TECHNISCHE UNIVERSITÄT WIEN

Introduction to WIEN2k

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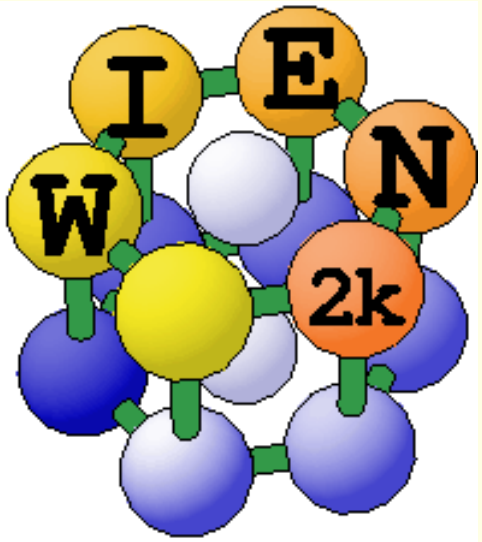


Concepts when solving Schrödingers-equation

Treatment of spin

Non-spinpolarized
Spin polarized
(with certain magnetic order)

Form of potential

"Muffin-tin" MT
atomic sphere approximation (ASA)
pseudopotential (PP)
Full potential : FP

Relativistic treatment of the electrons

non relativistic
semi-relativistic
fully-relativistic

exchange and correlation potential

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

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

Schrödinger - equation

Representation of solid

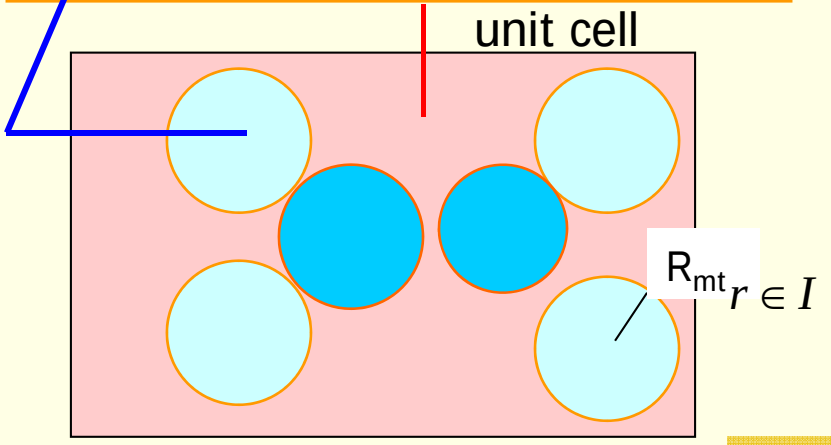
non periodic
(cluster, individual MOs)
periodic
(unit cell, Blochfunctions, "bandstructure")

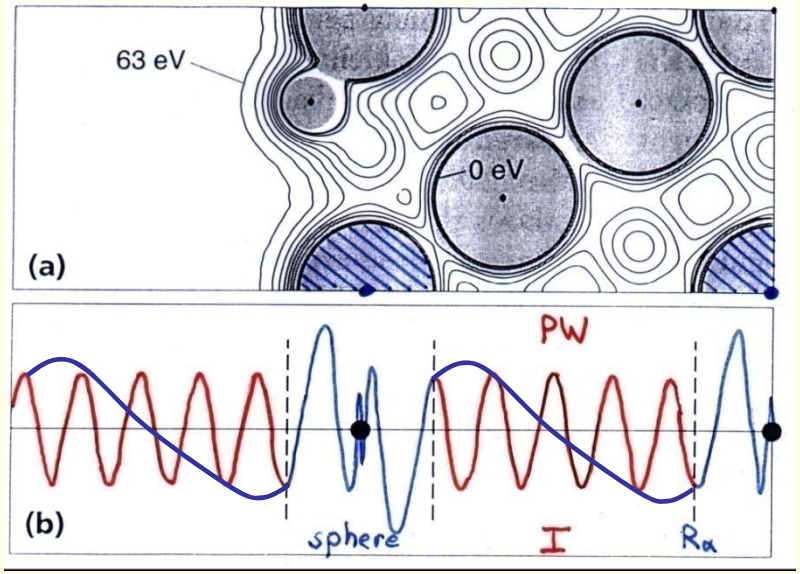
Basis functions

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

APW Augmented Plane Wave method

The unit cell is partitioned into:
- atomic spheres
- Interstitial region





"exact" solutions, but energy dependent

Basisset:

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

Atomic partial waves

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

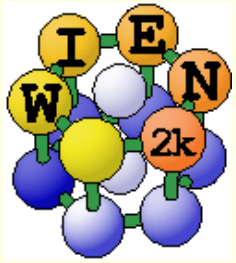
join

$u_l(r,\varepsilon)$ 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* ⟹ *Non-linear eigenvalue problem*
    - Computationally very demanding
- LAPW (O.K.Andersen 1975)
  - ***Linearization*** *of E-dependency* ⟹ *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.Nordstörm, D.J.Singh 2000)
  - ***E-independent*** *APWs + local orbitals (to describe the E-dependency)*
  - *Efficience of APW + convenience of LAPW*
  - *Basis for*

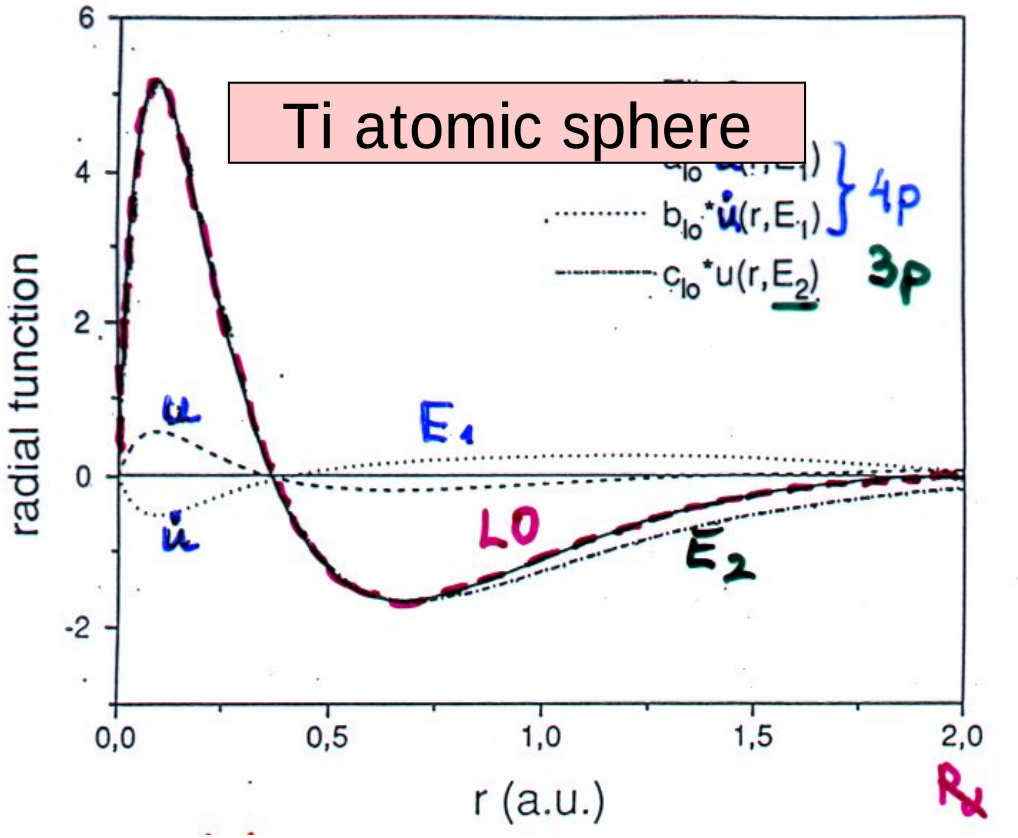


K.Schwarz, P.Blaha, G.K.H.Madsen,
Comp.Phys.Commun.**147**, 71-76 (2002)

Extending the basis: Local orbitals (LO)

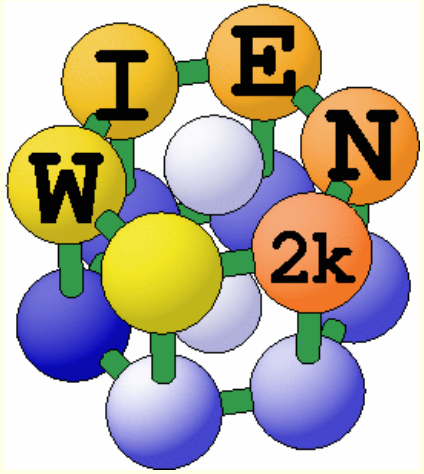
$$\Phi_{LO} = [A_{\ell m} u_\ell^{E_1} + B_{\ell m} \dot{u}_\ell^{E_1} + C_{\ell m} u_\ell^{E_2}] Y_{\ell m}(\hat{r})$$

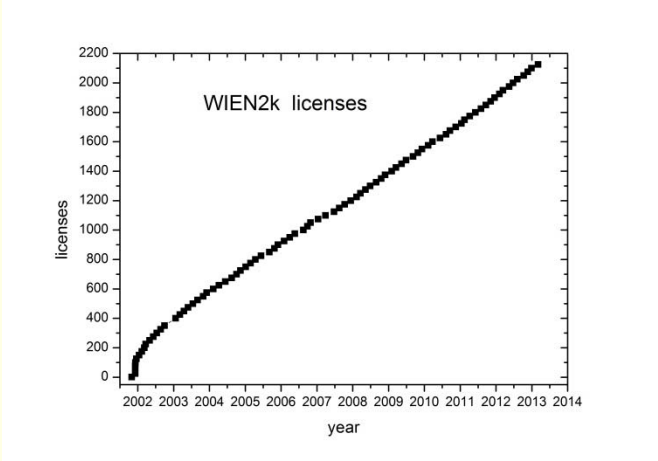
- LO: contains a second $u_l(E_2)$
  - *is confined to an atomic sphere*
  - *has zero value and slope at R*
  - *can treat two principal QN n for each azimuthal QN ℓ (3p and 4p)*
  - *corresponding states are strictly orthogonal (no "ghostbands")*
  - *tail of semi-core states can be represented by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



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

WIEN2k software package





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

Peter Blaha
Karlheinz Schwarz
Georg Madsen
Dieter Kvasnicka
Joachim Luitz

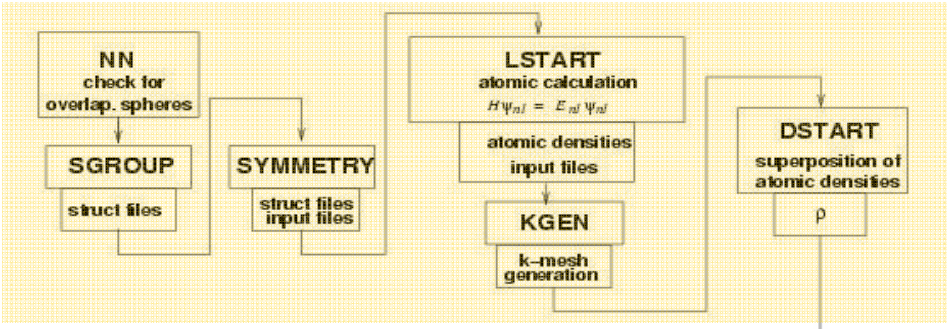
November 2001
Vienna, AUSTRIA
Vienna University of Technology

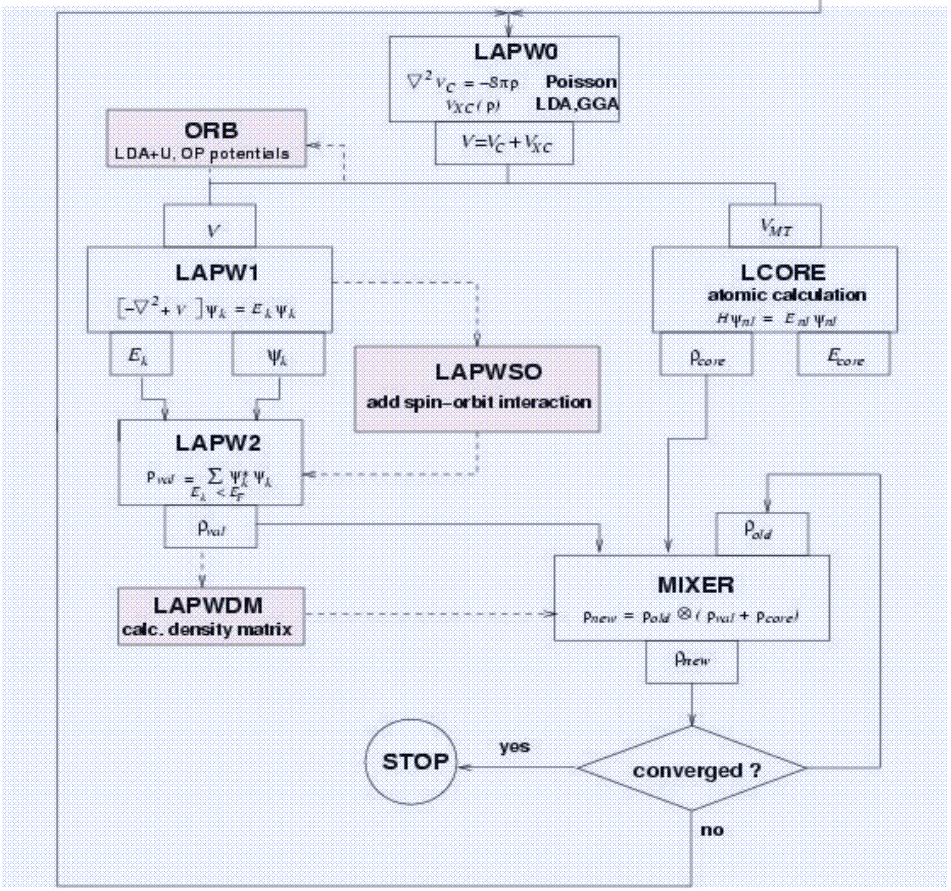
http://www.wien2k.at

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

Program structure of WIEN2k

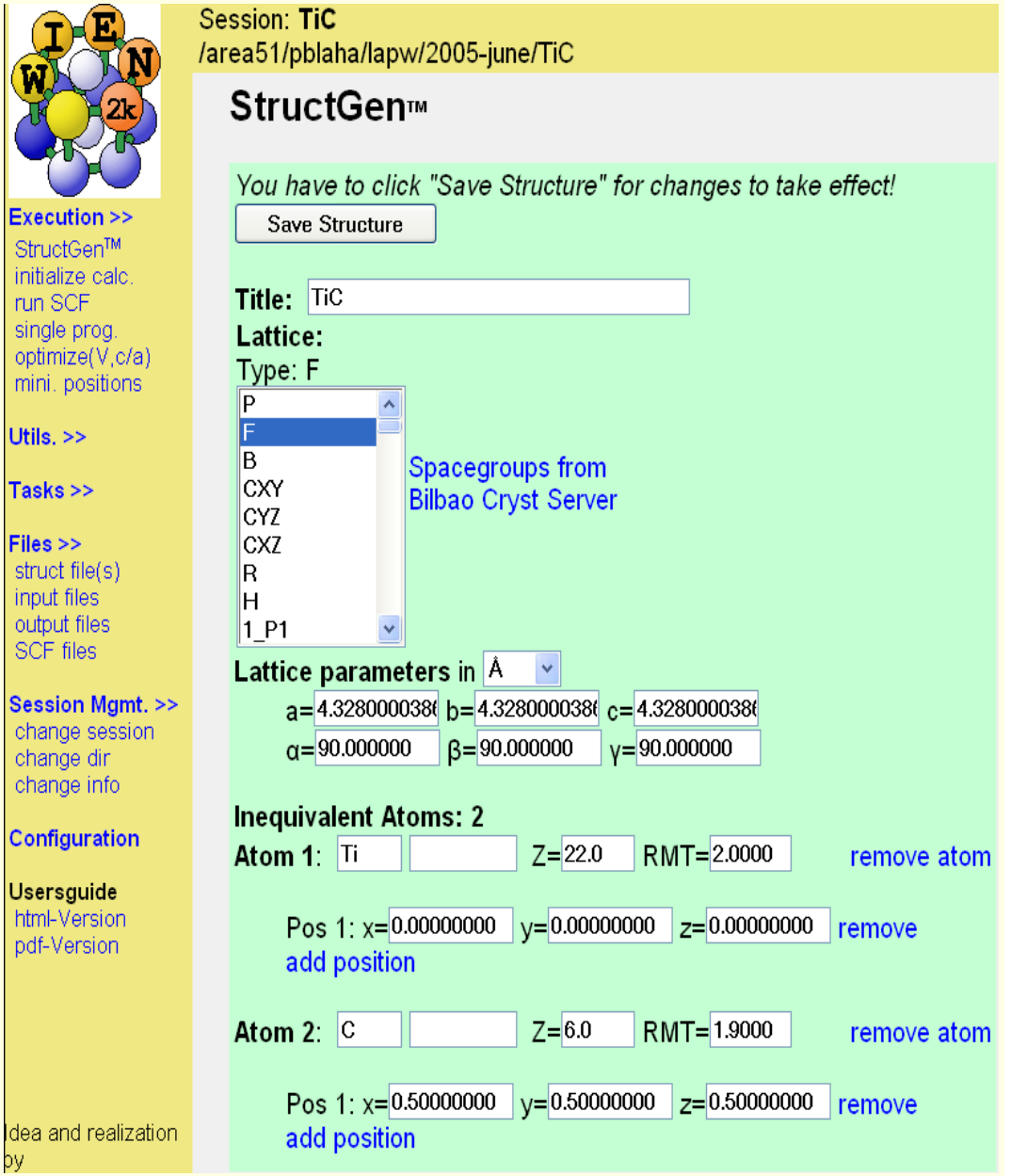
- create a structure
- init_lapw
  - *step-by-step or batch initialization*
  - *symmetry detection (F, I, C-centering, inversion)*
  - *input generation with recommended defaults*
  - *quality (and computing time) depends on k-mesh and R.Kmax (determines #PW)*
- run_lapw
  - *scf-cycle*
  - *optional with SO and/or LDA+U*
  - *different convergence criteria (energy, charge, forces)*
- save_lapw tic_gga_100k_rk7_vol0
  - *cp case.struct 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*



O-NMR of tetragonal $BaTiO_3$

- cd work; mkdir BaTiO3; cd BaTiO3
- **makestruct** (and type in the following information)
  - *$BaTiO_3$: 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)

DFT Density Functional Theory

Hohenberg-Kohn theorem: (exact)

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

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

Kohn-Sham: (still exact!)

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

$E_{kinetic}$ non interacting

E_{ne}

$E_{coulomb}$ E_{ee}

E_{xc} exchange-correlation

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

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

LDA } treats both, exchange and

GGA } correlation effects approximately

Success and failure of “standard” DFT in solids

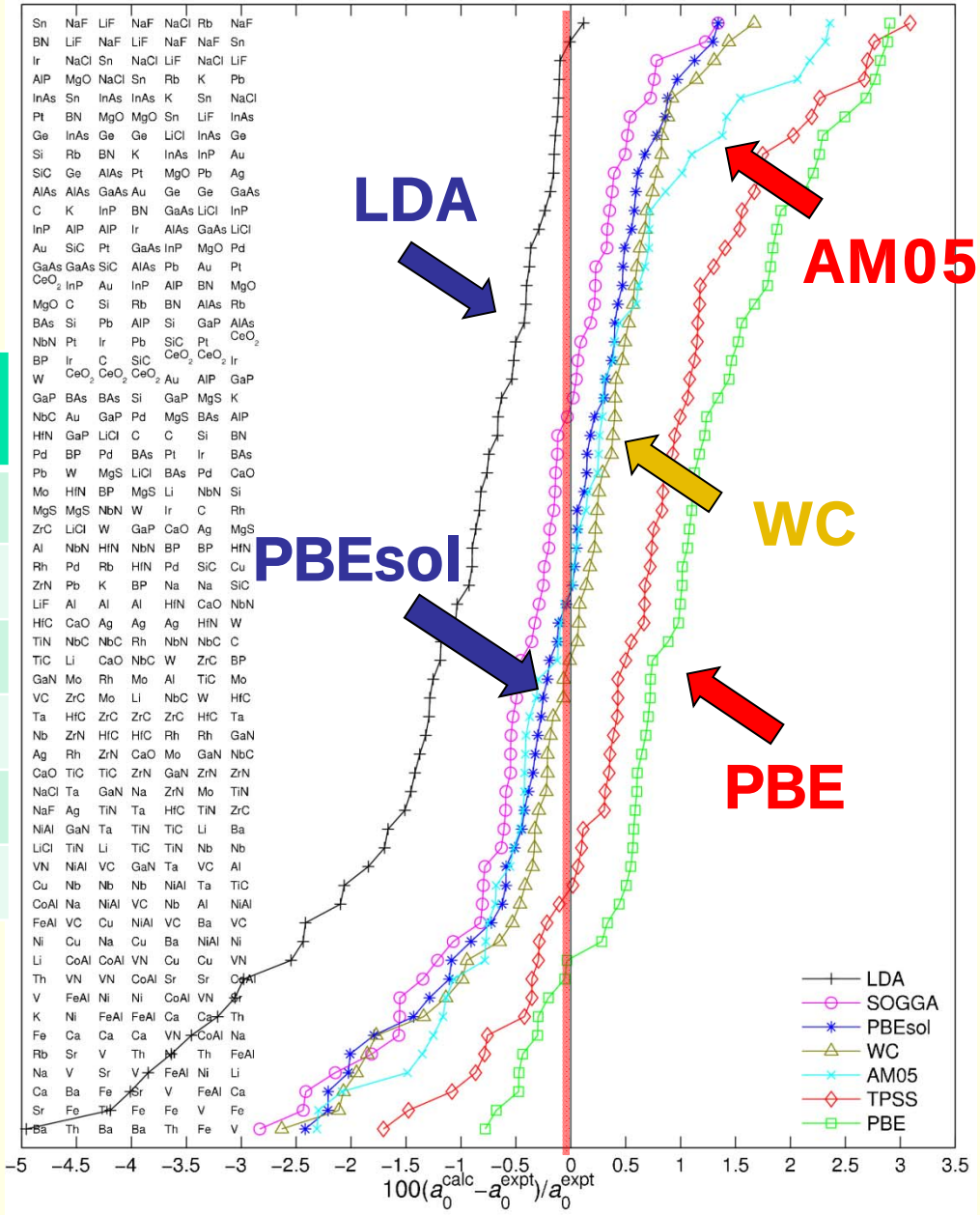
- Standard LDA (GGA) gives good description of most solids
- Problems:
  - *accuracy : functional “adapted” for specific materials or properties*
    - solids - molecules; metals - insulators - van der Waals bonds
    - elements: trends within up - down and left - right in periodic table
    - geometry - binding energies - spectroscopy
  - *“correlated” (localized) electrons: 3d transition metal oxides, 4f,5f e⁻*
    - metals instead of insulators (FeO, FeF_2, cuprates, ...)
    - nonmagnetic instead of anti-ferromagnetic (La_2CuO_4, $YBa_2Cu_3O_6$)
  - *band gaps in semiconductors/insulators*
    - gap typically underestimated by 50%
- Possible improvements (depend on case and property):
  - *ground state: better GGAs, LDA+U, hybrid-DFT, OEP, RPA, DMFT, QMC*
  - *excited states: GW, TB-mBJ, BSE, TD-DFT*

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 !!



semilocal functionals available in WIEN2k

Functional	Authors	Year	indxc (case.in0)
LDA	Dirac, Slater, etc.	1930 - ...	5
GGA:			
PBE	Perdew et al	1996	13
WC	Wu, Cohen	2005	11
PBEsol	Perdew et al.	2007	19
HTBS	Haas et al.	2011	46
TB-mBJ*	Tran, Blaha	2009	28, 50
meta-GGA:			
revTPSS**	Perdew et al.	2009	29

* only a potential (E_{xc} = LDA)

** only E_{xc} (V_{xc} = PBE)

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**

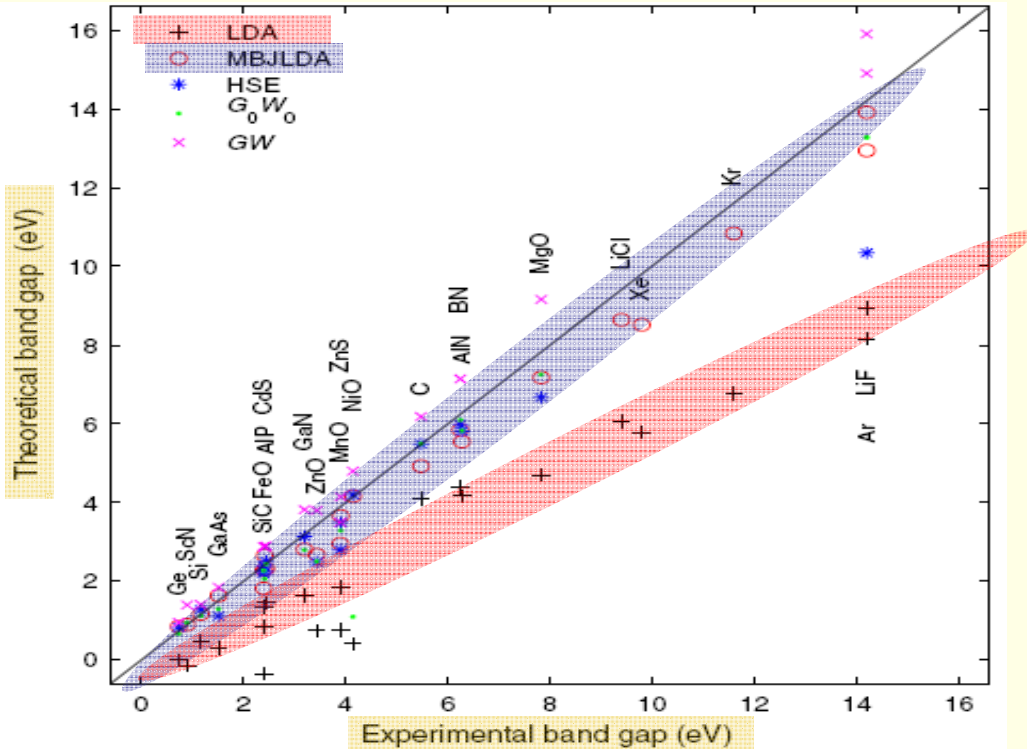
$$v_{x,\sigma}^{\mathrm{MBJ}}(\mathbf{r}) = c\,v_{x,\sigma}^{\mathrm{BR}}(\mathbf{r}) + (3c-2)\frac{1}{\pi}\sqrt{\frac{5}{12}}\sqrt{\frac{2t_\sigma(\mathbf{r})}{\rho_\sigma(\mathbf{r})}},$$

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

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

c depends on the density properties of a material

\+ gaps of „GW“ quality
\+ good for correlated TM-oxides
\- NO energy (only V)



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

- **LDA+U** ⟹ 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)

$$E_{\mathrm{xc}} = E_{\mathrm{xc}}^{\mathrm{SL}} + \alpha_{\mathrm{x}} \left(E_{\mathrm{x}}^{\text{SR-HF}} - E_{\mathrm{x}}^{\text{SR-SL}} \right)$$

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

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

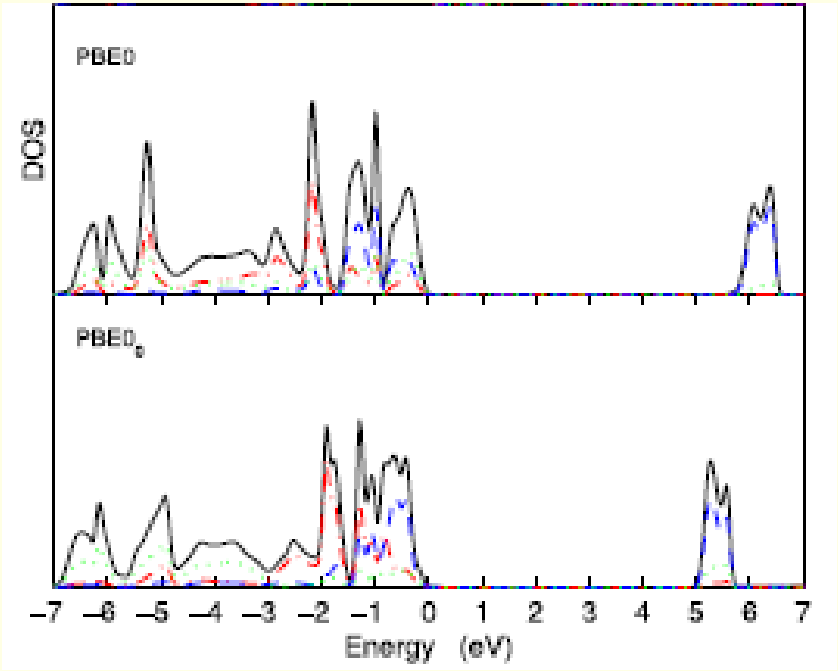
$$\varepsilon_{nk}^{QP} = \varepsilon_{nk}^{LDA} - \langle nk | \Sigma(\varepsilon_{nk}^{QP}) - V_{xc}^{LDA} | nk \rangle$$

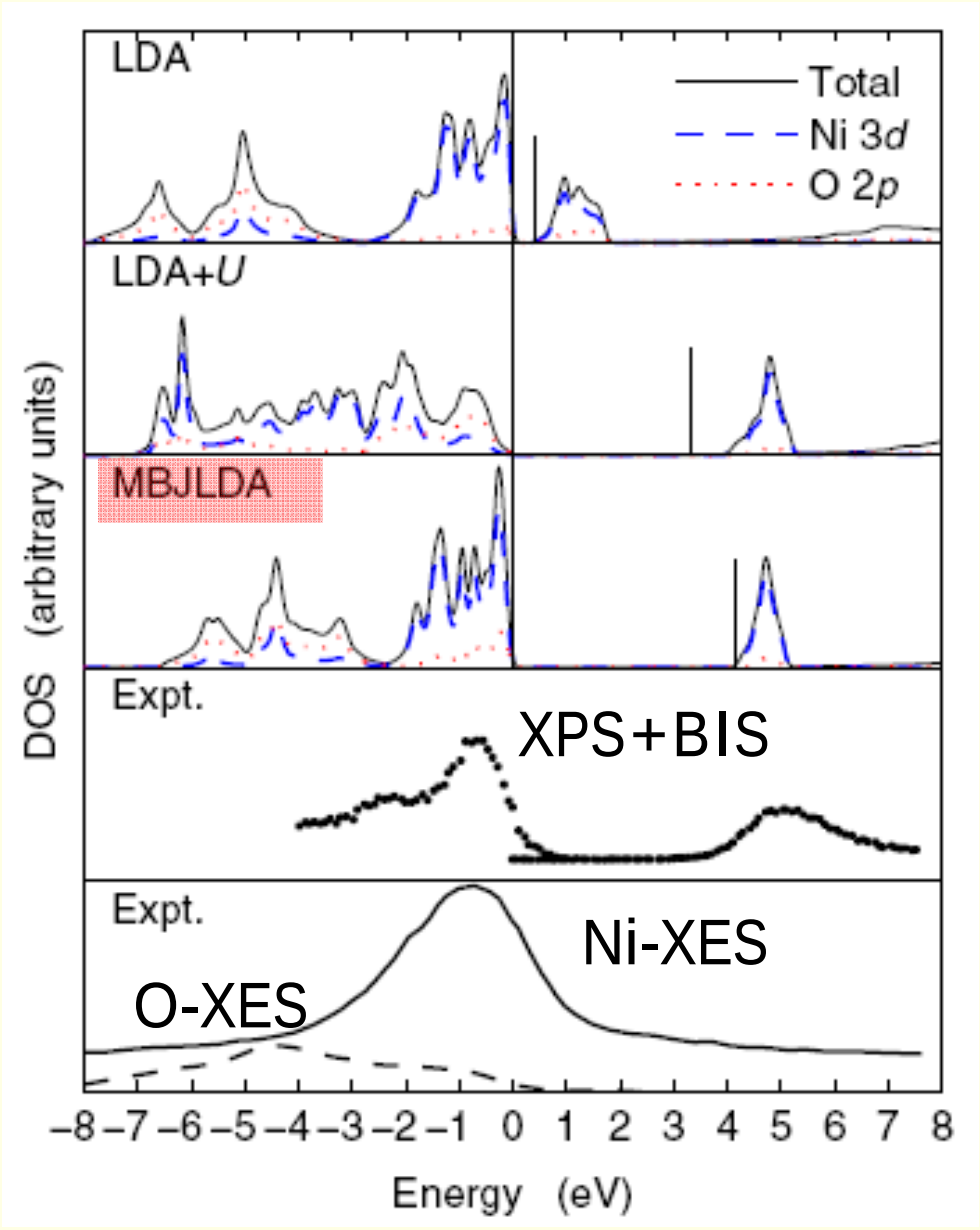
available for WIEN2k
M. Scheffler et al.
(very expensive)

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

DOS of NiO

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





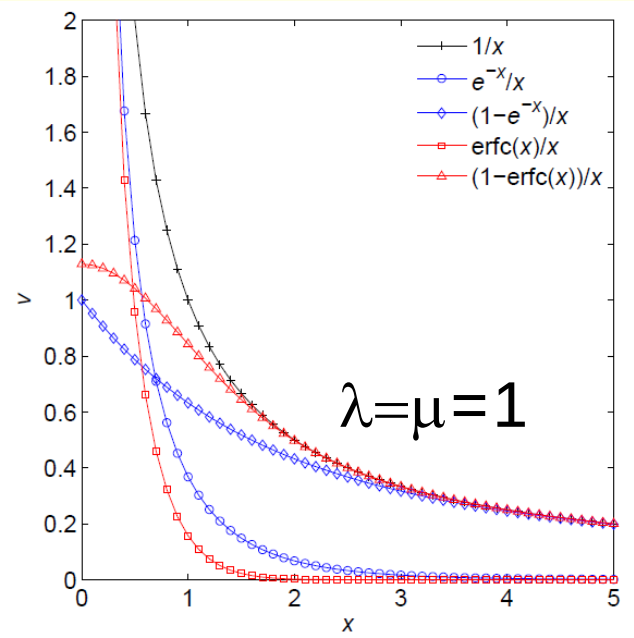
screened full-hybrid functionals

$$E_{\mathrm{xc}} = E_{\mathrm{xc}}^{\mathrm{SL}} + \alpha_{\mathrm{x}} \left(E_{\mathrm{x}}^{\mathrm{SR\text{-}HF}} - E_{\mathrm{x}}^{\mathrm{SR\text{-}SL}} \right)$$

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

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

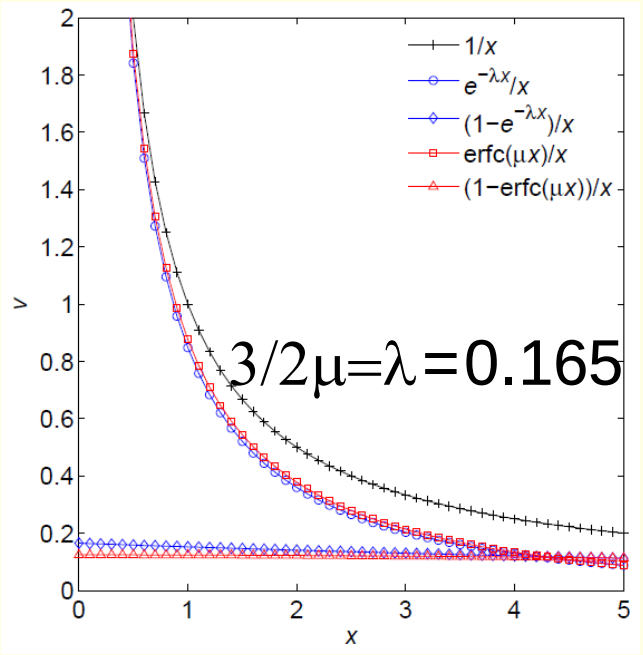
$$\left(1-\mathrm{erfc}(\mu x)\right)/x$$



HSE06 functional: μ=0.11 bohr^{-1}

exponential with λ=3/2 μ is very similar

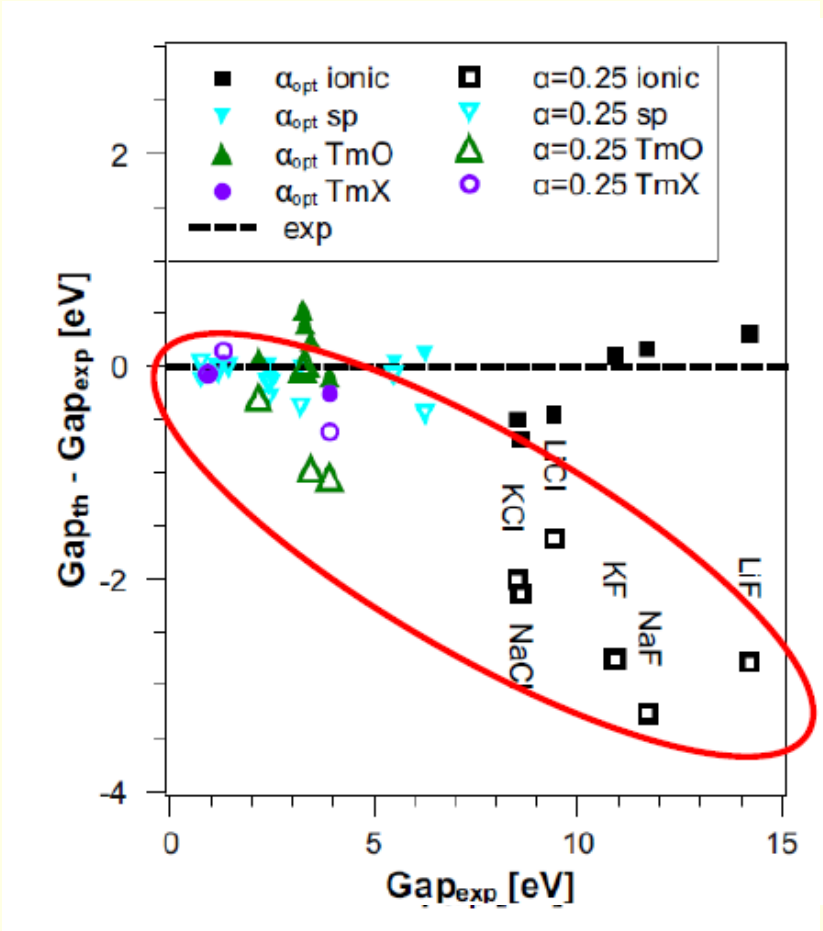
YS-PBE0: Tran,Blaha, PRB **83**, 235118 (2011)

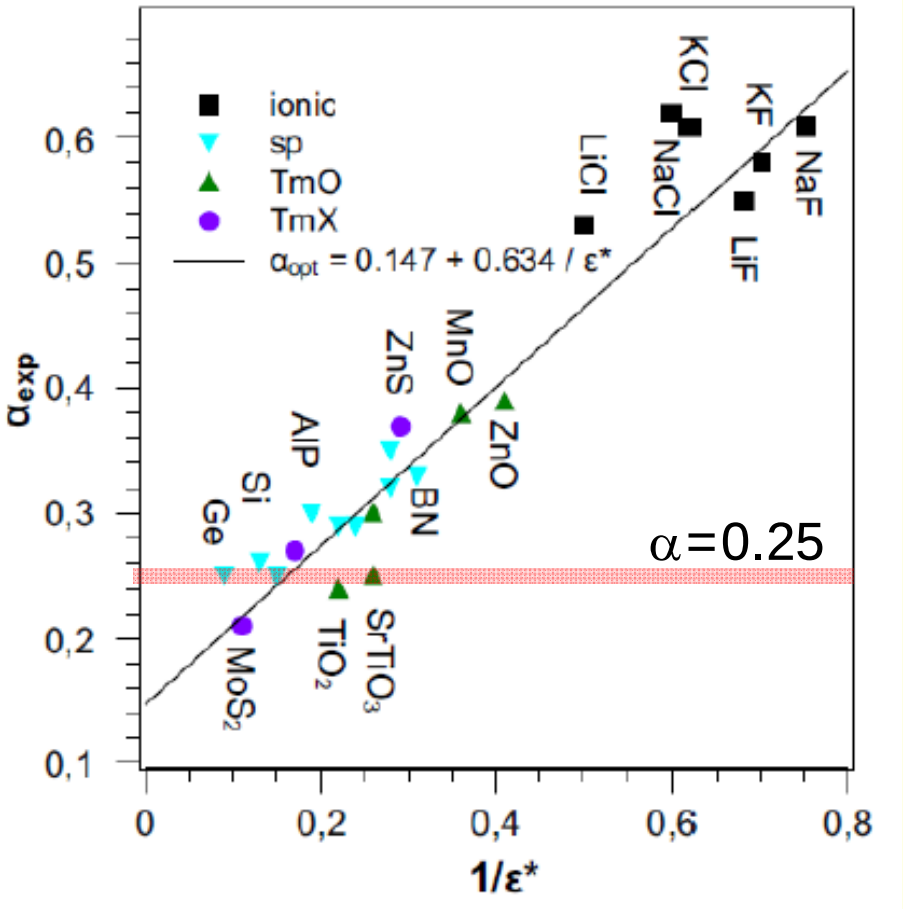


screened functionals improve k-mesh convergence dramatically

hybrid-DFT with individual α

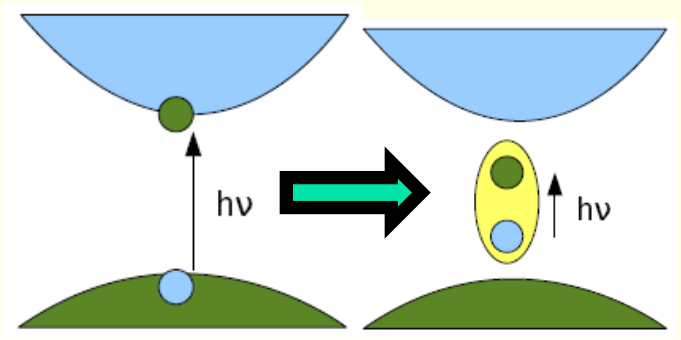
- **standard** hybrid-DFT **underestimates** gaps for insulators
- **optimal** α found by fit to exp. as function of $\mathbf{1/\varepsilon_0}$





fully relativistic electron-hole interaction (BSE)

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



$$\sum_{v'c'k'} (H^{eh}_{v'c'k',vck}) A^{\lambda}_{v'c'k'} = E^{\lambda} A^{\lambda}_{vck}$$

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

single particle APW (WIEN2k)

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

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

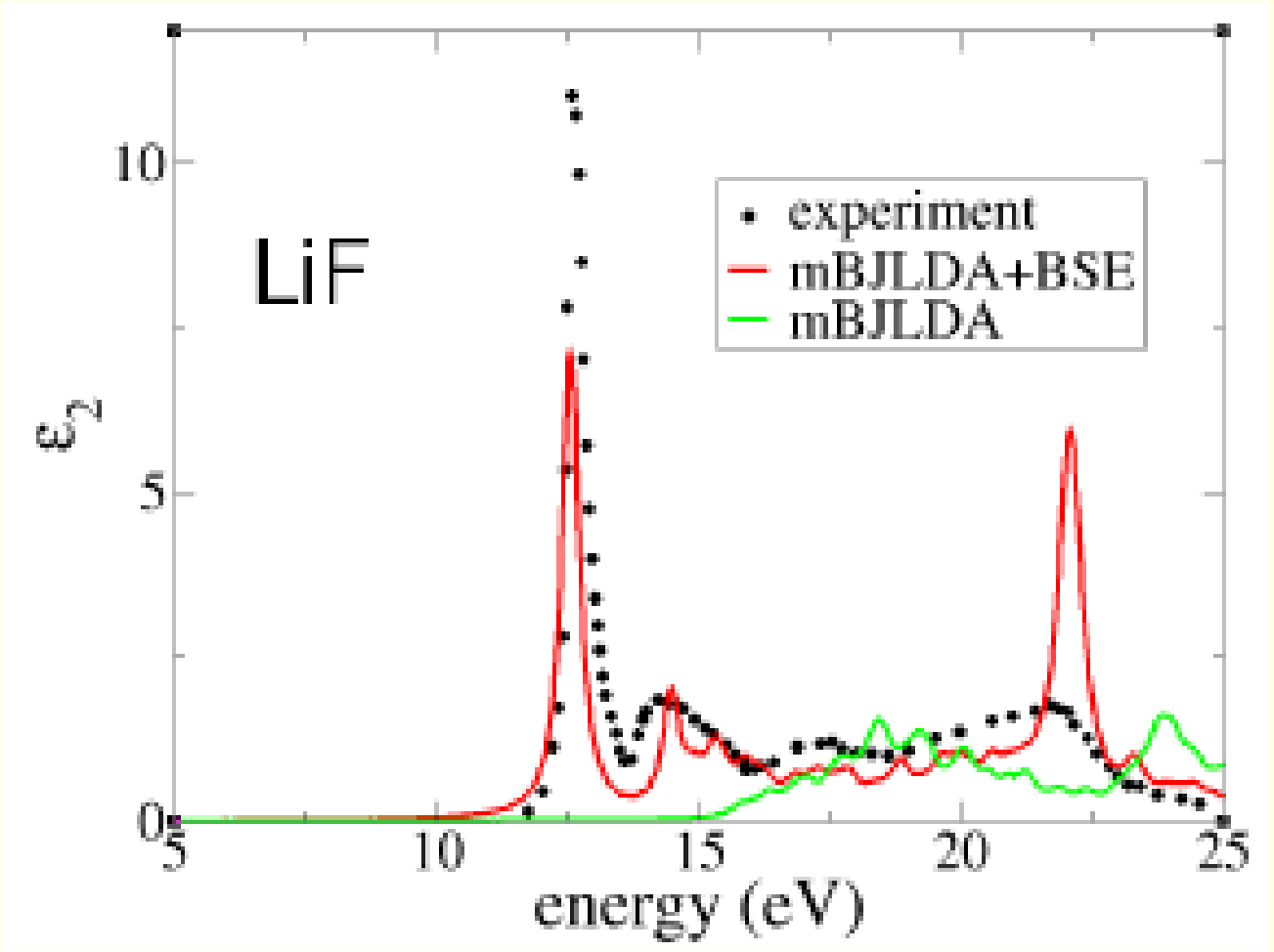
$$H^{dir}_{vckv'c'k'} = -\int d^3r\, d^3r'\, \Psi_{vk}(r)\Psi^*_{ck}(r')W(r,r')\Psi^*_{v'k'}(r)\Psi_{c'k'}(r')$$

attractive screened static Coulomb interaction *W; W~ε^{-1}*

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

e-h exchange with bare Coulomb potential *v*

Excitons in LiF

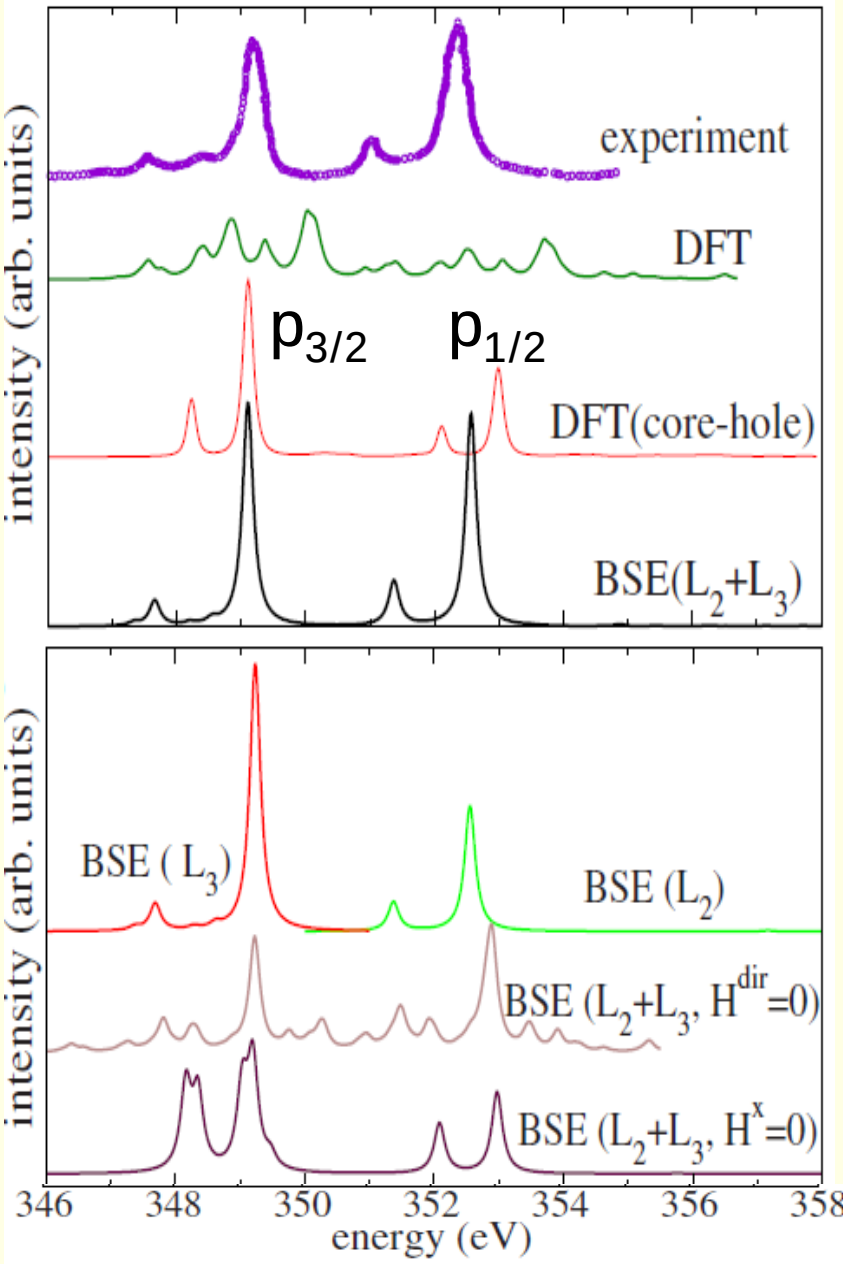


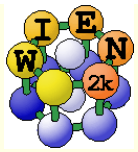
- BSE calculations are very expensive
  - *(code available on request, needs hundreds of cores .... + memory)*

R. Laskowski, P. Blaha, Phys. Rev. B, 81, 075418 (2010)

Ca-L_{23} edge in CaF_2 (Ca-2p → Ca-3d)

- **experiment**
- "ground-state" DOS





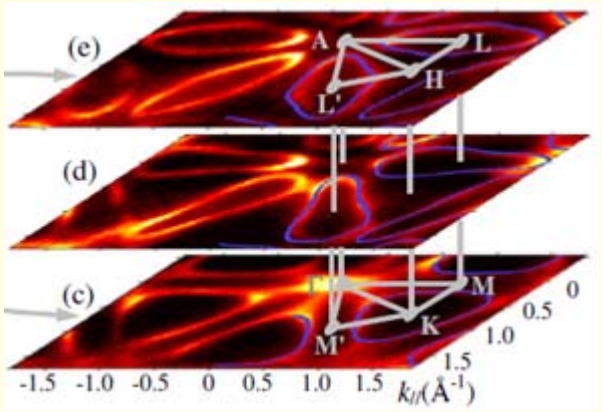
TU WIEN

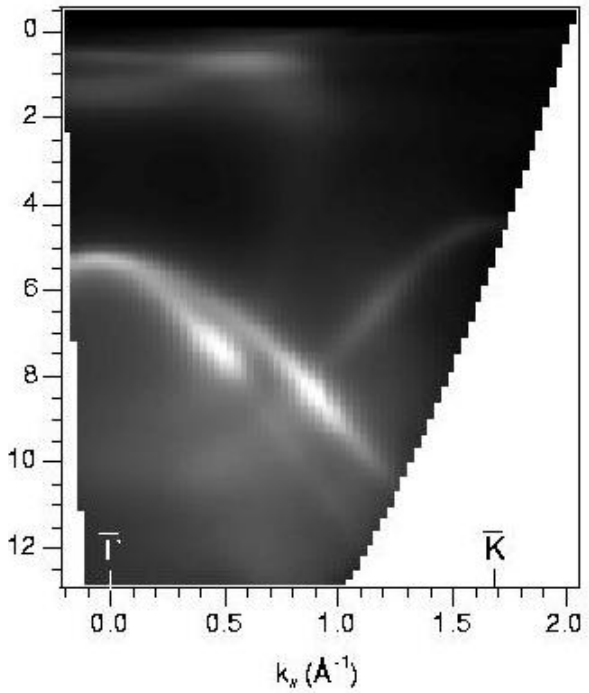
properties with WIEN2k

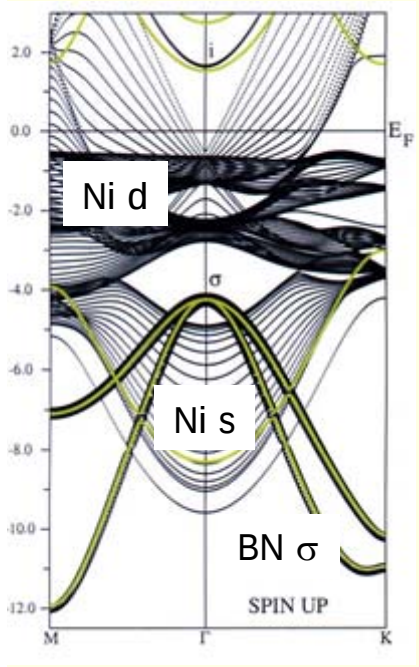
Properties with WIEN2k - I

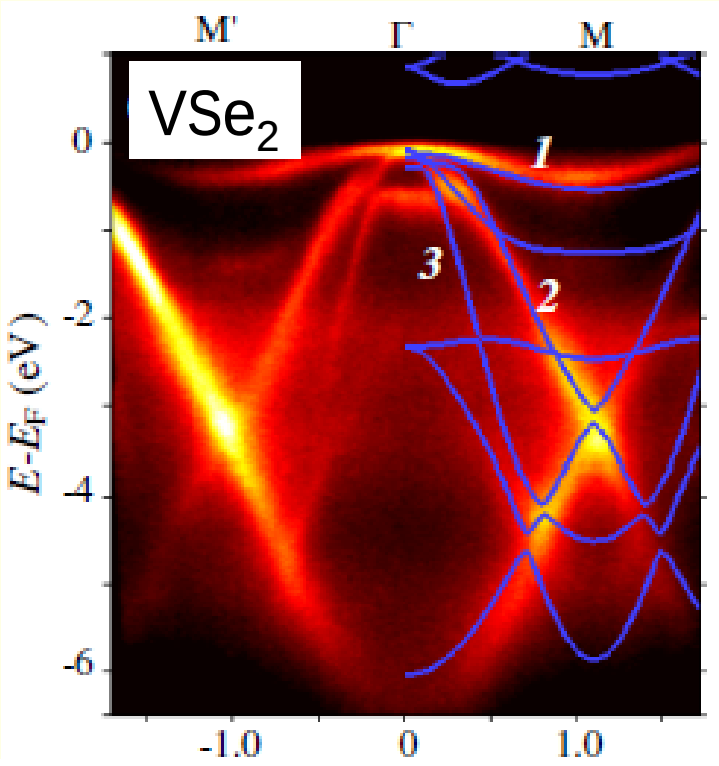
- Energy bands
  - *classification of irreducible representations*
  - *´character-plot´ (emphasize certain band-character)*
- Density of states
  - *including partial DOS with l and m- character*
- Fermi surfaces

h-BN / Ni(111): σ and π bands





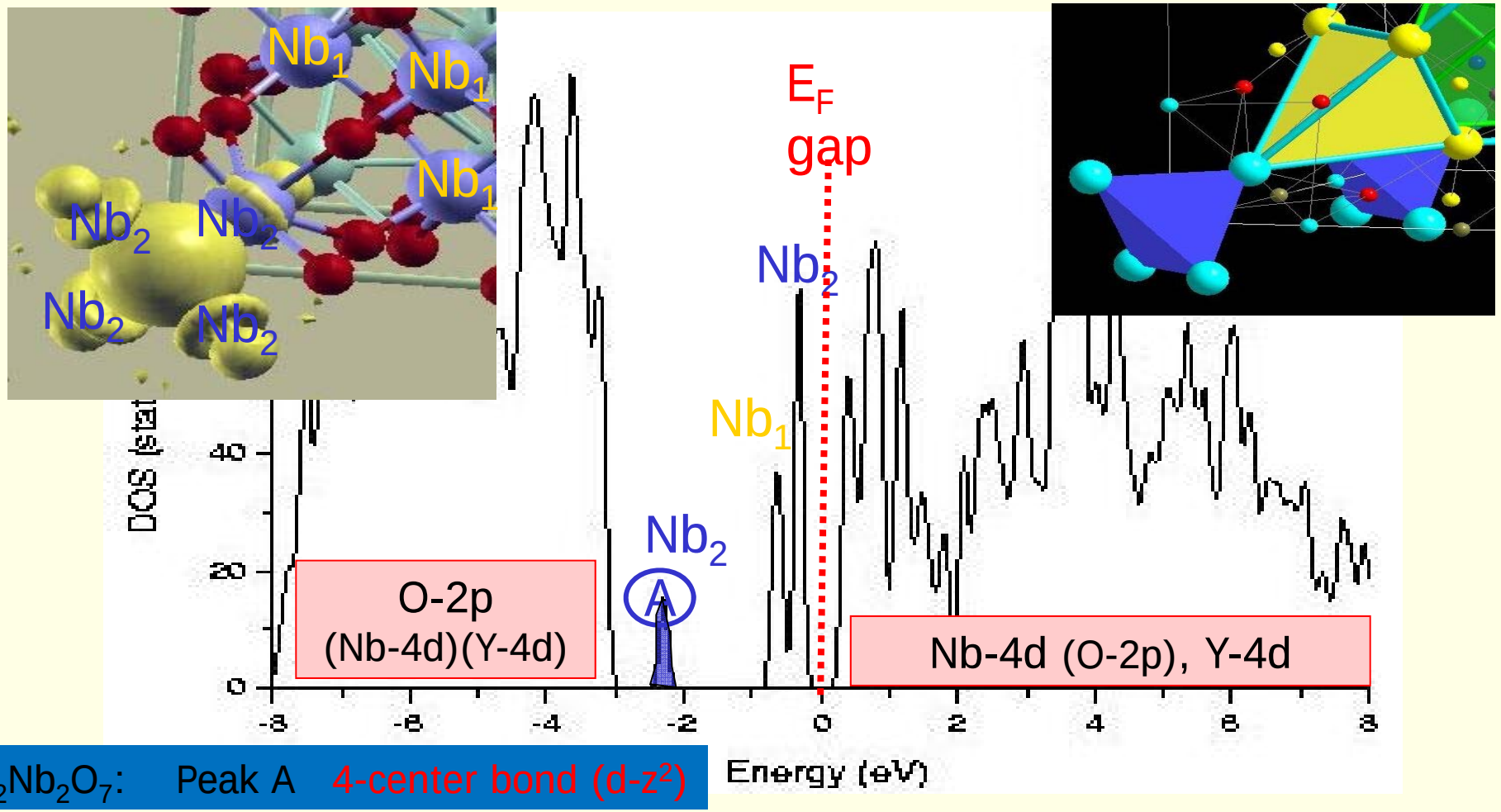




V.Strocov et al., PRL **109** (2012), 086401

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 ($\nabla\rho.\vec{n}=0$)*



$Y_2Nb_2O_7$: Peak A 4-center bond (d-z^2)

Properties with WIEN2k - II

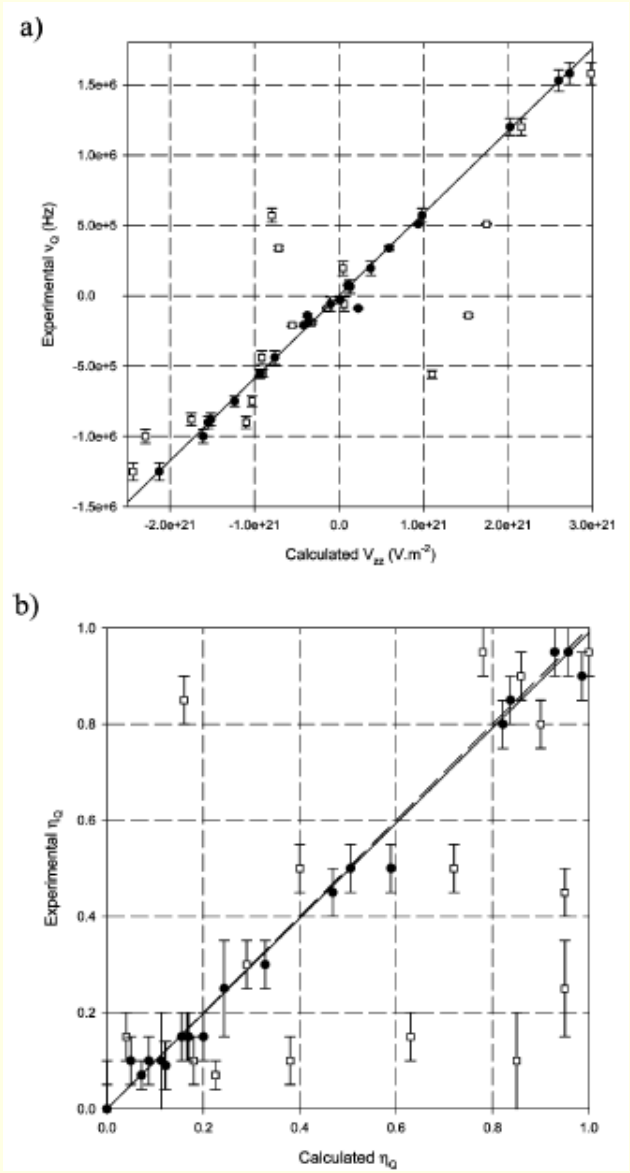
- **Hyperfine parameters** (NMR, Mössbauer, PAC)
  -
  - **hyperfine fields** (contact + dipolar + orbital contribution)
  - **NMR chemical shifts**
  - **Mössbauer Isomer shifts**
  - **Electric field gradients**

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

$$\nu_Q = \frac{3eQV_{zz}}{2I(2I-1)h} \qquad \eta_Q = \frac{V_{yy} - V_{xx}}{V_{zz}}$$

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

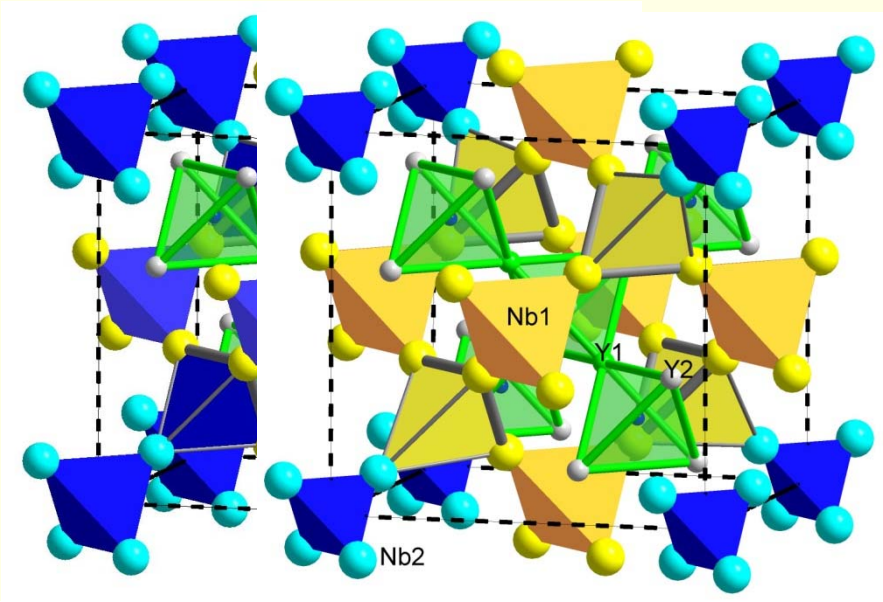
M.Body et al., *J.Phys.Chem. A 2007, 111, 11873*

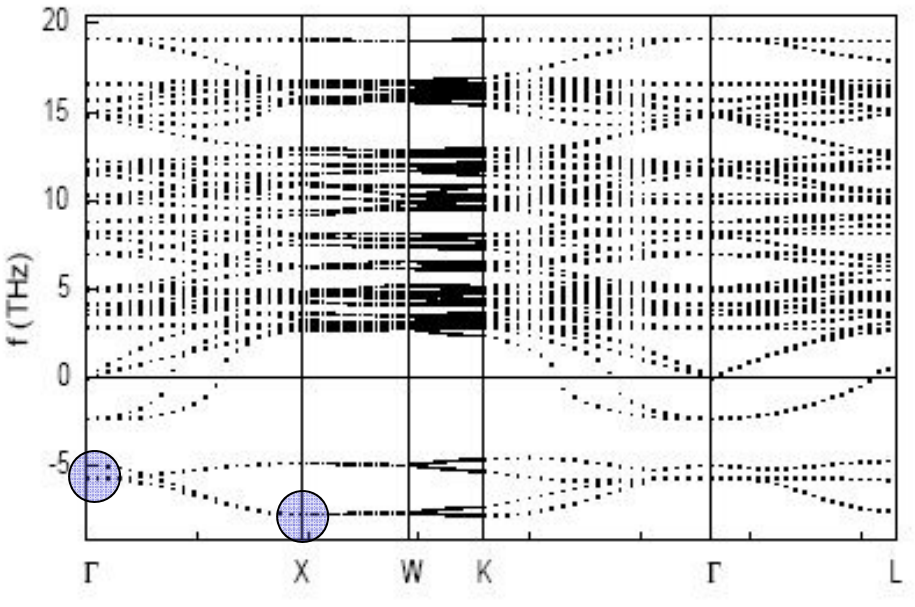


Properties with WIEN2k - III

- Total energy and forces
  - *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

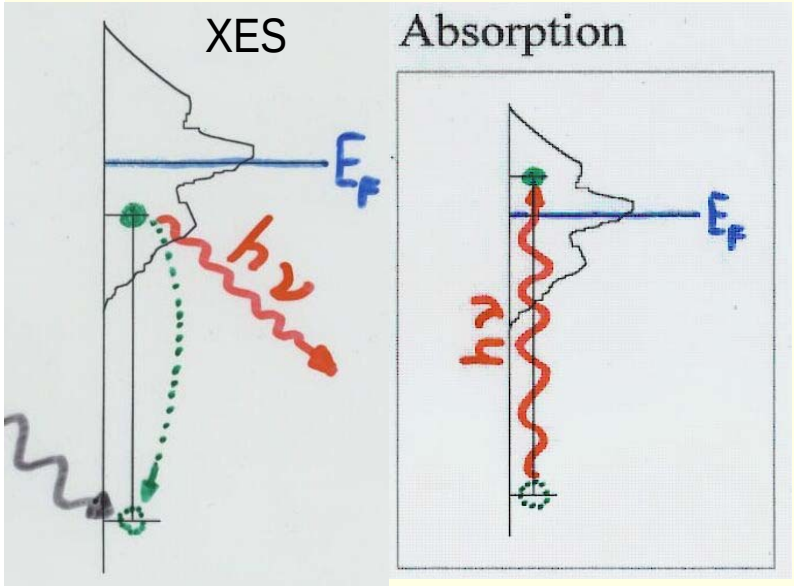
Pyrochlore structure of $Y_2Nb_2O_7$: **metallic** instead of an **insulator**
strong **phonon instabilities** → phase transition → **insulator**





Properties with WIEN2k - IV

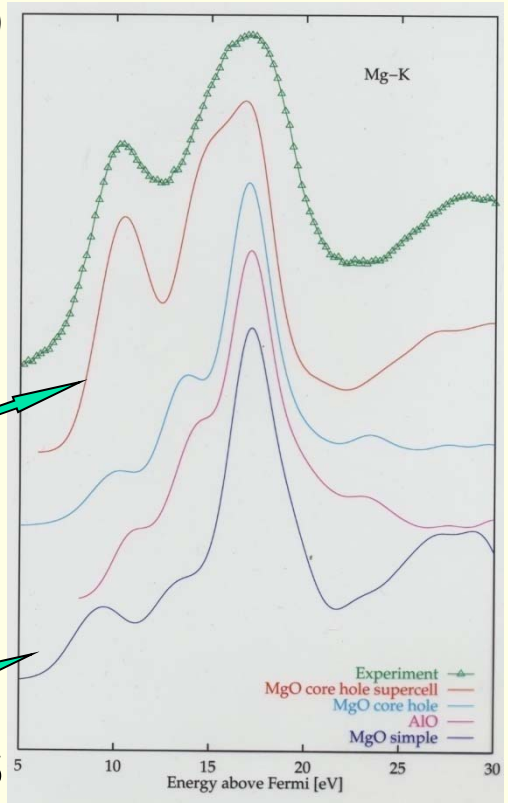
- Spectroscopy
  - *XPS core levelshifts (with half-core holes, Slater's transition state)*
  - *X-ray emission, absorption, electron-energy-loss*
    - (core - valence/conduction-band transitions with matrix elements and angular dep.)
    - EELS including possible non-dipol transititons (momentum transfer)
  - *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

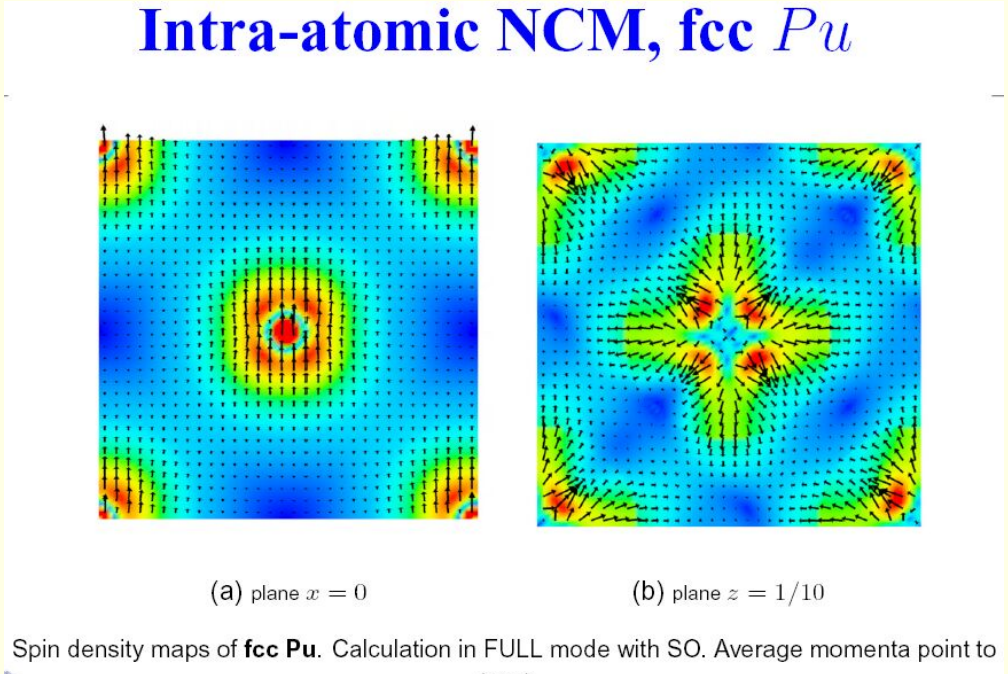
including a core-hole
in supercell
(Final state rule)

from ground-state DOS



Properties with WIEN2k - V

- WIENNCM: non-collinear magnetism (spin-spirals to fully-relativistic) (R.Laskowski)
- BOLTZTRAP by G.Madsen: (transport, fermi velocities, Seebeck, conductivity, thermoelectrics)
- ATAT@WIEN2k (C.Draxl) : alloy theoretical automatic toolkit
- BSE (R.Laskowski) Bethe-Salpether equation for electron-hole interactions; excitons
- Berry-PI: (O. Rubel): berry-phases for electric fields, polarization, Born charges, piezoelectricity
- GW (M.Scheffler):
- **w2wannier** (J.Kunes et al)
- interfaced with TRIQS (M. Aichhorn)



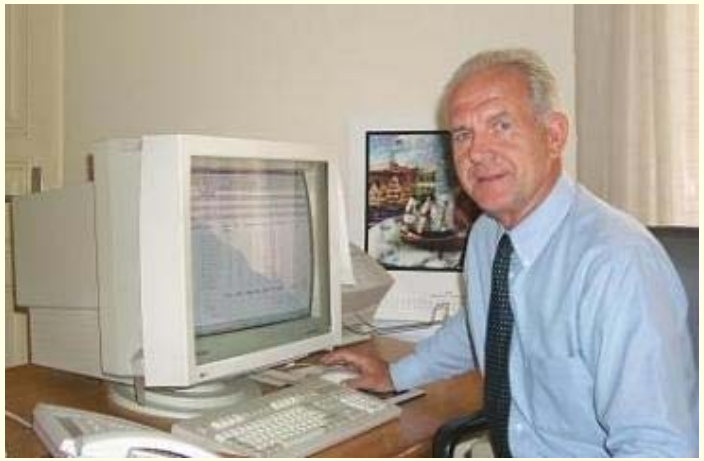
Advantage/disadvantage of WIEN2k

+ robust all-electron full-potential method (new effective mixer by L.Marks)
+ unbiased basisset, single convergence parameter (LDA-limit)
+ all elements of periodic table (equal expensive), metals
+ LDA, GGAs, meta-GGA, LDA+U, hybrid-DFT, spin-orbit
+ many properties and tools (supercells, structeditor, 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: scales as n^3, but:*
  - *+ fast iterative diagonalization and good parallelelization (k-points and mpi-fine-grain)*
  - *- full H, S matrix stored → large memory required*
  - *+ many k-points do not require more memory*
- no stress tensor

Acknowledgment

F.Tran

R.Laskowski



K.Schwarz

Thank you for
your attention !