UNIVERSITÉ DE NANTES

IMN

Région PAYS DE LA LOIRE

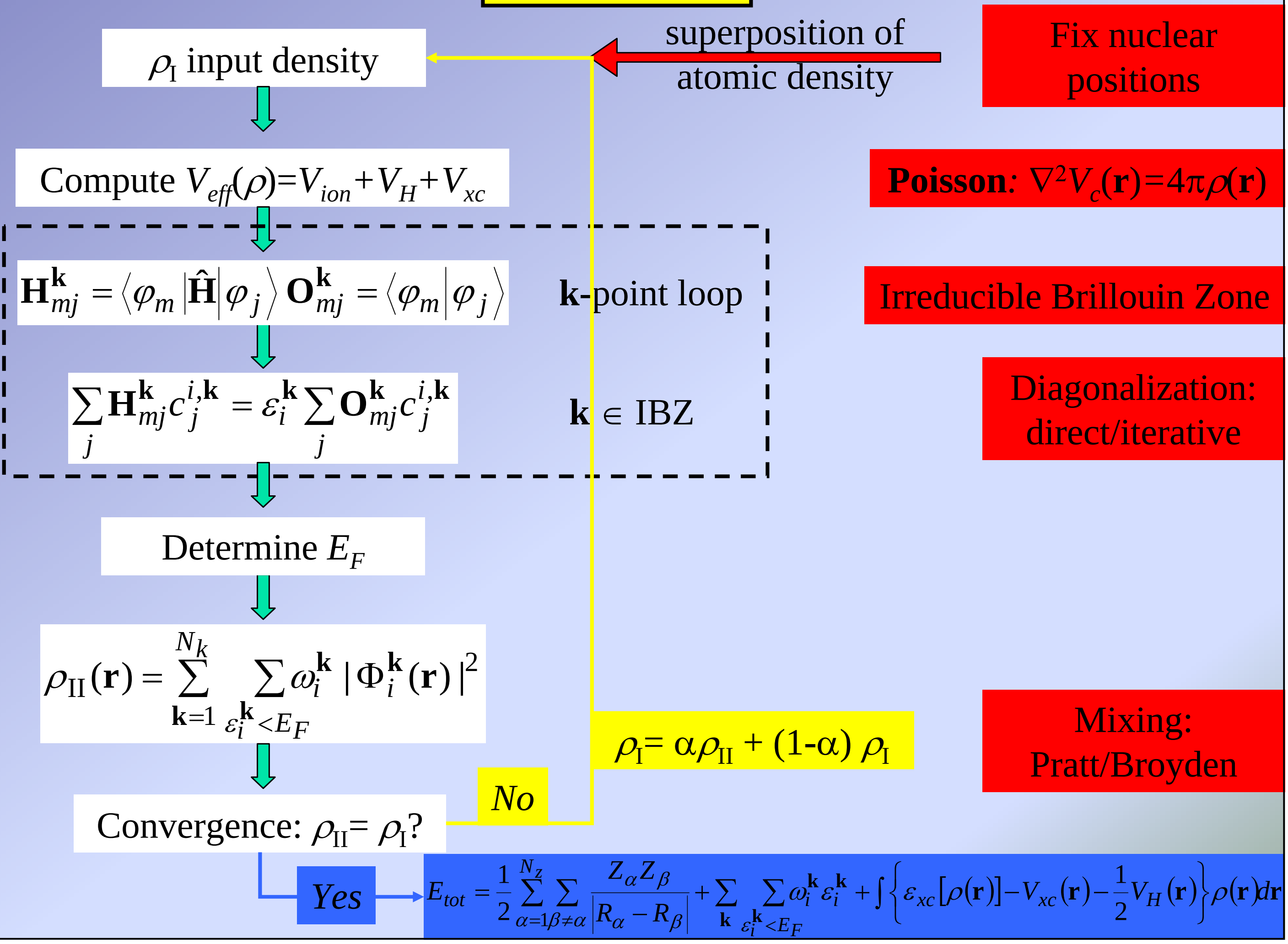
Calcul DFT périodique avec une base tous électrons

Présentation de la méthode FLAPW et du code WIEN2k

Réseau Français de Chimie Théorique

CCIPL

SCF procedure



ρ_{I} input density

superposition of atomic density

Fix nuclear positions

Compute $V_{eff}(\rho)=V_{ion}+V_H+V_{xc}$

Poisson: $\nabla^2 V_c(\mathbf{r})=4\pi\rho(\mathbf{r})$

$\mathbf{H}^{\mathbf{k}}_{mj}=\langle\varphi_m|\hat{\mathbf{H}}|\varphi_j\rangle \quad \mathbf{O}^{\mathbf{k}}_{mj}=\langle\varphi_m|\varphi_j\rangle$

k-point loop

Irreducible Brillouin Zone

$\sum_j \mathbf{H}^{\mathbf{k}}_{mj}c^{i,\mathbf{k}}_j=\varepsilon^{\mathbf{k}}_i\sum_j \mathbf{O}^{\mathbf{k}}_{mj}c^{i,\mathbf{k}}_j$

$\mathbf{k}\in$ IBZ

Diagonalization: direct/iterative

Determine E_F

$\rho_{\mathrm{II}}(\mathbf{r})=\sum_{\mathbf{k}=1}^{N_k}\sum_{\varepsilon^{\mathbf{k}}_i<E_F}\omega^{\mathbf{k}}_i|\Phi^{\mathbf{k}}_i(\mathbf{r})|^2$

$\rho_{\mathrm{I}}=\alpha\rho_{\mathrm{II}}+(1\text{-}\alpha)\,\rho_{\mathrm{I}}$

Mixing: Pratt/Broyden

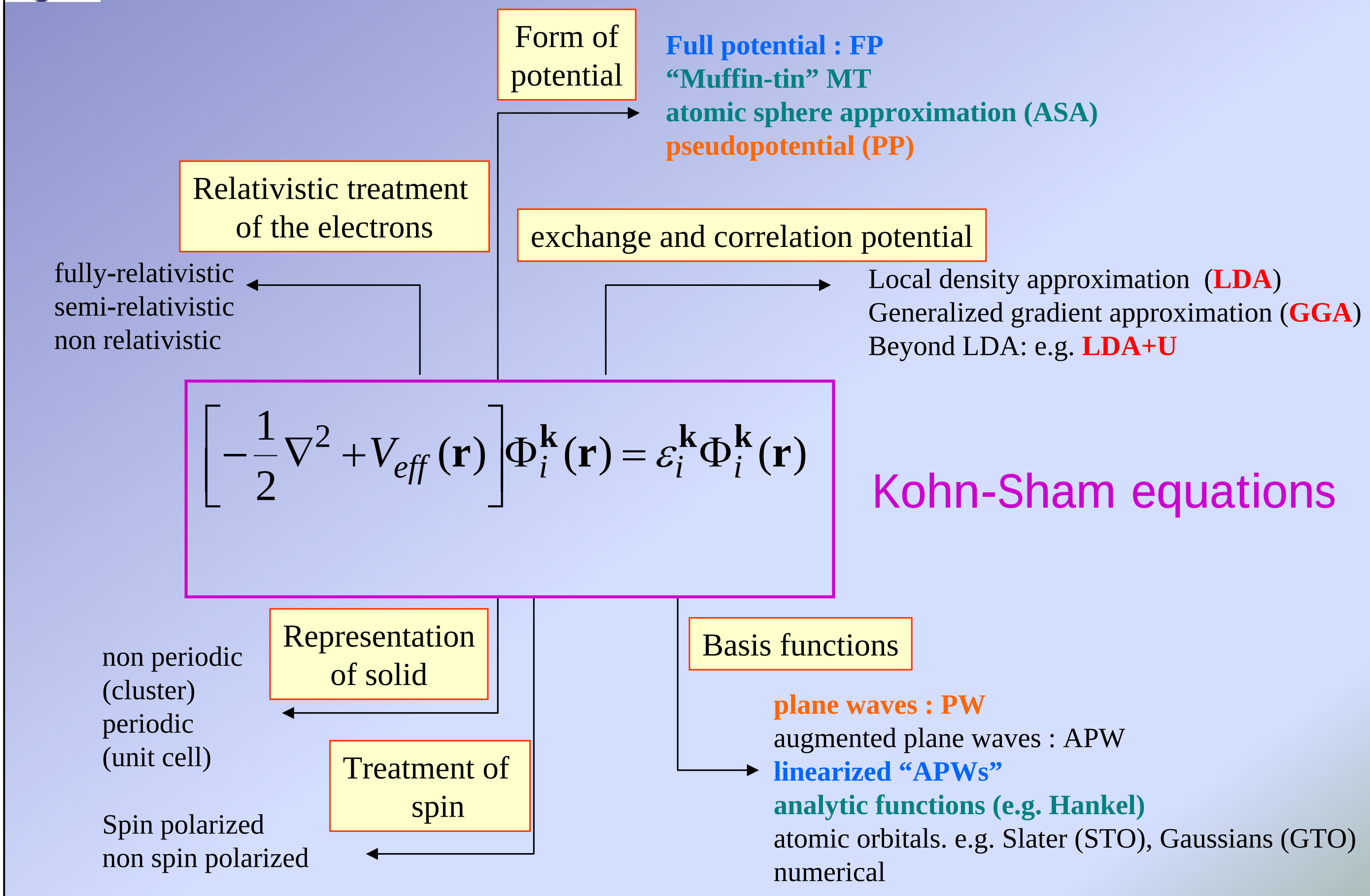
Convergence: $\rho_{\mathrm{II}}=\rho_{\mathrm{I}}$?

No

Yes

$$E_{tot}=\frac{1}{2}\sum_{\alpha=1}^{N_Z}\sum_{\beta\neq\alpha}\frac{Z_\alpha Z_\beta}{|R_\alpha-R_\beta|}+\sum_{\mathbf{k}}\sum_{\varepsilon^{\mathbf{k}}_i<E_F}\omega^{\mathbf{k}}_i\varepsilon^{\mathbf{k}}_i+\int\left\{\varepsilon_{xc}[\rho(\mathbf{r})]-V_{xc}(\mathbf{r})-\frac{1}{2}V_H(\mathbf{r})\right\}\rho(\mathbf{r})d\mathbf{r}$$

Overview of DFT concepts*



Form of potential

Full potential : FP
"Muffin-tin" MT
atomic sphere approximation (ASA)
pseudopotential (PP)

Relativistic treatment of the electrons

fully-relativistic
semi-relativistic
non relativistic

exchange and correlation potential

Local density approximation (LDA)
Generalized gradient approximation (GGA)
Beyond LDA: e.g. LDA+U

$$\left[-\frac{1}{2}\nabla^2 + V_{eff}(\mathbf{r})\right]\Phi_i^{\mathbf{k}}(\mathbf{r}) = \varepsilon_i^{\mathbf{k}}\Phi_i^{\mathbf{k}}(\mathbf{r})$$

Kohn-Sham equations

Representation of solid

non periodic
(cluster)
periodic
(unit cell)

Treatment of spin

Spin polarized
non spin polarized

Basis functions

plane waves : PW
augmented plane waves : APW
linearized "APWs"
analytic functions (e.g. Hankel)
atomic orbitals. e.g. Slater (STO), Gaussians (GTO)
numerical

*Thanks to Prof. K. H. Schwarz (WIEN WORKSHOP)

The basis set

$$|\Phi_i^{\mathbf{k}}(\mathbf{r})\rangle = \sum_{j=1}^{P} c_j^{i,\mathbf{k}}|\varphi_j^{\mathbf{k}}(\mathbf{r})\rangle$$

$$\begin{bmatrix} \cdots & \cdots & \cdots \\ \vdots & \langle \varphi_m^{\mathbf{k}}|\hat{\mathbf{H}}|\varphi_n^{\mathbf{k}}\rangle - \varepsilon_i^{\mathbf{k}}\langle\varphi_m^{\mathbf{k}}|\varphi_n^{\mathbf{k}}\rangle & \vdots \\ \cdots & \cdots & \cdots \end{bmatrix}\begin{bmatrix} c_1^{i,\mathbf{k}} \\ \vdots \\ c_P^{i,\mathbf{k}} \end{bmatrix} = \begin{bmatrix} 0 \\ \vdots \\ 0 \end{bmatrix}$$

What is a good Basis Set (BS)?

- the BS should be efficient: P should be as low as possible for a given accuracy

- the BS should be unbiased: it should not impose (or force) the solution into a built-in direction. Completeness of the BS has to be checked !

- better if the basis functions are mathematically simple

Plane waves BS

$$\Phi_i^{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{K}=1}^{\mathbf{K}_{\max}} c_{\mathbf{K}}^{i,\mathbf{k}} \cdot \exp\left(j(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}\right)$$

$$E_{cutoff} = \frac{\hbar^2}{2m_e}\left|\mathbf{K}_{\max} + \mathbf{k}\right|^2$$

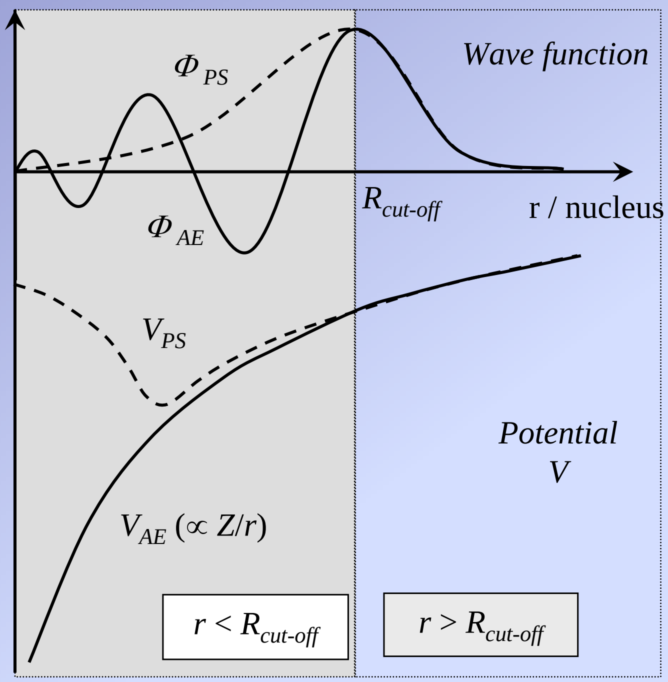
The advantages

- completeness can be checked easily by increasing the energy cut-off
- "easy mathematics": fast-Fourier-transforms can be used
- the Hamiltonian matrix expression is simple
- *forces on the atoms and stress on the unit cell are just evaluated via the Hellmann-Feynman theorem* (no further correction needed)

The drawback

- the PW basis set is not efficient to describe core wave functions
- pseudopotential should be used instead of the full potential to replace the strong electron-ion interaction
- a large effort has to be spent to construct "good" pseudopotentials (libraries are "available")

Plane Waves/Pseudopotential



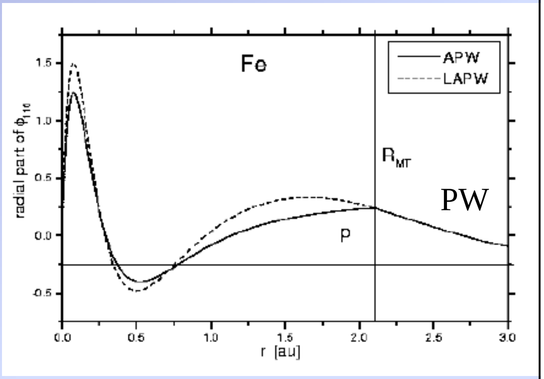
Commonly used potential:

-norm-conserving pseudopotentials

-ultra-soft pseudopotentials

-PAW potentials

LAPW's methods



The advantages

- completeness can be checked easily by increasing the energy cut-off

- the BS is efficient: size of the basis is less compared to PW/PP methods

- core levels are well described: possibility to calculate core level excitations, hyperfine interactions…

- nearly "parameter free" and easy for beginners

The drawback

- the mathematics are not easy

- time is needed to calculate H and O (non orthogonal BS)

- *forces on the atoms need Pulay corrections and stress on the unit cell are hard to calculate*

General recommendations for the BS

-check the completeness of the BS: evolution of total energy as a function of the size of the BS

- use exactly the same BS for total energy comparisons

-check the convergence of the total energy and all the quantity you are interested in: EFG…

-use a BS adapted for what you a looking for !

APW based schemes

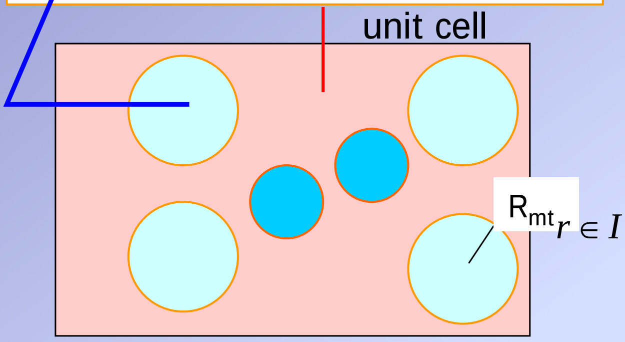
- APW (J.C.Slater 1937)
  - *Non-linear eigenvalue problem*
  - *Computationally very demanding*
- LAPW (O.K.Anderssen 1975)
  - *Generalized eigenvalue problem*
  - *Full-potential*
- Local orbitals (D.J.Singh 1991)
  - *treatment of semi-core states (avoids ghostbands)*
- APW+lo (E.Sjöstedt, L.Nordstörm,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

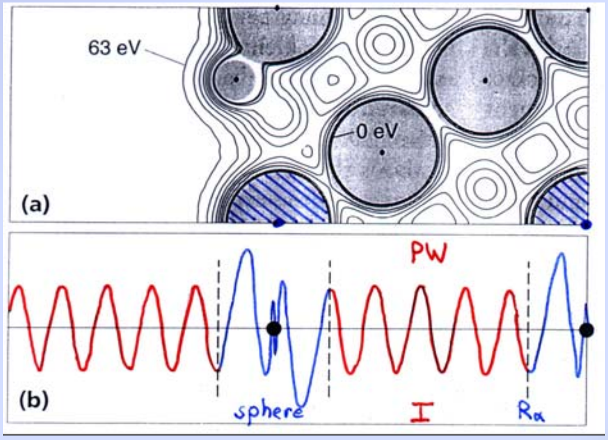
K.Schwarz, P.Blaha, G.K.H.Madsen, Comp.Phys.Commun.**147**, 71-76 (2002)

APW Augmented Plane Wave method

The unit cell is partitioned into:
atomic spheres
Interstitial region

Bloch wave function:
atomic partial waves
Plane Waves (PWs)





Full potential

$$\sum_{LM} V_{LM} Y_{LM}(\hat{r}) \qquad r < R_\alpha$$

$$\sum_{K} V_K e^{i\vec{K}.\vec{r}} \qquad r \in I$$

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

join

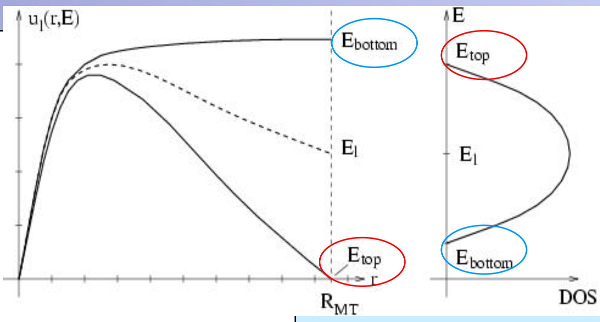
Atomic partial wave

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

Linearization of energy dependence

LAPW suggested by

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

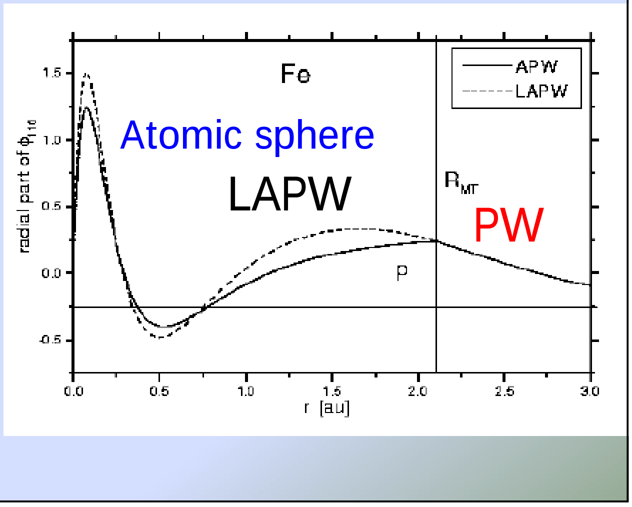


$$\Phi_{k_n} = \sum_{\ell m} [A_{\ell m}(k_n) u_\ell(E_\ell, r) + B_{\ell m}(k_n) \dot{u}_\ell(E_\ell, r)] Y_{\ell m}(\hat{r})$$

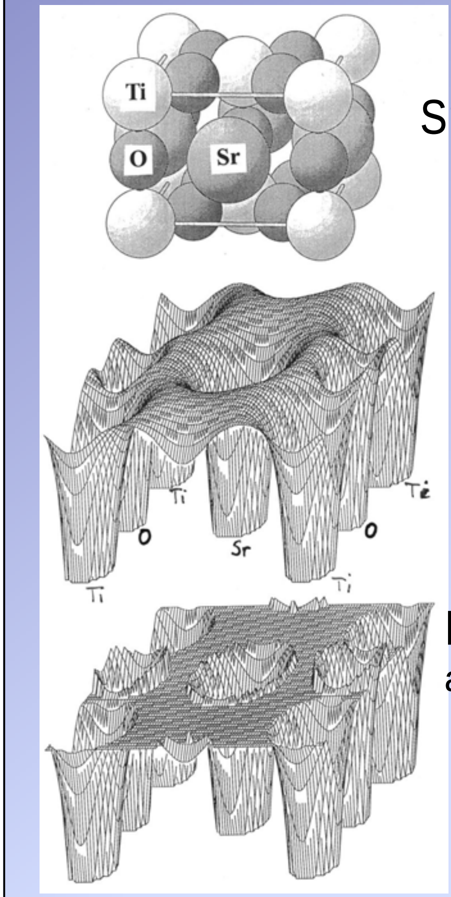
join PWs in value and slope

Plane Waves (PWs)

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



Full-potential in LAPW



SrTiO$_3$

Full potential

Muffin tin approximation

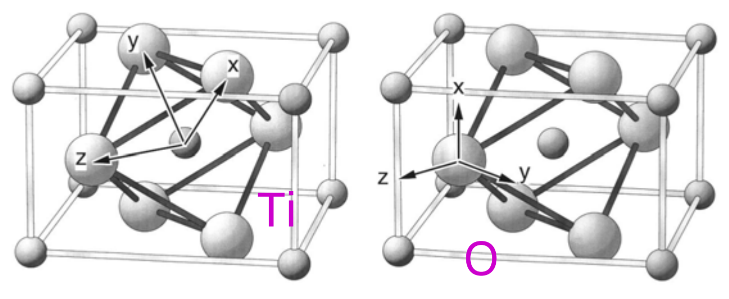
TiO$_2$ rutile

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

  (no shape approximation)

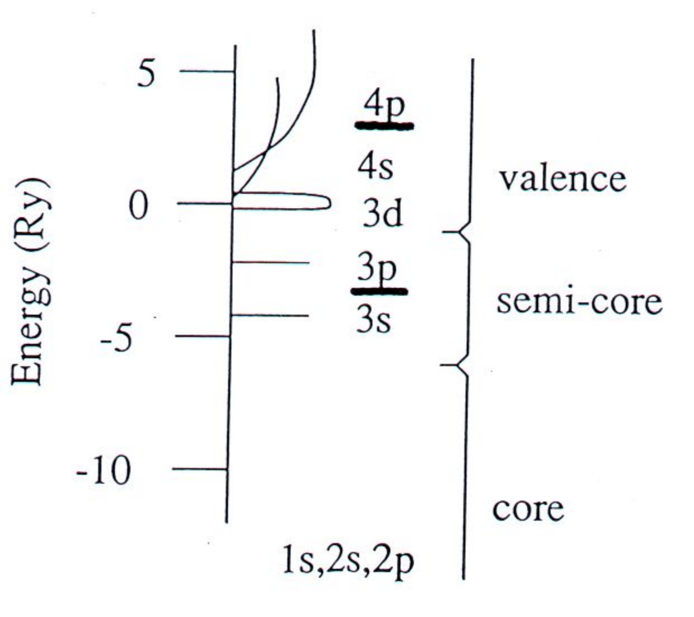
$$V(r) = \begin{cases} \sum_{LM} V_{LM}(r) Y_{LM}(\hat{r}) & r < R_\alpha \\ \sum_{K} V_K e^{i\vec{K}.\vec{r}} & r \in I \end{cases}$$

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



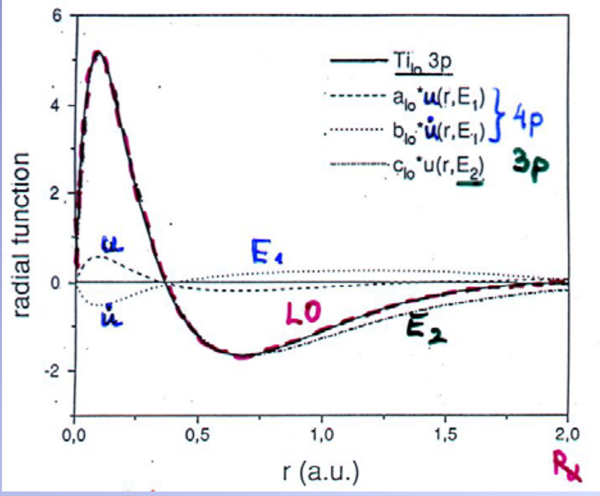
Core, semi-core and valence states

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*

Local orbitals (LO)



- LOs are
  - *confined to an atomic sphere*
  - *have zero value and slope at R*
  - *Can treat two principal QN n for each azimuthal QN ℓ (e.g. 3p and 4p)*
  - *Corresponding states are strictly orthogonal*
    - (e.g.semi-core and valence)
  - *Tail of semi-core states can be represented by plane waves*
  - *Only slightly increases the basis set (matrix size)*

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

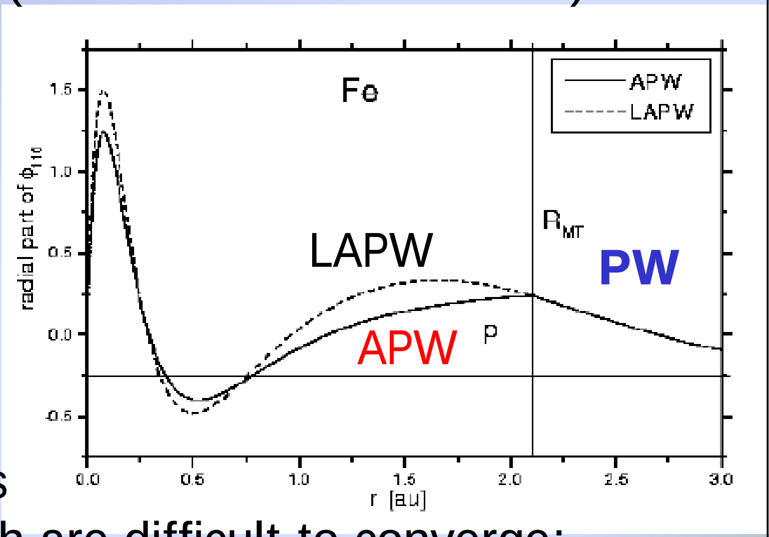
New ideas from Uppsala and Washington

E.Sjöststedt, L.Nordström, D.J.Singh, SSC 114, 15 (2000)

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

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

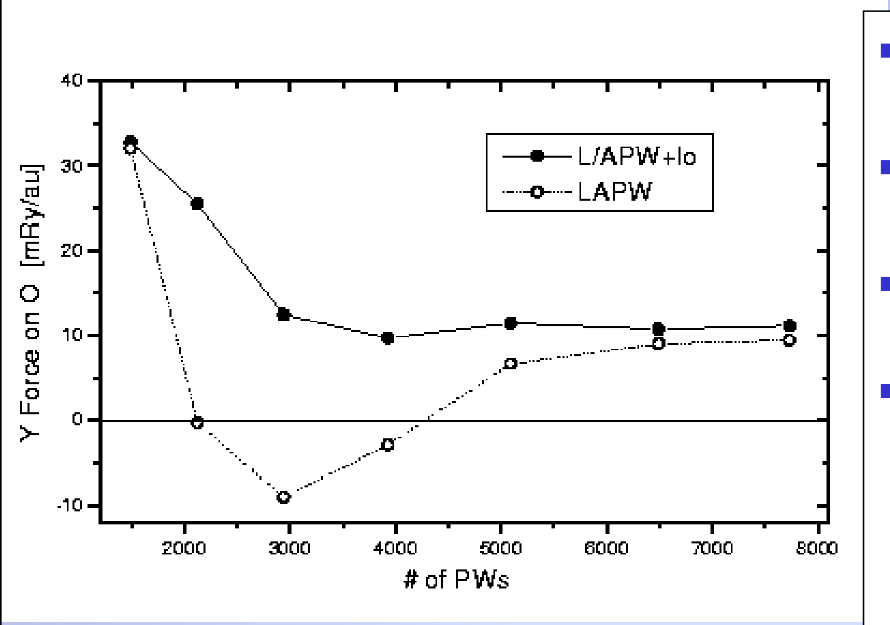
$$\Phi_{lo} = [A_{\ell m} u_\ell^{E_1} + B_{\ell m} \dot{u}_\ell^{E_1}] Y_{\ell m}(\hat{r})$$



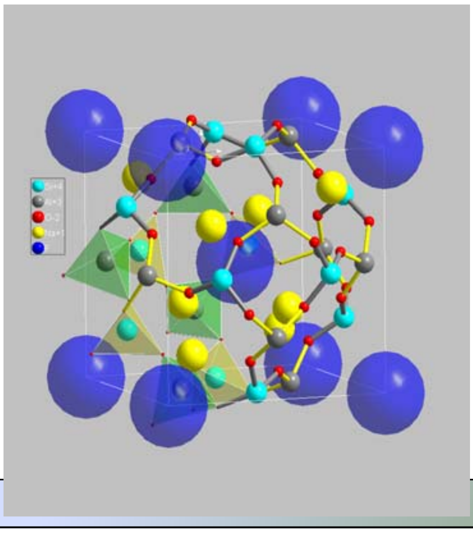
optimal solution: mixed basis

- 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

Improved convergence of APW+lo



- force (Fy) on oxygen in SES vs. # plane waves
- in **LAPW** changes sign and converges slowly
- in **APW+lo** better convergence
- to same value as in LAPW



SES (sodium electro solodalite)

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

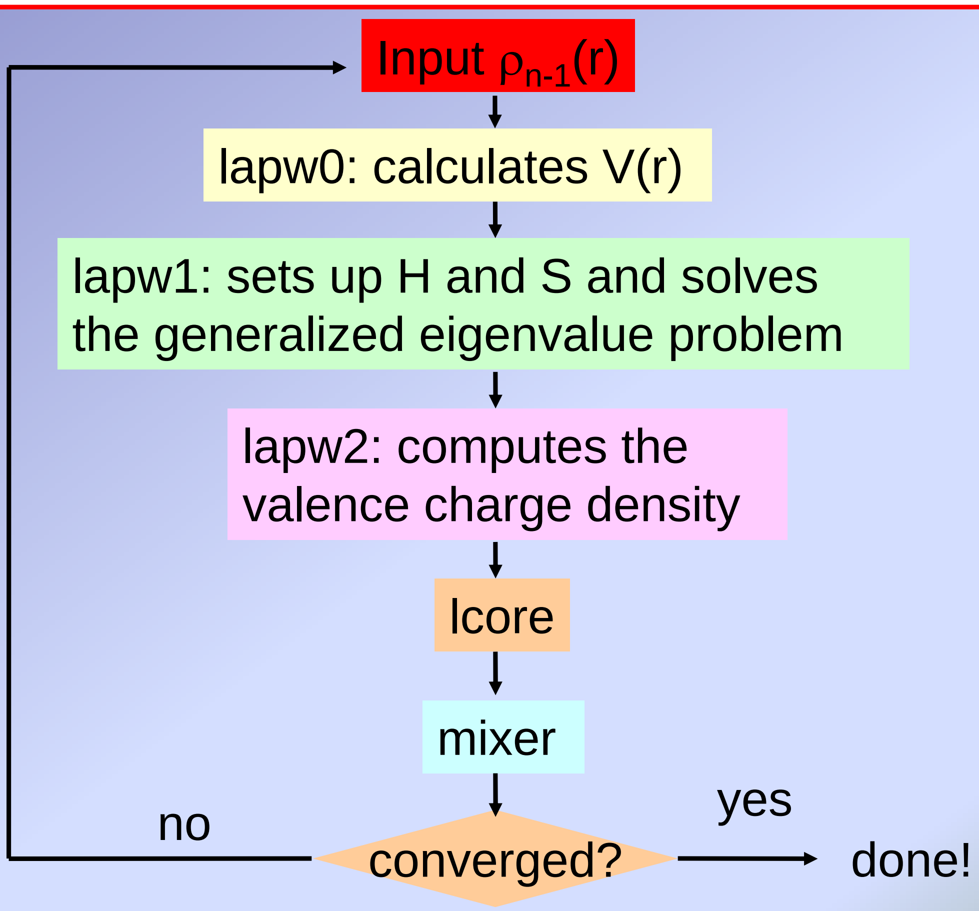
WIEN2k software package

**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

Flow Chart of WIEN2k (SCF)



Input $\rho_{n-1}(r)$

lapw0: calculates V(r)

lapw1: sets up H and S and solves the generalized eigenvalue problem

lapw2: computes the valence charge density

lcore

mixer

converged?

WIEN2k: *P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, and J. Luitz*

General remarks on WIEN2k

- WIEN2k consists of many independent F90 programs, which are linked together via C-shell scripts.
- 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 of 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) and init_lapw

Program execution:

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

```
x  lapw2  –up  –c
```

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

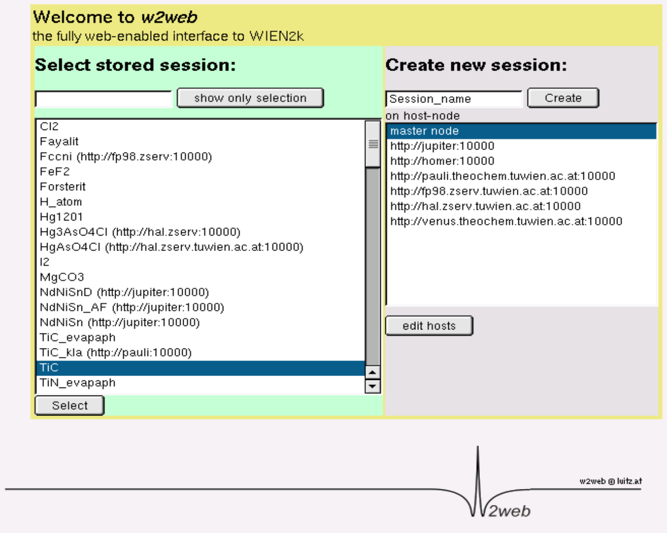
```
5,'tin.in2c',        'old',    'formatted'
6,'tin.output2up',   'unknown','formatted'
8,'tin.clmvalup',    'unknown','formatted'
10,'./tin.vectorup','unknown','unformatted'
```

- 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*

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:port*
    - opera 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:

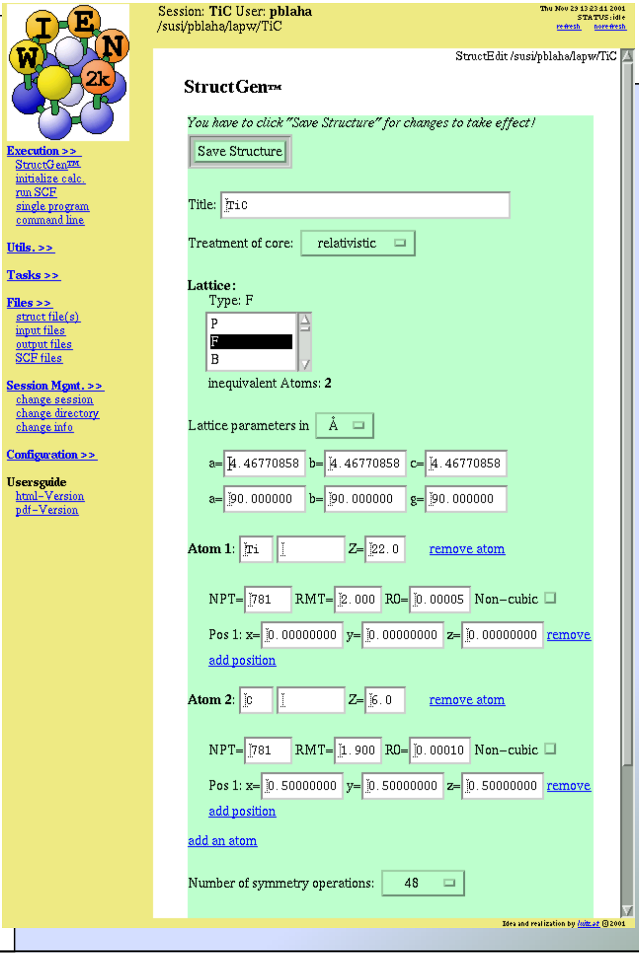
Cl2
Fayalit
Fccni (http://fp98.zserv:10000)
FeF2
Forsterit
H_atom
Hg1201
Hg3AsO4Cl (http://hal.zserv:10000)
HgAsO4Cl (http://hal.zserv.tuwien.ac.at:10000)
I2
MgCO3
NdNiSnD (http://jupiter:10000)
NdNiSn_AF (http://jupiter:10000)
NdNiSn (http://jupiter:10000)
TiC_evapaph
TiC_kla (http://pauli:10000)
TiC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

Thu Nov 29 13:23:41 2001
STATUS: idle

StructEdit /susi/pblaha/lapw/TiC

StructGen™

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

Title: TiC

Treatment of core: relativistic

Lattice:
Type: F
P
F
B
inequivalent Atoms: **2**

Lattice parameters in Å

a= 4.46770858 b= 4.46770858 c= 4.46770858
a= 90.000000 b= 90.000000 g= 90.000000

Atom 1: Ti Z= 22.0 remove atom
NPT= 781 RMT= 2.000 R0= 0.00005 Non-cubic □
Pos 1: x= 0.00000000 y= 0.00000000 z= 0.00000000 remove
add position

Atom 2: C Z= 6.0 remove atom
NPT= 781 RMT= 1.900 R0= 0.00010 Non-cubic □
Pos 1: x= 0.50000000 y= 0.50000000 z= 0.50000000 remove
add position

add an atom

Number of symmetry operations: 48

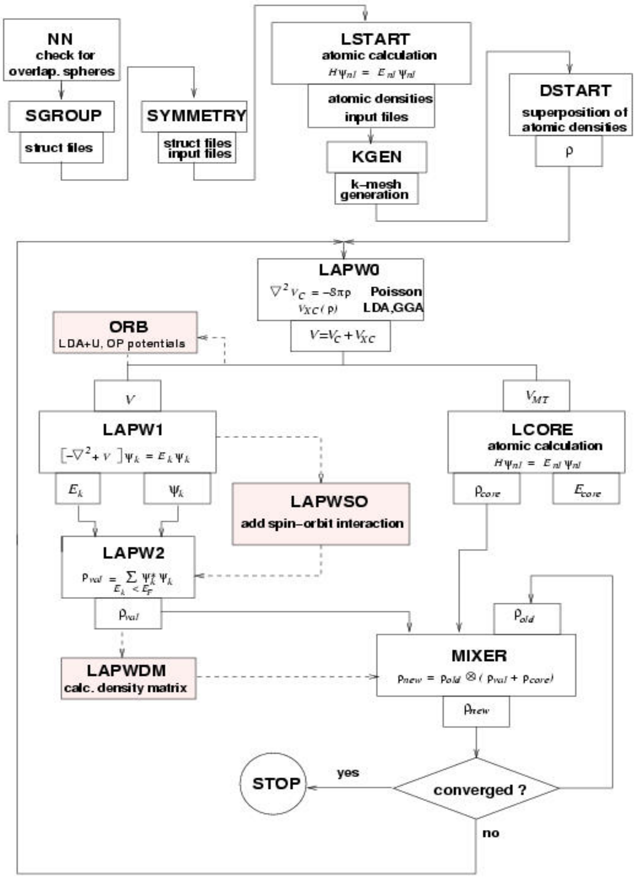
Idea and realization by luitz.at ©2001

Structure generator

- Specify:
  - *Number of nonequivalent atoms*
  - *lattice type (P, F, B, H, CXY, CXZ, CYZ) or spacegroup symbol*
  - *lattice parameters a,b,c (in Ang or bohr)*
  - *name of atoms (Si) and fractional coordinates (position)*
    - as numbers (0.123); fractions (1/3); simple expressions (x-1/2,...)
    - in fcc (bcc) specify just one atom, not the others in (1/2,1/2,0; ...)
- „save structure – continue editing – save structure – save+cleanup
  - *updates automatically Z, r0, equivalent positions and generates case.inst*
- After „init_lapw / nn“ you know the distances between the atoms. Go back to structgen and specify RMT:
  - *non-overlapping „as large as possible“ (saves time), but not larger than 3 bohr*
  - *RMT for sp-elements 10-20 % smaller than for d (f) elements*
  - *largest spheres not more than 50 % larger than smallest sphere*
  - *Exception: H in C-H or O-H bonds: RMT~0.6 bohr (RKMAX~3-4)*
  - *Do not change RMT in a „series“ of calculations*

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*



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)*
  - *-p* *parallel calculation (needs .machines file)*
  - *-so* *add spin-orbit*
  - *Spacegroups without inversion use automatically lapw1c, lapw2c (case.in1c,in2c)*
  - *If scf-cycle diverges (grep :DIS case.scf): check struture; reduce mixing in case.inm; rm *.bro* case.scf; x dstart*
- runsp_lapw (for magnetic cases, case.clmup/dn)
  - *-orb* *use LDA+U (needs case.indm, case.inorb)*
- runfsm_lapw –m Moment (fixed-spin-moment calc.)
- runafm_lapw (Antiferromagnetic, use with care)

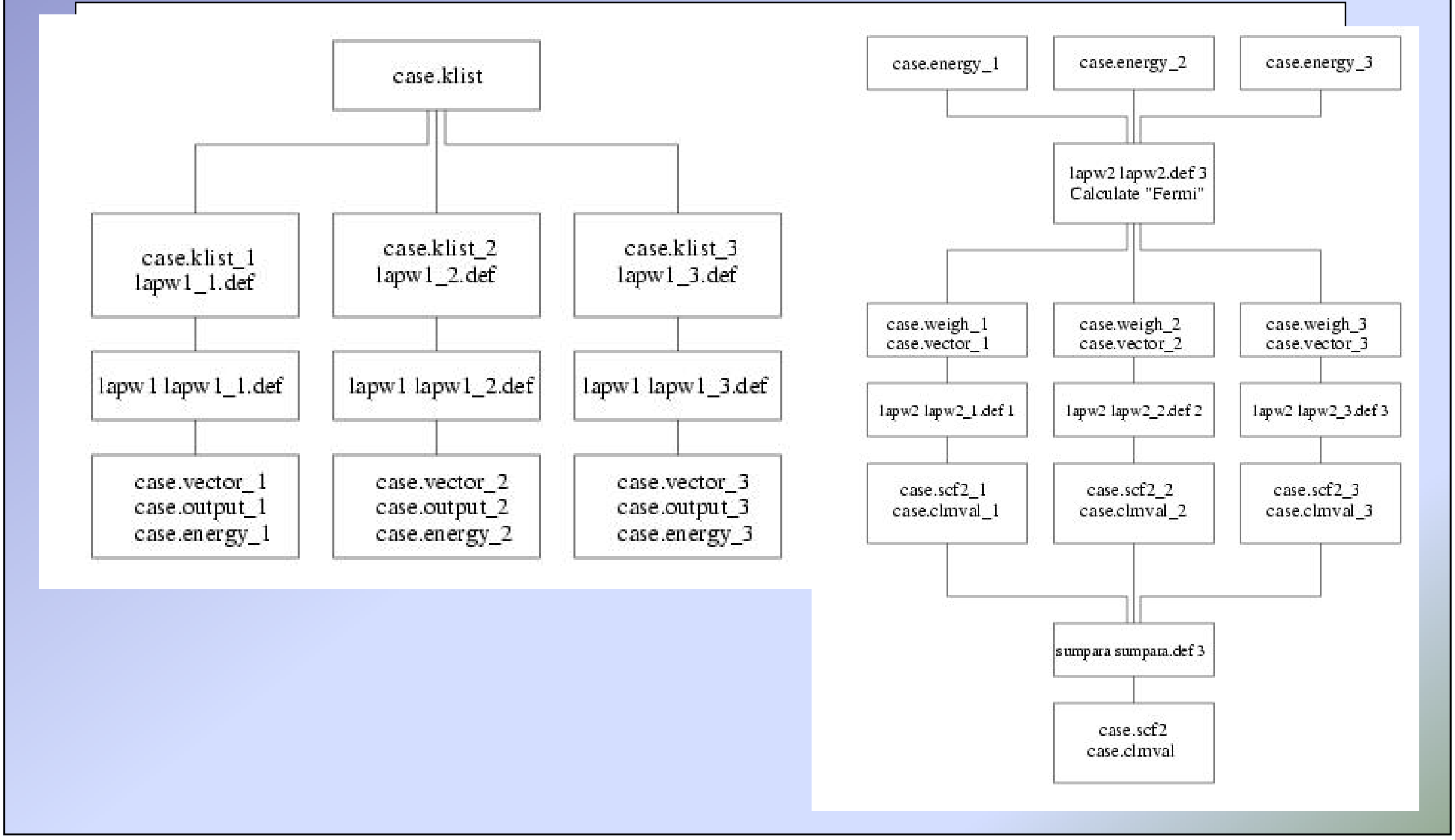
Installation of WIEN2k

- Register via http://www.wien2k.at
- Create your $WIENROOT directory (e.g. ./WIEN2k)
- Download wien2k_03.tar and examples (executables)
- Uncompress and expand all files using:
  - *tar –xvf wien2k_03.tar*
  - *gunzip *.gz*
  - *chmod +x ./expand_lapw*
  - *./expand_lapw*
- This leads to the following directories:
  - *./SRC* *(scripts, ug.ps)*
  - *./SRC_aim* *(programs)*
  - *…*
  - *SRC_templates* *(example inputs)*
  - *…*
  - *SRC_usersguide_html (HTML-version of UG)*
  - *example_struct_files* *(examples)*
  - *TiC*

Parallelization

- k-point parallel on clusters (slow network): lapw1+lapw2
  - *common NFS filesystem (files must be accessable with the same path on all machines)*
  - *rsh/ssh without password (.rhosts; private/public keys)*
    - .machines file:
      - 1:host1 (speed:hostname)
      - 2:host2
      - granularity:1 (1:10k+10k; 3: 3+3+3+3+3+3+rest ➔load balancing)
      - extrafine (rest in junks of 1 k)
    - testpara (tests distribution); run_lapw -p
- fine-grain parallelization for big cases (>50 atoms) and fast network (shared memory machines)
  - *mpi + scalapack*
    - .machines file:
      - 1:host1:4 4 mpi-parallel jobs on host1
      - lapw0:host1:4 host2:4 8 parallel jobs; atom-loops only!!!

Flow of parallel execution



case.klist

case.klist_1 lapw1_1.def

case.klist_2 lapw1_2.def

case.klist_3 lapw1_3.def

lapw1 lapw1_1.def

lapw1 lapw1_2.def

lapw1 lapw1_3.def

case.vector_1 case.output_1 case.energy_1

case.vector_2 case.output_2 case.energy_2

case.vector_3 case.output_3 case.energy_3

case.energy_1

case.energy_2

case.energy_3

lapw2 lapw2.def 3 Calculate "Fermi"

case.weigh_1 case.vector_1

case.weigh_2 case.vector_2

case.weigh_3 case.vector_3

lapw2 lapw2_1.def 1

lapw2 lapw2_2.def 2

lapw2 lapw2_3.def 3

case.scf2_1 case.clmval_1

case.scf2_2 case.clmval_2

case.scf2_3 case.clmval_3

sumpara sumpara.def 3

case.scf2 case.clmval

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*
  - *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)*