

DE LA RECHERCHE À L'INDUSTRIE



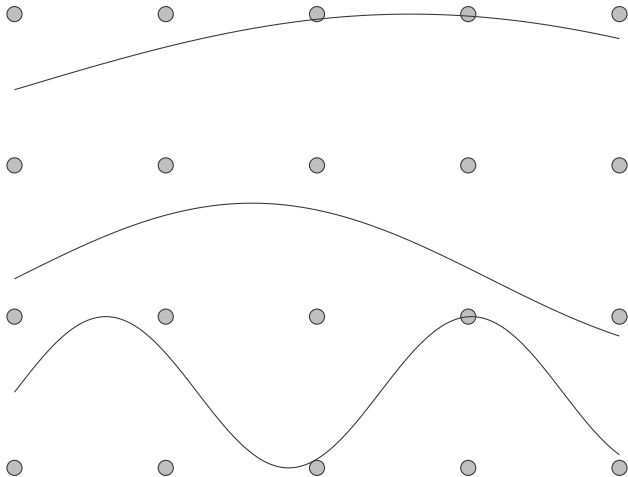
Strong electronic correlations in solid states physics: how to handle it with ABINIT ? Presentation of cRPA, DFT+U and DFT+DMFT

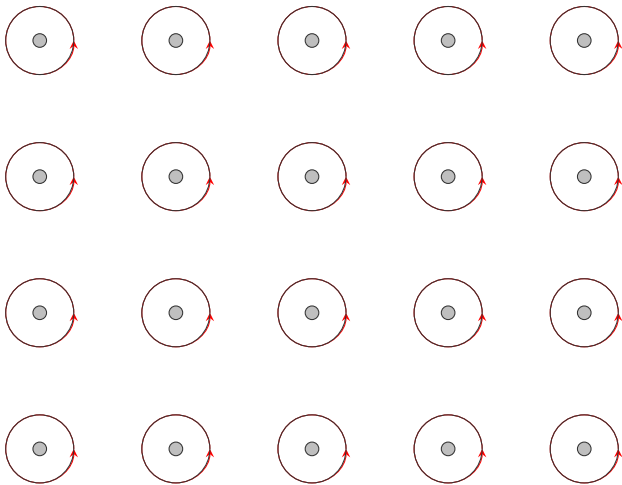
Bernard Amadon
CEA/DAM, DIF, France

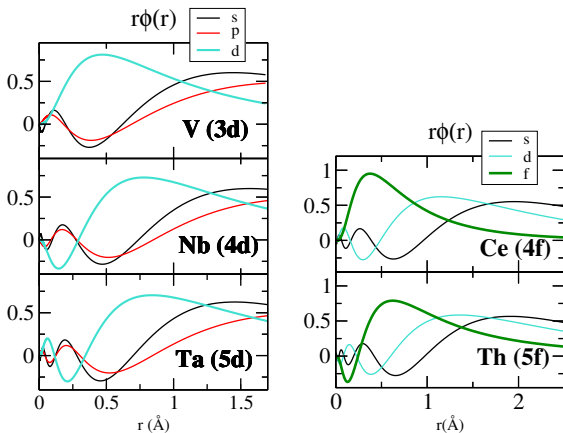
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ABINIT School 2017

1. Introduction to strong correlation

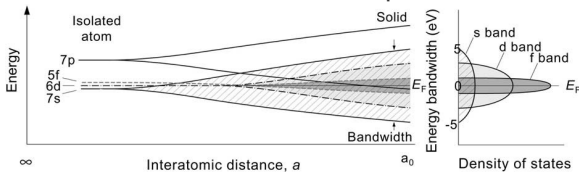






$3d$ and $4f$ orbitals are more localized.

- Localized orbitals \Rightarrow two consequences:



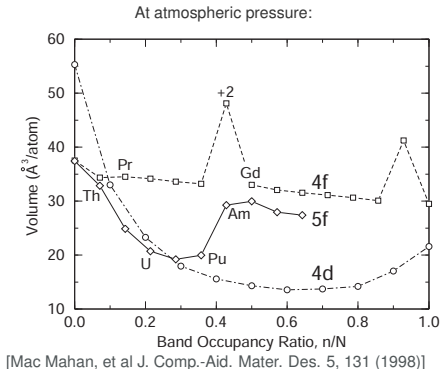
- overlap is weak: energy bands are **narrow (width: W)**.
 - Strong **interactions " U "** between electrons inside these orbitals.
- \Rightarrow The **ratio of U and W** , governs the importance of correlations.

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.

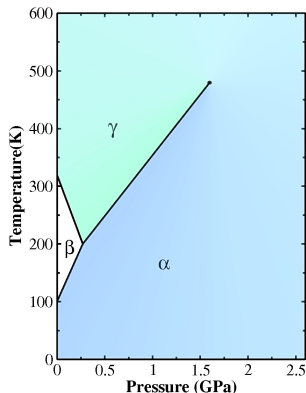
Actinide: **intermediate case** of
localization.



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

Electronic configuration $4f^1$.

- α phase: Pauli paramagnetism
⇒ α phase: $f e^-$ more delocalized.
- γ phase: Curie Paramagnetism
⇒ γ phase: $f e^-$ is localized

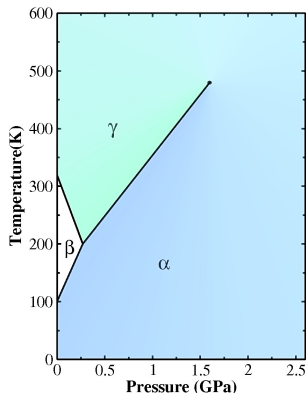


[Johansson, B. Phil. Mag. **30**, 469 (1974)]

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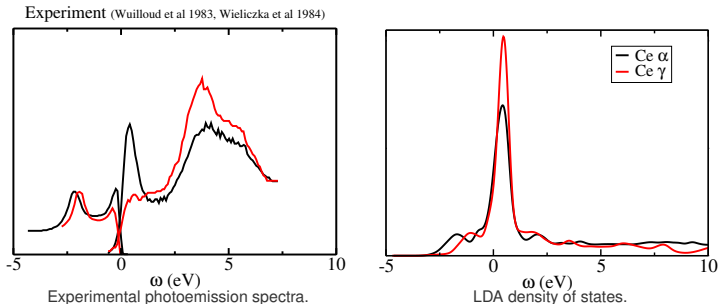
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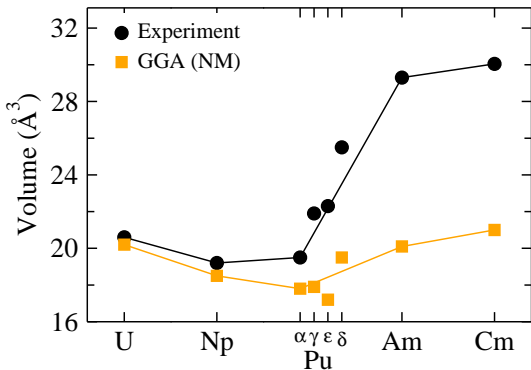


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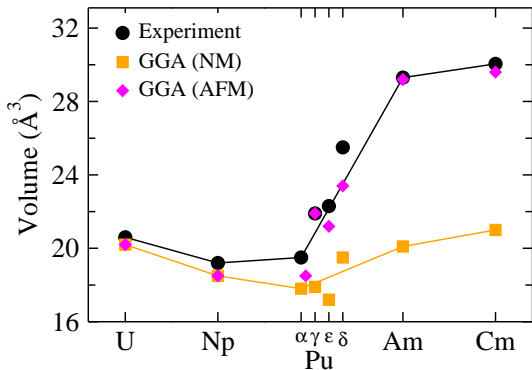
Only the α phase is described by DFT/LDA/GGA.



- Peak at the Fermi level **only in the α phase**.
 γ **and** α 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**
- $E_{\text{dft-lda}}(V)$: γ phase **not stable**



GGA: Cohesion is overestimated, not enough correlation

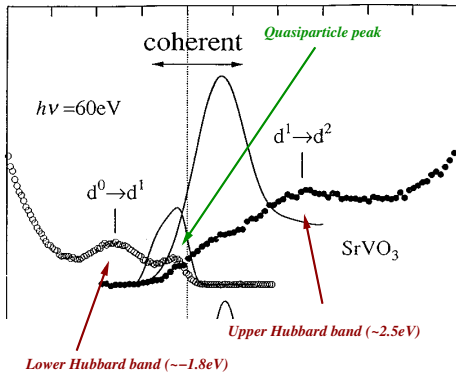
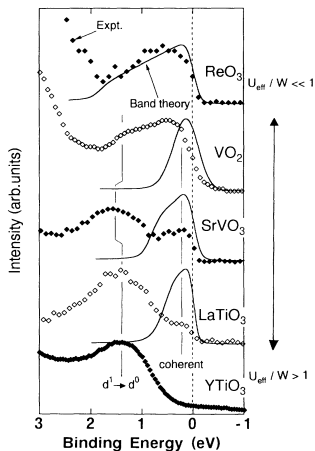


GGA-AFM: good description of volumes but magnetism is wrong

GGA(AFM) G. Robert, A. Pasturel, and B. Siberchicot *et al* Journal of Phys: Cond. Matter 15 8377 (2003), A.

Kutepov and S. Kutepova J. Magn. Mater. 272, E329 (2004)

GGA+OP P. Söderlind and B. Sadigh Phys. Rev. Lett. 92, 185702 (2004), P. Söderlind *et al* MRS Bull. 35, 883 (2010)



From Morikawa et al (1995)

Sekiyama 1992

⇒ YTiO₃ insulator: metal in LDA.

⇒ SrVO₃ is a metal: metal in LDA, but without the peak at -1.8 eV.

PERIODIC TABLE OF THE ELEMENTS

<http://www.ktf-split.hr/periodni/en/>

PERIOD	GROUP I		GROUP NUMBERS IUPAC RECOMMENDATION (1985)										GROUP NUMBERS CHEMICAL ABSTRACT SERVICE (1986)						GROUP VIII	
	1A	2A	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18		
1	1 1.0079 H HYDROGEN																	2 4.0026 He HELIUM		
2	3 6.941 Li LITHIUM	4 9.0122 Be BERYLLIUM											5 10.811 B BORON	6 12.011 C CARBON	7 14.007 N NITROGEN	8 15.999 O OXYGEN	9 18.998 F FLUORINE	10 20.180 Ne NEON		
3	11 22.990 Na SODIUM	12 24.305 Mg MAGNESIUM											13 26.982 Al ALUMINIUM	14 28.086 Si SILICON	15 30.974 P PHOSPHORUS	16 32.065 S SULFUR	17 35.453 Cl CHLORINE	18 39.948 Ar ARGON		
4	19 39.098 K POTASSIUM	20 40.078 Ca CALCIUM	21 44.956 Sc SCANDIUM	22 47.867 Ti TITANIUM	23 50.942 V VANADIUM	24 51.996 Cr CHROMIUM	25 54.938 Mn MANGANESE	26 55.945 Fe IRON	27 58.933 Co COBALT	28 58.693 Ni NICKEL	29 63.546 Cu COPPER	30 65.39 Zn ZINC	31 69.723 Ga GALLIUM	32 72.64 Ge GERMANIUM	33 74.922 As ARSENIC	34 78.96 Se SELENIUM	35 79.904 Br BROMINE	36 83.80 Kr KRYPTON		
5	37 85.468 Rb RUBIDIUM	38 87.62 Sr STRONTIUM	39 86.909 Y YTRBIUM	40 91.224 Zr ZIRCONIUM	41 92.906 Nb NIOBIUM	42 95.94 Mo MOLYBDENUM	43 (98) Tc TECHNETIUM	44 101.07 Ru RUTHENIUM	45 102.91 Rh RHODIUM	46 106.42 Pd PALLADIUM	47 107.87 Ag SILVER	48 112.41 Cd CADMIUM	49 114.82 In INDIUM	50 118.71 Sn TIN	51 121.76 Sb ANTIMONY	52 127.60 Te TELLURIUM	53 126.90 I IODINE	54 131.29 Xe XENON		
6	55 132.91 Cs CAESIUM	56 137.33 Ba BARIUM	57-71 La-Lu Lanthanide	72 178.49 Hf HAFNIUM	73 180.95 Ta TANTALUM	74 183.84 W WOLYBDENUM	75 186.21 Re RHENIUM	76 190.23 Os OSMIUM	77 192.22 Ir IRIDIUM	78 195.08 Pt PLATINUM	79 196.97 Au GOLD	80 200.59 Hg MERCURY	81 204.38 Tl THALLIUM	82 207.2 Pb LEAD	83 208.98 Bi BISMUTH	84 209 Po POLONIUM	85 (210) At ASTATINE	86 (222) Rn RADON		
7	87 (223) Fr FRANCIUM	88 (226) Ra RADIUM	89-103 Ac-Lr Actinide	104 (261) Rf RUFORDIUM	105 (262) Db DUBNIUM	106 (266) Sg SEABORGIUM	107 (264) Bh BOHRLIUM	108 (277) Hs HASSIUM	109 (268) Mt MEITNERIUM	110 (281) Uu UNUNILNIUM	111 (272) Uu UNUNILVIUM	112 (285) Uu UNUNILVIUM	114 (289) Uu UNUNQUADRIUM							

(1) Pure Appl. Chem., 73, No. 4, 987-833 (2001)
Relative atomic mass is shown with five significant figures. For elements having no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotopes of the element.
However, three such elements (Tl, Po, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

LANTHANIDE															
57 138.91 La LANTHANUM	58 140.12 Ce CESIUM	59 140.91 Pr PRASEODYMIUM	60 144.24 Nd NEODYMIUM	61 (145) Pm PROMETHIUM	62 150.36 Sm SAMARIUM	63 151.96 Eu EUROPIUM	64 157.25 Gd GADOLINIUM	65 158.93 Tb TERBIUM	66 162.50 Dy DYSPROSIUM	67 164.93 Ho HOLMIUM	68 167.26 Er ERBIUM	69 168.93 Tm THULIUM	70 173.04 Yb YTTERIUM	71 174.97 Lu LUTETIUM	
ACTINIDE															
89 (227) Ac ACTINIUM	90 232.04 Th THORIUM	91 231.04 Pa PROTACTINIUM	92 238.03 U URANIUM	93 (237) Np NEPTUNIUM	94 (244) Pu PLUTONIUM	95 (243) Am AMERICIUM	96 (247) Cm CURIUM	97 (247) Bk BERKELIUM	98 (251) Cf CALIFORNIUM	99 (252) Es EINSTEINIUM	100 (257) Fm FERMIUM	101 (268) Md MESENERIUM	102 (269) No NOBELIUM	103 (262) Lr LAWRENCIUM	

(table from de www.ktf-split.hr/periodni/en/)

Oversimplified...4d and 5d elements exhibits non negligible strong correlation effects

The exact hamiltonien is:

$$H = \sum_{i=1}^N \left[-\frac{1}{2} \nabla_{\mathbf{r}_i}^2 + V_{\text{ext}}(\mathbf{r}_i) \right] + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

It can be exactly rewritten in second quantization as:

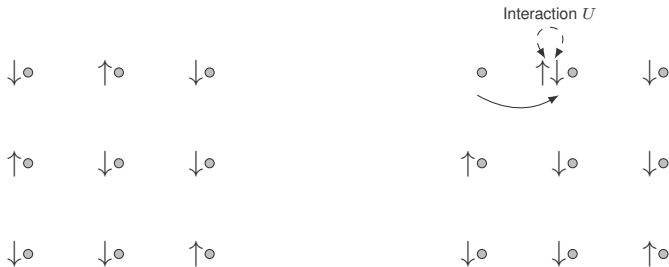
$$H = \sum_{i,j} \langle i|h|j \rangle c_i^\dagger c_j + \sum_{i,j,k,l} \langle ij|v|kl \rangle c_i^\dagger c_j^\dagger c_k c_l \quad (1)$$

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

$$H = \underbrace{\sum_{\mathbf{R}, \mathbf{R}'} t_{\mathbf{R}, \mathbf{R}'} c_{\mathbf{R}}^\dagger c_{\mathbf{R}'}}_{\text{one electron term : delocalization}} + \underbrace{\sum_{\mathbf{R}} U \hat{n}_{\mathbf{R}\uparrow} \hat{n}_{\mathbf{R}\downarrow}}_{\text{interaction term : localization}}$$

Competition between **delocalization** and **localization**

$$H = \underbrace{\sum_{\mathbf{R}, \mathbf{R}'} t_{\mathbf{R}, \mathbf{R}'} c_{\mathbf{R}}^{\dagger} c_{\mathbf{R}'}}_{\text{one electron term : delocalization}} + \underbrace{\sum_{\mathbf{R}} U \hat{n}_{\mathbf{R}\uparrow} \hat{n}_{\mathbf{R}\downarrow}}_{\text{interaction term : localization}}$$



- 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)

$$H = \sum_{i=1}^N \left[-\frac{1}{2} \nabla_{\mathbf{r}_i}^2 + V_{\text{ext}}(\mathbf{r}_i) \right] + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

- DFT solution

$$\frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \Rightarrow \sum_i V_{\text{Ha+xc}}(\mathbf{r}_i)$$

- Better: Keep local interaction between correlated localized orbitals.

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

- We need to solve:

$$H = \underbrace{\sum_{\mathbf{R}, \mathbf{R}'} \sum_{i, j} t_{ij}^{\mathbf{R}, \mathbf{R}'} c_{\mathbf{R}i}^\dagger c_{\mathbf{R}'j}}_{\text{one electron term (lda)}} + \underbrace{\frac{1}{2} \sum_{\mathbf{R}, f \neq f'} U_{ff'} \hat{n}_{\mathbf{R}f} \hat{n}_{\mathbf{R}f'}}_{\text{many body term : interactions}}$$

- 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 $n_f = \langle \hat{n}_f \rangle$

- Hamiltonian to solve (i : électrons):

$$H = \sum_{i=1}^N \left[-\frac{1}{2} \nabla_{\mathbf{r}_i}^2 + V_{\text{ext}}(\mathbf{r}_i) \right] + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

- Strong correlation in Localized orbitals (f, d)
- Other orbitals: DFT(LDA/GGA) could be tried..

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

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

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:

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

- $n_f = 0$, $V = V_{\text{LDA}} + \frac{U}{2}$
- $n_f = 1$, $V = V_{\text{LDA}} - \frac{U}{2}$
- ⇒ 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.
 $U = E(N+1) + E(N-1) - 2E(N) = I - A.$

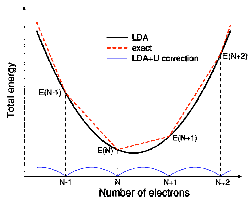


FIG. 1. (Color online) Sketch of the total energy profile as a function of number of electrons in a generic atomic system in contact with a reservoir. The bottom curve is simply the difference between the other two (the LDA energy and the “exact” result for an open system).

- Atom (integer nb of e^-) = The LDA+U correction disappears.
- ⇒ Self-interaction correction.
- ⇒ Discontinuity of the exchange and correlation potential.

From Cococcioni *et al* PRB 71 (2005)

see also Solovyev *et al* PRB 50

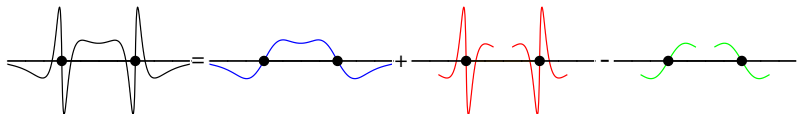
16861 (1994)

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

- The localized f orbital: What is its radial part ? \Rightarrow important but not discussed here.
- What is the value of effective Coulomb interaction U between these f orbitals ?

$$|\Psi_{\mathbf{k}\nu}\rangle = \underbrace{|\tilde{\Psi}_{\mathbf{k}\nu}\rangle}_{\text{On plane waves}} + \underbrace{\sum_i |\varphi_i\rangle \langle \tilde{p}_i | \tilde{\Psi}_{\mathbf{k}\nu}\rangle - \sum_i |\tilde{\varphi}_i\rangle \langle \tilde{p}_i | \tilde{\Psi}_{\mathbf{k}\nu}\rangle}_{\text{On a local radial grid}}$$

Blöchl PRB 1994



[Developed in ABINIT by the CEA group]

[M. Torrent, F. Jollet, F. Bottin, G. Zérah, X. Gonze Comp. Mat. Science 42 (2), 337-351 (2008)]

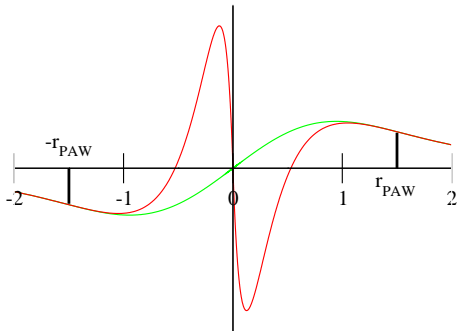
A grid devoted to local properties : well adapted to correlated systems and to compute:

- DFT+ U density matrix.
- Projected Wannier orbitals.

A Kohn-Sham function can be written:

$$|\Psi_{\mathbf{k}\nu}\rangle = \underbrace{|\tilde{\Psi}_{\mathbf{k}\nu}\rangle}_{\text{On plane waves}} + \underbrace{\sum_i |\varphi_i\rangle \langle \tilde{p}_i | \tilde{\Psi}_{\mathbf{k}\nu}\rangle - \sum_i |\tilde{\varphi}_i\rangle \langle \tilde{p}_i | \tilde{\Psi}_{\mathbf{k}\nu}\rangle}_{\text{On a local radial grid}}$$

- φ_i : atomic wavefunction
- $\tilde{\varphi}_i$: pseudo atomic wavefunction



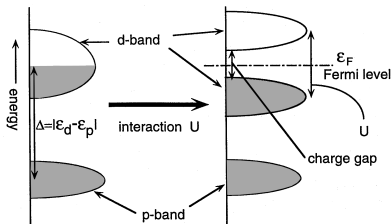
Double counting corrections: Atomic limit (or Full localized limit)
[Lichtenstein(1995), Anisimov (1991)]:

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

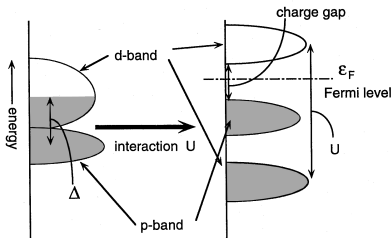
Around mean field version [Czyzyk(1994)] (delocalized limit):

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

(Made to correct the delocalized limit.)



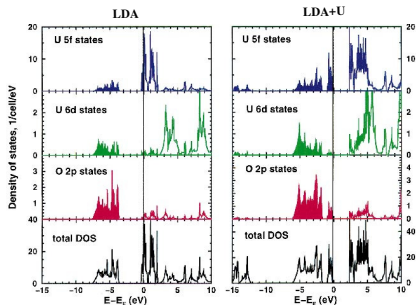
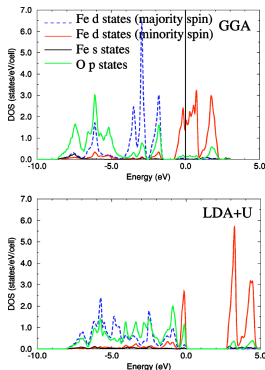
(a) Mott-Hubbard Insulator



(b) Charge Transfer Insulator

Mott insulators: Gap excitations are d-d (or f-f) ie between **Hubbard bands**.

Charge Transfer insulators: Gap excitations are **Op-d** (Or **Op-f**)



UO_2 (f^2): antiferromagnetic, insulator

$\text{Gap}_{\text{exp}} = 2.1 \text{ eV}$

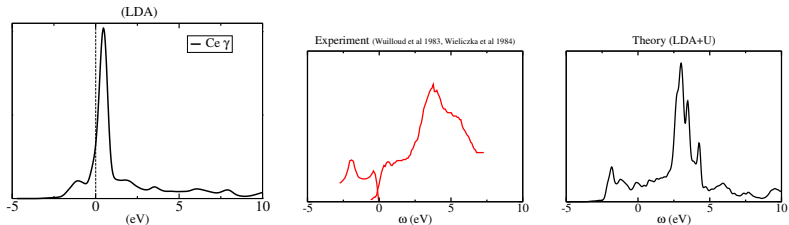
electrons localization: volume increases in LDA+U

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

Cococcioni *et al* PRB 71 2005

Dudarev *et al* Micron 31 2000

- Spectral functions: basic features are reproduced.



- Structural data

⇒ Electron repulsion induces a weakening of the bonding.

(1) Shick, Pickett, Lichtenstein 2000,
Amadon, Jollet, Torrent PRB 2008.

	Exp	LDA+U ¹	LDA
alat (au)	9.76	9.83/9.54	8.54
B_0 (GPa)	19	29.6/34	55

- But: The α phase is not correctly described, magnetism is incorrect (except for the β 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:

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

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.

$$|a\rangle = \sum_{m, L=l_{\text{cor}}} \langle m|a\rangle|m\rangle + \dots \text{terms neglected}$$

and show that (blackboard or exercise):

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

it can be rewritten as:

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

with

$$n_{m_1, m_2}^{\sigma} = \sum_a \langle m_1 | a \rangle f_a \langle a | m_2 \rangle = \sum_{\nu, \mathbf{k}} \langle m_1 | \Psi_{\nu, \mathbf{k}} \rangle f_{\nu, \mathbf{k}} \langle \Psi_{\nu, \mathbf{k}} | m_2 \rangle$$

One uses $\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \sum_{m=-k}^k \frac{4\pi}{2k+1} \frac{r_{<}^k}{r_{>}^{k+1}} Y_k^m(\theta_1, \phi_1) Y_k^{m*}(\theta_2, \phi_2)$ 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 of
pawu   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
  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 0.0 # dn density matrix
```

On the board...

A binit