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Electronic Correlations in Condensed Matter:
From Models to Materials

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 Outline:

- Electronic correlation effects
- Dynamical Mean-Field Theory (DMFT)
- LDA+DMFT
- V-3d\(^1\) system: \((\text{Sr,Ca})\text{VO}_3\)
- V-3d\(^2\) system: \(\text{V}_2\text{O}_3\)
- Ferromagnetic materials, e.g., \(\text{Ni}\)
- Electron Transfer in Donor-Acceptor Systems
Correlated Electron Materials
Photoemission spectra for $\text{La}_{1-x}\text{Sr}_x\text{TiO}_3$

Comparison of the experimental photoemission spectrum [Fujimori et al., PRL 69, 1796 (1992)] to the LDA result [Nekrasov et al. EPJB 18, 55 (2000)].
Mott-Hubbard metal insulator transition in $V_2O_3$

- PI $\leftrightarrow$ PM: 1. order transition without lattice symmetry change
- Anomalous slope of $P(T)$

Electronic correlation effect
Mott-Hubbard metal insulator transition in $V_2O_3$

- PI  PM: 1st order transition without lattice symmetry change
- Anomalous slope of $P(T)$

Pomeranchuk effect in $^3$He

Rice, McWhan (1970);
McWhan, Menth, Remeika,
Brinkman, Rice (1973)
Mott-Hubbard metal insulator transition in $V_2O_3$
Mott-Hubbard metal insulator transition in V$_2$O$_3$

V$_2$O$_3$: metal-insulator transition

$^{3}$He: liquid-solid transition

$S = \gamma T$

$S = k_B \ln 2$

$\text{Liquid} \quad \text{Solid}$

$S = \gamma T$

$S = k_B \ln 2$
-6 eV satellite in Nickel

Guillot, ..., Falicov (1977)

Not reproducible by DFT/LDA

FIG. 1. Photoemission spectra of a clean Ni(100) surface for photon energy $h\nu$ between 63 and 85 eV. The peak A corresponds to the d bands; B (dashed area) is the structure located at 6 eV from the Fermi level. The arrows indicate the Auger transition.
Transition metals: correlated $d$-electrons

Periodic Table of the Elements
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

"Complexity"

⇒ Technological applications:
- catalyzers
- sensors
- cables
- spintronics
- magnets/magnetic storage,...
Dynamical Mean-Field Theory
Theory of strongly correlated electrons

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

Coordination number \( Z \):
\( Z = 6 \) (simple cubic)
Theory of strongly correlated electrons

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

Coordination number Z:
Z=8 (body-centered cubic)
Theory of strongly correlated electrons

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

Coordination number Z:
Z=12 (face-centered cubic)

Metzner + DV (1989)

\[ \Sigma(\omega) \]

\[ G(\omega) \]

"single-site" mean field theory
Theory of strongly correlated electrons

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

Georges and Kotliar (1992)

Hubbard model \( d \to \infty \) single-impurity Anderson model + self-consistency
Time resolved treatment of local electronic interactions:

⇒ proper treatment of electronic correlations

Dynamical Mean-Field Theory (DMFT)

DMFT study of Mott-Hubbard metal-insulator transition

Hubbard model, $n=1$

Georges; Kotliar, Krauth, Rozenberg (1996)

Characteristic three-peak structure
LDA+DMFT
Computational scheme for correlated electron materials:

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

Electronic correlations (Many-body theory/DMFT)

\[ \text{LDA+DMFT} \]

Anisimov, Poteryaev, Korotin, Anokhin, Kotliar (1997)
Lichtenstein, Katsnelson (1998)
Nekrasov, Held, Blümer, Poteryaev, Anisimov, DV (2000)
LDA+DMFT (simplest version)

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

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

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

\[
\text{LDA}
\]

\[
\text{double counting correction}
\]

\[
+ \sum_{i=i_d, m\sigma, m'\sigma'} \sum_{l=l_d} \frac{U_{mm'}}{2} \hat{n}_{ilm\sigma} \hat{n}_{ilm'\sigma'} - \sum_{i=i_d, m\sigma, m'\sigma'} \sum_{l=l_d} \sum_{m'\sigma'} \hat{J}_{mm'} \hat{c}_{ilm\sigma}^{\dagger} \hat{c}_{ilm'\sigma} \hat{c}_{ilm'\sigma'}^{\dagger} \hat{c}_{ilm'\sigma} \hat{c}_{ilm\sigma'}
\]

\[
\text{local Coulomb interaction}
\]

\[
\text{Hund's rule coupling}
\]
3) Solve by DMFT (⇔ multi-band single-impurity Anderson model) using QMC: LDA+DMFT(QMC)

Solve self-consistently:

(i) Single impurity part

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

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

\[ G_{mm'}^\sigma(\omega) = \frac{1}{V_B} \int d^3 k \left[ (\omega - \Sigma^\sigma(\omega)) \delta_{m,m'} - \left( H_{LDA}^0(k) \right)_{m,m'} \right]^{-1} \]
Application of LDA+DMFT to specific materials
3d$^1$ system: (Sr,Ca)VO$_3$
3d$^1$ system: (Sr,Ca)VO$_3$

Inoue et al., PRL (1995)
3d$^1$ system: (Sr,Ca)VO$_3$

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

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**Band scheme**

$3d^1$

$e_g$

$t_{2g}$

isotropic cubic

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**LDA density of states**

SrVO$_3$

CaVO$_3$

- $V-3d(t_{2g})$
- $V-3d(e_g)$

SrVO$_3$ → CaVO$_3$

only 4% bandwidth reduction
LDA+DMFT results

$k$-integrated spectral function

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

U=5.55 eV, J=1.0 eV

SrVO$_3$ and CaVO$_3$

- Stronger correlations in CaVO$_3$
- Curves nearly identical around $E_F$

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)

(Ca,Sr)VO\textsubscript{3}: Experiment and theory (LDA+DMFT)

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

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

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

matrices in orbital space

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

![Graph showing quasiparticle bands](image)

ARPES spectra

![Graph showing ARPES spectra](image)

Finite lifetime due to correlations
3d\(^2\) system: V\(_2\)O\(_3\)
3d² system: V₂O₃

Crossover
Critical point
PI  PM
Corundum + trigonal distort.
AFI  Monoclinic

increasing interaction U

isotropic cubic trigonal
3d² system: V₂O₃

Castellani, Natoli, Ranninger (1978)

AFI
Monoclinic

Corundum + trigonal distort.

PI
PM

Crossover

Increasing interaction U

Increasing pressure

\( a_{1g} \) singlet \( S=1/2 \)
$V_2O_3$: LDA+DMFT Spectra

Metallic $V_2O_3$: Photoemission Spectra

Ann Arbor - Osaka - Augsburg - Ekaterinburg collaboration; Mo et al., PRL (2003)
Metallic $V_2O_3$: Photoemission and XAS Spectra in Theory and Experiment

Ann Arbor - Osaka - Augsburg - Ekaterinburg collaboration; Mo et al., PRL (2003)
Insulating \( V_2O_3 \): Filling of the Mott gap

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

Filling of gap with increasing temperature
→ genuine feature of Mott-Hubbard MIT
Local magnetic moment and orbital occupation

$$\langle m_z^2 \rangle = \left\langle \left( \sum_m \left[ n_{m\uparrow} - n_{m\downarrow} \right] \right)^2 \right\rangle$$

$$\langle m_z^2 \rangle \approx 4 \Leftrightarrow 2 \text{ spin-aligned electrons in } (a_{1g}, e_{g1}, e_{g2}) \text{ orbitals}$$

$S=1$ state agrees with Park et al.; PRL (2000)
Generalized fcc lattice ($\mathcal{Z} \to \infty$)

Microscopic conditions for ferromagnetism:
Wahle, Blümer, Schlipf, Held, DV (1998)

DMFT results for ferromagnetism in the one-band Hubbard model

Ulmke (1998)
DMFT results for ferromagnetism in the one-band Hubbard model

Ulmke (1998)

Application of LDA+DMFT to ferromagnetic Ni

Lichtenstein et al. (2004)
Other applications:  

- Half-metallic ferromagnets  
- Correlation effects in Co/Cu and Fe/Cr magnetic multilayers

Application of LDA+DMFT to ferromagnetic Ni

Lichtenstein et al. (2004)
Electronic correlations in complex adaptive matter:

Electron Transfer in Donor-Acceptor Systems
Electron Transfer (ET) in Donor-Acceptor Systems: Many-Particle Effects and Influence of Electronic Correlations
S. Tornow, N.-H. Tong, R. Bulla

**Fundamental process in chemistry, biology, physics:**

- corrosion of metals
- charge transfer in semi-conductors
- enzymatic activities
- photosynthesis, ...

**Electronic correlations are important**
Electron Transfer (ET) in Donor-Acceptor Systems: Many-Particle Effects and Influence of Electronic Correlations
S. Tornow, N.-H. Tong, R. Bulla

Model: Generalized single-impurity Anderson model

Influence of many-electron effects on ET

Method of solution: (bosonic) NRG
Conclusion

Electronic Correlations in Condensed Matter:

1. Application of LDA+DMFT(QMC) to TM+TMO
   - (Sr,Ca)VO₃
   - V₂O₃
   - Ni

2. Electron-transfer in donor-acceptor systems

Unifying concept: local correlation effects