Correlated metals and LDA+U

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On n'est pas tout à fait sincère sans être un peu ennuyex.

One cannot be fully honest without being somewhat boring.

Anatole France

Correlation effects manifest themselves in many ways
The two most common are:

A) Strongly localized electrons - examples:

1) Shallow levels - Cu metal, d-band

2) Mott-Hubbard insulators - NiO, FeO, La_2CuO_4

3) f-metals

(2–3: Classic domain for LDA+U)

B) Magnetic correlations - examples:

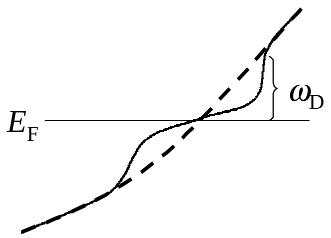
1) Exchange splitting in Ni

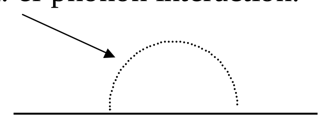
2) Spin-fluctuation induced mass renormalization - Sr_2RuO_4, CrO_2

3) Quantum Critical Point and suppression of magnetism by fluctuations - $ZrZn_2$, $Sr_3Ru_2O_7$, FeAl

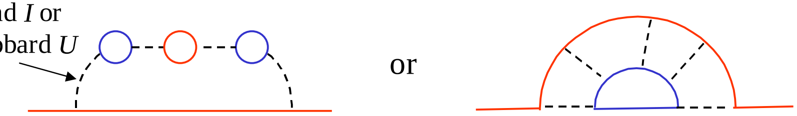
Spin-fluctuation induced mass renormalization

Cf. el-phonon interaction:



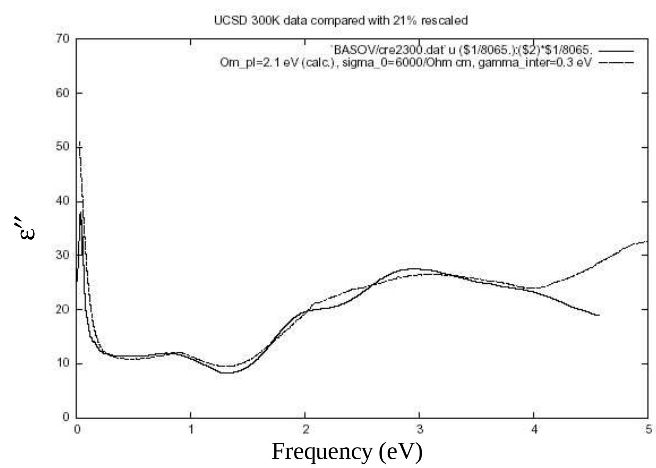


Let's say, we have spin fluctuations a la Berk-Schrieffer:



We expect bands to become heavier within several eV of the Fermi level (comparable to the bandwidth). Indeed...

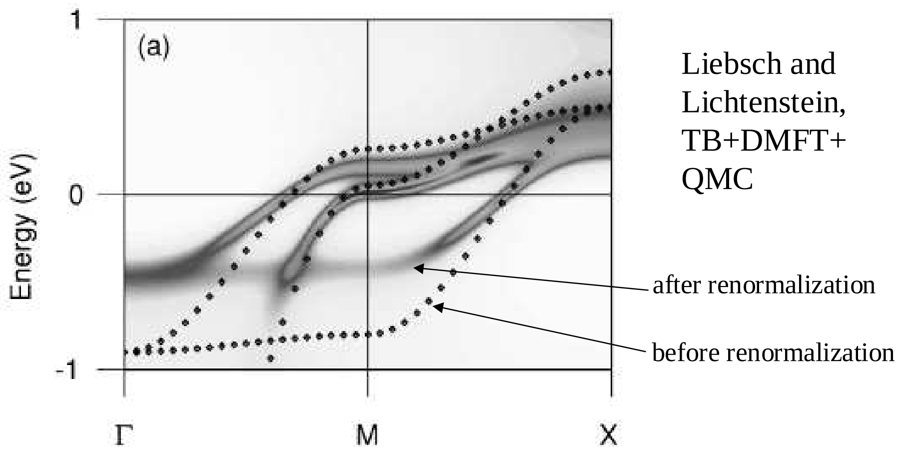
An example of mass renormalization: CrO_2 optics.



Expt: Basov et al, Theory: Ambrosh-Draxl, Singh, IIM

theoretical curve is downscaled by 21%!

Sr_2RuO_4: de Haas-van Alphen mass renormalization of the order 3-4 (depending on the band)



Liebsch and Lichtenstein, TB+DMFT+ QMC

Ferromagnetic Quantum Critical Point and related issues

For strongly correlated systems LSDA consistently underestimates the tendency to magnetism (cuprates, NiO etc)

For strongly *fluctuating* systems LSDA consistently *over*estimates it.

FeAl: M=0.7 μ_B, exp paramagnetic
$Sr_3Ru_2O_7$: M=0.6 μ_B, exp paramagnetic
$ZrZn_2$: M=0.7 μ_B, exp 0.2 μ_B
Pd: χ/χ_0=10-12, exp.: 5-6
Ni: Exchange splitting in LDA twice larger than in the exp.

All these are close to a QCP

LiV_2O_4: M=1 μ_B exp paramagnetic. Frustrated AFM, fluctuations...

Does LDA+U help?
First, *which* LDA+U? ("My name is Legion, for we are many.")

LDA+U

$$\Delta H^0_{LDA+U} = \frac{U}{2}\sum_{m\sigma \neq m'\sigma'} n_{m\sigma}n_{m'\sigma'} - \frac{J}{2}\sum_{m\neq m',\sigma} n_{m\sigma}n_{m'\sigma}$$

$$= \frac{UN^2}{2} - \frac{J}{2}\sum_{\sigma} N_\sigma^2 - \frac{U-J}{2}\sum_{m\sigma} n^2_{m\sigma}$$

Need to subtract double counting!

Hartree part is done exceedingly well in LDA - so one need to remove the corresponding part from the "+U" terms

The "+U" potential is $V_{m\sigma} = Un - Jn_\sigma - (U-J)n_{m\sigma}$

LDA=mean-field;
the m.f. part is $V_{m.f.a.} = Un - Jn_\sigma - (U-J)x_\sigma$

What is *x*?

1) "AMF-LDA+U" (Around Mean Field)

$$V_{m\sigma} = Un - Jn_\sigma - (U-J)n_{m\sigma}$$
$$V_{m.f.a.} = Un - Jn_\sigma - (U-J)x_\sigma$$

$\Longrightarrow$

$$x_\sigma = \langle n_{m\sigma}\rangle = \frac{n_\sigma}{2l+1}$$

This leads to

$$H_{m.f.a.} = \frac{Un^2}{2} - \sum_\sigma \frac{Jn_\sigma^2}{2} - \sum_\sigma \frac{(U-J)n_\sigma^2}{2(2l+1)}$$

and

$$\Delta E_{AMF.} = \frac{(U-J)}{2}\left(\sum_{m\sigma} n^2_{m\sigma} - \sum_\sigma \frac{n_\sigma^2}{2l+1}\right) = \frac{(U-J)}{2}\sum_{m\sigma}\left(n_{m\sigma} - \frac{n_\sigma}{2l+1}\right)^2$$

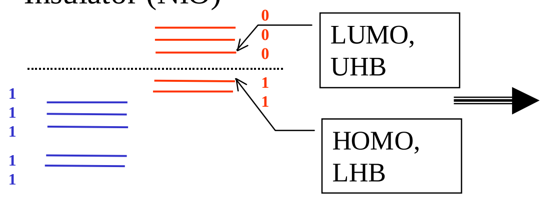
$$\Delta V_{AMF}(m) = (U-J)\left[n_{m\sigma} - n_\sigma/(2l+1)\right]$$

This mean field is similar to Slater X_α method: averaging potential over all occupied states. The "Kohn-Sham mean field" potential is the potential at μ.

Note: if all $n_{m\sigma} = \langle n_\sigma \rangle$ then $\Delta V_{AMF}=0$, $\Delta E_{AMF}=0$, and AMF *is* Kohn-Sham! But not if $n_{m\sigma}$ *are different!*

2) "FLL -LDA+U" (fully localized, AKA as SIC)

Insulator (NiO)



$$x_\sigma = \frac{n_{LUMO} + n_{HOMO}}{2} = \frac{1}{2}$$

This leads to

$$H_{m.f.a.} = \frac{Un^2}{2} - \sum_\sigma \frac{Jn_\sigma^2}{2} - \left(\frac{Un}{2} - \sum_\sigma \frac{Jn_\sigma}{2} \right) = \frac{Un(n-1)}{2} - \sum_\sigma \frac{Jn_\sigma (n_\sigma - 1)}{2}$$

Thus SIC!

and

$$\Delta E_{SIC.} = \frac{(U-J)}{2} \left(\sum_{m\sigma} n_{m\sigma}^2 - \sum_\sigma n_\sigma \right)$$

$$\Delta V_{SIC}(m) = (U-J)\left[n_{m\sigma} - 1/2 \right]$$

Note: if $n_{m\sigma}$= {0,1} then ΔE_{SIC}=0, but $\Delta V_{SIC} \neq 0$ -- right in the DFT spirit!

(nearly) most general formula

$$H_{m.f.a.} = \frac{Un^2}{2} - \sum_\sigma \frac{Jn_\sigma^2}{2} - \sum_\sigma \left[\frac{U-J}{2} (S_\sigma n_\sigma^2 + P_\sigma n_\sigma) \right]$$

AMF: $S = 1/(2l+1),\ P = 0$

SIC: $S = 0,\ P = 1/2$

SIC is the right "DFT" mean field for localized systems, $n_{m\sigma}$= 1 or 0
AMF is the right "DFT" mean field for for uniform occupancy, $n_{m\sigma} = \langle n_\sigma \rangle$

How can we generalize it onto arbitrary $n_{m\sigma}$? Let's impose that at the self-consistency ΔE_{DFT}=0 ("DFT" of the Hubbard part gives the right Hubbard energy).

The following inequality holds: $n_\sigma^2/(2l+1) \leq \sum_m n_{m\sigma}^2 \leq n_\sigma$

So let us set $(2l+1)S_\sigma + P_\sigma = 1$

Alternative formula

$$H_{m.f.a.} = \frac{Un^2}{2} - \sum_{\sigma} \frac{Jn_\sigma^2}{2} - \sum_{\sigma} \left[\frac{U-J}{2} \left((1-\alpha_\sigma) n_\sigma^2 /(2l+1) + \alpha_\sigma n_\sigma \right) \right]$$

AMF: α_σ=0 FLL: α_σ=1

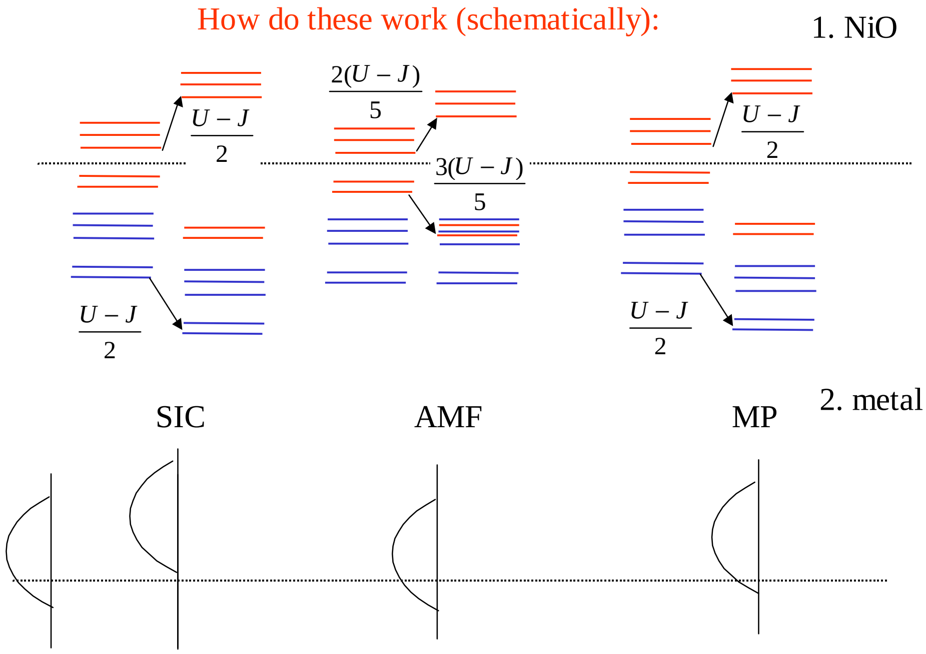
$$\Delta E_{KS} = -\frac{(U-J)}{2} \left(\sum_{m\sigma} n_{m\sigma}^2 - \sum_{\sigma} (\alpha_\sigma n_\sigma + (1-\alpha_\sigma) n_\sigma^2 /(2l+1)) \right) = 0; \quad \Rightarrow$$

$$\Rightarrow \quad \alpha_\sigma = \frac{\sum_m (n_{m\sigma} - \langle n_\sigma \rangle)^2}{(2l+1)\langle n_\sigma \rangle (1 - \langle n_\sigma \rangle)}, \qquad \text{where} \quad \langle n_\sigma \rangle = n_\sigma /(2l+1)$$

$$\Delta V_{KS}(m) = -(U-J)\left(n_{m\sigma} - \alpha_\sigma /2 - (1-\alpha_\sigma) n_\sigma /(2l+1) \right)$$

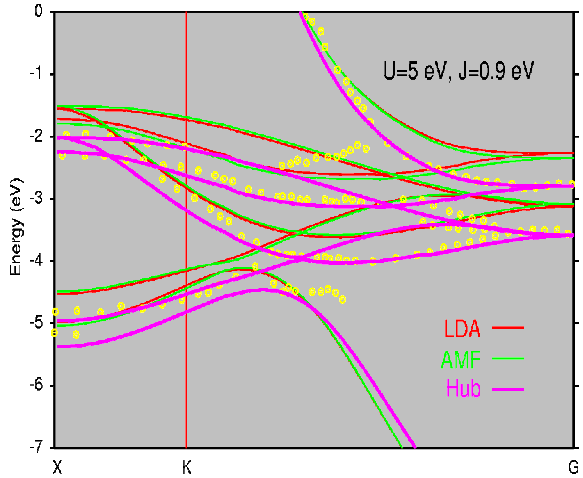
Note: it looks like α depends on n_m. It does not. It is a constant for a given system, determined by n_m in the self-consistent state. But in practice, it will change from iteration to iteration.

How do these work (schematically):



Some application examples

Localized states - Cu metal: AMF fails, FLL works



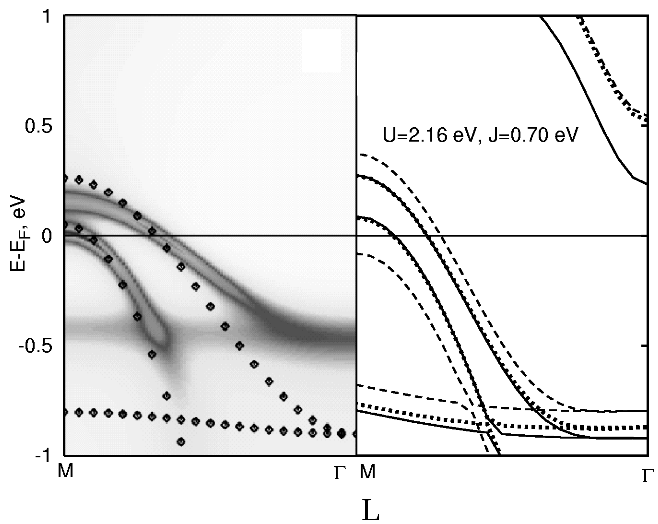
LDA: d-band 0.4 eV too high.

LDA+U(AMF): no change

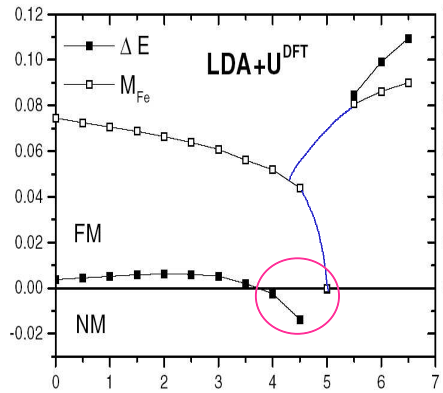
LDA+U(FLL): excellent agreement with the experiment, but somewhat smallish U.

A weakly correlated metal: Sr_2RuO_4

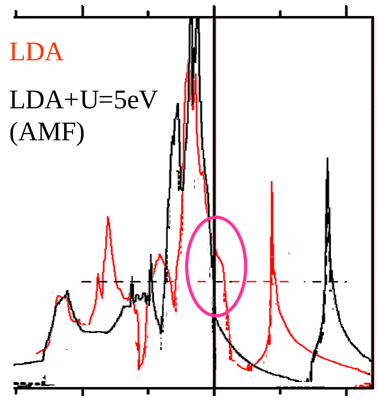
Neither LDA+U works



Spin fluctuations near a Quantum Critical point: FeAl
LDA: M=0.7 μ_B, exp: paramagnetic
FLL fails, AMF *seems* to work.



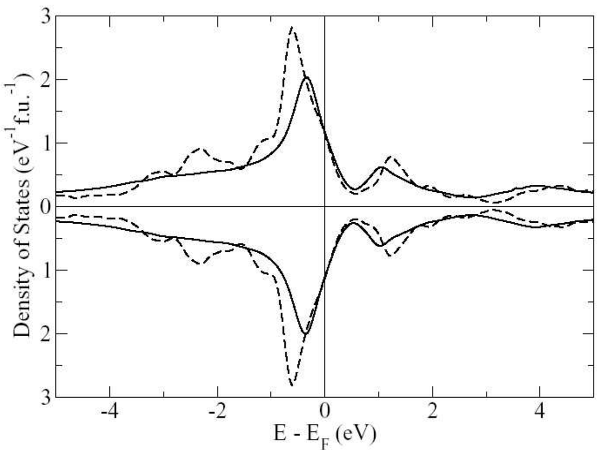
Mohn et al. PRL,'02



Magnetism is lost because of reduced DOS

Why LDA+U(AMF) at small U makes FeAl less magnetic?
Because LDA+U increases the crystal field.

Is this the right physics?
SF renormalization makes bands heavier ⇒ should *reduce* DOS!



Lichtenstein and Chioncel, DMFT

What ***do*** we believe to be the right physics near QCP?

$$\Delta E_{LSDA}(m) = \frac{m^2}{4}[N_{\uparrow}^{-1}(E_F) - I] + am^4$$

Fluctuations of magnetization add a 2nd order term $\propto a\langle \delta m^2 \rangle$

Stoner I is reduced *because of the zero-point spin fluctuations*.

How do LDA+U's fare? — *N* diagonal

$$-\frac{2d^2E(m)}{dm^2} = \Delta I_{AMF} = (U-J)\left[\mathrm{Tr}(N\square N) - \frac{(\mathrm{Tr}N)^2}{2l+1}\right] / N_{tot}^2 \qquad 0$$

$$-\frac{2d^2E(m)}{dm^2} = \Delta I_{SIC} = (U-J)\mathrm{Tr}(N\square N)/N_{tot}^2 \qquad \frac{U-J}{2l+1}$$

.

<u>Main problems of LDA+U</u>

Problem one: LDA+U is static — Corrected in DMFT

Problem two: spatial dependence of Coulomb potential is primitive!

Problem three: There is no unique recipe.

} DMFT as well

Conclusion: weakly correlated metals remain a challenge.