Realistic modeling of materials with strongly correlated electrons: LDA+DMFT and beyond

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Correlated electron materials: Sensitivity to small changes in control parameters (T, P, H, n, ...)

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

⇒ Technological applications:
  - catalyzers
  - sensors
  - cables
  - spintronics
  - magnets/magnetic storage,...
Outline:

- LDA+DMFT
- V-3d¹ system: (Sr,Ca)VO₃
  \( k \)-integrated + ARPES spectra
- V-3d² system: V₂O₃
  \( k \)-integrated spectra, Mott gap
- Full-orbital, self-consistent LDA+DMFT scheme
Computational scheme for correlated electron materials:

Material specific electronic structure
(Density functional theory: \textbf{LDA}, \textbf{GW}, ...)

+ Electronic correlations
(Many-body theory: \textbf{DMFT})

\textbf{LDA+DMFT}

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

Computational scheme for correlated electron materials:

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

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

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

\[
\hat{\mathcal{H}} = \sum_{klm,l'm'} \varepsilon_{lml'm'}(k) \hat{c}_{klm\sigma}^\dagger \hat{c}_{kl'm'\sigma} - \sum_{i=d, m\sigma} \sum_{l=l_d} \Delta \varepsilon_{d} \hat{n}_{ilm\sigma} \\
\text{LDA} \\
\text{double counting correction} \\
+ \sum_{i=i_d, m\sigma, m'\sigma'} U_{mm'} \frac{1}{2} \hat{n}_{ilm\sigma} \hat{n}_{ilm'\sigma'} \\
\text{local Coulomb interaction} \\
- \sum_{i=i_d, m\sigma, m'\sigma'} \sum_{l=l_d} J_{mm'} \hat{c}_{ilm\sigma}^\dagger \hat{c}_{ilm'\sigma'}^\dagger \hat{c}_{ilm'\sigma} \hat{c}_{ilm\sigma'} \\
\text{Hund's rule coupling}
3) Solve model by DMFT with, e.g., QMC: LDA+DMFT(QMC)

Solve self-consistently:

(i) Effective single impurity part

\[ G = -\frac{1}{Z} \int \mathcal{D}[\psi \psi^*] \psi \psi^* e^{\psi^* [G^{-1} + \Sigma]} \psi - U \psi^* \psi \psi^* \psi + J \psi^* \psi \psi^* \psi \]

(ii) \( k \)-integrated Dyson equ.

\[ G_{mm'}^\sigma(\omega) = \frac{1}{V_B} \int d^3k \left[ (\omega - \Sigma^\sigma(\omega)) \delta_{m,m'} - \left( H_{LDA}^0 \text{eff}(k) \right)_{m,m'} \right]^{-1} \]
3) Solve model by DMFT with, e.g., QMC: LDA+DMFT(QMC)

Solve self-consistently:

(i) Effective single impurity part

\[ G = -\frac{1}{Z} \int D[\psi \psi^*] \psi \psi^* \epsilon \psi^* [G^{-1} + \Sigma] \psi - U \psi^* \psi \psi^* \psi + J \psi^* \psi \psi^* \psi \]

(ii) \( k \)-integrated Dyson equ. (orbital degeneracy)

\[ G(\omega) = \int d\epsilon \frac{N^0_{\text{LDA}}(\epsilon)}{\omega - \Sigma(\omega) - \epsilon} \]
Application of LDA+DMFT to specific materials
Augsburg
G. Keller
M. Kollar
I. Leonov
X. Ren
V. Eyert
DV
----------------------------
K. Held (MPI Stuttgart)
T. Pruschke (Göttingen)

Ekaterinburg
V. I. Anisimov
I. A. Nekrasov,
...

Osaka
S. Suga et al.

Ann Arbor
J. W. Allen et al.
3d$^1$ system: (Sr,Ca)VO$_3$

Photoemission spectroscopy (PES)

Inoue et al., PRL (1995)
Experiment

Photoemission spectra at high photon energies

 Comparison of SrVO$_3$ spectra for different photon energies. All curves are normalized to 1. (Sekiyama et al. 0206471)

 Comparison of CaVO$_3$ spectra for different photon energies. All curves are normalized to 1. (Sekiyama et al. 0206471)

 SrVO$_3$

 CaVO$_3$

Spectra after subtraction of estimated surface contribution:

Theory

Electronic structure

Crystal structure

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

↓

orthorhombic distortion

↓

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

10% reduction in V-O-V angle

Band scheme

isotropic cubic

3d$^1$

t$_{2g}$

e$_g$

LDA density of states

SrVO$_3$

\( V-3d(t_{2g}) \)

CaVO$_3$

\( V-3d(t_{2g}) \)

\( V-3d(e_g) \)

\( V-3d(e_g) \)

SrVO$_3$ \( \rightarrow \) CaVO$_3$

only 4% bandwidth reduction
LDA+DMFT results

$k$-integrated spectral function

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

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

SrVO$_3$ and CaVO$_3$

- Stronger correlations in CaVO$_3$

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)
40 years „Kondo effect“

Single-impurity Anderson model

One-band Hubbard model (DMFT) (Bulla, 1999)

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

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

\[
LDA + \text{DMFT} \xrightarrow{QMC} \Sigma(i\omega), G(i\omega) \xrightarrow{\text{MEM}} \text{Im } G(\omega) \xrightarrow{k.-K.} G(\omega) \xrightarrow{} \Sigma(\omega)
\]

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

matrices in orbital space

\[
\rightarrow \text{ } k\text{-resolved spectral function}
\]

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

Ekaterinburg - Augsburg - O. K. Andersen - collaboration

LMTO: N=1

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

Quasiparticle bands/ARPES spectra

Finite lifetime due to correlations
3d² system: V₂O₃

Paramagnetic

Metal

Antiferromagnetic

Insulator

Pressure

T(K)

Interaction U

3d

e_{\sigma}
e_{g}
t_{2g}
a_{1g}

isotropic cubic trigonal
$V_2O_3$: LDA Spectra


metallic:

insulating:

U=5.0 eV, J=0.93 eV
$V_2O_3$: LDA+DMFT Spectra

Metallic $V_2O_3$: Photoemission Spectra

Ann Arbor - Osaka - Augsburg - Ekaterinburg collaboration; Mo et al., PRL (2003)
Insulating $\text{V}_2\text{O}_3$: Small Mott gap due to Hund’s rule splitting

$U=5.5 \text{ eV}, J=0.93 \text{ eV}, V=U-2J=3.6 \text{ eV}$

Keller, Held, Eyert, Vollhardt, and Anisimov; PRB (2004)
Insulating $V_2O_3$: Filling of the Mott gap

Filling of the gap with increasing temperature $\rightarrow$ genuine feature of Mott-Hubbard MIT

$Mo\ et\ al.,\ PRL\ (2004)$
$Held\ et\ al.\ (2004)$

$\rightarrow$ Poster K. Held
**Full-orbital, self-consistent LDA+DMFT scheme**

Ekaterinburg - Augsburg - Ann Arbor - Osaka - collaboration, cond-mat/ 0407359 [PRB, (2005)]

**LDA: LMTO basis**
- large band width
- long tails
- non-integer electron number

Unfavorable for DMFT
Wannier functions more suitable:

- Localized, site-centered, atomic-like orbitals
- Can reproduce partially filled bands
- Permits projection of $H, \Sigma$ etc. from/to full/few-orbital space without loss of information
- Makes self-consistent merging of LDA and DMFT possible
Full-orbital DMFT scheme with Wannier functions

Ekaterinburg - Augsburg - Ann Arbor - Osaka - collaboration,
cond-mat/ 0407359 [PRB (2005)]

LDA+DMFT(QMC) with full-orbital self-energy (O-2p + V-3d states)
Conclusion

Application of LDA+DMFT(QMC) to

1. V-3d\textsuperscript{1} system: (Sr,Ca)VO\textsubscript{3}
   k-integrated and ARPES spectra

2. V-3d\textsuperscript{2} system: V\textsubscript{2}O\textsubscript{3}
   Spectra, filling of Mott gap, orbital structure, spin state

3. Wannier function formalism for DMFT
   Full-orbital, self-consistent LDA+DMFT scheme
**ab initio**, self-consistent Wannier function for LDA+DMFT

\[ |W_{n\kappa}\rangle = \sum_\mu \phi_{\mu n}^k \phi_{\mu}^k \]

\(\mu, \nu\): full-orbital basis; \(n, n'\): few-orbital basis
LDA+DMFT for NiO

FIG. 1. XPS and BIS spectra of NiO showing the 4.3-eV band gap. Both were collected with a photon energy of 1486.6 eV.