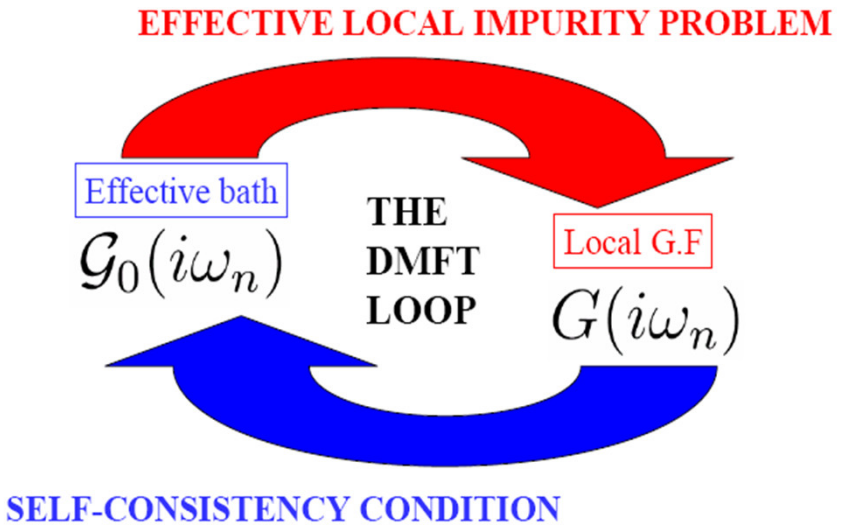
An introduction to the dynamical mean-field theory

L. V. Pourovskii



Nordita school on Photon-Matter interaction, Stockholm, 06.10.2016

OUTLINE

- **The standard density-functional-theory (DFT) framework**
- **An overview of correlated materials and DFT limitations in decscribing them**
- **Models of correlated systems**
- **Dynamical mean-field theory (DMFT) and Mott transition in the model context**
- **DFT+DMFT: an *ab initio* framework for correlated materials**

DFT: an effective one-electron theory

The conventional (density functional theory) approach to electronic structure:

$$\hat{H}\Psi = E\Psi$$

$$\Psi_k(\ldots, \vec{r}_i\sigma_i, \ldots, \vec{r}_j\sigma_j, \ldots)$$

$$\hat{H} = \sum_{n=1}^{N} -\frac{1}{2}\nabla_i^2 + \sum_{n=1}^{N} v(\vec{r}_i) + \frac{1}{2}\sum_i \sum_{j\neq i} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

Many-body theory
(Many-electron Schrödinger eq. For Interacting electrons)

$$H_{KS}\psi_i^\sigma(r, \mathrm{R}_1, \mathrm{R}_2, \ldots \mathrm{R}_M) = \varepsilon_i^\sigma \psi_i^\sigma(r, \mathrm{R}_1, \mathrm{R}_2, \ldots \mathrm{R}_M)$$

$$H_{KS} = -\frac{1}{2}\nabla^2 + V_{KS}^\sigma[n(r, \mathrm{R}_1, \mathrm{R}_2, \ldots \mathrm{R}_M)]$$

$$V_{KS}^\sigma[n(r, \mathrm{R}_1, \mathrm{R}_2, \ldots \mathrm{R}_M)] = V_H[n] + V_{EXT}[n] + V_{XC}^\sigma[n]$$

$$n(r, \mathrm{R}_1, \mathrm{R}_2, \ldots \mathrm{R}_M) = \sum_\sigma n^\sigma(r, \mathrm{R}_1, \mathrm{R}_2, \ldots \mathrm{R}_M) = \sum_\sigma \sum_{OCC} \psi_i^{\sigma *} \psi_i^\sigma$$

Effective one-electron theory:
No interaction term in H_{KS}
All many-body effects are taken into account implicitly in V_{KS} within LDA/GGA

Provides good description for *itinerant* electron states characterized by wide bands
Often fails for (partially) *localized* states in narrow bands

Kinetic vs. potential energy competition and electronic correlations

Simple estimate of the key energy scales in solids (see A. Georges arXiv:0403123) :

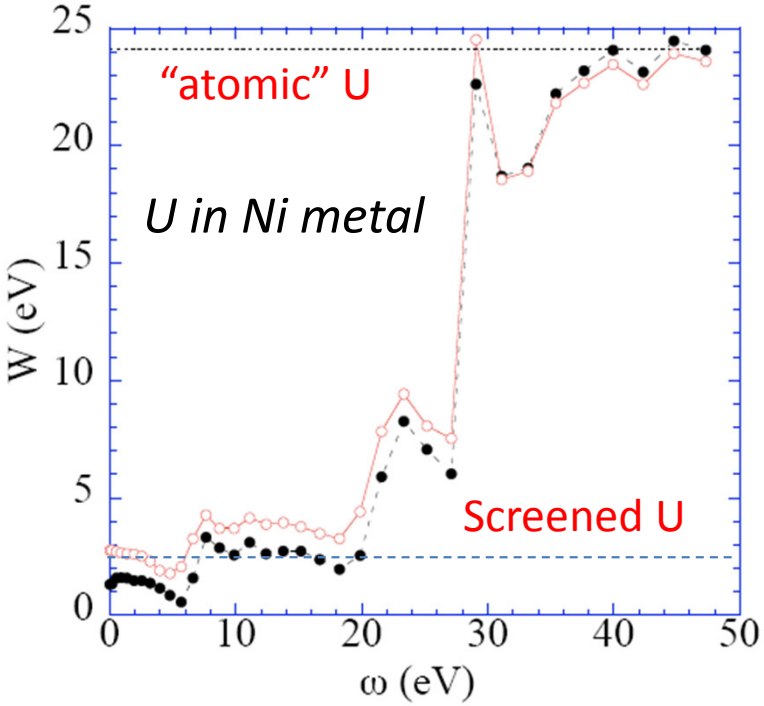
$\chi_L(\mathbf{r}-\mathbf{R})$ is an orbital for *L={l,m}* centered at cite ***R***

$$t_{\mathbf{RR}'}^{LL'} \sim \int d\mathbf{r}\, \chi_L^*(\mathbf{r}-\mathbf{R}) \frac{\hbar^2\nabla^2}{2m} \chi_{L'}(\mathbf{r}-\mathbf{R}')$$

hopping matrix element, estimate for the kinetic energy, determining the **bandwidth W**

$$U \sim \int d\mathbf{r}d\mathbf{r}' |\chi_L(\mathbf{r}-\mathbf{R})|^2 U_s(\mathbf{r}-\mathbf{r}') |\chi_L(\mathbf{r}'-\mathbf{R})|^2$$

Screened Coulomb repulsion between orbitals on the same site



1). $W >> U$: ***kinetic energy dominates;*** electrons behave as weakly-renormalized quasiparticles

2) $W << U$: **on-site repulsion dominates**, at each site electrons adopt a configuration minimizing potential energy, no conduction

3). $W \sim U$: electrons moves in a strongly correlated fashion. **Strongly-correlated bad metals at the verge of Mott insulating behavior**

Strongly-correlated materials

Systems with *U≥bandwidth* are not described correctly within DFT-LDA/GGA
Important classes of those materials:

- Transition metal compounds:
  TM-oxides (**NiO, CoO, Fe_2O_3, V_2O_3…**)
  TM perovskites (**$SrVO_3$, $CaVO_3$, LaTiO3, YTiO3**…)
  cuprate superconductors (**$La_{2-x}Sr_xCuO_4$, $Nd_{2-x}Ce_xCuO_4$…**)
  manganites (**$LaMnO_3$**).
  Parameters controlling correlation strength: **U, W, Δ_{dp}, Δ_{CF}**.

- Localized *f*- electron compounds:
  lanthanide metals (**Pr-Yb**), oxides (***Ln*$_2$O$_3$**…), pnictides (***Ln*N, *Ln*P, *Ln*As**)
  heavy actinides (**Am-Cf**) and their compounds
  Relevant parameters: intra-atomic ***U, J***, Δ_{SO}, crystal field Δ_{CF} much smaller
  f-states localized and posses local moments, often order magnetically at low *T*.

- Heavy-fermion compounds, Kondo lattices:
  mainly **Ce, Yb**, and **U** compounds: **CeAl3**, **CeCu2Si2**, **UPt3**, **CeRhIn5**…
  At high T ~ localized *f*-el. compounds. At low T the local *f*-moments *screened* by cond. electrons. $C(T)=\gamma T$ with very large γ (correspond. to m^* ~100÷1000). Often superconducting at low *T.*

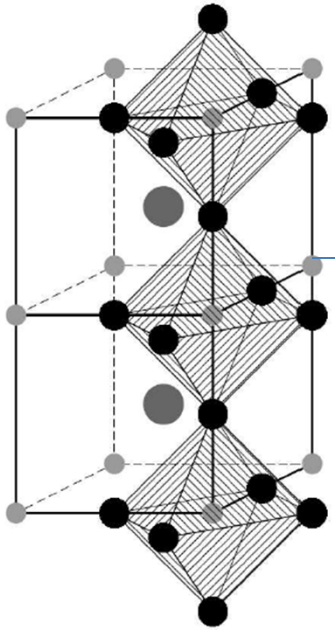
* More exotic systems: organic conductors, optical lattices

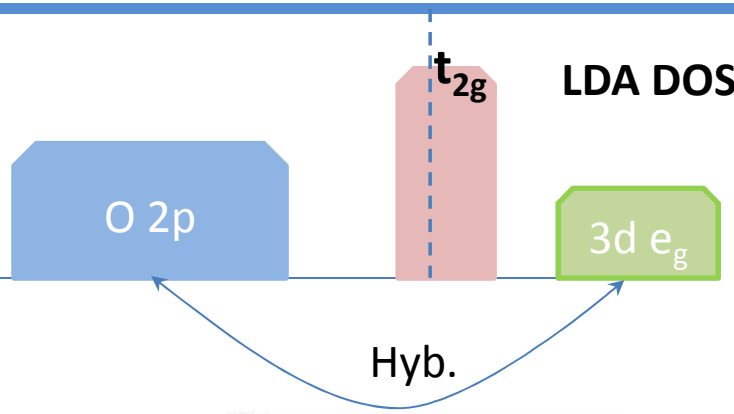
Transition-metal oxides and peroxides

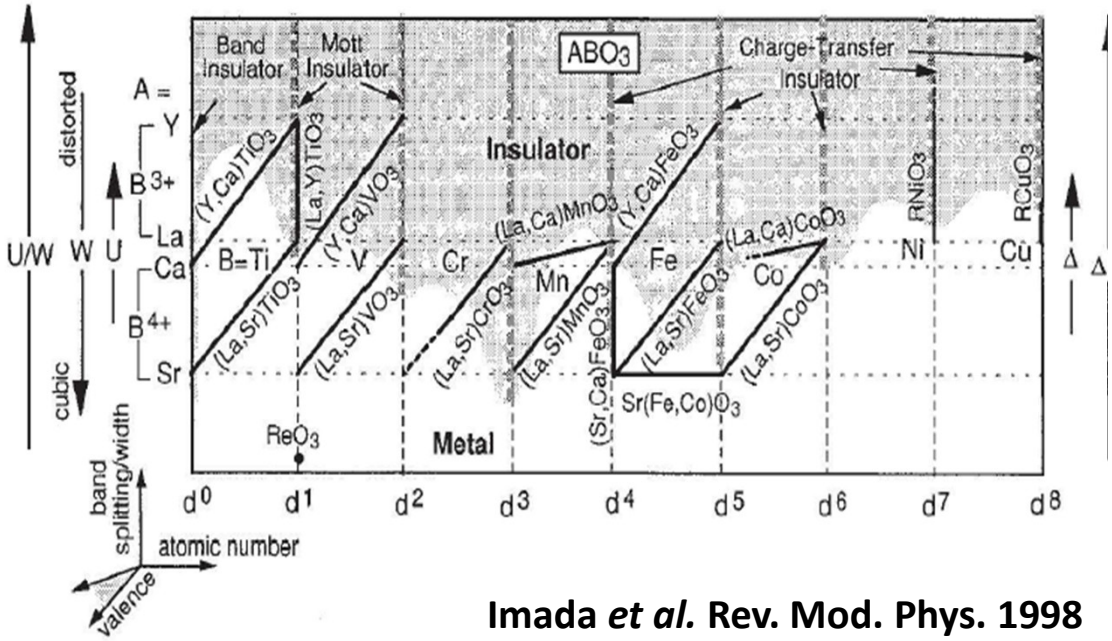
$SrVO_3$, $CaVO_3$, $LaTiO_3$, $YTiO_3$

Basic electronic structure:

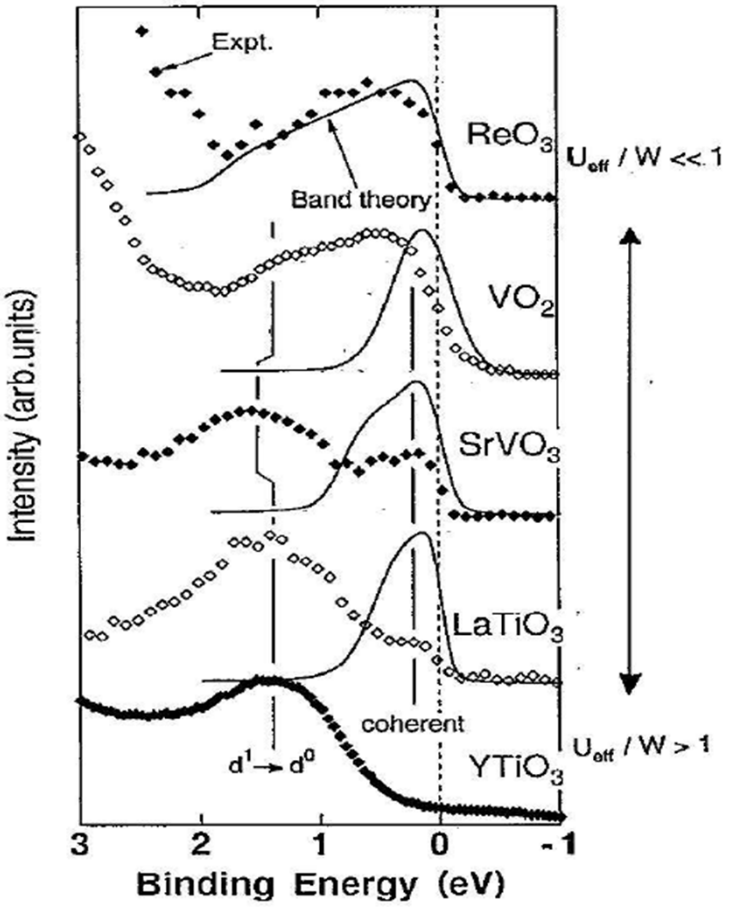
- O 2*p* and TM e_g (d_{x2-y2} , d_{z2-r2}) form bonding anti-bonding states
- TM t_{2g} (xy,xz,yz) are pinned at E_F
- t_{2g} states are quite localized, *U*~3-5eV





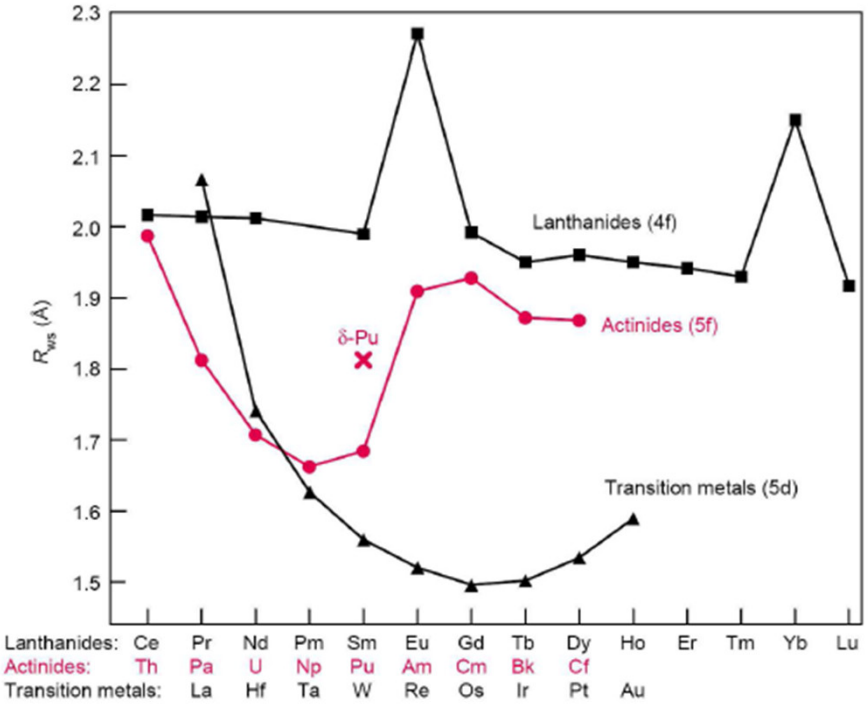


Imada *et al.* Rev. Mod. Phys. 1998

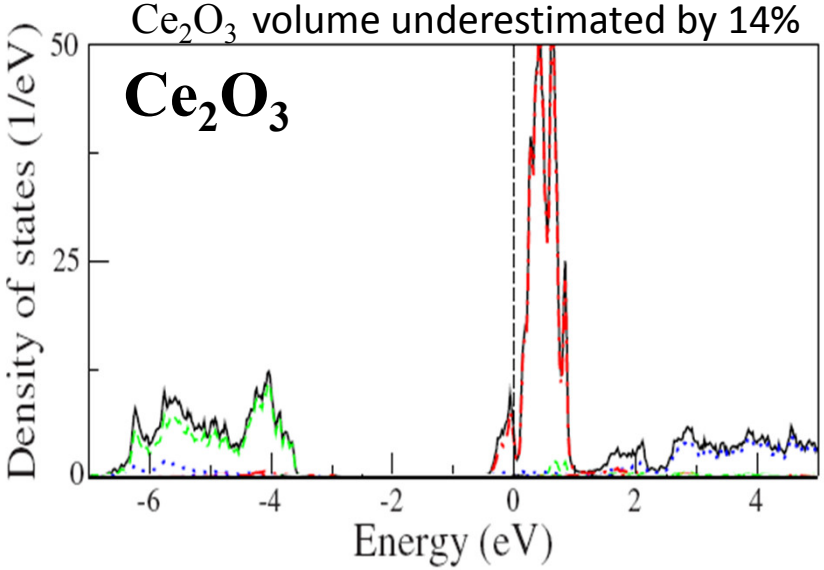


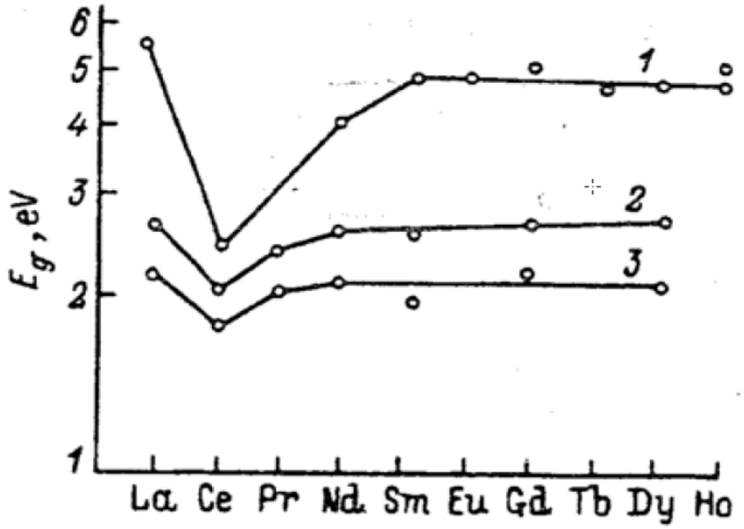
Localized Rare-earth compounds

- In majority of lanthanides **4*f*s** are localized and do not contribute to bonding, **W << U** They form local moments (a Curie susceptibility) ordering at low T.
- In LDA 4*f* states *itinerant, pinned at* E_F, *contribute to bonding* $\rightarrow$ *too small volume, metallic state*



Ce_2O_3 volume underestimated by 14%

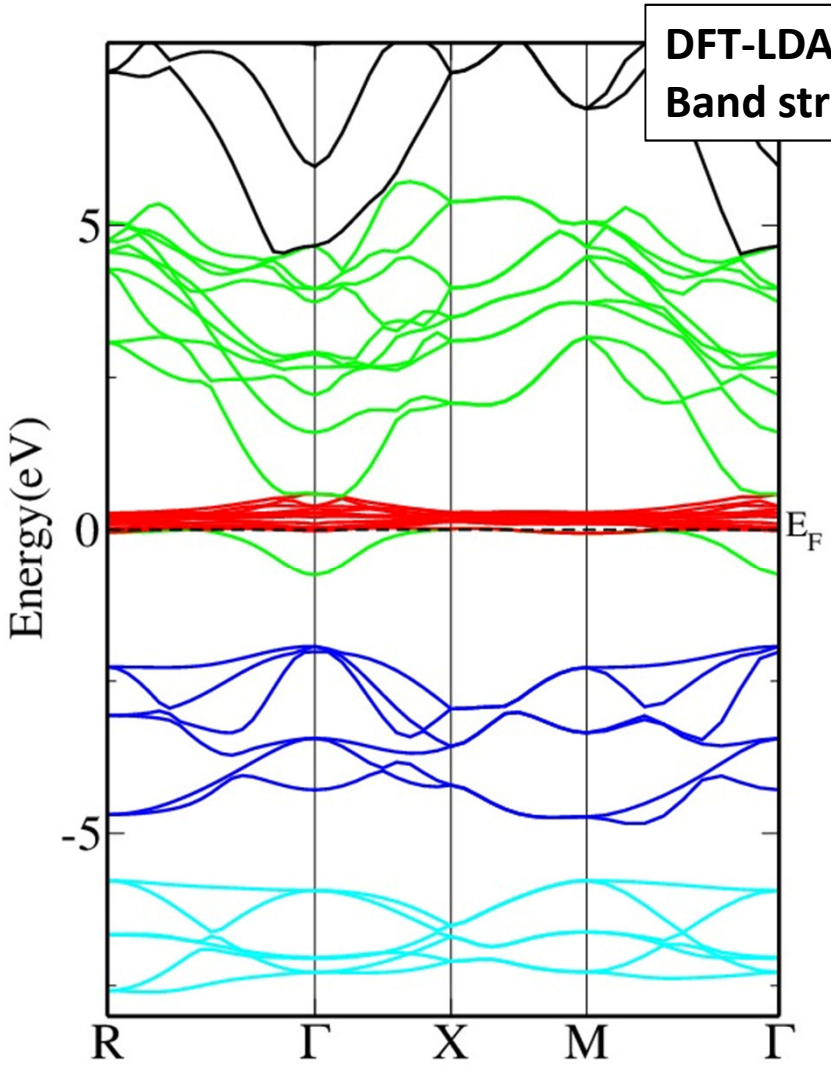


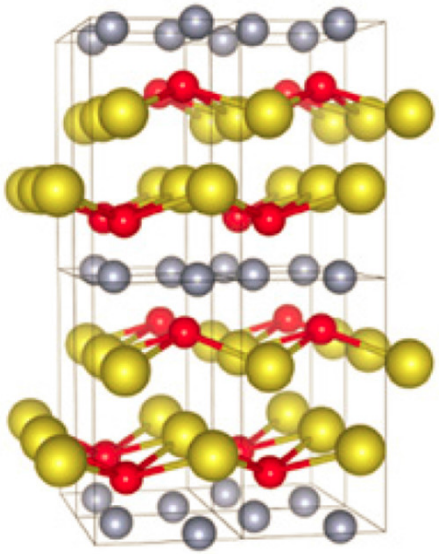


Optical gaps in 1. Ln_2O_3; *2.* Ln_2S_3; *3.* Ln_2Se_3

Golubkov *et al.*, Phys. Solid State 37, 1028 (1995).

An example: CeSF – an *f*-electron pigment





NEOLOR®

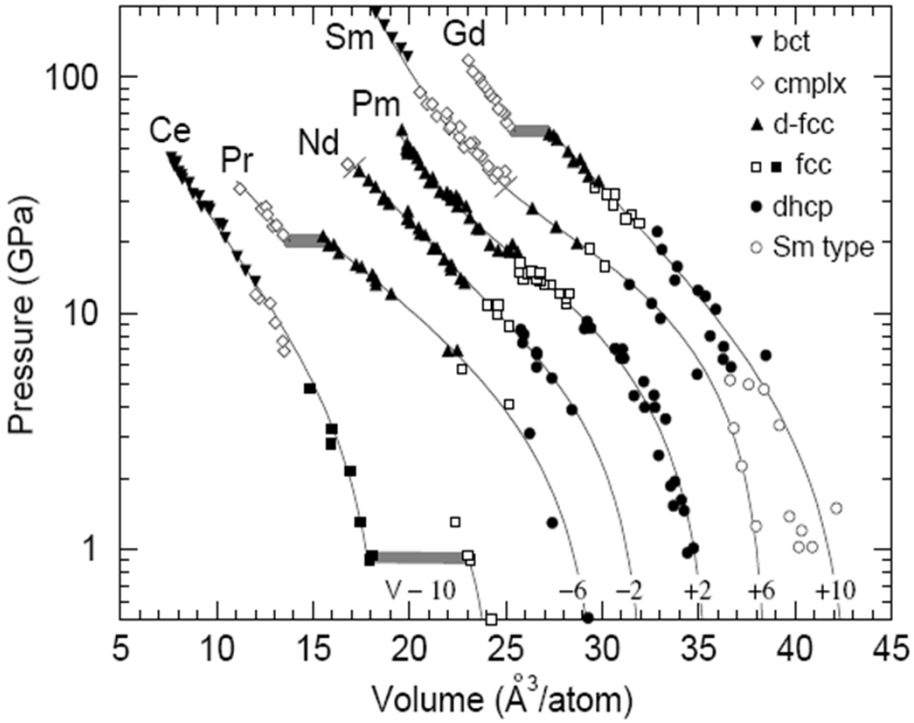
Ce: $4f^1$ configuration, paramagnetic

CeSF is a wide-gap semiconductor with a sharp absorption edge however, DFT predicts it to be a metal...

Volume collapse in rare-earth and heavy actinides

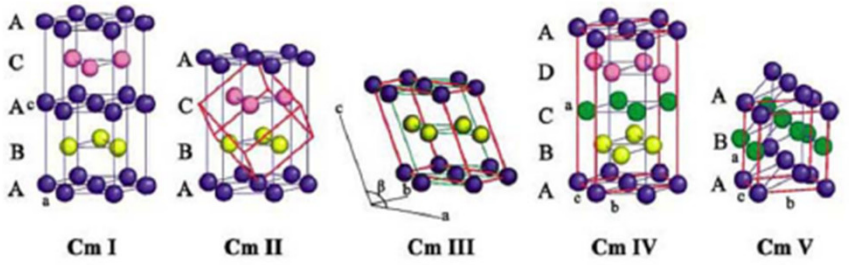
Under pressure bandwidth increases and U/W↓
In result, *f* electrons delocalize, V↓ and crystal. structure usually changes

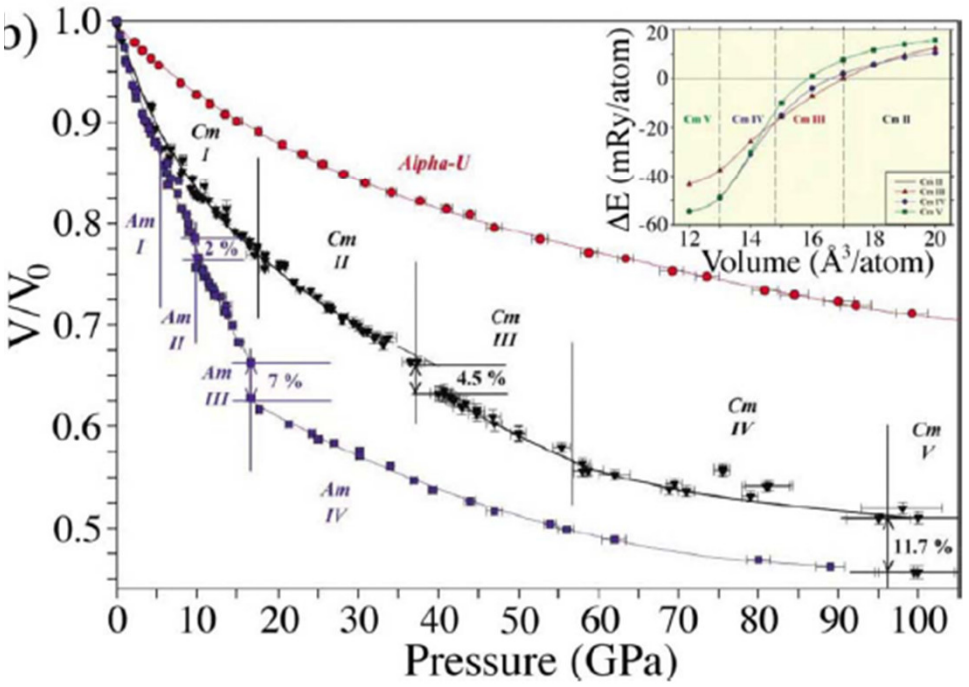
Rare-earth metals



Am and Cm metals under P

(Rev. Mod. Phys. **81** 235 (2009)





Due to complicated shapes of *f*-el. wave functions low-volume structures of RE and AC metals are often quite complex

Lattice models of correlated materials

Several famous models have been proposed to capture strongly-correlated behavior while keeping only most relevant parameters describing the competition between the hopping and local Coulomb repulsion

Hubbard model (1b): The simplest model including only nearest neighbor hopping + on-site U

$$H = -\sum_{\mathbf{R}\mathbf{R}',\sigma} t_{\mathbf{R}\mathbf{R}'}\, c^{+}_{\mathbf{R}\sigma} c_{\mathbf{R}'\sigma} + \varepsilon_0 \sum_{\mathbf{R}\sigma} n_{\mathbf{R}\sigma} + U \sum_{\mathbf{R}} n_{\mathbf{R}\uparrow} n_{\mathbf{R}\downarrow}$$

Extended Hubbard model: includes as well the hopping between the correlated (*d*) and ligand (*p*) band for a more realistic description of TM-oxides

$$H_{pd} = -\sum_{\mathbf{R}\mathbf{R}',\sigma} t_{pd}\left(d^{+}_{\mathbf{R}\sigma} p_{\mathbf{R}'\sigma} + h.c\right) + \varepsilon_d \sum_{\mathbf{R}\sigma} n^{d}_{\mathbf{R}\sigma} + \varepsilon_p \sum_{\mathbf{R}'\sigma} n^{p}_{\mathbf{R}'\sigma} + U_{dd} \sum_{\mathbf{R}} n^{d}_{\mathbf{R}\uparrow} n^{d}_{\mathbf{R}\downarrow}$$

Periodic Anderson model: discards direct hopping between correlated orbitals, relevant for localized RE, heavy-fermion compounds with very localized *f*-electrons:

$$H_{PAM} = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}}\, c^{\dagger}_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma} + \sum_{\mathbf{k}\sigma m} \left(V_{\mathbf{k}}\, c^{\dagger}_{\mathbf{k}\sigma} f_{m\mathbf{k}\sigma} + h.c\right) + \varepsilon_f \sum_{\mathbf{R}\sigma m} n^{f}_{\mathbf{R}\sigma m} + U \sum_{\mathbf{R}} \left(\sum_{\sigma m} n^{f}_{\mathbf{R}\sigma m}\right)^{2}$$

Even those simplified lattice models cannot be solved exactly apart from limiting cases (zero U or hopping, 1*d* cases)

Impurity models

Impurity models (the Anderson model, P. W. Anderson 1961) were originally proposed to describe formation local magnetic moments of TM impurities in metallic hosts

Anderson impurity model: $H = H_c + H_{mix} + \overbrace{H_d + H_U}^{H_{atomic}}$

describes a single impurity $H_{atomic} = H_d + H_U = E_d \sum_\sigma \hat{n}_{d\sigma} + U n_{d\uparrow} n_{d\downarrow}$

embedded into a host of non-interacting delocalized electrons: $H_c = \sum_{\vec{k}\sigma} \varepsilon_{\vec{k}} c^\dagger_{\vec{k}\sigma} c_{\vec{k}\sigma}$

localized impurity and itinerant states hybridize $H_{mix} = \sum_{j\sigma} [V_{\vec{k}} c^\dagger_{k\sigma} d_\sigma + \text{H.c.}]$

For $U >> |V_k|$ AIM may be reduced to the **Kondo model:**

$$H = \sum_{k\sigma} \varepsilon_k c^\dagger_{k\sigma} c_{k\sigma} + \sum_{k,k'} J_{k,k'} c^\dagger_{k\alpha} \vec{\sigma} c_{k'\beta} \cdot \vec{S}_d$$

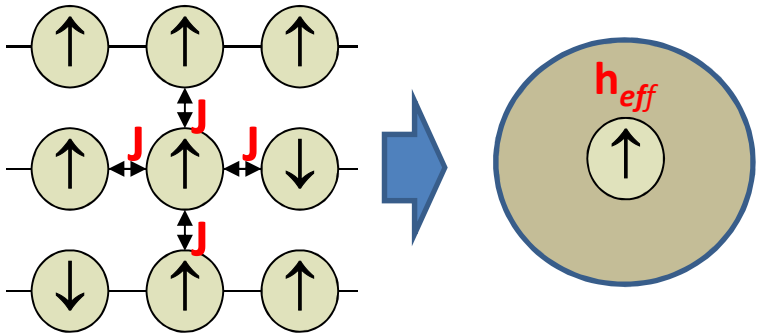
describing interaction of itinerant electrons with localized spins

AIM and Kondo model were solved in 70s-80s by several techniques (renormalization group, Bethe anzatz, large N-expansion), other numerical and analytical methods are available now

Mean-field theories: example of the Ising model

Ising model:

$$H = -\sum_{(ij)} J_{ij} S_i S_j - h \sum_i S_i$$



The average on-site magnetization is $m_i = \langle S_i \rangle$

We introduce a **mean field** $H_{eff} = -\sum_i h_i^{eff} S_i$ that reproduces given m_i :

$$m_i = \frac{e^{-\beta h_i^{eff}} - e^{\beta h_i^{eff}}}{e^{-\beta h_i^{eff}} + e^{\beta h_i^{eff}}} = \tanh(\beta h_i^{eff}) \longrightarrow \beta h_i^{eff} = \tanh^{-1} m_i$$

MF approximation= neglecting fluctuations of magnetization on neighboring sites:

$$h_i^{eff} = h + \sum_j J_{ij} m_j \simeq h + zJm$$

MF approximation

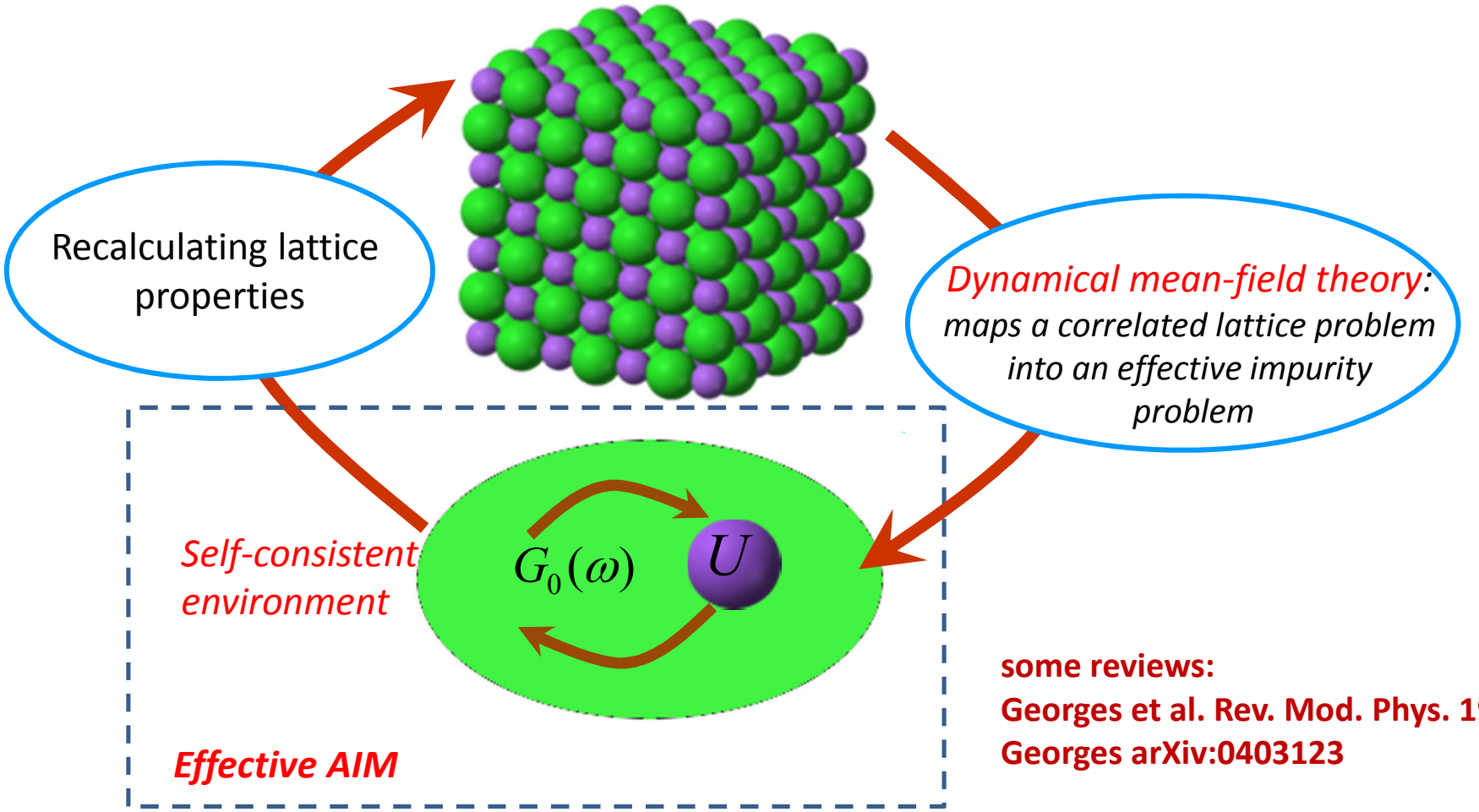
which allows one to obtain a closed equation for the magnetization:

$$m = \tanh(\beta h + z\beta J m)$$

It becomes exact in the limit of coordination number $z \to \infty$

Dynamical mean-field theory(DMFT)

Dynamical mean-field theory (**Metzner/Vollhard PRL 89** and **Georges/Kotliar PRB 92**) relates a correlated lattice problem (e.g. Hubbard model) to an auxiliary Anderson impurity model, which can then be solved

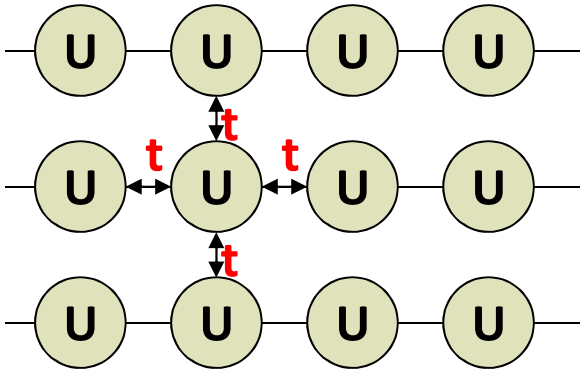


some reviews:
Georges et al. Rev. Mod. Phys. 1996
Georges arXiv:0403123

The dynamical mean-field theory: local GF and the bath

The lattice (Hubbard) model is described by the Hamiltonian:

$$H = -\sum_{ij,\sigma} t_{ij}\, c^{\dagger}_{i\sigma} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow} + \varepsilon_0 \sum_{i\sigma} n_{i\sigma}$$



and we may introduce local GF (in the imaginary time domain)

for a representative site: $G^{\sigma}_{ii}(\tau - \tau') \equiv -\langle T c_{i\sigma}(\tau) c^{\dagger}_{i\sigma}(\tau') \rangle$

and its Fourier transform $G_{ii}(i\omega_n)$

which is the *local* quantity («m_i ») coupled to *an effective bath* (the rest of the lattice)

The representative site is described by effective AIM:

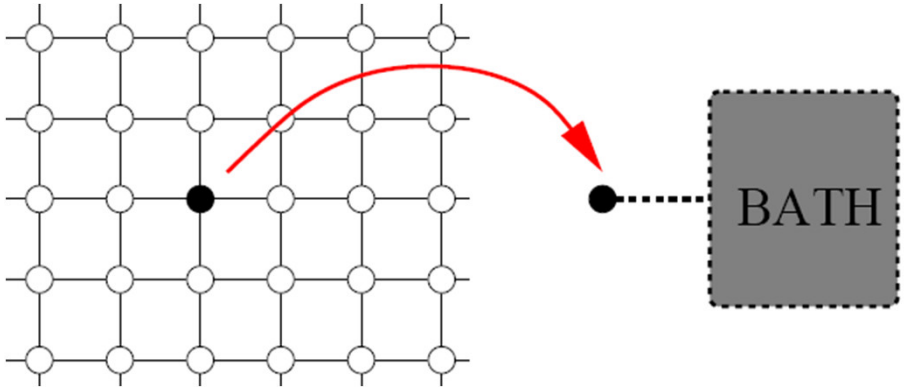
$$H_{AIM} = H_{atom} + H_{bath} + H_{coupling}$$

where

$$H_{atom} = U\, n^{c}_{\uparrow} n^{c}_{\downarrow} + (\varepsilon_0 - \mu)\,(n^{c}_{\uparrow} + n^{c}_{\downarrow})$$

$$H_{bath} = \sum_{l\sigma} \tilde{\varepsilon}_l\, a^{\dagger}_{l\sigma} a_{l\sigma}$$

$$H_{coupling} = \sum_{l\sigma} V_l\,(a^{\dagger}_{l\sigma} c_{\sigma} + c^{\dagger}_{\sigma} a_{l\sigma})$$



where $a^{\dagger}_{l\sigma}$ / $a_{l\sigma}$ are the *bath* degrees of freedom

DMFT: the hybridization and bath Green's functions

The electron hopping on/off the impurity is thus described by the ***bath Green's function***:

$$\mathcal{G}_0^{-1}(i\omega_n) = i\omega_n + \mu - \varepsilon_0 - \Delta(i\omega_n)$$

and the **interaction term** $U\hat{n}_\uparrow\hat{n}_\downarrow$ it defines an effective Anderson impurity problem for a single correlated atom. Solution of this **quantum impurity problem** gives one the local Green's function.

One needs then to obtain the **effective field** $\mathcal{G}_0(\tau - \tau')$ in terms of a **local quantity**.

defining the **local self-energy** : $\Sigma_{imp}(i\omega_n) \equiv \mathcal{G}_0^{-1}(i\omega_n) - G^{-1}(i\omega_n)$

and lattice GF and self-energy**:** $G(\mathbf{k}, i\omega_n) = \dfrac{1}{i\omega_n + \mu - \varepsilon_0 - \varepsilon_\mathbf{k} - \Sigma(\mathbf{k}, i\omega_n)}$

we introduce the key **mean-field approximation**:

$$\Sigma(k, i\omega_n) \cong \Sigma_{imp}(i\omega_n)$$

i.e. **the self-energy is purely local.** One obtains the DMFT **self-consistency condition**:

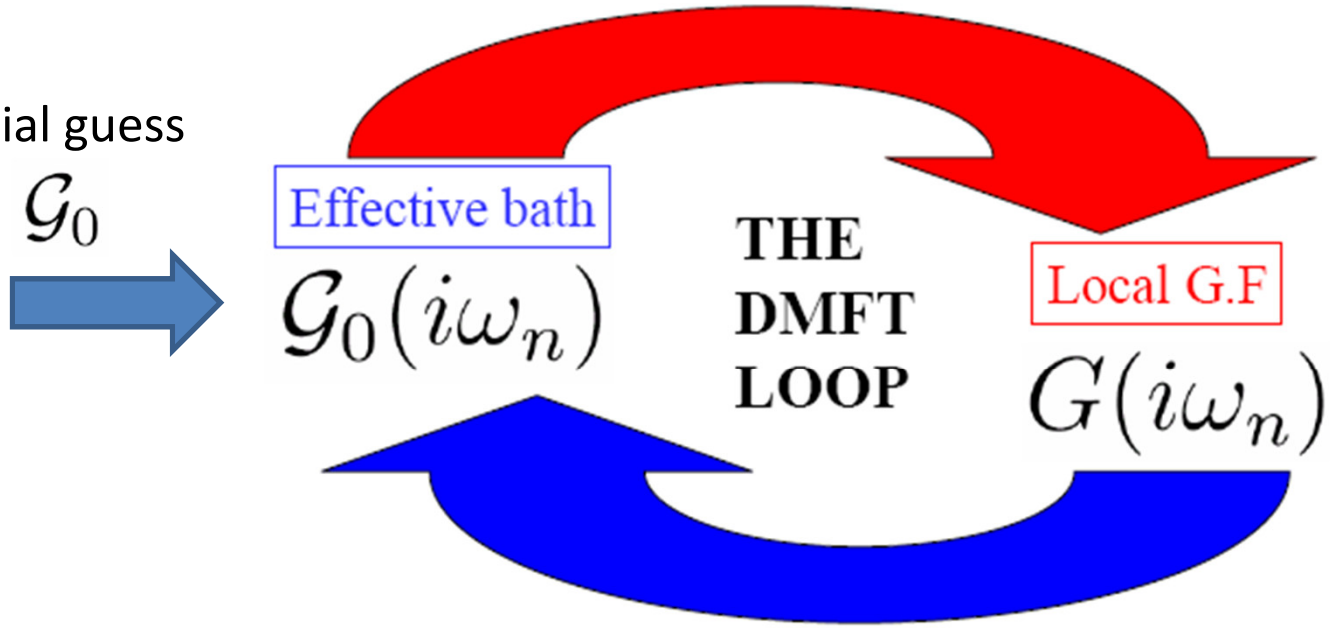
$$\sum_\mathbf{k} \frac{1}{\Delta(i\omega_n) + G(i\omega_n)^{-1} - \varepsilon_\mathbf{k}} = G(i\omega_n)$$

Iterative solution of DMFT equations

In practice one searches for the true Weiss field $\mathcal{G}_0(\tau-\tau')$ using an iterative procedure

EFFECTIVE LOCAL IMPURITY PROBLEM

Initial guess for $\mathcal{G}_0$



SELF-CONSISTENCY CONDITION

$$\Sigma_{imp} = \mathcal{G}_0^{-1}(i\omega_n) - G_{imp}^{-1}(i\omega_n)$$

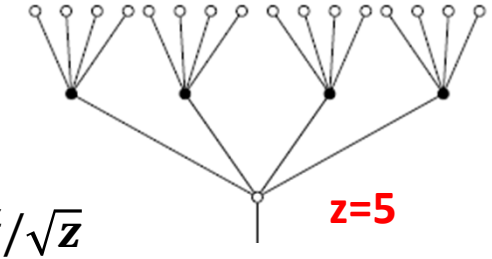
$$G_{loc} = \sum_{\mathbf{k}} [i\omega_n + \mu - \varepsilon_{\mathbf{k}} - \Sigma_{imp}(i\omega_n)]^{-1}$$

updated $\mathcal{G}_0$ $\quad \mathcal{G}_{0,new}^{-1} = G_{loc}^{-1} + \Sigma_{imp}$

DMFT capturing the Mott transition: d→∞ 1-band case

$$\hat{H}_{\mathrm{Hub}} = -t \sum_{\langle i,j\rangle,\sigma} \left(\hat{c}^{\dagger}_{i\sigma} \hat{c}_{j\sigma} + \mathrm{h.c.} \right) + U \sum_{i} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$

on the « tree-like » Bethe lattice



with z→∞ : $t = \tilde{t}/\sqrt{z}$

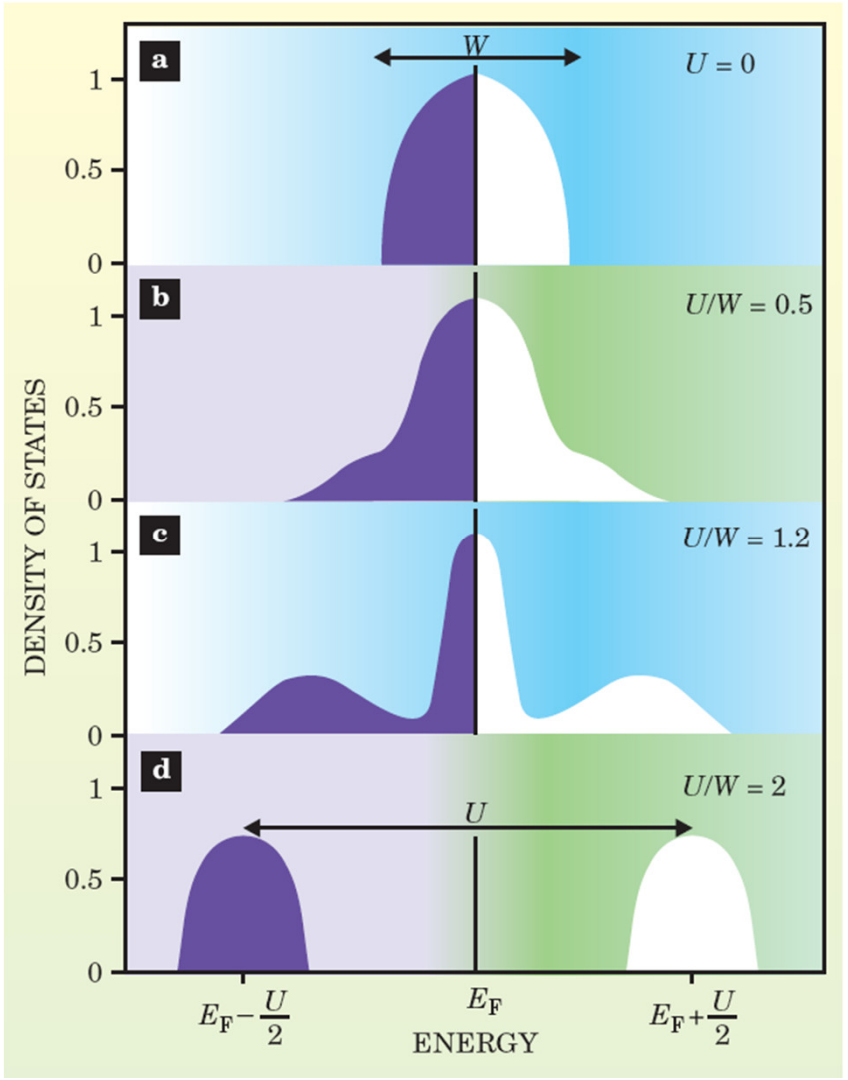
has a particular simple DMFT self-consistency condition (see **Georges et al. Rev. Mod. Phys. 96**)

- **Non-interacting case:** metal with semi-circular DOS
- **Insulating limit:** lower and upper Hubbard bands each containing 1electron/site and separated by the gap ~U
- Conecting those two limits:

  with increasing U/W the system passes through a correlated metal regime (3-peak structure)

  followed by **the Mott transition**.

1b Model evolution vs. U/W



G. *Kotliar* and D. Vollhardt, *Physics Today* 57, 53 (2004).

An approach for real materials: DFT+DMFT framework

Combining ab initio band DFT methods with a DMFT treatment of correlated shells

$$H = -\sum_{\substack{i,j \\ \Lambda,\Lambda'}} t_{ij}^{\Lambda\Lambda'} c_{i\Lambda}^{+} c_{j\Lambda'} + \sum_{i,\lambda_{1\ldots4}} U_{\lambda_1\lambda_2\lambda_3\lambda_4} c_{i\lambda_1}^{+} c_{i\lambda_2}^{+} c_{i\lambda_3} c_{i\lambda_4} = H_{one-el} + H_{\mathrm{int}\,r} - H_{DC}$$

from DFT-LDA

Crucial ingredients:

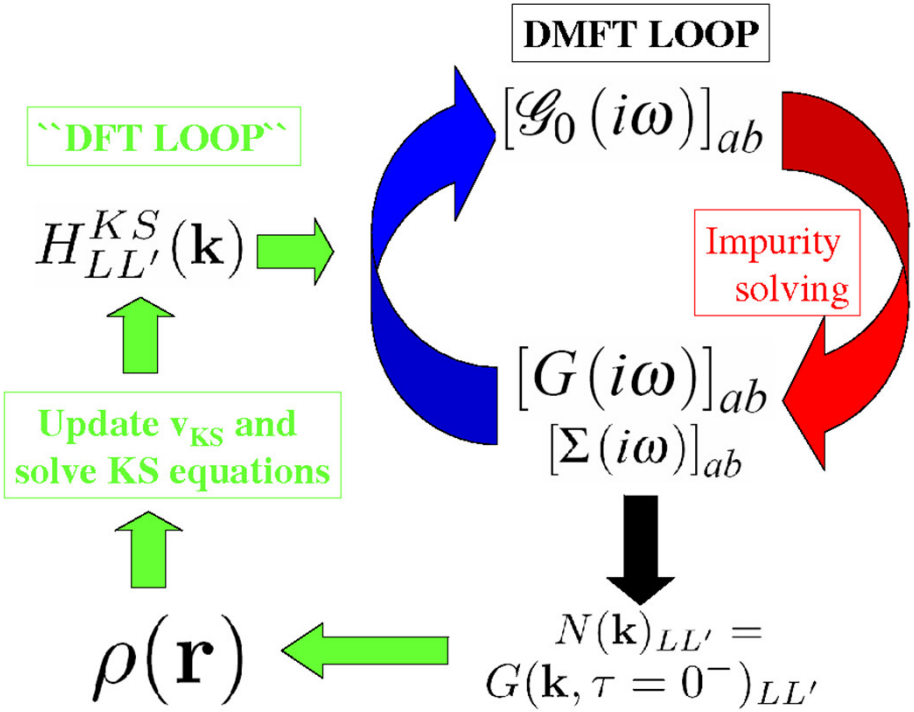
→ choice of the **localized basis** representing correlated states

→ choice of the **interaction vertex**

→ DMFT **impurity solvers**

→ self-consistency in the charge density

(Anisimov et al. 1997, Lichtenstein et al. 1998, Review: Kotliar et al. Rev. Mod. Phys. 2006)



Choice of the correlated basis: Wannier functions

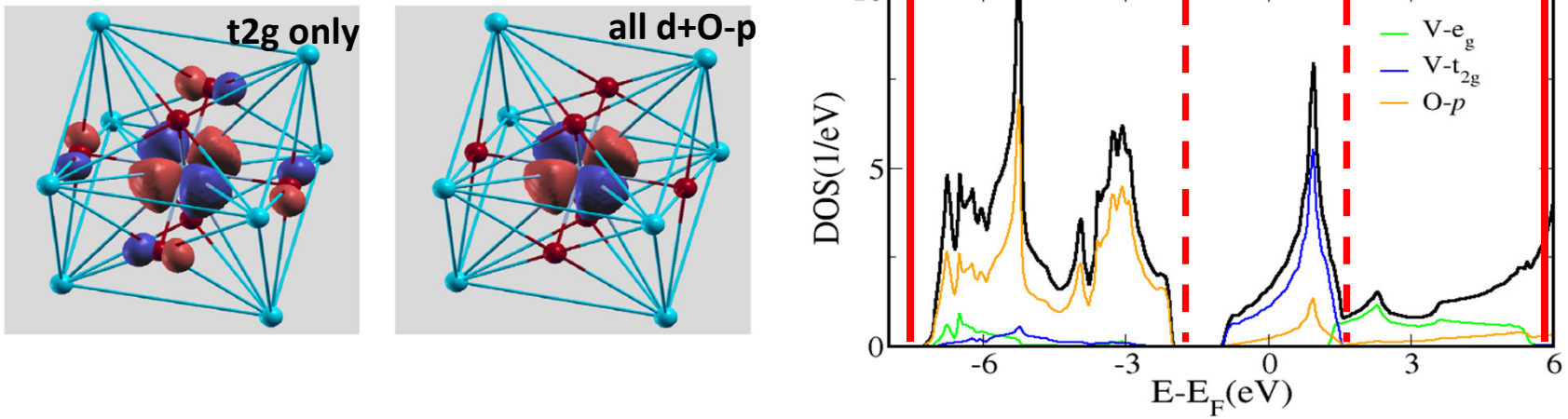
Wannier functions are constructed from Bloch eigenstates of the KS problem

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

or in the *k*-space: $\left|w_{i\vec{k}}\right\rangle = \sum_{\nu\in W} U^{(k)}_{i\nu}\left|\psi_{\vec{k}\nu}\right\rangle$

Optimizing $\boldsymbol{U}^{(\vec{k})}$ and increasing the range of bands $\boldsymbol{W}$ one may increase the localization of WF

Example: peroxide SrVO3



Advantage: **flexible, can be interfaced with any band structure method**

Disadvantage: **requires Wannier orbitals' construction**

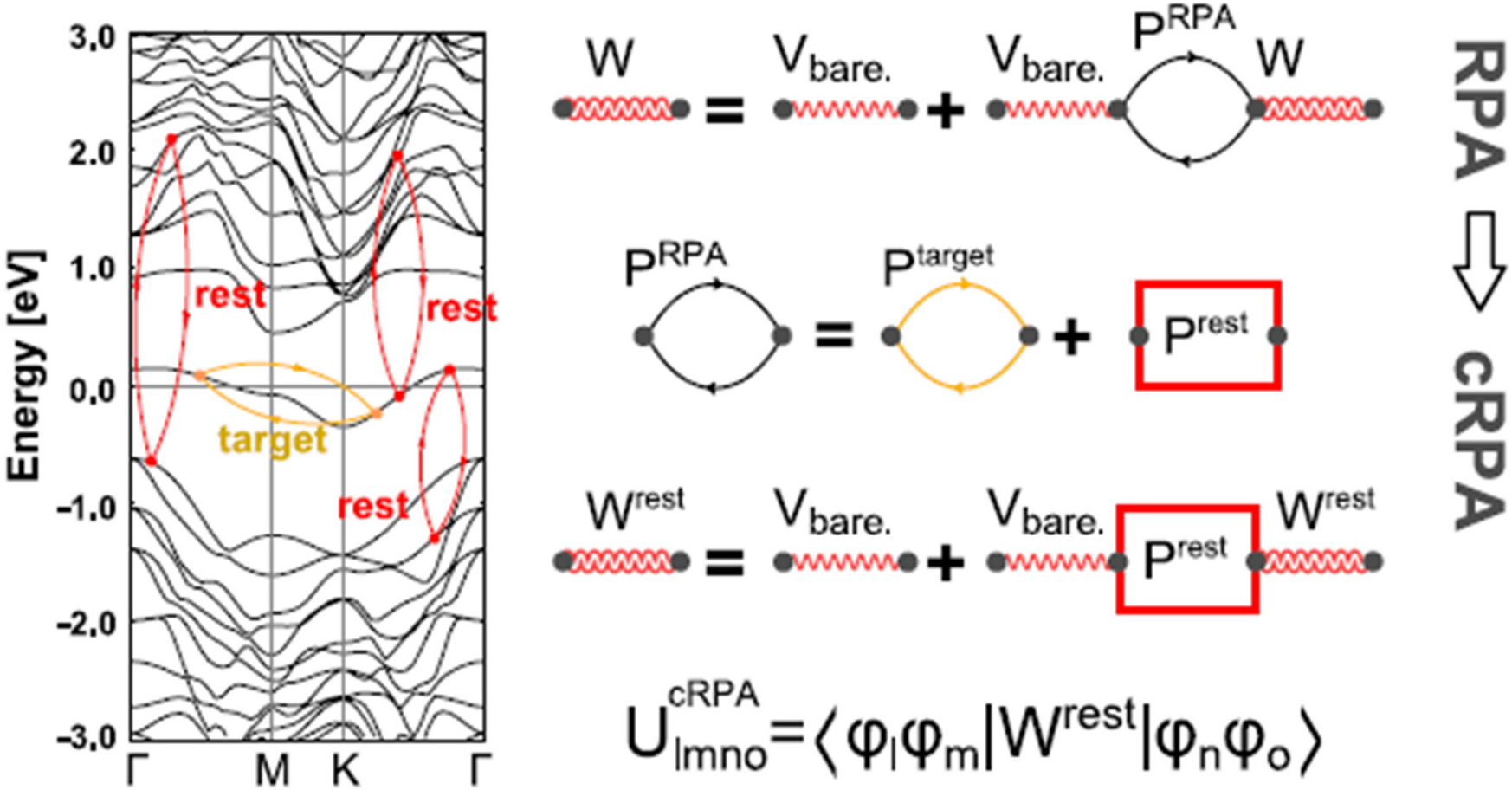
(see Marzari and Vanderbilt PRB 1997, Amadon *et al.* PRB 2008, Aichhorn *et al.* PRB 2009)

other choices for correlated basis: atomic-like "partial waves", NMTO etc.

Evaluating local Coulomb interaction

U can be adjusted to some experiment, or evaluated, e.g., by

Constrained Random Phase Approximation



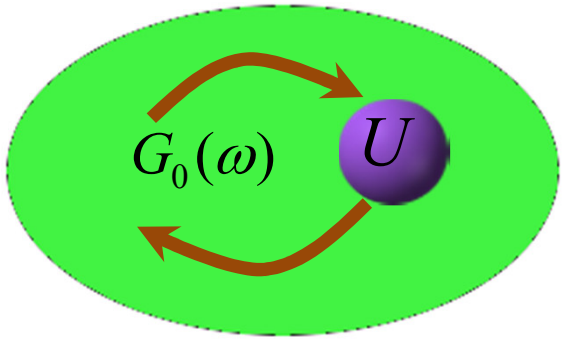
Aryasetiawan, Imada, Georges, Kotliar, Biermann, Lichtenstein, PRB 2004.

[Figure from Hansmann et al., JPCM 2013]

Quantum impurity solvers

Impurity problem defined by the following action:

$$S = -\int_0^\beta \mathrm{d}\tau \mathrm{d}\tau' \sum_{\alpha,\beta} c_\alpha^\dagger(\tau) G_{0,\alpha\beta}^{-1}(\tau,\tau') c_\beta(\tau') + \int_0^\beta \mathrm{d}\tau H_{\mathrm{int}}$$



Effective impurity problem

Result: $G_{\alpha\beta}(\tau) = -\left\langle T\left[c_\alpha(\tau)c_\beta^\dagger(0)\right]\right\rangle \rightarrow \Sigma(i\omega_n)$

- **Numerical methods:**

  Quantum Monte-Carlo (QMC) family, e.g. **continious-time QMC**: stochastic summation of diagramatic contributions into one-electron Green's function G(τ) and/or more complicated two-electron GF $G_{\alpha\beta\gamma\delta}(\tau,\tau_1,\tau_2) = \left\langle T\left[c_\beta^\dagger(\tau)c_\alpha(\tau_1)c_\beta^\dagger(\tau_2)c_\alpha(0)\right]\right\rangle$

  Exact diagonalization method: G_0 is approximated by a discrete set of fictitious atomic levels coupled to the physical ones:

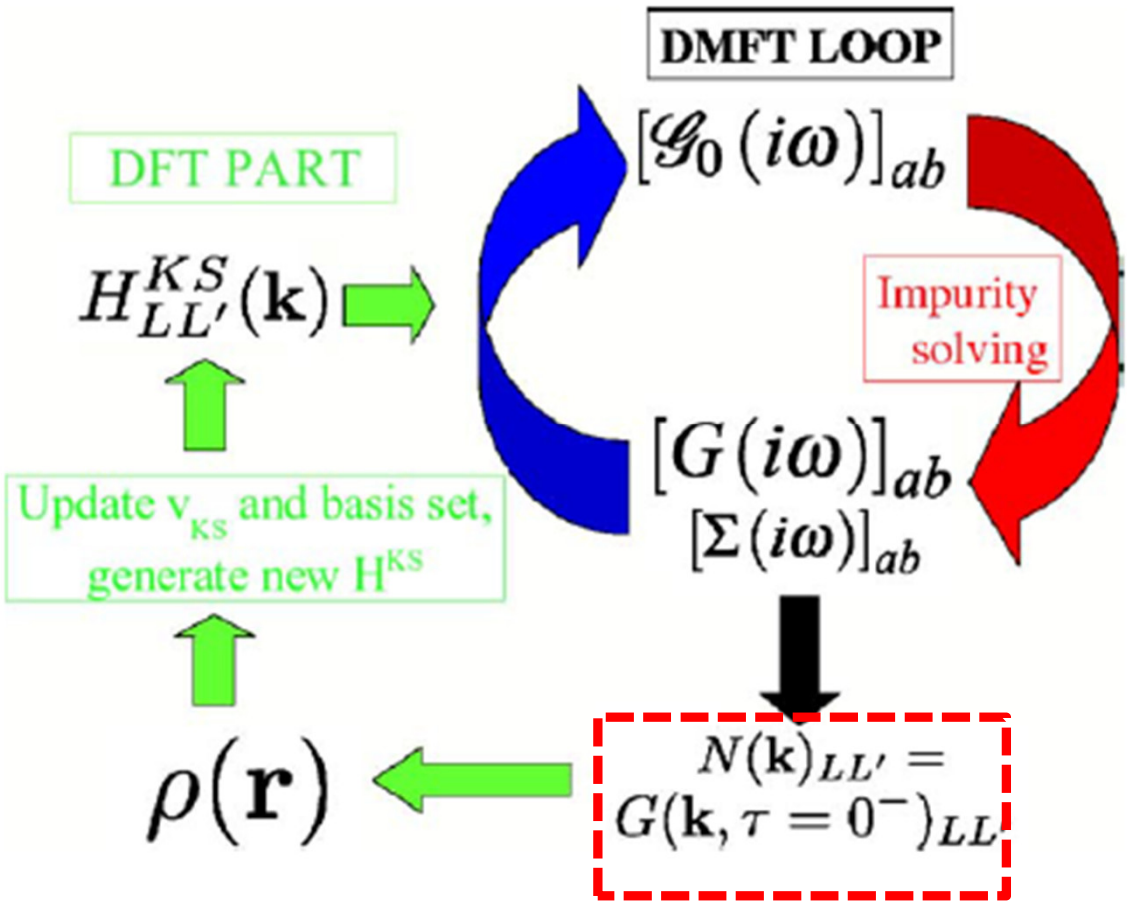
$$G_0 = i\omega_n + \mu - \sum_{p=2}^{n_s} \frac{V_p^2}{i\omega_n - \tilde{\epsilon}_p}$$

  the Hamiltonian describing the real interacting level coupled to n_s fictitious ones is then diagonalized

- **Analytical methods:** resummation of a subset of diagrams around non-interacting (FLEX,RPA) or atomic (non-crossing (NCA), one-crossing (OCA) approximations

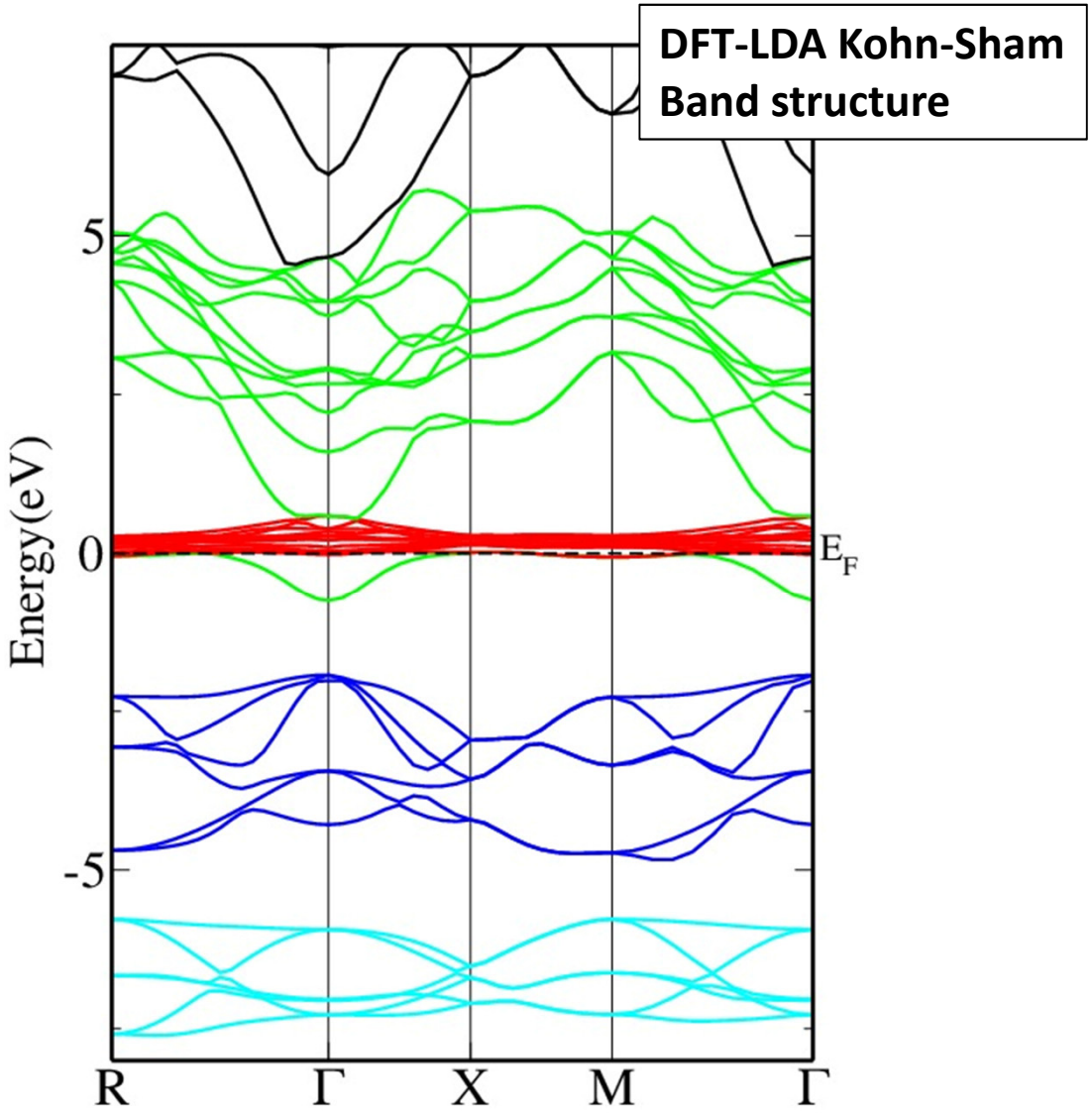
see more in, e.g., Kotliar *et al.* Rev. Mod. Phys. 2006, Gull *et al.* Rev. Mod. Phys. 2010

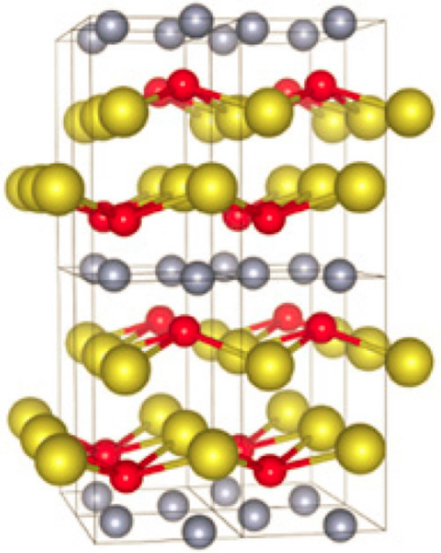
Fully self-consistent DFT+DMFT: updating charge



See Pourovskii et al. PRB 2007, Aichhorn et al., PRB 2011; Haule PRB 2009.

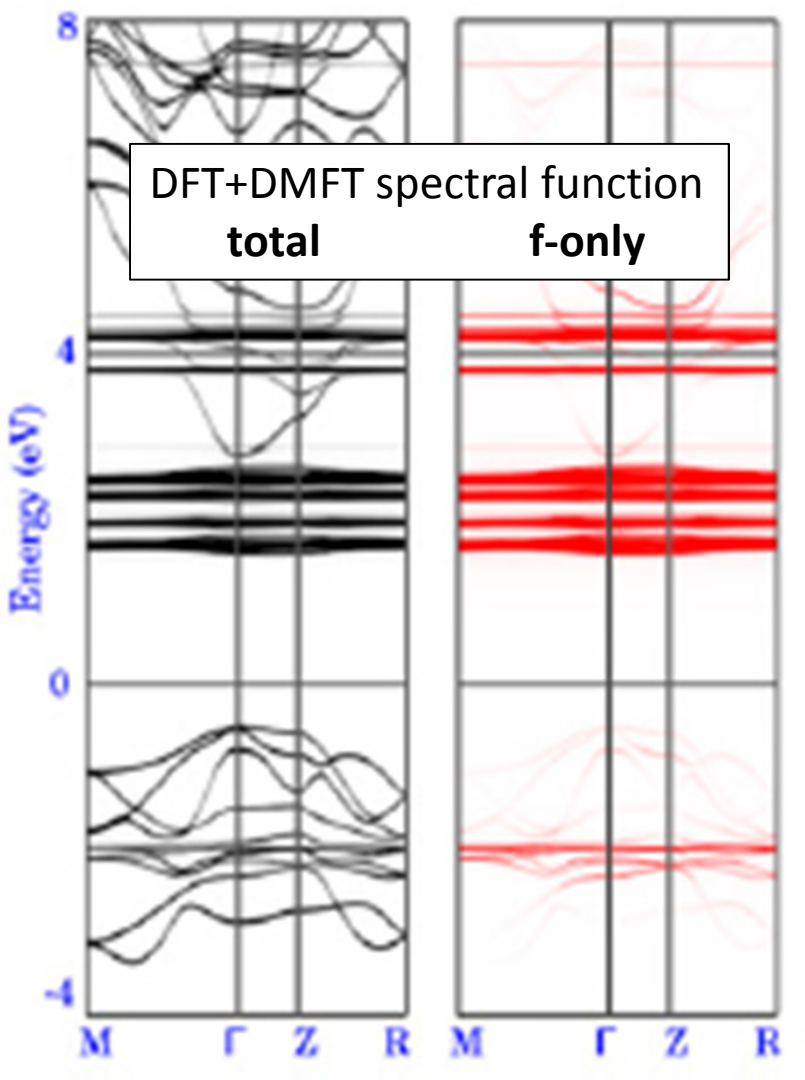
Reminder: DFT picture for the red pigment CeSF



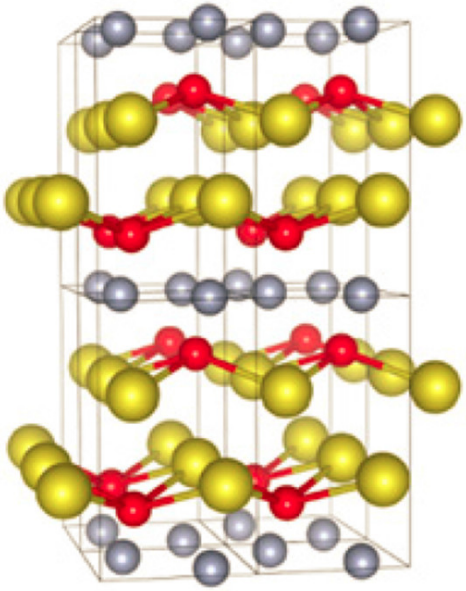


A metal!

4*f*-electron pigment CeSF with DFT+DMFT



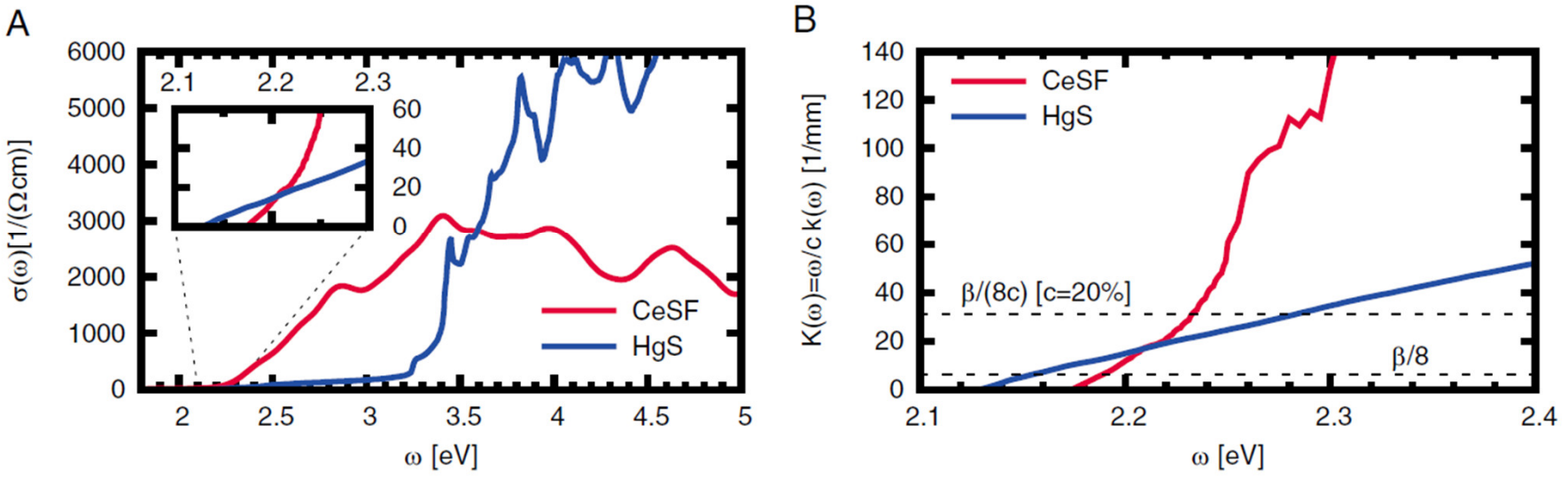
Ce: $4f^1$ configuration, paramagnetic



U=4.8 eV and J=0.7 eV from cRPA

Tomczak, Pourovskii, Vaugier, Georges, Biermann, PNAS 2013

4*f*-electron pigment CeSF with DFT+DMFT: optical conductivity (A) and absorption (B)



diffuse reflectance

Calculated color of CeSF:

Tomczak, Pourovskii, Vaugier, Georges, Biermann, PNAS 2013