Electronic Correlations in Models and Materials

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University of Warsaw; November 13, 2009

Supported by Deutsche Forschungsgemeinschaft through SFB 484
Outline:

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

Grammar: either ... or

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: Effects beyond factorization approximations
Temporal/spatial correlations in everyday life
Electronic Correlations in the Periodic Table
Partially filled d-orbitals

Partially filled f-orbitals

Narrow d,f-orbitals → strong electronic correlations
1. Simple metals

"Heavy Fermions"

Steglich et al. (1979)

\[ \lim_{T \to 0} \frac{C_V}{T} \approx \gamma_0 \Rightarrow m^* \approx m \]

Consequence of elementary excitations (quasiparticles)

\[ \lim_{T \to 0} \frac{C_V}{T} = \gamma \propto \frac{m^*}{m}, \quad v_F = \frac{\hbar k_F}{m^*} \]

Potassium

\[ C/T = 2.08 + 2.57 T^2 \]

\[ T^2 (K^2) \]

\[ C/T (mJ/mole K^2) \]

\[ m^* \approx 1000 m \]

Stewart et al. (1983)

CeCu$_2$Si$_2$, UBe$_{13}$: very heavy quasiparticles

\[ C/T (mJ/mole K^2) \]

\[ T^2 (K^2) \]
Photoemission spectra of (Sr, Ca)VO₃

Reason for shift of spectral weight?

Osaka - Augsburg - Ekaterinburg collaboration: Sekiyama et al., 2004
Metal-insulator transition in $\text{V}_2\text{O}_3$

- PL $\rightarrow$ PM: 1st order transition without lattice symmetry change
- Anomalous slope of $P(T)$
  $\Rightarrow$ Pomeranchuk effect in $^3\text{He}$

Microscopic explanation?
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

Large susceptibilities

Technological applications:
- sensors, switches
- magnetic storage
- refrigerators
- functional materials, ...
Correlated Electrons: Models
Hubbard model

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

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

Correlation phenomena:
Metal-insulator transition, Ferromagnetism, ...

Many-body dynamics essential

$$\langle n_{i \uparrow} n_{i \downarrow} \rangle \neq \langle n_{i \uparrow} \rangle \langle n_{i \downarrow} \rangle$$

→ Hartree-(Fock) mean-field theory generally insufficient
Dynamical Mean-Field Theory (DMFT)
Theory of strongly 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

Hypercubic lattices: Coordination number \( Z = 2d \)

Dimension \( d = 1 \)

\[ Z = 2 \]
Theory of strongly 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

Hypercubic lattices: Coordination number \( Z=2d \)

Dimension \( d=2 \)

\[ Z=4 \]
Theory of strongly correlated electrons

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

Hypercubic lattices: Coordination number \( Z = 2d \)

Dimension \( d = 3 \)

\( Z = 6 \)
Theory of strongly 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

Body-centered cubic lattice

Dimension \( d=3 \)

\[ Z=8 \]
Theory of strongly 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

Dimension \(d=3\)

Metzner, DV (1989)

\[ Z \to \infty \]

\[ d \to \infty \]

\[ \Sigma(\omega) \]

\[ G(\omega) \]


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

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

Face-centered cubic lattice

Dimension \( d=3 \)

\[ Z=12 \]

Metzner, DV (1989)

Self-consistent "single-impurity Anderson model"

Proper time resolved treatment of local electronic interactions:

→ **Dynamical Mean-Field Theory (DMFT)**

**Correlations (I):**

Interaction effects beyond Hartree-Fock (= *static* mean-field theory)

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**DMFT self-consistency equations**

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

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

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,…
Application of DMFT:
Mott-Hubbard metal-insulator transition
1. Squeezable nanocrystal film switching between metal and insulator

Compressed film: metal
(metallic sheen)

Uncompressed film: insulator
(shininess is gone)

Discontinuous transition

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

McWhan et al. (1971)  
Kuwamoto, Honig, Appel (1980)
Spectral weight

Hubbard model, n=1

Density of states

Quasiparticle renormalization, $Z^{-1} = \frac{m^*}{m} \to \infty$

Correlations (II):
Interaction effects leading to transfer of spectral weight
Incoherent states (Hubbard bands)

Correlations (II):
Interaction effects leading to transfer of spectral weight
DMFT: Metal-insulator transition in the one-band Hubbard model

1994

Iterated perturbation theory  Rozenberg et al. (1994)
DMFT: Metal-insulator transition in the one-band Hubbard model

Blümer, Dissertation 2002
Strongly correlated electron materials: $V_2O_3$, $NiSe_{2-x}S_x$, $\kappa$-organics, ...

Mott-Hubbard metal-insulator transition

Hubbard model (n=1)

Universality due to Fermi statistics
Models meet Materials:
LDA+DMFT
### DFT/LDA

| + | material specific: “ab initio” |
| - | fails for strong correlations |
| + | fast code packages |

### Model Hamiltonians

| - | input parameters unknown |
| + | systematic many-body approach |
| - | computationally expensive |

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How to combine?
Computational scheme for correlated electron materials:

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

+ 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)
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)

\[
\hat{\mathcal{H}} = \sum_{klm, l'm'} \epsilon_{lm'l''m'}(k) \hat{c}_{klm\sigma}^\dagger \hat{c}_{kl'm'\sigma} - \sum_{i=\text{i}_d, m\sigma} \sum_{\ell=\text{l}_d} \Delta \varepsilon_{d} \hat{n}_{ilm\sigma} \\
\text{LDA} \\
+ \sum_{i=\text{i}_d, m\sigma, m'\sigma'} \sum_{l=\text{l}_d} \frac{U_{mm'}^{\sigma\sigma'}}{2} \hat{n}_{ilm\sigma} \hat{n}_{ilm'\sigma'} - \sum_{i=\text{i}_d, m\sigma, m'\sigma'} \sum_{l=\text{l}_d} J_{mm'}^{\sigma\sigma'} \hat{c}_{ilm\sigma}^\dagger \hat{c}_{ilm'\sigma'}^\dagger \hat{c}_{ilm'\sigma} \hat{c}_{ilm\sigma'} \\
\text{local Coulomb interaction} \\
\text{double counting correction} \\
\text{Hund's rule coupling}
\]
3) Solve self-consistently with an impurity solver, e.g., QMC: LDA+DMFT(QMC)

(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. (orbital degeneracy)

\[ G(\omega) = \int d\epsilon \frac{N^{LDA}(\epsilon)}{\omega - \Sigma(\omega) - \epsilon} \]
3) Solve self-consistently with an impurity solver, e.g., QMC: LDA+DMFT(QMC)

(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)

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

1. **Photoemission Spectroscopy (PES)**

Angular Resolved PES = ARPES

Measures *occupied* states of electronic spectral function
Ideal spectral function of a material
Ideal spectral function of a material
Occupied states (ideal)
Occupied states (measured)
2. Inverse Photoemission Spectroscopy (IPES)

Measures unoccupied states of electronic spectral function

Information also available by:

X-ray absorption spectroscopy (XAS)
Ideal spectral function of a material

IPES/XAS

1-f(\omega)
Unoccupied states (ideal)
Unoccupied states
(measured)
1. Application:

$3d^1$ system $(\text{Sr}, \text{Ca})\text{VO}_3$
Experiment

Photoemission spectra at high photon energies

SrVO$_3$  
CaVO$_3$

Bulk spectra

**Theory**

**Electronic structure**

**Crystal structure**

SrVO$_3$: $\angle V - O - V = 180^\circ$

\[ V \quad O \quad V \]

\[ \downarrow \text{orthorhombic distortion} \]

CaVO$_3$: $\angle V - O - V \approx 162^\circ$

\[ V \quad O \quad V \]
**Theory**

**Electronic structure**

**Crystal structure**

\[ \angle V - O - V = 180^\circ \]

SrVO\(_3\): \( \angle V - O - V \approx 180^\circ \)

SrVO\(_3\): orthorhombic distortion

CaVO\(_3\): \( \angle V - O - V \approx 162^\circ \)

CaVO\(_3\): isotropic cubic

**Band scheme**

\[ 3d^{1} \]

\[ t_{2g} \]

\[ e_{g} \]

**LDA density of states**

\[ \text{SrVO}_3 \]

\[ \text{CaVO}_3 \]

\[ \text{SrVO}_3 \rightarrow \text{CaVO}_3 \]

**No correlation effects/spectral transfer**
LDA+DMFT results

Density of states ("Spectral function"): 

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

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

\( \text{SrVO}_3 \) and \( \text{CaVO}_3 \)

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)

Experimental confirmation of three-peak structure in correlated bulk systems
2. Application:

Kinks in the electronic dispersion
Kinks in high-$T_c$ cuprates

- Kinks at $\omega_* \approx 40$-70 meV
- Due to coupling of electrons to phonons !?
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
Kinks: Metal surfaces

PES of quasi-1D electronic structures on Platinum(110) surface

Kinks due to “coupling” of electrons to what?

Menzel et al. (2005)

300meV: too high for phonons or spin fluctuations
Kinks due to electronic interaction in high-$T_c$ cuprates (non-phononic)

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

$$A(\omega) = -\text{Im} G(\omega)/\pi$$

- **Meaning of** $\omega_*$ ?
- **Consequences** ?

Byczuk, Kollar, Held, Yang, Nekrasov, Pruschke, DV; *Nature Physics* (2007)
Byczuk, Kollar, Held, Yang, Nekrasov, Pruschke, DV; Nature Physics (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

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

Byczuk, Kollar, Held, Yang, Nekrasov, Pruschke, DV; Nature Physics (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

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

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

Byczuk, Kollar, Held, Yang, Nekrasov, Pruschke, DV; Nature Physics (2007)
Kinks in high-resolution ARPES of Ni(110)


Energy scale for magnons in Ni (large k) ~ 270-370 meV

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

- Electronic correlation effects
- Dynamical Mean-Field Theory (DMFT)
- Models meet materials: LDA+DMFT
- Applications:
  - (Sr,Ca)VO$_3$ → experimental three-peak structure explained
  - Kinks → generic electronic correlation effect