TECHNISCHE UNIVERSITÄT WIEN

The FP-LAPW and APW+lo methods

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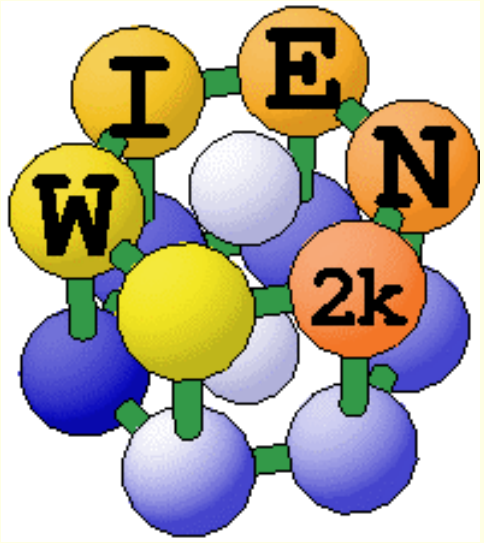
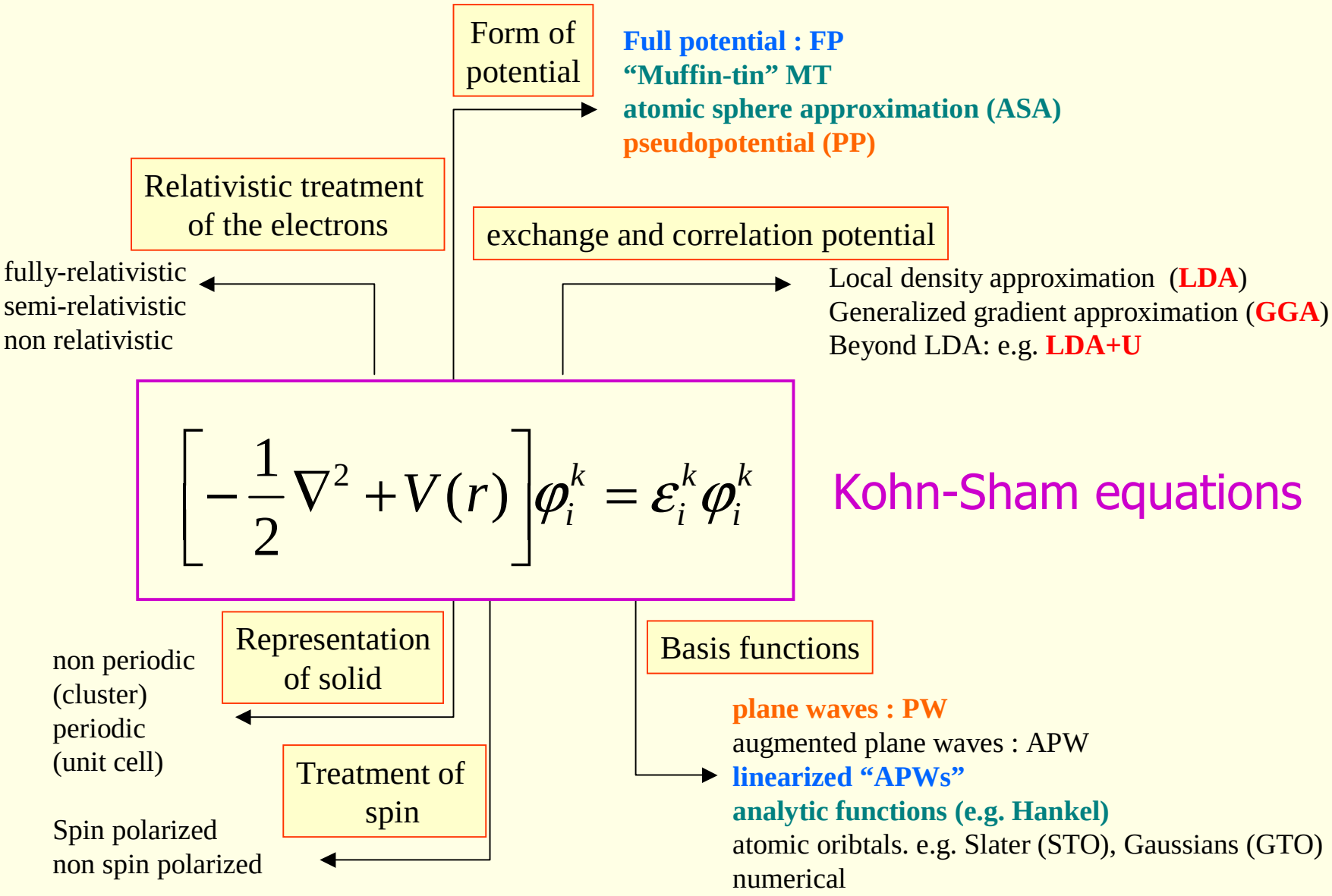
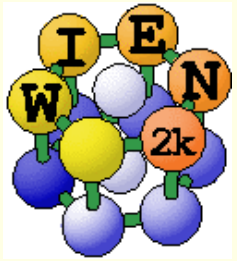


Overview of DFT concepts



APW based schemes

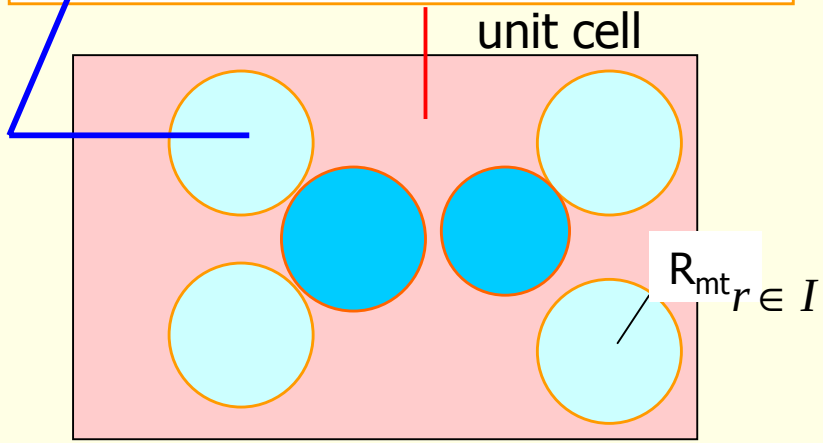
- APW (J.C.Slater 1937)
  - *Non-linear eigenvalue problem*
  - *Computationally very demanding*
- LAPW (O.K.Anderssen 1975)
  - *Generalized eigenvalue problem*
  - *Full-potential*
- Local orbitals (D.J.Singh 1991)
  - *treatment of semi-core states (avoids ghostbands)*
- APW+lo (E.Sjöstedt, L.Nordstörm,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

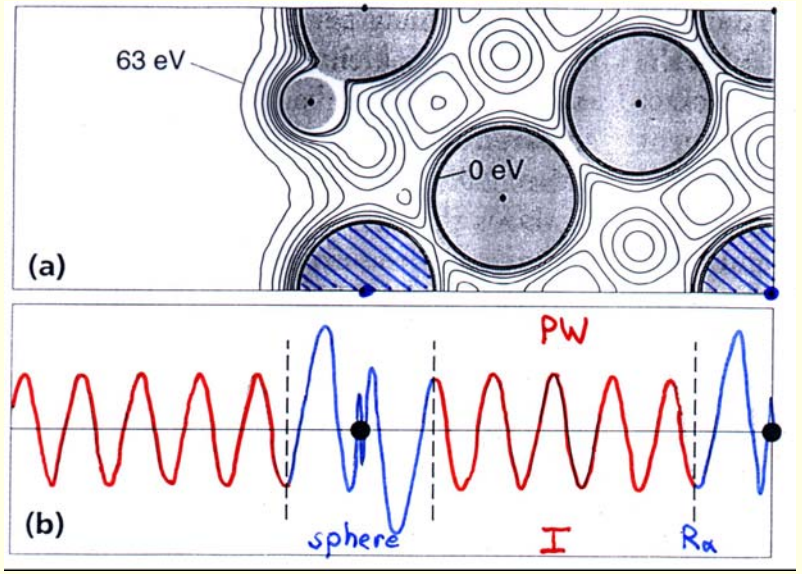


K.Schwarz, P.Blaha, G.K.H.Madsen,
Comp.Phys.Commun.**147**, 71-76 (2002)

APW Augmented Plane Wave method

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





Basisset:

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

Atomic partial waves

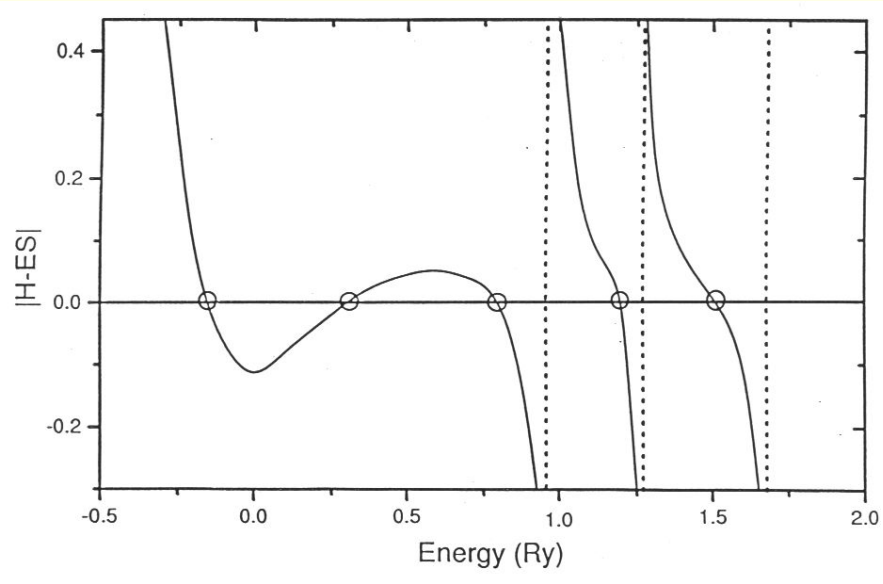
$$\sum_{\ell m} A^K_{\ell m} u_\ell(r',\varepsilon) Y_{\ell m}(\hat{r}')$$

join

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

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

Slater's APW (1937)



Atomic partial waves

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

Energy dependent basis functions lead to ➔

Non-linear eigenvalue problem

H Hamiltonian
S overlap matrix

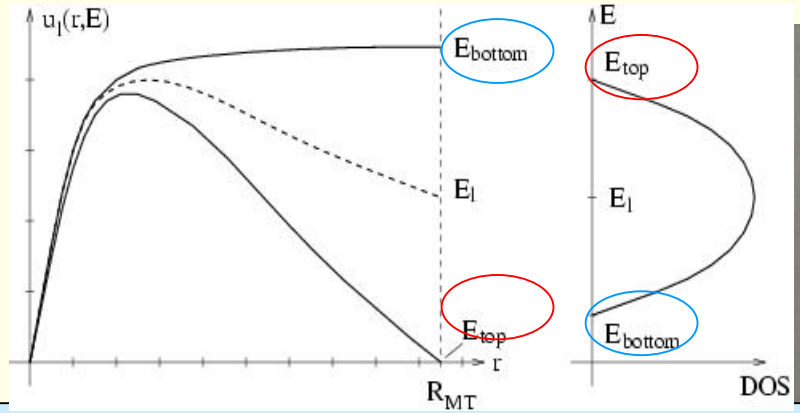
One had to numerically search for the energy, for which the det|H-ES| vanishes. Computationally very demanding.

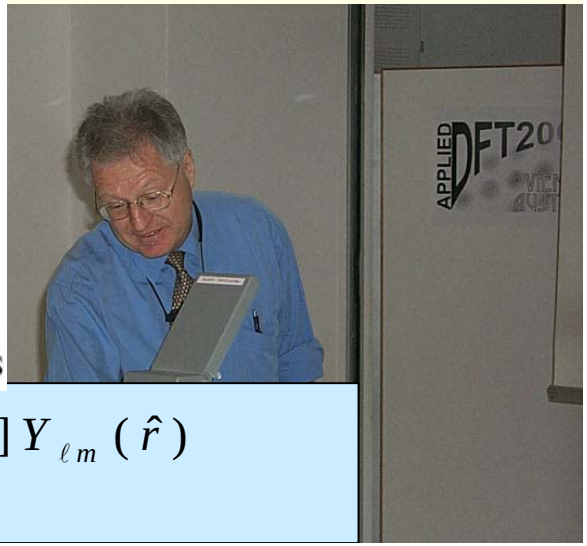
"Exact" solution for given MT potential!

Linearization of energy dependence

LAPW suggested by

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

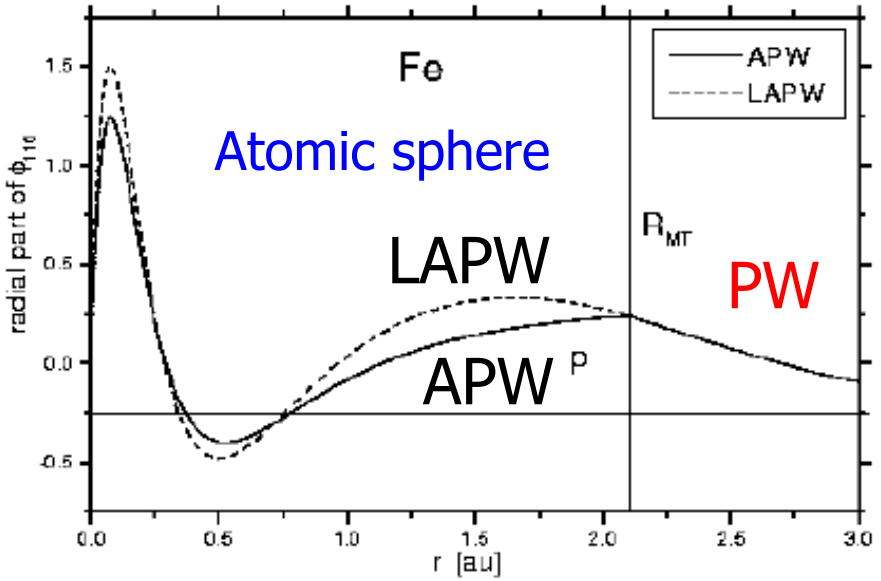




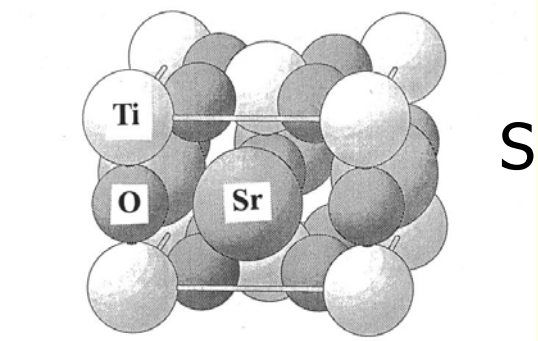
$$\Phi_{k_n} = \sum_{\ell m} [A_{\ell m}(k_n) u_\ell(E_\ell, r) + B_{\ell m}(k_n) \dot{u}_\ell(E_\ell, r)] Y_{\ell m}(\hat{r})$$

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

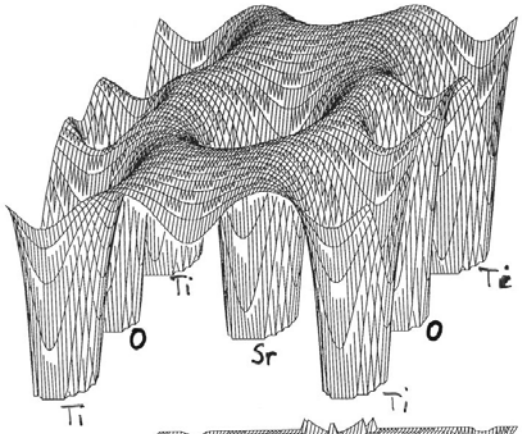
A_{lm}^k, B_{lm}^k: join PWs in value and slope
→additional constraint requires more PWs than APW
→basis flexible enough for single diagonalization



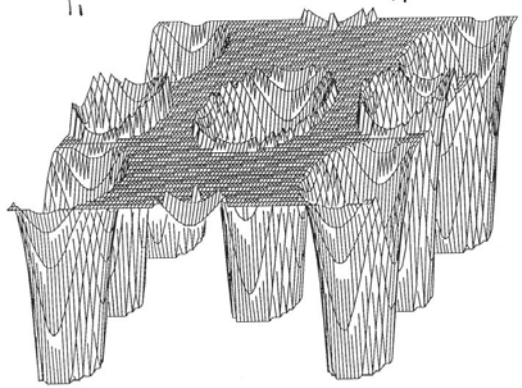
Full-potential in LAPW (A.Freeman etal.)



$SrTiO_3$



Full potential



Muffin tin approximation

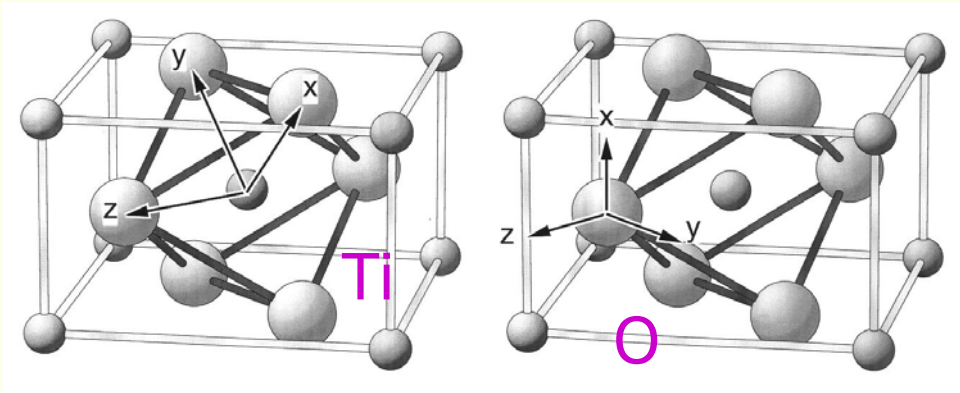
TiO_2 rutile

- The potential (and charge density) can be of general form

  (no shape approximation)

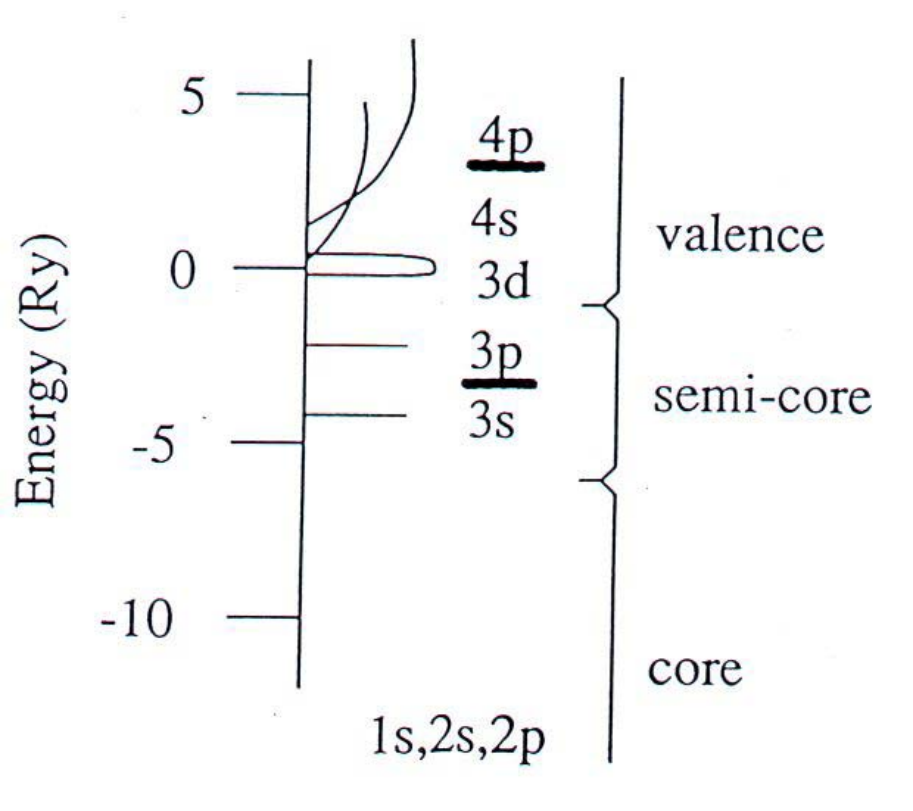
$$V(r) = \begin{cases} \sum_{LM} V_{LM}(r) Y_{LM}(\hat{r}) & r < R_\alpha \\ \sum_{K} V_K e^{i\vec{K}.\vec{r}} & r \in I \end{cases}$$

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



Core, semi-core and valence states

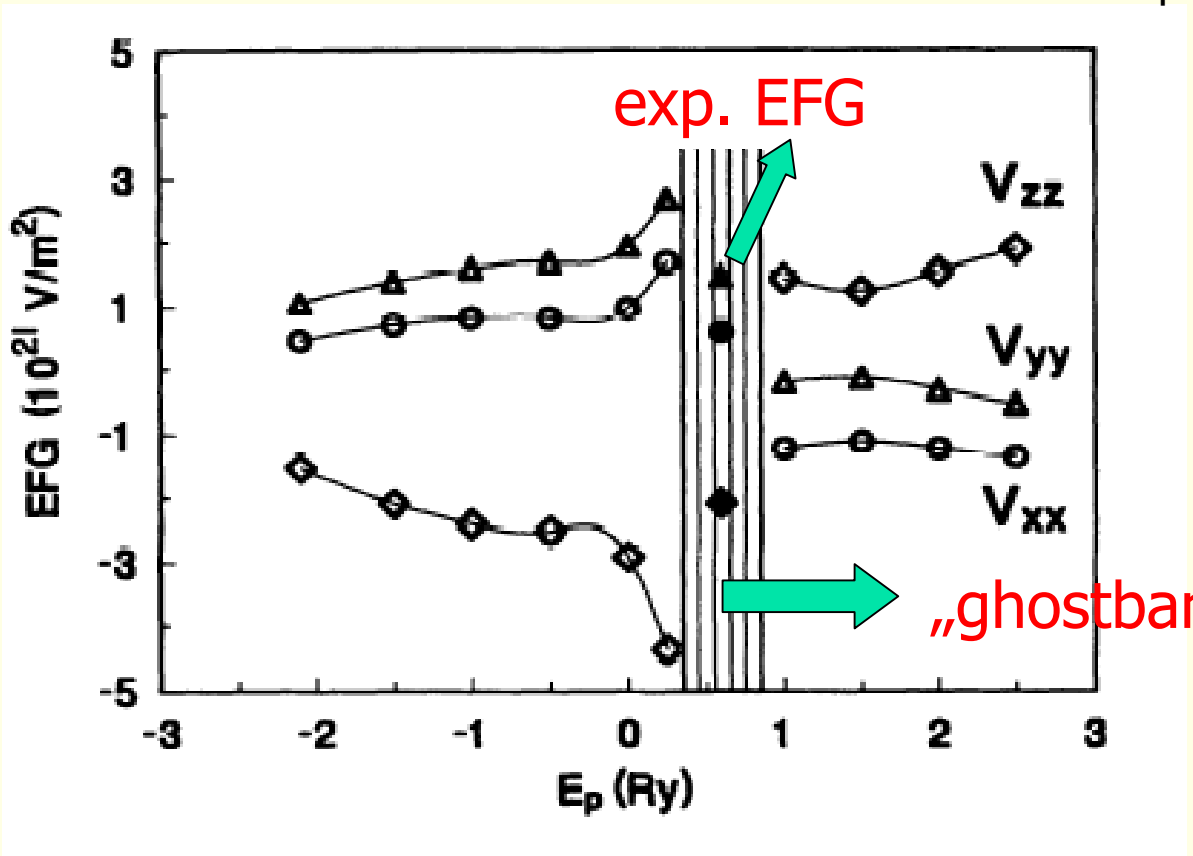
For example: Ti



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

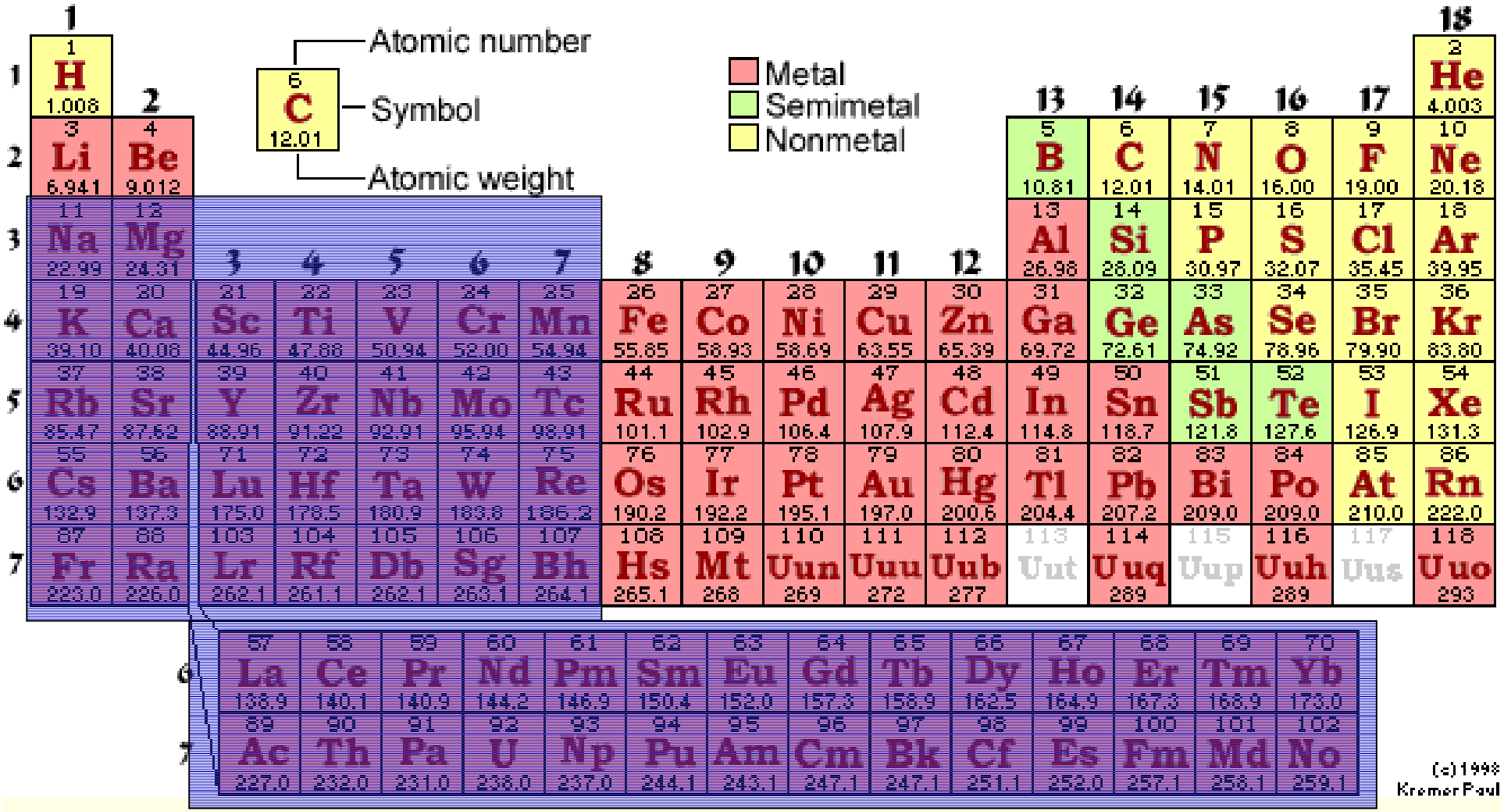
Problems of the LAPW method:

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



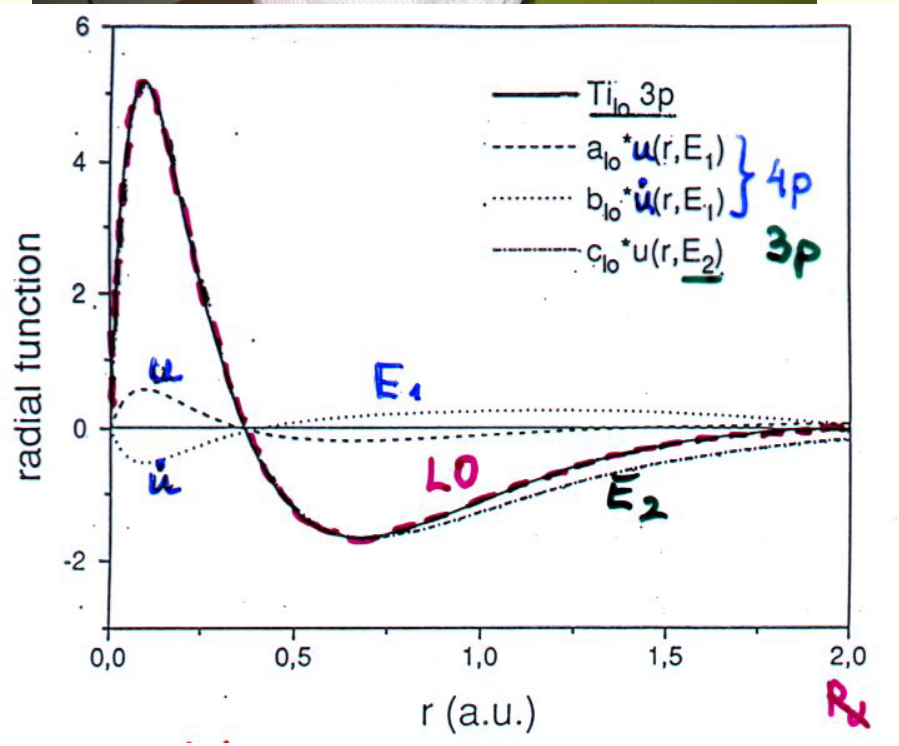
P. Blaha, D.J. Singh, P.I. Sorantin and K. Schwarz,
Phys. Rev. B **46**, 1321 (1992).

Problems of the LAPW method



Problems with semi-core states

Extending the basis: Local orbitals (LO)

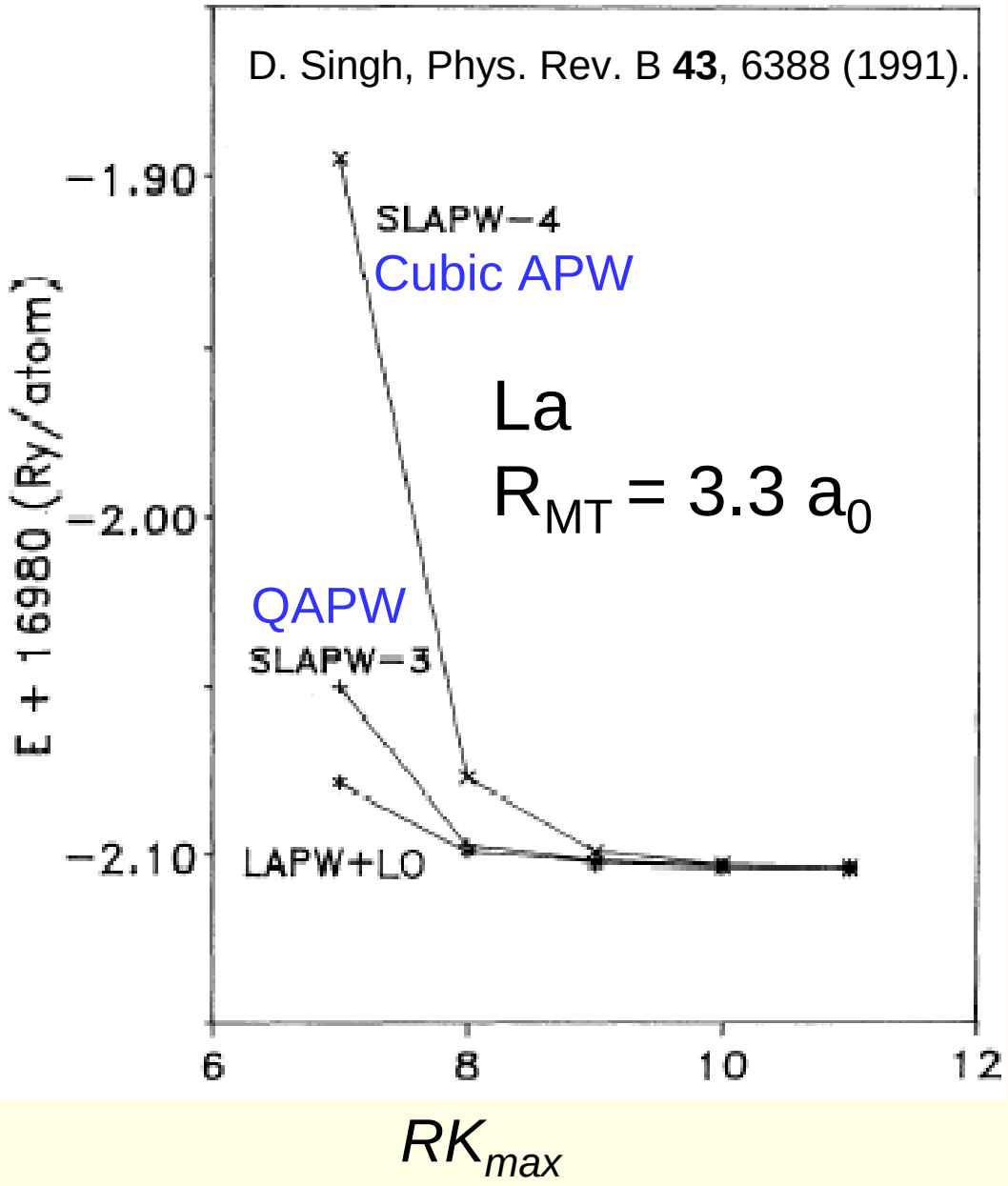


$$\Phi_{LO} = [A_{\ell m} u_\ell^{E_1} + B_{\ell m} \dot{u}_\ell^{E_1} + C_{\ell m} u_\ell^{E_2}] Y_{\ell m}(\hat{r})$$

- 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)

The LAPW+LO Method



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.

New ideas from Uppsala and Washington

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)

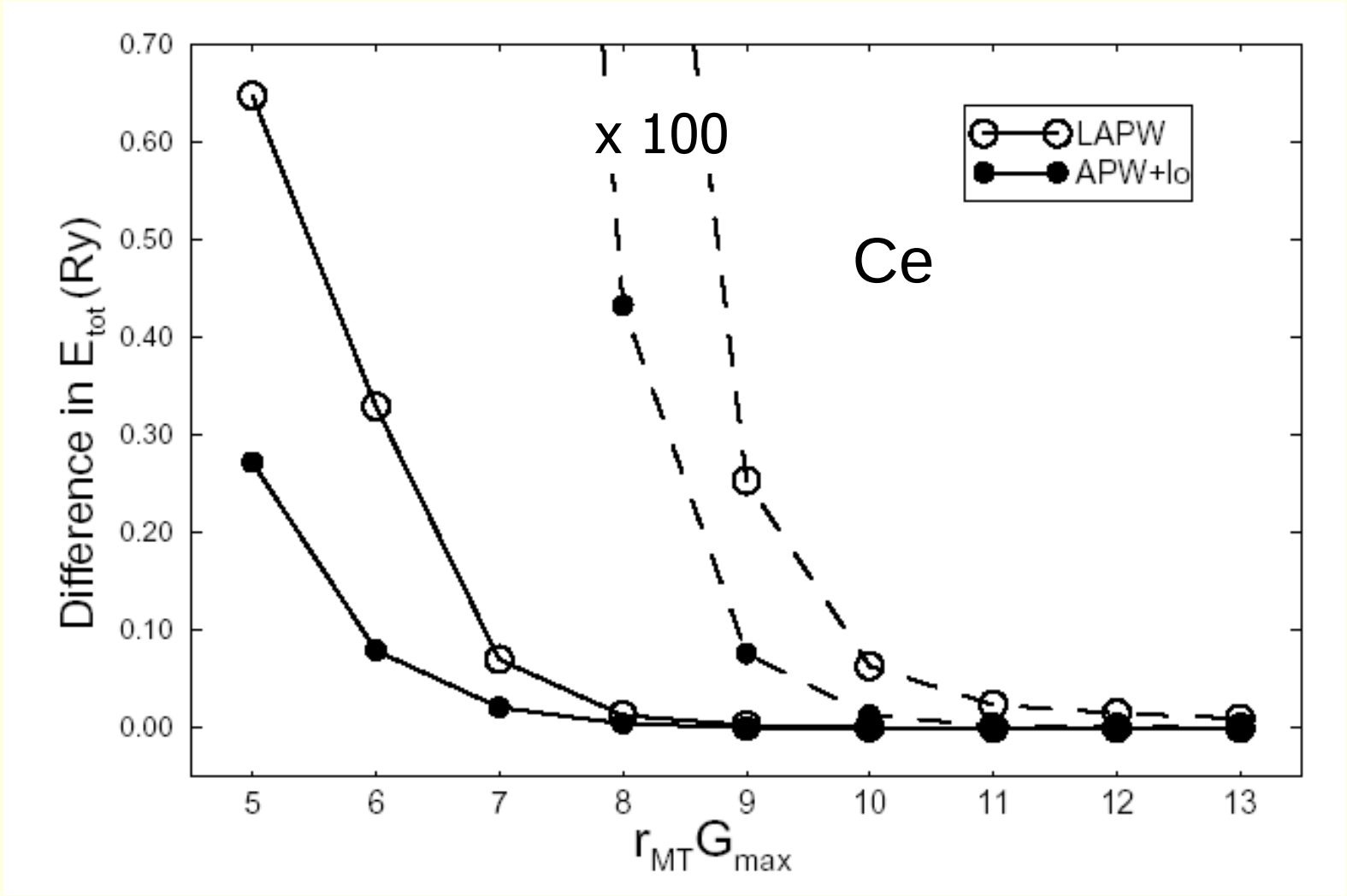
$$\Phi_{k_n} = \sum_{\ell m} A_{\ell m}(k_n) u_\ell(E_\ell, r) Y_{\ell m}(\hat{r})$$

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

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 angular momenta

Convergence of the APW+LO Method

E. Sjostedt, L. Nordstrom and D.J. Singh, Solid State Commun. **114**, 15 (2000).

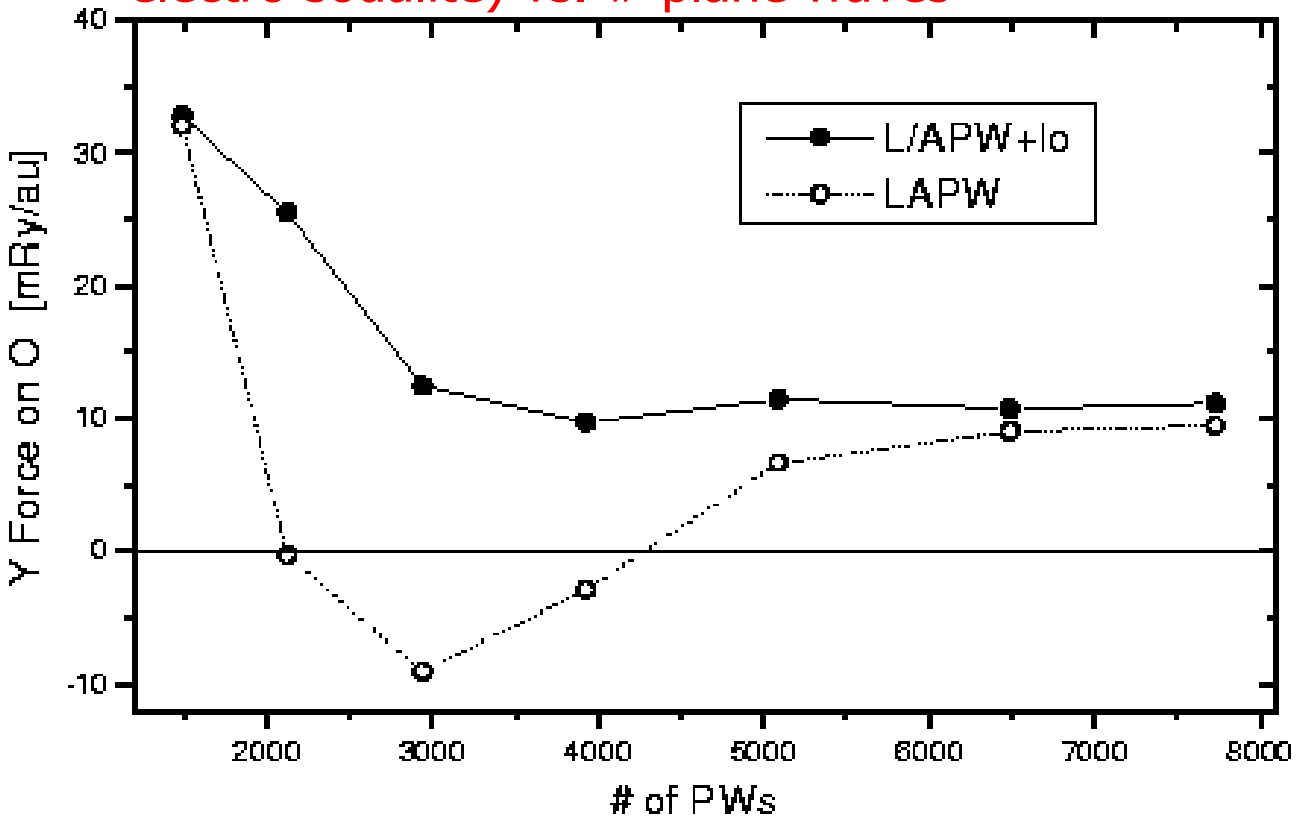


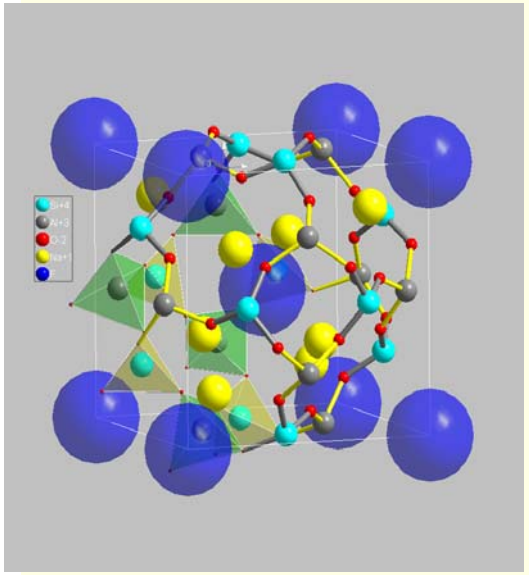
Improved convergence of APW+lo

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**

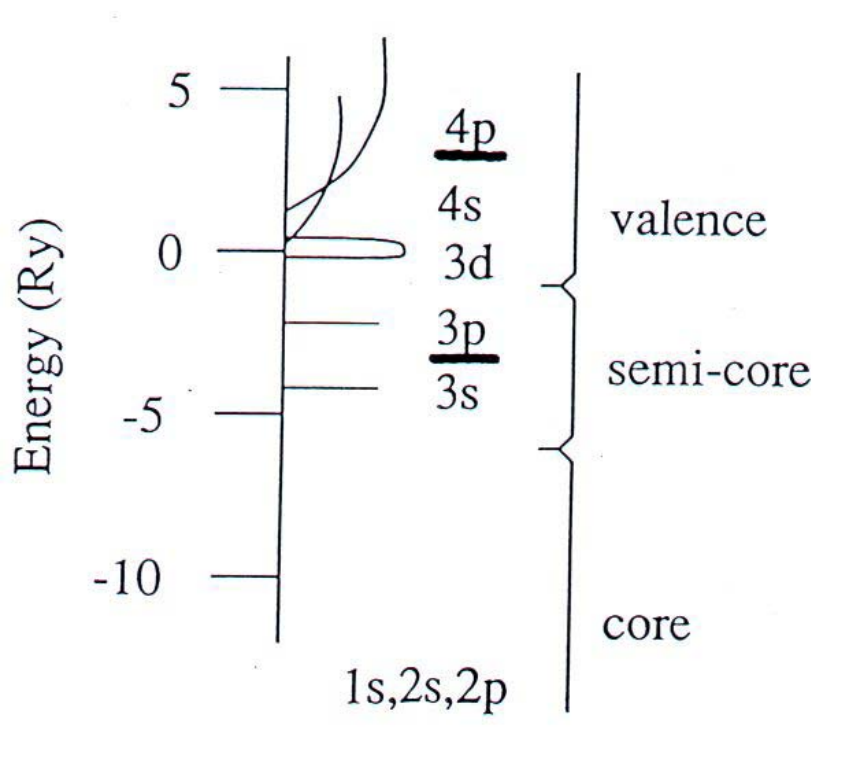
Force (Fy) on oxygen in SES (sodium electro sodalite) vs. # plane waves





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

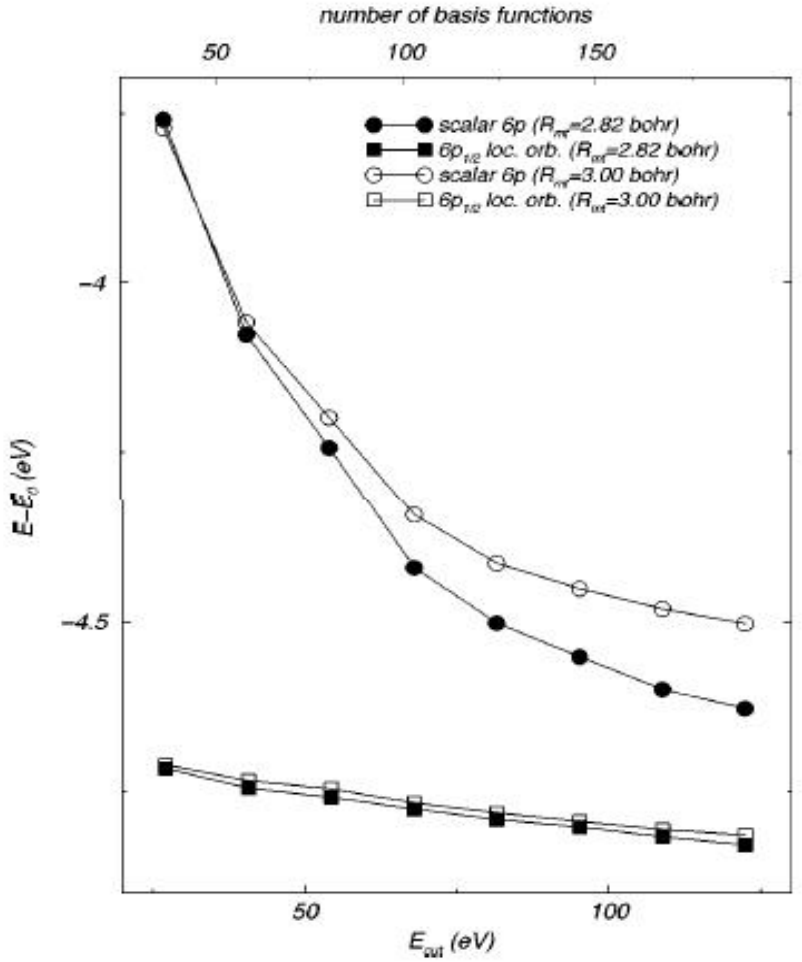


FIG. 1. The total energy E as a function of the second-variation cutoff energy E_{cut} (the approximate size of the second-variational-step basis, including spin, is marked on the top axis) for two different muffin-tin radii. The standard FLAPW results are marked with circles, the results obtained with 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)

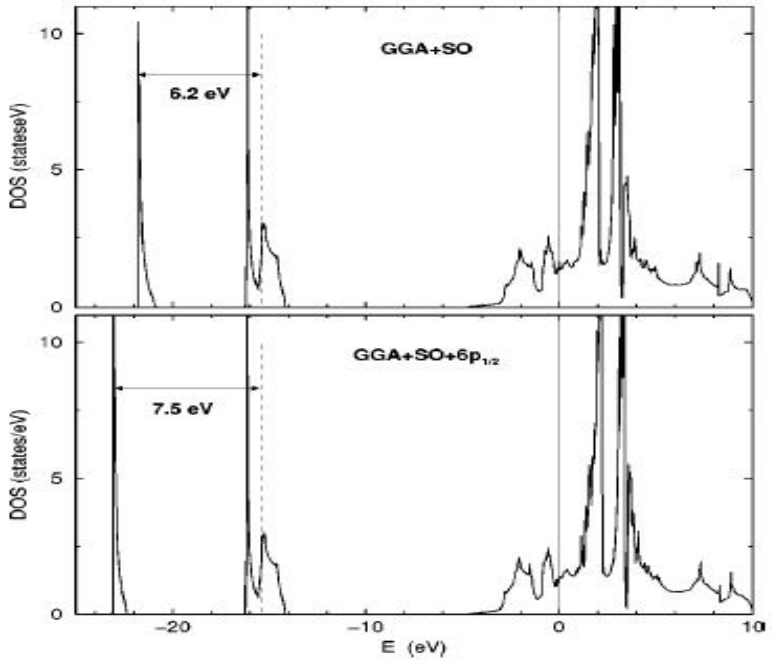


FIG. 2. Density of states calculated with the scalar relativistic basis (top panel) and with the $p_{1/2}$ local orbitals extended basis (bottom panel). The splitting between the centers of $6p_{1/2}$ and $6p_{3/2}$ bands is shown.

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*

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

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

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

- 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*

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

  - *Pulay corrections*
    - Core

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

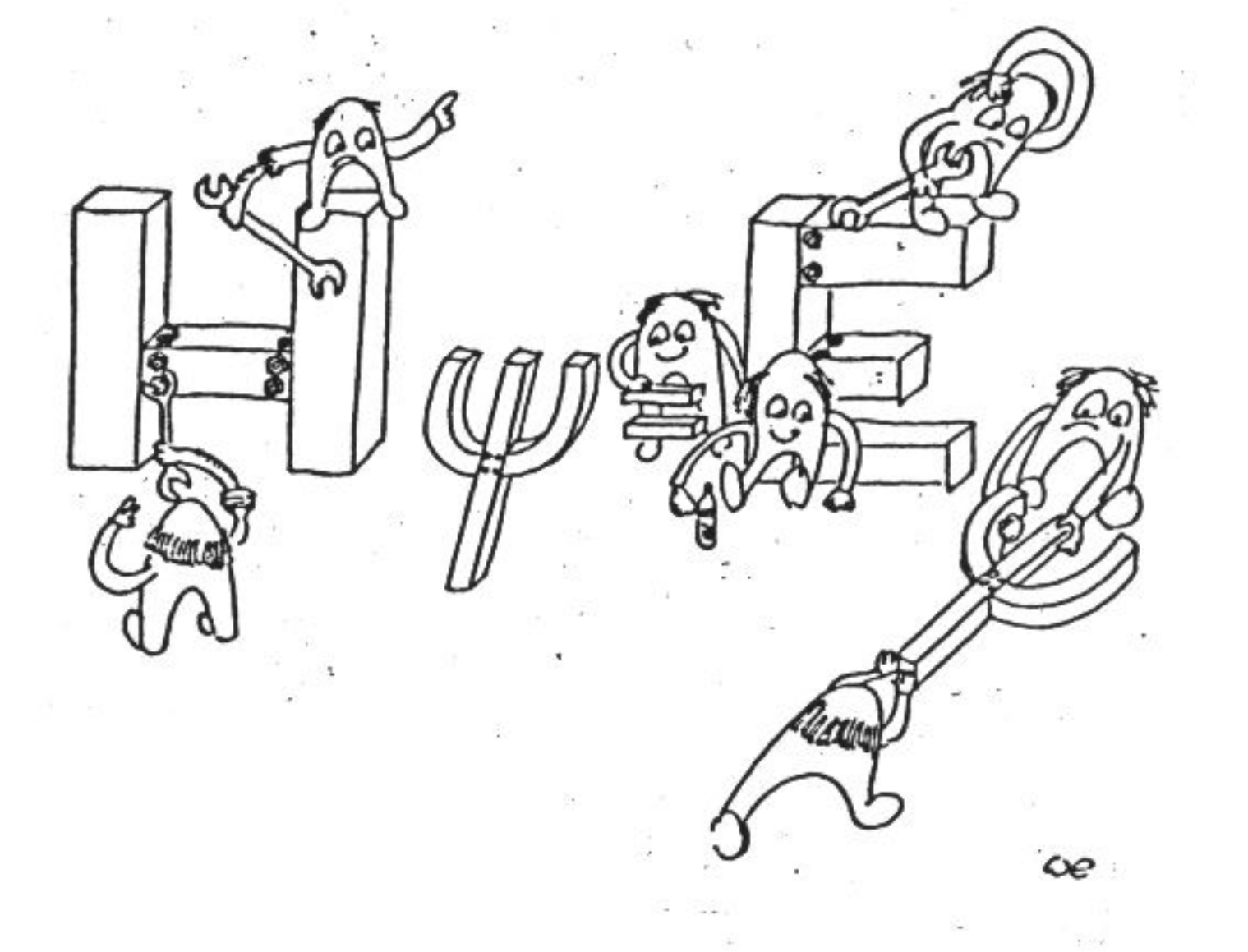
    - Valence

$$F_{val}^\alpha = \int_\alpha V_{eff}(r)\nabla_\alpha\rho_{val}(r)\,d\vec{r} + \sum_{k,i} n_i \sum_{K,K'} c_i^*(K')c_i(K)\times$$

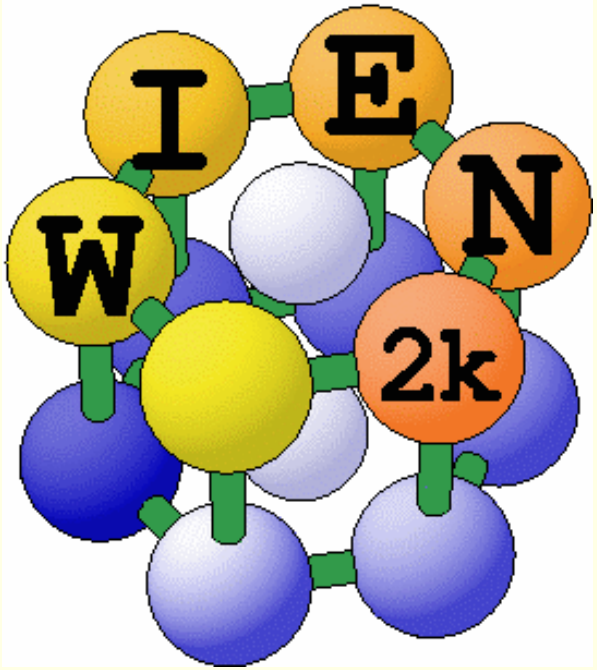
$$\left[(K^2-\varepsilon_i)\oint\phi_{K'}^*(r)\phi_K(r)\,dS_\alpha - i(K-K')\left\langle\phi_{K'}\middle|H-\varepsilon_i\middle|\phi_K\right\rangle_\alpha\right]$$

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

Quantum mechanics at work



WIEN2k software package



WIEN97: ~500 users
WIEN2k: ~500 users
mailinglist: 800 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*
  - *D.J.Singh (NRL, Washington D.C.), local oribtals (LO), APW+lo*
  - *U. Birkenheuer (Dresden), wave function plotting*
  - *T. Charpin (Paris), elastic constants*
  - *R. Dohmen und J. Pichlmeier (RZG, Garching), parallelization*
  - *P. Novák and J. Kunes (Prague), LDA+U, SO*
  - *C. Persson (Uppsala), irreducible representations*
  - *M. Scheffler (Fritz Haber Inst., Berlin), forces*
  - *E. Sjöstedt and L Nordström (Uppsala, Sweden), APW+lo*
  - *J. Sofo and J. Fuhr (Barriloche), Bader analysis*
  - *B. Yanchitsky and A. Timoshevskii (Kiev), spacegroup*
  - *R. Laskowski (Vienna), non-collinear magnetism*
  - *B. Olejnik (Vienna), non-linear optics*
- and many others ….

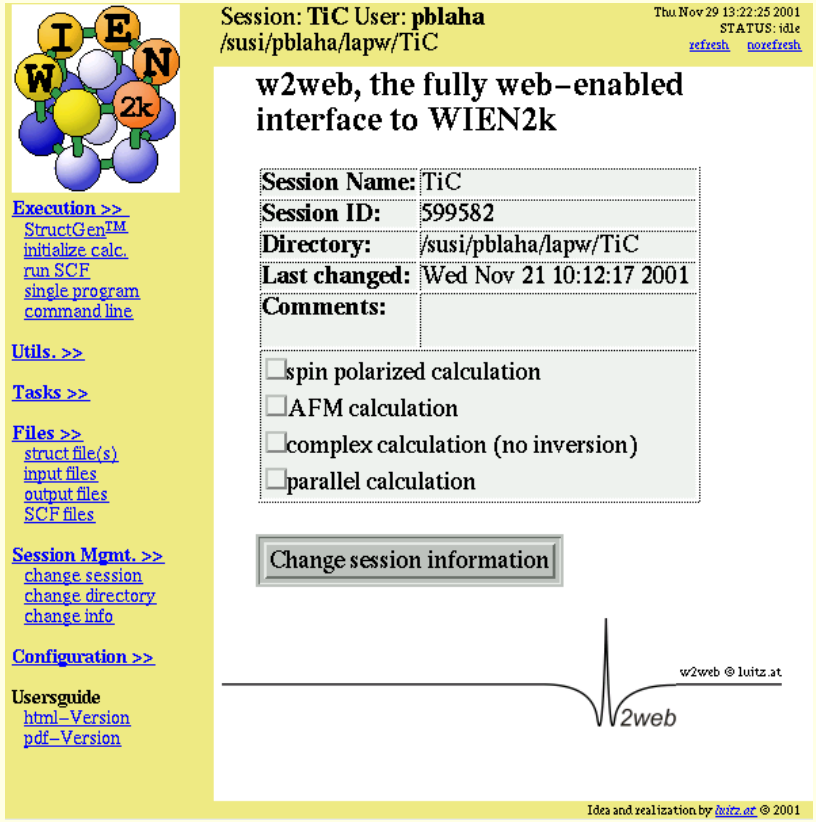
International co-operations

- More than 500 user groups worldwide
  - *Industries (Canon, Eastman, Exxon, Fuji, A.D.Little, Mitsubishi, Motorola, NEC, Norsk Hydro, Osram, Panasonic, Samsung, Sony, Sumitomo).*
  - *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- hardware/software

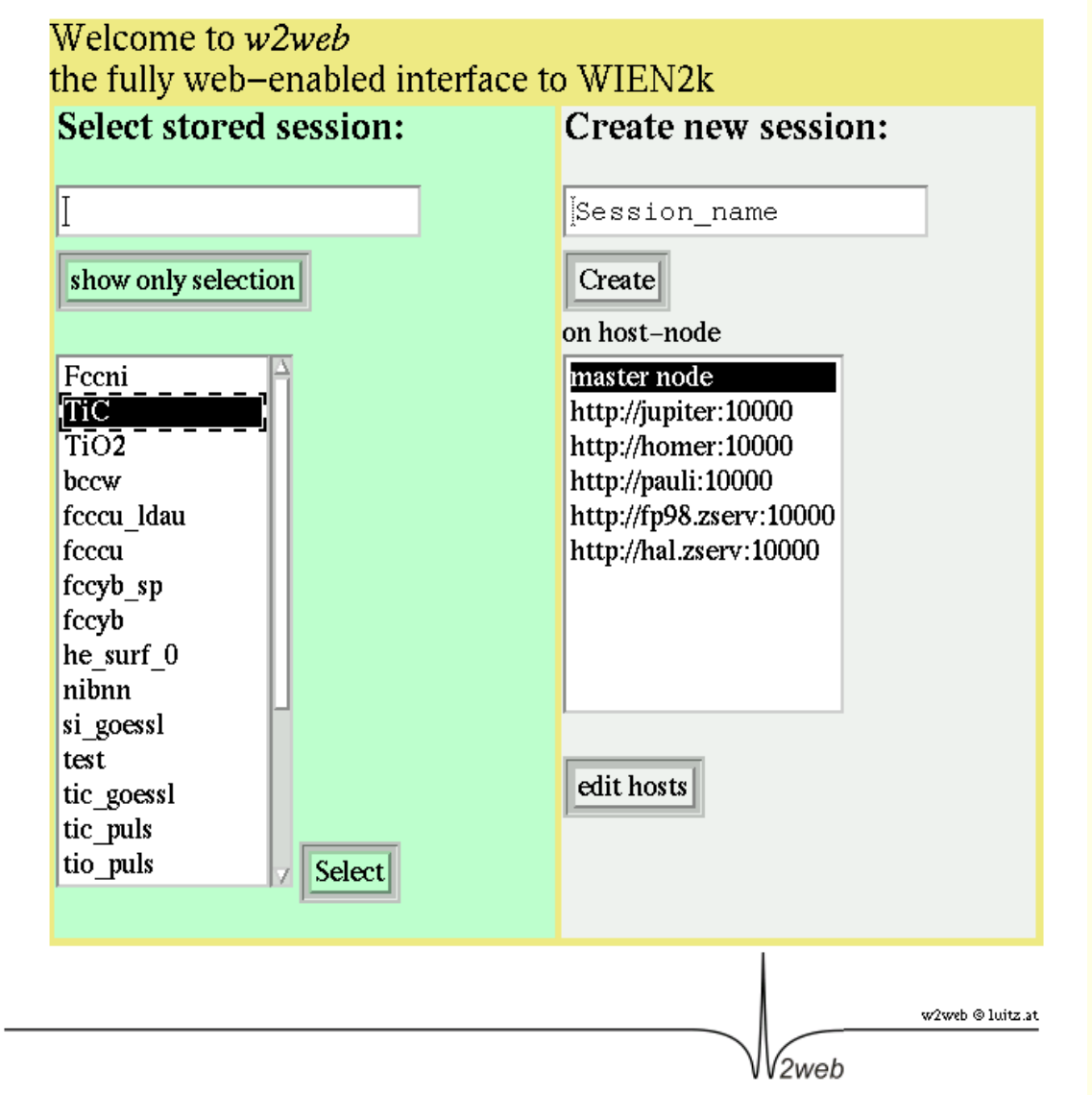
- WIEN2k runs on any Unix/Linux platform from PCs, workstations, clusters to supercomputers
- Fortran90 (dynamical allocation)
- many individual modules, linked together with C-shell or perl-scripts
- f90 compiler, BLAS-library, perl5, ghostview, gnuplot, Tcl/Tk (Xcrysden), pdf-reader, www-browser

•web-based GUI – w2web
•real/complex version (inversion)
•10 atom cells on 128Mb 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 (>50 atoms) and fast network
•installation support for most platforms



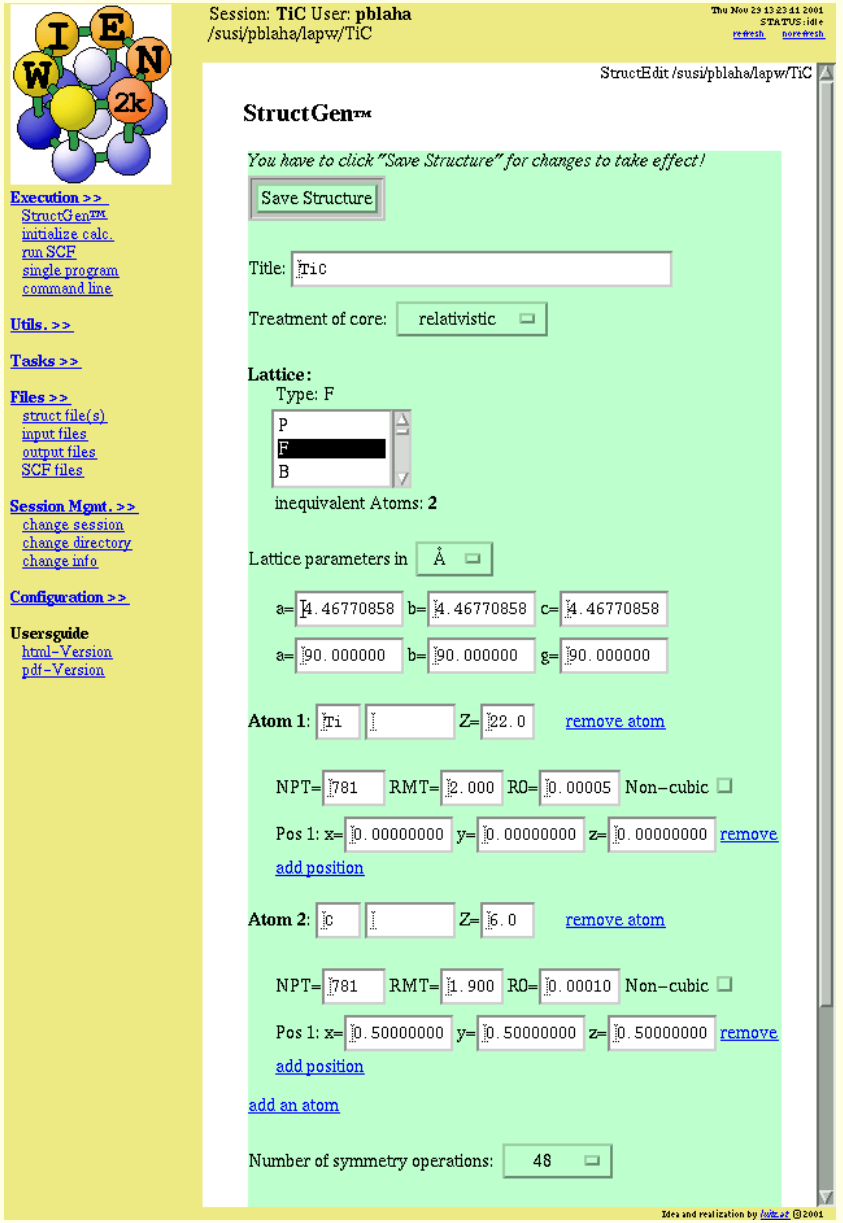
w2web

- Based on www
  - *WIEN2k can be managed remotely via w2web*
  - *Secure (Password)*
- Important steps:
  - *start w2web on all your hosts*
  - *use your favorite browser and connect to the master host*
  - *define a session on the desired host*



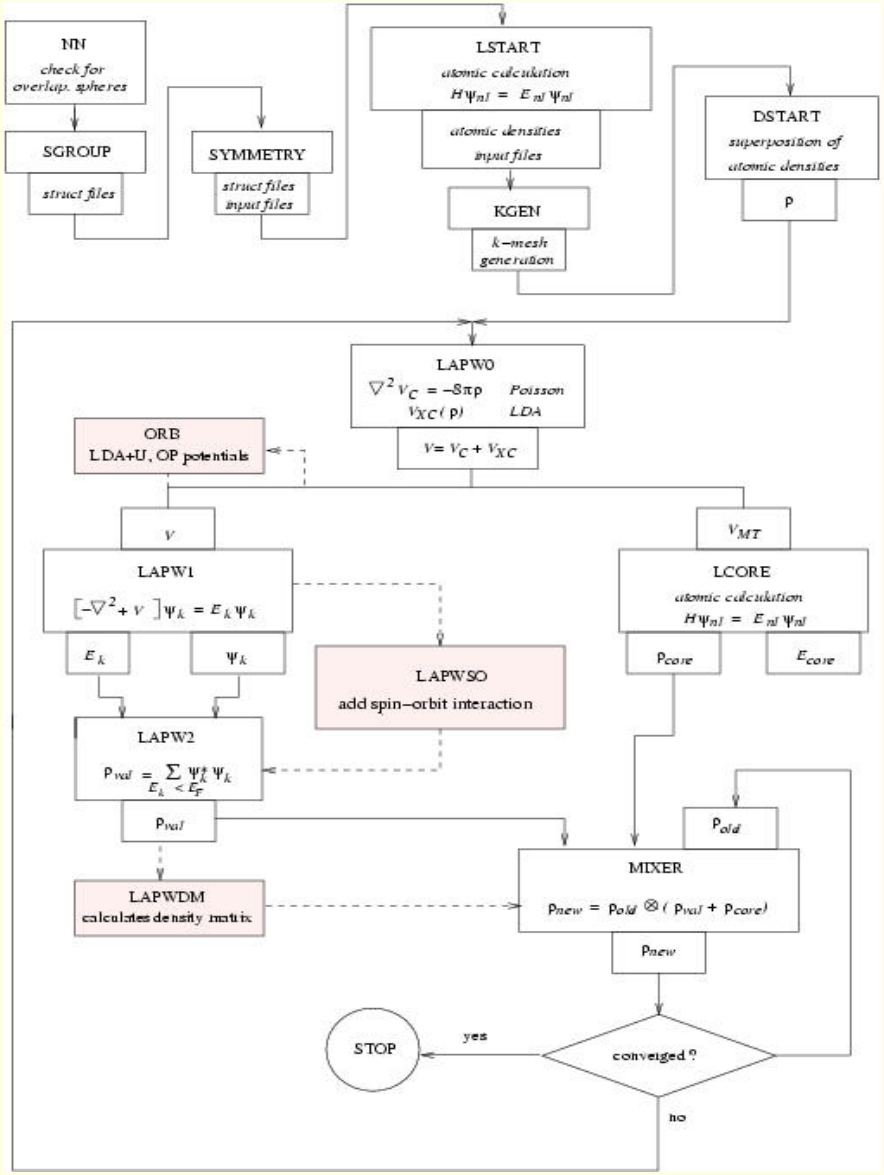
GUI (Graphical user interface)

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



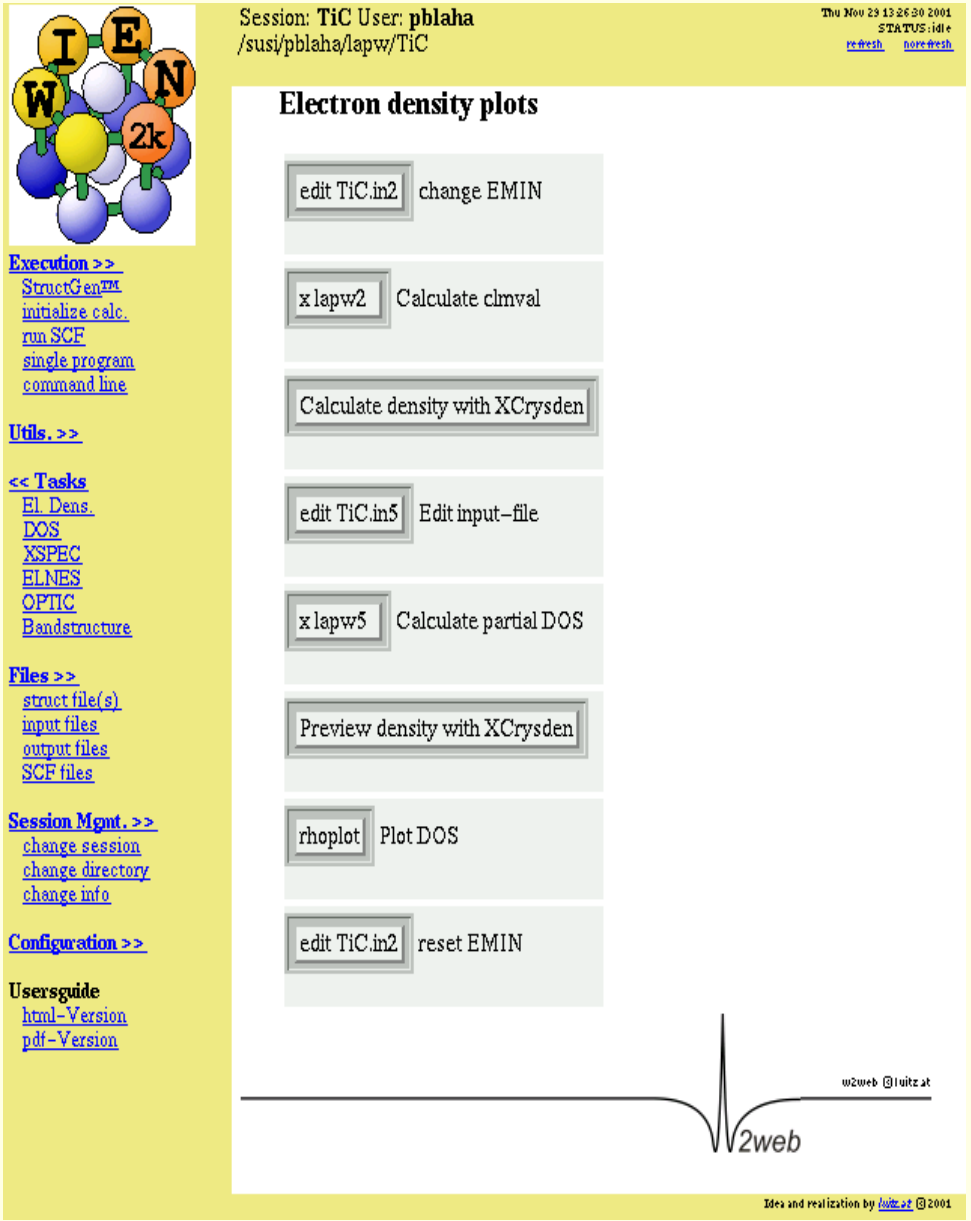
Program structure of WIEN2k

- 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)*



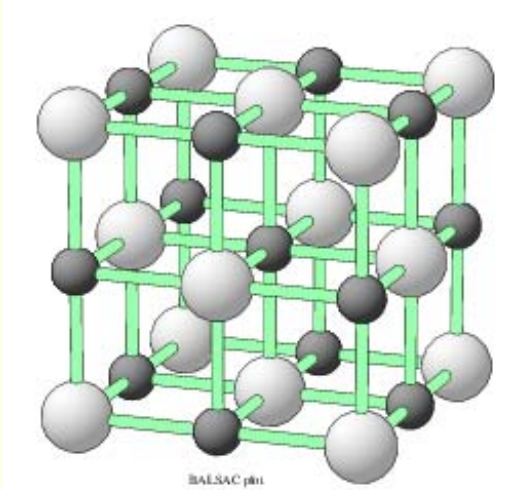
Task for electron density plot

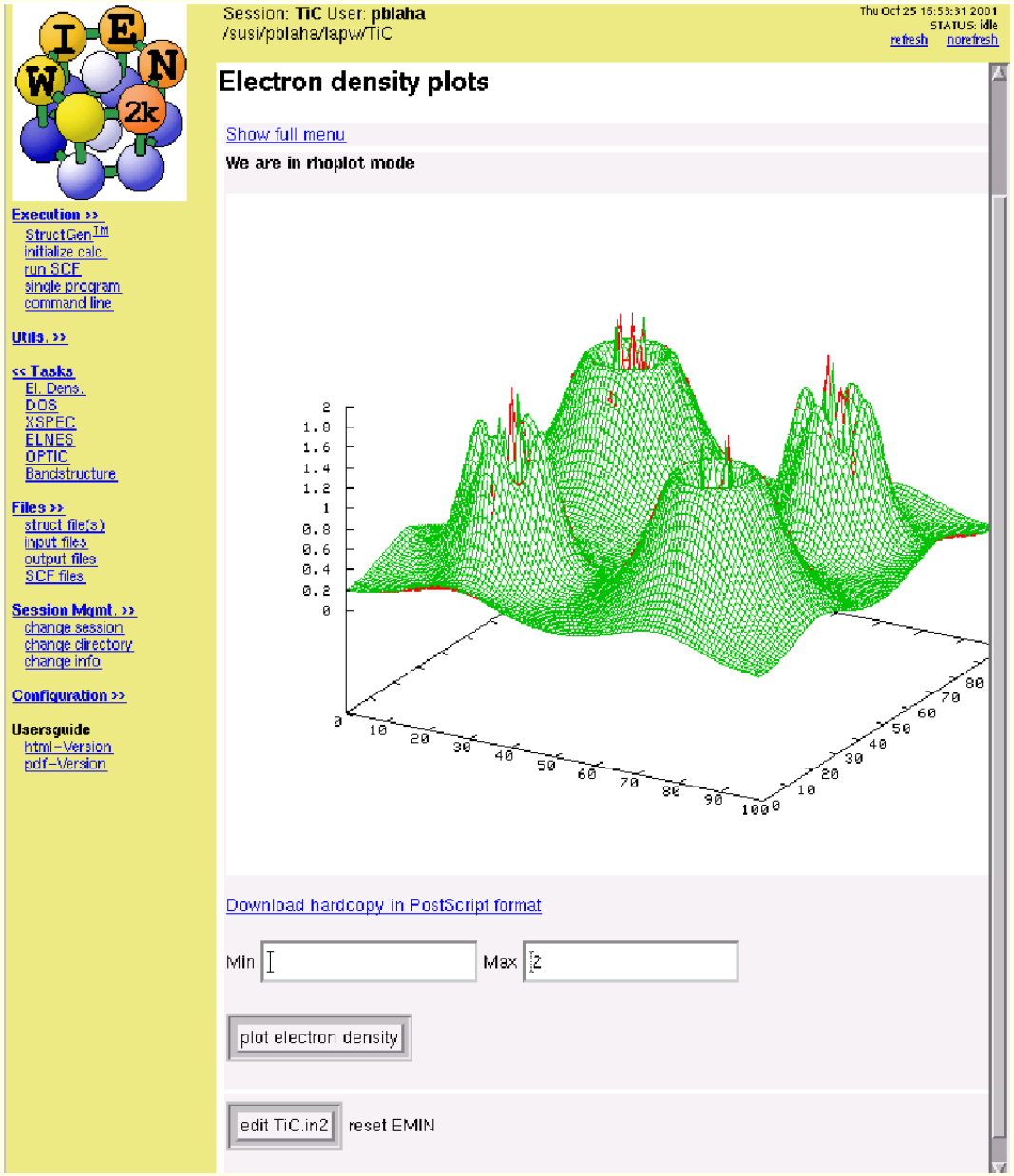
- A task consists of
  - *a series of steps*
  - *that must be executed*
  - *to generate a plot*
- For electron density plot
  - *select states (e.g. valence e^-)*
  - *select plane for plot*
  - *generate 3D or contour plot with gnuplot or Xcrysden*



TiC electron density

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





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*

Properties with WIEN2k - II

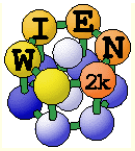
- Total energy and forces
  - *optimization of internal coordinates, (MD, BROYDEN)*
  - *cell parameter only via E_{tot} (no stress tensor)*
  - *elastic constants for cubic cells*
  - *Phonons via supercells*
    - interface to PHONON (K.Parlinski) – bands, DOS, thermodynamics, neutrons
- Spectroscopy
  - *core levels (with core holes)*
  - *X-ray emission, absorption, electron-energy-loss (core-valence/conduction bands including matrix elements and angular dep.)*
  - *optical properties (dielectric function, JDOS including momentum matrix elements and Kramers-Kronig)*
  - *fermi surface (2D, 3D)*

Properties with WIEN2k - III

- New developments (in progress)
  - *non-linear optics*
  - *non-collinear magnetism*
  - *transport properties (Fermi velocities, Seebeck, conductivity, thermoelectrics, ..)*
  - *Compton profiles*
  - *linear response (phonons, E-field) (C.Ambrosch-Draxl)*
  - *stress tensor (C.Ambrosch-Draxl)*
  - *exact exchange, GW, … ??*
  - *grid-computing*

Advantage/disadvantage of WIEN2k

+ 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
+ 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 (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



TU WIEN

Thank you for your attention !