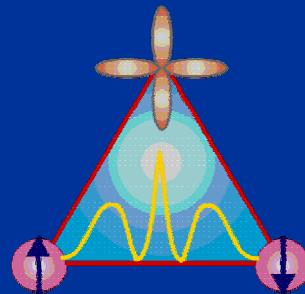


Electronic structure of strongly correlated materials from a Dynamical Mean-Field Theory perspective



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IHP Paris, 2006

<http://www.cpht.polytechnique.fr/cpht/correl/mainpage.htm>

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)

$$H = -\frac{\hbar^2}{2m} \sum_i \Delta_i + \sum_i v_{cryst}(i) + e^2 \sum_{i < j} \frac{1}{|x_i - x_j|}$$

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


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

Γ_0 can be obtained by solving an effective one-particle problem


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

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


(Kohn-Sham) **ALL THIS IS EXACT**: no approximation (yet)

 The Nobel Prize in Chemistry 1998

"for his development of the density-functional theory" "for his development of computational methods in quantum chemistry"



Walter Kohn
🏆 1/2 of the prize
 USA
 University of California
 Santa Barbara, CA, USA
 b. 1923
 (in Vienna, Austria)



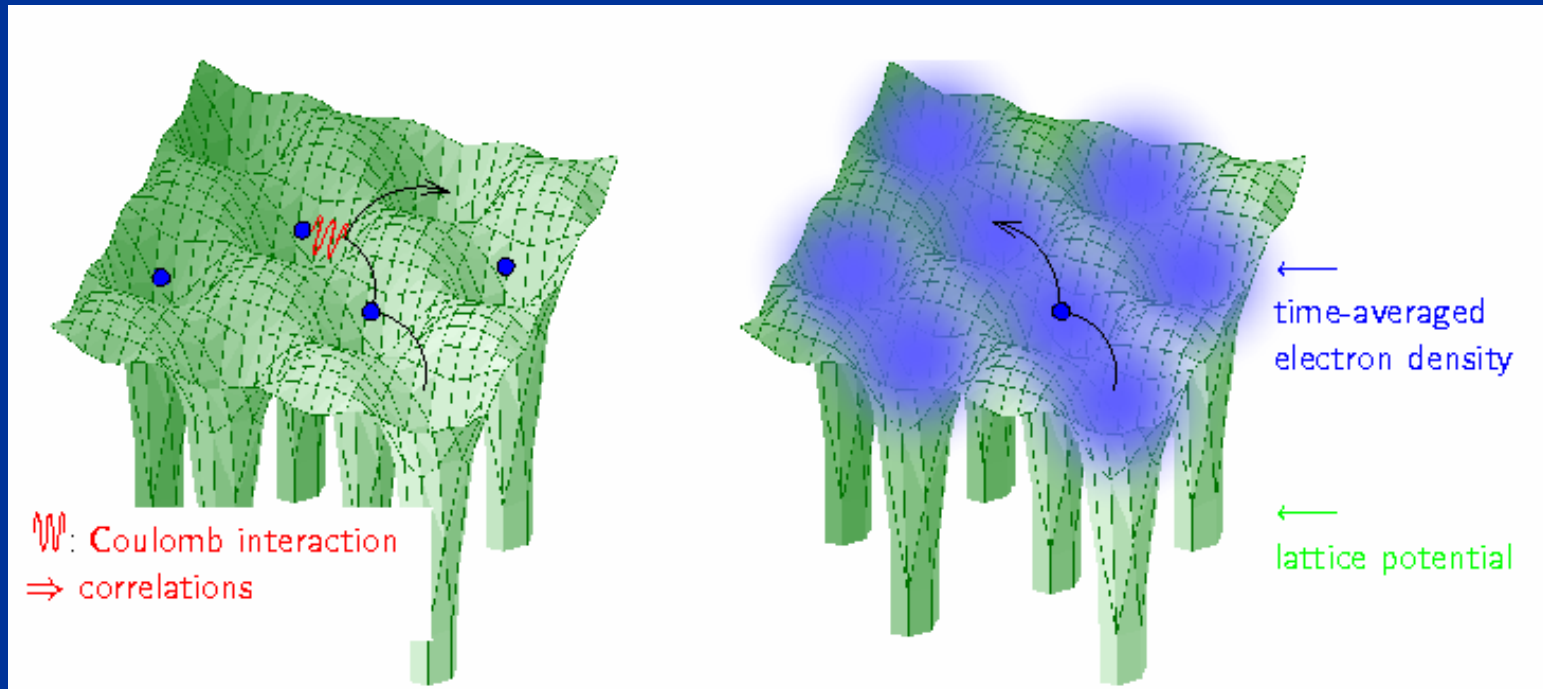
John A. Pople
🏆 1/2 of the prize
 United Kingdom
 Northwestern University
 Evanston, IL, USA
 b. 1925
 d. 2004

$\Gamma_{xc}[n(x)]$

Exchange-correlation functional [Exact form unknown]

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

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



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

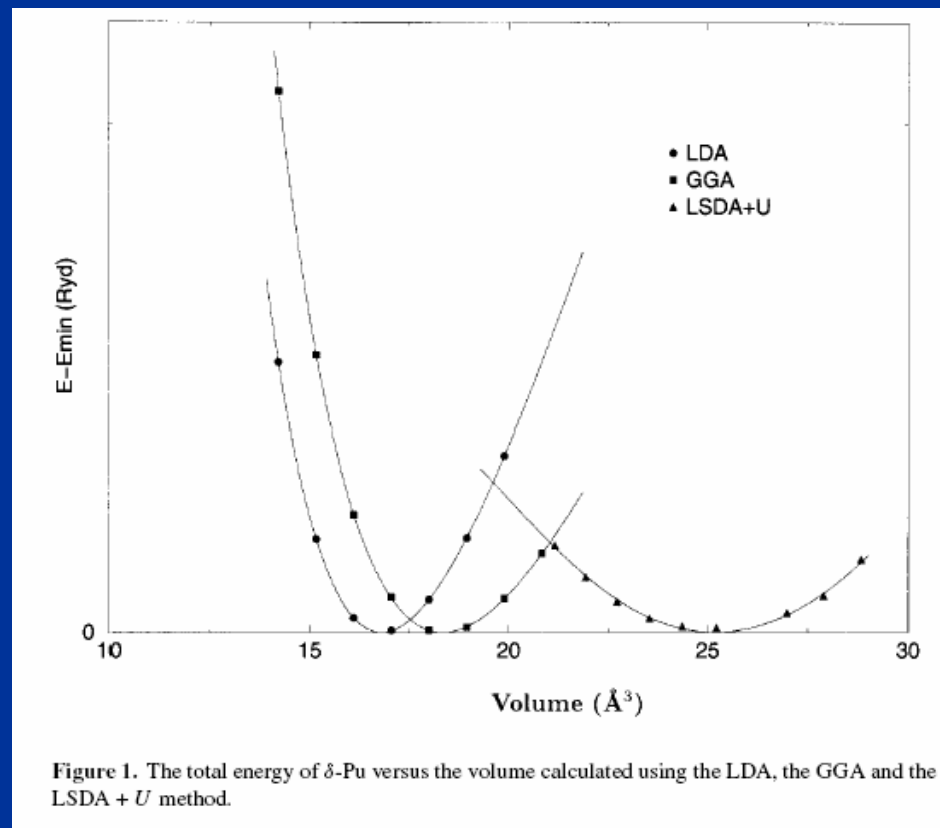
Example (a dramatic one): delta-Plutonium

**GGA underestimates
unit-cell volume
by ~ 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**



Bouchet et al. J.Phys.C 2000

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)

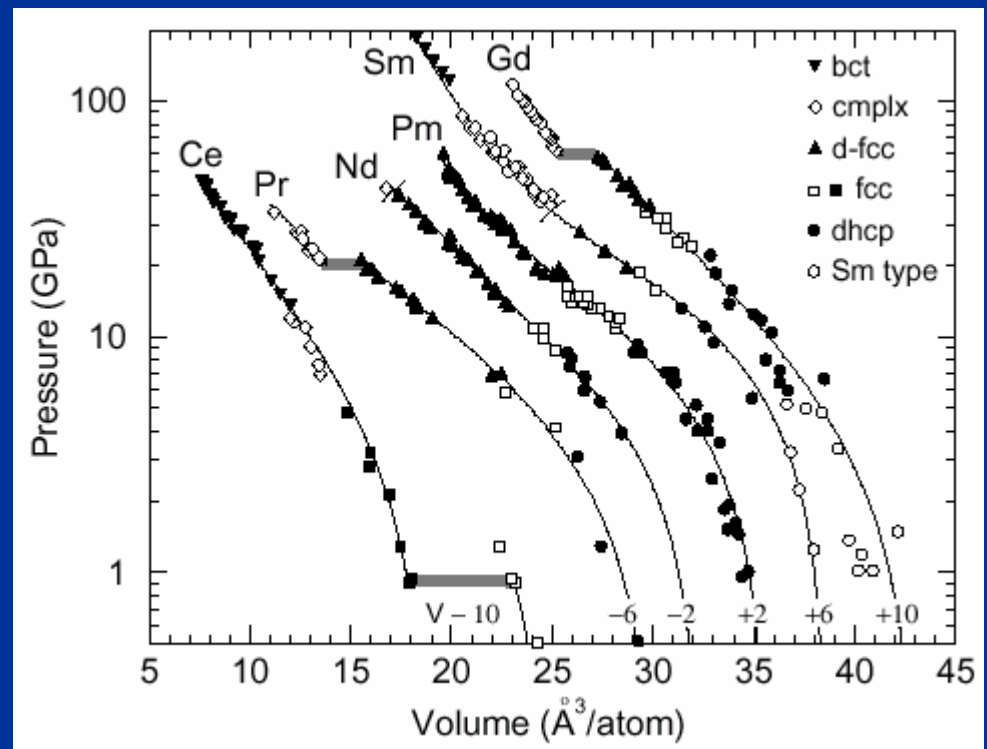
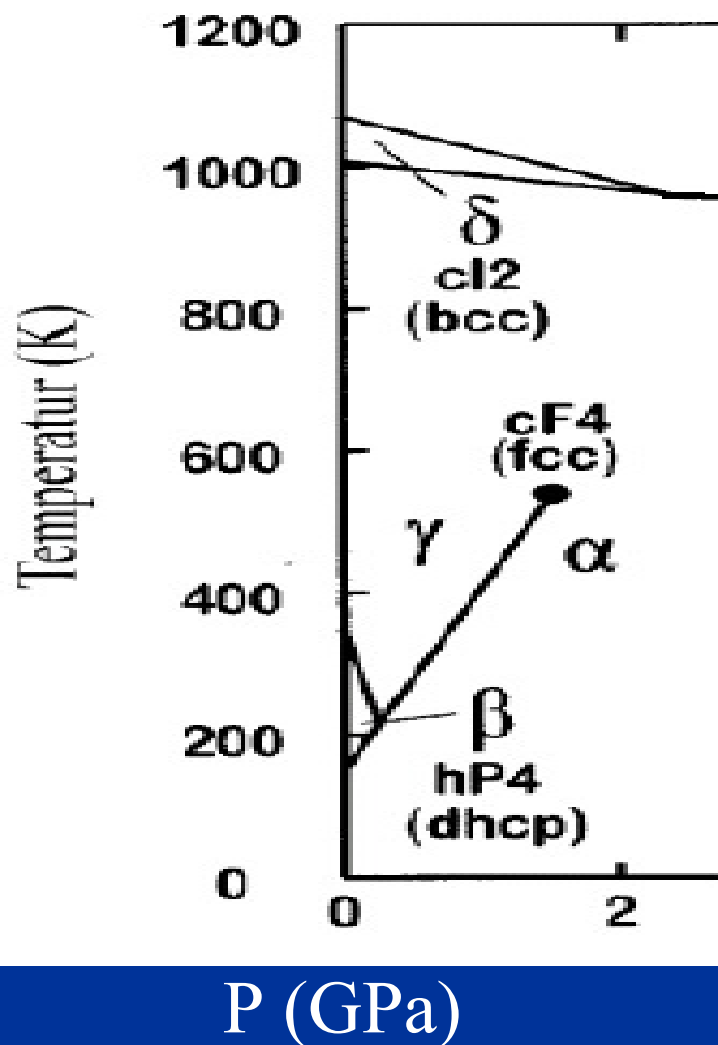
The problem becomes crucial when electrons are in **an intermediate regime between being localized and being itinerant**, and especially when a phase transition takes place from one behaviour to the other (as a function of e.g pressure)

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 α - γ)



II) Difficulties with excited states

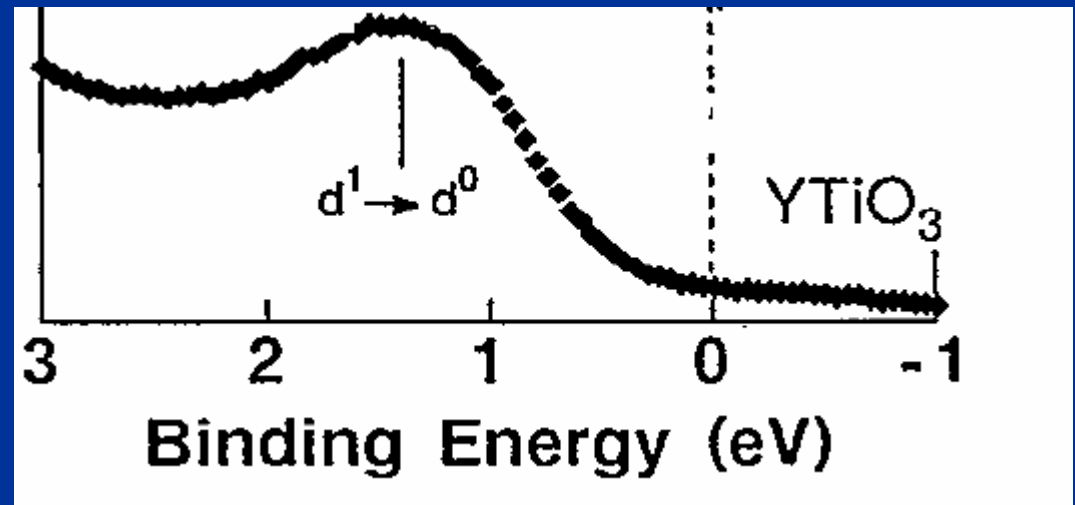
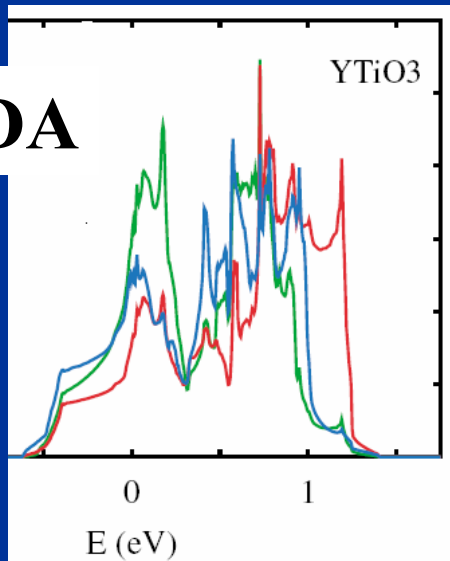
The interpretation of Kohn-Sham spectra as excitations is in serious trouble in the case of correlated materials

- **The most dramatic examples are Mott insulators:**



Hubbard satellite

LDA



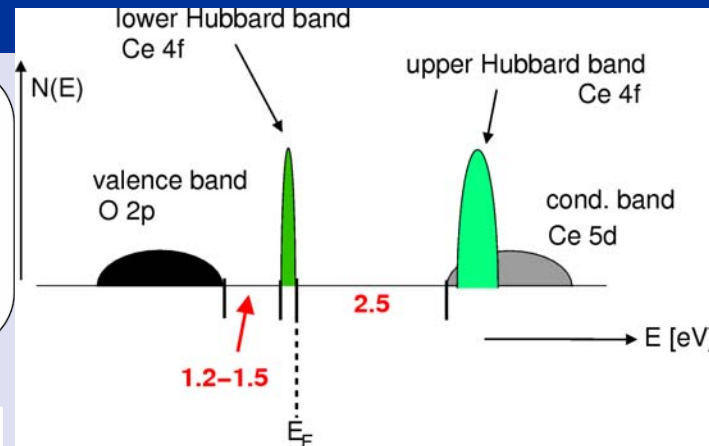
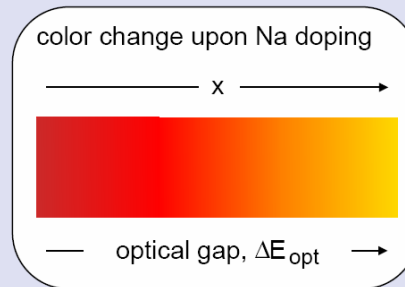
Photoemission: Fujimori et al., PRL 1992

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)



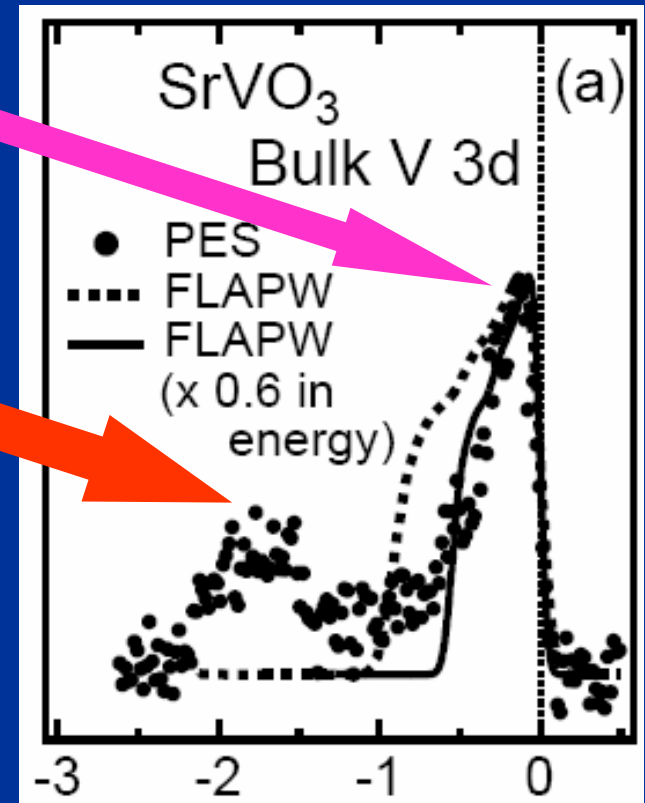
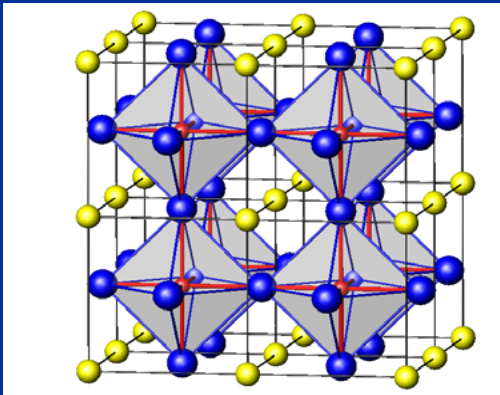
http://www.rhodia-rare-earths.com/site_ec_us/other_markets/index_neolor.htm

Ce2O3: R. Windiks et al.

Correlated metals:

Even when ground-state is indeed metallic,
KS spectra from LDA fail to reproduce:

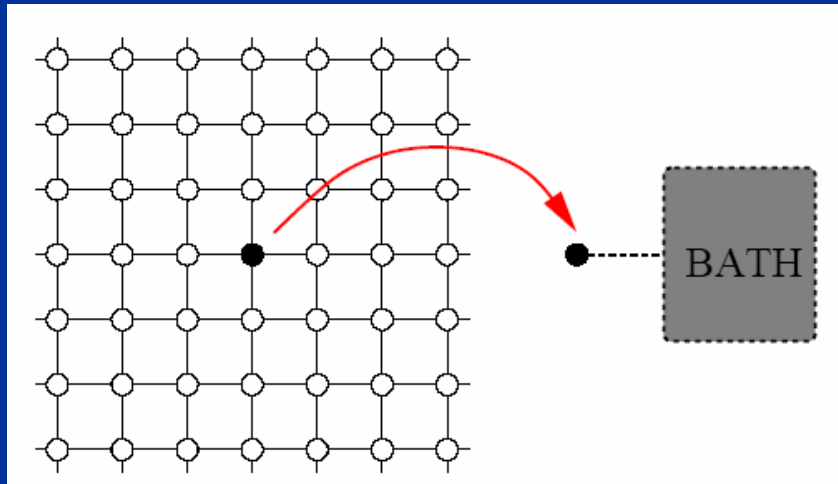
- **Narrowing of quasiparticle bands** due to correlations (the Brinkman-Rice phenomenon)
- **Hubbard satellites** (i.e. extension to the solid of atomic-like transitions)



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:

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

e.g Hubbard model: $H_{\text{atom}}^{\mathbf{R}} = U \hat{n}_{\mathbf{R}\uparrow}^f \hat{n}_{\mathbf{R}\downarrow}^f + \epsilon_0 [\hat{n}_{\mathbf{R}\uparrow}^f + \hat{n}_{\mathbf{R}\downarrow}^f]$

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 G_{RR}) 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:

$$G_{RR}(\omega) = \sum_{\mathbf{k}} \frac{1}{\omega + \mu - \varepsilon_{\mathbf{k}} - \Sigma(\mathbf{k}, \omega)}$$

In which $\varepsilon_{\mathbf{k}}$ 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}

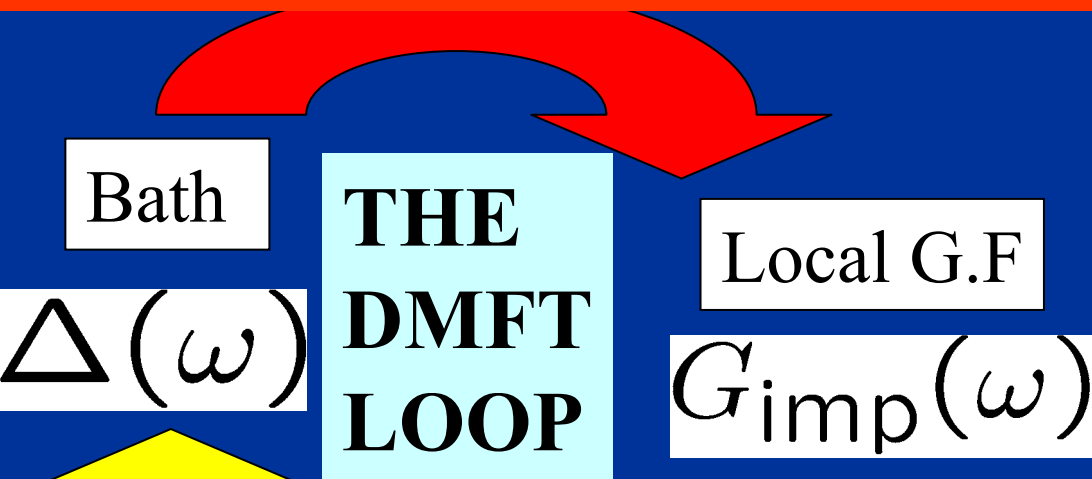
Let us now make the **APPROXIMATION** that the lattice self-energy is **k-independent** and coincides with that of the effective impurity problem:

$$\Sigma(\mathbf{k}, \omega) \simeq \Sigma_{\text{imp}}(\omega)$$

This yields a self-consistency condition which fully determines both the local G and Δ :

$$G_{\text{imp}}[\Delta(\omega)] = \sum_{\mathbf{k}} \frac{1}{\omega + \mu - \Sigma_{\text{imp}}[\Delta(\omega)] - \epsilon_{\mathbf{k}}}$$

EFFECTIVE LOCAL IMPURITY PROBLEM



(Kotliar&A.G, PRB 1992)

In the large-d limit pioneered by Metzner&Vollhardt (PRL 1989) this construction becomes exact

SELF-CONSISTENCY CONDITION

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:

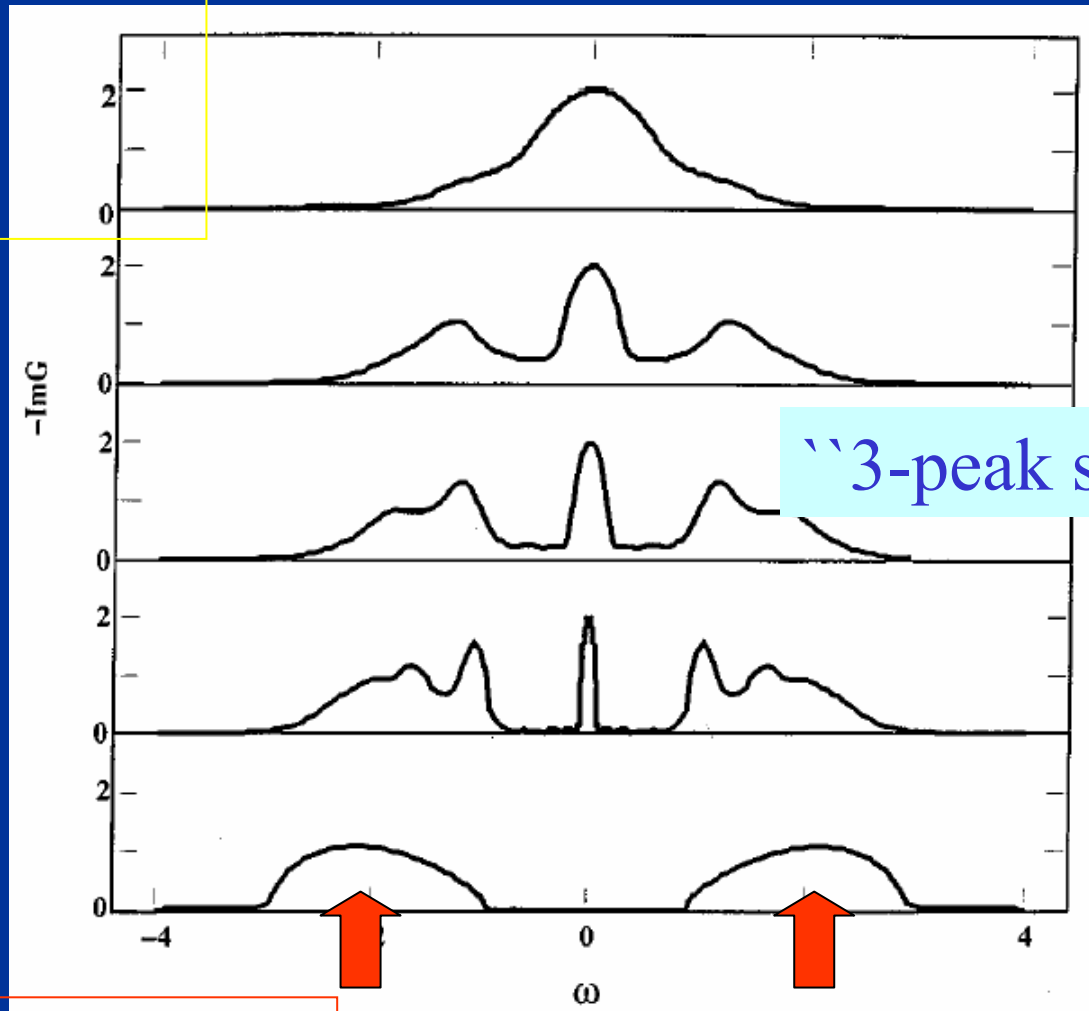
early DMFT results

(AG&G.Kotliar 1992,
AG&W.Krauth,
M.Rozenberg et al.
1992-94)

Increasing U

Quasiparticle peak

QP bandwidth \mathcal{E}_F^*



“3-peak structure”

Hubbard bands

> GAP <

A.Fujimori et al.

**Low-energy quasiparticles
and
high-energy Hubbard bands
coexist**
in a strongly-correlated metal:
early evidence from
photoemission (1992).

Tremendous
experimental progress
over the last ~ 15 years !

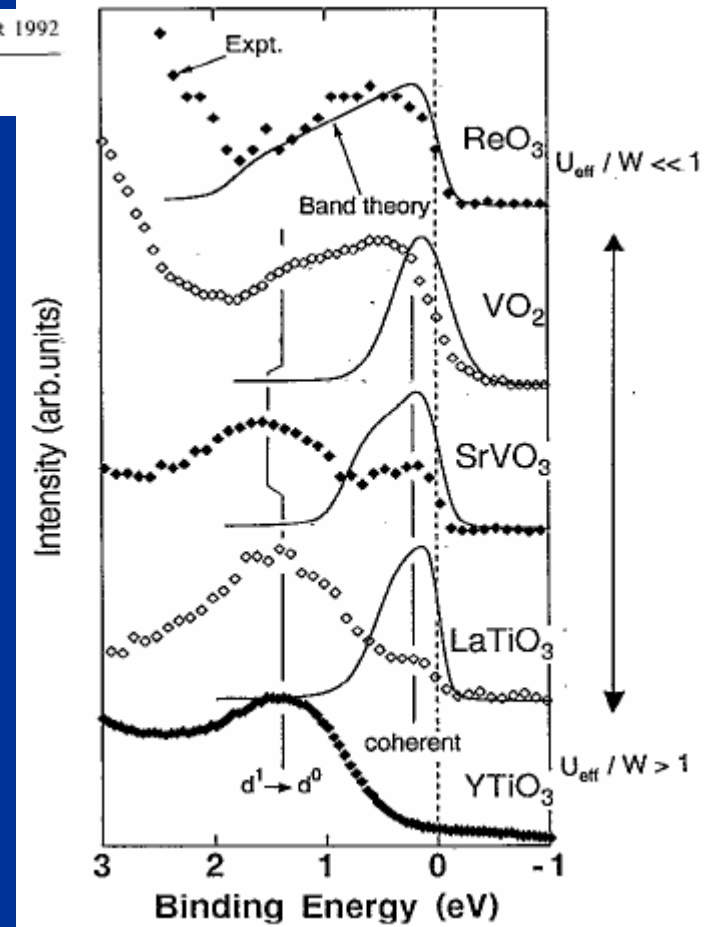


FIG. 2. Photoemission spectra (diamond symbols) of YTiO_3 ($h\nu=21.2$ eV), LaTiO_3 ($h\nu=48$ eV), and SrVO_3 ($h\nu=55$ eV) in the d -band region. The spectra of VO_2 in the metallic phase ($h\nu=60$ eV) and ReO_3 ($h\nu=40.8$ eV) are taken from Refs. [9] and [14], respectively. They are compared with the DOS given by band-structure calculations [13,15] (solid curves). The instrumental resolution is ~ 0.5 eV for VO_2 and ~ 0.2 – 0.3 eV otherwise.

Quasiparticle excitations

Wave-like

Momentum (k-) space

Atomic-like excitations (Hubbard satellites)

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

- Anisimov, Poteryaev, Korotin, Anokhin and Kotliar J.Phys C 1997
- Lichtenstein and Katsnelson PRB 1998
- cf. also A.G et al. Rev Mod Phys 1996

Focus here on:

-Basis-set independent formulation

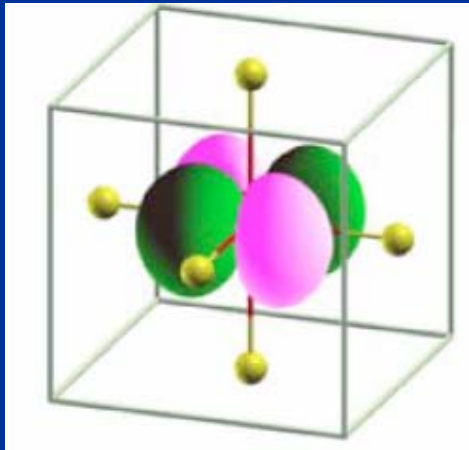
- Flexible implementation using Wannier functions

(combines w/ any kind of electronic structure method)

cf: F.Lechermann, AG, S.Biermann, A.Poteryaev,
M.Posternak, O.K. Andersen, A. Yamazaki PRB 74, 125120 (2006)

Identify set of `correlated` orbitals for which many-body effects will be treated w/DMFT, beyond LDA:

e.g d- or f- subset denoted $\{|\chi_{R_m}\rangle\}$



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) $\rho(\mathbf{r})$
- Components of on-site Green's function (and self-energy) projected on the correlated subset:

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

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

projection on correlated space

* Add to the exchange-correlation functional $E_{\text{LDA}}^{\text{xc}}[\rho]$ on-site many-body terms of the form:

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

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:

$$\begin{aligned} \Delta\Sigma(\mathbf{r}, \mathbf{r}'; i\omega_n) \\ \equiv \sum_{\mathbf{T}mm'} \chi_m^*(\mathbf{r} - \mathbf{R} - \mathbf{T}) \chi_{m'}(\mathbf{r}' - \mathbf{R} - \mathbf{T}) \Delta\Sigma_{mm'}(i\omega_n) \end{aligned}$$

Incidentally: what is really the (in)famous Hubbard U in a solid ?

~ something like :

$$U \sim \int d\mathbf{r} d\mathbf{r}' |\chi_m(\mathbf{r})|^2 W_{\text{screened}}^{\text{int}}(\mathbf{r} - \mathbf{r}') |\chi_m(\mathbf{r}')|^2$$

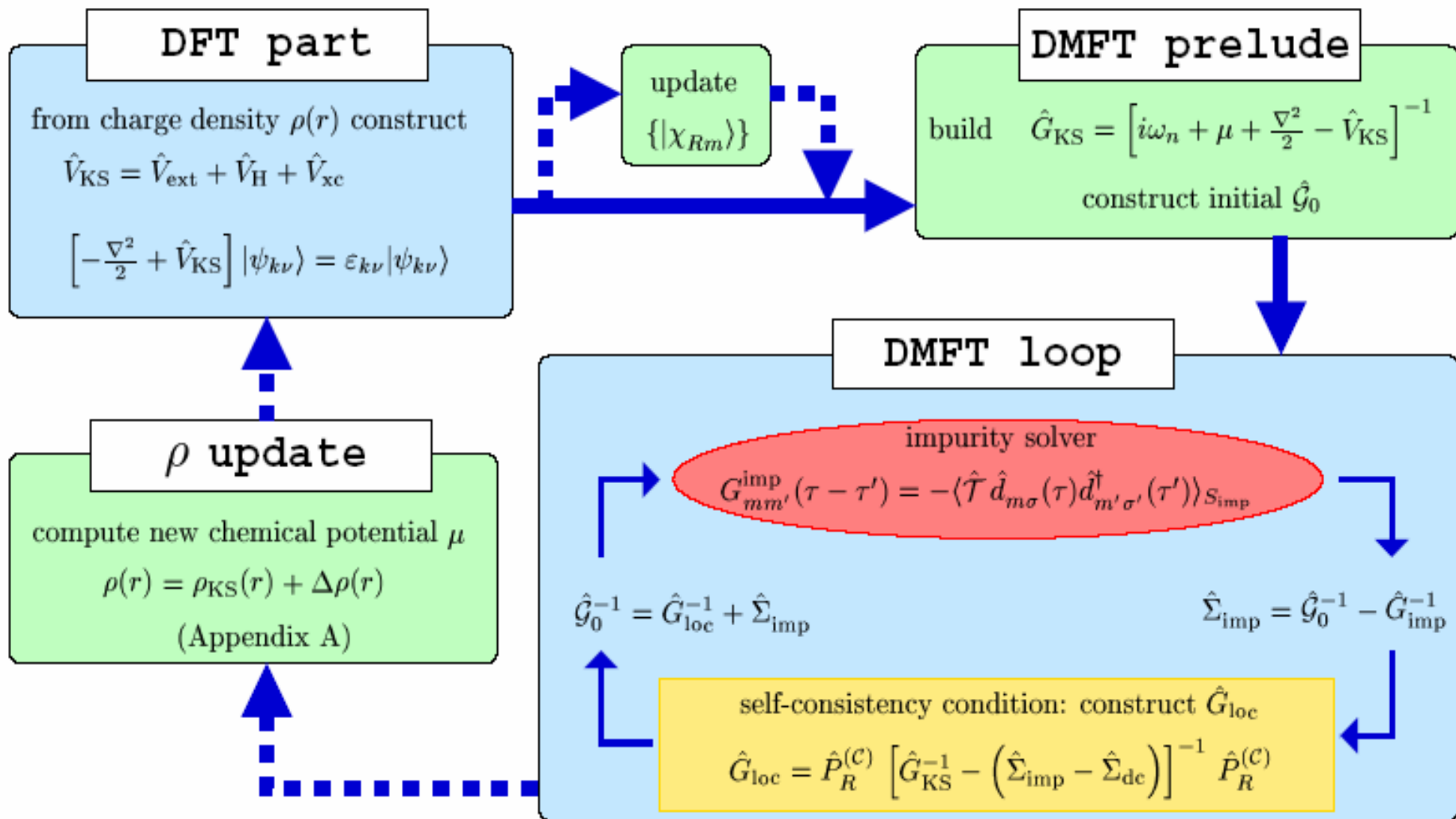
SCREENING plays a key role

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...



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 (\sim 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

$$B_{\mathbf{k},\alpha} \ ; \ \alpha = \mathbf{R}, l, m, \text{ etc...}$$

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

$$\hat{H}_{\text{KS}}(\mathbf{k}) = \sum_{\alpha\alpha'} |B_{\mathbf{k}\alpha}\rangle \langle B_{\mathbf{k}\alpha'}| \left(\sum_{\nu} \varepsilon_{\mathbf{k}\nu} \langle B_{\mathbf{k}\alpha} | \psi_{\mathbf{k}\nu} \rangle \langle \psi_{\mathbf{k}\nu} | B_{\mathbf{k}\alpha'} \rangle \right)$$

$$\Delta\Sigma_{\alpha\alpha'}(\mathbf{k}, i\omega_n) = \sum_{mm'} \langle B_{\mathbf{k}\alpha} | \chi_m^{\mathbf{k}} \rangle \langle \chi_{m'}^{\mathbf{k}} | B_{\mathbf{k}\alpha'} \rangle \\ \times [\Sigma_{mm'}^{\text{imp}}(i\omega_n) - \Sigma_{mm'}^{\text{dc}}]$$

DMFT self-consistency condition reads:

$$G_{mm'}^{\text{imp}}(i\omega_n) = \sum_{\mathbf{k}} \sum_{\alpha\alpha'} \langle \chi_m^{\mathbf{k}} | B_{\mathbf{k}\alpha} \rangle \langle B_{\mathbf{k}\alpha'} | \chi_{m'}^{\mathbf{k}} \rangle \\ \times \{ [i\omega_n + \mu - \mathbf{H}_{\text{KS}}(\mathbf{k}) - \Delta\Sigma(\mathbf{k}, i\omega_n)]^{-1} \}_{\alpha\alpha'}$$

*Inversion of matrix of size $N_B * N_B$ at each k -point and each frequency !*

The Wannier route

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

$$w_{\alpha}(\mathbf{r} - \mathbf{T}) = \frac{V}{(2\pi)^3} \int_{\text{BZ}} d\mathbf{k} e^{-i\mathbf{k}\cdot\mathbf{T}} \sum_{\nu \in W} U_{\alpha\nu}^{(\mathbf{k})} \psi_{\mathbf{k}\nu}(\mathbf{r}),$$

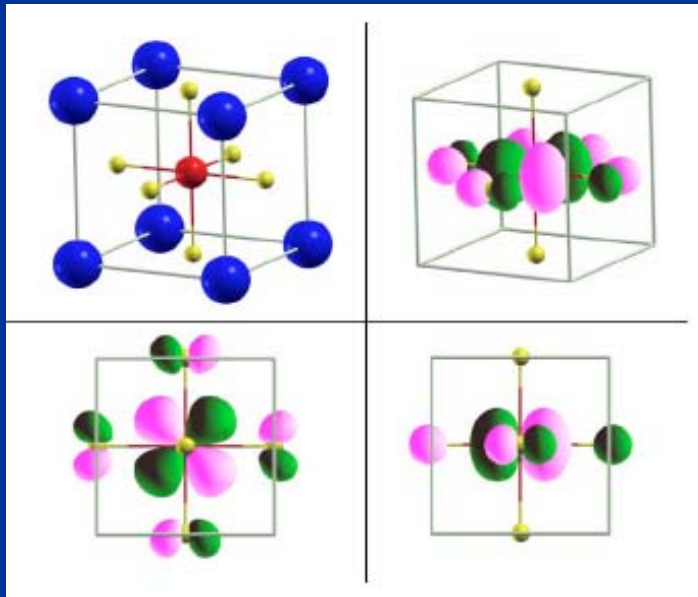
- Select a subset C of W as defining the correlated orbitals:

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

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

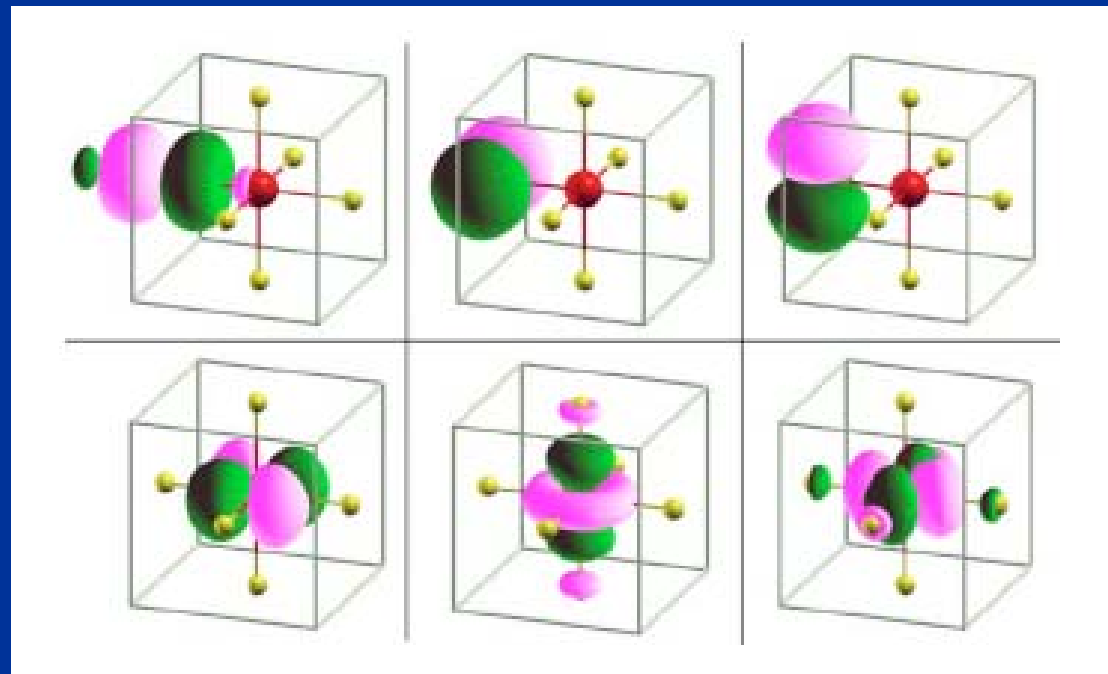
Easily implemented in any electronic structure method (e.g localized LMTO/NMTO or FLAPW, pseudopotential,...)

Example: SrVO₃ Wannier functions



← t_{2g} only

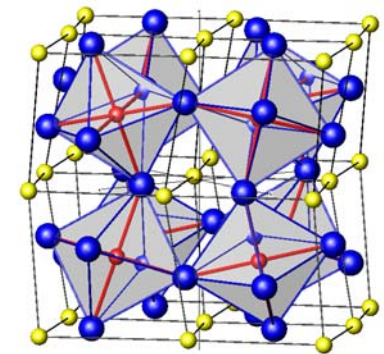
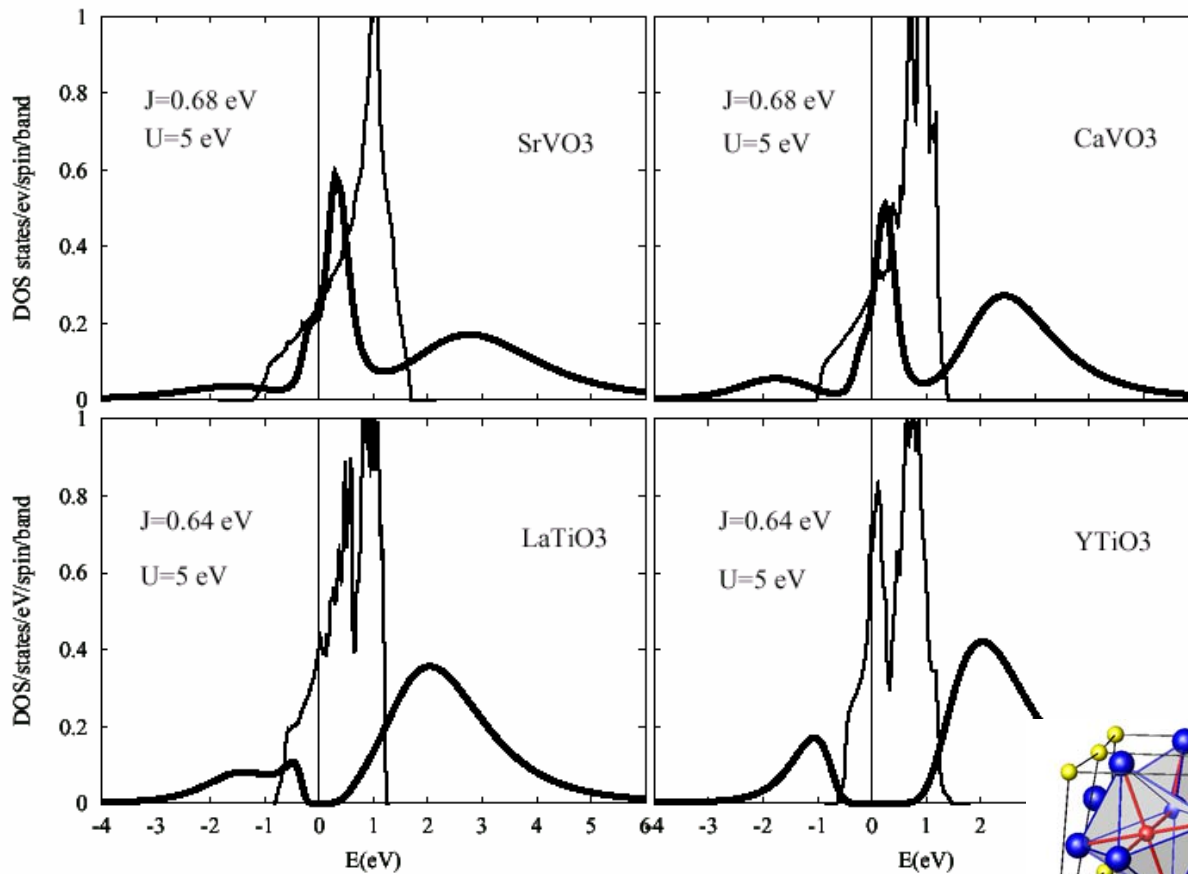
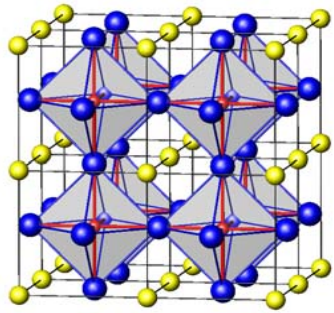
O2p+Vt_{2g} and e_g



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

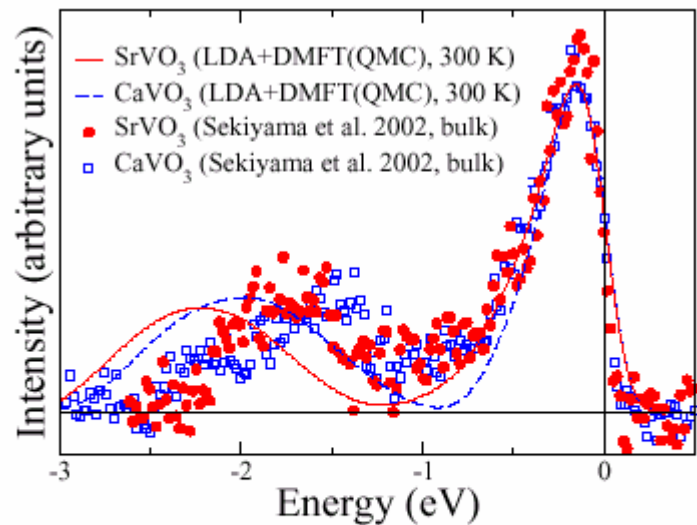
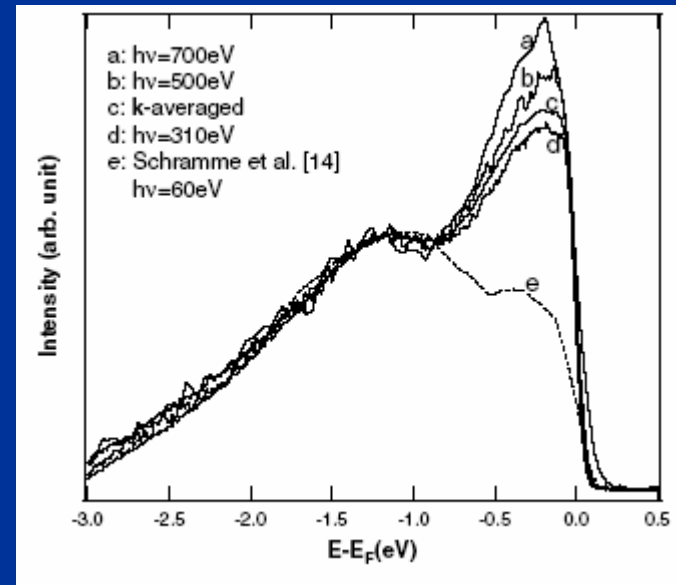


FIG. 4: Comparison of the calculated, parameter-free LDA+DMFT(QMC) spectra of SrVO₃ (solid line) and CaVO₃ (dashed line) with bulk-sensitive high-resolution PES (SrVO₃: circles; CaVO₃: rectangles) [4]. Horizontal line: experimental subtraction of the background intensity.

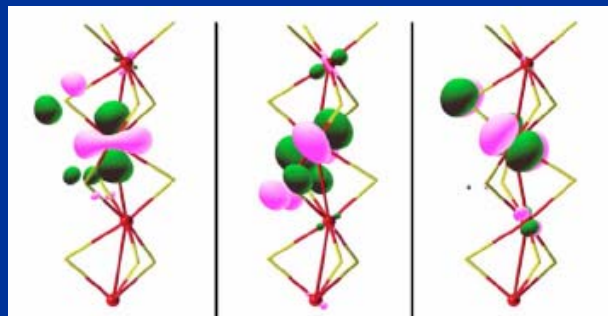
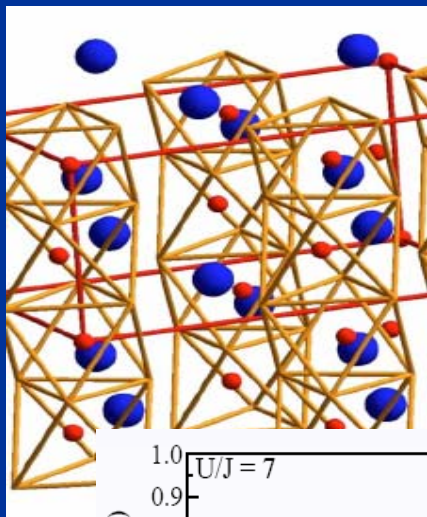
Sekiyama et al, Ca/SrVO₃



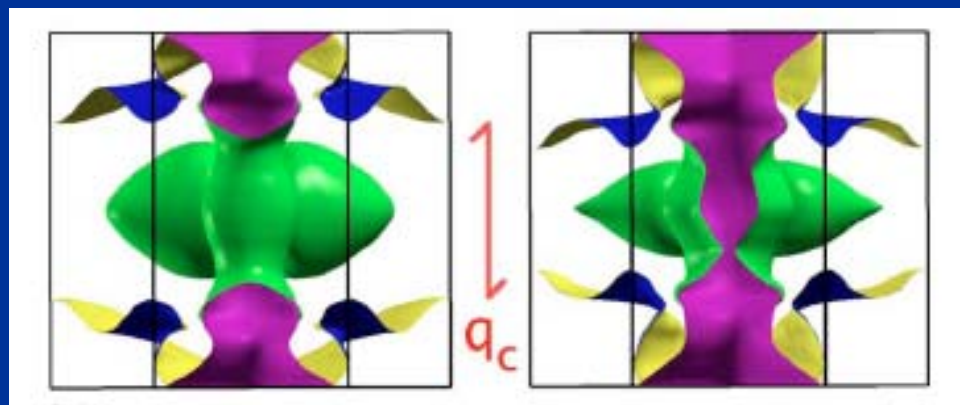
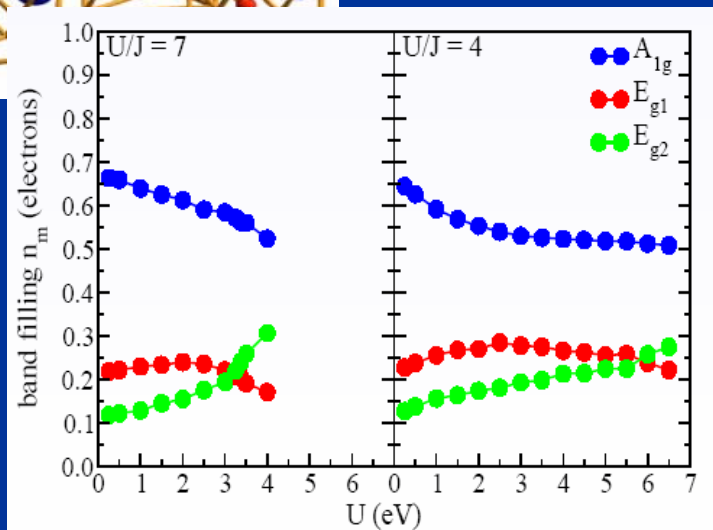
Mo et al, V₂O₃
(DMFT calculations by Keller, Held et al.
cf. also Poteryaev et al.

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



Correlation-induced nesting
of the Fermi surface:



LDA

Correlated

Total energy: the LDA+DMFT free-energy functional

$$\begin{aligned} \Gamma[\rho, G_{mm'}] &= \\ &= T[\rho, G_{mm'}] + E_H[\rho] + E_{xc}[\rho, G_{mm'}] \\ &\quad - \text{tr} \ln[i\omega_n + \mu + \frac{1}{2}\nabla^2 - v_{KS}(\mathbf{r}) - \chi^* \cdot \Delta\Sigma \cdot \chi] - \int d\mathbf{r} (v_{KS} - v_c)\rho(\mathbf{r}) - \text{tr}[G \cdot \Delta\Sigma] \\ &\quad + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r}) U(\mathbf{r} - \mathbf{r}') \rho(\mathbf{r}') + E_{xc}[\rho(\mathbf{r})] + \sum_{\mathbf{R}} (\Phi_{imp}[G_{ab}^{RR}] - \Phi_{DC}[G_{ab}^{RR}]) \end{aligned}$$

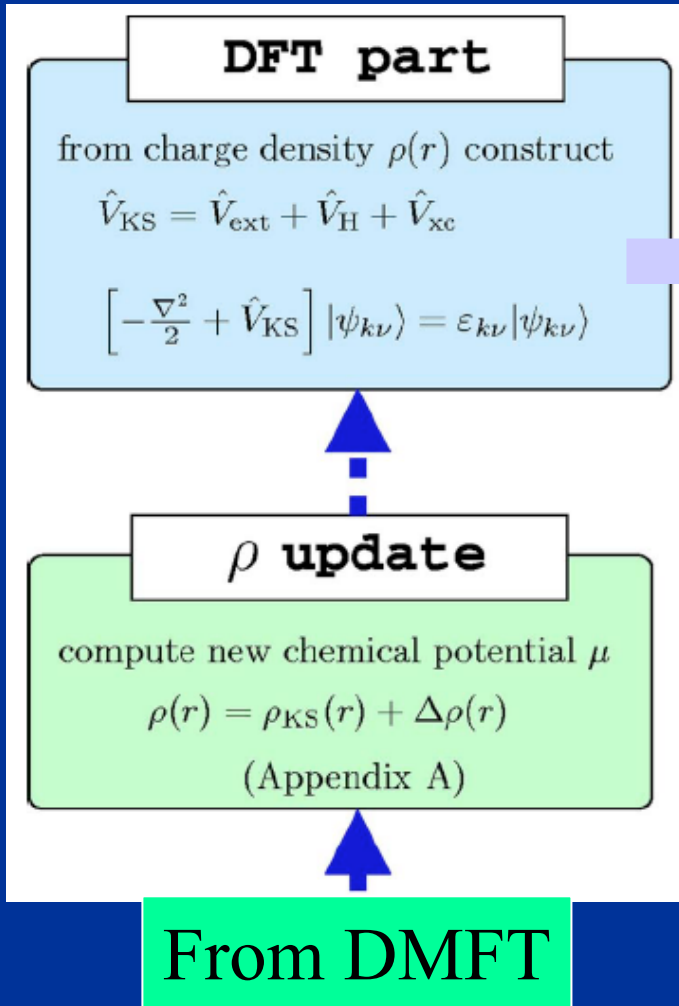
In these expressions,

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:

$$\begin{aligned} E_{LDA+DMFT} &= E_{DFT} - \sum_{\lambda} \epsilon_{\lambda}^{KS} + \langle H_{KS} \rangle + \langle H_U \rangle - E_{DC} \\ &= E_{DFT} + \sum_{\mathbf{k}, LL'} h_{LL'}^{KS} [\langle c_{L\mathbf{k}}^{\dagger} c_{L'\mathbf{k}} \rangle_{DMFT} - \langle c_{L\mathbf{k}}^{\dagger} c_{L'\mathbf{k}} \rangle_{KS}] + \langle H_U \rangle - E_{DC} \end{aligned}$$



Update of charge density

Construct G_{KS} and back to DMFT

$$\rho(\mathbf{r}) = \sum_{\mathbf{k}\nu\nu'} D_{\nu'\nu}^{(\mathbf{k})}(\mathbf{r}) \Delta N_{\nu\nu'}^{(\mathbf{k})} + \sum_{\nu} \Theta(\mu - \varepsilon_{\mathbf{k}\nu}) D_{\nu\nu}^{(\mathbf{k})}(\mathbf{r}).$$

KS density matrix:

$$D_{\nu'\nu}^{(\mathbf{k})}(\mathbf{r}) = \psi_{\mathbf{k}\nu}(\mathbf{r}) \psi_{\mathbf{k}\nu'}^*(\mathbf{r}).$$

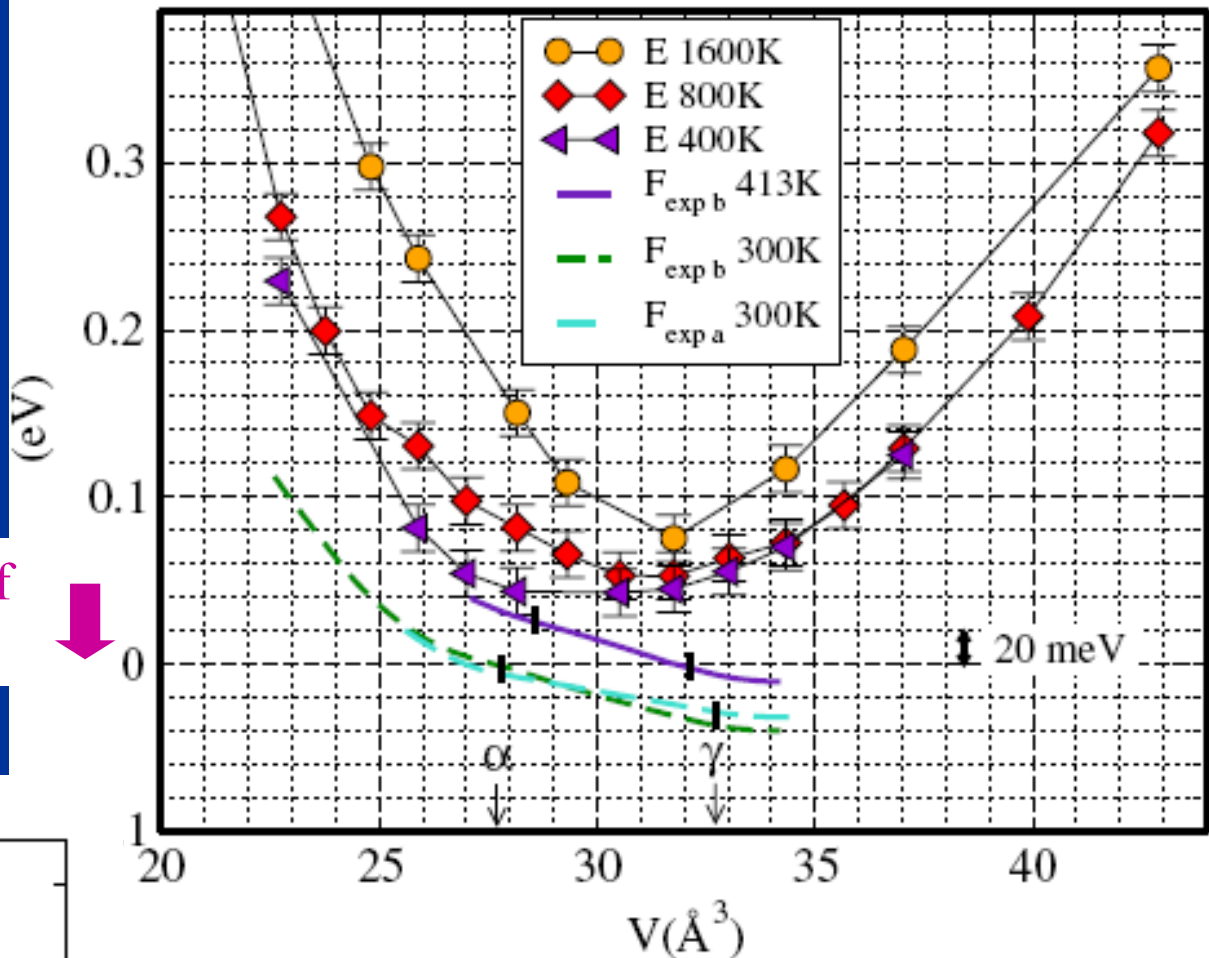
Many-body correction:

$$\Delta N_{\alpha\alpha'}^{(\mathbf{k})} \equiv \frac{1}{\beta} \sum_{nmm'} G_{\alpha m}^{\text{KS}}(\mathbf{k}, i\omega_n) \Delta \Sigma_{mm'}(i\omega_n) G_{m'\alpha'}(\mathbf{k}, i\omega_n)$$

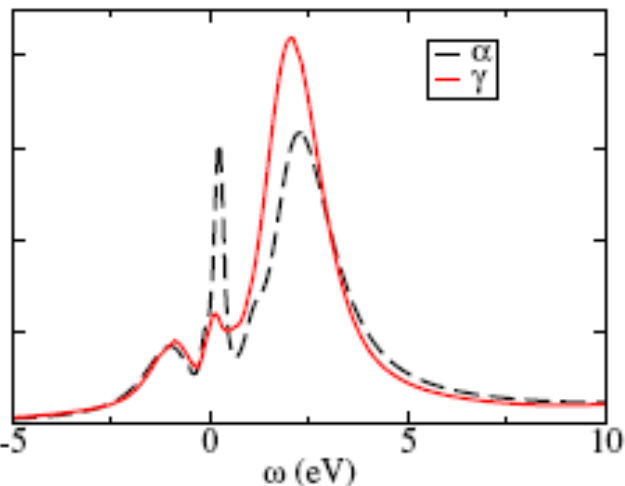
KS system is updated
and modified by many-body
effects...

Consistent with LDA+DMFT calculations of total energy

Entropic stabilisation of
gamma phase

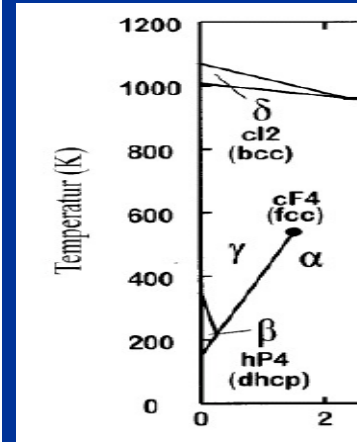
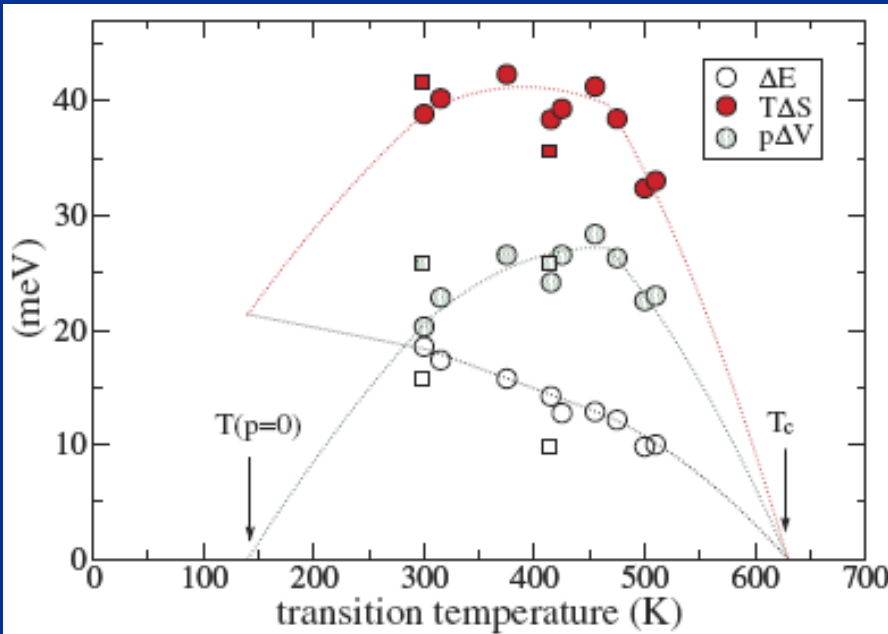


LDA+DMFT (800K)



The α - γ transition of cerium is entropy-driven...

Amadon et al. PRL 2006

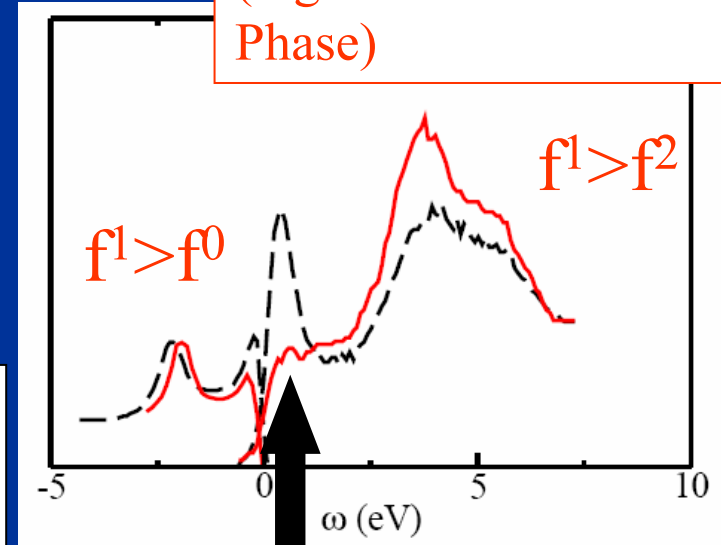


Red:
 γ -cerium
 (higher volume
 Phase)

Entropy and energy
 Across transition from
 Experimental equation of state

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

Black:
 α -cerium
 (lower volume
 Phase)



Kondo resonance

Cerium: the α - γ transition, photoemission and optical spectra, total energy

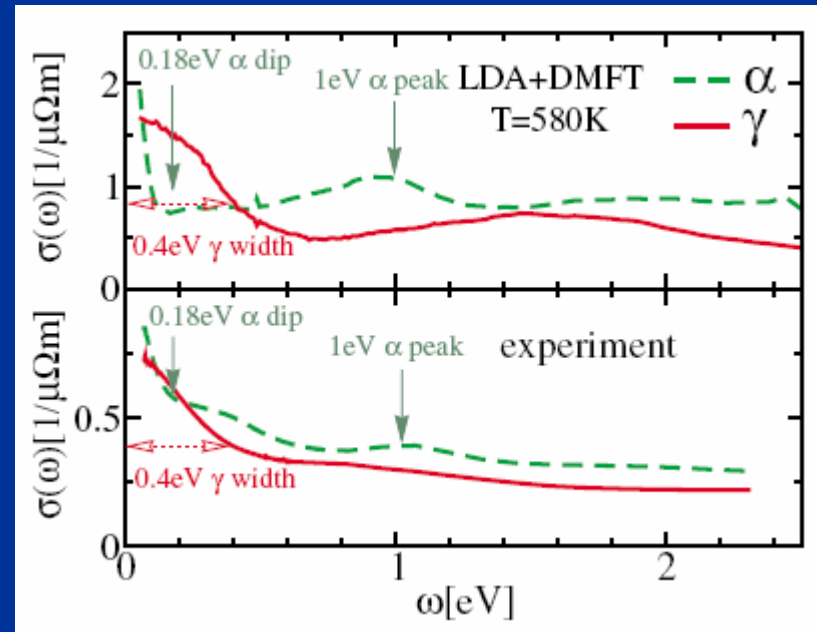
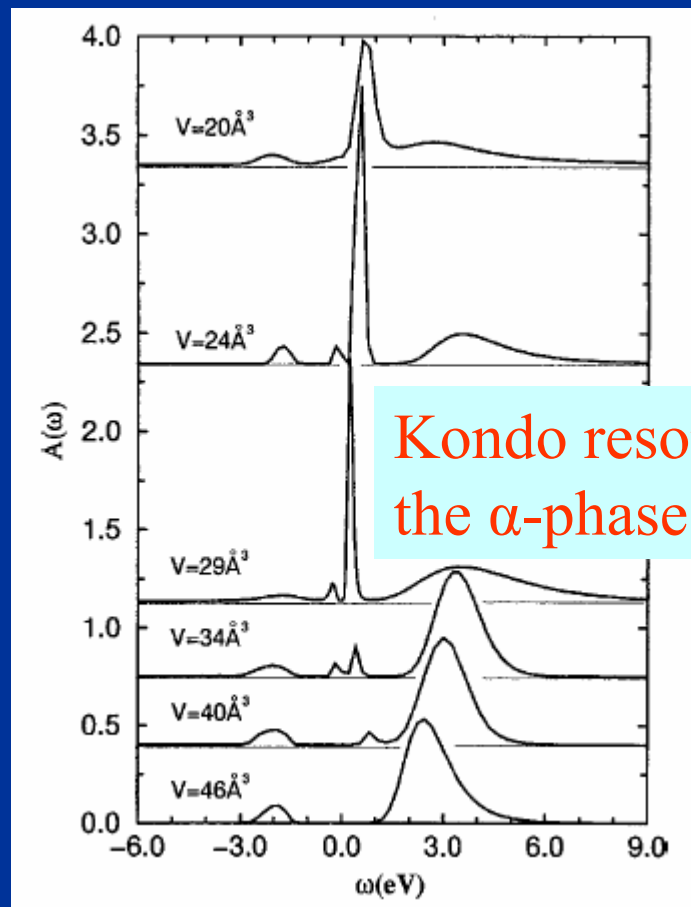


FIG. 1 (color online). The top panel shows the calculated optical conductivity for both α and γ phase of cerium. The temperature used in calculation is 580 K while the volume of α and γ phase is 28.06 \AA^3 and 34.37 \AA^3 , respectively. The bottom panel shows experimental results measured by the group of van der Marel [2]. The measurements for α phase were done at 5 K and for γ phase at 400 K.

(f-d.o.s at $T \sim 600\text{K}$)

Held, McMahan & Scalettar, PRL2001, PRB2003

Zolfl et al, PRL2001. Amadon et al, PRL 2006

Haule et al, PRL 2005

Expts: van der Eeb,
PRL 2001

Total energy of fcc-Plutonium (δ -phase)

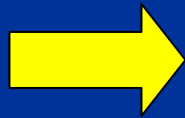
S.Savrasov, G. Kotliar and E.Abrahams Nature 410 (2001) 793

LDA+DMFT

total energy

vs.

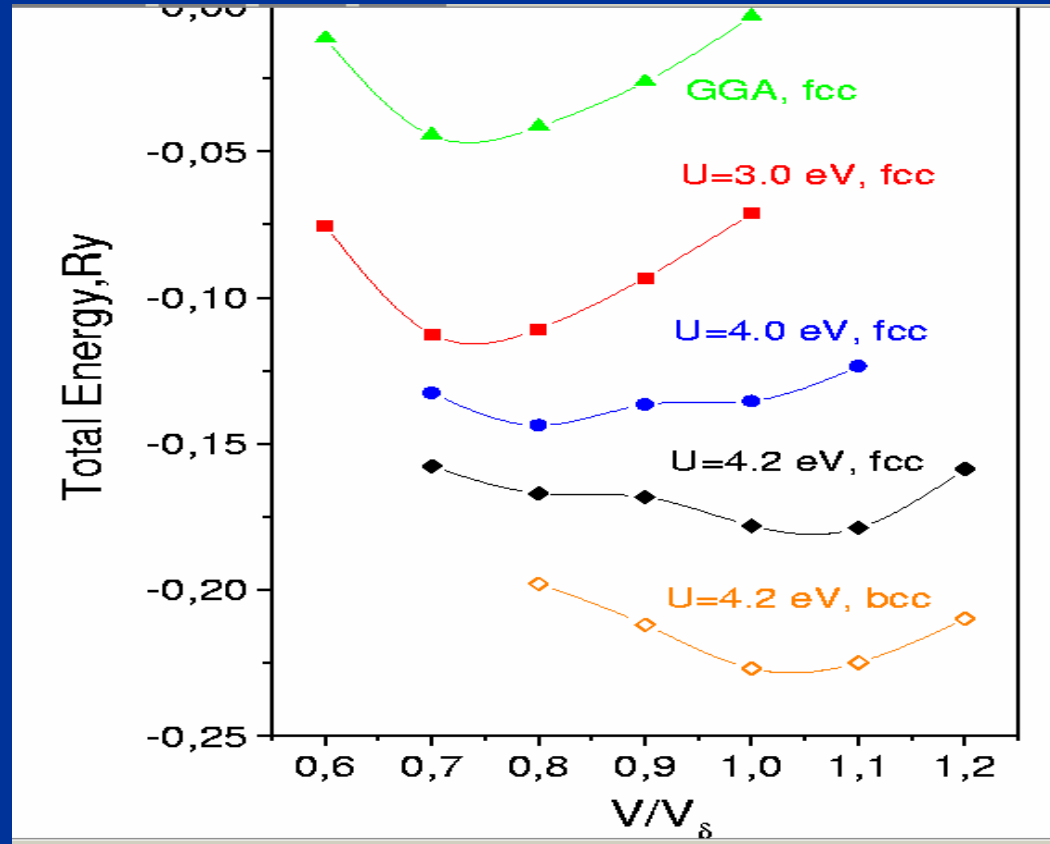
unit-cell volume



Double-well

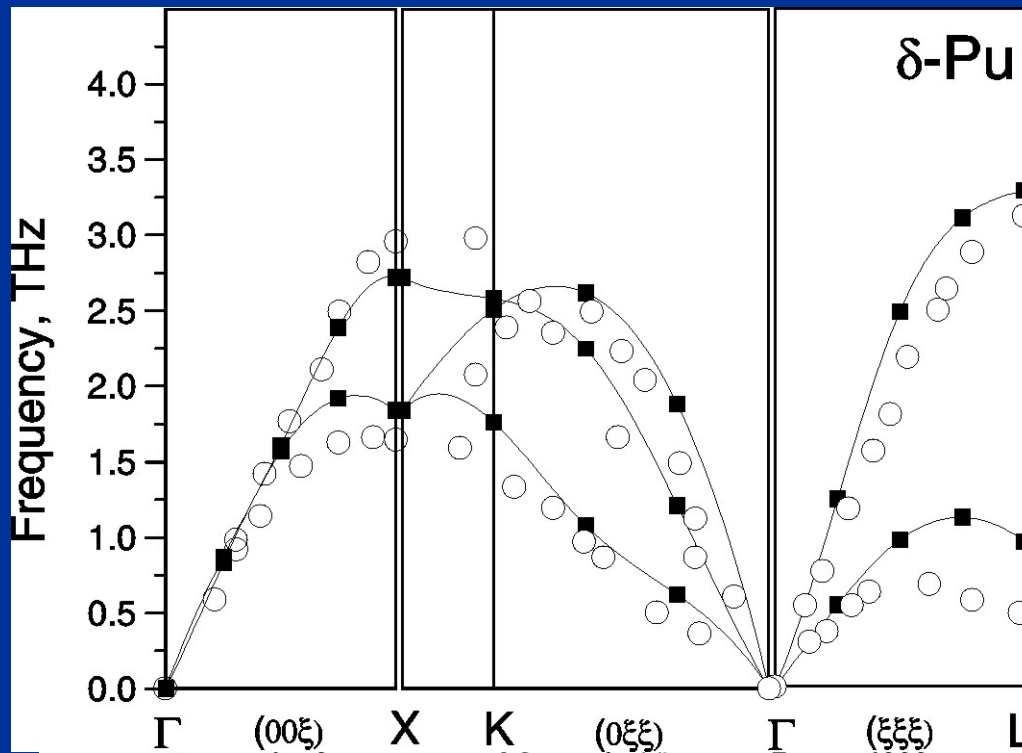
Structure:

Alpha-like phase ?



Also: Kondo-like quasiparticle peak at Fermi level,
in agreement with photoemission (Arko).

Phonons in fcc δ -Pu PREDICTED from DMFT



Phonons
From
Linear-response
In DMFT:
Savrasov&Kotliar,
PRL 2003
[MnO,NiO]

	C_{11} (GPa)	C_{44} (GPa)	C_{12} (GPa)	C' (GPa)
Theory	34.56	33.03	26.81	3.88
Experiment	36.28	33.59	26.73	4.78

(Dai, Savrasov, Kotliar, Ledbetter, Migliori, Abrahams, Science, 9 May 2003)

(experiments from Wong et.al, Science, 22 August 2003)

[Squares]

[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 Ti_2O_3 and VO_2 , Poteryaev, Biermann et al.)

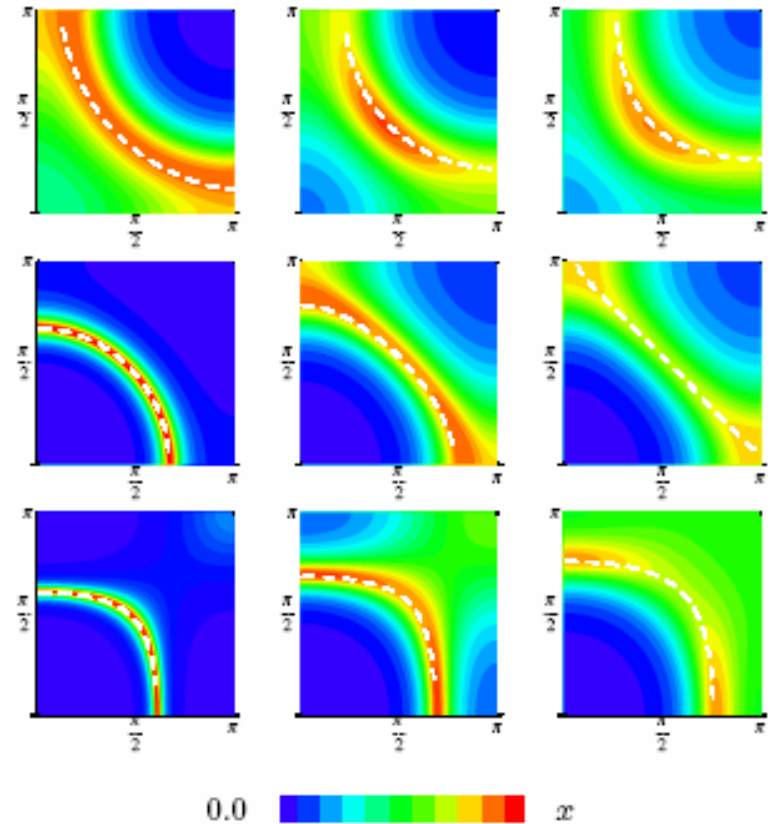
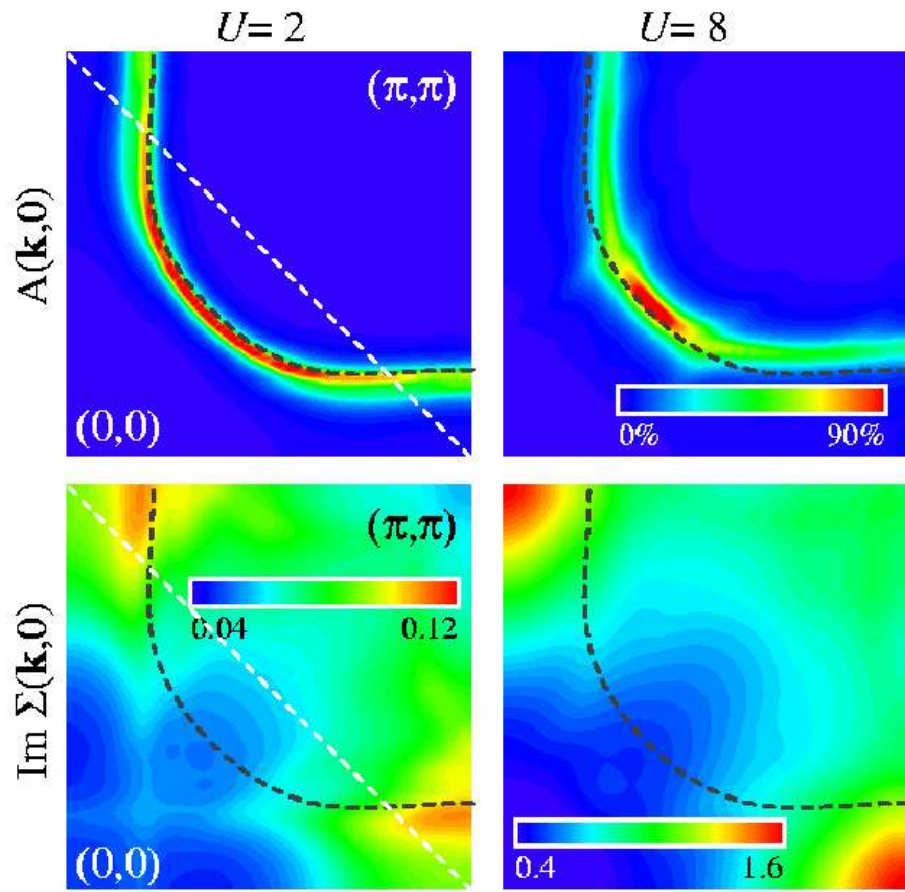


FIG. 4: $A(k, \omega = 0^+)$ in the first quadrant of the Brillouin zone. From the top: in the first row $t' = -0.3t$, $n = 0.73, 0.89, 0.96$, color scale $x = 0.28, 0.22, 0.12$; in the second $t' = +0.3t$, $n = 0.70, 0.90, 0.95$, color scale $x = 0.82, 0.34, 0.27$; in the lowest row $t' = +0.9t$, $n = 0.69, 0.92, 0.96$, 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

[published as: Lectures on the Physics of Highly Correlated Electron Systems VIII (2004) 3, American Institute of Physics Conference Proceedings Vol. 715]

- **Review articles:** A.G, G.Kotliar, W.Krauth and M.Rozenberg, Rev.Mod.Phys. **68** (1996) 13; G.Kotliar et al. (2006), K.Held (2006)

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

A collective enterprise ...



Silke Biermann



Frank Lechermann

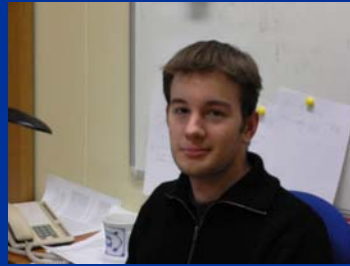


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Pablo Cornaglia

And also...
Bernard Amadon (CEA)
Ferdi Arvasetiawan

Towards (truly) first-principles DMFT

Or...

“A life without (ad-hoc) U ”
(and perhaps also... without LDA ?!)

- 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:

$$H = -\sum_i \frac{1}{2} \nabla_i^2 + \sum_i v(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j} u(\mathbf{r}_i - \mathbf{r}_j)$$

Density-density correlation function:

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

Screened interaction:

$$W(\mathbf{r}, \mathbf{r}', i\omega) = u(\mathbf{r} - \mathbf{r}') - \int d\mathbf{r}_1 d\mathbf{r}_2 u(\mathbf{r} - \mathbf{r}_1) \chi(\mathbf{r}_1 - \mathbf{r}_2; i\omega) u(\mathbf{r}_2 - \mathbf{r}')$$

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)

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

$$G_H^{-1} = i\omega_n + \mu + \nabla^2/2 - v_H$$

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

$\delta\Gamma/\delta G = \delta\Gamma/\delta W = 0$ yields:

$$G^{-1} = G_H^{-1} - \Sigma^{xc}, \quad \Sigma^{xc} = \frac{\delta\Psi}{\delta G}; \quad W^{-1} = u^{-1} - P, \quad P = -2\frac{\delta\Psi}{\delta W}$$

Approximations to the Psi-functional:

e.g. the GW approximation:

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

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-):

$$\Psi_{GW+DMFT}[G_{L_1L'_1}^{\mathbf{R}\mathbf{R}'}, W_{L_1L_2L'_1L'_2}^{\mathbf{R}\mathbf{R}'}] = \Psi_{GWA}^{non-loc} + [\Psi_{GWA}^{loc} - \Delta\Psi] + \sum_{\mathbf{R}} \Psi_{imp}[G_{ab}^{\mathbf{R}\mathbf{R}}, W_{abcd}^{\mathbf{R}\mathbf{R}}] \quad (147)$$

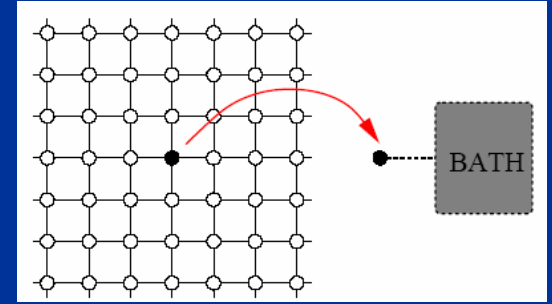
In this expression, Ψ_{imp} is the Ψ -functional corresponding to the local effective model (142), while $\Delta\Psi$ removes the components from Ψ_{GWA}^{loc} which will be taken into account in Ψ_{imp} , namely:

$$\Delta\Psi = -\frac{1}{2} \sum_{\mathbf{R}} \int d\tau \sum_{abcd} G_{ab}^{\mathbf{R}}(\tau) W_{abcd}^{\mathbf{R}\mathbf{R}}(\tau) G_{DC}^{\mathbf{R}\mathbf{R}}(-\tau) \quad (148)$$

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):

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

Can be viewed as a way to **REPRESENT** the (exact) local G and local W

Self-consistency:

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

$$W_{loc}(i\nu_n) = \sum_{\mathbf{q}} [V_{\mathbf{q}}^{-1} - P(\mathbf{q}, i\nu_n)]^{-1}$$

$$\mathcal{G}^{-1} = G_{loc}^{-1} + \Sigma_{imp}$$

$$\mathcal{U}^{-1} = W_{loc}^{-1} + P_{imp}$$

With:

$$\Sigma^{LL'}(\mathbf{k}, i\omega_n) = \Sigma_{GW}^{LL'}(\mathbf{k}, i\omega_n) - \sum_{\mathbf{k}} \Sigma_{GW}^{LL'}(\mathbf{k}, i\omega_n) + \Sigma_{imp}^{LL'}(i\omega_n)$$

$$P^{\alpha\beta}(\mathbf{k}, i\omega_n) = P_{GW}^{\alpha\beta}(\mathbf{k}, i\omega_n) - \sum_{\mathbf{k}} P_{GW}^{\alpha\beta}(\mathbf{k}, i\omega_n) + P_{imp}^{\alpha\beta}(i\omega_n)$$

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)