Realistic Modeling of Materials with Strong Electronic Correlations

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Okinawa, Japan; March 5, 2009

Supported by Deutsche Forschungsgemeinschaft through SFB 484
Outline

• LDA+DMFT approach to correlated electron materials

• Applications

1. (Sr,Ca)VO$_3$: spectral transfer in a paramagnetic metal
2. NiO: Mott-Hubbard vs. charge-transfer insulator
3. KCuF$_3$: correlation induced structural transformation
4. Kinks in the electronic dispersion (e.g., SrVO$_3$, Ni)
LDA+DMFT: Theory of correlated electron materials
### How to combine?

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

- **Coulomb interaction**: correlations
- **time-averaged electron density**
- **lattice potential**
Dynamical Mean-Field Theory of Electronic Correlations

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

Dynamical treatment of local interaction required:

Hubbard model \[ \rightarrow \]

single-impurity Anderson model
+ self-consistency

Metzner, DV (1989)
Georges, Kotliar (1992)
Dynamical mean-field theory (DMFT):

Proper time resolved treatment of local electronic interactions:

Kotliar, DV (Physics Today, March 2004)

Electronic correlations → Transfer of spectral weight
Computational scheme for correlated electron materials:

- **Material specific electronic structure**
  - (Density functional theory: LDA, GGA, KKR, ...)
- **Local electronic correlations**
  - (Many-body theory: DMFT)

\[ \text{LDA+DMFT} \]

References:
- Anisimov et al. (1997)
- Lichtenstein, Katsnelson (1998)
- Nekrasov et al. (2000)
- Kotliar, DV (Physics Today, March 2004)
- Kotliar et al. (RMP, 2006)
Computational scheme for correlated electron materials:

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

+ Local electronic correlations
(Many-body theory: DMFT)
1) Calculate LDA band structure: \( \varepsilon_{lm\ell'm'}(k) \rightarrow \hat{H}_{LDA} \)

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

\[
\hat{H} = \sum_{klm,l'm'\sigma} \epsilon_{lm\ell'm'}(k) \hat{c}_{klm\sigma}^\dagger \hat{c}_{klm'\sigma} - \sum_{i=i_d, m\sigma} \sum_{\ell=l_d} \Delta \varepsilon_d \hat{n}_{ilm\sigma}
\]

- double counting correction

\[
+ \sum_{i=i_d, m\sigma, m'\sigma'} \sum' \frac{U_{mm'}}{2} \hat{n}_{ilm\sigma} \hat{n}_{ilm'\sigma'}
\]

- local Coulomb interaction

\[
- \sum_{i=i_d, m\sigma, m'\sigma'} \sum' J_{mm'} \hat{c}_{ilm\sigma}^\dagger \hat{c}_{ilm'\sigma'}^\dagger \hat{c}_{ilm'\sigma} \hat{c}_{ilm\sigma}
\]

- Hund's rule coupling

3) Solve \( \hat{H} \) by DMFT with an "impurity solver“, e.g., QMC
Spectral function in DMFT

**k-integrated spectral function**

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

**k-resolved spectral function**

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

\[ A(k, \omega) = -\frac{1}{\pi} \text{Im} \, Tr G(k, \omega) \]  \( \rightarrow \) ARPES
1. Application:

Strongly correlated paramagnetic metal

(Sr, Ca)VO₃
Experiment

Fujimori, Hase, Namatame, Fujishima, Tokura, Eisaki, Uchida, Takegahara, de Groot (1992)

Photoemission spectra at high photon energies

Photoemission spectra at high photon energies

Theory

Electronic structure

Crystal structure

SrVO₃: \( \angle V - O - V = 180^\circ \)

\[ \text{SrVO}_3: \quad \angle V - O - V = 180^\circ \]

\( \downarrow \text{orthorhombic distortion} \)

CaVO₃: \( \angle V - O - V \approx 162^\circ \)

\[ \text{CaVO}_3: \quad \angle V - O - V \approx 162^\circ \]

Band scheme

LDA density of states

No correlation effects/spectral transfer
LDA+DMFT results

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

constrained LDA: 
\( U=5.55 \text{ eV}, \ J=1.0 \text{ eV} \)

SrVO\(_3\) and CaVO\(_3\)

Correlation induced spectral transfer → 3-peak structure

Strongly correlated paramagnetic metal 
(Mott-Hubbard system)

Comparison with experiment

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

Osaka - Augsburg - Ekaterinburg collaboration,
Sekiyama et al., PRL (2004)
Nekrasov et al., PRB (2005)

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

Confirmation of three-peak structure in correlated bulk systems
2. Application:
Mott-Hubbard vs. charge-transfer insulator

NiO
NiO

“Surprising properties of materials with incompletely filled 3d bands”

- Antiferromagnet, $T_N = 523$ K
- Insulator with gap $\sim 4$ eV; persists up to $> 1000$ K

Prototypical Mott-Hubbard insulator?

Exact diagonalization on small clusters

\[ \rightarrow \text{Include correlated Ni-3d + O-2p states (p-d hybridization)} \]
NiO: LDA+DMFT in Wannier function basis

p-d hybridization in LDA+DMFT $\rightarrow$ 8-band Hamiltonian

Kunes, Anisimov, Lukoyanov, DV; PRB (2007)

- charge-transfer gap clearly seen
- correct position of p-band
- valence band: p-d character
- conduction band: d-character
- lower Hubbard at -9 eV

PES experiment

- mainly Ni 3d
- mainly O 2p
- 120 eV
- 66 eV

Theory

p-d hybridization is essential
NiO: LDA+DMFT in Wannier function basis

p-d hybridization in LDA+DMFT $\rightarrow$ 8-band Hamiltonian

Kunes, Anisimov, Lukoyanov, DV; PRB (2007)

Hole doping of NiO

$$x\text{Ni}^{2+} \rightarrow \text{Li}^{1+} \Rightarrow n_h \approx \frac{x}{1-x} \quad \text{per Ni site}$$

$$\text{Li}_{0.38}\text{Ni}_{0.62}\text{O}$$  \(n_h=0.6\)

• Spectral transfer $\rightarrow$ Mott gap filled
• Doped holes go to O sites
NiO: LDA+DMFT in Wannier function basis

p-d hybridization in LDA+DMFT $\rightarrow$ 8-band Hamiltonian

Kunes, Anisimov, Lukoyanov, DV; PRB (2007)

Exp.: Shen et al. (1990, 1991)

Theory: Kunes, Anisimov, Skornyakov, Lukoyanov, DV; PRL (2007)

- Ni-d bands only weakly dispersive
- O-p bands dispersive
- Result of d-correlations + p-d hybridization
3. Application:
Correlation induced structural transformation

KCuF$_3$
**KCuF$_3$: Prototypical Jahn-Teller system**

Room temperature crystal structure:

- insulating, pseudo-cubic perovskite
- $T_{\text{Neel}} \sim 38$ K

- cooperative JT distortion = spontaneous lifting of orbital degeneracy
  → orbital order → structural relaxation with symmetry reduction

Kugel, Khomskii (1982)
Liechtenstein, Anisimov, Zaanen (1995)
**KCuF₃: Prototypical Jahn-Teller system**

Room temperature crystal structure:

Kugel, Khomskii (1982)
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**Cooperative JT distortion**
**KCuF₃:** Prototypical Jahn-Teller system

Room temperature crystal structure:

Kugel, Khomskii (1982)
Liechtenstein, Anisimov, Zaanen (1995)

Undistorted structure
**KCuF₃: Prototypical Jahn-Teller system**

Room temperature crystal structure:

![Crystal Structure Diagram]

**Kugel, Khomskii (1982)**  
Liechtenstein, Anisimov, Zaanen (1995)

**JT-distortion** \( \delta_{JT} = (d_l - d_s)/a \)

\( T > T_N \sim 38 \text{ K} \): Correlated paramagnetic insulator with strong JT distortion

LDA/GGA+U predicts magnetic LRO

How to determine  
- cooperative JT-distortion?  
- correct orbital order?
**KCuF₃: GGA+DMFT results**

Implementation with plane-wave pseudo-potentials

**GGA:**
- metallic solution
- very shallow minimum of energy at $\delta_{JT} = 2.5\%$
  $\Rightarrow \delta_{JT} = 0$ for $T > 100$ K
  (no orbital order)
- Inconsistent with experiment

**U = 7.0 eV, J = 0.9 eV**

![Total energy graph](image)
**KCuF$_3$: GGA+DMFT results**

Leonov, Bingelli, Korotin, Anisimov, Stojic, DV; PRL (2008)

Implementation with plane-wave pseudo-potentials

**GGA:**
- metallic solution
- very shallow minimum of energy at $\delta_{JT} = 2.5\%$
  $\rightarrow \delta_{JT} = 0$ for $T > 100\,K$
  (no orbital order)
- Inconsistent with experiment

**GGA+DMFT:**
- paramagnetic insulator
- $\delta_{JT}^{opt} = 4.13\% \rightarrow$ JT distortion persists up to 1000 K (melting)
- AF orbital order
- Good agreement with experiment at 300 K

**Total energy**

$U = 7.0\,eV, J = 0.9\,eV$

→ Structural transformation caused by electronic correlations

Even stronger effects, e.g., in LaMnO$_3$, Mott transition in V$_2$O$_3$
4. Application:
Kinks in the electronic dispersion
Kinks in the electronic dispersion: High-$T_c$ cuprates

"Kinks" in the electronic dispersion at 40-70 meV

Zhou et al. (2006)

Phonons !?
Electron-phonon (boson) correction of electronic dispersion
Ashcroft, Mermin; *Solid State Physics* (1976)
Kinks in strongly correlated electron systems


Kinks at $|\omega_*| \approx 0.24$ eV

Strongly correlated paramagnetic metal

**SrVO$_3$**

$\omega \approx$ Kinks at

$W_{LDA} = 2.9$ eV

$W_{QP} = 1.5$ eV

$m^*/m = 1.9$

Yoshida, Tanaka, Yagi, Ino, Eisaki, Fujimori, Shen (2005)
Kinks in strongly correlated electron systems

Conventional wisdom for the origin of kinks:

Kinks due to electron-boson coupling

Kinks due to electron-electron hybridization


Kinks at $|\omega_*| \approx 0.24$ eV

Strongly correlated paramagnetic metal
Kinks in strongly correlated electron systems

Kinks due to electronic interaction in high-$T_c$ cuprates (non-phononic)

Coupling of quasiparticles to spin fluctuations

Manske, Eremin, Bennemann (2001)
Randeria, Paramekanti, Trivedi (2004)
Kordyuk et al. (2004)
Kakehashi, Fulde (2005)
Borisenko et al. (2006)

$k$-dependence of self-energy $\Sigma(k, \omega)$ essential


Kinks at $|\omega_*| \approx 0.24$ eV

Strongly correlated paramagnetic metal

Origin of kinks?
Strongly correlated paramagnetic metal: Kinks without “coupling” to anything

Strongly correlated paramagnetic metal: Kinks without “coupling” to anything

\[ A(\omega) = -\text{Im} \, G(\omega)/\pi \]

\begin{equation*}
G(\omega) \xrightarrow{\text{DMFT}} \Sigma(\omega)
\end{equation*}

$$\omega_* = Z_{FL} D_{0/LDA}$$

$$E_k = \begin{cases} Z_{FL} E_k^{0/LDA} \\ Z_{CP} E_k^{0/LDA} + c \end{cases}$$

Landau FL regime
Central Peak, outside Landau FL regime

Example: Electronic dispersion $E_k$: Hubbard model, cubic lattice, DMFT(NRG)

Strong correlations: $U=0.96W$, $Z_{FL}=0.086$
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Strong correlations: $U=0.96W$, $Z_{FL}=0.086$

Non-interacting dispersion $E^0_k$

Fermi liquid dispersion $E_k = Z_{FL}E^0_k$
Example: Electronic dispersion $E_k$: Hubbard model, cubic lattice, DMFT(NRG)

Strong correlations: $U=0.96W$, $Z_{FL}=0.086$

Non-interacting dispersion $E_k^0$

Fermi liquid dispersion $E_k = Z_{FL} E_k^0$

Dispersion outside Fermi liquid regime $E_k = Z_{CP} E_k^0 + c$
Fermi liquid dispersion

\[ E(k) = \text{dispersion outside Fermi liquid regime} \]

Example: Electronic dispersion \( E_k \): Hubbard model, cubic lattice, DMFT(NRG)

Strong correlations: \( U=0.96W, Z_{FL}=0.086 \)

\[ \log A(k,\omega) \text{ [1/eV]} \]

\[ k (\sqrt{3} \pi / a) \]

\[ \text{Energy (eV)} \]

X-over

→ Kinks
\[ \omega_* = Z_{FL} D_{LDA} \]

LDA bandwidth

\[ E_k = \begin{cases} 
Z_{FL} E_k^{LDA} \\
Z_{CP} E_k^{LDA} \pm c 
\end{cases} \]

Landau FL regime

Central Peak, outside Landau FL regime

(Sr,Ca)VO$_3$

Kinks:
- Generic features of strongly correlated electrons
- No “coupling” to other excitations required

Kinks in high-resolution ARPES of Ni(110)

Kinks in high-resolution ARPES of Ni(110)


Energy scale for magnons in Ni (large $k$) \( \sim 270-370 \) meV

Byczuk et al. (2007):
Kink energy caused by local spin fluctuations $\omega^* \sim 300$ meV

Consistent with KK-relation → “electron-magnon” coupling
LDA+DMFT

Material specific theory of correlated electron materials with predictive power

Goal: Explain and predict properties of complex correlated materials