Electronic Correlations in Solids

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Supported by Deutsche Forschungsgemeinschaft through SFB 484

Colloquium, University of Dortmund; October 23, 2007
Outline:

- Correlations
- Correlated Electrons
- Dynamical Mean-Field Theory
- Models meet materials
- Applications: (Sr,Ca)VO$_3$ Kinks
"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

Time/space average inappropriate
Correlations vs. long-range order

(Sempe)
Correlated Electrons
Consequences?

Partially filled d-orbitals

Partially filled f-orbitals

Narrow d,f-orbitals → strong electronic correlations

Consequences?
1. Magnetic impurity in a metallic host: The Kondo effect

Explanation of the three peak structure?
2. Photoemission spectra of Ni: -6 eV satellite

Guillot, ..., Falicov (1977)

Not reproducible by Density Functional Theory/
Local Density Approximation

Explanation of the -6 eV satellite?
Metal-insulator transition in $V_2O_3$

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

Rice, McWhan (1970)
McWhan et al. (1973)

Microscopic explanation of the transition?
Transition metal oxides: Spin, charge, orbital order; coupling to lattice; Mott-Hubbard metal-insulator transitions, high $T_c$
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

with

Technological applications:
• sensors, switches
• superconducting cables
• magnets/magnetic storage
• spintronics, …
Hubbard model

\[ H = -t \sum_{\langle i,j \rangle, \sigma} c_i^\dagger c_j + U \sum_i n_{i \uparrow} n_{i \downarrow} \]
Hartree-(Fock) mean-field theory generally insufficient

Correlation phenomena:
Metal-insulator transition, ...

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

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

Hartree-(Fock) mean-field theory generally insufficient
Dynamical Mean-Field Theory (DMFT)
Coordination number $Z$: 
$Z=6$ (simple cubic)

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
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

Coordination number \( Z \):
\( Z=8 \) (body-centered cubic)
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

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

\[ \Sigma(\omega) \]

Metzner + Vollhardt (1989)

\[ d \to \infty \]

Dynamical "single-site" mean-field theory

Theory of strongly correlated electrons

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

Hubbard model

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

Metzner + Vollhardt (1989)

Excursion: Single-impurity Anderson model

Non-interacting conduction (s-) electrons

+ single d-orbital ("impurity")

+ s,d-hybridization $V$

Density of states $N(E)$

$\sim V^2/W$
Excursion: Single-impurity Anderson model

Non-interacting conduction (s-) electrons + single d-orbital ("impurity")
Excursion: Single-impurity Anderson model

Non-interacting conduction (s-) electrons

+ single d-orbital ("impurity") with interaction $U$

Excursion: Single-impurity Anderson model
**Excursion: Single-impurity Anderson model**

- Non-interacting conduction (s-) electrons
- Single d-orbital ("impurity") with interaction $U$
- $s,d$-hybridization $V$

**Characteristics:**
- 3-peak structure
- Non-perturbative energy scale ("Kondo physics")

**Bulk systems ($Z \to \infty$):**
- Connection with DMFT

![Graph showing the single-impurity Anderson model](image)
Dynamical Mean-Field Theory (DMFT)

Proper time resolved treatment of local electronic interactions:

Kotliar, Vollhardt; Physics Today (March 2004)

Correlations (I):
Interaction effects beyond Hartree-Fock (= static mean-field theory)
Mott-Hubbard metal-insulator transition

**Hubbard model, n=1**

- **Density of states**
- **Quasiparticle renormalization**: $Z^{-1} = \frac{m^*}{m} \rightarrow \infty$

**Correlations (II):** Interaction effects leading to transfer of spectral weight
Mott-Hubbard metal-insulator transition

Hubbard model, \( n=1 \)

Correlations (II):
Interaction effects leading to transfer of spectral weight
Universality due to Fermi statistics

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

Mott-Hubbard metal-insulator transition

Hubbard model ($n=1$)

Helium-3

Universality due to Fermi statistics
Characteristic three-peak structure

Single-impurity Anderson model

Two types of electrons

Only one type of electron

Experimentally detectable?
Structure of the single-particle spectral function $A(\omega)$

DMFT(IPT): Georges et al. (1996)


DMFT(QMC): Schlipf et al. (1999)

Signature of a composite excitation? Experimentally detectable?
Models meet Materials: LDA+DMFT
DFT/LDA

- material specific: “ab initio”
- fails for strong correlations
- fast code packages
### 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>

*How to combine:*
1. Gutzwiller density functional theory

Gutzwiller approximation exact in $d \to \infty$

Metzner, DV (1989)

d $\to \infty$: Evaluation of $E_G$ for arbitrary $\left| \psi_0 \right>$

Gebhard (1990)

Multi-band generalization:

„Gutzwiller DFT“

Ferromagnetic Ni: Cut of Fermi surface

Bünemann, Gebhard, Ohm, Weiser, Weber (2005)
2. Dynamical computational scheme for correlated electron materials

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

+ Local electronic correlations
  Many-body theory: DMFT

LDA+DMFT

Anisimov et al. (1997)
Lichtenstein, Katsnelson (1998)
Kotliar, Vollhardt (2004)
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
Unoccupied states (ideal)
Unoccupied states (measured)
1. Application: 
3d\(^1\) system \((\text{Sr,Ca})\text{VO}_3\)
Experiment

Photoemission spectra at high photon energies

SrVO$_3$  CaVO$_3$

Bulk spectra

Theory

Electronic structure

Crystal structure

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

↓

orthorhombic distortion

↓

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

10% reduction in V-O-V angle
Theory

Electronic structure

Crystal structure
SrVO₃: $\angle V-O-V = 180^\circ$

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

orthorhombic distortion

10% reduction in V-O-V angle

10% reduction in V-O-V angle

Band scheme

3d¹

isotropic cubic

t₂g

e₉

LDA density of states

SrVO₃

CaVO₃

SrVO₃  $\rightarrow$  CaVO₃

only 4% bandwidth reduction
LDA+DMFT results

Density of states ("Spectral function"): \[ A(\omega) = -\frac{1}{\pi} \text{Im} G(\omega) \]

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

\( \text{SrVO}_3 \) 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)
2. Application:

Kinks in the electronic dispersion
“Kinks” at 40-70 meV due to coupling of electrons to phonons or spin fluctuations?

Zhou et al. (2006)
Electron-phonon (boson) correction of electronic dispersion

Ashcroft, Mermin; *Solid State Physics* (1976)
Kinks: Metal surfaces

Adsorbate (Hydrogen) on Tungsten (110) surface

$\omega^* = 160$ meV: Surface phonon

Rotenberg et al. (2000)

Kink due to electron-phonon coupling
Kinks: Metal surfaces

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

300meV: too high for phonons or spin fluctuations

Menzel et al. (2005)

Kinks due to coupling of electrons to what?
Kinks due to electron-boson coupling

Conventional wisdom

Kinks due to electron-electron hybridization
Kinks in strongly correlated electron systems


Kinks at $\omega_0 \approx 0.2$ eV

Origin of kinks in a purely electronic theory with one type of electron?
Strongly correlated paramagnetic metal: Kinks without “coupling”

Byczuk, Kollar, Held, Yang, Nekrasov, Pruschke, DV; Nature Physics (2007)
\[ G(\omega) \xrightarrow{\text{DMFT}} \Sigma(\omega) \]

Byczuk, Kollar, Held, Yang, Nekrasov, Pruschke, DV; Nature Physics (2007)
\[
G(\omega) \overset{DMFT}{\longrightarrow} \Sigma(\omega)
\]

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

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

- FL regime
- Central Peak, outside FL regime

Byczuk, Kollar, Held, Yang, Nekrasov, Pruschke, DV; Nature Physics (2007)
\[ G(\omega) \xrightarrow{\text{DMFT}} \Sigma(\omega) \]

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

\[ E_k = \begin{cases} \frac{Z_{FL} E_k^{0/LDA}}{Z_{CP}} & \text{FL regime} \\ \pm c & \text{Central Peak,} \\ & \text{outside FL regime} \end{cases} \]

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

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