Lecture Notes

Introduction to Strongly Correlated Electron Systems

WS 2014/ 2015

Mohsen Abd-Elmeguid

II. Institute of Physics, University of Cologne, Germany
Introduction to strongly correlated electron systems

I. Introduction
   Brief summary of electrons in solids, origin of strong electron correlations

II. Classes of strongly correlated electron systems
   (a) Transition metal compounds: 3d-electrons
       - Hubbard model, Mott insulator, metal-insulator transition
       - Spin, charge, and orbital degrees of freedom and ordering phenomena, selected materials
   (b) Heavy fermion systems: 4f (5f) – electrons
       - The Kondo effect, heavy fermion systems, non-Fermi liquid behavior,
       - Quantum phase transitions, unconventional superconductivity, selected materials
   (c) Nanoscale structures:
       - Quantum confinement, unusual properties for potential applications

III. Pressure effect on the ground state properties:
    - Recent experimental results on heavy fermions and transition metal compounds

IV. Summary and open discussion
Some comments on electrons in Solids:

Theoretical description using **two different approaches/approximations** without taking into account electron-electron correlations:

- The nearly-free electron model (itinerant electrons in very weak periodic potential)

- The tight-binding model (electrons localized on an atomic site but weakly coupled to all other atoms—use Linear Combination of Atomic Orbitals, LCAO)

Both models qualitatively yield the same results and are well known to most of you in details from the lectures on Solid State Physics by Prof. M. Grüninger and Pd Dr. T. Lorenz.

To remind you, I just will go briefly through the two models and stress on some relevant points!
Bloch theorem for non-interacting electrons in a periodic potential

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(r) + U(\vec{r})\psi(r) = E\psi(r)$$

$$U(\vec{r}) = U(\vec{r} + R)$$

**R is a Bravais lattice vector!**

… where $U(\vec{r})$ is a function with the periodicity of the lattice …

Bloch’s theorem tells us that eigenstates have the form

$$\psi(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} U(\vec{r})$$

Energy eigenvalues $E_n(\vec{k})$  **Band structure!**
Copper: Valence States
Some comments to the effective mass of electrons
The effective mass of Bloch electrons

The motion of electrons is modified by the crystal potential through which it moves

\[
m^* = \left( \frac{1}{\hbar^2} \frac{d^2 E}{dk^2} \right)^{-1}
\]

1/ curvature of the band is proportional to \( m^* \)

Heavy effective mass implies high density of states \( D(E) \) and high ~\( \gamma \) and vice versa

Electrons in a crystal are accelerated in response to an external force just as though they were free electrons with effective mass \( m^* \)
The effective mass of electrons and density of states

\[ D(E_F) = \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} E_F^{1/2} \]

\[ C_{el} = \frac{\pi^2}{3} k_B^2 D(E_F) T = \gamma T \]

, hence \( \gamma \propto m \)

For free electrons \( \gamma \) calculated per mole:

\[ \gamma_{th} = \frac{\pi^2}{3} k_B^2 D(E_F) = \frac{\pi^2 k_B^2 m N_0 z}{\hbar^2 (3\pi^2 N/V)^{2/3}} \]

\( N_0 \) Avogadro's number and \( z \) number of conduction electrons per formula unit
Comparison of $\gamma_{th}$ with experimental $\gamma$ values

\[
\begin{array}{cccc}
\text{Metal} & \gamma & \gamma_{th} & \text{Metal} \\
\hline
\text{Li} & 1.63 & 0.749 & \text{Fe} & 5.0 \\
\text{Na} & 1.38 & 1.094 & \text{Co} & 4.7 \\
\text{K} & 2.08 & 1.668 & \text{Ni} & 7.1 \\
\text{Cu} & 0.69 & 0.505 & \text{La} & 10 \\
\text{Ag} & 0.64 & 0.645 & \text{Ce} & 21 \\
\text{Au} & 0.69 & 0.642 & \text{Er} & 13 \\
\text{Al} & 1.35 & 0.912 & \text{Pt} & 6.8 \\
\text{Ga} & 0.60 & 1.025 & \text{Mn} & 14 \\
\end{array}
\]

$\frac{\gamma}{\gamma_{th}} \approx 1 - 1.5$

mainly s-electrons, broad bands

$\frac{\gamma}{\gamma_{th}} \approx 10 - 30$

partially filled d-bands

$\frac{\gamma}{\gamma_{th}} \approx 100 - 1000$

heavy fermion compounds 4f (5f)-orbitals strong electron-electron correlations SCES

Why $m^*$ is so large in some 4f and 5f electron system?

No answer from the band theory (one electron approximation), neglecting electron-electron interactions. This will be discussed in Chapter II (b).
The tight-binding model

- Electrons (inner shells) are strongly localized and mainly see the atomic potential
  \[ \Rightarrow \text{use Linear Combination of Atomic Orbitals (LCAO)} \]

- The atomic wave function of level \( i \) \( \Phi_A^i \) at site \( \vec{R} \) (\( \vec{R} \) site of Bravais lattice) is defined by
  \[ H_A(\vec{R} - \vec{r}) \Phi_A^i(\vec{r} - \vec{R}) = E_A^i \Phi_A^i(\vec{r} - \vec{R}) \]
  \[ \Rightarrow H_A(\vec{r} - \vec{R}) = -\frac{\hbar^2}{2m} \nabla^2 + V_A(\vec{r} - \vec{R}) \]

- Lattice periodic potential
  \[ V(\vec{r}) = \sum_{\vec{R}} V_A(\vec{r} - \vec{R}) \]
  \[ = V_A(\vec{r} - \vec{R}) + \sum_{\vec{R} \neq \vec{R}'} V_A(\vec{r} - \vec{R}') \]
  \[ = \tilde{V}(\vec{r} - \vec{R}) \]

\( \Rightarrow \) lattice: single atom at \( \vec{R} \) + rest!
tight binding energy bands

\[ E(k) = E_A - A - 2t_x \cos(k_x a) - 2t_y \cos(k_y b) - 2t_z \cos(k_z c) \]

atomic level

binding energy
(electrons at site \(R\) feel
the attraction potential
of all other ions)

Schematic representation of formation of TB bands

<table>
<thead>
<tr>
<th>Energy levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Spacing) (^{-1})</td>
</tr>
</tbody>
</table>

\( n = 1 \) \( n = 2 \) \( n = 3 \)

\( N \)-fold degenerate levels

\( (\text{Singlet}) \)

Band width \( W = 12t \) in 3D cubic lattice

\( \cos \text{ from } -1 \text{ to } +1 \)

dispersion results from finite overlap (hopping)

in general:

\[ \psi_i \propto (\frac{r_i}{r_i}) \mid \tilde{V} \mid \phi_A (r_i - r) \]

\( R \) nearest neighbor

Notes:
Band width depends on the spatial extent
of \( \phi_A \), interatomic distance, and on
the number of nearest neighbors (nn)

\[ W \propto 2zt \]

\( z = 2 \) for 1D

\( n \geq \frac{1}{2} \) nn

eq 8 for 1D

\[ \Rightarrow E(k) = E_A - 2t \cos k_x a \]

\( \text{B'} \)
Electron Density of States: LCAO

bcc tungsten
We now discuss the breakdown of the band theory in describing the ground states of strongly correlated transition oxide systems.
Insulator vs. Metal

Only full and empty shells
⇒ **Insulator** (NaCl, Si)

Partially filled shells
⇒ **Metal** (Na, Cu)

**Examples of correlated Insulators with partially filled shells:**

La$_2$CuO$_4$: Cu$^{2+}$: [Ar]3d$^9$    La$^{3+}$: [Xe] O$^{2-}$: [Ne]
V$_2$O$_3$:    V$^{3+}$: [Ar]3d$^2$    O$^{2-}$: [Ne]
Nd$_2$O$_3$:    Nd$^{3+}$: [Xe]4f$^3$    O$^{2-}$: [Ne]

**breakdown of band theory?**
High-$T_c$-Superconductivity in La$_{2-x}$Sr$_x$CuO$_4$

La$_2$CuO$_4$: antiferromagnetic Mott-Insulator.  
Doping with Sr$^{2+}$ for La$^{3+}$, high-$T_c$-Superconductor La$_{2-x}$Sr$_x$CuO$_4$

Metal-Insulator transition in $\text{V}_2\text{O}_3$

Mott-Hubbard-System: Metal-insulator transition as a function of temperature (factor $10^8$!) as a function of temperature $T \sim 150\,\text{K}$ without structural phase transition!

Energy gap $\sim 0.6\,\text{eV} \sim 7000\,\text{K}$
Mott-Hubbard-Insulators \( \text{LaM} \text{O}_3 \)

\[ M = \text{Cu, Ni: 3d}^8, \text{3d}^7, \text{Metal} \]
\[ M = \text{Sc 3d}^0, \text{Band insulator} \]

\[ M = \text{Ti, V, Cr, Mn, Fe, Co,} \]
3d partially filled (3d\(^1\) – 3d\(^6\)),
Mott-Hubbard insulators
Energy gap ~ 0.2 - 3 eV

Perowskit-structure
(distorted)
\( \text{LaM} \text{O}_3 \)
A closer look to “half filling”
Gedankenexperiment

Consider a half-filled band, e.g. Na metal
Na: 1 e in 3s shell with 2 states per atom (spin↑↓)

Metallic for any interatomic distance?
(expected from the band theory)

Obviously not, for a very large distances we have individual atoms insulating, not metallic state. The 3s band becomes very narrow, but its always half-filled!!

Question: what suppresses the transfer of an electron from one atom to another atom?
In SCES: Coulomb repulsion between 2 electrons at the same atom must be taken into account beyond one electron approximation.

**Explanation**

**Small distances:** electrons are smeared out (large bandwidth, \(W\)), charge fluctuations do not alter the average occupation (k-space picture)

**Large distances:** electronic transition yields \(\text{Na}^+ & \text{Na}^- \rightarrow 2\ e\) in same orbital \(\rightarrow\) large on-site Coulomb repulsion \(U\) (local picture)

Competition between kinetic energy and on-site energy \(U\) determines the nature of the ground state

- Metallic state: if \(W >> U\)
- Insulating state: if \(U >> W\)
Dealing with electron-electron correlations

Hubbard model

simplest (!) microscopic Model for correlated electrons (1963) introduced at the same time by Gutzwiller, Hubbard und Kanamori

(a) kinetic energy: electron hopping between next nearest neighbors

(b) Interaction only between electrons at the same site:

on-site e-e-repulsion = Hubbard $U$

Hamiltonian in 2nd quantization:

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

$\langle i,j\rangle$ next nearest neighbors site; $c_{i\sigma}^+, c_{i\sigma}$ creation, annihilation operators of an occupied electronic state at site $i$ with spin $\sigma$

$c_{i\sigma}^+ c_{i\sigma}$ Electron hops from $j$ to $i$ without spin flip

$n_{i\uparrow} n_{i\downarrow}$ counts doubly occupied sites ($n_{i\uparrow} = c_{i\uparrow}^+ c_{i\uparrow}$, number operator )
Hubbard model

\[ H_{\text{Hubbard}} = \sum_{\langle i,j \rangle, \sigma} t_{ij} c_{i\sigma}^+ c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} \]

**kinetic energy**
- Hopping of \( e^- \) between next neighbors
- Hopping matrix element \( t \) large = strong intersite overlap, large \( W \)

**electron interaction**
- Only between \( e^- \) on the same site *on-site* e-e repulsion = Hubbard U ( \( \sim \) eV)
- Hubbard U punishes double occupancy

\( U \) wants to localize \( t \) rewards delocalization

\( \rightarrow \) competition:
see Board!
\[ \Delta E = U = (N-2)E_N + E_{N+1} + E_{N-1} - N E_N \]

\[ \Rightarrow U = \frac{E_{N+1} + E_{N-1} - 2E_N}{2} \quad \text{Hubbard \ } U \]
Hubbard model describes two opposite limits:

(a) Weak interacting electrons $\Rightarrow U \ll t$; and

(b) Strongly interacting, or strongly correlated electrons $\Rightarrow U \gg t$

(a) $U \ll t \Rightarrow \text{tight-binding approximation (} U \sim 0 \text{)}$

$$H_{\text{Hubbard}} \sim t \sum_{i,j} c^+_i \sigma c_j$$

$\Rightarrow E(k) \leq 2t \cos(k_x a) - 2ty \cos(k_y b) + \cdots$ (see eqs. B)

or in 1D $E(k) = -2t \cos(k_x a)$ (eqs. B')
(b) $U \gg t$

Collection of isolated atoms; each has 4 electronic many-body states:

| State $|N, S^o, S_z \rangle$ | total $n^o$ of electrons $N$ | total spin $S^o$ |
|--------------------------|--------------------------|-----------------|
| $|0, 0, 0 \rangle = |0 \rangle$ | 0 | 0 |
| $|1, \frac{1}{2}, \uparrow \rangle = c_i \uparrow |0 \rangle$ | 1 | $\frac{1}{2}$ |
| $|1, \frac{1}{2}, \downarrow \rangle = c_i \downarrow |0 \rangle$ | 1 | $\frac{1}{2}$ |
| $|2, 0, 0 \rangle = c_i \uparrow c_i \downarrow |0 \rangle$ | 2 | 0 |
Hubbard model

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

**kinetic energy**

- Hopping of \( e^- \) between next neighbors

**electron interaction**

- Only between \( e^- \) on the same site on-site e-e repulsion = Hubbard \( U \) ( \( \sim \) eV)

Hopping matrix element \( t \) large = strong intersite overlap, large \( W \)

**competition:**

- \( U \) wants to localize
- \( t \) rewards delocalization

Hubbard \( U \) punishes double occupancy
calculation of Hubbard $U$

Simple case: one electron per site (half band filling)
Coulomb repulsion between electrons causes localization when the intersite interaction and (thus $W$) is small. Coulomb repulsion drives a half-filled band insulating, with Mott-Hubbard gap ($U$):

$$U = E_{N+1} + E_{N-1} - 2E_N$$
Double occupation costs energy $(U)$ splitting of the energy band into Upper and Lower Hubbard bands.
Types of Mott-Insulators

(a) Mott-Hubbard insulator:

\[ \Delta = |\epsilon_d - \epsilon_p| \]

\[ W_d \] charge gap

\[ U_{dd} \] on-site Coulomb interaction

LaMO3 for M = Co, Fe

(b) Charge-transfer insulator:

\[ W_p \] charge transfer energy

\[ U_{dd} \] bandwidth; (hopping t)

LaMO3 for M = Ti, V
Metal-insulator transition: Bandwidth

with half filling:

U > W $\rightarrow$ LHB full, UHB empty $\rightarrow$ Mott-Hubbard-Isolator

U < W $\rightarrow$ kinetic energy dominates $\rightarrow$ Metal-insulator transition

Kotliar, Vollhard, Physics Today, March 2004, 39

PES

Ti$^{3+}$, V$^{4+}$: 3d$^1$
Re$^{6+}$: 5d$^1$
variation of W (t) with structure (bonding angles) and from 3d to 5d

(stoichiometric LaTiO$_3$ is Mott-insulator)

2) Metal-Insulator transition as a function of doping
e.g.: replace La\textsuperscript{3+} (or Y\textsuperscript{3+}) by Sr\textsuperscript{2+} (or Ca\textsuperscript{2+}) \rightarrow hole-doping

Hoping of a doped hole costs no energy
Hoping of a doped electron costs no energy

Doping Mott-insulator
Induced a metallic, superconducting state
e.g. La\textsubscript{2-x}Sr\textsubscript{x}CuO\textsubscript{4}

Uchida et al, PRB 43, 7942 (91)

More later ....
doped Mott-insulators

HTC-Superconductors

Complexity in Strongly Correlated Electronic Systems

Science 8 July 2005: Vol. 309 no. 5732 pp. 257-262
Transition metal systems and electron correlations

Systems can be quite close to the borderline $U \sim W (t)$

Thus many interesting transitions can occur by changing $T, P, \text{filling, structure, etc}$

more discussion with examples later!