24th Wien2k Workshop, 18. - 22.Sept. 2017, Vienna

Dynamical mean-field theory (DMFT)

ELECTRONIC STRUCTURE OF CORRELATED MATERIALS

Jan M. Tomczak, Vienna University of Technology

Outline

I. Introduction

- when do we need to go beyond DFT? **Electronic correlations!**
- how to treat them: rationale of **dynamical mean-field theory (DMFT)**

II. Example applications of DMFT

- rare-earth eco-friendly pigment **CeSF** (issue: **localized orbitals**)
- intermetallic **FeSi** (issues: **lifetime effects, finite temperatures**)
- ($SrVO_3$ thin film: **Mott transistor**)

III. Summary

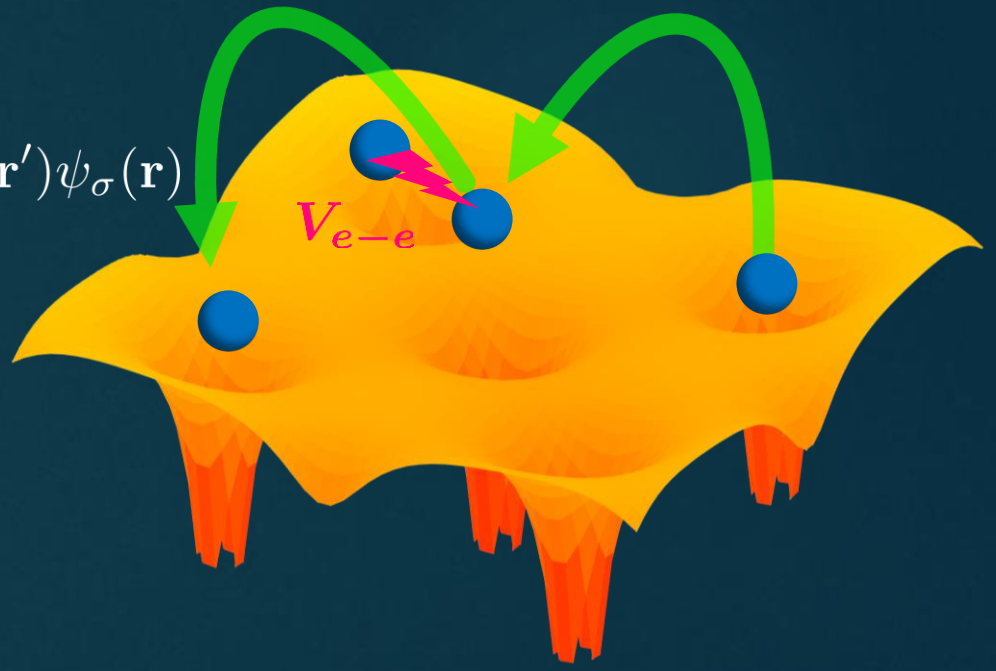
Electronic Structure of Solids

- Hamiltonian

$$H = \sum_{\sigma} \psi_{\sigma}^{\dagger}(\mathbf{r}) \left[-\frac{\hbar^2}{2m_e}\Delta + \underbrace{\sum_{l} \frac{-e^2}{4\pi\epsilon_0} \frac{Z_l}{|\mathbf{r}-\mathbf{R}_l|}}_{V_{ion}(\mathbf{r})} \right] \psi_{\sigma}(\mathbf{r})$$
$$+ \frac{1}{2} \sum_{\sigma\sigma'} \int d^3r d^3r' \psi_{\sigma}^{\dagger}(\mathbf{r}) \psi_{\sigma'}^{\dagger}(\mathbf{r}') \underbrace{\frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}-\mathbf{r}'|}}_{V_{e-e}(\mathbf{r}-\mathbf{r}')} \psi_{\sigma'}(\mathbf{r}') \psi_{\sigma}(\mathbf{r})$$

- impossible to solve, even numerically for N>10.

"motion" of electrons *correlated* !



non-relativistic, Born-Oppenheimer approximation

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$$+\frac{1}{2}\sum_{\sigma\sigma'}\int d^3r d^3r' \psi_\sigma^\dagger(\mathbf{r})\psi_{\sigma'}^\dagger(\mathbf{r}') \underbrace{\frac{e^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}-\mathbf{r}'|}}_{V_{e-e}(\mathbf{r}-\mathbf{r}')} \psi_{\sigma'}(\mathbf{r}')\psi_\sigma(\mathbf{r})$$

"motion" of electrons independent!
→ 1-particle Hamiltonian

- density functional theory (DFT):

$$H^{DFT} = \sum_\sigma \psi_\sigma^\dagger(\mathbf{r}) \left[-\frac{\hbar^2}{2m_e}\Delta + V_{ion}(\mathbf{r}) + V_{e-e}^{eff}[\rho](\mathbf{r}) \right] \psi_\sigma(\mathbf{r})$$

"time-averaged" interaction, typically obtained from homogeneous electron gas of density ρ

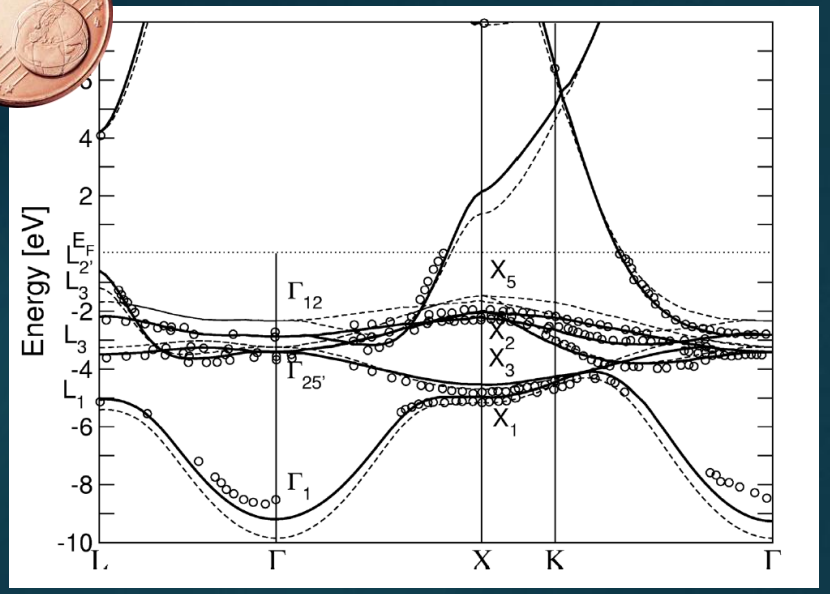
non-relativistic, Born-Oppenheimer approximation

[Hohenberg & Kohn, Kohn & Sham]

Standard electronic structure theory

DFT: treat solid as <u>electron gas</u> subject to <u>periodic potential</u> of ions

Cu=[Ar] $3d^{10}$ $4s^{1}$



[Courths & Hüfner 1984 / Marini et al 2002]

bandwidth W

Why does this work?

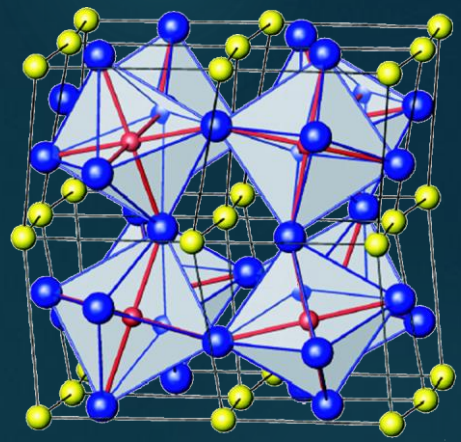
- **screening** reduces bare Coulomb interaction

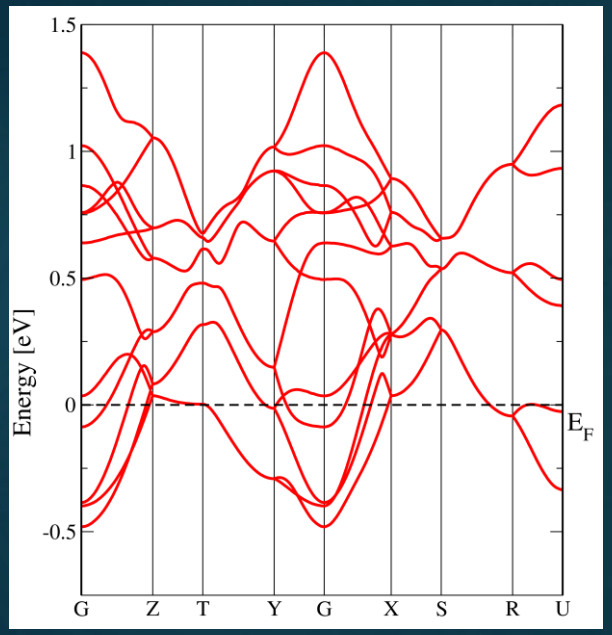
$$V = \frac{e^2}{r-r'} \quad \longrightarrow \quad V^{eff} = \frac{e^2}{r-r'} \frac{1}{\epsilon} e^{-\lambda(r-r')}$$

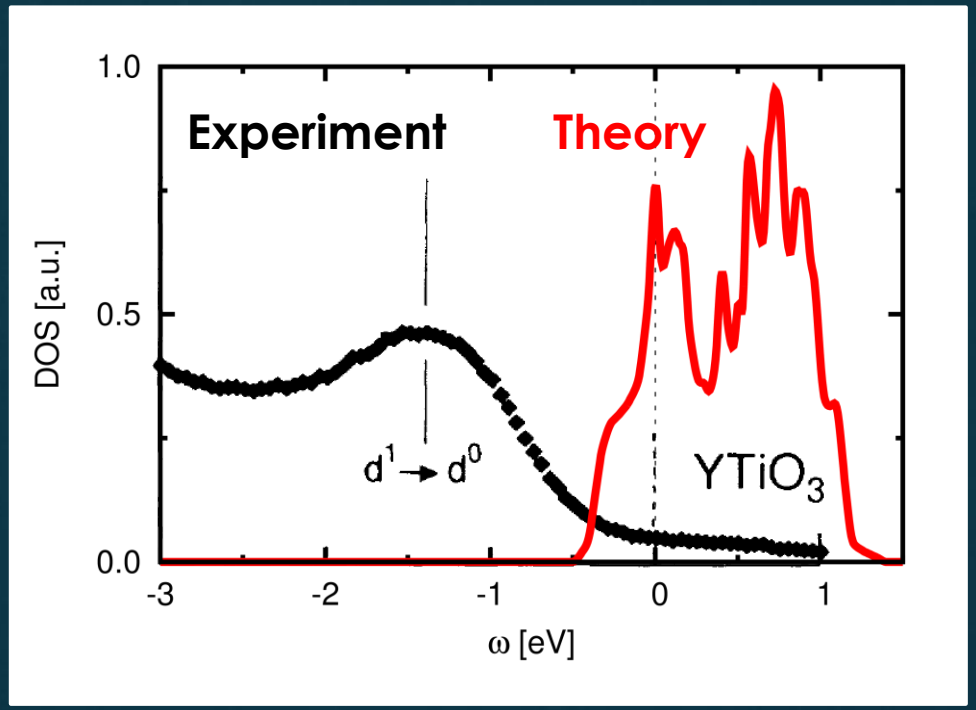
- **large kinetic energy** = large bandwidth W

→ V^{eff}/W small
→ kinetic energy dominates
→ quasi-particle picture applies

Breakdown of band-theory: The Mott insulator $YTiO_3$





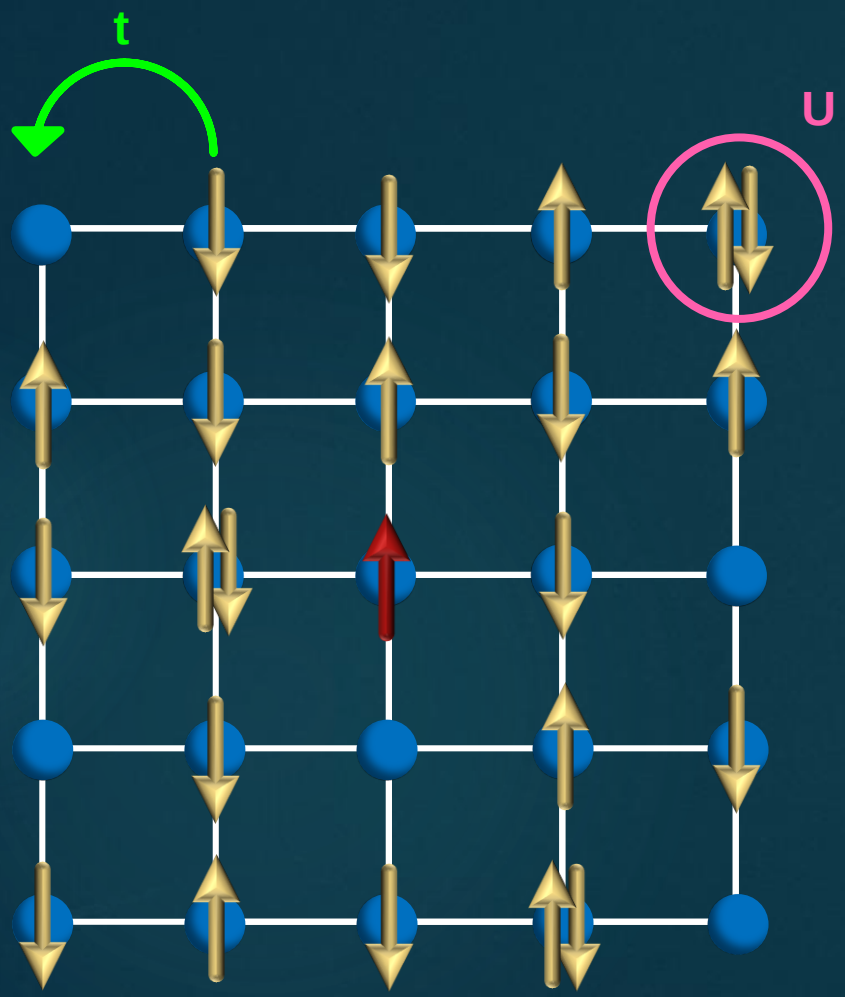


[Fujimori et al. PRB 69, 1796 (1992)]

Q:
Why does DFT fail?

- interpreting KS spectrum as excitations…
- GW also fails for $YTiO_3$

Time & energy scales



Hubbard model

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

long time scales (=low energy)

- delocalized → quasi-particles in Fermi liquid

short time scales (=high energy)

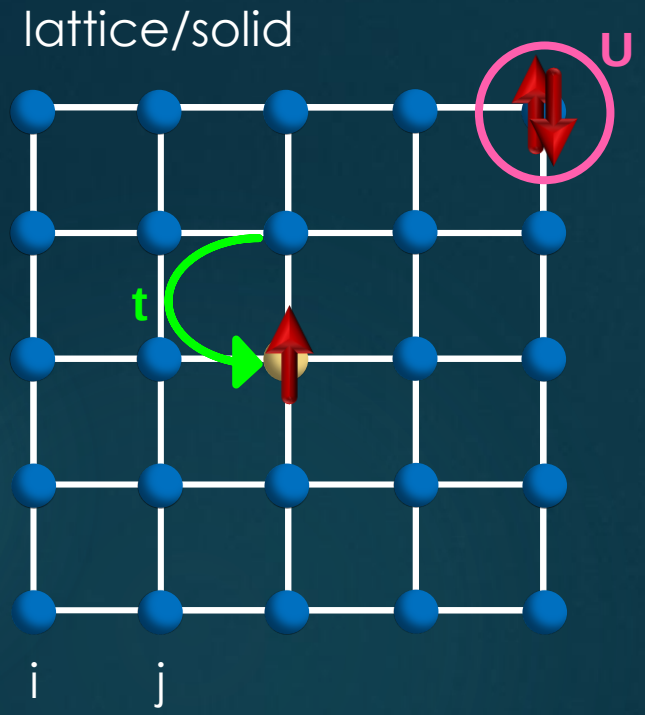
- localized → Hubbard bands / local moments

dynamical effects:

"time-averaged" potential $V^{eff}(r)$ insufficient!

Dynamical mean-field theory (DMFT)

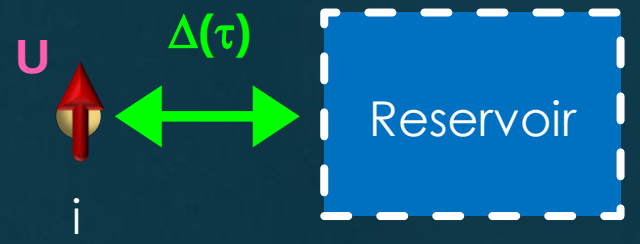
[Metzner & Vollhardt '89, Georges & Kotliar '92]



mapping to

reference system

(effective)
Anderson impurity model



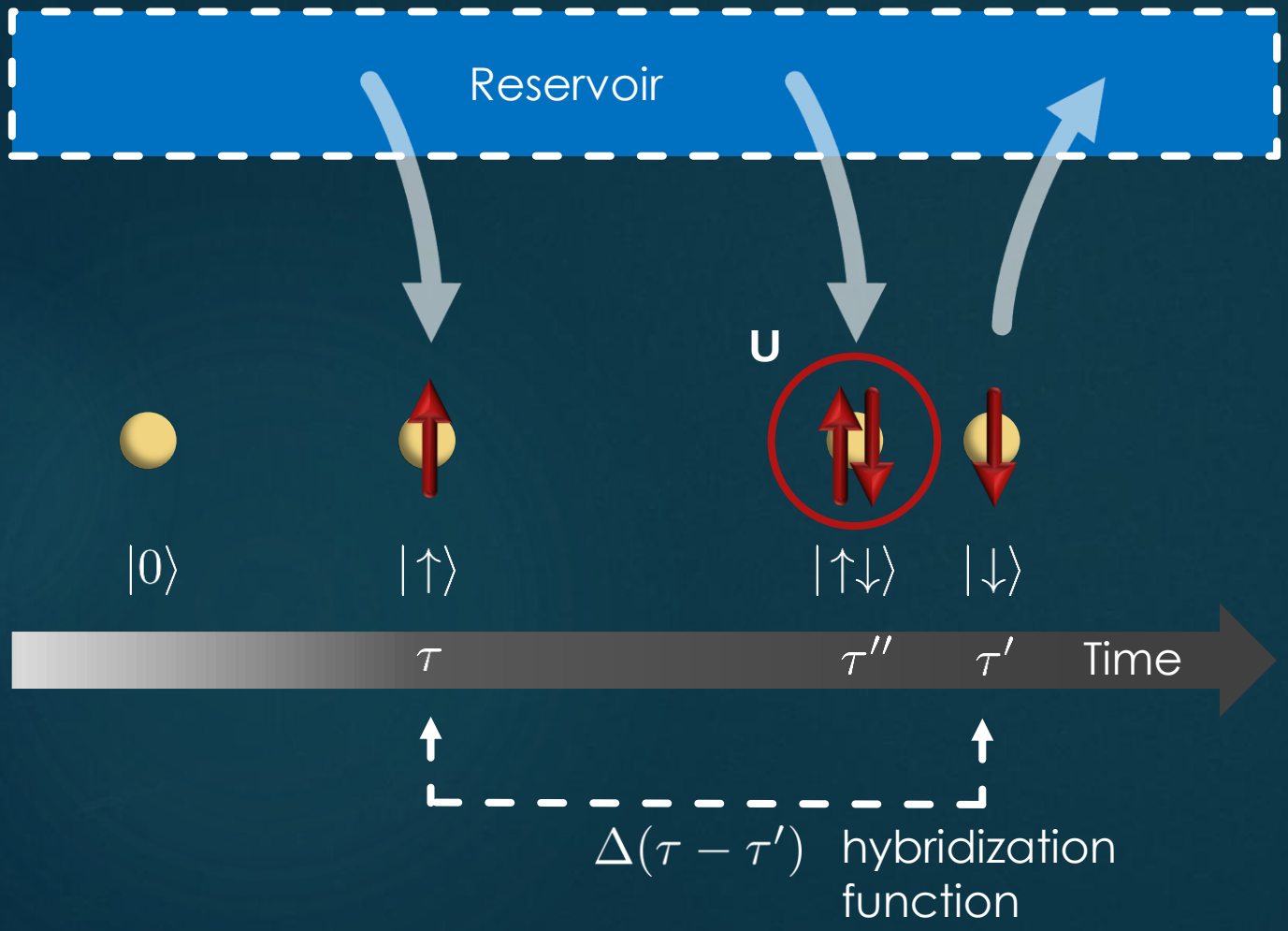
solve

- exact diagonalization
- QMC
- …

self-energy: $\Sigma(\omega)$

embedding:
approximate $\Sigma_{ij} = \Sigma\, \delta_{ij}$

Fluctuations of atomic configurations

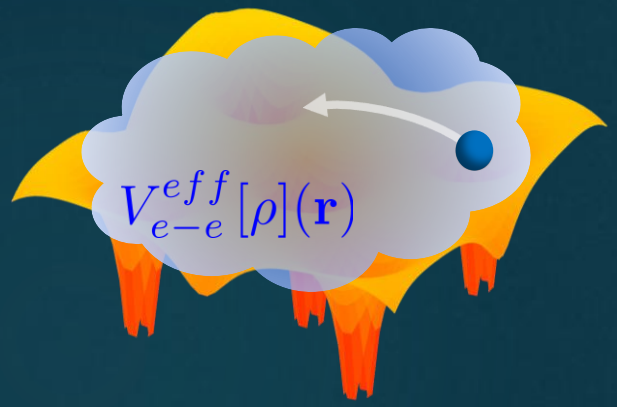


- Time history (dynamics) of **local** quantum fluctuations
- Neglects spatial fluctuations: Mean-field in space

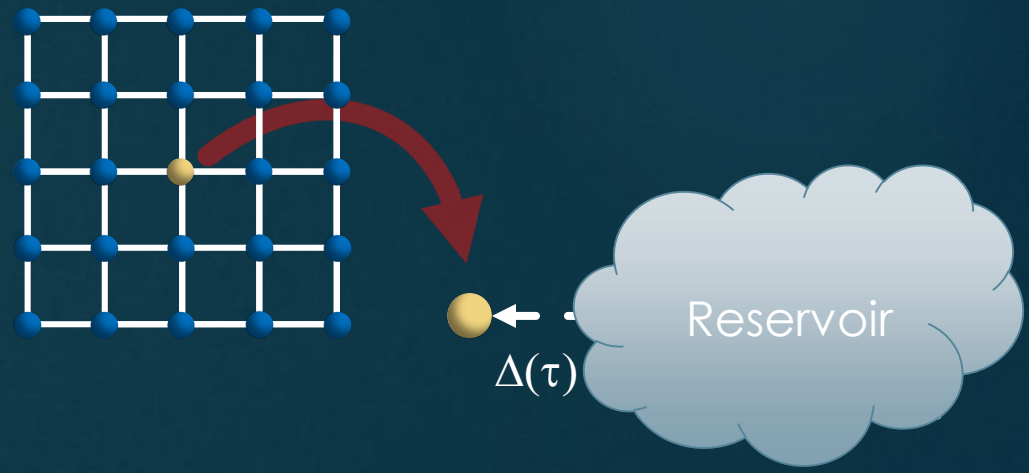
[adapted from: Kotliar & Vollhardt, Physics Today 3, 53 (2004)]

Self-consistency

- **DFT**
  - reference mapping: electron gas
  - *time* averaged potential → $V^{eff}[\rho](r)$
  - self-consistent density $\rho(r)$



- **DMFT**
  - reference mapping: Anderson impurity model
  - mean-field in space → local $\Sigma[\Delta](\omega)$
  - self-consistent bath Δ



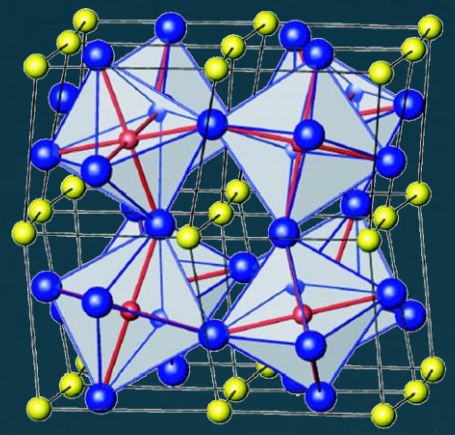
$$H^{DFT} = \sum_{\sigma} \psi^{\dagger}_{\sigma}(\mathbf{r}) \left[-\frac{\hbar^2}{2m_e}\Delta + V_{ion}(\mathbf{r}) + V^{eff}_{e-e}[\rho](\mathbf{r}) \right] \psi_{\sigma}(\mathbf{r})$$

$$H^{DFT} + \Sigma(\omega) - \Sigma_{dc}$$

"DFT+DMFT"

[Anisimov et al '97]
[Lichtenstein and Katsnelson '98]

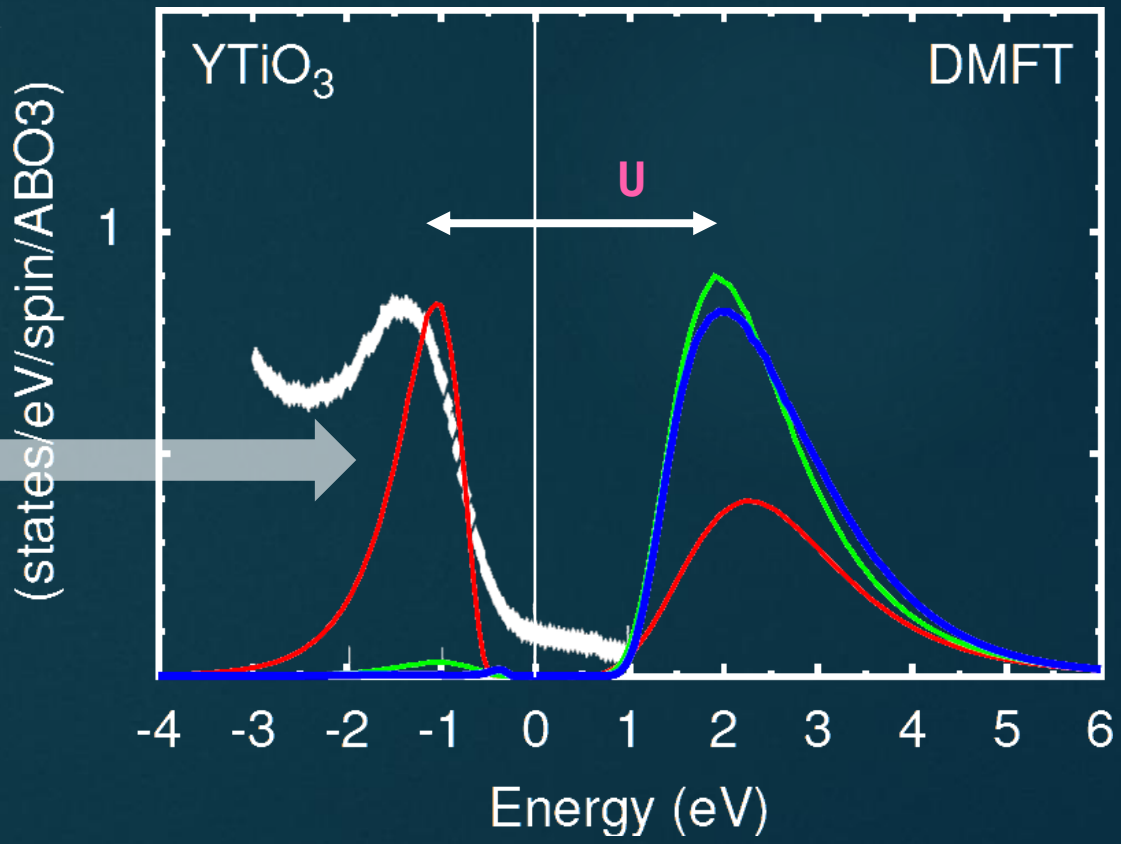
$YTiO_3$: Ti $3d^1$



U/t ≫1

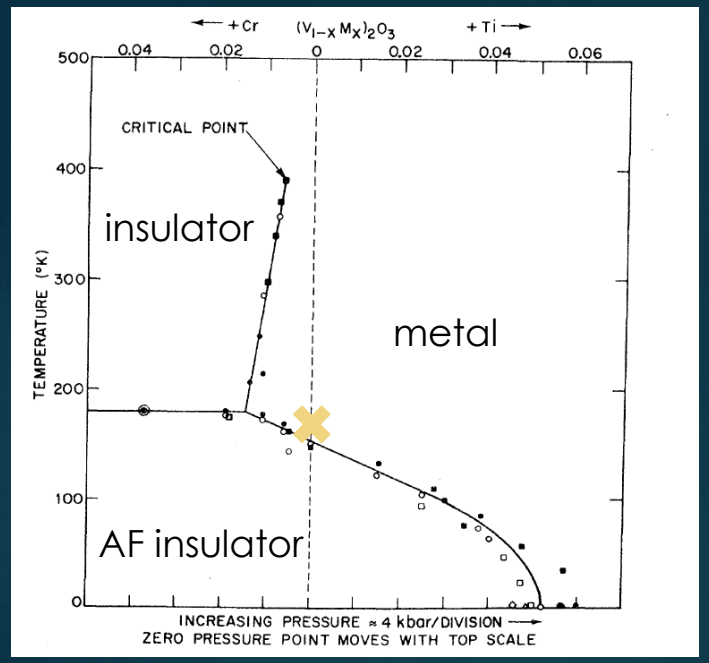
- **Mott insulator**

[Pavarini et al, NJP '05, Fujimori et al, PRB'92]

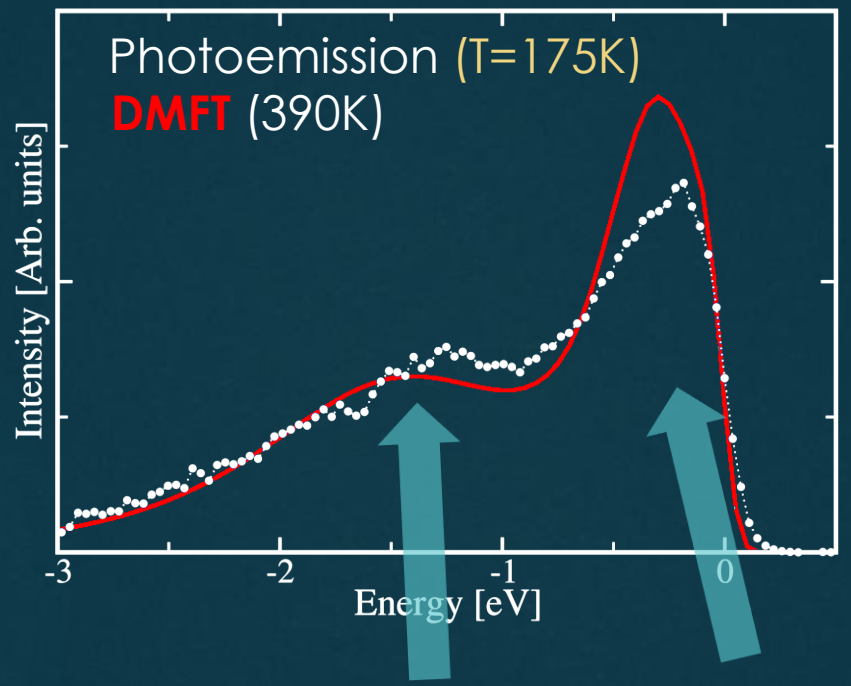


V_2O_3: band *and* atomic characteristics

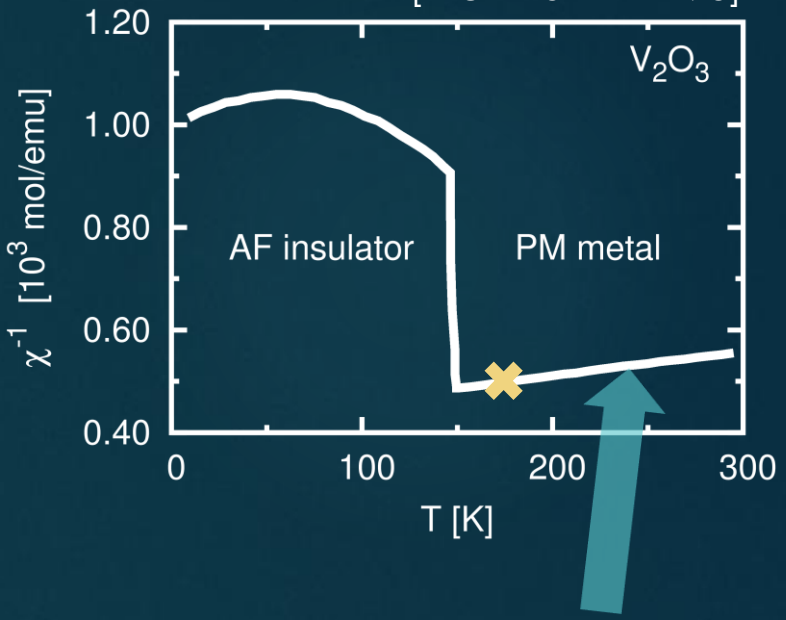
V $3d^2$



[Poteryaev, JMT et al, PRB '07]
[Mo et al, PRL '03]



[McWhan PRB '73]



short time-scales :
$d^2 \rightarrow d^1$ atomic like

large time-scales :
quasi-particles

$\chi \sim 1/(T-\theta)$ Curie-Weiss-like
fluctuating local moments

Self-energy Σ & spectral function

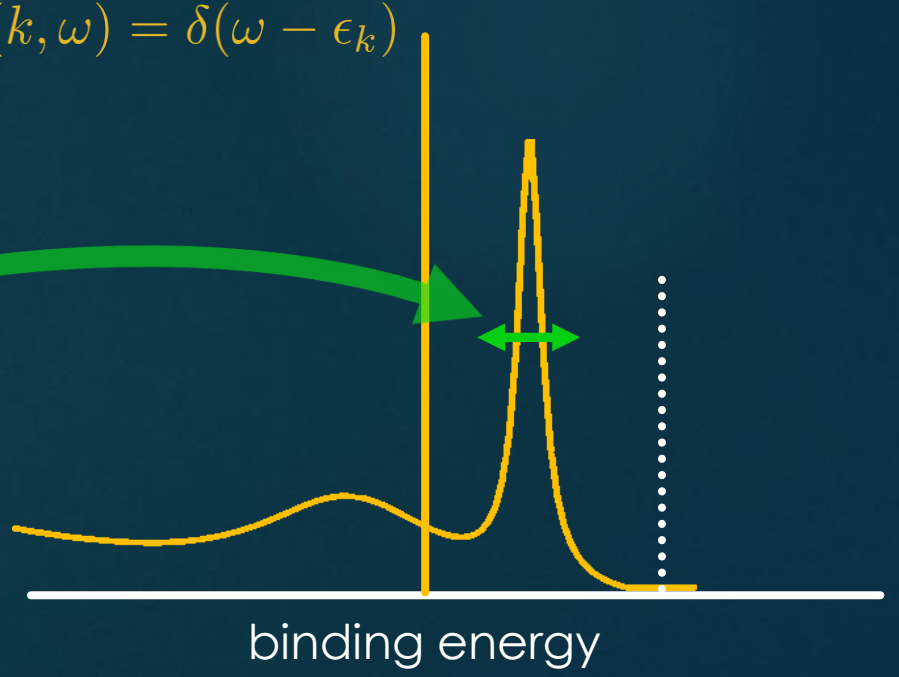
spectral function $A(k,\omega) = -\frac{1}{\pi}\frac{Im\Sigma}{(\omega - \epsilon_k - Re\Sigma)^2 + (Im\Sigma)^2}$ renormalized "Lorentzian"

- no correlations: $\Sigma(k,\omega) = -i0^+$
- Fermi liquid

$$\Sigma(k,\omega) = (1 - Z_k^{-1})\omega - iB_k(\omega^2 + (\pi k_B T)^2) + \mathcal{O}(\omega^3)$$

$$A(k,\omega) = Z_k \frac{(Z_k Im\Sigma/\pi)}{(\omega - Z_k\epsilon_k)^2 + (Z_k Im\Sigma)^2} + \cdots$$

$A(k,\omega) = \delta(\omega - \epsilon_k)$



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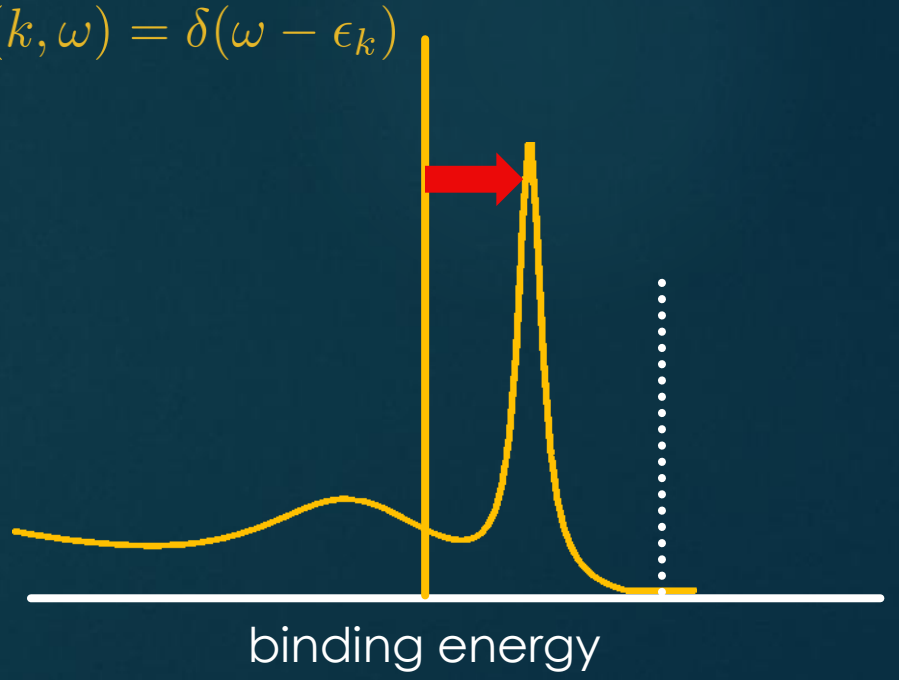

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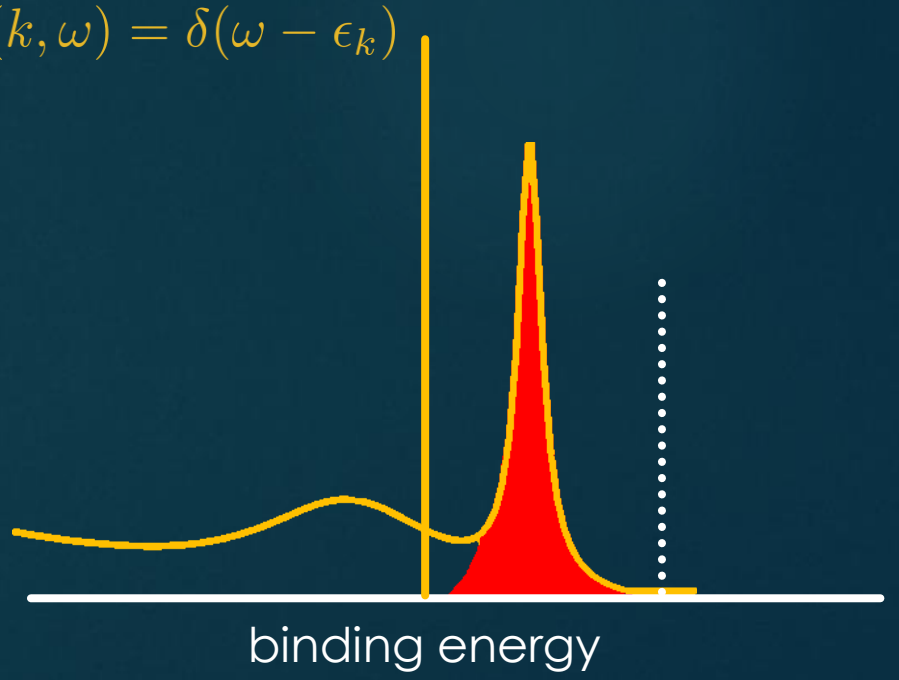

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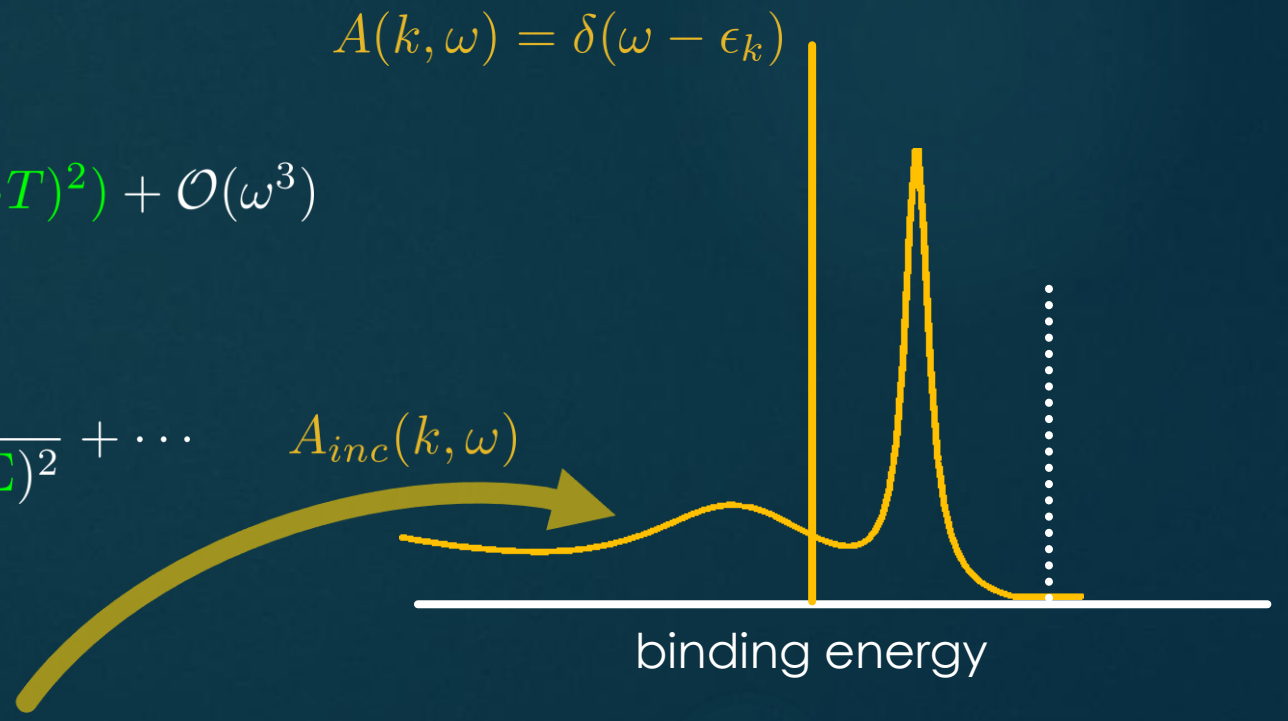
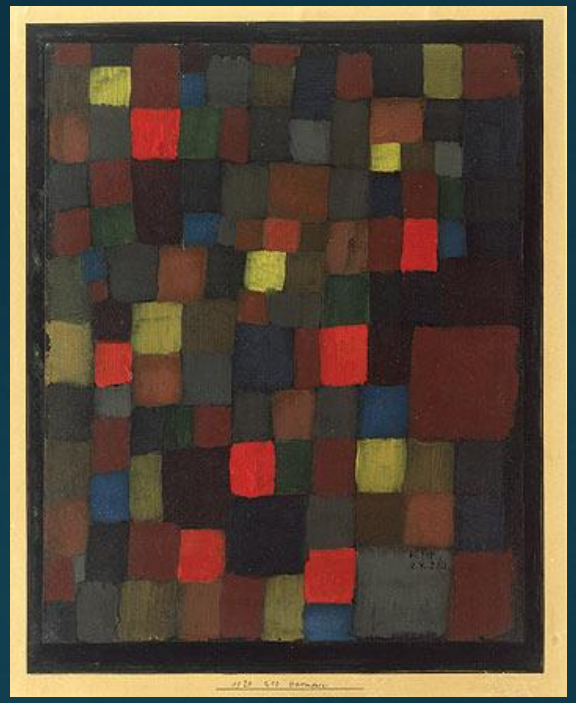
$$A(k,\omega) = Z_k \frac{(Z_k Im\Sigma/\pi)}{(\omega - Z_k\epsilon_k)^2 + (Z_k Im\Sigma)^2} + \cdots \qquad A_{inc}(k,\omega)$$



Hubbard bands, plasmons, couplings to bosons (e.g. phonons)

1) pigments



"Colour Harmony in Squares with **Vermillion** Accents"
[P. Klee (1924)]

In fact, researchers have found evidence that at least some of the old masters were affected by the materials they used to create their masterpieces. According to physicians Lisbet Milling Pedersen and Henrik Permin at Hviolovre Hospital in Copenhagen, Denmark, the rheumatoid arthritis suffered by Paul Rubens (who had one of the first cases of the disease described in the literature), Auguste Renoir, and Raoul Dufy, and the scleroderma that plagued Paul Klee can be linked to the bright and clear colors that dominated their canvases.

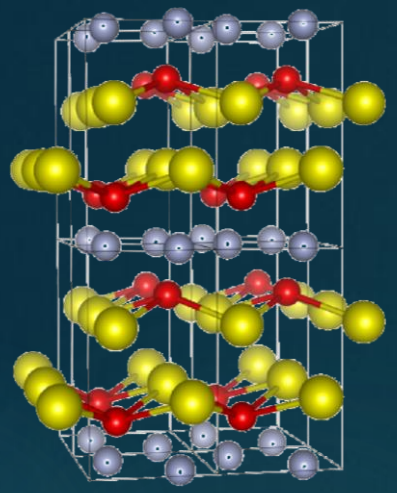
These afflicted artists depended on colors based on toxic heavy metals more often than their contemporaries, who favored earth colors based on harmless iron and carbon compounds. Prolonged exposure to these substances—including mercury, cadmium, arsenic, lead, antimony, tin, cobalt, manganese, and chromium—can promote the development of inflammatory rheumatic diseases, as well as chronic lead and manganese poisoning.

[Environmental health perspectives 105, 284 (1997)]

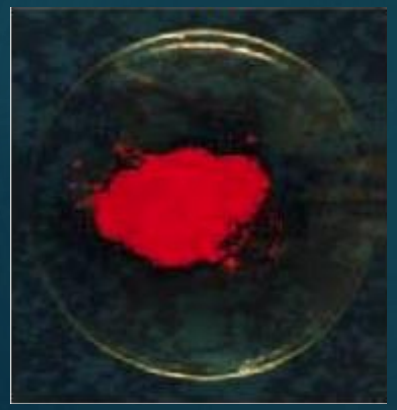
- many "classical" pigments contain toxic heavy metals (Hg, Cd, Pb…)
  - red: vermillion (cinnabar): α-HgS

Q: Alternatives…?

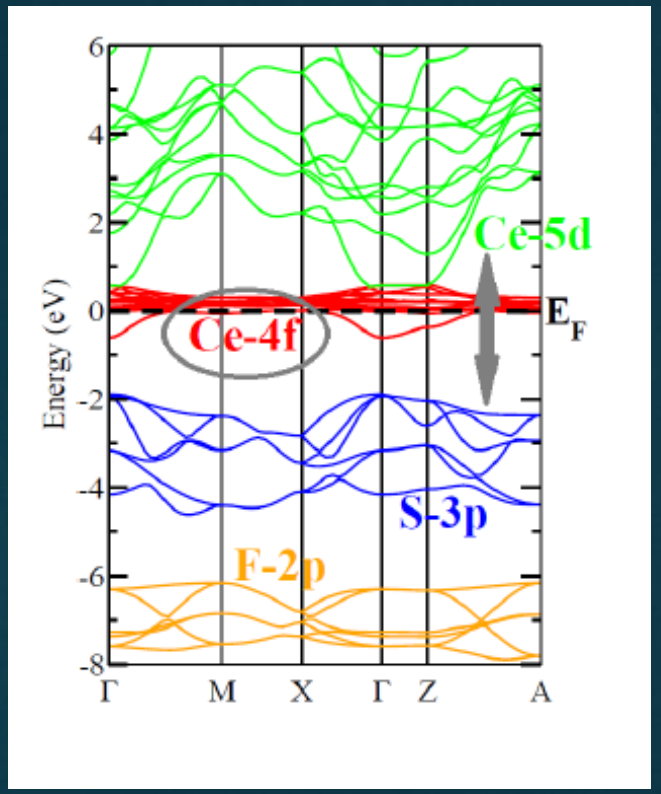
Eco-friendly rare-earth pigment: CeSF



[Demourges et al, '01]



DFT



Ce $4f^1$ configuration
odd #valence electrons

- quasi localized 4f states

  DFT: metal
  exp: paramagnetic (Mott) insulator

  → need DMFT

- S3p-Ce5d gap too small

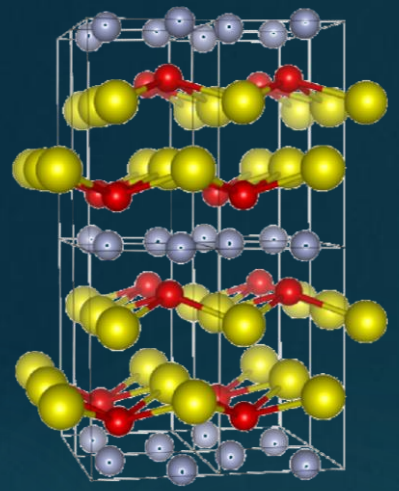
LaSF (f^0)	Exp	LDA	GW
Δ_{pd} [eV]	2.8	1.3	2.45

→ need GW

here: poor man's GW+DMFT

[JMT et al, PNAS 110, 904 (2013)]

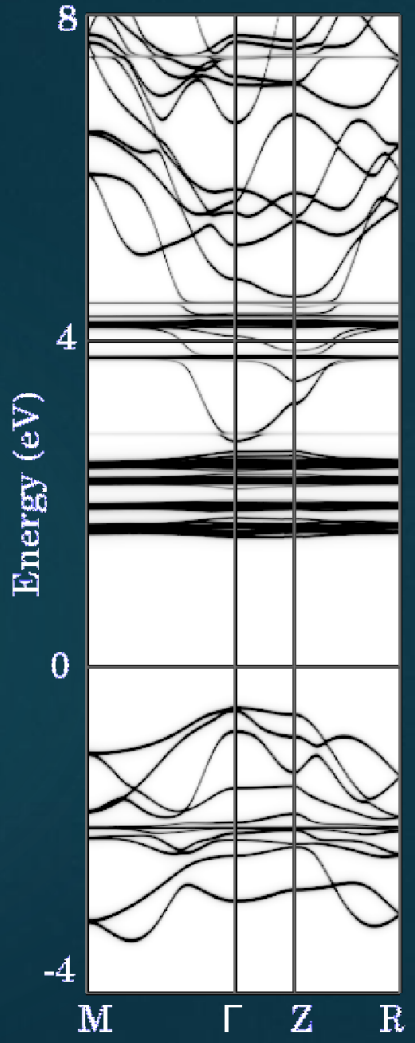
Eco-friendly rare-earth pigment: CeSF



CeSF

[Demourges et al, '01]

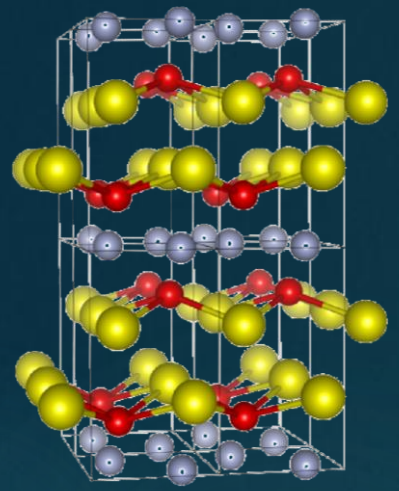
DFT/GW+DMFT



- "atomic physics" of localized 4f states embedded in itinerant bands
- multiplet structure
- microscopic understanding of good absorption properties

[JMT et al, PNAS 110, 904 (2013)]

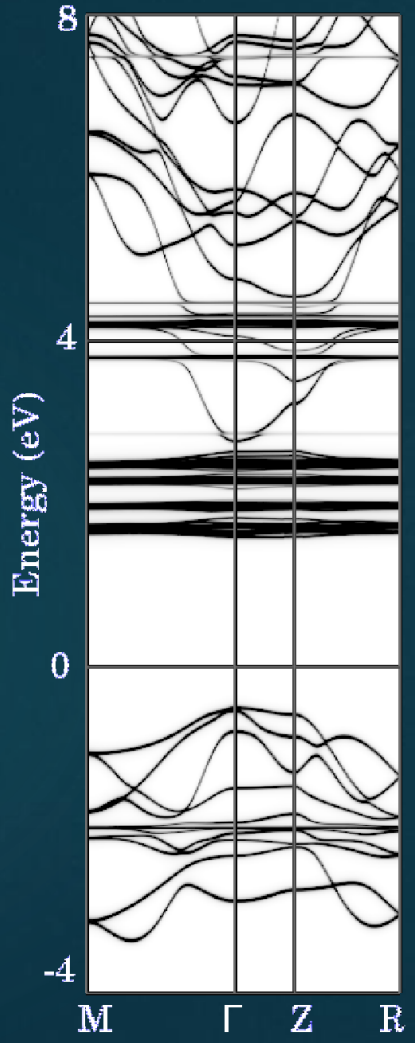
Eco-friendly rare-earth pigment: CeSF



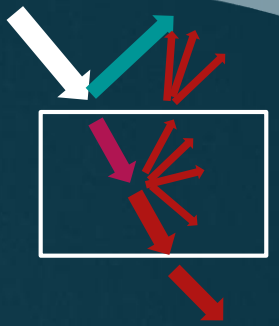
CeSF

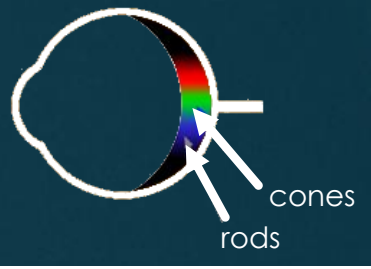
[Demourges et al, '01]

DFT/GW+DMFT



- scattering
- color perception





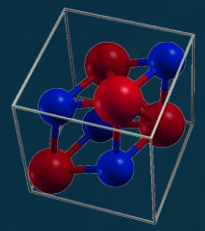
bulk

20% in 10μm film

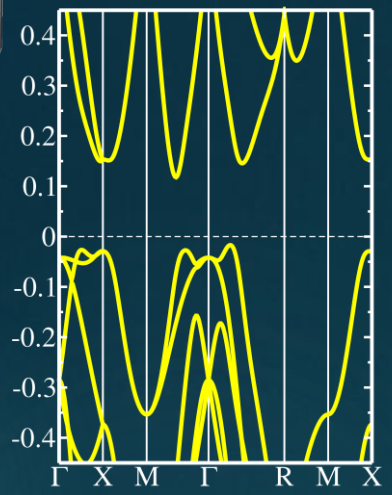
"Neolor" of Solvay/Rhodia

[www.solvay.com/en/markets-and-products/featured-products/neolor.html]

2) intermetallic FeSi

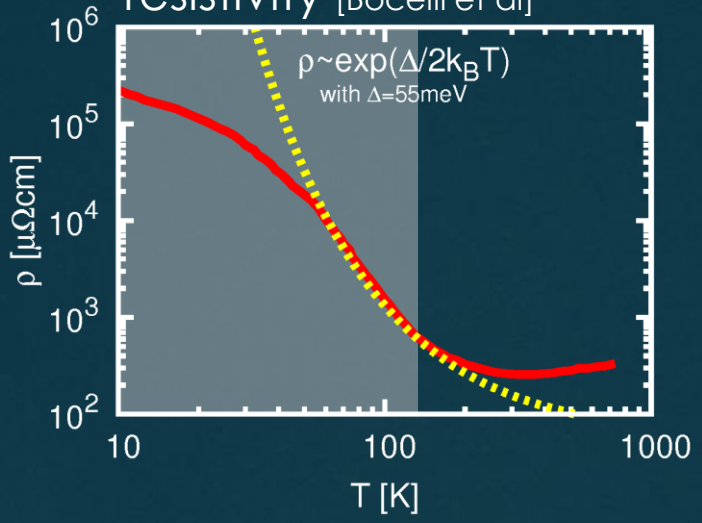


DFT

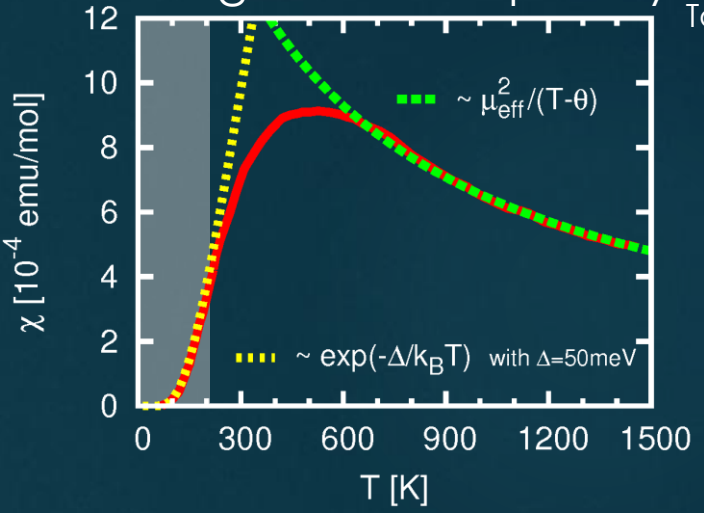


Δ_{DFT}~120meV

resistivity [Bocelli et al]



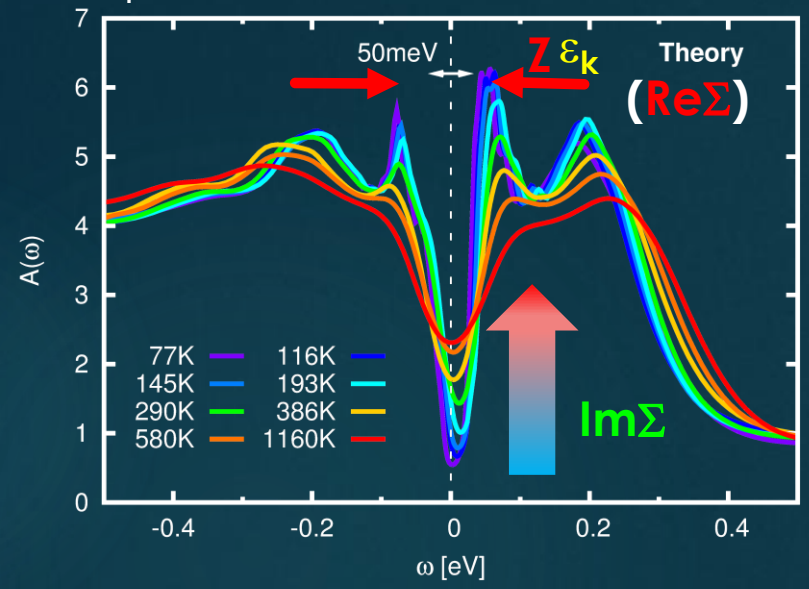
magnetic susceptibility [Jaccarino et al, Takagi et al]

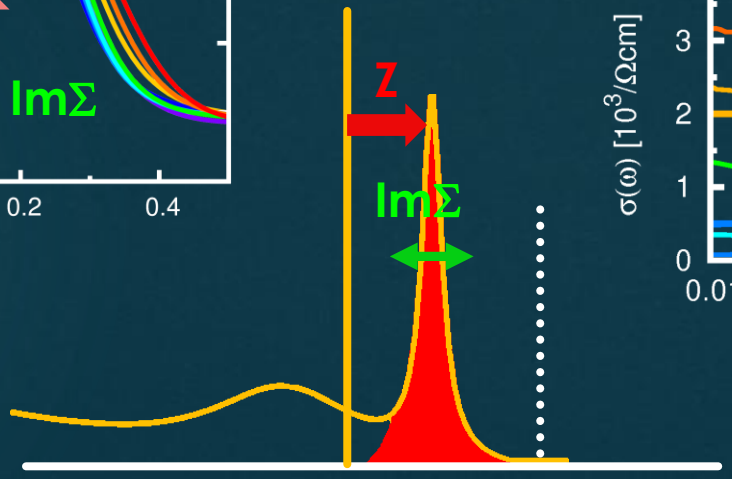


- band-gap too large by factor of 2! Δ_{DFT}~120meV, Δ_{exp}~55meV
- crossover to metallic state for $k_BT \sim k_B 100K = 17meV \ll \Delta$ (beyond thermal activation)
- Curie-Weiss-like magnetic susceptibility

FeSi: DMFT 1-particle spectroscopies

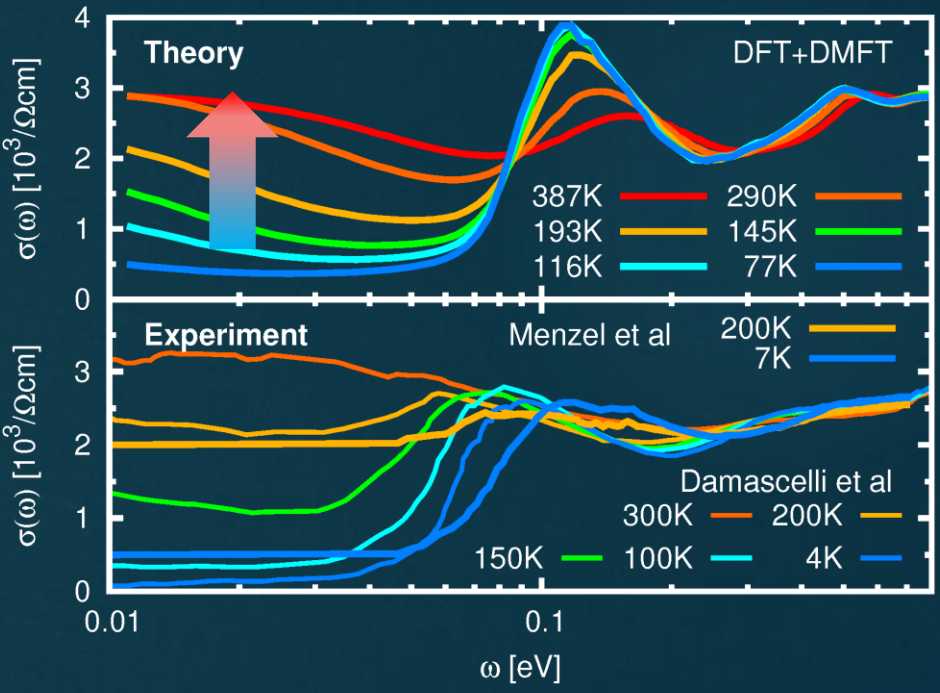
local
spectral function DFT+DMFT





binding energy

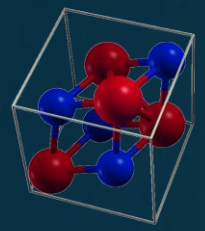
optical conductivity



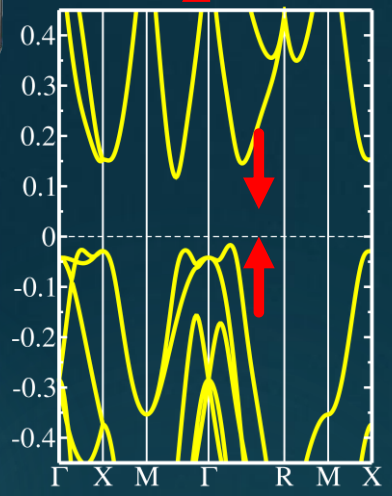
[JMT et al, PNAS 109, 3243 (2012)]

[JMT et al, PNAS 109, 3243 (2012)]

FeSi: physical picture

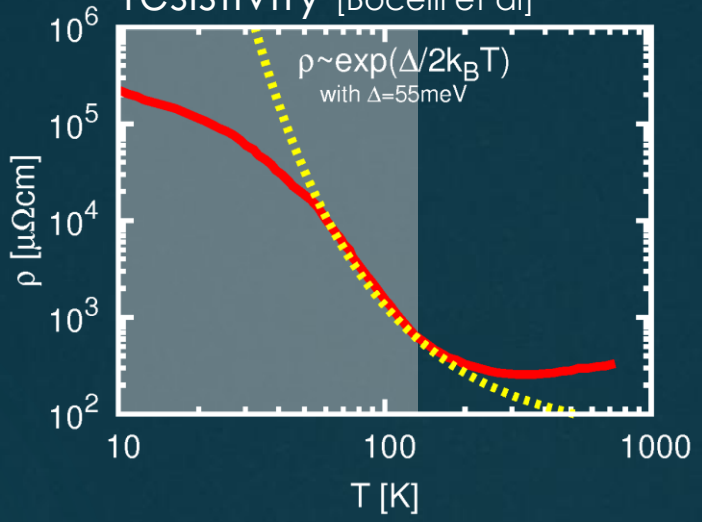


DFT+Z

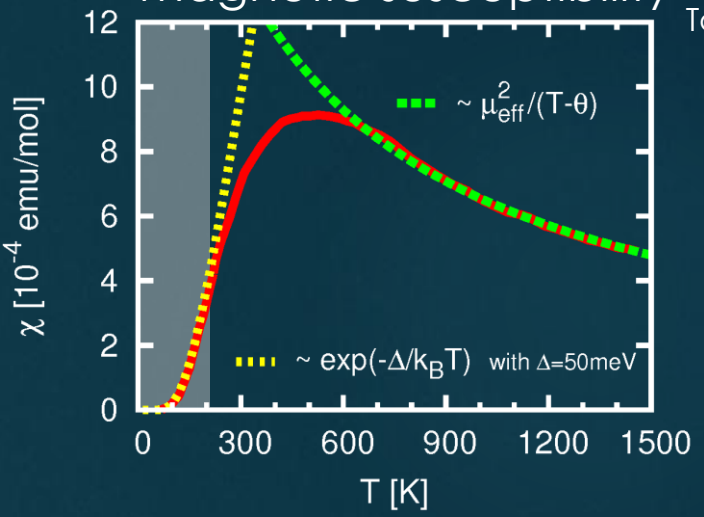


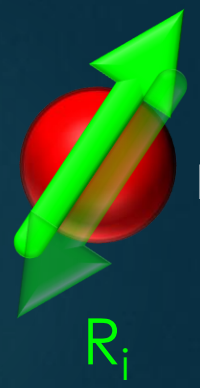
$Z\varepsilon_k$

resistivity [Bocelli et al]



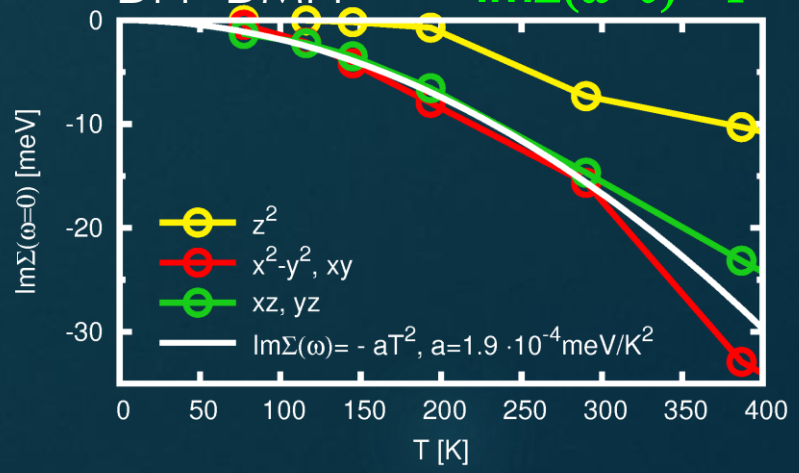
magnetic susceptibility [Jaccarino et al, Takagi et al]





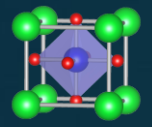
electronic structure:

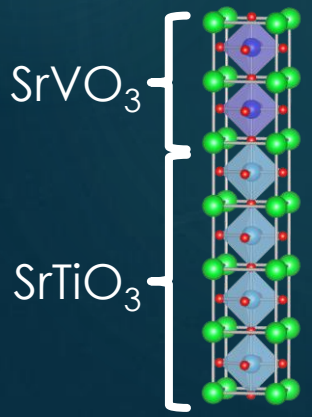
DFT+DMFT $\mathrm{Im}\Sigma(\omega=0) = \Gamma$

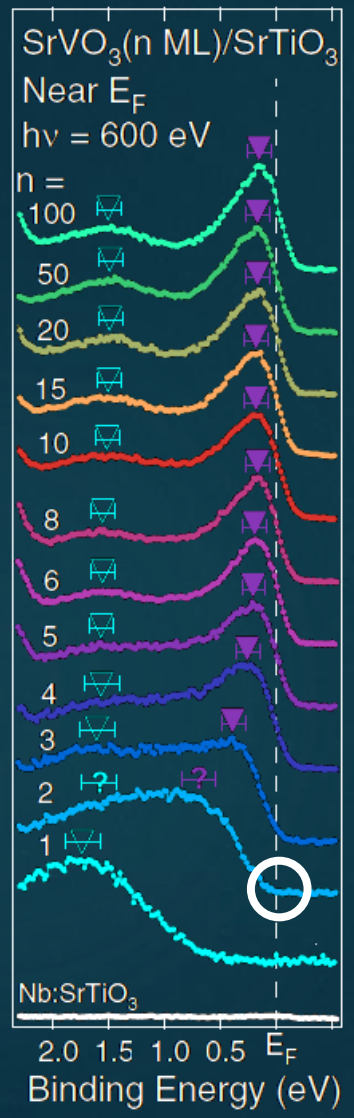


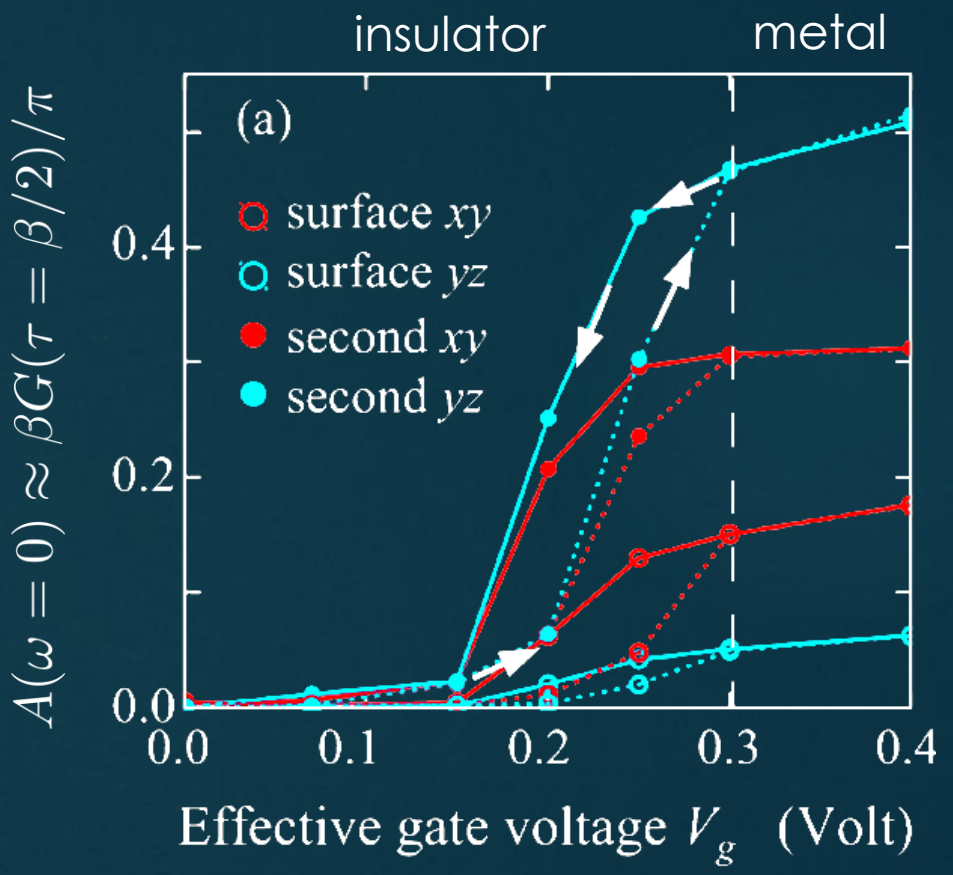
[See also: Fu & Doniach PRB '95, Kunes & Anisimov PRB '08, Sentef et al, PRB '09]

3) $SrVO_3$ films: Mott transistor





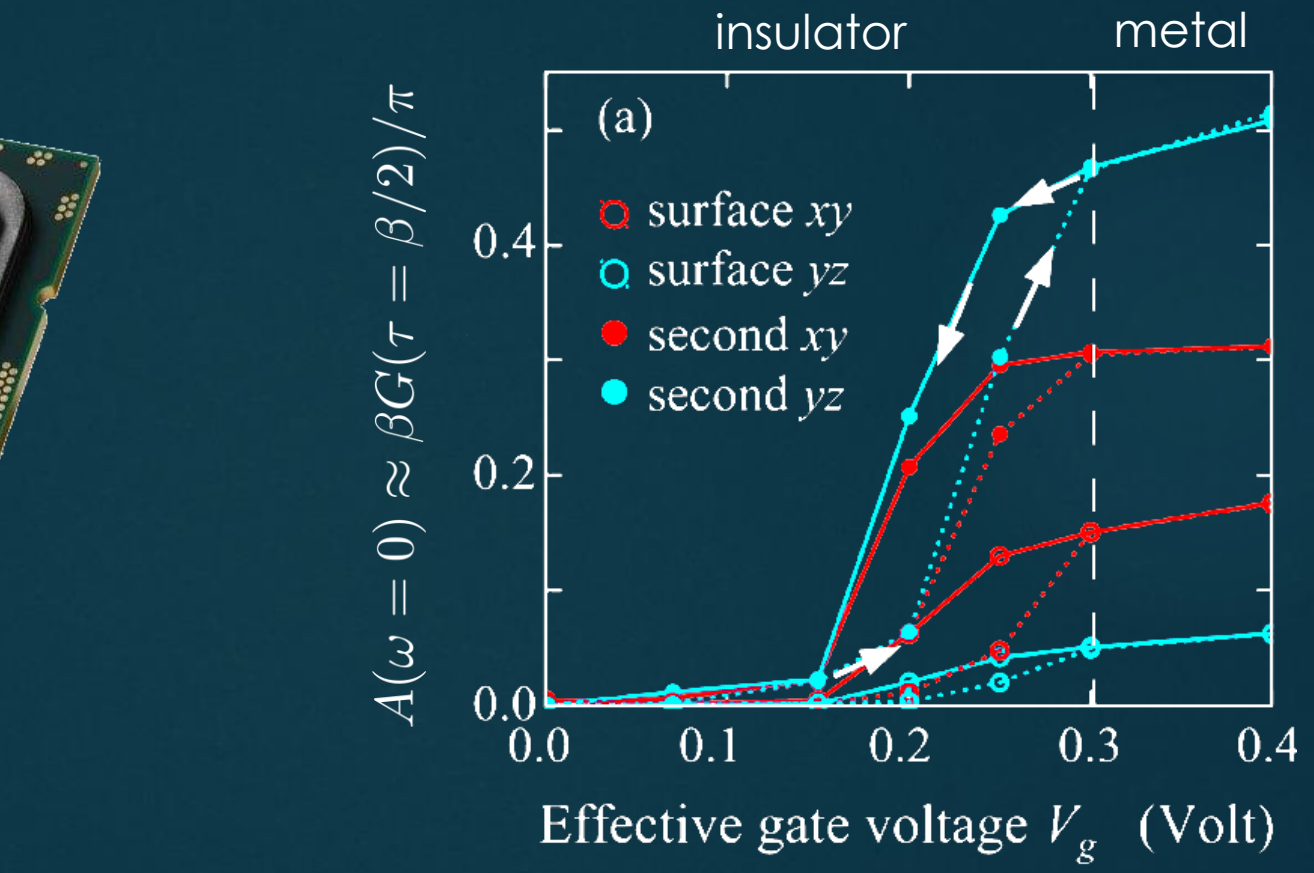




Experiment: [Yoshimatsu et al, Science '11] Theory: [Zhong, Wallerberger, JMT et al, PRL '15]

3) $SrVO_3$ films: Mott transistor

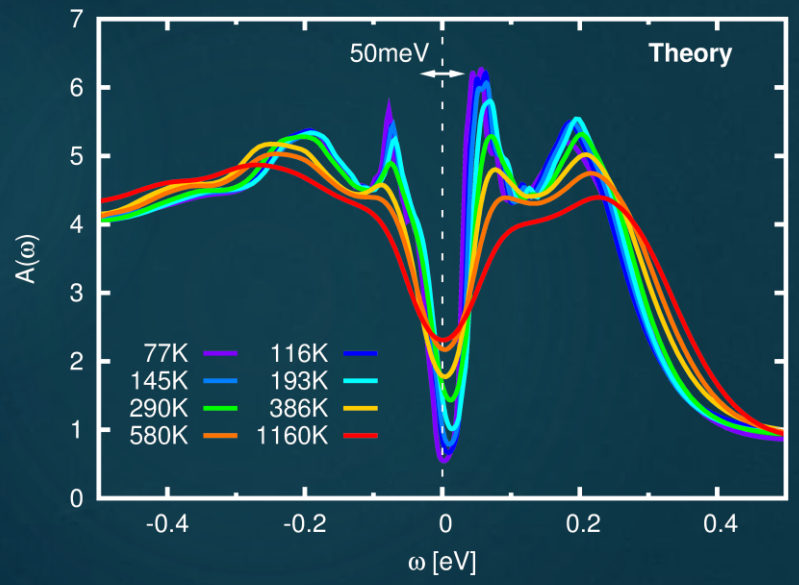
~1V (silicon diode: 0.7eV)

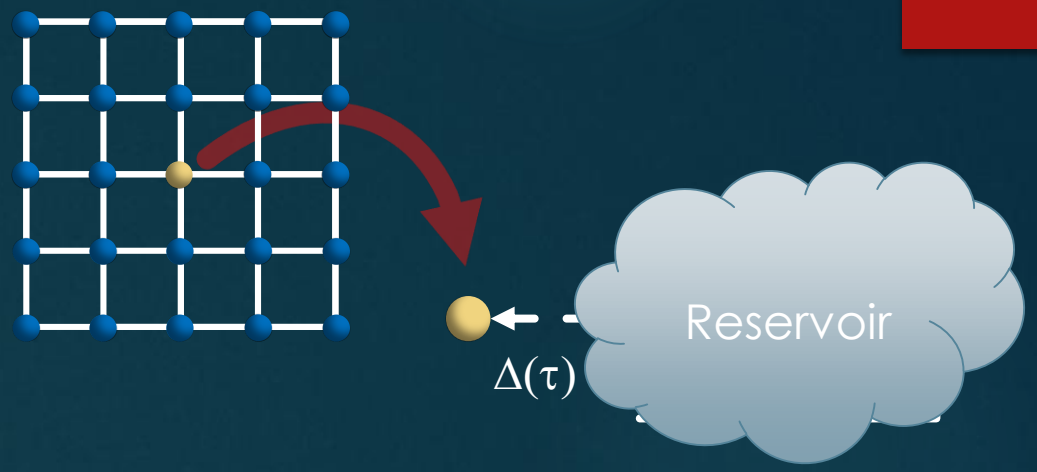


Experiment: [Yoshimatsu et al, Science '11] Theory: [Zhong, Wallerberger, JMT et al, PRL '15]

Summary

- DMFT
  - many-body renormalizations
  - excited states
  - finite temperature





- public codes (with wien2k interfaces, e.g., wien2wannier)
  - w2dynamics [Wuerzburg+Wien] → $SrVO_3$ thin films
  - TRIQS [O. Parcollet et al, Paris] → CeSF
  - DFT+Embedded DMFT Functional [K. Haule, Rutgers] → FeSi
  - ALPS [Switzerland], …

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Der Wissenschaftsfonds.