Electronic Correlation in Solids – what is it and how to tackle it ?

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“Correlations”?

What is it ?

“Correlations”?

Ashcroft-Mermin, “Solid state physics” gives ...

... the “beyond Hartree-Fock” definition”:

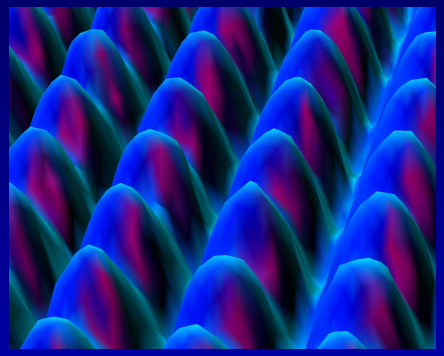
The correlation energy of an electronic system is the difference between the exact energy and its Hartree-Fock energy.

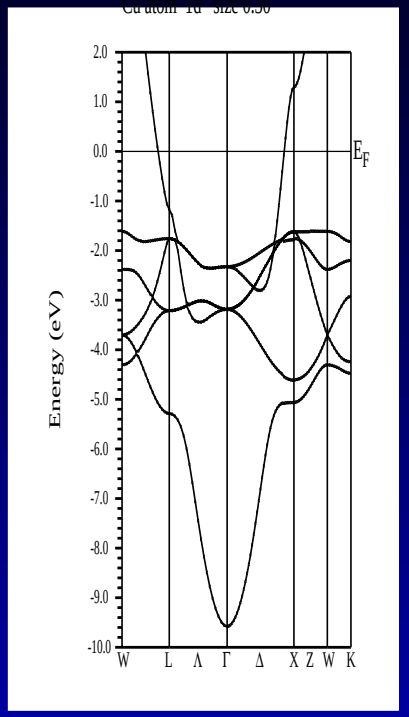
“Correlations”?

- “Correlatio” (lat.): mutual relationship

  $\rightarrow$ The behavior of a given electron is not independent of the behavior of the others!

The “standard model” of solids:





F. Bloch

Electrons in a periodic potential

- occupy *one-particle* (Bloch) states, delocalised over the solid.
- feel each other only through an effective mean potential (and the Pauli principle).

$\rightarrow$ *independent particle picture*

“Correlations”?

- “Correlatio” (lat.): mutual relationship

  $\rightarrow$ The behavior of a given electron is not independent of the behavior of the others!

- Mathematically:

$$\langle AB \rangle \neq \langle A \rangle \langle B \rangle \tag{1}$$

“Correlations”?

50 % have blue eyes
50 % have yellow eyes

“Correlations”?

50 % are left-handed
50 % are right-handed

“Correlations”?

What’s the probability for a left-handed yellow-eyed kangaroo ???

“Correlations”?

probability for a left-handed yellow-eyed kangaroo = $1/2 \cdot 1/2 = 1/4$ **only if the two properties are uncorrelated**

Otherwise: anything can happen ....

“Correlations”?

- “Correlatio” (lat.): mutual relationship

  $\rightarrow$ The behavior of a given electron is not independent of the behavior of the others!

- Mathematically:

$$\langle AB \rangle \neq \langle A \rangle \langle B \rangle \tag{2}$$

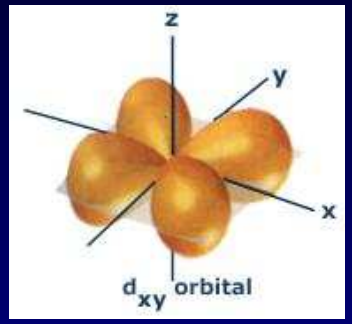
  For electrons (in a given atomic orbital):

$$\langle n_\uparrow n_\downarrow \rangle \neq \langle n_\uparrow \rangle \langle n_\downarrow \rangle$$

  n_σ = number operator for electrons with spin σ.

“Correlations”?

Count electrons on a given atom in a given orbital:



n_σ = counts electrons with spin σ

$n_\uparrow n_\downarrow$ counts “double-occupations”

$\langle n_\uparrow n_\downarrow \rangle = \langle n_\uparrow \rangle \langle n_\downarrow \rangle$ **only if the “second” electron does not care about the orbital being already occupied or not**

Exercise (!):

Does

$$\langle n_\uparrow n_\downarrow \rangle = \langle n_\uparrow \rangle \langle n_\downarrow \rangle \text{hold?}$$

1. Hamiltonian: $H_0 = \epsilon(n_\uparrow + n_\downarrow)$

2. Hamiltonian: $H = \epsilon(n_\uparrow + n_\downarrow) + U n_\uparrow n_\downarrow$

Correlations $\langle n_\uparrow n_\downarrow \rangle = \langle n_\uparrow \rangle \langle n_\downarrow \rangle$?

(1) Hamiltonian: $H_0 = \epsilon(n_\uparrow + n_\downarrow)$
Operators $n_\uparrow$ and $n_\downarrow$ have eigenvalues 0 and 1.

Correlations $\langle n_\uparrow n_\downarrow \rangle = \langle n_\uparrow \rangle \langle n_\downarrow \rangle$?

(1) Hamiltonian: $H_0 = \epsilon(n_\uparrow + n_\downarrow)$
Operators $n_\uparrow$ and $n_\downarrow$ have eigenvalues 0 and 1.

$$\begin{aligned}
\langle n_\uparrow n_\downarrow \rangle &= \frac{1}{Z} \sum_{n_\uparrow=0,1,\ n_\downarrow=0,1} n_\uparrow n_\downarrow e^{-\beta\epsilon(n_\uparrow+n_\downarrow)} \\
&= \frac{1}{Z} \sum_{n_\uparrow=0,1} n_\uparrow e^{-\beta\epsilon n_\uparrow} \sum_{n_\downarrow=0,1} n_\downarrow e^{-\beta\epsilon n_\downarrow} \\
&= \langle n_\uparrow \rangle \langle n_\downarrow \rangle
\end{aligned}$$

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\end{aligned}$$

No correlations! (Hamiltonian separable)

Correlations $\langle n_\uparrow n_\downarrow \rangle = \langle n_\uparrow \rangle \langle n_\downarrow \rangle$?

(2) Hamiltonian: $H = \epsilon(n_\uparrow + n_\downarrow) + U n_\uparrow n_\downarrow$
Operators $n_\uparrow$ and $n_\downarrow$ have eigenvalues 0 and 1.

Correlations $\langle n_\uparrow n_\downarrow \rangle = \langle n_\uparrow \rangle \langle n_\downarrow \rangle$?

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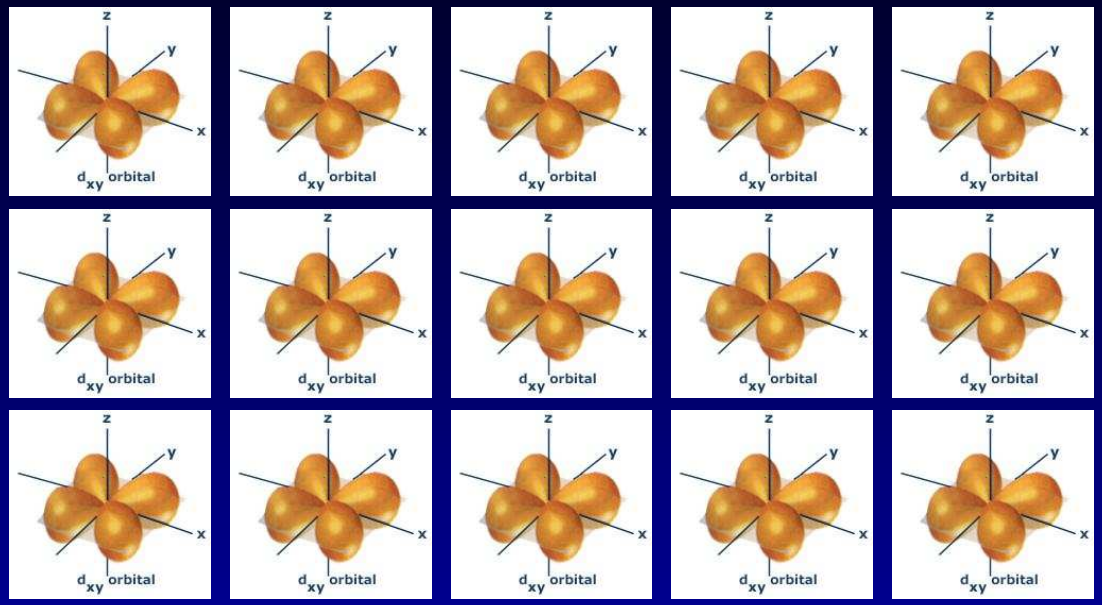
Correlations! (Hamiltonian not separable)

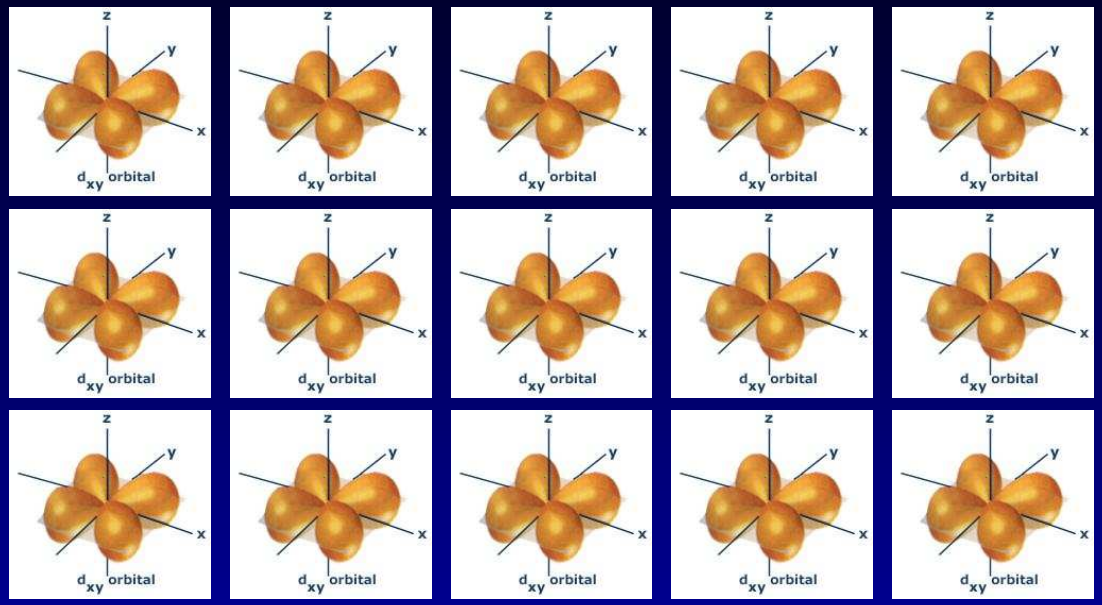
Periodic array of sites with one orbital



We can have $\langle n_\uparrow + n_\downarrow \rangle = 1$ for each site, but yet $\langle n_\uparrow n_\downarrow \rangle = 0$ (insulator!)

Is this possible within a one-particle picture?

Periodic array of sites with one orbital



$\langle n_\uparrow + n_\downarrow \rangle = 1$ for each site, and $\langle n_\uparrow n_\downarrow \rangle = 0$

$\rightarrow$ only possible in a one-particle picture if we allow for symmetry breaking (e.g. magnetic), such that $\langle n_\uparrow \rangle \langle n_\downarrow \rangle = 0$

Mott's ficticious H-solid:

Hydrogen atoms with lattice spacing 1 m

H H H H H H H H
H H H H H H H H
H H H H H H H H
H H H H H H H H
H H H H H H H H

(not to scale ...)

Metal or insulator?

Mott's ficticious H-solid:

Hydrogen atoms with lattice spacing 1 m

H H H H H H H H
H H H H H H H H
H H H H H H H H (not to scale ...)
H H H H H H H H
H H H H H H H H

Metal or insulator?

Band structure: $\rightarrow$ metal
Reality: $\rightarrow$ "Mott insulator"!

Mott's ficticious H-solid:

Hydrogen atoms with lattice spacing 1 m

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Metal or insulator?

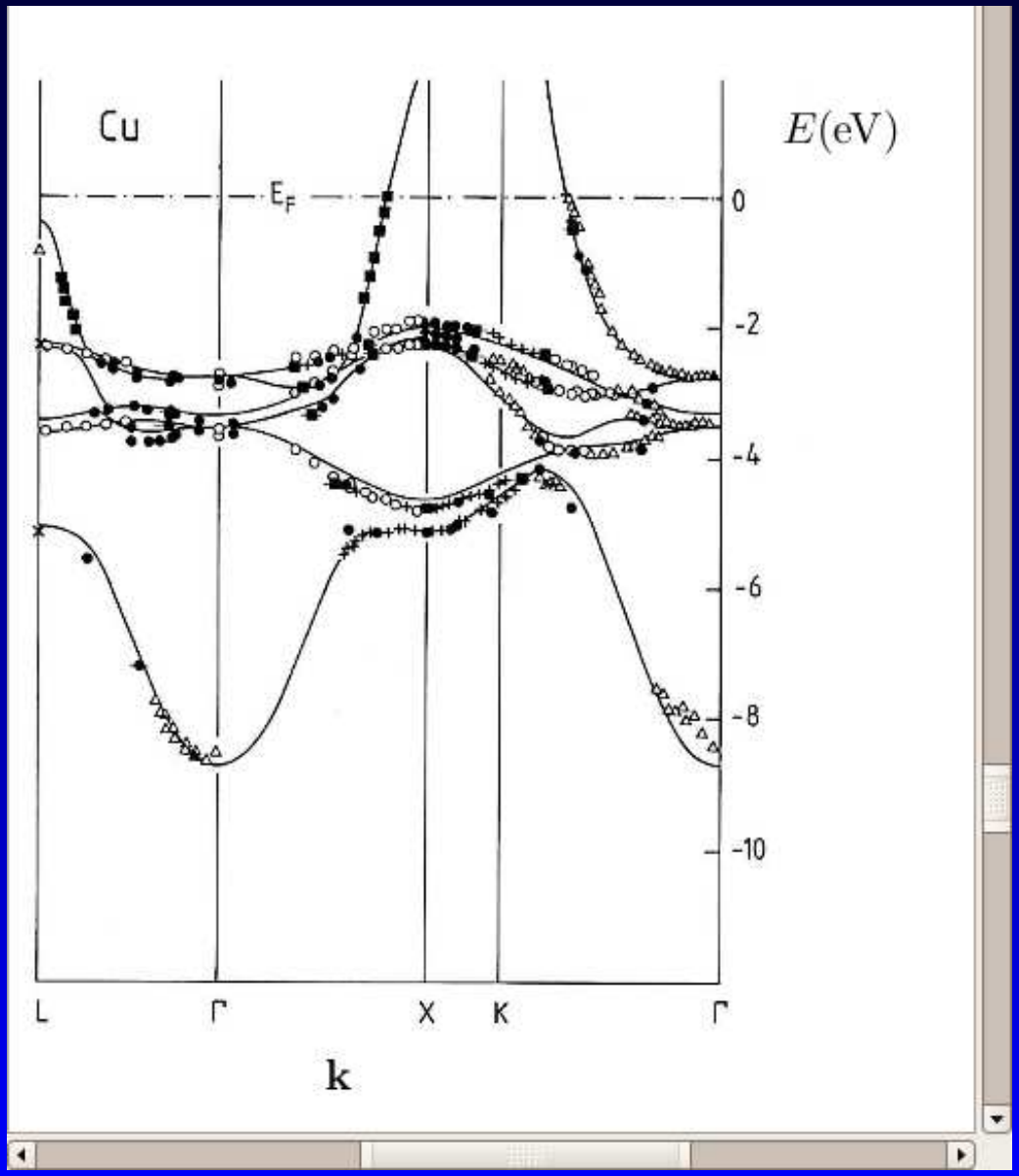
Band structure: $\rightarrow$ metal
Reality: $\rightarrow$ "Mott insulator"!

Coulomb repulsion dominates over kinetic energy!

Why does band theory work at all?

Band structure ...

... from photoemission – Example: Copper



Why does band theory work at all?

Band structure relies on *one-electron* picture
But: electrons interact !

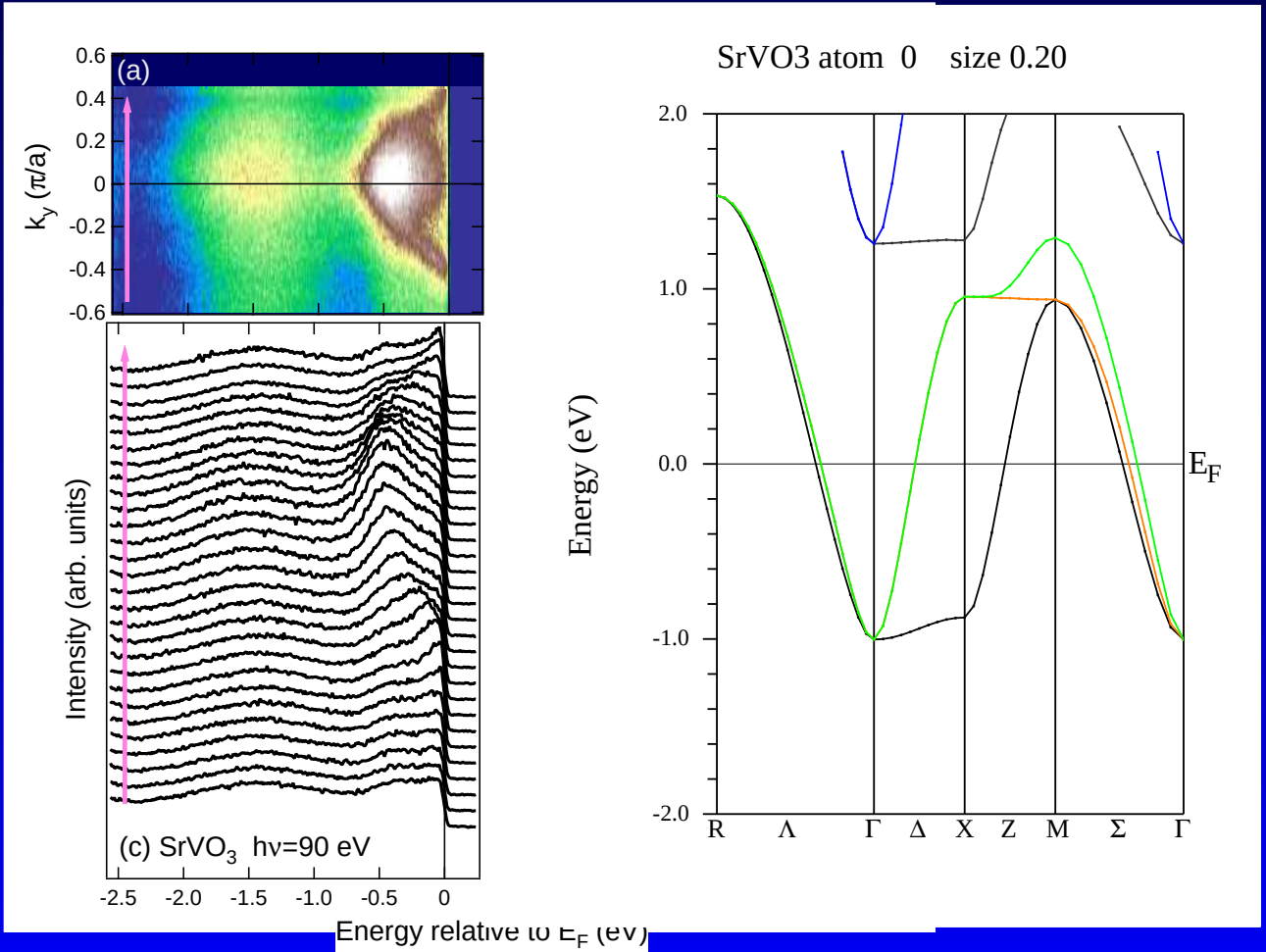
Several answers ...:

- Pauli principle
Screening } reduce effects of interactions

  Landau's Fermi liquid theory: quasi-particles

The “standard model” (contd.)

Landau theory of quasiparticles:
$\rightarrow$ one-particle picture as a low-energy theory with renormalized parameters



(cf. Patrick Rinke’s lecture!)

Why does the “standard model” work?

Band structure relies on *one-electron* picture
But: electrons interact !

Several answers ...:

- Pauli principle
Screening } reduce effects of interactions

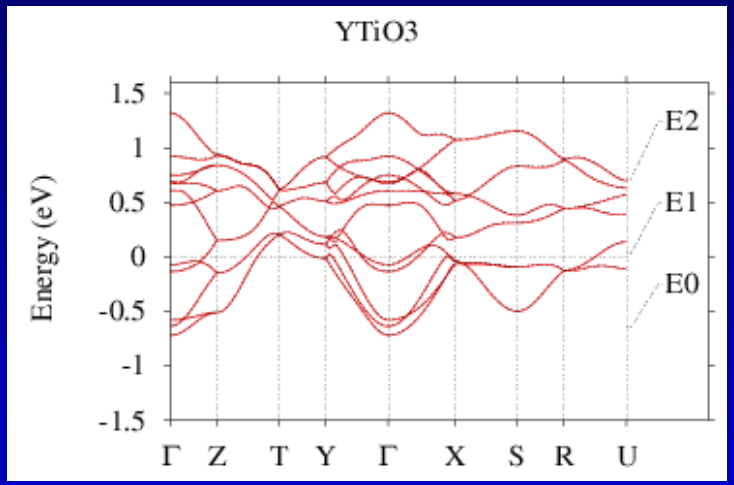
  Landau’s Fermi liquid theory: quasi-particles

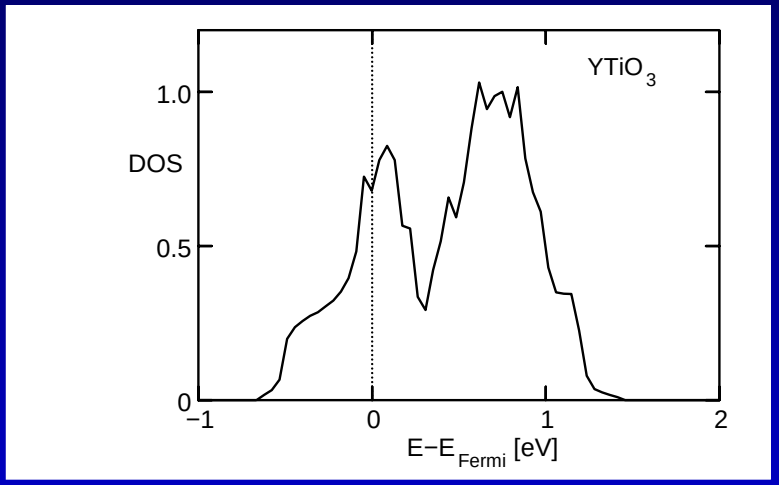
- It does not always work ....

$YTiO_3$ in LDA

$YTiO_3$: a distorted perovskite compound with d^1 configuration (i.e. 1 electron in t_{2g} orbitals), paramagnetic above 30 K.

DFT-LDA results:



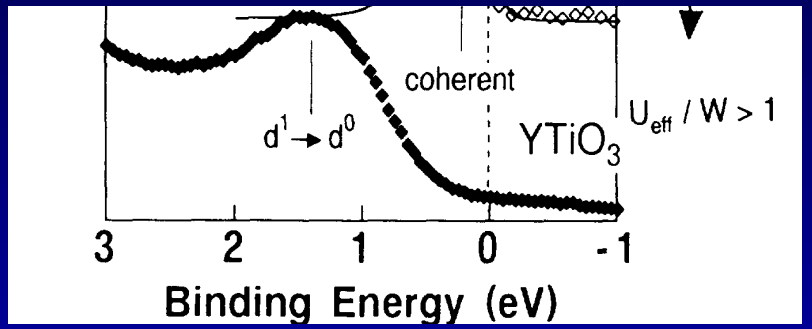


(∗) DFT-LDA = Density Functional Theory within the local density approximation

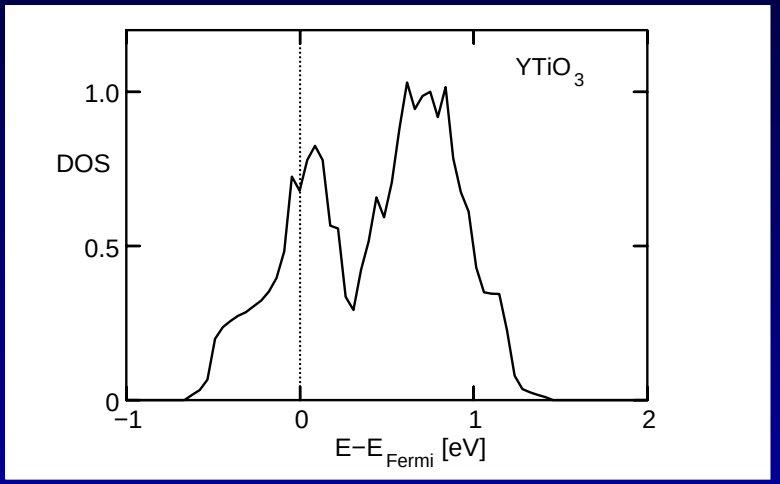
$YTiO_3$: in reality ...

Photoemission reveals a (Mott) insulator:

(Fujimori et al.)



LDA



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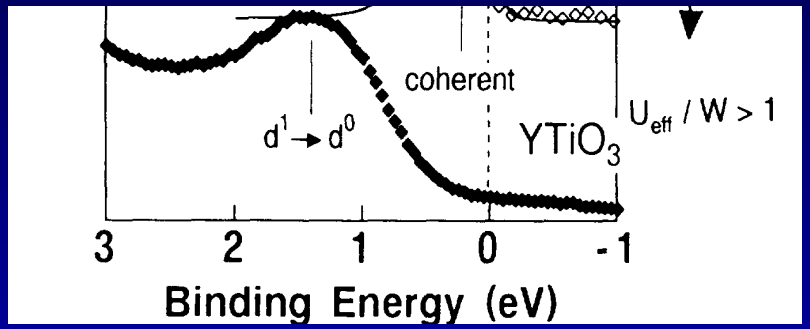
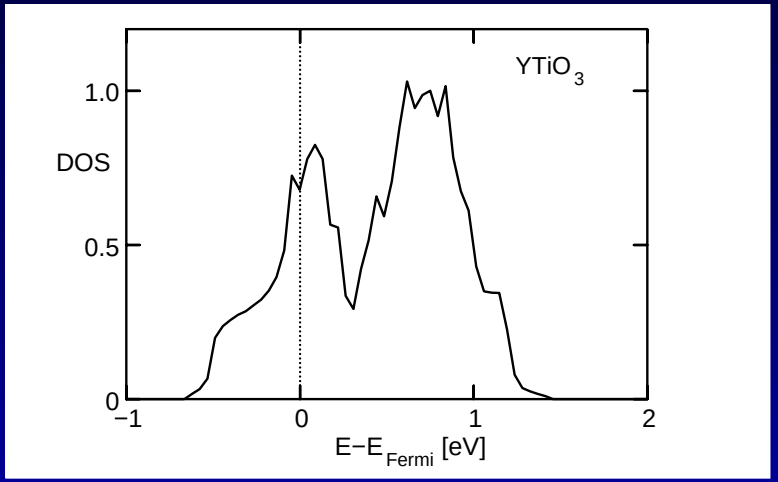


LDA



How to produce a paramagnetic insulating state with 1 electron in 3 bands?

$\rightarrow$ not possible in band theory

$\rightarrow$ breakdown of independent particle picture

Further outline

- From N-particle to 1-particle Hamiltonians
- Problems of DFT-LDA
- Modelling correlated behavior: the Hubbard model
- The Mott metal-insulator transition
- Dynamical mean field theory
- Dynamical mean field theory within electronic structure calculations ("LDA+DMFT")
- Examples:

  Typical examples: d^1 perovskites $SrVO_3$, $CaVO_3$, $LaTiO_3$, $YTiO_3$
  A not typical one ...: VO_2
- Conclusions and perspectives

The N particle problem ...

and its mean-field solution:
N-electron Schrödinger equation

$$\mathcal{H}_N \Psi(r_1, r_2, ..., r_N) = E_N \Psi(r_1, r_2, ..., r_N)$$

with

$$\mathcal{H}_N = H_N^{kinetic} + H_N^{external} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|}$$

becomes separable in mean-field theory:

$$\mathcal{H}_N = \sum_i h_i$$

For example, using the Hartree(-Fock) mean field:

$$h_i = h_i^{kinetic} + h_i^{external} + e^2 \int dr \frac{n(r)}{|r_i - r|}$$

Solutions are Slater determinants of *one-particle* states, fulfilling

$$h_i \phi(r_i) = \epsilon \phi(r_i)$$

Bloch's theorem => use quantum numbers k, n for 1-particle states
1-particle energies ϵ_{kn} => band structure of the solid

Density functional theory ...

... achieves a mapping onto a separable system (mapping of interacting system onto non-interacting system of the same density *in an effective potential*) for the ground state.
However:

- effective potential unknown => local density approximation
- strictly speaking: not for excited states

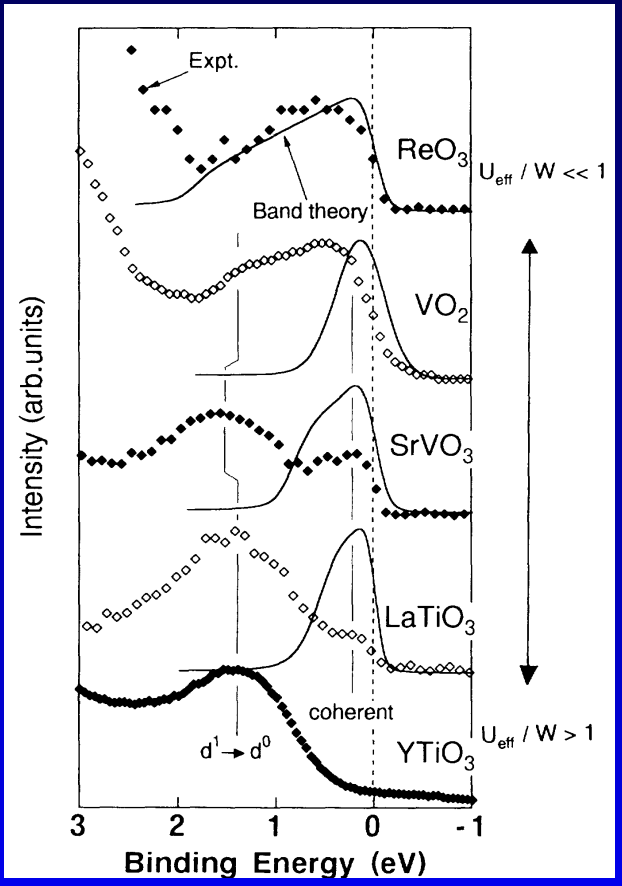
In practice (and with the above caveats):
DFT-LDA can be viewed as a specific choice for a mean field

Electronic Correlations

General definition:
Electronic correlations are those effects of the inter-actions between electrons that cannot be described by a mean field.

More specific definitions:
Electronic correlations are effects beyond

- ... Hartree(-Fock)
- ... DFT-LDA$^{(*)}$
- ... the “best possible” one-particle picture



(from Fujimori et al., 1992)

Two regimes of failures of LDA

1. “weak coupling”: moderate correlations, perturbative approaches work (e.g. “GW approximation”) (see Patrick Rinke’s lecture)

2. “strong coupling”: strong correlations, non-perturbative approaches needed (e.g dynamical mean field theory)

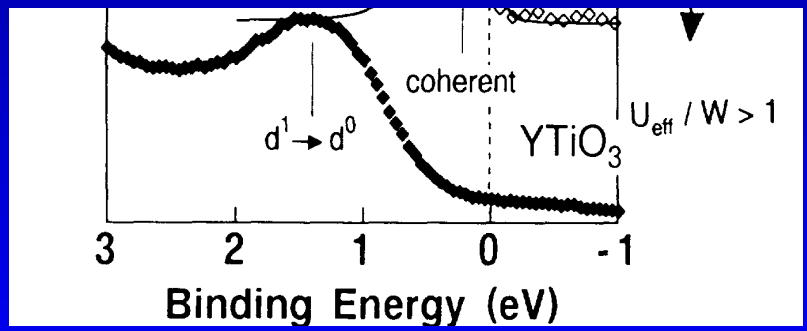
NB. Traditionally two communities, different techniques, but which in recent years have started to merge ...

NB. Correlation effects can show up in some quantities more than in others!

Problems of DFT-LDA...

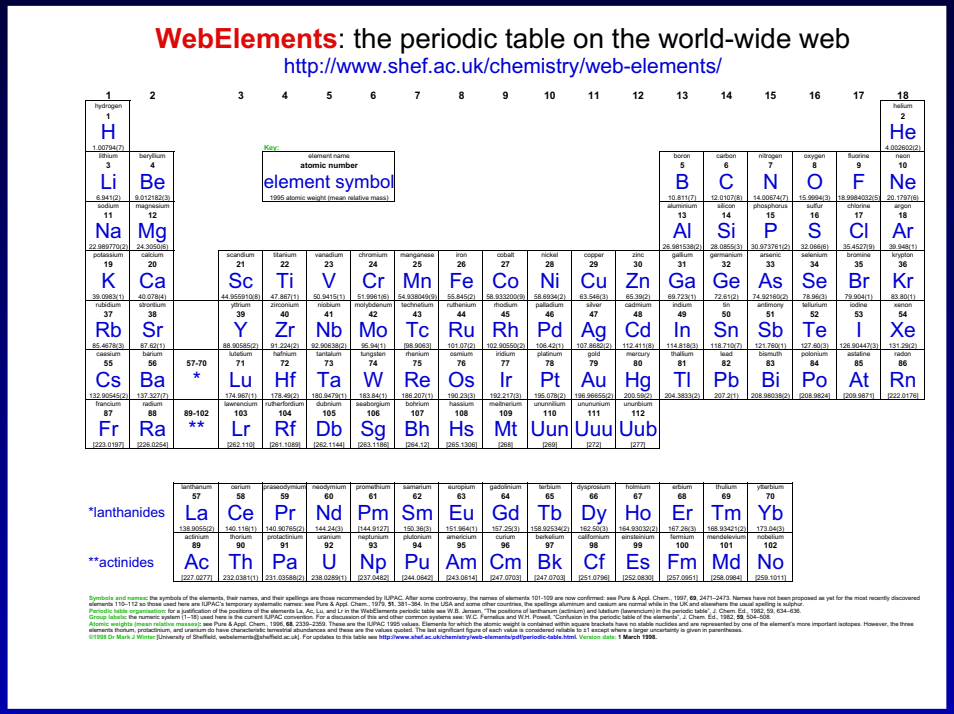
- 30% error in volume of δ-Pu by DFT-LDA$^{(*)}$
- α-γ transition in Ce not described by LDA
- correlation effects in Ni, Fe, Mn ...
- LDA misses insulating phases of certain oxides (VO_2, V_2O_3, $LaTiO_3$, $YTiO_3$, Ti_2O_3 ...)
- bad description of spectra of some metallic compounds ($SrVO_3$, $CaVO_3$ ...)

E.g. photoemission of $YTiO_3$:



Correlated Materials ...

... typically contain partially filled d- or f-shells



WebElements: the periodic table on the world-wide web

http://www.shef.ac.uk/chemistry/web-elements/

1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
hydrogen 1 H 1.00794(7)																		helium 2 He 4.002602(2)
lithium 3 Li 6.941(2)	beryllium 4 Be 9.012182(3)												boron 5 B 10.811(7)	carbon 6 C 12.0107(8)	nitrogen 7 N 14.00674(7)	oxygen 8 O 15.9994(3)	fluorine 9 F 18.9984032(5)	neon 10 Ne 20.1797(6)
sodium 11 Na 22.989770(2)	magnesium 12 Mg 24.3050(6)												aluminium 13 Al 26.981538(2)	silicon 14 Si 28.0855(3)	phosphorus 15 P 30.973761(2)	sulfur 16 S 32.066(6)	chlorine 17 Cl 35.4527(9)	argon 18 Ar 39.948(1)
potassium 19 K 39.0983(1)	calcium 20 Ca 40.078(4)		scandium 21 Sc 44.955910(8)	titanium 22 Ti 47.867(1)	vanadium 23 V 50.9415(1)	chromium 24 Cr 51.9961(6)	manganese 25 Mn 54.938049(9)	iron 26 Fe 55.845(2)	cobalt 27 Co 58.933200(9)	nickel 28 Ni 58.6934(2)	copper 29 Cu 63.546(3)	zinc 30 Zn 65.39(2)	gallium 31 Ga 69.723(1)	germanium 32 Ge 72.61(2)	arsenic 33 As 74.92160(2)	selenium 34 Se 78.96(3)	bromine 35 Br 79.904(1)	krypton 36 Kr 83.80(1)
rubidium 37 Rb 85.4678(3)	strontium 38 Sr 87.62(1)		yttrium 39 Y 88.90585(2)	zirconium 40 Zr 91.224(2)	niobium 41 Nb 92.90638(2)	molybdenum 42 Mo 95.94(1)	technetium 43 Tc [98.9063]	ruthenium 44 Ru 101.07(2)	rhodium 45 Rh 102.90550(2)	palladium 46 Pd 106.42(1)	silver 47 Ag 107.8682(2)	cadmium 48 Cd 112.411(8)	indium 49 In 114.818(3)	tin 50 Sn 118.710(7)	antimony 51 Sb 121.760(1)	tellurium 52 Te 127.60(3)	iodine 53 I 126.90447(3)	xenon 54 Xe 131.29(2)
caesium 55 Cs 132.90545(2)	barium 56 Ba 137.327(7)	57-70 *	lutetium 71 Lu 174.967(1)	hafnium 72 Hf 178.49(2)	tantalum 73 Ta 180.9479(1)	tungsten 74 W 183.84(1)	rhenium 75 Re 186.207(1)	osmium 76 Os 190.23(3)	iridium 77 Ir 192.217(3)	platinum 78 Pt 195.078(2)	gold 79 Au 196.96655(2)	mercury 80 Hg 200.59(2)	thallium 81 Tl 204.3833(2)	lead 82 Pb 207.2(1)	bismuth 83 Bi 208.98038(2)	polonium 84 Po [208.9824]	astatine 85 At [209.9871]	radon 86 Rn [222.0176]
francium 87 Fr [223.0197]	radium 88 Ra [226.0254]	89-102 **	lawrencium 103 Lr [262.110]	rutherfordium 104 Rf [261.1089]	dubnium 105 Db [262.1144]	seaborgium 106 Sg [263.1186]	bohrium 107 Bh [264.12]	hassium 108 Hs [265.1306]	meitnerium 109 Mt [268]	ununnilium 110 Uun [269]	unununium 111 Uuu [272]	ununbium 112 Uub [277]						

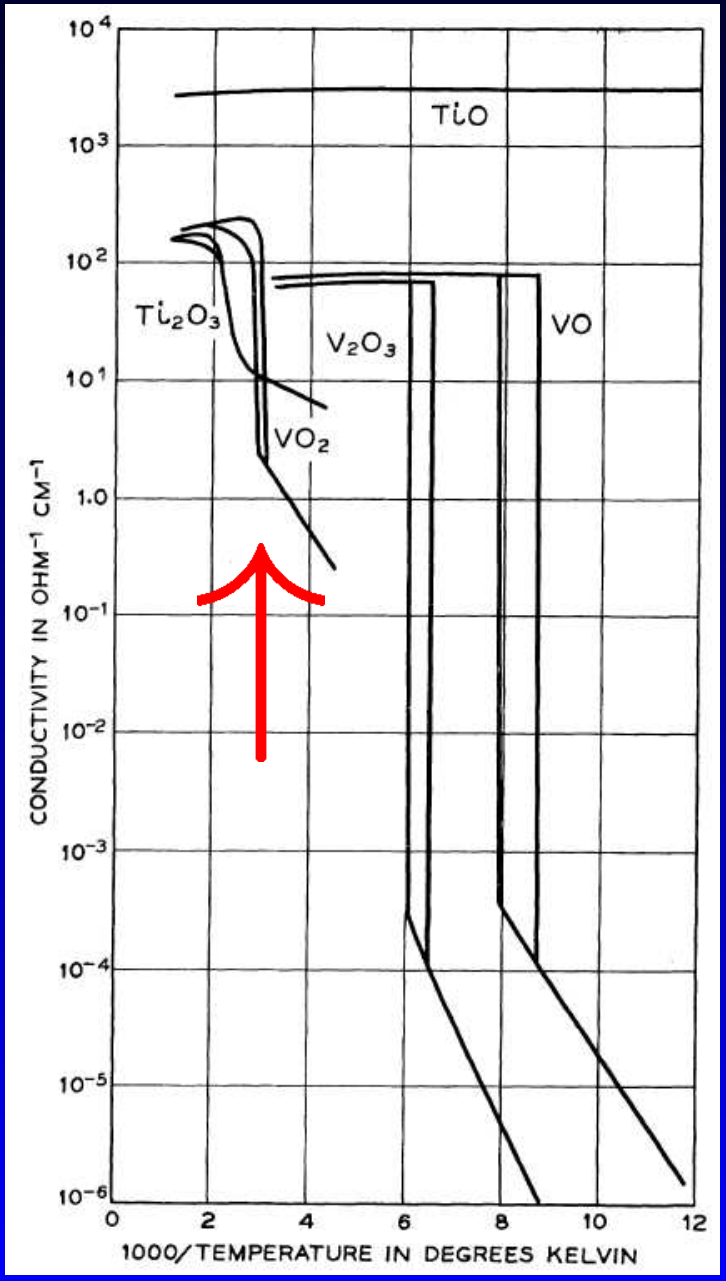
*lanthanides	lanthanum 57 La 138.9055(2)	cerium 58 Ce 140.116(1)	praseodymium 59 Pr 140.90765(2)	neodymium 60 Nd 144.24(3)	promethium 61 Pm [144.9127]	samarium 62 Sm 150.36(3)	europium 63 Eu 151.964(1)	gadolinium 64 Gd 157.25(3)	terbium 65 Tb 158.92534(2)	dysprosium 66 Dy 162.50(3)	holmium 67 Ho 164.93032(2)	erbium 68 Er 167.26(3)	thulium 69 Tm 168.93421(2)	ytterbium 70 Yb 173.04(3)
**actinides	actinium 89 Ac [227.0277]	thorium 90 Th 232.0381(1)	protactinium 91 Pa 231.03588(2)	uranium 92 U 238.0289(1)	neptunium 93 Np [237.0482]	plutonium 94 Pu [244.0642]	americium 95 Am [243.0614]	curium 96 Cm [247.0703]	berkelium 97 Bk [247.0703]	californium 98 Cf [251.0796]	einsteinium 99 Es [252.0830]	fermium 100 Fm [257.0951]	mendelevium 101 Md [258.0984]	nobelium 102 No [259.1011]

Key: element name, atomic number, element symbol, 1995 atomic weight (mean relative mass)

Symbols and names: the symbols of the elements, their names, and their spellings are those recommended by IUPAC. After some controversy, the names of elements 101-109 are now confirmed: see Pure & Appl. Chem., 1997, **69**, 2471–2473. Names have not been proposed as yet for the most recently discovered elements 110–112 so those used here are IUPAC's temporary systematic names: see Pure & Appl. Chem., 1979, **51**, 381–384. In the USA and some other countries, the spellings aluminum and cesium are normal while in the UK and elsewhere the usual spelling is sulphur.
Periodic table organisation: for a justification of the positions of the elements Lu, Ac, Lr, and Lr in the WebElements periodic table see W.B. Jensen, "The positions of lanthanum (actinium) and lutetium (lawrencium) in the periodic table", J. Chem. Ed., 1982, **59**, 634–636.
Group labels: the numeric system (1–18) used here is the current IUPAC convention. For a discussion of this and other common systems see: W.C. Fernelius and W.H. Powell, "Confusion in the periodic table of the elements", J. Chem. Ed., 1982, **59**, 504–508.
Atomic weights (mean relative masses): see Pure & Appl. Chem., 1998, **68**, 2339–2359. These are the IUPAC 1995 values. Elements for which the atomic weight is contained within square brackets have no stable nuclides and are represented by one of the element's more important isotopes. However, the three elements thorium, protactinium, and uranium do have characteristic terrestrial abundances and these are the values quoted. The last significant figure of each value is considered reliable to ±1 except where a larger uncertainty is given in parentheses.
©1998 Dr Mark J Winter (University of Sheffield, webelements@sheffield.ac.uk). For updates to this table see http://www.shef.ac.uk/chemistry/web-elements/pdf/periodic-table.html. Version date: 1 March 1998.

→ transition metal oxides/sulfides, rare earth or actinide compounds
(but also: low-dimensional systems, organics ...)

Metal-Insulator Transitions

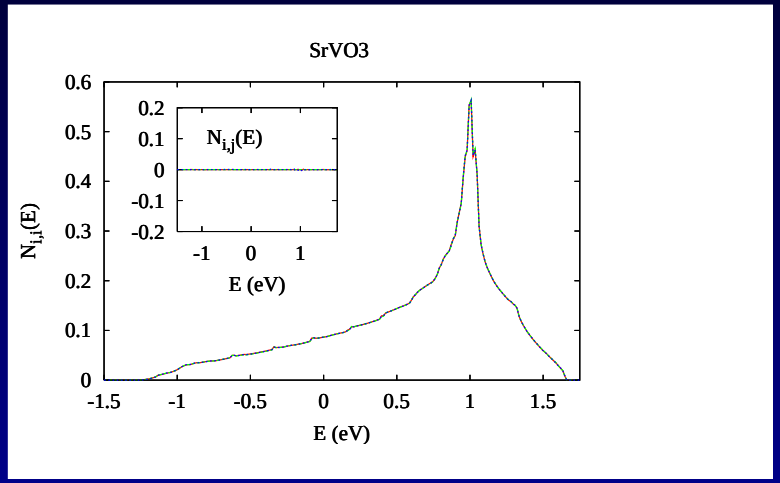


Metal-insulator transition in VO_2 at T_c=340 K

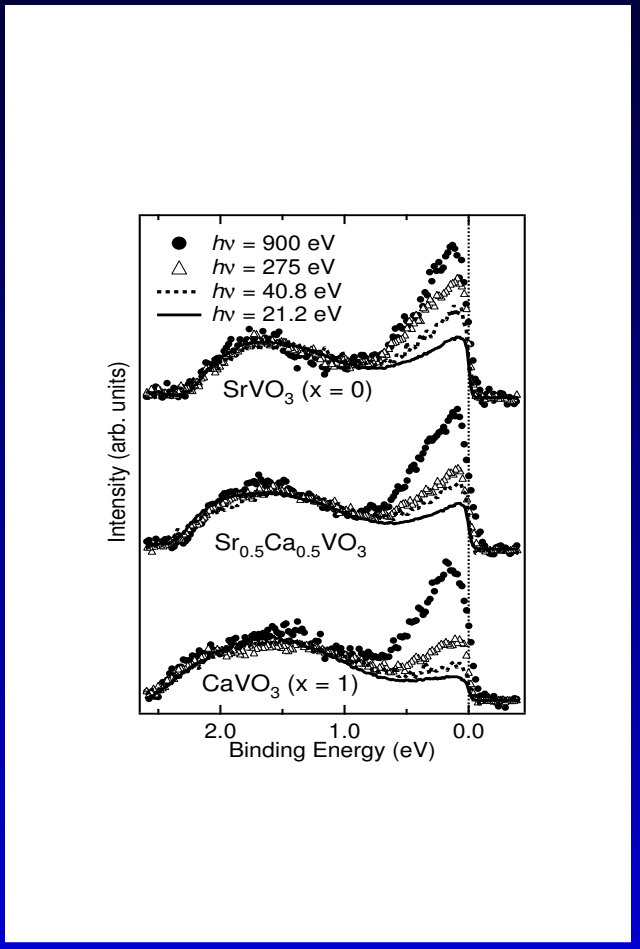
Morin et al., 1959

$SrVO_3$: a correlated metal

$SrVO_3$ within DFT-LDA



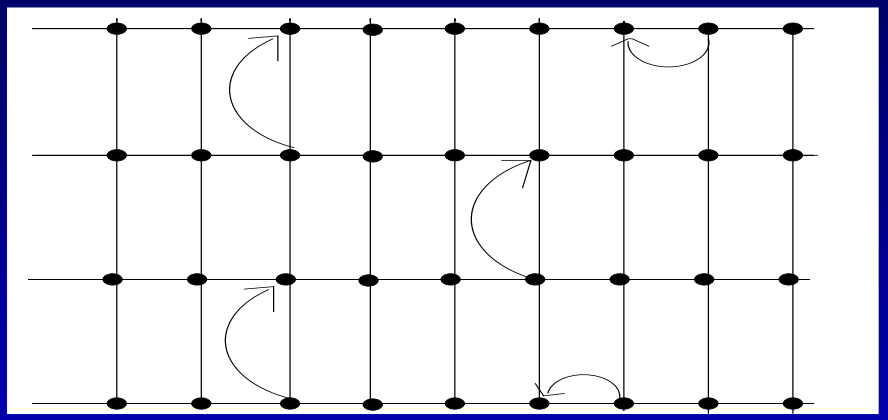
Photoemission



(Sekiyama et al. 2003)

The Hubbard model

$$H = -\frac{D}{2} \sum_{<ij>\sigma} \left(c^{\dagger}_{i\sigma} c_{j\sigma} + c^{\dagger}_{j\sigma} c_{i\sigma} \right) + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$



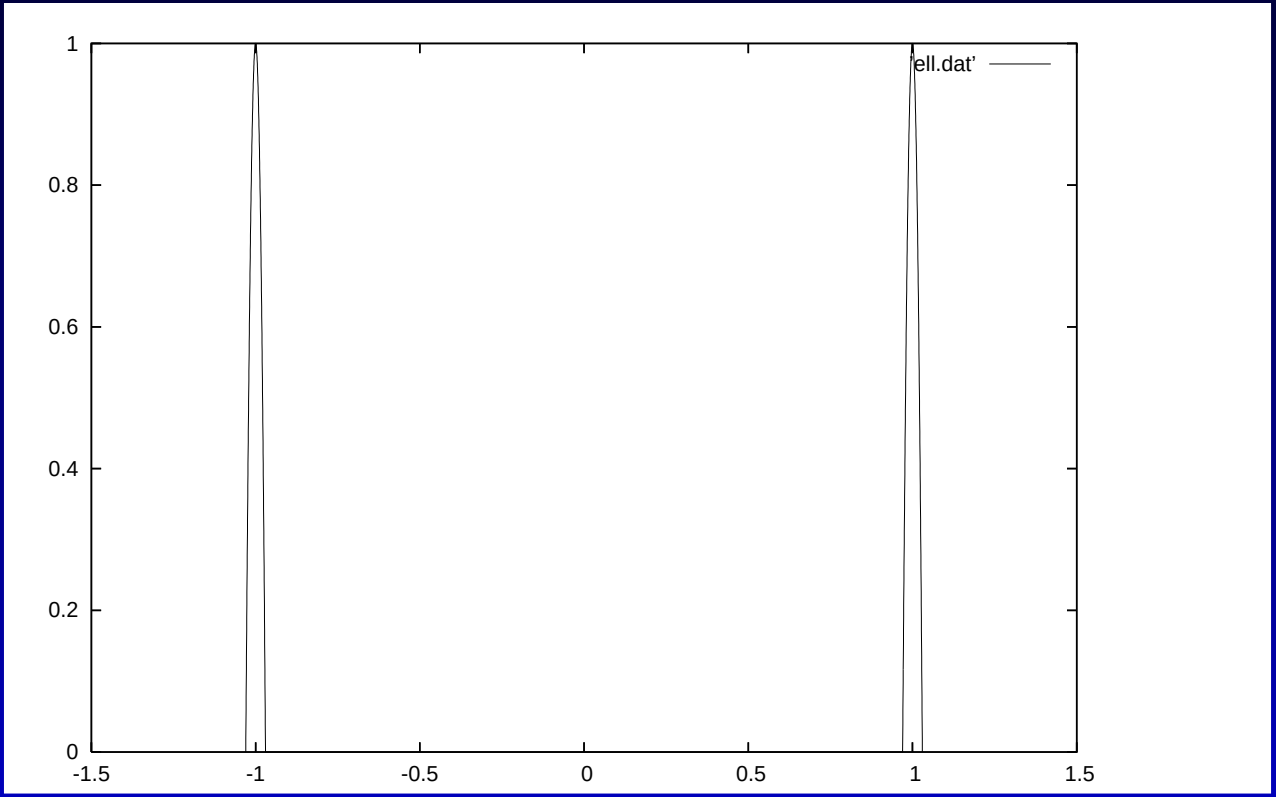
(Hubbard, 1963)

Ground state at half-filling and finite U: antiferromagnetic

Frustrated model $\rightarrow$ paramagnetic solution ?

Spectra for one atom

Electron removal and addition spectra



$E = \epsilon$ $E = \epsilon + U$

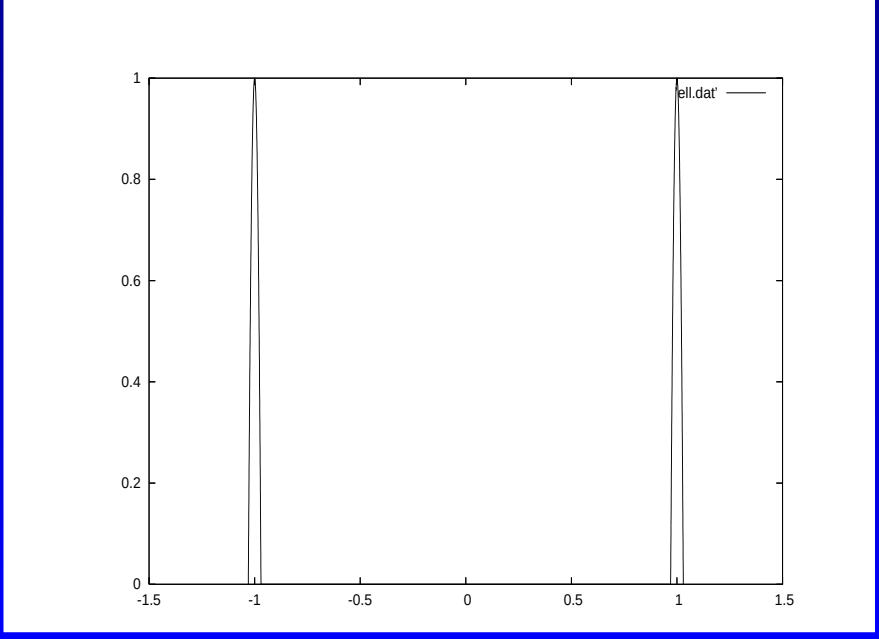
U=Coulomb interaction between two 1s electrons

Atomic limit: D=0

$$H = U \sum_i n_{i\uparrow} n_{i\downarrow}$$

$\rightarrow$ atomic eigenstates, localized in *real* space

Spectral function = discrete peaks separated by U

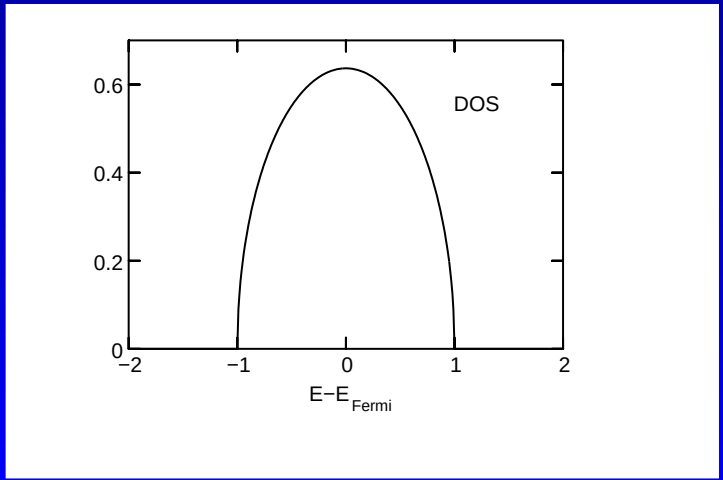


Non-interacting limit: U=0

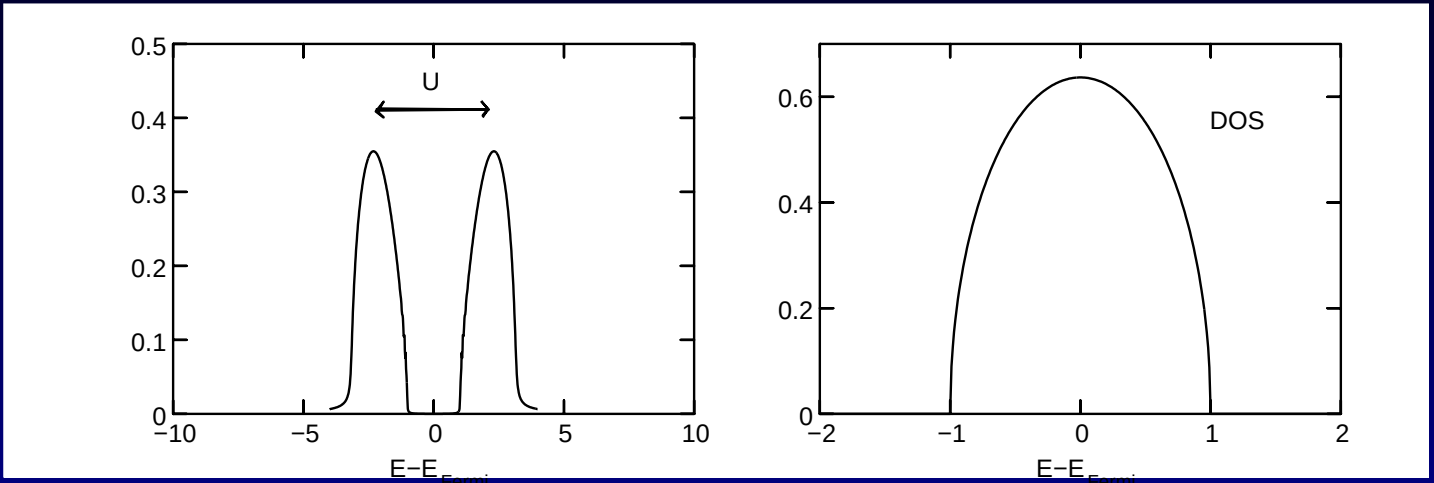
$$H = -\frac{D}{2} \sum_{<ij>\sigma} \left(c^{\dagger}_{i\sigma} c_{j\sigma} + c^{\dagger}_{j\sigma} c_{i\sigma} \right) = \sum_{k\sigma} \epsilon_k c^{\dagger}_{k\sigma} c_{k\sigma}$$

with e.g. $\epsilon_k = -D[cos(k_x) + cos(k_y) + cos(k_z))$ on a 3D square lattice (lattice constant 1) with nearest neighbor hopping.

Spectral function = non-interacting DOS



“Atomic” and “band-like” spectra



“Spectral function” $\rho(\omega)$ probes possibility of adding/removing an electron at energy ω.

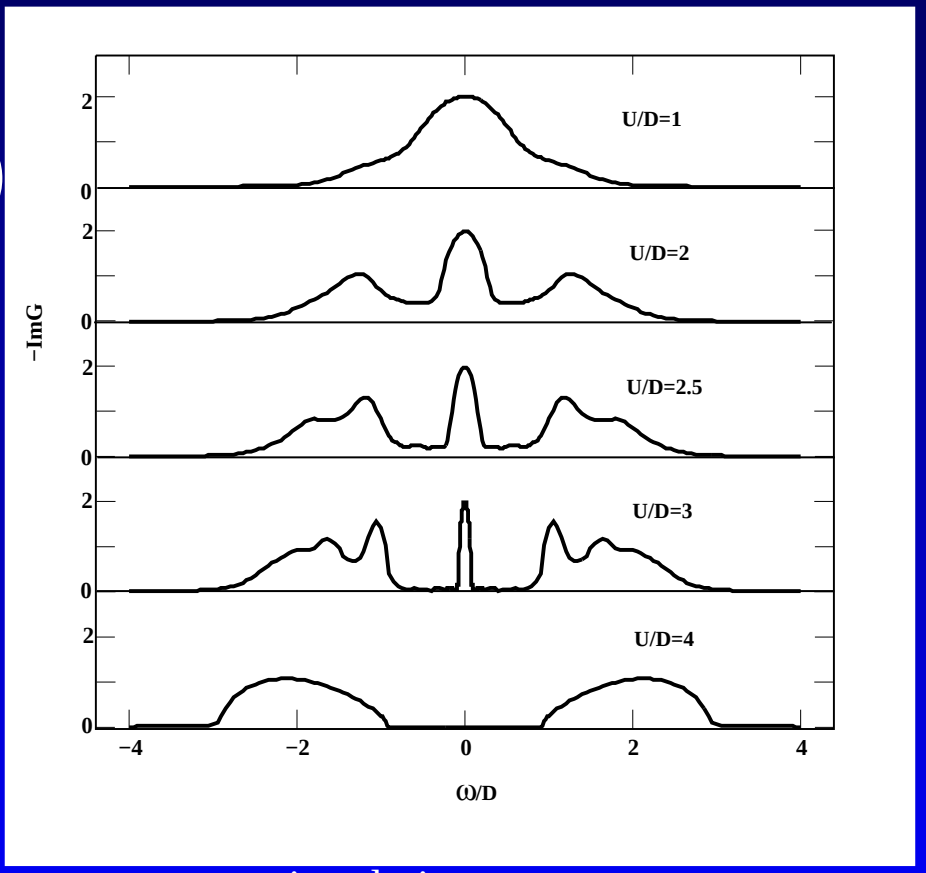
In non-interacting case: $\rho(\omega)$= DOS.
In general case: relaxation effects!
In “atomic limit”: probe local Coulomb interaction

Hubbard model within DMFT$^{(*)}$

$$H = -\frac{D}{2} \sum_{<ij>\sigma} \left(c^{\dagger}_{i\sigma} c_{j\sigma} + c^{\dagger}_{j\sigma} c_{i\sigma} \right) + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$

(Hubbard, 1963)

$\rho(\omega)$



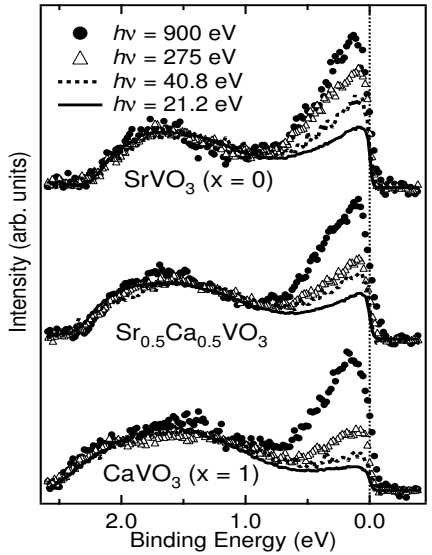
Quasi-particle peak
Hubbard bands

Georges & Kotliar 1992

$(*)$ DMFT = Dynamical Mean Field Theory, paramagnetic solution

Spectra of perovskites

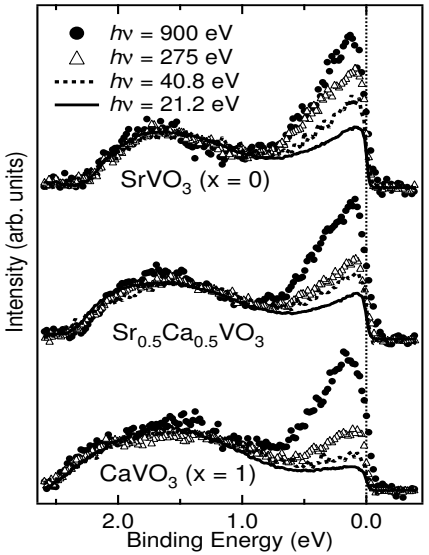
Photoemission

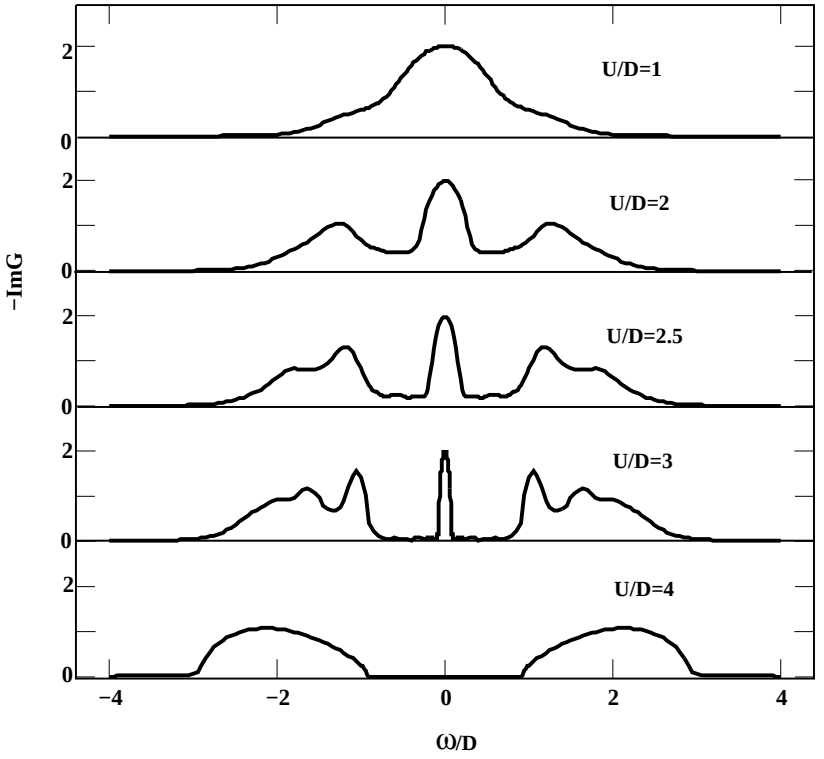


(Sekiyama et al. 2003)

Spectra of perovskites

Photoemission





(Sekiyama et al. 2003)

Green's function – survival kit

$$\rho(\omega) = -\frac{1}{\pi}\Im G_{ii}(\omega)$$

Definition of Green's function:

$$G_{ij}(t) = -\langle \hat{T} c_i(t) c_j^\dagger(0) \rangle$$

Quasi-particles are poles of

$$G(k,\omega) = \frac{1}{\omega + \mu - \epsilon_o(k) - \Sigma(k,\omega)}$$

All correlations are hidden in the *self-energy*:

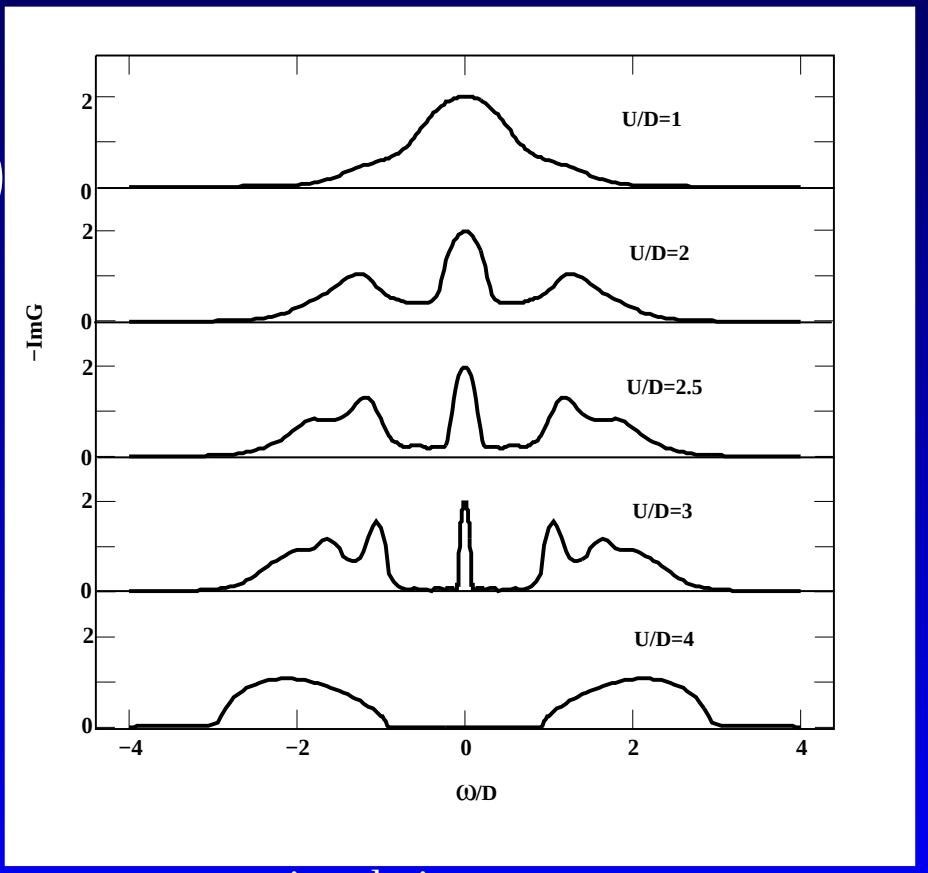
$$\Sigma(k,\omega) = G_0^{-1}(k,\omega) - G^{-1}(k,\omega)$$

Hubbard model within DMFT$^{(*)}$

$$H = -\frac{D}{2} \sum_{<ij>\sigma} \left(c^{\dagger}_{i\sigma} c_{j\sigma} + c^{\dagger}_{j\sigma} c_{i\sigma} \right) + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$

(Hubbard, 1963)

$\rho(\omega)$



Quasi-particle peak
Hubbard bands

Georges & Kotliar 1992

$(*)$ DMFT = Dynamical Mean Field Theory, paramagnetic solution

The “mechanism” ?

$\Sigma''(\omega)$ diverges for $\omega \to 0$ (i.e. at the Fermi level):
Quasi-particle lifetime ($\sim 1/\Sigma''(\omega = 0)$) vanishes!
$\to$ Opening of a gap at the Fermi level $\omega = 0$

$$\begin{aligned} A(k,\omega) &= ImG(k,\omega) \\ &= Im\frac{1}{\omega + \mu - \epsilon_o(k) - \Sigma(k,\omega)} \\ &= -\frac{1}{\pi}\frac{\Sigma''(k,\omega)}{(\omega + \mu - \epsilon_o(k) - \Sigma'(k,\omega))^2 + \Sigma''(k,\omega)^2} \end{aligned}$$

Here (particle-hole symetry and local self-energy):

$$A(k,\omega) = -\frac{1}{\pi}\frac{\Sigma''(\omega)}{(\omega - \epsilon_o(k))^2 + \Sigma''(\omega)^2}$$

What about the metal?

In a Fermi liquid (local self-energy, for simplicity ...):

$$\begin{aligned} Im\Sigma(\omega) &= -\Gamma\omega^2 + O(\omega^3) \\ Re\Sigma(\omega) &= Re\Sigma(0) + (1 - Z^{-1})\omega + O(\omega^2) \end{aligned}$$

$$A(k,\omega) = \frac{Z^2}{\pi} \frac{-\Im\Sigma(\omega)}{\left(\omega - Z\epsilon_0(k)\right)^2 + \left(-Z\Im\Sigma(\omega)\right)^2} + A_{inkoh}$$

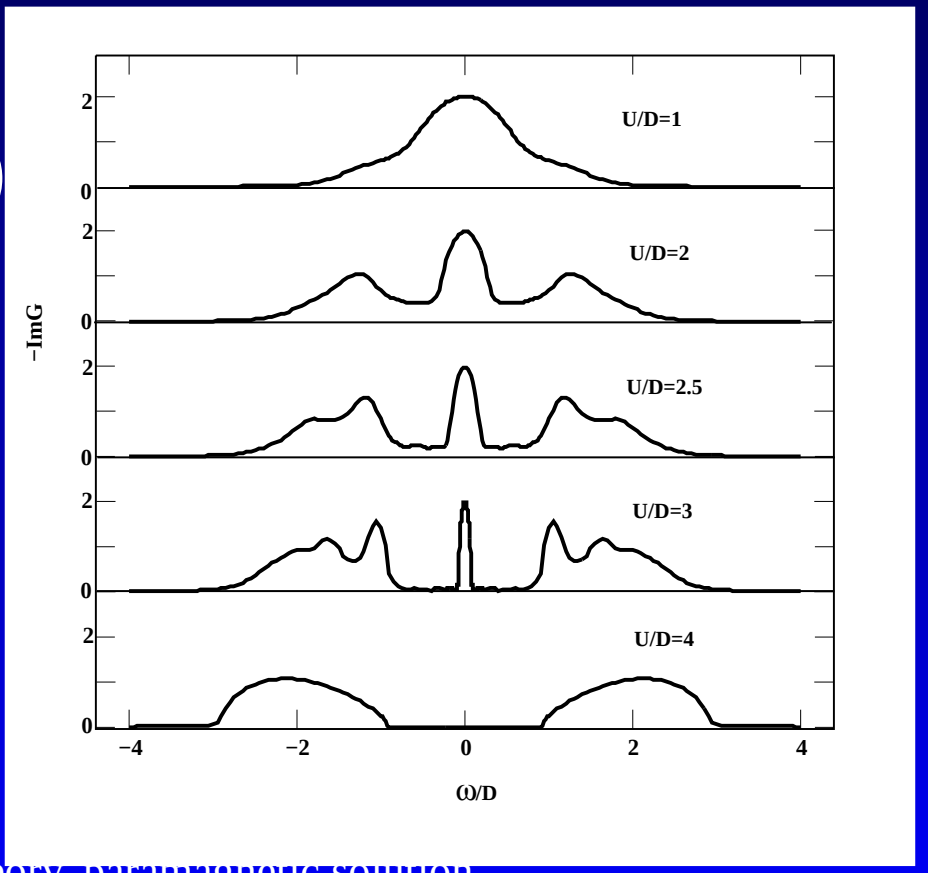
For small Im Σ (i.e. well-defined quasi-particles):
Lorentzian of width ZIm Σ,
poles at renormalized quasi-particle bands $Z\epsilon_0(k)$,
weight Z (instead of 1 in non-interacting case)

Hubbard model within DMFT$^{(*)}$

$$H = -\frac{D}{2} \sum_{<ij>\sigma} \left(c^{\dagger}_{i\sigma} c_{j\sigma} + c^{\dagger}_{j\sigma} c_{i\sigma} \right) + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$

(Hubbard, 1963)

$\rho(\omega)$



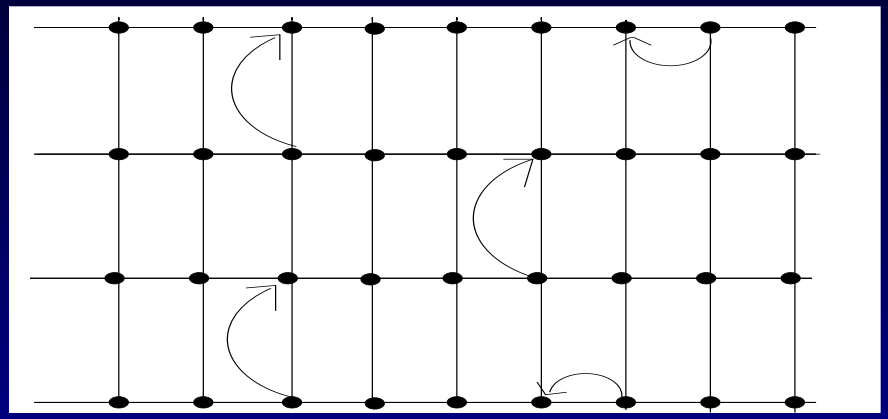
Quasi-particle peak
Hubbard bands

Georges & Kotliar 1992

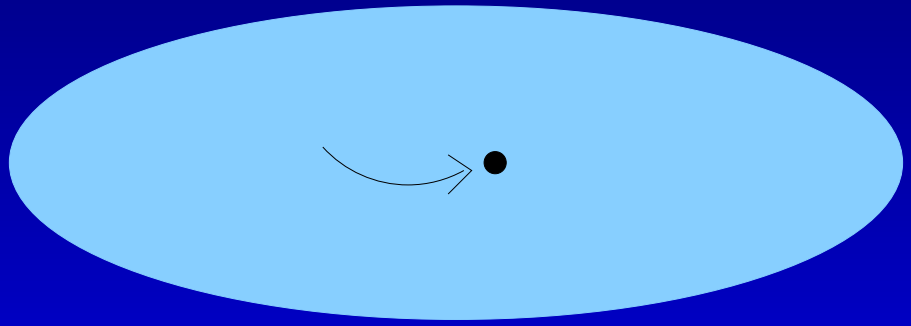
$(*)$ DMFT = Dynamical Mean Field Theory, paramagnetic solution

Dynamical mean field theory ...

... maps a lattice problem



onto a single-site (Anderson impurity) problem



with a self-consistency condition

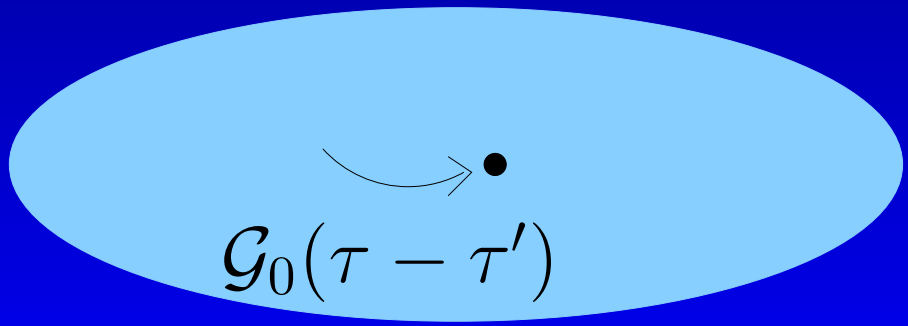
(see e.g. Georges et al., Rev. Mod. Phys. 1996)

Effective dynamics ...

... for *single-site* problem

$$S_{eff} = -\int_0^\beta d\tau \int_0^\beta d\tau' \sum_\sigma c_\sigma^\dagger(\tau)\mathcal{G}_0^{-1}(\tau-\tau')c_\sigma(\tau')$$
$$+ U\int_0^\beta d\tau n_\uparrow n_\downarrow$$

with the dynamical mean field $\mathcal{G}_0^{-1}(\tau-\tau')$

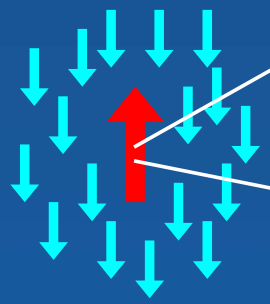


Déjà vu !

ESRF

A Light for Science

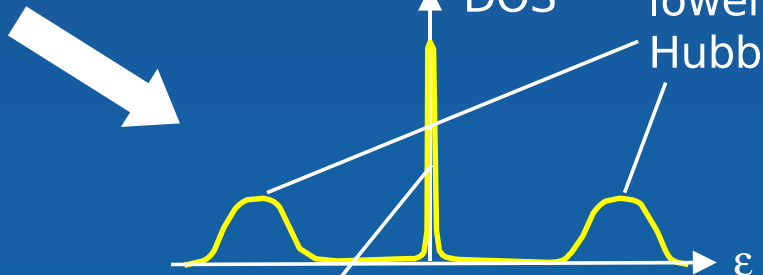
probing magnetic interactions by means of the Kondo effect



magnetic impurity

conduction electrons of host material

correlated singlet state



Kondo resonance near the Fermi level (width $\approx k_B T_K$)

European Synchrotron Radiation Facility

DMFT (contd.)

Green's function:

$$G_{imp}(\tau) = -\langle \hat{T} c(\tau) c^{\dagger}(0) \rangle$$

Self-energy (k-independent):

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

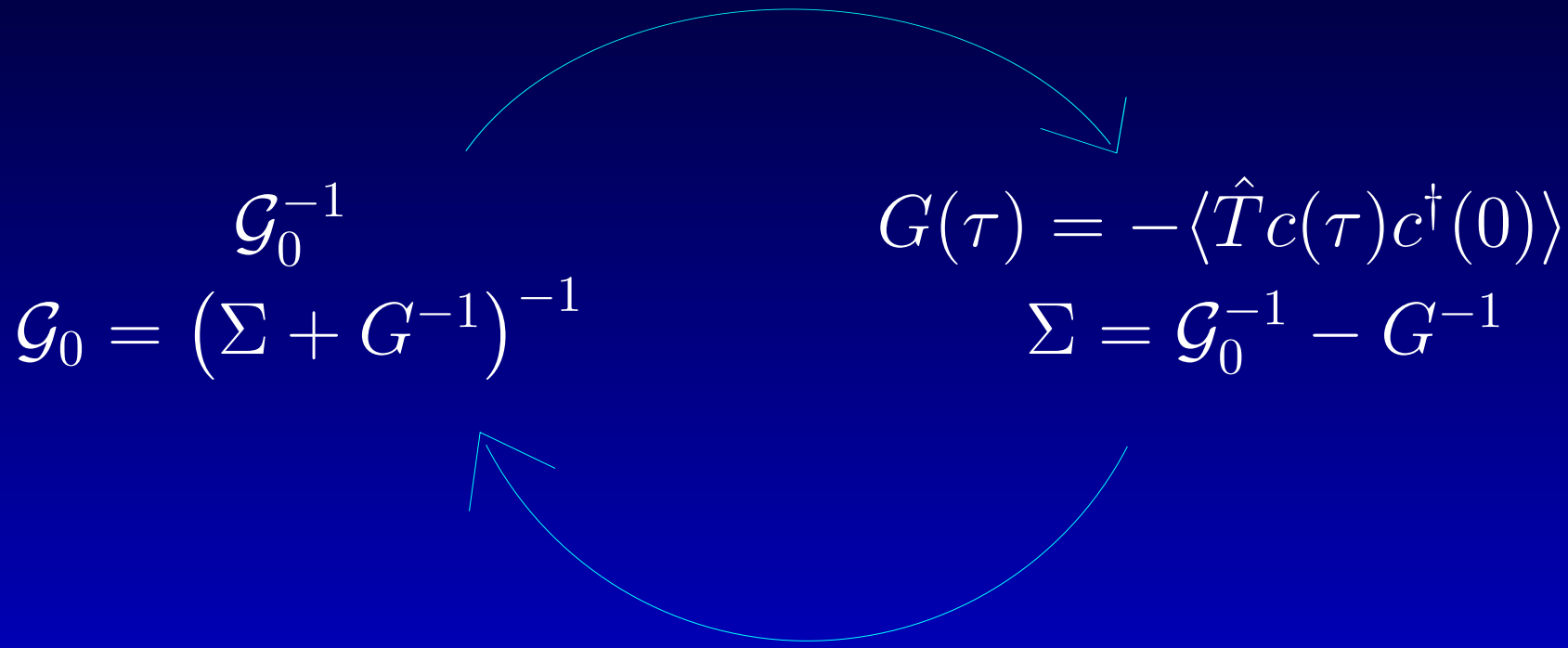
DMFT assumption :

$$\begin{aligned} \Sigma_{imp} &= \Sigma^{lattice} \\ G_{imp} &= G_{local}^{lattice} \end{aligned}$$

$\rightarrow$ Self-consistency condition for $\mathcal{G}_0^{-1}$

The DMFT self-consistency cycle

Anderson impurity model solver

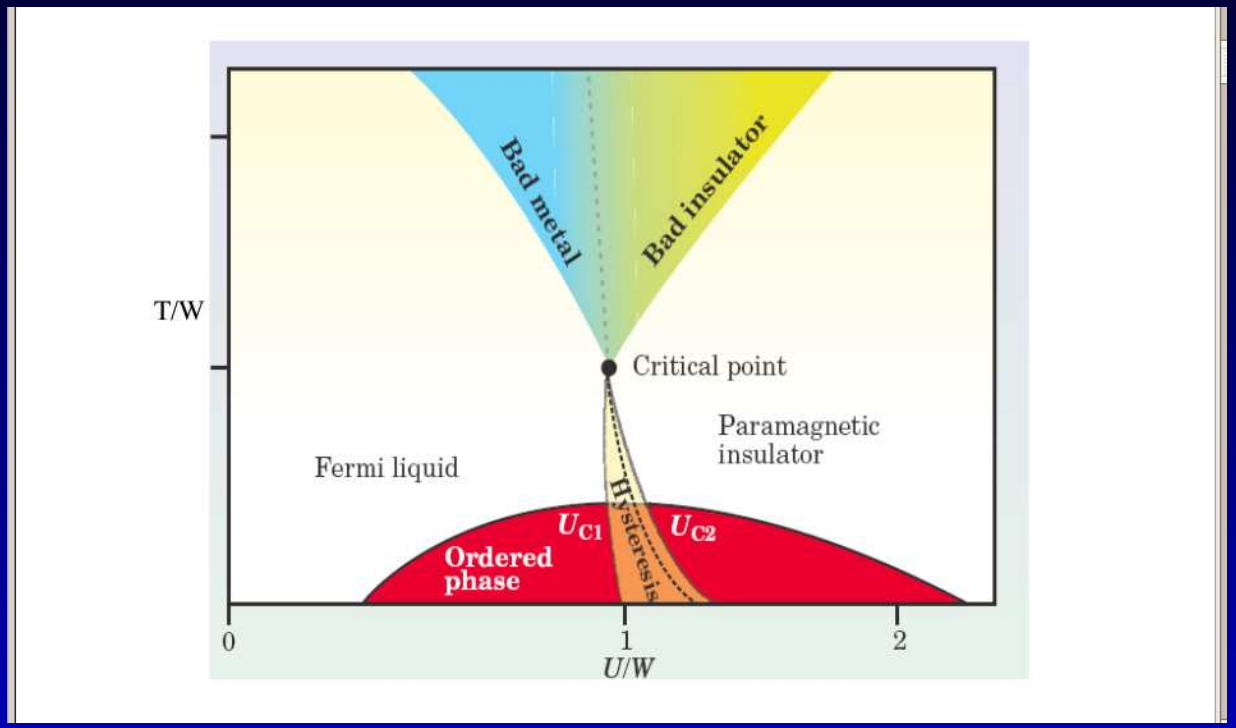


Self-consistency condition:

$$G(\omega) = \sum_k \frac{1}{\omega + \mu - \epsilon_k - \Sigma(\omega)}$$

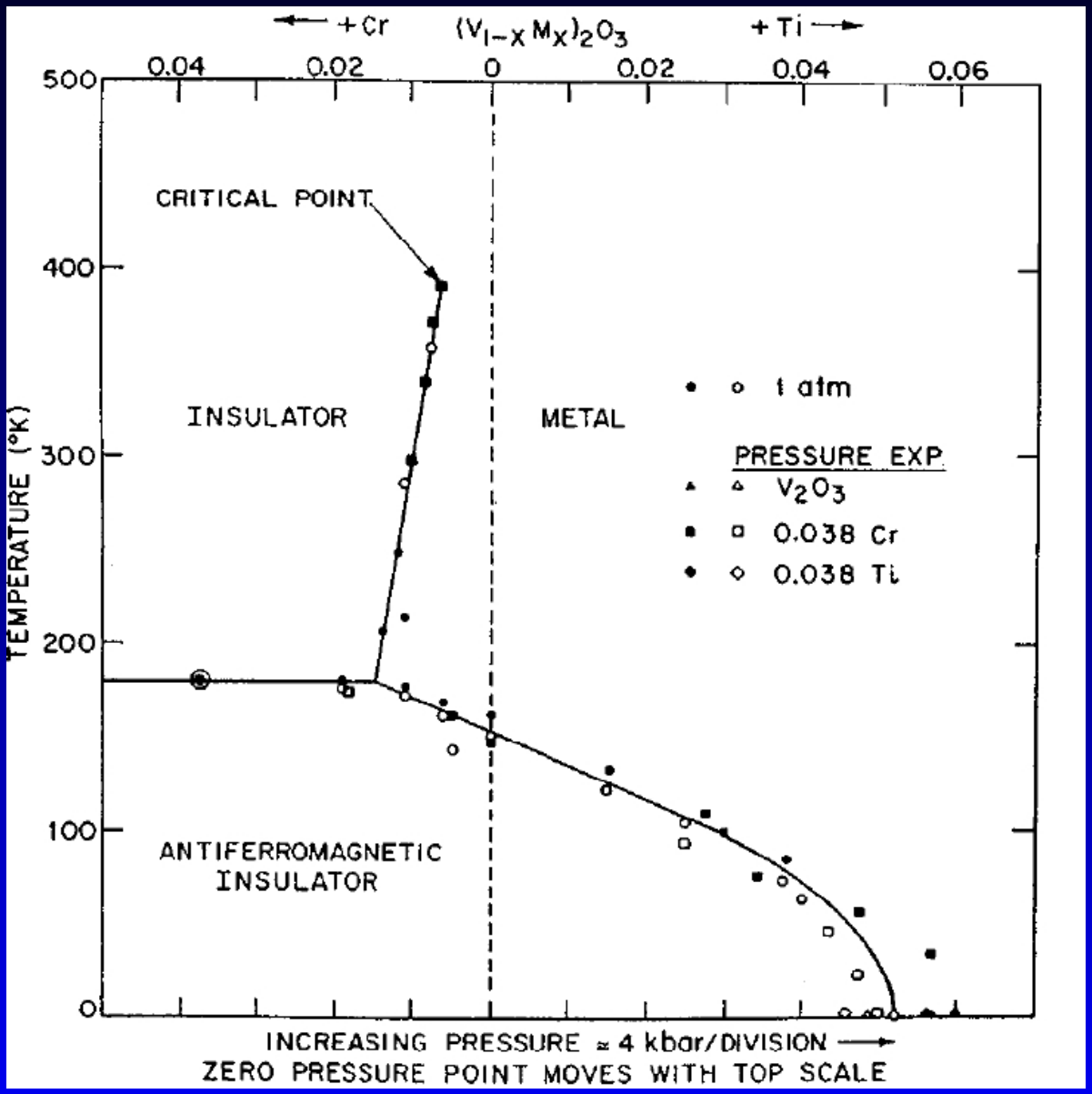
Hubbard model – again

Phase diagram of half-filled model within DMFT:



First order metal-insulator transition (ending in 2nd order critical points)

Real materials ... : V_2O_3



Realistic Approach to Correlations

Combine DMFT with band structure calculations
(Anisimov et al. 1997, Lichtenstein et al. 1998)

$\rightarrow$ effective one-particle Hamiltonian within LDA
$\rightarrow$ represent in localized basis
$\rightarrow$ add Hubbard interaction term for correlated orbitals
$\rightarrow$ solve within Dynamical Mean Field Theory

LDA+DMFT

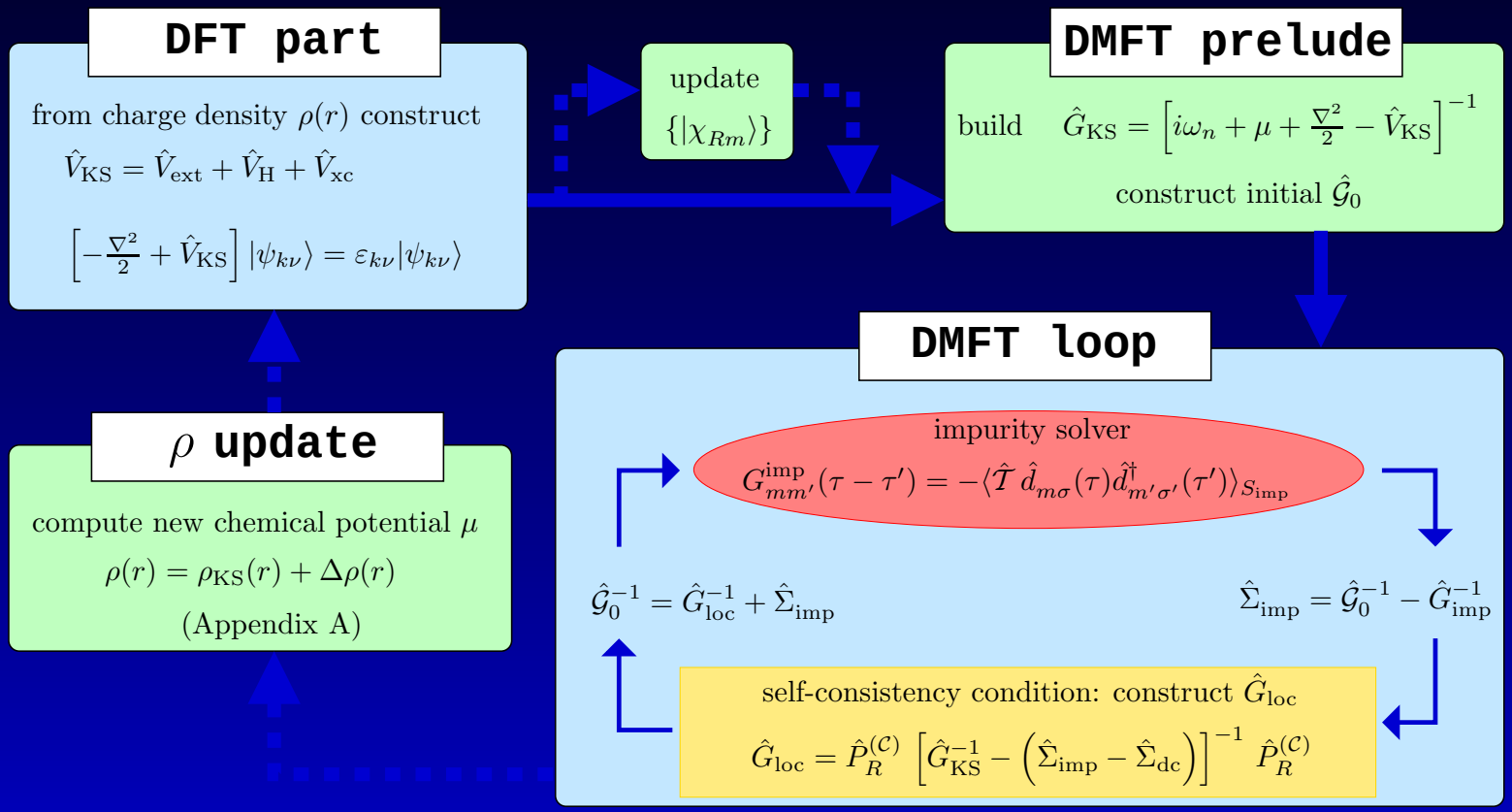
$$H = \sum_{\{im\sigma\}} (H^{LDA}_{im,i'm'} - H^{double\ counting}_{im,i'm'}) a^{+}_{im\sigma} a_{i'm'\sigma}$$

$$+ \frac{1}{2} \sum_{imm'\sigma \text{ (correl. orb.)}} U^{i}_{mm'} n_{im\sigma} n_{im'-\sigma}$$

$$+ \frac{1}{2} \sum_{im\neq m'\sigma \text{ (correl. orb.)}} (U^{i}_{mm'} - J^{i}_{mm'}) n_{im\sigma} n_{im'\sigma}$$

$\rightarrow$ solve withing DMFT

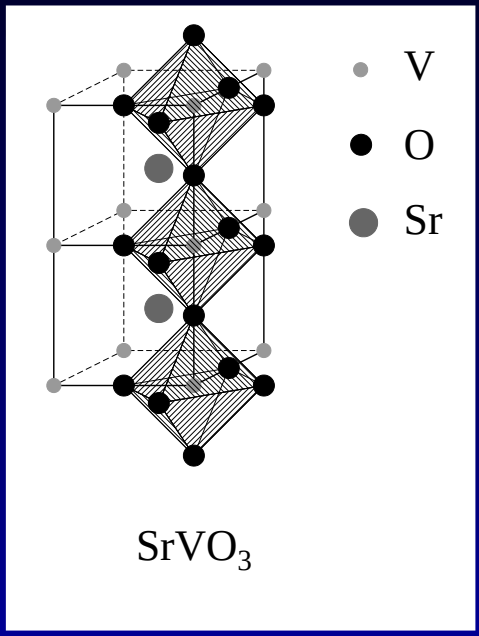
LDA+DMFT – the full scheme



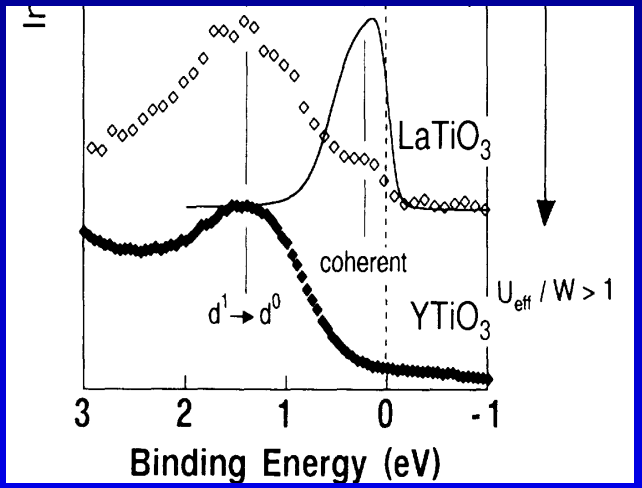
F. Lechermann, A. Georges, A. Poteryaev, S. B., M. Posternak, A. Yamasaki, O. K. Andersen, Phys. Rev. B **74** 125120 (2006)

Some examples

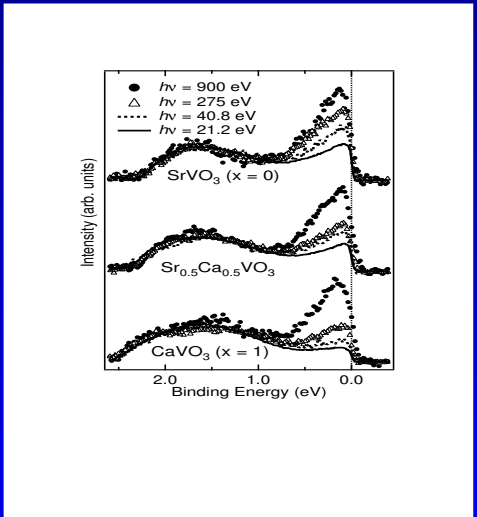
$SrVO_3$: (correlated) metal
$CaVO_3$: (correlated) metal
$LaTiO_3$: at Mott transition
$YTiO_3$: insulator



Photoemission spectra:

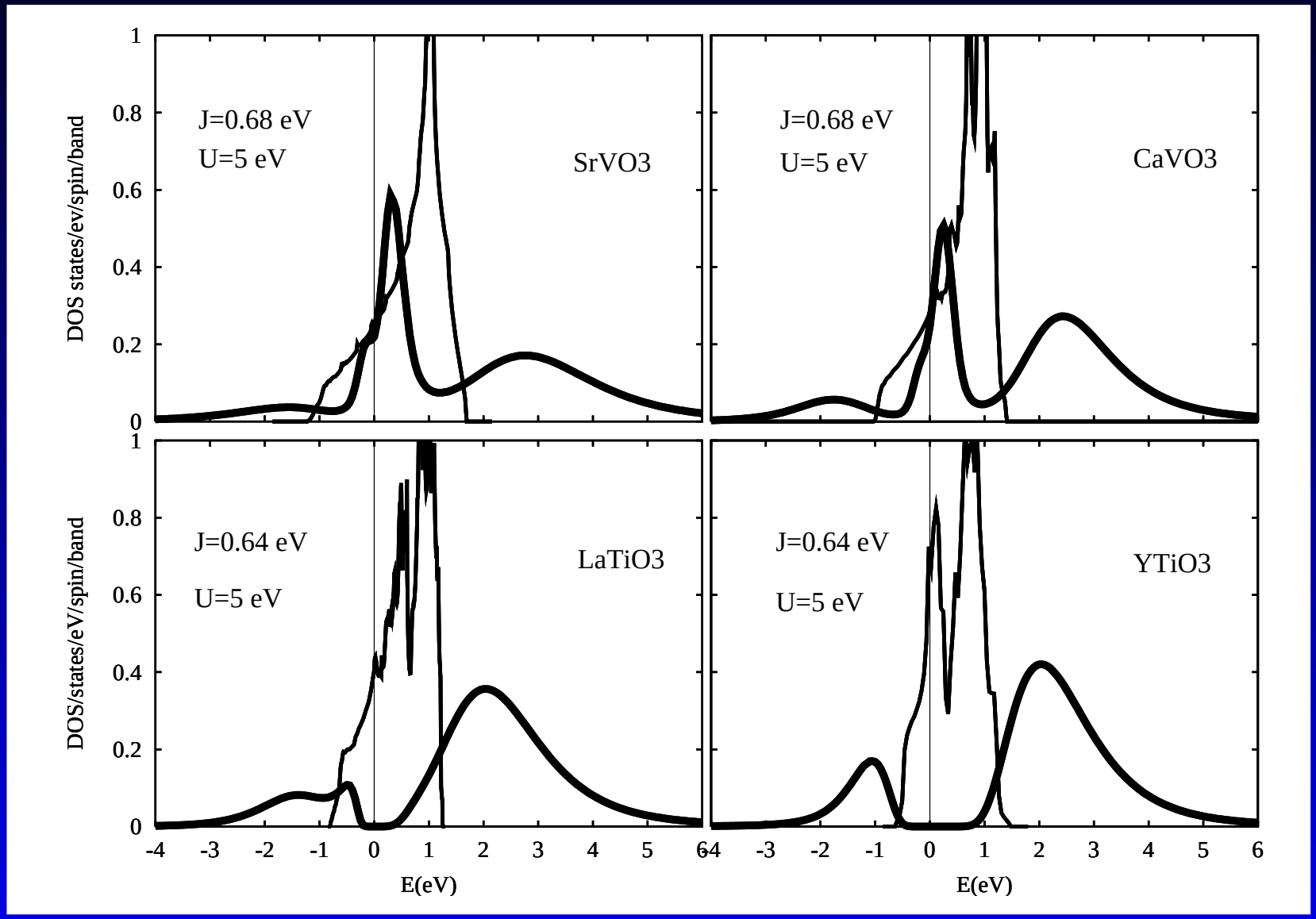


Fujimori et al. 1992



Sekiyama et al., 2002

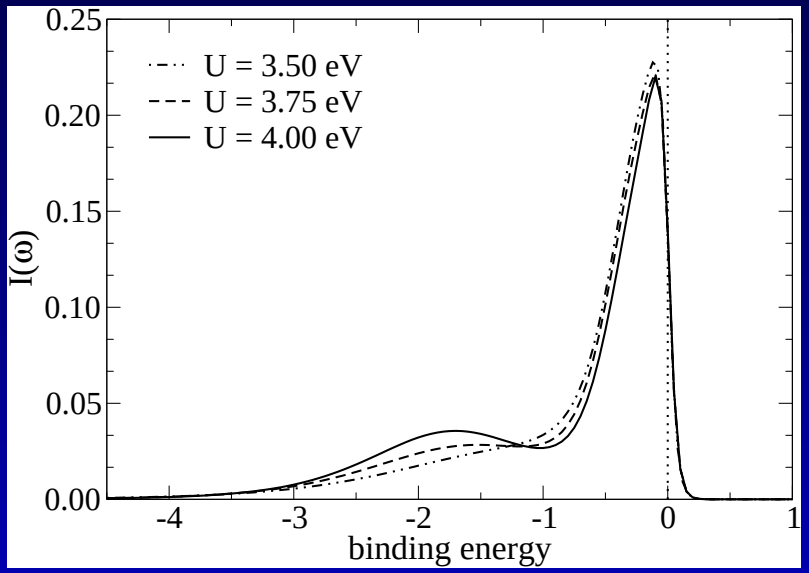
LDA+DMFT: spectra of perovskites



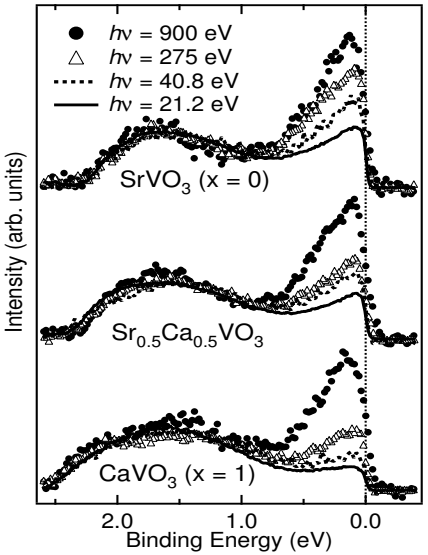
(E. Pavarini, S. B. et al., Phys. Rev. Lett. **92** 176403 (2004))

Spectra of perovskites

$SrVO_3$ LDA+DMFT



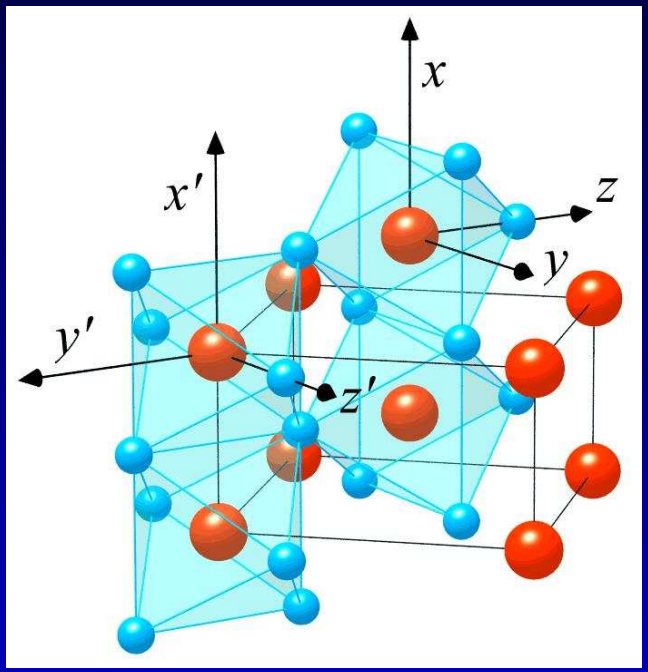
Photoemission

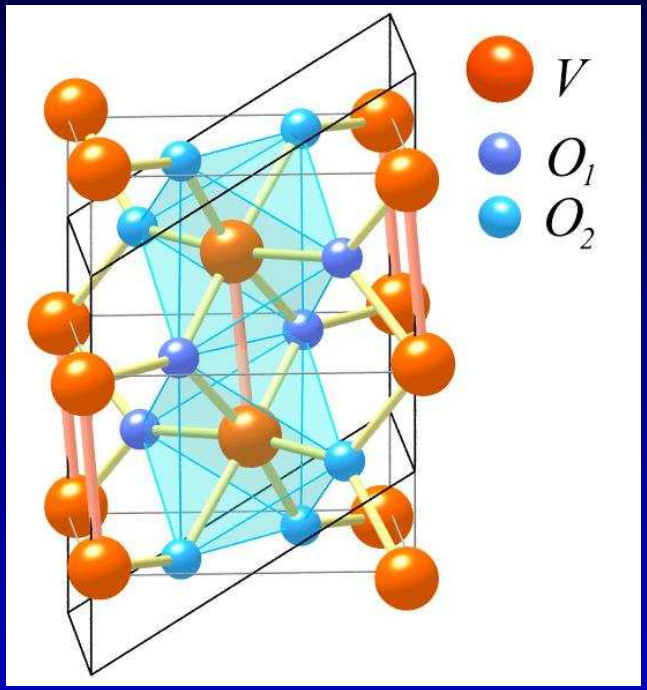


(see also Sekiyama et al. 2003, Lechermann et al. 2006)

Vanadium dioxide: VO_2

Metal-insulator transition accompanied by dimerization of V atoms:





VO_2: Peierls or Mott ?

PHYSICAL REVIEW B VOLUME 11, NUMBER 11 1 JUNE 1975

Metal-insulator transition in vanadium dioxide*

A. Zylbersztejn
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N. F. Mott
Cavendish Laboratory, University of Cambridge, Cambridge, England

(Received 27 November 1974)

VOLUME 35, NUMBER 13 PHYSICAL REVIEW LETTERS 29 SEPTEMBER 1975

Electron Localization Induced by Uniaxial Stress in Pure VO_2

J. P. Pouget and H. Launois
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and

J. P. D'Haenens and P. Merenda
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and

T. M. Rice
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(Received 7 August 1975)

VOLUME 72, NUMBER 21 PHYSICAL REVIEW LETTERS 23 MAY 1994

VO_2: Peierls or Mott-Hubbard? A View from Band Theory

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Department of Physics, State University of New York at Stony Brook, Stony Brook, New York 11794-3800

(Received 24 November 1993)

The electronic and structural properties of VO_2 across its metal-insulator transition are studied using the local-density approximation. Band theory finds a monoclinic distorted ground state in good agreement with experiment, and an almost open gap to charge excitations. Although rigid criteria for distinguishing correlated from band insulators are not available, these findings suggest that VO_2 may be more bandlike than correlated.

Evidence for a Mott-Hubbard metal-insulator transition in VO_2

R. Eguchi,[1,*] M. Taguchi,[1] M. Matsunami,[1] K. Horiba,[1] K. Yamamoto,[1] Y. Ishida,[1] A. Chainani,[1] Y. Takata,[1] M. Yabashi,[2,3] D. Miwa,[2] Y. Nishino,[2] K. Tamasaku,[2] T. Ishikawa,[2,3] Y. Senba,[3] H. Ohashi,[3] Y. Muraoka,[4] Z. Hiroi,[4] and S. Shin[1,4]

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[3]*JASRI/SPring-8, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan*
[4]*Institute for Solid State Physics, University of Tokyo, Kashiwanoha, Kashiwa, Chiba 277-8581, Japan*

(Dated: July 28, 2006)

PRL 97, 266401 (2006) PHYSICAL REVIEW LETTERS week ending 31 DECEMBER 2006

Monoclinic and Correlated Metal Phase in VO_2 as Evidence of the Mott Transition: Coherent Phonon Analysis

in-Tak Kim,[1,*] Yong Wook Lee,[1] Bong-Jun Kim,[1] Byung-Gyu Chae,[1] Sun Jin Yun,[1] Kwang-Yong Kang,[1] Kang-Jeon Han,[2] Ki-Ju Yee,[2] and Yong-Sik Lim[3]

[1]*IT Convergence and Components Research Laboratory, ETRI, Daejeon 305-350, Republic of Korea*
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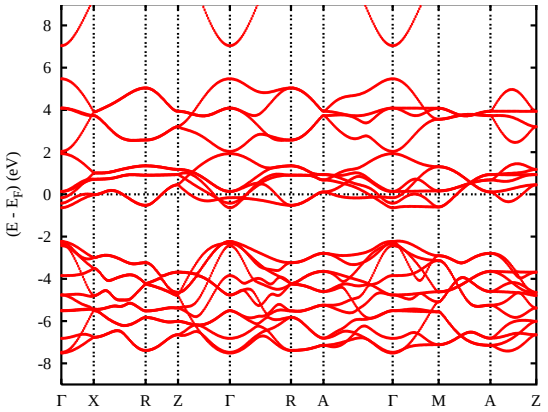
(Received 23 July 2006; published 26 December 2006)

In femtosecond pump-probe measurements, the appearance of coherent phonon oscillations at 4.5 and 6.0 THz indicating the rutile metal phase of VO_2 does not occur simultaneously with the first-order metal-insulator transition (MIT) near 68 °C. The monoclinic and correlated metal (MCM) phase between the MIT and the structural phase transition (SPT) is generated by a photoassisted hole excitation, which is evidence of the Mott transition. The SPT between the MCM phase and the rutile metal phase occurs due to subsequent Joule heating. The MCM phase can be regarded as an intermediate nonequilibrium state.

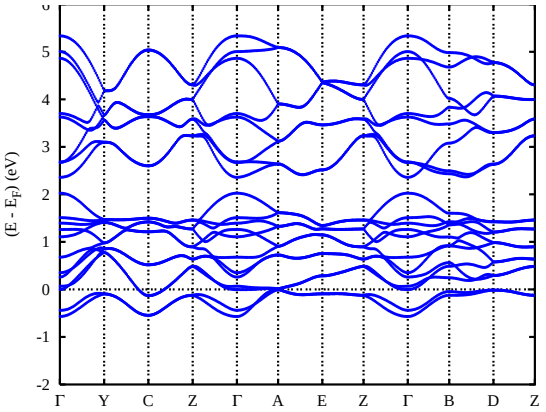
How far do we get ...

... using Density Functional Theory for VO_2 ?

metallic phase



”insulating“ phase



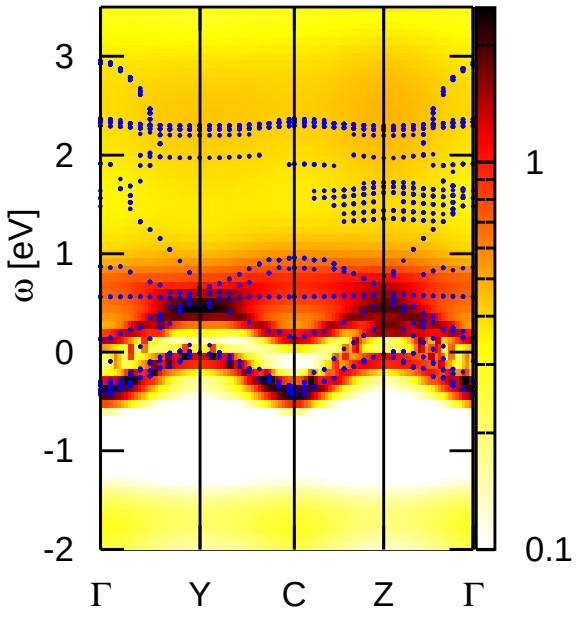
DFT-LDA : no incoherent weight not insulating

(from V. Eyert)

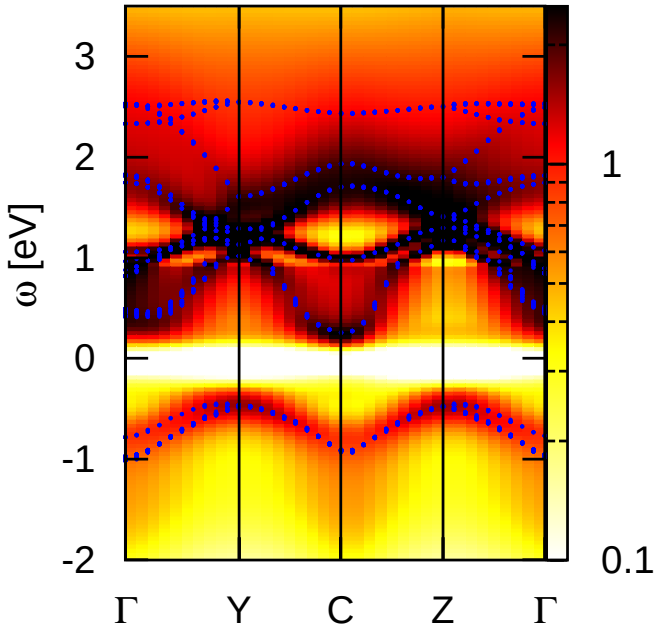
VO_2 : the physical picture

Charge transfer $e_g^\pi \rightarrow a_{1g}$ and bonding-antibonding splitting

metallic phase:



insulating phase:

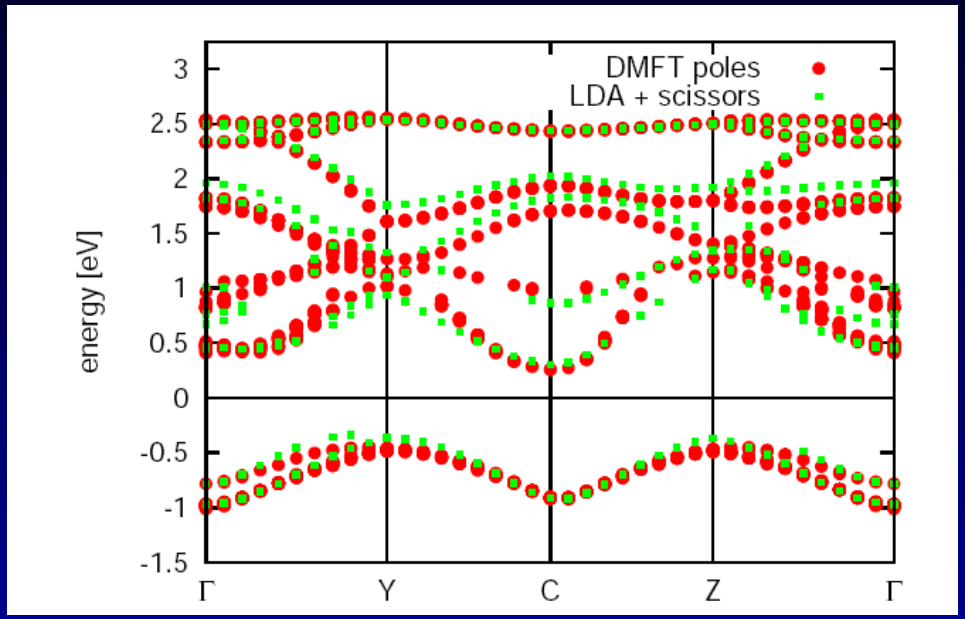


Spectral functions and "band structure"

$$\det\left(\omega_{\mathbf{k}} + \mu - H^{\mathrm{LDA}}(\mathbf{k}) - \Re\Sigma(\omega_{\mathbf{k}})\right) = 0$$

J.M. Tomczak, S.B., J.Phys.:Cond.Mat. 2007; J.M. Tomczak, F. Aryasetiawan, S.B., PRB 2008

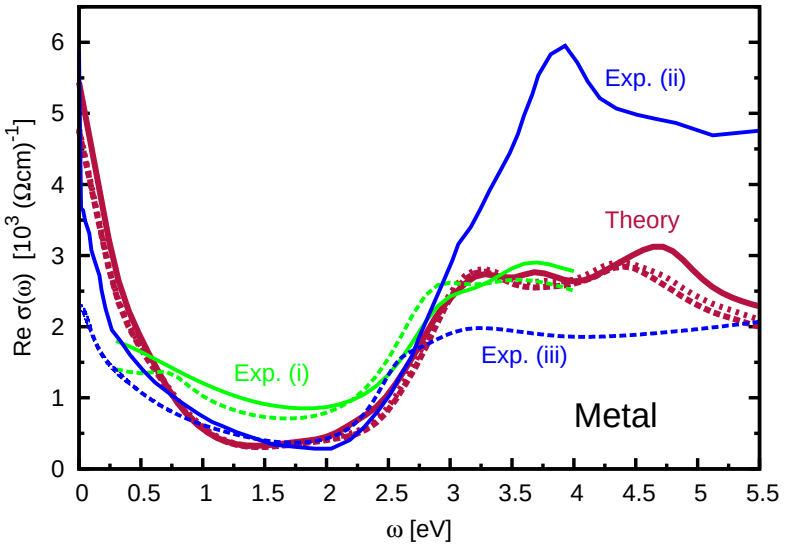
VO_2 monoclinic phase

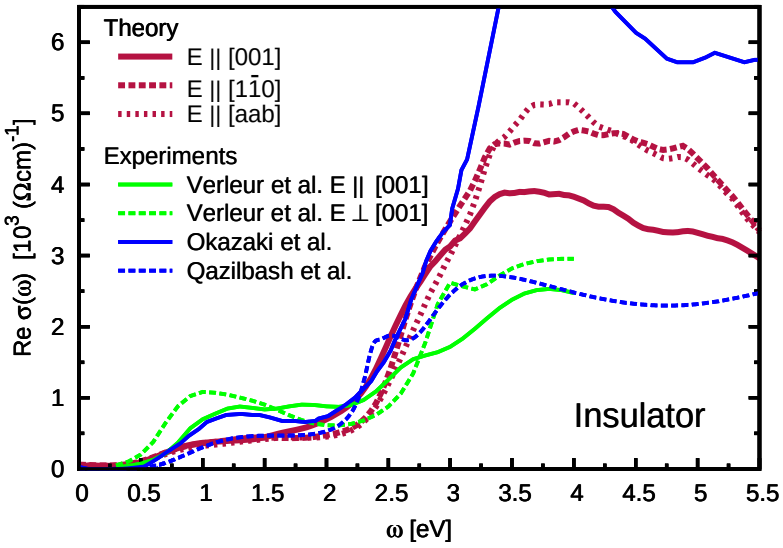


quasi-particle poles (solutions of $\det[\omega + \mu - H(k) - \Sigma(\omega)]=0$) and band structure from effective (orbital-dependent) potential

($\rightarrow$ for spectrum of insulating VO_2: independent particle picture not so bad!! (but LDA is!))

Optical Conductivity of VO_2





[Verleur *et al.*] : single crystals

[Okazaki *et al.*] : thin films $E \perp [001]$, T_c=290 K

[Qazilbash *et al.*] : polycrystalline films, preferential $E \perp [010]$, T_c=340 K

Conclusions?

Not everything ...

... depends only on the average occupation!

Not everything ...

... depends only on the average occupation!

Not everything ...

... depends only on the average occupation!

$$\langle n_\uparrow n_\downarrow \rangle \neq \langle n_\uparrow \rangle \langle n_\downarrow \rangle$$

Conclusion and perspectives

There is a world beyond the one-electron approximation!

- Mott insulators
- Correlated metals (electrons become schizophrenic ...)

How to describe these phenomena on an equal footing?

- Hubbard model: kinetic energy $\leftrightarrow$ Coulomb cost
- Hubbard goes realistic: "LDA+DMFT"
  $\rightarrow$ correlated d- and f-electron materials accessible to first principles calculations!
- What's next? $\rightarrow$ "GW+DMFT" (or on how to get rid off U – and LDA ...!)

Useful Reading (not complete)

- DMFT - Review:

  A. Georges et al., Rev. Mod. Phys., 1996

- LDA+DMFT - Reviews:

  G. Kotliar et al., Rev. Mod. Phys. (2007)

  D. Vollhardt et al., J. Phys. Soc. Jpn. 74, 136 (2005)

  A. Georges, condmat0403123

  S. Biermann, in Encyclop. of Mat. Science. and Technol., Elsevier 2005.

  F. Lechermann et al., Phys. Rev. B **74** 125120 (2006)

References, continued

Some recent applications of LDA+DMFT:

- VO_2: J. Tomczak, S.B., Psik-Newsletter, Aug. 2008, J. Phys. Cond. Mat. 2007; EPL 2008, PRB 2008, Phys. stat. solidi 2009.
  J. Tomczak, F. Aryasetiawan, S.B., PRB 2008;
  S.B., A. Poteryaev, A. Georges, A. Lichtenstein, PRL 2005
- V_2O_3: A. Poteryaev, J. Tomczak, S.B., A. Georges, A.I. Lichtenstein, A.N. Rubtsov, T. Saha-Dasgupta, O.K. Andersen, PRB 2007.
- Cerium: Amadon, S. B., A. Georges, F. Aryasetiawan, PRL 2006
- d^1 Perovskites: E. Pavarini, S. B. et al., PRL 2004

You want to know still more?

Send us your postdoc application! Join the crew ...