Vienna Computational Materials Laboratory ViCoM

TECHNISCHE UNIVERSITÄT WIEN

VIENNA SCIENTIFIC CLUSTER

The FP-LAPW and APW+lo bandstructure methods as implemented in WIEN2k

Peter Blaha

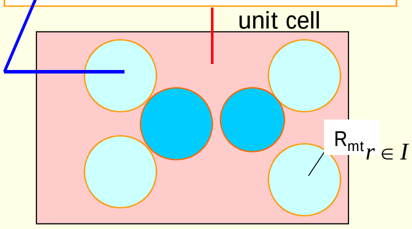
Institute of Materials Chemistry

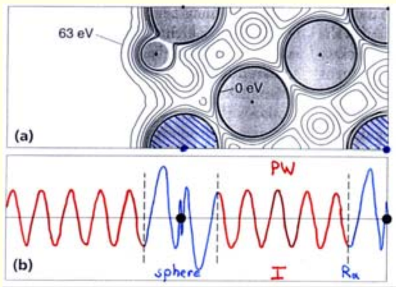
TU Wien

http://wien2k.at/events/vicom_wien2k.pdf

APW Augmented Plane Wave method

The unit cell is partitioned into:
- atomic spheres
- Interstitial region





Basisset:

PW: $e^{i(\vec{k}+\vec{K}).\vec{r}}$

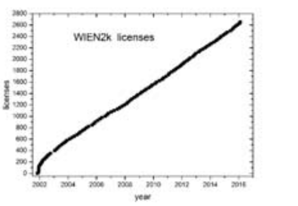
Atomic partial waves

$$\sum_{\ell m} A^K_{\ell m} u_\ell(r',\varepsilon) Y_{\ell m}(\hat{r}')$$

join

$u_l(r,\varepsilon)$ are the numerical solutions of the radial Schrödinger equation in a given spherical potential for a particular energy ε

$A_{lm}{}^K$ coefficients for matching the PW



WIEN2k software package

An Augmented Plane Wave Plus Local Orbital
Program for Calculating Crystal Properties

Peter Blaha
Karlheinz Schwarz
Georg Madsen
Dieter Kvasnicka
Joachim Luitz

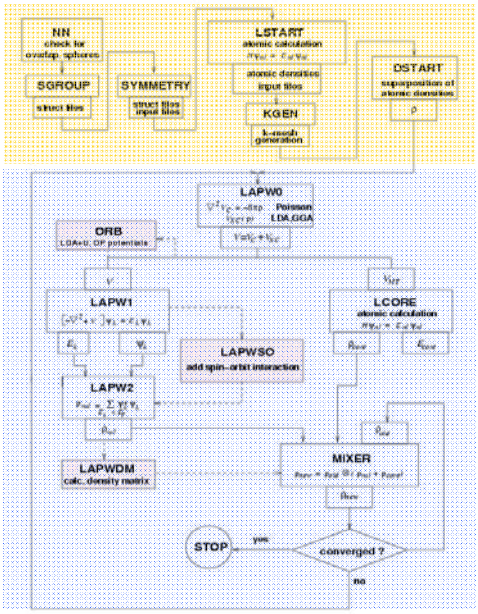
November 2001
Vienna, AUSTRIA
Vienna University of Technology

http://www.wien2k.at

WIEN97: ~500 users
WIEN2k: ~2800 users

WIEN2k: many independent **f90** programs, linked together and executed by **csh-scripts**

- init_lapw
  - *step-by-step or batch initialization*
  - *symmetry detection (F, I, C-centering, inversion)*
  - *input generation with recommended defaults*
  - *quality (and computing time) depends on k-mesh and R.Kmax (determines #PW)*
- run_lapw
  - *scf-cycle (optional position optim.)*
  - *optional with SO and/or LDA+U*
  - *different convergence criteria (energy, charge, forces)*
- save_lapw tic_gga_100k_rk7_vol0
  - *cp case.struct and clmsum files,*
  - *mv case.scf file*
  - *rm case.broyd* files*

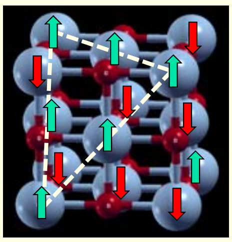


WIEN2k and the w2web GUI

- Structure generator
  - *spacegroup selection*
  - *import cif or xyz file*
- step by step initialization
  - *symmetry detection*
  - *automatic input generation*
- SCF calculations
  - *Magnetism (spin-polarization)*
  - *Spin-orbit coupling*
  - *Forces (automatic geometry optimization)*
- Guided Tasks
  - *Energy band structure*
  - *DOS*
  - *Electron density*
  - *X-ray spectra*
  - *Optics*

exercises: NiO an AFM insulator

- nonmagnetic NiO
  - *basics of wien2k, basis for DMFT calculations*
  - *partial DOS*
  - *volume optimization*
- ferromagnetic NiO
  - *partial DOS*
  - *DFT+U calculations*
  - *spin-orbit coupling*
  - *band structure plotting*
- antiferromagnetic NiO
  - *creation of supercells*
  - *DFT and DFT+U calculations*
  - *spin- and charge-densities*
  - *comparisons of total energies, magnetic moments, gaps, ...*

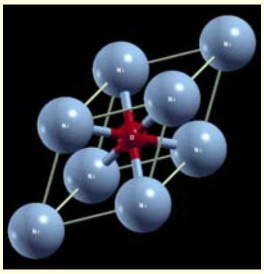


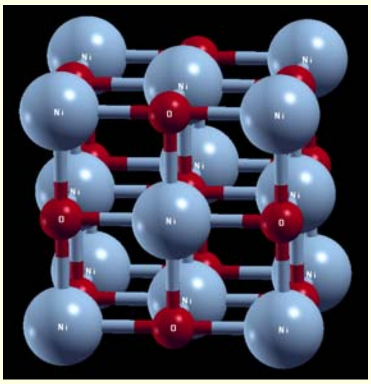
exercises: computer setup

- open the userguide in a browser: http://wien2k.at/reg_user/textbooks
- open 2 windows and connect to the vsc3 frontend
  - *ssh -X training@vsc3.vsc.ac.at (Vicom_2017)*
- salloc -J pc## (## is your PC number: 01-29)
- srun hostname (find the allocated compute node)
  - *ssh -X nAA-BBB (see previous line on your screen, on all windows)*
- on ALL windows: cd ##/wien2k (see label on your screen)
  - *since we all use the same account , it is ESSENTIAL that you create data only in YOUR „home-directory“ !!*
- the „text-version“ of the instructions (for „cut and paste“) can be opened using
  - *$EDITOR ~/blaha/wien2k_exercises.txt & (or use less/ vi / emacs)*

NiO: nonmagnetic calculation

- mkdir NiO-nm; cd NiO-nm
- makestruct_lapw # define the NaCl structure of NiO
  - *lattice: F (one does not need to know the spacegroup)*
  - *lattice parameter: 4.186 Ang*
  - *Ni (0,0,0)*
  - *O (0.5,0,0)*
- cp init.struct NiO-nm.struct
- xcrysden --wien_struct .





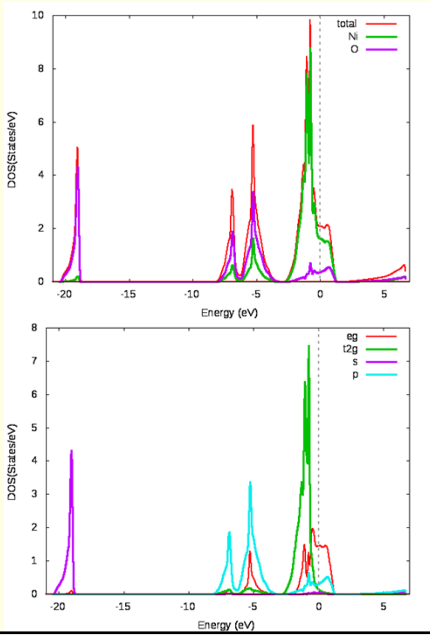
primitive and conventional cell

NiO-nm: initialization and scf

- init_lapw –h # help switch to see all options
- init_lapw –b –numk 300 # batch initialization with 6x6x6 kmesh
  # what are the valence and core states ?
- run_lapw # scf cycle with default convergence
- save_lapw pbe # save a calculation
- # check scf convergence:
- grep :ENE pbe.scf # observe convergence and warnings
- grep :WAR pbe.scf # linearization warning for state above EF
- grep :FER pbe.scf
- grep :GAP pbe.scf # metal !!
- grep :DIS pbe.scf # charge convergence
- grep :CTO001 pbe.scf # charge in Ni sphere (~constant, Ni^{2+}, $3d^8$)
- grep :CTO002 pbe.scf # O charge (increases, O^{2-}, Ni-$4s^2$ → O-$2p^6$)

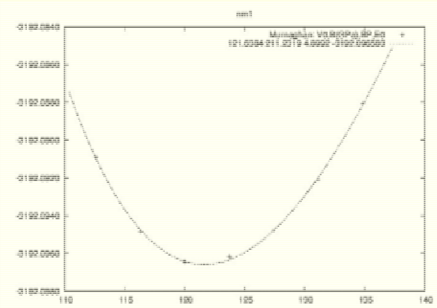
DOS (total, Ni-$d_{eg/t2g}$, O-s,p)

- x lapw2 –qtl
- configure_int_lapw
  - *select: total*
  - *1 (tot,d-eg,d-t2g)*
  - *2 (tot,s,p)*
  - *E-min/Emax: -1.0 to 1.0 Ry*
- x tetra
- dosplot2
  - *produce 2 plots:*
  - *total, Ni-tot, O-tot*
  - *Ni-eg,t2g,O-s,p)*



Volume optimization

- x optimize # create a series of struct files with different volume
  - *select option 1 (volume) and 7 cases: -9 -6 -3 0 3 6 9 % change of vol*
- ./optimize.job # run scf for all volumes.
  - *this takes 2-3 min and while this is running, you may continue in the other window with the ferromagnetic calculation and come back later*
- grepline :ene '*scf' 1 # get E-tot for all volumes
- eplot -a default # fit EOS and plot E vs. vol
  - *what is a_0 (compare to experiment) and B_0 ?*

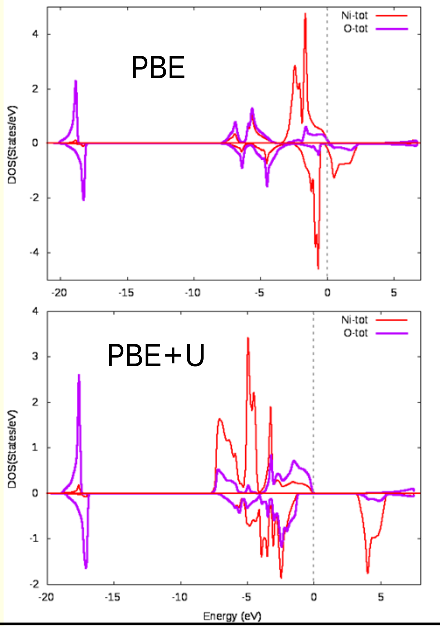


NiO: ferromagnetic calculation

- cd ..; mkdir NiO-fm; cd NiO-fm
- cp ../NiO-nm/NiO-nm.struct NiO-fm.struct #copy nm struct file
-
- init_lapw –b –sp –numk 300 # spin-polarized initialization
- runsp_lapw # spin-polarized scf cycle
- save_lapw pbe
- # check convergence and compare with NiO-nm
- grep :ENE *.scf # fm or nm lower in energy ?
- grep :GAP *scf # still metallic, (exp. gap ~4eV)
- grep :MMT *scf # total spin magnetic moment / cell
- grep :MMI001 *scf # exp. moment: ~2uB

DOS (total, Ni-$d_{eg/t2g}$, O-s,p)

- x lapw2 –qtl –up
- x lapw2 –qtl -dn
- configure_int_lapw
  - *select: total*
  - *1 (tot,d-eg,d-t2g)*
  - *2 (tot,s,p)*
  - *E-range = -1.0 / 1.0*
- x tetra –up / -dn
- dosplot2 -up
  - *produce a spin-pol. plot:*
  - *Ni-tot, O-tot up+dn*

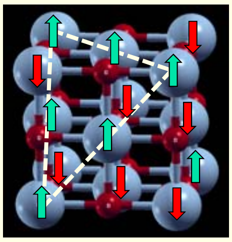


NiO: fm PBE+U calculation

- x orb -up
- x lapwdm -up # create input templates
- $EDITOR NiO-fm.indm # density matrix for only 1atom (Ni, l=2; delete 2nd atom)
- $EDITOR NiO-fm.inorb # only 1 atom (Ni), SIC-method, U= 7eV)
- runsp_lapw -orb # spin-polarized scf cycle with GGA+U
- save_lapw pbe+u
- # compare with fm calculation
- grepline :GAP '*.scf' 2 # shows last 2 :GAP lines of all scf files
- grepline :MMI001 '*scf' 1 # observe creation of gap and larger moment
- plot DOS in the same way as for PBE calculation

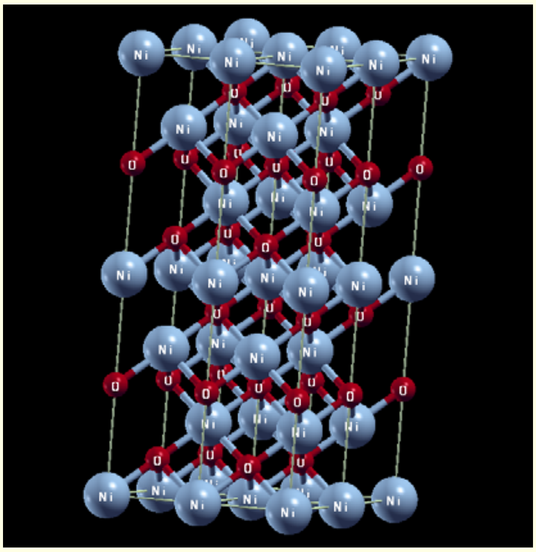
NiO: AFM-II (fm Ni(111) layers)

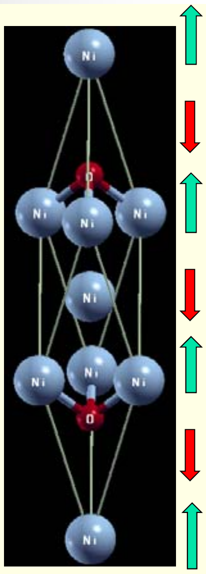
- cd ..; mkdir NiO-afm; cd NiO-afm
- cp ../NiO-nm/NiO-nm.struct fcc.struct #copy nm struct file as start
- create a supercell with 2 Ni and O atoms along (111)-direction
- octave # a „free“ matlab
- helpstruct # list all structeditor commands
- help loadstruct # help for specific command
- s=loadstruct(“fcc.struct“);
- sp=makeprimitive(s); # create primitive (rhombohedral) cell
- su=makesupercell(sp,[1 1 0; 1 0 1; 0 1 1]);
- showstruct(su)
- savestruct(su,“NiO-afm.struct“)
- quit



hexagonal and rhombohedral cell

up
dn
up
dn
up
dn
up





AFM-II NiO

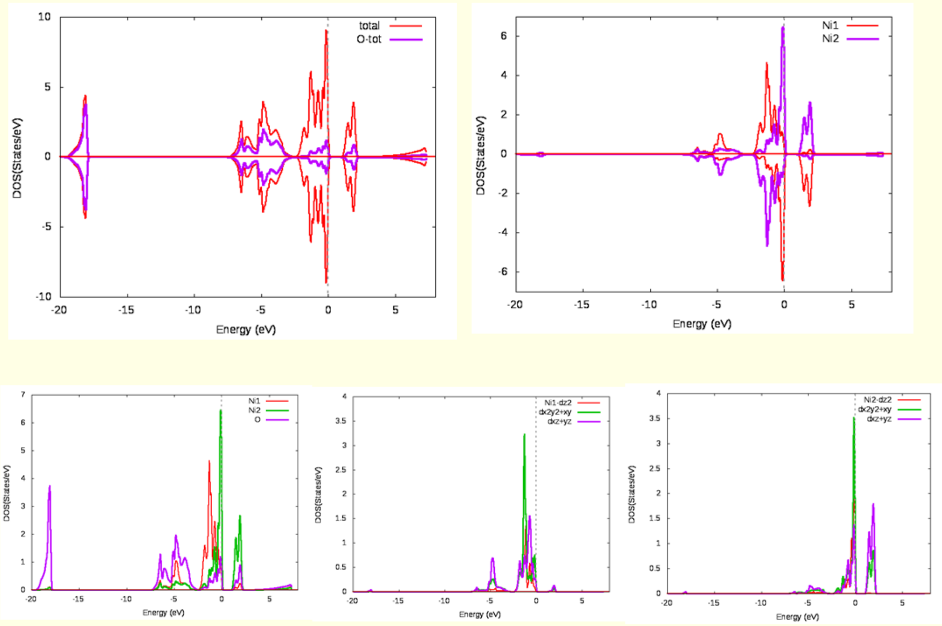
- less NiO-afm.struct # observe the 4 atoms in R cell
- x sgroup # run spacegroup program
- less NiO-afm.struct_sgroup # back to original NaCl structure
- $EDITOR NiO-afm.struct # „label Ni1 and Ni2“ (overwrite mode). This directs sgroup to treat Ni1 and Ni2 as different atoms
- x sgroup
- less NiO-afm.struct_sgroup # 3 non-equivalent atoms !
- cp NiO-afm.struct_sgroup NiO-afm.struct # take this struct file
- instgen_lapw –ask # starting spin-structure: u, d, n
- init_lapw –b –sp –numk 100 # (4x4x4 k-mesh)
- runsp_lapw # spin-polarized scf cycle
- save_lapw pbe

AFM NiO: convergence and DOS

- # check convergence and compare with NiO-nm, NiO-fm
- grep :ENE *.scf # afm, fm or nm lower in energy ?
- grep :GAP *scf # small gap opened, (exp. gap ~4eV)
- grep :MMT *scf # total spin magnetic moment / cell
- grep :MMI001 *scf # small moment (exp. ~2uB)

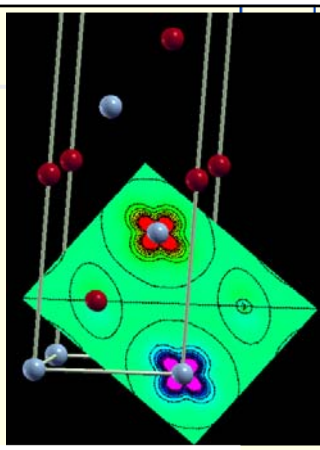
- # plot DOS (observe „symmetry“ between up and dn-DOS)
- x lapw2 –qtl –up /-dn
- configure_int_lapw # select total and all „meaningful“ splittings (they are automatically symmetry adapted), E-range
- x tetra –up / -dn
- dosplot2 –up # Ni1/2-up/dn; d-split (eg/t2g does not exist in this coordinate system); Ni1,Ni2,O-tot up

AFM NiO: PBE DOS

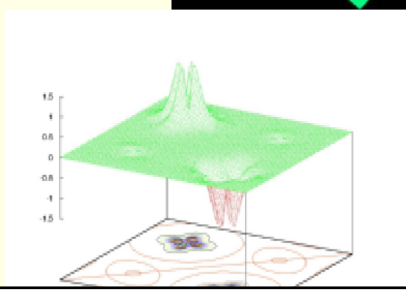


spin-density

- xcrysden --wien_density .
  - *2D plot*
  - *80 points (in first line)*
  - *3 atoms spanning rectangular „fcc"-100-plane (2Ni at different z-values)*
  - *enlarge plane by 0.5*
  - *submit and change „ADD" to „SUB"*
  - *plot with „rainbow", thermometer, ranges: -0.4/0.40, small atoms, ball/stick ratio=0*



- rhoplot # 3D-plot

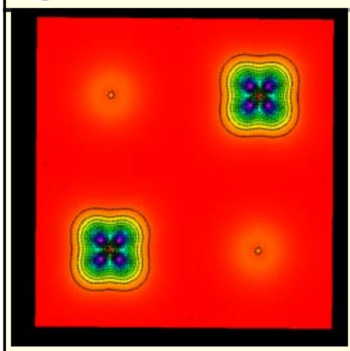


density of occupied and empty Ni-d states

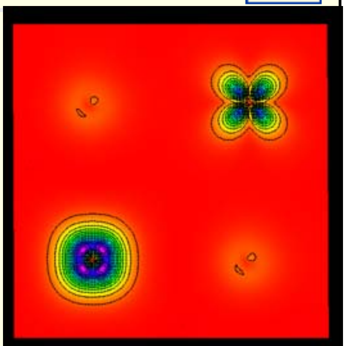
- grep band NiO-afm.output2up # find the energy-ranges (xxx and yyy) around EF to plot occupied (8 bands) and empty (2 bands) Ni-d states
- x lapw2 -up -emin xxx # calculate ρ_{up} for states from xxx to EF
- x lapw2 -dn -emin xxx # calculate ρ_{dn} for states from xxx to EF
- $EDITOR NiO-afm.in5 # change "SUB" to "ADD"
- x lapw5 -up # generate density in plane
- rhoplot / xcrysden --wien_renderdensity . # plot total density of occupied Ni-d band - which symmetry is present around Ni
- rm NiO-afm.clmvaldn # remove spin-dn density
- x lapw5 -up
- rhoplot / xcrysden --wien_renderdensity . # plot spin-up density of occupied Ni-d band - which symmetry is present around Ni

- x lapw2 -all xxx yyy -up # calculate spin-up density for unoccupied Ni-d band
- x lapw5 -up
- xcrysden --wien_renderdensity . # plot spin-up density of unoccupied Ni-d band - symmetry around Ni ?

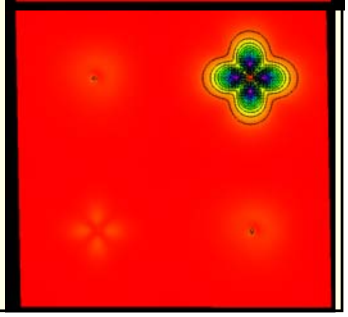
Ni-d bands in AFM NiO



total density of occupied Ni-d bands (8 bands below EF) t_{2g} symmetry dominates e_g



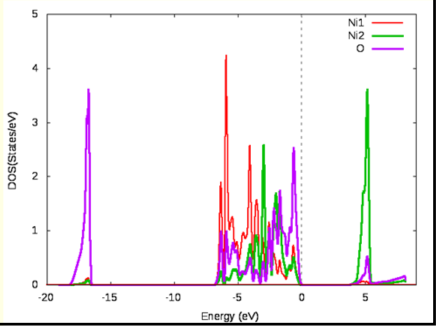
spin-up density of occupied Ni-d bands
Ni1: all 5 d-bands occupied
Ni2: only 3 t_{2g} bands occupied



empty Ni-d bands
Ni1: nothing
Ni2: 2 e_g bands

AFM-II NiO with PBE+U

- x orb –up # create default inputs, (templates are for AFM NiO,
- x lapwdm –up # no editing necessary)
- runsp_lapw –orb
- save_lapw pbe+u
- grepline :GAP '*scf' 2 # observe the larger gap than with GGA
- grepline :MMI001 '*scf' 1 # observe the larger magnetic moment
- # you can now plot the DOS in the same way as for the PBE calculation. Compare the DOS
- where is the lower and upper Hubbard band ?



Compare the different calculations

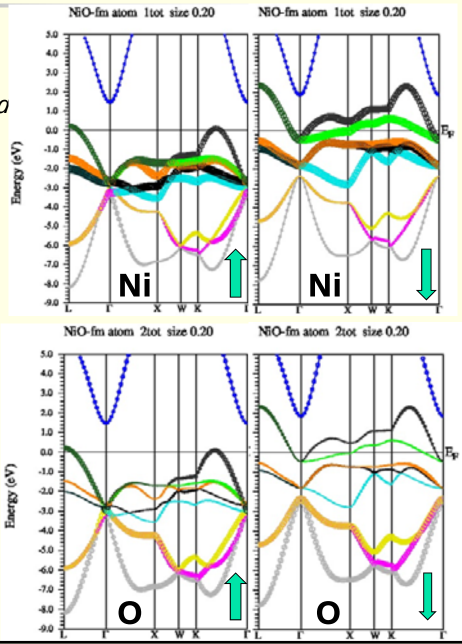
- cd ..
- grepline :ENE '*/pbe.scf' 1 # which case has the lowest energy, what are the differences ?
- grepline :ENE '*/pbe+u.scf' 1 # which case has the lowest energy, what are the differences ? What are the differences between PBE and PBE+U ?
- # from an analysis of total energies for different spin structures (including other AFM settings) a Heisenberg model can be set up and the exchange parameters J_i could be determined.
- grepline :GAP '*/pbe.scf' 2 # which case has a gap in PBE ?
- grepline :GAP '*/pbe+u.scf' 2 # which case has a gap in PBE+U ?

FM NiO with GGA+U and spin-orbit coupling

- cd NiO-fm
- initso_lapw # define magnetization direction along (001), use defaults; continue setup with "spin-polarization": symmetso will detect the symmetry break and create a new structure, commit all changes
- runsp_lapw -orb -so # scf cycle with PBE+U and spin-orbit
- save_lapw pbe+u_so
- grepline :GAP '*scf' 2 # compare the gaps
- grepline :MMI001 '*scf' 1 # compare the spin magnetic moments
- grepline :ORB001 '*scf' 1 # get the orbital magnetic moment (only in the so-calc.)
- get the DOS as above (use x lapw2 -up -so -qtl)

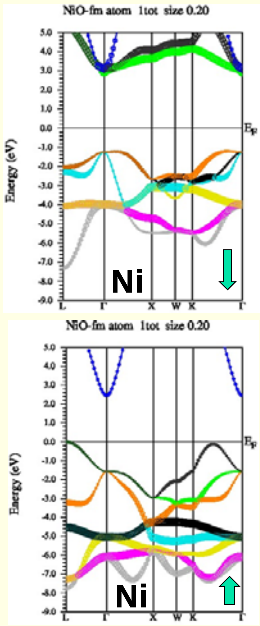
bandstructure plots: fm NiO (pbe)

- xcrysden --wien_kpath .
  - *click L-Gamma-X-W-K-Gamma,*
  - *100 points, save as NiO-fm.klist_band*
- restore_lapw pbe
- x lapw1 –band –up/dn
- x lapw2 -band –qtl –up/dn
- x spaghetti -up
- grep :FER pbe.scf
- $EDITOR NiO-fm.insp
  - *insert EF, emin=-9.*
  - *plot Ni or O-tot (1 1 0.2 or 2 1 0.2)*
- x spaghetti –up/dn
- gs NiO-fm.spaghettiup_ps
- gs NiO-fm.spaghettidn_ps
- save_lapw –band pbe



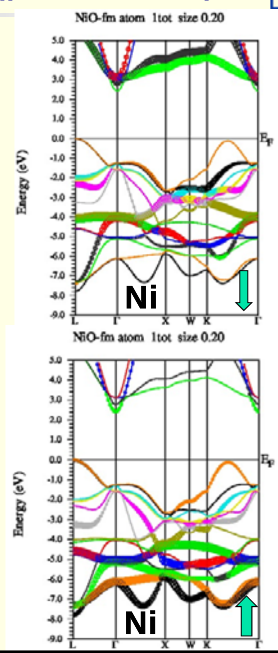
bandstructure plots: fm NiO (pbe+u)

- restore_lapw pbe+u
- x lapw1 –band –orb –up/dn
- x lapw2 -band –qtl –up/dn
- grep :FER pbe+u.scf
- $EDITOR NiO-fm.insp
  - *insert EF*
- x spaghetti –up/dn
- gs NiO-fm.spaghettiup_ps
- gs NiO-fm.spaghettidn_ps
  - *where are the „lower“ and „upper“ Hubbard bands ?*
- save_lapw –band pbe+u



bandstructure: fm NiO (pbe+u+so)

- restore_lapw pbe+u_so
- x lapw1 –band –up/dn
- x lapwso –up -orb
- x lapw2 -band –qtl –so –up/dn
- grep :FER pbe+u_so.scf
- $EDITOR NiO-fm.insp
  - *insert EF*
- x spaghetti –so –up/dn
- gs NiO-fm.spaghettiup_ps
- gs NiO-fm.spaghettidn_ps
  - *what is the difference to calc. without spin-orbit ?*
- save_lapw –band pbe+u_so



other DFT options

- Tran-Blaha modified Becke-Johnson potential
  - *a meta-GGA potential giving gaps of GW quality. XES spectra ok.*
  - *fast, but no total energy ! init_mbj_lapw (see UG)*
- EECE (onsite hybrid-DFT for correlated electrons only).
  - *fast, similar to GGA+U, good gaps with proper HF fraction (see UG)*
- Hybrid-DFT (PBE0, HSE, ...)
  - *rather time consuming, run in k-parallel (or mpi-) mode, good gaps with proper HF fraction. init_hf_lapw (see UG)*

DOS of NiO

- mBJ DOS agrees with
  - *XPS/BIS*
  - *Ni-XES, O-XES*
- LDA+U gives similar gap, but cannot explain XES
- PBE0: gap too large