Outline:

- Electronic correlations
- Dynamical Mean-Field Theory
- Mott-Hubbard metal-insulator transition
- Models meet materials
- Applications: PES/XAS spectra of (Sr,Ca)VO$_3$
  Kinks in the electronic dispersion
Correlations
Correlation [lat.]: con + relatio ("with relation")

Correlations in mathematics, natural sciences:

\[ \langle AB \rangle \neq \langle A \rangle \langle B \rangle \]

e.g., densities:

\[ \langle \rho(r) \rho(r') \rangle \neq \langle \rho(r) \rangle \langle \rho(r') \rangle \]

Correlations (I):
Effects beyond factorization approximations (e.g., Hartree-Fock)
Temporal/spatial correlations in everyday life

Beware: External periodic potential
Temporal/spatial correlations in everyday life

Time/space average insufficient
Electronic Correlations in Solids
Partially filled d-orbitals

Partially filled f-orbitals

Narrow d,f-orbitals/bands → strong electronic correlations
Correlated electron materials

Fascinating topics for fundamental research

- large resistivity changes
- gigantic volume changes
- high-\(T_c\) superconductivity
- strong thermoelectric response
- colossal magnetoresistance
- huge multiferroic effects

with

Technological applications:
- sensors, switches
- magnetic storage
- thermoelectrics
- functional materials, …
Electronic Correlations: Models
**Hubbard model**

\[
H = -t \sum_{\langle i,j \rangle, \sigma} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}
\]

Purely numerical approaches (d=2,3): hopeless

**Theoretical challenge:**
Construct reliable, comprehensive
**non-perturbative** approximation scheme

Gutzwiller, 1963
Hubbard, 1963
Kanamori, 1963

\[\langle n_{i\uparrow} n_{i\downarrow} \rangle \neq \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle\]

Static (Hartree-Fock-type)
mean-field theories
generally insufficient
Dynamical Mean-Field Theory (DMFT) of Correlated Electrons
Theory of correlated electrons

\[ H = -t \sum_{\langle i,j \rangle, \sigma} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} \]  

Hubbard model

Face-centered cubic lattice (d=3)

\[ Z=12 \]
Theory of correlated electrons

\[ H = -t \sum_{\langle i,j \rangle, \sigma} c^\dagger_{i\sigma} c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} \]

Hubbard model

Face-centered cubic lattice (d=3)

Metzner, DV (1989); Müller-Hartmann (1989); Brandt, Mielsch (1989)

Dynamical single-site problem
Theory of correlated electrons

\[ H = -t \sum_{\langle i,j \rangle, \sigma} c_{i \sigma}^\dagger c_{j \sigma} + U \sum_i n_{i \uparrow} n_{i \downarrow} \]

Hubbard model

Face-centered cubic lattice (d=3)

- Metzner, DV (1989)
- Janiš (1991): Generalization of „coherent potential approx.“
- Georges, Kotliar (1992)

Self-consistency problem

Dynamical single-site mean-field theory
Theory of correlated electrons

\[ H = -t \sum_{\langle i,j \rangle, \sigma} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} \]

Hubbard model

Face-centered cubic lattice (d=3)

Strong simplifications

"Dynamical mean-field theory" (DMFT)
DMFT self-consistency equations for $G$ and $\Sigma$

(i) Effective single impurity problem: “local propagator“

$$G = -\frac{1}{Z} \int D[\psi, \psi^*] \psi \psi^* \exp i \int d\omega \left[ G^{-1} + \Sigma \right] \psi - U \psi^* \psi \psi^* \psi$$

single-site ("impurity") action $A$

(ii) $k$-integrated Dyson equation ("lattice Green function“: lattice enters)

$$G(\omega) = \int d\varepsilon \frac{N^0(\varepsilon)}{\omega - \Sigma(\omega) - \varepsilon} = G^0(\omega - \Sigma(\omega))$$

$\rightarrow$ free electrons in a dynamic potential $\Sigma(\omega)$

Solve with an „impurity solver“, e.g., QMC, NRG, ED, DMRG, …

$\Sigma(\omega)$: mean field ("dynamical potential“)
Dynamical mean-field theory (DMFT) of correlated electrons

Proper time resolved treatment of local electronic interactions

Kotliar, DV (2004)
Application of DMFT:
Mott-Hubbard metal-insulator transition
1. Squeezable nanocrystal film switching between metal and insulator

Uncompressed film: insulator

Compressed film: metal (metallic sheen)

Discontinuous transition

Collier, Saykally, Shiang, Henrichs, Heath (1997)
2. Mott metal-insulator transition in $V_2O_3$

McWhan et al. (1971)  
Kuwamoto, Honig, Appel (1980)
Correlations (II):
Interaction effects leading to transfer of spectral weight

Hubbard model, n=1

Spectral weight

Mott-Hubbard metal-insulator transition
DMFT: Metal-insulator transition in the one-band Hubbard model

1994

Rozenberg, Kotliar, Zhang (1994)

Iterated perturbation theory
DMFT: Metal-insulator transition in the one-band Hubbard model

2002

Blümer, Dissertation 2002
Universality due to Fermi statistics

Mott-Hubbard metal-insulator transition

Kotliar, DV (2004)

Hubbard model (n=1)

Strongly correlated electron materials:
- \( V_2O_3 \)
- \( NiSe_{2-x}S_x \)
- \( \kappa \)-organics, ...

Universality due to Fermi statistics
Mott-Hubbard metal-insulator transition

Kotliar, DV (2004)

Hubbard model (n=1)

Strongly correlated electron materials: V$_2$O$_3$, NiSe$_{2-x}$S$_x$, $\kappa$-organics, ...

4-site cluster-DMFT

Park, Haule, Kotliar (2008)
Models meet Materials: LDA+DMFT
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>
</tr>
</tbody>
</table>

Held (2004)

- time-averaged electron density
- lattice potential

Held (2004)
Computational scheme for correlated electron materials:

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

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

Anisimov, Poteryaev, Korotin, Anokhin, Kotliar (1997)
Lichtenstein, Katsnelson (1998)
Nekrasov, Held, Blümer, Poteryaev, Anisimov, DV (2000)
Computational scheme for correlated electron materials:

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

+ 

**Local electronic correlations**
(Many-body theory: DMFT)

Held, Nekrasov, Keller, Eyert, Blümer, McMahan, Scalettar, Pruschke, Anisimov, DV (Psi-k 2003)
**LDA+DMFT (simplest version)**

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

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

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

\[
\hat{H}_{LDA} = \underbrace{\sum_{l m l' m' \sigma} \varepsilon_{lm l' m'}(k) \hat{c}_{kl m \sigma}^\dagger \hat{c}_{kl' m' \sigma}}_{\text{LDA band structure}} - \underbrace{\sum_{i=i_d, m \sigma} \sum_{\ell=\ell_d} \Delta \varepsilon_d \hat{n}_{ilm \sigma}}_{\text{double counting correction}}
\]

\[
\hat{\mathcal{H}} = \underbrace{\sum_{i=i_d, m \sigma, m' \sigma'} \frac{U_{mm'}}{2} \hat{n}_{ilm \sigma} \hat{n}_{ilm' \sigma'}}_{\text{local Coulomb interaction}} - \underbrace{\sum_{i=i_d, m \sigma, m' \sigma'} J_{mm'} \hat{c}_{ilm \sigma}^\dagger \hat{c}_{ilm' \sigma'} \hat{c}_{ilm' \sigma} \hat{c}_{ilm \sigma'}}_{\text{Hund's rule coupling}}
\]
Self-consistent LDA+DMFT equations

(i) Effective single impurity problem

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

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

\[ G(\omega) = \int d\varepsilon \frac{N^{\text{LDA}}(\varepsilon)}{\omega - \Sigma(\omega) - \varepsilon} \]

Solve with an impurity solver, e.g., QMC
Self-consistent LDA+DMFT equations

(i) Effective single impurity problem

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

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

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

Solve with an impurity solver, e.g., QMC
Application of LDA+DMFT
Application of LDA+DMFT:

1. Mott-Hubbard systems
Electronic structure

Crystal structure

SrVO₃: $\angle V - O - V = 180^\circ$

CaVO₃: $\angle V - O - V \approx 162^\circ$

No correlation effects

LDA density of states
LDA+DMFT results

SrVO$_3$ / CaVO$_3$

k-integrated spectral function

Energy (eV)

Mott-Hubbard system

Constrained LDA: U=5.55 eV, J=1.0 eV

Osaka - Augsburg - Ekaterinburg collaboration:

Measure by electron spectroscopy
Comparison with experiment


Bulk sensitive photoemission spectroscopy → occupied states: \( A(E) \cdot f(E,T) \)

X-ray absorption spectroscopy → unoccupied states: \( A(E) \cdot [1 - f(E,T)] \)

3-peak structure detected
State-of-the-art LDA+DMFT: Electronic correlations & structural transformations

Electron correlations can induce structural transformations

Examples: Cooperative Jahn-Teller distortion in KCuF$_3$  
Leonov et al., (2010)
Incorporating Strong Correlations into the Design of Transport Properties of Nuclear Fuel Materials

Quan Yin, Andrey Kutepov, Kristjan Haule, and Gabriel Kotliar

Department of Physics and Astronomy, Rutgers University, Piscataway, NJ 08854

Sergey Y. Savrasov and Warren E. Pickett

Department of Physics, University of California, Davis, CA 95616

(Dated: December 14, 2010)

arXiv:1012.2412
Phase diagram of light actinide series

Perspective of the LDA+DMFT approach

Explain and predict properties of complex correlated materials

Phase diagram connecting individual binary alloy diagrams

Black: two-phase regions; Brown: details unknown

Boring and Smith (2000)
Perspective of the LDA+DMFT approach

Explain and predict properties of complex correlated materials

Phase diagram of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$

Hemberger et al. (2002)

1, 2, ... multi-electron transfer in metalloprotein complexes

$\rightarrow$ Photosynthesis
Goal: Dynamical mean-field approach with predictive power for strongly correlated materials
Application of LDA+DMFT:
2. Kinks in the electronic dispersion
Kinks in high-$T_c$ cuprates

- Kinks at $\omega_\star \approx 40$-70 meV
- Due to coupling of electrons to phonons !?

Valla et al. (1999)
Bogdanov et al. (2000)

Lanzara et al. (2001)
Kinks in conventional superconductivity

Electron-phonon correction of electronic dispersion
Ashcroft, Mermin; *Solid State Physics* (1976)
Known origin of kinks in solid-state physics

Kinks due to electron-phonon (boson) coupling

Kinks due to electron-electron hybridization
PES of quasi-1D electronic structures on Platinum(110) surface

300 meV: too high for phonons or spin fluctuations

Kinks due to “coupling” of electrons to what?

Menzel et al. (2005)
Kinks due to electronic interaction in high-$\mathcal{T}_c$ cuprates
(non-phononic)

• Manske, Eremin, Bennemann (2001, 2003, ...)
  
  Coupling of quasiparticles to spin fluctuations
  [FLEX]

• Randeria, Paramekanti, Trivedi (2004)
  
  Different high/low energy dispersion of nodal quasiparticles (origin?)
  [Gutzwiller projected wave functions]

• Kordyuk et al. (2004 -), Borisenko et al. (2006)
  
  Spin-fluctuation mediated electronic interaction
  [KK-consistent extraction of self-energy]

• Kakehashi, Fulde (2005)
  
  Coupling of quasiparticles to short-range magnetic fluctuations
  [Self-consistent projection operator method]

**k**-dependence of self-energy $\Sigma(k, \omega)$ essential
Kinks in strongly correlated electron systems


Kinks at $|\omega_*| \approx 0.2$ eV

Origin of kinks in a purely electronic theory with one type of electron?

Yoshida et al. (2005)
Strongly correlated paramagnetic metal: Kinks without “coupling” to anything

Byczuk, Kollar, Held, Yang, Nekrasov, Pruschke, DV; Nature Physics (2007)
Electronic dispersion outside Fermi liquid regime?

\[ G(\omega) \xrightarrow{DMFT} \Sigma(\omega) \]

**Fermi liquid regime restricted to**

\[ |\omega| \leq \omega_* \]

\[ \omega_* = (\sqrt{2} - 1)Z_{FL}D_0 \]

\[ \Omega \sim \sqrt{Z_{FL}} \]

Electronic dispersion outside Fermi liquid regime?

Byczuk, Kollar, Held, Yang, Nekrasov, Pruschke, DV; *Nature Phys.* (2007)
\[ \omega_* = Z_{FL} D_{0/LDA} \]

\[ E_k = \begin{cases} 
Z_{FL} E_k^{0/LDA} \\
Z_{CP} E_k^{0/LDA} \pm c
\end{cases} \]

Landau FL regime

Central Peak, outside Landau FL regime

analytically derivable

Byczuk, Kollar, Held, Yang, Nekrasov, Pruschke, DV; Nature Physics (2007)
\( \omega_\ast = Z_{FL} D_{0/LDA} \)

\[ E_k = \begin{cases} Z_{FL} E_k^{0/LDA} \\ Z_{CP} E_k^{0/LDA} \pm c \end{cases} \]

**SrVO_3 and CaVO_3**

**SrVO_3**

**Effective dispersion**

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

*Byczuk, Kollar, Held, Yang, Nekrasov, Pruschke, DV; Nature Physics (2007)*
\[ \omega_* = Z_{FL} D_{0/\text{LDA}} \]

\[ E_k = \begin{cases} Z_{FL} E_k^{0/\text{LDA}} \\ Z_{CP} E_k^{0/\text{LDA}} \pm c \end{cases} \]

- Landau FL regime
- Central Peak, outside Landau FL regime

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

Kinks in high-resolution ARPES of Ni(110)  
Hofmann et al.; PRL (2009)
Generalization: p-d model

Greger (2010, unpublished)

\[ \varepsilon_{k,\text{Num}} \]
\[ \varepsilon_k \]
\[ U = 7.2 \text{ eV} \]
\[ \varepsilon_d = 0 \text{ eV} \]
\[ \varepsilon_p = 3.6 \text{ eV} \]
\[ t = 1 \text{ eV} \]
## Conclusion

- **DMFT:** canonical mean-field theory for correlated electrons
- **LDA+DMFT:** computational scheme for the investigation of correlated materials
- **Goal:** Dynamical mean-field approach with predictive power for strongly correlated materials