First-principles description of correlated electron materials: LDA+U and beyond

Purpose:

- Understanding the limitation of standard local approximations to describe correlated electron systems
- Understanding the basic idea of LDA+U and other related methods
- Understanding recent progress on LDA+U functionals
Contents:

✓ Failure of LDA and similar approximations to describe correlated electron physics
✓ Basics of LDA+U: Idea, technical and physical issues…
✓ DMFT (dynamical mean field theory) and others

Suggested Reading:


R. M. Martin, “Electronic structure: Basic theory and practical methods (CUP 2004)”

V. I. Anisimov et al., “Strong Coulomb correlations in electronic structure calculations: Beyond the local density approximation (Gordon & Breach 2000)”


Local Density Approximation

✓ ‘Local’ approximation based on the solution of ‘homogeneous’ electron gas

✓ Get in trouble whenever these approximations become invalidated:
   For examples,

   (Weak) van der Waals interaction originating from the fluctuating dipole moments

   (Strong) On-site Coulomb repulsion which is originated from the atomic nature of localized d- or f- electrons in solids
A material with partially-filled band(s) should be metallic

Kittel, *Introduction to Solid State Physics*
Insulator: Pauli and Mott

Pauli exclusion: band insulator

Coulomb repulsion: Mott (-Hubbard) insulator
Localized Orbital and Hubbard Model

Hubbard Model (1964)

\[ H = - \sum_{i,j,\sigma} t_{ij} (c_{i\sigma}^\dagger c_{j\sigma} + \text{H.c.}) + U \sum_i n_{i\uparrow} n_{i\downarrow} \]

- **‘Hopping’ term between the sites**
- **On-site Coulomb repulsion in the correlated orbitals**

Additional electron occupation requires the energy cost:

\[ U = E(d^{n+1}) + E(d^{n-1}) - 2E(d^n) \]


http://theor.jinr.ru/~kuzemsky/jhbio.html
Actually Happening Quite Often

Localized valence wavefunctions

Partially filled 3d, 4f, 5f orbitals → magnetism and others
Applying LDA to ‘Mott’ Insulators

Oguchi et al., PRB (1983)
Terakura et al., PRB (1984)

- Too small or zero band gap
- Magnetic moment underestimated
- Too large exchange coupling (Tc)

TABLE III. Experimental and theoretical exchange parameters (in K) of the first and the second neighbors.

<table>
<thead>
<tr>
<th></th>
<th>MnO</th>
<th>MnS</th>
<th>NiO</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>J₁</td>
<td>J₂</td>
<td>J₁</td>
<td>J₂</td>
<td>J₁</td>
</tr>
<tr>
<td>-14.4</td>
<td>-7.0</td>
<td>-8.0</td>
<td>-9.0</td>
<td>-50</td>
</tr>
<tr>
<td>-9.0</td>
<td>-10.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-10.0</td>
<td>-11.0</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>-28</td>
<td>-28</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-30.3</td>
<td>-29.8</td>
<td>-10</td>
<td>-27</td>
<td>61</td>
</tr>
</tbody>
</table>
Combining LDA with Hubbard Model

Band theory and Mott insulators: Hubbard $U$ instead of Stoner $I$

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(Received 4 September 1990; revised manuscript received 5 March 1991)

We propose a form for the exchange-correlation potential in local-density band theory, appropriate for Mott insulators. The idea is to use the “constrained-local-density-approximation” Hubbard parameter $U$ as the quantity relating the single-particle potentials to the magnetic- (and orbital-) order parameters. Our energy functional is that of the local-density approximation plus the mean-field approximation to the remaining part of the $U$ term. We argue that such a method should make sense, if one accepts the Hubbard model and the success of constrained-local-density-approximation parameter calculations. Using this ab initio scheme, we find that all late-3$d$-transition-metal monoxides, as well as the parent compounds of the high-$T_c$ compounds, are large-gap magnetic insulators of the charge-transfer type. Further, the method predicts that LiNiO$_2$ is a low-spin ferromagnet and NiS a local-moment $p$-type metal. The present version of the scheme fails for the early-3$d$-transition-metal monoxides and for the late 3$d$ transition metals.

**Basic idea:** Introduce Hubbard-like term into the energy functional (and subtract the equivalent LDA term to avoid the double counting)

$$E_{LDA+U} = E_{LDA} + E_U - E_{dc}$$

where $E_U = \frac{1}{2} \sum_{ilm\sigma} U n_{ilm}^\sigma n_{ilm'}^{\sigma'}$
LDA+U Functional

The (original) form of energy functional (Anisimov et al. 1991)

\[ E = E^{\text{LDA}} + \frac{1}{2} \sum_{m,m',\sigma} U(n_{im\sigma} - n^0)(n_{im'\sigma} - n^0) \]
\[ + \frac{1}{2} \sum_{m,m',\sigma} (U - J)(n_{im\sigma} - n^0)(n_{im'\sigma} - n^0). \]

\( i \): site index (orbitals)

\( n^0 \): average d-orbital occupation (no double counting correction)

\( J \): Hund coupling constant

Orbital-dependent potential

\[ V_{m\sigma} = U \sum_{m'} (n_{m'\sigma} - n^0) \]
\[ + (U - J) \sum_{m' \neq m} (n_{m'\sigma} - n^0) + V^{\text{LDA}}. \]
LDA+U Result

- **Band gap (in eV):**

<table>
<thead>
<tr>
<th>( U ) (eV)</th>
<th>MnO</th>
<th>FeO</th>
<th>CoO</th>
<th>NiO</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.04</td>
<td>0.00</td>
<td>0.00</td>
<td>0.36</td>
</tr>
<tr>
<td>2</td>
<td>1.68</td>
<td>0.76</td>
<td>1.20</td>
<td>1.56</td>
</tr>
<tr>
<td>4</td>
<td>2.12</td>
<td>1.96</td>
<td>2.20</td>
<td>2.53</td>
</tr>
<tr>
<td>6</td>
<td>4.21</td>
<td>2.77</td>
<td>3.01</td>
<td>3.89</td>
</tr>
<tr>
<td>Calc. (LSDA)</td>
<td>0.8(^a)</td>
<td>0.0(^a)</td>
<td>0.0(^a)</td>
<td>0.2(^a)</td>
</tr>
<tr>
<td>Calc. (LDA+U)</td>
<td>3.5(^b)</td>
<td>3.2(^c)</td>
<td>3.2(^d)</td>
<td>3.1(^e)</td>
</tr>
<tr>
<td>Expt.</td>
<td>3.6-3.8(^f)</td>
<td>2.4(^g)</td>
<td>2.4(^h)</td>
<td>4.0(^i), 4.3(^j)</td>
</tr>
</tbody>
</table>

- **Magnetic moment of NiO (in \( \mu_B \)):**

<table>
<thead>
<tr>
<th>( U ) (eV)</th>
<th>Mulliken</th>
<th>Voronoi</th>
<th>Other group results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Full</td>
<td>Dual</td>
<td>On-site</td>
</tr>
<tr>
<td>0</td>
<td>1.30</td>
<td>1.30</td>
<td>1.30</td>
</tr>
<tr>
<td>2</td>
<td>1.48</td>
<td>1.54</td>
<td>1.59</td>
</tr>
<tr>
<td>4</td>
<td>1.59</td>
<td>1.66</td>
<td>1.71</td>
</tr>
<tr>
<td>6</td>
<td>1.66</td>
<td>1.74</td>
<td>1.79</td>
</tr>
<tr>
<td>Expt.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

MJH, Ozaki and Yu
PRB (2006)
Further Issues

✓ Rotational invariance and several different functional forms

\[ E^U[n] = \frac{1}{2} \sum_{\{m\}, \sigma} \left\{ \langle m, m'' | V_{ee} | m', m''' \rangle n^\sigma m_m n^{-\sigma}_{m'' m'''} + \langle m, m'' | V_{ee} | m', m''' \rangle - \langle m, m'' | V_{ee} | m''', m' \rangle n^\sigma_{m_m} n^\sigma_{m'' m'''} \right\}, \]

\[ E_{dc}[n^\sigma] = \frac{1}{2} Un(n - 1) - \frac{1}{2} J [n^\uparrow (n^\uparrow - 1) + n^\downarrow (n^\downarrow - 1)]. \]

(So-called) fully localized limit: Liechtenstein et al. PRB (1995)

\[ E^{\text{LSDA+AMF}} = E^{\text{LSDA}} + \frac{1}{2} \sum_{m, m', \sigma} U_{mm'} (n_{m\sigma} - n^0_{\sigma}) \times (n_{m'-\sigma} - n^0_{-\sigma}) \]

\[ + \frac{1}{2} \sum_{m, m', m \neq m', \sigma} (U_{mm'} - J_{mm'}) (n_{m\sigma} - n^0_{\sigma}) \times (n_{m'\sigma} - n^0_{\sigma}). \]  

(So-called) around the mean field limit: Czyzyk et al. PRB (1994)
Numerically generated (pseudo-) atomic orbital basis set:
Non-orthogonal multiple d-/f-orbitals with arbitrarily-chosen cutoff radii

LDA+U based on LCPAO (2)

✓ Non-orthogonality and no guarantee for the sum rule

See, for example, Pickett et al. PRB (1998)

‘On-site’ representation

‘Full’ representation

Non-orthogonality and no guarantee for the sum rule

Proposed ‘dual’ representation:

\[
\hat{\rho}_{smm'} = \frac{1}{2} (|s\bar{m}\sigma\rangle\langle sm'\sigma| + |sm\sigma\rangle\langle s\bar{m}'\sigma|)
\]

Sum rule satisfied:

\[
\sum_\sigma Tr(n^\sigma) = \sum_\sigma \frac{1}{2} [Tr(S\rho^\sigma) + Tr(\rho^\sigma S)] = N_{ele}
\]

where \( n^\sigma \) is the density matrix.
LDA+U based on LCPAO (3)


- LCPAO and O(N) LDA+U: Large-scale correlated electron systems

Limitations

✓ How to determine the U and J values?
   No fully satisfactory way to determine the key parameters
   c-LDA (e.g., Hybersen, Andersen, Anisimov et al 1980s, Cococcioni et al. 2005),
   (Sakakibara, MJH et al. 2016)

✓ How to define the double-counting energy functional?
   Fully-localized limit, Around-the-mean-field form, Simplified rotationally
   invariant from, etc
   See, Anisimov et al. (1991); Czyzyk and Sawatzky (1994); Dudarev et al. (1998)

✓ It is a static Hartree-Fock method
   The correlation effect beyond this static limit cannot be captured
   → Dynamical mean-field theory
Dynamical Correlation and DMFT

✔ Dynamical mean-field theory

Mapping ‘**Hubbard Hamiltonian**’ into ‘**Anderson Impurity Hamiltonian**’ plus ‘**self-consistent equation**’

Georges et al., Rev. Mod. Phys.(1996); Kotliar et al., Rev. Mod. Phys.(2006);
DMFT Result

Impurity level (atomic-like): width $\sim V^2$ (hybridization)

On-site correlation at the impurity site (or orbital): $E_d + U/2$

Zhang et al., PRL (1993)

LaTiO$_3$/LaAlO$_3$ superlattice: calculated by J.-H. Sim (OpenMX + ALPS-DMFT solver)
Comparison

**LDA**
No on-site correlation (homogeneous electron gas)

**LDA+U**
Hubbard-U correlation
Static approximation

**LDA+DMFT**
Hubbard-U correlation
Dynamic correlation

Application to high-$T_c$ cuprate

LDA+U and DMFT

✓ LDA+U is the static (Hartree) approximation of DMFT:
  - Temperature dependency
  - Electronic property near the phase boundary
  - Paramagnetic insulating and correlated metallic phase

LaTiO$_3$/LaAlO$_3$ superlattice: calculated by J.-H. Sim (OpenMX + ALPS-DMFT solver)
Other Methods

✓ Hybrid functionals, self-interaction correction, etc
  • Inclusion of atomic nature can always be helpful
  • ‘Controllability’ versus ‘parameter-free’-ness
  • Hidden parameters (or factors)
  • Computation cost (→ relaxation etc)

✓ (Self-consistent) GW
  • Parameter-free way to include the well-defined self energy
  • No way to calculate total energy, force,…etc
  • Fermi liquid limit
PART 2

Purpose:

✓ Introducing recent progress on understanding LDA+U functionals

Contents:

✓ LDA+U functionals reformulated
✓ Comparison of LDA+U with LSDA+U
✓ Case studies and Perspective

Suggested Reading:

**DFT+U (or +DMFT) Formalism: Basic Idea**

\[ E^{\text{DFT+U}}[\rho^\sigma, n^\sigma] = E^{\text{DFT}}[\rho^\sigma] + E^{\text{int}}[n^\sigma] - E^{\text{dc}} \]

where \( E^{\text{int}}[n^\sigma] \): Hubbard-type on-site interaction term

\( E^{\text{dc}} \): (conceptually) the same interaction energy in LDA/GGA
DFT+U (or +DMFT) Formalism: The Issue (1)

\[ E^{\text{DFT+U}}[\rho^\sigma, n^\sigma] = E^{\text{DFT}}[\rho^\sigma] + E^{\text{int}}[n^\sigma] - E^{\text{dc}} \]

where \( E^{\text{int}}[n^\sigma] \): Hubbard-type on-site interaction term

\( E^{\text{dc}} \): (conceptually) the same interaction energy in LDA/GGA

- \( E^{\text{int}} \): Expression, basis-set dependence, rotational invariance, … etc
- \( E^{\text{dc}} \): No well-established prescription

→ FLL (fully localized limit) vs AMF (around the mean field)

Anisimov, Solovyev et al., PRB (1993)
Czyzyk & Sawatzky, PRB (1994)
Liechtenstein et al., PRB (1995)
Petukhov, Mazin et al., PRB (2003)
Pourovskii, Amadon et al., PRB (2007)
Amadon, Lechermann et al., PRB (2008)
X. Wang, MJH et al., PRB (2012)
H. Park, Millis, Marianetii, PRB (2014)
Haule, PRL (2015)
…
DFT+U (or +DMFT) Formalism: The Issue (2)

\[ E^{\text{DFT+U}}[\rho^\sigma, n^\sigma] = E^{\text{DFT}}[\rho^\sigma] + E^{\text{int}}[n^\sigma] - E^{\text{dc}} \]

where \( E^{\text{int}}[n^\sigma] \): Hubbard-type on-site interaction term

\( E^{\text{dc}} \): (conceptually) the same interaction energy in LDA/GGA

- \( E^{\text{int}} \): Expression, basis-set dependence, rotational invariance,… etc
- \( E^{\text{dc}} \): No well-established prescription

→ FLL (fully localized limit) vs AMF (around the mean field)

- \( E^{\text{DFT}} \): charge-only-density XC (LDA) or spin-density XC (LSDA) ??

<table>
<thead>
<tr>
<th>CDFT+U</th>
<th>SDFT+U</th>
</tr>
</thead>
</table>
No systematic formal analysis on this fundamental issue
(Some case studies and internal agreement in DMFT community)

Density functional plus dynamical mean-field theory of the spin-crossover molecule Fe(phen)$_2$(NCS)$_2$

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Density functional versus spin-density functional and the choice of correlated subspace in multivariable effective action theories of electronic structure

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Spin-density functional theories and their $+U$ and $+J$ extensions: A comparative study of transition metals and transition metal oxides

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(Received 18 November 2015; published 26 January 2016)
The Issue Formulated

- Total energy; CDFT+U and SDFT+U

\[
E^{\text{CDFT+U}} = T_s[\rho^\sigma] + \int dr v_{\text{ext}}(r) \rho + E_{\text{HXC}}[\rho] + E^{\text{int}}[n^\sigma] - E^{\text{de}}[N]
\]

\[
E^{\text{SDFT+U}} = T_s[\rho^\sigma] + \int dr v_{\text{ext}}(r) \rho + E_{\text{HXC}}[\rho^\sigma] + E^{\text{int}}[n^\sigma] - E^{\text{de}}[N^\sigma]
\]

where \( E^{\text{int}} = \frac{1}{2} \sum_{\{m_i\}, \sigma, \sigma'} n_{m_1m_2}^\sigma \{ \langle m_1, m_3 | V_{ee} | m_2, m_4 \rangle - \langle m_1, m_3 | V_{ee} | m_4, m_2 \rangle \delta_{\sigma\sigma'} \} n_{m_3m_4}^{\sigma'} \)

Coulomb interaction tensor using two input parameters; \( U \) and \( J \)

- The choice of XC functional: charge-only (LDA/GGA) or spin (LSDA/SGGA)

- The expression of interactions (including double counting)

- FLL (fully localized limit)

- AMF (around mean-field)

Liechtenstein et al., PRB (1995)
Dudarev et al., PRB (1998)
Anisimov et al., PRB (1991)
‘FLL (fully localized limit)’ Formalism

- Total energy; CDFT+U and SDFT+U

\[ E^{\text{CDFT+U}} = T_s[\rho^\sigma] + \int d\nu_{\text{ext}}(r)\rho + E_{\text{HXC}}[\rho] + E^{\text{int}}[n^\sigma] - E^{\text{dc}}[N] \]

\[ E^{\text{SDFT+U}} = T_s[\rho^\sigma] + \int d\nu_{\text{ext}}(r)\rho + E_{\text{HXC}}[\rho^\sigma] + E^{\text{int}}[n^\sigma] - E^{\text{dc}}[N^\sigma] \]

- Potential

\[ V^{U,\sigma}_{m_1 m_2} = \frac{\delta E^U}{\delta n^\sigma_{m_1 m_2}} = \delta(E^{\text{int}} - E^{\text{dc}})/\delta n^\sigma_{m_1 m_2} = V^{\text{int},\sigma}_{m_1 m_2} - V^{\text{dc},\sigma}_{m_1 m_2} \]

- FLL formulations: \textbf{cFLL (CDFT+U version)} and \textbf{sFLL (SDFT+U version)}

\[ E^{\text{int}} = \frac{1}{2} \sum_{\{m_i\}, \sigma, \sigma'} n^\sigma_{m_1} \{\langle m_1, m_2 | V_{ee} | m_1, m_2 \rangle - \langle m_1, m_2 | V_{ee} | m_2, m_1 \rangle \delta_{\sigma \sigma'} \} n^{\sigma'}_{m_2} \]

\[ V^{\text{dc}}_{\text{cFLL}, m_1 m_2} = \left\{ U \left( N - \frac{1}{2} \right) - J \left( \frac{N}{2} - \frac{1}{2} \right) \right\} \delta_{m_1 m_2} \]

\[ V^{\text{dc}}_{\text{sFLL}, m_1 m_2} = \left\{ U \left( N - \frac{1}{2} \right) - J \left( N^\sigma - \frac{1}{2} \right) \right\} \delta_{m_1 m_2} \]

\[ E^{\text{dc}}_{\text{cFLL}} = \frac{1}{2} U N (N-1) - J \frac{N}{2} \left( \frac{N}{2} - 1 \right) \]

\[ E^{\text{dc}}_{\text{sFLL}} = \frac{1}{2} U N (N-1) - J \frac{N}{2} \left( \frac{N}{2} - 1 \right) - \frac{1}{4} J M^2 \]

- sFLL double counting with \(-\frac{1}{4} J M^2\) : in competition with spin-density XC energy

- Double counting potential: cFLL (spin-independent) vs sFLL (spin-dependent)
‘AMF (around mean-field)’ Formalism

- **Total energy; CDFT+U and SDFT+U**
  \[ E^{\text{CDFT+U}} = T_s[\rho^\sigma] + \int d\mathbf{r} \nu_{\text{ext}}(\mathbf{r}) \rho + E_{\text{HXC}}[\rho] + E^{\text{int}}[n^\sigma] - E^{\text{dc}}[N] \]
  \[ E^{\text{SDFT+U}} = T_s[\rho^\sigma] + \int d\mathbf{r} \nu_{\text{ext}}(\mathbf{r}) \rho + E_{\text{HXC}}[\rho^\sigma] + E^{\text{int}}[n^\sigma] - E^{\text{dc}}[N^\sigma] \]

- **Potential**
  \[ V_{m_1m_2}^{U,\sigma} = \frac{\delta E^U}{\delta n_{m_1m_2}^{\sigma}} = \delta(E^{\text{int}} - E^{\text{dc}})/\delta n_{m_1m_2}^{\sigma} = V^{\text{int},\sigma}_{m_1m_2} - V^{\text{dc},\sigma}_{m_1m_2} \]

- **AMF formulations:** **cAMF (CDFT+U version)** and **sAMF (SDFT+U version)**

  \[ E^{U}_{\text{AMF}} = E^{\text{int}}_{\text{AMF}} - E^{\text{dc}}_{\text{AMF}} = \frac{1}{2} \sum_{\{m_1,\sigma,\sigma'\}} \tilde{n}_{m_1m_2}^{\sigma} \left( \langle m_1, m_3 | V_{ee} | m_2, m_4 \rangle - \langle m_1, m_3 | V_{ee} | m_4, m_2 \delta_{\sigma\sigma'} \rangle \right) \tilde{n}_{m_3m_4}^{\sigma'} \]

  **cAMF**
  \[ \tilde{n}_{m_1m_2}^{\sigma} = n_{m_1m_2}^{\sigma} - \frac{1}{2(2l + 1)} (N \delta_{m_1m_2}) \]

  **sAMF**
  \[ \tilde{n}_{m_1m_2}^{\sigma} = n_{m_1m_2}^{\sigma} - \frac{1}{2(2l + 1)} (N + \text{sgn}(\sigma) M) \delta_{m_1m_2} \]

- ✔ In cAMF/sAMF, the interaction is described by the fluctuation w.r.t. the average charge/spin occupation (double counting implicit).
**Analysis (1): Energetics**

- **cFLL:** $E^{U+XC} = E^{\text{int}}[n^\sigma] - \left[ \frac{1}{2} UN(N - 1) - J \frac{N}{2} \left( \frac{N}{2} - 1 \right) \right]$
  
- **sFLL:** $E^{U+XC} = E^{\text{int}}[n^\sigma] - \left[ \frac{1}{2} UN(N - 1) - \frac{J}{2} \sum_\sigma N^\sigma (N^\sigma - 1) \right] - IM^2/4$

- **Spin-polarization energy of LDA/GGA** is also present in SDFT+U (but not in CDFT+U)

  - Represented by **Stoner I** (in general material dependent)

  (cf) In general, for real materials, $I_{\text{SGGA}} > I_{\text{LSDA}}$. See, for example, S. Ryee and MJH, Sci. Rep. (2017)

- **“Model” d-shell electronic configurations**

  - All possible integer-occupancy configurations
    
    e.g.) $10C_5 = 252$ configurations for 5 electrons

  - Hund $J$ and Stoner $I$ used as the control parameters

---

Analysis (1): Energetics (FLL)

* U = 5 eV  

* (a) – (d): sFLL  

* (e): cFLL

✓ cFLL (charge-only density functional formulation)

→ The moment formation is favored as J increases.

✓ sFLL (spin-density functional formulation)

→ J in competition with $I_{\text{Stoner}}$ : even for sufficiently large J, high-spin state can be unfavored.
Analysis (1): Energetics (AMF)

\[ E_{U+XC} \]  

- \[ U = 5 \text{ eV} \]
- \( f \) – \( i \): sAMF  
- \( j \): cAMF

\[
\text{cAMF} \rightarrow \text{The moment formation is favored as } J \text{ increases.}
\]

\[
\text{sFLL} \rightarrow J \text{ in competition with } I_{\text{Stoner}} : \text{high-spin state is hardly favored.}
\]

\[
\text{sDFT+U (based on spin-density XC) can easily give unphysical electronic and magnetic solutions...!}
\]

(consistent with the previous case studies)
Analysis (2): Potentials

- J-only contribution of DFT+U potential:

\[ \tilde{V}_{J,m_1}^{\text{int},\sigma} = \sum_{m_2,\sigma'} \left\{ \langle m_1, m_2 | V_{J,ee} | m_1, m_2 \rangle - \langle m_1, m_2 | V_{J,ee} | m_2, m_1 \rangle \delta_{\sigma\sigma'} \right\} n_{m_2}^{\sigma'} \]

J-only (excluding \( U \)-related terms) contribution to the Coulomb interaction tensor:

\[ \langle m_1, m_2 | V_{J,ee} | m_1, m_2 \rangle = \sum_{\{m'_i\}} \left[ S_{m_1m'_1} S_{m_2m'_3} \left\{ \sum_{k \neq 0} \alpha_k(m'_1, m'_3, m'_2, m'_4) F^k \right\} S^{-1}_{m'_2m_1} S^{-1}_{m'_4m_2} \right] \]

\( \alpha_k \): Racah-Wigner numbers

\( F^k \): Slater integrals

**CDFT+U**

\[ \tilde{V}_{c\text{FLL},m}^{U,\sigma} = \tilde{V}_{J,m}^{\text{int},\sigma} + J \left( \frac{N}{2} - \frac{1}{2} \right) \]

\[ \tilde{V}_{c\text{AMF},m}^{U,\sigma} = \tilde{V}_{J,m}^{\text{int},\sigma} + J \left( \frac{2l}{2l + 1} \frac{N}{2} \right) \]

**SDFT+U**

\[ \tilde{V}_{s\text{FLL},m}^{U,\sigma} = \tilde{V}_{J,m}^{\text{int},\sigma} + J \left( N^\sigma - \frac{1}{2} \right) \]

\[ \tilde{V}_{s\text{AMF},m}^{U,\sigma} = \tilde{V}_{J,m}^{\text{int},\sigma} + J \left( \frac{2l}{2l + 1} N^\sigma \right) \]

*spin-independent ‘d-c’ potentials*

*spin-dependent ‘d-c’ potentials*
Analysis (2): Potentials

In $\text{CDFT+U}$, the spin splitting is nothing to do with double counting.

In $\text{SDFT+U}$, the double-counting potential is not cancelled out by SDFT contribution ($\sim IM$): Ambiguity in describing spectral property.

$$\Delta \tilde{V}_{\alpha}^U \equiv \tilde{V}_{\alpha\downarrow}^U - \tilde{V}_{\alpha\uparrow}^U: J\text{-induced spin-splitting}$$

No. 8:
- $e_g$
- $t_{2g}$

No. 12:
- $e_g$
- $t_{2g}$

$$V_{\text{cFLL},m_1m_2}^{\text{dc,}\sigma} = \left\{ U \left( N \frac{1}{2} \right) - J \left( \frac{N}{2} \frac{1}{2} \right) \right\} \delta_{m_1m_2}$$

$$V_{\text{sFLL},m_1m_2}^{\text{dc,}\sigma} = \left\{ U \left( N \frac{1}{2} \right) - J \left( N^\sigma \frac{1}{2} \right) \right\} \delta_{m_1m_2}: \text{competes with XC spin splitting } \sim IM$$
Application to real materials: MnO and NiO

- cFLL and cAMF: Low-spin to high-spin transition is well described as a function of J, which is not the case for sFLL and sAMF.

(cf) For half-filled d-shell,

\[ J_{ex} \sim - \frac{t^2}{U + 4J} \]

Application to real materials: \( \text{BaFe}_2\text{As}_2 \) (AF metal)

- LSDA overestimates the moments of Fe-pnictides (Exp. ~ 1 \( \mu_B \))

\[
\begin{array}{|c|c|c|c|c|c|c|}
\hline
\text{System} & \text{Moment} & J_{1a} & J_2 & J_{1b} & J_{1a}/2J_2 & J_{1a} + 2J_2 \\
\hline
\text{LaFeAsO} & 1.69 & 47.4 & 22.4 & -6.9 & 1.06 & 92.2 \\
\text{CeFeAsO} & 1.79 & 31.6 & 15.4 & 2.0 & 1.03 & 62.4 \\
\text{PrFeAsO} & 1.76 & 57.2 & 18.2 & 3.4 & 1.57 & 93.6 \\
\text{NdFeAsO} & 1.49 & 42.1 & 15.2 & -1.7 & 1.38 & 72.5 \\
\text{CaFe}_2\text{As}_2 & 1.51 & 36.6 & 19.4 & -2.8 & 0.95 & 75.4 \\
\text{SrFe}_2\text{As}_2 & 1.69 & 42.0 & 16.0 & 2.6 & 1.31 & 74.0 \\
\text{BaFe}_2\text{As}_2 & 1.68 & 43.0 & 14.3 & -3.1 & 1.51 & 71.5 \\
\text{KFe}_2\text{As}_2 & 1.58 & 42.5 & 15.0 & -2.9 & 1.42 & 72.5 \\
\text{LiFeAs} & 1.69 & 43.4 & 22.9 & -2.5 & 0.95 & 89.2 \\
\hline
\end{array}
\]

M. J. Han et al., PRL (2009)

1) Empirical way of accounting for spin-fluctuations; \( I_R \sim sI \)

L. Ortenzi et al., PRL (2015)
J. Lischner et al., PRB (2015)

2) Using negative \( U \) in sFLL

M. Yi et al., PRB (2009)

\[
\begin{array}{|c|c|c|c|c|c|}
\hline
U \text{ [eV]} & J \text{ [eV]} & \text{DM} & M^{\text{FLL}} \text{ [\( \mu_B/\text{Fe} \)]} & M^{\text{sFLL}} \text{ [\( \mu_B/\text{Fe} \)]} \\
\hline
2.3 & 0.3 & \text{dual} & \boxed{0.94} & 2.82 \\
& & \text{full} & 0.29 & 2.63 \\
0.5 & & \text{dual} & 1.78 & 2.77 \\
& & \text{full} & \boxed{0.75} & 2.59 \\
0.7 & & \text{dual} & 2.34 & 2.73 \\
& & \text{full} & 1.33 & 2.56 \\
\hline
\end{array}
\]

S. Ryee and MJH, arXiv:1709.03214
Application to real materials: LaMnO$_3$

S. W. Jang et al, arXiv:1803.00213

The first CDFT+U calculation for this classical material. The detailed electronic structure and orbital-dependent magnetic interaction analyzed.
The Case for Non-collinear Orders

Summary and Perspective (Part 2)

- Formal analysis clearly shows that the use of spin-density XC functionals in combination with +U or +DMFT can easily lead to unphysical and uncontrollable errors.

- As a rule of thumb, cDFT+U with FLL double counting can be recommended.

- For non-collinear magnetism, further analysis and development are certainly requested. Probably also for other issues like RKKY-type magnetism.