(Approximate) Exact Exchange for correlated electrons.

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Plan

- Hartree-Fock vs. DFT
- LDA+U $\Rightarrow$ Approximate Exact Exchange
- Implementation to WIEN2k
- Examples: hcp Gd, NiO, FeF_2, (FeAl, Ni_3Ga, Ni_3Al)
- Bad and good aspects
- What next
- Conclusions

Hartree-Fock vs. DFT

H-F	DFT (LSDA, GGA)
no correlation	correlation included
wrong for delocalized states	exact for jellium
one particle excitations	only ground state
no selfinteraction	selfinteraction
	(for localized states)
overshoots localization	wrong ground state
	(sometimes)
too large gaps	too small gaps
difficult for crystals	easy for crystals
corrections transparent	corrections difficult

Hartree-Fock

Hartree-Fock equations:

$$\left[-\Delta_i + V(\vec{r}_1) + \sum_i \int d\vec{r}_2 \frac{|\varphi_i(\vec{r}_2)|^2}{|\vec{r}_1 - \vec{r}_2|}\right] \varphi_j(\vec{r}_1) -$$

$$\sum_{\vec{s}_i \| \vec{s}_j} \int d\vec{r}_2 \frac{\varphi_j^*(\vec{r}_2)\varphi_i(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} \varphi_i(\vec{r}_1) = E_i \varphi_j(\vec{r}_1)$$

no selfinteraction, but
iteration requires knowledge of all occupied orbitals.
Program CRYSTAL
(V.R. Saunders, R. Dovesi, Daresbury, Turin)
CRYSTAL03 - LSDA as an option

$\Rightarrow$ hybrid HF-DFT methods F. Cora et al. 2004

Exact Exchange

Exact Exchange in DFT:
construct density dependent, local functional
that provides the same solution as the functional with nonlocal, exact exchange.
Program EXCITING

(Graz group, Claudia Ambrosch-Draxl, 2005)

LDA+U $\Rightarrow$ '$\approx$' Exact Exchange

Select subspace of states of correlated electrons
Construct DFT functional:

$$E = E_{LSDA}(\rho) + [\mathcal{E}^{screen}_{H-F}(\varphi^{m,\sigma}_{corr}) - E_{dc}(\rho_{corr})]$$

Screened Hartree-Fock interaction

$$\mathcal{E}^{screen}_{H-F} = \frac{U}{2} tr(\hat{n}\hat{n}) - \frac{J}{2}\sum_{\sigma} tr(\hat{n}^{\sigma}\hat{n}^{\sigma})$$

Double-counting term (Fully Localized Limit)

$$E_{dc} = \frac{U}{2} N_{corr}(N_{corr} - 1) - \frac{J}{2}\sum_{\sigma=\downarrow,\uparrow} N^{\sigma}_{corr}(N^{\sigma}_{corr} - 1)$$

LDA+U problems

Is LDA+U a DFT scheme?
YES, but
U, J are parameters that are fixed.

Often more solutions of scf procedure depending on starting density matrix.

Several schemes for double counting:

- Fully Localized Limit
- Around the Mean Field
- ...

U, J must be inserted $\Rightarrow$ not fully *ab-initio*

Our proposal

- Instead of double counting term:
  subtract all interactions between correlated electrons.
- Consider only atomic spheres (as in LDA+U)
- Use unscreened H-F energy.

$$E = E_{LSDA}(\rho) + [\mathcal{E}_{H-F}(\varphi^{m,\sigma}_{corr}) - \mathcal{E}_{LSDA}(\rho_{corr})]$$

$\mathcal{E}_{LSDA}$ includes Hartree and XC energy
Hartree term is the same in H-F and LSDA

$\Rightarrow$ only H-F (exact) exchange remains.

Hartree-Fock term

$$\mathcal{E}_{H-F} = \mathcal{E}_C + \mathcal{E}_X; \quad V_{ee} = \frac{1}{2}\sum_{i\neq j}\frac{1}{|\vec{r}_i - \vec{r}_j|}$$

$$\mathcal{E}_C = \frac{1}{2}\sum_{m_1..m_4}^{\sigma,\sigma'} n^{\sigma}_{m_1,m_2} < m_1, m_3|V^{ee}|m_2, m_4 > n^{\sigma'}_{m_3,m_4}$$

$$\mathcal{E}_X = -\frac{1}{2}\sum_{m_1..m_4}^{\sigma,\sigma'} n^{\sigma}_{m_1,m_2} < m_1, m_3|V^{ee}|m_4, m_2 > \delta_{\sigma,\sigma'} n^{\sigma'}_{m_3,m_4}.$$

$$< m_1, m_3|V^{ee}|m_2, m_4 >= \sum_k a_k(m_1, m_2, m_3, m_4)F^k$$

Slater integrals

$$F^k = \int_0^{r_s} \frac{r_<^k}{r_>^{k+1}} |u_l(r_1)|^2 |u_l(r_2)|^2 r_1^2 r_2^2 dr_1 dr_2$$

$$r_< = min(r_1, r_2),\ r_> = max(r_1, r_2)$$

$$\text{In WIEN}: \quad r^2 |u_l(r)|^2 = \rho_{00}(r)/(N_{corr}\sqrt{4\pi})$$

$$F^k = \frac{1}{4\pi N_{corr}^2} \int dr \int dr' \rho_{00}(r)\rho_{00}(r') \frac{r_<^k}{r_>^{k+1}}$$

Implementation

Three WIEN modules modifi ed: LAPW0 ($\rho \rightarrow V$), LAPW2 (ρ_{corr}), ORB

LAPW0

JOBEXEX

LAPW1 −up −orb

LAPW1 −dn −orb

LAPW2 −up

LAPW2 −dn

LCORE −up

LCORE −dn

MIXER

JOBEXEX

LAPW2 −up

LAPW2 −dn

LAPWDM −up

LAPWDM −dn

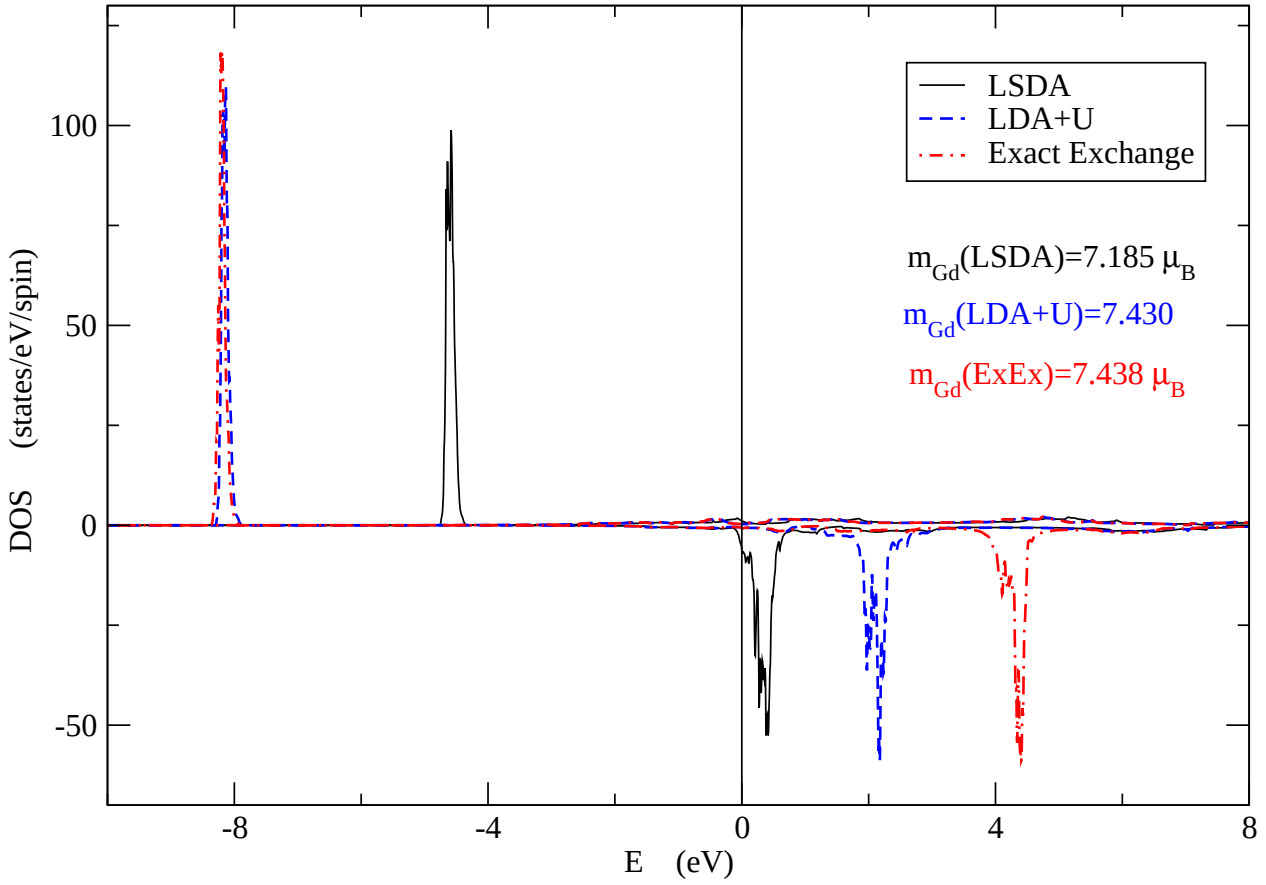
MIXER

LAPW0 −ex

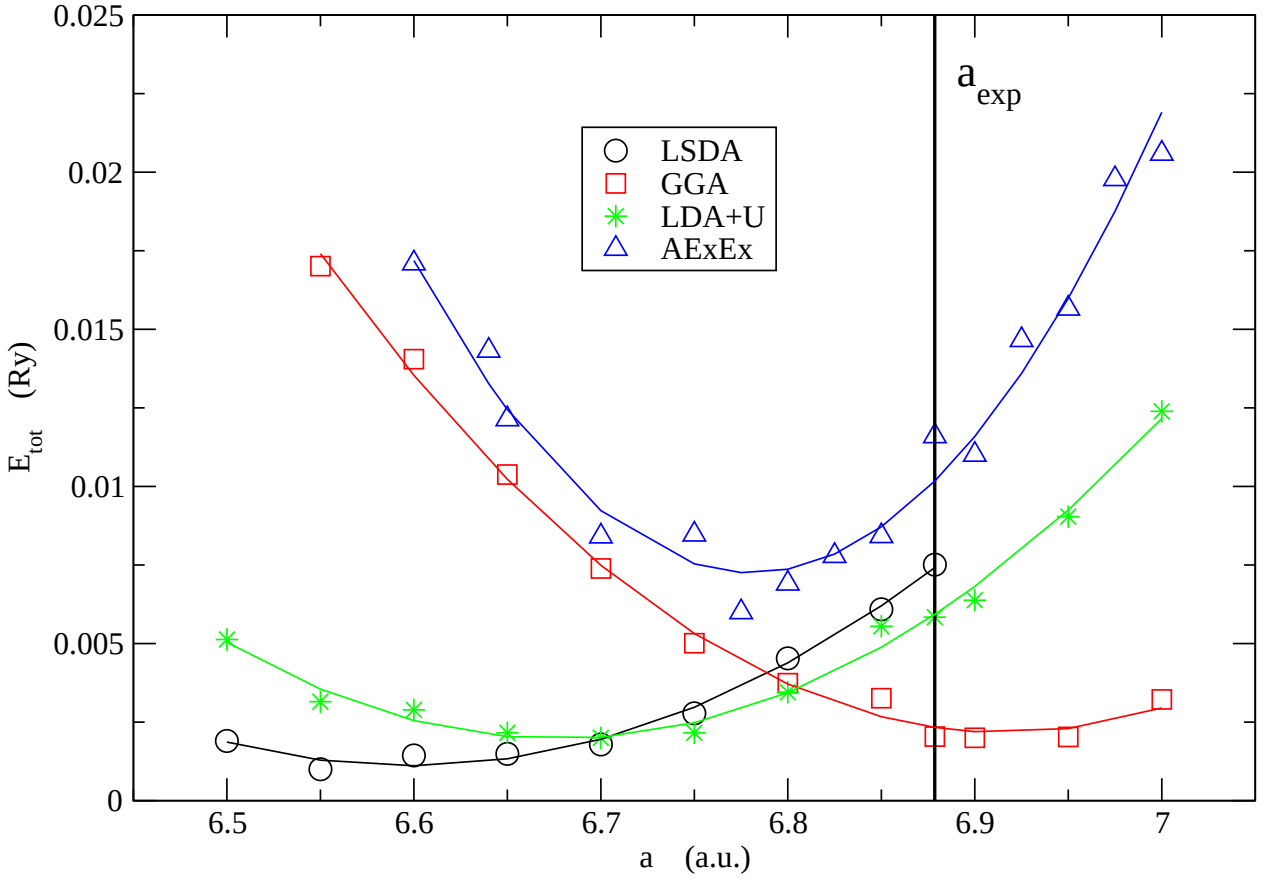
ORB −up −ex

ORB −dn −ex

Examples:hcp Gd



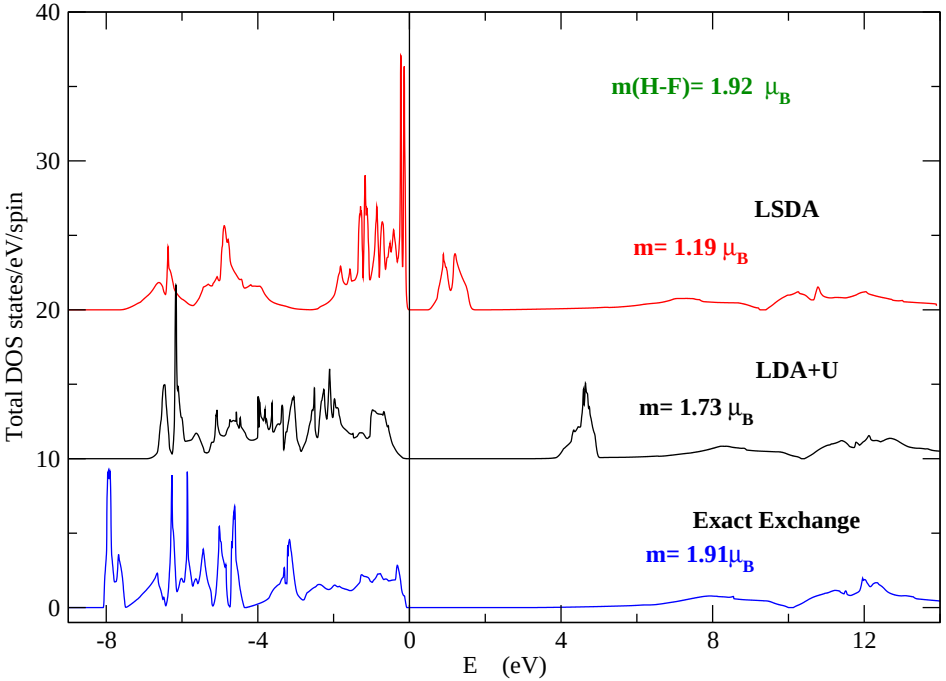
Examples:hcp Gd



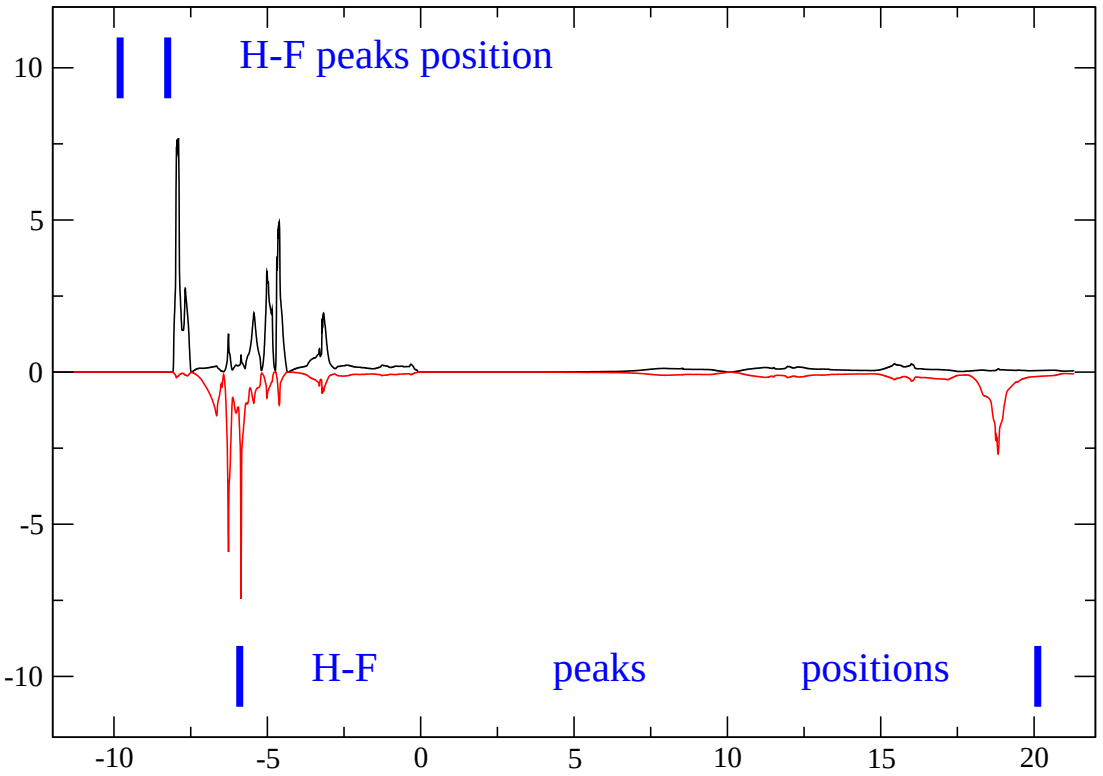
Examples:NiO

H-F calculation (CRYSTAL):

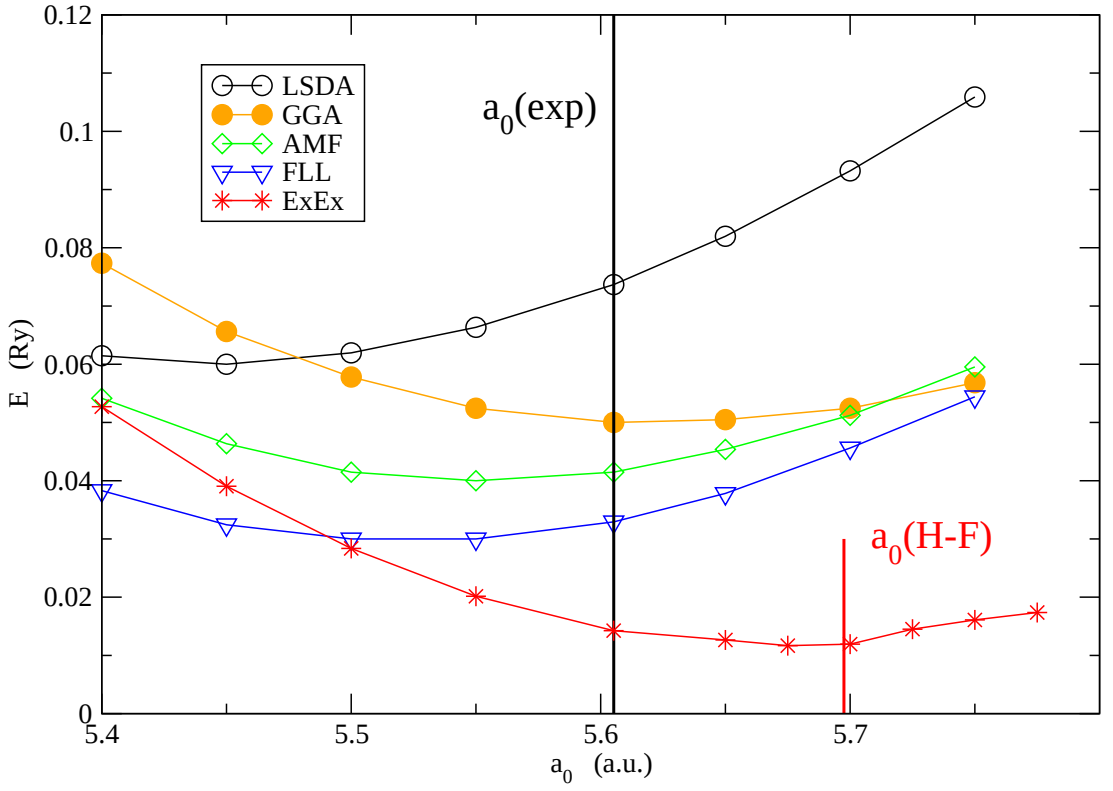
Towler et al. PRB 50,5041(1994)



NiO, continue

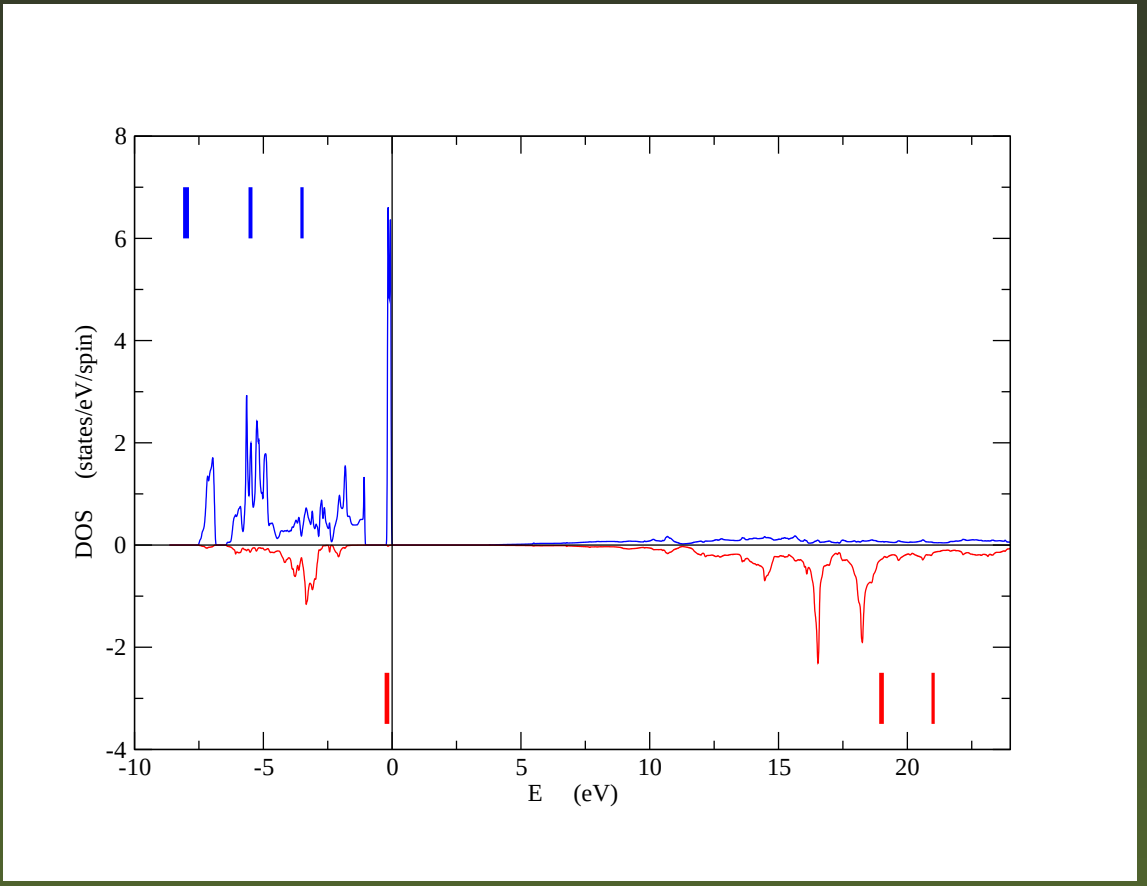


NiO, continue

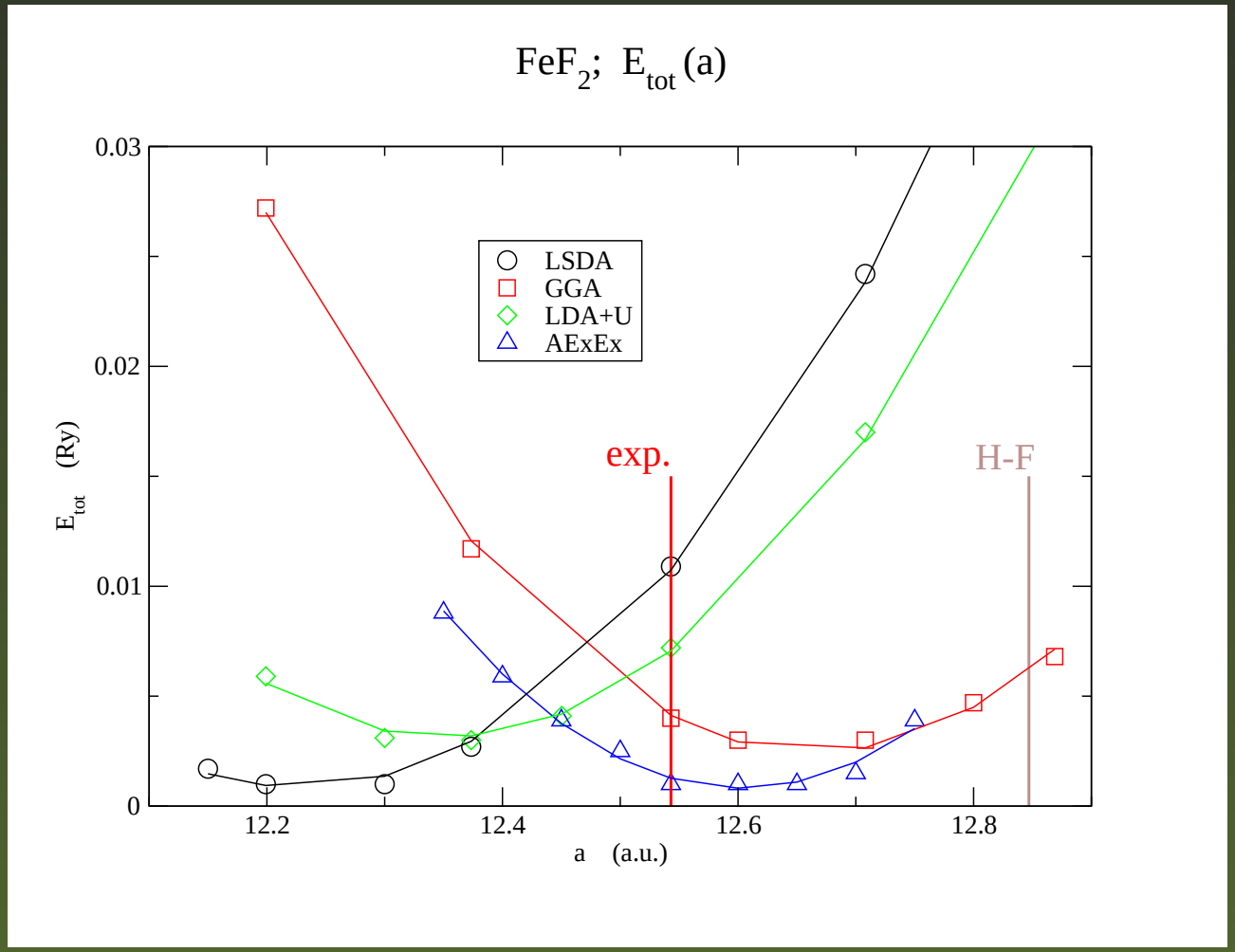


Examples:FeF_2

H-F calculation (CRYSTAL):
Valerio et al. PRB **52**, 2422 1995



FeF_2 continue



Magnetism

		LSDA	GGA	LDA+U	AExEx	HF	exp.
hcp Gd	m_s	7.356	7.567	7.762	7.792		
	m_l	0.310	0.230	0.008	0.002		
	m_{tot}	7.666	7.797	7.770	7.794		7.63
FeF_2	m_s	3.466	3.502	3.718	3.752	3.934	3.75
	m_l	0.247	0.098	0.097	0.100		
	m_{tot}	3.713	3.600	3.815	3.852		
NiO	m_s	1.199	1.378	1.734	1.913	1.924	1.90 (20)
	m_l	0.143	0.118	0.253	0.421		0.32 (5)
	m_{tot}	1.342	1.496	1.987	2.334		2.22 (25)

Bad aspects

- Still not fully ab-initio: correlated states must be selected.
- What to do with the interstitial?
  Results depend on muffin-tin radii to some extent.
- More solutions of scf procedure?
- More difficult to converge relative to LDA+U.
  Technical?
- Excessive localization.

Good aspects

- No parameters.
- Simple implementation.
- Little extra CPU and memory needed.
- Reasonable description of occupied states.
- Good starting point for
  - screened exchange
  - hybrid methods

What next?

- Screened exchange - very simple to implement.
- Hybrid functionals
  $(1-\alpha)$V(AExEx) + αV_{corr}(LSDA).
- Implementation to FPLO - no interstitial.
- More checks, more systems.

Conclusion

Leave LDA+U

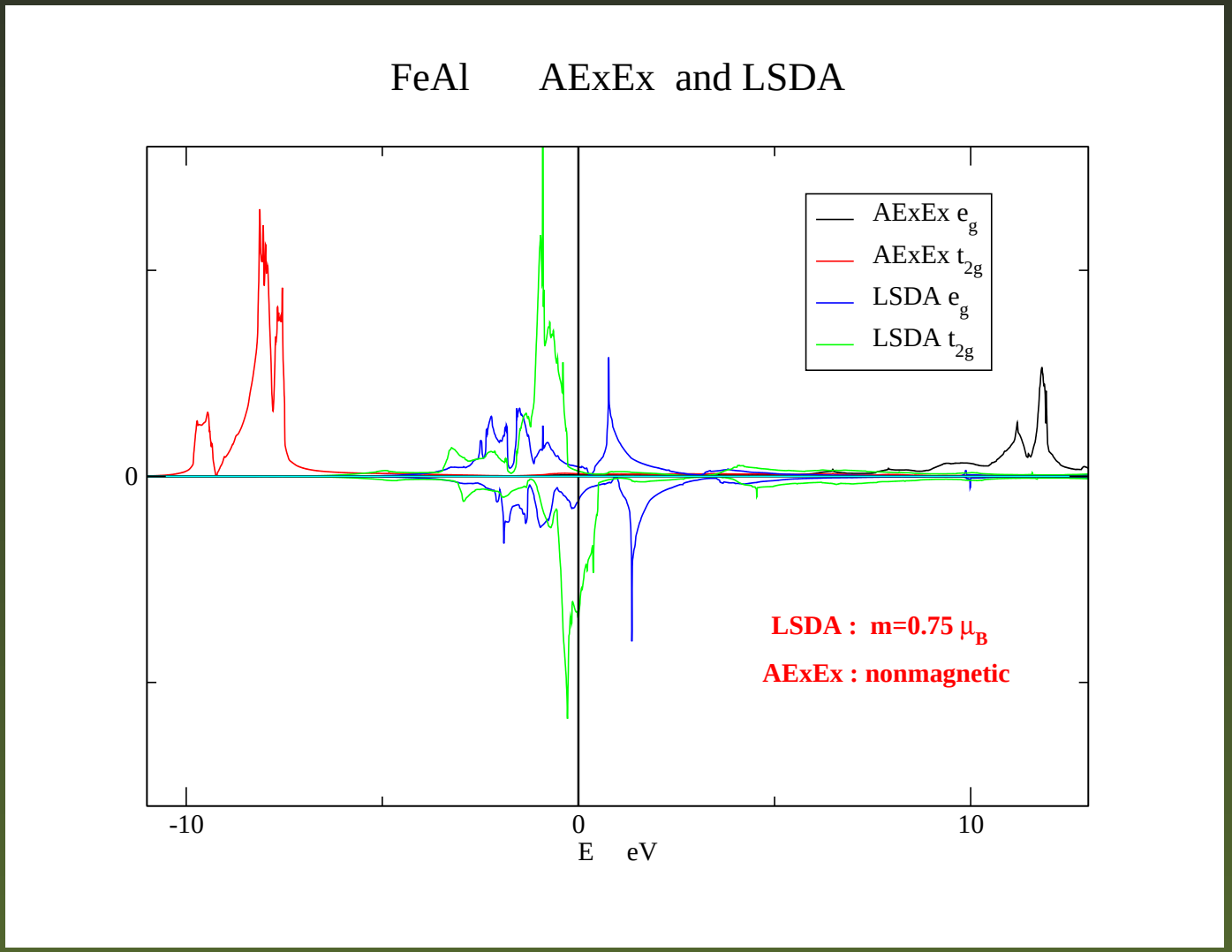
use AExEx instead

Collaboration

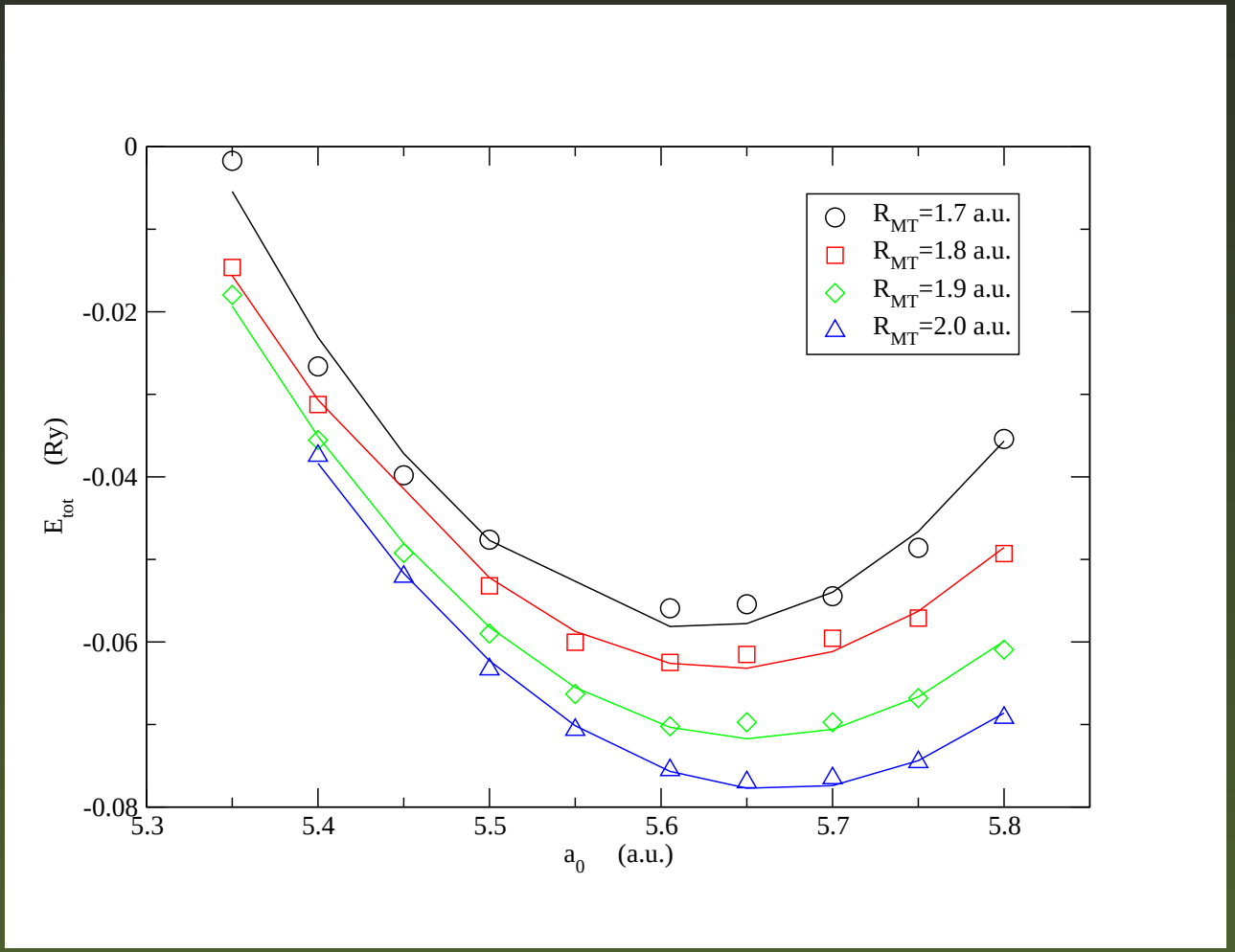
Warren E. Pickett, UC Davis
Jan Kuneš, UC Davis and Inst. of Physics

Laurent Chaput, Univ. Nancy

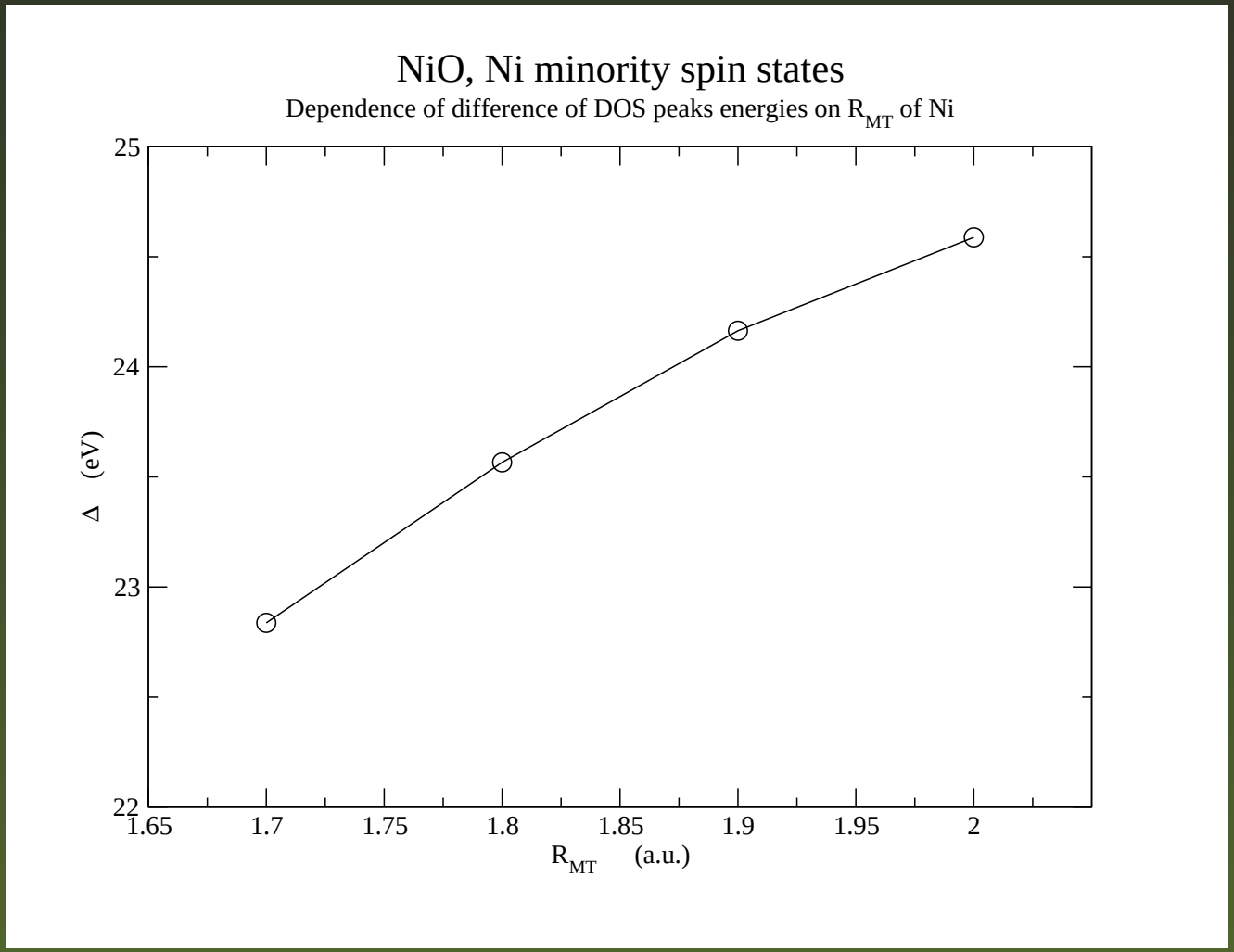
FeAl


FeAl AExEx and LSDA
AExEx e_g
AExEx t_{2g}
LSDA e_g
LSDA t_{2g}
0
-10
0
10
E eV
LSDA : m=0.75 μ_B
AExEx : nonmagnetic

NiO: RMT, E_{tot}


0
-0.02
-0.04
-0.06
-0.08
E_tot (Ry)
5.3
5.4
5.5
5.6
5.7
5.8
a_0 (a.u.)
R_MT=1.7 a.u.
R_MT=1.8 a.u.
R_MT=1.9 a.u.
R_MT=2.0 a.u.

NiO: RMT, DOS


NiO, Ni minority spin states
Dependence of difference of DOS peaks energies on R_{MT} of Ni
25
24
23
22
Δ (eV)
1.65
1.7
1.75
1.8
1.85
1.9
1.95
2
R_{MT} (a.u.)