Dynamical Mean Field Theory (DMFT) and DFT+DMFT

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DFT: an electron in the **effective field** of other electrons
DMFT: a correlated atom in the **effective field** of other atoms

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  - The effective field is frequency dependent = energy levels generating the field are distributed in energy.
  - In contrast to static mean field theory of ferromagnetism in the Ising model.
  - The frequency dependence of this field is not created by interactions but is required to treat the correlated atom.

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    - In contrast to static mean field theory of ferromagnetism in the Ising model.
    - The frequency dependence of this field is not created by interactions but is required to treat the correlated atom.
- **Dynamical** : the self-energy is frequency dependent, in contrast to DFT+U and DFT, allowing to describe strong correlations and its features in photoemission.

Why using Dynamical Mean Field Theory ?

Describe solids with strong correlations, static correlations

	Correlation		Can compute		Solids	No Parameters	Non Perturbative
	Weak correlation	Strong correlation	Spectra	Structure			
Single reference methods							
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Other methods							

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Other methods							
QMC	+			+	+	+	+

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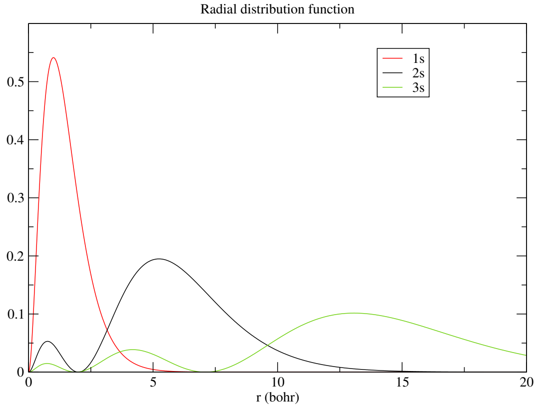
Other methods							
QMC	+			+	+	+	+
RDMFT	+		+	+	+	+	+

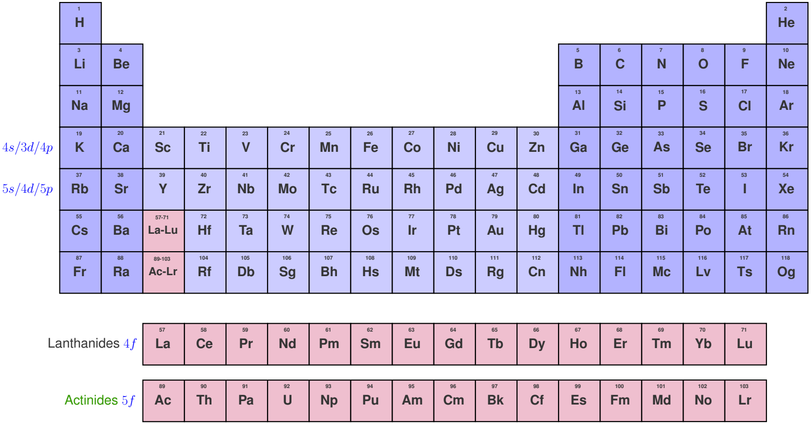
Atomic orbitals 1s, 2s and 3s



$\Psi_{nlm}(\mathbf{r}) = R_{nl}(r)Y_{lm}(\theta, \phi)$

Radial distribution function is $(rR_{nl}(r))^2$

THE PERIODIC TABLE



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	55 Cs	56 Ba	57-71 La-Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
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Actinides $5f$			89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

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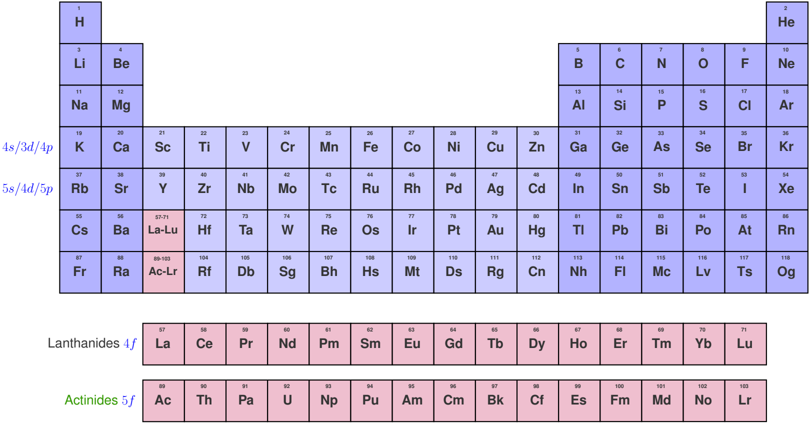

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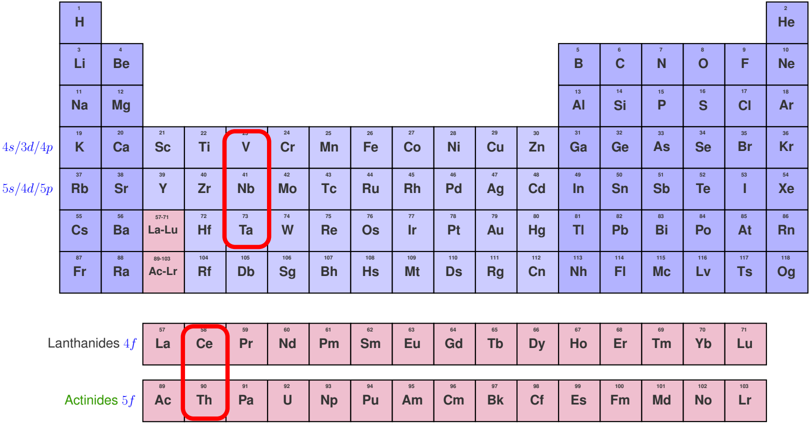

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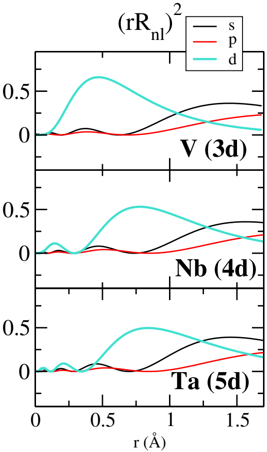
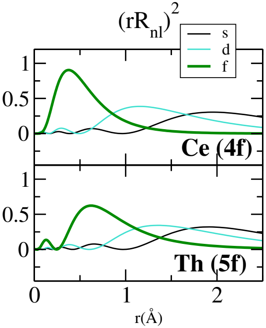
Localization of $3d$, $4f$ and $5f$ orbitals.



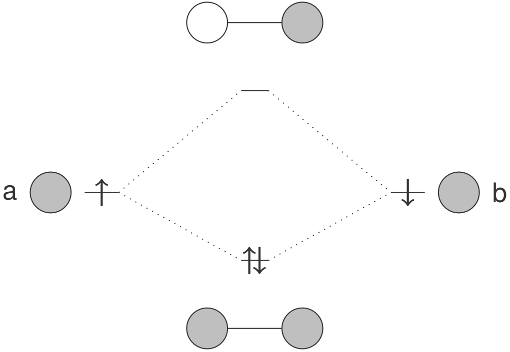


- $\Psi_{nlm}(\mathbf{r}) = R_{nl}(r)Y_{lm}(\theta, \phi)$
- For $1s, 2p, 3d, 4f$, R has no node, their maxima are thus closer to the nucleus
- $3d$ and $4f$ orbitals are more localized.

Hydrogen Molecule

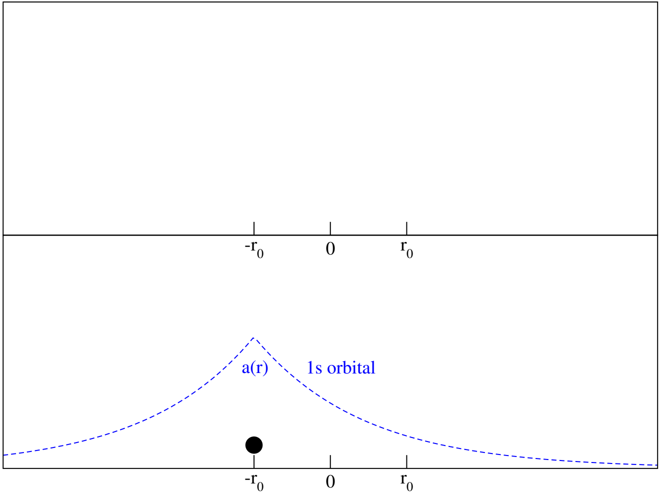
Non diagonal elements of the Hamiltonian creates chemical bonding

antibonding state $\sigma_u = \frac{a-b}{\sqrt{2}}$

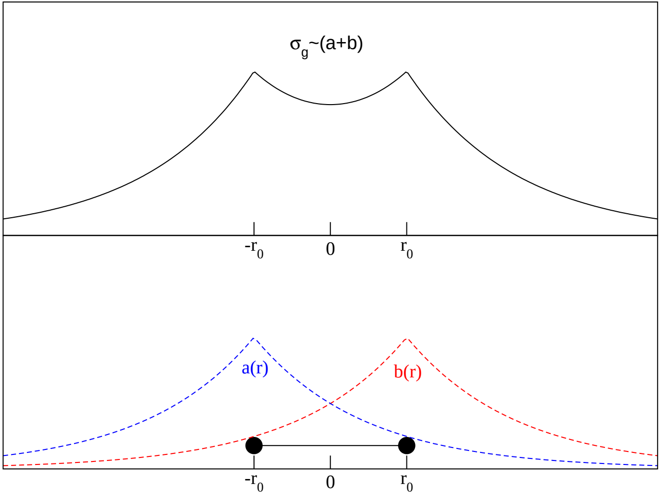


bonding state $\sigma_g = \frac{a+b}{\sqrt{2}}$

Hydrogen atom: 1s orbital

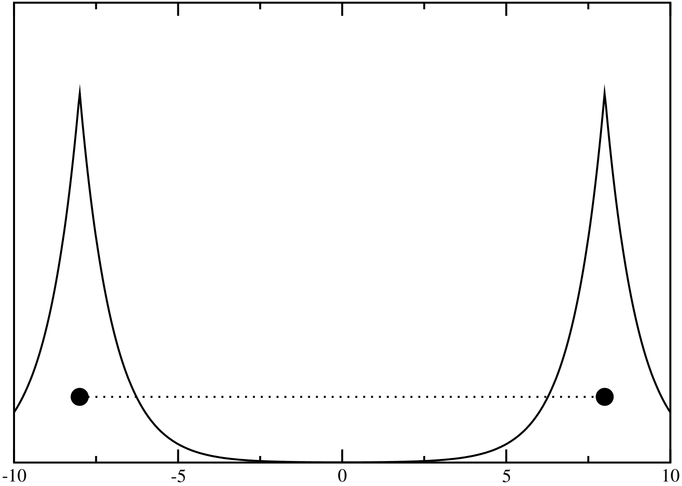


Hydrogen molecule: molecular orbital.

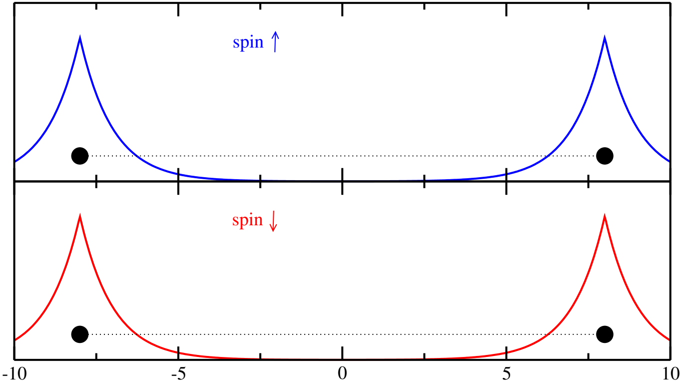


$$\sigma_g = \frac{a+b}{\sqrt{2}}$$

Hydrogen molecule: stretched.



Hydrogen molecule: same orbital for both spins !



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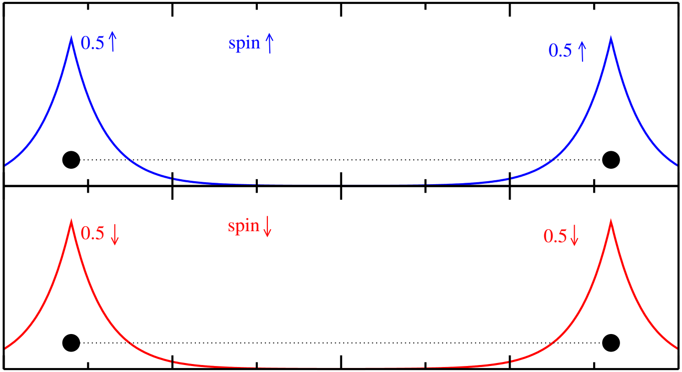
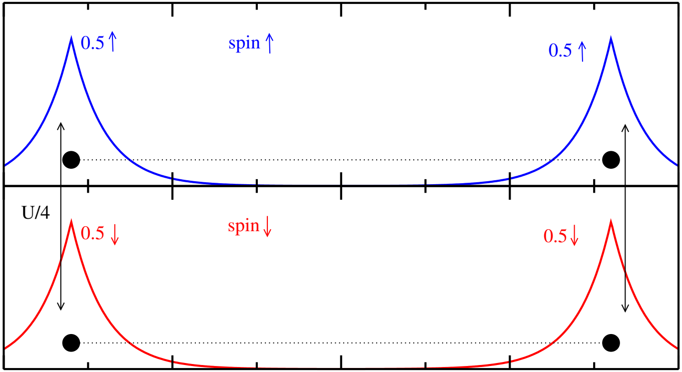
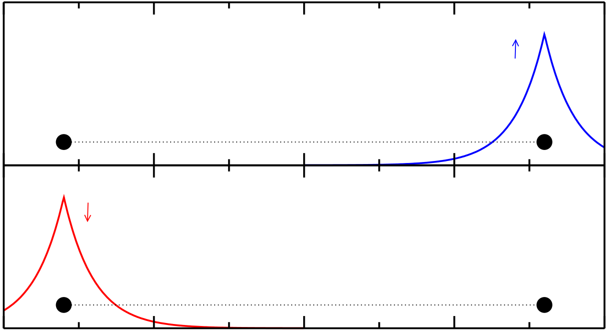


Hydrogen molecule: dissociation limit is bad



A solution: break symmetry

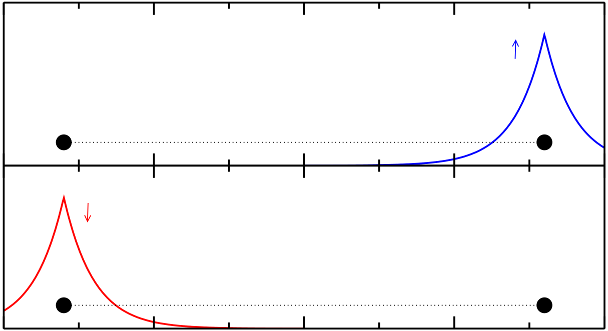


no more artificial delocalization, no more interaction

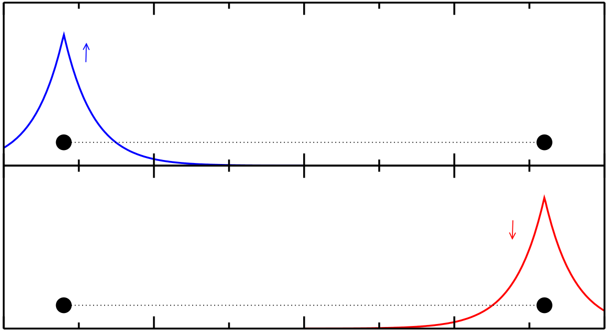
But

- Symmetry breaking. An artificial magnetism is induced.
- A static theory, which overestimates localization.

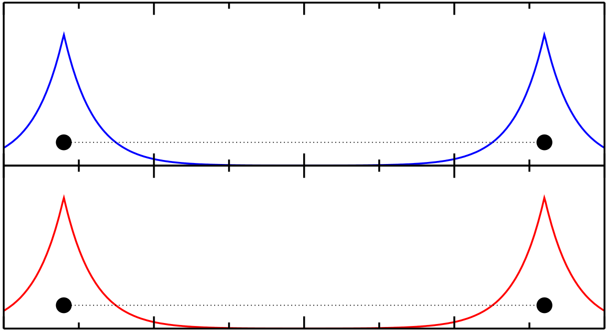
Solution 1: localization: lowers interaction



Solution 2: localization: lowers interaction

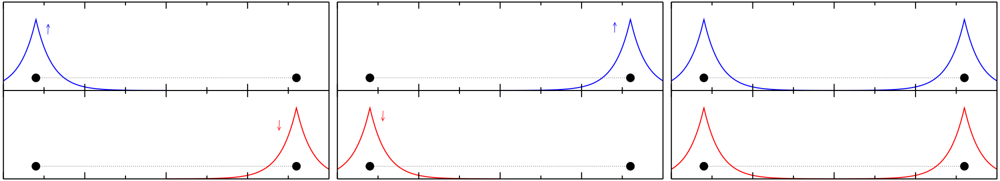


Solution 3: delocalization: lowers kinetic energy



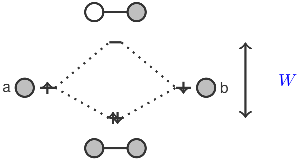
The exact solution

$$|\Psi\rangle = c_1|1 : \text{localized} \uparrow\downarrow\rangle \quad + c_2|2 : \text{localized} \downarrow\uparrow\rangle \quad + c_3|3 : \text{delocalized}\rangle$$



- This mixing of configuration correctly describes the system (magnetism, structural properties).
    - $c_1 = c_2$: no ordered magnetism.
    - c_3 increases if distance between atoms lowers.

- If $W >> U$ then $c_1 = c_2 << c_3$
- If $W << U$ then $c_1 = c_2 >> c_3$



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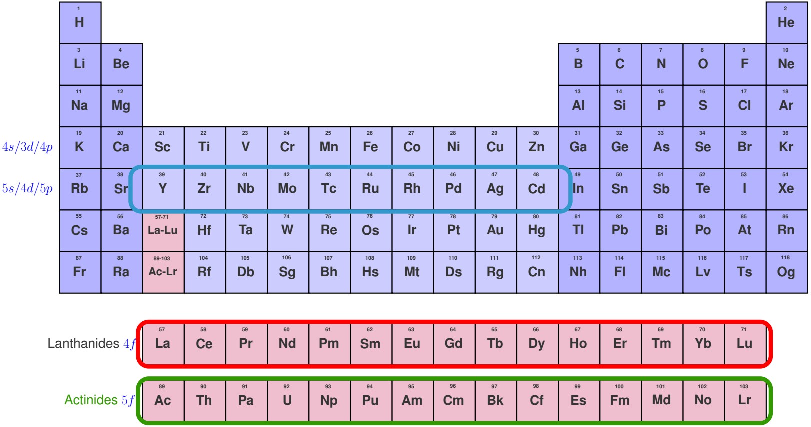

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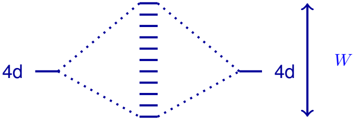
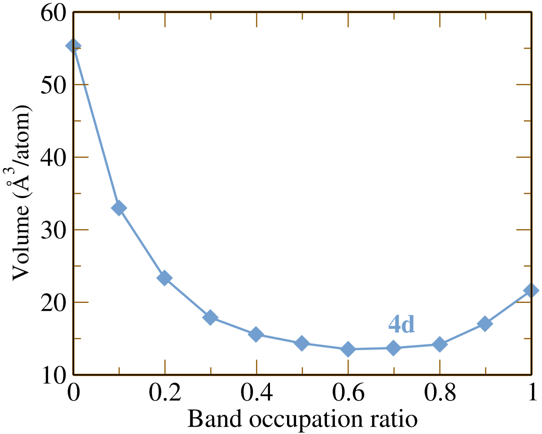
Localization in f electrons systems

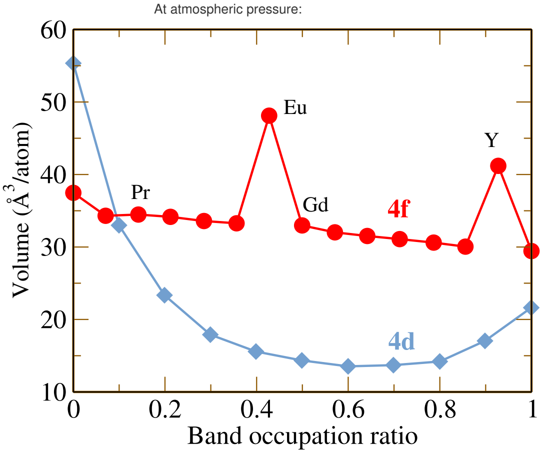


At atmospheric pressure:



[Mac Mahan, et al J. Comp.-Aid. Mater. Des. 5, 131 (1998)]

Localization in f electrons systems



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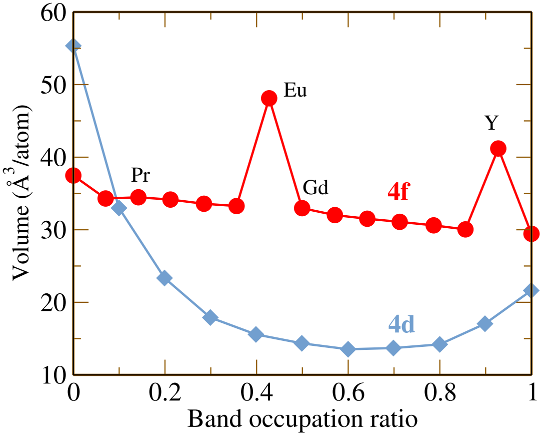
Localization in f electrons systems

Ln $4f^n(6s5d)^3$

Eu $4f^6(6s5d)^3 \Rightarrow 4f^7(6s5d)^2$

Yb $4f^{13}(6s5d)^3 \Rightarrow 4f^{14}(6s5d)^2$

At atmospheric pressure:



[Mac Mahan, et al J. Comp.-Aid. Mater. Des. 5, 131 (1998)]

Isostructural transition in Cerium

Isostructural transition $\frac{V_\gamma - V_\alpha}{V_\gamma} = 15\%$, ends at a critical point

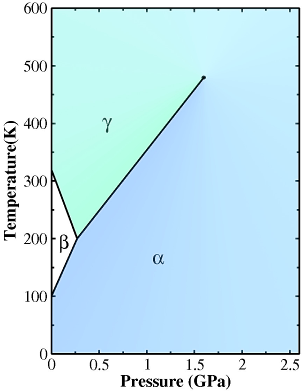
Electronic configuration 4f^1.

- α phase: Pauli paramagnetism

  $\Rightarrow$ α phase: f e^- more delocalized.

- γ phase: Curie Paramagnetism

  $\Rightarrow$ γ phase: f e^- is localized



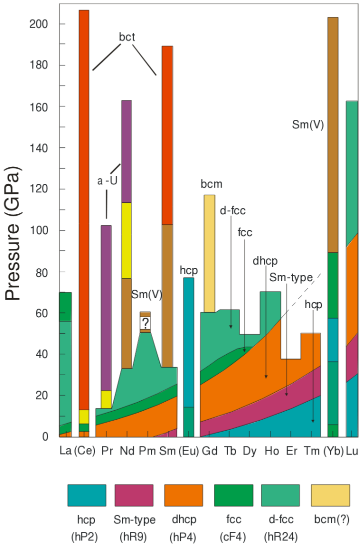
[Johansson, B. Phil. Mag. **30**, 469 (1974)]

Transition in lanthanides.

We now discuss the equation of states of lanthanides as a function of pressure.

- At low pressure, compact structures.
- Under pressure, more distorted structure
  - f electrons participate to the bonding

Figure from [Schiwek, (2002)]



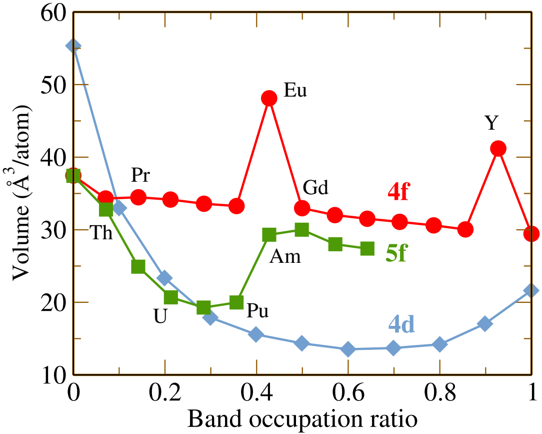
Localization in f electrons systems

$4d$ element: filling of the $4d$ band (Bonding states and antibonding): $4d$ electrons are **delocalized**.

Lanthanides: $4f$ electrons **localized**, negligible overlap between $4f$ orbitals .

Actinides: intermediate case of localization.

At atmospheric pressure:



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THE EXACT HAMILTONIAN

The exact hamiltonien is (i, j are electrons)

$$H = \sum_{i=1}^{N} [-\frac{1}{2}\nabla^2_{\mathbf{r}_i} + V_{\text{ext}}(\mathbf{r}_i)] + \frac{1}{2}\sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

THE EXACT HAMILTONIAN

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$$H = \sum_i \epsilon_0 (\underbrace{n_{i\uparrow}}_{c^\dagger_{i\uparrow} c_{i\uparrow}} + n_{i\downarrow}) + \underbrace{\sum_{j \neq i, \sigma = \uparrow,\downarrow} t_{ij} c^\dagger_{i\sigma} c_{j\sigma}}_{\text{one electron term : delocalization}} + \underbrace{\sum_i U \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}}_{\text{interaction term : localization}}$$

The Hubbard model: Competition between localization and delocalization

$$H = \sum_i \epsilon_0 (n_{i\uparrow} + n_{i\downarrow}) + \sum_{j \neq i, \sigma=\uparrow,\downarrow} t_{ij} c^\dagger_{i\sigma} c_{j\sigma} + \sum_i U \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$

U is the energy repulsion of two electrons on the same site.

- For large value of the interaction U, electrons are localized
- For low value of the interaction U, electrons are delocalized

The Hubbard model $U = 0$

In this limit, we neglect the interaction term.

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$$|\psi_k\rangle = \frac{1}{\sqrt{N}} \sum_i |\phi_{T_i}\rangle \mathrm{e}^{ikT_i}$$

where $|\phi_{T_i}\rangle$ are atomic orbitals: $\langle r|\phi_{T_i}\rangle = \phi(r - T_i)$ on site i. Does it satisfy the Bloch theorem (cf lecture by V. Robert) ?

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$$\psi_k(r+T) = \frac{1}{\sqrt{N}} \sum_i \phi_{T_i}(r+T) \mathrm{e}^{ikT_i} = \frac{1}{\sqrt{N}} \sum_i \phi(r + T - T_i))\rangle \mathrm{e}^{ikT_i}$$

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We also have the change of basis for creation and annihilation operators:

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As a consequence, one can show that (using that $\frac{1}{N}\sum_i \mathrm{e}^{i(k-k')T_i} = \delta_{kk'}$ show it!).

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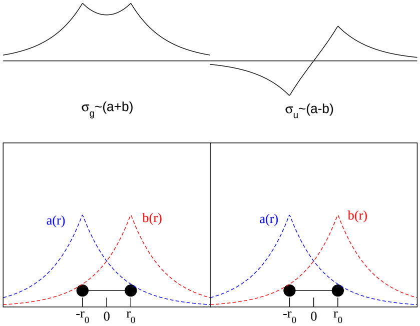
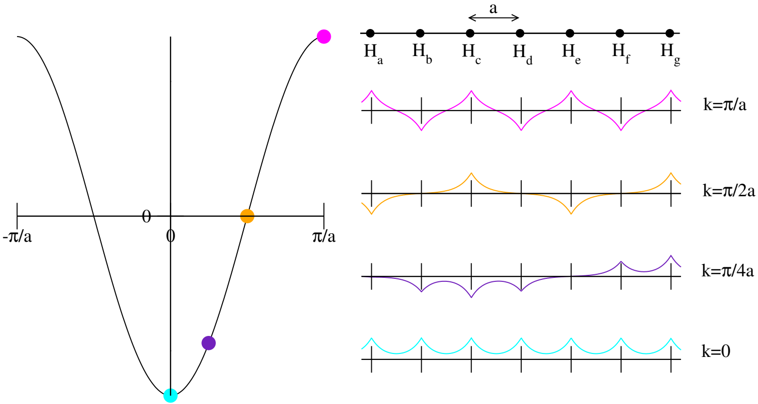
Toward the 1D chain: H_2

- **For hydrogen molecule**, hopping t induces a bonding state and an antibonding states for the molecule.



The chain of atoms: $\epsilon_k = \epsilon_0 + 2t\cos(ka)$ $\qquad t < 0$



$$\psi_k(\mathbf{r}) = \sum_i \mathrm{e}^{i\mathbf{k}T_i}\phi(\mathbf{r}-T_i) = \mathrm{e}^{i\mathbf{k}(\mathbf{r})}\sum_n \mathrm{e}^{-i\mathbf{k}(\mathbf{r}-T_i)}\phi(\mathbf{r}-T_i) = \mathrm{e}^{i\mathbf{k}(\mathbf{r})}u_{\mathbf{k}}(\mathbf{r}) \qquad [T_i = ia]$$

Hubbard model with $t = 0$

$$H = \sum_i \epsilon_0 (n_{i\uparrow} + n_{i\downarrow}) + \cancel{\sum_{j \neq i, \sigma = \uparrow, \downarrow} t_{ij} c^\dagger_{i\sigma} c_{j\sigma}} + \sum_i U \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$

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Atoms are disconnected, one can study one single atom !

$$H = \sum_i [\epsilon_0 (n_{i\uparrow} + n_{i\downarrow}) + U \hat{n}_{i\uparrow}\hat{n}_{i\downarrow}] = \sum_i H^i_{\text{atomic}}$$

Hubbard model with $t = 0$

The isolated atom limit: $t = 0$

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How many electrons can we put in this system ?

Hubbard model with $t = 0$

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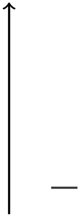

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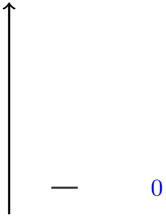

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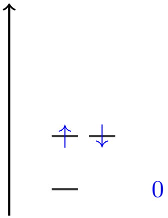

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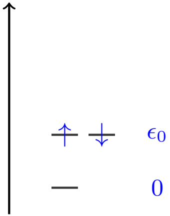

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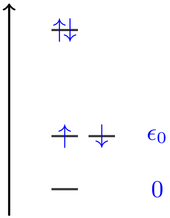

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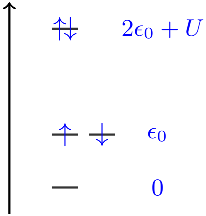

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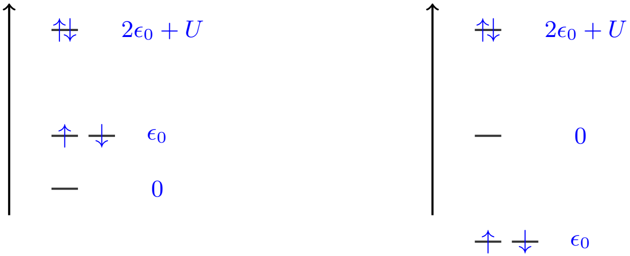

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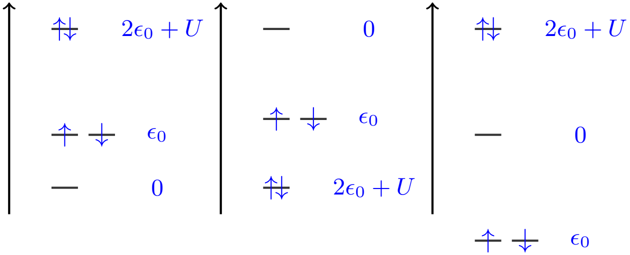
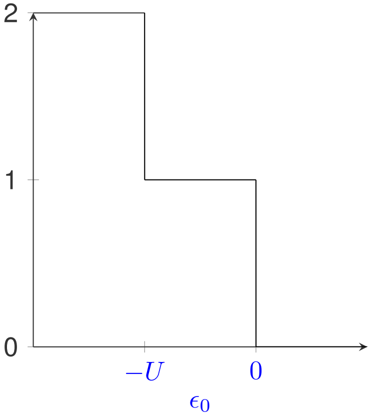
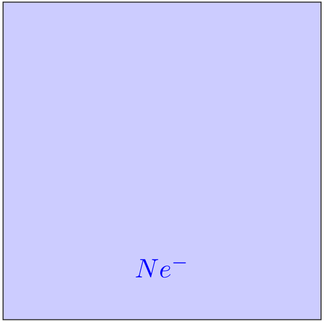
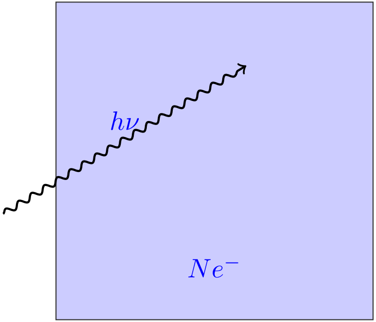




Direct photoemission


Ne^-

Direct photoemission



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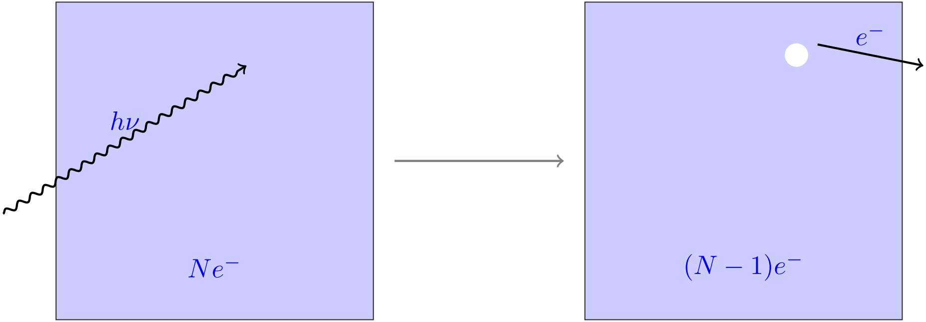
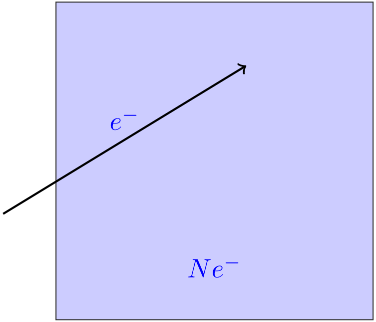


$$h\nu + E_N = E_{\rm kin} + E_{N-1}$$

One can measure $E_N - E_{N-1}$

cf also F. Bruneval lecture.

Inverse photoemission



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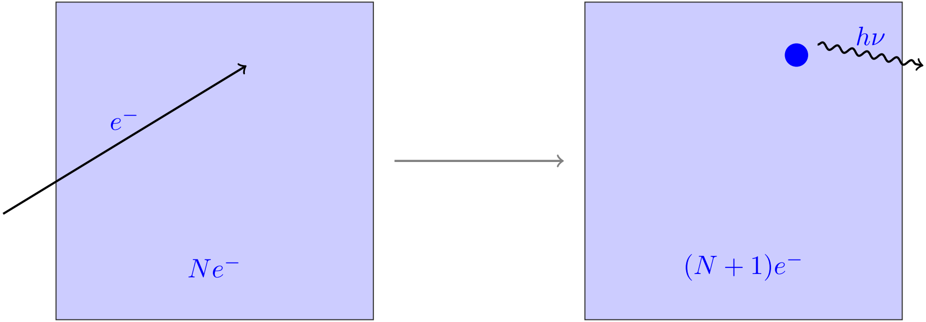


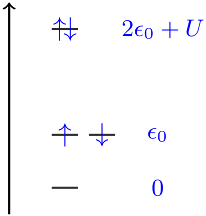
$$E_{\text{kin}} + E_N = h\nu + E_{N+1}$$

One can measure $E_{N+1} - E_N$

Hubbard bands

The isolated atom limit: $t = 0$

$$H = U n_\uparrow n_\downarrow + \epsilon_0 (n_\uparrow + n_\downarrow) = U n_\uparrow n_\downarrow + \epsilon_0 (n_\uparrow + n_\downarrow)$$



$2\epsilon_0 + U$

ϵ_0

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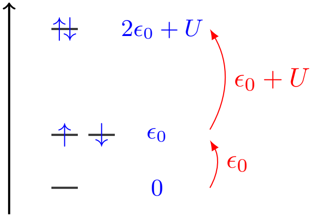

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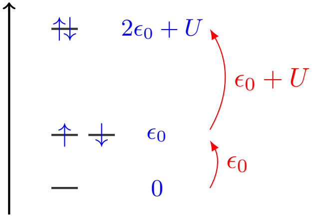
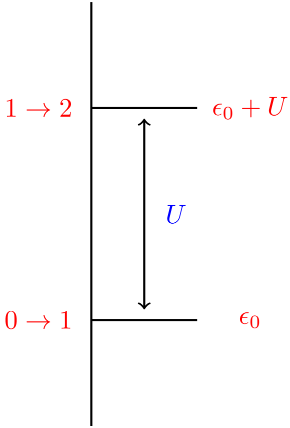




Atomic case: Green’s function

- We study the atomic problem with 1 electron.
- Green’s function of the atom and Self-energy. Let’s use $\epsilon_0 = -U/2$ and the Lehman representation of the

$$iG(\mathbf{r},\mathbf{r}',t-t')=\langle N,0|T[\Psi(\mathbf{r}t)\Psi^{+}(\mathbf{r}'t')]|N,0\rangle$$

Closure relation

$$\sum_{M,i}|M,i\rangle\langle M,i|$$

Lehman representation:

$$G(\mathbf{r},\mathbf{r}',\omega)=\sum_{i}\frac{f_i(\mathbf{r})f_i^{*}(\mathbf{r}')}{\omega-\epsilon_i\pm i\eta}$$

Green’s function (F. Bruneval Lecture):

$$G(\omega) = \frac{1/2}{\omega + U/2} + \frac{1/2}{\omega - U/2} = \frac{\omega}{\omega^2 - (U/2)^2}$$

Equation of motion for the non interacting Green’s function.

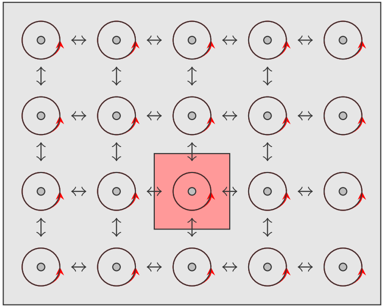
$$(\omega - \epsilon_0)\mathcal{G}_0(\omega) = 1 \Rightarrow \mathcal{G}_0(\omega) = \frac{1}{\omega - \epsilon_0} = \frac{1}{\omega + U/2}$$

- The Dyson eq writes:

$$\Sigma(\omega) = \mathcal{G}_0^{-1} - G^{-1} = \omega + U/2 - \frac{\omega^2 - (U/2)^2}{\omega} = U/2 + \frac{(U/2)^2}{\omega}$$

Dynamical Mean Field Theory

The Hubbard model physics can be mimicked by an Anderson model + Self-consistency



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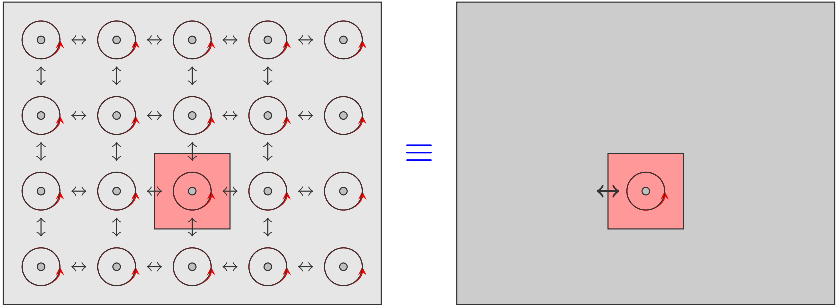

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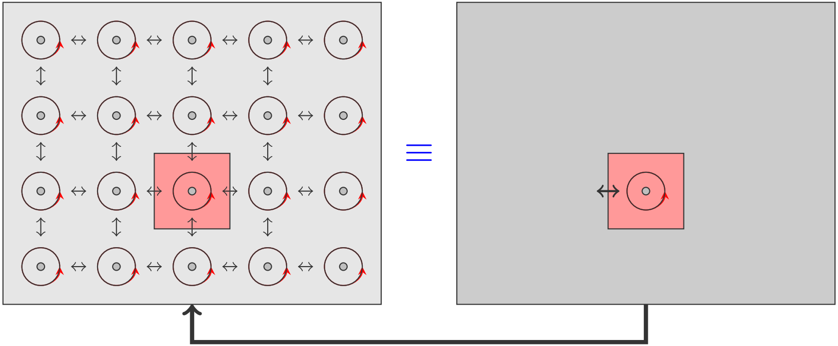
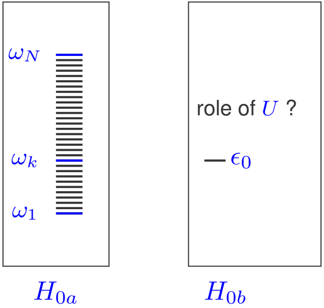


W. Metzner and D. Vollhardt Phys. Rev. Lett. 62 (3) 324 (1989)
A. Georges and G.Kotliar Phys. Rev. B 45 (12) 6479 (1992)
Antoine Georges, Gabriel Kotliar, Werner Krauth, and Marcelo J. Rozenberg Rev. Mod. Phys. 68, 13 (1996)

Anderson Hamiltonian in the DMFT



$$H_{\text{Anderson}} = \underbrace{\sum_{\sigma,k=1}^{N} \omega_k a^{+}_{k,\sigma} a_{k\sigma}}_{H_{0a}} + \underbrace{\epsilon_0 (n_\uparrow + n_\downarrow) + U n_\uparrow n_\downarrow}_{H_{0b}}$$

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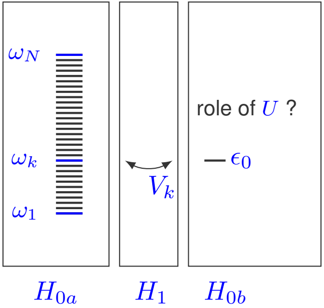

$$H_{\text{Anderson}} = \underbrace{\sum_{\sigma,k=1}^{N} \omega_k a^+_{k,\sigma} a_{k\sigma}}_{H_{0a}} + \underbrace{\sum_{k,\sigma} V_k (a^+_{k,\sigma} c_\sigma + c^+_\sigma a_{k,\sigma})}_{H_1} + \underbrace{\epsilon_0 (n_\uparrow + n_\downarrow) + U n_\uparrow n_\downarrow}_{H_{0b}}$$

Anderson Hamiltonian with $V_k = 0$: Hubbard bands

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H_{0a} and H_{0b} are not coupled. Solution is equivalent to Hubbard model with $t = 0$: Hubbard bands.

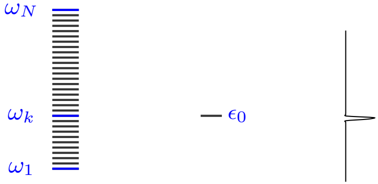
Anderson hamiltonian $U = 0$

The hamiltonian writes:

$$H_{\mathrm{Anderson}} = \sum \omega_k a^+_{k,\sigma} a_{k\sigma} + \sum_{k,\sigma} V_k (a^+_{k,\sigma} c_\sigma + c^+_\sigma a_{k,\sigma}) + \epsilon_0 (n_\uparrow + n_\downarrow)$$

With only one bath state, H is:

$$\begin{pmatrix} \epsilon_0 & V_1 & \dots & V_k & \dots & V_N \\ V_1 & \omega_1 & 0 & 0 & 0 & 0 \\ \dots. & 0 & \dots\dots.. & 0 & 0 & 0 \\ V_k & 0 & 0 & \omega_k & 0 & 0 \\ \dots & 0 & 0 & 0 & \dots.. & 0 \\ V_N & 0 & 0 & 0 & 0 & \omega_N \end{pmatrix}$$



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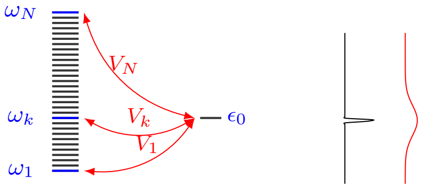

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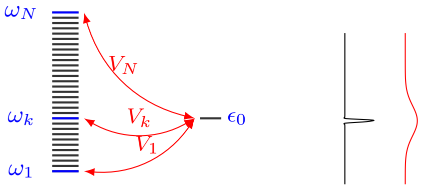

This hamiltonian contains the hybridization of a single level ϵ_0 to other levels. The level with move and will be broadened by hybridization on other levels.

Anderson hamiltonian $U = 0$

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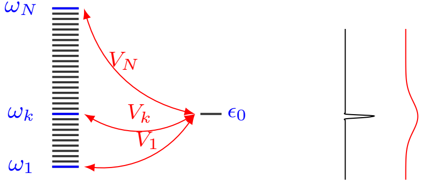
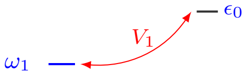


H is:

$$\begin{pmatrix} \epsilon_0 & V_1 \\ V_1 & \omega_1 \end{pmatrix}$$



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Let’s now compute Green’s function poles, using the following relation, which comes from the equation of motion of the Green’s function (which comes from the time Schrodinger eq (see lecture of P. Romaniello)).

$$G = (\omega I - H)^{-1}$$

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$$G = (\omega I - H)^{-1}$$

$$G = \begin{pmatrix} \omega - \epsilon_0 & V_1 \\ V_1 & \omega - \omega_1 \end{pmatrix}^{-1} = \frac{1}{(\omega - \epsilon_0)(\omega - \omega_1) - V_1^2} \begin{pmatrix} \omega - \epsilon_1 & -V_1 \\ -V_1 & \omega - \omega_0 \end{pmatrix}$$

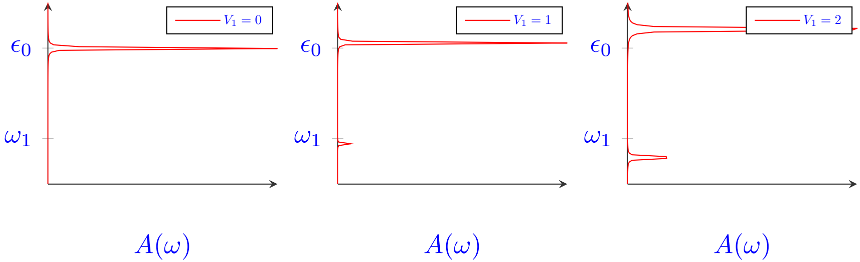
The pole of G are indeed the eigenvalues of this two orbital model.
Let's now focus on the element of the Greens function on the correlated orbitals G_{00}

$$G_{00} = \frac{\omega - \epsilon_1}{(\omega - \epsilon_0)(\omega - \omega_1) - V_1^2} = \frac{1}{\omega - \epsilon_0 - \frac{V_1^2}{\omega - \omega_1}}$$

Spectral function

We can now compute the spectral function of this system by computing:

$$A(\omega) = -\frac{1}{\pi}\mathrm{Im}G^R(\omega + i\delta) = -\frac{1}{\pi}\mathrm{Im}\frac{1}{\omega + i\delta - \epsilon_0 - \frac{V_1^2}{\omega+i\delta-\omega_1}}$$



Anderson Hamiltonian with $U = 0$.

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$$G = (\omega I - H)^{-1}$$

We can inverse this matrix and compute the Green's function of the correlated orbital (Using $A^{-1} = \mathrm{Com}(A)^T / \mathrm{det} A$ to inverse $I - H$). We obtain as a generalisation of the previous result:

$$G(\omega) = \frac{1}{\omega - \epsilon_0 - \Delta(\omega)} \quad \text{with} \quad \Delta(\omega) = \sum_k \frac{V_k^2}{\omega - \omega_k}$$

Where $\Delta(\omega)$ is called the hybridization function.

Anderson Hamiltonian with $U = 0$.

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$$A(\omega) = -\frac{1}{\pi}\mathrm{Im}G^R(\omega + i\delta) = -\frac{1}{\pi}\mathrm{Im}\frac{1}{\omega + i\delta - \epsilon_0 - \Delta(\omega + i\delta)}$$

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We need

$$\Delta(\omega + i\delta) = \sum_k \frac{V_k^2}{\omega + i\delta - \omega_k}$$

$$\mathrm{Re}\Delta = \sum_k \frac{V_k^2}{(\omega - \omega_k)^2 + \delta^2} \qquad \mathrm{Im}\Delta = \sum_k \frac{-\delta V_k^2}{(\omega - \omega_k)^2 + \delta^2}.$$

And with $\lim_{\delta \to 0} \frac{1}{\pi} \frac{\delta}{x^2 + \delta^2} = \delta(x)$

$$\mathrm{Im}\Delta = -\pi \sum_k V_k^2 \delta(\omega - \omega_k) \simeq -\pi |V|^2 \rho(\omega)$$

Anderson Hamiltonian with $U = 0$.

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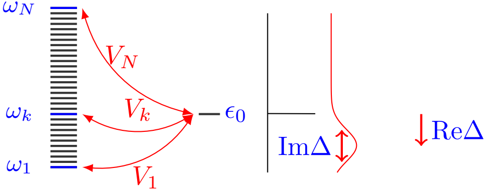

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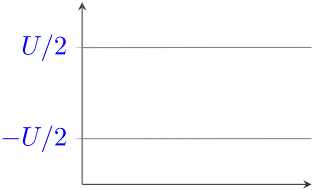
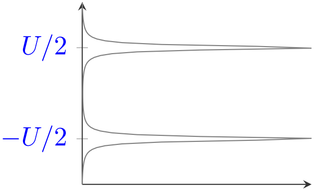
Anderson Hamiltonian; Hubbard band with hybridization ?





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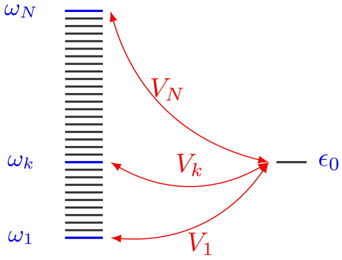
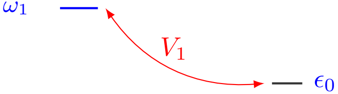
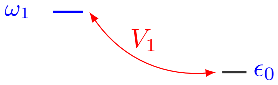




- Size of the Hilbert space ?
- If N=2 electrons ?
- If $U = \infty$?

Anderson Hamiltonian: one orbital for the bath.



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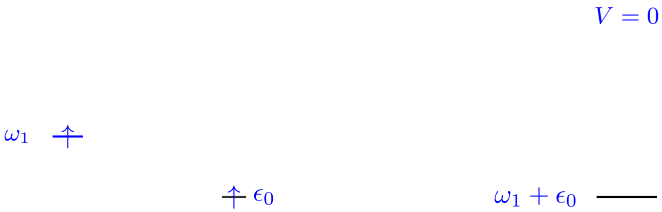

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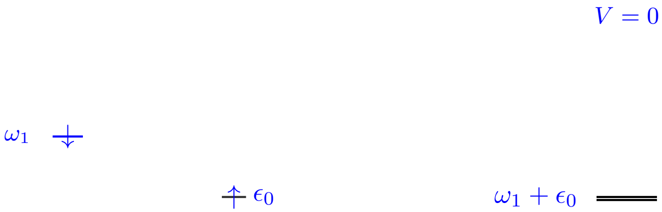

$V = 0$

ω_1

ϵ_0

$\omega_1 + \epsilon_0$

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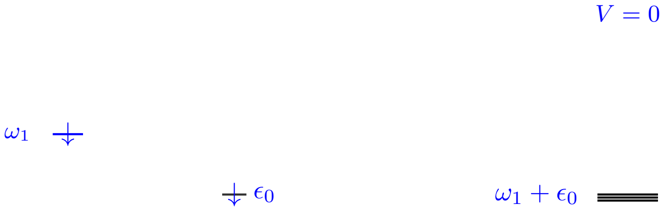

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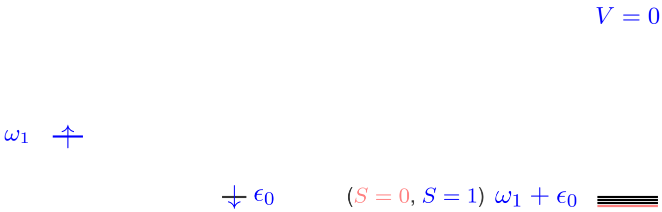

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ω_1

ϵ_0

$(S = 0, S = 1)\ \omega_1 + \epsilon_0$

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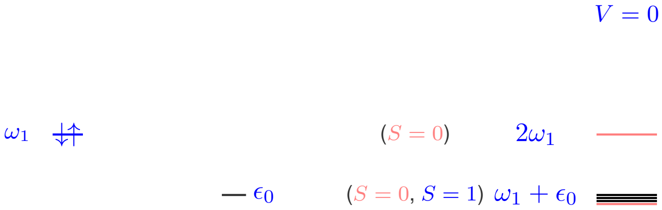

$V = 0$

ω_1 $\uparrow\downarrow$

ϵ_0

$(S = 0)$ $2\omega_1$

$(S = 0, S = 1)$ $\omega_1 + \epsilon_0$

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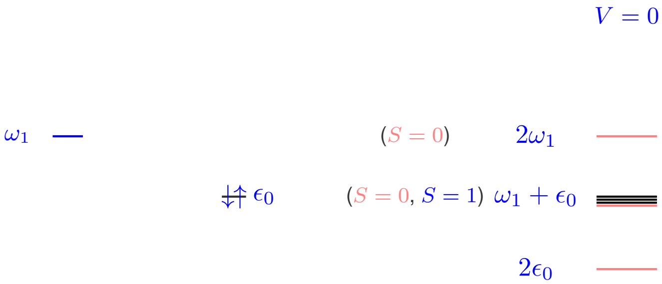

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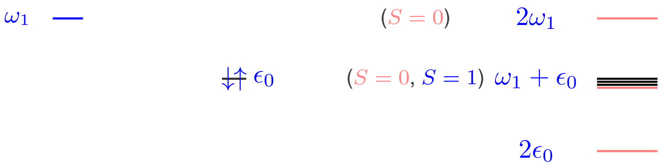
$2\epsilon_0$

Anderson Hamiltonian: one orbital for the bath.

$2\epsilon_0 + U = \infty$

$V = 0$



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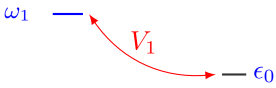

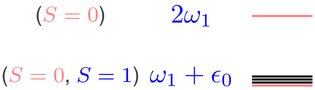

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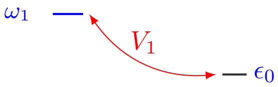

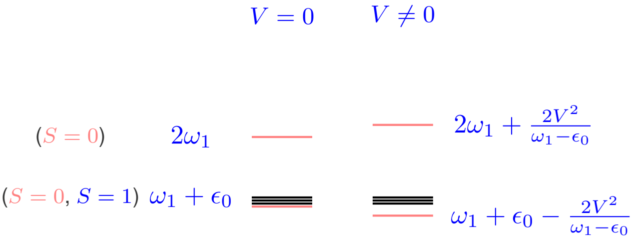

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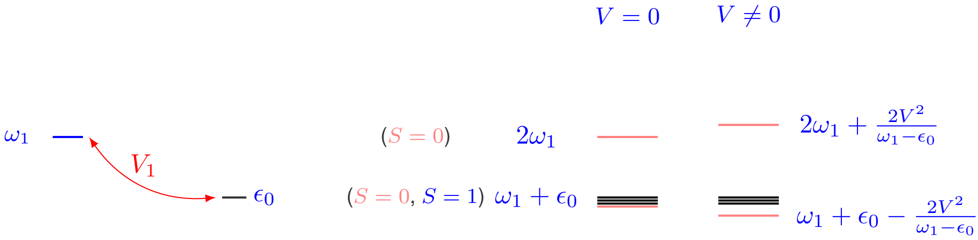
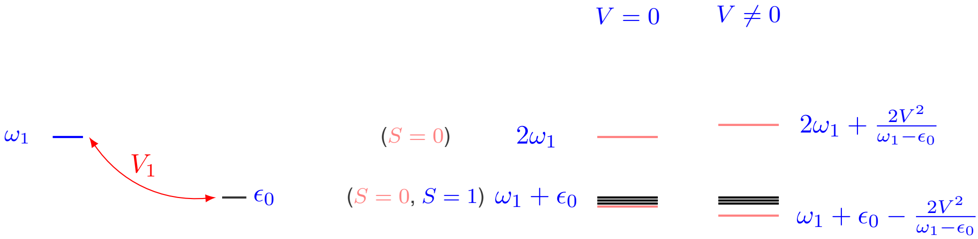


Because of hybridization, the ground state is a many body problem

Anderson Hamiltonian: one orbital for the bath.

$$2\epsilon_0 + U = \infty$$



$V = 0$ $\quad V \neq 0$

ω_1

V_1

ϵ_0

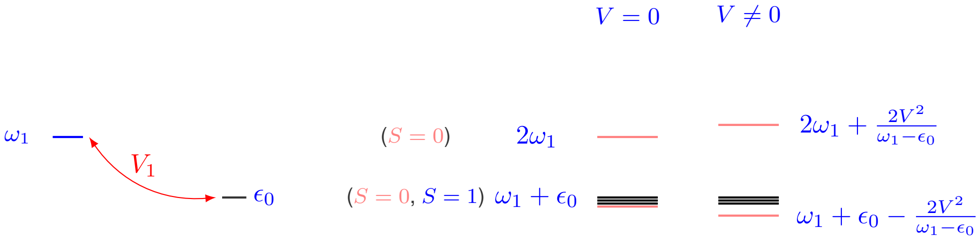
$(S = 0)$ $\quad 2\omega_1$ $\quad 2\omega_1 + \frac{2V^2}{\omega_1 - \epsilon_0}$

$(S = 0,\ S = 1)$ $\quad \omega_1 + \epsilon_0$ $\quad \omega_1 + \epsilon_0 - \frac{2V^2}{\omega_1 - \epsilon_0}$

Because of hybridization, the ground state is a many body problem
Because of U, the ground state is a many body problem

Anderson Hamiltonian: one orbital for the bath.

$$2\epsilon_0 + U = \infty$$



$V = 0$ $V \neq 0$

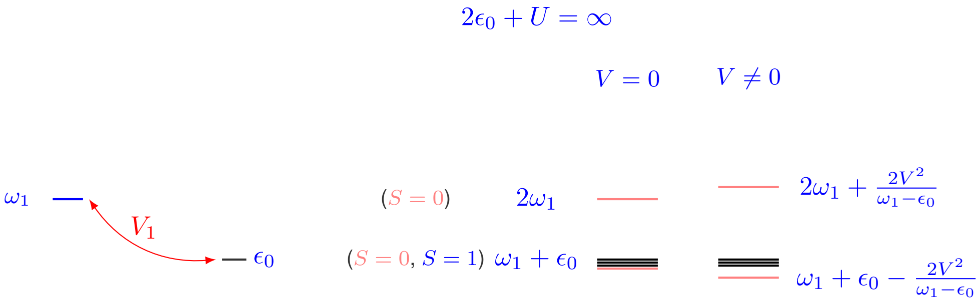
ω_1 V_1 ϵ_0

$(S = 0)$ $2\omega_1$ $2\omega_1 + \frac{2V^2}{\omega_1 - \epsilon_0}$

$(S = 0, S = 1)$ $\omega_1 + \epsilon_0$ $\omega_1 + \epsilon_0 - \frac{2V^2}{\omega_1 - \epsilon_0}$

Because of hybridization, the ground state is a many body problem
Because of U, the ground state is a many body problem
Because of U and hybridization, the ground state is not magnetic.

Anderson Hamiltonian: one orbital for the bath.



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The formation of a singlet is the essence of the Kondo effect.

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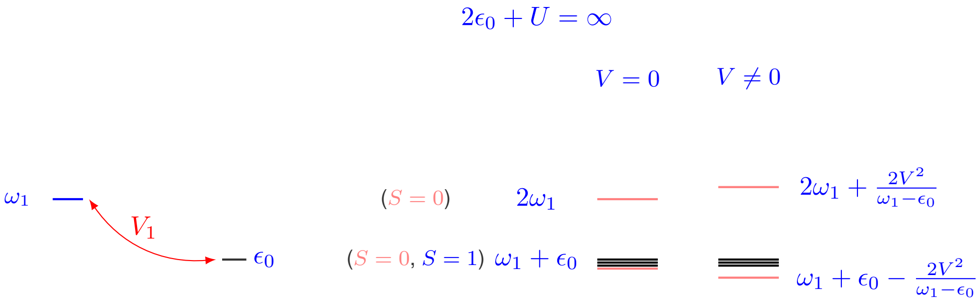

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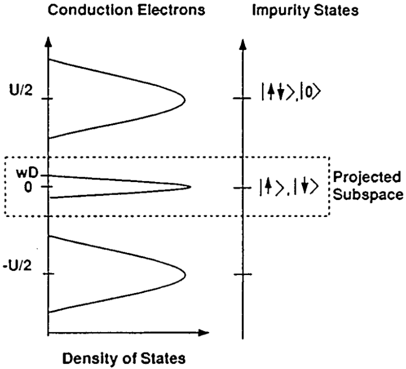
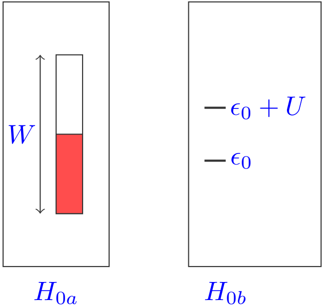
Because of hybridization, the ground state is a many body problem
Because of U, the ground state is a many body problem
Because of U and hybridization, the ground state is not magnetic.
The formation of a singlet is the essence of the Kondo effect.
There is a low energy excitation $\simeq \frac{V^2}{\omega_1 - \epsilon_0}$
Fulde 1988

The Anderson model: 3 peak structure



Hubbard bands are due to charge fluctuations (as in the atomic case)
Quasiparticle peak is linked to spin fluctuations (see Anderson molecule)
(from Georges et al RMP 1996)

The Anderson Hamiltonian (solved by CTQMC)



E Gull, AJ Millis, AI Lichtenstein, AN Rubtsov, M Troyer, P Werner Reviews of Modern Physics 83 (2), 349 (2011)

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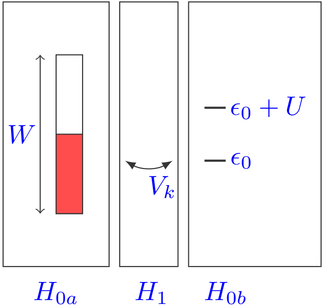

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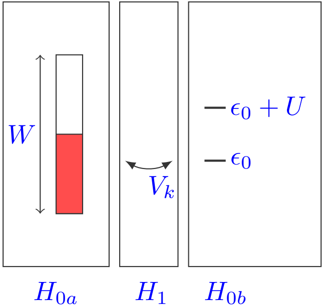
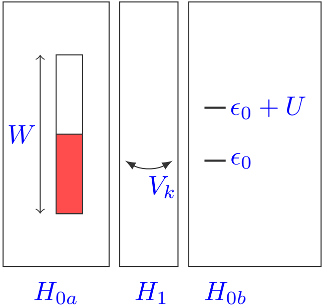


$$H_{\text{Anderson}} = \underbrace{\sum \omega_k a^+_{k,\sigma} a_{k\sigma}}_{H_{0a}} + \underbrace{\sum_{k,\sigma} V_{kf} a^+_{k,\sigma} f_\sigma}_{H_1} + \underbrace{\sum_\sigma \epsilon_f f^+_\sigma f_\sigma + U n_{f\uparrow} n_{f\downarrow}}_{H_{0b}}$$

E Gull, AJ Millis, AI Lichtenstein, AN Rubtsov, M Troyer, P Werner Reviews of Modern Physics 83 (2), 349 (2011)

The Anderson Hamiltonian (solved by CTQMC)



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Continuous Time Quantum Monte Carlo: Expansion as a function of H_1

[P. Werner, A. Comanac, L. de medici, M. Troyer and A. J. Millis Phys. Rev. Lett. 97, 076405 (2006)] E Gull, AJ Millis, AI Lichtenstein, AN Rubtsov, M Troyer, P Werner Reviews of Modern Physics 83 (2), 349 (2011)

The self consistency condition and the DMFT loop

The equation of Motion of the Green's function (see lecture from P. Romaniello) is

$$(\omega - H - \Sigma)G = 1$$

It is an equation for operators and it directly comes from the time dependent Schrödinger Eq. for creation and annihilation operators. One can insert the closure relation for Bloch states which is

$$\sum_{k'} |\psi_{k'}\rangle\langle\psi_{k'}| = 1$$

We thus have:

$$(\omega - H - \Sigma) \sum_{k'} |\psi_{k'}\rangle\langle\psi_{k'}|G = 1$$

We can project on the left and right by ψ_k:

$$\langle\psi_k|(\omega - H - \Sigma) \sum_{k'} |\psi_{k'}\rangle\langle\psi_{k'}|G|\psi_k\rangle = 1$$

thus

$$[\omega - \epsilon_{\mathbf{k}} - \Sigma_{\mathbf{k}}(\omega)]G_{\mathbf{k}}(\omega)$$

the lattice Green's function for the Hubbard model is written:

$$G_{\mathbf{k}}(\omega) = \frac{1}{\omega - \epsilon_{\mathbf{k}} - \Sigma_{\mathbf{k}}(\omega)}$$

Green’s function of the lattice

The Green’s function of the lattice in real space writes:

$$G_{ij}^{\mathrm{local}}(\omega) = \frac{1}{N}\sum_{\mathbf{k}} \mathrm{e}^{ik(T_i - T_j)} G_{\mathbf{k}}(\omega) = \frac{1}{N}\sum_{\mathbf{k}} G_{\mathbf{k}}(\omega)$$

The local Green’s function of the lattice is

$$G_{ii}^{\mathrm{local}}(\omega) = \frac{1}{N}\sum_{\mathbf{k}} \mathrm{e}^{ik(T_i - T_i)} G_{\mathbf{k}}(\omega) = \frac{1}{N}\sum_{\mathbf{k}} G_{\mathbf{k}}(\omega)$$

$$\boxed{G_{ii}^{\mathrm{local}}(\omega) = \frac{1}{N}\sum_{\mathbf{k}} \frac{1}{\omega - \epsilon_{\mathbf{k}} - \Sigma_{\mathbf{k}}(\omega)}}$$

Green's function of the Anderson model

- From the equation of motion:
  $G = (\omega I - H - \Sigma)^{-1}$
  with $H + \Sigma$ is:

$$\begin{pmatrix} \epsilon_0 + \Sigma & V_1 & \ldots & V_k & \ldots & V_N \\ V_1 & \omega_1 & 0 & 0 & 0 & 0 \\ \ldots. & 0 & \ldots\ldots.. & 0 & 0 & 0 \\ V_k & 0 & 0 & \omega_k & 0 & 0 \\ \ldots & 0 & 0 & 0 & \ldots.. & 0 \\ V_N & 0 & 0 & 0 & 0 & \omega_N \end{pmatrix}$$

we can show using exactly the same derivation as for $U = 0$:

$$\boxed{G_{\text{Anderson}}(\omega) = \frac{1}{\omega - \epsilon_0 - \Delta(\omega) - \Sigma(\omega)}}$$

Green's function of the Anderson model

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  we can show using exactly the same derivation as for $U = 0$:
  $$\boxed{G_{\text{Anderson}}(\omega) = \frac{1}{\omega - \epsilon_0 - \Delta(\omega) - \Sigma(\omega)}}$$

- or equivalently using the Dyson equation using the expression of $\mathcal{G}_0^{-1}$
  $G^{-1} = \mathcal{G}_0^{-1} - \Sigma = \omega I - H - \Delta - \Sigma$
  $$\boxed{G_{\text{Anderson}}(\omega) = \frac{1}{\omega - \epsilon_0 - \Delta(\omega) - \Sigma(\omega)}}$$

The self consistency condition and the DMFT loop

For one atom in the solid, the local Green's function is

$$\boxed{G_{ii}^{\text{local}}(\omega) = \frac{1}{N}\sum_{\mathbf{k}} \frac{1}{\omega - \epsilon_{\mathbf{k}} - \Sigma_{\mathbf{k}}(\omega)}}$$

For the Anderson model, the correlated orbital Green's function is:

$$\boxed{G_{\text{Anderson}}(\omega) = \frac{1}{\omega - \epsilon_0 - \Delta(\omega) - \Sigma(\omega)}}$$

What could be the self-consistency relation ?

The self consistency condition and the DMFT loop

For one atom in the solid, the local Green's function is

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Identity of spectral functions for the lattice and for the Anderson model

$$\boxed{-\frac{1}{\pi}\text{Im}[G_{ii}^{\text{local}}(\omega)] = -\frac{1}{\pi}\text{Im}[G_{\text{Anderson}}]}$$

The self consistency condition and the DMFT loop

For one atom in the solid, the local Green's function is

$$\boxed{G_{ii}^{\text{local}}(\omega) = \frac{1}{N}\sum_{\mathbf{k}} \frac{1}{\omega - \epsilon_{\mathbf{k}} - \Sigma_{\mathbf{k}}(\omega)}}$$

For the Anderson model, the correlated orbital Green's function is:

$$\boxed{G_{\text{Anderson}}(\omega) = \frac{1}{\omega - \epsilon_0 - \Delta(\omega) - \Sigma(\omega)}}$$

The DMFT idea is to identify the two Green's function and the Self-energies:

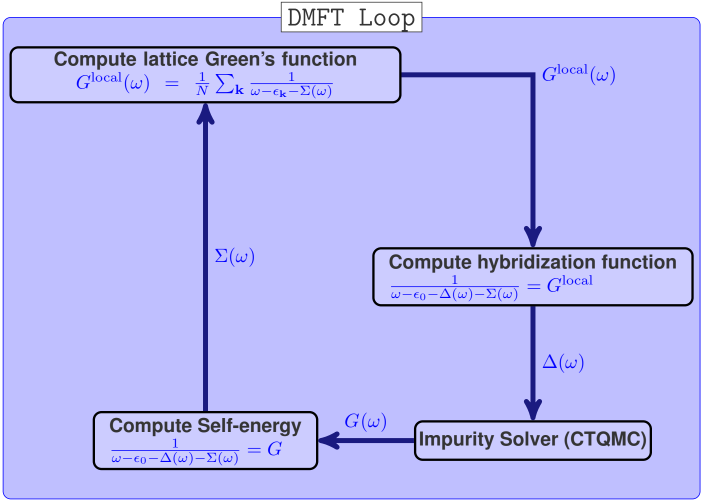
$$\boxed{G_{ii}^{\text{local}}(\omega) = G_{\text{Anderson}}(\omega) \qquad \Rightarrow \frac{1}{N}\sum_{k} \frac{1}{\omega - \epsilon_{\mathbf{k}} - \Sigma(\omega)} = \frac{1}{\omega - \epsilon_0 - \Delta(\omega) - \Sigma(\omega)}}$$

DMFT scheme

$$\boxed{G_{ii}^{\mathrm{local}}(\omega) = \frac{1}{N}\sum_{\mathbf{k}} \frac{1}{\omega - \epsilon_{\mathbf{k}} - \Sigma_{\mathbf{k}}(\omega)}}$$

$$\boxed{G_{\mathrm{Anderson}}(\omega) = \frac{1}{\omega - \epsilon_0 - \Delta(\omega) - \Sigma(\omega)}}$$

$$\boxed{G_{ii}^{\mathrm{local}}(\omega) = G_{\mathrm{Anderson}}(\omega)}$$



`DMFT Loop`

Compute lattice Green's function

$$G^{\mathrm{local}}(\omega) \;=\; \frac{1}{N}\sum_{\mathbf{k}} \frac{1}{\omega-\epsilon_{\mathbf{k}}-\Sigma(\omega)}$$

$G^{\mathrm{local}}(\omega)$

Compute hybridization function

$$\frac{1}{\omega-\epsilon_0-\Delta(\omega)-\Sigma(\omega)} = G^{\mathrm{local}}$$

$\Delta(\omega)$

Impurity Solver (CTQMC)

$G(\omega)$

Compute Self-energy

$$\frac{1}{\omega-\epsilon_0-\Delta(\omega)-\Sigma(\omega)} = G$$

$\Sigma(\omega)$

The self consistency condition and the DMFT loop

$$\boxed{\frac{1}{N}\sum_{k}\frac{1}{\omega-\epsilon_{\mathbf{k}}-\Sigma(\omega)}=\frac{1}{\omega-\epsilon_0-\Delta(\omega)-\Sigma(\omega)}}$$

- If $t=0$, then $\epsilon_k=\epsilon_0$ and $\Delta=0$ thus, the self-consistency is always fulfilled. The Anderson model can be solved only one time to give the exact solution.

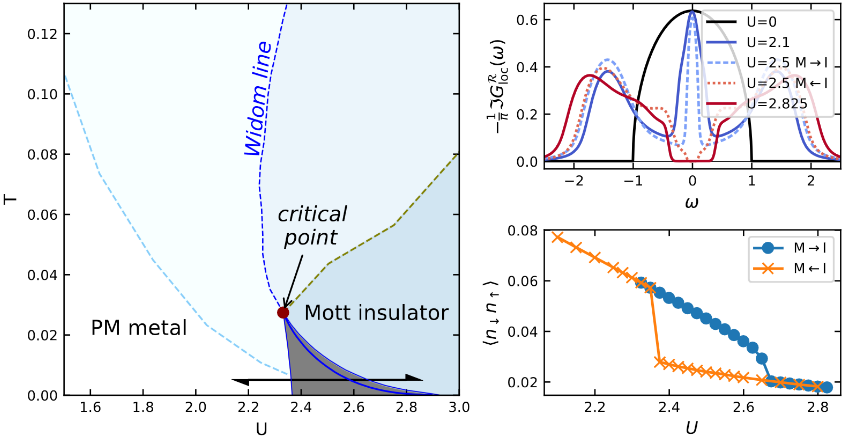
$$\frac{1}{N}\sum_{k}\frac{1}{\omega-\epsilon_0-\Sigma(\omega)}=\frac{1}{\omega-\epsilon_0-\Sigma(\omega)}$$

- If $U=0$, then the lattice Green's function and the local Green's function are exact.

$$\frac{1}{N}\sum_{k}\frac{1}{\omega-\epsilon_{\mathbf{k}}}=\frac{1}{\omega-\epsilon_0-\Delta(\omega)}$$

The Green's function is exact in the two cases. The self-consistency has no effect.

Phase diagram of Hubbard model in DMFT



Watzenböck et al Scipost (2022)

Phase diagram of Hubbard model in DMFT

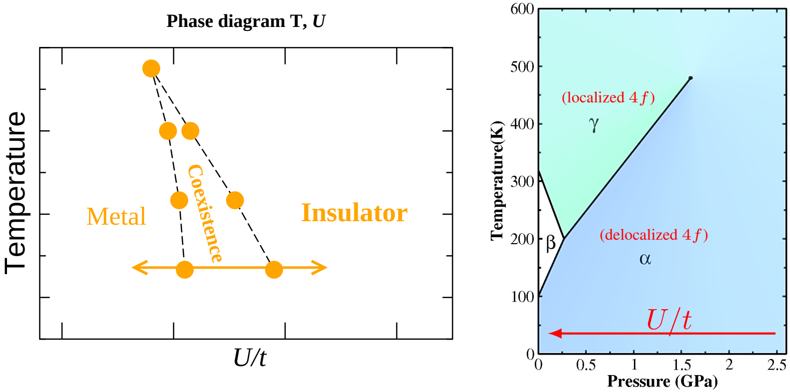


FIGURE: Phase diagram of the Hubbard model in DMFT compared to phase diagram of Cerium.

Phase diagram of Hubbard model in DMFT

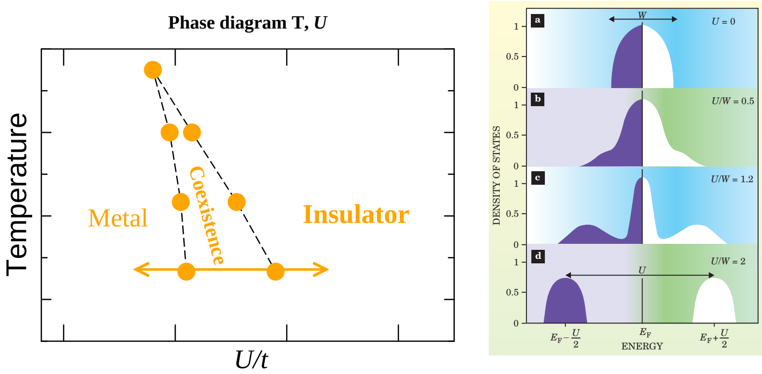
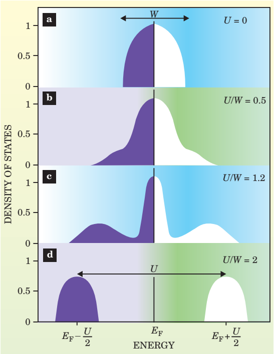
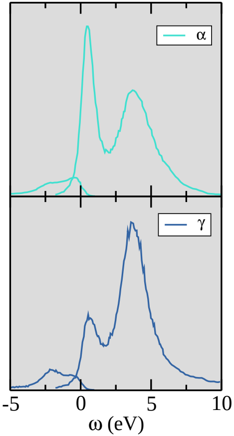


FIGURE: Phase diagram of the Hubbard model in DMFT and evolution of the spectral function

Spectral function of Hubbard model in DMFT





[G.Kotliar *et al* Phys. Today, AIP, 57, 53-59 (2004)]

[E. Weschke, *et al* Phys. Rev. B 44, 8304 (1991)
M. Grioni, *et al* Phys. Rev. B 55, 2056 (1997)]

DFT : The Kohn Sham Equations

- The total energy expression as a function of $\phi(\mathbf{r})$ is

$$E_{v_{\text{ext}}}[n(\mathbf{r})] = -\sum_i \int \phi_i^*(\mathbf{r}) \frac{\nabla^2}{2} \phi_i(\mathbf{r}) d\mathbf{r} + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) + E_{\text{Hartree}}[n(\mathbf{r})] + E_{\text{xc}}[n(\mathbf{r})]$$

  and can be minimized.

- One obtains the one electron Kohn-Sham Equations

$$\left[-\frac{\nabla^2}{2} + V_{\text{KS}}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

- The effective Kohn Sham potential $V_{\text{KS}}(\mathbf{r})$ is defined as a the functional derivative of the last three terms of the energy:

$$V_{\text{KS}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{\text{xc}}[n(\mathbf{r})](\mathbf{r})$$

- The exchange and correlation potential $v_{\text{xc}}(\mathbf{r})$ is

$$v_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$$

From DFT to DFT+DMFT

$$\boxed{\text{DMFT}}$$

$$\boxed{\text{DFT} + \text{DMFT}}$$

$$G_k^{\text{lattice}}(\omega) = \frac{1}{\omega - \epsilon_{\mathbf{k}} - \Sigma_{\mathbf{k}}(\omega)}$$

$$G_{ii}^{\text{local}}(\omega) = \frac{1}{N}\sum_{\mathbf{k}} G_k^{\text{lattice}}(\omega)$$

For the Anderson model, the correlated orbital Green's function is:

$$G_{\text{Anderson}}(\omega) = \frac{1}{\omega - \epsilon_0 - \Delta(\omega) - \Sigma(\omega)}$$

From DFT to DFT+DMFT

$$\boxed{\text{DMFT}}$$

$$G_k^{\text{lattice}}(\omega) = \frac{1}{\omega - \epsilon_{\mathbf{k}} - \Sigma_{\mathbf{k}}(\omega)}$$

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$$\boxed{\text{DFT} + \text{DMFT}}$$

- ϵ_k= Kohn Sham eigenvalues - double counting correction

From DFT to DFT+DMFT

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$$\boxed{\text{DFT} + \text{DMFT}}$$

- ϵ_k= Kohn Sham eigenvalues - double counting correction
- The local Green's function is defined on correlated orbitals. $\Rightarrow G$ and Σ are matrices

From DFT to DFT+DMFT

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$$\boxed{\text{DFT} + \text{DMFT}}$$

- ϵ_k= Kohn Sham eigenvalues - double counting correction
- The local Green's function is defined on correlated orbitals. $\Rightarrow$ G and Σ are matrices
- Need a projection from Kohn Sham states to correlated orbitals. $\langle \Psi_{nk} | \chi_{lm} \rangle$

From DFT to DFT+DMFT

$$\boxed{\text{DMFT}}$$

$$G_k^{\text{lattice}}(\omega) = \frac{1}{\omega - \epsilon_{\mathbf{k}} - \Sigma_{\mathbf{k}}(\omega)}$$

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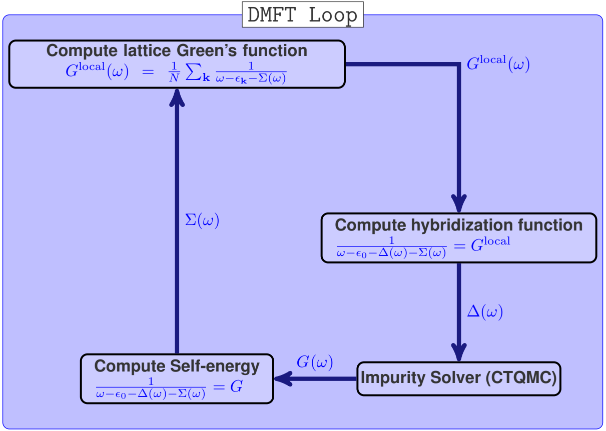
$$\boxed{\text{DFT} + \text{DMFT}}$$

- ϵ_k= Kohn Sham eigenvalues - double counting correction
- The local Green's function is defined on correlated orbitals. $\Rightarrow G$ and Σ are matrices
- Need a projection from Kohn Sham states to correlated orbitals. $\langle \Psi_{nk} | \chi_{lm} \rangle$
- The Anderson model is multiorbital, e.g. 10 (d) or 14 (f) orbitals.

The DMFT Loop



DMFT Loop

Compute lattice Green's function

$$G^{\mathrm{local}}(\omega) \;=\; \frac{1}{N}\sum_{\mathbf{k}} \frac{1}{\omega-\epsilon_{\mathbf{k}}-\Sigma(\omega)}$$

$G^{\mathrm{local}}(\omega)$

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$\Delta(\omega)$

Impurity Solver (CTQMC)

$G(\omega)$

Compute Self-energy

$$\frac{1}{\omega-\epsilon_0-\Delta(\omega)-\Sigma(\omega)} = G$$

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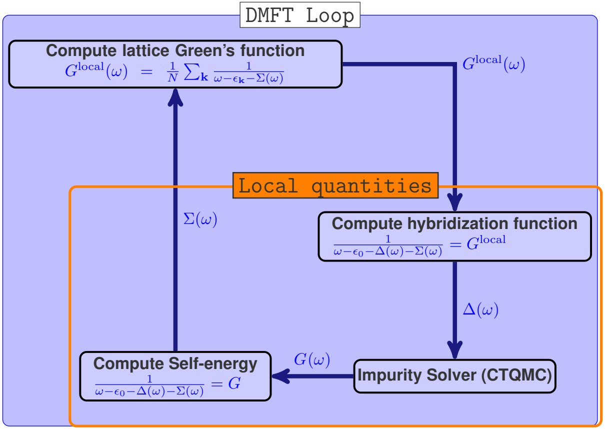
The DMFT Loop



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$G^{\text{local}}(\omega)$

Local quantities

Compute hybridization function

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$\Delta(\omega)$

Impurity Solver (CTQMC)

$G(\omega)$

Compute Self-energy

$$\frac{1}{\omega-\epsilon_0-\Delta(\omega)-\Sigma(\omega)} = G$$

$\Sigma(\omega)$

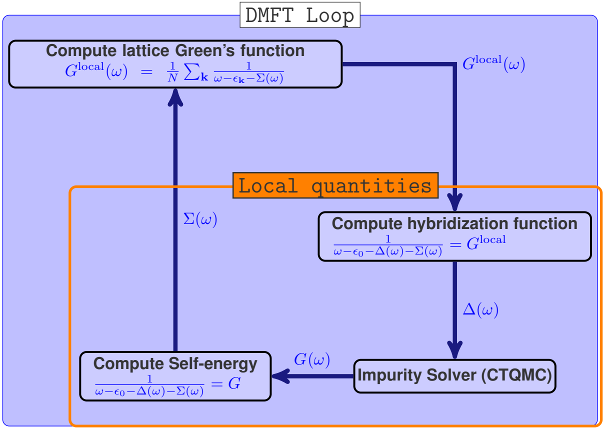
Reminder about Hubbard model

- Local quantities are expressed in a basis of correlated orbitals.

  $$\widehat{\Sigma}(\omega) = \sum_{\mathbf{T}} |\chi_{\mathbf{T}}\rangle \Sigma(\omega) \langle \chi_{\mathbf{T}}|$$

  where $\chi_{\mathbf{T}}$ is the unique orbital on the atom at $\mathbf{T}$ and $\mathbf{T}$ are the lattice vectors.

The DMFT Loop



DMFT Loop

Compute lattice Green's function

$$G^{\mathrm{local}}(\omega) = \frac{1}{N}\sum_{\mathbf{k}} \frac{1}{\omega - \epsilon_{\mathbf{k}} - \Sigma(\omega)}$$

$G^{\mathrm{local}}(\omega)$

Local quantities

Compute hybridization function

$$\frac{1}{\omega - \epsilon_0 - \Delta(\omega) - \Sigma(\omega)} = G^{\mathrm{local}}$$

$\Delta(\omega)$

Impurity Solver (CTQMC)

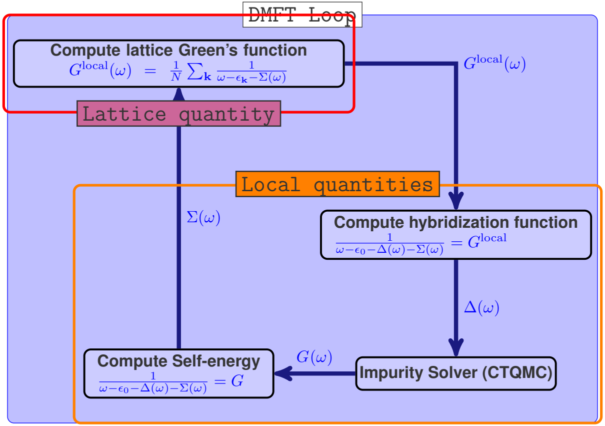
$G(\omega)$

Compute Self-energy

$$\frac{1}{\omega - \epsilon_0 - \Delta(\omega) - \Sigma(\omega)} = G$$

$\Sigma(\omega)$

The DMFT Loop



DMFT Loop

Compute lattice Green's function

$$G^{\text{local}}(\omega) = \frac{1}{N}\sum_{\mathbf{k}} \frac{1}{\omega - \epsilon_{\mathbf{k}} - \Sigma(\omega)}$$

Compute hybridization function

$$\frac{1}{\omega - \epsilon_0 - \Delta(\omega) - \Sigma(\omega)} = G^{\text{local}}$$

Impurity Solver (CTQMC)

Compute Self-energy

$$\frac{1}{\omega - \epsilon_0 - \Delta(\omega) - \Sigma(\omega)} = G$$

Reminder about Hubbard model

- Lattice Green's functions are expressed in Bloch eigenvectors of the non interacting Hamiltonian ($\epsilon_{\mathbf{k}} = \frac{1}{N} \sum_{ij} t_{ij} \mathrm{e}^{-i\mathbf{k}(\mathbf{T}_i - \mathbf{T}_j)}$)

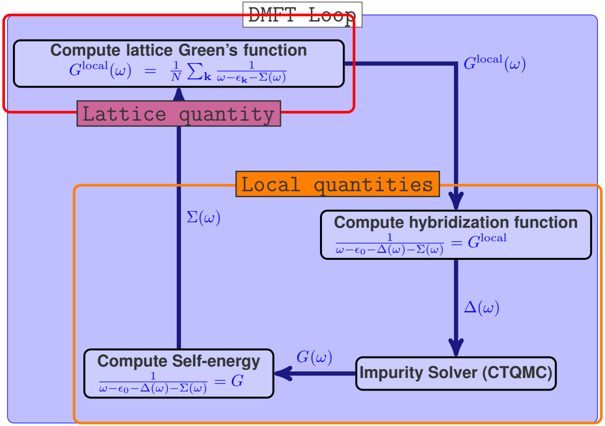
  $$\widehat{H}_0 = |\chi_{\mathbf{k}}\rangle \epsilon_{\mathbf{k}} \langle \chi_{\mathbf{k}}|$$

  with

  $$|\chi_{\mathbf{k}}\rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{T}} |\chi_{\mathbf{T}}\rangle \mathrm{e}^{i\mathbf{k}\mathbf{T}}$$

  where $\mathbf{T}$ are lattice vectors.

The DMFT Loop



DMFT Loop

Lattice quantity

Compute lattice Green's function

$G^{\text{local}}(\omega) = \frac{1}{N}\sum_{\mathbf{k}} \frac{1}{\omega-\epsilon_{\mathbf{k}}-\Sigma(\omega)}$

$G^{\text{local}}(\omega)$

Local quantities

Compute hybridization function

$\frac{1}{\omega-\epsilon_0-\Delta(\omega)-\Sigma(\omega)} = G^{\text{local}}$

$\Delta(\omega)$

Impurity Solver (CTQMC)

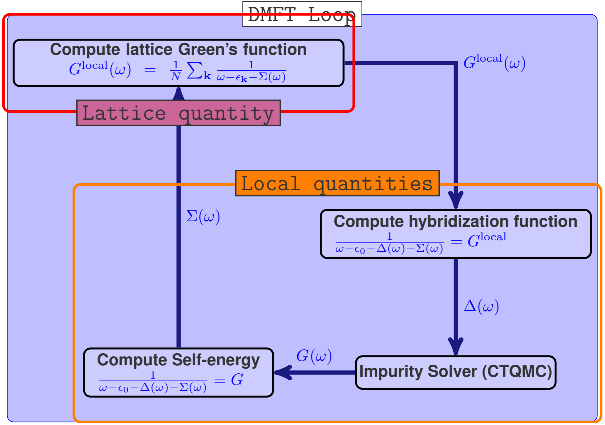
$G(\omega)$

Compute Self-energy

$\frac{1}{\omega-\epsilon_0-\Delta(\omega)-\Sigma(\omega)} = G$

$\Sigma(\omega)$

The DMFT Loop



DMFT Loop

Compute lattice Green's function

$G^{\text{local}}(\omega) = \frac{1}{N}\sum_{\mathbf{k}} \frac{1}{\omega-\epsilon_{\mathbf{k}}-\Sigma(\omega)}$

$G^{\text{local}}(\omega)$

Lattice quantity

Local quantities

$\Sigma(\omega)$

Compute hybridization function

$\frac{1}{\omega-\epsilon_0-\Delta(\omega)-\Sigma(\omega)} = G^{\text{local}}$

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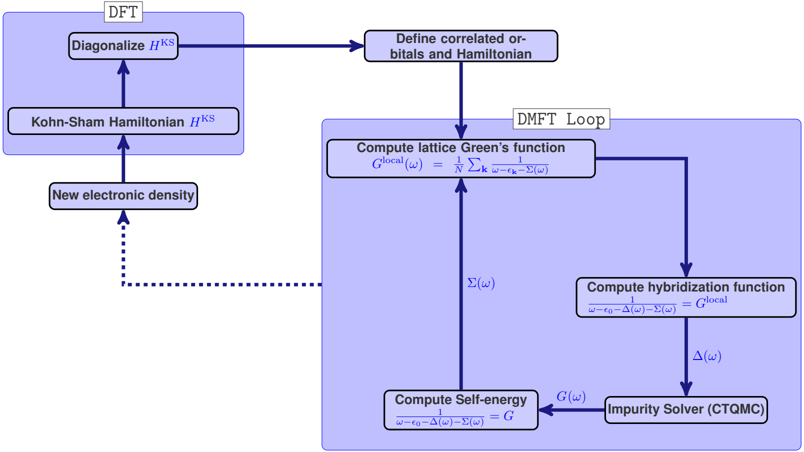
Impurity Solver (CTQMC)

How to apply such idea for a real solid, with both **strongly interacting orbitals**, and **weakly interacting orbitals**

DFT+DMFT scheme



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Kohn-Sham Hamiltonian H^{KS}

New electronic density

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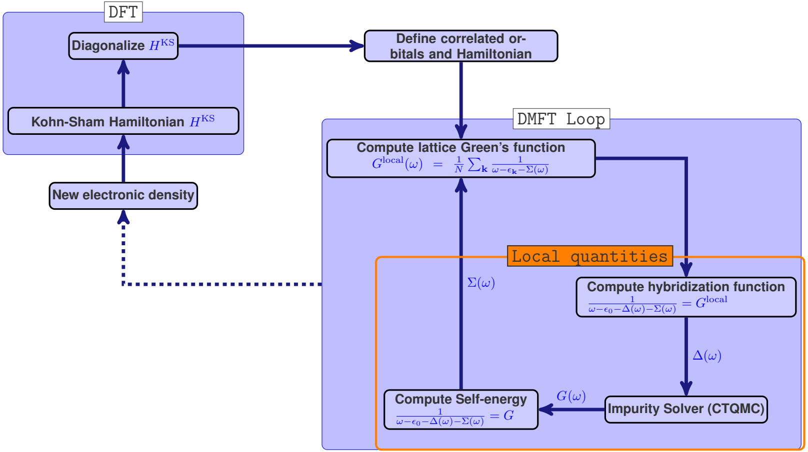

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Correlated orbitals: what are they

For d orbitals (l=2), $m \in \{-2,-1,0,1,2\}$, a correlated atomic orbital writes:

$$\chi_m(\mathbf{r}) = \langle \mathbf{r}|\chi_m\rangle = R(r)Y_m(\theta,\phi)$$

- The angular part $Y_m(\theta,\phi)$ is well defined.
- The radial part $R(r)$ is not defined in a solid.

In a first step, let's assume that we have found a good choice for $R(r)$ and thus $|\chi_m\rangle$ is defined.

In a real system in DFT+DMFT

- Local Quantity are expressed in a basis of correlated orbitals.

$$\widehat{\Sigma}(\omega) = \sum_{m,m',\mathbf{T}} |\chi^{\mathbf{R}}_{\mathbf{T}m}\rangle \Sigma_{m,m'}(\omega) \langle \chi^{\mathbf{R}}_{\mathbf{T}m'}|$$

where $m, m' \in -l, ..., l$ and $\chi^{\mathbf{R}}_{\mathbf{T}m}$ is an orbital whose angular part is Y_{lm}. Note that $\Sigma_{m,m'}$ can be a matrix and have non diagonal elements.

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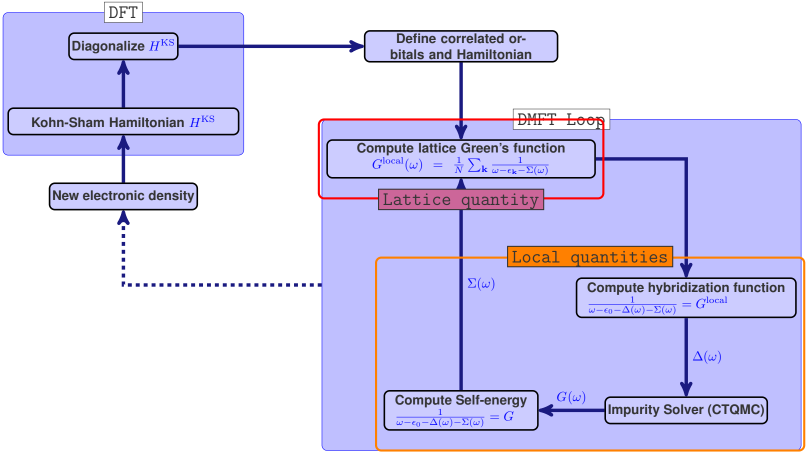
[for Hubbard model

$$\widehat{\Sigma}(\omega) = \sum_{\mathbf{T}} |\chi_{\mathbf{T}}\rangle \Sigma(\omega) \langle \chi_{\mathbf{T}}|$$

]

DFT+DMFT scheme



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Impurity Solver (CTQMC)

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In a real system in DFT+DMFT

- DFT Hamiltonian and thus lattice Green's functions are more easily expressed in Bloch eigenvectors of the DFT Kohn Sham Hamiltonian.

  $$\widehat{H}_{\mathrm{KS}} = |\Psi_{\mathbf{k}\nu}\rangle \epsilon_{\mathbf{k}\nu} \langle \Psi_{\mathbf{k}\nu}|$$

  Where $\Psi_{\mathbf{k}\nu}$ are one electron Kohn Sham wave function for the k-point $\mathbf{k}$ and band number ν.
  $\Psi_{\mathbf{k}\nu}$ contains both correlated atomic orbitals and other non correlated orbitals.
  (Reminder: in the Hubbard model, the analogue of $\Psi_{\mathbf{k}\nu}$ was just the Bloch transform of atomic orbitals.)

In a real system in DFT+DMFT

- Local quantities such as $\widehat{\Sigma}$ can be computed in the Bloch basis:

$$\Sigma_{\nu\nu'\mathbf{k}}(\omega) = \langle \Psi_{\mathbf{k}\nu} | \widehat{\Sigma}(\omega) | \Psi_{\mathbf{k}\nu'} \rangle = \sum_{m,m',\mathbf{T}} \langle \Psi_{\mathbf{k}\nu} | \chi^{\mathbf{R}}_{\mathbf{T}m} \rangle \Sigma_{mm'}(\omega) \langle \chi^{\mathbf{R}}_{\mathbf{T}m'} | \Psi_{\mathbf{k}\nu'} \rangle$$

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  Using $|\chi^{\mathbf{R}}_{\mathbf{T}m}\rangle = \frac{1}{\sqrt{N}}\sum_{\mathbf{k}}|\chi^{\mathbf{R}}_{\mathbf{k}m}\rangle \mathrm{e}^{-i\mathbf{k}\mathbf{T}}$, one arrive to

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- From the Self energy, the full lattice Green's function in the Kohn Sham basis

  $$G^{-1}(\omega) = G^{-1}_{\mathrm{KS}}(\omega) - \Delta\Sigma(\omega) = (\omega - H_{\mathrm{KS}})\mathcal{I} - \Delta\Sigma(\omega)$$

  $$G_{\nu\nu'\mathbf{k}}(\omega) = [\omega - \epsilon_{\mathbf{k}\nu} - \Delta\Sigma_{\nu\nu'\mathbf{k}}(\omega)]^{-1}_{\nu\nu'\mathbf{k}}$$

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In a real system in DFT+DMFT

- Using the operator expression of the lattice Green's function

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- One can write the local Green's function as:

$$G_{mm'}(\omega) = \sum_{\nu\nu'\mathbf{k}} \langle \chi^{\mathbf{R}}_{\mathbf{T}m} | \Psi_{\mathbf{k}\nu}\rangle G_{\nu\nu'\mathbf{k}}(\omega) \langle \Psi_{\mathbf{k}\nu'} | \chi^{\mathbf{R}}_{\mathbf{T}m'}\rangle$$

for Hubbard model $G(\omega) = \sum_{\mathbf{k}} G_{\mathbf{k}}(\omega)$

From DFT to DFT+DMFT

$$\boxed{\text{DMFT}}$$

$$G_k^{\text{lattice}}(\omega) = \frac{1}{\omega - \epsilon_{\mathbf{k}} - \Sigma_{\mathbf{k}}(\omega)}$$

$$G^{\text{local}}(\omega) = \frac{1}{N}\sum_{\mathbf{k}} G_k^{\text{lattice}}(\omega)$$

For the Anderson model, the correlated orbital Green's function is:

$$G_{\text{Anderson}}(\omega) = \frac{1}{\omega - \epsilon_0 - \Delta(\omega) - \Sigma(\omega)}$$

$$\boxed{\text{DFT} + \text{DMFT}}$$

$$G_{n,n'\mathbf{k}}^{\text{lattice}}(\omega) = \frac{1}{\omega - \epsilon_{n\mathbf{k}} - \Sigma_{nn'\mathbf{k}}(\omega)}$$

$$G_{mm'}^{\text{local}}(\omega) = \sum_{\mathbf{k},n,n'} \langle \chi_{\mathbf{k}m} | \Psi_{\mathbf{k}n} \rangle G_{nn'}(\mathbf{k},\omega) \langle \Psi_{\mathbf{k}n'} | \chi_{\mathbf{k}m'} \rangle$$

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$$G_{mm'}^{\text{Anderson}}(\omega) = \left[\omega I - E_0 - \Delta(\omega) - \Sigma(\omega)\right]^{-1}\Big|_{mm'}$$

Definition of correlated orbitals: example of SrVO$_3$.

Need a projection from Kohn Sham states to correlated orbitals. $\langle \Psi_{nk} | \chi_{lm} \rangle$
A possible choice for correlation orbitals is Wannier functions.

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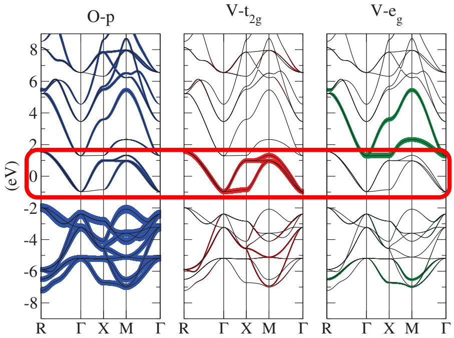

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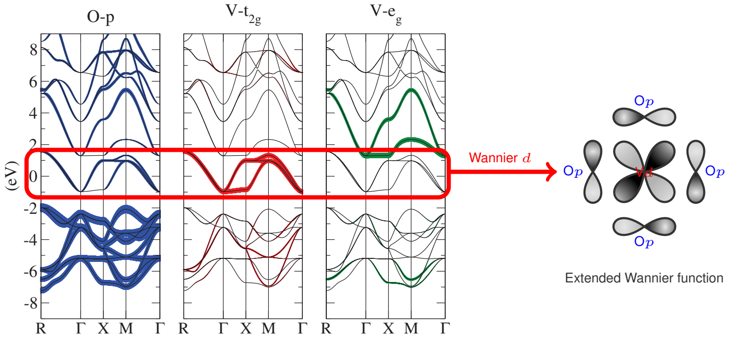

Extended Wannier function

Wannier orbitals are made from Vdt_{2g} bands so, they are not pure dt_{2g} orbitals because of the hybridization

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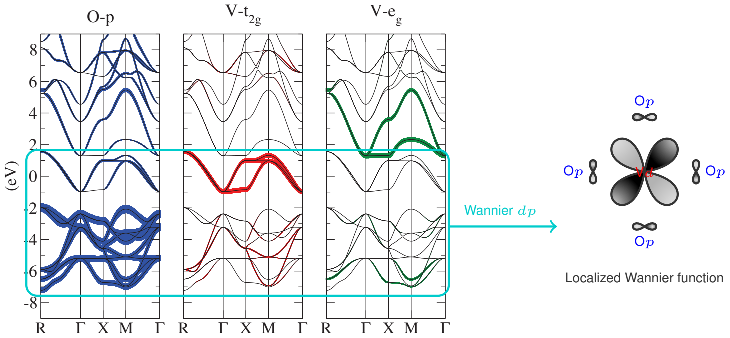


Localized Wannier function

Wannier orbitals are made from Vdt_{2g} bands and O p bands so, they are closer to dt_{2g} orbitals because more t_{2g} character is taken into account.

Double counting of interactions

Double counting corrections: Atomic limit (or Full localized limit) [Lichtenstein(1995), Anisimov (1991)]:

$$E_{\text{dc}}^{\text{FLL}} = \sum_t (\frac{U}{2} N(N-1) - \sum_\sigma \frac{J}{2} N^\sigma (N^\sigma - 1))$$

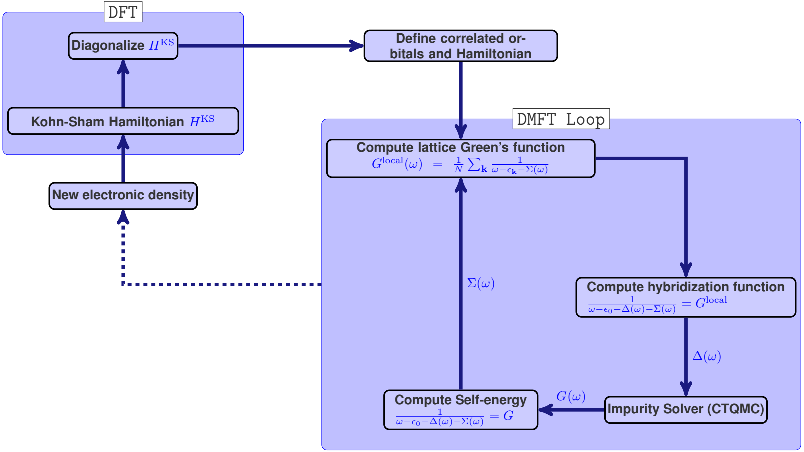
Around mean field version [Czyzyk(1994)] (delocalized limit):

$$E_{\text{dc}}^{\text{AMF}} = \sum_t (U N_\uparrow N_\downarrow + \frac{1}{2}(N_\uparrow^2 + N_\downarrow^2) \frac{2l}{2l+1}(U - J))$$

(Made to correct the delocalized limit.)

$$G_{\text{Anderson}}(\omega) = \frac{1}{\omega - \epsilon_0 - \Delta(\omega) - [\Sigma(\omega) - \Sigma_{dc}(\omega)]}$$

DFT+DMFT scheme



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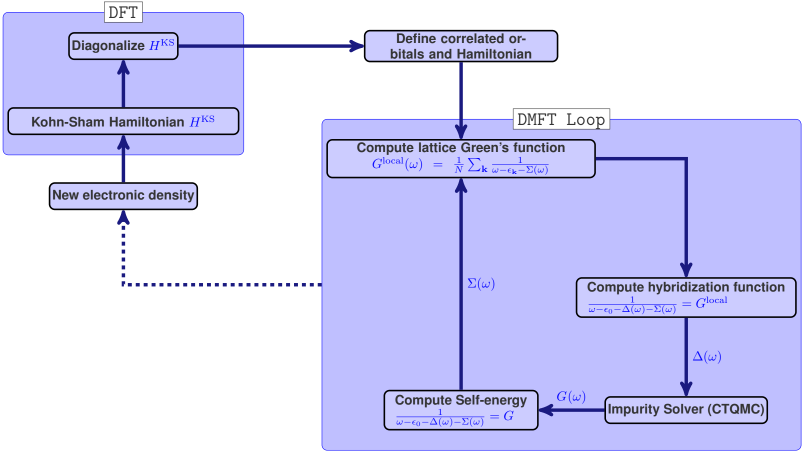

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More generally, DFT+DMFT can be expressed as functional of the local Green's function and the electronic density ⇒ Internal and free energies can be computed.

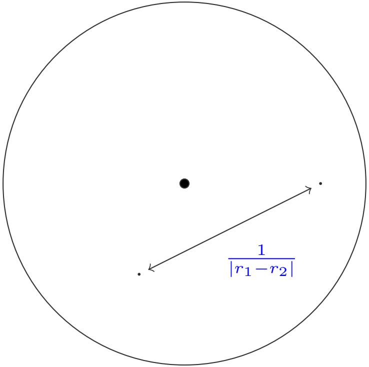
A functional of the density and the local Green's function

Theory	DFT	Green's fct Functional Theory
Interaction functional Interaction potential Equivalent system	$E_{\mathrm{Ha+xc}}[n(\mathbf{r})]$ $v_{\mathrm{Ha+xc}}$ non interacting system with a effective potential	$\widehat{\Phi}_U[G]$ Self energy Σ non interacting system with a frequency dependent potential (self energy)
Approximation Reference system	LDA Homogeneous electron gas	DMFT Anderson Impurity model

DFT+U

- Introduction to correlations.
- Dynamical Mean Field Theory (DMFT).
- Density Functional Theory and DMFT
- Calculation of effective interaction U.
- DFT+U.

How to compute the effective interaction ?



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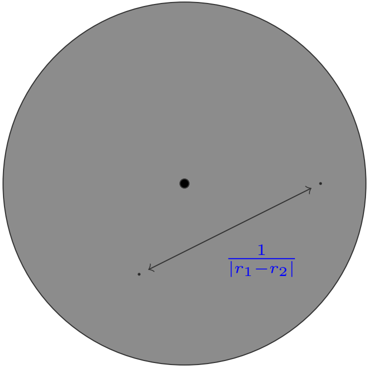

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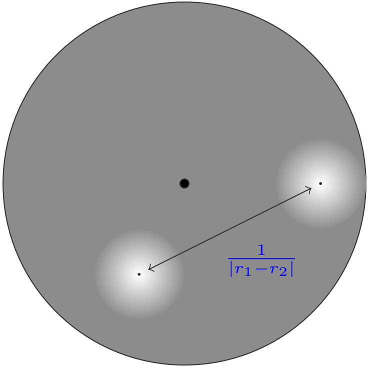

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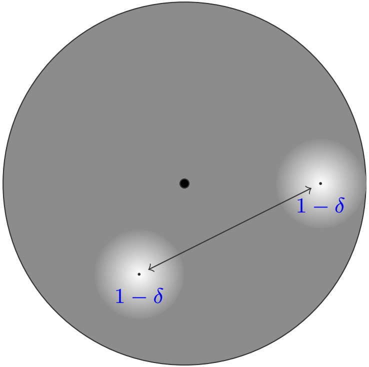

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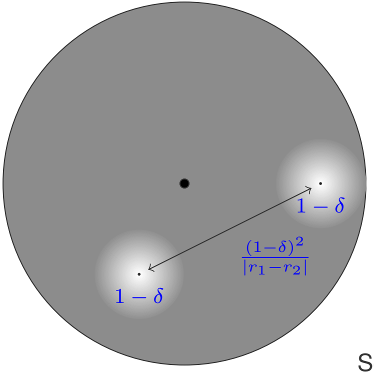


Screening

Methods to compute U

U is the screened interaction between electrons:

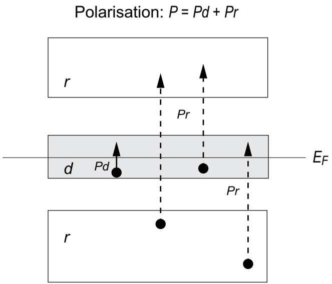
- Direct calculation of interactions in LDA by constraint LDA ^{1}
  - The coupling between d electrons and others is removed for the calculation.
- Direct approach by linear response theory ^{3}
  - The d local potential is modified, the number of correlated electrons changes, and the rearrangement of electrons around the atom describes the screening
- Calculation using the screening from LDA (cRPA formalism ^{2})
  - Frequency dependent interaction.
- Empirical determination.

(1) Anisimov and Gunnarsson PRB **43** 7570 (1991)

(2) Aryasetiawan, *et al* PRB **70** 195104 (2004)

(3) Cococcioni and de Gironcoli PRB **71** 035105 (2006)

The cRPA approach.



- In cRPA, all excitations are taken into account except the one belonging to the correlated subshell.

$$\varepsilon_r(\omega) = 1 - vP_r(\omega).$$

and P_r is the cRPA non interacting polarisability (see lectures of F. Bruneval) which describes transitions between occupied and empty states.

Picture from F. Aryasetiawan, The LDA+DMFT approach to strongly correlated materials E. Pavarini, E. Koch, D. Vollhardt, A. Lichtenstein (Eds.), Forschungszentrum JÃ$\frac{1}{4}$lich (2011).
F. Aryasetiawan, Imada, Georges, Kotliar, Biermann et Lichtenstein PRB 2004.

The cRPA approach.

We call here χ_0 the non interacting (Kohn-Sham) polarizability of the system. Let's now separate the correlated states (They could be d states but the method is more general and correlated orbitals could gather several orbitals from e.g different atoms) from the rest (r). We thus have:

$$\chi_0 = \chi_0^{\mathrm{correl}} + \chi_0^r$$

thus, we can rewrite the inverse dielectric matrix as:

$$\epsilon^{-1} = \frac{1}{1 - v(\chi_0^{\mathrm{correl}} + \chi_0^r)}$$

We now define the dielectric function due to correlated electrons as

The cRPA approach.

$$\epsilon_{\text{correl}}^{-1} \hat{=} \frac{1}{1 - W_r \chi_0^{\text{correl}}},$$

the dielectric function of the other electrons as

$$\epsilon_r^{-1} \hat{=} \frac{1}{1 - v\chi_0^r},$$

and the interaction screened only by the other (r) electrons as:

$$W_r = \frac{v}{1 - v\chi_0^r}$$

The cRPA approach.

With these definitions, one shows that

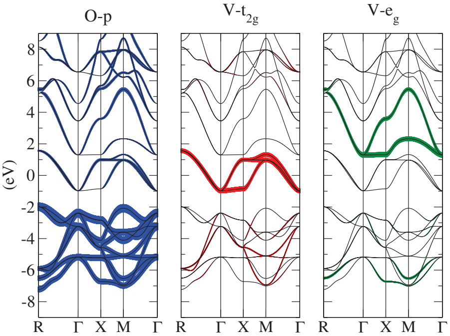
$$\epsilon_{\mathrm{correl}}^{-1}\epsilon_r^{-1} = ... = \frac{1}{1 - v\chi_0^r - v\chi_0^{\mathrm{correl}}} = \frac{1}{1 - v\chi_0} = \epsilon^{-1}$$

Thus, we have

$$W \hat{=} \epsilon^{-1} v = \epsilon_{\mathrm{correl}}^{-1}\epsilon_r^{-1} v$$

We can interpret this result: The fully screened RPA interaction is the combination of two screening processes. First, the bare interaction is screened by non-correlated electrons (r), and it gives rises to a screened interaction W_r. Secondly the screening of this interaction by correlated electrons recovers the fully screened interaction.

Definition of correlated orbitals: example of SrVO .



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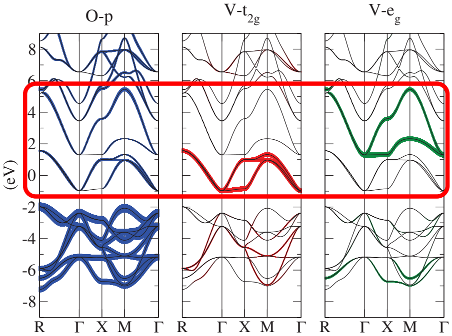

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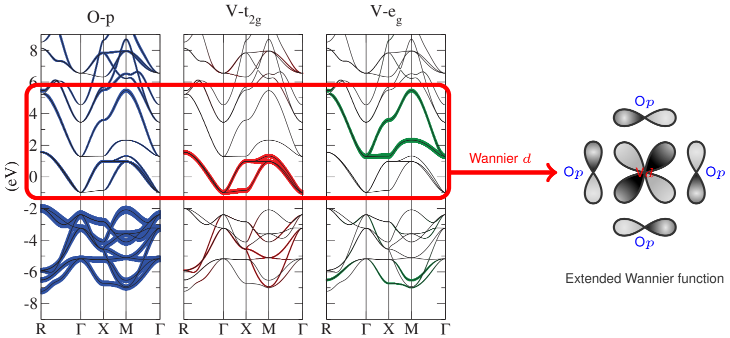

Extended Wannier function

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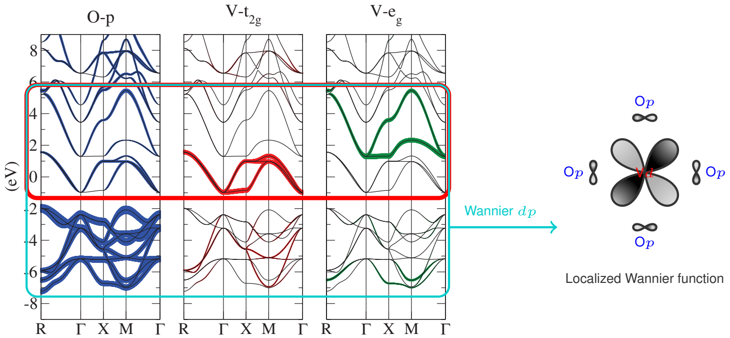
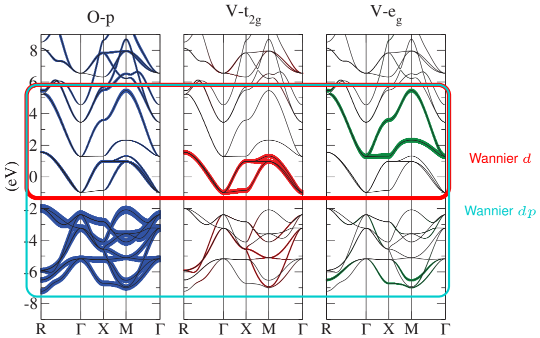


Localized Wannier function

Definition of correlated orbitals: example of SrVO .



Wannier d

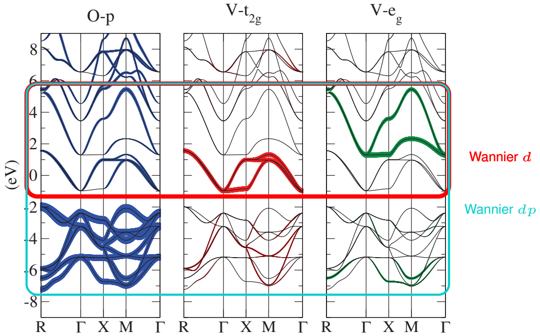
Wannier dp

Bare interaction can be computed as:

$$v = \langle \chi\chi | \frac{1}{r_1 - r_2} | \chi\chi \rangle$$

Wannier function	bare interaction v (eV)
Wannier d	15.3
Wannier dp	19.4

Definition of correlated orbitals: example of SrVO .



Effective interaction can be computed as:

$$U = \langle \chi\chi | \epsilon^{-1}_{\mathrm{cRPA}} v | \chi\chi \rangle$$

Wannier function	bare interaction v (eV)	effective interaction U (eV)	Name of the model
Wannier d	15.3	2.8	$d-d$
Wannier dp	19.4	10.8	$dp-dp$

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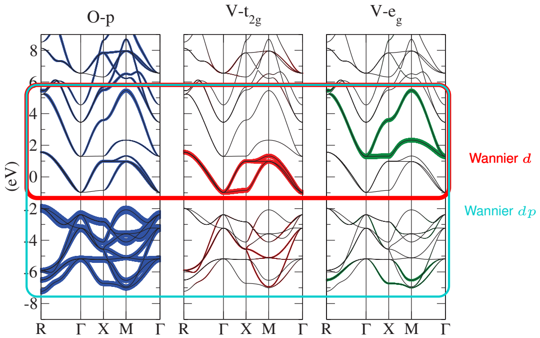

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DFT+U

- Introduction to correlations.
- Dynamical Mean Field Theory (DMFT).
- Density Functional Theory and DMFT
- Calculation of effective interaction U.
- DFT+U.

Rotationnaly invariant DFT+U [Lichtenstein et al (1995)]

The interaction part corresponds to :

$$E_{\mathrm{HF}}^{\mathrm{Coulomb}} = \frac{1}{2}\sum_{i,j}\left[\int \phi_i(\mathbf{r})\phi_j(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_i(\mathbf{r})\phi_j(\mathbf{r}') - \int \phi_i(\mathbf{r})\phi_j(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_j(\mathbf{r})\phi_i(\mathbf{r}')\right]$$

Expand the wavefunctions on a new basis: the basis of Vanadium d orbitals and Oxygen p orbitals:

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$$|\phi_i\rangle = \sum_{d,m=-2\ldots2}\langle\chi_{d,m}|\phi_i\rangle|\chi_{d,m}\rangle + \underbrace{(\sum_{p,m=-1\ldots1}\langle\chi_{p,m}|\phi_i\rangle|\chi_{p,m}\rangle) + \ldots\ldots}_{\text{neglected}}$$

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and show that (blackboard or exercice):

$$E_{\mathrm{HF}}^{\mathrm{Coulomb}} = \frac{1}{2}\sum_{m_1,m_2,m_3,m_4}\Bigg[\langle\chi_{m_1}\chi_{m_2}|\frac{1}{|\mathbf{r}-\mathbf{r}'|}|\chi_{m_3}\chi_{m_4}\rangle n_{m_4,m_2}n_{m_3,m_1} - \langle\chi_{m_1}\chi_{m_2}|\frac{1}{|\mathbf{r}-\mathbf{r}'|}|\chi_{m_3}\chi_{m_4}\rangle n_{m_3,m_2}$$

$$n_{V\,d,m_1,m_2} = \sum_i\langle\phi_i|\chi_{d,m_1}\rangle\langle\chi_{V\,d,m_2}|\phi_i\rangle$$

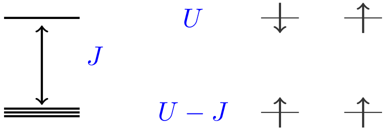
In the cubic symmetry, density matrices are diagonal and thus

$$E_{\mathrm{HF}}^{\mathrm{Coulomb}} = \frac{1}{2}\sum_{m_1,m_2}\left[\langle\chi_{m_1}\chi_{m_2}|V|\chi_{m_1}\chi_{m_2}\rangle n_{m_2,m_2}n_{m_1,m_1} - \langle\chi_{m_1}\chi_{m_2}|V|\chi_{m_2}\chi_{m_1}\rangle n_{m_2,m_2}n_{m_1,m_1}\right]$$

DFT+U

Thus , in the simplest case (restoring spin):

$$
\begin{aligned}
E_{\mathrm{HF}}^{\mathrm{U}} &= \frac{1}{2} \sum_{m_1,m_2,\sigma} U_{m_1,m_2} n_{m_2}^{\sigma} n_{m_1}^{-\sigma} \\
&+ \sum_{m_1,m_2,\sigma} (U_{m_1,m_2} - J_{m_1,m_2}) n_{m_2}^{\sigma} n_{m_1}^{\sigma}
\end{aligned}
$$



DFT+U

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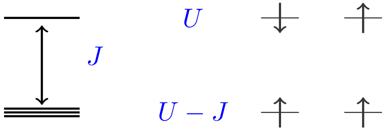
$$\begin{aligned} E^{\mathrm{U}}_{\mathrm{HF}} &= \frac{1}{2}\sum_{m_1,m_2,\sigma} U_{m_1,m_2} n^{\sigma}_{m_2} n^{-\sigma}_{m_1} \\ &+ \sum_{m_1,m_2,\sigma} (U_{m_1,m_2} - J_{m_1,m_2}) n^{\sigma}_{m_2} n^{\sigma}_{m_1} \end{aligned}$$



Let’s simplify even more, neglecting J and using a constant U.

$$E^{\mathrm{U}}_{\mathrm{HF}} = \frac{1}{2}\sum_{m_1,m_2} U n_{m_2} n_{m_1} = \sum_{m_1>m_2} U n_{m_2} n_{m_1}$$

DFT+U

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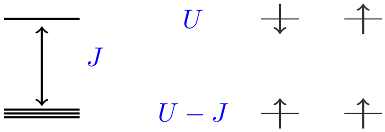

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$$

If we have $2l+1$ orbitals, the number of interactions is $2l(2l+1)$. The interaction is taken into account twice ! One in E_{xc}, one in E^{Coulomb} ! We need to cancel the DFT contribution, a proposition is:

$$
E_{\mathrm{HF}}^{\mathrm{dc(=double\ \ counting)}} = U\frac{N(N-1)}{2} \quad \text{with} \quad N = \mathrm{Tr}[n_{m_1}]
$$

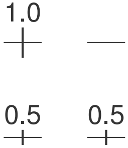
Basic effects of the static mean field approximation (DFT+U)

$$E^{\mathrm{U}} = \sum_{m_1 > m_2} U n_{m_2} n_{m_1}$$

- U favors integer occupation of orbitals
- It penalizes non integer values.

$$E_U = 0 \times 1U = 0$$

$$E^U = 0.5 \times 0.5U = 0.125U$$



Basic effects of the static mean field approximation (DFT+U)

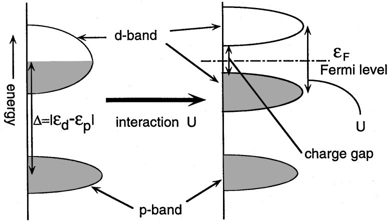
$$E = E_{\mathrm{DFT}} - U\frac{N(N-1)}{2} + \frac{U}{2}\sum_{m \neq m'} n_m n_{m'} \quad \Rightarrow \quad V = V_{\mathrm{DFT}} - \sum_m |\chi_m\rangle U(n_m - \frac{1}{2})\langle\chi_m|$$

(do it in exercice !)

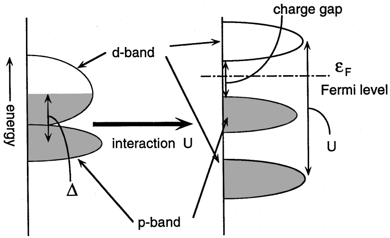
- $n_m = 0$, $V = V_{\mathrm{DFT}} + \frac{U}{2}$
- $n_m = 1$, $V = V_{\mathrm{DFT}} - \frac{U}{2}$

$\Rightarrow$ A gap is opened among correlated orbitals.

Charge transfert insulators and Mott Hubbard insulators



(a) Mott-Hubbard Insulator



(b) Charge Transfer Insulator

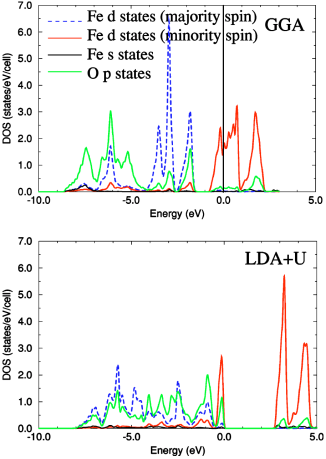
Mott insulators: Gap excitations are d-d (or f-f)
ie between Hubbard bands.

Charge Transfert insulators: Gap excitations are Op-d (Or Op-f)
Correlation opens the gap in the two cases !

Imada RMP (1998)

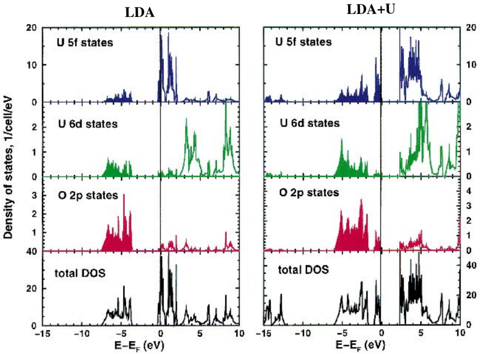
Zaanen, Sawatzky, and Allen PRL (1985)

Main effects of Mean Field approximation (DFT+U)



FeO (d^6): insulator in DFT+U

Cococcioni *et al* PRB **71** 2005



UO$_2$ (f^2): antiferromagnetic, insulator

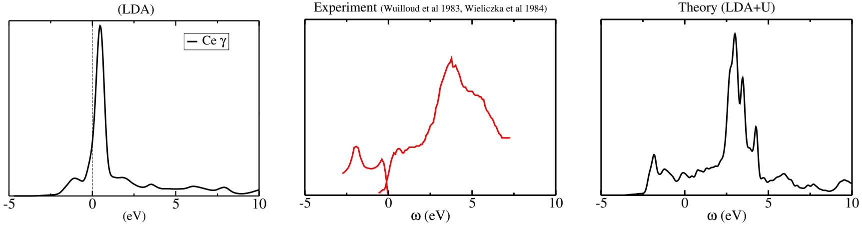
Gap$_{exp}$=2.1 eV

electrons localization: volume increases in DFT+U

Dudarev *et al* Micron **31** 2000

γ cerium (paramagnetic)

- Spectral functions: basic features are reproduced.



(LDA)

Experiment (Wuilloud et al 1983, Wieliczka et al 1984)

Theory (LDA+U)

- Structural data

$\Rightarrow$ Electron repulsion induces a weakening of the bonding.

(1) Shick, Pickett, Lichtenstein 2000, Amadon, Jollet, Torrent PRB 2008.

	Exp	DFT+U[1]	DFT
alat (au)	9.76	9.83/9.54	8.54
B_0 (GPa)	19	29.6/34	55

- But: The α phase is not correctly described, magnetism is incorrect (except for the β phase), no transitions.

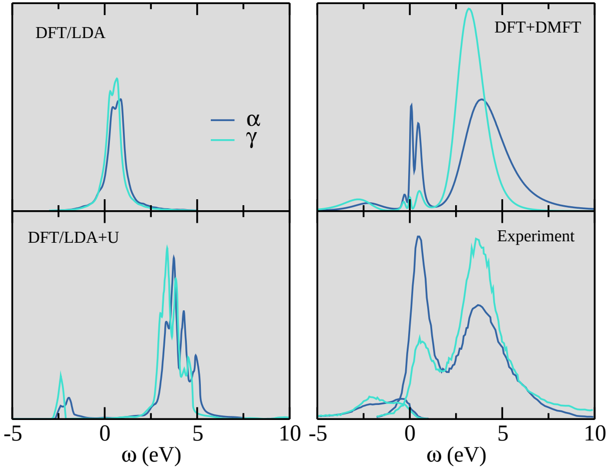
Some limitations of the DFT+U method

Mean Field solution : Fixed (frozen) occupancies.

- Magnetic order: Paramagnetic insulators cannot be described.
  - V_2O_3, γ Cerium.
- Orbital order and anisotropy are overestimated
  - Electrons are frozen.
- Metallic and correlated phase are out of reach (α Cerium, $SrVO_3$).
- Transition induced by localization cannot be described.

Spectral functions of cerium

Theoretical spectral functions compared to photoemission spectra



Amadon et al PRB 2015

Conclusion

- Strong correlations
  - Localized orbitals induce strong electronic Coulomb interaction.
  - This repulsion can induce strong localization of electrons and creates Mott insulator.
  - Hubbard bands and Kondo effects are signatures of strong interaction.
  - DMFT can describe both localized and delocalized electron and metal insulator transition.

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  - DMFT is exact in infinite dimensions, at $U = 0$ and $t = 0$.
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  - Photoemission spectra and various core spectroscopies.
  - Total and free energy.
  - Phonons and elastic properties.
  - Magnetic susceptibility (Curie, Pauli), Curie temperature.

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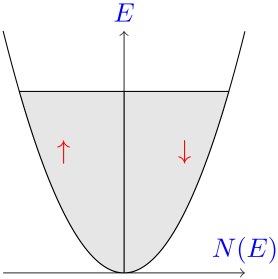
- Perspectives
  - Include non local interactions and correlations: Cluster-DMFT
  - Treat also weak correlation effects and more ab-initio (no parameters): GW+DMFT

THANK YOU

Pauli paramagnetism



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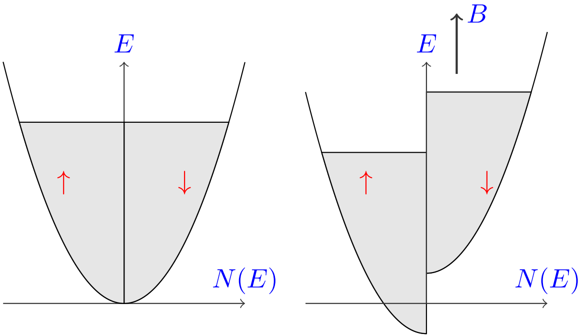

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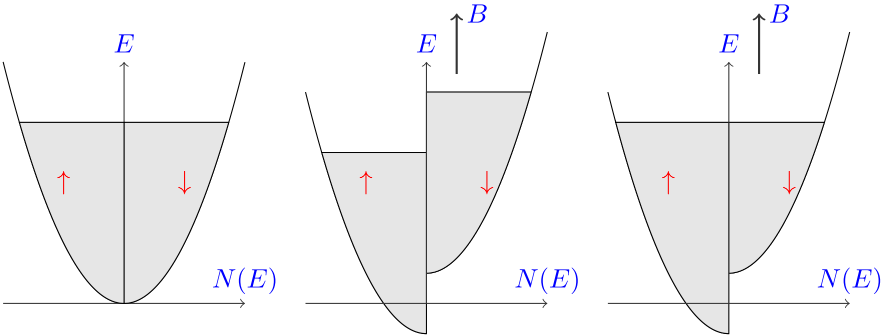
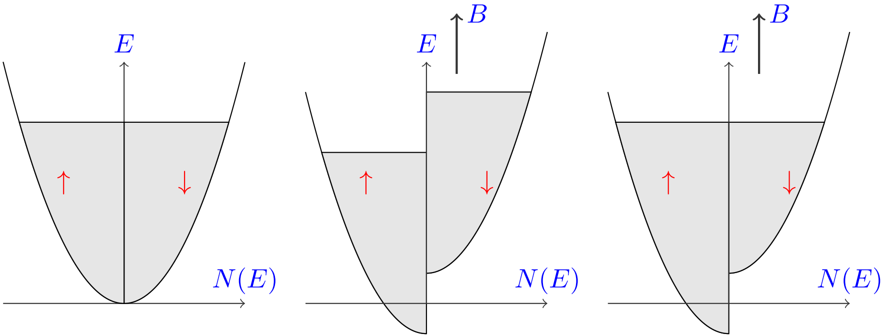


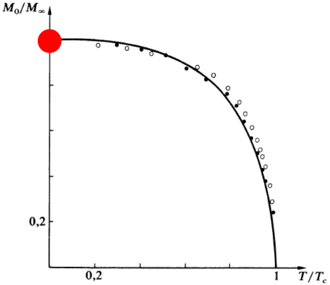
Pauli paramagnetism



- Small magnetic moment, linear with B.
- Pauli paramagnetism (temperature independent)
- For simple metals (Na,Al): Pauli paramagnetism
- Exercice : Derive the susceptibility and show that it is independent of temperature.

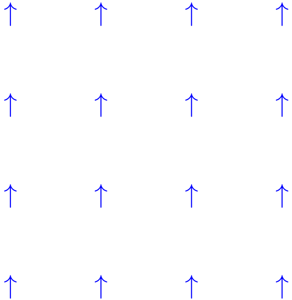
Curie Weiss paramagnetism and ferromagnetism

- Ferromagnetism



Ronds vides: fer
Ronds pleins: cobalt et nickel

- T=0 large magnetic moment



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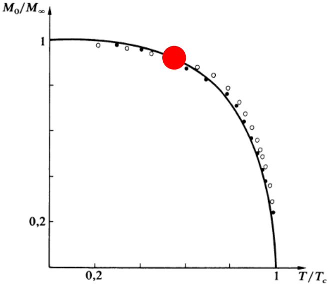

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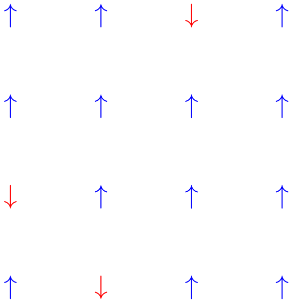
- T=0 large magnetic moment
- T increases, magnetic moment lowers (thermal effect).



Curie Weiss paramagnetism and ferromagnetism

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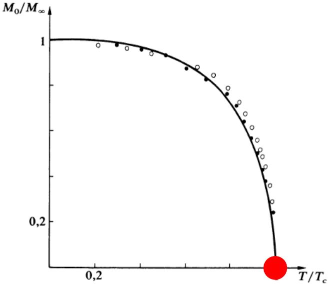

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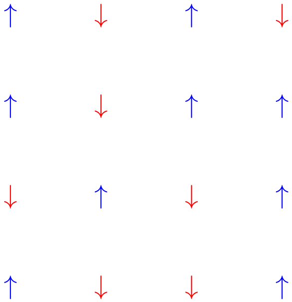
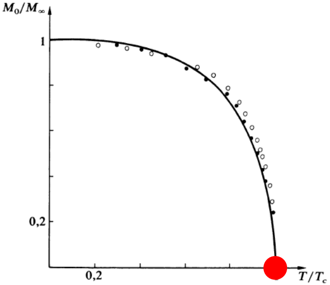
- Curie temperature (disordered fluctuating moments)



Curie Weiss paramagnetism and ferromagnetism

- Ferromagnetism



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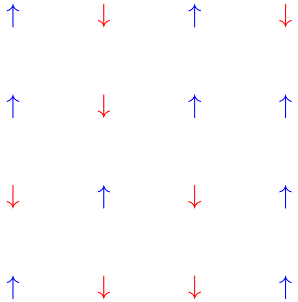
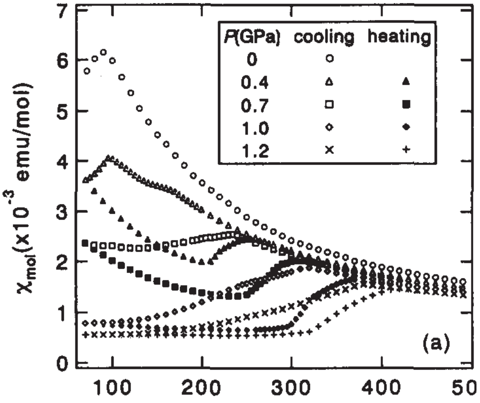
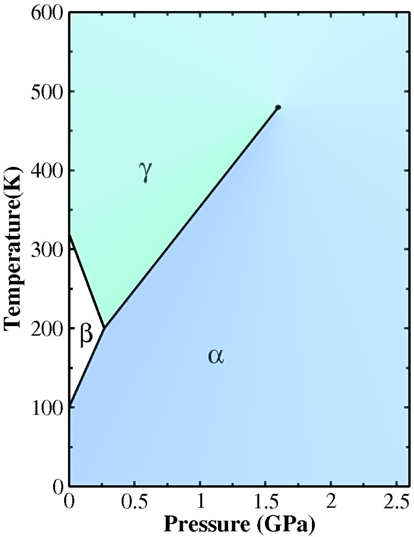


- What happens at large temperature ?

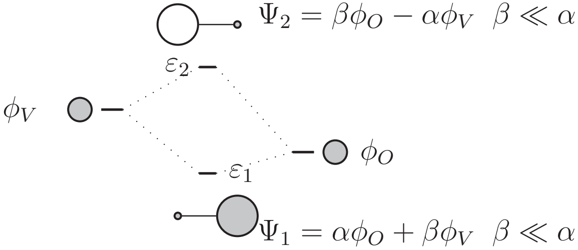
Susceptibility in cerium





Naka et al (1995)

An oversimplified derivation



Two windows of energy are possible to compute

$$|\widetilde{\chi}\rangle = \sum_{i\in\mathcal{W}} \langle\Psi_i|\phi_V\rangle|\Psi_i\rangle$$

- If $\mathcal{W} = \{\varepsilon_2\}$, the correlated wavefunction is $|\widetilde{\chi}\rangle = |\Psi_2\rangle = \beta|\phi_O\rangle - \alpha|\phi_V\rangle$. No renormalization is necessary thus $|w\rangle = |\widetilde{\chi}\rangle$. It contains an Oxygen contribution
- If $\mathcal{W} = \{\varepsilon_1, \varepsilon_2\}$, the correlated wavefunction is $|\widetilde{\chi}\rangle = \sum_i \langle\Psi_i|\phi_V\rangle|\Psi_i\rangle = |\phi_V\rangle$ and is much more localized.

Calculation of $\langle m_1 m_3 | V | m_2 m_4 \rangle$

One uses $\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \sum_{m=-k}^{k} \frac{4\pi}{2k+1} \frac{r_<^k}{r_>^{k+1}} Y_k^m(\theta_1, \phi_1) Y_k^{m*}(\theta_2, \phi_2)$ and after some manipulations: $\langle m_1 m_3 | V_{\text{ee}} | m_2 m_4 \rangle$ contains an angular and a radial part.

$$\langle m_1 m_3 | V_{\text{ee}} | m_2 m_4 \rangle = 4\pi \sum_{k=0,2,4,6} \frac{F_k}{2k+1} \sum_{m=-k}^{+k} \langle m_1 | m | m_2 \rangle \langle m_3 | m | m_4 \rangle$$

$$\begin{aligned} U &= \frac{1}{(2l+1)^2} \sum_{m_1, m_2} \langle m_1 m_2 | V_{\text{ee}} | m_1 m_2 \rangle = F_0 \ \ \text{coulomb} \ \ \text{term} \\ J &= \frac{1}{2l(2l+1)} \sum_{m_1 \neq m_2} \langle m_1 m_2 | V_{\text{ee}} | m_2 m_1 \rangle = \frac{F_2 + F_4}{14} \ \ \text{exchange} \ \ \text{term} \end{aligned}$$

The DFT+U method

$$E_{\mathrm{DFT+U}} = E_{\mathrm{DFT}} - \overbrace{U\frac{N(N-1)}{2}}^{E_{\mathrm{DC}}} + \overbrace{\frac{U}{2}\sum_{m\neq m'} n_m n_{m'}}^{E_{\mathrm{ee}}} = U\sum_m (n_m - n_m^2)$$

In the atom (n_f=1,0) $E_{\mathrm{ee}} = E_{\mathrm{DC}} = U\frac{N(N-1)}{2}$

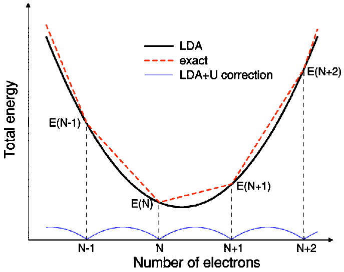


FIG. 1. (Color online) Sketch of the total energy profile as a function of number of electrons in a generic atomic system in contact with a reservoir. The bottom curve is simply the difference between the other two (the LDA energy and the "exact" result for an open system).

- Atom (integer nb of e^-)=The DFT+U correction disappears.

$\Rightarrow$ Self-interaction correction.

From Cococcioni *et al* PRB **71** (2005)

see also Solovyev *et al* PRB **50** 16861 (1994)