

Electronic States in Solids from First Principles: Band Theory and beyond

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Le Menu ...

- Le "modèle standard" de la physique des solides:
la théorie des bandes
 - De l'Hamiltonien à N particules aux électrons indépendants: Hartree, Hartree-Fock ...
 - Etats électroniques dans un potentiel périodique: rappels sur le théoreme de Bloch
- Les calculs “ab initio”
 - La théorie de la fonctionnelle de la densité (DFT)
 - L'approximation de la densité locale (LDA)
 - Les calculs ab initio "en pratique"

Le Menu ... (cont.)

- Exemples de structures de bandes
 - Structure de bandes mesurées en ARPES
 - Prédictions théoriques
- Les limites et les défis
 - Au-delà de la LDA: corrélations électroniques – des quasi-particules de Landau à l'isolant de Mott
 - Fonctions spectrales de "systèmes complexes"



What do the electrons do in Copper?

The N particle Hamiltonian ...

... and its mean-field solution:

N-electron Schrödinger equation

$$\mathcal{H}_N \Psi(r_1, r_2, \dots, r_N) = E_N \Psi(r_1, r_2, \dots, r_N) \quad (1)$$

with

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

becomes separable in mean-field theory:

$$\mathcal{H}_N = \sum_i h_i \quad (3)$$

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

$$h_i = -\frac{\hbar^2}{2m} \nabla_i^2 + v^{external}(r_i) + e^2 \int dr \frac{n(r)}{|r_i - r|} \quad (4)$$

Solutions are Slater determinants

$$\Psi(r_1, r_2, \dots, r_N) \sim \det(\phi_j(r_i)) \quad (5)$$

of *one-particle* states, fulfilling

$$h_i \phi(r_i) = \epsilon \phi(r_i) \quad (6)$$

We are left with a *1-electron problem*:

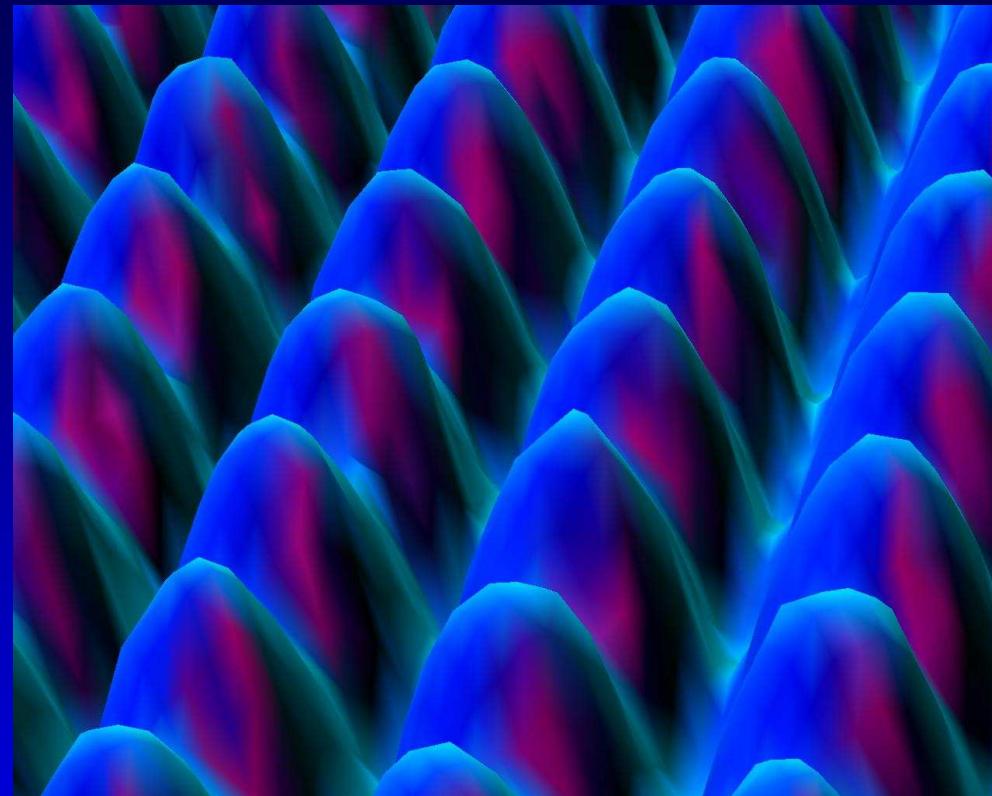
$$h_i \phi(r_i) = \epsilon \phi(r_i) \quad (7)$$

where h_i is the (1-particle) Hamiltonian of a single electron in the solid!



What does 1 electron do in Copper?

What are the eigenstates of an electron
in a periodic potential?



F. Bloch's theorem

Soit $V(x) = V(x + a)$ un potentiel périodique. Alors:
Les fonctions propres de l'Hamiltonien

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \quad (8)$$

peuvent se mettre sous la forme

$$\Psi_k(x) = e^{ikx} u_k(x)$$

avec $u_k(x + a) = u_k(x)$ périodique et $k \in [-\frac{\pi}{a}, \frac{\pi}{a}]$.

(NB. La généralisation à plus d'une dimension est immédiate.)

Que font les électrons?

"When I started to think about it, I felt that the main problem was to explain how the electrons could sneak by all the ions in a metal so as to avoid a mean free path of the order of atomic distances. Such a distance was much too short to explain the observed resistances... To make my life easy, I began by considering wavefunctions in a one-dimensional periodic potential. By straight Fourier analysis I found to my delight that the wave differed from the plane wave of free electrons only by a periodic modulation.

[Felix Bloch, in "Reminiscences of Heisenberg and the early days of quantum mechanics", 1976, p.26.]

(suite)

This was so simple that I couldn't think it could be much of a discovery, but when I showed it to Heisenberg he said right away: 'That's it!' Well that wasn't quite it yet , and my calculations were only completed in the summer when I wrote my thesis on "The Quantum Mechanics of Electrons in Crystal Lattices."



[Felix Bloch, in "Reminiscences of Heisenberg and the early days of quantum mechanics", 1976, p.26.]

F. Bloch's theorem

Soit $V(r) = V(r + R)$ un potentiel périodique. Alors:
Les fonctions propres de l'Hamiltonien

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V(r) \quad (9)$$

peuvent se mettre sous la forme

$$\Psi_k(r) = e^{ikr} u_k(r)$$

avec $u_k(r + R) = u_k(r)$ périodique et $k \in$ the first Brillouin zone

Les nombres quantiques \mathbf{k}

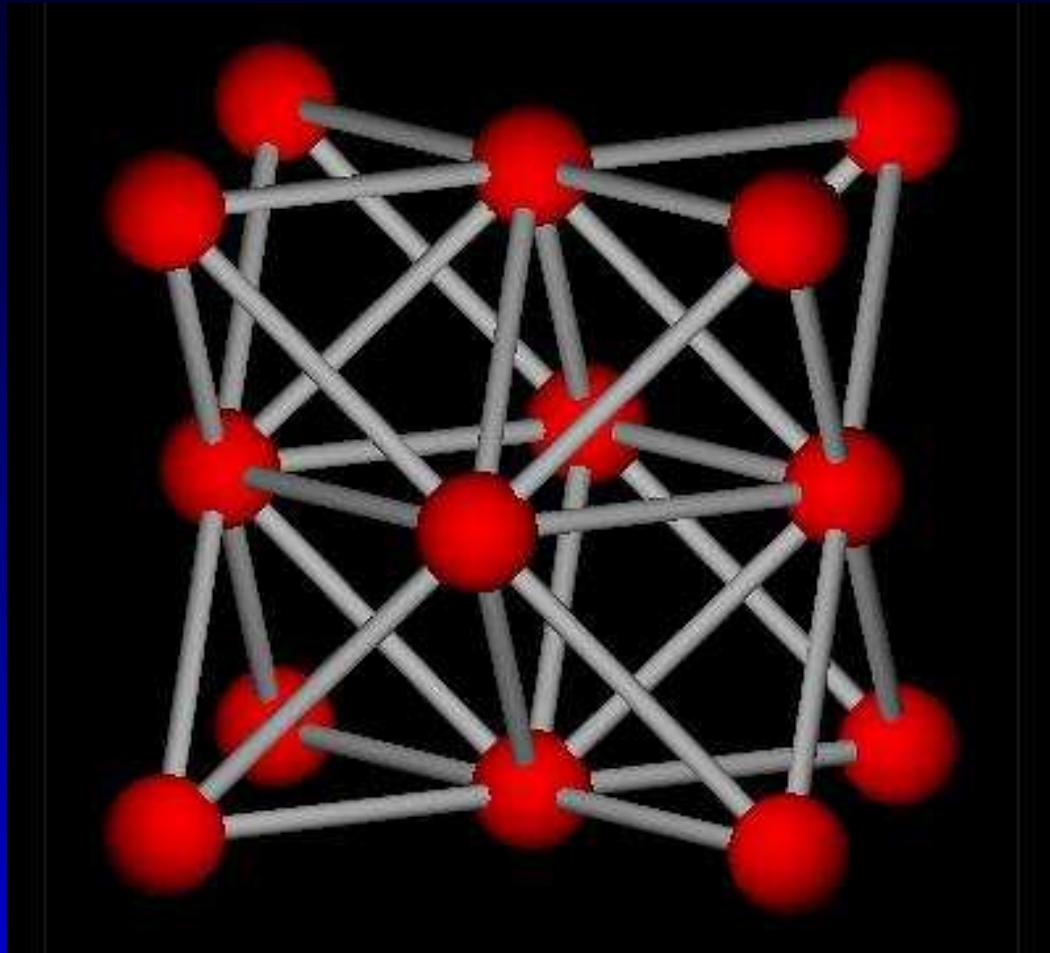
Définition:

$K \in$ Réseau Réciproque $\leftrightarrow e^{iKR} = 1$ pour toutes les translations \mathbf{R} du réseau

Définition:

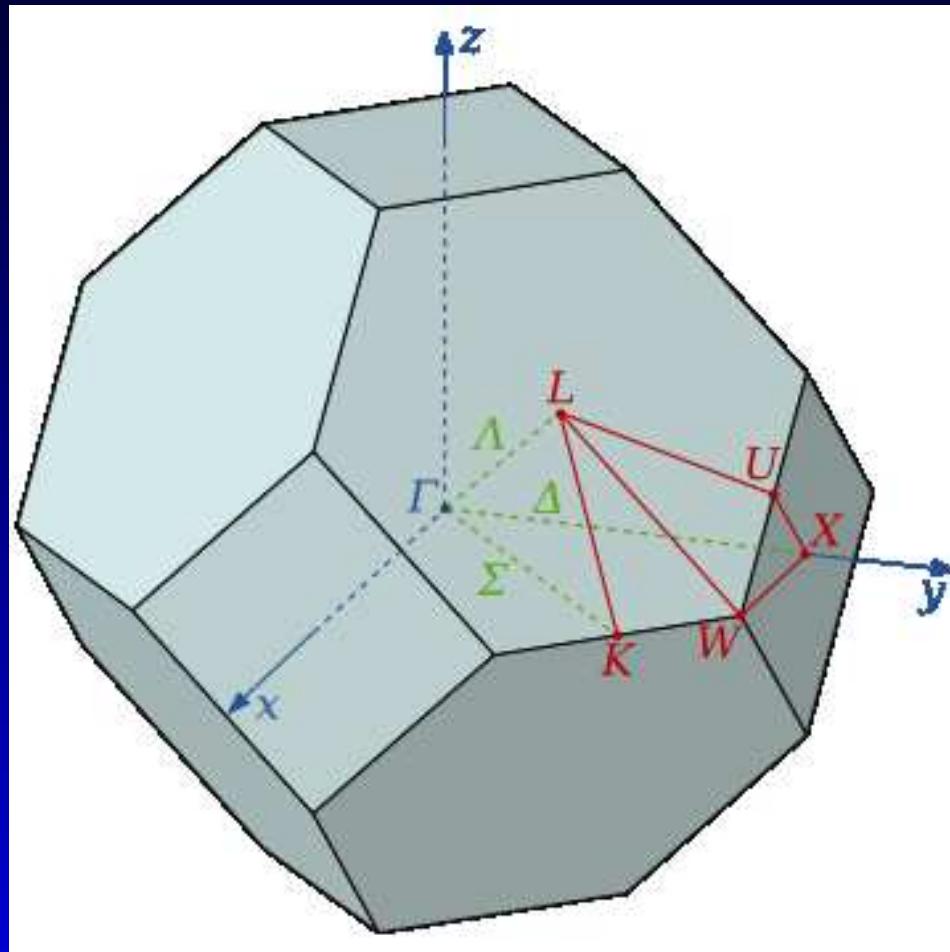
$k \in$ 1ere zone de Brillouin $\leftrightarrow |k| \leq |k - K|$ pour tous $K \in$ Réseau Réciproque

fcc-Copper



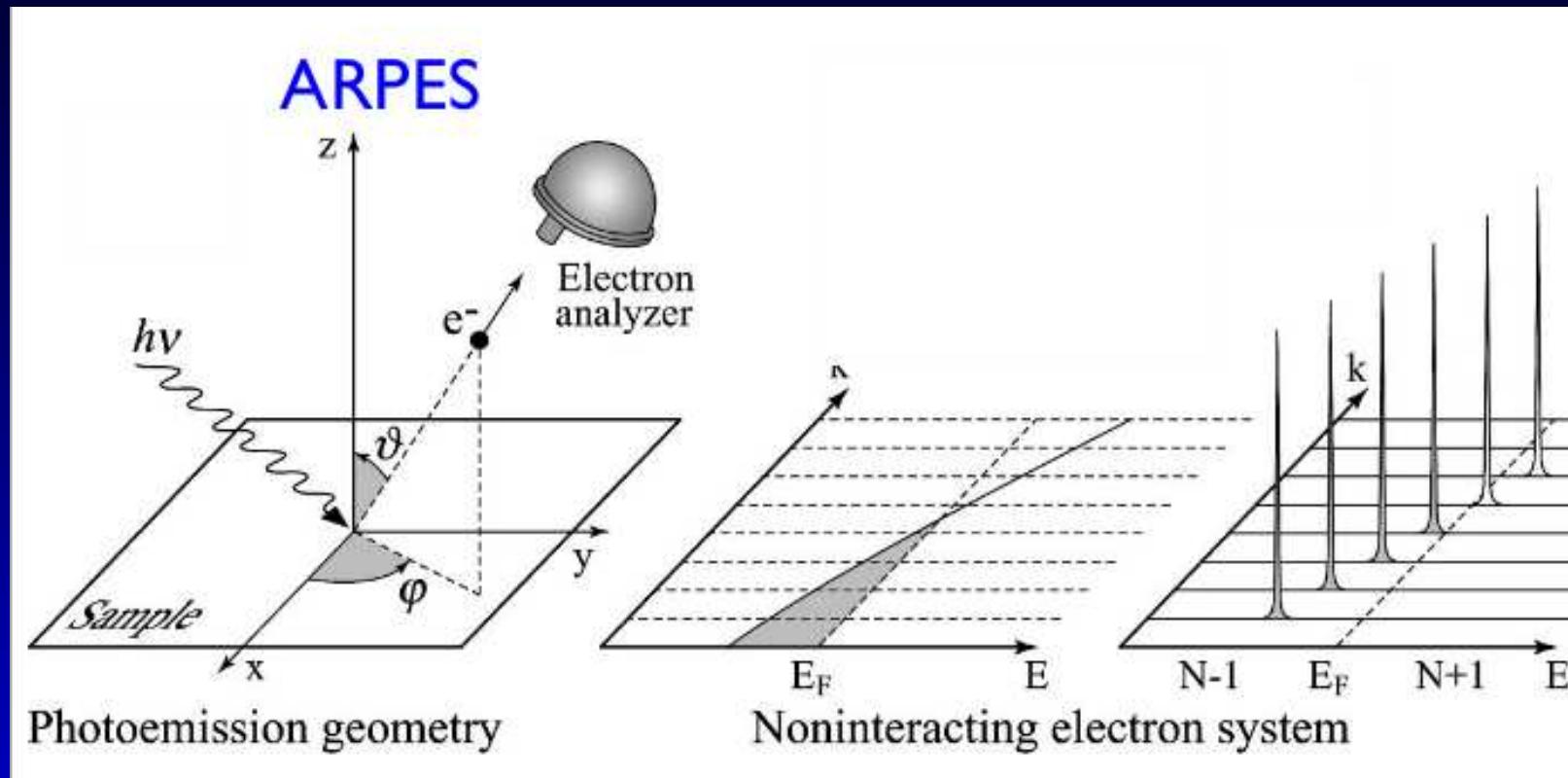
fcc-Copper

First Brillouin zone:



How can we measure bands?

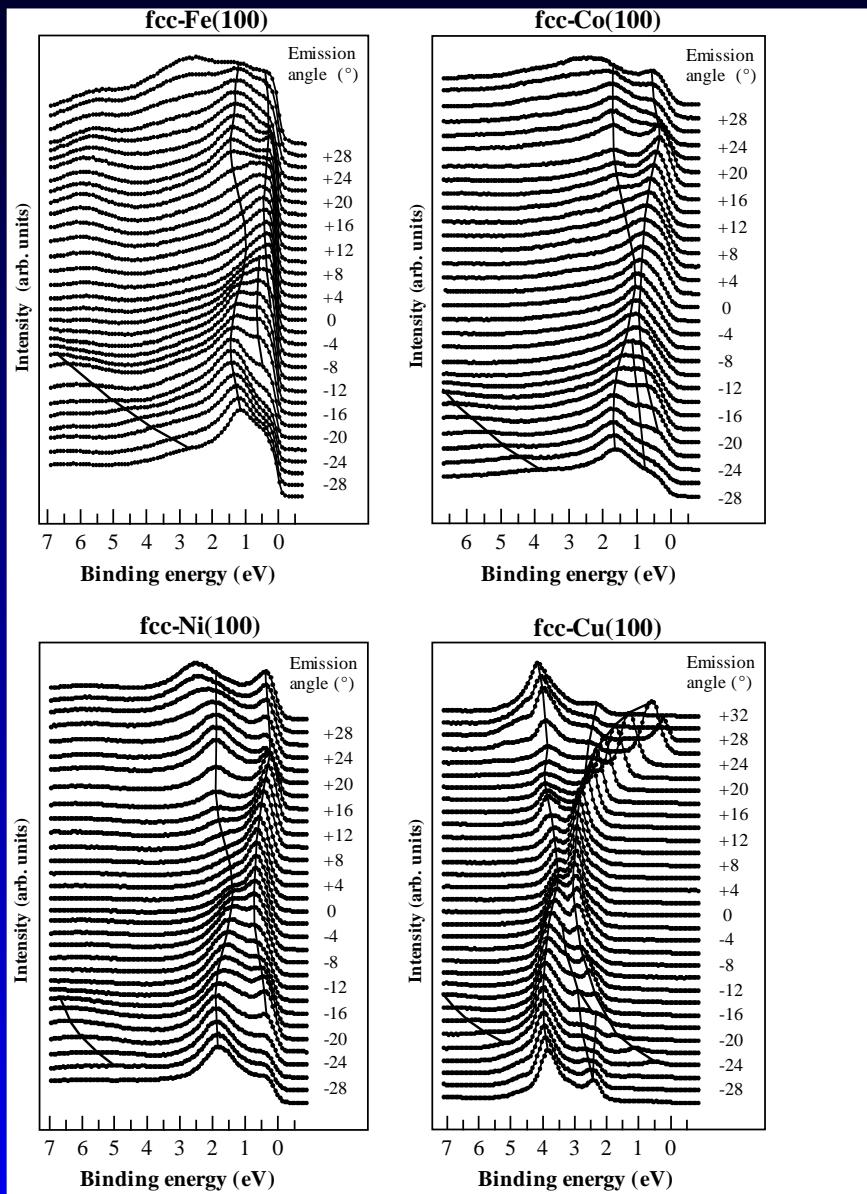
Photoemission:



Photoemission: Electron removal spectra

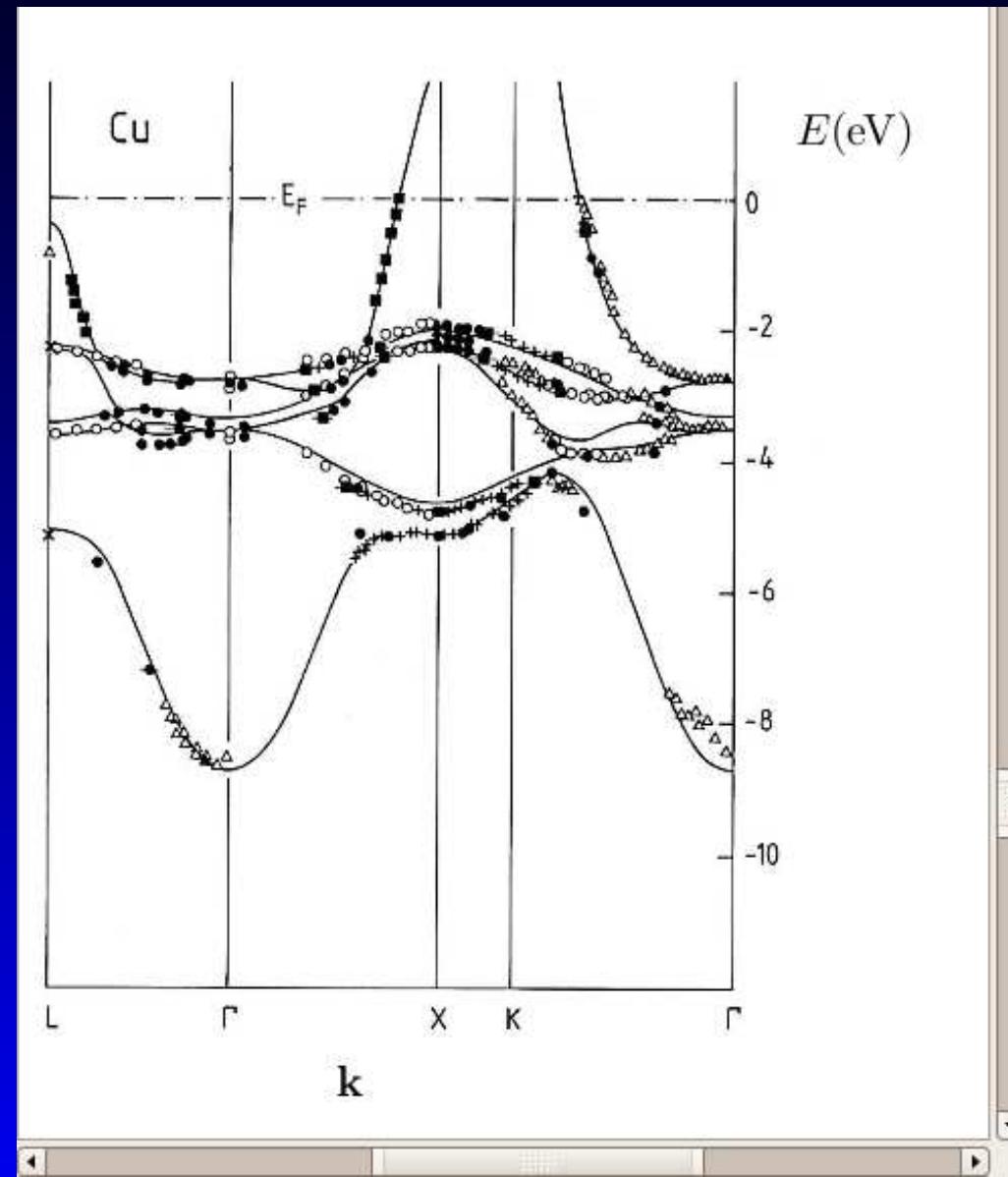
Inverse photoemission (“BIS”): Electron addition spectra

Photoemission spectra



Energies and k -vectors of intensity maxima \rightarrow band structure ϵ_k

Structure de bande



Exemple: Cuivre

Why does it work?

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

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Several answers:

- Pauli principle }
 - Screening }
- reduce effects of interactions

Landau's Fermi liquid theory: quasi-particles
cf. Thierry Giamarchi's lecture

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Landau's Fermi liquid theory: quasi-particles
cf. Thierry Giamarchi's lecture

- It does not always work

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Density Functional Theory

- most widely used framework for *ab initio* electronic structure calculations
- strictly speaking, a theory for ground state properties only
- in practice, however, often used also for excitations (bands!)

Nobel Price in Chemistry, 1998



Nobel Lecture: Electronic structure of matter—wave functions and density functionals^a

W. Kohn

Department of Physics, University of California, Santa Barbara, California 93106
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I. INTRODUCTION

The citation for my share of the 1998 Nobel Prize in Chemistry refers to the development of the density-functional theory.^b The initial work on Density Functional Theory (DFT) was reported in two papers from the first half of the 1960s (Hohenberg and Kohn, 1964) and the next with L. J. Sham (Kohn and Sham, 1965). This was almost 40 years after E. Schrödinger (1927) published his first quantum paper marking the beginning of what we call “The Thomas-Fermi theory,” the most rudimentary form of DFT, was not pursued shortly afterwards (Fermi, 1927), however, it received only modest attention.

There is no need to tell the story of the development of the Kohn-Sham wave function. It has been set forward and spectroscopically validated for small systems like He and H₂, F. M. DiStasio and his colleagues have calculated the electronic energy and entropy of an entire alkali series, and the results were compared to their powerful equation (see below); it is said to have added “in a most natural way” to the Kohn-Sham wave function. The Kohn-Sham equation was born to incorporate in allow solutions

^aThe 1998 Nobel Prize in Chemistry was shared by W. Kohn and John A. Pople. The lecture is the part of the prize lecture address to the Association of the Award.

In the intervening more than six decades enormous progress has been made in finding approximate solutions of Schrödinger's wave equation for systems with several electrons, especially since the concept of density functionals. Thus, the breaking contributions of my Nobel Prize co-winner John Pople are in this area. The main objective of his present lecture is to explain DFT, which is an alternative approach to the theory of electronic structure, in which the electron density distribution $\rho(r)$, rather than the wave function $\psi(r)$, fulfills a primary central role. I feel that it would be useful to do this in a nontechnical context; hence the wording “Wave Functions and Density Functionals” in the title.

In my view DFT makes two kinds of contribution to the science of “the” electronic structure of molecules and of extended matter:

(1) This is the one of fundamental understanding: Theoretical chemists and physicists, following the path of the Schrödinger equation, have become somewhat familiar in terms of the untrusted Hilbert space of single-particle streams. The spectacular advances achieved in this way attest to the triumphs of this perspective. However, when high accuracy is required, so many Slater determinants are required (in some calculations up to 10¹⁰) that the computation becomes difficult. DFT provides a complementary perspective. It focuses on quantities in the real, finite-dimensional coordinate space, namely on the electron density $\rho(r)$. Other quantities of great interest are the exchange correlation potential, $v_{xc}(r)$, which describes how the potential $V(r)$ at a location r depends on the total density of the other electrons at the point r' , and the mean response function, $g(r,r')$, which uses on the electron density at the point r' with frequency ω as the perturbing potential at the point r , with frequency ω . These quantities are universal, independent of representation, and easily visualized even for very large systems. Their understanding provides complementary and complementary insight into the nature of electronic systems.

(2) This is a combination’s method. Traditional multigrid calculations methods, while applied to systems of many particles, can never win. They can experience well when the number of atoms N exceeds a critical value while “current” ϵ in the neighborhood of $\Delta\epsilon_0$ (ϵ is within a factor of about 2) for a system without symmetries. A major improvement in the analytical and/or computational aspects of these methods alone, plus new ones will lead to only modest increases in N_c . Consequently problems involving the simultaneous com-

The Hohenberg-Kohn Theorem

The ground state density $n(r)$ of a bound system of interacting electrons in some external potential $v(r)$ determines this potential uniquely (up to a constant).

Remarks:

- In the case of a degenerate ground state: *any* ground state density
- Proof uses Rayleigh-Ritz variational principle: see Noble lecture in Rev. Mod. Phys. by W. Kohn or do it as an exercise!

Interpretation

Two different external potentials, say $v_{Cu}(r)$ and $v_{Ni}(r)$, cannot have the same ground state density.

→ One-to-one-correspondance between the external potential and the ground state density:

$$v(r) \leftrightarrow n(r)$$

Since $v(r)$ determines the Hamiltonian:
Ground state properties of an interacting many-electron system are *functionals of the density only*.

Density functional theory

Why was this worth the Noble prize
in chemistry???

Density functional theory –

– The Kohn-Sham formalism:

Energy = functional of the density $n(r)$:

$$E[n(r)] = T_0[n(r)] + E_{external}[n(r)] + E_{Hartree}[n(r)] + E_{xc}[n(r)]$$

$T_0[n(r)]$ = kinetic energy of a **non-interacting reference** system
("Kohn-Sham system") of density $n(r)$

(Hohenberg & Kohn (1964), Kohn & Sham (1965))

Density functional theory –

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Schrödinger equation for the reference system (“Kohn-Sham equation”): $(-\frac{1}{2}\Delta + v_{eff})\phi_l(r) = \epsilon_l\phi_l(r)$

“Kohn-Sham orbitals” ϕ_l parametrize the density:

$$\sum_{occ} |\phi_l(r)|^2 = n(r)$$

(Hohenberg & Kohn (1964), Kohn & Sham (1965))

Density Functional Theory –

– so far an *exact* theory, but :

Approximations for E_{xc} required, e.g. the “local density approximation” (LDA):

$$E_{xc}^{LDA}[n(r)] = \int dr n(r) \epsilon_{xc}^{HEG}(n(r))$$

→ DFT-LDA most commonly used method in modern electronic structure calculations

(Hohenberg & Kohn (1964), Kohn & Sham (1965))

Density Functional Theory ...

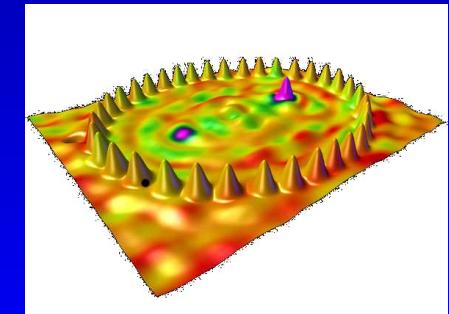
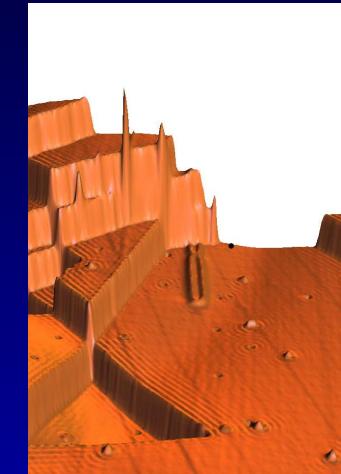
... within the local density approximation (LDA)

– a success story !

- Total energy calculations, phonons
- Band structures, densities of states

Applications to

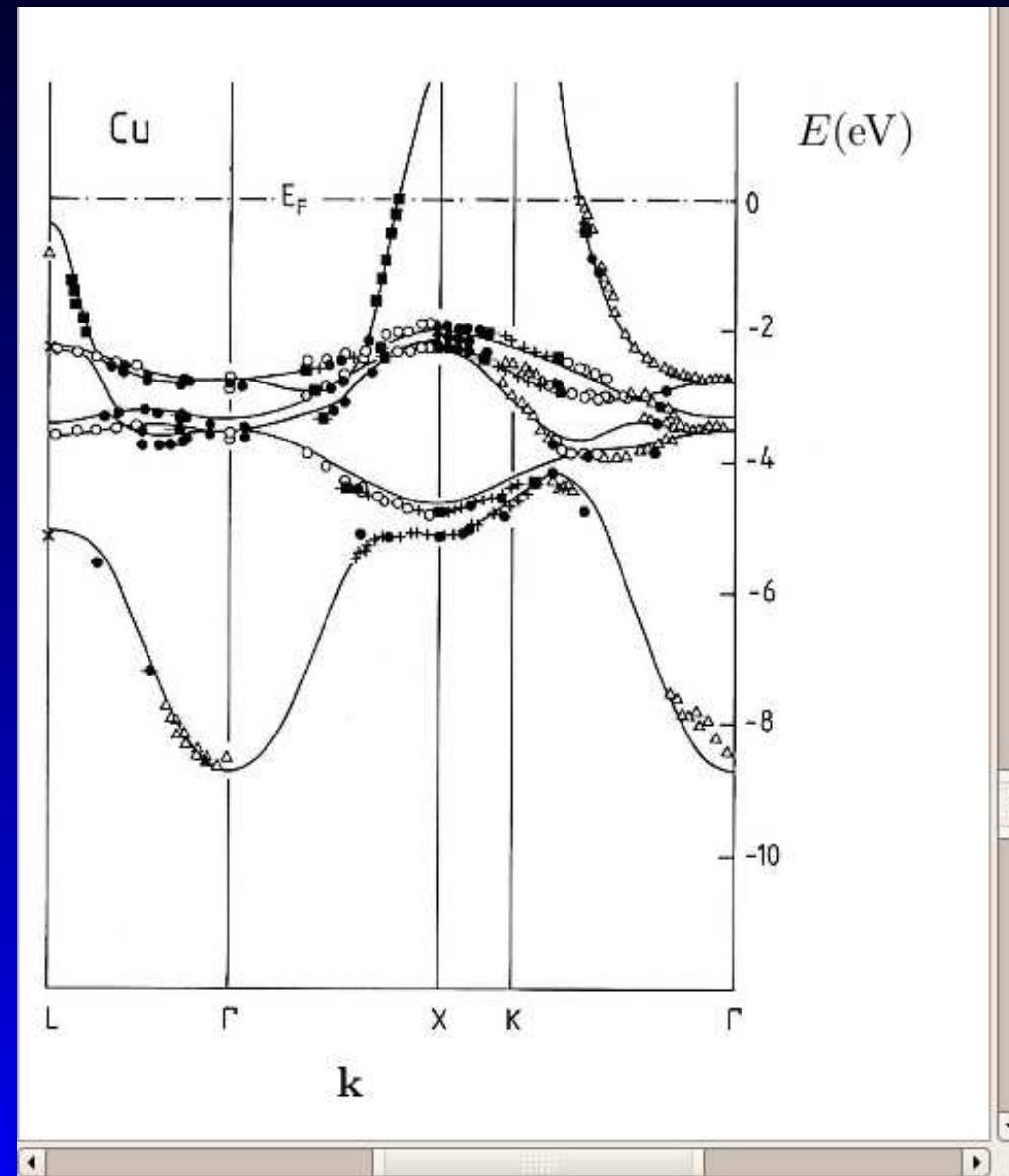
- nanostructures
- surface problems, quantum corrals, ...
- magnetic exchange constants
- dilute magnetic semiconductors
-



Le Menu ... (cont.)

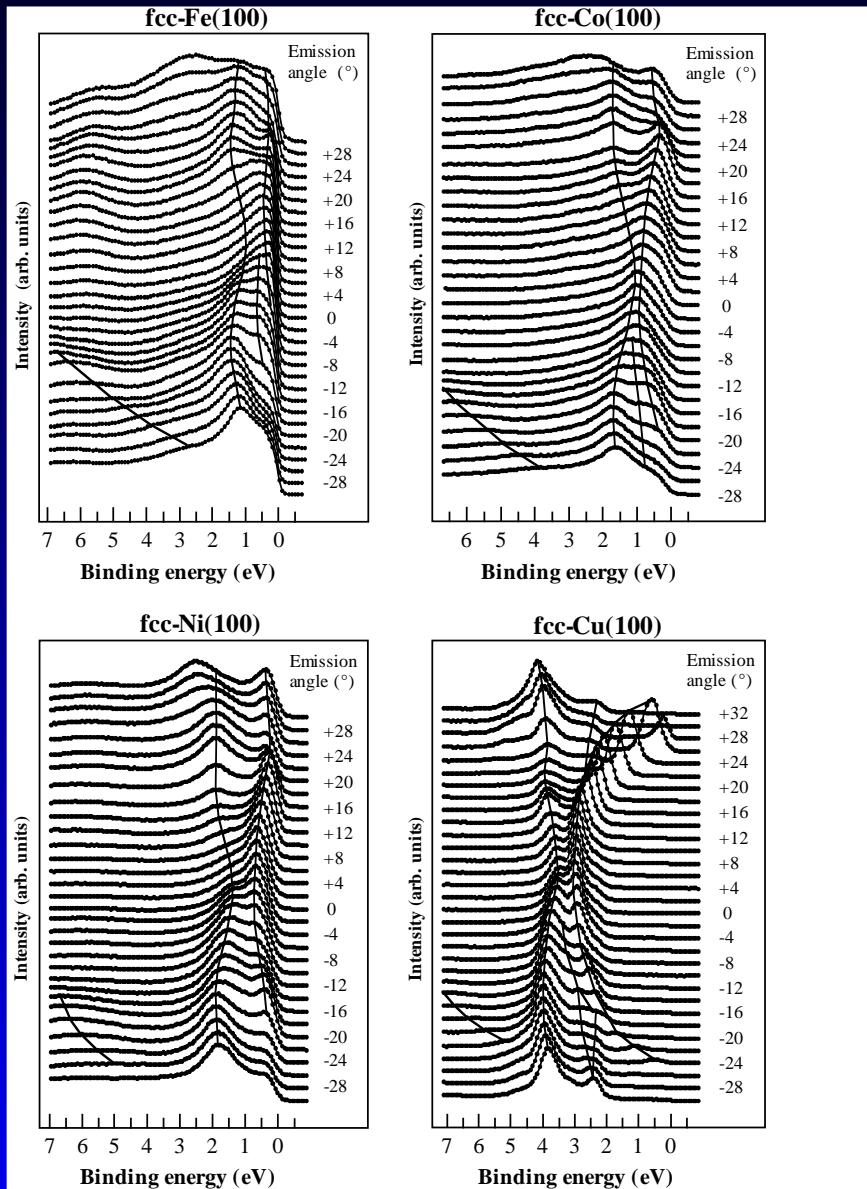
- Exemples de structures de bandes
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Structure de bande



Exemple: Cuivre

Photoemission of fcc-metals



Atomic configuration:

Fe: $3d^6 4s^2$

Co: $3d^7 4s^2$

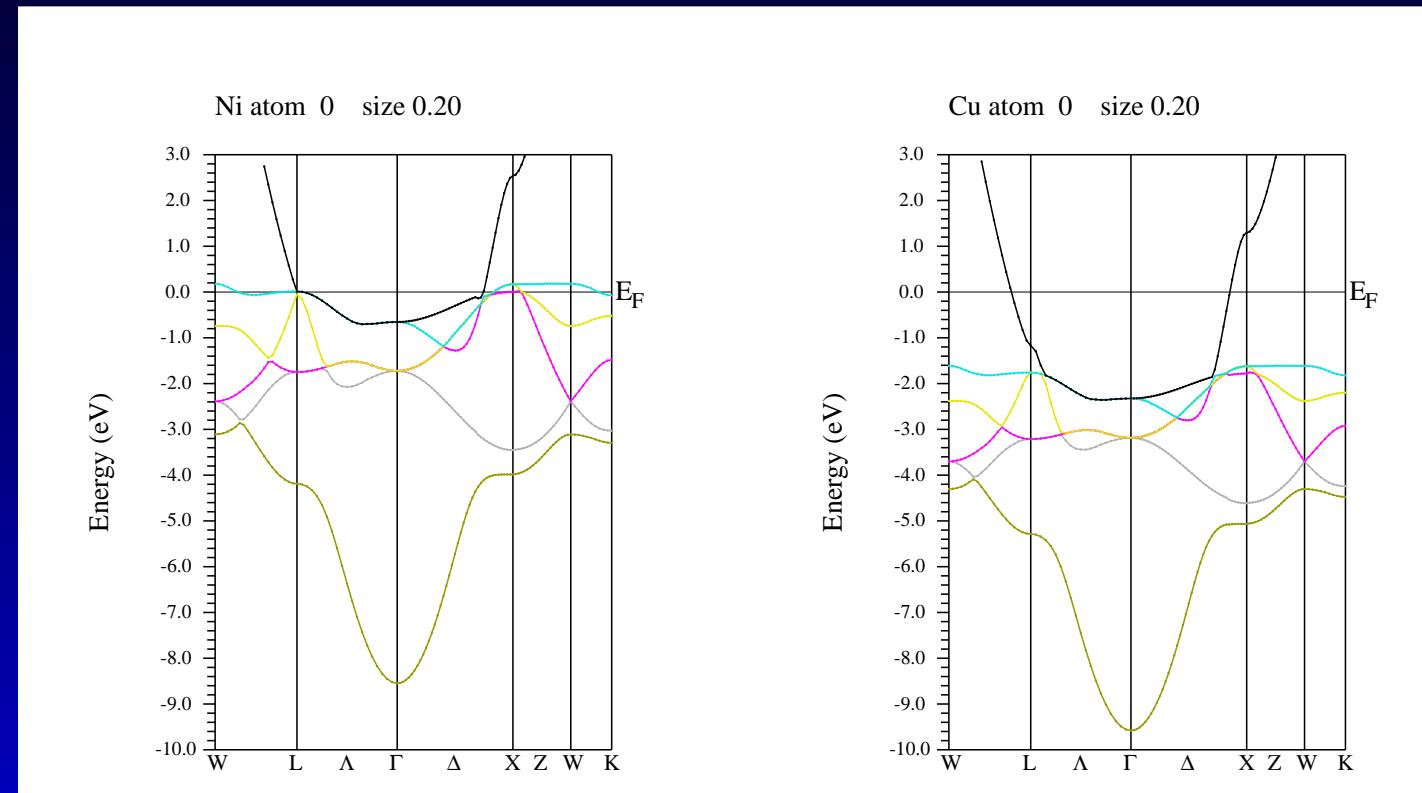
Ni: $3d^8 4s^2$

Cu: $3d^{10} 4s^1$

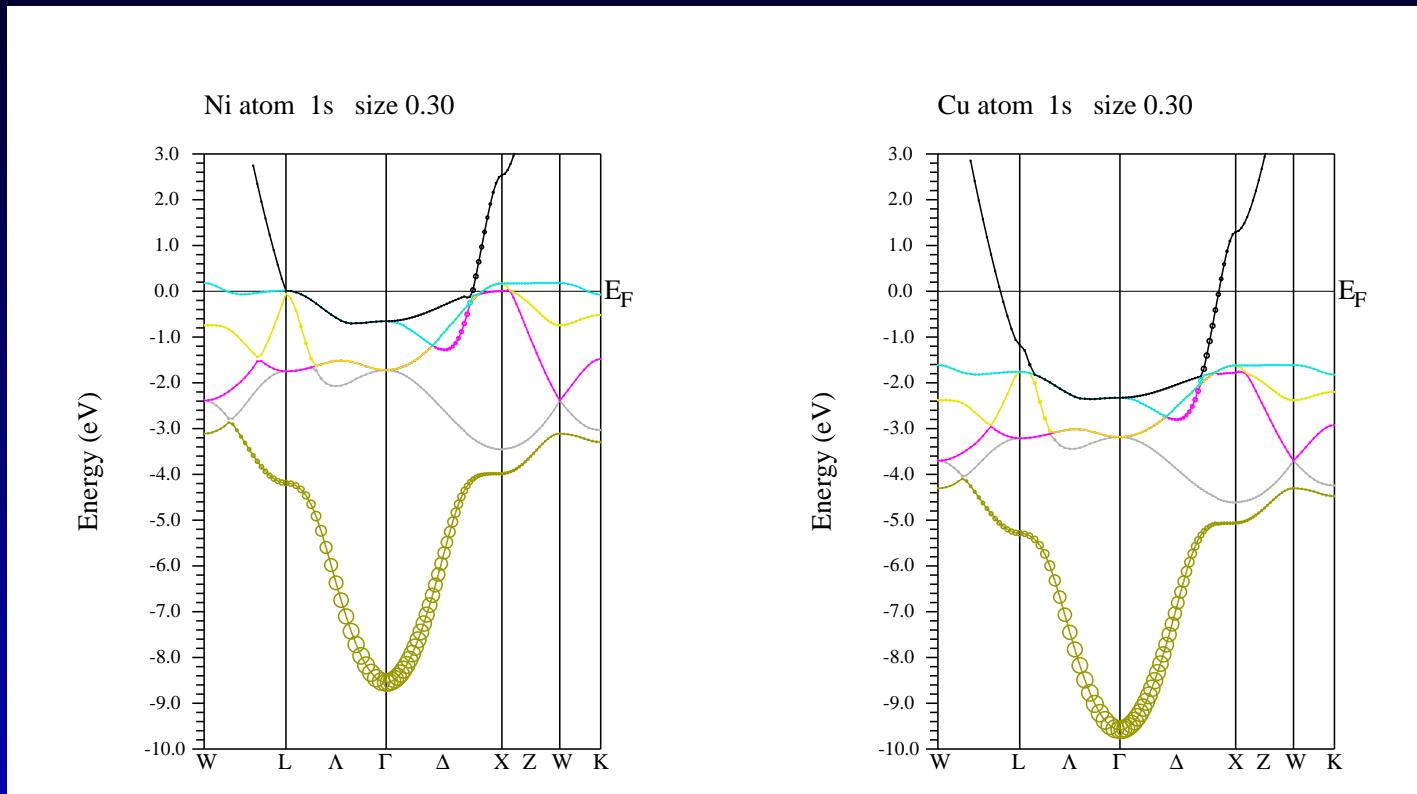
Bands of fcc-metals

Ni: $3d^8 4s^2$

Cu: $3d^{10} 4s^1$

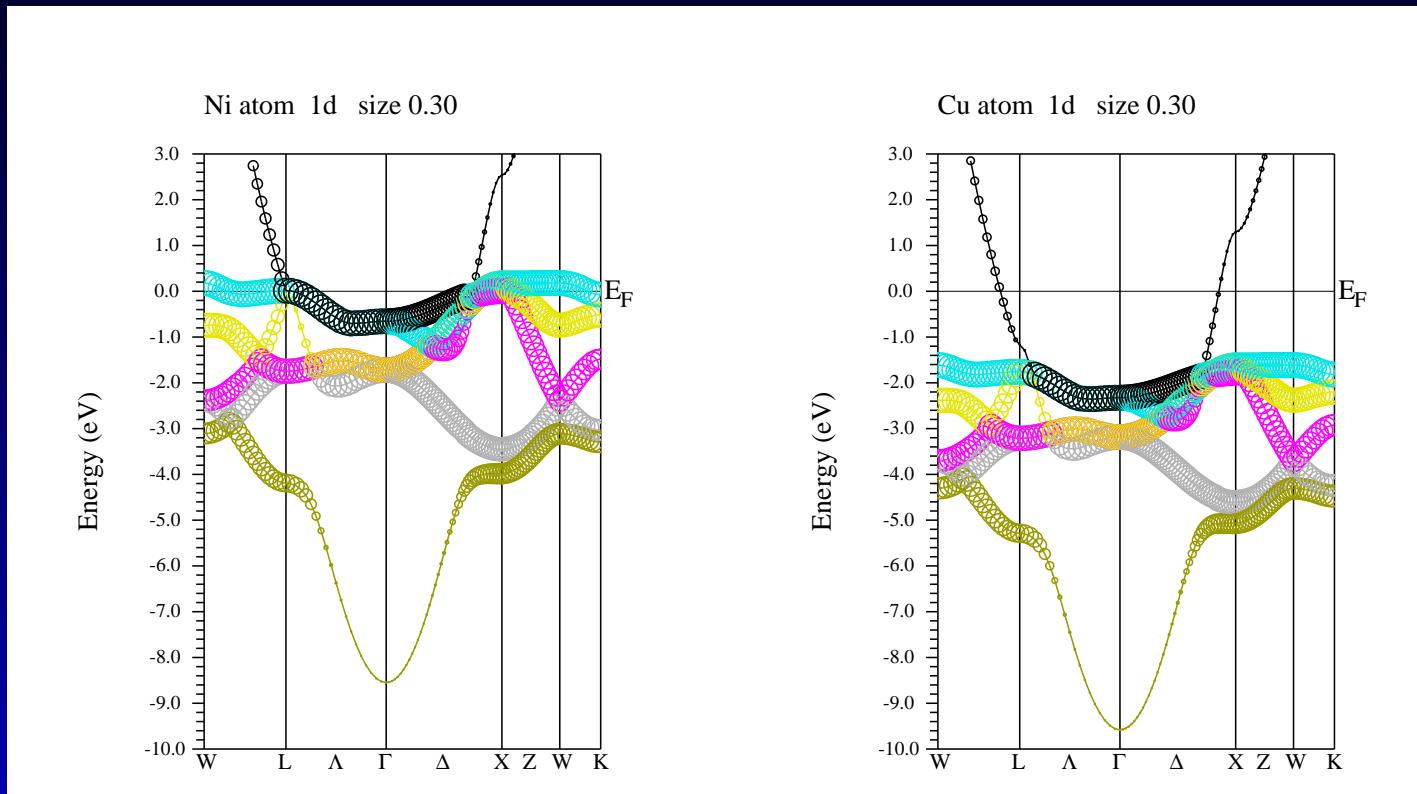


“Fatbands” of fcc-metals



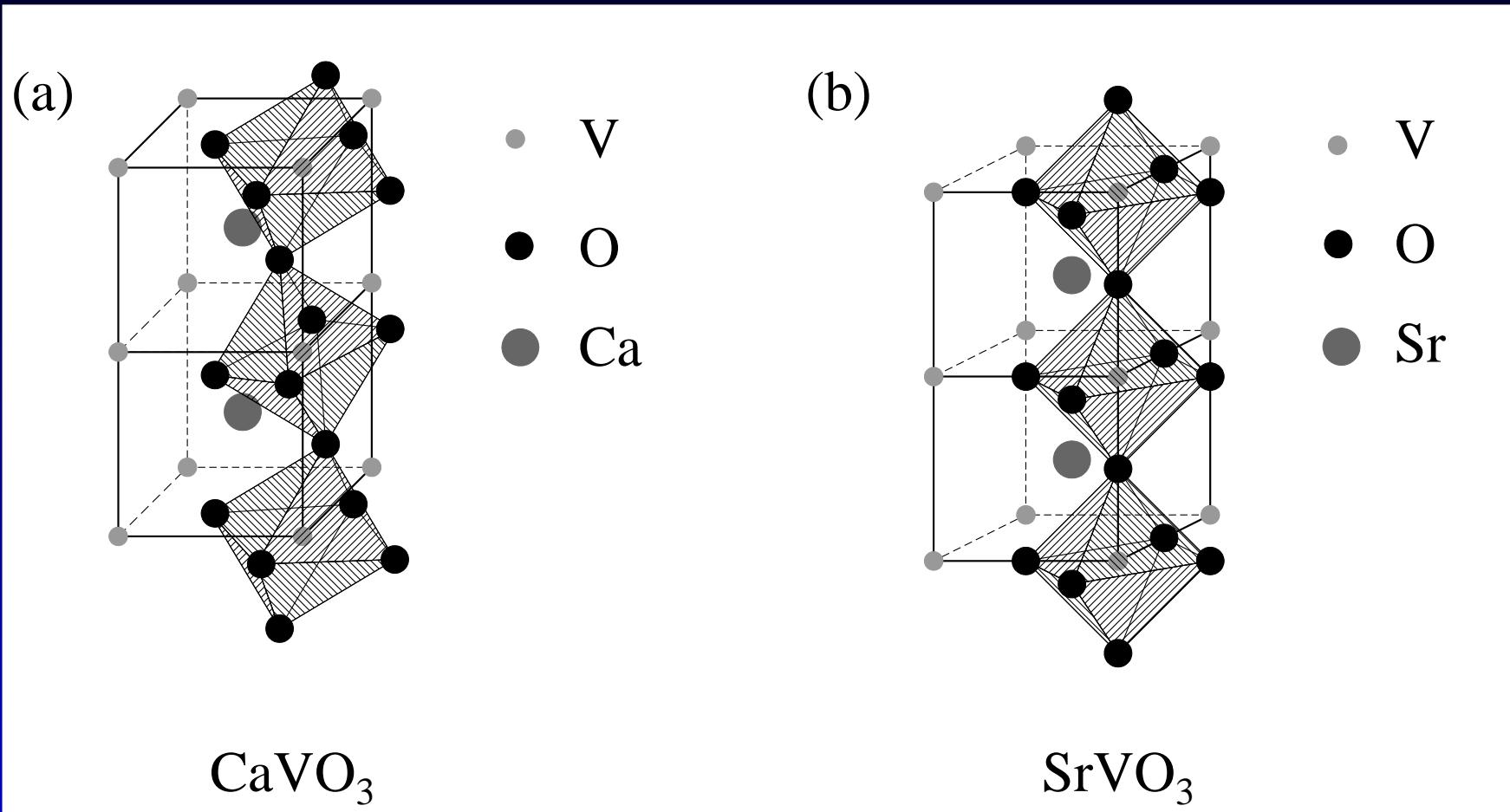
Graphical “fatness” proportional to orbital character
of eigenvector: $|\langle \chi_{klm} | \Psi_{kn} \rangle|^2$
Here, e.g. for $(l,m)=(0,0)$, s-character

“Fatbands” of fcc-metals



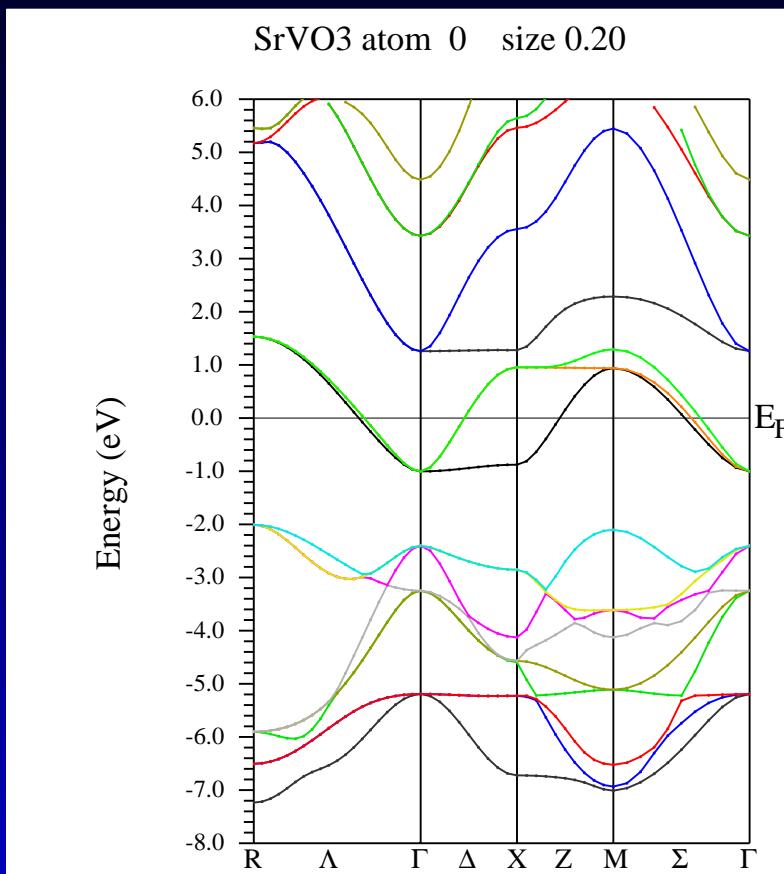
Graphical “fatness” proportional to orbital character
of eigenvector: $|\langle \chi_{klm} | \Psi_{kn} \rangle|^2$
Here, e.g. for $(l,m)=(2,m)$, d-character

Structure of $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$



SrVO_3 cubic, CaVO_3 , LaTiO_3 , YTiO_3 orthorhombic
with increasing (GdFeO_3 -type) distortions
(From K. Maiti, PhD (1998))

SrVO₃: LDA bands



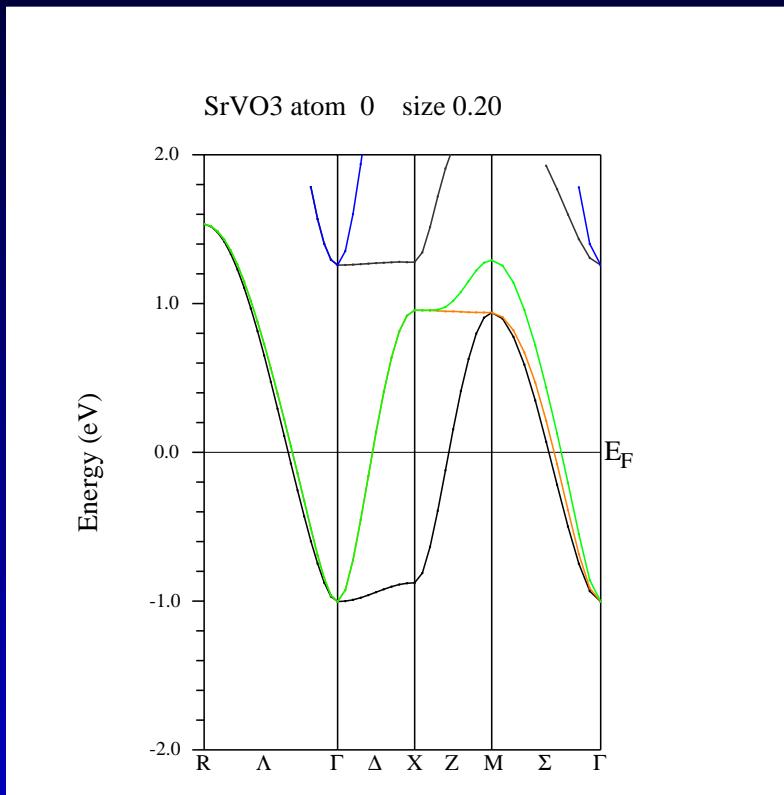
V d-states: e_g –
twofold degenerate

V d-states: t_{2g} –
threefold degenerate

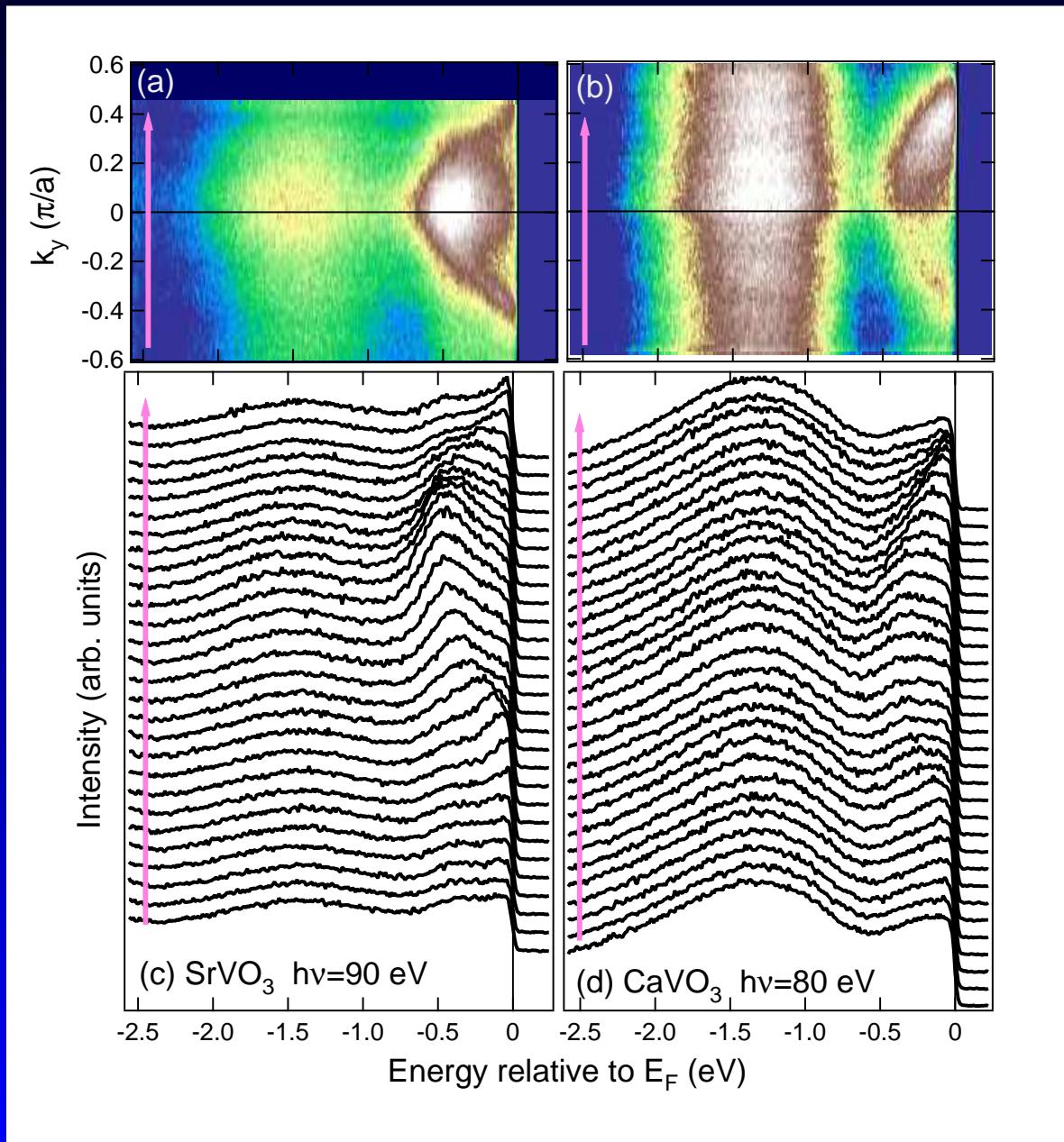
O p-states: $3 \times 3 =$
ninefold degenerate

SrVO₃: LDA bands

t_{2g} states:

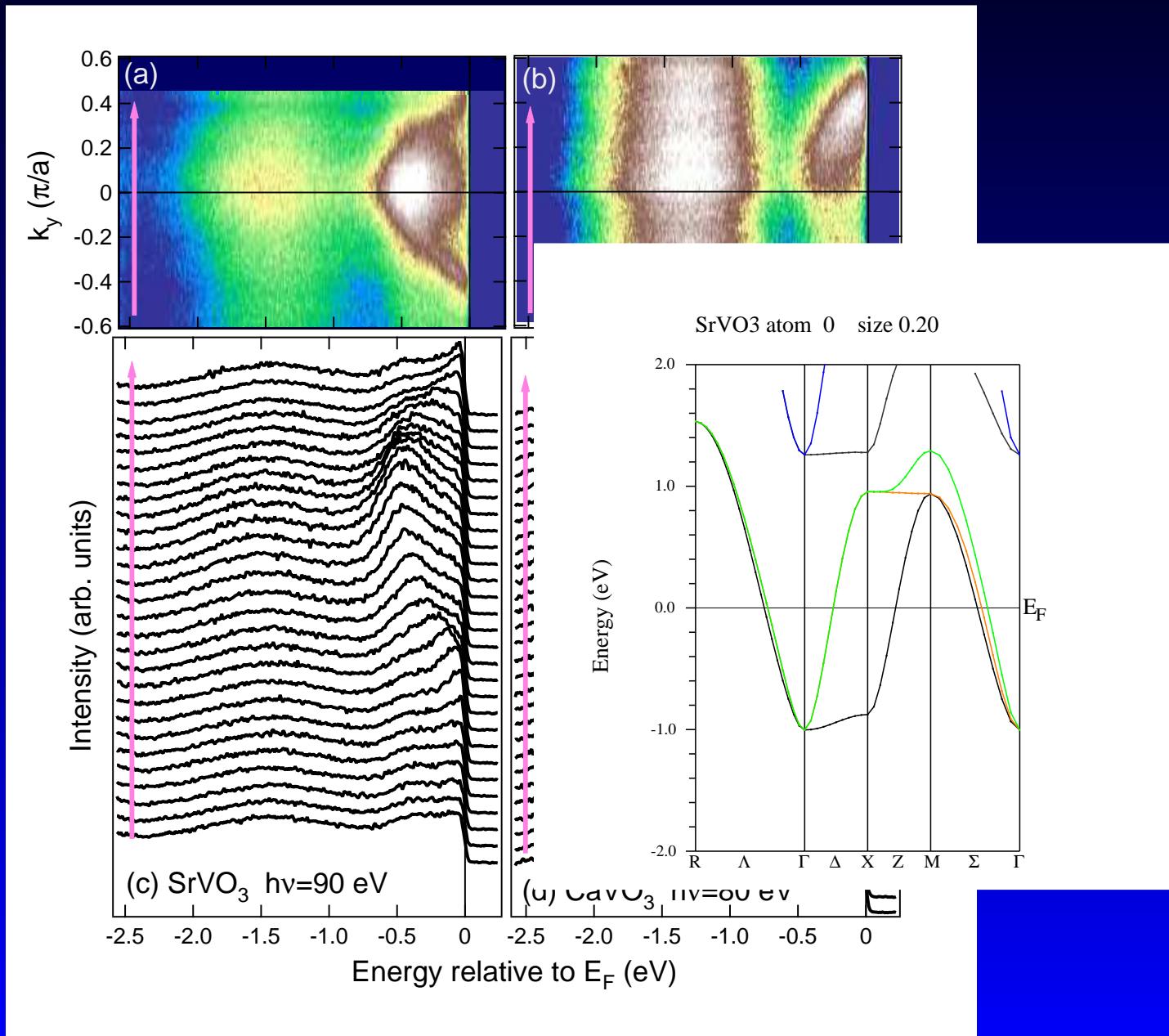


SrVO₃: ARPES



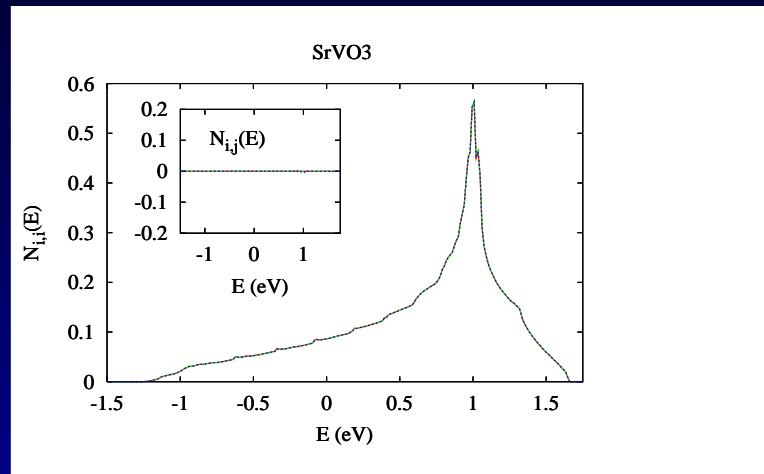
(Yoshida et al.,
2010)

SrVO₃: ARPES

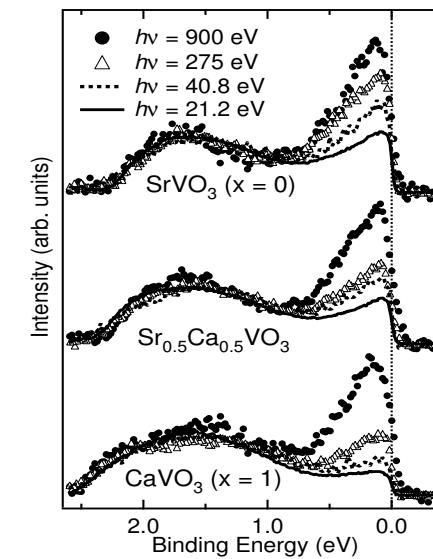


SrVO_3 : a correlated metal

DOS within DFT-LDA



Photoemission



Band narrowing and shift of spectral weight!

(Sekiyama et al. 2003)

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Not everything ...

... depends only on the average occupation!

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Correlations: $\langle AB \rangle \neq \langle A \rangle \langle B \rangle$

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Example: $A = n_\uparrow, B = n_\downarrow$, eigenvalues 0 or 1

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

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

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No correlations! (Hamiltonian separable)

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Correlations! (Hamiltonian not separable)

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/>

The table is organized into 18 groups and 7 periods. Key features include:

- Element Name:** The official name of each element.
- Atomic Number:** The number of protons in the nucleus.
- Element Symbol:** The standard one- or two-letter symbol used by chemists.
- Atomic Weight:** The mean relative mass of the element's isotopes.
- Discovery:** The year and location where each element was first identified.
- Properties:** A brief summary of physical and chemical properties for each element.
- Groups:** Elements with similar properties are grouped together.
- Periods:** Elements are arranged in horizontal rows based on their atomic number.

Lanthanides: Elements 57-71 (Ce-Lu) are listed separately below the main table.

Actinides: Elements 89-102 (Fr-Ra) are listed separately below the lanthanides.

Copyright © Dr Mark J Winter (University of Sheffield). webelements@shef.ac.uk. For updates to this table see <http://www.shef.ac.uk/chemistry/web-elements/p/periodic-table.html>. Version date: 1 March 1998.

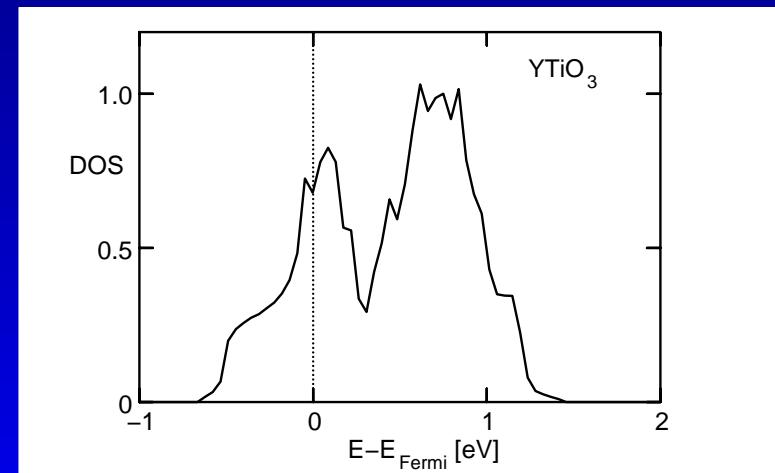
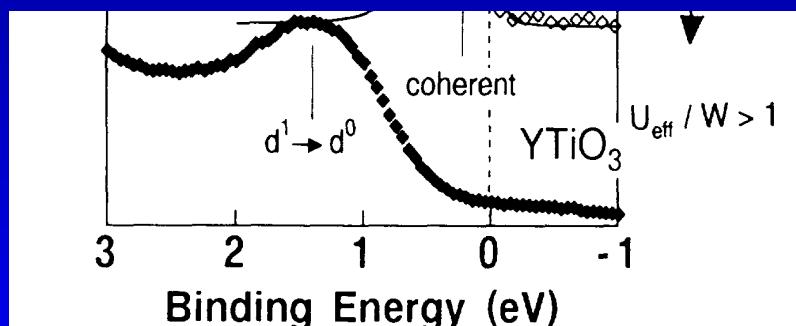
→ transition metal oxides/sulfides, rare earth or actinide compounds
(but also: low-dimensional systems, organics ...)

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 ...)

E.g. photoemission of YTiO_3 :

(Fujimori et al.)



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

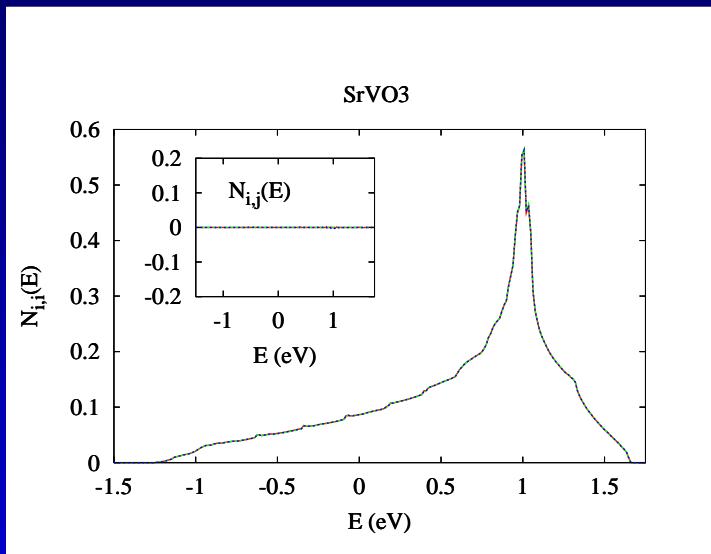
Spectral function – survival kit

Add/remove an electron – at which energy?

Non-interacting limit:

state of N electrons = Slater determinant

(N+1)th electron can jump into any (unoccupied) band
→ probe unoccupied **density of states**

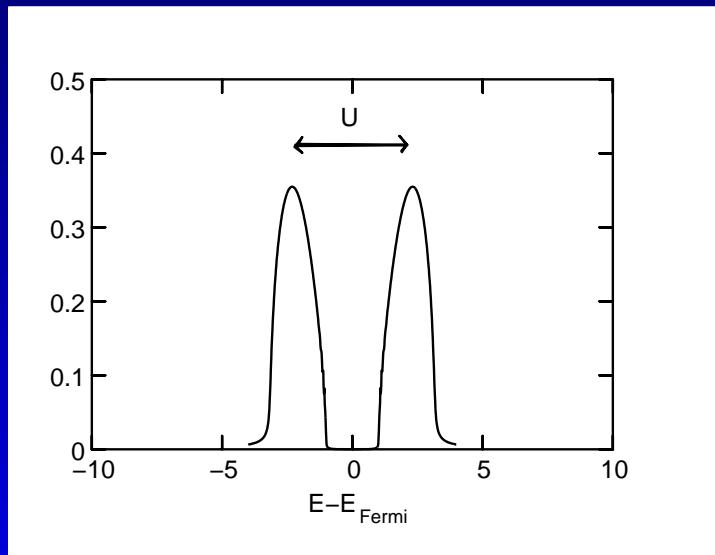


Spectral function – survival kit

In the general, interacting case: relaxation effects!!

Spectral function $\rho(\omega)$ describes the possibility of adding an electron with energy ω

“Atomic limit” (complete localization):
probe local Coulomb interaction!



Green's function – survival kit

(cf. lecture by T. Giamarchi)

$$A(k, \omega) = -\frac{1}{\pi} \Im G(k, \omega)$$

Definition of Green's function:

$$G(k, t) = -\langle \hat{T} c_k(t) c_k^\dagger(0) \rangle$$

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*:

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

Band narrowing by correlations?

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

$$Im\Sigma(\omega) = -\Gamma\omega^2 + O(\omega^3)$$

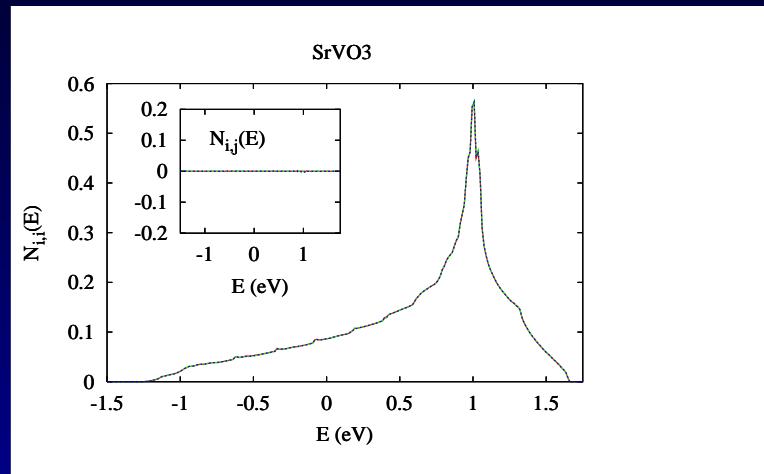
$$Re\Sigma(\omega) = Re\Sigma(0) + (1 - Z^{-1})\omega + O(\omega^2)$$

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

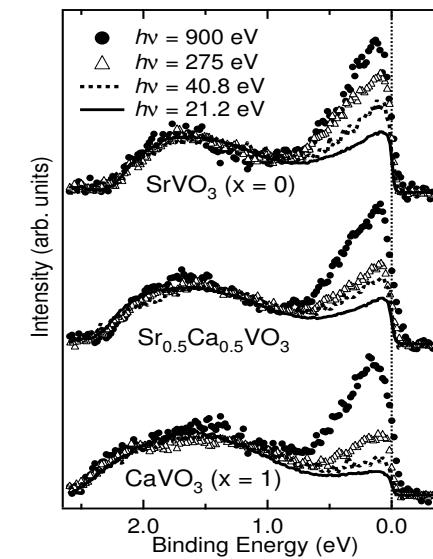
For small $\text{Im } \Sigma$ (i.e. well-defined quasi-particles):
Lorentzian of width $Z\text{Im } \Sigma$,
poles at renormalized quasi-particle bands $Z\epsilon_0(k)$,
weight Z (instead of 1 in non-interacting case)

SrVO_3 : a correlated metal

DOS within DFT-LDA



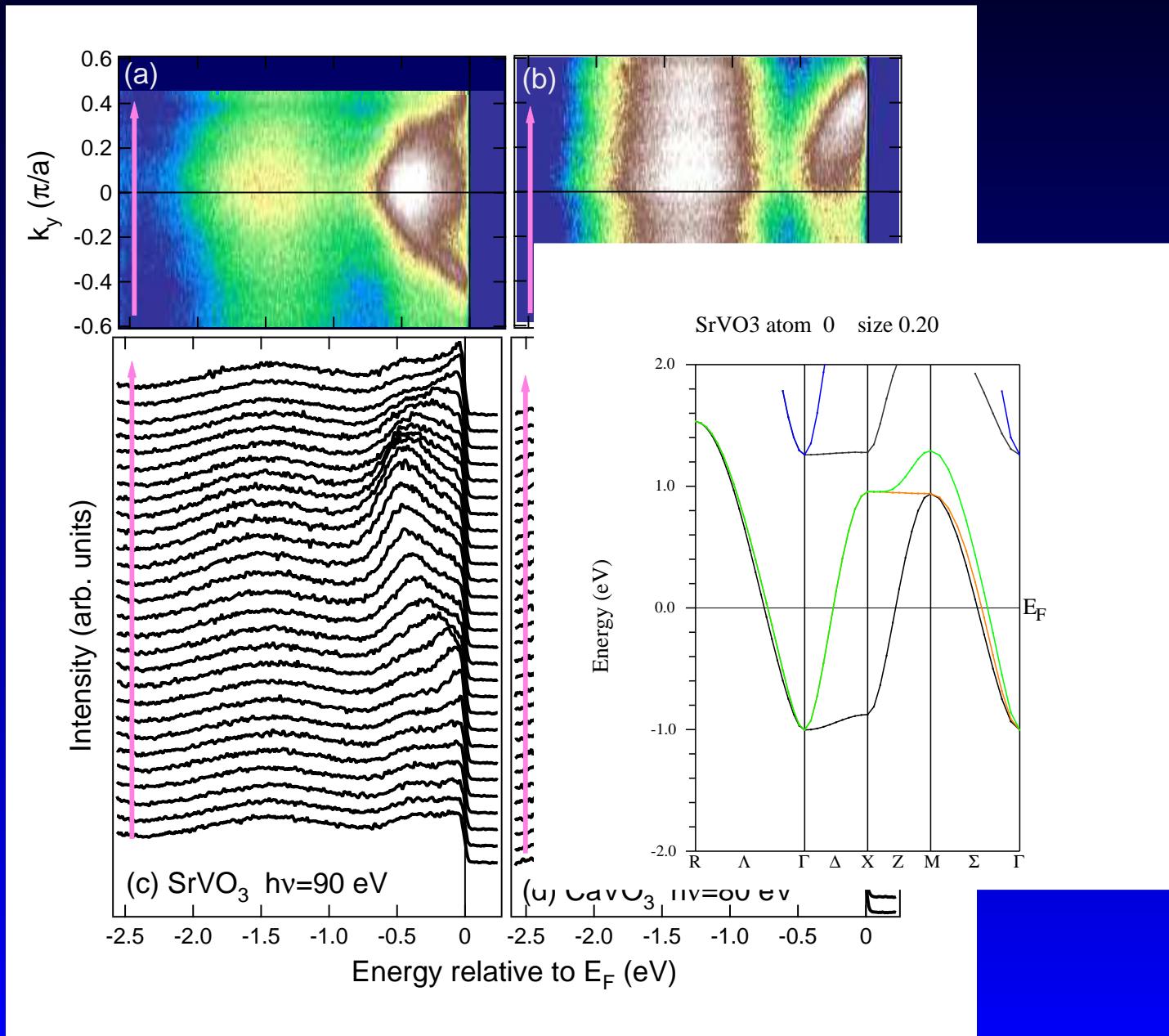
Photoemission



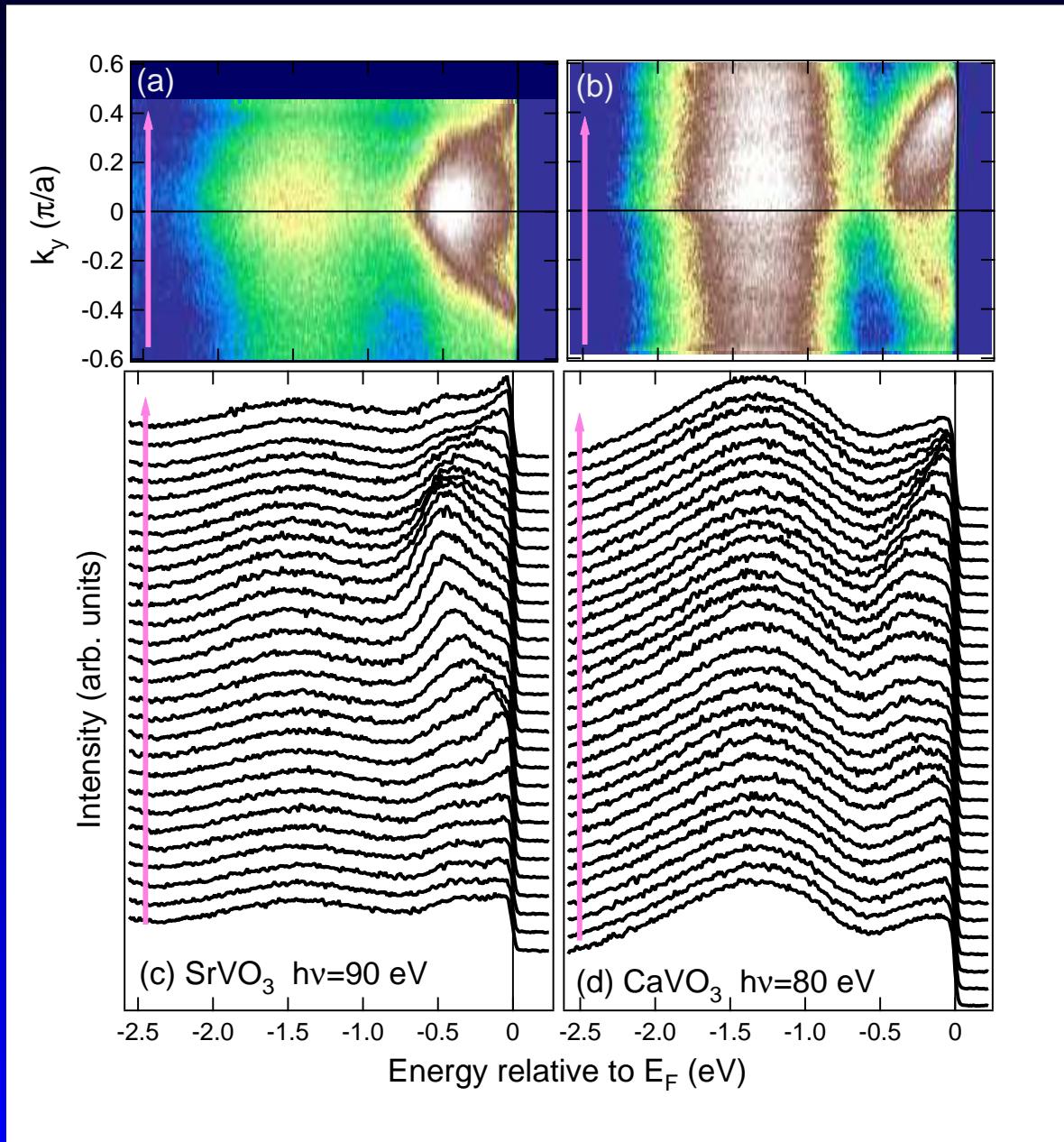
Band narrowing and shift of spectral weight!

(Sekiyama et al. 2003)

SrVO₃: ARPES



SrVO₃: ARPES



Theoretical description ...

... requires explicit calculation of self-energy!



Theoretical description ...

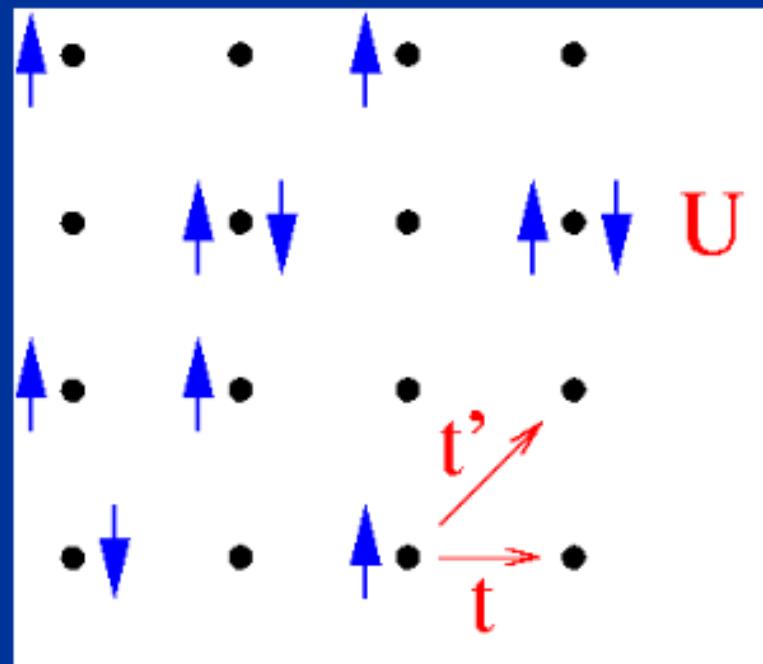
... requires explicit calculation of self-energy!



Here: dynamical mean field theory (DMFT)
→ yields self-energy in local (k -indep.)
approximation

Example

Hubbard model (1963)



$$H = -t \sum_{\langle i,j \rangle, \sigma} (c_{i,\sigma}^\dagger c_{j,\sigma} + h.c.) + U \sum_{i=1}^N n_{i\uparrow} n_{i\downarrow}$$

stolen from T.Giamarchi's lecture

What's a mean field theory?

Two ingredients:

1. Reference system: single site (or cluster of sites) in an effective mean field
2. Self-consistency condition relating the effective problem to the original one

... a *dynamical* mean field theory?

Two ingredients:

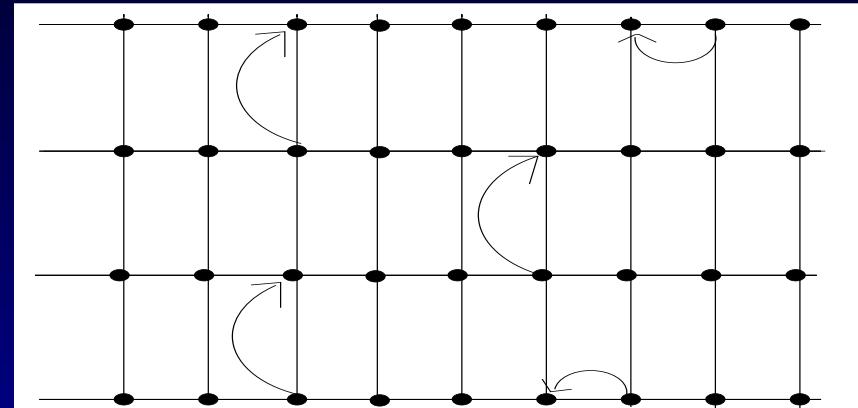
1. Reference system: single site (or cluster of sites) in an effective mean field

- Mean field can be **energy-dependent** (\rightarrow **dynamical**)
- Reference system can be **interacting**

2. Self-consistency condition relating the effective problem to the original one

Dynamical mean field theory ...

... maps the lattice problem



onto a single-site (Anderson impurity) problem

with a self-consistency condition

(for a review see Georges et al., Rev. Mod. Phys. 1996)

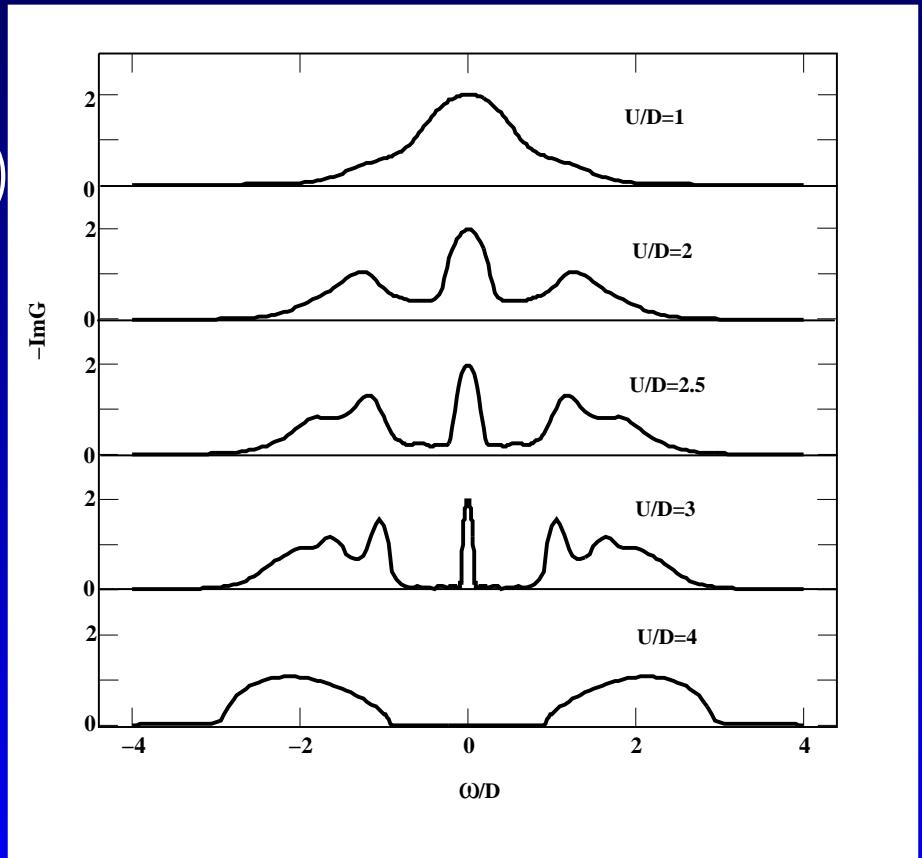
Hubbard model within DMFT

$$H = -\frac{D}{2} \sum_{\langle ij \rangle \sigma} \left(c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma} \right) + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

(Hubbard, 1963)

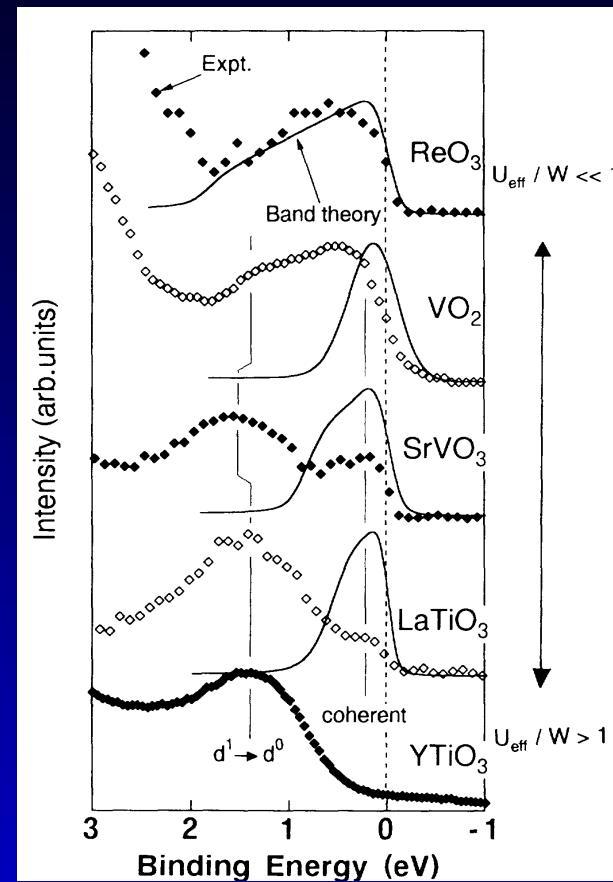
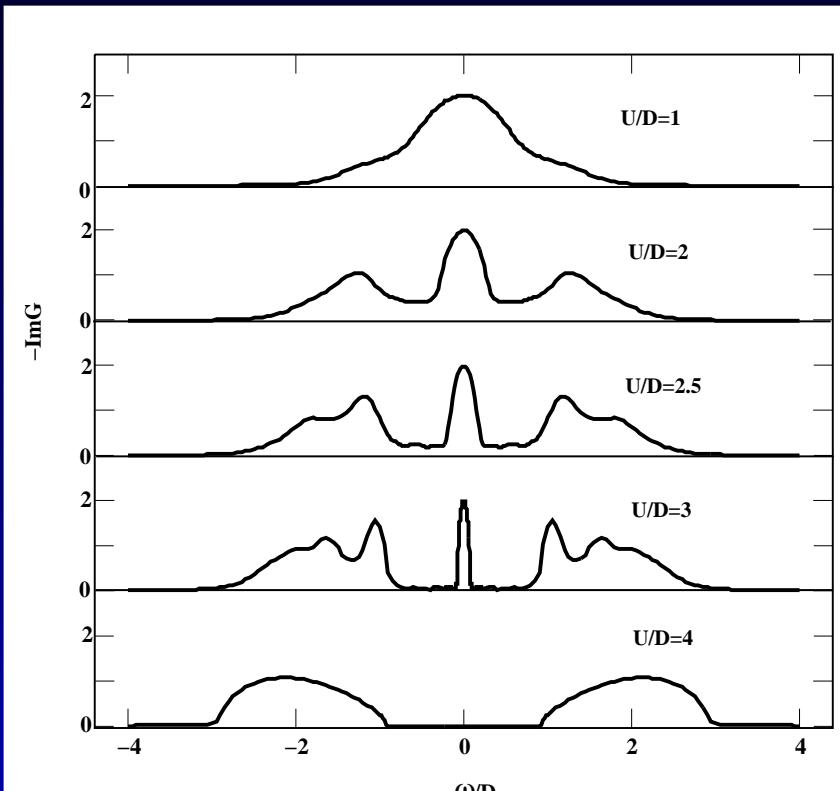
$\rho(\omega)$
Quasi-particle peak
Hubbard bands

Georges & Kotliar 1992



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

Photoemission vs. Hubbard model spectral function



(from Fujimori et al., 1992)

Calculate Correlated Materials ...?

Wanted: techniques for **materials-specific** calculations
of electronic properties **beyond band theory**

Strategy:

- materials-specific → “first principles” (i.e. without adjustable parameters)
- beyond band theory → many-body techniques based on dynamical mean field theory (DMFT)

→ combine both ...

“LDA+DMFT” – basic strategy

- effective one-particle Hamiltonian within LDA
- represent in localized basis
- add Hubbard interaction terms

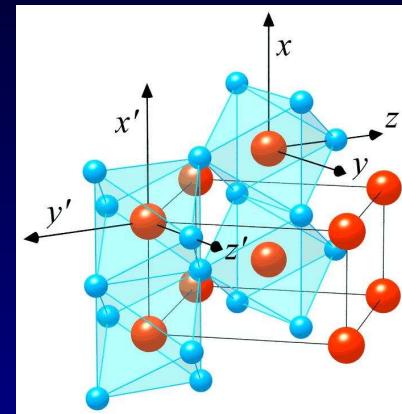
$$\begin{aligned} H = & \sum_{\{im\sigma\}} (H_{im,i'm'}^{LDA} - H_{im,i'm'}^{double counting}) a_{im\sigma}^+ a_{i'm'\sigma} \\ & + \frac{1}{2} \sum_{imm'\sigma \text{ (correl. orb.)}} U_{mm'} n_{im\sigma} n_{im'-\sigma} \\ & + \frac{1}{2} \sum_{im \neq m' \sigma \text{ (correl. orb.)}} (U_{mm'} - J_{mm'}) n_{im\sigma} n_{im'\sigma} \end{aligned}$$

- solve within Dynamical Mean Field Theory

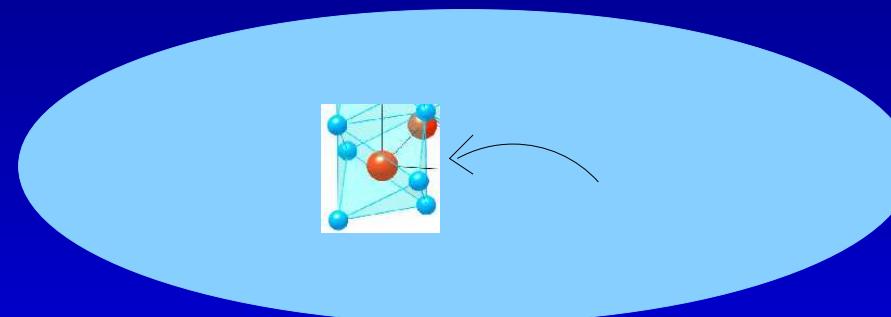
(Anisimov et al. 1997, Lichtenstein et al. 1998)

Dynamical mean field theory ...

... maps a lattice problem [a solid]



onto a single-site problem [an effective atom]

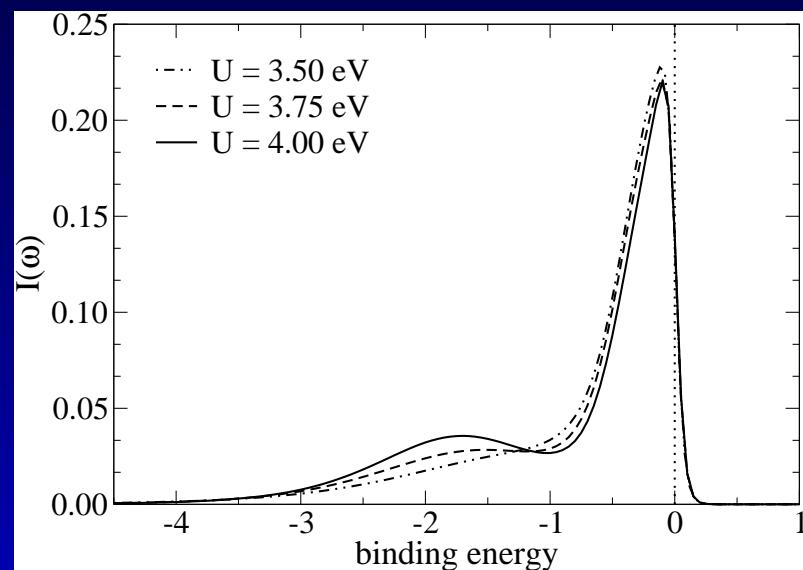


with a self-consistency condition

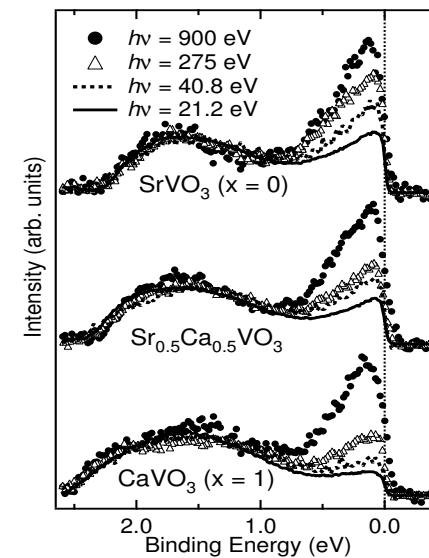
Spectra of perovskites

SrVO_3

LDA+DMFT

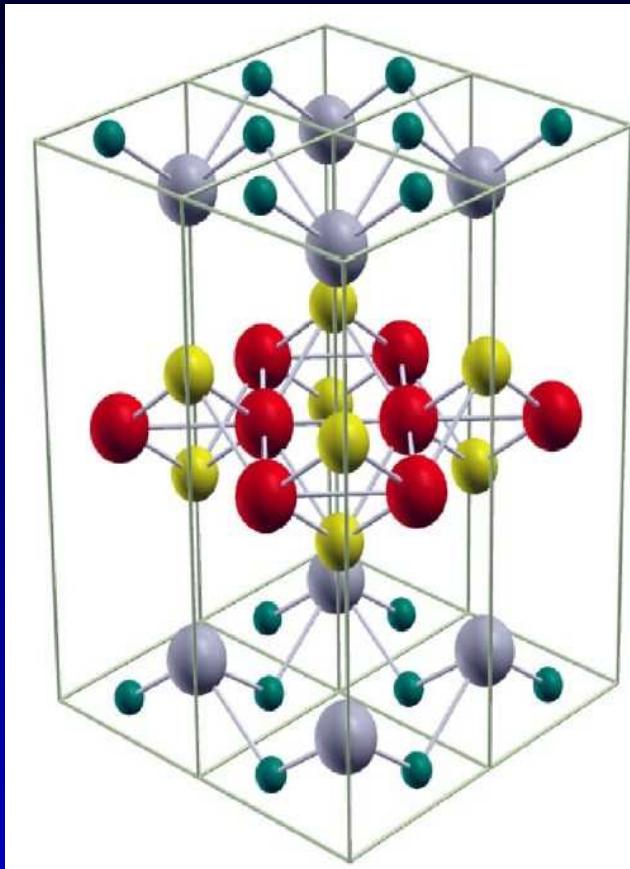


Photoemission



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

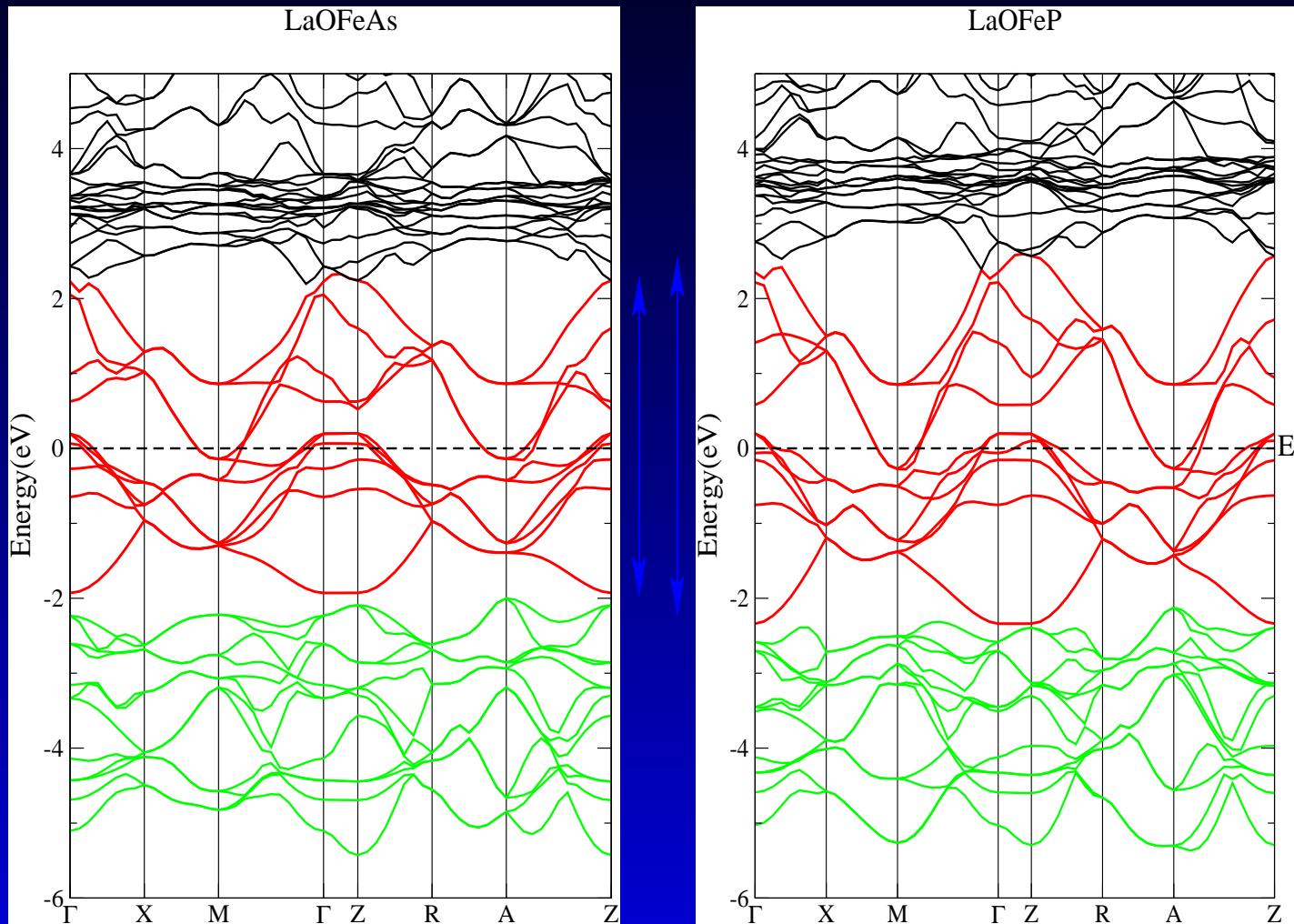
LaFeAsO



Fe
As
RE=La, Ce,
Pr, Sm,...
O

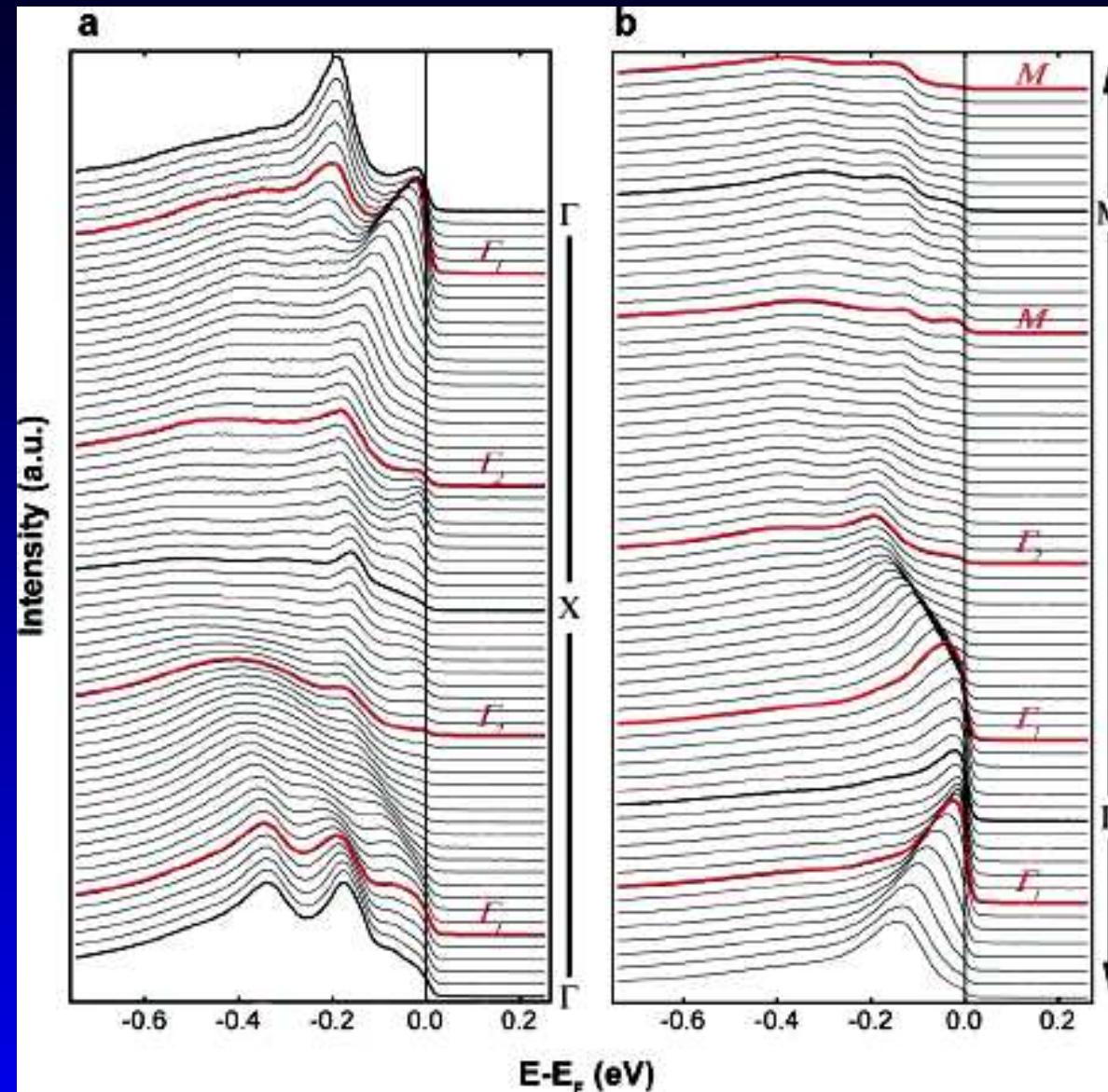
Parent compound of new iron oxypnictide superconductors
Fe-d states, hybridising with As-p and O-p bands

LaFeAsO and LaFePO



Fe-d states (red), hybridising with As-p and O-p bands (green)

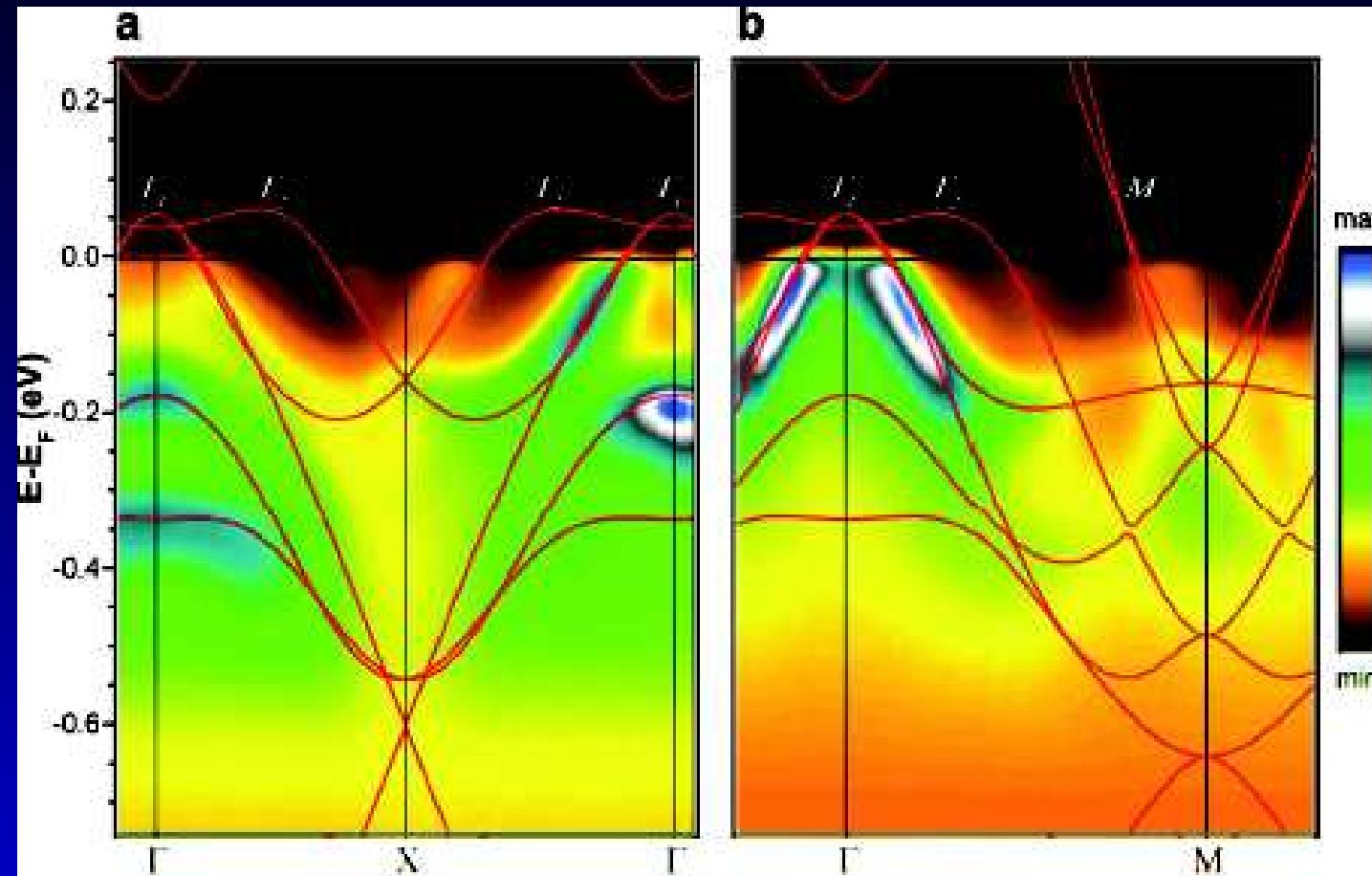
LaFePO



Fe-d states

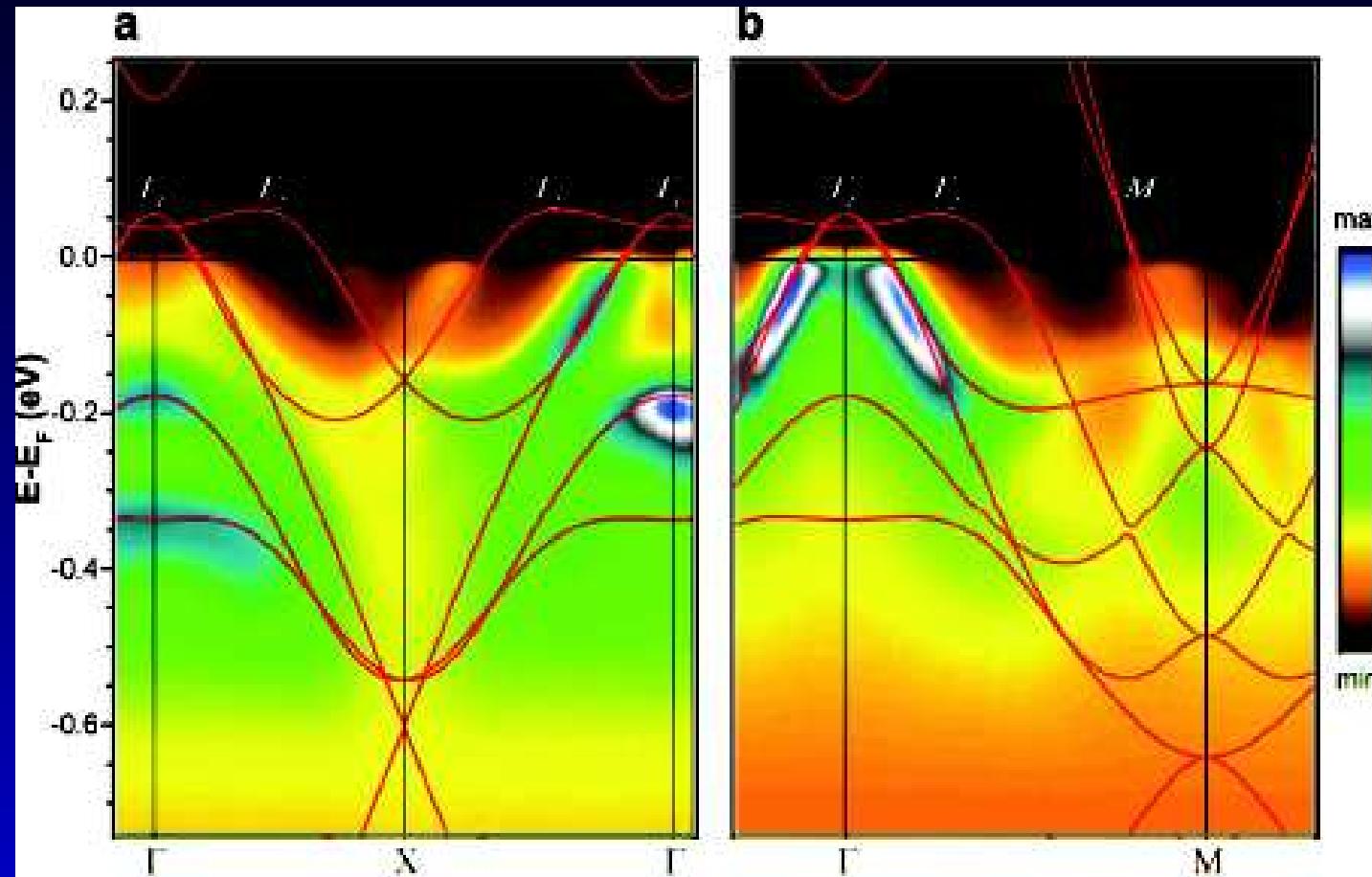
(Lu et al., 2008)

LaFePO



Fe-d states

LaFePO



Fe-d states

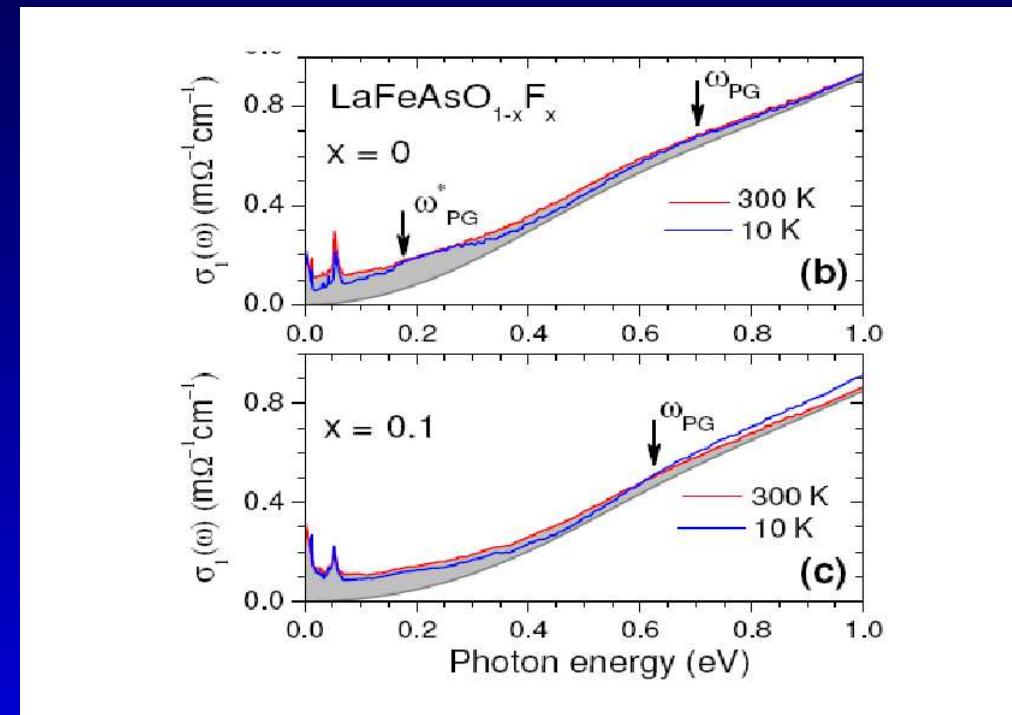
“after shifting the calculated bands up by 0.11 eV and then renormalizing by a factor 2.2” ...

Correlations in LaFeAsO?

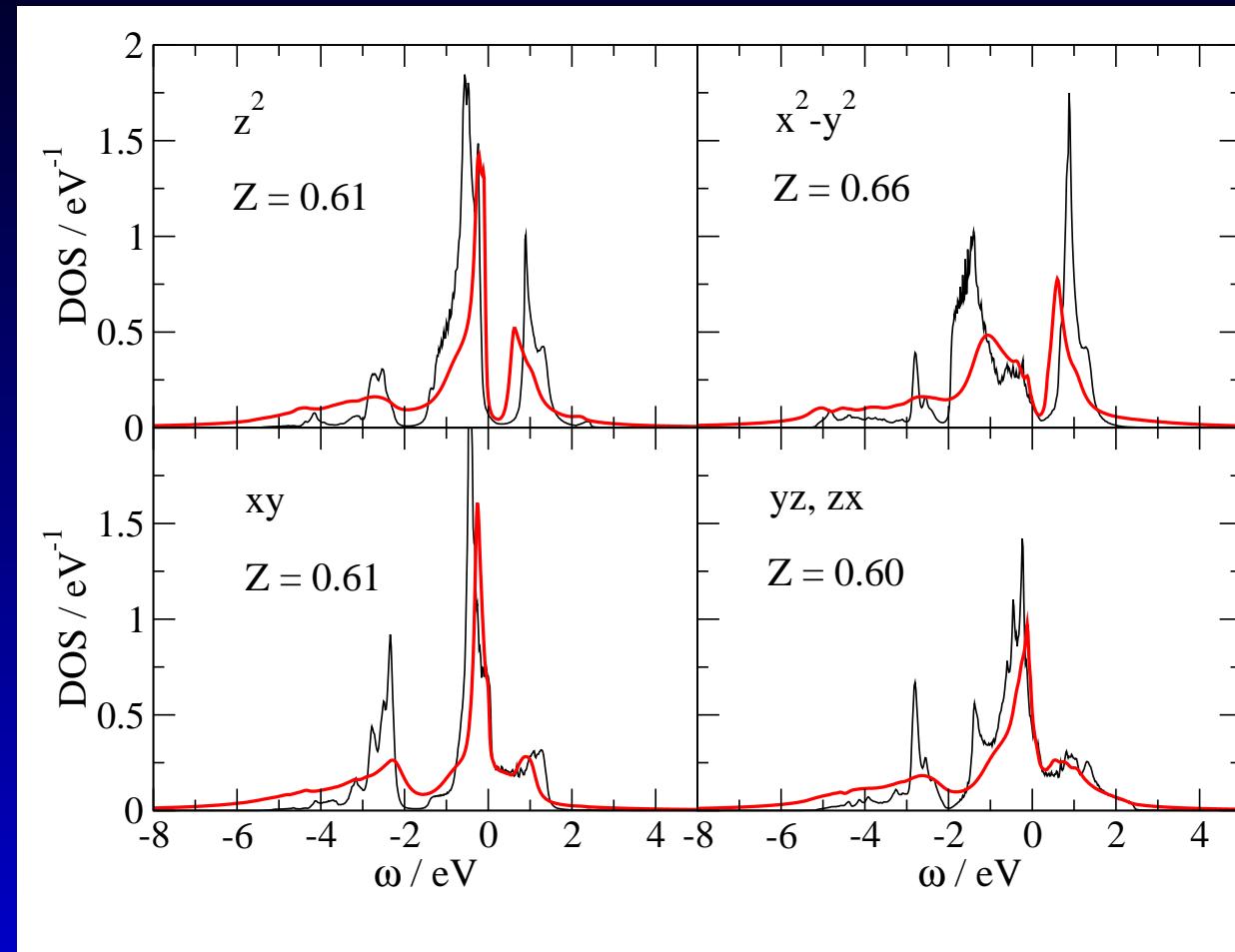
Experimental (ARPES, XAS, optics ...) indications of moderate correlations

Mass enhancement from ARPES $\sim 1.8 - 2.2$

Optics (Boris et al.):

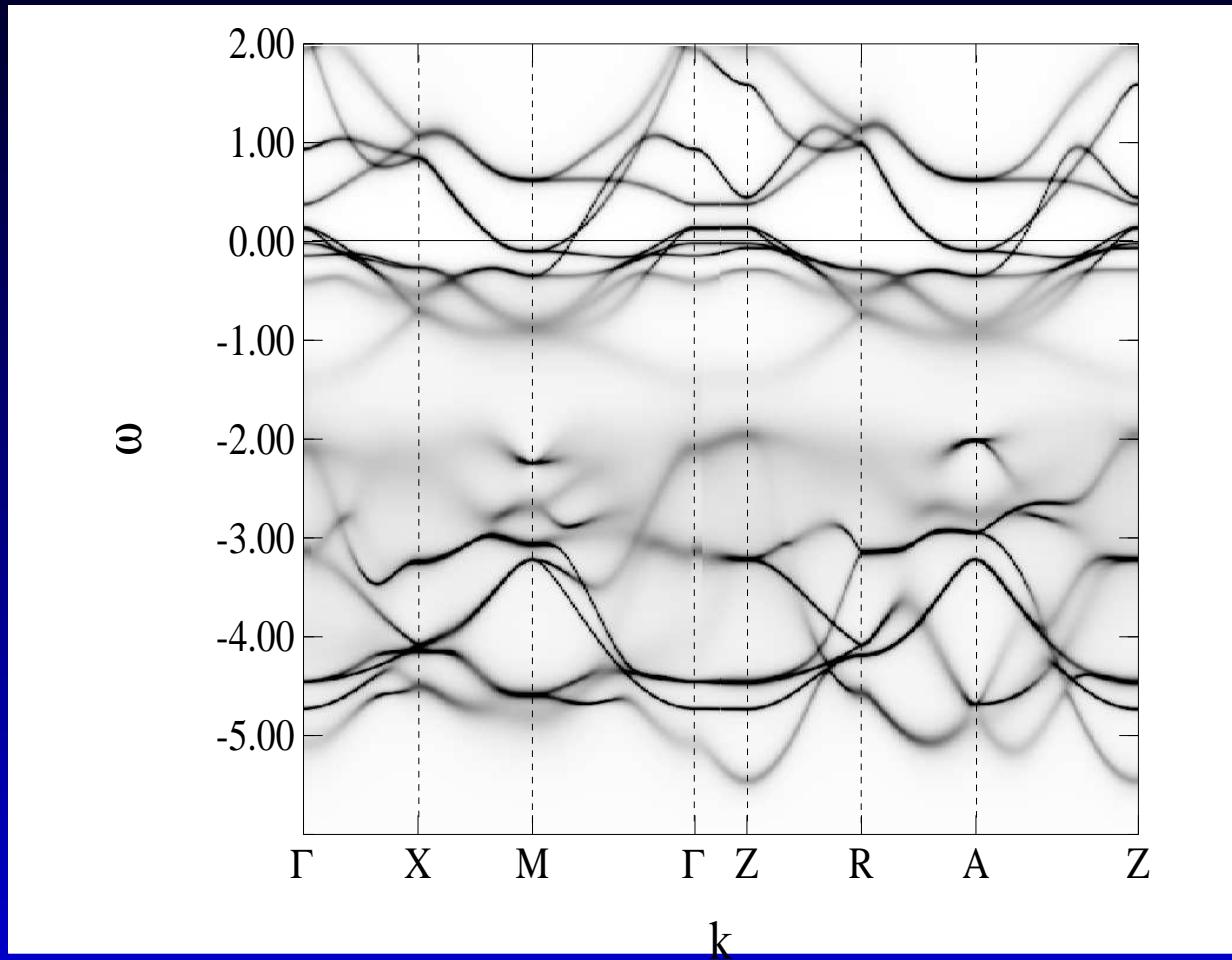


LaFeAsO with many-body effects



Aichhorn, Pourovskii, Vildosola, Ferrero, Parcollet, Miyake,
Georges, SB, PRB 2009

LaFeAsO with many-body effects



Well-defined quasi-particles close to E_F , damping effects beyond ~ 0.5 eV.

Aichhorn, Pourovskii, Vildosola, Ferrero, Parcollet, Miyake, Georges, SB, PRB 2009

Conclusions

- First principles calculations possible, based on density functional theory within the local density approximation
- Strictly: ground state properties only!
- For simple metals: LDA bands often a good first approximation to excited states
- For band insulators: gaps too small

Nobel Price in Chemistry, 1998



Conclusions

For “correlated materials”:

- metals: renormalised bands, shift of spectral weight
- “Mott insulators”: breakdown of band picture

→ many-body techniques necessary to calculate self-energy effects (e.g. dynamical mean field theory)



What's U in a solid?

... an answer from RPA:

Divide $P = P_d + P_r$ where P_d = polarization of the correlated orbitals (e.g. 3d orbitals)

Then:

$$\begin{aligned} W &= [1 - vP]^{-1}v \\ &= [1 - W_r P_d]^{-1} W_r \end{aligned}$$

where W_r that does not include 3d-3d screening:

$$W_r(\omega) = [1 - vP_r(\omega)]^{-1}v$$

Identify $U = W_r$!

*F. Aryasetiawan, M. Imada, A. Georges, G. Kotliar, S.B., A. I. Lichtenstein PRB **70** 195104 (2004)*