Electronic Correlation in Solids
– what is it and how to tackle it?

Silke Biermann
Centre de Physique Théorique
Ecole Polytechnique, Palaiseau, France
“Correlations”? What is it?
“Correlations”? Ashcroft-Mermin, “Solid state physics” gives ...

... the “beyond Hartree-Fock” definition”:

The correlation energy of an electronic system is the difference between the exact energy and its Hartree-Fock energy.
“Correlations”?  

- “Correlatio” (lat.): mutual relationship  

→ The behavior of a given electron is not independent of the behavior of the others!
The “standard model” of solids:

Electrons in a periodic potential

- occupy *one-particle* (Bloch) states, delocalised over the solid.
- feel each other only through an effective mean potential (and the Pauli principle).

→ *independent particle picture*
“Correlations”?

• “Correlatio” (lat.): mutual relationship

   → The behavior of a given electron is not independent of the behavior of the others!

• Mathematically:

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

(1)
“Correlations”?  

50 % have blue eyes  
50 % have yellow eyes
“Correlations”? 

50% are left-handed
50% are right-handed
“Correlations”?

What’s the probability for a left-handed yellow-eyed kangaroo ??
“Correlations”? 

probability for a left-handed yellow-eyed kangaroo  
= $1/2 \cdot 1/2 = 1/4$  **only if the two properties are uncorrelated**  
Otherwise: anything can happen ....
“Correlations”?  

- “Correlatio” (lat.): mutual relationship

→ The behavior of a given electron is not independent of the behavior of the others!

- Mathematically:

\[ \langle AB \rangle \neq \langle A \rangle \langle B \rangle \]  \hspace{1cm} (2)

For electrons (in a given atomic orbital):

\[ \langle n_\uparrow n_\downarrow \rangle \neq \langle n_\uparrow \rangle \langle n_\downarrow \rangle \]

\( n_\sigma = \text{number operator for electrons with spin } \sigma. \)
“Correlations”? Count electrons on a given atom in a given orbital:

\[ n_\sigma = \text{counts electrons with spin } \sigma \]

\[ n_{\uparrow} n_{\downarrow} \text{ counts “double-occupations”} \]

\[ \langle n_{\uparrow} n_{\downarrow} \rangle = \langle n_{\uparrow} \rangle \langle n_{\downarrow} \rangle \text{ only if the “second” electron does not care about the orbital being already occupied or not} \]
Exercise (!):

Does

$$\langle n_{\uparrow}n_{\downarrow} \rangle = \langle n_{\uparrow} \rangle \langle n_{\downarrow} \rangle \text{ hold?}$$

1. Hamiltonian: $$H_0 = \epsilon(n_{\uparrow} + n_{\downarrow})$$

2. Hamiltonian: $$H = \epsilon(n_{\uparrow} + n_{\downarrow}) + U n_{\uparrow} n_{\downarrow}$$
Correlations $\langle n^{\uparrow} n^{\downarrow} \rangle = \langle n^{\uparrow} \rangle \langle n^{\downarrow} \rangle$?

(1) Hamiltonian: $H_0 = \varepsilon (n^{\uparrow} + n^{\downarrow})$
Operators $n^{\uparrow}$ and $n^{\downarrow}$ have eigenvalues 0 and 1.
Correlations $\langle n_\uparrow n_\downarrow \rangle = \langle n_\uparrow \rangle \langle n_\downarrow \rangle$?

(1) Hamiltonian: $H_0 = \epsilon (n_\uparrow + n_\downarrow)$
Operators $n_\uparrow$ and $n_\downarrow$ have eigenvalues 0 and 1.

$$\langle n_\uparrow n_\downarrow \rangle = \frac{1}{\mathcal{Z}} \sum_{n_\uparrow=0,1, \ n_\downarrow=0,1} n_\uparrow n_\downarrow e^{-\beta\epsilon (n_\uparrow+n_\downarrow)}$$

$$= \frac{1}{\mathcal{Z}} \sum_{n_\uparrow=0,1} n_\uparrow e^{-\beta\epsilon n_\uparrow} \sum_{n_\downarrow=0,1} n_\downarrow e^{-\beta\epsilon n_\downarrow}$$

$$= \langle n_\uparrow \rangle \langle n_\downarrow \rangle$$
Correlations \[ \langle n^{\uparrow} n^{\downarrow} \rangle = \langle n^{\uparrow} \rangle \langle n^{\downarrow} \rangle ? \]

(1) Hamiltonian: \[ H_0 = \epsilon (n^{\uparrow} + n^{\downarrow}) \]
Operators \( n^{\uparrow} \) and \( n^{\downarrow} \) have eigenvalues 0 and 1.

\[
\langle n^{\uparrow} n^{\downarrow} \rangle = \frac{1}{Z} \sum_{n^{\uparrow}=0,1, n^{\downarrow}=0,1} n^{\uparrow} n^{\downarrow} e^{-\beta \epsilon (n^{\uparrow} + n^{\downarrow})}
\]

\[
= \frac{1}{Z} \sum_{n^{\uparrow}=0,1} n^{\uparrow} e^{-\beta \epsilon n^{\uparrow}} \sum_{n^{\downarrow}=0,1} n^{\downarrow} e^{-\beta \epsilon n^{\downarrow}}
\]

\[
= \langle n^{\uparrow} \rangle \langle n^{\downarrow} \rangle
\]

No correlations! (Hamiltonian separable)
Correlations $\langle n^\uparrow n^\downarrow \rangle = \langle n^\uparrow \rangle \langle n^\downarrow \rangle$?

(2) Hamiltonian: $H = \epsilon (n^\uparrow + n^\downarrow) + U n^\uparrow n^\downarrow$

Operators $n^\uparrow$ and $n^\downarrow$ have eigenvalues 0 and 1.
Correlations $\langle n_{\uparrow} n_{\downarrow} \rangle = \langle n_{\uparrow} \rangle \langle n_{\downarrow} \rangle$?

(2) Hamiltonian: $H = \epsilon (n_{\uparrow} + n_{\downarrow}) + U n_{\uparrow} n_{\downarrow}$

Operators $n_{\uparrow}$ and $n_{\downarrow}$ have eigenvalues 0 and 1.

$$
\langle n_{\uparrow} n_{\downarrow} \rangle = \frac{1}{Z} \sum_{n_{\uparrow}=0,1, \ n_{\downarrow}=0,1} n_{\uparrow} n_{\downarrow} e^{-\beta \epsilon (n_{\uparrow} + n_{\downarrow}) - \beta U n_{\uparrow} n_{\downarrow}}
\neq \langle n_{\uparrow} \rangle \langle n_{\downarrow} \rangle
$$
Correlations $\langle n^\uparrow n^\downarrow \rangle = \langle n^\uparrow \rangle \langle n^\downarrow \rangle$?

(2) Hamiltonian: $H = \epsilon (n^\uparrow + n^\downarrow) + U n^\uparrow n^\downarrow$

Operators $n^\uparrow$ and $n^\downarrow$ have eigenvalues 0 and 1.

$$\langle n^\uparrow n^\downarrow \rangle = \frac{1}{\mathbb{Z}} \sum_{n^\uparrow = 0,1, \ n^\downarrow = 0,1} n^\uparrow n^\downarrow e^{-\beta \epsilon (n^\uparrow + n^\downarrow)} - \beta U n^\uparrow n^\downarrow$$

$\neq \langle n^\uparrow \rangle \langle n^\downarrow \rangle$

Correlations! (Hamiltonian not separable)
Periodic array of sites with one orbital

We can have $\langle n_\uparrow + n_\downarrow \rangle = 1$ for each site, but yet $\langle n_\uparrow n_\downarrow \rangle = 0$ (insulator!)

Is this possible within a one-particle picture?
Periodic array of sites with one orbital

\[ \langle n_{\uparrow} + n_{\downarrow} \rangle = 1 \text{ for each site, and } \langle n_{\uparrow} n_{\downarrow} \rangle = 0 \]

→ only possible in a one-particle picture if we allow for symmetry breaking (e.g. magnetic), such that
\[ \langle n_{\uparrow} \rangle \langle n_{\downarrow} \rangle = 0 \]
Mott’s ficticious H-solid:

Hydrogen atoms with lattice spacing 1 m

H H H H H H H H H H H
H H H H H H H H H H H
H H H H H H H H H H H
H H H H H H H H H H H
H H H H H H H H H H H
H H H H H H H H H H H

(not to scale ...)

Metal or insulator?
Mott’s ficticious H-solid:
Hydrogen atoms with lattice spacing 1 m

H H H H H H H H H H H H
H H H H H H H H H H H H
H H H H H H H H H H H H
H H H H H H H H H H H H
H H H H H H H H H H H H
H H H H H H H H H H H H
H H H H H H H H H H H H
H H H H H H H H H H H H
H H H H H H H H H H H H
H H H H H H H H H H H H
H H H H H H H H H H H H

(not to scale ...)

Metal or insulator?

Band structure: $\rightarrow$ metal
Reality: $\rightarrow$ “Mott insulator”!
Mott’s ficticious H-solid:
Hydrogen atoms with lattice spacing 1 m

H H H H H H H H H H H H H
H H H H H H H H H H H H H
H H H H H H H H H H H H H
H H H H H H H H H H H H H
H H H H H H H H H H H H
H H H H H H H H H H H
H H H H H H H H H H H
H H H H H H H H H H
H H H H H H

(not to scale ...)

Metal or insulator?

Band structure: $\rightarrow$ metal
Reality: $\rightarrow$ “Mott insulator”!

Coulomb repulsion dominates over kinetic energy!
Why does band theory work at all?
Band structure ...

... from photoemission – Example: Copper
Why does band theory work at all?

Band structure relies on *one-electron* picture
But: electrons interact!

Several answers ...:

- Pauli principle
- Screening

\{ \text{reduce effects of interactions} \}

Landau’s Fermi liquid theory: quasi-particles
The “standard model” (contd.)

Landau theory of quasiparticles:
→ one-particle picture as a low-energy theory with renormalized parameters

(cf. Patrick Rinke’s lecture!)
Why does the “standard model” work?

Band structure relies on \textit{one-electron} picture
But: electrons interact!

Several answers ...:

- Pauli principle
- Screening

\{ \text{reduce effects of interactions} \}

Landau’s Fermi liquid theory: quasi-particles

- It does not always work ....


**YTiO$_3$ in LDA**

YTiO$_3$: a distorted perovskite compound with d$^1$ configuration (i.e. 1 electron in $t_{2g}$ orbitals), paramagnetic above 30 K.

**DFT-LDA results:**

*(*) DFT-LDA = Density Functional Theory within the local density approximation
YTiO$_3$: in reality ...

Photoemission reveals a (Mott) insulator:

(Fujimori et al.)
**YTiO$_3$: in reality ...**

Photoemission reveals a (Mott) insulator:

(Fujimori et al.)

How to produce a paramagnetic insulating state with 1 electron in 3 bands?

→ not possible in band theory

→ breakdown of independent particle picture
Further outline

- From N-particle to 1-particle Hamiltonians
- Problems of DFT-LDA
- Modelling correlated behavior: the Hubbard model
- The Mott metal-insulator transition
- Dynamical mean field theory
- Dynamical mean field theory within electronic structure calculations (“LDA+DMFT”)
- Examples:
  Typical examples: $d^1$ perovskites $\text{SrVO}_3$, $\text{CaVO}_3$, $\text{LaTiO}_3$, $\text{YTiO}_3$
  A not typical one ...: $\text{VO}_2$
- Conclusions and perspectives
The N particle problem ...

and its mean-field solution:
N-electron Schrödinger equation

\[ \mathcal{H}_N \Psi(r_1, r_2, ..., r_N) = E_N \Psi(r_1, r_2, ..., r_N) \]

with

\[ \mathcal{H}_N = H_{kinetic}^N + H_{external}^N + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} \]

becomes separable in mean-field theory:

\[ \mathcal{H}_N = \sum_i h_i \]
For example, using the Hartree(-Fock) mean field:

\[
    h_i = h_i^{\text{kinetic}} + h_i^{\text{external}} + e^2 \int dr \frac{n(r)}{|r_i - r|}
\]

Solutions are Slater determinants of one-particle states, fulfilling

\[
    h_i \phi(r_i) = \epsilon \phi(r_i)
\]

Bloch’s theorem => use quantum numbers k, n for 1-particle states
1-particle energies \( \epsilon_{kn} \) => band structure of the solid
Density functional theory ...

... achieves a mapping onto a separable system (mapping of interacting system onto non-interacting system of the same density \textit{in an effective potential}) for the ground state. However:

• effective potential unknown => local density approximation

• strictly speaking: not for excited states

In practice (and with the above caveats): \textit{DFT-LDA can be viewed as a specific choice for a mean field}
Electronic Correlations

General definition:
Electronic correlations are those effects of the interactions between electrons that cannot be described by a mean field.

More specific definitions:
Electronic correlations are effects beyond

- ... Hartree(-Fock)
- ... DFT-LDA(*)
- ... the “best possible” one-particle picture

(from Fujimori et al., 1992)
Two regimes of failures of LDA

1. “weak coupling”: moderate correlations, perturbative approaches work (e.g. “GW approximation”) (see Patrick Rinke’s lecture)

2. “strong coupling”: strong correlations, non-perturbative approaches needed (e.g. dynamical mean field theory)

NB. Traditionally two communities, different techniques, but which in recent years have started to merge ...

NB. Correlation effects can show up in some quantities more than in others!
Problems of DFT-LDA...

- 30% error in volume of $\delta$-Pu by DFT-LDA (*)
- $\alpha$-$\gamma$ transition in Ce not described by LDA
- correlation effects in Ni, Fe, Mn ...
- LDA misses insulating phases of certain oxides (VO$_2$, V$_2$O$_3$, LaTiO$_3$, YTiO$_3$, Ti$_2$O$_3$ ...)
- bad description of spectra of some metallic compounds (SrVO$_3$, CaVO$_3$ ...)

E.g. photoemission of YTiO$_3$:

![Photoemission plot of YTiO$_3$.](image)
Correlated Materials ...

... typically contain partially filled d- or f-shells

→ transition metal oxides/sulfides, rare earth or actinide compounds
(but also: low-dimensional systems, organics ...)
Metal-Insulator Transitions

Metal-insulator transition in VO$_2$ at $T_c = 340$ K

Morin et al., 1959
**SrVO₃ : a correlated metal**

**SrVO₃ within DFT-LDA**

![Graph of Nᵢ,E vs E (eV) for SrVO₃ within DFT-LDA.]

**Photoemission**

![Graph of binding energy vs intensity for SrVO₃ and CaVO₃ with different photon energies.]

(Sekiyama et al. 2003)
The Hubbard model

\[ H = -\frac{D}{2} \sum_{\langle ij \rangle \sigma} \left( c_{i\sigma}^{\dagger} c_{j\sigma} + c_{j\sigma}^{\dagger} c_{i\sigma} \right) + U \sum_{i} n_{i\uparrow} n_{i\downarrow} \]

(Hubbard, 1963)

Ground state at half-filling and finite U: antiferromagnetic
Frustrated model → paramagnetic solution ?
Spectra for one atom

Electron removal and addition spectra

\[ E = \epsilon \]

\[ E = \epsilon + U \]

U=Coulomb interaction between two 1s electrons
Atomic limit: $D=0$

$$H = U \sum_i n_i \uparrow n_i \downarrow$$

→ atomic eigenstates, localized in \textit{real} space

Spectral function = discrete peaks separated by $U$
Non-interacting limit: \( U=0 \)

\[
H = -\frac{D}{2} \sum_{\langle ij \rangle \sigma} \left( c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma} \right) = \sum_{k\sigma} \epsilon_k c_{k\sigma}^\dagger c_{k\sigma}
\]

with e.g. \( \epsilon_k = -D \left[ \cos(k_x) + \cos(k_y) + \cos(k_z) \right] \) on a 3D square lattice (lattice constant 1) with nearest neighbor hopping.

Spectral function = non-interacting DOS
“Atomic” and “band-like” spectra

“Spectral function” $\rho(\omega)$ probes possibility of adding/removing an electron at energy $\omega$.

In non-interacting case: $\rho(\omega)=\text{DOS}$.
In general case: relaxation effects!
In “atomic limit”: probe local Coulomb interaction
Hubbard model within DMFT\(^{(\ast)}\)

\[
H = -\frac{D}{2} \sum_{<i,j>\sigma} \left( c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma} \right) + U \sum_i n_{i\uparrow} n_{i\downarrow}
\]

(Hubbard, 1963)

\(\rho(\omega)\)

Quasi-particle peak
Hubbard bands

Georges & Kotliar 1992

(\ast) DMFT = Dynamical Mean Field Theory, paramagnetic solution
Spectra of perovskites

Photoemission

(Sekiyama et al. 2003)
Spectra of perovskites

Photoemission

(Sekiyama et al. 2003)
Green’s function – survival kit

$$\rho(\omega) = -\frac{1}{\pi} \Im G_{ii}(\omega)$$

Definition of Green’s function:

$$G_{ij}(t) = -\langle \hat{T} c_i(t) c_j^\dagger(0) \rangle$$

Quasi-particles are poles of

$$G(k, \omega) = \frac{1}{\omega + \mu - \epsilon_o(k) - \Sigma(k, \omega)}$$

All correlations are hidden in the self-energy:

$$\Sigma(k, \omega) = G^{-1}_0(k, \omega) - G^{-1}(k, \omega)$$
Hubbard model within DMFT\(^(*)\)

\[
H = -\frac{D}{2} \sum_{<ij>\sigma} \left( c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma} \right) + U \sum_i n_{i\uparrow} n_{i\downarrow}
\]

(Hubbard, 1963)

\[\rho(\omega)\]

Quasi-particle peak
Hubbard bands

Georges & Kotliar 1992

\((*)\) DMFT = Dynamical Mean Field Theory, paramagnetic solution
The “mechanism”?

Σ''(ω) diverges for ω → 0 (i.e. at the Fermi level):
Quasi-particle lifetime (≈ 1/Σ''(ω = 0)) vanishes!

Opening of a gap at the Fermi level ω = 0

\[ A(k, \omega) = \text{Im}G(k, \omega) \]

\[ = \text{Im} \frac{1}{\omega + \mu - \epsilon_o(k) - \Sigma(k, \omega)} \]

\[ = -\frac{1}{\pi} \frac{\Sigma''(k, \omega)}{\omega + \mu - \epsilon_o(k) - \Sigma'(k, \omega))^2 + \Sigma''(k, \omega)^2} \]

Here (particle-hole symmetry and local self-energy):

\[ A(k, \omega) = -\frac{1}{\pi} \frac{\Sigma''(\omega)}{\omega - \epsilon_o(k))^2 + \Sigma''(\omega)^2} \]
What about the metal?

In a Fermi liquid (local self-energy, for simplicity ...):

\[
\begin{align*}
Im \Sigma(\omega) &= -\Gamma \omega^2 + O(\omega^3) \\
Re \Sigma(\omega) &= Re\Sigma(0) + (1 - Z^{-1})\omega + O(\omega^2)
\end{align*}
\]

\[
A(k, \omega) = \frac{Z^2}{\pi} \frac{-\Im \Sigma(\omega)}{(\omega - Z\epsilon_0(k))^2 + (-Z\Im \Sigma(\omega))^2} + A_{inkoh}
\]

For small \(Im \Sigma\) (i.e. well-defined quasi-particles):
Lorentzian of width \(ZIm \Sigma\),
poles at renormalized quasi-particle bands \(Z\epsilon_0(k)\),
weight \(Z\) (instead of 1 in non-interacting case)
Hubbard model within DMFT$^\ast$

\[
H = -\frac{D}{2} \sum_{<i,j>\sigma} \left( c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma} \right) + U \sum_i n_{i\uparrow} n_{i\downarrow}
\]

(Hubbard, 1963)

ρ(ω)

Quasi-particle peak
Hubbard bands

Georges \& Kotliar 1992

\(\ast\) DMFT = Dynamical Mean Field Theory, paramagnetic solution
Dynamical mean field theory ...

... maps a lattice problem onto a single-site (Anderson impurity) problem

with a self-consistency condition (see e.g. Georges et al., Rev. Mod. Phys. 1996)
Effective dynamics ...

... for single-site problem

\[ S_{\text{eff}} = - \int_{0}^{\beta} d\tau \int_{0}^{\beta} d\tau' \sum_{\sigma} c_{\sigma}^{\dagger}(\tau) G_{0}^{-1}(\tau - \tau') c_{\sigma}(\tau') \]

\[ + \ U \int_{0}^{\beta} d\tau n_{\uparrow} n_{\downarrow} \]

with the dynamical mean field \( G_{0}^{-1}(\tau - \tau') \)
Déjà vu!

**probing magnetic interactions by means of the Kondo effect**

- magnetic impurity
- conduction electrons of host material
- correlated singlet state
- DOS
  - lower and upper Hubbard bands
  - Kondo resonance near the Fermi level (width \( \approx k_B T_K \))
DMFT (contd.)

Green’s function:

\[ G_{imp}(\tau) = -\langle \hat{T}c(\tau)c^\dagger(0) \rangle \]

Self-energy (k-independent):

\[ \Sigma_{imp}(\omega) = G_0^{-1}(\omega) - G_{imp}^{-1}(\omega) \]

DMFT assumption:

\[ \Sigma_{imp} = \Sigma_{lattice} \]
\[ G_{imp} = G_{lattice}^{local} \]

→ Self-consistency condition for \( G_0^{-1} \)
The DMFT self-consistency cycle

Anderson impurity model solver

\[ G_0^{-1} \]

\[ G_0 = (\Sigma + G^{-1})^{-1} \]

\[ G(\tau) = -\langle \hat{T}c(\tau)c^\dagger(0) \rangle \]

\[ \Sigma = G_0^{-1} - G^{-1} \]

Self-consistency condition:

\[ G(\omega) = \sum_k \frac{1}{\omega + \mu - \epsilon_k - \Sigma(\omega)} \]
Hubbard model – again

Phase diagram of half-filled model within DMFT:

First order metal-insulator transition (ending in 2nd order critical points)
Real materials ... : V$_2$O$_3$
Realistic Approach to Correlations

Combine DMFT with band structure calculations (Anisimov et al. 1997, Lichtenstein et al. 1998)

→ effective one-particle Hamiltonian within LDA
→ represent in localized basis
→ add Hubbard interaction term for correlated orbitals
→ solve within Dynamical Mean Field Theory
**LDA+DMFT**

\[
H = \sum_{\{i m \sigma\}} \left( H_{i m, i'm'}^{LDA} - H_{i m, i'm'}^{\text{double counting}} \right) a_{i m \sigma}^{+} a_{i'm' \sigma}^{\phantom{+}} \\
+ \frac{1}{2} \sum_{i m m' \sigma \text{ (correl. orb.)}} U_{i m m' \sigma}^{i} n_{i m \sigma} n_{i m' \sigma} - \sigma \\
+ \frac{1}{2} \sum_{i m \neq m' \sigma \text{ (correl. orb.)}} (U_{i m m' \sigma}^{i} - J_{i m m' \sigma}^{i}) n_{i m \sigma} n_{i m' \sigma}
\]

→ solve withing DMFT
LDA+DMFT – the full scheme

**DFT part**
from charge density \( \rho(r) \) construct
\[
\hat{V}_{KS} = \hat{V}_{\text{ext}} + \hat{V}_{H} + \hat{V}_{xc}
\]
\[
\left[-\frac{\nabla^2}{2} + \hat{V}_{KS}\right] |\psi_{k\nu}\rangle = \varepsilon_{k\nu} |\psi_{k\nu}\rangle
\]

**DMFT prelude**
build
\[
\hat{G}_{KS} = \left[i\omega_n + \mu + \frac{\nabla^2}{2} - \hat{V}_{KS}\right]^{-1}
\]

**DMFT loop**
impurity solver
\[
C_{\text{imp}}^{\text{imp}}(\tau - \tau') = -\langle \hat{T} \hat{d}_{m\sigma}(\tau) \hat{d}^{\dagger}_{m'\sigma'}(\tau') \rangle \Sigma_{\text{imp}}
\]
\[
\hat{G}_0^{-1} = \hat{G}_{\text{loc}}^{-1} + \hat{\Sigma}_{\text{imp}}
\]
\[
\hat{\Sigma}_{\text{imp}} = \hat{G}_0^{-1} - \hat{G}_{\text{imp}}^{-1}
\]
self-consistency condition: construct \( \hat{G}_{\text{loc}} \)
\[
\hat{G}_{\text{loc}} = \hat{P}_R^{(C)} \left[ \hat{G}_{KS}^{-1} - \left( \hat{\Sigma}_{\text{imp}} - \hat{\Sigma}_{\text{dc}} \right) \right]^{-1} \hat{P}_R^{(C)}
\]

**ρ update**
compute new chemical potential \( \mu \)
\[
\rho(r) = \rho_{KS}(r) + \Delta \rho(r)
\]
(Appendix A)

F. Lechermann, A. Georges, A. Poteryaev, S. B., M. Posternak, A. Yamasaki, O. K. Andersen,
Some examples

SrVO$_3$: (correlated) metal
CaVO$_3$: (correlated) metal
LaTiO$_3$: at Mott transition
YTiO$_3$: insulator

Photoemission spectra:

Fujimori et al. 1992
Sekiyama et al., 2002
LDA+DMFT: spectra of perovskites

Spectra of perovskites

SrVO$_3$ LDA+DMFT

(see also Sekiyama et al. 2003, Lechermann et al. 2006)
Vanadium dioxide: VO$_2$

Metal-insulator transition accompanied by dimerization of V atoms:
VO$_2$: Peierls or Mott?

**Physical Review B**

**Volume 11, Number 11**

1 June 1975

Metal-insulator transition in vanadium dioxide

A. Zylbersztejn

Laboratoire Central de Recherches, Thomson-CSF, 91401 Orsay, France

N. F. Mott

Cavendish Laboratory, University of Cambridge, Cambridge, England

(Received 27 November 1974)

---

**Physical Review Letters**

**Volume 35, Number 13**

20 September 1975

Electron Localization Induced by Uniaxial Stress in Pure VO$_2$

J. P. Pouget and H. Launois

Laboratoire de Physique des Solides, Université Paris XI, 91405 Orsay, France

and

J. P. D'Hanoens and P. Morenca

Laboratoire Central de Recherches, Thomson-CSF, 91401 Orsay, France

and

T. M. Rice

Bell Laboratories, Murray Hill, New Jersey 07974

(Received 7 August 1975)

---

**Physical Review Letters**

**Volume 72, Number 21**

23 May 1994

VO$_2$: Peierls or Mott-Hubbard? A View from Band Theory

Renata M. Wenezeworschi

Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, United Kingdom

Werner W. Schultz and Philip L. Allen

Department of Physics, State University of New York at Stony Brook, Stony Brook, New York 11794-3800

(Received 21 November 1993)

The electronic and structural properties of VO$_2$ across its metal-insulator transition are studied using the local-density approximation. Band theory finds a monoclinic distorted ground state in good agreement with experiment, and an almost open gap to charge excitations. Although rigid criteria for distinguishing correlations from band insulators are not available, these findings suggest that VO$_2$ may be more bandlike than correlated.

---

**Physical Review Letters**

**Volume 97, Number 21**

11 December 2006

Evidence for a Mott-Hubbard metal-insulator transition in VO$_2$

R. Eguchi,$^1$ M. Taguchi,$^1$ M. Matsunami,$^1$ K. Horiba,$^1$ K. Yamanoto,$^1$ Y. Ishida,$^1$

A. Chaimait,$^1$ Y. Takata,$^1$ M. Yabuhashi,$^2,3$ D. Miwa,$^2$ Y. Nishino,$^2$ K. Tanaka,$^2$

T. Ishikawa,$^2,3$ Y. Senda,$^2$ H. Ohishi,$^3$ Y. Murakami,$^1$ Z. Hiroi,$^4$ and S. Shin$^1,4$

$^1$Soft X-ray Spectroscopy Laboratory, RIKEN SPring-8 Center, Sayo-cho, Sayo-gun, Hyogo 679-5118, Japan

$^2$Coherent X-ray Optics Laboratory, RIKEN SPring-8 Center, Sayo-cho, Sayo-gun, Hyogo 679-5118, Japan

$^3$JASRI/SPring-8, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan

$^4$Institute for Solid State Physics, University of Tokyo, Kashiwanoha, Kashiwa, Chiba 277-8581, Japan

(Date: July 28, 2006)

---

**Physical Review Letters**

**Volume 97, Number 21**

23 May 2006

Monoclinic and Correlated Metal Phase in VO$_2$ as Evidence of the Mott Transition: Coherent Phonon Analysis

n-Tak Kim,$^1,4$ Yong-Weok Lee,$^1$ Dong-Jun Kim,$^1$ Byung-Gyu Chun,$^1$ Sun Jin Yon,$^1$ Kwang-Yong Kang,$^1$

Kang-Joon Han,$^2$ K. Lee Yoo,$^2$ and Young-Sik Lim$^1$

$^1$Advanced Condensed Matter Research Laboratory, KIST, Daejon 305-340, Republic of Korea

$^2$Department of Physics, Chonnam National University, Daejeon 305-764, Republic of Korea

$^3$Department of Applied Physics, Konkuk University, Chungju, Chungbuk 380-701, Republic of Korea

(Received 23 July 2006; published 26 December 2006)

In femtosecond pump-probe measurements, the appearance of coherent phonon oscillations at 4.5 and 60 THz indicating the metallic phase of VO$_2$ does not occur simultaneously with the ferromagnetic metal-insulator transition (MIF) near 68 °C. The monoclinic and correlated metal (MCM) phase between the MIF and the structural phase transition (SPT) is generated by a photo-assisted hole excitation, which is evidence of the Mott transition. The SPT between the MCM phase and the metallic phase occurs due to subsequent phase heating. The MCM phase can be regarded as an intermediate nonequilibrium state.
How far do we get ... 
... using Density Functional Theory for VO$_2$ ?

DFT-LDA: no incoherent weight not insulating
(from V. Eyert)
**VO$_2$: the physical picture**

Charge transfer $e^{\pi g} \rightarrow a_{1g}$ and bonding-antibonding splitting

**metallic phase:**

**insulating phase:**

Spectral functions and “band structure”

$$\det \left( \omega_{\mathbf{k}} + \mu - H^{\text{LDA}}(\mathbf{k}) - \Re \Sigma(\omega_{\mathbf{k}}) \right) = 0$$

**VO$_2$ monoclinic phase**

Quasi-particle poles (solutions of $\det[\omega + \mu - H(k) - \Sigma(\omega)] = 0$) and band structure from effective (orbital-dependent) potential

($\rightarrow$ for spectrum of insulating VO$_2$: independent particle picture not so bad!! (but LDA is!!))
Optical Conductivity of VO$_2$

[Verleu et al.] : single crystals
[Okazaki et al.] : thin films $E \perp [001]$, $T_c=290$ K
[Qazilbash et al.] : polycrystalline films, preferential $E \perp [010]$, $T_c=340$ K
Conclusions?
Not everything ...

... depends only on the average occupation!
Not everything ...

... depends only on the average occupation!
Not everything ...

... depends only on the average occupation!

\[ \langle n_{\uparrow}n_{\downarrow} \rangle \neq \langle n_{\uparrow} \rangle \langle n_{\downarrow} \rangle \]
Conclusion and perspectives

There is a world beyond the one-electron approximation!

- Mott insulators
- Correlated metals (electrons become schizophrenic ...)

How to describe these phenomena on an equal footing?

- Hubbard model: kinetic energy ↔ Coulomb cost
- Hubbard goes realistic: “LDA+DMFT” → correlated d- and f-electron materials accessible to first principles calculations!
- What’s next? → “GW+DMFT” (or on how to get rid off U – and LDA ...!)
Useful Reading (not complete)

• DMFT - Review:
  A. Georges et al., Rev. Mod. Phys., 1996

• LDA+DMFT - Reviews:
  A. Georges, condmat0403123
  S. Biermann, in Encyclop. of Mat. Science. and Technol.,
References, continued

Some recent applications of LDA+DMFT:

  J. Tomczak, F. Aryasetiawan, S.B., PRB 2008;
  S.B., A. Poteryaev, A. Georges, A. Lichtenstein, PRL 2005


- **Cerium:** Amadon, S. B., A. Georges, F. Aryasetiawan, PRL 2006

- **d$^1$ Perovskites:** E. Pavarini, S. B. et al., PRL 2004
You want to know still more?
Send us your postdoc application! Join the crew ...