Theory of Electronic Correlations in Transition Metal Oxides:

From simple models to real materials

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Outline:

- Introduction: Electronic Correlations
- LDA+DMFT
- \( k \)-integrated + ARPES spectra for
  - V-3d\(^1\) system: (Sr,Ca)VO\(_3\)
  - Ru-4d\(^4\) system: Sr\(_2\)RuO\(_4\)
Correlation [lat.]: con + relatio ("with relation")

Mathematics, natural sciences:
\[ \langle AB \rangle \neq \langle A \rangle \langle B \rangle \]

e.g., densities:
\[ \langle \rho(r) \rho(r') \rangle \neq \langle \rho(r) \rangle \langle \rho(r') \rangle \]

Beyond (standard) mean-field theory [Weiss/Hartree-Fock,...]
Short-range spatial **correlations** in everyday life

Time average is insufficient
Partially filled 3d bands

Partially filled 4f bands

Narrow 3d, 4f orbitals → strong electronic correlations
Electronic correlations relevant, e.g., in Transition metals and their oxides

Perovskites
Correlated electron materials

Fascinating topics for fundamental research

- large resistivity changes
- huge volume changes
- high $T_c$ superconductivity
- strong thermoelectric response
- colossal magnetoresistance
- gigantic non-linear optical effects

with

Technological applications:
- switches
- sensors
- cables
- spintronics
- magnets/magnetic storage,...

"Complexity"
Theory of Electronic Correlations in Transition Metal Oxides
DFT/LDA

+ material specific: “ab initio”
- fails for strong correlations
+ fast code packages
Proper treatment of local correlations?

<table>
<thead>
<tr>
<th>DFT/LDA</th>
<th>Model Hamiltonians</th>
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<tr>
<td>+ material specific: “ab initio”</td>
<td>− input parameters unknown</td>
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<tr>
<td>− fails for strong correlations</td>
<td>+ systematic many-body approach</td>
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<tr>
<td>+ fast code packages</td>
<td>− computationally expensive</td>
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Correlation (Mott-Hubbard) physics

\[ H = \sum_{i,j,\sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} \]

Time resolved treatment of local interaction required:
Correlation (Mott-Hubbard) physics

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Time resolved treatment of local interaction required:

Metzner, DV (1989)

"Single-site" mean-field theory with full many-body dynamics
Correlation (Mott-Hubbard) physics

\[ H = \sum_{i,j,\sigma} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow} \]

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"Single-site" mean-field theory with full many-body dynamics

\[ \Sigma(\omega) \]

\[ G(\omega) \]

\[ d \rightarrow \infty \]

\[ \leftrightarrow \]

Single-impurity Anderson model + self-consistency

Dynamical Mean-Field Theory (DMFT)

Georges, Kotliar (1992)
Jarrell (1992)
Computational scheme for correlated electron materials:

Material specific electronic structure
(Density functional theory: LDA, …)

+ 

Local electronic correlations
(Many-body theory: DMFT)

LDA+DMFT

Anisimov, Poteryaev, Korotin, Anokhin, Kotliar (1997)
Lichtenstein, Katsnelson (1998)
Nekrasov, Held, Blümer, Poteryaev, Anisimov, DV (2000)

Physics Today, March 2004; Kotliar, DV
Computational scheme for correlated electron materials:

Material specific electronic structure
(Density functional theory: LDA, GW, ...)

+ Local electronic correlations
(Many-body theory: DMFT)
LDA+DMFT (simplest version)

1) Calculate LDA band structure: \( \varepsilon_{lm,m'}(k) \rightarrow \hat{H}_{LDA} \)

2) Supplement LDA by local Coulomb interaction (only for correlated bands)

3) Solve model by DMFT with, e.g., QMC: LDA+DMFT(QMC)

\[
G_{mm'}^{\sigma}(\omega) = \frac{1}{V_B} \int d^3 k \left[ (\omega - \Sigma^{\sigma}(\omega)) \delta_{m,m'} - \left( H_{LDA}^{0 \, \text{eff}}(k) \right)_{m,m'} \right]^{-1}
\]
LDA+DMFT (simplest version)

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Orbital degeneracy, no hybridization:

\[
G(\omega) = \int d\varepsilon \frac{N^{LDA}(\varepsilon)}{\omega - \Sigma(\omega) - \varepsilon}
\]
Application of LDA+DMFT to specific materials

- LaTiO$_3$
- (Sr,Ca)VO$_3$
- V$_2$O$_3$
- LiV$_2$O$_4$
- Sr$_2$RuO$_4$
3d$^1$ system: (Sr,Ca)VO$_3$
3d$^1$ system: (Sr,Ca)VO$_3$

Photoemission spectroscopy (PES)

Inoue *et al.*, PRL (1995)
Experiment

**Photoemission spectra at high photon energies**

![Graphs showing photoemission spectra for SrVO$_3$ and CaVO$_3$.]

**SrVO$_3$**

**CaVO$_3$**

**Transfer of spectral weight: Correlation effect**

(Sr, Ca)VO$_3$: Spectra after subtraction of estimated surface contribution

**Theory**

**Electronic structure**

**Crystal structure**

SrVO$_3$: $\angle 123 = 180^\circ$

$\uparrow$ orthorhombic distortion

CaVO$_3$: $\angle 123 \approx 162^\circ$

10% reduction in V-O-V angle

**Band scheme**

3$d^1$

$^{t_2_g}$

isotropic cubic

**LDA density of states**

SrVO$_3$

CaVO$_3$

SrVO$_3$ \rightarrow CaVO$_3$

only 4% bandwidth reduction

V-3d($t_{2g}$)  
V-3d($e_g$)
**LDA+DMFT results**

\[ A(\omega) = -\frac{1}{\pi} \text{Im} G(\omega) \]

- **k-integrated spectral function**

   **LDA+DMFT** explains transfer of spectral weight

   **SrVO\textsubscript{3} and CaVO\textsubscript{3}**

   **constrained LDA:**
   \[ U=5.55 \text{ eV}, \ J=1.0 \text{ eV} \]

   - Stronger correlations in \textit{CaVO\textsubscript{3}}

Comparison with experiment

- (i) bulk-sensitive high-resolution photoemission spectra (PES)
- (ii) 1s x-ray absorption spectra (XAS)

Measurement at O K-edge: no symmetry breaking of V 2p shell in final state (XAS ≈ IPES)
Three-peak structure of spectral function

Single-impurity Anderson model

One-band Hubbard model (DMFT)

(Ca,Sr)VO₃: Experiment and theory (LDA+DMFT)

Bulk system
**k**-resolved spectra (ARPES) in DMFT

\[ G(k, \omega) = \left[ \omega - \Sigma(\omega) - H_{LDA}^0(k) \right]^{-1} \]

matrices in orbital space

→ **k**-resolved spectral function

\[ A(k, \omega) = -\frac{1}{\pi} \text{Im} \, Tr \, G(k, \omega) \]
NMTO downfolded vs. LDA+DMFT bands

Renormalization of LDA bands by LDA+DMFT self-energy; 1/Z = m*/m = 1.9

Ekaterinburg - Augsburg - MPI Stuttgart collaboration (2004); cond-mat/0508313

LMTO: N=1

Kinks
High-resolution photoemission results on SrVO$_3$

Fujimori et al., cond-mat/0504576
$4d^4$ system: $\text{Sr}_2\text{RuO}_4$
Sr$_2$RuO$_4$

- First non-cuprate superconductor ($T_c=1.5$K)
  isostructural with La$_2$CuO$_4$
- Quasi 2D structure

Band scheme:

Non-degenerate $t_{2g}$-orbitals
Strong admixture of Ru(4d) states with O(2p) states

Input for LDA+DMFT(QMC):
- 3x3 LDA Hamiltonian for Ru-4d(t_{2g}) orbitals
- Constrained LDA: $U=3.1$ eV, $J=0.7$ eV
Is $\text{Sr}_2\text{RuO}_4$ a correlated electron system?
Sr$_2$RuO$_4$: Full-orbital LDA+DMFT results vs. XPS

E = 1486.6 eV

- XPS, $E_{ph} = 1486.6$ eV (Tran et al. '04, PRB 70, 153106)
  - see also Yokoya et al. (1996)
- LDA
- LDA+DMFT(QMC) ($t_{2g}$ only)
- LDA+DMFT(QMC) (full-orbital)

Linear broadening: $-0.1*E+0.4$

Crosssection ratio: Ru-4d:O-2p = 40:1

T=300 K

Sr$_2$RuO$_4$ is a correlated electron system
Sr$_2$RuO$_4$: Full-orbital LDA+DMFT results vs. ARPES

LDA+DMFT bands


Suga et al., unpublished

Conclusion

1. V-3d\textsuperscript{1} system: SrVO\textsubscript{3} ↔ CaVO\textsubscript{3}
   - almost identical spectral functions
   - LDA+DMFT explains bulk sensitive PES+XAS experiments
   - why are PES at surfaces so different?

2. Ru-4d\textsuperscript{4} system: Full-orbital LDA+DMFT explains
   - XPS, PES, ARPES spectra

3. LDA+DMFT predicts kinks in ARPES
   - Microscopic origin of kinks in the dispersion near $E_F$?