Density functional theory (DFT) and the concepts of the augmented-plane-wave plus local orbital (L)APW+lo method

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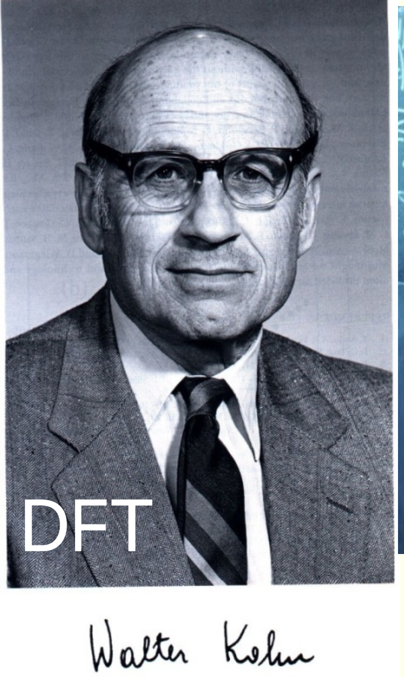
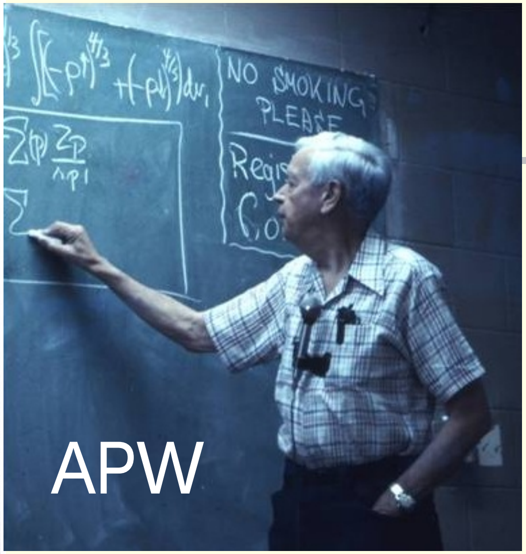
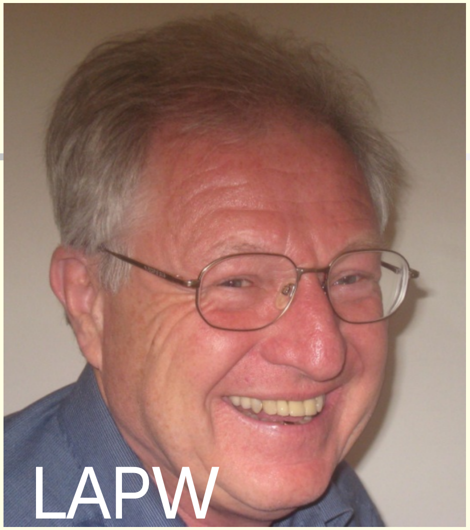




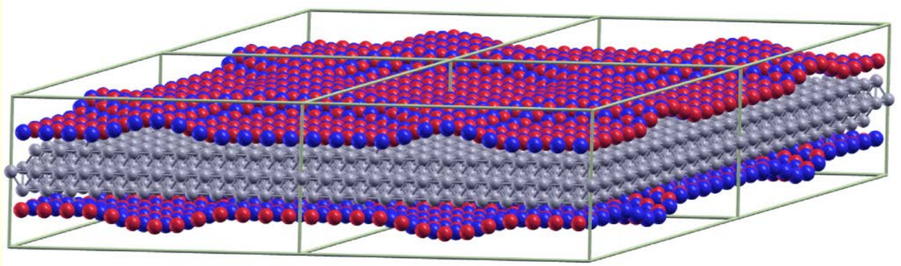
J.C.Slater



O.K.Andersen

WIEN 2k

Electronic structure of
solids and surfaces



hexagonal boron nitride on Rh(111)
2x2 supercell (1108 atoms per cell)

Phys.Rev.Lett. 98, 106802 (2007)

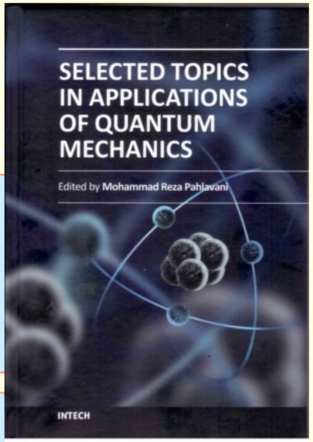
K.Schwarz, P.Blaha, S.B.Trickey,
Molecular physics, **108**, 3147 (2010)

Wien2k is used worldwide
by about 2500 groups

The WIEN2k code: comments

- Walter Kohn: density functional theory (DFT), 1965
- J.C.Slater: augmented plane wave (APW) method, 1937
- O.K.Andersen: Linearized APW (LAPW), 1975
- Wien2k code: developed during the last 35 years
  - *In the year 2000 (2k) the WIEN code (from Vienna) was called wien2k*
  - *One of the most accurate DFT codes for solids*
  - *All electron, relativistic, full- potential method*
  - *Widely used in academia and industry*
- Applications:
  - *solids: insulators , covalently bonded systems, metals*
  - *Surfaces: catalysis*
  - *Electronic, magnetic, elastic , optical ,…properties*
  - *Many application in literature*
  - *See www.wien2k.at*

Review articles


SELECTED TOPICS
IN APPLICATIONS
OF QUANTUM
MECHANICS

Edited by Mohammad Reza Pahlavani

INTECH

K.Schwarz, *Computation of Materials Properties at the Atomic Scale*
InTech, (2015) Chapter 10, 275-310, open access book
ISBN 978-953-51-2126-8 (2015) dx.doi.org/10.5772/59108

K.Schwarz, P.Blaha, *Electronic structure of solids and surfaces with WIEN2k*
in *Practical Aspects of Computational Chemistry I: An Overview of the Last Two Decades and Current Trends*,
J.Leszczyncski, M.K.Shukla (Eds),
Springer Science+Business Media B.V. (2012) Chapter 7, 191-207,
ISBN 978-94-007-0918-8

S.Cottenier, *Density Functionl Theory and the famliy of (L)APW methods :*
A step by step introduction
2002-2012 /(2nd edition); ISBN 978-90-807215-1-7
Freely available at: *http://www.wien2k.at/reg-user/textbooks*

K.Schwarz, P.Blaha, S.B.Trickey, *Electronic structure of solids with WIEN2k*
Molecular physics, **108**, 3147 (2010)

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

K.Schwarz, P.Blaha, G.K.H.Madsen,
Electronic structure calculations of solids using the WIEN2k package for material Sciences
Comp.Phys.Commun.**147**, 71-76 (2002)

Aspects at this workshop

- Atomic structure
  - *Periodic boundary condition (approximation)*
- Quantum mechanical treatment
  - *DFT (functionals) and beyond (GW, DMFT, RPA, BSE, ...)*
- How to solve the QM (basis set)
  - *LAPW method and local orbitals as implemented in WIEN2k*
- Applications
  - *Verwey transition, EFG, NMR, surfaces, spectra ....*
- Software development
  - *Accuracy, efficiency, system size, user-friendliness, commercial*
- Insight and understanding
  - *Analysis to find trends, computer experiments (artificial cases)*
- Combination of expertise
  - *Chemistry, physics, mathematics, computer science, application*

Four big challenges for theorists :

- *large scale applications to simulate "real" materials*
  - at the atomic scale
- *A proper quantum mechanical treatment (accurate)*
  - develop more accurate DFT functionals
  - beyond DFT (GW, DMFT, BSE, RPA...)
- *Efficiency (make calculations faster):*
  - improve numerics, parallelization, algorithms (iterative diagonalization)
- *calculate "new" properties*
  - for direct comparison with experiment

The atomic structure

- A crystal is represented by a unit cell
  - *We assume periodic boundary condition (approximation)*
  - *The unit cell is repeated to infinity (makes calculations feasible)*
  - *A real crystal is finite (with surfaces, impurities, defects …)*
  - *Nano materials differ from bulk*
  - *Symmetry helps (space group, Bloch theorem, …)*
- In theory
  - *The atomic structure is an input and thus well defined.*
  - *Artificial structures can be studied too*
- In experiment
  - *The atomic structure is not perfectly known*
  - *Single crystals, micro crystals, powder samples, nano*
  - *e.g. by X-ray: averaged with uncertainties (defects, disorder)*

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

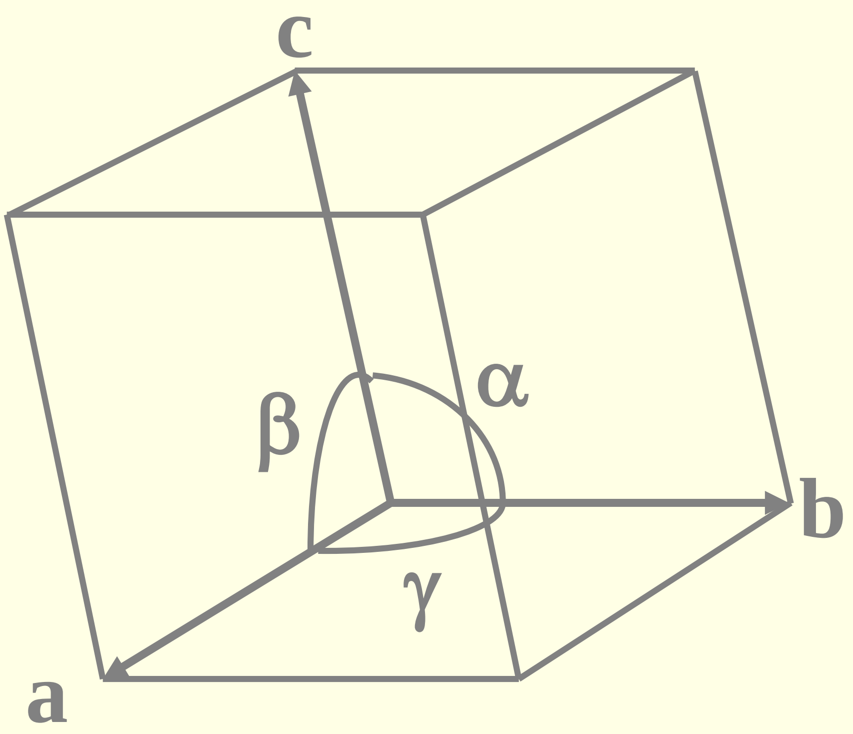
Unit cell: a volume in space that fills space entirely when translated by all lattice vectors.

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)



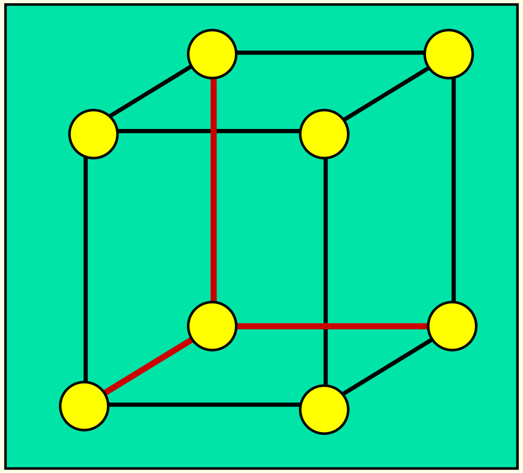
A unit cell containing one lattice point is called primitive cell.

Crystal system: e.g. cubic

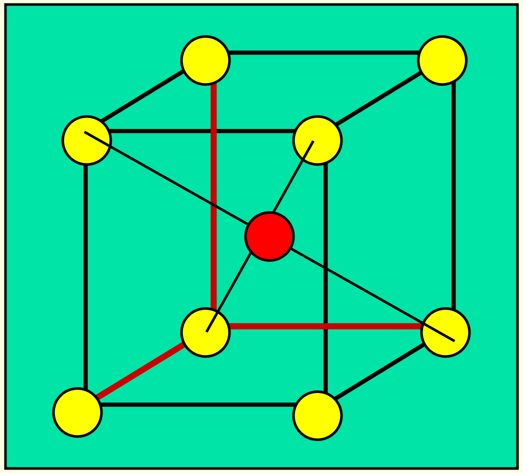
Axis system **a = b = c**

$\alpha = \beta = \gamma = 90°$

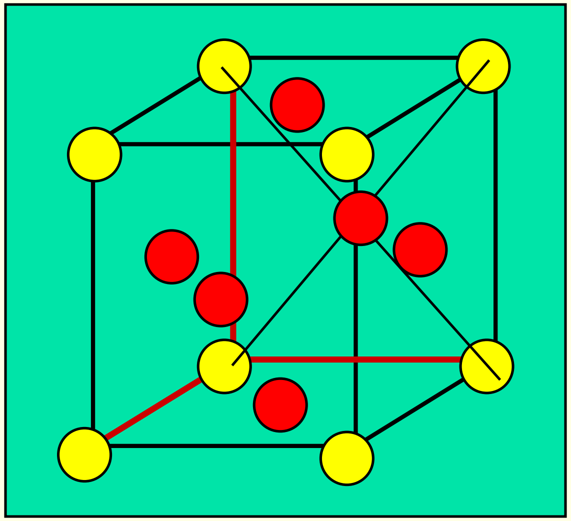
primitive **body centered** **face centered**



P (cP)



I (bcc)



F (fcc)

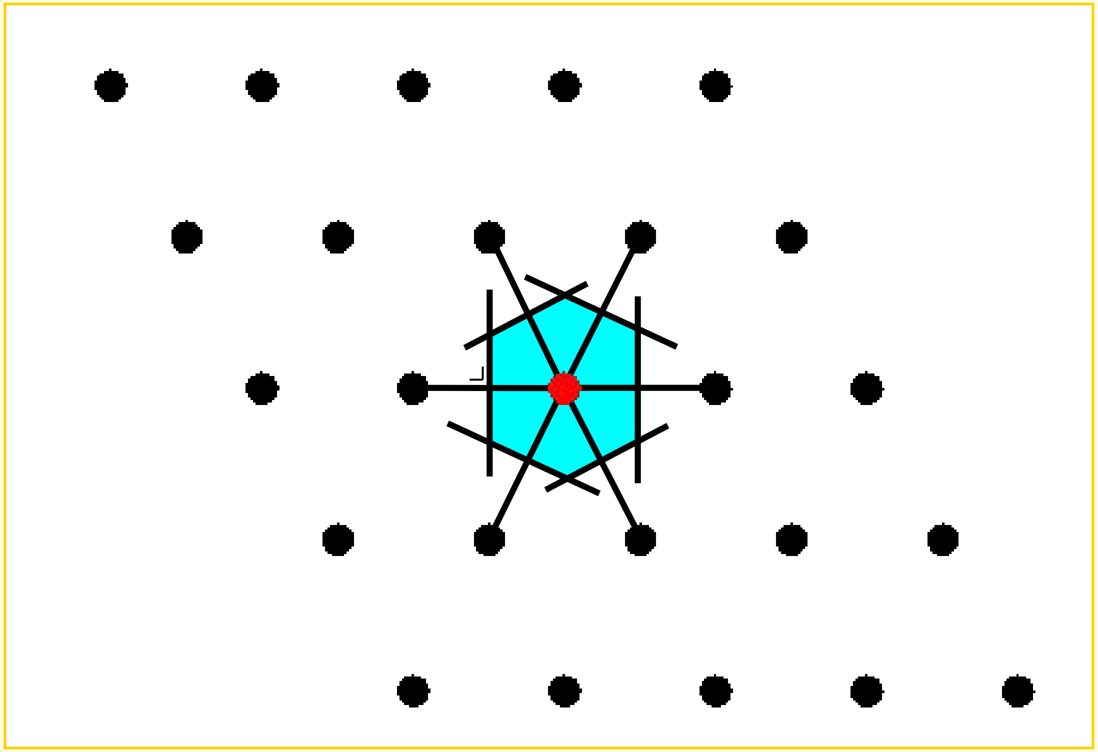
3D lattice types:

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 (≠ 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



The quantum mechanical treatment

- The electronic structure requires a QM treatment
- The main scheme is density functional theory (DFT)
  - *It is a mean field approach and requires approximations*
  - *According to Hohenberg Kohn it is sufficient to know the electron density of a system to determine its total energy. The many electron wave function (which depends on many variables) is not needed. In principle this is an enormous simplification, but in practice approximations must be made.*
  - *The direction of improving the QM treatment is summarized pictorially in Jabob's ladder:*
- There are schemes which go beyond DFT:
  - *GW method (for excitations or band gaps)*
  - *The Bethe Salpeter equation (BSE) for excitons (core hole - electron)*
  - *Dynamical mean field theory (DMFT) based on DFT (wien2wannier)*

Bloch-Theorem:

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

1-dimensioanl case:

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:

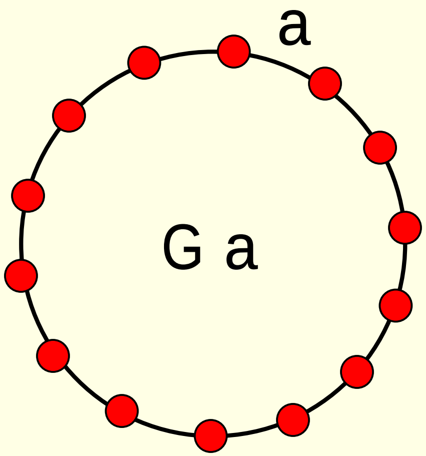
$$\tau^g\Psi(x) = \Psi(x+ga) = \mu^g\Psi(x)$$

periodic boundary conditions:

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

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

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



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

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

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

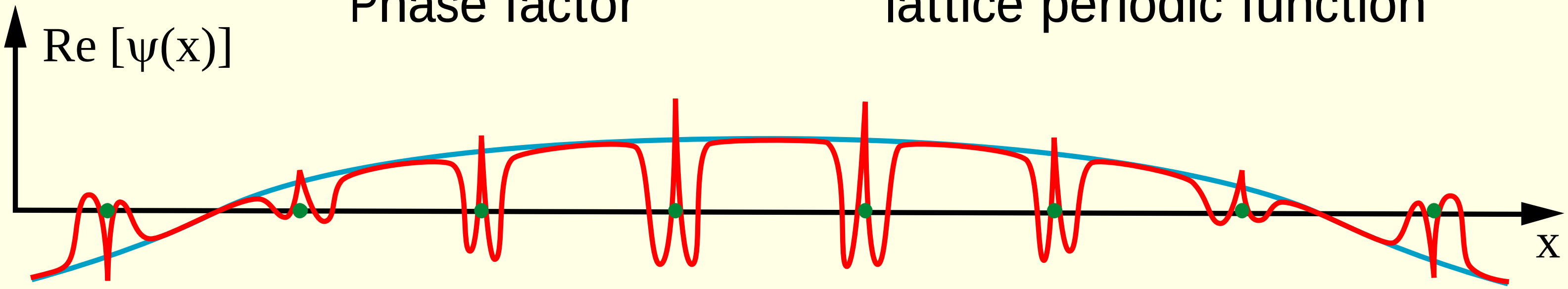
Bloch functions:

- 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 .

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

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
(Kohn-Sham equation)

Representation of solid

non periodic
(cluster)
periodic
(unit cell)

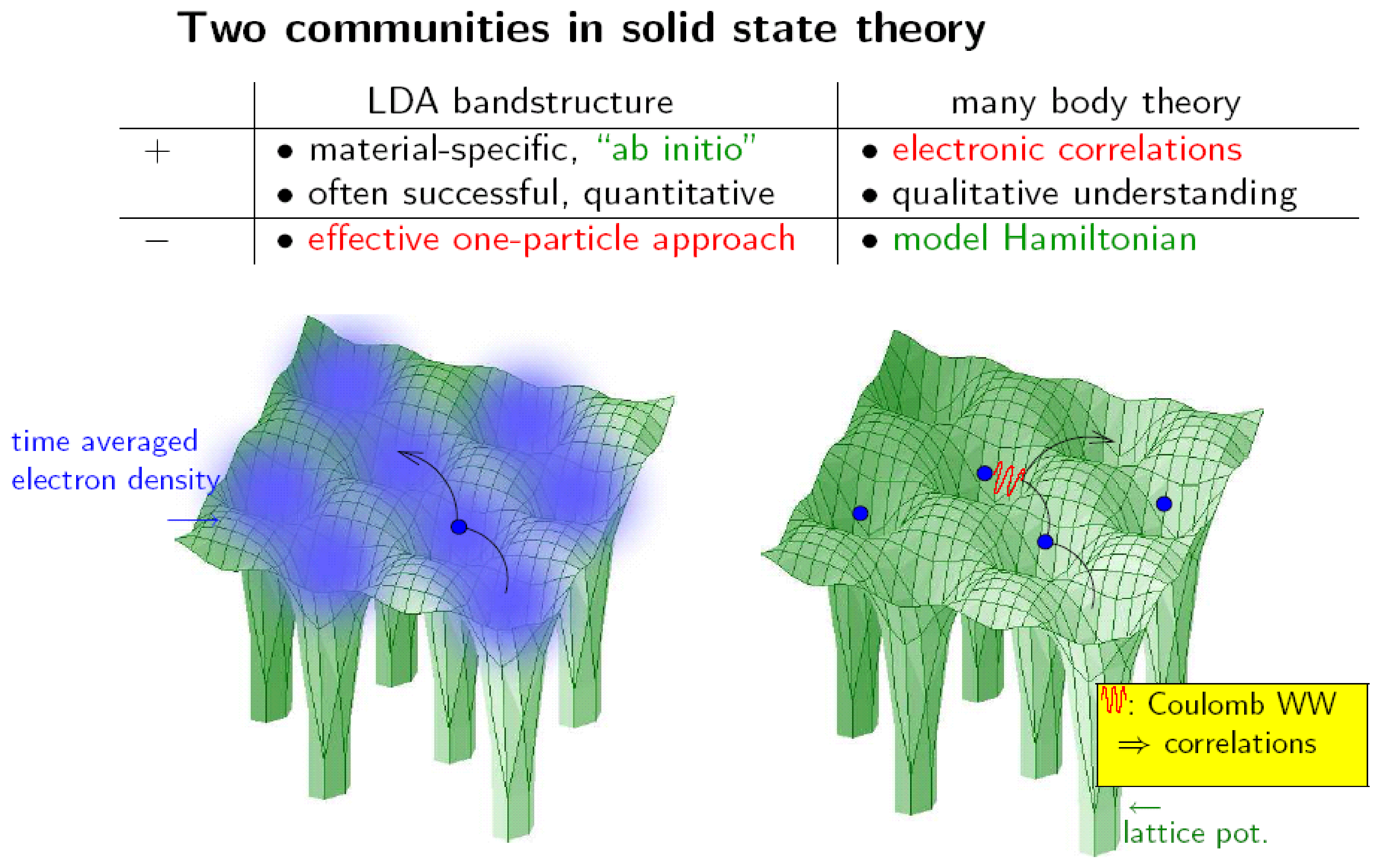
Treatment of spin

Non-spinpolarized
Spin polarized
(with certain magnetic order)

Basis functions

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

DFT vs. MBT (many body theory)

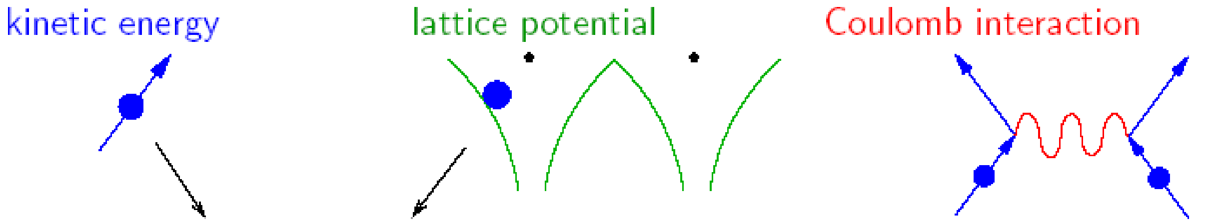


Two communities in solid state theory

	LDA bandstructure	many body theory
+	• material-specific, "ab initio" • often successful, quantitative	• electronic correlations • qualitative understanding
–	• effective one-particle approach	• model Hamiltonian

Ab-initio Hamiltonian

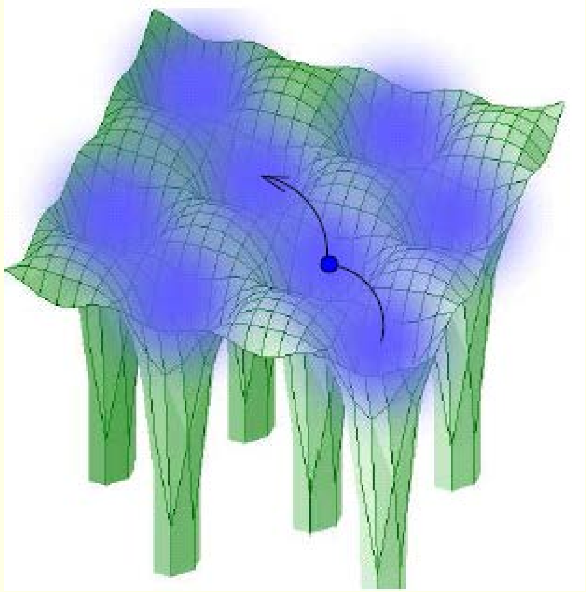
(non-relativistic/Born-Oppenheimer approximation)



$$H = \sum_i \left[-\frac{\hbar^2\Delta_i}{2m_e} + \sum_l \frac{-e^2}{4\pi\epsilon_0}\frac{Z_l}{|\mathbf{r}_i-\mathbf{R}_l|}\right] + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}$$

LDA bandstructure corresponds to

$$H_{\mathrm{LDA}} = \sum_i \left[-\frac{\hbar^2\Delta_i}{2m_e} + \sum_l \frac{-e^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}_i-\mathbf{R}_l|} + \int \mathrm{d}^3r\, \frac{e^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}_i-\mathbf{r}|}\rho(\mathbf{r}) + V_{xc}^{\mathrm{LDA}}(\rho(\mathbf{r}_i))\right]$$



Coulomb potential:

- nuclei
- all electrons
- including self-interaction

Quantum mechanics:

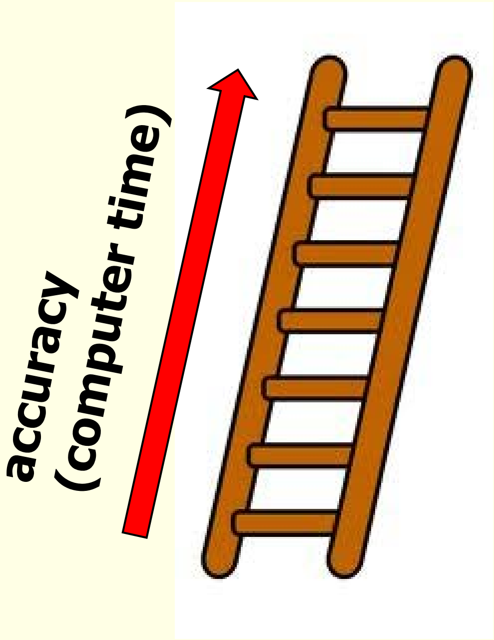
- exchange
- correlation
- (partly) cancel self-interaction

Jacob‘s ladder: The grand challenge:

- Find a functional which leads to “DFT heaven”: →

  predictive power with chemical accuracy

- J. Perdew‘s „Jacob‘s ladder“ into DFT heaven:



- DFT heaven
- unoccupied orbitals (ACFDT-RPA)
- occupied orbitals (hybrid-DFT)
- meta-GGAs (kinetic energy density τ)
- GGA ($\nabla\rho$)
- LDA (ρ)
- Hartree

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}

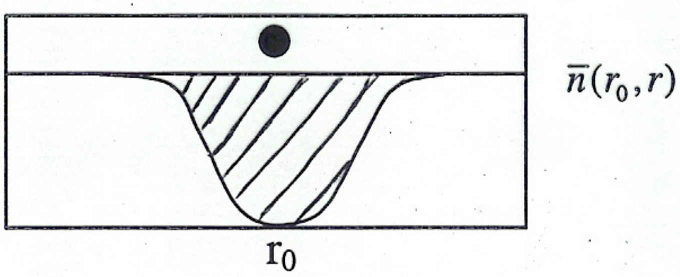
E_{xc} exchange-correlation

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

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

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



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

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

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

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

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

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

LDA

GGA

treats both,
exchange and correlation effects,
but approximately

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

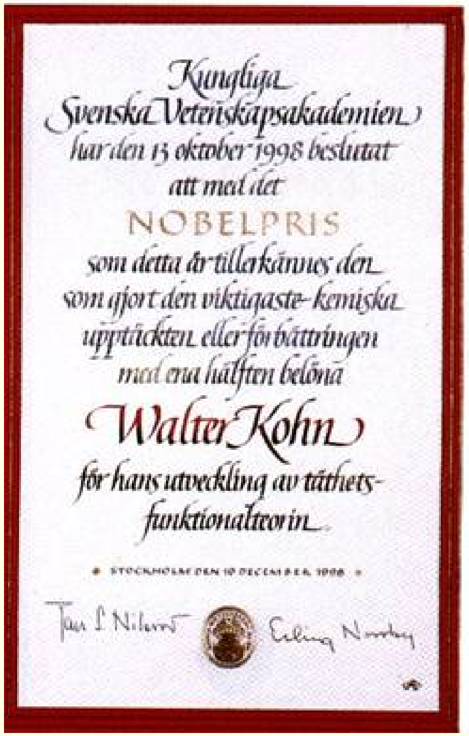
ESSENCE OF DENSITY-FUNTIONAL THEORY

- **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

Walter Kohn



Kungliga
Svenska Vetenskapsakademien
har den 15 oktober 1998 beslutat
att med det
NOBELPRIS
som detta år tillerkännes den
som gjort den viktigaste kemiska
upptäckten eller förbättringen
med ena hälften belöna
Walter Kohn
för hans utveckling av täthets-
funktionalteorin

◆ STOCKHOLM DEN 10 DECEMBER 1998 ◆

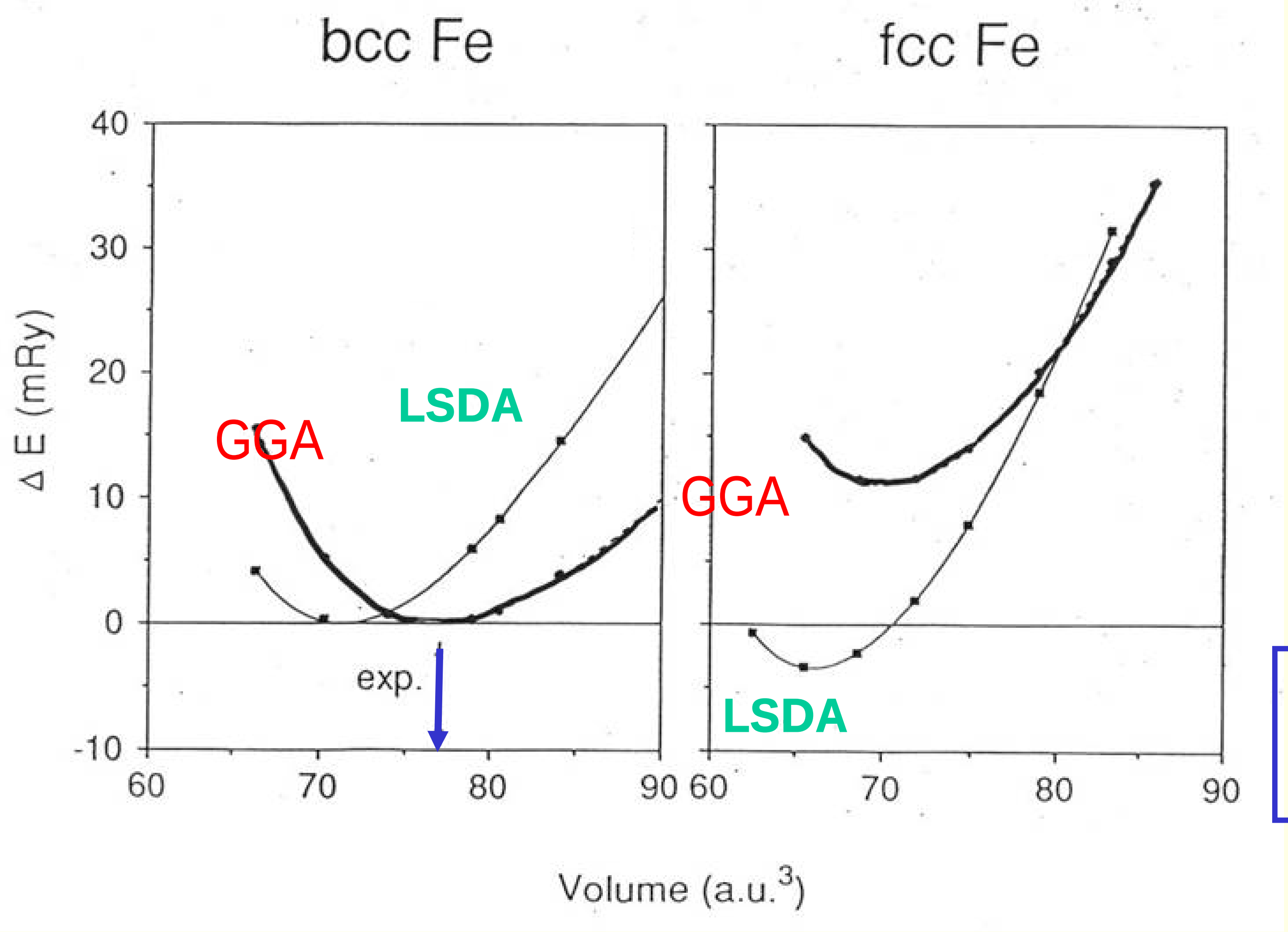
Jan S Nilsson Erling Norrby

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

50 years ago

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

DFT ground state of iron



LSDA

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

GGA

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

Experiment

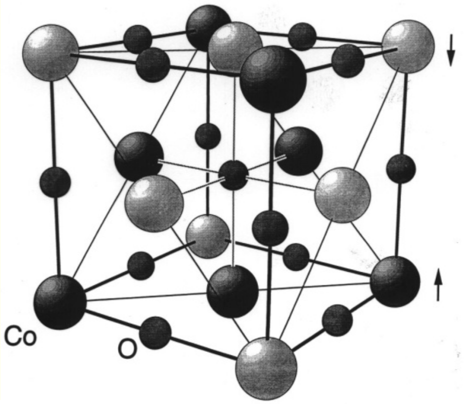
- *FM*
- *bcc*

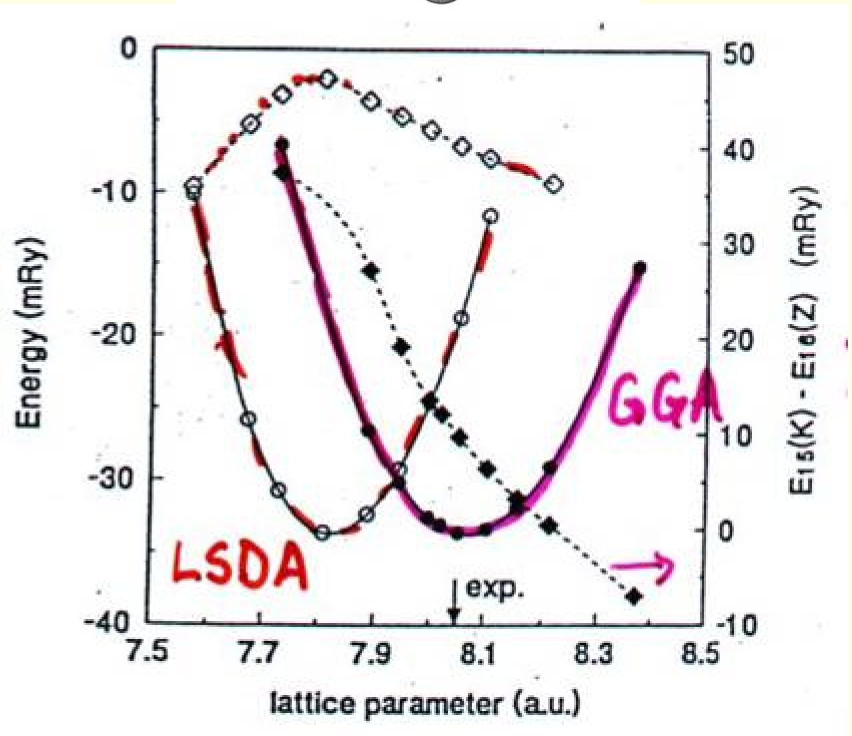
DFT thanks to Claudia Ambrosch (previously in Graz)

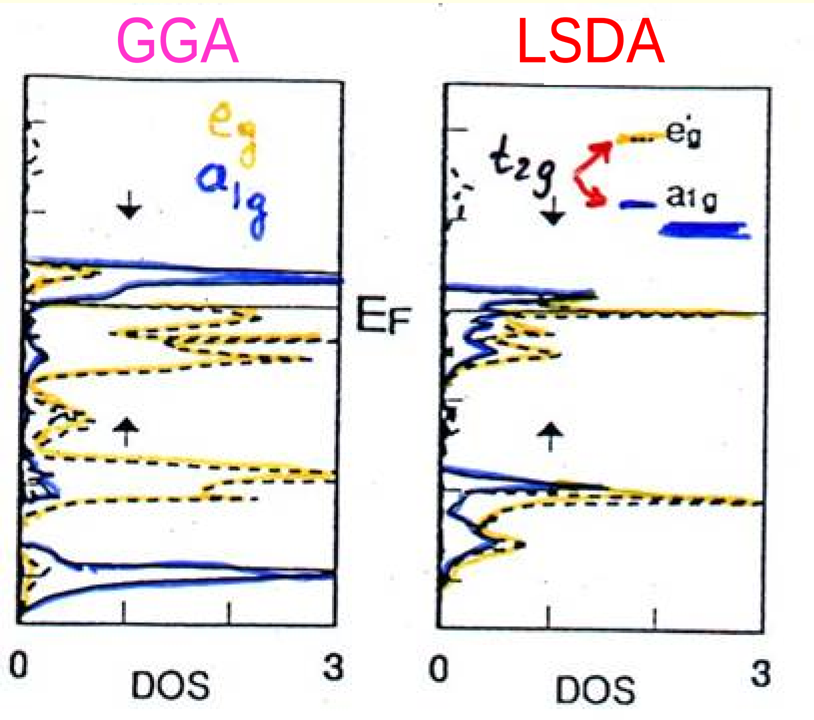
GGA follows LDA

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*

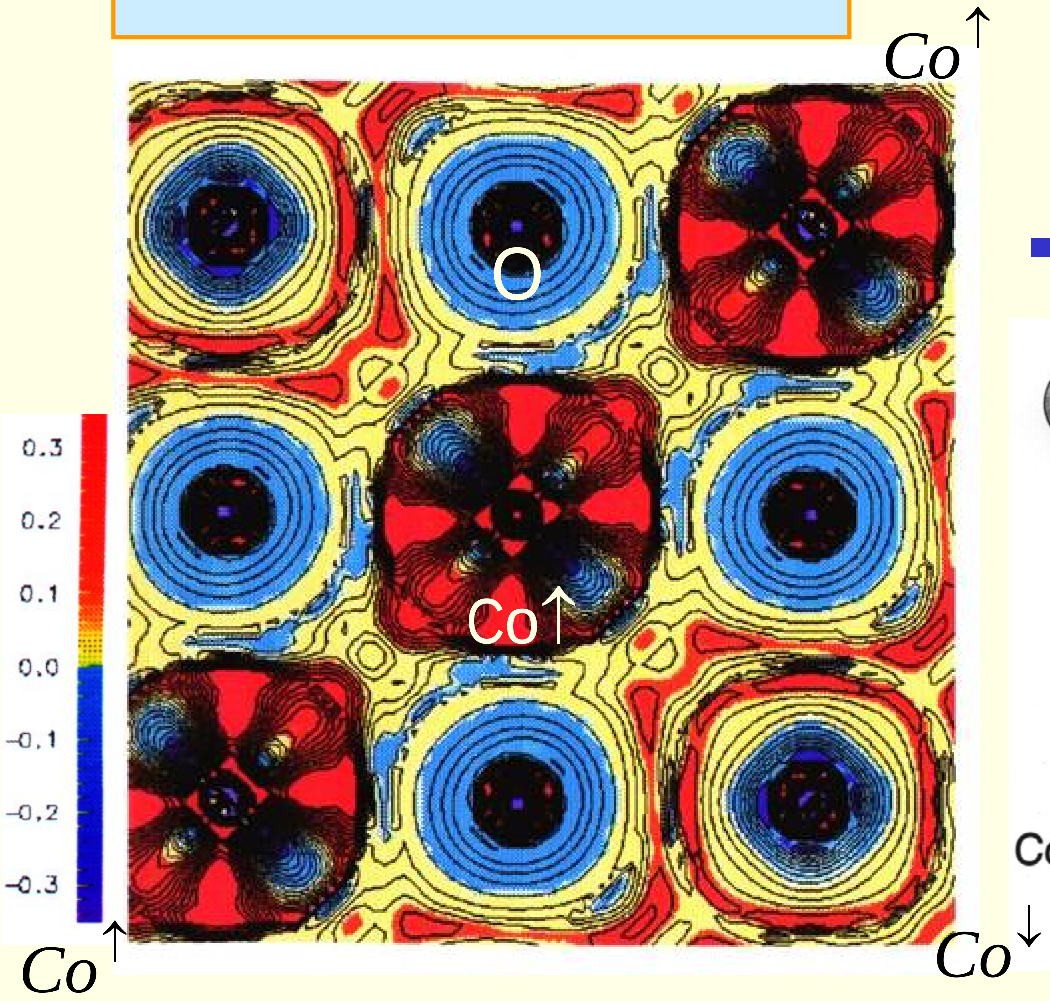




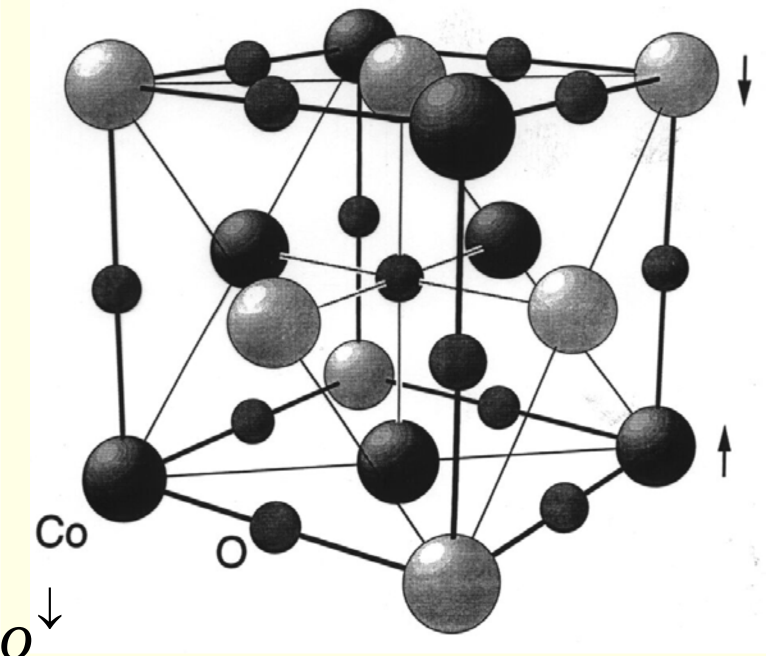


CoO why is GGA better than LSDA

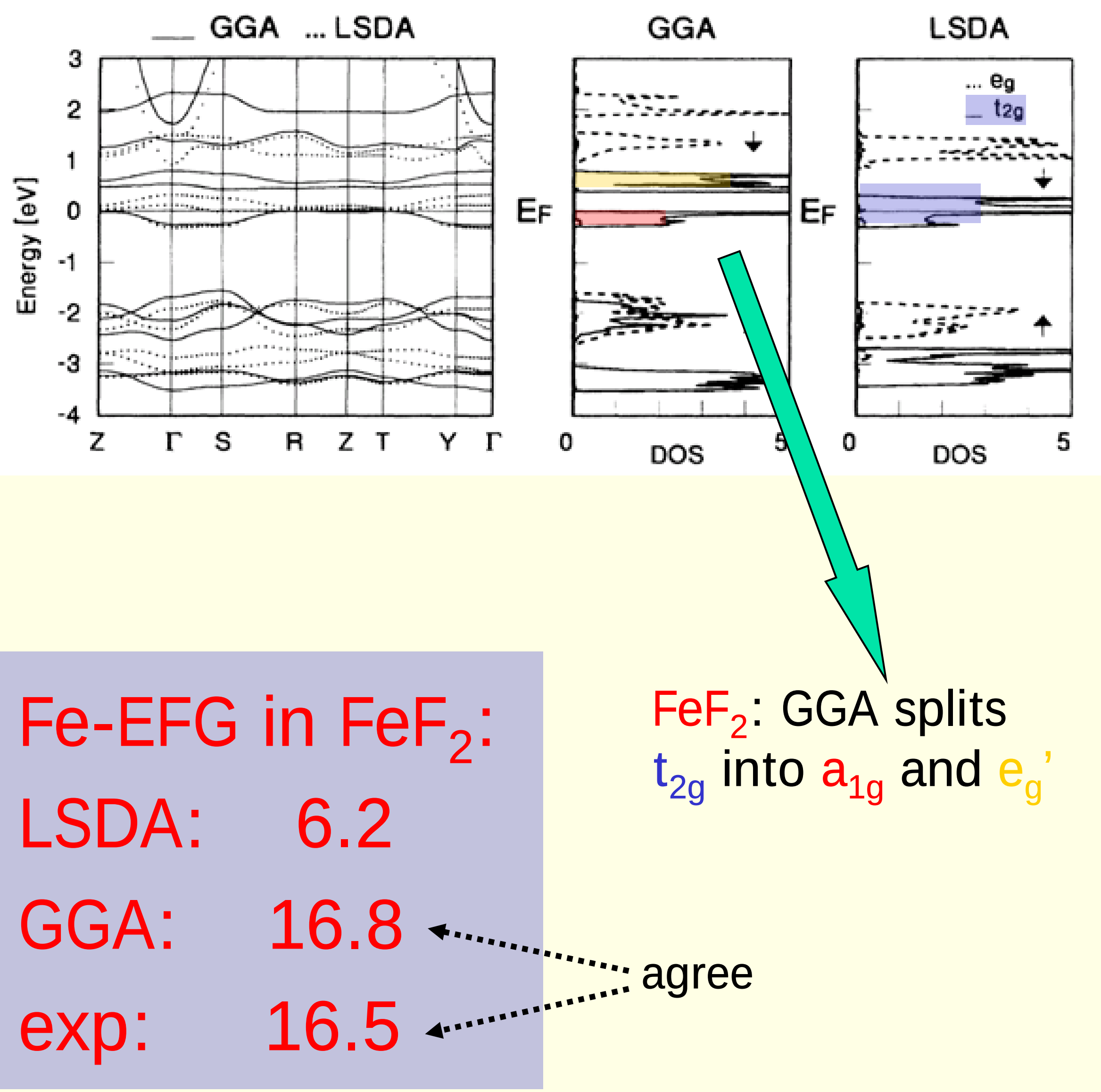
$$\Delta V_{xc}^{\uparrow} = V_{xc}^{\uparrow GGA} - V_{xc}^{\uparrow LSDA}$$



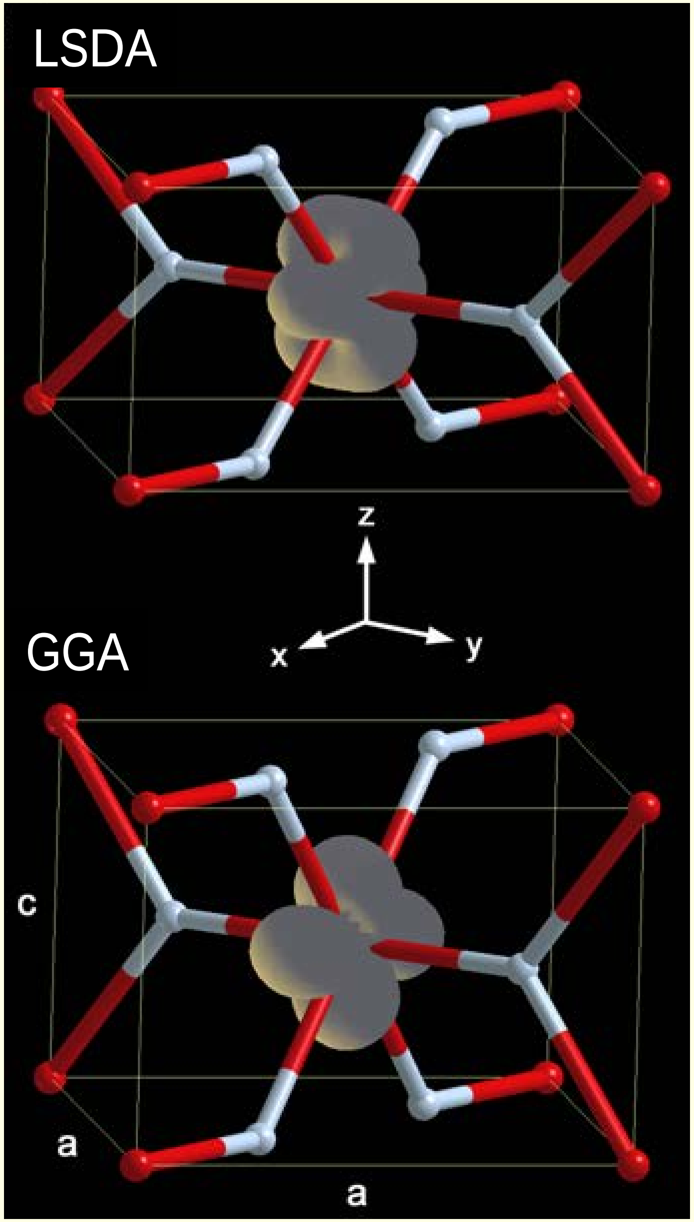
- Central Co atom distinguishes
  - *between* $Co^{\uparrow}$
  - *and* $Co^{\downarrow}$
- Angular correlation



FeF$_2$: GGA works surprisingly well



FeF$_2$: GGA splits t_{2g} into a_{1g} and e_g'



Fe-EFG in FeF$_2$:

LSDA: 6.2

GGA: 16.8

exp: 16.5

agree

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)*

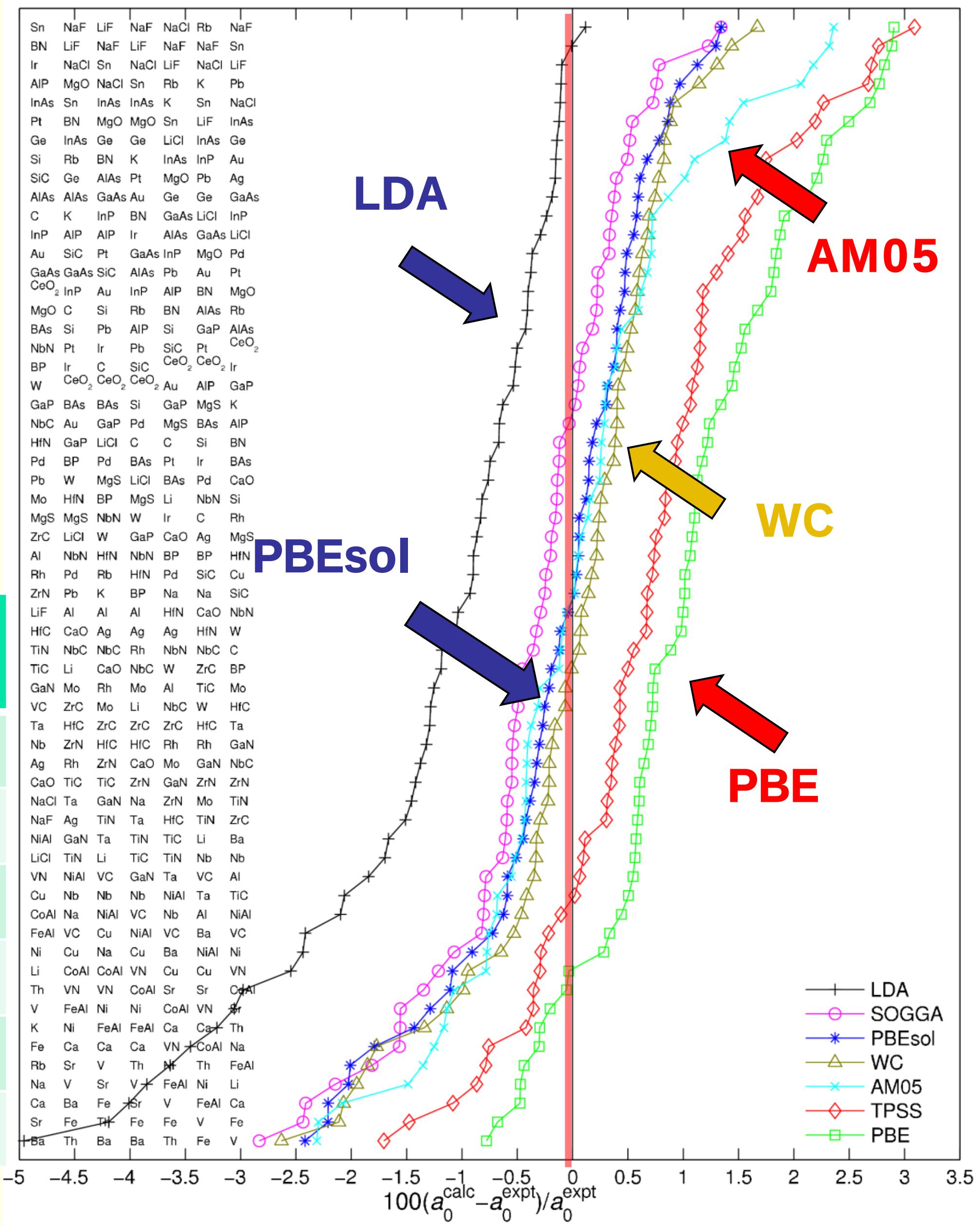
Z.Wu, R.E.Cohen,
PRB 73, 235116 (2006)

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

accuracy: "DFT limit"

- Testing of DFT functionals:
  - *error of theoretical lattice parameters for a large variety of solids (Li-Th)*

	me (Å)	mae (Å)	mre (%)	mare (%)
LDA	-0.058	0.058	-1.32	1.32
SO-GGA	-0.014	0.029	-0.37	0.68
PBEsol	-0.005	0.029	-0.17	0.67
WC	0.000	0.031	-0.03	0.68
AM05	0.005	0.035	0.01	0.77
PBE	0.051	0.055	1.05	1.18



Can LDA be improved ?

- better GGAs and meta-GGAs (ρ, $\nabla\rho$, τ):
  - *usually improvement, but often too small.*
- LDA+U: for correlated 3d/4f electrons, treat strong Coulomb repulsion via Hubbard U parameter (cheap, “empirical U” ?)
- Exact exchange: imbalance between exact X and approximate C
  - *hybrid-DFT (mixing of HF + GGA; “mixing factor” ?)*
  - *exact exchange + RPA correlation (extremely expensive)*
- GW: gaps in semiconductors, expensive!
- Quantum Monte-Carlo: very expensive
- DMFT: for strongly correlated (metallic) d (f) -systems (expensive)

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

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

Hybrid functional: only for (correlated) electrons

- Only for certain atoms

  and electrons of a given angular momentum ℓ

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

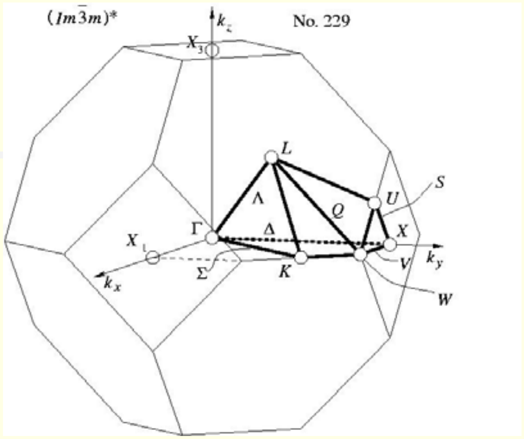
$$E_{\mathrm{x}}^{\mathrm{HF}}[n_{m_i m_j}^\sigma] = -\frac{1}{2}\sum_\sigma \sum_{m_1,m_2,m_3,m_4}^{\ell} n_{m_1 m_2}^\sigma n_{m_3 m_4}^\sigma \langle m_1 m_3 | v_{\mathrm{ee}} | m_4 m_2\rangle$$

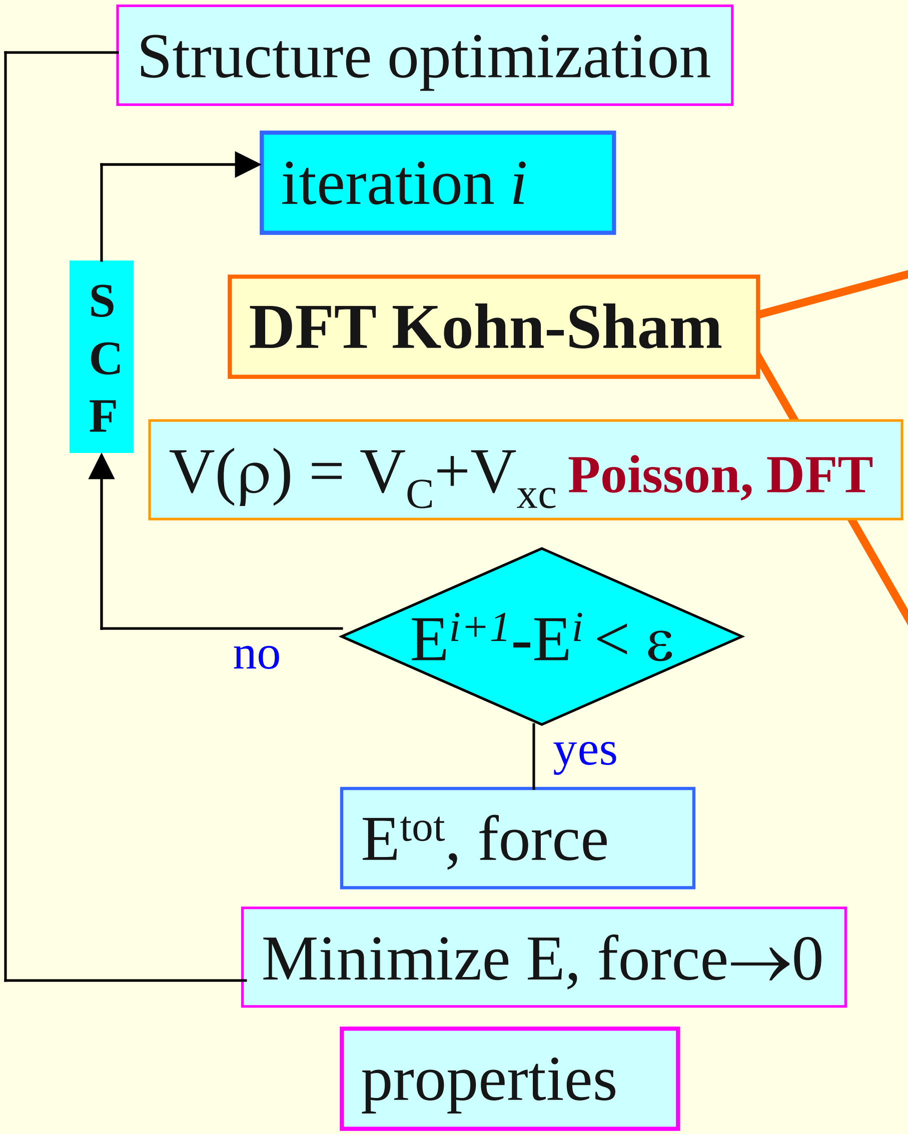
$$\langle m_1 m_2 | v_{\mathrm{ee}} | m_3 m_4\rangle = \sum_{k=0}^{2\ell} a_k F_k$$

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

Structure: $\underbrace{a,b,c,\alpha,\beta,\gamma,}_{\text{unit cell}}$ R_α , ...

unit cell atomic positions





Structure optimization

iteration *i*

S
C
F

DFT Kohn-Sham

V(ρ) = $V_C + V_{xc}$ **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

$$\frac{\delta\langle E\rangle}{\delta C_{k_n}} = 0$$

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:*

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

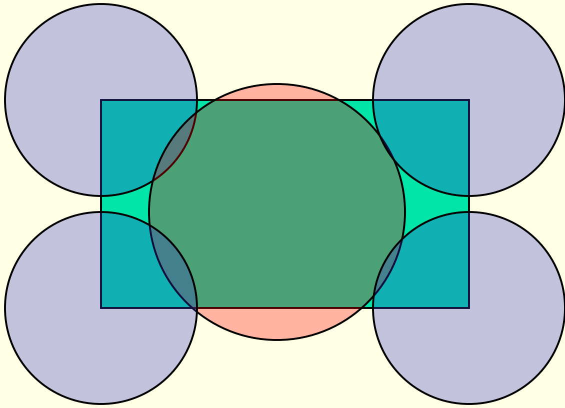
  - *this leads to the famous “Secular equations”, i.e. a set of linear equations which in matrix representation is called “generalized eigenvalue problem”*

$$H\,C = E\,S\,C$$

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

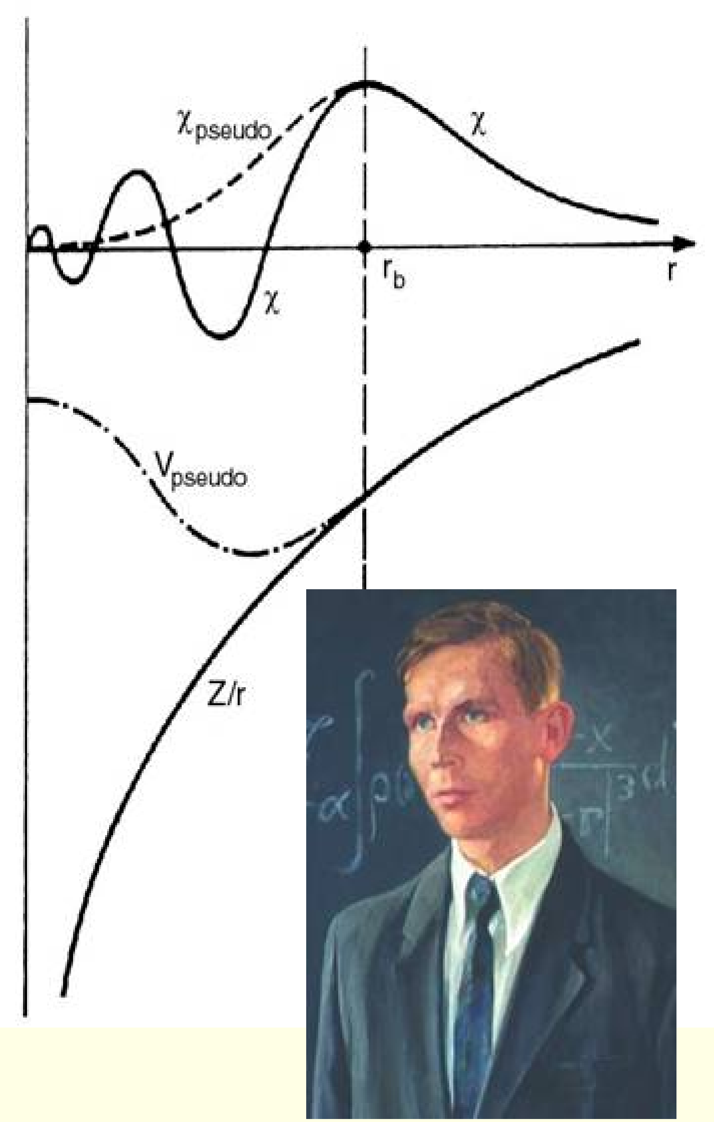
Basis Sets for Solids

- 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)*



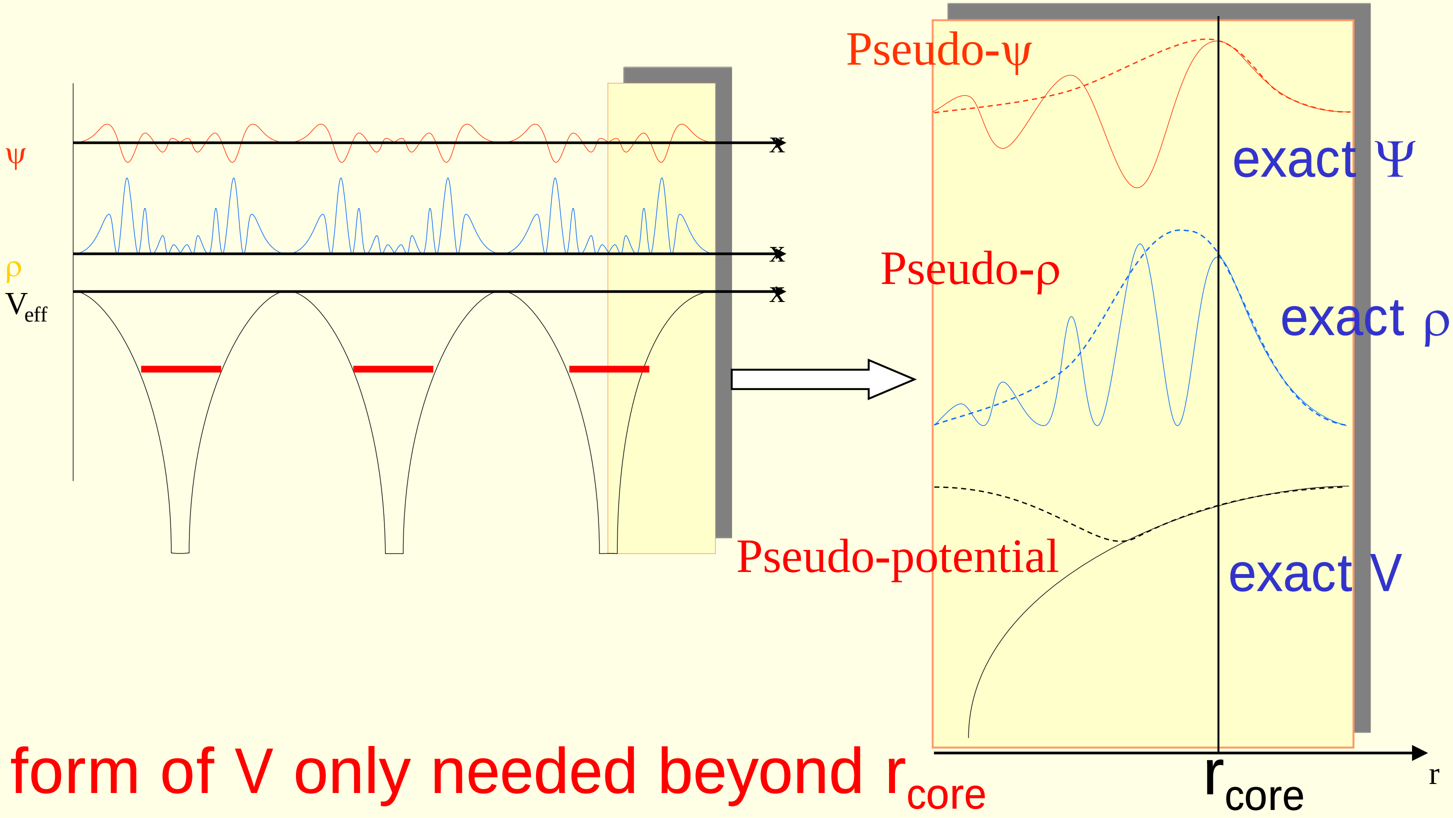
pseudopotential plane wave methods

- 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*

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

- LAPW (O.K.Anderssen 1975)
  - *Generalized eigenvalue problem*
  - *Full-potential*

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

- 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

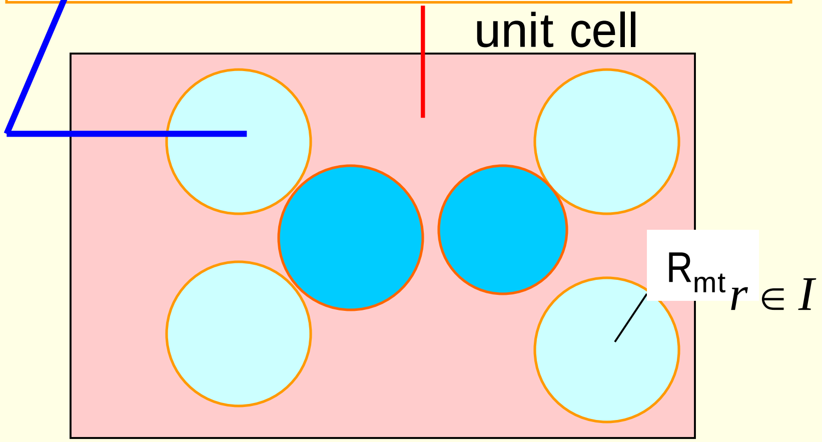
K.Schwarz, P.Blaha, S.B.Trickey,
Molecular physics, **108**, 3147 (2010)

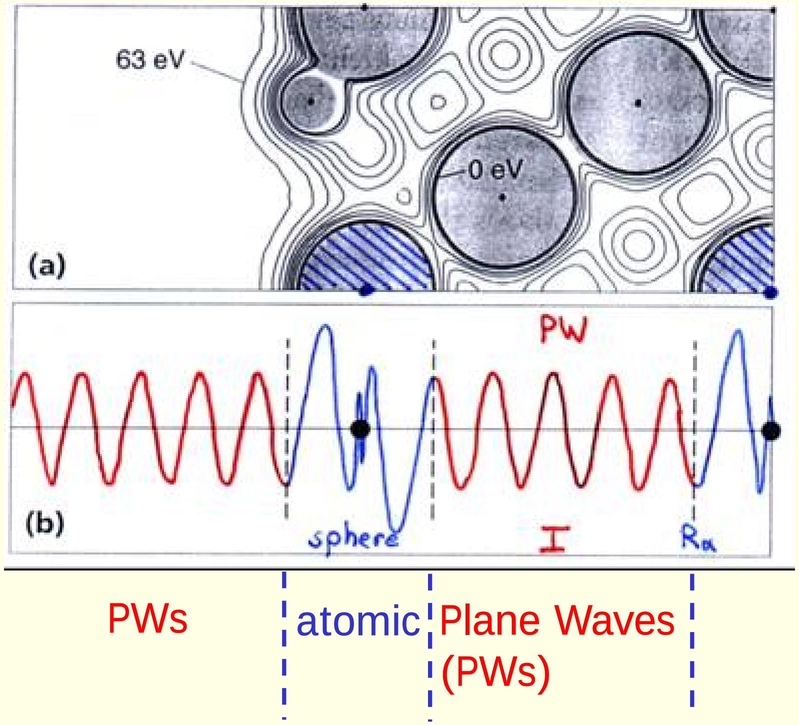
APW Augmented Plane Wave method

The unit cell is partitioned into:

atomic spheres

Interstitial region





Basis set:

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

join

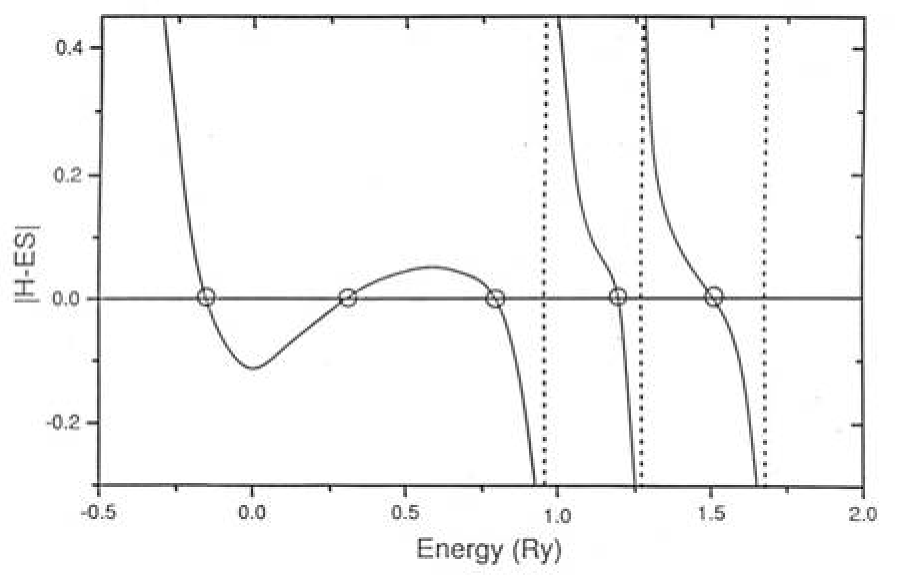
Atomic partial waves

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

$u_l(r,\varepsilon)$ 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

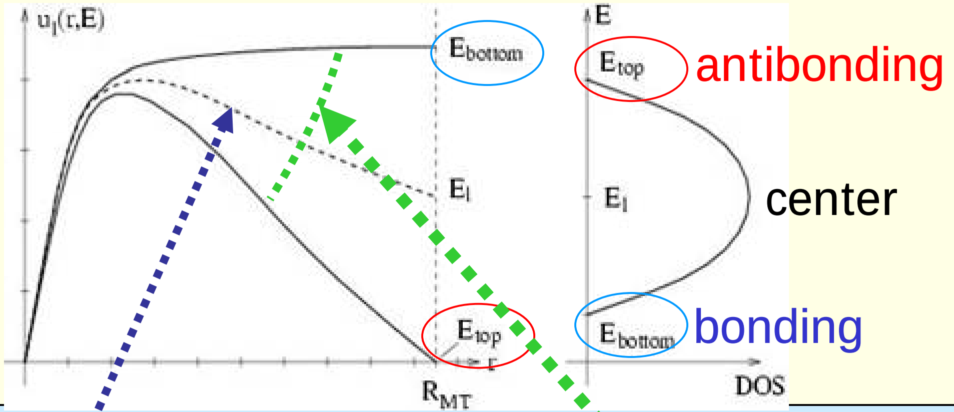
Numerical search for those energies, for which the det|H-ES| vanishes. Computationally very demanding.

“Exact” solution for given MT potential!

Linearization of energy dependence

LAPW suggested by

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



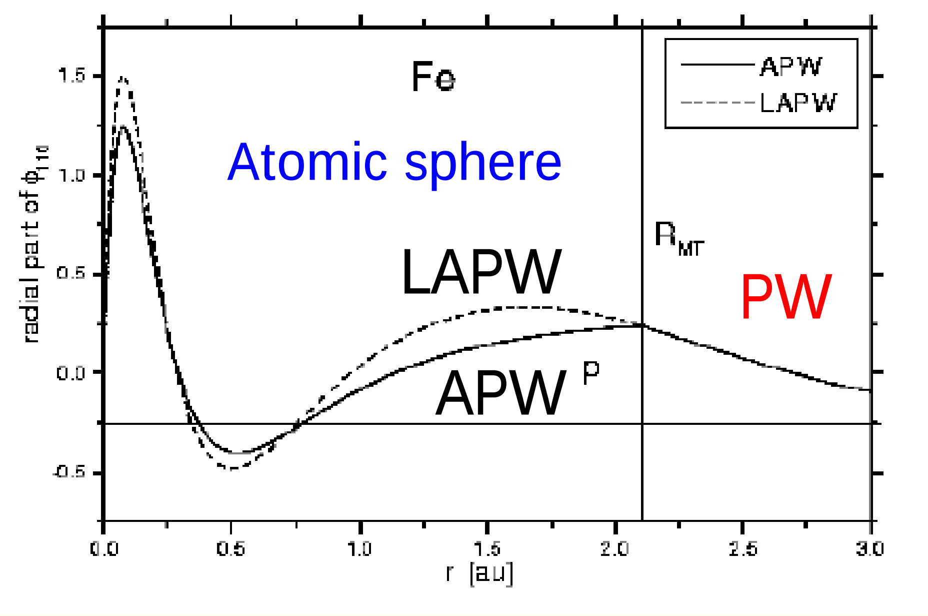
$$\Phi_{k_n} = \sum_{\ell m} [\underline{A_{\ell m}}(k_n) u_\ell(E_\ell, r) + \underline{B_{\ell m}}(k_n) \dot{u}_\ell(E_\ell, r)] Y_{\ell m}(\hat{r})$$

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

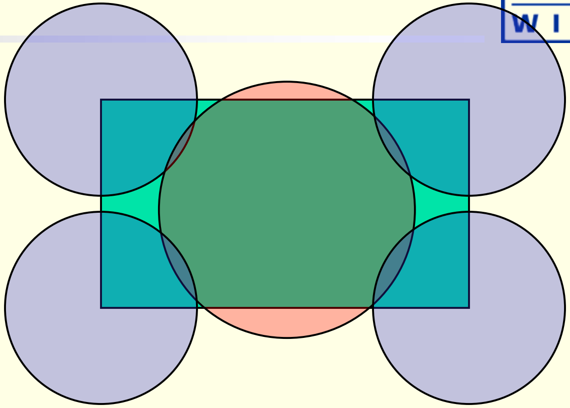
→ General eigenvalue problem (diagonalization)

→ additional constraint requires more PWs than APW

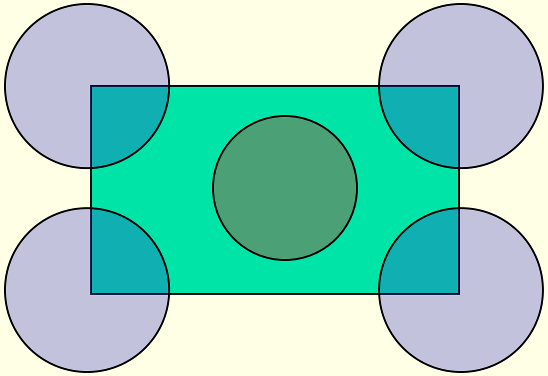


shape approximations to “real” potentials

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

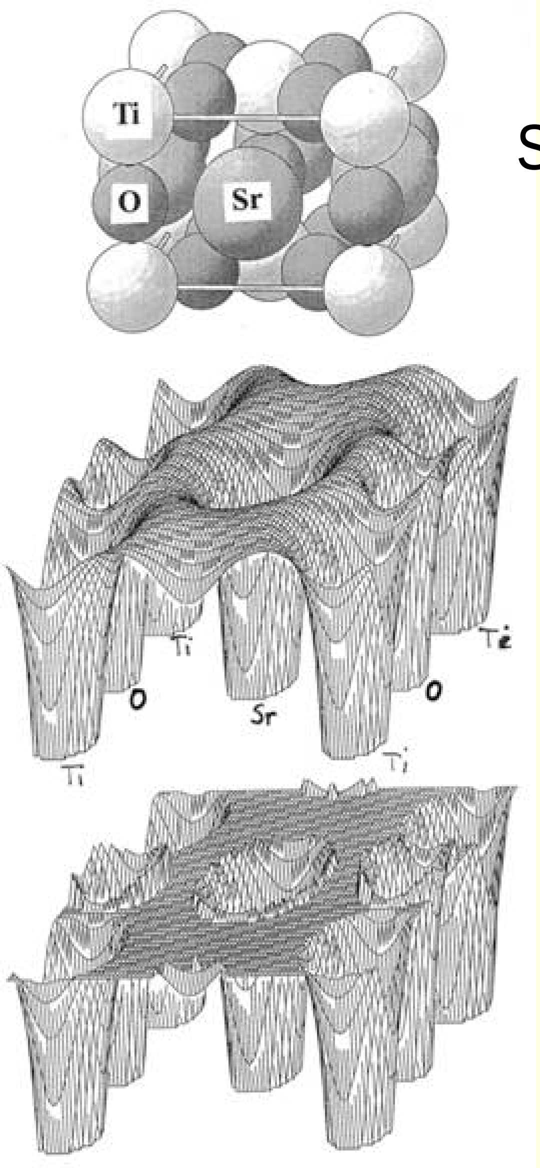


- “muffin-tin” approximation (MTA)
  - *non-overlapping spheres with spherically symmetric potential +*
  - *interstitial region with V=const.*



- “full”-potential
  - *no shape approximations to V*

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



SrTiO$_3$

Full potential

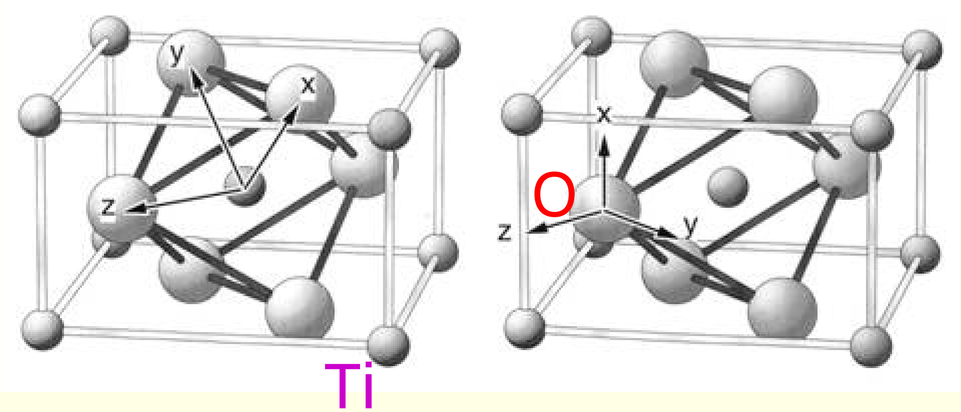
Muffin tin approximation

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

  (no shape approximation)

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

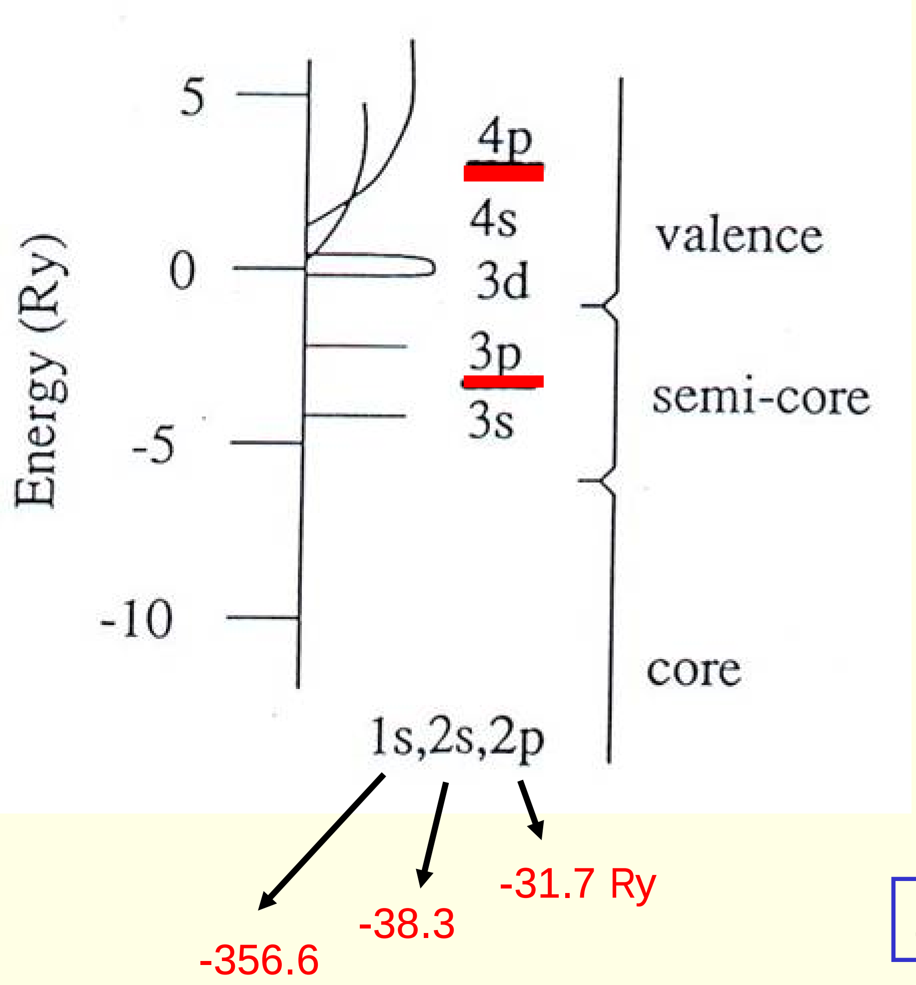
- Inside each atomic sphere a local coordinate system is used (defining LM)



TiO$_2$ rutile

Core, semi-core and valence states

For example: Ti

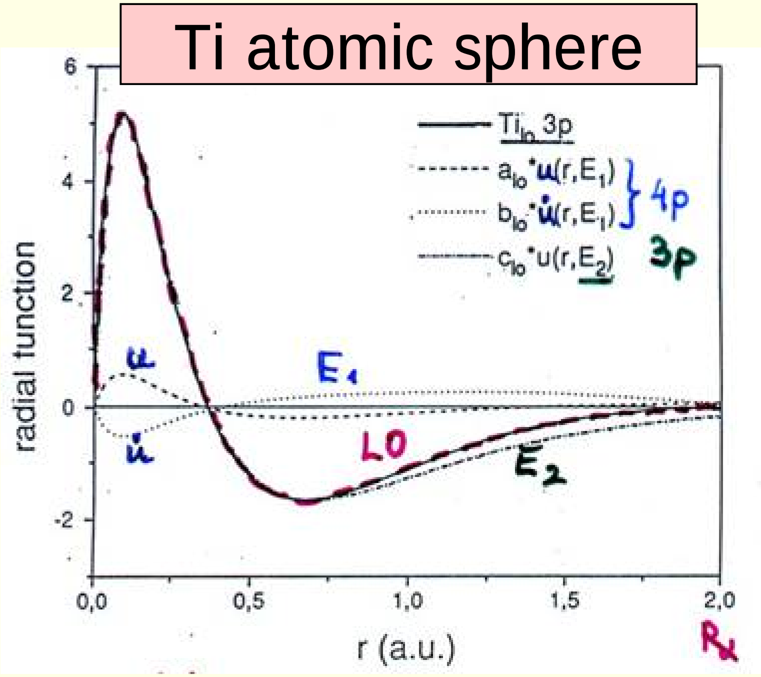


- Valences states
  - ***High*** *in energy*
  - ***Delocalized*** *wavefunctions*
- Semi-core states
  - ***Medium*** *energy*
  - *Principal **QN** one less than valence (e.g. in Ti **3**p and **4**p)*
  - ***not completely confined*** *inside sphere (charge leakage)*
- Core states
  - ***Low*** *in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

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

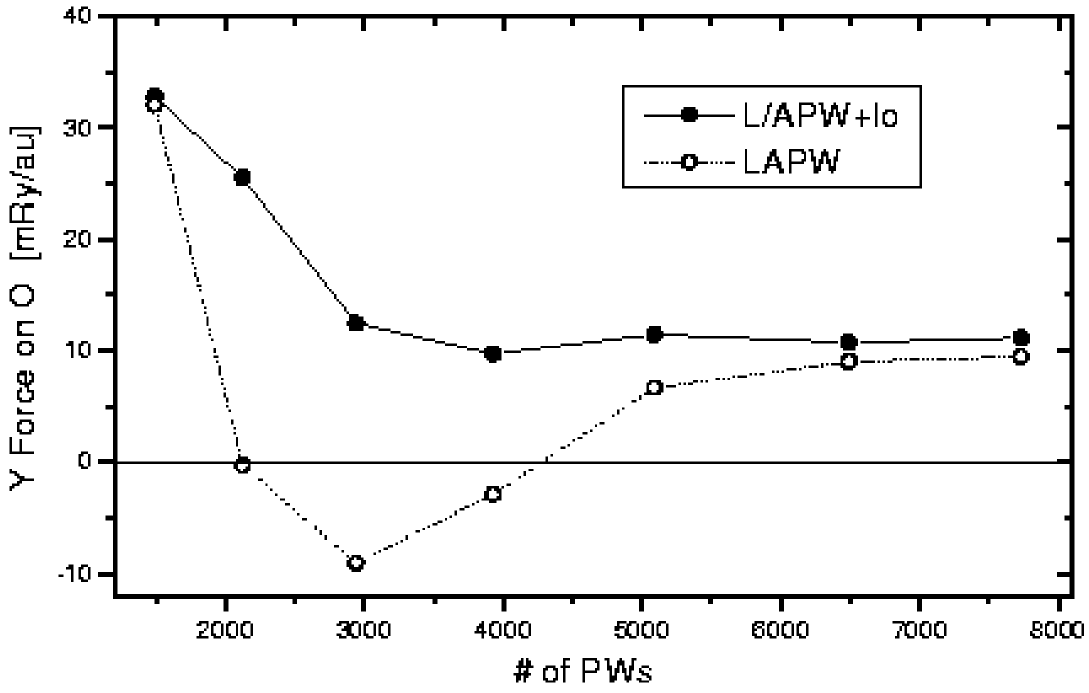
$$\Phi_{lo} = [A_{\ell m} u_\ell^{E_1} + B_{\ell m} \dot{u}_\ell^{E_1}] Y_{\ell m}(\hat{r})$$

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

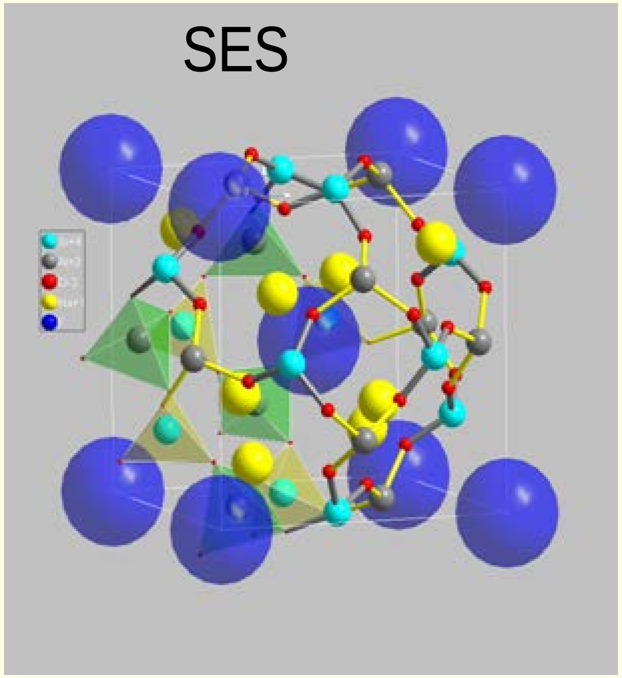
Improved convergence of APW+lo

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 (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*

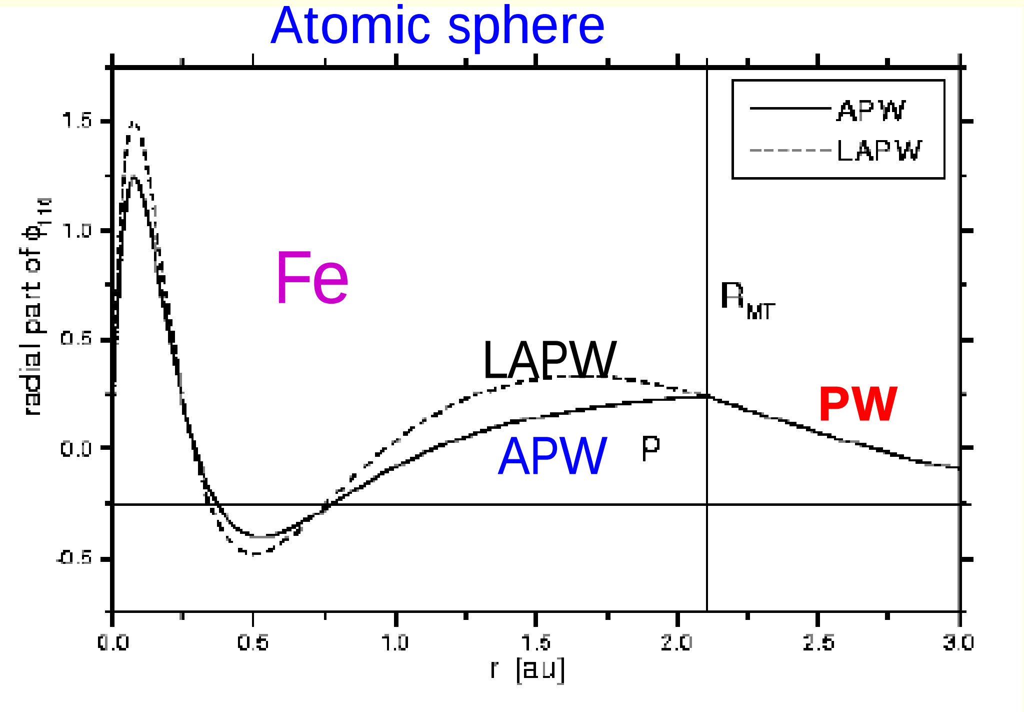
$$\Phi_{k_n} = \sum_{\ell m} A_{\ell m}(k_n) u_\ell(E_\ell, r) Y_{\ell m}(\hat{r})$$

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)

The WIEN2k authors

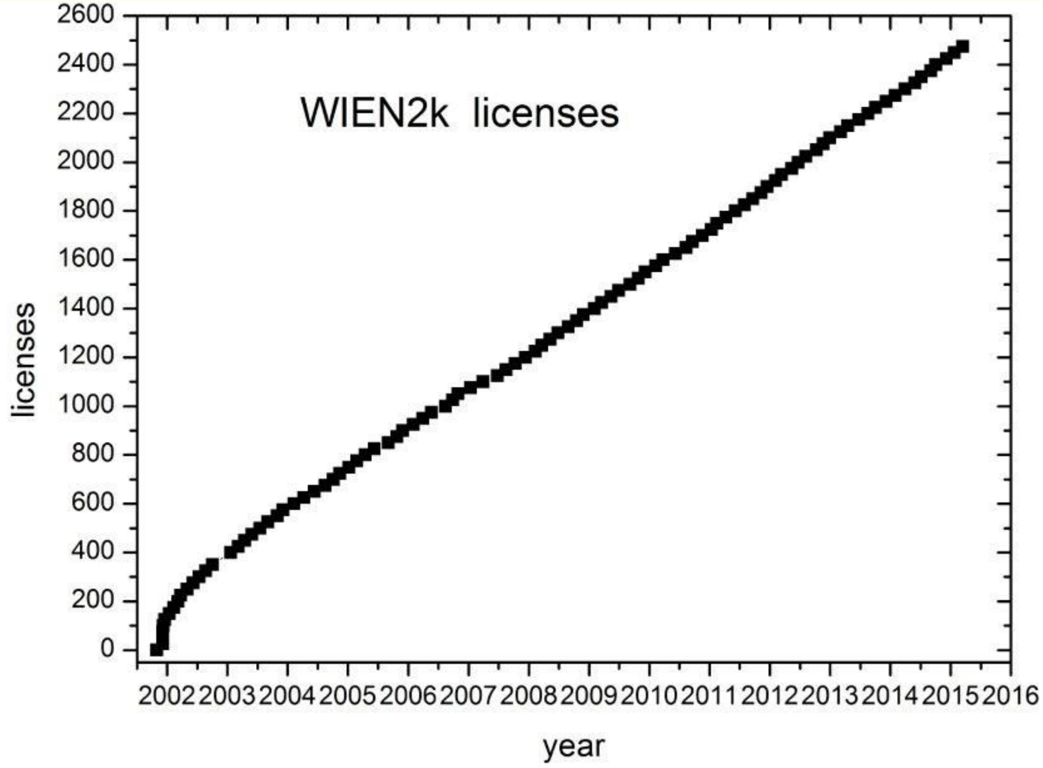
An Augmented Plane Wave
Plus Local Orbital Program for
Calculating Crystal Properties

Peter Blaha
Karlheinz Schwarz
Georg Madsen
Dieter Kvasnicka
Joachim Luitz

November 2001
Vienna, AUSTRIA
Vienna University of Technology

http://www.wien2k.at

International users



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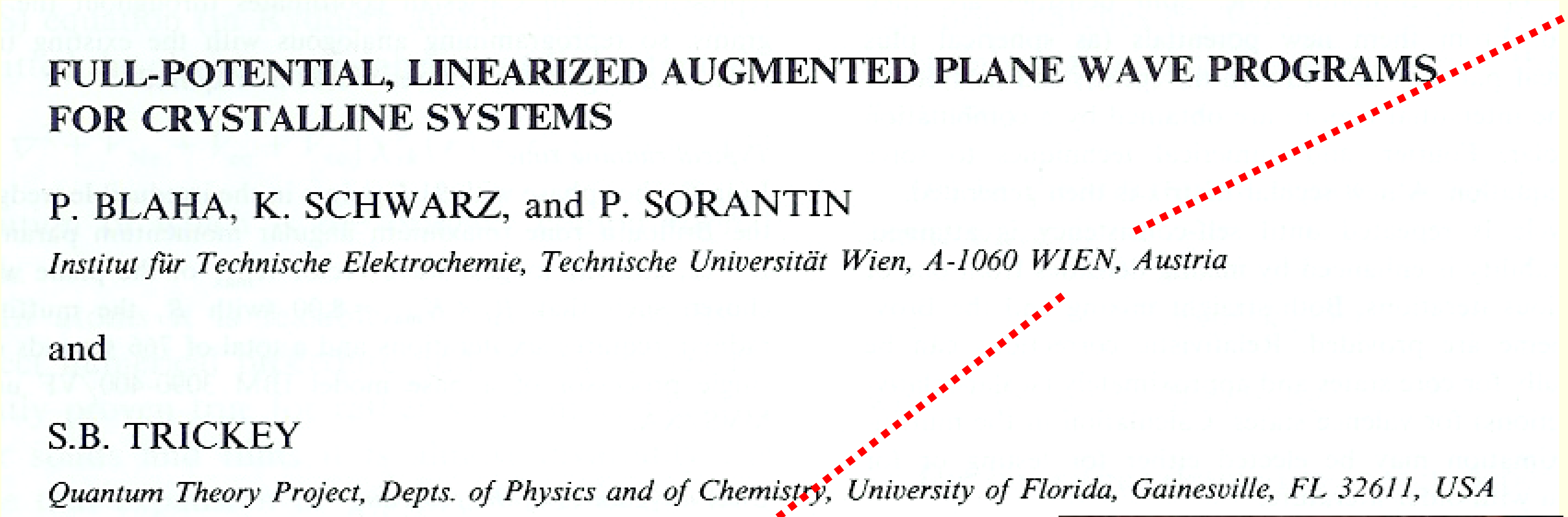
mailinglist: 10.000 emails/6 years

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

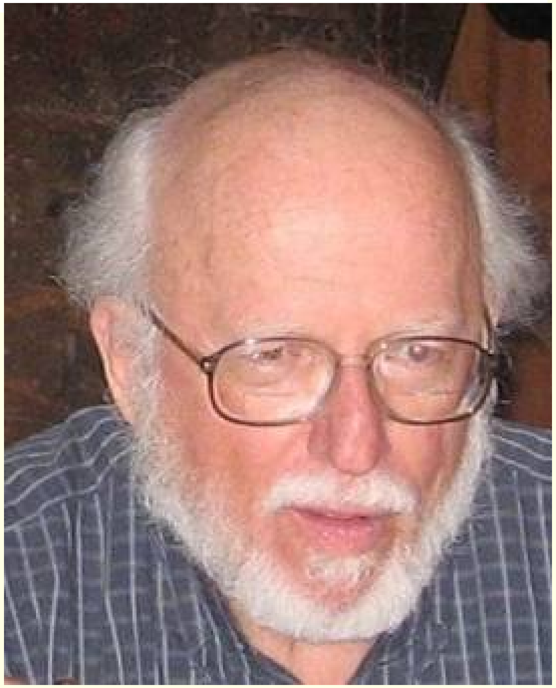
S.B. TRICKEY

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

PROGRAM SUMMARY

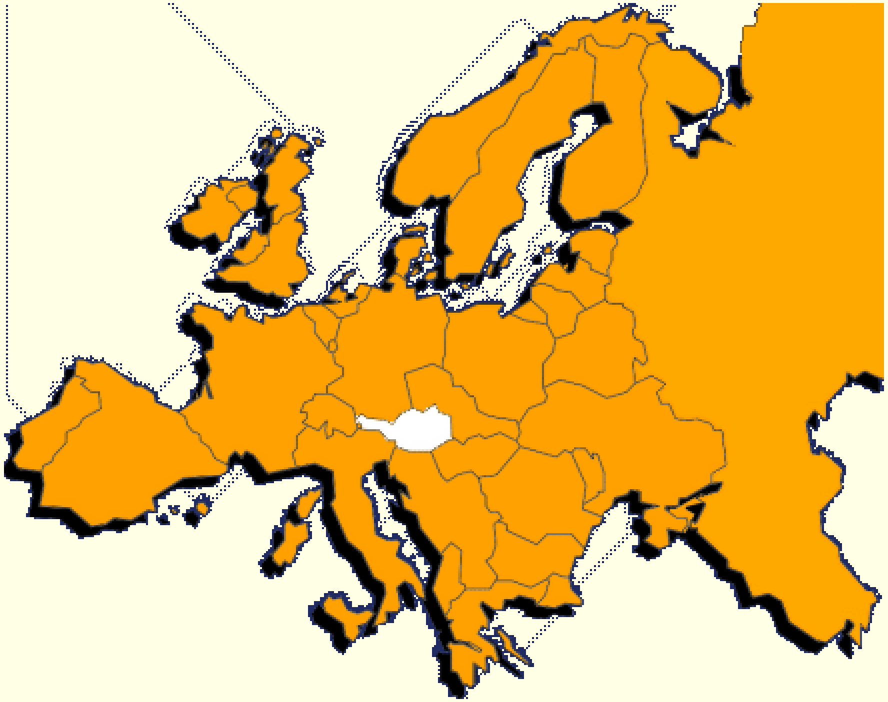
Title of program: WIEN

Computer Physics Communications 59 (1990) 399–415



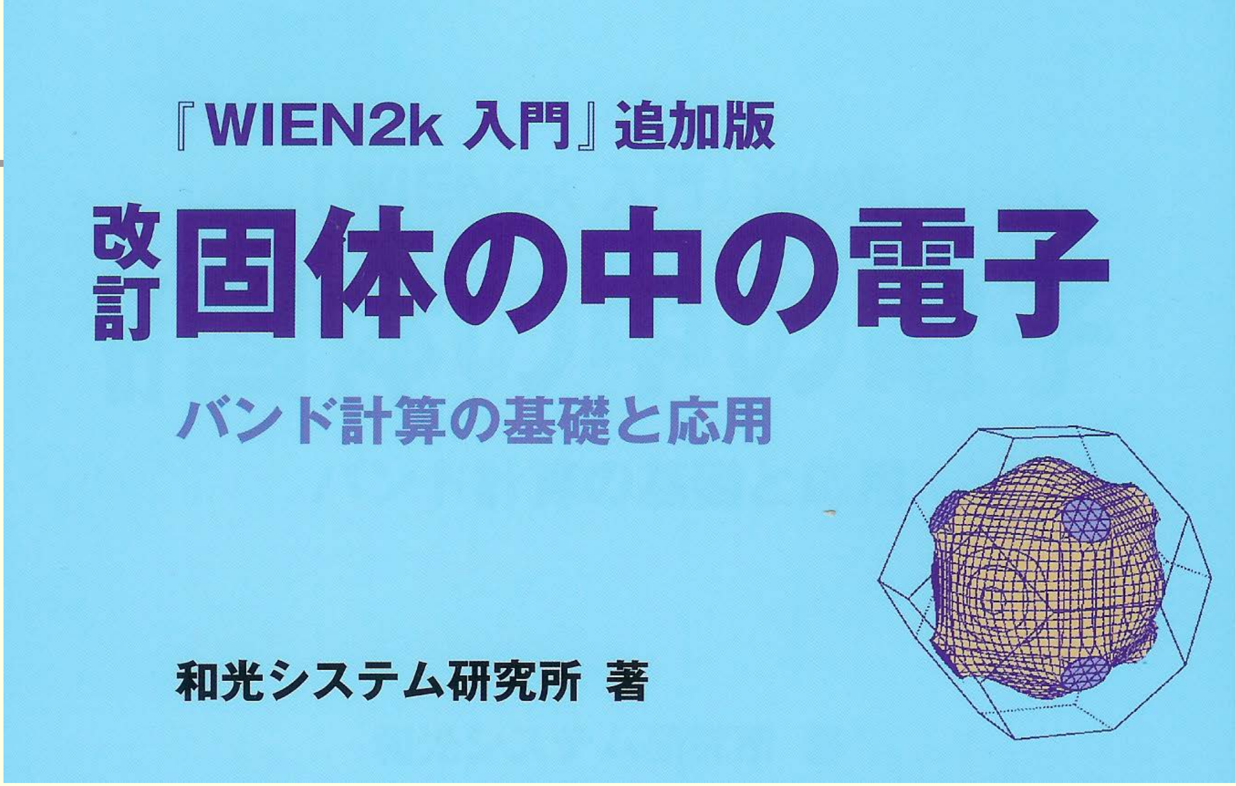
Europa Austria Vienna → WIEN

In the Heart of EUROPE



In Japan

- Book published by
  Shinya Wakoh (2006)

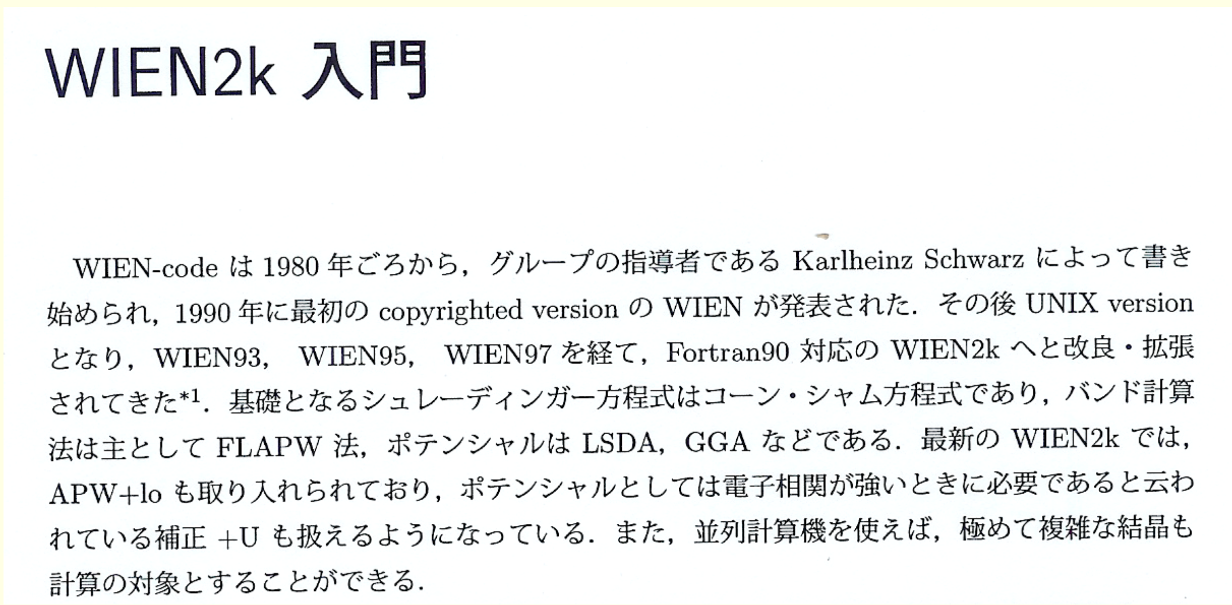


『WIEN2k 入門』追加版

改訂 固体の中の電子

バンド計算の基礎と応用

和光システム研究所 著



WIEN2k 入門

WIEN-code は 1980 年ごろから，グループの指導者である Karlheinz Schwarz によって書き始められ，1990 年に最初の copyrighted version の WIEN が発表された．その後 UNIX version となり，WIEN93， WIEN95， WIEN97 を経て，Fortran90 対応の WIEN2k へと改良・拡張されてきた[*1]．基礎となるシュレーディンガー方程式はコーン・シャム方程式であり，バンド計算法は主として FLAPW 法，ポテンシャルは LSDA，GGA などである．最新の WIEN2k では，APW+lo も取り入れられており，ポテンシャルとしては電子相関が強いときに必要であると云われている補正 +U も扱えるようになっている．また，並列計算機を使えば，極めて複雑な結晶も計算の対象とすることができる．

Development of WIEN2k

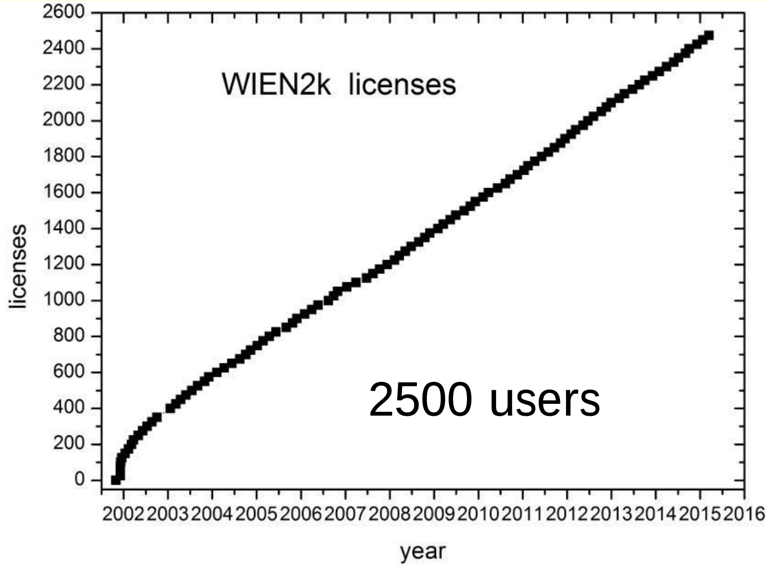
- Authors of WIEN2k

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

- Other contributions to WIEN2k
  - *C. Ambrosch-Draxl (Univ. Graz, Austria), optics*
  - *E. Assmann (Vienna) Wannier functions*
  - *F. Karsai (Vienna) parallelization*
  - ***R. Laskowski (Singapore),** non-collinear magnetism, NMR chemical shifts, BSE*
  - ***L. Marks (Northwestern, US)** , various optimizations, new mixer*
  - *P. Novák and J. Kunes (Prague), LDA+U, SO*
  - *B. Olejnik (Vienna), non-linear optics,*
  - *C. Persson (Uppsala), irreducible representations*
  - *V. Petricek (Prague) 230 space groups*
  - *O. Rubel (Lakehead) Berry phases*
  - *M. Scheffler (Fritz Haber Inst., Berlin), forces*
  - ***D.J.Singh** (NRL, Washington D.C., Oak Ridge), local oribtals (LO), APW+lo*
  - *E. Sjöstedt and **L Nordström** (Uppsala, Sweden), APW+lo*
  - *J. Sofo (Penn State, USA) and J. Fuhr (Barriloche), Bader analysis*
  - *F. Tran (Vienna) Hartree Fock, DFT functionals*
  - *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	
16th	Penn State, USA	June	2009	
17th	Nantes, France	July	2010	
18th	Penn State, USA	June	2011	
19th	Tokyo, Japan	Sept	2012	
20th	Penn State, USA	Aug.	2013	
21th	Nantes, France	July	2014	
	Warsaw, Poland	Oct.	2014	
22nd	Singapore	Aug.	2015	



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

upper bound

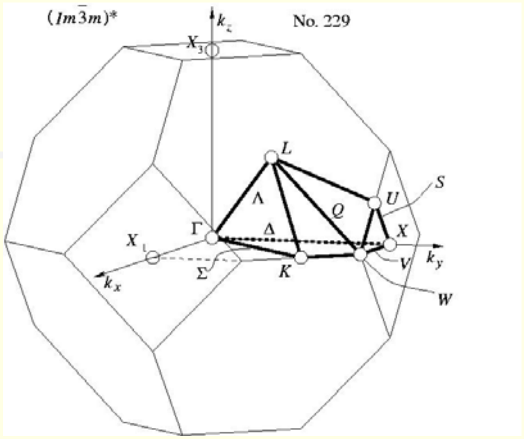
minimum

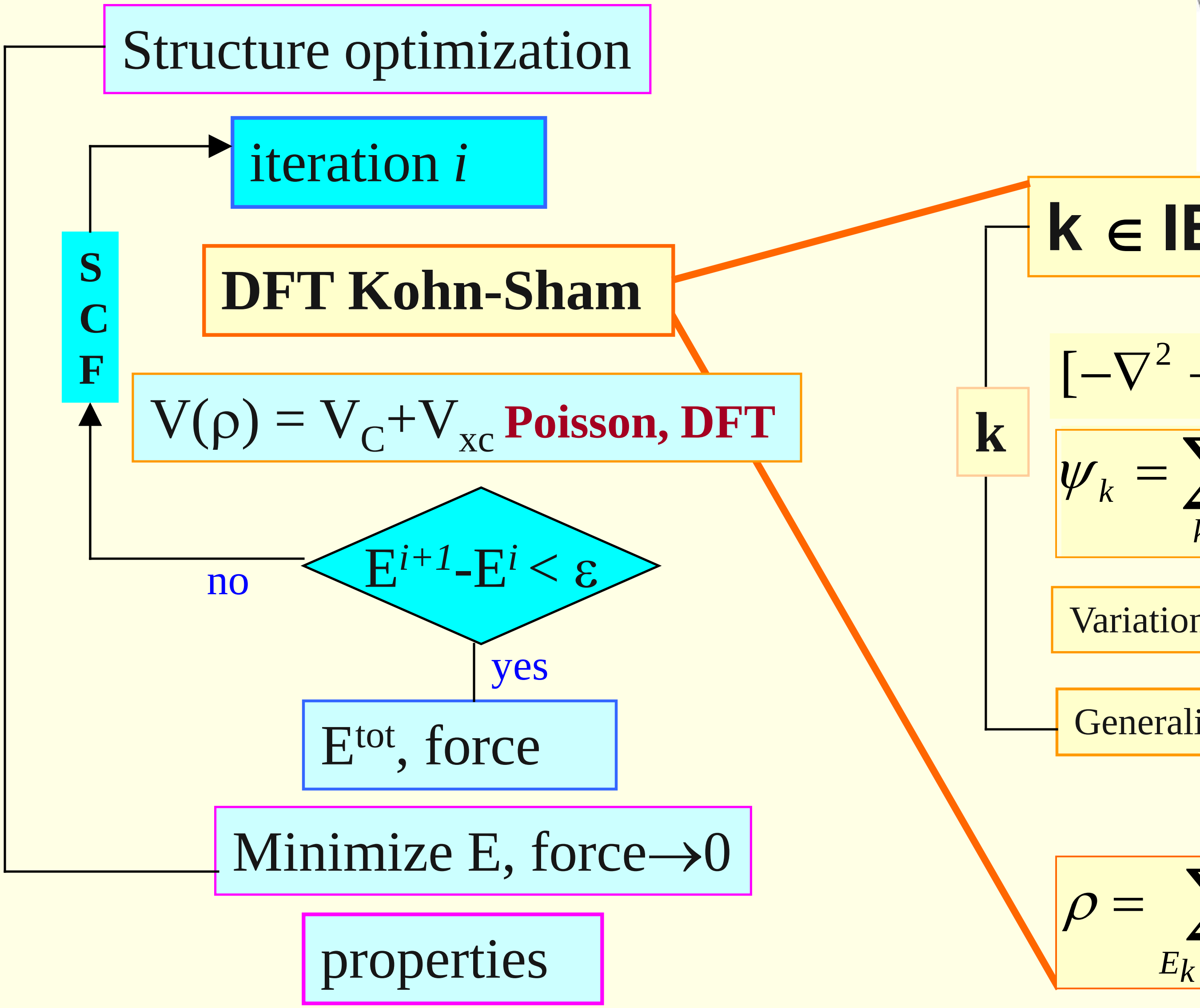
Generalized eigenvalue problem: H C=E S C

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

Structure: $\underbrace{a,b,c,\alpha,\beta,\gamma,}_{\text{unit cell}}$ R_α , ...

atomic positions





Structure optimization

iteration *i*

S C F

DFT Kohn-Sham

V(ρ) = $V_C + V_{xc}$ **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

$$\frac{\delta \langle E \rangle}{\delta C_{k_n}} = 0$$

Generalized eigenvalue problem

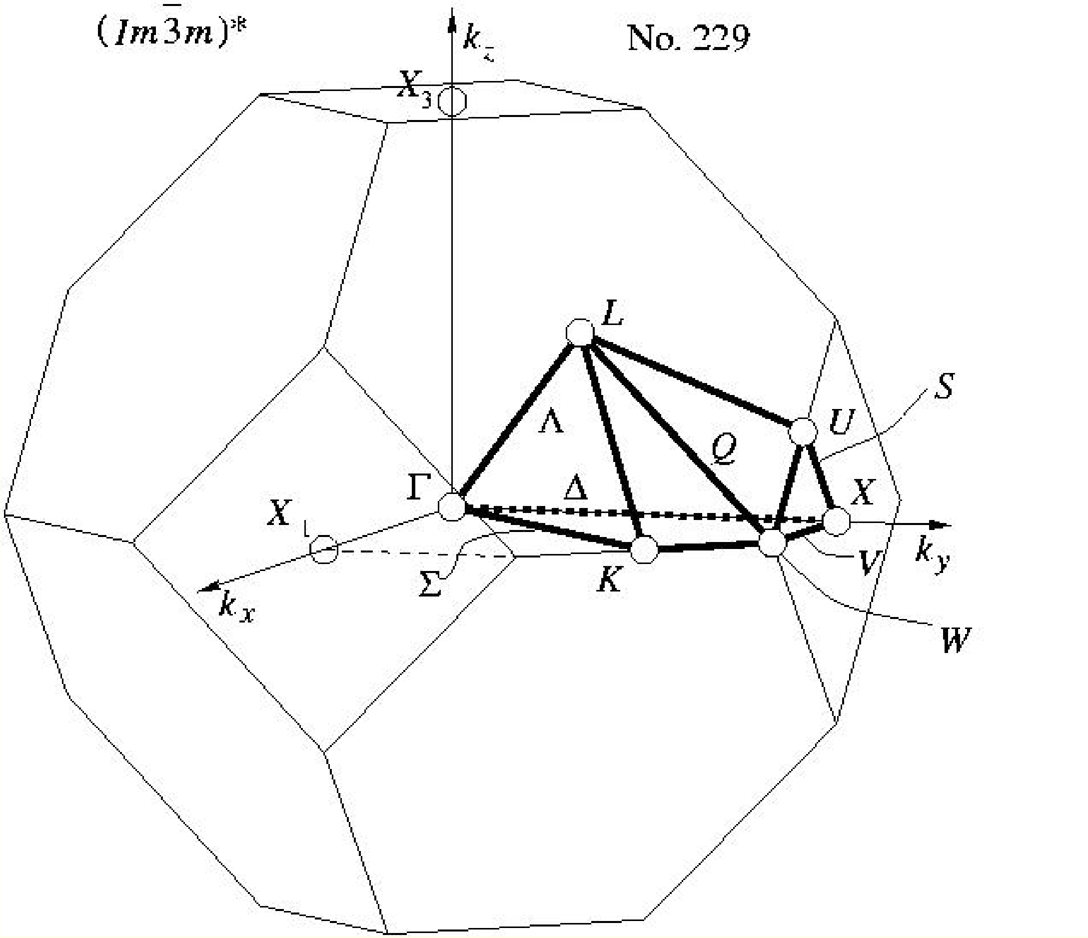
$$HC = ESC$$

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

The Brillouin zone (BZ)

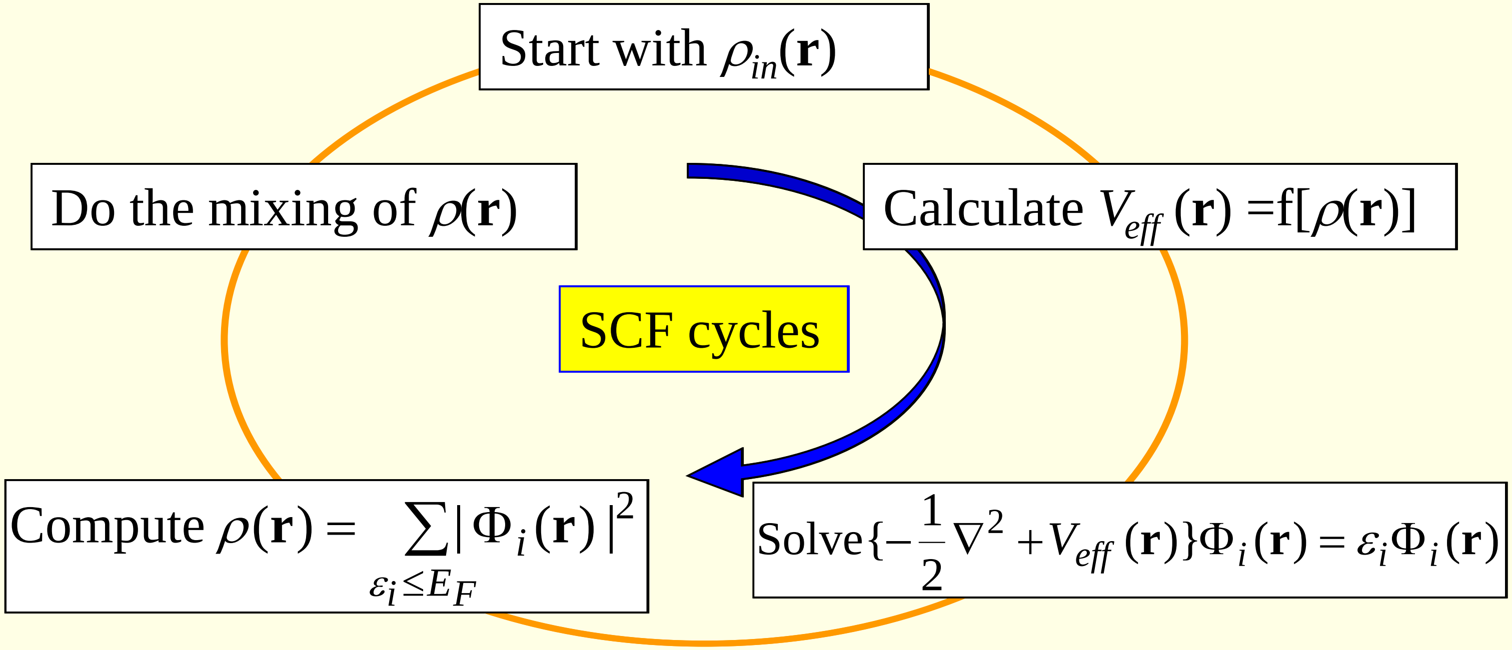
- Irreducible BZ (IBZ)
  - *The irreducible wedge*
  - *Region, from which the whole BZ can be obtained by applying all symmetry operations*

- 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 ρ(r)
- the density ρ(r) can be obtained from $\Psi(r)^*\Psi(r)$
- ?? Ψ(r) is unknown before $H\Psi=E\Psi$ is solved ??



SCF cycles

Start with $\rho_{in}(\mathbf{r})$

Calculate $V_{eff}(\mathbf{r}) = f[\rho(\mathbf{r})]$

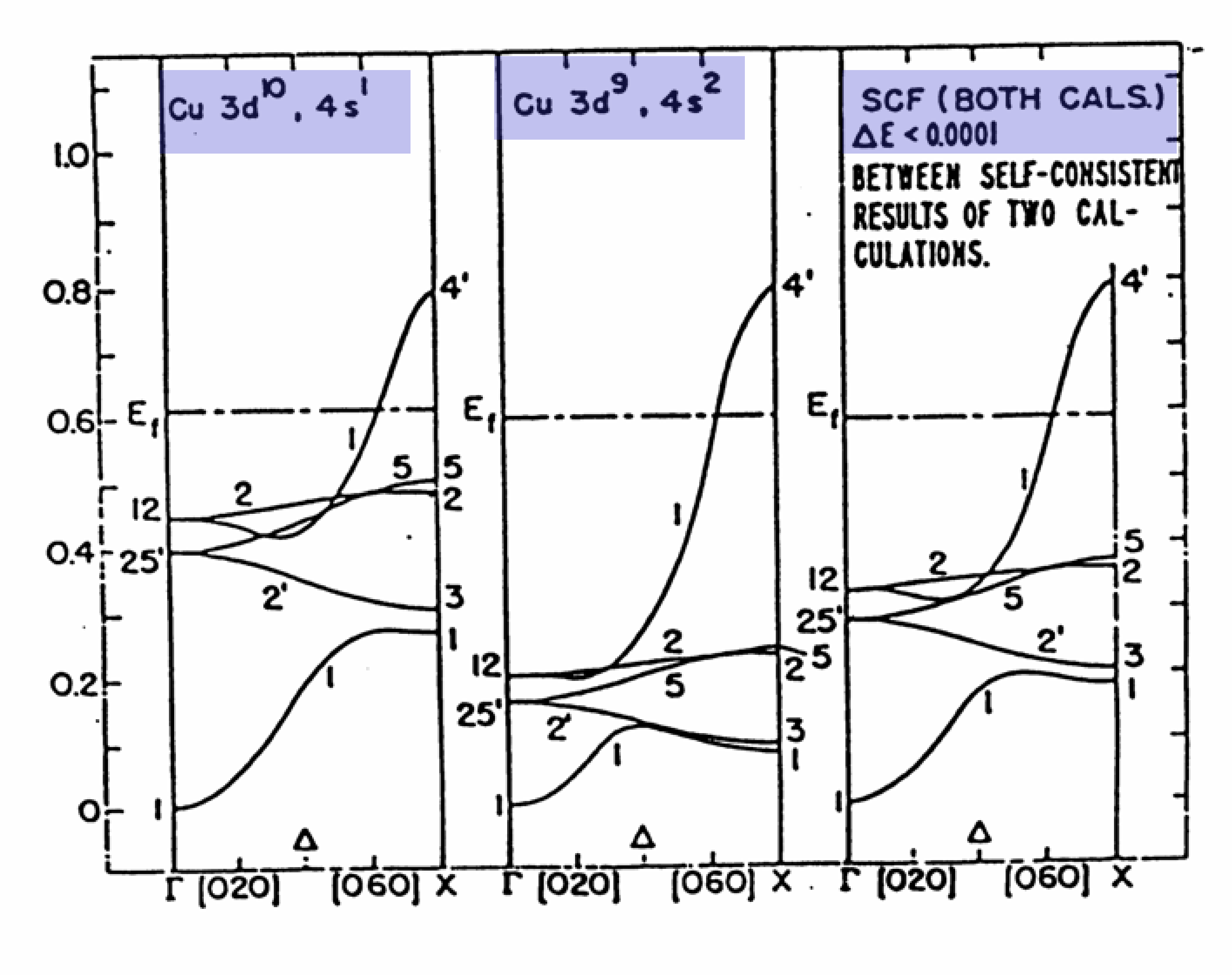
$\text{Solve}\{-\frac{1}{2}\nabla^2 + V_{eff}(\mathbf{r})\}\Phi_i(\mathbf{r}) = \varepsilon_i\Phi_i(\mathbf{r})$

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

Do the mixing of $\rho(\mathbf{r})$

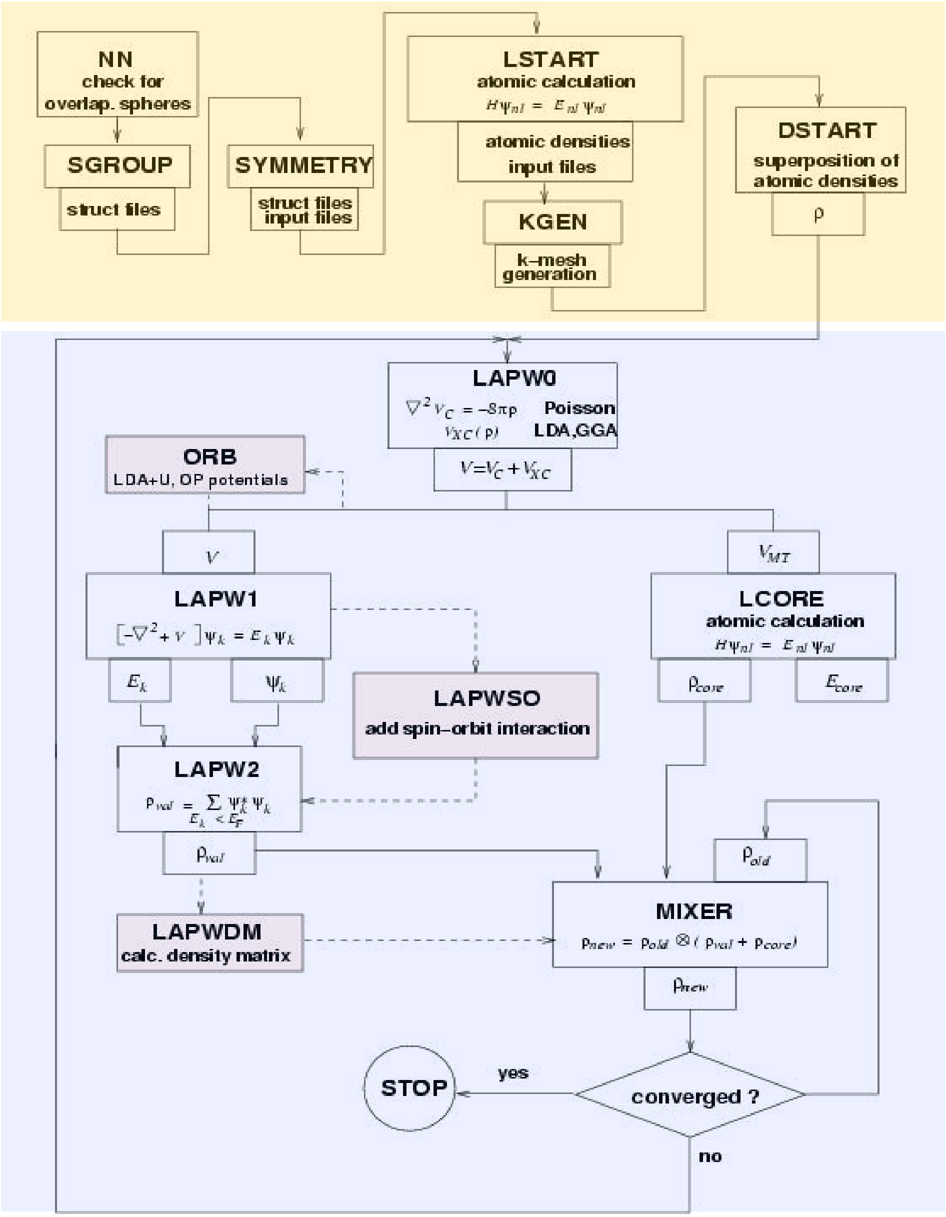
Effects of SCF

Band structure of fcc Cu

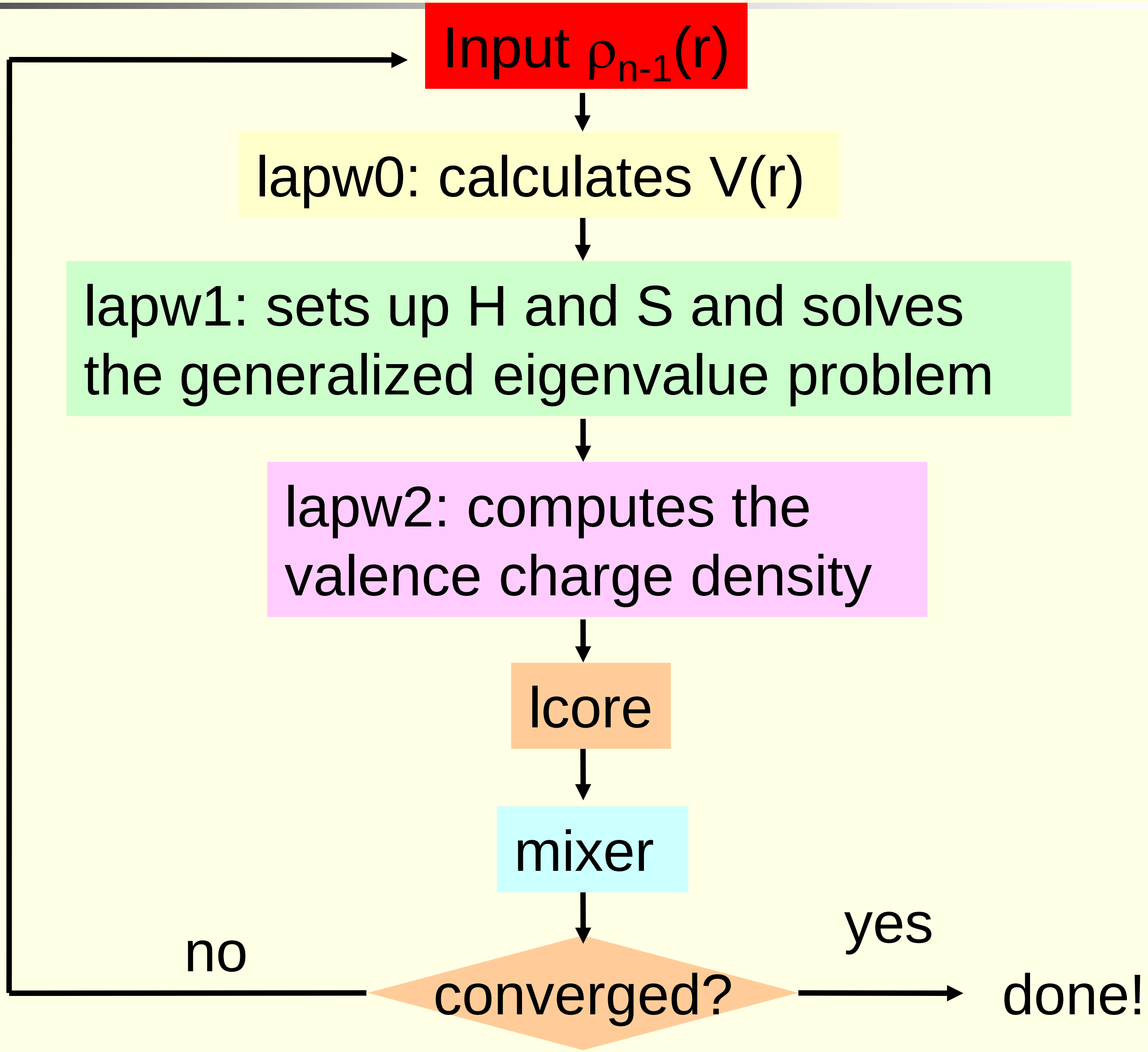


Program structure of WIEN2k

- 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*



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?

no

yes

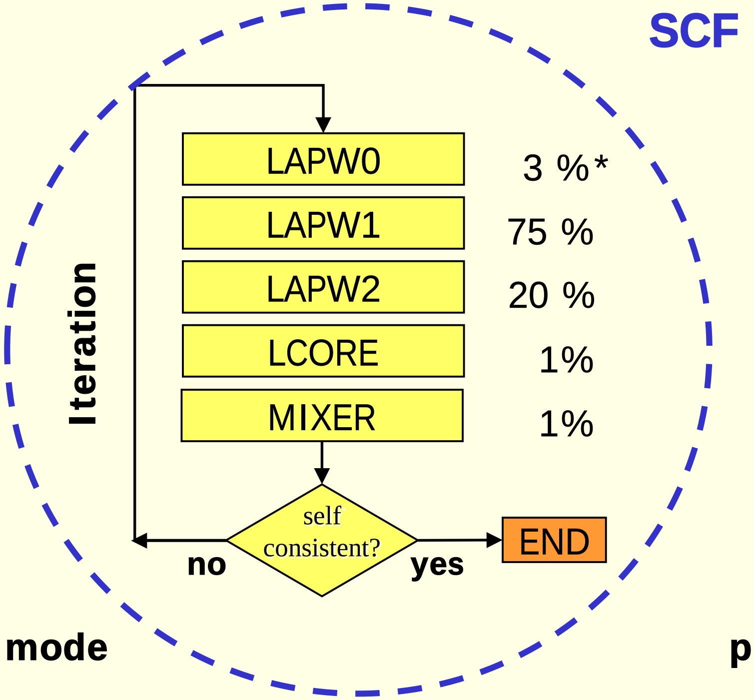
done!

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

SCF cycle



Iteration

LAPW0	3 %*
LAPW1	75 %
LAPW2	20 %
LCORE	1%
MIXER	1%

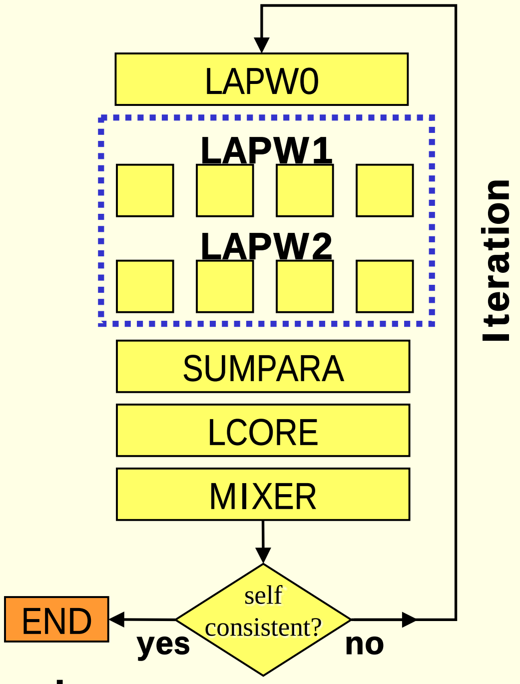
self consistent?

no

yes

END

single mode



LAPW0

LAPW1

LAPW2

SUMPARA

LCORE

MIXER

self consistent?

yes

no

END

Iteration

parallel mode

k-point parallelization

* fraction of total computation time

Advantage/disadvantage of WIEN2k

\+ robust all-electron full-potential method (new effective mixer)

\+ unbiased basisset, one convergence parameter (LDA-limit)

\+ all elements of periodic table (comparable in CPU time), metals

\+ LDA, GGA, meta-GGA, LDA+U, spin-orbit

\+ many properties and tools (supercells, symmetry)

\+ w2web (for novice users)

? speed + memory requirements

  + very efficient basis for large spheres (2 bohr) (Fe: 12Ry, O: 9Ry)

  - less efficient for small spheres (1 bohr) (O: 25 Ry)

  - large cells, many atoms (n^3, but new iterative diagonalization)

  - full H, S matrix stored → large memory required

  + effective dual parallelization (k-points, mpi-fine-grain)

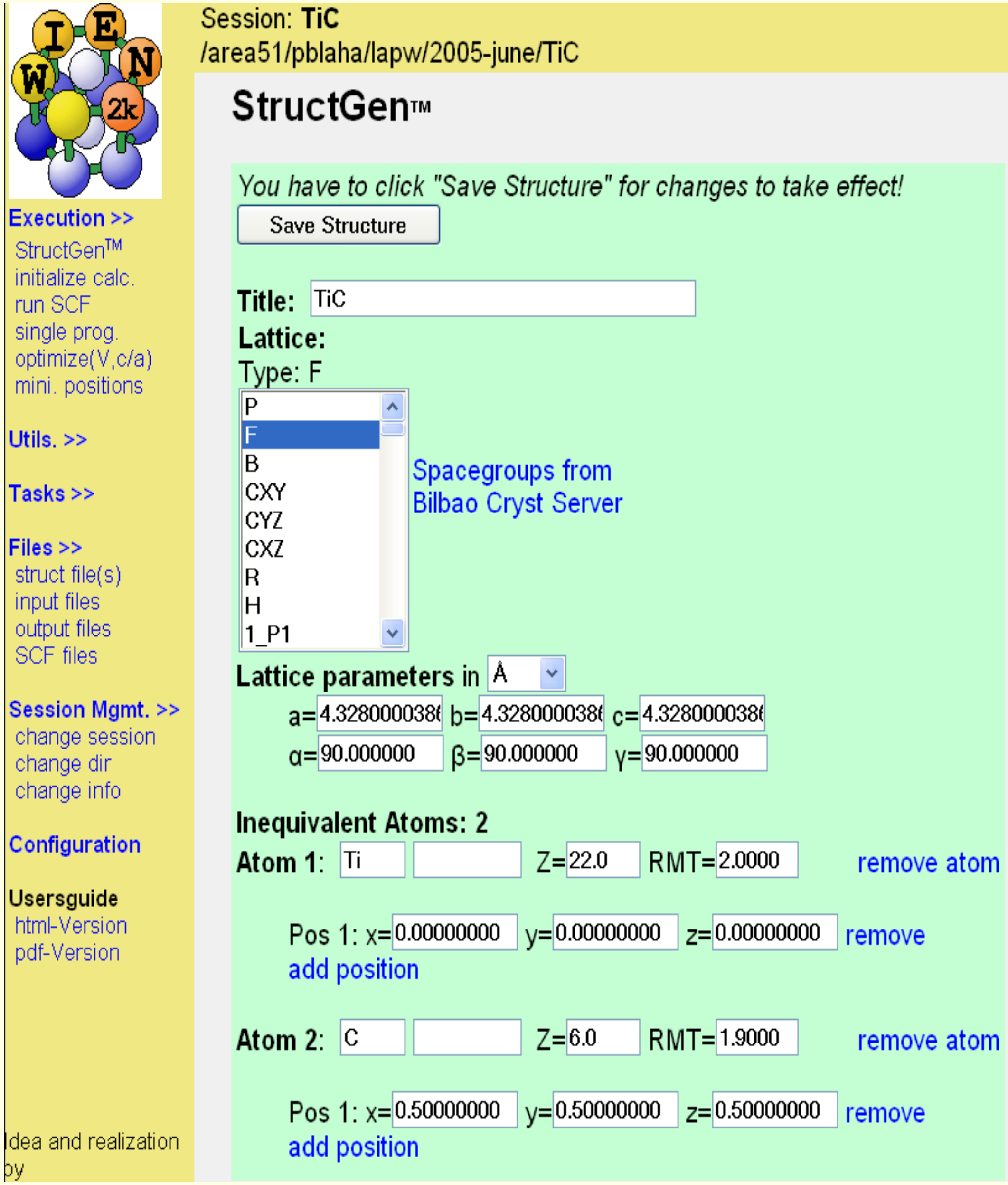
  + many k-points do not require more memory

\- no stress tensor

\- no linear response

w2web GUI (graphical user interface)

- Structure generator
  - *spacegroup selection*
  - *import cif file*
- step by step initialization
  - *symmetry detection*
  - *automatic input generation*
- SCF calculations
  - *Magnetism (spin-polarization)*
  - *Spin-orbit coupling*
  - *Forces (automatic geometry optimization)*
- Guided Tasks
  - *Energy band structure*
  - *DOS*
  - *Electron density*
  - *X-ray spectra*
  - *Optics*



Session: **TiC**
/area51/pblaha/lapw/2005-june/TiC

StructGen™

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

Title: TiC

Lattice:

Type: F

Lattice parameters in Å

a=4.328000038 b=4.328000038 c=4.328000038

α=90.000000 β=90.000000 γ=90.000000

Inequivalent Atoms: 2

Atom 1: Ti Z=22.0 RMT=2.0000

Pos 1: x=0.00000000 y=0.00000000 z=0.00000000

Atom 2: C Z=6.0 RMT=1.9000

Pos 1: x=0.50000000 y=0.50000000 z=0.50000000

Spacegroup P4$_2$/mnm

Structure given by:

- spacegroup
- lattice parameter
- positions of atoms (basis)

Rutile TiO$_2$:

P4$_2$/mnm (136)

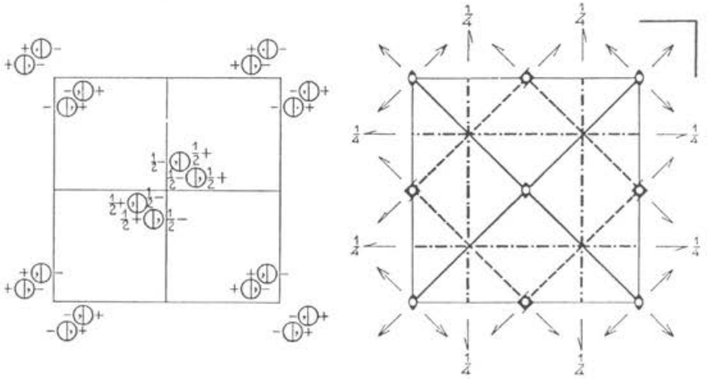
a=8.68, c=5.59 bohr

Ti: (0,0,0) 2a

O: (0.304,0.304,0)

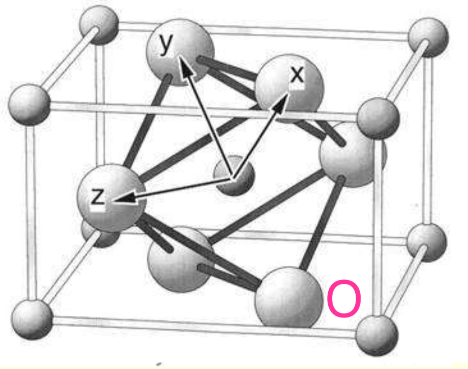
Wyckoff position: x, x, 0 4f

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

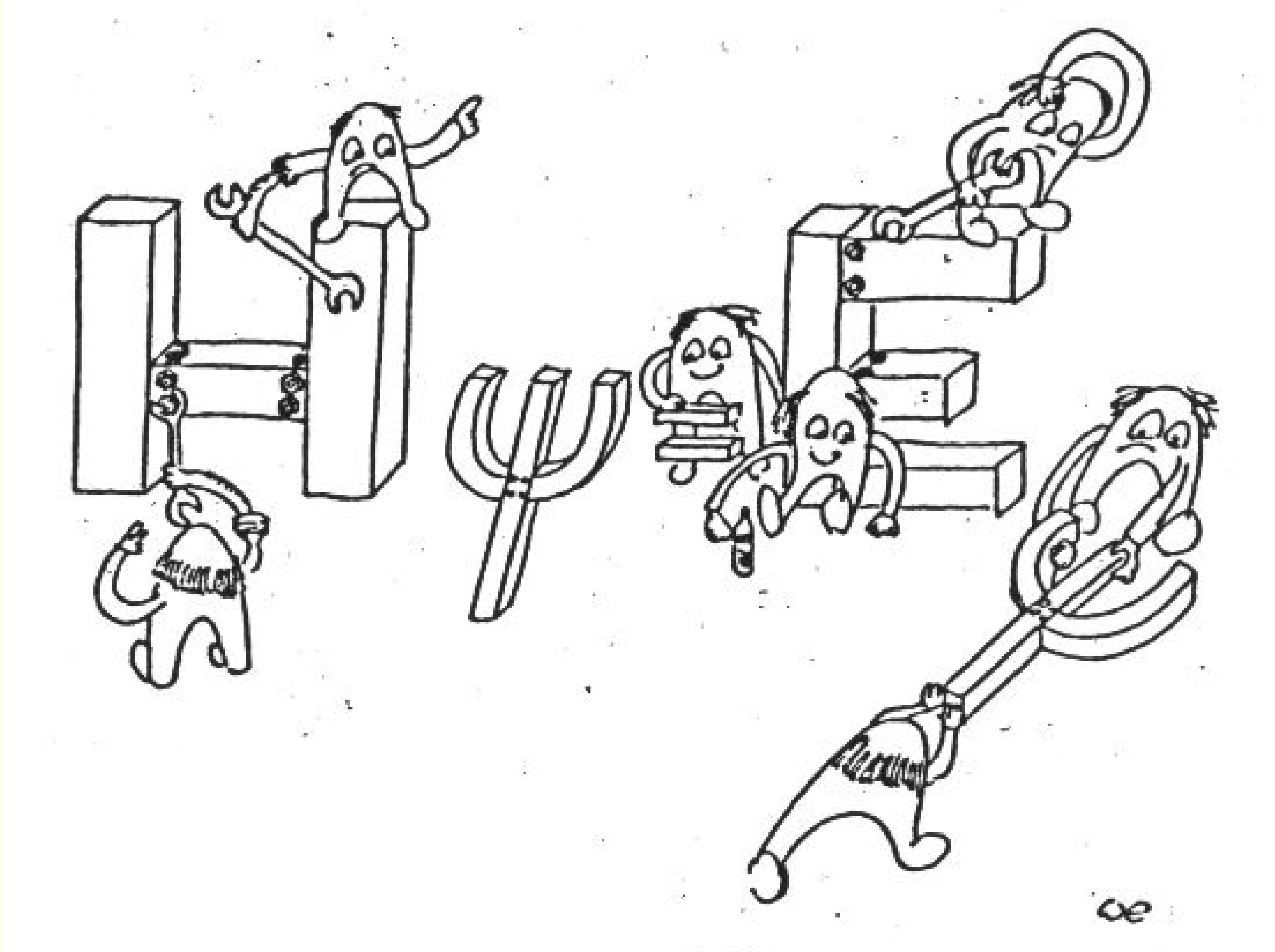


Origin at centre (*mmm*)

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*	$0,0,0;\ \frac{1}{2},\frac{1}{2},\frac{1}{2}.$	



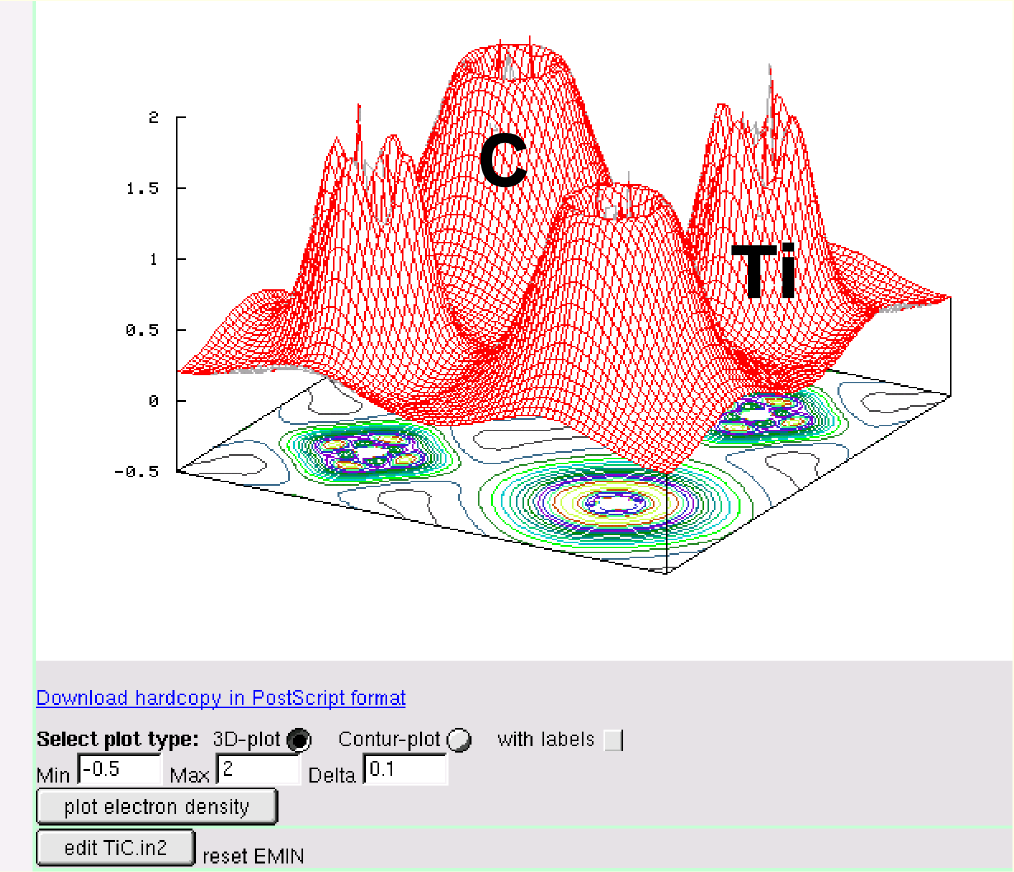
Quantum mechanics at work



thanks to Erich Wimmer

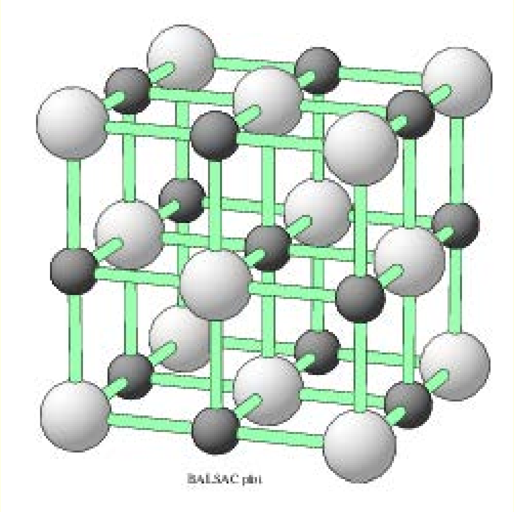
TiC electron density

- 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*



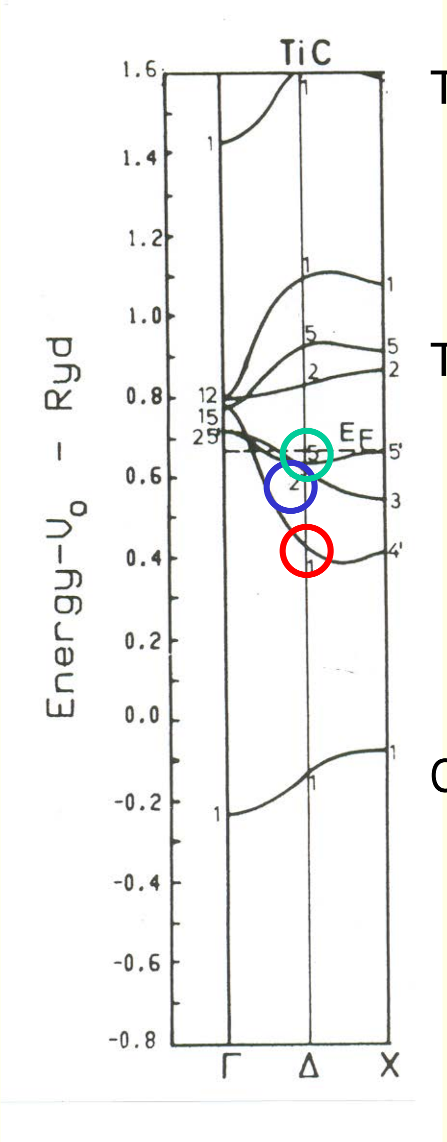
Select plot type: 3D-plot ● Contur-plot ○ with labels ☐

Min -0.5 Max 2 Delta 0.1



TiC, three valence states at Δ

Energy bands

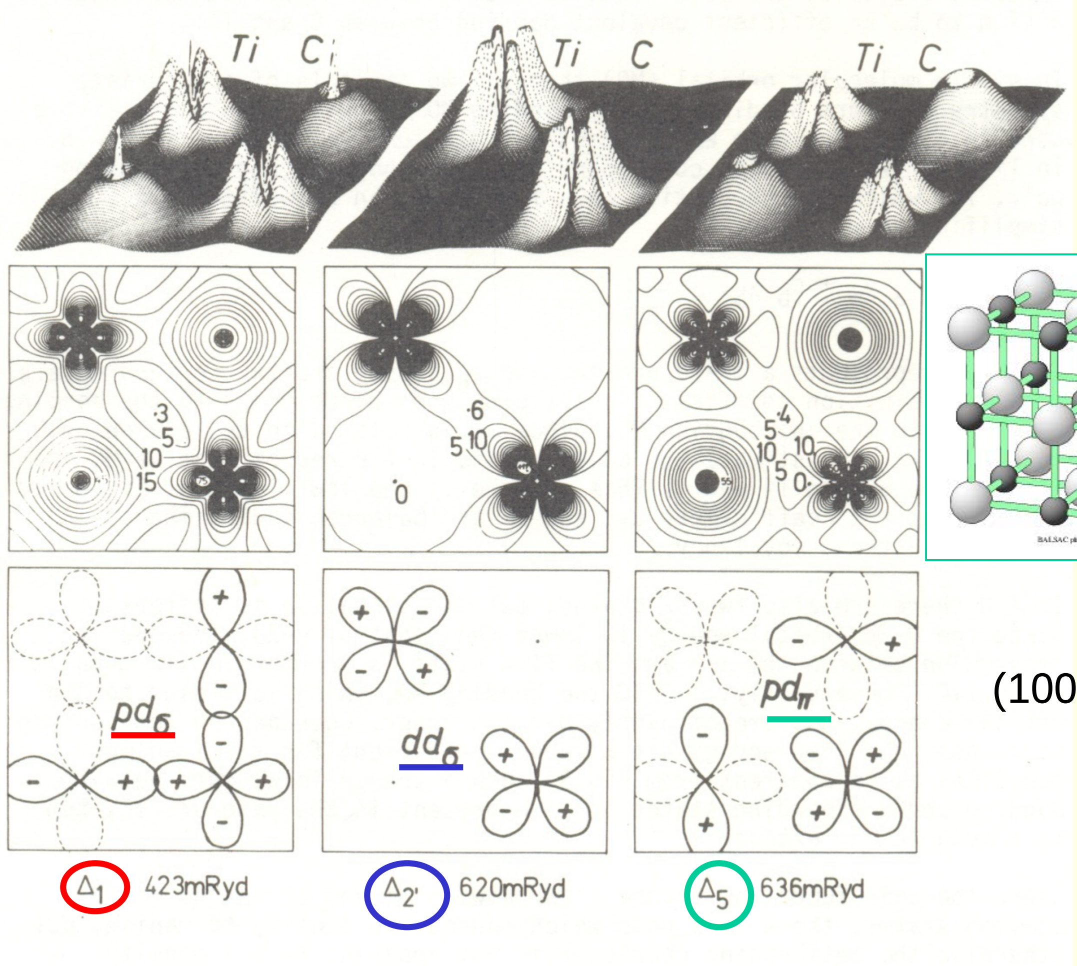


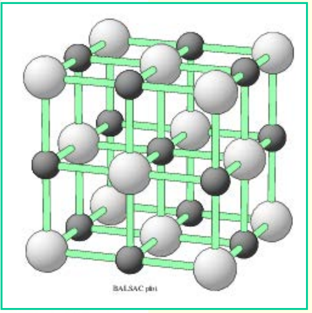
Ti-4s

Ti-3d

C-2p

C-2s





(100) plane

C_p-Ti_d σ

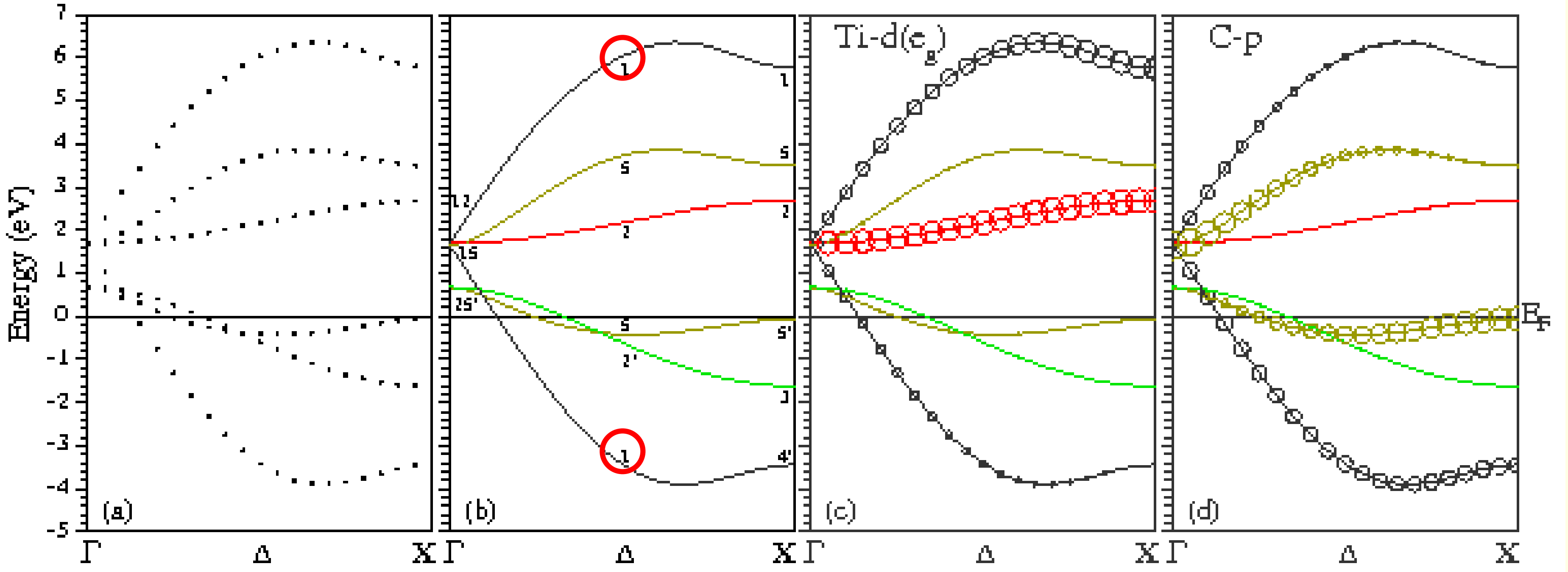
Ti_d-Ti_d σ

C_p-Ti_d π

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

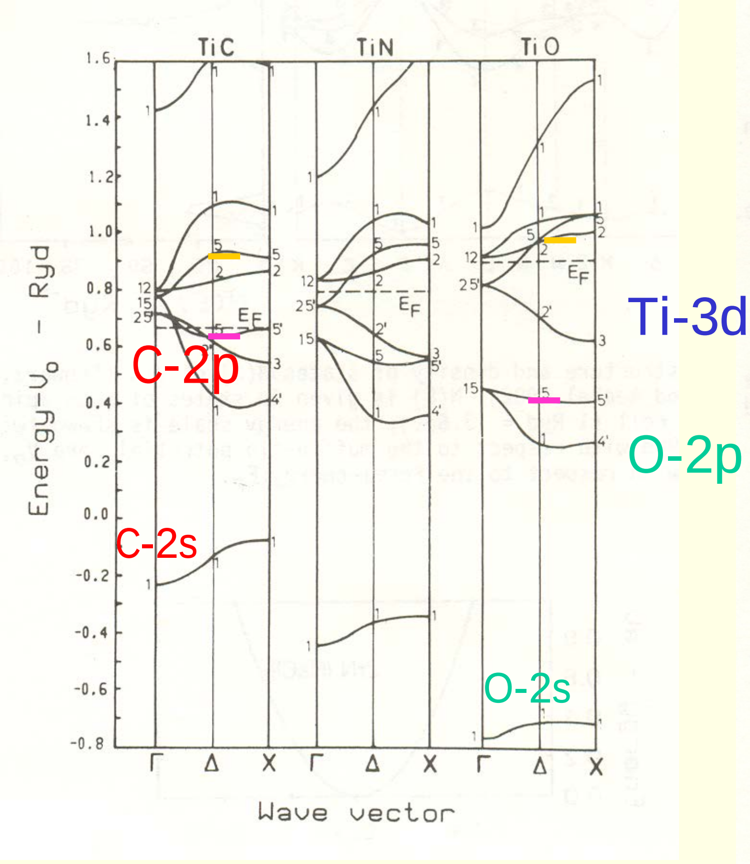
TiC, energy bands

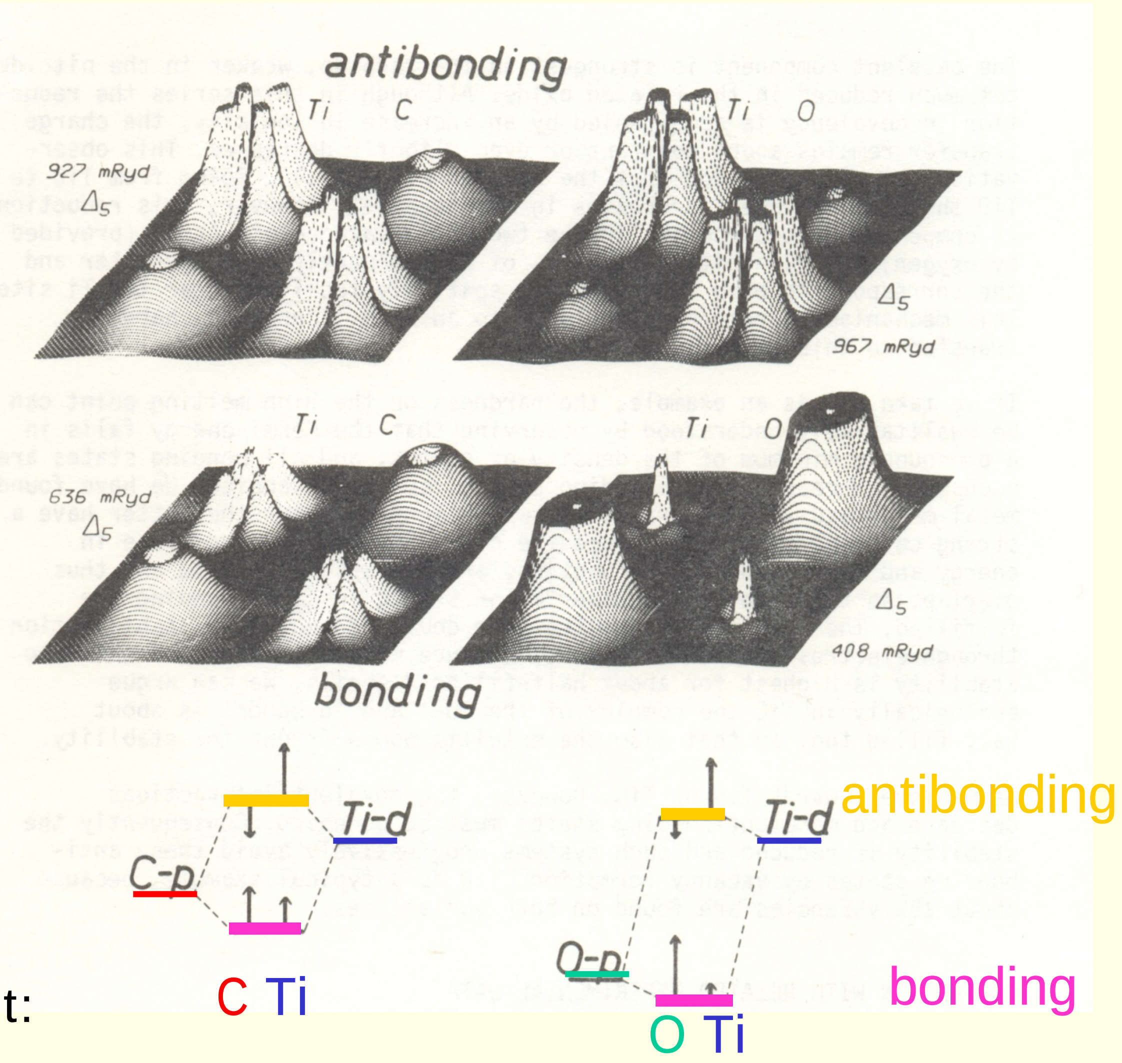
spaghetti irred.rep. character bands



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

TiC, bonding and antibonding states





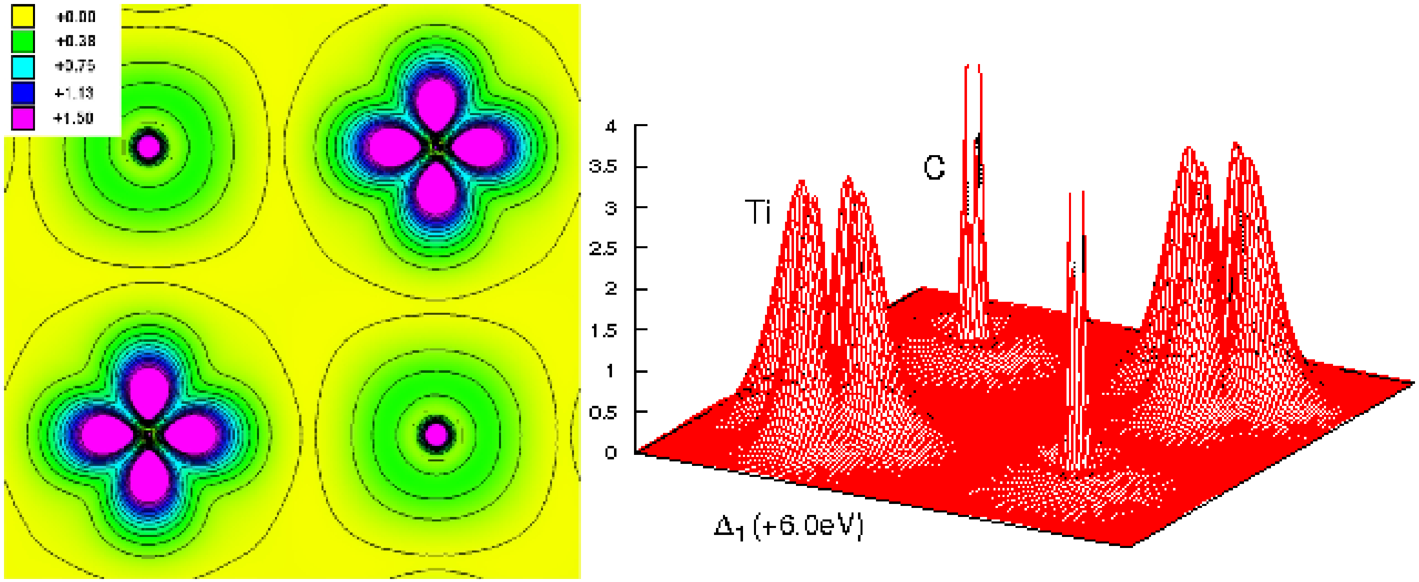
weight:

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

Bonding and antibondig state at Δ1

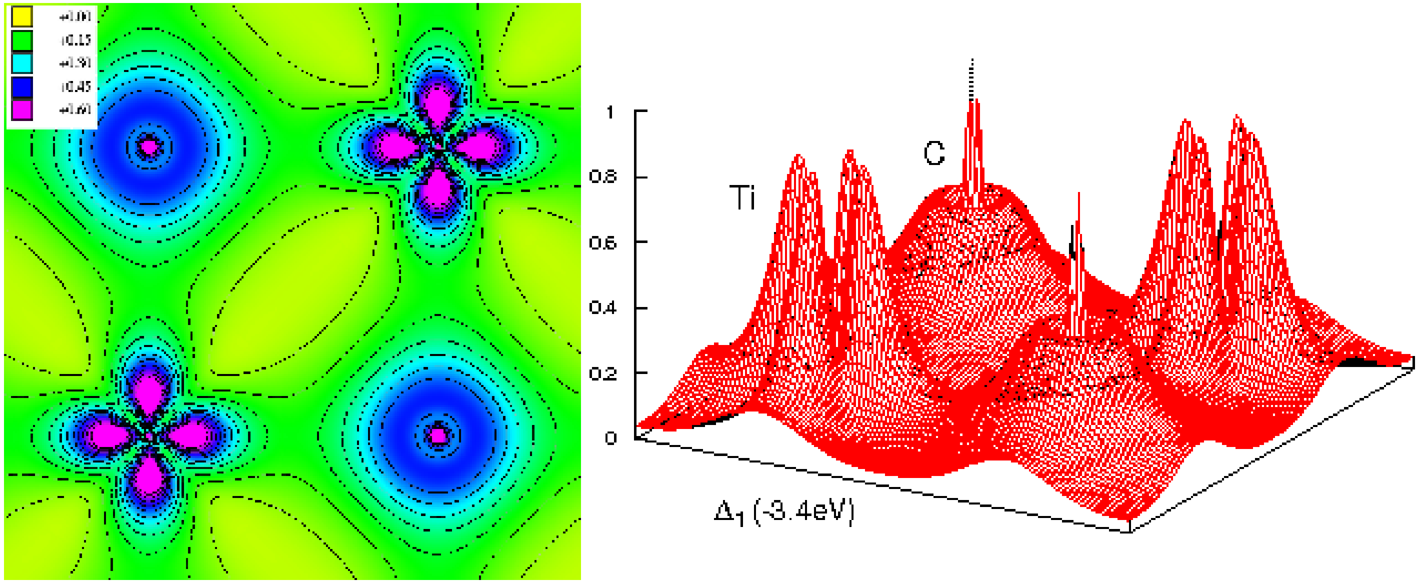
antibonding

C_p-Ti_d σ

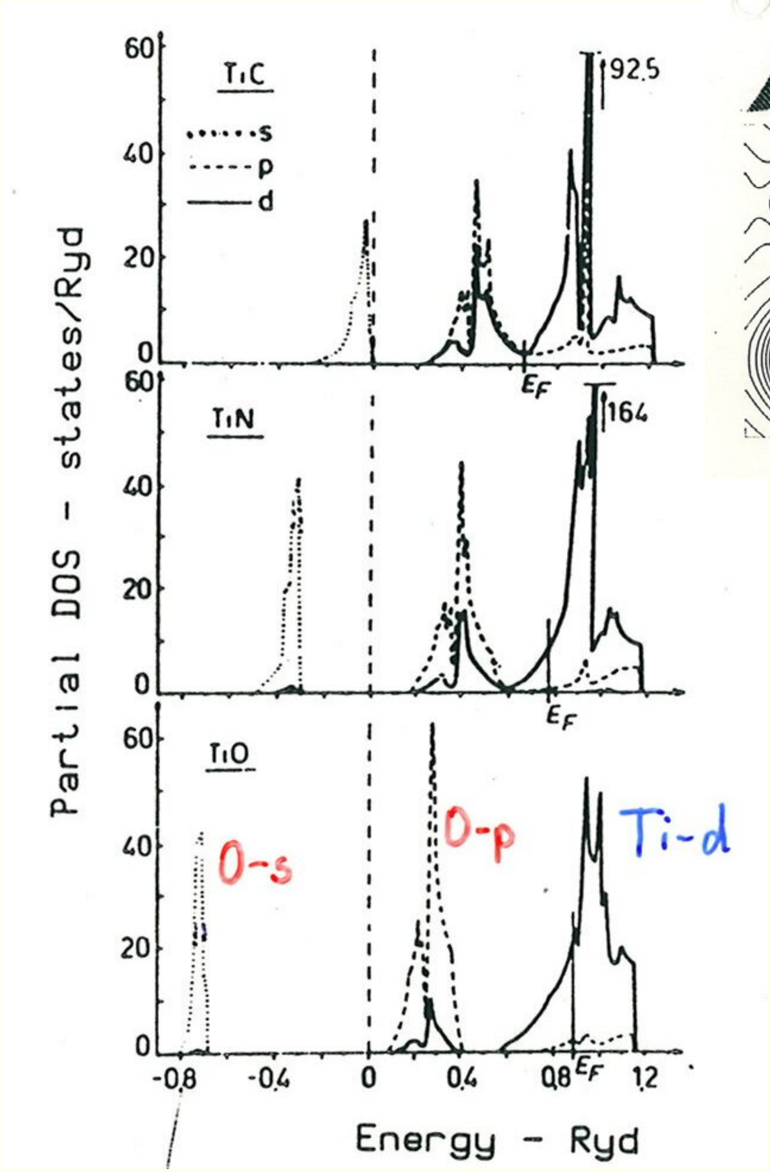


bonding

C_p-Ti_d σ



TiC, TiN, TiO



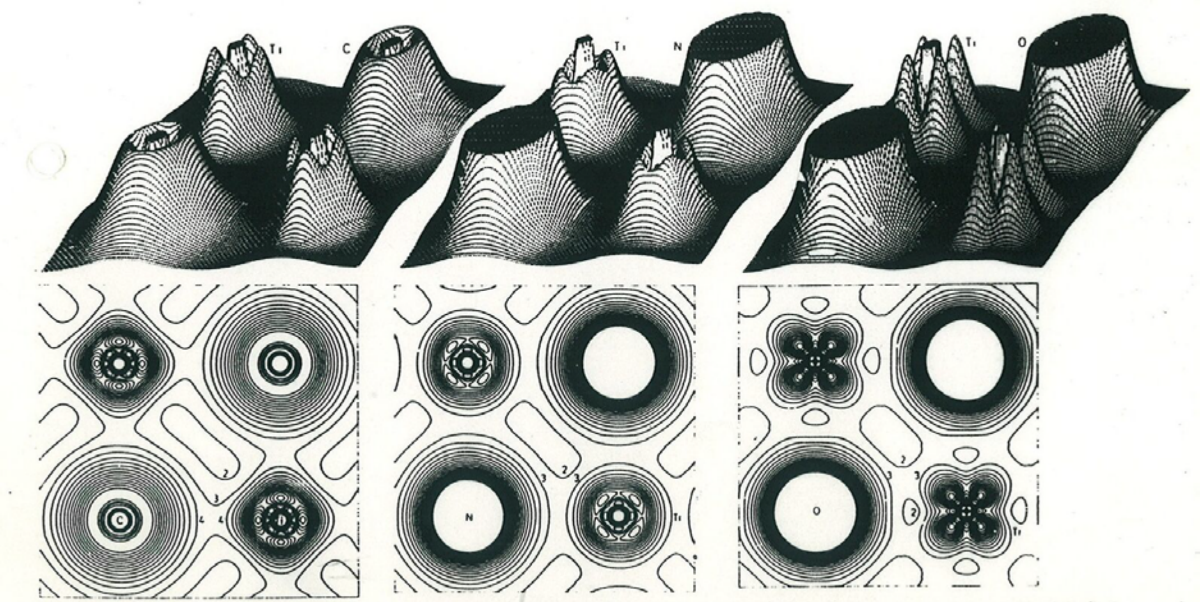


Figure 3. Valence charge densities in the (100) plane. Contour intervals $0.1 e\text{Å}^{-3}$ (numbers are in these units), cutoff at $1.7 e\text{Å}^{-3}$.

TiC **TiN** **TiO**

Rigid band model: limitations

Electron density ρ: decomposition

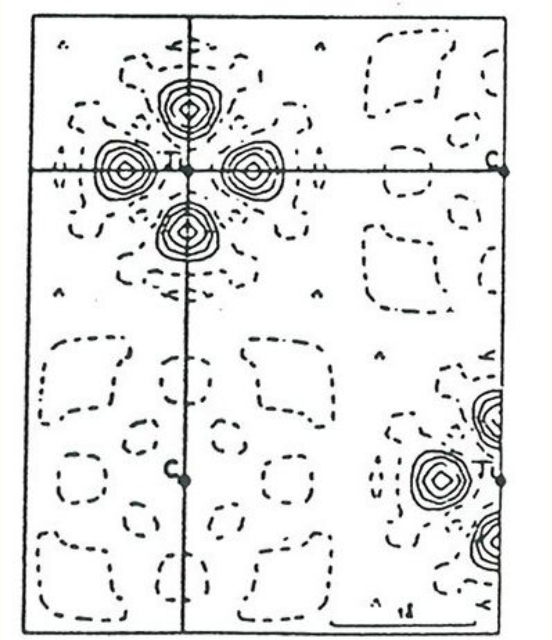
$$1 = q_{out} + \sum_{t} \sum_{\ell} q_{t\ell}$$

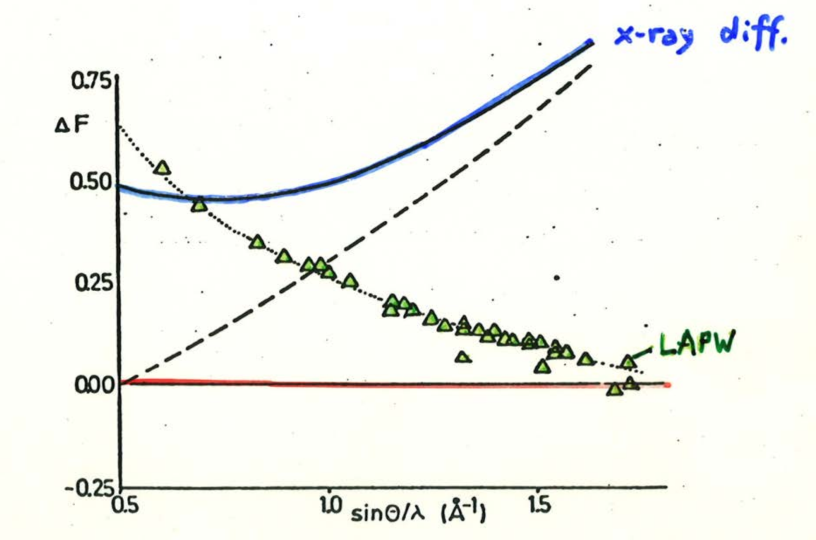
unit cell interstitial atom t ℓ=s, p, d, ...

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

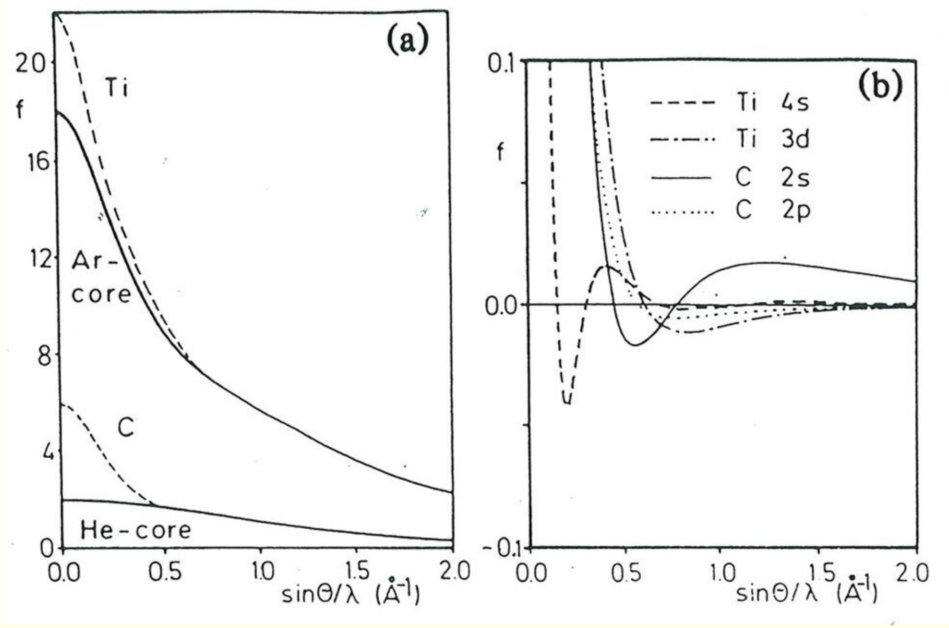
TiC, TiN, TiO

Experimental difference electron density

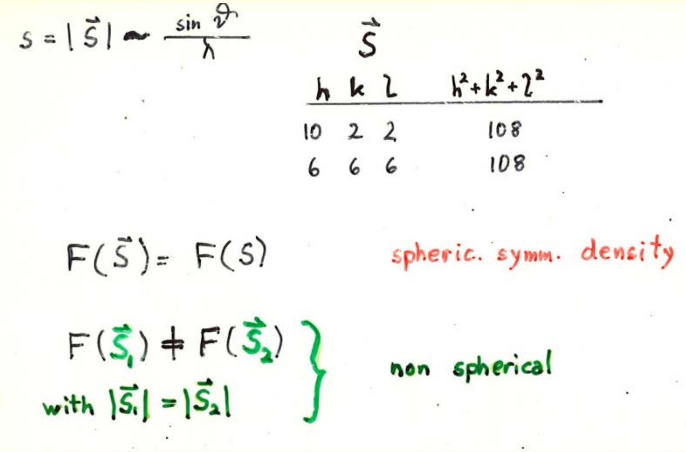




Atomic form factors for Ti and C



Paired reflections



$s = |\vec{S}| \sim \frac{\sin \vartheta}{\lambda}$

$\vec{S}$

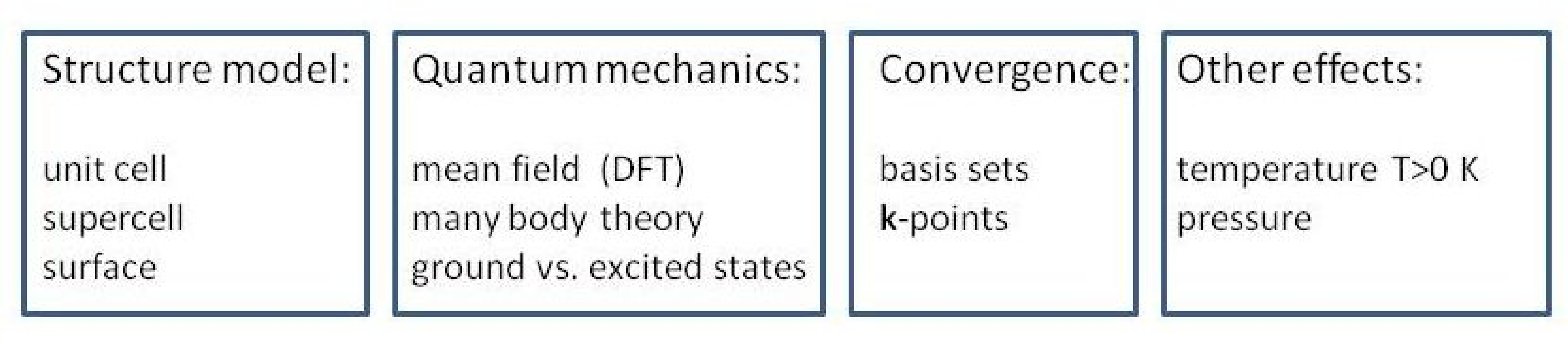
h	k	l	$h^2+k^2+l^2$
10	2	2	108
6	6	6	108

$F(\vec{S}) = F(s)$ spheric. symm. density

$\left.\begin{array}{l} F(\vec{S}_1) \neq F(\vec{S}_2) \\ \text{with } |\vec{S}_1| = |\vec{S}_2| \end{array}\right\}$ non spherical

Crucial aspects for a simulation

Theory vs. experiment: Agreement or disagreement:
What can cause it?



Structure model:

unit cell
supercell
surface

Quantum mechanics:

mean field (DFT)
many body theory
ground vs. excited states

Convergence:

basis sets
k-points

Other effects:

temperature T>0 K
pressure

stoichiometry
disorder
impurities, defects

electron core-hole
satellites
all electron

vacuum
supercell
ℓ quantum n.

average
vibrations

These aspects need to be considered when comparing **theory** with **experiment**.

Vienna, city of music and the Wien2k code