Strong electronic correlations in solid states physics: how to handle it with ABINIT?

Presentation of cRPA, DFT+U and DFT+DMFT

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1. Introduction to strong correlation
Electronic structure: Bloch states $= u_k(r)e^{ikr}$
Localization of $3d$, $4f$ and $5f$ orbitals.

$3d$ and $4f$ orbitals are more localized.
Localized orbitals ⇒ two consequences:

- overlap is weak: energy bands are narrow (width: \( W \)).
- Strong interactions "\( U \)" between electrons inside these orbitals.

⇒ The ratio of \( U \) and \( W \), governs the importance of correlations.
4d element: filling of the 4d band (Bonding states and antibonding): 4d electrons are delocalized.

Lanthanides: 4f electrons are localized, negligible overlap between 4f orbitals.

Actinide: intermediate case of localization.

At atmospheric pressure:

![Graph showing band occupancy ratio and volume as functions of band occupancy ratio.](image-url)

Isostructural transition $\frac{V_\gamma - V_\alpha}{V_\gamma} = 15\%$, ends at a critical point

Electronic configuration $4f^1$.
- $\alpha$ phase: Pauli paramagnetism
  $\Rightarrow$ $\alpha$ phase: $f\,e^-$ more delocalized.
- $\gamma$ phase: Curie Paramagnetism
  $\Rightarrow$ $\gamma$ phase: $f\,e^-$ is localized

[Johansson, B. Phil. Mag. 30, 469 (1974)]
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- **$\alpha$ phase**: Pauli paramagnetism
  - $\Rightarrow$ **$\alpha$ phase**: $f\,e^-$ more delocalized.

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  - $\Rightarrow$ **$\gamma$ phase**: $f\,e^-$ is localized

[Johansson, B. Phil. Mag. 30, 469 (1974)]

**Only the $\alpha$ phase is described by DFT/LDA/GGA.**
Peak at the Fermi level only in the $\alpha$ phase.

- $\gamma$ and $\alpha$ phase: high energy bands (-2 eV and 5 eV).
- Bands at high energy not described in LDA.
- Peak at the Fermi level not correct in LDA.
- $E_{\text{dft-lda}}(V)$: $\gamma$ phase not stable.
Non magnetic GGA underestimates volume for late actinides

GGA: Cohesion is overestimated, not enough correlation
GGA-AFM: good description of volumes but magnetism is wrong

Photoemission spectra of $d$ elements.

From Morikawa et al (1995)

Sekiyama 1992

⇒ YTiO$_3$ insulator: metal in LDA.

⇒ SrVO$_3$ is a metal: metal in LDA, but without the peak at -1.8eV.
Oversimplified... 4d and 5d elements exhibit non negligible strong correlation effects.
Towards more explicit local correlation

The exact hamiltonian is:

\[ H = \sum_{i=1}^{N} \left[ -\frac{1}{2} \nabla^2_{r_i} + V_{\text{ext}}(r_i) \right] + \frac{1}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|} \]

It can be exactly rewritten in second quantization as:

\[ H = \sum_{i,j} \langle i|h|j \rangle c_i^\dagger c_j + \sum_{i,j,k,l} \langle ij|v|kl \rangle c_i^\dagger c_j^\dagger c_k c_l \] (1)

If interactions are purely local (and with only one (correlated) orbital per atom), one can write the Hubbard model

\[ H = \sum_{R,R'} t_{R,R'} c_R^\dagger c_{R'} + \sum_{R} U \hat{n}_{R\uparrow} \hat{n}_{R\downarrow} \]

one electron term : delocalization  interaction term : localization

Competition between delocalization and localization
The Hubbard model: Competition between localization and delocalization

\[ H = \sum_{R,R'} t_{R,R'} c_R^\dagger c_{R'} + \sum_R U \hat{n}_{R\uparrow} \hat{n}_{R\downarrow} \]

- **One electron term**: delocalization
- **Interaction term**: localization

- For large value of the interaction \(U\), electrons are localized
- For low value of the interaction \(U\), electrons are delocalized
2. The DFT+\(U\) method
Hamiltonian to solve ($i$ represents an electron)

$$H = \sum_{i=1}^{N} \left[ -\frac{1}{2} \nabla^2 r_i + V_{\text{ext}}(r_i) \right] + \frac{1}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|}$$

DFT solution

$$\frac{1}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|} \Rightarrow \sum_i V_{\text{Ha+xc}}(r_i)$$

Better: Keep local interaction between correlated localized orbitals.

$$\frac{1}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|} \Rightarrow \frac{1}{2} \sum_{i \neq j} U_{ij} \hat{n}_i \hat{n}_j$$
Explicit description of correlations

- We need to solve:

\[ H = \sum_{R,R'} \sum_{i,j} t_{ij}^{R,R'} c_{R_i}^{\dagger} c_{R'_j} + \frac{1}{2} \sum_{R,f \neq f'} U_{ff'} \hat{n}_{R_f} \hat{n}_{R_{f'}} \]

one electron term (lda)  
many body term: interactions

- **Static mean field approximation**: \( \langle AB \rangle = \langle A \rangle \langle B \rangle \)
- Fluctuations \( \langle (A - \langle A \rangle)(B - \langle B \rangle) \rangle \) are neglected
- The energy thus writes:

\[
\frac{1}{2} \langle \sum_{f,f'} \hat{n}_f \hat{n}_{f'} \rangle = \frac{1}{2} \sum_{f,f'} n_f n_{f'}
\]

with \( n_f = \langle \hat{n}_f \rangle \)

Anisimov, Zaanen, and Andersen, PRB 44 943 (1991)
Strong local correlations: Introduction

- Hamiltonian to solve ($i$: électrons):

$$H = \sum_{i=1}^{N} \left[ -\frac{1}{2} \nabla^2 r_i + V_{\text{ext}}(r_i) \right] + \frac{1}{2} \sum_{i\neq j} \frac{1}{|r_i - r_j|}$$

- Strong correlation in Localized orbitals ($f, d$)

- Other orbitals: DFT(LDA/GGA) could be tried.

$$H_{\text{LDA+Manybody}} = \text{one electron term (DFT/LDA)} + \frac{U}{2} \sum_{i\neq j} \hat{n}_i \hat{n}_j$$

$$E_{\text{LDA+U}} = E_{\text{LDA}} - U \frac{N(N-1)}{2} + \frac{U}{2} \sum_{i\neq j} n_i n_j$$
The LDA+U Method

Replace operators by their mean value (static approximation)

\[
E = E_{\text{one body term}} + U \sum_{\mathbf{R}} U n_{\mathbf{R}\uparrow} n_{\mathbf{R}\downarrow}
\]

In a DFT context:

\[
E = E_{\text{LDA}} - U \frac{N(N-1)}{2} + \frac{U}{2} \sum_{f \neq f'} n_f n_{f'} \quad \Rightarrow \quad V = V_{\text{LDA}} - U(n_f - \frac{1}{2})
\]

- \( n_f = 0 \), \( V = V_{\text{LDA}} + \frac{U}{2} \)
- \( n_f = 1 \), \( V = V_{\text{LDA}} - \frac{U}{2} \)

⇒ A gap is opened among correlated orbitals.

⇒ Oxides: U/crystal field ⇒ Mott-Hubbard/Charge-transfer insulator.

⇒ \( U \) is, in the atomic limit the energy which is necessary to promote one electron from a correlated orbital to another.

\[ U = E(N+1) + E(N-1) - 2E(N) = I - A. \]
The LDA+U method

Atom (integer nb of $e^{-}$) = The LDA+U correction disappears.

$\Rightarrow$ Self-interaction correction.

$\Rightarrow$ Discontinuity of the exchange and correlation potential.

From Cococcioni et al PRB 71 (2005)

see also Solovyev et al PRB 50 16861 (1994)
What is not yet defined: orbital and interaction

\[ \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \Rightarrow \frac{1}{2} \sum_{i \neq j} U_{ij} \hat{n}_i \hat{n}_j \]

- The localized \( f \) orbital: What is its radial part? ⇒ important but not discussed here.
- What is the value of effective Coulomb interaction \( U \) between these \( f \) orbitals?
The PAW method: Expression of a Kohn Sham function of Cl$_2$.

\[ |\Psi_{k\nu}\rangle = \frac{1}{\sqrt{N}} \sum_i \langle \tilde{\phi}_i | \tilde{p}_i | \tilde{\Psi}_{k\nu}\rangle - \frac{1}{\sqrt{N}} \sum_i \langle \tilde{\phi}_i | \tilde{p}_i | \tilde{\Psi}_{k\nu}\rangle \]

On plane waves

On a local radial grid

Blöchl PRB 1994

[Developed in ABINIT by the CEA group]


A grid devoted to local properties: well adapted to correlated systems and to compute:

- DFT+\(U\) density matrix.
- Projected Wannier orbitals.
A Kohn-Sham function can be written:

\[ |\Psi_{k\nu}\rangle = \left|\tilde{\Psi}_{k\nu}\right\rangle + \sum_i \left| \varphi_i \right\rangle \langle \tilde{p}_i | \tilde{\Psi}_{k\nu}\rangle - \sum_i \left| \tilde{\varphi}_i \right\rangle \langle \tilde{p}_i | \tilde{\Psi}_{k\nu}\rangle \]

On plane waves

On a local radial grid

- \( \varphi_i \): atomic wavefunction
- \( \tilde{\varphi}_i \): pseudo atomic wavefunction
Double counting corrections: Atomic limit (or Full localized limit) [Lichtenstein(1995), Anisimov (1991)]:

\[
E_{\text{dc}}^{\text{FLL}} = \sum_{t} \left( \frac{U}{2} N(N - 1) - \sum_{\sigma} \frac{J}{2} N^{\sigma}(N^{\sigma} - 1) \right)
\]

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

\[
E_{\text{dc}}^{\text{AMF}} = \sum_{t} \left( U N_{\uparrow} N_{\downarrow} + \frac{1}{2} \left( N_{\uparrow}^2 + N_{\downarrow}^2 \right) \frac{2l}{2l + 1} (U - J) \right)
\]

(Made to correct the delocalized limit.)
Mott insulators: Gap excitations are d-d (or f-f) ie between Hubbard bands.
Charge Transfert insulators: Gap excitations are Op-d (Or Op-f)
Main effects of Mean Field approximation (DFT+U)

FeO (d^6): insulator in LDA+U

Cococcioni et al PRB 71 2005

UO_2 (f^2): antiferromagnetic, insulator

\( \text{Gap}_{\text{exp}} = 2.1 \text{ eV} \)

Electrons localization: volume increases in LDA+U

Dudarev et al Micron 31 2000

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Spectral functions: basic features are reproduced.

Structural data

$\Rightarrow$ Electron repulsion induces a weakening of the bonding.


But: The $\alpha$ phase is not correctly described, magnetism is incorrect (except for the $\beta$ phase), no transitions.
We start from the Hartree Fock result

\[ E_{HF} = \sum_{a,occ} h_{a,a} + \frac{1}{2} \sum_{a,b} (aa, bb) - (ab, ba) \]

The interaction part corresponds to, taking into account the spin:

\[
E_{HF}^{\text{interaction}} = \frac{1}{2} \sum_{a,b} \sum_{\sigma,\sigma'} \left[ \int \Psi_{\sigma}^a(r) \Psi_{\sigma'}^b(r') \frac{1}{|r - r'|} \Psi_{\sigma}^a(r) \Psi_{\sigma'}^b(r') \right. \\
- \left. \delta_{\sigma,\sigma'} \int \Psi_{\sigma}^a(r) \Psi_{\sigma}^b(r') \frac{1}{|r - r'|} \Psi_{\sigma}^a(r) \Psi_{\sigma}^b(r') \right]
\]

or

\[
E_{HF}^{\text{interaction}} = \frac{1}{2} \sum_{a,b} \sum_{\sigma,\sigma'} \left[ \langle a^\sigma b^\sigma' | V | a^\sigma b^\sigma' \rangle - \delta_{\sigma,\sigma'} \langle a^\sigma b^\sigma | V | b^\sigma a^\sigma \rangle \right]
\]

Then, we keep only the terms in \(|a\rangle\) in the correlated subsets of orbitals.
\[ |a\rangle = \sum_{m, L=\text{Lcor}} \langle m|a|m \rangle + \ldots \text{terms neglected} \]

and show that (blackboard or exercise):

\[
E_{\text{interaction LDA+U}} = \frac{1}{2} \sum_{m_1, m_2, m_3, m_4} \sum_{\sigma, \sigma'} \left[ \langle m_1 m_2|V|m_3 m_4 \rangle n_{m_4, m_2}^{\sigma'} n_{m_3, m_1}^{\sigma} - \delta_{\sigma, \sigma'} \langle m_1 m_2|V|m_3 m_4 \rangle n_{m_3, m_2}^{\sigma} n_{m_4, m_1}^{\sigma} \right]
\]

it can be rewritten as:

\[
E_{\text{interaction LDA+U}} = \frac{1}{2} \sum_{1, 2, 3, 4, \sigma} \left[ \langle 12|V|34 \rangle n_{4, 2}^{\sigma} n_{3, 1}^{\sigma} + (\langle 12|V|34 \rangle - \langle 12|V|43 \rangle) n_{4, 2}^{\sigma} n_{3, 1}^{\sigma} \right]
\]

with

\[
n_{m_1, m_2}^{\sigma} = \sum_a \langle m_1|a \rangle f_a \langle a|m_2 \rangle = \sum_{\nu, k} \langle m_1|\Psi_{\nu, k} \rangle f_{\nu, k} \langle \Psi_{\nu, k}|m_2 \rangle
\]
Calculation of $\langle m_1 m_3 | V | m_2 m_4 \rangle$

One uses $\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \sum_{m=-k}^{k} \frac{4\pi}{2k+1} \frac{r^k}{r_{12}^{k+1}} Y^m(\theta_1, \phi_1) Y^m_*(\theta_2, \phi_2)$ and after some manipulations: $\langle m_1 m_3 | V_{ee} | m_2 m_4 \rangle$ contains an angular and a radial part.

$$\langle m_1 m_3 | V_{ee} | m_2 m_4 \rangle = 4\pi \sum_{k=0,2,4,6} \frac{F_k}{2k+1} \sum_{m=-k}^{+k} \langle m_1 | m | m_2 \rangle \langle m_3 | m | m_4 \rangle$$

$$U = \frac{1}{(2l + 1)^2} \sum_{m_1, m_2} \langle m_1 m_2 | V_{ee} | m_1 m_2 \rangle = F_0 \text{ coulomb term}$$

$$J = \frac{1}{2l(2l+1)} \sum_{m_1 \neq m_2} \langle m_1 m_2 | V_{ee} | m_2 m_1 \rangle = \frac{F_2 + F_4}{14} \text{ exchange term}$$
# == LDA+U

usepawu 1  # activate DFT+U
lpawu 2 -1  # apply DFT+U for d orbitals for the first species only
upawu 8.0 0.0  # Value of U
jpawu 1.0 0.0  # Value of J

usedmatpu 10  # Number of steps to impose a density matrix
dmatpawu

1.0 0.0 0.0 0.0 0.0  # up density matrix
0.0 1.0 0.0 0.0 0.0  # up density matrix
0.0 0.0 1.0 0.0 0.0  # up density matrix
0.0 0.0 0.0 1.0 0.0  # up density matrix
0.0 0.0 0.0 0.0 1.0  # up density matrix

1.0 0.0 0.0 0.0 0.0  # dn density matrix
da 0.0 1.0 0.0 0.0 0.0  # dn density matrix
0.0 0.0 0.0 0.0 0.0  # dn density matrix
0.0 0.0 0.0 1.0 0.0  # dn density matrix
0.0 0.0 0.0 0.0 1.0  # dn density matrix
0.0 0.0 0.0 0.0 0.0  # dn density matrix
On the board...