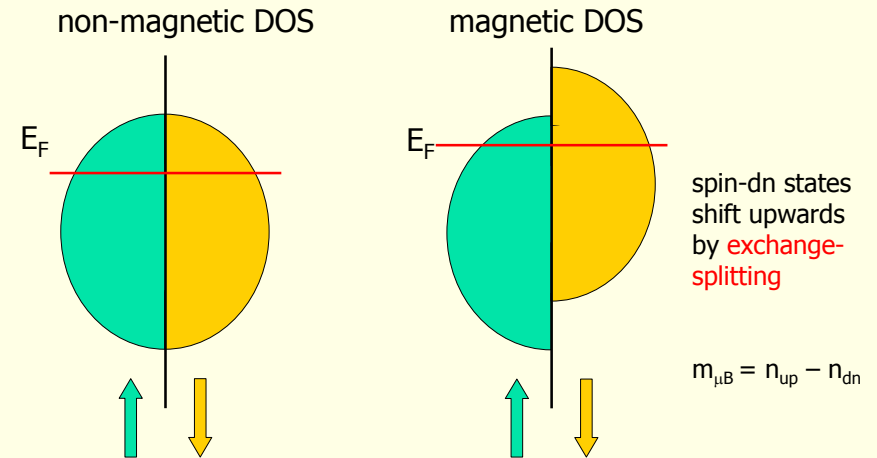
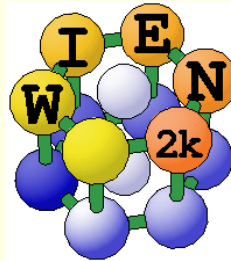


# Magnetism, relativistic effects strongly correlated solids

**Peter Blaha**

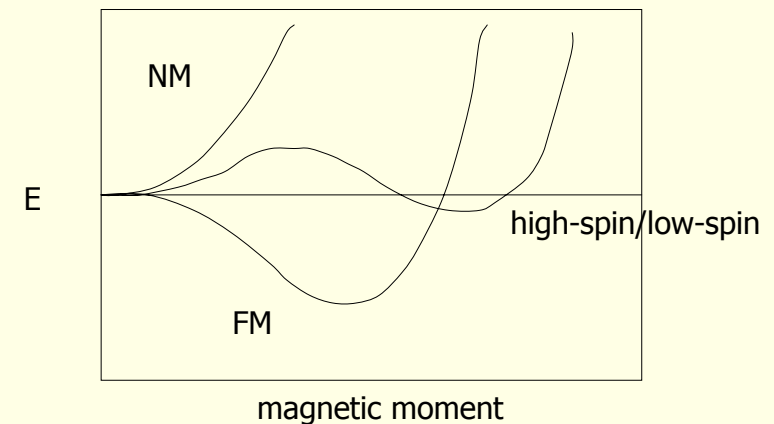
Institute of Materials Chemistry  
TU Vienna



## "Spin-polarized calculations"

- **runsp\_lapw** (for magnetic cases, case.clmup/dn)
  - runs lapw1/2 for both spins independently
- **case.scf** contains additional information:
  - :MMT total moment
  - :MMI001 moment within 1<sup>st</sup> atomic sphere
  - :HFF001 contact hyperfine field
- **runfsm\_lapw -m Moment** (fixed-spin-moment calc.)
  - for difficult to converge magnetic cases or simply to constrain a moment
- **runafm\_lapw** (Antiferromagnetic, use with care)
  - calculates only spin-up, uses symmetry to generate spin-dn
  - faster, more stable convergence
  - afminput requires "original" struct file or a symmetry operation which transforms the AFM-atoms into each other. The AFM subgroup can be "klassengleich" (bcc Cr) or "translationengleich" (same lattice, less symmetry)

## FSM curves





# Relativistic effects



## Relativistic effects:



### Dirac equation in central field (spherical symmetry):

$$\left[ \frac{p^2}{2m} + V - \frac{p^4}{8m^3c^2} - \frac{\hbar^2}{4m^2c^2} \frac{dV}{dr} \frac{\partial}{\partial r} + \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV}{dr} (\vec{l}\vec{s}) \right] \Phi = \varepsilon \Phi$$

non-rel.SE

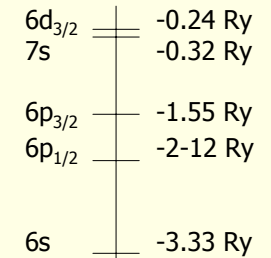
mass+Darwin

spin-orbit

Due to SO spin  $s$  and orbital angular momentum  $l$  are no longer good quantum numbers. Instead use total angular momentum  $j = l + s$

	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

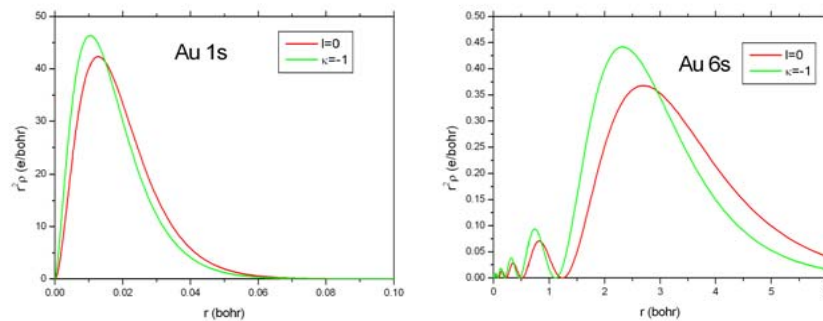
Thorium



## Relativistic orbital contraction



### Au s orbital (no SOC)

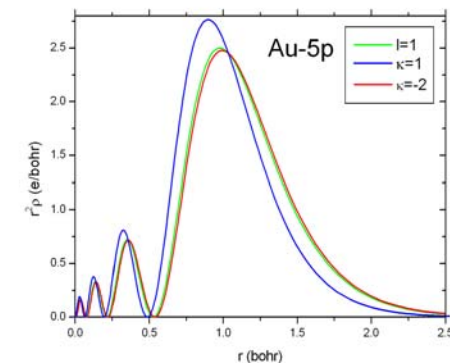


- 1s contracts due to relativistic mass enhancement
- 2s - 6s contract due to orthogonality to 1s

$$M = m / \sqrt{1 - (v/c)^2} \quad v \text{ proportional } Z: \text{ Gold: } Z = 79; M = 1.2 m$$



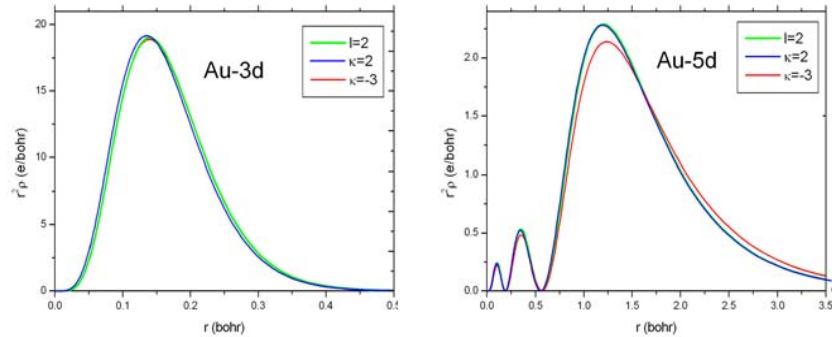
## SOC splitting: Au 5p state



- Spin Orbit splitting of l-quantum number.
- p<sub>1/2</sub> ( $\kappa=1$ ): markedly different behavior than non-relativistic p-state
- g <sub>$\kappa=1$</sub>  : non-zero at nucleus



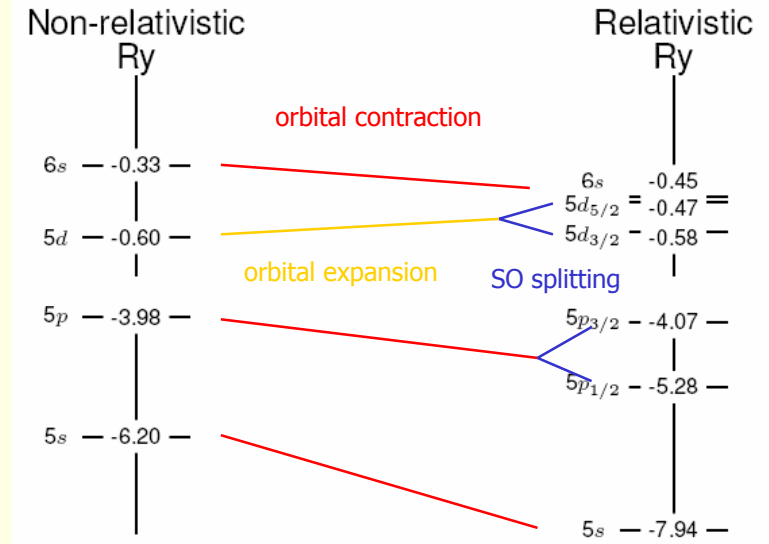
## Orbital expansion: Au d states



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



## Gold – atomic spectra



## Scalar relativistic approximation



Drop all terms which depend on  $\kappa$ , keep Darwin and enhanced mass  $M$  and modified large  $\tilde{g}$  and small  $\tilde{f}$  component of  $\Phi$

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

$$\text{with } M = m + \frac{\varepsilon - V}{2c^2} \quad \tilde{f} = \frac{1}{2Mc} \frac{d\tilde{g}}{dr}$$

Spin  $s$  and  $l$  are still good quantum numbers.  
The four-component wave function  $\tilde{\Psi}$  contains  $\tilde{\Phi}$  as pure spin state

$$\tilde{\Psi} = \begin{pmatrix} \tilde{\Phi} \\ \tilde{\chi} \end{pmatrix} \quad \tilde{\Phi} = \tilde{g} Y_{lm} \chi_s$$



## Spin-orbit in second variation



Use the scalar-relativistic (pure-spin) eigenstates  $\tilde{\Psi}_n$  (with  $E_n < E_{\text{cut}}$ ) as basis and add Spin-orbit interaction:

$$H \tilde{\Psi} = \varepsilon \tilde{\Psi} + H_{so} \tilde{\Psi} \quad H_{so} = \frac{1}{4M^2c^2} \frac{1}{r} \frac{dV}{dr} \begin{pmatrix} \vec{\sigma} \vec{l} & 0 \\ 0 & 0 \end{pmatrix}$$

SO mixes spin-up and dn states (“doubles matrixsize”).

Scalar-relativistic p-orbital is similar to  $p_{3/2}$  wave function, but  $\tilde{\Psi}$  does not contain  $p_{1/2}$  radial basis function:

Add “Local orbital” with  $p_{1/2}$  radial function



# Relativistic semi-core states in fcc Th

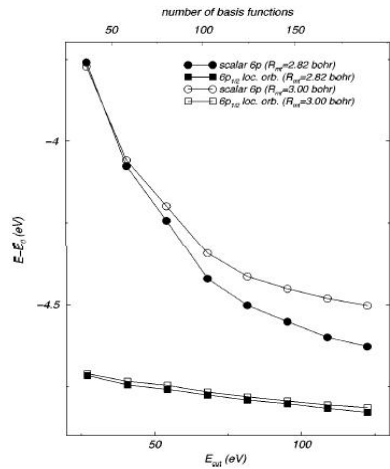


FIG. 1. The total energy  $E$  as a function of the second-variation cutoff energy  $E_{cut}$  (the approximate size of the second-variational-step basis, including spin, is marked on the top axis) for two different muffin-tin radii. The standard FLAPW results are marked with circles, the results obtained with the additional  $p_{1/2}$  local orbitals are marked with squares (the latter energies were increased by 3 eV in order to show the curves on the same plot).

- additional local orbitals for  $6p_{1/2}$  orbital in Th
- Spin-orbit (2<sup>nd</sup> variational method)

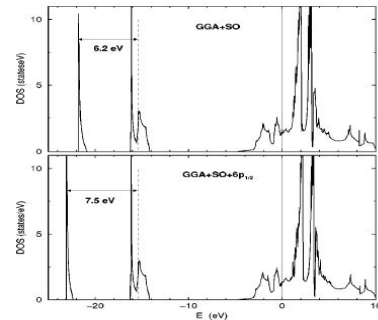


FIG. 2. Density of states calculated with the scalar relativistic basis (top panel) and with the  $p_{1/2}$  local orbitals extended basis (bottom panel). The splitting between the centers of  $6p_{1/2}$  and  $6p_{3/2}$  bands is shown.

J.Kuneš, P.Novak, R.Schmid, P.Blahá, K.Schwarz, Phys.Rev.B. 64, 153102 (2001)

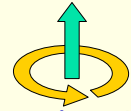


# Spin-orbit coupling: magnetic systems



## ■ magnetic systems:

- Define direction of magnetism (coupled to the lattice only by SO, magneto crystalline anisotropy)
- Possible reduction of symmetry: magnetic field breaks time-inversion and spin transforms like a pseudovector (current due to magn.field)



- number of symmetry operations reduced
- Irreducible BZ enlarged (do NOT "add" Inversion!)
- atoms may become non-equivalent, reduced local symmetry (more LM)
- *initso\_lapw* (with *symmetso*) dedects new symmetry and creates new files (*case.struct*, *in\**, *clm\**).
- Symmetry operations are classified into
  - 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.

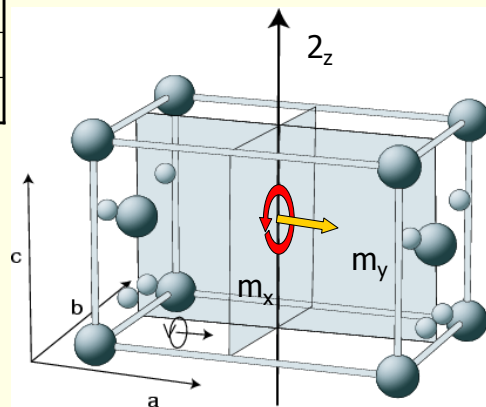


# spin-orbit coupling: symmetry



## 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



# Spin-orbit coupling



## ■ WIEN2k offers several levels of treating relativity:

- *non-relativistic*: select *NREL* in *case.struct* (not recommended)
- *standard*: fully-relativistic core, scalar-relativistic valence
  - mass-velocity and Darwin s-shift, no spin-orbit interaction
- "fully"-relativistic:
  - adding SO in "second variation" (using previous eigenstates as basis)
  - adding p-1/2 LOs to increase accuracy (caution!!!)
    - x lapw1 (increase E-max for more eigenvalues, to have a better basis for lapwso)
    - x lapwso
    - x lapw2 -so -c SO ALWAYS needs complex lapw2 version
- Non-magnetic systems:
  - SO does NOT reduce symmetry. *initso\_lapw* just generates *case.inso* and *case.in2c*.
- Magnetic systems:
  - *symmetso* dedects proper symmetry and rewrites *case.struct/in\*/clm\**



# case.inso



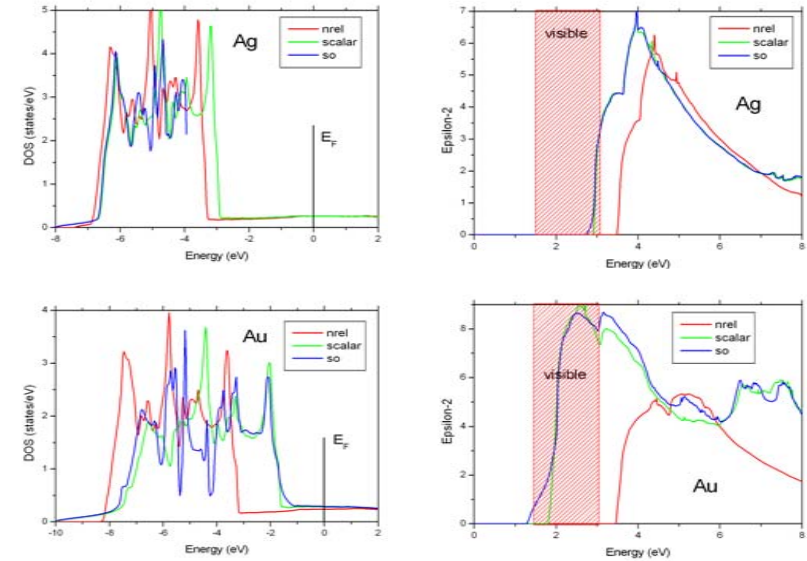
```

WFFIL
4 1 0
-10.0000 1.50000
0. 0. 1.
1
2 -0.97 0.005
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



# Ag – Au: the difference



# Spin-orbit splitting of the L-gap surface state on Au-111 and Ag-111



G. Nicolay, F. Reinert, S. Hüfner, P.Blaha, PRB 65,33407

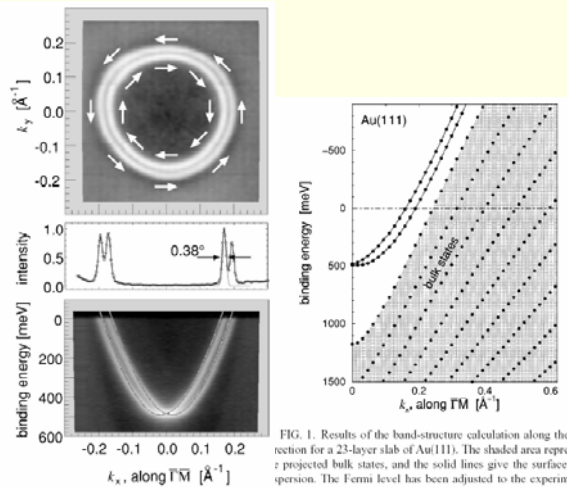


FIG. 1. Results of the band-structure calculation along the direction for a 23-layer slab of Au(111). The shaded area represents projected bulk states, and the solid lines give the surface dispersion. The Fermi level has been adjusted to the experimental position.

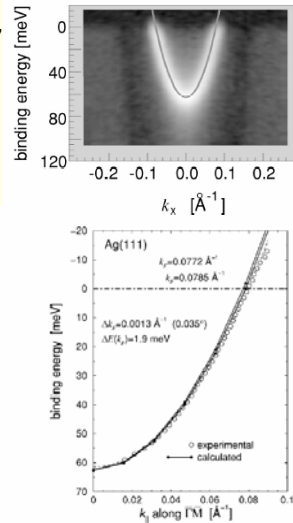


FIG. 4. Comparison of experimental (open circles) and calculated results (filled circles) of the L-gap surface state of Ag(111). The SO splitting in momentum is only  $\Delta k=0.0013 \text{ \AA}^{-1}$ , equivalent to an angle of  $0.035^\circ$  at  $\text{HeI}$ . At the Fermi level the corresponding splitting in the EDC's is  $\Delta E=1.9 \text{ meV}$ .



# Beyond LDA (GGA)



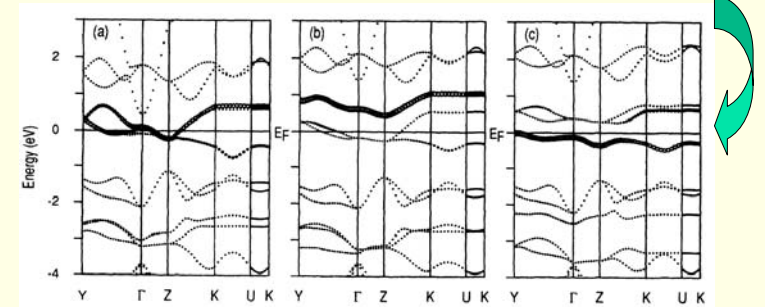
# LDA+U



- Standard LDA (GGA) gives good description of structural and electronic properties of most solids (lattice parameters within 1-2%, at least qualitatively correct bandstructure, metal-insulator, magnetism,...)
- Problems: "localized" (correlated) electrons
  - late 3d transition metal oxides/halides
    - metals instead of insulators (FeO, FeF<sub>2</sub>, cuprates, ...)
    - nonmagnetic instead of anti-ferromagnetic (La<sub>2</sub>CuO<sub>4</sub>, YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub>)
  - 4f, 5f electrons
    - all f-states pinned at the Fermi energy, "always" metallic
    - orbital moments much too small
  - "weakly" correlated metals
    - FeAl is ferromagnetic in theory, but nonmagnetic experimentally
    - 3d-band position, exchange splitting,...

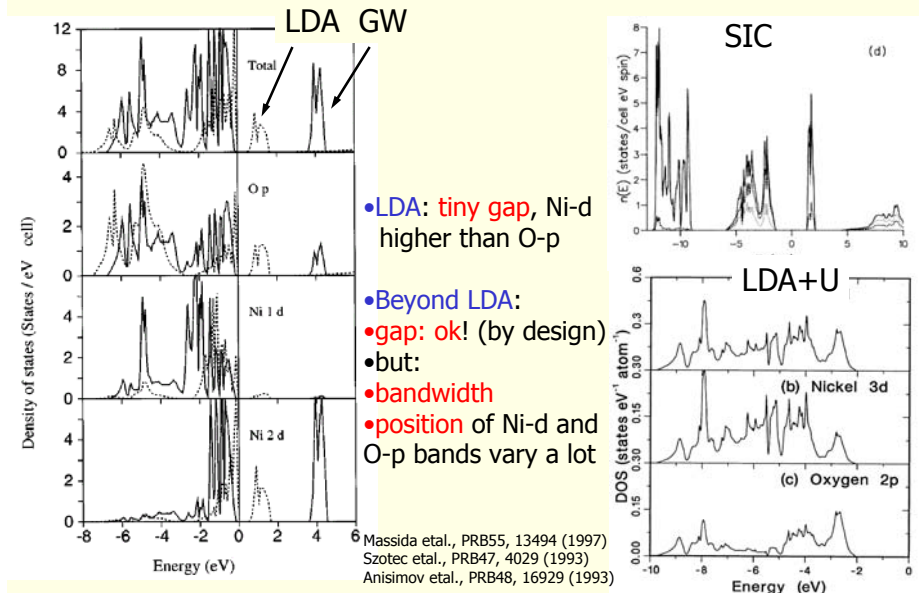


- FeO
  - PBE-GGA
  - EV-GGA (splits bands with good "start")
- Cuprates (La<sub>2</sub>CuO<sub>4</sub>, YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub>)
  - LDA and GGA yields non-magnetic metals instead of AFM insulators



ab initio methods

- GGA: usually improvement, but often too small.
- Exact exchange: imbalance between exact X and approximate C
- Hybrid functionals: Hartree-Fock + LDA/GGA mix (adiabatic connection)
- GW: gaps in semiconductors, but groundstate? expensive!
- Quantum Monte-Carlo: very expensive
- not fully ab initio
  - Self-interaction-correction: vanishes for Bloch states
  - Orbital polarization: Hund's 2<sup>nd</sup> rule by atomic Slater-parameter
  - LDA+U: strong Coulomb repulsion via external Hubbard U parameter
  - DMFT: extension of LDA+U for weakly correlated systems



Massida et al., PRB55, 13494 (1997)  
 Szotec et al., PRB47, 4029 (1993)  
 Anisimov et al., PRB48, 16929 (1993)



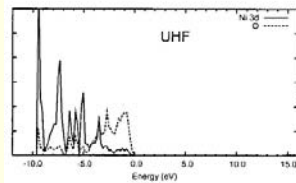
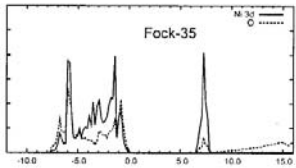
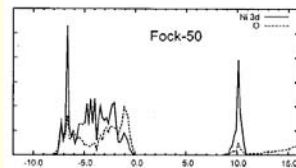
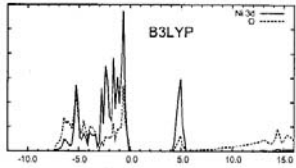
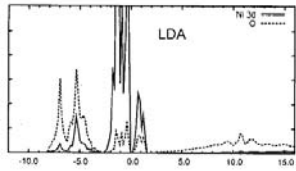


# "Beyond-LDA" results for NiO



I. Moreira et al., PRB65,155102 (2002)

LDA, hybrid-DFT or Hartree-Fock:



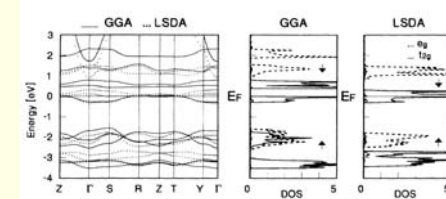
# Beyond LDA:



- gaps, bandstructure (spectra): not groundstate properties
  - validity is difficult to judge
  - some properties (like gaps or magnetic moments) are obtained by "design"
- compare electron density (or "related" quantities)
  - X-ray diffraction has improved (synchrotrons, detectors), but only for Si it might be accurate enough to test DFT-methods

➔ Electric field gradients

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



# LDA+U method



Separation of electrons into two subsystems:

- itinerant electrons (described by LSDA)
- Localized d (f) electrons:

$$E^{ee} = \frac{1}{2}UN^2 - \frac{1}{2}J\sum_{\sigma}N_{\sigma}^2 - \frac{1}{2}(U-J)\sum_{\sigma}n_{m,\sigma}^2$$

N...total number of e n<sub>m,σ</sub>...orbital occupancies

Hubbard U describes the coulomb energy cost to place two electrons at the same site:

$$U = E(n+1) + E(n-1) - 2E(n) \quad \begin{matrix} n & n & n+1 & n-1 \\ \bullet & \bullet & \bullet & \bullet \end{matrix}$$

J is the averaged intraatomic exchange parameter



# LDA+U Functional



Define a new energy functional:

$$F^{LDA+U} = F^{LDA} + E^{ee}(n_m) - F^{dc}(n_m)$$

Double counting term F<sup>dc</sup> can be approximated in several ways

- Fully localized limit (Anisimov et al.): Assumes that the total number of d (f) electrons N=Σ n<sub>m</sub> is given properly by LDA (but not the eigenvalues). Their energy is (SIC free Hartree energy):

$$E^{dc} = \frac{U}{2}N(N-1) - \frac{J}{2}\sum_{\sigma}N_{\sigma}^2$$

➔ V<sub>m,m',σ</sub> = (U - J)(1/2 - n<sub>m,m',σ</sub>) can shift center of bands

- Around mean field approximation (Czyzyk&Sawatzky):

$$E^{dc} = \frac{1}{2}UN^2 - \frac{1}{2}J\sum_{\sigma}N_{\sigma}^2 - \frac{1}{2}(U-J)\sum_{\sigma}n_{aver,\sigma}^2$$

➔ V<sub>m,m',σ</sub> = (U - J)(n<sub>aver,σ</sub> - n<sub>m,m',σ</sub>) leaves center unchanged

- Orbitals with occupancies n<sub>m,m',σ</sub> larger than 1/2 (or n<sub>average</sub>) become more occupied, others become depopulated.



# rotational invariant LDA+U



- In essence, LDA+U shifts occupied states ( $n_i > 1/2$ ) down in energy by  $U/2$  (increasing the occupation  $n_i$ ) and empty states up (decreasing their occupation).
- A generalization leads to the "rotational invariant LDA+U" method, which is independent of coordinate systems, uses the full density matrix  $n_{m,m'}$  and two parameters, Hubbard  $U$  and Stoner exchange  $J$ .
- $U$  and  $J$  can be taken from experiment or estimated by constraint LDA calculations (see recipe on our website).  
( $U \dots 2-10$  eV,  $J \dots 1-2$  eV)



# LDA+U in WIEN2k:



cp \$WIENROOT/SRC\_templates/case.inorb .  
cp \$WIENROOT/SRC\_templates/case.indm .  
(done automatically in w2web)

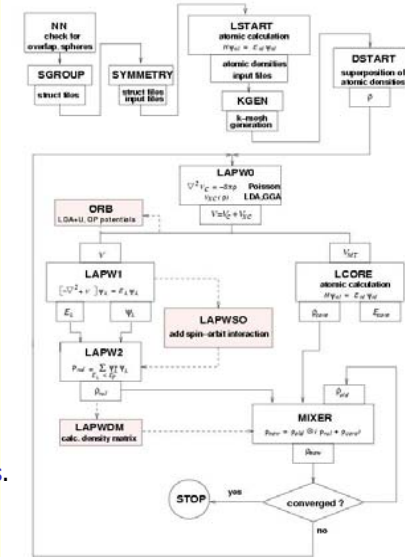
Specify atoms, orbitals, double counting correction (FLL) and  $U$  ( $J=0$ )

runsp\_lapw -orb

for nonmagnetic cases use

runsp\_c\_lapw -orb

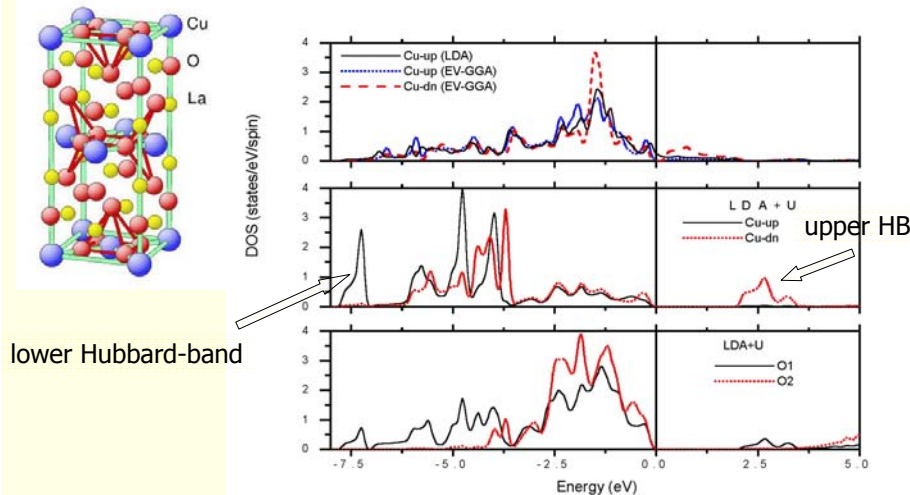
Note: Different solutions may be obtained when starting from different density matrices.



# Cuprates



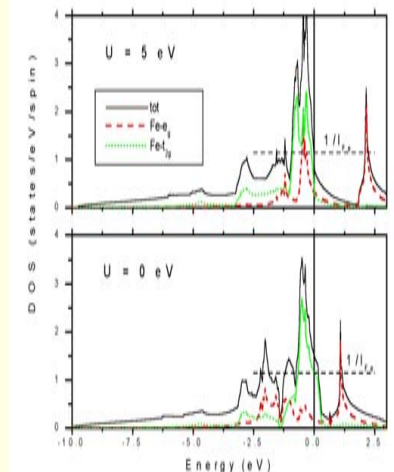
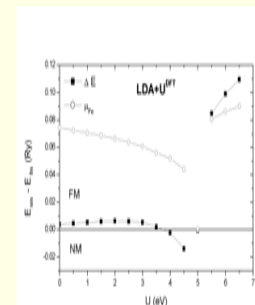
- $La_2CuO_4$ : nonmagnetic metal instead of AFM insulator



# LDA+U in weakly correlated metals: FeAl



- Experimentally
  - $FeAl$  is nonmagnetic
- DFT
  - Conventional LSDA calculation
    - yields a ferromagnetic ground state
  - LDA+U(AFM)
    - nonmagnetic
    - $Fe-t_{2g}$  and  $Fe-e_g$  affected differently



P.Mohn, C.Persson, P.Blaha, K.Schwarz, P.Novak, H.Eschrig,  
Correlation induced paramagnetic ground state in FeAl  
Phys.Rev.Lett. 87, 196401 (2001)