Determination of *U* in the PAW approximation in ABINIT

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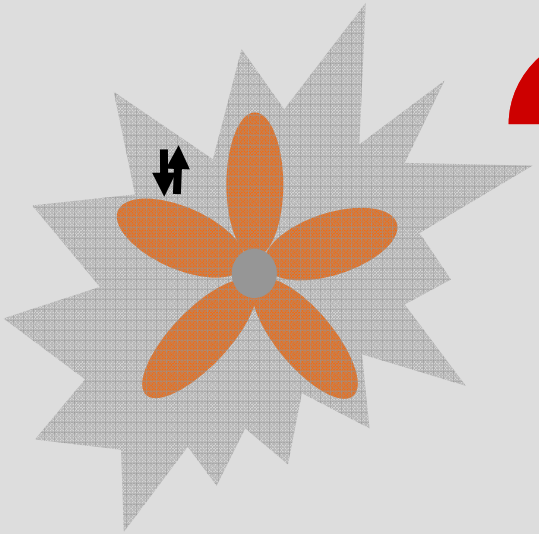
OVERVIEW

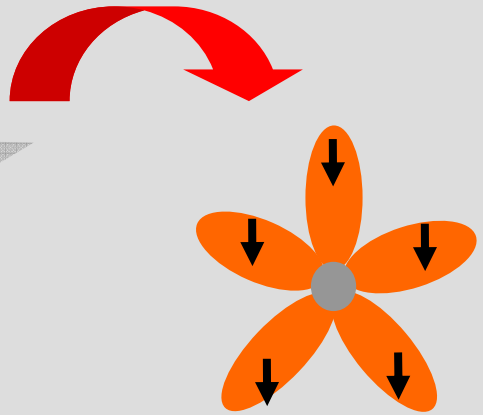
- MOTIVATION: DFT+U (DMFT)
- DETERMINATION U
- THEORY
- IMPLEMENTATION
- OUTLOOK
- CONCLUSIONS

MOTIVATION: LDA+U

LDA



LDA+U



$$E_U = E_{ee} - E_{d.c.} = \frac{U-J}{2}\sum_{i,\sigma} n_i^{\sigma} - (n_i^{\sigma})^2$$

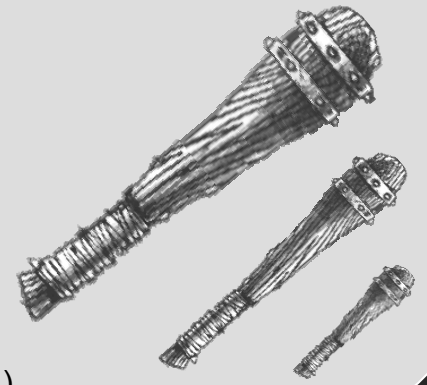
$$E_{ee} = U\sum_{i,j} n_i^{\uparrow} n_j^{\downarrow} + (U-J)\sum_{\sigma, i>j} n_i^{\sigma} n_j^{\sigma}$$

$$n = 0.5 \Rightarrow n - n^2 = 0.25$$

$$n = 0.1 \Rightarrow n - n^2 = 0.09$$

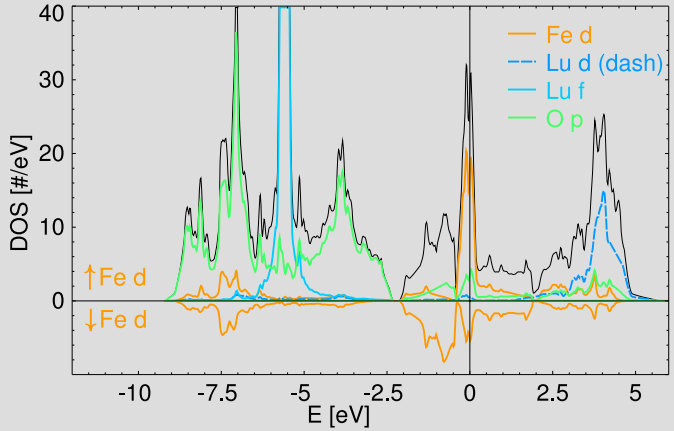
$$n = 0.9 \Rightarrow n - n^2 = 0.09$$

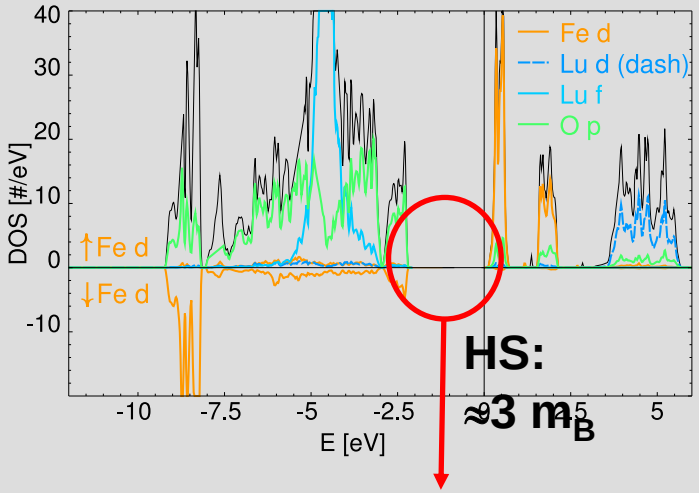
Anisimov, Gunnarsson PRB 43 (1991)



MOTIVATION: LDA+U

LDA:

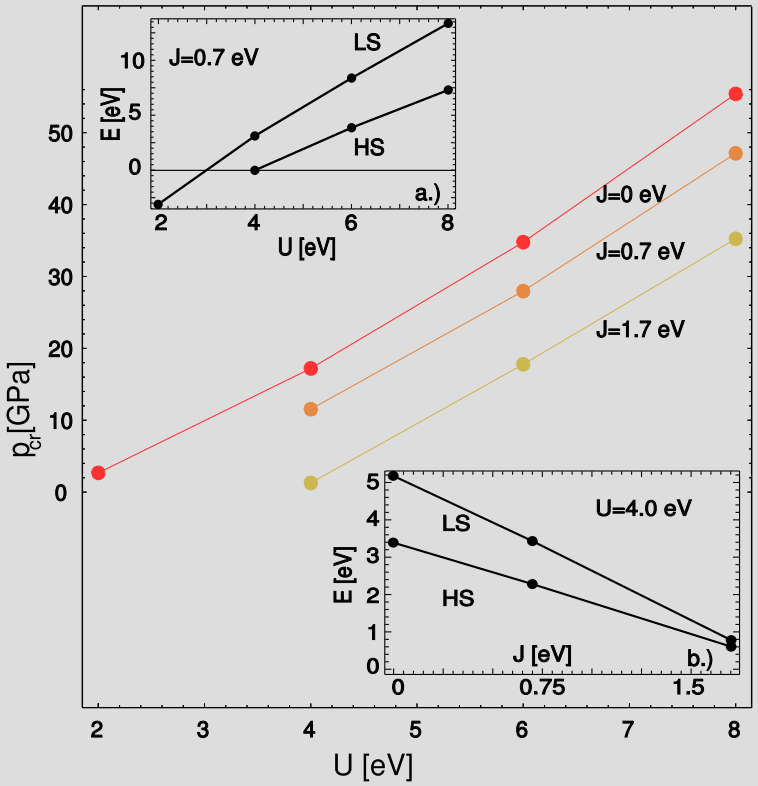




Spectroscopy

- New solutions: LDA+U, LDA+DMFT, self-interaction corrected LSDA, hybrid functionals, GW

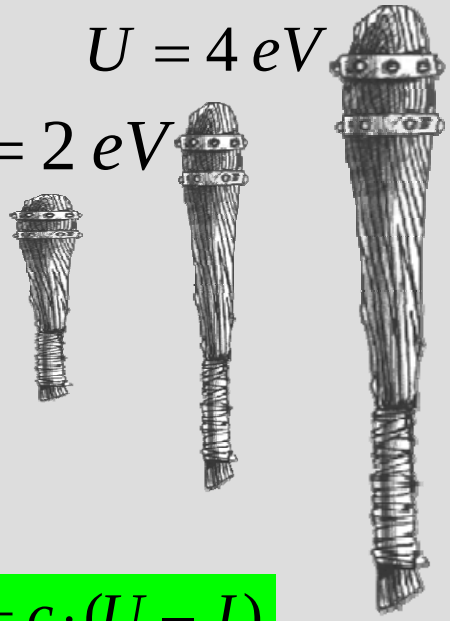
MOTIVATION: $p_{cr}(U,J)$ in $LuFeO_3$



$U = 8\,eV$

$U = 4\,eV$

$U = 2\,eV$



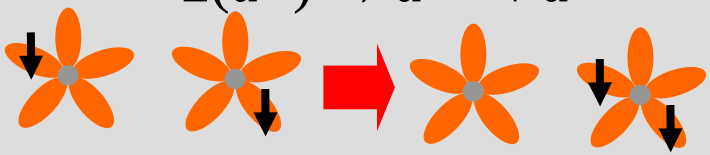
$$p_{cr} = c \cdot (U - J)$$

$$c \approx 10\ \mathrm{GPa/eV}$$

D.J. Adams and B. Amadon, PRB 79, 115114 (2009).

DETERMINATION *U*: THEORY

$$2(d^n) \rightarrow d^{n+1} + d^{n-1}$$



$$U = E(n+1) + E(n-1) - 2E(n)$$

$$U = \frac{\partial^2 E}{\partial^2 n}$$

$$\frac{dE}{dn} = -\alpha$$

$$U = \frac{d}{dn}\frac{dE}{dn} = -\frac{d}{dn}\alpha$$

Accessible:

$$\chi_{IJ} = \frac{dn_I}{d\alpha_J}$$

$$U = -(\chi^{-1})_{II}$$

Anisimov, Gunnarsson PRB 43 (1991)
M. Cococcioni, Ph.D. thesis, International School for Advanced Studies (SISSA), Trieste (2002).
M. Cococcioni and S. de Gironcoli, Phys. Rev. B 71, 035105 (2005).
W. E. Pickett, S. C. Erwin, and E. C. Ethridge, Phys. Rev. B 58, 1201 (1998).
P. H. Dederichs, S. Blügel, R. Zeller, and H. Akai, Phys. Rev. Lett. 53, 2512 (1984).

DETERMINATION *U*: THEORY

$$U = \frac{\partial^2 E}{\partial^2 n}$$

$$E[n] = E_{kin}[n] + E_{ext}[n] + E_{xc}[n] + E_{hart}[n]$$

linear

desired

Non self-consistent evaluation:

$$E^0[n_0 + dn] = E_{kin}[n_0 + dn] + (V_{ext} + V_{xc}[n_0] + V_{hart}[n_0]) \cdot dn$$

$$\frac{\partial^2 E_{\mathrm{kin}}[n_i]}{\partial^2 n} \neq 0$$

$$U = \frac{\partial^2 E}{\partial^2 n} - \frac{\partial^2 E_0}{\partial^2 n}$$

Pickett et al. (1998), Cococcioni and de Gironcoli (2002),

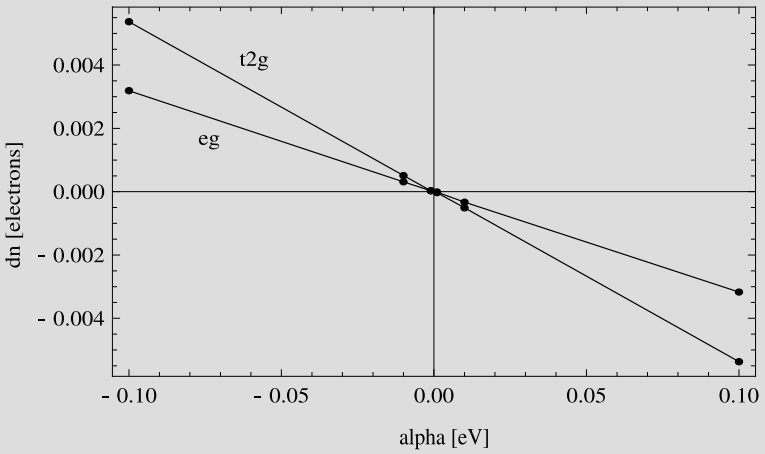
$$\chi^{ee^{-1}} = \chi^{-1} - \chi_0^{-1}$$

e-e interaction

Kinetic (Kohn-Sham)

DETERMINATION *U*: THEORY

- Implementation of method by Cococcioni and de Gironcoli (2005) in ABINIT (Gonze et al. 2006, Torrent et al. 2008).
- Linear response: Dederichs et al. (1984), Pickett et al. (1998) and Cococcioni and de Gironcoli (2002).
- No artificial constraints due to change of independent variable (use of lagrange multipliers).
- Subtraction of kinetic (Kohn-Sham) contribution.

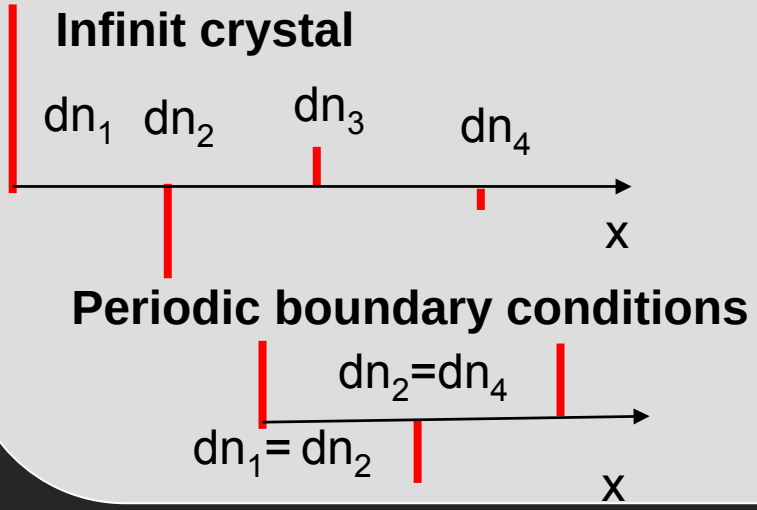


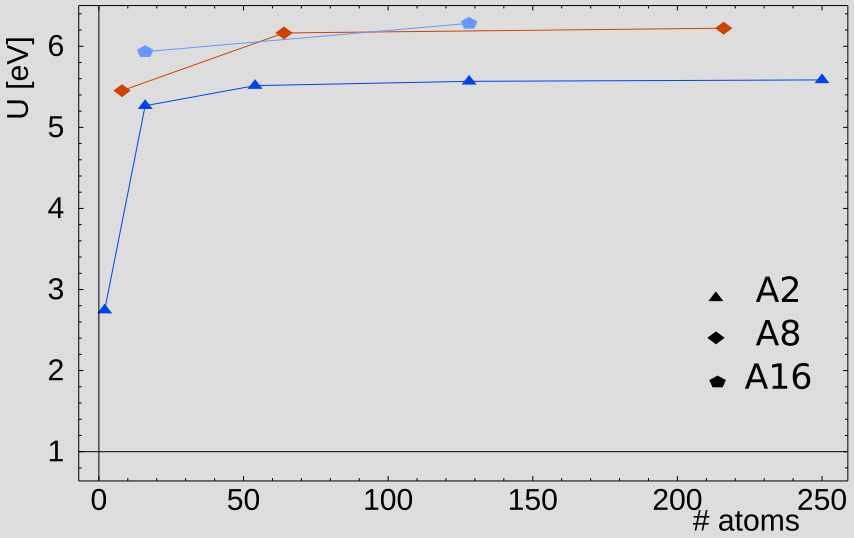
$$E(n+1)+E(n-1)-2E(n)$$

$$\chi_{IJ} = \frac{dn_I}{d\alpha_J}$$

DETERMINATION *U*: THEORY

- Extrapolation to supercells (calculate Coulomb interaction in presence of crystal)





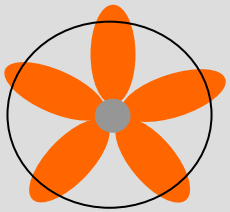
Calculation of *U* for *bcc* Fe using 2, 8 and 16 atoms in the actual calculation. Comparision with extrapolated results.

Normalization of localized states (e.g. Fe 3*d* within PAW region)

$$n_0(r) = \phi_0^*(r) \cdot \phi_0(r)$$

$$n'_0(r) = \frac{n_0(r)\Theta(r - r_{PAW})}{\langle \phi_0 \Theta(r - r_{PAW}) \rangle}$$

Atomic orbitals



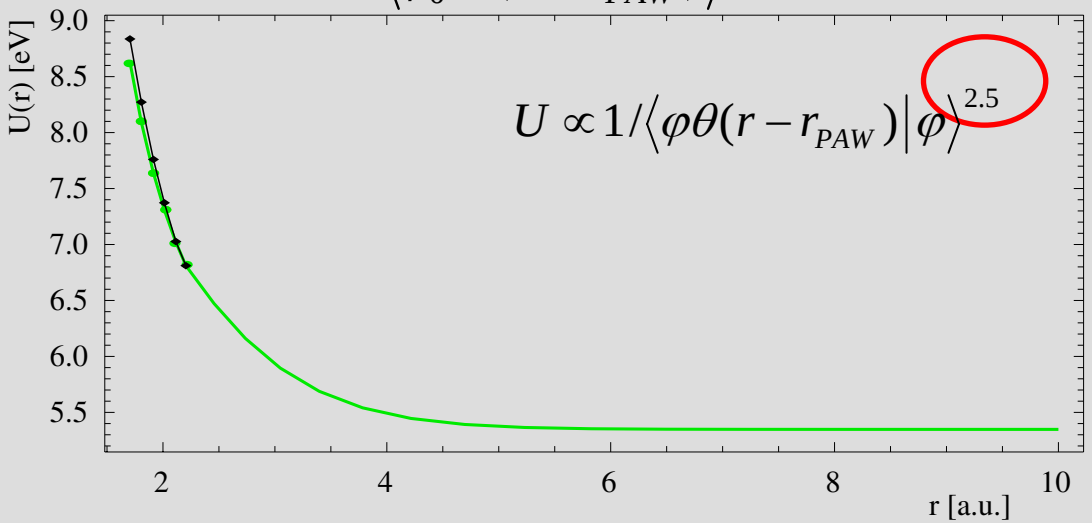
PAW-sphere

$$U = \int\int_0^\infty \; n_0(r) \cdot n_0(r') \frac{1}{|r - r'|} \varepsilon^{-1} r'^2 \, r^2 dr dr'$$

$$U = \frac{1}{\langle \phi_0 \Theta(r - r_{PAW}) \rangle^2} \underbrace{\int\int_0^{r_{PAW}} \; n_0(r) \cdot n_0(r') \frac{1}{|r - r'|} \varepsilon^{-1} r'^2 \, r^2 dr dr'}_{\approx U_\infty}$$

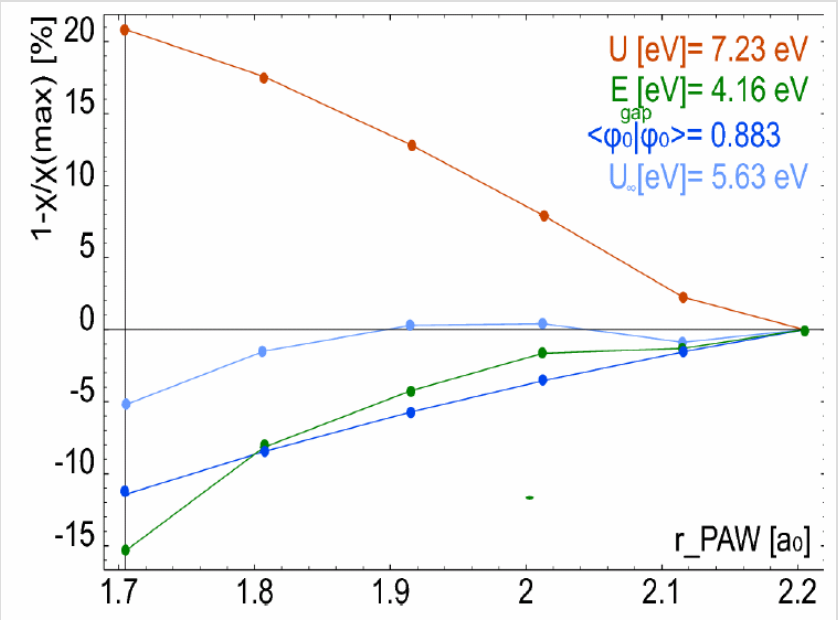
DETERMINATION *U*: RESULTS

$$U \approx \frac{U_\infty}{\left\langle \phi_0 \Theta(r - r_{PAW}) \right\rangle^f} \qquad f = 2$$



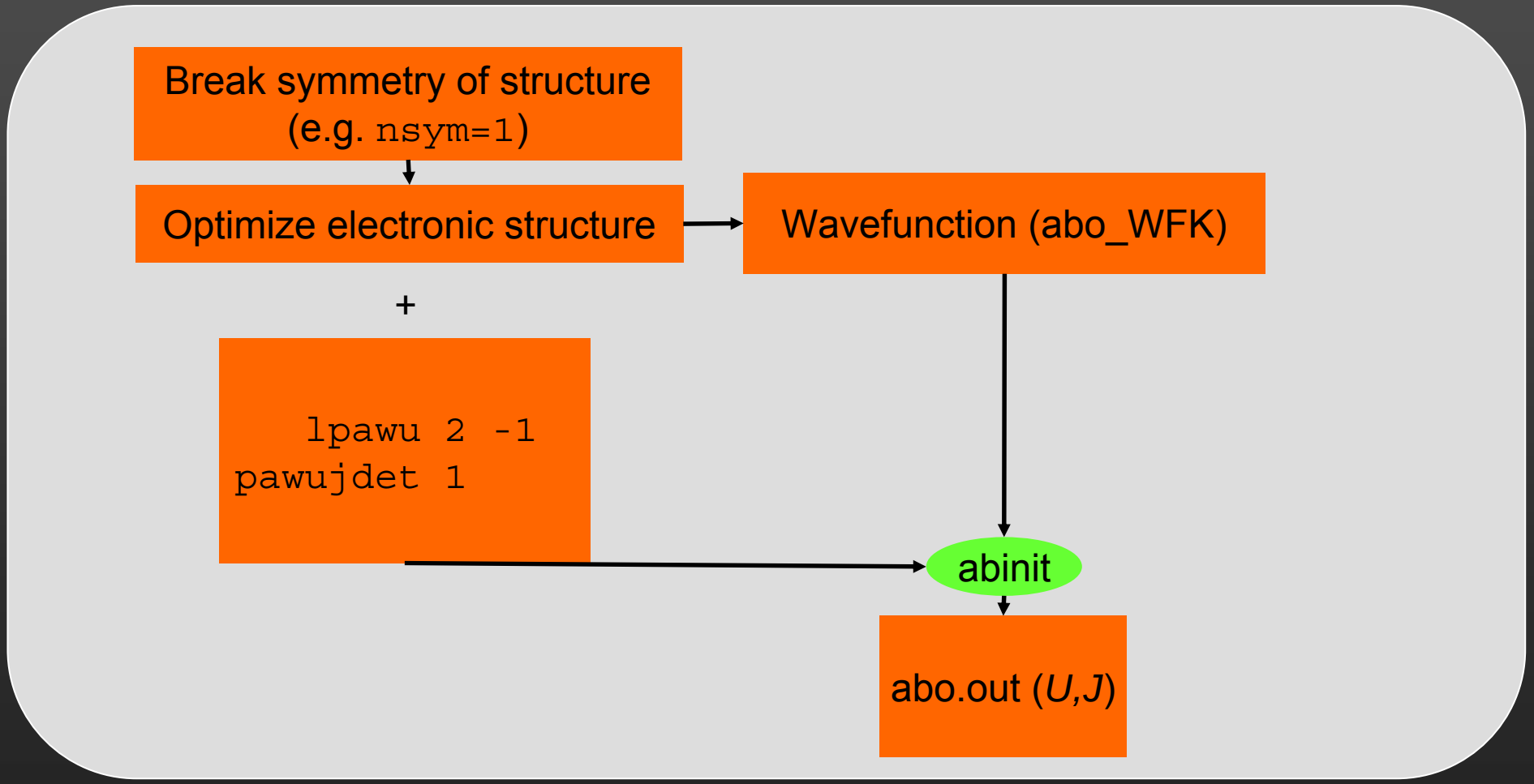
(black) Calculated values of *U* in *bcc* Fe. Green : Extrapolated values. *U(r)* has a universal behavior: It allows to extrapolate to arbitrary *r*.

DETERMINATION *U*: RESULTS



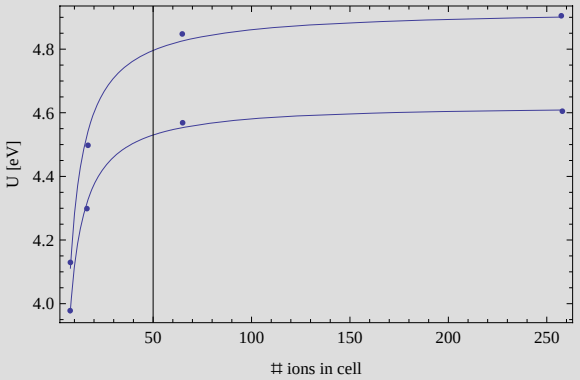
FeO: dependence of physical quantities upon PAW-radius. The gap varies little: An increase of *U* compensates the effect of the decrease of r_{PAW}.

DETAILS IMPLEMENTATION



DETAILS IMPLEMENTATION

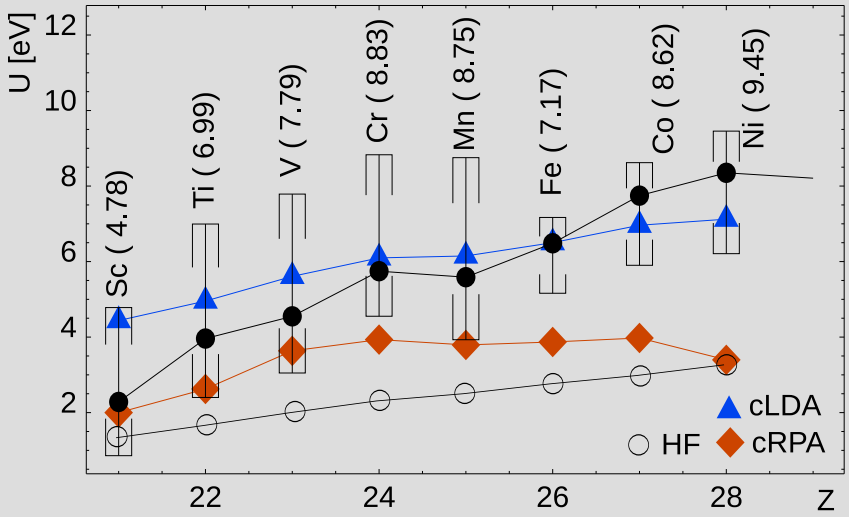
- pawujdet
  - activates determination of *U* (or *J*)
    - pawujdet = 1 : standard determination
    - pawujdet = 2 : determination of *U* on one spin channel (test)
    - pawujdet = 3 : determination of *J* (test)
- pawujv (optional)
  - Size of potential shift. Typically 0.1 -0.5 eV.
  - Default 0.1 eV
- pawujat (optional)
  - Determines atom *U* is determined on
  - Default: first atom lpaw>0



Calculated Hubbard *U* on Fe1 and Fe2 in Fayalite. From Ref. 1.

[1] M. Cococcioni and S. de Gironcoli, Phys. Rev. B 71, 035105 (2005).

DETERMINATION *U*: RESULTS



U calculated on the transition metal series. Top of errorbars: U(r_{PAW}), bottom of error-bars U(r), dots (●) U(d_0/2), (d_0 interatomic distance). Reference data from Aryasetiawan et al. (2006): diamonds (♦), *U* from cRPa; triangles (▲) U from cLDA, circles (○) from HF calculations of Cox et al. (1974).

F. Aryasetiawan, K. Karlsson, O. Jepsen, and U. Schönberger, Physical Review B 74, 125106 (2006).
B. N. Cox, M. A. Coulthard, and P. Lloyd, Journal of Physics F: Metal Physics 4, 807 (1974)

DETERMINATION *U*: RESULTS

U calculated on the reference transition metal oxydes: MnO, FeO, CoO and NiO

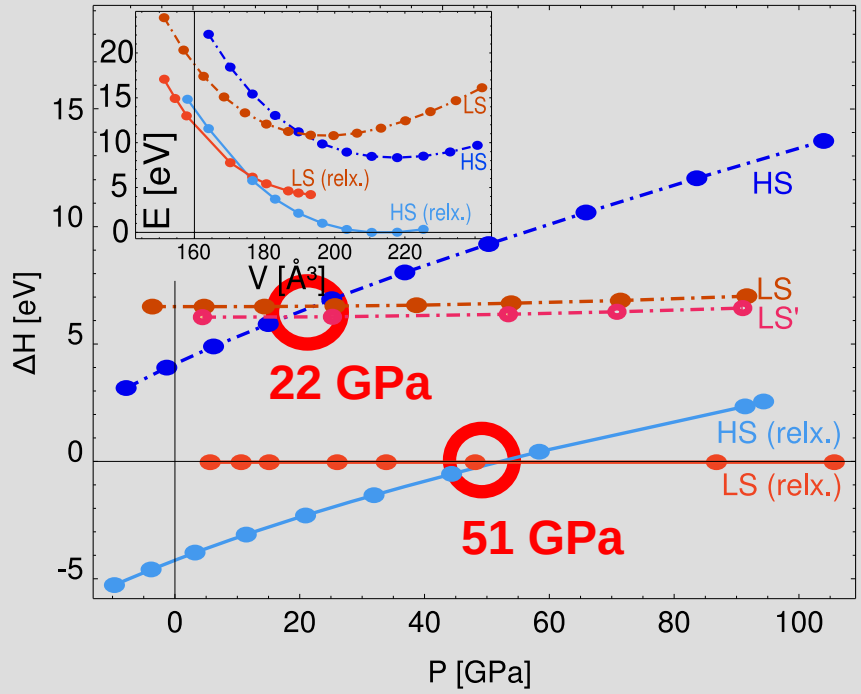
-	r_{PAW} a.u.	E_g [eV]	E_g [eV][a]	μ [μ_B]	μ [μ_B] [a]	U [eV]	U_{ASA} [eV]	U [eV][a]	U_∞ [eV]	n_{TO}	r_{AS} a.u.
MnO	1.654	2.05	3.5	4.05	4.79	9.23	6.9	4.20	4.14	4.87	3.00
FeO	2.013	2.68	3.2	3.66	3.32	9.53	6.8	5.69	6.86	7.52	3.01
CoO	1.911	2.95	3.2	2.74	3.35	10.23	7.8	6.59	7.00	7.75	2.96
NiO	1.972	3.05	3.1	1.62	1.77	10.95	8.0	7.82	7.19	8.40	2.91

a.) V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B 44, 943 (1991)

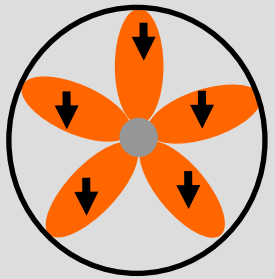
DETERMINATION *U*: CONCLUSIONS

- Consistent determination of *U* is important
- Strong (physical) dependence of *U* upon the sphere radius
- Universal behavior *U*(r)
- Upon extrapolation to U_{ASA} (or U_{∞}) good agreement with literature
- Fast & easy to use (no scripts needed, no further treatment)
- Treatment of all compounds (metals, transition metal oxides, *f*-electron systems)
- No constraints (all e-e interactions included), use LDA or GGA, use same basis as in DFT+*U*

$LuFeO_3$, a high precision calculation

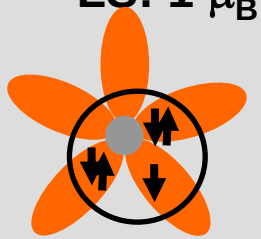


Fe^{3+} HS: 5 μ_B



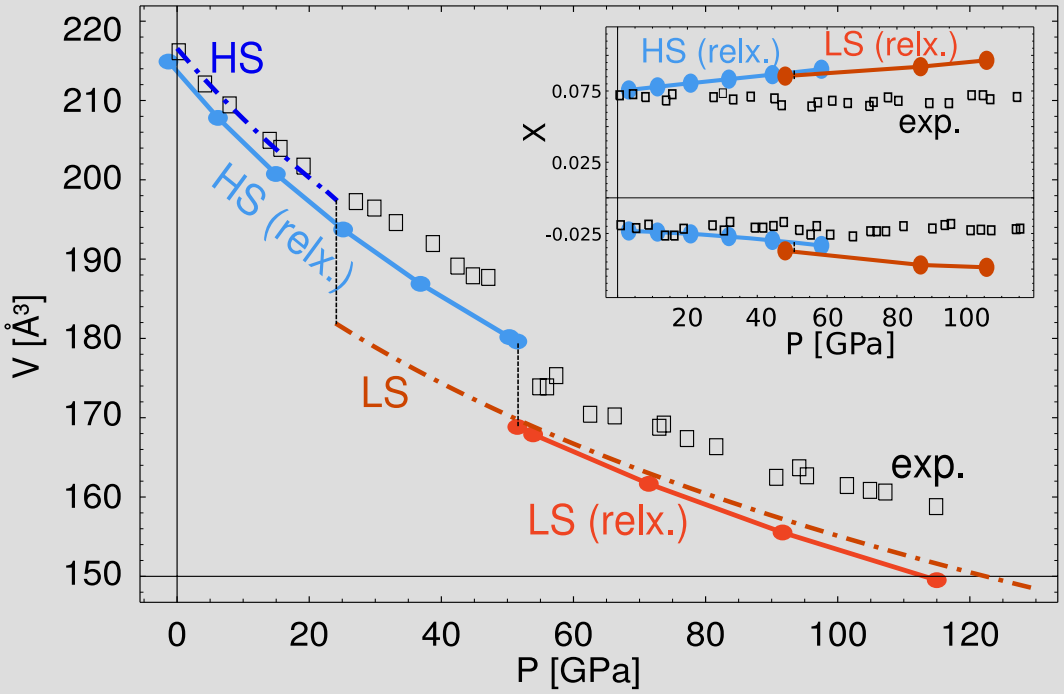
$r_{HS} > r_{LS}$

Fe^{3+} LS: 1 μ_B



The enthalpy of the HS, the LS, and the LS phases of $LuFeO_3$ in the pressure range of 0–100 GPa; relaxed (relx) and unrelaxed LDA+*U* calculations. Inset: the energy of the HS and LS phases at the corresponding volumes. D.J. Adams and B. Amadon, PRB 79, 115114 (2009).

$LuFeO_3$, a high precision calculation



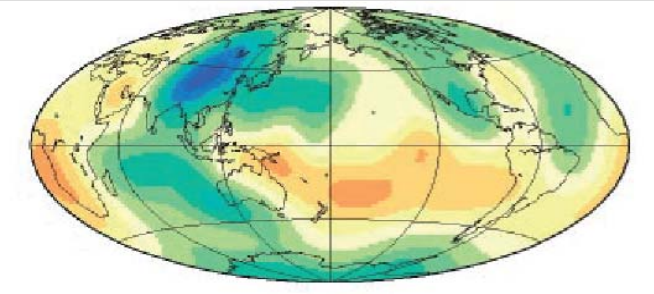
Volume collapse
6% (Exp. 5.5%)

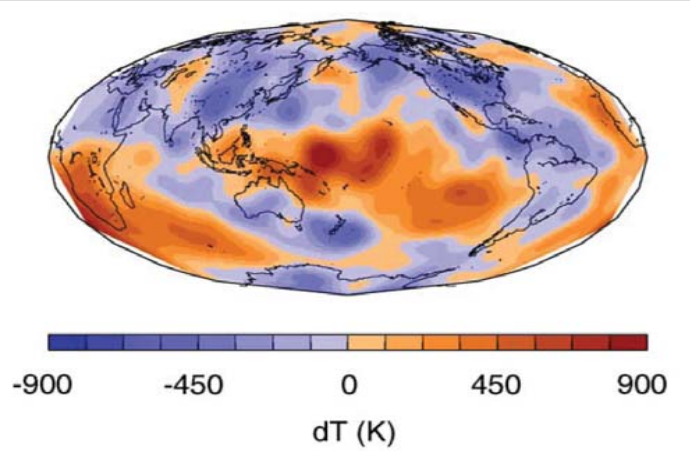
G. K. Rozenberg, M. P. Pasternak, W. M. Xu et al. Europhys. Lett. **71**, 228 (2005).

D. J. Adams and B. Amadon, Study of the volume and spin collapse in orthoferrite LuFeO3 using LDA+U, Phys. Rev. **B** 79, 115114 (2009)

Ab initio + Geophysics

- Measured wave velocities





- Numerical inversion =>
  - composition (*C*), temperature (*T*), fraction of partial melt (*F*)

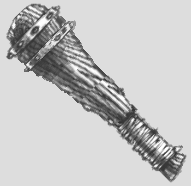
$$d\ln V_p = \frac{\partial \ln V_p}{\partial T} dT + \frac{\partial \ln V_p}{\partial C} dC + \frac{\partial \ln V_p}{\partial F} dF$$

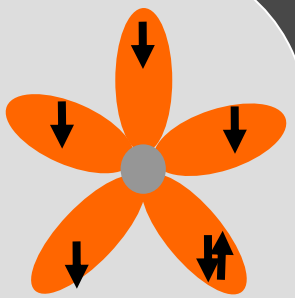
$$d\ln V_s = \frac{\partial \ln V_s}{\partial T} dT + \frac{\partial \ln V_s}{\partial C} dC + \frac{\partial \ln V_s}{\partial F} dF$$

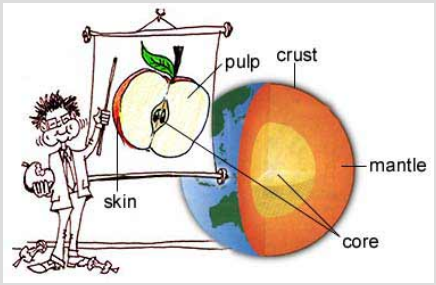
Masters, G. et. al. (2000). In Karato, S. et al. Deep Interior: Mineral Physics and Tomography from the Atomic to the Global Scale, Washington, Am. Geophys. Union.
Deschamps, F. and Trampert, J. (2003). Phys. Earth Planet. Int., 140:277–291

OVERVIEW

- MOTIVATIONMOTIVATION: LDA+U
- DETERMINATION of *U*
- Outlook: GEOPHYSICS







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