Implementation of LDA+U in the PAW framework, Applications

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The Local Correlation Problem

- Density functional theory: In practice LDA, GGA.
- Fails to describe strong correlations.
- Excited states are not correctly described (ex: Gap in oxydes).
- Even ground states property can be wrong (ex: Ce, Pu)
- Need for an explicit description of correlations.

Explicit description of Correlation

Hamiltonian to solve (Generalized Hubbard model):

$$H = \underbrace{\sum_{m,m'} \sum_{R,R'} (h^{m,m'}_{\mathrm{lda},RR'} - h^{m,m'}_{\mathrm{DC},RR'}) c^{\dagger}_{R,m} c_{R',m'}}_{\text{1 electron term (lda-DC term)}} + \underbrace{\frac{1}{2} {\sum_{R}}' \sum_{f \neq f'} U_{f f'} n_{\mathrm{f},\mathrm{R}'} n_{\mathrm{f}',\mathrm{R}'}}_{\text{N electrons term: interactions}} .$$

Mean field approximation:

$$E = E_{\mathrm{LDA}} - E_{\mathrm{DC}} + \frac{1}{2} \sum_{i \neq j} U n_i n_j$$

$$V = V_{\mathrm{LDA}} + U(n_i - \frac{1}{2})$$

Not rotationnaly invariant !!

Rotationaly invariant LDA+U (Lichtenstein et al (1995))

Energy can be computed directly

$$E_{\mathrm{LDA+U}}[n_{\mathrm{LDA+U}}] = E_{\mathrm{LDA}}[n_{\mathrm{LDA+U}}] + E_{\mathrm{ee}} - E_{\mathrm{dc}}$$

$$E_{\mathrm{ee}} = \frac{1}{2}\sum_{1,3}^{\sigma}\left[U n_1^{\sigma} n_3^{-\sigma} + (U-J)\delta_{13} n_1^{\sigma} n_3^{\sigma}\right]$$

$$E_{\mathrm{ee}} = \frac{1}{2}\sum_{1,2,3,4}^{\sigma}\left[\langle 13|V_{\mathrm{ee}}|24\rangle n_{1,2}^{\sigma} n_{3,4}^{-\sigma} + (\langle 13|V_{\mathrm{ee}}|24\rangle - \langle 13|V_{\mathrm{ee}}|42\rangle) n_{1,2}^{\sigma} n_{3,4}^{\sigma}\right]$$

$\langle 13|V_{\mathrm{ee}}|24\rangle$ contains an angular and a radial part.

$$\langle 13|V_{\mathrm{ee}}|24\rangle = 4\pi \sum_{k=0,2,4,6} \frac{F_k}{2k+1} \sum_{m=-k}^{+k} \langle m1|m|m2\rangle\langle m3|m|m4\rangle$$

U, J $\Rightarrow F_k$.

How to define $n_{1,2}^{\sigma}$?

LDA+U in the PAW framework 1/3

cf also Bengone et al (2000)
Preceding formulas are for a given n_{12}.
Occupation matrix n:

$$n^{\sigma}_{m,m'} = \sum_{\mathbf{k},n} f_n^{\mathbf{k},\sigma} \langle \Psi_n^{\mathbf{k},\sigma} | P_{m,m'} | \Psi_n^{\mathbf{k},\sigma} \rangle = \sum_{\mathbf{k},n} f_n^{\mathbf{k},\sigma} \langle \widetilde{\Psi}_n^{\mathbf{k},\sigma} | \widetilde{P}_{m,m'} | \widetilde{\Psi}_n^{\mathbf{k},\sigma} \rangle$$

and $P_{m,m'} = |\chi_m\rangle\langle\chi_{m'}|$.

$$n^{\sigma}_{m,m'} = \sum_{n_i,n_j} \rho^{\sigma}_{ij} \langle \phi_{n_i,m,l} | \chi_{m,l} \rangle \langle \chi_{m',l} | \phi_{n_j,m,l} \rangle = \sum_{n_i,n_j} \rho^{\sigma}_{ij} C_{n_i,n_j}$$

$\chi_{m,l}$: an atomic orbital (computed inside sphere). For Cerium, $\langle\chi|\chi\rangle \simeq 0.96$
Other choices for $C_{n_i n_j}$ exists (in practice similar results).

LDA+U in the PAW framework 2/3

$$H^\sigma = \frac{dE_U}{d\widetilde{\rho}^\sigma} = \sum_{i,j}^{l_i=l_j=l_U} \underbrace{\frac{dE_U}{dn_{m_i m_j}{}^\sigma}}_{V^{\mathrm{LDA+U}}_{m_i m_j}} \underbrace{\frac{dn_{m_i m_j}{}^\sigma}{d\rho_{ij}{}^\sigma}}_{C_{n_i,n_j}} \underbrace{\frac{d\rho_{ij}{}^\sigma}{d\widetilde{\rho}^\sigma}}_{|\widetilde{p}_i\rangle\langle\widetilde{p}_j|} = \sum_{i,j}^{l_i=l_j=l_U} |\widetilde{p}_i\rangle D^U_{ij} \langle\widetilde{p}_j|$$

So that: $D^U_{ij} = V^{\mathrm{LDA+U}}_{m_i m_j} C_{n_i,n_j}$.

This new D_{ij} is simply added to others in `pawdij.F90`

Hellman Feynman $\Rightarrow$ no modifications for forces and stress in LDA+U (only through the electronic density).

LDA+U in the PAW framework 3/3

Calculation of energy. Direct way:

$$E_{\mathrm{LDA+U}}[n_{\mathrm{LDA+U}}] = E_{\mathrm{LDA}}[n_{\mathrm{LDA+U}}] + E_{\mathrm{e-e}} - E_{\mathrm{dc}} \qquad (1)$$

Double counting way (be careful: double counting (DC) way of calculating energy in DFT and double counting (dc) correction in LDA+U are two different things):

$$E_{\mathrm{LDA+U}} = \sum_i \epsilon_i^{KS} + E_{\mathrm{LDA}}^{\mathrm{DC}} + E_{\mathrm{U}}^{\mathrm{DC}}$$

With

$$E_{\mathrm{U}}^{\mathrm{DC}} = E_{\mathrm{ee}} - E_{\mathrm{dc}} - \sum_\sigma \langle V_{\sigma U}^{\mathrm{KS}} \rangle$$

$V_{\mathrm{U}}^{\mathrm{KS}}$ contains a LDA+U double counting term.

$$E_{\mathrm{U}}^{\mathrm{DC}} = -E_{\mathrm{ee}} - E_{\mathrm{dc}}^{\mathrm{DC}}$$

LDA+U : double counting corrections

Double counting corrections: Atomic limit (or Full localized limit) [Lichtenstein(1995), Anisimov (1991)]:

$$E_{\rm dc}^{\rm FLL} = \sum_t (U\frac{1}{2}N(N-1) - J\sum_\sigma \frac{1}{2}N^\sigma(N^\sigma-1))$$

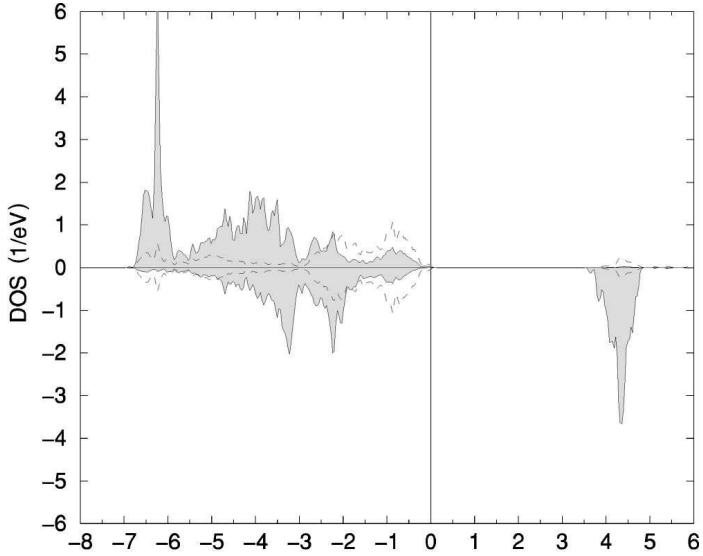
Around mean field version [Czyzyk(1994)] (delocalized limit):

$$E_{\rm dc}^{\rm AMF} = \sum_t (U N_\uparrow N_\downarrow + \frac{1}{2}(N_\uparrow^2+N_\downarrow^2)\frac{2l}{2l+1}(U-J))$$

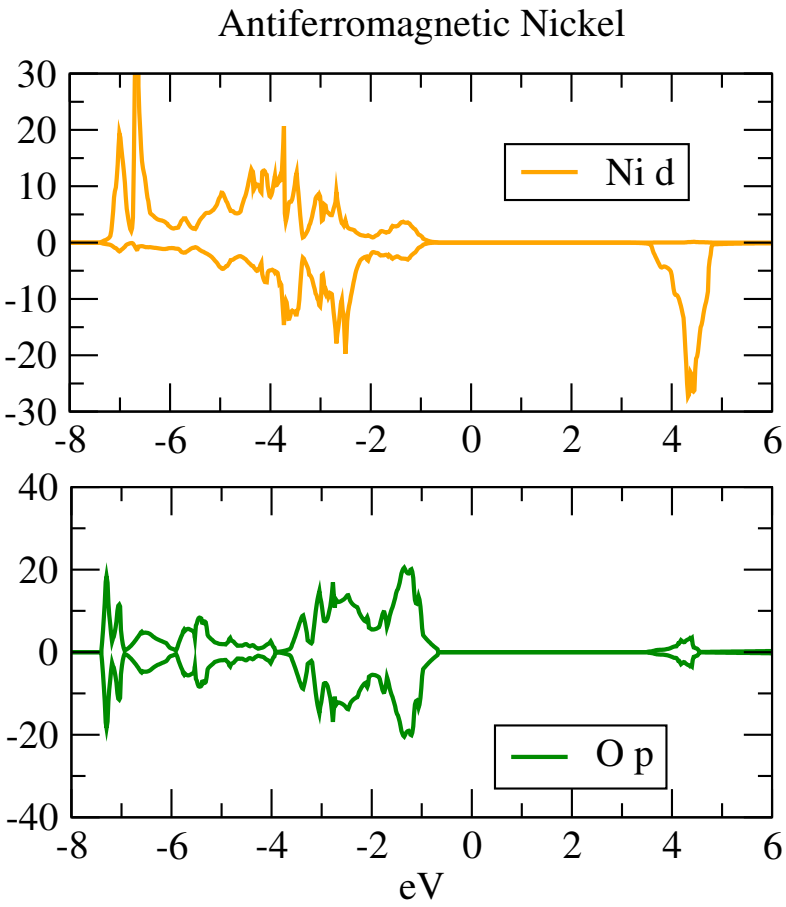
(*not extensively tested: calculations are scarced in AMF*)

Tests of physical systems I:NiO

NiO is an antiferromagnetic insulator correctly described in LDA but the gap is too small. Results are in accordance to other existing calculations.



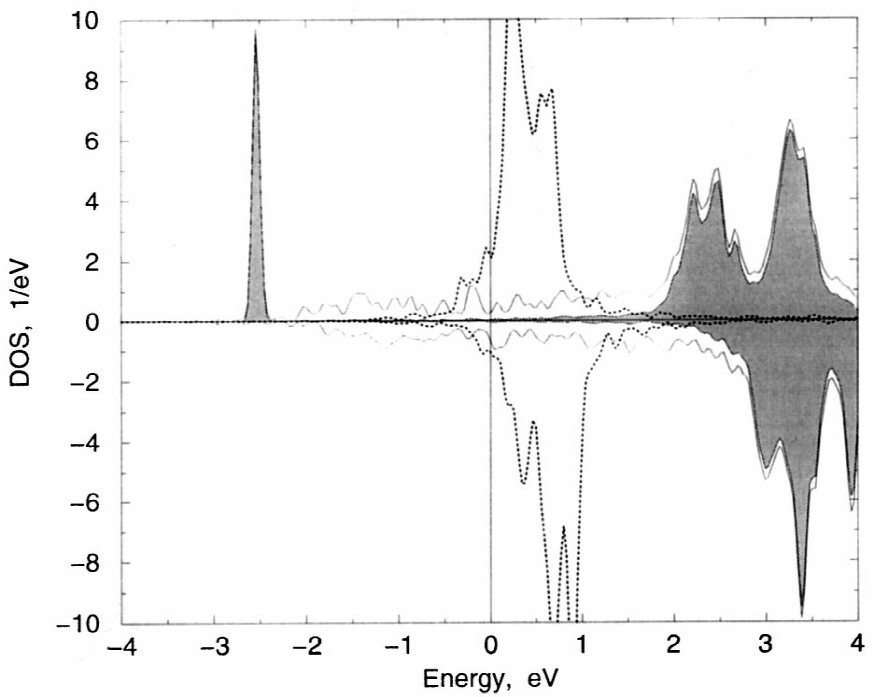
FLAPW (Shick et al 1999)



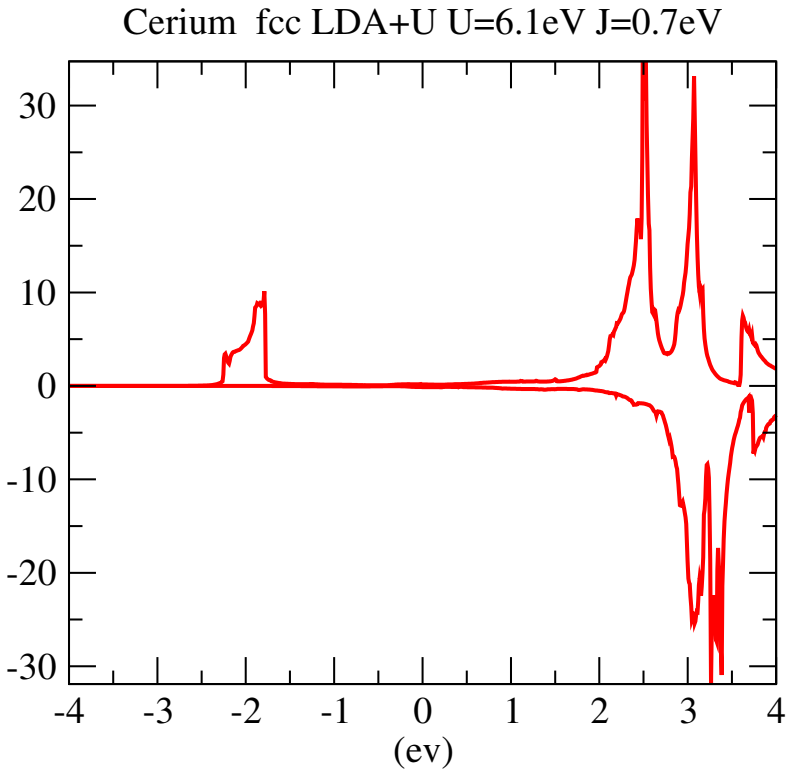
PAW (Our calculation)

Tests of physical systems II:Cerium

Cerium γ: a paramagnetic correlated system. Spectral functions



FLAPW (Shick et al 2000)



PAW (Our calculation)

We have also compared with another PAW/LDA+U code; very good agreement on spectra and lattice parameter (less 0.2%)

New variables (see list of variables)

`usepawu`: 1 or 2 in LDA+U (for FLL and AMF double counting terms).
`lpawu`: value of l on which to apply LDA+U (for each type).
`upawu`: value of U for each type.
`jpawu`: value of J for each type.
On output:
Direct decomposition of LDA+U correction to energy.
Matrix of occupations.

LDA+U

- Application to β Cerium: a dhcp antiferromagnetic structure (8 atoms/cell).
- Relaxation of forces and stress in LDA+U
- We found the same volume per atom as for γ Cerium to 0.3 % (all are closed packed structure).
- The antiferromagnetic ordering of the structure is described correctly in contrast to GGA calculation.

Wannier Function: an alternate localized basis

Main ingredient to compute Maximaly localised Wannier function: The overlap:

$$M_{mn}^{(\mathbf{k},\mathbf{b})} = \langle u_{m\mathbf{k}} | u_{n,\mathbf{k}+\mathbf{b}} \rangle$$

Easy in a plane waves framework. Extension to Ultra Soft pseudopotential has been developped by Ferretti et al (cond-mat/0603256). Implementation of this framework in PAW in progress:

$$M_{mn}^{\mathbf{k},\mathbf{b}} = \langle \widetilde{u}_{\mathbf{k},m} | \widetilde{u}_{\mathbf{k}+\mathbf{b},n} \rangle + \sum_{I,ij} Q_{ij}^{I}(\mathbf{b}) \langle \widetilde{\Psi}_{\mathbf{k},m} | \widetilde{p}_{Ii} \rangle \langle \widetilde{p}_{Ij} | \widetilde{\Psi}_{\mathbf{k}+\mathbf{b},m} \rangle ,$$

where we have defined $Q_{ij}^{I}(\mathbf{b}) = \int d\mathbf{r}\, Q_{ij}^{I}(\mathbf{r})\, e^{-i\mathbf{b}\cdot\mathbf{r}}$.

Conclusion

- An implementation of LDA+U inside spheres.
- Tests on NiO and Ce.
- Comparison with FLAPW spectra, and with other PAW code.
- Relaxation of a complex cell (β Ce) gives physical results. The magnetic ordering is correctly described.
- Wannier functions are an alternate basis for electronic structure calculations.