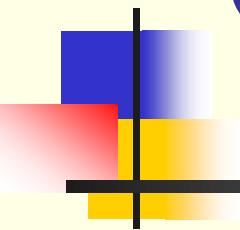
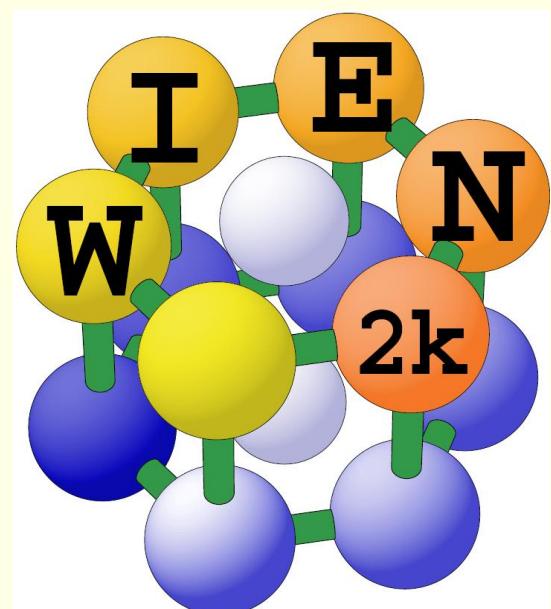
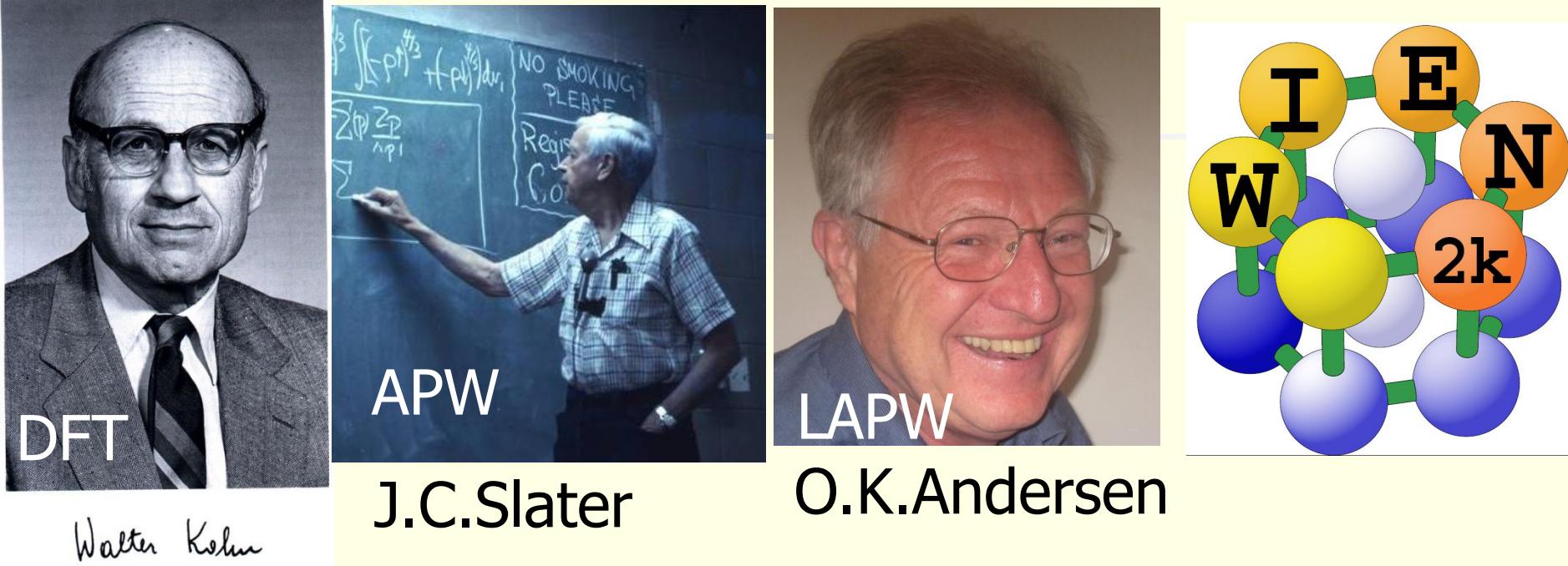


# Density functional theory (DFT) and the concepts of the augmented-plane-wave plus local orbital (L)APW+lo method

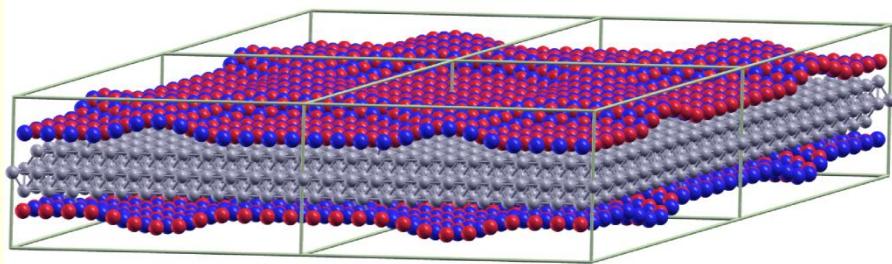


**Karlheinz Schwarz**  
Institute for Material Chemistry  
TU Wien  
Vienna University of Technology





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 2600 groups

- 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](http://www.wien2k.at)



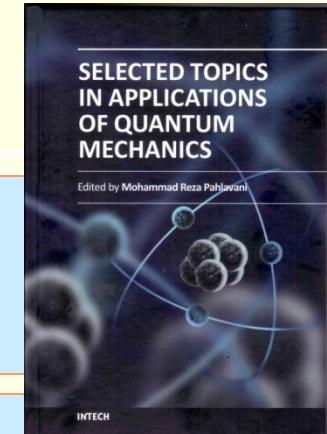
# Review articles

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](https://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.Leszczynski, 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> I

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)

- 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
  - *Structure, surfaces, core-level spectra, NMR, hyperfine, Wannier,...*
- 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

## ■ 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)*

## ■ 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)*

Assuming an ideal infinite crystal we define a unit cell by

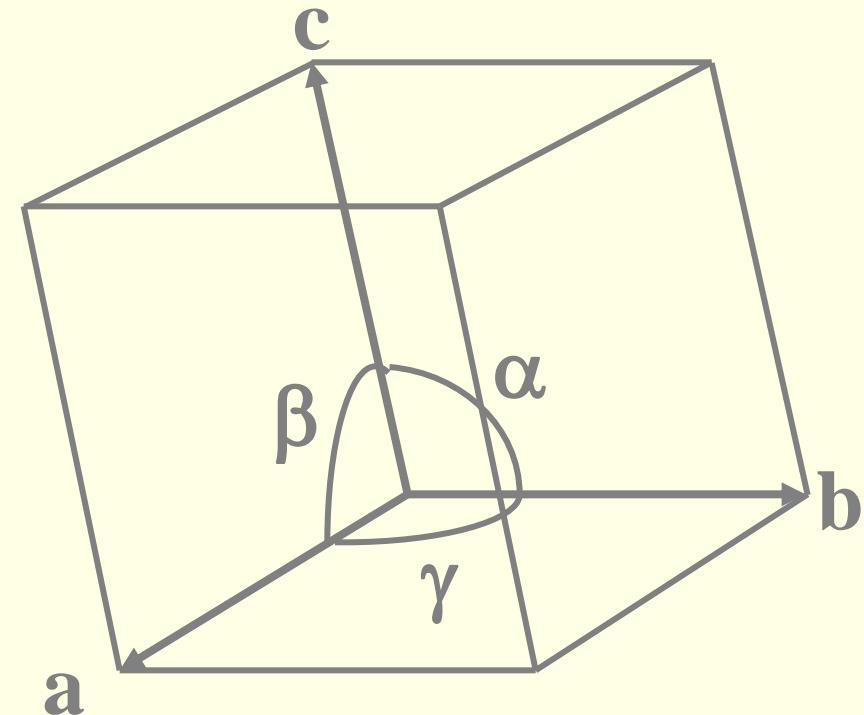
Unit cell: a volume in space that fills space entirely when translated by all lattice vectors.

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)



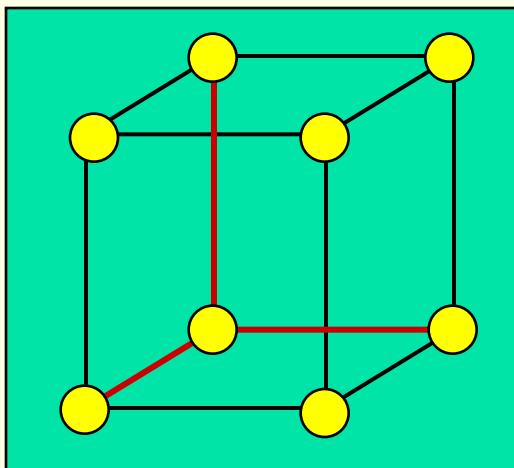
A unit cell containing one lattice point is called primitive cell.

Axis system

$$a = b = c$$

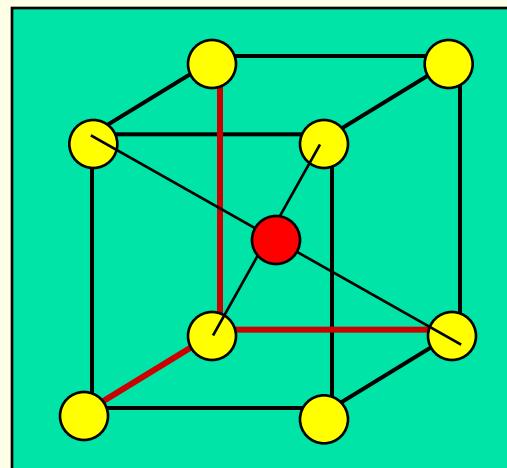
$$\alpha = \beta = \gamma = 90^\circ$$

**primitive**



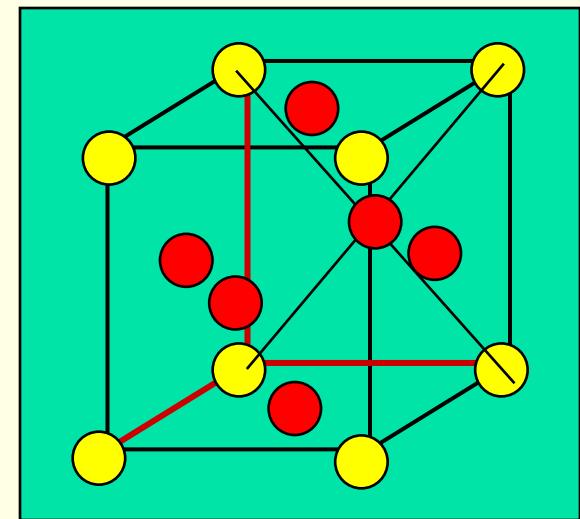
**P (cP)**

**body centered**



**I (bcc)**

**face centered**



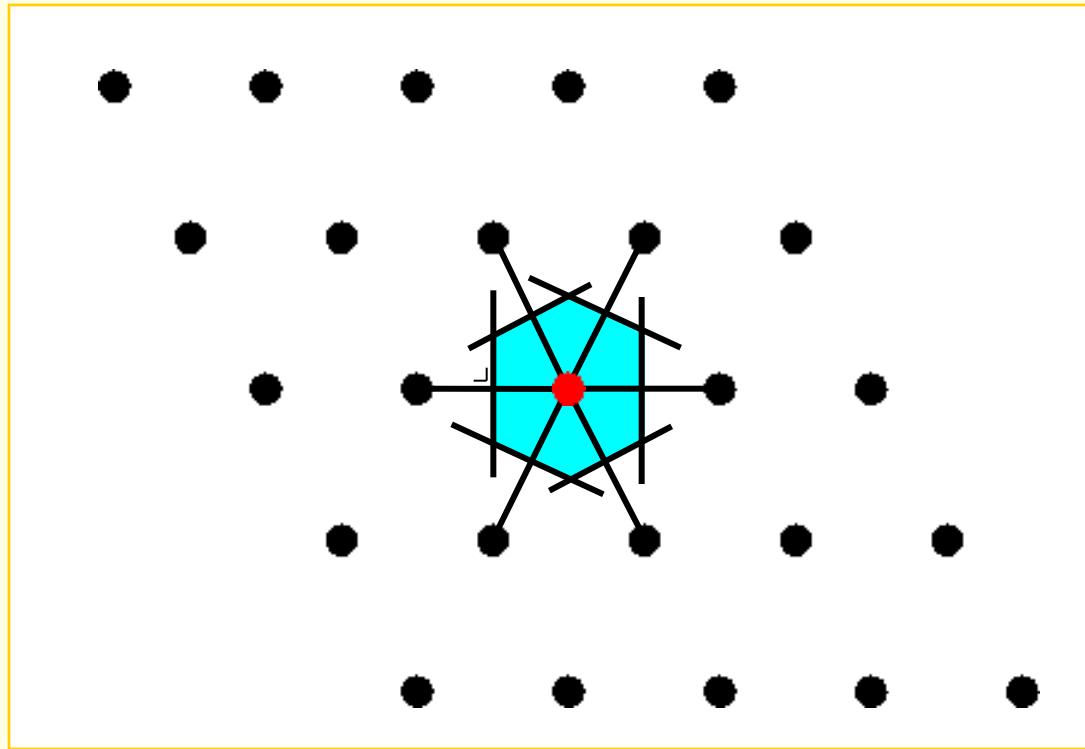
**F (fcc)**

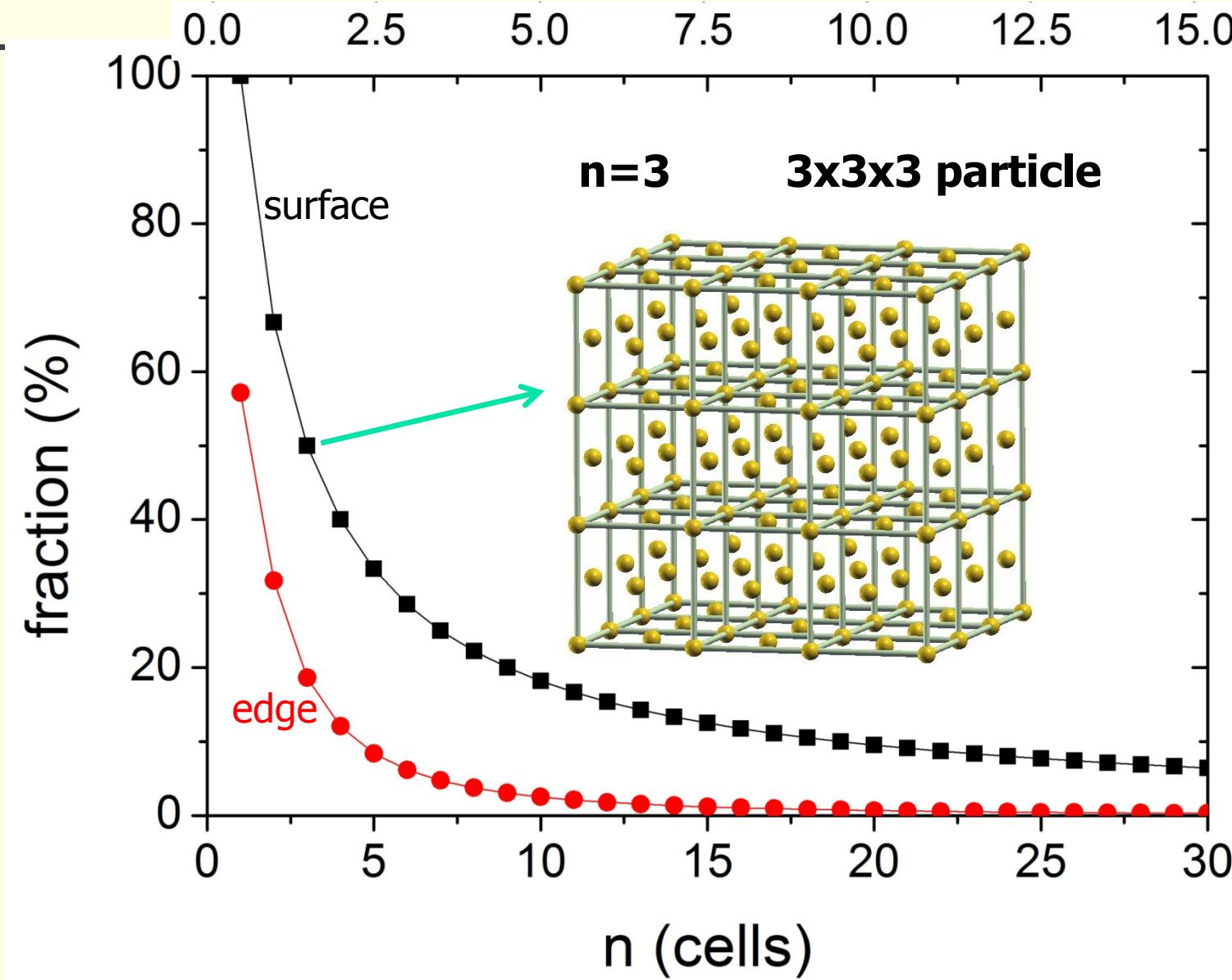
# 3D lattice types:

## 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 ( $\neq 90^\circ$ ) + 3 fold
Hexagonal	1	Two right and one $120^\circ$ angle + 6 fold

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





Fraction of atoms on surface (black) or edge (red) as function of particle size  $n$

- 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)*

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

1-dimensioanl case:

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

$$V(x) = V(x+a)$$

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

$$\rho(x) = \rho(x+a) = \Psi^*(x)\Psi(x) \quad \text{but :}$$

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

Application of the translation  $\tau$  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):

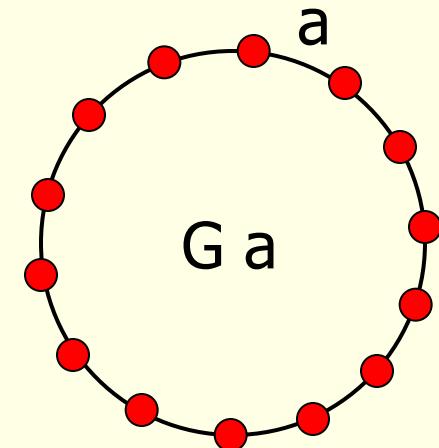
$$\tau^G \Psi(x) = \Psi(x + Ga) = \mu^G \Psi(x) = \Psi(x)$$

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

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

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

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



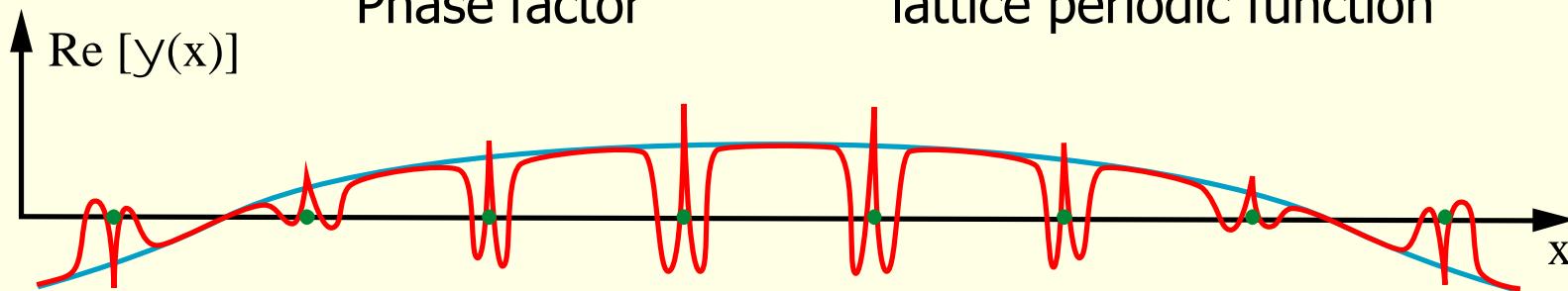
## Bloch functions:

- Wave functions with Bloch form:

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

Phase factor

lattice periodic function

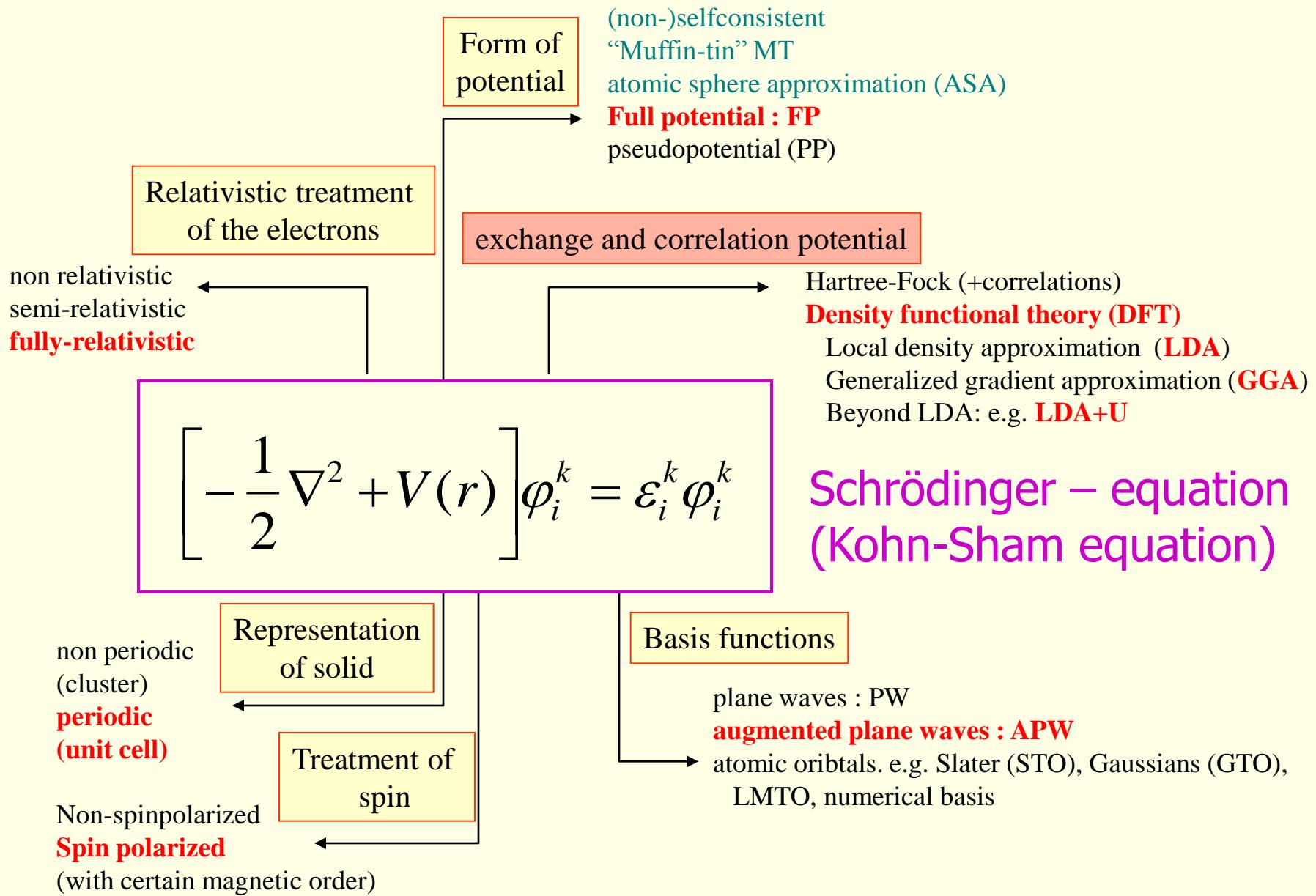


Replacing  $\mathbf{k}$  by  $\mathbf{k}+\mathbf{K}$ , where  $\mathbf{K}$  is a reciprocal lattice vector, fulfills again the Bloch-condition.

→  $\mathbf{k}$  can be restricted to the first Brillouin zone .

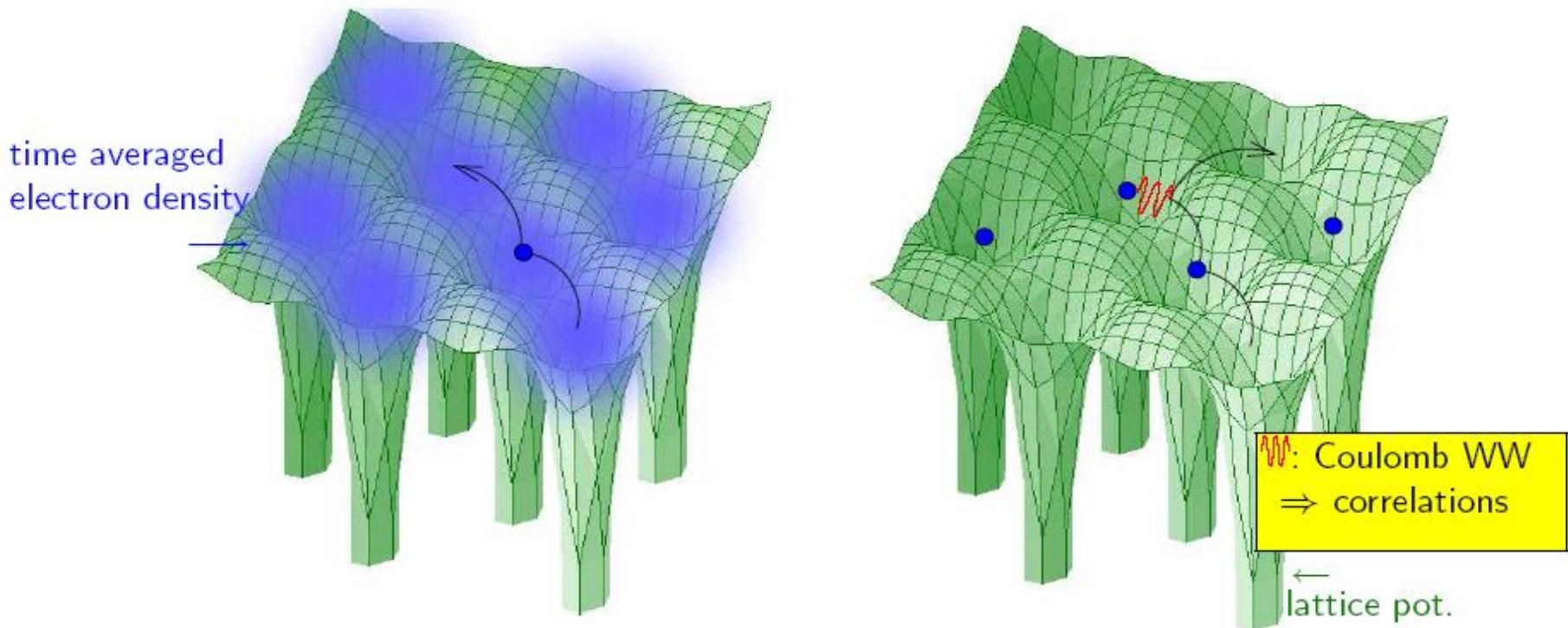
$$e^{i\frac{2\pi}{a}K} = 1$$

$$-\frac{\pi}{a} < k < \frac{\pi}{a}$$



## Two communities in solid state theory

	LDA bandstructure	many body theory
+	<ul style="list-style-type: none"><li>material-specific, "ab initio"</li><li>often successful, quantitative</li></ul>	<ul style="list-style-type: none"><li>electronic correlations</li><li>qualitative understanding</li></ul>
-	<ul style="list-style-type: none"><li>effective one-particle approach</li></ul>	<ul style="list-style-type: none"><li>model Hamiltonian</li></ul>

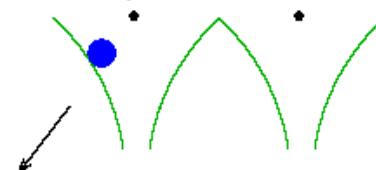


(non-relativistic/Born-Oppenheimer approximation)

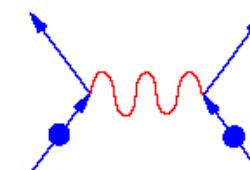
kinetic energy



lattice potential



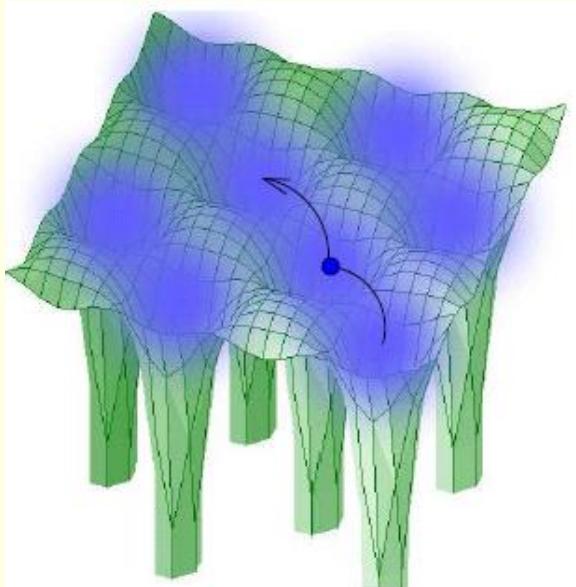
Coulomb interaction



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

**LDA bandstructure** corresponds to

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



Coulomb potential:

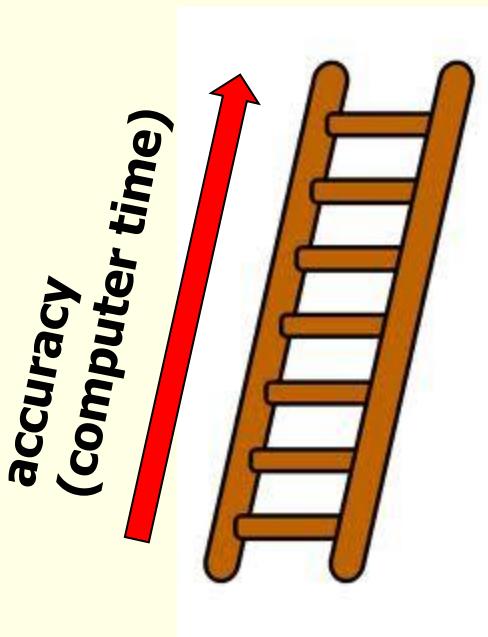
- nuclei
- all electrons
- including self-interaction

Quantum mechanics:

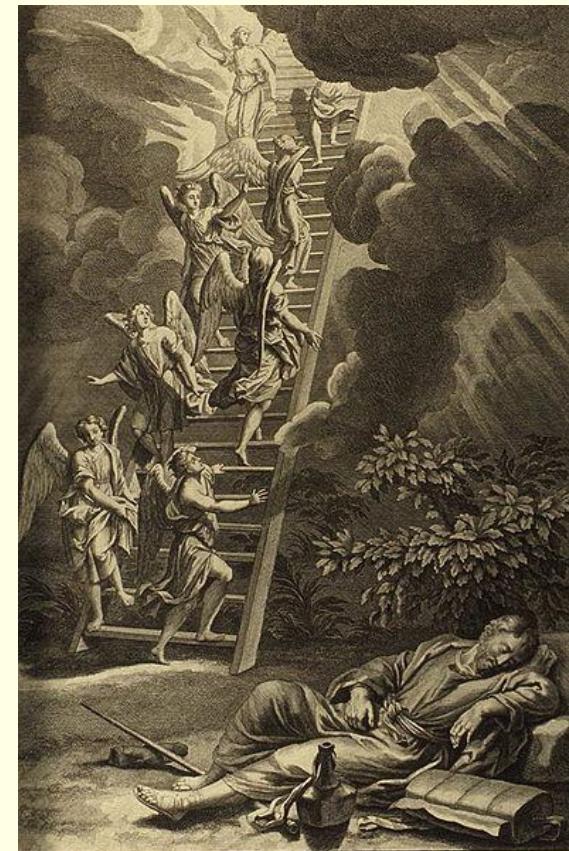
- exchange
- correlation
- (partly) cancel self-interaction

# 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  $\tau$ )
- GGA ( $\nabla \rho$ )
- LDA ( $\rho$ )
- Hartree



## Hohenberg-Kohn theorem: (exact)

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

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

## Kohn-Sham: (still exact!)

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

$E_{kinetic}$

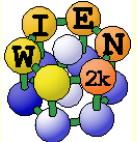
non interacting

$E_{ne}$

$E_{coulomb}$   $E_{ee}$

$E_{xc}$  exchange-correlation

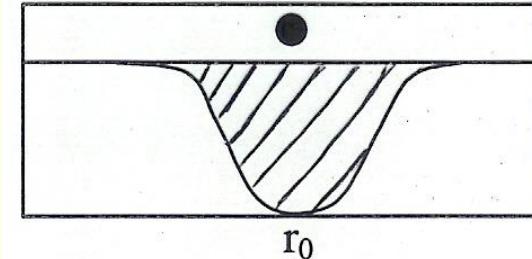
In KS the **many body problem** of interacting electrons and nuclei is **mapped** to a **one-electron reference system** that leads to the **same density** as the real system.



# Exchange and correlation

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

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



$$\overline{n}(r_0, r)$$

## Properties of the exchange-correlation hole:

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

$$h(r_0, r) \xrightarrow{|r-r_0| \rightarrow \infty} 0$$

$$h(r_0, r) \xrightarrow{|r-r_0| \rightarrow 0} -n(r_0)$$

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

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

- 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:

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

LDA, GGA

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

1-electron equations (Kohn Sham)

vary  $\rho$

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

$$-Z/r$$

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

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

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

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

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

**LDA**

**GGA**

treats both,  
exchange and correlation effects,  
but approximately

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

- 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's 80



With 80 years

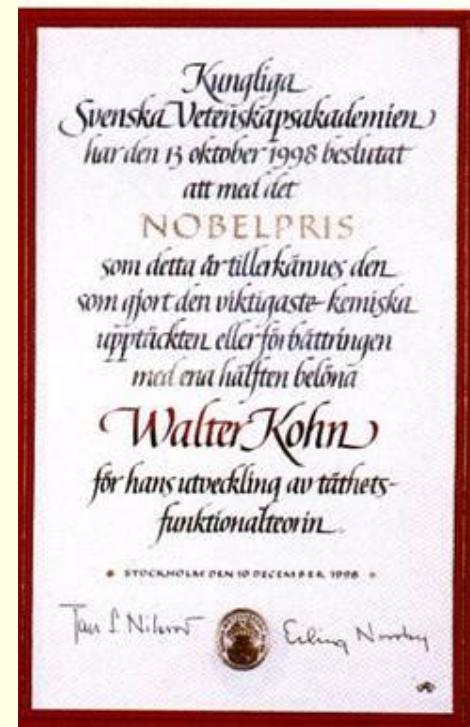


- 1923 born in Vienna
- 1938 had to leave Vienna
- 1946 Univ. Toronto (master, Math)
- 1948 Harvard (PhD, Schwinger)
- Carnegie Mellon, Pittsburgh (Luttinger), Bell Labs, Copenhagen, Washington (Seattle), Paris, Imperial College (London), ETH Zürich, Univ. California, San Diego
- 1979 Founding director Santa Barbara, California
- 1964 **Hohenberg Kohn**
- 1965 **Kohn Sham**
- 1998 **Nobel prize**: Chemistry
- 2016, he died on April 19

# Walter Kohn, Nobel Prize 1998 Chemistry



Walter Kohn

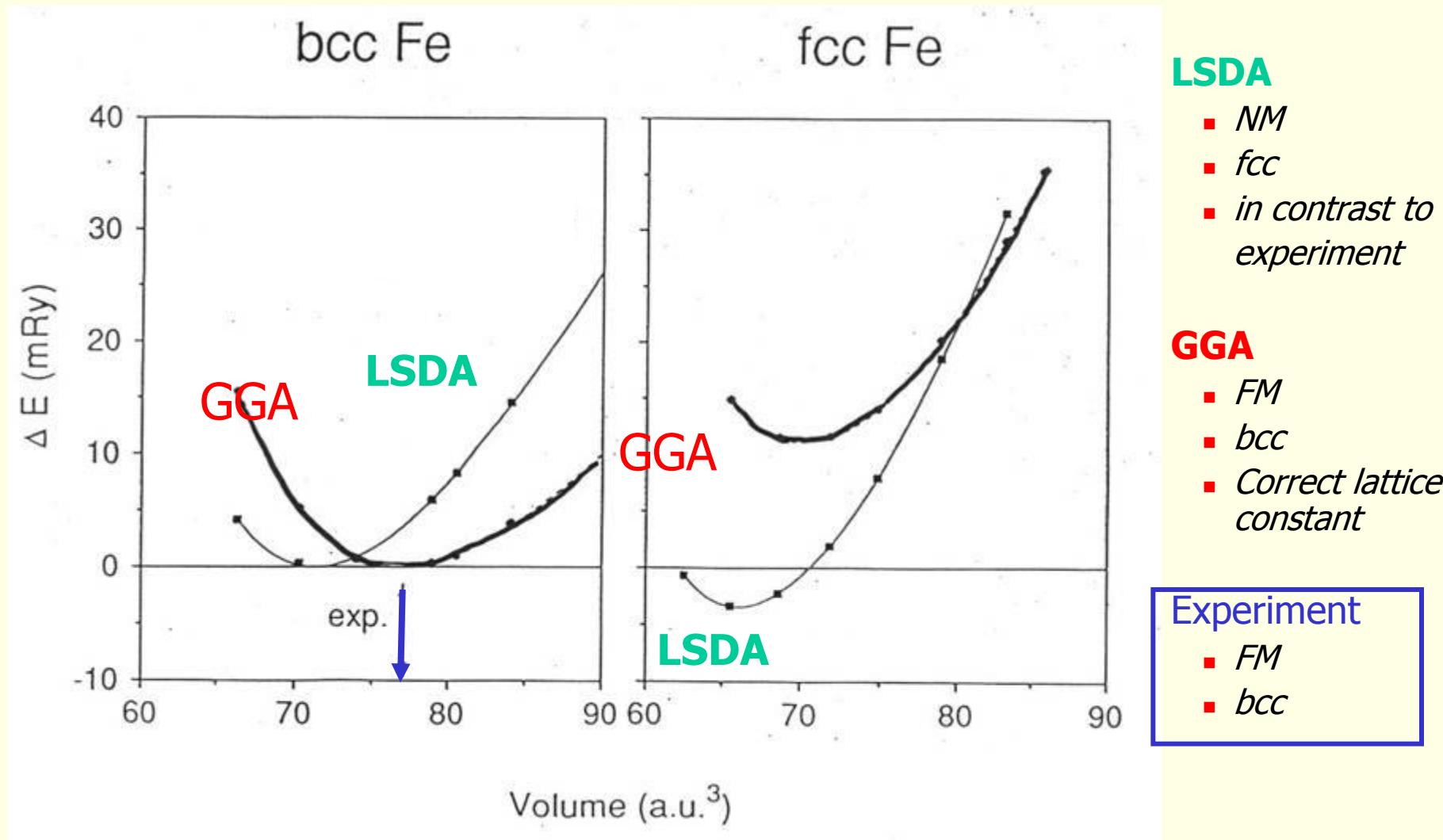


“Self-consistent Equations including Exchange and Correlation Effects”

**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 thanks to Claudia Ambrosch (previously in Graz)



GGA follows LDA



# Kopmanns' and Janak's theorem

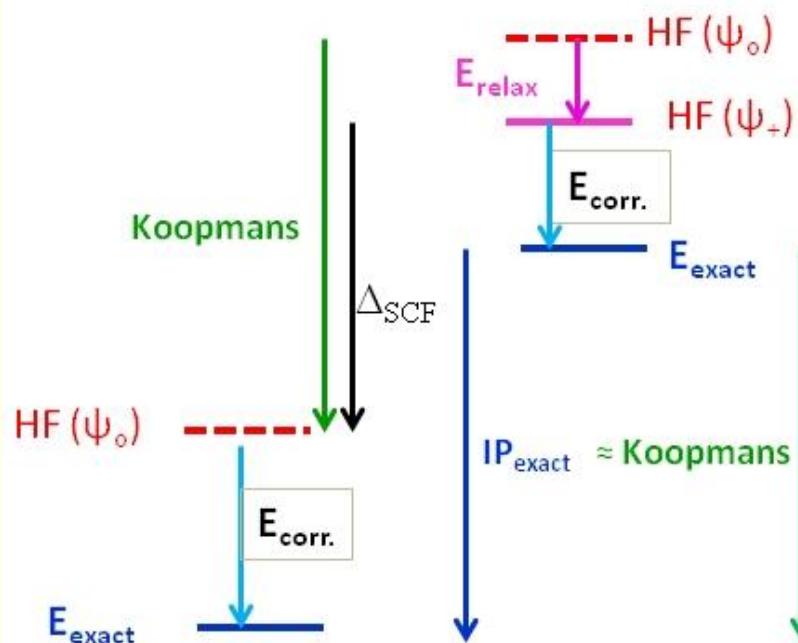
Single-electron picture

**Koopmans  
theorem:**

$$IP = \Delta E \approx \epsilon_i$$

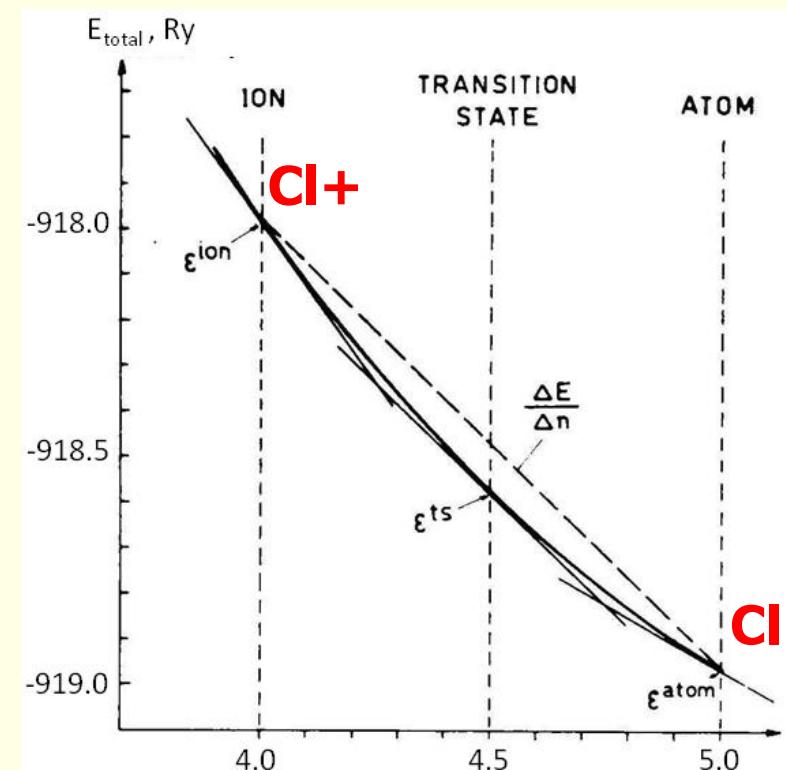
Atom A

Ion A<sup>+</sup>

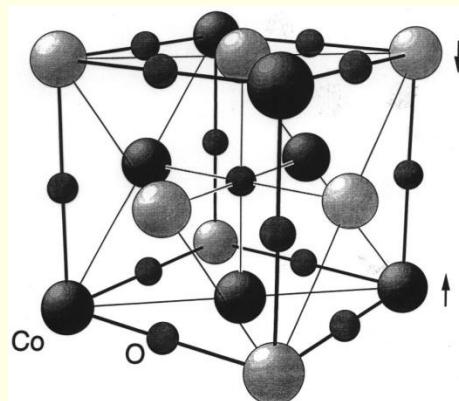


**Janak's theorem:**  $\epsilon_i = \frac{\partial E}{\partial n_i}$

**Slater's transition state:**  
Cl atom

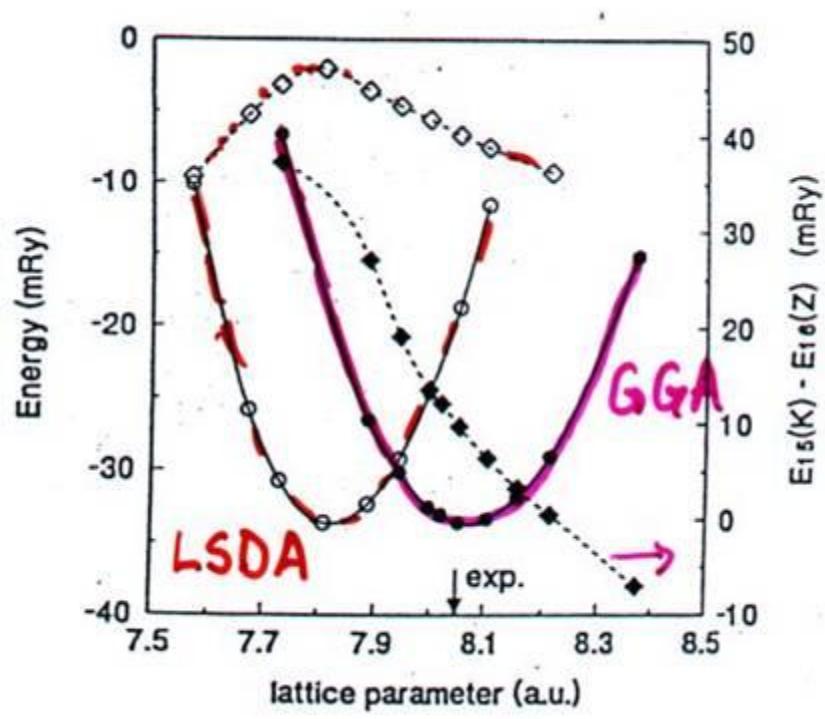


K.Schwarz  
Chem. Physics Z, 100 (1975)

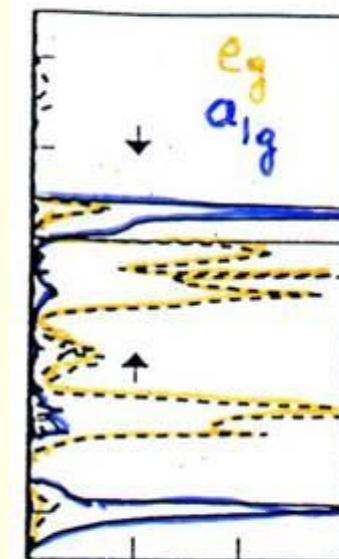


## ■ CoO

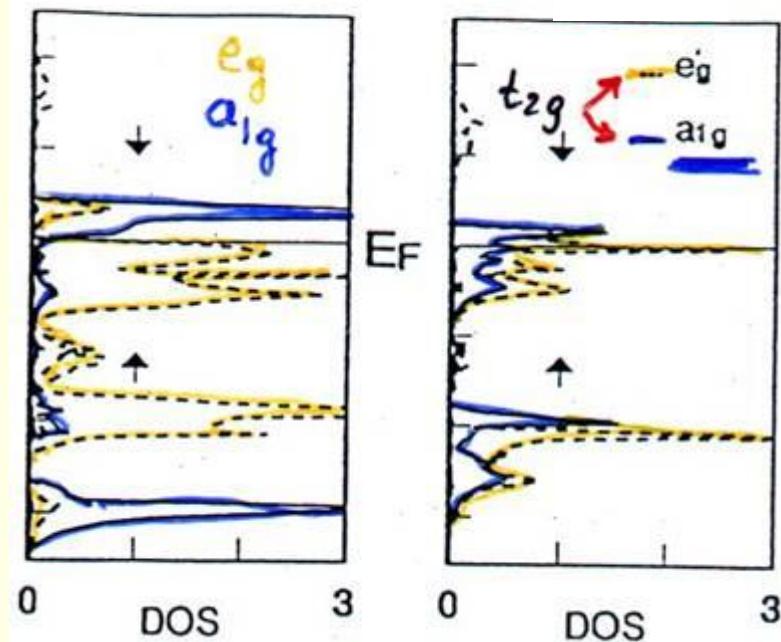
- *in NaCl structure*
- *antiferromagnetic: AF II*
- *insulator*
- *$t_{2g}$  splits into  $a_{1g}$  and  $e_g'$*
- *GGA almost splits the bands*



GGA

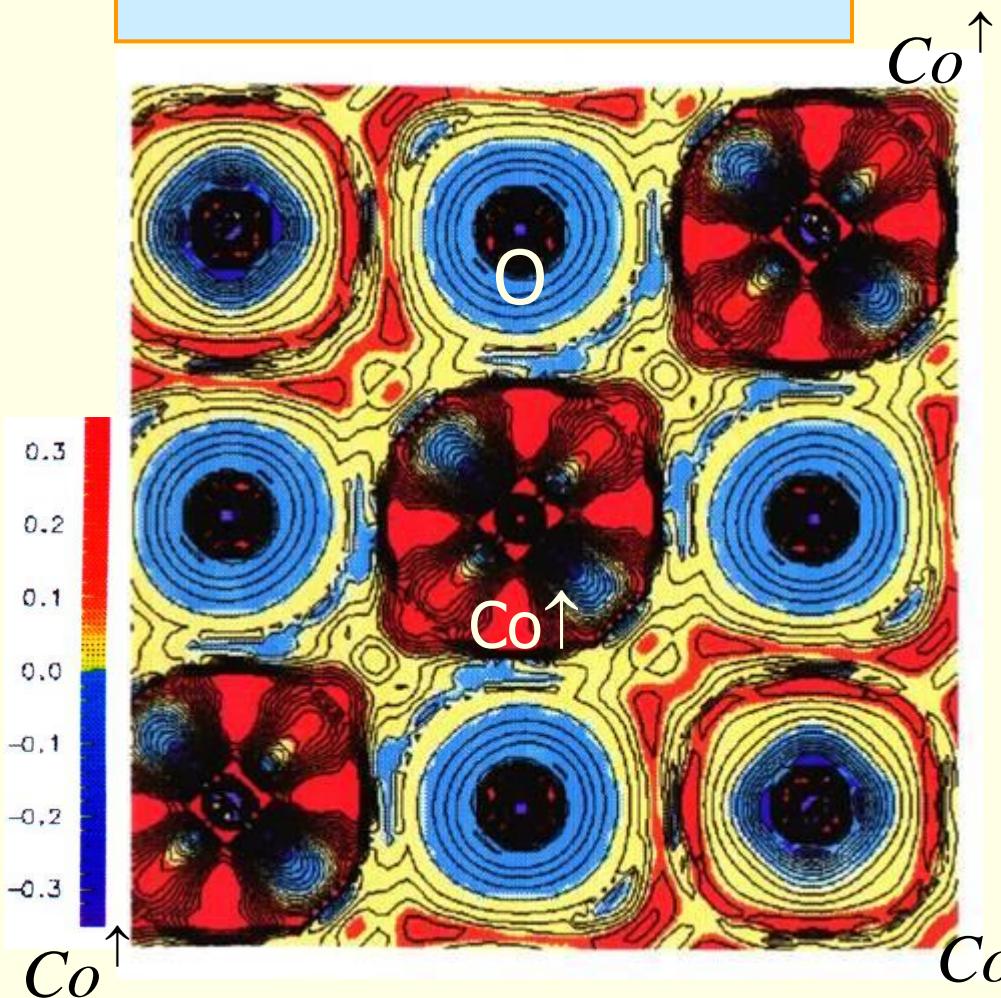


LSDA



# CoO why is GGA better than LSDA

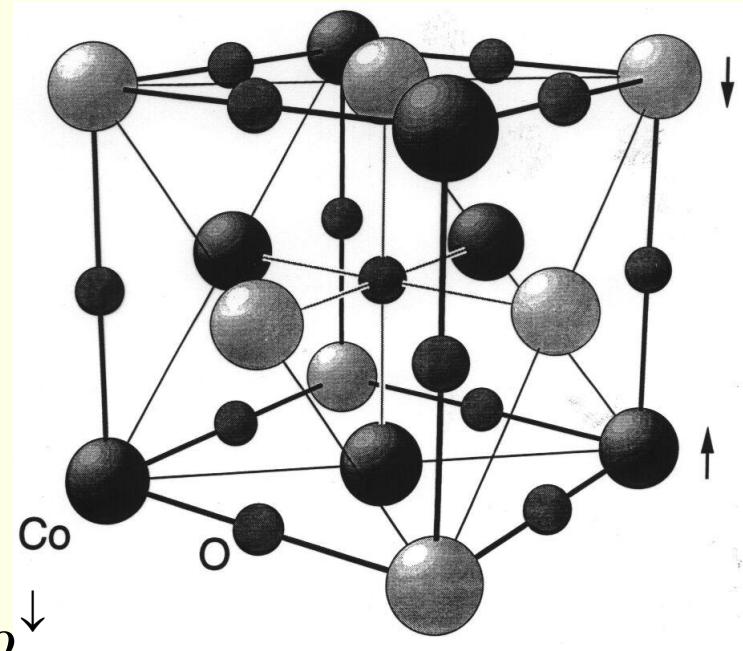
$$\Delta V_{xc}^{\uparrow} = V_{xc}^{\uparrow GGA} - V_{xc}^{\uparrow LSDA}$$



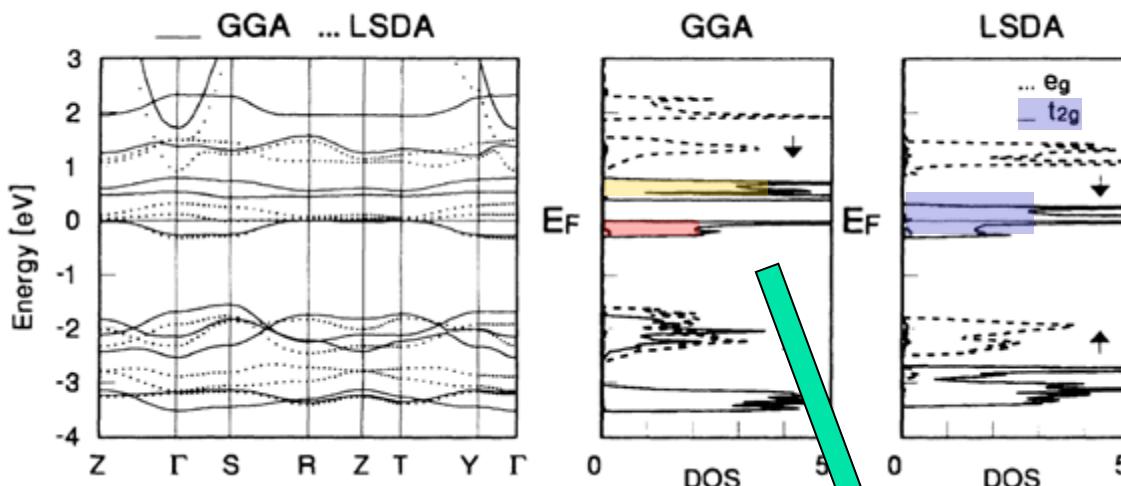
- Central Co atom distinguishes

- *between*  $Co^{\uparrow}$   
and  $Co^{\downarrow}$

- Angular correlation



# FeF<sub>2</sub>: GGA works surprisingly well



Fe-EFG in FeF<sub>2</sub>:

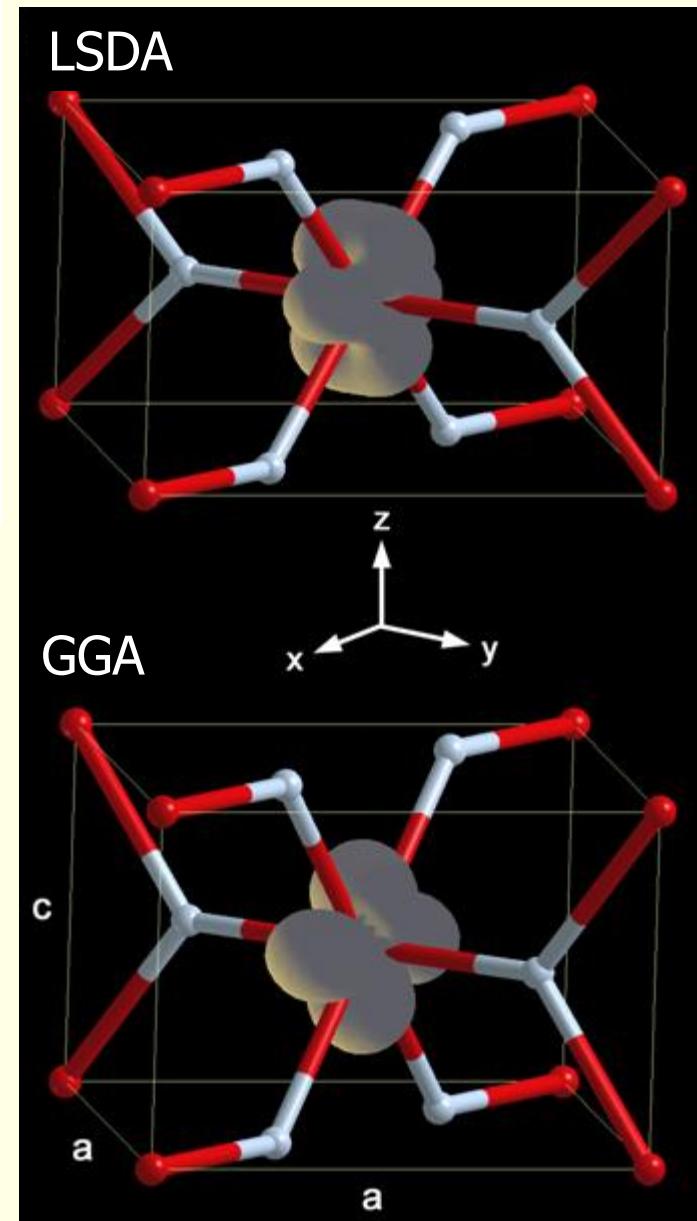
LSDA: 6.2

GGA: 16.8

exp: 16.5

agree

FeF<sub>2</sub>: GGA splits  
 $t_{2g}$  into  $a_{1g}$  and  $e_g'$



## Lattice parameters ( $\text{\AA}$ )

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

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

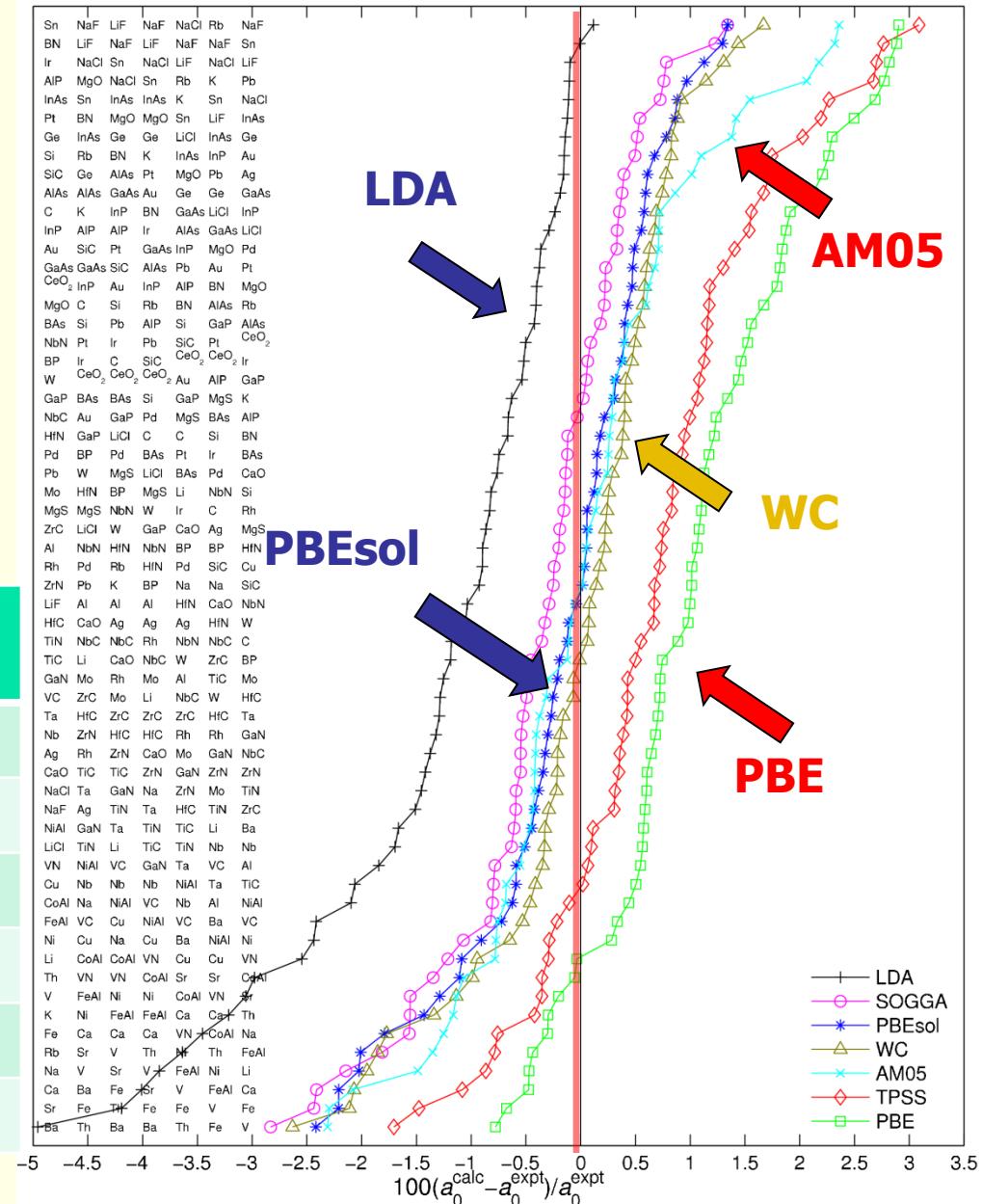
- 4d elements:
  - LDA too small, PBE too large
  - New functional  
Wu-Cohen (WC)

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

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

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

	<b>me (Å)</b>	<b>mae (Å)</b>	<b>mre (%)</b>	<b>mare (%)</b>
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



- better GGAs and meta-GGAs ( $\rho, \nabla\rho, \tau$ ):
  - *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)

## Approximations for $E_{xc}$

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



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

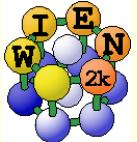
- Only for certain atoms  
and electrons of a given  
angular momentum  $\ell$

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

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

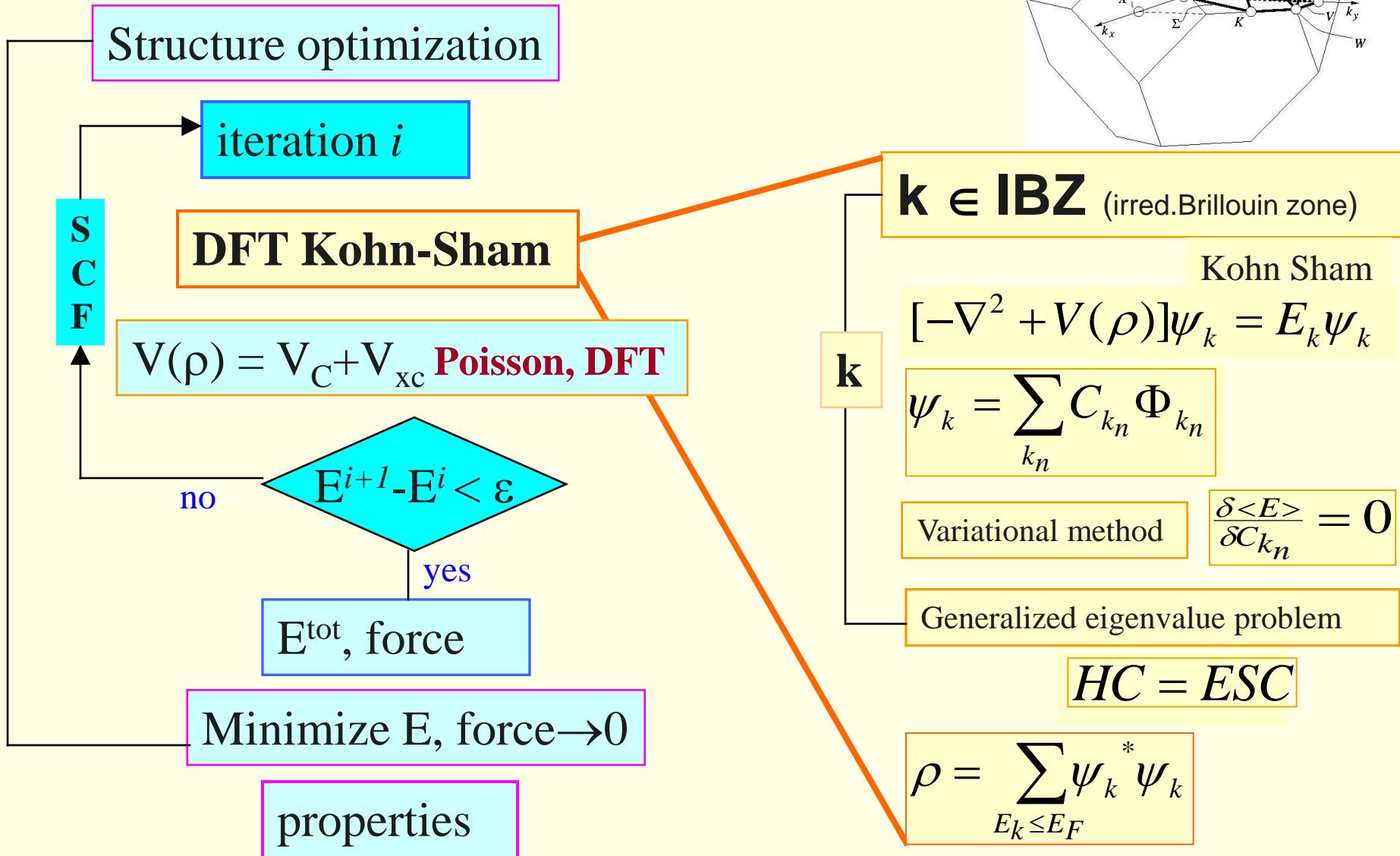
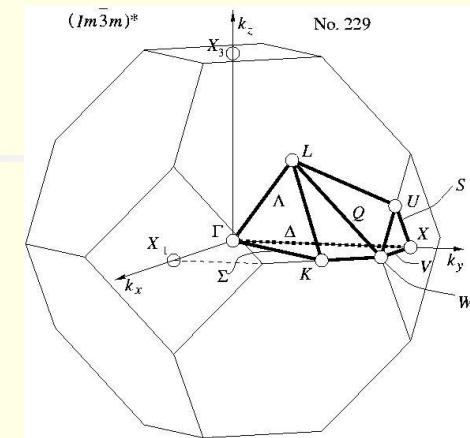
$$\langle m_1 m_2 | v_{ee} | m_3 m_4 \rangle = \sum_{k=0}^{2\ell} a_k F_k$$

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



# Structure: $a, b, c, \alpha, \beta, \gamma, R_\alpha, \dots$

unit cell      atomic positions





# Solving Schrödinger's equation:

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



- $\Psi$  cannot be found analytically
- complete “numerical” solution is possible but inefficient
- Ansatz:

- *linear combination of some "basis functions"*
  - different methods use different basis sets !
- *finding the "best" wave function using the **variational principle**:*

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

- *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

## ■ plane waves

- *pseudo potentials*
- *PAW (projector augmented wave) by P.E.Blöchl*

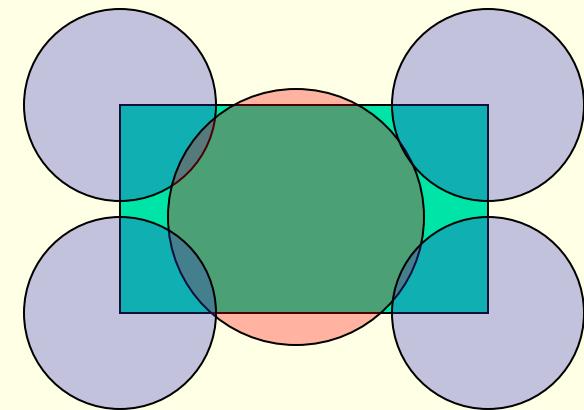
## ■ space partitioning (augmentation) methods

- *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)*

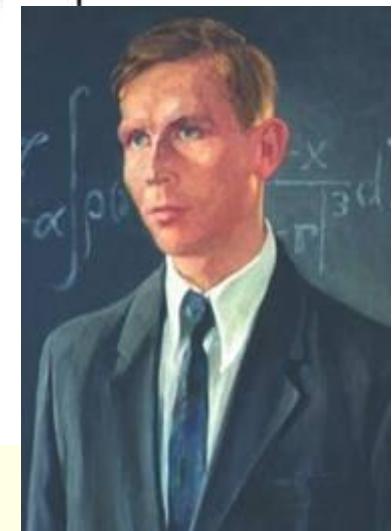
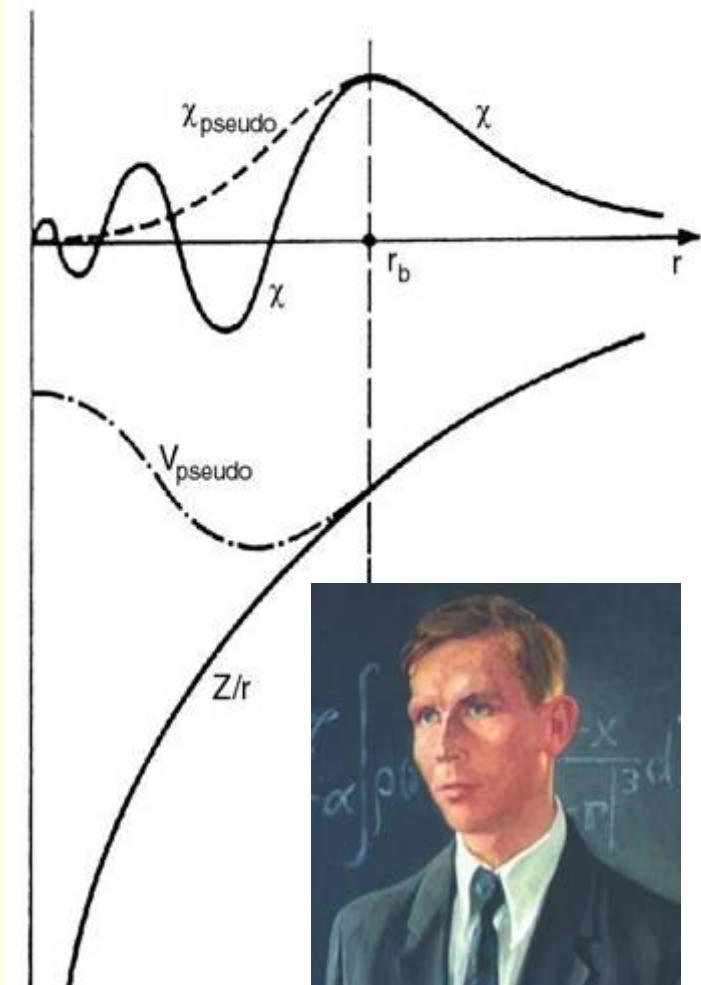


## ■ LCAO methods

- *Gaussians, Slater, or numerical orbitals, often with PP option*)

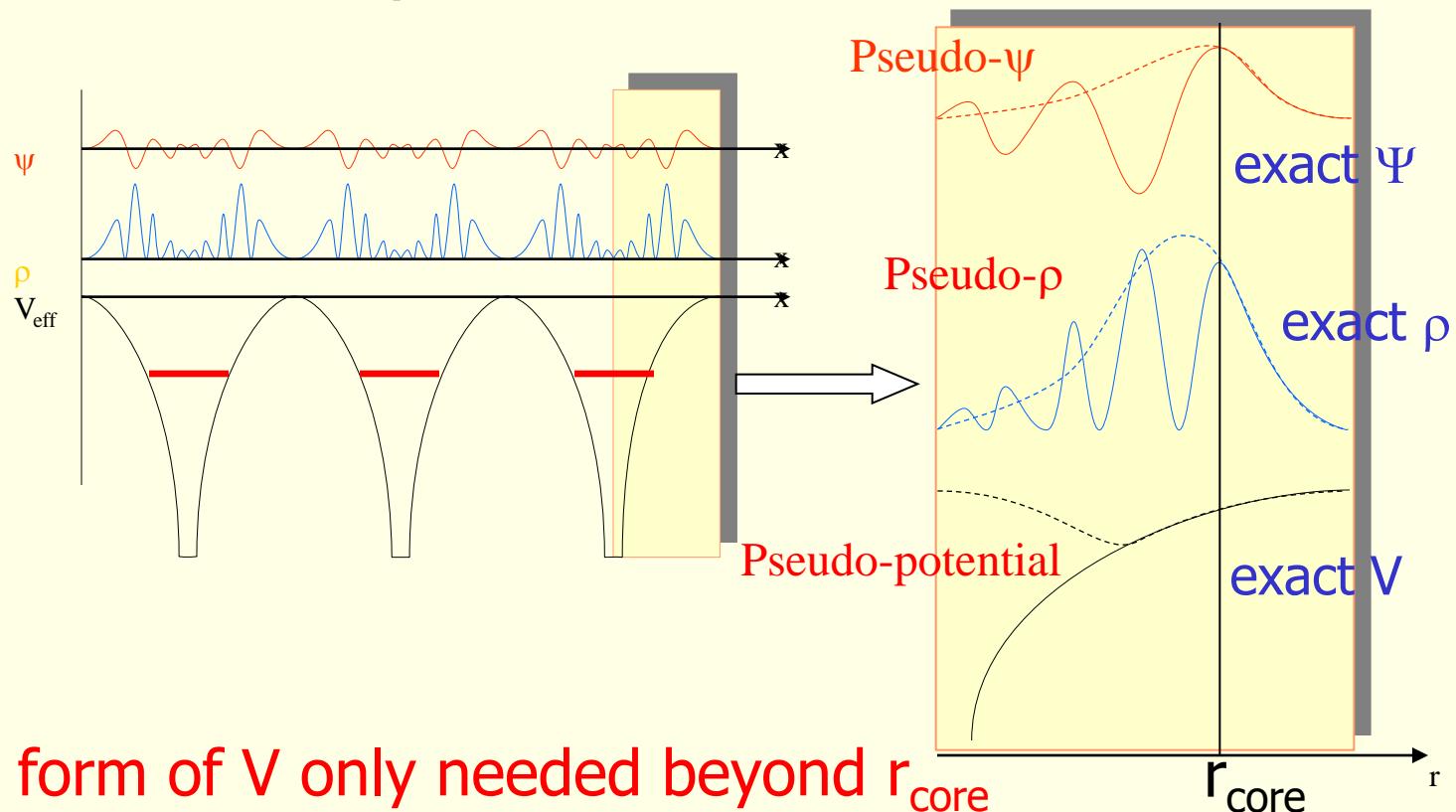


- **plane waves** form a “complete” basis set, however, they “never” converge due to the rapid oscillations of the atomic wave functions  $\chi$  close to the nuclei
- let’s get rid of all **core electrons** and **these oscillations** by replacing the strong ion–electron potential by a much weaker (and 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) →



## ■ 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*

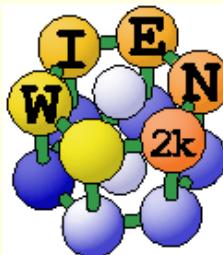
K.Schwarz,  
DFT calculations of solids with LAPW and WIEN2k  
Solid State Chem.**176**, 319-328 (2003)

## ■ Local orbitals (D.J.Singh 1991)

- *treatment of semi-core states (avoids ghostbands)*

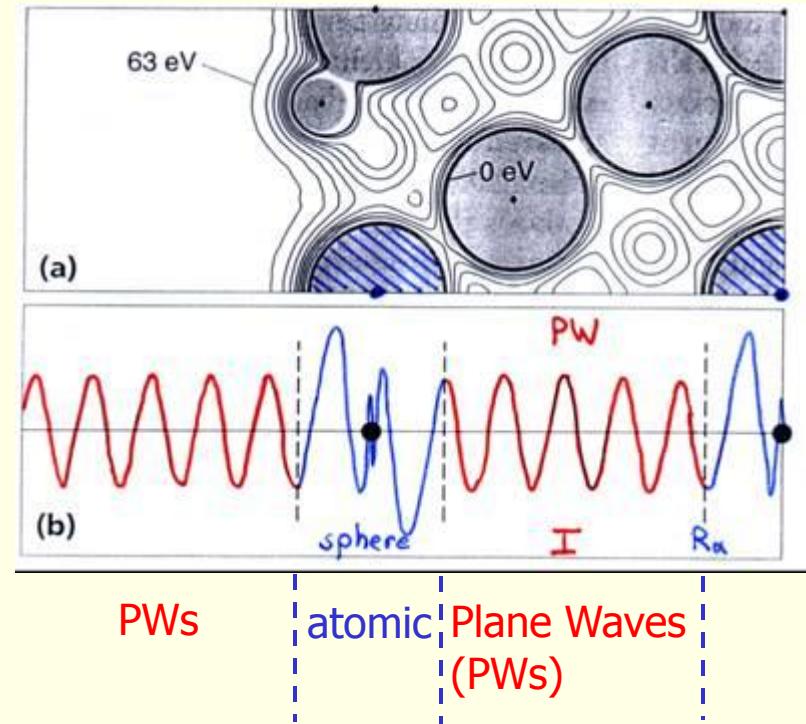
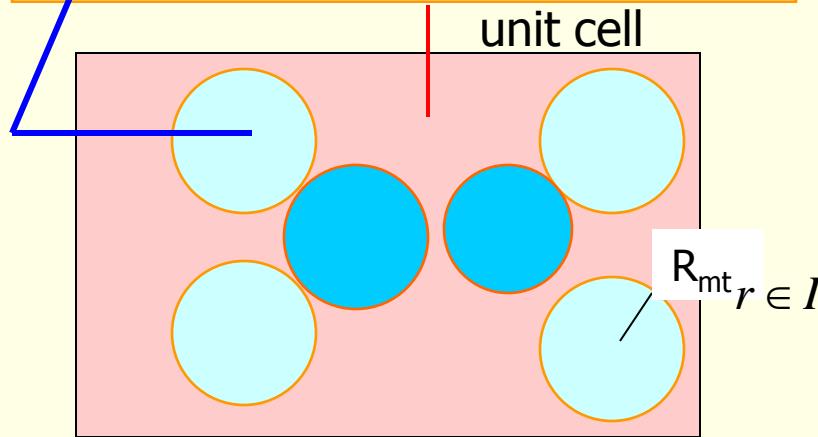
## ■ APW+lo (E.Sjöstedt, L.Nordstörm, D.J.Singh 2000)

- *Efficiency of APW + convenience of LAPW*
- *Basis for*



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

The unit cell is partitioned into:  
 atomic spheres  
 Interstitial region



Basis set:

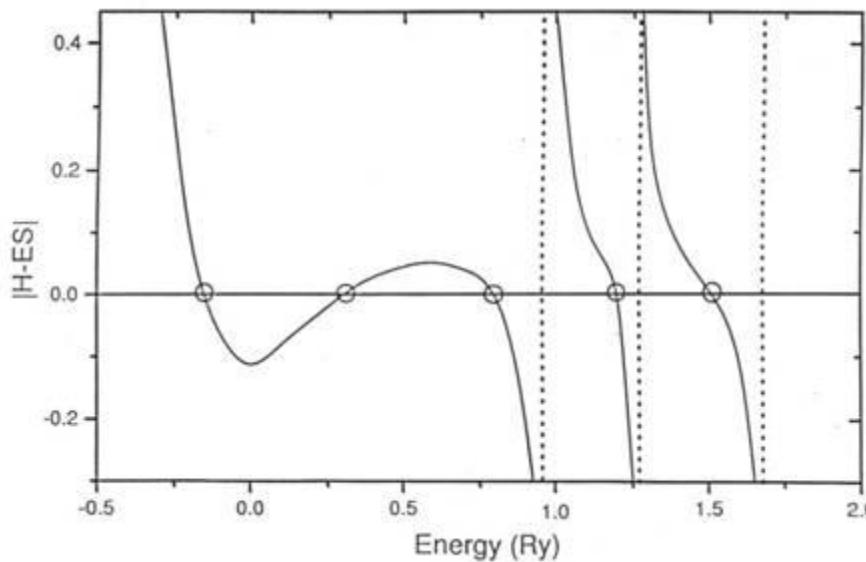
$$\text{PW: } e^{i(\vec{k} + \vec{K}) \cdot \vec{r}}$$

join

Atomic partial waves

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

$u_\ell(r, \varepsilon)$  are the numerical solutions of the radial Schrödinger equation in a given spherical potential for a particular energy  $\varepsilon$   
 $A_{\ell m}^K$  coefficients for matching the PW



H Hamiltonian  
S overlap matrix

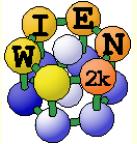


Atomic partial waves

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

Energy dependent basis functions  
lead to a  
Non-linear eigenvalue problem

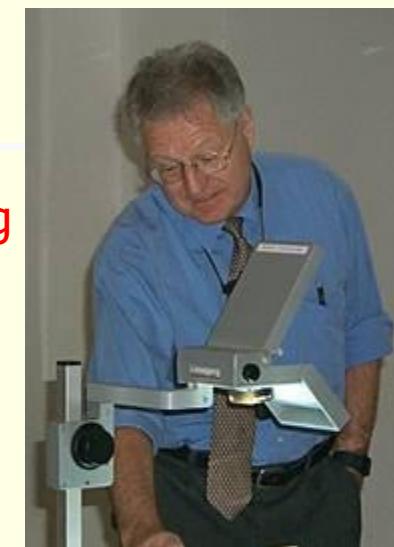
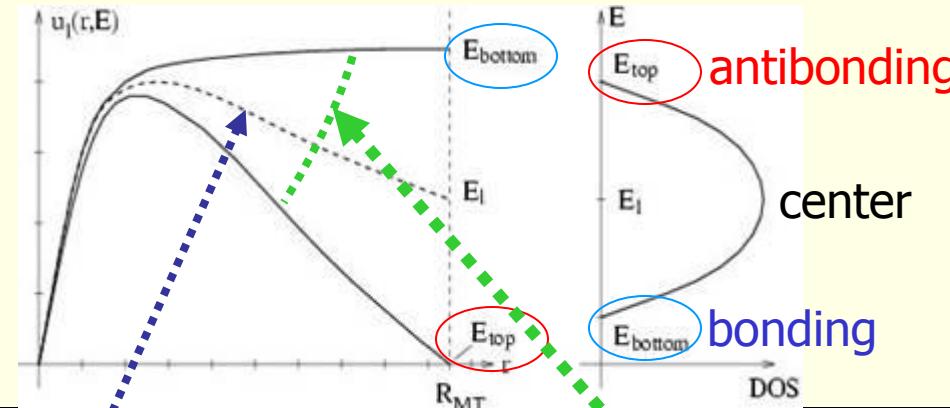
Numerical search for those energies, for which  
the  $\det|H-ES|$  vanishes. **Computationally very demanding.**  
“Exact” solution for given MT potential!



# Linearization of energy dependence

LAPW suggested by

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



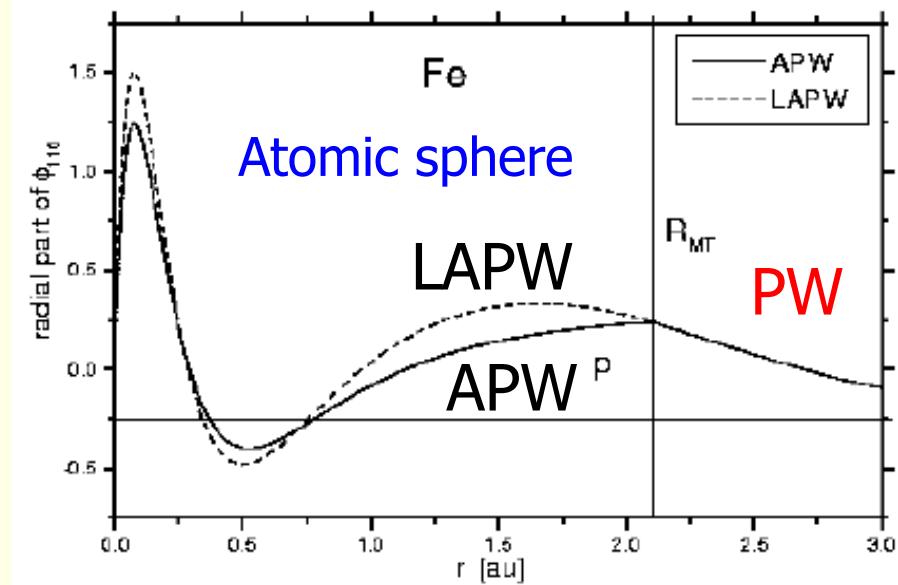
$$\Phi_{k_n} = \sum_{\ell m} [A_{\ell m}(k_n)u_\ell(E_\ell, r) + B_{\ell m}(k_n)\dot{u}_\ell(E_\ell, r)]Y_{\ell m}(\hat{r})$$

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

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

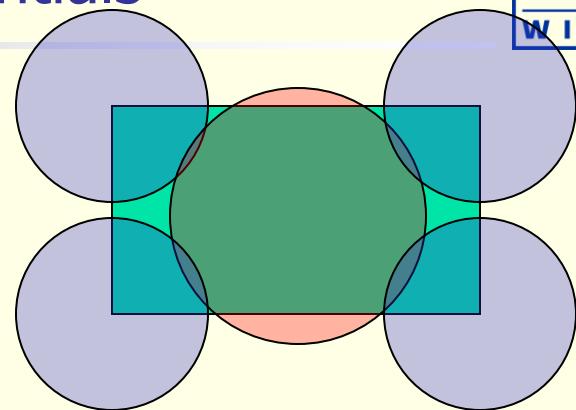
→ General eigenvalue problem  
(diagonalization)

→ additional constraint requires  
more PWs than APW



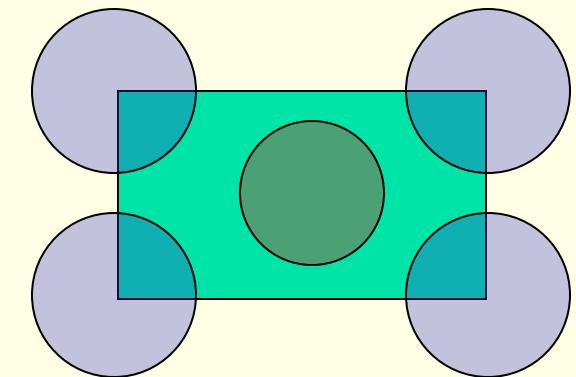
## ■ Atomic sphere approximation (ASA)

- *overlapping spheres “fill” all volume*
- *potential spherically symmetric*



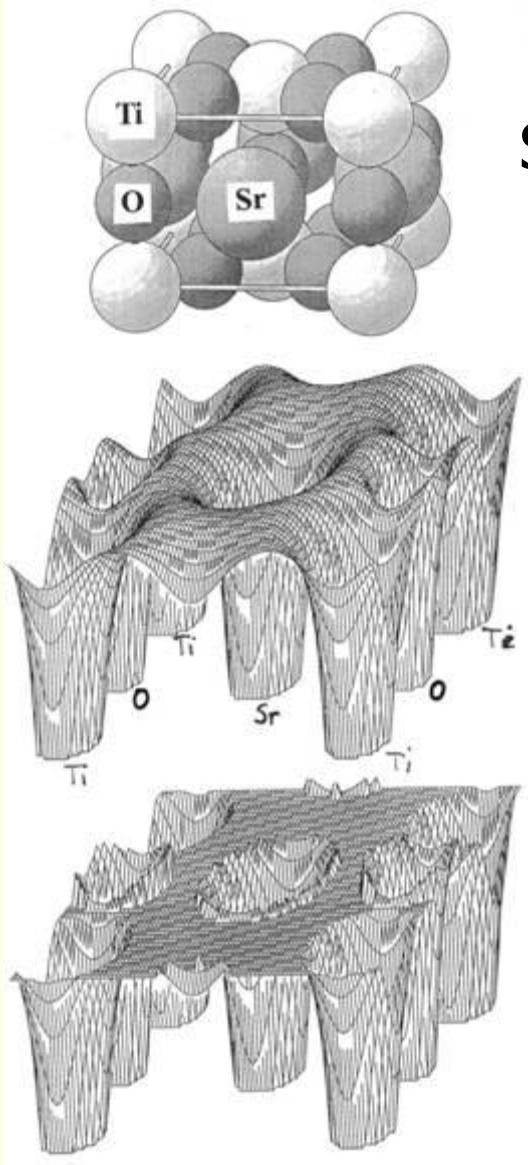
## ■ “muffin-tin” approximation (MTA)

- *non-overlapping spheres with spherically symmetric potential +*
- *interstitial region with  $V=const.$*



## ■ “full”-potential

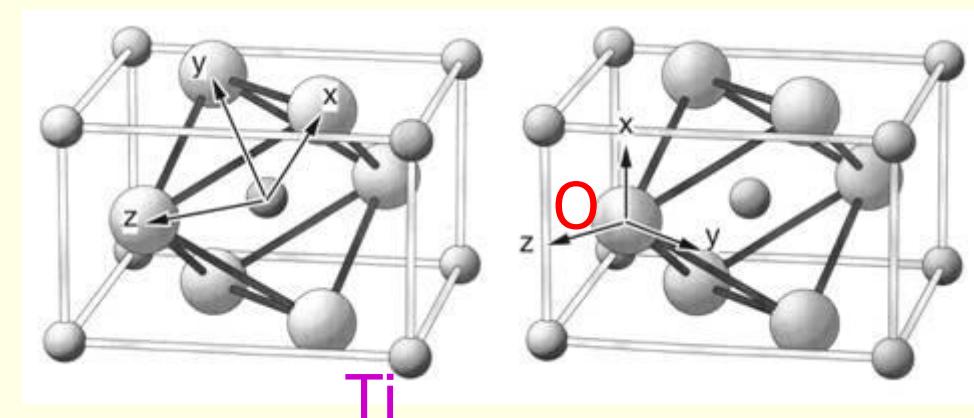
- *no shape approximations to  $V$*



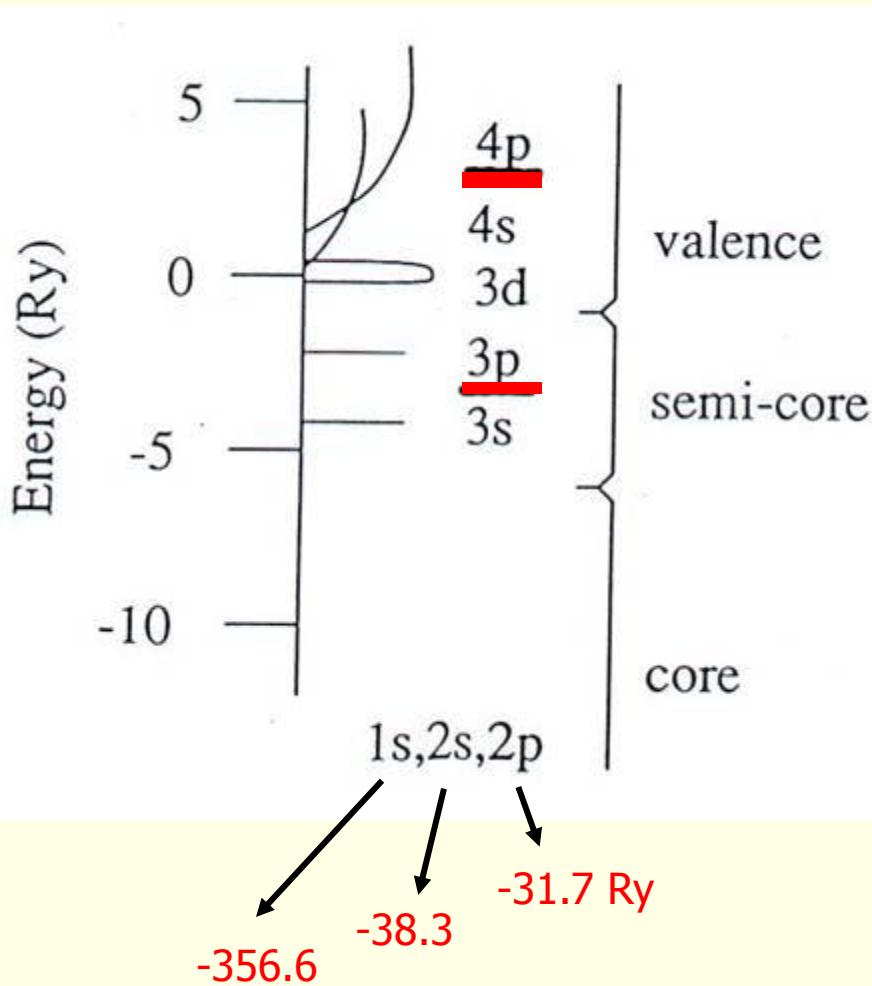
- The potential (and charge density) can be of general form (no shape approximation)

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

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



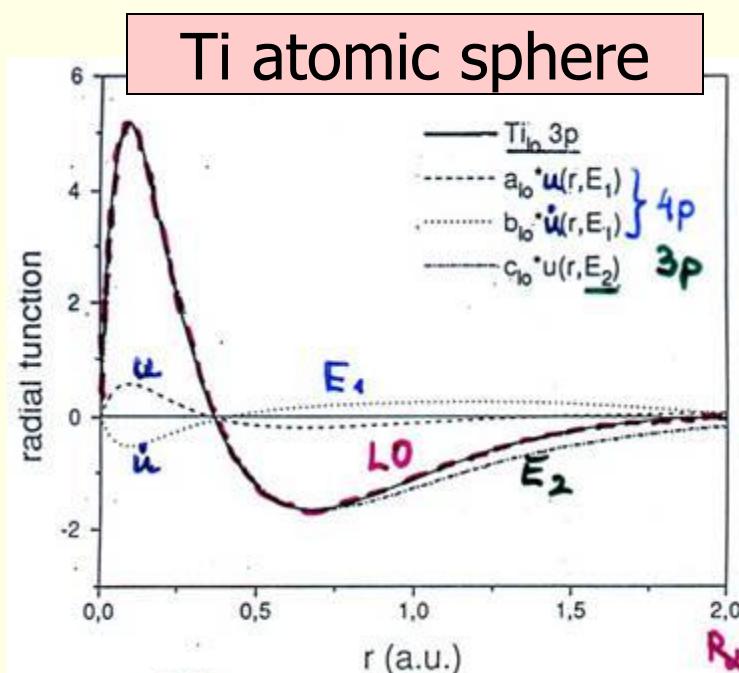
For example: Ti



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

$$1 \text{ Ry} = 13.605 \text{ eV}$$

# Local orbitals (LO)



## ■ LOs

- are confined to an atomic sphere
- have zero value and slope at  $R$
- Can treat two principal QN  $n$  for each azimuthal QN  $\ell$   
(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)

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  $E$** , (superior PW convergence)
- Linearize with **additional local orbitals (lo)**  
(add a few extra basis functions)

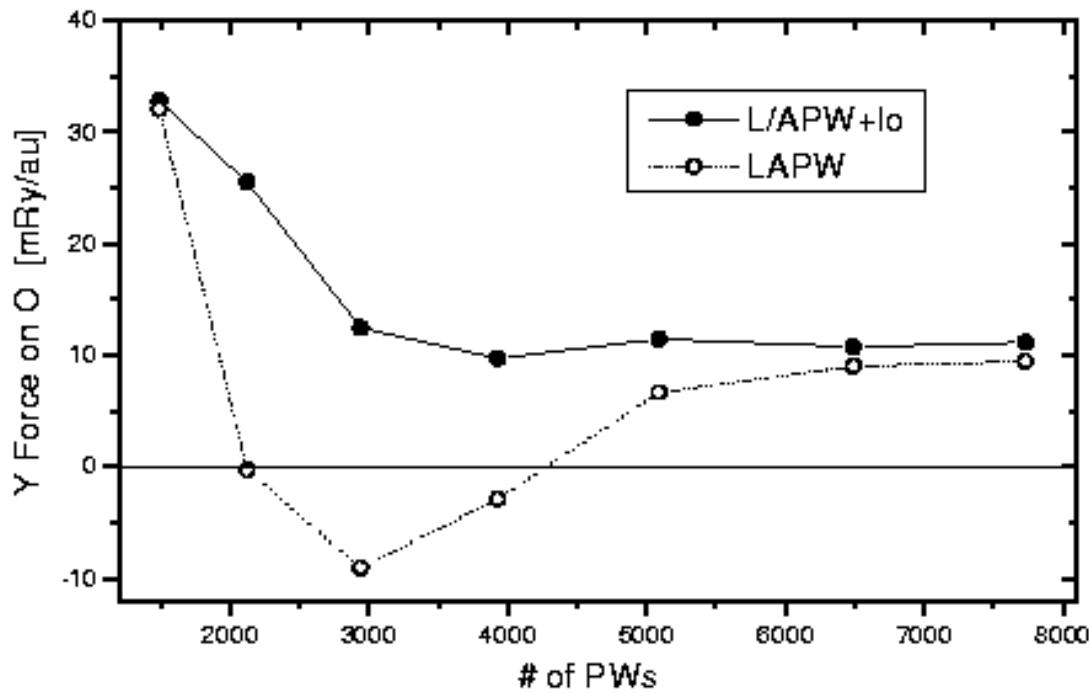
$$\Phi_{k_n} = \sum_{\ell m} A_{\ell m}(k_n) u_{\ell}(E_{\ell}, r) Y_{\ell m}(\hat{r})$$

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

**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

## Representative Convergence:

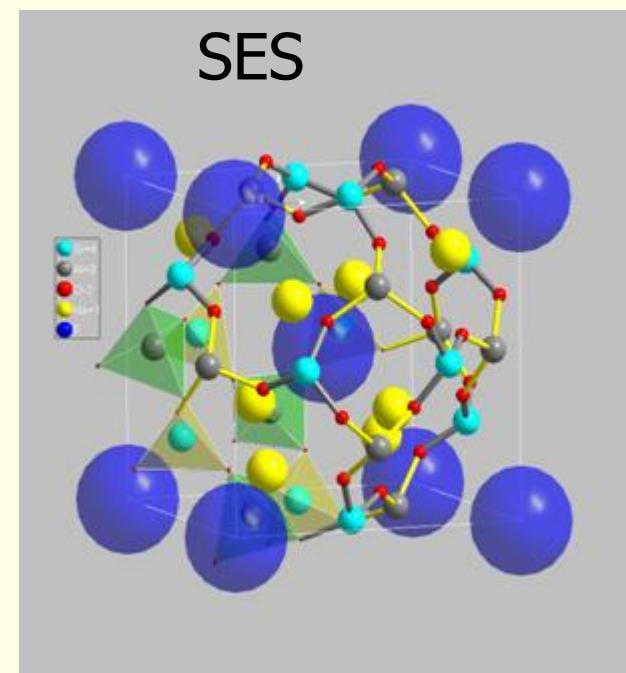


SES (sodium electro solodalite)

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

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



## ■ 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)

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

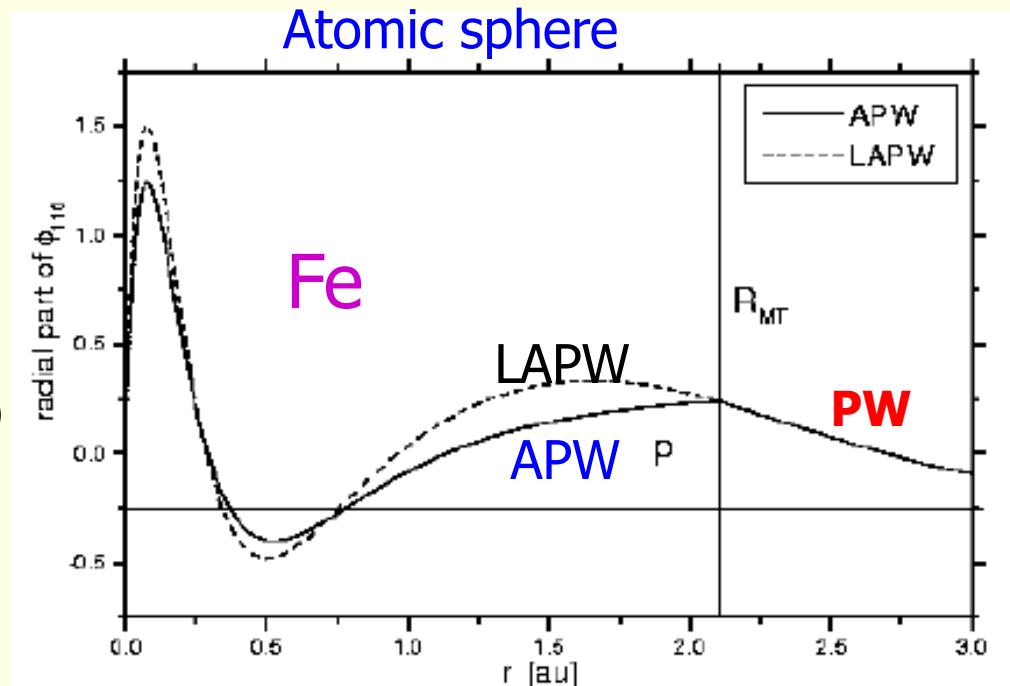
## ■ match at sphere boundary

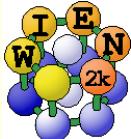
- LAPW

value and slope  $A_{\ell m}(k_n), B_{\ell m}(k_n)$

- APW

value  $A_{\ell m}(k_n)$





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

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

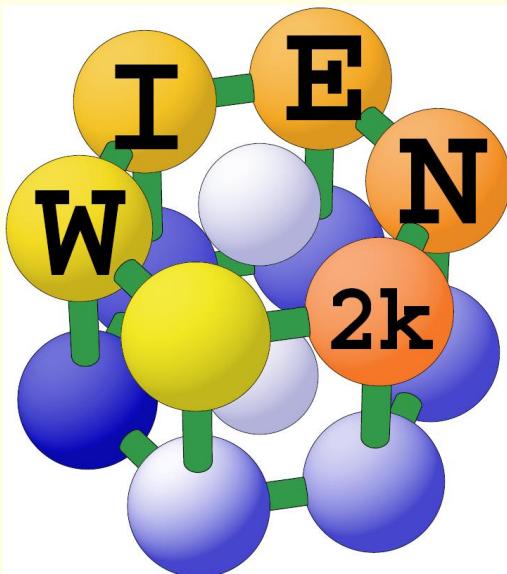
optimal solution: mixed basis

- 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



G.Madsen

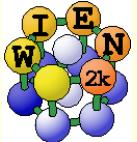
P.Blahा

D.Kvasnicka

K.Schwarz

J.Luitz

<http://www.wien2k.at>



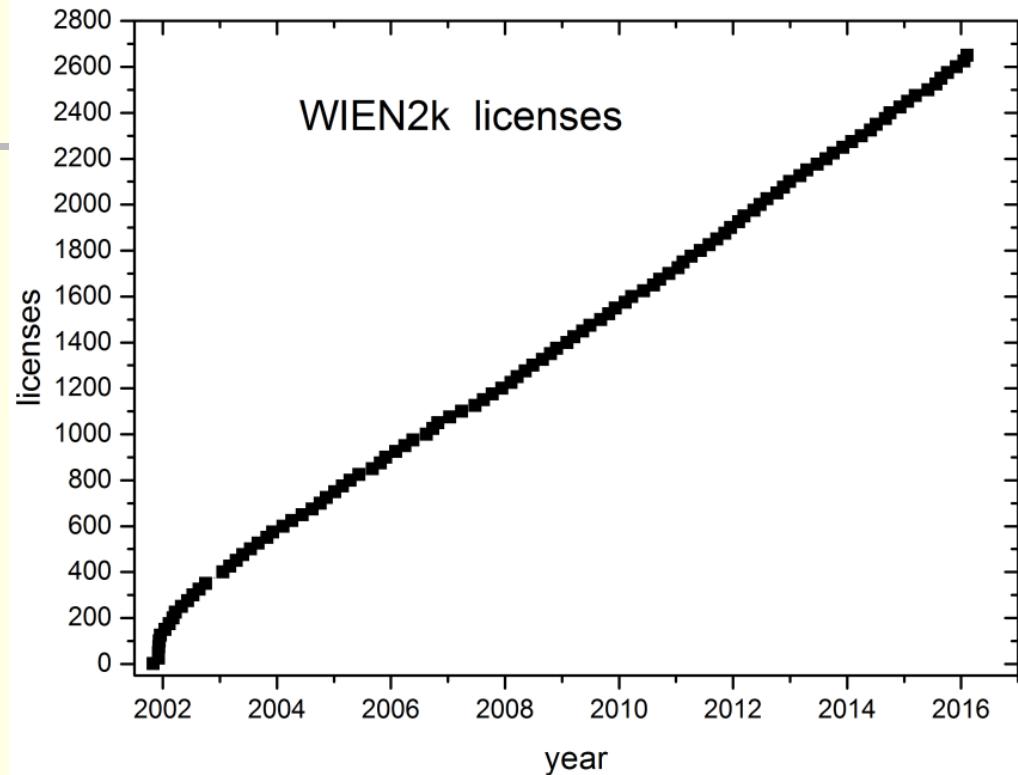
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mailinglist: 10.000 emails/6 years



# 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*

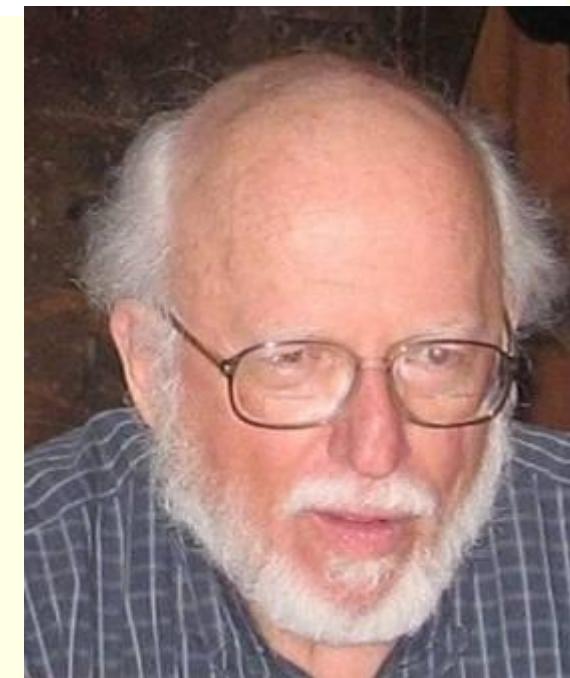
and

S.B. TRICKEY

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

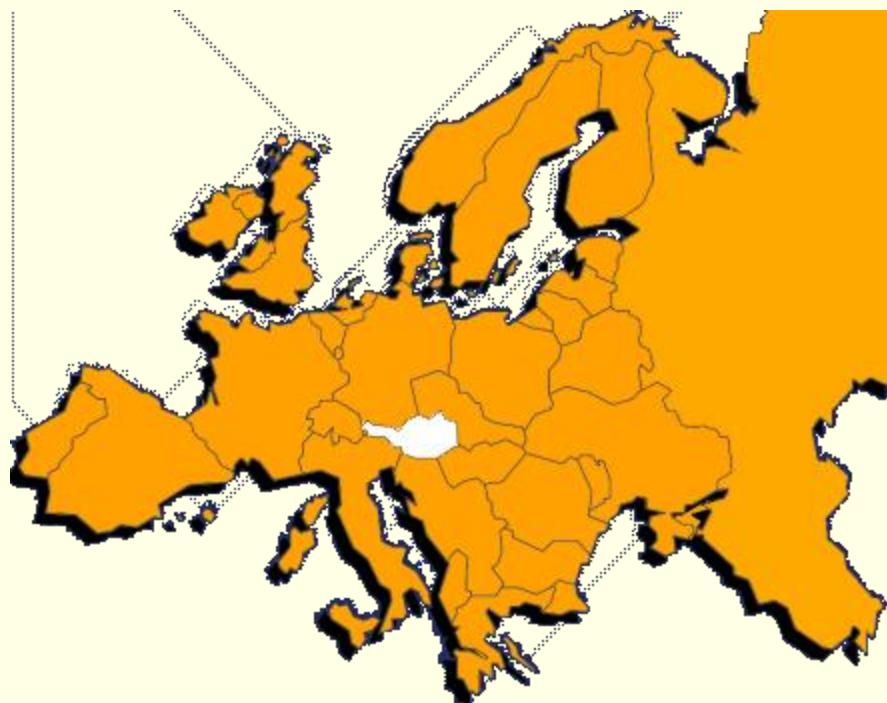
### PROGRAM SUMMARY

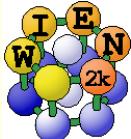
*Title of program:* WIEN



Computer Physics Communications 59 (1990) 399–415

In the Heart of EUROPE





# In Japan

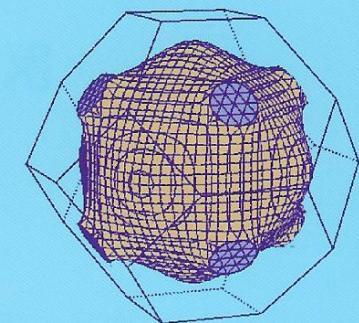
- Book published by  
Shinya Wakoh (2006)

『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<sup>\*1</sup>。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ます。

# Development of WIEN2k

## ■ Authors of WIEN2k

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

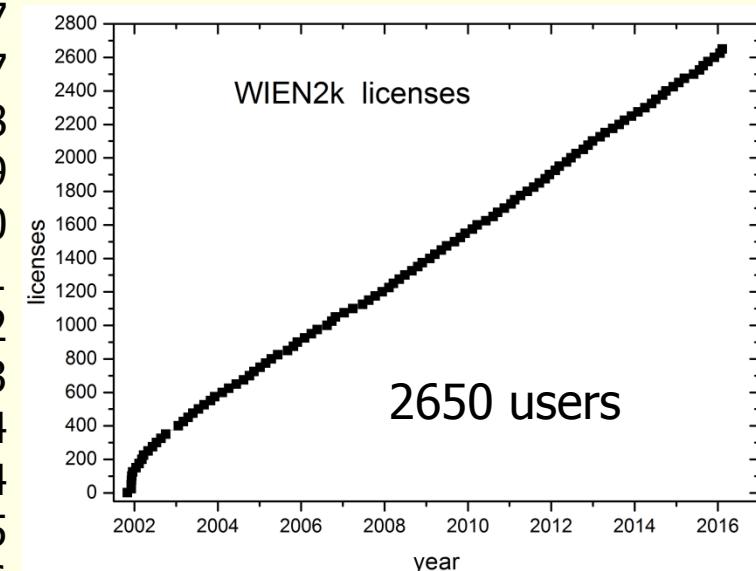
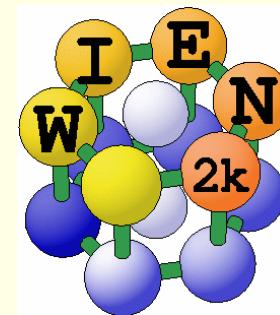
## ■ Other contributions to WIEN2k

- *C. Ambrosch-Draxl (Free Univ. Berlin) 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 (McMaster Univ. Hamilton, ON) Berry phases*
- *M. Scheffler (Fritz Haber Inst., Berlin), forces*
- *D.J.Singh (NRL, Washington D.C., Oak Ridge), local orbitals (LO), APW+lo*
- *E. Sjöstedt and L Nordström (Uppsala, Sweden), APW+lo*
- *J. Sofo (Penn State, USA) and J. Fuhr (Bariloche), 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	
■ 23rd	McMaster, Canada	June	2016	



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:

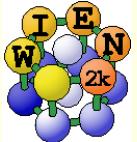
$$\langle E \rangle = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad \frac{\delta \langle E \rangle}{\delta C_{k_n}} = 0$$

upper bound

minimum

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

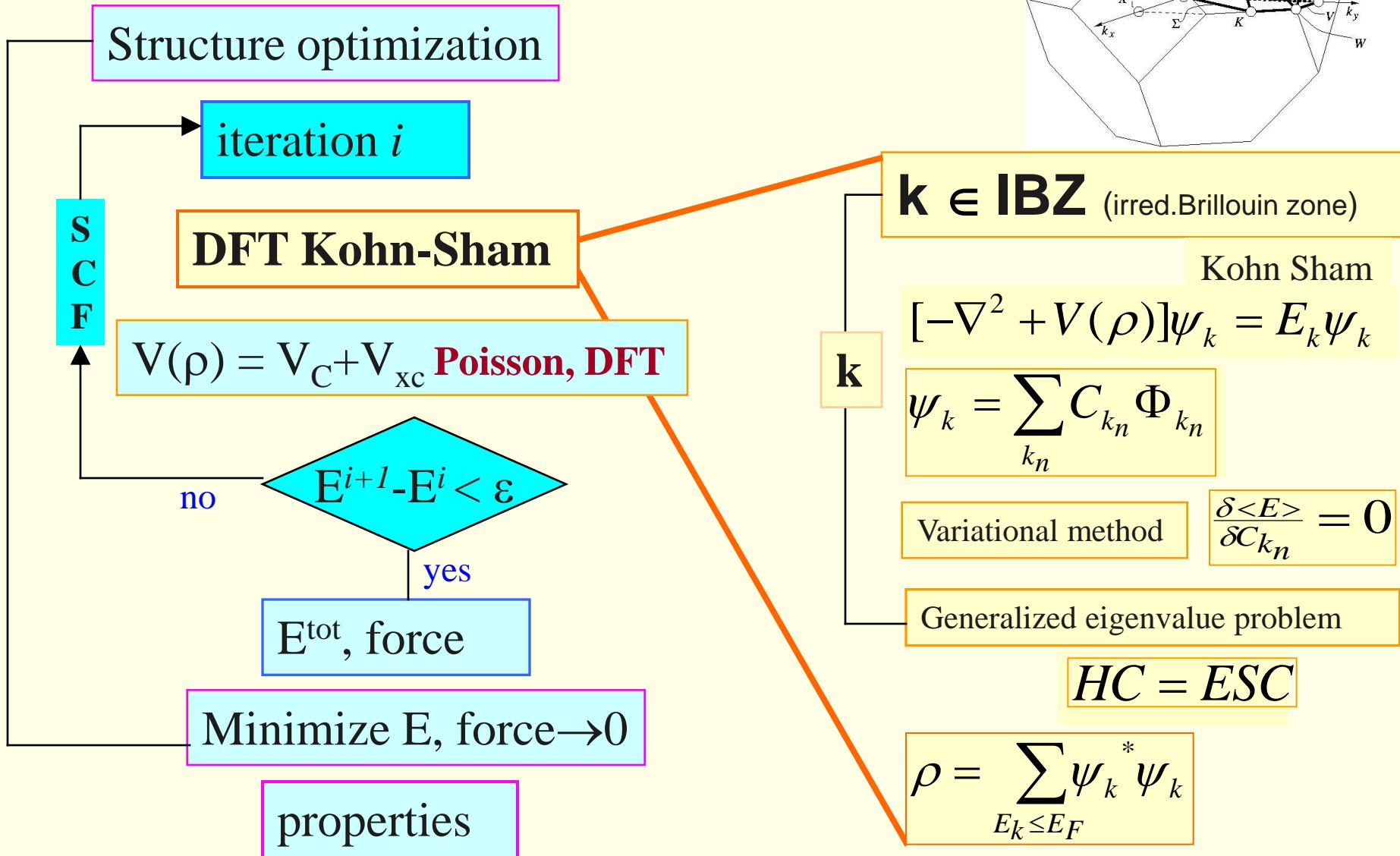
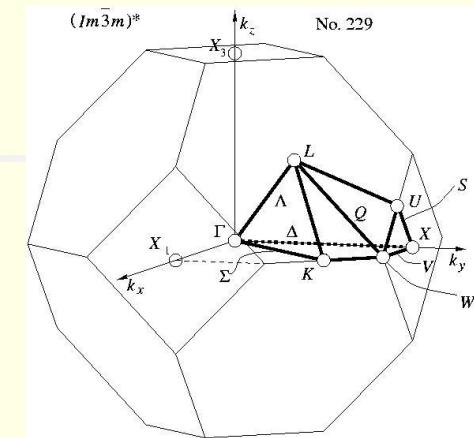
Diagonalization of (real or complex) matrices of size 10.000 to 50.000 (up to 50 Gb memory)



# Structure: $a, b, c, \alpha, \beta, \gamma, R_\alpha, \dots$

unit cell

atomic positions

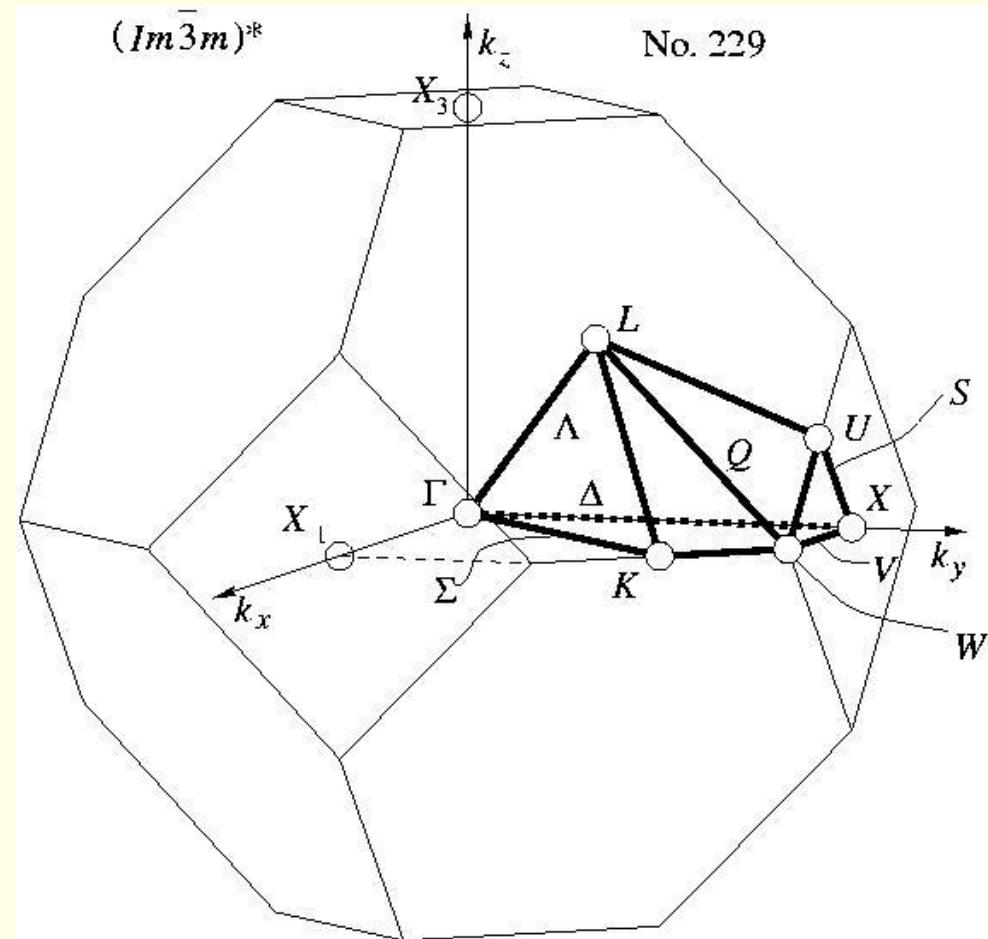


## ■ Irreducible BZ (IBZ)

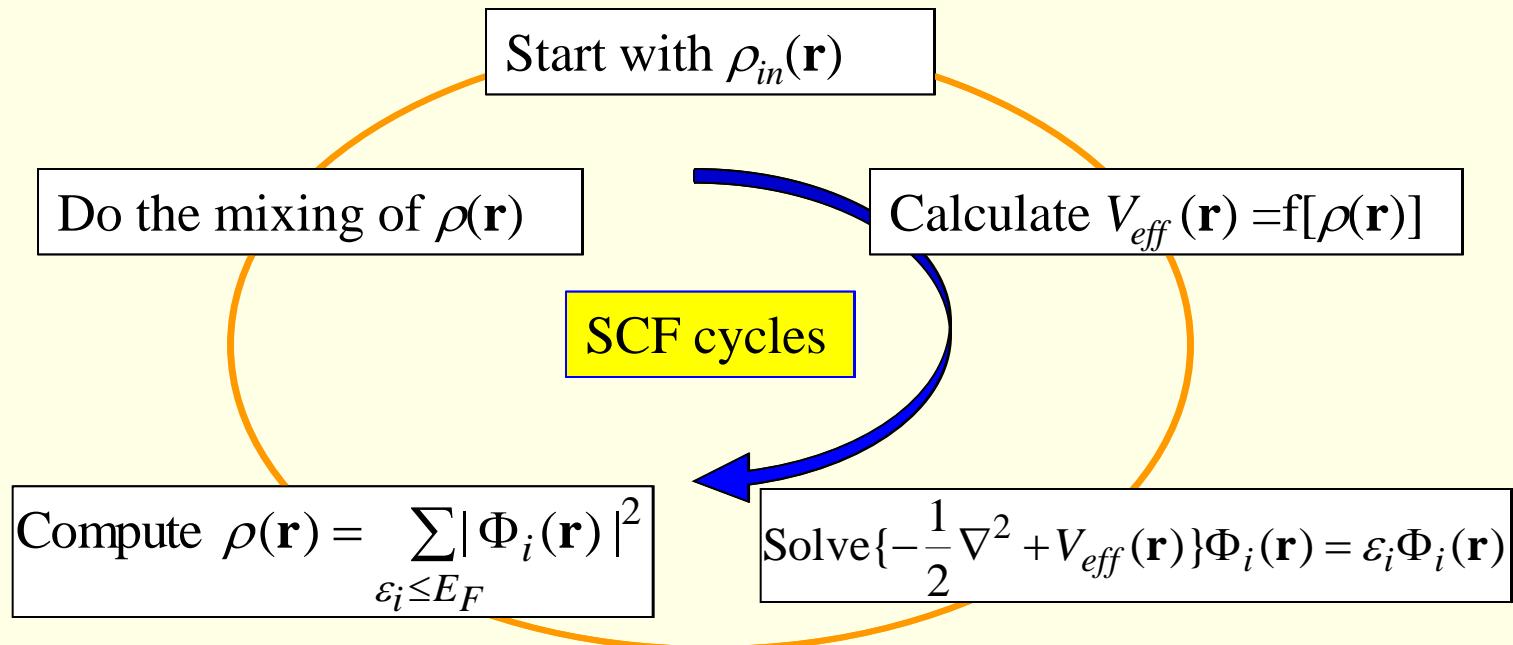
- *The irreducible wedge*
- *Region, from which the whole BZ can be obtained by applying all symmetry operations*

## ■ Bilbao Crystallographic Server:

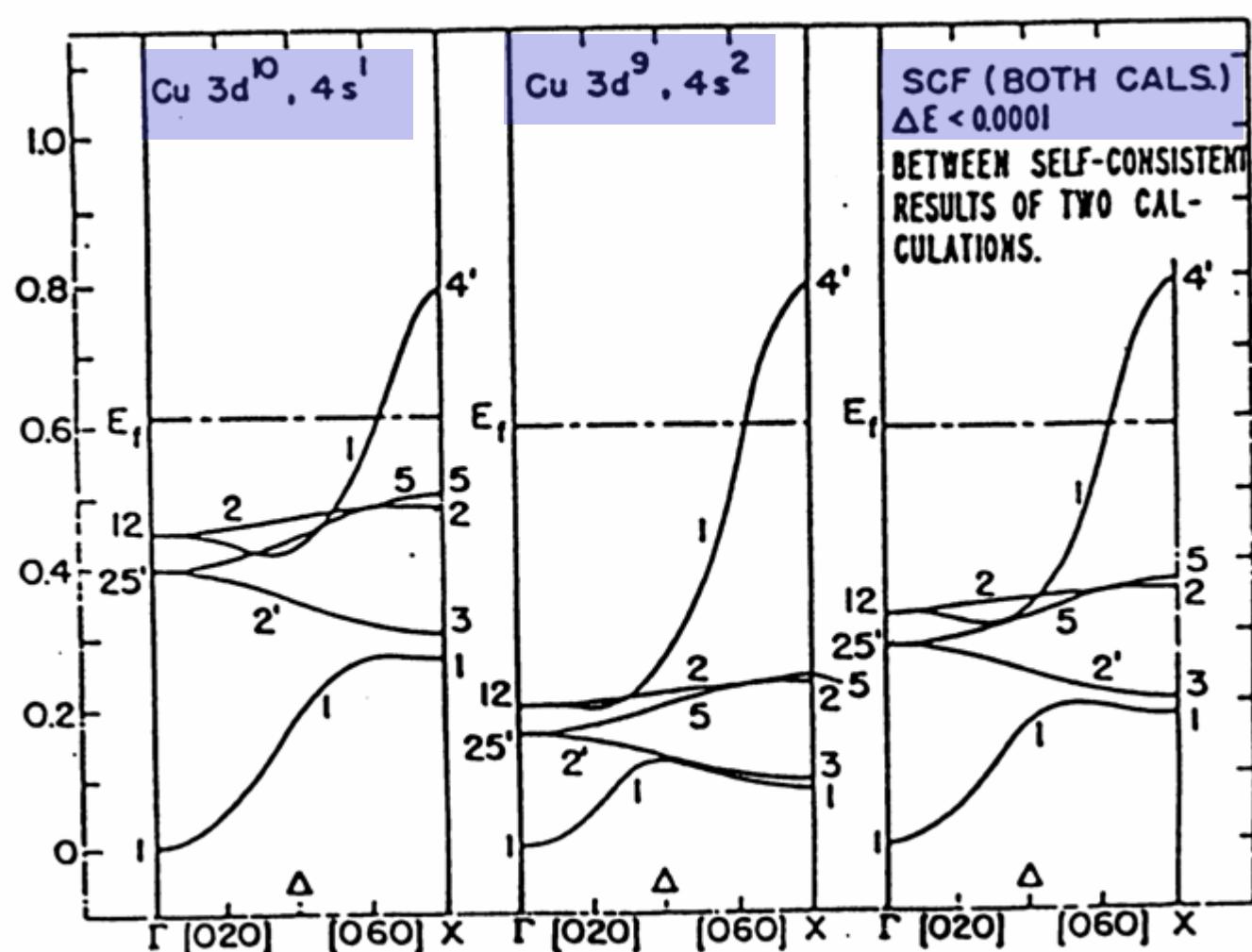
- [www.cryst.ehu.es/cryst/](http://www.cryst.ehu.es/cryst/)
- *The IBZ of all space groups can be obtained from this server*
- *using the option KVEC and specifying the space group (e.g. No.225 for the fcc structure leading to bcc in reciprocal space, No.229 )*



- 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 ??



## Band structure of fcc Cu



## ■ init\_lapw

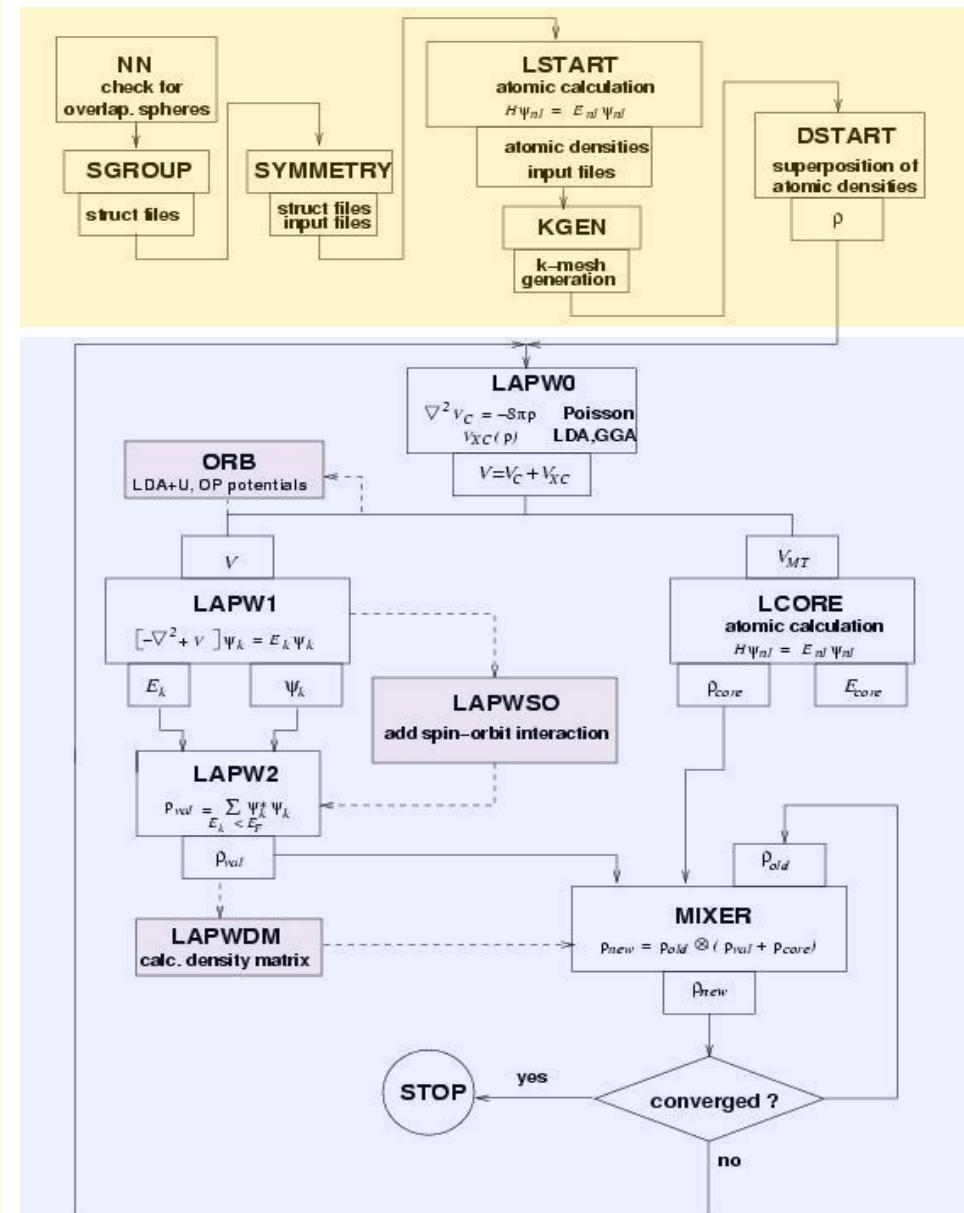
- *initialization*
- *symmetry detection ( $F$ ,  $I$ ,  $C$ -centering, inversion)*
- *input generation with recommended defaults*
- *quality (and computing time) depends on k-mesh and R.Kmax (determines #PW)*

## ■ run\_lapw

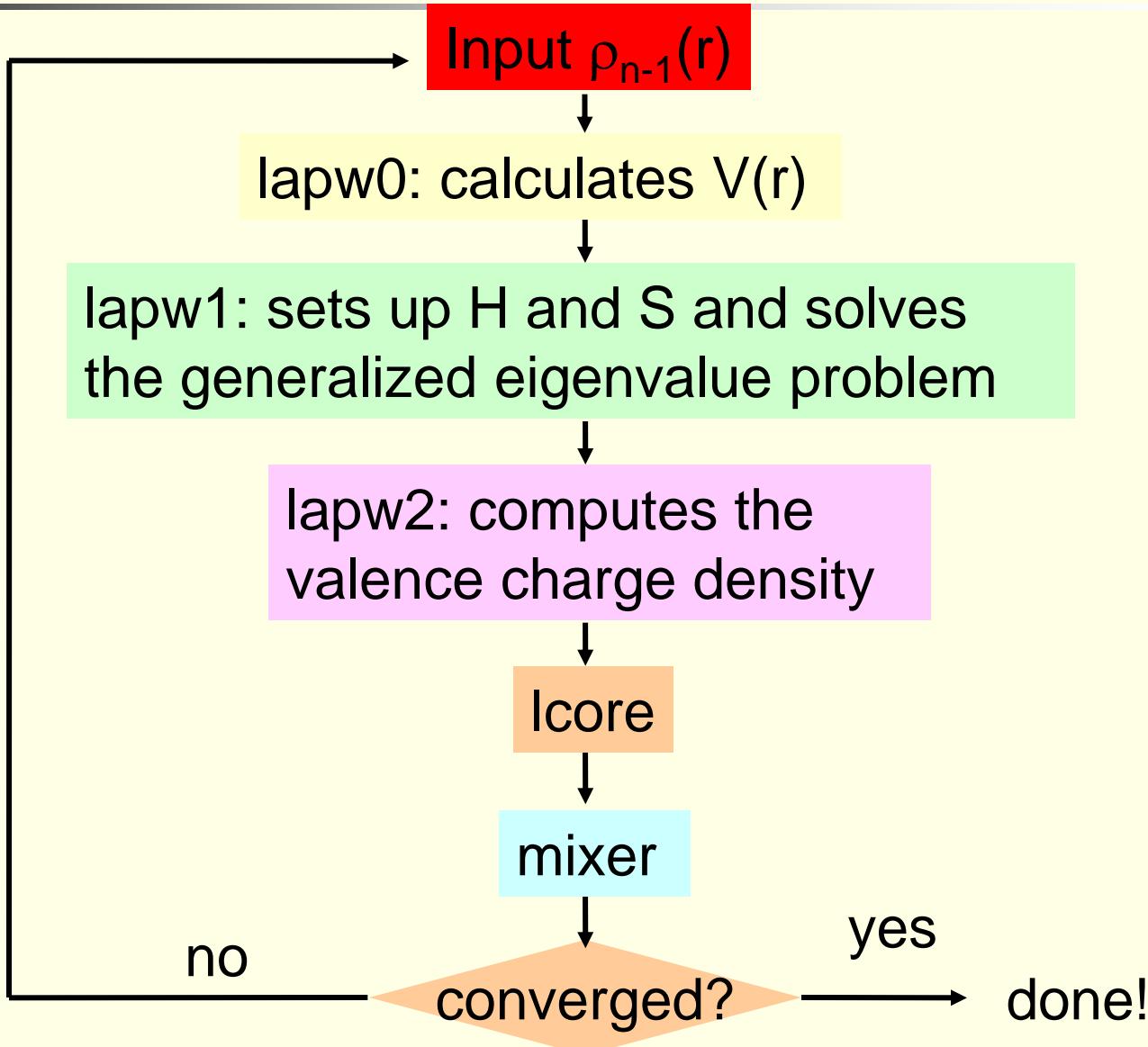
- *scf-cycle*
- *optional with SO and/or LDA+U*
- *different convergence criteria (energy, charge, forces)*

## ■ save\_lapw tic\_gga\_100k\_rk7\_vol0

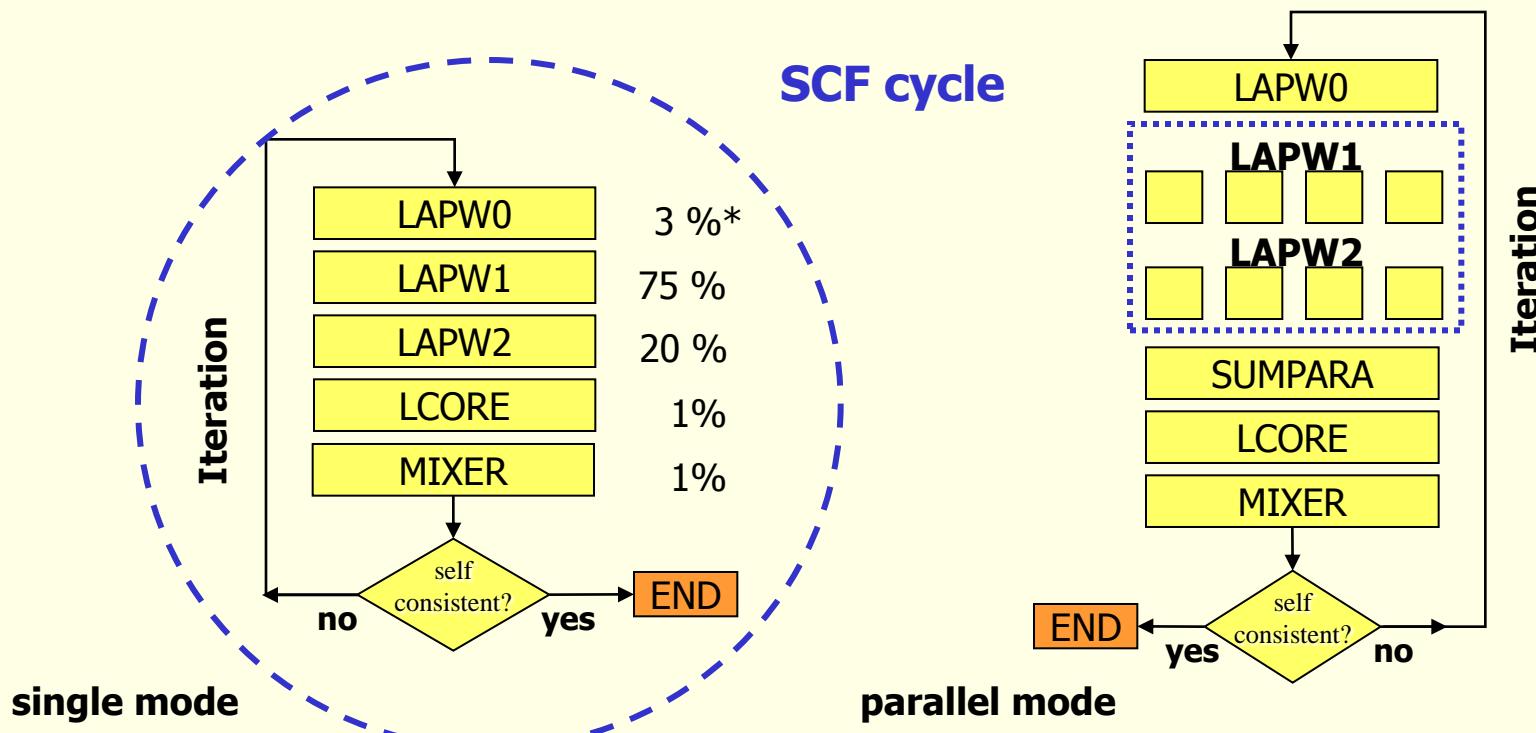
- *cp case.struct and clmsum files,*
- *mv case.scf file*
- *rm case.broyd\* files*



# Flow Chart of WIEN2k (SCF)



- 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



\* fraction of total computation time

- + 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

- **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/pbla/laapw/2005-june/TiC

**StructGen™**

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

**Save Structure**

**Title:** TiC

**Lattice:**

**Type:** F

Spacegroups from Bilbao Cryst Server

P  
F  
B  
CXY  
CYZ  
CXZ  
R  
H  
1\_P1

**Lattice parameters in Å**

a=4.3280000386 b=4.3280000386 c=4.3280000386  
α=90.000000 β=90.000000 γ=90.000000

**Inequivalent Atoms: 2**

Atom 1: Ti    Z=22.0    RMT=2.0000    remove atom  
Pos 1: x=0.00000000 y=0.00000000 z=0.00000000 remove  
add position

Atom 2: C    Z=6.0    RMT=1.9000    remove atom  
Pos 1: x=0.50000000 y=0.50000000 z=0.50000000 remove  
add position

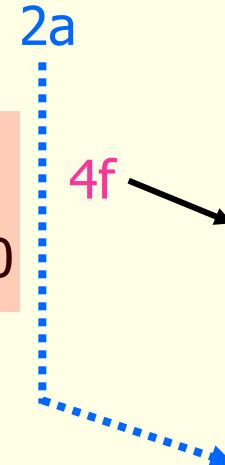


# Spacegroup $P4_2/mnm$

**Structure given by:**  
 spacegroup  
 lattice parameter  
 positions of atoms  
 (basis)

**Rutile  $TiO_2$ :**  
 $P4_2/mnm$  (136)  
 $a=8.68$ ,  $c=5.59$  bohr  
 $Ti: (0,0,0)$

O: (0.304,0.304,0)  
 Wyckoff position: x, x, 0

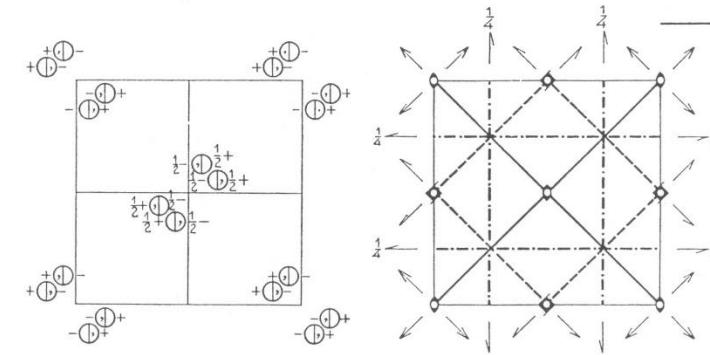


$P4_2/mnm$   
 $D_{4h}^{14}$

No. 136

$P4_2/m\ 2_1/n\ 2/m$

$4/m\ m\ m$  Tetragonal



Origin at centre (mmm)

Number of positions,  
 Wyckoff notation,  
 and point symmetry

Co-ordinates of equivalent positions

Conditions limiting  
 possible reflections

16	<i>k</i>	1	$x, y, z; \bar{x}, \bar{y}, z; \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z; \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z;$	$x, y, \bar{z}; \bar{x}, \bar{y}, \bar{z}; \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z; \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z;$	$y, x, z; \bar{y}, \bar{x}, z; \frac{1}{2} + y, \frac{1}{2} - x, \frac{1}{2} + z; \frac{1}{2} - y, \frac{1}{2} + x, \frac{1}{2} + z;$	$y, x, \bar{z}; \bar{y}, \bar{x}, \bar{z}; \frac{1}{2} + y, \frac{1}{2} - x, \frac{1}{2} - z; \frac{1}{2} - y, \frac{1}{2} + x, \frac{1}{2} - z.$
----	----------	---	---	---	---	---

General:  
 $hkl$ : No conditions  
 $hk0$ : No conditions  
 $0kl$ :  $k+l=2n$   
 $hhl$ : No conditions

8	<i>j</i>	<i>m</i>	$x, x, z; \bar{x}, \bar{x}, z; \frac{1}{2} + x, \frac{1}{2} - x, \frac{1}{2} + z; \frac{1}{2} - x, \frac{1}{2} + x, \frac{1}{2} + z;$	$x, x, \bar{z}; \bar{x}, \bar{x}, \bar{z}; \frac{1}{2} + x, \frac{1}{2} - x, \frac{1}{2} - z; \frac{1}{2} - x, \frac{1}{2} + x, \frac{1}{2} - z.$
---	----------	----------	---	---

Special: as above, plus  
 } no extra conditions

8	<i>i</i>	<i>m</i>	$x, y, 0; \bar{x}, \bar{y}, 0; \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2}; \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2};$	$y, x, 0; \bar{y}, \bar{x}, 0; \frac{1}{2} + y, \frac{1}{2} - x, \frac{1}{2}; \frac{1}{2} - y, \frac{1}{2} + x, \frac{1}{2}.$
---	----------	----------	---	---

8	<i>h</i>	2	$0, \frac{1}{2}, z; 0, \frac{1}{2}, \bar{z}; 0, \frac{1}{2}, \frac{1}{2} + z; 0, \frac{1}{2}, \frac{1}{2} - z;$	$\frac{1}{2}, 0, z; \frac{1}{2}, 0, \bar{z}; \frac{1}{2}, 0, \frac{1}{2} + z; \frac{1}{2}, 0, \frac{1}{2} - z.$
---	----------	---	---	---

4	<i>g</i>	<i>mm</i>	$x, \bar{x}, 0; \bar{x}, x, 0; \frac{1}{2} + x, \frac{1}{2} + x, \frac{1}{2}; \frac{1}{2} - x, \frac{1}{2} - x, \frac{1}{2}.$	
---	----------	-----------	---	--

4	<i>f</i>	<i>mm</i>	$x, x, 0; \bar{x}, \bar{x}, 0; \frac{1}{2} + x, \frac{1}{2} - x, \frac{1}{2}; \frac{1}{2} - x, \frac{1}{2} + x, \frac{1}{2}.$	
---	----------	-----------	---	--

4	<i>e</i>	<i>mm</i>	$0, 0, z; 0, 0, \bar{z}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2} + z; \frac{1}{2}, \frac{1}{2}, \frac{1}{2} - z.$	
---	----------	-----------	---	--

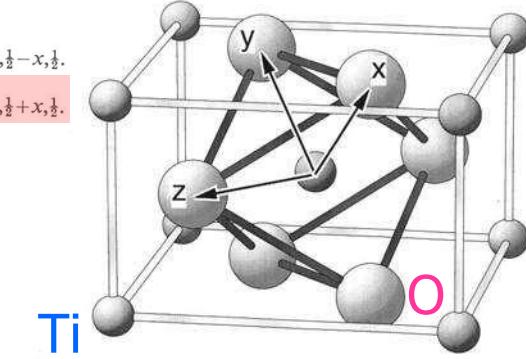
4	<i>d</i>	4	$0, \frac{1}{2}, \frac{1}{4}; \frac{1}{2}, 0, \frac{1}{4}; 0, \frac{1}{2}, \frac{3}{4}; \frac{1}{2}, 0, \frac{3}{4}.$	
---	----------	---	---	--

4	<i>c</i>	2/m	$0, \frac{1}{2}, 0; \frac{1}{2}, 0, 0; 0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, \frac{1}{2}.$	
---	----------	-----	---	--

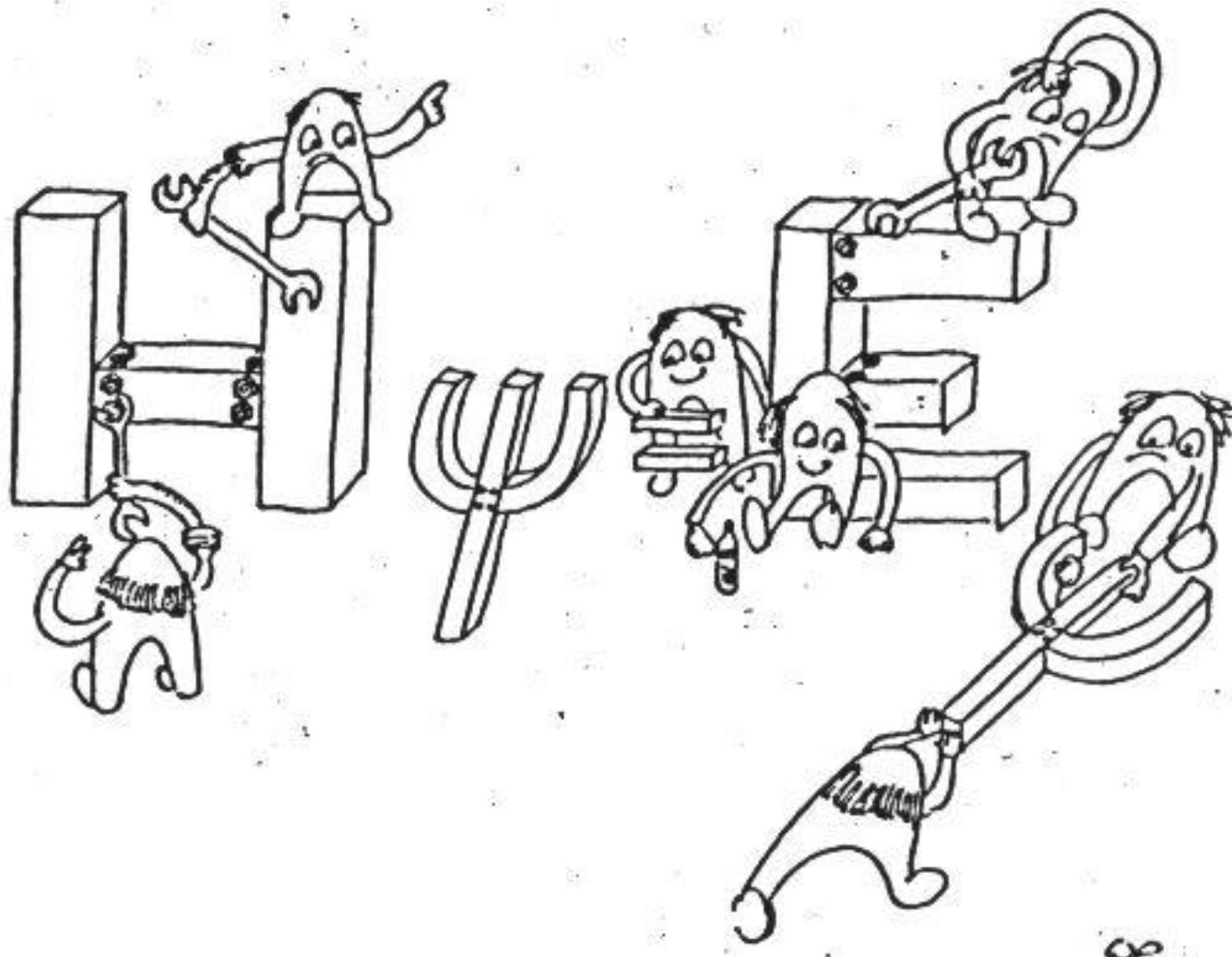
2	<i>b</i>	mmm	$0, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, 0.$	
---	----------	-----	---	--

2	<i>a</i>	mmm	$0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}.$	
---	----------	-----	---	--

$hkl$ :  $h+k=2n$ ;  $t=2n$

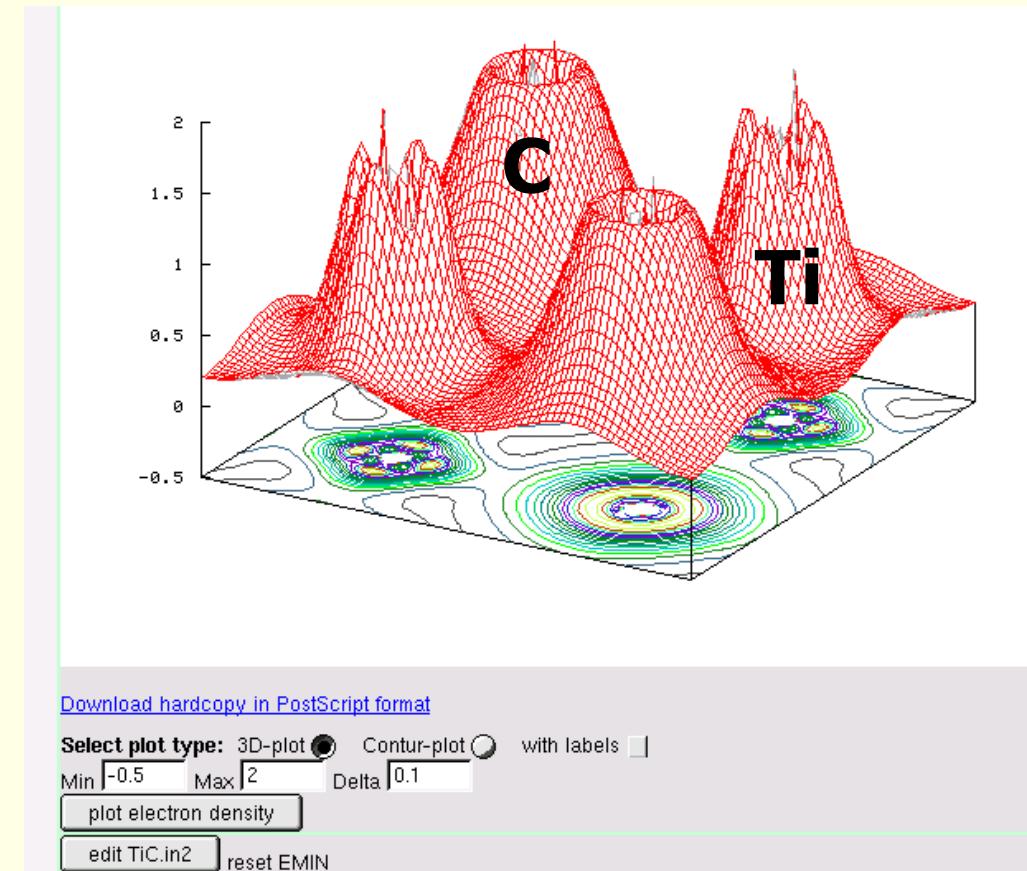
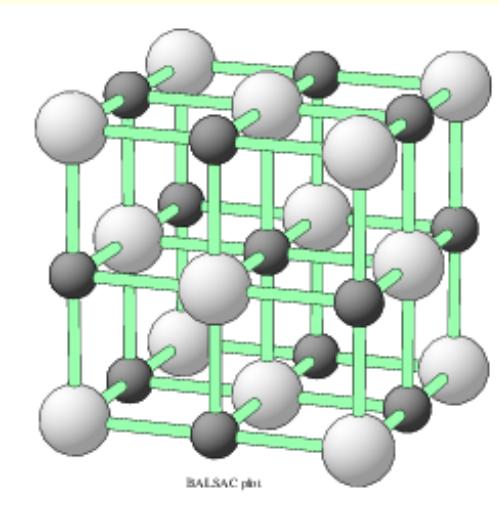


# Quantum mechanics at work

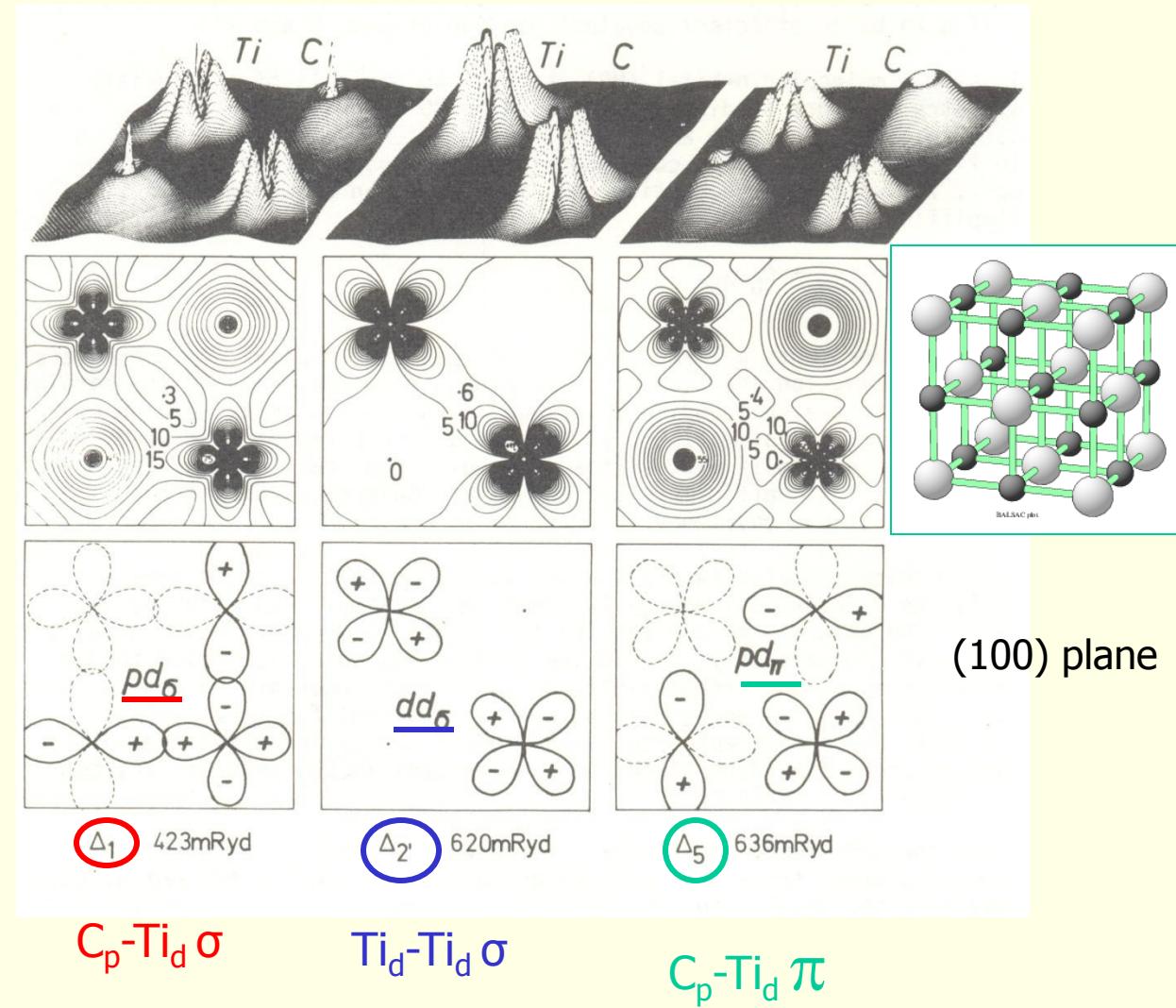
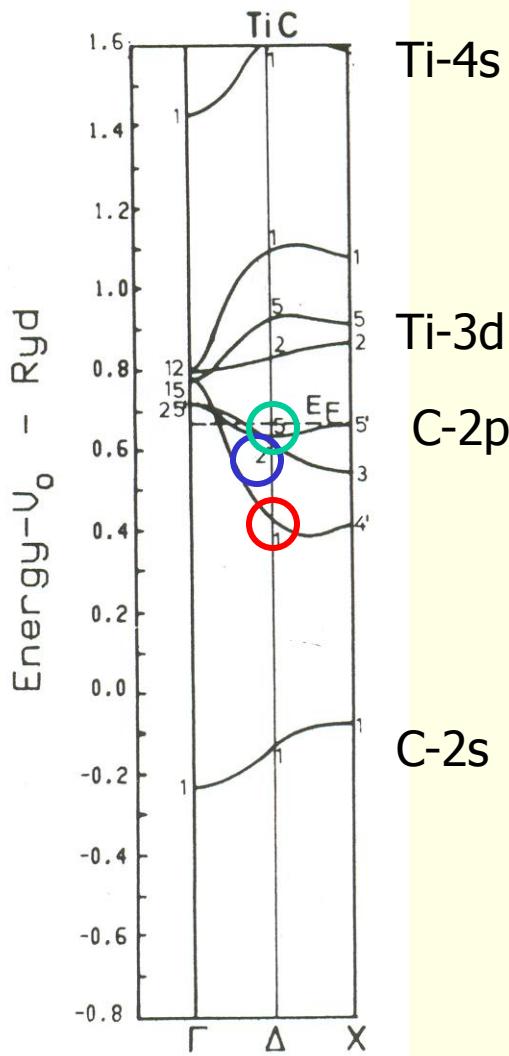


thanks to Erich Wimmer

- 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



## Energy bands

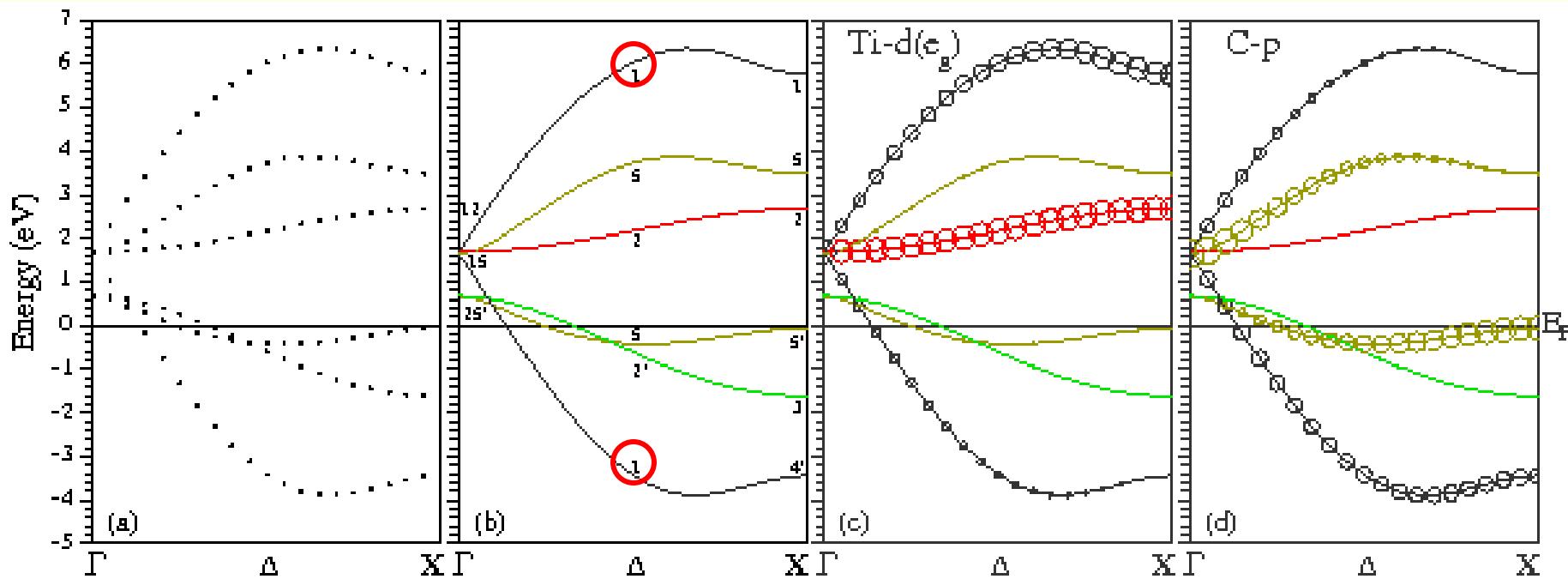


P.Blaha, K.Schwarz,  
Int.J.Quantum Chem. 23, 1535 (1983)

spaghetti

irred.rep.

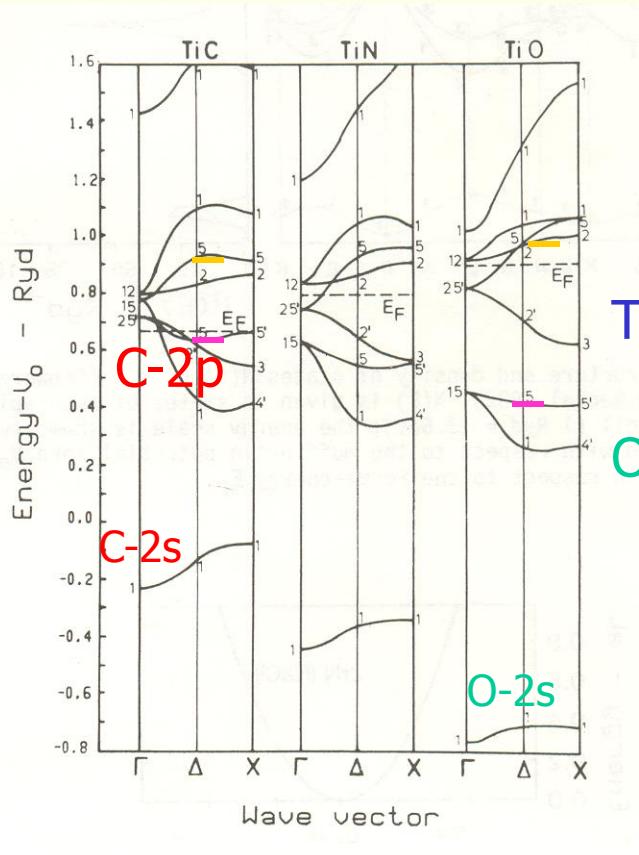
character bands



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

unit cell      interstitial      atom t       $\ell = s, p, d, \dots$

# TiC, bonding and antibonding states

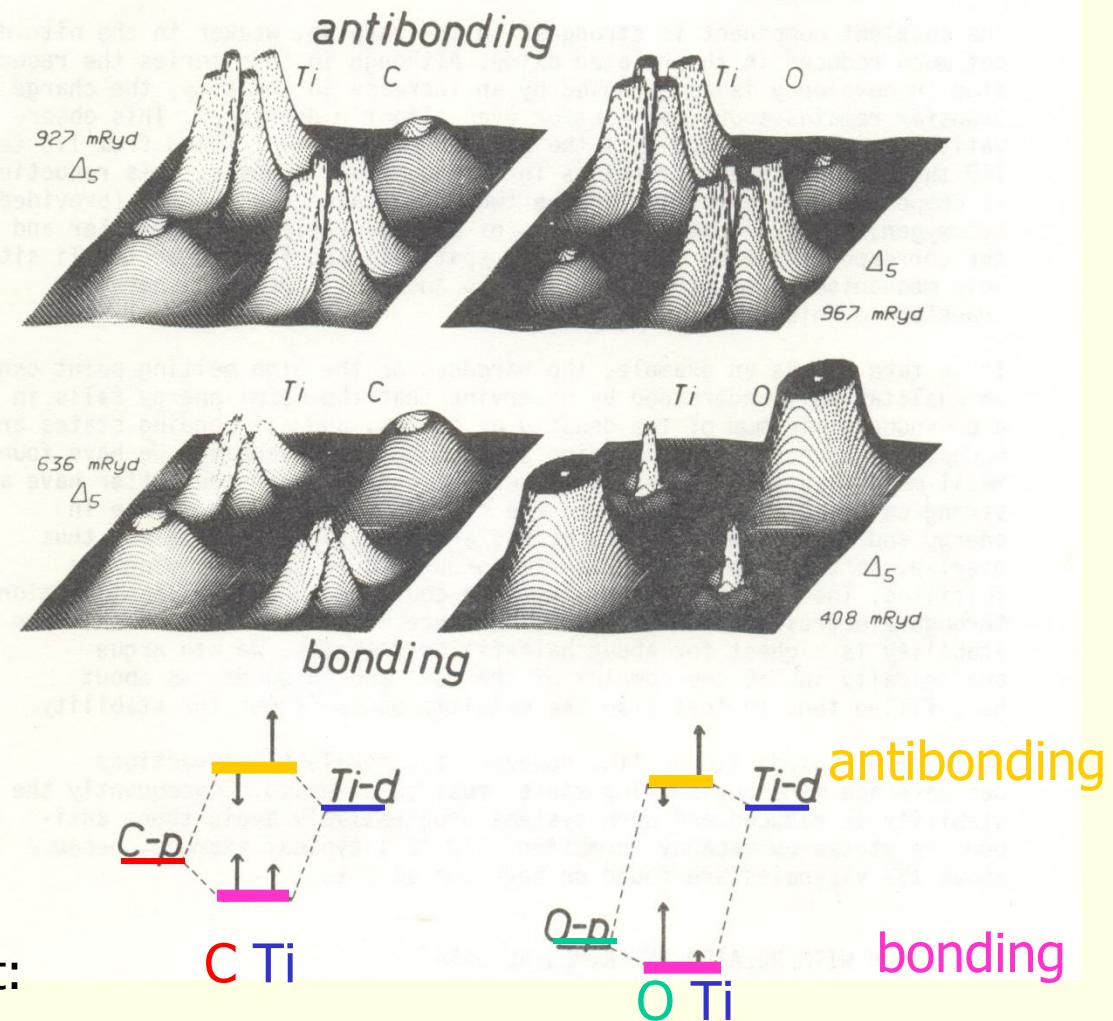


Ti-3d  
O-2p

O-2s

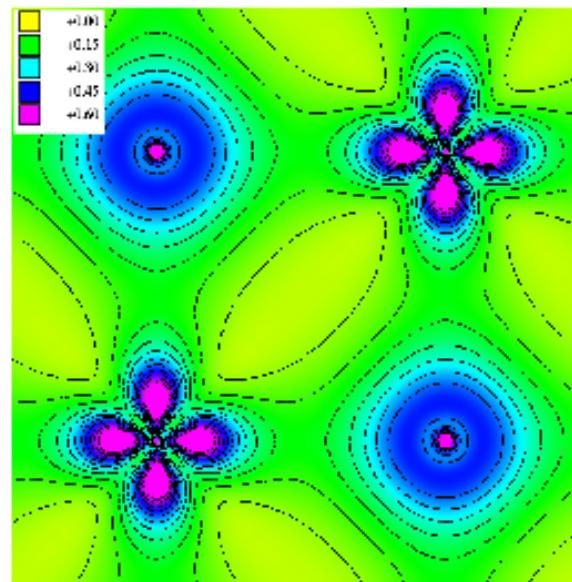
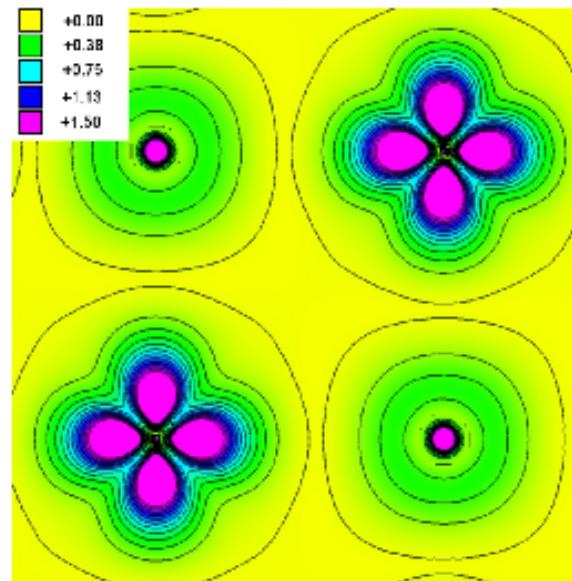
C-2s

weight:

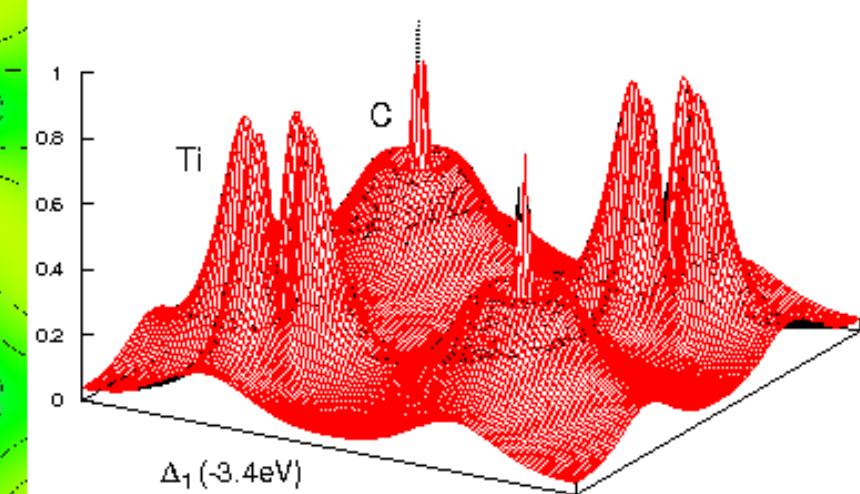
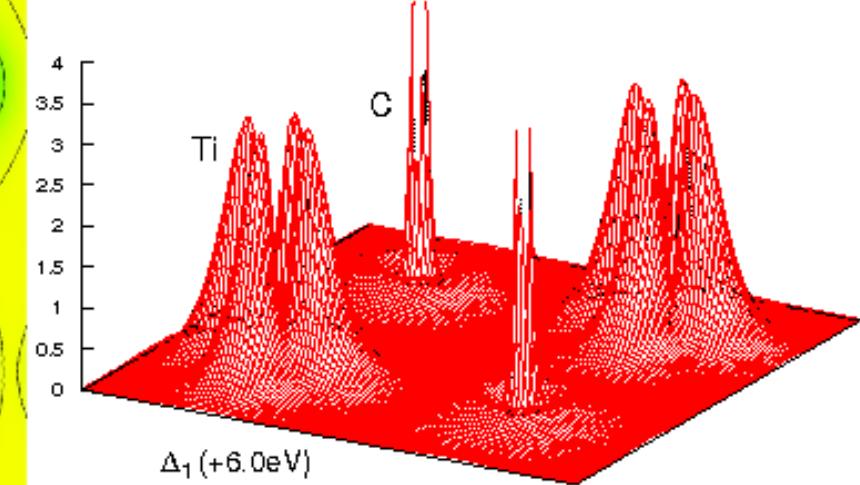


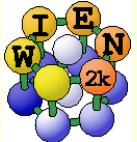
P.Blaha, K.Schwarz,  
Int.J.Quantum Chem. 23, 1535 (1983)

antibonding  
 $C_p\text{-}Ti_d \sigma$



bonding  
 $C_p\text{-}Ti_d \sigma$





# TiC, TiN, TiO

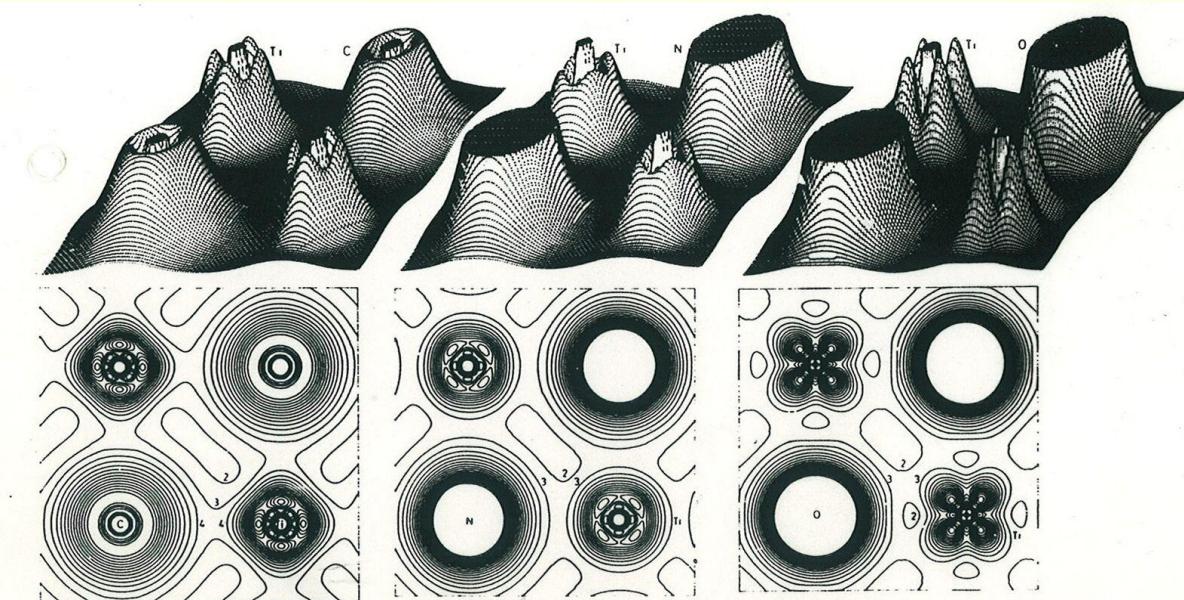
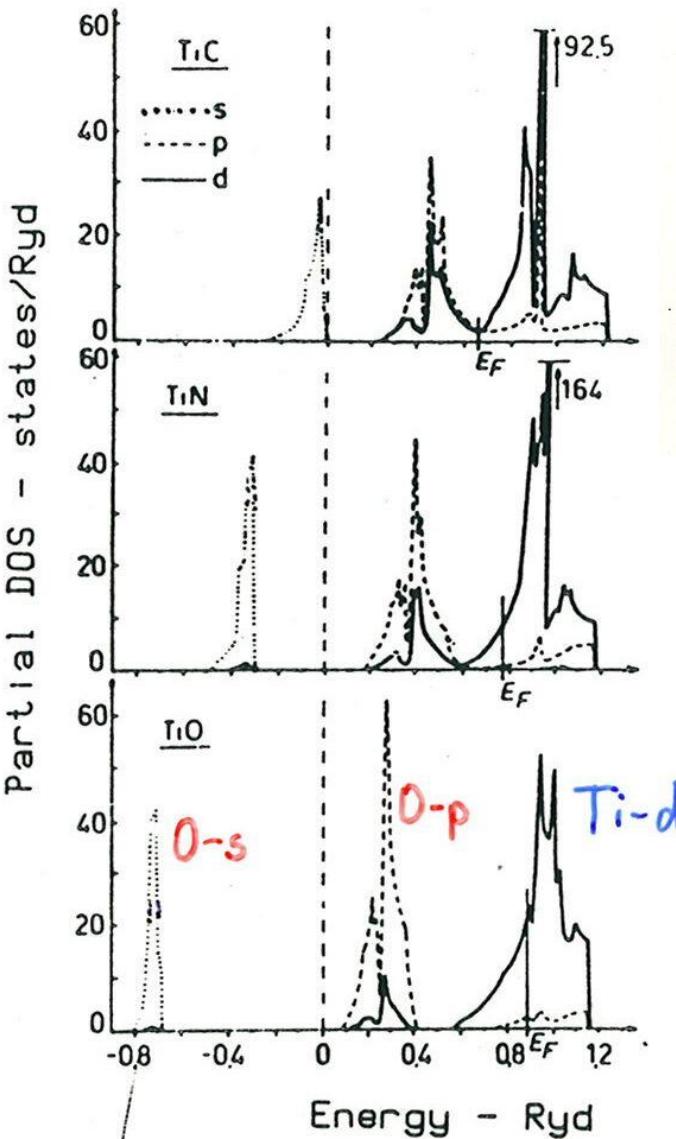


Figure 3. Valence charge densities in the (100) plane. Contour intervals  $0.1e\text{\AA}^{-3}$  (numbers are in these units), cutoff at  $1.7e\text{\AA}^{-3}$ .

**TiC**

**TiN**

**TiO**

Rigid band model: limitations

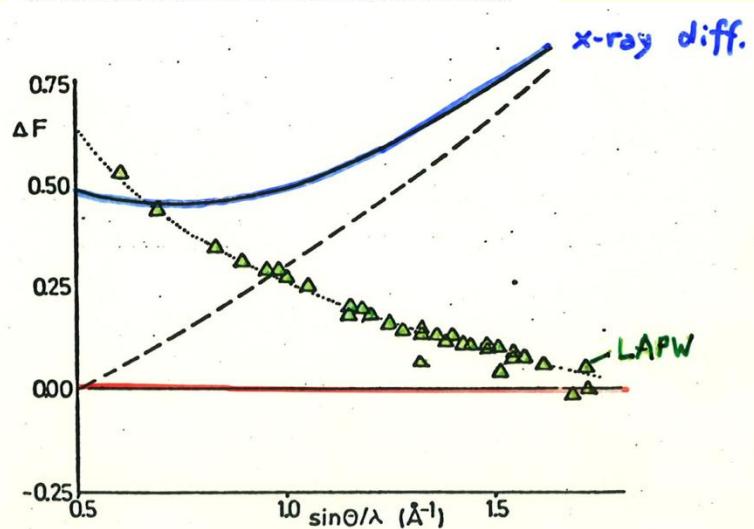
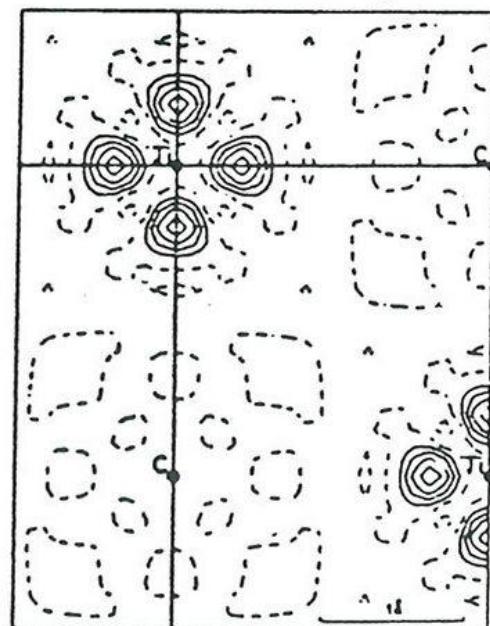
Electron density  $\rho$ : decomposition

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

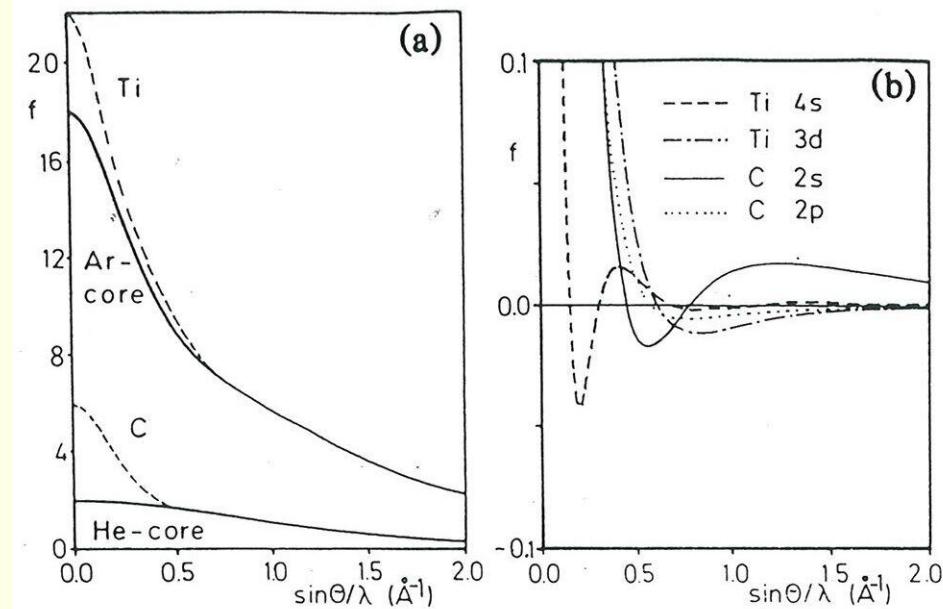
unit cell    interstitial    atom t     $\ell = s, p, d, \dots$

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

## Experimental difference electron density



## Atomic form factors for Ti and C



## Paired reflections

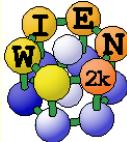
$$s = |\vec{S}| \approx \frac{\sin \vartheta}{\lambda}$$

$$\begin{array}{ll} \vec{S} & \\ h k l & h^2 + k^2 + l^2 \\ \hline 10 & 2 & 2 & 108 \\ 6 & 6 & 6 & 108 \end{array}$$

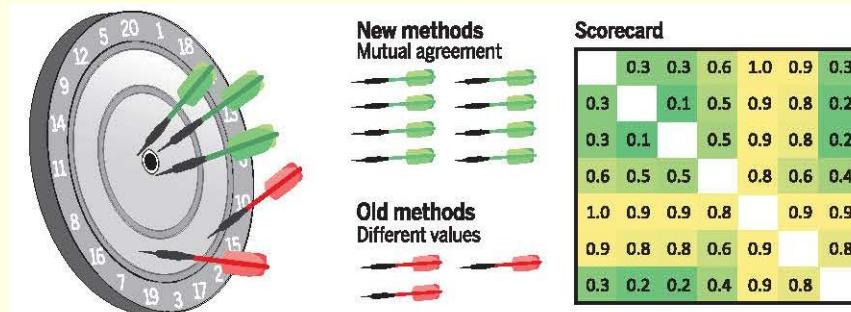
$$F(\vec{S}) = F(S) \quad \text{spher. symm. density}$$

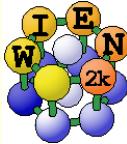
$$F(\vec{S}_1) + F(\vec{S}_2) \quad \left. \right\} \quad \text{non spherical}$$

with  $|\vec{S}_1| = |\vec{S}_2|$



Kurt Lejaeghere,<sup>1\*</sup> Gustav Bihlmayer,<sup>2</sup> Torbjörn Björkman,<sup>3,4</sup> Peter Blaha,<sup>5</sup>  
Stefan Blügel,<sup>2</sup> Volker Blum,<sup>6</sup> Damien Caliste,<sup>7,8</sup> Ivano E. Castelli,<sup>9</sup> Stewart J. Clark,<sup>10</sup>  
Andrea Dal Corso,<sup>11</sup> Stefano de Gironcoli,<sup>11</sup> Thierry Deutsch,<sup>7,8</sup> John Kay Dewhurst,<sup>12</sup>  
Igor Di Marco,<sup>13</sup> Claudia Draxl,<sup>14,15</sup> Marcin Dulak,<sup>16</sup> Olle Eriksson,<sup>13</sup>  
José A. Flores-Livas,<sup>12</sup> Kevin F. Garrity,<sup>17</sup> Luigi Genovese,<sup>7,8</sup> Paolo Giannozzi,<sup>18</sup>  
Matteo Giantomassi,<sup>19</sup> Stefan Goedecker,<sup>20</sup> Xavier Gonze,<sup>19</sup> Oscar Gränäs,<sup>13,21</sup>  
E. K. U. Gross,<sup>12</sup> Andris Gulans,<sup>14,15</sup> François Gygi,<sup>22</sup> D. R. Hamann,<sup>23,24</sup>  
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François Jollet,<sup>28</sup> Daniel Jones,<sup>29</sup> Georg Kresse,<sup>30</sup> Klaus Koepernik,<sup>31,32</sup>  
Emine Küçükbenli,<sup>9,11</sup> Yaroslav O. Kvashnin,<sup>13</sup> Inka L. M. Locht,<sup>13,33</sup> Sven Lubeck,<sup>14</sup>  
Martijn Marsman,<sup>30</sup> Nicola Marzari,<sup>9</sup> Ulrike Nitzsche,<sup>31</sup> Lars Nordström,<sup>13</sup>  
Taisuke Ozaki,<sup>34</sup> Lorenzo Paulatto,<sup>35</sup> Chris J. Pickard,<sup>36</sup> Ward Poelmans,<sup>1,37</sup>  
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Santanu Saha,<sup>20</sup> Matthias Scheffler,<sup>15,40</sup> Martin Schlipf,<sup>22</sup> Karlheinz Schwarz,<sup>5</sup>  
Sangeeta Sharma,<sup>12</sup> Francesca Tavazza,<sup>17</sup> Patrik Thunström,<sup>41</sup> Alexandre Tkatchenko,<sup>15,42</sup>  
Marc Torrent,<sup>28</sup> David Vanderbilt,<sup>23</sup> Michiel J. van Setten,<sup>19</sup>  
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Guo-Xu Zhang,<sup>44</sup> Stefaan Cottenier<sup>1,45\*</sup>

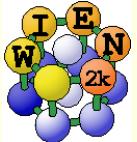




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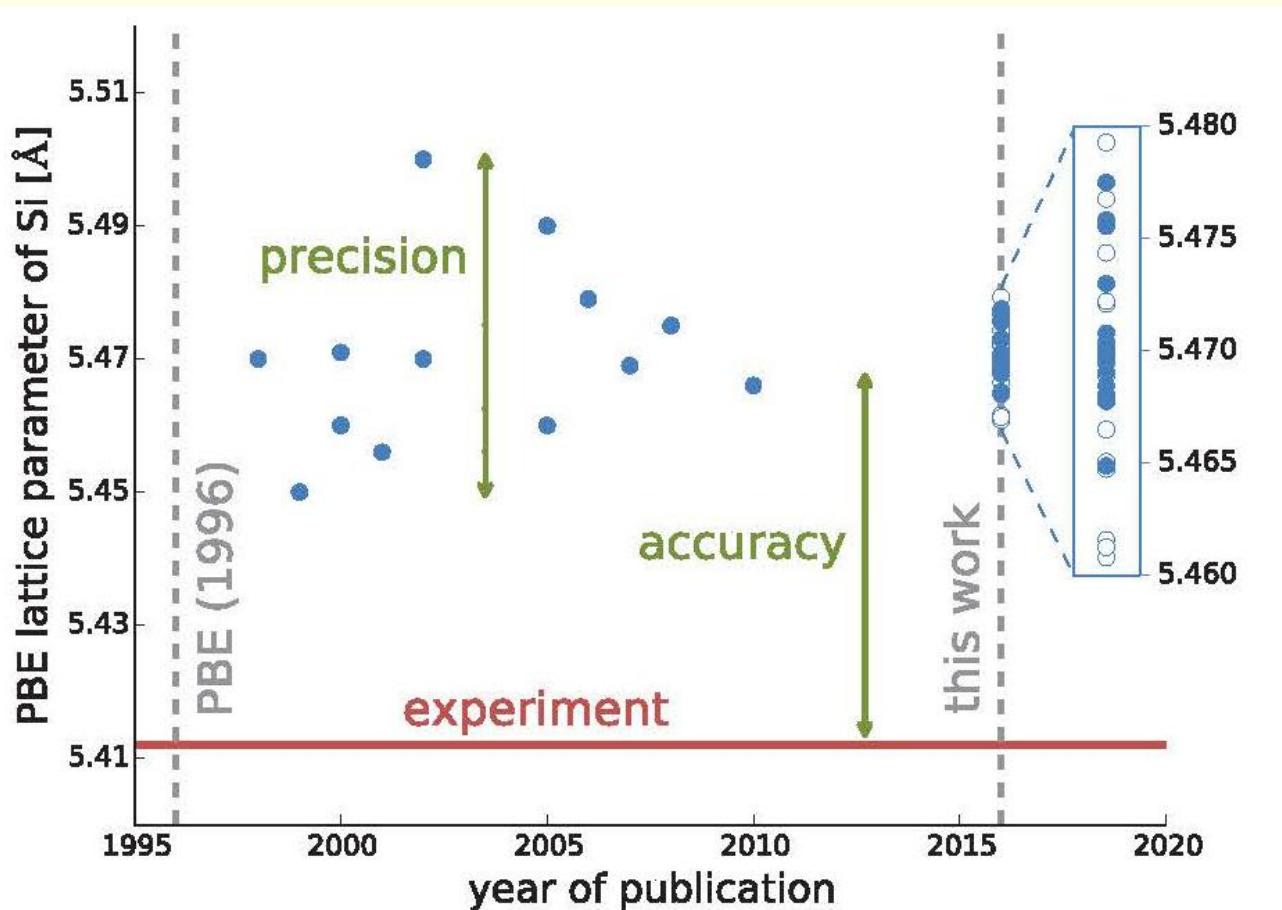


## The most accurate code

**AE:** all electron

		average $\langle \Delta \rangle$	Elk	exciting	FHI-aims/tier2	FLEUR	FPLO/T+F+e	RSPT	WIEN2k/acc	AE
AE	Elk	0.6	0.3	0.3	0.6	1.0	0.9	0.3		
	exciting	0.5	0.3		0.1	0.5	0.9	0.8	0.2	
	FHI-aims/tier2	0.5	0.3	0.1		0.5	0.9	0.8	0.2	
	FLEUR	0.6	0.6	0.5	0.5		0.8	0.6	0.4	
	FPLO/T+F+e	0.9	1.0	0.9	0.9	0.8		0.9	0.9	
	RSPT	0.8	0.9	0.8	0.8	0.6	0.9		0.8	
PAW	WIEN2k/acc	0.5	0.3	0.2	0.2	0.4	0.9	0.8		
	GBRV12/ABINIT	0.9	0.9	0.8	0.8	0.9	1.3	1.1	0.8	
	GPAW09/ABINIT	1.4	1.3	1.3	1.3	1.3	1.7	1.5	1.3	
	GPAW09/GPAW	1.6	1.5	1.5	1.5	1.5	1.8	1.7	1.5	
	JTH02/ABINIT	0.6	0.6	0.6	0.6	0.6	0.9	0.7	0.5	
	PS11b100/QE	0.9	0.9	0.8	0.8	0.8	1.3	1.1	0.8	
USPP	VASP/GW2015/VASP	0.6	0.4	0.4	0.4	0.6	1.0	0.8	0.3	
	GBRV14/CASTEP	1.1	1.1	1.1	1.0	1.0	1.4	1.3	1.0	
	GBRV14/QE	1.1	1.0	1.0	0.9	1.0	1.4	1.3	1.0	
	OTFG9/CASTEP	0.7	0.4	0.5	0.5	0.7	1.0	1.0	0.5	
	SSSP/QE	0.5	0.4	0.3	0.3	0.5	0.9	0.8	0.3	
	Vdb2/DACAPo	6.3	6.3	6.3	6.3	6.3	6.4	6.5	6.2	
NCP	FHI98pp/ABINIT	13.3	13.5	13.4	13.4	13.2	13.0	13.2	13.4	
	HGH/ABINIT	2.2	2.2	2.2	2.2	2.0	2.3	2.2	2.1	
	HGH-NLCC/BigDFT	1.1	1.1	1.1	1.1	1.0	1.2	1.1	1.0	
	MK2013/OpenMK	2.0	2.1	2.1	2.1	1.9	1.8	1.8	2.0	
	ONCVPPSP (PD0.1)/ABINIT	0.7	0.7	0.7	0.7	0.6	1.0	0.8	0.6	
	ONCVPPSP (SG15)1/QE	1.4	1.4	1.3	1.3	1.3	1.6	1.5	1.3	
NCP	ONCVPPSP (SG15)2/CASTEP	1.4	1.4	1.4	1.4	1.3	1.6	1.5	1.4	

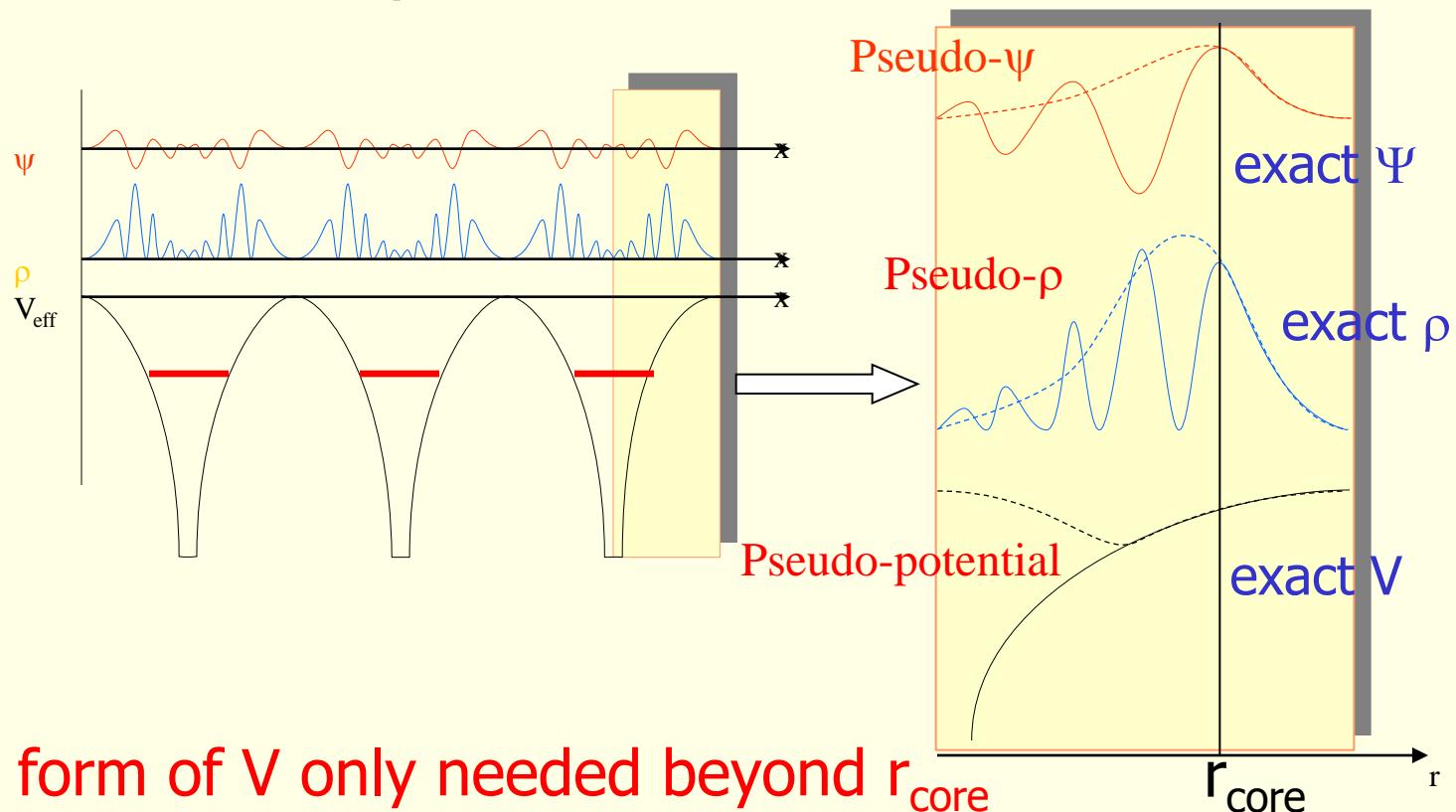
**Fig. 4.  $\Delta$  values for comparisons between the most important DFT methods considered (in millielectron volts per atom).** Shown are comparisons of all-electron (AE), PAW, ultrasoft (USPP), and norm-conserving pseudopotential (NCP) results with all-electron results (methods are listed in alphabetical order in each category). The labels for each method stand for code, code/specification (AE), or potential set/code (PAW, USPP, and NCP) and are explained in full in tables S3 to S42. The color coding illustrates the range from small (green) to large (red)  $\Delta$  values. The mixed potential set SSSP was added to the ultrasoft category, in agreement with its prevalent potential type. Both the code settings and the DFT-predicted EOS parameters behind these numbers are included in tables S3 to S42, and fig. S1 provides a full  $\Delta$  matrix for all methods mentioned in this article.



**Fig. 1. Historical evolution of the predicted equilibrium lattice parameter for silicon.** All data points represent calculations within the DFT-PBE framework. Values from literature (data points before 2016) (15, 16, 18, 56–62, 63–65) are compared with (i) predictions from the different codes used in this study (2016 data points, magnified in the inset; open circles indicate data produced by older methods or calculations with lower numerical settings) and (ii) the experimental value, extrapolated to 0 K and corrected for zero-point effects (red line) (26). The concepts of precision and accuracy are illustrated graphically.

# “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) →



# 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  
relativistic effects

vacuum  
supercell  
 $\ell$  quantum n.

average  
vibrations

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



# Vienna, city of music and the Wien2k code

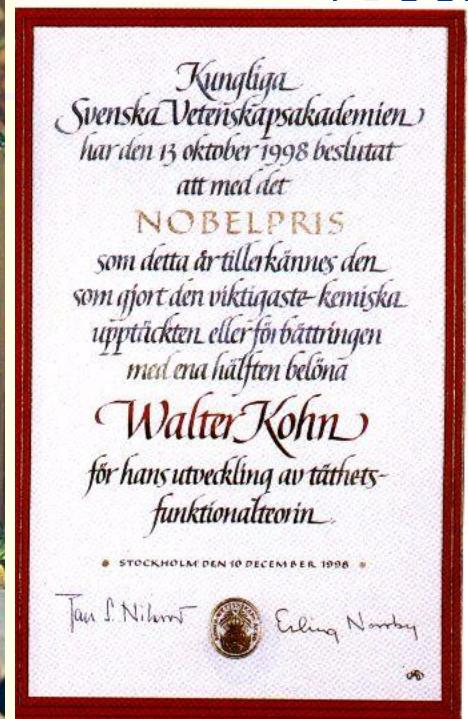




# Walter Kohn

- 1997 DFT Conference in Vienna

- *Walter Kohn Main speaker*



- 1998 Nobel Prize

for Chemistry

- 2001 invited lecturer

- My 60th birthday



International Conference on  
Applied Density Functional  
Theory

January 14-17, 2001  
Vienna/Austria

dedicated to Karlheinz Schwarz  
on occasion of his 60<sup>th</sup> birthday

Honorary Chairman: Walter Kohn

16. 1. 2001

Walter Kohn

Peter & Claude Skopky



Walter Kohn's 80

Ecole Normale Supérieur

- World of
  - Interacting
  - Electrons and
  - Nuclei
- due ■ 2
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