From APW to LAPW to (L)APW+lo

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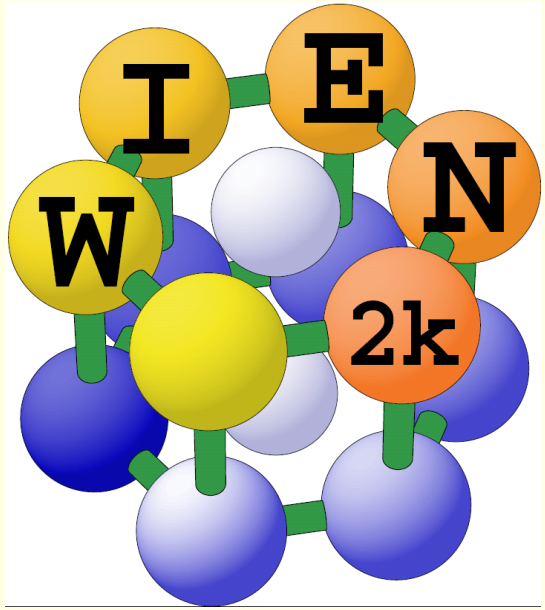


Computational Chemistry Group

- Authors of WIEN2k
  - *Peter Blaha* — *WIEN2k*
  - *Karlheinz Schwarz* — *WIEN2k*
  - *Dieter Kvasnicka* — *mathematician, computer scientist*
  - *Georg Madsen* — *APW+lo, crystallographer*
  - *Joachim Luitz* — *GUI, chemist*
- Other members working on WIEN2k
  - *Bernd Sonalkar* — *non linear optics (NLO)*
  - *Johannes Schweifer* — *Grid computing (w2grid)*
  - *Thomas Gallauner* — *Nanoparticles*
  - *Günther Schmidt* — *structure optimization, sulfosalts*
  - *Robert Laskowski* — *LDA+U (physicists)*
  - *Fabien Tran* — *exchange correlation, HF, hybrid*
  - *Christian Spiel* — *mixed valence compounds*
  - *Andreas Mattern* — *high-spin low-spin transitions*
  - *Othmar Koch* — *general eigensolver (mathematician)*

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

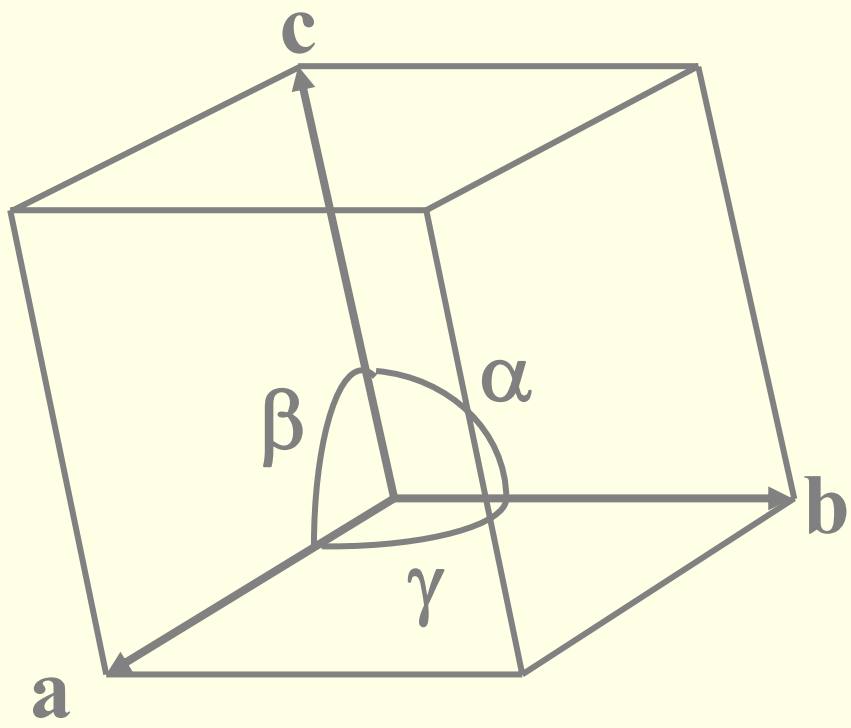
Unit cell: a volume in space that fills space entirely when translated by all lattice vectors.

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)



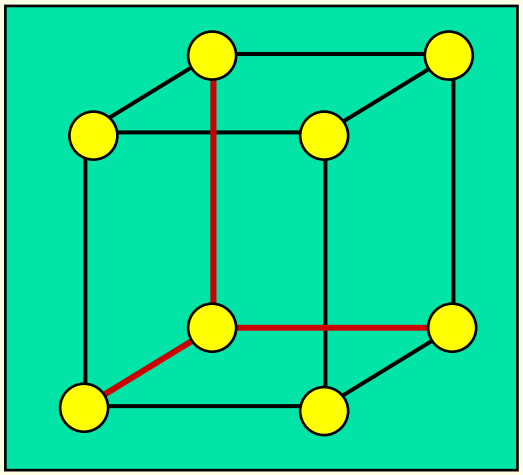
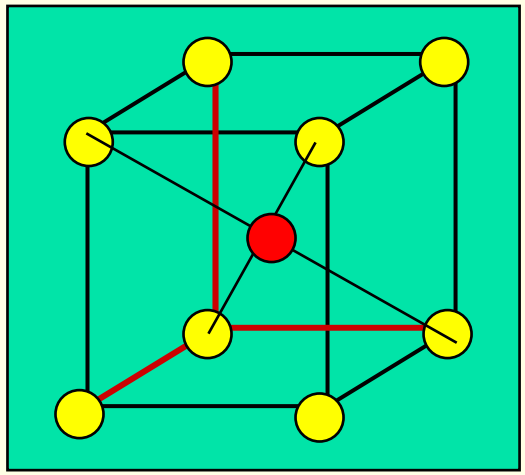
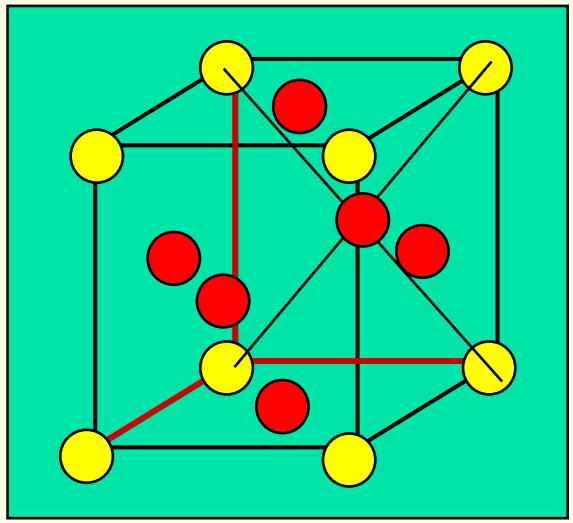
A unit cell containing one lattice point is called primitive cell.

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)**

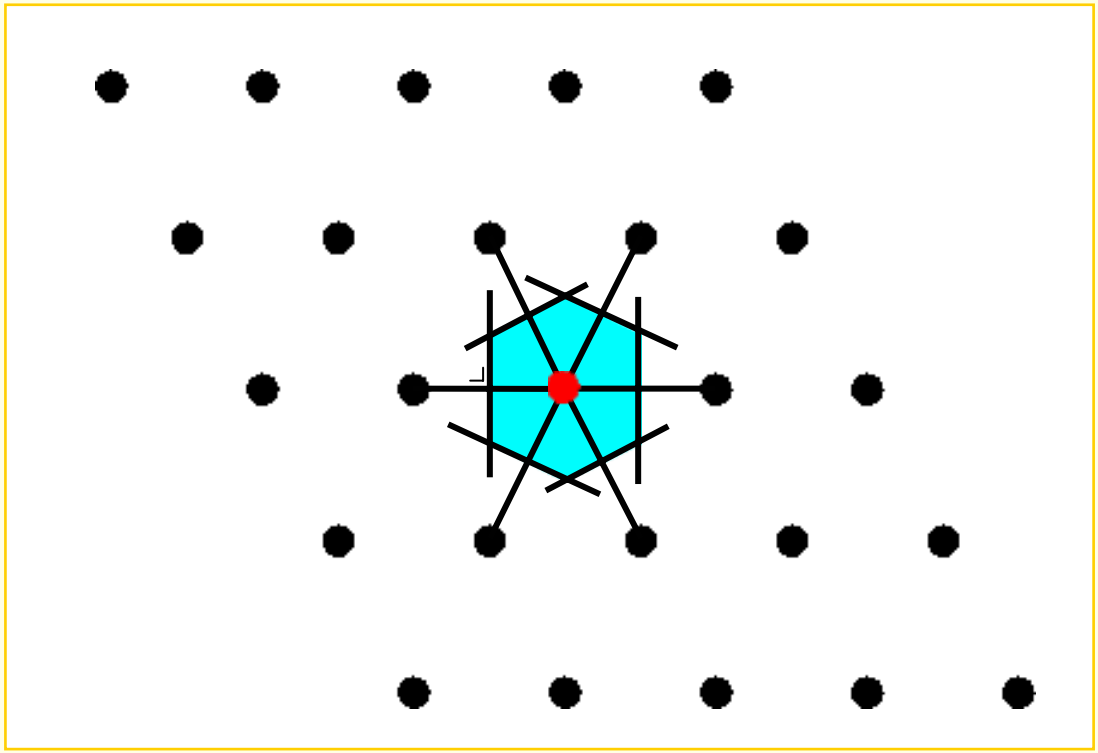
3D lattice types:

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:

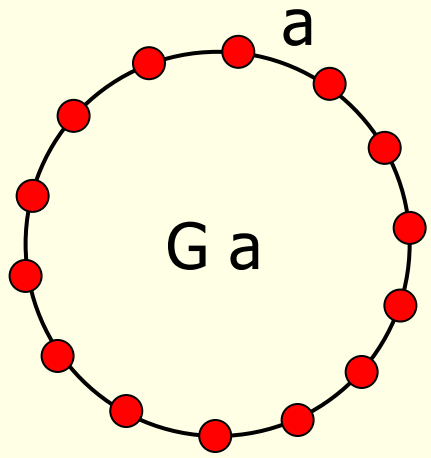
$$\tau^g\Psi(x) = \Psi(x+ga) = \mu^g\Psi(x)$$

periodic boundary conditions:

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

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

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



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

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

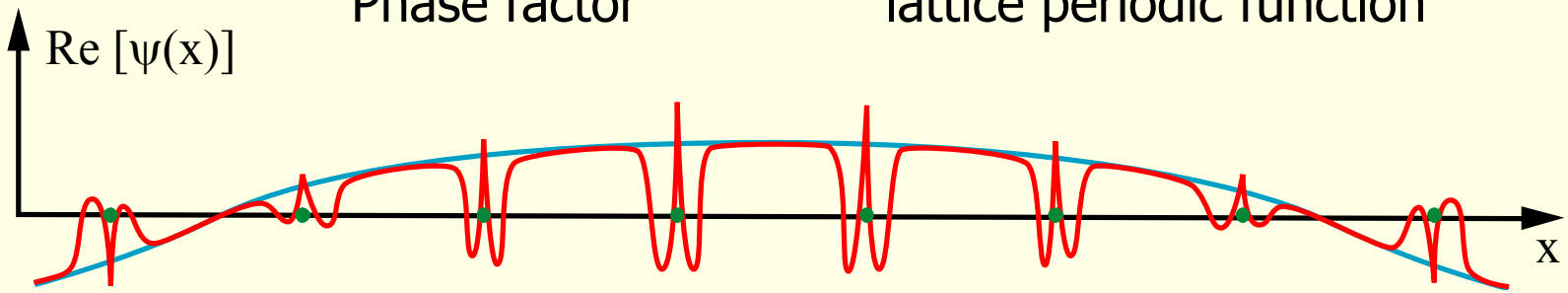
$$Bloch\ condition: \quad \Psi(x + a) = e^{ika}\Psi(x) = \Psi_k$$

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

Form of potential

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

Relativistic treatment of the electrons

non relativistic
semi-relativistic
fully-relativistic

exchange and correlation potential

Hartree-Fock (+correlations)
Density functional theory (DFT)
Local density approximation (**LDA**)
Generalized gradient approximation (**GGA**)
Beyond LDA: e.g. **LDA+U**

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

Schrödinger - equation

Representation of solid

non periodic
(cluster)
periodic
(unit cell)

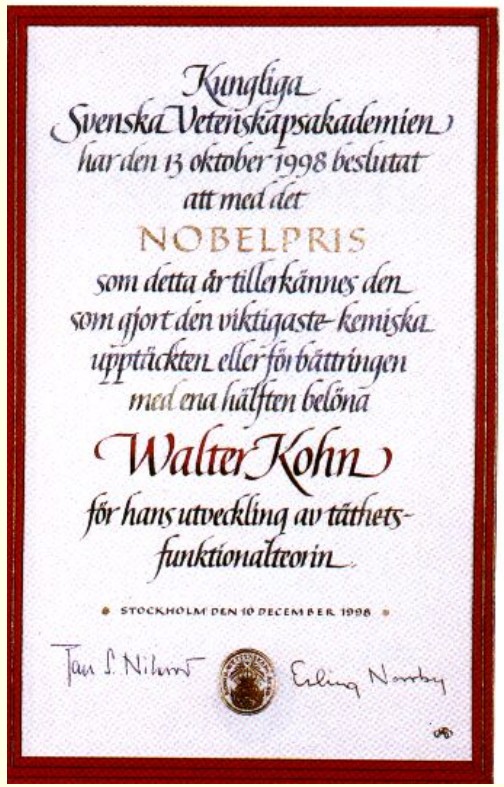
Basis functions

plane waves : PW
augmented plane waves : APW
atomic oribtals. e.g. Slater (STO), Gaussians (GTO), LMTO, numerical basis

Treatment of spin

Non-spinpolarized
Spin polarized
(with certain magnetic order)

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}

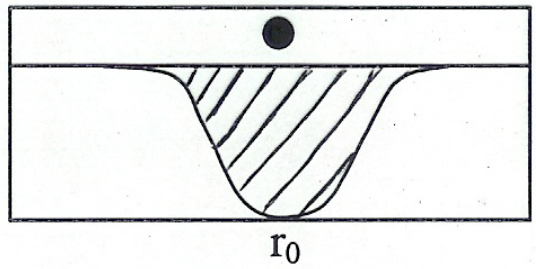
$E_{coulomb}$ E_{ee}

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 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

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

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

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

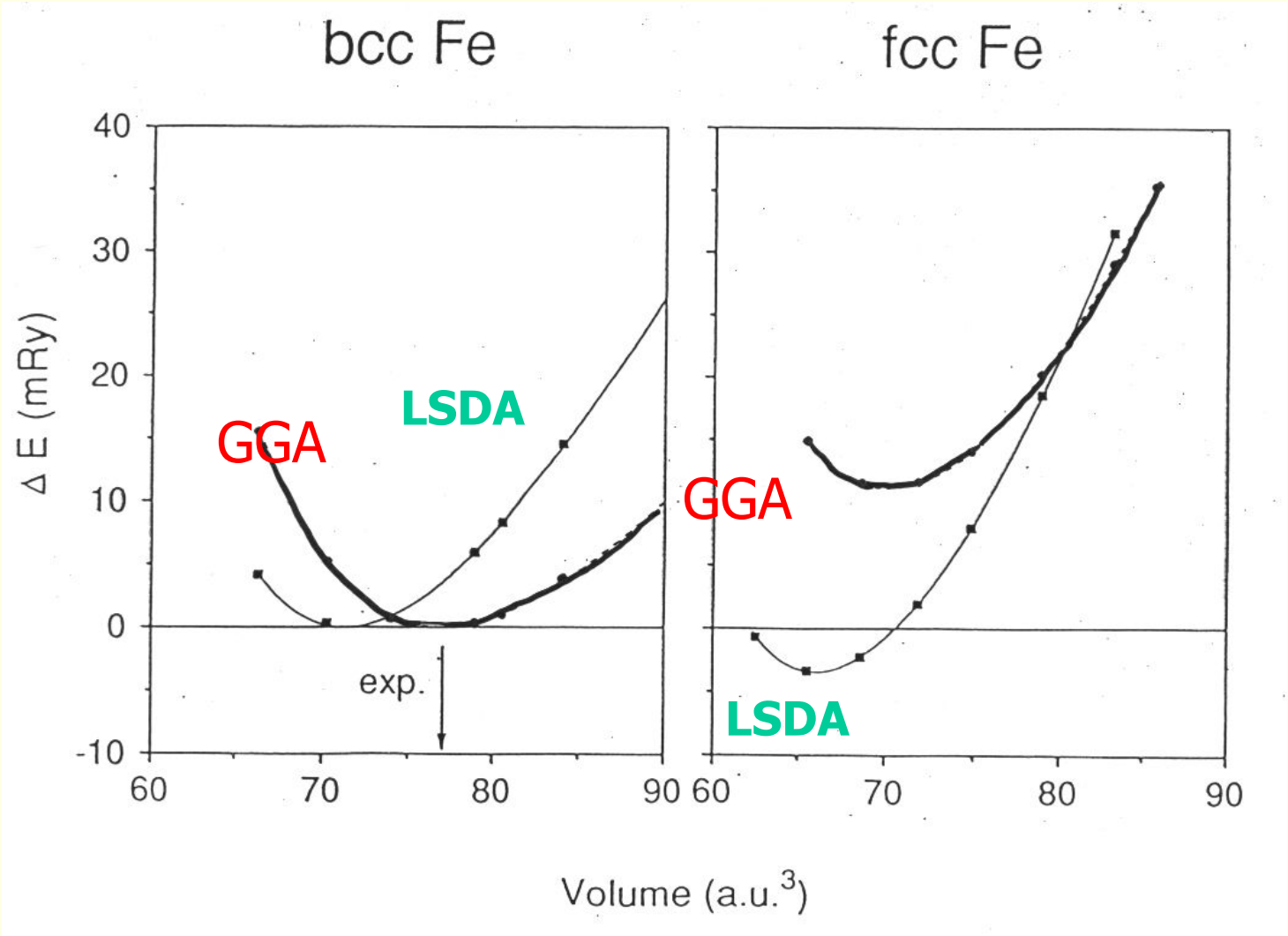
$$E_{xc}^{LDA} \propto \int \rho(r)\ \varepsilon_{xc}^{\text{hom.}}[\rho(r)]\ dr$$

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

LDA and **GGA** treat both, exchange and correlation effects, but approximately

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

DFT ground state of iron



LSDA

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

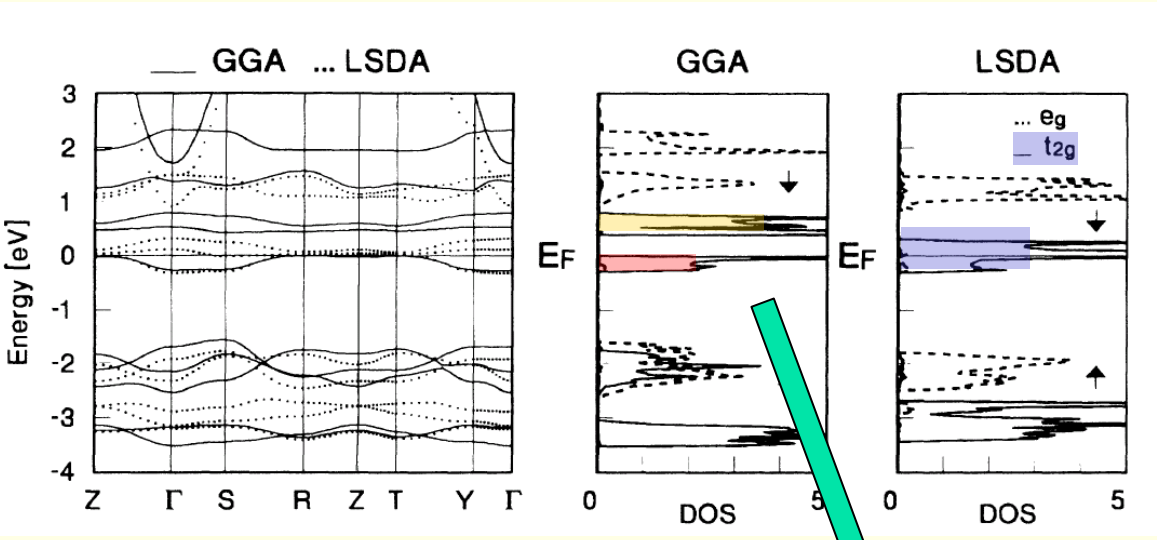
GGA

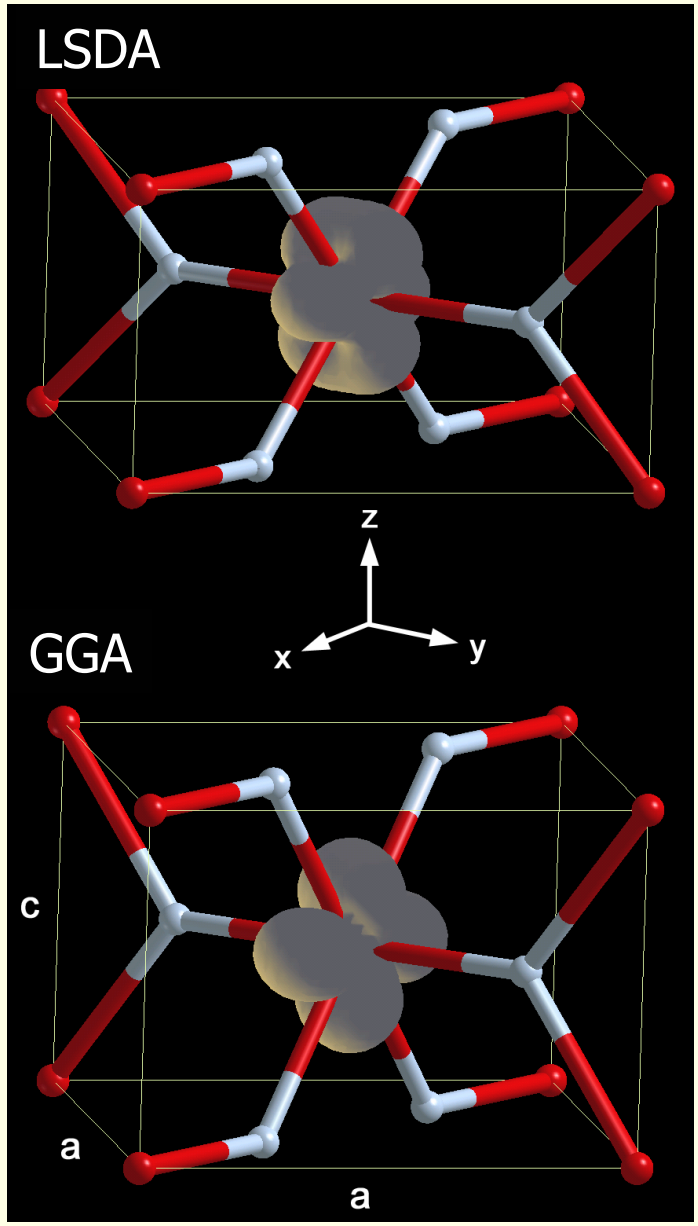
- *FM*
- *bcc*
- *Correct lattice constant*

Experiment

- *FM*
- *bcc*

FeF_2: GGA works surprisingly well





Fe-EFG in FeF_2:

LSDA: 6.2

GGA: 16.8

exp: 16.5

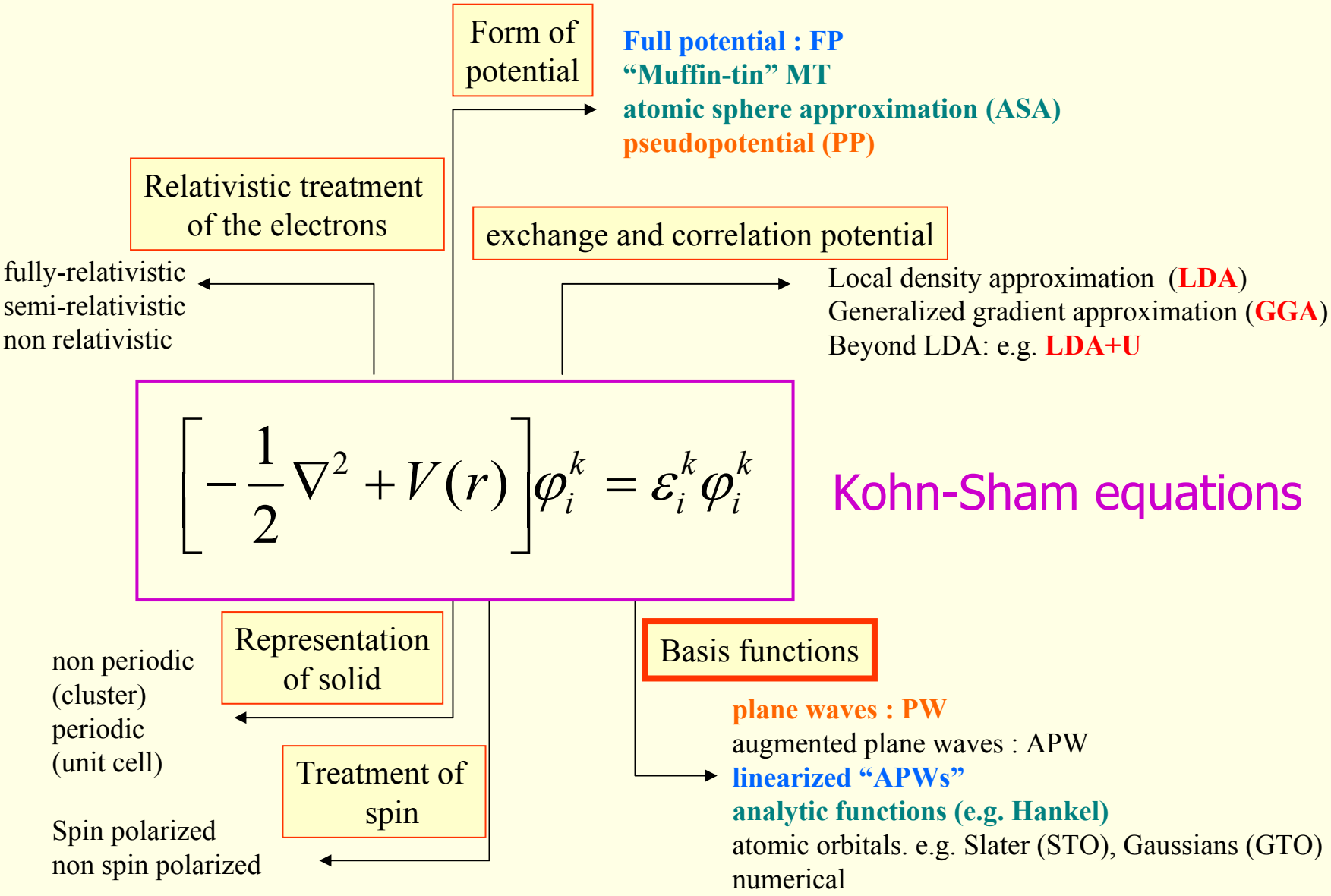
FeF_2: GGA splits t_{2g} into a_{1g} and e_g'

Austria knows about the importance of DFT

(thanks to Claudia Ambrosch (Graz))

GGA follows LDA

Overview of DFT concepts



Kohn Sham equations

How

to solve

them ?

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"*
    - different methods use different basis sets !

$$\Psi_k = \sum_{K_n} c_{k_n} \Phi_{k_n}$$

  - *finding the "best" wave function using the variational principle:*

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

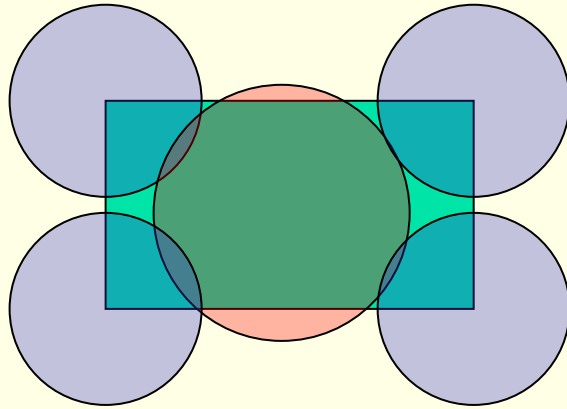
  - *this leads to the famous "Secular equations", i.e. a set of linear equations which in matrix representation is called "generalized eigenvalue problem"*

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

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

Basis Sets for Solids

- plane waves (pseudo potentials)
- space partitioning (augmentation) methods
  - *LMTO (linear muffin tin orbitals)*
    - ASA approx., linearized numerical radial function
    + Hankel- and Bessel function expansions
  - *ASW (augmented spherical wave)*
    - similar to LMTO
  - *FP-LMTO (full-potential LMTO)*
    - similar to LAPW, space partitioned with non-overlapping spheres
  - *KKR (Kohn, Koringa, 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)*

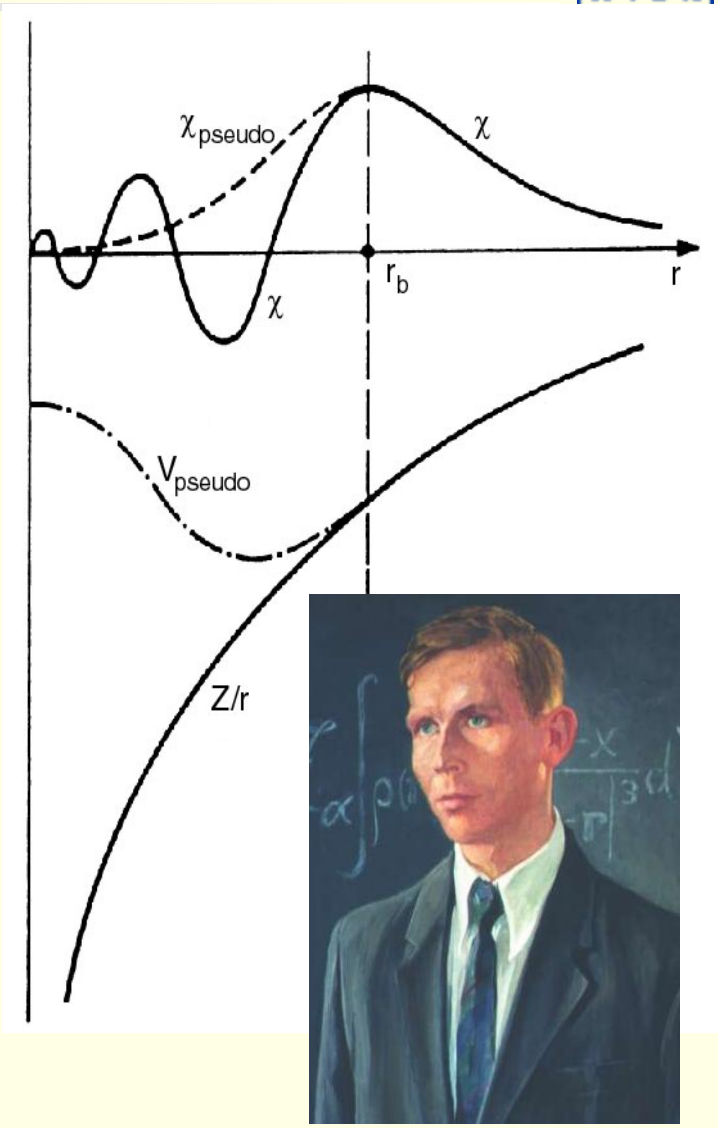


pseudopotential plane wave methods

- 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

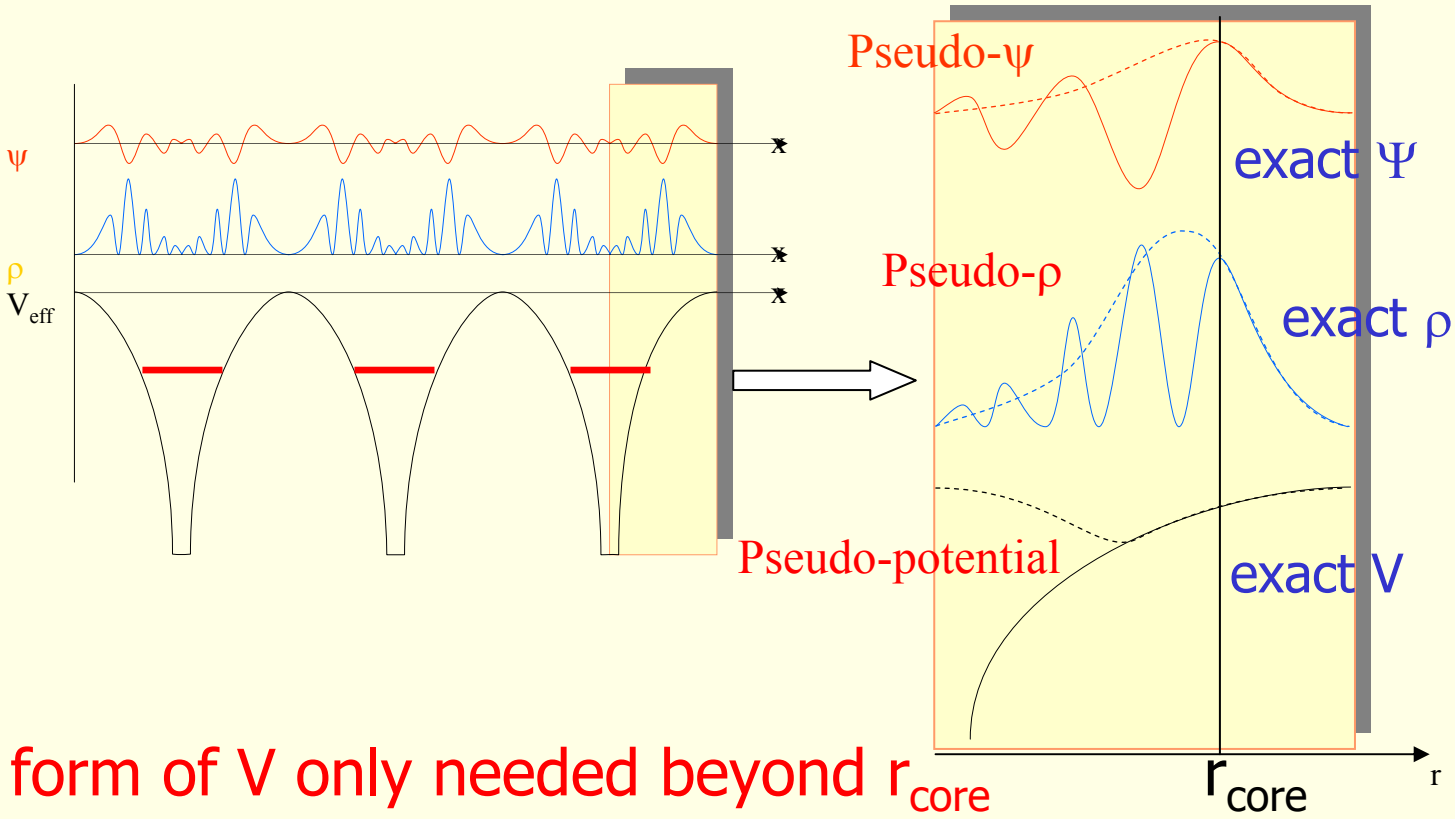
- let´s get rid of all core electrons and these oscillations by replacing the strong ion–electron potential by a much weaker (and physically dubious) *pseudopotential*

- 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}

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

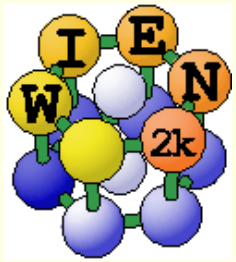
upper bound | minimum

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)

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*

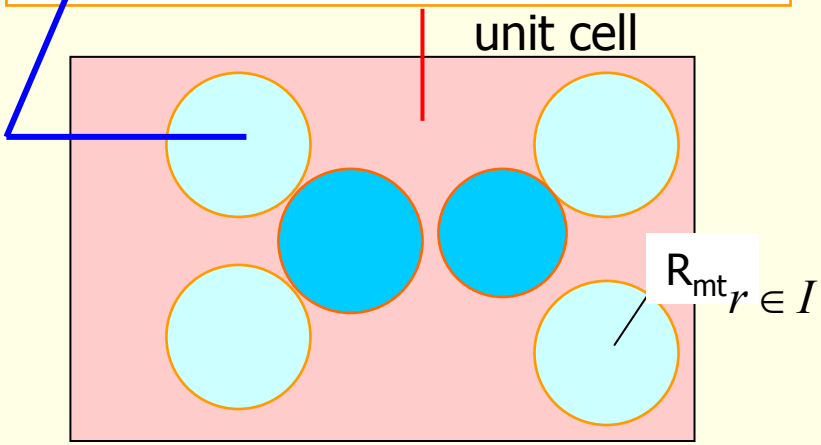


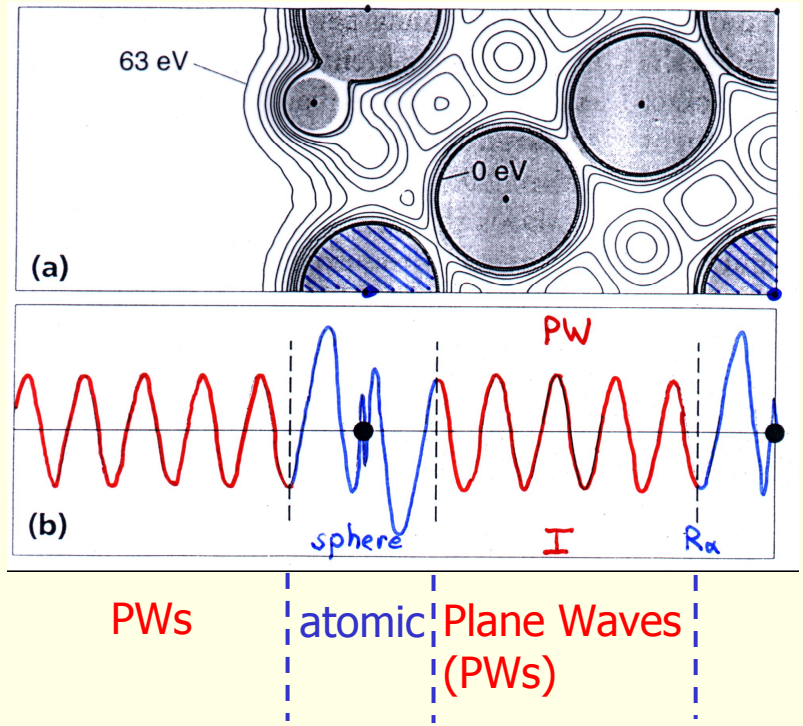
K.Schwarz, P.Blaha, G.K.H.Madsen, Comp.Phys.Commun.**147**, 71-76 (2002)

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

- Assuming a spherically symmetric potential we can use the Ansatz:

$$\psi_{n\ell m}(r,\vartheta,\varphi) = R_{n\ell}(r)\, Y_\ell^m(\vartheta,\varphi)$$

- This leads to the radial Schrödinger equation:

$$-\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR_{n\ell}}{dr}\right)+\left[\underbrace{\frac{\ell(\ell+1)}{r^2}+V(r)-E}_{g(r)}\right]R_{n\ell}(r)=0$$

$$\textit{Substitute}: \quad R(r)=\frac{P(r)}{r} \qquad P'=\frac{dP}{dr}$$

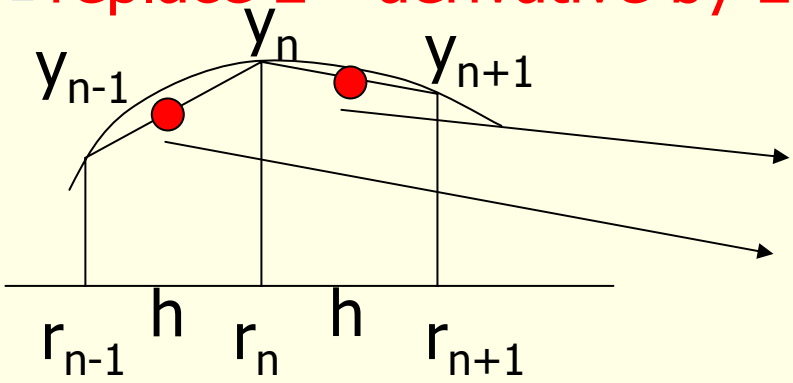
$$-\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{\mathrm{P'r}-P}{r^2}\right]+g(r)\frac{P}{r}=0$$

$$-\frac{1}{r^2}\left[\mathrm{P''r}+P'-P'\right]+g(r)\frac{P}{r}=0$$

$$P''=g(r)P$$

numerical calculation of P″

- assume an equidistant radial mesh ($h=r_{n+1}-r_n$; $y_n=y(r_n)$)
- replace 2nd derivative by 2nd differences δ^2:



1st diff.

$$\frac{y_{n+1}-y_n}{h}$$

$$\frac{y_n-y_{n-1}}{h}$$

2nd diff.

$$\frac{y_{n+1}-2y_n+y_{n-1}}{h^2}\approx y_n''$$

- Taylor-expansion of y_n at r_n:

$$y_{n\pm1}=y_n\pm y_n'h+y_n''h^2/2\pm y_n'''h^3/3!+y_n^{IV}h^4/4!\pm y_n^{V}h^3/5!+y_n^{VI}h^6/6!$$

$$\delta^2 y_n\equiv y_{n+1}-2y_n+y_{n-1}$$

$$\delta^2 y_n=y''h^2+y_n^{IV}h^4/12+y_n^{VI}h^6/360$$

Numerov method

- By a clever Ansatz one can find even better agreement:
- Ansatz:

$$y_n = P_n - h^2/12\, P_n''$$

$$y_n'' = P_n'' - h^2/12\, P_n^{IV}$$

$$y_n^{IV} = P_n^{IV} - h^2/12\, P_n^{VI} \quad .....$$

- substitute this Ansatz into the previous result:

$$\delta^2 y_n = y'' h^2 + y_n^{IV}\, h^4/12 + y_n^{VI}\, h^6/360$$

$$\delta^2 y_n = P'' h^2 - P_n^{IV}\, h^4/12 + P_n^{IV}\, h^4/12 - P_n^{VI}\, h^6/144 + P_n^{VI}\, h^6/360 .12 - \dots$$

$$\delta^2 y_n = P'' h^2 \qquad - P_n^{VI}\, h^6/240 \quad ....$$

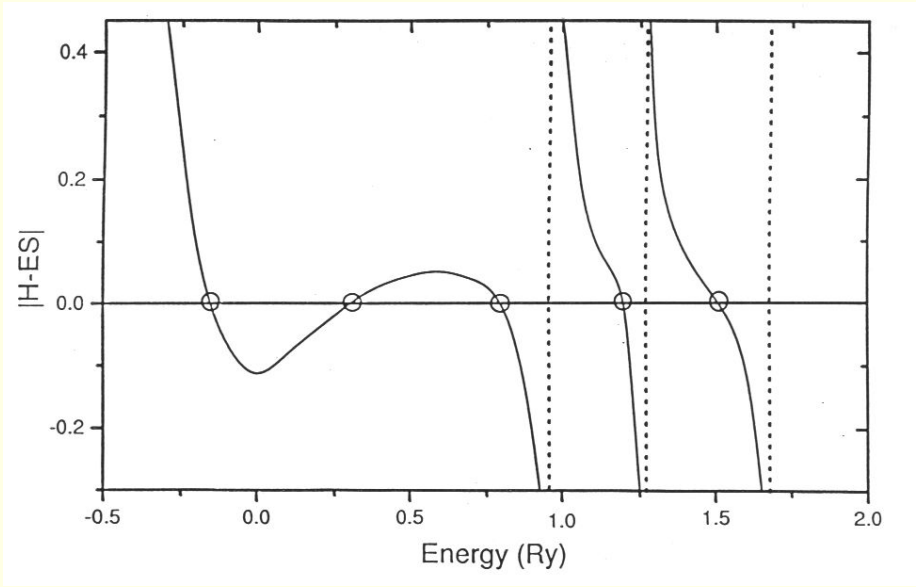
Recursion formula:

- The Numerov solution yields a recursion formula for P:

$$P_{n+1} = \frac{2P_n\left(12/h^2 + 5g_n\right) - P_{n-1}\left(12/h^2 - g_{n-1}\right)}{12/h^2 - g_{n+1}}$$

- P(r) = R(r) . r and $g(r)=\ell(\ell+1)/r^2 + V(r) - E$
- solve P for given ℓ, V and E
- the first two points from P(0)=0 and $P \sim r^{\ell}$
- (today even faster and more accurate solvers are available)

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 a

Non-linear eigenvalue problem

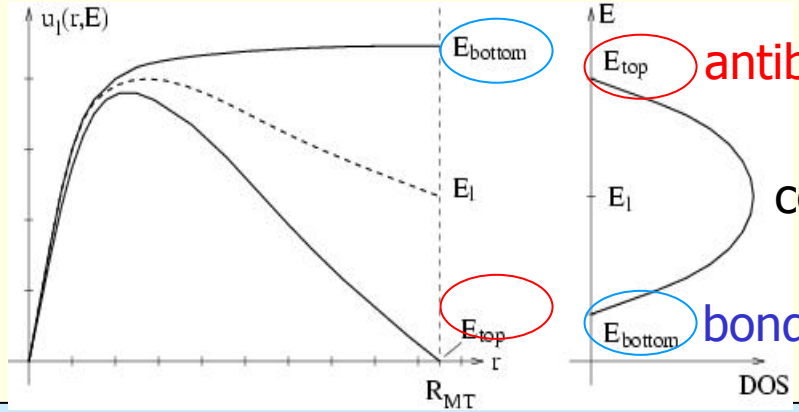
Numerical search for those energies, for which the det|H-ES| vanishes. Computationally very demanding.

"Exact" solution for given MT potential!

Linearization of energy dependence

LAPW suggested by

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



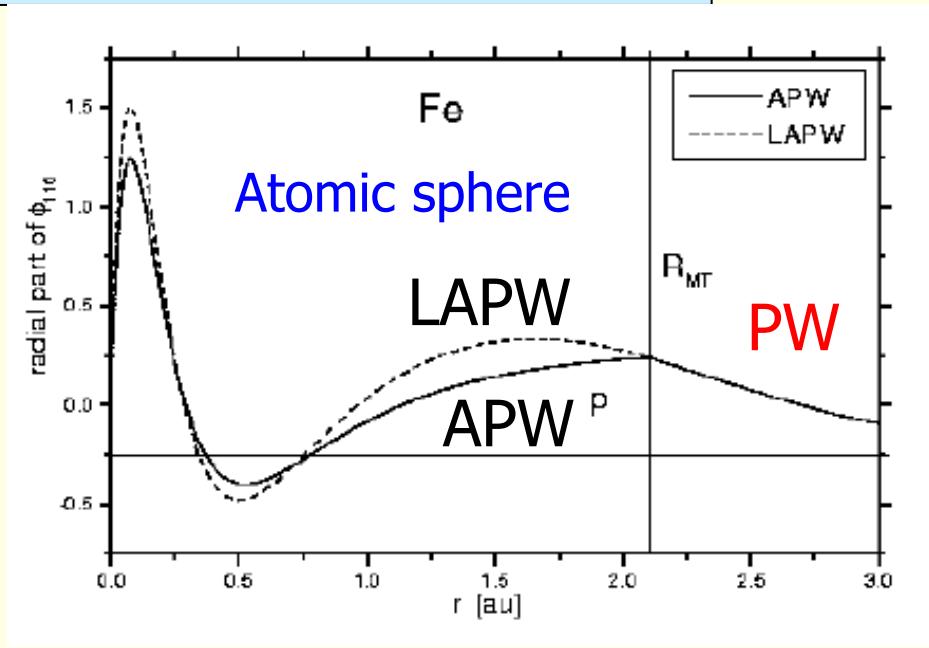
$$\Phi_{k_n} = \sum_{\ell m} [A_{\ell m}(k_n) u_\ell(E_\ell, r) + B_{\ell m}(k_n) \dot{u}_\ell(E_\ell, r)] Y_{\ell m}(\hat{r})$$

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

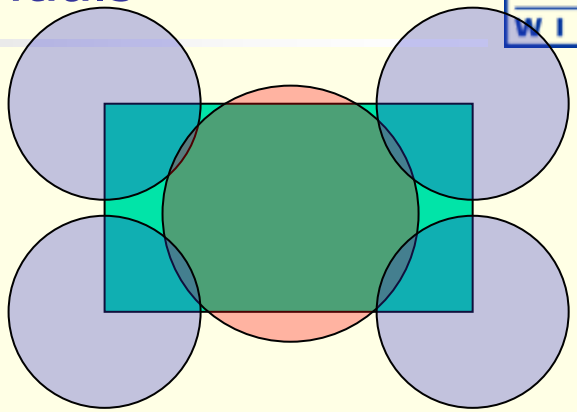
→ General eigenvalue problem (diagonalization)

→ additional constraint requires more PWs than APW

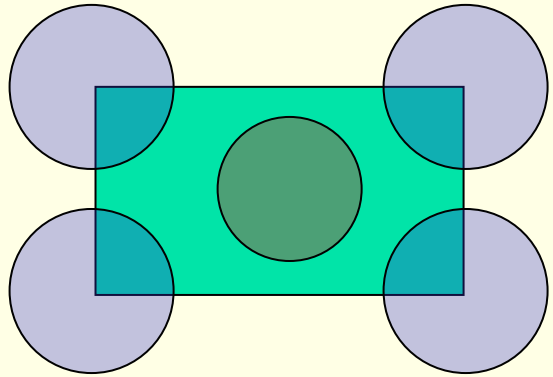


shape approximations to "real" potentials

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

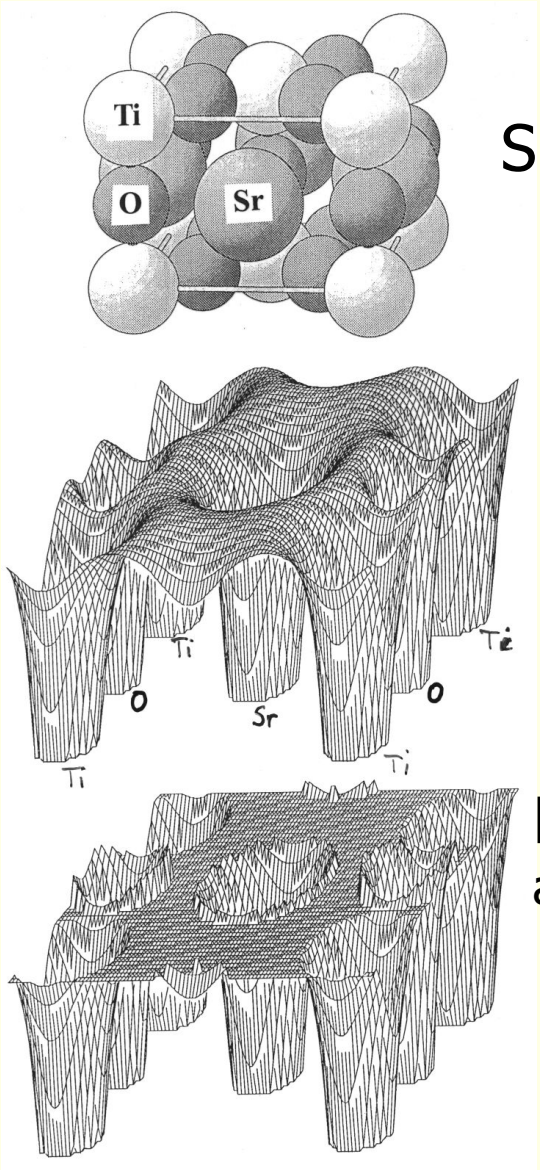


- "muffin-tin" approximation (MTA)
  - *non-overlapping spheres with spherically symmetric potential +*
  - *interstitial region with V=const.*



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

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



$SrTiO_3$

Full potential

Muffin tin approximation

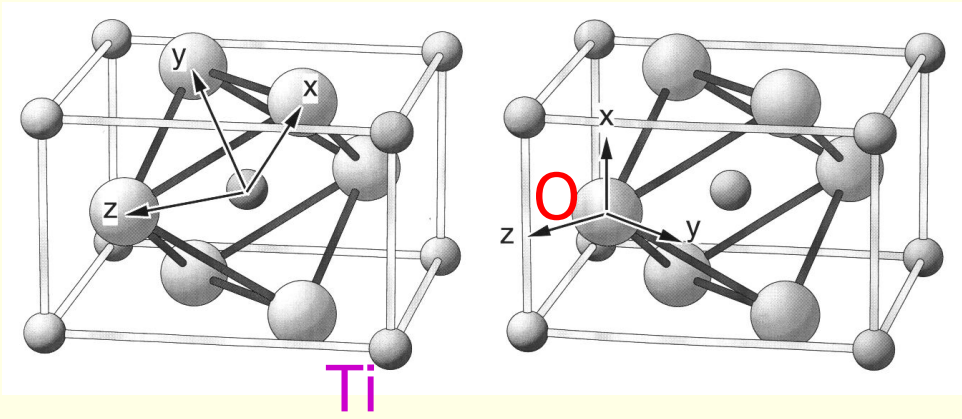
TiO_2 rutile

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

  (no shape approximation)

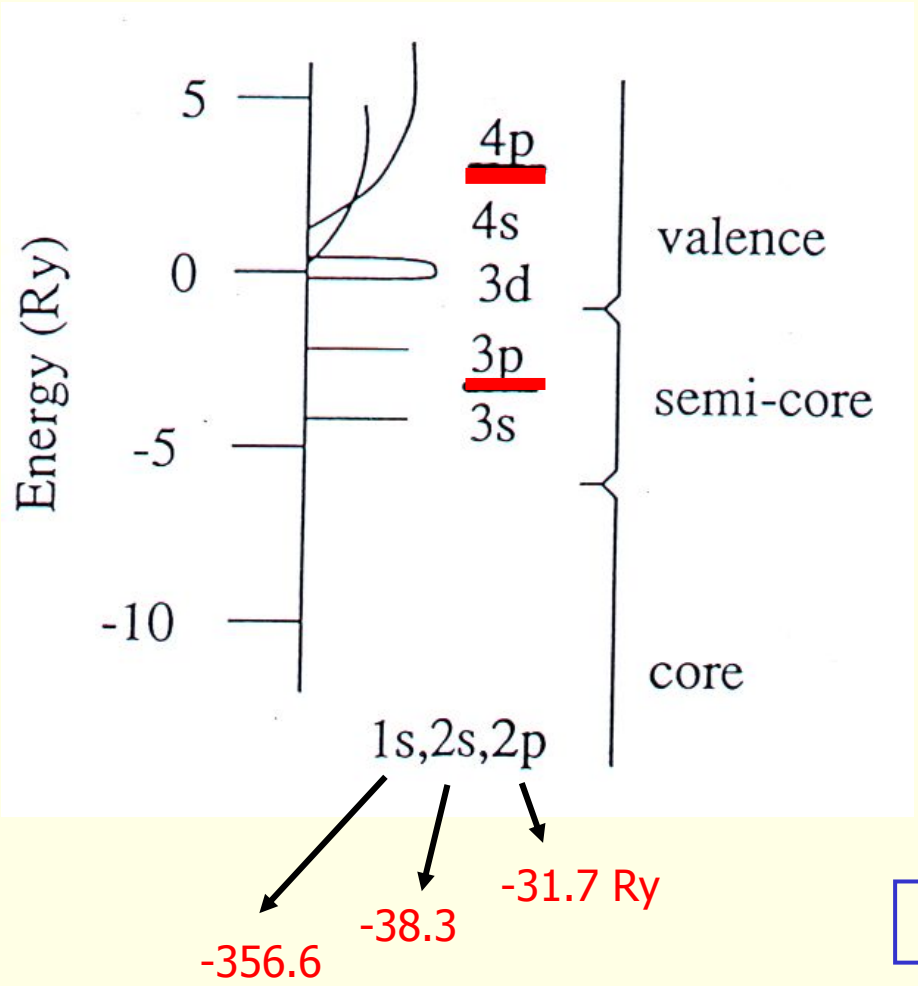
$$V(r) = \begin{cases} \sum_{LM} V_{LM}(r) Y_{LM}(\hat{r}) & r < R_\alpha \\ \sum_{K} V_K e^{i\vec{K}.\vec{r}} & r \in I \end{cases}$$

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



Core, semi-core and valence states

For example: Ti

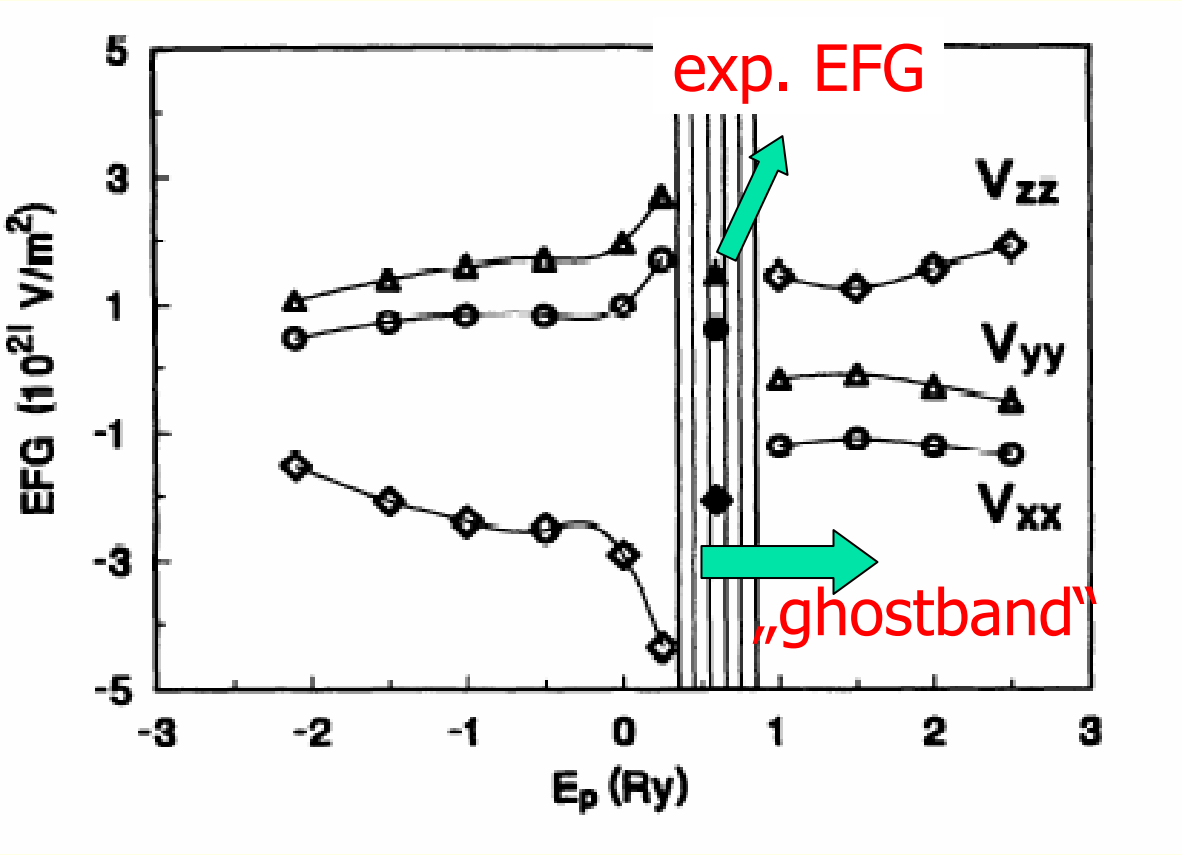


- Valences states
  - ***High*** *in energy*
  - ***Delocalized*** *wavefunctions*
- Semi-core states
  - ***Medium*** *energy*
  - *Principal* ***QN*** *one less than valence (e.g. in Ti* ***3****p and* ***4****p)*
  - ***not completely confined*** *inside sphere*
- Core states
  - ***Low*** *in energy*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

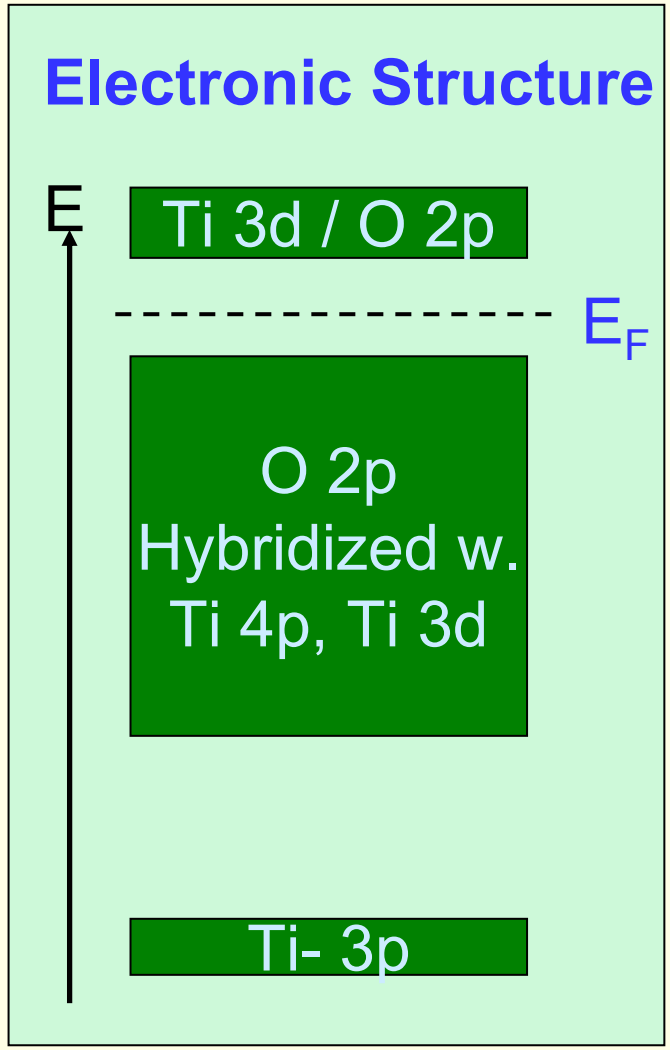
1 Ry =13.605 eV

Problems of the LAPW method:

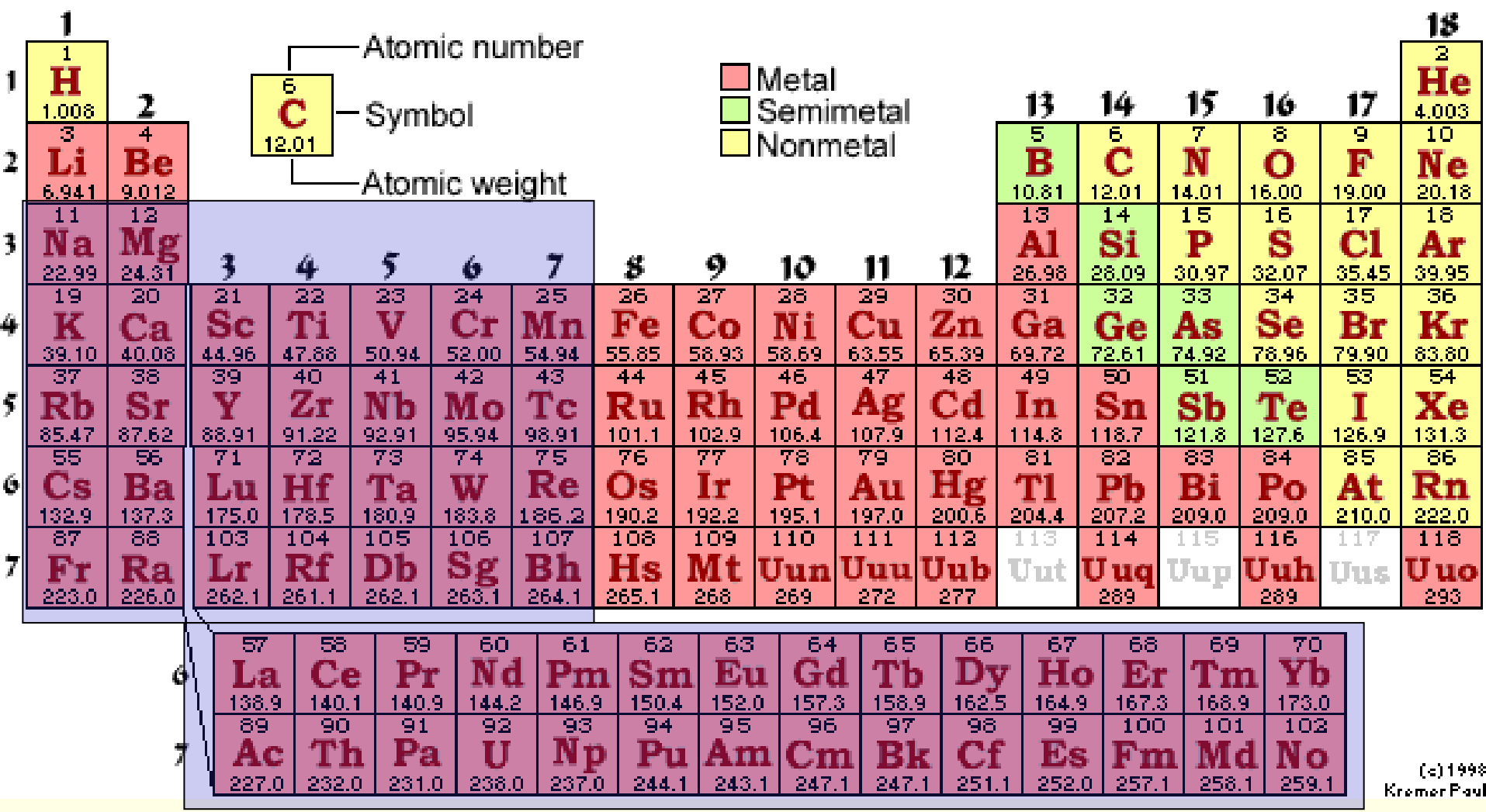
EFG Calculation for Rutile TiO_2 as a function of the Ti-*p* linearization energy E_p



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



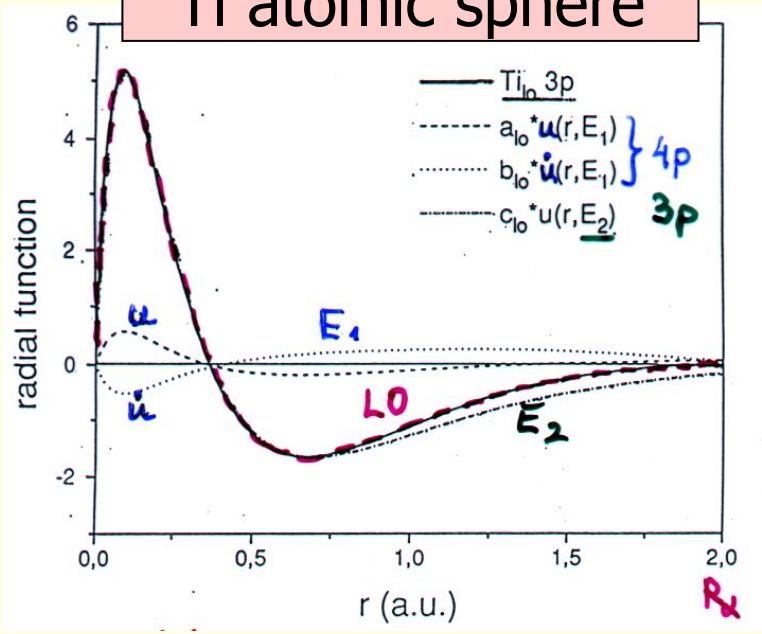
Semi-core problems in LAPW



Problems with semi-core states

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)

The LAPW + LO method

The LAPW+LO basis is:

$$\varphi(\mathbf{r}) = \begin{cases} \Omega^{-1/2} \sum_{\mathbf{K}} c_{\mathbf{K}}\, e^{i(\mathbf{K}+\mathbf{k})\cdot\mathbf{r}} \\ \sum_{lm} \left(A_{lm} u_l(r) + B_{lm} \mathring{u}_l(r)\right) Y_{lm}(\mathbf{r}) + \\ \sum_{lm} \mathbf{c_{lm}} \left(A'_{lm} u_l(r) + B'_{lm} \mathring{u}_l(r) + u^{(2)}_l(r)\right) Y_{lm}(\mathbf{r}) \end{cases}$$

The variational coefficients are: (1) $c_{\mathbf{K}}$ and (2) c_{lm}

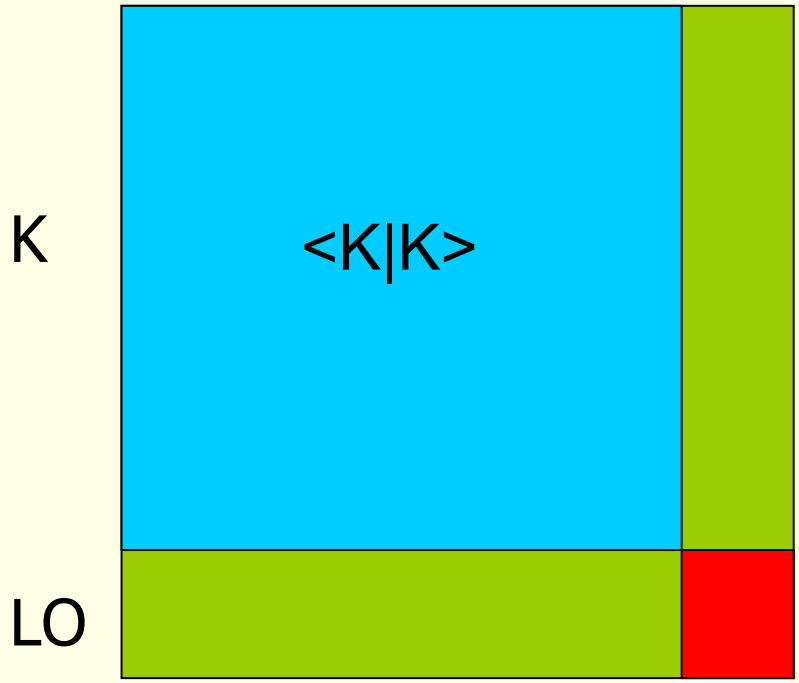
Subsidiary (non-variational) coefficients are A_{lm} B_{lm} A'_{lm} & B'_{lm}

- A_{lm} and B_{lm} are determined by matching the value and derivative on the sphere boundary to the plane waves as usual.
- A'_{lm} and B'_{lm} are determined by forcing the value and derivative of the LO on the sphere boundary to zero. The part $\left(A'_{lm} u_l(r) + B'_{lm} \mathring{u}_l(r) + u^{(2)}_l(r)\right) Y_{lm}(\mathbf{r})$ is formally a local orbital.

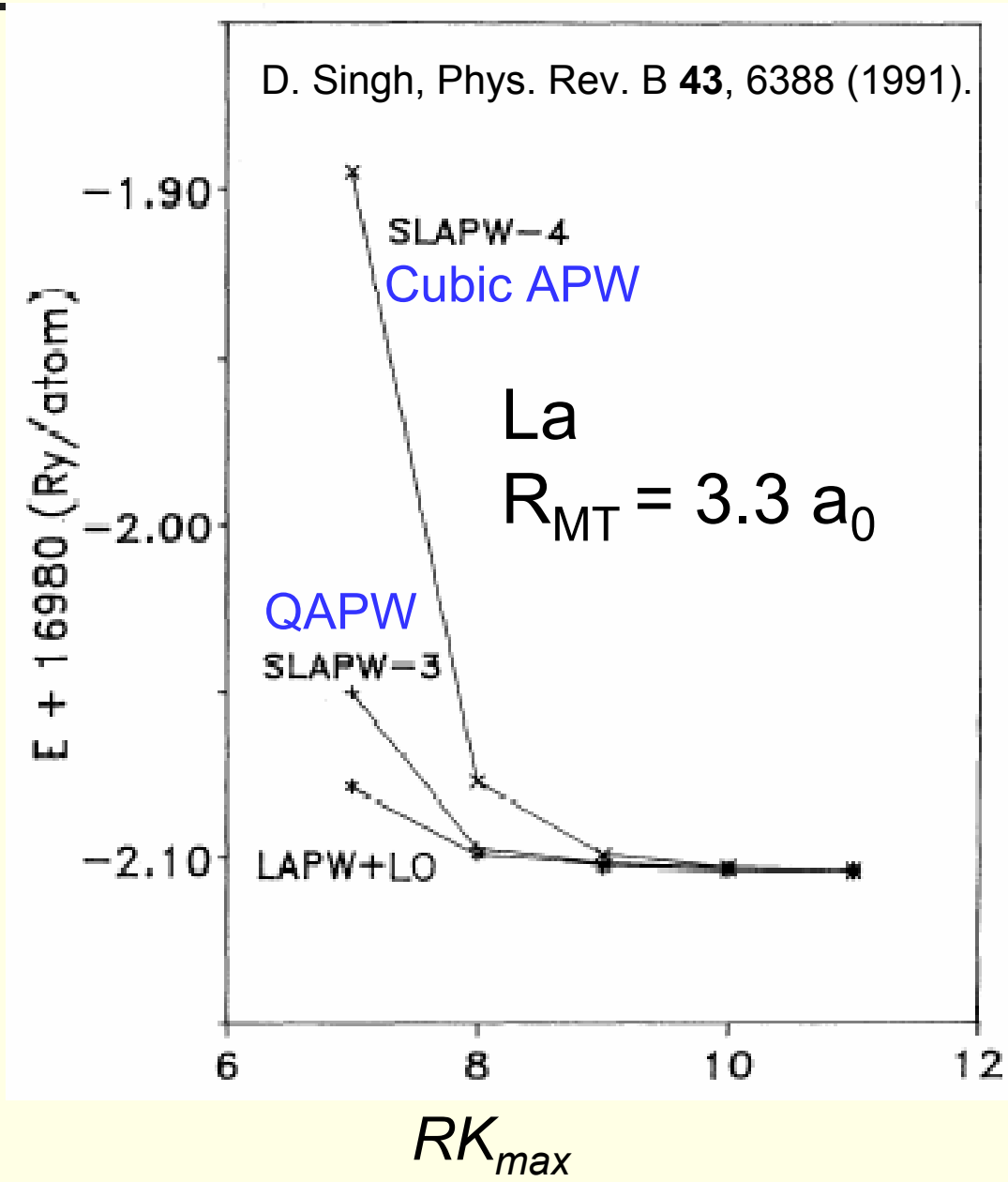
Key Points:

1. The local orbitals should only be used for those atoms and angular momenta, for which they are needed.
2. The local orbitals are just another way to handle the augmentation. They look very different from atomic functions.
3. We are trading a large number of extra plane wave coefficients for some c_{lm}.

Shape of H and S



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.

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)

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

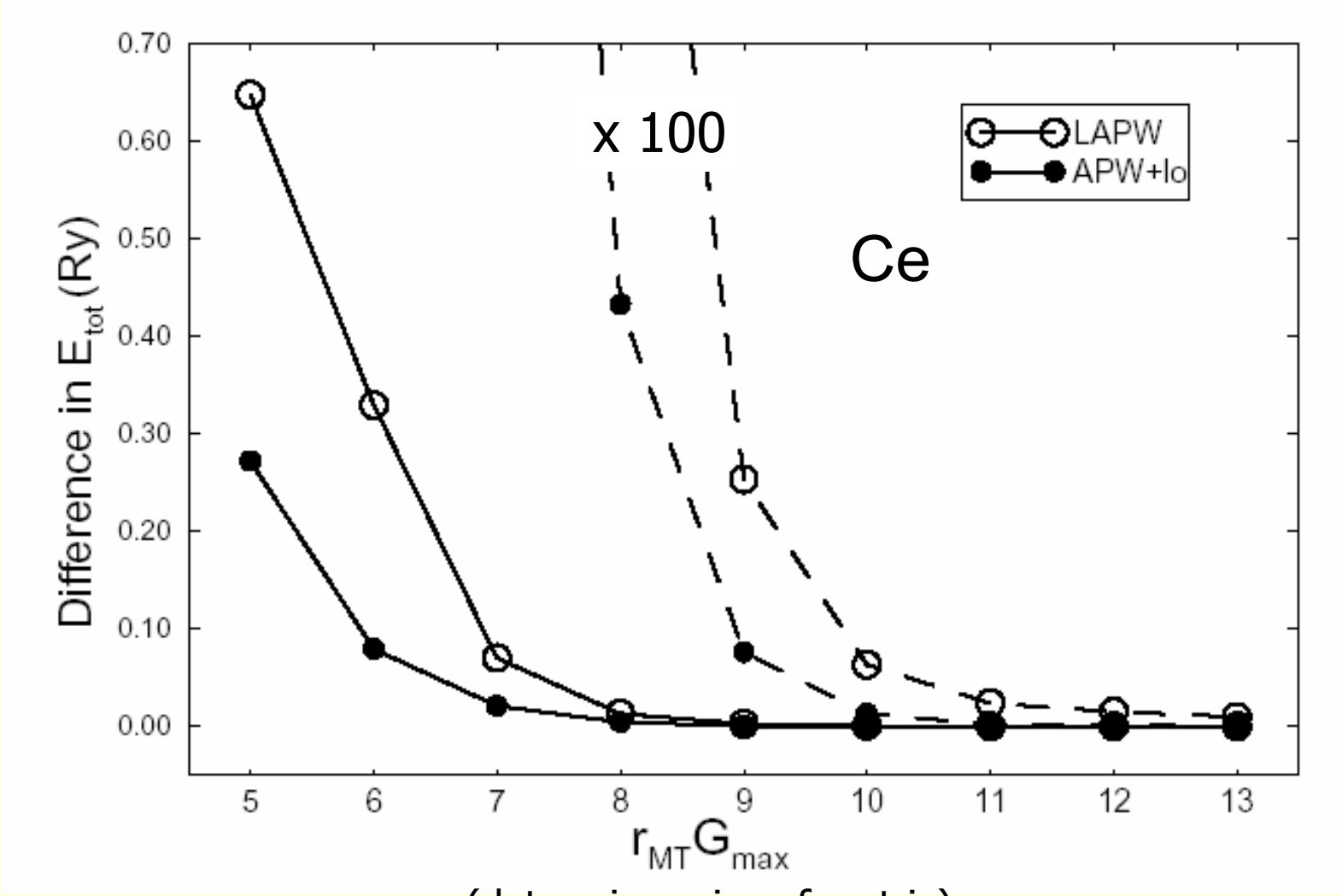
$$\Phi_{lo} = [A_{\ell m} u_\ell^{E_1} + B_{\ell m} \dot{u}_\ell^{E_1}] Y_{\ell m}(\hat{r})$$

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

Convergence of the APW+lo Method

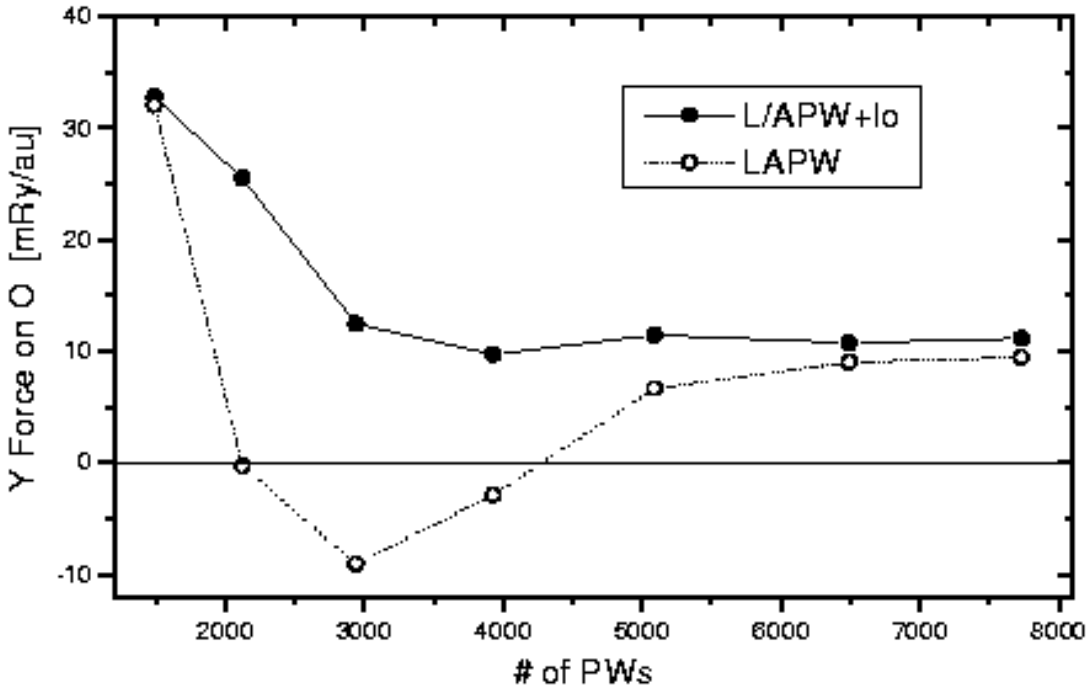
E. Sjostedt, L. Nordstrom and D.J. Singh, Solid State Commun. **114**, 15 (2000).



(determines size of matrix)

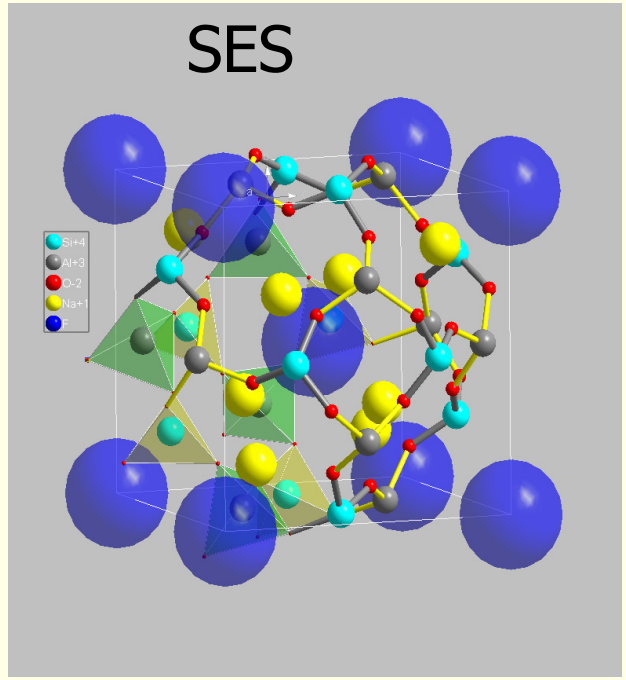
Improved convergence of APW+lo

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 (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*

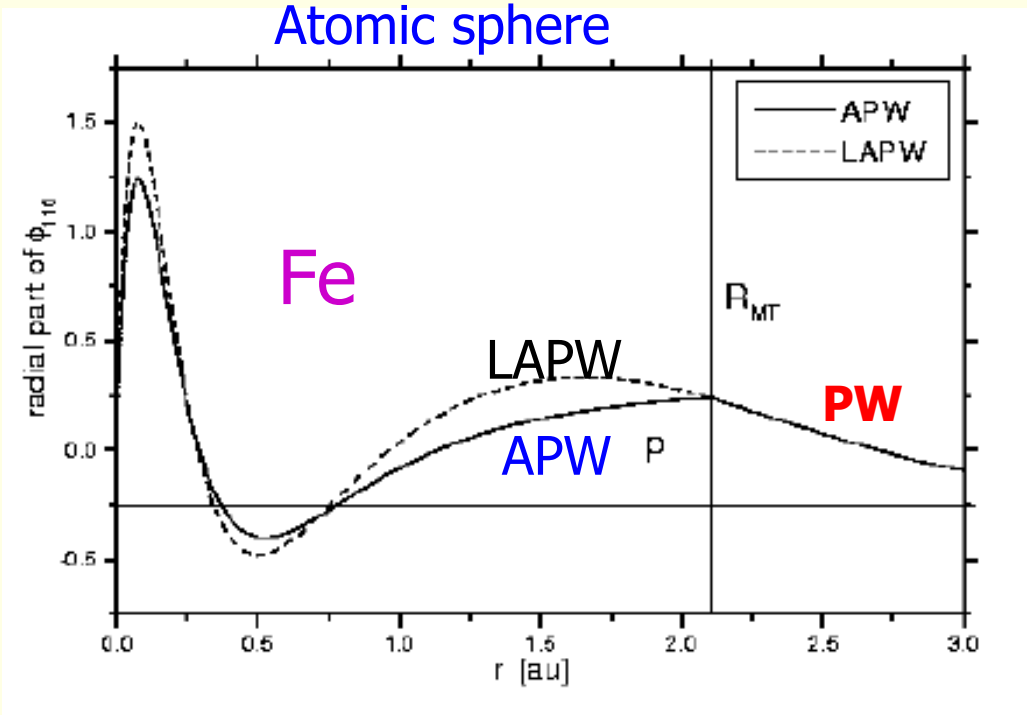
$$\Phi_{k_n} = \sum_{\ell m} A_{\ell m}(k_n) u_\ell(E_\ell, r) Y_{\ell m}(\hat{r})$$

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 $A_{\ell m}(k_n)$



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

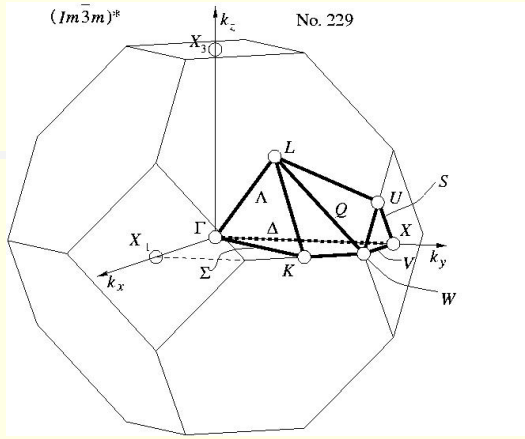
- use APW+lo for states which are difficult to converge: (f- or d- states, atoms with small spheres)
- use LAPW+LO for all other atoms and angular momenta

A summary is given in

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

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

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

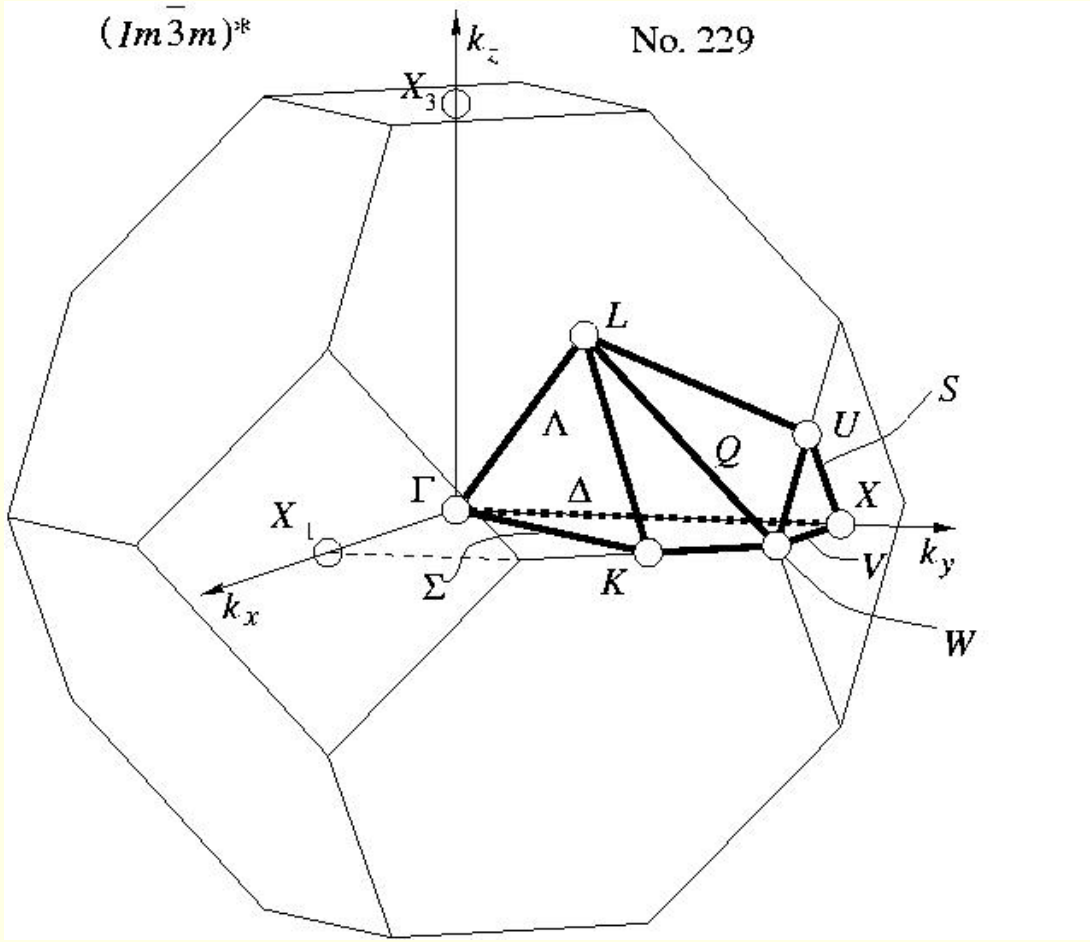
Generalized eigenvalue problem

$$HC = ESC$$

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

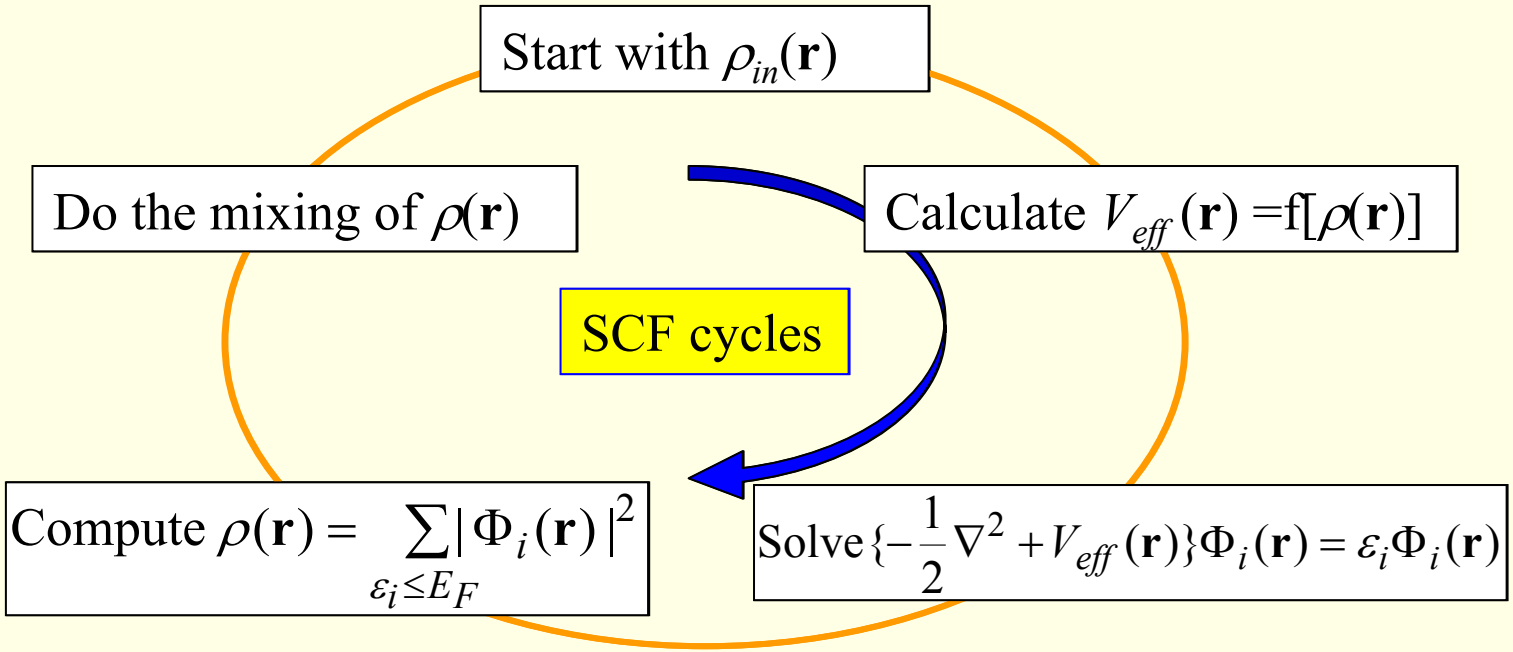
The Brillouin zone (BZ)

- 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)*

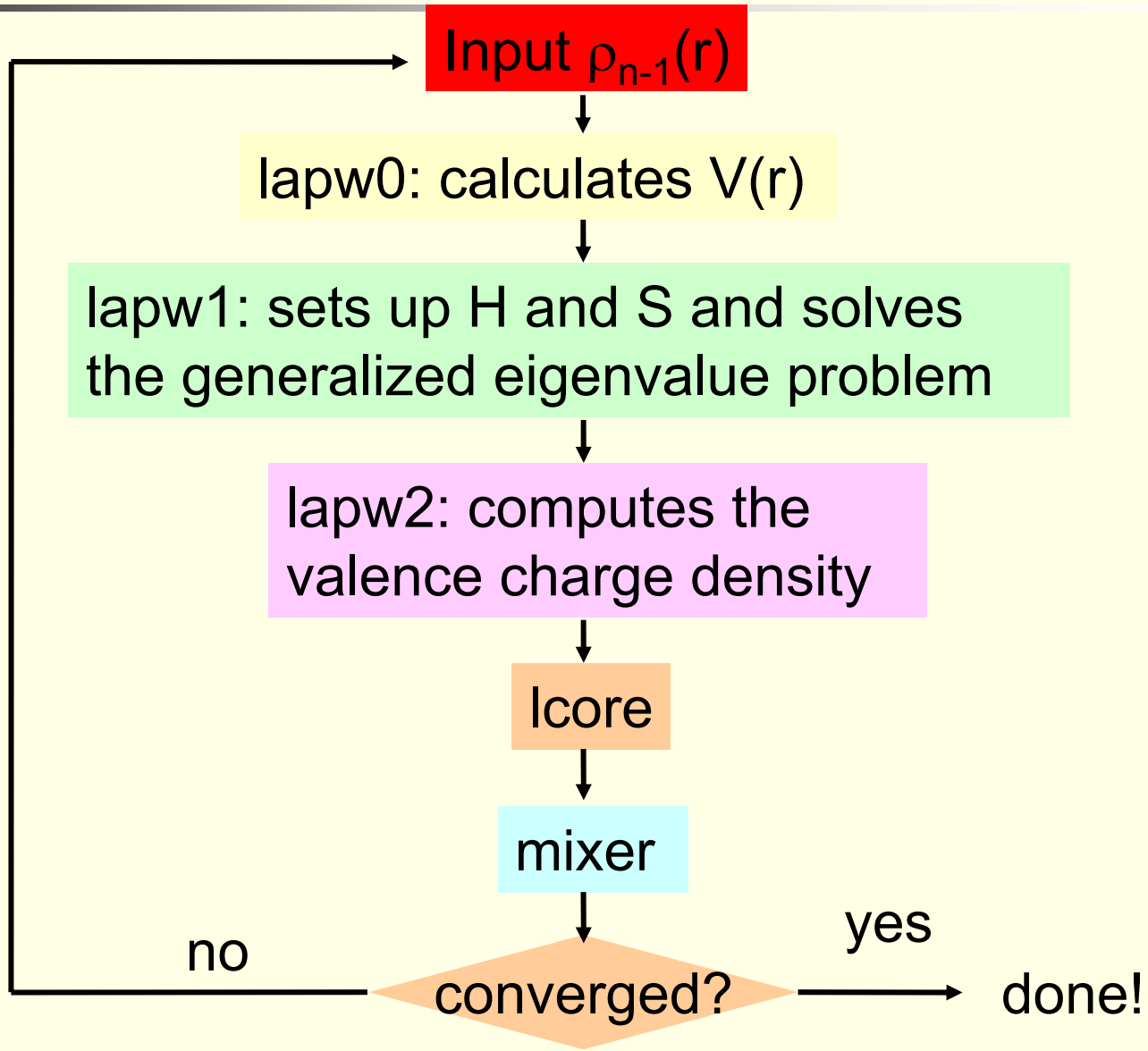


Self-consistent field (SCF) calculations

- 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 ??



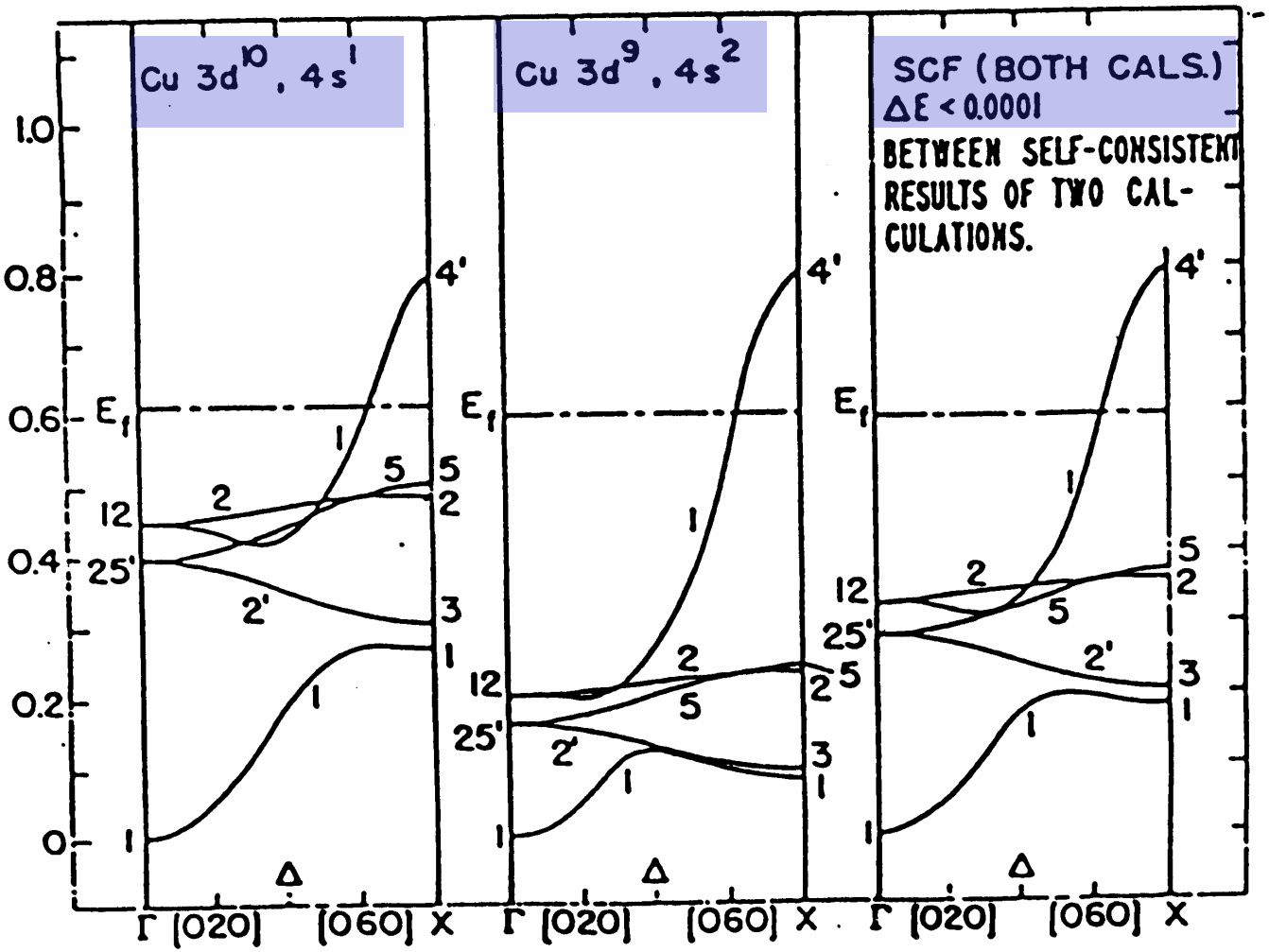
Flow Chart of WIEN2k (SCF)



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

Effects of SCF

Band structure of fcc Cu



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

Computer Physics Communications 59 (1990) 399–415

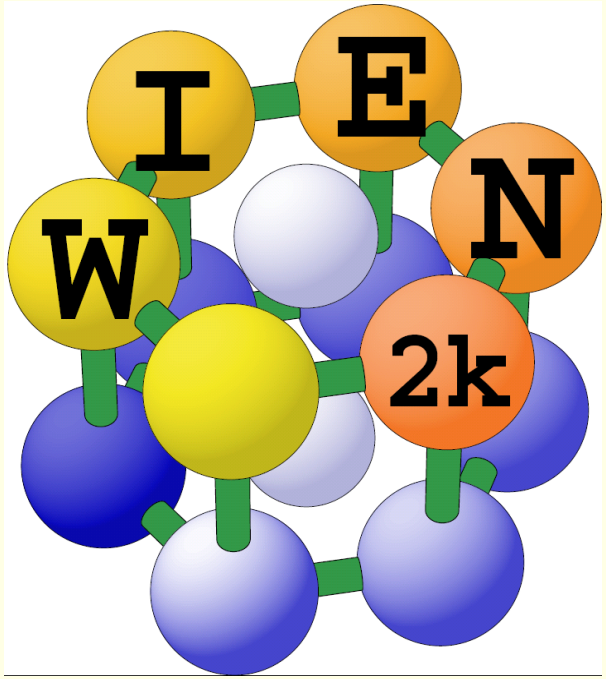
PROGRAM SUMMARY

Title of program: WIEN

Europa Austria Vienna → WIEN

In the Heart of EUROPE

WIEN2k software package



WIEN2k:
~950 groups worldwide

Based on DFT-LDA (GGA)
Accuracy determined by one parameter: number of PW

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

The WIEN2k authors

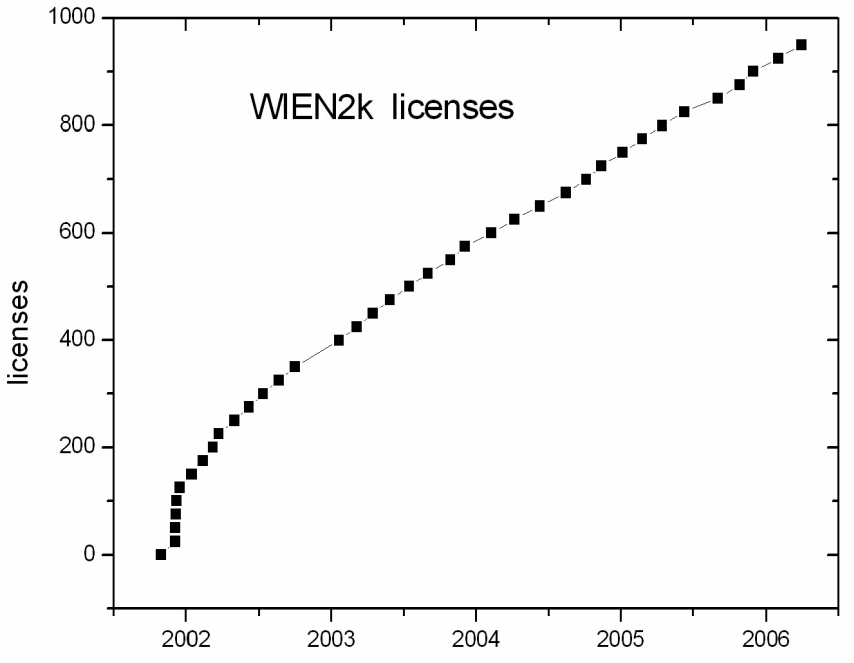
Main developers of WIEN2k

- Authors of WIEN2k

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

- Other contributions to WIEN2k
  - *C. Ambrosch-Draxl (Univ. Leoben, Austria), optics*
  - *U. Birkenheuer (Dresden), wave function plotting*
  - *R. Dohmen und J. Pichlmeier (RZG, Garching), parallelization*
  - *C. Först (Vienna), afminput*
  - *R. Laskowski (Vienna), non-collinear magnetism*
  - *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 ….

International users



More than **950** user groups worldwide

- *35 industries (Canon, Eastman, Exxon, Fuji, Hitachi, IBM, Idemitsu Petrochem., Kansai, Komatsu, A.D.Little, Mitsubishi, Mitsui Mining, Motorola, NEC, Nippon Steel, Norsk Hydro, Osram, Panasonic, Samsung, Siemens, Sony, Sumitomo,TDK,Toyota).*
- *Europe: A, B, CH, CZ, D, DK, ES, F, FIN, GR, H, I, IL, IRE, N, NL, PL, RO, S, SK, SL, SI, UK (ETH Zürich, MPI Stuttgart, FHI Berlin, DESY, TH Aachen, ESRF, Prague, IJS Ljubjlana, Paris, Chalmers, Cambridge, Oxford)*
- *America: ARG, BZ, CDN, MX, USA (MIT, NIST, Berkeley, Princeton, Harvard, Argonne NL, Los Alamos NL, Oak Ridge NL, Penn State, Georgia Tech, Lehigh, John Hopkins, Chicago, Stony Brook, SUNY, UC St.Barbara, UCLA)*
- *far east: AUS, China, India, JPN, Korea, Pakistan, Singapore,Taiwan (Beijing, Tokyo, Osaka, Kyoto, Sendai, Tsukuba, Hong Kong)*

WIEN code as benchmark

Vienna city of music and the WIEN2k code

Thank you for your attention