Electronic structure of strongly correlated materials from a Dynamical Mean-Field Theory perspective

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Aim of this lecture...

- **Provide an introduction to DMFT =**
  a method to handle strong correlation effects, both for models and in a realistic context (the happy marriage of LDA and DMFT).

- **Review some of the key achievements of**
  this approach over the last ~ 5 years.

- **Recent experimental developments.**

- **Frontier of the field: challenges ahead.**
Modern electronic structure: density-functional theory (DFT) and the local-density approximation (LDA)

Focus on local electronic density \( n(x) \) and construct an energy functional:

\[
\Gamma[n(x)] = \Gamma_0[n(x)] + E_{\text{Hartree}}[n(x)] + \Gamma_{xc}[n(x)]
\]

\( \Gamma_0 \) can be obtained by solving an effective one-particle problem

\[
\left( -\frac{1}{2} \Delta + v_{\text{eff}}(x) \right) \phi_l(x) = \varepsilon_l \phi_l(x)
\]

\[
\sum_l |\phi_l(x)|^2 f_{FD}(\varepsilon_l) = n(x)
\]

(Kohn-Sham) ALL THIS IS EXACT: no approximation (yet)
Exchange-correlation functional
[Exact form unknown]

``Local Density Approximation” (LDA) : use the xc-energy density of the Homogeneous Electron Gas!

\[ \Gamma_{xc}[n(x)]|_{LDA} = \int dx \, n(x) \epsilon_{xc}^{HEG}[n(x)] \]

From K.Held’s website
DMFT aims at overcoming some of the limitations of DFT-LDA for correlated materials, which are twofold:

• I) Ground-state issues

When some of the electrons are rather well localized in certain orbitals (typically, d- and f-orbitals), LDA has a tendency to **OVERBIND**

i.e the participation of those electrons in the electronic cohesive energy of the solid is overestimated, resulting in a too small (sometimes MUCH too small) value of the unit-cell volume at equilibrium
Example (a dramatic one): delta-Plutonium

GGA underestimates unit-cell volume by \( \sim 30\% \)!

(cf. work of several groups)

Bulk modulus one order of magnitude too large

L(S)DA+U corrects the volume but leads to long-range magnetic order, in contradiction to experiments

Savrasov & Kotliar, PRL 2000
When the electrons are well localized, the problem can be fixed (to some extent) by treating these orbitals as core. However:
- Generally leads to underestimate of cohesive energy
- Hence, too large volumes (cf. rare-earths)

The problem becomes crucial when electrons are in an intermediate regime between being localized and being itinerant, and especially when a phase transition takes place from one behaviour to the other (as a function of e.g pressure)

Well-known examples:
- **f-states**: alpha-gamma transition of Cerium, Americium under pressure, etc…
- **d-states**: metal- Mott insulator transition
Delocalization/localization transition in rare-earths (e.g. cerium $\alpha$-$\gamma$)

![Graph showing temperature vs. pressure, with phase transitions indicated.](image-url)
II) Difficulties with excited states

The interpretation of Kohn-Sham spectra as excitations is in serious trouble in the case of correlated materials.

- The most dramatic examples are Mott insulators:

Photoemission: Fujimori et al., PRL 1992
The Mott phenomenon also has implications for applications!!

γ-Cerium sulfides

\[ \text{Na}_{3x}\text{Ce}_{2-x}\text{S}_3 \ (0 \leq x \leq 1/8) \]

Industrial pigments which can be viewed as "f-electron Mott insulators", whose colour is tuned by the position of the localised f-orbitals > material design!

Environmentally-responsible pigments (NEOLOR™, Rhodia)

Ce2O3: R. Windiks et al.
Correlated metals:
Even when ground-state is indeed metallic, KS spectra from LDA fail to reproduce:

- Narrowing of quasiparticle bands due to correlations (the Brinkman-Rice phenomenon)
- Hubbard satellites (i.e. extension to the solid of atomic-like transitions)

Sekiyama et al., PRL 2004
Main concept behind DMFT:
Replace the full solid by an effective atom hybridized, in a self-consistent manner, to an energy-dependent environment (effective medium)
Illustrate first on simple one-band lattice model:

\[
H = - \sum_{RR'\sigma} t_{RR'} f_{R\sigma}^\dagger f_{R'\sigma} + \sum_{R} H_{\text{atom}}^R \quad \text{R= lattice (atomic) site}
\]

e.g Hubbard model:

\[
H_{\text{atom}}^R = U \hat{n}_{R\uparrow} \hat{n}_{R\downarrow} + \epsilon_0 [\hat{n}_{R\uparrow} + \hat{n}_{R\downarrow}]
\]

Focus on key observable: on-site Green’s function (of the whole lattice model):

\[
G_{RR}(\omega)
\]

Introduce a **REFERENCE SYSTEM** in order to represent \( G_{RR} \): **we are familiar with this concept from DFT** in which a reference system of non-interacting electrons is introduced, with a well-chosen (Kohn-Sham) potential such as to reproduce the local density \( \rho(\vec{r}) \), the key observable of DFT.
In DMFT, the REFERENCE SYSTEM is the atom coupled to a bath of (free) electrons, with appropriate energy levels $E_p$’s and hybridization $V_p$’s to the atomic orbital, chosen such that the Green’s function of this embedded atom reproduces $G_{RR}$.

For the simple Hubbard case, this yields:

\[ H_{\text{imp}} = H_{\text{atom}}[f_{\sigma}, f_{\sigma}^\dagger] + \sum_{p\sigma} [V_p f_{\sigma}^\dagger a_{p\sigma} + h.c.] + \sum_{p\sigma} E_p a_{p\sigma}^\dagger a_{p\sigma} \]

**This is the Anderson model of a magnetic “impurity” in a solid!**

$E_p$’s and $V_p$’s can be recast into a hybridization function:

\[ \Delta(\omega) = \sum_p \frac{|V_p|^2}{\omega - E_p} \]

It plays the role of an ENERGY-DEPENDENT mean-field, (Weiss field, conjugate to GRR) which must be chosen such that:

\[ G_{\text{imp}}[\Delta(\omega)] = G_{RR}(\omega) \]
On the other hand, $G_{RR}$ is related to the self-energy of the lattice (solid) by Dyson’s equation:

$$G_{RR}(\omega) = \sum_k \frac{1}{\omega + \mu - \varepsilon_k - \Sigma(k, \omega)}$$

In which $\varepsilon_k$ is the tight-binding band (FT of the hopping $t_{RR}$).

At this point, no approximation has been made: we have just used a reference system to represent $G_{RR}$.

Let us now make the APPROXIMATION that the lattice self-energy is $k$-independent and coincides with that of the effective impurity problem:

$$\Sigma(k, \omega) \simeq \Sigma_{imp}(\omega)$$
This yields a self-consistency condition which fully determines both the local $G$ and $\Delta$:

$$G_{\text{imp}}[\Delta(\omega)] = \sum_k \frac{1}{\omega + \mu - \Sigma_{\text{imp}}[\Delta(\omega)] - \varepsilon_k}$$

**EFFECTIVE LOCAL IMPURITY PROBLEM**

Bath

$\Delta(\omega)$

**THE DMFT LOOP**

Local G.F

$G_{\text{imp}}(\omega)$

**SELF-CONSISTENCY CONDITION**

(Kotliar&A.G, PRB 1992)

In the large-d limit pioneered by Metzner&Vollhardt (PRL 1989) this construction becomes exact.
Solving the impurity+bath problem: [MANY-BODY but local]

Several numerical algorithms, or semi-analytical approximation schemes have been developed over the years to this aim, starting in the early days of the Kondo effect (Anderson impurity model) e.g: Hirsch-Fye auxiliary field QMC, Resummed perturbation theories, Numerical Renormalisation Group, Hubbard approximations (insulators), etc...

``Impurity solvers``
k-integrated spectral Function:
early DMFT results
(AG&G.Kotliar 1992,
AG&W.Krauth,
M.Rozenberg et al. 1992-94)

Quasiparticle peak
QP bandwidth $\varepsilon_F^*$
``3-peak structure’’

Tremendous experimental progress over the last ~ 15 years!
Quasiparticle excitations

Atomic-like excitations (Hubbard satellites)

Wave-like

Momentum (k-) space

Particle-like (adding/removing charges locally)

Real (R-) space

Spectral weight transfers

Are treated on equal footing within DMFT
The (happy) marriage of DFT-LDA and DMFT. Extending the DMFT construction to real solids

- Lichtenstein and Katsnelson PRB 1998
- cf. also A.G et al. Rev Mod Phys 1996

Focus here on:
- Basis-set independent formulation
- Flexible implementation using Wannier functions
  (combines w/ any kind of electronic structure method)

Identify **set of ”correlated” orbitals** for which many-body effects will be treated w/DMFT, beyond LDA:
e.g d- or f- subset denoted \( \{ \chi_{Rm} \} \)

\[ t_{2g} d_{xy} \] orbital for cubic Perovskite SrVO\(_3\)

**In practice:**
- e.g LMTOs, or LMTO heads only (**not necessarily basis functions**) !
- Or Wannier functions e.g NMTOs, or maximally localized, etc.. (cf. Pavarini et al PRL2004, Anisimov et al. PRB2005, Lechermann et al. PRB2006)
* Focus on two key quantities:

- Total charge density in the solid (all orbitals) $\rho(r)$

- Components of on-site Green’s function (and self-energy) \textit{projected on the correlated subset}:

$$G_{mm'}^{\text{loc}}(i\omega_n) = \int \int dr\,d'r' \chi_m^*(r - R)\chi_{m'}(r' - R)G(r,r';i\omega_n).$$

$$= \hat{\mathcal{P}}_{R}^{(C)} \hat{G} \hat{\mathcal{P}}_{R}^{(C)}$$

projection on correlated space
* Add to the exchange-correlation functional \( E_{\text{LDA}}^{\text{exc}}[\rho] \) on-site many-body terms of the form:

\[
\sum_{R} \left( \Phi_{\text{imp}}[G_{mm'}^{\text{RR}}] - \Phi_{\text{dc}}[G_{mm'}^{\text{RR}}] \right)
\]

calculated from an effective embedded atom defined by on-site interaction parameters \( U_{abcd} \).

(The 2nd term is a double-counting correction, cf. LDA+U)

* The \`impurity\' self-energy is upfolded to the whole solid:

\[
\Delta \Sigma (r, r'; i \omega_n) = \sum_{T_{mm'}} \chi^*_m(r - R - T) \chi_{m'}(r' - R - T) \Delta \Sigma_{mm'}(i \omega_n)
\]
Incidentally: what is really the (in)famous Hubbard U in a solid?

~ something like:

\[ U \sim \int drdr' |\chi_m(r)|^2 W_{\text{screened}}^{\text{int}}(r - r') |\chi_m(r')|^2 \]

**SCREENING** plays a key role

Naive –unscreened- value is **HUGE** (10-20 eV !) and applies at high-energy while in fact low-energy U is a few eV’s

**Hence U is in fact an energy scale-dependent notion: U(\omega)**

This is an important question: see recent work by F.Aryasetiawan et al. I.Solovyev and M.Imada, *cf also current efforts on GW+DMFT*
Realistic DMFT, in a nutshell…

**DFT part**

from charge density $\rho(r)$ construct

$$\hat{V}_{KS} = \hat{V}_{ext} + \hat{V}_{H} + \hat{V}_{xc}$$

$$\left[-\frac{\nabla^2}{2} + \hat{V}_{KS}\right] |\psi_{k\nu}\rangle = \varepsilon_{k\nu} |\psi_{k\nu}\rangle$$

**$\rho$ update**

compute new chemical potential $\mu$

$$\rho(r) = \rho_{KS}(r) + \Delta\rho(r)$$

(Appendix A)

DMFT loop

**DMFT prelude**

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

construct initial $\hat{G}_0$

**impurity solver**

$$\hat{G}^{imp}_{mm'}(\tau - \tau') = -\langle \hat{T} \hat{d}^{\dagger}_{m\sigma}(\tau) \hat{d}_{m'\sigma'}(\tau') \rangle_{s_{imp}}$$

$$\hat{G}_0^{-1} = \hat{G}_{loc}^{-1} + \hat{\Sigma}_{imp}$$

$$\hat{\Sigma}_{imp} = \hat{G}_0^{-1} - \hat{G}_{imp}^{-1}$$

self-consistency condition: construct $\hat{G}_{loc}$

$$\hat{G}_{loc} = \hat{P}_R^{(C)} \left[ \hat{G}_{KS}^{-1} - \left( \hat{\Sigma}_{imp} - \hat{\Sigma}_{dc} \right) \right]^{-1} \hat{P}_R^{(C)}$$

NOTE: No basis set has been specified
Relation to LDA+U scheme

- Starting point is similar

- Within LDA+U, the many-body problem is treated in a highly simplified manner (~Hartree):
  a STATIC self-energy is used, which is ORBITAL- and SPIN- dependent
  but ENERGY-INDEPENDENT (a potential)

>> LDA+U is a static limit of LDA+DMFT

The key phenomenon of opening a large Mott gap in a PARAMAGNETIC insulator (e.g finite-T) cannot be described with LDA+U.
Paramagnetic Mott insulators, correlated metals need a frequency-dependent self-energy (DMFT)
Implementation in practice: introducing a basis set

\[ B_{k,\alpha} ; \quad \alpha = R, l, m, \text{etc...} \]

Can be any preferred basis: Bloch, LMTO, mixed (FLAPW)

\[
\hat{H}_{KS}(k) = \sum_{\alpha\alpha'} |B_{k\alpha}\rangle \langle B_{k\alpha'}| \left( \sum_{\nu} \epsilon_{k\nu} |B_{k\alpha}\rangle \langle \psi_{k\nu}| \langle \psi_{k\nu}| B_{k\alpha'}\rangle \right)
\]

\[
\Delta \Sigma_{\alpha\alpha'}(k, i\omega_n) = \sum_{mm'} \langle B_{k\alpha}| \chi^k_m \rangle \langle \chi^k_m| B_{k\alpha'}\rangle \times \left[ \Sigma^{\text{imp}}_{mm'}(i\omega_n) - \Sigma^{\text{dc}}_{mm'} \right]
\]

DMFT self-consistency condition reads:

\[
G^{\text{imp}}_{mm'}(i\omega_n) = \sum_k \sum_{\alpha\alpha'} \langle \chi^k_m| B_{k\alpha}\rangle \langle B_{k\alpha'}| \chi^k_{m'}\rangle \times \left( [i\omega_n + \mu - H_{KS}(k) - \Delta \Sigma (k, i\omega_n)]^{-1} \right)_{\alpha\alpha'}
\]

*Inversion of matrix of size \( N_B \times N_B \) at each \( k \)-point and each frequency!"
The Wannier route

- Perform Wannier construction for some set of bands $W$ (aka some energy window)

$$w_{\alpha}(r-T) = \frac{V}{(2\pi)^3} \int_{BZ} dk e^{-ik\cdot T} \sum_{\nu \in W} U^{(k)}_{\alpha \nu} \psi_{\nu}(r),$$

- Select a subset $C$ of $W$ as defining the correlated orbitals:

$$G_{mm',(i\omega_n)}^{imp} = \sum_{k} \{[(i\omega_n + \mu)I - H^{(W)}_{KS}(k) - \Delta \Sigma^{(C)}(i\omega_n)]^{-1}\}_{mm'},$$

$W=C$ most economical choice when possible
(e.g isolated set of `correlated’ bands), but perhaps
more localised $C$-set preferable ??

Easily implemented in any electronic structure method (e.g localized LMTO/NMTO or FLAPW, pseudopotential, …)
Example: SrVO$_3$ Wannier functions

- t$_2g$ only

- O$_2p$+Vt$_2g$ and eg
Examples of applications to the electronic structure of correlated materials
(far from exhaustive selection among the numerous works of the last few years, for illustrative purposes)
Photoemission spectra of correlated metals and (paramagnetic) Mott insulators

E. Pavarini et al., PRL 2004

cf. also Sekiyama et al. (Ca/SrVO3) PRL 2004
3-peak structure clearly revealed in recent high-photon energy PES experiments w/relative intensities between QP and Hubbard satellites in good agreement w/DMFT

Mo et al, V2O3
(DMFT calculations by Keller, Held et al.
cf. also Poteryaev et al.)
Correlation-induced inter-orbital charge transfers and modifications of the Fermi surface wrt/LDA: the example of BaVS3
Lechermann, Biermann and A.G, PRL 2005
Total energy: the LDA+DMFT free-energy functional

\[
\Gamma [\rho, G_{mm'}] = \\
= T [\rho, G_{mm'}] + E_H [\rho] + E_{xc} [\rho, G_{mm'}] \\
- \text{tr } \ln [i\omega_n + \mu + \frac{1}{2} \nabla^2 - \nu_{KS}(r) - \chi^* \Delta \Sigma \chi] - \int dr \left( \nu_{KS} - \nu_c \right) \rho (r) - \text{tr } [G \Delta \Sigma] \\
+ \frac{1}{2} \int dr \int dr' \rho (r) U (r - r') \rho (r') + E_{xc} [\rho (r)] + \Sigma_R \left( \Phi_{imp}[G_{ab}^{RR}] - \Phi_{DC}[G_{ab}^{RR}] \right)
\]

In these expressions, 
\(V_{KS}\) is the Kohn-Sham potential 
and \(\Delta \Sigma\) is the (dc-corrected) local self-energy in ``correlated'' subset

Finally, total energy is calculated as:

\[
E_{LDA+DMFT} = E_{DFT} - \Sigma'_{\lambda} \varepsilon_{\lambda}^{KS} + \langle H_{KS} \rangle + \langle H_{U} \rangle - E_{DC} \\
= E_{DFT} + \Sigma_{k,LL'} h_{LL'}^{KS} \left[ \langle c_{Lk}^{\dagger} c_{L'k} \rangle_{DMFT} - \langle c_{Lk}^{\dagger} c_{L'k} \rangle_{KS} \right] + \langle H_{U} \rangle - E_{DC}
\]
Update of charge density

From DMFT

KS system is updated and modified by many-body effects...

Construct $G_{KS}$ and back to DMFT

KS density matrix:

$$
\rho(r) = \sum_{k\nu\nu'} D^{(k)}_{\nu'\nu}(r) \Delta N^{(k)}_{\nu\nu'} + \sum_{\nu} \Theta(\mu - \varepsilon_{k\nu}) D^{(k)}_{\nu\nu}(r).
$$

Many-body correction:

$$
\Delta N^{(k)}_{\alpha\alpha'} = \frac{1}{\beta} \sum_{nmn'm'} G^{KS}_{\alpha\alpha}(k,i\omega_n) \Delta \Sigma_{nmn'}(i\omega_n) G_{m'n'}(k,i\omega_n).
$$
Entropic stabilisation of gamma phase

Consistent with LDA+DMFT calculations of total energy
The $\alpha$-$\gamma$ transition of cerium is entropy-driven...

Entropy and energy
Across transition from
Experimental equation of state

PES experiments
(Wuilloud et al, Weliczka et al.)

Amadon et al. PRL 2006

Black: $\alpha$-cerium
(lower volume Phase)

Red: $\gamma$-cerium
(higher volume Phase)

Kondo resonance

$\Delta f > f^0$
Cerium: the $\alpha$-$\gamma$ transition, photoemission and optical spectra, total energy

Kondo resonance in the $\alpha$-phase, not in $\gamma$

(f-d.o.s at $T\sim600K$)

Held, McMahan & Scalettar, PRL2001, PRB2003

Haule et al, PRL 2005

Expts: van der Eeb, PRL 2001

FIG. 1 (color online). The top panel shows the calculated optical conductivity for both $\alpha$ and $\gamma$ phase of cerium. The temperature used in calculation is 580 K while the volume of $\alpha$ and $\gamma$ phase is 28.06 Å$^3$ and 34.37 Å$^3$, respectively. The bottom panel shows experimental results measured by the group of van der Marel [2]. The measurements for $\alpha$ phase were done at 5 K and for $\gamma$ phase at 400 K.
Total energy of fcc-Plutonium (δ-phase)
S. Savrasov, G. Kotliar and E. Abrahams Nature 410 (2001) 793

LDA+DMFT
total energy
vs.
unit-cell volume

Double-well
Structure:
Alpha-like phase?

Also: Kondo-like quasiparticle peak at Fermi level,
in agreement with photoemission (Arko).
Phonons in fcc $\delta$-Pu PREDICTED from DMFT

Phonons From Linear-response In DMFT: Savrasov & Kotliar, PRL 2003

$[MnO,NiO]$ [Squares]

<table>
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<th></th>
<th>$C_{11}$ (GPa)</th>
<th>$C_{44}$ (GPa)</th>
<th>$C_{12}$ (GPa)</th>
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<td>4.78</td>
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</table>

(Dai, Savrasov, Kotliar, Ledbetter, Migliori, Abrahams, Science, 9 May 2003)
(experiments from Wong et.al, Science, 22 August 2003) [Open dots]
CONCLUSION / OVERVIEW

- DMFT is an energy-dependent mean-field approach aimed at treating strong correlation effects

- The frequency-dependent on-site self-energy is calculated through an effective atomic problem embedded in a self-consistent medium

- Quasiparticle excitations (and bandwidth narrowing) as well as Hubbard satellites are treated on equal footing

- The method has been happily blended with DFT-LDA, and applied to long-standing problems in electronic structure calculations of strongly correlated materials
Frontiers (I)

- Fully first-principle scheme: ab-initio calculation of (frequency-dependent) U, GW-functionals
- Technical challenge: ever-more efficient "impurity solvers" (recent progress from CT-QMC)
- Optimal choice of correlated orbitals
- Implementations within a wider range of electronic structure methods (at present: LMTO/NMTO, FLAPW, mixed-basis pseudopotential)
Frontiers (II) …
Beyond a purely-local self-energy: restoring some momentum-dependence

>> CLUSTER extensions of DMFT: C-DMFT

This is needed both in the context of MODELS of strongly-correlated electrons, to explain some of the key aspects of the cuprates (differentiation of the Fermi surface into hot and cold regions, cf. work by Sherbrooke and Rutgers/Saclay/Rome group) AND in a realistic electronic-structure context, for some materials e.g w/ Peierls insulator character (cf. recent work on Ti2O3 and VO2, Poteryaev, Biermann et al.)
FIG. 4: $A(k, \omega = 0^\dagger)$ in the first quadrant of the Brillouin zone. From the top: in the first row $t' = -0.3t$, $n = 0.73, 0.89, 0.96$, color scale $x = 0.28, 0.22, 0.12$; in the second $t' = +0.3t$, $n = 0.70, 0.90, 0.95$, color scale $x = 0.82, 0.34, 0.27$; in the lowest row $t' = +0.9t$, $n = 0.69, 0.92, 0.96$, color scale $x = 0.90, 0.32, 0.22$. The white dashed line is the FS given by $t_{\text{eff}}(k) = \mu$. 

Senechal, A.M Tremblay, PRL 2004

Civelli et al., PRL 2005
Cluster-DMFT
Some general references…

- Lecture notes (A.G) cond-mat/0403123

  *Strongly Correlated Electron Materials: Dynamical Mean-Field Theory and Electronic Structure*


- **Overview article:** G.Kotliar and D.Vollhardt, Physics Today, March 2004

http://www.cpht.polytechnique.fr/cpht/correl/mainpage.htm
A collective enterprise ...

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And also…

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Towards (truly) first-principles DMFT

Or…
``A life without (ad-hoc) U''
(and perhaps also… without LDA ?!)

Biermann, Aryasetiawan, A.G PRL 2003
Kotliar and Savrasov
- Give a proper meaning to “U” and bypass the tricky question of “’improving LDA’”

>> Deal with first-principle screened interaction (W)

- Excited states >> use a Green’s function approach

- Calculate total energy

>> Use a FUNCTIONAL as a guiding principle
What is really the (in)famous Hubbard U in a solid?

~ something like:

\[
U \sim \int dr \, dr' |W_i(r)|^2 V_{\text{screened}}^{\text{int}}(r - r') |W_i(r')|^2
\]

SCREENING plays a key role

Naive –unscreened- value is HUGE (10-20 eV !)
and applies at high-energy
while in fact low-energy U is a few eV’s

Hence U is in fact an energy scale-dependent notion: \(U(\omega)\)

This is an important question: see recent work by F.Aryasetiawan et al.
I.Solovyev and M.Imada (cf. F.Aryasetiawan’s talk)
Define screened interaction:

\[ H = -\sum_i \frac{1}{2} \nabla_i^2 + \sum_i v(r_i) + \frac{1}{2} \sum_{i \neq j} u(r_i - r_j) \]

Density-density correlation function:

\[ \chi(r, r'; \tau - \tau') = \langle T (\hat{n}(r, \tau) - \rho(r)) (\hat{n}(r', \tau') - \rho(r')) \rangle \]

Screened interaction:

\[ W(r, r', i\omega) = u(r - r') - \int dr_1 \, dr_2 \, u(r - r_1) \chi(r_1 - r_2; i\omega) u(r_2 - r') \]

Exact polarizability:

\[ P \equiv -\chi \cdot [1 - u \cdot \chi]^{-1} \]
Exact functional of $G$ and $W$:
(Almbladh, von Barth and van Leeuwen; Chitra and Kotliar)

$$
\Gamma(G, W) = Tr \ln G - Tr[(G^{-1}_H - G^{-1})G] - \frac{1}{2} Tr \ln W + \\
+ \frac{1}{2} Tr[(u^{-1} - W^{-1})W] + \Psi[G, W]
$$

Hartree's G.F: LDA is NOT the starting point

$$
G^{-1}_H = i\omega_n + \mu + \nabla^2/2 - \nu_H
$$

$$
\frac{\delta \Gamma}{\delta G} = \frac{\delta \Gamma}{\delta W} = 0
$$

yields:

$$
G^{-1} = G^{-1}_H - \Sigma^{xc}, \quad \Sigma^{xc} = \frac{\delta \Psi}{\delta G}; \quad W^{-1} = u^{-1} - P, \quad P = -2 \frac{\delta \Psi}{\delta W}
$$
Approximations to the Psi-functional:

e.g. the GW approximation:

\[ \Psi_{GW_A} = -\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \int d\tau d\tau' G(\mathbf{r}, \mathbf{r}', \tau - \tau') W(\mathbf{r}, \mathbf{r}', \tau - \tau') G(\mathbf{r}', \mathbf{r}, \tau' - \tau) \]

Use a localised basis set (LMTO, NMTO, other Wannier’s) and consider matrix elements:

\[ G_{ab}(i\omega) = \langle \chi_a \mathbf{R} | G | \chi_b \mathbf{R} \rangle \]

\[ W_{a_1 a_2 a_3 a_4}(i\omega) = \langle \chi_{a_1 \mathbf{R}} \chi_{a_2 \mathbf{R}} | W | \chi_{a_3 \mathbf{R}} \chi_{a_4 \mathbf{R}} \rangle \]
Improve on the GW approximation (which includes the dominant screening effects) by doing a better treatment of local (on-atom) terms, perhaps for a selected set of orbitals only (e.g. d- or f-):

\[
\Psi_{GW+DMFT}^{RR'}[G_{L_1'L_1}, W_{L_2'L_2}] = \Psi_{GW}^{non-loc} + [\Psi_{GW}^{loc} - \Delta\Psi] + \sum_R \Psi_{imp}^{RR'}[G_{ab}, W_{abcd}]
\]

In this expression, \(\Psi_{imp}\) is the \(\Psi\)-functional corresponding to the local effective model (142), while \(\Delta\Psi\) removes the components from \(\Psi_{GW}^{loc}\) which will be taken into account in \(\Psi_{imp}\), namely:

\[
\Delta\Psi = -\frac{1}{2} \sum_R \int d\tau \sum_{abcd} G_{ab}^R(\tau) W_{abcd}^{RR}(\tau) G_{DC}^{RR}(-\tau)
\]

If all valence orbitals are included in the DMFT treatment, the second term in the r.h.s of (147) is absent altogether. If only a correlated subset is treated with DMFT, \(\Delta\Psi\) can be thought of as a term preventing double-counting of interactions in the correlated subset.

NO AD-HOC double-counting!
What is the local part of the functional?

Constructed as that of an effective atom embedded (self-consistently) in the solid (w/ retardation):

\[
S = \int d\tau d\tau' \left[ -\sum c_a^+(\tau) \mathcal{G}_{ab}^{-1}(\tau - \tau') c_b(\tau') + \frac{1}{2} \sum :c_{a_1}^+(\tau)c_{a_2}(\tau) : \mathcal{U}_{a_1a_2a_3a_4}(\tau - \tau') :c_{a_3}^+(\tau')c_{a_4}(\tau') : \right] 
\]

Can be viewed as a way to REPRESENT the (exact) local G and local W.
Self-consistency:

\[ G_{loc}(i\omega_n) = \sum_k [G_H^{-1}(k, i\omega_n) - \Sigma(k, i\omega_n)]^{-1} \]

\[ W_{loc}(i\nu_n) = \sum_q [V_q^{-1} - P(q, i\nu_n)]^{-1} \]

With:

\[ \Sigma^{LL'}(k, i\omega_n) = \Sigma_{GW}^{LL'}(k, i\omega_n) - \sum_k \Sigma_{GW}^{LL'}(k, i\omega_n) + \Sigma_{imp}^{LL'}(i\omega_n) \]

\[ P^\alpha\beta(k, i\omega_n) = P_{GW}^\alpha\beta(k, i\omega_n) - \sum_k P_{GW}^\alpha\beta(k, i\omega_n) + P_{imp}^\alpha\beta(i\omega_n) \]
In this approach, $U_{abcd}(\omega)$ is determined self-consistently, on the same footing than the effective hybridization function

LDA+DMFT can be viewed as a simplified form of this approach, in which a static (frequency-independent) $U$ is used, and chosen empirically or from independent methods (constrained LDA, GW, etc…)

Some work on (highly) simplified (static) implementations of ``GW+DMFT’’ approach for Ni (Biermann et al.).

Much more work to be developed along these lines, starting w/ evaluations of U’s (various groups currently working on this)