Matteo Gatti, Federico Iori, and Angel Rubio

Beyond the Hubbard model: a realistic description of metal-insulator transitions

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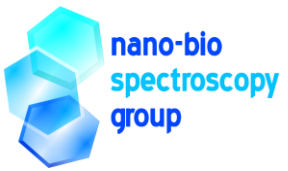
TDDFT Workshop 2012 - Benasque



Outline

- Introduction
- GW approximation: exchange and dynamical screening
- Metal-insulator transition in MnO under pressure
- Excitons in VO_2 from the Bethe-Salpeter equation
- Conclusions

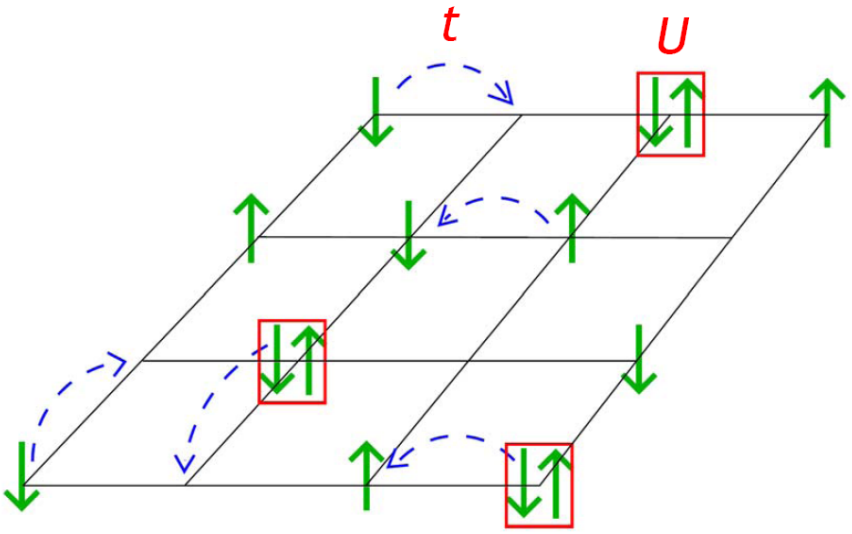
Hubbard model

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

Single-band Hubbard model:

competition between tendency

- to localise (on-site Coulomb repulsion U)
- to spread over other lattice sites (bandwidth W)



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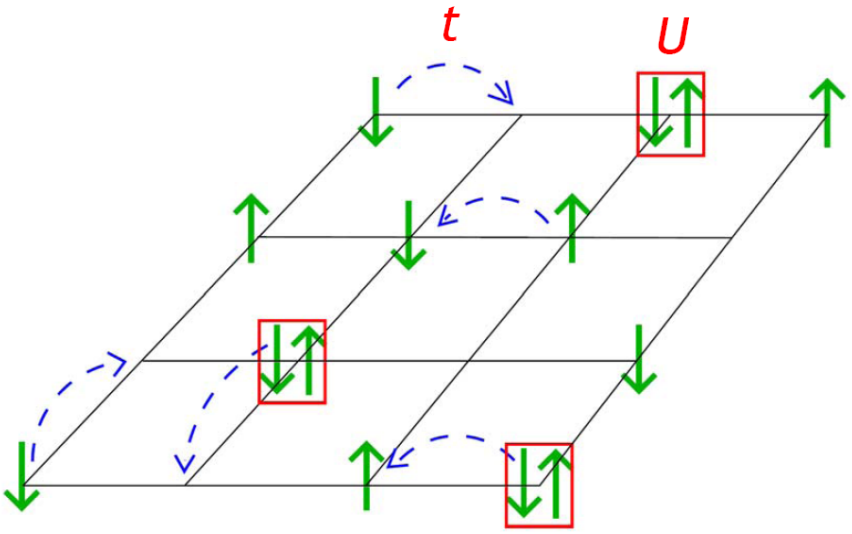
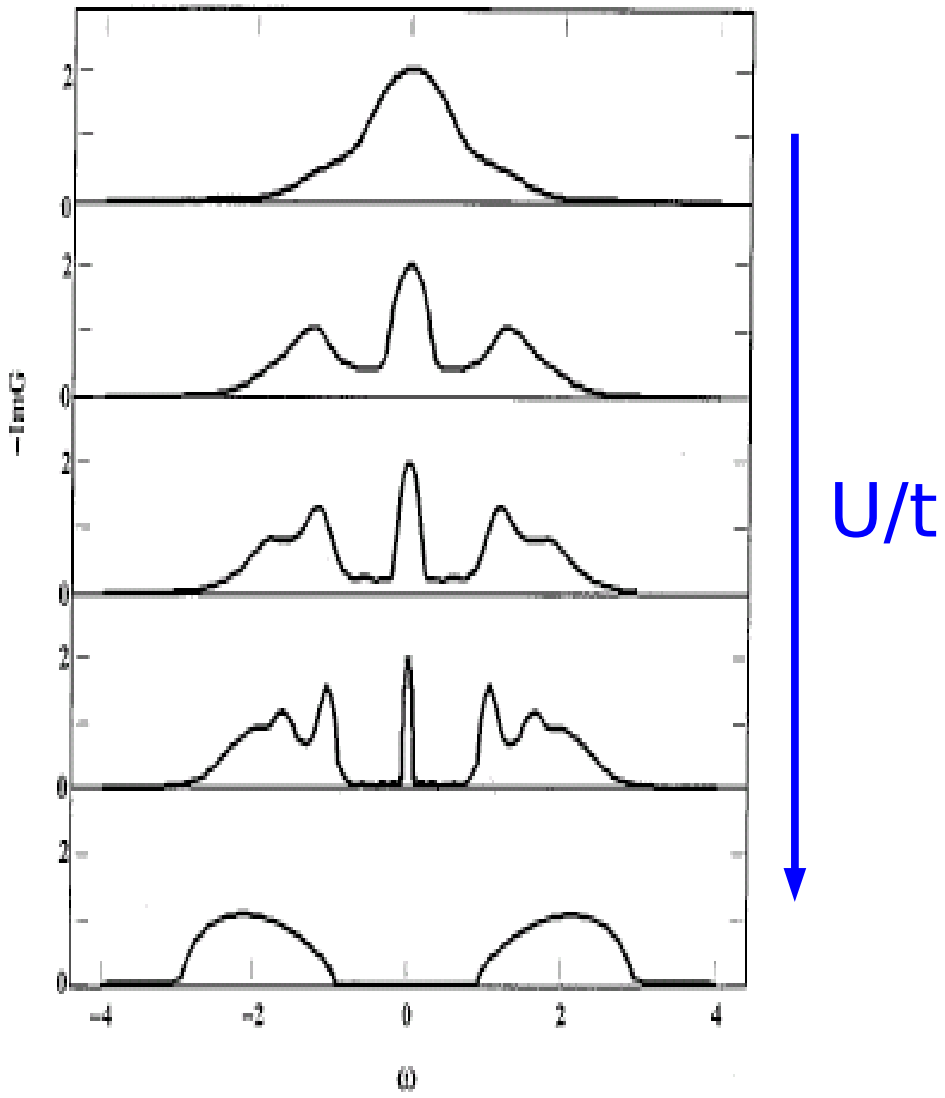


LDA+U, LDA+DMFT, LDA+....

Hubbard Model
DMFT solution



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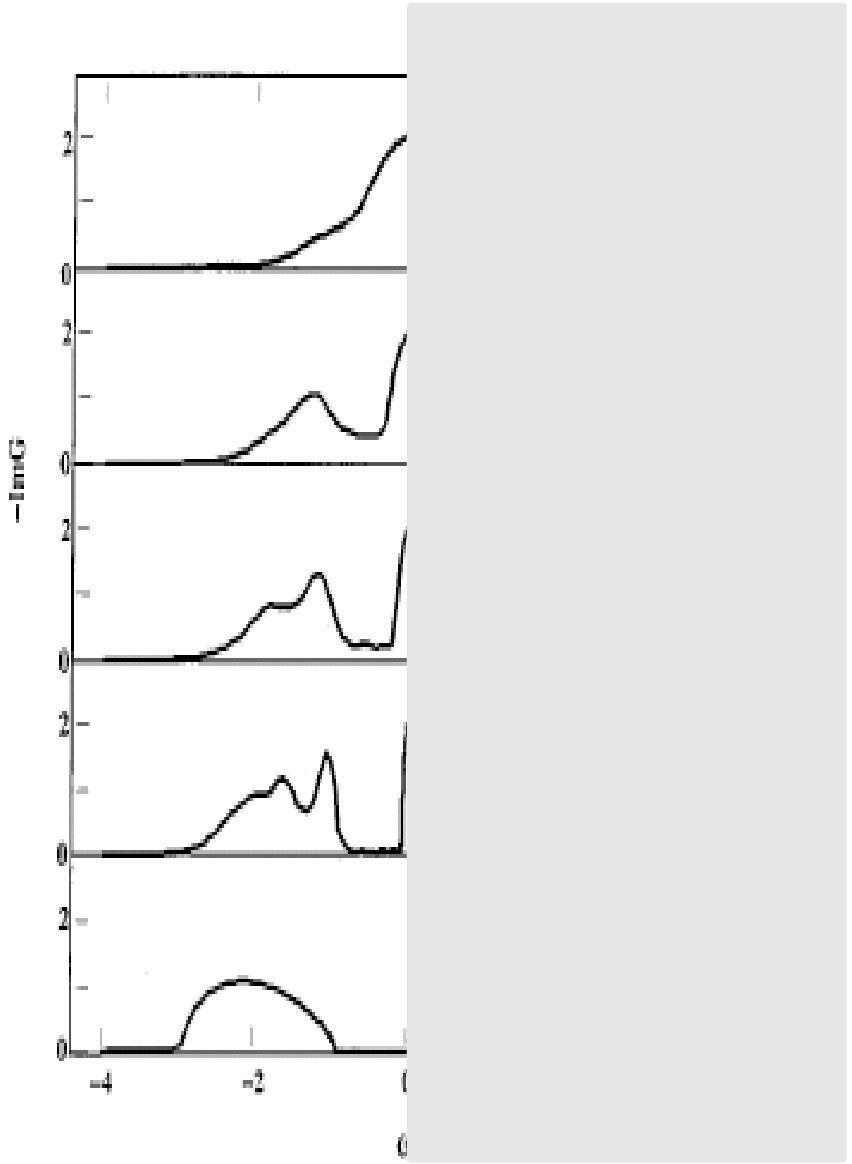
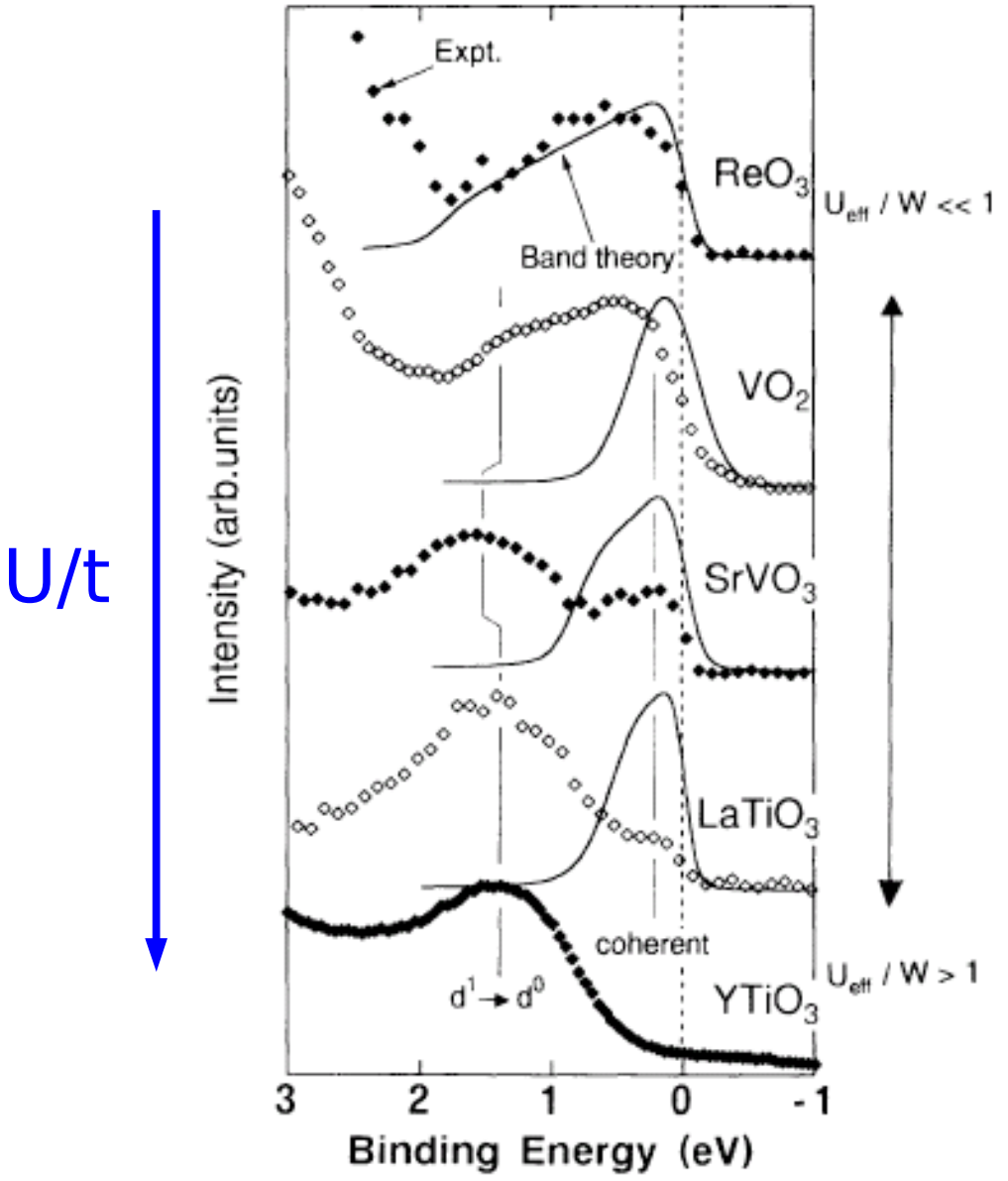


Photoemission spectra of d^1 oxides



Fujimori et al, PRL 69 (1992)

Can we describe metal-insulator transitions
in transition-metal oxides
independently from the Hubbard model?

Methodology: ab initio GW approximation

Standard perturbative G_0W_0

$$H_0(\mathbf{r})\varphi_i(\mathbf{r}) + V_{xc}(\mathbf{r})\varphi_i(r) = \epsilon_i\varphi_i(\mathbf{r})$$

$$H_0(\mathbf{r})\phi_i(\mathbf{r}) + \int d\mathbf{r}'\ \Sigma(\mathbf{r},\mathbf{r}',\omega = E_i)\ \phi_i(\mathbf{r}') = E_i\,\phi_i(\mathbf{r})$$

First-order perturbative corrections with $\Sigma = iGW$:

$$E_i - \epsilon_i = \langle\varphi_i|\Sigma(E_i) - V_{xc}|\varphi_i\rangle$$

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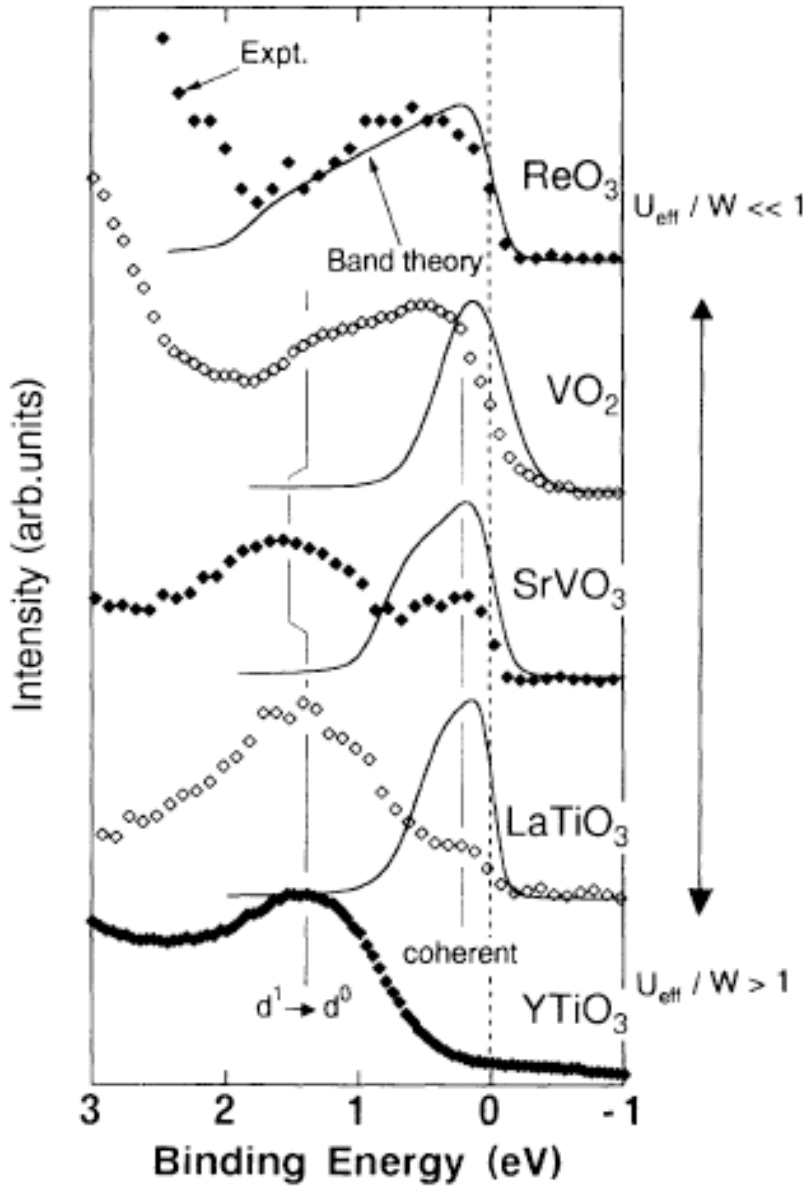
First-order perturbative corrections with $\Sigma = iGW$:

$$E_i - \epsilon_i = \langle\varphi_i|\Sigma(E_i) - V_{xc}|\varphi_i\rangle$$

Beyond G_0W_0: self-consistent COHSEX + GW

See: F. Bruneval, N. Vast, and L. Reining, PRB 74 (2006).
Similar results to QPscGW scheme: S. Faleev *et al.* PRL 93 (2004).

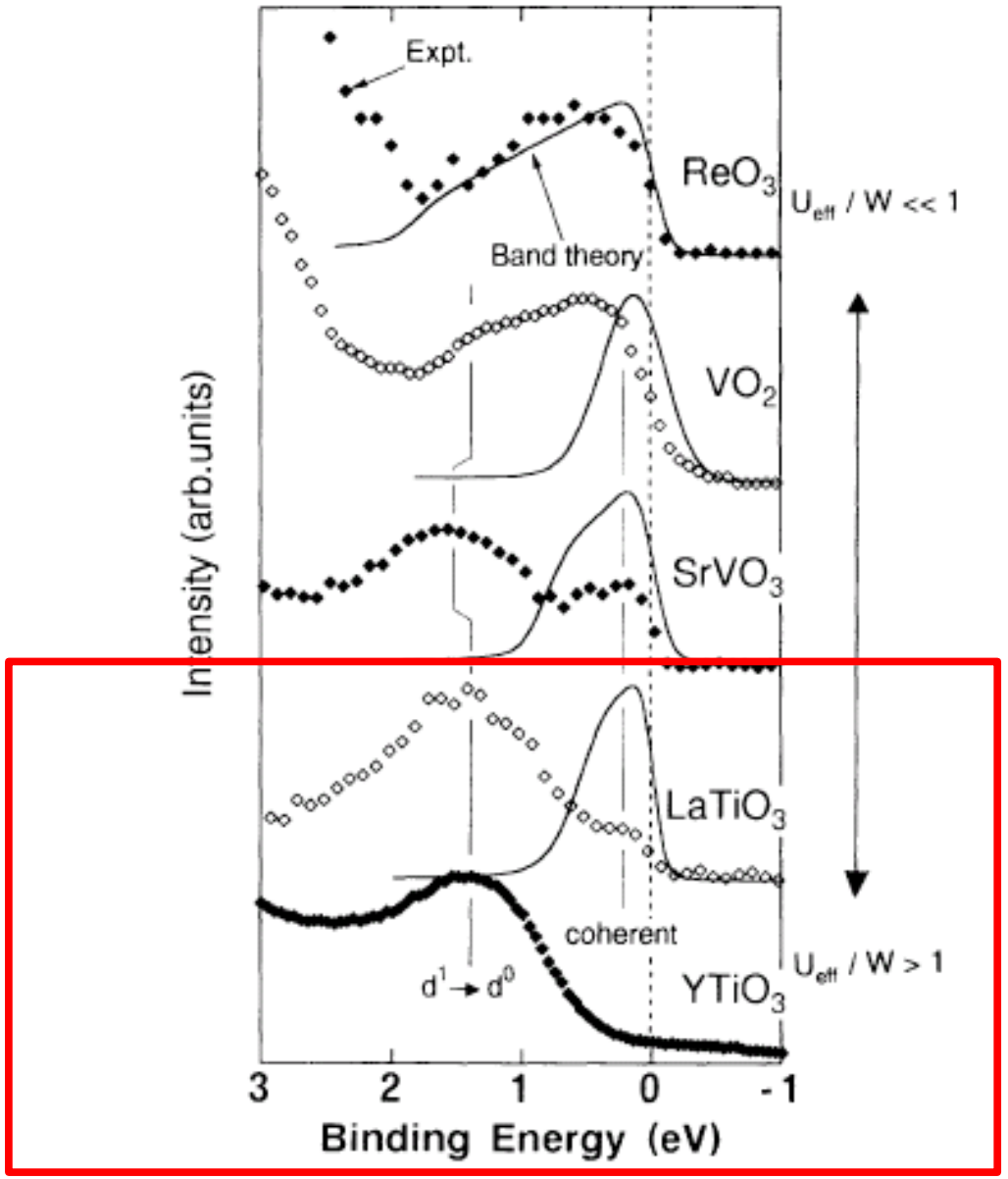
Photoemission spectra of d^1 oxides



Fujimori et al, PRL 69 (1992)

Two problems:

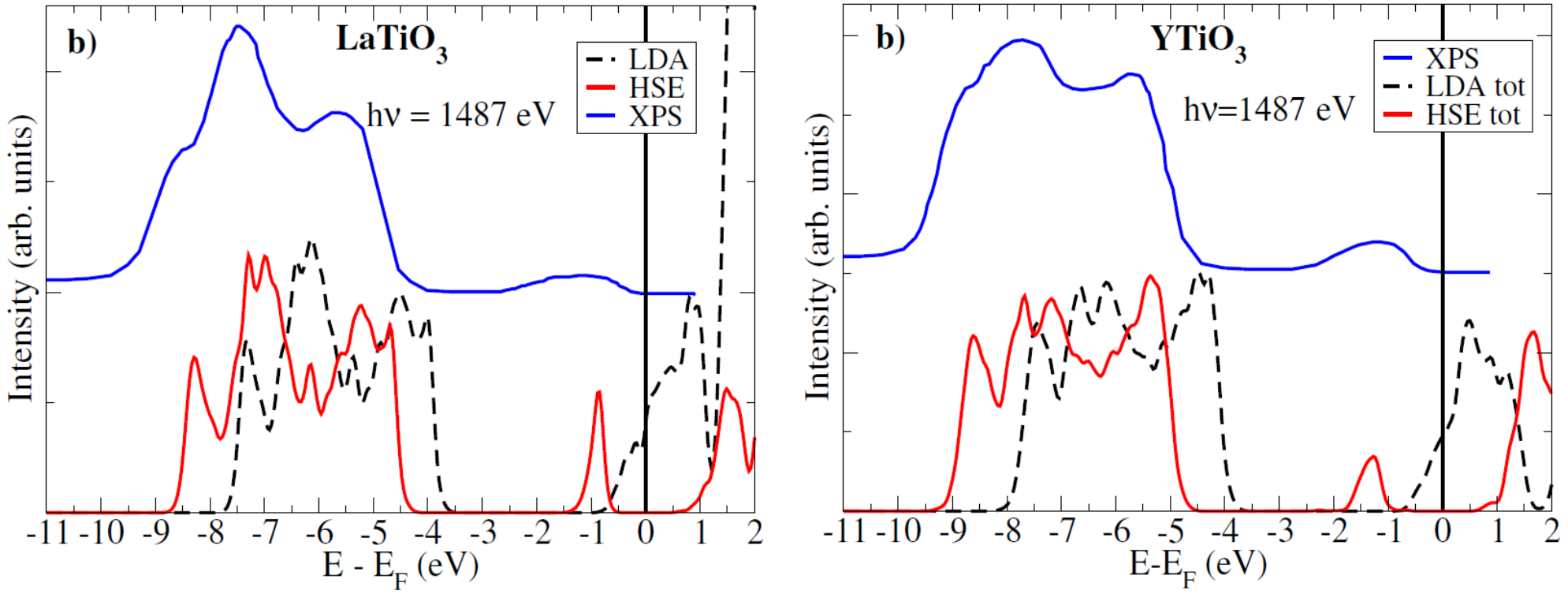
- bulk-sensitive spectra ?
- LDA = “band theory” ?



Fujimori et al, PRL 69 (1992)

Mott insulators?

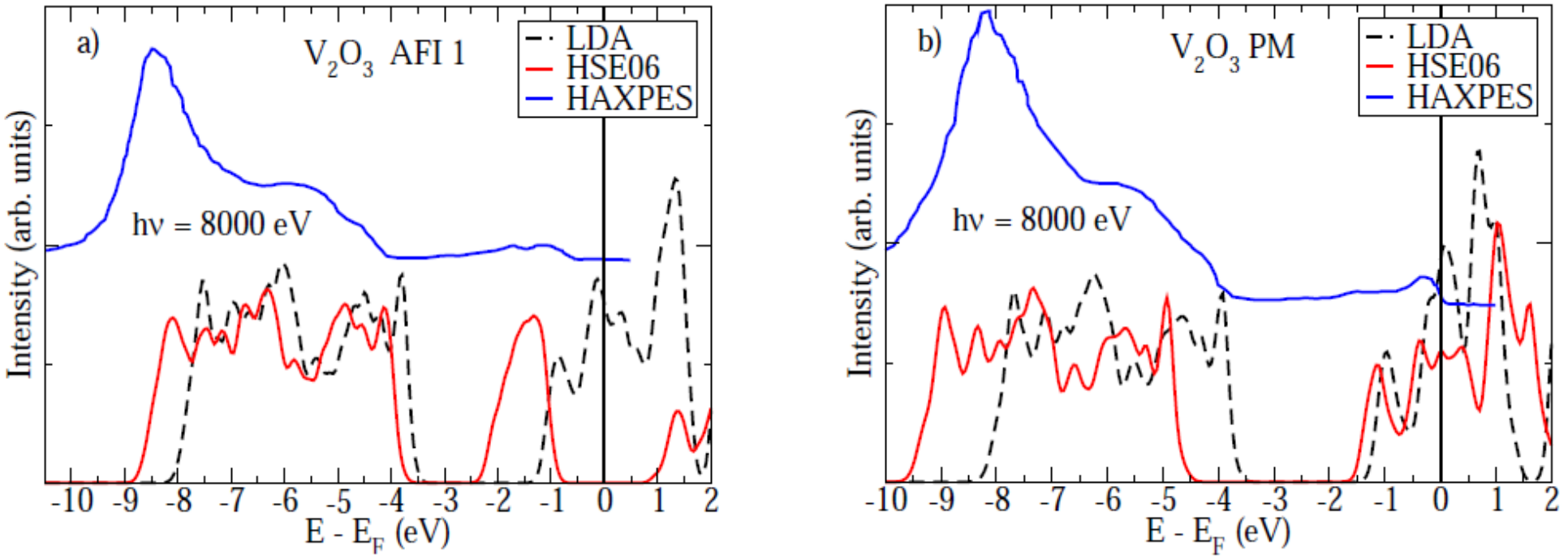
The role of nonlocal exchange



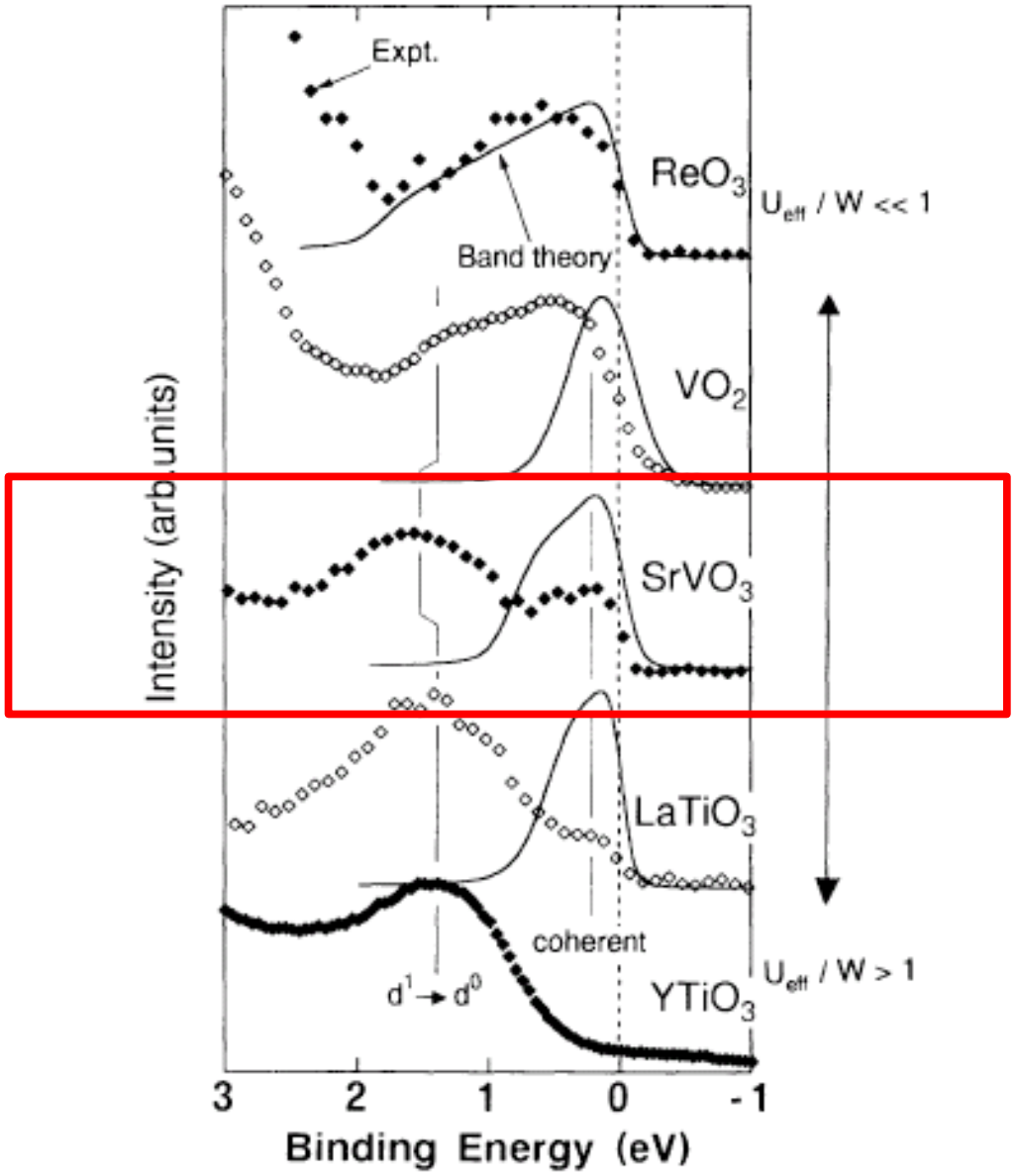
Hybrid functional HSE06 - Federico Iori, UPV San Sebastian (2011)
Exp. from H. Roth PhD thesis – Köln 2008

The role of nonlocal exchange

Metal-insulator transition in V_2O_3

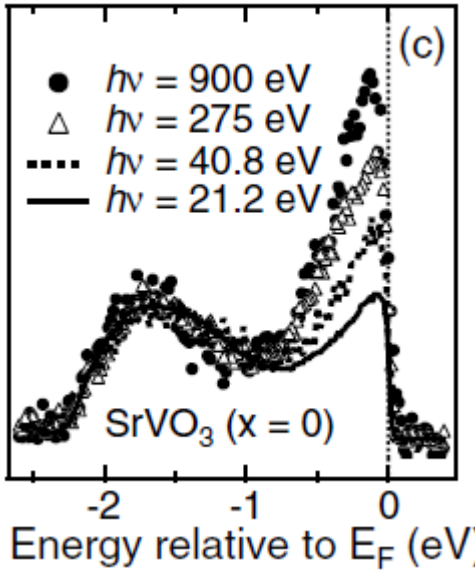


Hybrid functional HSE06 - Federico Iori, UPV San Sebastian (2011)
Exp. from H. Fujiwara et al, PRB 84 (2011).



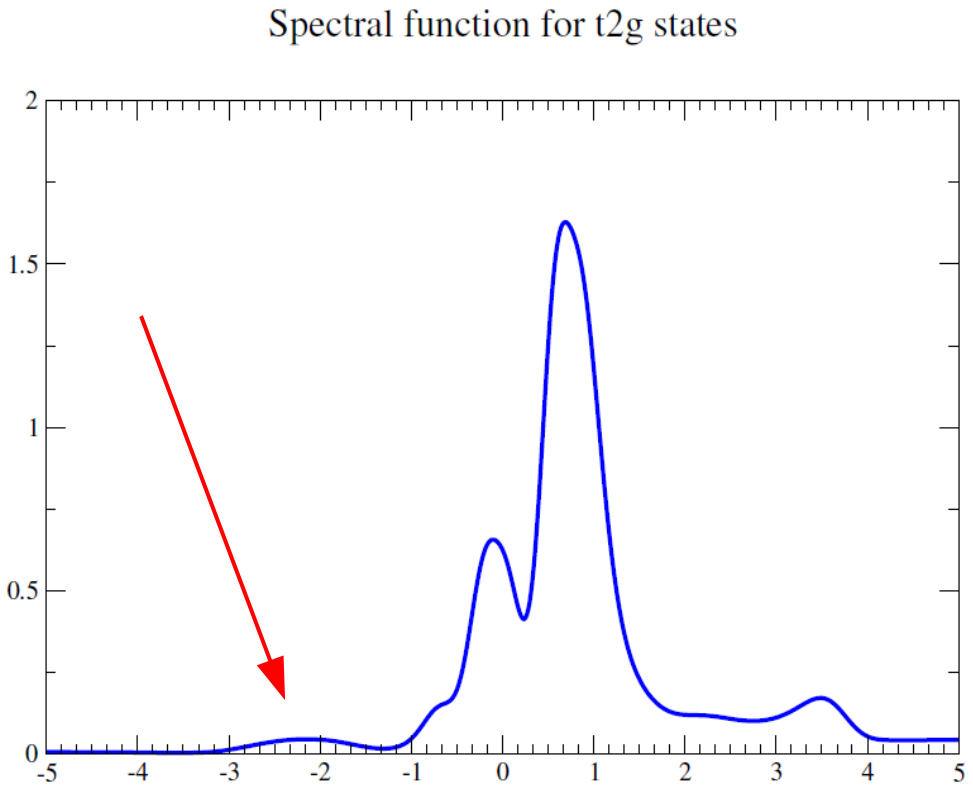
Fujimori et al, PRL 69 (1992)

Correlated metal:
Hubbard band?

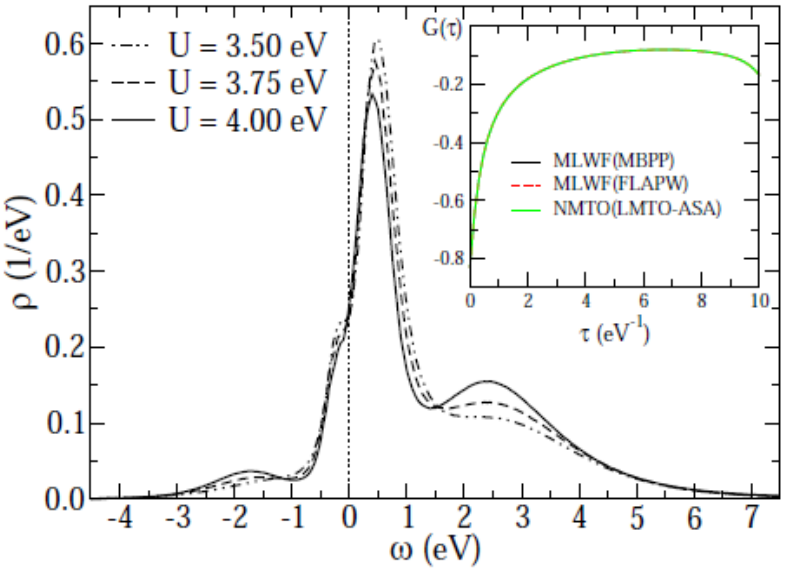


A. Sekiyama et al PRL 93 (2004)

The role of dynamical screening



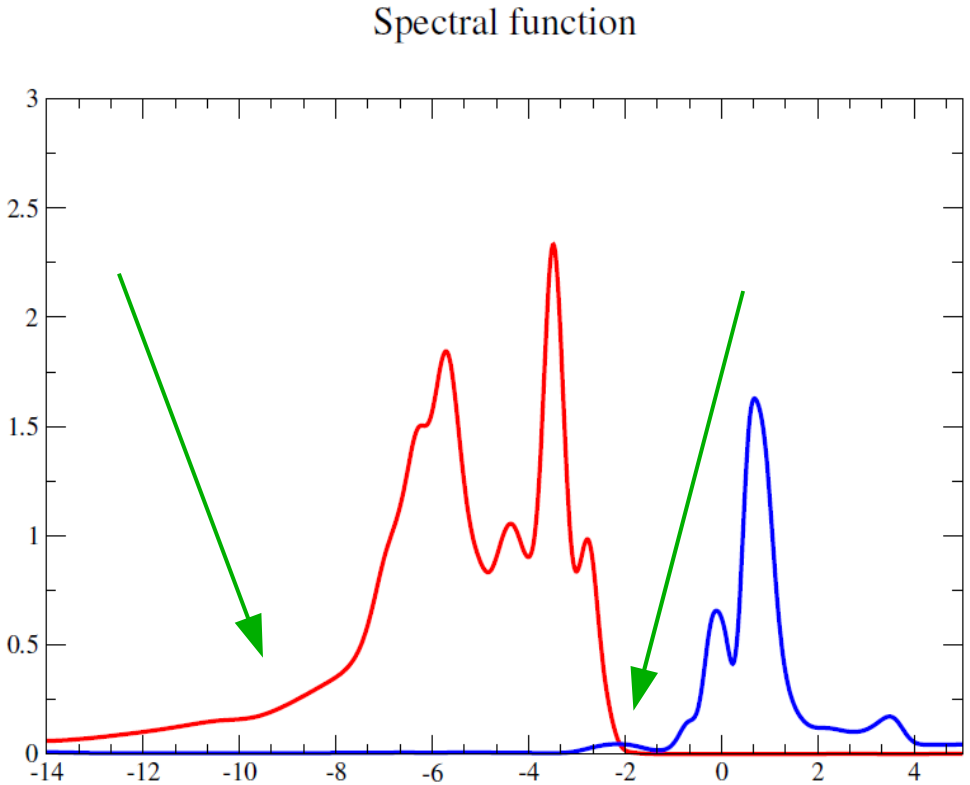
GW approximation



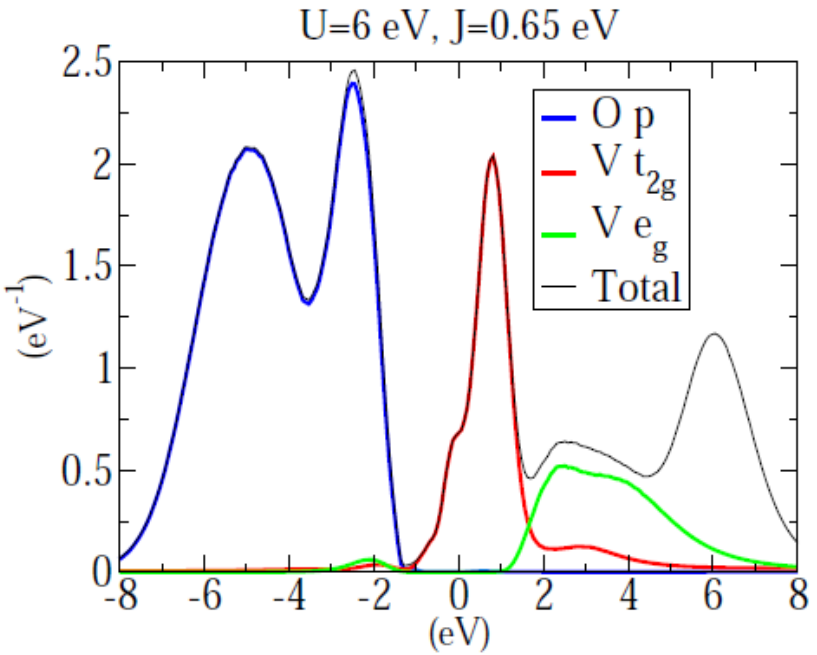
F. Lechermann et al, PRB 74 (2006)

LDA + DMFT

The role of dynamical screening



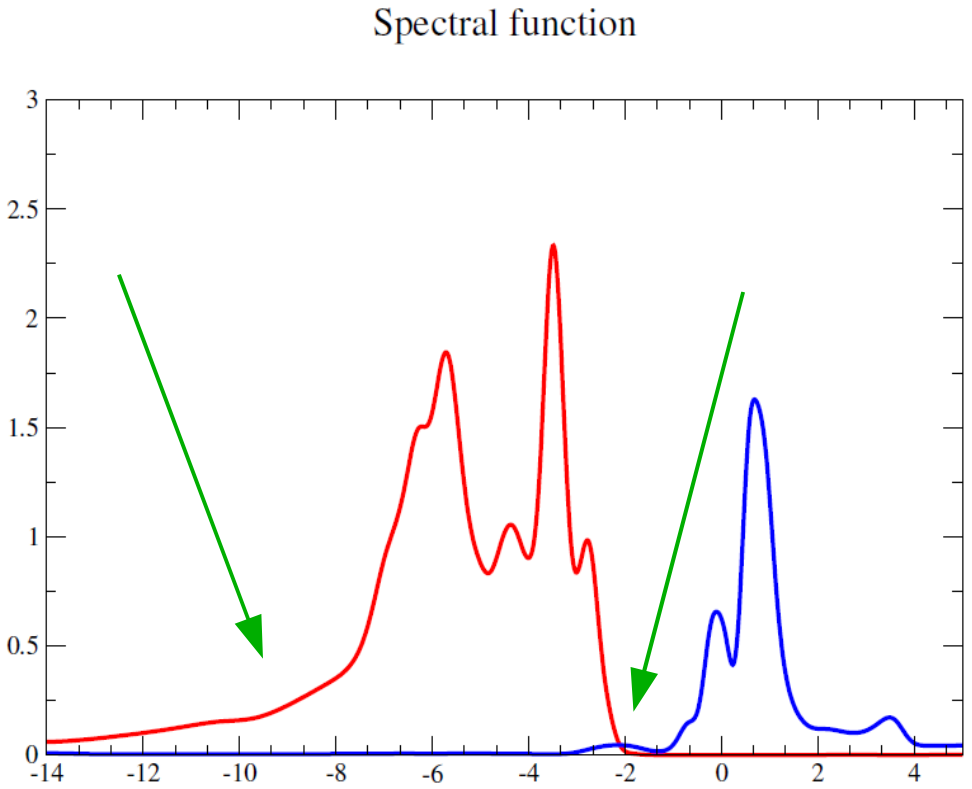
GW approximation



B. Amadon et al. PRB 77 (2008)

LDA + DMFT

The role of dynamical screening



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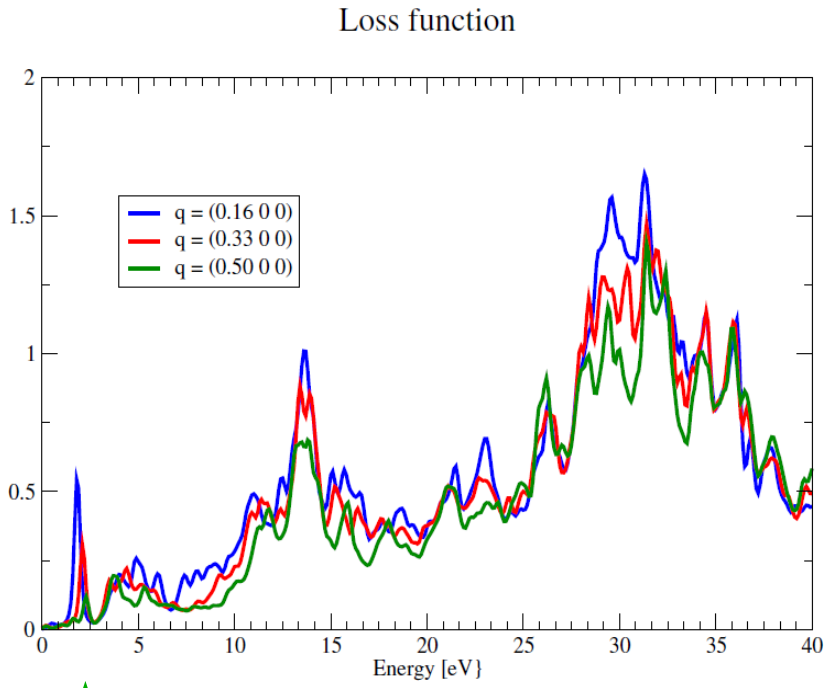
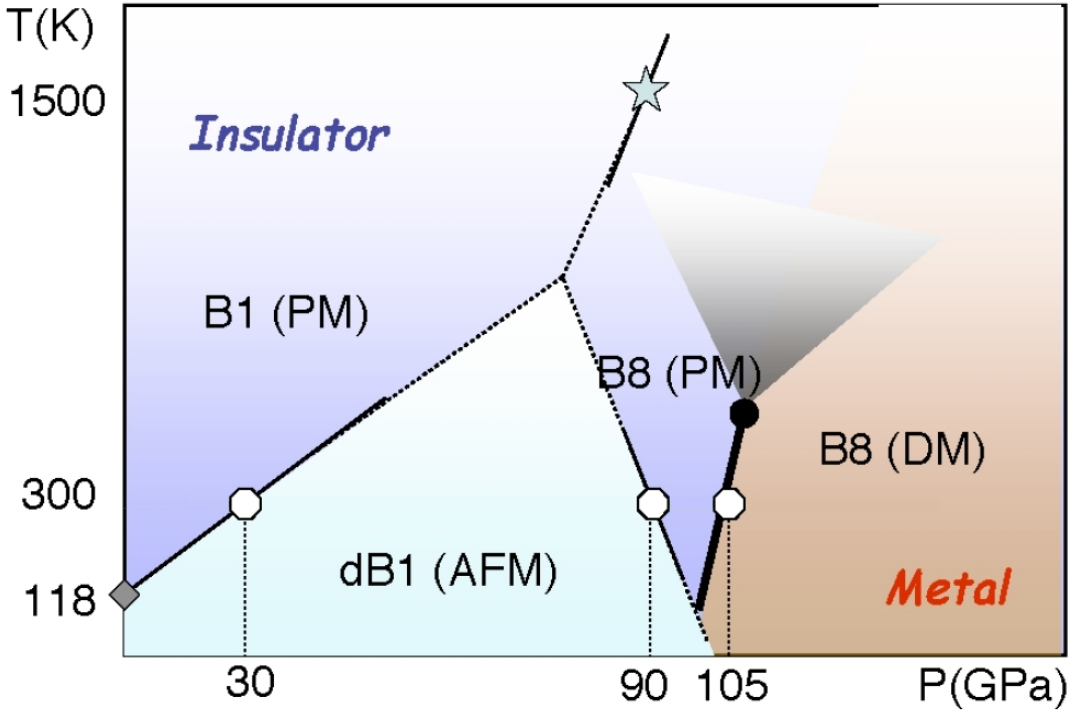


$-\mathrm{Im}\ \varepsilon^{-1}(q,\omega)$

Mott transition in MnO

Apply pressure = reduce U/W
Transition from localized to itinerant state (Mott transition)

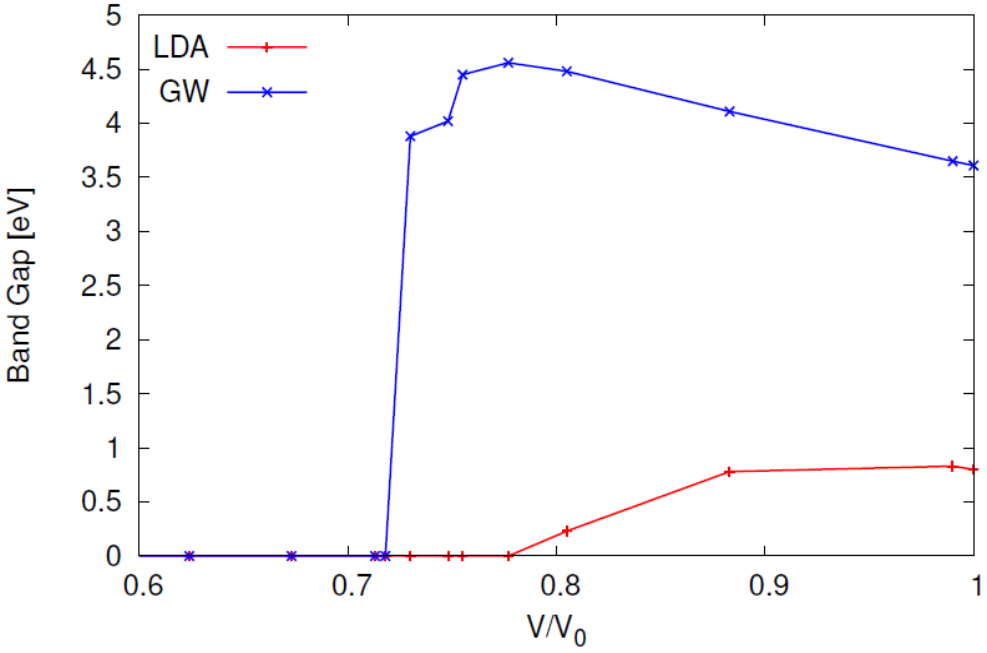
MnO: a prototypical real system
Insulator → Metal
High spin (5/2) → Low spin (1/2)

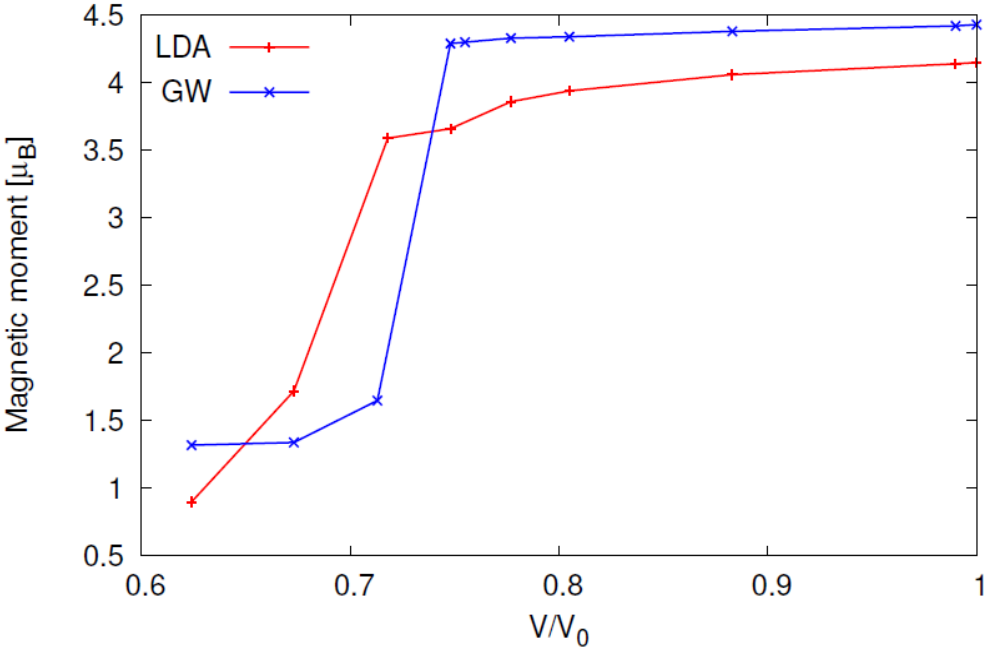


d^5 configuration = multiorbital character
structural distortion

C. S. Yoo et al., PRL 94 (2005)
R.E. Cohen et al., Science 275 (1997)
D. Kasinathan et al., PRB 74 (2006)
J. Kunes et al., Nature Materials 7 (2008)
J.M. Tomczak et al, PRB 81 (2010)

Mott transition in MnO: FCC model

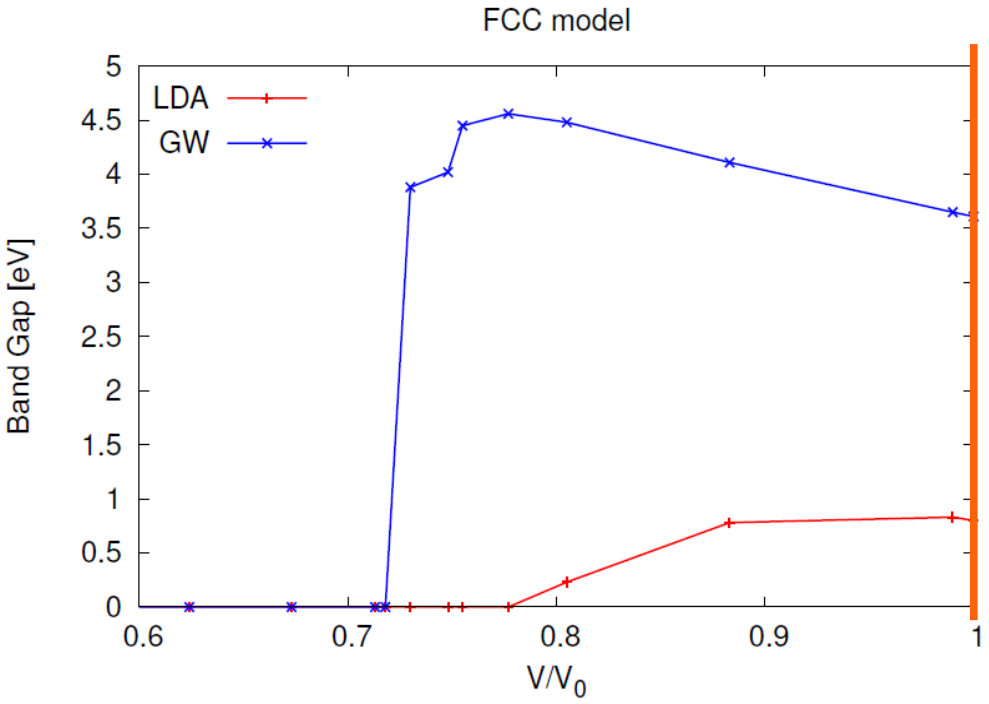


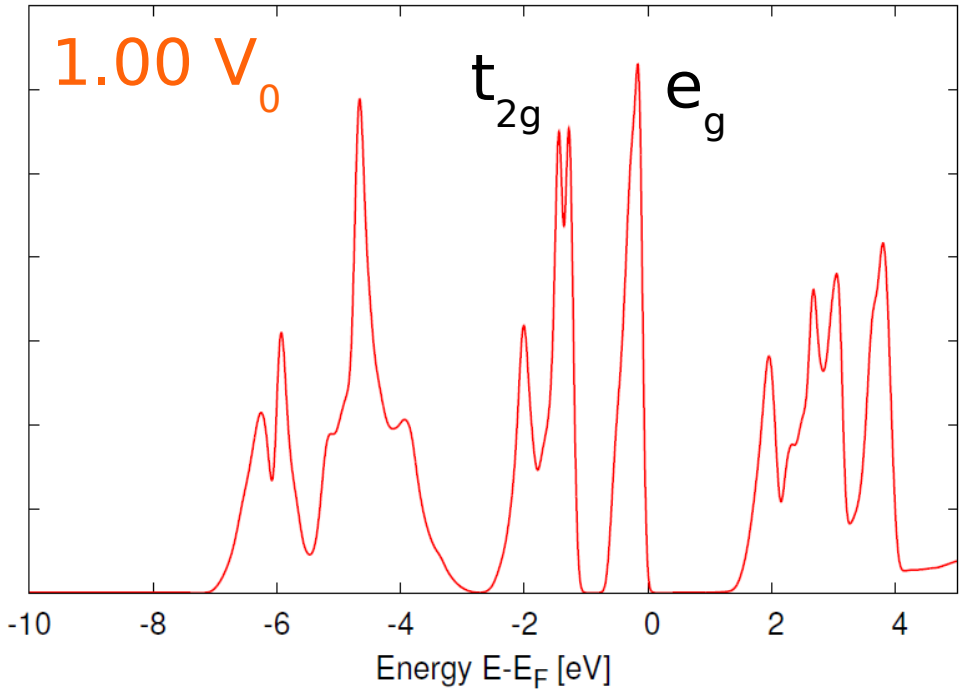


LDA: metal at too large volume
magnetic moment decreases continuously

GW: metallization & magnetic moment collapse
are simultaneous: Mott transition

Mott transition in MnO: LDA





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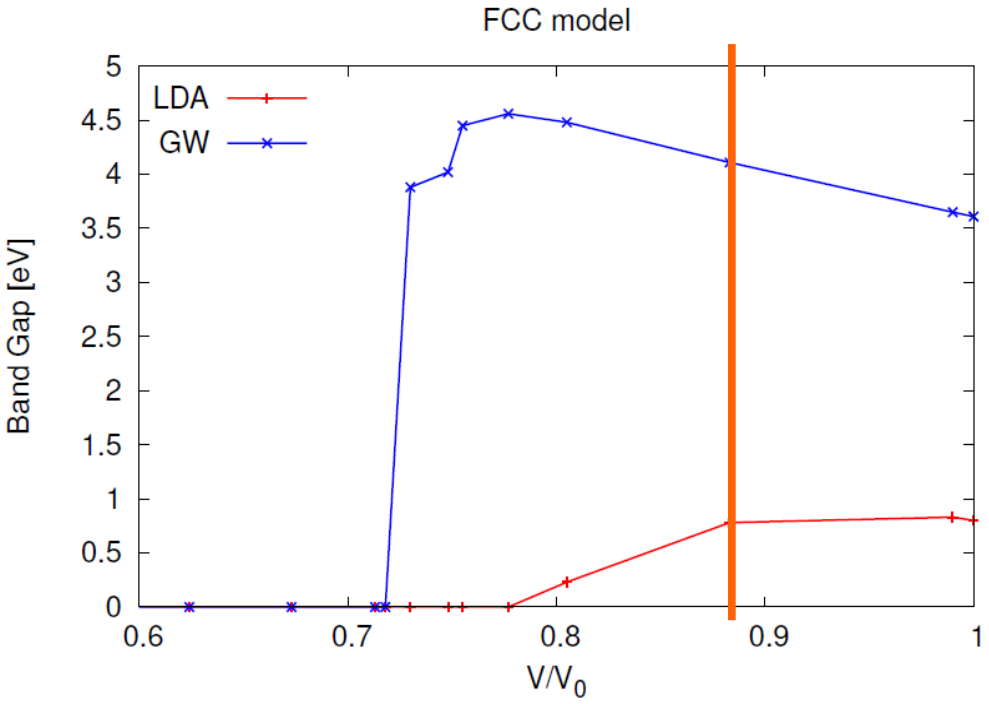
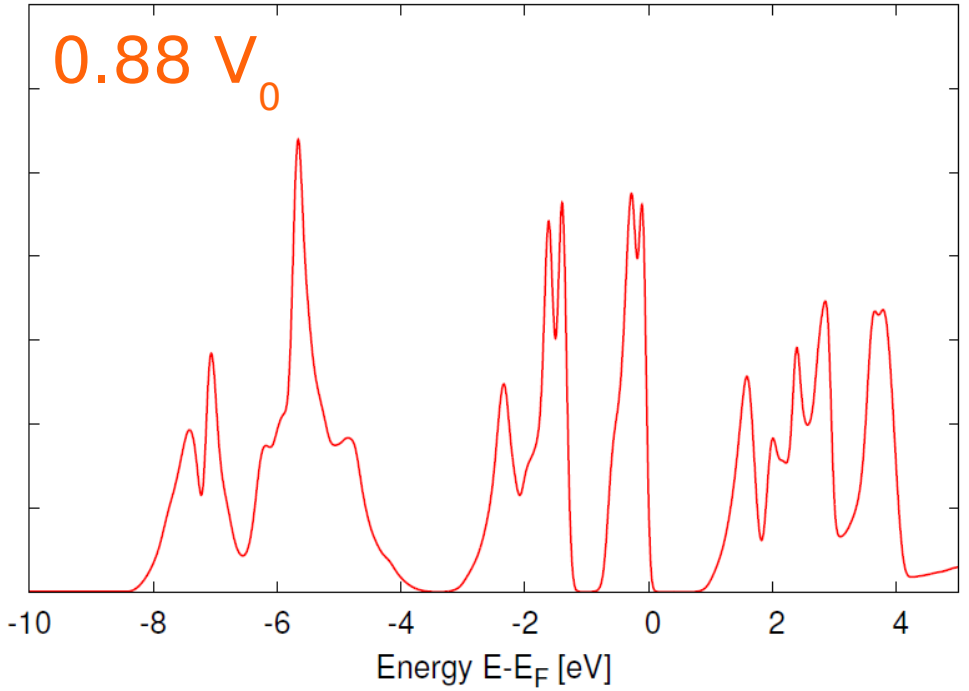
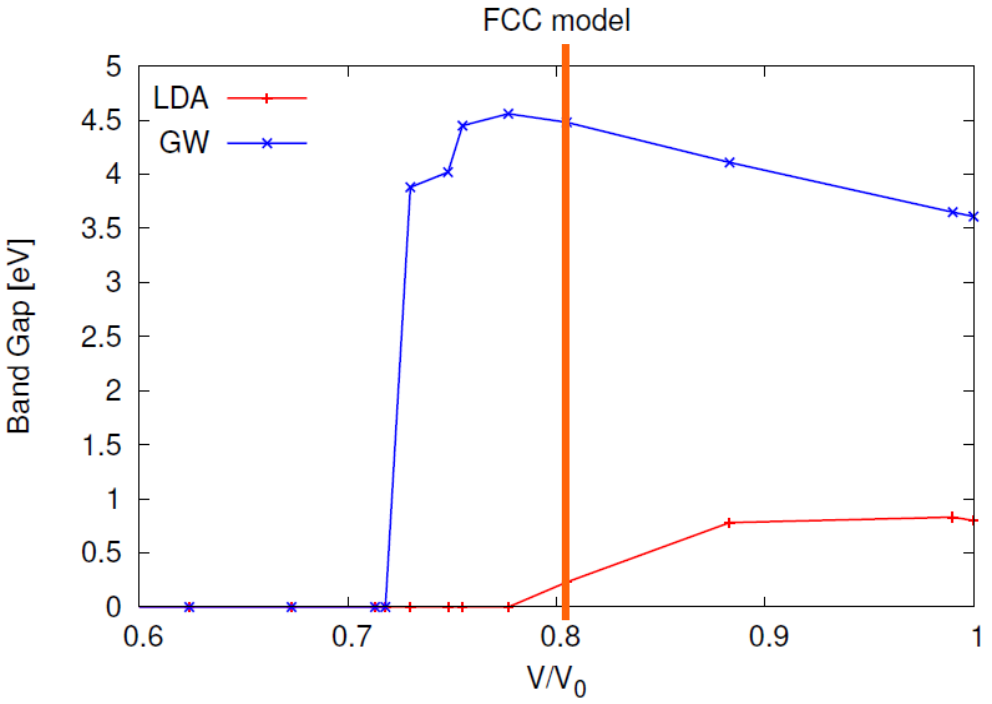
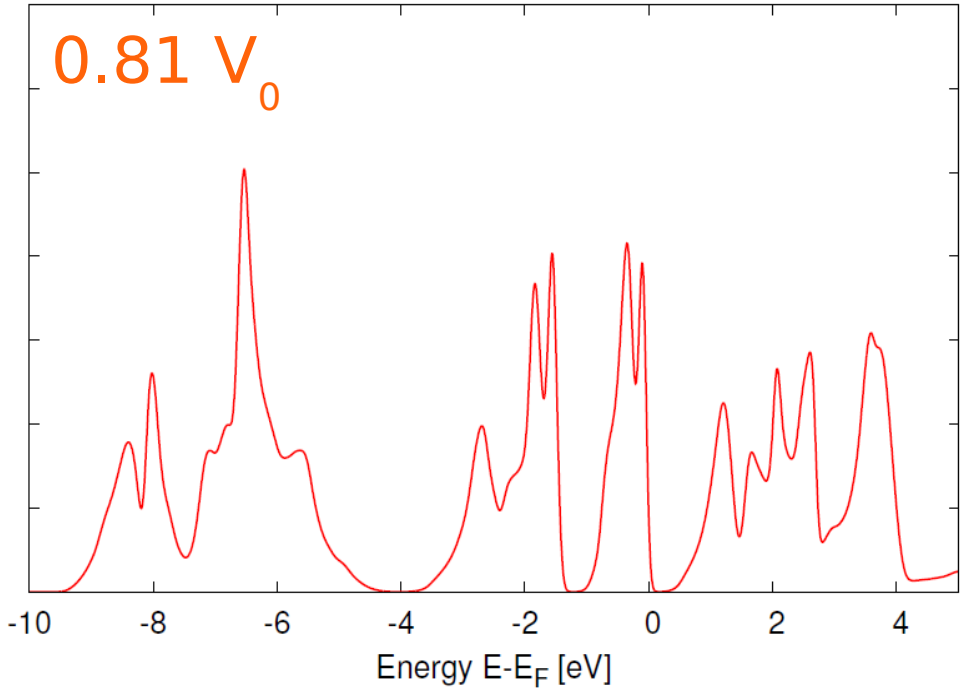




LDA: band broadening leads to metallic phase

Mott transition in MnO: LDA





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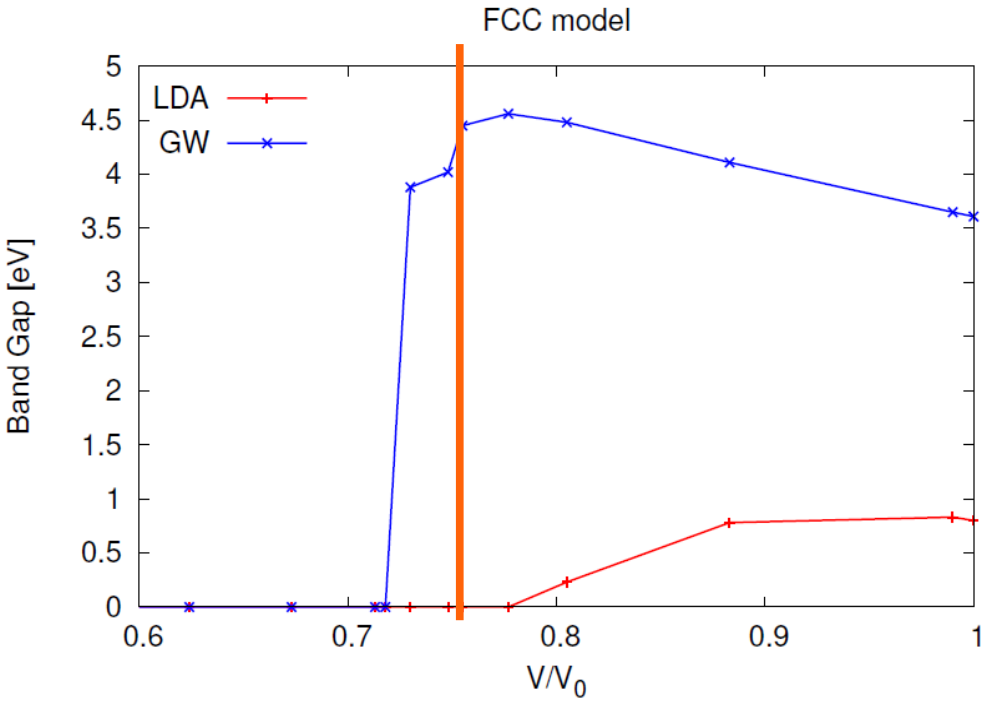
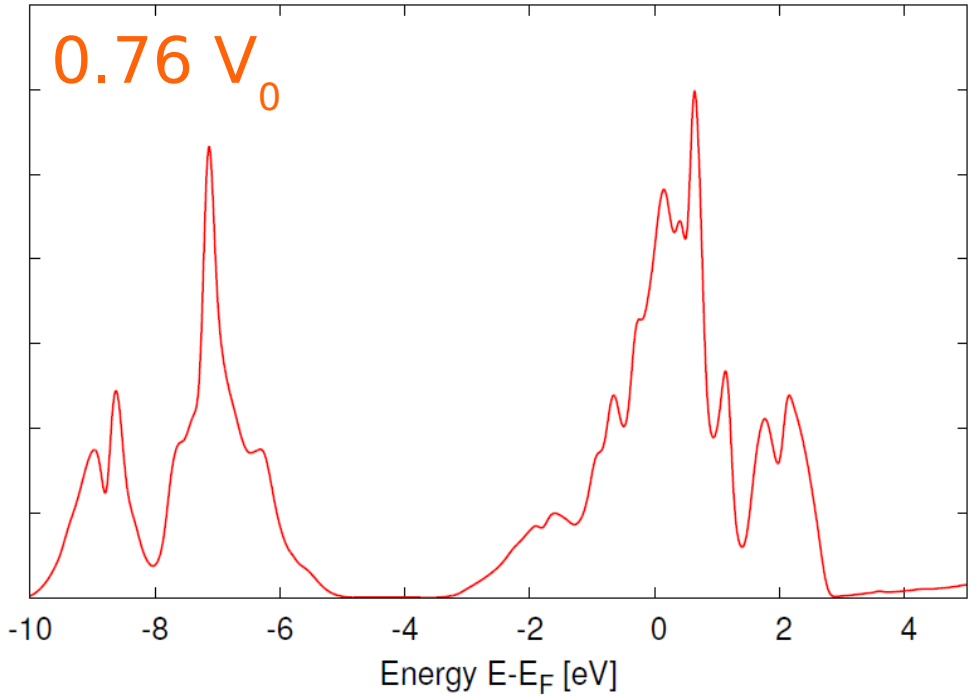
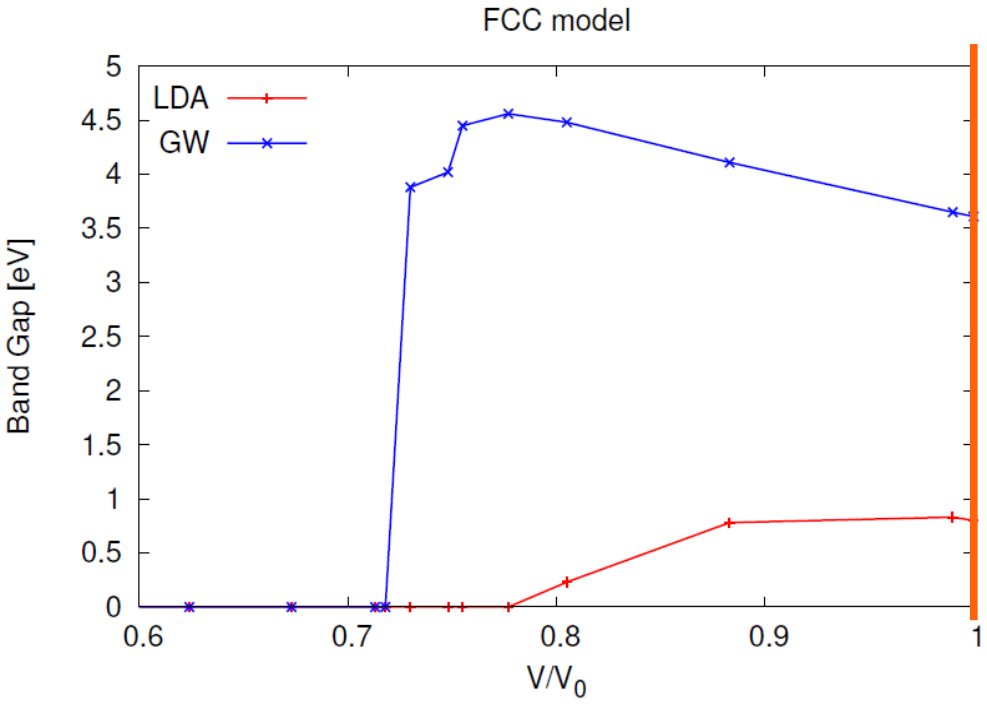
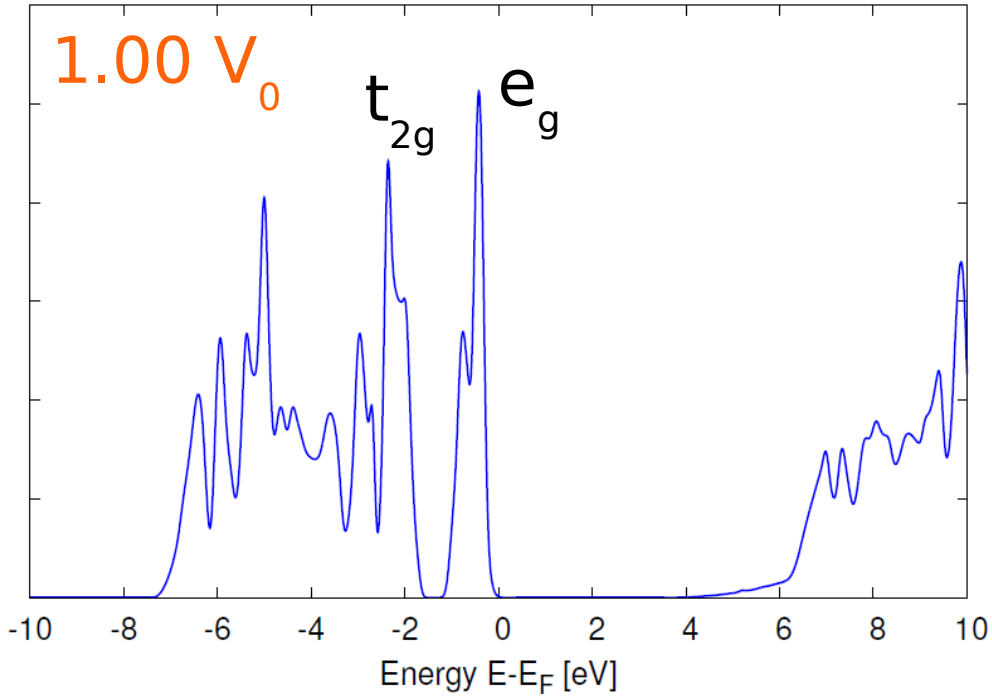




LDA: band broadening leads to metallic phase

Mott transition in MnO: GW

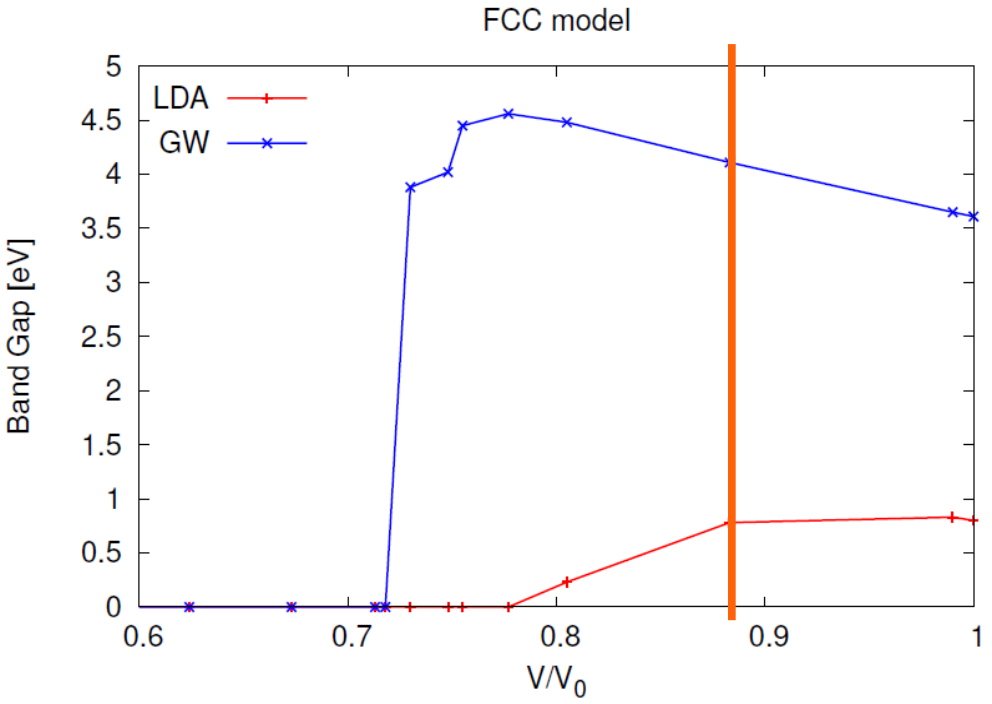


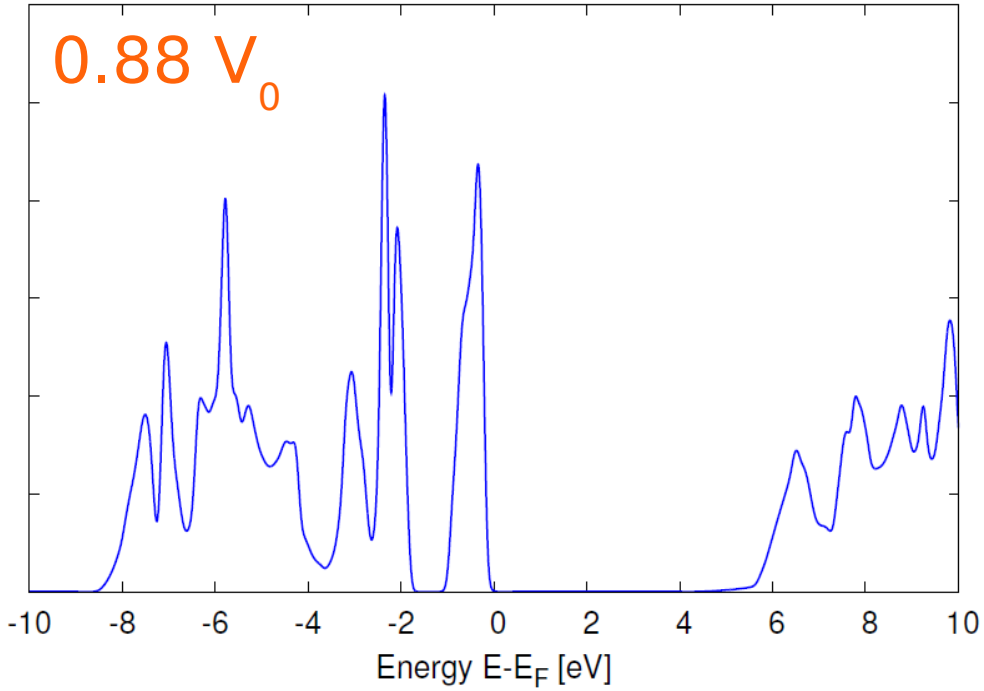


GW gap = 3.64 eV
(exp 3.9±0.4 eV)

See also: S. Faleev *et al*. PRL **93** (2004); C. Roedl *et a*l. PRB **77** (2008).

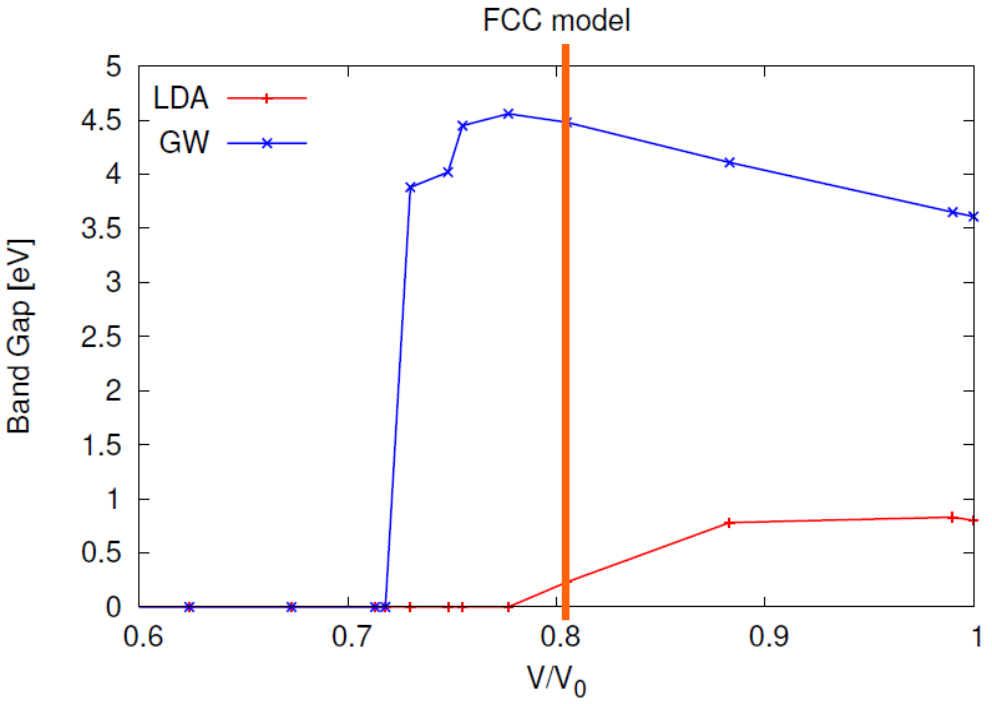
Mott transition in MnO: GW

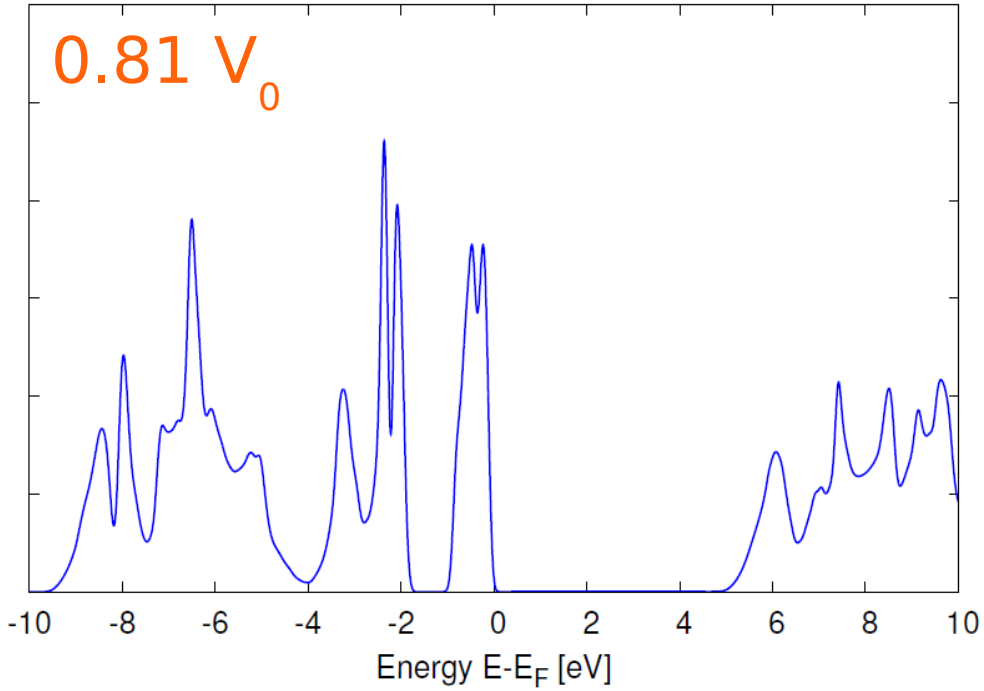




GW: increase of crystal-field splitting drives the transition
(d bandwidths constant)

Mott transition in MnO: GW





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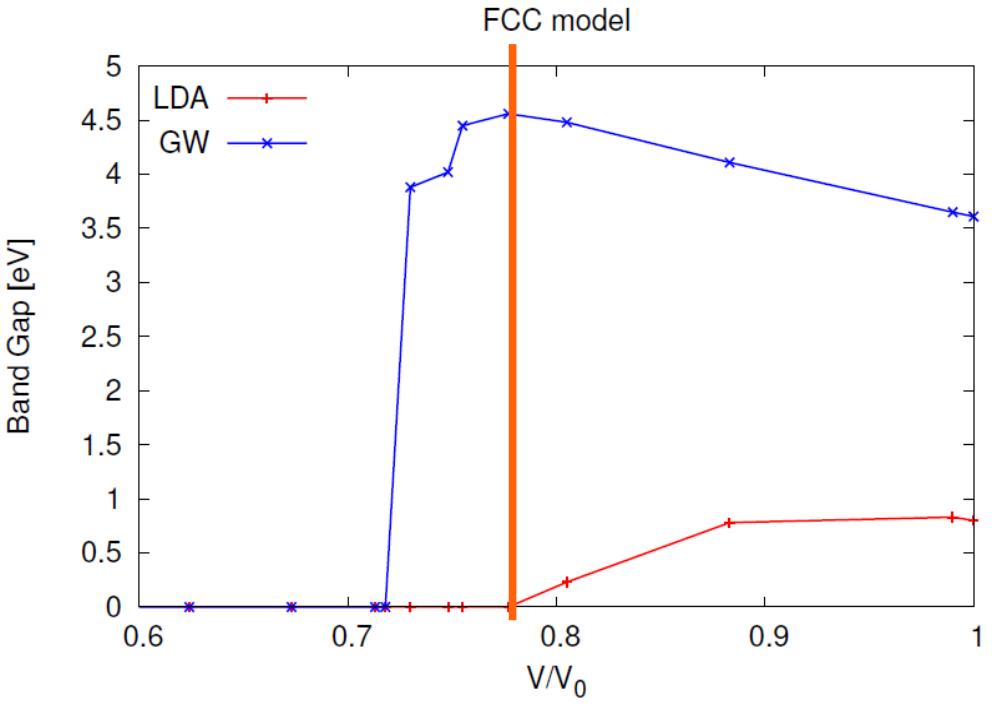

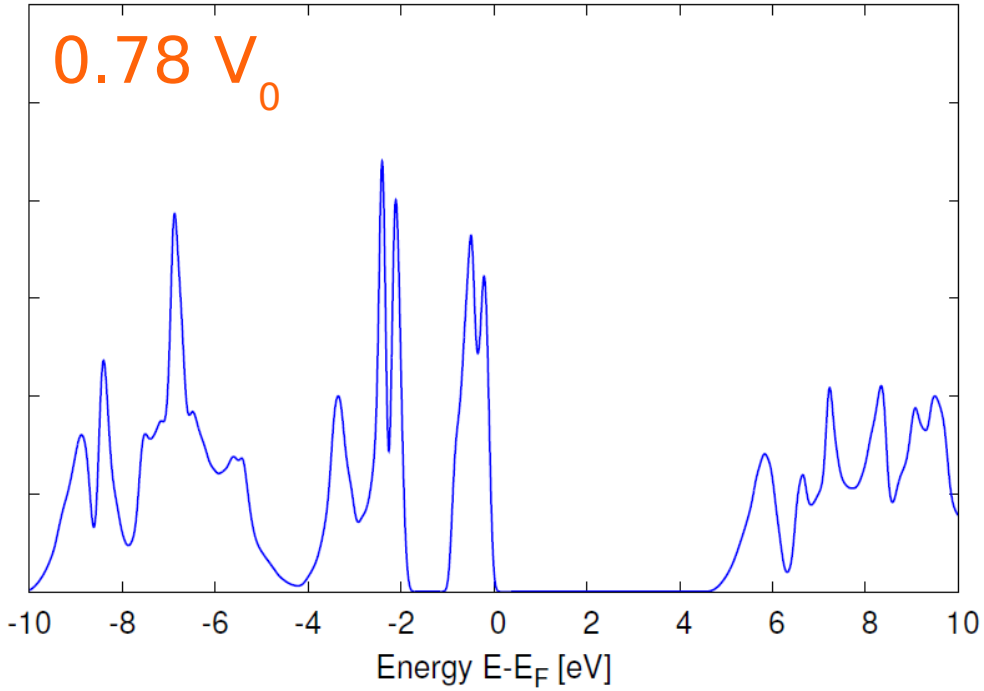

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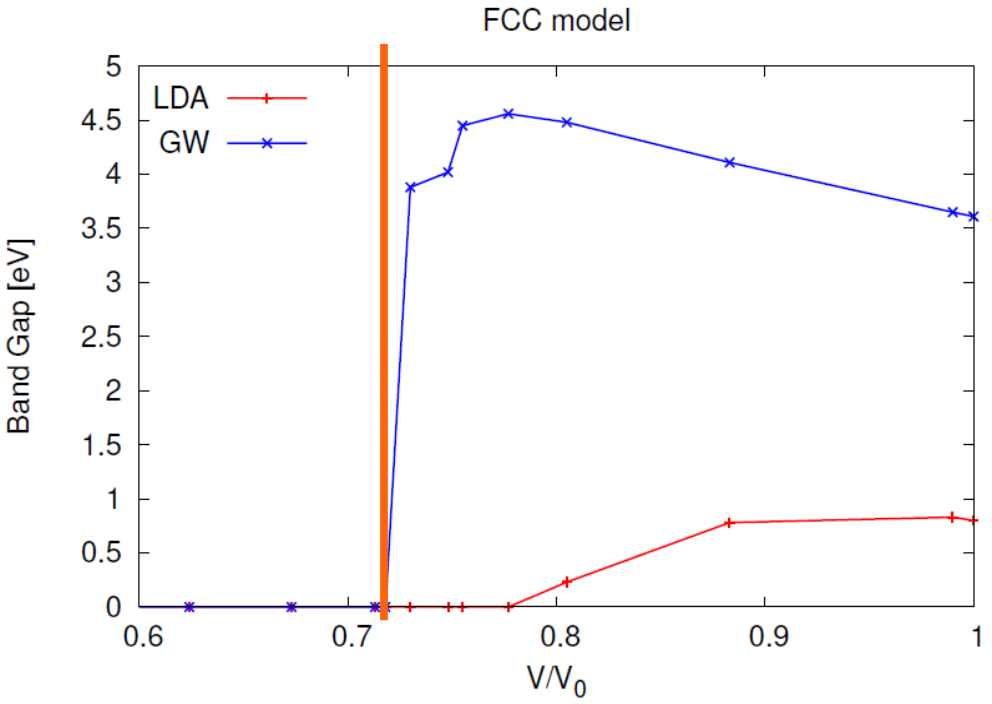
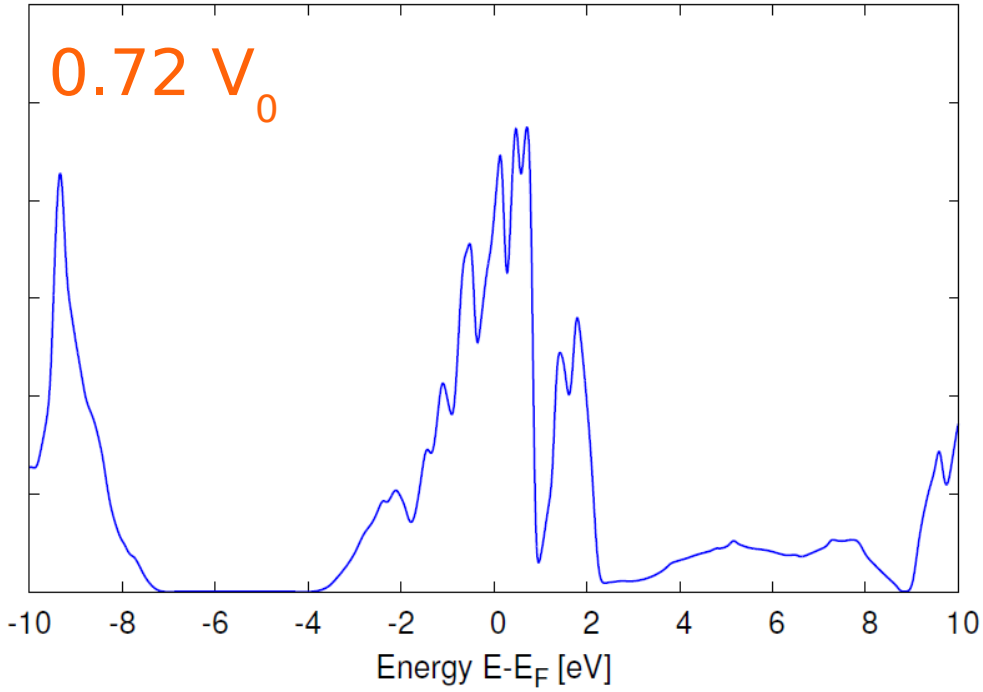
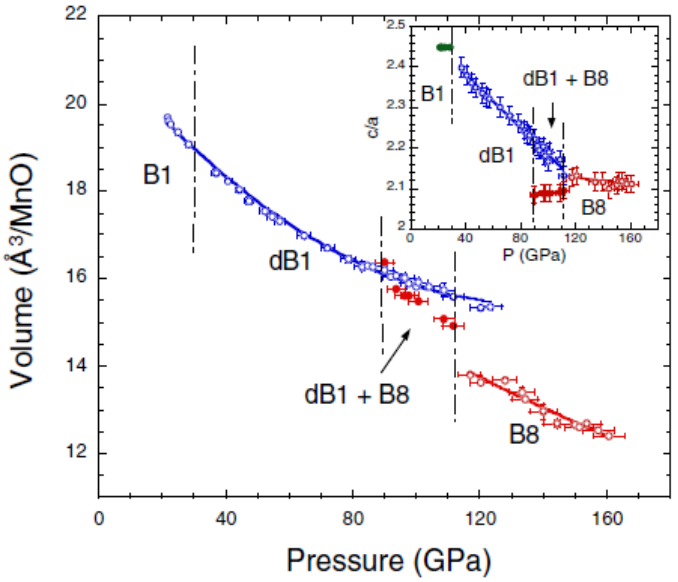
Mott transition in MnO: GW



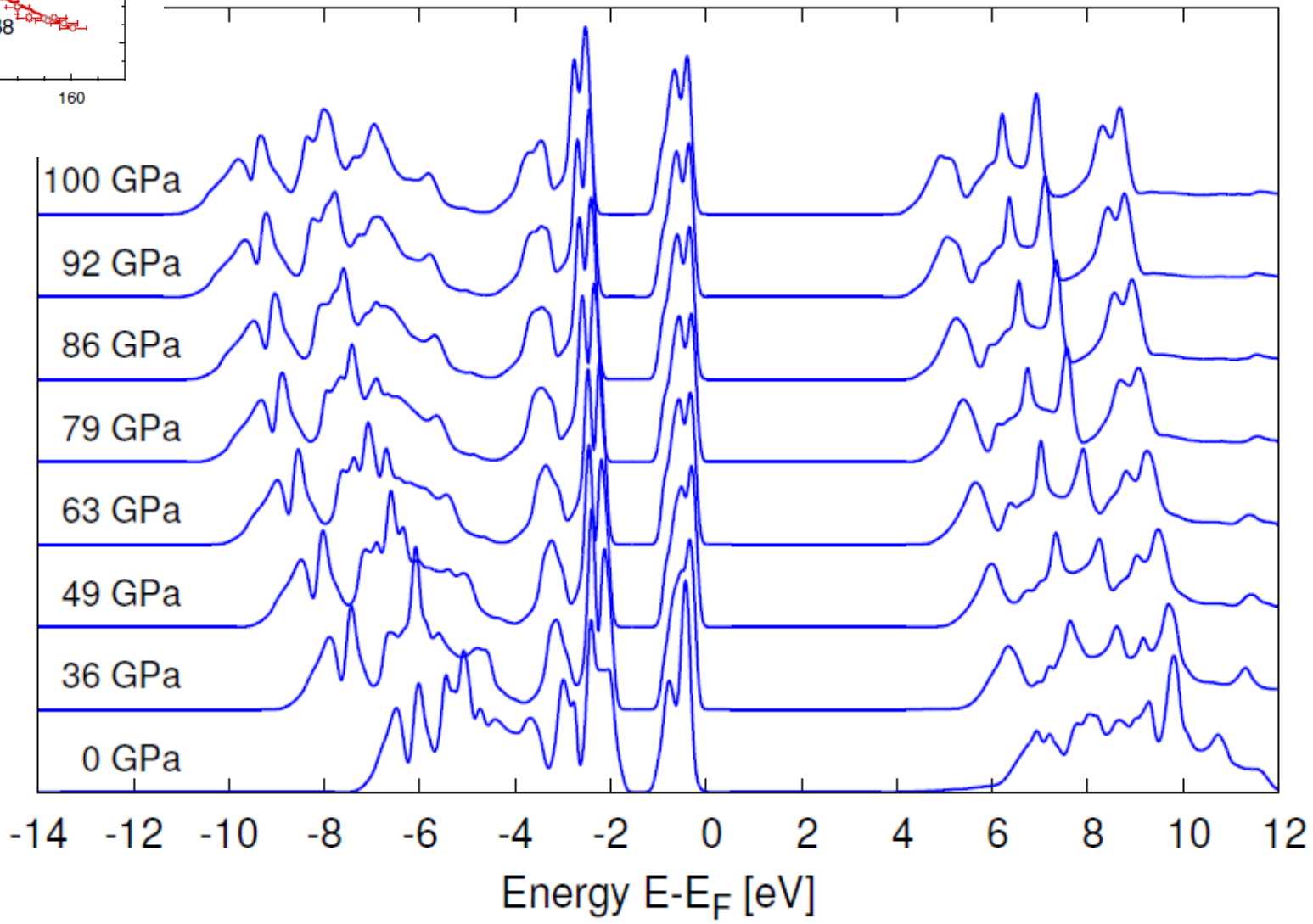


GW: increase of crystal-field splitting drives the transition
(d bandwidths constant)

Structural distortion enhances crystal-field splitting



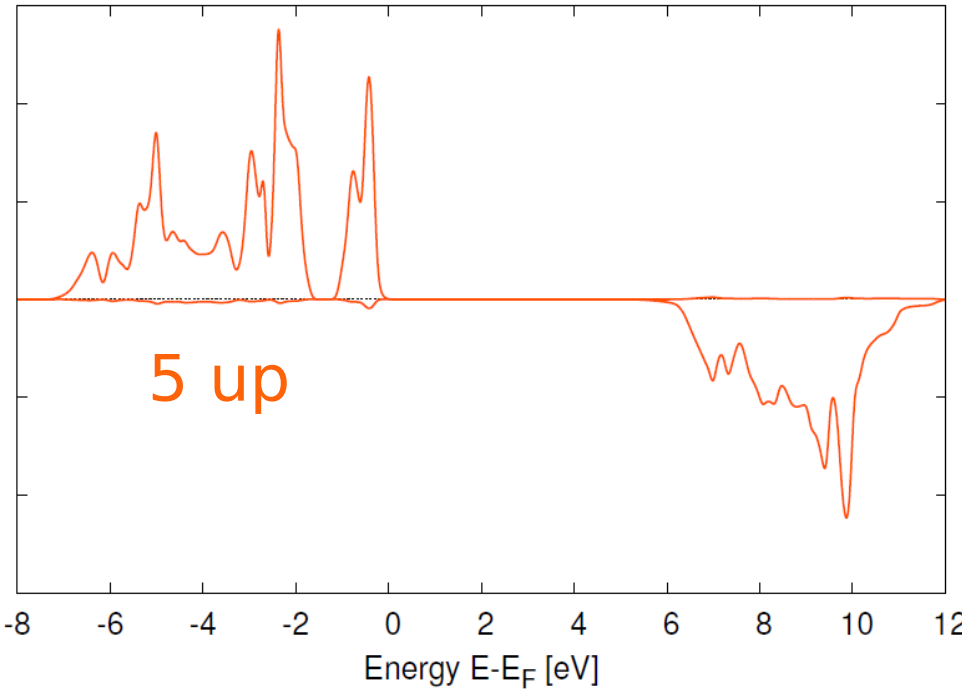
C. S. Yoo et al., PRL 94 (2005)



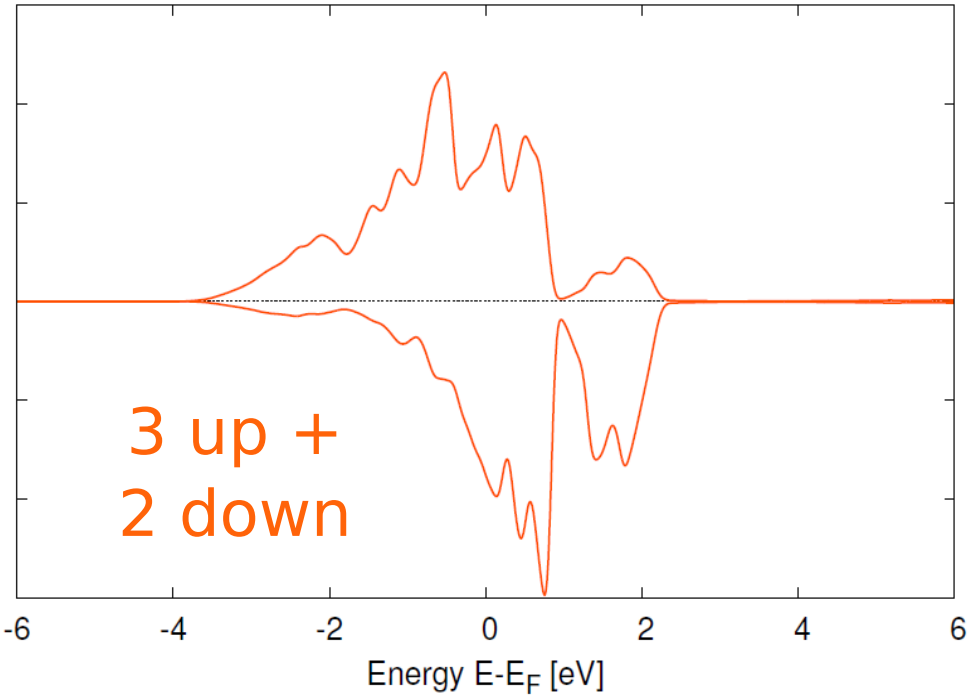
See also: J. M. Tomczak, T. Miyake, and F. Aryasetiawan, PRB 81 (2010)

Mott transition in MnO: d states

High spin

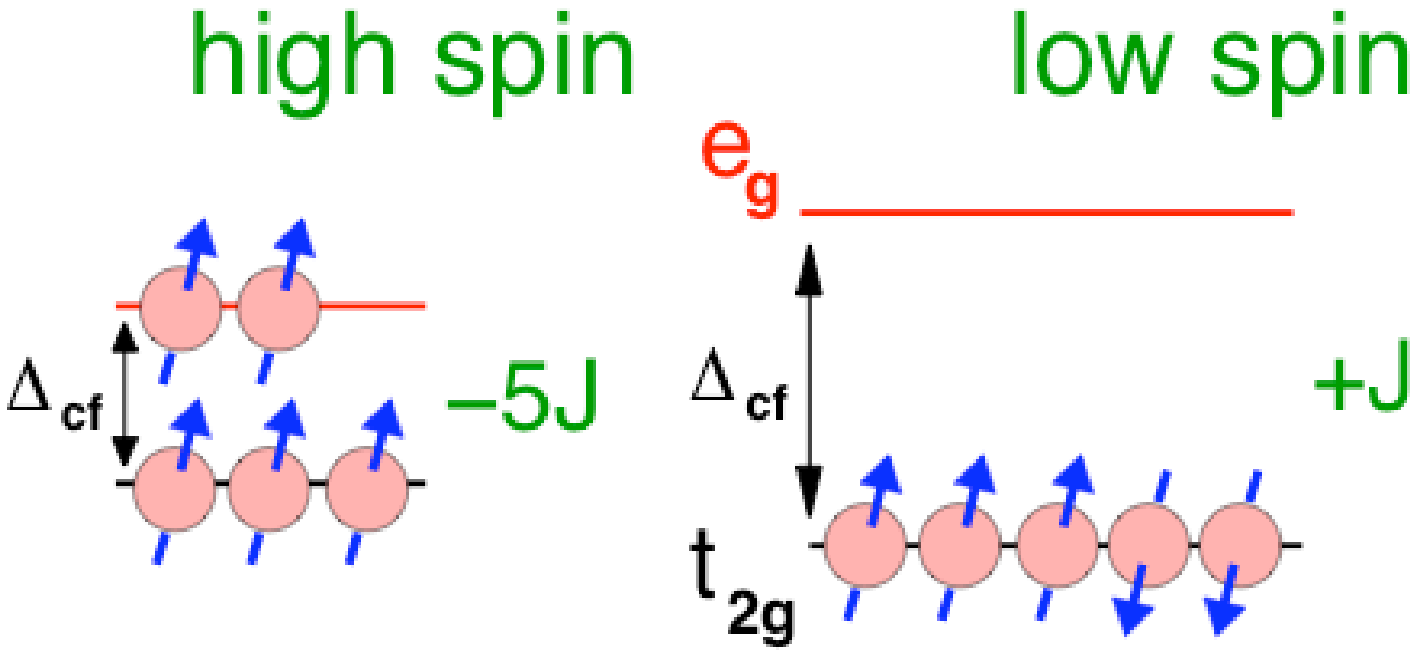


Low spin



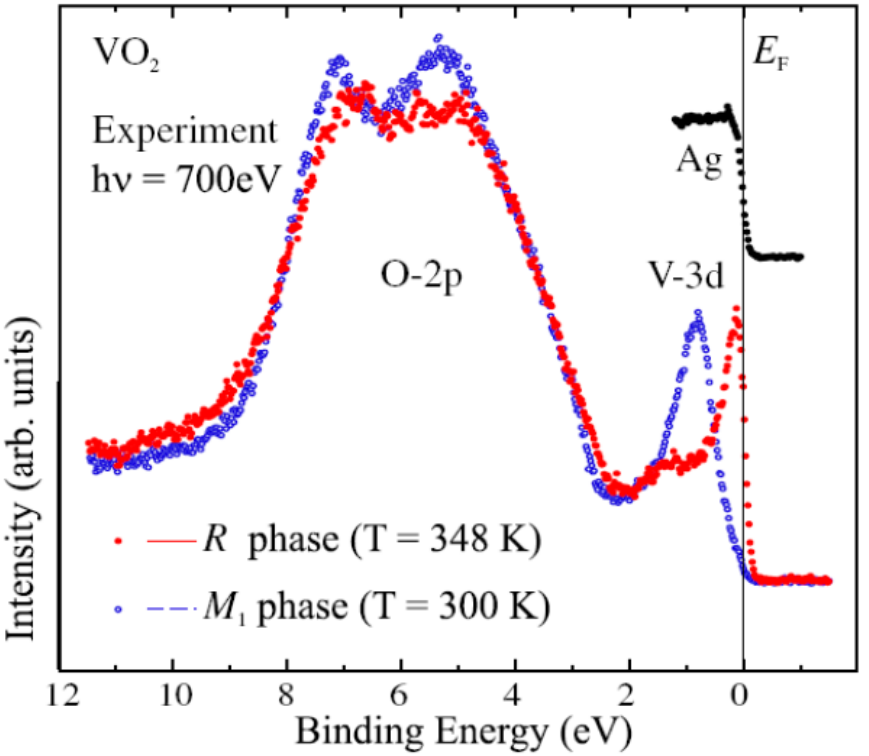
magnetic moment collapse ↔ change of occupations

Mott transition in MnO: d states



J. Kunes et al., Nature Materials 7 (2008).

VO_2: Photoemission spectra



From: Koethe *et al*. PRL 97 (2006)

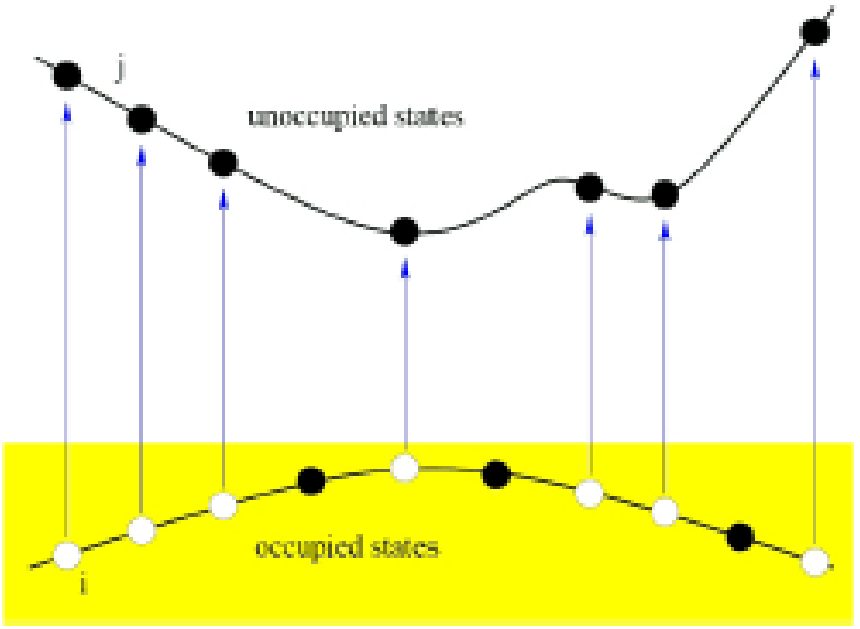
Insulator: metallic in LDA
OK in COHSEX+ GW

See: PRL 99 (2007)

Optical absorption: independent particles

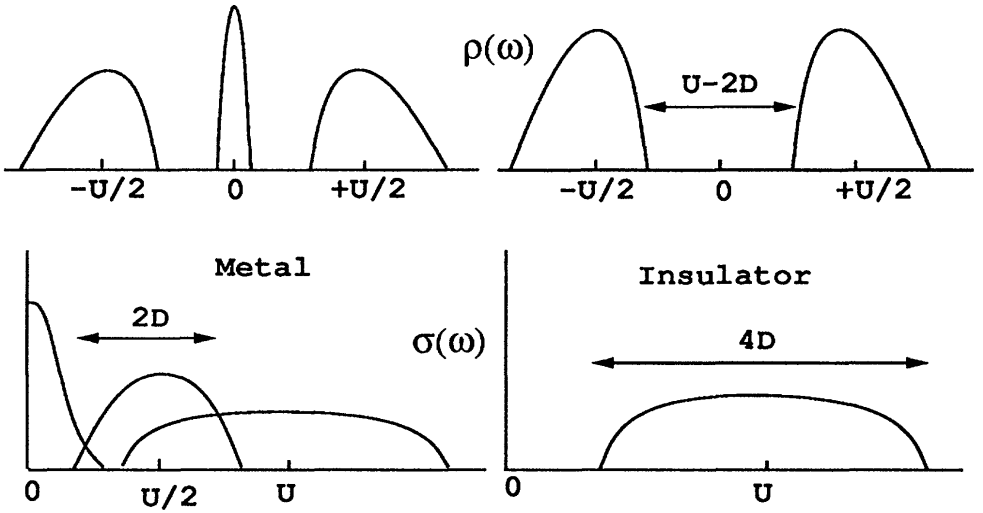
Independent transitions:

$$\epsilon_2(\omega) = \frac{8\pi^2}{\Omega\omega^2} \sum_{ij} |\langle\varphi_j|\mathbf{e}\cdot\mathbf{v}|\varphi_i\rangle|^2 \delta(\epsilon_j - \epsilon_i - \omega)$$



Optical absorption: DMFT approach

Hubbard model

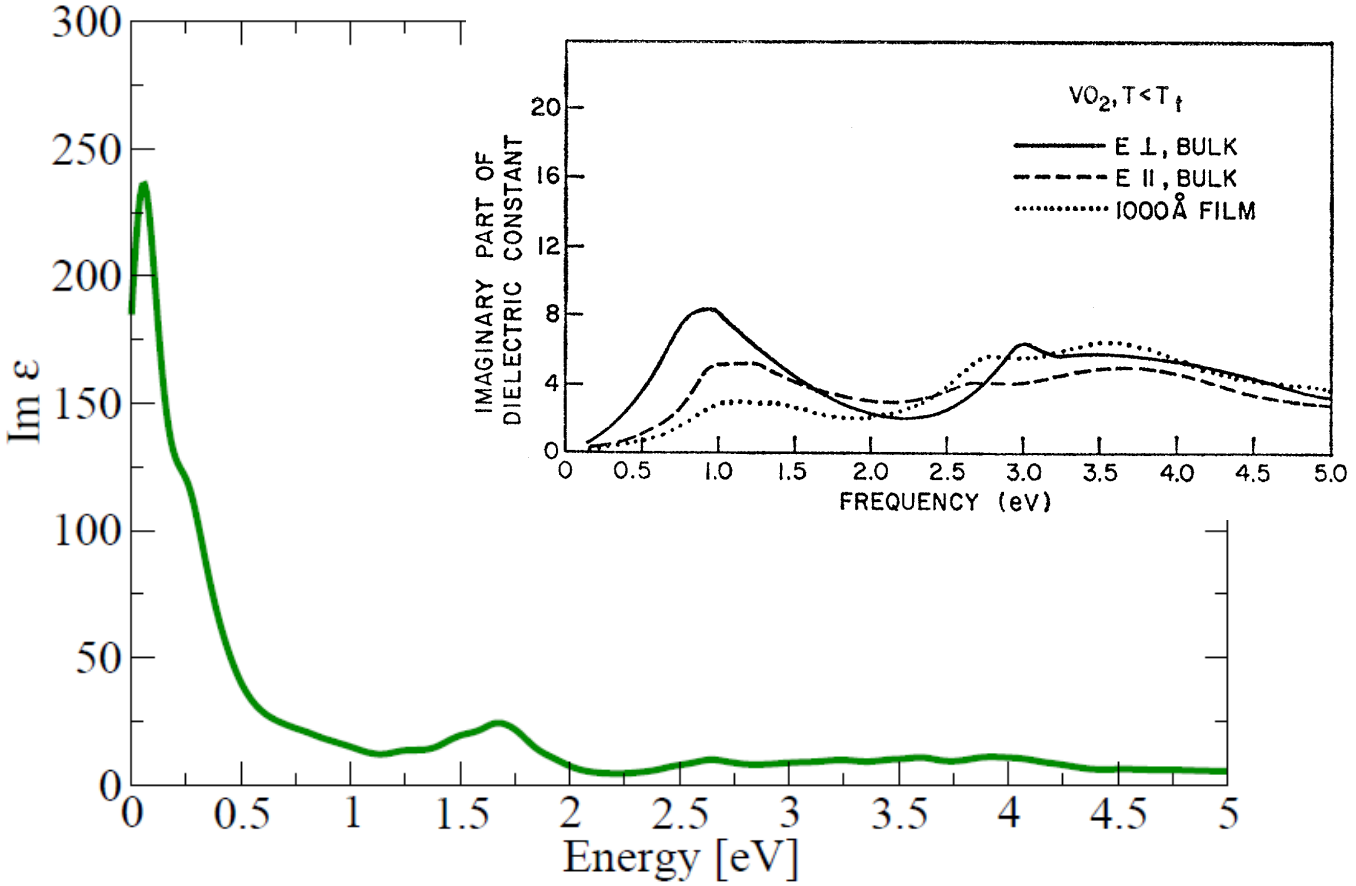


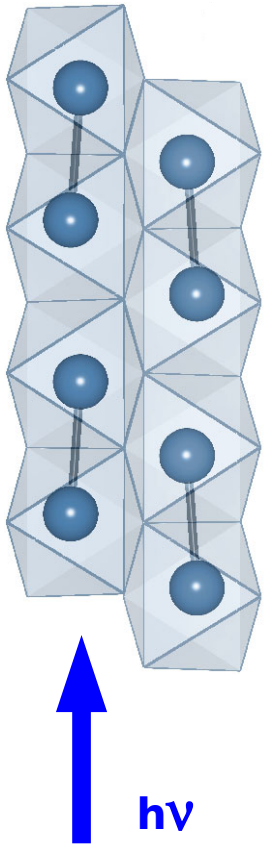
From Rozenberg *et al*. PRL 75 (1995):

$$\sigma(\omega) = \frac{1}{\omega}\frac{2e^2t^2a^2}{\nu\hbar^2}\int_{-\infty}^{\infty} d\epsilon\,\rho^0(\epsilon)\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}A_\epsilon(\omega')A_\epsilon(\omega'+\omega)[n_f(\omega')-n_f(\omega'+\omega)]$$

Optical absorption: independent particles

LDA energies, KS wavefunctions

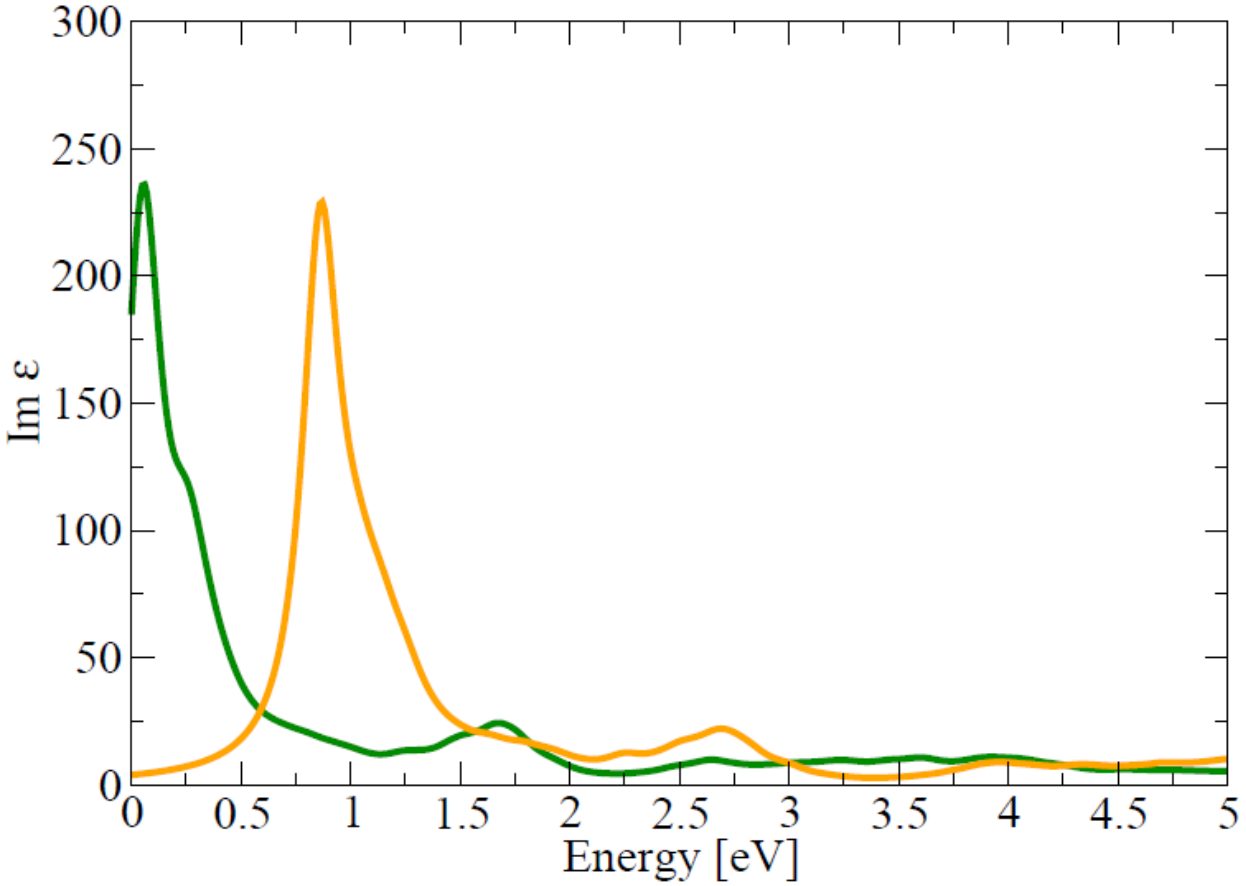




Exp. from Verleur, *et al.*, PR 172 (1968)

Optical absorption: independent particles

GW energies, KS wavefunctions

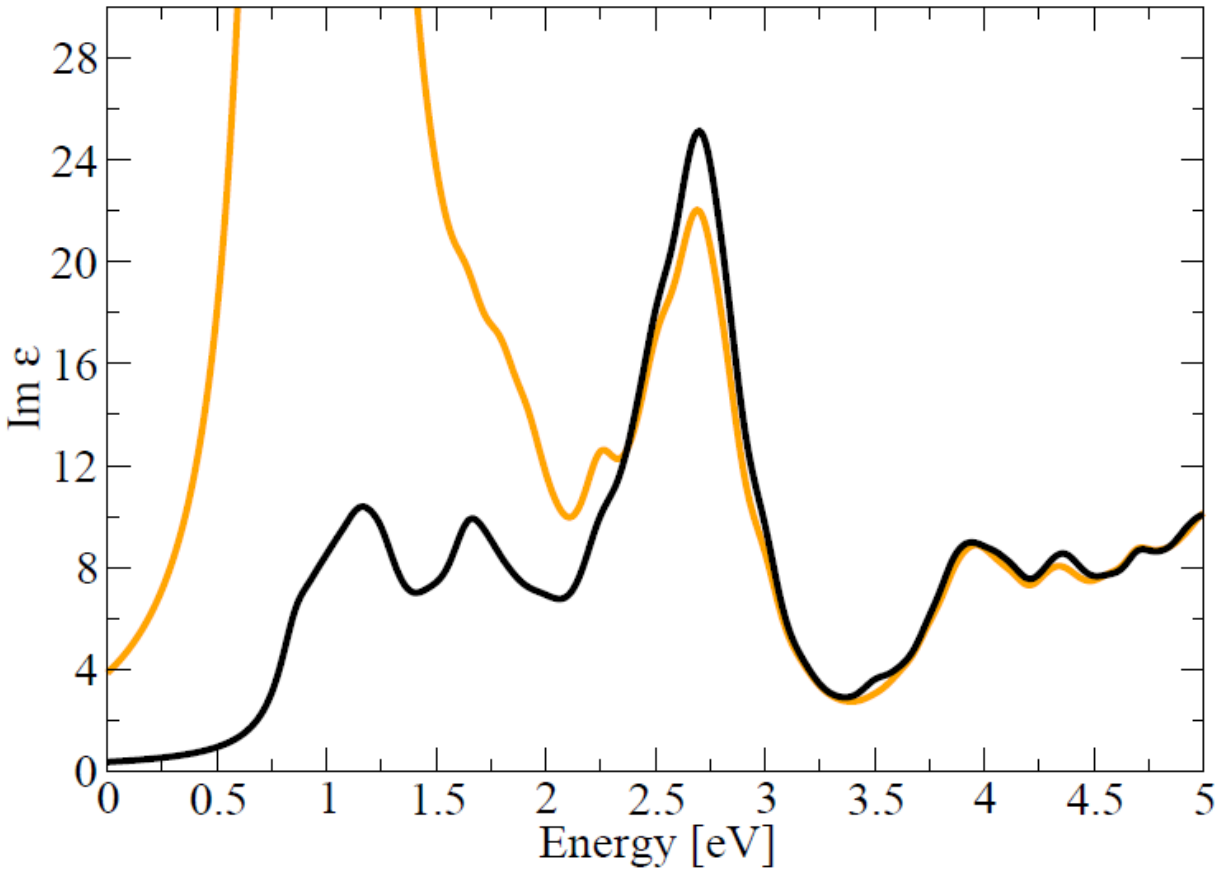


$$\lim_{\mathbf{q}\to 0}\langle\varphi^{KS}_{n,\mathbf{k}-\mathbf{q}}|e^{-i\mathbf{qr}}|\varphi^{KS}_{n',\mathbf{k}}\rangle =$$

$$= \frac{\langle\varphi^{KS}_{n,\mathbf{k}}|[H^{KS}, i\mathbf{qr}]|\varphi^{KS}_{n',\mathbf{k}}\rangle}{\epsilon^{KS}_{n',\mathbf{k}} - \epsilon^{KS}_{n,\mathbf{k}}}$$

Optical absorption: independent particles

GW energies, QP wavefunctions

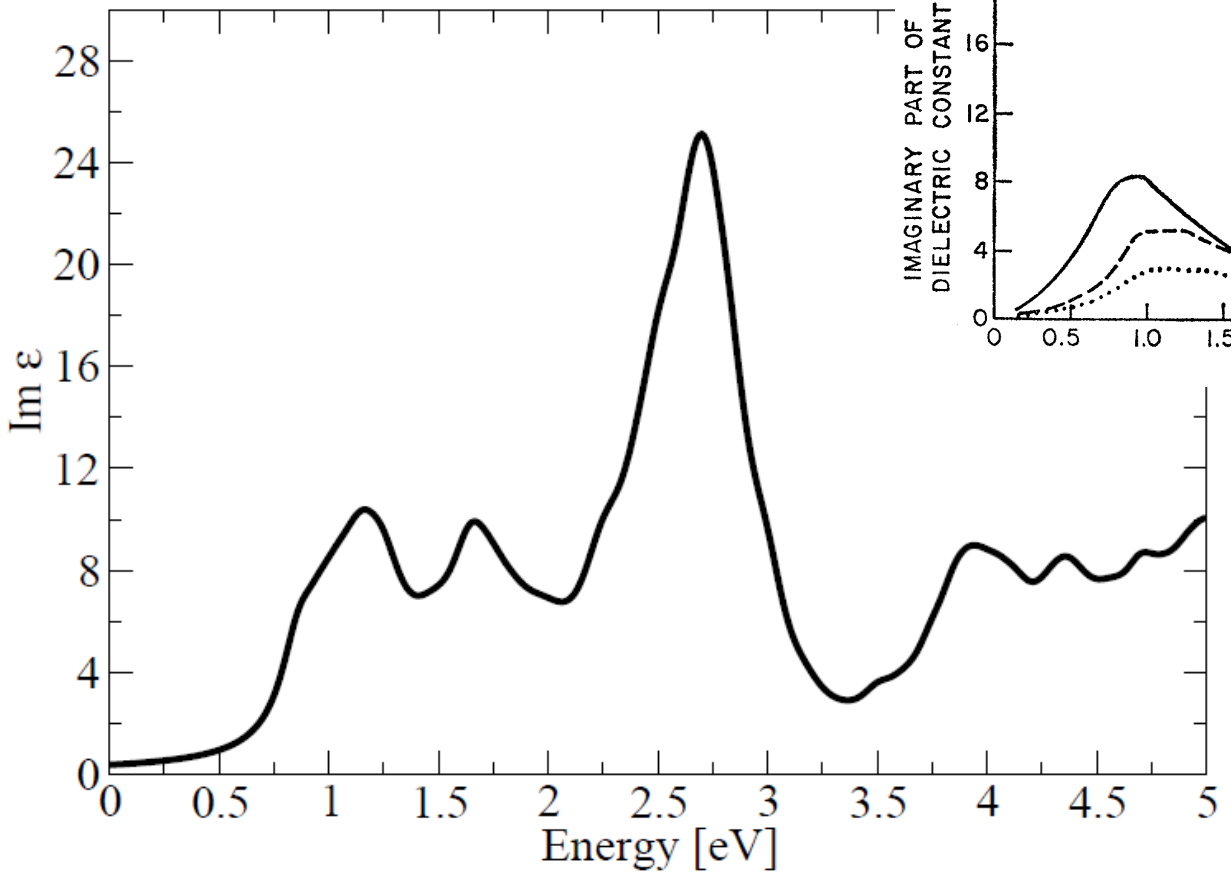


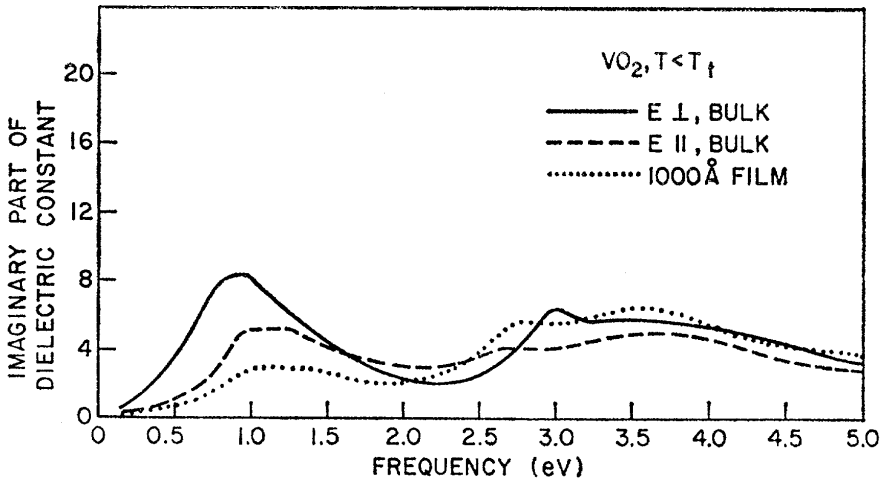
$$\lim_{\mathbf{q}\to 0} \langle \varphi^{QP}_{n,\mathbf{k}-\mathbf{q}} | e^{-i\mathbf{qr}} | \varphi^{QP}_{n',\mathbf{k}} \rangle =$$

$$= \frac{\langle \varphi^{QP}_{n,\mathbf{k}} | [H^{QP}, i\mathbf{qr}] | \varphi^{QP}_{n',\mathbf{k}} \rangle}{\epsilon^{QP}_{n',\mathbf{k}} - \epsilon^{QP}_{n,\mathbf{k}}}$$

Optical absorption: independent particles

GW energies, QP wavefu



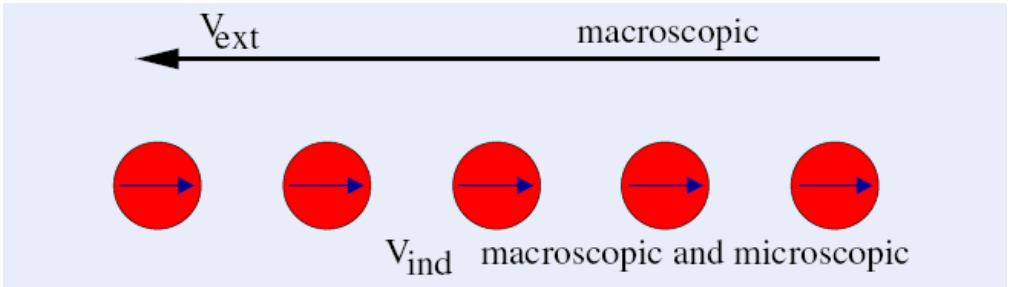


Optical absorption: Bethe Salpeter (BSE)

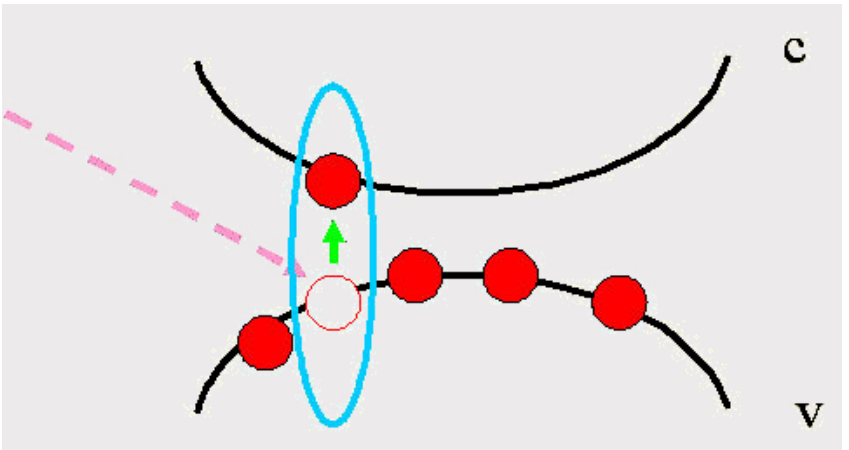
Beyond independent particles

$$L = L_0 + L_0(v - W)L$$

Crystal local fields

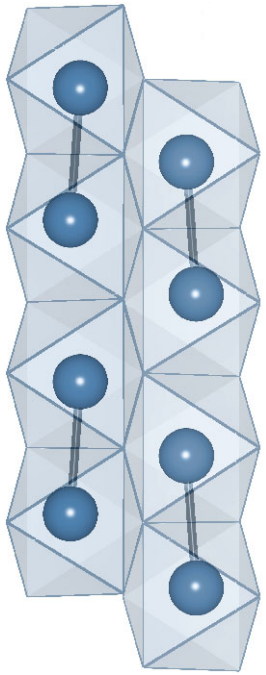


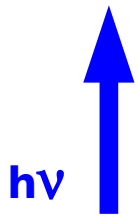
Excitonic effects

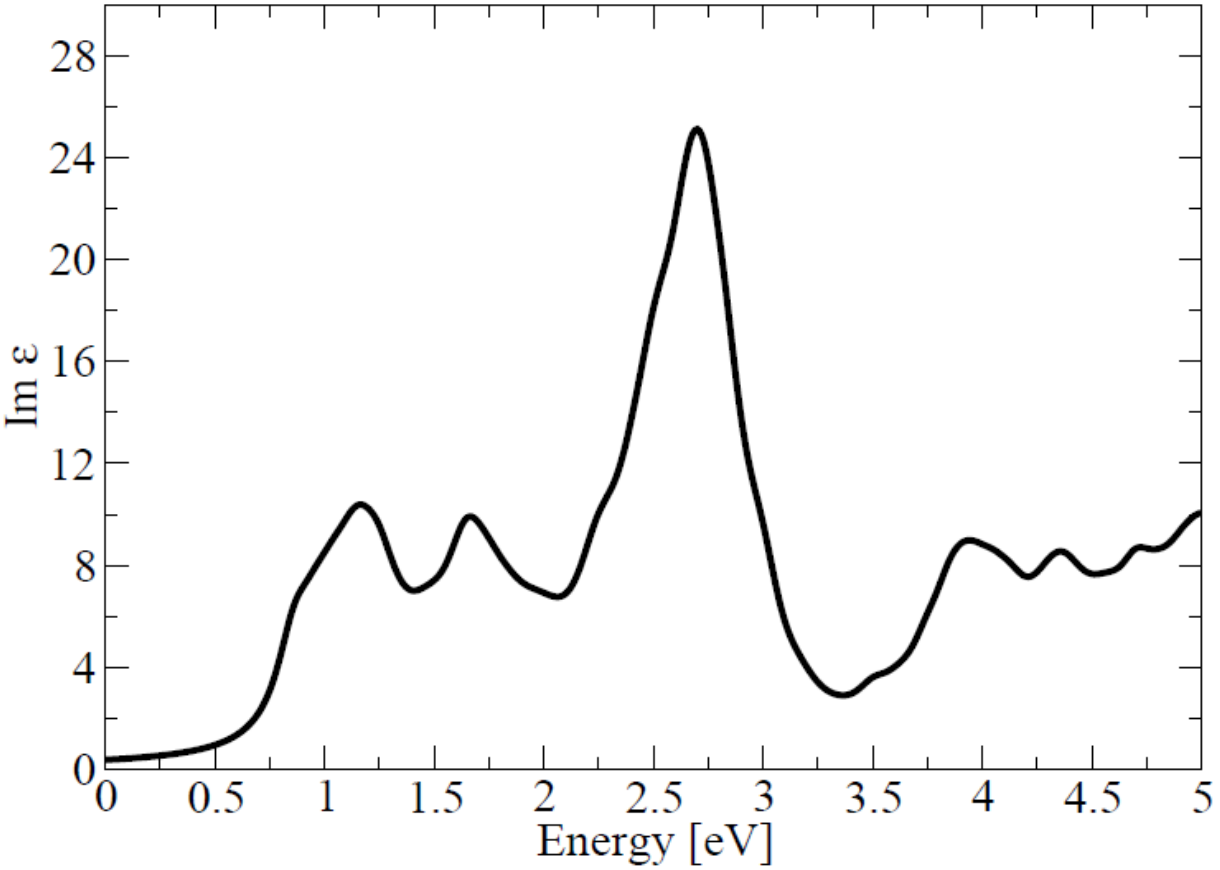


Optical absorption: local fields

Local fields

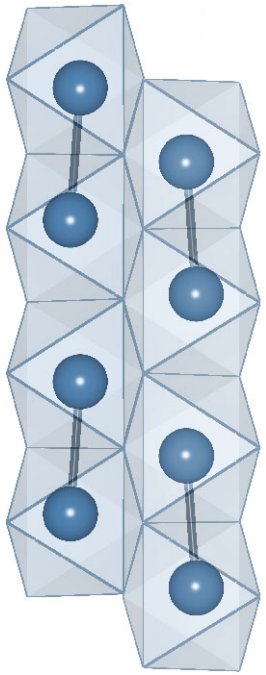


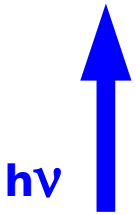


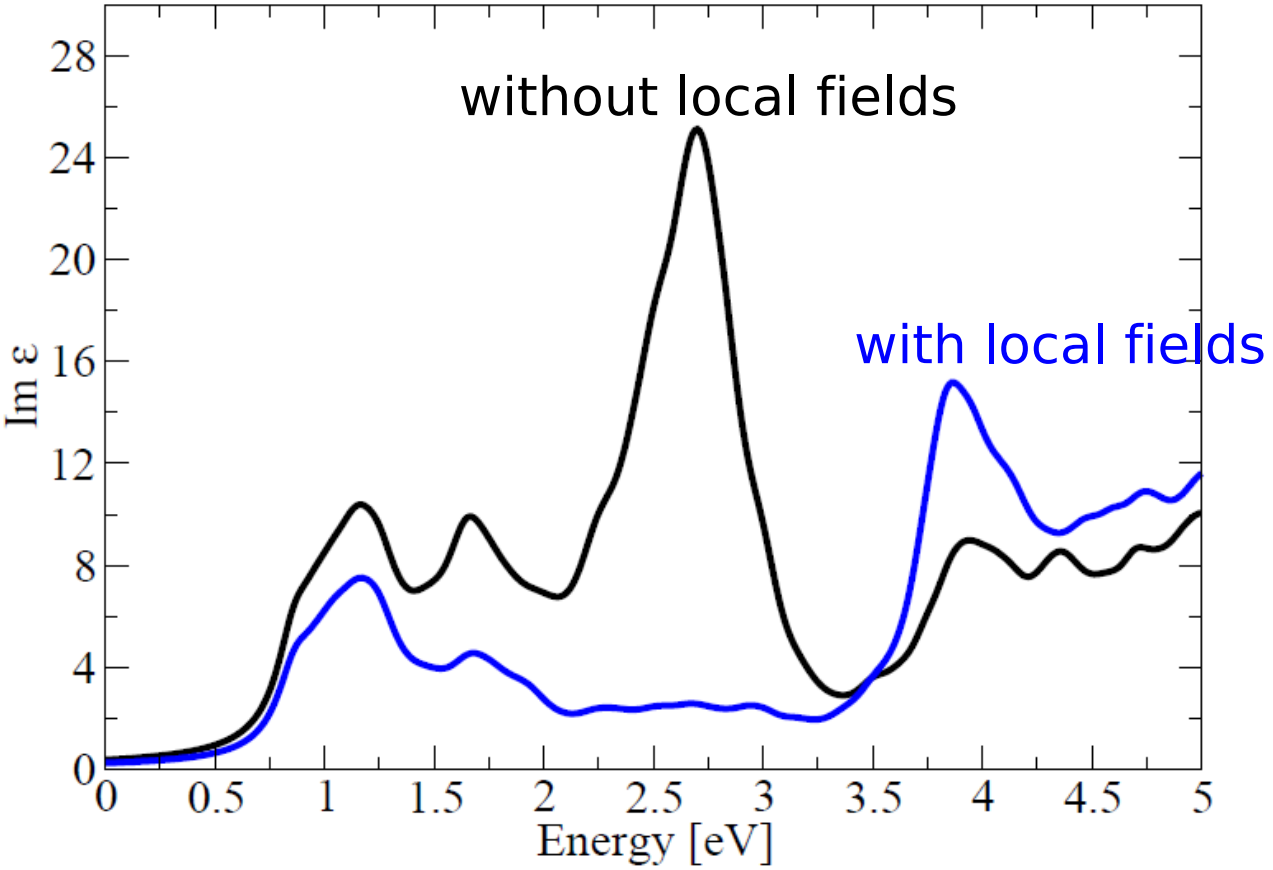


Optical absorption: local fields

Local fields

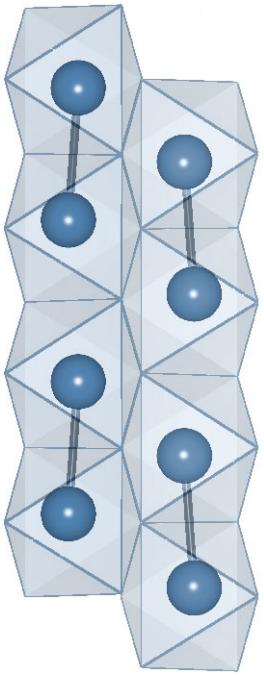




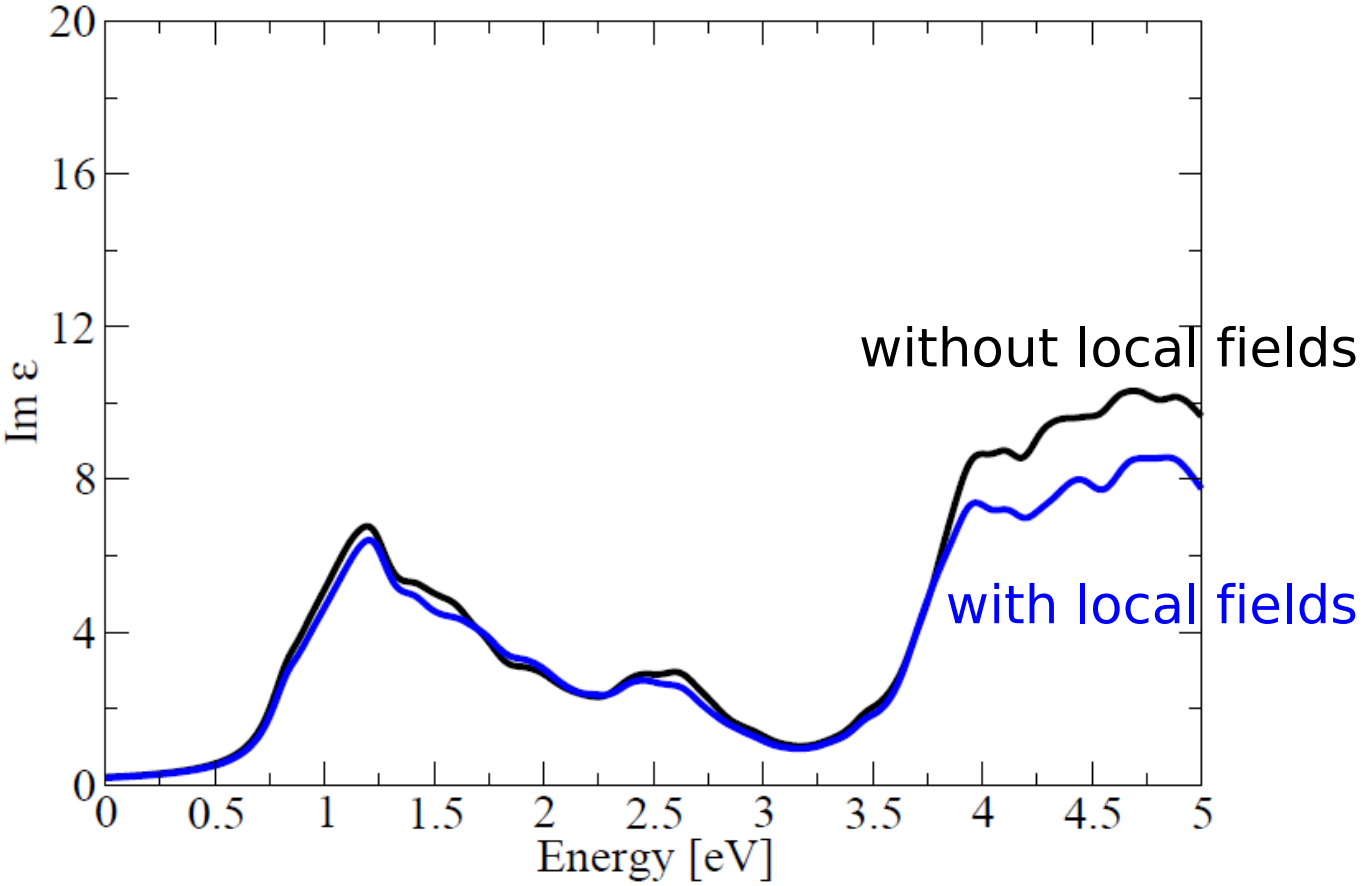


Optical absorption: local fields

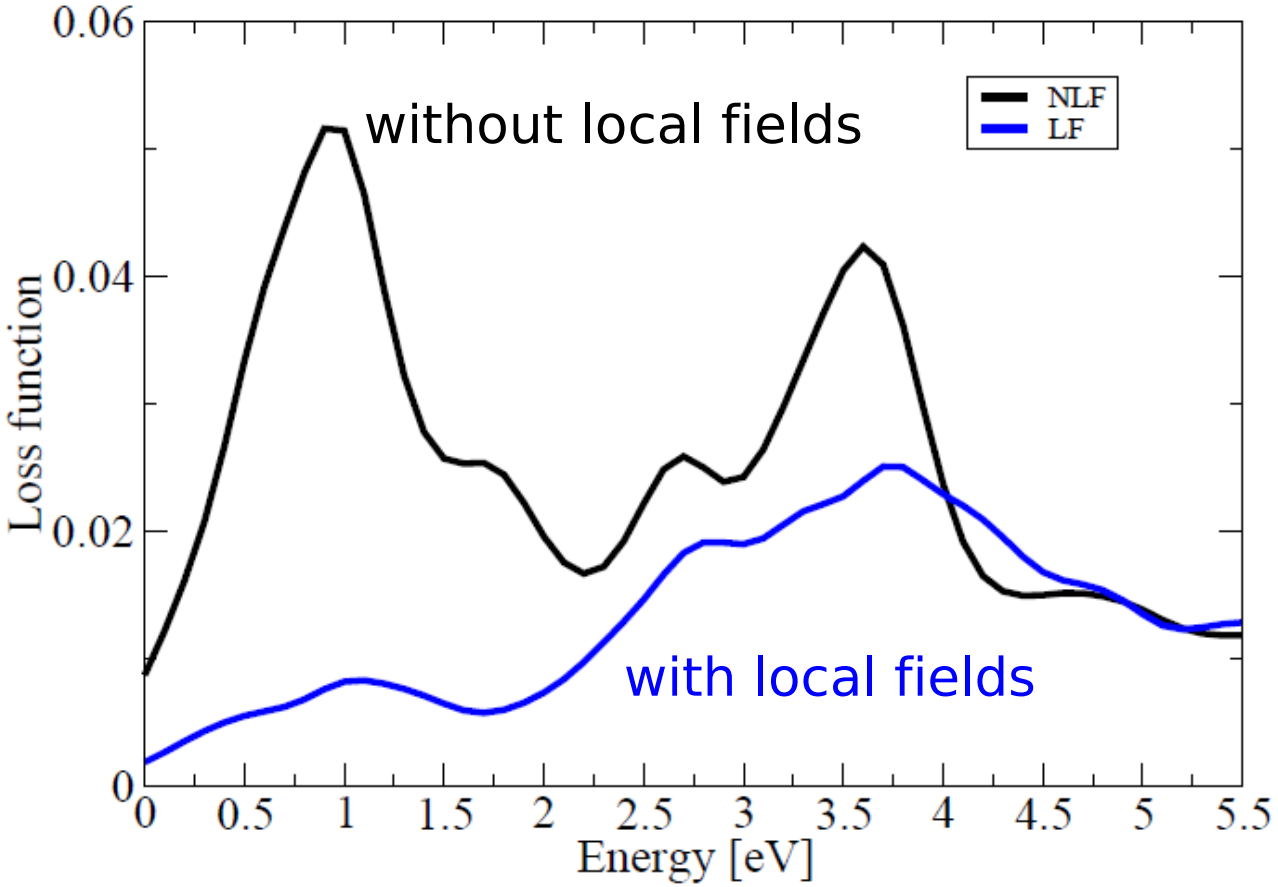
Local fields



hν



Local fields in a correlated metal: V_2O_3

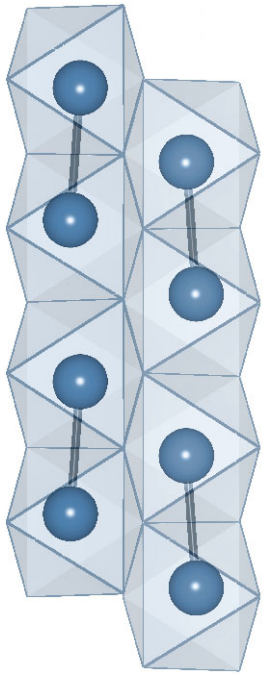


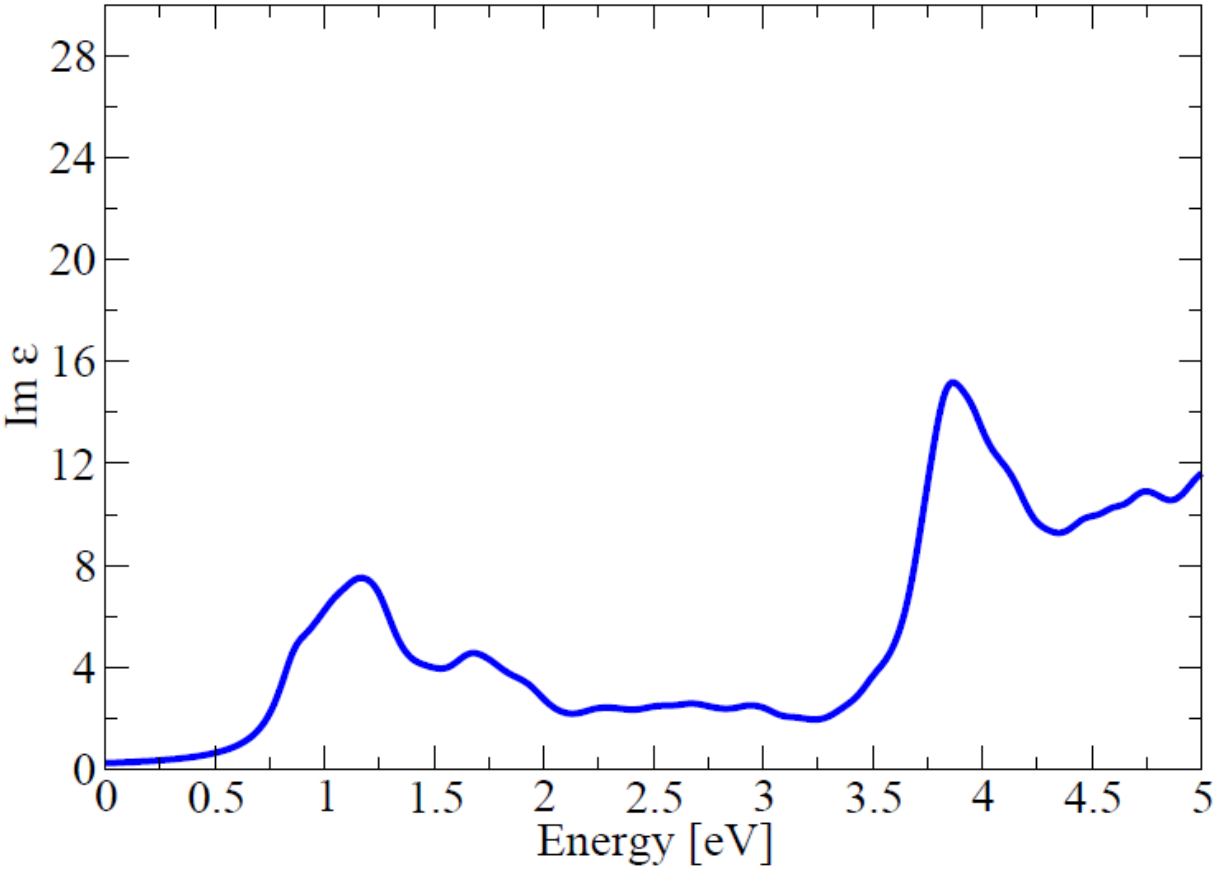
Q = (0 0 10)

Federico Iori, et al., in preparation.

Optical absorption: excitons

Excitons

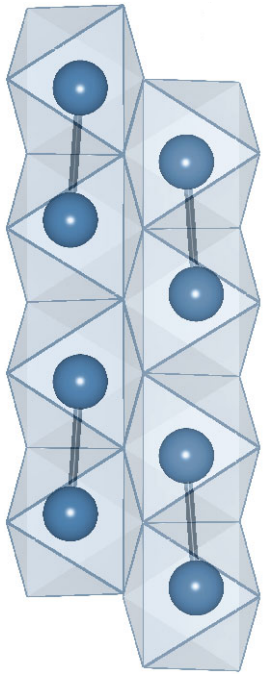


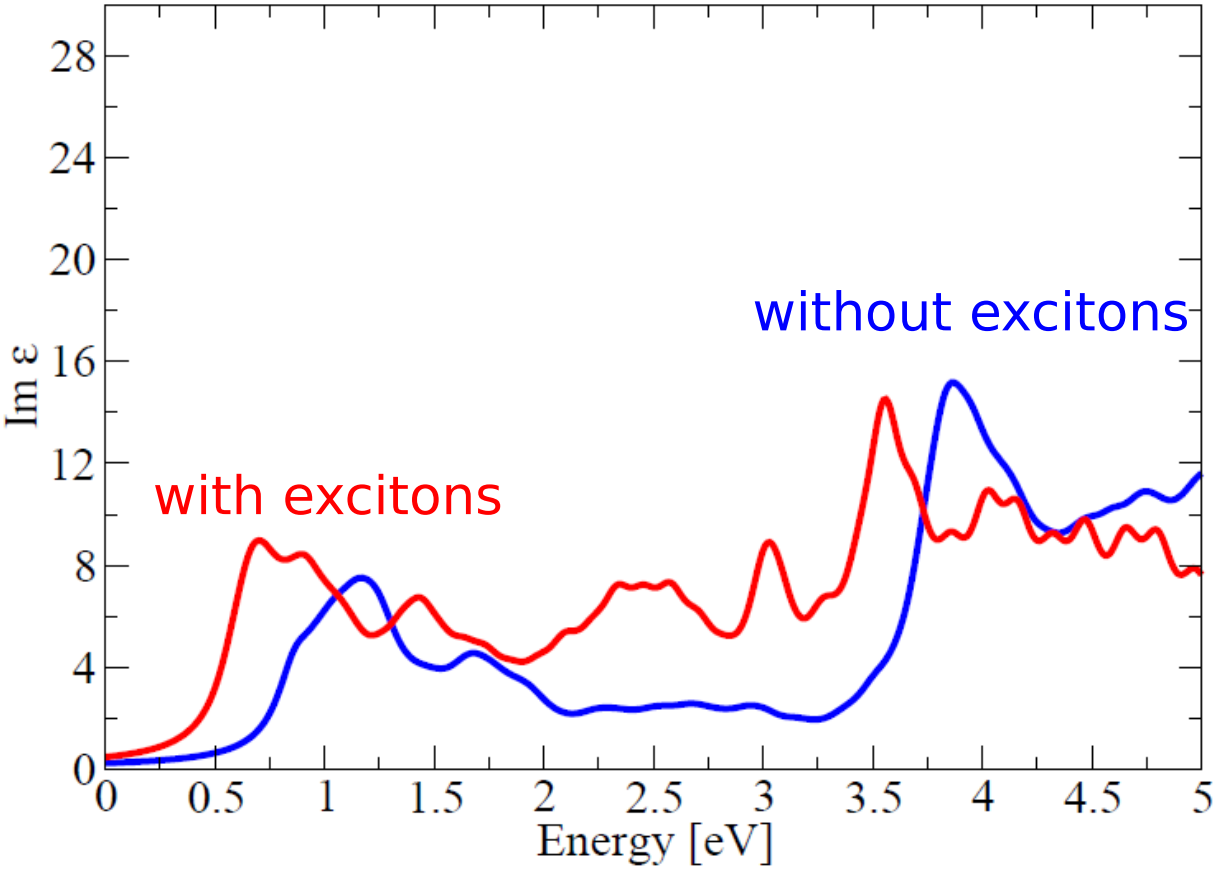


hν

Optical absorption: excitons

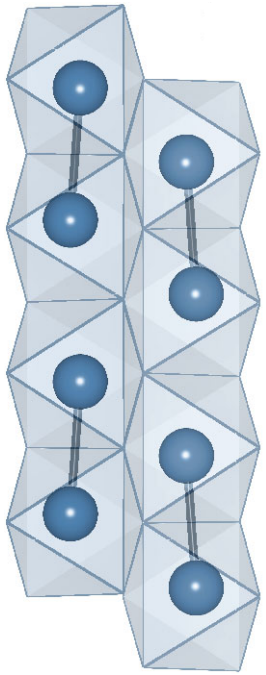
Excitons





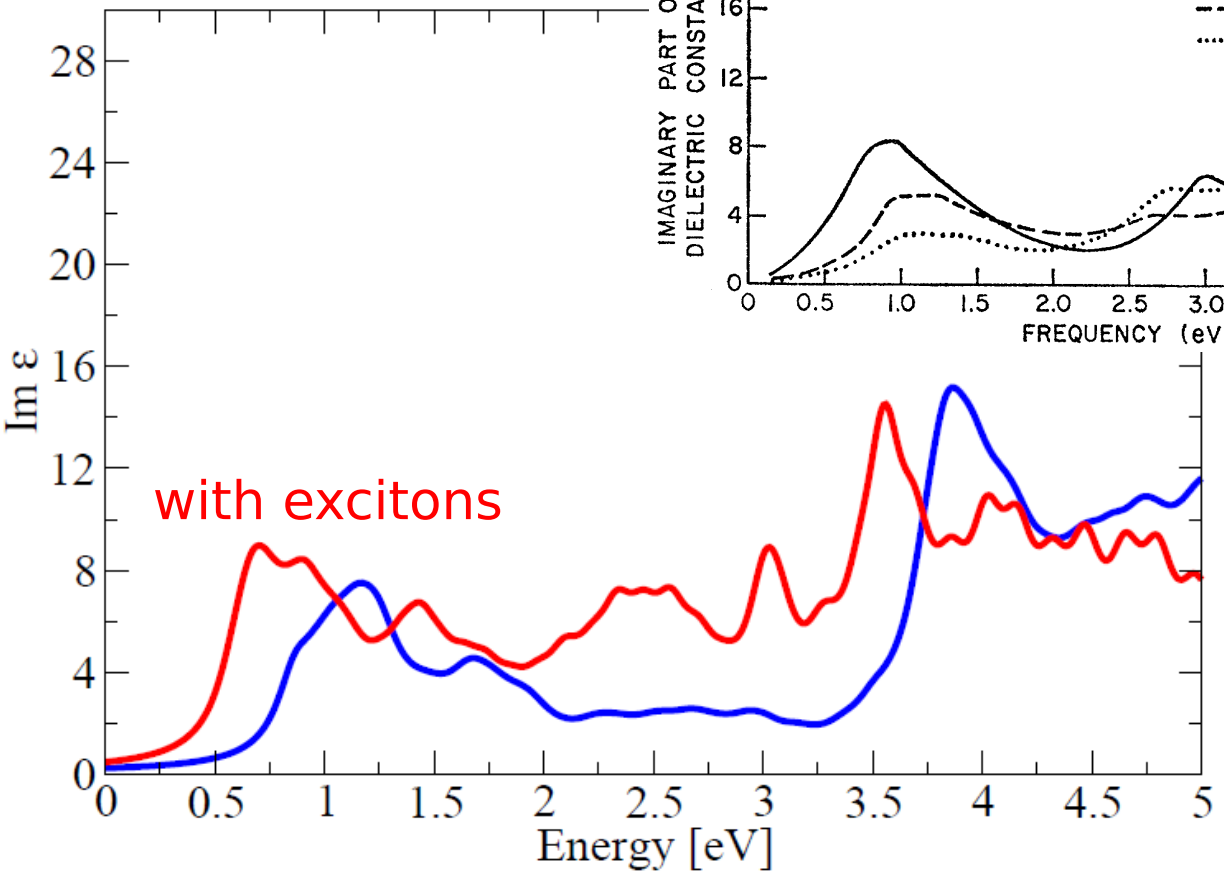
hν

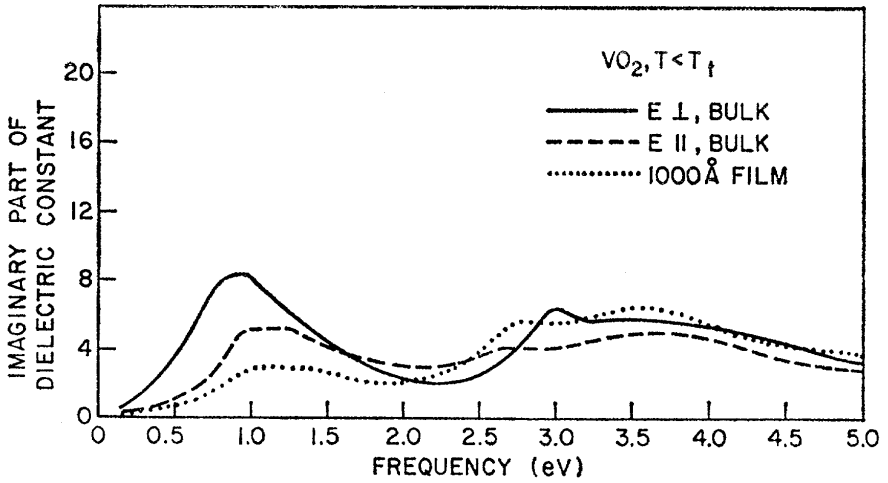
Optical absorption: excitons



hν

Excit





... and in TDDFT?

Excitons in Mott insulators?

$$\chi(\omega) = \chi_s(\omega) + \chi_s(\omega)(v + f_{xc}(\omega))\chi(\omega)$$

$$L(\omega) = L_0(\omega) + L_0(\omega)(v - W(0))L(\omega)$$

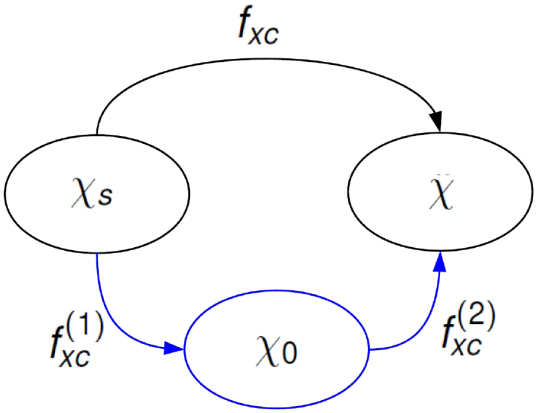
excitons from W

... and in TDDFT?

Excitons in Mott insulators?

$$\chi(\omega) = \chi_s(\omega) + \chi_s(\omega)(v + f_{xc}(\omega))\chi(\omega)$$

$$f_{xc}(\omega) = f_{xc}^{(1)}(\omega) + f_{xc}^{(2)}(\omega)$$



$$\chi_0(\omega) = \chi_s(\omega) + \chi_s(\omega) f_{xc}^{(1)}(\omega)\chi_0(\omega)$$

from KS to QP energies/orbitals

$$\chi(\omega) = \chi_0(\omega) + \chi_0(\omega)(v + f_{xc}^{(2)}(\omega))\chi(\omega)$$

excitons

$$L(\omega) = L_0(\omega) + L_0(\omega)(v - W(0))L(\omega)$$

excitons from W

... and in TDDFT?

Excitons in Mott insulators?

$$f_{xc}^{(2)}(\omega) = -\chi_0^{-1}\chi_0^3 W(0)\chi_0^3\chi_0^{-1}$$

Local in space

Non-local in time

Non-local in space

Local in time

... and in TDDFT?

Excitons in Mott insulators?

$$f_{xc}^{(2)}(\omega) = -\chi_0^{-1}\chi_0^3 W(0)\chi_0^3\chi_0^{-1}$$

Local in space

Non-local in time

Non-local in space

Local in time

But what about ? $f_{xc}(\omega) = f_{xc}^{(1)}(\omega) + f_{xc}^{(2)}(\omega)$

Imagine an insulator for which exact KS is “metallic”.

Summary

Theoretical spectroscopy:

Parameter-free analysis of phase transitions in correlated materials

Electronic properties: ab initio GW (exchange + dynamical screening)

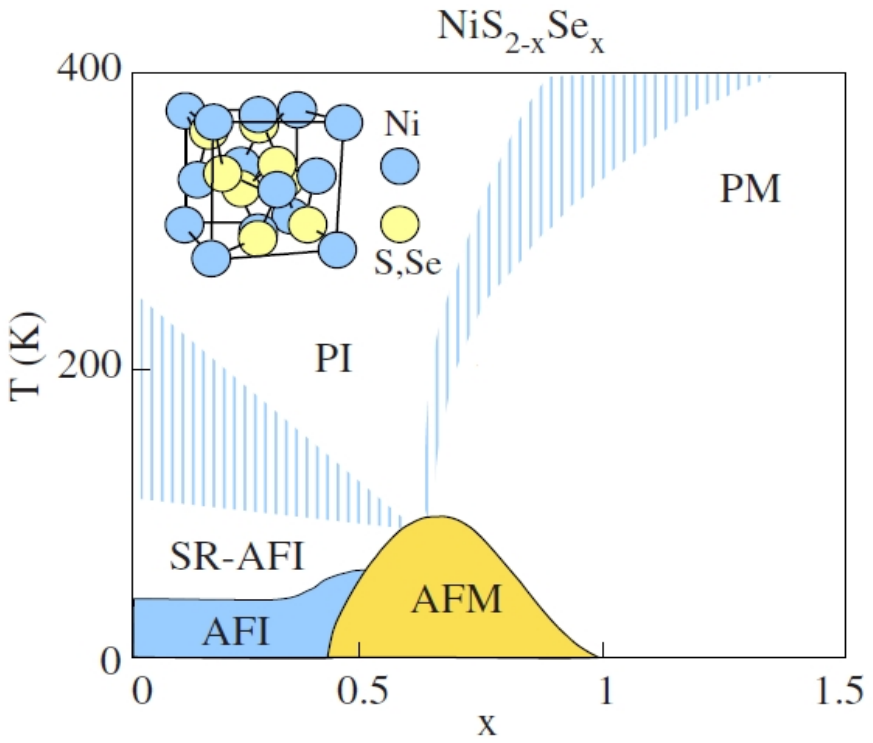
- Mott transition in MnO: the role of crystal-field splitting

Optical properties: Bethe-Salpeter equation

- crystal local fields and excitons in VO_2

Many Thanks!

Phase diagram of $NiS_{2-x}Se_x$



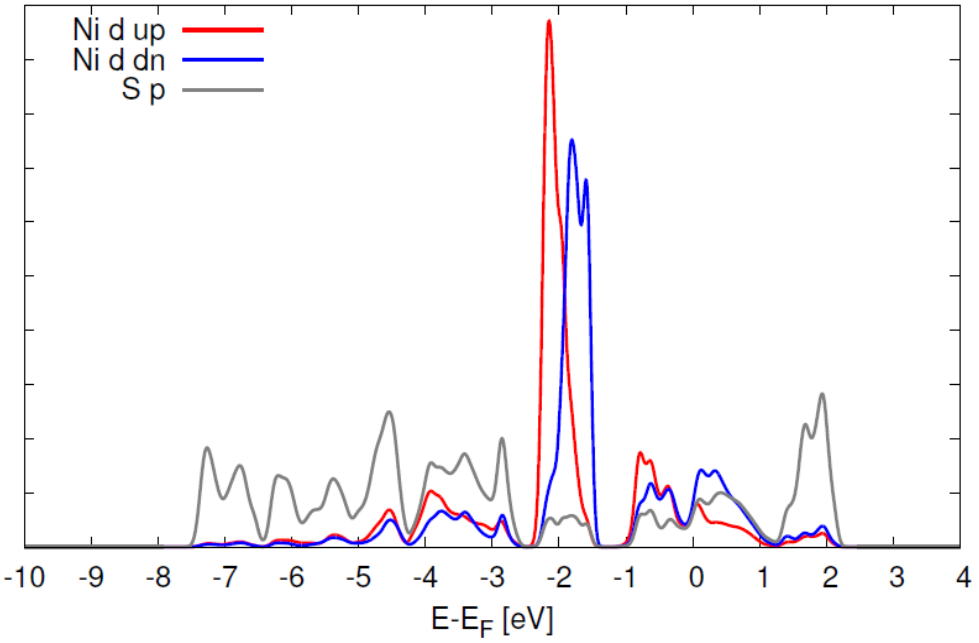
Isostructural transitions
(pyrite structure)

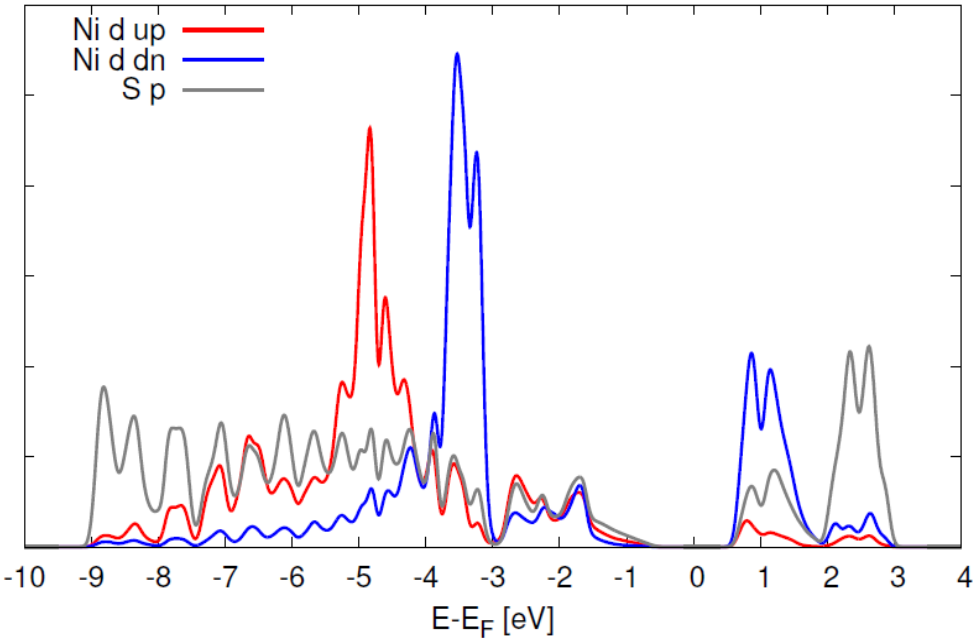
Under pressure:
from antiferromagnetic insulator to paramagnetic metal
Band broadening effect.

With Se doping:
first electronic transition (from insulator to metal) then magnetic transition (from antiferromagnetic to paramagnetic)

Lattice is expanded by Se alloying.

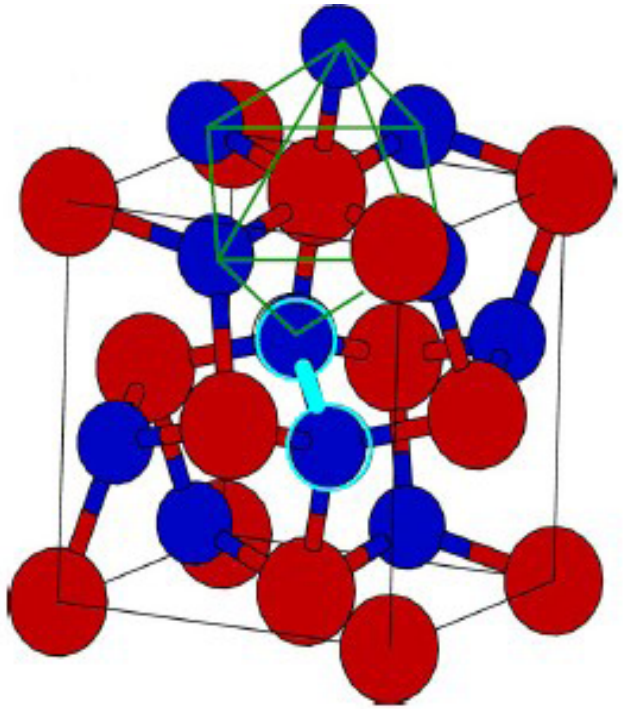
NiS_2: antiferromagnetic insulator



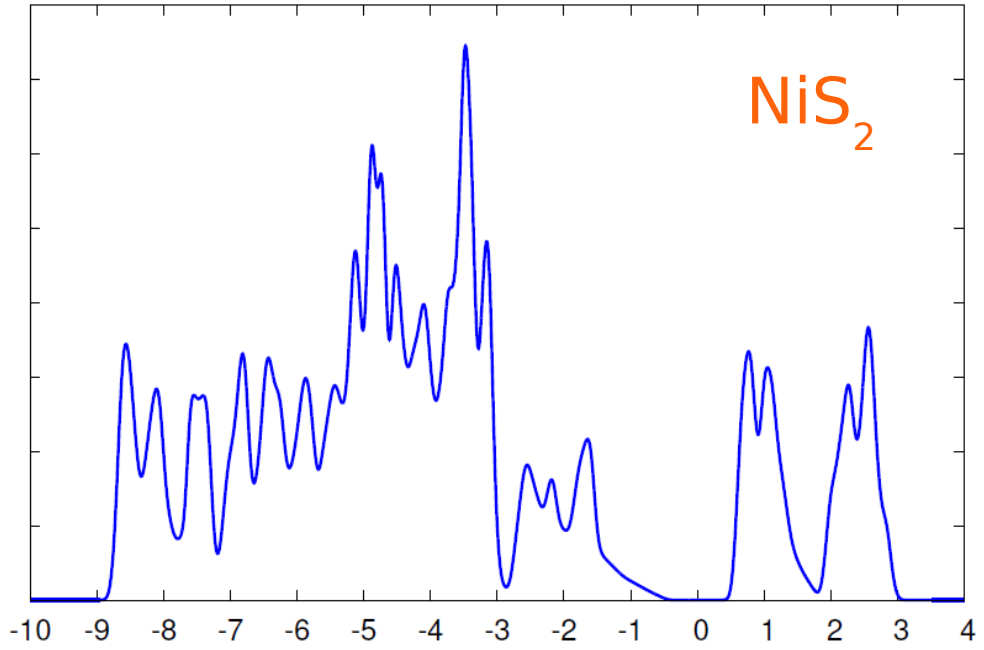


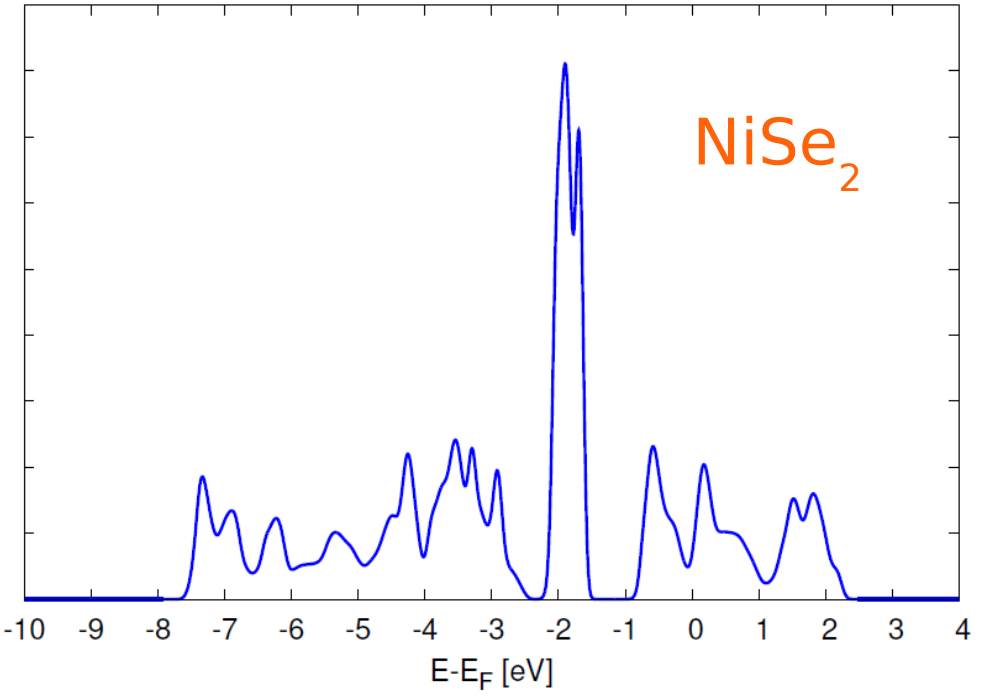
NiS_2 is metallic in LDA

GW: charge-transfer insulator

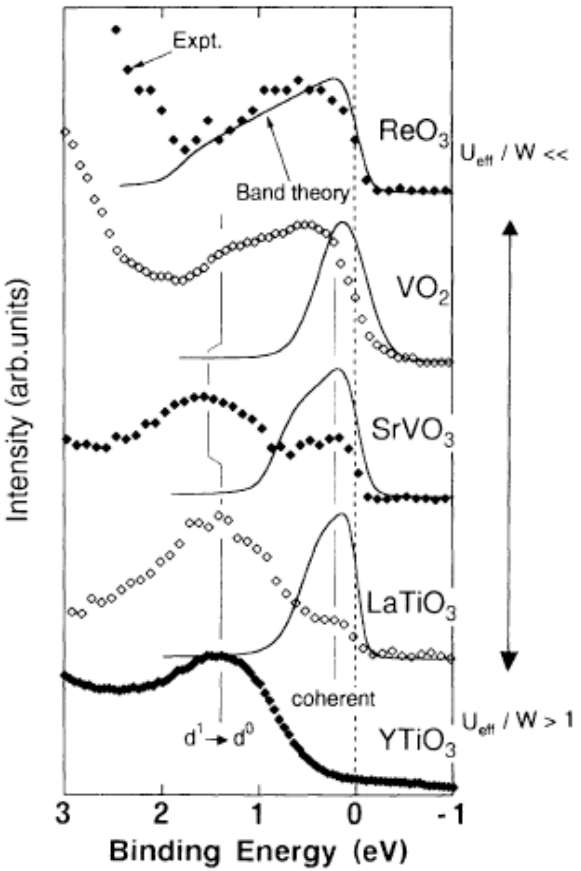


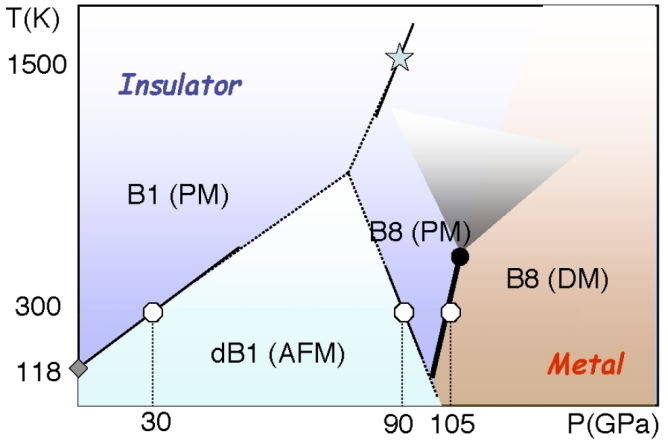
Se-Se dimers longer than S-S dimers
→ reduced p bonding-antibonding splitting
→ metal

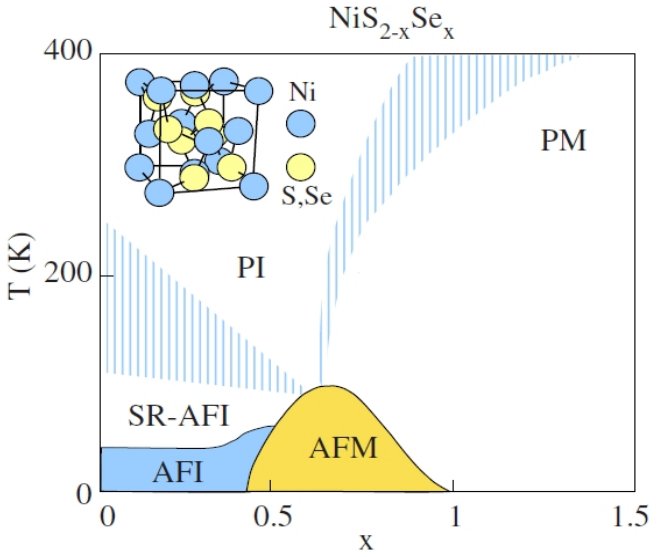




Phase transitions beyond Hubbard model



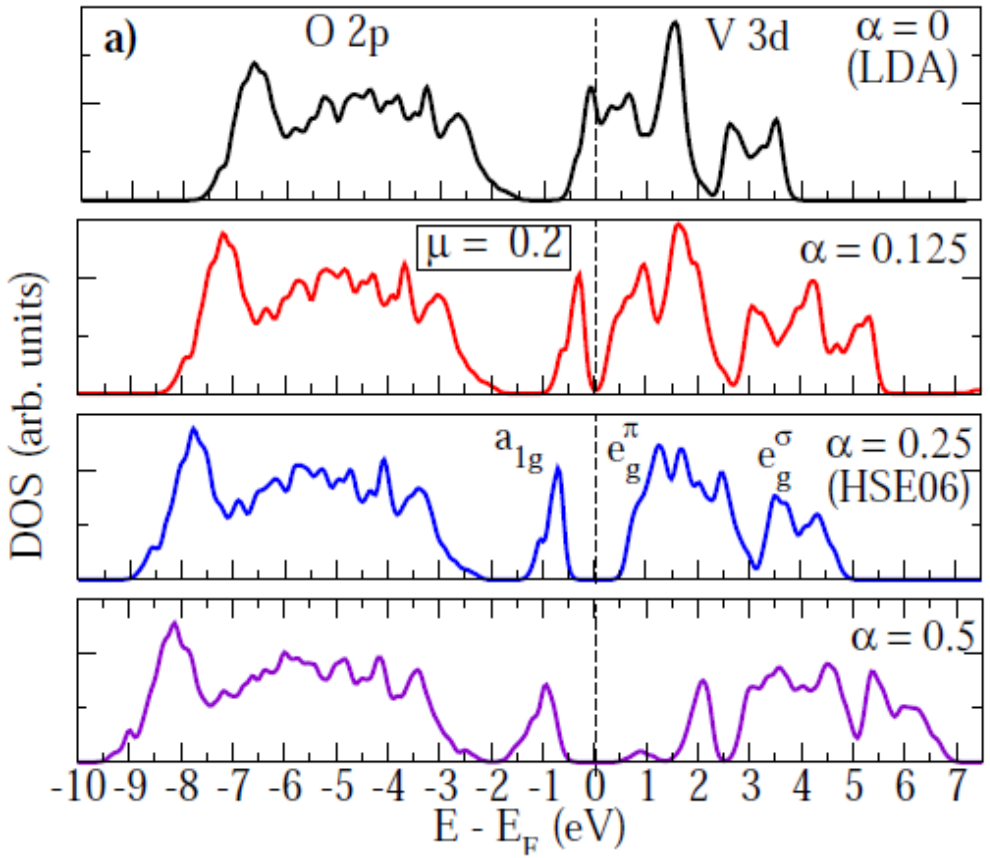


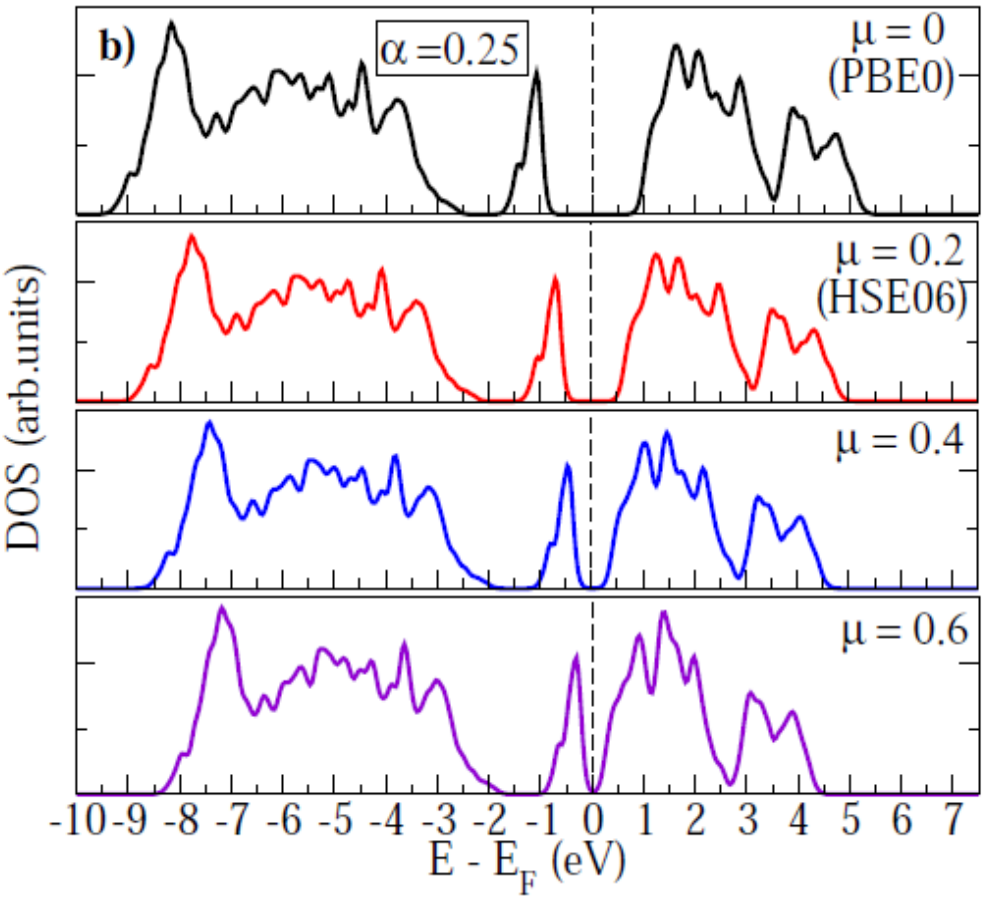


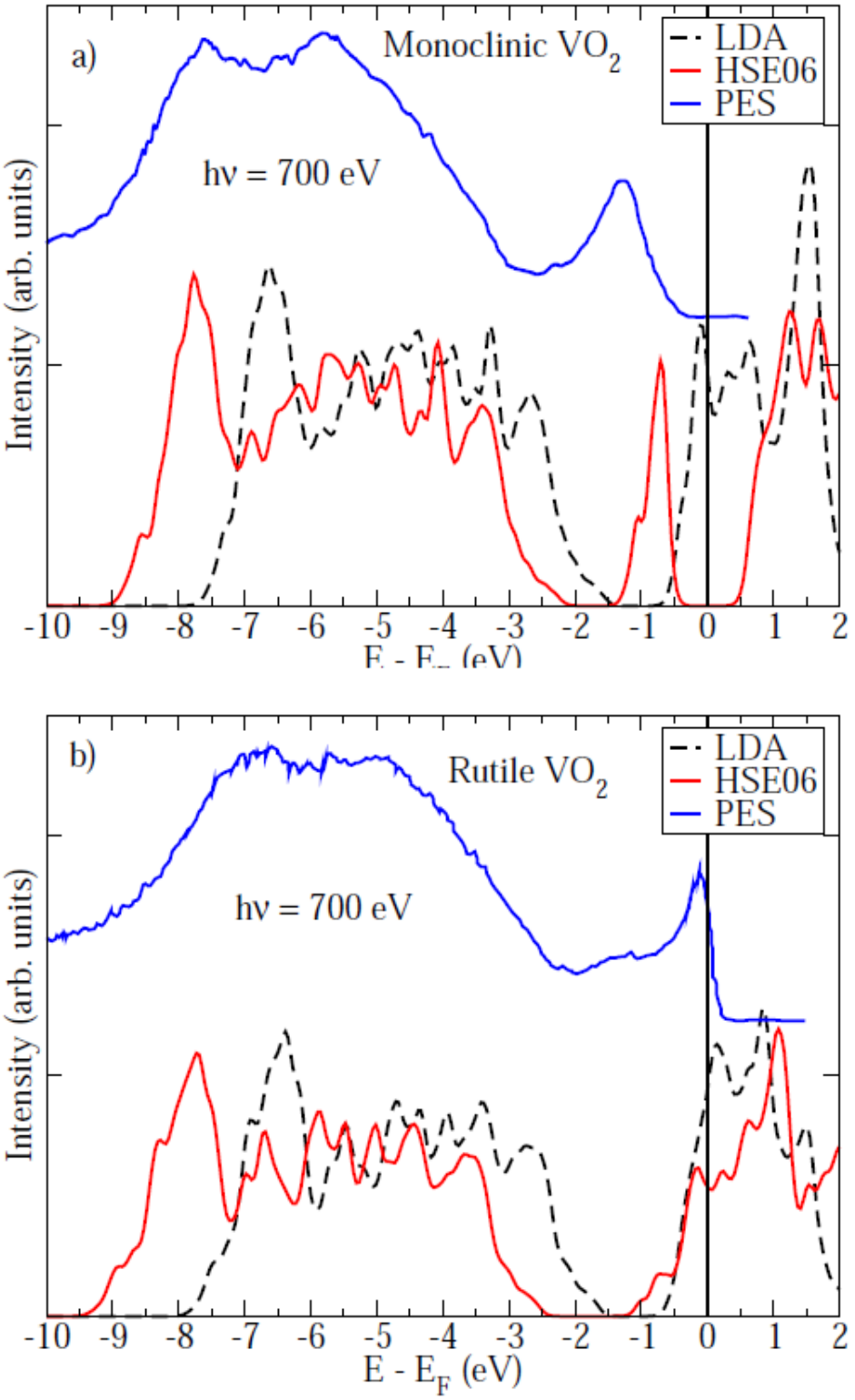
- Role of nonlocal exchange
- Role of dynamical screening

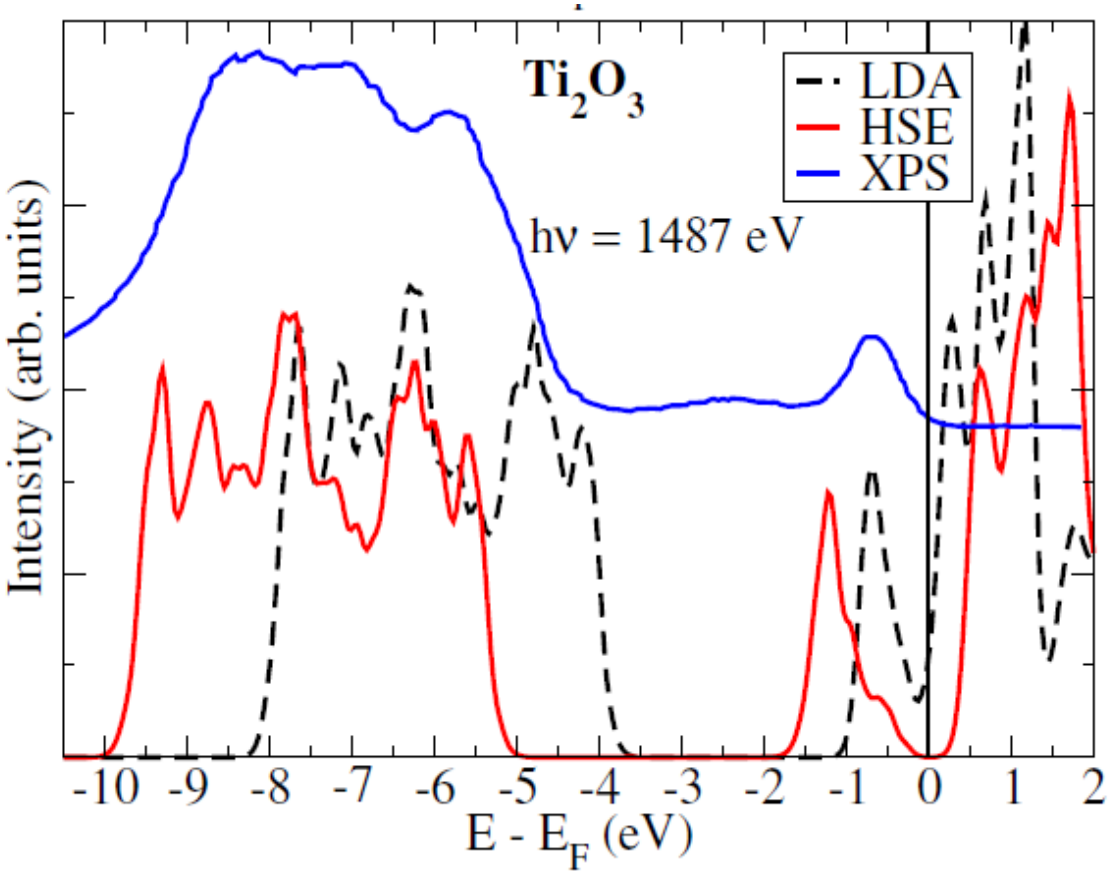
→ GW approximation

Mott insulators/transitions revisited

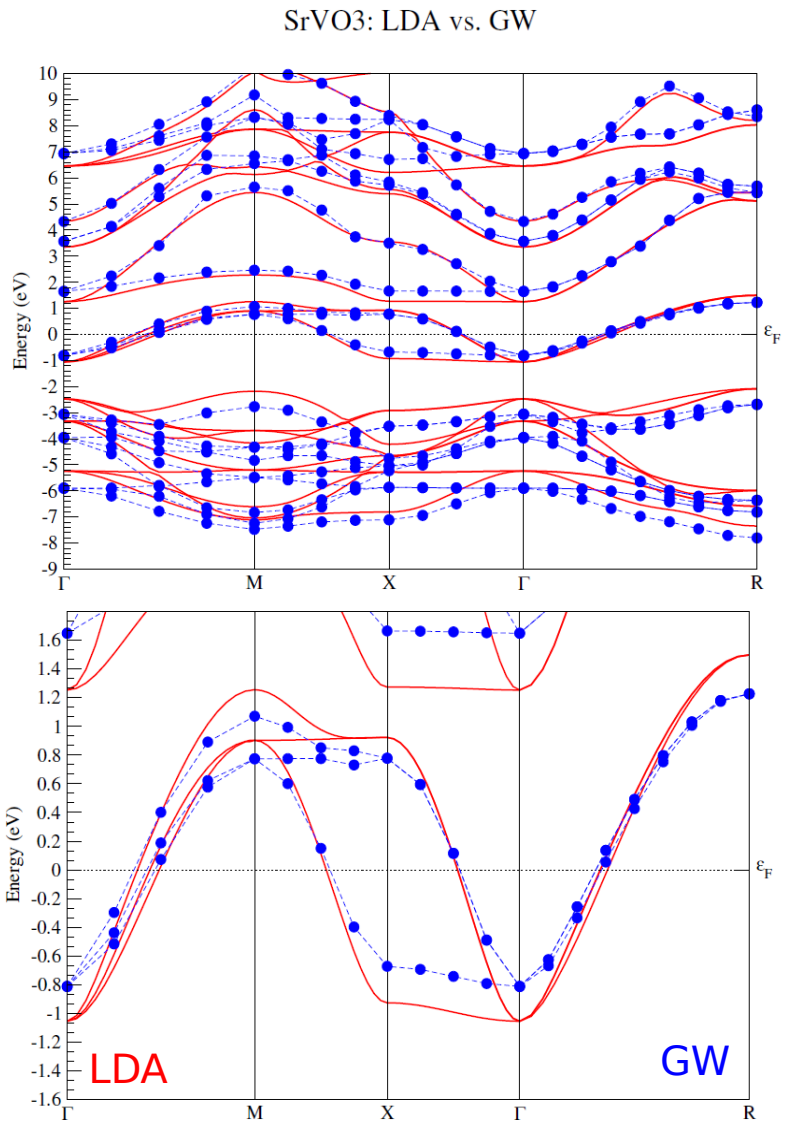

a)
O 2p
V 3d
α = 0
(LDA)
μ = 0.2
α = 0.125
a1g
e_g^π
e_g^σ
α = 0.25
(HSE06)
α = 0.5
DOS (arb. units)
-10 -9 -8 -7 -6 -5 -4 -3 -2 -1 0 1 2 3 4 5 6 7
E - E_F (eV)

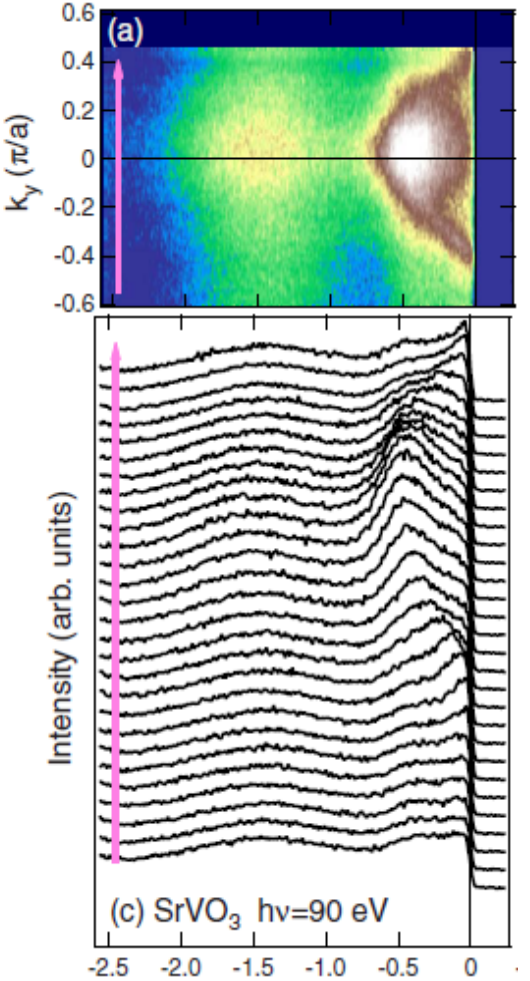

b)
α =0.25
μ = 0
(PBE0)
μ = 0.2
(HSE06)
μ = 0.4
μ = 0.6
DOS (arb.units)
-10 -9 -8 -7 -6 -5 -4 -3 -2 -1 0 1 2 3 4 5 6 7
E - E_F (eV)

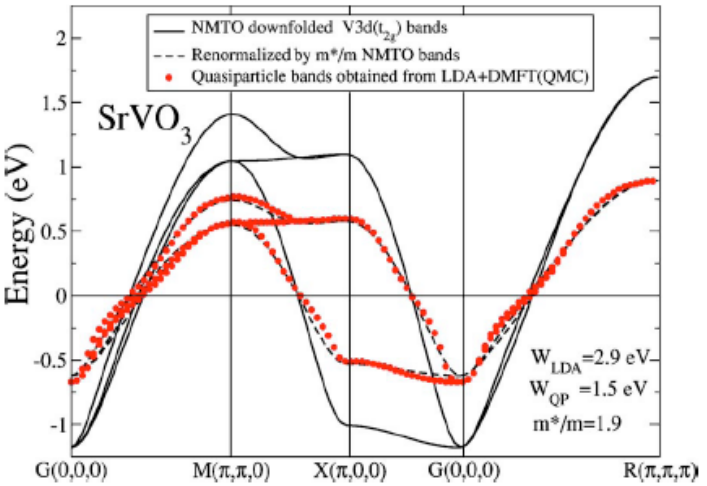

a)
Monoclinic VO2
LDA
HSE06
PES
hν = 700 eV
Intensity (arb. units)
-10 -9 -8 -7 -6 -5 -4 -3 -2 -1 0 1 2
E - EF (eV)
b)
Rutile VO2
LDA
HSE06
PES
hν = 700 eV
Intensity (arb. units)
-10 -9 -8 -7 -6 -5 -4 -3 -2 -1 0 1 2
E - EF (eV)


Ti2O3
LDA
HSE
XPS
hν = 1487 eV
Intensity (arb. units)
-10 -9 -8 -7 -6 -5 -4 -3 -2 -1 0 1 2
E - EF (eV)

$SrVO_3$: Band structure







ARPES: Yoshida et al, PRB 82 (2010).
DMFT: I. A. Nekrasov et al, PRB 73 (2006).

Mott insulator

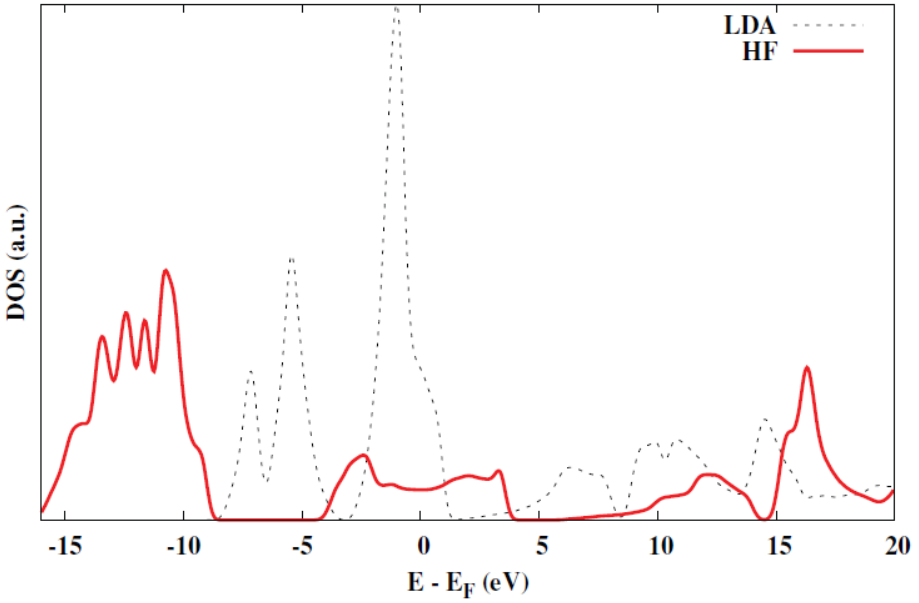
latter is purely electronic. This is a matter of definition; we describe a Mott insulator as an antiferromagnetic material that would be a metal if no moments were formed. Probably this is true of all antiferromagnetic insulators, for instance compounds of the rare earths; without moments we might expect a partially filled

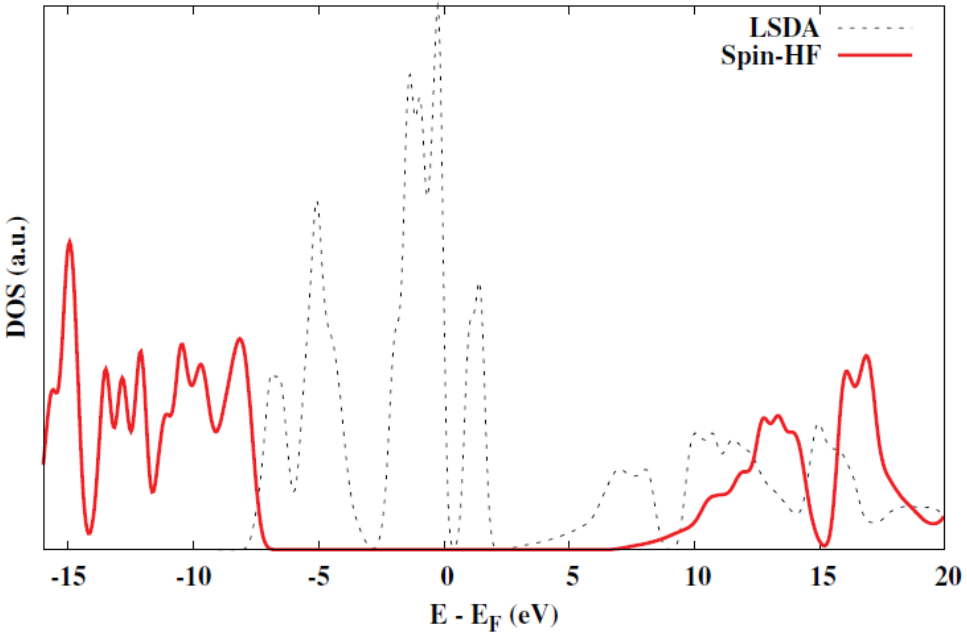
Mott, *Metal-Insulator transitions,* p. 138 (1974)

We emphasize that, in the insulating state, the gap is given by $U - \frac{1}{2}(B_1 + B_2)$, and that it depends on the existence of moments and not on whether or not they are ordered. The gap is not related to the crystal structure. Indeed, if the crystal structure is such as to predict a gap, no antiferromagnetic lattice can form, unless the gap resulting from the Hubbard U is greater than that derived from the crystal structure.

Mott, *Metal-Insulator transitions,* p. 139 (1974)

Mott insulator: NiO

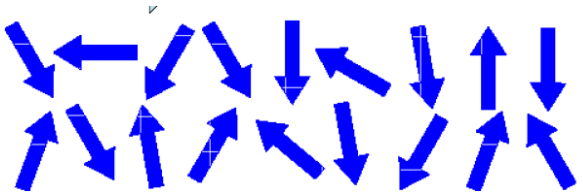




Matteo Guzzo, Master thesis, Uni Milan Bicocca (2009)

Mott insulator: NiO

Disordered local moments + SIC



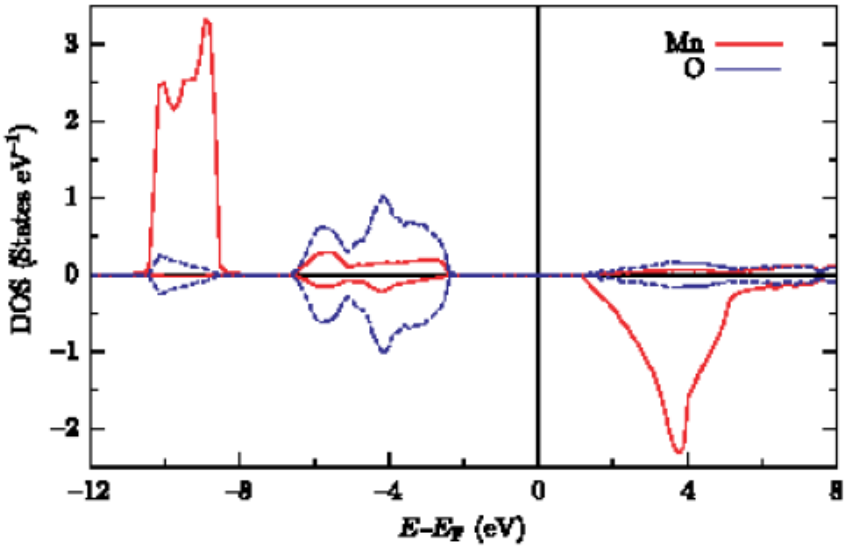
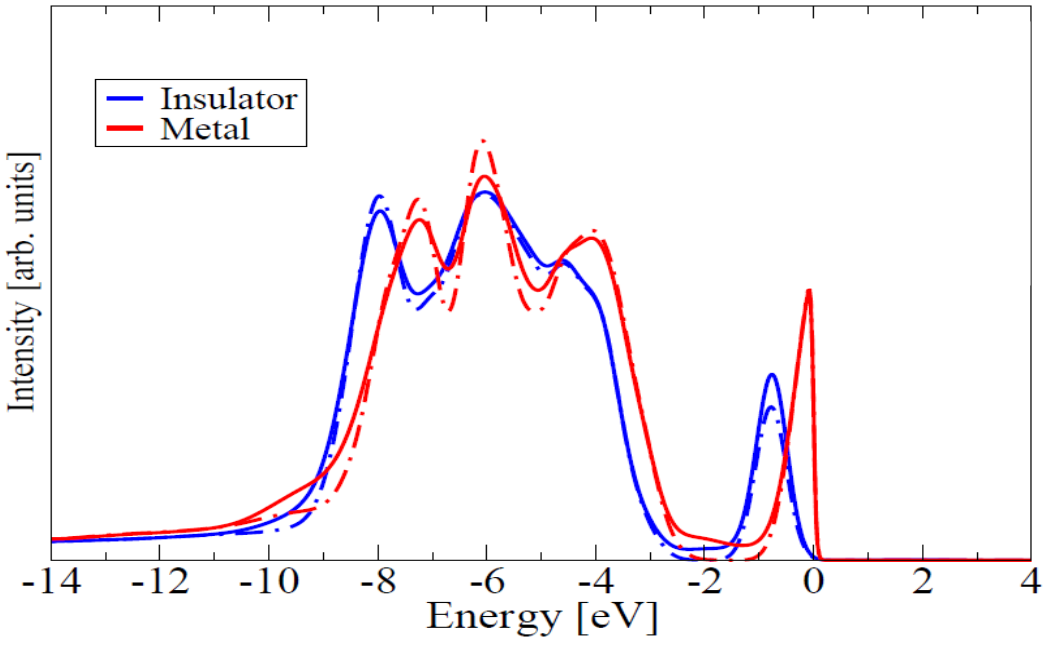
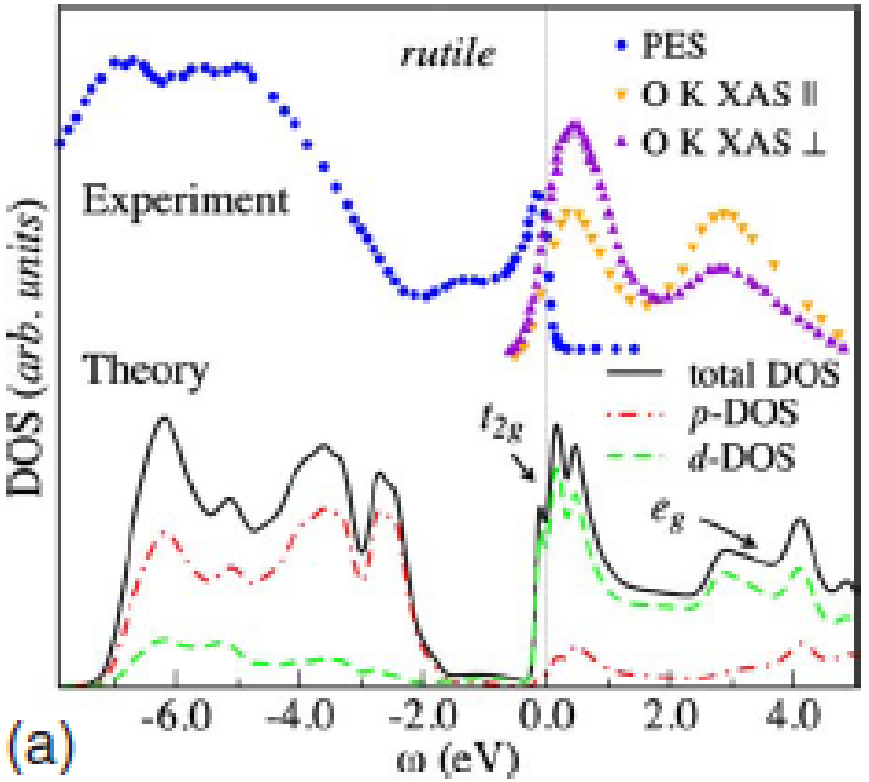


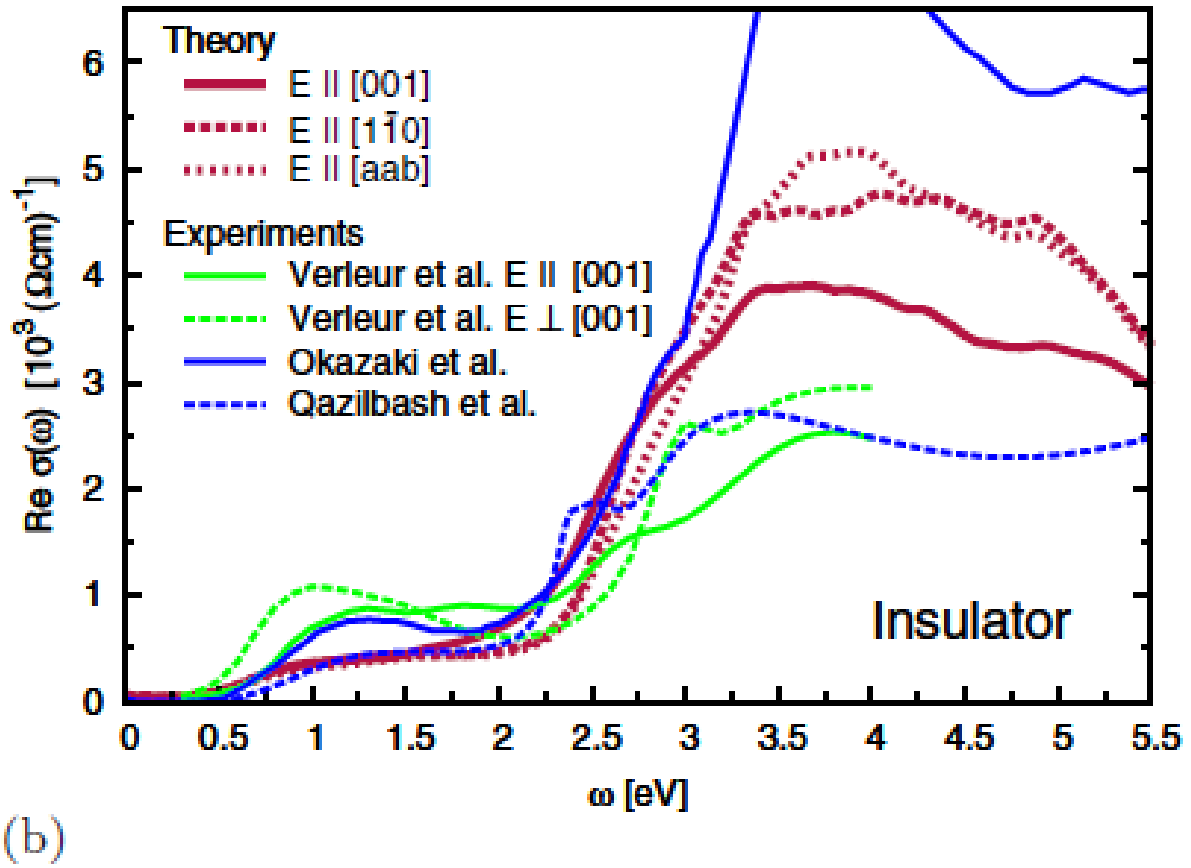
Figure 1. The local DOS for MnO in its paramagnetic (DLM) state on Mn (full line) and O sites (dashed). The upper (lower) panel shows the DOS associated with electrons with spins parallel (anti-parallel) to the local moment on the site. Note that a sizeable gap persists in the paramagnetic state.

D. Hughes *et al.*, New Journal of Physics 10 (2008)

DMFT vs. GW in VO_2



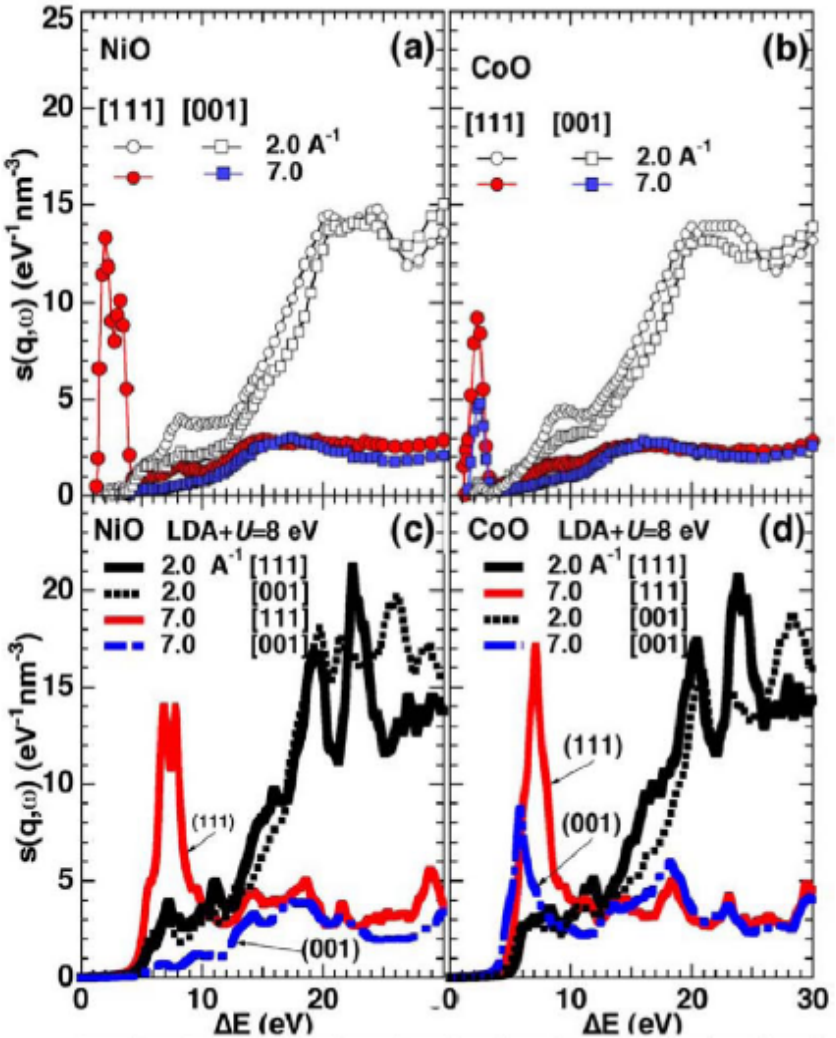




(b)

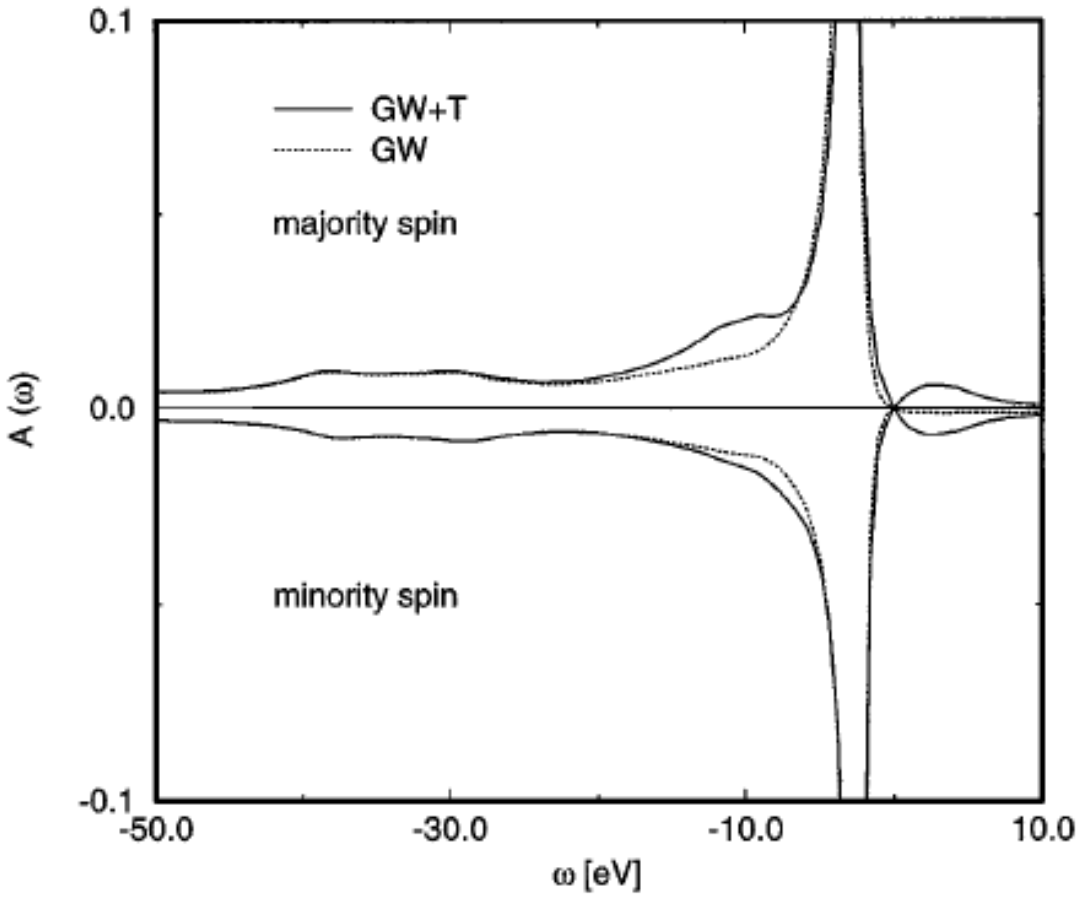
J. Tomczak and S. Biermann, EPL 86 (2009)

Excitons in screening



B. C. Larson et al., PRL 99 (2007)

When the coupling is not with plasmons...



6 eV satellite in Ni: 2-hole bound state

Springer, Aryasetiawan, Karlsson, PRL 80, 2389 (1998)