From APW to LAPW to (L)APW+lo

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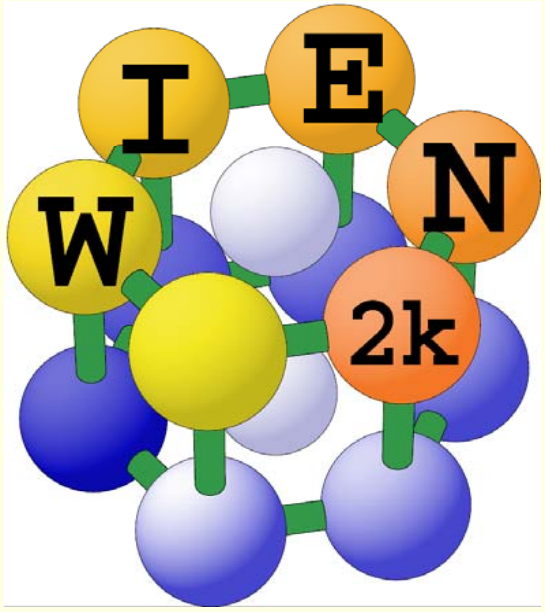


A few solid state concepts

- Crystal structure
  - *Unit cell (defined by 3 lattice vectors) leading to 7 crystal systems*
  - *Bravais lattice (14)*
  - *Atomic basis (Wyckoff position)*
  - *Symmetries (rotations, inversion, mirror planes, glide plane, screw axis)*
  - *Space group (230)*
  - *Wigner-Seitz cell*
  - *Reciprocal lattice (Brillouin zone)*
- Electronic structure
  - *Periodic boundary conditions*
  - *Bloch theorem (k-vector), Bloch function*
  - *Schrödinger equation (HF, DFT)*

Unit cell

Assuming an ideal infinite crystal we define a unit cell by

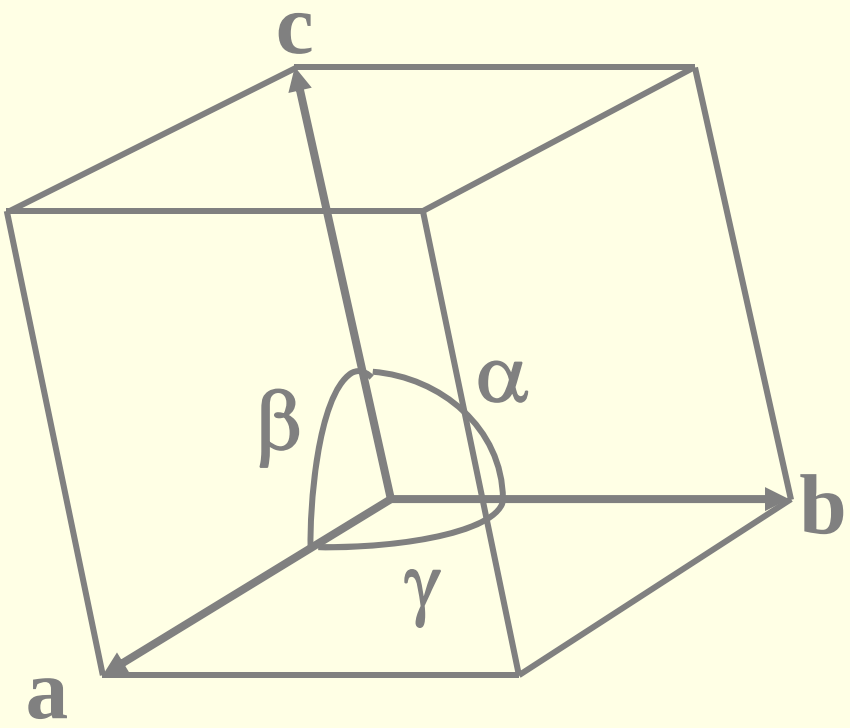
Unit cell: a volume in space that fills space entirely when translated by all lattice vectors.

The obvious choice:

a parallelepiped defined by **a**, **b**, **c**, three basis vectors with

the best **a**, **b**, **c** are as orthogonal as possible

the cell is as symmetric as possible (14 types)



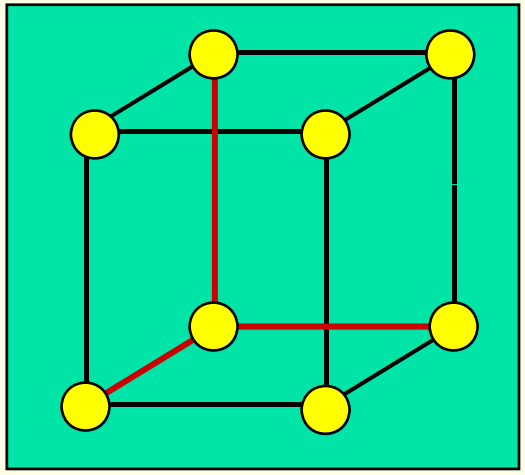
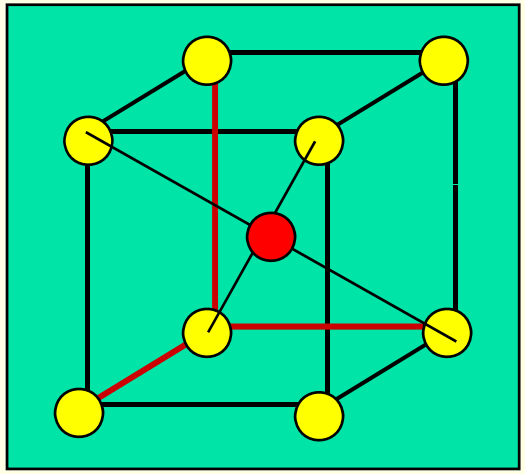
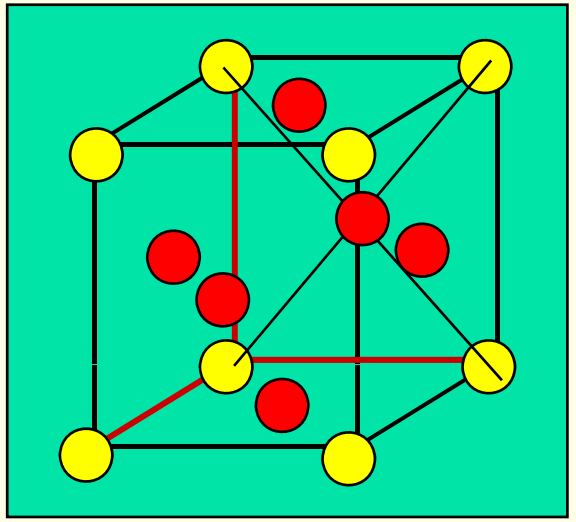
A unit cell containing one lattice point is called primitive cell.

Crystal system: e.g. cubic

Axis system

a = b = c

$\alpha = \beta = \gamma = 90°$

primitive	**body centered**	**face centered**
		
P (cP)	**I (bcc)**	**F (fcc)**

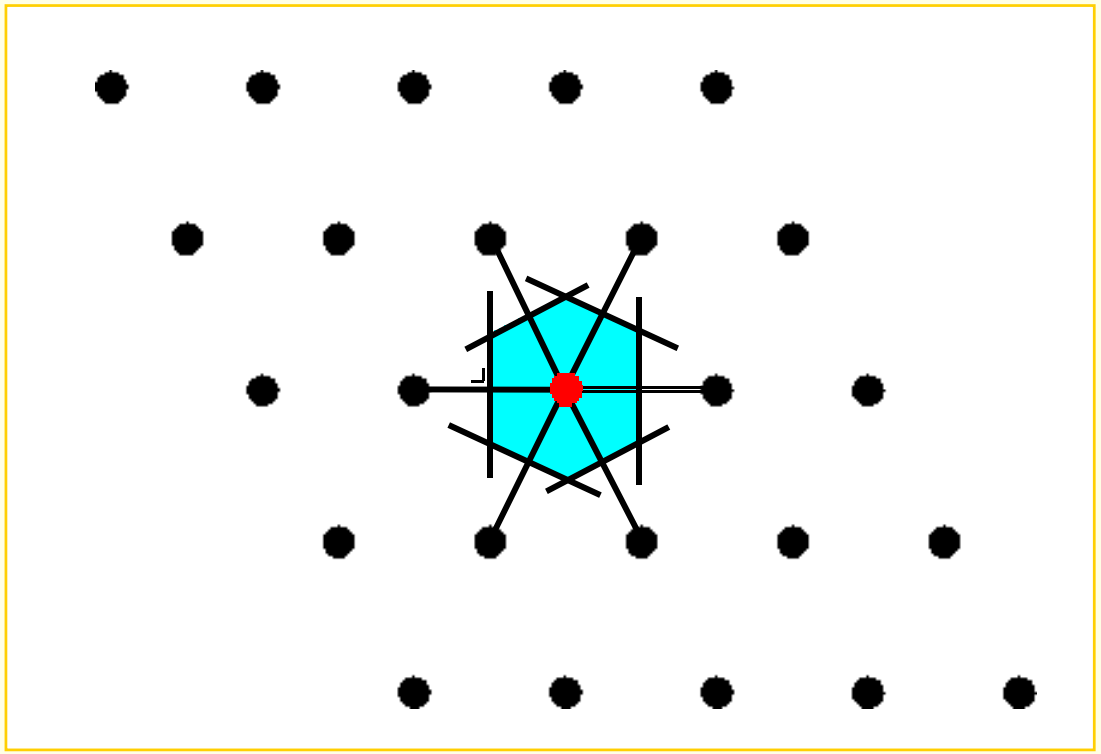
3D lattice types:

7 **Crystal systems** and 14 **Bravais lattices**

Triclinic	1	“no” symmetry
Monoclinic (P, C)	2	Two right angles
Orthorhombic (P, C, I, F)	4	Three right angles
Tetragonal (P, I)	2	Three right angles + 4 fold rotation
Cubic (P, I, F)	3	Three right angles + 4 fold + 3 fold
Trigonal (Rhombohedral)	1	Three equal angles ($\neq 90^{o}$)+ 3 fold
Hexagonal	1	Two right and one 120^{o} angle + 6 fold

Wigner-Seitz Cell

Form connection to all neighbors and span a plane normal to the connecting line at half distance



Bloch-Theorem:

$$\left[-\frac{1}{2}\nabla^2 + V(r) \right]\Psi(r) = E\Psi(r)$$

V(x) has lattice periodicity ("translational invariance"):

V(x)=V(x+a)

The electron density ρ(x) has also lattice periodicity, however, the **wave function** does **NOT**:

$$\rho(x) = \rho(x+a) = \Psi^*(x)\Psi(x) \qquad but:$$

$$\Psi(x+a) = \mu\Psi(x) \quad \Rightarrow \quad \mu^*\mu = 1$$

Application of the translation τ g-times:

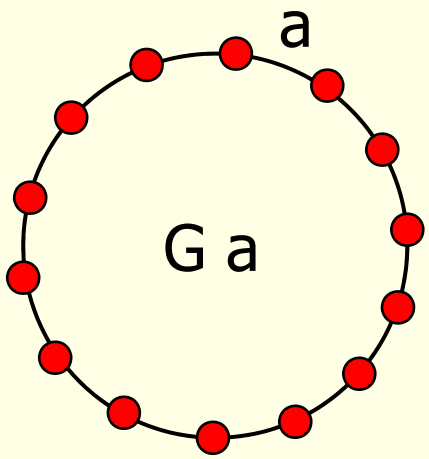
$$\tau^g\Psi(x) = \Psi(x+ga) = \mu^g\Psi(x)$$

periodic boundary conditions:

- The wave function must be uniquely defined: after G translations it must be identical (G a: periodicity volume):

$$\tau^G \Psi(x) = \Psi(x + Ga) = \mu^G \Psi(x) = \Psi(x)$$

$$\Rightarrow \quad \mu^G = 1$$



$$\mu = e^{2\pi i \frac{g}{G}} \qquad g = 0, \pm 1 \pm 2, ...$$

$$Def.: \quad k = \frac{2\pi}{a}\frac{g}{G} \qquad \mu = e^{ika}$$

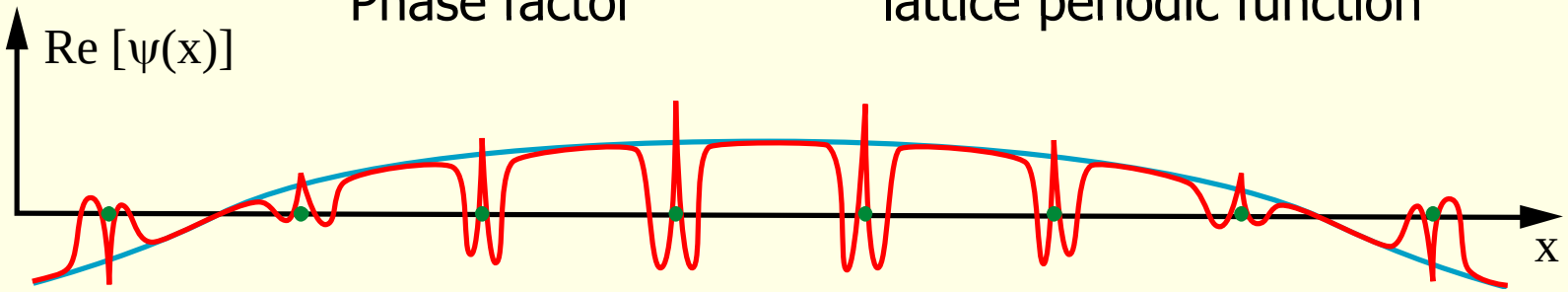
$$Bloch\ condition: \quad \Psi(x + a) = e^{ika}\Psi(x) = \Psi_k$$

Bloch functions:

- Wave functions with Bloch form:

$$\Psi_k(x) = e^{ikx}u(x) \qquad where: \qquad u(x) = u(x+a)$$

Phase factor — lattice periodic function

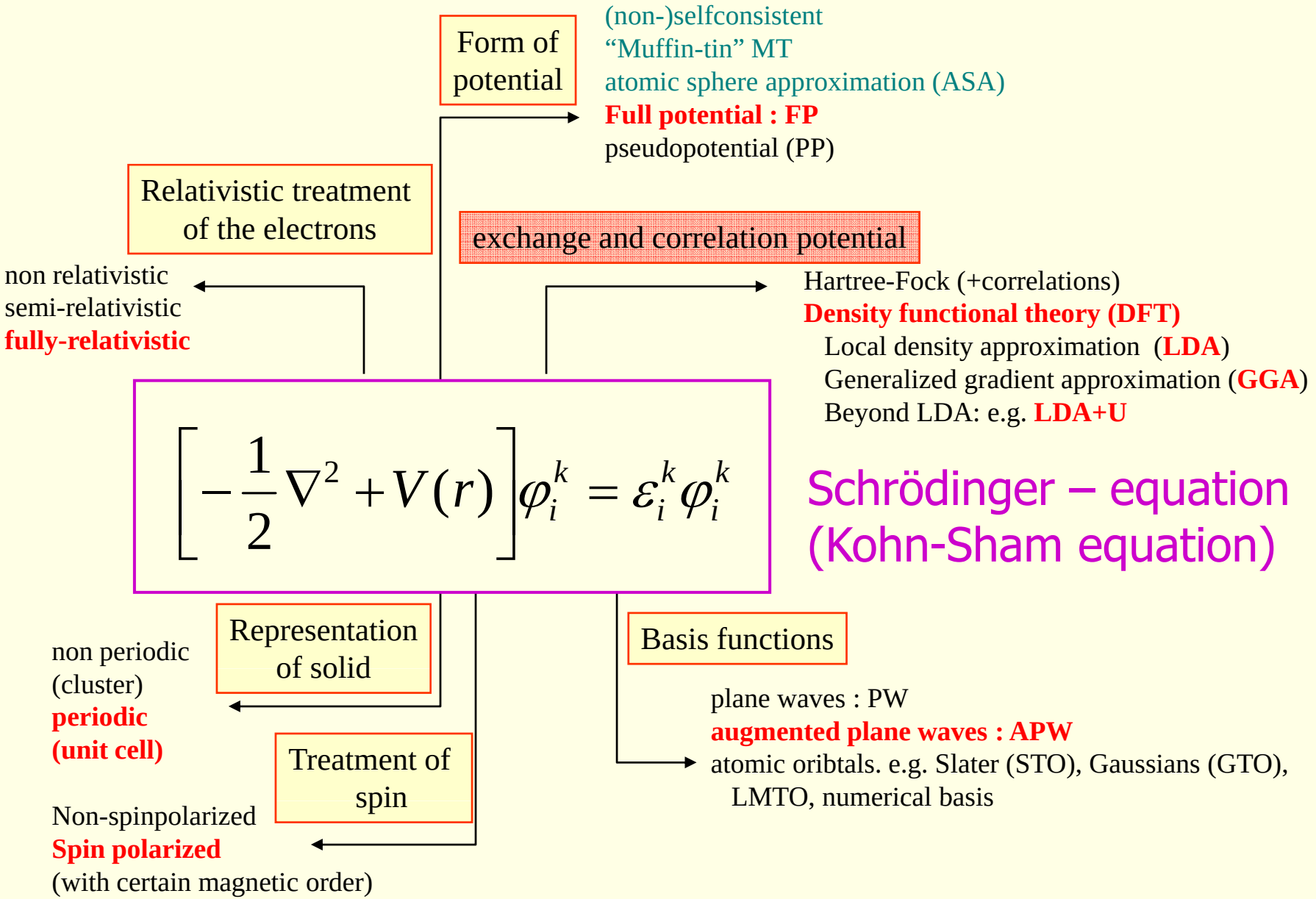


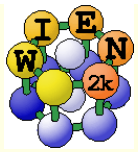
Replacing ***k*** by ***k***+***K***, where ***K*** is a reciprocal lattice vector, fulfills again the Bloch-condition.

→ ***k*** can be restricted to the first Brillouin zone .

$$e^{i\frac{2\pi}{a}K} = 1 \qquad -\frac{\pi}{a} < k < \frac{\pi}{a}$$

Concepts when solving Schrödingers-equation in solids





ESSENCE OF DENSITY-FUNTIONAL THEORY

TU WIEN

- **Every observable quantity of a quantum system can be calculated from the density of the system ALONE (Hohenberg, Kohn, 1964).**

- **The density of particles interacting with each other can be calculated as the density of an auxiliary system of non-interacting particles (Kohn, Sham, 1965).**

Walter Kohn, Nobel Prize 1998 Chemistry

"Self-consistent Equations including Exchange and Correlation Effects"
W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965)

Literal quote from Kohn and Sham's paper:"... We do not expect an accurate description of chemical binding."

DFT Density Functional Theory

Hohenberg-Kohn theorem: (exact)

The total energy of an interacting inhomogeneous electron gas in the presence of an external potential $V_{ext}(r)$ is a functional of the density ρ

$$E = \int V_{ext}(\vec{r})\rho(\vec{r})d\vec{r} + F[\rho]$$

Kohn-Sham: (still exact!)

$$E = T_o[\rho] + \int V_{ext}\rho(\vec{r})d\vec{r} + \frac{1}{2}\int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}' - \vec{r}|}d\vec{r}d\vec{r}' + E_{xc}[\rho]$$

$E_{kinetic}$ non interacting

E_{ne}

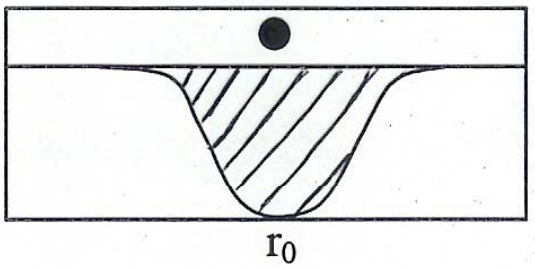
$E_{coulomb}$ E_{ee}

E_{xc} exchange-correlation

In KS the many body problem of interacting electrons and nuclei is mapped to a one-electron reference system that leads to the same density as the real system.

Exchange and correlation

$$\bar{n}(r_0, r) = n(r) + h(r_0, r)$$



- We divide the density of the N-1 electron system into the total density n(r) and an exchange-correlation hole:

Properties of the exchange-correlation hole:

- Locality
- Pauli principle
- the hole contains ONE electron
- The hole must ne negative

$$h(r_0, r) \xrightarrow[|r-r_0|\to\infty]{} 0$$

$$h(r_0, r) \xrightarrow[|r-r_0|\to 0]{} -n(r_0)$$

$$\int dr\; h(r_0, r) = -1$$

$$h(r_0, r) \le 0$$

- The exchange hole affects electrons with the same spin and accounts for the Pauli principle
- In contrast, the correlation-hole accounts for the Coulomb repulsion of electrons with the opposite spin. It is short range and leads to a small redistribution of charge. The correlation hole contains NO charge:

$$\int dr\; h_c(r_0, r) = 0$$

Kohn-Sham equations

LDA, GGA

$$E = T_o[\rho] + \int V_{ext}\,\rho(\vec{r})\,d\vec{r} + \frac{1}{2}\int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}' - \vec{r}|} d\vec{r}\,d\vec{r}' + E_{xc}[\rho]$$

vary ρ

1-electron equations (Kohn Sham)

$$\{-\frac{1}{2}\nabla^2 + V_{ext}(\vec{r}) + V_C(\rho(\vec{r})) + V_{xc}(\rho(\vec{r}))\}\Phi_i(\vec{r}) = \varepsilon_i \Phi_i(\vec{r})$$

-Z/r

$$\int \frac{\rho(\vec{r})}{|\vec{r}' - \vec{r}|} d\vec{r}$$

$$\frac{\partial E_{xc}(\rho)}{\partial \rho}$$

$$\rho(\vec{r}) = \sum_{\varepsilon_i \le E_F} |\Phi_i|^2$$

$$E_{xc}^{LDA} \propto \int \rho(r)\ \varepsilon_{xc}^{\text{hom.}}[\rho(r)]\ dr$$

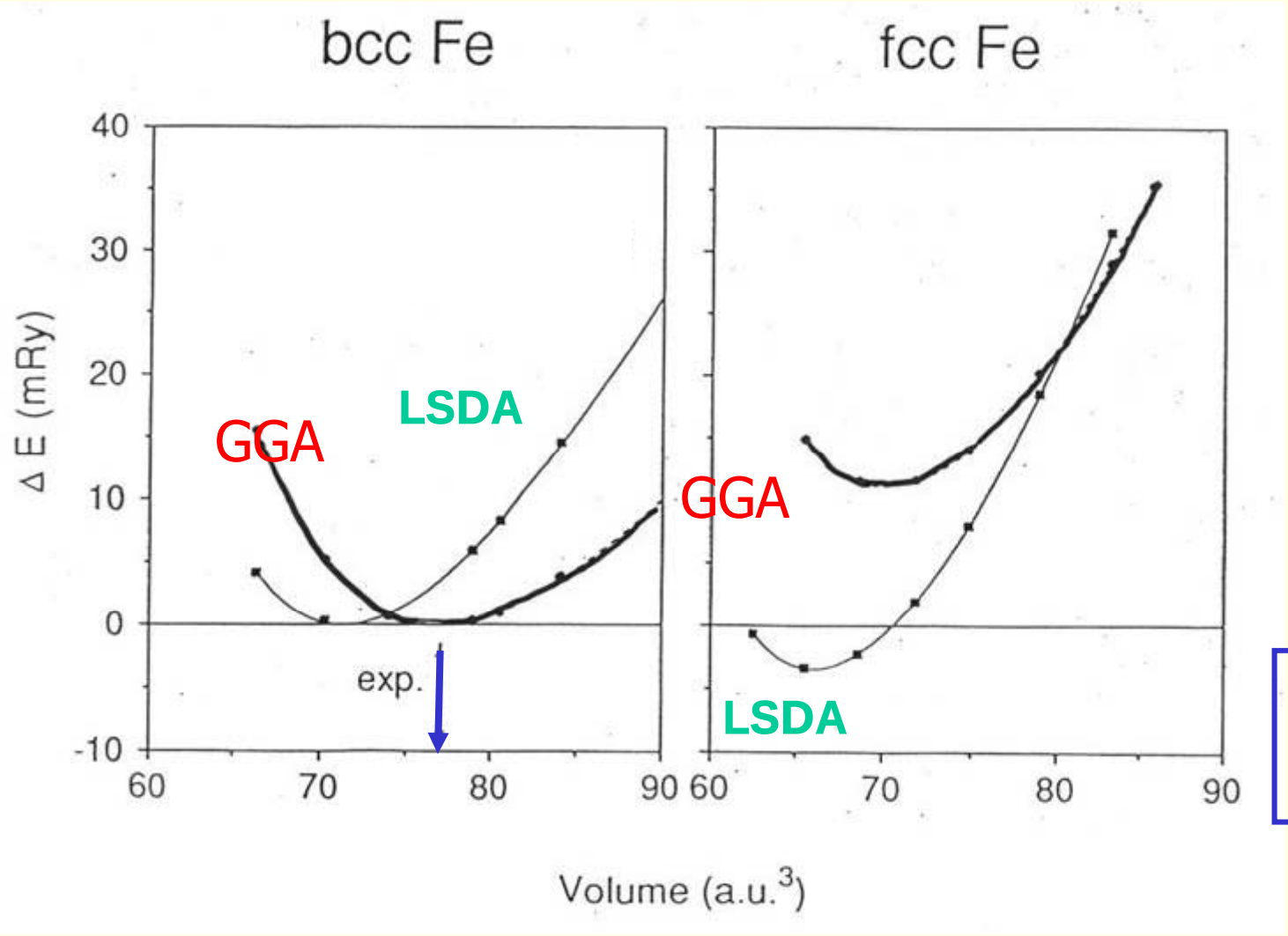
$$E_{xc}^{GGA} \propto \int \rho(r)\ F[\rho(r), \nabla\rho(r)]\ dr$$

LDA treats both, exchange and correlation effects,

GGA but approximately

New (better ?) functionals are still an active field of research

DFT ground state of iron



LSDA

- *NM*
- *fcc*
- *in contrast to experiment*

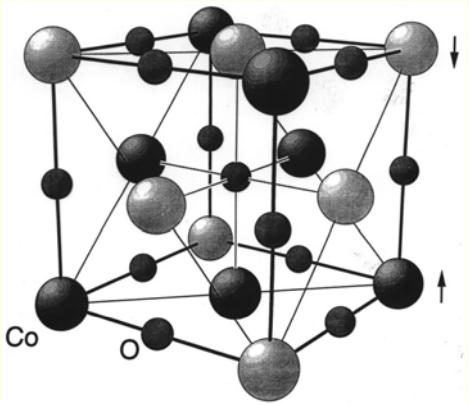
GGA

- *FM*
- *bcc*
- *Correct lattice constant*

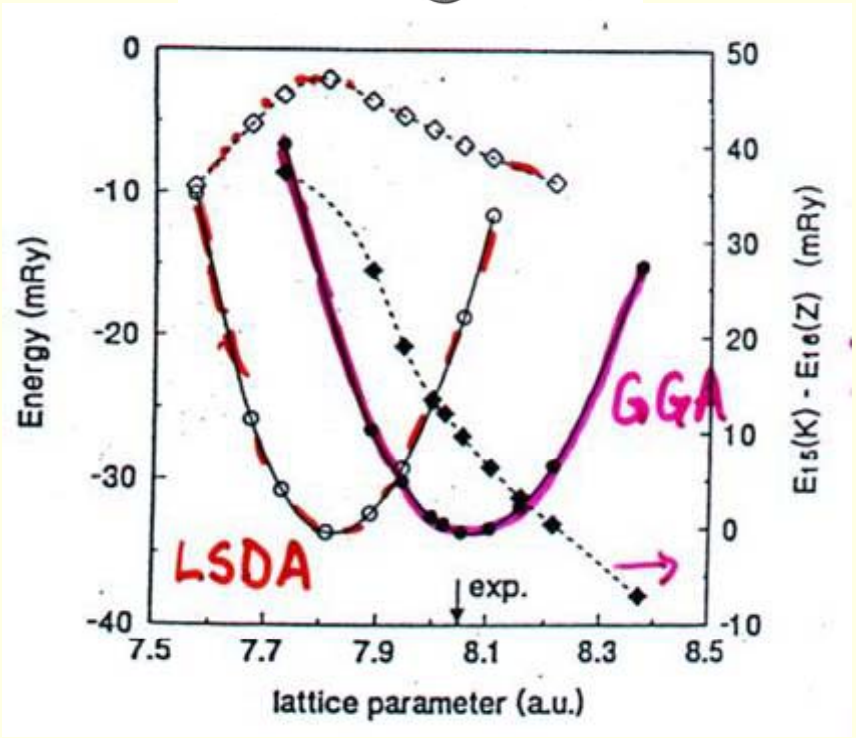
Experiment

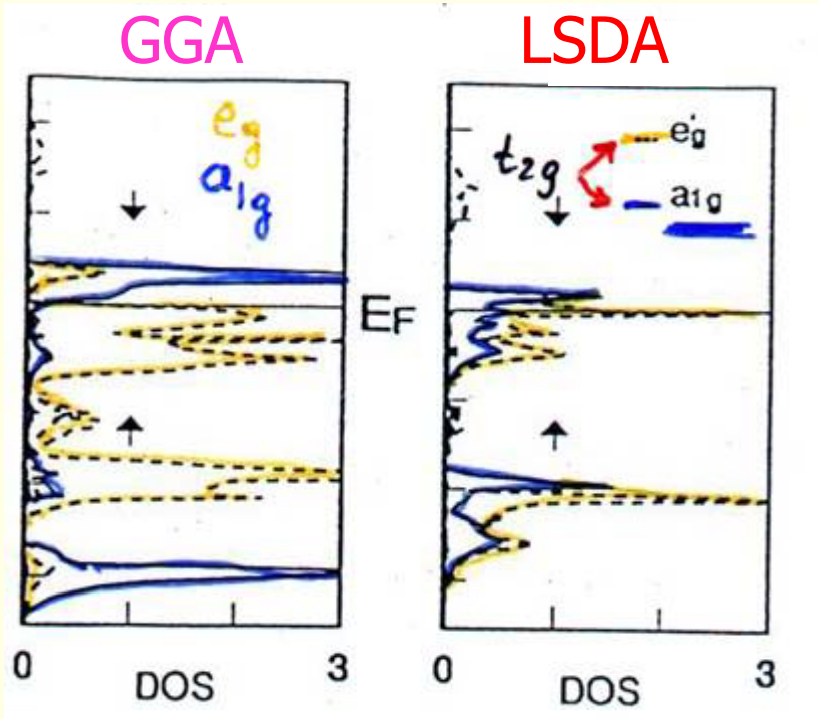
- *FM*
- *bcc*

CoO AFM-II total energy, DOS



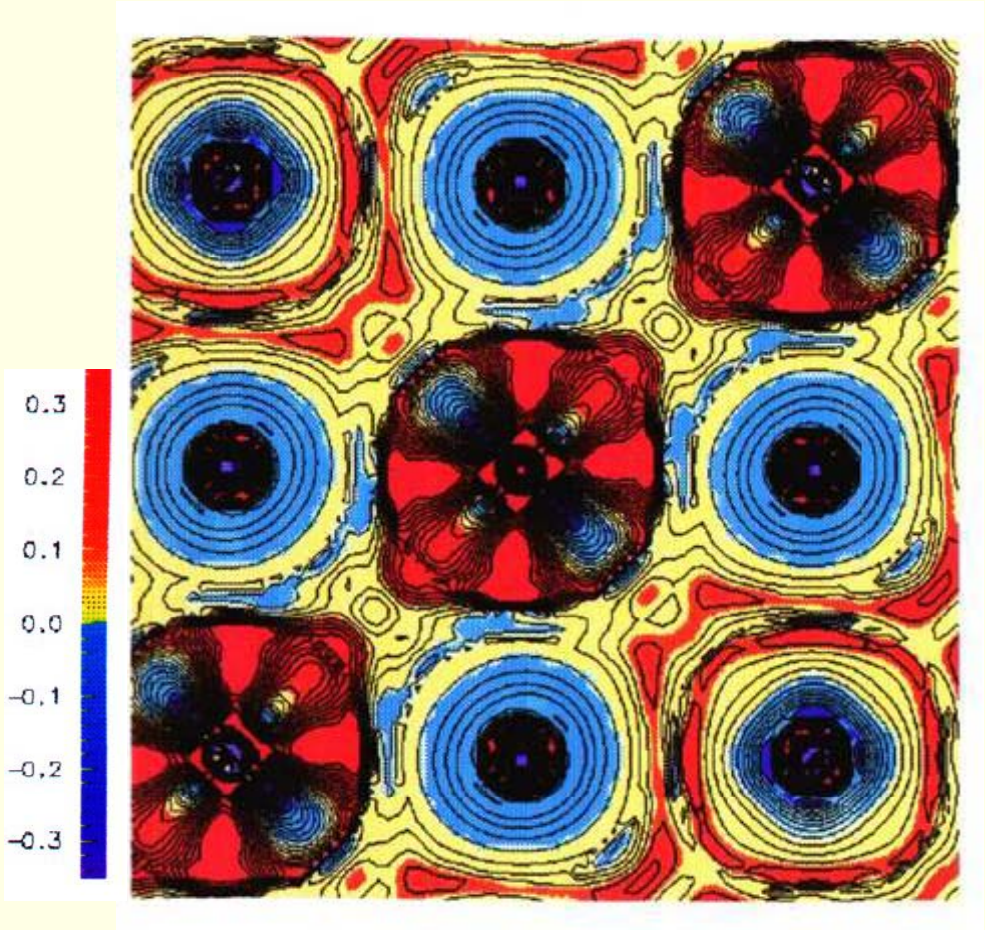
- CoO
  - *in NaCl structure*
  - *antiferromagnetic: AF II*
  - *insulator*
  - *t_{2g} splits into a_{1g} and e_g'*
  - *GGA almost spilts the bands*



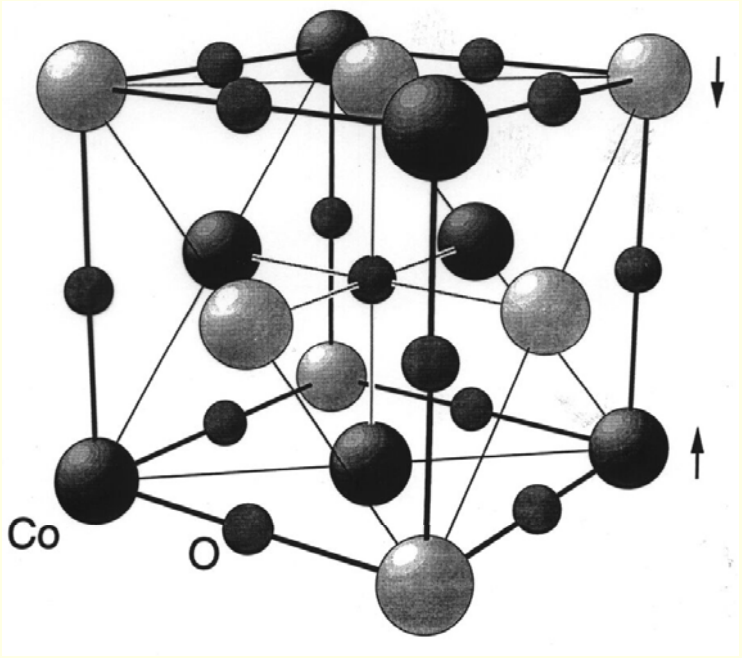


CoO why is GGA better than LSDA

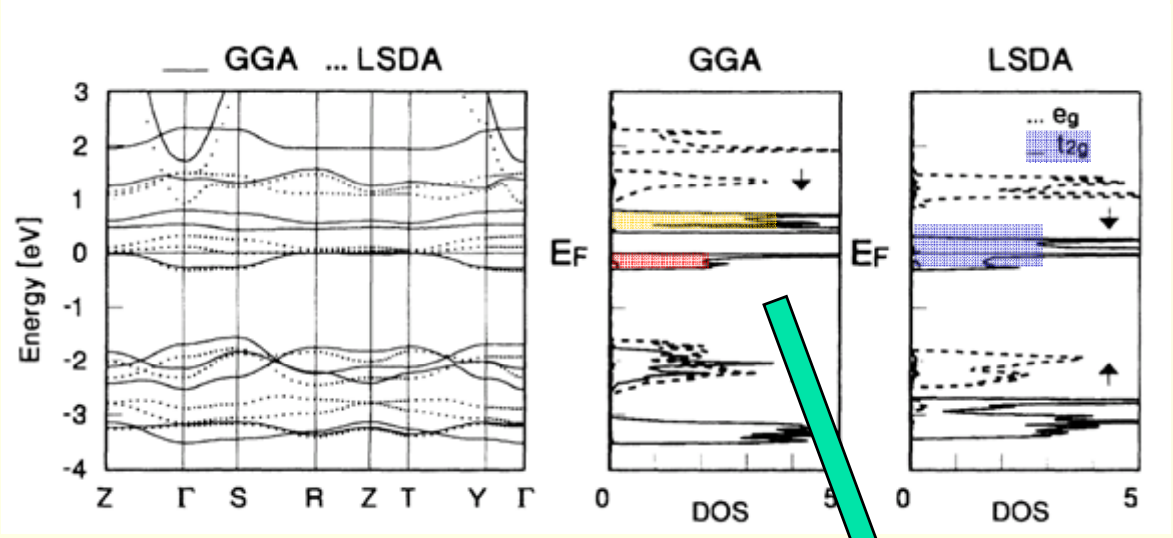
$$\Delta V_{xc}^{\uparrow} = V_{xc}^{\uparrow GGA} - V_{xc}^{\uparrow LSDA}$$

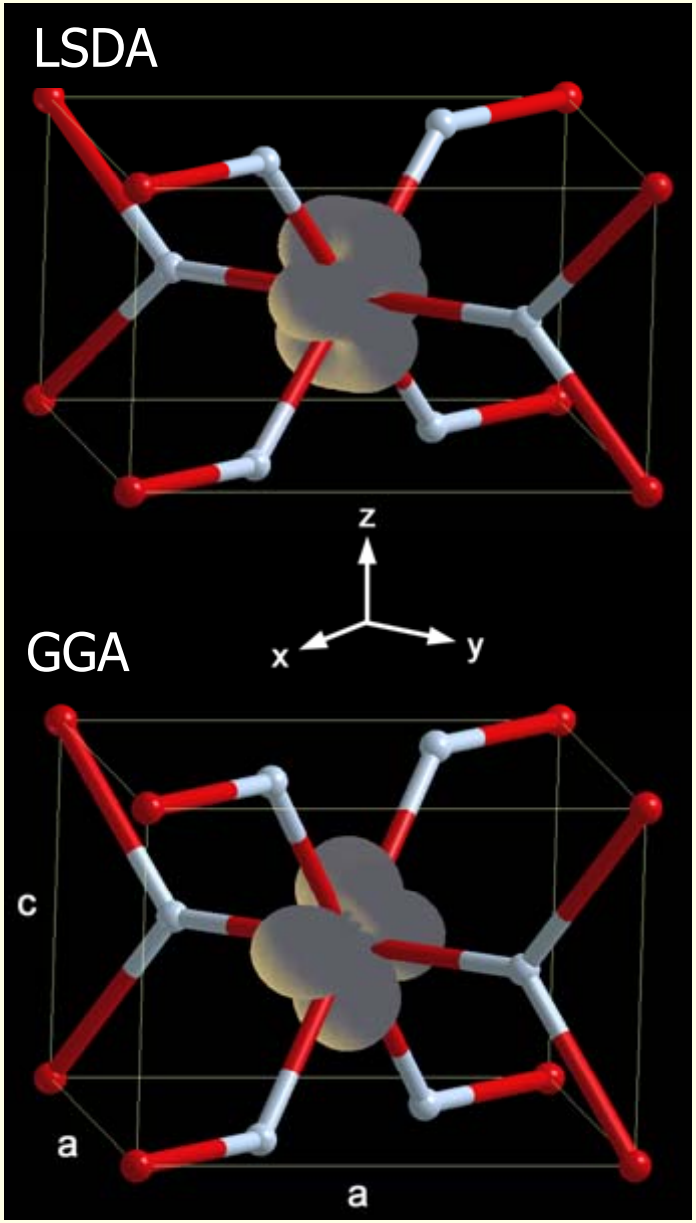


- Central Co atom distinguishes
  - *between* $Co^{\uparrow}$
  - *and* $Co^{\downarrow}$
- Angular correlation



FeF_2: GGA works surprisingly well





Fe-EFG in FeF_2:

LSDA: 6.2

GGA: 16.8

exp: 16.5

agree

FeF_2: GGA splits t_{2g} into a_{1g} and e_g'

Accuracy of DFT for transition metals

Lattice parameters (Å)

	Exp.	LDA	PBE	WC
Co	2.51	2.42	**2.49**	2.45
Ni	3.52	3.42	**3.52**	3.47
Cu	3.61	3.52	**3.63**	3.57
Ru	2.71	2.69	2.71	**2.73**
Rh	3.80	3.76	3.83	**3.80**
Pd	3.88	3.85	3.95	**3.89**
Ag	4.07	4.01	4.15	**4.07**
Ir	3.84	**3.84**	3.90	3.86
Pt	3.92	**3.92**	4.00	3.96
Au	4.08	**4.07**	4.18	4.11

- 3d elements:
  - *PBE superior, LDA much too small*
- 4d elements:

LDA too small, PBE too large

  - *New functional Wu-Cohen (WC)*

Z.Wu, R.E.Cohen,
PRB 73, 235116 (2006)

- 5d elements:
  - *LDA superior, PBE too large*

Treatment of exchange and correlation

Approximations for E_{xc}

- LDA: $E_{\mathrm{xc}}^{\mathrm{LDA}} = \int f(\rho(\mathbf{r}))d^3r$
- GGA: $E_{\mathrm{xc}}^{\mathrm{GGA}} = \int f(\rho(\mathbf{r}), |\nabla\rho(\mathbf{r})|)d^3r$
- MGGA: $E_{\mathrm{xc}}^{\mathrm{MGGA}} = \int f(\rho(\mathbf{r}), |\nabla\rho(\mathbf{r})|, \nabla^2\rho(\mathbf{r}), t(\mathbf{r}))d^3r$
- LDA+U: $E_{\mathrm{xc}}^{\mathrm{LDA}+U} = E_{\mathrm{xc}}^{\mathrm{LDA}} + E_{\mathrm{ee}} - E_{\mathrm{dc}}$
- GGA+U: $E_{\mathrm{xc}}^{\mathrm{GGA}+U} = E_{\mathrm{xc}}^{\mathrm{GGA}} + E_{\mathrm{ee}} - E_{\mathrm{dc}}$
- hybrid: $E_{\mathrm{xc}}^{\mathrm{hybrid}} = E_{\mathrm{xc}}^{\mathrm{DFT}} + \alpha\left(E_{\mathrm{x}}^{\mathrm{HF}} - E_{\mathrm{x}}^{\mathrm{DFT}}\right)$
  where

$$E_{\mathrm{x}}^{\mathrm{HF}} = -\frac{1}{2}\sum_{\sigma}\sum_{\substack{n,\mathbf{k}\\ n',\mathbf{k}'}} w_{\mathbf{k}} w_{\mathbf{k}'} \int\int \frac{\psi_{n\mathbf{k}}^{\sigma *}(\mathbf{r})\psi_{n'\mathbf{k}'}^{\sigma *}(\mathbf{r}')\psi_{n'\mathbf{k}'}^{\sigma}(\mathbf{r})\psi_{n\mathbf{k}}^{\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r d^3r'$$

Hybrid functional: only for (correlated) electrons

- Only for certain atoms
  and electrons of a given
  angular momentum ℓ

$$E_{\mathrm{xc}}^{\mathrm{hybrid}} = E_{\mathrm{xc}}^{\mathrm{DFT}}[\rho^{\sigma}] + \alpha \left(E_{\mathrm{x}}^{\mathrm{HF}}[n_{m_i m_j}^{\sigma}] - E_{\mathrm{x}}^{\mathrm{DFT}}[\rho_{\ell}^{\sigma}] \right)$$

$$E_{\mathrm{x}}^{\mathrm{HF}}[n_{m_i m_j}^{\sigma}] = -\frac{1}{2} \sum_{\sigma} \sum_{m_1, m_2, m_3, m_4}^{\ell} n_{m_1 m_2}^{\sigma} n_{m_3 m_4}^{\sigma} \langle m_1 m_3 | v_{\mathrm{ee}} | m_4 m_2 \rangle$$

$$\langle m_1 m_2 | v_{\mathrm{ee}} | m_3 m_4 \rangle = \sum_{k=0}^{2\ell} a_k F_k$$

The Slater integrals F_k are calculated according to
P.Novák et al., phys.stat.sol (b) **245**, 563 (2006)

Application to FeO

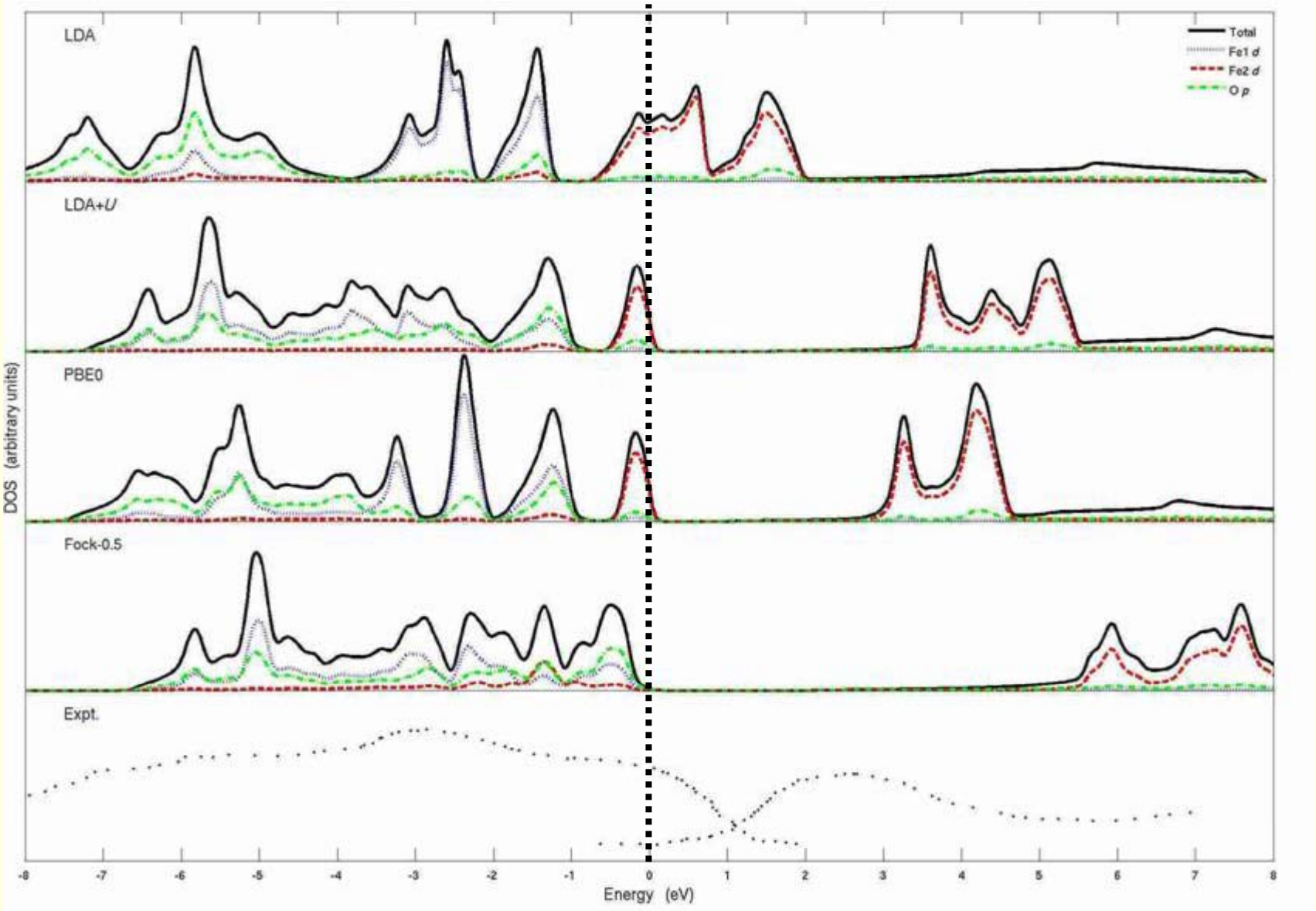
Table: Lattice constant a (Å), bulk modulus B (GPa), total and orbital magnetic moment M and M_ℓ (μ_B), fundamental band gap Δ_{fund} (eV), and optical band gap Δ_{opt} (eV) of AFII phase of FeO.

	a	B	M (M_ℓ)	Δ_{fund}	Δ_{opt}	
LDA	4.18	230	3.44 (0.09)	0.0	0.0	metallic
PBE	4.30	183	3.49 (0.08)	0.0	0.0	metallic
LDA+U	4.28	199	4.23 (0.63)	1.7	2.2	gap
B3PW91	4.35	172	4.15 (0.61)	1.3	1.8	gap
PBE0	4.40	155	4.30 (0.75)	1.2	1.6	gap
Fock-0.35	4.31	195	4.27 (0.68)	2.1	2.4	gap
Fock-0.5	4.34	189	4.32 (0.68)	2.2	2.7	gap
Expt.	4.334	150–180	3.32, 4.2	2.4	0.5[1], 2.4[2]	

[1]Assigned to Fe 3d/O 2sp→Fe 4s transitions.
[2]Assigned to Fe 3d/O 2sp→Fe 3d transitions.

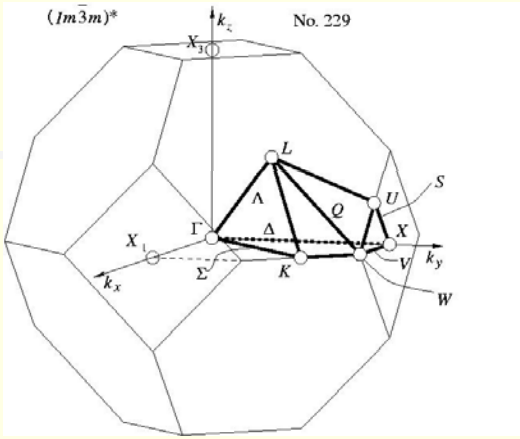
F.Tran, P.Blaha,K.Schwarz, P.Novák, PRB **74**, 155108 (2006)

FeO: LDA vs. LDA+U vs. Hybrids vs. exp



Structure: a,b,c,α,β,γ, R_α , ...

unit cell atomic positions



Structure optimization

iteration *i*

DFT Kohn-Sham

$V(\rho) = V_C + V_{xc}$ **Poisson, DFT**

$E^{i+1} - E^i < \varepsilon$

no

yes

E^{tot}, force

Minimize E, force→0

properties

SCF

k ∈ **IBZ** (irred.Brillouin zone)

k

Kohn Sham

$$[-\nabla^2 + V(\rho)]\psi_k = E_k\psi_k$$

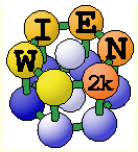
$$\psi_k = \sum_{k_n} C_{k_n}\Phi_{k_n}$$

Variational method $\frac{\delta < E >}{\delta C_{k_n}} = 0$

Generalized eigenvalue problem

$$HC = ESC$$

$$\rho = \sum_{E_k \le E_F} \psi_k^* \psi_k$$



Solving Schrödingers equation:

$$\left[-\frac{1}{2}\nabla^2 + V(r)\right]\Psi_i^k = \varepsilon_i^k \Psi_i^k$$

- Ψ cannot be found analytically
- complete "numerical" solution is possible but inefficient
- Ansatz:
  - *linear combination of some "basis functions"* $\Psi_k = \sum_{K_n} c_{k_n} \Phi_{k_n}$
    - different methods use different basis sets !
  - *finding the "best" wave function using the variational principle:*

$$\langle E_k \rangle = \frac{\langle \Psi_k^* | H | \Psi_k \rangle}{\langle \Psi_k^* | \Psi_k \rangle} \qquad \frac{\partial E_k}{\partial c_{k_n}} = 0$$

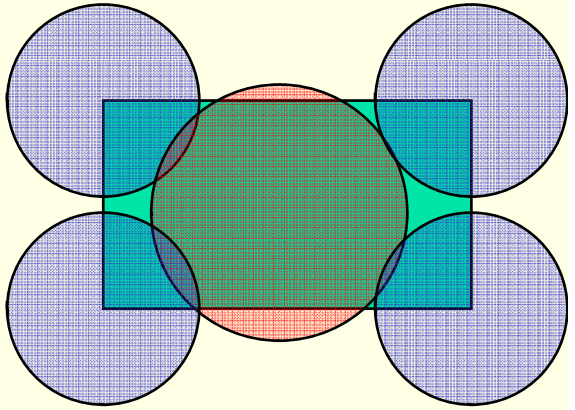
  - *this leads to the famous "Secular equations", i.e. a set of linear equations which in matrix representation is called "generalized eigenvalue problem"*

$$\boldsymbol{H\,C = E\,S\,C}$$

H, S : hamilton and overlap matrix; C: eigenvectors, E: eigenvalues

Basis Sets for Solids

- plane waves
  - *pseudo potentials*
  - *PAW (projector augmented wave) by P.E.Blöchl*
- space partitioning (augmentation) methods
  - *LMTO (linear muffin tin orbitals)*
    - ASA approx., linearized numerical radial function
    + Hankel- and Bessel function expansions
    - full-potential LMTO
  - *ASW (augmented spherical wave)*
    - similar to LMTO
  - *KKR (Korringa, Kohn, Rostocker method)*
    - solution of multiple scattering problem, Greens function formalism
    - equivalent to APW
  - *(L)APW (linearized augmented plane waves)*
- LCAO methods
  - *Gaussians, Slater, or numerical orbitals, often with PP option)*

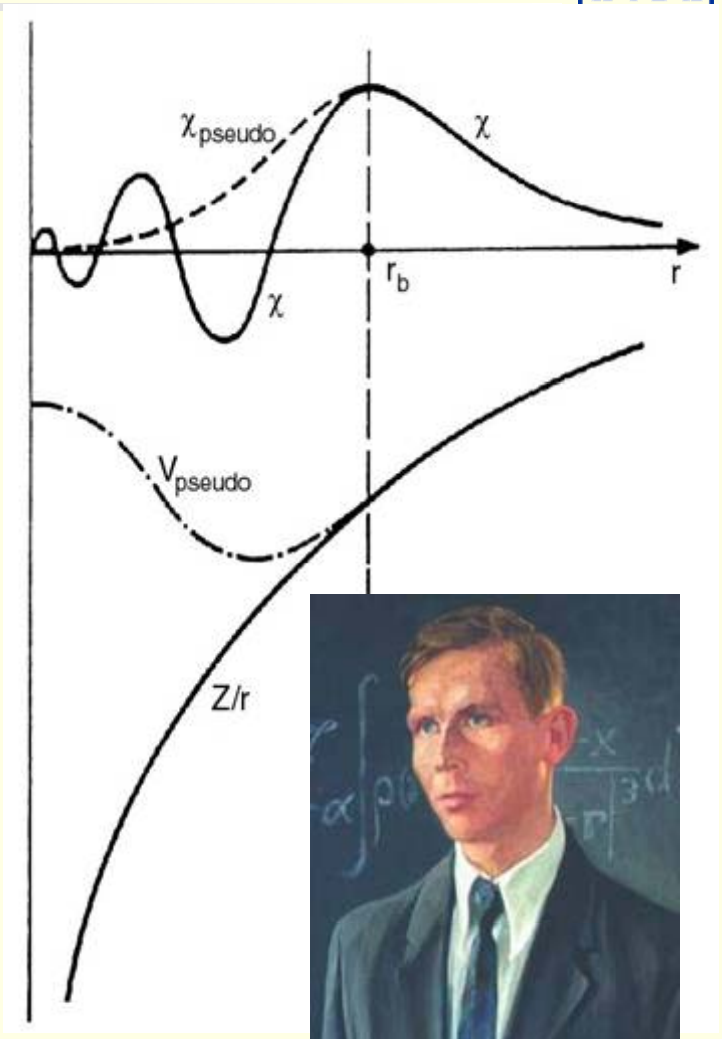


pseudopotential plane wave methods

- plane waves form a "complete" basis set, however, they "never" converge due to the rapid oscillations of the atomic wave functions χ close to the nuclei

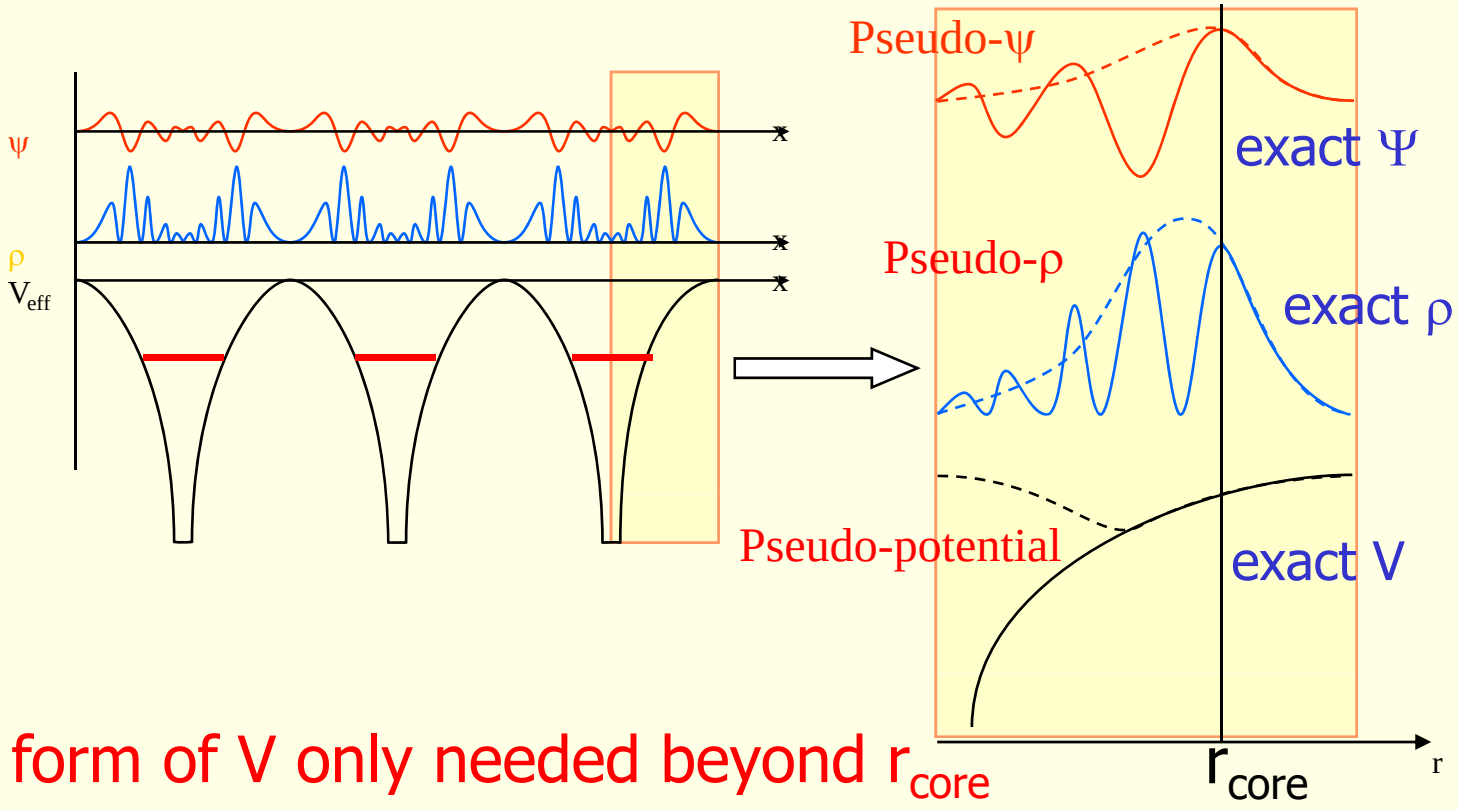
- let´s get rid of all core electrons and these oscillations by replacing the strong ion–electron potential by a much weaker (and physically dubious) *pseudopotential*

- Hellmann´s 1935 *combined approximation method*



"real" potentials vs. pseudopotentials

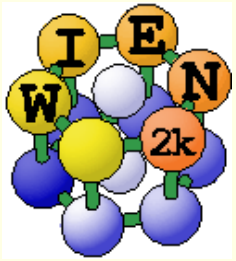
- "real" potentials contain the Coulomb singularity -Z/r
- the wave function has a cusp and many wiggles,
- chemical bonding depends mainly on the overlap of the wave functions between neighboring atoms (in the region between the nuclei) →



→exact form of V only needed beyond r_{core}

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*

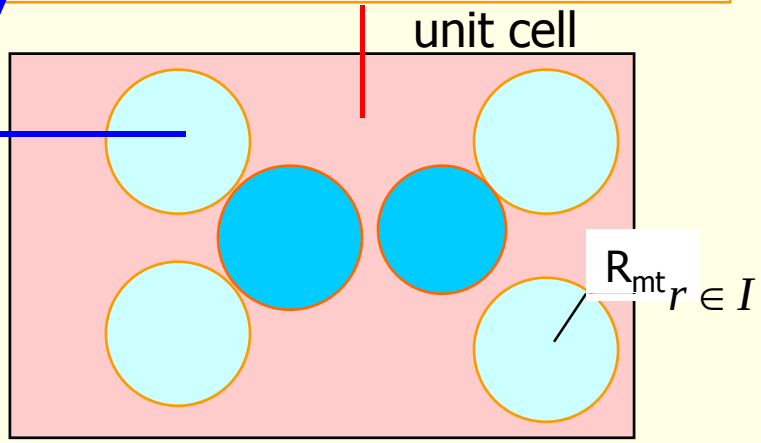


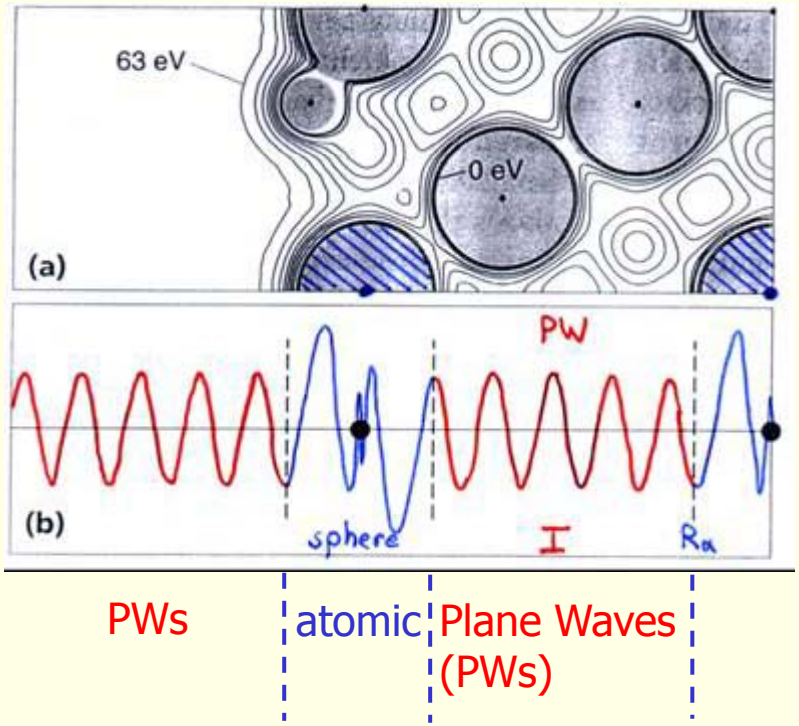
K.Schwarz, P.Blaha, G.K.H.Madsen,
Comp.Phys.Commun.**147**, 71-76 (2002)

K.Schwarz,
DFT calculations of solids with LAPW and WIEN2k
Solid State Chem.**176**, 319-328 (2003)

APW Augmented Plane Wave method

The unit cell is partitioned into:
atomic spheres
Interstitial region





Basis set:

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

Atomic partial waves

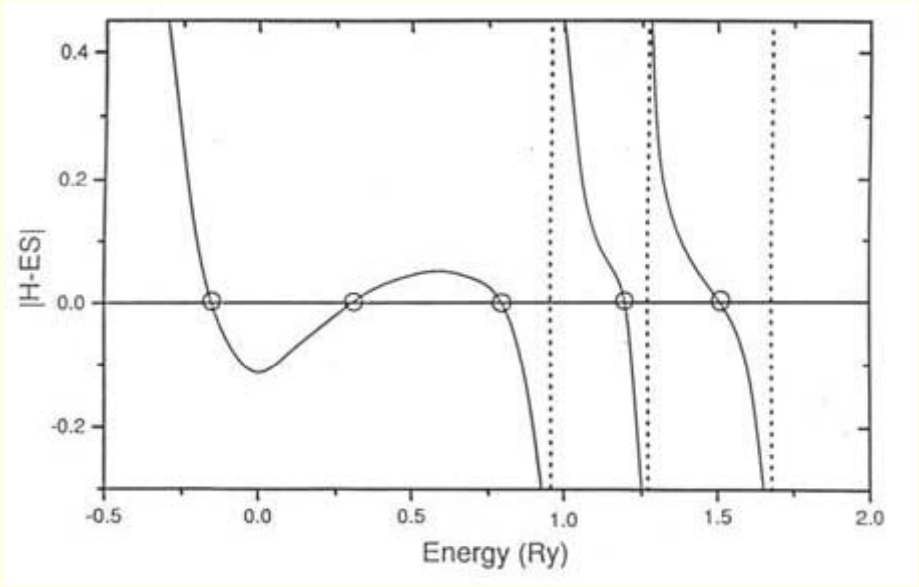
$$\sum_{\ell m} A^K_{\ell m} u_\ell(r',\varepsilon) Y_{\ell m}(\hat{r}')$$

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)



H Hamiltonian
S overlap matrix

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 a

Non-linear eigenvalue problem

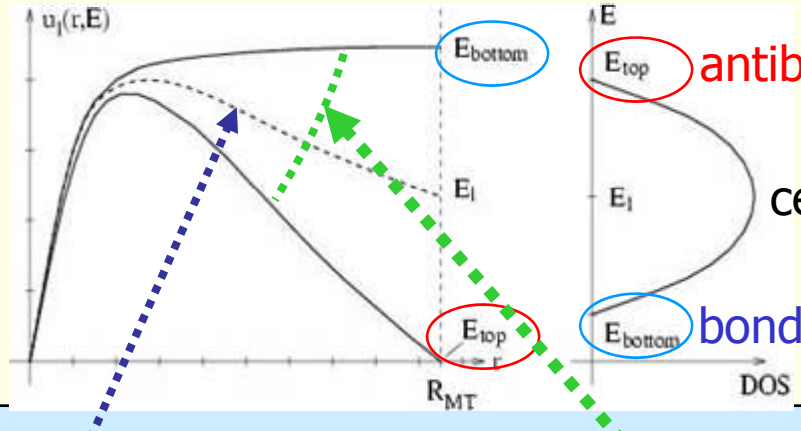
Numerical search for those energies, for which the det|H-ES| vanishes. Computationally very demanding.

"Exact" solution for given MT potential!

Linearization of energy dependence

LAPW suggested by

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



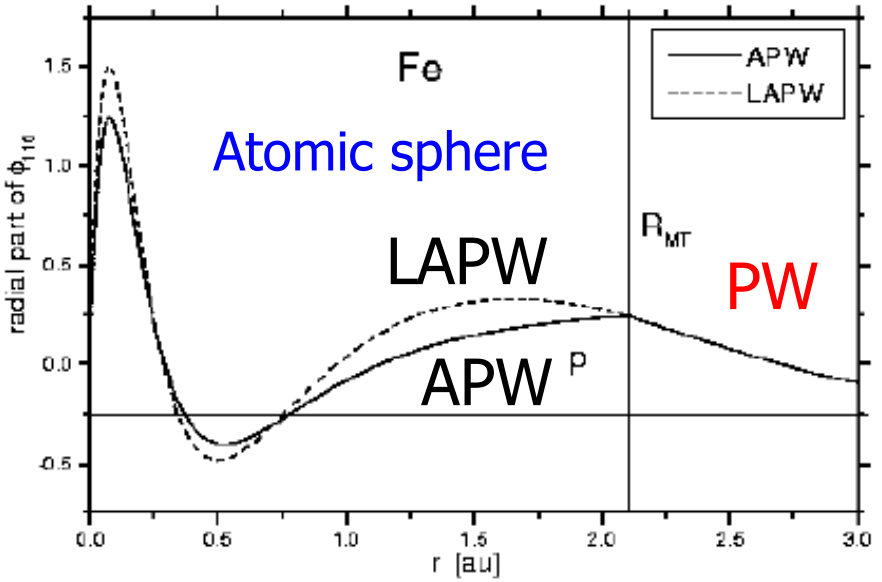
$$\Phi_{k_n} = \sum_{\ell m} [A_{\ell m}(k_n)\, u_\ell(E_\ell, r) + B_{\ell m}(k_n)\, \dot{u}_\ell(E_\ell, r)]\, Y_{\ell m}(\hat{r})$$

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

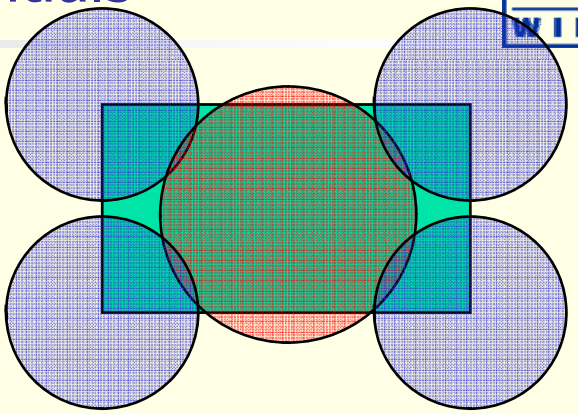
A_{lm}^k, B_{lm}^k: join PWs in value and slope

→ General eigenvalue problem (diagonalization)

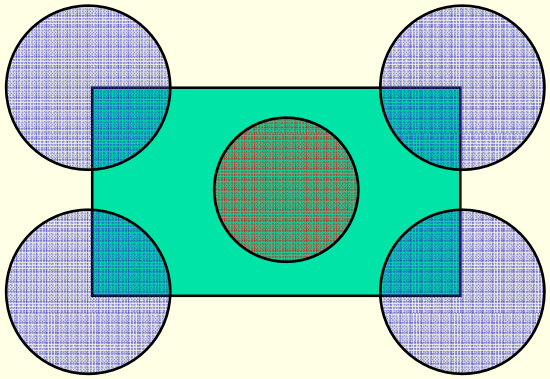
→ additional constraint requires more PWs than APW



shape approximations to "real" potentials



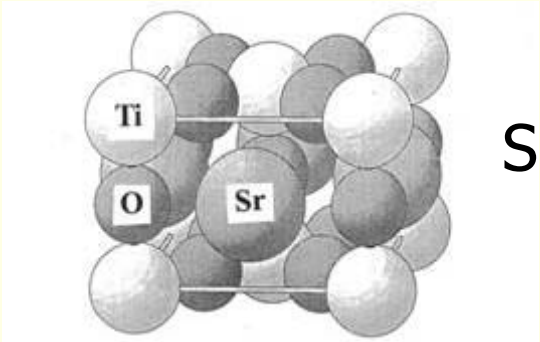
- Atomic sphere approximation (ASA)
  - *overlapping spheres "fill" all volume*
  - *potential spherically symmetric*



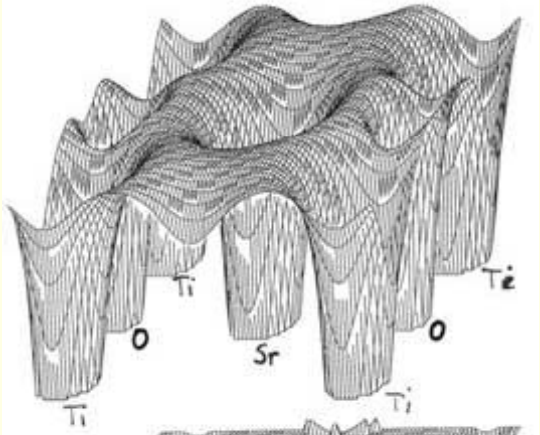
- "muffin-tin" approximation (MTA)
  - *non-overlapping spheres with spherically symmetric potential +*
  - *interstitial region with V=const.*

- "full"-potential
  - *no shape approximations to V*

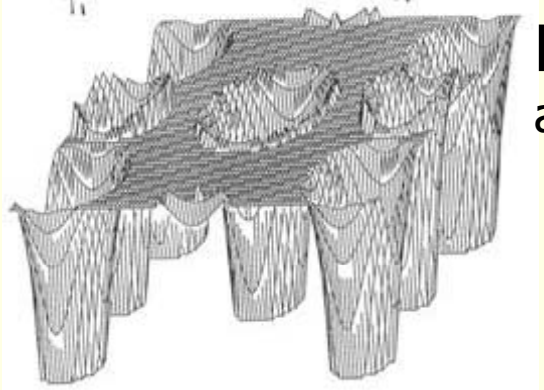
Full-potential in LAPW (A.Freeman et al)



$SrTiO_3$



Full potential



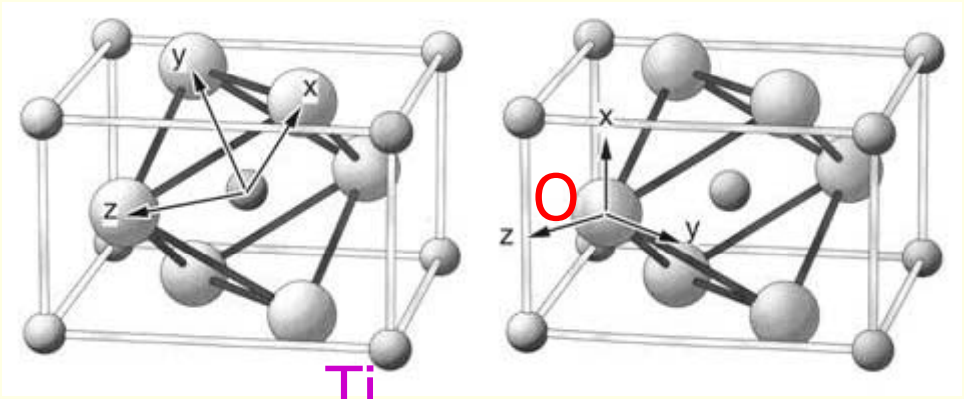
Muffin tin approximation

TiO_2 rutile

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

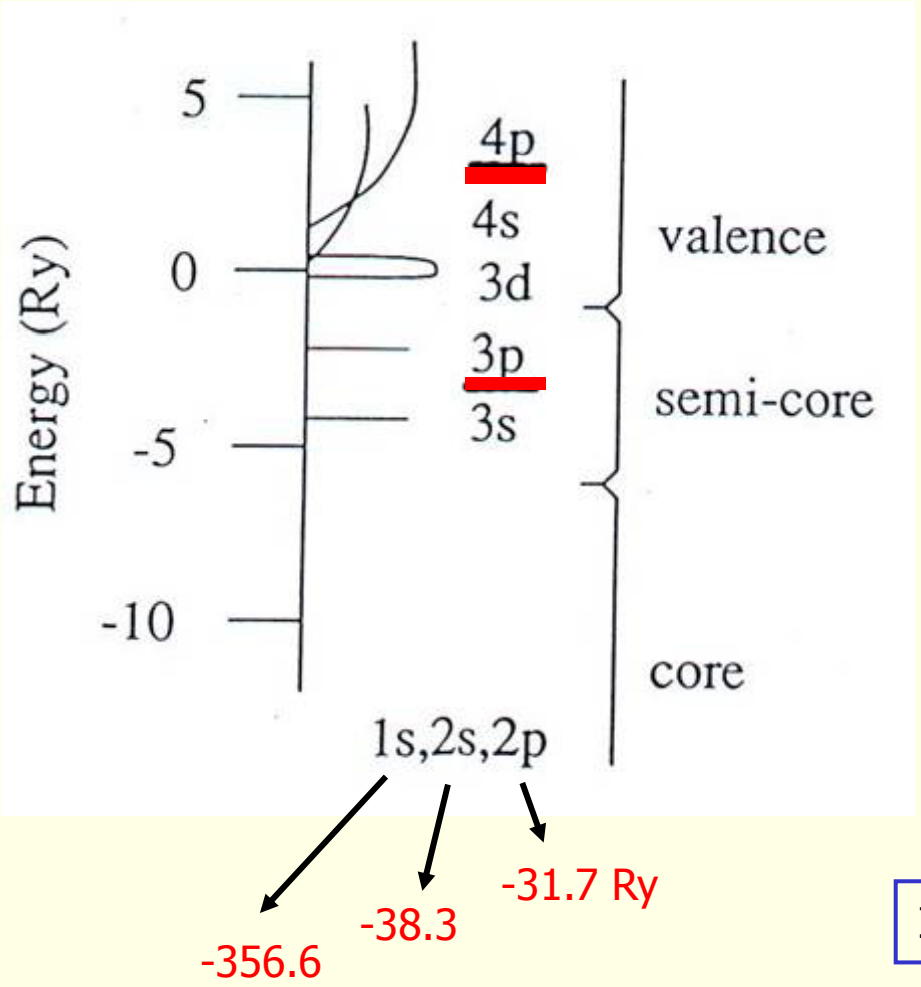
$$V(r) = \begin{cases} \sum_{LM} V_{LM}(r) Y_{LM}(\hat{r}) & r < R_\alpha \\ \sum_{K} V_K e^{i\vec{K}.\vec{r}} & r \in I \end{cases}$$

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



Core, semi-core and valence states

For example: Ti

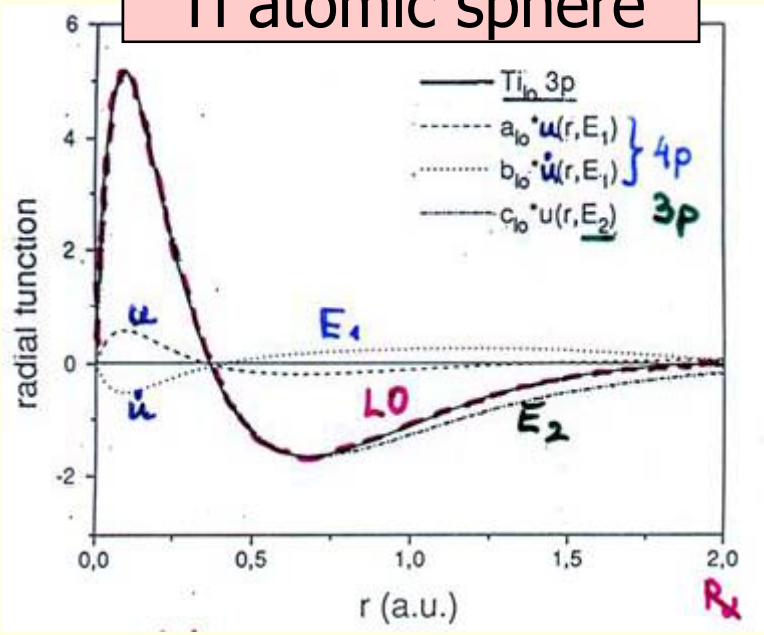


- Valences states
  - ***High*** *in energy*
  - ***Delocalized*** *wavefunctions*
- Semi-core states
  - ***Medium*** *energy*
  - *Principal* ***QN*** *one less than valence (e.g. in Ti* ***3****p and* ***4****p)*
  - ***not completely confined*** *inside sphere*
- Core states
  - ***Low*** *in energy*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

1 Ry =13.605 eV

Local orbitals (LO)

Ti atomic sphere



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

- 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)

An alternative combination of schemes

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 local orbitals (lo)
  (add a few extra basis functions)

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

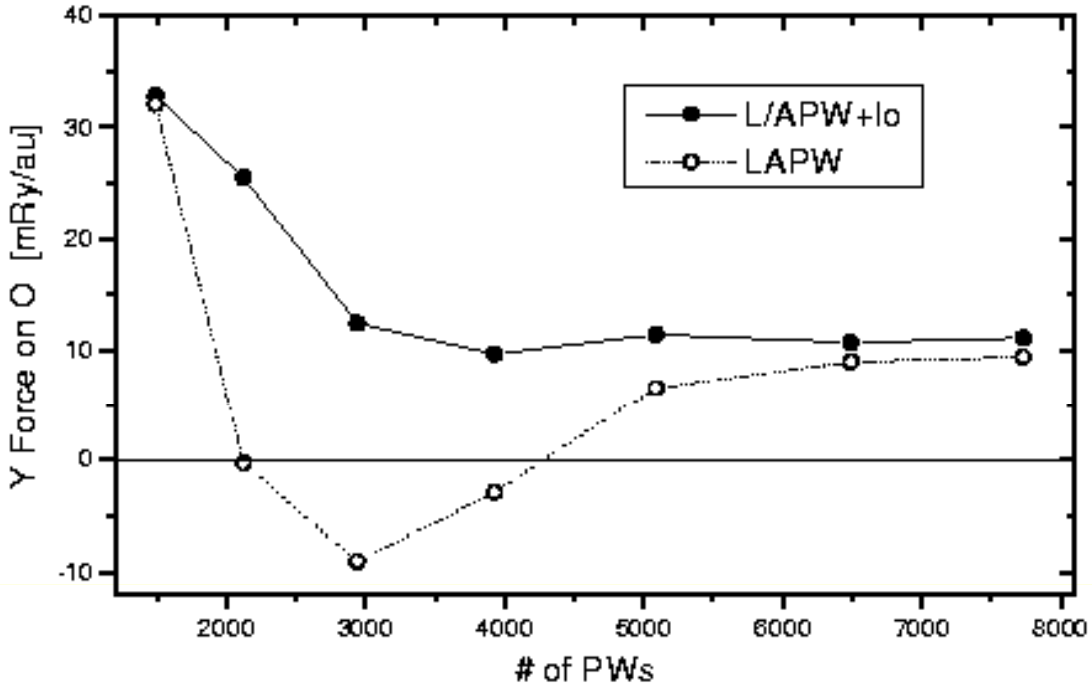
$$\Phi_{lo} = [A_{\ell m} u_\ell^{E_1} + B_{\ell m} \dot{u}_\ell^{E_1}] Y_{\ell m}(\hat{r})$$

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

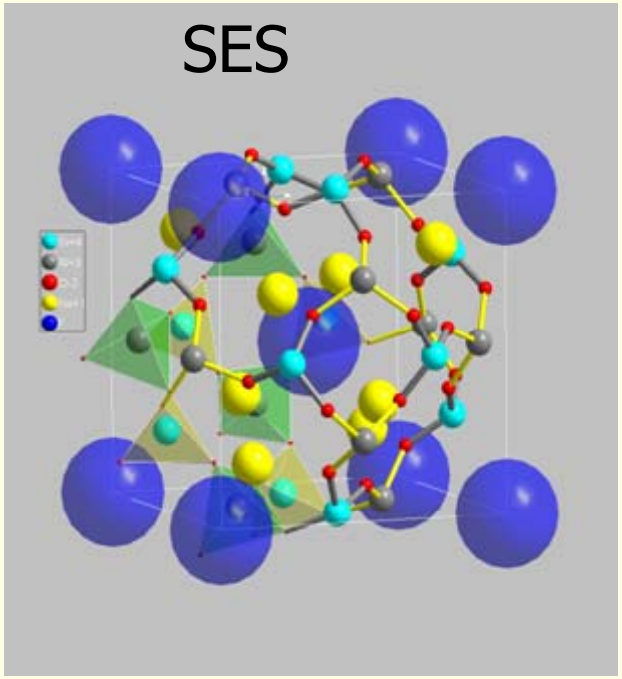
Representative Convergence:



e.g. force (F_y) 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



SES (sodium electro solodalite)

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

Summary: Linearization LAPW vs. APW

- Atomic partial waves
  - *LAPW*

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

  - *APW+lo*

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

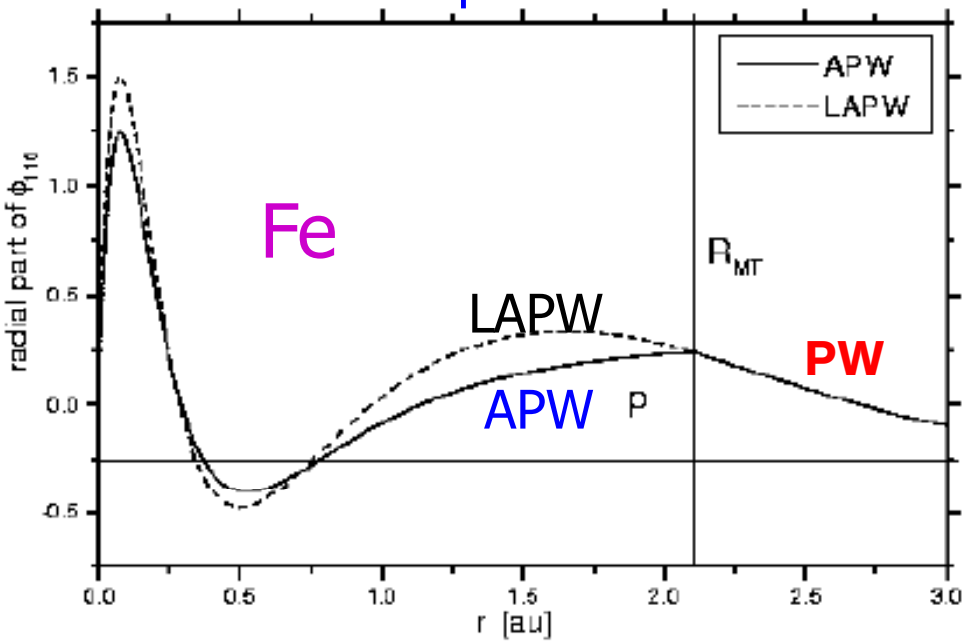
plus another type of local orbital (lo)

- Plane Waves (PWs)

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

- match at sphere boundary
  - *LAPW*
    value and slope $A_{\ell m}(k_n), B_{\ell m}(k_n)$
  - *APW*
    value $A_{\ell m}(k_n)$

Atomic sphere



Method implemented in WIEN2k

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)

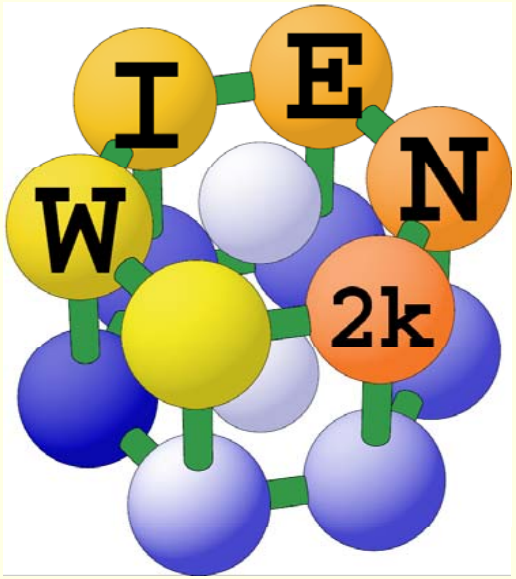
optimal solution: mixed basis

- 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

A summary is given in

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

The WIEN2k authors



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

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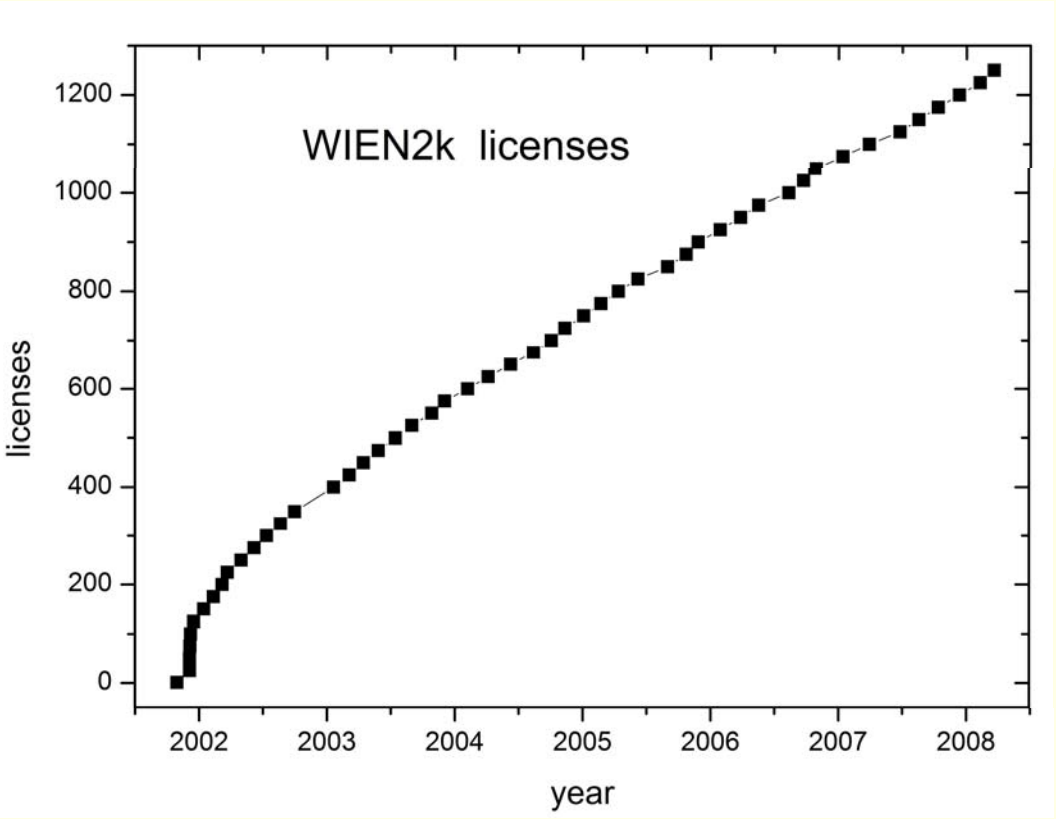
far east: ***AUS, China, India, JPN, Korea, Pakistan, Singapore,Taiwan (Beijing, Tokyo, Osaka, Kyoto, Sendai, Tsukuba, Hong Kong)***



50 industries ***(Canon, Eastman, Exxon, Fuji, Hitachi, IBM, Idemitsu Petrochem., Kansai, Komatsu, Konica-Minolta, A.D.Little, Mitsubishi, Mitsui Mining, Motorola, NEC, Nippon Steel, Norsk Hydro, Osram, Panasonic, Samsung, Seiko Epson, Siemens, Sony, Sumitomo,TDK,Toyota).***

The first publication of the WIEN code

FULL-POTENTIAL, LINEARIZED AUGMENTED PLANE WAVE PROGRAMS FOR CRYSTALLINE SYSTEMS

P. BLAHA, K. SCHWARZ, and P. SORANTIN

Institut für Technische Elektrochemie, Technische Universität Wien, A-1060 WIEN, Austria

and

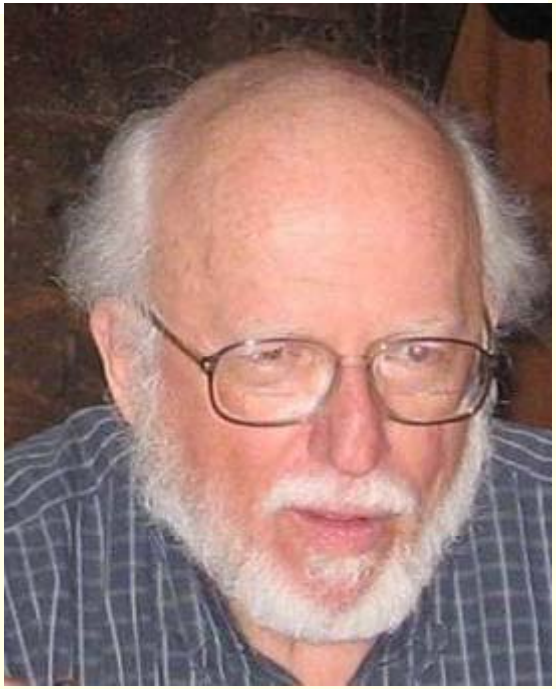
S.B. TRICKEY

Quantum Theory Project, Depts. of Physics and of Chemistry, University of Florida, Gainesville, FL 32611, USA

PROGRAM SUMMARY

Title of program: WIEN

Computer Physics Communications 59 (1990) 399–415



Main developers of WIEN2k

- Authors of WIEN2k

  P. Blaha, K. Schwarz, D. Kvasnicka, G. Madsen and J. Luitz
- Other contributions to WIEN2k
  - *C. Ambrosch (Univ. Leoben, Austria), optics*
  - *U. Birkenheuer (Dresden), wave function plotting*
  - *R. Dohmen und J. Pichlmeier (RZG, Garching), parallelization*
  - *C. Först (Vienna), afminput*
  - *K. Jorrisen (U.Washington) core-level spectra*
  - *R. Laskowski (Vienna), non-collinear magnetism*
  - *L.D. Marks (Northwestern U. , USA) density mixing*
  - *P. Novák and J. Kunes (Prague), LDA+U, SO*
  - *C. Persson (Uppsala), irreducible representations*
  - *V. Petricek (Prague) 230 space groups*
  - *M. Scheffler (Fritz Haber Inst., Berlin), forces, optimization*
  - *D.J.Singh (NRL, Washington D.C.), local orbitals (LO), APW+lo*
  - *E. Sjöstedt and L Nordström (Uppsala, Sweden), APW+lo*
  - *J. Sofo and J.Fuhr (Penn State, USA), Bader analysis*
  - *B. Sonalkar (Vienna), non-linear optics*
  - *B. Yanchitsky and A. Timoshevskii (Kiev), space group*
- and many others ….

A series of WIEN workshops were held

1st	Vienna	April	1995	Wien95
2nd	Vienna	April	1996	
3rd	Vienna	April	1997	Wien97
4st	Trieste, Italy	June	1998	
5st	Vienna	April	1999	
6th	Vienna	April	2000	
7th	Vienna	Sept.	2001	Wien2k
8th	Esfahan, Iran	April	2002	
	Penn State, USA	July	2002	
9th	Vienna	April	2003	
10th	Penn State, USA	July	2004	
11th	Kyoto, Japan	May	2005	
	IPAM, Los Angeles, USA	Nov.	2005	
12th	Vienna	April	2006	
13th	Penn State, USA	June	2007	
14th	Singapore	July	2007	
15th	Vienna	March	2008	

(L)APW methods

APW + local orbital method
(linearized) augmented plane wave method

Total wave function $\Psi_k = \sum_{K_n} C_{k_n} \phi_{k_n}$ n...50-100 PWs /atom

Variational method: $< E > = \frac{< \Psi \mid H \mid \Psi >}{< \Psi \mid \Psi >}$ $\frac{\delta < E >}{\delta C_{k_n}} = 0$

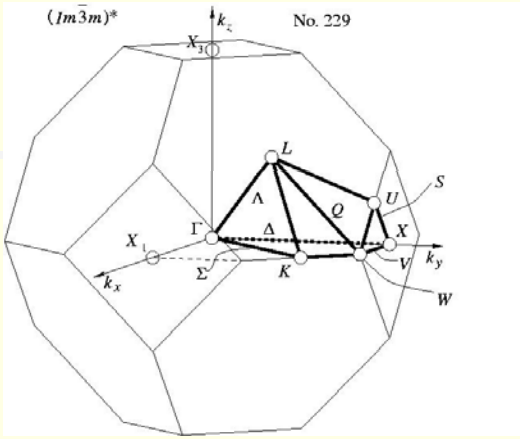
upper bound | minimum

Generalized eigenvalue problem: $H C = E S C$

Diagonalization of (real or complex) matrices of size 10.000 to 50.000 (up to 50 Gb memory)

Structure: a,b,c,α,β,γ, R_α , ...

unit cell atomic positions



Structure optimization

iteration *i*

SCF

DFT Kohn-Sham

$V(\rho) = V_C + V_{xc}$ **Poisson, DFT**

$E^{i+1} - E^i < \varepsilon$

no

yes

E^{tot}, force

Minimize E, force→0

properties

k ∈ **IBZ** (irred.Brillouin zone)

k

Kohn Sham

$$[-\nabla^2 + V(\rho)]\psi_k = E_k\psi_k$$

$$\psi_k = \sum_{k_n} C_{k_n}\Phi_{k_n}$$

Variational method $\frac{\delta < E >}{\delta C_{k_n}} = 0$

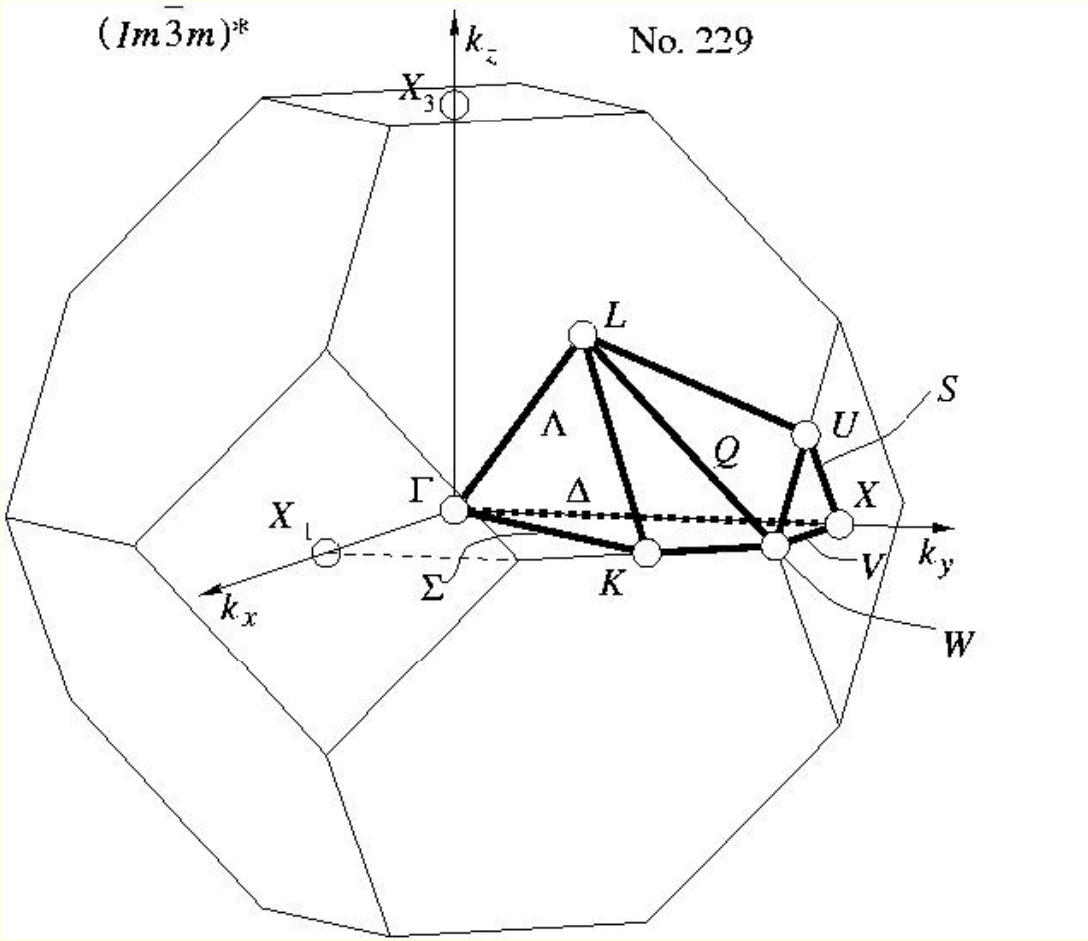
Generalized eigenvalue problem

$$HC = ESC$$

$$\rho = \sum_{E_k \le E_F} \psi_k^* \psi_k$$

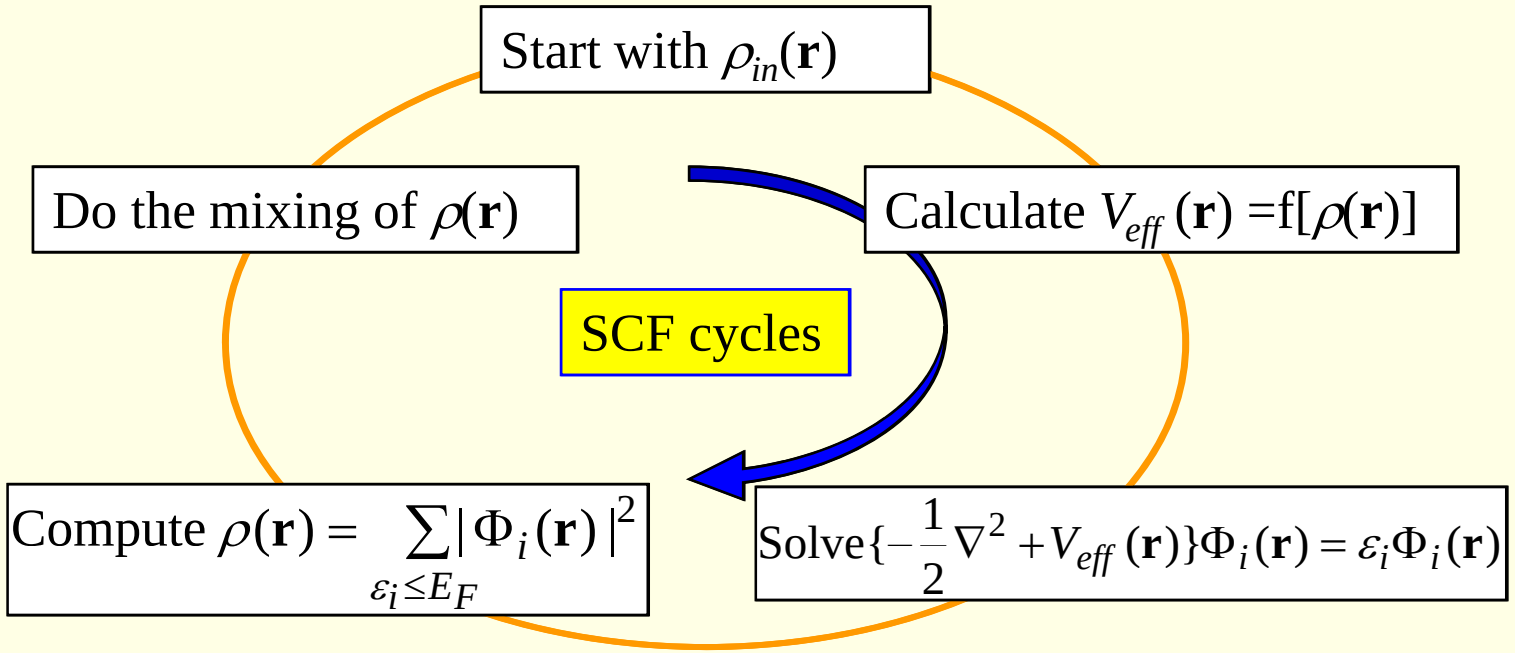
The Brillouin zone (BZ)

- Irreducible BZ (IBZ)
  - *The irreducible wedge*
  - *Region, from which the whole BZ can be obtained by applying all symmetry operations*
- Bilbao Crystallographic Server:
  - *www.cryst.ehu.es/cryst/*
  - *The IBZ of all space groups can be obtained from this server*
  - *using the option KVEC and specifying the space group (e.g. No.225 for the fcc structure leading to bcc in reciprocal space, No.229)*



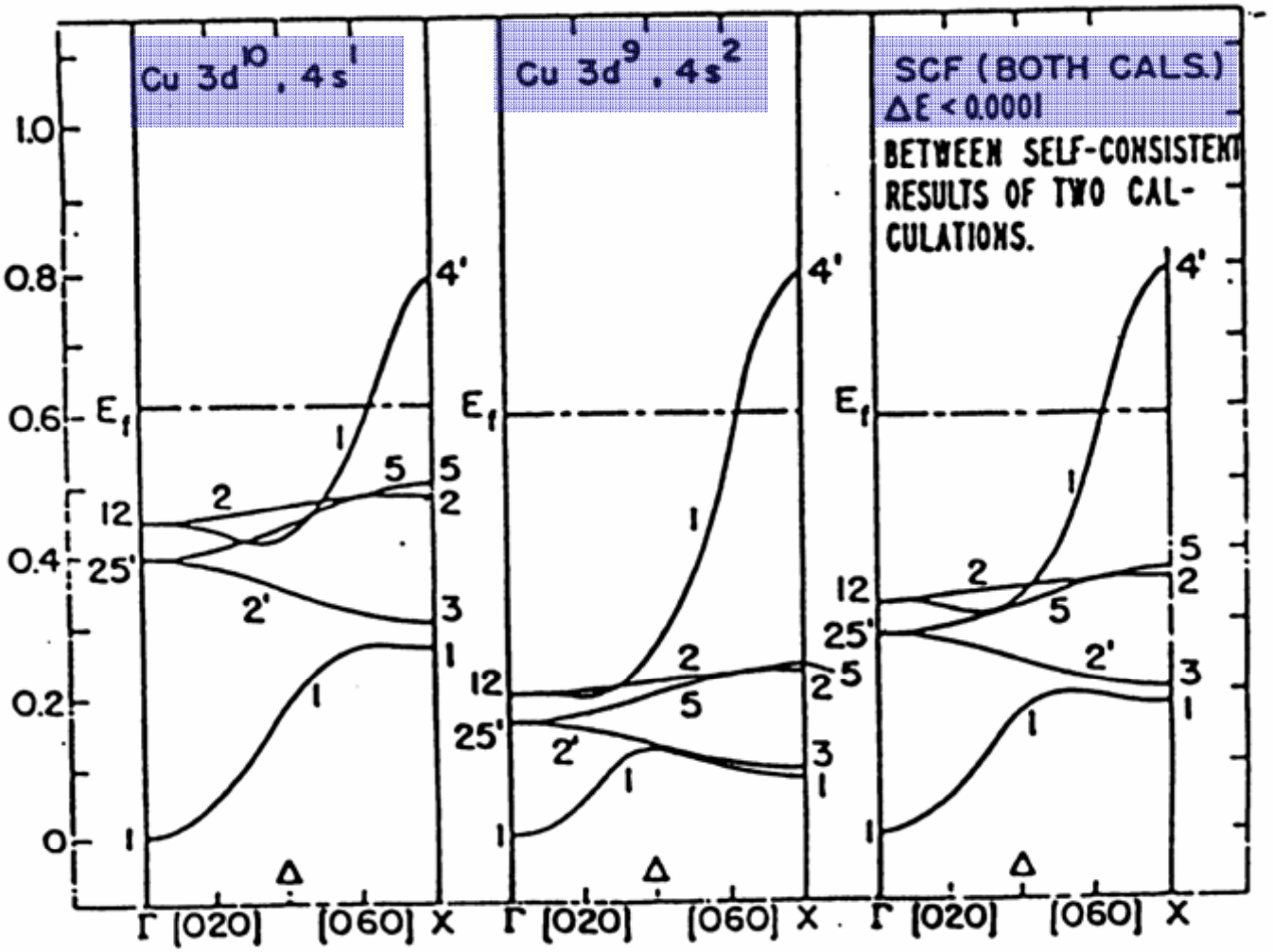
Self-consistent field (SCF) calculations

- In order to solve $H\Psi=E\Psi$ we need to know the potential V(r)
- for V(r) we need the electron density $\rho(r)$
- the density $\rho(r)$ can be obtained from $\Psi(r)^*\Psi(r)$
- ?? $\Psi(r)$ is unknown before $H\Psi=E\Psi$ is solved ??



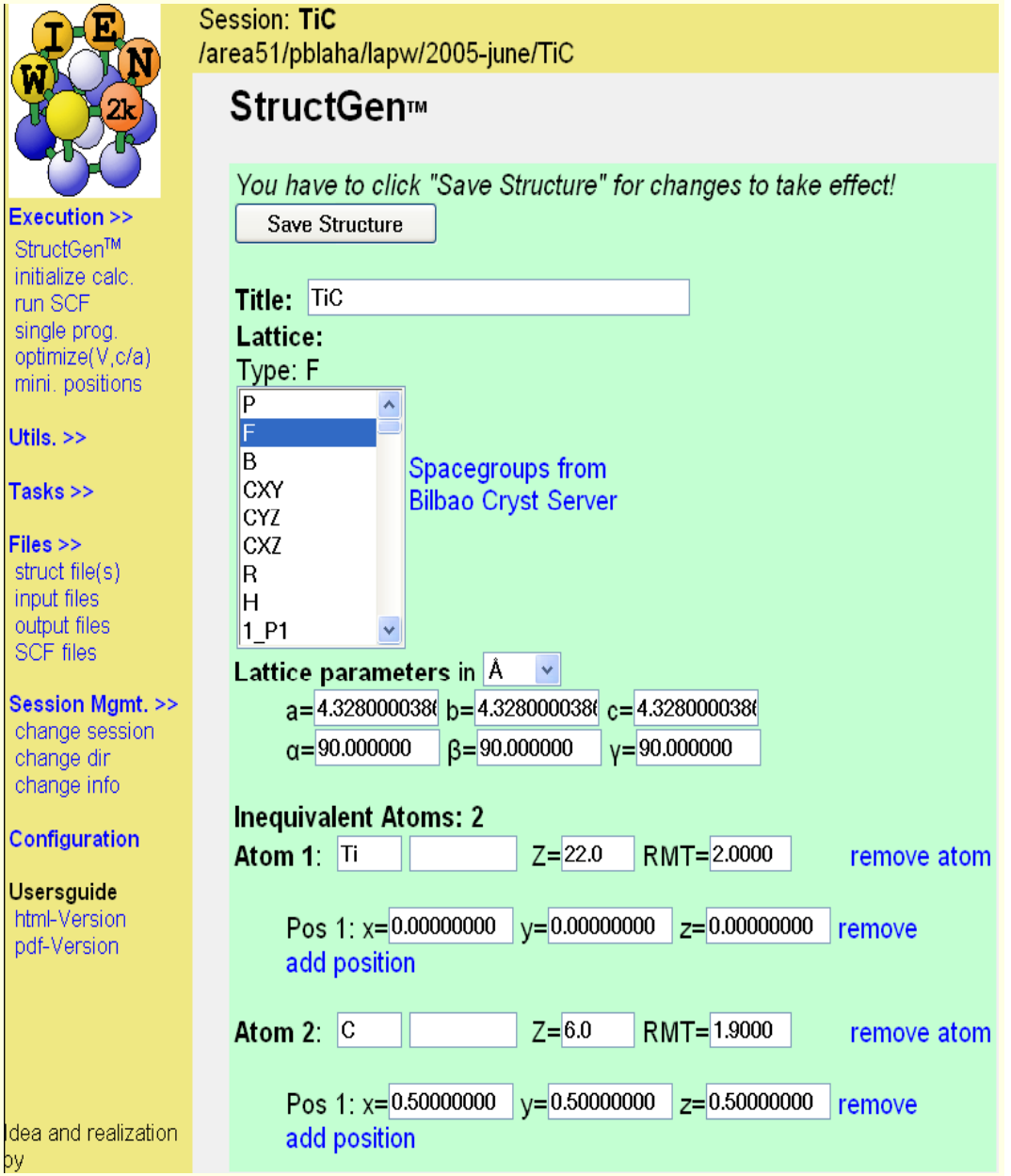
Effects of SCF

Band structure of fcc Cu



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*



Spacegroup $P4_2/mnm$

Structure given by:

spacegroup

lattice parameter

positions of atoms (basis)

Rutile TiO_2:

$P4_2/mnm$ (136)

a=8.68, c=5.59 bohr

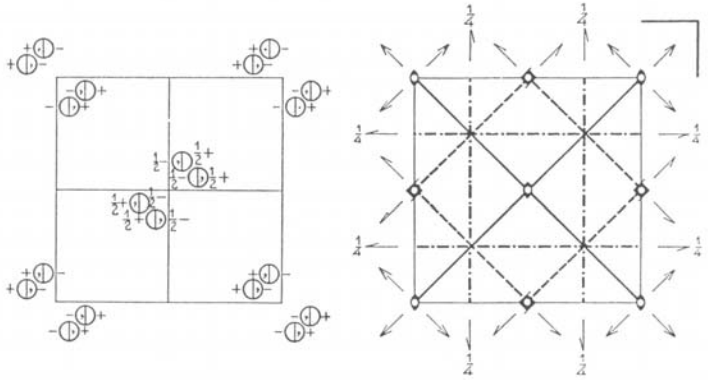
Ti: (0,0,0)

O: (0.304,0.304,0)

2a

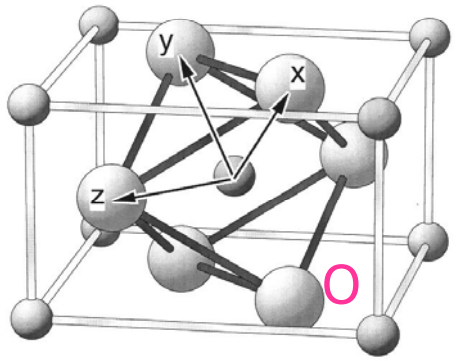
4f

$P4_2/mnm$ D_{4h}^{14} No. 136 $P\,4_2/m\,2_1/n\,2/m$ $4/m\,m\,m$ Tetragonal



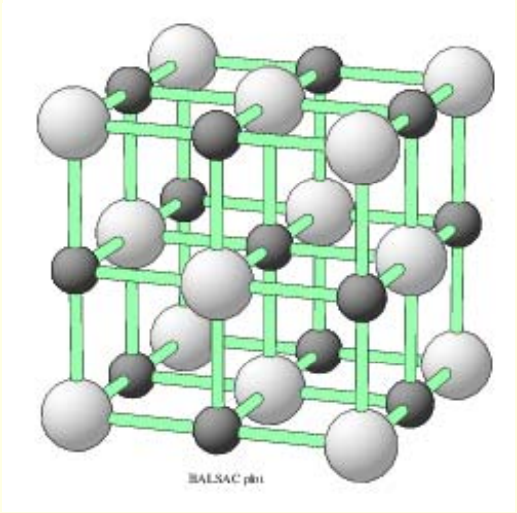
Origin at centre (*mmm*)

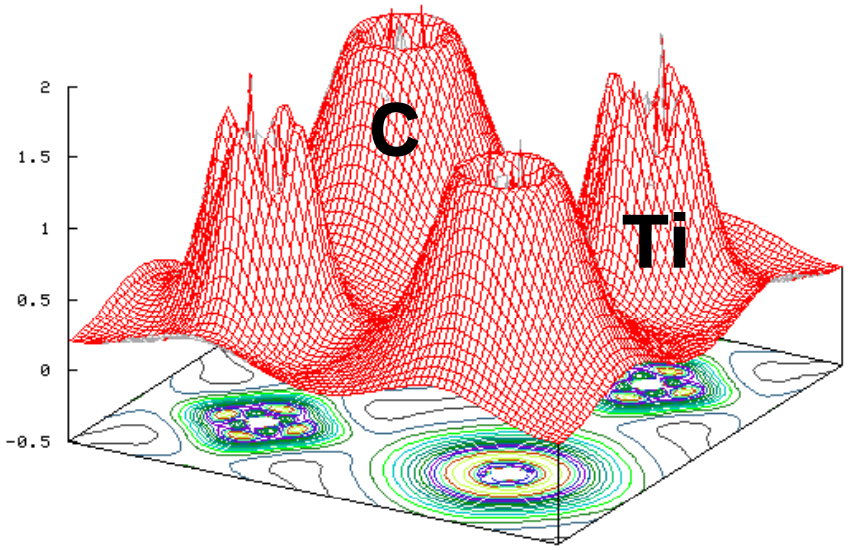
Number of positions, Wyckoff notation, and point symmetry			Co-ordinates of equivalent positions	Conditions limiting possible reflections
				General:
16	*k*	1	x,y,z; $\bar{x},\bar{y},z$; $\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z$; $\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}+z$; $x,y,\bar{z}$; $\bar{x},\bar{y},\bar{z}$; $\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}-z$; $\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z$; y,x,z; $\bar{y},\bar{x},z$; $\frac{1}{2}+y,\frac{1}{2}-x,\frac{1}{2}+z$; $\frac{1}{2}-y,\frac{1}{2}+x,\frac{1}{2}+z$; $y,x,\bar{z}$; $\bar{y},\bar{x},\bar{z}$; $\frac{1}{2}+y,\frac{1}{2}-x,\frac{1}{2}-z$; $\frac{1}{2}-y,\frac{1}{2}+x,\frac{1}{2}-z$.	*hkl*: No conditions *hk*0: No conditions 0*kl*: $k+l=2n$ *hhl*: No conditions
				Special: as above, plus
8	*j*	*m*	x,x,z; $\bar{x},\bar{x},z$; $\frac{1}{2}+x,\frac{1}{2}-x,\frac{1}{2}+z$; $\frac{1}{2}-x,\frac{1}{2}+x,\frac{1}{2}+z$; $x,x,\bar{z}$; $\bar{x},\bar{x},\bar{z}$; $\frac{1}{2}+x,\frac{1}{2}-x,\frac{1}{2}-z$; $\frac{1}{2}-x,\frac{1}{2}+x,\frac{1}{2}-z$.	no extra conditions
8	*i*	*m*	$x,y,0$; $\bar{x},\bar{y},0$; $\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}$; $\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}$; $y,x,0$; $\bar{y},\bar{x},0$; $\frac{1}{2}+y,\frac{1}{2}-x,\frac{1}{2}$; $\frac{1}{2}-y,\frac{1}{2}+x,\frac{1}{2}$.	
8	*h*	2	$0,\frac{1}{2},z$; $0,\frac{1}{2},\bar{z}$; $0,\frac{1}{2},\frac{1}{2}+z$; $0,\frac{1}{2},\frac{1}{2}-z$; $\frac{1}{2},0,z$; $\frac{1}{2},0,\bar{z}$; $\frac{1}{2},0,\frac{1}{2}+z$; $\frac{1}{2},0,\frac{1}{2}-z$.	*hkl*: $h+k=2n$; $l=2n$
4	*g*	*mm*	$x,\bar{x},0$; $\bar{x},x,0$; $\frac{1}{2}+x,\frac{1}{2}+x,\frac{1}{2}$; $\frac{1}{2}-x,\frac{1}{2}-x,\frac{1}{2}$.	
4	*f*	*mm*	$x,x,0$; $\bar{x},\bar{x},0$; $\frac{1}{2}+x,\frac{1}{2}-x,\frac{1}{2}$; $\frac{1}{2}-x,\frac{1}{2}+x,\frac{1}{2}$.	
4	*e*	*mm*	$0,0,z$; $0,0,\bar{z}$; $\frac{1}{2},\frac{1}{2},\frac{1}{2}+z$; $\frac{1}{2},\frac{1}{2},\frac{1}{2}-z$.	
4	*d*	$\bar{4}$	$0,\frac{1}{2},\frac{1}{4}$; $\frac{1}{2},0,\frac{1}{4}$; $0,\frac{1}{2},\frac{3}{4}$; $\frac{1}{2},0,\frac{3}{4}$.	
4	*c*	2/*m*	$0,\frac{1}{2},0$; $\frac{1}{2},0,0$; $0,\frac{1}{2},\frac{1}{2}$; $\frac{1}{2},0,\frac{1}{2}$.	
2	*b*	*mmm*	$0,0,\frac{1}{2}$; $\frac{1}{2},\frac{1}{2},0$.	
2	*a*	*mmm*	$0,0,0$; $\frac{1}{2},\frac{1}{2},\frac{1}{2}$.	



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 ☐

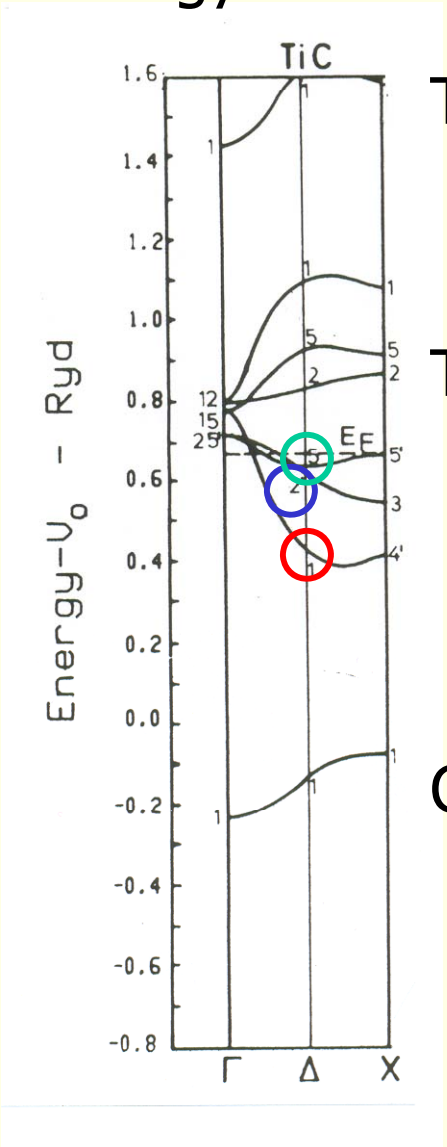
Min -0.5 Max 2 Delta 0.1

plot electron density

edit TiC.in2 reset EMIN

TiC, three valence states at Δ

Energy bands

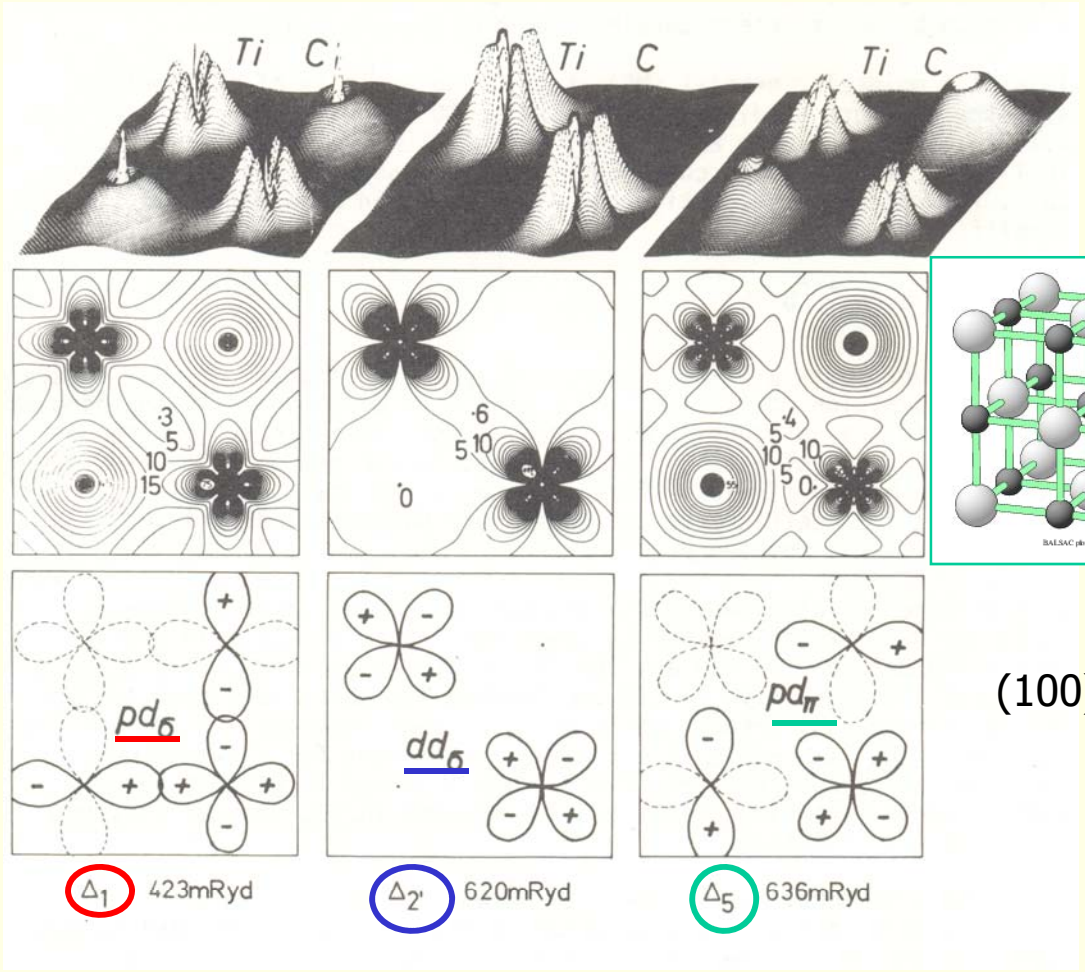


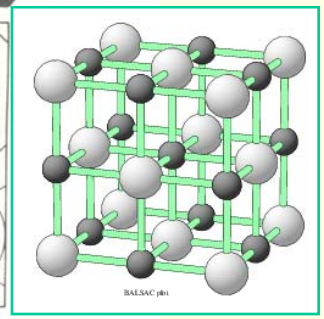
Ti-4s

Ti-3d

C-2p

C-2s



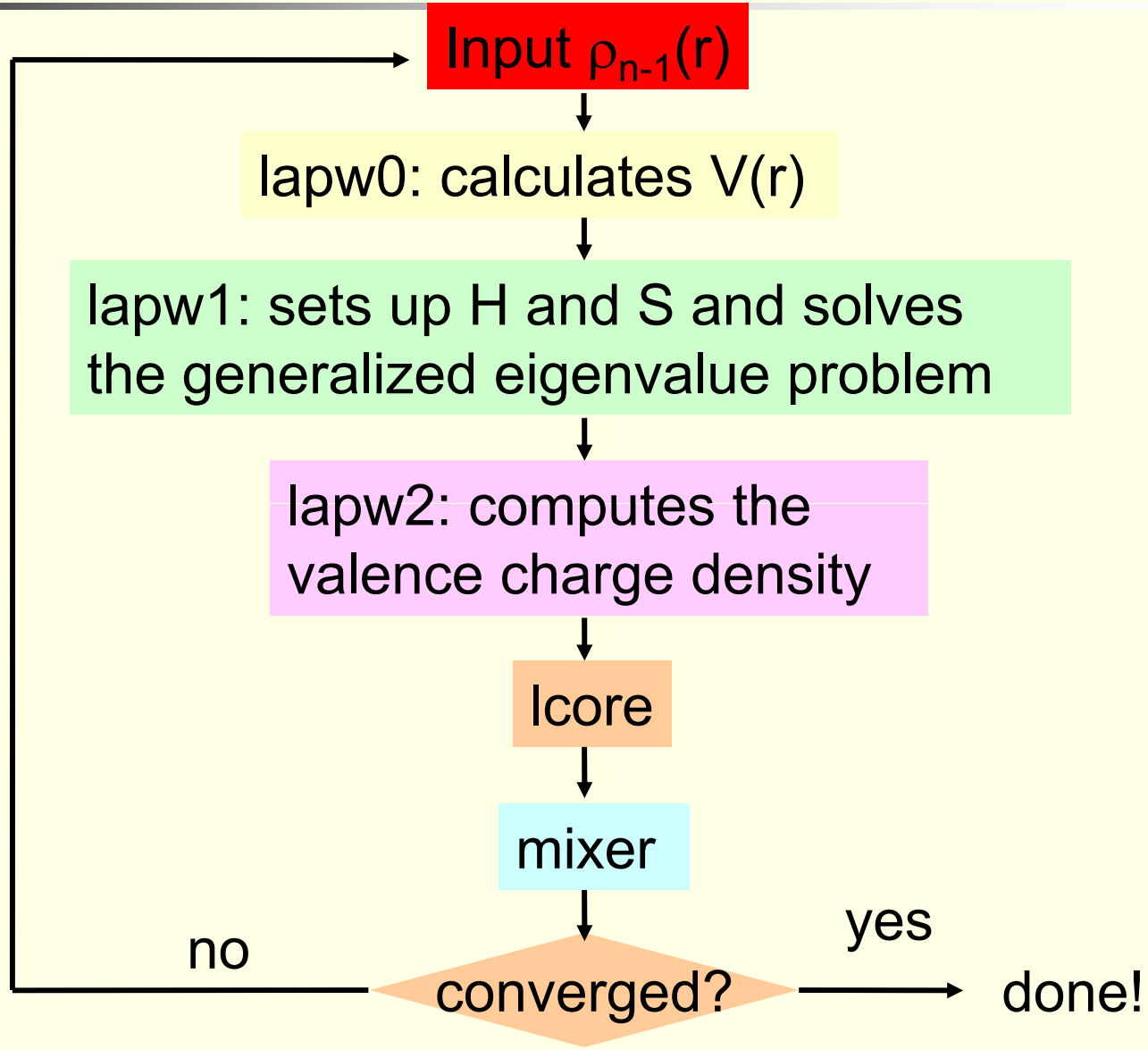


(100) plane

C_p-Ti_d σ Ti_d-Ti_d σ C_p-Ti_d □

P.Blaha, K.Schwarz,
Int.J.Quantum Chem. 23, 1535 (1983)

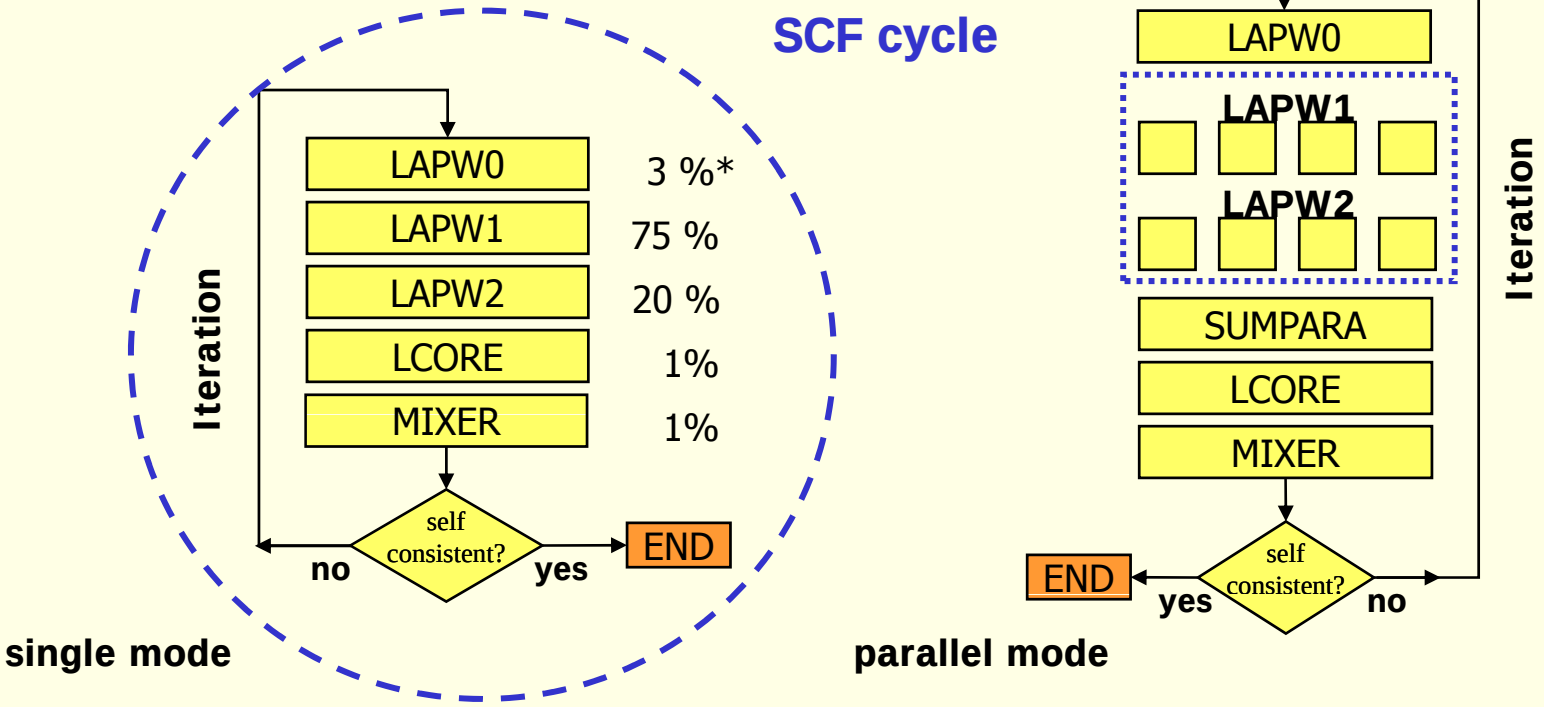
Flow Chart of WIEN2k (SCF)



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

Workflow of a WIEN2k calculation

- individual FORTRAN programs linked by shell-scripts
- the output of one program is input for the next
- lapw1/2 can run in parallel on many processors



k-point parallelization

* fraction of total computation time