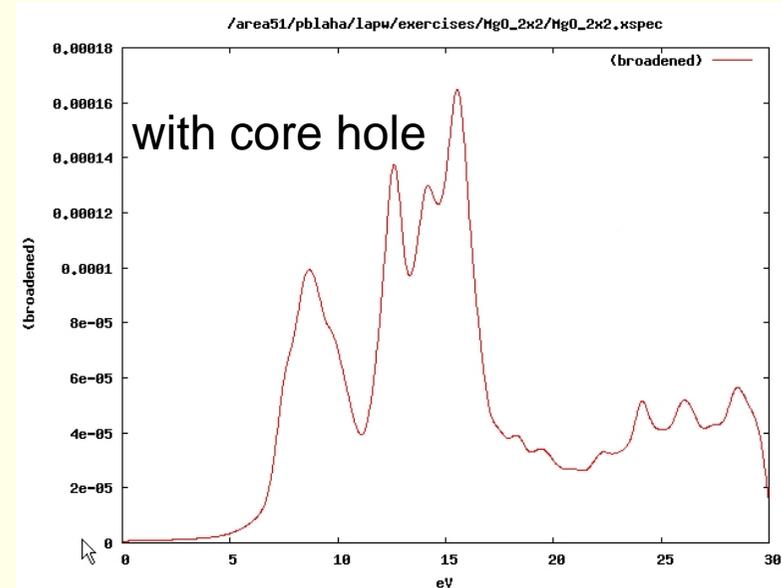
Exercise 9: Mg K-XAS in MgO

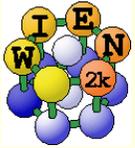


- **MgO** (NaCl structure, $a=7.96$ bohr; default initialization with 1000 k-points; scf-cycle)
 - *XSPEC task: larger EMAX in MgO.in1; select in MgO.inxs: Mg-K ABS from 0-30 eV, vary broadening)*
- **Supercells: MgO 2x2x2 FCC-supercell for core-hole simulation**
 - *create new "session", copy MgO.struct 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 \rightarrow 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



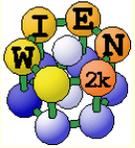


Exercise 10:



■ LDA+U: 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 \pm (.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: 1.41 μ B)
 - compare orbital moments for SO and SO+U calculations (0.12 and 0.09 μ B)
- *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...

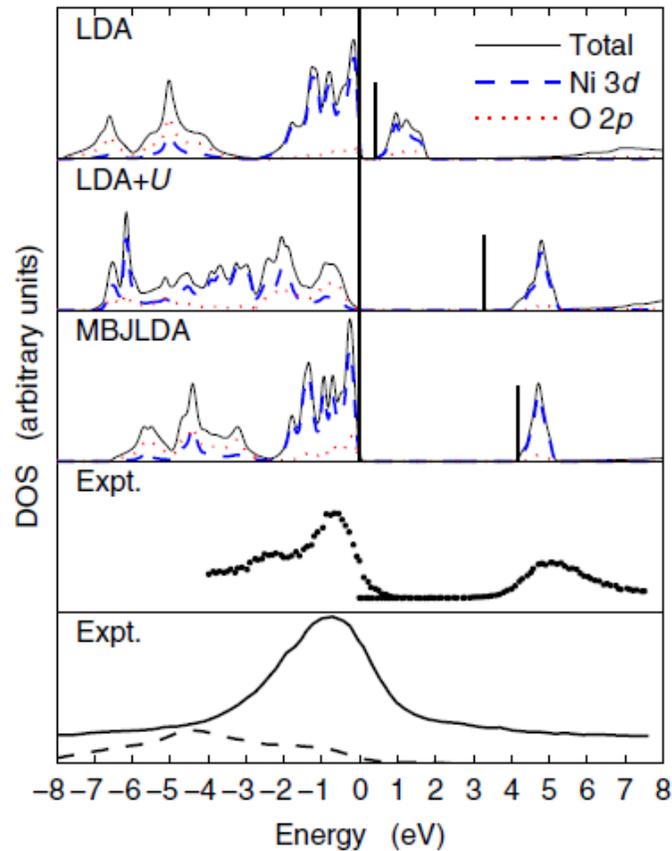
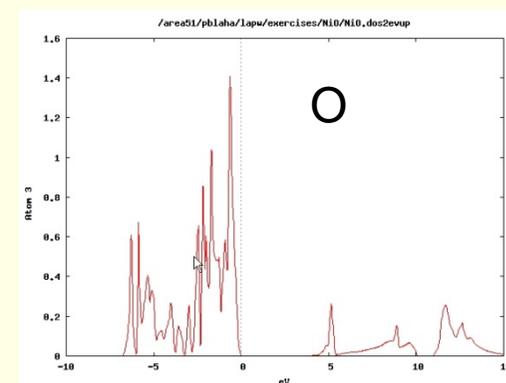
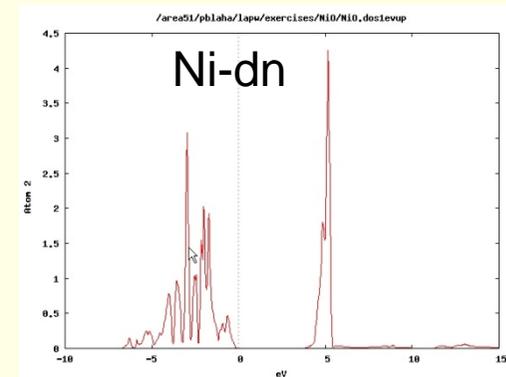
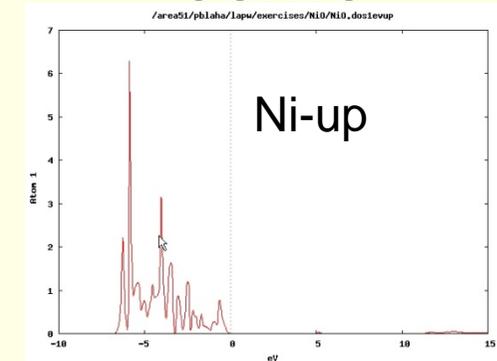


FIG. 2 (color online). DOS of NiO. The vertical bars indicate the end of the fundamental band gap which starts at $E = 0$ eV. The panels labeled “Expt.” show photoelectron [25] (upper panel) and XES [33] [lower panel, Ni (solid line) and O (dashed line) spectra] measurements.

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

GGA+U





Exercise 11:



■ Optical properties: fcc Al

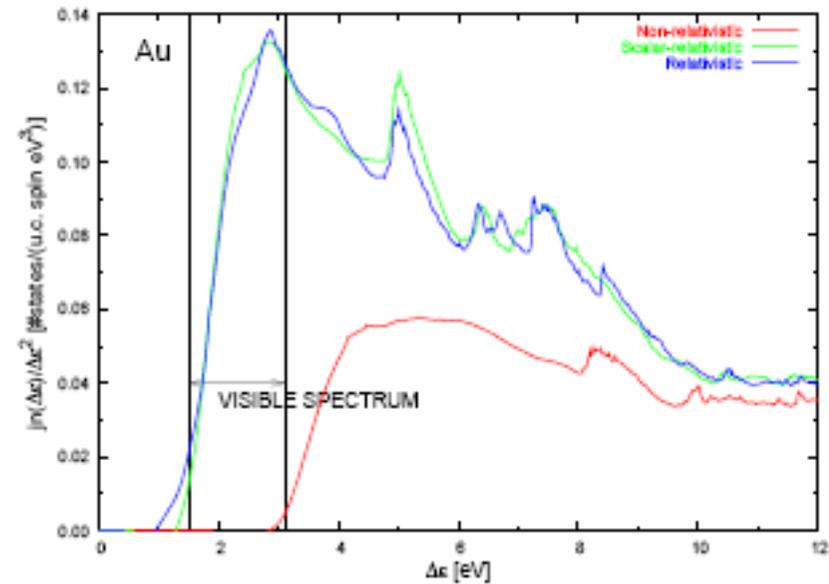
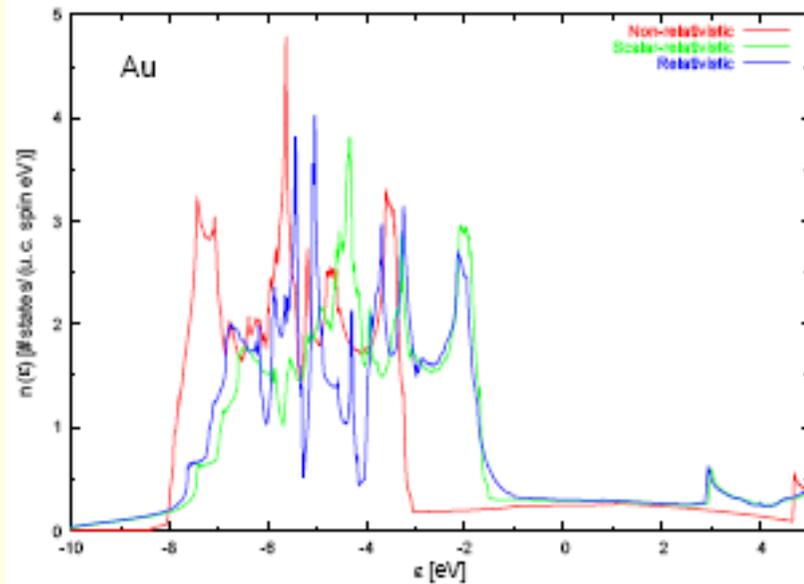
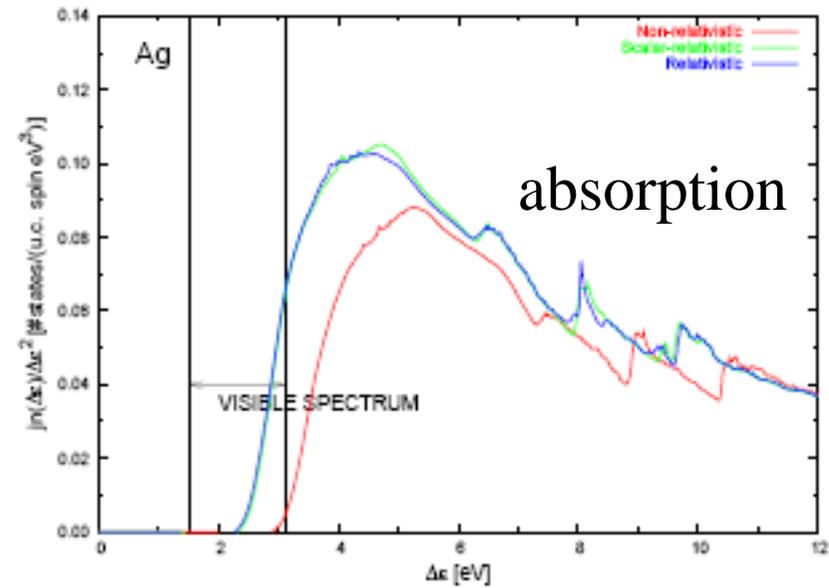
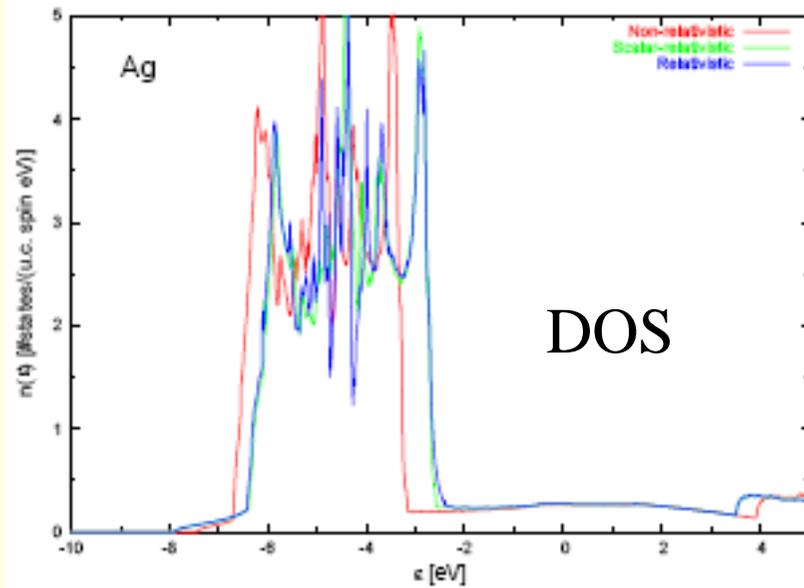
- $a_0 = 4.05 \text{ \AA}$
- *init_lapw* (use 165 **IBZ** k-points only!)
- *run_lapw*
- *calculate optics* (as described in the optics lecture, compare with the Al - Fig.)
 - calculate plasma frequency (case.outputjoint) and dielectric function
 - check your results with respect to k-mesh
 - x kgen (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 $a_0 = 4.08 \text{ \AA}$)

- *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

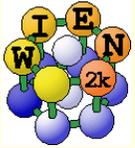




Exercise 12: O-NMR of cubic/tetragonal BaTiO₃



- 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)
 - *BaTiO₃: 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`
- `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 :EFG002 *scf`
 - `grep :EFG003 *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.
- *compare with experiment:*

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

- Estimate $\delta_{\text{iso}}(\text{th}) = (\sigma_{\text{iso}}(\text{th}) - \sigma_{\text{ref}}(\text{th}))$; estimate $\sigma_{\text{ref}}(\text{th})$ to obtain "best" agreement with exp.
- 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)