

# Hands-on Exercises

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The program package WIEN2k allows to perform electronic structure calculations of solids using density functional theory (DFT).  
First Polish workshop and the 22-nd workshop in the history of the WIEN2k code: "WIEN2k and SPECTROSCOPY: HANDS-ON WORKSHOP" which was held at Institute of Physics PAS, Warsaw, Poland in Fall 2014.



Group of X-ray Spectroscopy and Microanalysis, Laboratory of X-ray and Electron Microscopy Research, Institute of Physics, PAS:  
Dr. Iraida Demchenko, Mr. Yevgen Syryanyy, Dr. Pawel Rejmak

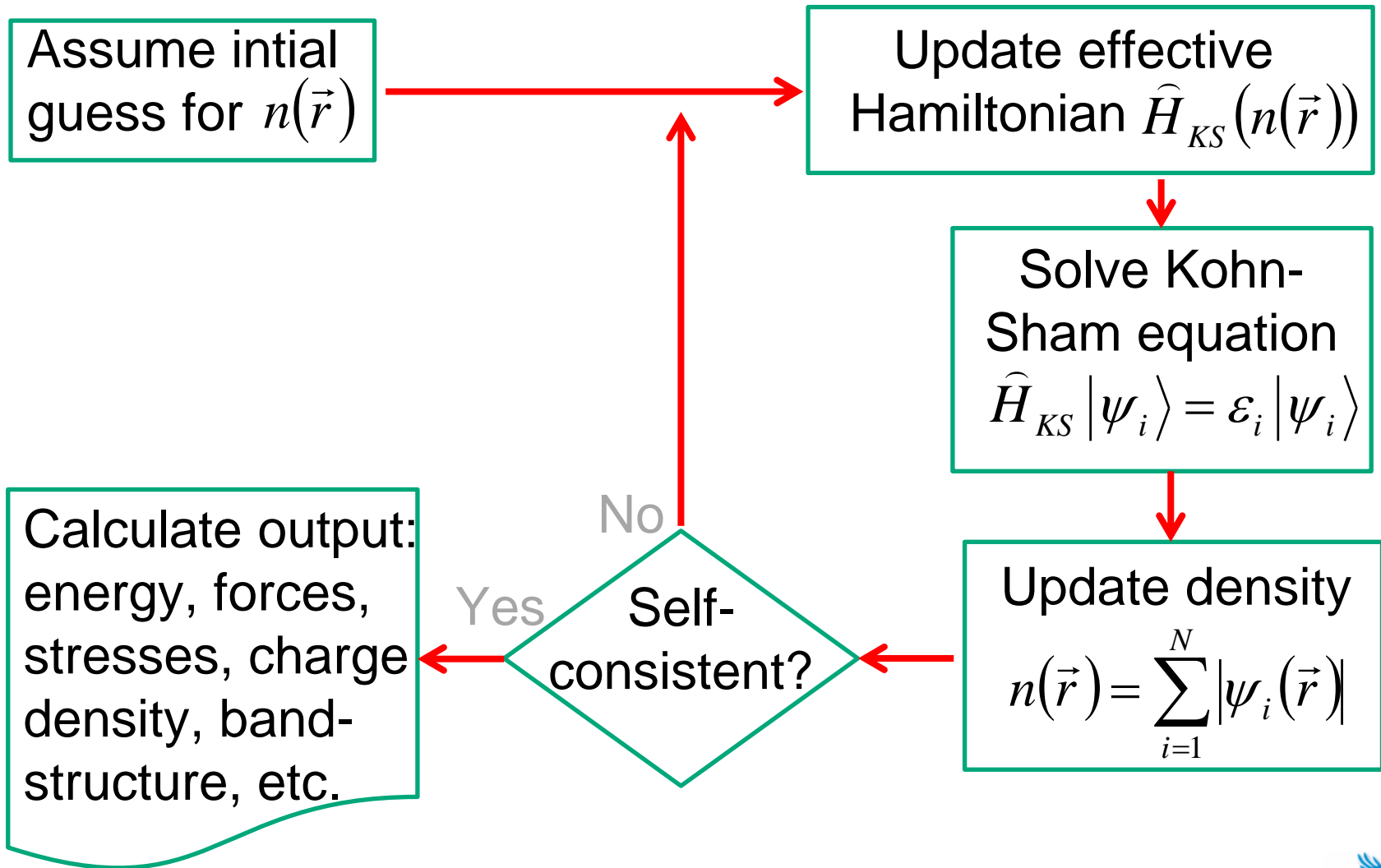


# Outline

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- Exercise I:** Getting started: struct file, init, scf, charge density, DOS, bands
- Exercise II:** Volume and structure optimization
- Exercise III:** Testing accuracy: RKmax and k-points
- Exercise IV:** Testing exchange potentials
- Exercise V:** Magnetism
- Exercise VI:** Hybrid-DFT
- Exercise VII:** Core level spectroscopy (XSPEC) and core-hole effects
- Exercise VIII:** LDA+U (if time permits)

# Solving Kohn-Sham equations





# Exercises

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The exercises presented here can be solved either via w2web or in terminal

The proposed “calculation parameters” are set to “minimal cpu-time” instead of “fully converged calculations”

For final results and publications, the “calculation parameters” have to be checked for convergence

As we saw in the “Introduction to DFT” lecture the SCF calculations must always be performed.



# Exercises

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Useful resources:

- [www.wien2k.at](http://www.wien2k.at) – WIEN2k webpage with tutorials from schools and workshops
- User guide (UG) available online
- WIEN2k forum (searchable, questions answered quite fast by WIEN2k code developers and users)
- [www.cryst.ehu.es](http://www.cryst.ehu.es) – Bilbao Crystallographic Server (for space groups, Wyckoff Positions, etc.)
- [www.crystallography.net](http://www.crystallography.net) – Crystallography Open Database (searchable, but use with care)
- XCrySDen – visualization code for structure and density
- cif2struct, xyz2struct
- dos2unix
- etc.

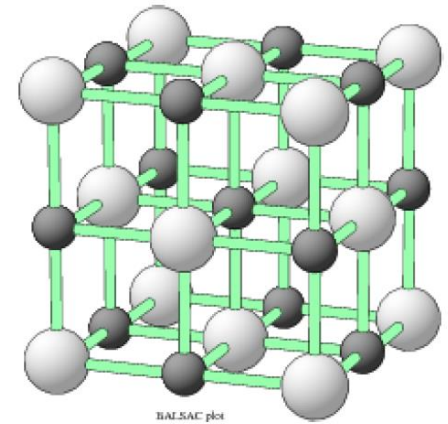
# Exercise I: Getting started

TiN:

F; Space group 225;  $a=4.235$  Ang

Ti 4a 0, 0, 0

N 4b 0.5, 0.5, 0.5



Construct structure in w2web or **makestruct lapw**

**init\_lapw -b** - to initialize everything by default

Visualize structure in XCrysDen

Check files created

**run\_lapw -p** - to run everything with default values in a parallel mode

Monitor the files: "STDOUT", "dayfile", ":log"

**utilities: analyse** - to analyse results in w2web (text or graphic)

Check files created

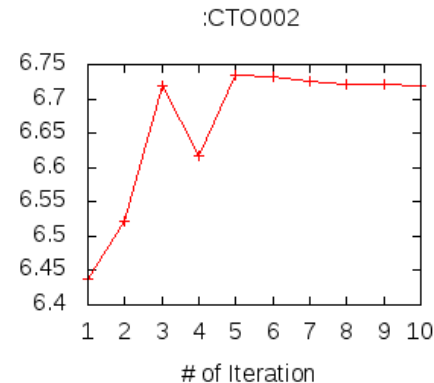
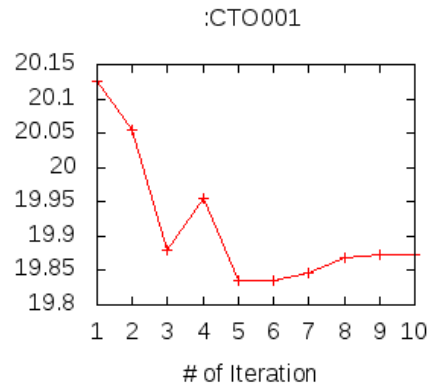
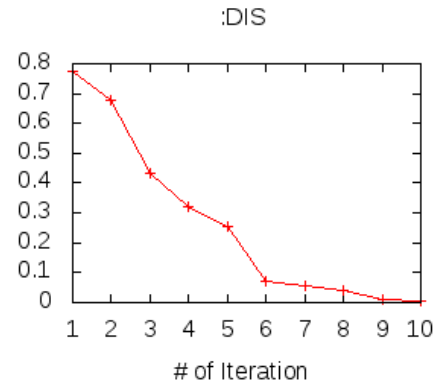
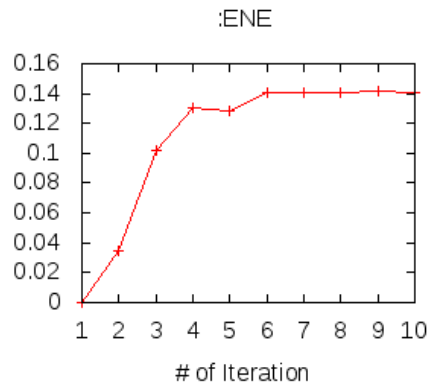
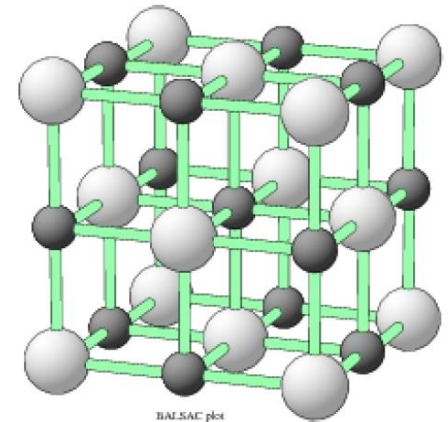
**save\_lapw TiN\_pbe\_rk7\_1000k**

Check files left

# Exercise I: Getting started

TiN:

**utilities: analyse** - to analyse results in w2web  
(text or graphic)  
(:ENE, :DIS, :CTO, :GAP)



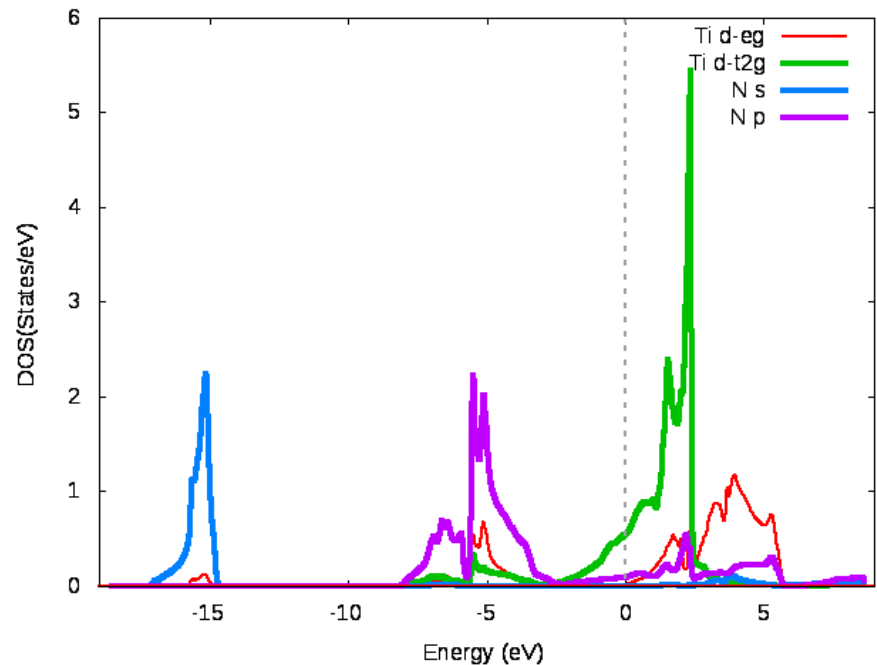
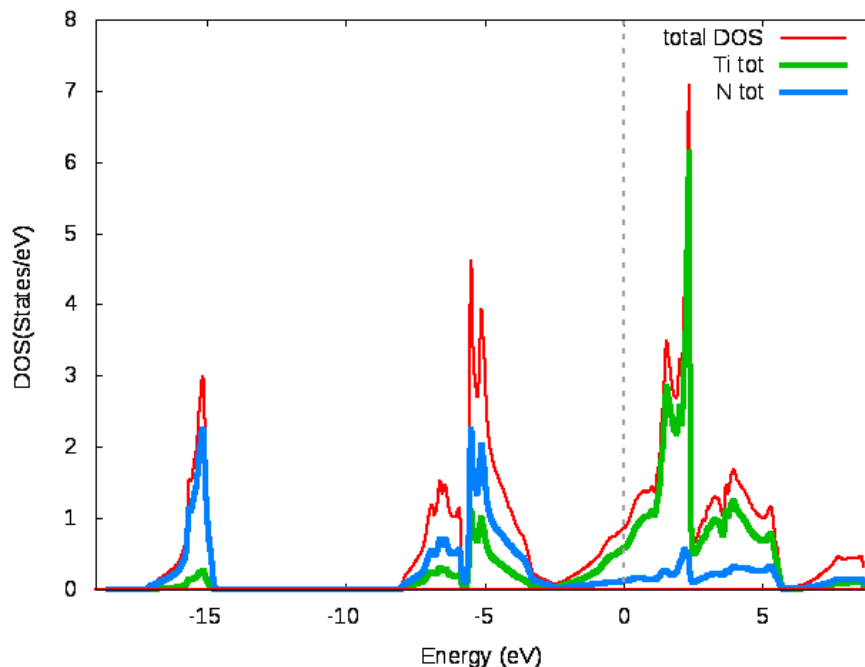


# Exercise I: Getting started

TiN:

DOS (plot 7 cases: total + Ti-tot + N-tot and Ti-eg + Ti-t2g + N-s + N-p)

- **x lapw2 -qtl**
- edit "TiC.int" to select what to plot
- **x tetra**
- view DOS plot

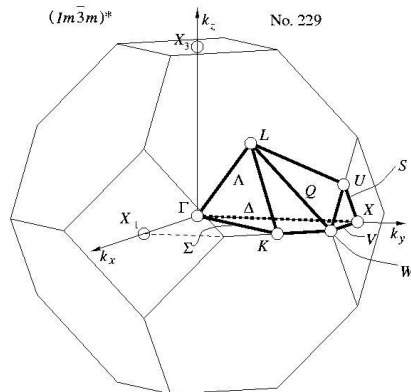


# Exercise I: Getting started

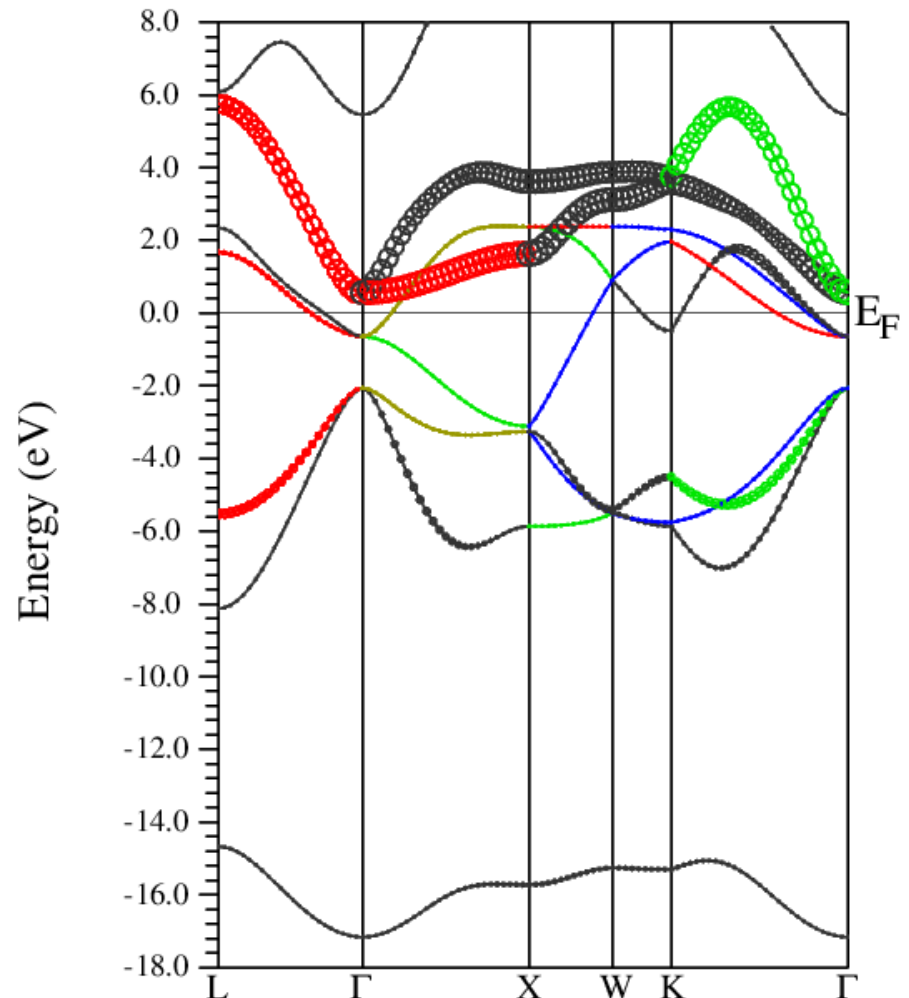
TiN:

## Bandstructure

- Create mesh along which bands will be calculated
- **x lapw1 -band**
- **x lapw2 -qtl -band**
- Edit "TiC.insp" for correct value of  $E_f$  and specify what to plot
- **x spaghetti -p**
- View bandstructure



TiN atom 1D-eg size 0.20

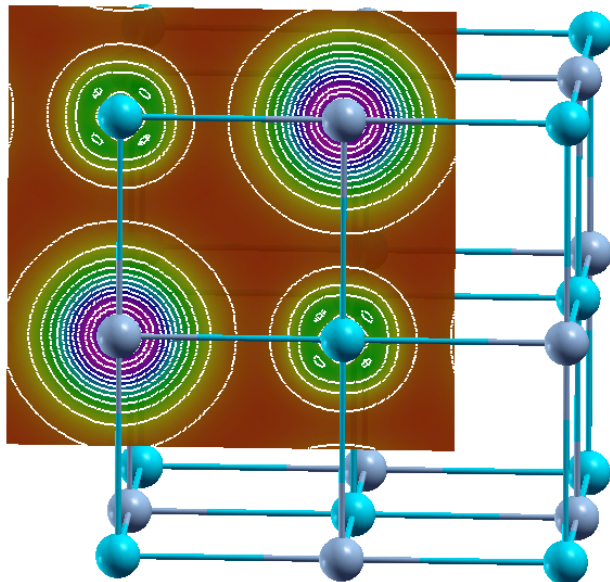


# Exercise I: Getting started

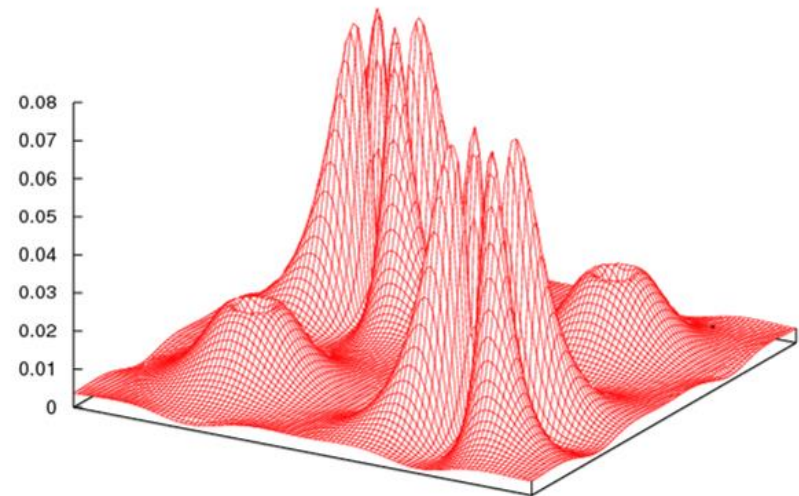
TiN:

Electron density

- **x lapw2 -emin** X\_putNumberHere
- edit "TiN.in5" to choose the plane for plotting
- **x lapw5** – to calculate electron density
- Plot results in XCrysDen and/or **rhoplot**



valence  $\rho$



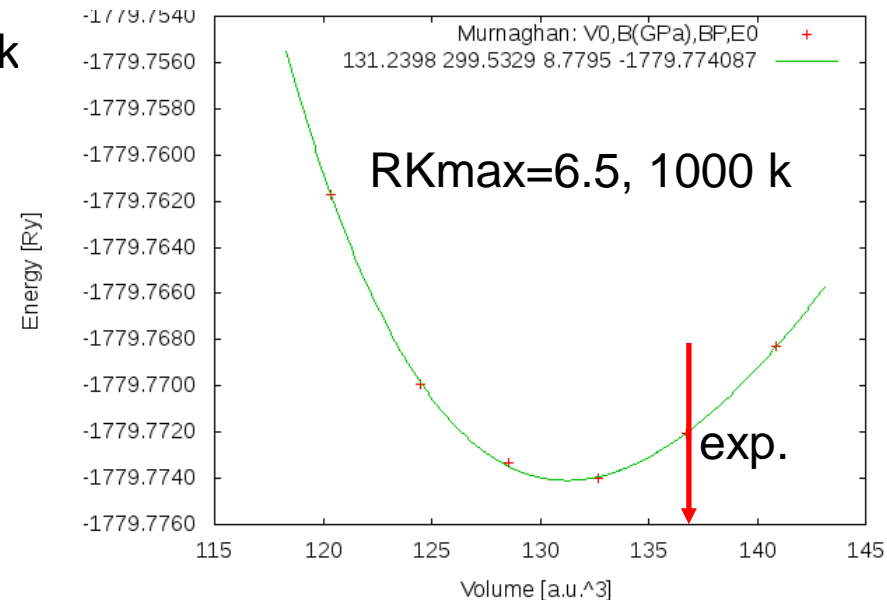
Ti-d band

# Exercise II: volume optimiz.

TiC:

TiC (F; Space group 225;  $a=4.328$  Ang; Ti= $4a=(0,0,0)$ ; C= $4b=(0.5,0.5,0.5)$ )

- a) initialize in expert mode with **LDA, RKmax=6.5, 1000 k-points, setrmt 5%**
- b) run x optimize and generate 6 structures (-9, -6, -3, 0, 3, 9% volume change)
- 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\_rkm6.5\_1000k
- d) run optimize.job,
- e) plot the results (using \*rkm5\_200k)



# Exercise II: structure optimiz.

**Structure given by:**

spacegroup

lattice parameter

positions of atoms

(basis)

**Rutile  $\text{TiO}_2$ :**

$P4_2/mnm$  (136)

$a=8.68$ ,  $c=5.59$  bohr

Ti:  $(0,0,0)$   $2a$

O:  $(0.304,0.304,0)$

Wyckoff position:  $x, x, 0$

$4f$

$P4_2/mnm$   
 $D_{4h}^{14}$

No. 136

$P 4_2/m 2_1/n 2/m$

$4/m m m$  Tetragonal

Origin at centre ( $mmm$ )

Number of positions,  
Wyckoff notation,  
and point symmetry

Co-ordinates of equivalent positions

Conditions limiting  
possible reflections

General:

$hkl$ : No conditions

$hk0$ : No conditions

$0kl$ :  $k+l=2n$

$hhl$ : No conditions

Special: as above, plus

no extra conditions

$hkl$ :  $h+k=2n$ ;  $l=2n$

16	$k$	1	$x, y, z$ ; $\bar{x}, \bar{y}, z$ ; $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$ ; $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$ ; $x, y, \bar{z}$ ; $\bar{x}, \bar{y}, \bar{z}$ ; $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$ ; $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$ ; $y, x, z$ ; $\bar{y}, \bar{x}, z$ ; $\frac{1}{2}+y, \frac{1}{2}-x, \frac{1}{2}+z$ ; $\frac{1}{2}-y, \frac{1}{2}+x, \frac{1}{2}+z$ ; $y, x, \bar{z}$ ; $\bar{y}, \bar{x}, \bar{z}$ ; $\frac{1}{2}+y, \frac{1}{2}-x, \frac{1}{2}-z$ ; $\frac{1}{2}-y, \frac{1}{2}+x, \frac{1}{2}-z$ .
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8	$j$	$m$	$x, x, z$ ; $\bar{x}, \bar{x}, z$ ; $\frac{1}{2}+x, \frac{1}{2}-x, \frac{1}{2}+z$ ; $\frac{1}{2}-x, \frac{1}{2}+x, \frac{1}{2}+z$ ; $x, x, \bar{z}$ ; $\bar{x}, \bar{x}, \bar{z}$ ; $\frac{1}{2}+x, \frac{1}{2}-x, \frac{1}{2}-z$ ; $\frac{1}{2}-x, \frac{1}{2}+x, \frac{1}{2}-z$ .
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8	$i$	$m$	$x, y, 0$ ; $\bar{x}, \bar{y}, 0$ ; $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}$ ; $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}$ ; $y, x, 0$ ; $\bar{y}, \bar{x}, 0$ ; $\frac{1}{2}+y, \frac{1}{2}-x, \frac{1}{2}$ ; $\frac{1}{2}-y, \frac{1}{2}+x, \frac{1}{2}$ .
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8	$h$	2	$0, \frac{1}{2}, z$ ; $0, \frac{1}{2}, \bar{z}$ ; $0, \frac{1}{2}, \frac{1}{2}+z$ ; $0, \frac{1}{2}, \frac{1}{2}-z$ ; $\frac{1}{2}, 0, z$ ; $\frac{1}{2}, 0, \bar{z}$ ; $\frac{1}{2}, 0, \frac{1}{2}+z$ ; $\frac{1}{2}, 0, \frac{1}{2}-z$ .
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4	$g$	$mm$	$x, \bar{x}, 0$ ; $\bar{x}, x, 0$ ; $\frac{1}{2}+x, \frac{1}{2}+x, \frac{1}{2}$ ; $\frac{1}{2}-x, \frac{1}{2}-x, \frac{1}{2}$ .
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4	$f$	$mm$	$x, x, 0$ ; $\bar{x}, \bar{x}, 0$ ; $\frac{1}{2}+x, \frac{1}{2}-x, \frac{1}{2}$ ; $\frac{1}{2}-x, \frac{1}{2}+x, \frac{1}{2}$ .
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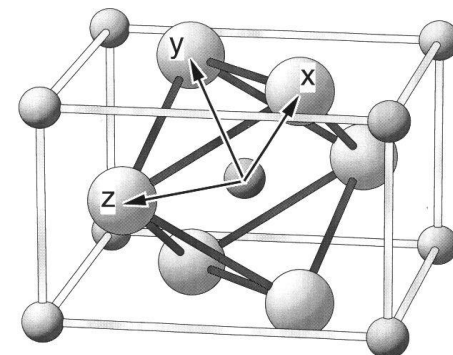
4	$e$	$mm$	$0, 0, z$ ; $0, 0, \bar{z}$ ; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}+z$ ; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}-z$ .
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4	$d$	$\bar{4}$	$0, \frac{1}{2}, \frac{1}{4}$ ; $\frac{1}{2}, 0, \frac{1}{4}$ ; $0, \frac{1}{2}, \frac{3}{4}$ ; $\frac{1}{2}, 0, \frac{3}{4}$ .
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4	$c$	$2/m$	$0, \frac{1}{2}, 0$ ; $\frac{1}{2}, 0, 0$ ; $0, \frac{1}{2}, \frac{1}{2}$ ; $\frac{1}{2}, 0, \frac{1}{2}$ .
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2	$b$	$mmm$	$0, 0, \frac{1}{2}$ ; $\frac{1}{2}, \frac{1}{2}, 0$ .
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2	$a$	$mmm$	$0, 0, 0$ ; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ .
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# Exercise II: structure optimiz.

TiO<sub>2</sub> (rutile):

TiO<sub>2</sub> (Space group 136; a=b=8.682 B; c=5.593 B; Ti=2a=(0,0,0); O=4f=(0.3,0.3,0)

**This is minimization using PORT**

a) initialize in expert mode with **PBE, RKmax=7.0, 1000 k-points, setrmt 0%**

`init_lapw -b -vxc 13 -red 0 -ecut -6.0 -rkmax 7.0 -numk 1000`

b) Visualize structure

c) `run_lapw -p -fc 1 -NI`

- to see how big are the forces

d) `min_lapw -p`

- performs all dirty work

e) `save_lapw case_relaxed_rkm7`

f) `analyze case.scf_mini`

`:ENE :FGL002z :POS002z`

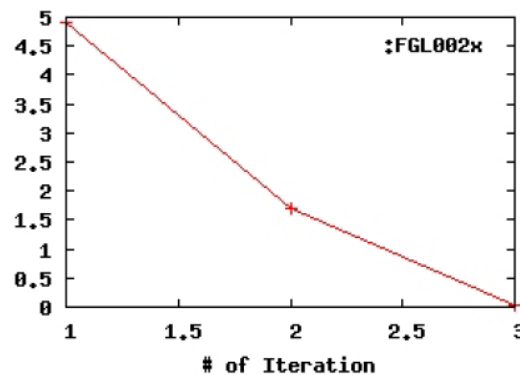
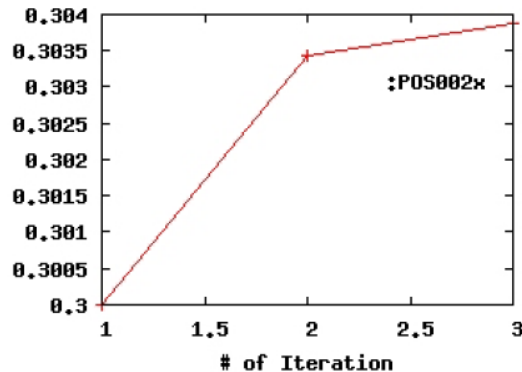
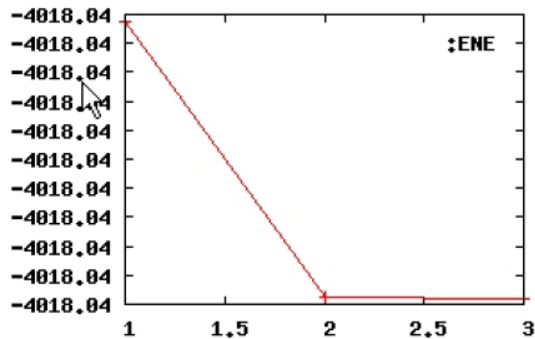
g) The final structural parameter of the O-atom should be close to x=0.304, which compares well with the experimental x=0.305.

# Exercise II: structure optimiz.

TiO<sub>2</sub> (rutile):

TiO<sub>2</sub> (Space group 136; a=b=8.682 B; c=5.593 B; Ti=2a=(0,0,0); O=4f=(0.3,0.3,0))

This is minimization using PORT



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:

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

Analysis of: ☐ TiO2.scf with 10 lines.  
or of alternate scf-files: ☒ TiO2.scf\_mini with 10 lines.

☒ Graphics using scfmonitor (only for single scf file)



# Exercise II: structure optimiz.

TiO<sub>2</sub> (rutile):

TiO<sub>2</sub> (Space group 136; a=b=8.682 B; c=5.593 B; Ti=2a=(0,0,0); O=4f=(0.3,0.3,0)

**This is minimization using MSR1a**

a) initialize in expert mode with **PBE, RKmax=7.0, 1000 k-points, setrmt 0%**

`init_lapw -b -vxc 13 -red 0 -ecut -6.0 -rkmax 7.0 -numk 1000`

b) Visualize structure

c) `run_lapw -p -fc 1 -NI`

- to see how big are the forces

d) `run -min -fc 1 -cc 0.001 -ec 0.0001`

- min sets MSR1a in case.inm

e) `save_lapw case_relaxed_rkm7`

f) `analyze case.scf`

`:ENE :FGL002z :POS002z :ITE`

g) The final structural parameter of the O-atom should be close to x=0.304, which compares well with the experimental x=0.305.





# Exercise III: testing accuracy

hcp-Fe (exp, 12.7 GPa):

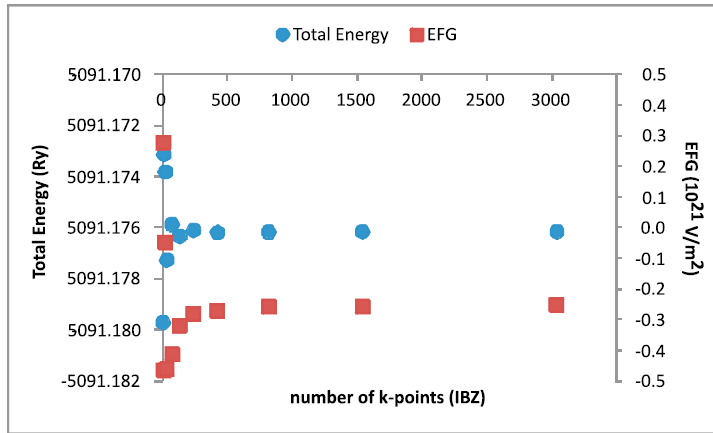
hcp-Fe (Space group 194;  $a=b=4.673$  B;  $c=7.487$  B;  $\alpha=\beta=90^\circ$   $\gamma=120^\circ$ ;  
 $\text{Fe}=2d=(1/3, 2/3, 3/4)$ ; non-magnetic

- `init_lapw -b -vxc 13 -ecut -7.0 -rkmax 7.0 -numk 30`
- How many k-points?
- `run_lapw -cc 0.0001`
- Record the total energy with Linux command or WIEN2k command
  - `grep :ENE case.scf`
  - `grep line :KPT '*.scf' 1`
  - `grep line :ENE '*.scf' 1`
- Save calculation `save -a hcp-Fe_RKM70_k0006`
- Repeat everything doubling number of k-points: 30, 60, 120, etc., 30720
  - `x kgen 120`
  - No need to run `init_lapw` again

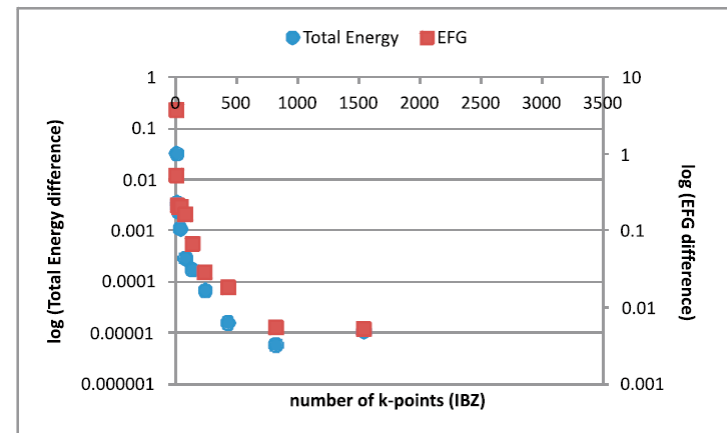
# Exercise III: testing accuracy

hcp-Fe (exp, 12.7 GPa):

hcp-Fe (Space group 194;  $a=b=4.673$  B;  $c=7.487$  B;  $\alpha=\beta=90^\circ$   $\gamma=120^\circ$ ;  
 $\text{Fe}=2d=(1/3, 2/3, 3/4)$ ; non-magnetic



Total energy and electric Field Gradient (EFG) as a function of the number of k-points in the irreducible part of the first Brillouin zone (IBZ).



The logarithm of the difference between total energy (EFG) at the largest number of k-points and at the present number of k-points.



# Exercise III: testing accuracy

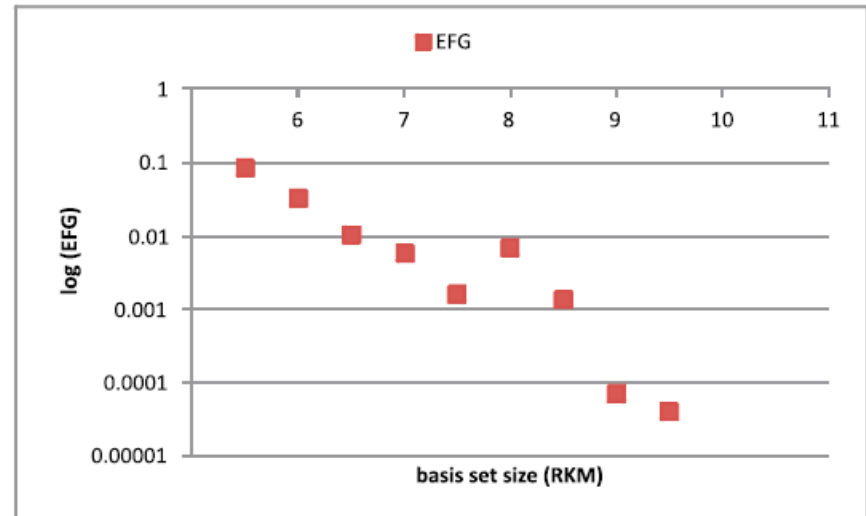
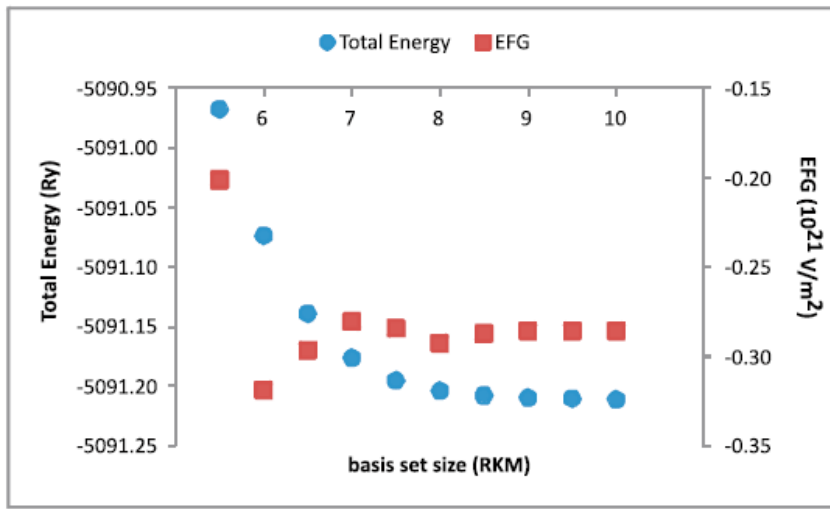
hcp-Fe (exp, 12.7 GPa):

hcp-Fe (Space group 194;  $a=b=4.673$  B;  $c=7.487$  B;  $\alpha=\beta=90^\circ$   $\gamma=120^\circ$ ;  
 $\text{Fe}=2d=(1/3, 2/3, 3/4)$ ; non-magnetic

- Suppose 240 k-points in IBZ (3840 k-points in the full BZ) is enough
- RKmax vary from 5.5 till 9.5 (in steps of 0.5)
- `init_lapw -b -vxc 13 -ecut -7.0 -rkmax 5.5 -numk 3840`
  - Change case.in1, run, save, repeat
- Check the basis set size and total energy with Linux command or WIEN2k command
  - `grep line :RKM '*.scf' 1`
  - `grep line :ENE '*.scf' 1`
- Basis set increased 4 times: from 61LOs (for RKM=5) to 223LOs (RKM= 9.5). The calculation time increased 64 times (it scales with the third power of the basis set size)

# Exercise III: testing accuracy

hcp-Fe (exp, 12.7 GPa):



- We knew that with 240 k-points the EFG is known with an accuracy  $\sim 0.05$
- It does not make sense to ask for a basis set that offers a better accuracy
- Even a small basis set as RKM=6.5 offers this accuracy:
  - `init_lapw -b -vxc 13 -ecut -7.0 -rkmax 6.5 -numk 3840`
- If EFG is searched with accuracy of  $\sim 0.01$ , then:
  - `init_lapw -b -vxc 13 -ecut -7.0 -rkmax 8.5 -numk 30720`



# Exercise IV: Testing exchange potentials

GaAs:

GaAs (Space group 216;  $a=b=c=10.683136$  B; Ga=4a=(0,0,0); As=4c=(1/4,1/4,1/4)

- Make 4 folders to test
  - PBE (13), LDA (5), PBEsol (19), WC (11) exchange potentials
- run optimization problem:
  - x optimize and generate 7 structures (-9, -6, -3, 0, 3, 6, 9% volume change)
  - edit "optimize.job"
  - run optimize.job
  - plot the results
- If run from terminal:
  - eosfit
  - Check the file case.outputeos
  - Plot "volume, E-tot"
- If run from w2web:
  - Finish analysis and plot "volume, E-tot" which automatically gives minimum



# Exercise IV: Testing exchange potentials

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GaAs:

GaAs (Space group 216;  $a=b=c=10.683136$  B; Ga=4a=(0,0,0); As=4c=(1/4,1/4,1/4))

	lattice, Bohr	GAP, eV
LDA (5),	10.5946	0.466
Experiment	10.68309	1.52
PBEsol (19),	10.6977	0.411
WC (11),	10.7009	0.350
PBE (13)	10.8534	0.164



# Exercise V: Magnetism

## Cr (nonmagnetic)

Cr (Space group 229;  $a=b=c=2.885$  Å;  $\text{Cr}=2a=(0,0,0)$ )

- `instgen_lapw` allows to define the spin-state of all/certain atoms:
  - `case.struct` must be present with specified RMT
  - If does not exist, it is produced automatically during `init_lapw`
  - Otherwise, first thing after `case.struct` is generated run `instgen_lapw`
- `instgen_lapw -up` spin-up configuration for all atoms (default)
- `instgen_lapw -nm` non-magnetic configuration for all atoms
- `instgen_lapw -ask` asks for each atom which configuration it should be
- If from terminal
  - `printf 'u\nd\nn\n' | instgen_lapw -ask -s` 3 atoms: up down nonmagn
- If run from `w2web`:
  - Select manually, the `w2web` will run the command above in background



# Exercise V: Magnetism

Cr (nonmagnetic)

Cr (Space group 229;  $a=b=c=2.885$  Å; Cr=2a=(0,0,0))

- Cr = [Ar] 3d5 4s1
- instgen\_lapw -nm
- Initialize
  - everything default
  - 5000k
- run\_lapw -cc 0.001
- grepline :ENE `\*.scf' 1

```
Cr
Ar 3
3, 2, 2.0 N
3, 2, 2.0 N
3, -3, 0.5 N
3, -3, 0.5 N
4, -1, 0.5 N
4, -1, 0.5 N
****
****
```

END of input (instgen\_lapw)



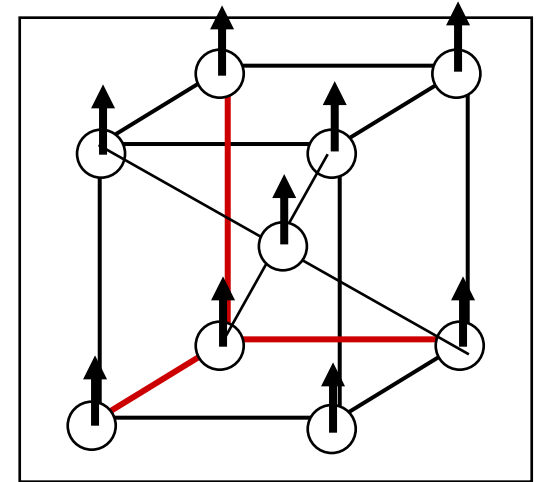
# Exercise V: Magnetism

## Cr (ferromagnetic)

Cr (Space group 229;  $a=b=c=2.885$  Å;  $\text{Cr}=2a=(0,0,0)$ )

- Cr = [Ar] 3d5 4s1
- instgen\_lapw -up
- Initialize
  - everything default
  - 5000k
  - -sp option must be used now
- runsp\_lapw -cc 0.001
- grepline :ENE '\*.scf' 1
- Plot DOS and bandstructure
  - Create case.klist\_band
  - x lapw1 -band -p -up
  - x lapw1 -band -p -dn
  - x lapw2 -band -p -qtl -up
  - Edit case.insp to enter correct EF
  - x spaghetti -p -up
  - Plot bandstructure

```
Cr
Ar 3
3, 2, 2.0 N
3, 2, 2.0 N
3, -3, 1.0 N
3, -3, 0.0 N
4, -1, 1.0 N
4, -1, 0.0 N
****
****
```

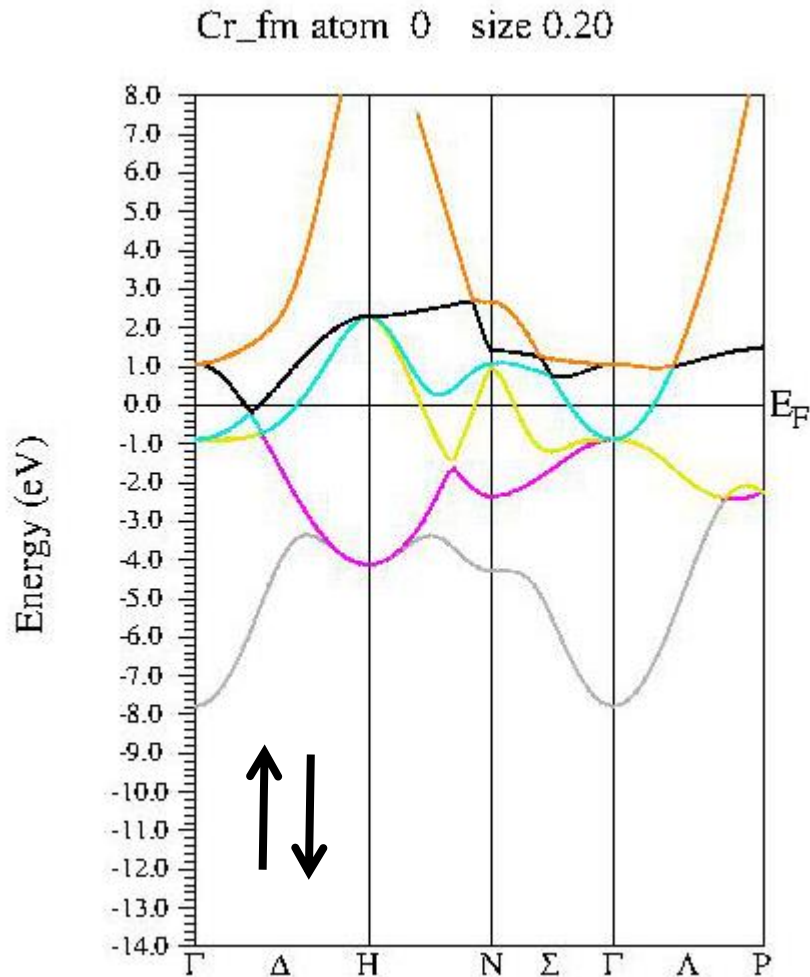


END of input (instgen\_lapw)

(just to find out that the  
solution is nonmagnetic)

# Exercise V: Magnetism

## Cr (ferromagnetic)



grepline :ENE '\*.scf' 1

grepline :MMTOT '\*.scf' 1

grep :MMI001 \*.scf

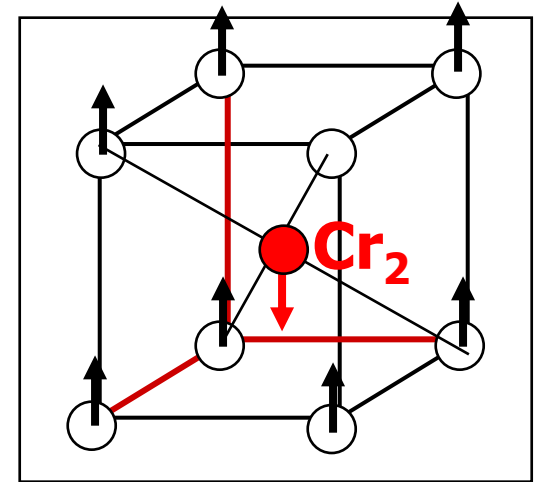
To observe that magnetic moment in sphere 1 decreases with iterations reaching 0 at the final converged iteration

# Exercise V: Magnetism

## Cr (antiferromagnetic)

Cr (Space group 229;  $a=b=c=2.885$  Å;  $\text{Cr}=2a=(0,0,0)$ )

- Cr = [Ar] 3d<sup>5</sup> 4s<sup>1</sup>
- Where to take 2 atoms of Cr?
- Starting from case.struct of ferromagnetic
- Run supercell with case.struct, 1, 1, 1, 0, 0, 0, P
  - New structure is in case\_super.struct
  - Rename this file to case\_struct (you may want to keep the old case.struct file)
  - What is space group? Symmetry operations?
  - Rename necessary atoms in case\_struct: Cr1 and Cr2, for example
- `printf 'u\nd\n' | instgen_lapw -ask -s` 2 atoms: up down
- `init_lapw -b -sp -numk 5000`
- `runsp_lapw -p -cc 0.001`
- `grepline :ENE '*.scf' 1`
- Plot bandstructure and DOS



# Exercise V: Magnetism

## Cr (antiferromagnetic)

### ■ Plot bandstructure

- Edit case.in1 to enter large Emax
- x lkgen 10000 to generate denser mesh
- x lapw1 -p -up
- x lapw1 -p -dn
- x lapw2 -p -qtl -up
- Edit case.int to select what is wanted
- x tetra -up
- Plot DOS (case.dos1evup)

### ■ Is FM/NM or AFM Cr more stable?

- AFM -4203.54296998
- FM -2101.76940377
- NM -2101.76940618

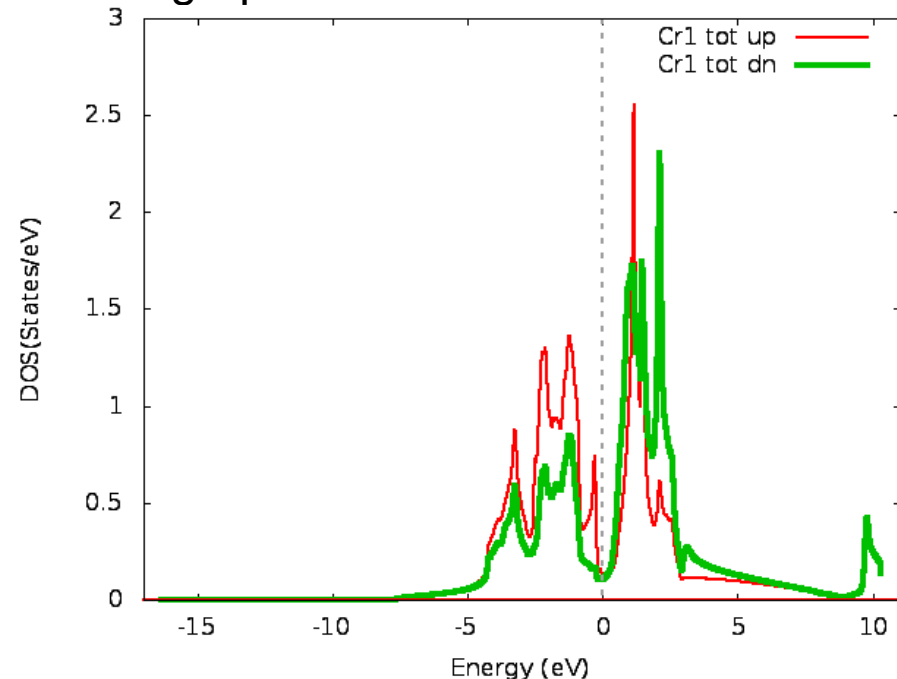
### ■ Is it necessary to plot DOS for down spin

```
grepline :ENE '*.scf' 1
```

```
grepline :MMTOT '*.scf' 1
```

```
grep :MMI001 *.scf
```

```
grep :VOL *.scf
```





# Exercise VI: Hybrid-DFT

MgO: Identification of bandgap (PBE vs mBJ vs YS-PBE0)

MgO (Space group 225;  $a=b=c=7.96$  Å;  $\text{Mg}=4a=(0,0,0)$ ;  $\text{O}=4b=(0.5,0.5,0.5)$ )

- *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, or increase allowed number of cycles via option “-i 80”)
  - monitor the change of the :GAP
  - plot a band structure (fcc) and compare with PBE



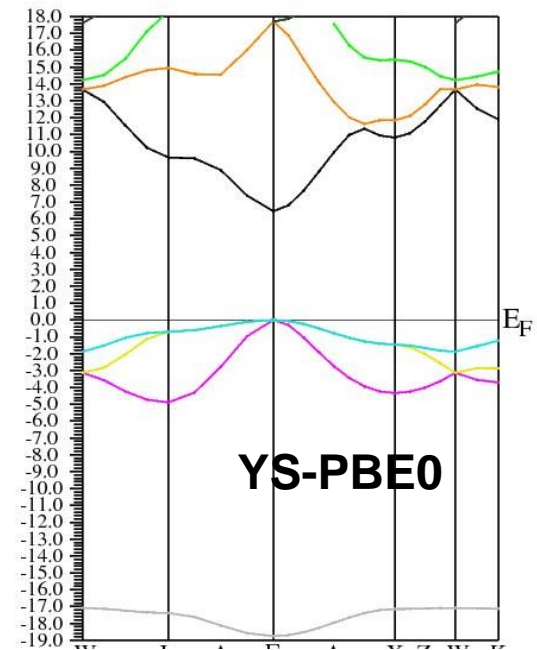
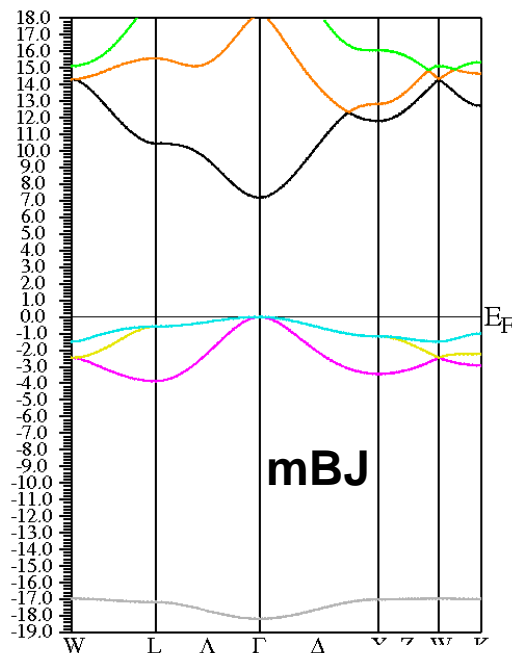
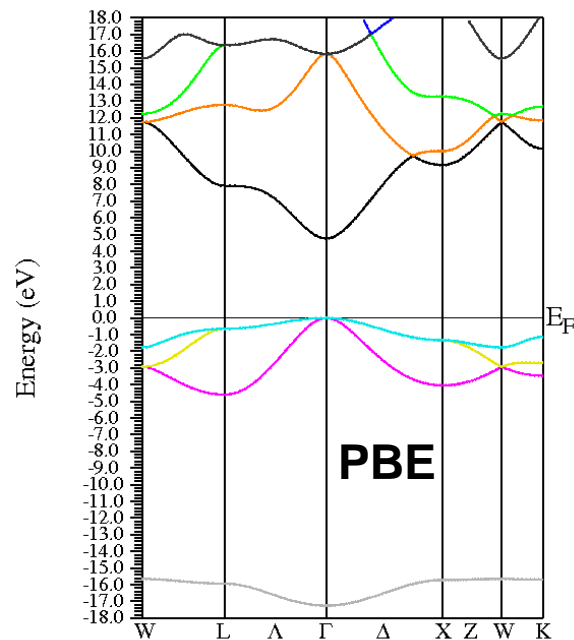
# Exercise VI: Hybrid-DFT

## MgO: Identification of bandgap (PBE vs mBJ vs YS-PBE0)

- *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 Userguide 4.5.8)
    - Select NBAND=12 (case.inhf)
    - and a 4x4x4 / 4x4x4 k-point mesh (no reduction)
    - Another option to add reduced k-mesh
  - scf cycle with **-hf**
  - monitor the change of the :GAP and compare it with mBJ and exp. gaps (only every 2<sup>nd</sup> 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 VI: Hybrid-DFT

## MgO: Identification of bandgap (PBE vs mBJ vs YS-PBE0)

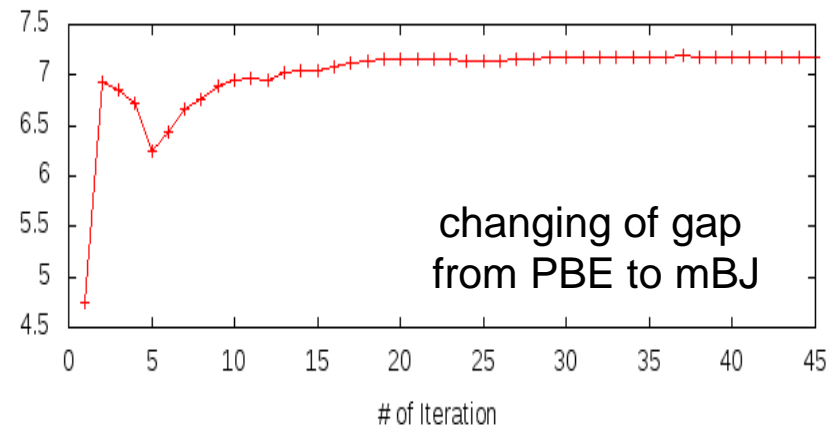


Experimental value of bandgap is 7.8 eV

PBE: 4.75 eV

mBJ: 7.20 eV

HF: 6.45 eV





# Exercise VII: XSPEC and core-hole

---

## MgO (Mg K-XAS)

MgO (Space group 225;  $a=b=c=7.96$  Å; Mg=4a=(0,0,0); O=4b=(0.5,0.5,0.5))

- instgen\_lapw -up
- Initialize
  - everything default
  - 1000k
- Perform SCF calculations
- XSPEC task:
  - Larger Emax in MgO.in1
  - Select in MgO.inxs
  - Mg-K ABS from 0-30 eV
  - Vary broadening





# Exercise VII: XSPEC and core-hole

- 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 sgroupp` 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 VII: XSPEC and core-hole

- **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 VII: XSPEC and core-hole

---

## MgO (Mg K-XAS)

MgO (Space group 225;  $a=b=c=7.96$  Å; Mg=4a=(0,0,0); O=4b=(0.5,0.5,0.5))

- instgen\_lapw -up
- Initialize
  - everything default
  - 1000k
- Perform SCF calculations
- XSPEC task:
  - Larger Emax in MgO.in1
  - Select in MgO.inxs
  - Mg-K ABS from 0-30 eV
  - Vary broadening



# Exercise VII: XSPEC and core-hole

## MgO (Mg K-XAS)

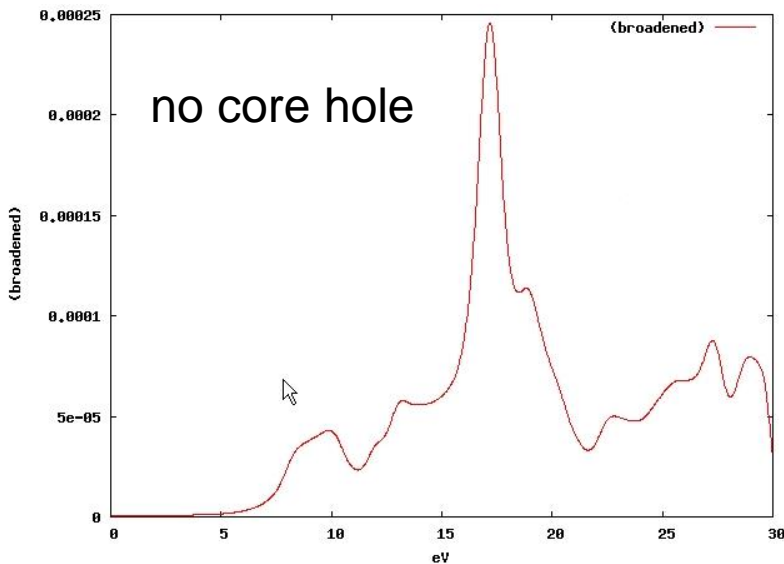
MgO (Space group 225;  $a=b=c=7.96$  Å;  $\text{Mg}=4a=(0,0,0)$ ;  $\text{O}=4b=(0.5,0.5,0.5)$ )

- Why supercell?
- 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**" 1<sup>st</sup> atom (Mg → Mg1)
  - init\_lapw (with 200k, RKmax=6.5)
  - edit case.inc (remove a core electron from 1<sup>st</sup> atom)
  - edit case.in2 (add one valence electron)
  - run\_lapw (for bigger calc. use -it and compare timings for 1<sup>st</sup> and later iterations!)
  - edit case.in2 (remove extra valence electron)
  - XSPEC task for Mg-K XAS (see above)

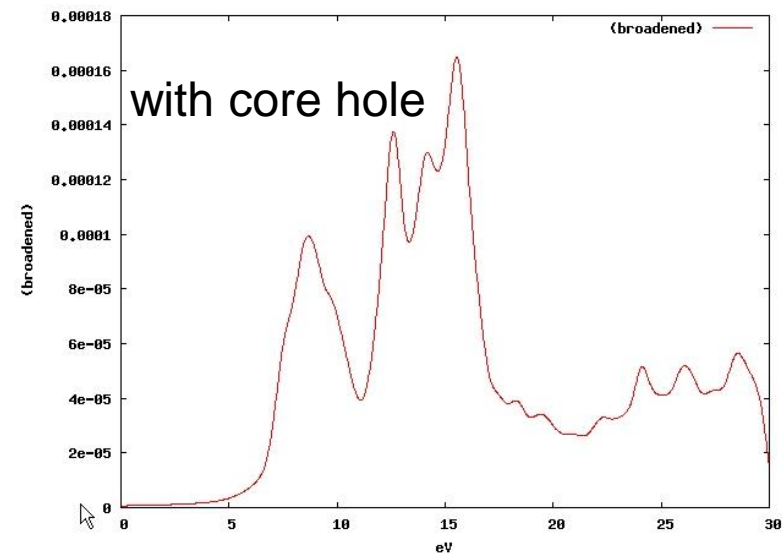
# Exercise VII: XSPEC and core-hole

## MgO (Mg K-XAS)

MgO (Space group 225;  $a=b=c=7.96$  Å; Mg=4a=(0,0,0); O=4b=(0.5,0.5,0.5))



## Mg-K XAS



# Exercise VIII: DFT+U

if time  
permits

## NiO (antiferromagnetic)

NiO (Space group 166;  $a=b=5.605236$  B;  $c=13.729967$  B;  $\alpha=\beta=90$   $\gamma=120$ ;  
Ni=3a=(0,0,0) i.e. add (0,0,0) (2/3,1/3,1/3) (1/3,2/3,2/3)  
O=3b=(0,0,1/2)

- Crystallography.net gives R -3 m: H (H stands for hexagonal, WIEN2k needs rhombohedral axes: R -3 m: R, which will produce Ni=1a=(0,0,0)  
O=1b=(1/2,1/2,1/2)
- How to make antiferromagnetic
  - supercell to convert from R into H (primitive)
  - supercell to add 2<sup>nd</sup> cell in z-direction
  - Check how many inequivalent atoms
  - Which to pick as Ni1 and Ni2?
- To pick antiferromagnetic along [111] direction choose:
  - Ni1 = (0,0,0) (1/3,2/3,2/3) (2/3,1/3,1/3)
  - Ni2 = (0,0,1/2) (1/3,2/3,2/3-1/2) (2/3,1/3,1/3+1/2)
- Run sgrouop which will generate the structure:
  - NiO (Space group 166;  $a=b=5.605236$  B;  $c=27.459934$  B;  $\alpha=\beta=90$   $\gamma=120$
  - Ni1=1a=(0,0,0) Ni2=1b=(1/2,1/2,1/2) O=2c=( $\pm 1/4, \pm 1/4, \pm 1/4$ )

## NiO (antiferromagnetic)

- GGA calculations
  - Initialize (with AFM)
  - Run SCF calculations (with AFM)
  - Compute GAP, DOS and magnetic moment of Ni1, Ni2 and O
  - `save_lapw NiO_gga`
- GGA+U calculations
  - Initialize (with AFM)
  - Edit two files:
    - `case.indm` and `case.inorb` where to enter number of atoms, details for each atom and value of U
  - In this case:  $U=7\text{eV}$ ,  $J=0$
  - `runsp_lapw -p -orb -i 80 -ec 0.0001 -cc 0.001 -NI`
  - Compute GAP, DOS and magnetic moment of Ni1, Ni2 and O
  - `save_lapw NiO_gga+u`
- TB-mBJ calculation for NiO
  - start new case
  - Compute GGA
  - add mBJ
  - Compute GAP, DOS and magnetic moment of Ni1, Ni2 and O

# Exercise VIII: DFT+U

if time  
permits

## NiO (antiferromagnetic)

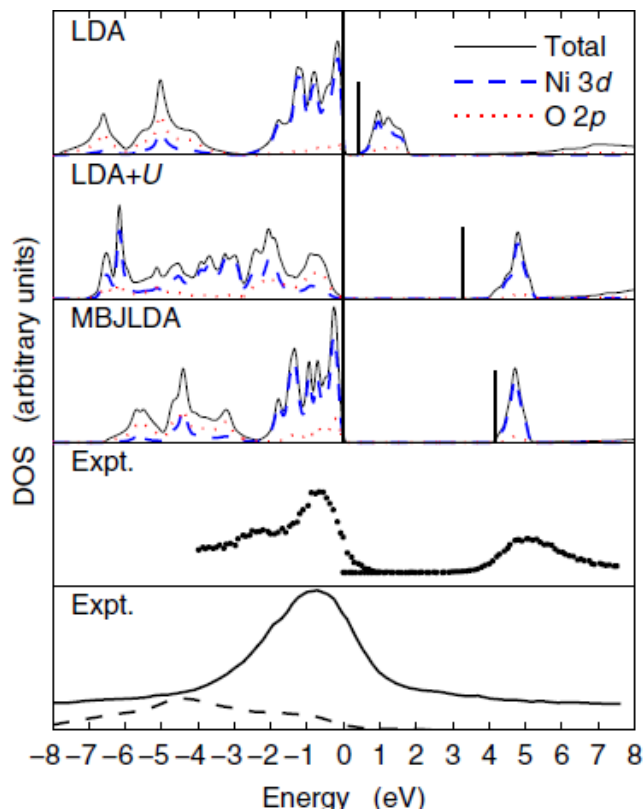


FIG. 2 (color online). DOS of NiO. The vertical bars indicate the end of the fundamental band gap which starts at  $E = 0$  eV. The panels labeled “Expt.” show photoelectron [25] (upper panel) and XES [33] [lower panel, Ni (solid line) and O (dashed line) spectral measurements.

	GAP, eV	Moment, $\mu_B$
LDA	1.12	$\pm 1.41$
LDA+U	3.54	$\pm 1.76$
mBJ	4.28	$\pm 1.76$
Exper.	4	

## GGA+U

