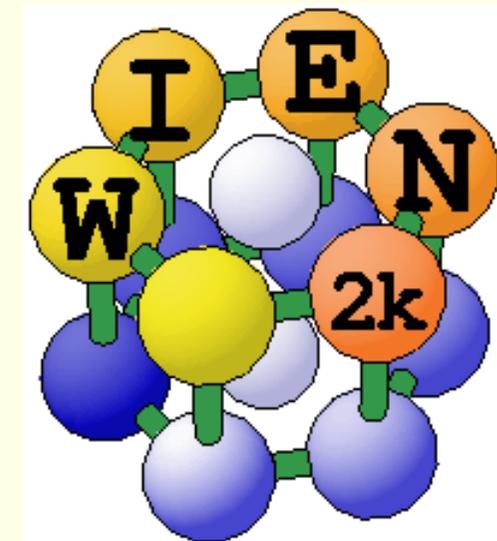


Basic concepts of bandstructure methods and the APW based methods

Peter Blaha

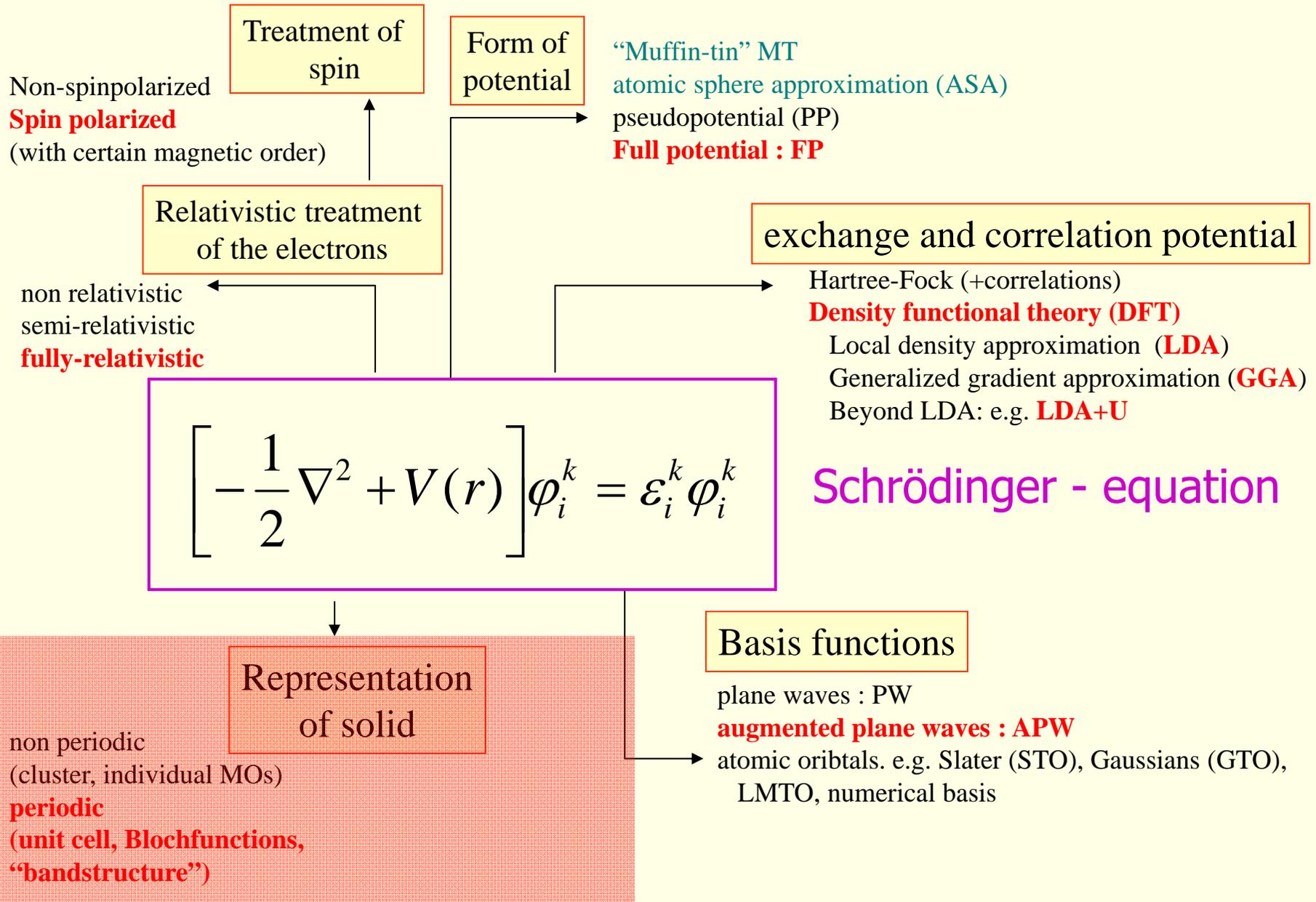
Institute of Materials Chemistry

TU Wien





Concepts when solving Schrödingers-equation





Representation of the solid

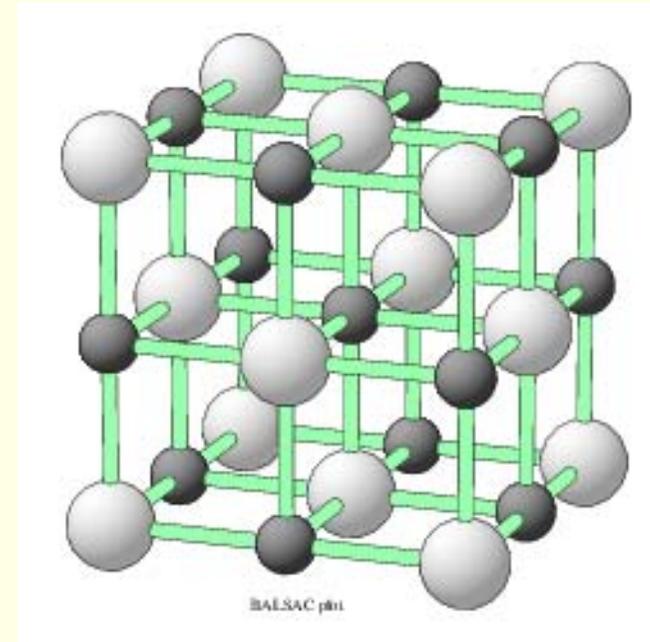


- **free cluster**

- *almost all atoms are at the "surface"*

- **cluster + embedding**

- *point charges*
- *auxiliary atoms (small basis set)*



- **infinite "ideal" crystal (with "small" unit cell) → band structure methods**

- *no surface*
- *no dislocations*
- *no impurities, vacancies*



A few solid state concepts

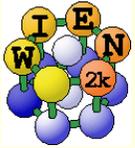


■ Crystal structure

- *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)*

■ Electronic structure

- *Periodic boundary conditions*
- *Bloch theorem (k -vector), Bloch function*
- *Reciprocal lattice (Brillouin zone)*
- *Bandstructure, density of states*



Spacegroup $P4_2/mnm$

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

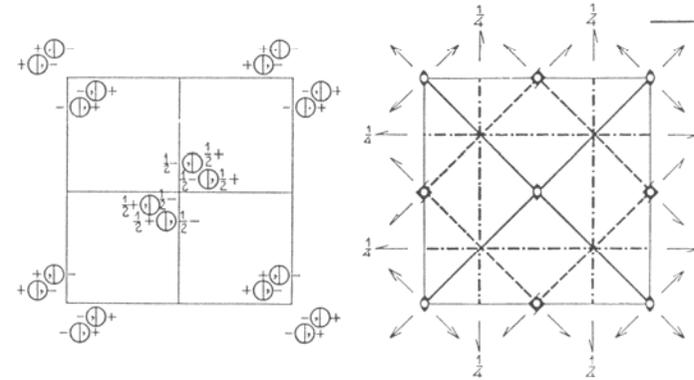
Rutile TiO_2 :
 $P4_2/mnm$ (136)
 $a=8.68, c=5.59$ bohr
Ti: (0,0,0)
O: (0.304,0.304,0)

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

No. 136

$P 4_2/m 2_1/n 2/m$

$4/m m m$ Tetragonal



Origin at centre (mmm)

Number of positions,
Wyckoff notation,
and point symmetry

Co-ordinates of equivalent positions

Conditions limiting
possible reflections

| Number of positions, Wyckoff notation, and point symmetry | | | Co-ordinates of equivalent positions |
|---|----------|------------|--|
| 16 | <i>k</i> | 1 | $x, y, z; \bar{x}, \bar{y}, z; \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z; \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z;$ $x, y, \bar{z}; \bar{x}, \bar{y}, \bar{z}; \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z; \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z;$ $y, x, z; \bar{y}, \bar{x}, z; \frac{1}{2} + y, \frac{1}{2} - x, \frac{1}{2} + z; \frac{1}{2} - y, \frac{1}{2} + x, \frac{1}{2} + z;$ $y, x, \bar{z}; \bar{y}, \bar{x}, \bar{z}; \frac{1}{2} + y, \frac{1}{2} - x, \frac{1}{2} - z; \frac{1}{2} - y, \frac{1}{2} + x, \frac{1}{2} - z.$ |
| 8 | <i>j</i> | <i>m</i> | $x, x, z; \bar{x}, \bar{x}, z; \frac{1}{2} + x, \frac{1}{2} - x, \frac{1}{2} + z; \frac{1}{2} - x, \frac{1}{2} + x, \frac{1}{2} + z;$ $x, x, \bar{z}; \bar{x}, \bar{x}, \bar{z}; \frac{1}{2} + x, \frac{1}{2} - x, \frac{1}{2} - z; \frac{1}{2} - x, \frac{1}{2} + x, \frac{1}{2} - z.$ |
| 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> | $0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}.$ |

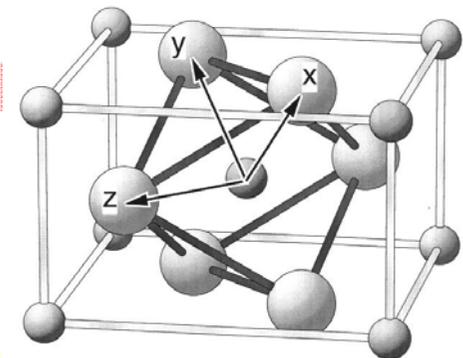
General:

hkl: No conditions
hk0: No conditions
Ok: $k+l=2n$
hhl: No conditions

Special: as above, plus

no extra conditions

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





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)*

■ Electronic structure

- *Periodic boundary conditions*
- *Bloch theorem (k -vector), Bloch function*
- *Reciprocal lattice (Brillouin zone)*
- *Bandstructure, density of states*



periodic boundary conditions:



- The electron density (potential) must be periodic, but not the wave function

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

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

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

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

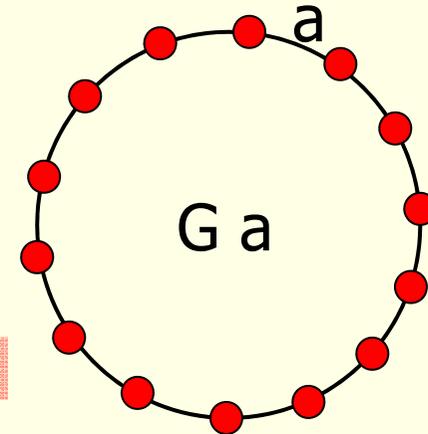
$$\Rightarrow \mu^G = 1$$

$$\mu = e^{2\pi i \frac{g}{G}}$$

$$g = 0, \pm 1, \pm 2, \dots$$

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

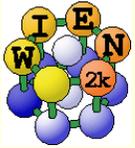
$$\text{Bloch condition} : \Psi(x+a) = e^{ika} \Psi(x) = \Psi_k$$



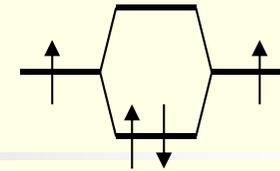
- Bloch function: $\Psi_k(r) = e^{ikr} u(r)$ periodic part $u(r)$



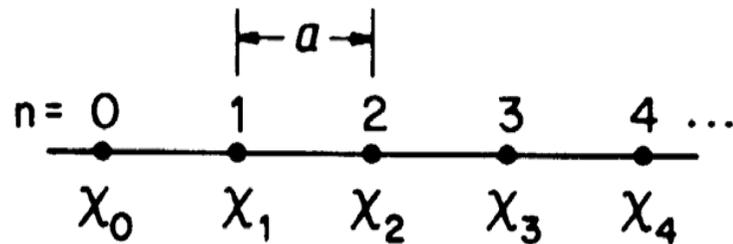
band structure



The Simple Machinery



- written in LCAO (linear combination of atomic orbitals) style, Bloch's theorem simply reads:



$$\psi_k = \sum_n e^{ikna} \chi_n$$

bonding

$k=0$

$$\psi_0 = \sum_n e^{i0} \chi_n = \sum_n \chi_n$$

$$= \chi_0 + \chi_1 + \chi_2 + \chi_3 + \dots$$

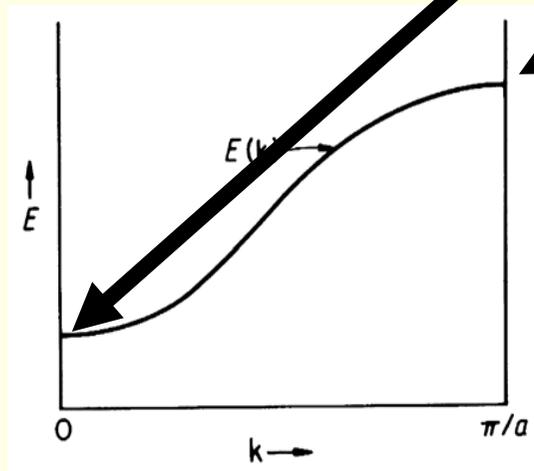
$k=\frac{\pi}{a}$

$$\psi_{\frac{\pi}{a}} = \sum_n e^{i\pi n} \chi_n = \sum_n (-1)^n \chi_n$$

$$= \chi_0 - \chi_1 + \chi_2 - \chi_3 + \dots$$

antibonding

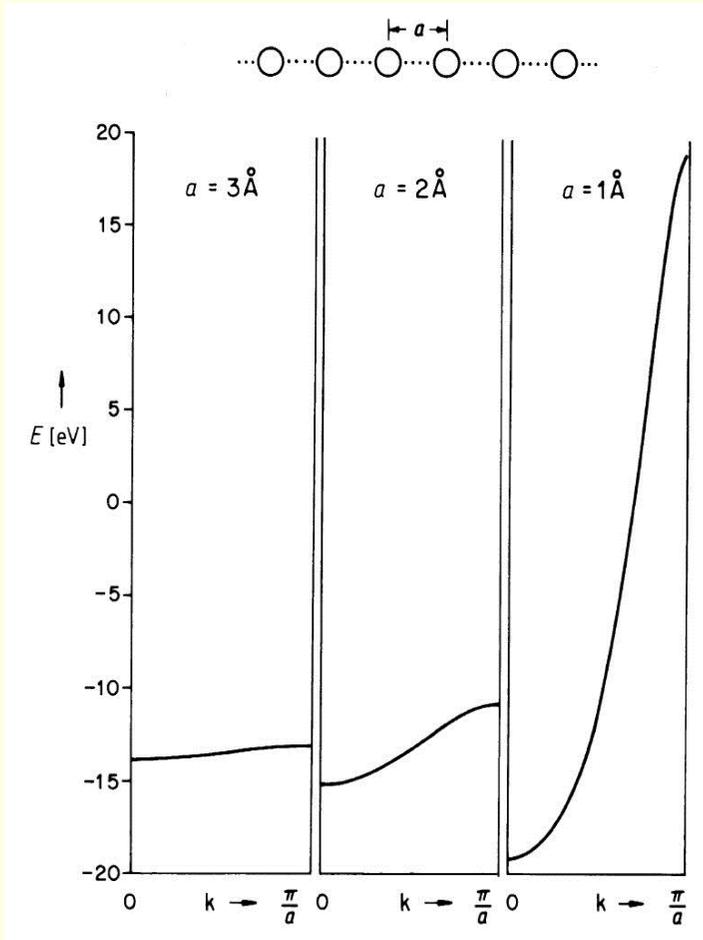
intermediate k : partial bonding



MO diagramm of a "long" chain



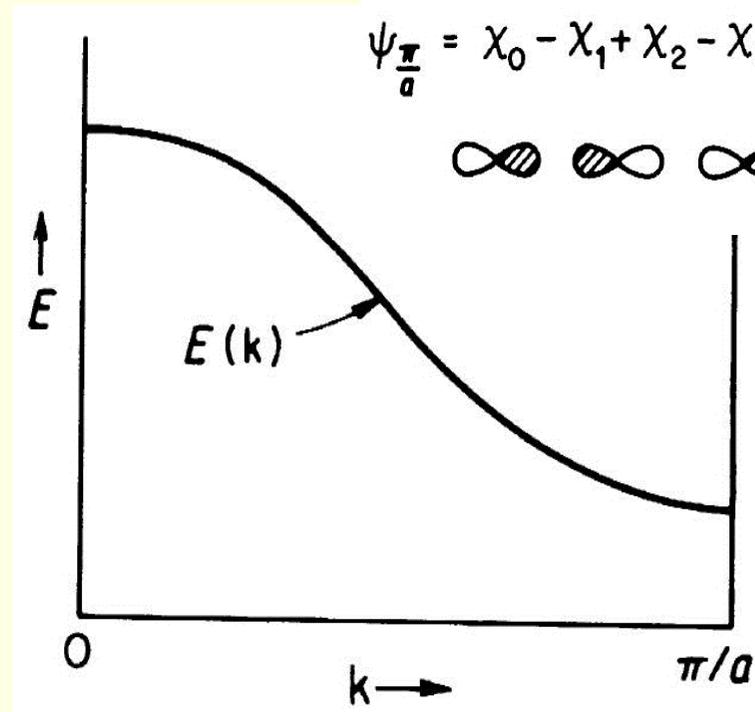
Dispersion and Course of Bands



$$\psi_0 = \chi_0 + \chi_1 + \chi_2 + \chi_3 + \dots$$



$$\psi_{\frac{\pi}{a}} = \chi_0 - \chi_1 + \chi_2 - \chi_3 + \dots$$



- *dispersion* (band width) set by inter-unit-cell *overlap*,
band course determined by *topology* of overlap



Bandstructure and DOS of Cu ($a_0=3.6\text{\AA}$)



flat bands \rightarrow high DOS, steep bands \rightarrow low DOS

- low effective mass (curvature)

Cu-3d band

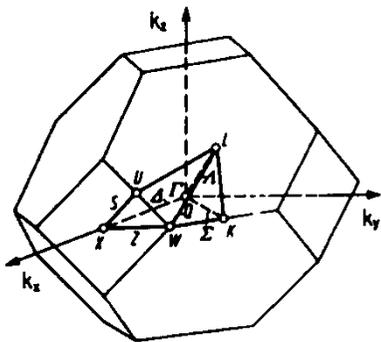
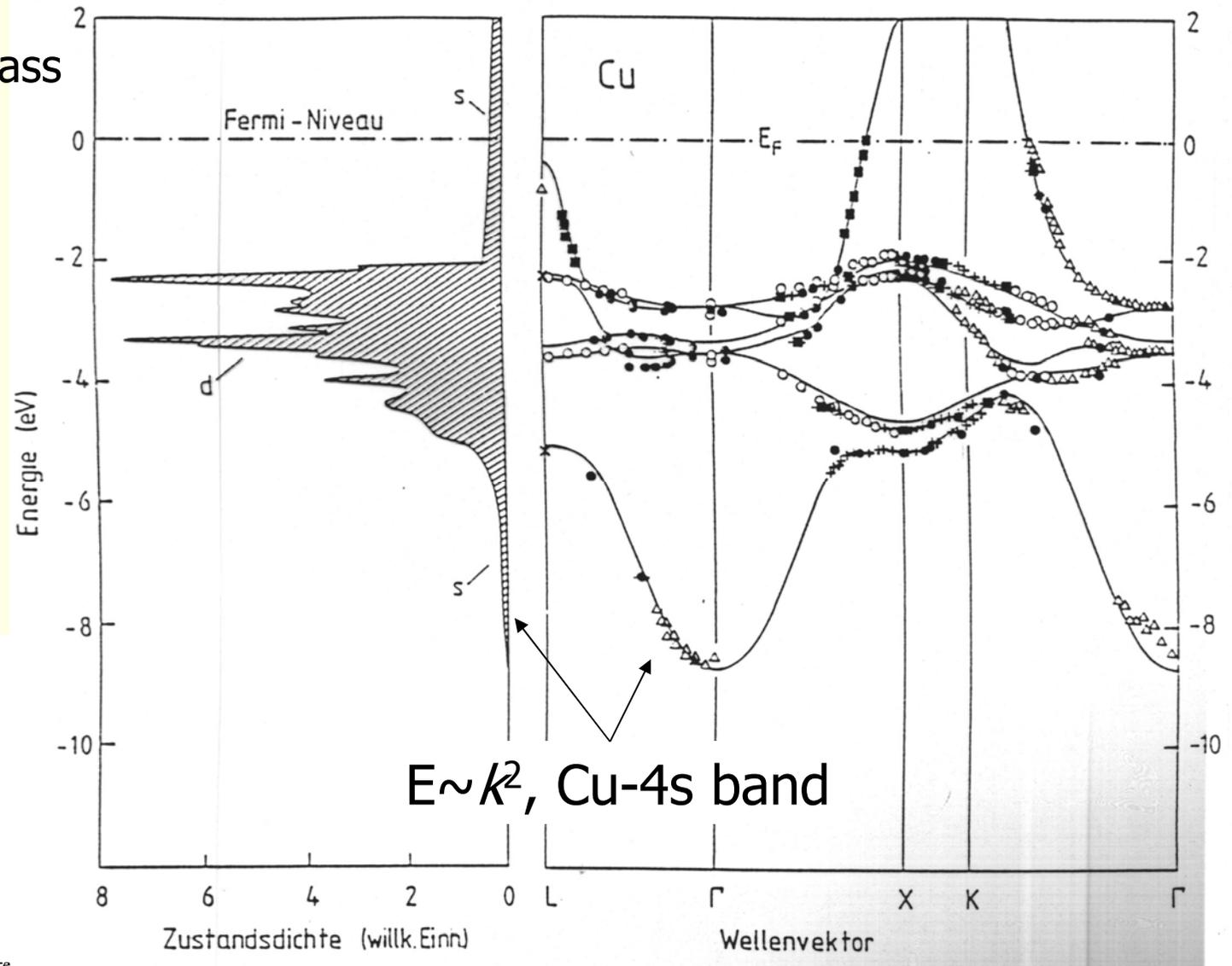
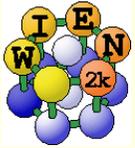
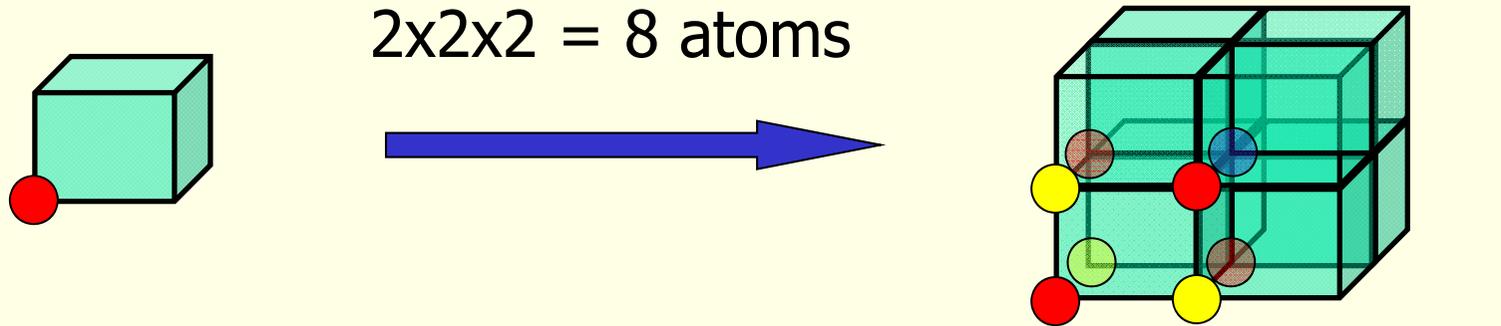


Figure 5.19. First Brillouin zone of the fcc structure.



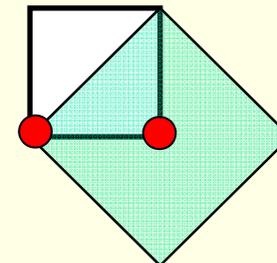
„Real materials“: Supercells

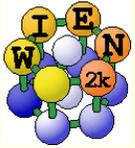


| | | | | | |
|-----------|---------------------------------|-----------|------------|-------------|--------------|
| $(0,0,0)$ | $P \rightarrow 8 \text{ atoms}$ | $(0,0,0)$ | $(.5,0,0)$ | $(.5,.5,0)$ | $(.5,.5,.5)$ |
| | | | $(0,.5,0)$ | $(.5,0,.5)$ | |
| | | | $(0,0,.5)$ | $(0,.5,.5)$ | |
| | $B \rightarrow 4 \text{ atoms}$ | yes | yes | no | no |
| | $F \rightarrow 2 \text{ atoms}$ | yes | no | no | yes |

4x4x4 supercells: P (64), B (32), F (16) atoms

$\sqrt{2} \times \sqrt{2}$ supercells (1 \rightarrow 2 atoms)



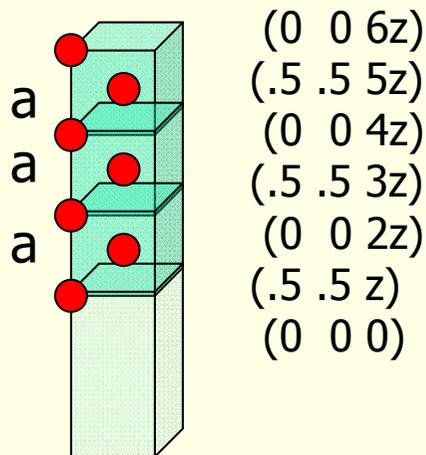


Supercells for surfaces



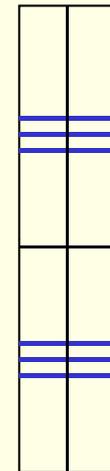
- 2D-slabs with finite number of layers with „vacuum“ in 3rd dimension

bcc (001) 7 layers:

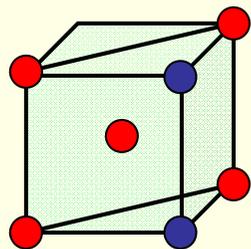


(0 0 6z)
 (.5 .5 5z)
 (0 0 4z)
 (.5 .5 3z)
 (0 0 2z)
 (.5 .5 z)
 (0 0 0)

with lattice parameters:
 $a, a, c=(3a+15-20\text{bohr vacuum})$
 shift to
 $(.5 .5 +/-3z)$
 $(0 0 +/-2z)$
 $(.5 .5 +/-z)$
 $(0 0 0)$
 inversion $z = a/2c$

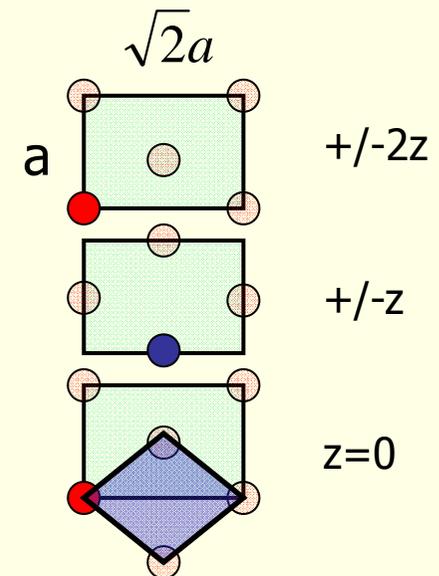


bcc (110):



orthorhombic CXY-lattice: $a, \sqrt{2}a, c$

(0 0 0) $z = a/\sqrt{2}a c$
 (0 .5 +/-z)
 (0 0 +/-2z)



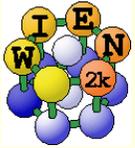


structure utilities in WIEN2k:



- **x supercell**
 - *simple $H \times K \times L$ supercells (+ vacuum) from small structure*
- **Structeditor-scripts for octave (matlab)**
 - *allows complex operations on struct files (surfaces, rotations, merging ..)*

```
octave
s=loadstruct("GaN.struct")
# make an orthorhombic supercell and visualize it
a=[1 0 0; 1 1 0; 0 0 2]
sout=makesupercell (s,a);
showstruct(sout);
# save it as test.struct
savestruct (sout,"test.struct");
# get help on all commands
helpstruct
```

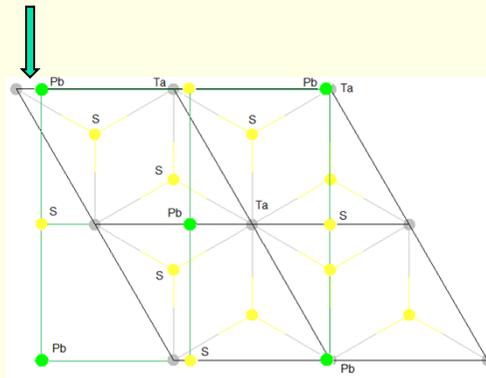


create an atomic model for real materials

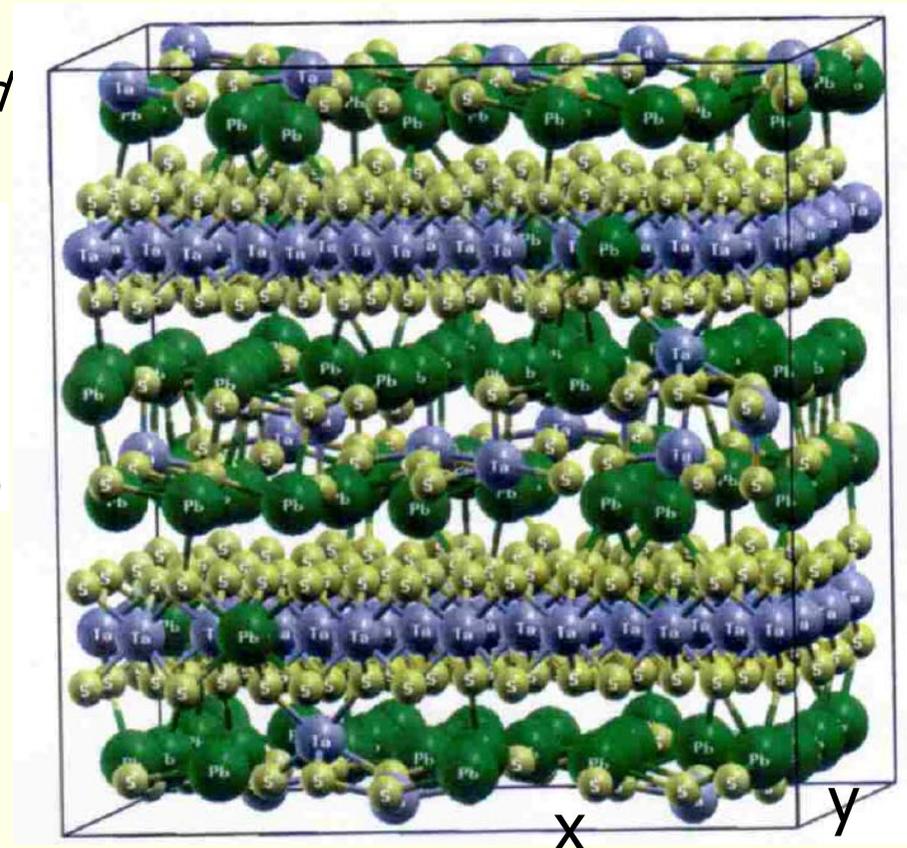


- make it "realistic" (as big as possible)
- make it as "small" as possible (cpu-time scales with n^3)
 - 64 atom unit cells on a single PC (k -parallel on a few PCs)
 - parallelization on hundreds of cores (mpi, Scalapack)

disorder in misfit layer compound
 $(PbS)_{1.14}TaS_2$

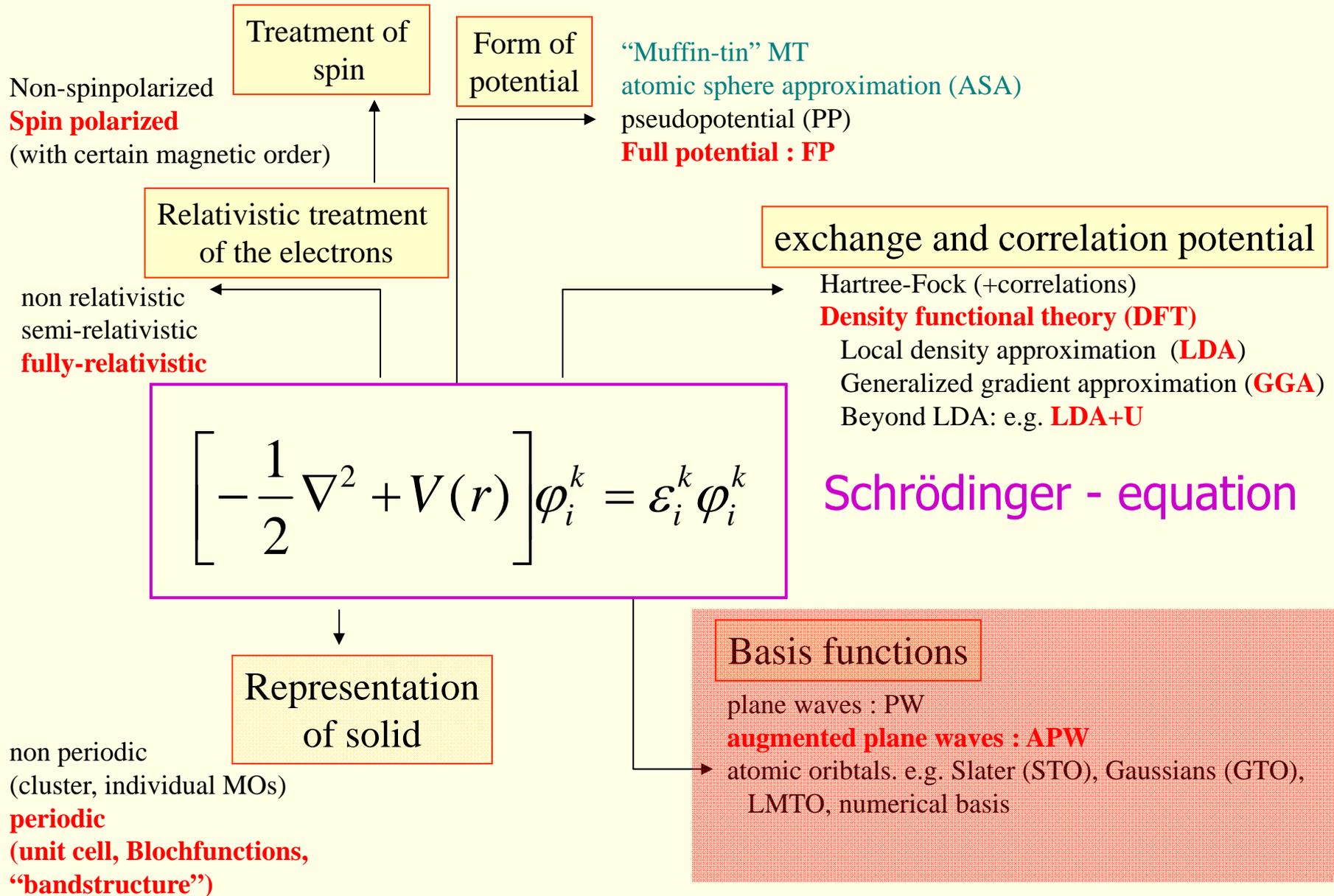


4 PbS x 7 TaS₂ unit cells in "x"
4 unit cells in "y" for "disorder"
➡ *296 atoms*



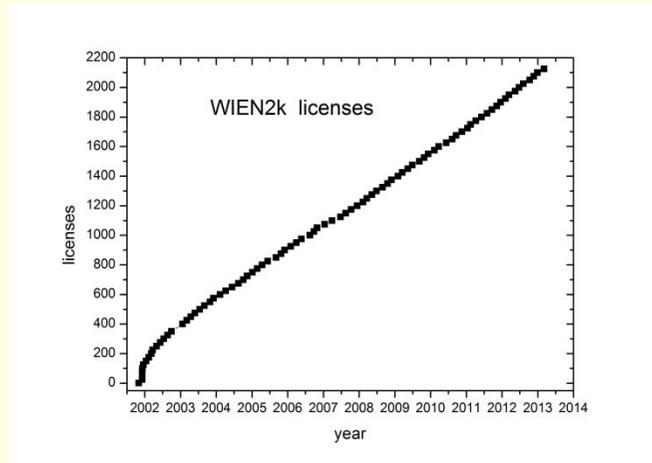
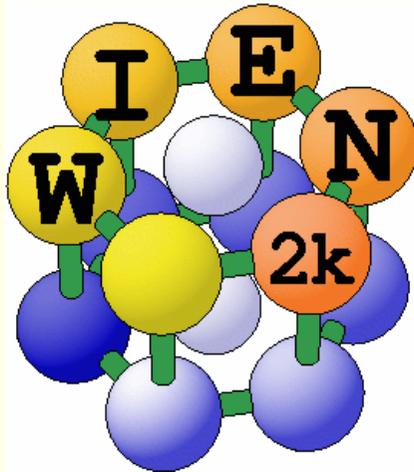


Concepts when solving Schrödingers-equation





WIEN2k software package



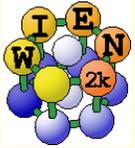
WIEN2k: ~2200 groups
mailinglist: 1.500 emails/year
20 WIEN2k-workshops (Europe, USA, Japan, Singapore, Iran)

**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

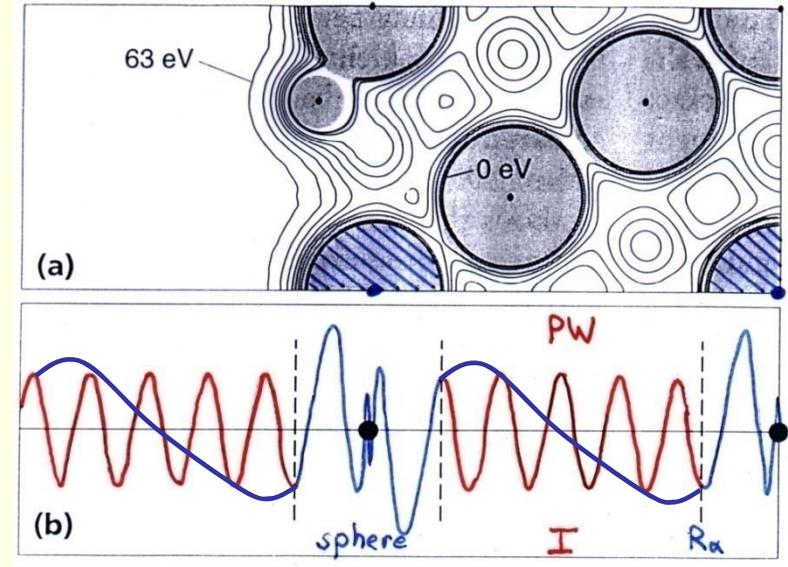
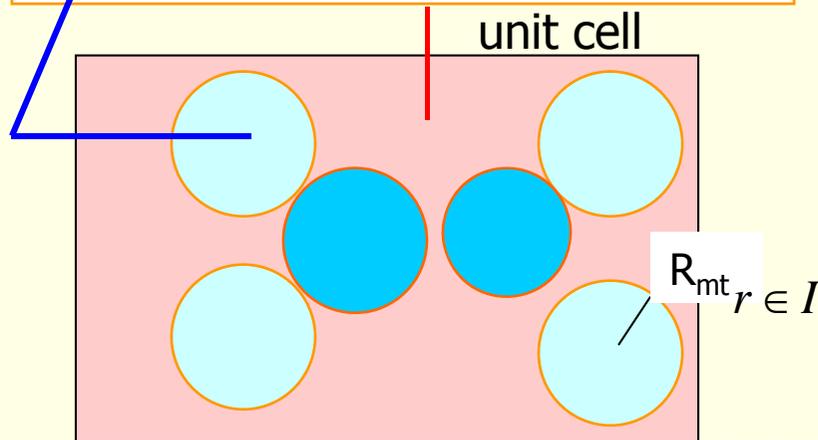
<http://www.wien2k.at>



APW Augmented Plane Wave method



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

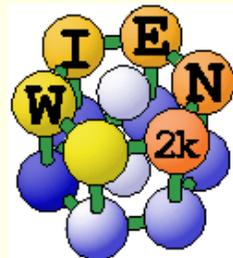
$u_l(r, \varepsilon)$ are the numerical solutions of the radial Schrödinger equation in a given spherical potential for a particular energy ε
 A_{lm}^K coefficients for matching the PW



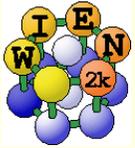
APW based schemes



- **APW (J.C.Slater 1937)**
 - ***E-dependent basis*** \longrightarrow *Non-linear eigenvalue problem*
 - Computationally very demanding
- **LAPW (O.K.Andersen 1975)**
 - ***Linearization of E-dependency*** \longrightarrow *Generalized eigenvalue problem*
 - *Full-potential (A. Freeman et al.)*
 - ghostbands (problem with 2 principal QN; Ti: 3p + 4p)
- **Local orbitals (D.J.Singh 1991)**
 - *treatment of semi-core states (avoids ghostbands)*
- **APW+lo (E.Sjöstedt, L.Nordström, D.J.Singh 2000)**
 - ***E-independent APWs + local orbitals (to describe the E-dependency)***
 - *Efficiency of APW + convenience of LAPW*
 - *Basis for*



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

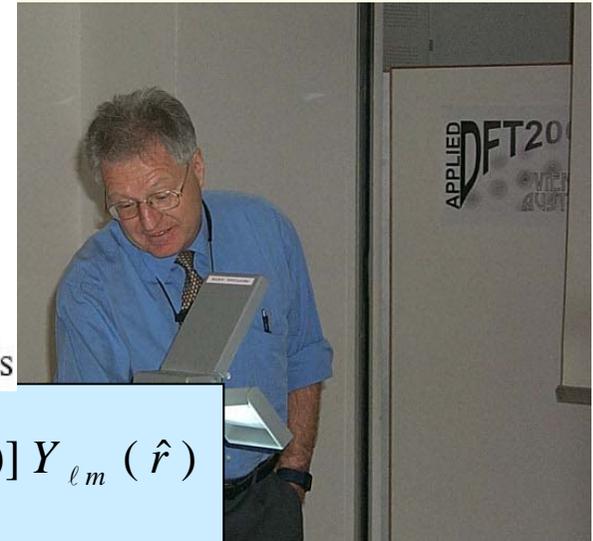
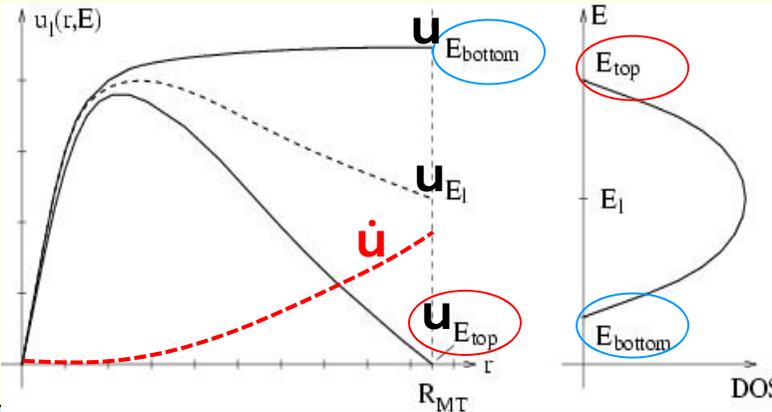


Linearization of energy dependence



LAPW suggested by

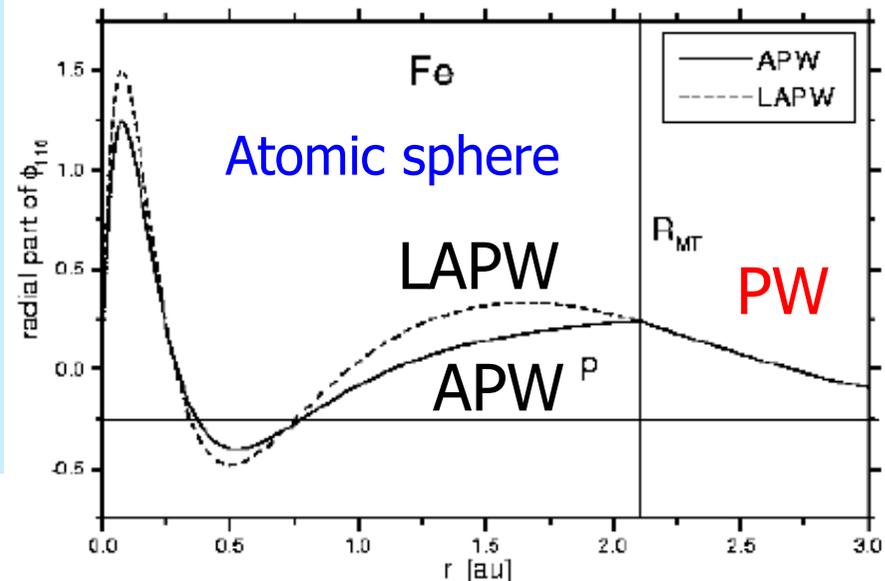
O.K.Andersen,
Phys.Rev. B 12, 3060
(1975)



$$\Phi_{k_n} = \sum_{l m} [A_{l m}(k_n) u_l(E_l, r) + B_{l m}(k_n) \dot{u}_l(E_l, r)] Y_{l m}(\hat{r})$$

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

$A_{l m}^k, B_{l m}^k$: join PWs in value and slope
→ additional constraint requires **more PWs** than APW
→ basis flexible enough for **single diagonalization**



only ONE principle QN (3s OR 4s) → ghostband problem

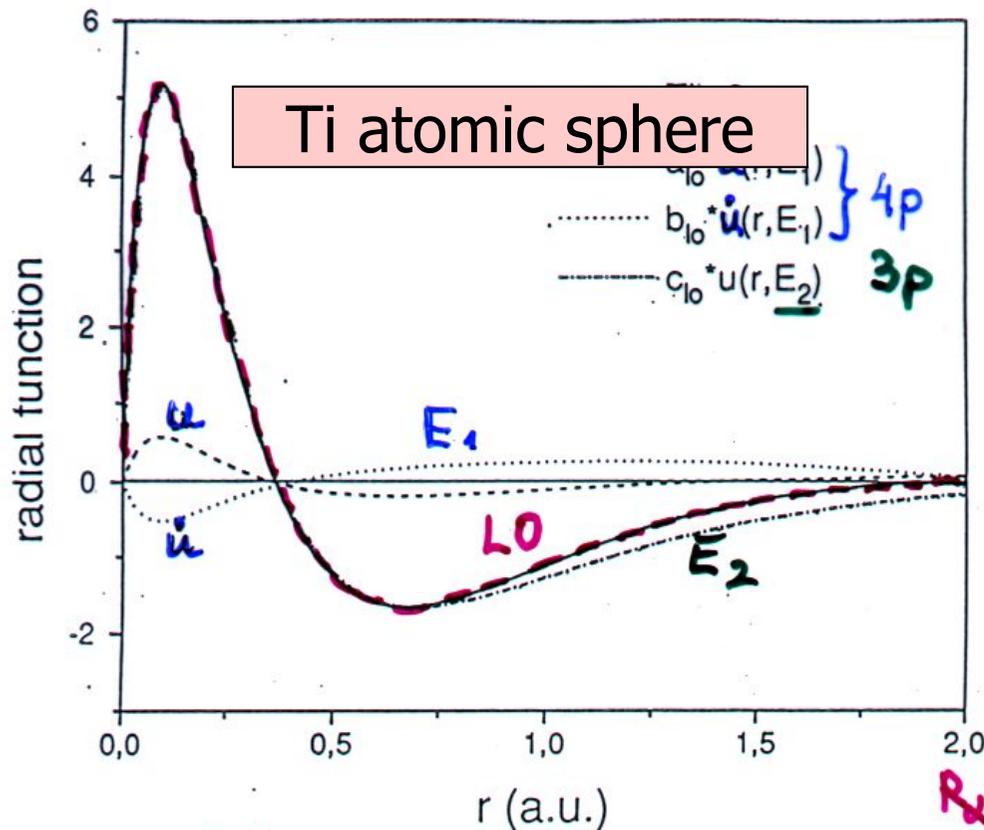


Extending the basis: Local orbitals (LO)



$$\Phi_{LO} = [A_{lm} u_l^{E_1} + B_{lm} \dot{u}_l^{E_1} + C_{lm} u_l^{E_2}] Y_{lm}(\hat{r})$$

- LO: contains a second $u_l(E_2)$
 - *is confined to an atomic sphere*
 - *has zero value and slope at R*
 - *can treat two principal QN n for each azimuthal QN ℓ (3p and 4p)*
 - *corresponding states are strictly orthogonal (no "ghostbands")*
 - *tail of semi-core states can be represented by plane waves*
 - *only slight increase of basis set (matrix size)*



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



New ideas from Uppsala and Washington



E.Sjöstedt, L.Nordström, D.J.Singh,
An alternative way of linearizing the augmented plane wave method,
Solid State Commun. 114, 15 (2000)

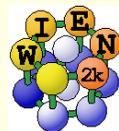
- Use **APW**, but at **fixed E** , (superior PW convergence)
- **Linearize** with **additional lo** (add a few basis functions)

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

$$\Phi_{lo} = [A_{lm} u_l^{E_1} + B_{lm} \dot{u}_l^{E_1}] Y_{lm}(\hat{r})$$

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



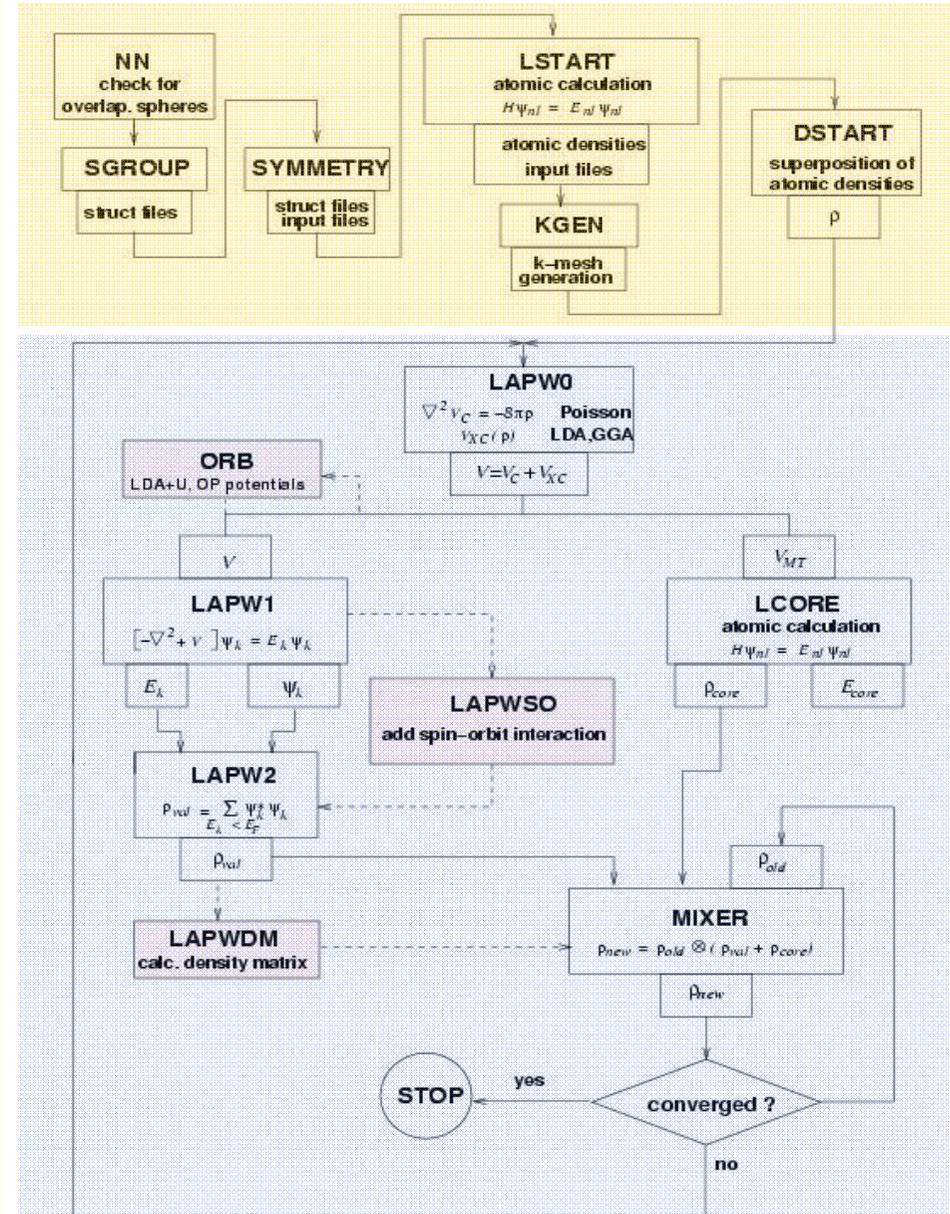
K.Schwarz, P.Blaho, G.K.H.Madsen,
Comp.Phys.Commun. **147**, 71-76 (2002)



Program structure of WIEN2k



- create a structure
- **init_lapw**
 - *step-by-step or batch 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, input and clmsum files,*
 - *mv case.scf file*
 - *rm case.broyd* files*

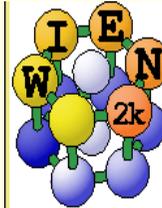




w2web GUI (graphical user interface)



- **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*



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

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



O-NMR of tetragonal BaTiO₃



- `cd work; mkdir BaTiO3; cd BaTiO3`
- **makestruct** (and type in the following information)
 - *BaTiO₃*: *SG 99 (P 4 m m), a = 3.9926 3.9926 4.0294 Ang*
 - *Ba (0,0, 0.0217), Ti (0.5,0.5, 0.5363), O_1 (0.5,0.5, 0.99805), O_2 (0,0.5, 0.50663)*
- `cp init.struct BaTiO3.struct`
- `init_lapw -b` (batch mode with defaults) [`-sp -numk 100 -rkmax 6 -vxc 11`]
- `edit .machines` (insert 4 lines with 1:localhost to run 4-fold k-parallel)
- `run_lapw -p -fc 10` (scf-cycle with crude force convergence)
- `edit BaTiO3.inm` (put "MSR1a" instead of "MSR1")
- `run_lapw -p -fc 1 -cc 0.001` (optimize position of all atoms + scf simultaneously)
- `grep :ENE BaTiO3.scf (:FGLxxx :POSxxx)` and verify E-minimum, forces are "small", change in atomic positions
- Now calculate "properties":
- `x_nmr_lapw -mode in1 -focus O` (and view the resulting *in1c_nmr file)
- `x_nmr_lapw -p`
 - `tail BaTiO3.outputnmr_integ` (chemical shift)
 - `grep :EFG *scf0` (quadrupole splitting + asymmetry)
 - `grep :ETA *scf0`



accuracy and applicability of specific DFT- approximations

*(development of better exchange and correlation
functionals)*



Schrödinger's equation:



Ab-initio Hamiltonian

(non-relativistic/Born-Oppenheimer approximation)

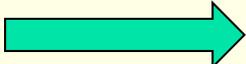
$$H = \sum_i \left[-\frac{\hbar^2 \Delta_i}{2m_e} + \sum_l \frac{-e^2}{4\pi\epsilon_0} \frac{Z_l}{|\mathbf{r}_i - \mathbf{R}_l|} \right] + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

- for a system with N electrons, Ψ depends on $3N$ coordinates

$$H \Psi(r_1, r_2, \dots, r_n) = E \Psi(r_1, r_2, \dots, r_n)$$

- Hartree-Fock ansatz: "Slater determinant" (exchange only)
 - Ψ as antisymmetric product of single electron wavefunctions

$$\Psi_{HF} = \frac{1}{\sqrt{N!}} \det[\Phi_1 \Phi_2 \dots \Phi_n]$$

- Correlation via MP2, CC, CI  terrible scaling with N



DFT Density Functional Theory



Hohenberg-Kohn theorem: (exact)

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

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

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_{kinetic}

non interacting

E_{ne}

E_{coulomb} E_{ee}

E_{xc} exchange-correlation

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

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

LDA

GGA

treats both, **exchange** and

correlation effects **approximately**

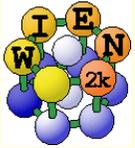


Success and failure of "standard" DFT in solids



- Standard LDA (GGA) gives good description of most solids
- Problems:
 - *accuracy : functional "adapted" for specific materials or properties*
 - solids - molecules; metals - insulators - van der Waals bonds
 - elements: trends within up - down and left - right in periodic table
 - geometry - binding energies - spectroscopy
 - *"correlated" (localized) electrons: 3d transition metal oxides, 4f,5f e*
 - metals instead of insulators (FeO, FeF₂, cuprates, ...)
 - nonmagnetic instead of anti-ferromagnetic (La₂CuO₄, YBa₂Cu₃O₆)
 - *band gaps in semiconductors/insulators*
 - gap typically underestimated by 50%
- Possible improvements (depends on case and property):
 - *ground state: better GGAs, LDA+U, hybrid-DFT, OEP, RPA, DMFT, QMC*
 - *excited states: TB-mBJ, TD-DFT, GW,BSE,*

DFT: groundstate



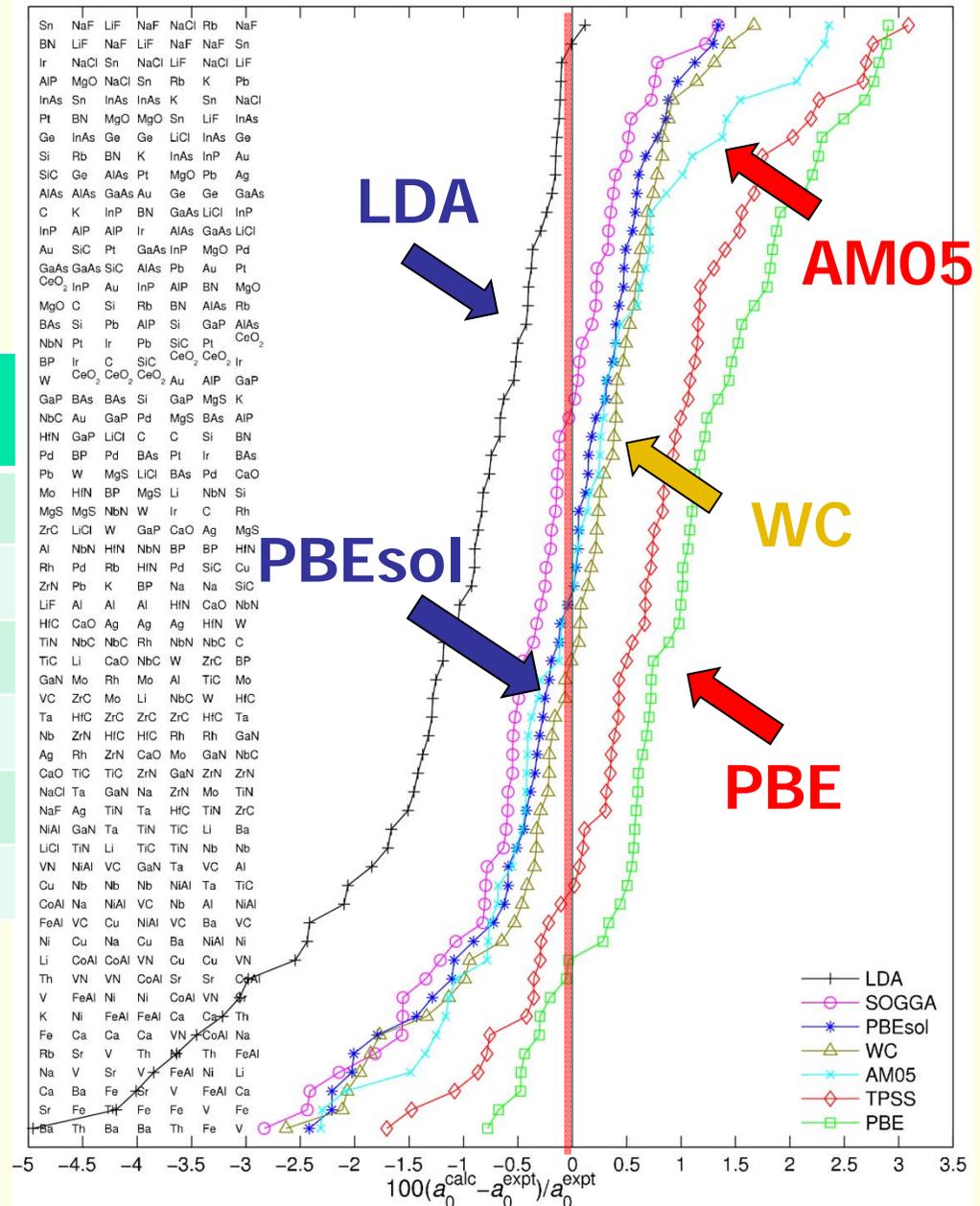
accuracy: "DFT limit"



- Testing of DFT functionals:
 - error of theoretical lattice parameters for 60 different simple 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 |

- but: better GGAs for solids are worse for molecules !!





Band gaps by a semi-local potential



- Becke-Johnson potential (J. Chem. Phys. 124, 221101 (2006))
 - *local* potential designed to reproduce *non-local* OEP potentials in *atoms*
- **modified Becke-Johnson potential**

$$v_{x,\sigma}^{\text{MBJ}}(\mathbf{r}) = c v_{x,\sigma}^{\text{BR}}(\mathbf{r}) + (3c - 2) \frac{1}{\pi} \sqrt{\frac{5}{12}} \sqrt{\frac{2t_{\sigma}(\mathbf{r})}{\rho_{\sigma}(\mathbf{r})}},$$

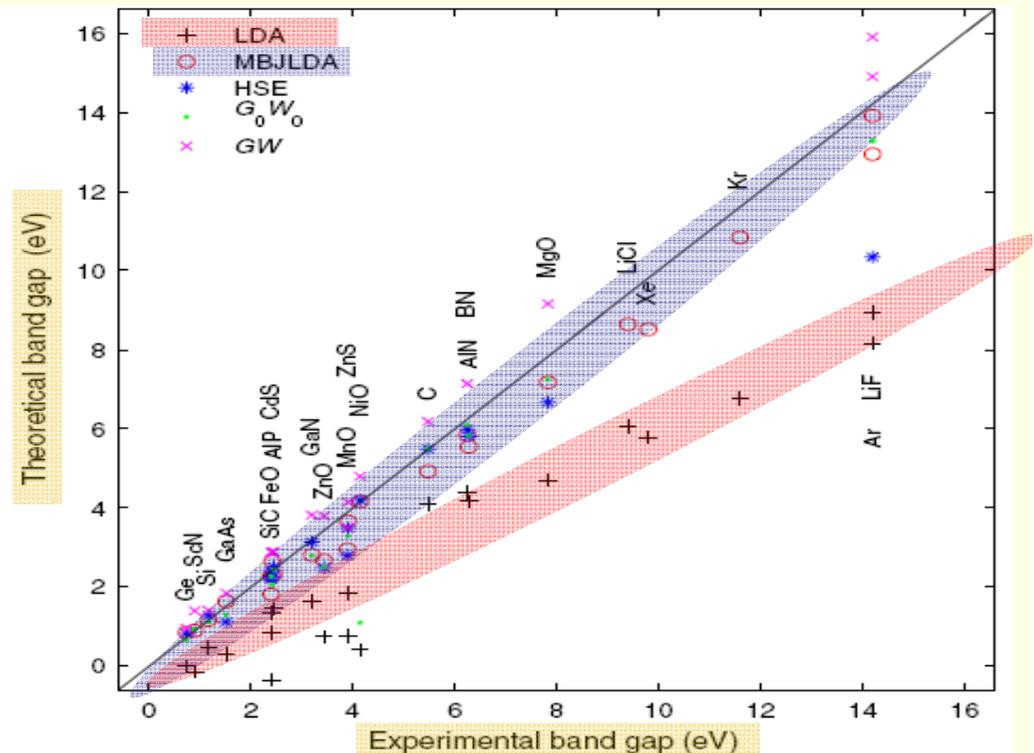
F. Tran P. Blaha
PRL 102, 226401 (2009)

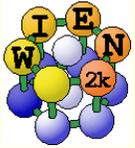
$$c = \alpha + \beta \left(\frac{1}{V_{\text{cell}}} \int_{\text{cell}} \frac{|\nabla \rho(\mathbf{r}')|}{\rho(\mathbf{r}')} d^3 r' \right)^{1/2}$$

c depends on the density properties of a material

+ as cheap as GGA

- NO energy (only V)





mBJ gaps



- accuracy of a few tenths of an eV (like GW)
- works for small gap semiconductors to large gap insulators (Ne!!!)
- works for TM-oxides (in contrast to G_0W_0)
- improves unoccupied bands
- nearly unchanged occupied bands, but too strong localization
- fails for magn. metals

| Solid | LDA | MBJLDA | HSE | G_0W_0 | GW | Expt. |
|-----------|-------|--------|--------------------|--------------------|-------------------|-----------|
| Ne (A1) | 11.42 | 22.72 | | 19.59 ^c | 22.1 ^g | 21.70 |
| Ar (A1) | 8.16 | 13.91 | 10.34 ^a | 13.28 ^e | 14.9 ^g | 14.20 |
| Kr (A1) | 6.76 | 10.83 | | | | 11.6 |
| Xe (A1) | 5.78 | 8.52 | | | | 9.8 |
| C (A4) | 4.11 | 4.93 | 5.49 ^b | 5.50 ^e | 6.18 ^g | 5.48 |
| Si (A4) | 0.47 | 1.17 | 1.28 ^b | 1.12 ^e | 1.41 ^g | 1.17 |
| Ge (A4) | 0.00 | 0.85 | 0.83 ^b | 0.66 ^f | 0.95 ^g | 0.74 |
| LiF (B1) | 8.94 | 12.94 | | 13.27 ^e | 15.9 ^g | 14.20 |
| LiCl (B1) | 6.06 | 8.64 | | | | 9.4 |
| MgO (B1) | 4.70 | 7.17 | 6.67 ^b | 7.25 ^e | 9.16 ^g | 7.83 |
| ScN (B1) | -0.14 | 0.90 | | 0.95 ^f | 1.4 ^h | ~0.9 |
| MnO (B1) | 0.76 | 2.95 | 2.8 ^c | | 3.5 ⁱ | 3.9 ± 0.4 |
| FeO (B1) | -0.35 | 1.82 | 2.2 ^c | | | 2.4 |
| NiO (B1) | 0.42 | 4.16 | 4.2 ^c | 1.1 ^f | 4.8 ⁱ | 4.0, 4.3 |
| SiC (B3) | 1.35 | 2.28 | 2.40 ^b | 2.27 ^e | 2.88 ^g | 2.40 |
| BN (B3) | 4.39 | 5.85 | 5.99 ^b | 6.10 ^e | 7.14 ^g | ~6.25 |
| GaN (B3) | 1.63 | 2.81 | 3.14 ^b | 2.80 ^e | 3.82 ^g | 3.20 |
| GaAs (B3) | 0.30 | 1.64 | 1.12 ^b | 1.30 ^e | 1.85 ^g | 1.52 |
| AlP (B3) | 1.46 | 2.32 | 2.51 ^b | 2.44 ^e | 2.90 ^g | 2.45 |
| ZnS (B3) | 1.84 | 3.66 | 3.49 ^b | 3.29 ^e | 4.15 ^g | 3.91 |
| CdS (B3) | 0.86 | 2.66 | 2.25 ^b | 2.06 ^e | 2.87 ^g | 2.42 |
| AlN (B4) | 4.17 | 5.55 | 5.81 ^b | 5.83 ^f | | 6.28 |
| ZnO (B4) | 0.75 | 2.68 | 2.49 ^d | 2.51 ^f | 3.8 ^g | 3.44 |



more “non-local” functionals (“beyond DFT”)



- **LDA+U** \longrightarrow **DMFT** (dynamical mean field theory)
 - *approximate screened HF for selected “highly-correlated” electrons (3d,4f,5f)*
 - *empirical parameter U*

- **Hartree-Fock**
 - *neglects correlation, which for most solids is essential*

- **Hybrid functionals:** mixing of DFT+ HF (“onsite”, “diagonal”, “full”-hybrids)

$$E_{xc} = E_{xc}^{SL} + \alpha_x (E_x^{SR-HF} - E_x^{SR-SL})$$

- **GW method:** calculate the quasiparticle self energy Σ

$$\Sigma(r, r', \omega) = \frac{i}{2\pi} \int d\omega' G(r, r, \omega - \omega') W(r, r', \omega)$$

$$\epsilon_{nk}^{QP} = \epsilon_{nk}^{LDA} - \langle nk | \Sigma(\epsilon_{nk}^{QP}) - V_{xc}^{LDA} | nk \rangle$$

available for WIEN2k
M. Scheffler et al.
(very expensive)

- **BSE** (Bethe-Salpeter equ.): e^-h^+ interactions, excitons
 - *2 particle wavefunctions with screened (nonlocal, but static ϵ) coulomb and full exchange*

LDA+U

Anisimov *et al* PRB 48, 16929 (1993)

- add local orbital dependent energy

$$E_{LDA+U} = E_{LDA} + \frac{U}{2} \sum_{i \neq j} n_i n_j - \underbrace{\frac{U}{2} N(N-1)}_{E_{dc}}$$

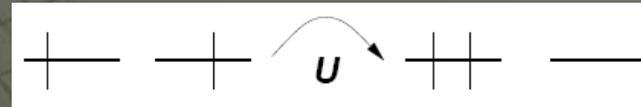
$$E_{dc} = E_{dc}(\text{atomic limit})$$

$$\varepsilon_i = \frac{\partial E}{\partial n_i} = \varepsilon_{LDA} + U\left(\frac{1}{2} - n_i\right)$$

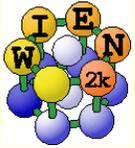
- other choices for E_{dc}

$$E_{dc}(\text{around mean field}) = \frac{U}{2} N(N - \bar{n})$$

Czyzyk and Sawatzky PRB 49, 14211 (1994)



Hubbard-U describes coulomb energy for $2e^-$ at the same site



screened full-hybrid functionals

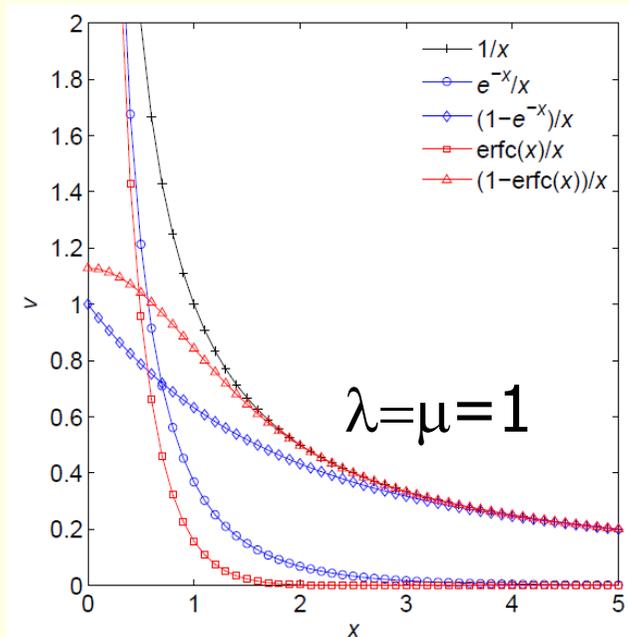


$$E_{xc} = E_{xc}^{SL} + \alpha_x (E_x^{SR-HF} - E_x^{SR-SL}) \quad \alpha=0.25$$

- $1/r$ is decomposed into a short-range and long-range component using an **exponential** (or the error function)

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \underbrace{\frac{e^{-\lambda|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|}}_{\text{SR}} + \underbrace{\frac{1 - e^{-\lambda|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|}}_{\text{LR}}$$

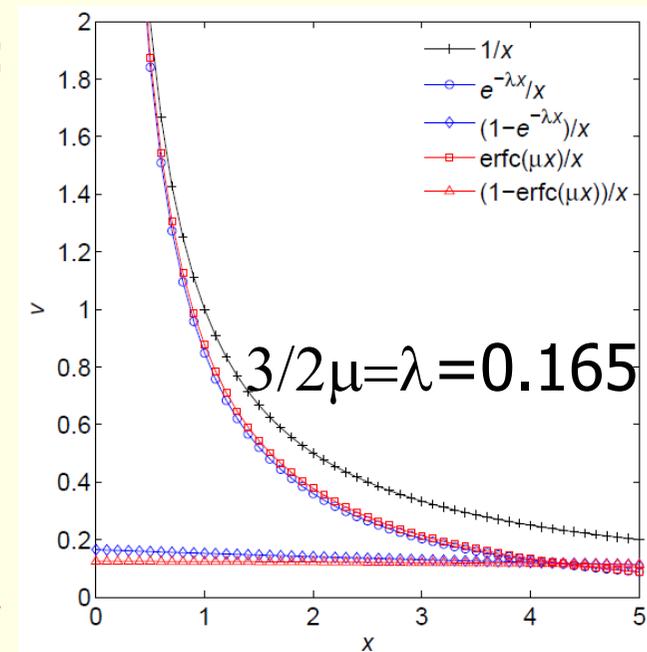
$$(1 - \text{erfc}(\mu x)) / x$$



HSE06 functional:
 $\mu=0.11 \text{ bohr}^{-1}$

exponential with
 $\lambda=3/2$ μ is very
similar

YS-PBE0: Tran, Blaha,
PRB 83, 235118 (2011)



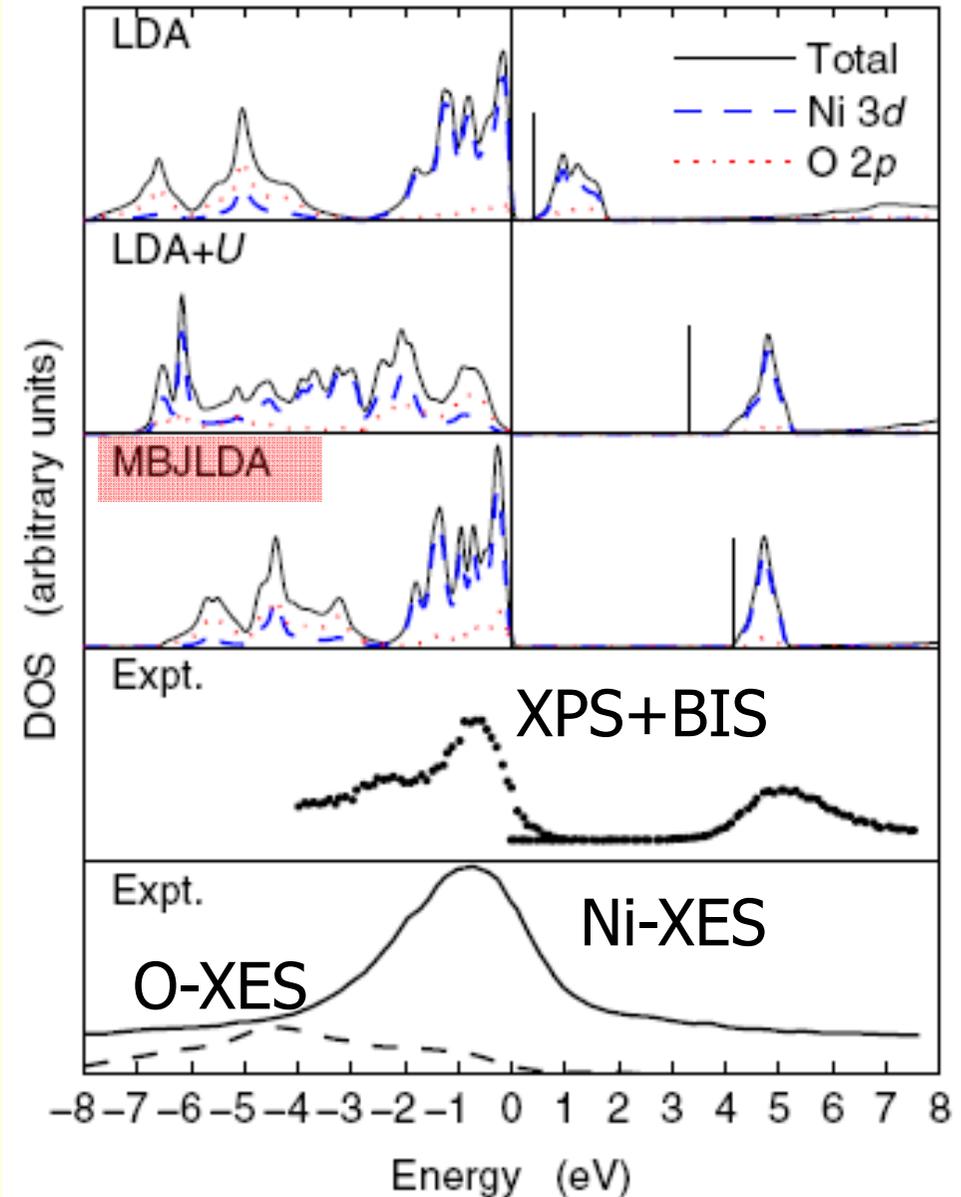
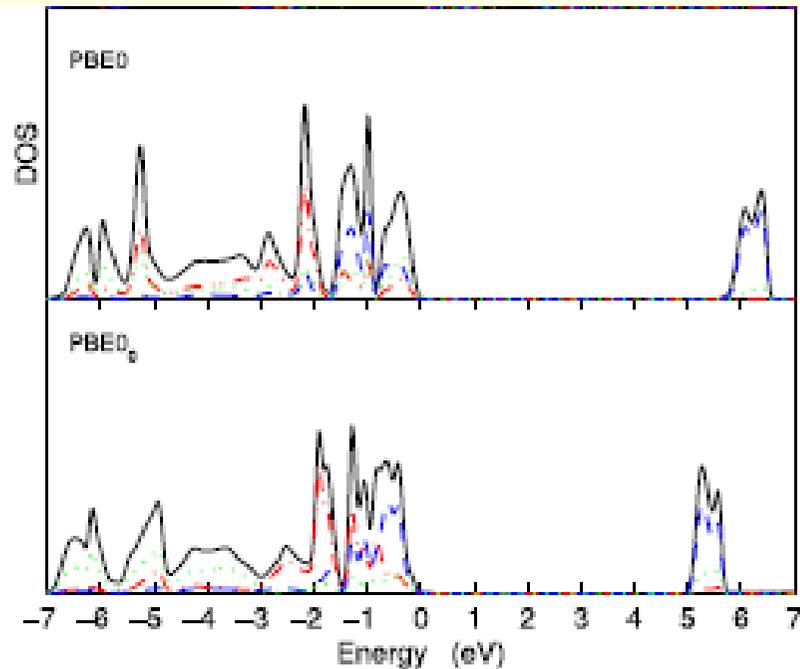
screened functionals improve k-mesh convergence dramatically



DOS of AFM-NiO



- mBJ DOS agrees with
 - XPS/BIS
 - Ni-XES, O-XES
- LDA+U gives similar gap, but cannot explain XES
- PBE0: gap too large

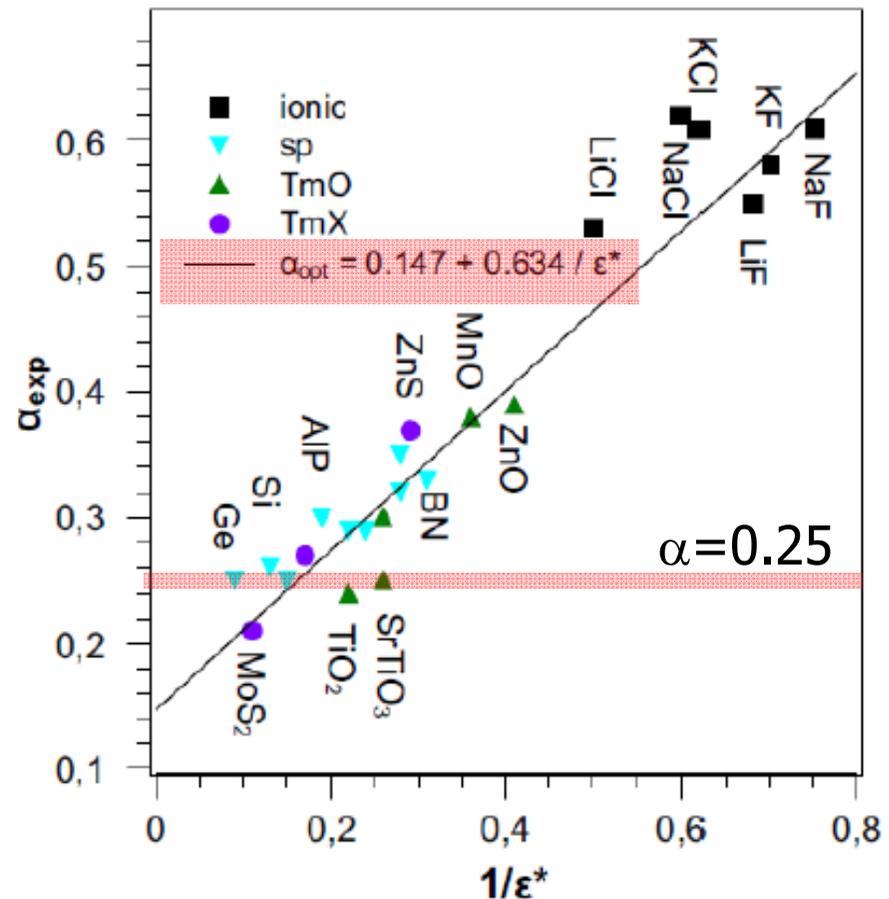
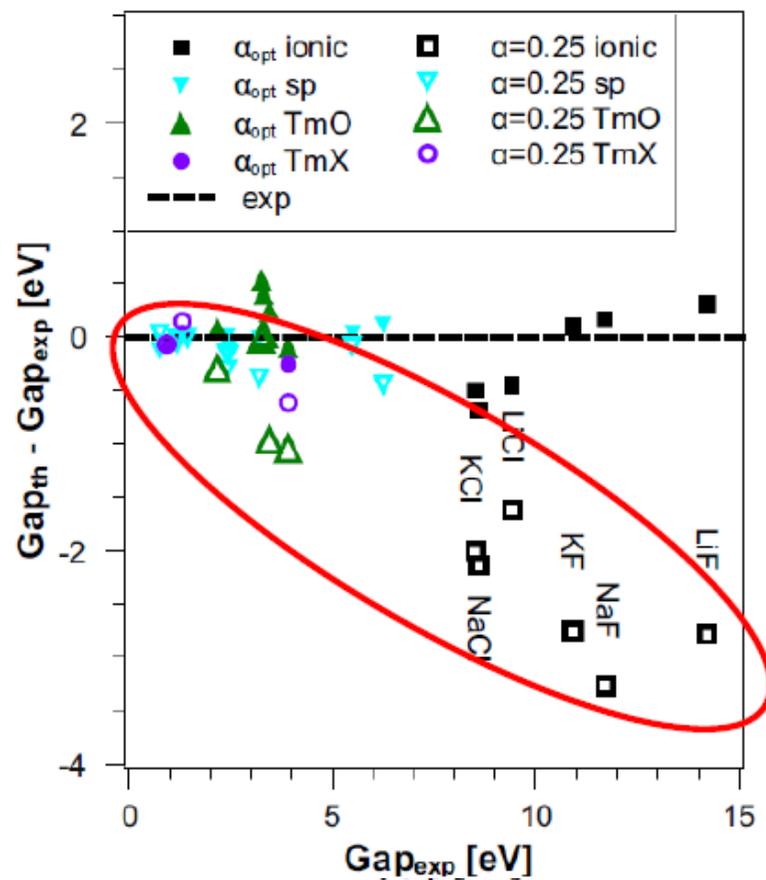


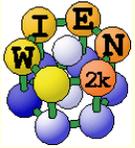


hybrid-DFT with individual α

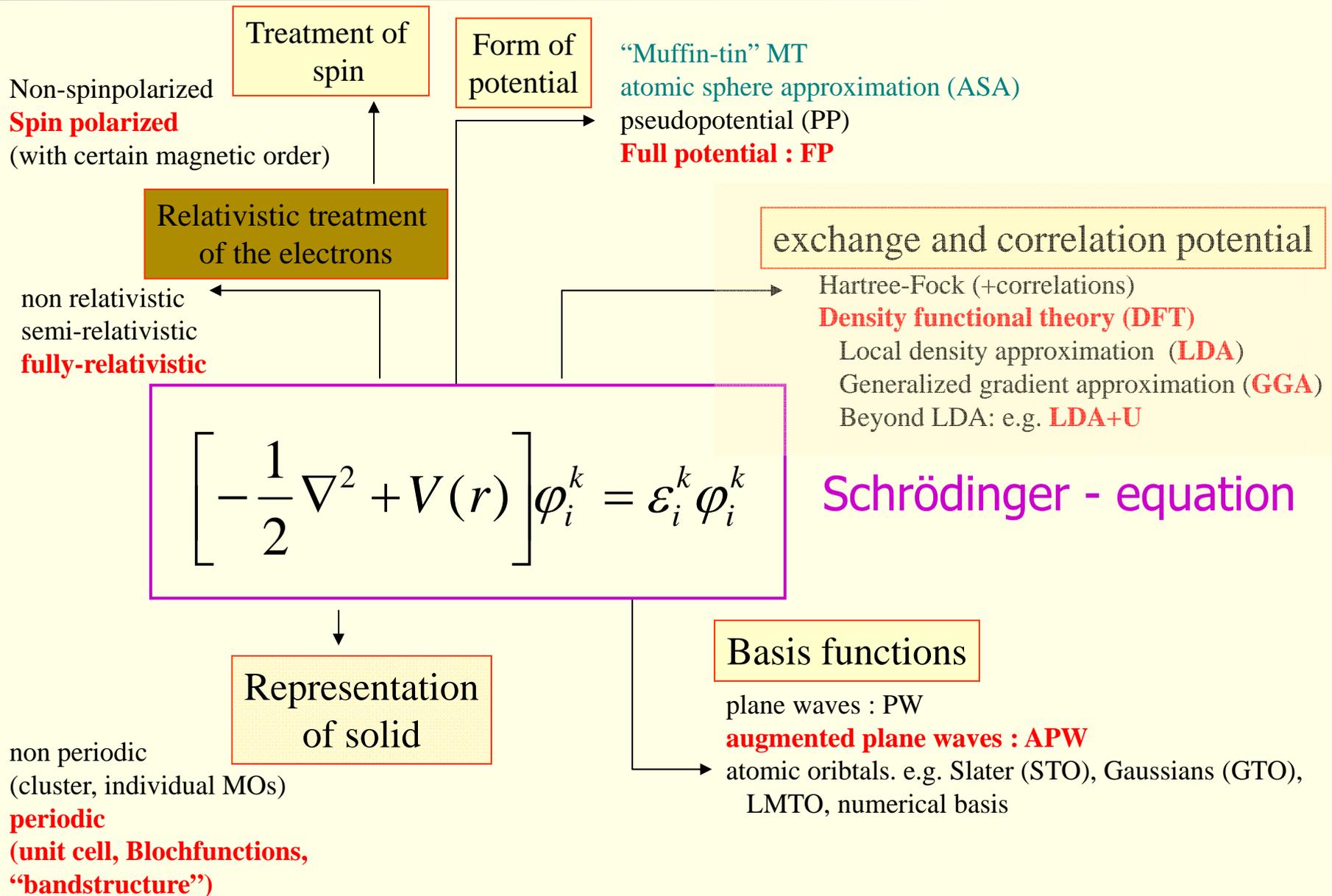


- **standard** hybrid-DFT underestimates gaps for insulators
- **optimal** α found by fit to exp. as function of $1/\epsilon_0$





Concepts when solving Schrödingers-equation





Dirac Hamiltonian: a brief description

Dirac relativistic Hamiltonian provides a quantum mechanical description of electrons, consistent with the theory of special relativity.

$$E^2 = p^2 c^2 + m^2 c^4$$

$$H_D \Psi = \mathcal{E} \Psi \quad \text{with} \quad H_D = c \vec{\alpha} \cdot \vec{p} + \beta m_e c^2 + V$$

Momentum operator (pointing to \vec{p})
Rest mass (pointing to $m_e c^2$)
Electrostatic potential (pointing to V)

$$\alpha_k = \begin{pmatrix} 0 & \sigma_k \\ \sigma_k & 0 \end{pmatrix} \quad \beta_k = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

(2x2) unit and zero matrices

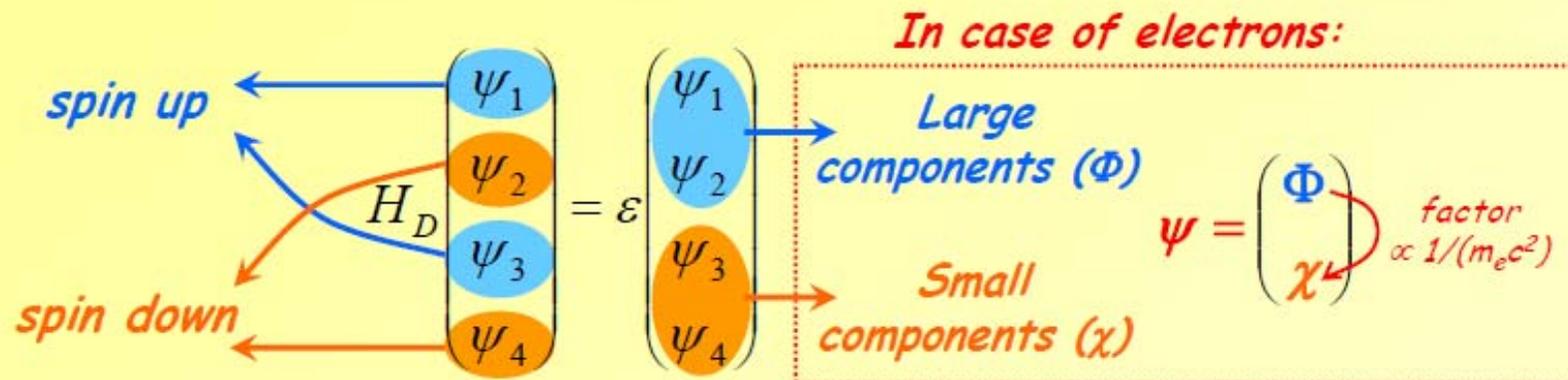
$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

(2x2) Pauli spin matrices



Dirac equation: H_D and Ψ are 4-dimensional

Ψ is a four-component single-particle wave function that describes spin-1/2 particles.



Φ and χ are time-independent two-component spinors describing the spatial and spin-1/2 degrees of freedom

➔ Leads to a set of coupled equations for Φ and χ :

$$c(\sigma \cdot \vec{p}) \chi = (\epsilon - V - m_e c^2) \phi$$

$$c(\sigma \cdot \vec{p}) \phi = (\epsilon - V + m_e c^2) \chi$$



Dirac equation in a spherical potential

→ For a spherical potential $V(r)$:

The resulting equations for the radial functions ($g_{n\kappa}$ and $f_{n\kappa}$) are simplified if we define:

$$\text{Energy: } \varepsilon' = \varepsilon - m_e c^2 \quad \text{Radially varying mass: } M_e(r) = m_e + \frac{\varepsilon' - V(r)}{2c^2}$$

Then the coupled equations can be written in the form of the radial eq.:

$$-\frac{\hbar^2}{2M_e} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dg_{n\kappa}}{dr} \right) + \left[V + \frac{\hbar^2}{2M_e} \frac{l(l+1)}{r^2} \right] g_{n\kappa} - \underbrace{\frac{\hbar^2}{4M_e^2 c^2} \frac{dV}{dr} \frac{dg_{n\kappa}}{dr}}_{\text{Darwin term}} - \underbrace{\frac{\hbar^2}{4M_e^2 c^2} \frac{dV}{dr} \frac{(1+\kappa)}{r} g_{n\kappa}}_{\text{Spin-orbit coupling}} = \varepsilon' g_{n\kappa}$$

and **Mass-velocity effect**

Darwin term

Spin-orbit coupling

$$\frac{df_{n\kappa}}{dr} = \frac{1}{\hbar c} (V - \varepsilon') g_{n\kappa} + \frac{(\kappa - 1)}{r} f_{n\kappa}$$

→ Due to **spin-orbit coupling**, Ψ is not an eigenfunction of spin (s) and angular orbital momentum (l).

Instead the good quantum numbers are j and κ

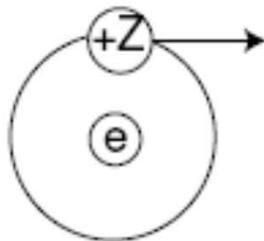
$$\begin{aligned} j &= l + s/2 \\ \kappa &= -s(j + 1/2) \\ s &= +1, -1 \end{aligned}$$

Note that: $\kappa(\kappa + 1) = l(l + 1)$



spin-orbit coupling

Classic view of SOC



electrons rest frame.

current from circling nucleus
gives rise to magnetic field

$$\mathbf{B} = \frac{1}{em_e c^2} \frac{1}{r} \frac{dV(r)}{dr} \mathbf{L}$$

Interaction energy between magnetic field and
spin moment of electron

$$\Delta E = \frac{gS\mu_B}{\hbar} \mathbf{B} \cdot \mathbf{S} = -\frac{1}{em_e^2 c^2} \frac{1}{r} \frac{dV(r)}{dr} \mathbf{L} \cdot \mathbf{S}$$

correct except for a factor of two

Due to SO spin s and orbital angular
momentum l are no longer good quantum
numbers.

Instead use total angular momentum

$$\vec{j} = \vec{l} + \vec{s}$$

| | l | $j=l+s/2$ | | $\kappa=-s(j+1/2)$ | | occupation | |
|---|-----|-----------|--------|--------------------|--------|------------|--------|
| | | $s=-1$ | $s=+1$ | $s=-1$ | $s=+1$ | $s=-1$ | $s=+1$ |
| s | 0 | | 1/2 | | -1 | | 2 |
| p | 1 | 1/2 | 3/2 | 1 | -2 | 2 | 4 |
| d | 2 | 3/2 | 5/2 | 2 | -3 | 4 | 6 |
| f | 3 | 5/2 | 7/2 | 3 | -4 | 6 | 8 |



Dirac equation in a spherical potential

→ Scalar relativistic approximation

Approximation that the spin-orbit term is small
 ⇒ neglect SOC in radial functions

No SOC ⇒ Approximate radial functions: $g_{nk} \rightarrow \tilde{g}_{nl}$ $f_{nk} \rightarrow \tilde{f}_{nl}$

$$-\frac{\hbar^2}{2M_e} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\tilde{g}_{nl}}{dr} \right) + \left[V + \frac{\hbar^2}{2M_e} \frac{l(l+1)}{r^2} \right] \tilde{g}_{nl} - \frac{\hbar^2}{4M_e^2 c^2} \frac{dV}{dr} \frac{d\tilde{g}_{nl}}{dr} = \varepsilon' \tilde{g}_{nl}$$

and $\tilde{f}_{nl} = \frac{\hbar}{2M_e c} \frac{d\tilde{g}_{nl}}{dr}$ with the normalization condition: $\int (\tilde{g}_{nl}^2 + \tilde{f}_{nl}^2) r^2 dr = 1$

→ The four-component wave function is now written as:

$$\tilde{\Psi} = \begin{pmatrix} \tilde{\Phi} \\ \tilde{\chi} \end{pmatrix} = \begin{pmatrix} \tilde{g}_{nl}(r) Y_{lm} \\ -i \tilde{f}_{nl}(r) Y_{lm} \end{pmatrix}$$

Inclusion of the spin-orbit coupling in "second variation" (on the large component only)

$$H\tilde{\Psi} = \varepsilon\tilde{\Psi} + H_{so}\tilde{\Psi}$$

$\tilde{\Phi}$ is a pure spin state

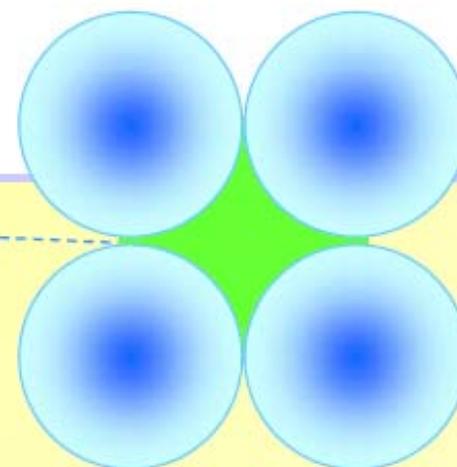
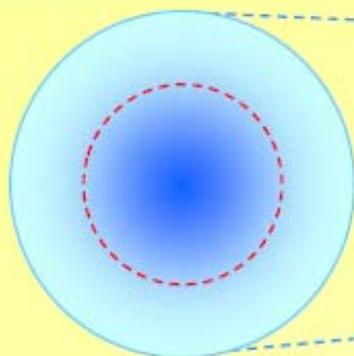
$\tilde{\chi}$ is a mixture of up and down spin states

with

$$H_{so} = \frac{\hbar^2}{4M_e^2 c^2} \frac{1}{r} \frac{dV}{dr} \begin{pmatrix} \vec{\sigma} & 0 \\ 0 & 0 \end{pmatrix}$$



Implementation in WIEN2k



Atomic sphere (RMT) Region

Core electrons

« Fully » relativistic

Spin-compensated Dirac equation

Valence electrons

Scalar relativistic (no SOC)

Possibility to add SOC (2nd variational)

Interstitial Region

Valence electrons

Not relativistic

SOC: Spin orbit coupling



Implementation in WIEN2k: valence electrons

→ *SOC is added in a second variation (lapwso):*

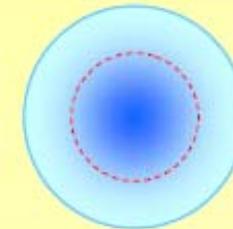
- First diagonalization (lapw1): $H_1 \Psi_1 = \varepsilon_1 \Psi_1$
- Second diagonalization (lapwso): $(H_1 + H_{SO}) \Psi = \varepsilon \Psi$

The second equation is expanded in the basis of first eigenvectors (Ψ_1)

$$\sum_i^N \left(\delta_{ij} \varepsilon_1^j + \langle \Psi_1^j | H_{SO} | \Psi_1^i \rangle \right) \langle \Psi_1^i | \Psi \rangle = \varepsilon \langle \Psi_1^j | \Psi \rangle$$

sum include both up/down spin states

→ *N is much smaller than the basis size in lapw1*



Atomic sphere (RMT) Region

Valence electrons

Scalar relativistic
(no SOC)

Possibility to add SOC
(2nd variational)

- ♦ SOC is active only inside atomic spheres, only spherical potential (V_{MT}) is taken into account, in the polarized case spin up and down parts are averaged.
- ♦ Eigenstates are not pure spin states, SOC mixes up and down spin states
- ♦ Off-diagonal term of the spin-density matrix is ignored. It means that in each SCF cycle the magnetization is projected on the chosen direction (from case.inso)

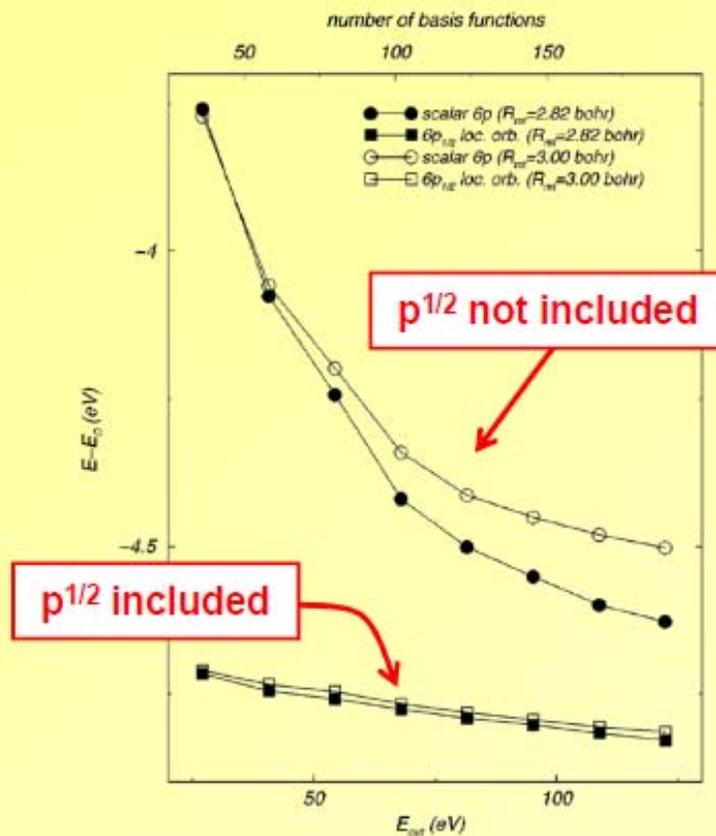
V_{MT} : Muffin-tin potential (spherically symmetric)



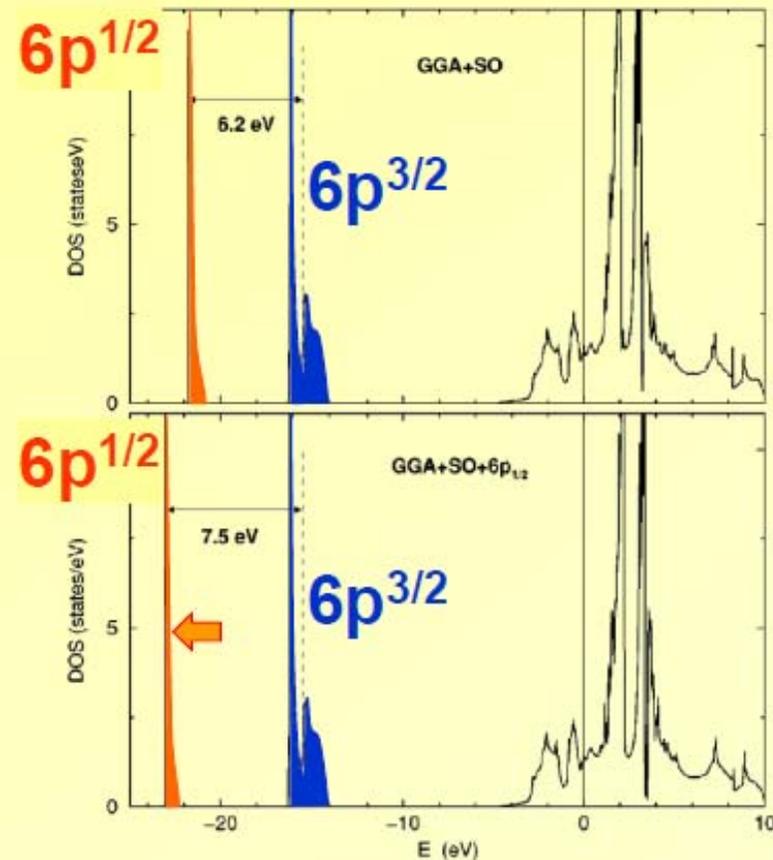
Relativistic semicore states: $p^{1/2}$ orbitals

Electronic structure of fcc Th, SOC with $6p^{1/2}$ local orbital

Energy vs. basis size



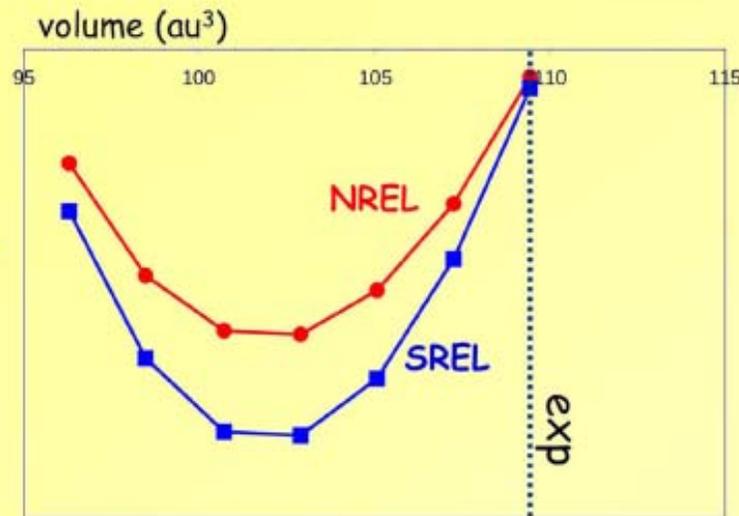
DOS with and without $p^{1/2}$





Relativistic effects in the solid: Illustration

hcp-Be
Z = 4



LDA overbinding (7%)

No difference NREL/SREL

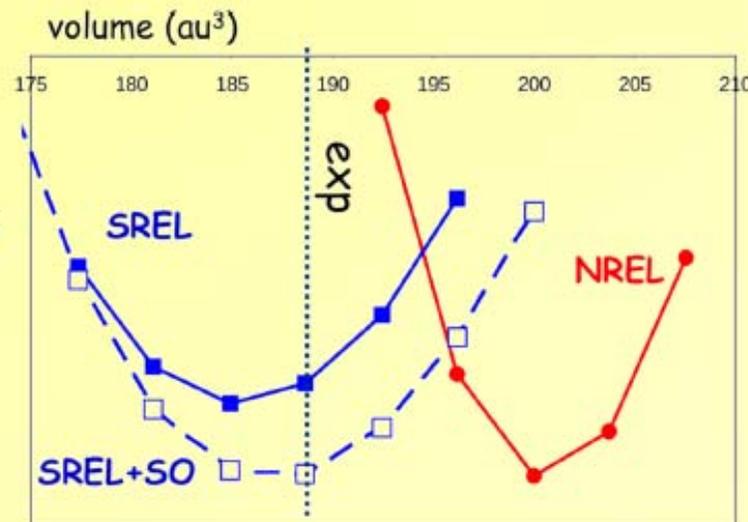
Bulk modulus:

- NREL: 131.4 GPa

- SREL: 131.5 GPa

- Exp.: 130 GPa

hcp-Os
Z = 76



♦ Scalar-relativistic (SREL):

- LDA overbinding (2%)

- Bulk modulus: 447 GPa

+ spin-orbit coupling (SREL+SO):

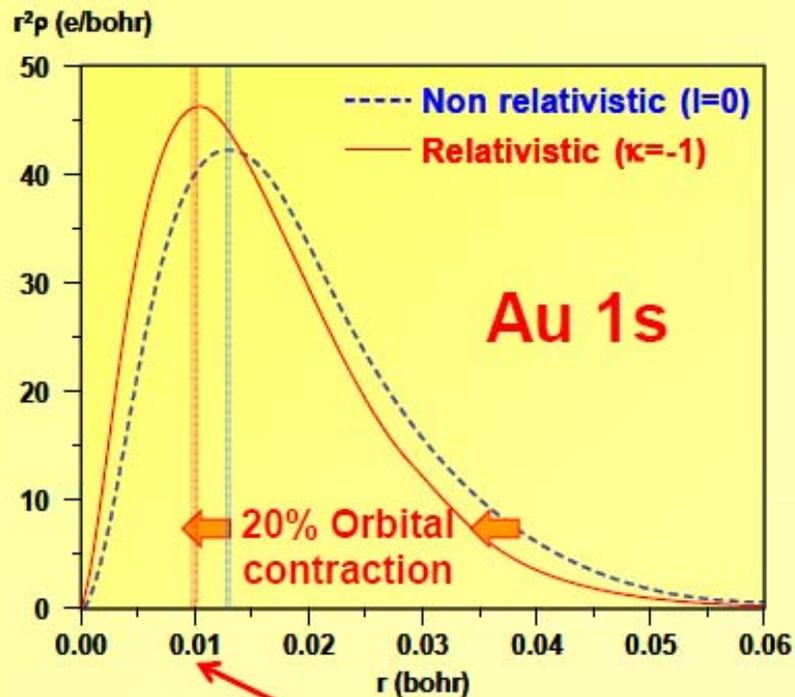
- LDA overbinding (1%)

- Bulk modulus: 436 GPa

⇒ Exp. Bulk modulus: 462 GPa



(1) Relativistic orbital contraction



Radius of the 1s orbit (Bohr model):



$$r(1s) = \frac{n^2 a_0}{Z} \quad \text{AND} \quad a_0 = \frac{\hbar}{m c \alpha} = 1 \text{ bohr}$$

$$r(1s) = \frac{1}{79} = 0.013 \text{ bohr}$$

In Au atom, the relativistic mass (M) of the 1s electron is 22% larger than the rest mass (m)

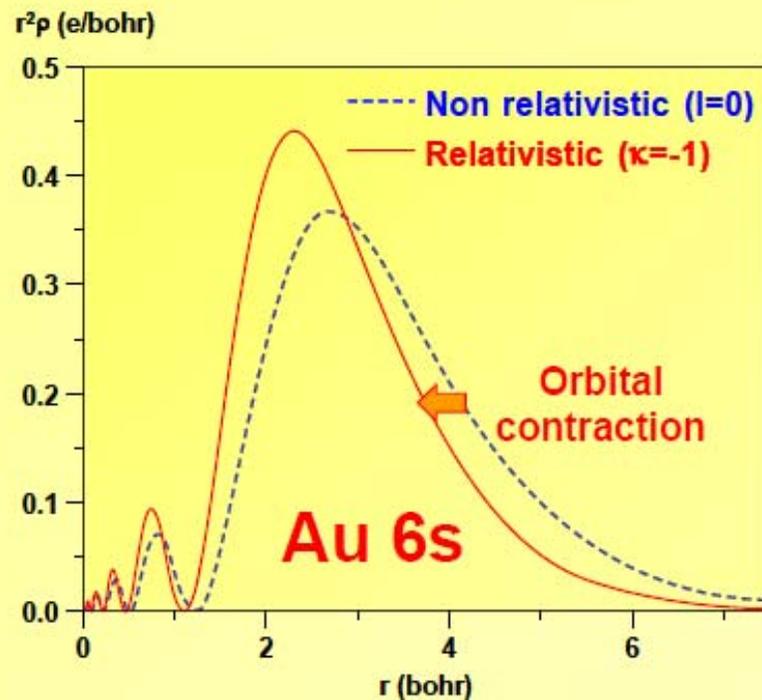
$$r(1s) = \frac{n^2 a_0}{Z \gamma} = \frac{1}{79} \frac{1}{1.22} = 0.010 \text{ bohr}$$

$$M = \gamma \cdot m_e = 1.22 m_e$$

$$a_0[RELA] = \frac{\hbar}{M_e c \alpha} = \frac{a_0}{\gamma}$$



(1) Relativistic orbital contraction



$$v_e(6s) = \frac{Z}{n} = \frac{79}{6} = 13.17 = 0.096c$$

$$\gamma = \frac{1}{\sqrt{1 - \left(\frac{v_e}{c}\right)^2}} = \frac{1}{\sqrt{1 - (0.096)^2}} = 1.0046$$

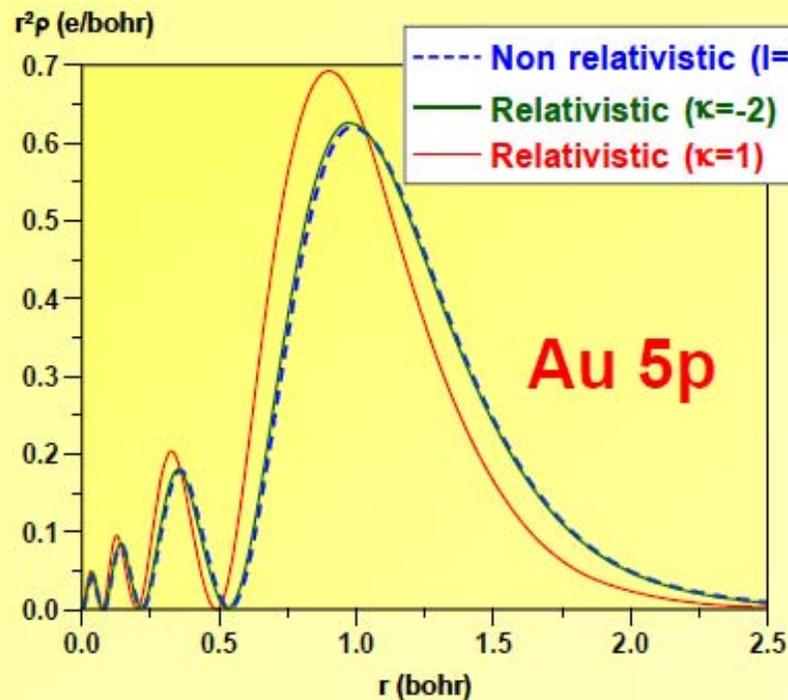
Direct relativistic effect (mass enhancement) → contraction of 0.46% only

However, the relativistic contraction of the 6s orbital is large (>20%)

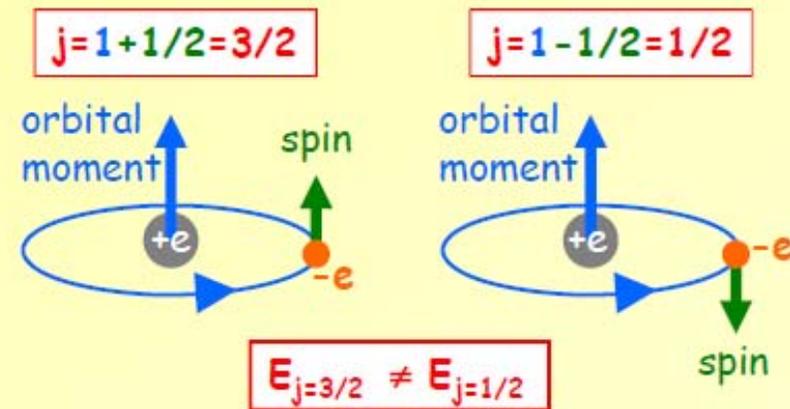
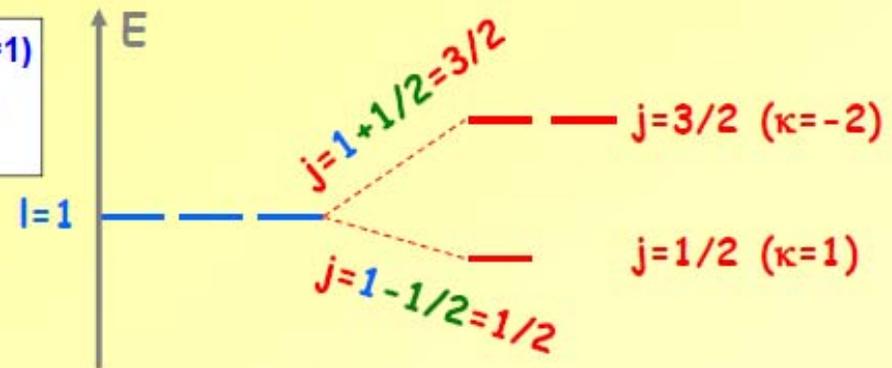
ns orbitals (with $n > 1$) contract due to orthogonality to 1s



(2) Spin-Orbit splitting of p states



♦ Spin-orbit splitting of l-quantum number



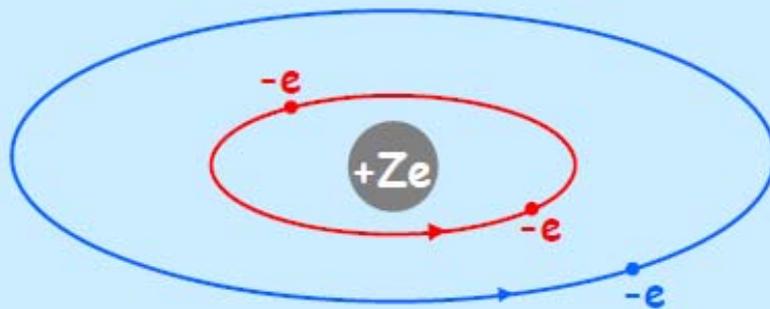
- ♦ $p_{1/2}$ ($\kappa=1$): markedly different behavior than non-relativistic p-state
 $g_{\kappa=1}$ is non-zero at nucleus



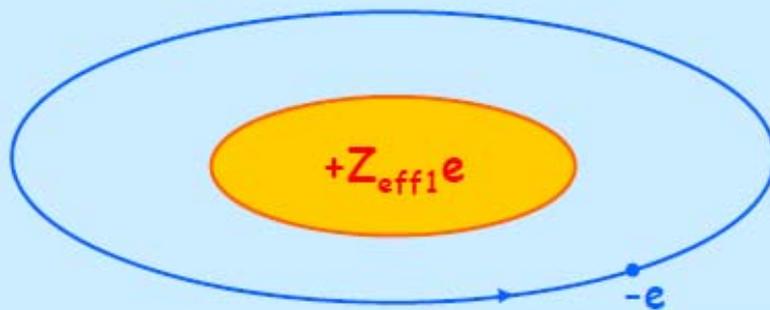
(3) Orbital expansion: Au(d) states

Higher l-quantum number states expand due to **better shielding** of nucleus charge from contracted s-states

Non-relativistic (NREL)

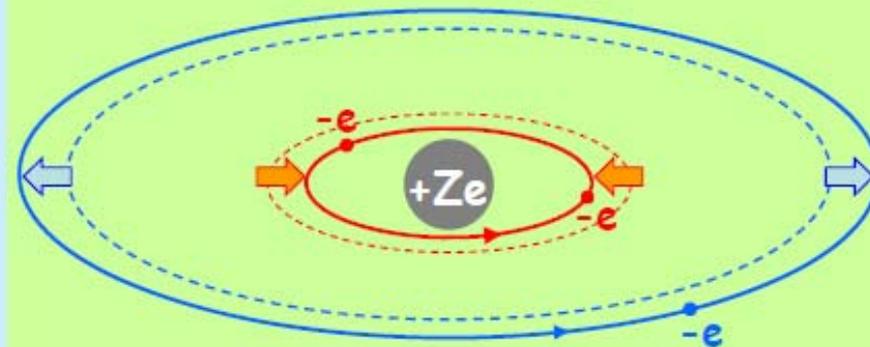


$$Z_{\text{eff1}} = Z - \sigma(\text{NREL})$$

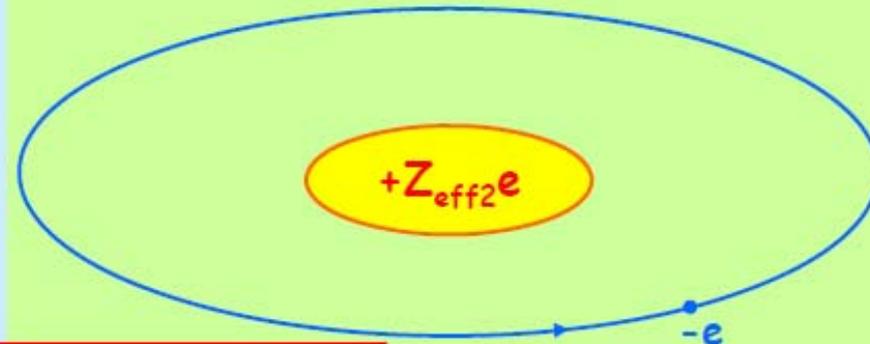


$$Z_{\text{eff1}} > Z_{\text{eff2}}$$

Relativistic (REL)



$$Z_{\text{eff2}} = Z - \sigma(\text{REL})$$



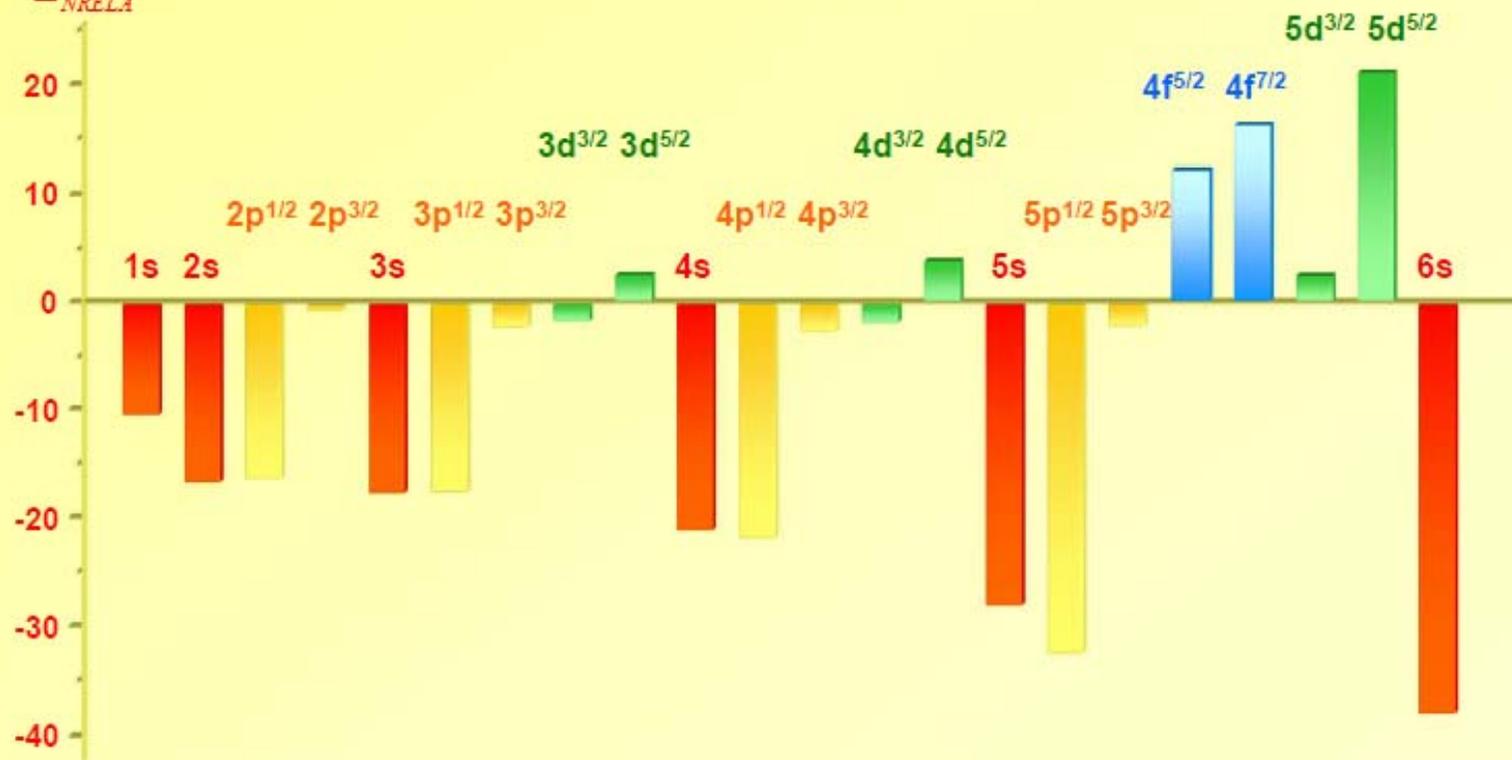
Indirect relativistic effect



Relativistic effects on the Au energy levels

Relativistic correction (%)

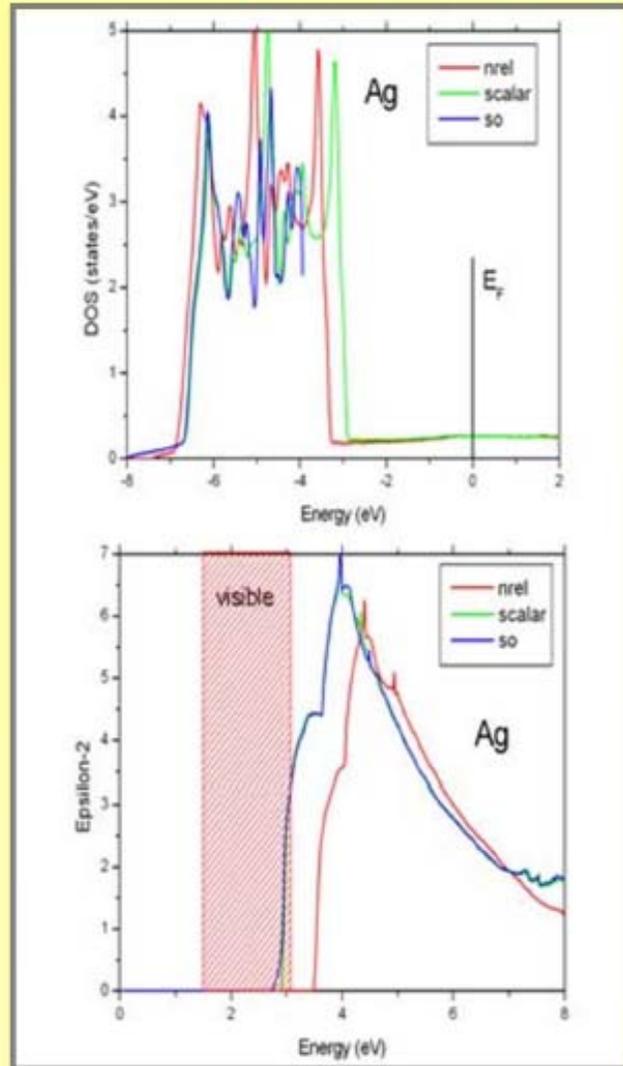
$$\frac{(E_{RELA} - E_{NRELA})}{E_{NRELA}}$$



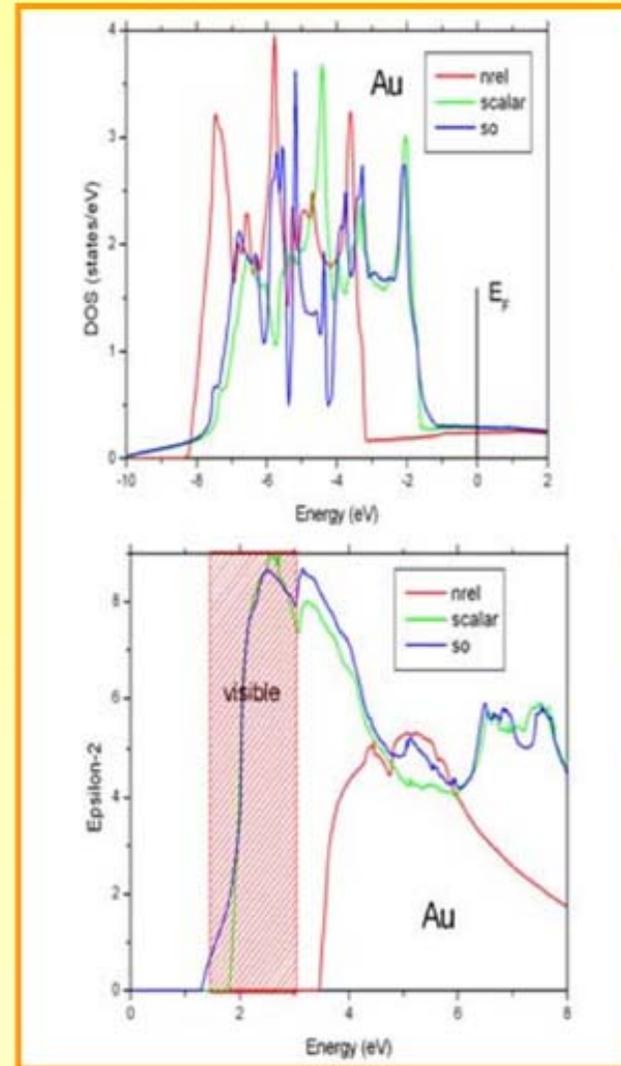


Ag - Au: the differences (DOS & optical prop.)

Ag



Au





Relativistic effects



1) The mass-velocity correction

Relativistic increase in the mass of an electron with its velocity (when $v_e \rightarrow c$)



Relativistic effects



1) *The mass-velocity correction*

Relativistic increase in the mass of an electron with its velocity (when $v_e \rightarrow c$)

2) *The Darwin term*

It has no classical relativistic analogue

Due to small and irregular motions of an electron about its mean position (*Zitterbewegung**)

**Analysis of Erwin Schrödinger of the wave packet solutions of the Dirac equation for relativistic electrons in free space: The interference between positive and negative energy states produces what appears to be a fluctuation (at the speed of light) of the position of an electron around the median.*



Relativistic effects



1) *The mass-velocity correction*

Relativistic increase in the mass of an electron with its velocity (when $v_e \rightarrow c$)

2) *The Darwin term*

It has no classical relativistic analogue
Due to small and irregular motions of an electron about its mean position (*Zitterbewegung*)

3) *The spin-orbit coupling*

It is the interaction of the spin magnetic moment (s) of an electron with the magnetic field induced by its own orbital motion (l)



Relativistic effects



1) *The mass-velocity correction*

Relativistic increase in the mass of an electron with its velocity (when $v_e \rightarrow c$)

2) *The Darwin term*

It has no classical relativistic analogue
Due to small and irregular motions of an electron about its mean position (*Zitterbewegung*)

3) *The spin-orbit coupling*

It is the interaction of the spin magnetic moment (s) of an electron with the magnetic field induced by its own orbital motion (l)

4) *Indirect relativistic effect*

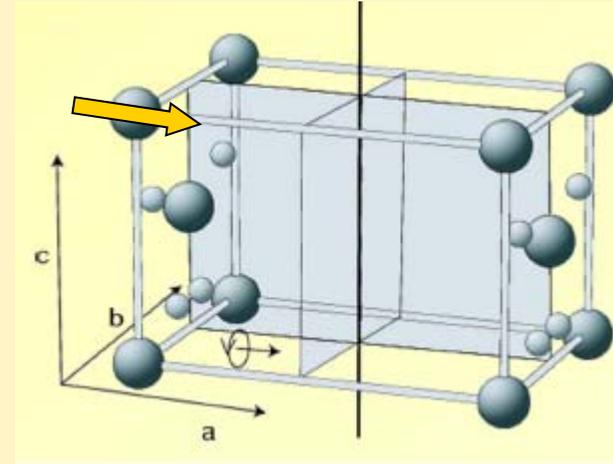
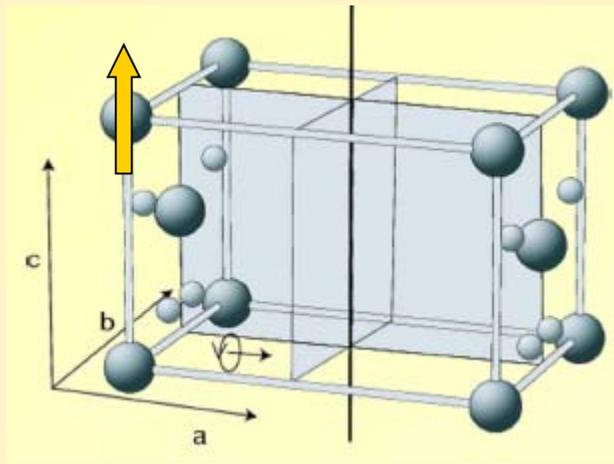
Orthogonality constrain of valence electrons; modified electrostatic potential acting on the valence e- because the core e- are contracted.



SOC in magnetic systems

→ *SOC couples magnetic moment to the lattice*

- *without spin-orbit there is only a spin-magnetic moment (if $n_{up} \neq n_{dn}$) and its direction is not coupled to the lattice (only α and β spin)*
- *with spin-orbit there could also be an orbital-magnetic moment and this “defines” a “direction” of the total magnetic moment with respect to the lattice*



- *the direction of the exchange field has to be given as input (case.inso)*
- *calculations of the total energy as function of this direction allows to calculate*
 - *easy and hard axis of magnetization*
 - *magnetocrystalline anisotropy*



SOC in magnetic systems

→ **SOC couples magnetic moment to the lattice**

◆ direction of the exchange field matters (input in case.inso)

- easy - hard axis
- magneto crystalline anisotropy

→ **Symmetry operations acts in real and spin space**

(pseudovector)

◆ number of symmetry operations may be reduced (reflections act differently on spins than on positions) **(atoms may become inequivalent)**

◆ time inversion is not symmetry operation (do not add an inversion for klist) $\epsilon_k \neq \epsilon_{-k}$

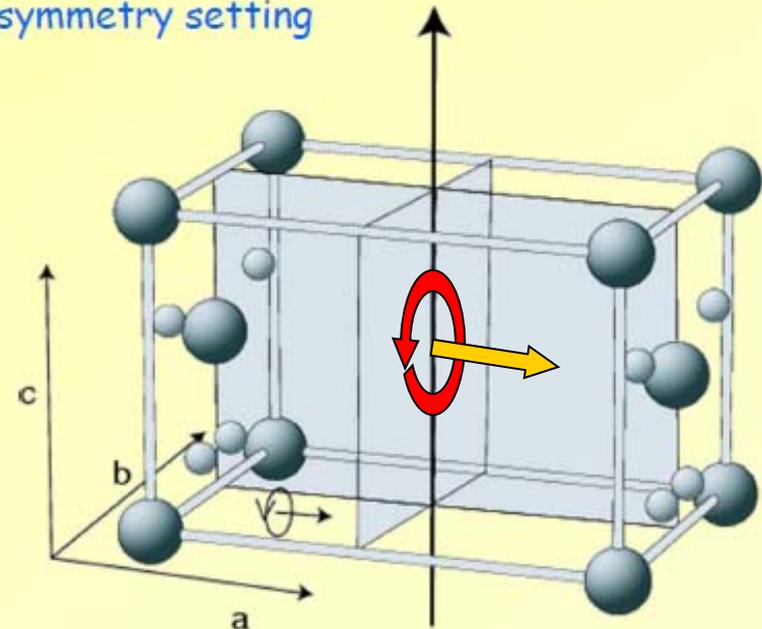
◆ initso_lapw (must be executed) detects new symmetry setting

| | Direction of magnetization | | | |
|-------|----------------------------|-------|-------|-------|
| | [100] | [010] | [001] | [110] |
| 1 | A | A | A | A |
| m_x | A | B | B | - |
| m_y | B | A | B | - |
| 2_z | B | B | A | B |

A (preserves real space AND direction of spin)

B (preserves real space, inverts magnetic moment).

Together with time-inversion this is still a valid symmetry operation





Pauli Hamiltonian for magnetic systems

⇒ 2x2 matrix in spin space, due to Pauli spin operators

$$H_P = -\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{eff}} + \mu_B \vec{\sigma} \cdot \vec{B}_{\text{eff}} + \zeta (\vec{\sigma} \cdot \vec{l}) + \dots$$

Effective electrostatic potential

$$V_{\text{eff}} = V_{\text{ext}} + V_H + V_{xc}$$

Exchange-correlation potential

Effective magnetic field

$$B_{\text{eff}} = B_{\text{ext}} + B_{xc}$$

Exchange-correlation field

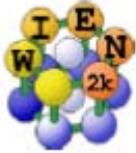
Spin-orbit coupling

$$\zeta = \frac{\hbar^2}{2M_e^2 c^2} \frac{1}{r} \frac{dV}{dr}$$

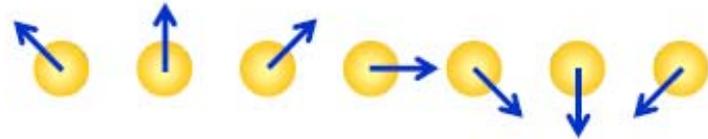
Many-body effects which are defined within DFT LDA or GGA

$$\vec{B}_{xc} = \rho \frac{\partial \varepsilon_{xc}^{\text{hom}}(\rho, \vec{m})}{\partial \vec{m}} \hat{m}$$

B_{xc} is parallel to the magnetization density vector (\hat{m})



Non-collinear magnetism



⇒ Direction of magnetization vary in space, thus spin-orbit term is present

$$H_P = -\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{eff}} + \mu_B \vec{\sigma} \cdot \vec{B}_{\text{eff}} + \zeta (\vec{\sigma} \cdot \vec{l}) + \dots$$

$$\left(\begin{array}{cc} -\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{eff}} + \mu_B B_z + \dots & \mu_B (B_x - iB_y) \\ \mu_B (B_x + iB_y) & -\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{eff}} - \mu_B B_z + \dots \end{array} \right) \psi = \varepsilon \psi$$

$$\psi = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} \Rightarrow \psi_1 \text{ and } \psi_2 \text{ are non-zero}$$

- ◆ Solutions are non-pure spinors
- ◆ Non-collinear magnetic moments



Collinear magnetism



⇒ Magnetization in z-direction / spin-orbit is not present

$$H_P = -\frac{\hbar^2}{2m_e} \nabla^2 + V_{eff} + \mu_B \vec{\sigma} \cdot \vec{B}_{eff} + \zeta (\vec{\sigma} \cdot \vec{l}) + \dots$$

$$\begin{pmatrix} -\frac{\hbar^2}{2m_e} \nabla^2 + V_{eff} + \mu_B B_z + \dots & 0 \\ 0 & -\frac{\hbar^2}{2m_e} \nabla^2 + V_{eff} - \mu_B B_z + \dots \end{pmatrix} \psi = \varepsilon \psi$$

$$\psi_{\uparrow} = \begin{pmatrix} \psi_1 \\ 0 \end{pmatrix} \quad \psi_{\downarrow} = \begin{pmatrix} 0 \\ \psi_2 \end{pmatrix}$$

$$\varepsilon_{\uparrow} \neq \varepsilon_{\downarrow}$$

- ◆ Solutions are pure spinors
- ◆ Collinear magnetic moments
- ◆ Non-degenerate energies



Non-magnetic calculation

⇒ No magnetization present, $B_x = B_y = B_z = 0$ and no spin-orbit coupling

$$H_P = -\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{eff}} + \mu_B \cancel{\vec{\sigma}} \cdot \cancel{\vec{B}_{\text{eff}}} + \zeta \cancel{(\vec{\sigma} \cdot \vec{l})} + \dots$$

$$\begin{pmatrix} -\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{eff}} & 0 \\ 0 & -\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{eff}} \end{pmatrix} \psi = \varepsilon \psi$$

$$\psi_{\uparrow} = \begin{pmatrix} \psi \\ 0 \end{pmatrix} \quad \psi_{\downarrow} = \begin{pmatrix} 0 \\ \psi \end{pmatrix}$$

$$\varepsilon_{\uparrow} = \varepsilon_{\downarrow}$$

- ◆ Solutions are pure spinors
- ◆ Degenerate spin solutions



Magnetism and WIEN2k

⇒ *Spin-polarized calculations*

- ◆ `runsp_lapw` script (unconstrained magnetic calc.)
- ◆ `runfsm_lapw -m` value (constrained moment calc.)
- ◆ `runafm_lapw` (constrained anti-ferromagnetic calculation)

- ◆ **spin-orbit coupling** can be included in second variational step
- ◆ **never mix polarized and non-polarized calculations in one case directory !!!**



Non-collinear magnetism



⇒ *In case of non-collinear spin arrangements WIENncm (WIEN2k clone) has to be used:*

- ◆ SOC in first variational step, LDA+U
- ◆ Spin spirals



WFFIL

4 1 0

-10.0000 1.50000

0. 0. 1.

1

2 -0.97 0.005

0 0 0 0 0

lmax,ipr,kpot

emin,emax (output energy window)

direction of magnetization (lattice vectors)

number of atoms for which **RLO** is added

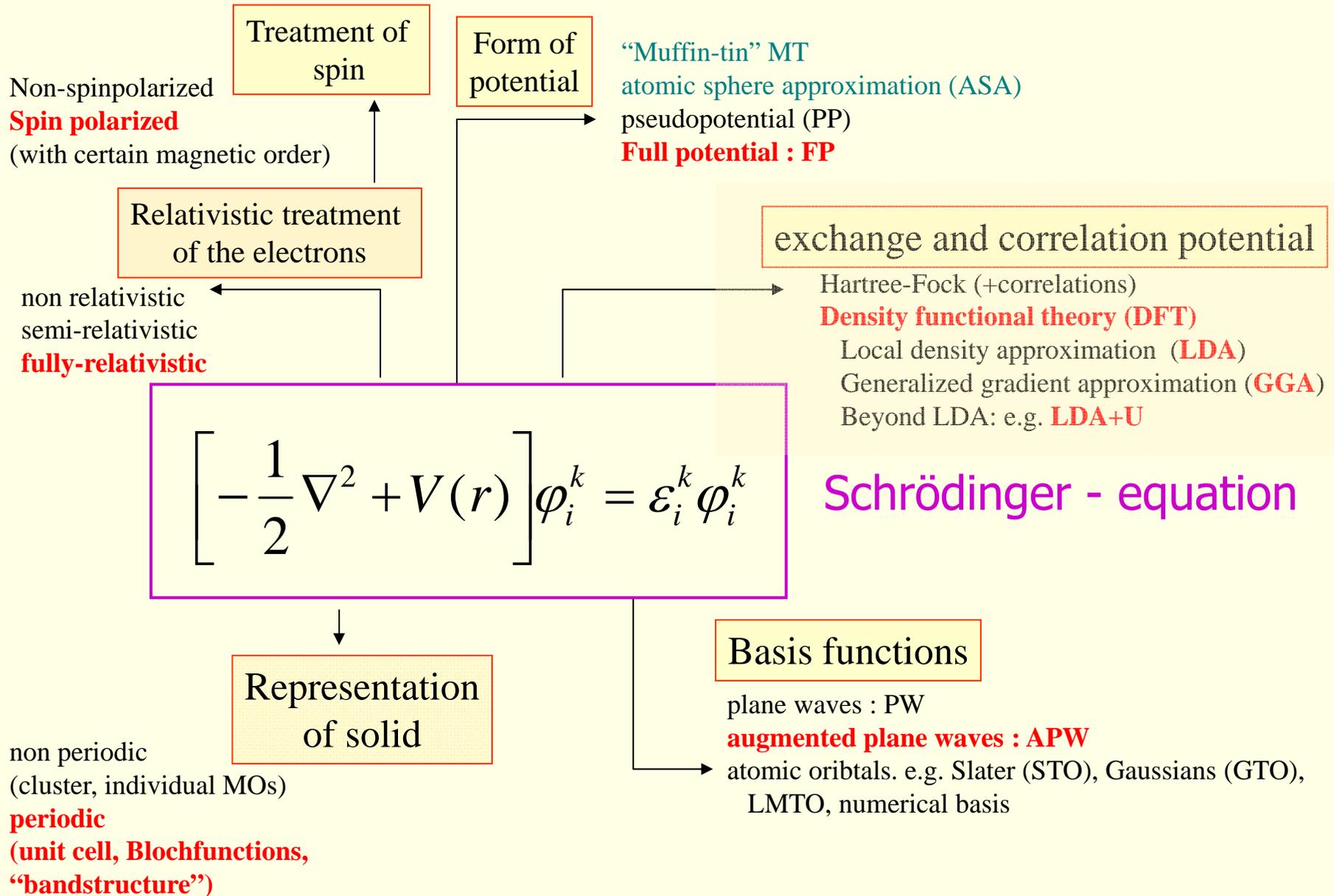
atom number,e-lo,de (case.in1), repeat NX times

number of atoms for which SO is **switched off**; atoms

- RLOs important for semicore p-states ($p_{1/2}$ - $p_{3/2}$ splitting)
- forces are not implemented together with SO
- switching off SO for "light" elements allows to optimize their positions even when SO is included for a heavy element (eg. in Sr_2IrO_4)



Concepts when solving Schrödingers-equation





Solving Schrödinger's equation:

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



- Ψ cannot be found analytically
- complete "numerical" solution is possible but inefficient

■ Ansatz:

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

$$\Psi_k = \sum_{K_n} c_{k_n} \Phi_{k_n}$$

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

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

$$H C = E S C$$

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



(L)APW+lo Method:

- dual basisset:

$$\phi_{\mathbf{k},\mathbf{G}}^{\text{LAPW}}(\mathbf{r}) = \begin{cases} \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}}, & \mathbf{r} \in I, \\ \sum_{lm} [A_{lm}^{\alpha,\mathbf{k}+\mathbf{G}} u_l^\alpha(r, E_l) + B_{lm}^{\alpha,\mathbf{k}+\mathbf{G}} \dot{u}_l^\alpha(r, E_l)] Y_{lm}(\hat{r}), & \mathbf{r} \in S_\alpha, \end{cases}$$

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

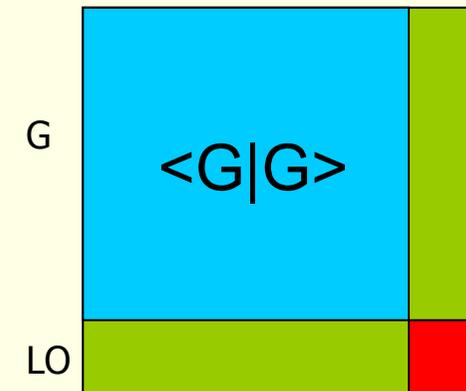
- Total wavefunction as linear combination of basis functions

- $n \dots 50-100$ APW/atom

$$\Psi_k = \sum_{G_n} c_{G_n} \Phi_{G_n}$$

- Variational method → General eigenvalue problem: **$HC=ESC$**

- setup of H and S (Hamilton- und overlap matrix)
 - diagonalisation
 - → eigenvalues E_k^n , eigenvectors c_k^n (n: band index)



- Variational calculation for many k -points,

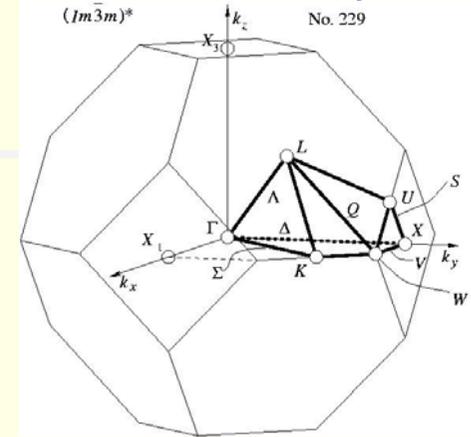
- BZ-integration → new electron density

- → new potential → SCF cycle



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

unit cell atomic positions



Structure optimization

iteration i

DFT Kohn-Sham

S
C
F

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

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

no

yes

E^{tot} , force

Minimize E, force $\rightarrow 0$

properties

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

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

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

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

Generalized eigenvalue problem

$HC = ESC$

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



Total energy and Atomic forces



Total Energy:

- *Electrostatic energy*
- *Kinetic energy*
- *XC-energy*

$$U[\rho] = \frac{1}{2} \int d^3\vec{r} \rho(\vec{r}) V_{es}(\vec{r}) + \frac{1}{2} \sum_{\alpha} Z_{\alpha} V_{es}^{\alpha}(\vec{r})$$

$$T[\rho] = \sum_i n_i \varepsilon_i - \int d^3\vec{r} \rho(\vec{r}) V_{eff}(\vec{r})$$

$$E_{xc}[\rho] = \int d^3\vec{r} \rho(\vec{r}) \varepsilon_{xc}(\vec{r})$$

Force on atom α :

$$\vec{F}^{\alpha} = \frac{-dE_{tot}}{d\vec{R}_{\alpha}} = F_{HF}^{\alpha} + F_{core}^{\alpha} + F_{val}^{\alpha}$$

- *Hellmann-Feynman-force*
- *Pulay corrections*

- *Core*
- *Valence*

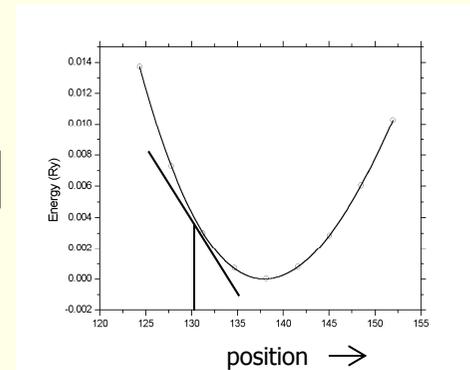
$$F_{HF}^{\alpha} = Z_{\alpha} \sum_{m=-1}^1 \lim_{r_{\alpha} \rightarrow 0} \frac{V_{1m}^{es}(r_{\alpha})}{r_{\alpha}} \nabla_{\alpha} [r_{\alpha} Y_{1m}(\hat{r})]$$

$$F_{core}^{\alpha} = - \int \rho_{core}(r) \nabla_{\alpha} V_{eff}(r) d\vec{r}$$

- *expensive, contains a summation of matrix elements over all occupied states*

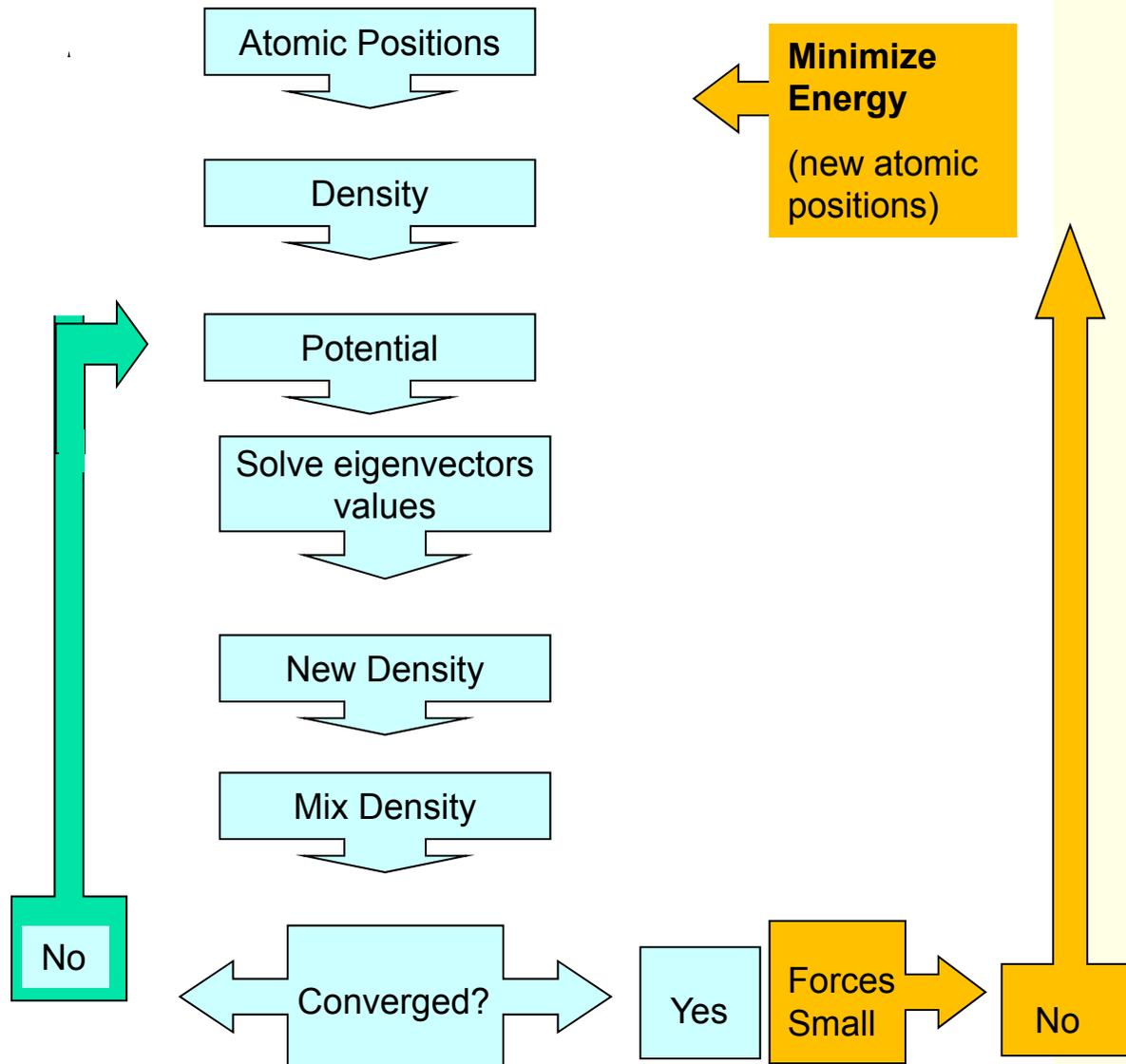
$$F_{val}^{\alpha} = \int_{\alpha} V_{eff}(r) \nabla_{\alpha} \rho_{val}(r) d\vec{r} + \sum_{k,i} n_i \sum_{K,K'} c_i^*(K') c_i(K) \times$$

$$\left[(K^2 - \varepsilon_i) \oint \phi_{K'}^*(r) \phi_K(r) dS_{\alpha} - i(K - K') \langle \phi_{K'} | H - \varepsilon_i | \phi_K \rangle_{\alpha} \right]$$





Structure optimization (atomic positions)



Traditional way:

- Inner loop: obtain fixed-point for given atom positions
- Outer loop: optimize atomic positions

New approach:

- optimize positions and density simultaneously using approximate forces

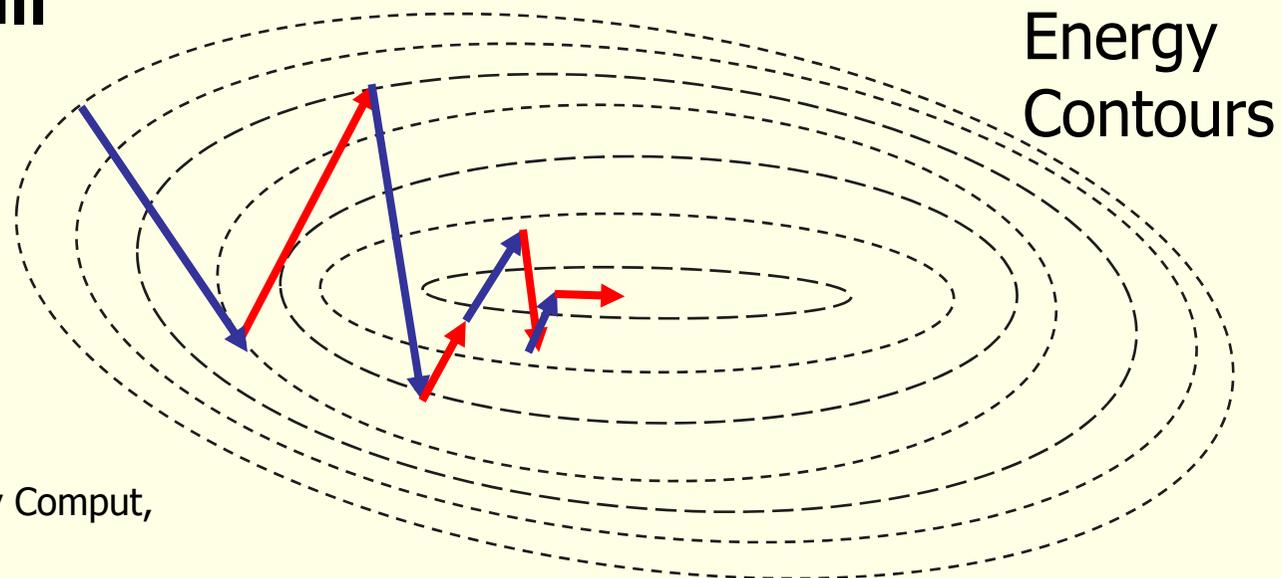


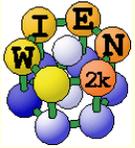
Current algorithms



- Calculate SCF mapping, time T_0
- Broyden expansion for fixed-point problem, self-consistent density, N_{SCF} iterations
- BFGS is most common for optimizing the atomic positions (Energy), N_{BFGS}
- Time scales as $N_{\text{SCF}} * N_{\text{BFGS}} * T_0$

each step is a **full**
scf calculation
producing
accurate forces



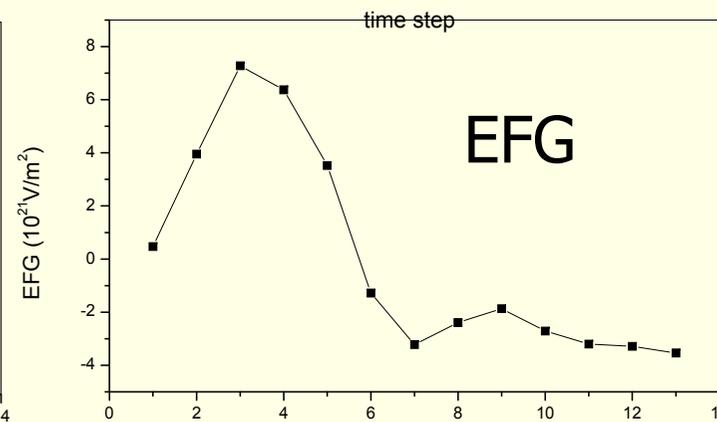
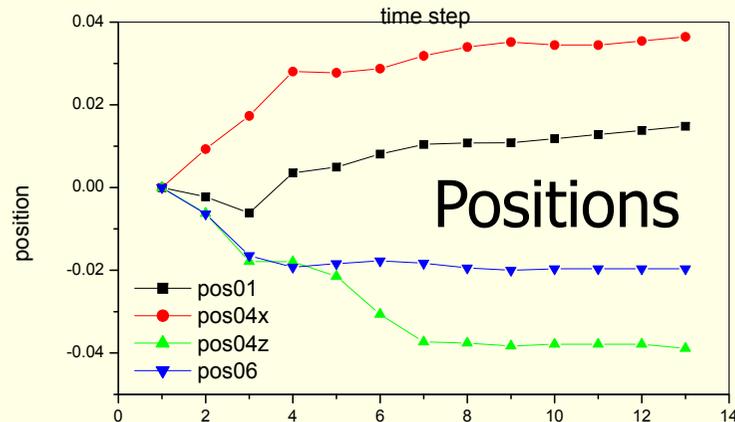
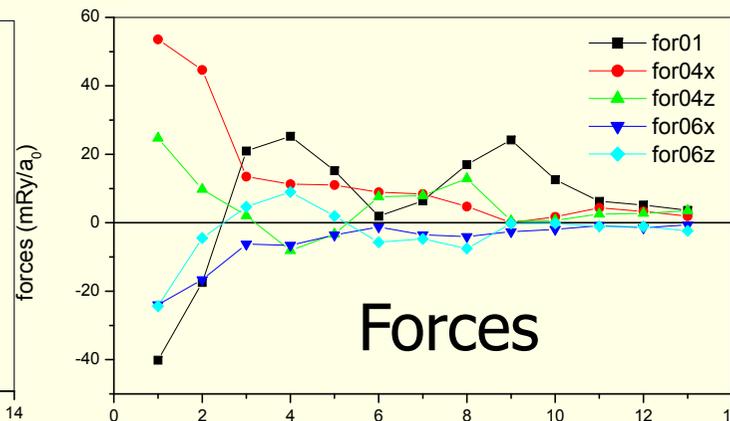
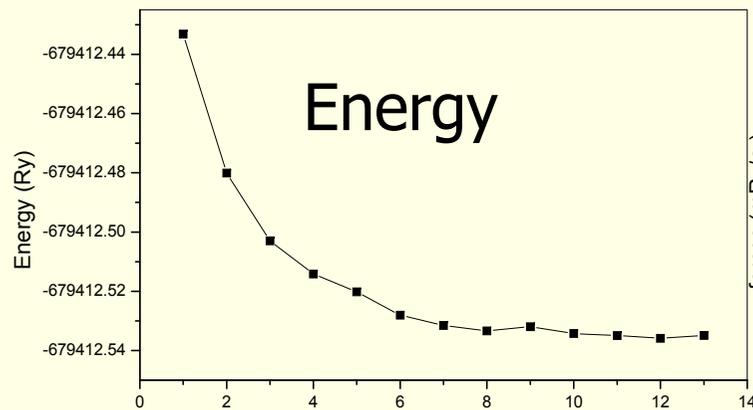
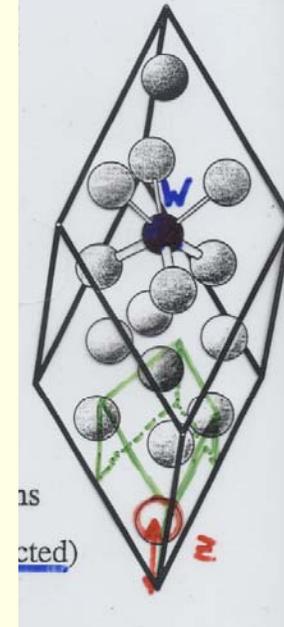


- quite efficient Broyden scheme (PORT)

exp.EFG ($Q=-.46b$)

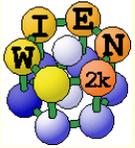
$4.6 \cdot 10^{21} \text{V/m}^2$ (NQR, $^{209}\text{Bi}(9/2)$)

W impurity in Bi (2x2x2 cell: Bi_{15}W)





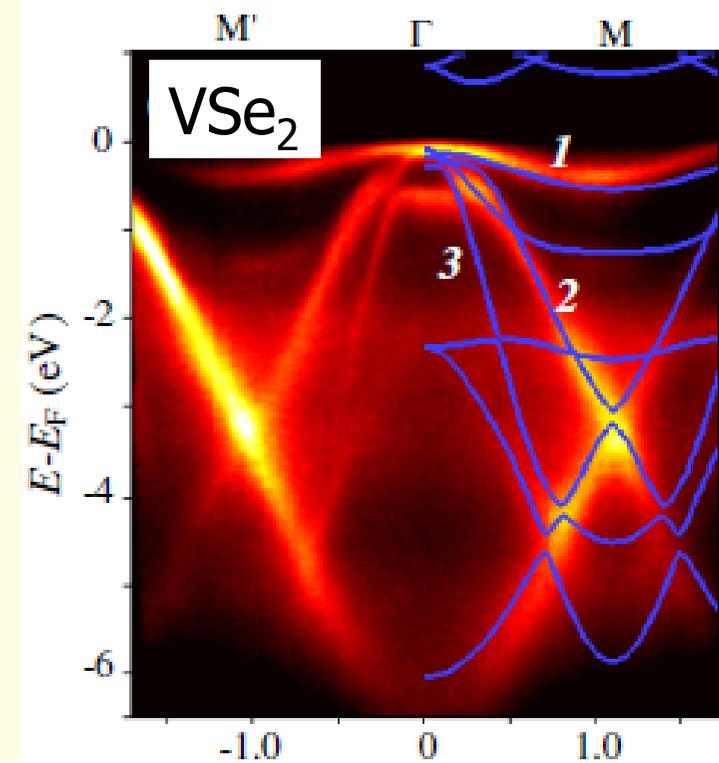
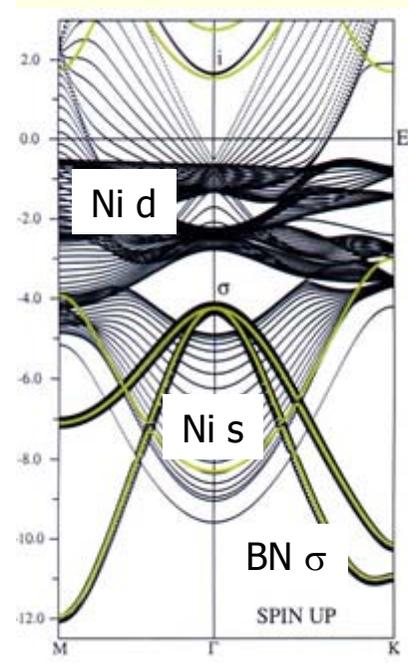
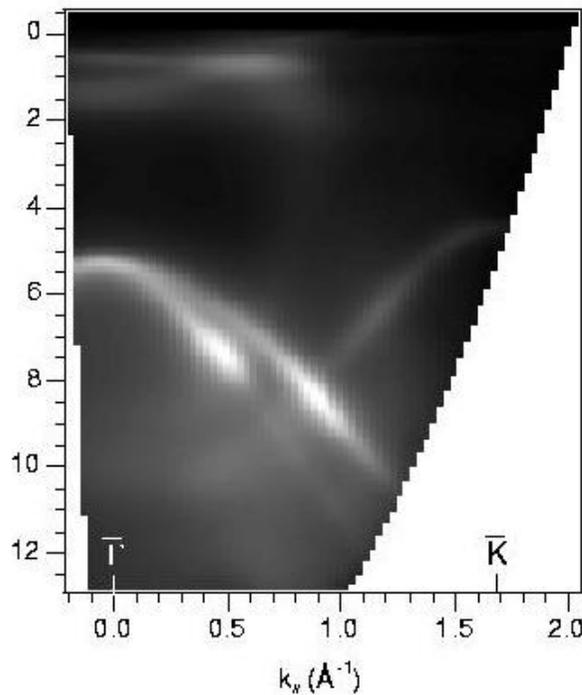
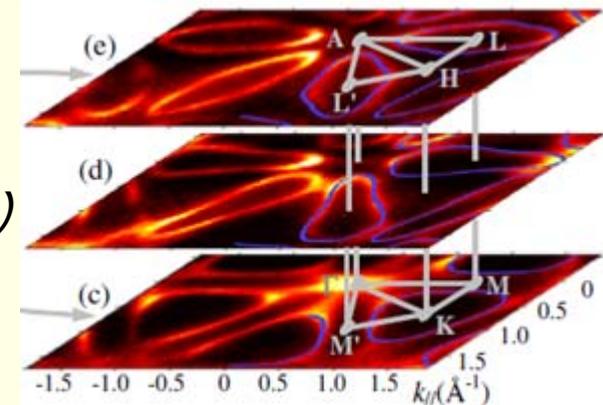
properties with WIEN2k



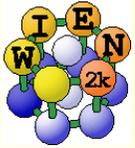
Properties with WIEN2k - I



- Energy bands
 - classification of irreducible representations
 - 'character-plot' (emphasize certain band-character)
 - Density of states
 - including partial DOS with l and m -character
 - Fermi surfaces
- h-BN/Ni(111): σ and π bands



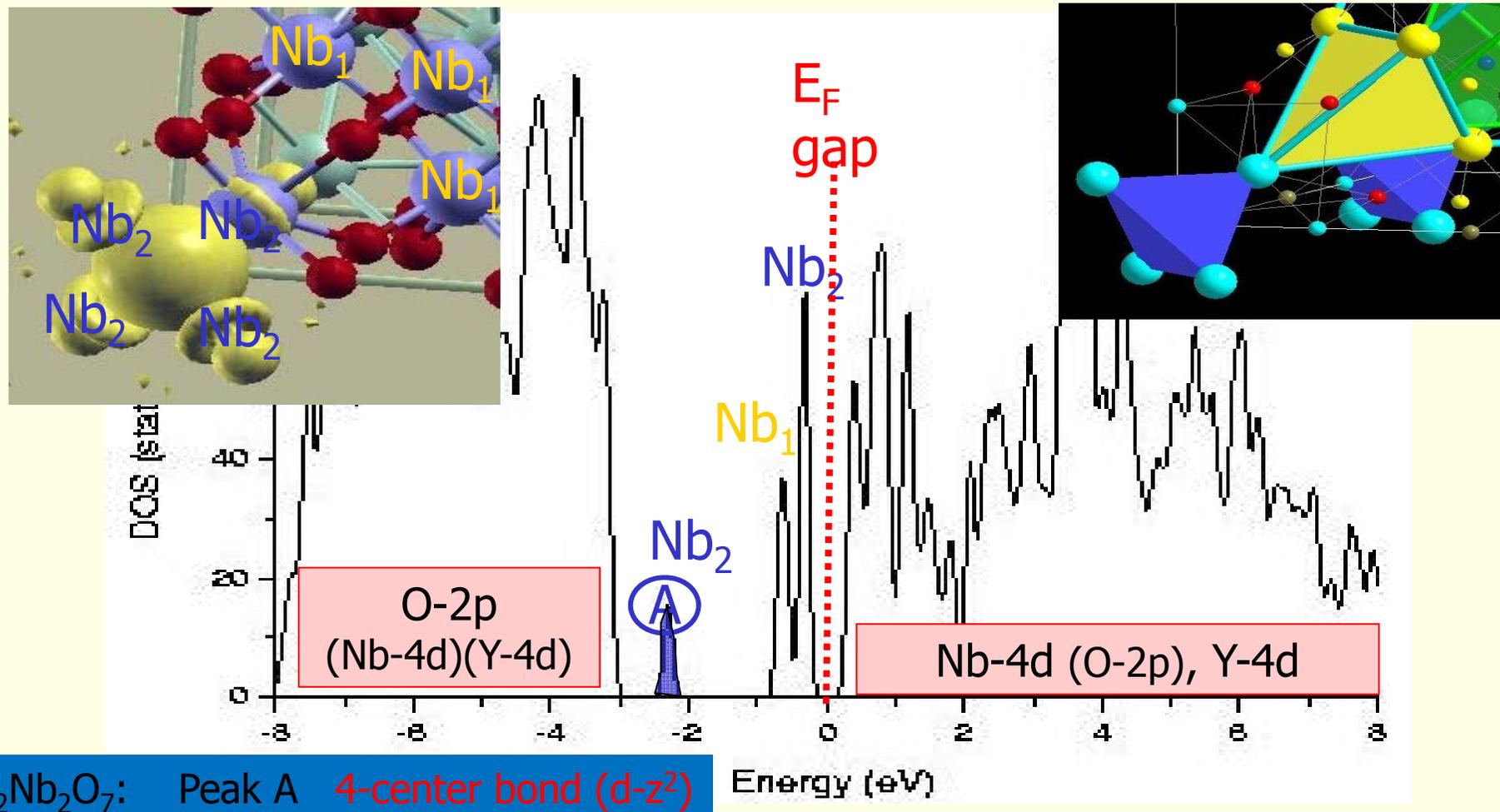
V.Strocov et al., PRL 109 (2012), 086401



Properties with WIEN2k - II



- Electron density, potential, X-ray structure factors, spin + orbital moments
 - total-, valence-, difference-, spin-densities, ρ of selected states
 - Bader's atom-in-molecule analysis, BCP, atomic basins and charges ($\nabla\rho\cdot\vec{n} = 0$)





Properties with WIEN2k - II



- **Hyperfine parameters** (NMR, Mössbauer, PAC)
 - **hyperfine fields** (contact + dipolar + orbital contribution)
 - **Mössbauer Isomer shifts**
 - **NMR chemical shifts**
 - **Electric field gradients**

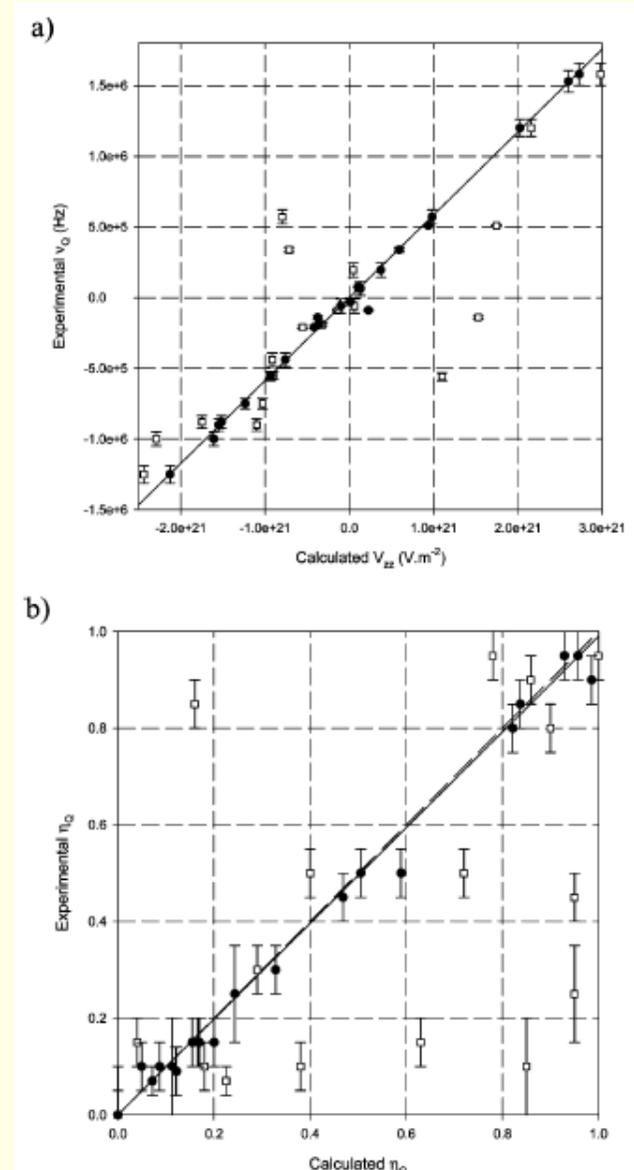
$$V_{zz} = \int \frac{\rho(r)Y_{20}}{r^3} dr$$

$$\nu_Q = \frac{3eQV_{zz}}{2I(2I - 1)h}$$

$$\eta_Q = \frac{V_{yy} - V_{xx}}{V_{zz}}$$

- Al-EFG of 16 different Al-fluorides
- **before** (open symbols)
- **after** (filled symbols) **structural optimization**

M.Body et al., *J.Phys.Chem. A* 2007, 111, 11873



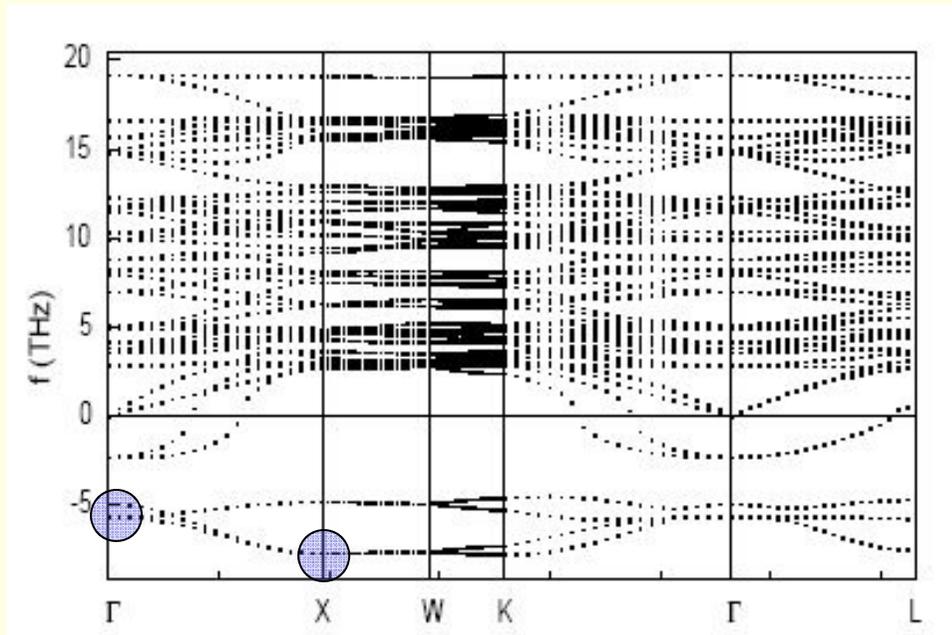
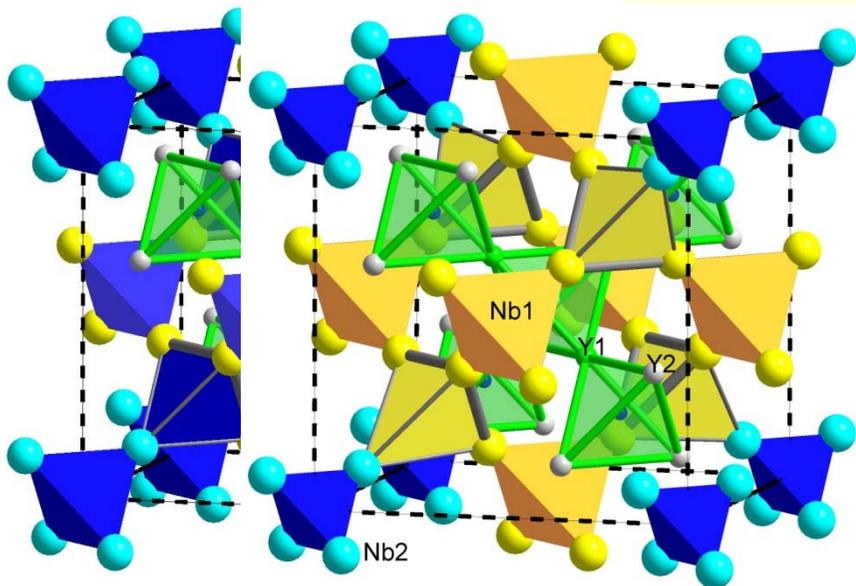


Properties with WIEN2k - III



- **Total energy, forces and structural optimization**
 - *optimization of internal coordinates, (damped MD, BROYDEN)*
 - *cell parameter only via E_{tot} (no stress tensor)*
 - *Phonons via a direct method (based on forces from supercells)*
 - interface to PHONON (K.Parlinski) – bands, DOS, thermodynamics, neutrons

Pyrochlore structure of $Y_2Nb_2O_7$: **metallic** instead of an **insulator**
strong **phonon instabilities** → phase transition → **insulator**



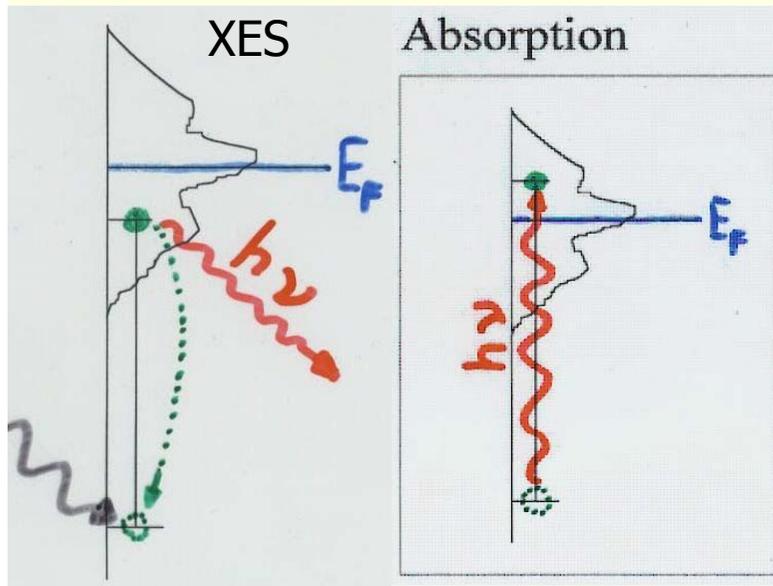


Properties with WIEN2k - IV



■ Spectroscopy

- **XPS core levelshifts** (with half-core holes, Slater's transition state)
- **X-ray emission, absorption, electron-energy-loss**
 - (core - valence/conduction-band transitions with matrix elements and angular dep.)
 - EELS including possible non-dipol transistions (momentum transfer)
- **optical properties (UV-VIS): dielectric function in IPA, JDOS including momentum matrix elements and Kramers-Kronig**
- **BSE for excitonic effects (both, for UV-VIS AND XAS)**

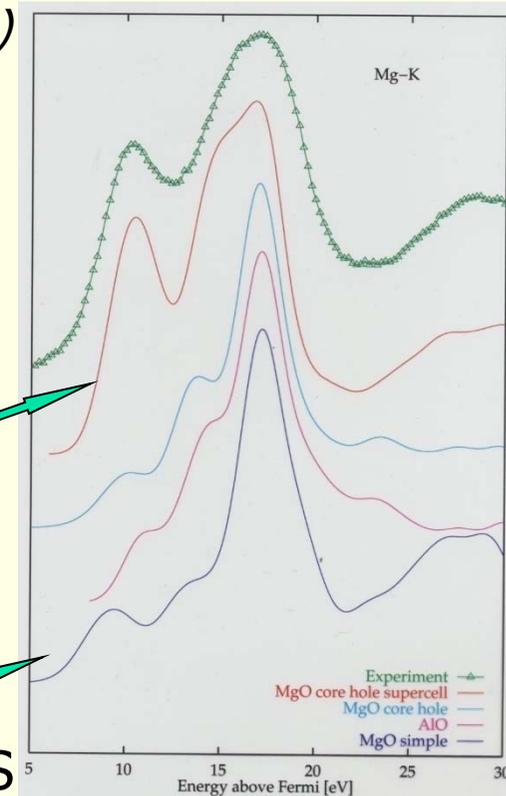


Mg-K XAS

probes empty Mg-p

including a core-hole
in supercell
(Final state rule)

from ground-state DOS





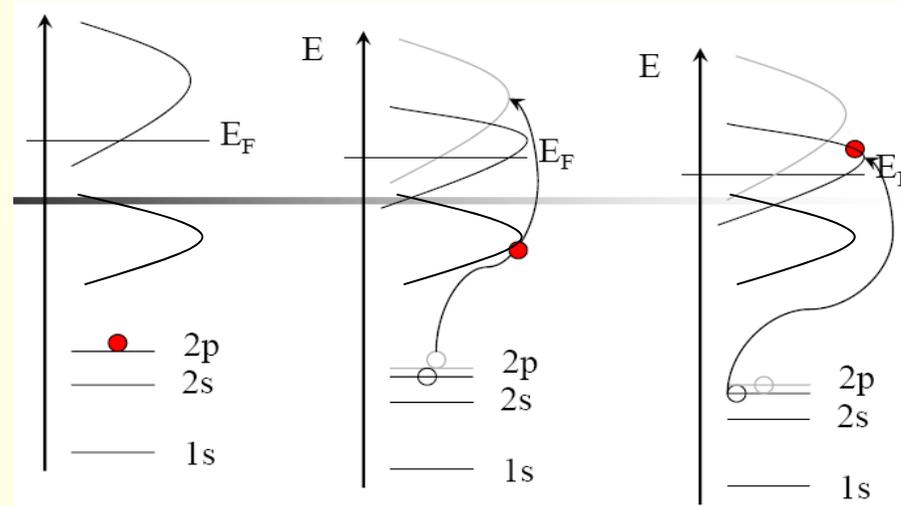
Absorption spectroscopy: Final state rule



Dipole matrix elements determine spectrum: $\frac{\partial^2 \sigma}{\partial E \partial \Omega} \propto \sum_{I,F} \left| \langle I | \vec{\epsilon} \vec{R} | F \rangle \right|^2$

- Final state has a "hole" in core/valence state, but additional e^- in conduction band.
- Core/valence-hole has large effect on the spectrum

➔ electron – hole interaction, "excitonic effects"



$$\Delta l = \pm 1$$

$$s \rightarrow p$$

$$p \rightarrow s+d$$

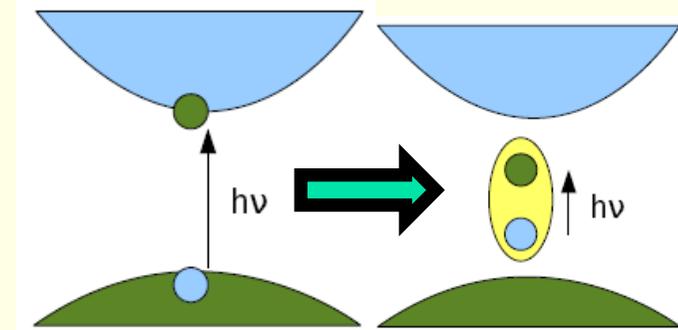
K-edge XANES can be modeled with static core-hole supercell calculations
L-edges require often a more sophisticated treatment (Bethe-Salpeter equ.)



fully relativistic electron-hole interaction (BSE)



- *Bethe-Salpeter-equation: $L(12;1'2')$*
- *solving a 2-particle ($e - h$) equation of large dimension ($N_v N_c N_k \sim 100000$)*



$$\sum_{v'c'k'} (H_{v'c'k',vck}^{eh}) A_{v'c'k'}^\lambda = E^\lambda A_{vck}^\lambda$$

$$H^{eh} = H^{diag} + H^{dir} + 2H^x$$

$$H^{diag} = (E_{v,k} - E_{c,k}) \delta_{cc'} \delta_{vv'} \delta_{kk'}$$

eigenvalue difference between hole (c) and electron(v) state

$$H_{vckv'c'k'}^{dir} = - \int d^3r d^3r' \Psi_{vk}(r) \Psi_{ck'}^*(r') W(r,r') \Psi_{v'k'}^*(r) \Psi_{c'k'}(r')$$

attractive screened static Coulomb interaction W ; $W \sim \epsilon^{-1}$

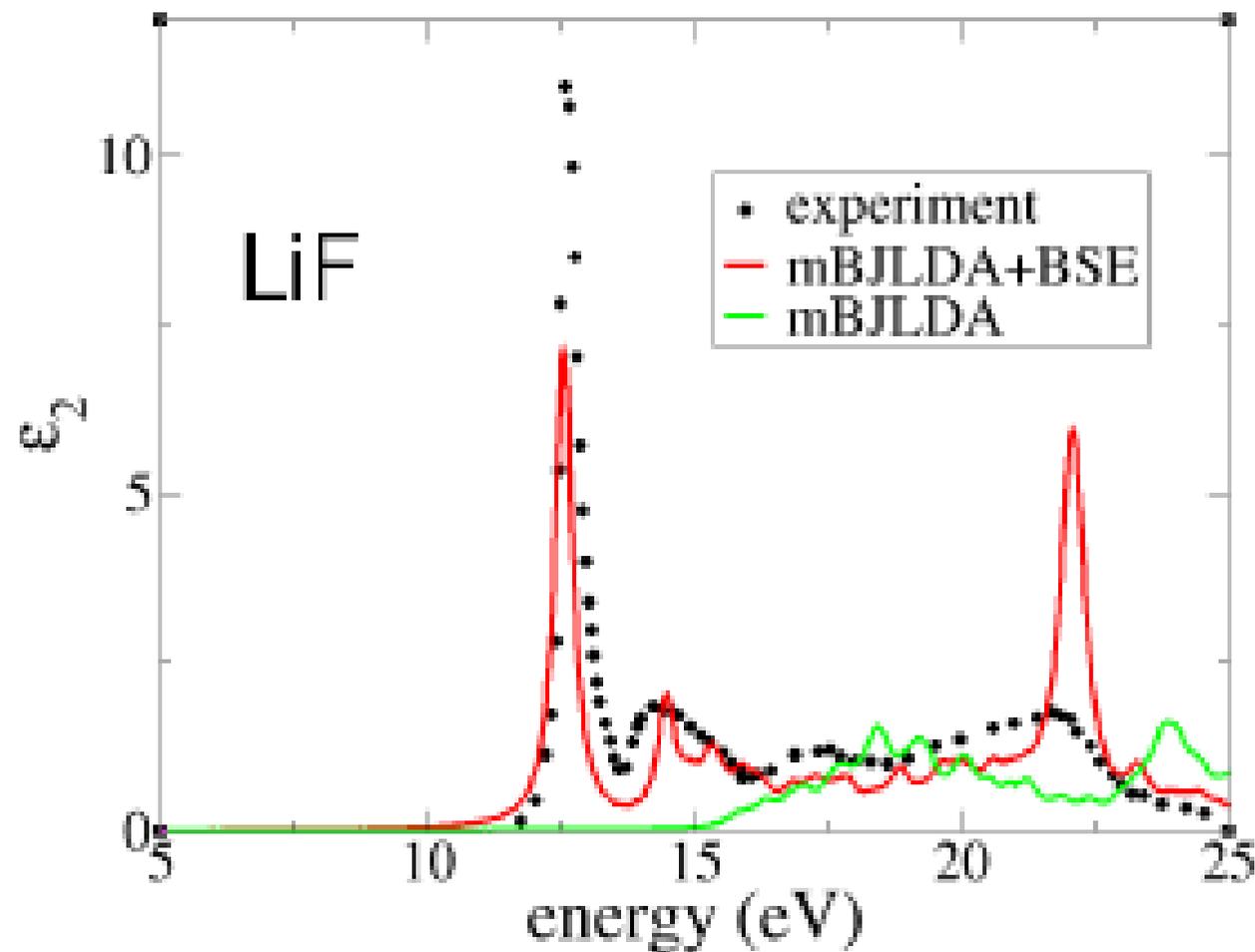
$$H_{vckv'c'k'}^x = \int d^3r d^3r' \Psi_{vk}(r) \Psi_{ck'}^*(r) \bar{v}(r,r') \Psi_{v'k'}^*(r') \Psi_{c'k'}(r')$$

e-h exchange with bare Coulomb potential v

single particle APW (WIEN2k)



Excitons in LiF



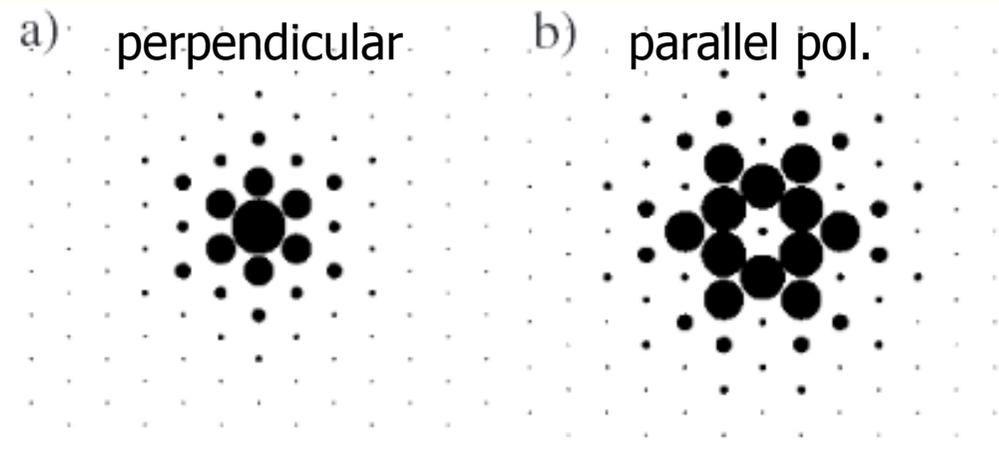
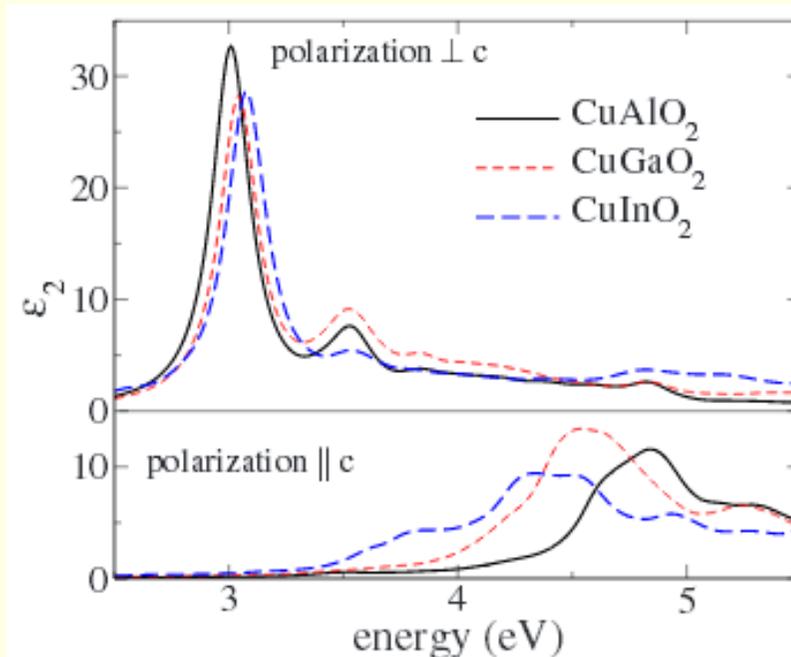
- BSE calculations are very expensive
 - *(code available on request, needs hundreds of cores + memory)*
R. Laskowski, P. Blaha, Phys. Rev. B, 81, 075418 (2010)



electron - hole separation



- BSE calculation can give you information about the **spatial correlation** between the **hole** and the **electrons**



each dot corresponds to a unit cell
 h^+ : center; e^- : black dots

Laskowski et al, PRB 79, 165209 (2009)



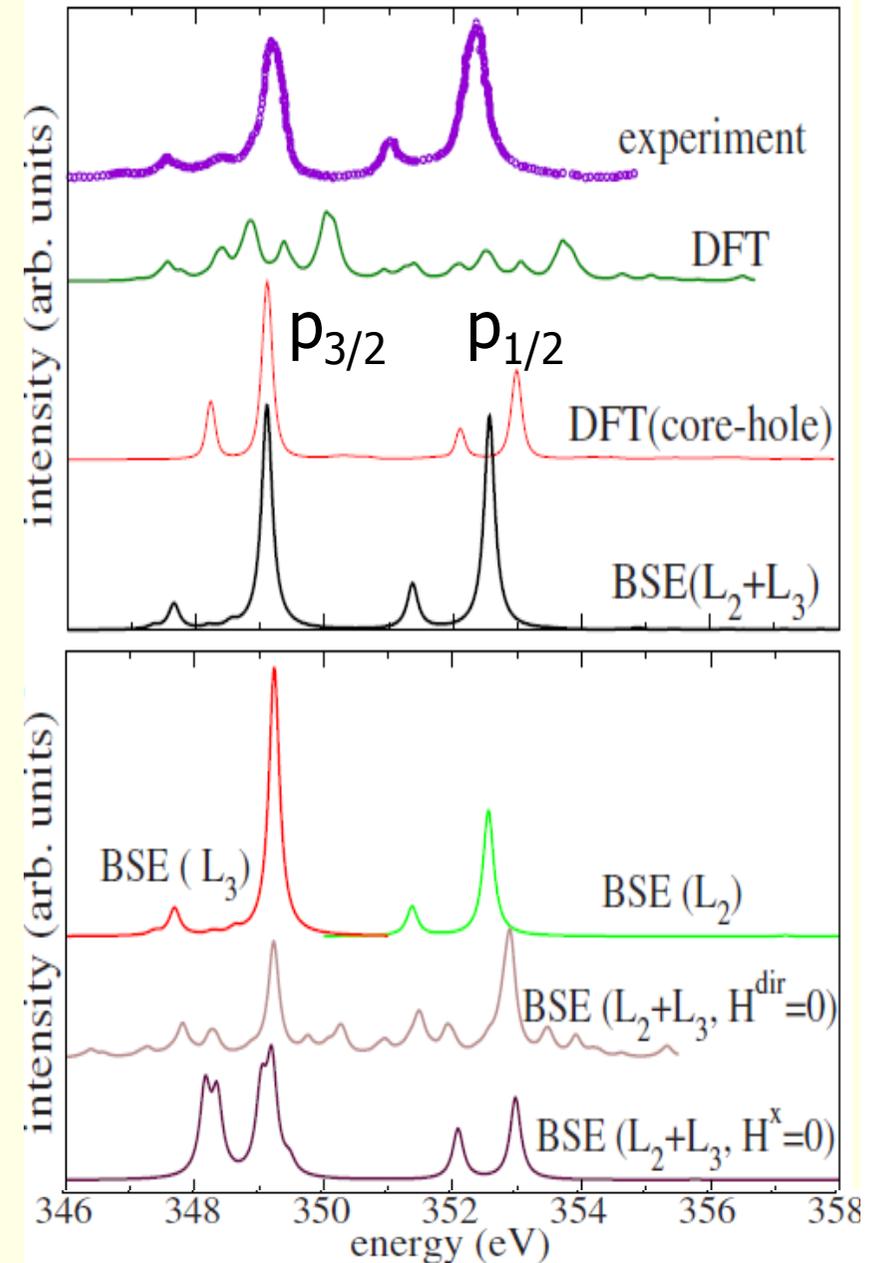
Ca-L₂₃ edge in CaF₂ (Ca-2p → Ca-3d)

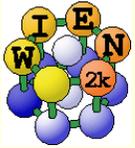


■ experiment



■ "ground-state" DOS

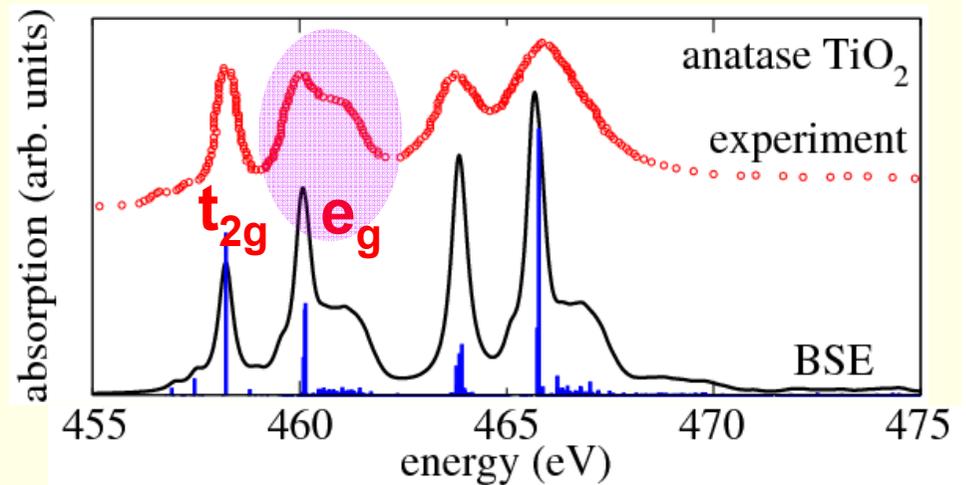
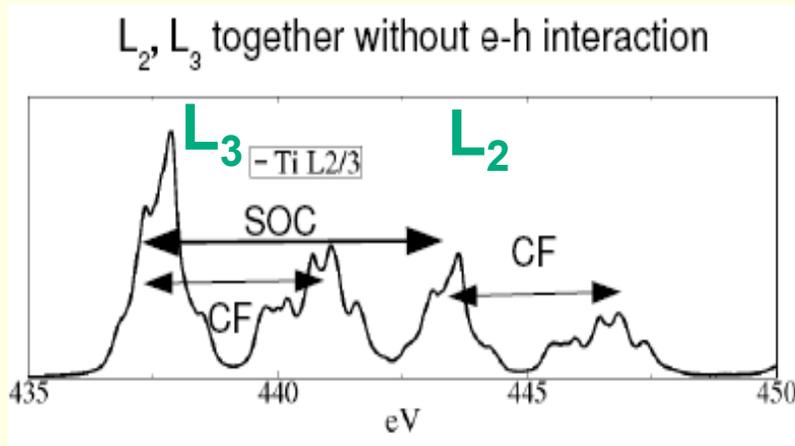




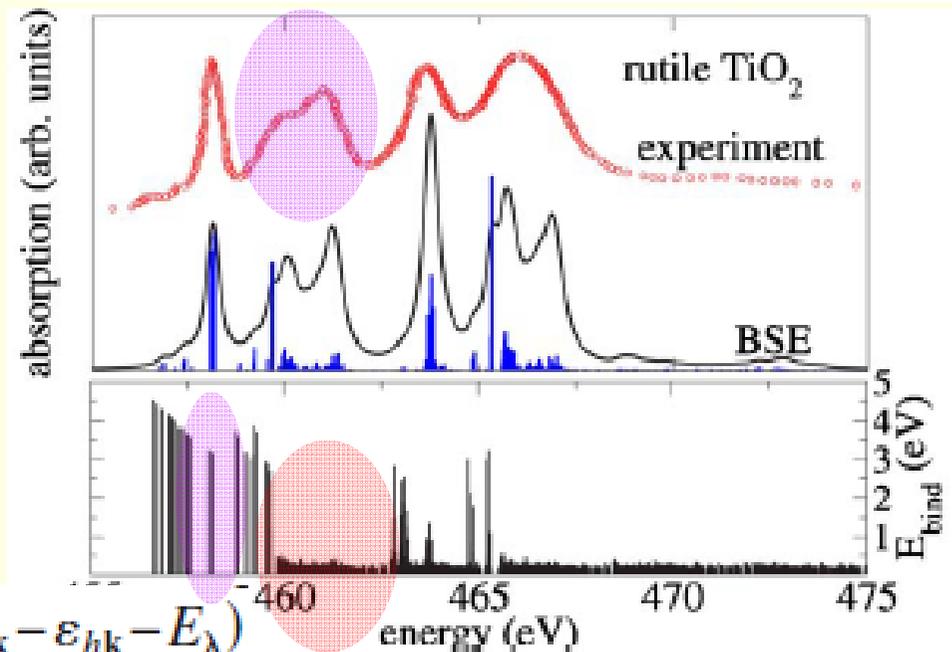
Ti $L_{2,3}$ XANES in rutile- TiO_2 , anatase- TiO_2



fully relativistic BSE calc. $\text{Ti } 2p_{1/2}, 2p_{3/2} \rightarrow$ conduction bands



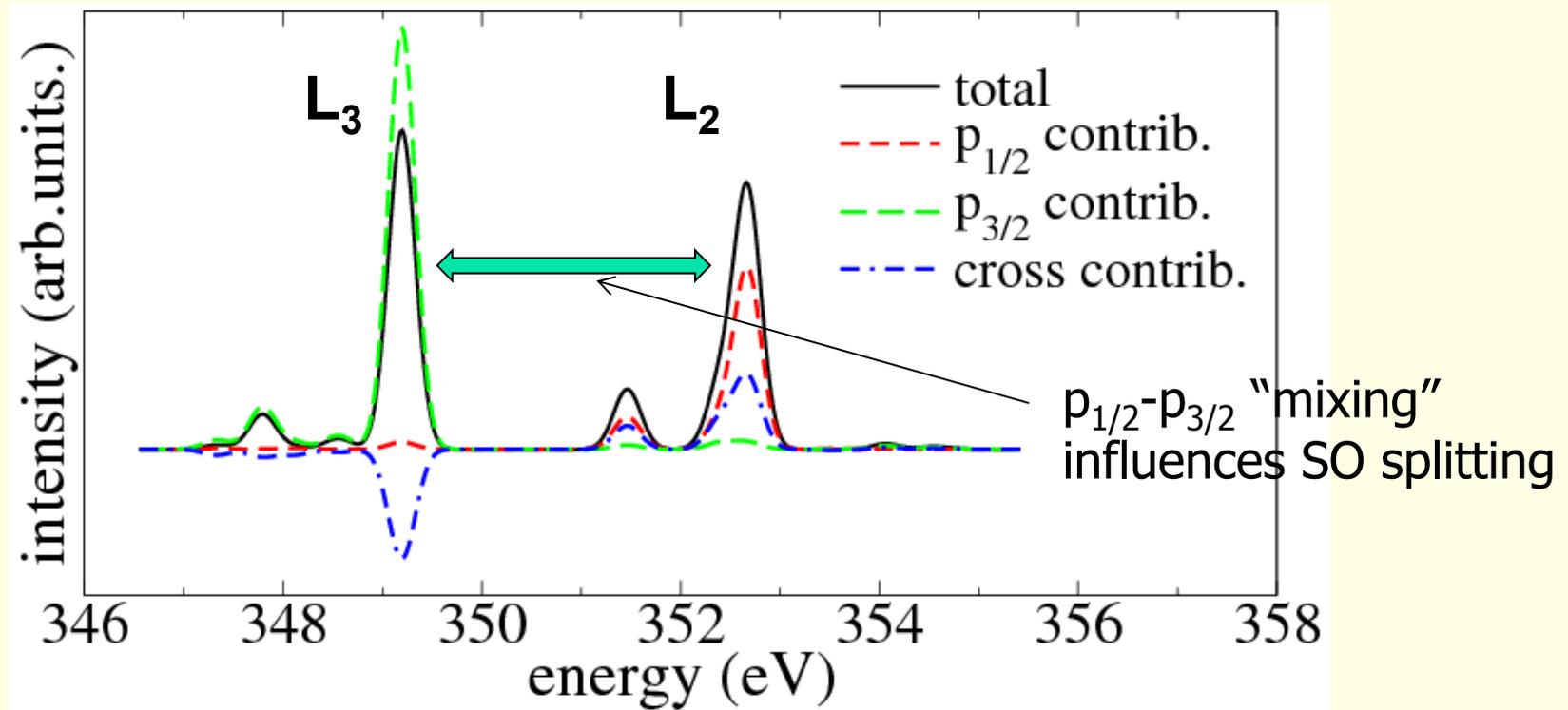
- The experimental Ti $L_{2,3}$ edges are rather well reproduced.
- intensity ratio L_3/L_2 (not 2:1)
- „ t_{2g}/e_g “ ratio (not 3:2)
- left/right shoulder in L_3 -„ e_g “ peak of rutile/anatase
- crystal field splitting influenced by excitonic binding energy



$$E_{bind}^{\lambda} = \sum_{k,e,h} A_{k,h,e}^2 (\epsilon_{ek} - \epsilon_{hk} - E_{\lambda})$$



$L_{2,3}$ edge for Ca in CaF_2



Decomposition of ϵ_2 into the excitation from $p_{1/2}$ and $p_{3/2}$ states
cross terms suppress the L_3 branch and enhance L_2

$$\epsilon_2^{xx}(\omega) = \frac{8\pi^2}{\Omega} \sum_{\lambda} \left| \sum_{hek} A_{hek}^{\lambda} \frac{\langle hk | -i\nabla_x | ek \rangle}{\epsilon_{ek} - \epsilon_{hk}} \right|^2 \times \delta(E^{\lambda} - \omega)$$



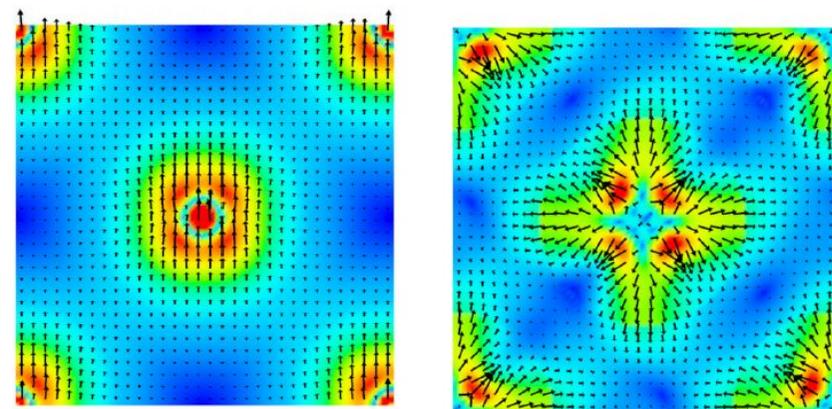
Properties with WIEN2k - V



- WIENNCM: non-collinear magnetism (spin-spirals to fully-relativistic) (R.Laskowski)
- BOLTZTRAP by G.Madsen: (transport, fermi velocities, effective masses, Seebeck, conductivity, thermoelectrics)
- ATAT@WIEN2k (C.Draxl) : alloy theoretical automatic toolkit (cluster expansion)
- Berry-PI: (O. Rubel): berry-phases for electric fields, polarization, Born charges, piezoelectricity
- GW: (M.Scheffler et al.)

- **w2wannier** (J.Kunes et al)
- interfaces with DMFT-codes (M. Aichhorn/S.Biermann, K. Held)

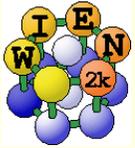
Intra-atomic NCM, fcc *Pu*



(a) plane $x = 0$

(b) plane $z = 1/10$

Spin density maps of **fcc Pu**. Calculation in FULL mode with SO. Average momenta point to $\langle 001 \rangle$



GW (MBPT on one page)



- Self-energy $\Sigma(r, r', \omega) = \frac{i}{2\pi} \int d\omega' G(r, r, \omega - \omega') W(r, r', \omega)$

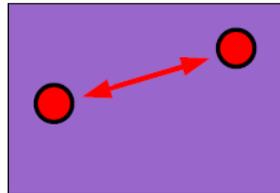
- Green's function $G(\mathbf{r}_1, \mathbf{r}_2, \omega) = \sum_i \frac{\phi_i^{KS}(\mathbf{r}_1) \phi_i^{KS*}(\mathbf{r}_2)}{\omega - \epsilon_i^{KS} \pm i\eta}$ describes propagation of e^-, h^+ from $\mathbf{r}_1 \rightarrow \mathbf{r}_2$ with time (ω)

- screened coulomb interaction W :

Interaction between electrons in a homogeneous polarizable medium:

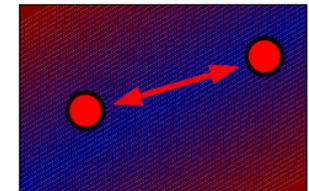
$$W(r, r') = \frac{1}{4\pi\epsilon_0\epsilon_r} \frac{e^2}{|r - r'|}$$

Dielectric constant of the medium



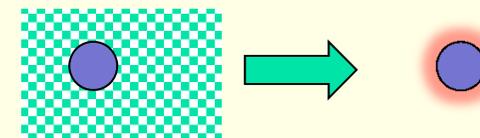
Dynamically screened interaction between electrons in a general medium:

$$W(r, r', \omega) = \frac{e^2}{4\pi\epsilon_0} \int d r'' \frac{\epsilon^{-1}(r, r'', \omega)}{|r'' - r'|}$$



- GW: screened HF approximation $\Sigma_x(r_1, r_2) + \Sigma_c(r_1, r_2, \omega)$

- calculation of "quasiparticle energies":



$$\epsilon_{nk}^{QP} = \epsilon_{nk}^{LDA} - \langle nk | \Sigma(\epsilon_{nk}^{QP}) - V_{xc}^{LDA} | nk \rangle$$



Summary



- **DFT can give you insight**
- **DFT can help to interpret your data**
- **DFT can narrow the design space**



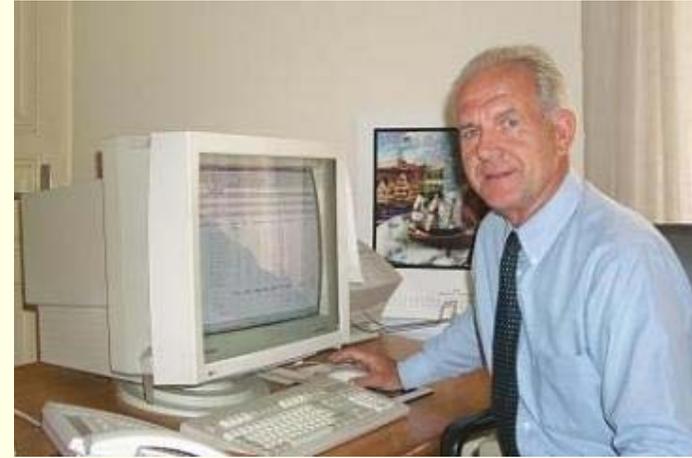
Acknowledgment



F. Tran



R. Laskowski



K. Schwarz

Thank you for
your attention !