Spectroscopy: Photoemission

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VII.

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Outline

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How to study microscopic (nanoscopic...) structure

Dimensions of the probe have to be comparable to the dimensions of the investigated system.

One cannot see inside the material: wave-length of visible light is by orders of magnitude larger than interatomic distances.

Only indirect methods are available if you want to study interiour of a material: blackbox techniques.
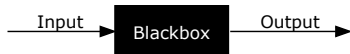
Diffraction: studying geometric structure (positions of ions)

Spectroscopy: studying electronic structure (energies $\varepsilon_{\mathbf{k}}^n$ and crystal momenta $\mathbf{k}$ of electrons)
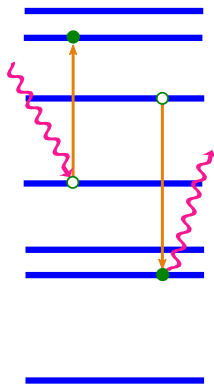
Modeling and comparing with theory is often indispensable.

Atomic levels

Atoms:
By measuring the energies at which the light is emitted or absorbed, a good picture of the positioning of the energy levels can be obtained.

$$E_2 - E_1 = \hbar\omega$$

Density of states

Solids:
Density of states (DOS) describes how many electron states are there at certain energy ε.

$$n(\varepsilon) \;=\; \sum_n \int_{1\mathrm{BZ}} \frac{\mathrm{d}\mathbf{k}}{4\pi} \,\delta(\varepsilon - \varepsilon_{\mathbf{k}}^n) \quad \text{density of states at energy } \varepsilon$$

$$N(E) = \int_{-\infty}^{E} \mathrm{d}\varepsilon \; n(\varepsilon) \qquad\qquad \text{number of states up to energy } E$$

Knowing the DOS for a solid is analogous to knowing the energy levels for an atom.

If we want to know other quantum numbers of stationary states (e.g., crystal momentum $\mathbf{k}$), we need to study more than just DOS.

Photoemission as a probe of occupied DOS
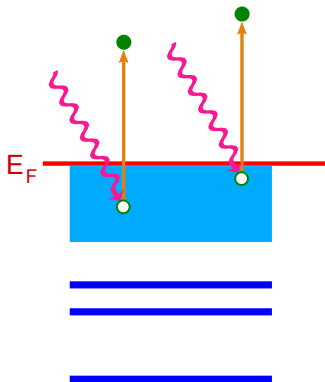
Exciting electrons from the valence band.

Having more electrons at our disposal means getting a higher intensity of the photoemission spectrum.

Higher DOS for particular energy E means that more electrons with that energy are available for being excited.

Higher DOS $\Rightarrow$ higher photoemission intensity.

Emission and absorption of light quanta

- Assume a system is described by an unperturbed Hamiltonian H_0. Consider its two eigenstates $|\psi_i\rangle$ and $|\psi_f\rangle$ (i.e., stationary states).

- This system is perturbed by Hamiltonian H_{int} which represents the interaction between the electrons and the photons,

$$H_{\text{int}} = -\frac{e}{m}\,\mathbf{A}(\mathbf{x}) \cdot \mathbf{p} \ .$$

The vector potential $\mathbf{A}(\mathbf{x})$ represents the quantized electromagnetic field and $\mathbf{p}$ is the momentum operator acting on the electron states.

The above Hamiltonian makes used of the so-called Coulomb calibration (not important for us). Moreover, it neglects terms proportional to $|\mathbf{A}|^2$, which may be important — we cannot describe two-photon transitions in this way.

Fermi's Golden Rule

Time-dependent first order perturbation theory:
Probability (per unit time) that a perturbation H_{int} causes a
transition between eigenstates $|\psi_i\rangle$ and $|\psi_f\rangle$ of the unperturbed
Hamiltonian is

$$w = \frac{2\pi}{\hbar} \, |M_{fi}|^2 \, \delta(E_f - E_i \pm \hbar\omega) \ .$$

The δ-function guarantees conservation of energy:
"+" for emission of photons, "-" for absorption of photons.

Transition matrix element M_{fi} is

$$M_{fi} \approx \left\langle \psi_f \left| e^{\pm\frac{i}{\hbar}\mathbf{q}\cdot\mathbf{x}} \, \epsilon \cdot \mathbf{p} \right| \psi_i \right\rangle \ ,$$

where $\mathbf{q}$ is the photon wave vector ($cq = \hbar\omega$) and ϵ is the
polarization vector of the radiation.

How the DOS enters the business

Do not get intimidated by the δ-function!

Probability of a radiative transition:

$$w = \frac{2\pi}{\hbar} \left| M_{fi} \right|^2 \delta(E_f - E_i \pm \hbar\omega) \ .$$

Recall DOS: $\qquad n(\varepsilon) = \sum_j \delta(\varepsilon - \varepsilon_j) = \sum_n \int_{(1\mathrm{BZ})} \frac{\mathrm{d}\mathbf{k}}{4\pi} \delta(\varepsilon - \varepsilon_{\mathbf{k}}^n).$

In photoemission we are interested in the probability that a final state "f" is created via incoming radiation.
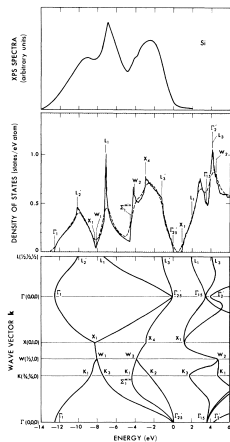
Therefore, we have to *integrate over all the initial states "i"*.
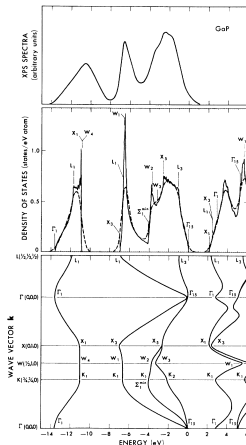
If the matrix elements do not depend on $\mathbf{k}$,

$$I(\hbar\omega) \approx \frac{2\pi}{\hbar} \left| M_{fi} \right|^2 n(E_f - \hbar\omega) \ .$$

The photoemission (and other) spectra thus reflect DOS weighted by transition matrix elements M_{fi}.

PES and DOS examples: when the nature is nice

PES

DOS

$\varepsilon^n(\mathbf{k})$

Si

GaP

Multicomponent systems: go for the local DOS

If we have a multicomponent system, it is desirable to get information about the local DOS.

Recall: Local density of states (LDOS) at **r** is the density of states with energy ε which results exclusively from electron states at site **r**.

DOS $\quad n(\varepsilon) \,=\, \sum_n \int_{1\mathrm{BZ}} \frac{\mathrm{d}\mathbf{k}}{4\pi}\, \delta(\varepsilon - \varepsilon_\mathbf{k}^n)$

LDOS $\quad n(\mathbf{r}, \varepsilon) \,=\, \sum_n \int_{1\mathrm{BZ}} \frac{\mathrm{d}\mathbf{k}}{4\pi}\, |\psi_\mathbf{k}^n(\mathbf{r})|^2\, \delta(\varepsilon - \varepsilon_\mathbf{k}^n)$

Integral of $n(\mathbf{r}, \varepsilon)$ over the unit cell gives total DOS $n(\varepsilon)$.

Integral of $n(\mathbf{r}, \varepsilon)$ over a sphere drawn around an atom in a solid gives the density of states associated with that atom.
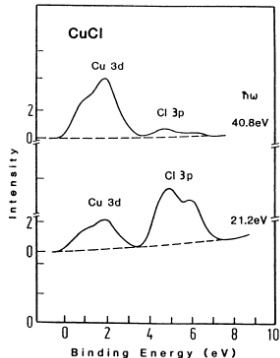
In this way the spatial inhomogeneity of the electronic structure is taken into acount.

Making use of the photoemission matrix elements

Photoemission matrix element $M_{fi} \approx \epsilon \cdot \langle \psi_f |\mathbf{p}| \psi_i \rangle$ depends on the difference $E_f - E_i$, i.e., on the exciting photon energy.
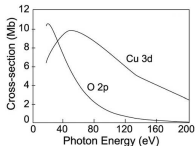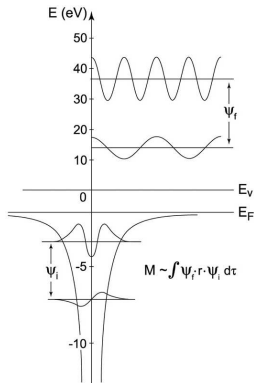
Phys. Scr. **T109**, 61 (2004)

Hüfner, Photoelectron spec. (1994)

By varying the energy of the incoming radiation $\hbar\omega$ we can put emphasis on one element or another.

Outline

ARPES — basic principle

Ejected photoelectron with energy $E_{\rm kin}$ is detected.

Wave-vector is determined by the energy $E_{\rm kin}$ and the direction θ ϕ.

Wave vector of the photoelectron in vacuum:

$$
\begin{aligned}
K_{\rm out,x} &= \frac{1}{\hbar}\sqrt{2mE_{\rm kin}}\,\sin\theta\cos\phi \\
K_{\rm out,y} &= \frac{1}{\hbar}\sqrt{2mE_{\rm kin}}\,\sin\theta\sin\phi \\
K_{\rm out,z} &= \frac{1}{\hbar}\sqrt{2mE_{\rm kin}}\,\cos\theta
\end{aligned}
$$
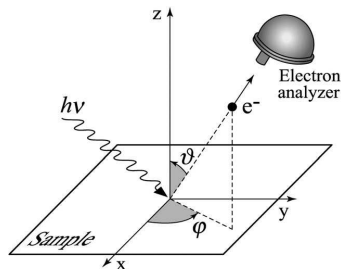
Photoemission geometry

Three steps model of photoemission

Not very accurate but transparent and intuitive.
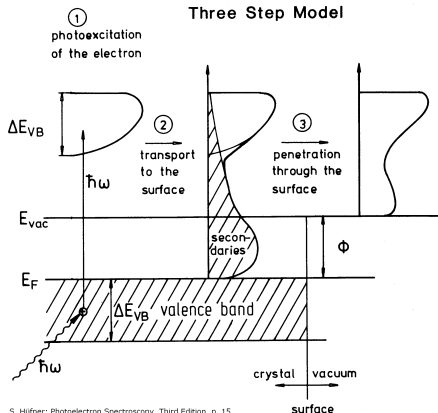
S. Hüfner: Photoelectron Spectroscopy, Third Edition, p. 15
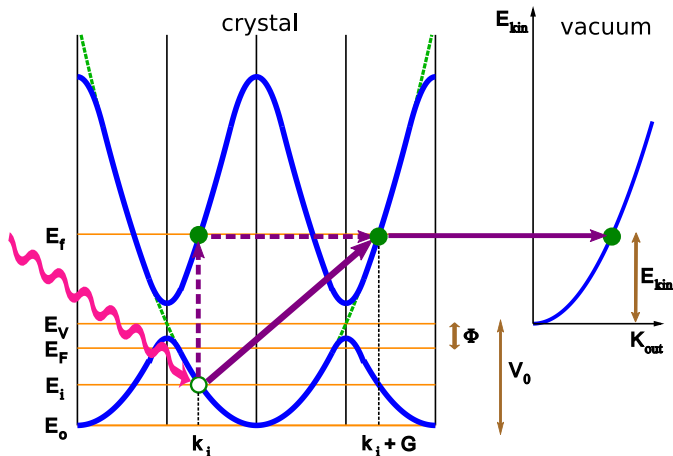
Hüfner, Photoelectron spectroscopy (1994)

The following processes are treated separately:

1. Photoexcitation of an electron in the bulk.

2. Propagation of the excited electron to the surface.

3. Escape of the electron from the bulk into the vacuum.

Recovering $\varepsilon_{\mathbf{k}}^n$ and $\mathbf{k}$ (1)

Conservation of energy: $E_{\mathrm{kin}} = \hbar\omega - \Phi - (E_F - E_i)$

Energy bands plotted in the extended zone scheme for convenience (the range of $\mathbf{k}$ is not restricted to 1BZ).

Recovering $\varepsilon_{\mathbf{k}}^n$ and $\mathbf{k}$ (2)
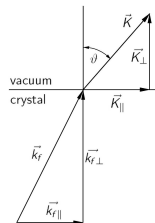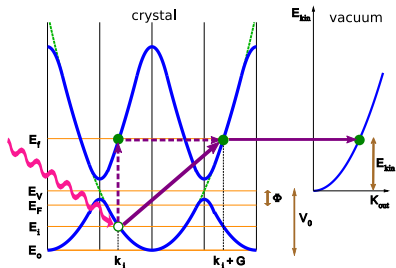
Momentum:

Parallel component $\mathbf{k}_{\parallel}$ is conserved up to a reciprocal lattice vector:

$$\mathbf{k}_{\parallel} = \mathbf{K}_{\mathrm{out},\parallel} - \mathbf{G}_{\parallel} \quad .$$

Recovering $\varepsilon_{\mathbf{k}}^n$ and $\mathbf{k}$ (3)
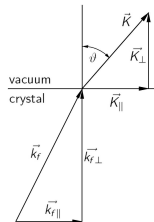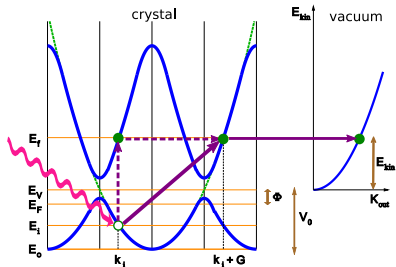
Perpendicular component can be recovered if assumptions about the bulk final state (in the solid) are made.

Assuming the free-electron-like character of the final state inside the crystal one gets

$$E_f - E_0 = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m} \left[(k_\perp + G_\perp)^2 + (\mathbf{k}_\parallel + \mathbf{G}_\parallel)^2 \right] \quad .$$

Recovering $\varepsilon_{\mathbf{k}}^n$ and $\mathbf{k}$ (4)
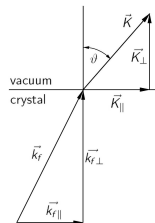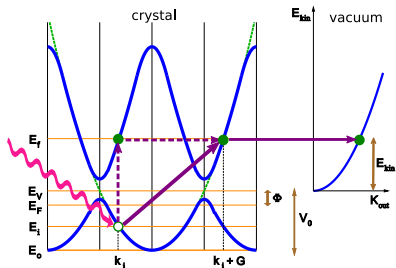
Energy balance: $\qquad E_f - E_0 \;=\; E_{\text{kin}} + (E_V - E_0)$

Free-electron approx.: $\quad E_f - E_0 \;=\; \dfrac{\hbar^2}{2m}\left[(k_\perp + G_\perp)^2 + (\mathbf{k}_\parallel + \mathbf{G}_\parallel)^2\right]\quad$.

Recovering $\varepsilon_{\mathbf{k}}^n$ and $\mathbf{k}$ (5)

$$\frac{\hbar^2}{2m} \left[(k_\perp + G_\perp)^2 + (\mathbf{k}_\parallel + \mathbf{G}_\parallel)^2 \right] = E_{\mathrm{kin}} + (E_V - E_0)$$

$$\mathbf{k}_\parallel = \mathbf{K}_{\mathrm{out},\parallel} - \mathbf{G}_\parallel$$

$$
\begin{aligned}
k_\perp + G_\perp &= \sqrt{\frac{2m}{\hbar^2} \left[E_{\mathrm{kin}} + (E_V - E_0) \right] - K_{\mathrm{out},\parallel}^2} \\
&= \sqrt{\frac{2m}{\hbar^2} \left[E_{\mathrm{kin}} + (E_V - E_0) - E_{\mathrm{kin}} \sin^2 \theta \right]} \\
&= \sqrt{\frac{2m}{\hbar^2} \left[E_{\mathrm{kin}} \cos^2 \theta + (E_V - E_0) \right]} \\
&= \sqrt{\frac{2m}{\hbar^2} \left[E_{\mathrm{kin}} \cos^2 \theta + V_0 \right]}
\end{aligned}
$$

V_0 is the difference between the zero vacuum energy and bottom of the band in a crystal.

Few more notes
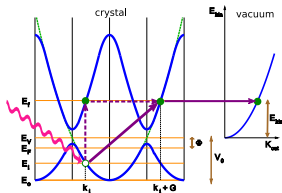
$$k_\perp + G_\perp = \sqrt{\frac{2m}{\hbar^2} \left[E_{\text{kin}} \cos^2 \theta + V_0 \right]}$$

The inner potential V_0 has to be determined by an educated quess (by fitting it so that experiment matches the theory or by imposing symmetry requirements — to make the bands have the symmetry of the solid).

Weak point:
Nearly-free electron approximation for the final states in the bulk will work well only for "nice" materials (such as alkali or simple metals) and/or for high energies.

Surface sensitivity of PES

The depth from which the photoelectrons can be detected is restricted by the mean free path of electrons in a solid.
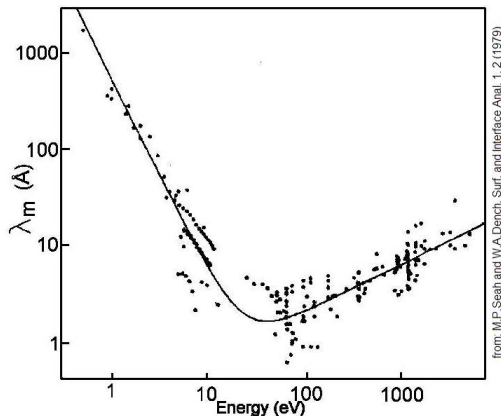
To probe bulk, either very low $\hbar\omega$ (threshold PES) or very high $\hbar\omega$ (HAXPES) is needed.

Depth-dependence of spectra: Where the bulk begins?

Cu(100) surface.
Layer-resolved spectral functions corresponding to photoemission at angle $38°$ for the surface layer and the first nine subsurface layers.
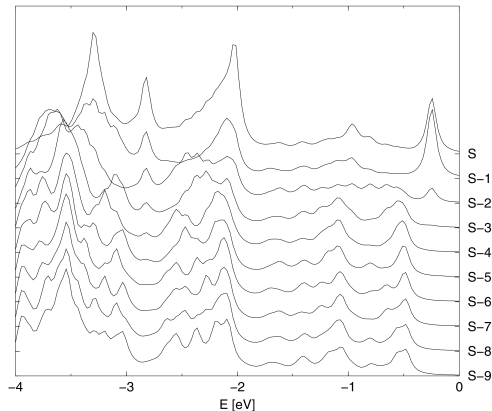
Lüdders *et al.* JPCM **13**, 8587
(2001)

Figure 3. Layer-resolved spectral functions corresponding to an emission angle of $38°$ for the surface layer and the first nine subsurface layers.

Beyond the order of five layers one basically recovers bulk behaviour.

Probing the surface, probing the bulk

By varying the energy, different depths are probed.

$\hbar\omega$=1000 eV

Fe(001)
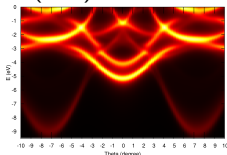
$\hbar\omega$=6000 eV

Fe(001)
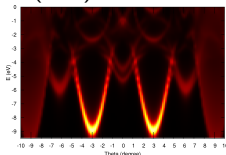
8 ML MgO/Fe(001)
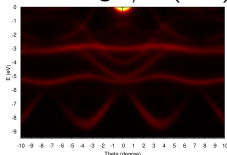
8 ML MgO/Fe(001)
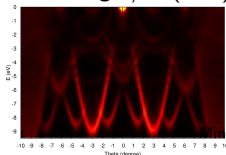
ár *et al.* JESRP (2011)

Fe-related features recovered for high photon energies $\Rightarrow$ access to buried interfaces.

Surface states vers. bulk states

How to distinguish one from the other in the photoemission spectra?

- Surface states have no dispertion along $k_\perp$.

- Energies and momenta of surface and bulk states cannot overlap (otherwise, it would be a bulk state...)

- Surface state have sharper linewidths (DOS in surface layers is more atomic-like).

Example of $\varepsilon_{\mathbf{k}}^n$ reconstruction: HgSe(110)

Model of nearly-free electron final states:
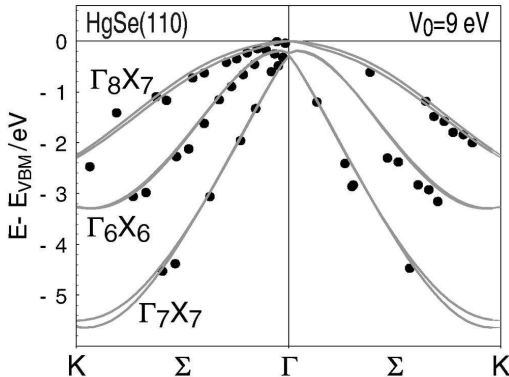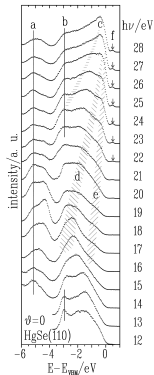
$$k_\perp = \sqrt{\frac{2m}{\hbar^2}(E_{\mathrm{kin}} + V_0)} - G_\perp$$

Normal ARPES ($\theta = 0°$).

Surface states: no dispersion
(marked by solid vertical lines)

Orlowski *et al.* 2001

Example of ε_k^n reconstruction: HgTe(110)

Model of nearly-free electron final states:
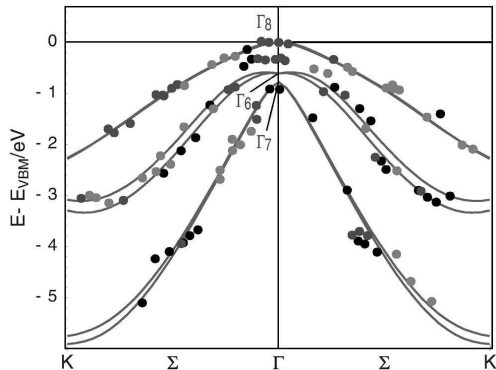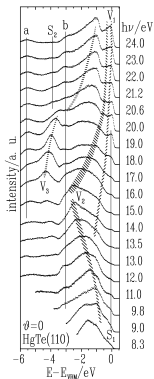
$$k_\perp = \sqrt{\frac{2m}{\hbar^2}\left(E_{\mathrm{kin}} + V_0\right)} - G_\perp$$

Normal ARPES ($\theta=0°$).

Surface states: no dispersion
(marked by solid vertical lines)

Orlowski *et al.* 2001

Outline

One step model of photoemission: Less is more
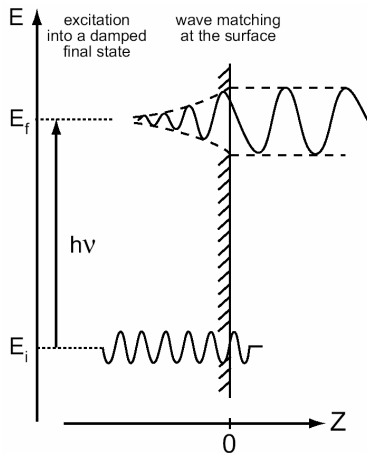
Not so intuitive but more accurate.

No hand-waving arguments, one has to calculate it.

Why:
A lot of spectra, a lot of details, a lot of opportunities to find a disagreement (a scientific prediction should be falsifiable).

One step model: Formal description

Probability of a radiative transition:

$$I(\hbar\omega) \approx \left| \langle \varepsilon_f, \mathbf{k}_\| \, | H_{\mathrm{int}} | \, \psi_i \rangle \right|^2 \, \delta(\varepsilon_f - \varepsilon_i \pm \hbar\omega) \ .$$

The proper final state is an "inverse LEED state" $|\varepsilon_f, \mathbf{k}_\|\rangle$:

▶ at infinity, it approaches a free-electron with parallel momentum $\mathbf{k}_\|$ and kinetic energy ε_f,

▶ in the solid, it attenuates when going deep beneath the surface to account for the finite mean-free path of the photoelectron.

The $|\varepsilon_f, \mathbf{k}_\|\rangle$ state should be computed accounting for the surface barrier. This can be conveniently achieved via multiple-scattering (a.k.a. KKR) or Green function formalism.

The attenuation of the final state is achieved through an imaginary component of the effective one-electron potential.

One step model: spectrum of Cu(111)
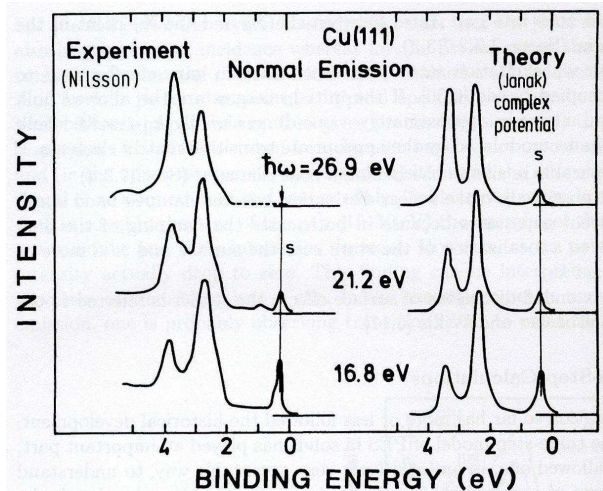
Spectra change if the energy of the exciting photon changes.

Hüfner, Photoelectron spectroscopy (1994)

Good agreement between LDA calculation and theory (in this case...).

ARPES — necessity of "non-conservation of momentum"

(Conservation) laws must be obeyed:
$$E_f^{(\text{system})} - E_i^{(\text{system})} = \hbar\omega$$
$$\mathbf{k}_f^{(\text{system})} - \mathbf{k}_i^{(\text{system})} = \mathbf{k}_\gamma$$

The problem: change of electron momentum cannot be catched up by change of incoming photon momentum ($|\mathbf{k}|_\gamma = \frac{2\pi}{\lambda}$).

Typical (crystal) momentum of electrons: $2\pi/a \approx 2\text{Å}^{-1}$
Typical momenta of photons in incoming UV light:

$\hbar\omega = 100$ eV $\quad \Rightarrow \quad |\mathbf{k}|_\gamma = 0.05$ Å^{-1}
$\hbar\omega = 21.2$ eV $\quad \Rightarrow \quad |\mathbf{k}|_\gamma = 0.008$ Å^{-1}

Photon provides the electron with the energy, crystal potential provides the momentum needed for reaching the excited state.

For individual electron the crystal momentum is conserved, i.e., momentum $\mathbf{k}$ is conserved up to a reciproval lattice vector $\mathbf{G}$.

Photon momentum effect

For (hard) x-rays, photon momentum $|\mathbf{k}|_\gamma = \frac{2\pi}{\lambda}$ cannot be neglected any more.

Ag(001) photoemission intensities along ΓK with LCP-light at $h\nu=552$ eV
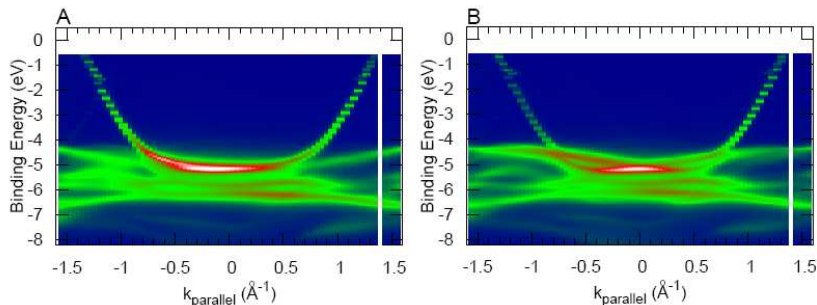
q_{photon} ignored

q_{photon} included

Matrix elements: dipole approximation

Transition matrix element: $\quad M_{fi} \approx \left\langle \psi_f \left| \mathrm{e}^{\pm \frac{\mathrm{i}}{\hbar} \mathbf{q} \cdot \mathbf{x}} \, \epsilon \cdot \mathbf{p} \right| \psi_i \right\rangle$.

Taylor expansion: $\mathrm{e}^{\pm \frac{\mathrm{i}}{\hbar} \mathbf{q} \cdot \mathbf{x}} = 1 \pm \frac{\mathrm{i}}{\hbar} \mathbf{q} \cdot \mathbf{x} + \frac{1}{2} (\frac{\mathrm{i}}{\hbar} \mathbf{q} \cdot \mathbf{x})^2 + \ldots$

If the quantum system is localised within a characteristic length a (the processes occur at this length scale),

$$\frac{1}{\hbar} a q \ll 1 \Leftrightarrow a \ll \frac{\hbar}{q} = \frac{\hbar}{\frac{\hbar \omega}{c}} = \frac{c}{\omega} = \frac{\lambda}{2\pi} \ ,$$

then the term $\frac{\mathrm{i}}{\hbar} \mathbf{q} \cdot \mathbf{x}$ and its powers can be neglected.

We thus have just $M_{fi} \approx \langle \psi_f \left| 1 \cdot \epsilon \cdot \mathbf{p} \right| \psi_i \rangle = \epsilon \cdot \langle \psi_f \left| \mathbf{p} \right| \psi_i \rangle$.
This is called the dipole approximation.

It can be used if the emission/absorption process happens at lengths much smaller than the wavelength of the radiation.
Usually it is the case.

Other forms of matrix elements

"Primordial" dipole matrix element:

$$M_{fi} \approx \epsilon \cdot \langle \psi_f \left| \mathbf{p} \right| \psi_i \rangle \quad .$$

Using the coordinate-momentum commutation relations
$[\mathbf{r}_i, \mathbf{p}_j] = i\hbar \delta_{ij}$ (and few other tricks), the matrix element in dipole
approximation can be written as

$$M_{fi} \approx \epsilon \cdot \langle \psi_f \left| \mathbf{p} \right| \psi_i \rangle = i m \omega \epsilon \cdot \langle \psi_f \left| \mathbf{r} \right| \psi_i \rangle = \frac{i}{\omega} \epsilon \cdot \langle \psi_f \left| \nabla V \right| \psi_i \rangle$$

In *most* situations, all these forms are equivalent.

For practical reasons, the $\langle \psi_f \left| \nabla V \right| \psi_i \rangle$ form mostly used in PES.

(Dipole) selection rules: where do they come from?

Dipole transition matrix element: $\epsilon \cdot \langle \psi_f | \mathbf{r} | \psi_i \rangle$

Analogy:
Integral of a product of an even and an odd functions will be identically zero.

Likewise:
If wave functions $|\psi_i\rangle$ and $|\psi_f\rangle$ have certain symmetries, the (dipole) matrix element will be identically zero.

Such transitions are called forbidden transitions.

Transitions forbidden by the dipole selection rule are accessible via higher-order terms in the $\exp(\pm \frac{i}{\hbar} \mathbf{q} \cdot \mathbf{x})$ expansion, their intensity is usually much less than intensity of the dipole-allowed transitions.

Selection rules in PES: what do they do?

Assuming a sample with a mirror plane, photoemission from a *d* orbital.

To have non-vanishing intensity, the whole integrand must be even w.r.t. the mirror plane (like integrating from $-\infty$ to ∞).

- Plane wave $\psi_f\rangle$ is always even w.r.t. sample mirror plane.
- $\epsilon \cdot \mathbf{r}$ is even if ϵ is in-plane and odd if ϵ is perpendicular to the plane
- $|\psi_i\rangle$ may be even or odd (here it is $d_{x^2-y^2}$, i.e., even).

Different polarizations probe different states: ϵ_p probes $d_{x^2-y^2}$, ϵ_s probes d_{xy}.

$\epsilon \cdot \langle \psi_f \,|\mathbf{r}|\, \psi_i \rangle$
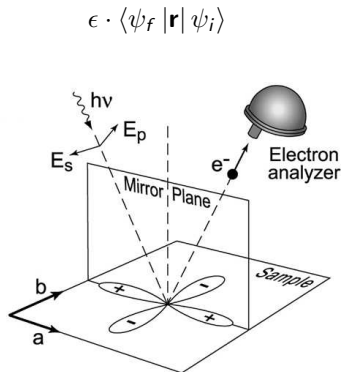
Example: polarization-dependence of PES of Cu(111)
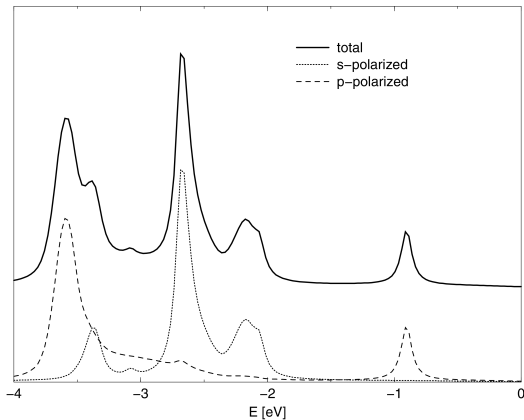
Lüdders *et al.* JPCM **13**, 8587

(2001)

Figure 5. Polarization-resolved photocurrents of Cu(111) at 21.2 eV normal emission.

Calculated total photocurrent for normal emission at 21.2 eV photon energy.

Outline

One step model: spectrum of Ni

Single particle (LDA)

Calculation done using the local density approximation (LDA) to the DFT yields a very poor agreement with experiment !

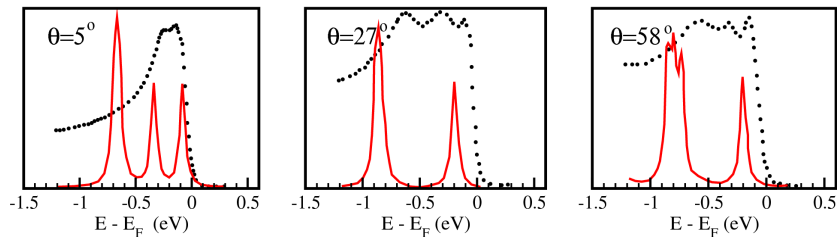# Beyond (effective) one-electron description (1)

One electron formalism:

$$I(\hbar\omega) \approx \left| \langle E_f, \mathbf{k}_\parallel | H_{\mathrm{int}} | \psi_i \rangle \right|^2 \, \delta(E_f - E_i - \hbar\omega) \ .$$

Assuming N interacting electrons:

$$I(\hbar\omega) \approx \left| \left\langle \Psi_f^{(N)} | \mathcal{H}_{\mathrm{int}} | \Psi_i^{(N)} \right\rangle \right|^2 \, \delta(E_f^{(N)} - E_i^{(N)} - \hbar\omega) \ .$$

$|\Psi_i^{(N)}\rangle = |\Psi_0^{(N)}\rangle$ \qquad many-body ground state

Sudden approximation: Interaction of the excited outgoing photoelectron with the rest system is neglected.

$a_{f,\mathbf{k}_\parallel}^\dagger |\Psi_S^{(N-1)}\rangle$ \qquad\qquad $a_{f,\mathbf{k}_\parallel}^\dagger$ creates $|\varepsilon_f, \mathbf{k}_\parallel\rangle$

Beyond (effective) one-electron description (2)

Factorization into single particle and many-body terms using a representation by single-particle states ϕ_m:

$$I(\hbar\omega) \approx \sum_{mm'} \sum_{S} \left\langle \phi_{f,\mathbf{k}_\parallel} | H_{\mathrm{int}} | \phi_m \right\rangle \left\langle \Psi_0^{(N)} | a_m^\dagger | \Psi_S^{(N-1)} \right\rangle$$

$$\times \delta(\varepsilon_f - \hbar\omega + E_S^{(N-1)} - E_0^{(N)})$$

$$\times \left\langle \Psi_S^{(N-1)} | a_{m'} | \Psi_0^{(N)} \right\rangle \left\langle \phi_{m'} | H_{\mathrm{int}}^\dagger | \phi_{f,\mathbf{k}_\parallel} \right\rangle$$

$$I(\hbar\omega) \approx \sum_{mm'} \left\langle \phi_{f,\mathbf{k}_\parallel} | H_{\mathrm{int}} | \phi_m \right\rangle A_{mm'}(\varepsilon_f - \hbar\omega) \left\langle \phi_{m'} | H_{\mathrm{int}}^\dagger | \phi_{f,\mathbf{k}_\parallel} \right\rangle$$

$$A_{mm'}(\varepsilon) := \sum_{S} \left\langle \Psi_0^{(N)} \left| a_m^\dagger \right| \Psi_S^{(N-1)} \right\rangle \delta(\epsilon + E_S^{(N-1)} - E_0^{(N)})$$

$$\times \left\langle \Psi_S^{(N-1)} \left| a_{m'} \right| \Psi_0^{(N)} \right\rangle$$

Spectral function $A(\varepsilon)$

Photoemission-specific part: $\left\langle \phi_{f,\mathbf{k}_\parallel} | H_{\mathrm{int}} | \phi_m \right\rangle$

Many-body ground-state-specific part:

$$A_{mm'}(\varepsilon) \ := \ \sum_S \left\langle \Psi_0^{(N)} \left| a_m^\dagger \right| \Psi_S^{(N-1)} \right\rangle \delta(\epsilon + E_S^{(N-1)} - E_0^{(N)})$$
$$\times \left\langle \Psi_S^{(N-1)} \left| a_{m'} \right| \Psi_0^{(N)} \right\rangle$$

m stands for any representation (quantum number). Typically, it denotes a Bloch state.

Spectral function $A(\varepsilon)$ is a generalization of DOS.
For non-interacting electrons:

$$A_{mm}(\varepsilon) \ = \ \delta(\varepsilon - \varepsilon_m)$$

Recall the definition of DOS: $n(\varepsilon) \ = \ \sum_m \delta(\varepsilon - \varepsilon_m)$

Crash course on Green's functions in quantum theory

To get wave function of a quantum system, we may either solve the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi = H\Psi ,$$

or "take" the Green's function (operator) and apply it on the wave function at t_0,

$$|\Psi(t)\rangle = G^{(+)}(t, t_0) |\Psi(t_0)\rangle .$$

For time-independent solutions, we can either solve

$$E|\psi\rangle = (H_0 + V)|\psi\rangle ,$$

or use a solution of a simpler problem

$$E|\psi_0\rangle = H_0|\psi_0\rangle ,$$

and apply the Green's function:

$$|\psi\rangle = (1 + G^{(+)}V)|\psi_0\rangle .$$

Why Green's functions?

Working with Green's functions does not bring anything really new.

Nominally, it is just another formal complication to please the mathematical gods.

However, working with Green's functions is (often) practical in many-body physics: various approximations can be more easily introduced and step-by-step improved in the Green's functions formalism.

Spectral function $A(\varepsilon)$, important in describing PES, is part of the Green's functions world.

Spectral function $A(\varepsilon)$ is related to retarded Green function:

$$A_{mm'}(\varepsilon) := -\frac{1}{\pi} \operatorname{Im} G^{(+)}_{mm'}(\varepsilon)$$

Dyson equation

Single-particle situation:
Hamiltonian H_0 has got a corresponding Green's function G_0,
Hamiltonian $H_0 + V$ has got Green's function G:

$$G(E) = G_0(E) + G_0(E)\, V\, G(E) \ .$$

The perturbing potential V does not depend on energy.

Many-body situation:
One-particle Green's function of an interacting many-body system $G(E)$ is related to Green's function of a non-interacting system $G_0(E)$ via

$$G(E) = G_0(E) + G_0(E)\, \Sigma(E)\, G(E) \ .$$

Self-energy $\Sigma(E)$ depends on energy, it incorporates all the many-body physics.

Self-energy: quick and dirty view

Green's function of interacting system $G(E)$, Green's functin of non-interacting system $G_0(E)$, self-energy $\Sigma(E)$:

$$G(E) = G_0(E) + G_0(E)\,\Sigma(E)\,G(E) \ .$$

In representation of single-particle Bloch waves:

$$G(\mathbf{k}, \varepsilon) = \frac{1}{\epsilon - \varepsilon_{\mathbf{k}} + \Sigma(\mathbf{k}, \varepsilon)}$$

Self-energy $\Sigma(\mathbf{k}, \varepsilon)$ describes how binding energies are modified by the many-body effects.
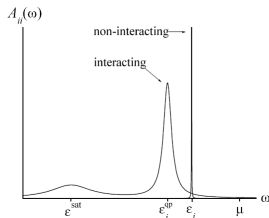
Spectral function and spectral lines

Many-body effects change a sharp energy level into a broader peak plus a satelite.

$$I(\hbar\omega) \approx \sum_{mm'} \left\langle \phi_{f,\mathbf{k}_\parallel} | H_{\text{int}} | \phi_m \right\rangle A_{mm'}(\varepsilon_f - \hbar\omega) \left\langle \phi_{m'} | H_{\text{int}}^\dagger | \phi_{f,\mathbf{k}_\parallel} \right\rangle$$

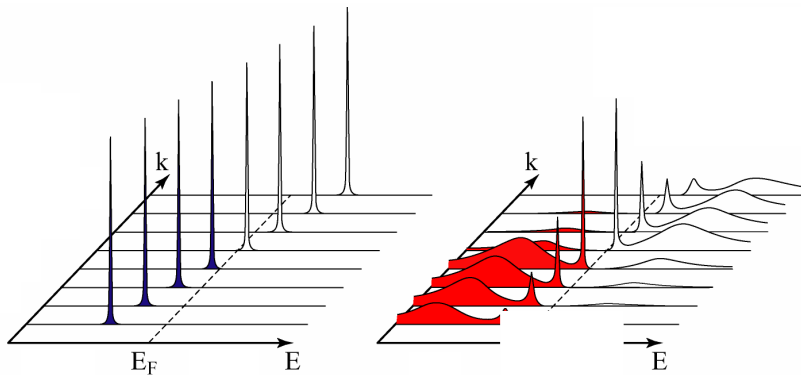$$A(\mathbf{k}, \varepsilon) = \frac{1}{\pi} \frac{\Sigma(\mathbf{k}, \varepsilon)}{[\epsilon - \varepsilon_\mathbf{k} + \text{Re}\Sigma(\mathbf{k}, \varepsilon)]^2 + [\text{Im}\Sigma(\mathbf{k}, \varepsilon)]^2}$$

$\text{Re}\Sigma(\mathbf{k}, \varepsilon)$ describes energy shift of the spectral peak.

$\text{Im}\Sigma(\mathbf{k}, \varepsilon)$ describes the change of the width of the spectral peak.

Generalizing the $\varepsilon_n(\mathbf{k})$ picture

States are represented not by single peaks in the spectral function $A_{\mathbf{k}}(\varepsilon)$ but by broadened elastic resonances followed by satelite structures.

Adding correlations explicitly

$$\hat{H} \;=\; \sum_{\mathbf{k}\,\ell m\,\ell'\,m'\,\sigma} \varepsilon_{\ell m\,\ell'\,m'\,\sigma}(\mathbf{k})\, \hat{c}^{\dagger}_{\mathbf{k}\ell m\sigma}\hat{c}_{\mathbf{k}\ell'\,m'\,\sigma}$$

LDA

Adding correlations explicitly

For correlated bands, add Coulomb interaction between electrons at the same sites

$$
\begin{aligned}
\hat{H} &= \sum_{\mathbf{k}\,\ell m\,\ell'\,m'\,\sigma} \varepsilon_{\ell m\ell'm'\sigma}(\mathbf{k})\,\hat{c}^{\dagger}_{\mathbf{k}\ell m\sigma}\,\hat{c}_{\mathbf{k}\ell'm'\sigma} \\[2mm]
&+ \sum_{i_d,\ell_d}\,{\sum_{m\sigma,m'\sigma'}}' \frac{U^{\sigma\sigma'}_{mm'}}{2}\,\hat{n}_{\mathbf{k}i_d\ell_d m\sigma}\,\hat{n}_{\mathbf{k}i_d\ell_d m'\sigma'} \\[2mm]
&- \sum_{i_d,\ell_d}\,{\sum_{m\sigma,m'\sigma'}}' J_{mm'}\,\hat{c}^{\dagger}_{\mathbf{k}i_d\ell_d m\sigma}\,\hat{c}^{\dagger}_{\mathbf{k}i_d\ell_d m'\sigma'}\,\hat{c}_{\mathbf{k}i_d\ell_d m'\sigma}\,\hat{c}_{\mathbf{k}i_d\ell_d m\sigma'}
\end{aligned}
$$

LDA   local Coulomb   Hund's rule

Adding correlations explicitly

For correlated bands, add Coulomb interaction between electrons at the same sites

$$
\begin{aligned}
\hat{H} \;=\; & \sum_{\mathbf{k}\,\ell m\,\ell'\,m'\,\sigma} \varepsilon_{\ell m\ell'm'\sigma}(\mathbf{k})\,\hat{c}^{\dagger}_{\mathbf{k}\ell m\sigma}\hat{c}_{\mathbf{k}\ell'm'\sigma} \\[2mm]
& + \sum_{i_d,\ell_d} \sideset{}{'}\sum_{m\sigma,m'\sigma'} \frac{U^{\sigma\sigma'}_{mm'}}{2}\,\hat{n}_{\mathbf{k}i_d\ell_d m\sigma}\,\hat{n}_{\mathbf{k}i_d\ell_d m'\sigma'} \\[2mm]
& - \sum_{i_d,\ell_d} \sideset{}{'}\sum_{m\sigma,m'\sigma'} J_{mm'}\,\hat{c}^{\dagger}_{\mathbf{k}i_d\ell_d m\sigma}\hat{c}^{\dagger}_{\mathbf{k}i_d\ell_d m'\sigma'}\hat{c}_{\mathbf{k}i_d\ell_d m'\sigma}\hat{c}_{\mathbf{k}i_d\ell_d m\sigma'} \\[2mm]
& - \sum_{i_d,\ell_d} \sideset{}{'}\sum_{m\sigma} \Delta\epsilon_d\,\hat{n}_{\mathbf{k}i_d\ell_d m\sigma}
\end{aligned}
$$

LDA   local Coulomb   Hund's rule   double counting

Going beyond the LDA

The LDA is a goose that lays golden eggs.

Direct approaches to many-body physics are not even close to being materially-specific (save few "singular cases").

You want to leave as much of LDA it as possible.

LDA+*something* methods: electron-electron interaction is added explicitly on top of the LDA Hamiltonian.

You describe localized electrons in a suitable LDA-generated basis and add Hubbard U and J to describe on-site interaction between electrons.

Caveat: The U and J values are basis-dependent, therefore not blindly transferrable from one calculations to the another.

Double counting problem: Some electron-electron interaction has been included in the LDA already so care has to be taken not to count it twice. An educated guess it needed.
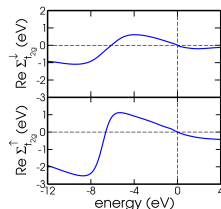
Describing many electron effects: LDA+DMFT
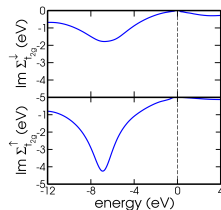
DMFT = Dynamical Mean Field Theory

Formalism to transform many-body
interactions among electrons in a solid into
interaction of a single impurity with a
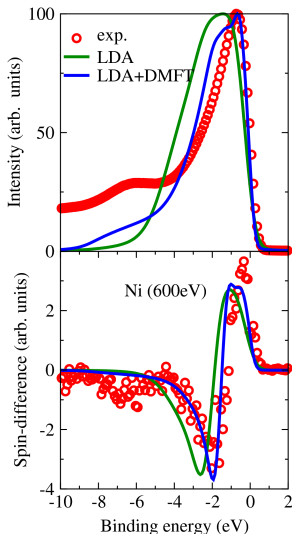suitable constructed environment (bath).
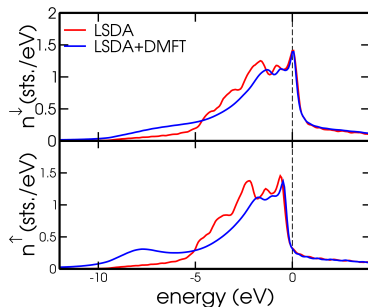
Bulk Ni: the DOS

$\mathrm{Re}\Sigma(\varepsilon)$

$\mathrm{Im}\Sigma(\varepsilon)$

LDA and LDA+DMFT: angle-integrated spectrum of Ni

Minar *et al.* PRL **95**, 166401 (2005)
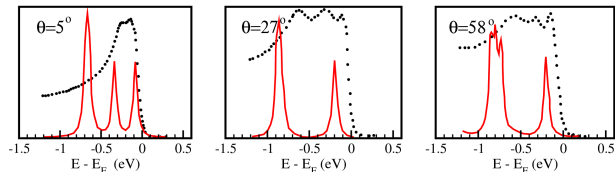
Main effects of LDA+DMFT:

1. Narrowing of the main peak.
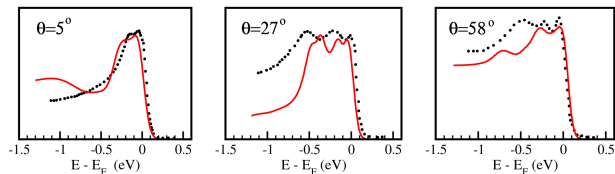2. Appearence of satellite peak ("lower Hubbard band").

Fano effect:
If the incoming x-rays are circularly polarized, there is a spin-imbalance in the ejected photoelectrons.

LDA and LDA+DMFT: ARPES of Ni

Single particle (LDA)

LSDA+DMFT

Braun *et al.* PRL **97**, 227601 (2008)

LDA+DMFT results are not perfect but present a significant improvement over plain LDA.