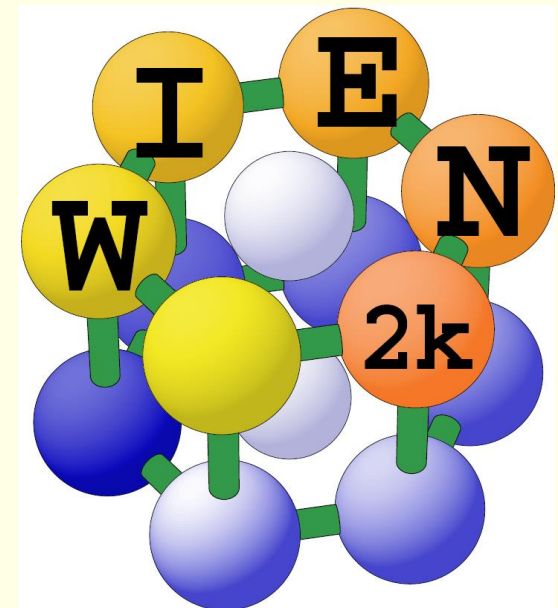# Density functional theory (DFT) and the concepts of the augmented-plane-wave plus local orbital (L)APW+lo method

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A series of **WIEN workshops** were held

- 1st   Vienna   Wien95   April 1995
- 2nd   Vienna   April 1996
- 3rd   Vienna   Wien97   April 1997
- 4st   Trieste Italy   June 1998
- 5st   Vienna   April 1999
- 6th   Vienna   April 2000
-     **Wien2k**
- 7th   Vienna   Sept 2001
- 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   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
- 24th   Vienna   Sept 2017
- 25th   Boston, USA   June 2018
- 26th   Vienna   Aug. 2019
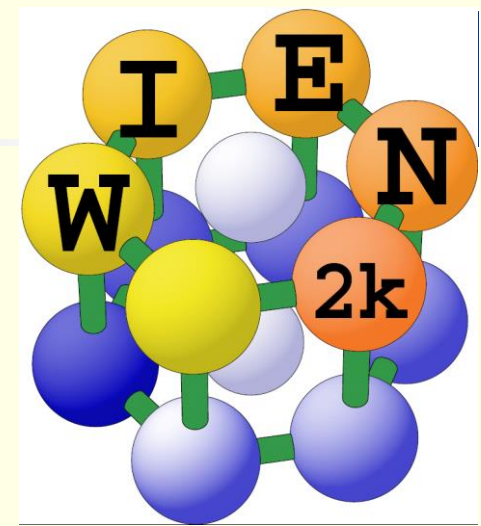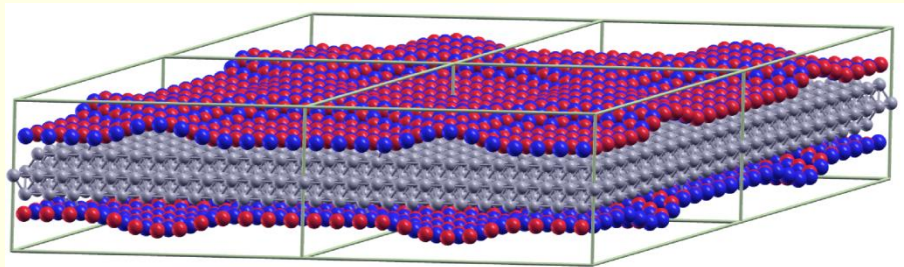- 27th   Triest, Italy   April 2024
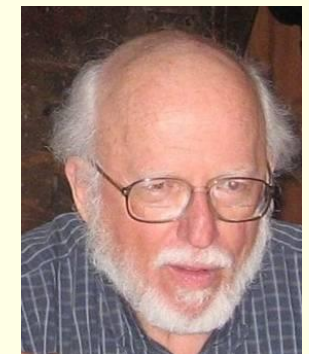
DFT

APW
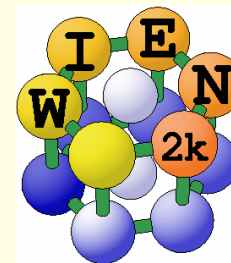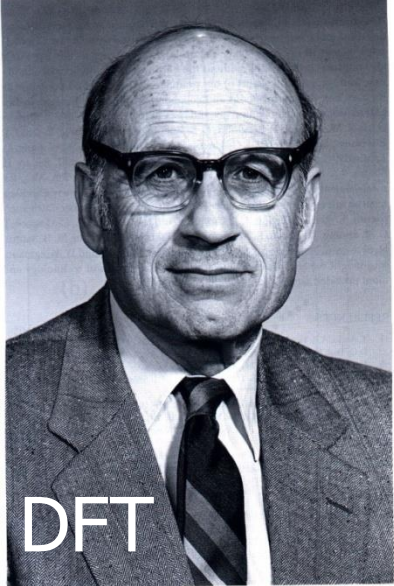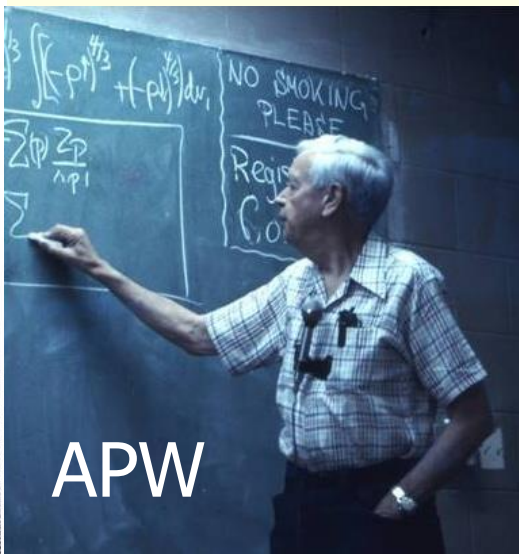
LAPW

J.C.Slater

O.K.Andersen

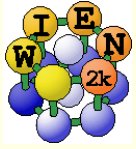Electronic structure of solids and surfaces

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
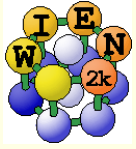by about 3800 groups

Walter Kohn

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 43 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*
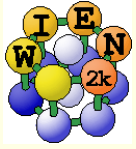 - *See www.wien2k.at*

- **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

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

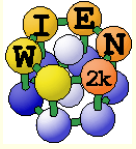| Structure model:	Quantum mechanics:	Convergence:	Other effects:
unit cell supercell surface	mean field (DFT) many body theory ground vs. excited states	basis sets **k**-points	temperature T>0 K pressure

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

These aspects need to be considered when comparing **theory** 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)*

A few solid state concepts

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

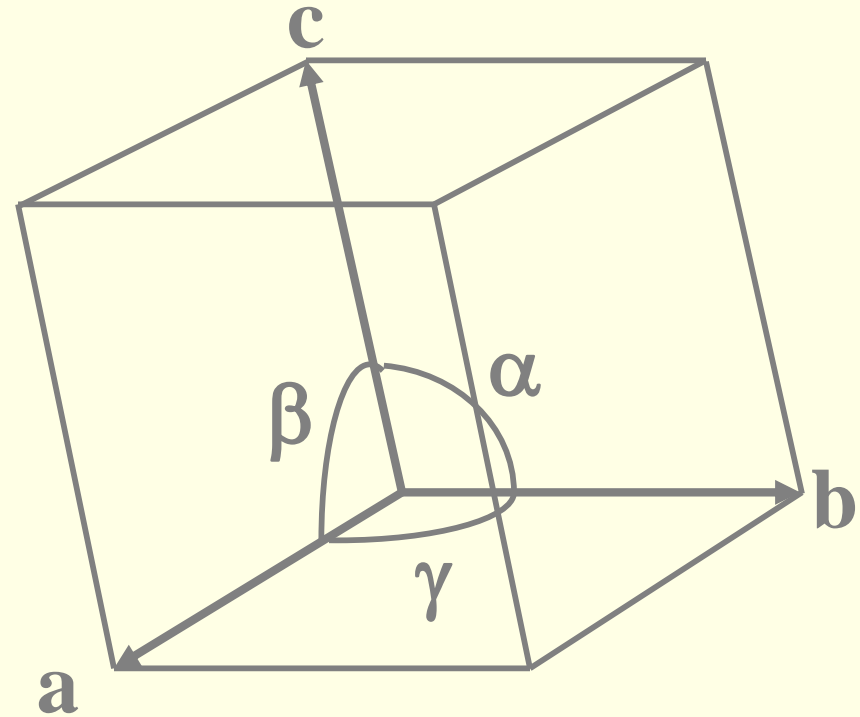Assuming an ideal infinite crystal we define a unit cell by

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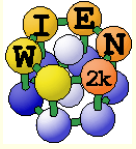
The obvious choice:

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

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

the cell is as symmetric as possible (14 types)

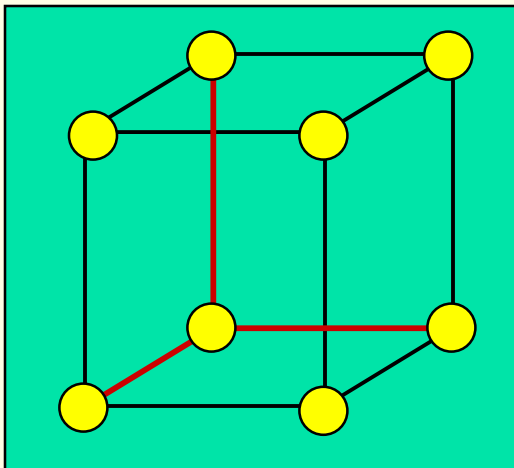A unit cell containing one lattice point is called primitive cell.
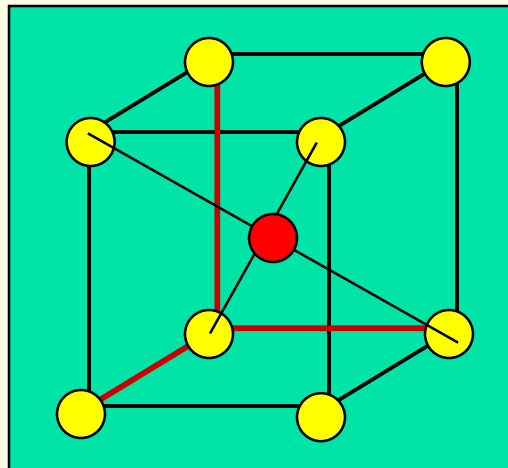
Crystal system: e.g. cubic

Axis system

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

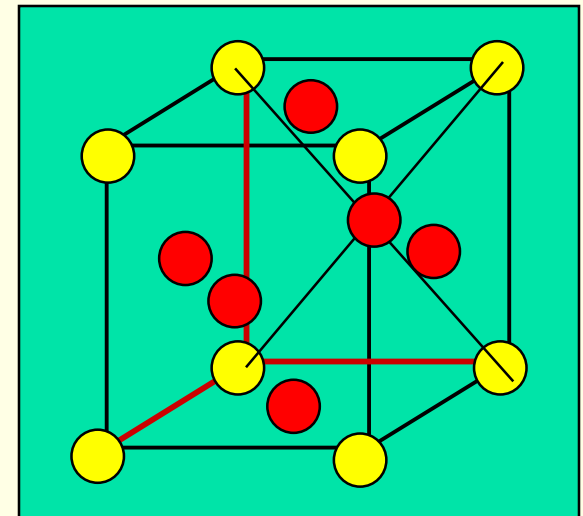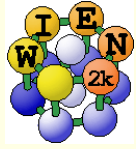**primitive**   **body centered**   **face centered**

P (cP)   **I (bcc)**   **F (fcc)**

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

triclinic ----- monoclinic -------------

-- orthorhombic ---------- --------

tetragonal   hexagonal   trigonal

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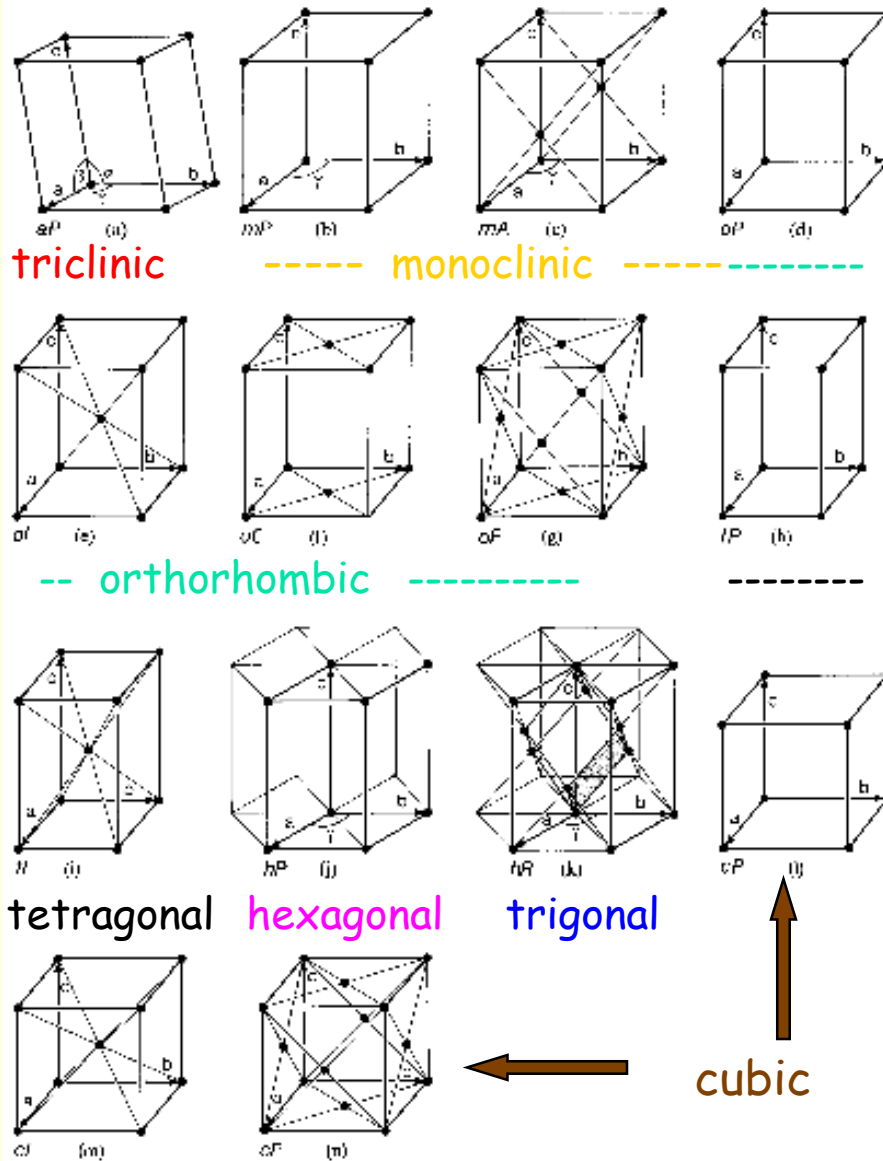
Form connection to all neighbors and span a plane normal to the connecting line at half distance

Finite particle with a length in nm

surface

n=3   3x3x3 particle
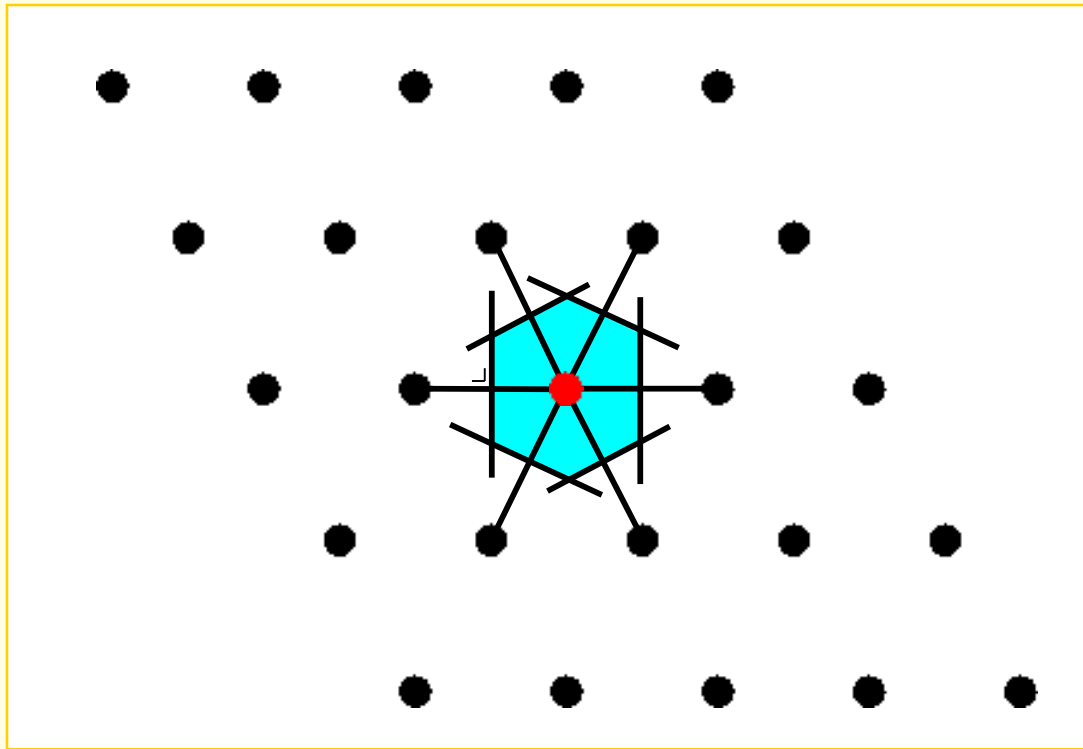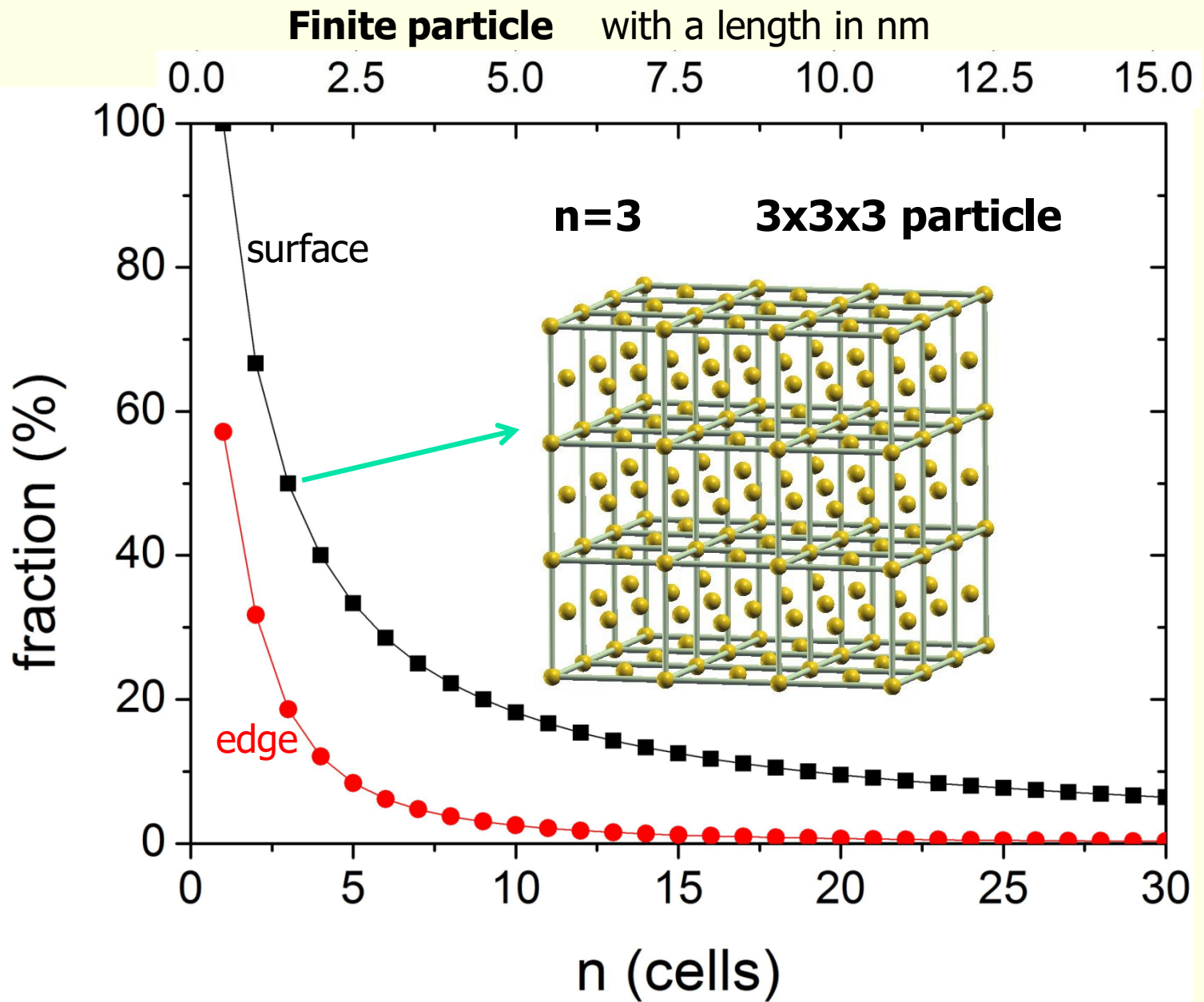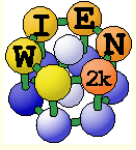
edge

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**:

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

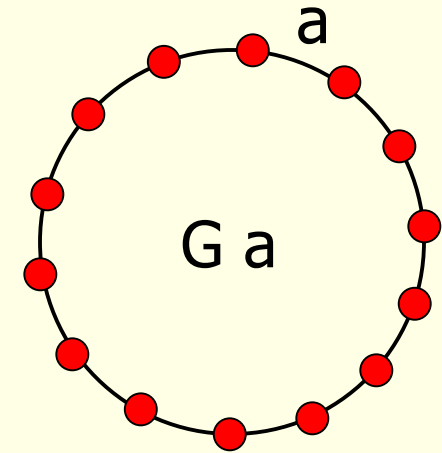$$\Psi(x+a) = \mu\Psi(x) \quad \Rightarrow \quad \mu^*\mu = 1$$

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):

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

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

a

G a

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

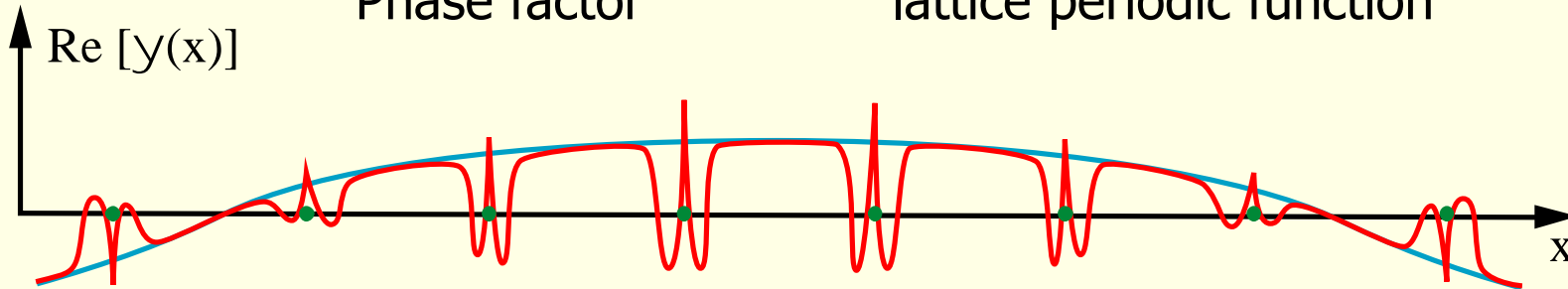$$Def.: \quad \boxed{k} = \frac{2\pi}{a} \frac{g}{G} \qquad \mu = e^{ika}$$

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

- **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 [y(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 .

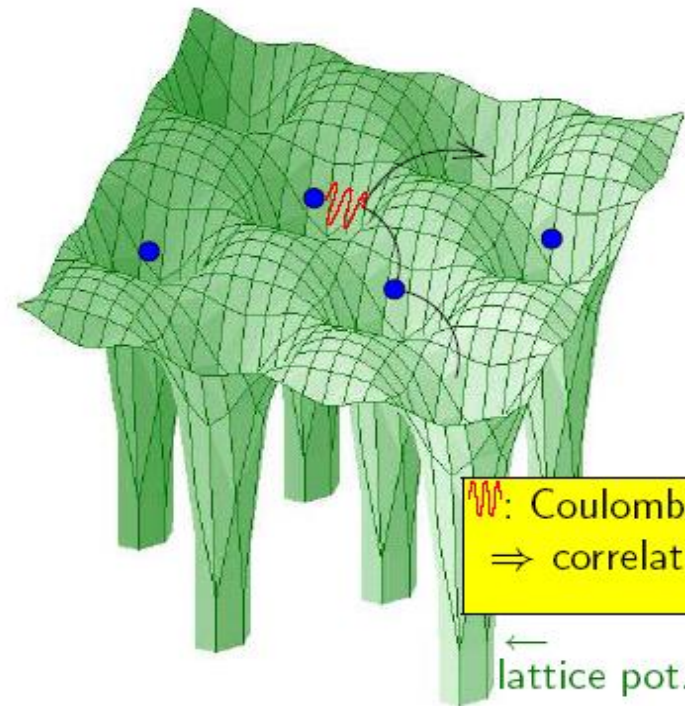$$e^{i\frac{2\pi}{a}K} = 1 \qquad\qquad -\frac{\pi}{a} < k < \frac{\pi}{a}$$

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
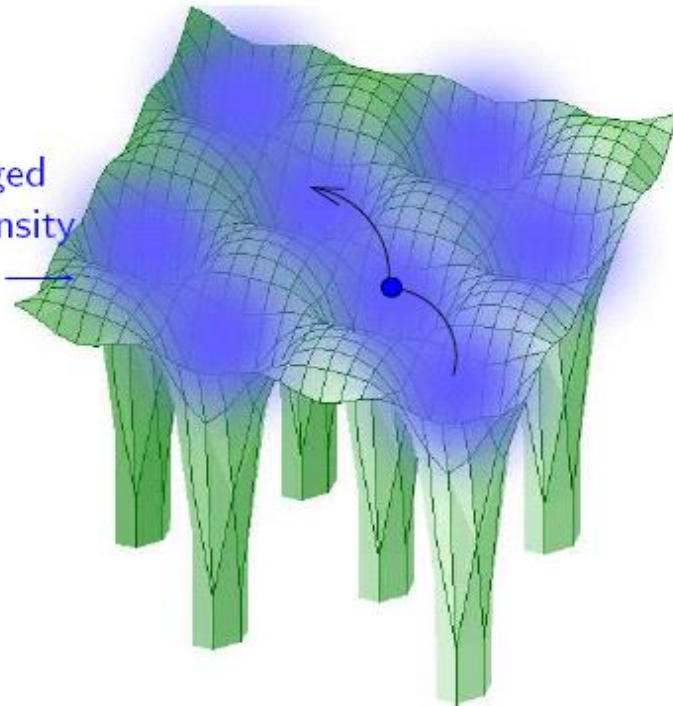
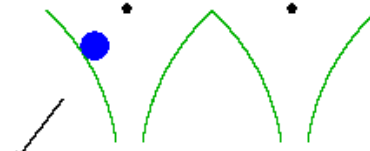: Coulomb WW
⇒ correlations

lattice pot.
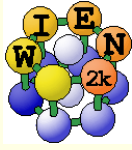
Ab-initio Hamiltonian

(non-relativistic/Born-Oppenheimer approximation)

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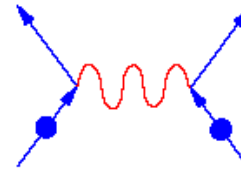
$$H = \sum_i \left[-\frac{\hbar^2 \Delta_i}{2m_e} + \sum_l \frac{-e^2}{4\pi\epsilon_0} \frac{Z_l}{|\mathbf{r}_i - \mathbf{R}_l|} \right] + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

LDA bandstructure corresponds to

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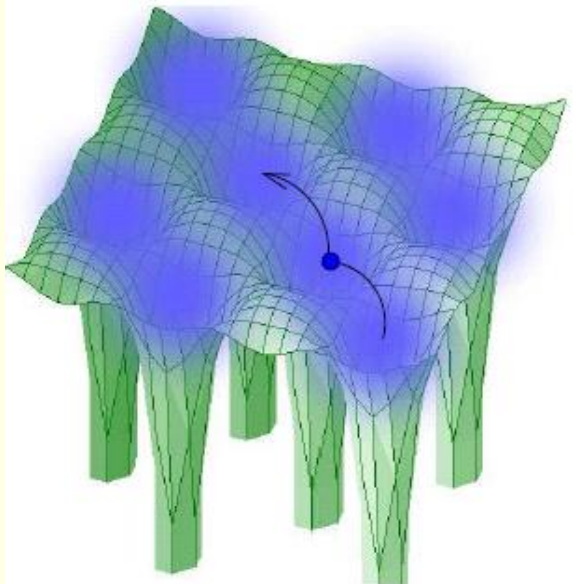
Coulomb potential:
- nuclei
- all electrons
- including self-interaction

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

Quantum mechanics

Time-independent (without relativistic effects)
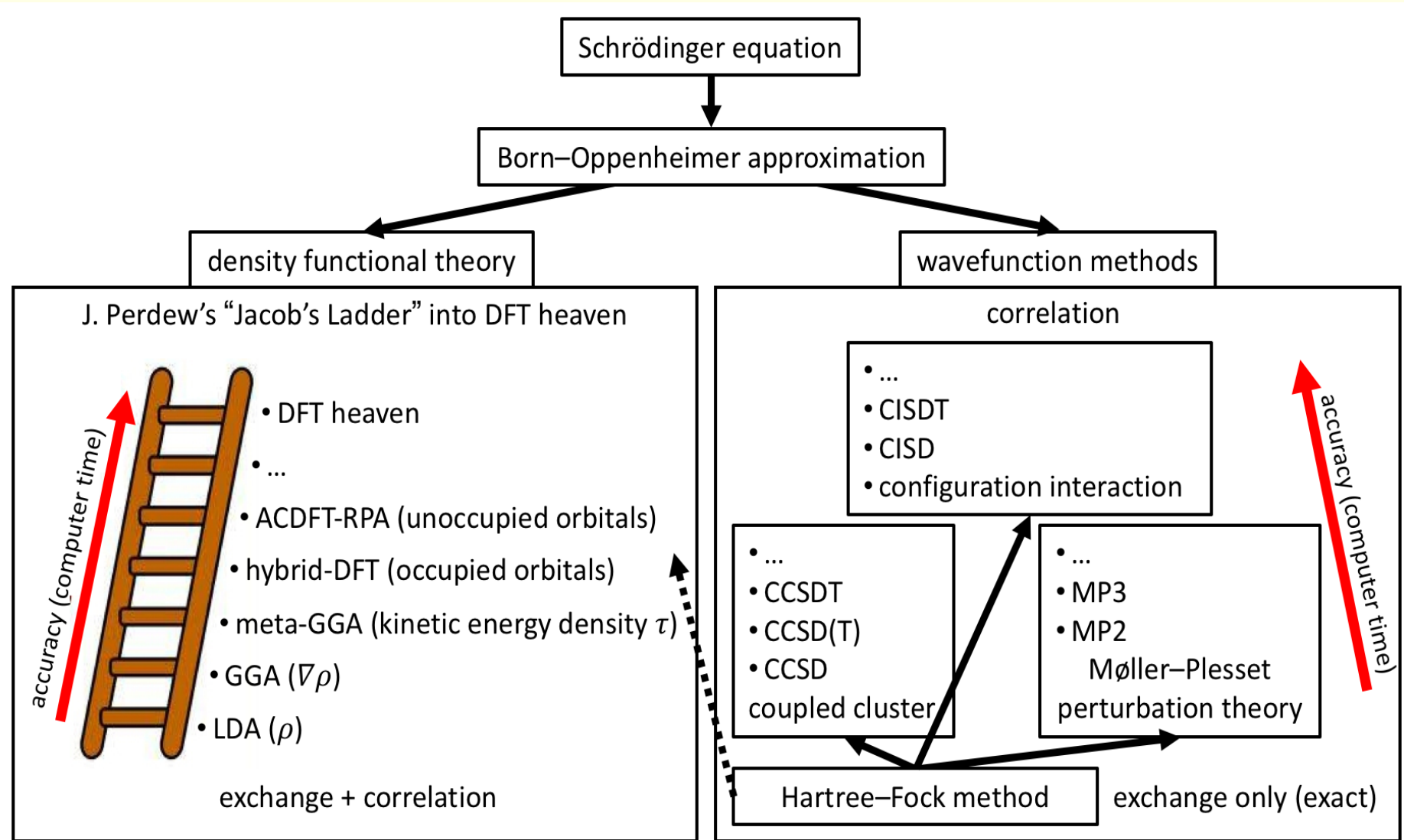
■ Find a functional which leads to "DFT heaven": ➡

predictive power with chemical accuracy

■ J. Perdew's „Jacob's ladder" into DFT heaven:

accuracy (computer time) →
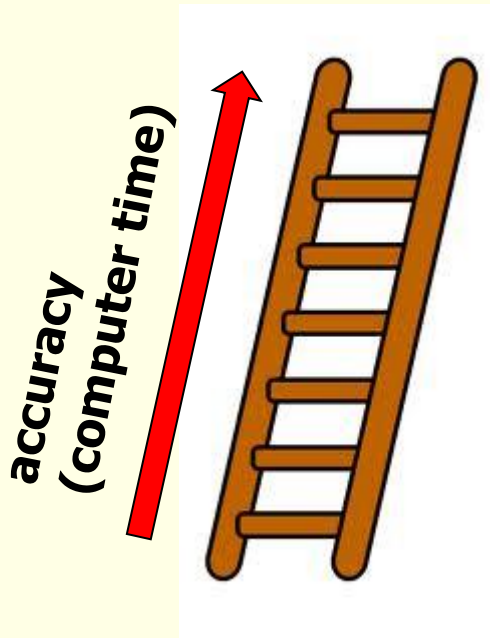
- DFT heaven

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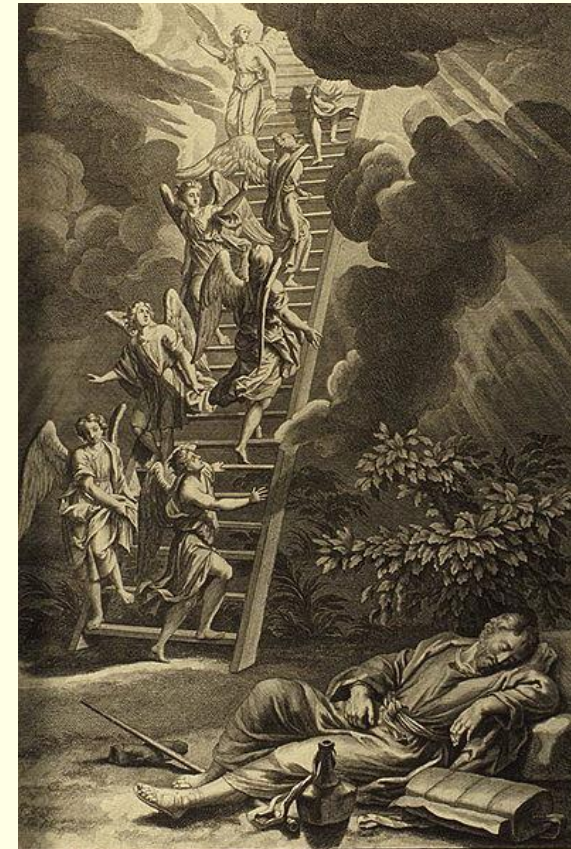
DFT versus the Schrödinger Equation

We have moved our problem from here ...

Properties of the system

SE

KS

Hard problem to solve

"Easy" problem to solve

Schrödinger view
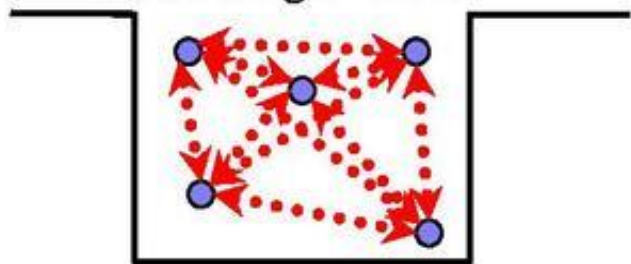
Formally equivalent

DFT view
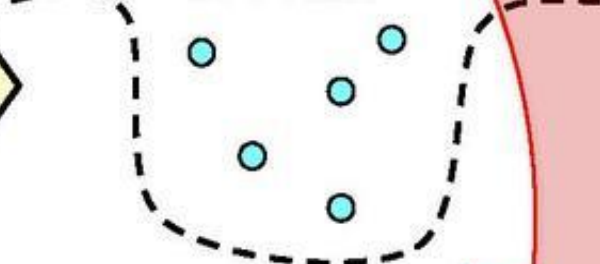
- electron
- interaction
- external potential

Kohn-Sham particle (non-interacting)

effective potential

$$v_{eff}(\boldsymbol{r}) = v(\boldsymbol{r}) + \int \frac{n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\,d\boldsymbol{r}' + \frac{\delta E_{xc}[n(\boldsymbol{r})]}{\delta n(\boldsymbol{r})}$$

... to here

All many-body effects are included in the effective potential via the Exchange-Correlation functional, $E_{xc}[n(\boldsymbol{r})]$.

LORD

Sandia National Laboratories

$$H = -\sum_{i=1}^{n} \frac{1}{2} \nabla_i^2 - \sum_{i=1}^{n} \frac{Z}{r_i} + \sum_{i<} \sum_{j} \frac{1}{r_{ij}}$$

Hamilton operator:

Indistinguishablility of electrons

t_1 (time) t_2 Ze

1   2

1
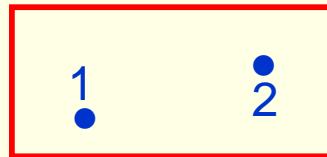
2
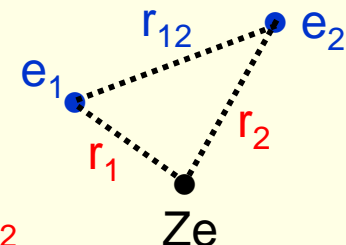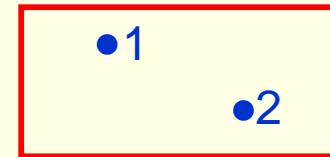
Many-electron wave function

$$\psi(r_1 \vartheta_1 \varphi_1 m_{s1}, r_2 \vartheta_2 \varphi_2 m_{s2}, ...) = \psi(1, 2, ...)$$

Permutation $P_{12}\psi(1,2) = \psi(2,1) = \frac{-}{+}\psi(1,2)$

- fermions   **+** bosons

half-integer   integer spin

electrons   photons

Pauli principle: (antisymmetric WF)

Wolfgang Pauli

Schrödinger equ. not exactly solvable due to el-el interaction

$\frac{1}{r_{ij}}$

Hartree approximation: effective Hamilton operator

$$H_{eff} = \sum_{i=1}^{n} [-\frac{1}{2}\nabla_i^2 + V_i(r_i)] = \sum_{i=1}^{n} H_i$$

effective potential (for el. i)   average over all other electrons

$$V_i = -\frac{Z}{r_i} + \sum_{j \neq i} \int \frac{\overline{u_j^* u_j}}{r_{ij}} d\tau$$ spherical averaged (only r dependent)

$$\psi(1,2,...n) = u_1(1)u_2(2)...u_n(n)$$

product:

many el. WF   1-el.WF

one-electron WF: $u_{n_i \ell_i m_i m_{si}}(r_i, \vartheta_i, \varphi_i, m_{s_i})$

Quantum numbers   coordinates

e⁻ are **fermions**, they must be

   antisymmetric $\Psi(2,1) = - \Psi(1,2)$

The wave function as "**Slater-Determinant**".

$$\Psi = \sqrt{\frac{1}{N!}} \begin{vmatrix} \psi_1(1) & \psi_2(1) & \cdots & \psi_N(1) \\ \psi_1(2) & \psi_2(2) & \cdots & \psi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(N) & \psi_2(N) & \cdots & \psi_N(N) \end{vmatrix}$$

The basic concept for the Hartree Fock method

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).**

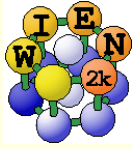- **The density of particles interacting with each other can be calculated as the density of an auxiliary system of non-interacting particles (Kohn, Sham, 1965).**

Walter Kohn's 80

Ecole Normale Supérieur

Kohn-Sham equations

LDA, GGA

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

vary ρ

1-electron equations (Kohn Sham)

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

-Z/r

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

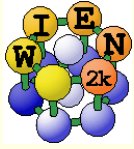$$\frac{\partial E_{xc}(\rho)}{\partial\rho}$$

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

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

LDA — treats both, exchange and correlation effects,

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

GGA — but approximately

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

Exchange and correlation

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

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

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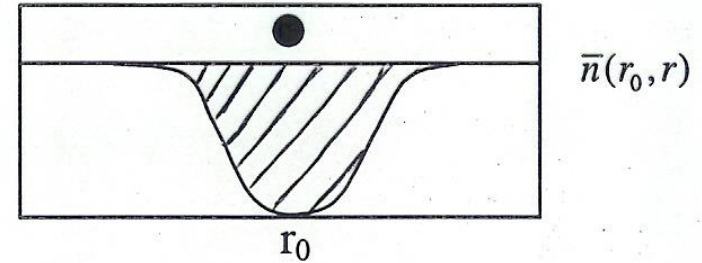
Properties of the exchange-correlation hole:
- Locality
- Pauli principle
- the hole contains ONE electron
- The hole must be negative

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

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

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

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

- 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:

$$\int dr\, h_c(r_0, r) = 0$$
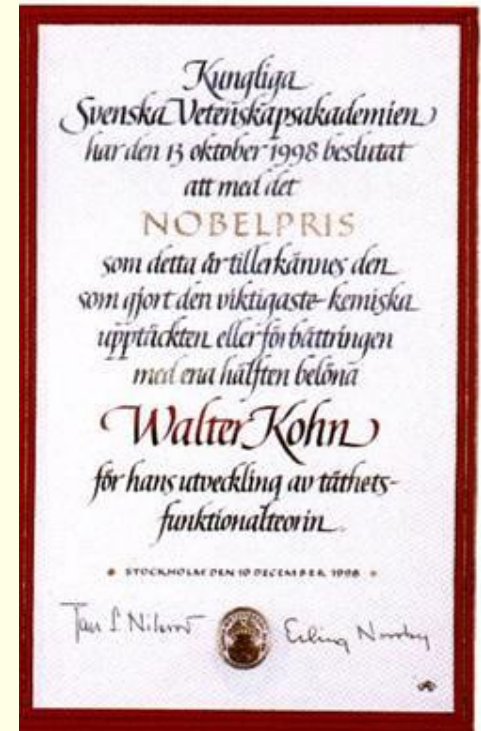
"Self-consistent Equations including Exchange and Correlation Effects"
W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965)

59 years ago

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

Walter Kohn

- 1923 he was born in Vienna (March 9, 1923)

- 1938 had to leave Vienna

- (England, Canada, Toronto, Havard)

- 1948 PhD Havard (with J.Schwinger)

- Active in many places: Pennsylvania, Michigan, Washington, Paris, Imperial College (London) ETH (Zürich),…

- 1960-79 Univ.of California, San Diego

- 1984 Founding director Inst. for Theoret.Physics, Santa Barbara, California

- 1964 **Hohenberg Kohn**

- 1965 **Kohn Sham**

- 1998 **Nobel prize**: Chemistry

- 2016, he died on April 19, Santa Barbara

Obituary for Walter Kohn (1923–2016)

Karlheinz **Schwarz**, Lu J. **Sham**, Ann E. **Mattsson**, Matthias **Scheffler,**
Obituary for Walter Kohn (1923-2016)
Computation, **4**, 40 (2016)

Walter was born in Vienna on 9 March 1923 into a Jewish family. As a child, he attended the renowned Academic Gymnasium, where he liked Latin the most, but had little interest in physics or mathematics. The situation changed drastically in 1938 when Austria joined Nazi Germany—*the Anschluss*—and Walter was forced to leave this gymnasium, but he was able to enroll in the Jewish Chajes Gymnasium. There were two teachers—especially Emil Nohel, a former assistant of Einstein—who initiated his ambition for physics and mathematics. In 1939, the Kohn parents sent their 16-year-old son to Great Britain with one of the last children's transport rescue missions (*Kindertransporte*). Walter never saw his parents again, as they were killed in Auschwitz. In 1940, when there was a risk of a UK invasion by Germany, he and other men who held German passports were considered to be "enemy aliens" and put in detention camps: first on the Isle of Man, and then Walter was shipped to Canada, where he worked in a woodcutter camp.

Approximations for E_{xc}

- LDA: $E_{xc}^{LDA} = \int f(\rho(\mathbf{r})) d^3 r$

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

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

- 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

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

Can LDA be improved ?

- **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)

DFT ground state of iron
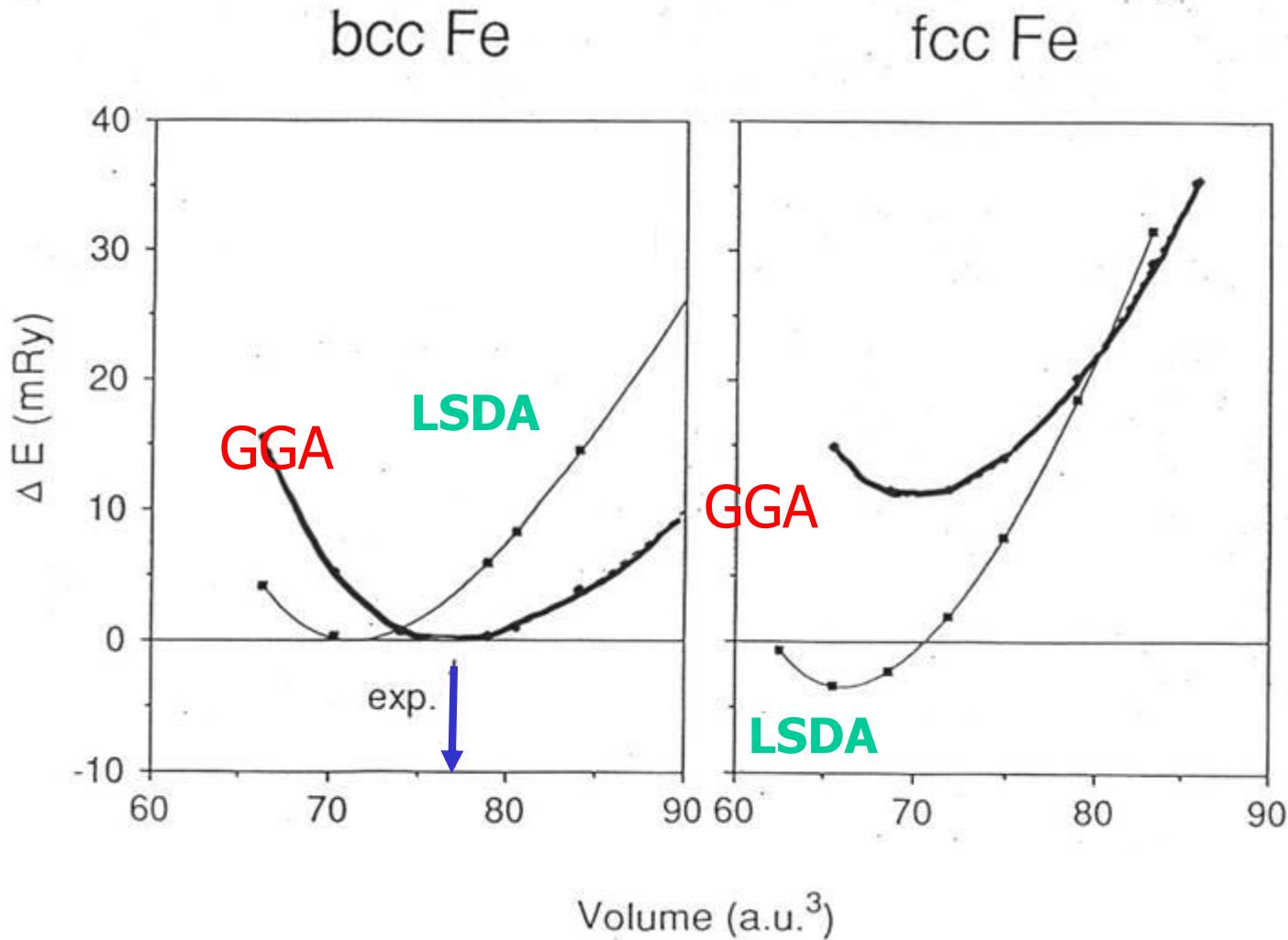
LSDA
- *NM*
- *fcc*
- *in contrast to experiment*

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

Experiment
- *FM*
- *bcc*

GGA follows LDA
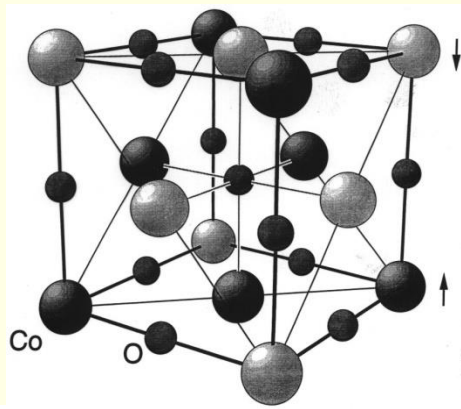
- **CoO**
  - *in NaCl structure*
  - *antiferromagnetic: AF II*
  - *insulator*
  - *t_{2g} splits into a_{1g} and e_g'*
  - *GGA almost spilts the bands*
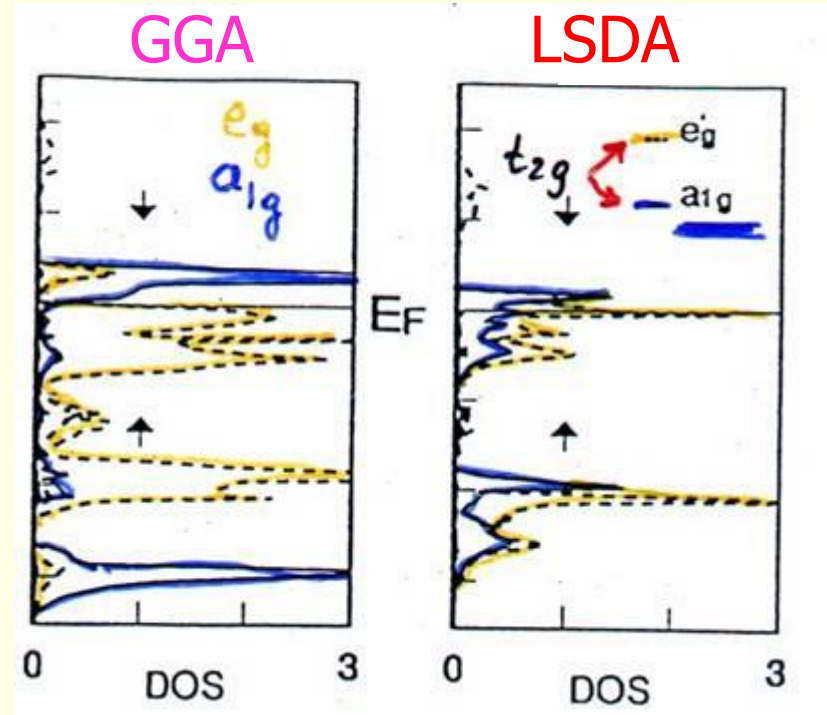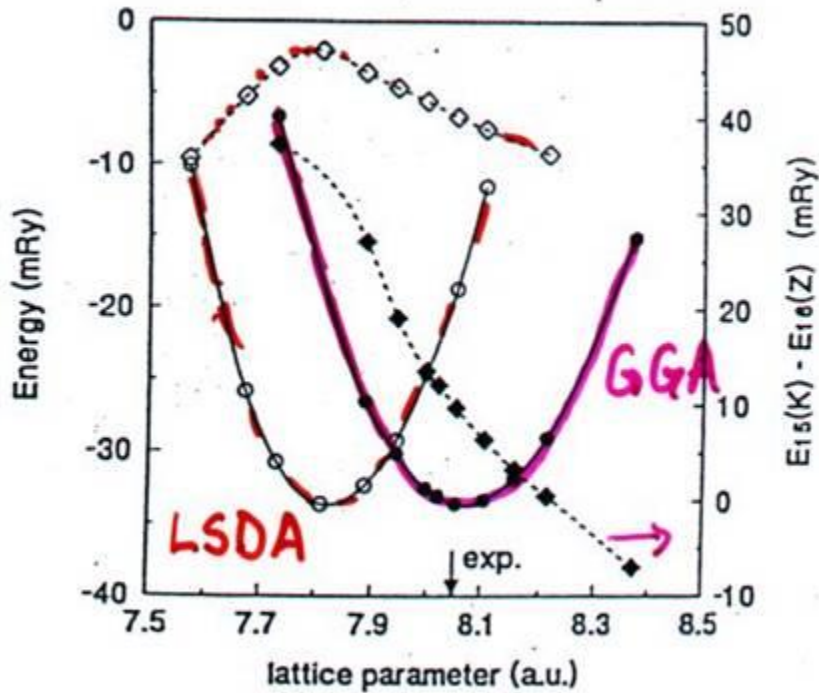
$$\Delta V_{xc}^{\uparrow} = V_{xc}^{\uparrow GGA} - V_{xc}^{\uparrow LSDA}$$
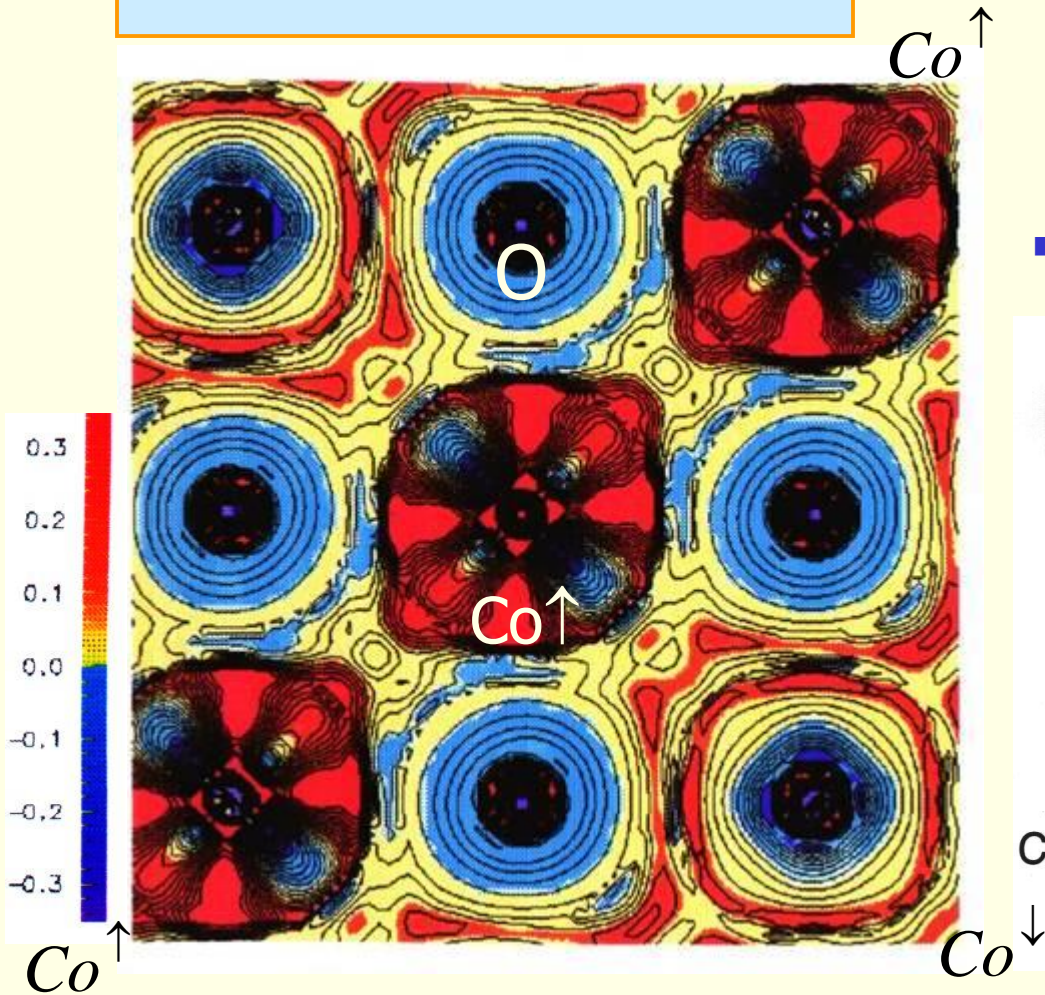
■ Central Co atom distinguishes

   ■ *between* $Co^{\uparrow}$

   ■ *and* $Co^{\downarrow}$

■ Angular correlation
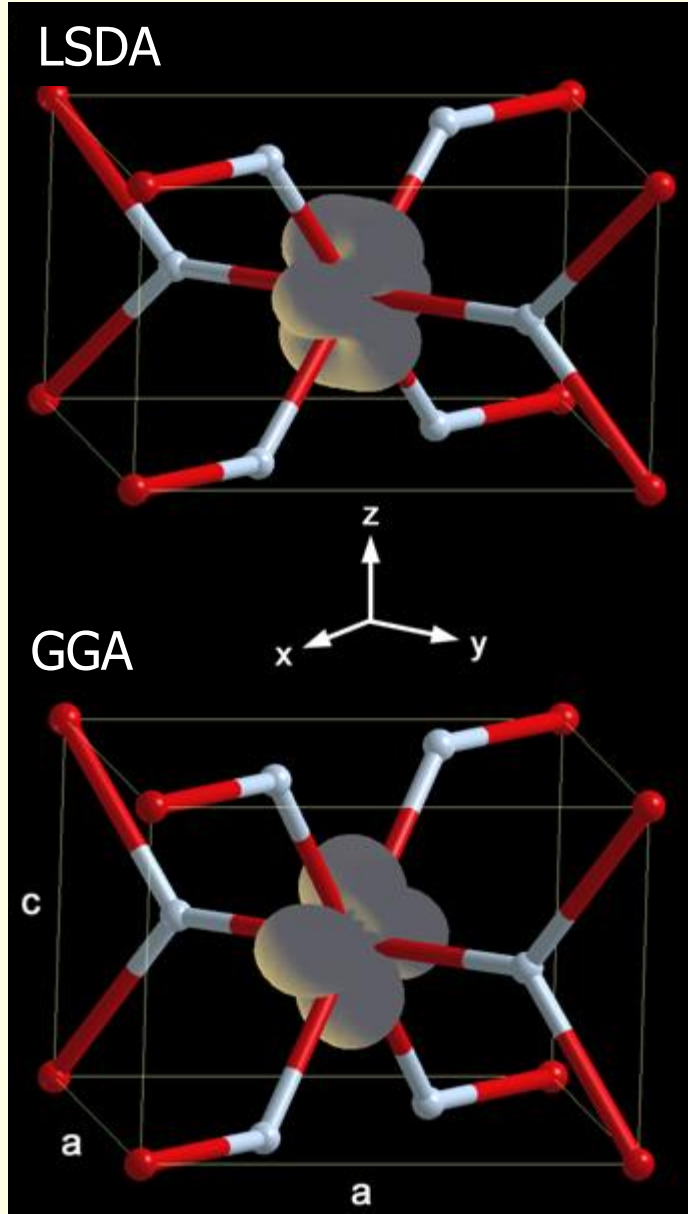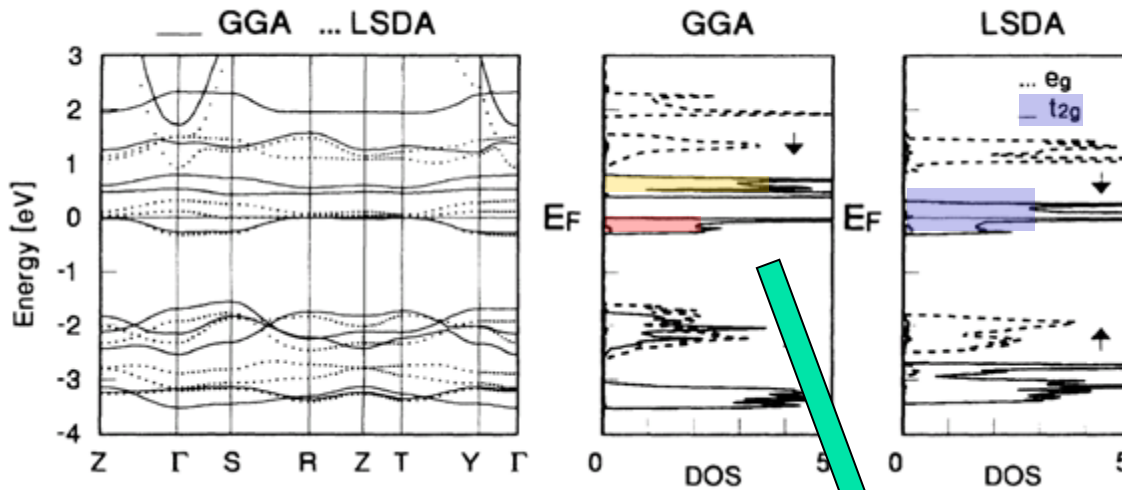
Fe-EFG in FeF$_2$:

LSDA: 6.2

GGA: 16.8

exp: 16.5

agree

FeF$_2$: GGA splits
t$_{2g}$ into a$_{1g}$ and e$_g$′

LSDA

GGA

Accuracy of DFT for transition metals

Lattice parameters (Å)

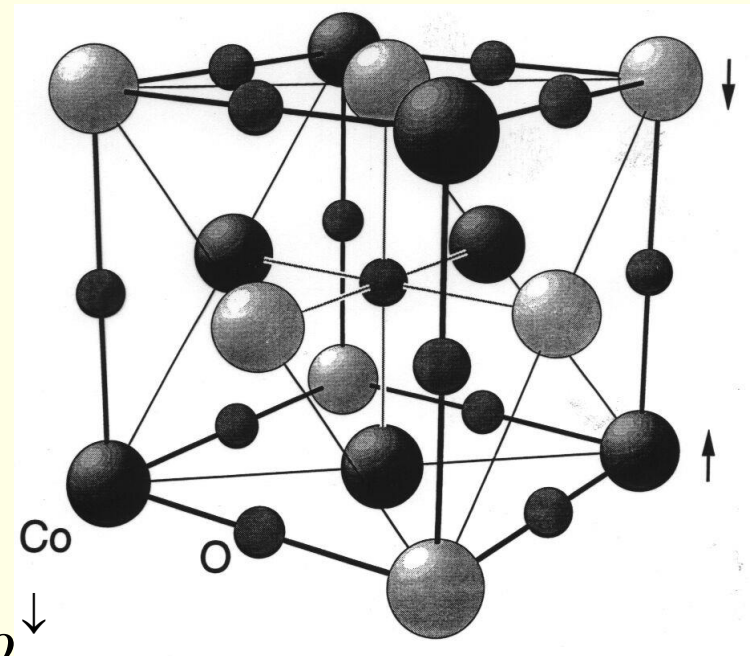|	Exp.	LDA	PBE	WC
Co	2.51	2.42	**2.49**	2.45
Ni	3.52	3.42	**3.52**	3.47
Cu	3.61	3.52	**3.63**	3.57
Ru	2.71	2.69	2.71	**2.73**
Rh	3.80	3.76	3.83	**3.80**
Pd	3.88	3.85	3.95	**3.89**
Ag	4.07	4.01	4.15	**4.07**
Ir	3.84	**3.84**	3.90	3.86
Pt	3.92	**3.92**	4.00	3.96
Au	4.08	**4.07**	4.18	4.11

- **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*

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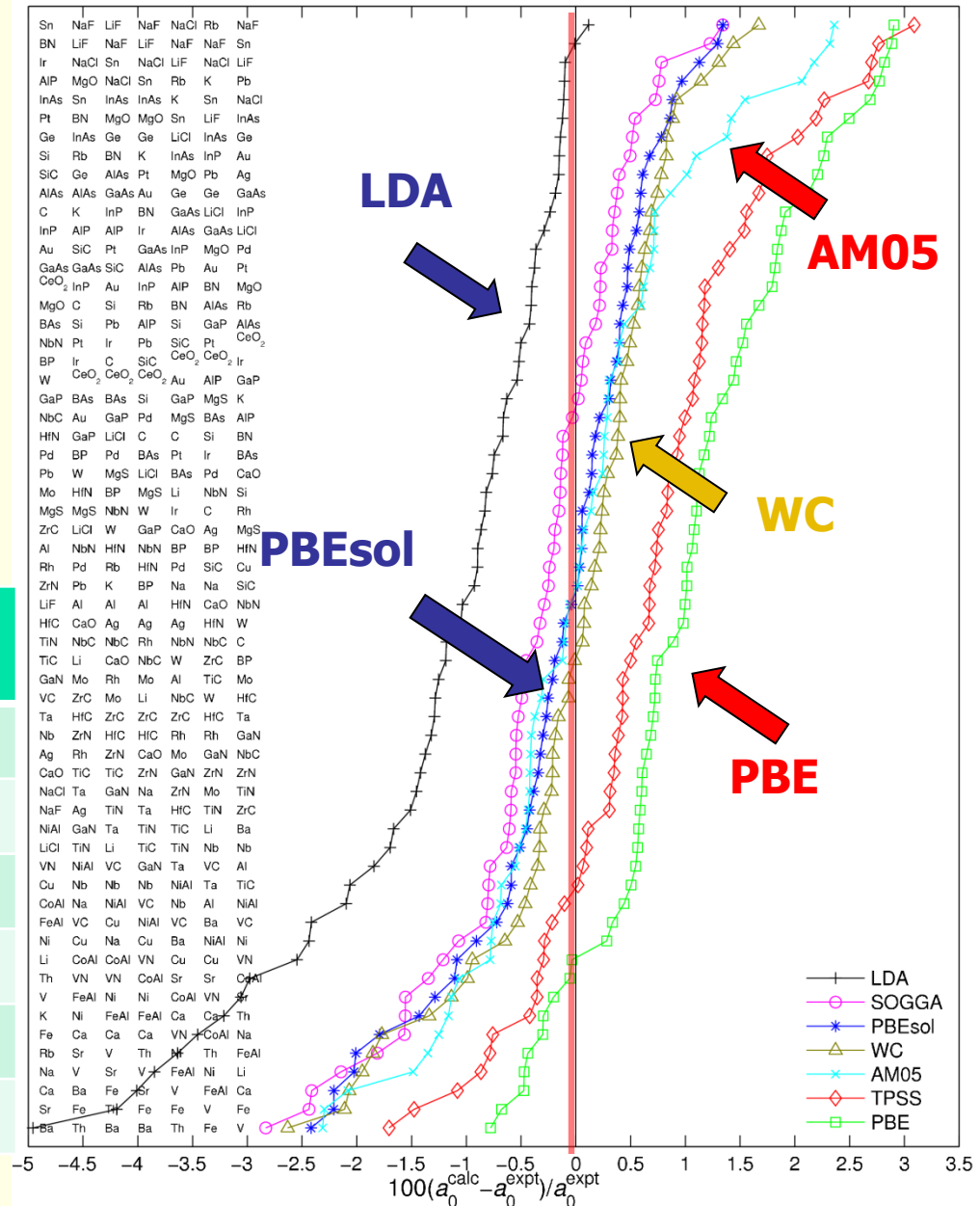
- **Only for certain atoms**
  and electrons of a given
  angular momentum ℓ

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

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

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

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

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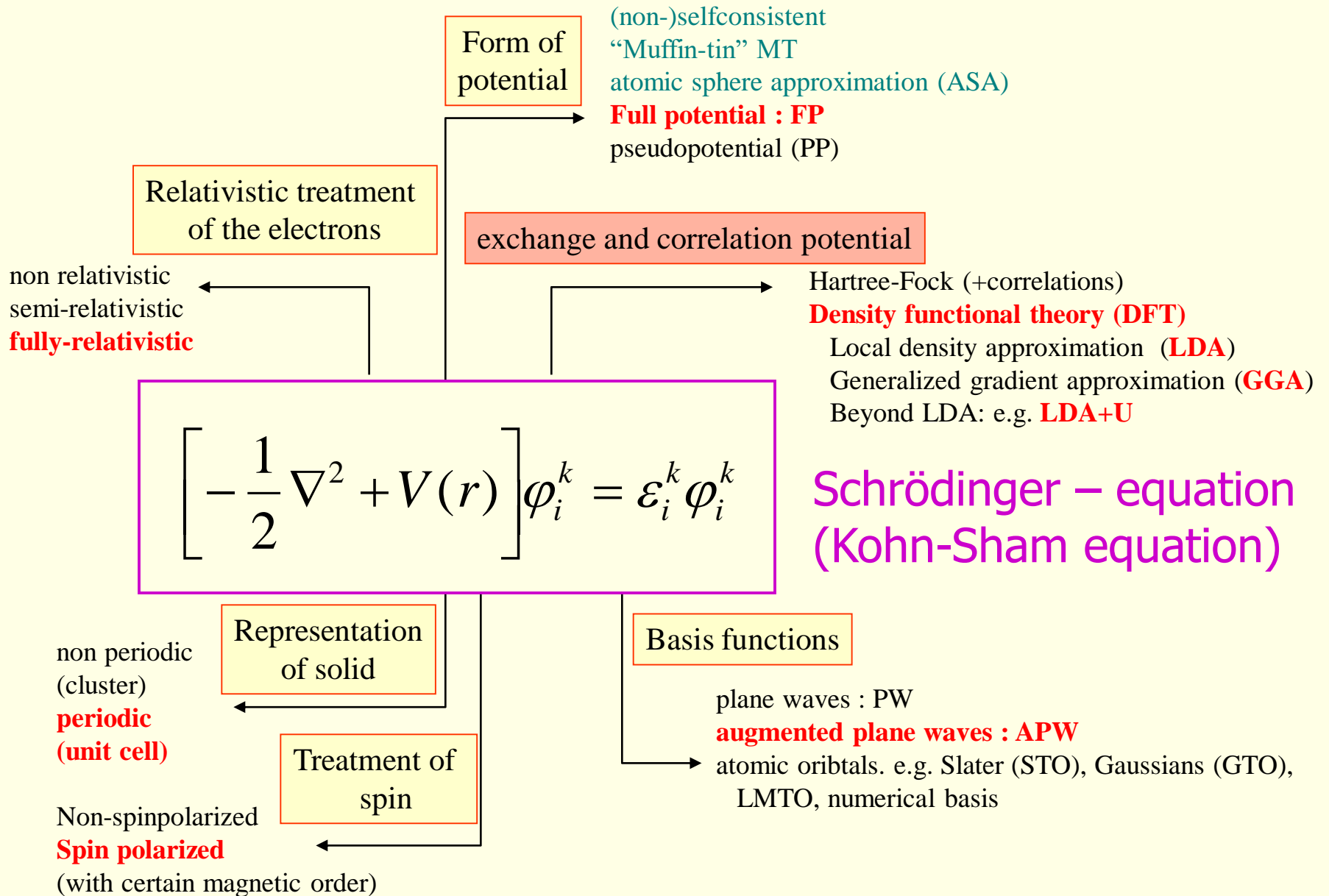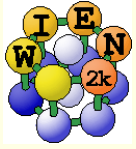
Hartree-Fock (+correlations)
Density functional theory (DFT)
    Local density approximation (**LDA**)
    Generalized gradient approximation (**GGA**)
    Beyond LDA: e.g. **LDA+U**

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

Schrödinger – equation
(Kohn-Sham equation)

Representation of solid

non periodic
(cluster)
**periodic
(unit cell)**

Basis functions

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

Treatment of spin

Non-spinpolarized
Spin polarized
(with certain magnetic order)

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

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

  - *this leads to the famous "Secular equations", i.e. a set of linear equations which in matrix representation is called "generalized eigenvalue problem"*
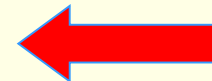
$$\boldsymbol{H\,C = E\,S\,C}$$

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

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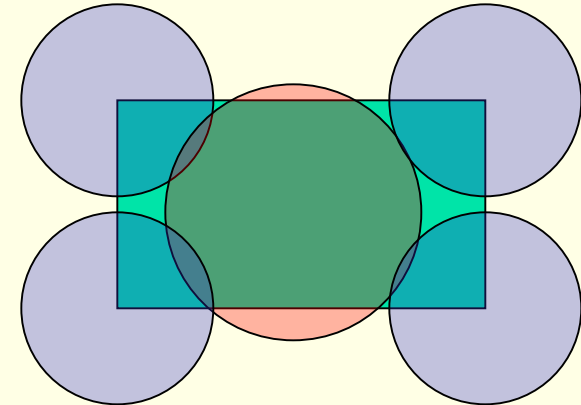
● plane waves form a "complete" basis set, however, they "never" converge due to the rapid oscillations of the atomic wave functions χ close to the nuclei

● 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*
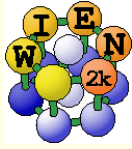
● Hellmann´s 1935 *combined approximation method*
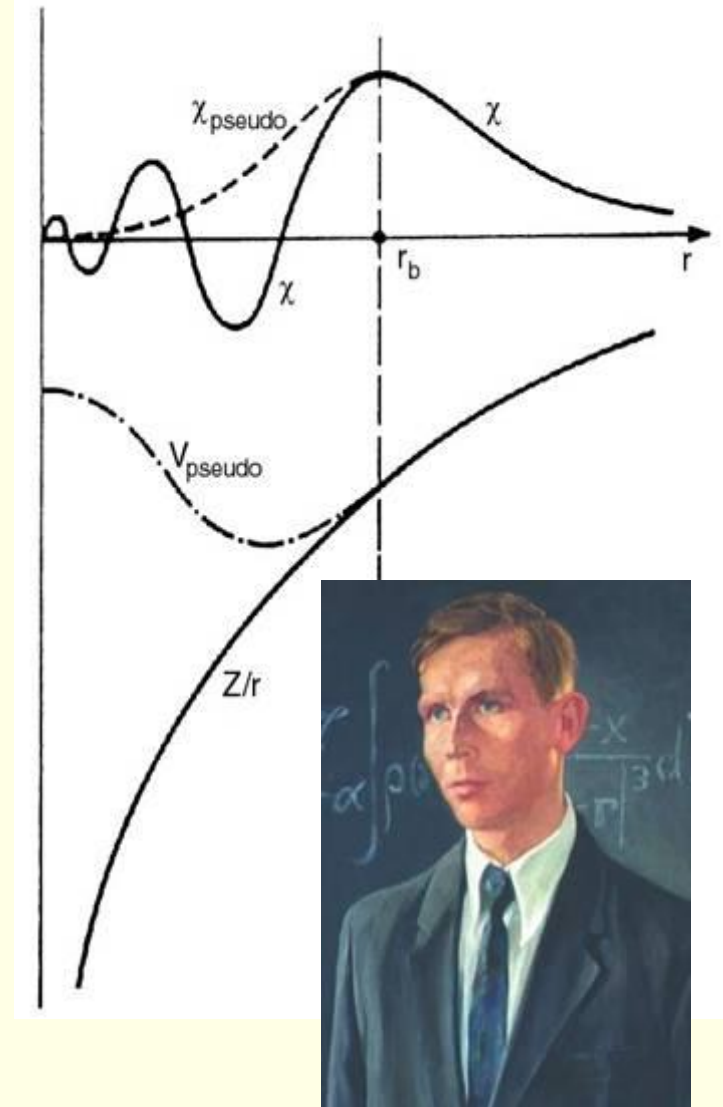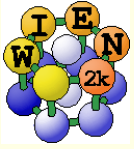
- "real" potentials contain the Coulomb singularity -Z/r
- the wave function has a cusp and many wiggles,
- chemical bonding depends mainly on the overlap of the wave functions between neighboring atoms (in the region between the nuclei) →

ψ

ρ

V_{eff}

Pseudo-ψ

exact Ψ

Pseudo-ρ

exact ρ

Pseudo-potential

exact V

r_{core}

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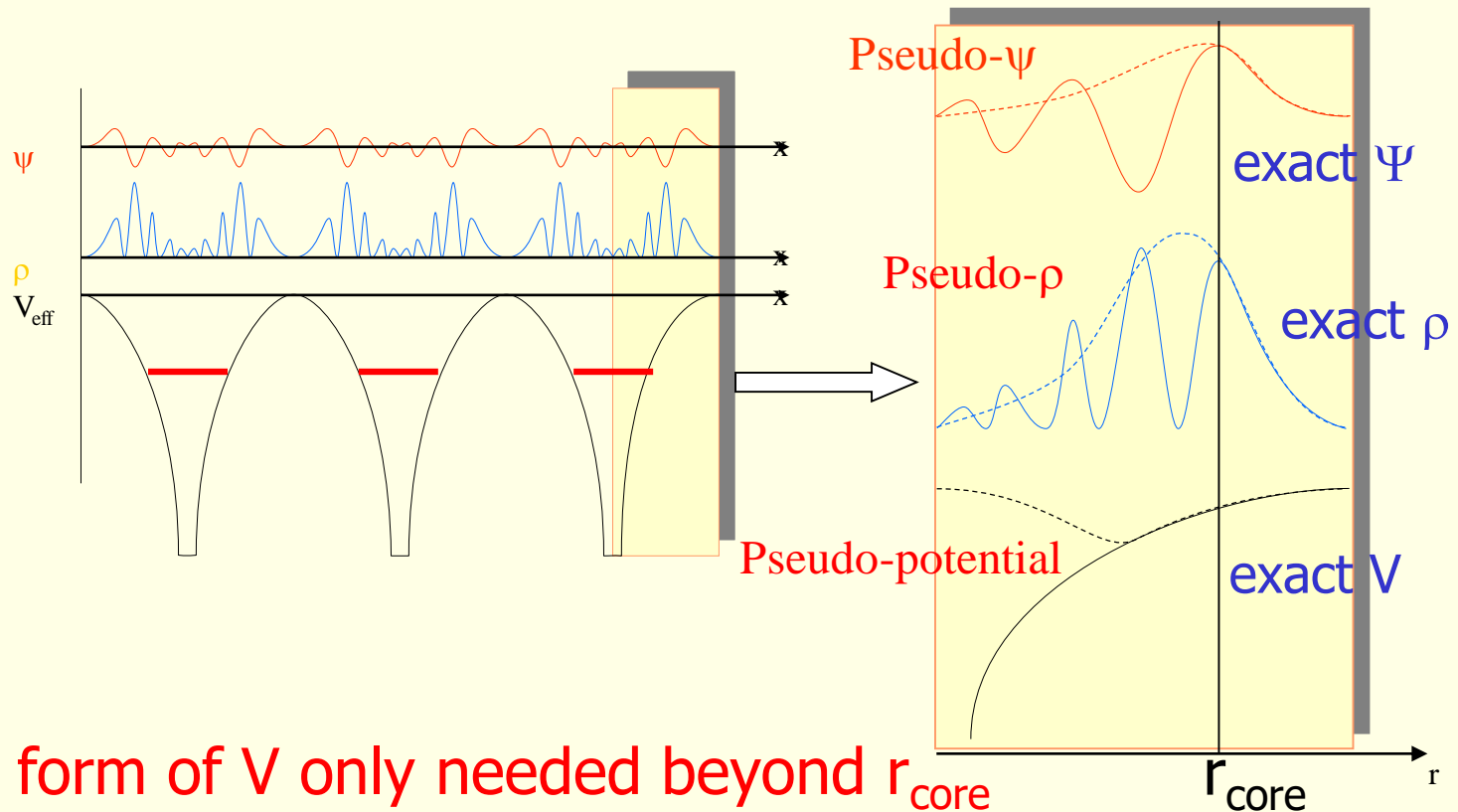
→exact form of V only needed beyond r_{core}

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)**
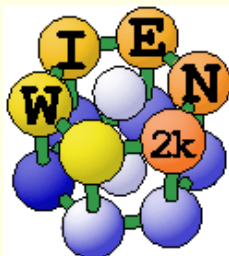 - *Generalized eigenvalue problem*
  - *Full-potential*

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

- **Local orbitals (D.J.Singh 1991)**
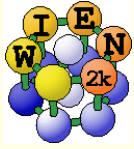 - *treatment of semi-core states (avoids ghostbands)*

- **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)

Review articles

P.Blaha, K.Schwarz, F.Tran, R.Laskowski, G.K.H.Madsen, L.D.Marks:
Wien2k: An APW+lo program for calculating the properties of solids
J.Chem.Phys. 152 074101 (2020)   dx.doi.org/10.1063/1.5143061

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
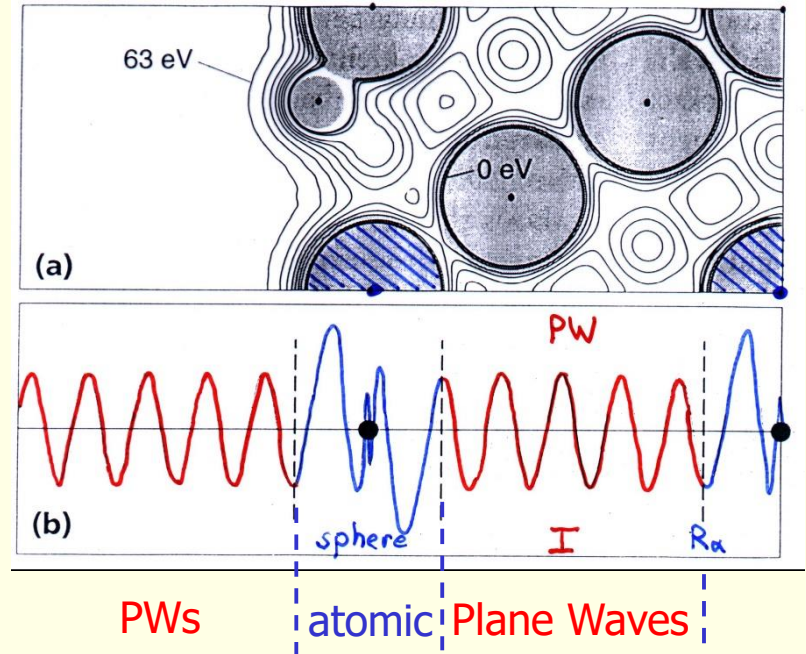*Freely available at:*   http://www.wien2k.at/reg-user/textbooks I
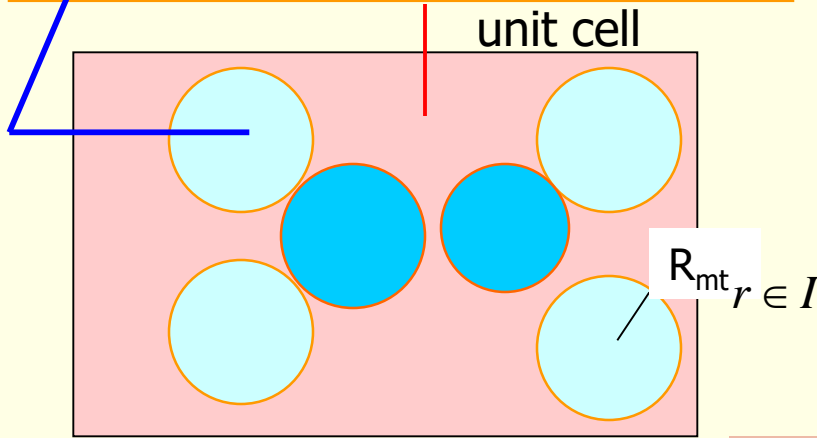
K.Schwarz, P.Blaha, S.B.Trickey, *Electronic structure of solids with WIEN2k*
Molecular physics, **108**, 3147 (2010)

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)

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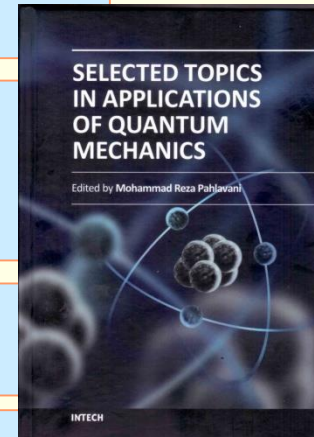
The unit cell is partitioned into:
 atomic spheres
 Interstitial region

unit cell

R_{mt} $r \in I$

(a) 63 eV   0 eV

(b) PW   sphere   I R_α

PWs   atomic   Plane Waves

"exact" solutions, but energy dependent

Basisset:

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

join
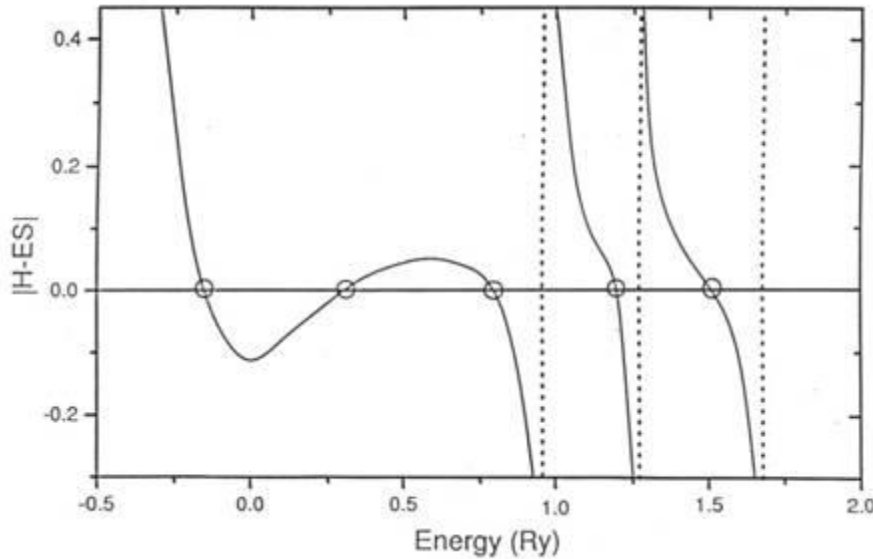
Atomic partial waves

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

$u_l(r,\varepsilon)$ are the numerical solutions of the radial Schrödinger equation in a spherical potential for energy ε
A_{lm}^{K} coefficients for matching the PW
$Y_{lm}(r)$: spherical harmonics

Slater's APW (1937)

H Hamiltonian
S overlap matrix

Atomic partial waves

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

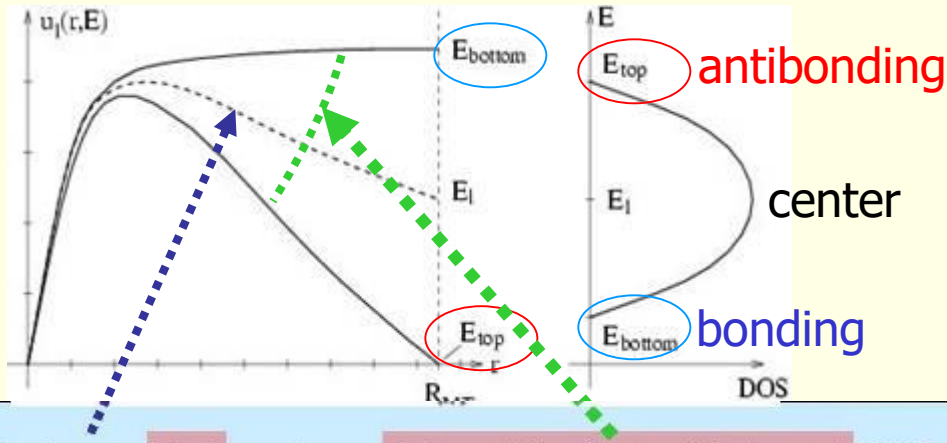**Energy dependent basis functions lead to a**

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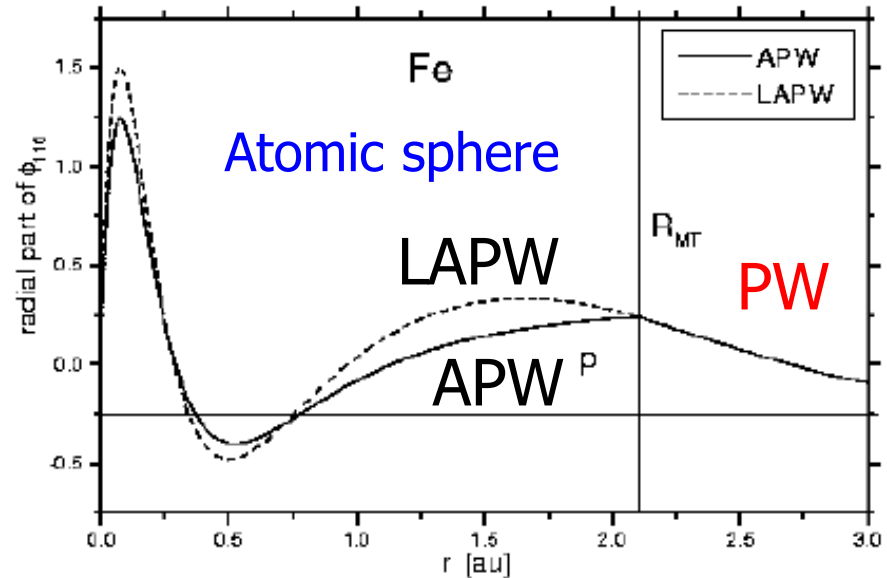
O.K.Andersen,
Phys.Rev. B 12, 3060
(1975)

antibonding

center

bonding

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

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

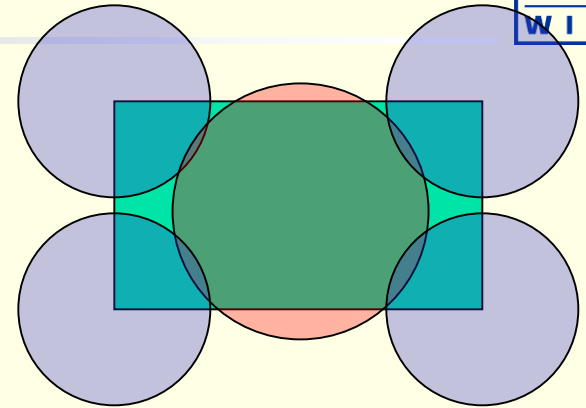$A_{lm}{}^k$, $B_{lm}{}^k$: join PWs in
value and slope

→ General eigenvalue problem
(diagonalization)

→ additional constraint requires
more PWs than APW

Atomic sphere

LAPW

APW ^{P}
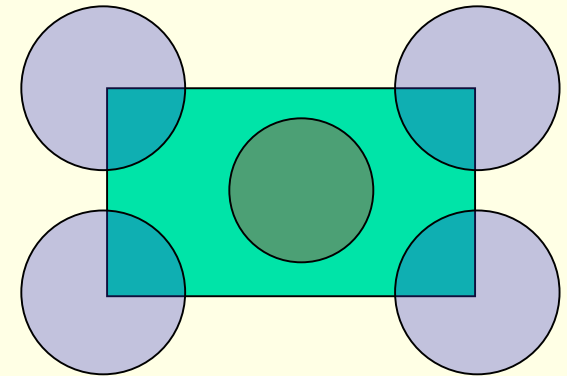
PW

shape approximations to "real" potentials

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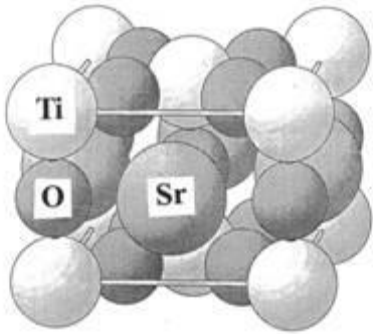 - *potential spherically symmetric*

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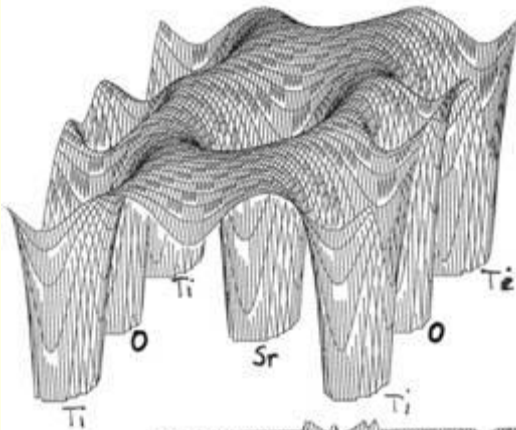 - *interstitial region with V=const.*

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

Full-potential in LAPW (A.Freeman et al)
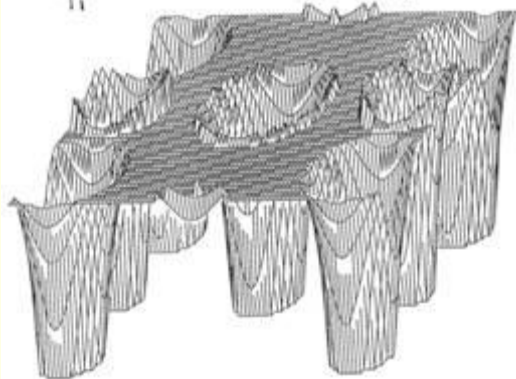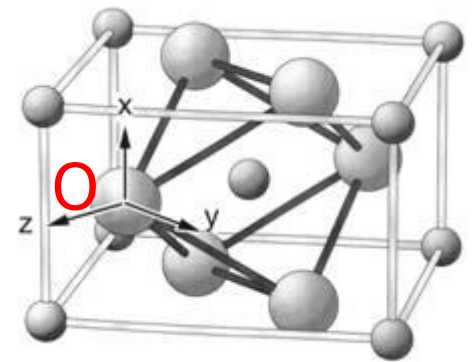
SrTiO$_3$

Full potential

Muffin tin approximation

TiO$_2$ rutile

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

(no shape approximation)

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

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

O

Ti
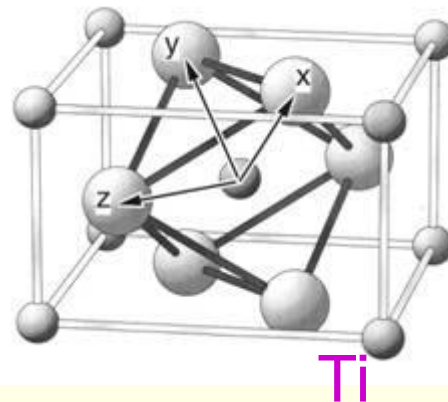
For example: Ti

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

-356.6   -38.3   -31.7 Ry

1 Ry =13.605 eV

Local orbitals (LO)

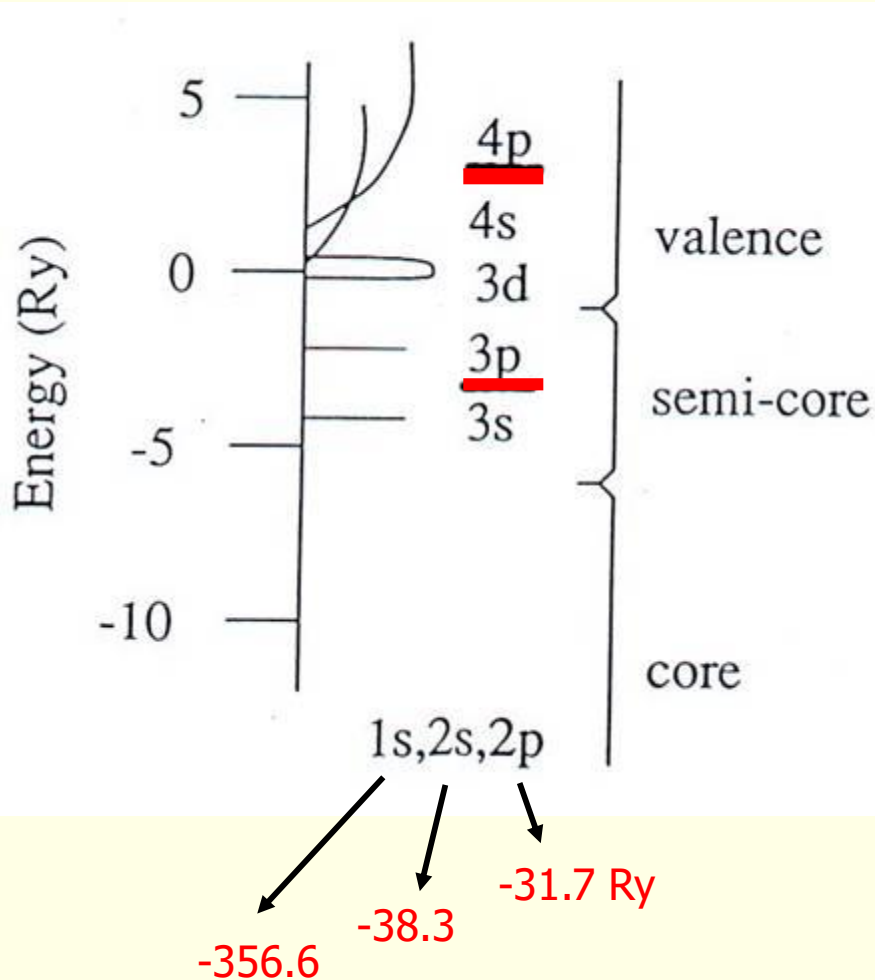$$\Phi_{LO} = [A_{\ell m} u_{\ell}^{E_1} + B_{\ell m} \dot{u}_{\ell}^{E_1} + C_{\ell m} u_{\ell}^{E_2}] Y_{\ell m}(\hat{r})$$

- **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)*

Ti atomic sphere
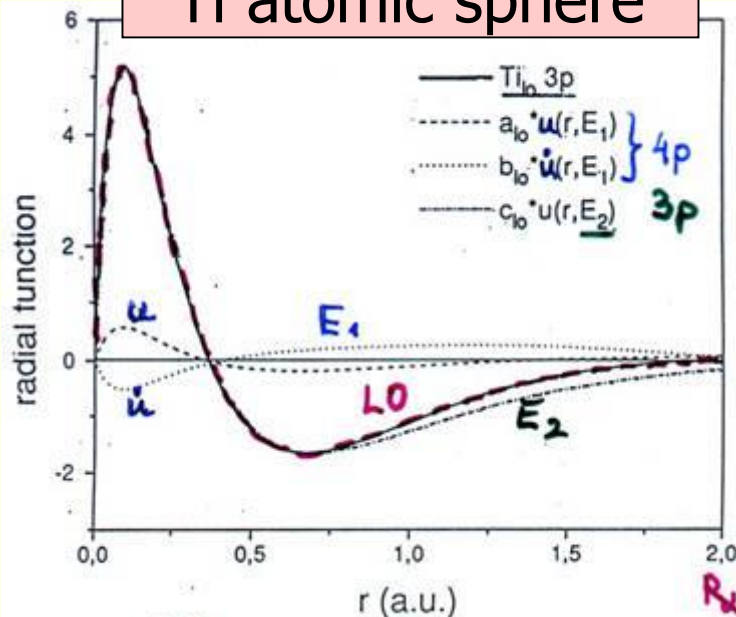
D.J.Singh,
Phys.Rev. B 43 6388 (1991)

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)
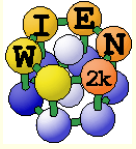 (add a few extra basis functions)

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

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

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

Representative Convergence:
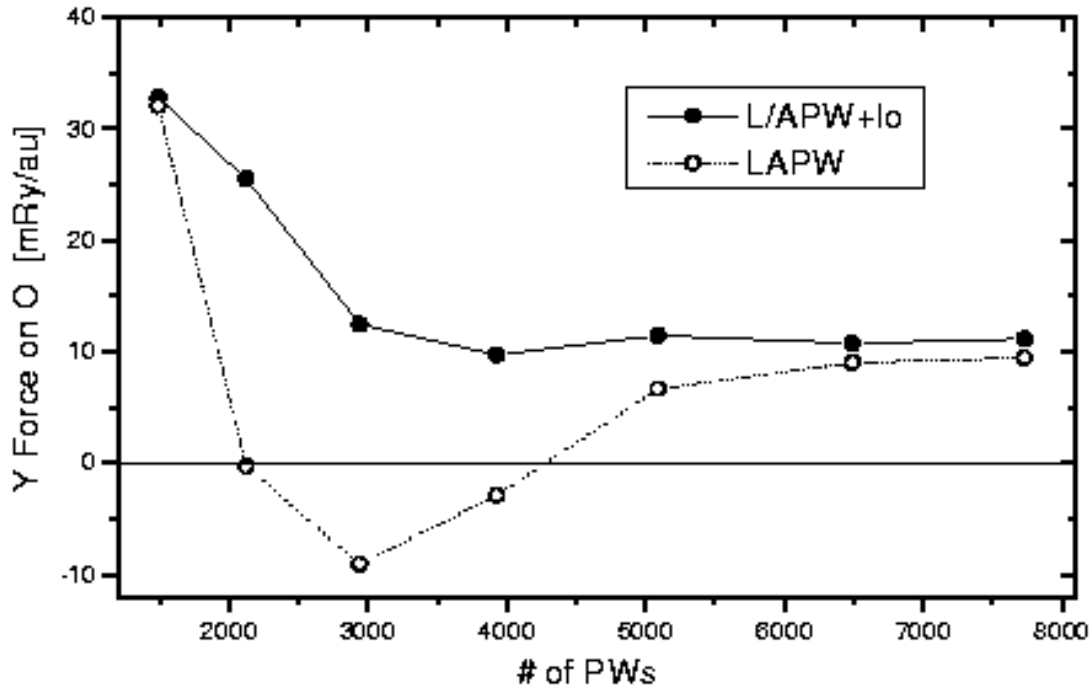
e.g. force (F_y) on oxygen in SES vs. # plane waves:

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

SES

SES (sodium electro solodalite)

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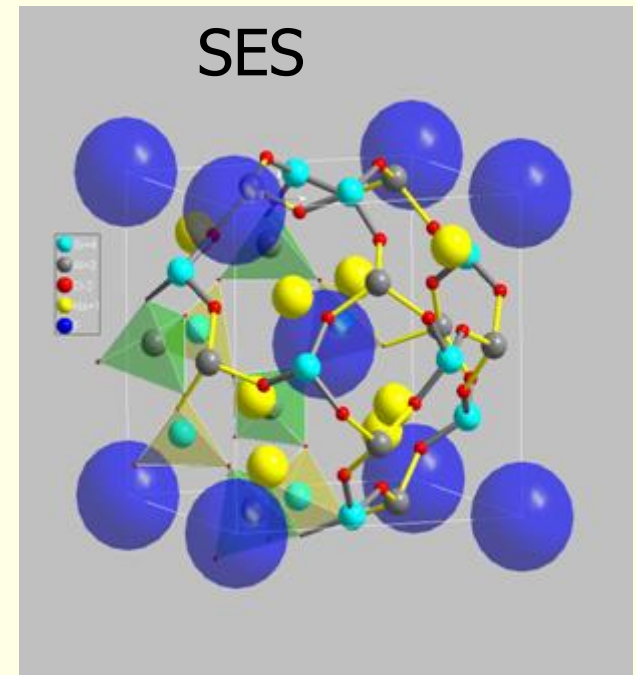
- **Atomic partial waves**
  - *LAPW*

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

  - *APW+lo*

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

  plus another type of local orbital (lo)

- **Plane Waves (PWs)**

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

- **match at sphere boundary**
  - *LAPW*

    value and slope $\quad A_{\ell m}(k_n), B_{\ell m}(k_n)$
  - *APW*

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

Atomic sphere

Fe

LAPW

APW

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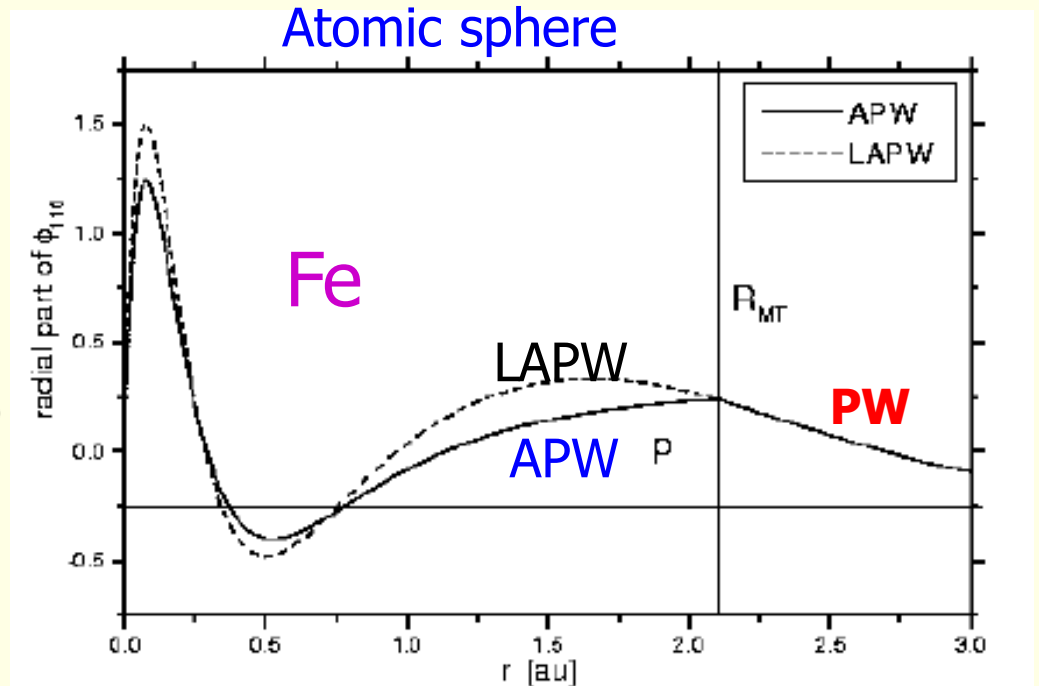
E.Sjöststedt, L.Nordström, D.J.Singh, SSC 114, 15 (2000)

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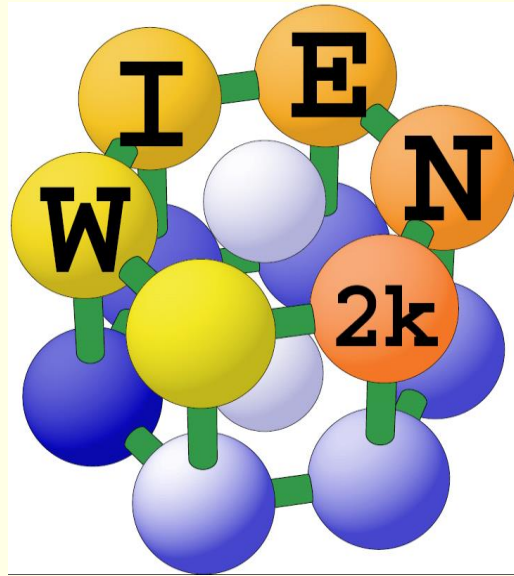
An Augmented Plane Wave Plus Local Orbital Program for Calculating Crystal Properties

Peter Blaha
Karlheinz Schwarz
Georg Madsen
Dieter Kvasnicka
Joachim Luitz

November 2001
Vienna, AUSTRIA
Vienna University of Technology

http://www.wien2k.at

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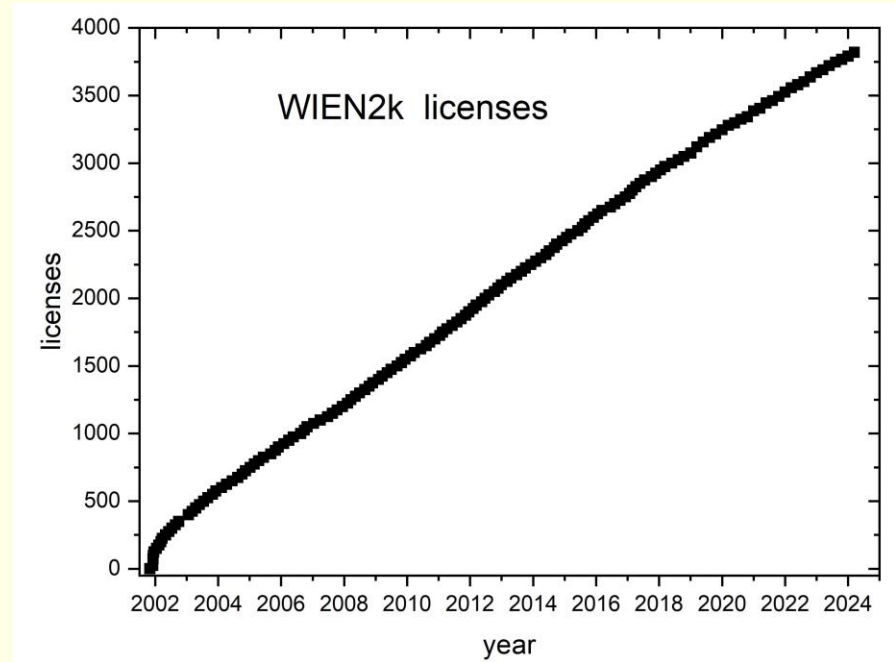
75 industries **(Canon, Eastman, Exxon, Fuji, Hitachi, IBM, Idemitsu Petrochem., Kansai, Komatsu, Konica-Minolta, A.D.Little, Mitsubishi, Mitsui Mining, Motorola, NEC, Nippon Steel, Norsk Hydro, Osram, Panasonic, Samsung, Seiko Epson, Siemens, Sony, Sumitomo,TDK,Toyota).**

mailinglist: 10.000 emails/6 years

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

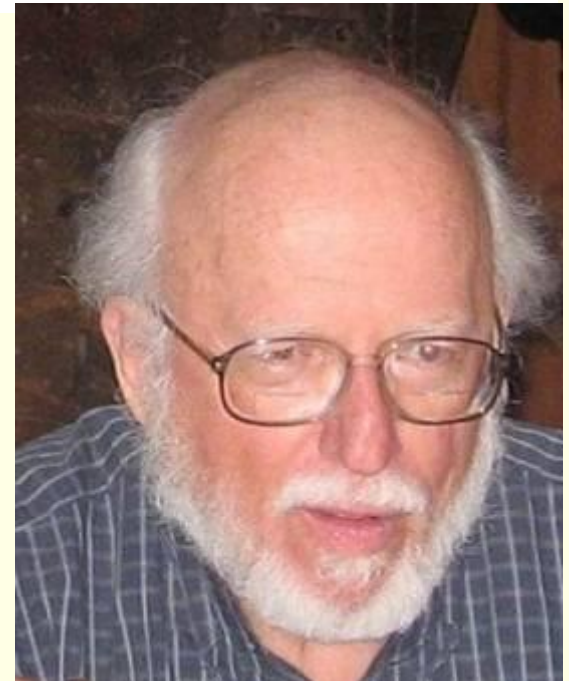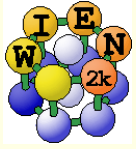*Quantum Theory Project, Depts. of Physics and of Chemistry, University of Florida, Gainesville, FL 32611, USA*

PROGRAM SUMMARY

Title of program: WIEN

In the Heart of EUROPE
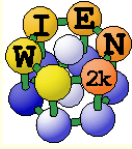
- **Authors of WIEN2k**

  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

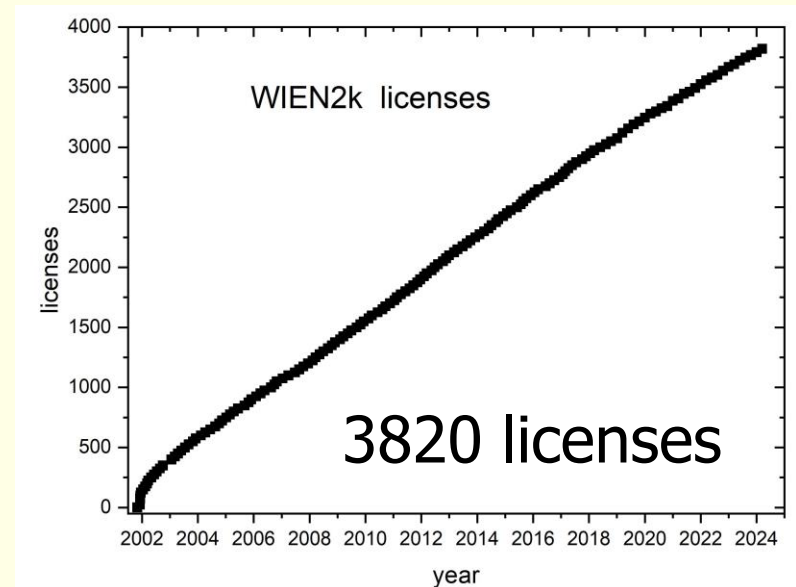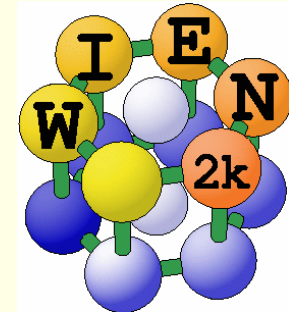|					
1st	Vienna		April	1995	Wien95
2nd	Vienna		April	1996	
3rd	Vienna		April	1997	Wien97
4st	Trieste, Italy		June	1998	
5st	Vienna		April	1999	
6th	Vienna		April	2000	
7th	Vienna		Sept.	2001	Wien2k
8th	Esfahan, Iran		April	2002	
	Penn State, USA		July	2002	
9th	Vienna		April	2003	
10th	Penn State, 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	
24th	Vienna		Sept	2017	
25th	Boston, USA		June	2018	
26th	Vienna		Aug.	2019	

WIEN2k licenses

3820 licenses

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

upper bound $\quad$ 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)
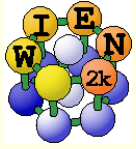
Structure: $a,b,c,\alpha,\beta,\gamma,$ R_α , ...

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$\to 0$

properties
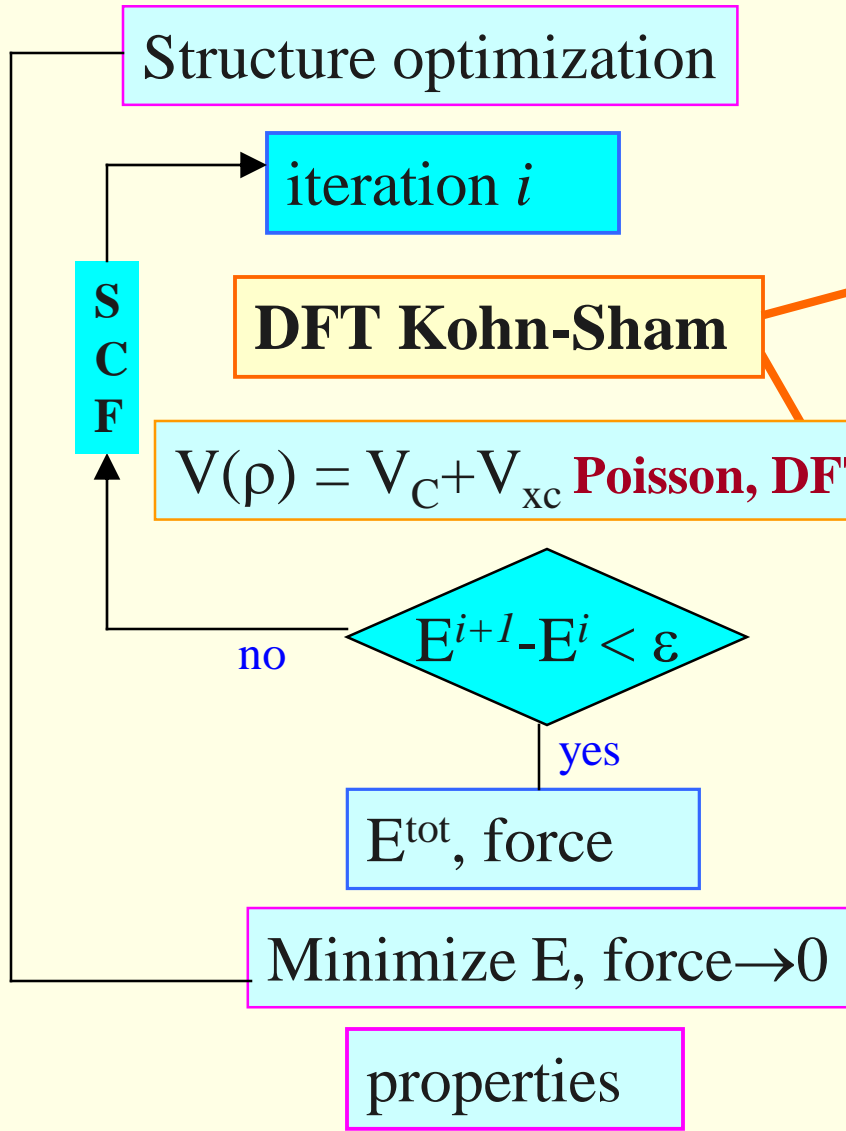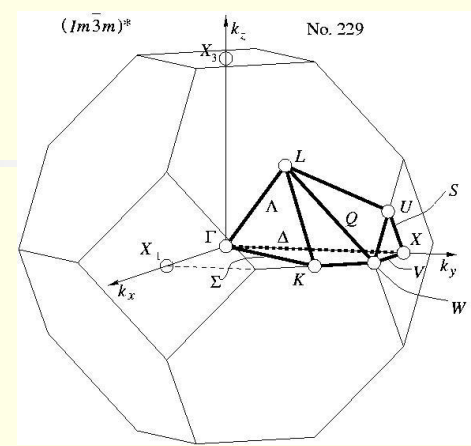
$k \in$ **IBZ** (irred. Brillouin zone)

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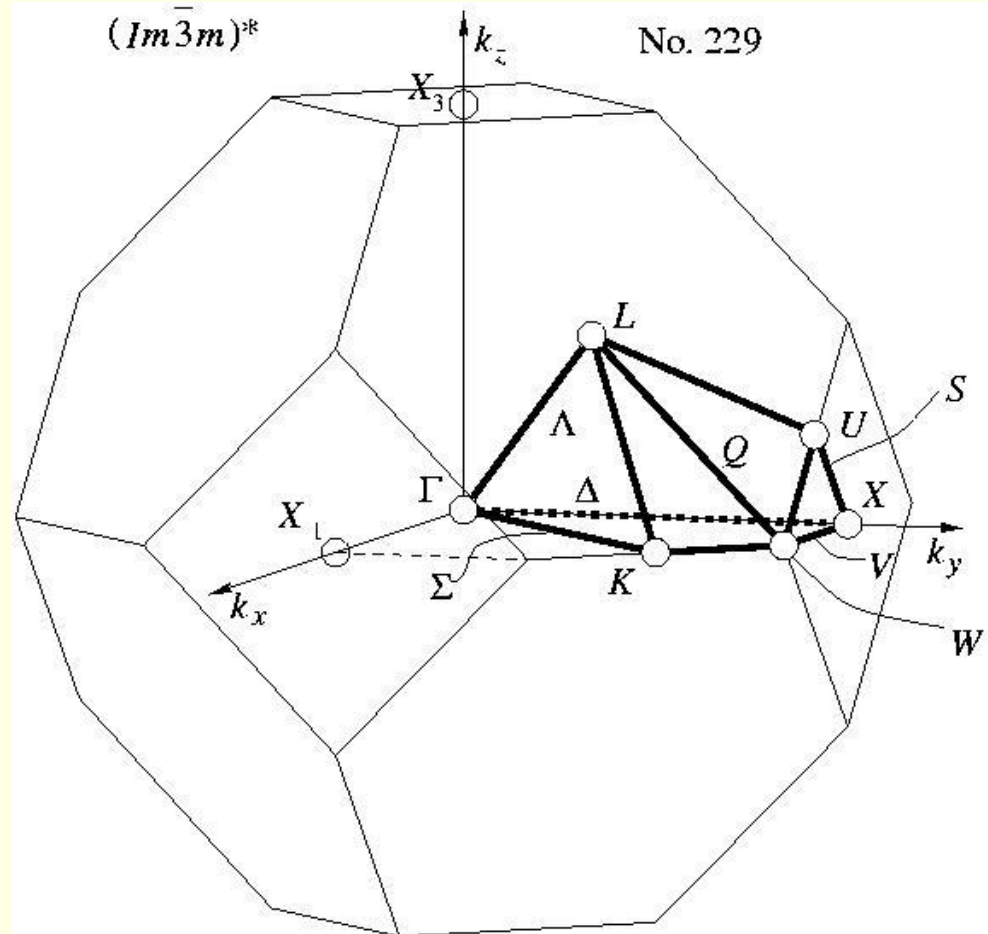
- In order to solve $H\Psi=E\Psi$ we need to know the potential V(r)
- for V(r) we need the electron density ρ(r)
- the density ρ(r) can be obtained from Ψ(r)*Ψ(r)
- ?? Ψ(r) is unknown before $H\Psi=E\Psi$ is solved ??

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

Solve $\{-\frac{1}{2}\nabla^2 + V_{eff}(\mathbf{r})\}\Phi_i(\mathbf{r}) = \varepsilon_i\Phi_i(\mathbf{r})$
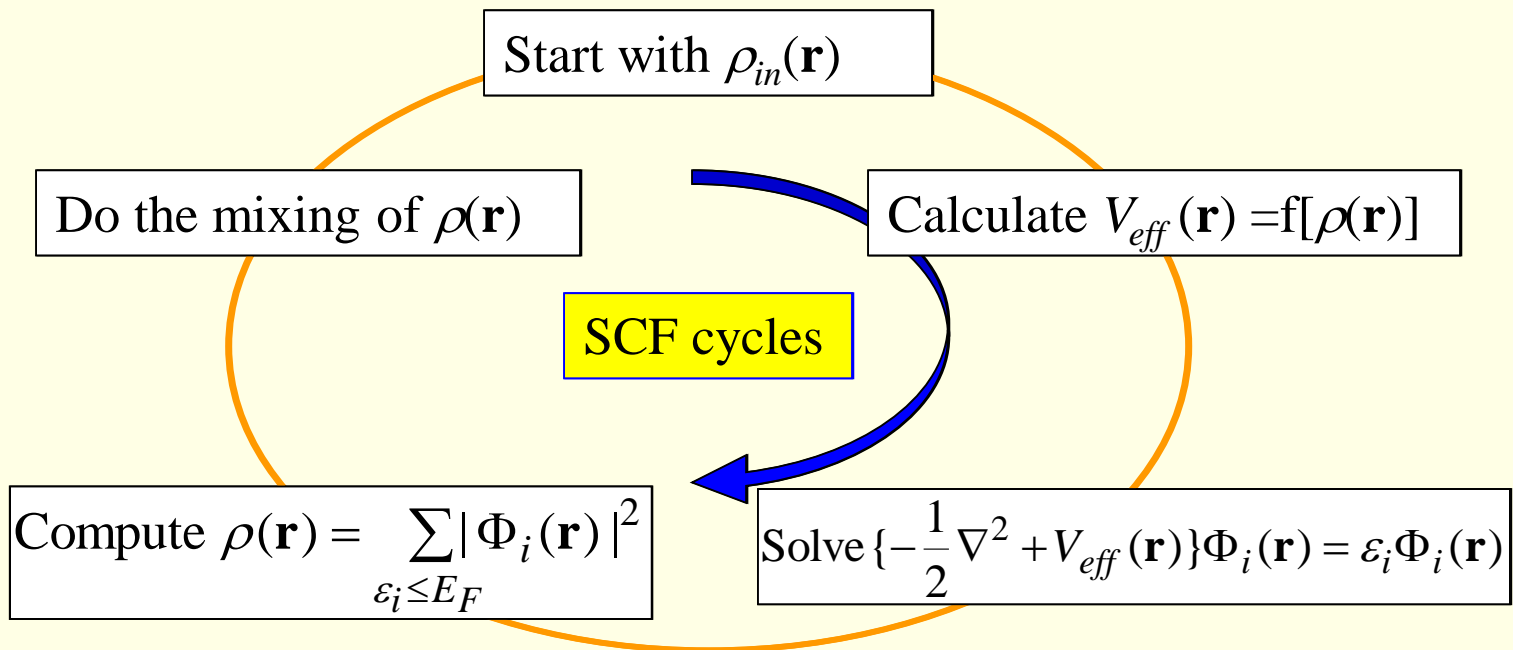
Band structure of fcc Cu
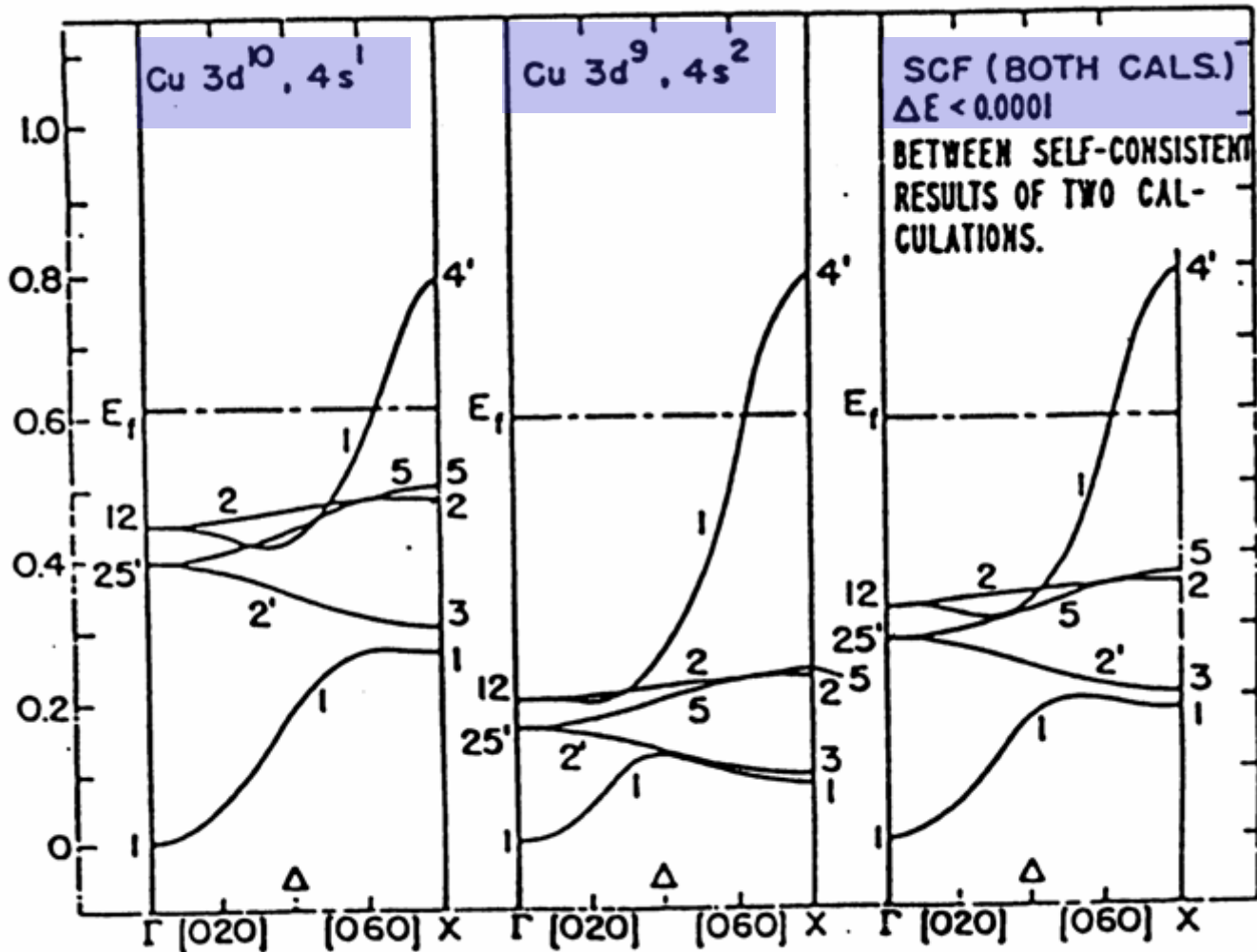
- **init_lapw**
  - *initialization*
  - *symmetry detection (F, I, C-centering, inversion)*
  - *input generation with recommended defaults*
  - *quality (and computing time) depends on k-mesh and R.Kmax (determines #PW)*
- **run_lapw**
  - *scf-cycle*
  - *optional with SO and/or LDA+U*
  - *different 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*

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*
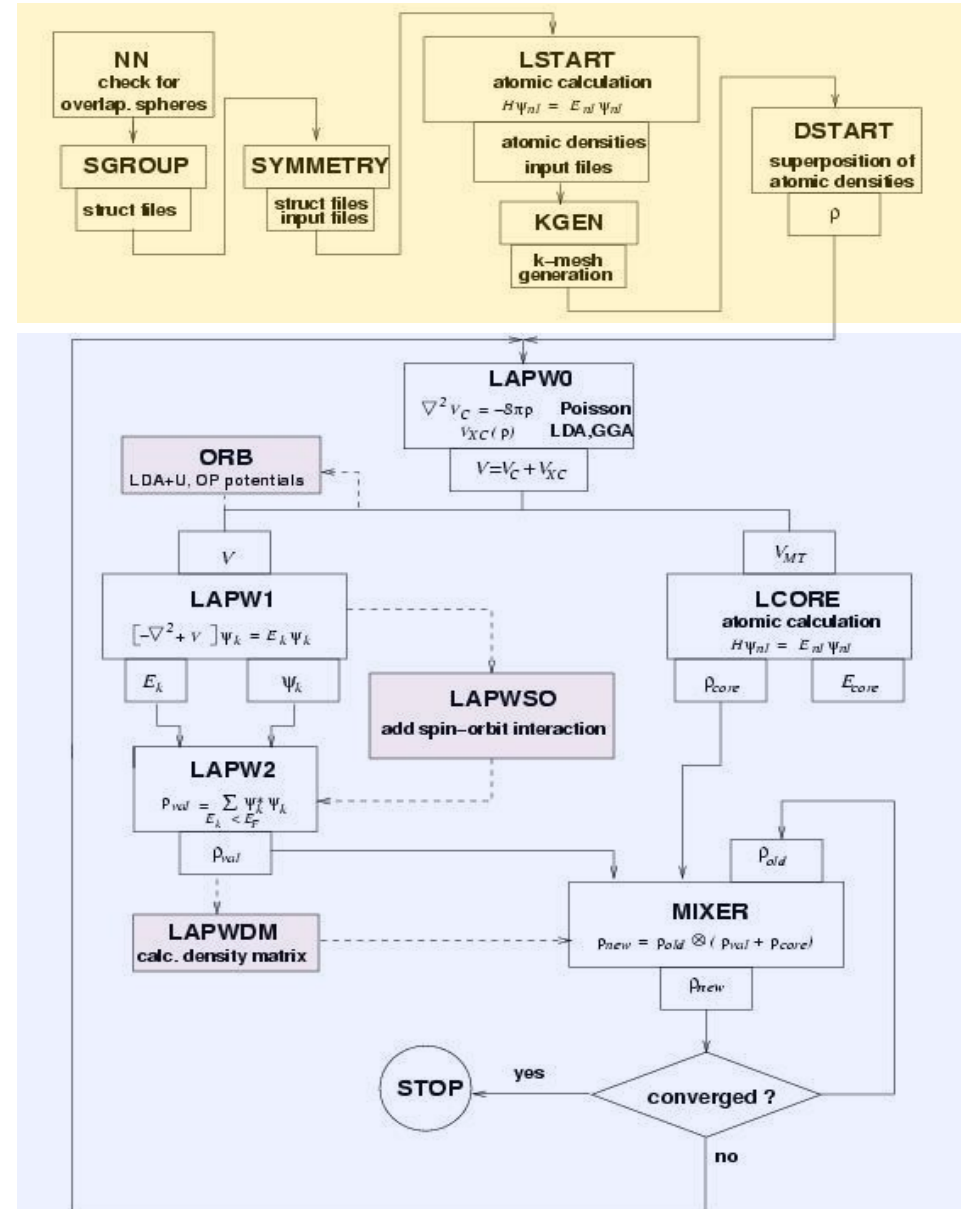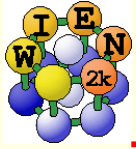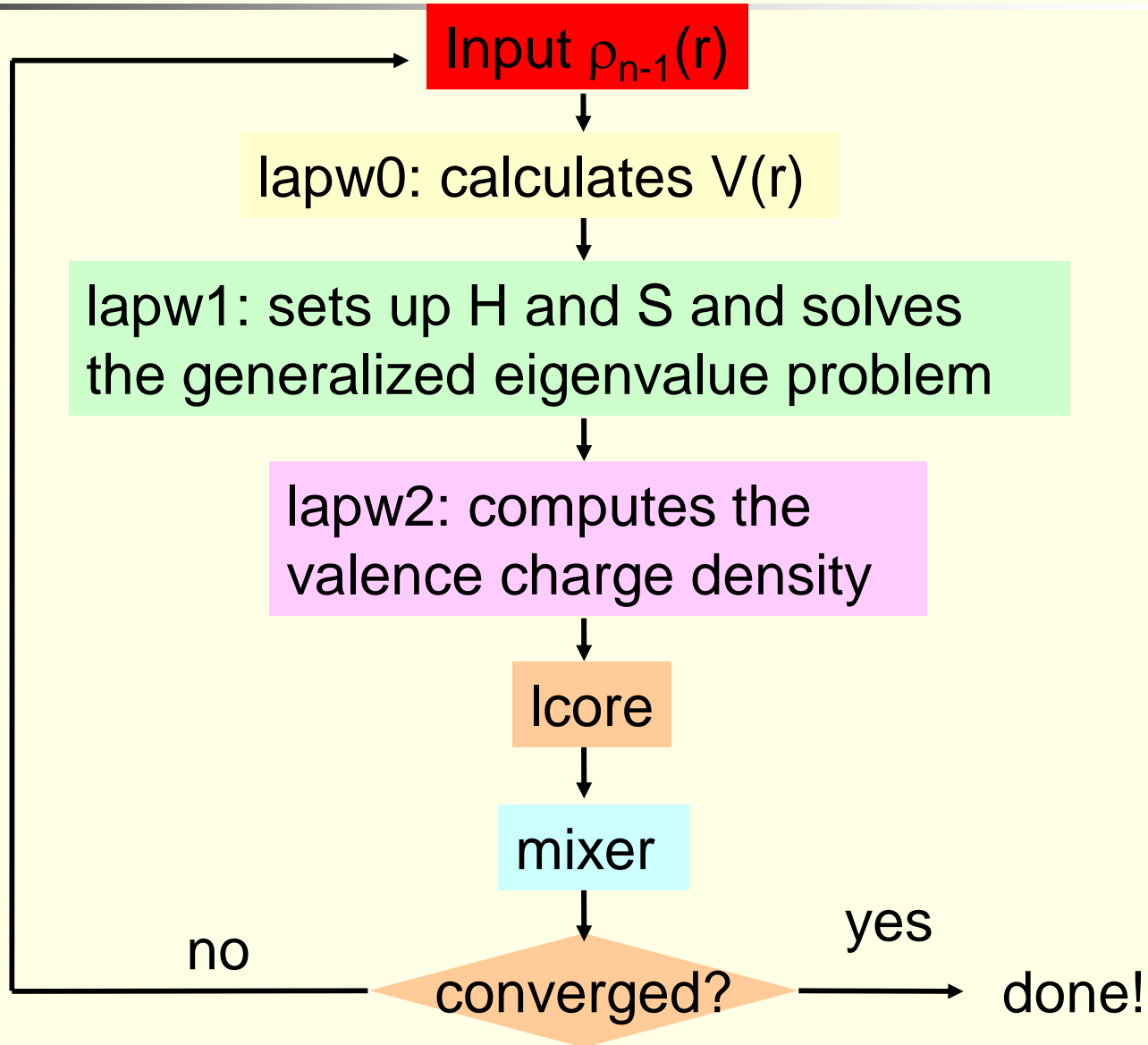
Workflow of a WIEN2k calculation

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

SCF cycle

single mode

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

Iteration

self consistent? — no / yes → END

parallel mode

Iteration

LAPW0

LAPW1

LAPW2

SUMPARA

LCORE

MIXER

self consistent? — yes → END / no

k-point parallelization
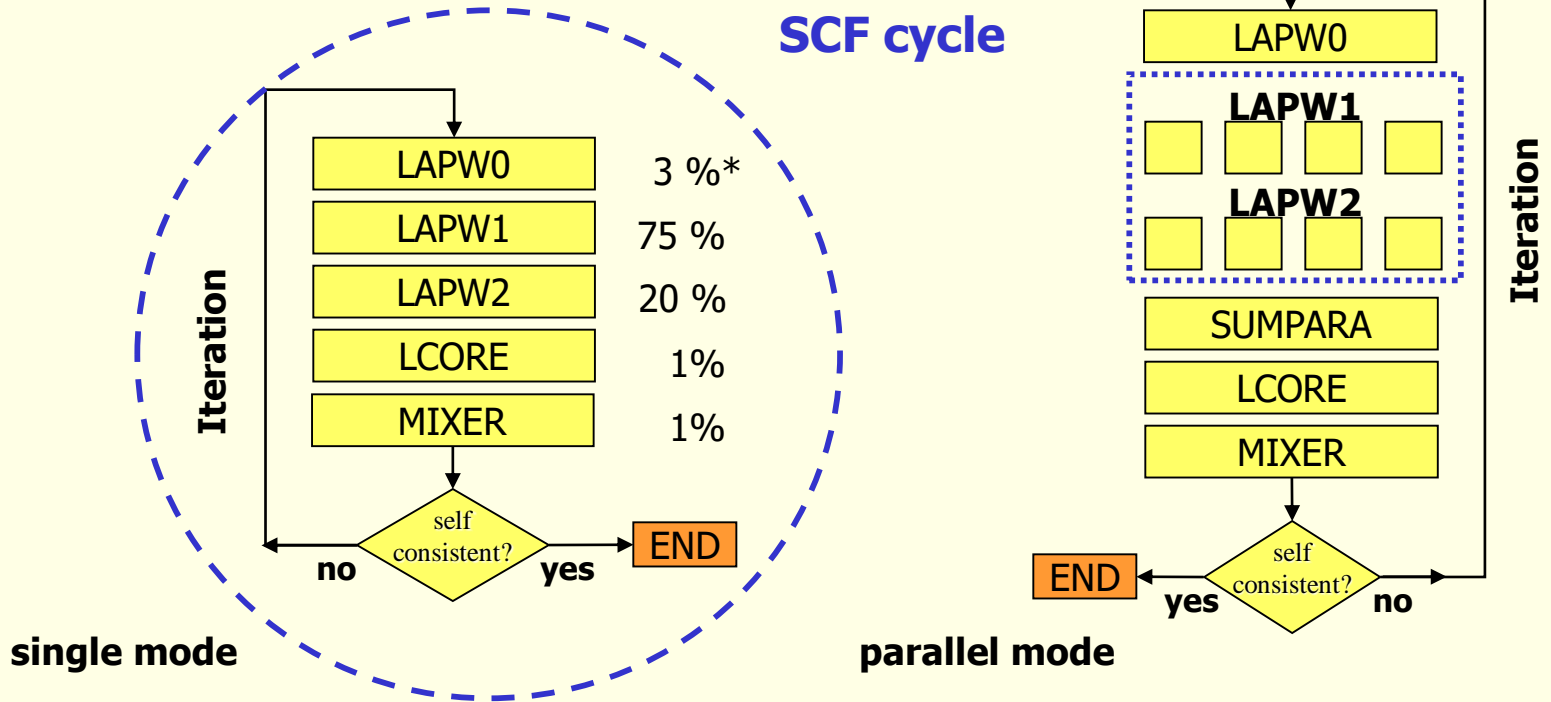
* fraction of total computation time

+ 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

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

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
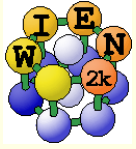
Spacegroup P4$_2$/mnm

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

Rutile TiO$_2$:
P4$_2$/mnm (136)
a=8.68, c=5.59 bohr
Ti: (0,0,0)

2a

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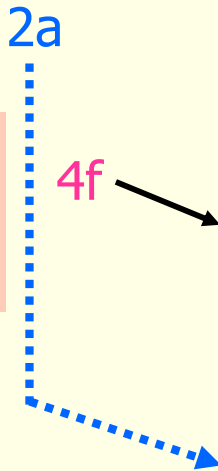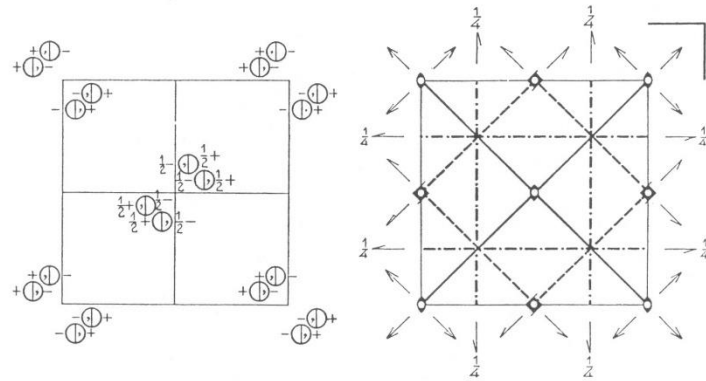Wyckoff position: x, x, 0

4f

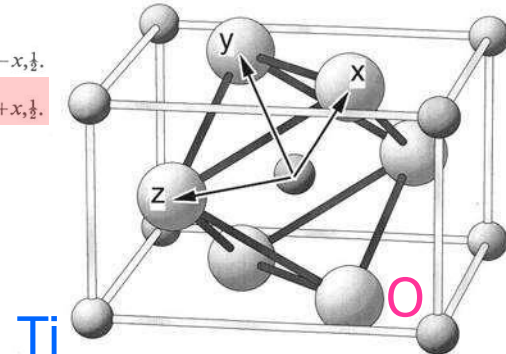$P4_2/mnm$ No. 136 $P\,4_2/m\,2_1/n\,2/m$ $4/m\,m\,m$ Tetragonal
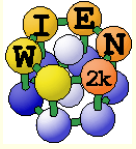D_{4h}^{14}

Origin at centre (mmm)

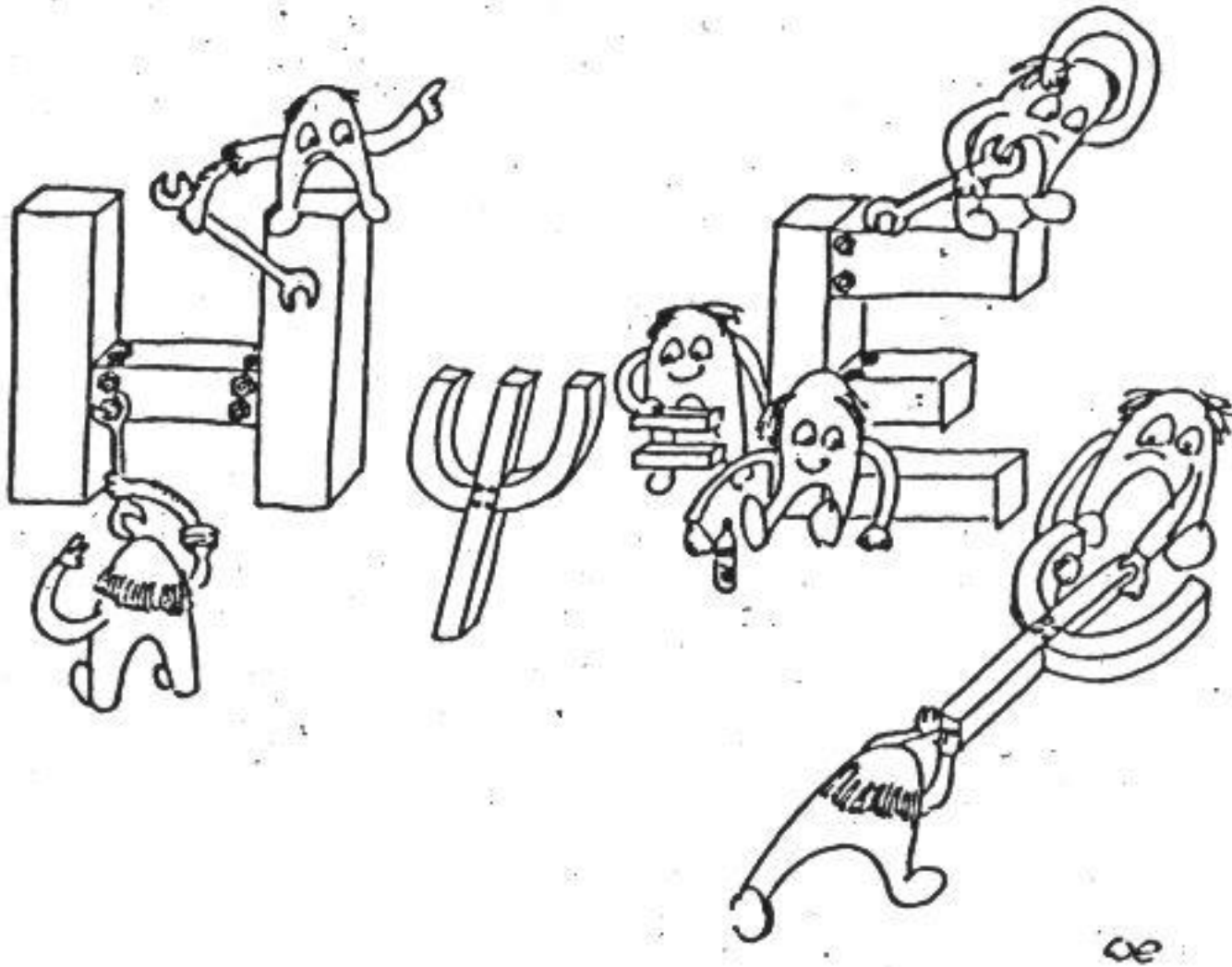| Number of positions, Wyckoff notation, and point symmetry			Co-ordinates of equivalent positions		Conditions limiting possible reflections

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

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

Special: as above, plus

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

no extra conditions

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

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

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

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

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

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

4 d $\bar{4}$ $0,\frac{1}{2},\frac{1}{4}$; $\frac{1}{2},0,\frac{1}{4}$; $0,\frac{1}{2},\frac{3}{4}$; $\frac{1}{2},0,\frac{3}{4}$.

4 c 2/m $0,\frac{1}{2},0$; $\frac{1}{2},0,0$; $0,\frac{1}{2},\frac{1}{2}$; $\frac{1}{2},0,\frac{1}{2}$.

2 b mmm $0,0,\frac{1}{2}$; $\frac{1}{2},\frac{1}{2},0$.

2 a mmm $0,0,0$; $\frac{1}{2},\frac{1}{2},\frac{1}{2}$.

Ti

O

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

C

Ti
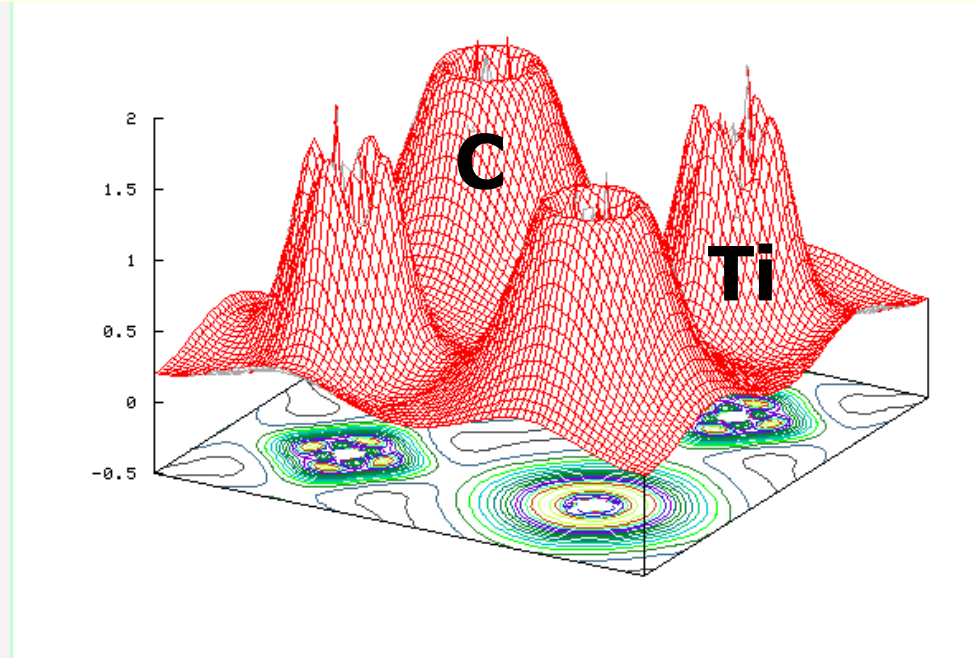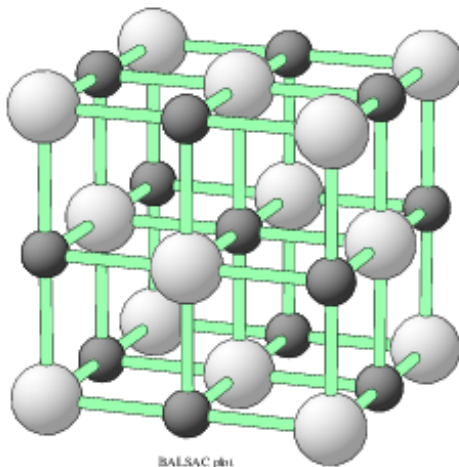
Download hardcopy in PostScript format

Select plot type: 3D-plot ● Contur-plot ○ with labels ☐
Min -0.5   Max 2   Delta 0.1
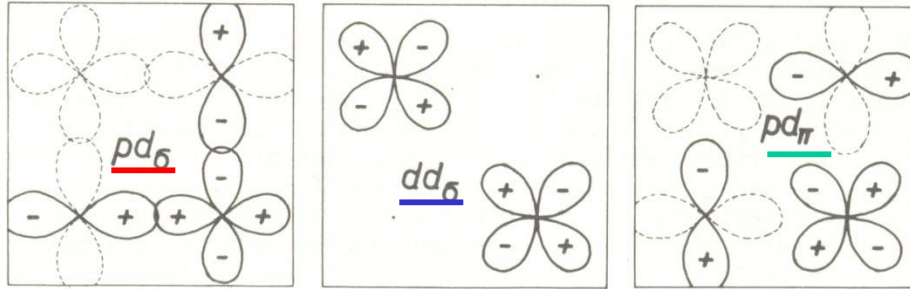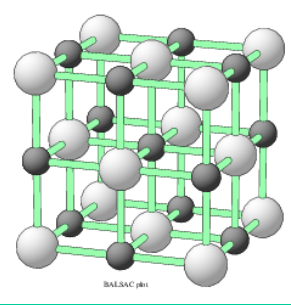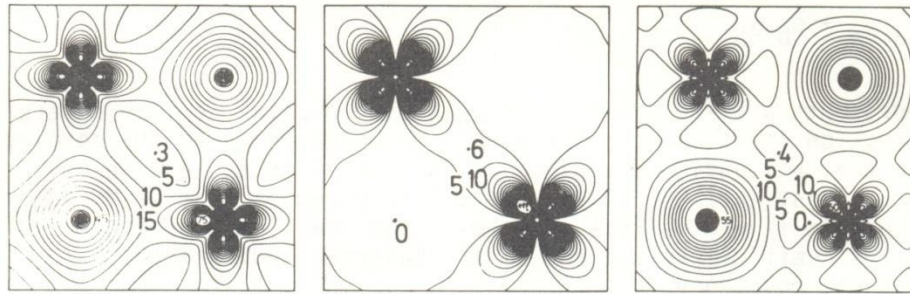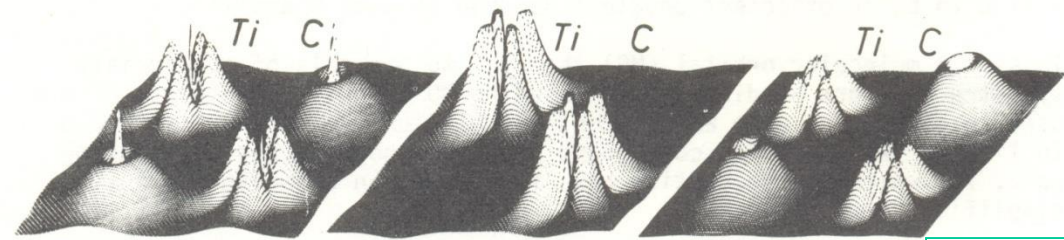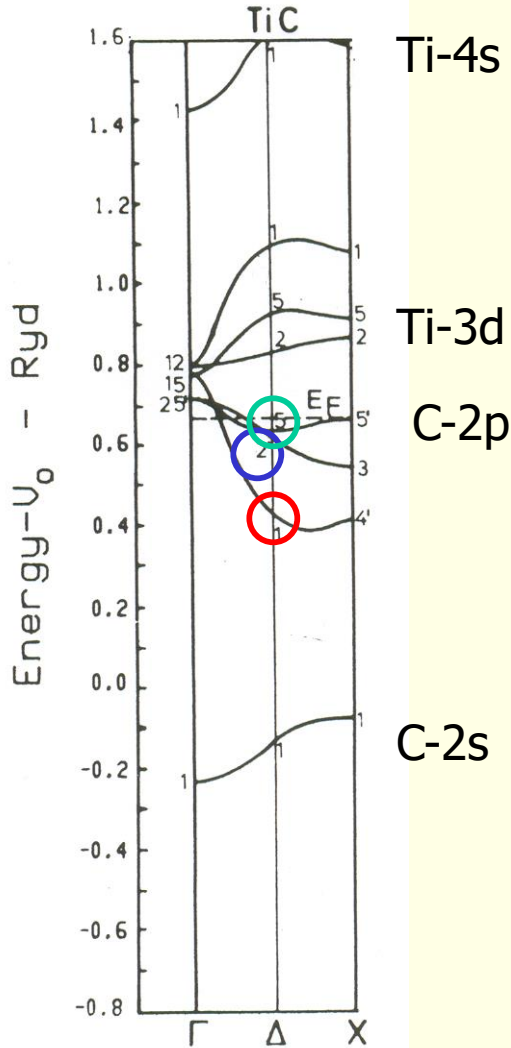
plot electron density

edit TiC.in2   reset EMIN

BALSAC plot

TiC, three valence states at Δ

Energy bands

Ti-4s

Ti-3d

C-2p

C-2s

(100) plane

pd_σ $Δ_1$ 423mRyd

dd_σ $Δ_{2'}$ 620mRyd

pd_π $Δ_5$ 636mRyd

C_p-Ti_d σ Ti_d-Ti_d σ C_p-Ti_d π

P.Blaha, K.Schwarz,
Int.J.Quantum Chem. <u>23</u>, 1535 (1983)

spaghetti   irred.rep.   character bands
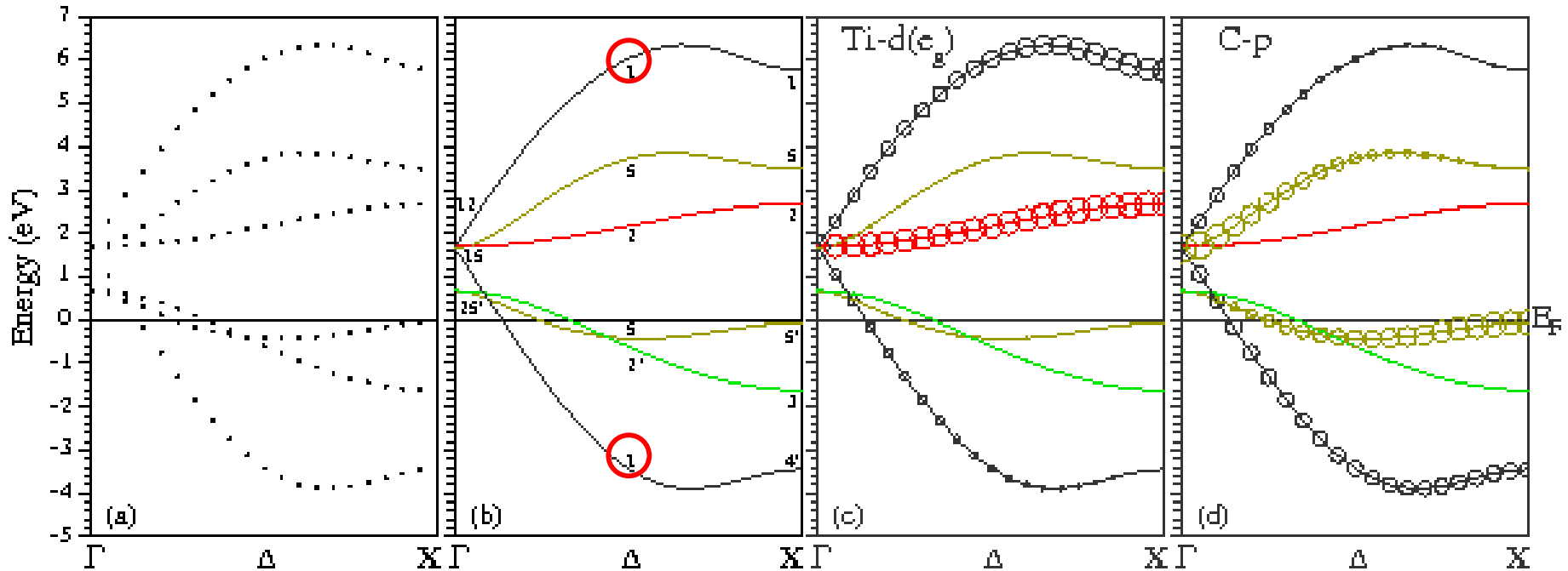
Normalized wave function (charges)

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

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

P.Blaha, K.Schwarz,
Int.J.Quantum Chem. <u>23</u>, 1535 (1983)

TiC, bonding and antibonding states

C-2p

C-2s

O-2p

O-2s

Ti-3d

antibonding

927 mRyd
Δ_5

967 mRyd
Δ_5

636 mRyd
Δ_5

408 mRyd
Δ_5

bonding

antibonding

Ti-d

C-p

C Ti

O-p

O Ti
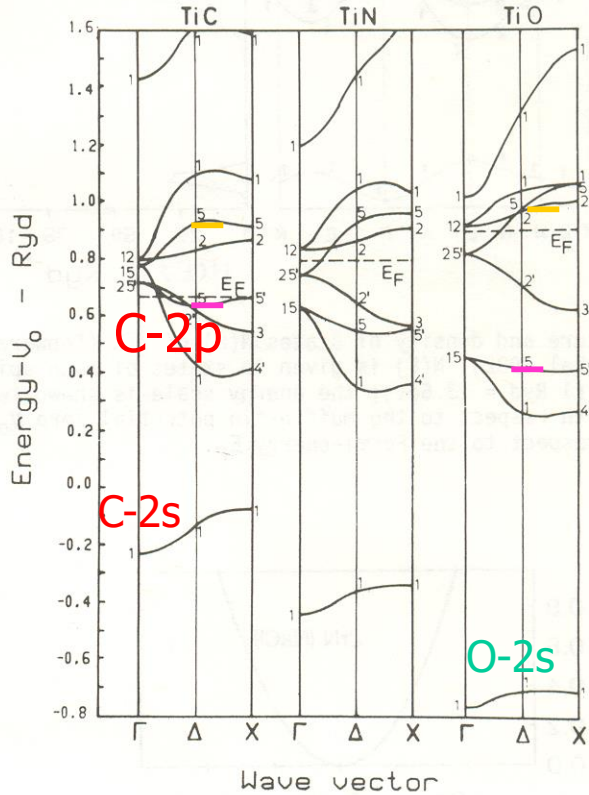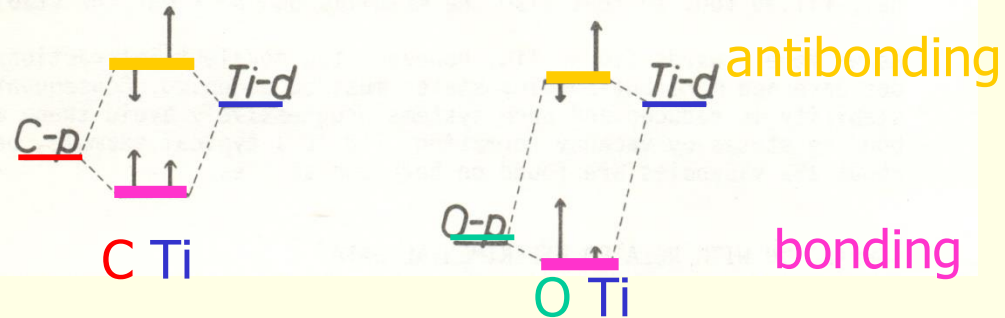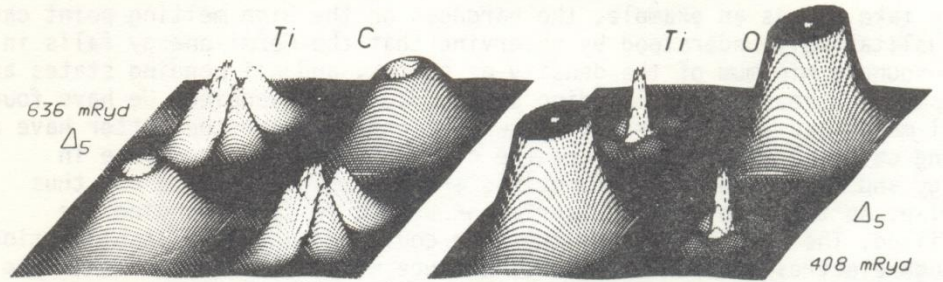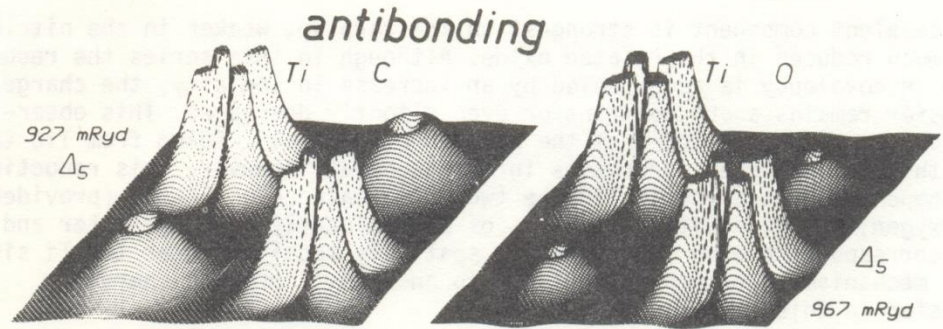
bonding

weight:

antibonding
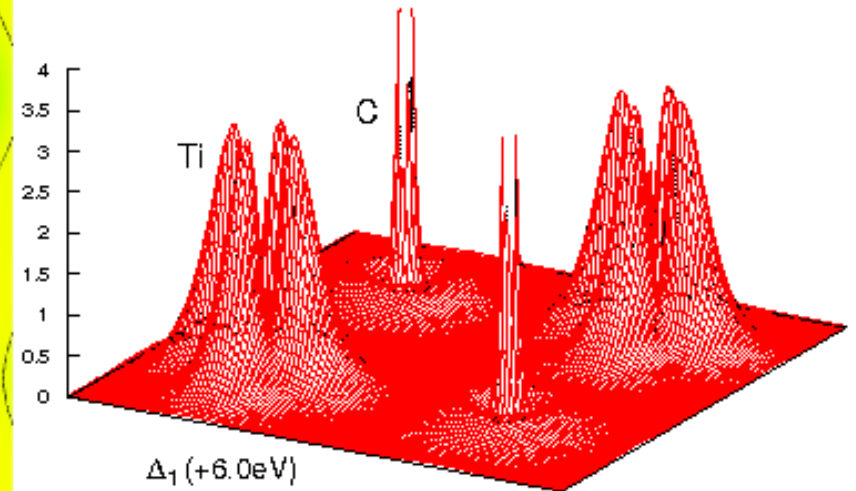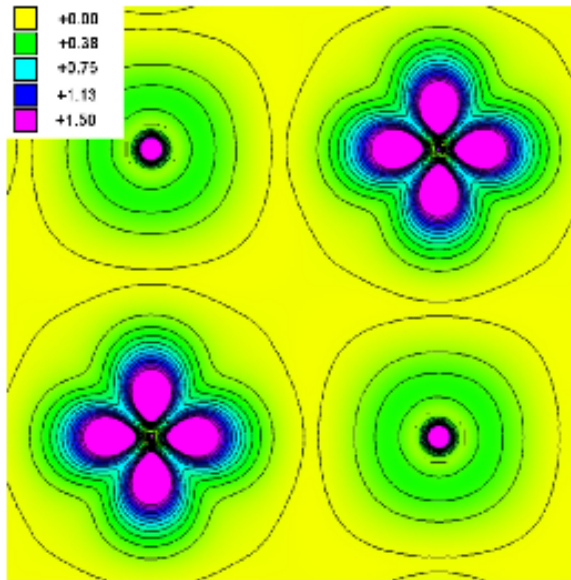
C_p-Ti_d σ

bonding

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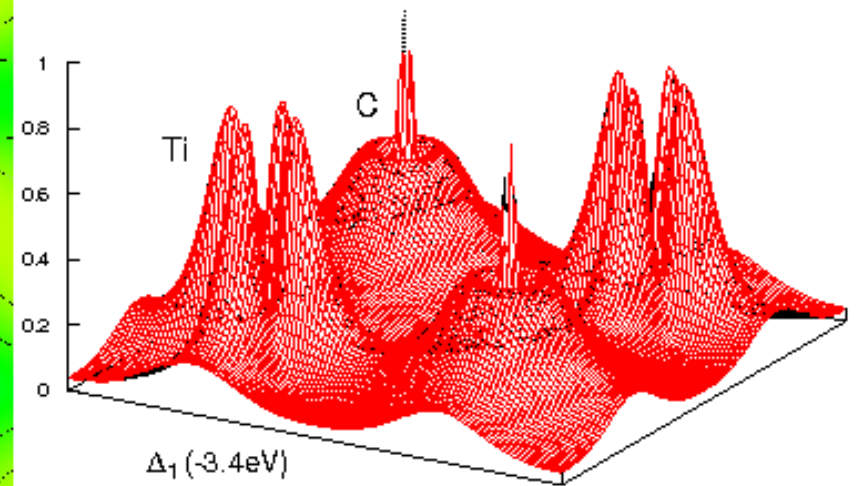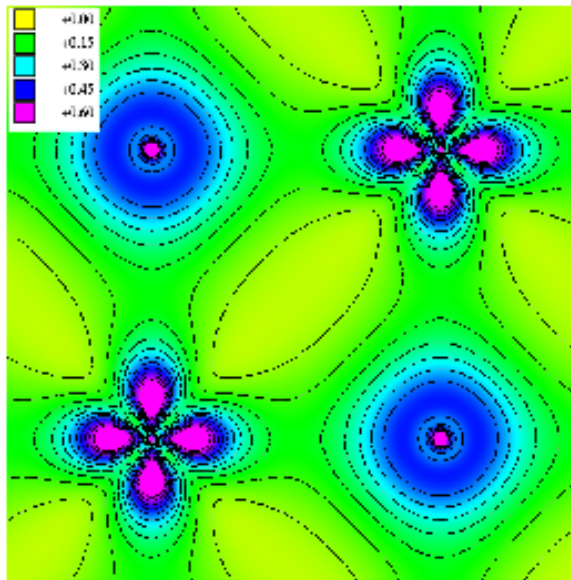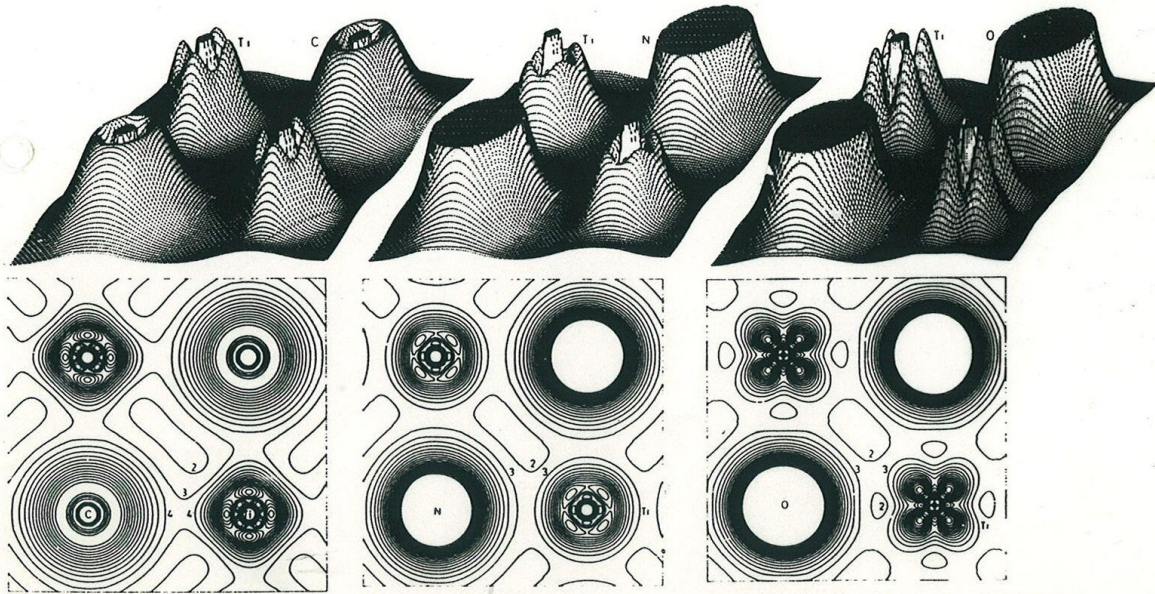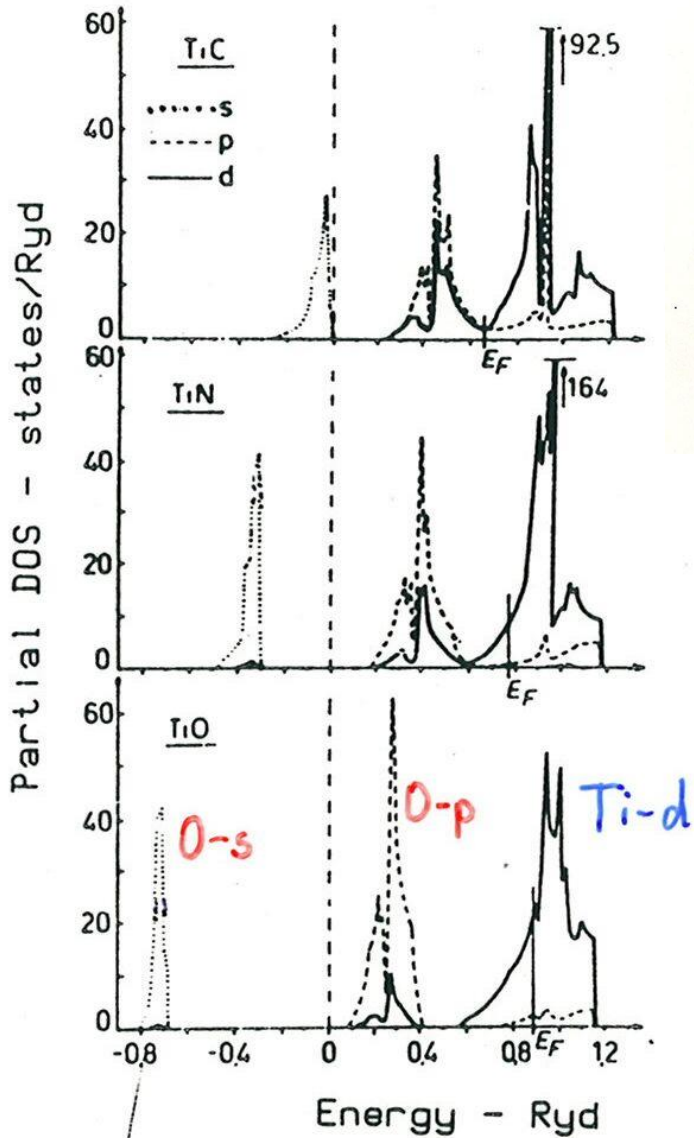
Figure 3. Valence charge densities in the (100) plane. Contour intervals $0.1 e\text{Å}^{-3}$ (numbers are in these units), cutoff at $1.7 e\text{Å}^{-3}$.

TiC   **TiN**   **TiO**

Rigid band model: limitations

Electron density ρ: decomposition

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

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

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

Experimental difference electron density
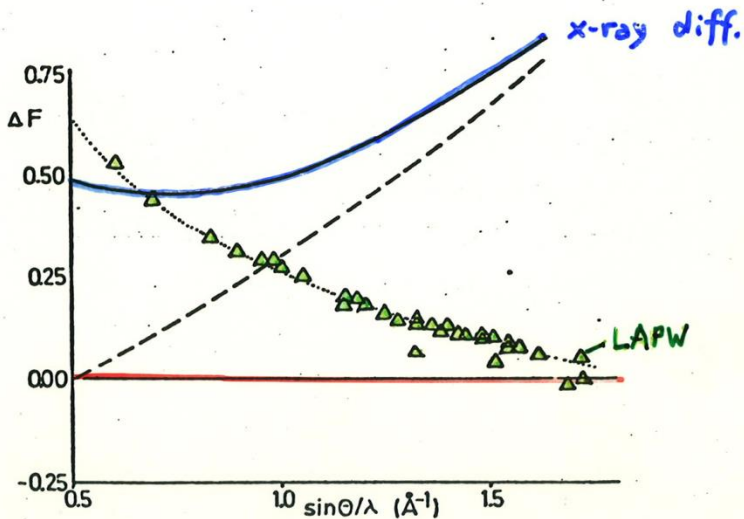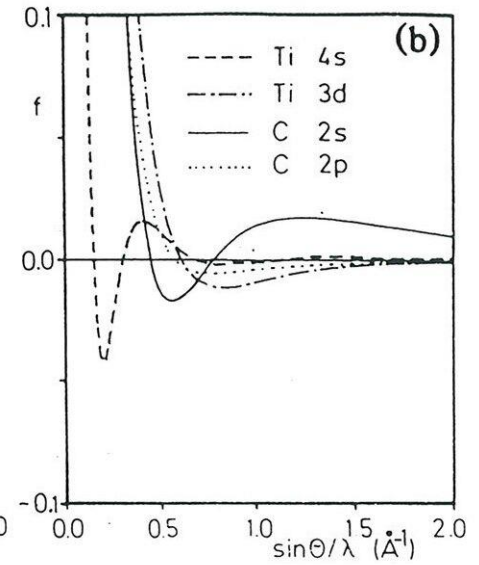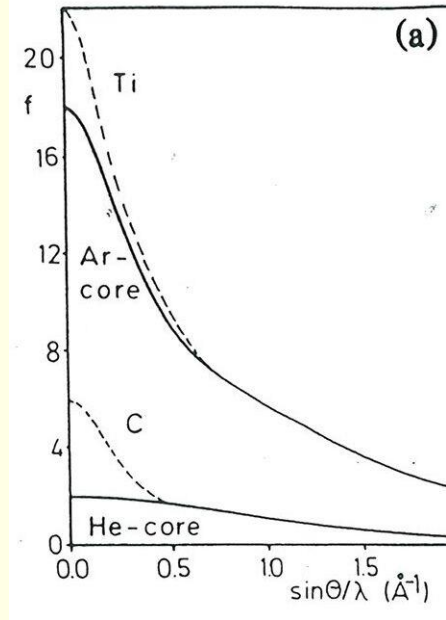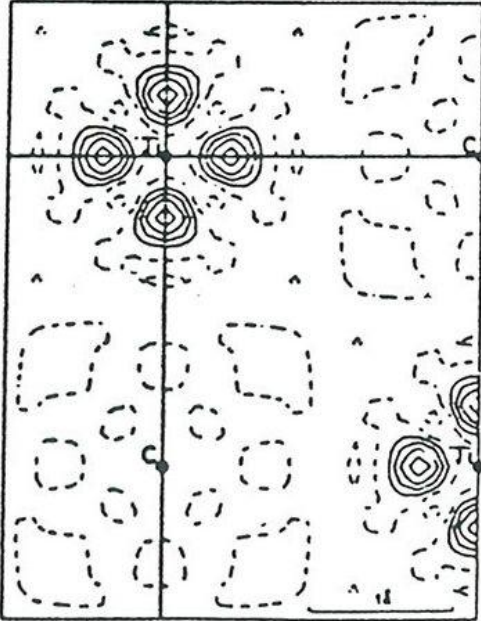
Paired reflections

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

$$\vec{S}$$

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

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

$$F(\vec{S_1}) \neq F(\vec{S_2}) \Big\} \quad \text{non spherical}$$
$$\text{with } |\vec{s_1}| = |\vec{s_2}|$$
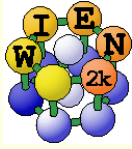
Kurt Lejaeghere,[1]* Gustav Bihlmayer,[2] Torbjörn Björkman,[3,4] Peter Blaha,[5]
Stefan Blügel,[2] Volker Blum,[6] Damien Caliste,[7,8] Ivano E. Castelli,[9] Stewart J. Clark,[10]
Andrea Dal Corso,[11] Stefano de Gironcoli,[11] Thierry Deutsch,[7,8] John Kay Dewhurst,[12]
Igor Di Marco,[13] Claudia 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]
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Sangeeta Sharma,[12] Francesca Tavazza,[17] Patrik Thunström,[41] Alexandre Tkatchenko,[15,42]
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Veronique Van Speybroeck,[1] John M. Wills,[43] Jonathan R. Yates,[29]
Guo-Xu Zhang,[44] Stefaan Cottenier[1,45]*
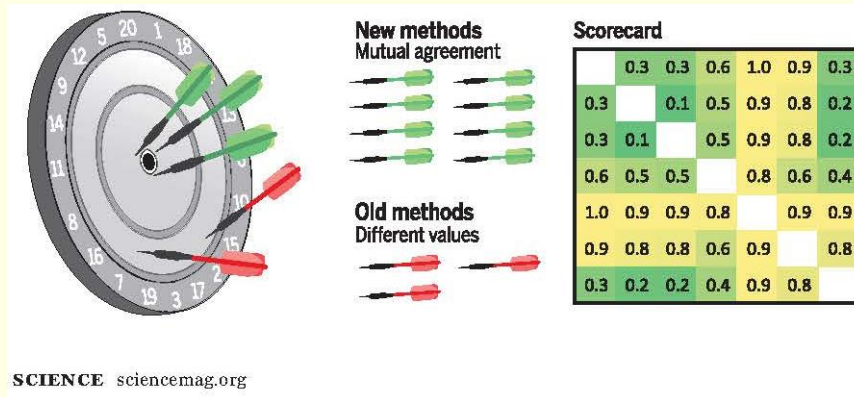
New methods
Mutual agreement

Old methods
Different values

Scorecard

	0.3	0.3	0.6	1.0	0.9	0.3
0.3		0.1	0.5	0.9	0.8	0.2
0.3	0.1		0.5	0.9	0.8	0.2
0.6	0.5	0.5		0.8	0.6	0.4
1.0	0.9	0.9	0.8		0.9	0.9
0.9	0.8	0.8	0.6	0.9		0.8
0.3	0.2	0.2	0.4	0.9	0.8	

from 45 institutions

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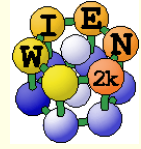
The most accurate code

AE: all electron

	average ⟨Δ⟩	AE						
		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.
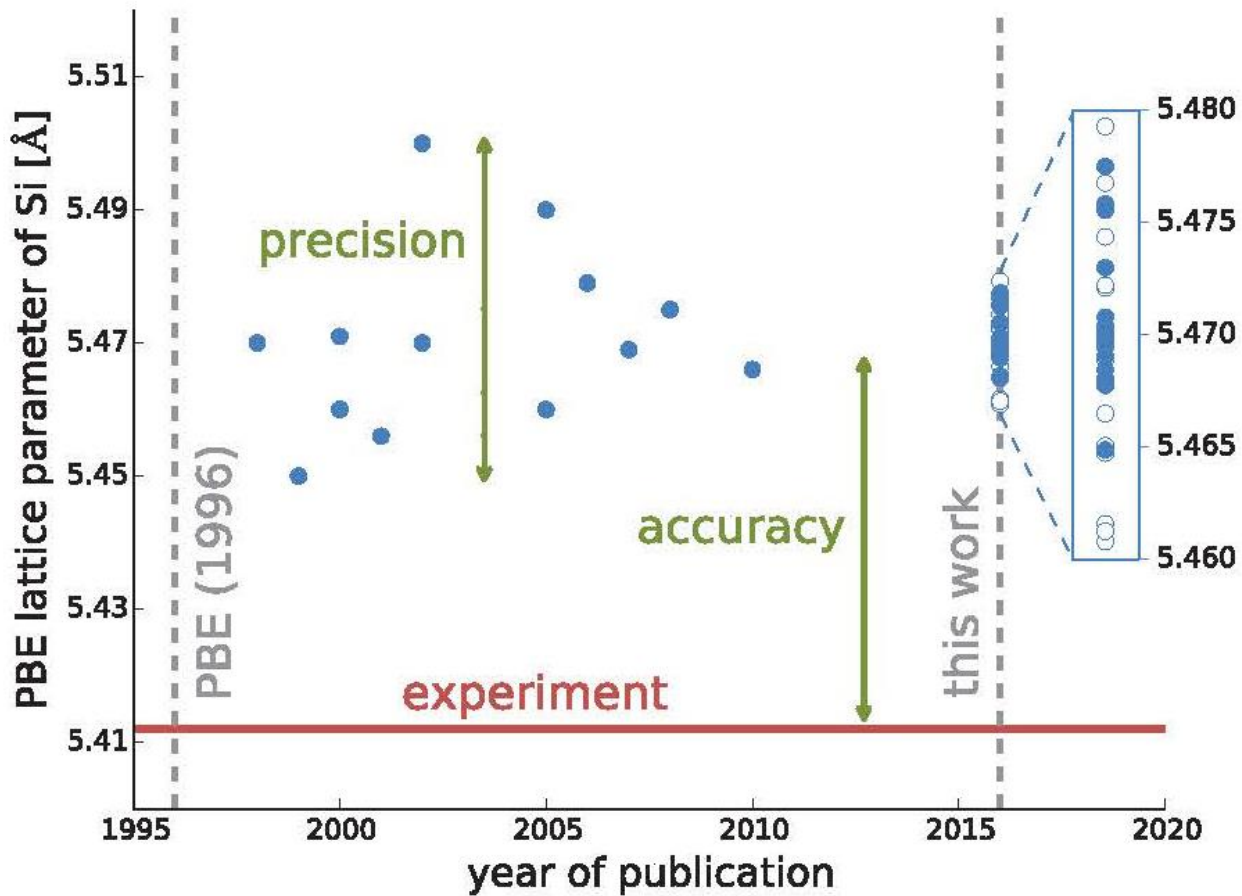
Fig. 1. Historical evolution of the predicted equilibrium lattice parameter for silicon. All data points represent calculations within the DFT-PBE framework. Values from literature (data points before 2016) (15, 16, 18, 56–62, 63–65) are compared with (i) predictions from the different codes used in 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.
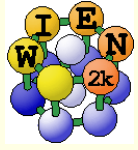
Vienna, city of music and the Wien2k code

WIEN2k

- **W**orld of
- **I**nteracting
- **E**lectrons and
- **N**uclei
- **2**

due walter kohn