

Charge Self-Consistency in Correlated Electronic Structure Calculations

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outline

- introduction
- self-consistency in numerical approaches to many-electron systems
 - Hartree-Fock method
 - density functional theory (DFT) in Kohn-Sham representation
 - dynamical mean-field theory (DMFT)
 - mixing
- realistic many-body account of correlated materials
 - combining DFT and DMFT: functionals
 - combining DFT and DMFT: in practise
 - relevance of charge self-consistency
- an illustrative materials example: metal-insulator transition in V_2O_3
 - phase diagram and basic materials characteristics
 - electronic correlations within DFT+DMFT
 - new results : Cr doping vs. Ti doping

introduction : basic concept of (charge) self-consistent calculations

fundamental for high-rank function f (e.g. a potential) and low-rank function ψ (e.g. a wave function)

general problem : $\mathcal{D} f(\psi) + \mathcal{D}' \psi = 0$, $\mathcal{D}, \mathcal{D}'$: generic operators

- problem results from explicit variational considerations
- problem results from other theory implications (e.g. crystal vacancy problem in thermodynamics)

→ solve problem by iterative means from initial guess $\{f^{(0)}, \psi^{(0)}\}$, until given relation is established

charge self-consistency in electronic structure problems

self-consistency : Hartree-Fock method, setting

describing an interacting electron system via the many-body wave function $\Psi(\{\mathbf{r}_i \sigma_i\}) =: \Psi(\{\mathbf{x}_i\})$

ansatz Slater determinant

$$\Psi_{\text{HF}}(\{\mathbf{x}\}) =: \hat{S}_- \prod_i^N \varphi_i(\mathbf{r}) \chi_i(\sigma) = \hat{S}_- \prod_i^N \phi_i(\mathbf{x}) \quad , \quad \text{with} \quad \varphi_i(\mathbf{r}) = \sum_{\nu}^M A_{i\nu} B_{\nu}(\mathbf{r})$$

Hamiltonian

$$\hat{H} = \sum_i^N \left[\frac{\hat{p}_i^2}{2m} + \hat{V}_i \right] + \frac{1}{2} \sum_{ij} \hat{v}_{ij} =: \sum_i^N \hat{h}_i + \frac{1}{2} \sum_{ij} \hat{v}_{ij}$$

Ritz' variational principle

$$\delta \left(\frac{\langle \Psi_{\text{HF}} | \hat{H} | \Psi_{\text{HF}} \rangle}{\langle \Psi_{\text{HF}} | \Psi_{\text{HF}} \rangle} \right) \stackrel{!}{=} 0 \quad \Rightarrow \quad \mathcal{F}[\Psi_{\text{HF}}] = \langle \Psi_{\text{HF}} | \hat{H} | \Psi_{\text{HF}} \rangle - \sum_i \varepsilon_i \langle \phi_i | \phi_i \rangle \quad , \quad \text{with} \quad \delta \mathcal{F} \stackrel{!}{=} 0$$

Hartree-Fock equations

$$\left[-\frac{1}{2m} \Delta + V(\mathbf{r}) + e^2 \sum_{j \neq i} \int d\mathbf{r}' \frac{|\varphi_j(\mathbf{r})|^2}{|\mathbf{r} - \mathbf{r}'|} \right] \phi_i(\mathbf{r}) - e^2 \sum_{j \neq i} \delta_{\sigma_i \sigma_j} \int d\mathbf{r}' \frac{\varphi_j^*(\mathbf{r}) \varphi_i^*(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \phi_j(\mathbf{x}) = \varepsilon_i \phi_i(\mathbf{x})$$
$$\Rightarrow \quad \left[-\frac{1}{2m} \Delta + V(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) \right] \varphi_i(\mathbf{r}) + \int d\mathbf{r}' v_{\text{X}}(\mathbf{r}, \mathbf{r}') \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})$$

comments

- ⊙ local Hartree potential v_{H} and nonlocal exchange potential v_{X} depend on the wave functions φ_i
- ⊙ Hartree-Fock cannot describe electronic correlations
- ⊙ no screening effects, ill-defined for metallic systems
- ⊙ accidentally : spectrum of Mott insulators may be described not too badly (i.e. careful not to be tricked...!)

self-consistency : Hartree-Fock method, solution

understanding the Hartree-Fock equations as self-consistent (SCF) field equations

iterative scheme

1. Start with an educated guess for the single-particle functions $\varphi_i(\mathbf{r}) = \varphi_i^{(1)}(\mathbf{r})$ by invoking suitable linear combinations of the basis functions.
For instance, an adequate kind of sp^n hybridization function might be meaningful for a carbon-based molecule.
2. Construct a first associated Hartree potential $v_H^{(1)}(\mathbf{r}) = v_H^{\{\varphi_i^{(1)}\}}(\mathbf{r})$
and exchange potential $v_X^{(1)}(\mathbf{r}) = v_X^{\{\varphi_i^{(1)}\}}(\mathbf{r}, \mathbf{r}')$,
solve the Hartree-Fock equations for a new set of eigenfunctions $\varphi_i^{(2)}(\mathbf{r})$.
3. Go back to step 2 and repeat p times until you reach convergence in the potentials,
i.e. $|v_H^{(p)} - v_H^{(p-1)}| < \eta$ and $|v_X^{(p)} - v_X^{(p-1)}| < \eta$ holds for small η .

comments

- ⊙ charge self-consistent, if all electrons treated equally

self-consistency : density functional theory, motivation

many-body wave functions are hard to compute and store

example : methane molecule CH_4 with $N=10$ electrons, M basis functions

$$\rightarrow \binom{2B}{N} = \frac{(2B)!}{N!(2B-N)!} \quad \text{possible many-body configurations}$$

minimal basis $B = 9$: $\binom{18}{10} = 43758 \xrightarrow{\text{symmetry}} \sim 16000$ relevant Slater determinants

good basis $M = 35$: $\binom{70}{10} = 4 \cdot 10^{11} \xrightarrow{\text{symmetry}} \sim 2 \cdot 10^{10}$ relevant Slater determinants

alternative : effective single-particle theory with individual electron in the mean field of the other electrons

electronic charge density $\rho(\mathbf{r})$ as observable 3 coordinates instead of $3N$

why promising?

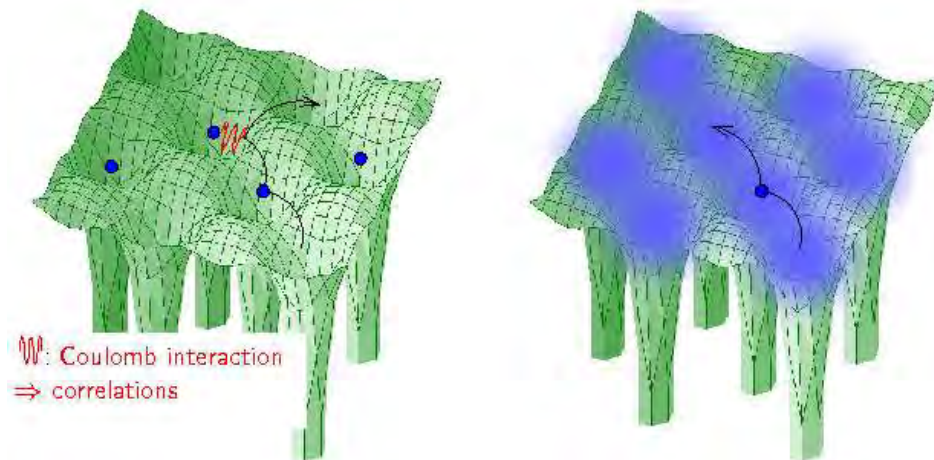
$\rho(\mathbf{r})$ sets . . .

... number N of electrons

... sites \mathbf{R}_i of nuclei

... charges Q_i of nuclei

\Rightarrow complete system information!



self-consistency : density functional theory, foundation and practise

describing an interacting electron system via the electronic charge density

Hohenberg-Kohn theorems

1. in principle, there is a unique one-to-one mapping between the charge density $\rho(\mathbf{r})$ and the many-body wave function $\psi(\{\mathbf{x}_i\})$, i.e. formally $\rho(\mathbf{r}) \Leftrightarrow \psi(\{\mathbf{x}_i\})$
2. there is an energy functional $E[n]$, which is minimal for the ground state energy E_0 . i.e. it holds $E_0 = \text{Min } E[n] = E[n_0]$

energy functional

$$E[\rho] = \underbrace{T[\rho]}_{\text{kin. Energie}} + \underbrace{V_{ee}[\rho]}_{\text{ee interaction}} + \underbrace{E_{\text{ext}}[\rho]}_{\text{e-nuclei energy}} = F_{\text{HK}}[\rho] + \int d^3 r \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r})$$

$=: F_{\text{HK}}[\rho]$

- Hohenberg-Kohn functional $F_{\text{HK}}[\rho]$ is unknown (extraordinarily complicated!)
- Use and variation of $E[\rho]$ remains open

Kohn-Sham idea mapping onto virtual, non-interacting electron system with one-body potential $v_{\text{eff}}(\mathbf{r})$
Slater determinant $\Phi(\{\mathbf{r}_i\})$ and charge density $\rho(\mathbf{r})$

$$\begin{aligned} \Rightarrow E[\rho] &= T[\rho] + V_{ee}[\rho] + \int d^3 r \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) \\ &\stackrel{!}{=} T_{\text{S}}[\rho] + \int d^3 r \rho(\mathbf{r}) v_{\text{eff}}(\mathbf{r}) \\ &= T_{\text{S}}[\rho] + \frac{e^2}{2} \int d^3 r \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}[\rho] + \int d^3 r \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) \end{aligned}$$

self-consistency : density functional theory, solution

variation now possible, since functionals become representable and $n\rho(\mathbf{r}) = \sum_{i, \text{occupied}} |\varphi_i(\mathbf{r})|^2$

$$\rightarrow \frac{\delta}{\delta \varphi_i^*} \left\{ E - \sum_i \varepsilon_i \int d^3 r |\varphi_i(\mathbf{r})|^2 \right\} \stackrel{!}{=} 0$$

$$\Rightarrow \text{Kohn-Sham equations} \quad \left[-\frac{1}{2m} \Delta_i + v_{\text{eff}}(\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})$$

exchange-correlation functional

effective potential $v_{\text{eff}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r})$, $v_{\text{xc}}(\mathbf{r}) := \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho}$ remains unknown!

approximation for $E_{\text{xc}}[n]$

use exchange-correlation density of the homogeneous electron gas $\epsilon_{\text{xc}}^{\text{hom}}(n)$ with $\rho = N/V$ and construct

$$E_{\text{xc}}[\rho] = \int d^3 r \rho(\mathbf{r}) \epsilon_{\text{xc}}^{\text{hom}}(\rho(\mathbf{r})) \quad \text{local density approximation (LDA)}$$

● $\epsilon_{\text{xc}}^{\text{hom}}(\rho)$ can be computed numerically exact by quantum Monte-Carlo techniques

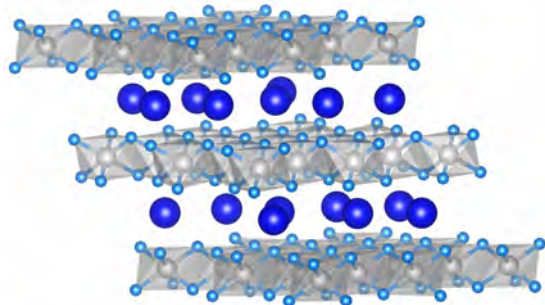
● parametrize $f = f(\rho)$, potential through differentiation

comments

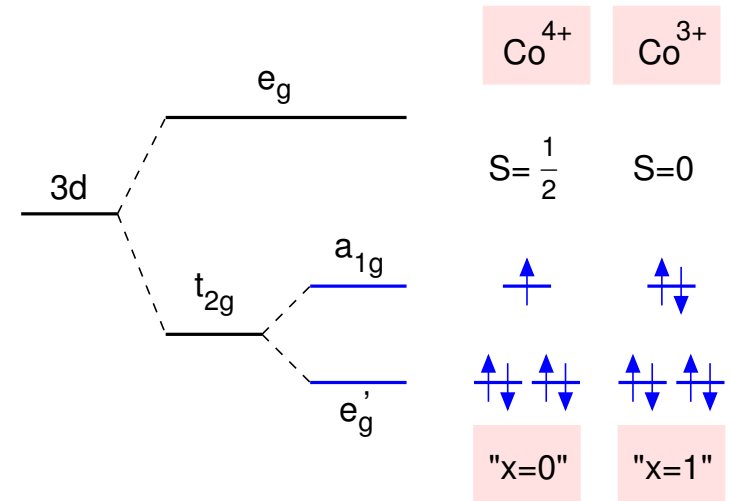
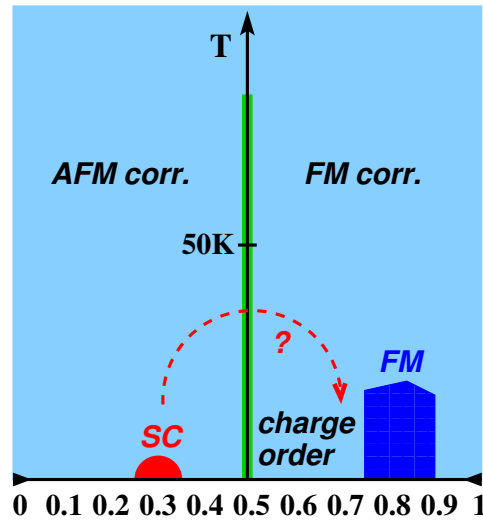
- the workhorse of materials science, all reliable over the periodic table
- new functionals: meta-GGA (e.g. SCAN), hybrids, etc.
- limitation : insufficient for physics of strong electronic correlations

self-consistency : density functional theory, challenging application

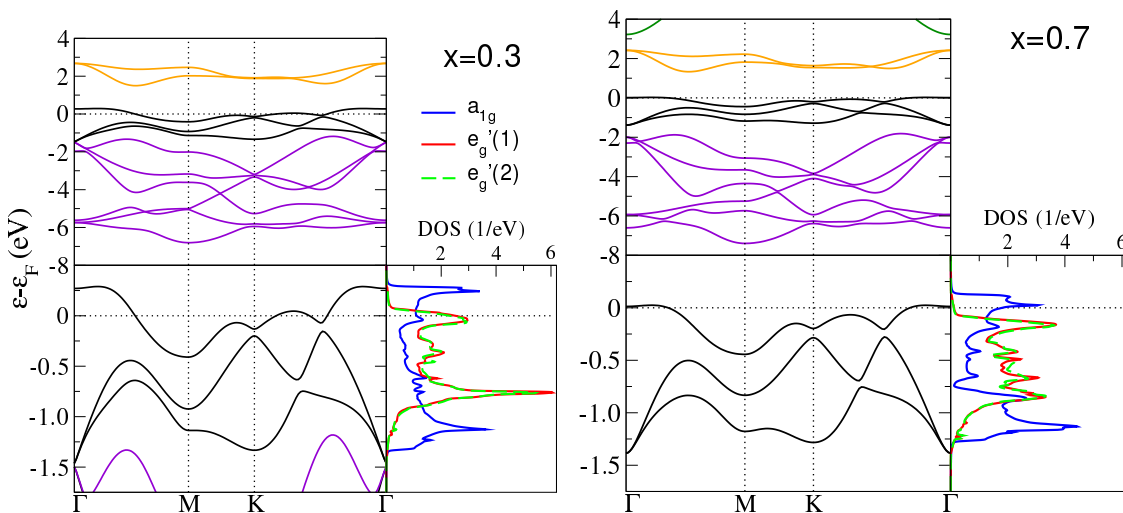
Na_xCoO_2 : a correlated materials system



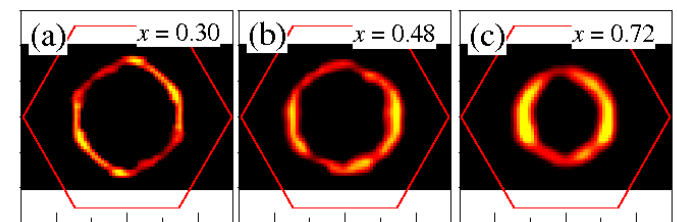
triangular CoO_2 lattice



DFT picture → band theory

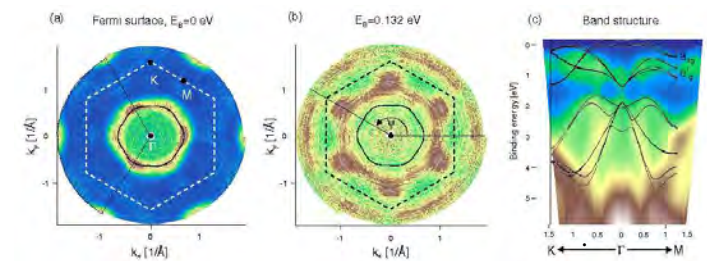


photoemission



[Yang et al., PRL 95, 146401 (2005)]

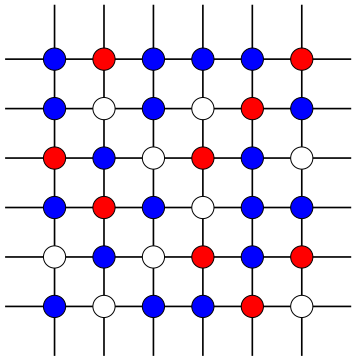
[Geck et al., PRL 99, 046403 (2007)]



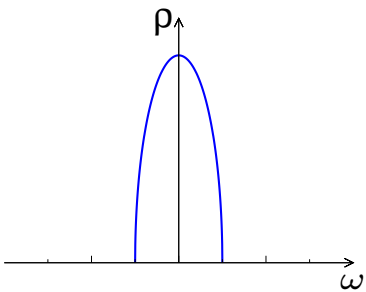
self-consistency : dynamical mean-field theory, motivation

Hubbard model:
$$H = -t \sum_{\langle ij \rangle \sigma} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}, \quad \text{for half filling } n = 1$$

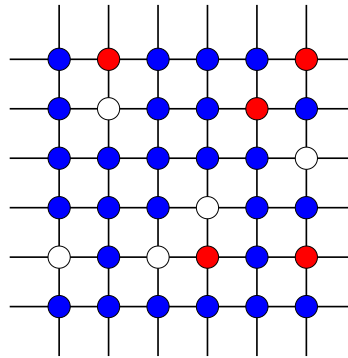
nonint. limit ($U = 0$)



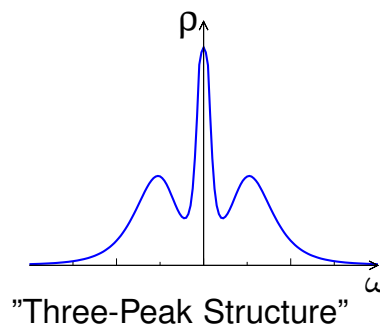
- $H = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma}$
- ideal metal, Fermi gas



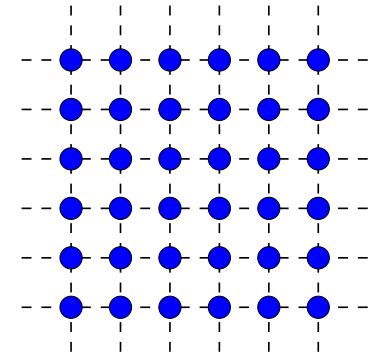
intermediate ($U \sim t$)



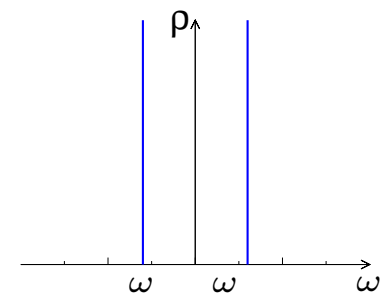
- correlated metal
- dominance of single occupations




atomic limit ($t = 0$)



- decoupled lattice sites
- only single occupations in ground state



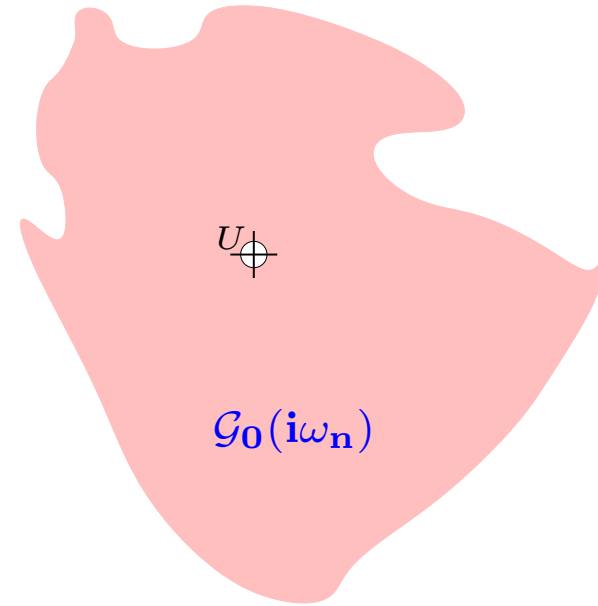
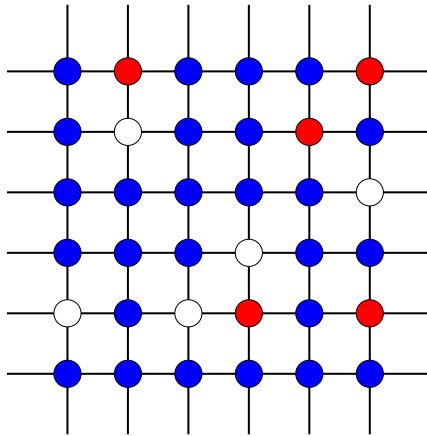
self-energy $\Sigma(\mathbf{k}, \omega)$ carries the effects of electron-electron interaction

 Kohn-Sham self energy
$$\Sigma_{\text{KS}}(\mathbf{k}, \omega) = \sum_{\mathbf{q}} (v_{\text{H}} + v_{\text{xc}})_{\mathbf{k}\mathbf{q}\mathbf{k}\mathbf{q}} \left(e^{\beta(\varepsilon_{\mathbf{q}} - \mu)} + 1 \right)^{-1}$$

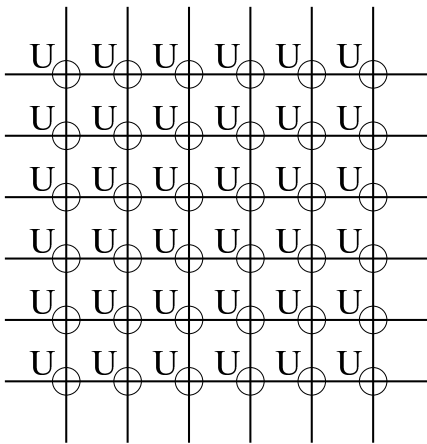
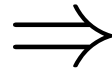
self-consistency : dynamical mean-field theory, impurity construction

[Metzner, Vollhardt, PRL (1989)] [Georges, Kotliar, PRB (1992)]

describing an interacting electron system with a given noninteracting Hamiltonian via a local self-energy



$$H = -t \sum_{\langle ij \rangle \sigma} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}$$



$$G_{\text{imp}}(i\omega_n) = \left[\mathcal{G}_0^{-1}(i\omega_n) - \Sigma_{\text{imp}}(i\omega_n) \right]^{-1}$$

DMFT approximation:

$$G_{\text{loc}}(i\omega_n) \stackrel{!}{=} G_{\text{imp}}(i\omega_n)$$

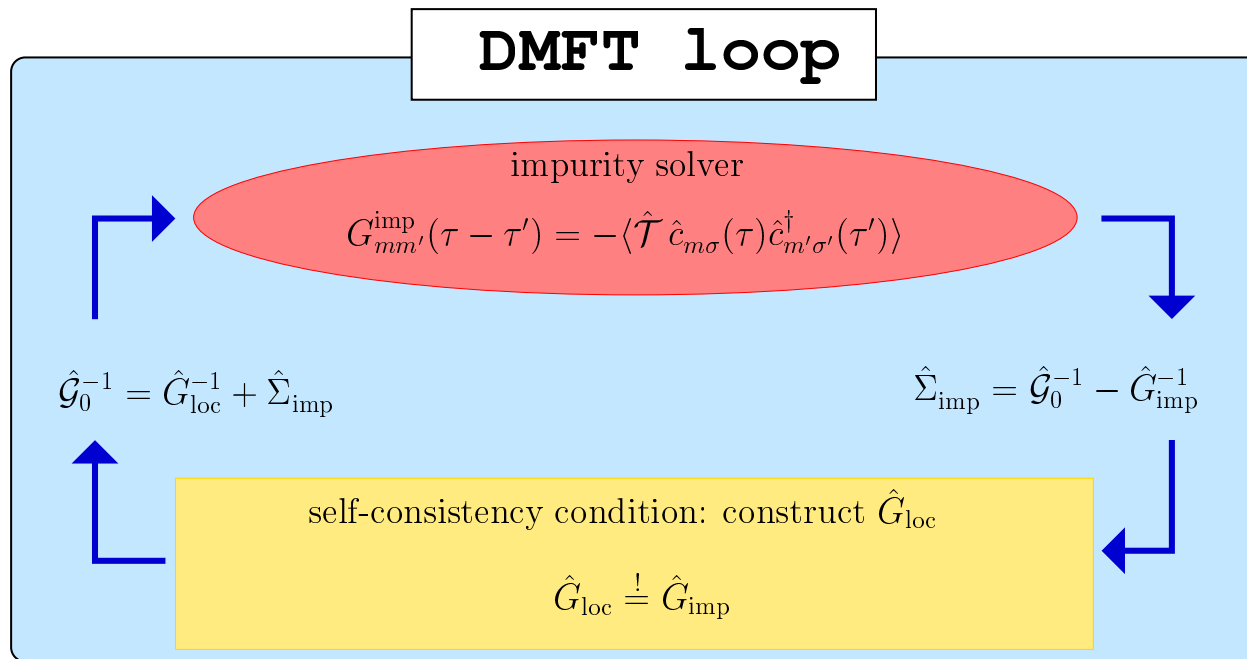
$$G_{\text{loc}}(i\omega_n) = \sum_{\mathbf{k}} [i\omega_n + \mu - \varepsilon_{\mathbf{k}} - \Sigma(\mathbf{k}, i\omega_n)]^{-1}$$

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

→ local correlations are fully taken into account non-pertubatively, explicit non-local correlations are neglected

self-consistency : dynamical mean-field theory, solution

iterative loop



comments

- ⊙ in principle, same self-consistency issues apply as in Hartree-Fock and DFT
- ⊙ but, explicit mean-field construction (and the resulting self-consistency loop) define here the approximation

self-consistency : mixing

[Broyden, Math. Comput. 19, 577 (1965)] [Vanderbilt and Louie, PRB 30, 6118 (1984)]...

usually, self-consistent loops do not converge that straightforwardly, but a 'mixing' of current and previous desired functions is necessary

$$v^{(p+1)} = v^{(p+1)}(v^{(p)}, v^{(p-1)}, \dots)$$

linear mixing

$$v_{\text{inp}}^{(p+1)} = (1 - \alpha) v_{\text{inp}}^{(p)} + \alpha v_{\text{out}}^{(p)}, \quad 0 < \alpha < 1$$

rigorous approach : e.g. quasi-Newton methods

$$\mathbf{F}(v_{\text{inp}}) = v_{\text{out}}(v_{\text{inp}}) - v_{\text{inp}} \stackrel{!}{=} 0$$

inspired by Newton-Raphson scheme : $f(x) \stackrel{!}{=} 0 \Rightarrow x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)}$

$\rightarrow \mathbf{F}(\mathbf{x}) = \mathbf{F}(\mathbf{x}^{(p)}) + \mathbf{J}^{(m)}(\mathbf{x} - \mathbf{x}^{(p)}) + \dots$ with Jacobian matrix $\mathbf{J}^{(m)} = \left. \frac{\partial \mathbf{F}}{\partial \mathbf{x}} \right|_{\mathbf{x}=\mathbf{x}^{(p)}}$

hence in linear order : $\mathbf{x}^{(p+1)} = \mathbf{x}^{(p)} - \left(\mathbf{J}^{(m)}\right)^{-1} \mathbf{F}(\mathbf{x}^{(p)})$

but mixing is 'hard' and in many cases, derivatives of \mathbf{F} are not simple.

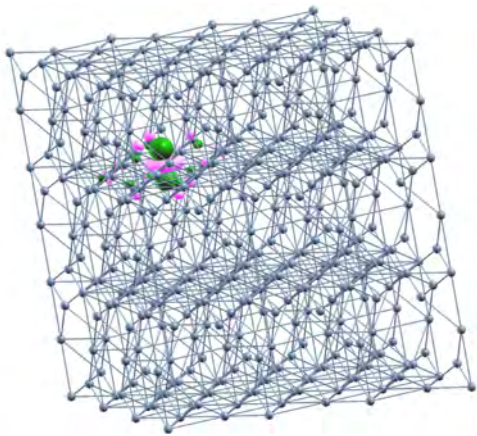
Therefore, various approximate step-by-step update formulas for the Jacobian matrix are available:

methods : Broyden, modified Broyden, inverse Broyden, BFGS, etc.

realistic many-body : marrying DFT and DMFT

density functional theory (DFT)

- Hohenberg-Kohn theorems, Kohn-Sham construction, exchange-correlation functional, local-density approximation, . . .
- mapping interacting electrons onto the problem of non-interacting electrons in a complicated effective potential
- very good description of the realistic, single-particle based chemical bonding (\rightarrow band structure for solids)



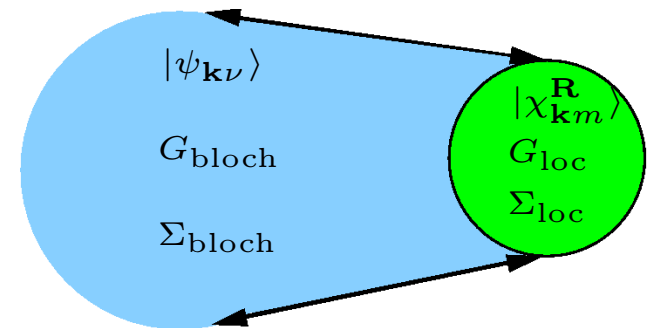
interface



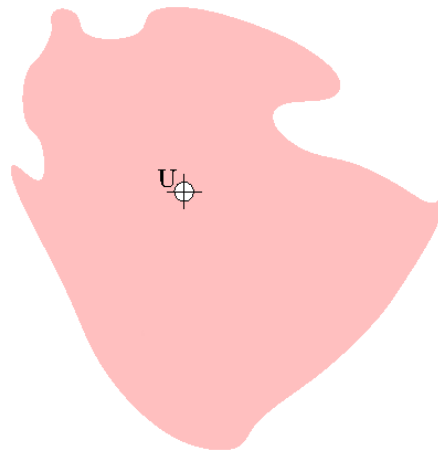
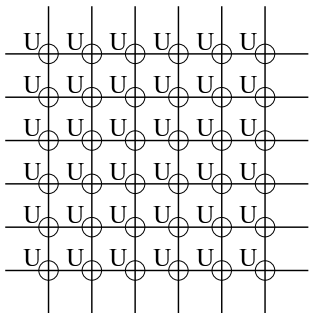
define

correlated subspace \mathcal{C}

by Wannier(-like) orbitals
from correlated sites



dynamical mean-field theory (DMFT)



many-body Green's functions, Hubbard model,
quasiparticles vs. Hubbard bands, quantum-impurity
solver, finite temperature, . . .



mapping interacting electrons onto the problem of
an interacting impurity in a self-consistent bath



very good description of interacting electrons on
a lattice in the model context

realistic many-body : DFT+DMFT, functionals

[Savrasov, Kotliar, PRB 69, 245101(2004)] [Georges, AIP Conference Proceedings 715 (2004)]

DMFT as well as the hybrid method DFT+DMFT may be derived from a functional form/variational principle

free energy of a many-body system

$$\Omega[\mathbf{G}] = \text{tr} \ln \mathbf{G} - \text{tr} \left[(\mathbf{G}_0^{-1} - \mathbf{G}^{-1}) \mathbf{G} \right] + \Phi[\mathbf{G}]$$

- \mathbf{G} : interacting Green's function
- \mathbf{G}_0 : noninteracting Green's function
- Φ : Luttinger-Ward functional

(compare with DFT energy $E_{\text{DFT}} = \sum_i \varepsilon_i - \frac{e^2}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \int d\mathbf{r} \rho(\mathbf{r})v_{\text{xc}}(\mathbf{r}) + E_{\text{xc}}[\rho]$)

DFT+DMFT free energy

$$\begin{aligned} \Omega_{\text{DFT+DMFT}}[\rho, G_{\mathcal{C}}; v_{\text{KS}}, \Sigma_{\mathcal{C}}] &= -\text{tr} \ln \left[i\omega_n + \mu + \frac{1}{2m} \Delta - v_{\text{KS}}(\mathbf{r}) - P^\dagger \Sigma_{\mathcal{C}}(i\omega_n) P \right] \\ &\quad - \int d\mathbf{r} (v_{\text{KS}}(\mathbf{r}) - v_{\text{ext}}(\mathbf{r})) \rho(\mathbf{r}) - \text{tr} [G_{\mathcal{C}}(i\omega_n) \Sigma_{\mathcal{C}}(i\omega_n)] \\ &\quad + E_{\text{H}}[\rho(\mathbf{r})] + E_{\text{xc}}[\rho(\mathbf{r})] + \Phi_{\mathcal{C}}[G_{\mathcal{C}}(i\omega_n)] \end{aligned}$$

- ρ : charge density
- v_{KS} : Kohn-Sham potential
- $G_{\mathcal{C}}$: interacting Green's function in correlated subspace \mathcal{C}
- $\Sigma_{\mathcal{C}}$: self-energy in correlated subspace \mathcal{C}
- P, P^\dagger : projection operators mediating between correlated subspace and complete space

realistic many-body : DFT+DMFT, functionals

minimization of functional

$$\frac{\delta \Omega}{\delta v_{\text{KS}}} = 0 \quad \Rightarrow \quad \rho(\mathbf{r}) = \frac{1}{\beta} \sum_n \langle \mathbf{r} | \hat{G} | \mathbf{r} \rangle$$

$$\frac{\delta \Omega}{\delta \Sigma_{\mathcal{C}}} = 0 \quad \Rightarrow \quad G_{\mathcal{C}}(i\omega_n) = P G(i\omega_n) P^\dagger$$

redefinition : $\tilde{\Omega}_{\text{DFT+DMFT}}[\rho, G_{\mathcal{C}}; v_{\text{KS}}, \Sigma_{\mathcal{C}}] = \Omega_{\text{DFT+DMFT}}[\rho, G_{\mathcal{C}}; v_{\text{KS}}[\rho, G_{\mathcal{C}}], \Sigma_{\mathcal{C}}[\rho, G_{\mathcal{C}}]]$

$$\frac{\delta \tilde{\Omega}}{\delta \rho} = 0 \quad \Rightarrow \quad v_{\text{KS}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r})$$

$$\frac{\delta \tilde{\Omega}}{\delta G_{\mathcal{C}}} = 0 \quad \Rightarrow \quad \Sigma_{\mathcal{C}}(i\omega_n) = \frac{\delta \Phi_{\mathcal{C}}}{\delta G_{\mathcal{C}}} := \Sigma_{\text{imp}}(i\omega_n) - \Sigma_{\text{DC}}$$

total energy

$$E_{\text{DFT+DMFT}} = E_{\text{DFT}} - \sum_{\mathbf{k}\nu} \varepsilon_{\mathbf{k}\nu}^{\text{KS}} + \text{tr}[GH_{\text{KS}}] + \text{tr}[G_{\mathcal{C}}\Sigma_{\text{imp}}] - E_{\text{DC}}$$

comments

- ⊙ correlations effect quasiparticle energies as well as local electronic energies

realistic many-body : practical DFT+DMFT, projections

constructing the correlated subspace \mathcal{C}

Wannier function

$$|\chi_{\mathbf{k}m}^{\mathbf{R}}\rangle := \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot(\mathbf{T}+\mathbf{R})} |\chi_m^{\mathbf{R}}\rangle =$$

$$\sum_{\nu} |\psi_{\mathbf{k}\nu}\rangle \langle \psi_{\mathbf{k}\nu} | \chi_{\mathbf{k}m}^{\mathbf{R}} \rangle = \sum_{\nu} \langle \psi_{\mathbf{k}\nu} | \chi_{\mathbf{k}m}^{\mathbf{R}} \rangle |\psi_{\mathbf{k}\nu}\rangle$$

→ efficient Wannier-like function

$$|w_{\mathbf{k}m}^{\mathbf{R}}\rangle = \sum_{\nu \in \mathcal{W}} P_{\nu m}^{\mathbf{R}*}(\mathbf{k}) |\psi_{\mathbf{k}\nu}\rangle$$

with
$$P_{m\nu}^{\mathbf{R}}(\mathbf{k}) := \sum_{\mathbf{R}'m'} \{O(\mathbf{k})^{-1/2}\}_{mm'}^{\mathbf{R}\mathbf{R}'} \langle \chi_{\mathbf{k}m}^{\mathbf{R}} | \psi_{\mathbf{k}\nu} \rangle$$

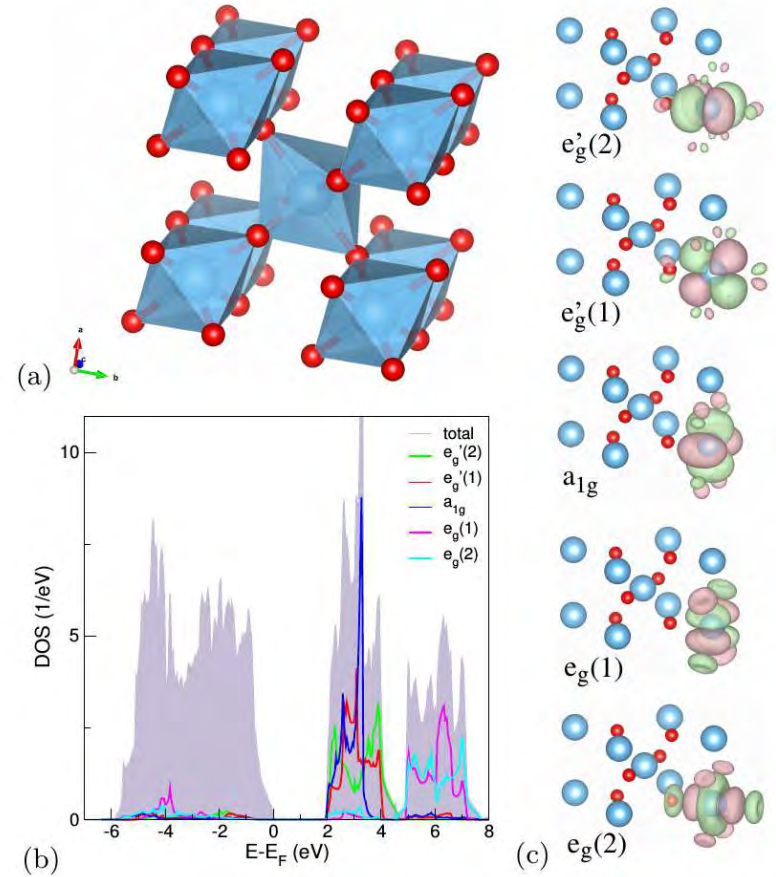
$$O_{mm'}^{\mathbf{R}\mathbf{R}'}(\mathbf{k}) := \langle \tilde{\chi}_{\mathbf{k}m}^{\mathbf{R}} | \tilde{\chi}_{\mathbf{k}m'}^{\mathbf{R}'} \rangle$$

key DFT+DMFT equations

$$G_{mm'}^{\mathbf{R}}(i\omega_n) = \sum_{\mathbf{k}, (\nu\nu') \in \mathcal{W}} P_{m\nu}^{\mathbf{R}}(\mathbf{k}) G_{\nu\nu'}^{\text{Bloch}}(\mathbf{k}, i\omega_n) P_{\nu'm'}^{\mathbf{R}*}(\mathbf{k})$$

$$\Sigma_{\nu\nu'}^{\text{Bloch}}(\mathbf{k}, i\omega_n) = \sum_{\mathbf{R}, mm'} P_{\nu m}^{\mathbf{R}*}(\mathbf{k}) \Sigma_{mm'}^{\mathbf{R}}(i\omega_n) P_{m'\nu'}^{\mathbf{R}}(\mathbf{k})$$

local self-energy : $\Sigma^{\mathbf{R}}(i\omega_n) = \Sigma_{\text{imp}}^{\mathbf{R}}(i\omega_n) - \Sigma_{\text{DC}}^{\mathbf{R}}$



realistic many-body : practical DFT+DMFT, charge self-consistency

feedback of the self-energy onto the full charge density

correlated charge density representation

$$\rho(\mathbf{r}) = \rho_{\text{KS}}(\mathbf{r}) + \Delta\rho(\mathbf{r}) = \frac{1}{\beta} \sum_n \left[\langle \mathbf{r} | \hat{G}_{\text{KS}} | \mathbf{r} \rangle + \langle \mathbf{r} | \hat{G} - \hat{G}_{\text{KS}} | \mathbf{r} \rangle \right]$$

with $G_{\text{KS}}(\mathbf{k}, i\omega_n) := [i\omega_n + \mu_{\text{KS}} - \varepsilon_{\mathbf{k}}^{\text{KS}}]^{-1}$

generic density matrix

using $\langle \mathbf{r} | \hat{G} - \hat{G}_{\text{KS}} | \mathbf{r} \rangle = \langle \mathbf{r} | \hat{G}_{\text{KS}} (\hat{G}_{\text{KS}}^{-1} - \hat{G}^{-1}) \hat{G} | \mathbf{r} \rangle = \langle \mathbf{r} | \hat{G}_{\text{KS}} (\hat{\Sigma}^{\text{Bloch}} - (\mu - \mu_{\text{KS}}) \hat{1}) \hat{G} | \mathbf{r} \rangle$

$$\Delta N_{\nu\nu'}(\mathbf{k}) := \frac{1}{\beta} \sum_{n, \nu''\nu'''} \in \mathcal{W} G_{\nu\nu''}^{\text{KS}}(\mathbf{k}, i\omega_n) (\Sigma_{\nu''\nu'''}^{\text{Bloch}}(\mathbf{k}, i\omega_n) - (\mu - \mu_{\text{KS}}) \delta_{\nu''\nu'''}) G_{\nu'''\nu'}(\mathbf{k}, i\omega_n)$$

hence $\Delta\rho(\mathbf{r}) = \sum_{\mathbf{k}, \nu\nu'} \langle \mathbf{r} | \psi_{\mathbf{k}\nu} \rangle \Delta N_{\nu\nu'}(\mathbf{k}) \langle \psi_{\mathbf{k}\nu'} | \mathbf{r} \rangle$

⇒ complete correlated charge density

$$\rho(\mathbf{r}) = \sum_{\mathbf{k}, \nu\nu'} \langle \mathbf{r} | \psi_{\mathbf{k}\nu} \rangle \left(f(\varepsilon_{\mathbf{k}\nu}^{\text{KS}}) \delta_{\nu\nu'} + \Delta N_{\nu\nu'}(\mathbf{k}) \right) \langle \psi_{\mathbf{k}\nu'} | \mathbf{r} \rangle$$

comments

- ⊙ increased numerical effort, i.e. larger number of self-consistency steps
- ⊙ charge self-consistency affects whole electronic structure, not only correlated subspace
- ⊙ impact depends on crystal symmetry, i.e. number of inequivalent orbitals, sites
- ⊙ general trend : reduced orbital polarization, less dependent on details of double counting

self-consistency : DFT+DMFT codes

[Anisimov, Poteryaev, Korotin et al., JPCM 9, 7359 (1997)]

[Held, Keller, Eyert et al., PRL 86, 5345 (2001)]

[Minár, Chioncel, Perlov, et al., PRB 72, 045125 (2005)]

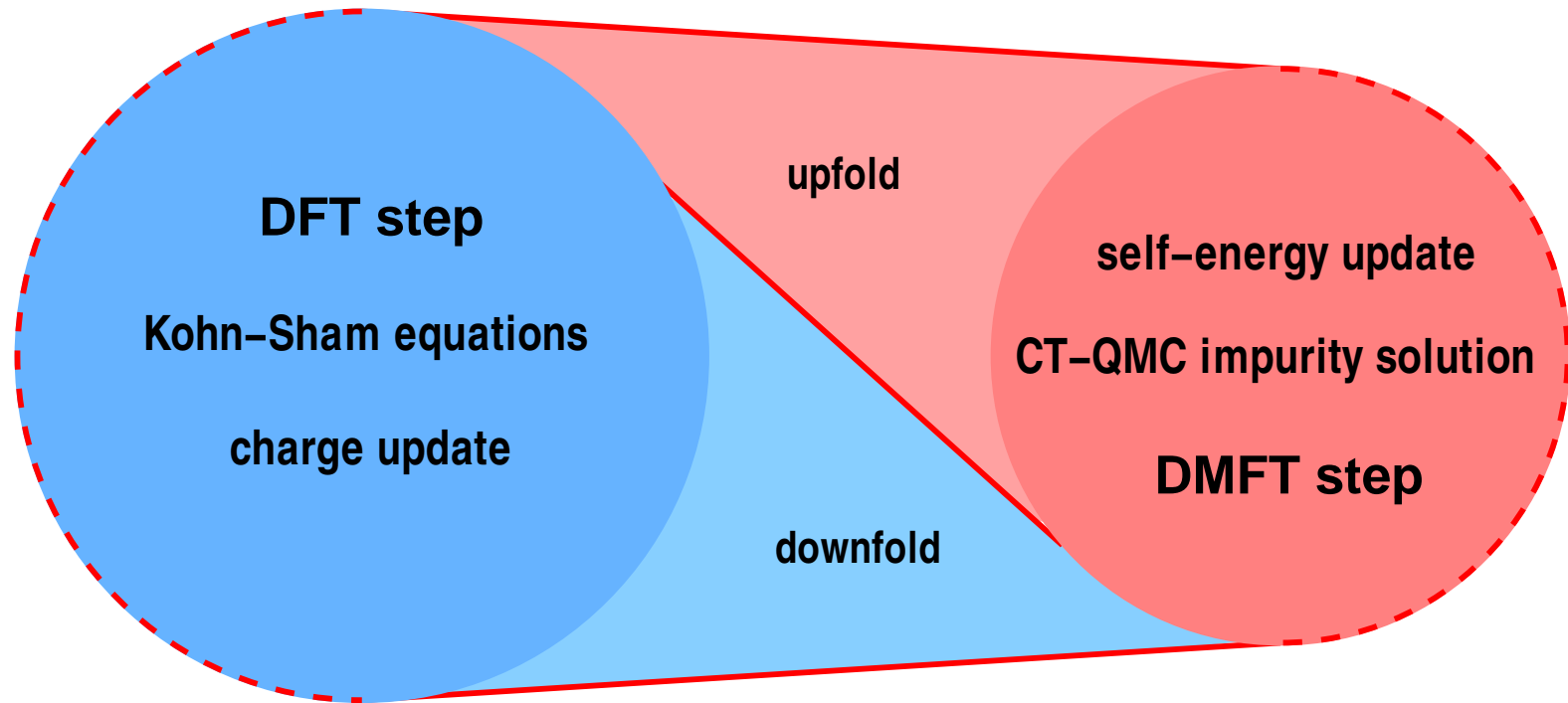
[FL, Georges, Poteryaev et al., PRB 74, 125120 (2006)]

[Lichtenstein and Katsnelson, PRB 57, 6884 (1998)]

[Pavarini, Biermann, Poteryaev et al., PRL 92, 176403 (2004)]

[Kotliar, S. Y. Savrasov, K. Haule et al, RMP 78, 865 (2006)]

[Grieger, Piefke, Peil and FL, PRB 86, 155121 (2012)] . . . , . . . , . . .



● DFT part : LMTO, KKR, pseudopotential, FLAPW, VASP

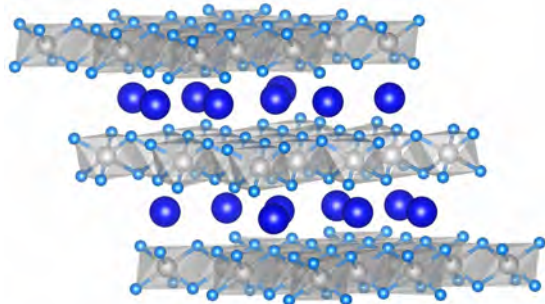
● DMFT impurity solver : Quantum Monte Carlo, ED, . . .

● 1-7 local correlated orbitals

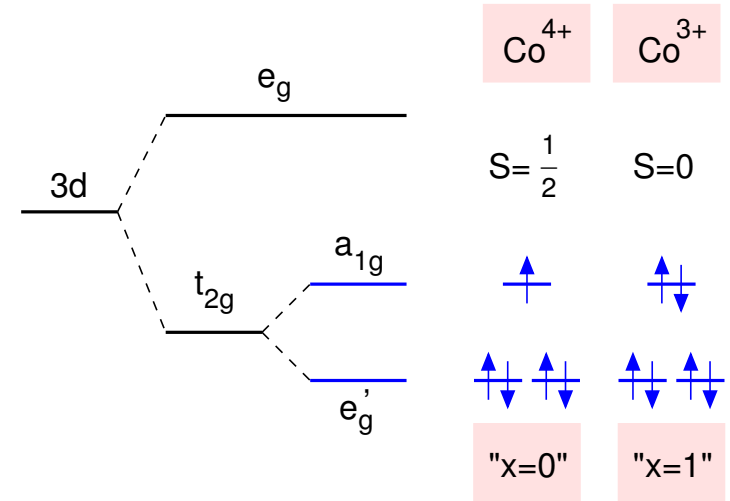
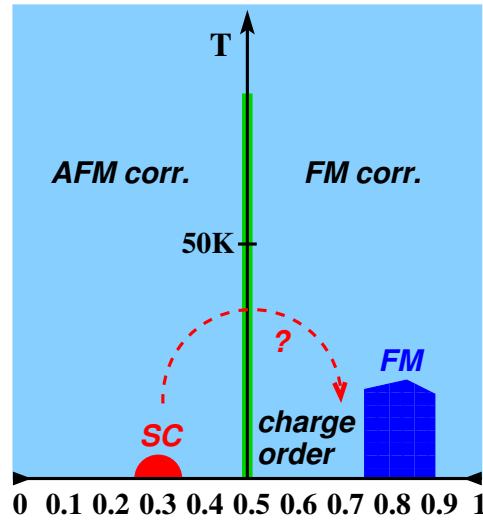
● up to 200-atom cells (pseudopotential)

self-consistency : density functional theory, challenging application

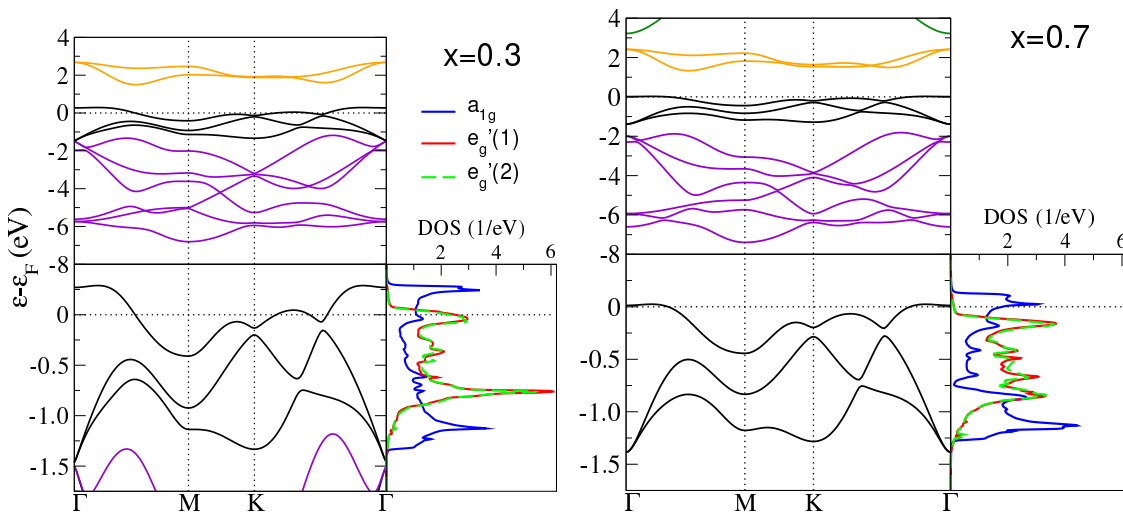
Na_xCoO_2 : a correlated materials system



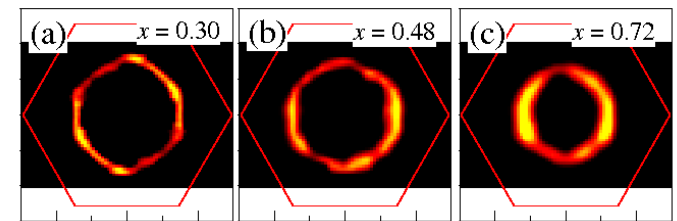
triangular CoO_2 lattice



DFT picture → band theory

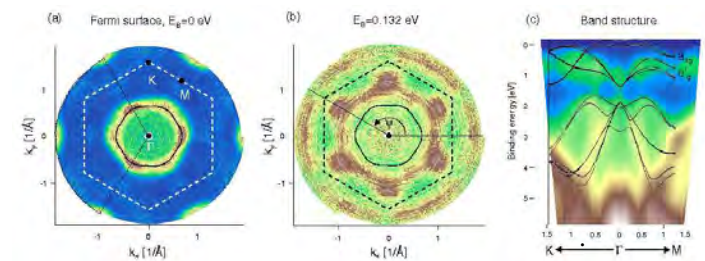


photoemission



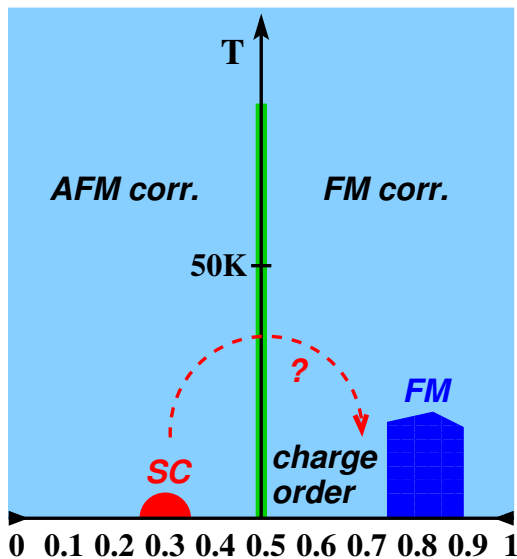
[Yang et al., PRL 95, 146401 (2005)]

[Geck et al., PRL 99, 046403 (2007)]



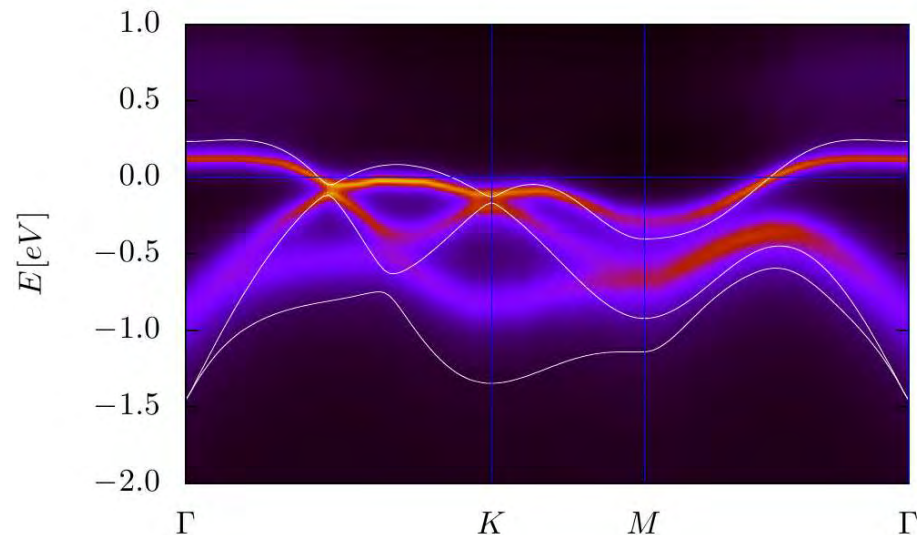
self-consistency : DFT+DMFT, resolving Na_xCoO_2 puzzle

[Boehnke and FL, phys. stat. sol. (a) 211, 1267 (2014)]

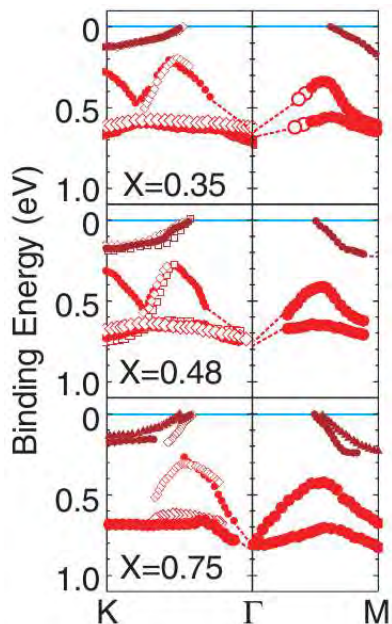
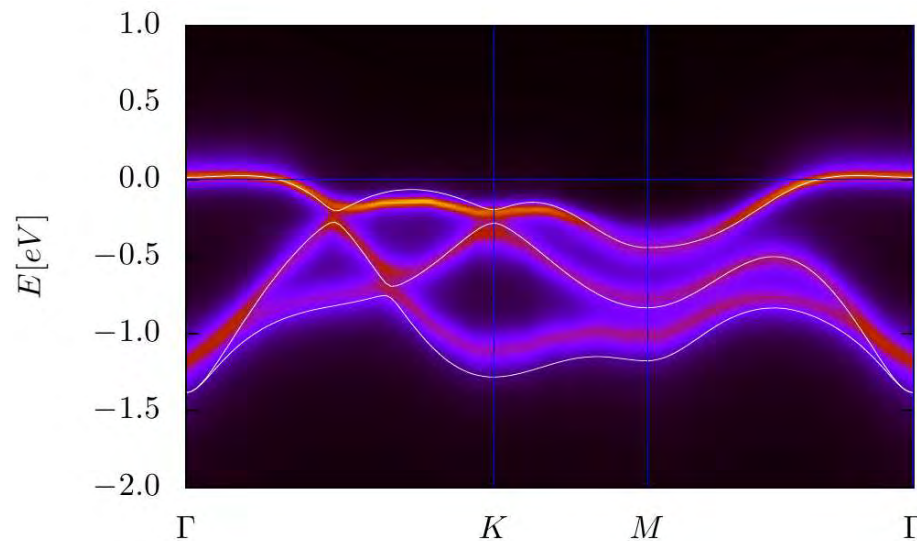


$$U = 5 \text{ eV}, J_H = 0.7 \text{ eV}$$

$x = 0.3$



$x = 0.7$



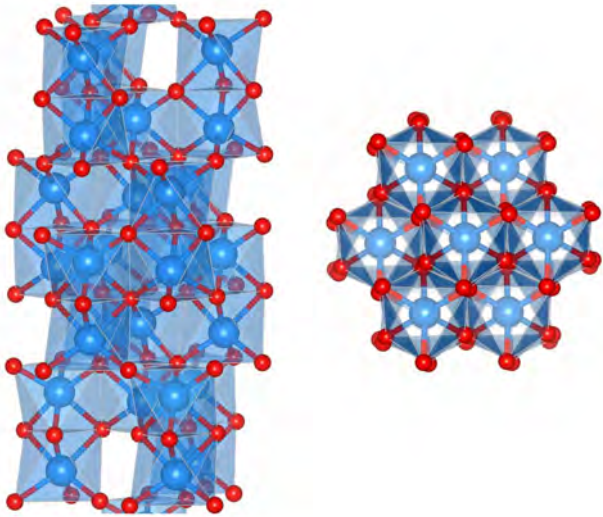
● suppressed e'_g hole pockets ✓

● significant band renormalizations ✓

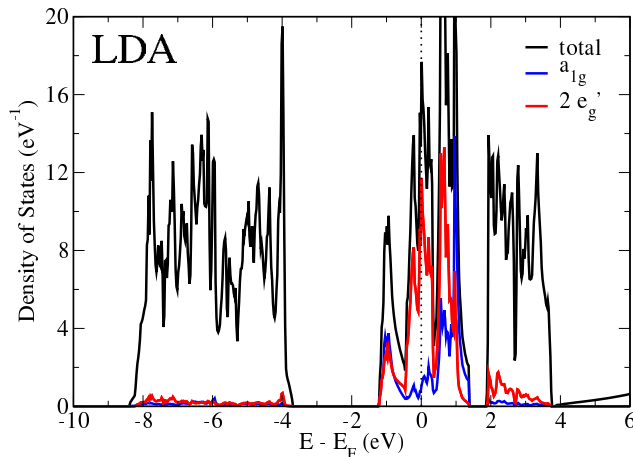
[Qian et al., PRL 97 (2006)]

V₂O₃ system : basics

V₂O₃ in corundum structure



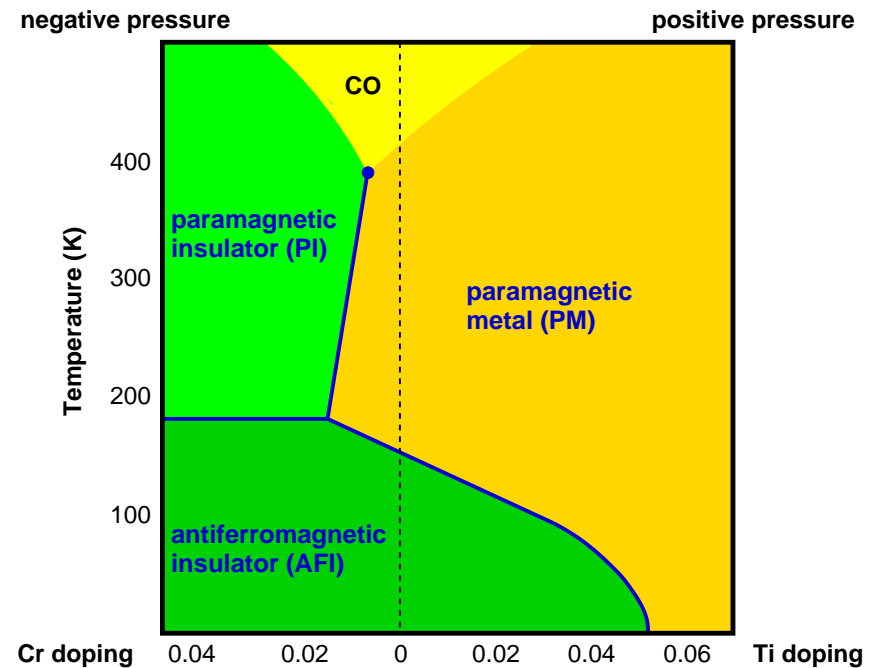
- V-V pairs along c , honeycomb lattice in ab
- V ions with $3d^2$ configuration (V^{3+})
- t_{2g} at low energy: a_{1g} and degenerate e_g^π



experimental phase diagram

[McWhan et al., PRL 27, 941 (1971)]

- phases : paramagnetic metal (PM), paramagnetic insulator (PI) and antiferromagnetic insulator (AFI)
- structural transition to monoclinic symmetry with magnetic order upon lowering of temperature

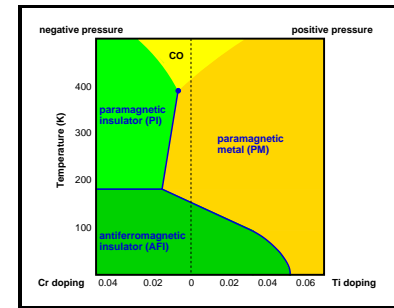


$U \geq W$: "model Mott-Hubbard system"?

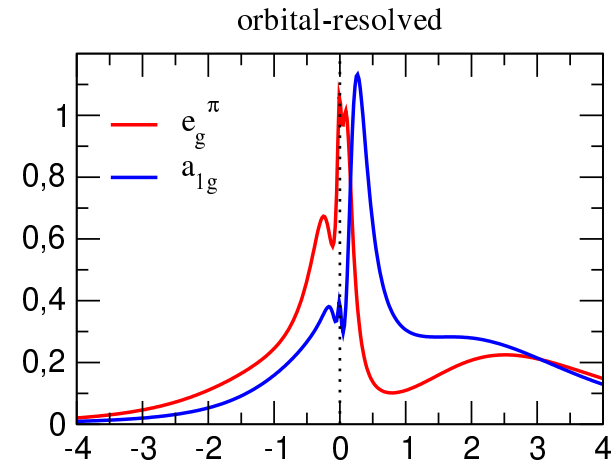
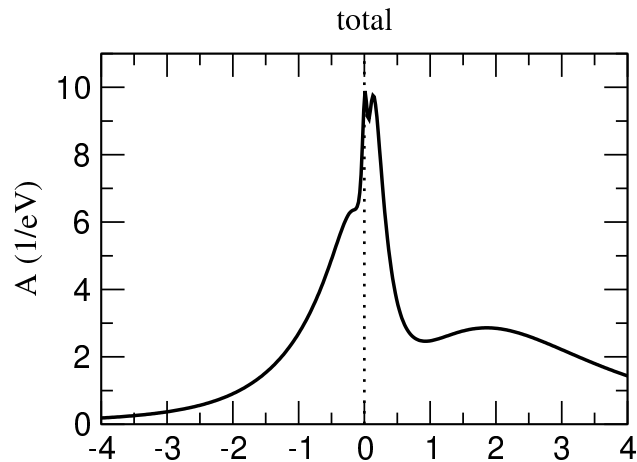
deviations from simplistic picture

- volume expansion for Cr and Ti doping

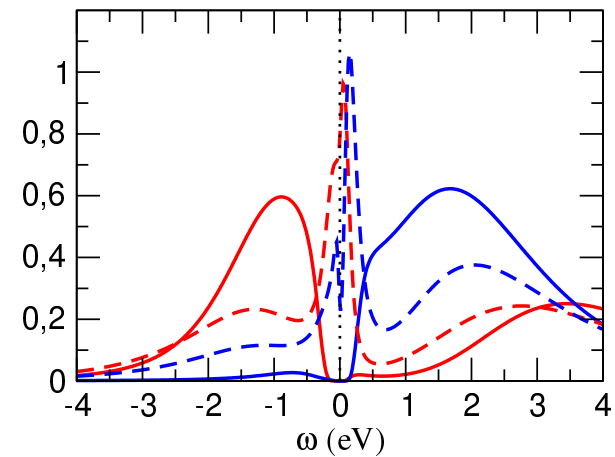
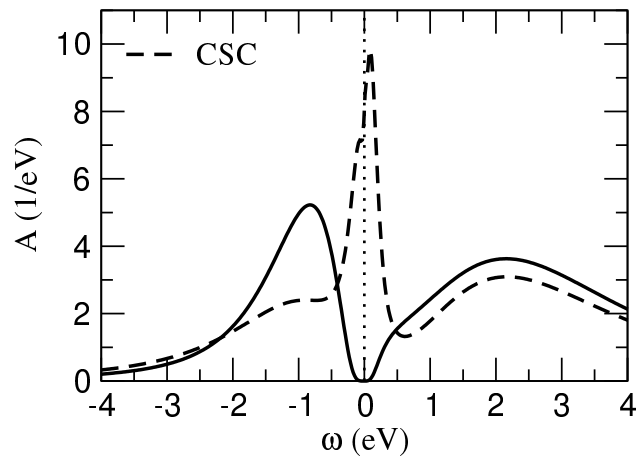
V_2O_3 system : DFT+DMFT at stoichiometry, corundum



$$U = 4 \text{ eV}, J_H = 0.7 \text{ eV}$$

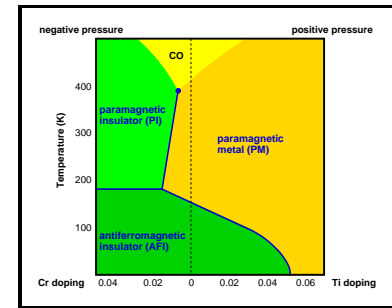
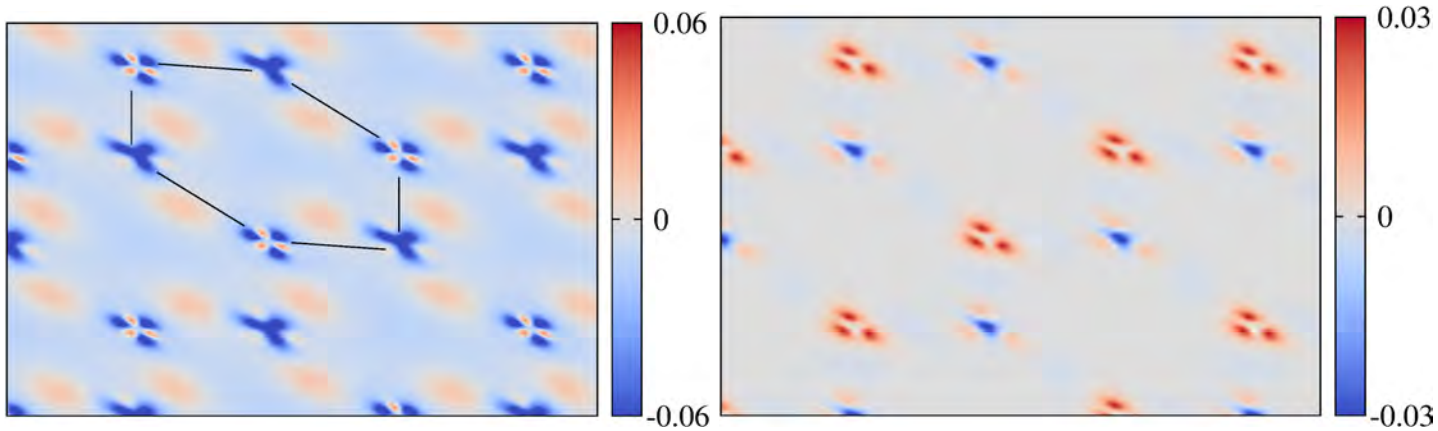


$$U = 5 \text{ eV}, J_H = 0.7 \text{ eV}$$

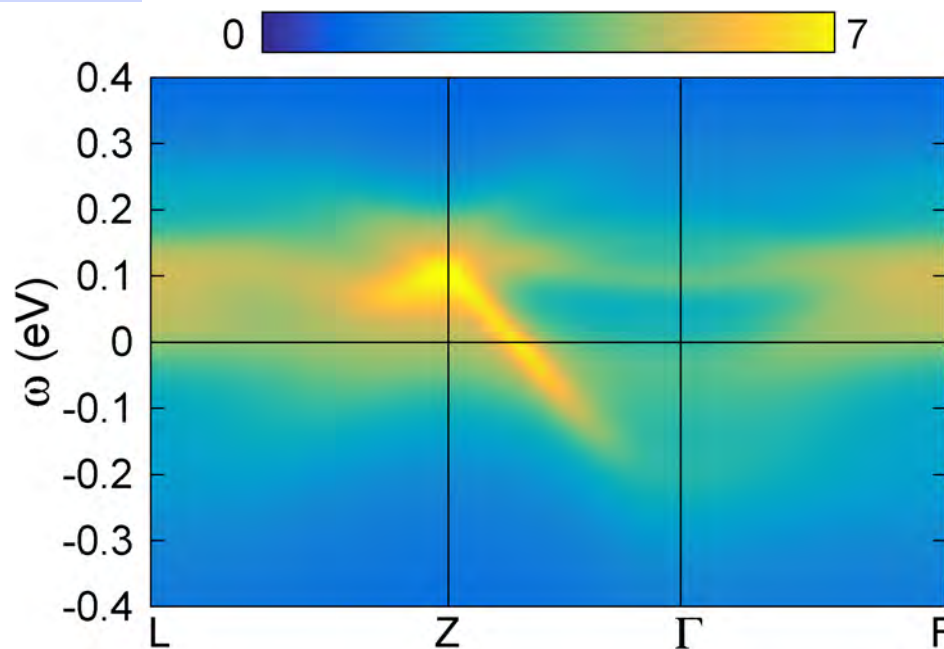


V_2O_3 system : DFT+DMFT at stoichiometry, corundum

correlated charge density



k -resolved spectral function



experiments on doped V_2O_3 : 'real-space integrated'

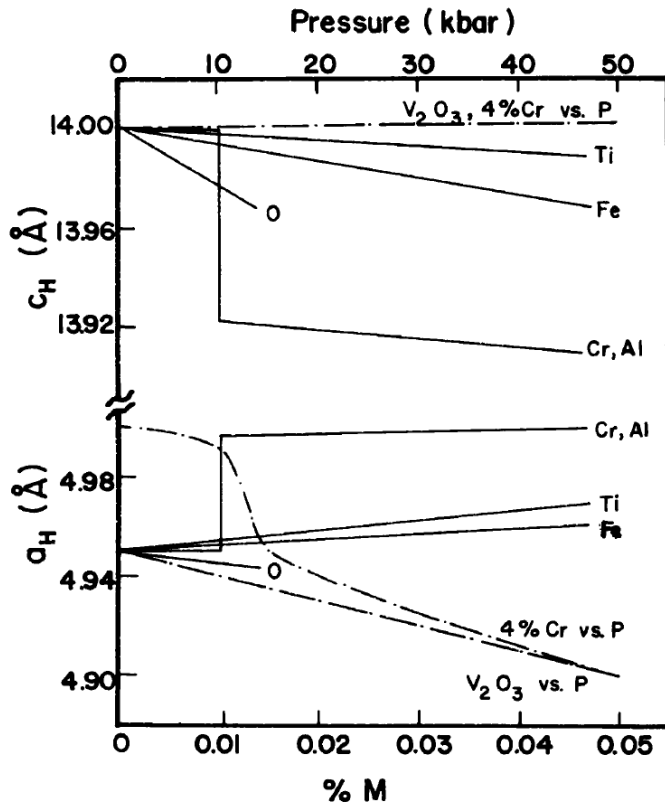
e_g^π/a_{1g} occupation ratio

[Park et al., PRB 61, 11506 (2000)]

Phase	V_2O_3	$(V_{0.996}Cr_{0.004})_2O_3$	$(V_{0.988}Cr_{0.012})_2O_3$	$(V_{0.982}Cr_{0.018})_2O_3$	Average	$e_g^\pi e_g^\pi : e_g^\pi a_{1g}$ occupation
AFI	34% (140 K)	30% (145 K)	32% (140 K)	35% (150 K)	33%	2:1
PM	18% (170 K)	19% (180 K)	18% (190 K)		18%	1:1
PI			27% (290 K)	27% (190 K)	27%	3:2

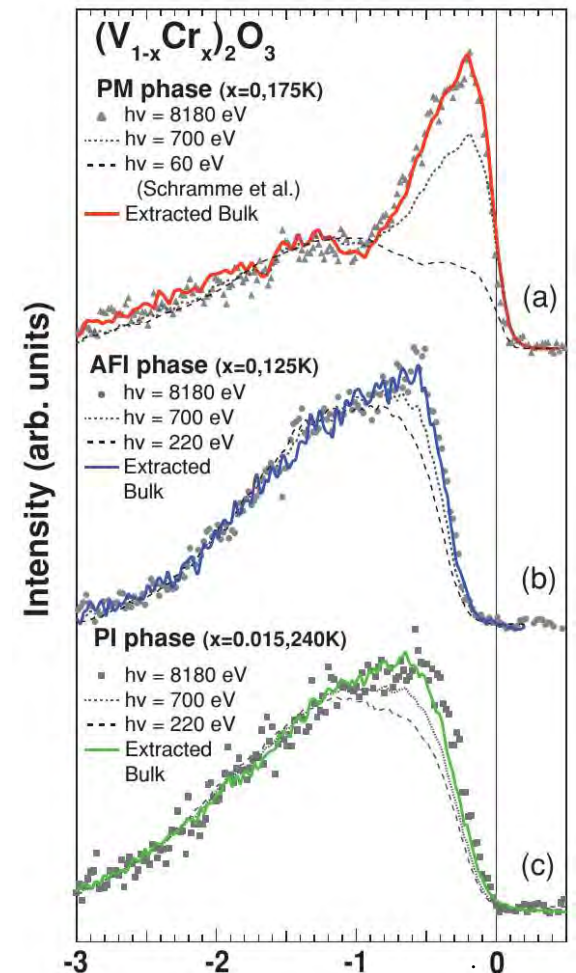
lattice parameters

[Kuwamoto and Honig., Phase Trans. 1, 289 (1980)]



photoemission

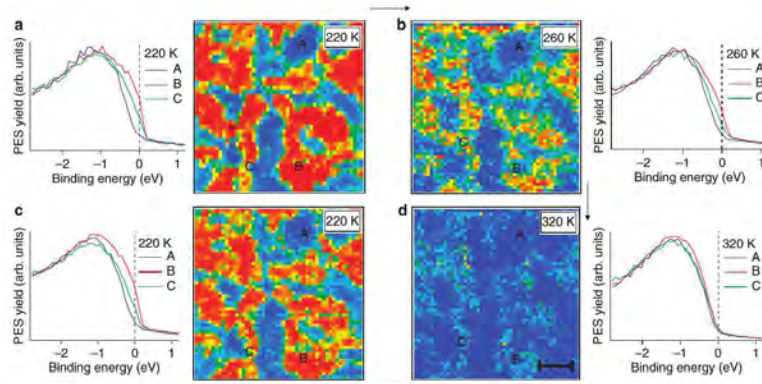
[Fujiwara, et al., PRB 84, 075117 (2011)]



experiments on Cr-doped V_2O_3 : 'real-space resolved'

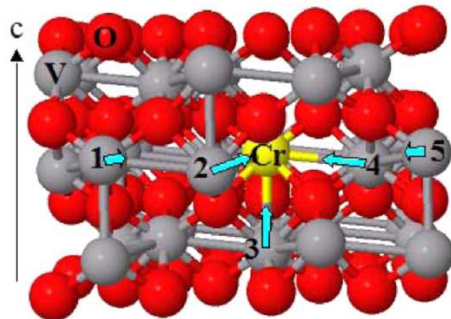
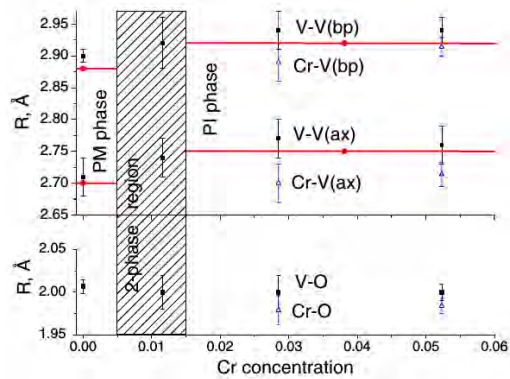
metal/insulator coexistence

[Lupi et al., Nat. Commun. 1, 105 (2010)]



interatomic distances

[Frenkel et al., PRL 97, 195502 (2006)]



local symmetry

[Bombardi et al., Physica B 345, 40 (2003)]

Physica B 345 (2004) 40–44

Precursor symmetry breaking in Cr doped V_2O_3

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P.A. Metcalf^c, J.M. Honig^c

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^dDipartimento di Fisica "E. Amaldi", Università di Roma III, via della Vasca Navale 84, 00146 Roma, Italy

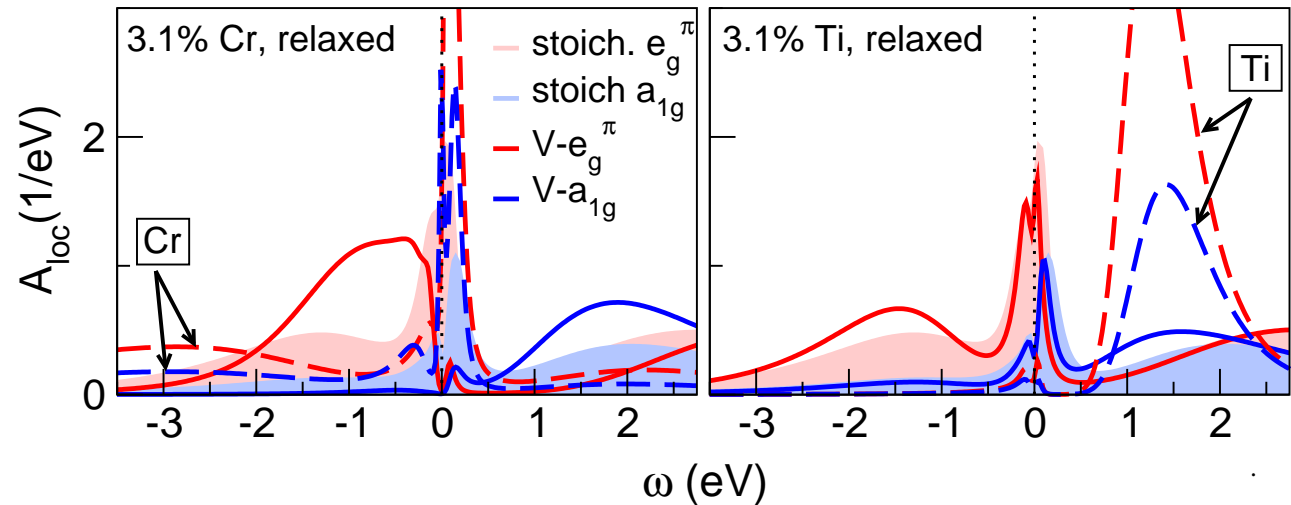
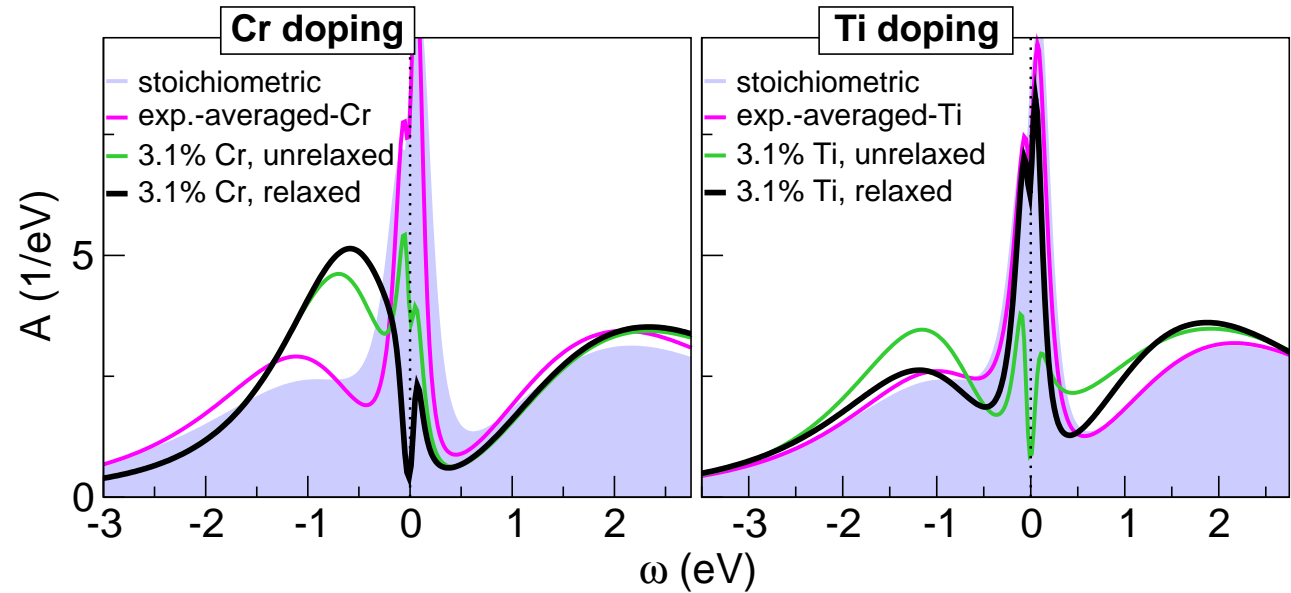
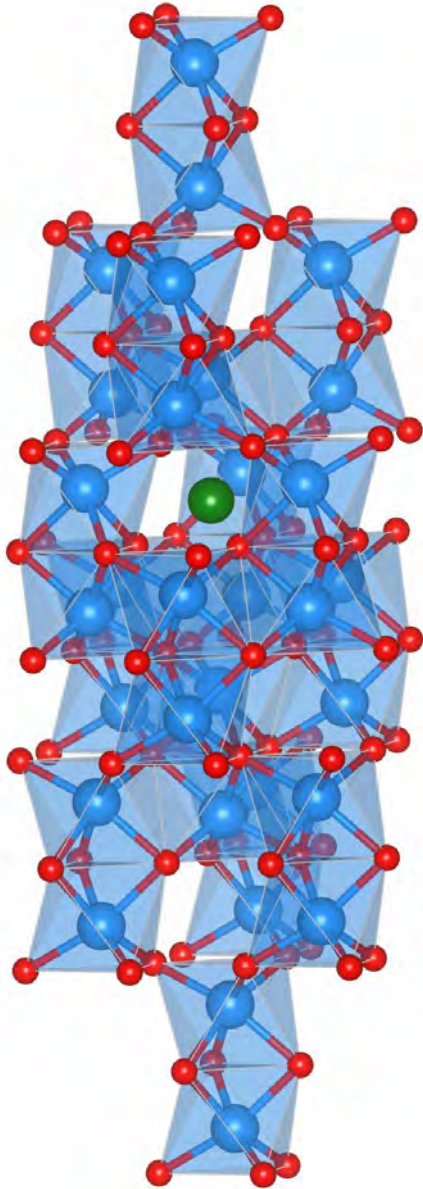
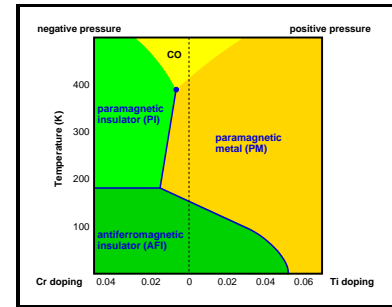
Abstract

The results of X-ray resonant scattering experiments performed on a $(V_{1-x}Cr_x)_2O_3$ sample with $x = 0.028$ are reported. This compound undergoes a first-order phase transition from paramagnetic insulator (PI) to antiferromagnetic insulator (AFI) at $T_N \approx 181$ K. At the same temperature a lattice distortion reduces the symmetry from $R\bar{3}c$ in the PI phase to $I2/a$ in the AFI phase. To get more insight into the transition driving mechanism, we studied the behaviour of the Bragg forbidden peak $(003)_h \equiv (10\bar{1})_m$, at V K edge, as a function of temperature, polarization, azimuthal angle and X-ray energy. On the contrary to what observed in the pure system and to what expected theoretically a non-vanishing signal is observed already at room temperature in the dipolar channel.

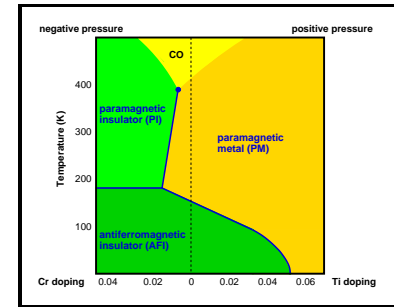
"... we believe that the E1 signal in the PI corundum phase must be related to the presence in the crystal of a second phase, probably monoclinic."

impurities in V_2O_3 : DFT+DMFT spectra

- Hubbard $U = 5$ eV, Hund's exchange $J_H = 0.7$ eV
- small unit cells : stoichiometric and experimentally-averaged structures
- 80-atom supercells: 31 V atoms, 1 Cr/Ti \rightarrow 3.1% doping



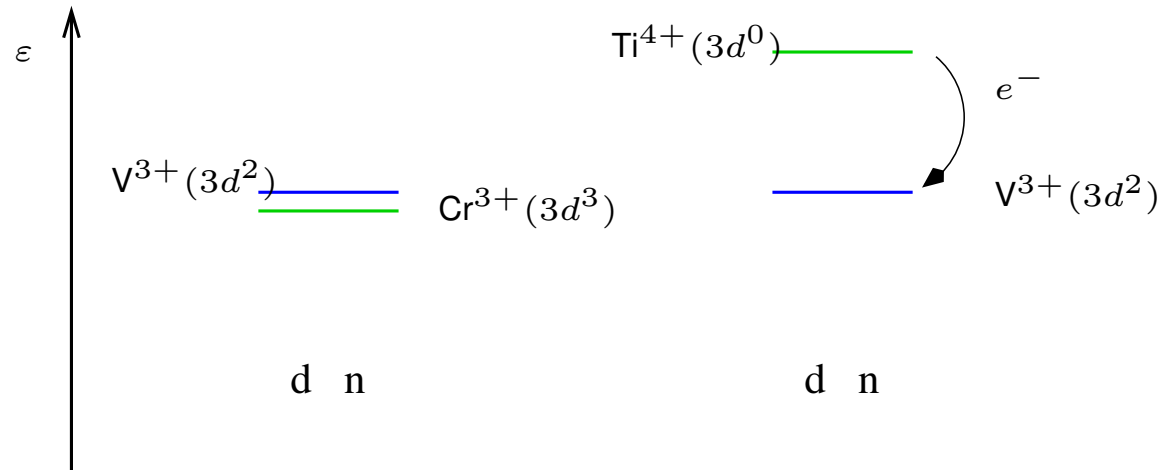
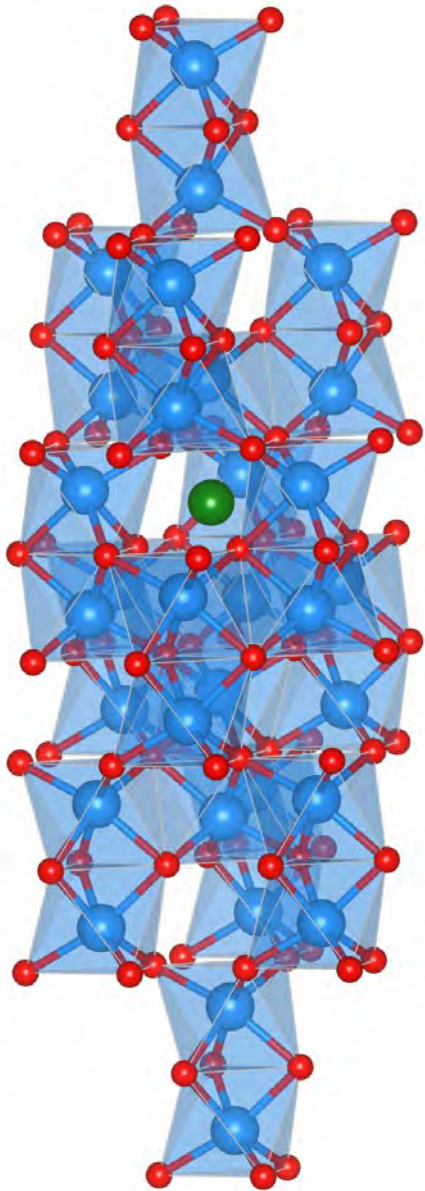
impurities in V_2O_3 : interpretation



[FL, Bernstein, Mazin and Valenti, PRL 121, 106401 (2018)]

summary of findings

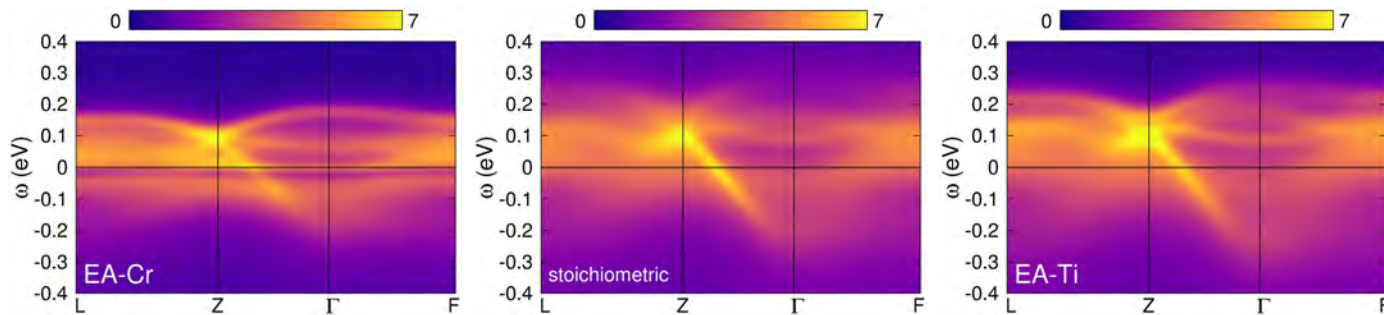
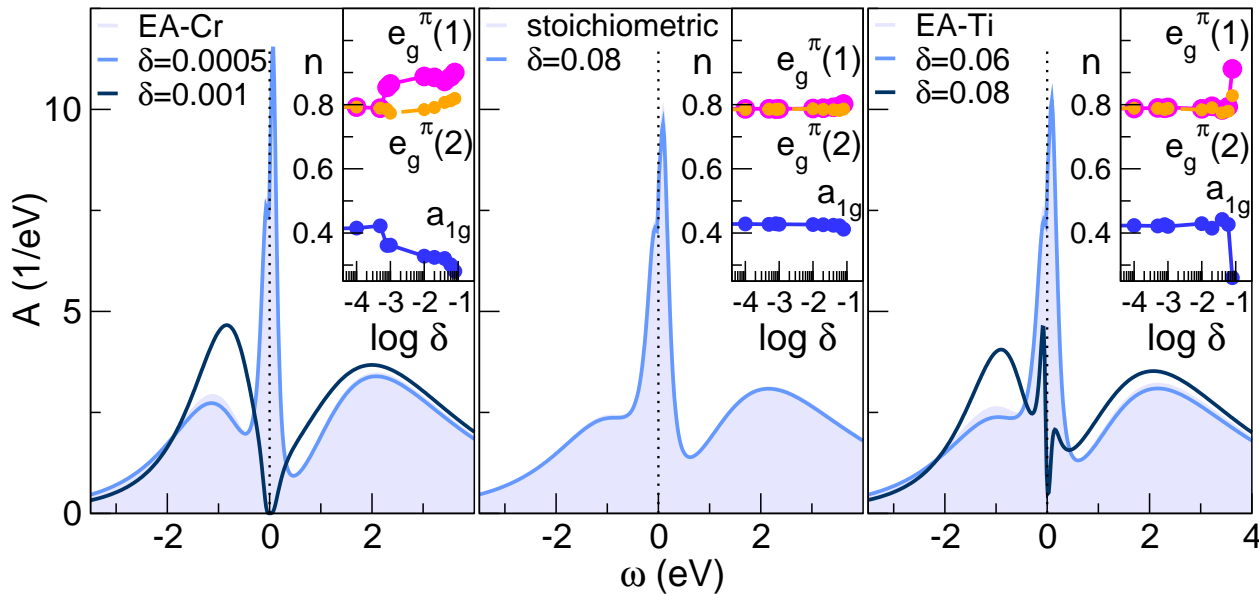
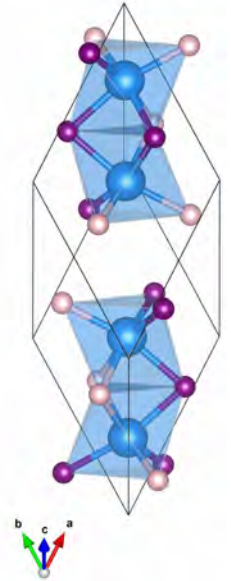
- sole experimental lattice expansion (i.e. no defect) of does not open a gap
- explicit Cr-defect treatment opens charge gap with experimental size (~ 0.1 eV)
- local monoclinic distortions for Cr doping are essential
- no local monoclinic distortions in case of Ti doping
- different valence of the dopants is important, especially titanium enters as Ti^{4+}
- strong orbital polariation towards e_g^π with doping
- lower Cr-based Hubbard peak in agreement with experiment



impurities in V_2O_3 : monoclinic instability with Cr doping

susceptibility towards structural symmetry breaking

- application of small low-symmetry field
- multi-site VCA calculation displays extreme sensitivity to charge modifications around the V sites
- introduce $\delta_{\pm}\delta O$ to replace δO
- important : umbrella distortion strongly enhanced in Cr-doped V_2O_3



conclusions

- charge self-consistent DFT+DMFT methodology is capable of addressing detailed challenges of many-body quantum materials on a realistic level
- self-consistency problems
- tier structure of system modelling(?)**
- find the key approximation element**
- be aware of mixing**
- PM—PI metal-insulator transition of V_2O_3
- impact of charge self-consistency on the degree of correlation, orbital polarization and temperature dependence**
- explicit Cr-and Ti-doping description via supercell approach**
- local symmetry breaking for Cr impurities, charge doping for Ti impurities**

