Part 1: Weakly Correlated Metals and LDA+U -- Shall We Try to be Honest?

Correlated metals and LDA+U
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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$_2$CuO$_4$
   3) f-metals

B) Magnetic correlations - examples:
   1) Exchange splitting in Ni
   2) Spin-fluctuation induced mass renormalization - Sr$_3$RuO$_4$, CrO$_2$
   3) Quantum Critical Point and suppression of magnetism by fluctuations - ZrZn$_2$, Sr$_3$Ru$_2$O$_7$, FeAl

On n’est pas tout à fait sincère sans être un peu ennuyeux.
One cannot be fully honest without being somewhat boring.

Anatole France

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Spin-fluctuation induced mass renormalization

Cf. el-phonon interaction:

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

Hund $I$ or Hubbard $U$

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%!*

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\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{Sr$_2$RuO$_4$: de Haas-van Alphen mass renormalization of the order 3-4 (depending on the band)}
\end{figure}

\textbf{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 overestimates it.

\begin{itemize}
  \item FeAl: $M=0.7 \, \mu_B$, exp paramagnetic
  \item Sr$_2$Ru$_2$O$_7$: $M=0.6 \, \mu_B$, exp paramagnetic
  \item ZrZn$_2$: $M=0.7 \, \mu_B$, exp 0.2 $\mu_B$
  \item Pd: $\chi/\chi_0=10$-$12$, exp.: 5-6
  \item Ni: Exchange splitting in LDA twice larger than in the exp.
\end{itemize}

All these are close to a QCP

\begin{itemize}
  \item LiV$_2$O$_4$: $M=1 \, \mu_B$ exp paramagnetic. Frustrated AFM, fluctuations...
\end{itemize}

Does LDA+U help?
First, \textit{which} LDA+U? (“My name is Legion, for we are many.”)
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LDA+U

\[
\Delta H_{\text{LDA+U}}^0 = \frac{U}{2} \sum_{m \neq m'} n_{m \sigma} n_{m' \sigma} - \frac{J}{2} \sum_{m \neq m', \sigma} n_{m \sigma} n_{m' \sigma}
\]

\[
= \frac{UN^2}{2} - \frac{J}{2} \sum_\sigma N_\sigma^2 - \frac{U - J}{2} \sum_{m \sigma} n_{m \sigma}^2
\]

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

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

What is \( x \)?

1) “AMF-LDA+U”
(Around Mean Field)

\[
V_{\text{m.f.}} = Un - Jn_\sigma - (U - J)n_{m \sigma}
\]

\[
V_{\text{m.f.}} = Un - Jn_\sigma - (U - J)x_\sigma
\]

This leads to \( H_{\text{m.f.}} = \frac{Un^2}{2} - \sum_\sigma \frac{n_\sigma^2}{2} - \sum_\sigma \frac{(U - J)n_{\sigma}^2}{2(2l + 1)} \)

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

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

This mean field is similar to Slater X_\alpha method: averaging potential over all occupied states. The “Kohn-Sham mean field” potential is the potential at \( \mu \).

Note: if all \( n_{m \sigma} = \langle n_\sigma \rangle \) then \( \Delta V_{\text{AMF}} = 0, \Delta E_{\text{AMF}} = 0 \), and AMF is Kohn-Sham! But not if \( n_{m \sigma} \) are different!
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<table>
<thead>
<tr>
<th>Insulator (NiO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LUMO, UHB</td>
</tr>
<tr>
<td>HOMO, LHB</td>
</tr>
</tbody>
</table>

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

\[
\begin{align*}
\chi_\sigma &= n_{LUMO} + n_{HOMO} \\
&\leq \frac{1}{2}
\end{align*}
\]

This leads to

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

and

\[
\Delta E_{\text{SIC}} = \frac{(U - J)}{2} \left( \sum_\sigma n_{\sigma}^2 - \sum_\sigma n_\sigma \right)
\]

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

Note: if \(n_{m\sigma} = \{0,1\}\) then \(\Delta E_{\text{SIC}} = 0\), but \(\Delta V_{\text{SIC}} \neq 0\) -- 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 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 \(\Delta E_{\text{DFT}} = 0\) (“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 \((2l+1)S_\sigma + P_\sigma = 1\)
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Alternative formula

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

AMF: \( \alpha_{\sigma} = 0 \)  
FLL: \( \alpha_{\sigma} = 1 \)

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

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

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

Note: it looks like \( \alpha \) 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):

1. NiO

2. metal

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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$_2$RuO$_4$
Neither LDA+U works

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Spin fluctuations near a Quantum Critical point: FeAl
LDA: M=0.7 $\mu_B$, exp: paramagnetic
FLL fails, AMF \textit{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 $\Rightarrow$ should \textit{reduce} DOS!

Lichtenstein and Chioncel, DMFT
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What do we believe to be the right physics near QCP?

\[ \Delta E_{LSDA}(m) = \frac{m^2}{4} \left[ N^{-1}_\uparrow(E_F) - I \right] + am^4 \]

Fluctuations of magnetization add a 2nd order term \( \propto a<\delta m^2> \)

Stoner \( I \) is reduced because of the zero-point spin fluctuations.

How do LDA+U’s fare? \( N \) diagonal

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

\[ \frac{-2d^2E(m)}{dm^2} = \Delta I_{SC} = (U - J) \text{Tr}(N\|N) / N_{\text{tot}}^2 \]

Main problems of LDA+U

Problem one: LDA+U is static \( \text{Corrected in DMFT} \)

Problem two: spatial dependence of Coulomb potential is primitive!

Problem three: There is no unique recipe.

Conclusion: weakly correlated metals remain a challenge.