

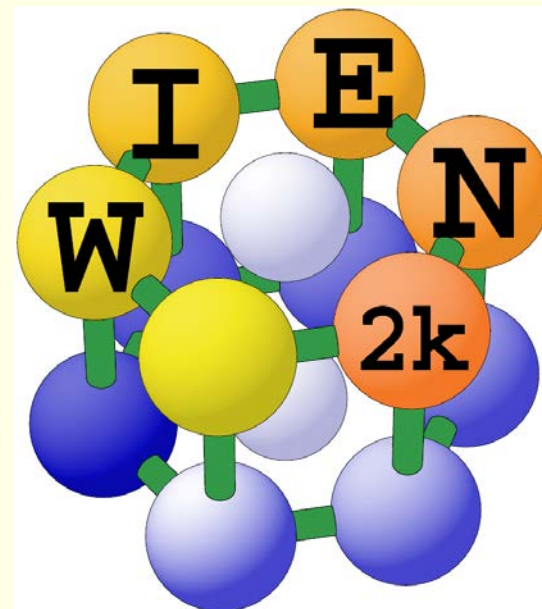
Density functional theory (DFT)  
and the concepts of the  
augmented-plane-wave plus local orbital  
(L)APW+lo method

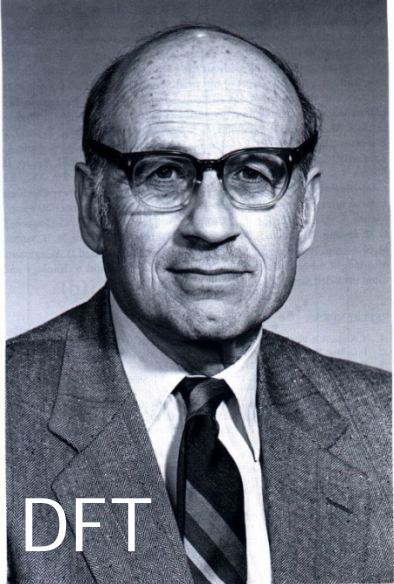
**Karlheinz Schwarz**

Institute for Material Chemistry

TU Wien

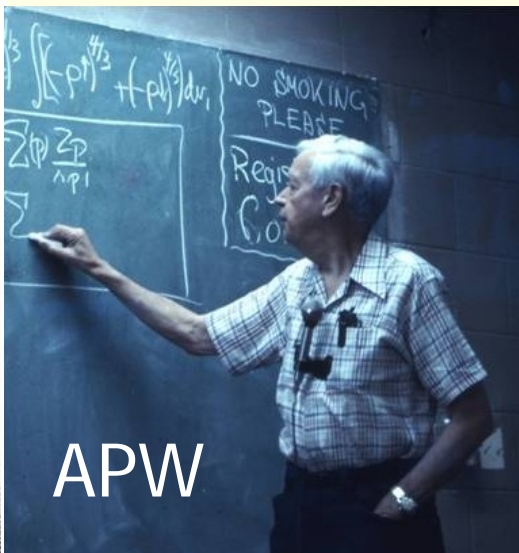
Vienna University of Technology





DFT

Walter Kohn



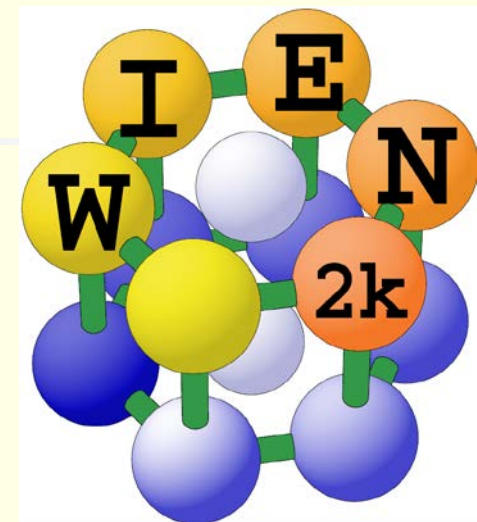
APW

J.C.Slater

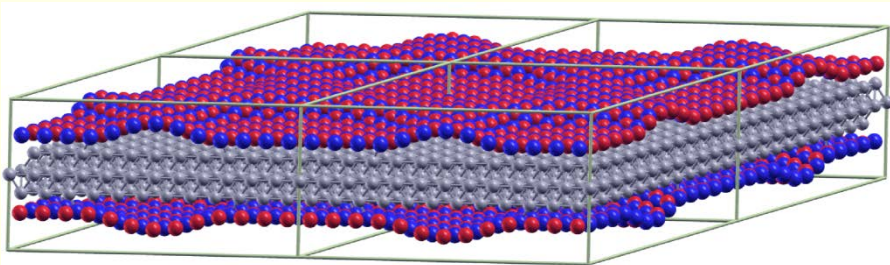


LAPW

O.K.Andersen

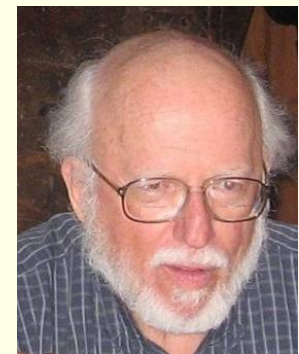


Electronic structure of solids and surfaces



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 3000 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 38 years
  - *In the year 2000 (2k) the WIEN code (from Vienna) was called wien2k*
  - *One of the most accurate DFT codes for solids*
  - *All electron, relativistic, full-potential method*
  - *Widely used in academia and industry*
- **Applications:**
  - *solids: insulators , covalently bonded systems, metals*
  - *Surfaces: catalysis*
  - *Electronic, magnetic, elastic , optical ,...properties*
  - *Many application in literature*
  - See [www.wien2k.at](http://www.wien2k.at)



# Aspects at this workshop



- Atomic structure
  - *Periodic boundary condition (approximation)*
- Quantum mechanical treatment
  - *DFT (functionals) and beyond (GW, DMFT, RPA, BSE, ...)*
- How to solve the QM (basis set)
  - *LAPW method and local orbitals as implemented in WIEN2k*
- Applications
  - *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



# Crucial aspects for a simulation



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

## Structure model:

unit cell  
supercell  
surface

## Quantum mechanics:

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

## Convergence:

basis sets  
**k**-points

## Other effects:

temperature  $T > 0$  K  
pressure

stoichiometry  
disorder  
impurities  
defects

electron core-hole  
satellites  
all electron  
relativistic effects

vacuum  
supercell  
 $\ell$  quantum nr.

average  
vibrations

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



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





# Unit cell

Assuming an ideal infinite crystal we define a unit cell by

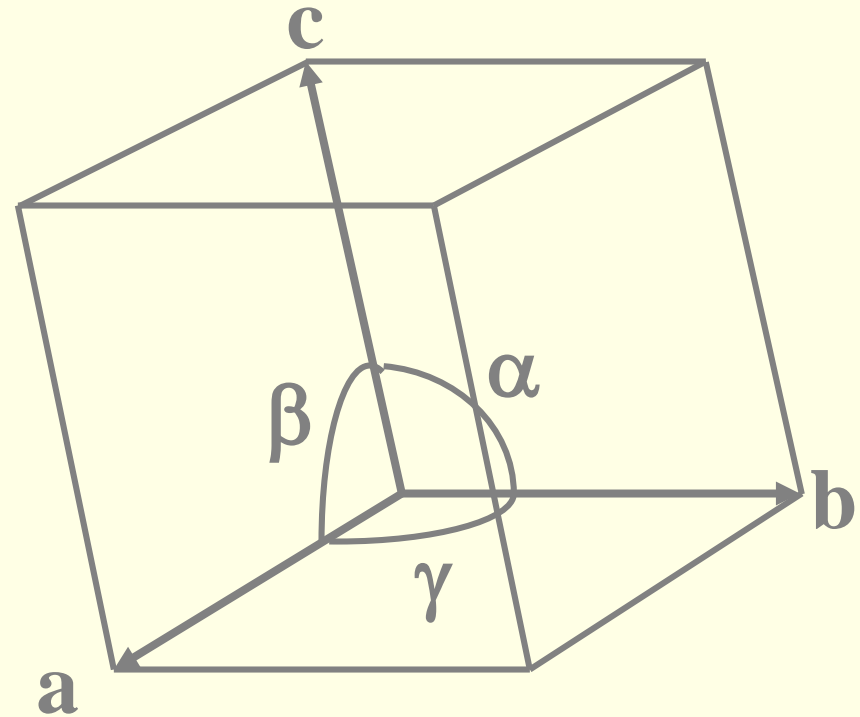
**Unit cell:** a volume in space that fills space entirely when translated by all lattice vectors.

The obvious choice:

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

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

the cell is as symmetric as possible (14 types)



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



# Crystal system: e.g. cubic

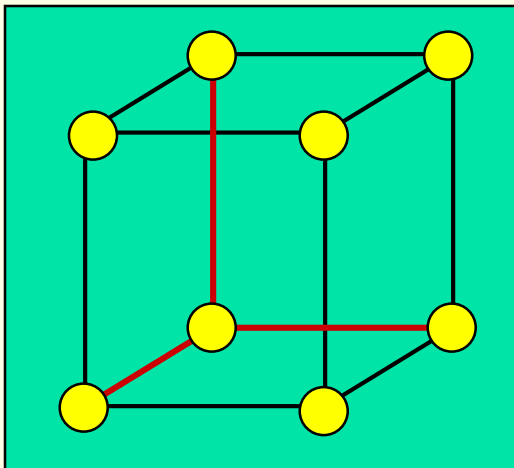


Axis system

$$a = b = c$$

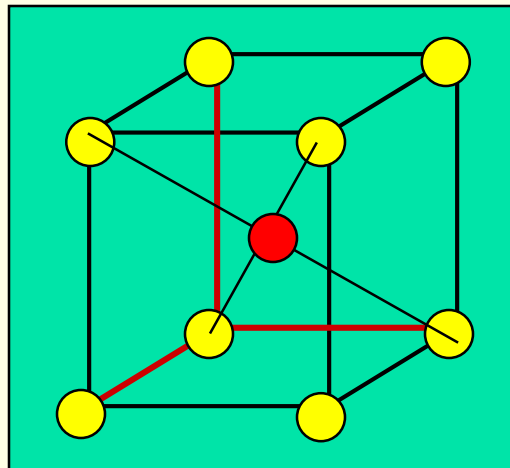
$$\alpha = \beta = \gamma = 90^\circ$$

**primitive**



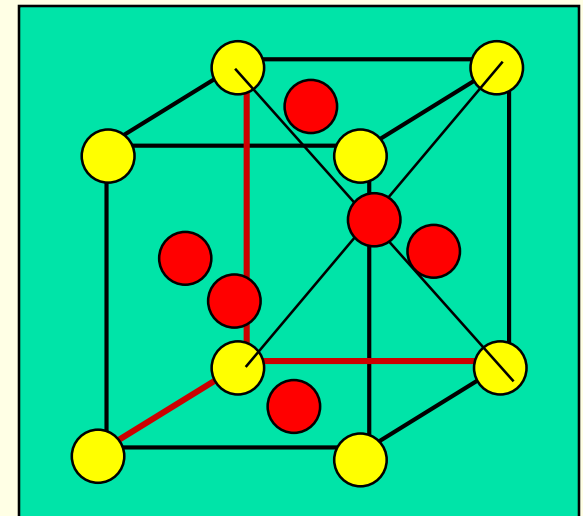
**P (cP)**

**body centered**



**I (bcc)**

**face centered**



**F (fcc)**



# 3D lattice types:

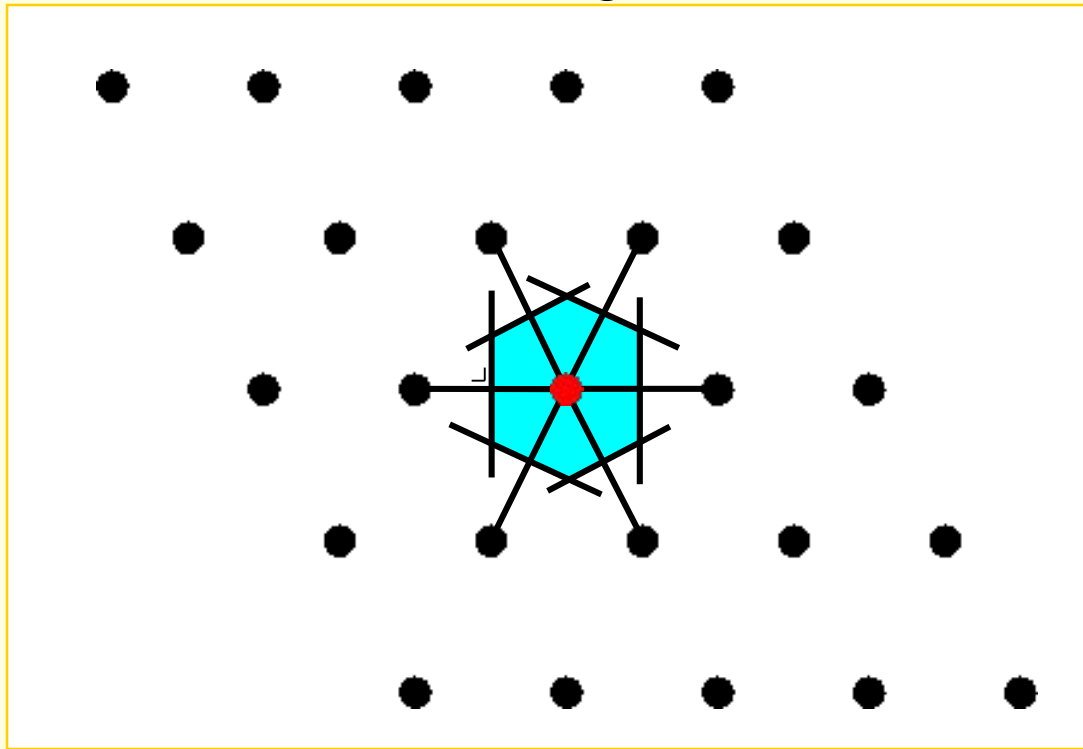
## 7 Crystal systems and 14 Bravais lattices

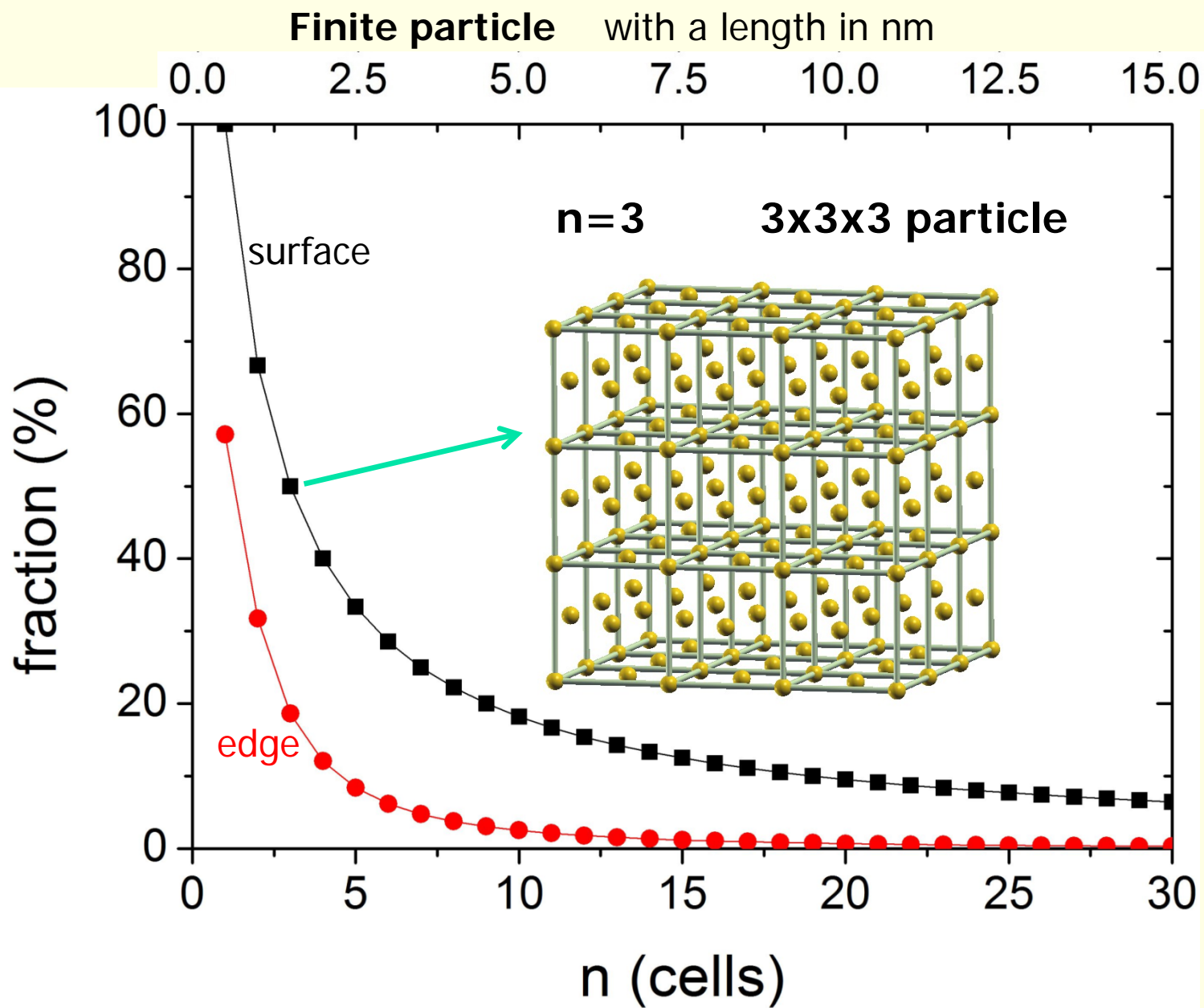
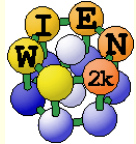
Triclinic	1	“no” symmetry
Monoclinic (P, C)	2	Two right angles
Orthorhombic (P, C, I, F)	4	Three right angles
Tetragonal (P, I)	2	Three right angles + 4 fold rotation
Cubic (P, I, F)	3	Three right angles + 4 fold + 3 fold
Trigonal (Rhombohedral)	1	Three equal angles ( $\neq 90^\circ$ ) + 3 fold
Hexagonal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



# Wigner-Seitz Cell

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





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



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



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

1-dimensional case:

$V(x)$  has lattice periodicity (“**translational invariance**”):

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

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

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

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

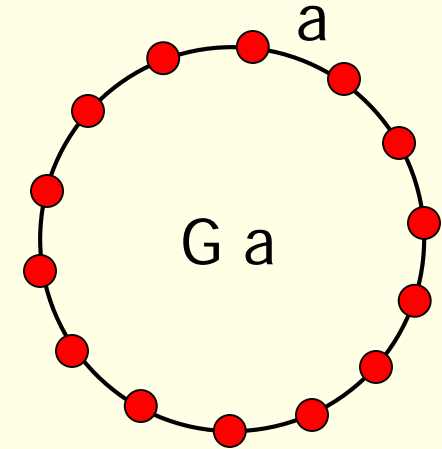
Application of the translation  $\tau$   $g$ -times:

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

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

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

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



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

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

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

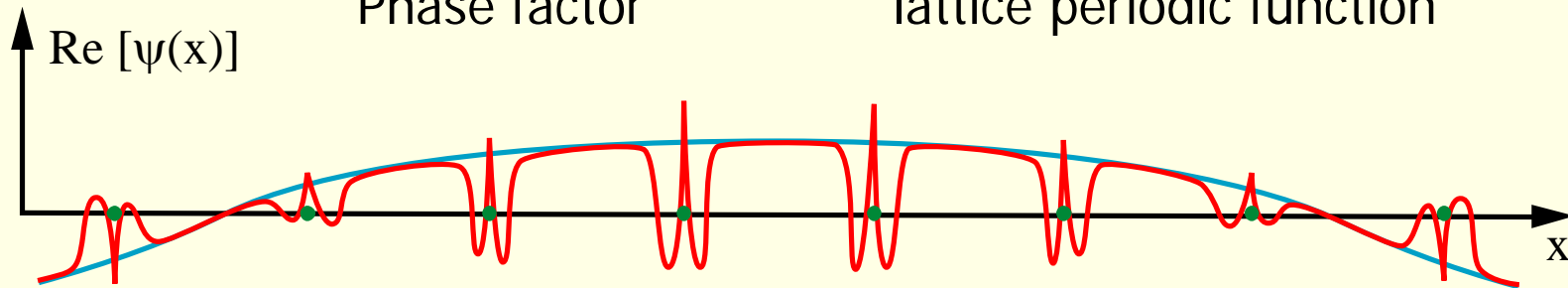


## Wave functions with Bloch form:

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

Phase factor

lattice periodic function



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

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

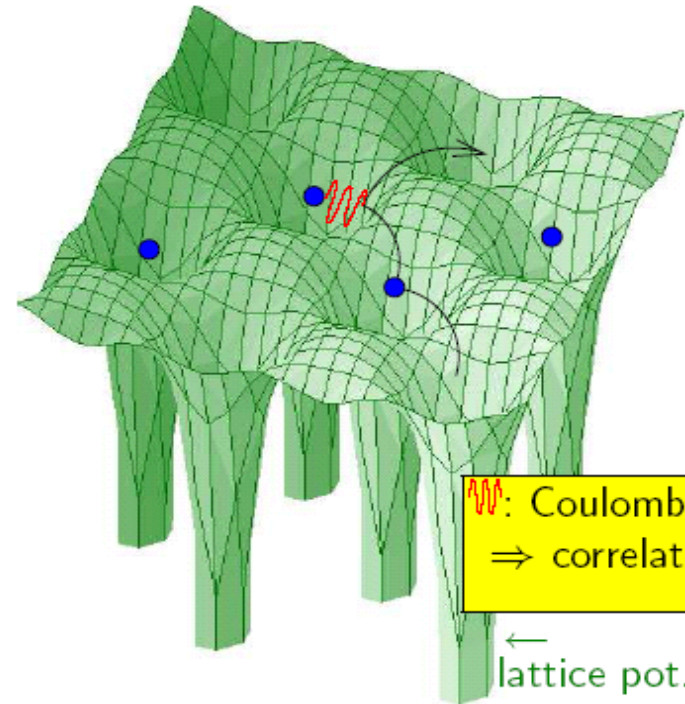
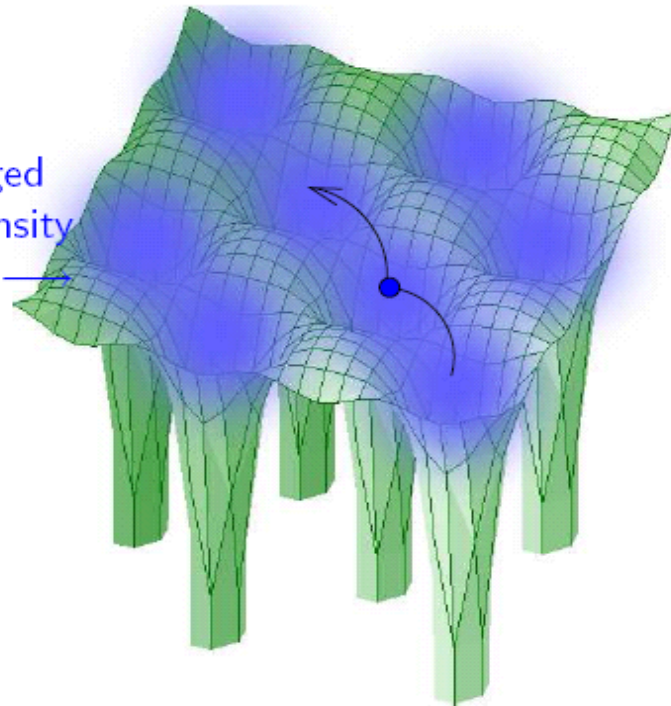
$$e^{i\frac{2\pi}{a}K} = 1$$

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

## Two communities in solid state theory

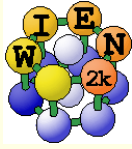
	LDA bandstructure	many body theory
+	<ul style="list-style-type: none"> <li>material-specific, "ab initio"</li> <li>often successful, quantitative</li> </ul>	<ul style="list-style-type: none"> <li>electronic correlations</li> <li>qualitative understanding</li> </ul>
-	<ul style="list-style-type: none">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

time averaged  
electron density



: Coulomb WW  
 ⇒ correlations

← lattice pot.



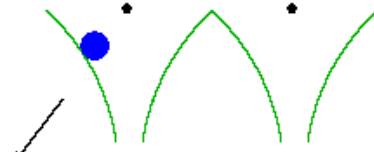
# Ab-initio Hamiltonian

(non-relativistic/Born-Oppenheimer approximation)

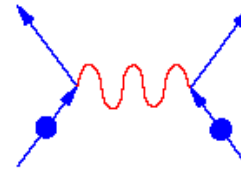
kinetic energy



lattice potential



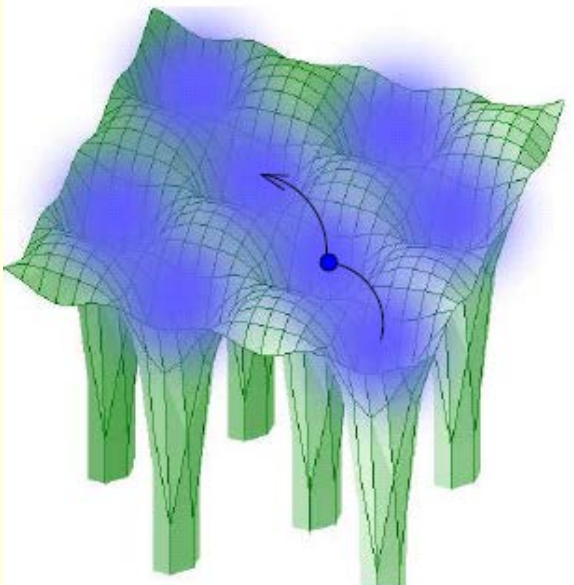
Coulomb interaction



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

LDA bandstructure corresponds to

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



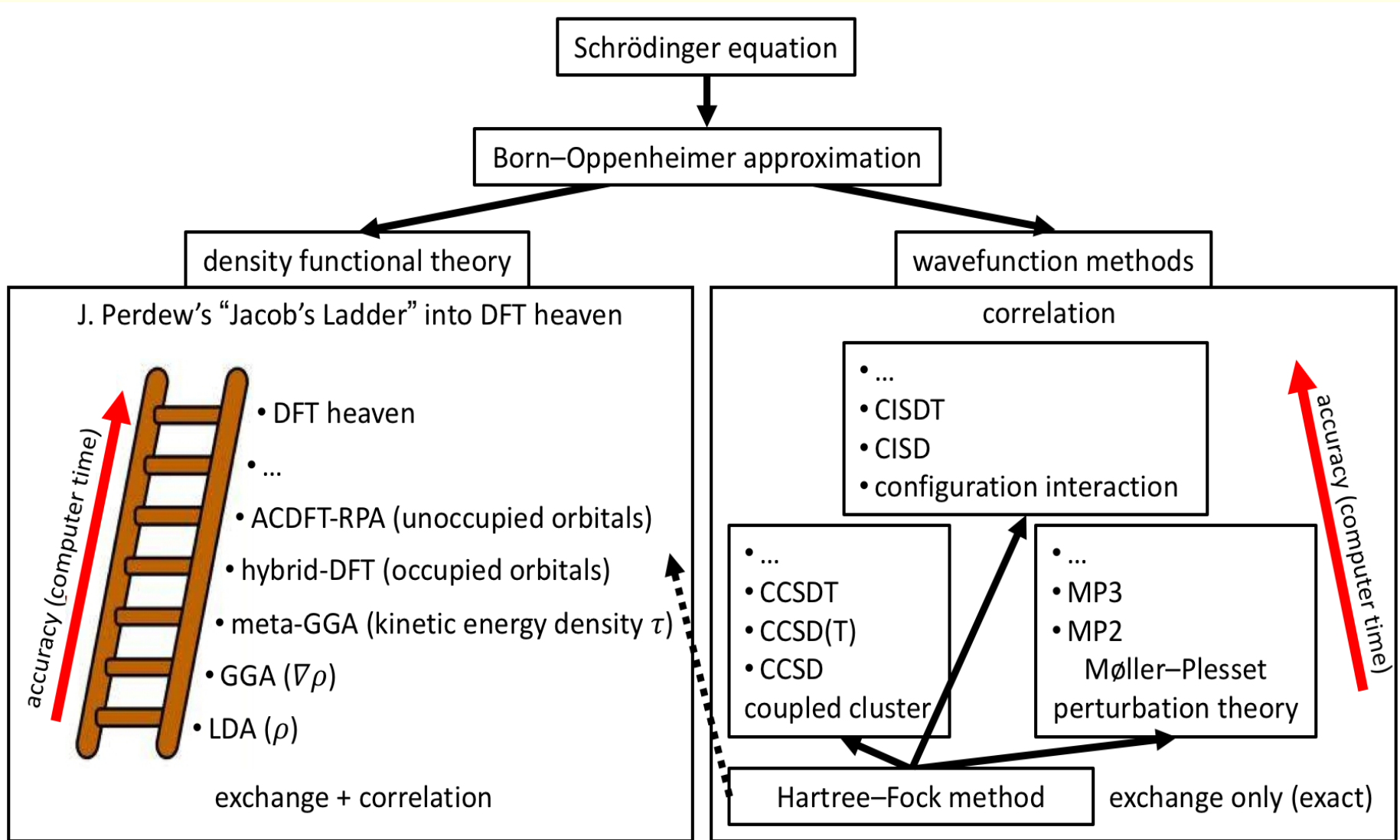
Coulomb potential:


- nuclei
- all electrons
- including self-interaction

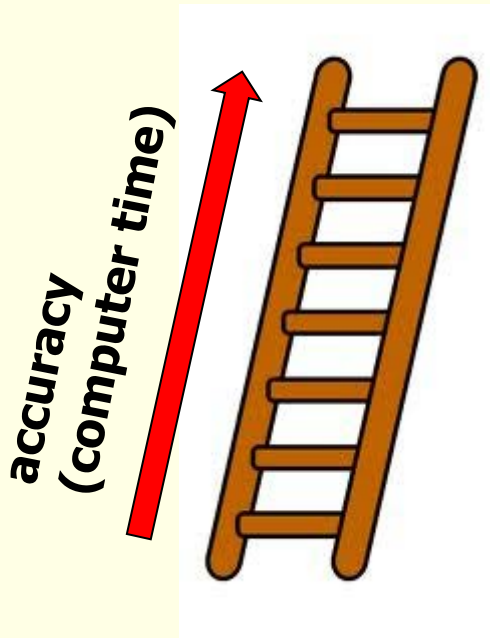
Quantum mechanics:

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

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:



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



# DFT versus the Schrödinger Equation

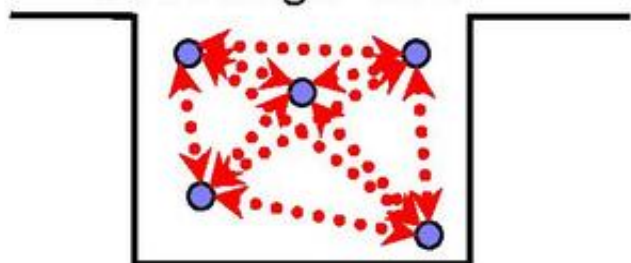
We have moved our problem from here ...

Properties of the system

Hard problem to solve

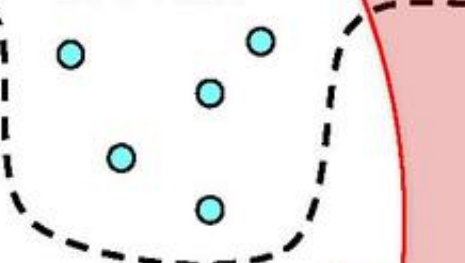
"Easy" problem to solve

Schrödinger view



Formally equivalent

DFT view



- electron
- electron interaction
- external potential

- Kohn-Sham particle (non-interacting)
- effective potential

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

... to here

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



## Hohenberg-Kohn theorem: (exact)

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

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

## Kohn-Sham: (still exact!)

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

$E_{\text{kinetic}}$   
non interacting

$E_{\text{ne}}$

$E_{\text{coulomb}}$   $E_{\text{ee}}$

$E_{\text{xc}}$  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.



# ESSENCE OF DENSITY-FUNCTIONAL THEORY



- **Every observable quantity of a quantum system can be calculated from the density of the system ALONE (Hohenberg, Kohn, 1964).**
- **The density of particles interacting with each other can be calculated as the density of an auxiliary system of non-interacting particles (Kohn, Sham, 1965).**







LDA, GGA

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

## 1-electron equations (Kohn Sham)

vary  $\rho$

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

$$-Z/r$$

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

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

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

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

**LDA** } treats both, exchange and correlation effects,  
**GGA** } but approximately

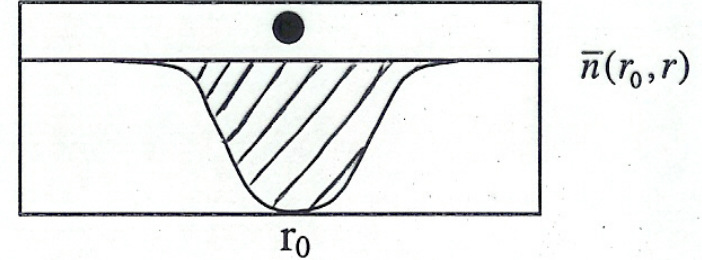
*New (better ?) functionals are still an active field of research*



# Exchange and correlation

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

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



Properties of the exchange-correlation hole:

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

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

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

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

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

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



With 80 years



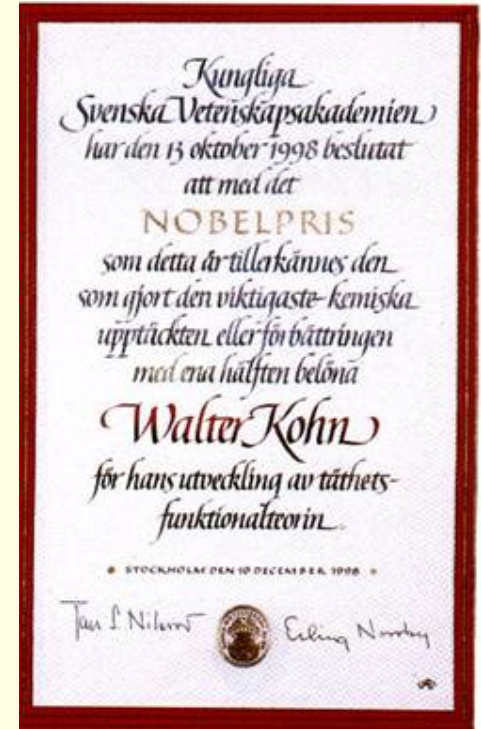
- 1923 born in Vienna
- 1938 had to leave Vienna
- 1946 Univ. Toronto (master, Math)
- 1948 Harvard (PhD, Schwinger)
- Carnegie Mellon, Pittsburgh (Luttinger), Bell Labs, Copenhagen, Washington (Seattle), Paris, Imperial College (London), ETH Zürich, Univ. California, San Diego
- 1979 Founding director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



# Walter Kohn, Nobel Prize 1998 Chemistry



Walter Kohn



“Self-consistent Equations including Exchange and Correlation Effects”

W. Kohn and L. J. Sham, *Phys. Rev.* 140, A1133 (1965)

54 years ago

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

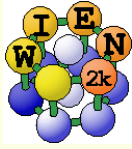


# Walter Kohn



- 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





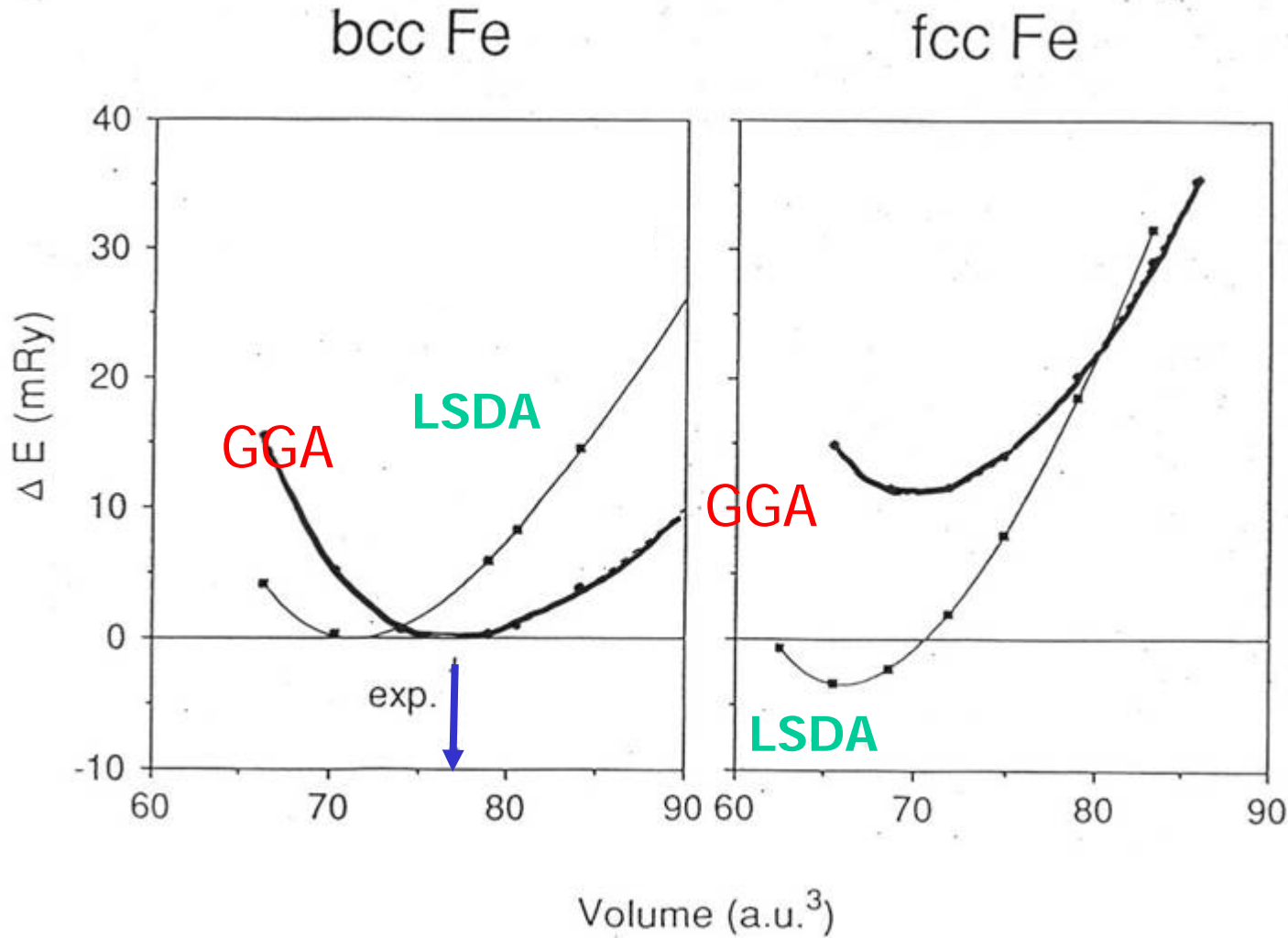
## Obituary for Walter Kohn (1923–2016)

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.



# DFT ground state of iron



## LSDA

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

## GGA

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

## Experiment

- *FM*
- *bcc*



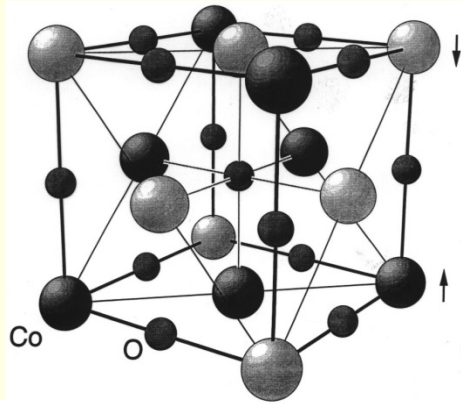
DFT thanks to Claudia Ambrosch (previously in Graz)



GGA follows LDA

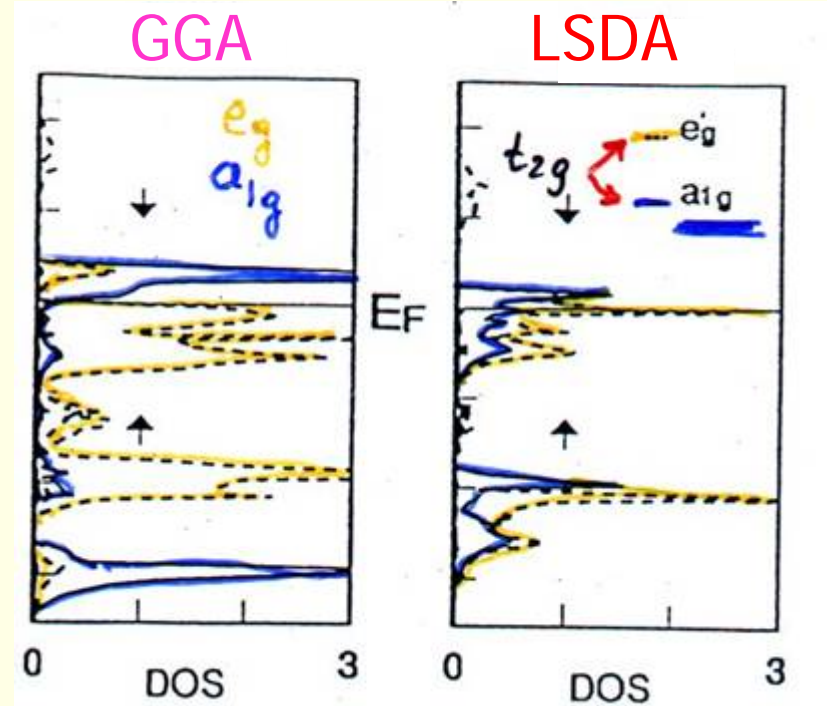
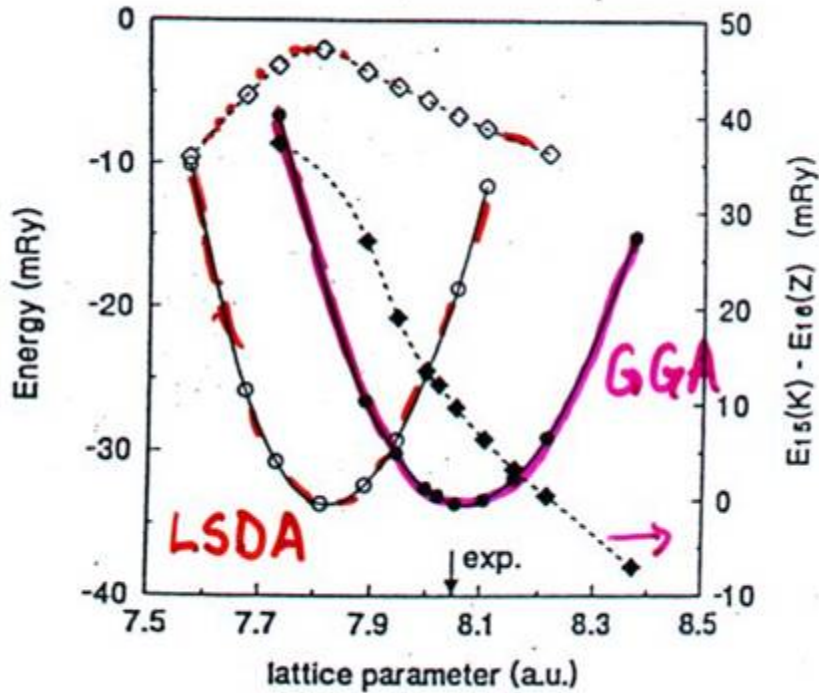




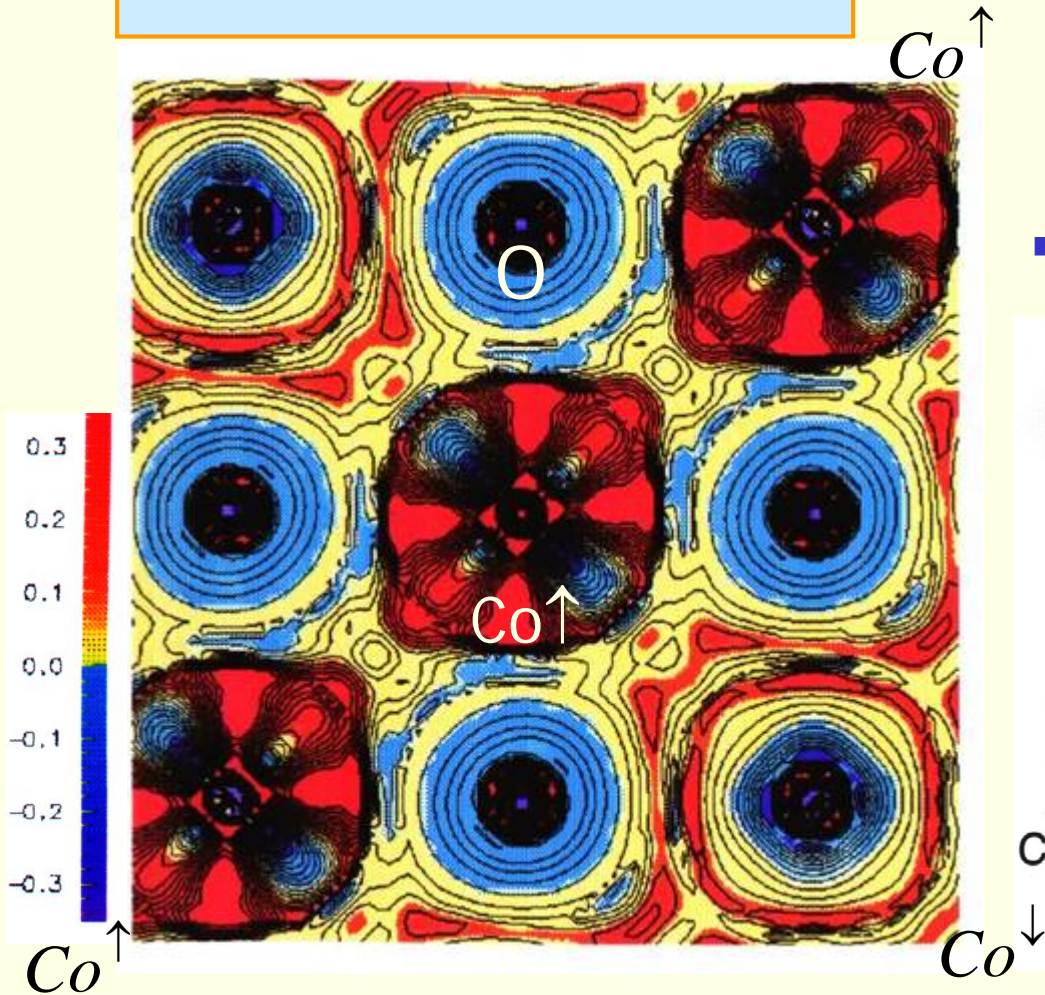


## ■ CoO

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



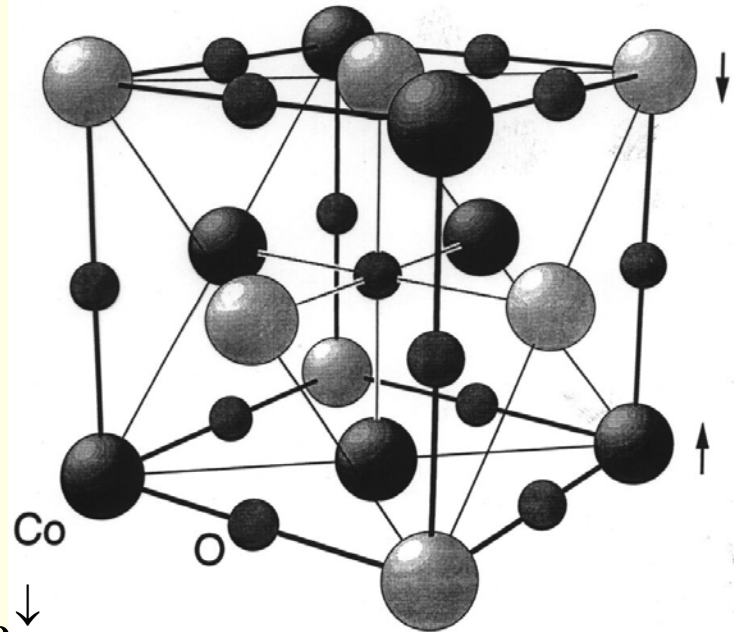
$$\Delta V_{xc}^{\uparrow} = V_{xc}^{\uparrow GGA} - V_{xc}^{\uparrow LSDA}$$



- Central Co atom distinguishes

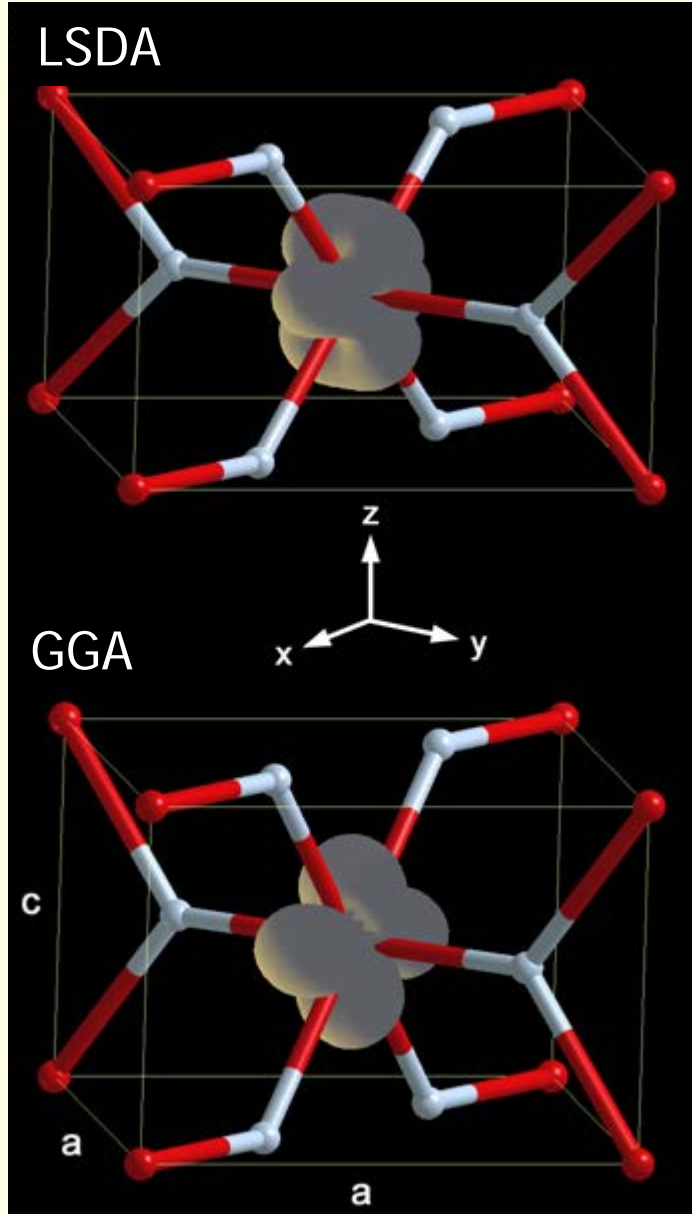
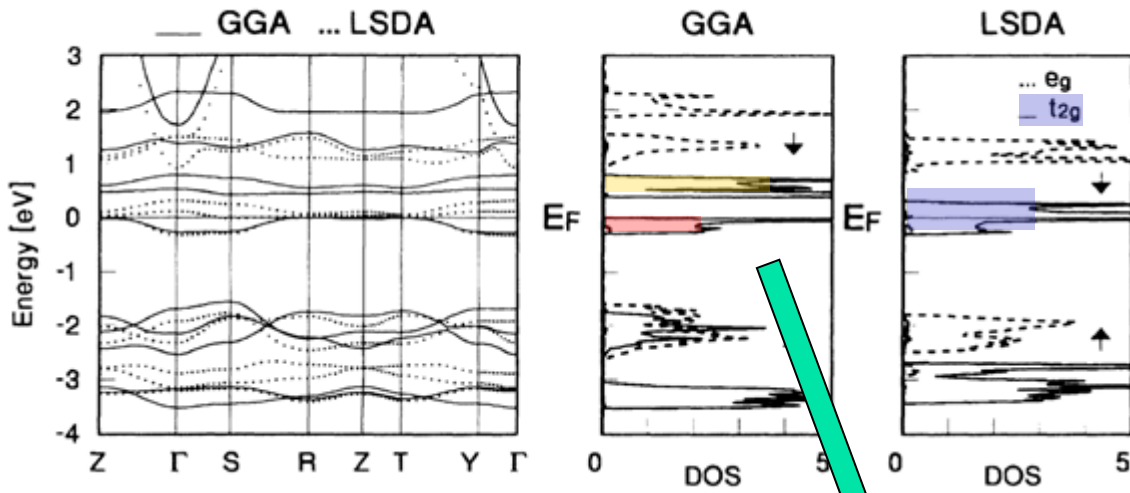
- *between*  $Co^{\uparrow}$
- *and*  $Co^{\downarrow}$

- Angular correlation





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



Fe-EFG in FeF<sub>2</sub>:  
LSDA: 6.2  
GGA: 16.8  
exp: 16.5

FeF<sub>2</sub>: GGA splits  
t<sub>2g</sub> into a<sub>1g</sub> and e<sub>g</sub>'

agree



# Accuracy of DFT for transition metals

## Lattice parameters (Å)

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

### ■ 3d elements:

- *PBE superior, LDA much too small*

### ■ 4d elements:

LDA too small, PBE too large

- *New functional Wu-Cohen (WC)*

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

### ■ 5d elements:

- *LDA superior, PBE too large*



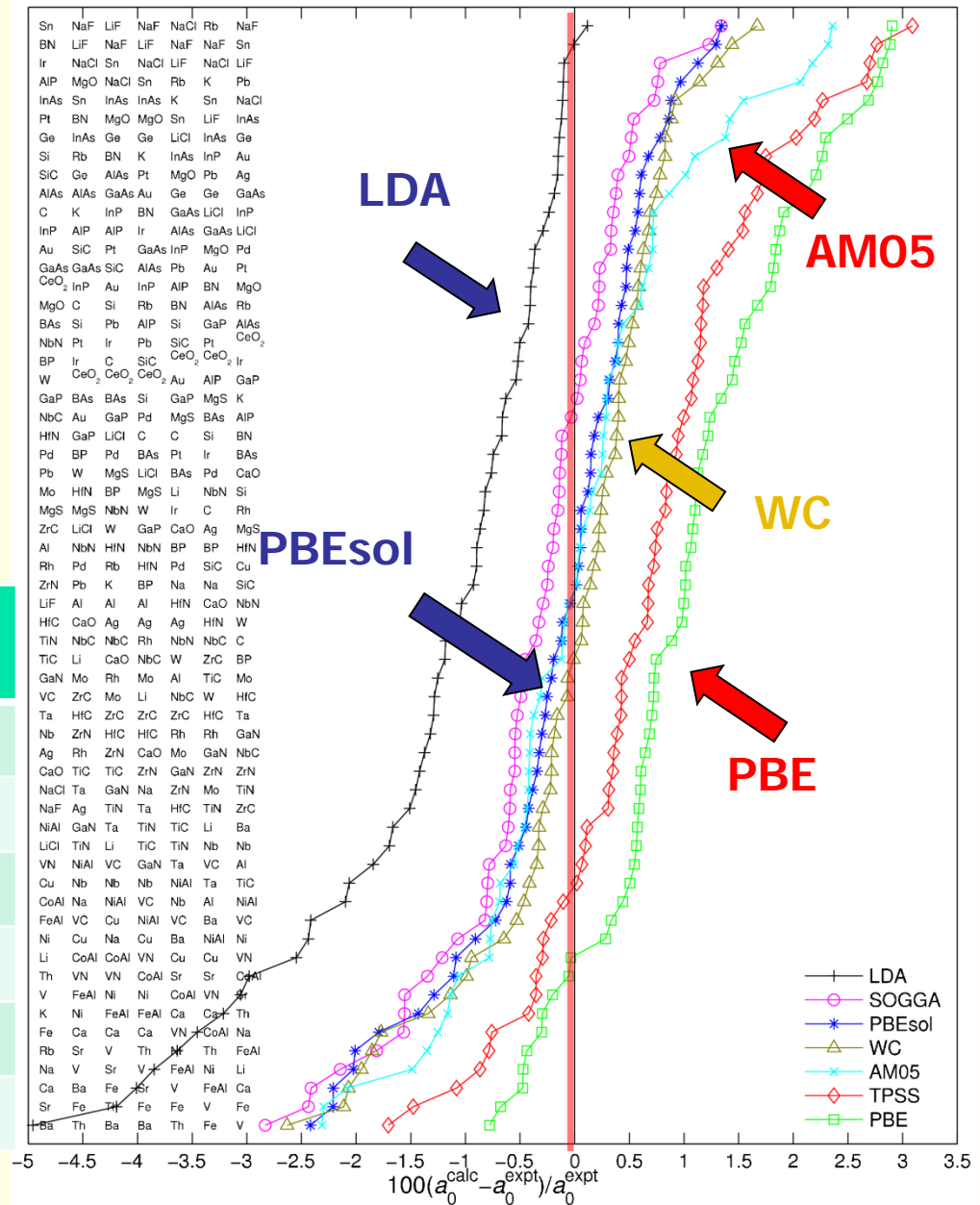
# accuracy: "DFT limit"



## Testing of DFT functionals:

- error of theoretical lattice parameters for a large variety of solids (Li-Th)

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





# Can LDA be improved ?



- **better GGAs and meta-GGAs** ( $\rho, \nabla\rho, \tau$ ):
  - *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:  $E_{xc}^{hybrid} = E_{xc}^{DFT} + \alpha (E_x^{HF} - E_x^{DFT})$   
where

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





# Hybrid functional: only for (correlated) electrons

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

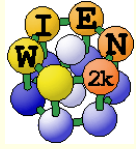
$$E_{xc}^{\text{hybrid}} = E_{xc}^{\text{DFT}}[\rho^\sigma] + \alpha \left( E_x^{\text{HF}}[n_{m_i m_j}^\sigma] - E_x^{\text{DFT}}[\rho_\ell^\sigma] \right)$$

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

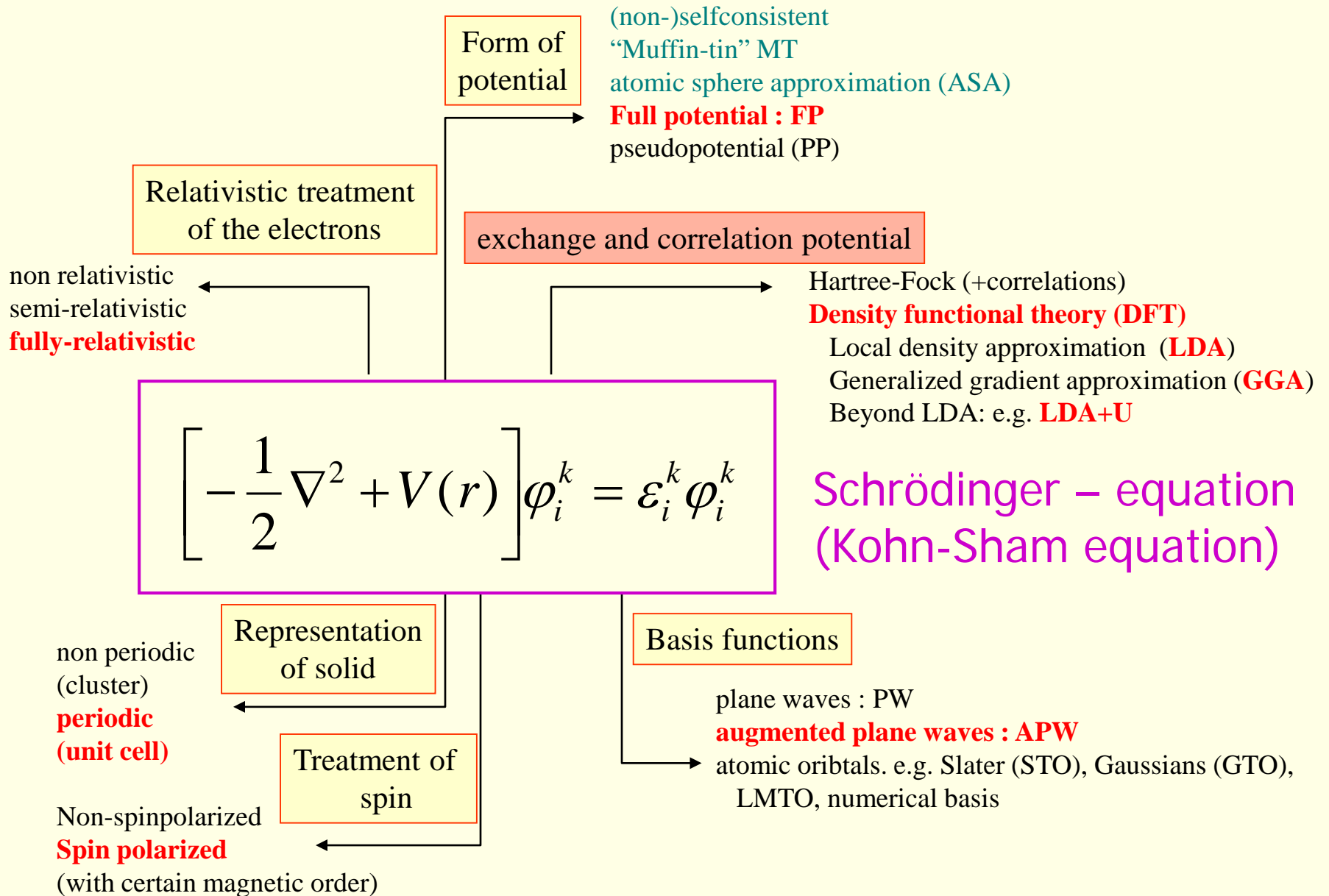
$$\langle m_1 m_2 | v_{ee} | m_3 m_4 \rangle = \sum_{k=0}^{2\ell} a_k F_k$$

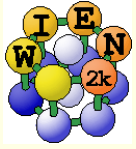
The Slater integrals  $F_k$  are calculated according to P. Novák et al., phys.stat.sol (b) **245**, 563 (2006)



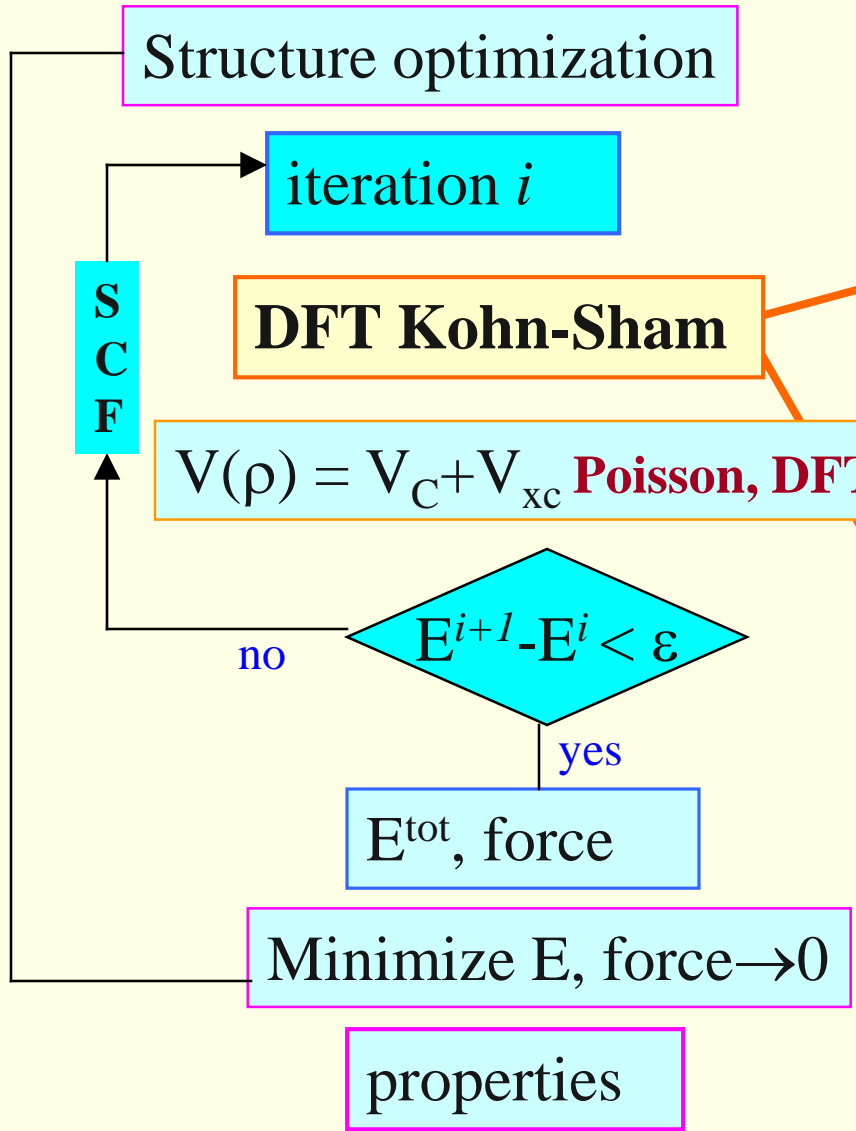
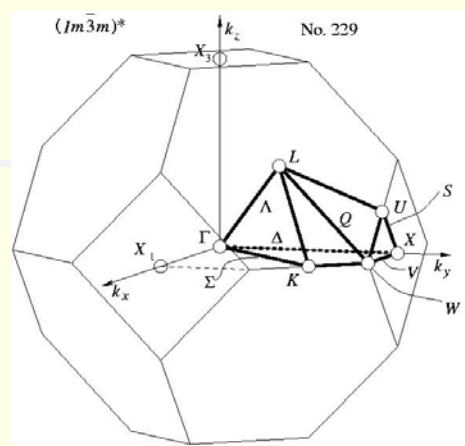


# Concepts when solving Schrödingers-equation in solids





Structure:  $\underbrace{a, b, c, \alpha, \beta, \gamma}_{\text{unit cell}}, \underbrace{R_\alpha, \dots}_{\text{atomic positions}}$



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

Kohn Sham

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

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

Variational method

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

Generalized eigenvalue problem

$$HC = ESC$$

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



# Solving Kohn-Sham's equation:



- $\Psi$  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"*

$$H C = E S C$$

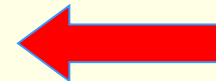
*H, S : hamilton and overlap matrix; C: eigenvectors, E: eigenvalues*

## ■ plane waves

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

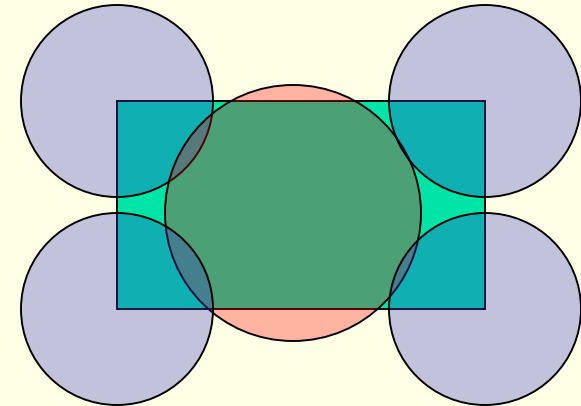
## ■ space partitioning (augmentation) methods

- *LMTO (linear muffin tin orbitals)*
  - ASA approx., linearized numerical radial function + Hankel- and Bessel function expansions
  - full-potential LMTO
- *ASW (augmented spherical wave)*
  - similar to LMTO
- *KKR (Korringa, Kohn, Rostocker method)*
  - solution of multiple scattering problem, Greens function formalism
  - equivalent to APW
- *(L)APW (linearized augmented plane waves)*



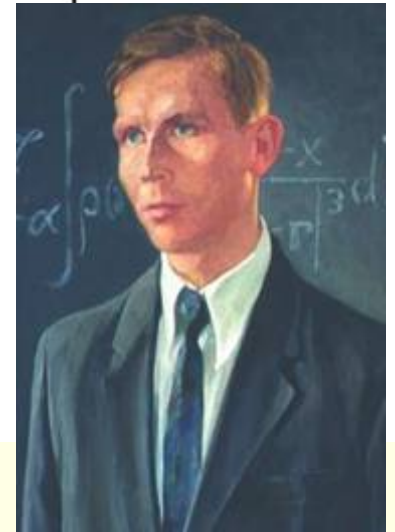
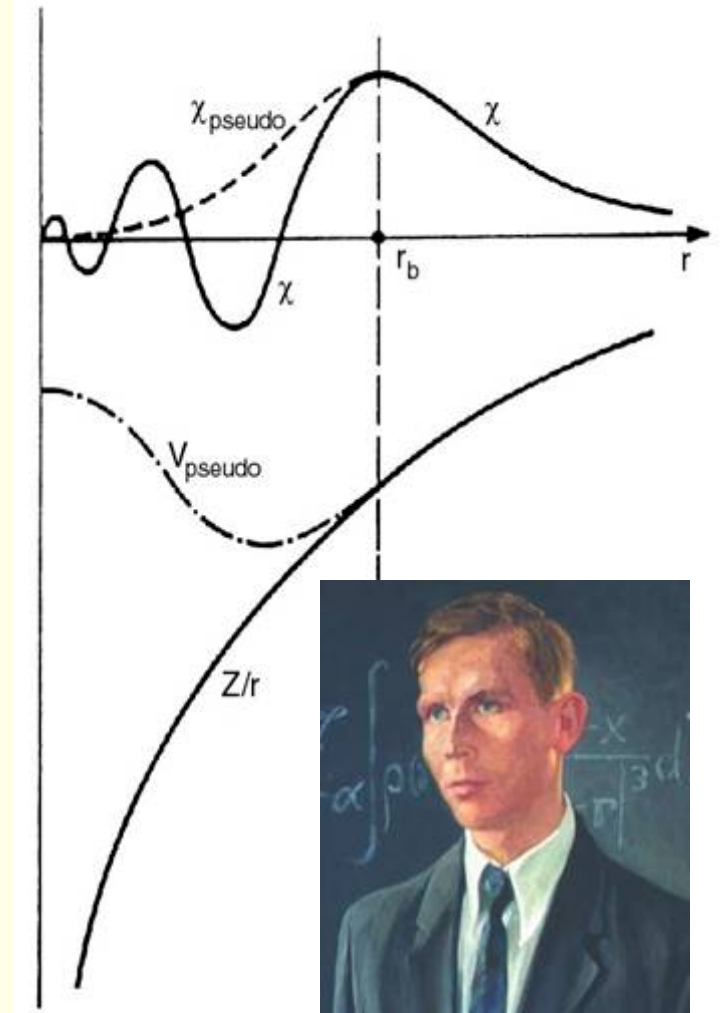
## ■ LCAO methods

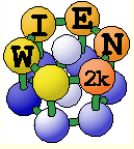
- *Gaussians, Slater, or numerical orbitals, often with PP option)*





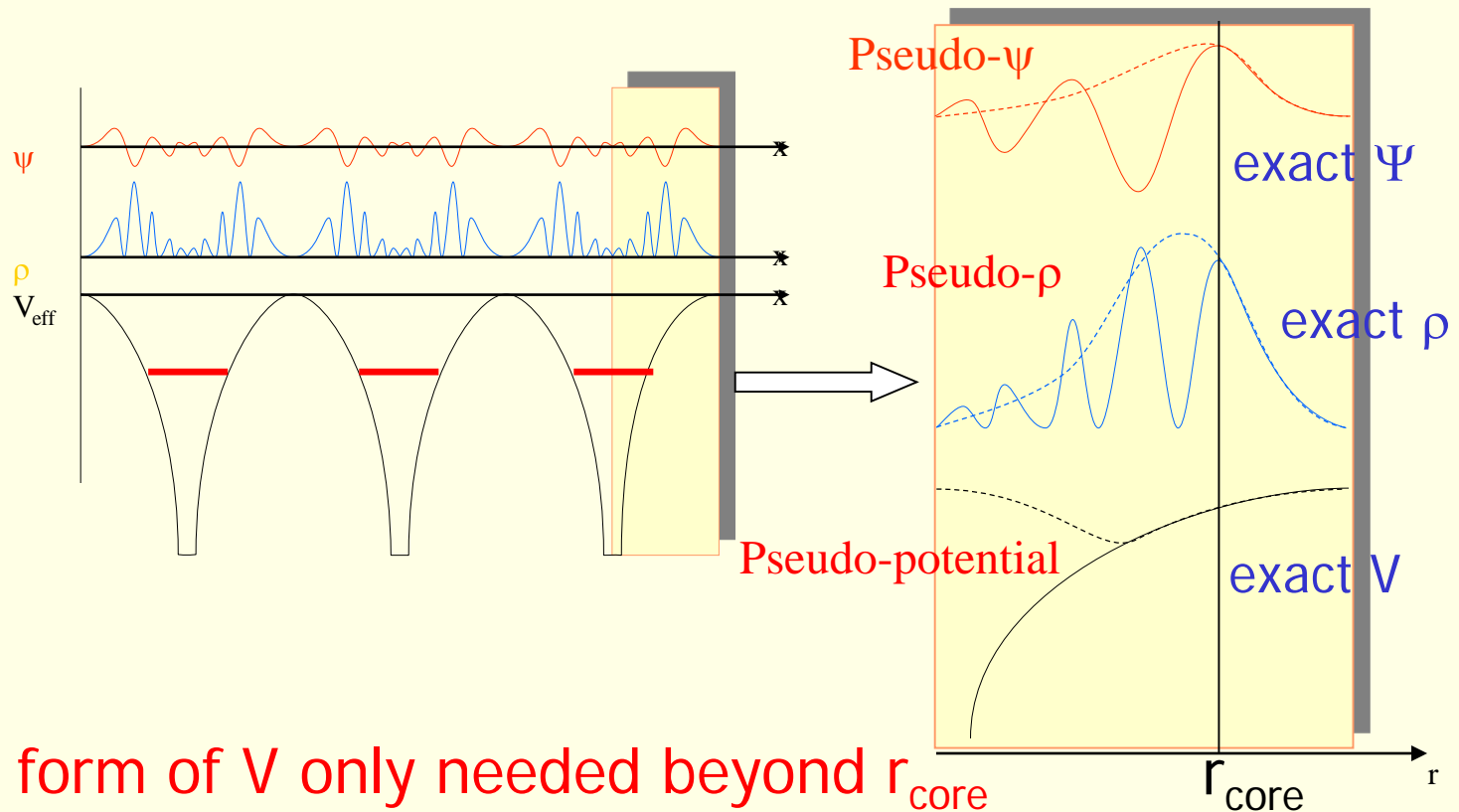
- **plane waves** form a “complete” basis set, however, they “never” converge due to the rapid oscillations of the atomic wave functions  $\chi$  close to the nuclei
- let’s get rid of all **core electrons** and **these oscillations** by replacing the strong ion–electron potential by a much weaker (and physically dubious) *pseudopotential*
- **Hellmann’s** 1935 *combined approximation method*



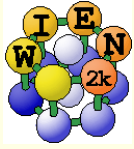


# "real" potentials vs. pseudopotentials

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



→ exact form of  $V$  only needed beyond  $r_{\text{core}}$



## ■ 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*

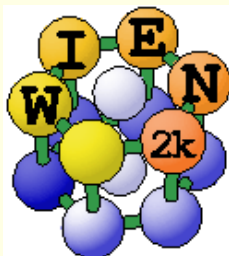
K.Schwarz,  
DFT calculations of solids with LAPW and WIEN2k  
Solid State Chem. **176**, 319-328 (2003)

## ■ Local orbitals (D.J.Singh 1991)

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

## ■ APW+lo (E.Sjöstedt, L.Nordström, 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

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

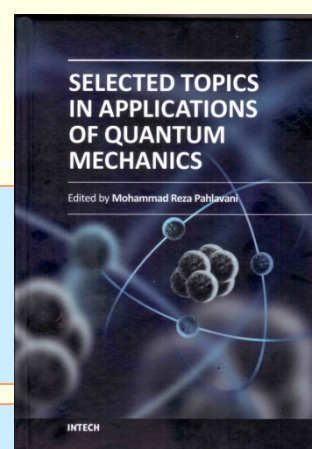
K.Schwarz, P.Blaha, *Electronic structure of solids and surfaces with WIEN2k*  
in *Practical Aspects of Computational Chemistry I: An Overview of the Last Two Decades and Current Trends*,  
J.Leszczynski, M.K.Shukla (Eds),  
Springer Science+Business Media B.V. (2012) Chapter 7, 191-207,  
ISBN 978-94-007-0918-8

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

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

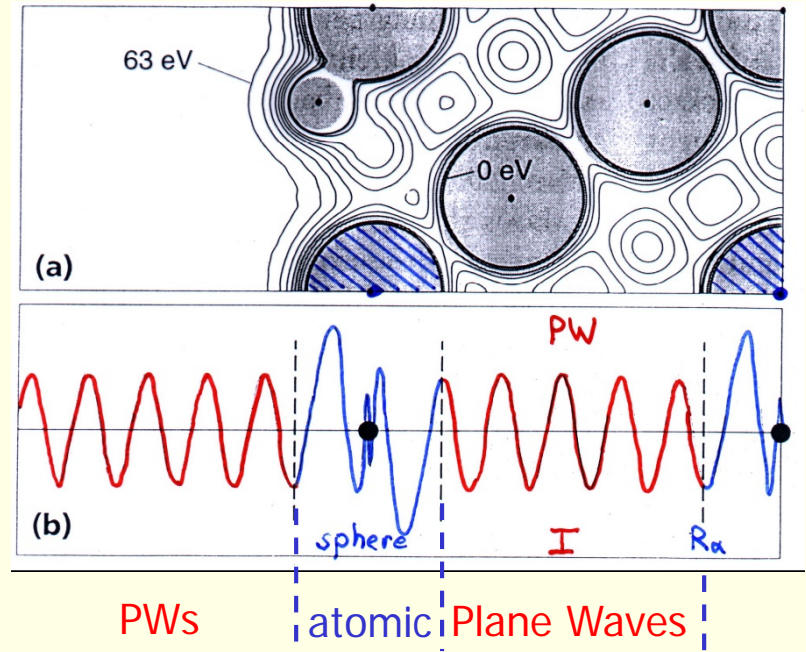
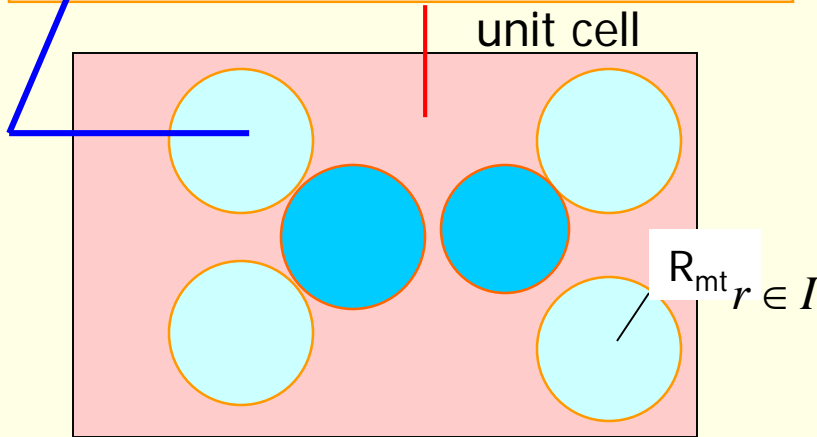
K.Schwarz, *DFT calculations of solids with LAPW and WIEN2k*  
Solid State Chem.**176**, 319-328 (2003)

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)





The unit cell is partitioned into:  
 atomic spheres  
 Interstitial region



"exact" solutions, but energy dependent

Basisset:

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

Atomic partial waves

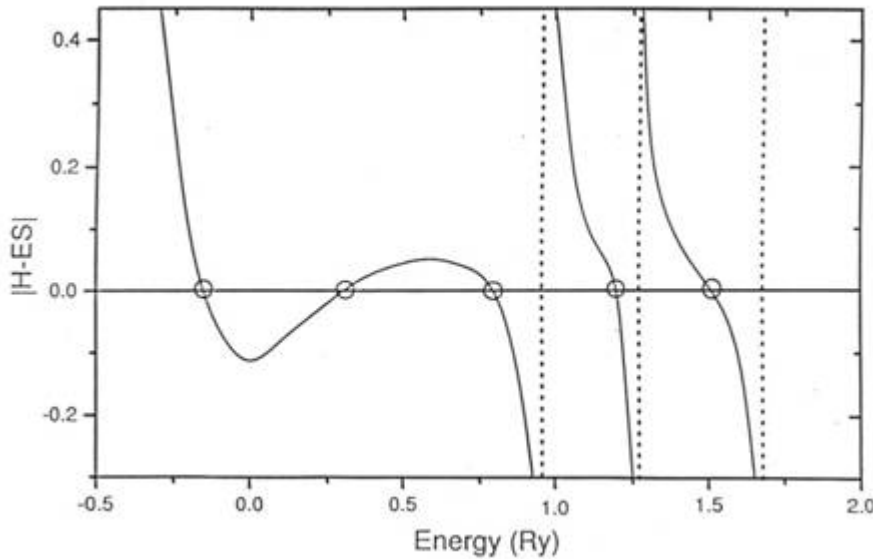
$$\sum_{lm} A_{lm}^K u_l(r', \varepsilon) Y_{lm}(\hat{r}')$$

join

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



# Slater's APW (1937)



H Hamiltonian  
S overlap matrix

Atomic partial waves

$$\sum_{lm} a_{lm}^K u_l(r', \varepsilon) Y_{lm}(\hat{r}')$$

Energy dependent basis functions  
lead to a

Non-linear eigenvalue problem

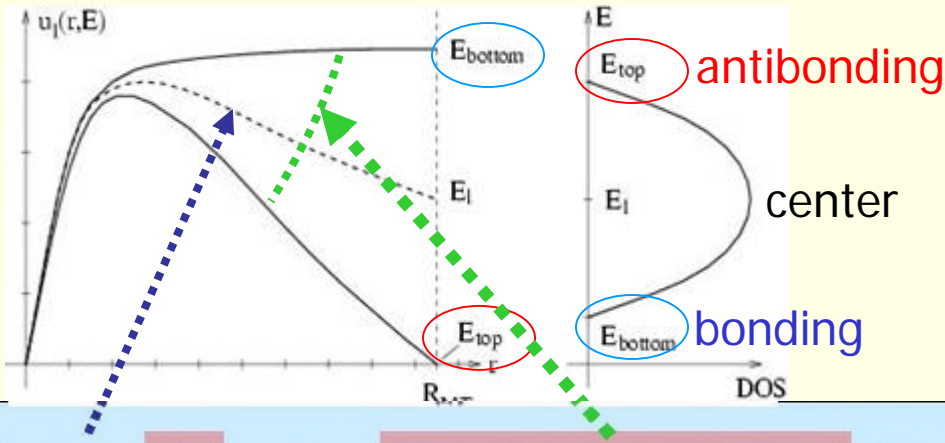
Numerical search for those energies, for which the  $\det|H-ES|$  vanishes. **Computationally very demanding.**  
"Exact" solution for given MT potential!



# Linearization of energy dependence

LAPW suggested by

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



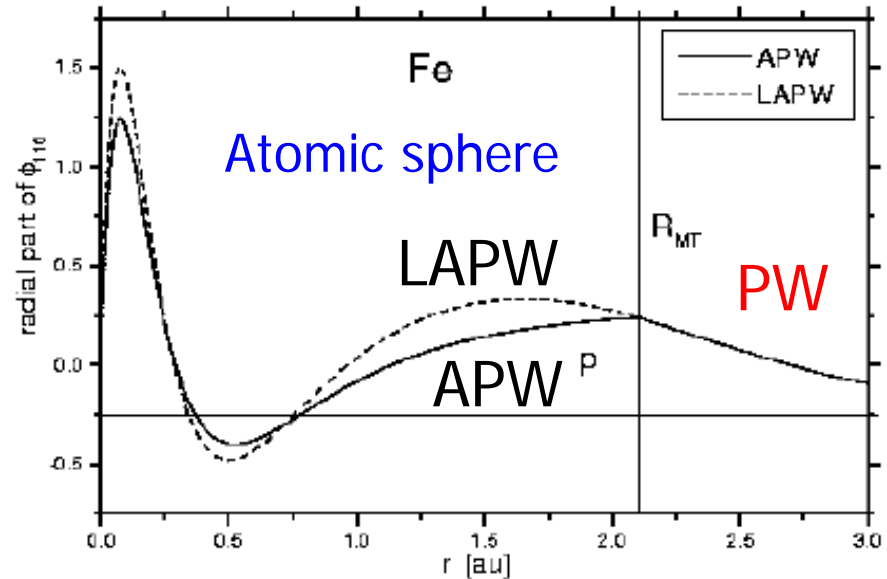
$$\Phi_{k_n} = \sum_{\ell m} [A_{\ell m}(k_n) u_{\ell}(E_{\ell}, r) + B_{\ell m}(k_n) \dot{u}_{\ell}(E_{\ell}, r)] Y_{\ell m}(\hat{r})$$

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

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

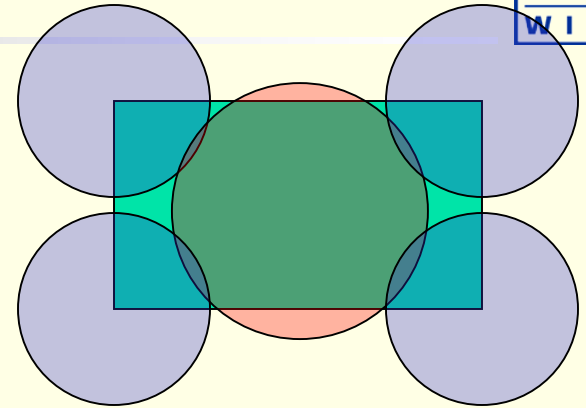
→ General eigenvalue problem  
(diagonalization)

→ additional constraint requires  
more **PWs** than APW



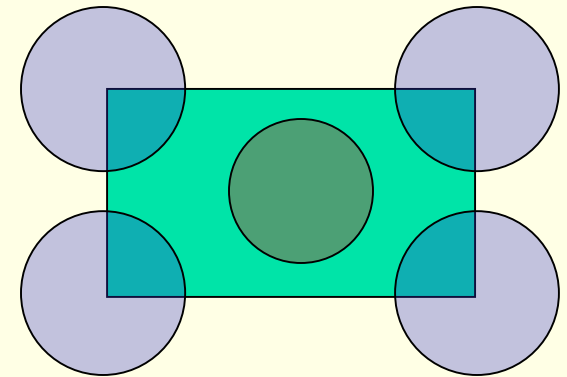
- **Atomic sphere approximation (ASA)**

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



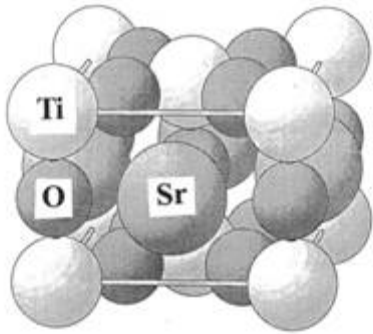
- **“muffin-tin” approximation (MTA)**

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

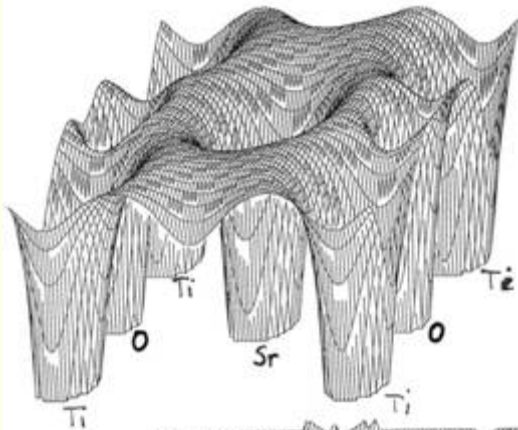


- **“full”-potential**

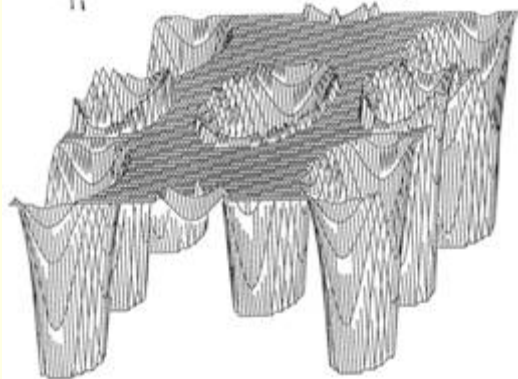
- *no shape approximations to  $V$*



SrTiO<sub>3</sub>



Full potential



Muffin tin approximation

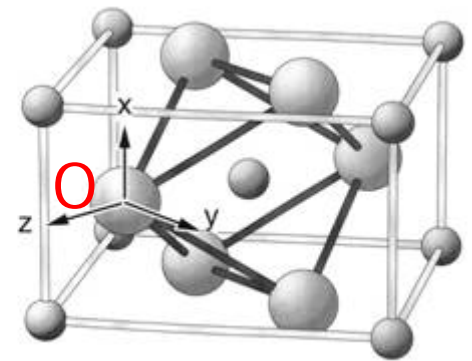
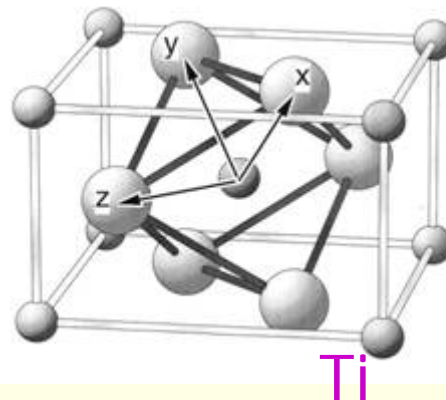


TiO<sub>2</sub> rutile

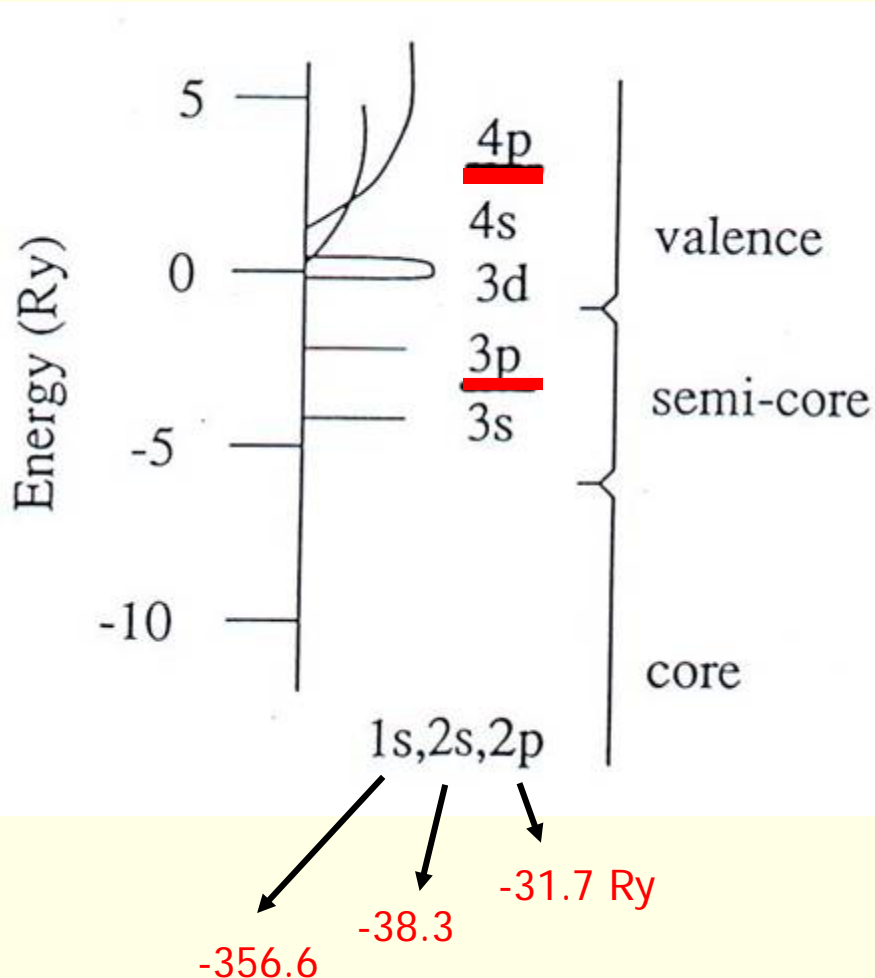
- The potential (and charge density) can be of general form (no shape approximation)

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

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



For example: **Ti**



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

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

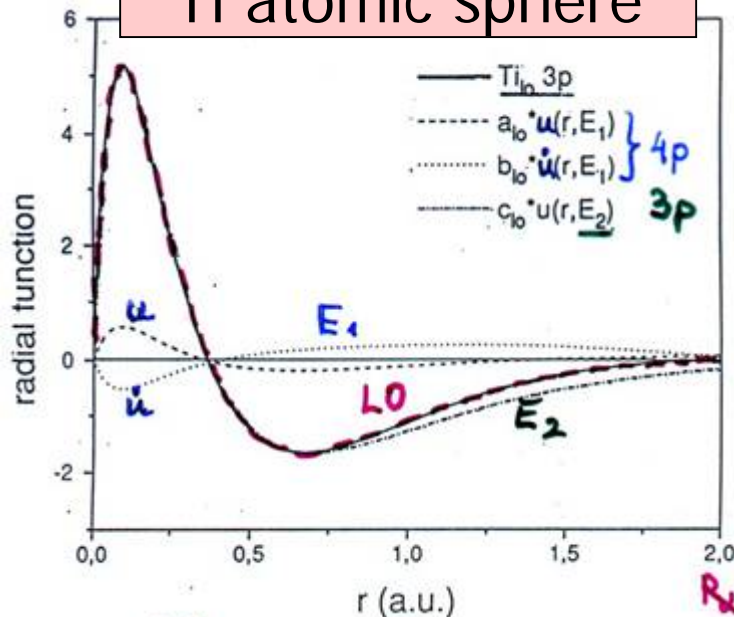


$$\Phi_{LO} = [A_{\ell m} u_{\ell}^{E_1} + B_{\ell m} \dot{u}_{\ell}^{E_1} + C_{\ell m} u_{\ell}^{E_2}] Y_{\ell m}(\hat{r})$$

## ■ LOs

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

$$\Phi_{k_n} = \sum_{lm} A_{lm}(k_n) u_l(E_l, r) Y_{lm}(\hat{r})$$

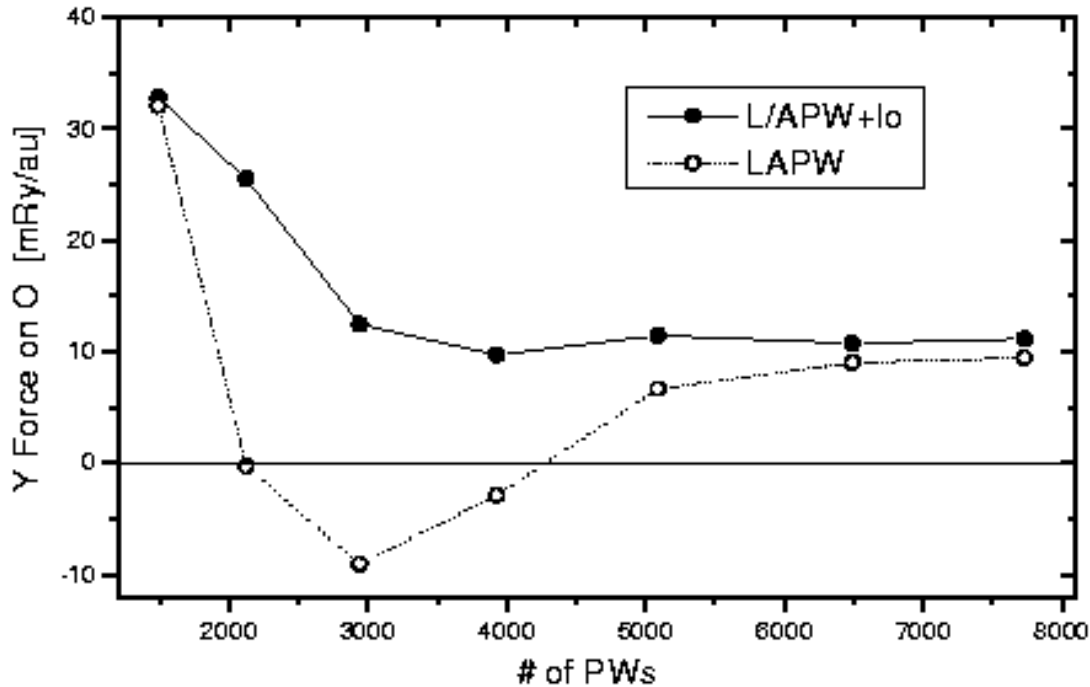
$$\Phi_{lo} = [A_{\ell m} u_{\ell}^{E_1} + B_{\ell m} \dot{u}_{\ell}^{E_1}] Y_{\ell m}(\hat{r})$$

**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:

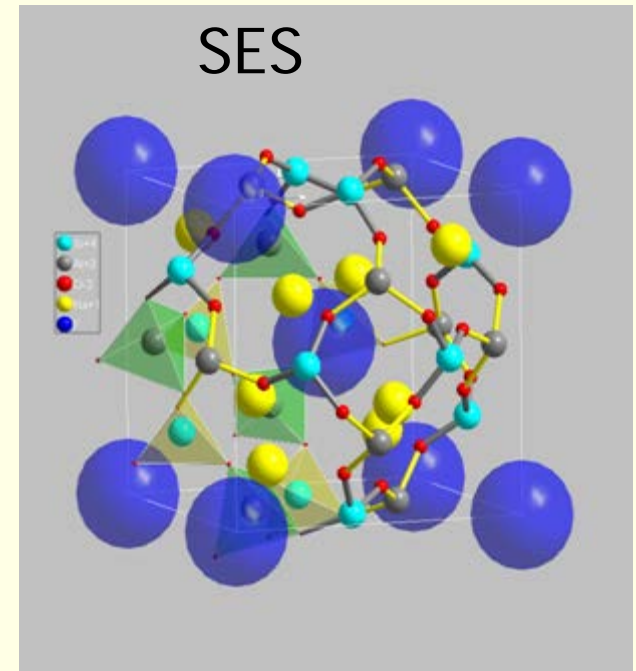


e.g. force ( $F_y$ ) on oxygen in SES vs. # plane waves:

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

SES (sodium electro solodalite)

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





# Summary: Linearization LAPW vs. APW

## Atomic partial waves

### LAPW

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

### APW+lo

$$\Phi_{k_n} = \sum_{l m} A_{l m}(k_n)u_l(E_l, r)Y_{l m}(\hat{r})$$

plus another type of local orbital (lo)

## Plane Waves (PWs)

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

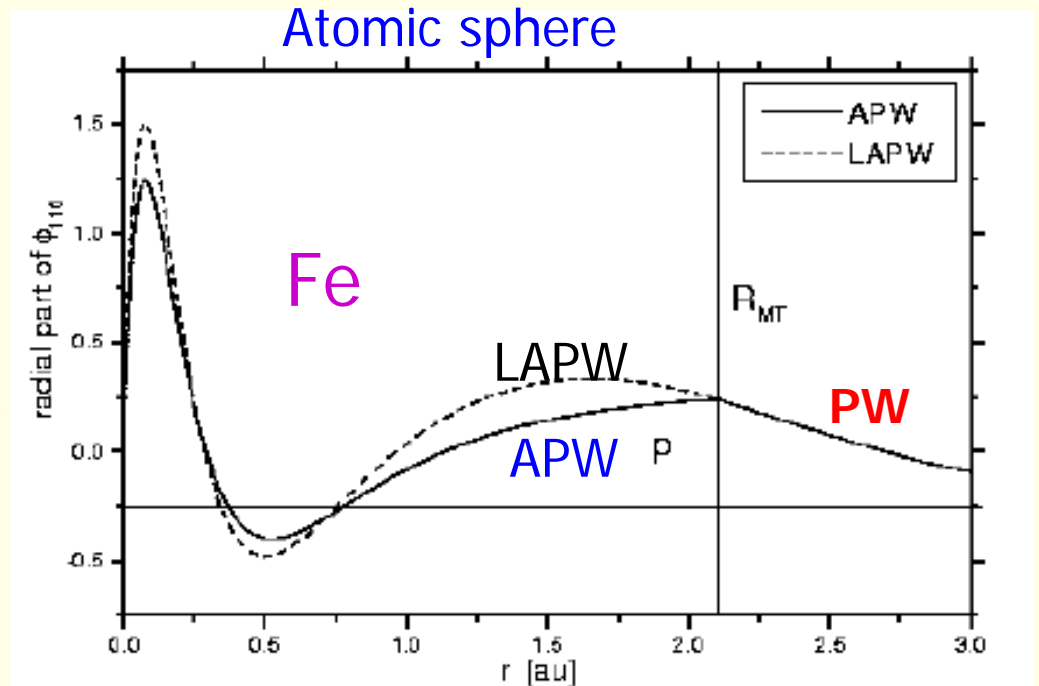
## match at sphere boundary

### LAPW

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

### APW

value  $A_{l m}(k_n)$





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

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

**optimal solution:** mixed basis

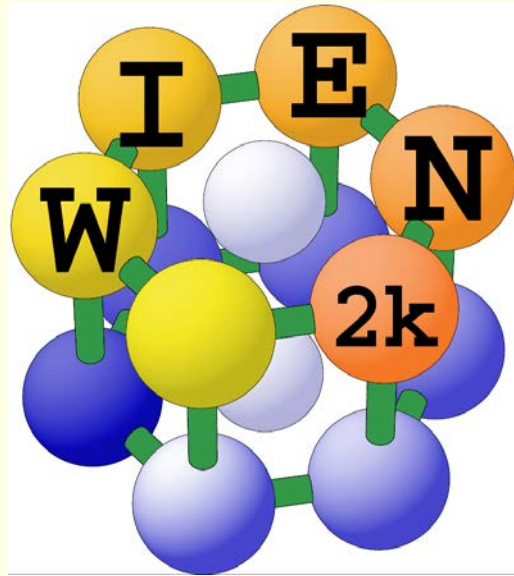
- use **APW+lo** for states which are difficult to converge:  
(**f-** or **d-** states, atoms with small spheres)
- use **LAPW+LO** for all **other** atoms and angular momenta

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>



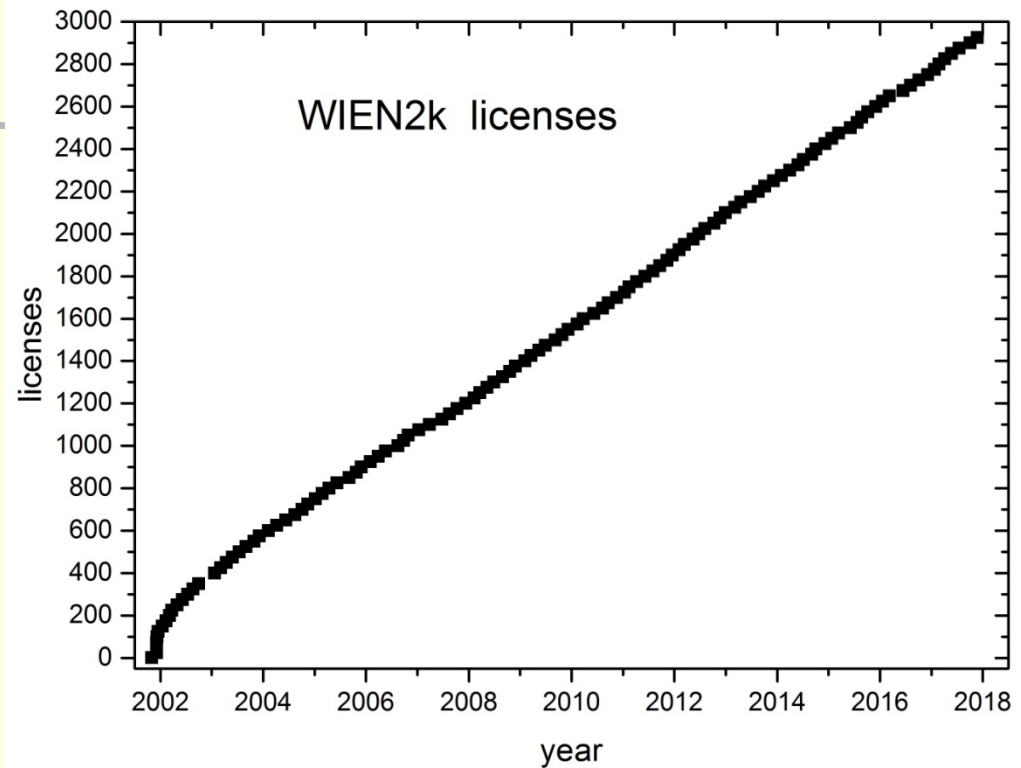
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mailinglist: 10.000 emails/6 years



# The first publication of the WIEN code



## FULL-POTENTIAL, LINEARIZED AUGMENTED PLANE WAVE PROGRAMS FOR CRYSTALLINE SYSTEMS

P. BLAHA, K. SCHWARZ, and P. SORANTIN

*Institut für Technische Elektrochemie, Technische Universität Wien, A-1060 WIEN, Austria*

and

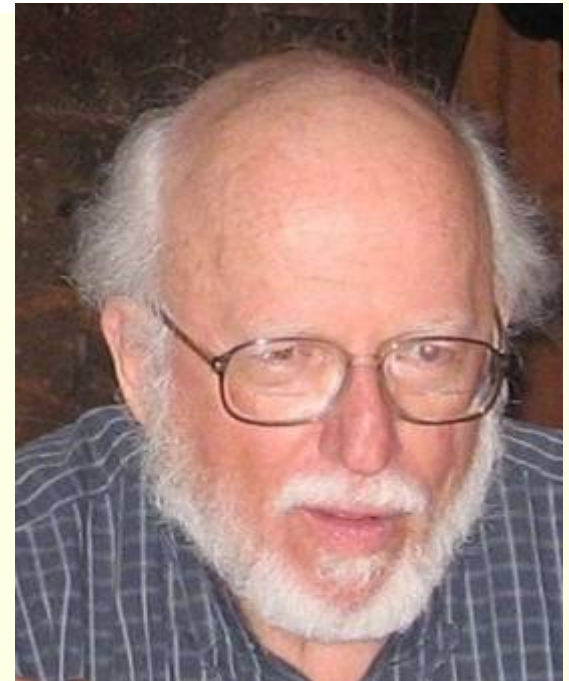
S.B. TRICKEY

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

### PROGRAM SUMMARY

*Title of program: WIEN*

Computer Physics Communications 59 (1990) 399–415

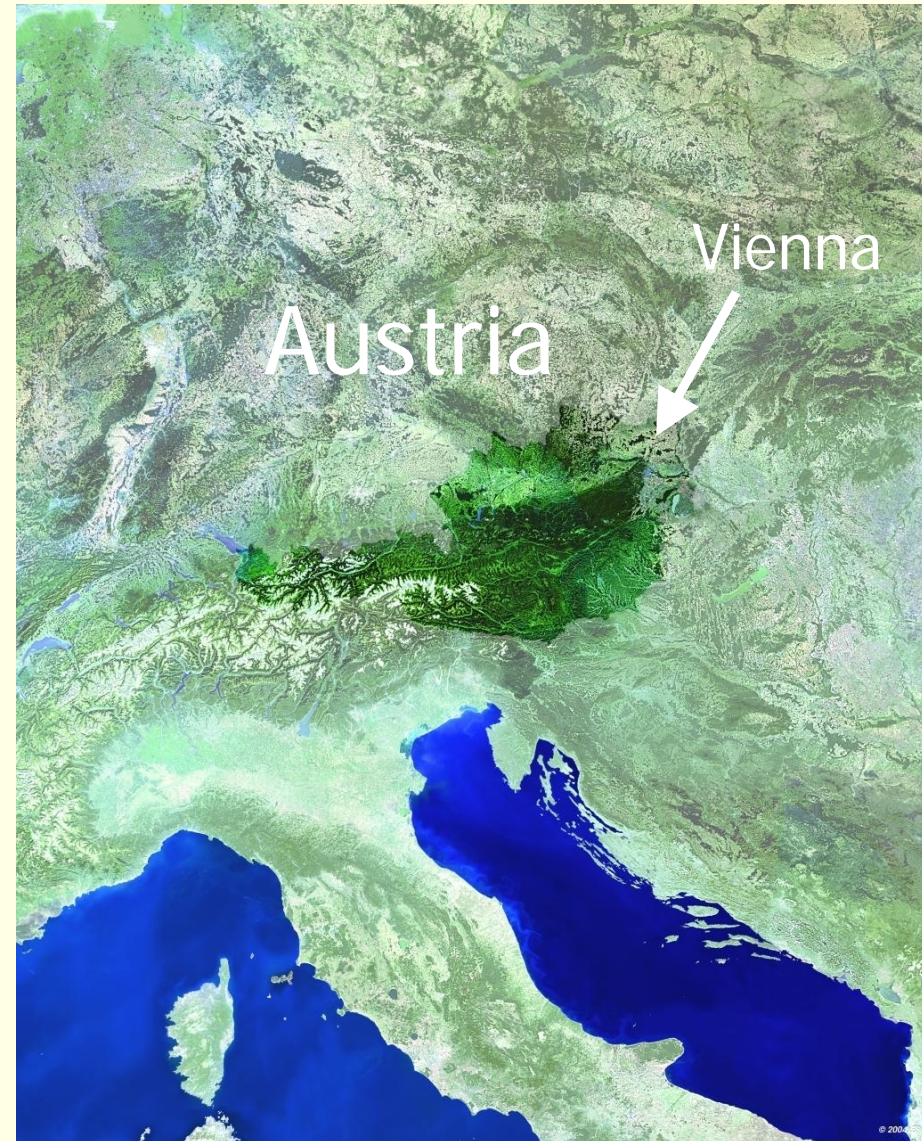


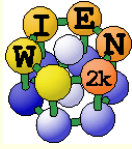


Europa Austria Vienna → WIEN



In the Heart of EUROPE





# Development of WIEN2k



## ■ Authors of WIEN2k

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

## ■ Other contributions to WIEN2k

- *C. Ambrosch-Draxl (Free Univ. Berlin) optics*
- *E. Assmann (Vienna) Wannier functions*
- *F. Karsai (Vienna) parallelization*
- *R. Laskowski (Singapore), non-collinear magnetism, NMR chemical shifts, BSE*
- *L. Marks (Northwestern, US) , various optimizations, new mixer*
- *P. Novák and J. Kunes (Prague), LDA+U, SO*
- *B. Olejnik (Vienna), non-linear optics,*
- *C. Persson (Uppsala), irreducible representations*
- *V. Petricek (Prague) 230 space groups*
- *O. Rubel (McMaster Univ. Hamilton, ON) Berry phases*
- *M. Scheffler (Fritz Haber Inst., Berlin), forces*
- *D.J.Singh (NRL, Washington D.C., Oak Ridge), local orbitals (LO), APW+lo*
- *E. Sjöstedt and L Nordström (Uppsala, Sweden), APW+lo*
- *J. Sofo (Penn State, USA) and J. Fuhr (Barriloche), Bader analysis*
- *F. Tran (Vienna) Hartree Fock, DFT functionals*
- *B. Yanchitsky and A. Timoshevskii (Kiev), space group*

## ■ and many others .....

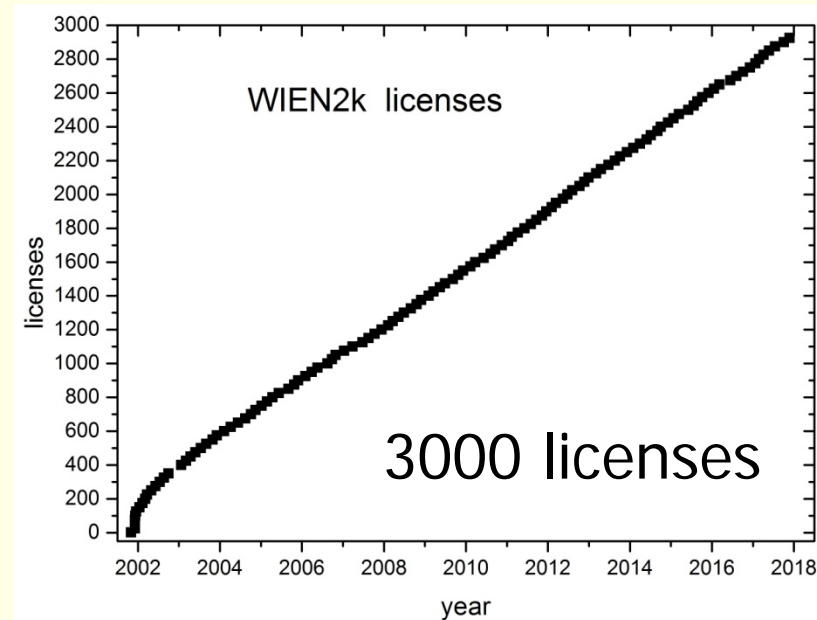
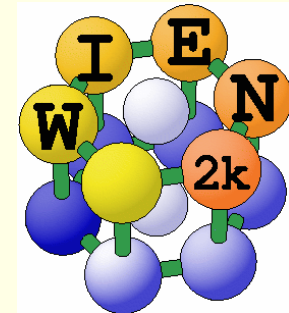




# A series of **WIEN** workshops were held



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	





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

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

Variational method:

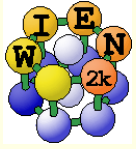
$$\langle E \rangle = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad \frac{\delta \langle E \rangle}{\delta C_{k_n}} = 0$$

upper bound

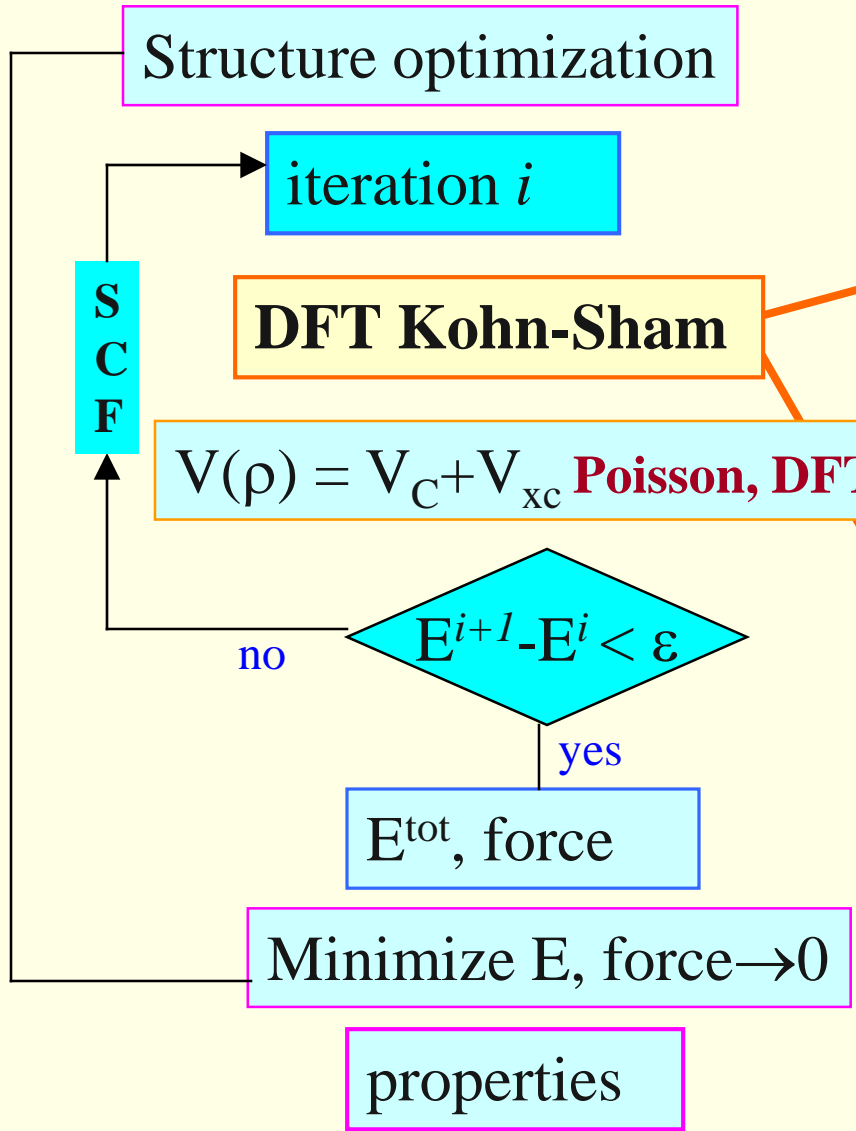
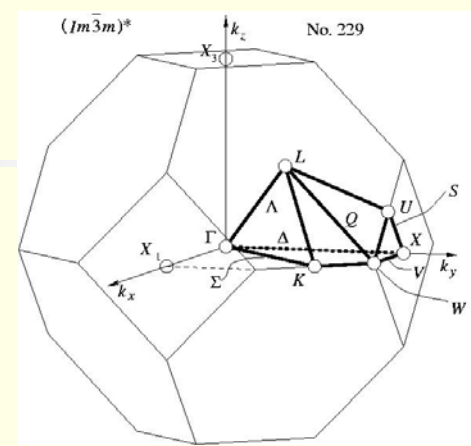
minimum

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

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



Structure:  $\underbrace{a, b, c, \alpha, \beta, \gamma}_{\text{unit cell}}, \underbrace{R_\alpha, \dots}_{\text{atomic positions}}$



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

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

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

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

Generalized eigenvalue problem

$$HC = ESC$$

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

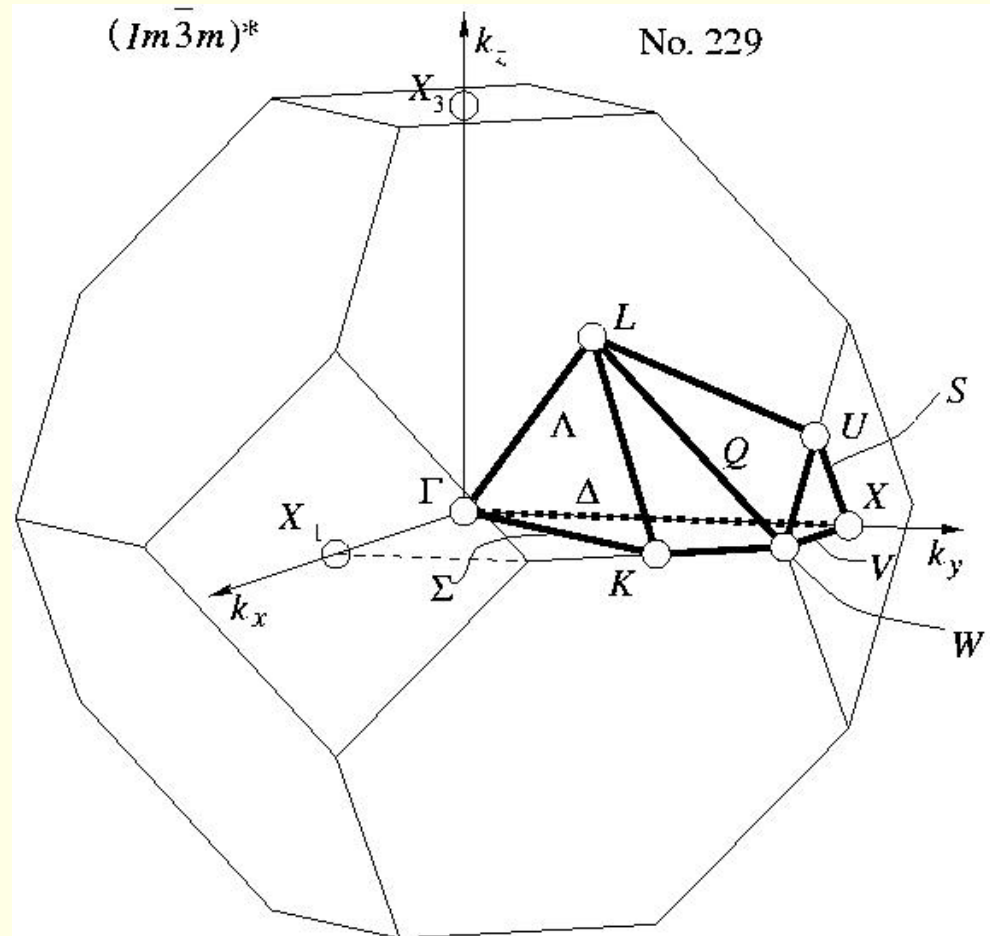
# The Brillouin zone (BZ)

## ■ Irreducible BZ (IBZ)

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

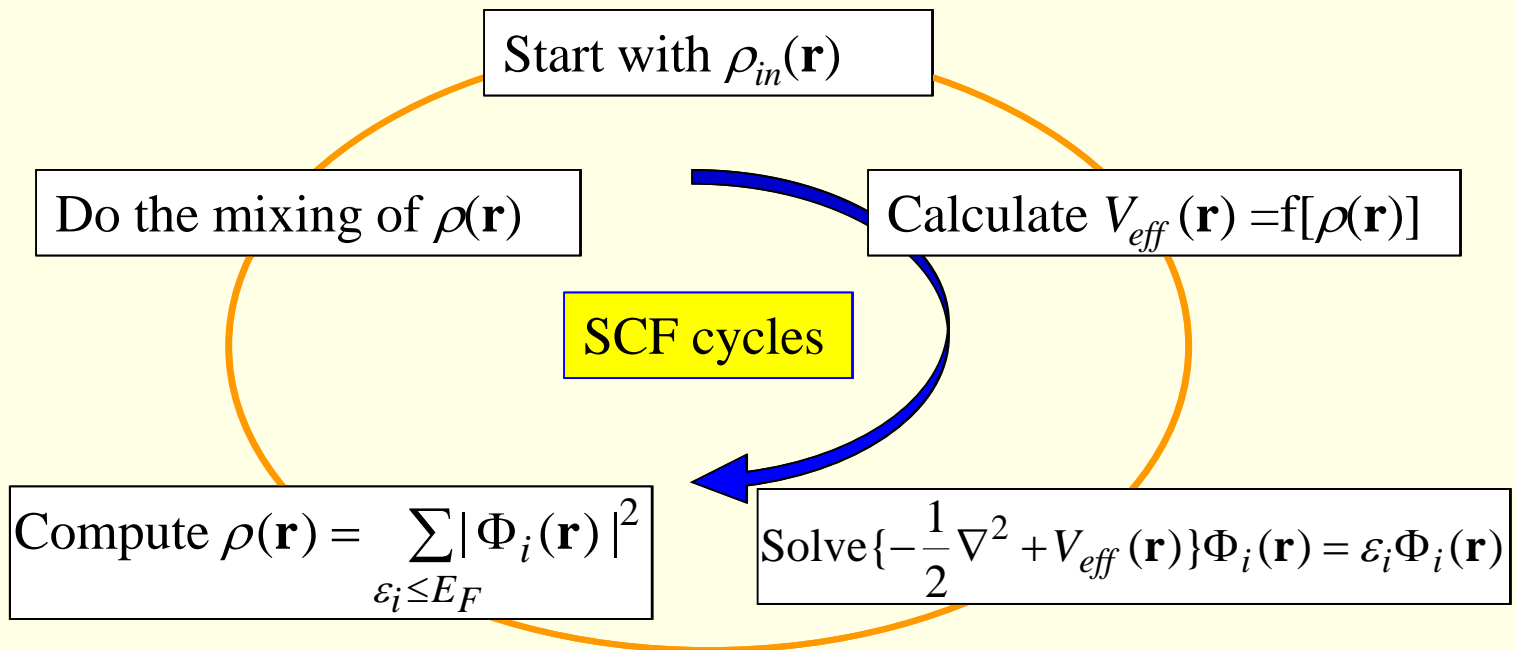
## ■ Bilbao Crystallographic Server:

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



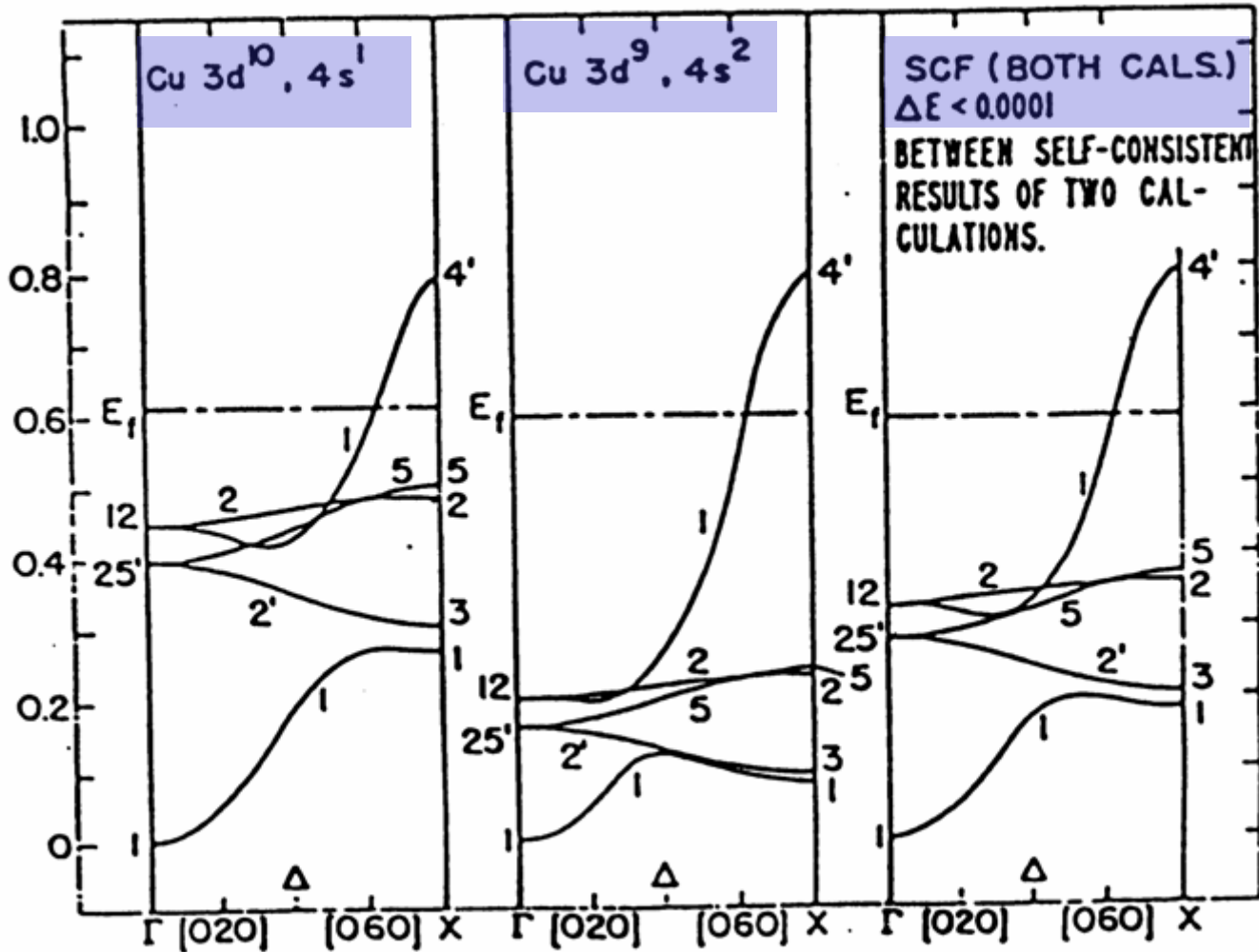


- In order to solve  $H\Psi = E\Psi$  we need to know the potential  $V(\mathbf{r})$
- for  $V(\mathbf{r})$  we need the electron density  $\rho(\mathbf{r})$
- the density  $\rho(\mathbf{r})$  can be obtained from  $\Psi(\mathbf{r})^* \Psi(\mathbf{r})$
- ??  $\Psi(\mathbf{r})$  is unknown before  $H\Psi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





## Band structure of fcc Cu





# Program structure of WIEN2k



## ■ `init_lapw`

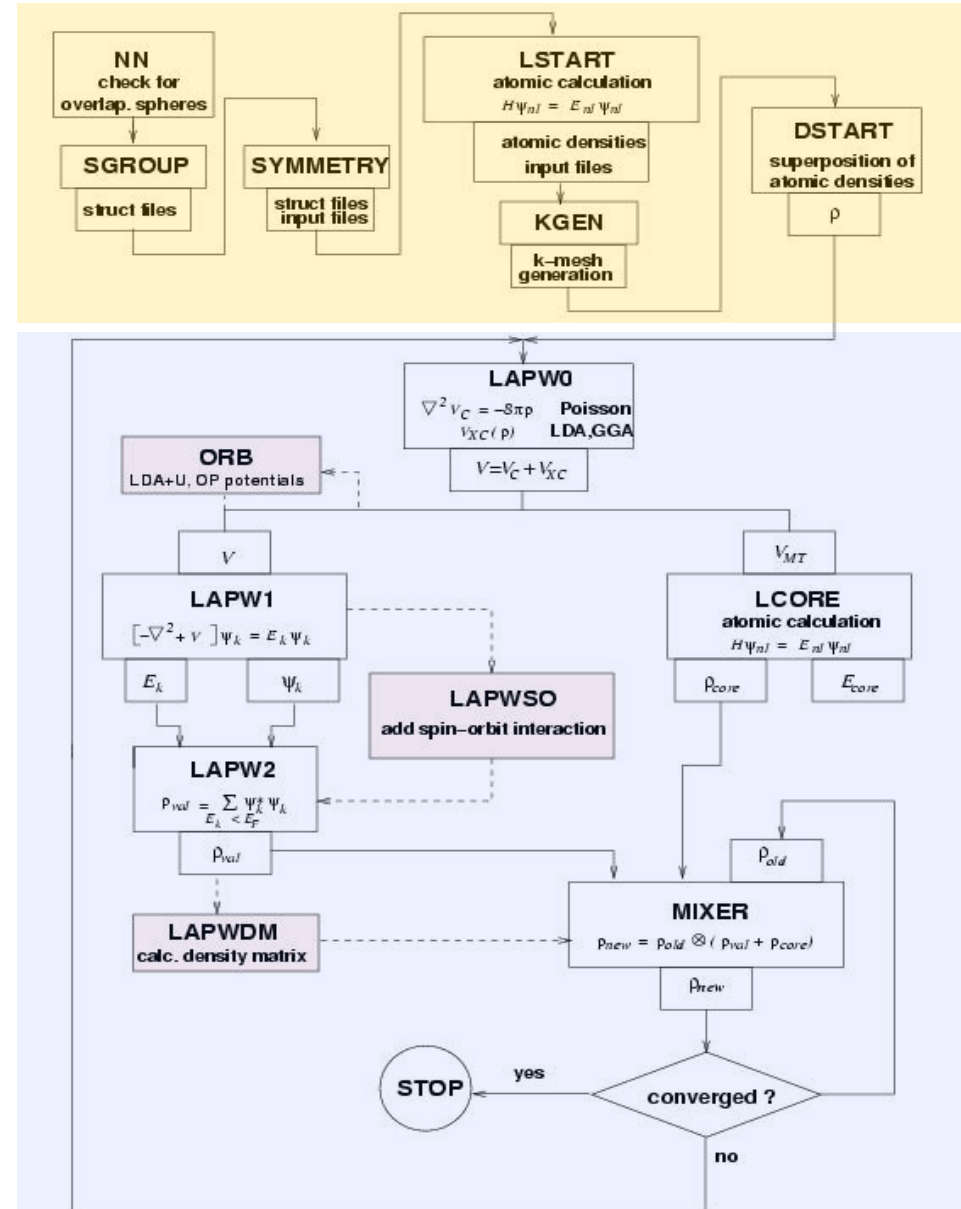
- *initialization*
- *symmetry detection (F, I, C-centering, inversion)*
- *input generation with recommended defaults*
- *quality (and computing time) depends on k-mesh and R.Kmax (determines #PW)*

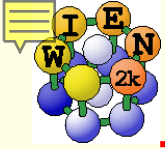
## ■ `run_lapw`

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

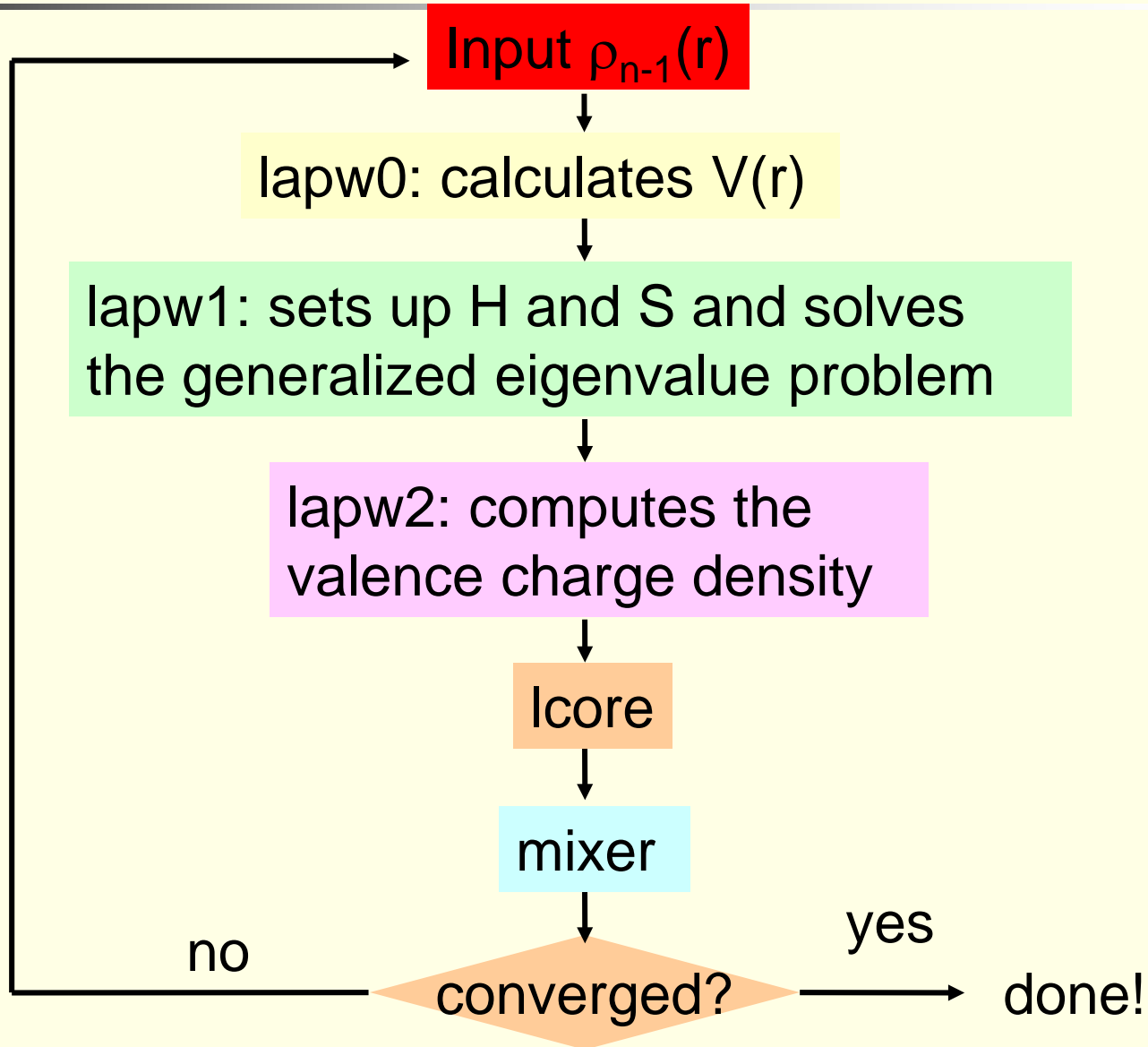
## ■ `save_lapw tic_gga_100k_rk7_vol0`

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





# Flow Chart of WIEN2k (SCF)

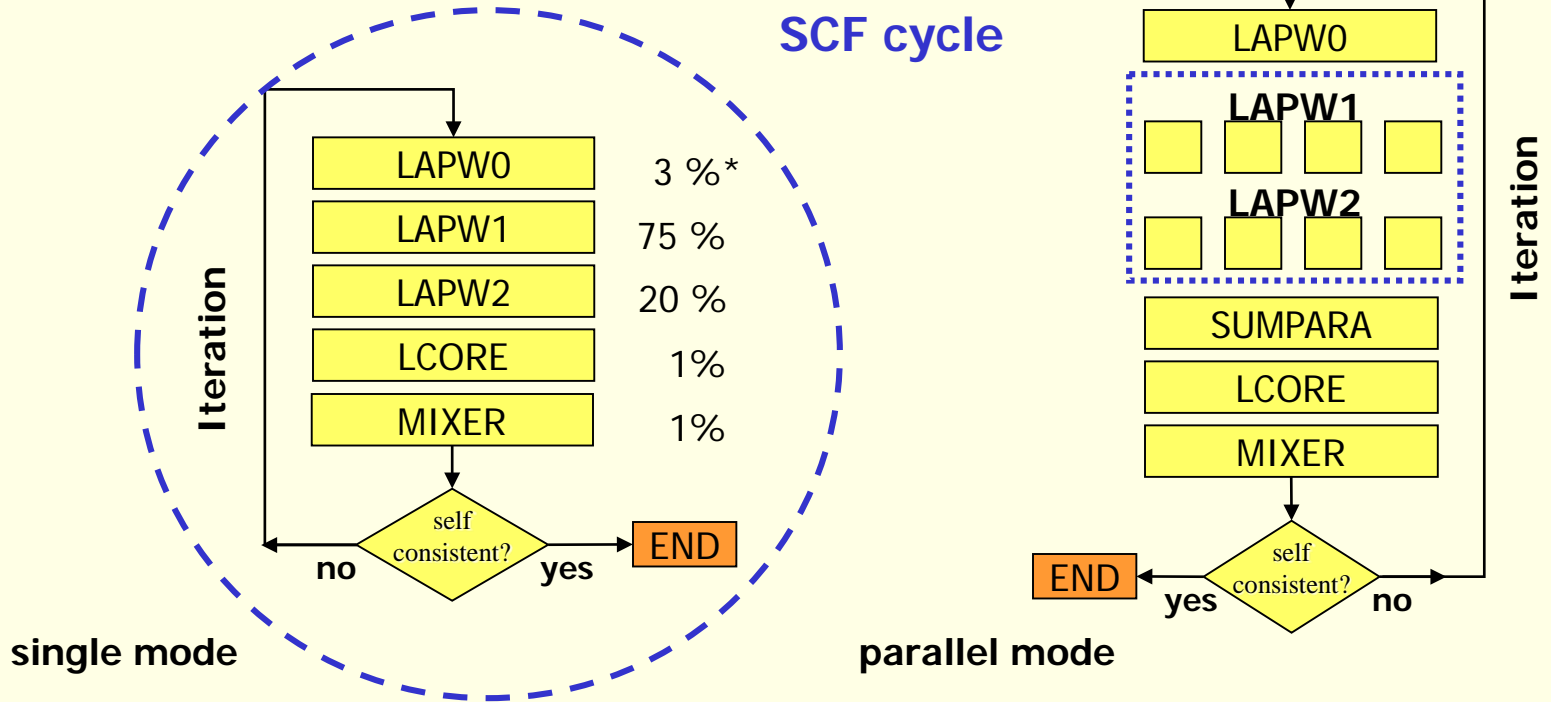






# Workflow of a WIEN2k calculation

- 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



\* fraction of total computation time



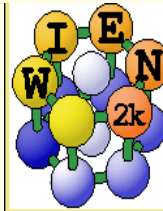
# Advantage/disadvantage of WIEN2k



- + robust all-electron full-potential method (new effective mixer)
- + unbiased basis set, 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  $\rightarrow$  large memory required*
  - + *effective dual parallelization (k-points, mpi-fine-grain)*
  - + *many k-points do not require more memory*
- no stress tensor
- no linear response



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



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

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

$\alpha=90.000000$   $\beta=90.000000$   $\gamma=90.000000$

Inequivalent Atoms: 2

Atom 1: Ti Z=22.0 RMT=2.0000 remove atom

Pos 1: x=0.00000000 y=0.00000000 z=0.00000000 remove  
 add position

Atom 2: C Z=6.0 RMT=1.9000 remove atom

Pos 1: x=0.50000000 y=0.50000000 z=0.50000000 remove  
 add position



# Spacegroup $P4_2/mnm$

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

## Rutile $TiO_2$ :

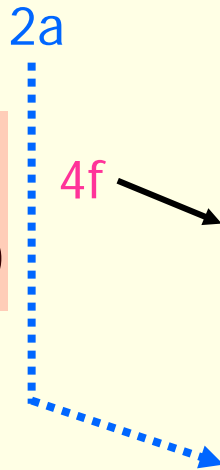
$P4_2/mnm$  (136)

$a=8.68, c=5.59$  bohr

Ti:  $(0,0,0)$

O:  $(0.304,0.304,0)$

Wyckoff position:  $x, x, 0$

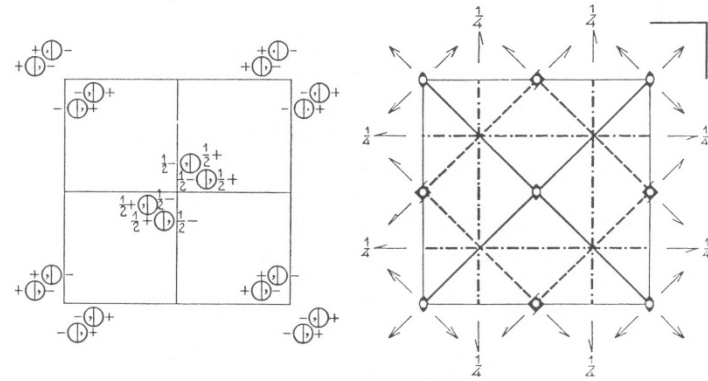


$P4_2/mnm$   
 $D_{4h}^{14}$

No. 136

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

$4/m m m$  Tetragonal



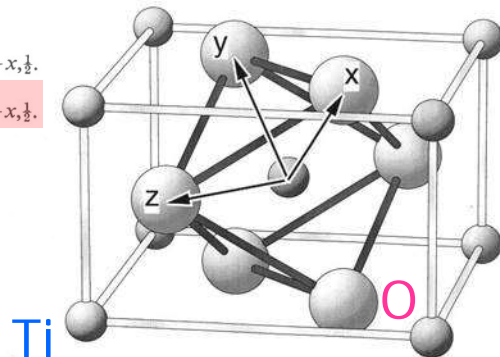
Origin at centre ( $mmm$ )

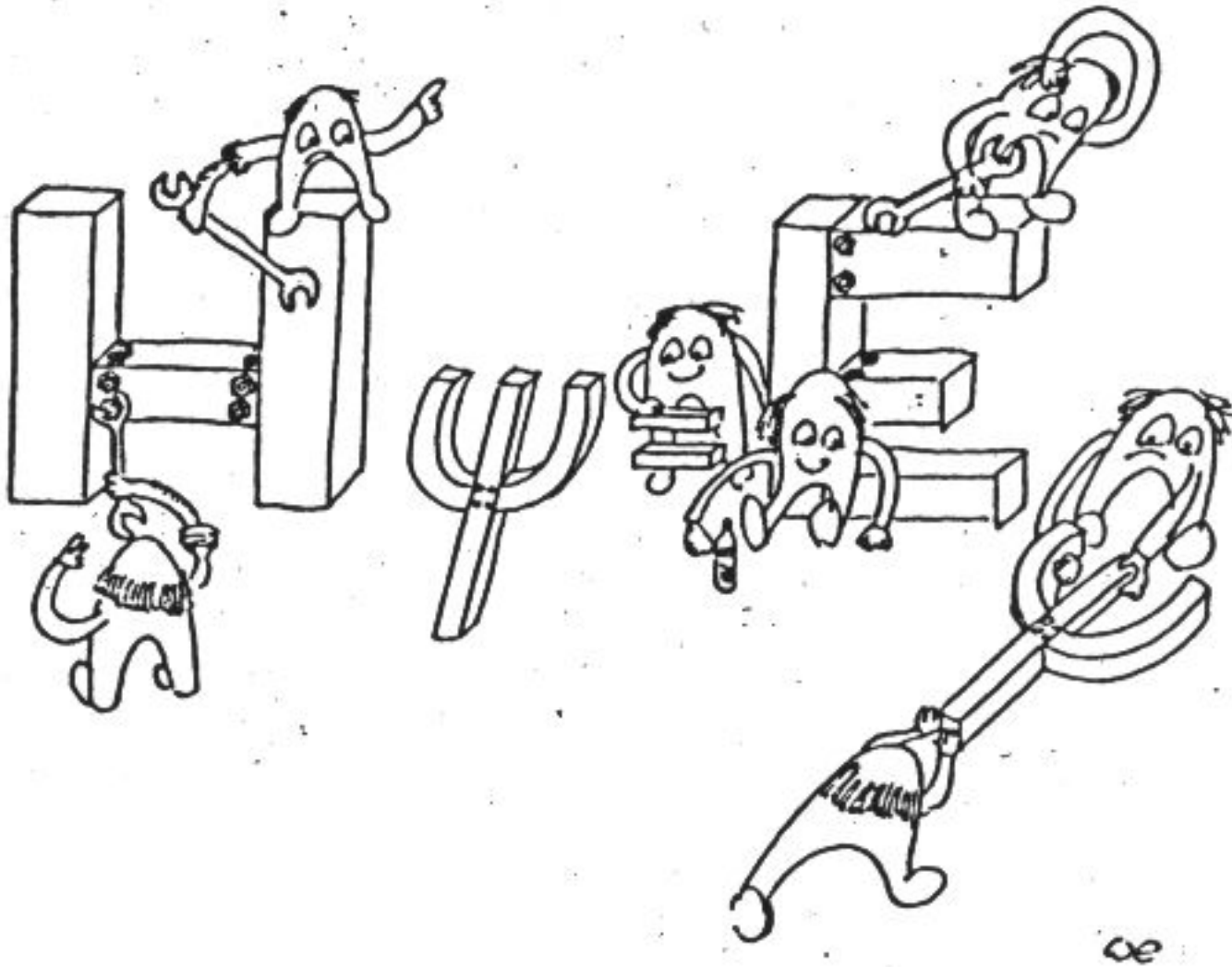
Number of positions,  
 Wyckoff notation,  
 and point symmetry

Co-ordinates of equivalent positions

Conditions limiting  
 possible reflections

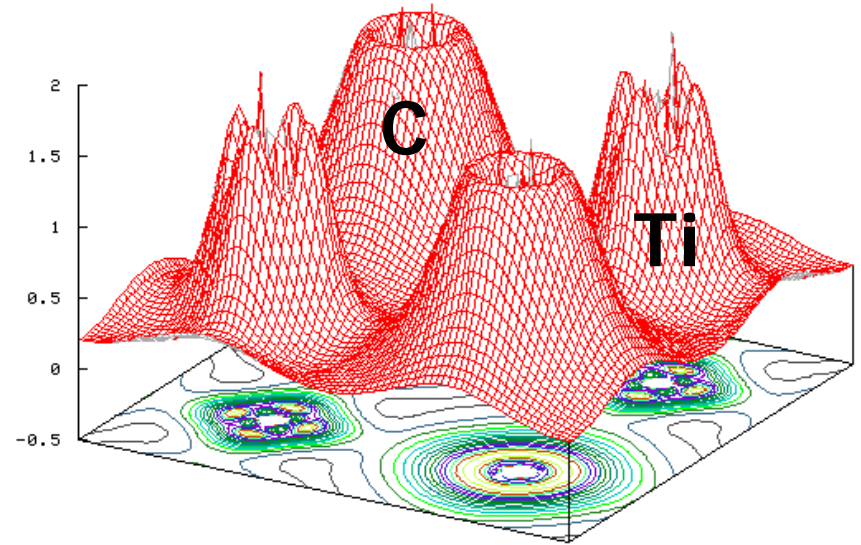
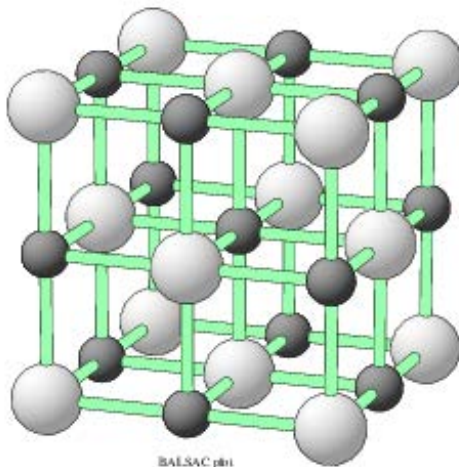
Number of positions, Wyckoff notation, and point symmetry	Co-ordinates of equivalent positions	Conditions limiting possible reflections
16 <i>k</i> 1	$x, y, z; \bar{x}, \bar{y}, z; \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z; \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z;$ $x, y, \bar{z}; \bar{x}, \bar{y}, \bar{z}; \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z; \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z;$ $y, x, z; \bar{y}, \bar{x}, z; \frac{1}{2} + y, \frac{1}{2} - x, \frac{1}{2} + z; \frac{1}{2} - y, \frac{1}{2} + x, \frac{1}{2} + z;$ $y, x, \bar{z}; \bar{y}, \bar{x}, \bar{z}; \frac{1}{2} + y, \frac{1}{2} - x, \frac{1}{2} - z; \frac{1}{2} - y, \frac{1}{2} + x, \frac{1}{2} - z.$	General: $hkl$ : No conditions $hk0$ : No conditions $0kl$ : $k+l=2n$ $hhl$ : No conditions
8 <i>j</i> <i>m</i>	$x, x, z; \bar{x}, \bar{x}, z; \frac{1}{2} + x, \frac{1}{2} - x, \frac{1}{2} + z; \frac{1}{2} - x, \frac{1}{2} + x, \frac{1}{2} + z;$ $x, x, \bar{z}; \bar{x}, \bar{x}, \bar{z}; \frac{1}{2} + x, \frac{1}{2} - x, \frac{1}{2} - z; \frac{1}{2} - x, \frac{1}{2} + x, \frac{1}{2} - z.$	Special: as above, plus $hkl$ : $h+k=2n; l=2n$ } no extra conditions
8 <i>i</i> <i>m</i>	$x, y, 0; \bar{x}, \bar{y}, 0; \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2}; \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2};$ $y, x, 0; \bar{y}, \bar{x}, 0; \frac{1}{2} + y, \frac{1}{2} - x, \frac{1}{2}; \frac{1}{2} - y, \frac{1}{2} + x, \frac{1}{2}.$	
8 <i>h</i> 2	$0, \frac{1}{2}, z; 0, \frac{1}{2}, \bar{z}; 0, \frac{1}{2}, \frac{1}{2} + z; 0, \frac{1}{2}, \frac{1}{2} - z;$ $\frac{1}{2}, 0, z; \frac{1}{2}, 0, \bar{z}; \frac{1}{2}, 0, \frac{1}{2} + z; \frac{1}{2}, 0, \frac{1}{2} - z.$	
4 <i>g</i> <i>mm</i>	$x, \bar{x}, 0; \bar{x}, x, 0; \frac{1}{2} + x, \frac{1}{2} + x, \frac{1}{2}; \frac{1}{2} - x, \frac{1}{2} - x, \frac{1}{2}.$	
4 <i>f</i> <i>mm</i>	$x, x, 0; \bar{x}, \bar{x}, 0; \frac{1}{2} + x, \frac{1}{2} - x, \frac{1}{2}; \frac{1}{2} - x, \frac{1}{2} + x, \frac{1}{2}.$	
4 <i>e</i> <i>mm</i>	$0, 0, z; 0, 0, \bar{z}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2} + z; \frac{1}{2}, \frac{1}{2}, \frac{1}{2} - z.$	
4 <i>d</i> $\bar{4}$	$0, \frac{1}{2}, \frac{1}{4}; \frac{1}{2}, 0, \frac{1}{4}; 0, \frac{1}{2}, \frac{3}{4}; \frac{1}{2}, 0, \frac{3}{4}.$	
4 <i>c</i> $2/m$	$0, \frac{1}{2}, 0; \frac{1}{2}, 0, 0; 0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, \frac{1}{2}.$	
2 <i>b</i> <i>mmm</i>	$0, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, 0.$	
2 <i>a</i> <i>mmm</i>	$0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}.$	





thanks to Erich Wimmer

- NaCl structure (100) plane
- Valence electrons only
- plot in 2 dimensions
- Shows
  - *charge distribution*
  - *covalent bonding*
    - between the Ti-3d and C-2p electrons
  - $e_g/t_{2g}$  symmetry

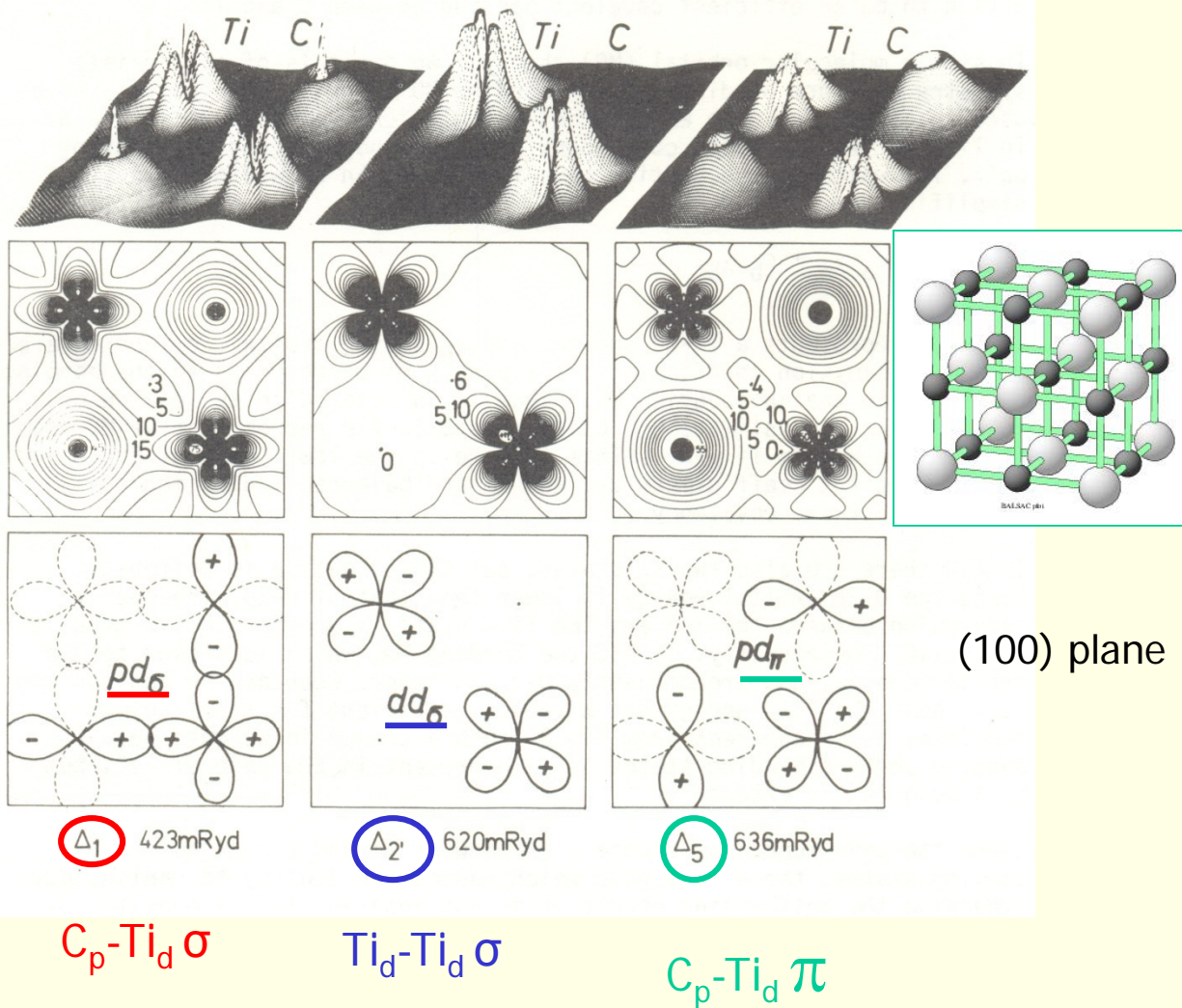
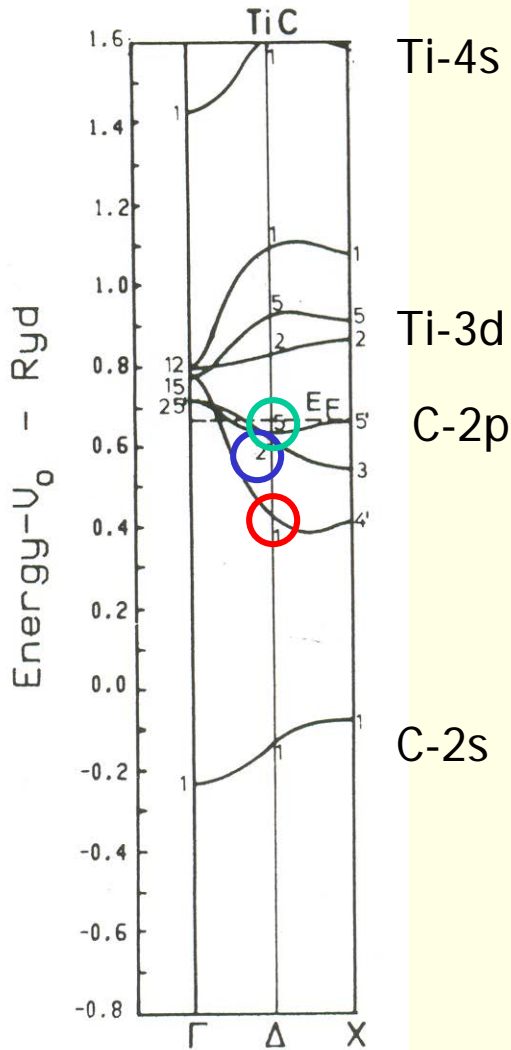


[Download hardcopy in PostScript format](#)

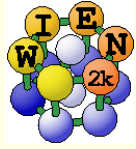
Select plot type: 3D-plot  Contur-plot  with labels

Min  Max  Delta

## Energy bands



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



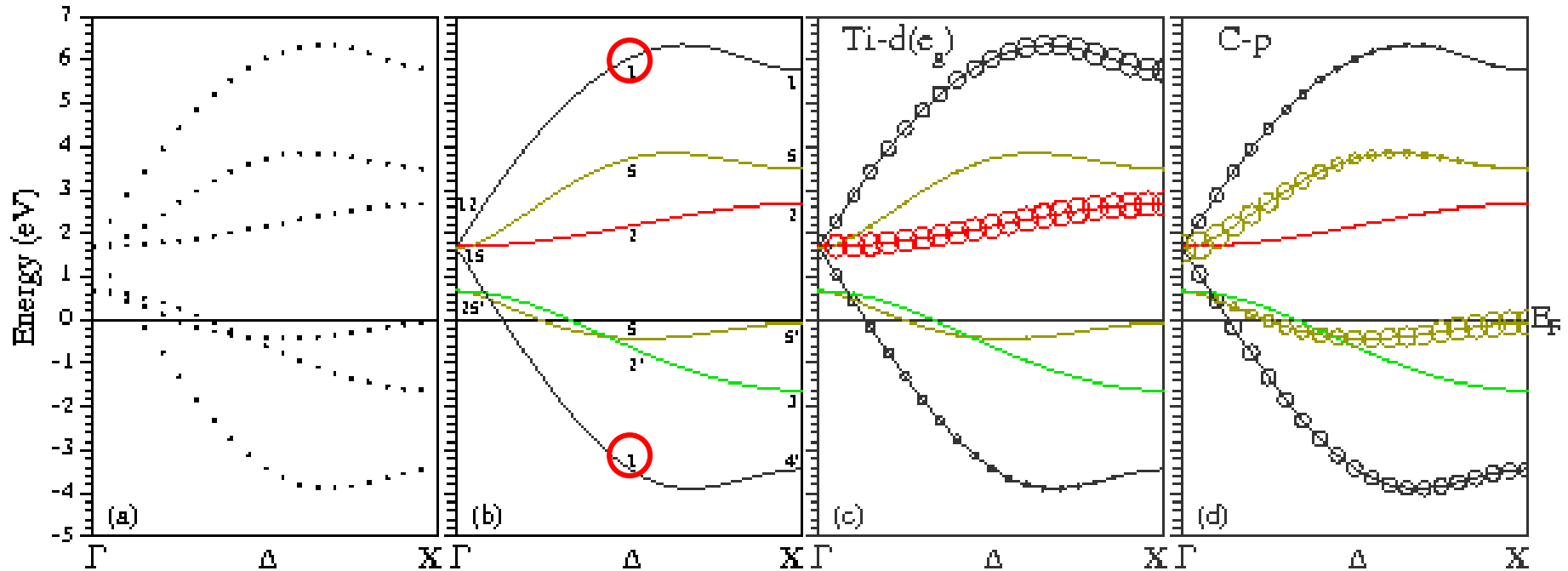
# TiC, energy bands



spaghetti

irred.rep.

character bands



Normalized wave function (charges)

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

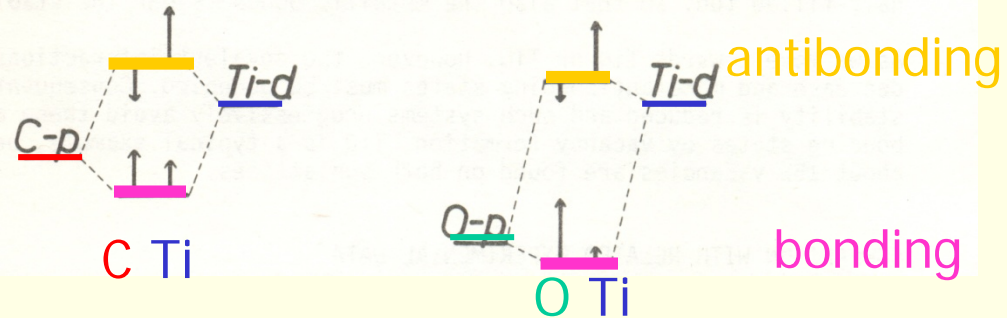
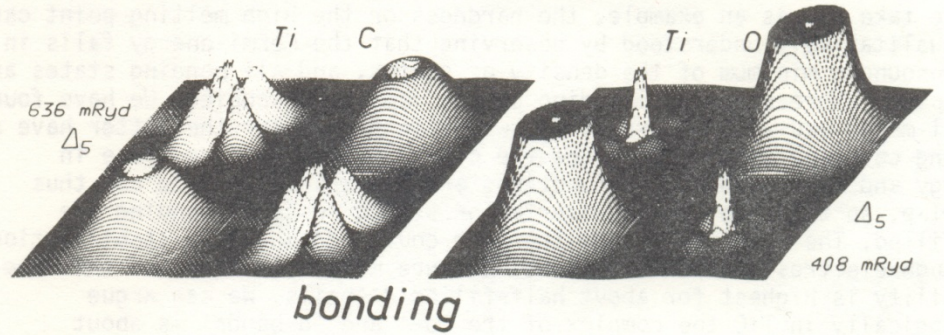
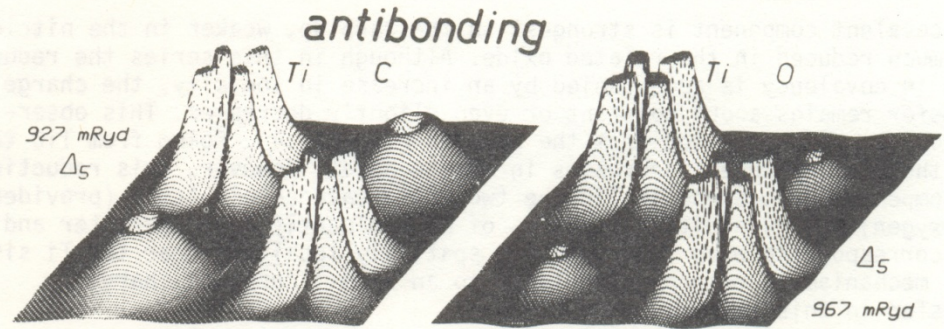
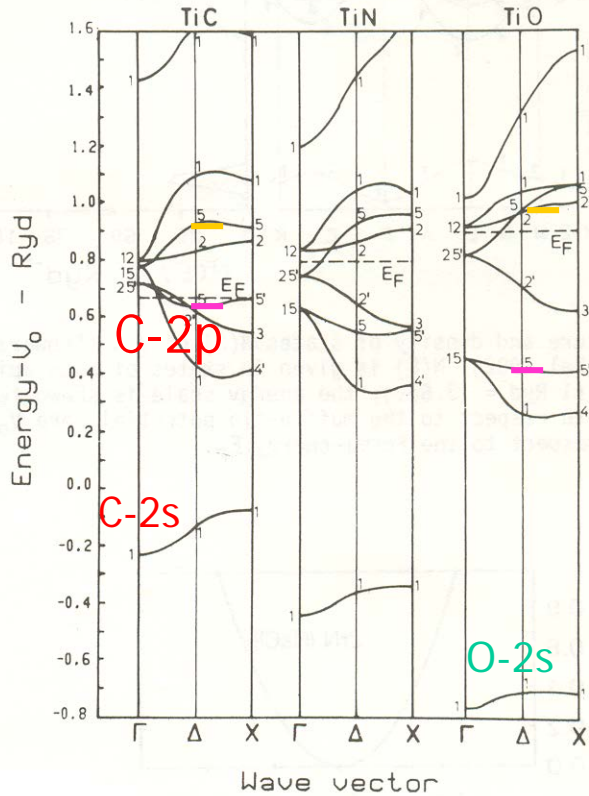
unit cell    interstitial    atom t     $\ell = s, p, d, \dots$

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





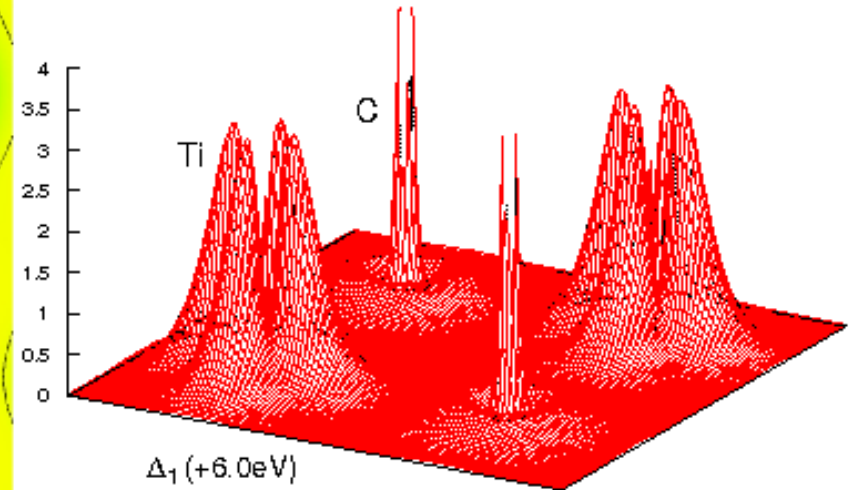
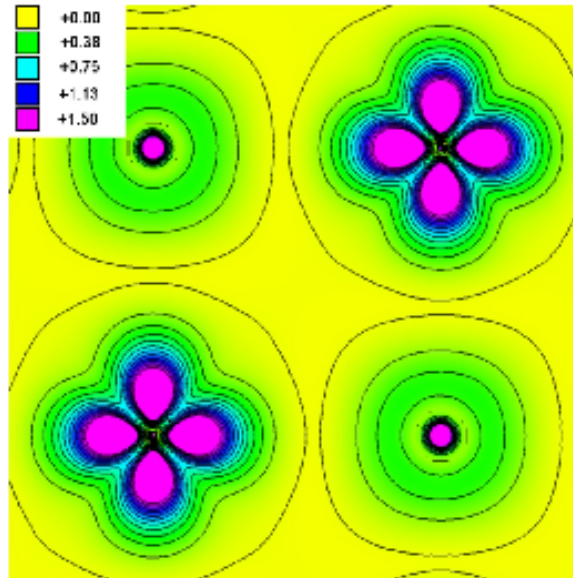
# TiC, bonding and antibonding states



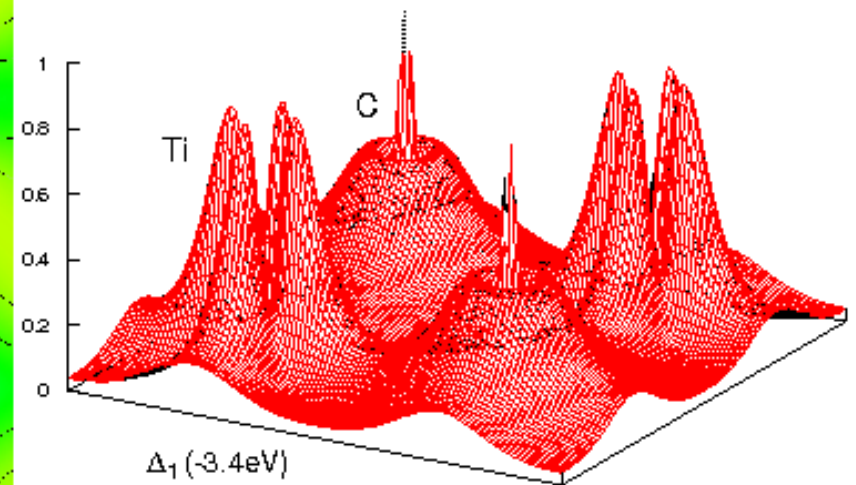
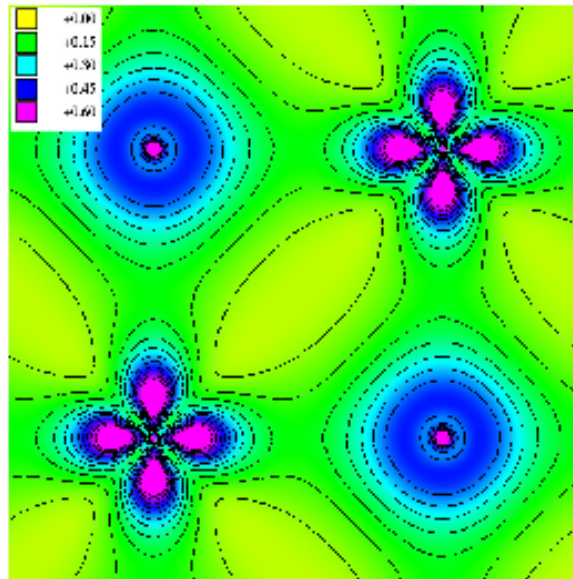
weight:

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

antibonding  
 $C_p-Ti_d \sigma$



bonding  
 $C_p-Ti_d \sigma$





# TiC, TiN, TiO

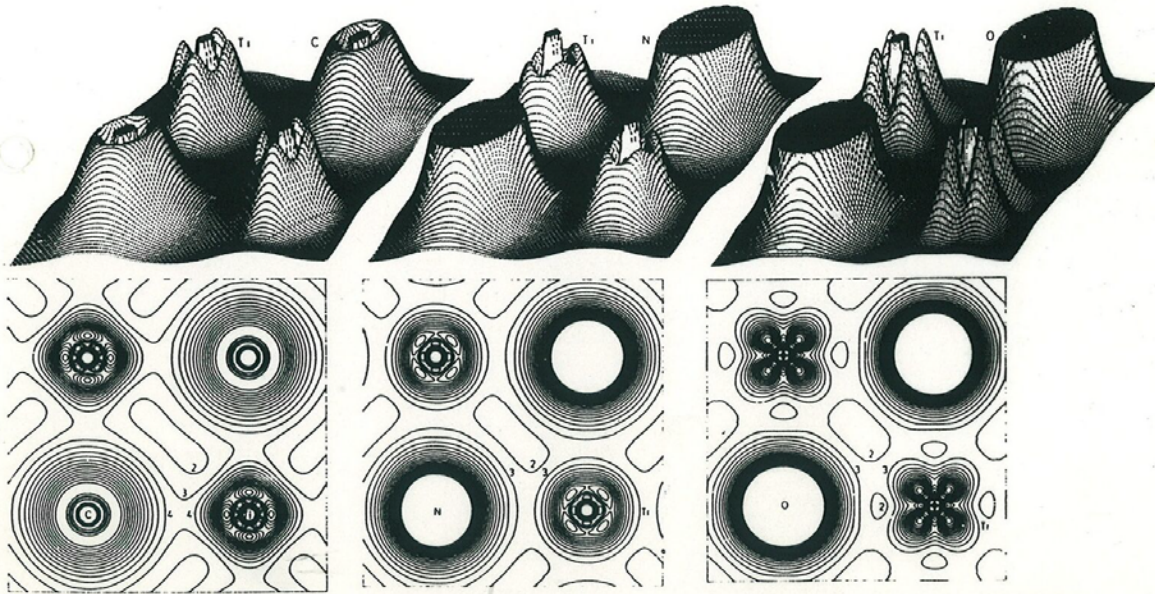
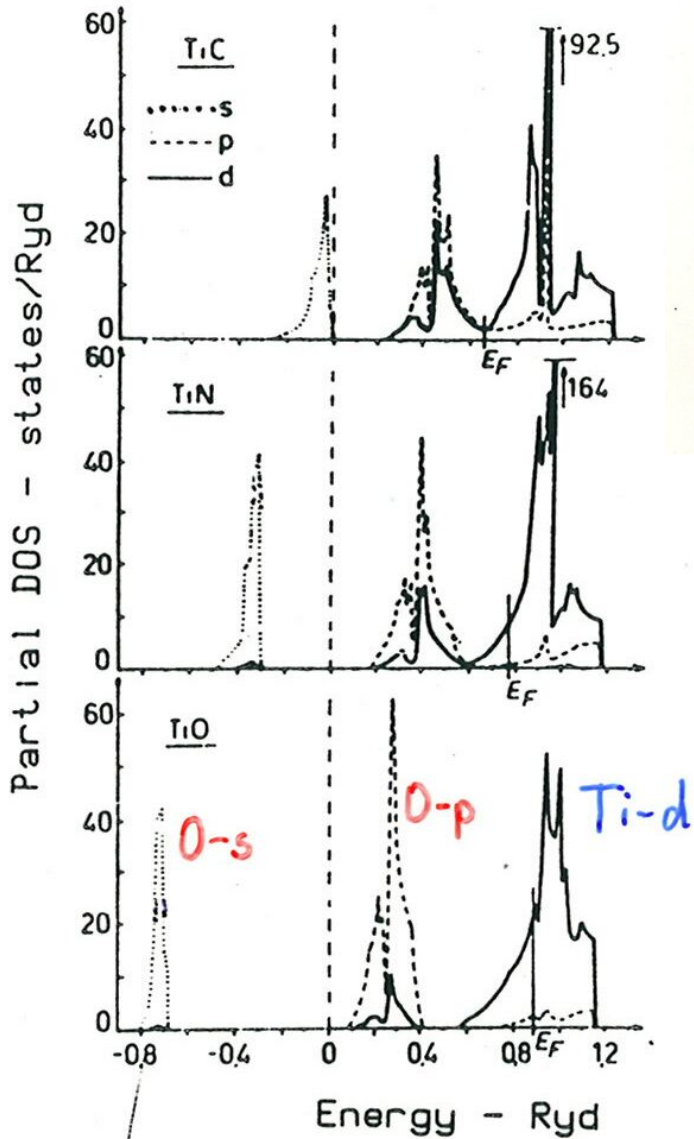


Figure 3. Valence charge densities in the (100) plane. Contour intervals  $0.1e\text{\AA}^{-3}$  (numbers are in these units), cutoff at  $1.7e\text{\AA}^{-3}$ .

**TiC**

**TiN**

**TiO**

Rigid band model: **limitations**

Electron density  $\rho$ : **decomposition**

$$1 = q_{out} + \sum_t \sum_l q_{tl}$$

unit cell

interstitial

atom  $t$

$l = s, p, d, \dots$

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

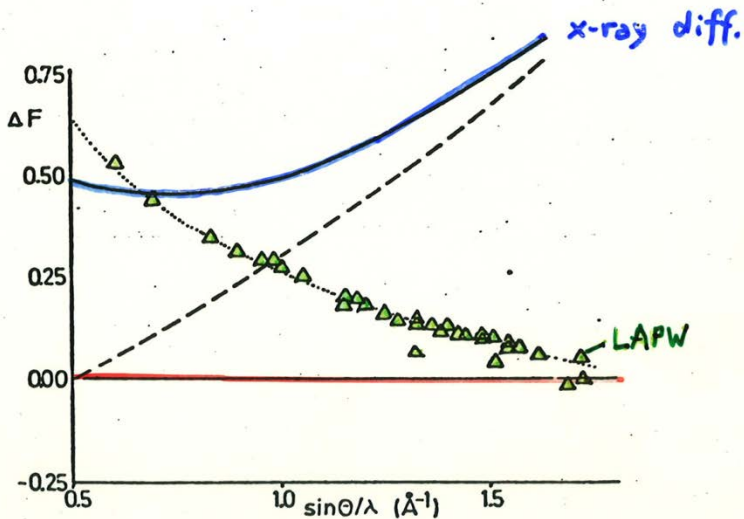
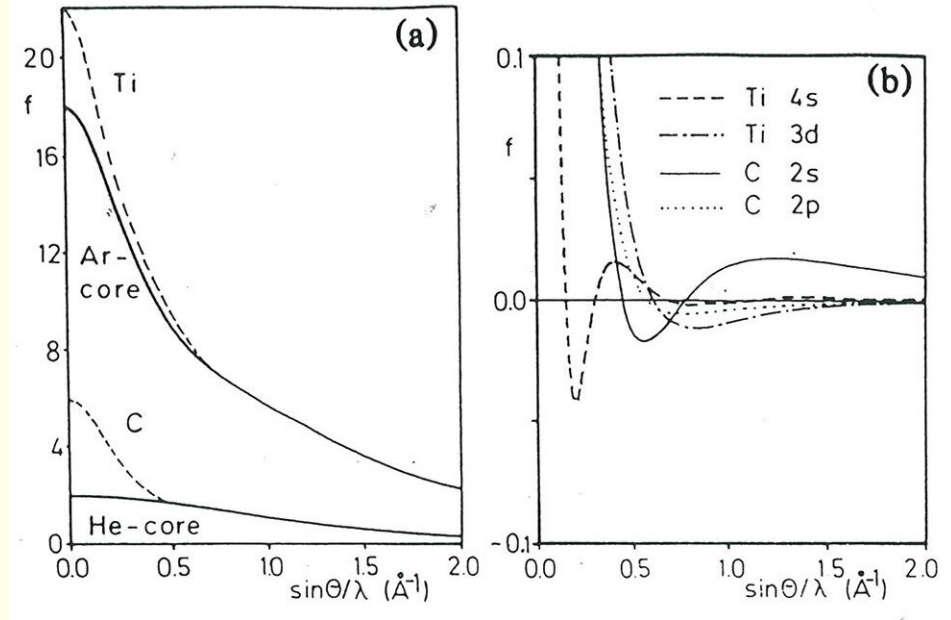
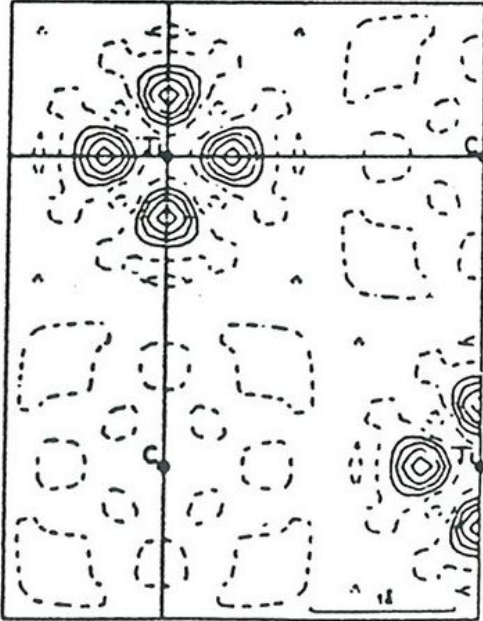


# TiC, TiN, TiO

## Atomic form factors for Ti and C



### Experimental difference electron density



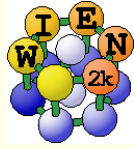
### Paired reflections

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

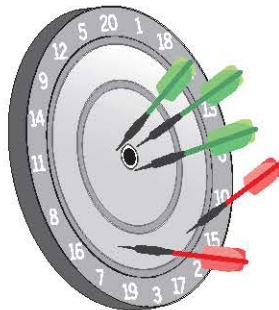
$\vec{S}$			$h^2+k^2+l^2$
h	k	l	
10	2	2	108
6	6	6	108

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

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



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 Marc Torrent,<sup>28</sup> David Vanderbilt,<sup>23</sup> Michiel J. van Setten,<sup>19</sup>  
 Veronique Van Speybroeck,<sup>1</sup> John M. Wills,<sup>43</sup> Jonathan R. Yates,<sup>29</sup>  
 Guo-Xu Zhang,<sup>44</sup> Stefaan Cottenier<sup>1,45\*</sup>



**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	



# Science

AAAS

## Reproducibility in density functional theory calculations of solids

Kurt Lejaeghere *et al.*

*Science* **351**, (2016);

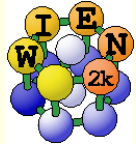
DOI: 10.1126/science.aad3000



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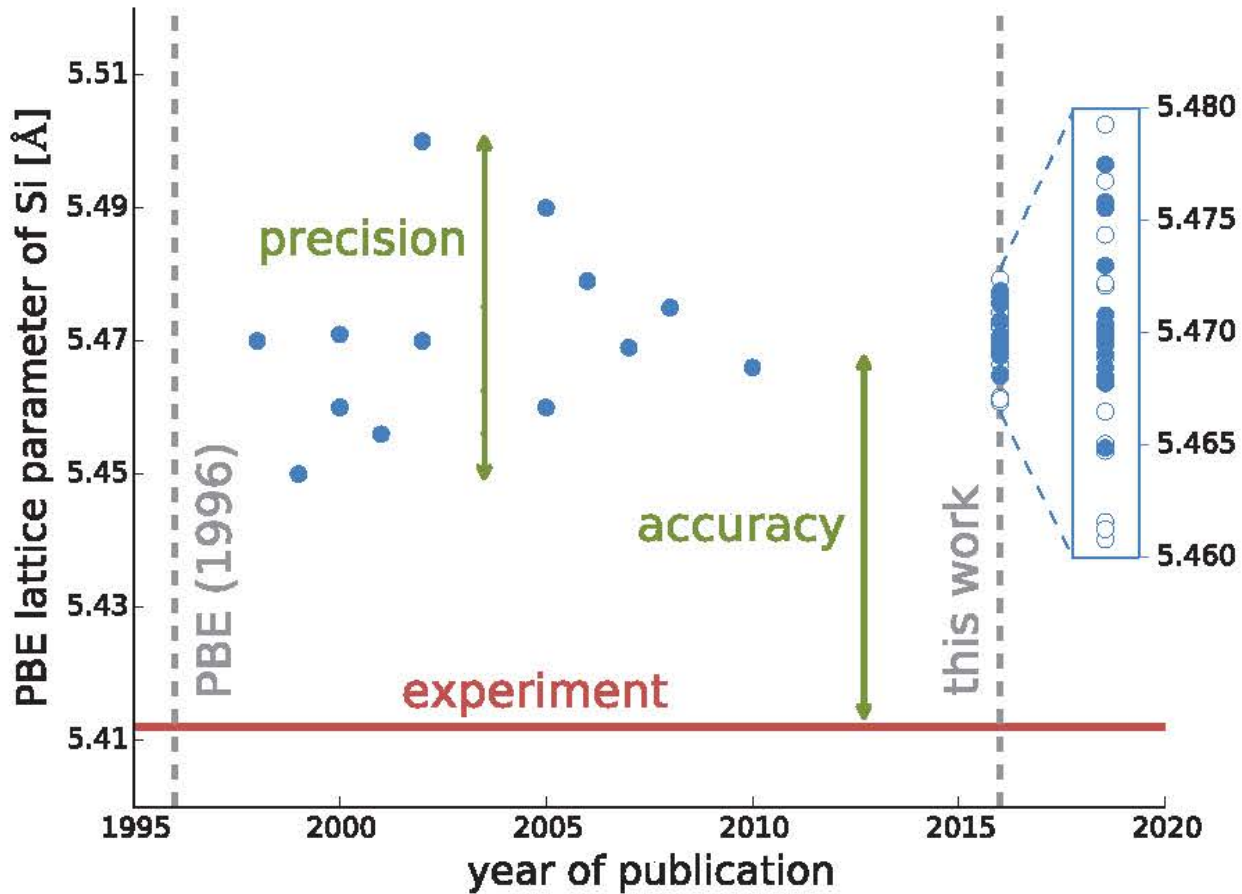


The most accurate code

AE: all electron

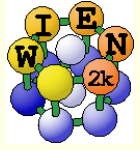
	average $\langle \Delta \rangle$	AE							
		Elk	exciting	FHI-aims/tier2	FLEUR	FPLO/T+T+s	RSPT	WIEN2k/acc	
AE	Elk	0.6		0.3	0.3	0.6	1.0	0.9	0.3
	exciting	0.5	0.3		0.1	0.5	0.9	0.8	0.2
	FHI-aims/tier2	0.5	0.3	0.1		0.5	0.9	0.8	0.2
	FLEUR	0.6	0.6	0.5	0.5		0.8	0.6	0.4
	FPLO/T+T+s	0.9	1.0	0.9	0.9	0.8		0.9	0.9
	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
	PS11b100/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/DACAP0	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
	ONCVFSP (FD0.1)/ABINIT	0.7	0.7	0.7	0.7	0.6	1.0	0.8	0.6
	ONCVFSP (SG15) 1/QE	1.4	1.4	1.3	1.3	1.3	1.6	1.5	1.3
ONCVFSP (SG15) 2/CASTEP	1.4	1.4	1.4	1.4	1.3	1.6	1.5	1.4	

Fig. 4.  $\Delta$  values for comparisons between the most important DFT methods considered (in millielectron volts per atom). Shown are comparisons of all-electron (AE), PAW, ultrasoft (USPP), and norm-conserving pseudopotential (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)  $\Delta$  values. The mixed potential set SSSP was added to the ultrasoft category, in agreement with its prevalent potential type. Both the code settings and the DFT-predicted EOS parameters behind these numbers are included in tables S3 to S42, and fig. S1 provides a full  $\Delta$  matrix for all methods mentioned in this article.



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





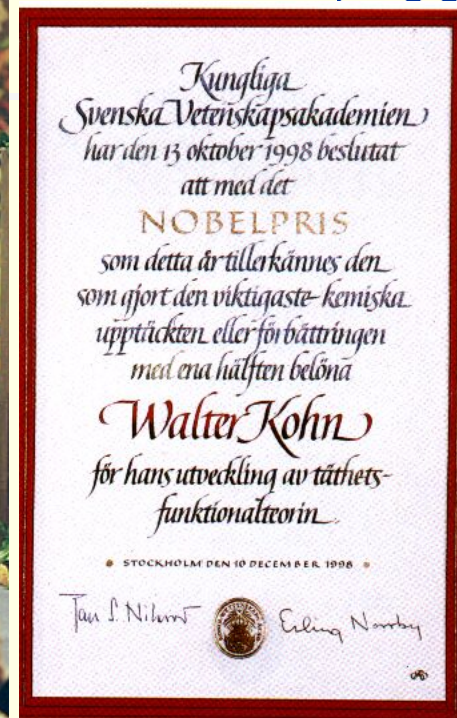
# Vienna, city of music and the **Wien2k** code





# 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 60<sup>th</sup> birthday

Honorary Chairman: Walter Kohn

16. 1. 2001

Walter Kohn  
Peter & Co. Laude S.K. P.icky



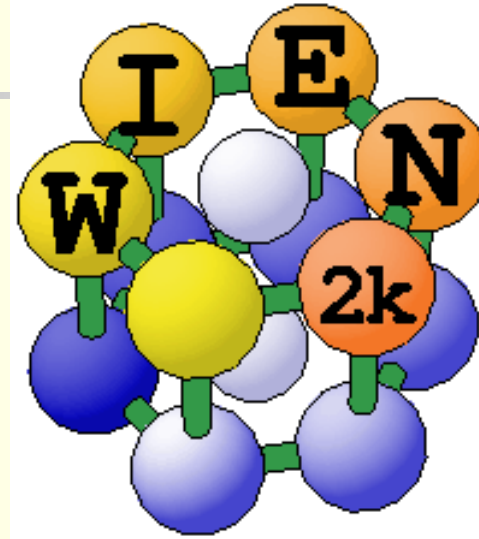


- **W**orld of
- **I**nteracting
- **E**lectrons and
- **N**uclei

due

■ **2**

walter ■ **k**ohn





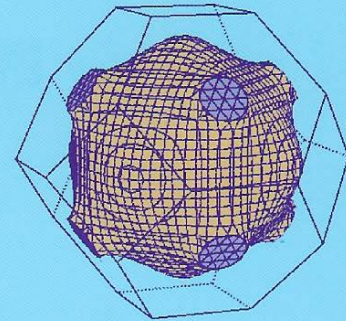
In Japan

- 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。