The FP-LAPW and APW+lo methods
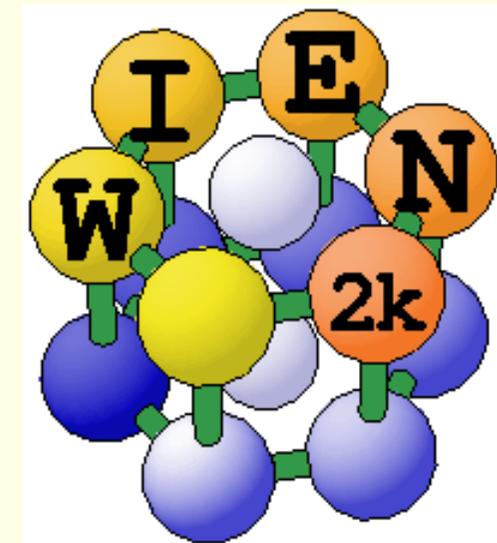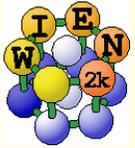
Peter Blaha

**Institute of Materials Chemistry**

TU Wien

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.Nordströrm, D.J.Singh 2000)**
  - *Efficiency of APW + convenience of LAPW*
  - *Basis for*
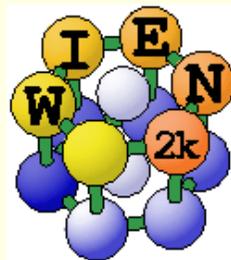
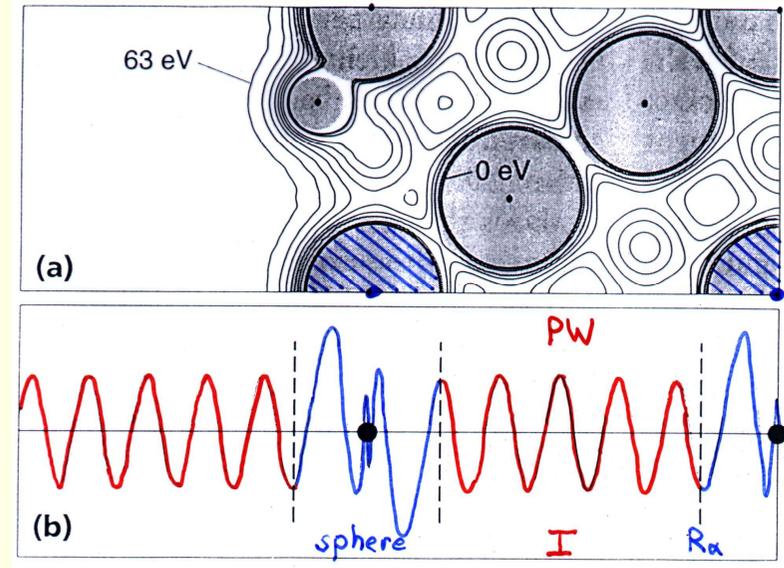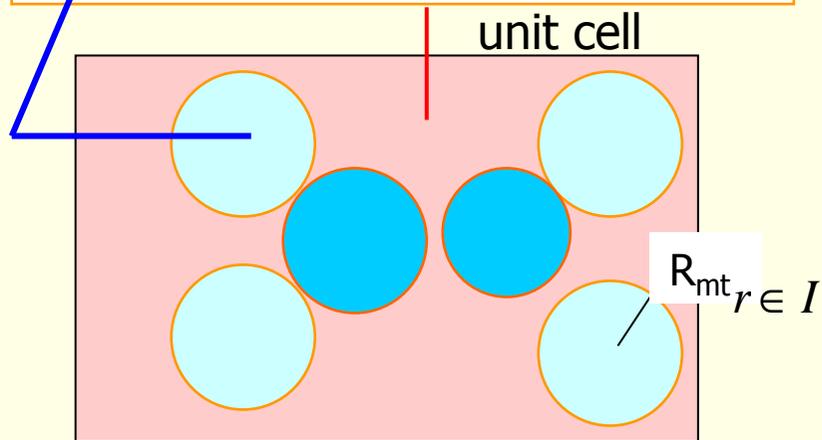K.Schwarz, P.Blaha, G.K.H.Madsen, Comp.Phys.Commun.**147**, 71-76 (2002)
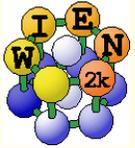
APW Augmented Plane Wave method

The unit cell is partitioned into:
  atomic spheres
  Interstitial region

unit cell

R_{mt} $r \in I$

$63\ eV$

$0\ eV$

(a)

PW

(b)   sphere   I R_α
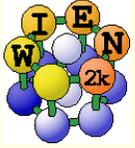
Basisset:

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

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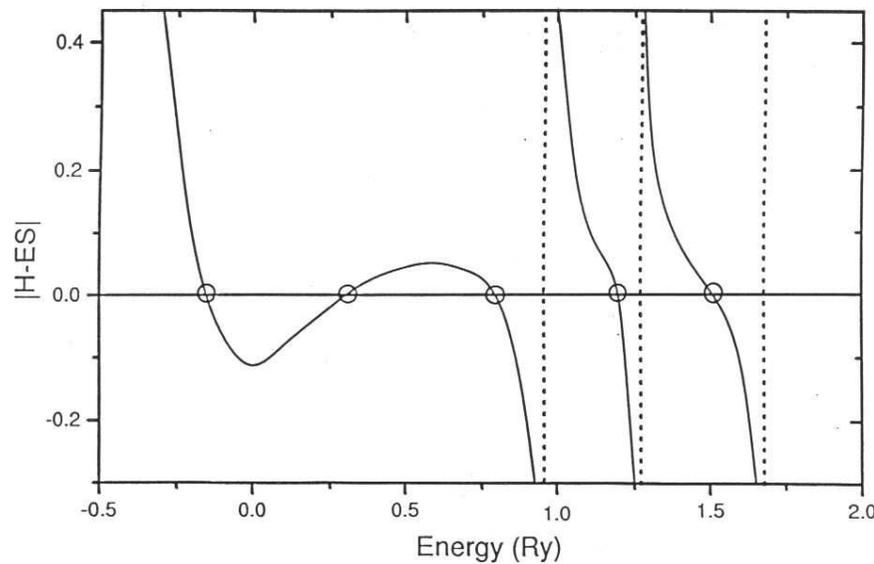
join

$u_l(r,\varepsilon)$ 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

Slater's APW (1937)

H Hamiltonian
S overlap matrix

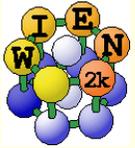**Atomic partial waves**

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

Energy dependent basis functions lead to ➔

Non-linear eigenvalue problem

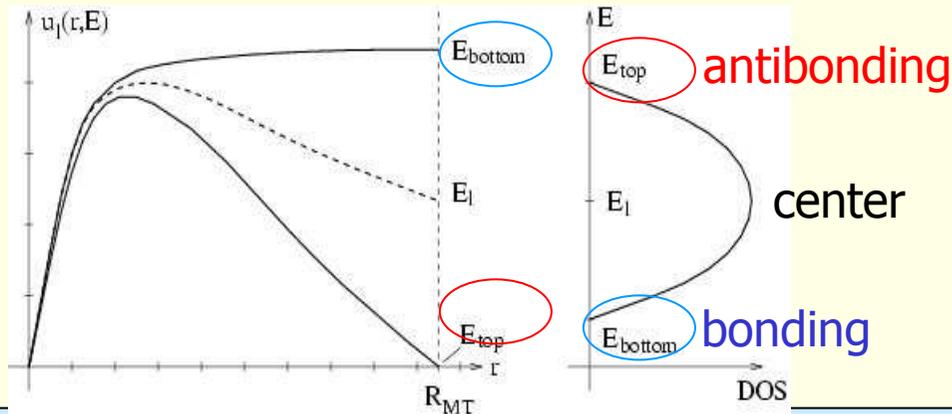One had to numerically search for the energy, for which the det|H-ES| vanishes. Computationally very demanding.
"Exact" solution for given (spherical) potential!

Linearization of energy dependence

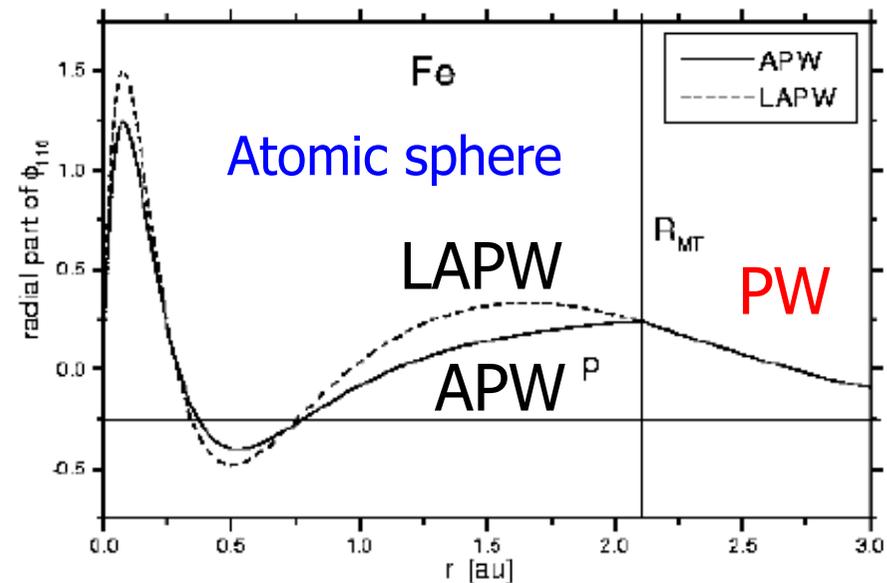**LAPW** suggested by

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

antibonding

center

bonding

$$\Phi_{k_n} = \sum_{\ell m} [\, A_{\ell m}(k_n)\, u_\ell(E_\ell, r) + B_{\ell m}(k_n)\, \dot{u}_\ell(E_\ell, r)]\, Y_{\ell m}(\hat{r})$$
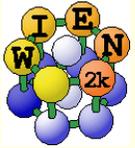
expand u_l at fixed energy E_l and
add $\dot{u}_l = \partial u_l / \partial \varepsilon$

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

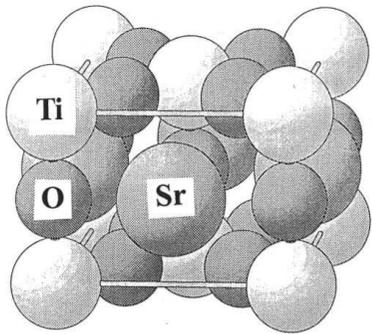→ General eigenvalue problem
(diagonalization)
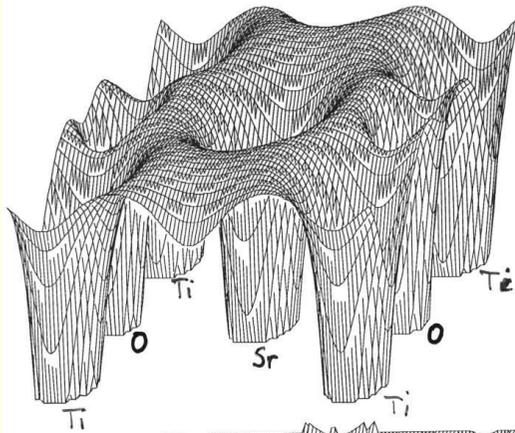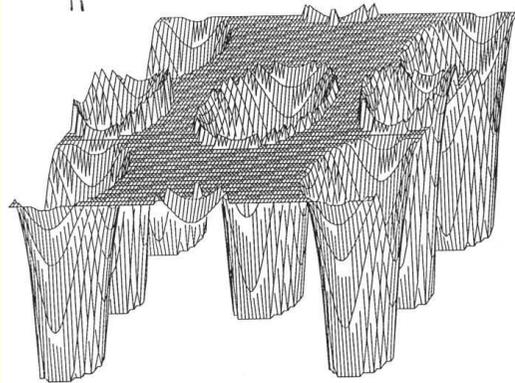
→ additional constraint requires
more PWs than APW

Fe

Atomic sphere

LAPW

APW

PW

Full-potential in LAPW (A.Freeman etal.)
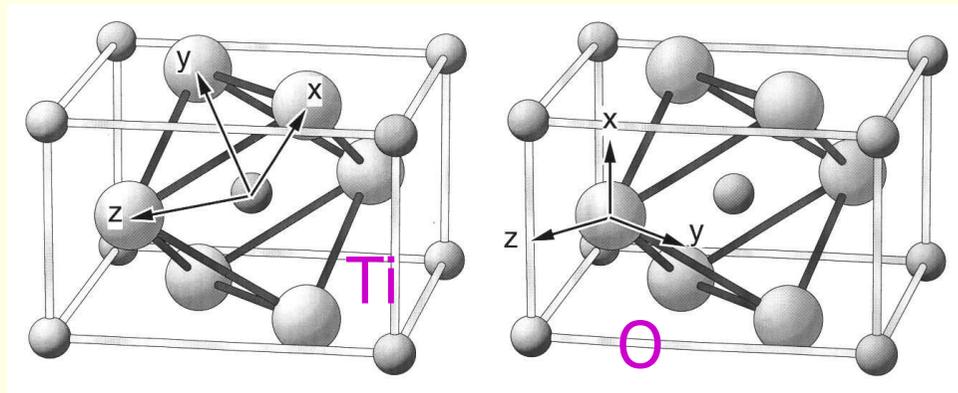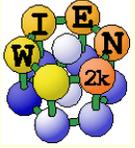
SrTiO$_3$

Full potential

Muffin tin approximation

TiO$_2$ rutile

- The potential (and charge density) can be of general form (no shape approximation)

$$V(r) = \begin{cases} \sum_{LM} V_{LM}(r) Y_{LM}(\hat{r}) & r < R_\alpha \\ \sum_{K} V_K e^{i\vec{K}.\vec{r}} & r \in I \end{cases}$$

- Inside each atomic sphere a local coordinate system is used (defining LM)

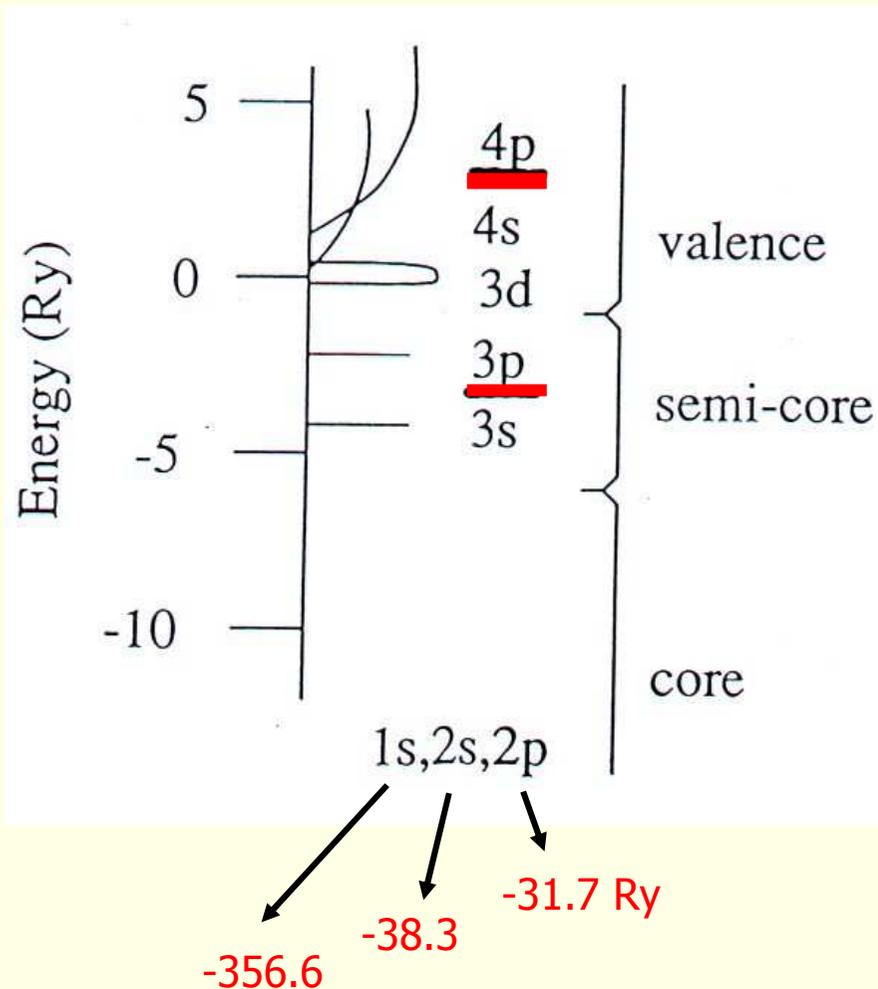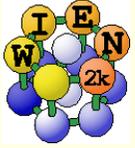Ti   O

Core, semi-core and valence states
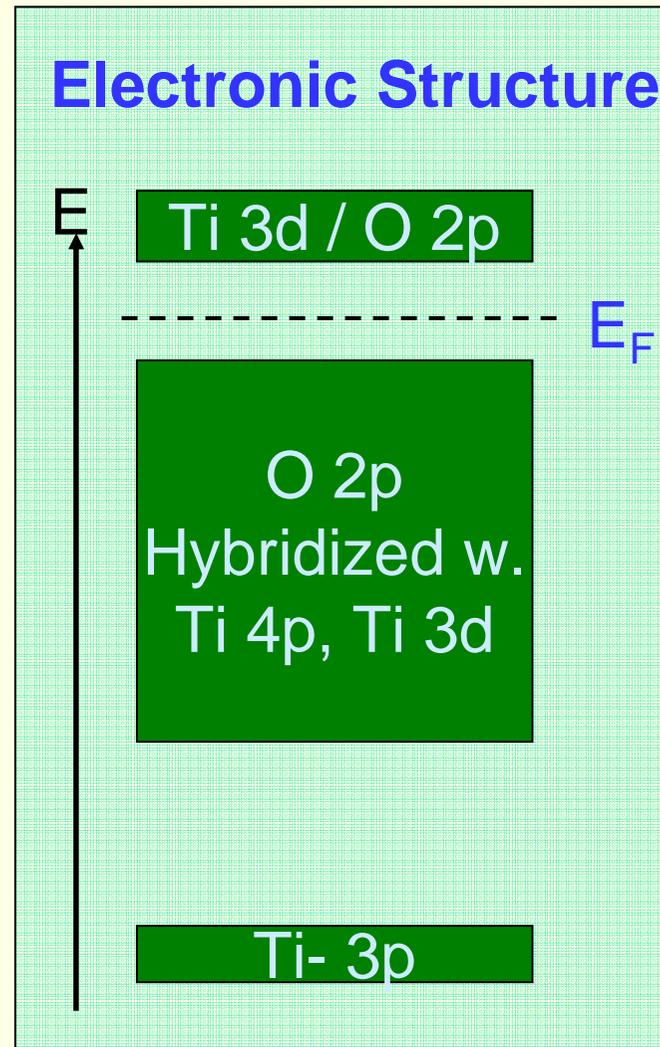
For example: Ti

- **Valences states**
  - **High** in energy
  - **Delocalized** wavefunctions
- **Semi-core states**
  - **Medium** energy
  - Principal **QN** one less than valence (e.g. in Ti **3**p and **4**p)
  - **not completely confined** inside sphere
- **Core states**
  - **Low** in energy
  - Reside **inside sphere**

1 Ry =13.605 eV

Problems of the LAPW method:

EFG Calculation for Rutile TiO_2 as a function of the Ti-p linearization energy E_p

exp. EFG

„ghostband"

Electronic Structure

Ti 3d / O 2p

E_F

O 2p
Hybridized w.
Ti 4p, Ti 3d

Ti- 3p
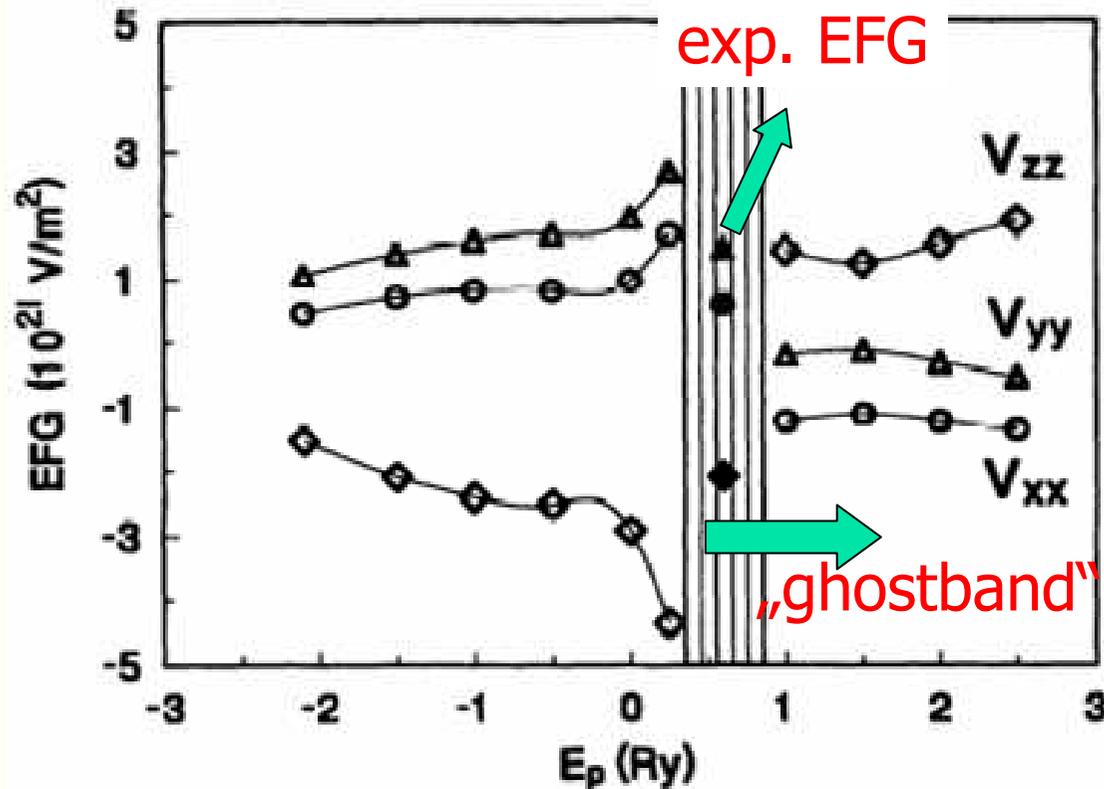
P. Blaha, D.J. Singh, P.I. Sorantin and K. Schwarz, Phys. Rev. B **46**, 1321 (1992).

Problems of the LAPW method

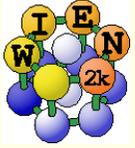**Problems with semi-core states**

Electronic Structure

E

Ti 3d / O 2p

---------------------------------- E_F

O 2p
Hybridized w
Ti 4p, Ti 3d

Ti- 3p
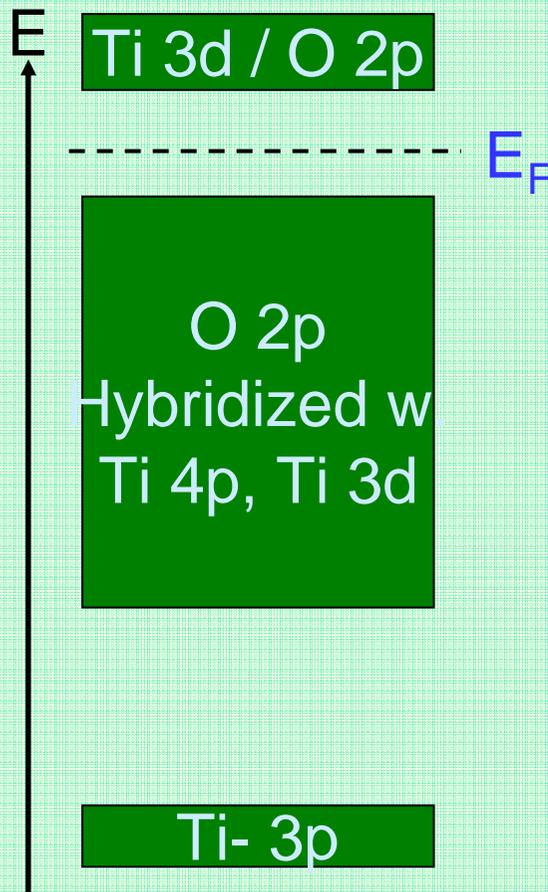
Treat all the states in a single energy window:

- Automatically orthogonal.
- Need to add variational freedom.
- Could invent quadratic or cubic APW methods.

$$\varphi(\mathbf{r}) = \left\{ \begin{array}{l} \Omega^{-1/2} \sum_{\mathbf{K}} c_{\mathbf{K}}\, e^{i(\mathbf{K}+\mathbf{k})\cdot\mathbf{r}} \\[2mm] \sum_{lm} \left(A_{lm} u_l(r) + B_{lm} \mathring{u}_l(r) + C_{lm} \ddot{u}_l(r)\right) Y_{lm}(\mathbf{r}) \end{array} \right.$$

Problem: *This requires an extra matching condition, e.g. second derivatives continuous ⇒method will be impractical due to the high planewave cut-off needed.*
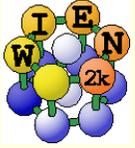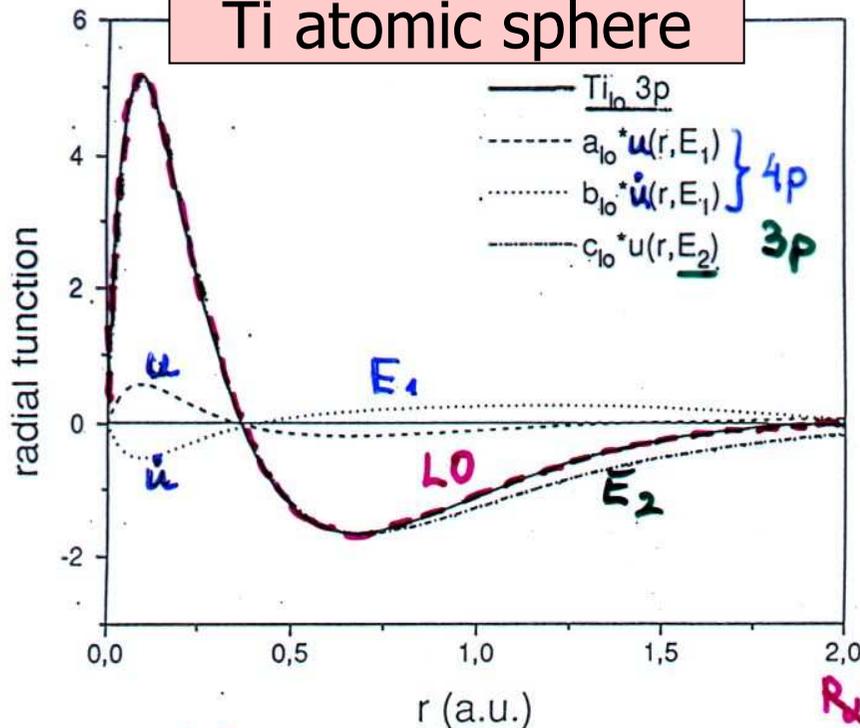
$$\Phi_{LO} = [A_{\ell m} u_\ell^{E_1} + B_{\ell m} \dot{u}_\ell^{E_1} + C_{\ell m} u_\ell^{E_2}] Y_{\ell m}(\hat{r})$$

- **LO: contains a second** $u_l(E_2)$
  - *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)

Ti atomic sphere

Ti$_{lo}$ 3p
a_{lo}*u(r,E$_1$) } 4p
b_{lo}*$\dot{u}$(r,E$_1$) }
c_{lo}*u(r,E$_2$) 3p

The LAPW+LO Method

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

SLAPW−4
QAPW

La
$R_{MT} = 3.3\ a_0$

Cubic APW
SLAPW−3

LAPW+LO

$E + 16980$ (Ry/atom)

RK_{max}
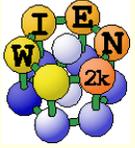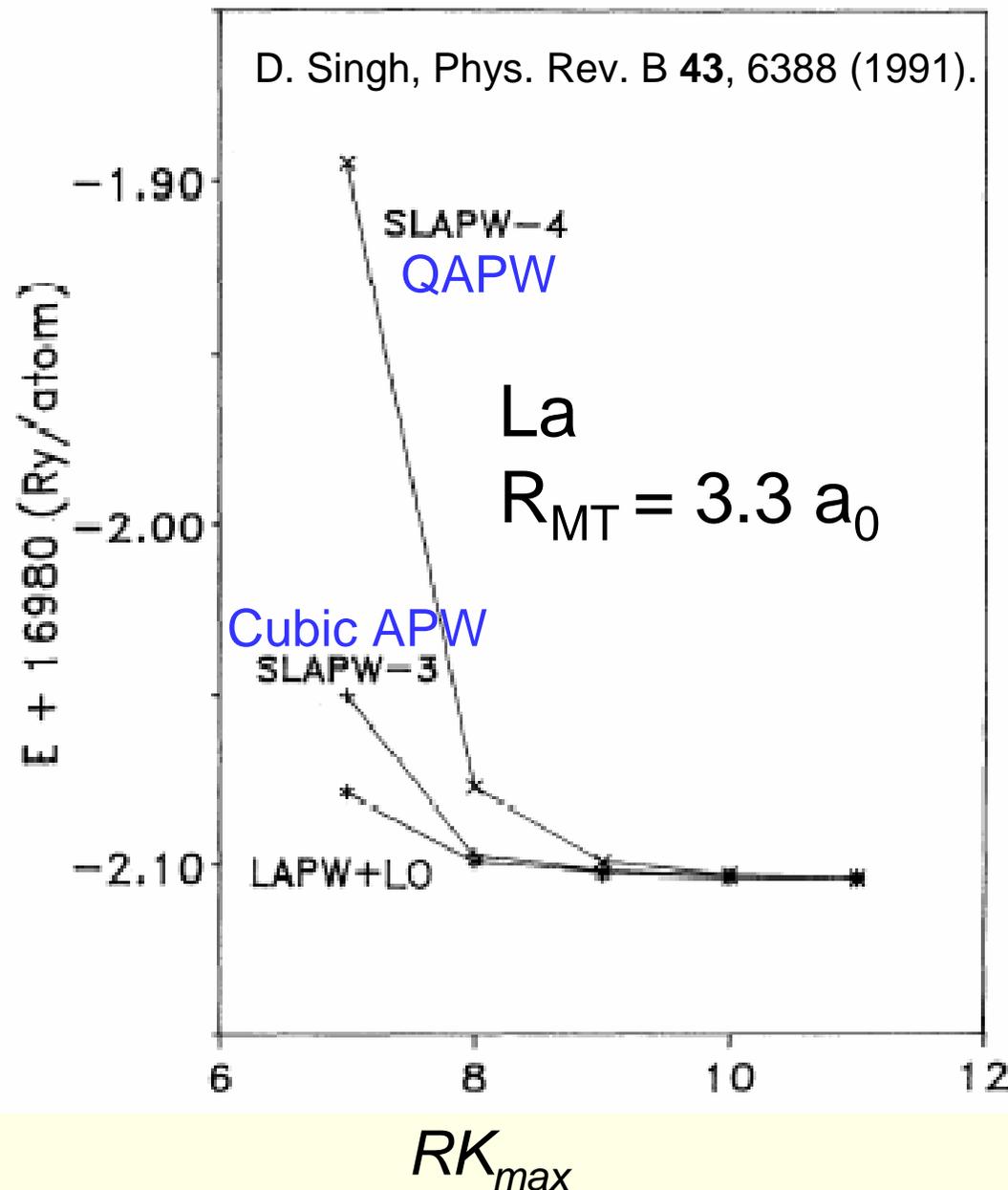
LAPW+LO converges like LAPW. The LO add a few basis functions (i.e. 3 per atom for p states). Can also use LO to relax linearization errors, e.g. for a narrow d or f band.

Suggested settings:

Two "energy" parameters, one for u and $\dot{u}$ and the other for $u^{(2)}$. Choose one at the semi-core position and the other at the valence.
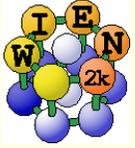
E.Sjöstedt, L.Nordström, D.J.Singh,
An alternative way of linearizing the augmented plane wave method,
Solid State Commun. 114, 15 (2000)

- Use APW, but at fixed E_l (superior PW convergence)
- Linearize with additional lo (add a few basis functions)

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

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

optimal solution: mixed basis
- use APW+lo for states which are difficult to converge:
(f or d- states, atoms with small spheres)
- use LAPW+LO for all other atoms and ℓ
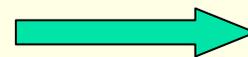
basis for
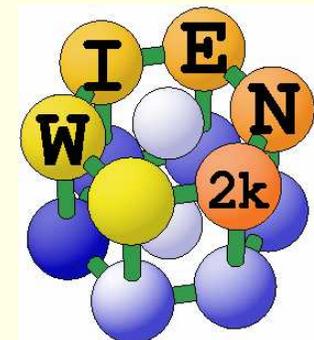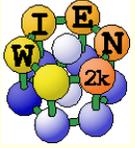
E. Sjostedt, L. Nordstrom and D.J. Singh, Solid State Commun. **114**, 15 (2000).
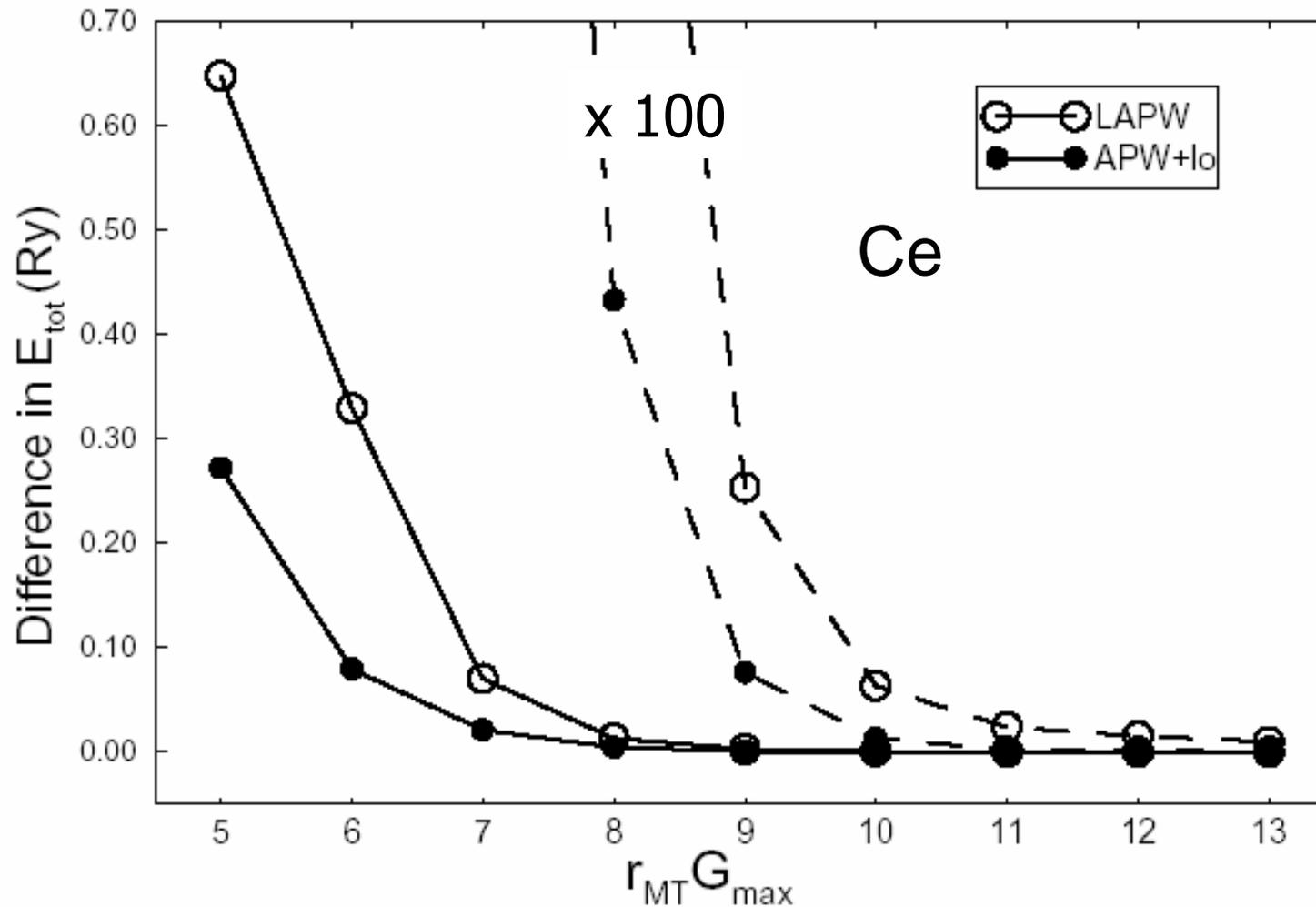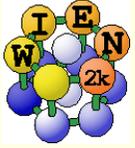
Improved convergence of APW+lo

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

- changes sign and converges slowly in **LAPW**

- better convergence in **APW+lo**

Force (Fy) on oxygen in SES (sodium electro sodalite) vs. # plane waves
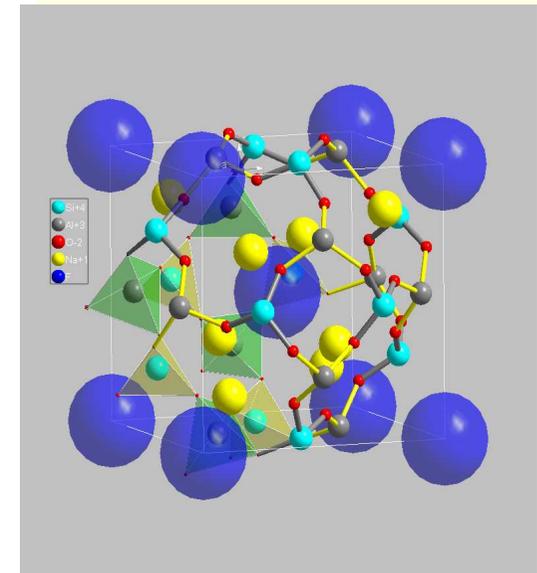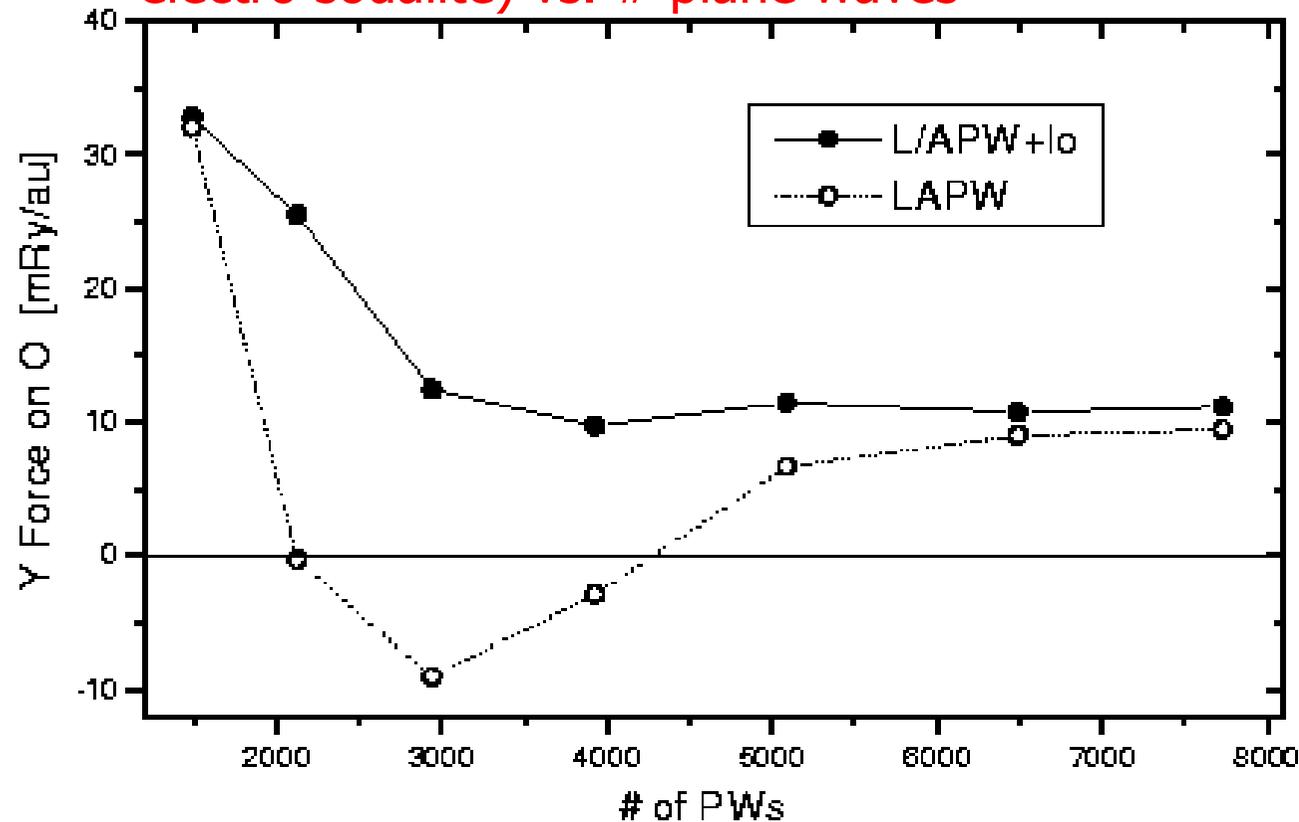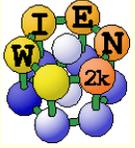
Relativistic treatment

For example: Ti
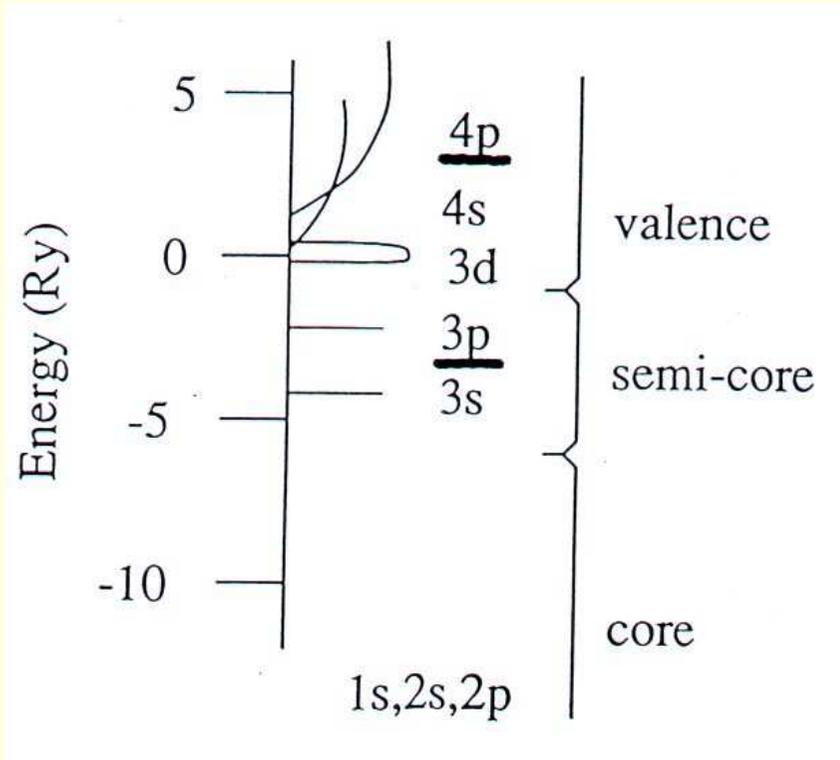
- **Valence states**
  - *Scalar relativistic*
    - mass-velocity
    - Darwin s-shift
  - *Spin orbit coupling **on demand** by second variational treatment*
- **Semi-core states**
  - *Scalar relativistic*
  - *No spin orbit coupling*
  - ***on demand***
    - spin orbit coupling by second variational treatment
    - Additional local orbital (see Th-6p$_{1/2}$)
- **Core states**
  - *Fully relativistic*
    - Dirac equation
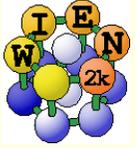
Relativistic semi-core states in fcc Th
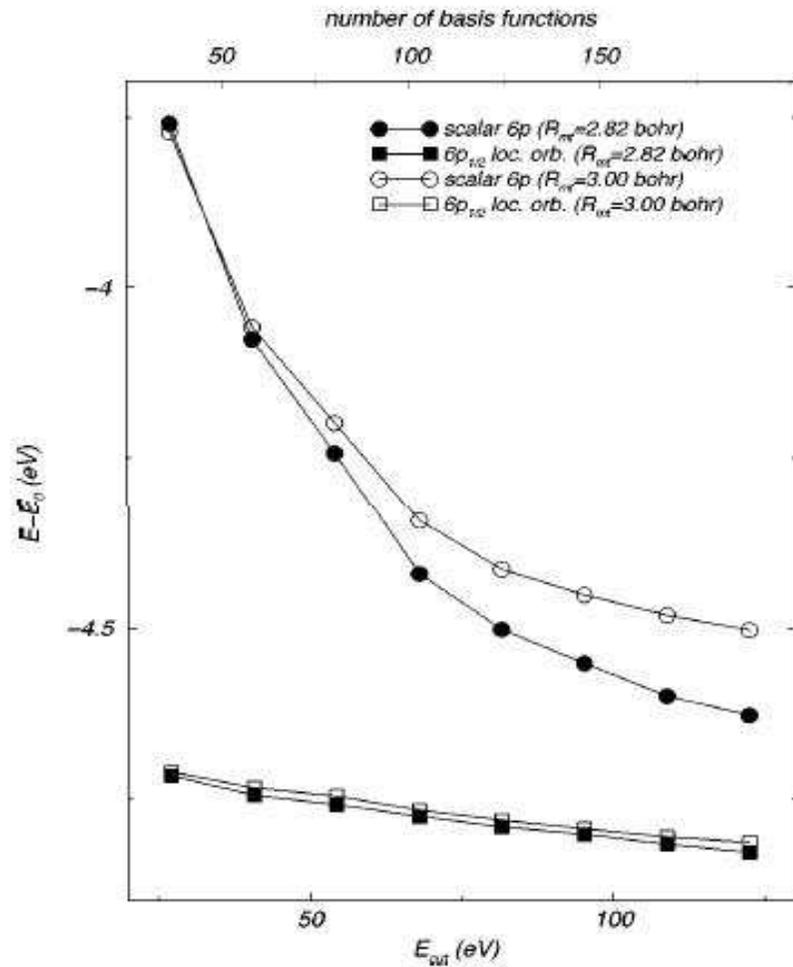
FIG. 1. The total energy E as a function of the second-variation cutoff energy E_{cut} (the approximate size of the second-variational-step basis, including spin, is marked on the top axis) for two different muffin-tin radii. The standard FLAPW results are marked with circles, the results obtained with the additional $p_{1/2}$ local orbitals are marked with squares (the latter energies were increased by 3 eV in order to show the curves on the same plot).

- additional local orbitals for 6p$_{1/2}$ orbital in Th
- Spin-orbit (2nd variational method)
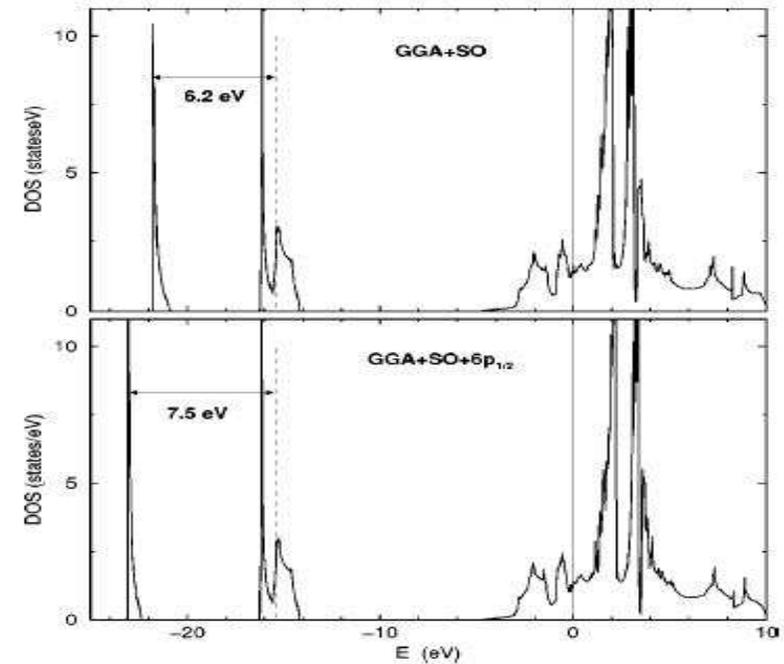
FIG. 2. Density of states calculated with the scalar relativistic basis (top panel) and with the $p_{1/2}$ local orbitals extended basis (bottom panel). The splitting between the centers of $6p_{1/2}$ and $6p_{3/2}$ bands is shown.

J.Kuneš, P.Novak, R.Schmid, P.Blaha, K.Schwarz, Phys.Rev.B. 64, 153102 (2001)

Atomic forces (Yu et al.; Kohler et al.)

- **Total Energy:**
  - *Electrostatic energy*
  - *Kinetic energy*
  - *XC-energy*

$$U[\rho] = \frac{1}{2} \int d^3\vec{r} \; \rho(\vec{r}) V_{es}(\vec{r}) + \frac{1}{2} \sum_{\alpha} Z_{\alpha} V_{es}^{\alpha}(\vec{r})$$

$$T[\rho] = \sum_i n_i \varepsilon_i - \int d^3\vec{r} \; \rho(\vec{r}) V_{eff}(\vec{r})$$

$$E_{xc}[\rho] = \int d^3\vec{r} \; \rho(\vec{r}) \varepsilon_{xc}(\vec{r})$$

- **Force on atom** α:

$$\vec{F}^{\alpha} = \frac{-dE_{tot}}{d\vec{R}_{\alpha}} = F_{HF}^{\alpha} + F_{core}^{\alpha} + F_{val}^{\alpha}$$

- *Hellmann-Feynman-force*

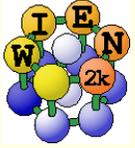$$F_{HF}^{\alpha} = Z_{\alpha} \sum_{m=-1}^{1} \lim_{r_{\alpha} \to 0} \frac{V_{1m}^{es}(r_{\alpha})}{r_{\alpha}} \nabla_{\alpha}[r_{\alpha} Y_{1m}(\hat{r})]$$

- *Pulay corrections*
  - Core

$$F_{core}^{\alpha} = -\int \rho_{core}(r) \nabla_{\alpha} V_{eff}(r) \, d\vec{r}$$

  - Valence

- expensive, contains a summation of matrix elements over all occupied states

$$F_{val}^{\alpha} = \int_{\alpha} V_{eff}(r) \nabla_{\alpha} \rho_{val}(r) \, d\vec{r} + \sum_{k,i} n_i \sum_{K,K'} c_i^*(K') c_i(K) \times$$
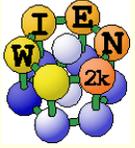
$$\left[(K^2 - \varepsilon_i) \oint \phi_{K'}^*(r) \phi_K(r) \, dS_{\alpha} - i(K - K') \langle \phi_{K'} | H - \varepsilon_i | \phi_K \rangle_{\alpha} \right]$$
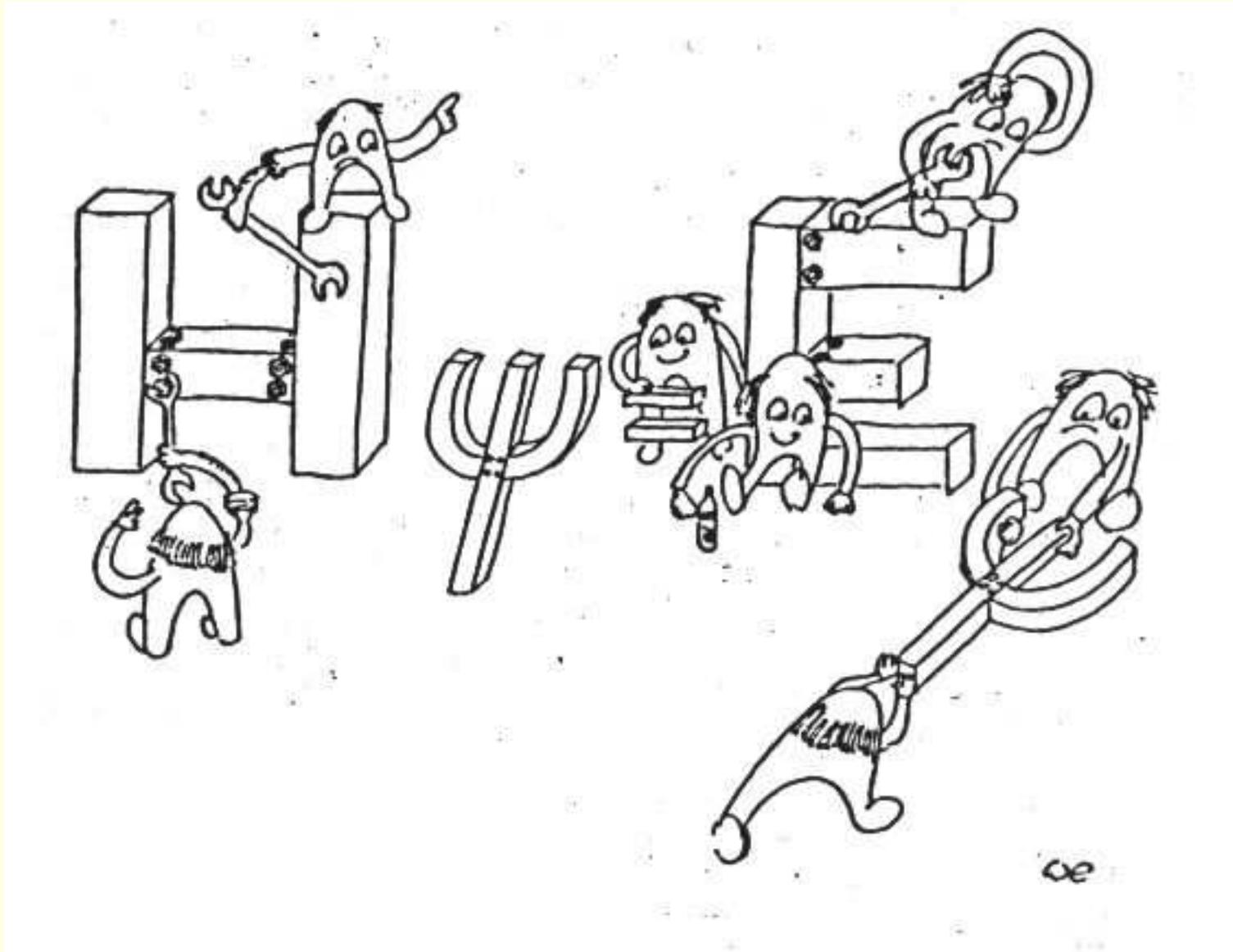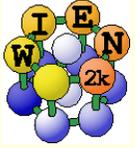
WIEN2k software package
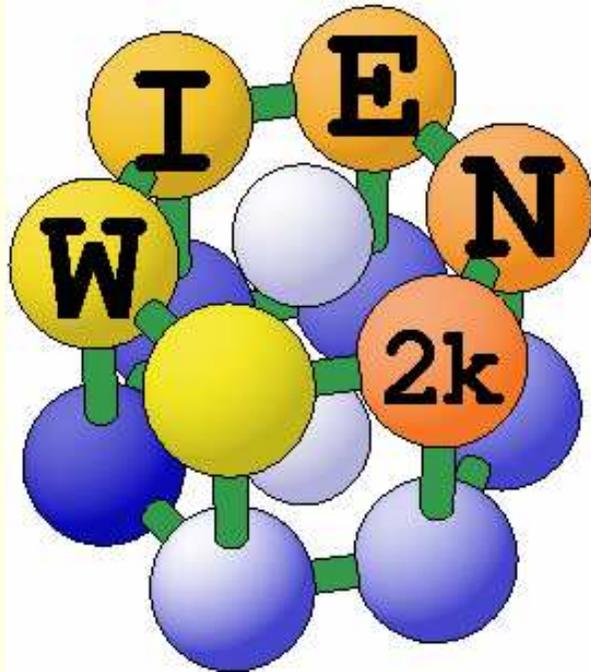
WIEN97: ~500 users
WIEN2k: ~1100 users
mailinglist: 1800 users

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

Development of WIEN2k

- **Authors of WIEN2k**

  P. Blaha, K. Schwarz, D. Kvasnicka, G. Madsen and J. Luitz

- **Other contributions to WIEN2k**

  - **C. Ambrosch-Draxl** *(Univ. Graz, Austria), optics*
  - *T. Charpin (Paris), elastic constants*
  - *R. Dohmen und J. Pichlmeier (RZG, Garching), parallelization*
  - **R. Laskowski (Vienna),** *non-collinear magnetism, parallelization*
  - *L. Marks (Northwestern, US) , various optimizations*
  - **P. Novák** *and J. Kunes (Prague), LDA+U, SO*
  - *B. Olejnik (Vienna), non-linear optics,*
 - *C. Persson (Uppsala), irreducible representations*
  - **M. Scheffler** *(Fritz Haber Inst., Berlin), forces*
  - **D.J.Singh** *(NRL, Washington D.C.), local oribtals (LO), APW+lo*
  - *E. Sjöstedt and **L Nordström** (Uppsala, Sweden), APW+lo*
  - *J. Sofo and J. Fuhr (Barriloche), Bader analysis*
  - *B. Yanchitsky and A. Timoshevskii (Kiev), spacegroup*

- **and many others ….**
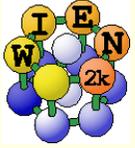
International co-operations

WIEN2k licenses

- **More than 1000 user groups worldwide**
  - *Industries* (Canon, Eastman, Exxon, Fuji, A.D.Little, Mitsubishi, Motorola, NEC, Norsk Hydro, Osram, Panasonic, Samsung, Sony).
 - *Europe:* (EHT Zürich, MPI Stuttgart, Dresden, FHI Berlin, DESY, TH Aachen, ESRF, Prague, Paris, Chalmers, Cambridge, Oxford)
  - *America:* ARG, BZ, CDN, MX, USA (MIT, NIST, Berkeley, Princeton, Harvard, Argonne NL, Los Alamos Nat.Lab., Penn State, Georgia Tech, Lehigh, Chicago, SUNY, UC St.Barbara, Toronto)
  - *far east:* AUS, China, India, JPN, Korea, Pakistan, Singapore,Taiwan (Beijing, Tokyo, Osaka, Sendai, Tsukuba, Hong Kong)
- **Registration at www.wien2k.at**
  - *400/4000 Euro for Universites/Industries*
  - *code download via www (with password), updates, bug fixes, news*
  - *usersguide, faq-page, mailing-list with help-requests*
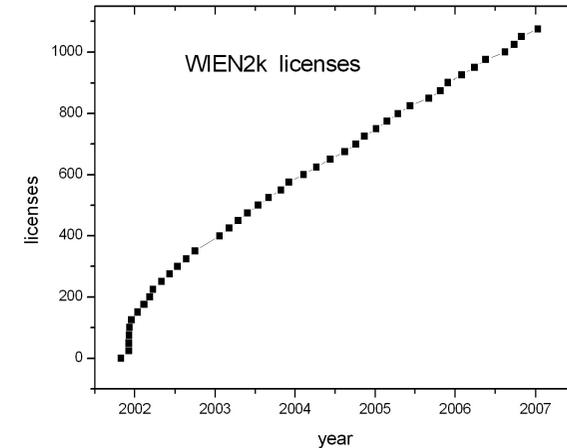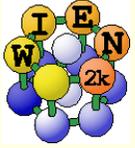
WIEN2k - WORKSHOPS

- "WIEN-workshops" started in 1993 in Vienna and subsequent workshops were held not only in Vienna, but also in Trieste, Isfahan (Iran), twice at PennState (US), in Kyoto (Japan) and at UCLA (California,US).

- **WIEN2007: Hands on Workshop on the WIEN2k package**

   Penn State University, USA, June 11-14, 2007

- **14th WIEN2k – WORKSHOP, a satellite meeting to ICMAT'07 (Symposium O)**

   **IHPC, Singapore, July 6-9, 2007**
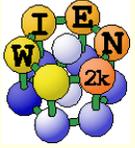
General remarks on WIEN2k

- WIEN2k consists of many independent F90 programs, which are linked together via C-shell scripts (needs Unix/Linux)
- real/complex version (inversion)
- 10 atom cells on 256Mb PC / 100 atom cells require 1-2 Gb RAM
- k-point parallel on clusters with common NFS (slow network)
- MPI/Scalapack parallelization for big cases (>100 atoms) and fast network
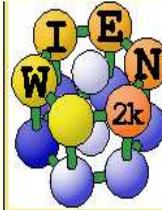   (h-BN/Rh(111) nanomesh: 1100 atoms+vacuum on 64-100 cpus)

- You can run WIEN2k using any www-browser and the w2web interface, but also at the command line of an xterm.
- 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)
- 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) and init_lapw
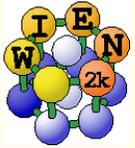
w2web GUI (graphical user interface)

- **Structure generator**
  - *spacegroup selection*
  - *import cif 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!

[Save Structure]

Execution >>
StructGen™
initialize calc.
run SCF
single prog.
optimize(V,c/a)
mini. positions

Utils. >>

Tasks >>

Files >>
struct file(s)
input files
output files
SCF files

Session Mgmt. >>
change session
change dir
change info

Configuration

Usersguide
html-Version
pdf-Version

Idea and realization by

Title: TiC
Lattice:
Type: F

P
F
B
CXY
CYZ
CXZ
R
H
1_P1

Spacegroups from
Bilbao Cryst Server

Lattice parameters in Å

a= 4.328000038 b= 4.328000038 c= 4.328000038

α= 90.000000 β= 90.000000 γ= 90.000000

Inequivalent Atoms: 2

Atom 1: Ti   Z= 22.0   RMT= 2.0000   remove atom

Pos 1: x= 0.00000000 y= 0.00000000 z= 0.00000000 remove
add position

Atom 2: C   Z= 6.0   RMT= 1.9000   remove atom

Pos 1: x= 0.50000000 y= 0.50000000 z= 0.50000000 remove
add position

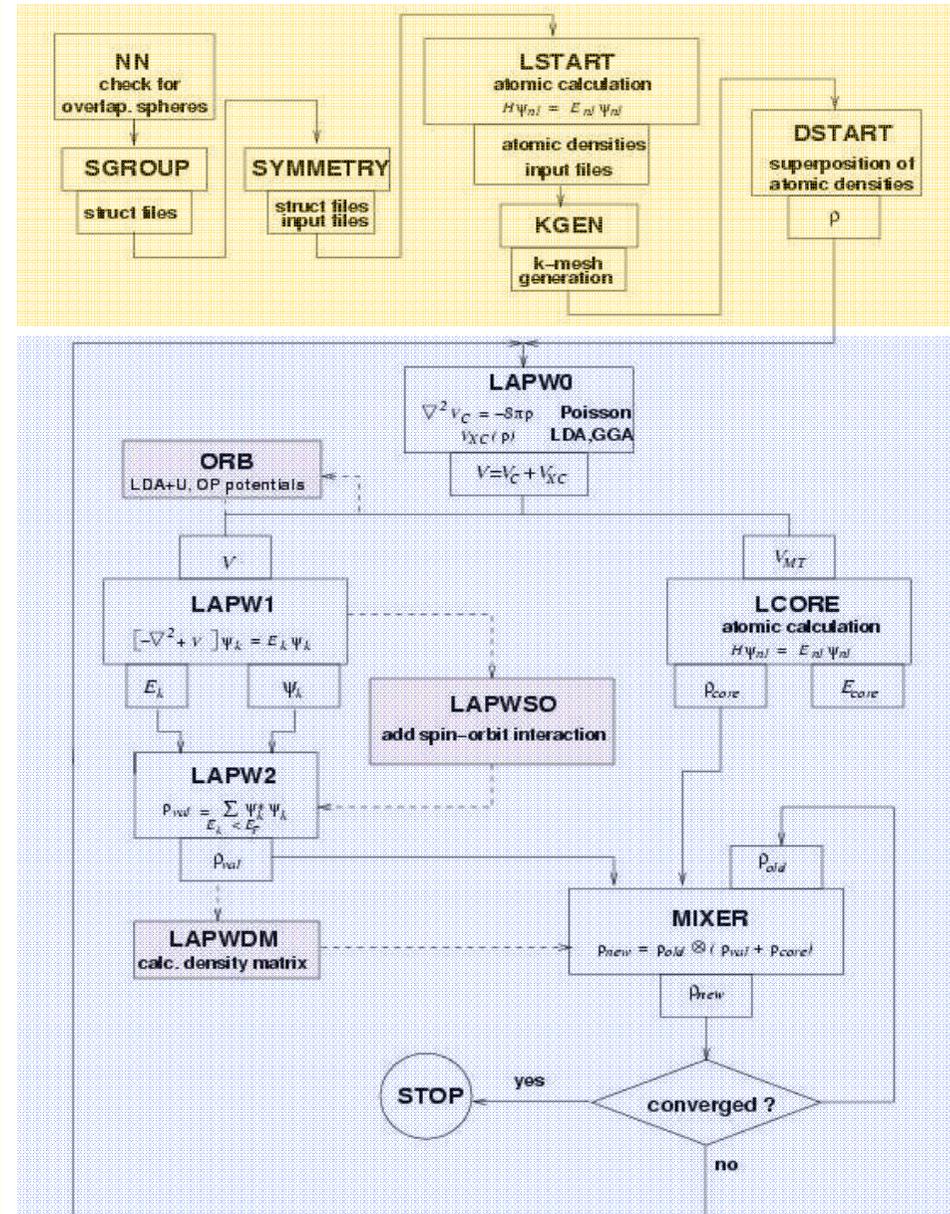# Program structure of WIEN2k

- **init_lapw**
  - *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**
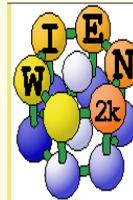 - *cp case.struct and clmsum files,*
  - *mv case.scf file*
  - *rm case.broyd* files*

Task for electron density plot

- **A task consists of**
  - *a series of steps*
  - *that must be executed*
  - *to generate a plot*
- **For electron density plot**
  - *select states by E-window in case.in2 (e.g. valence e^-: Ti-3d,4s, C-2s,2p)*
  - *for difference densities make sure you calculate the same states for the free atoms*
  - *select plane for plot (do not put an atom at the corner or edges)*
  - *generate 3D or contour plot with gnuplot or Xcrysden (Tone.Kokalj@ijs.si)*
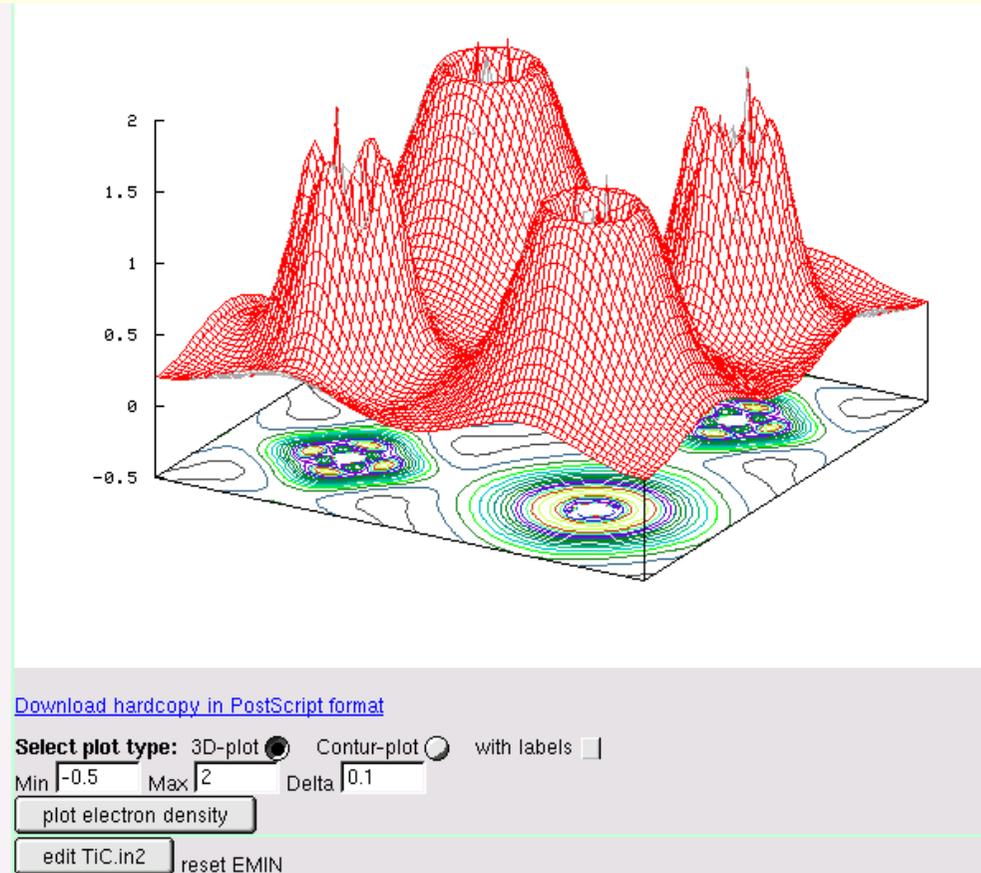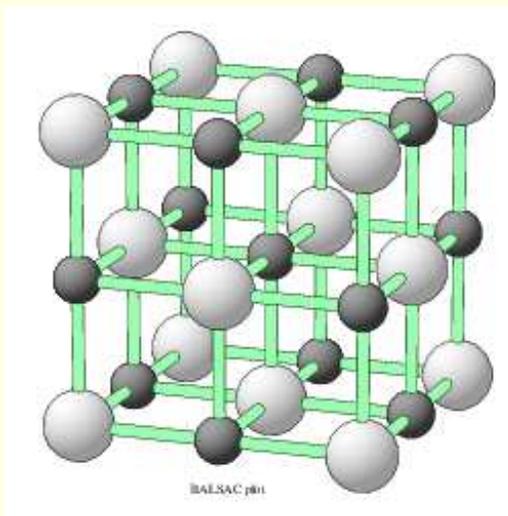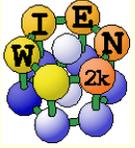 - *reset EMIN in case.in2*
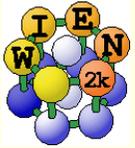
TiC electron density

- **NaCl structure (100) plane**
- **Valence electrons only**
- **plot in 2 dimensions**
- **Shows**
  - *charge distribution*
  - *covalent bonding*
    - between the Ti-3d and C-2p electrons
  - e_g/t_{2g} *symmetry*

Download hardcopy in PostScript format

Select plot type: 3D-plot ● Contur-plot ○ with labels ☐
Min `-0.5` Max `2` Delta `0.1`
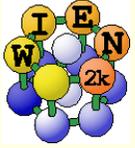plot electron density
edit TiC.in2 reset EMIN

BALSAC plot

Getting help

- ***_lapw –h**   „help switch" of all WIEN2k-scripts
- **help_lapw:**
  - *opens usersguide.pdf; Use ^f keyword to search for an item („index")*
- **html-version of the UG:** ($WIENROOT/SRC_usersguide/usersguide.html)
- **http://www.wien2k.at/reg_user**
  - *FAQ page with answers to common questions*
  - *Update information: When you think the program has an error, please check newest version*
  - *Textbook section: DFT and the family of LAPW methods by S.Cottenier*
  - *Mailing-list:*
    - subscribe to the list (always use the same email)
    - full text search of the „digest" (your questions may have been answered before)
    - posting questions: Provide sufficient information, locate your problem (case.dayfile, *.error, case.scf, case.outputX).
   - „My calculation crashed. Please help." This will most likely not be answered.
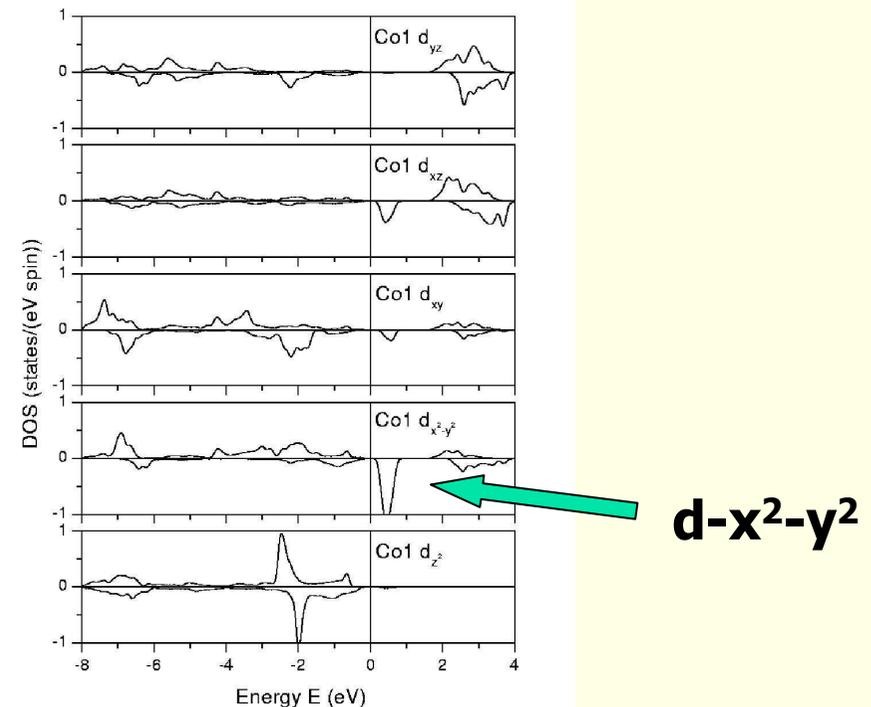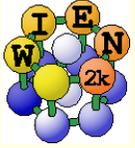
- **DFT:** LDA, various GGAs; meta-GGA, LDA+U; Hybrids for „correlated electrons")
- **Energy bands**
    - *classification of irreducible representations*
    - *´character-plot´ (emphasize a certain band-character)*
- **Density of states**
    - *including partial DOS with l and m- character (eg. p_x , p_y , p_z)*

h-BN/Ni(111): σ and π bands

BaCoO$_3$

d-x²-y²
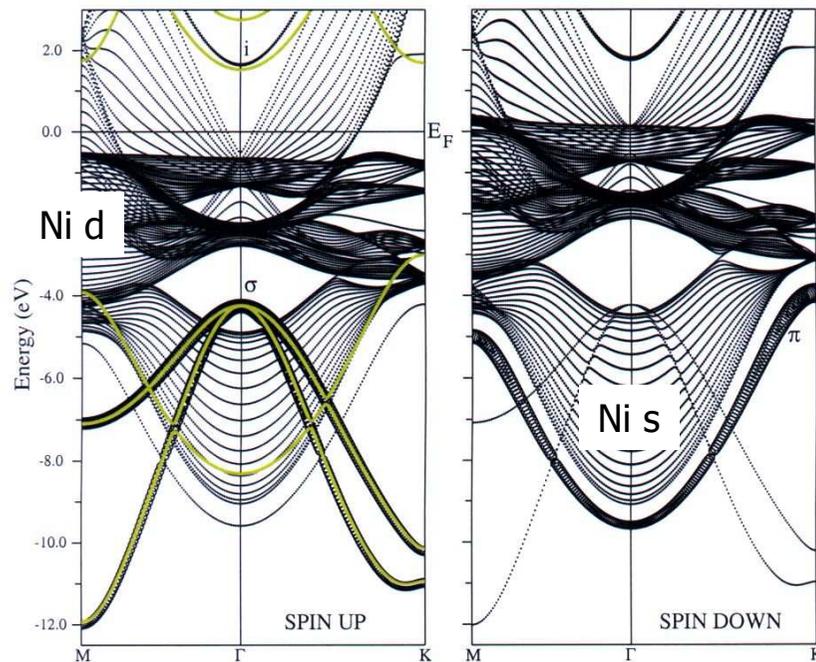
- **Electron density, potential**
  - *total-, valence-, difference-, spin-densities, ρ of selected states*
  - *1-D, 2D- and 3D-plots (Xcrysden)*
  - *X-ray structure factors*
  - *Bader´s atom-in-molecule analysis, critical-points, atomic basins and charges ($\nabla\rho.\vec{n} = 0$)*
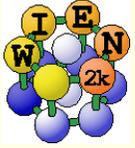 - *spin+orbital magnetic moments (+ spin-orbit)*
- **Hyperfine parameters**
  - *hyperfine fields (contact + dipolar + orbital contribution)*
  - *Isomer shift*
  - *Electric field gradients*
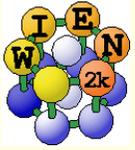
Y$_2$Nb$_2$O$_7$:   Peak A (Nb$_2$) 4-center bond (d-z^2)
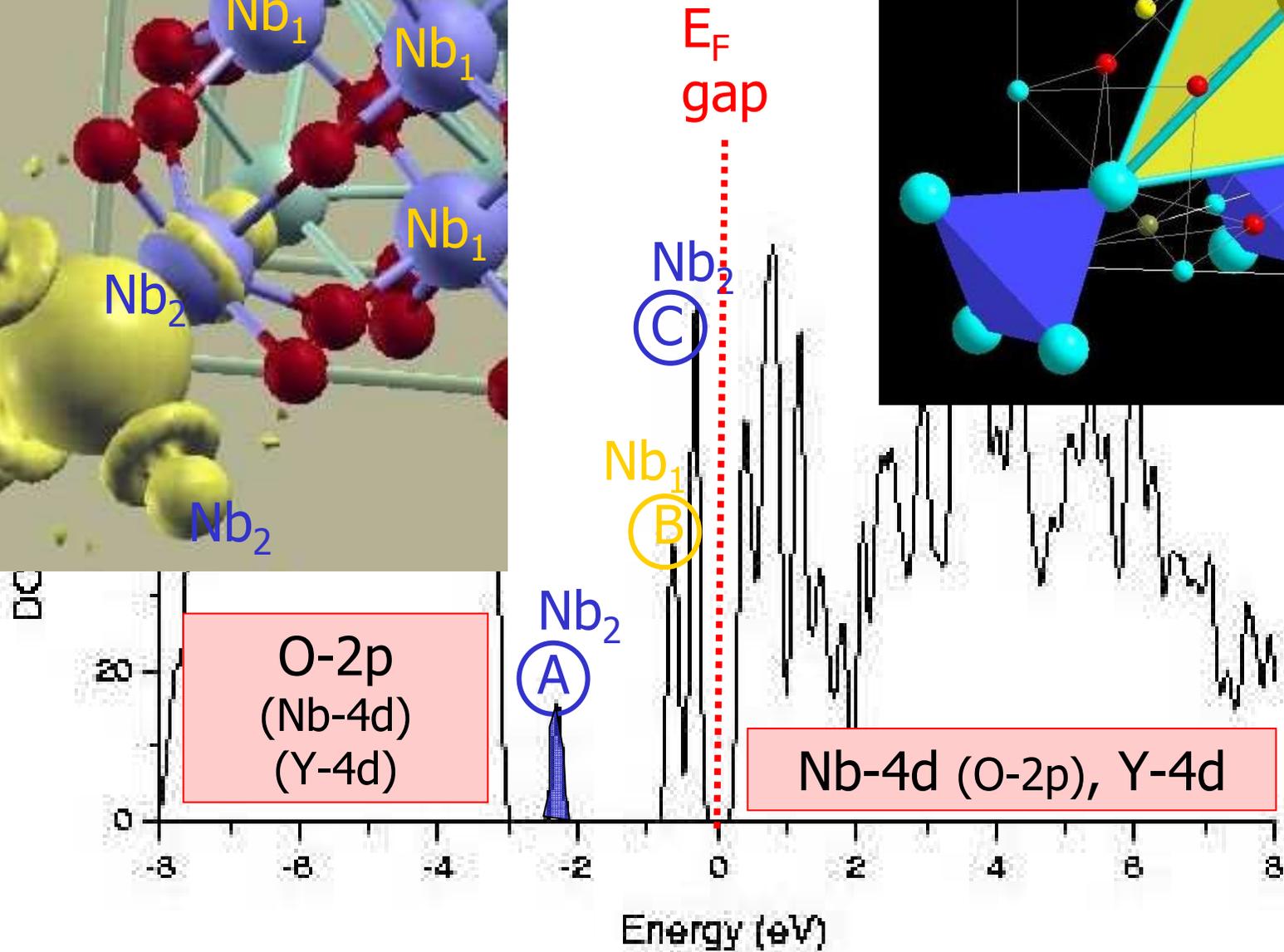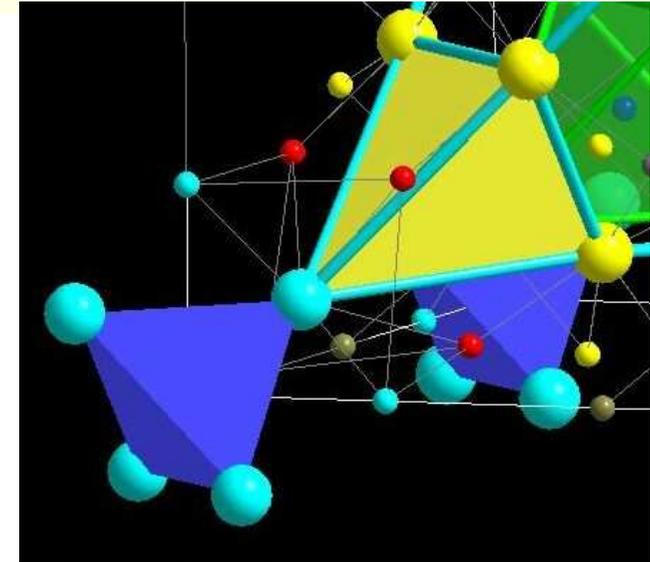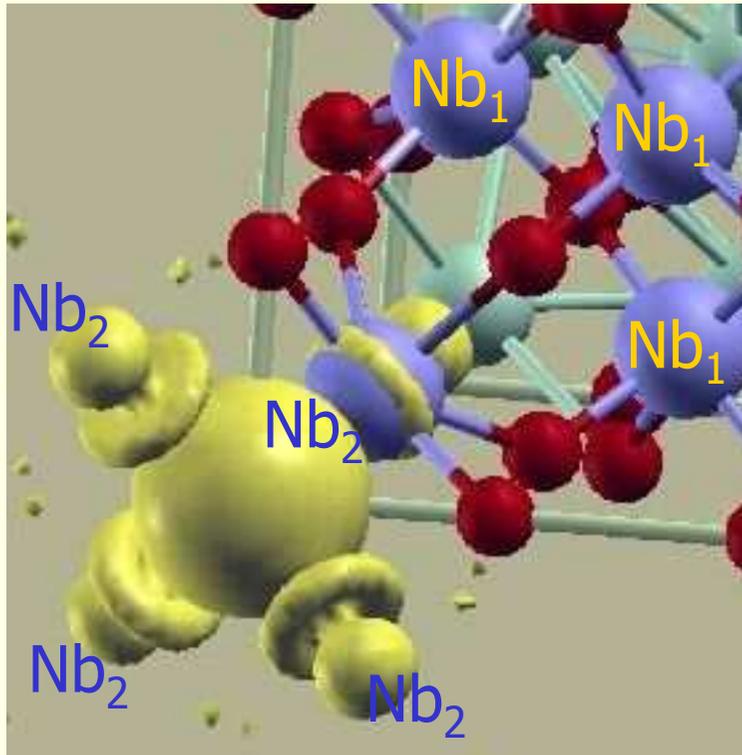
- ## Total energy and forces

  - *optimization of internal coordinates, (damped MD, BROYDEN)*
  - *cell parameter only via E_{tot} (no stress tensor)*
  - *elastic constants for cubic cells*
  - *Phonons via a direct method (based on forces from supercells)*
    - interface to PHONON (K.Parlinski) – bands, DOS, thermodynamics, neutrons

Pyrochlore structure of $Y_2Nb_2O_7$:   strong phonon instabilities→ phase transition
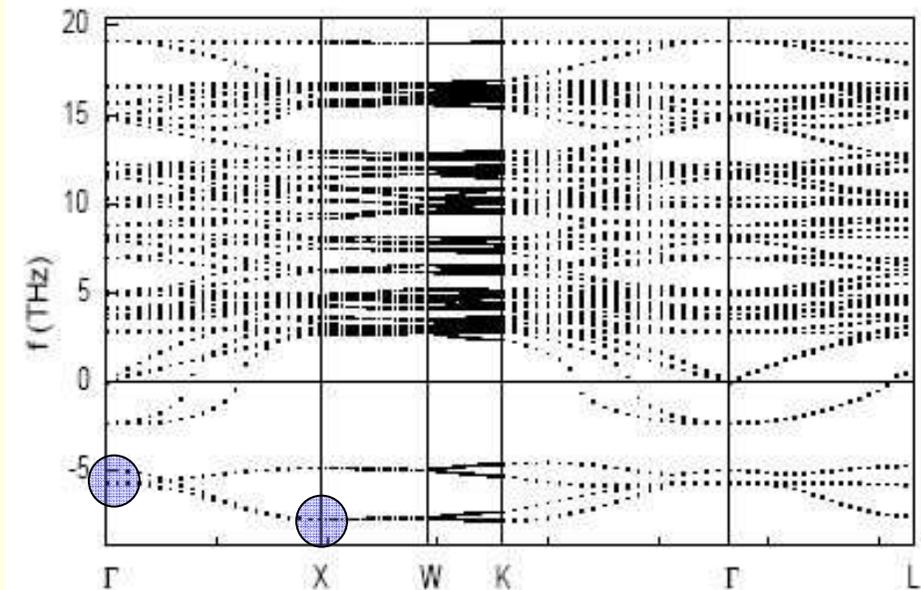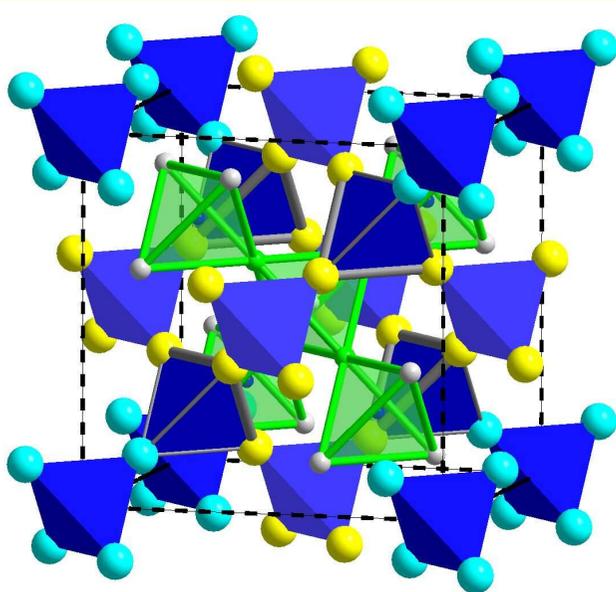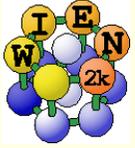
- **Spectroscopy**
  - *core levels (with core holes)*
  - *X-ray emission, absorption, electron-energy-loss*
    - (core - valence/conduction-band transitions including matrix elements and angular dep.)
    - EELS inclusion of possible non-dipol transititons (momentum transfer)
  - *optical properties (dielectric function in RPA, JDOS including momentum matrix elements and Kramers-Kronig)*
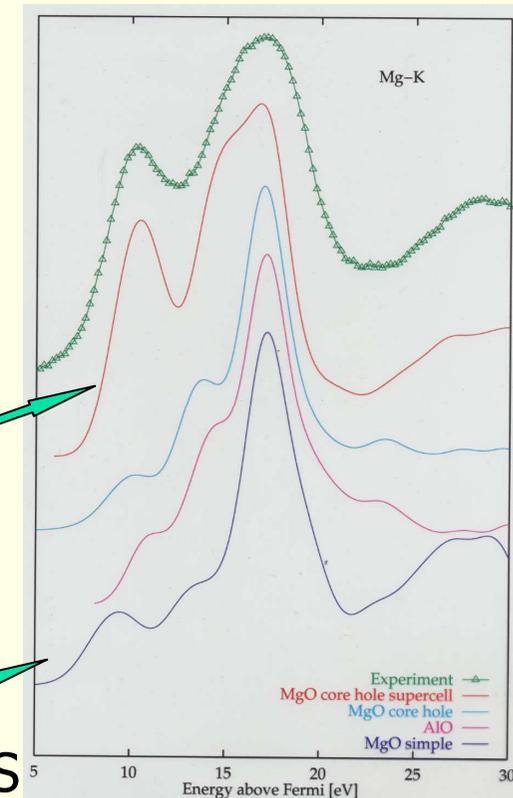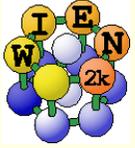 - *fermi surface (2D, 3D)*

XES
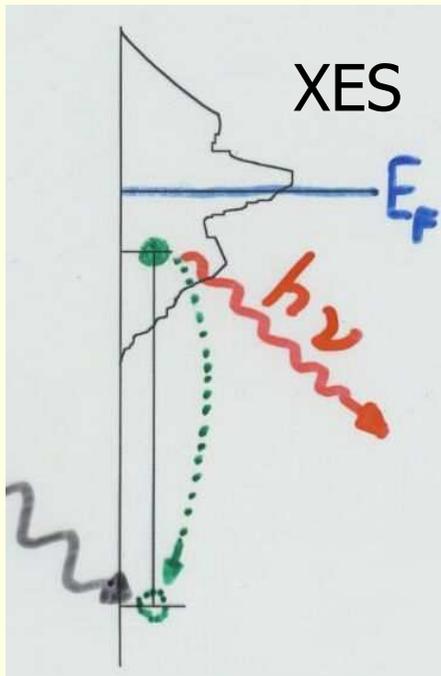
Mg-K XAS
probes empty Mg-p

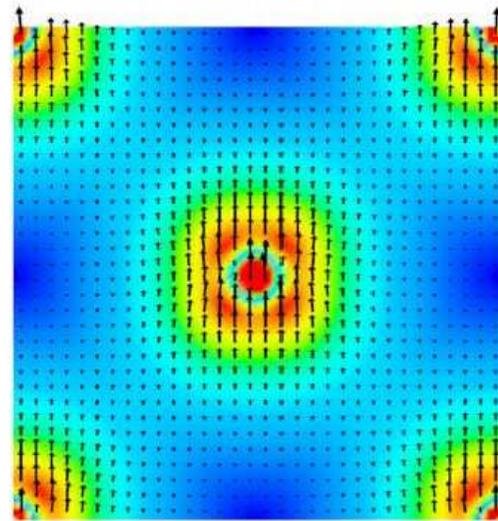including a core-hole
in supercell
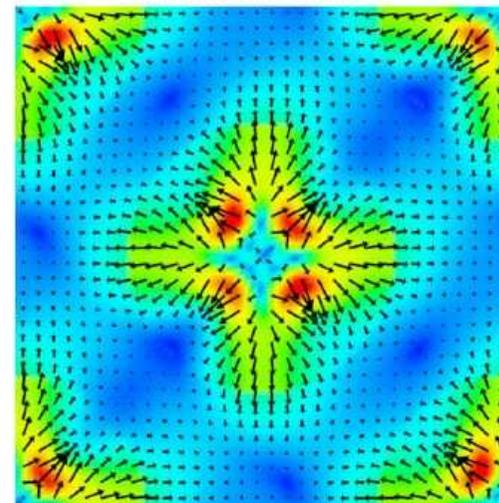(Final state rule)

from ground-state DOS

- **New developments (available)**
  - *non-linear optics (B.Olejnik)*
  - *non-collinear magnetism (spin-spirals to fully-relativistic) (R.Laskowski)*
  - *transport properties (Fermi velocities, Seebeck, conductivity, thermoelectrics, ..)* *(G.Madsen)*

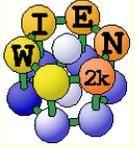**Intra-atomic NCM, fcc** Pu

(a) plane $x = 0$ (b) plane $z = 1/10$

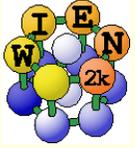Spin density maps of **fcc Pu**. Calculation in FULL mode with SO. Average momenta point to $\langle 001 \rangle$

+ robust all-electron full-potential method
+ unbiased basisset, one convergence parameter (LDA-limit)
+ all elements of periodic table (equal expensive), metals
+ LDA, GGA, meta-GGA, LDA+U, spin-orbit
+ many properties and tools (supercells, symmetry)
+ w2web (for novice users)
- ? speed + memory requirements
    + very efficient basis for large spheres (2 bohr) (Fe: 12Ry, O: 9Ry)
    - less efficient for small spheres (1 bohr) (O: 25 Ry)
    - large cells, many atoms (n^3, iterative diagonalization not perfect)
    - full H, S matrix stored → large memory required
    + many k-points do not require more memory
- no stress tensor
- no linear response
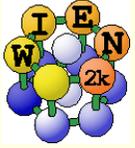
Conclusion

- **There are many ways to make efficient use of DFT calculations**
- **APW+lo method (as implemented in WIEN2k) is one of them**
  - *all electron*
  - *full-potential*
  - *highly accurate - benchmark for other methods*
  - *many properties*
  - *user friendly*
  - *widely used*
    - development by several groups
    - large user community
    - used by many experimental groups

Thank you for your attention !