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

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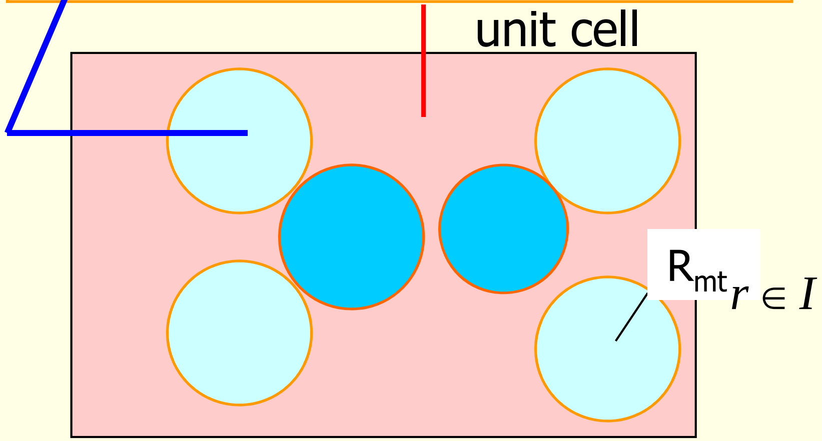
(You can find this pdf at $WIENROOT/wien2k.pdf)

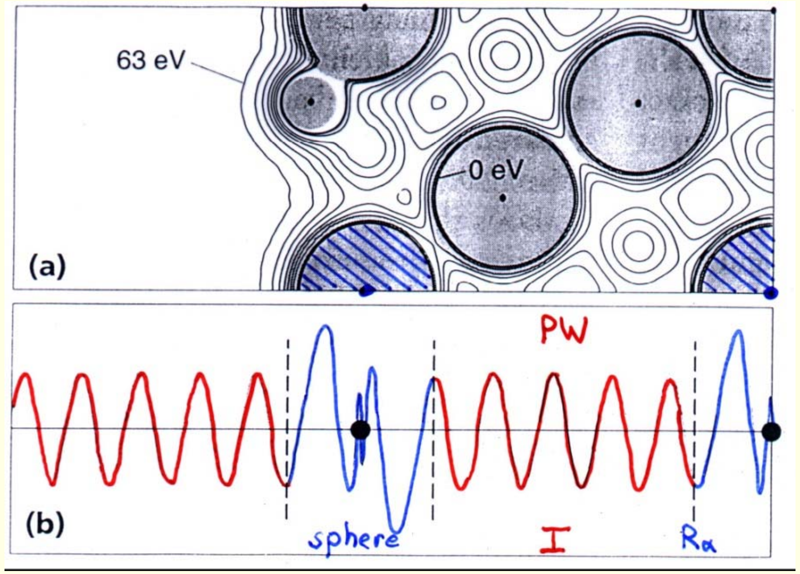
APW Augmented Plane Wave method

The unit cell is partitioned into:

atomic spheres

Interstitial region





Basisset:

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

Atomic partial waves

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

join

energy dependency !

$u_l(r,\varepsilon)$ 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

APW based schemes

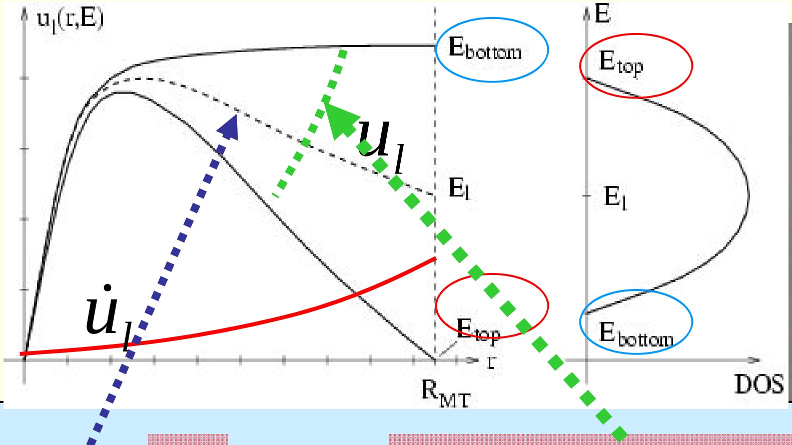
- APW (J.C.Slater 1937)
  - *Non-linear eigenvalue problem*
  - *Computationally very demanding*
- LAPW (O.K.Andersen 1975)
  - *Generalized eigenvalue problem*
  - *Full-potential (A. Freeman et al.)*
- Local orbitals (D.J.Singh 1991)
  - *treatment of semi-core states (avoids ghostbands)*
- APW+lo (E.Sjöstedt, L.Nordstörm, D.J.Singh 2000)
  - *Efficience of APW + convenience of LAPW*
  - *Basis for* WIEN2k

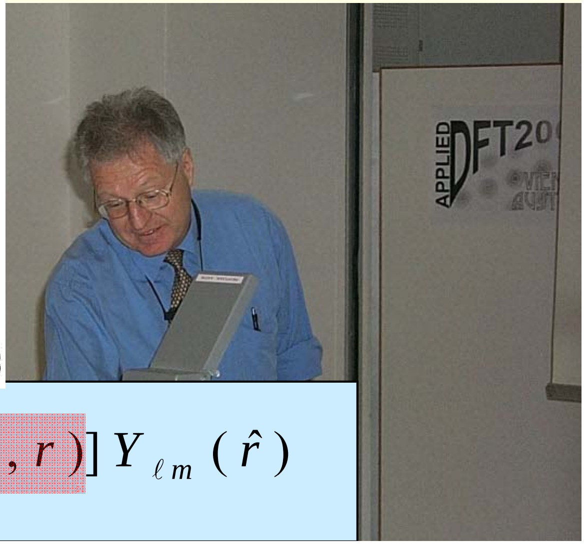
K.Schwarz, P.Blaha, G.K.H.Madsen,
Comp.Phys.Commun.**147**, 71-76 (2002)

Linearization of energy dependence

LAPW suggested by

O.K.Andersen,
Phys.Rev. B 12, 3060
(1975)





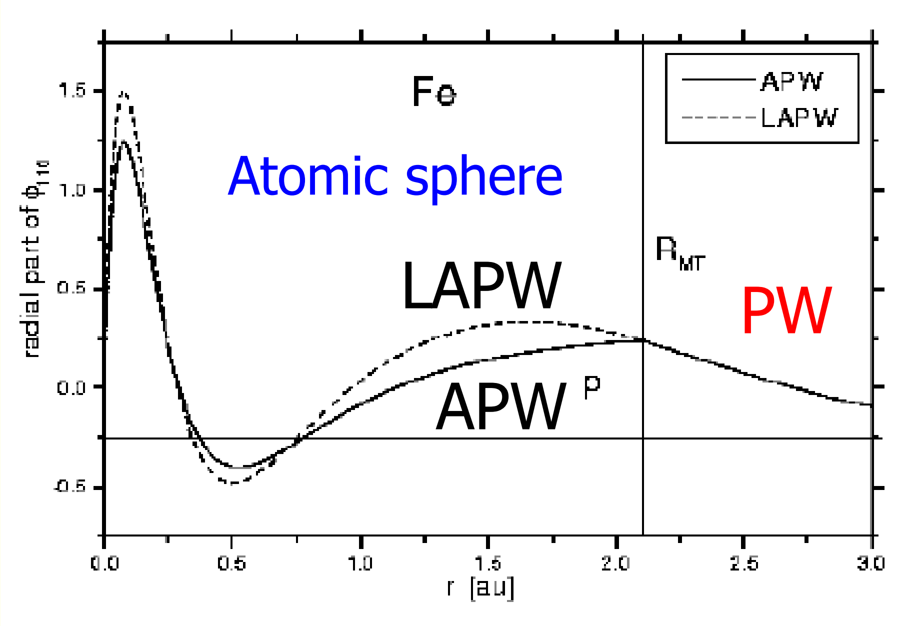
$$\Phi_{k_n} = \sum_{\ell m} [A_{\ell m}(k_n) u_\ell(E_\ell, r) + B_{\ell m}(k_n) \dot{u}_\ell(E_\ell, r)] Y_{\ell m}(\hat{r})$$

expand u_l at fixed energy E_l *and add* $\dot{u}_l = \partial u_l / \partial \varepsilon$

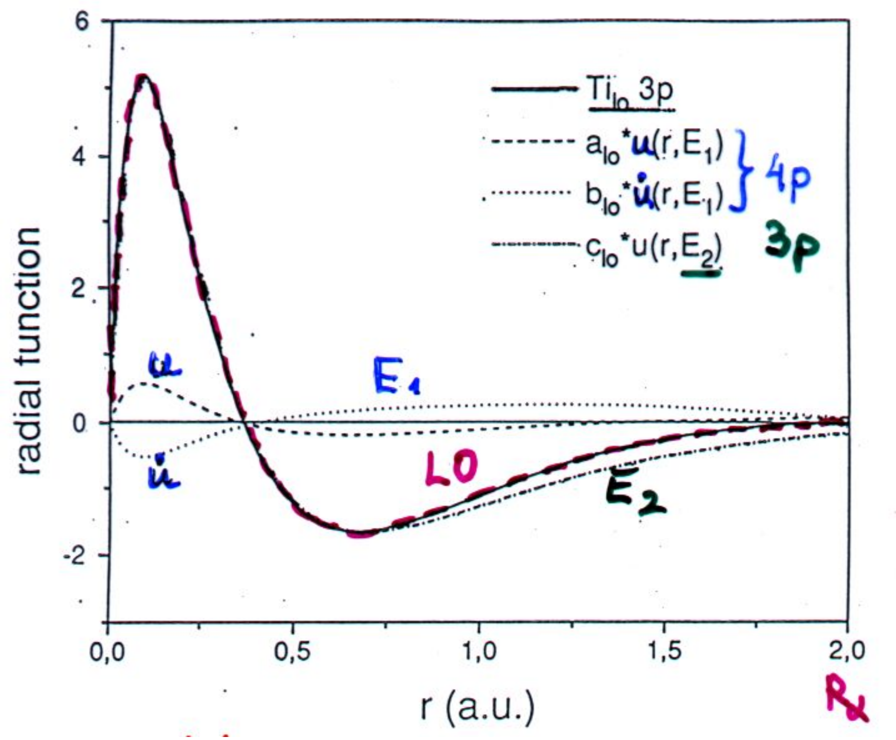
A_{lm}^k, B_{lm}^k: join PWs in value and slope

→basis flexible enough for single diagonalization

→additional constraint requires more PWs than APW



Extending the basis: Local orbitals (LO)



$$\Phi_{LO} = [A_{\ell m} u_\ell^{E_1} + B_{\ell m} \dot{u}_\ell^{E_1} + C_{\ell m} u_\ell^{E_2}] Y_{\ell m}(\hat{r})$$

- LO
  - *is confined to an atomic sphere*
  - *has zero value and slope at R*
  - *can treat two principal QN n for each azimuthal QN ℓ (3p and 4p)*
  - *corresponding states are strictly orthogonal (no "ghostbands")*
  - *tail of semi-core states can be represented by plane waves*
  - *only slight increase of basis set (matrix size)*

D.J.Singh,
Phys.Rev. B 43 6388 (1991)

Linearization LAPW vs. APW

- LAPW (for higher *l*) + LO

$$\Phi_{k_n} = \sum_{\ell m} [A_{\ell m}(k_n) u_\ell(E_\ell, r) + B_{\ell m}(k_n) \dot{u}_\ell(E_\ell, r)] Y_{\ell m}(\hat{r})$$

$$\Phi_{LO} = [A_{\ell m} u_\ell^{E_1} + B_{\ell m} \dot{u}_\ell^{E_1} + C_{\ell m} u_\ell^{E_2}] Y_{\ell m}(\hat{r})$$

- APW (for "chemical *l*") + lo

$$\Phi_{k_n} = \sum_{\ell m} A_{\ell m}(k_n) u_\ell(E_\ell, r) Y_{\ell m}(\hat{r})$$

$$\Phi_{lo} = [A_{\ell m} u_\ell^{E_1} + B_{\ell m} \dot{u}_\ell^{E_1}] Y_{\ell m}(\hat{r})$$

- Plane Waves (PWs) $e^{i(\vec{k}+\vec{K}_n).\vec{r}}$

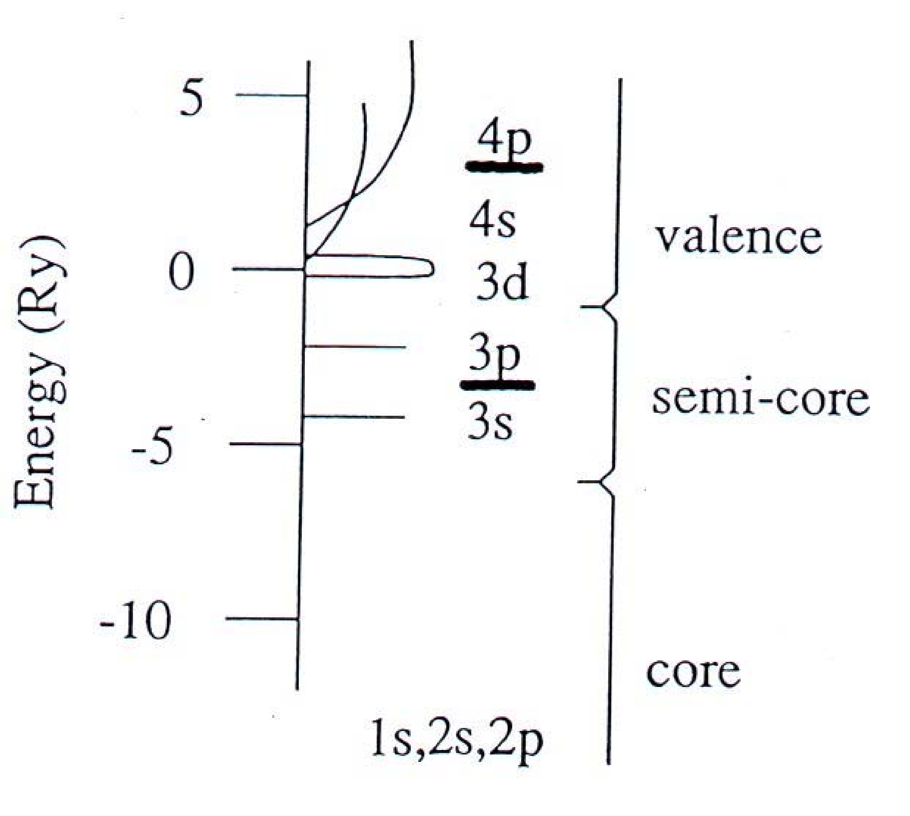
- match at sphere boundary (not stored)
  - *LAPW:* *value and slope* $A_{\ell m}(k_n), B_{\ell m}(k_n)$
  - *APW:* *value* $A_{\ell m}(k_n)$
  - *LO and lo:* *value (+slope) zero, normalization*

$$\Psi(r) = \sum_{k}^{k_{max}} c_{k_n} \Phi_{k_n}$$

- Variational coefficients: c_{kn}, c_{LO}, c_{lo}

Core, semi-core and valence states

For example: Ti



- Valences states
  - ***Scalar relativistic*** *wavefunctions with* ***large*** *and* ***small*** *component*
- Semi-core states
  - *Principal QN one less than valence (e.g.in Ti 3p and 4p)*
  - *not completely confined inside sphere*
  - *Treated by LOs*
- Core states (recalculated in scf)
  - *Reside completely inside sphere*
  - ***Fully relativistic*** *radial wf. (radial Dirac-equation)*
  - *Spherical symmetric*

DFT functionals available in WIEN2k

- various LDA, GGA, meta-GGA and DFT-D3 functionals
- interface to LIBXC (public domain XC-library)
- TB-mBJ (a XC-potential for band gaps)
- LDA+U
- “onsite” hybrid-DFT for “correlated electrons” (EECE)
  - *as cheap as LDA+U*
- hybrid functionals
  - *fairly expensive*

- additional packages: (very expensive !)
  - *GW calculations (GAP 2.0 code by Hong Jiang)*
  - *BSE calculations (obtainable on request)*

Band gaps by a semi-local **potential**

- Becke-Johnson potential (J. Chem. Phys. 124, 221101 (2006))
  - *local potential designed to reproduce non-local OEP potentials in atoms*
- modified Becke-Johnson potential

F.Tran P.Blaha
PRL **102**, 226401 (**2009**)

$$v_{x,\sigma}^{\mathrm{MBJ}}(\mathbf{r}) = c v_{x,\sigma}^{\mathrm{BR}}(\mathbf{r}) + (3c-2)\frac{1}{\pi}\sqrt{\frac{5}{12}}\sqrt{\frac{2t_\sigma(\mathbf{r})}{\rho_\sigma(\mathbf{r})}},$$

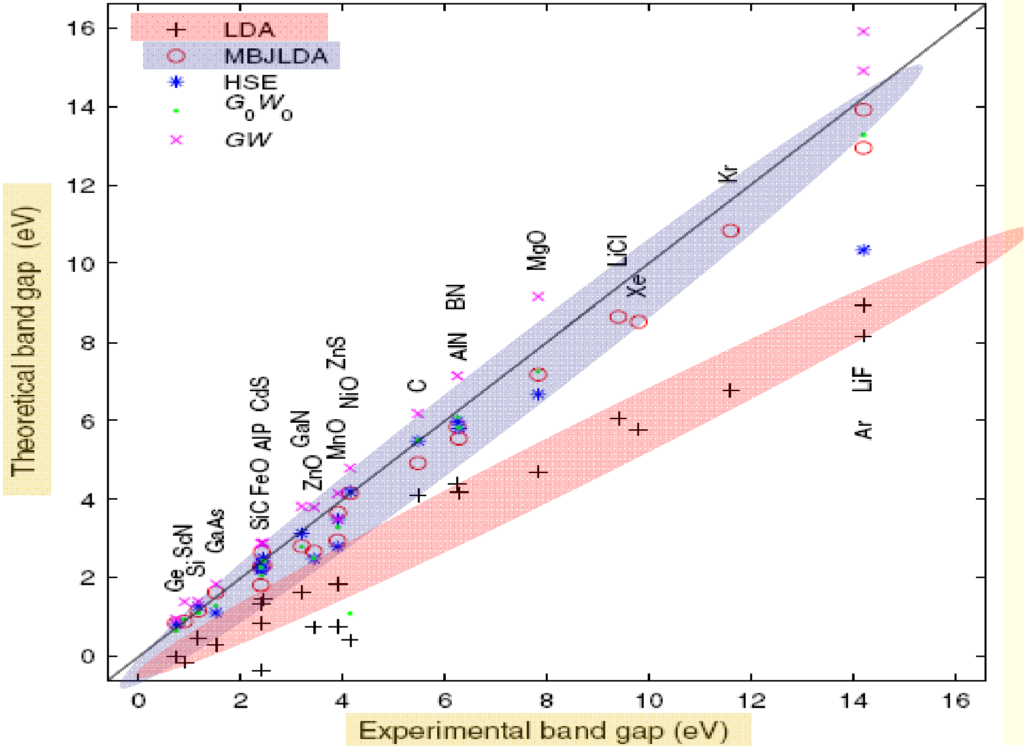
$$c = \alpha + \beta\left(\frac{1}{V_{\mathrm{cell}}}\int_{\mathrm{cell}}\frac{|\nabla\rho(\mathbf{r}')|}{\rho(\mathbf{r}')}d^3r'\right)^{1/2}$$

c depends on the density properties of a material

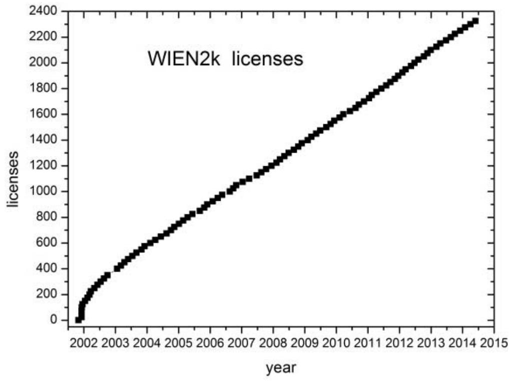
\+ gaps of „GW" quality

\+ good for correlated TM-oxides

\- NO energy (only V)



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: ~2600 users

23rd WIEN2k-workshop: 4.-7.June 2016
McMasters University, Hamilton, Canada

Properties with WIEN2k - I

- Energy bands
  - *classification of irreducible representations*
  - *´character-plot´ (emphasize a certain band-character)*
- Density of states
  - *including partial DOS with l and m- character (eg.* p_x *,* p_y *,* p_z *)*
- Electron density, potential
  - *total-, valence-, difference-, spin-densities,* ρ *of selected states*
  - *1-D, 2D- and 3D-plots (Xcrysden)*
  - *X-ray structure factors*
  - *Bader´s atom-in-molecule analysis, critical-points, atomic basins and charges* ($\nabla \rho . \vec{n} = 0$)
  - *spin+orbital magnetic moments (spin-orbit / LDA+U)*
- Hyperfine parameters
  - *hyperfine fields (contact + dipolar + orbital contribution)*
  - *Isomer shift*
  - *Electric field gradients (quadrupole splittings)*
  - *NMR Chemical shifts , Knight shifts*

Properties with WIEN2k - II

- Total energy and forces
  - *optimization of internal coordinates, (MD, BROYDEN)*
  - *cell parameter only via E_{tot} (no stress tensor)*
  - *elastic constants for cubic, hexagonal, and tetragonal cells*
  - *Phonons via supercells*
    - interface to PHONON (K.Parlinski) – bands, DOS, thermodynamics, neutrons
    - interface to PHONOPY (A. Togo)
      - http://www.wien2k.at/reg_user/unsupported
- Spectroscopy
  - *core level shifts*
  - *X-ray emission, absorption, electron-energy-loss (with core holes)*
    - core-valence/conduction bands including matrix elements and angular dep.
  - *optical properties (dielectric function in RPA approximation, JDOS including momentum matrix elements and Kramers-Kronig)*
- fermi surface: 2D, 3D (using XcrysDen)

Properties with WIEN2k - III

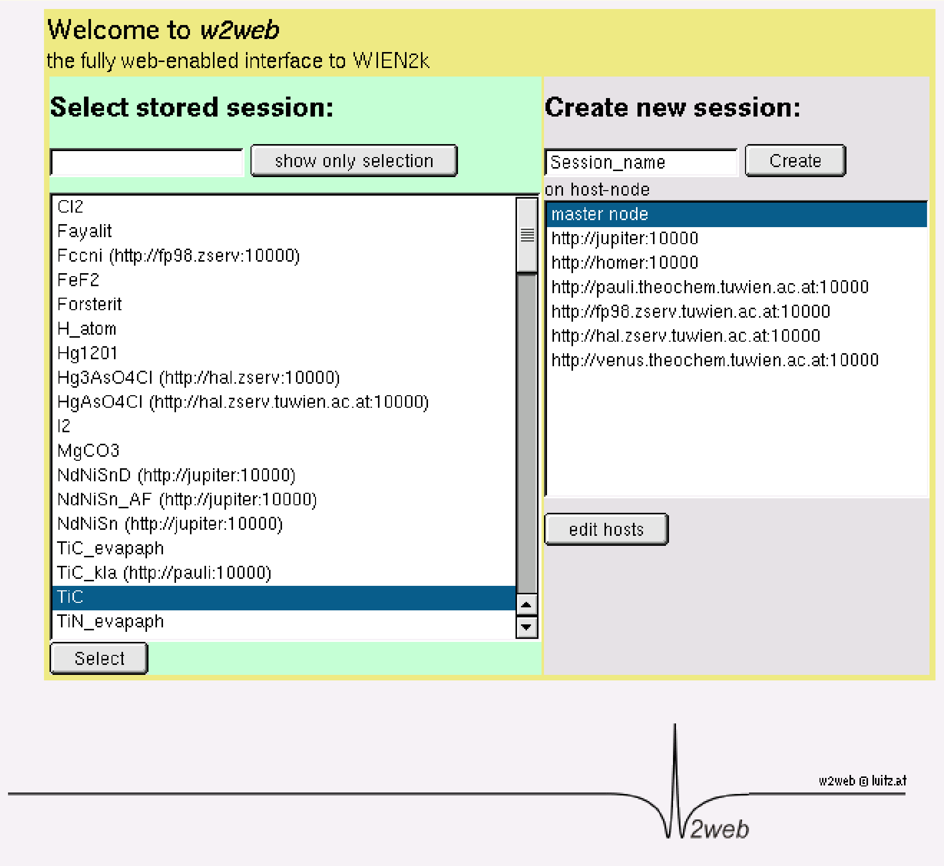
- advanced topics and developments
  - *non-collinear magnetism (available on request: www.wien2k.at)*
  - *transport properties (Fermi velocities, Seebeck, conductivity, thermoelectrics, ..): G. Madsen's BotzTrap code*
  - *(see http:www.wien2k.at/reg_user/unsupported)*
  - *Berry phases (BerryPI by O.Rubel etal.* (http:www.wien2k.at/reg_user/unsupported)
  - *Wannier functions (via Wannier90)*
  - *Bethe-Salpeter equation (for excitons, R.Laskowski)*
  - *GW (M.Scheffler, Hong Jiang)*

General remarks on WIEN2k

- WIEN2k consists of many independent F90 programs, linked together via C-shell scripts and executed via x PROGRAM.
- Each „case" runs in his own directory ./case
- The „master input" is called case.struct
- Initialize a calculation: init_lapw
- Run scf-cycle: run_lapw (runsp_lapw)
- You can run WIEN2k using any www-browser and the w2web interface, but also at the command line in an xterm.
- Input/output/scf files have endings as the corresponding programs:
  - *case.output1…lapw1; case.in2…lapw2; case.scf0…lapw0*
- Inputs are generated using STRUCTGEN(w2web, makestruct, cif2struct,xyz2struct) and init_lapw

w2web: the web-based GUI of WIEN2k

- Based on www
  - *WIEN2k can be managed remotely via w2web*
- Important steps:
  - *start w2web on all your hosts*
    - login to the desired host (ssh)
    - w2web (at first startup you will be asked for username/password, port-number, (master-)hostname. creates ~/.w2web directory)
  - *use your browser and connect to the (master) host:portnumber*
    - firefox http://fp98.zserv:10000
  - *create a new session on the desired host (or select an old one)*



Welcome to *w2web*

the fully web-enabled interface to WIEN2k

Select stored session:

Cl2
Fayalit
Fccni (http://fp98.zserv:10000)
FeF2
Forsterit
H_atom
Hg1201
Hg3AsO4Cl (http://hal.zserv:10000)
HgAsO4Cl (http://hal.zserv.tuwien.ac.at:10000)
I2
MgCO3
NdNiSnD (http://jupiter:10000)
NdNiSn_AF (http://jupiter:10000)
NdNiSn (http://jupiter:10000)
TiC_evapaph
TiC_kla (http://pauli:10000)
TiC
TiN_evapaph

Create new session:

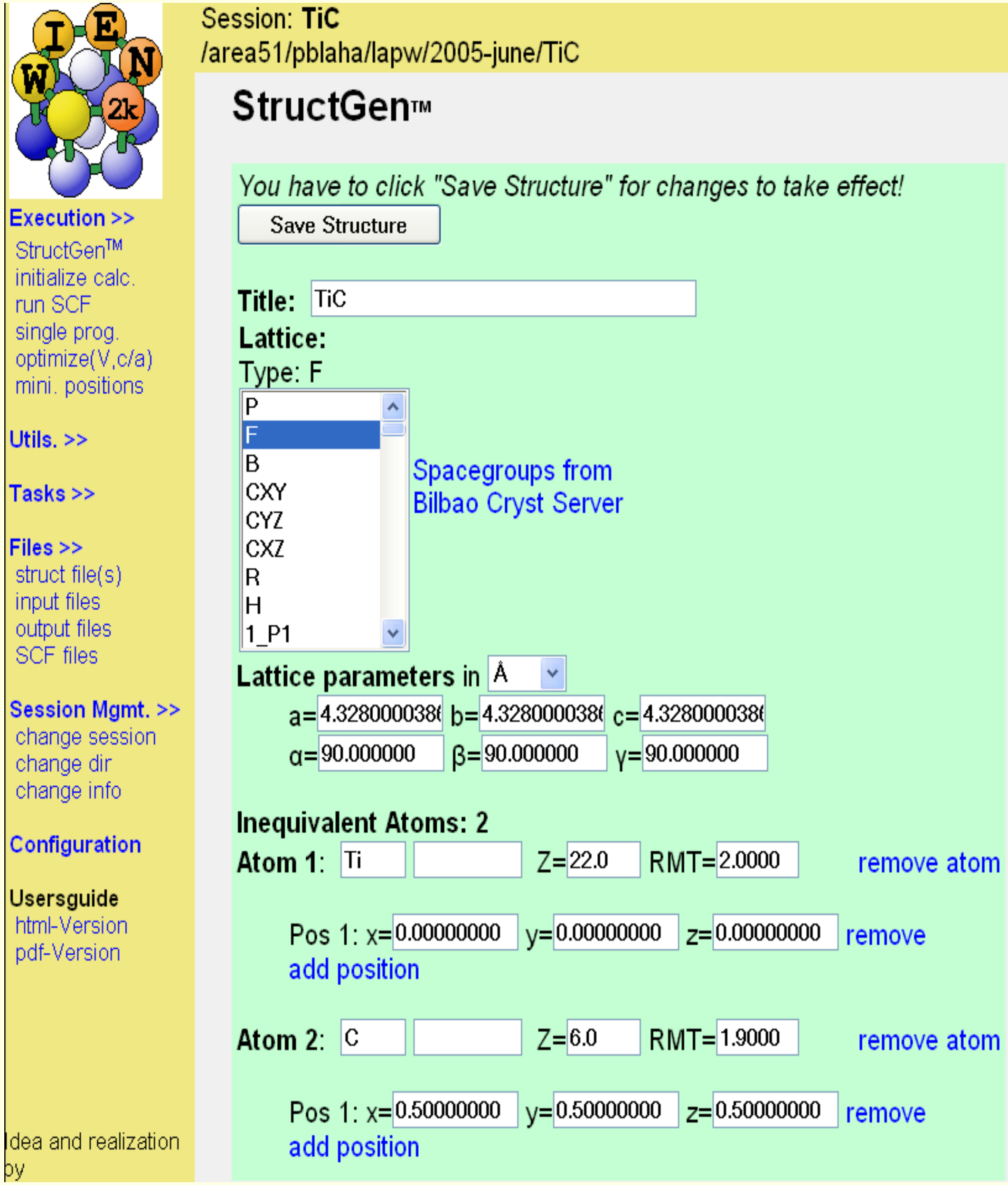
Session_name

on host-node

master node
http://jupiter:10000
http://homer:10000
http://pauli.theochem.tuwien.ac.at:10000
http://fp98.zserv.tuwien.ac.at:10000
http://hal.zserv.tuwien.ac.at:10000
http://venus.theochem.tuwien.ac.at:10000

w2web GUI (graphical user interface)

- 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*



Session: **TiC**
/area51/pblaha/lapw/2005-june/TiC

StructGen™

You have to click "Save Structure" for changes to take effect!

Title: TiC

Lattice:

Type: F

Lattice parameters in Å

a=4.3280000038 b=4.3280000038 c=4.3280000038

α=90.000000 β=90.000000 γ=90.000000

Inequivalent Atoms: 2

Atom 1: Ti Z=22.0 RMT=2.0000

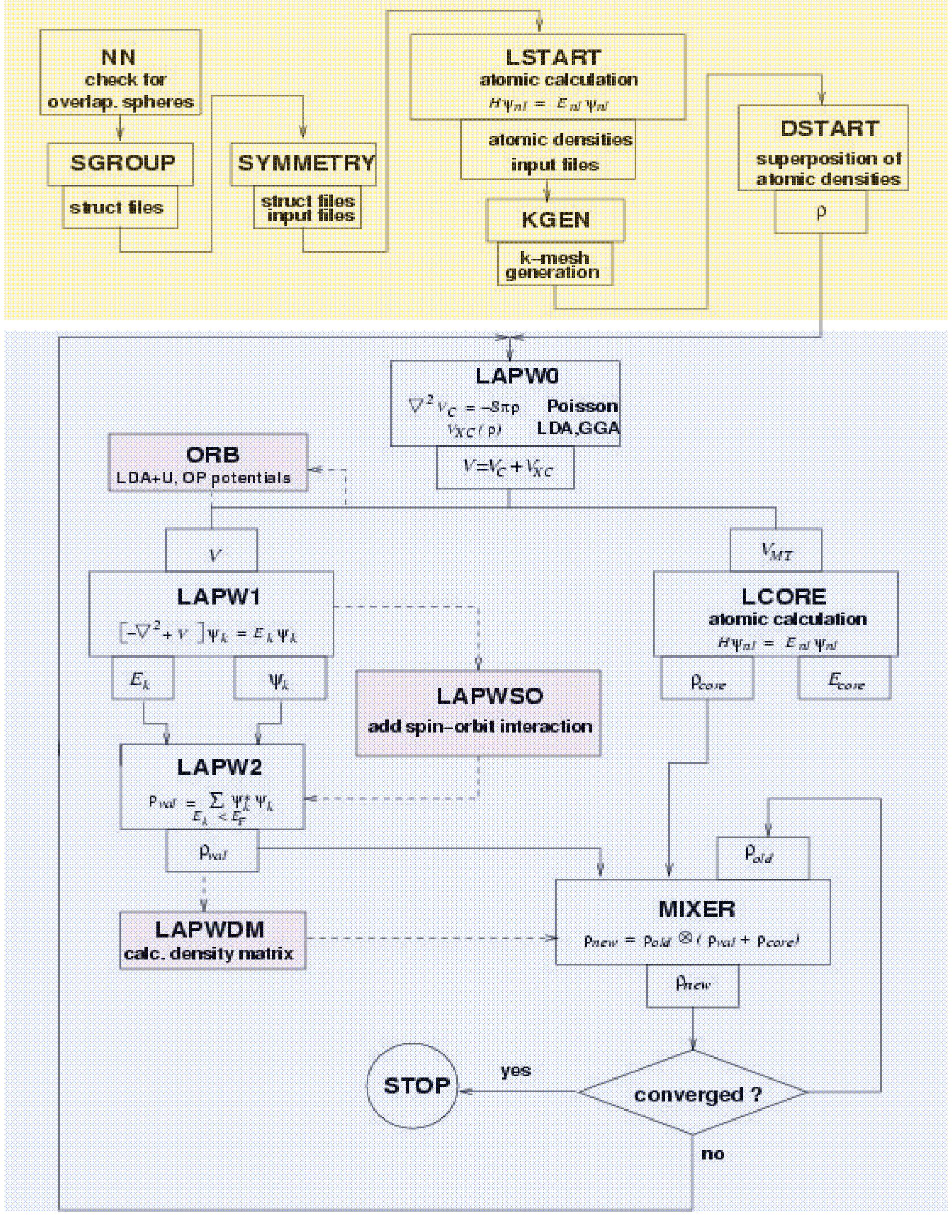
Pos 1: x=0.00000000 y=0.00000000 z=0.00000000

Atom 2: C Z=6.0 RMT=1.9000

Pos 1: x=0.50000000 y=0.50000000 z=0.50000000

Program structure of WIEN2k

- 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 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*



Program execution:

- All programs are executed via the „master“ shell-script „x“:

```
x  lapw2  –up  –c
```

- This generates a „def“ file: lapw2.def

```
5,'tin.in2c',         'old',     'formatted'
6,'tin.output2up',   'unknown','formatted'
8,'tin.clmvalup',    'unknown','formatted'
10,'./tin.vectorup','unknown','unformatted'
```

- and executes: lapw2c lapw2.def
- All WIEN2k-shell scripts have long and short names:
  - *x_lapw; runsp_lapw, runfsm_lapw ➔ x; runsp; runfsm*
- All scripts have a „help“ switch „-h“, which explains flags and options (without actually execution)

```
x  –h              x  lapw1  -h
```

scf-cycle

- run_lapw [options] (for nonmagnetic cases)

-ec 0.0001	*convergence of total energy (Ry)*
-cc 0.0001	*convergence of charge distance (e^-)*
-fc 1.0	*convergence of forces (mRy/bohr)*
-it (-it1,-it2 , -noHinv)	*iterative diagonalization (large speedup)*
-p	*parallel calculation (needs .machines file)*
-so	*add spin-orbit (only after „init_so")*

  - *Spacegroups without inversion use automatically lapw1c, lapw2c (case.in1c,in2c)*

- case.scf: master output file, contains history of the scf-cycle
  - *most information is stored with some „labels" (grep :label case.scf)*
    - :ENE :DIS :FER :GAP :CTO001 :NTO001 :QTL001
    - :FOR002: 2.ATOM 19.470 0.000 0.000 19.470
    - :FGL002: 2.ATOM 13.767 13.767 0.000 total forces
    - :LAT :VOL :POSxxx

exercises:

- connect to the compute nodes using:

- x2go   (hocXXX at rhea.cup.uni-muenchen.de)
  - *(or ssh -X hocXXX@rhea.cup.uni-muenchen.de*

- open at least 2 windows:
  - *on the frontend: for editing and small calculations, X-window graphics*
  - *qrsh_hoc: here you should do all the „calculations"*

- always work in $HOME/workdir

- you can find the „text-version" of the instructions (for „cut and paste") at $WIENROOT/wien2k.txt

Exercise #1

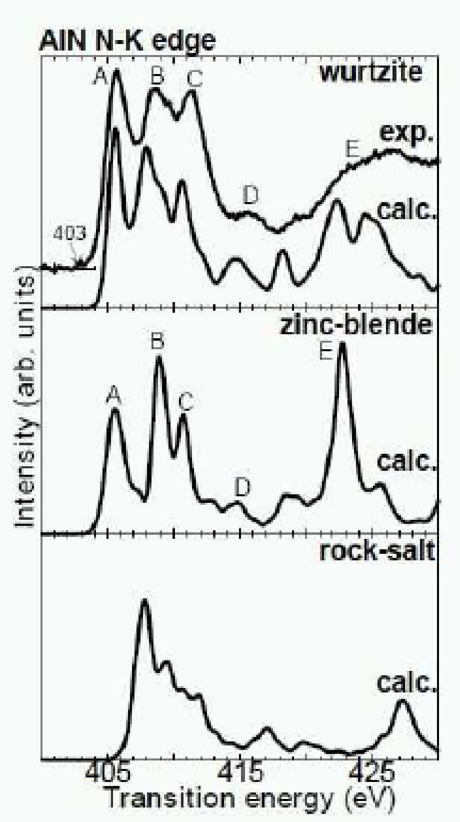
- **Electronic structure and N-K XAS of AlN**
  - T. Mizoguchi, Phys. Rev. B70 (2004) 045103

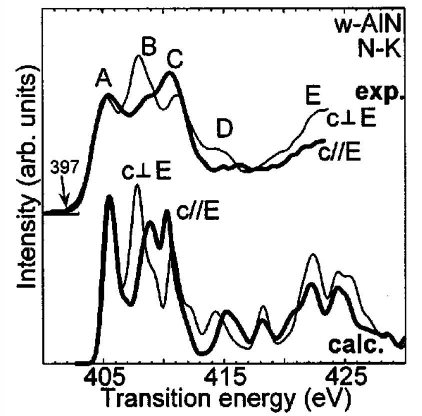
- Methods:
  - *ground state calculation*
  - *DOS, electron density, band structure*
  - *XAS (without core hole)*

  - *AlN 2x2x2 supercell with N-1s core hole*
  - *scf calculation*
  - *XSPEC with core hole*

  - *calculations using TB-mBJ (better gap)*

  - *PS: most parameters in the instructions are „underconverged" to save time*

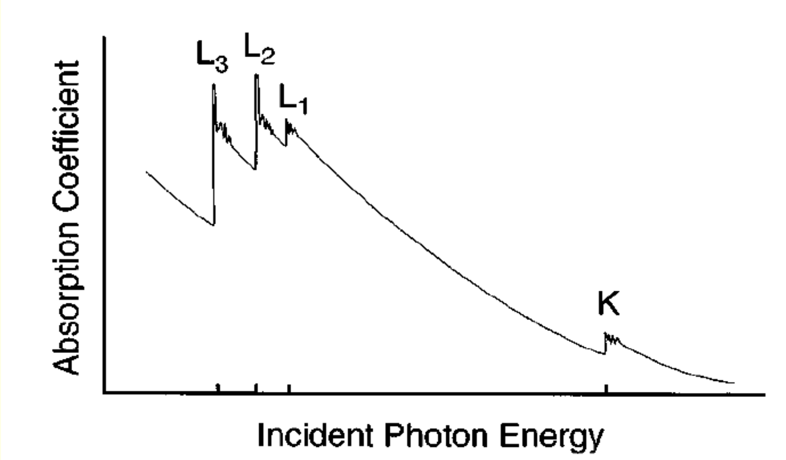




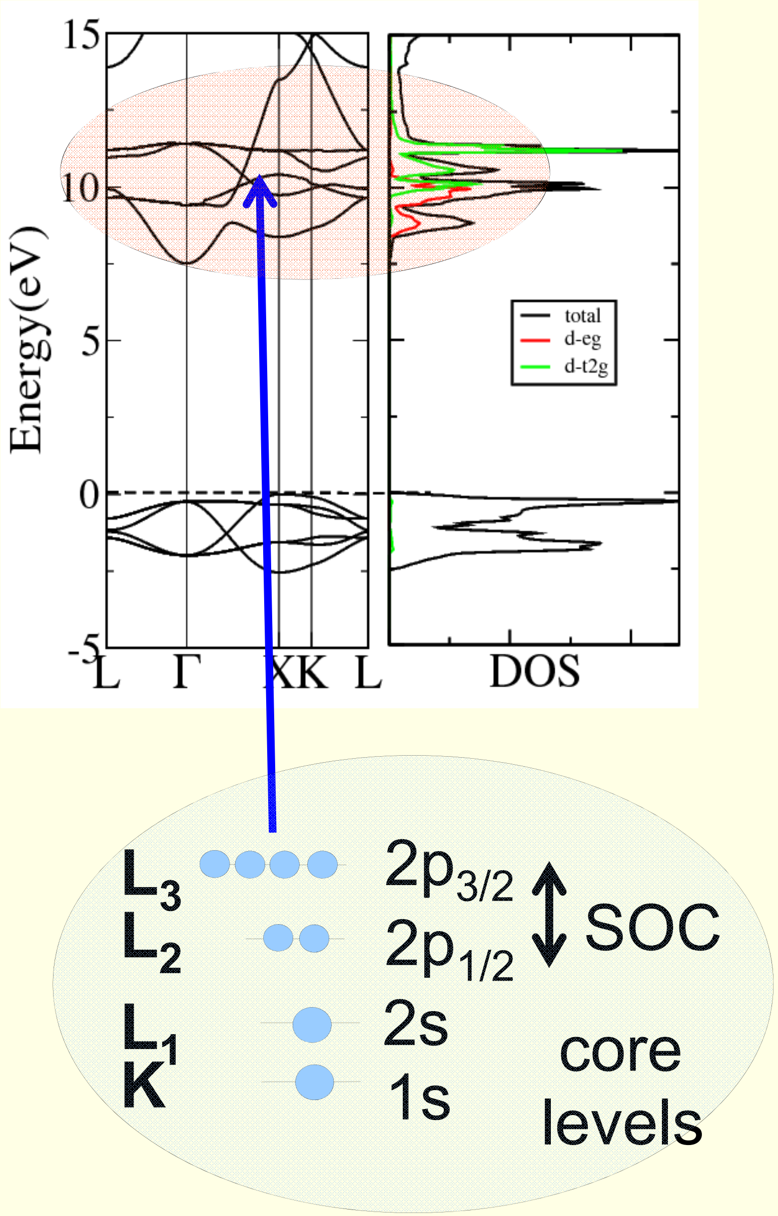
XAS (XANES), **EELS** (ELNES):

- **core electrons are excited into a conduction band**
- Each core shell introduces an absorption edge, (they are indexed by the principal number of a core level)

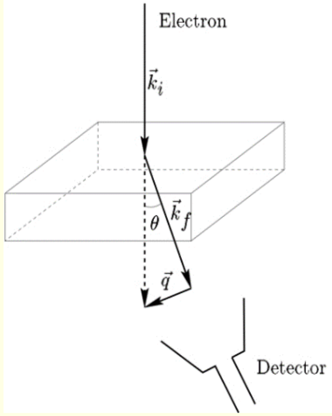
  K-1s, L_1-2s, L_2-2$p_{1/2}$, L_3-$p_{3/2}$

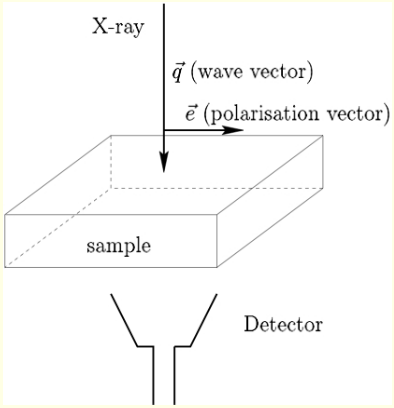


- **Due to localization of the core wave function, there is a strong interaction of an excited electron with a core hole**



EELS vs. XAS

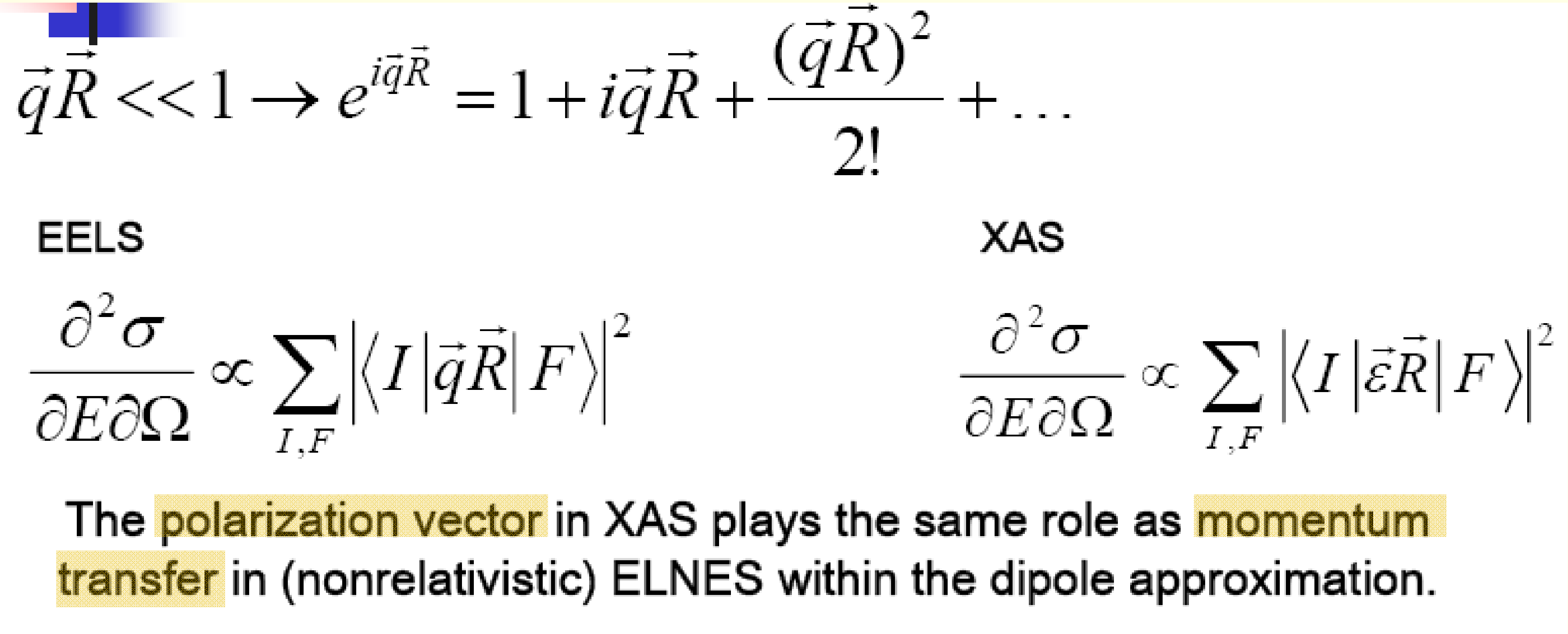




$$\frac{\partial^2 \sigma}{\partial E \partial \Omega} \propto \sum_{I,F} \left| \langle I | e^{i\vec{q}.\vec{R}} | F \rangle \right|^2$$

$$\frac{\partial \sigma}{\partial E} \propto \sum_{I,F} \left| \langle I | e^{i\vec{q}.\vec{R}} \vec{e}\vec{R} | F \rangle \right|^2$$

dipole approximation



$$\vec{q}\vec{R} << 1 \rightarrow e^{i\vec{q}\vec{R}} = 1 + i\vec{q}\vec{R} + \frac{(\vec{q}\vec{R})^2}{2!} + \ldots$$

EELS

$$\frac{\partial^2\sigma}{\partial E \partial\Omega} \propto \sum_{I,F} \left| \left\langle I \middle| \vec{q}\vec{R} \middle| F \right\rangle \right|^2$$

XAS

$$\frac{\partial^2\sigma}{\partial E \partial\Omega} \propto \sum_{I,F} \left| \left\langle I \middle| \vec{\varepsilon}\vec{R} \middle| F \right\rangle \right|^2$$

The polarization vector in XAS plays the same role as momentum transfer in (nonrelativistic) ELNES within the dipole approximation.

core-valence spectroscopies give information on the local DOS (because of $<\Psi_{core}|r|\Psi_{val}>$) of angular momentum character ℓ ± 1

Independent particle approximation: Final state rule

"Final state" determines the spectrum:

- Emission spectroscopy:

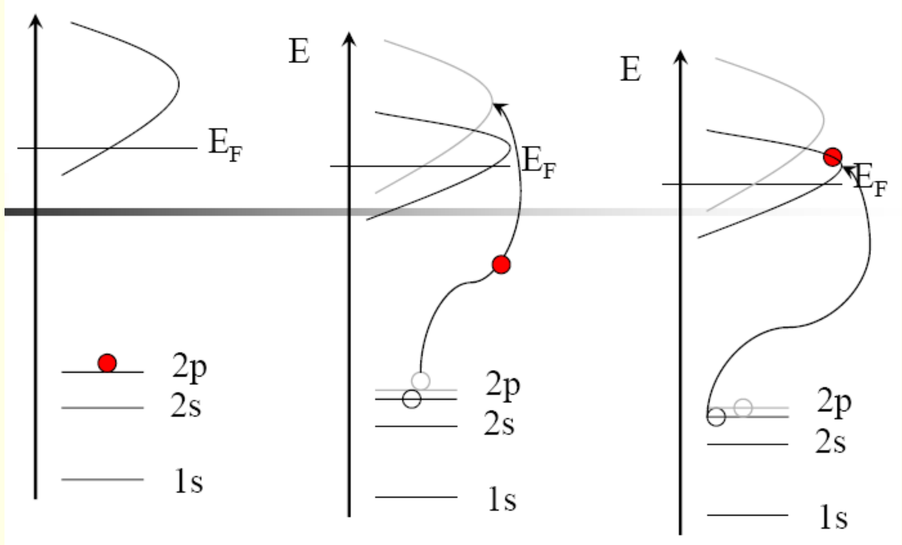
  Final state has filled core, but valence hole.
  This is usually well screened, thus one "sees" the groundstate.

- Absorption spectroscopy:

  Final state has a "hole" in core state, but additional e^- in conduction band.
  Core-hole has large effect on the spectrum

  - **electron – hole interaction, "excitonic effects"**

.



Core hole calc

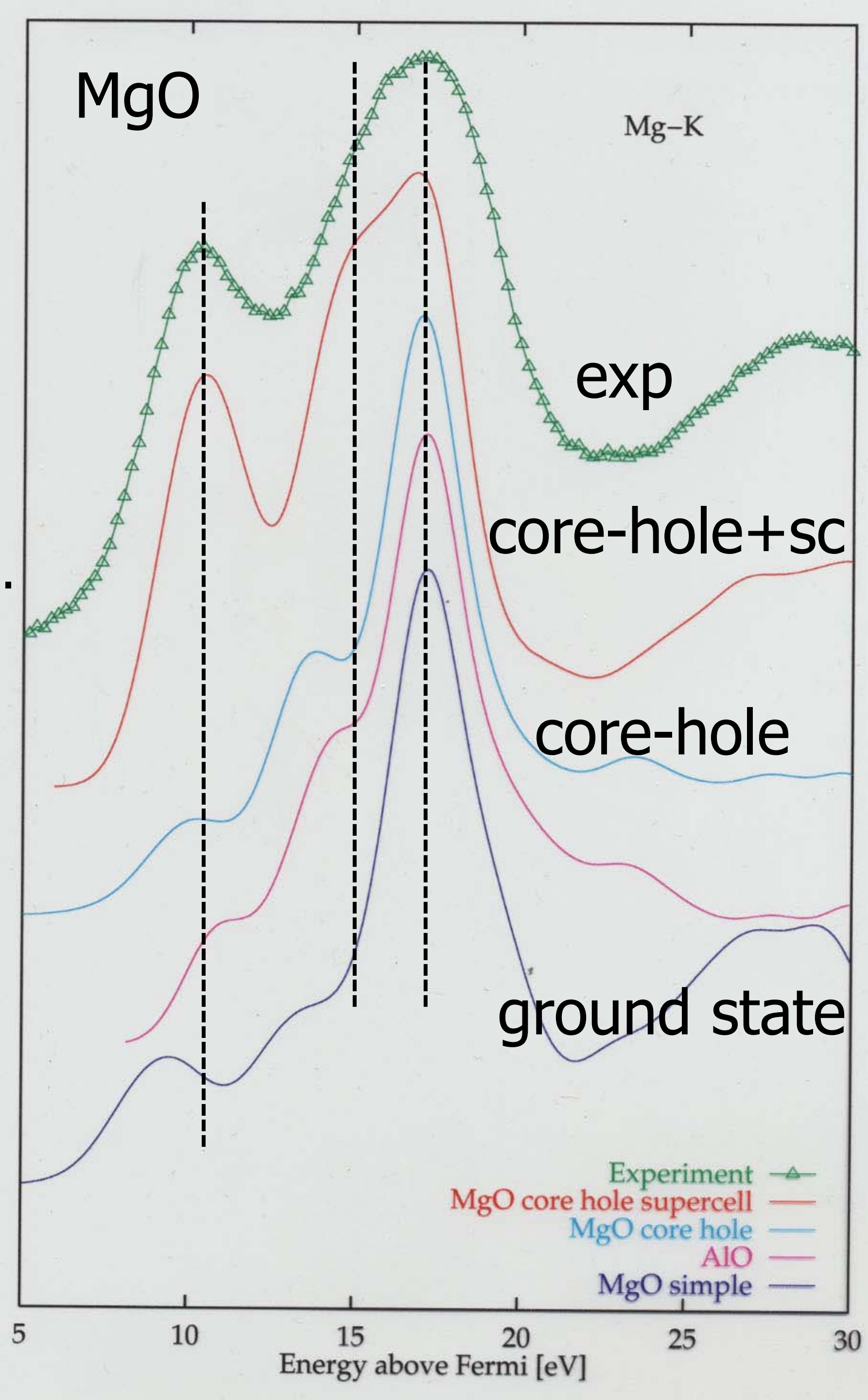
“Final state” determines the spectrum:

Selfconsistent supercell calculations:

- “hole” in core state of one of the atoms
- add e^- in conduction band or background.

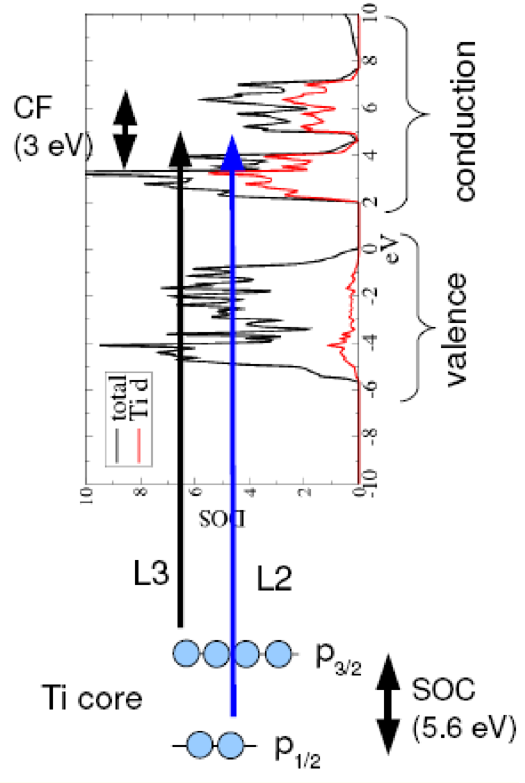
Static approximation:

- the scf calculation allows the conduction states to relax (adjust to the larger effective nuclear charge),
- the supercell allows for some static screening from the environment.

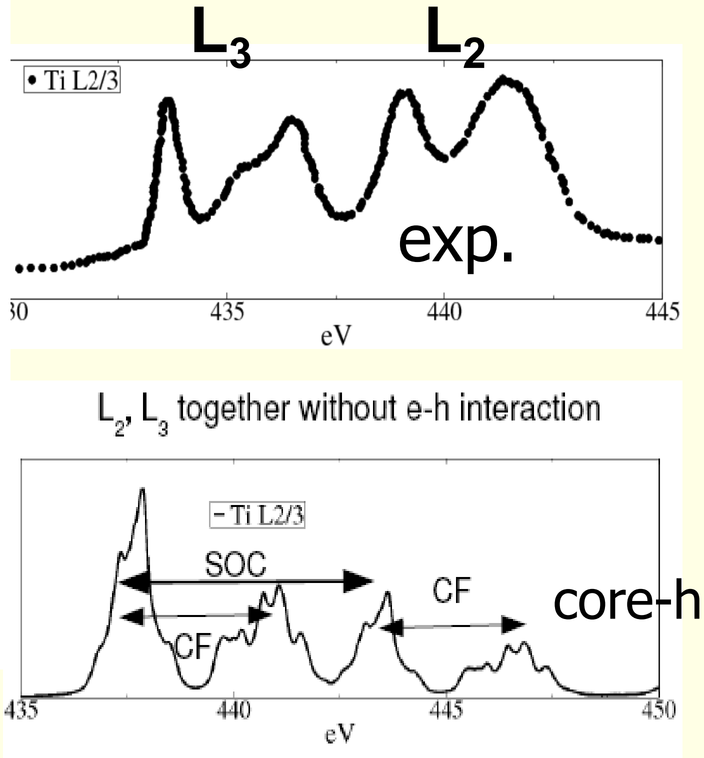


$L_{2,3}$ spectra: failure of the single particle approach

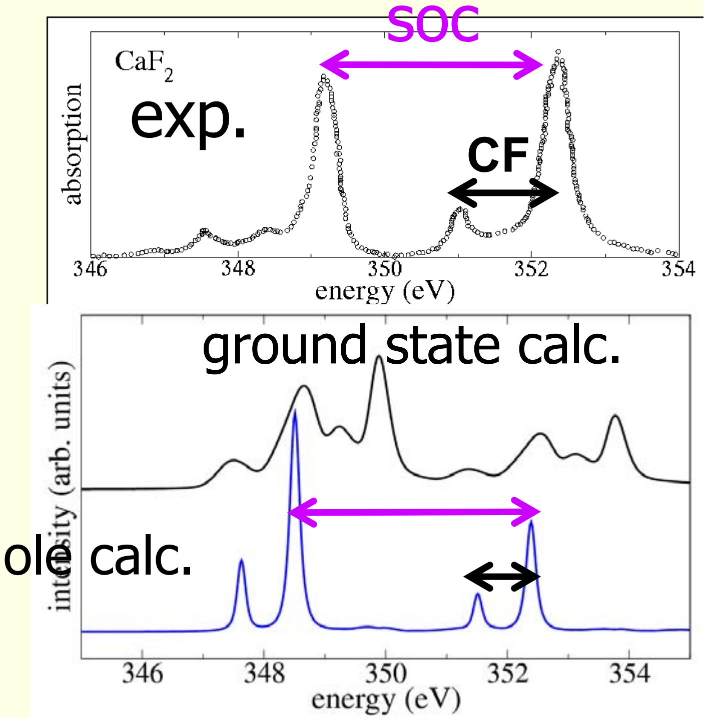
- In particular early 3d TM-compounds show a
  - *non-standard L_2/L_3 branching ratio (1:2)*
  - *sometimes a completely different lineshape (TiO_2)*
  - *„wrong" **SOC** or **CF** splittings*



rutile TiO_2

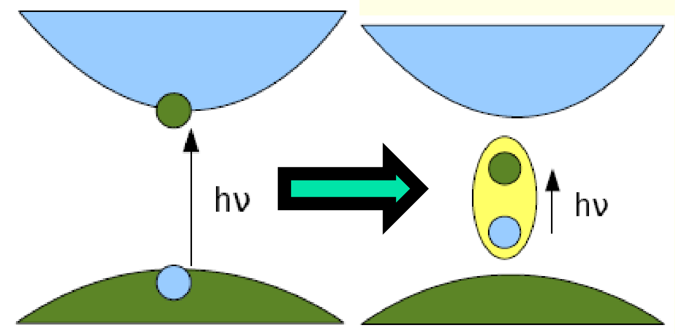


CaF_2



fully relativistic electron-hole interaction (BSE)

- *Bethe-Salpeter-equation: L(12;1'2')*
- *solving a 2-particle (e^- - h) equation of large dimension ($N_v N_c N_k$ ~ 100000)*



$$\boxed{\sum_{v'c'k'} \left(H^{eh}_{v'c'k',vck}\right) A^{\lambda}_{v'c'k'} = E^{\lambda} A^{\lambda}_{vck}}$$

single particle APW (WIEN2k)

$$H^{eh} = H^{diag} + H^{dir} + 2H^{x}$$

$$H^{diag} = (E_{v,k} - E_{c,k})\delta_{cc'}\delta_{vv'}\delta_{kk'}$$

eigenvalue difference between hole (c) and electron(v) state

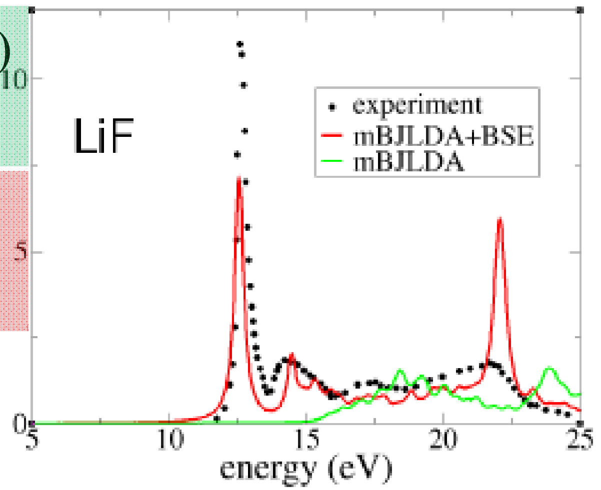
$$H^{dir}_{vckv'c'k'} = -\int d^3r\, d^3r'\, \Psi_{vk}(r)\Psi^*_{ck}(r')W(r,r')\Psi^*_{v'k'}(r)\Psi_{c'k'}(r')$$

attractive screened static Coulomb interaction *W; W~ε^{-1}(q)*

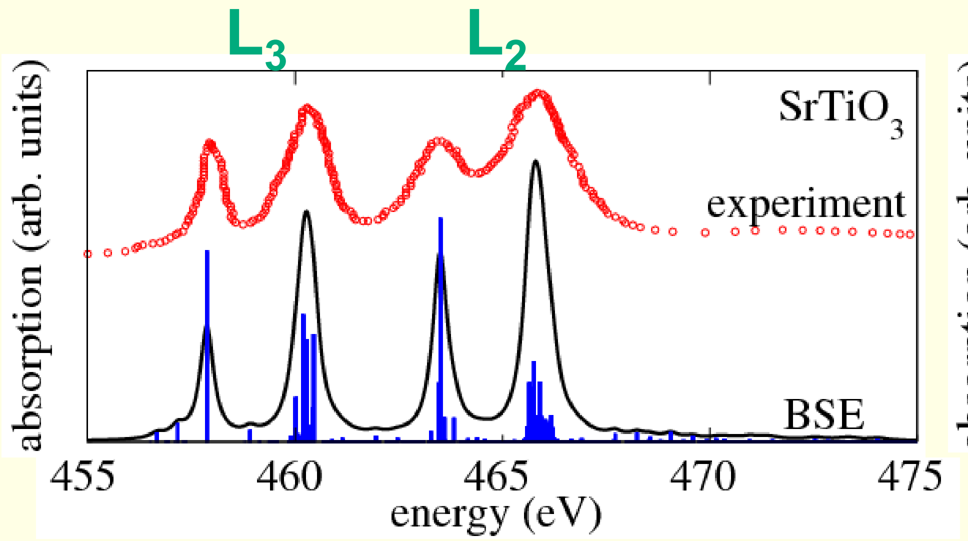
$$H^{x}_{vckv'c'k'} = \int d^3r\, d^3r'\, \Psi_{vk}(r)\Psi^*_{ck}(r)\bar{v}(r,r')\Psi^*_{v'k'}(r')\Psi_{c'k'}(r')$$

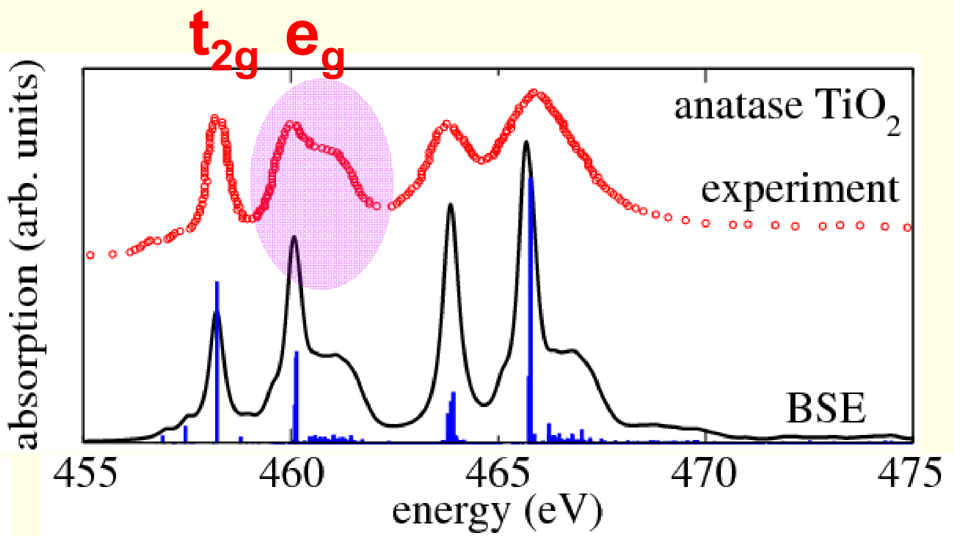
e-h exchange with bare Coulomb potential *v*

Excitons in LiF

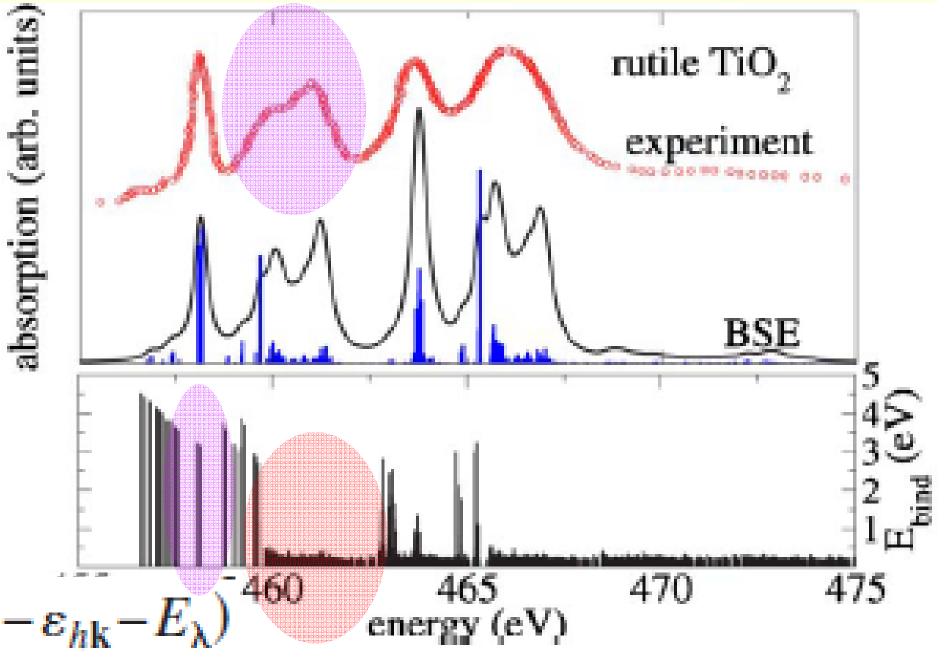


Ti $L_{2,3}$ in $SrTiO_3$, rutile-TiO_2, anatase-TiO_2



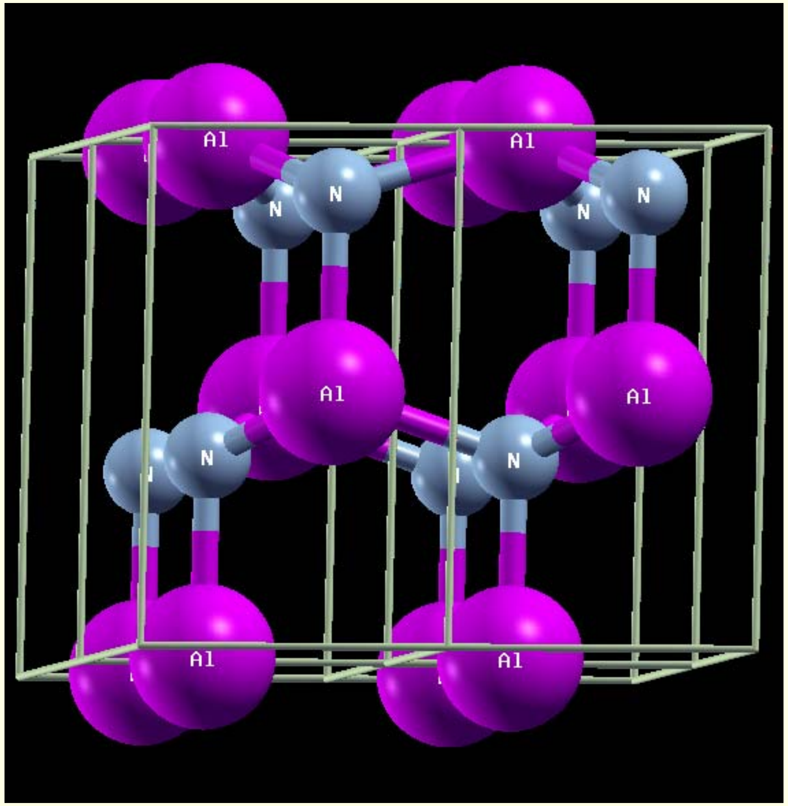


- The experimental Ti $L_{2,3}$ edges are rather well reproduced.
- intensity ratio L_3/L_2 (not 2:1)
- „t_{2g}/e_g“ ratio (not 3:2)
- left/right shoulder in L_3-„e_g“ peak of rutile/anatase
- crystal field splitting influenced by excitonic binding energy



$$E^{\lambda}_{bind} = \Sigma_{k,e,h} A^2_{k,h,e} (\varepsilon_{ek} - \varepsilon_{hk} - E_{\lambda})$$

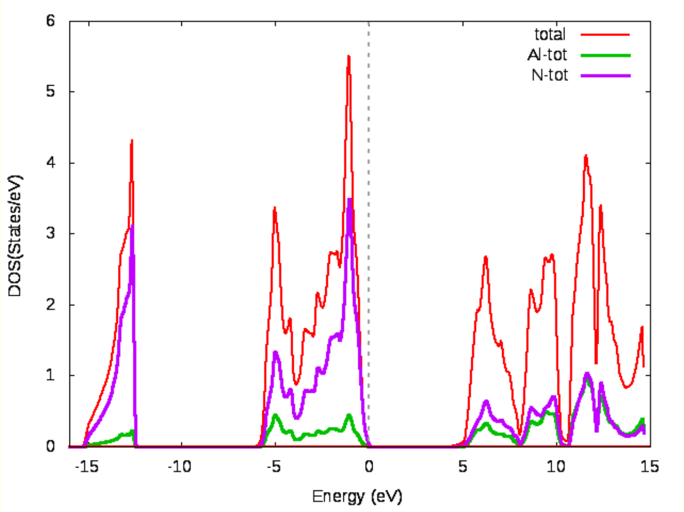
exercise #1: bulk w-AlN

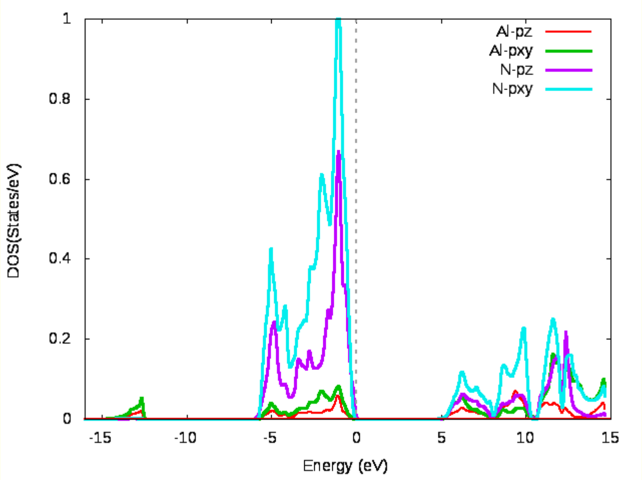


- cd workdir;mkdir AlN; cd AlN
- makestruct_lapw
  - *SG 186 (wurzite structure)*
  - *lattice parameter: 3.111, 4.978A*
  - *Al(1/3,2/3,0); N (1/3,2/3,0.385)*
  - *no reduction of RMT*
- cp init.struct AlN.struct
- xcrysden --wien_struct .
- init_lapw –b –rkmax 6 -numk 300
- in „exec" window: run_lapw
- # check convergence:
  - *grep :ENE AlN.scf (:DIS :FER :GAP)*
- save_lapw AlN_exp_rkm6_300k_pbe

AlN: DOS

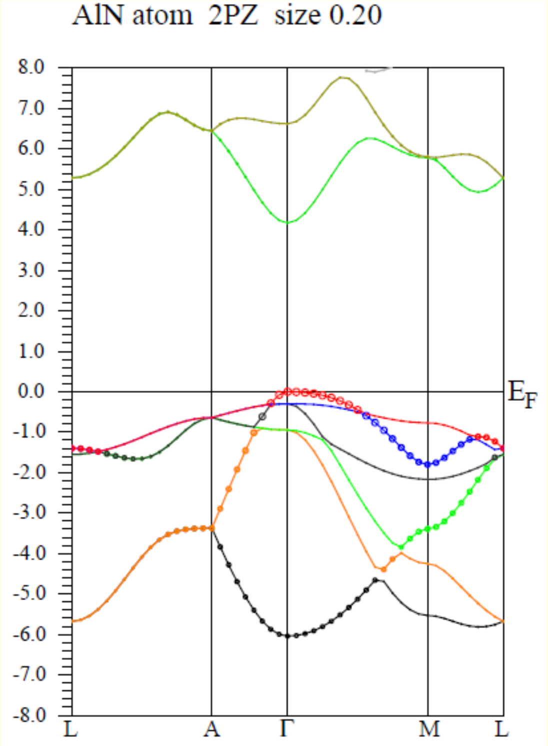
- x lapw2 -qtl
- cp $WIENROOT/SRC_templates/template.int AlN.int
- $EDITOR AlN.int
  - *emin=-1.0; 7 cases; total,Al-tot,N-tot,Al-pz,Al-pxy,N-pz,N-pxy*
- x tetra
- dosplot2
  - *a) total + Al-tot + N-tot*
  - *b) Al-pz, Al-px+py, N-pz, N-px+py*





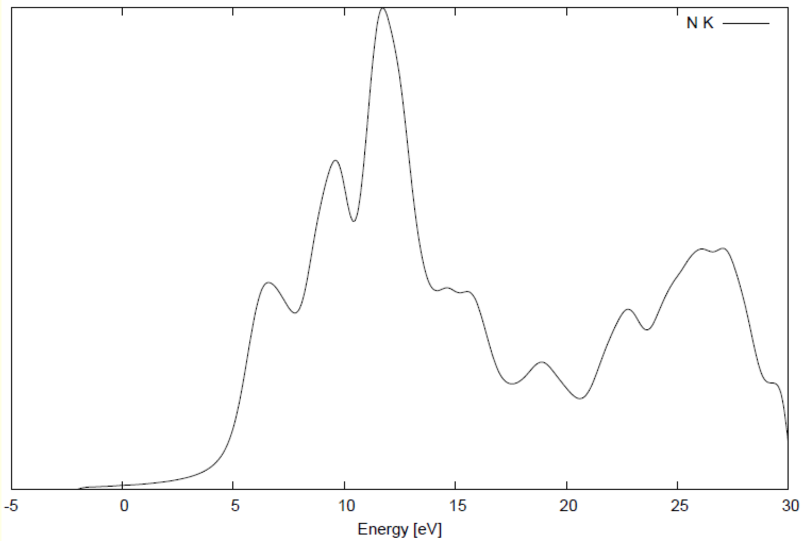
AlN bandstructure

- `xcrysden --wien_kpath .`
  - *click L-A-GAMMA-M-L, 50 total points, save as AlN.klist_band*
- `x lapw1 -band`
- `x lapw2 -band -qtl`
- `cp $WIENROOT/SRC_templates/template.insp AlN.insp`
- `grep :FER AlN.scf`
- `$EDITOR AlN.insp`
  - *insert EF, emin=-8.*
  - *plot N-p_z (and later p_{xy})*
- `x spaghetti`
- `gv AlN.spaghetti_ps`



AlN: xspec (groundstate)

- $EDITOR AlN.in1c # increase Emax to 5.0
- x lapw1
- x lapw2 -qtl
- cp $WIENROOT/SRC_templates/case.inxs AlN.inxs
  - *select N 1 s state; EMAX=30eV; broadening /2*
- x initxspec
- x tetra
- x txspec
- x lorentz
- specplot_lapw



- edit AlN.int and select N-p_z (p_{xy}) and repeat the steps from tetra

N-K XAS with core-hole

- copy AlN.struct into a new directory AlN_222, change into it
- x supercell
  - *AlN.struct*
  - *2x2x2 cells, no shift, no vacuum*
- cp AlN_super.struct AlN_222.struct
- $EDITOR AlN_222.struct
  - *increase NATO by 1; split the last N into 2 non-equivalent positions, label the last N as "N 1"*
- init_lapw -numk 40 -rkmax 5
- $EDITOR AlN_222.struct (reduce last N-1s occupation to 1)
- $EDITOR AlN_222.in2c (add one valence electron)
- $EDITOR .machines (insert 4 lines with: 1:localhost)

- run_lapw -p   (in execution window)

AlN supercell

- `grep :ENE AlN_222.scf` # observe the “warnings”
- `grep :WAR AlN_222.scf` # comes from large “QTL-B” values
- `less AlN_222.scf2` # find the reason (last N-p at 0.0 Ry)
- # check :EPH016 for proper E-parameter
- `$EDITOR AlN_222.in1c` # change for last N: E-p 0.3 → 0.0
- `rm *.broy*` # remove charge history
- `run_lapw -p` (on compute node)

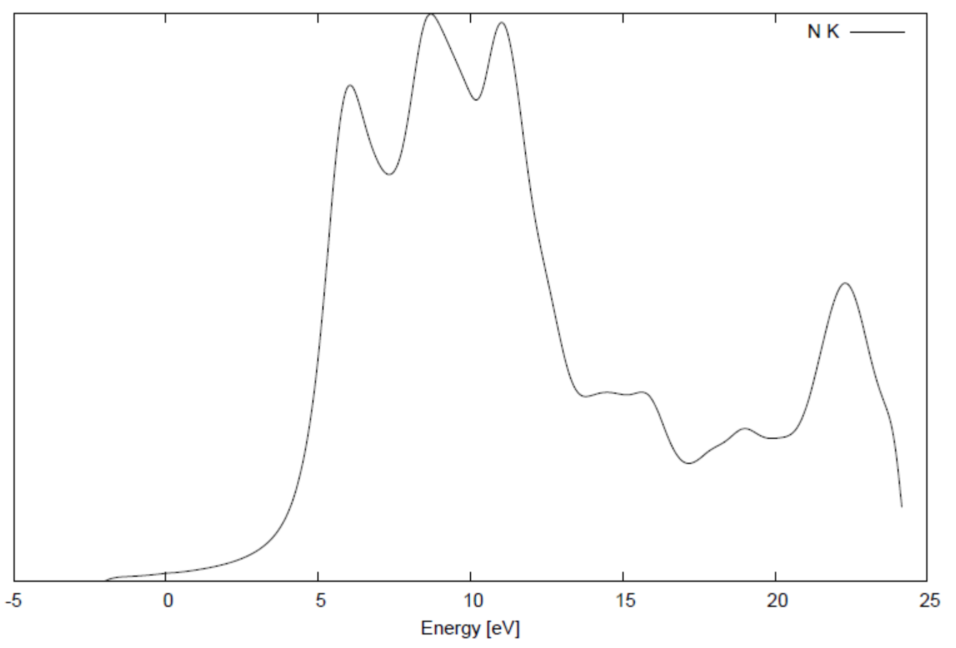
- `grep :ENE AlN_222.scf` # observe lower E

calculate AlN N-K XAS with core-hole

- $EDITOR AlN_222.in2c # reduce NE by 1
- x lapw2 -qtl -p

- …. follow the steps of the previous xspec

- compare the plots with experiments



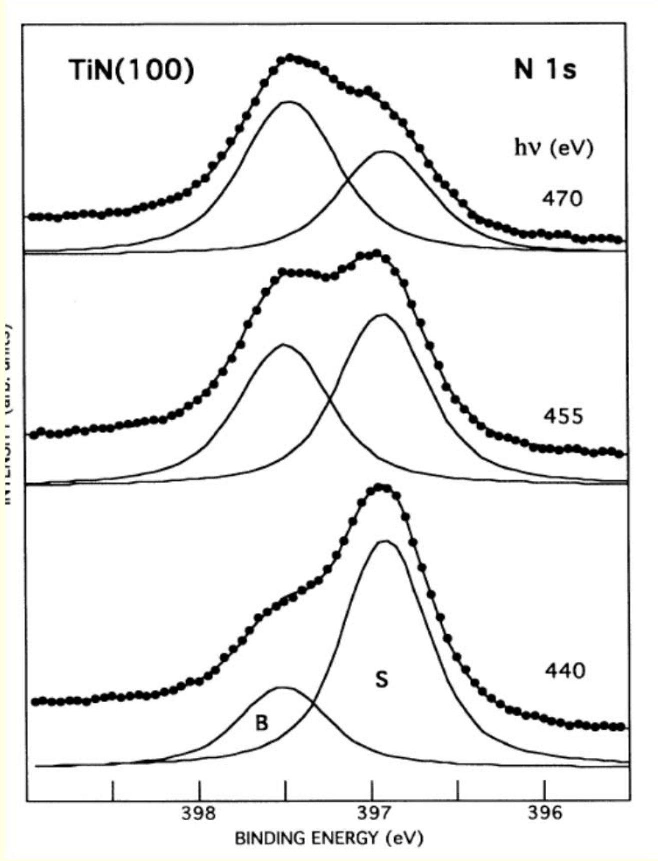
AlN: bandgap with TB-mBJ

- # go back into the AlN directory
- init_mbj_lapw # first step of mBJ initialization
- run -i 1 # prepare kinetic energy density for mBJ
- save_lapw AlN_PBE # save the PBE calculation
- init_mbj_lapw # 2nd step, select semiconductor param.
- run_lapw

- compare the PBE and mBJ band gaps (:GAP in the *.scf files) and experiment (6.13eV)

Exercise #2

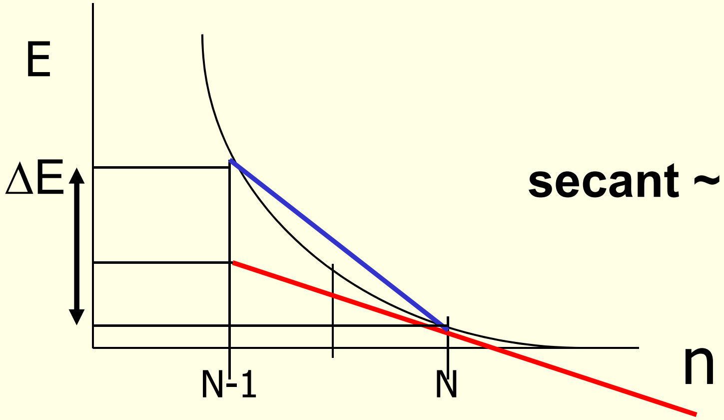
- **Surface XPS core-level shifts of N-1s in TiN(100)**
  - *L.I.Johansson et al., PRB 48, 14520 (1993)*
  - *N-1s in bulk has a ~0.5 eV larger BE than at the surface*



- Methods:
  - *lattice parameter optimization of bulk*
  - *creation of a (100) TiN surface model*
  - *relaxation of the surface slab*
    - check geometry
    - compare N-1s eigenvalues
    - analyse charge transfer at the surface
  - *XPS calculation using Slaters „transition state"*
    - 2x2x1 supercell
    - calculations with ½ core-hole at 2 N sites

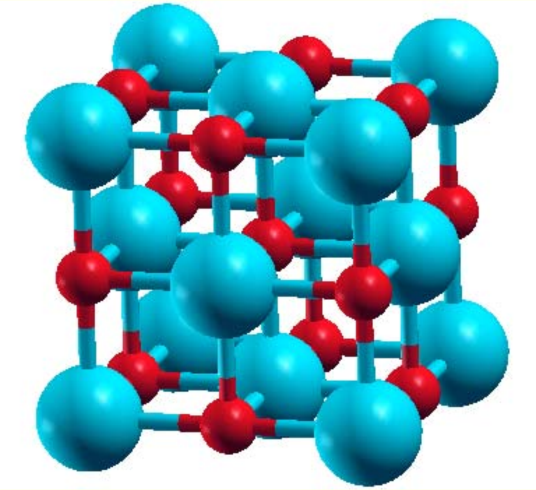
XPS, core-level shifts

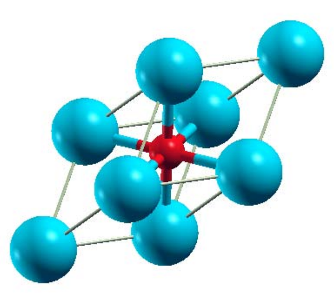
- Ionizationpotential of core-e$^-$, ***IP= $E^{tot}(N) - E^{tot}(N-1)$***
  - *gives information on charge state of the atom*
- core-eigenvalues ε_i are NOT a good approximation: ***$\varepsilon_i = dE/dn$***
  - *~10 % error, final state screening is not considered*
- Slater's "transition state": core-eigenvalues ε_i for half occupancy



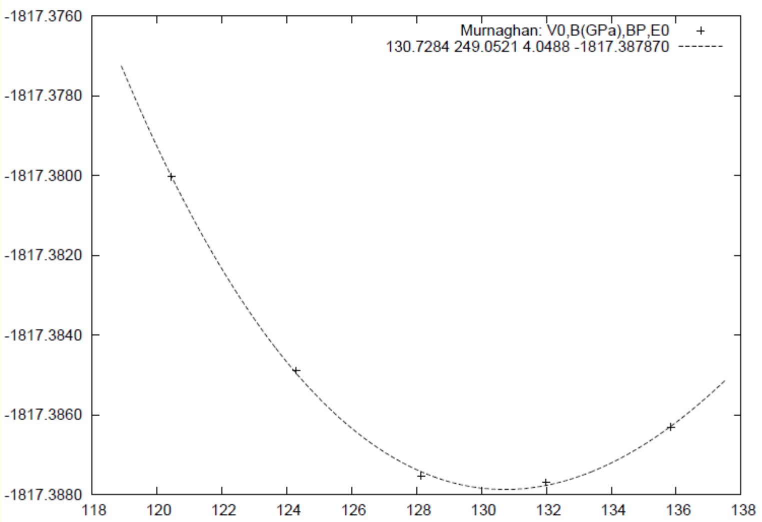
- Δ-SCF-calculation with and without core-hole: $E^{tot}(N) - E^{tot}(N-1)$
  - *supercells to reduce hole-hole interaction*
  - *error reduced to <1%; final state screening*

TiN





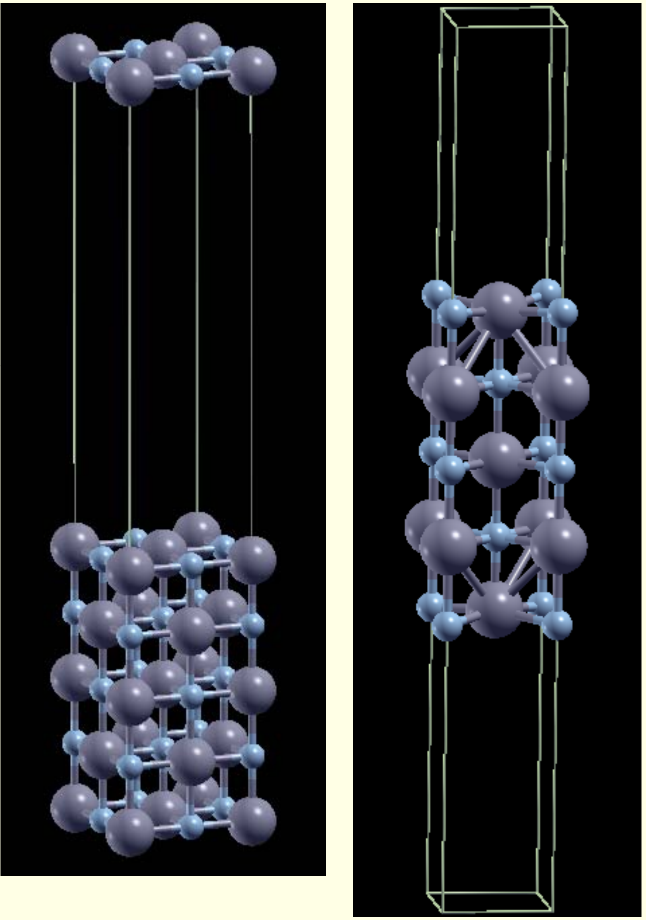
- cd workdir;mkdir TiN; cd TiN
- makestruct_lapw
  - *lattice type F (NaCl structure)*
  - *lattice parameter: 4.235 A*
  - *Ti (0,0,0); N (0.5,0,0)*
  - *3% reduction of RMT*
- cp init.struct TiN.struct
- xcrysden --wien_struct .
- init_lapw –b –rkmax 6
- x optimize
  - *volume opt. with -6,-3,0,3,6 %*
- now change into the other „window“
  - *./optimize.job*



- back in interactive window: eplot –a „ „   # (4.263)

TiN (100) surface (5 layers)

- cd ..; mkdir TiN100; cd TiN100
- cp ../TiN/TiN.struct .
- $EDITOR TiN.struct
  - *change lattice parameters to 8.0563 bohr*
  - *NOTE: struct file is fixed positioned (replace)*
- x supercell (TiN.struct; 1x1x2 cells; no shift;)
  - *30 bohr vacuum; repeat layer at z=0*
- cp TiN_super.struct TiN100.struct
- xcrysden --wien_struct .
- x sgroup
- less TiN100.outputsgroup
- cp TiN100.struct_sgroup TiN100.struct # and repeat xcrysden
- init_lapw –b –numk 60 –rkmax 6



TiN(100)

- in „exec-window“: run_lapw –fc 1 –min
- # analyse structural distortions and calc. BE of N-1s (from ε_i)
  - *xcrysden –wien_struct .*
  - *grep :1S TiN100.scf*
  - *grep :FER TiN100.scf # (376.9 and 377.3 eV; 20 eV too small)*

supercell for Slaters transition state

- # create a new directory (super); take optimized structure and generate 2x2x1 supercell; “label” a surface-N atom “N 1”
- x sgroup # regrouping of equivalent atoms
- # cp the generated struct file and initialize with 25 k and rkmax=6
- $EDITOR super.inc # change occupation of labelled “N 1” atom to 1.5
- $EDITOR super.in2 # increase NE by “MULT*0.5”
- $EDITOR .machines # insert 3 lines with: 1:localhost
- # in „exec-window“: run_lapw –fc 1 –min –p
- # calc. BE-N-1s (404.1 eV)

- # Repeat the scf cycle, but with a core-hole in a "bulk N-atom" (with mult=1). Check the struct file which N you should change and change occupancies in super.inc and NE in case.in2) (EB=404.55 eV)