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

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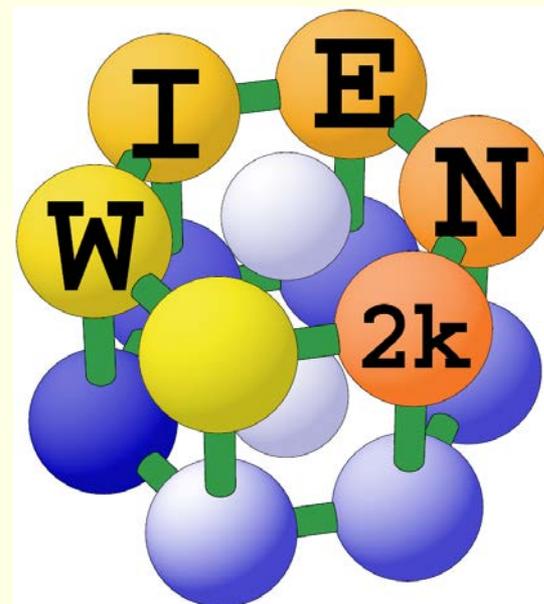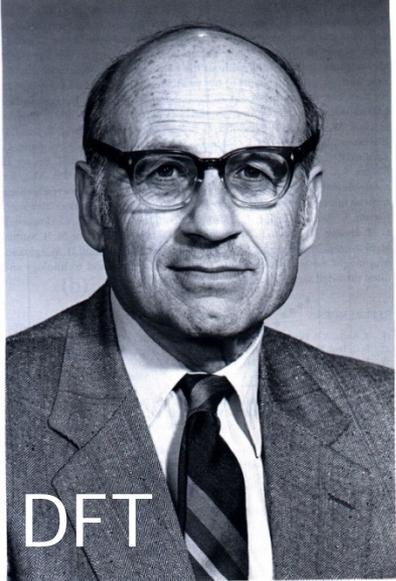
DFT
Walter Kohn
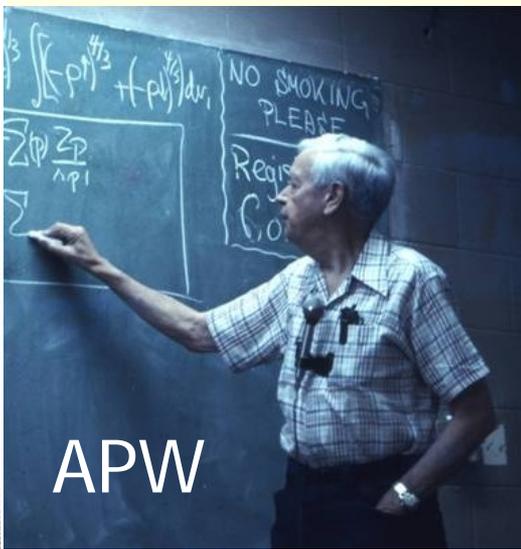
APW
J.C.Slater

LAPW
O.K.Andersen
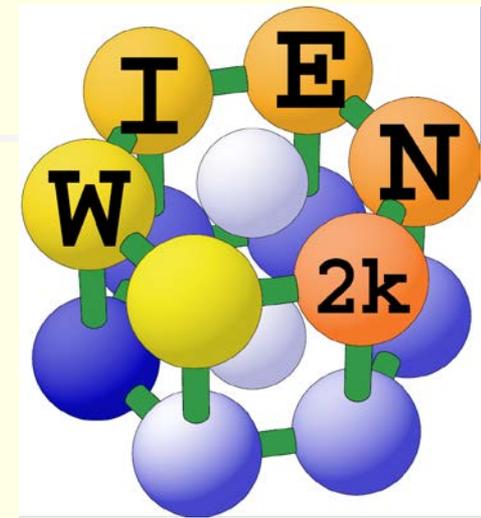
Electronic structure of
solids and surfaces
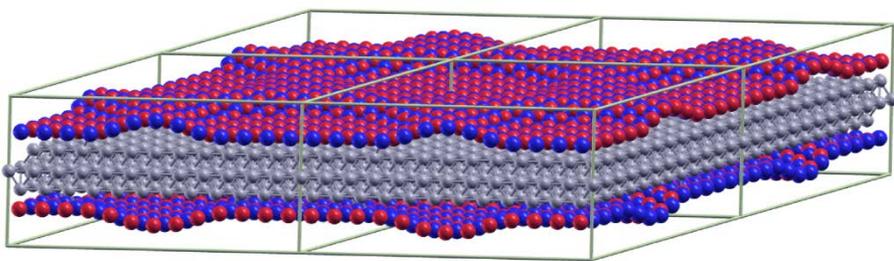
hexagonal boron nitride on Rh(111)
2x2 supercell (1108 atoms per cell)

Phys.Rev.Lett. 98, 106802 (2007)
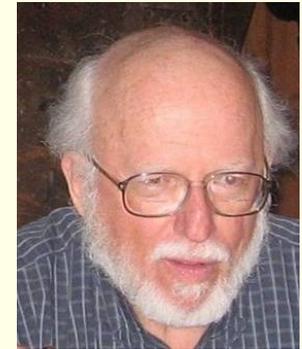
K.Schwarz, P.Blaha, S.B.Trickey,
Molecular physics, **108**, 3147 (2010)

Wien2k is used worldwide
by about 2900 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 37 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
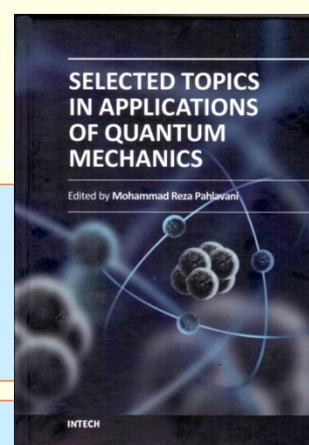
K.Schwarz, *Computation of Materials Properties at the Atomic Scale*
InTech, (2015) Chapter 10, 275-310,   open access book
ISBN 978-953-51-2126-8 (2015)   dx.doi.org/10.5772/59108

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 l

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*
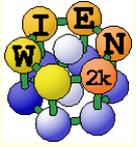
Four big challenges for theorists :

- *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

The atomic structure
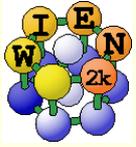
- **A crystal is represented by a unit cell**
  - *We assume periodic boundary condition (approximation)*
  - *The unit cell is repeated to infinity (makes calculations feasible)*
  - *A real crystal is finite (with surfaces, impurities, defects ...)*
  - *Nano materials differ from bulk*
  - *Symmetry helps (space group, Bloch theorem, ...)*
- **In theory**
  - *The atomic structure is an input and thus well defined.*
  - *Artificial structures can also be studied*
- **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)
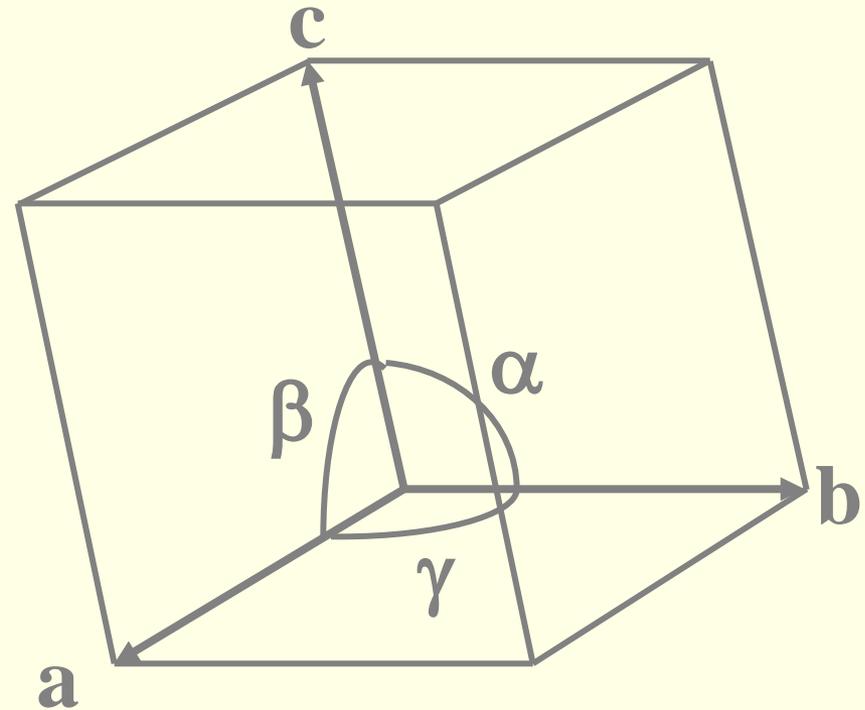
A unit cell containing one lattice point is called primitive cell.

Axis system

$$a = b = c$$
$$\alpha = \beta = \gamma = 90°$$

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

P (cP)   **I (bcc)**   **F (fcc)**
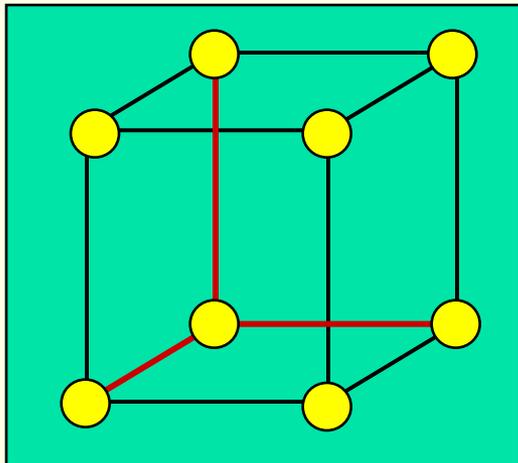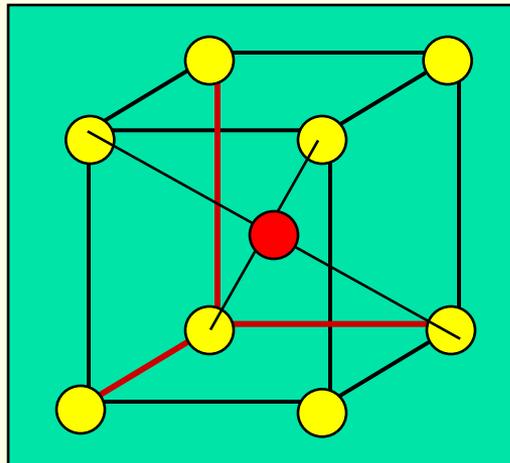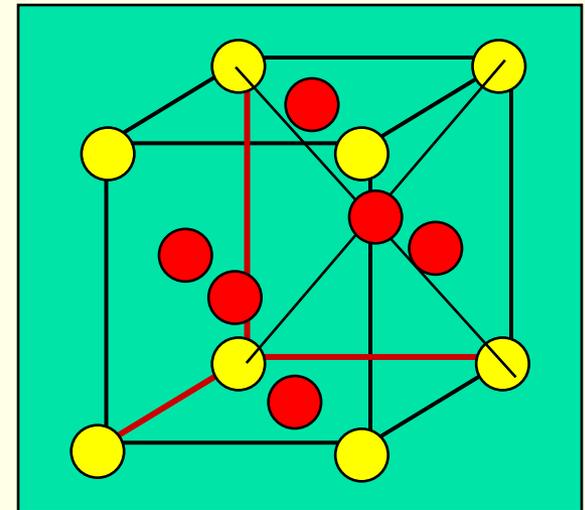
7 Crystal systems and 14 Bravais lattices

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

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

Finite particle with a length in nm

n=3   3x3x3 particle
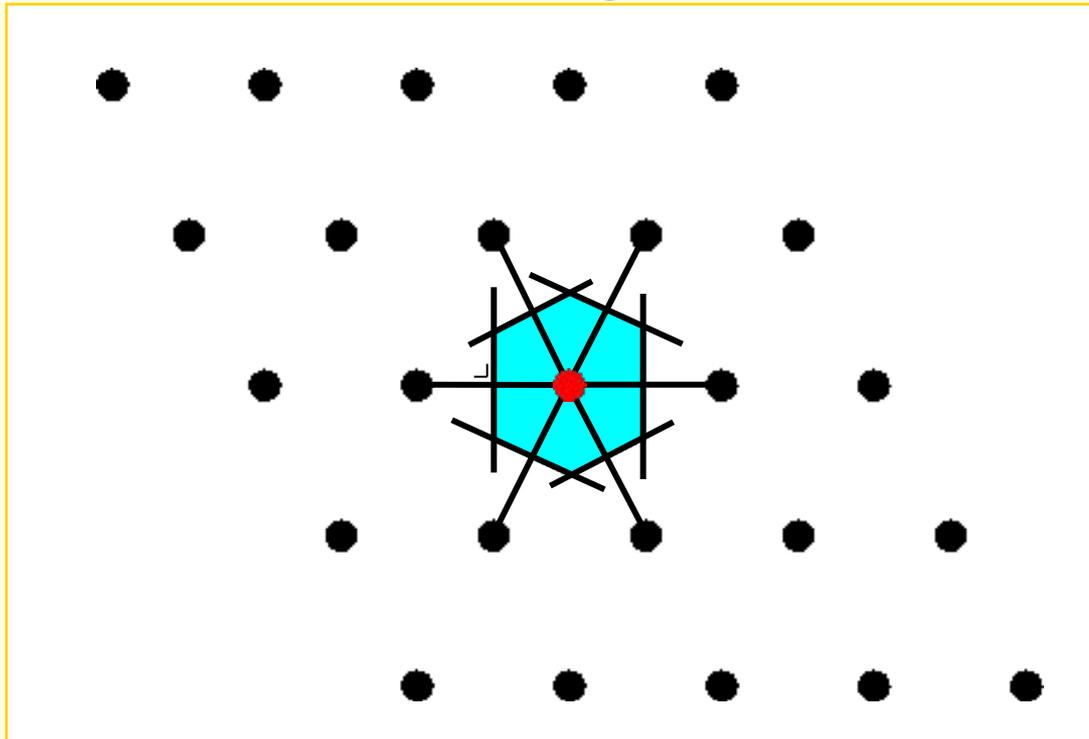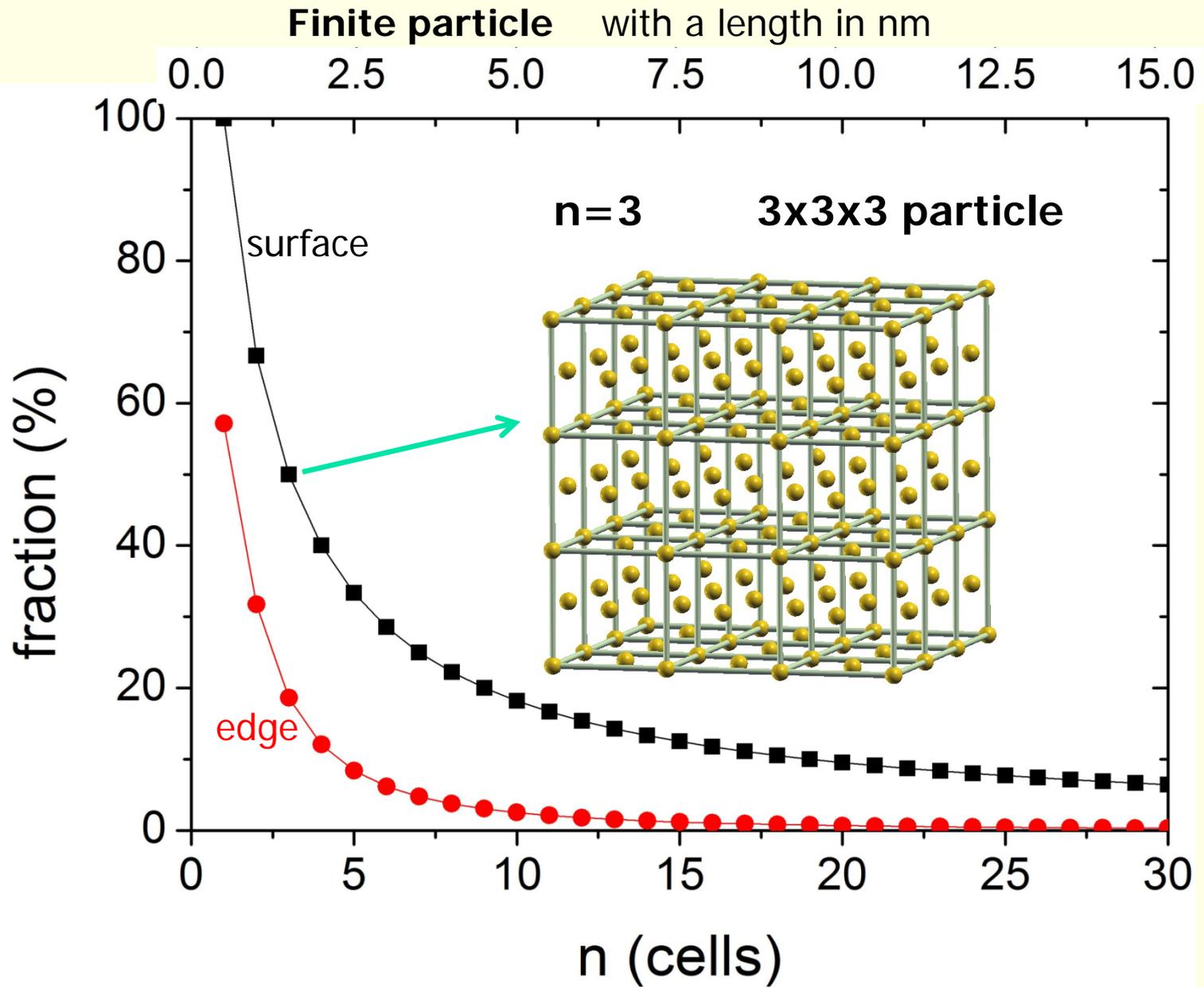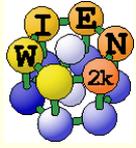
Fraction of atoms on surface (black) or edge (red) as function of particle size n
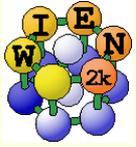
- **The electronic structure requires a QM treatment**
- **The main scheme is density functional theory (DFT)**
  - *It is a mean field approach and requires approximations*
  - *According to Hohenberg Kohn, it is sufficient to know the electron density of a system to determine its total energy. The 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 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:

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

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

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

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

a

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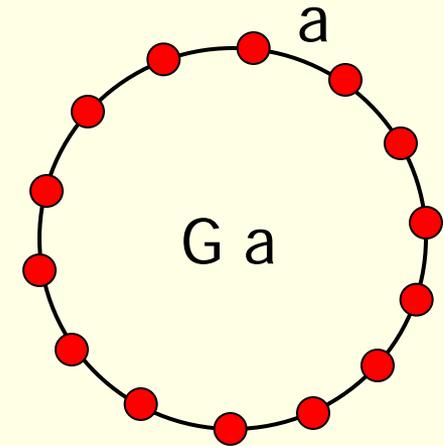
$$\mu = e^{2\pi i \frac{g}{G}} \qquad g = 0, \pm 1 \pm 2, \ldots.$$

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

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

- **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

Re $[\psi(x)]$

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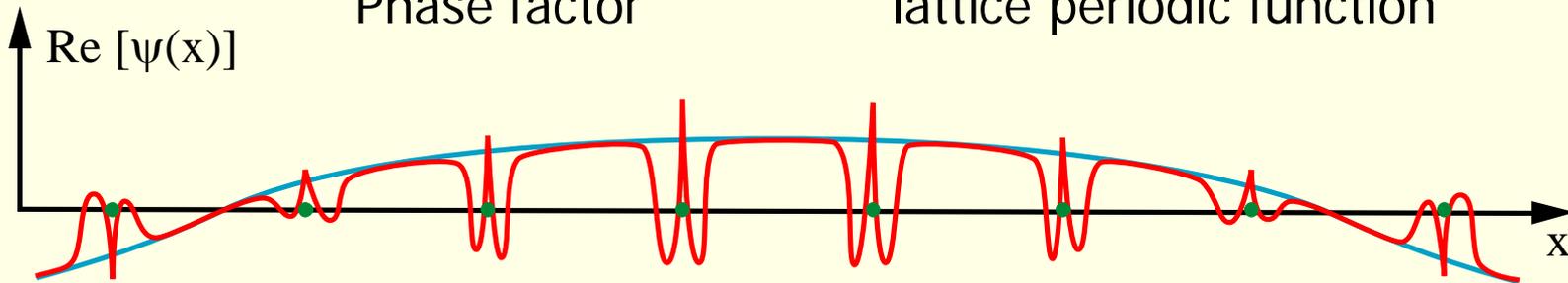
Replacing **k** by **k+K**, where **K** is a reciprocal lattice vector, fulfills again the Bloch-condition.

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

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

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

time averaged electron density

Ⓜ: Coulomb WW ⇒ correlations
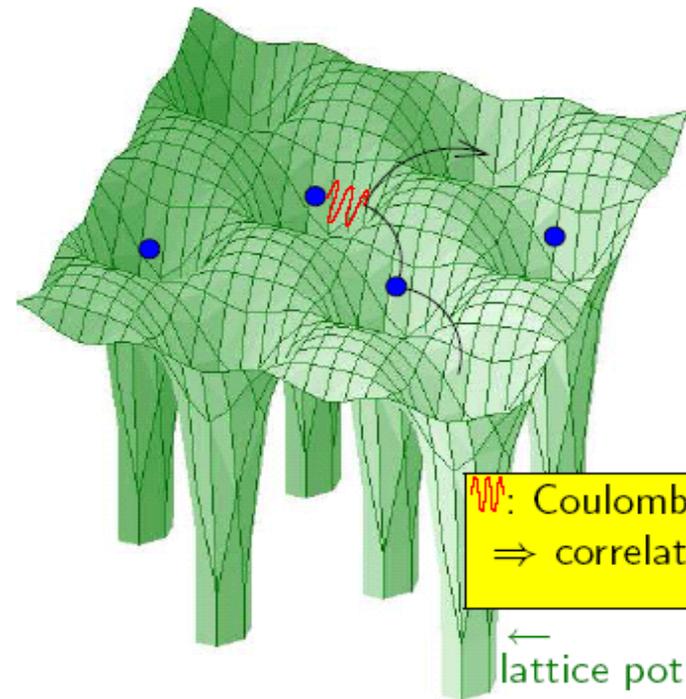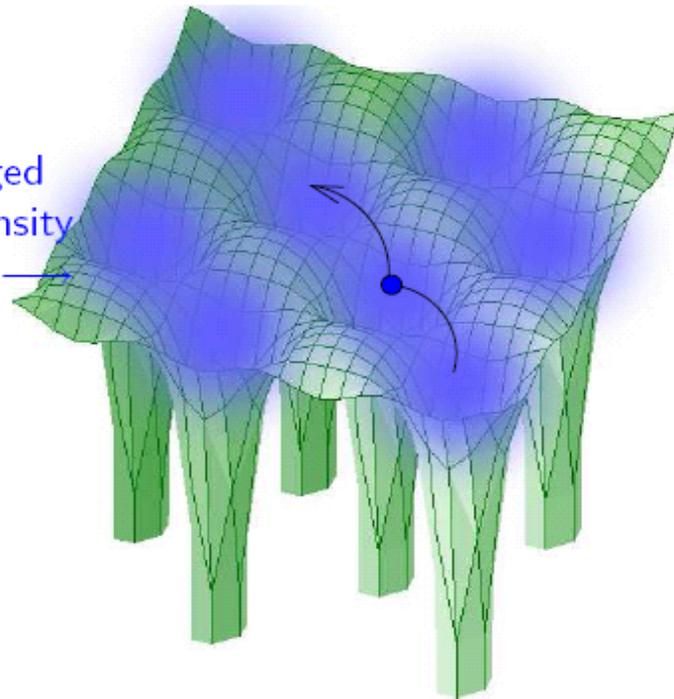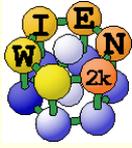
← lattice pot.

Ab-initio Hamiltonian

(non-relativistic/Born-Oppenheimer approximation)

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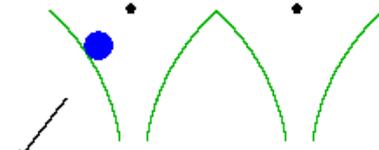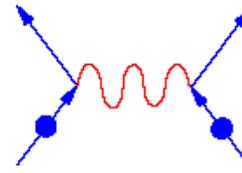
$$H = \sum_i \left[-\frac{\hbar^2 \Delta_i}{2m_e} + \sum_l \frac{-e^2}{4\pi\epsilon_0} \frac{Z_l}{|\mathbf{r}_i - \mathbf{R}_l|} \right] + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

LDA bandstructure corresponds to

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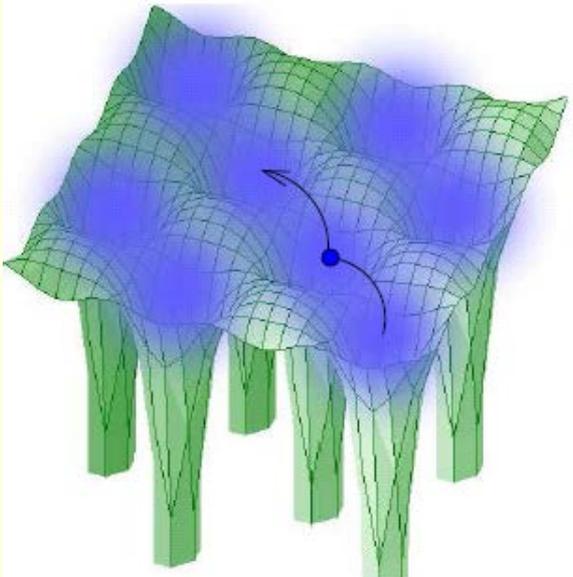
Coulomb potential:
- nuclei
- all electrons
- including
  self-interaction

Quantum mechanics:
- exchange
- correlation
- (partly) cancel
  self-interaction

Jacob's ladder: The grand challenge:
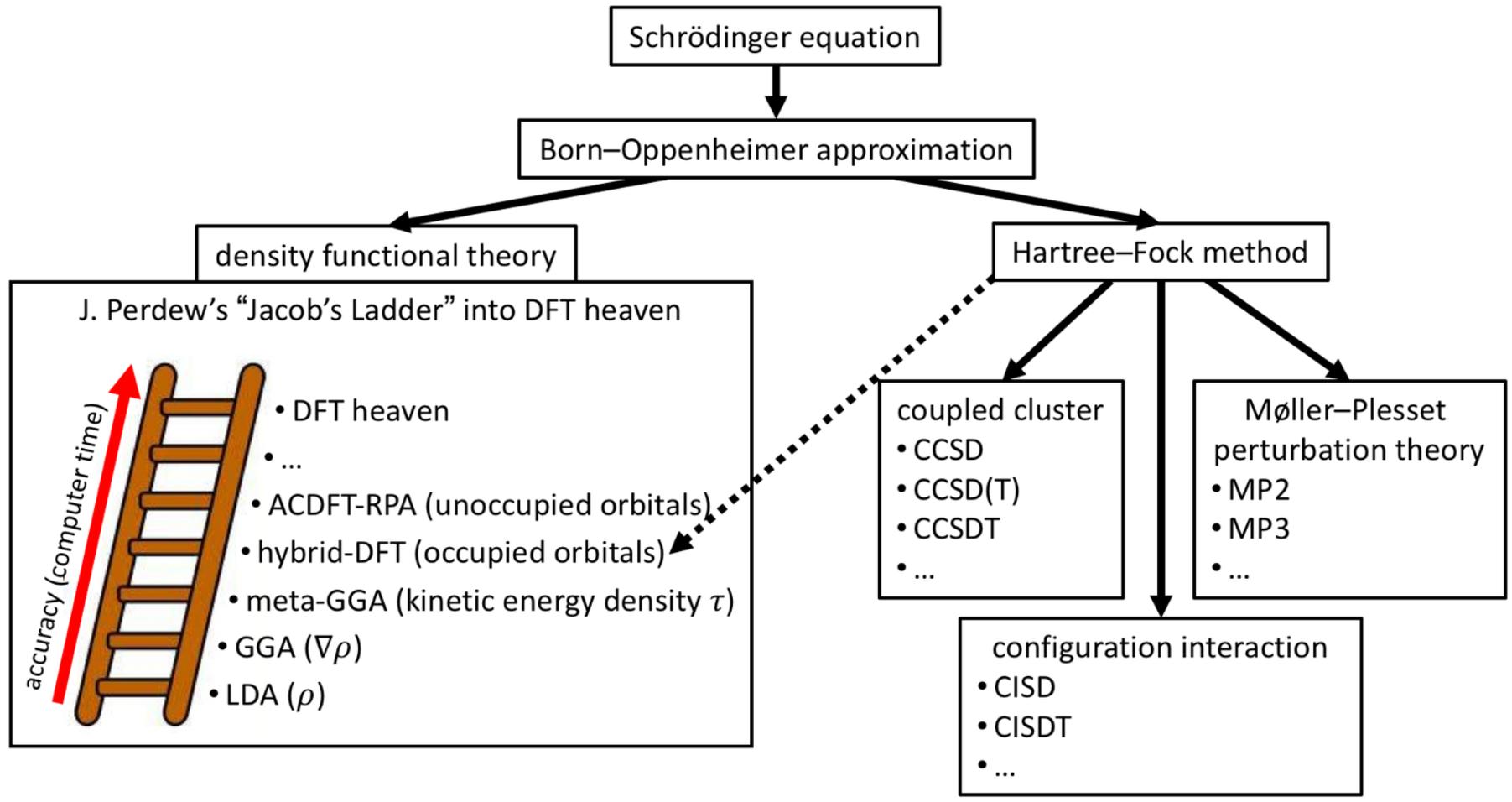
- **Find a functional which leads to "DFT heaven":** predictive power with chemical accuracy
- **J. Perdew's „Jacob's ladder" into DFT heaven:**

accuracy (computer time)
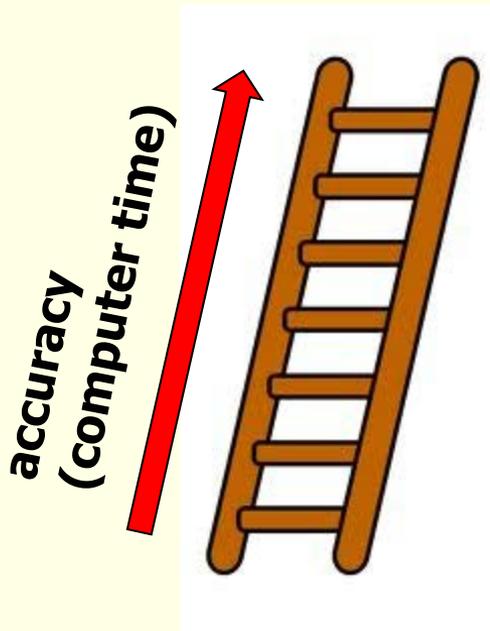
- DFT heaven

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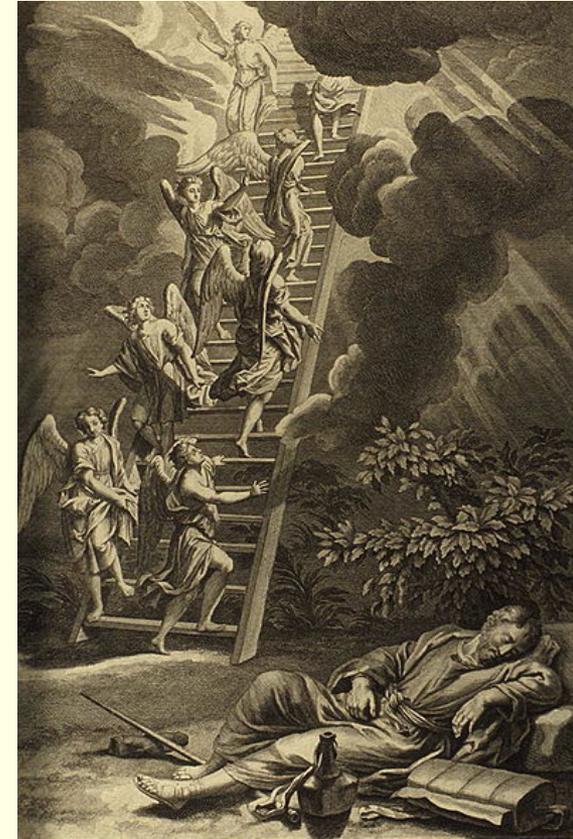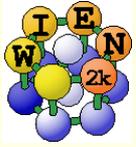
Hohenberg-Kohn theorem: (exact)

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.

- **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

Ecole Normale Supérieur

Kohn-Sham equations

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

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

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

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

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

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

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

LDA — treats both,

exchange and correlation effects,

GGA — but approximately

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

Exchange and correlation

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

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

r_0

- We divide the density of the N-1 electron system into the total density $n(r)$ and an exchange-correlation hole:
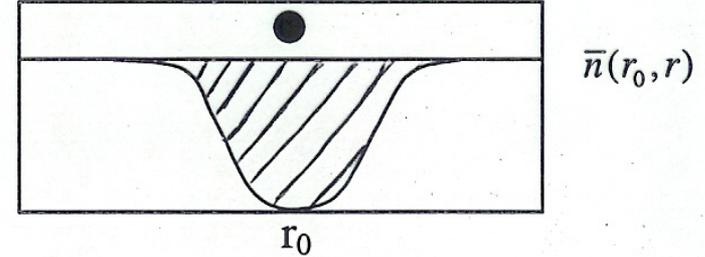
Properties of the exchange-correlation hole:
- Locality
- Pauli principle
- the hole contains ONE electron
- The hole must be negative

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

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

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

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

- 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:

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

Walter Kohn
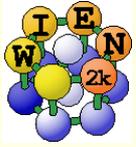
With 80 years

- 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, Washigton (Seattle), Paris, Imperial College (London), ETH Zürich, Unv. 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
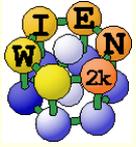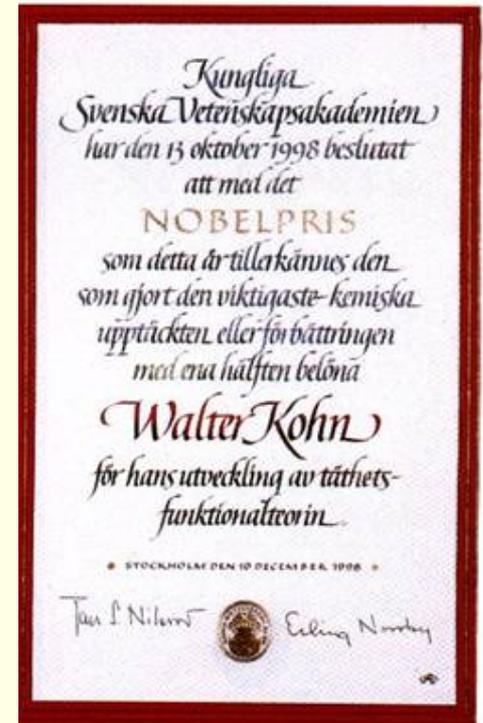
"Self-consistent Equations including Exchange and Correlation Effects"
W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965)

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

bcc Fe   fcc Fe

ΔE (mRy) vs Volume (a.u.³)

GGA   LSDA   exp.   GGA   LSDA
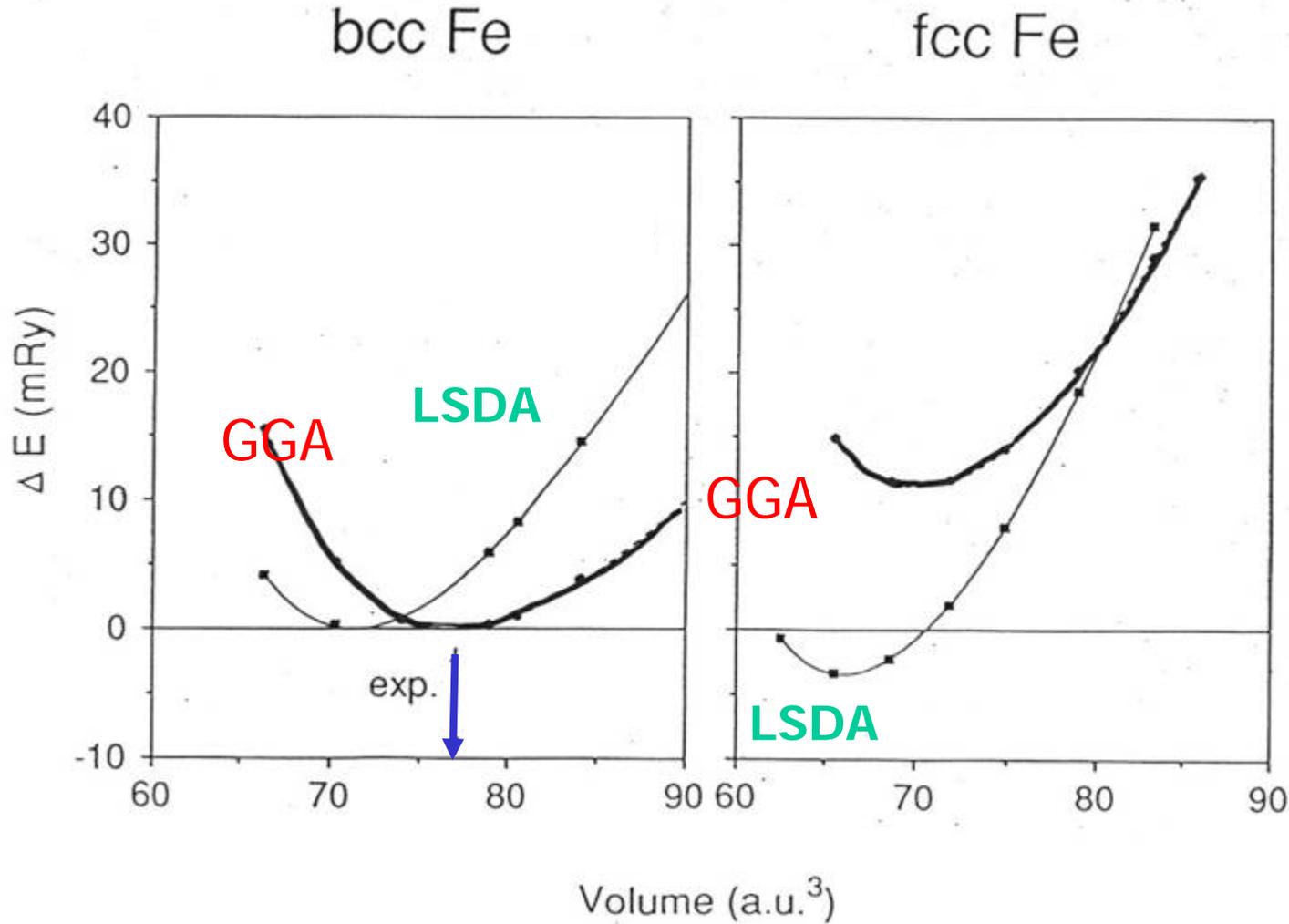
LSDA
- *NM*
- *fcc*
- *in contrast to experiment*

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

Experiment
- *FM*
- *bcc*

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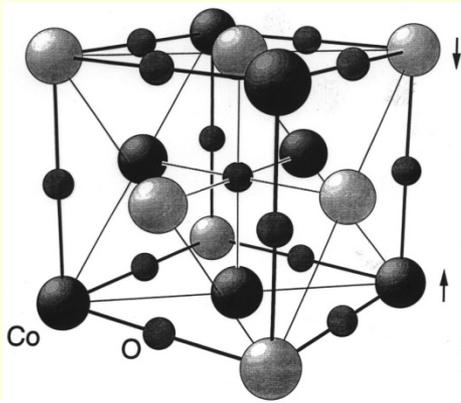
- **CoO**
  - *in NaCl structure*
  - *antiferromagnetic: AF II*
  - *insulator*
  - *t_{2g} splits into a_{1g} and e_g'*
  - *GGA almost spilts the bands*

GGA   LSDA

CoO why is GGA better than LSDA
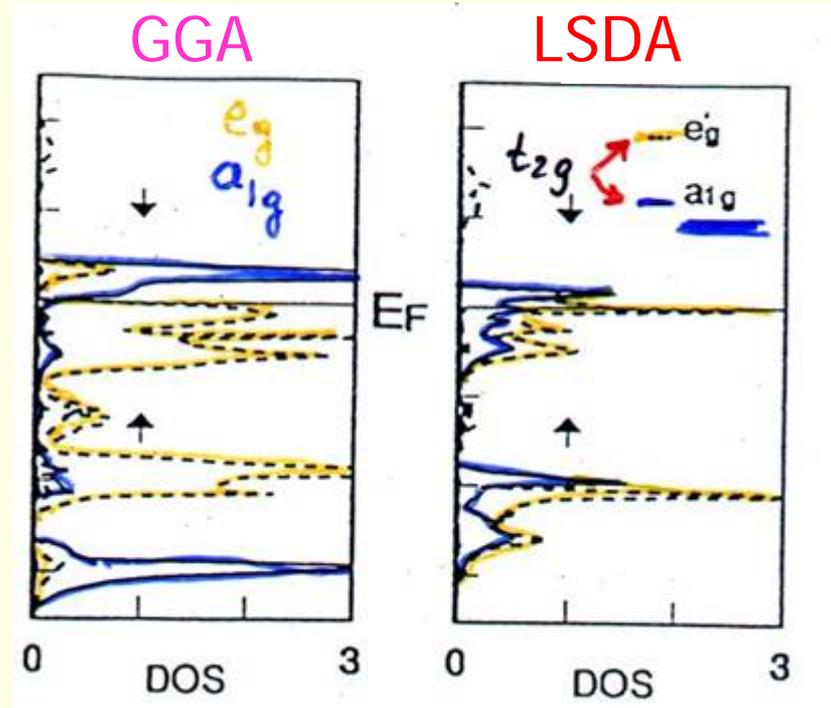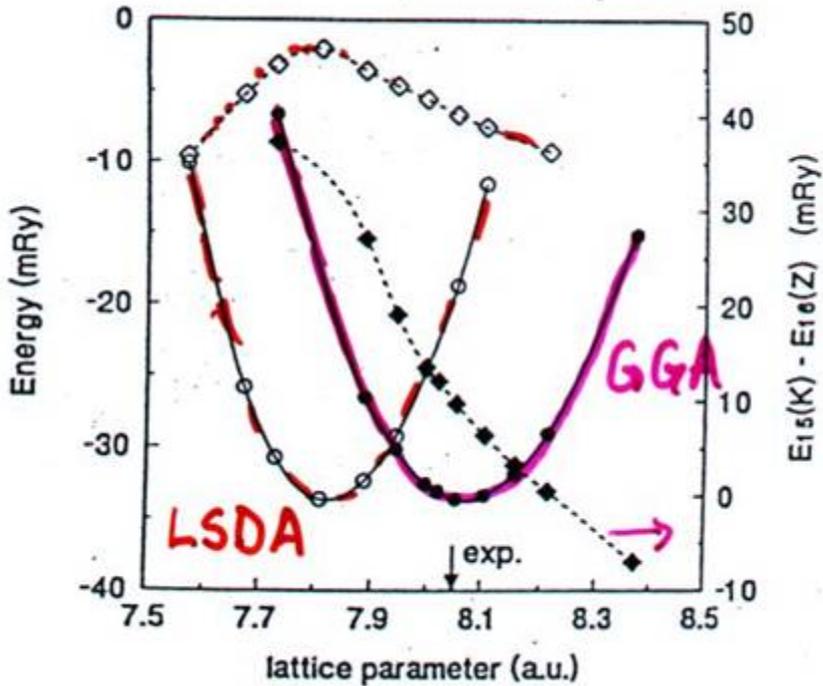
$$\Delta V_{xc}^{\uparrow} = V_{xc}^{\uparrow GGA} - V_{xc}^{\uparrow LSDA}$$
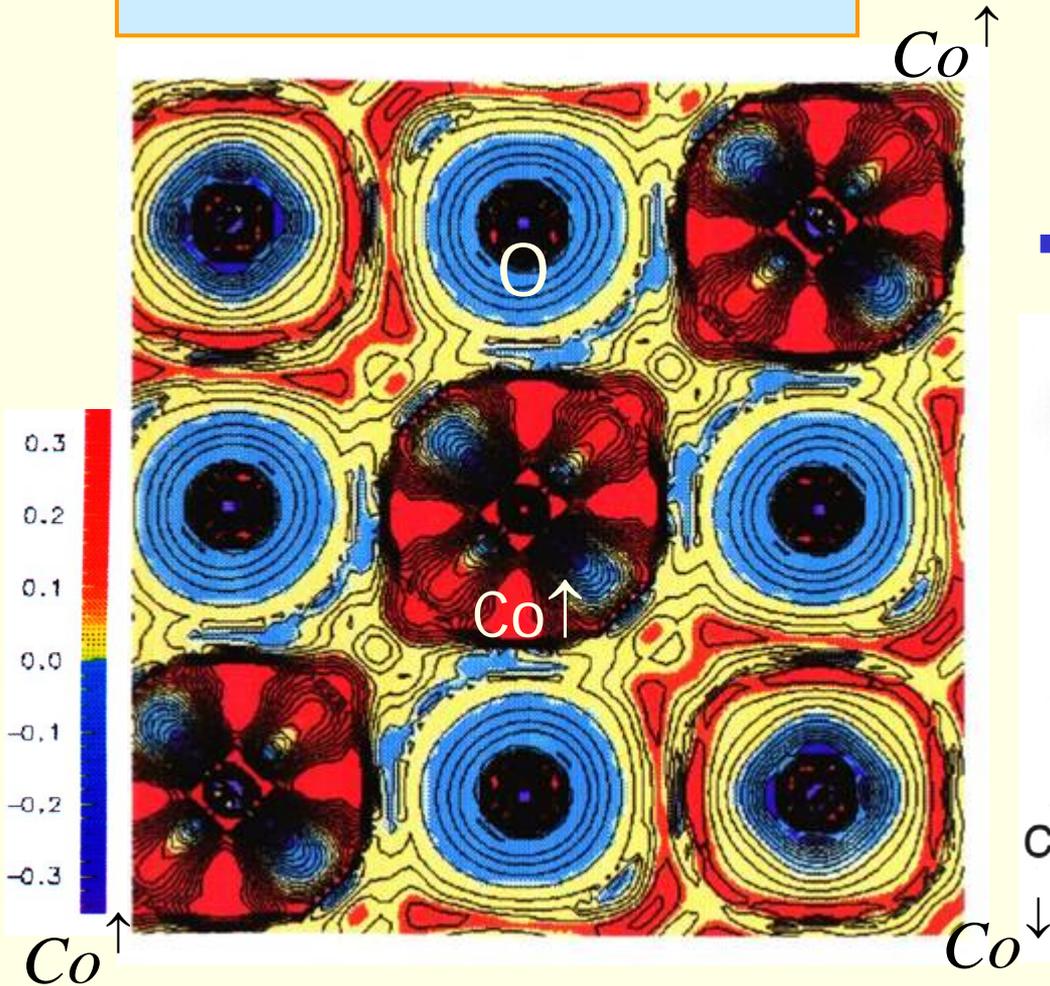
- Central Co atom distinguishes

  - between $Co^{\uparrow}$

  - and $Co^{\downarrow}$

- Angular correlation

$Co^{\uparrow}$

O

$Co^{\uparrow}$

$Co^{\uparrow}$

$Co^{\downarrow}$

0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3

Co   O
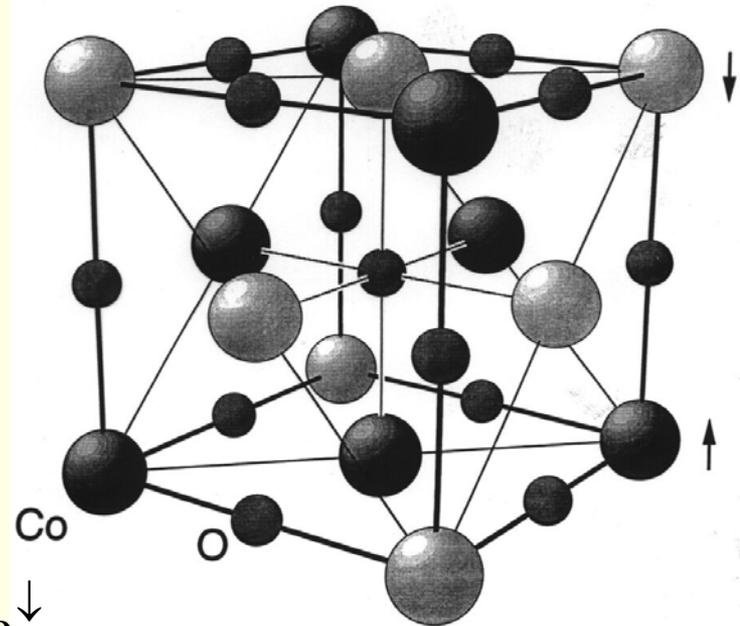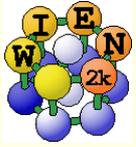
FeF$_2$: GGA splits
t$_{2g}$ into a$_{1g}$ and e$_g'$
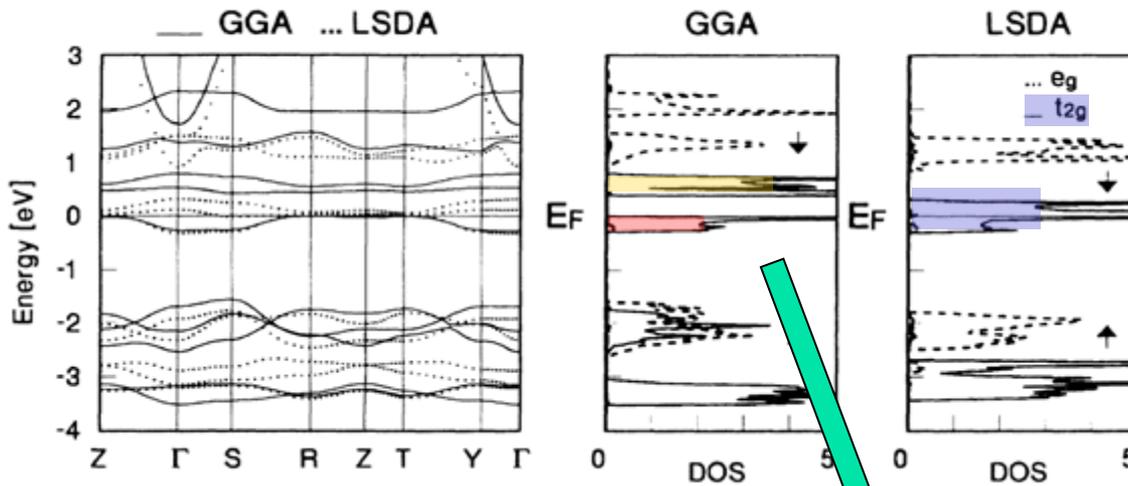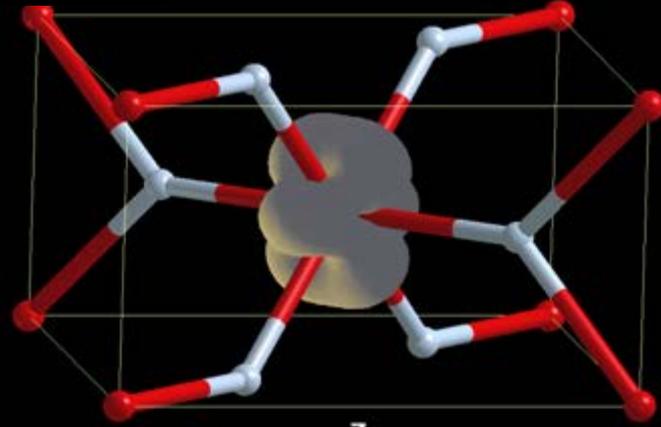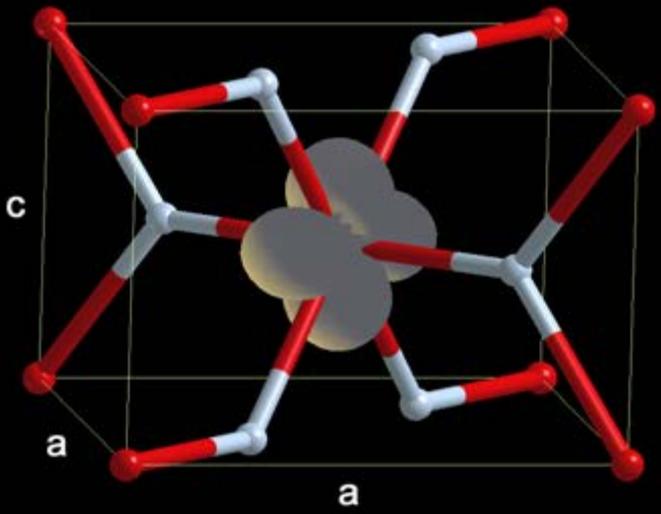
Fe-EFG in FeF$_2$:

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
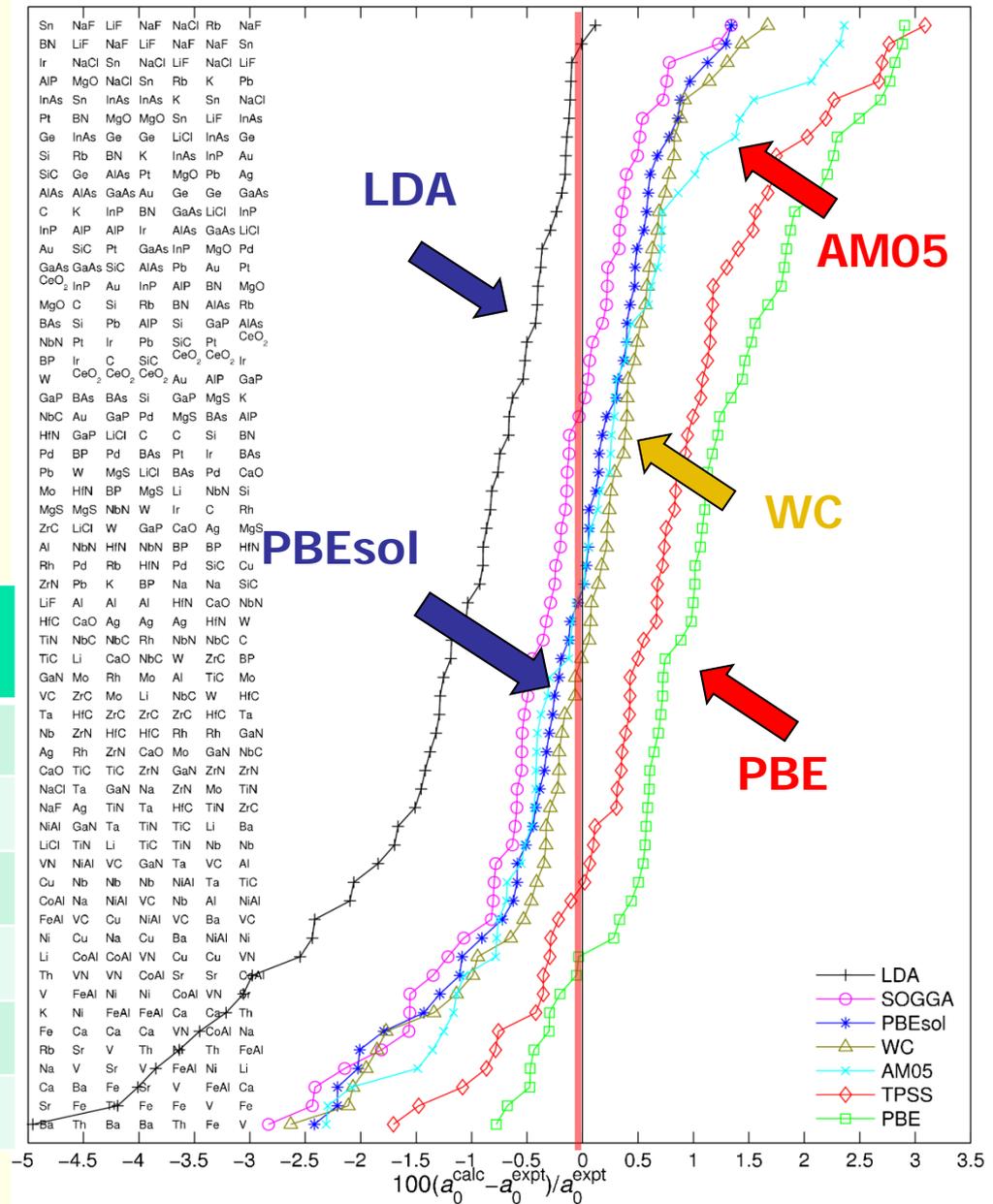
- **better GGAs and meta-GGAs ($\rho, \nabla\rho, \tau$):**
  - *usually improvement, but often too small.*
- **LDA+U: for correlated 3d/4f electrons,** treat strong Coulomb repulsion via Hubbard U parameter (cheap, "empirical U" ?)
- **Exact exchange:** imbalance between exact X and approximate C
  - *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: $E_{xc}^{LDA} = \int f(\rho(\mathbf{r}))d^3r$

- GGA: $E_{xc}^{GGA} = \int f(\rho(\mathbf{r}), |\nabla\rho(\mathbf{r})|)d^3r$

- MGGA: $E_{xc}^{MGGA} = \int f(\rho(\mathbf{r}), |\nabla\rho(\mathbf{r})|, \nabla^2\rho(\mathbf{r}), t(\mathbf{r}))d^3r$

- LDA+U: $E_{xc}^{LDA+U} = E_{xc}^{LDA} + E_{ee} - E_{dc}$

- GGA+U: $E_{xc}^{GGA+U} = E_{xc}^{GGA} + E_{ee} - E_{dc}$

- hybrid: $E_{xc}^{hybrid} = E_{xc}^{DFT} + \alpha\left(E_x^{HF} - E_x^{DFT}\right)$
  where

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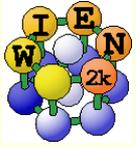
- **Only for certain atoms**

  and electrons of a given angular momentum ℓ

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

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

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

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

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

exchange and correlation potential

non relativistic
semi-relativistic
fully-relativistic

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

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

unit cell   atomic positions

$(Im\bar{3}m)^*$ No. 229

Structure optimization

iteration i

S C F

DFT Kohn-Sham

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

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

no

yes

E^{tot}, force

Minimize E, force$\rightarrow$0

properties

$k \in \mathbf{IBZ}$ (irred. Brillouin zone)

Kohn Sham

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

k

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

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

Generalized eigenvalue problem

$$HC = ESC$$

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

- **Ψ cannot be found analytically**
- **complete "numerical" solution is possible but inefficient**
- **Ansatz:**
  - *linear combination of some "basis functions"* $\qquad \Psi_k = \sum_{K_n} c_{k_n} \Phi_{k_n}$
    - 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

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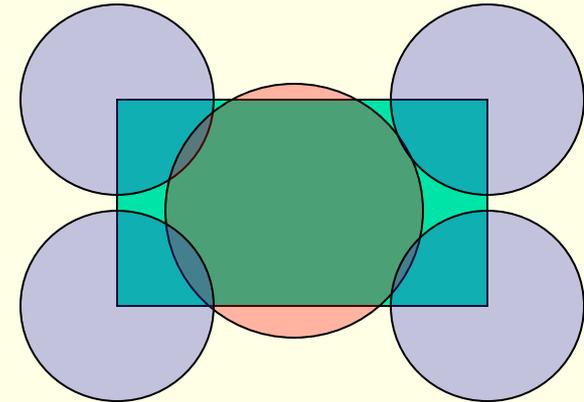
● **plane waves** form a "complete" basis set, however, they "never" converge due to the rapid oscillations of the atomic wave functions χ close to the nuclei

● 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*
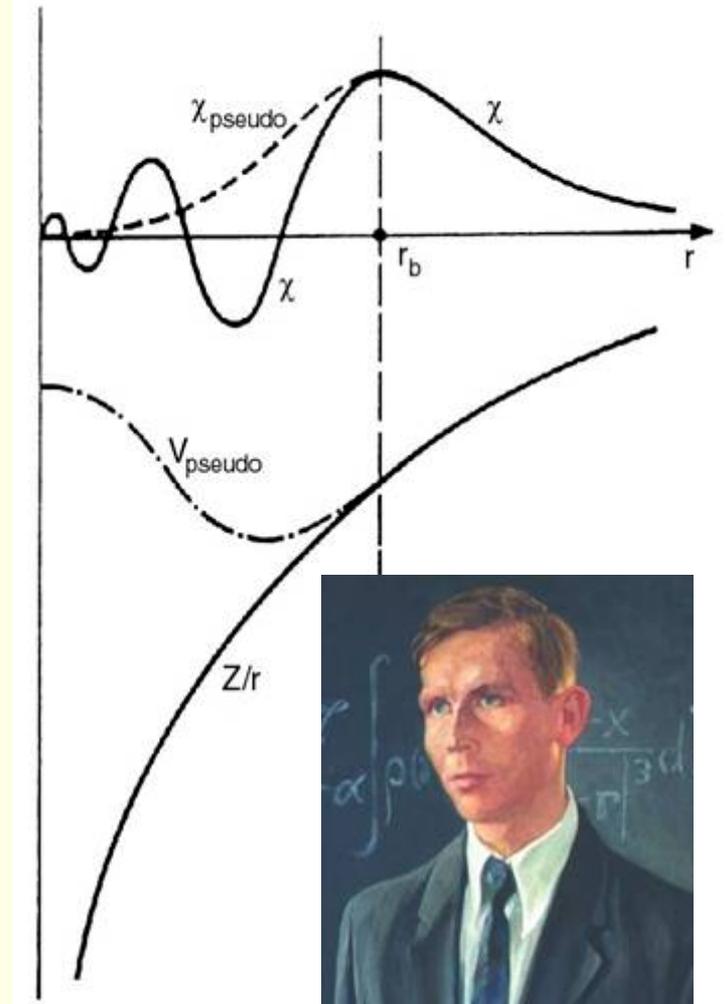
"real" potentials vs. pseudopotentials

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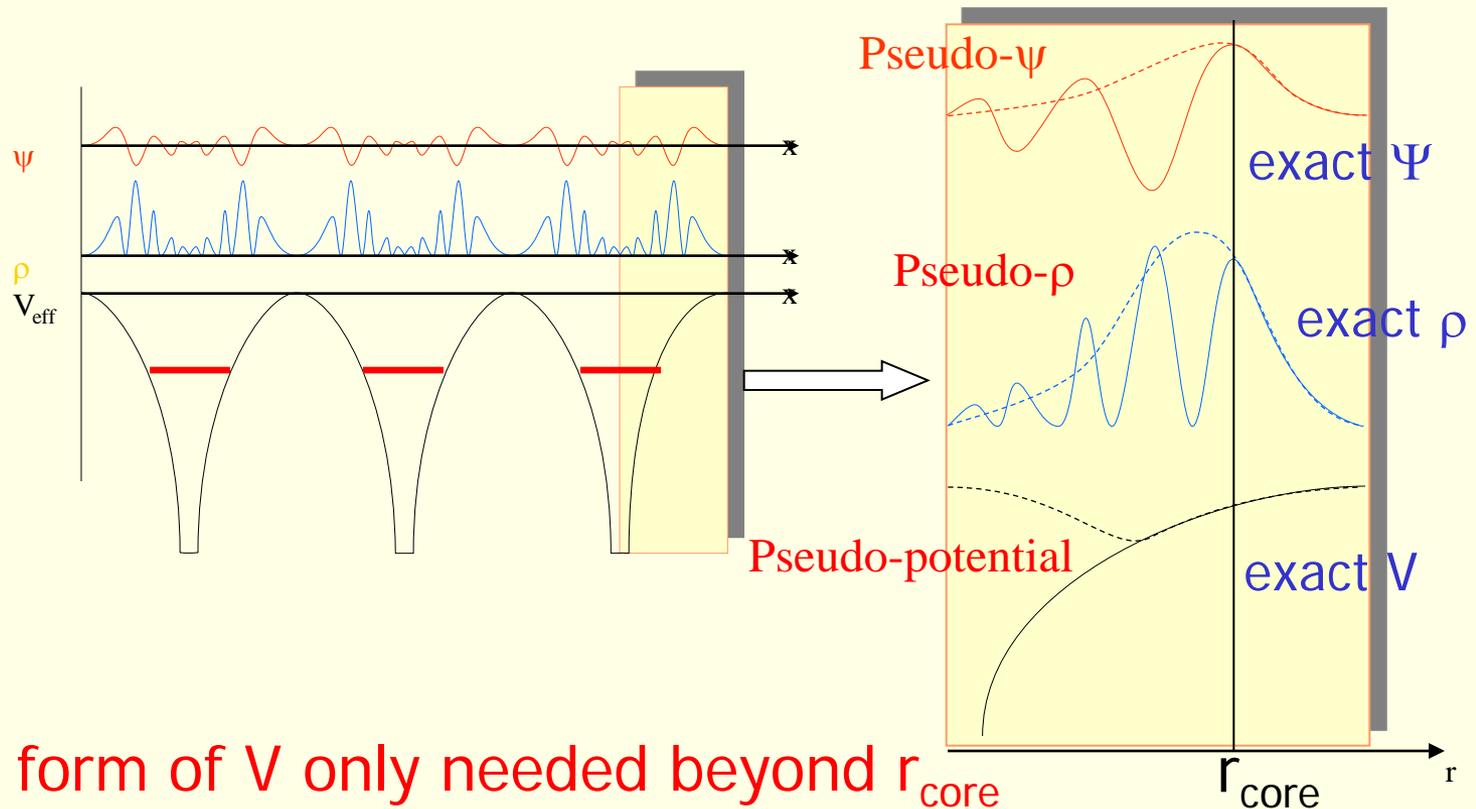
→exact form of V only needed beyond r_{core}

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*

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

APW Augmented Plane Wave method
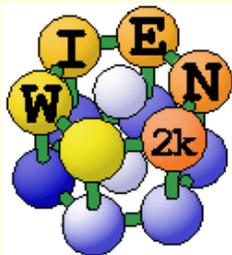
The unit cell is partitioned into:
  atomic spheres
  Interstitial region

unit cell

R_{mt} $r \in I$

63 eV

0 eV

(a)

PW

(b) sphere   I R_a

PWs   atomic   Plane Waves (PWs)

Basis set:

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

join

Atomic partial waves

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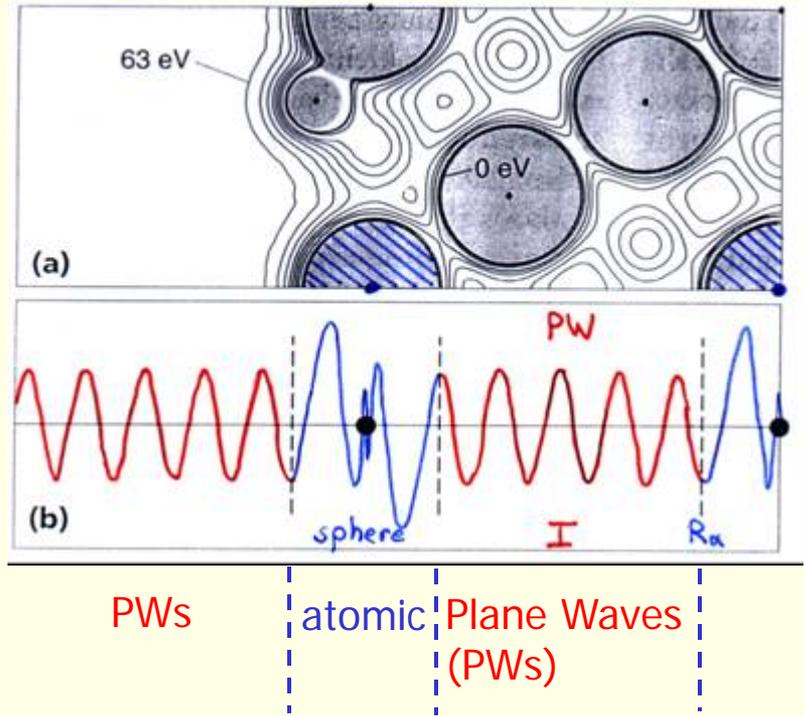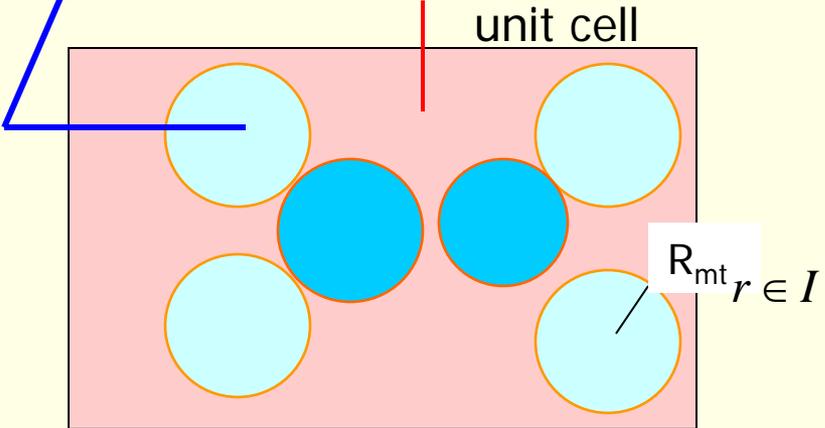
$u_l(r,\varepsilon)$ are the numerical solutions
of the radial Schrödinger equation
in a given spherical potential
for a particular energy ε
$A_{lm}{}^{K}$ coefficients for matching the PW

Slater's APW (1937)
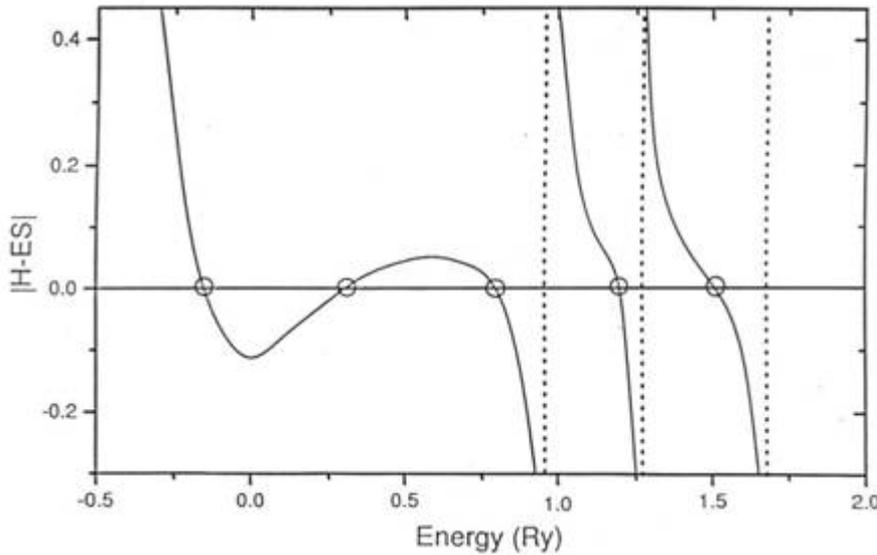
H Hamiltonian
S overlap matrix

Atomic partial waves

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

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!
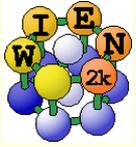
Linearization of energy dependence

LAPW suggested by

O.K.Andersen,
Phys.Rev. B 12, 3060
(1975)
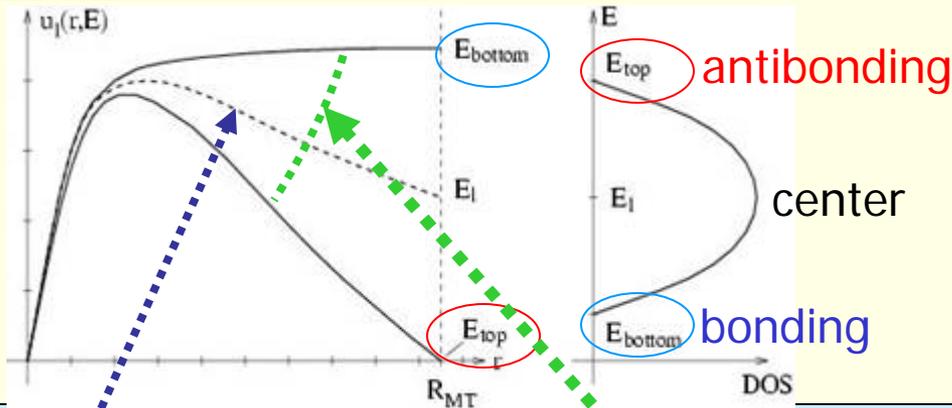
$$\Phi_{k_n} = \sum_{\ell m}[A_{\ell m}(k_n)u_\ell(E_\ell, r) + B_{\ell m}(k_n)\dot{u}_\ell(E_\ell, r)]Y_{\ell m}(\hat{r})$$

expand u_l at fixed energy E_l and

add $\quad \dot{u}_l = \partial u_l / \partial \varepsilon$

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

→ General eigenvalue problem (diagonalization)

→ additional constraint requires more PWs than APW
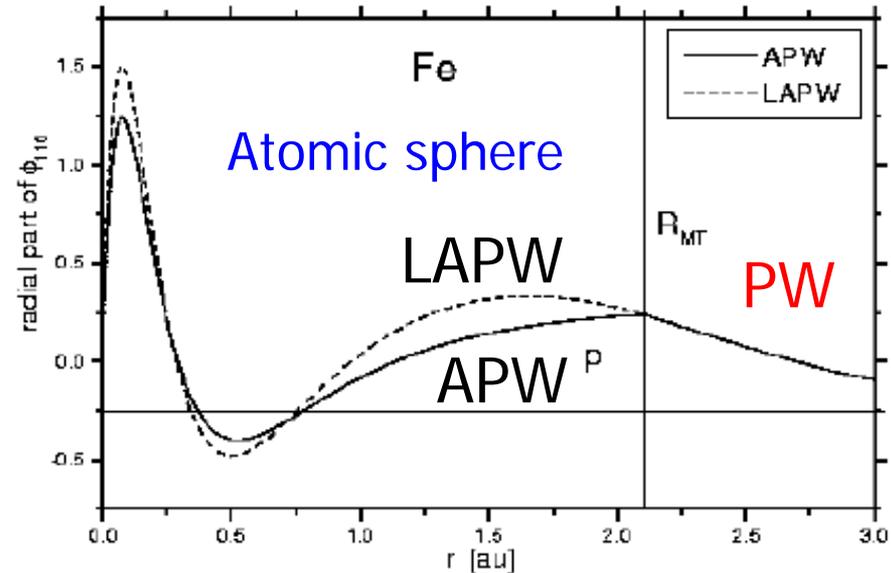
- **Atomic sphere approximation (ASA)**
  - *overlapping spheres "fill" all volume*
  - *potential spherically symmetric*
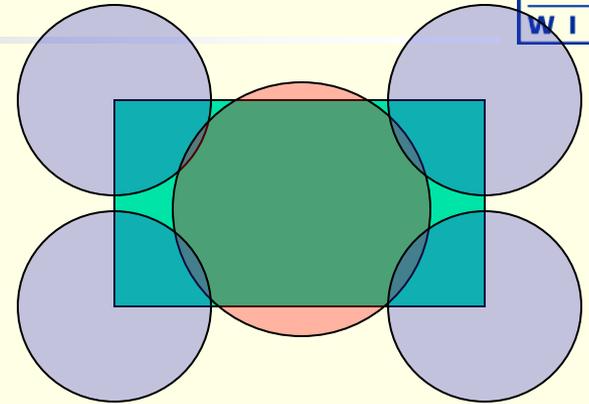
- **"muffin-tin" approximation (MTA)**
  - *non-overlapping spheres with spherically symmetric potential +*
 - *interstitial region with V=const.*
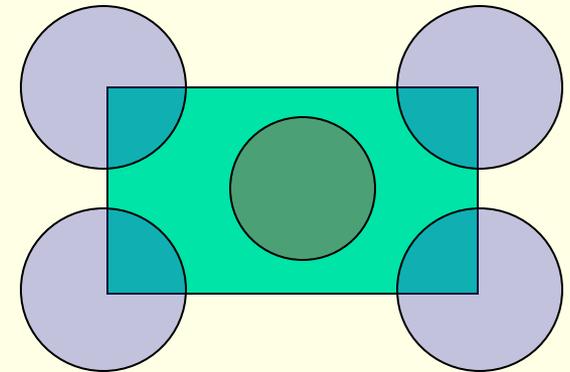

- **"full"-potential**
  - *no shape approximations to V*
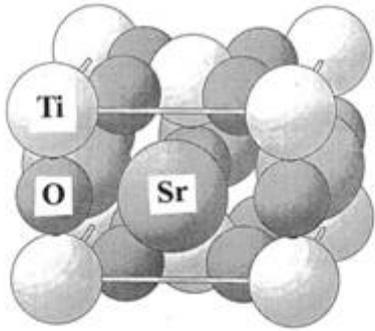
SrTiO$_3$
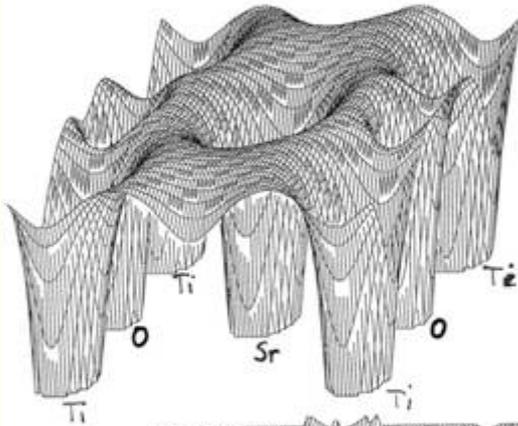
Full
potential
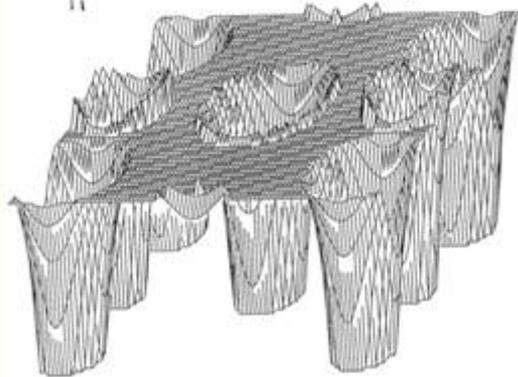
Muffin tin
approximation

TiO$_2$ rutile

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

(no shape approximation)

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

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

O

Ti

For example: Ti

-356.6

-38.3

-31.7 Ry
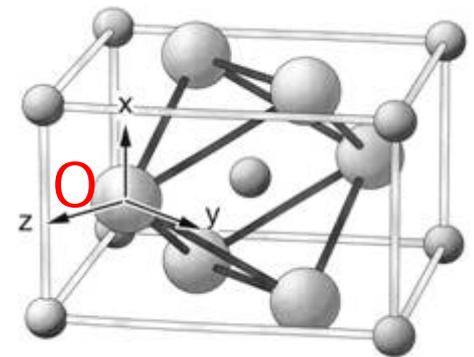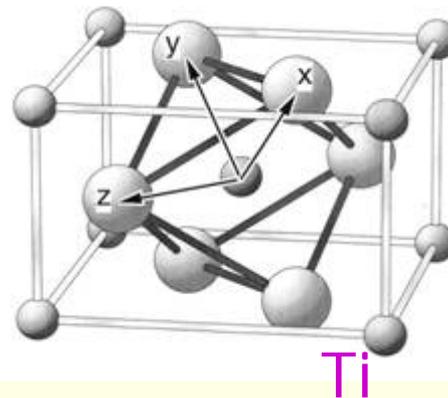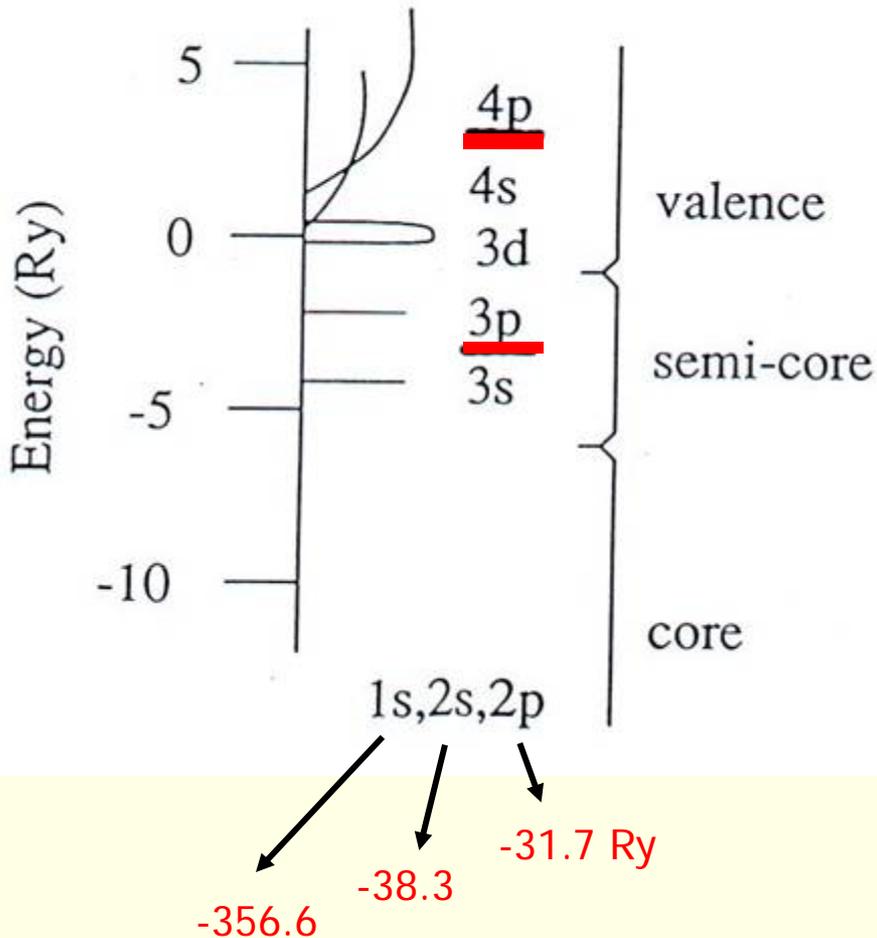
- **Valences states**
  - *High* in energy
  - *Delocalized* wavefunctions
- **Semi-core states**
  - *Medium* energy
  - Principal **QN** one less than valence (e.g. in Ti **3**p and **4**p)
  - *not completely confined* inside sphere (charge leakage)
- **Core states**
 - *Low* in energy
  - Reside *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)*
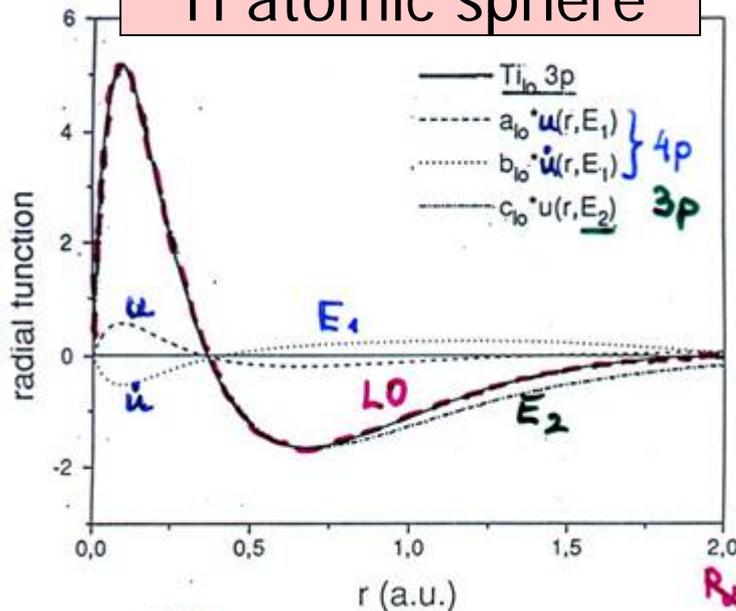
D.J.Singh,
Phys.Rev. B 43 6388 (1991)
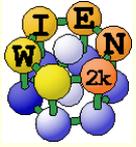
E.Sjöstedt, L.Nordström, D.J.Singh,
An alternative way of linearizing the augmented plane wave method,
Solid State Commun. 114, 15 (2000)

- 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:

SES (sodium electro solodalite)

K.Schwarz, P.Blaha, G.K.H.Madsen, Comp.Phys.Commun.**147**, 71-76 (2002)
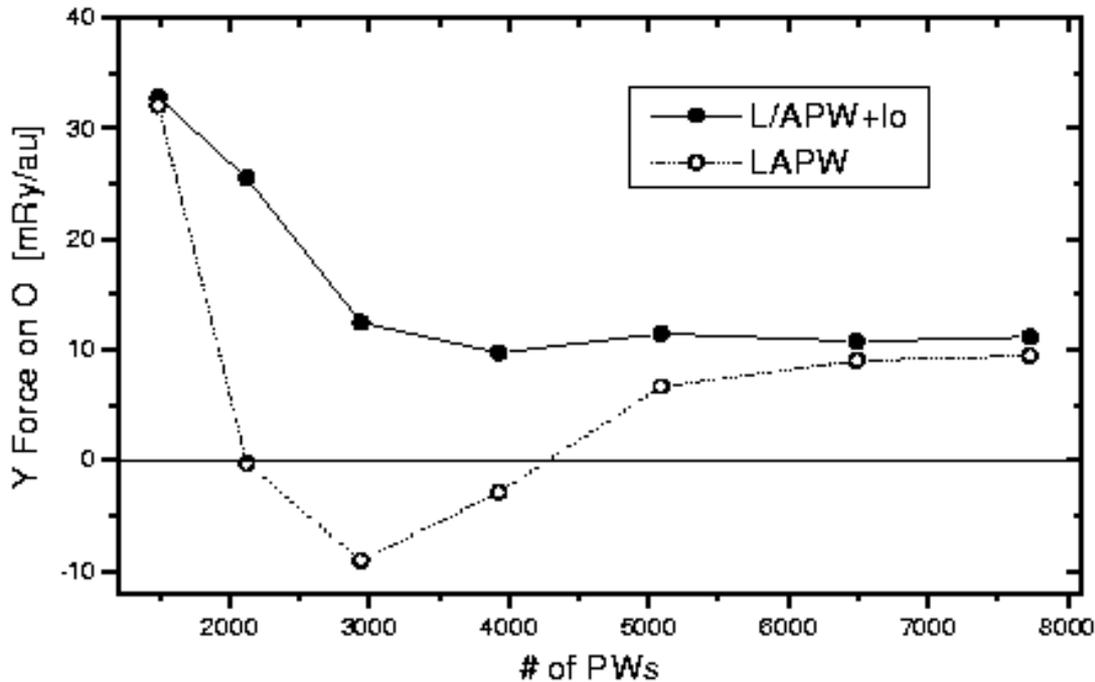
e.g. force (F_y) on oxygen in SES vs. # plane waves:

- in **LAPW** changes sign and converges slowly
- in **APW+lo** better convergence
- to same value as in LAPW

SES
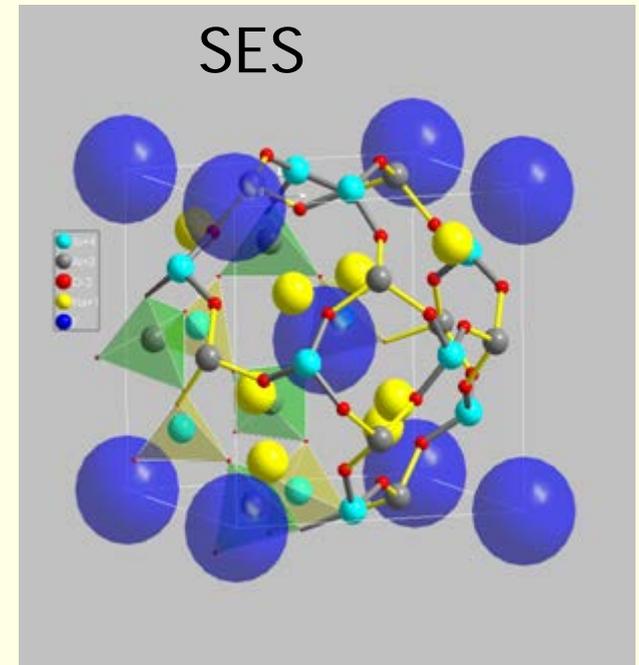
- **Atomic partial waves**
  - *LAPW*

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

  - *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 $A_{\ell m}(k_n)$

Atomic sphere

Fe

LAPW

APW

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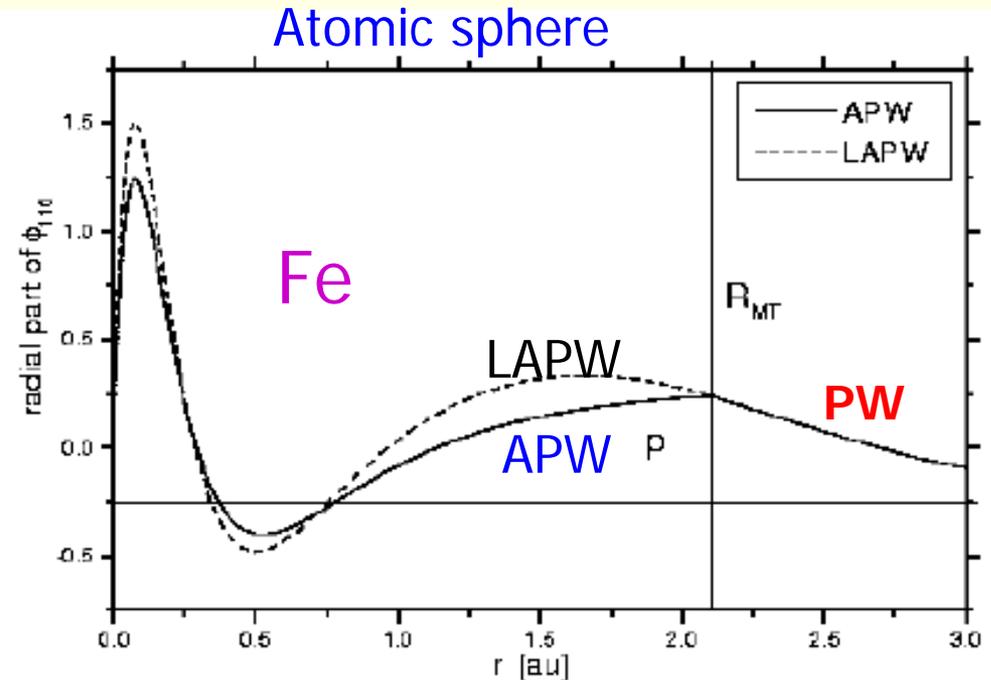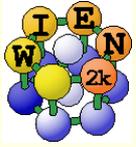
E.Sjöststedt, L.Nordström, D.J.Singh, SSC 114, 15 (2000)

- 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)
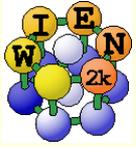
The WIEN2k authors
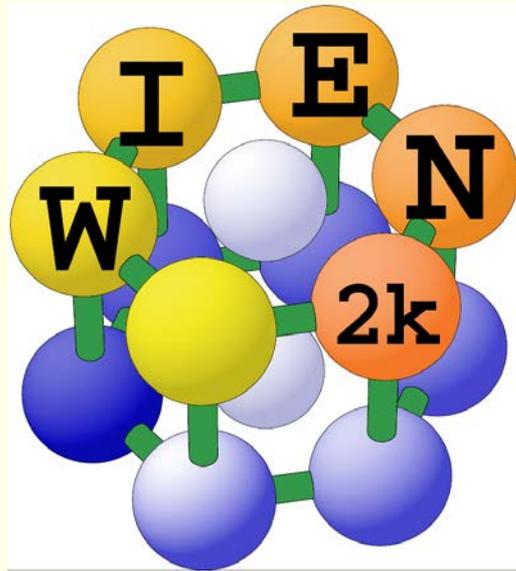
**An Augmented Plane Wave
Plus Local Orbital Program for
Calculating Crystal Properties**

**Peter Blaha
Karlheinz Schwarz
Georg Madsen
Dieter Kvasnicka
Joachim Luitz**

November 2001
Vienna, AUSTRIA
Vienna University of Technology

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

http://www.wien2k.at
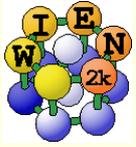
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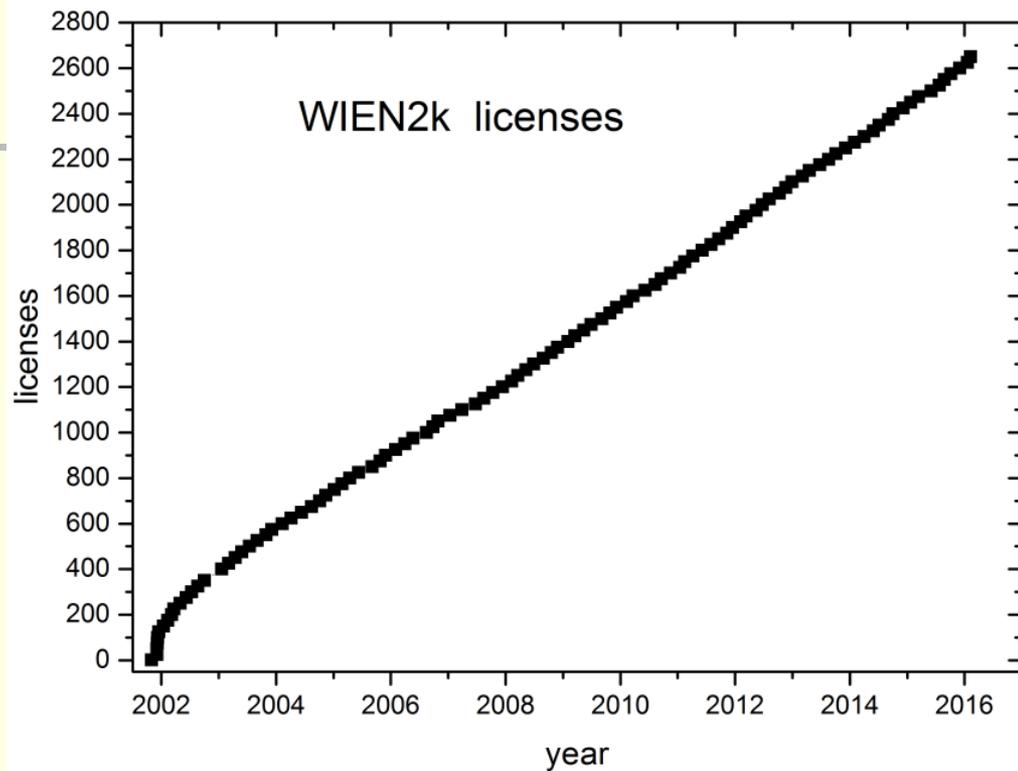
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mailinglist: 10.000 emails/6 years
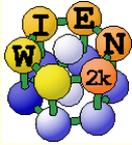
The first publication of the WIEN code

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
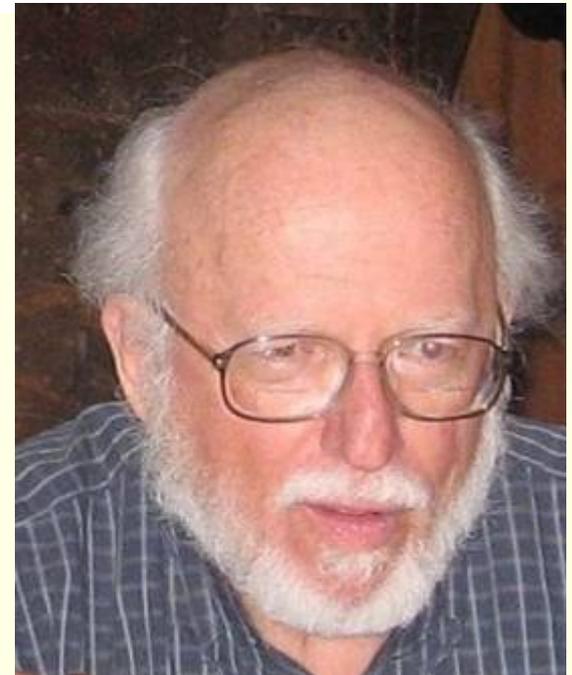
Europa Austria Vienna → WIEN

In the Heart of EUROPE
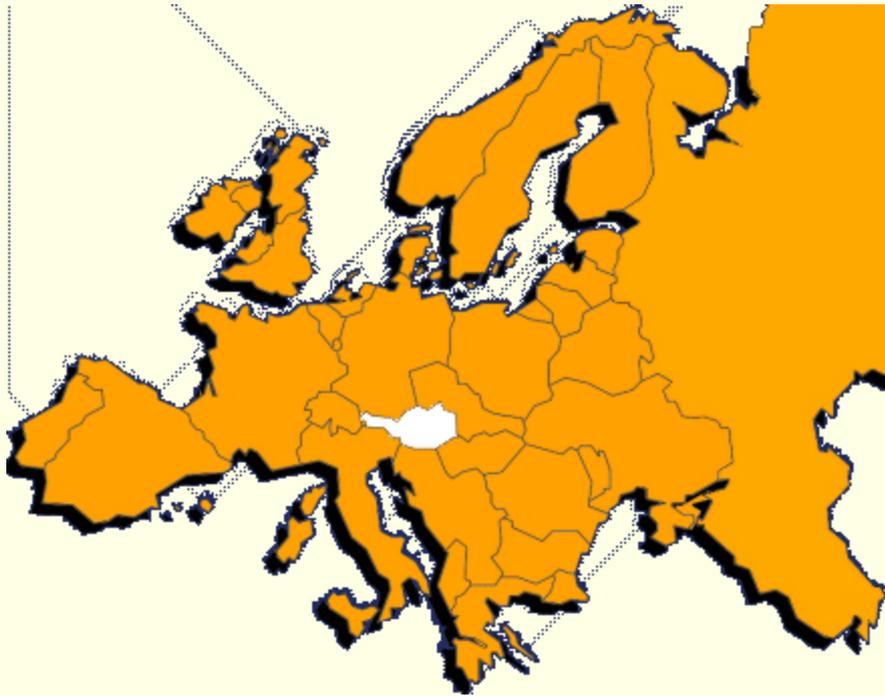
In Japan

- 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
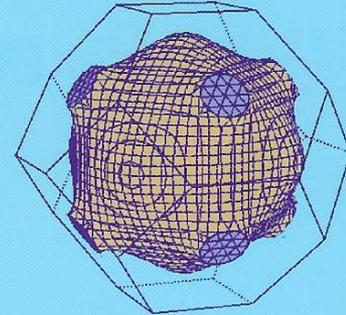
和光システム研究所 著

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 (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. Hamiton, ON) 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 ....**
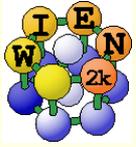
A series of **WIEN workshops** were held

■	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	
■	23rd	McMaster, Canada		June	2016	

WIEN2k licenses

2900 users
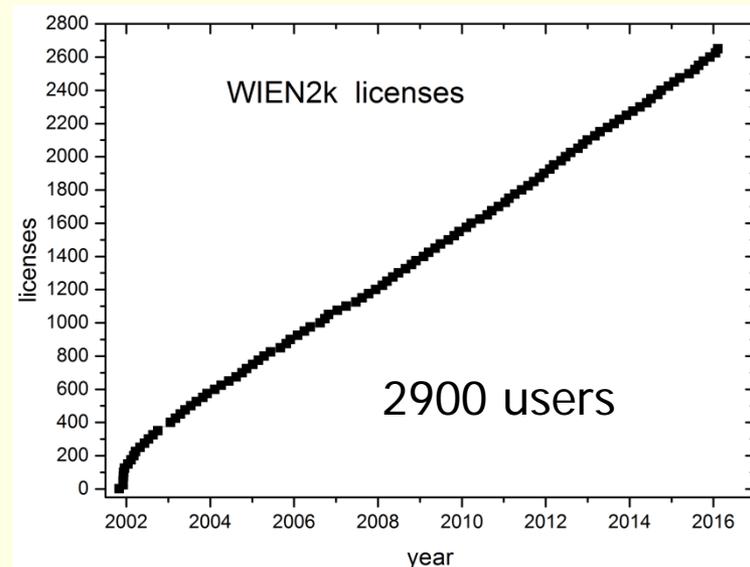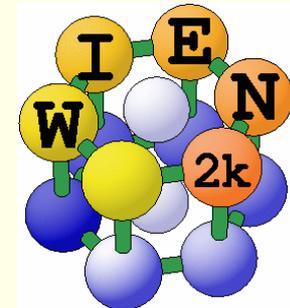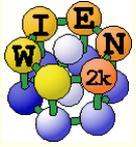
APW + local orbital method
(linearized) augmented plane wave method

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

Variational method: $\quad < E > = \dfrac{< \Psi / H / \Psi >}{< \Psi / \Psi >} \qquad \dfrac{\delta < E >}{\delta C_{k_n}} = 0$

| upper bound | minimum |

Generalized eigenvalue problem: $\quad H\,C = E\,S\,C$

Diagonalization of (real or complex) matrices of size 10.000 to 50.000 (up to 50 Gb memory)
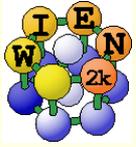
Structure: $a,b,c,\alpha,\beta,\gamma, R_\alpha$, …

unit cell   atomic positions
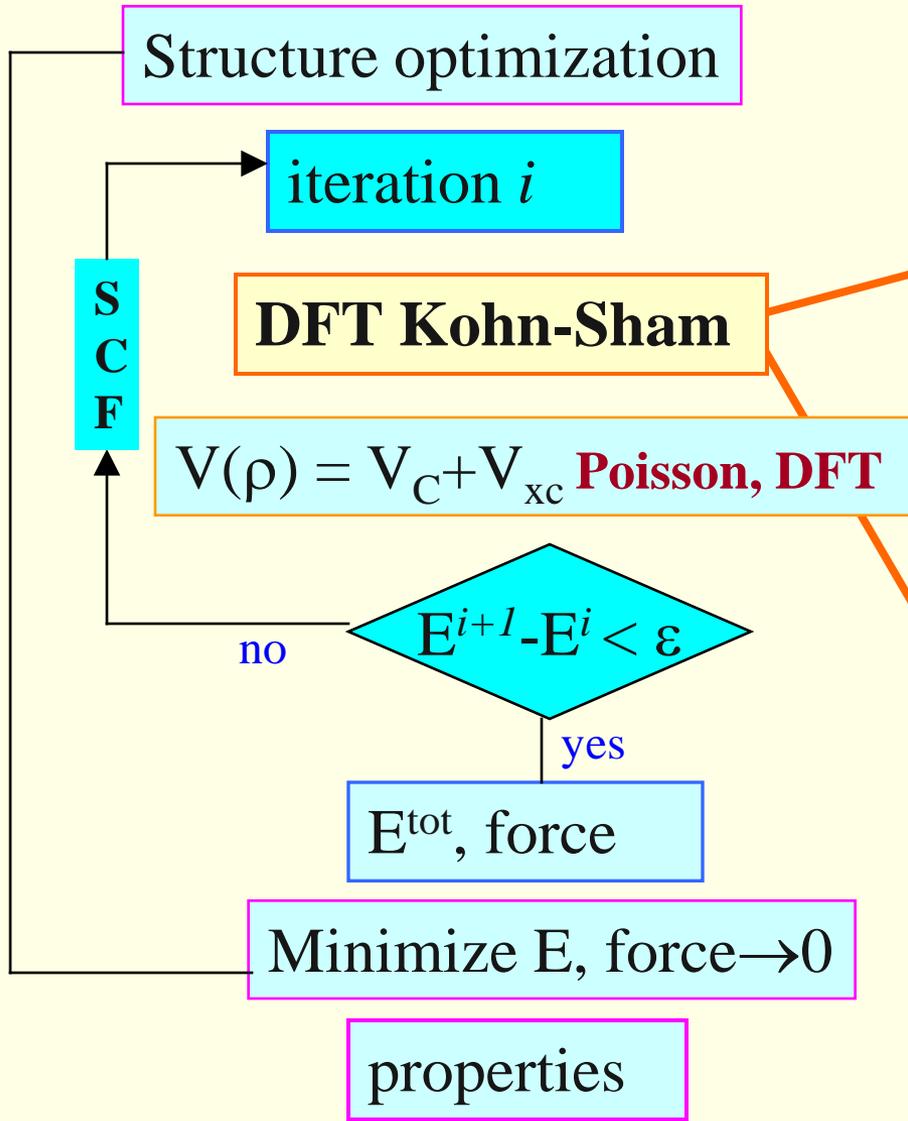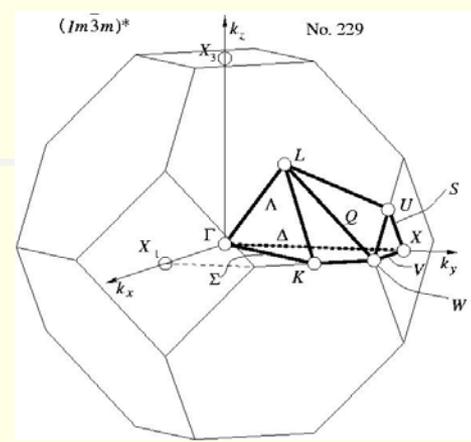
Structure optimization

iteration i

S C F

DFT Kohn-Sham

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

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

no

yes

E^{tot}, force

Minimize E, force$\to$0

properties

$k \in \mathbf{IBZ}$ (irred.Brillouin zone)

Kohn Sham

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

k

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

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

Generalized eigenvalue problem

$HC = ESC$

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

- **Irreducible BZ (IBZ)**

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

- Bilbao Crystallographic Server:

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

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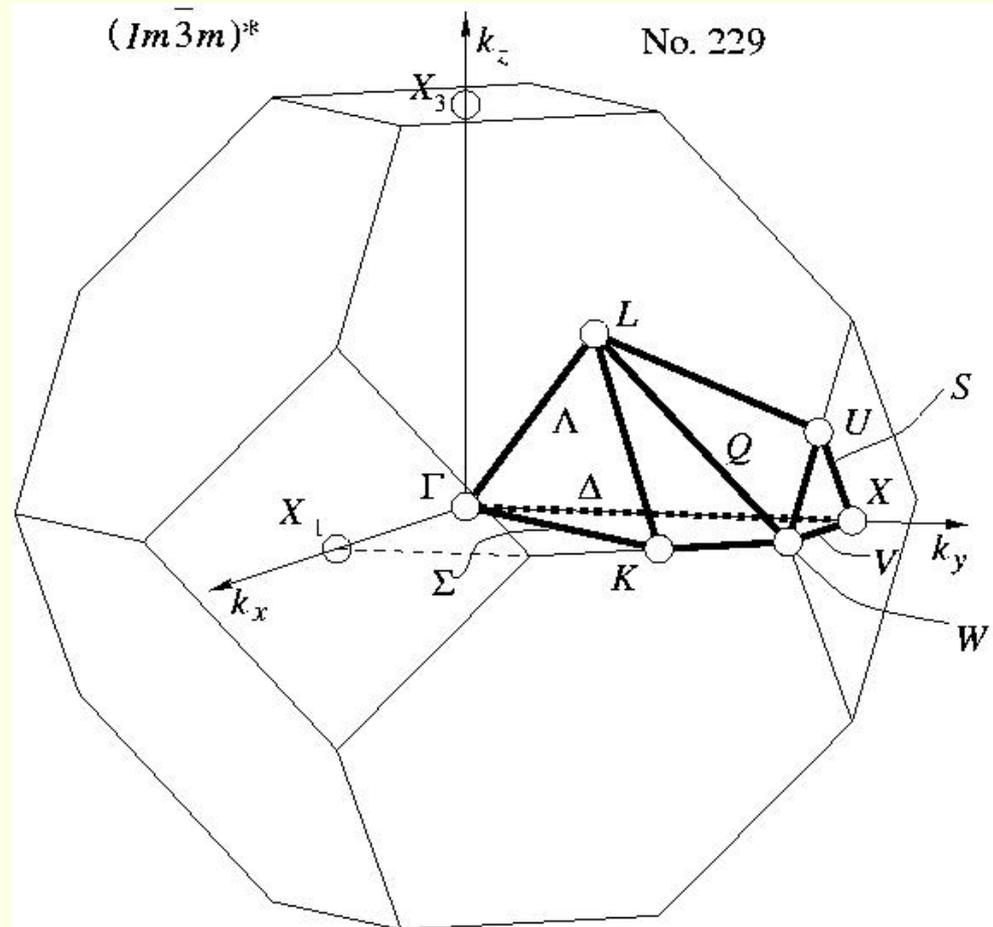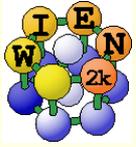
- In order to solve $H\Psi=E\Psi$ we need to know the potential $V(r)$
- for $V(r)$ we need the electron density $\rho(r)$
- the density $\rho(r)$ can be obtained from $\Psi(r)*\Psi(r)$
- ?? $\Psi(r)$ is unknown before $H\Psi=E\Psi$ is solved ??

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

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

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

SCF cycles

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

Solve $\{-\dfrac{1}{2}\nabla^2 + V_{eff}(\mathbf{r})\}\Phi_i(\mathbf{r}) = \varepsilon_i\Phi_i(\mathbf{r})$
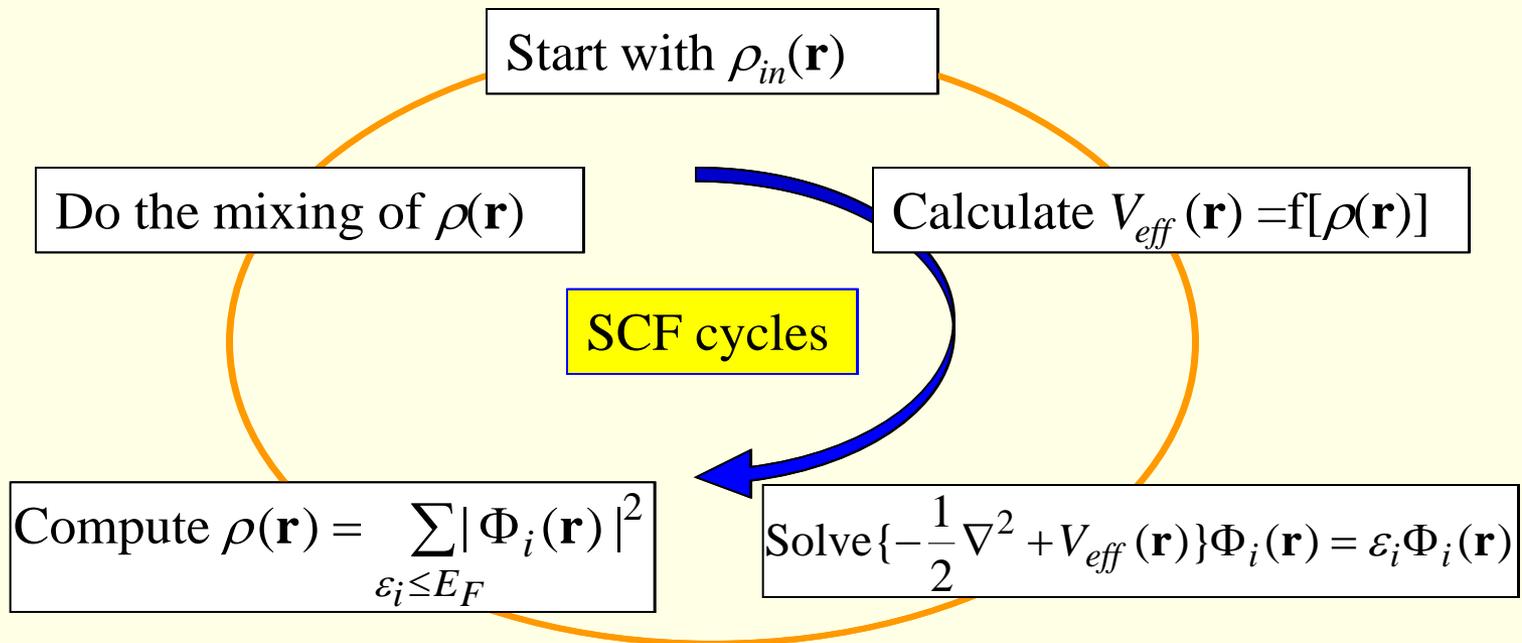
Band structure of fcc Cu
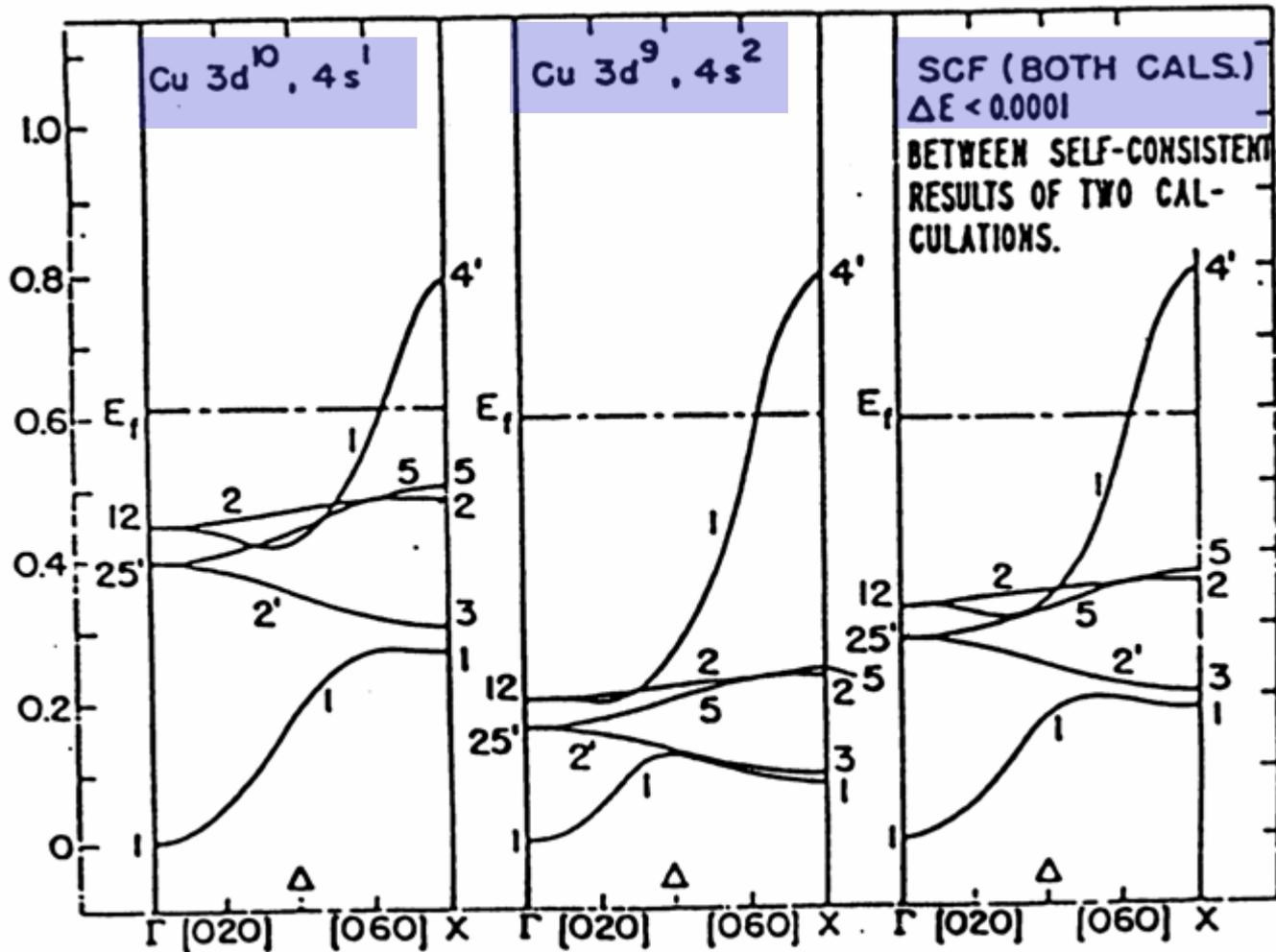
Program structure of WIEN2k

- **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*

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

no   converged?   yes → done!

WIEN2k: *P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, and J. Luitz*
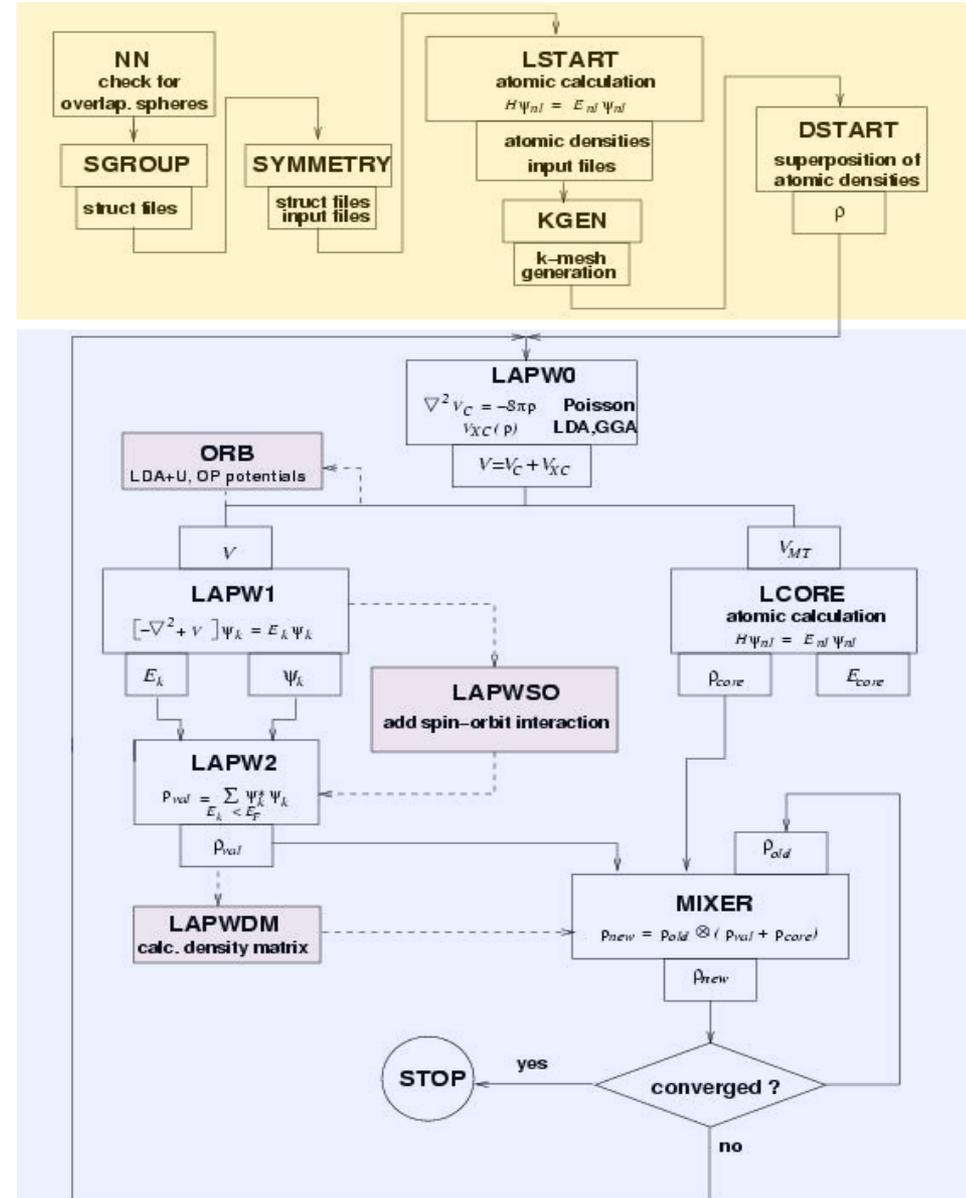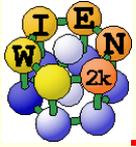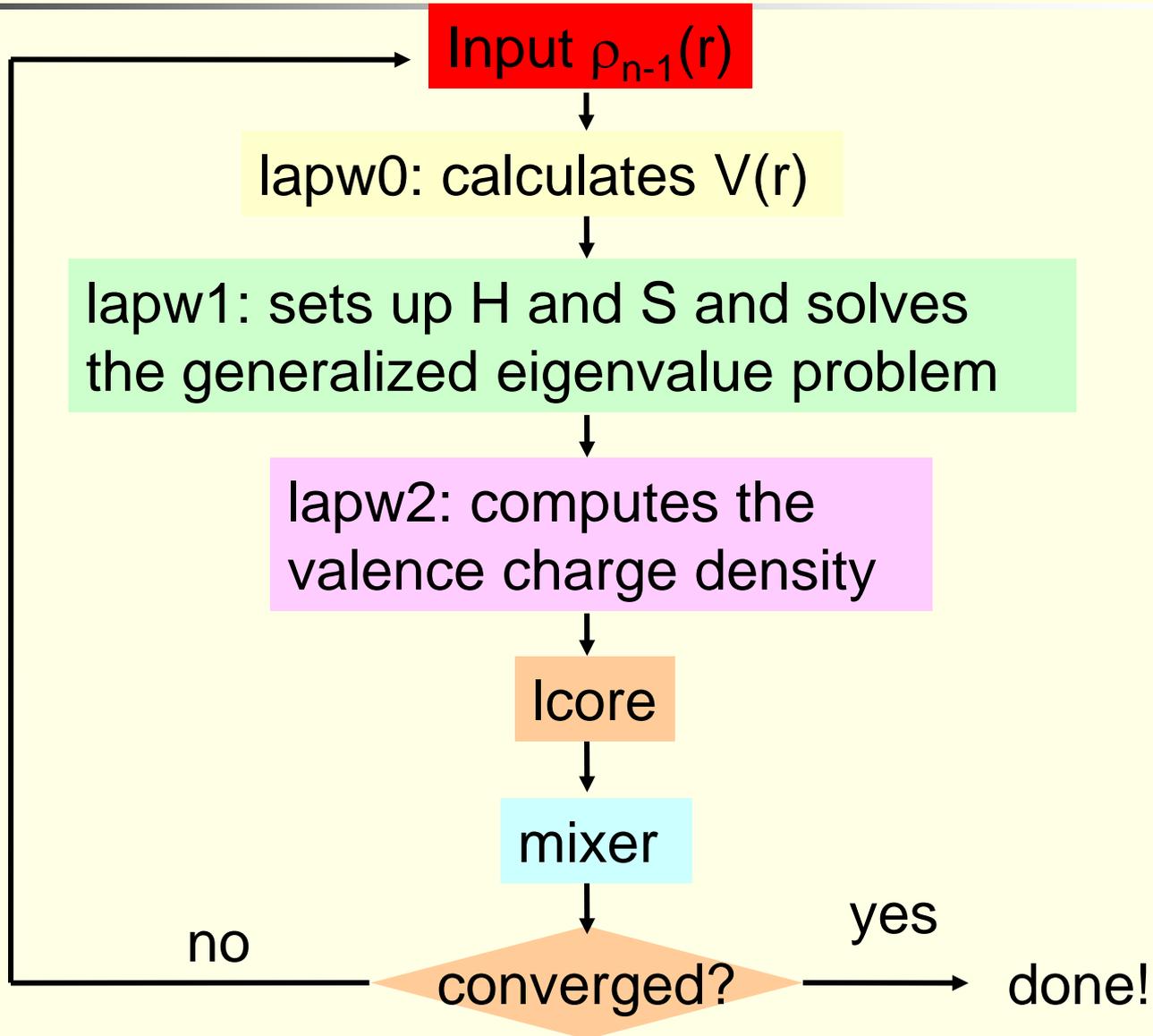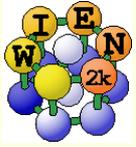
- individual FORTRAN programs linked by shell-scripts
- the output of one program is input for the next
- lapw1/2 can run in parallel on many processors

SCF cycle

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

Iteration

self consistent? no / yes → END

single mode

LAPW0

LAPW1

LAPW2

SUMPARA

LCORE

MIXER

Iteration

self consistent? yes → END / no

parallel mode

k-point parallelization
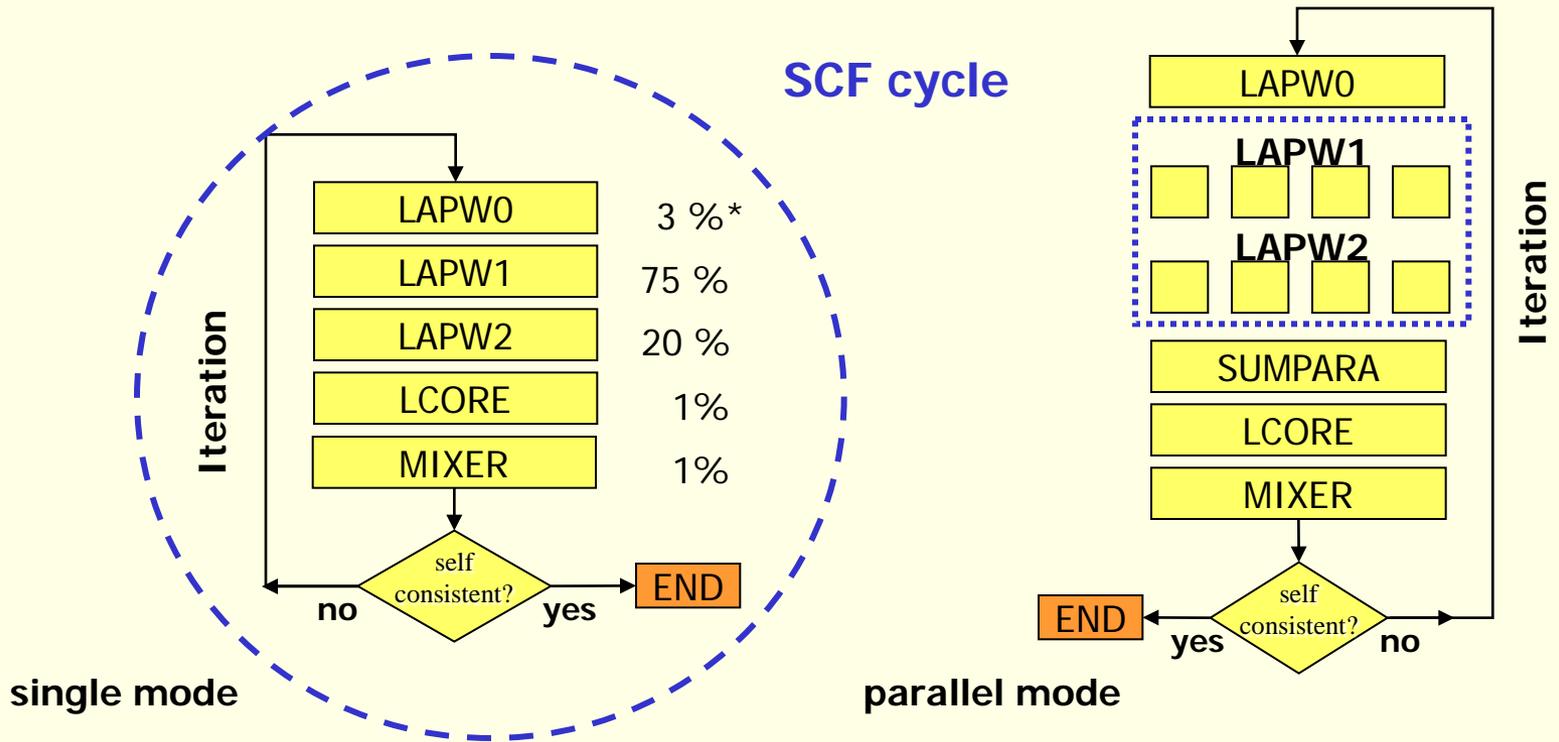
* fraction of total computation time
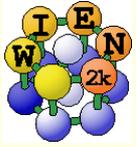
+ robust all-electron full-potential method (new effective mixer)

+ 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

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!

[Save Structure]
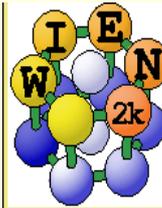
Execution >>
StructGen™
initialize calc.
run SCF
single prog.
optimize(V,c/a)
mini. positions

Utils. >>

Tasks >>

Files >>
struct file(s)
input files
output files
SCF files

Session Mgmt. >>
change session
change dir
change info

Configuration

Usersguide
html-Version
pdf-Version

Idea and realization
by

Title: TiC
Lattice:
Type: F

P
F
B
CXY
CYZ
CXZ
R
H
1_P1

Spacegroups from
Bilbao Cryst Server

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   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 P4₂/mnm

$P4_2/mnm$ Spacegroup — presentation slide

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

2a
4f
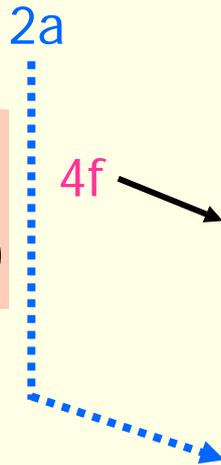
$P4_2/mnm$

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

Origin at centre (mmm)

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*

BALSAC plot
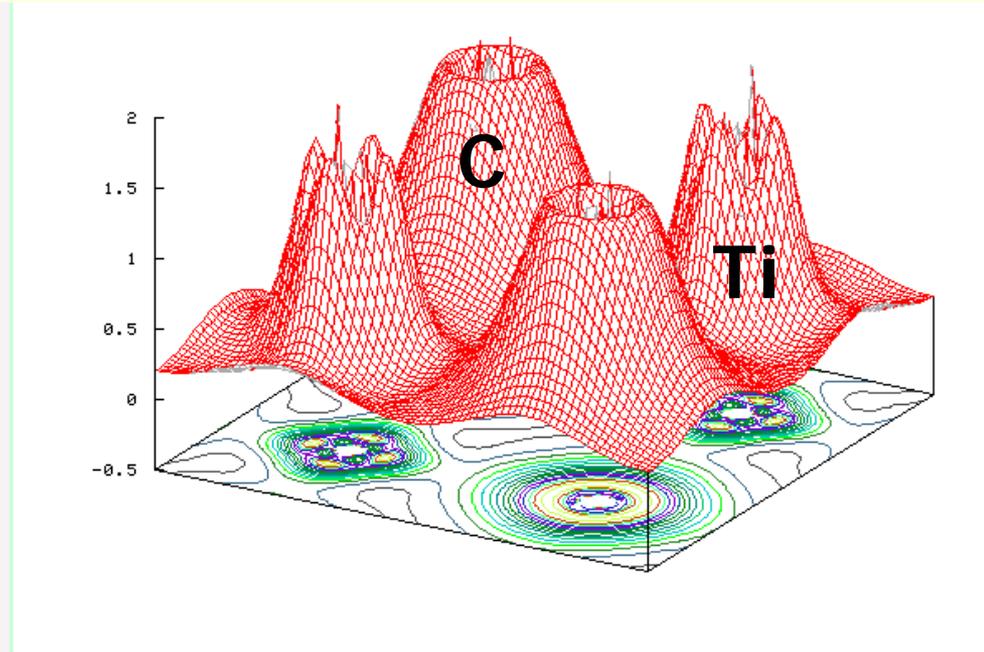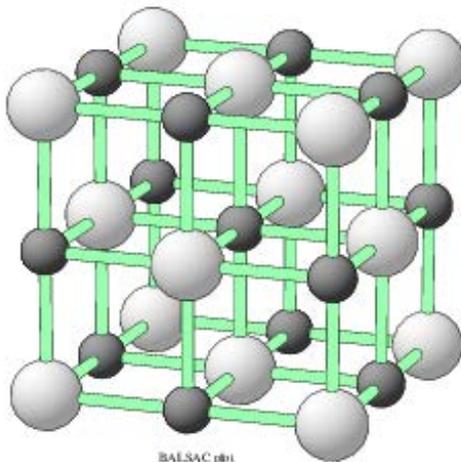
Download hardcopy in PostScript format

Select plot type: 3D-plot ● Contur-plot ○ with labels ☐|
Min -0.5   Max 2   Delta 0.1
[plot electron density]
[edit TiC.in2] reset EMIN
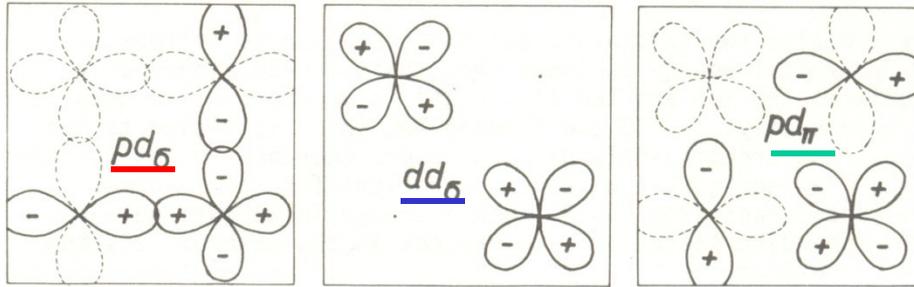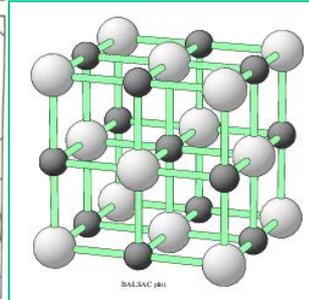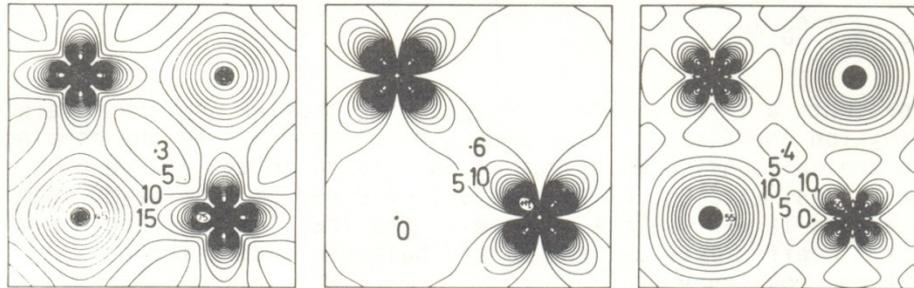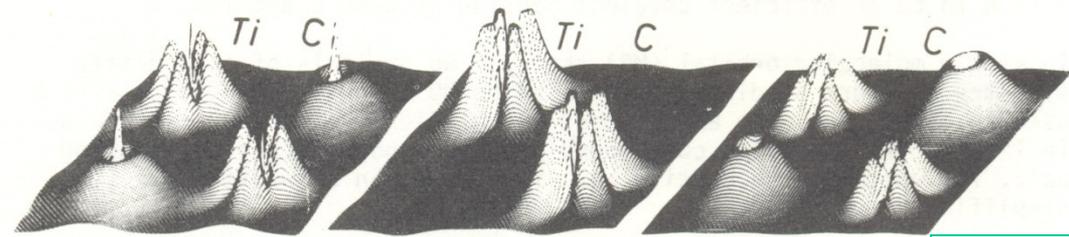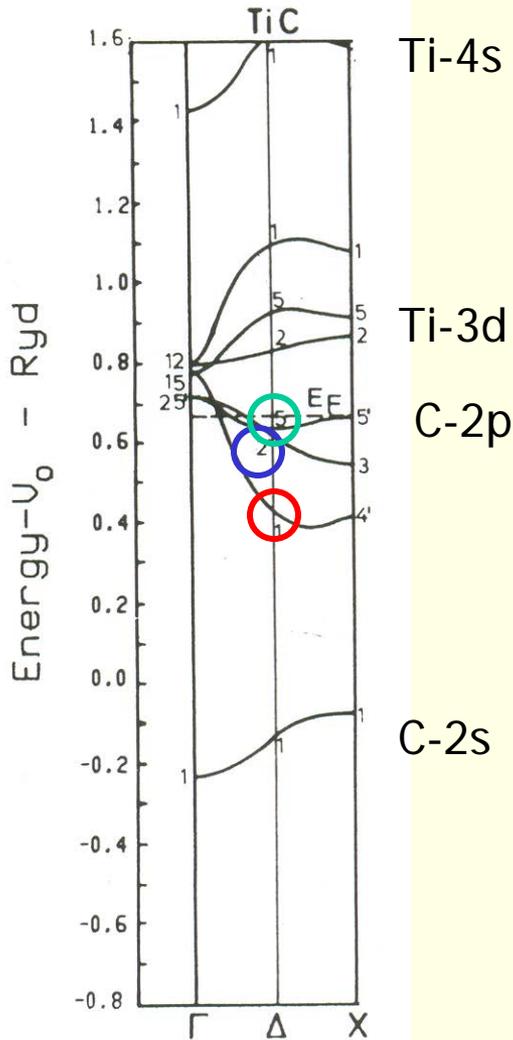
Energy bands

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

spaghetti   irred.rep.   character bands
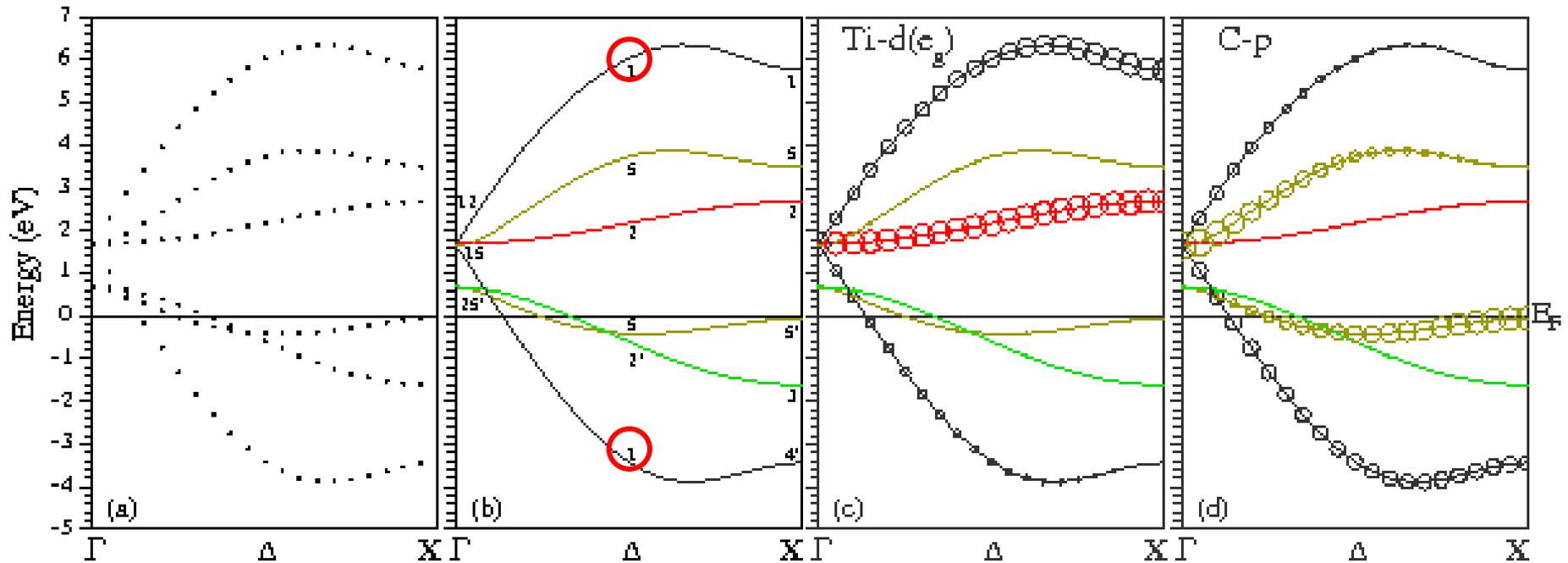
$$1 = q_{out} + \sum_t \sum_\ell q_{t\ell}$$

unit cell   interstitial   atom t ℓ=s, p, d, ...
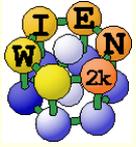
TiC, bonding and antibonding states

weight: C Ti   O Ti
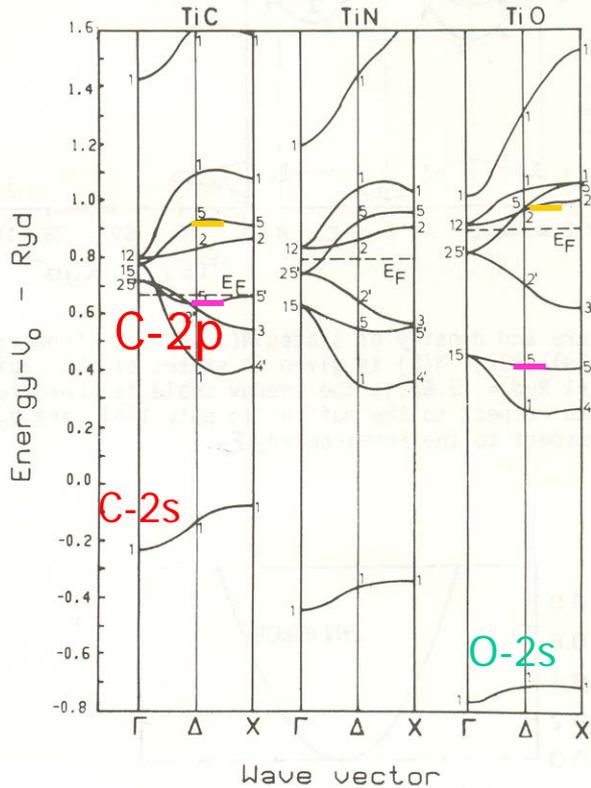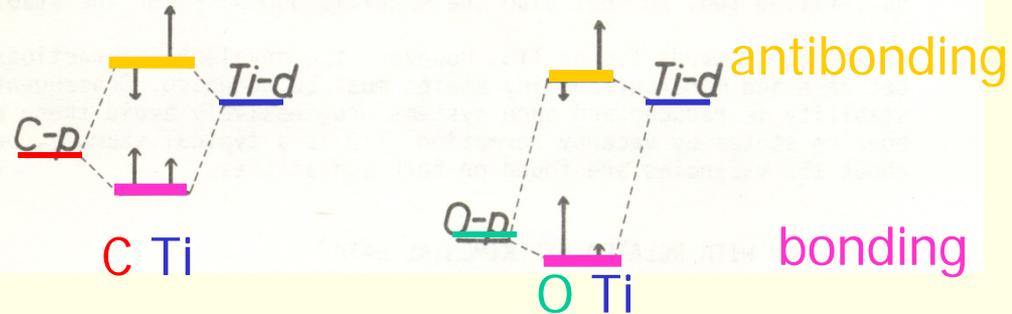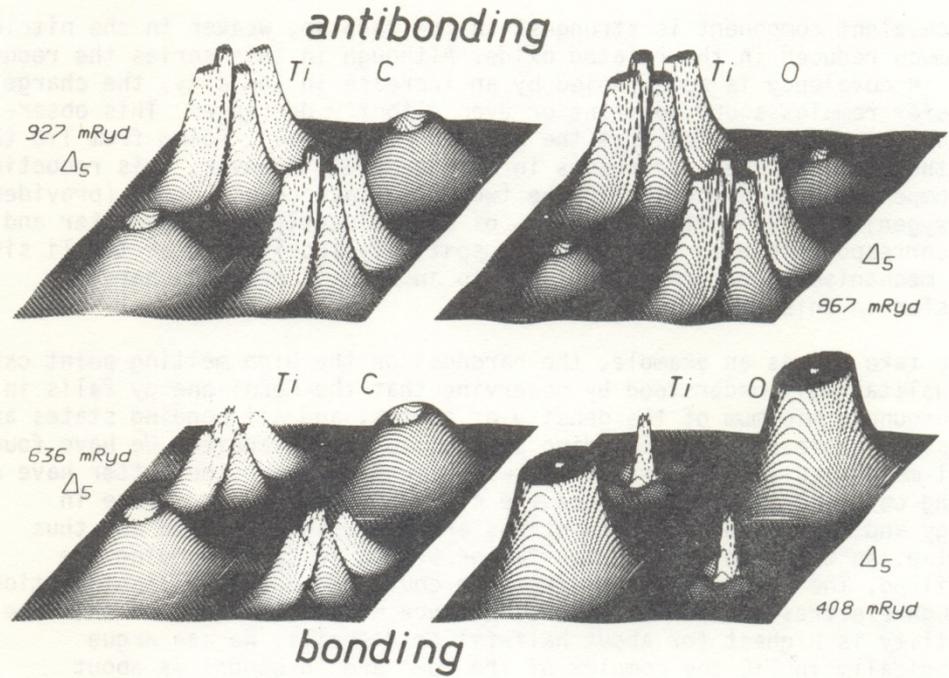
antibonding

bonding

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

antibonding

C_p-Ti_d σ
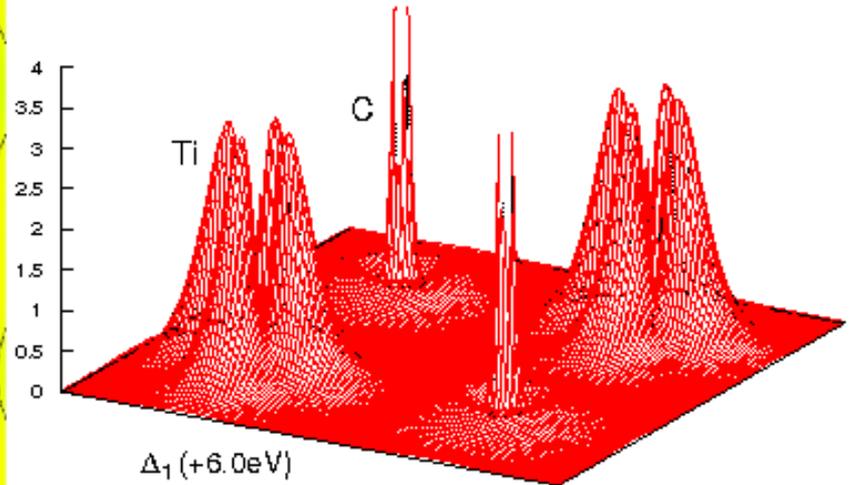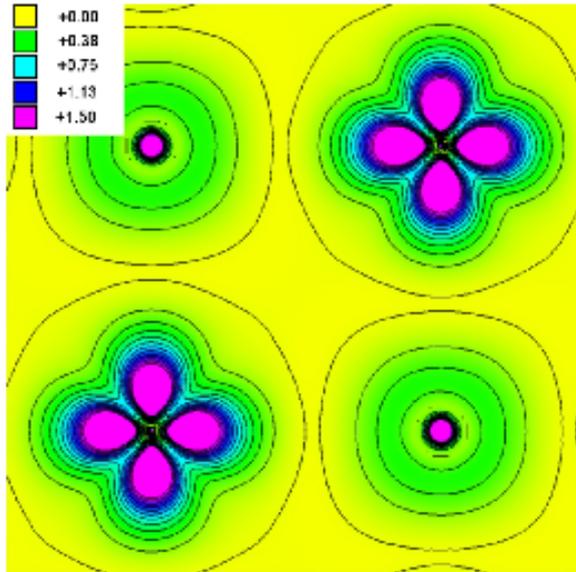
bonding

C_p-Ti_d σ
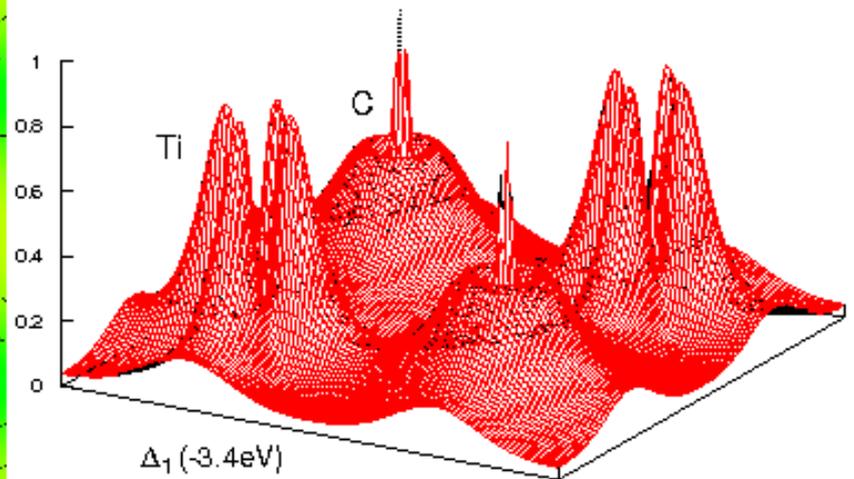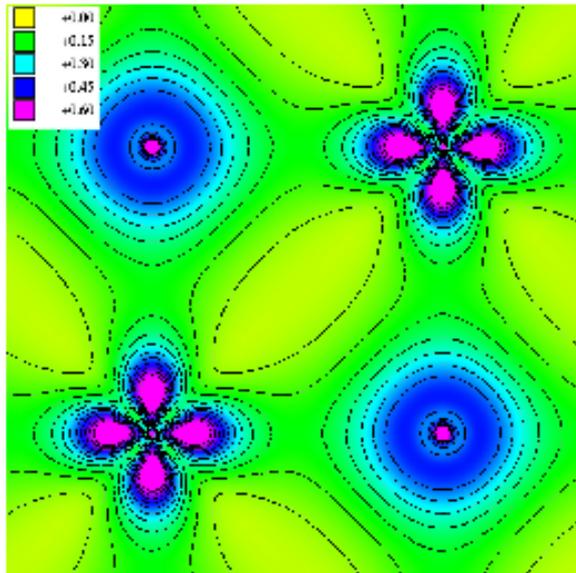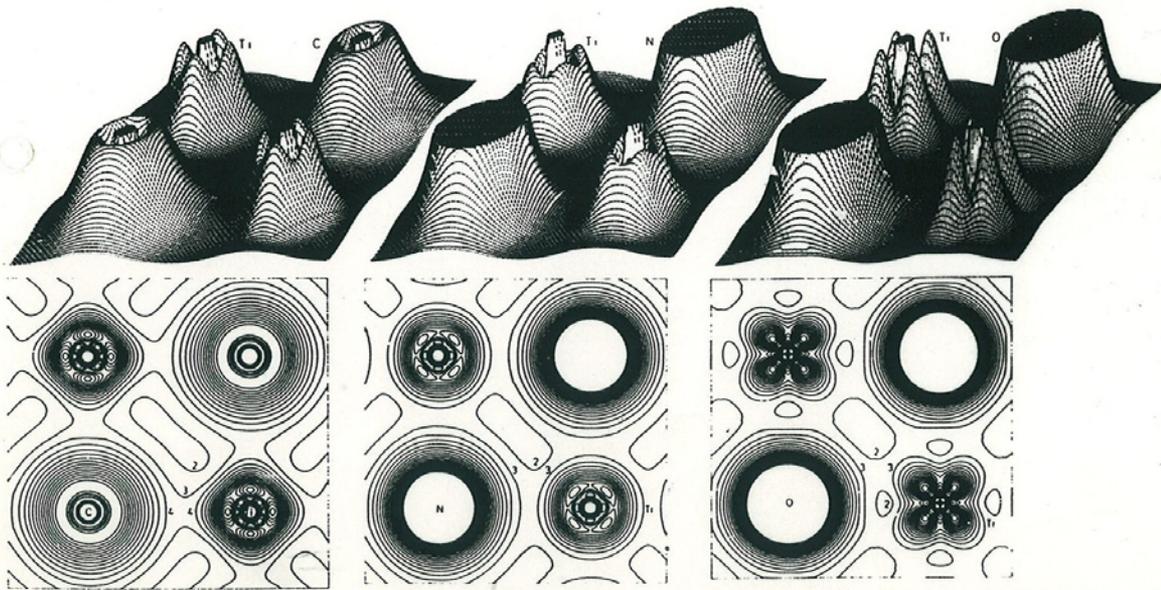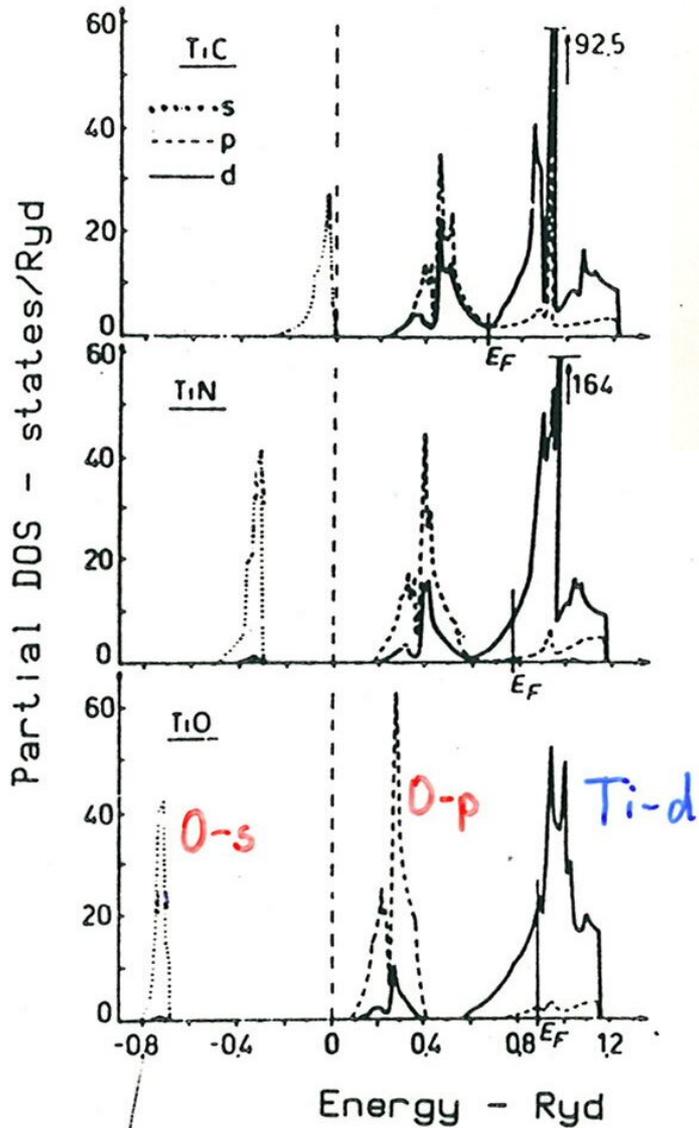
TiC, TiN, TiO

Figure 3. Valence charge densities in the (100) plane. Contour intervals 0.1e Å⁻³ (numbers are in these units), cutoff at 1.7e 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)

Experimental difference electron density
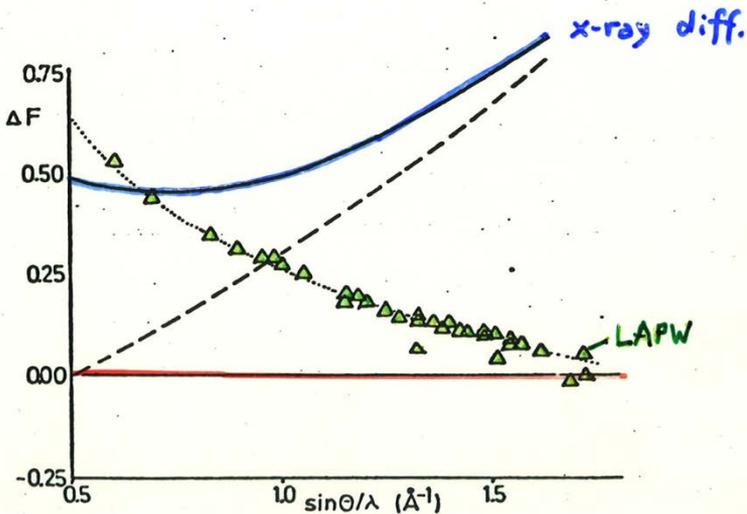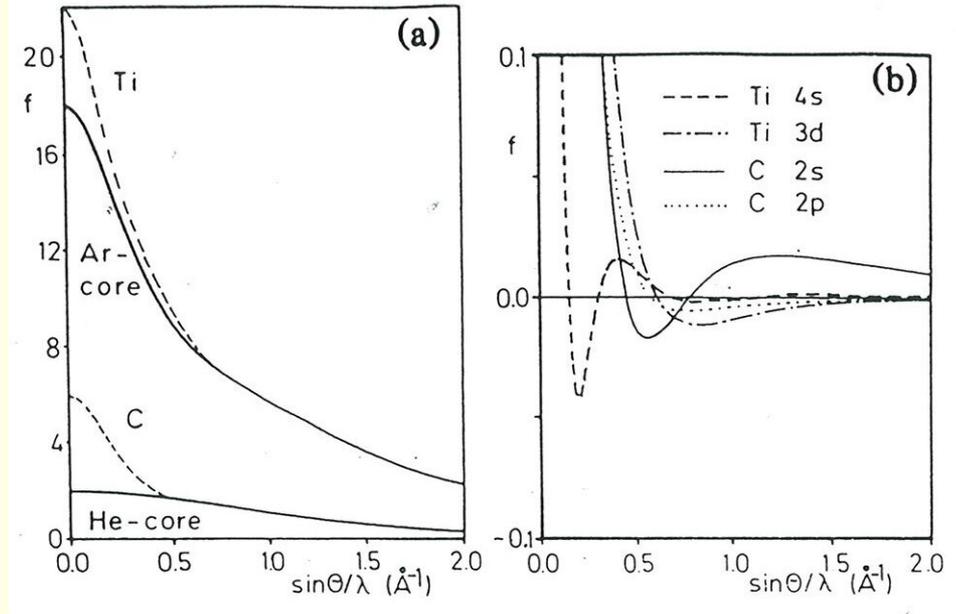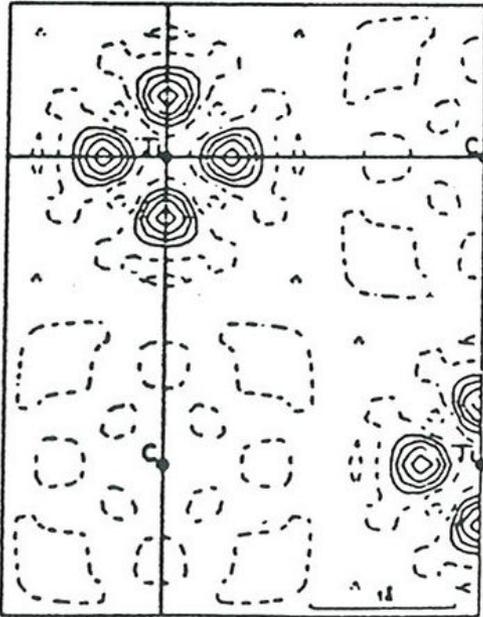
Paired reflections

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

$$\vec{S}$$

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

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

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

Kurt Lejaeghere,[1]* Gustav Bihlmayer,[2] Torbjörn Björkman,[3,4] Peter Blaha,[5]
Stefan Blügel,[2] Volker Blum,[6] Damien Caliste,[7,8] Ivano E. Castelli,[9] Stewart J. Clark,[10]
Andrea Dal Corso,[11] Stefano de Gironcoli,[11] Thierry Deutsch,[7,8] John Kay Dewhurst,[12]
Igor Di Marco,[13] Claudia Draxl,[14,15] Marcin Dułak,[16] Olle Eriksson,[13]
José A. Flores-Livas,[12] Kevin F. Garrity,[17] Luigi Genovese,[7,8] Paolo Giannozzi,[18]
Matteo Giantomassi,[19] Stefan Goedecker,[20] Xavier Gonze,[19] Oscar Grånäs,[13,21]
E. K. U. Gross,[12] Andris Gulans,[14,15] François Gygi,[22] D. R. Hamann,[23,24]
Phil J. Hasnip,[25] N. A. W. Holzwarth,[26] Diana Iuşan,[13] Dominik B. Jochym,[27]
François Jollet,[28] Daniel Jones,[29] Georg Kresse,[30] Klaus Koepernik,[31,32]
Emine Küçükbenli,[9,11] Yaroslav O. Kvashnin,[13] Inka L. M. Locht,[13,33] Sven Lubeck,[14]
Martijn Marsman,[30] Nicola Marzari,[9] Ulrike Nitzsche,[31] Lars Nordström,[13]
Taisuke Ozaki,[34] Lorenzo Paulatto,[35] Chris J. Pickard,[36] Ward Poelmans,[1,37]
Matt I. J. Probert,[25] Keith Refson,[38,39] Manuel Richter,[31,32] Gian-Marco Rignanese,[19]
Santanu Saha,[20] Matthias Scheffler,[15,40] Martin Schlipf,[22] Karlheinz Schwarz,[5]
Sangeeta Sharma,[12] Francesca Tavazza,[17] Patrik Thunström,[41] Alexandre Tkatchenko,[15,42]
Marc Torrent,[28] David Vanderbilt,[23] Michiel J. van Setten,[19]
Veronique Van Speybroeck,[1] John M. Wills,[43] Jonathan R. Yates,[29]
Guo-Xu Zhang,[44] Stefaan Cottenier[1,45]*
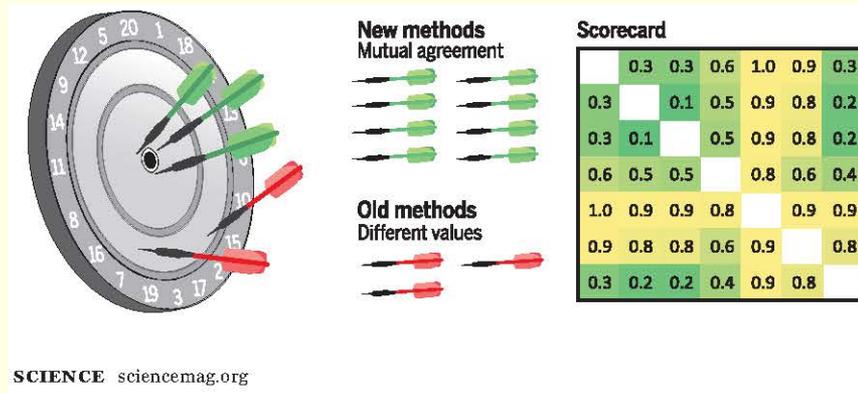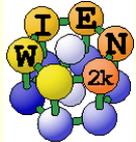
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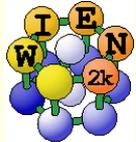
The most accurate code

AE: all electron

	average $\langle\Delta\rangle$	Elk	exciting	FHI-aims/tier2	FLEUR	FPLO/T+F+s	RSPt	WIEN2k/acc
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+s	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
WIEN2k/acc	0.5	0.3	0.2	0.2	0.4	0.9	0.8	
PAW								
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
PSlib100/QE	0.9	0.9	0.8	0.8	0.8	1.3	1.1	0.8
VASPGW2015/VASP	0.6	0.4	0.4	0.4	0.6	1.0	0.8	0.3
USPP								
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
NCPP								
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
MBK2013/OpenMX	2.0	2.1	2.1	2.1	1.9	1.8	1.8	2.0
ONCVPSP(PD0.1)/ABINIT	0.7	0.7	0.7	0.7	0.6	1.0	0.8	0.6
ONCVPSP(SG15)1/QE	1.4	1.4	1.3	1.3	1.3	1.6	1.5	1.3
ONCVPSP(SG15)2/CASTEP	1.4	1.4	1.4	1.4	1.3	1.6	1.5	1.4

Fig. 4. Δ 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 (NCPP) 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 NCPP) and are explained in full in tables S3 to S42. The color coding illustrates the range from small (green) to large (red) Δ 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 Δ matrix for all methods mentioned in this article.

# Precision of DFT calculations illustrated for Si
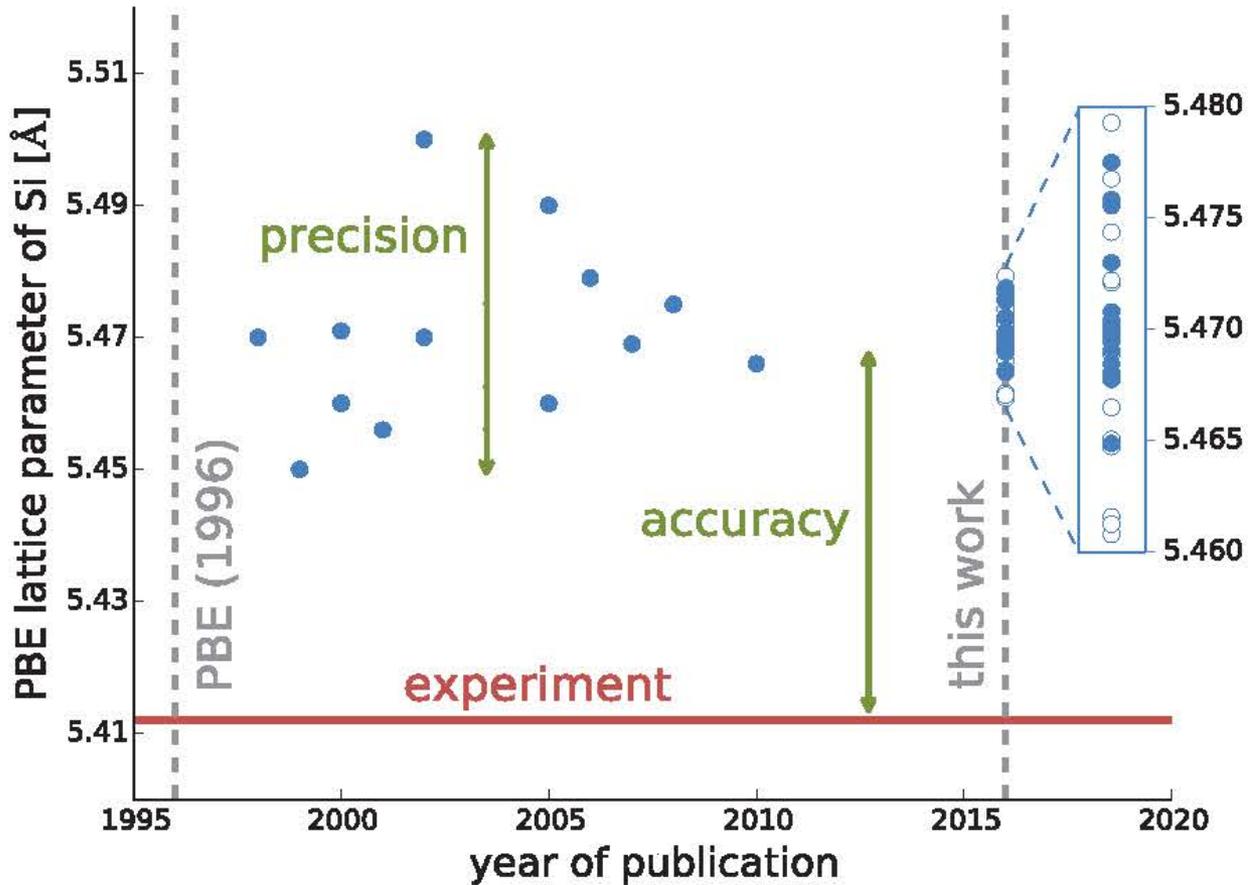
Fig. 1. Historical evolution of the predicted equilibrium lattice parameter for silicon. All data points represent calculations within the DFT-PBE framework. Values from literature (data points before 2016) (15, 16, 18, 56–62, 63–65) are compared with (i) predictions from the different codes used in 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 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) →
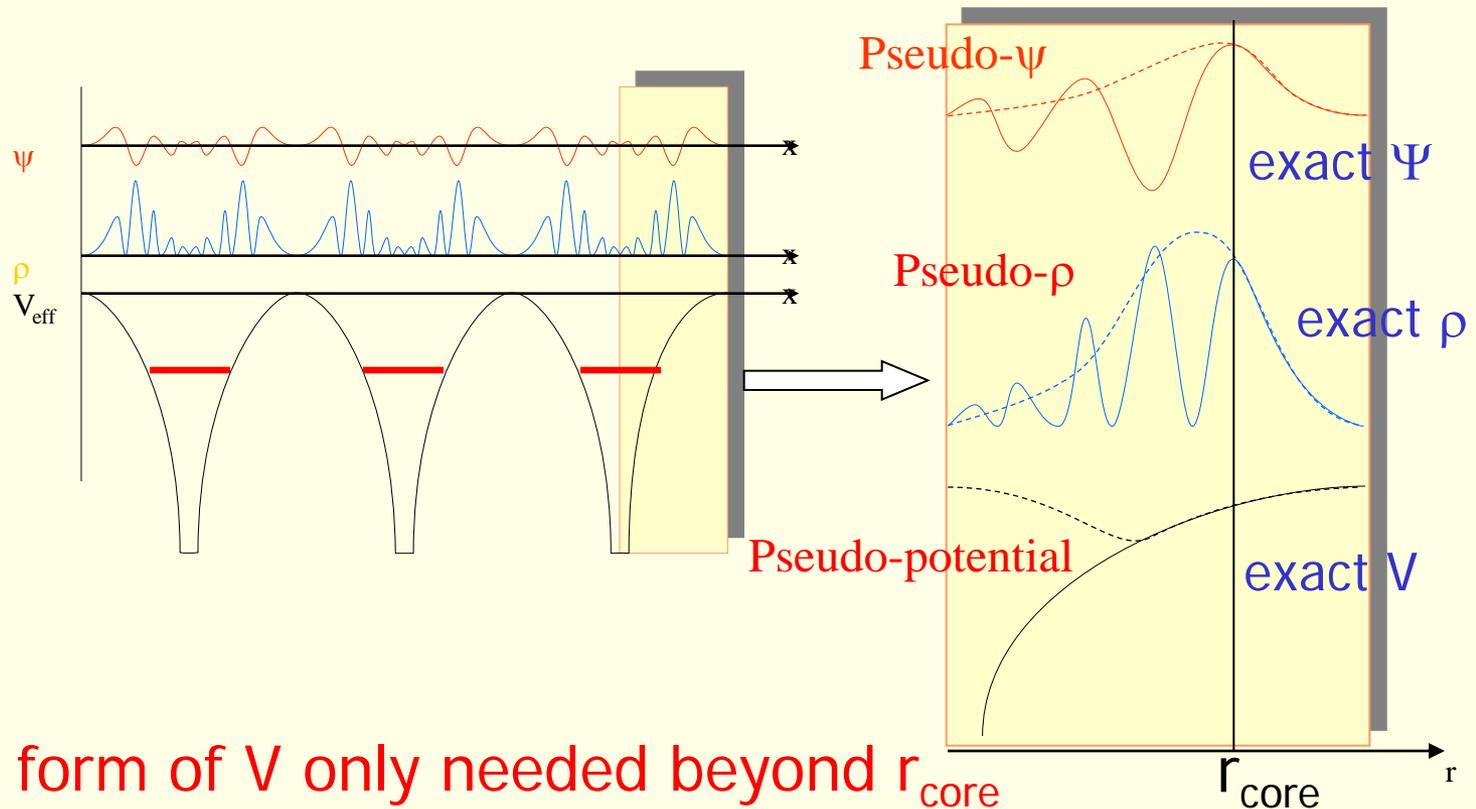
→exact form of V only needed beyond r_{core}
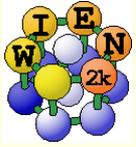
Crucial aspects for a simulation

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

Structure model:	Quantum mechanics:	Convergence:	Other effects:
unit cell	mean field (DFT)	basis sets	temperature T>0 K
supercell	many body theory	**k**-points	pressure
surface	ground vs. excited states		

stoichiometry	electron core-hole	vacuum	average
disorder	satellites	supercell	vibrations
impurities, defects	all electron	ℓ quantum n.	
	relativistic effects		

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

Vienna, city of music and the Wien2k code
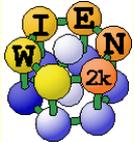
Walter Kohn

- **1997** DFT Conferene in Vienna
  - *Walter Kohn Main speaker*

- **1998** **Nobel Prize**
  for Chemmistry

- **2001** invited lecturer
  - *My 60th birthday*
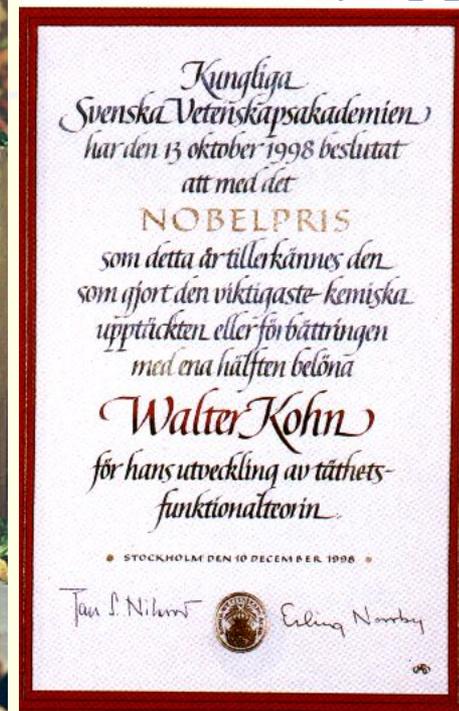
International Conference on
Applied Density Functional
Theory
January 14-17, 2001
Vienna/Austria

dedicated to Karlheinz Schwarz
on occasion of his 60th birthday
Honorary Chairman: Walter Kohn

16. 1. 2001

Walter Kohn
Peter & Claude Skplicky

Walter Kohn's 80

Ecole Normale Supérieur

WIEN2k
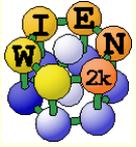
- **W**orld of
- **I**nteracting
- **E**lectrons and
- **N**uclei

due

walter **k**ohn **2**