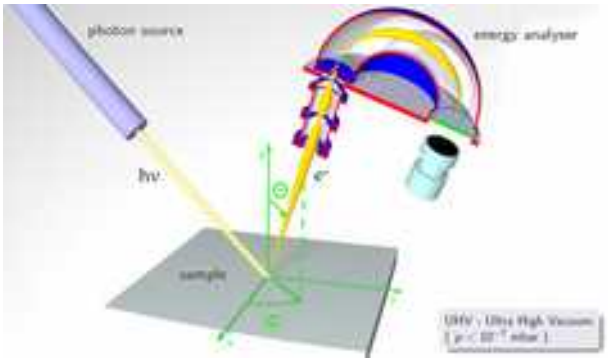
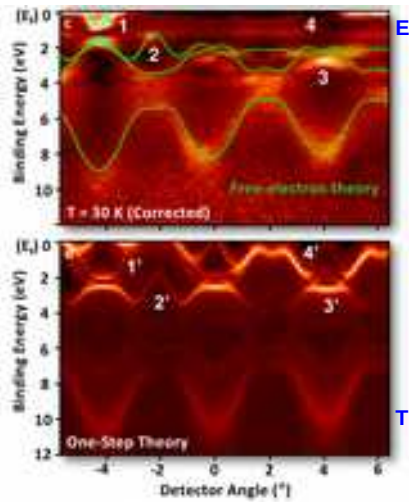
One step model of photoemission

Ján Minár

Ludwig-Maximilians-Universität München, Germany
and
University of West Bohemia, Pilsen
New Technologies - Research Center



$$\hat{G} = \hat{G}_0 + \hat{G}_0 \hat{V} \hat{G}$$



Outline of lecture

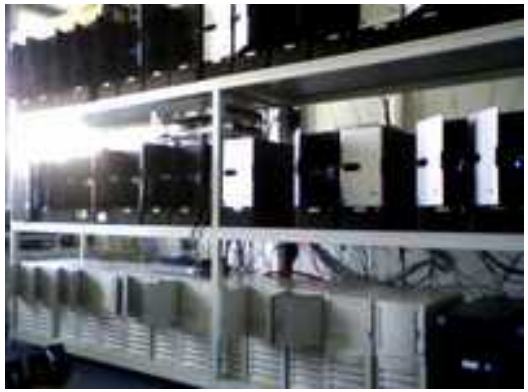
Theoretical ingredients

- Introduction
- Density functional theory
- Band structure methods
- Multiple scattering KKR method
  - Why to use Greens functions

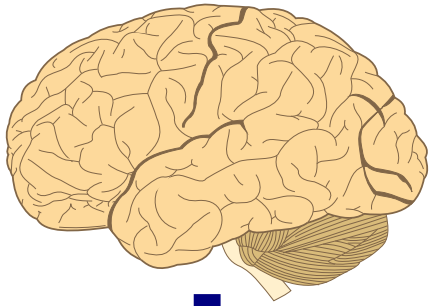
One step model of photoemission

- Three step model of PES
- One step model of PES
  - Surface states
  - Correlation effects
  - Aspects of HAXPES

Theory and experiments

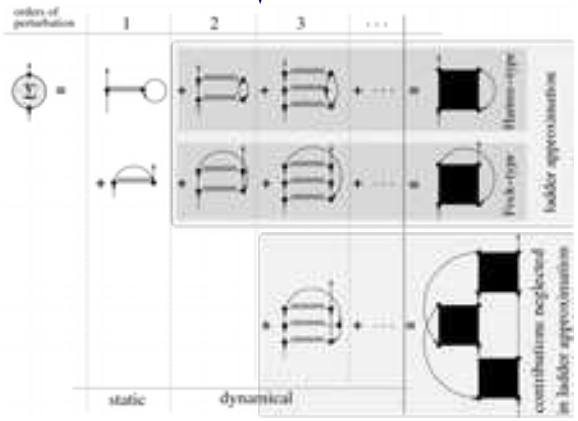


Brain extension

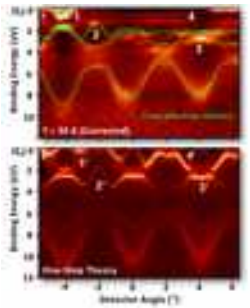


- One single high pressure experiment
  - repeated daily
  - chemistry of organic compounds

Approximations



Results ?

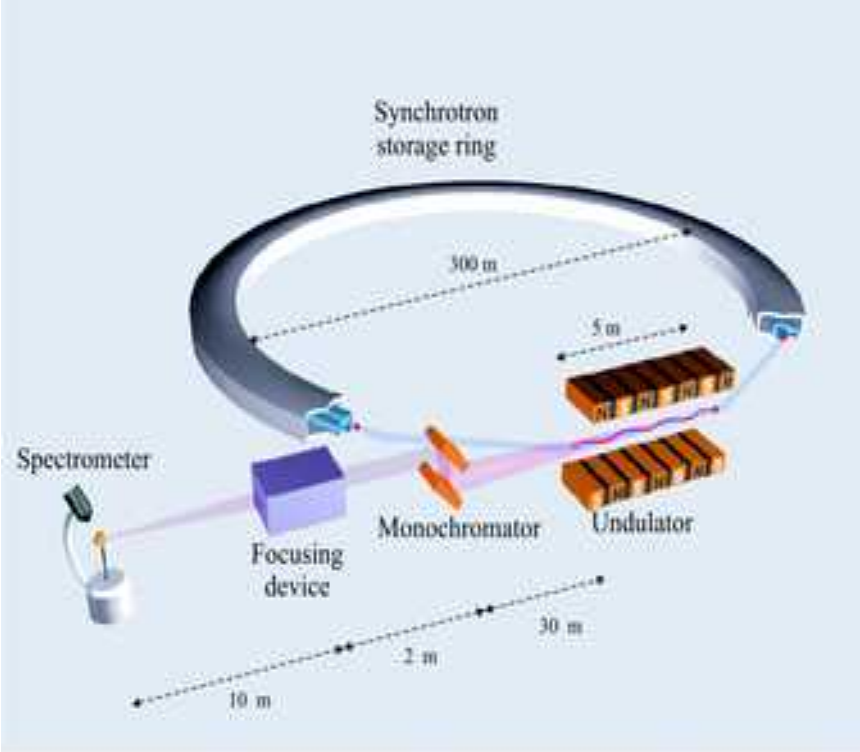


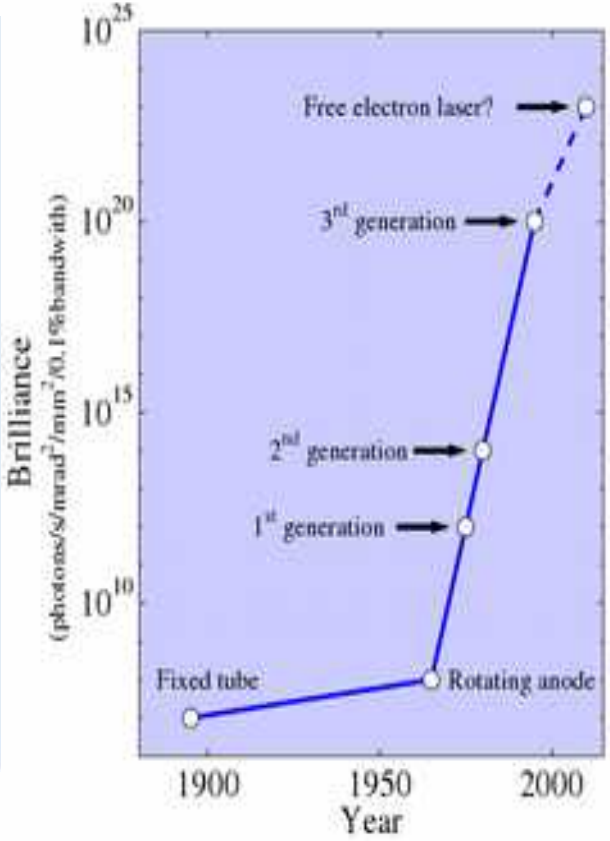
Exp.

Theory

Synchrotron radiation based techniques

New light sources

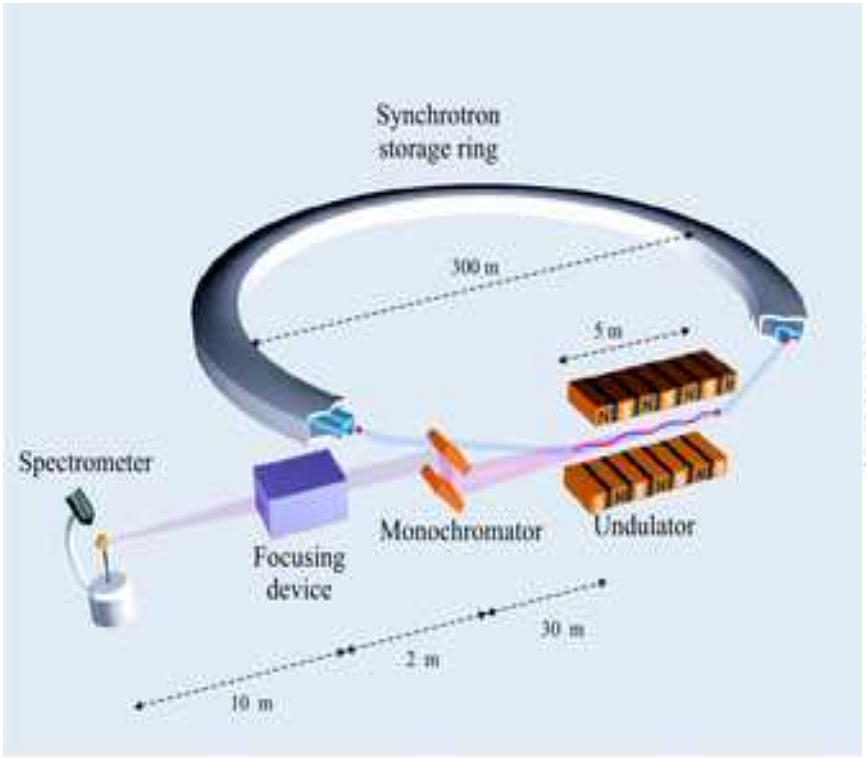


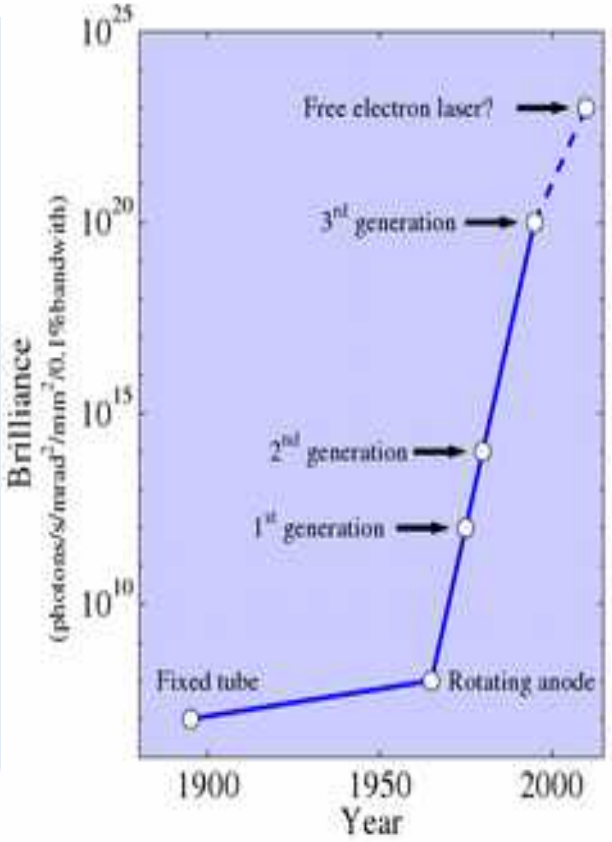


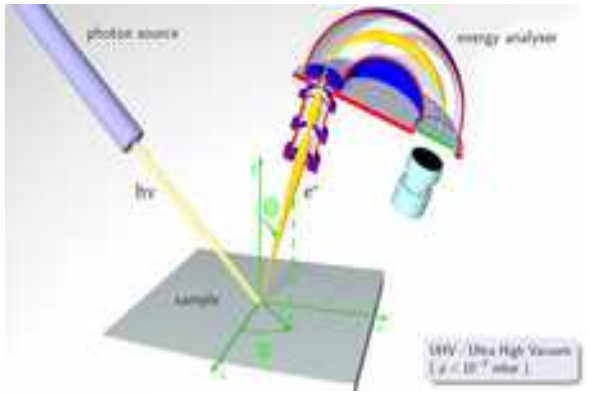
Synchrotron radiation based techniques

New light sources

Old
Solid state spectroscopies





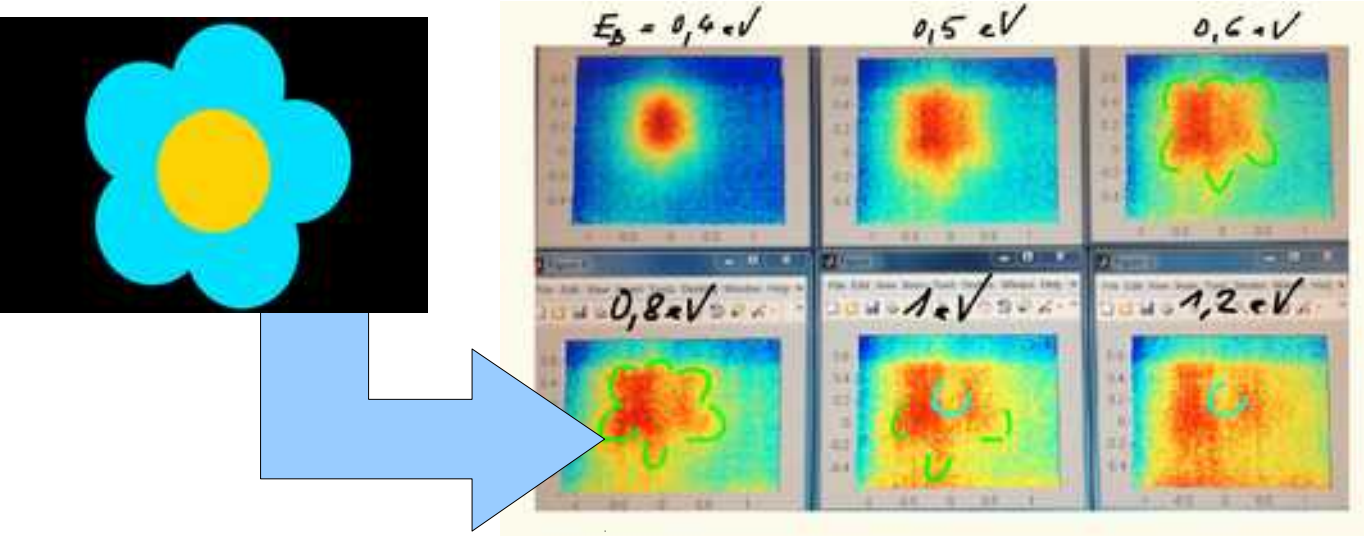


Strong need of
Theoretical support

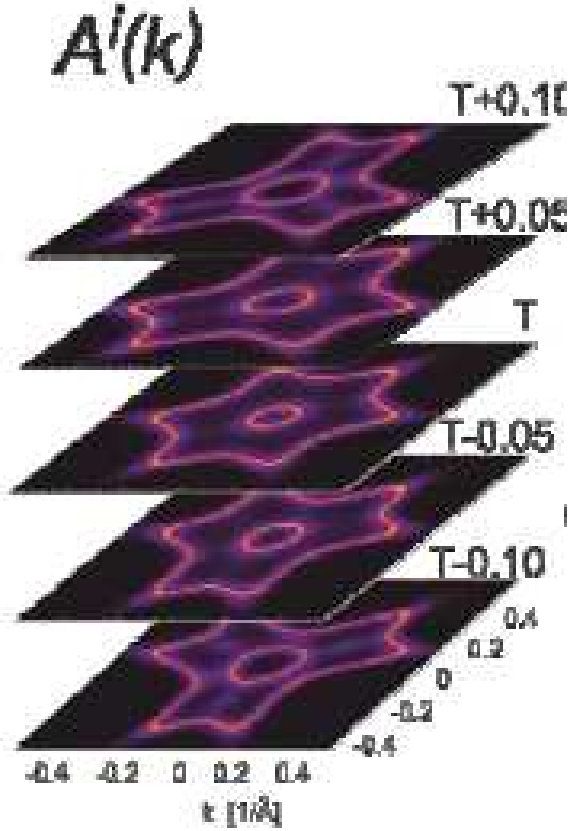
Interpretation

Ferroelectric material: GeTe

Photoemission data as measured



ARPES calculations



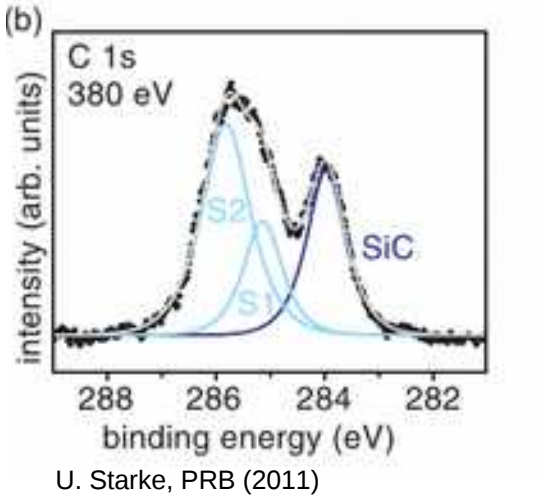
In collaboration with: J. Krempasky, H. Dill, S. Picozzi et al.

H. Volfova, Bachelor thesis (2013)

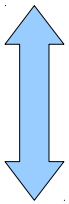
Necessary need for photoemission calculations

Photoemission spectroscopy: motivation

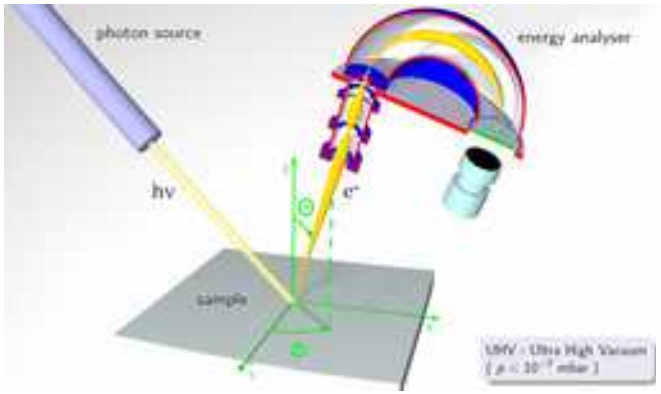
Core level (XPS, ESCA)



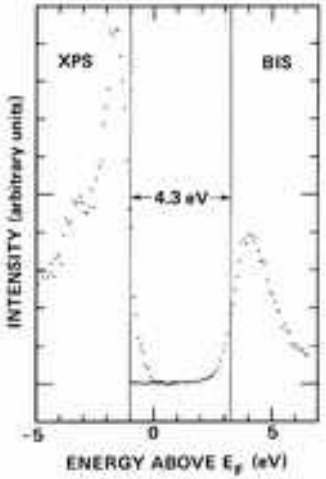
U. Starke, PRB (2011)



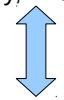
Chemical shift



Angle integrated (XPS)

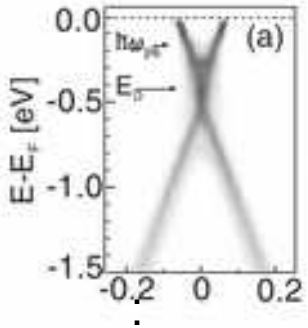


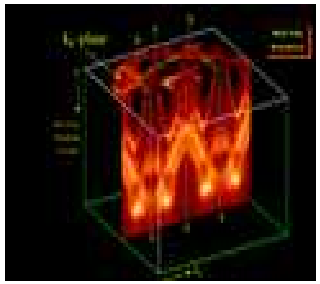
NiO: Sawatzky, Allen, PRL (1984)



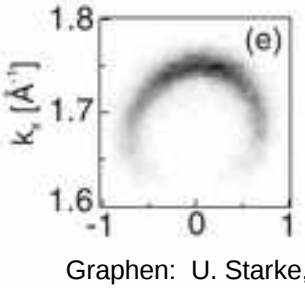
Total density of states

Angle resolved PES (ARPES)

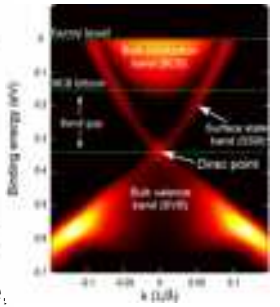




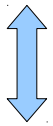
W(110): E. Rotenberg, PRB (2008)



Graphen: U. Starke, PRB (2011)



Bi_2Se_3: Y. Chen, Nature Mat. (2010)



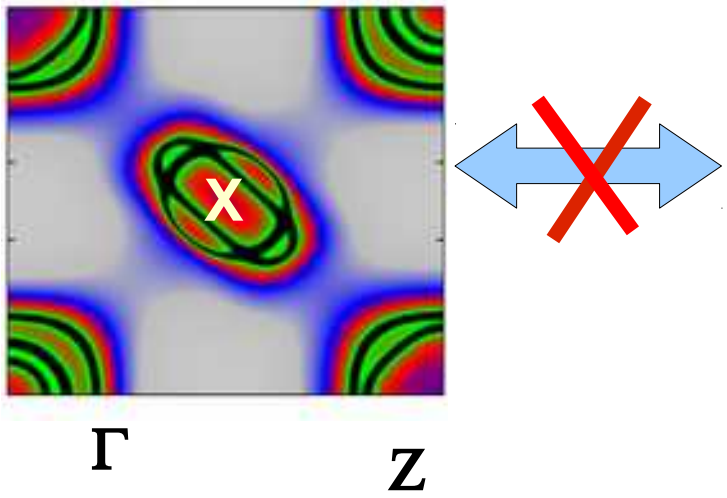
Band structure spectral function

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

Fermi surface of Fe-based HTC superconductor

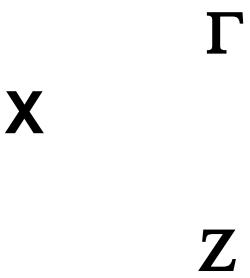
Bloch Spectral Functions

$BaFe_2As_2$

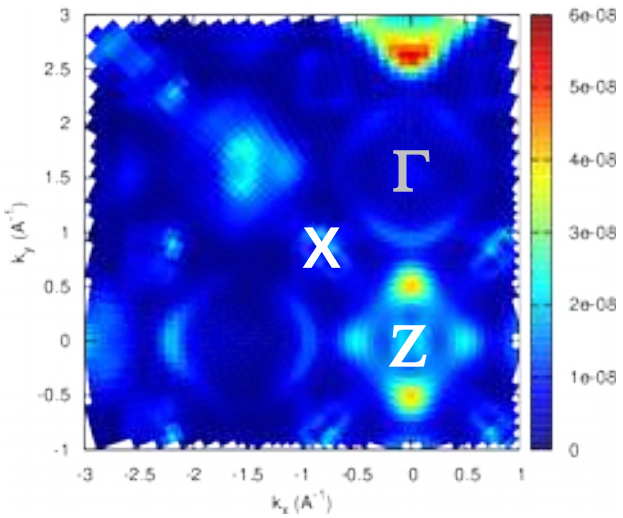


Experiment at 900 eV, p-pol light

$Ba_{0.6}K_{0.4}Fe_2As_2$



One-step model



Methodological requirements

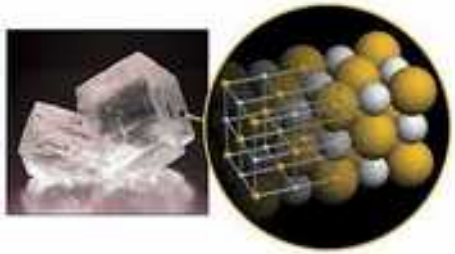
- Disorder (CPA)
- Correlation effects (DMFT)
- Surface effects
- Matrix elements
- High photon energy
- Bulk sensitivity

In collaboration with V. Strocov (Villingen, Paul Scherer Institut)

The many-electron problem (ground state)

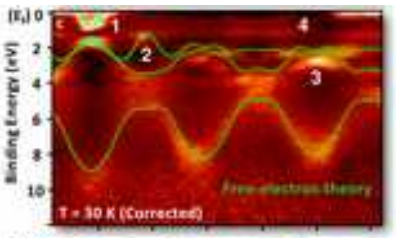
↓ Mapping to effective one-particle problem

Density functional theory (DFT)

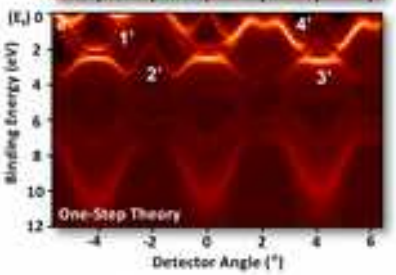


↓ Use of translational symmetry (Bloch's theorem)

Periodic lattice → Band structure methods



Exp.



Theory

↓

DFT and beyond → Inside DFT
SDFT, TD-DFT, GGA etc.

→ DFT + LSDA+U, +DMFT, +GW

Available band structure packages

Stuttgart TB-LMTO

http://www.fkf.mpg.de/andersen/LMTODOC/LMTODOC.html

LAPW

Wien2k http://www.wien2k.at/

Fleur http://www.flapw.de/pm/index.php

Elk http://elk.sourceforge.net/

FLPO

http://www.fplo.de/

Crystal

http://www.crystal.unito.it/

KKR-CPA

SPR-KKR http://ebert.cup.uni-muenchen.de/sprkkr

AkaiKKR http://kkr.phys.sci.osaka-u.ac.jp/

Pseudo potential codes

VASP http://cms.mpi.univie.ac.at/vasp/

CASTEP http://www.castep.org

Siesta http://www.icmab.es/siesta/

ABINIT http://www.abinit.org/

CPMD http://www.cpmd.org/

See also:

http://www.psi-k.org/codes.shtml

$$(-\frac{1}{2}\nabla^2 + V + V_{xc})\phi_i = \epsilon_i \phi_i$$

Variational

$$\phi_i = \sum_n C_n^i \phi_n$$

Scattering

P.W.

OPW
Pseudo Pot.
PAW

Localized

LCAO
FPLO

Augmented

APW
MTO

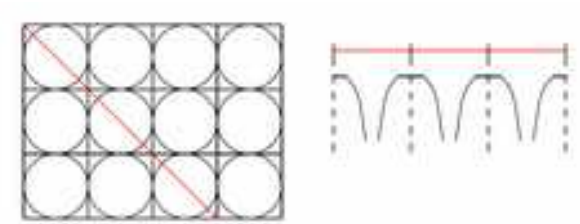
KKR
Old ~1960: Wave function
New: ~1970 Green's function

Linearized

LAPW
LMTO

Decomposition of space into atomic cells

E.g.: Muffin-tin potentials:



Different treatment of each region

- Atomic like in the spheres
- Free electron like in the interstitial

Matching of the wave functions at sphere boundaries

Combination of best of the two worlds

Augmented

KKR
Old: wave functions

Variational Principle

$$\left[\underline{\underline{H}}^{\vec{k}}(E) - E_{j\vec{k}}\,\underline{\underline{O}}^{\vec{k}}(E)\right]\ \underline{c}^{j\vec{k}} = \underline{0}$$

Energy dependent
eigenvalue problem

J. C. Slater, Phys. Rev. **51**, 846 (1937)

Linearized Methods

Idea: Taylor expand energy dependence of radial wave functions

$$\phi_n(E,r) \approx \phi_n(E_\nu,r) + \dot{\phi}_n(E_\nu,r)(E-E_\nu)$$

minimal basis-set

linearized APW: LAPW

- very accurate method
- can be generalized to full-potential (FP-LAPW)

linearized KKR/MTO: LMTO

- often in atomic sphere approximation (ASA):
  space-filling muffin-tin spheres, no interstitial
  very fast method
- FP-LMTO: comparable to FP-LAPW

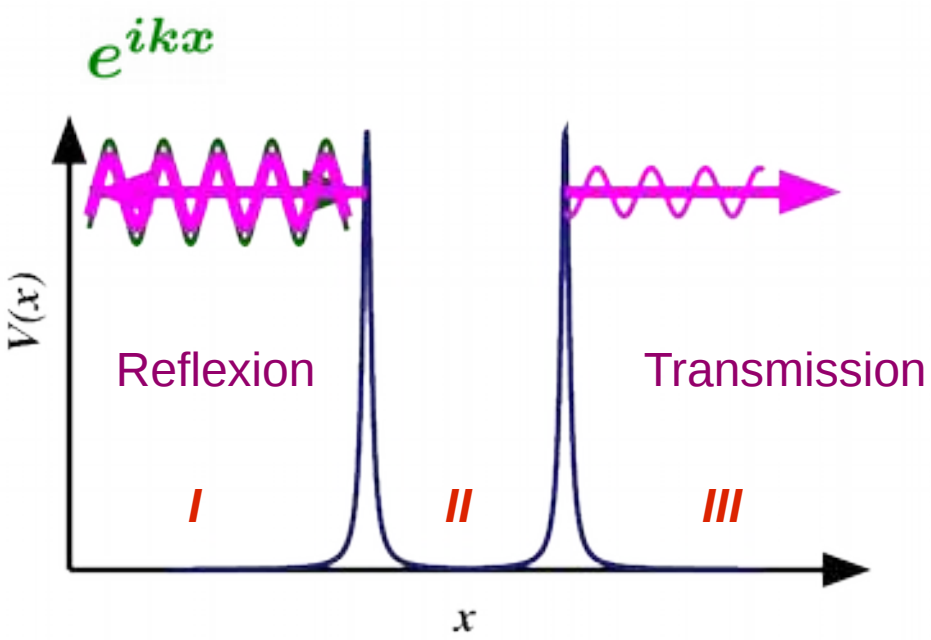
Problems for spectroscopies:
Linearisation not very good approx. far away from E_v

Multiple scattering – KKR formalism

Calculation of Greens function by means of multiple scattering theory

For reviews and overview of people working in this field see:
http://www.kkr-gf.org

Multiple scattering



- Traditional solution
  - solve Schrödinger's Eq. (SE): ***I,II,III***
  - match wave functions

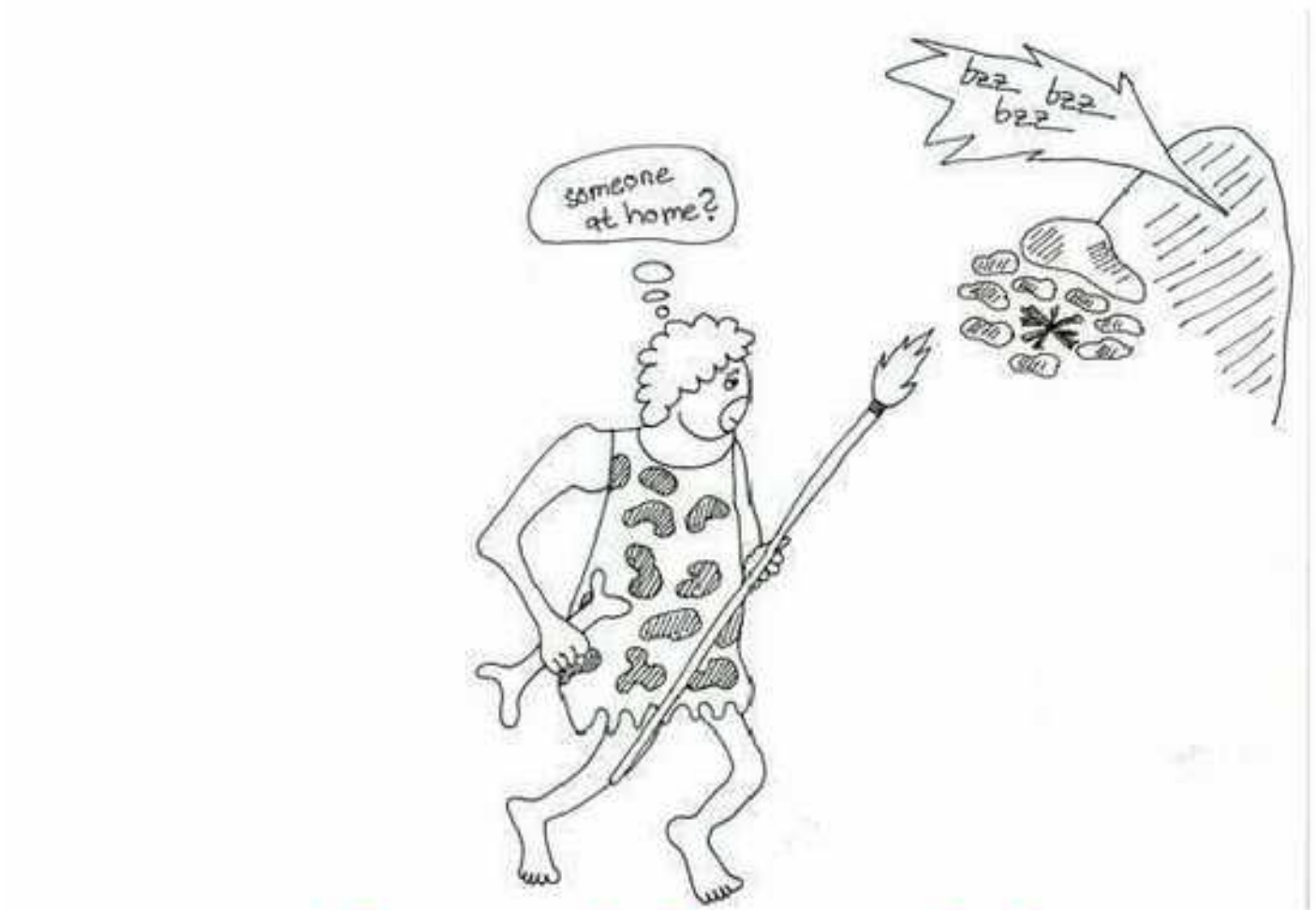
$$\left[-\frac{\hbar^2}{2m_e}\frac{d^2}{dx^2}+V(x)\right]\psi(x)=E\psi(x)$$

Is it possible to construct full solution from solutions of **single** barriers?

Yes!

Alternative: Multiple scattering and Green function

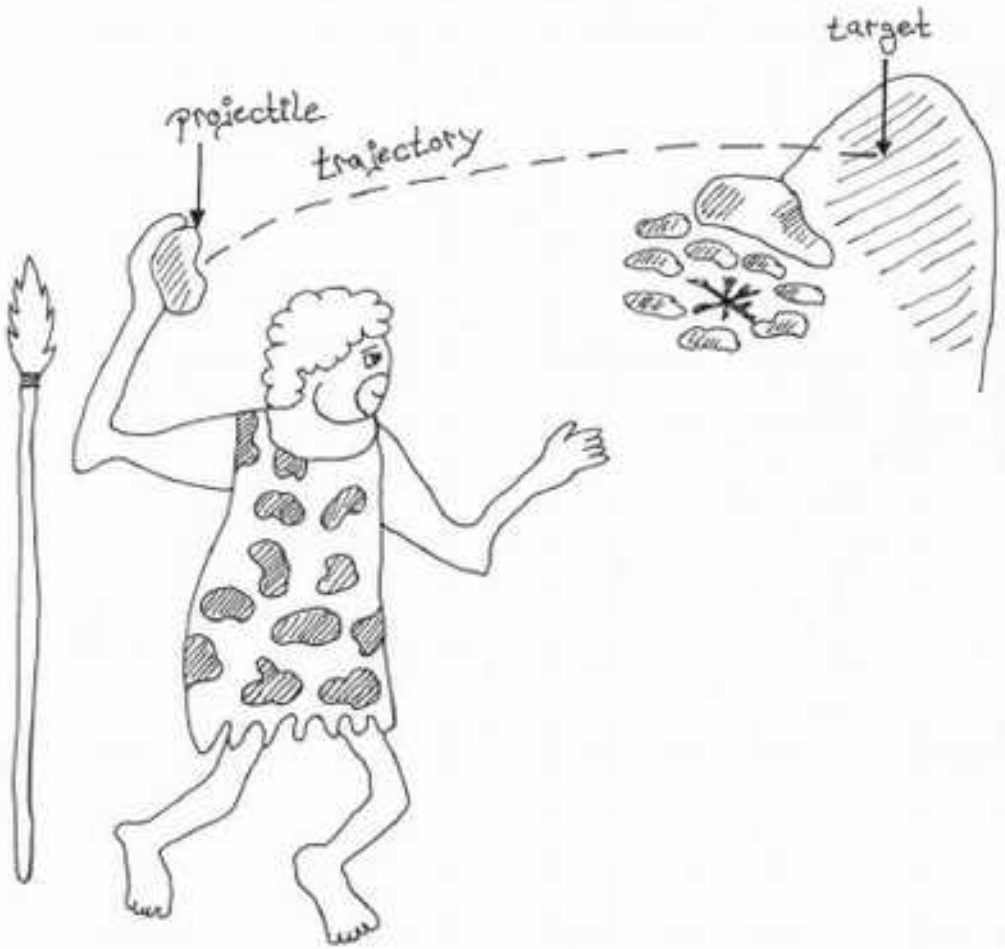
Early applications of scattering theory



... for solving problems

Thanks to Hubert Ebert

Principle of scattering theory



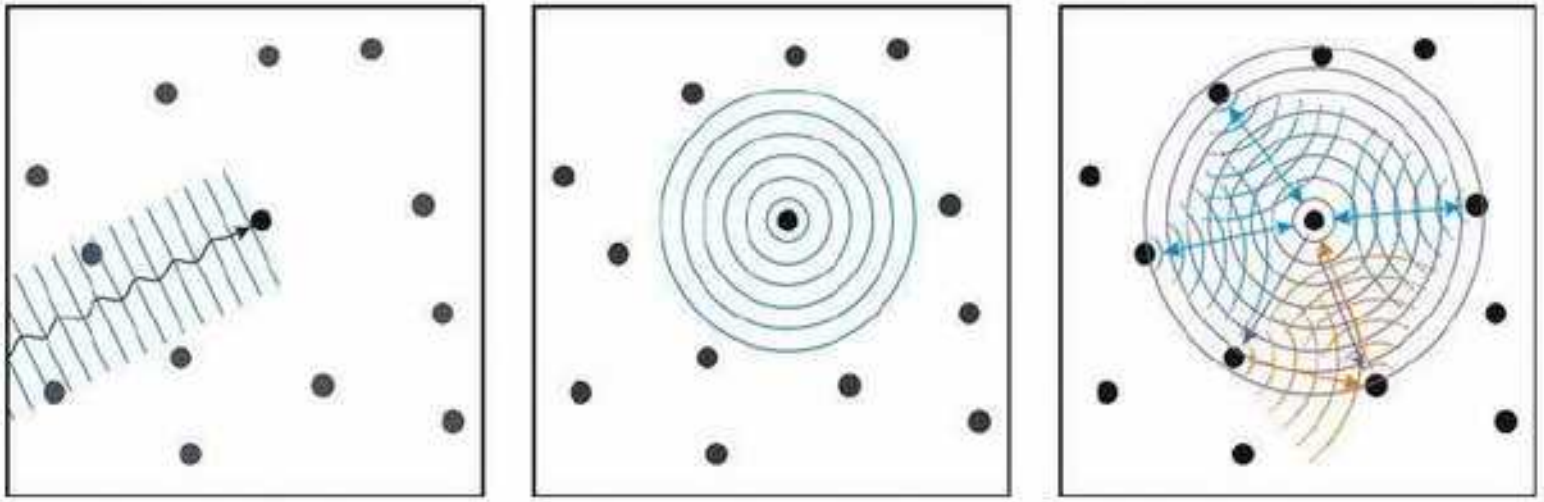
... to get information on a target

Sometimes solving a problem ....

... leads to another one

Calculation of Green function

Use the concept of EXAFS theory

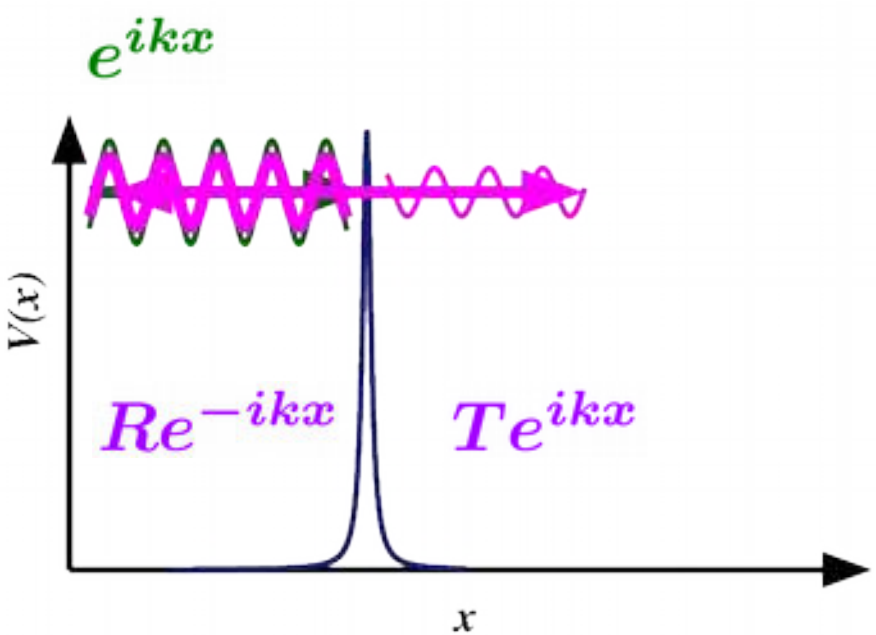


for electronic structure calculations

$\Rightarrow$ KKR $\equiv$ multiple scattering theory

e.g. J. Rehr, FEFF code

Multiple scattering and Green function *G*



$$G_0(x,x') = \frac{\alpha e^{ik|x-x'|}}{2ik}$$

Lippmann-Schwinger equation

$$|\psi\rangle = |k\rangle + \hat{G}_0\hat{t}|k\rangle$$

t – Matrix Operator

$$\hat{t} = \hat{v}(1 + \hat{G}_0\hat{t}) \quad (*)$$

$$|\psi\rangle = |k\rangle + \hat{G}_0\hat{t}|k\rangle$$

Green function without barrier (potential)

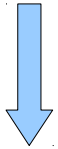
$$\hat{G}_0 = \lim_{\varepsilon\to 0} \frac{1}{E + i\varepsilon - \hat{H}_0}$$

Iterate (*) → $\hat{t}$ → $|\psi\rangle$ → Reflexion *R*, Transmission *T*

Equivalent to SE: Construction of Green function $\hat{G}$ of system with barrier

Multiple scattering and Green function *G*

Equivalent to SE: Construction of Green function $\hat{G}$ of total system



Expectation value of single particle observable (operator $\mathcal{A}$)

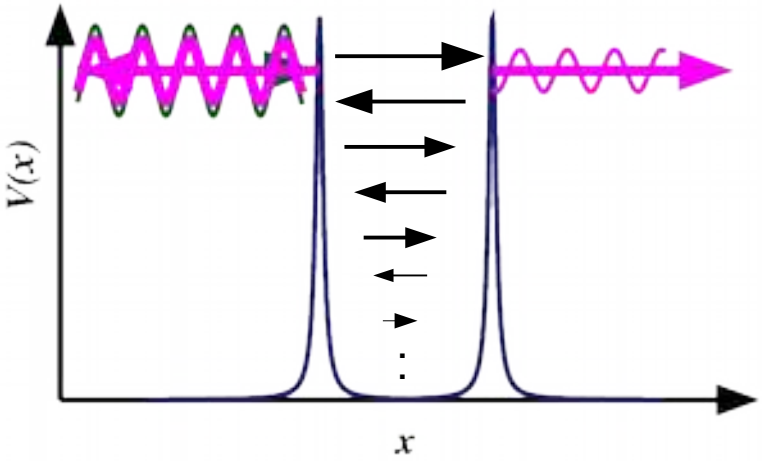
$$\langle \mathcal{A} \rangle = -\frac{1}{\pi} \mathrm{Im} \int_{-\infty}^{\infty} f_{\mathrm{FD}}(E)\ \mathcal{A}\ \hat{G}(E)$$

Dyson–Equation

Green function of total system

$$\hat{G} = \hat{G}_0 + \hat{G}_0 \hat{V} \hat{G}$$

Multiple scattering and Green function *G*



$$\hat{G} = \hat{G}_0 + \hat{G}_0 \hat{V} \hat{G}$$
$$= \hat{G}_0 + \hat{G}_0 \hat{T} \hat{G}_0$$

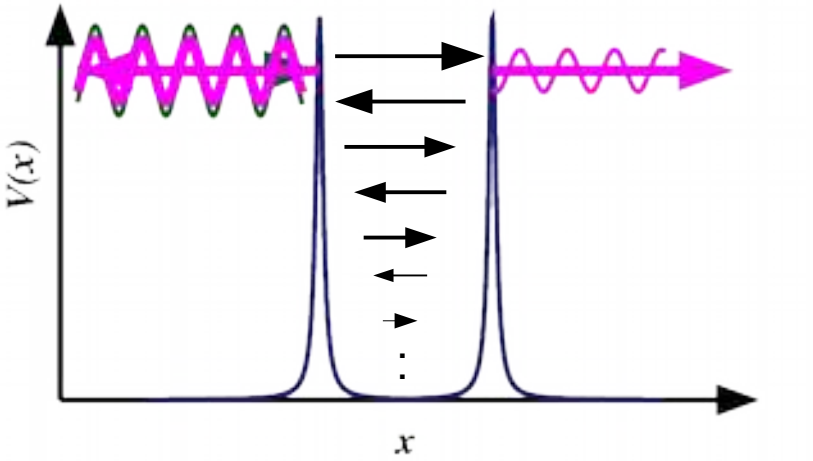
$$\begin{aligned}\hat{T} = & \hat{t}_1[1 + \hat{G}_0\hat{t}_2\hat{G}_0\hat{t}_1 + (\hat{G}_0\hat{t}_2\hat{G}_0\hat{t}_1)^2 + \ldots] \\ & + \hat{t}_2[1 + \hat{G}_0\hat{t}_1\hat{G}_0\hat{t}_2 + (\hat{G}_0\hat{t}_1\hat{G}_0\hat{t}_2)^2 + \ldots] \\ & + \hat{t}_1\hat{G}_0\hat{t}_2[1 + \hat{G}_0\hat{t}_2\hat{G}_0\hat{t}_1 + (\hat{G}_0\hat{t}_2\hat{G}_0\hat{t}_1)^2 + \ldots] \\ & + \hat{t}_2\hat{G}_0\hat{t}_1[1 + \hat{G}_0\hat{t}_1\hat{G}_0\hat{t}_2 + (\hat{G}_0\hat{t}_1\hat{G}_0\hat{t}_2)^2 + \ldots]\end{aligned}$$

$$= \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4$$

$$= \sum_{mn} \hat{\tau}^{mn}$$

scattering path operator

Multiple scattering and Green function *G*



$$\hat{G} = \hat{G}_0 + \hat{G}_0 \hat{V} \hat{G}$$
$$= \hat{G}_0 + \hat{G}_0 \hat{T} \hat{G}_0$$

$$\begin{aligned}\hat{T} = \; & \hat{t}_1[1 + \hat{G}_0\hat{t}_2\hat{G}_0\hat{t}_1 + (\hat{G}_0\hat{t}_2\hat{G}_0\hat{t}_1)^2 + \ldots] \\ & + \hat{t}_2[1 + \hat{G}_0\hat{t}_1\hat{G}_0\hat{t}_2 + (\hat{G}_0\hat{t}_1\hat{G}_0\hat{t}_2)^2 + \ldots] \\ & + \hat{t}_1\hat{G}_0\hat{t}_2[1 + \hat{G}_0\hat{t}_2\hat{G}_0\hat{t}_1 + (\hat{G}_0\hat{t}_2\hat{G}_0\hat{t}_1)^2 + \ldots] \\ & + \hat{t}_2\hat{G}_0\hat{t}_1[1 + \hat{G}_0\hat{t}_1\hat{G}_0\hat{t}_2 + (\hat{G}_0\hat{t}_1\hat{G}_0\hat{t}_2)^2 + \ldots]\end{aligned}$$

$$= \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4$$

$$= \sum_{mn} \hat{\tau}^{mn}$$

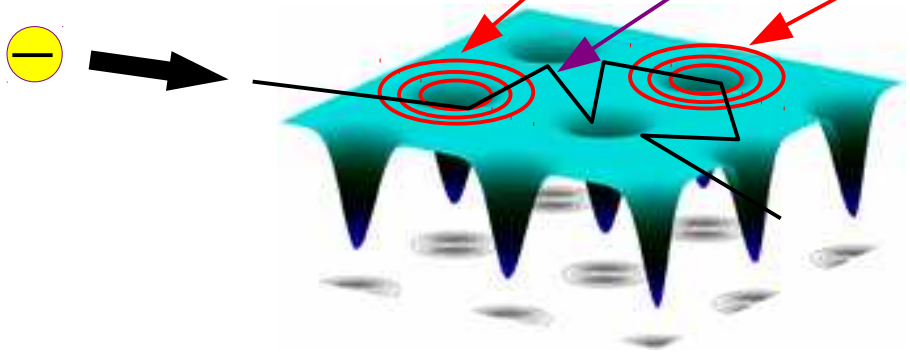
scattering path operator

Multiple scattering representation of *G* in KKR

$$\hat{H}^{\text{Dirac}} = c\alpha \cdot \vec{p} + \beta mc^2 + \bar{V} + \Sigma \cdot B$$

scattering path operator

$$G^{+}(\vec{r},\vec{r}',E) = G^{+,\text{irr}}_{nn}(\vec{r},\vec{r}',E) + \sum_{\Lambda\Lambda'} Z^{n}_{\Lambda}(\vec{r},E)\, \tau^{nm}_{\Lambda\Lambda'}(E)\, Z^{m\times}_{\Lambda'}(\vec{r}',E)$$



numerical,
relativistic
radial wavefunctions
&
rel. spin-angular functions

Muffin-Tin-Potential

Dyson–Equation

$\hat{H}_0$ Reference system

$$\hat{G} = \hat{G}_0 + \hat{G}_0 \hat{V} \hat{G}$$

$$\hat{H} = \hat{H}_0 + V$$

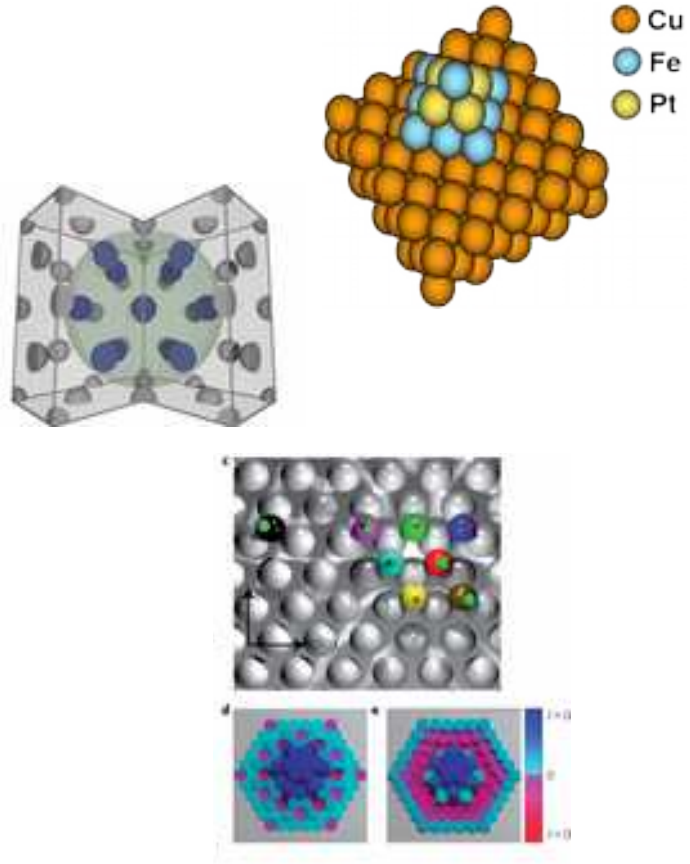
Dyson–Equation

$\hat{H}_0$ Reference system

$$\hat{G} = \hat{G}_0 + \hat{G}_0 \hat{V} \hat{G}$$

$$\hat{H} = \hat{H}_0 + V$$

- intuitive, physically transparent
- construction: Hierarchy of Dyson-Equations
- **Korringa-Kohn-Rostoker (KKR)**-GF method
  - spherical waves
  - accurate minimal basis set method
- efficient treatment of
  - Impurities, surfaces and interfaces
  - disorder (CPA)
  - Correlation effects (KKR+DMFT)



Lounis et al,
Nature Physics 6, 187 - 191 (2010)

Reviews: Ebert, Ködderitzsch, Minár, Rep. Prog. Phys. 74, 096501 (2011)
Papanikolaou, Zeller, Dederichs, JPCM **14**, 2799 (2002)

Why to use KKR Method for spectroscopy

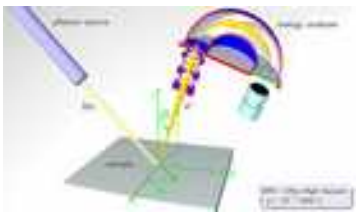
KKR represents electronic structure in terms of single particle Green's function

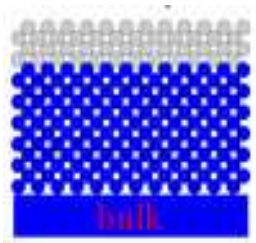
Multiple scattering formalism

with formal solution:

$$\underline{\underline{\tau}} = [\underline{\underline{t}}^{-1} - \underline{\underline{G_0}}]^{-1}$$

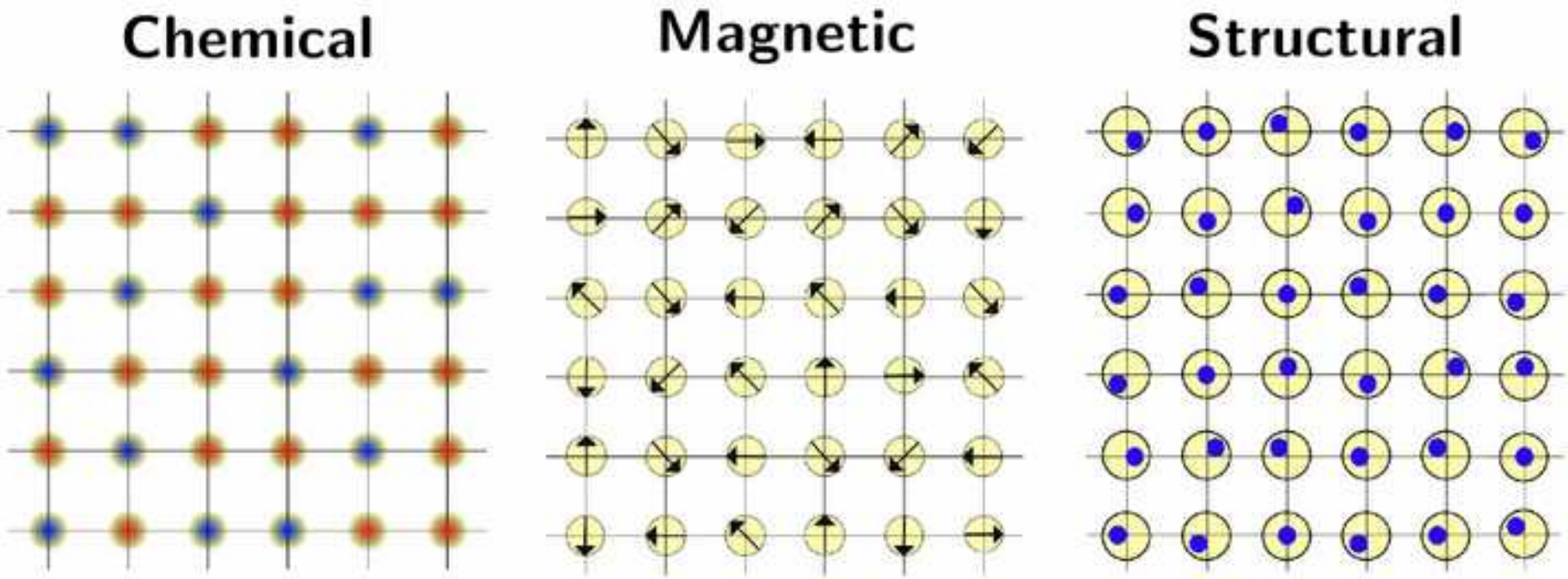
- Explicitly energy dependence of GF
- Energy dependent basis functions
- No problem to calculate states above E_F (~500eV)
- Scattering formalism: EXAFS, PES





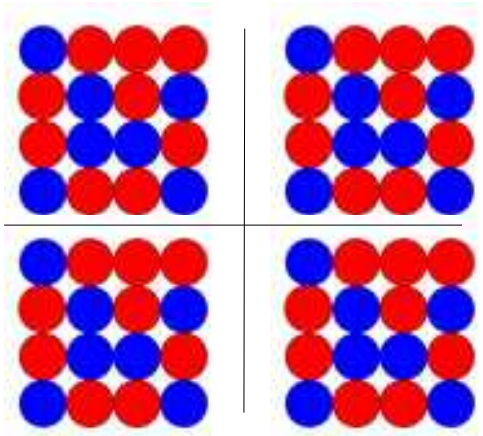
Treatment of substitutional disorder

Random disorder in solids
(how to avoid super-cells?)



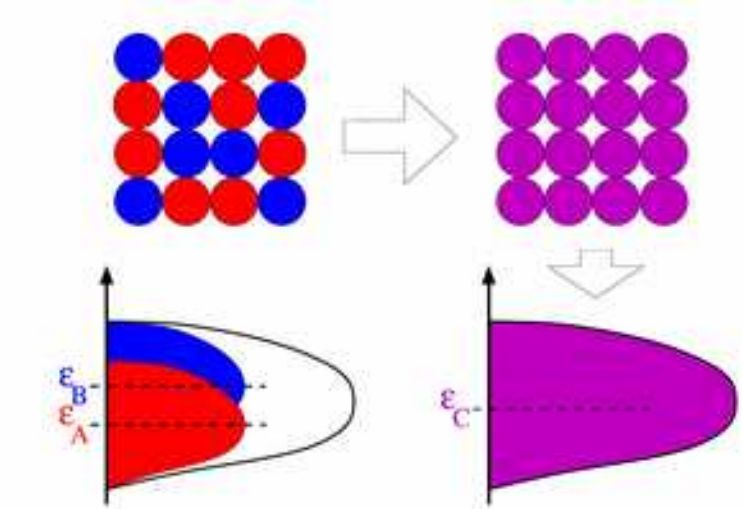
Overview of methods to deal with disorder

Supercell approach



- Applicable to any band structure method (Bloch theorem)
- Disadvantage: need for many calculations of big supercells
- “Up”-folding scheme (see eg. W. Ku, V. Popescu, A, Zunger)
- Advantage: Relaxation around impurities

Mean field approaches

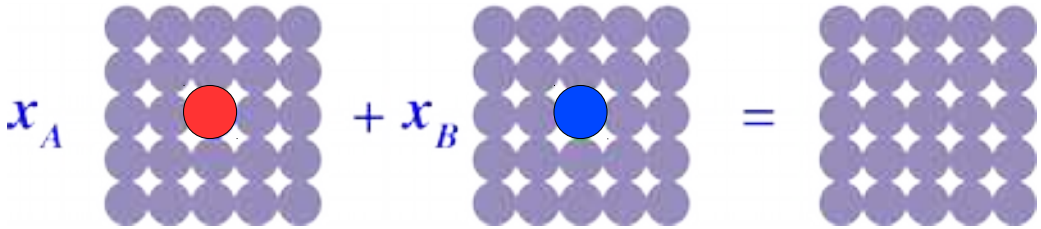


- Virtual crystal approximation (rigid band shift)
  - Implemented in most codes
  - Only applicable for systems having atoms with similar scattering properties
  - No finite life time broadening
  - No access to partial quantities –> as seen by core level spectroscopies
- Averaged t-matrix approximation (ATA)
- Coherent potential approximation (CPA): Averaging of Greens functions

Coherent potential approximation

Best Single site theory: $G_{AB} \approx xG_A + (1-x)G_B = G_C$

Coherent potetnial approximation (**CPA**)



$$x_A \underline{\tau}^{nn,A} + x_B \underline{\tau}^{nn,B} = \underline{\tau}^{nn,CPA}$$

$$\underline{\tau}^{nn,\alpha} = \underline{\tau}^{nn,CPA} \left[1 + \left(\underline{t}_\alpha^{-1} - \underline{t}_{CPA}^{-1} \right) \underline{\tau}^{nn,CPA} \right]^{-1}$$

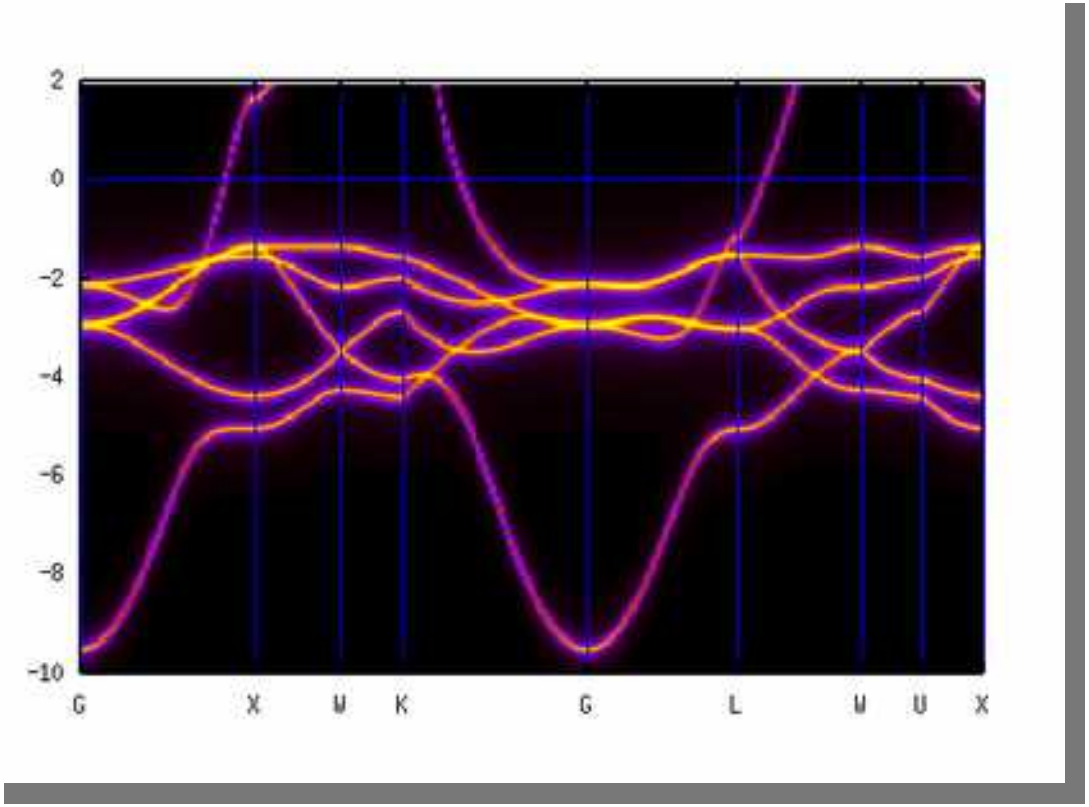
Self constituent construction of the mean field medium

Embedding of an A- or B-atom into the CPA-medium
- in the average - should not give rise to additional scattering

Soven, Physical Review **156**, 809 (1967)

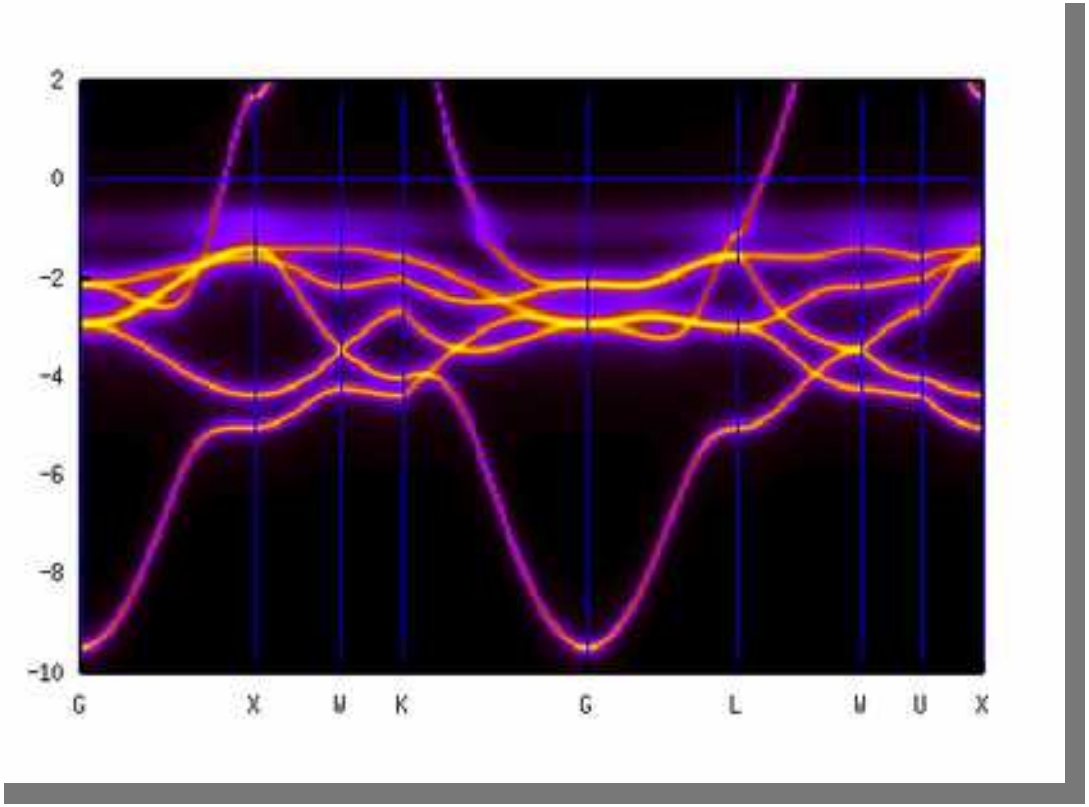
Coherent Potential Approximation

Example: Cu – Ni alloy: pure Cu



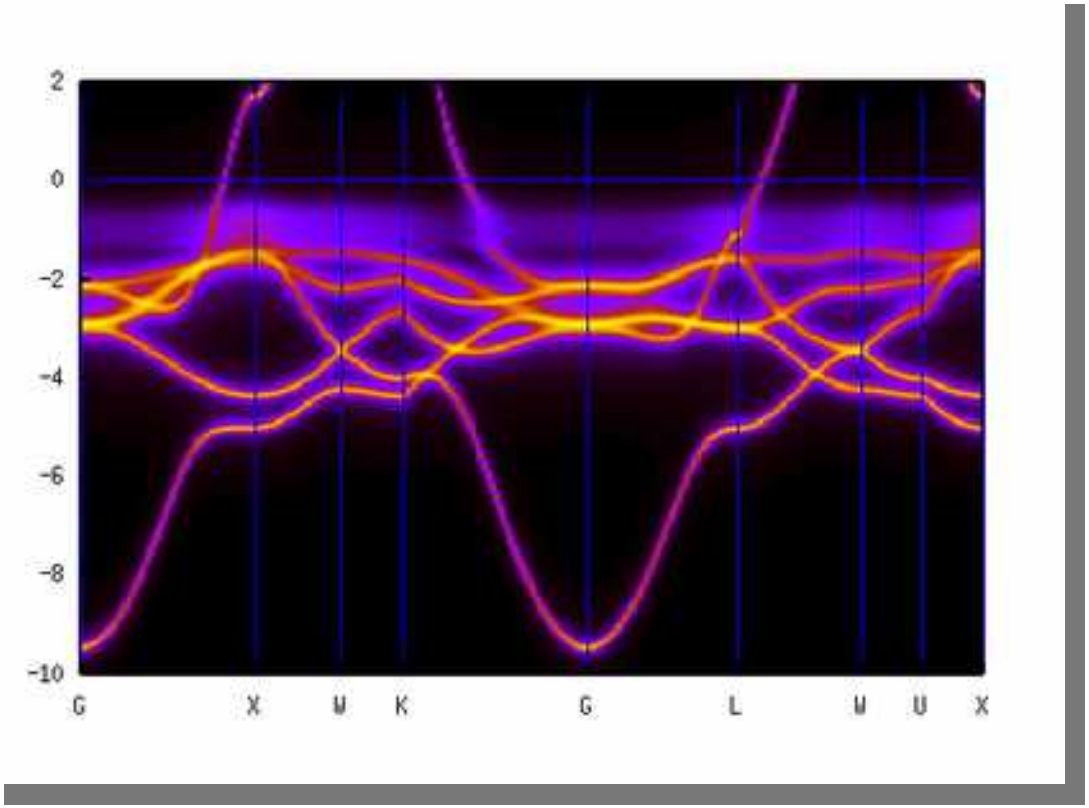
Coherent Potential Approximation

Example: Cu – Ni alloy: 5% Ni



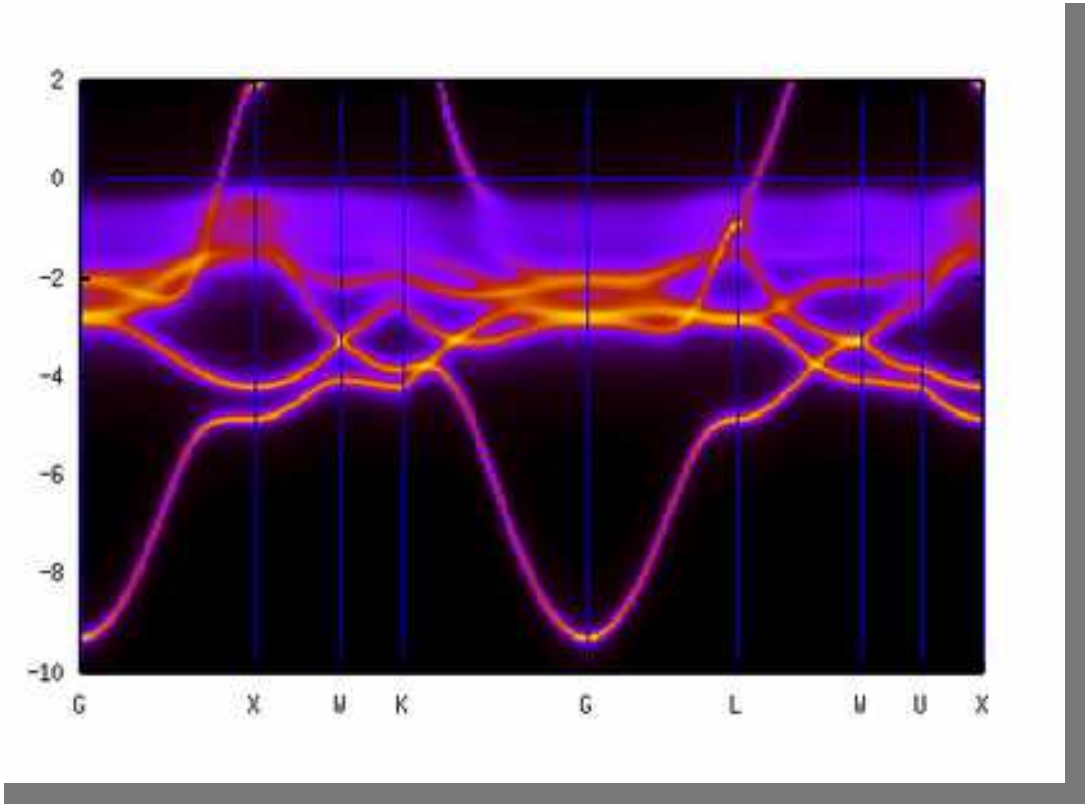
Coherent Potential Approximation

Example: Cu – Ni alloy: 10% Ni



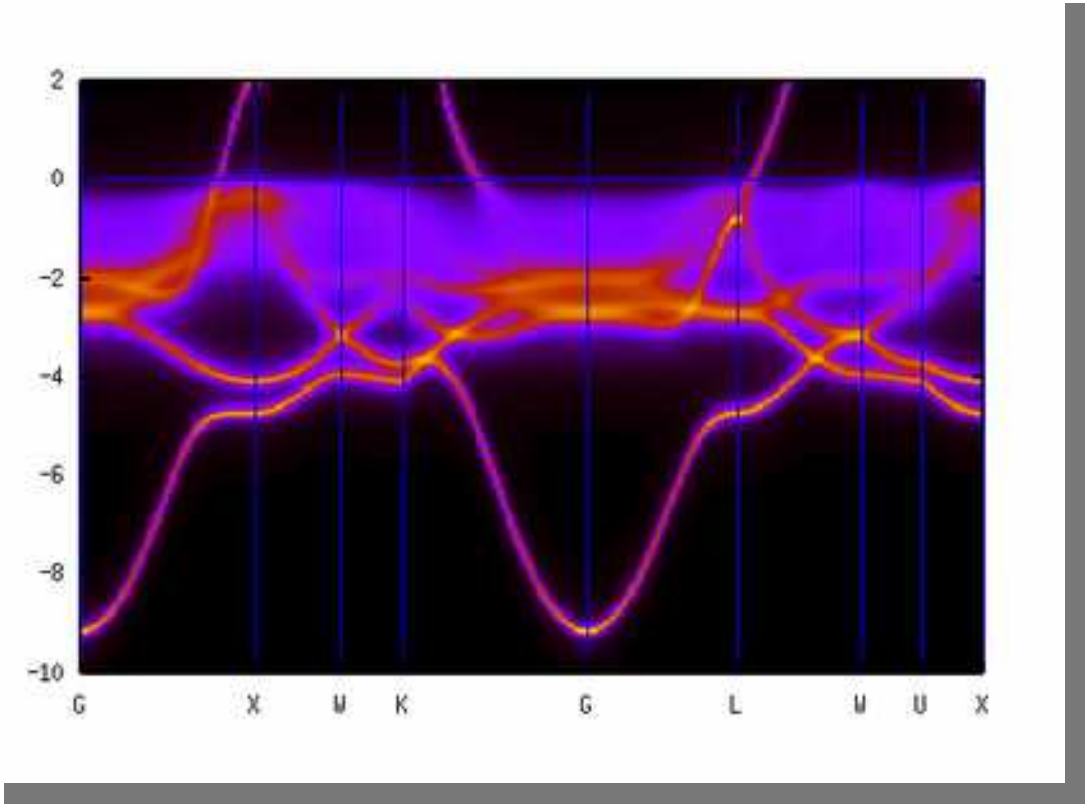
Coherent Potential Approximation

Example: Cu – Ni alloy: 20% Ni



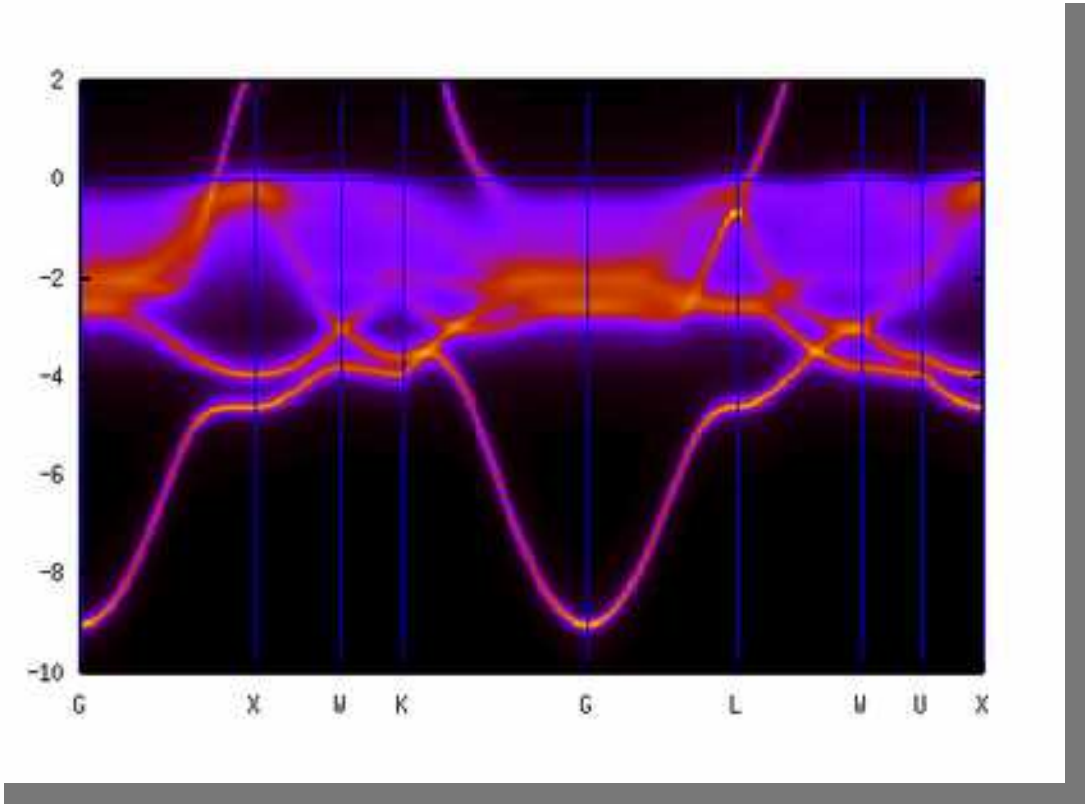
Coherent Potential Approximation

Example: Cu – Ni alloy: 30% Ni



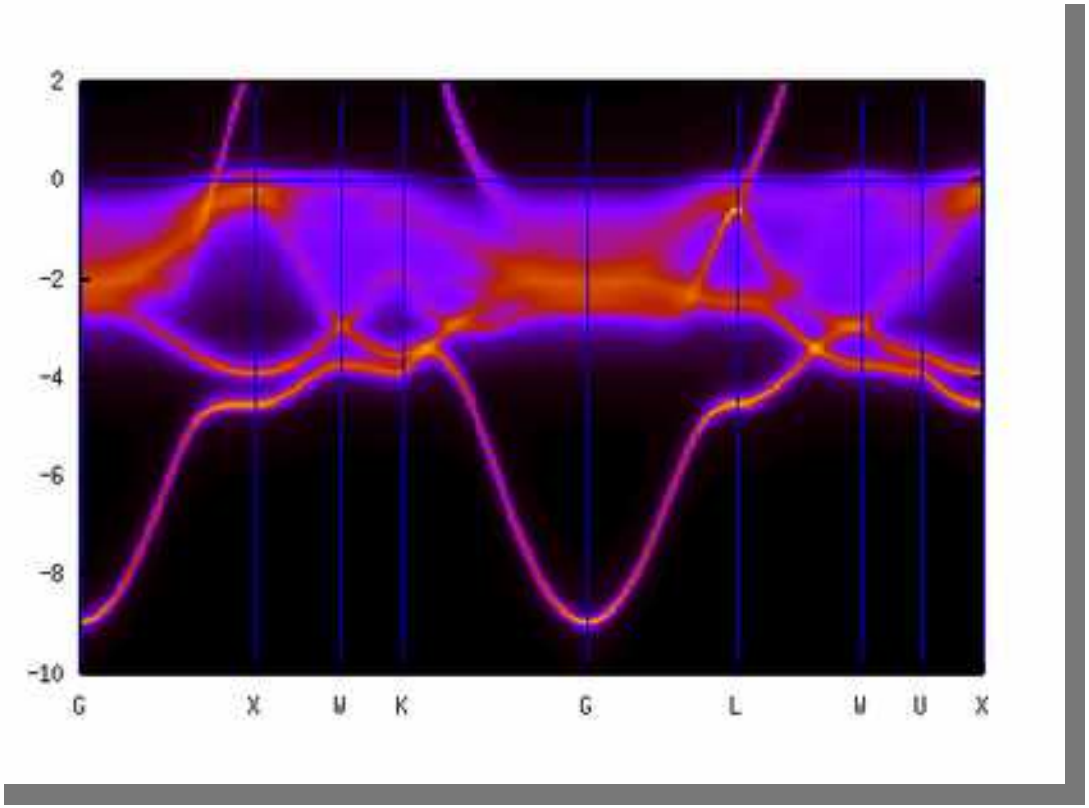
Coherent Potential Approximation

Example: Cu – Ni alloy: 40% Ni



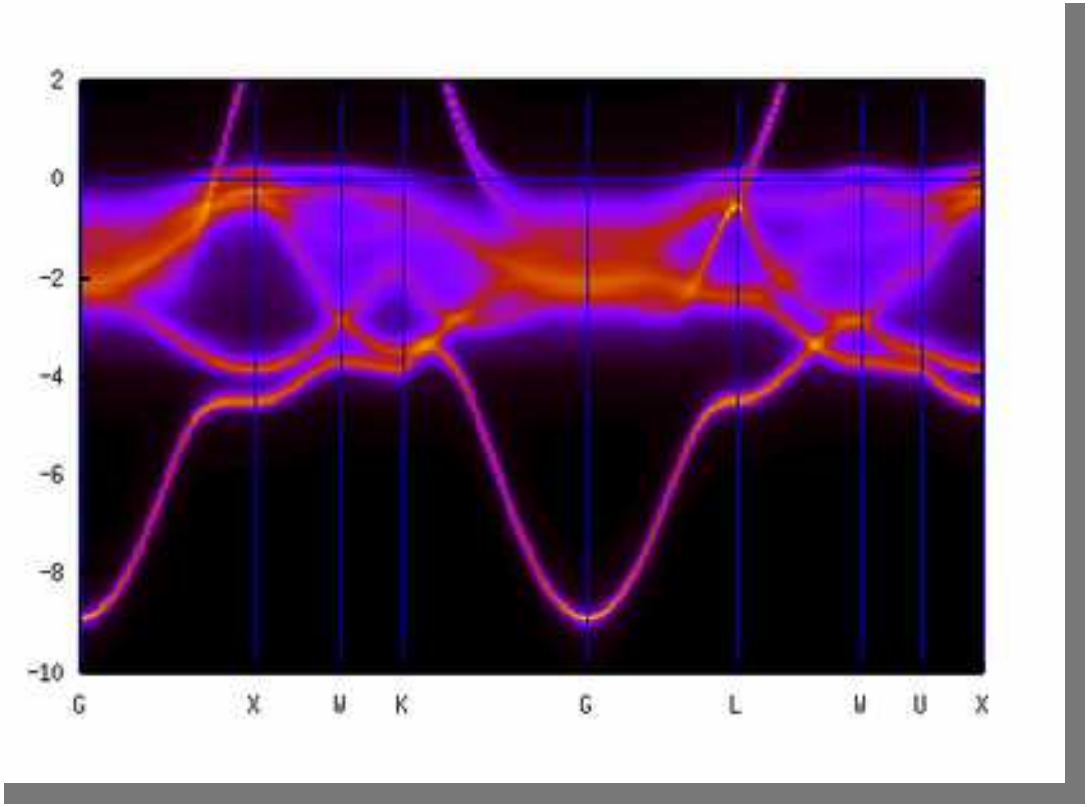
Coherent Potential Approximation

Example: Cu – Ni alloy: 50% Ni



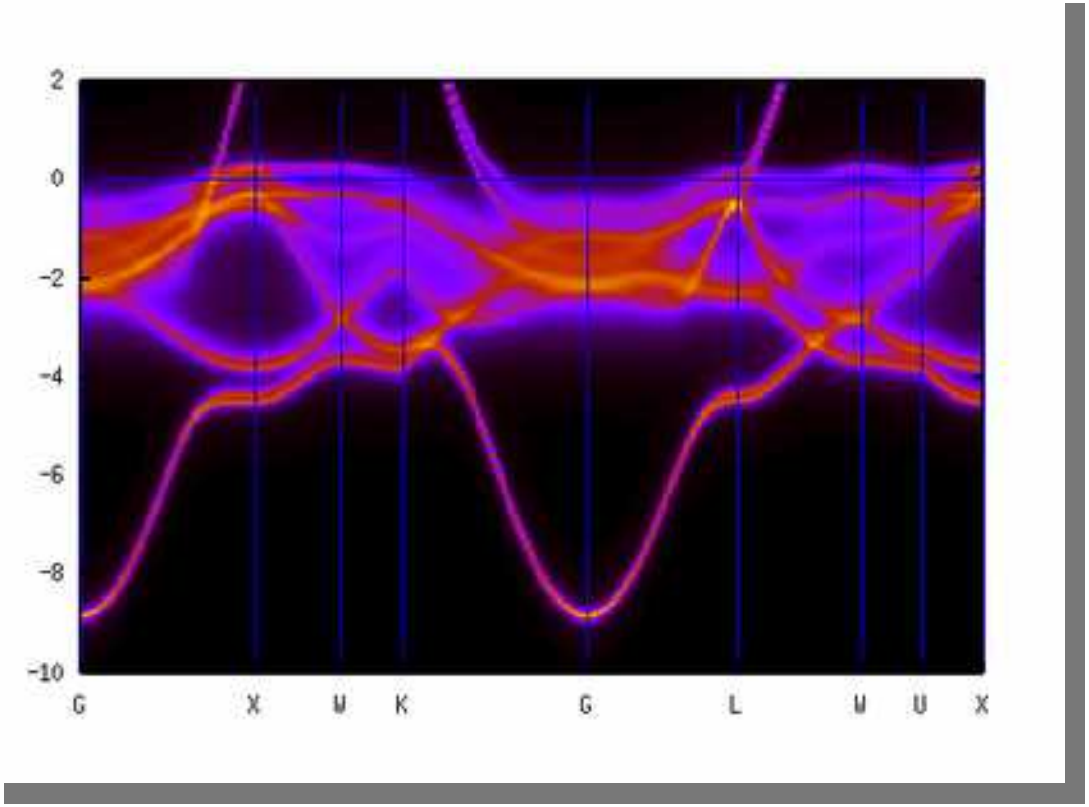
Coherent Potential Approximation

Example: Cu – Ni alloy: 60% Ni



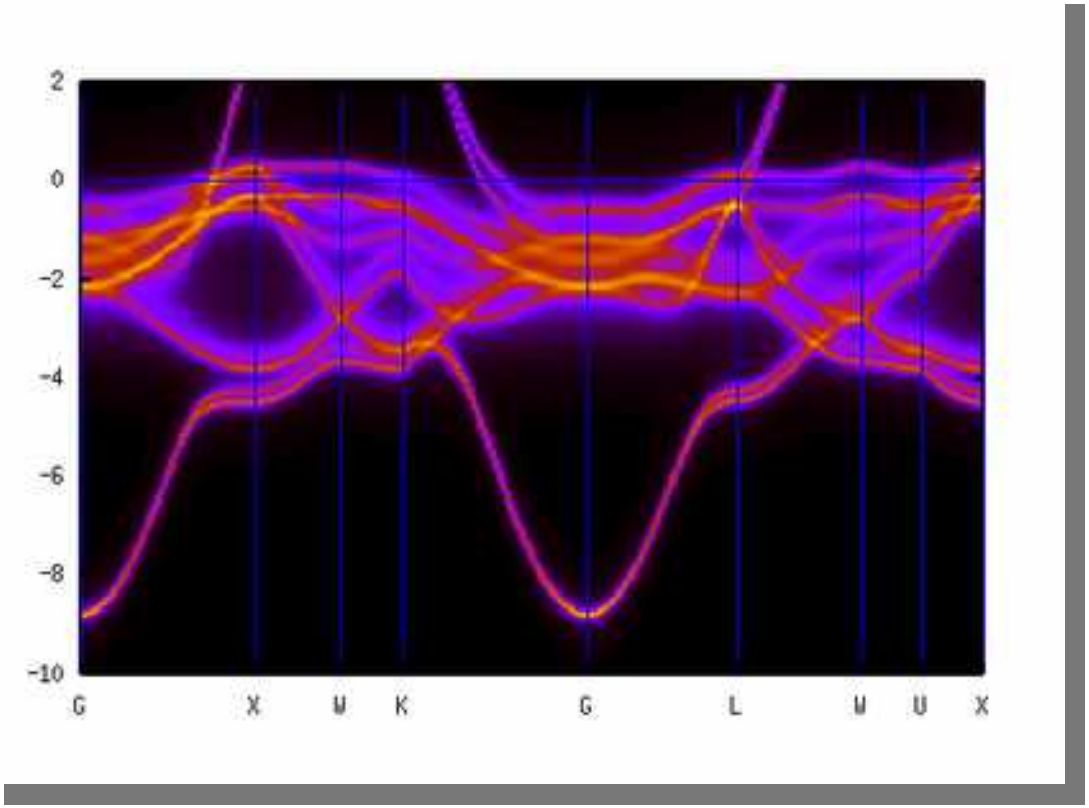
Coherent Potential Approximation

Example: Cu – Ni alloy: 70% Ni



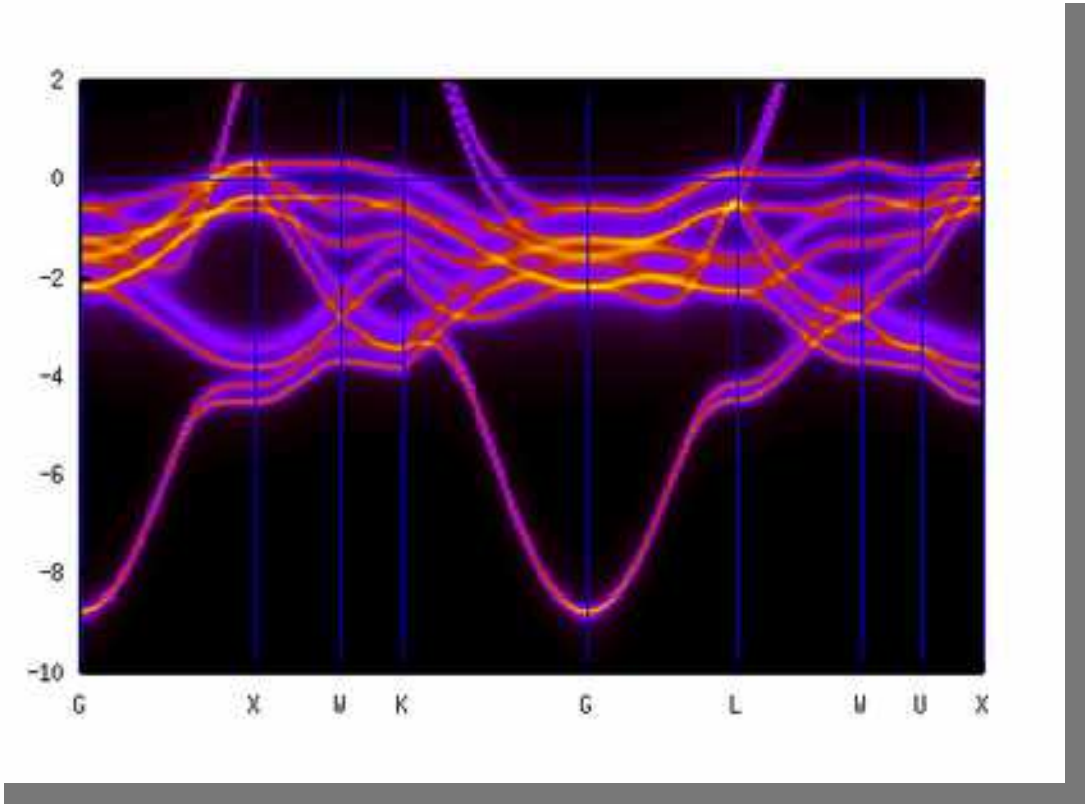
Coherent Potential Approximation

Example: Cu – Ni alloy: 80% Ni



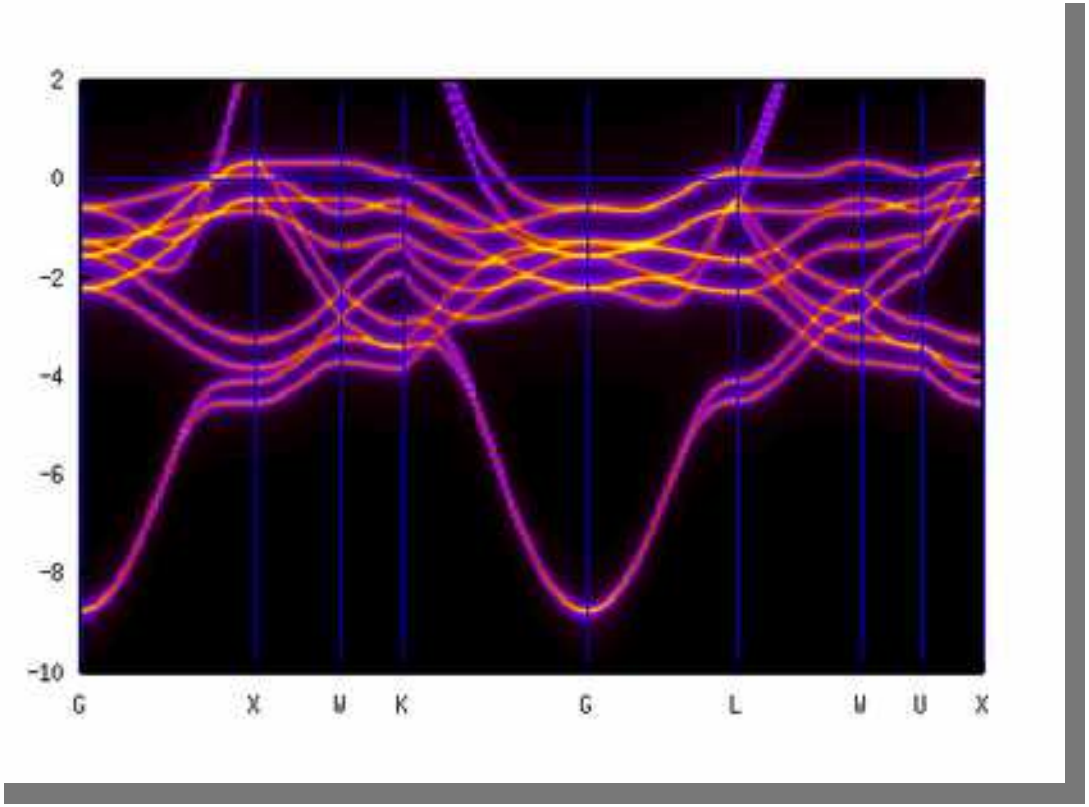
Coherent Potential Approximation

Example: Cu – Ni alloy: 90% Ni



Coherent Potential Approximation

Example: Cu – Ni alloy: pure Ni



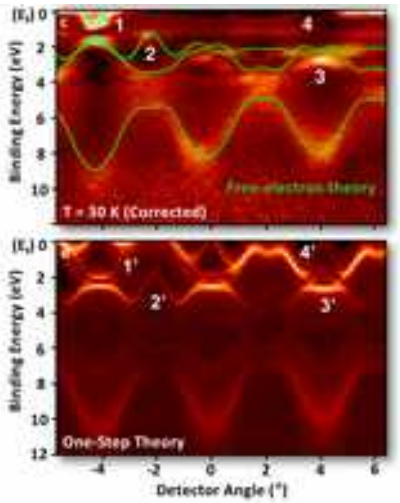
Outline

Angle resolved photoemission

↓ First interpretation

Three step model

↓ Many body physics



One step model → Direct comparison between Theory ↔ Experiment

↓

Surface states | **Correlation effects** | **Bulk sensitive ARPES**

Outline

Historical survey of the development of the theory of photoemission

1965 angle-integrated photoemission
- *three-step-model: Berglund, Spicer*
  - excitation, transport, emission

1972 many body theory of photoemission
- *one-step-model: Schaich, Ashcroft, Caroli ...*
  - current-current correlation function

1980 angle-resolved photoemission
- *one-step-model: Liebsch, Pendry, Inglesfield, Feibelmann,...*
  - dynamical ansatz, multiple scattering theory

1990 relativistic photoemission: non magnetic materials
- *one-step-model: Ginatempo, Durham, Henk, Halilov, Tamura, Feder, Ebert, Weinberger, Braun ...*
  - spin-orbit interaction

1995 full-potential photoemission
- *one-step-model: Braun*
  - complex structures and adsorbate

2000 full relativistic photoemission
- *one-step-model: Henk, Feder, Ebert, Minar, Fluchtmann, Braun*
  - magnetic dichroism
  - high Tc superconductors: *Lindroos*
  - inverse kp method: *Schattke, Krasovskii, Strocov …*

2004 extentions of full relativistic photoemission
- *One-step-model: Minar, Ebert, Braun*
  - dynamical mean field theory, CPA, HAXPES, Phonons, TD-PES ...

Schattke et al. ISBN: 3-527-40334-5 (2003)

Outline

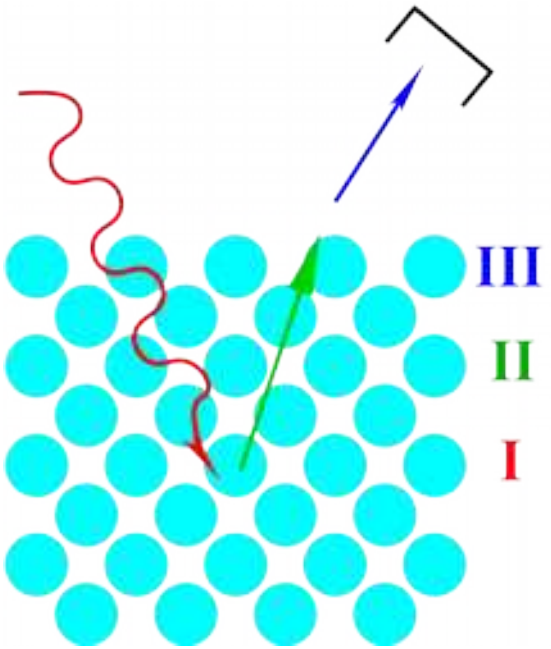
Angle resolved photoemission

First interpretation

Three step model

Description of PES via three-step model

three-step model of photo-emission (ARPES)
Berglund and Spicer (1964)



III Escape to the vacuum $\tilde{D}(E,\omega)$

II Transmission to surface $T(E,\vec{k})$

I Excitation $\langle n'\vec{k}|\vec{p}|n\vec{k}\rangle$

$$I \sim \tilde{D}(E,\omega)\sum_{nn'}\int d^3k\, T(E,\vec{k})\,|\langle n'\vec{k}|\vec{p}|n\vec{k}\rangle|^2$$
$$\times\delta(E-E_{n\vec{k}}-\omega)\delta(E_{n'\vec{k}}-E)\Theta(E-E_F)\Theta(E_F+\omega-E)$$

PES calculations based on three-step model

PES of polycrystalline Cu for $\hbar\omega = 8 - 17eV$

Theory: Janak et al. (1975)

three step-model
calculated from band structure data, e.g.:

$\langle n'\vec{k}|\vec{p}|n\vec{k}\rangle$

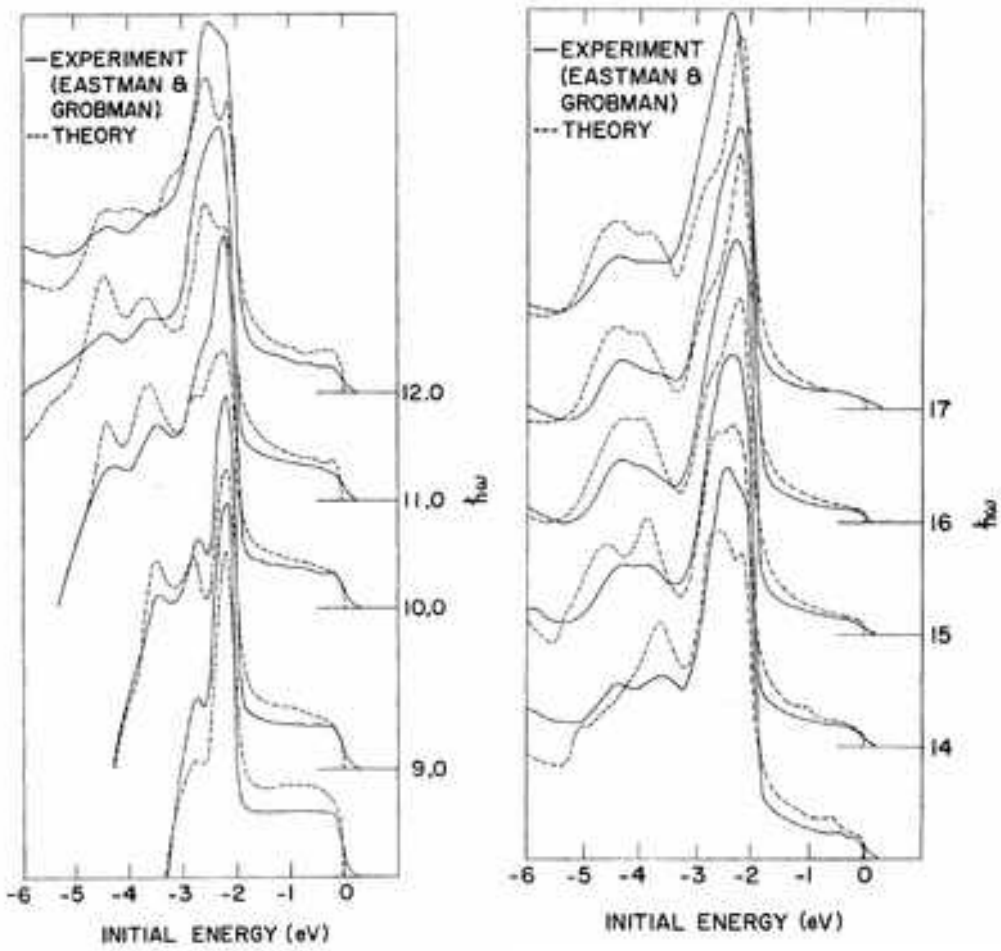
life times enter as parameters

$$T(E,\vec{k}) = \frac{\alpha(\omega)l(E,\vec{k})}{1+\alpha(\omega)l(E,\vec{k})}$$

$\tau_{phot} \rightarrow \alpha(\omega)$

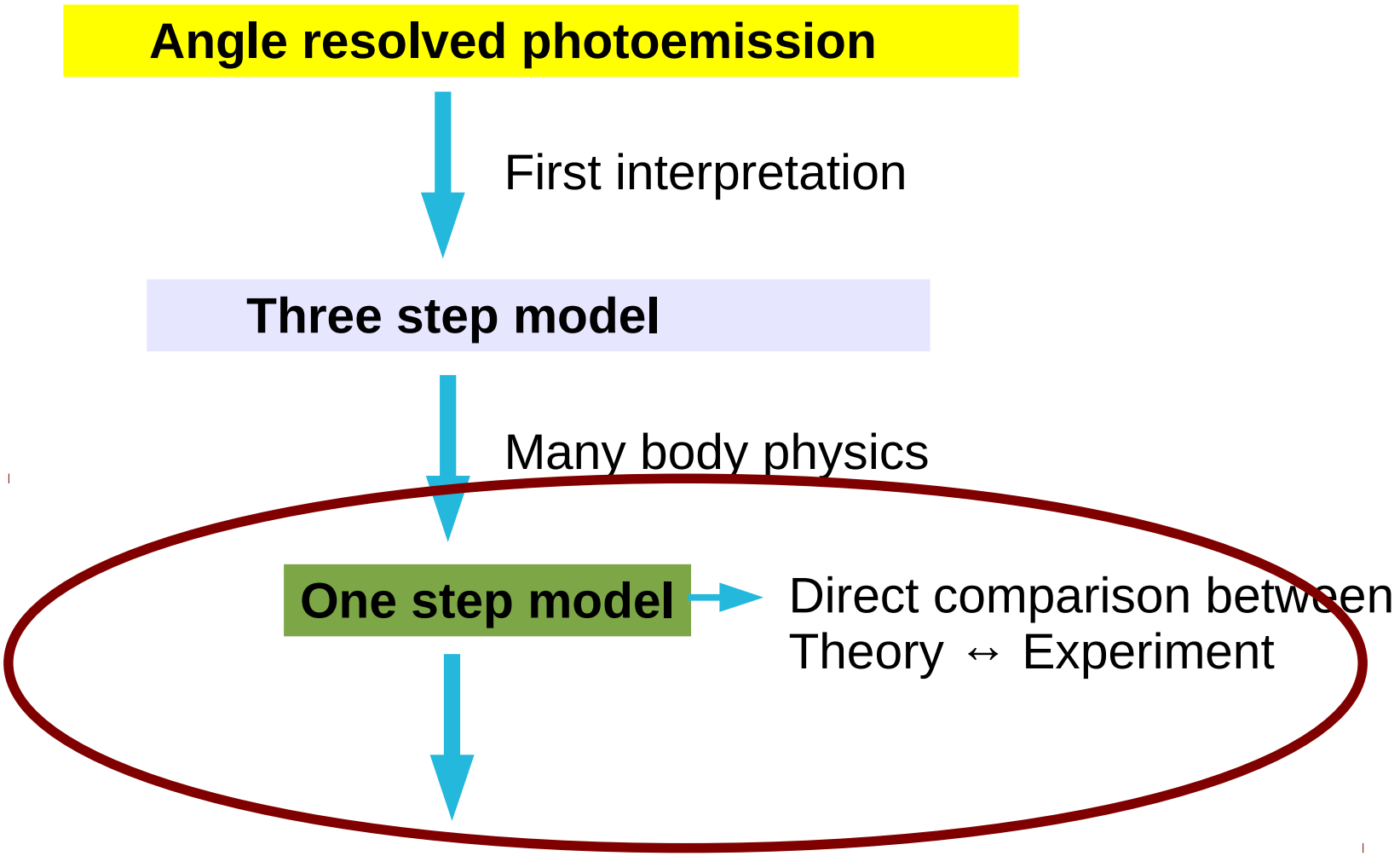
$\tau_{el} \rightarrow l(E,\vec{k})$

Expt: Eastman and Grobman



Expt. and Theor. photoemission distribution for 8 - 12 eV (left) and 13-17 eV (right)

Outline


Angle resolved photoemission
First interpretation
Three step model
Many body physics
One step model
Direct comparison between
Theory ↔ Experiment

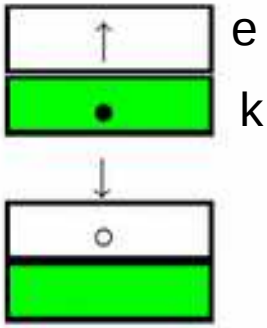
General theory of photoemission

Fermi's Golden Rule

$$\Gamma = -\frac{2\pi}{\hbar} |< \Psi_F|\Delta|\Psi_I >|^2 \, \delta(E_F - E_I - \epsilon_{ph})$$

$$\Delta^{PES} = \sum_{\mathbf{e},\mathbf{k}} M^P_{\mathbf{e},\mathbf{k}} \, a^\dagger_{\mathbf{e}} a_{\mathbf{k}}$$

$$\Delta^{IPE} = \sum_{\mathbf{e},\mathbf{k}} M^P_{\mathbf{k},\mathbf{e}} \, a^\dagger_{\mathbf{k}} a_{\mathbf{e}}$$

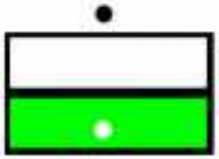


$$M^P_{\mathbf{e},\mathbf{k}} = < \phi^{SP}_{\mathbf{e}} | \mathbf{A_o} \cdot \mathbf{p} | \phi_{\mathbf{k}} >$$

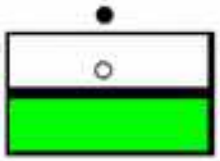
Sudden approximation

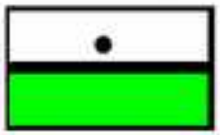
The interaction of the photoelectron with the rest system is neglected

PES:  $|\Psi_I >= |\Psi^N_0 >$

PES:  $|\Psi_F >= a^\dagger_{\mathbf{e}} |\Psi^{N-1}_S >$

$a_{\mathbf{e}} |\Psi^0_N >= 0$

IPE:  $|\Psi_I >= a^\dagger_{\mathbf{e}} |\Psi^N_0 >$

IPE:  $|\Psi_F >= |\Psi^{N+1}_S >$

Review: G. Brostel, Appl. Phys A **38,** 193 (1985)

General theory of photoemission

Inserting $|\Psi_I>$ and $|\Psi_F>$ in Fermi's Golden Rule
Summation over all possible final states
Averaging in the Grand Canonical Ensemble

$$\frac{1}{2\pi} < [T^\dagger(t), T(t')]_+ > \; = \; A^{(1)}(t,t') \; = \; \frac{1}{2\pi\hbar} \int dE e^{-\frac{i}{\hbar}E(t-t')} \, \mathrm{A}^{(1)}(\mathrm{E})$$

$$T^{PES} = \sum_{\mathbf{k}} M^P_{\mathbf{e},\mathbf{k}} \, a_{\mathbf{k}} \qquad\qquad T^{IPE} = \sum_{\mathbf{k}} M^P_{\mathbf{e},\mathbf{k}} \, a^\dagger_{\mathbf{k}}$$

Review: G. Brostel, Appl. Phys A **38,** 193 (1985)

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$$T^{PES} = \sum_{\mathbf{k}} M^P_{\mathbf{e},\mathbf{k}} \, a_{\mathbf{k}} \qquad\qquad T^{IPE} = \sum_{\mathbf{k}} M^P_{\mathbf{e},\mathbf{k}} \, a^\dagger_{\mathbf{k}}$$

$$A_{m,m'}(E_n) \, \frac{2}{\hbar} \sum_s \; < \Psi^0_N | \mathrm{a}^\dagger_m | \Psi^s_{N-1} > \delta(E_N - E_{N-1} - \hbar\omega) < \Psi^s_{N-1} | \mathrm{a}_{m'} | \Psi^0_N >$$

One step model of photoemission

$$I(\epsilon_e, \mathbf{k}_\parallel) \; = \; \int d\mathbf{r} \int d\mathbf{r}' \; \Psi^\dagger_e(\mathbf{r}) \; \boldsymbol{\alpha}\mathbf{A}_0 \; A^{(1)}(\mathbf{r}, \mathbf{r}', E) \; (\boldsymbol{\alpha}\mathbf{A}_0)^\dagger \; \Psi_e(\mathbf{r}')$$

$\hat{\boldsymbol{\alpha}} \cdot \mathbf{A}_0$: **relativistic form of electron-photon interaction**

Review: G. Brostel, Appl. Phys A **38,** 193 (1985)

Practical calculations of Photocurrent

One step model of photoemission

$$I(\mathbf{k}_\parallel, \epsilon_f) = -\frac{1}{\pi} Im < \mathbf{k}_\parallel, \epsilon_f \mid G_2^+ \triangle G_1^+ \triangle^\dagger G_2^- \mid \epsilon_f, \mathbf{k}_\parallel >$$

Pendry

DFT (e.g. N-1 → N)

Wave functions based methods

Initial state:
Supercell geometry (LAPW)
Systems with translational symmetry

Final state:
Solving Schrödinger Eq.
In plane wave basis
Limited to low photon energies (~30eV)

Nice feature:
simple initial and final state analysis

(Schattke, Krasovskii)

Green's function methods

Initial state:
Semi-infinite surface

Final state:
TR-LEED state
Proper Scattering solution

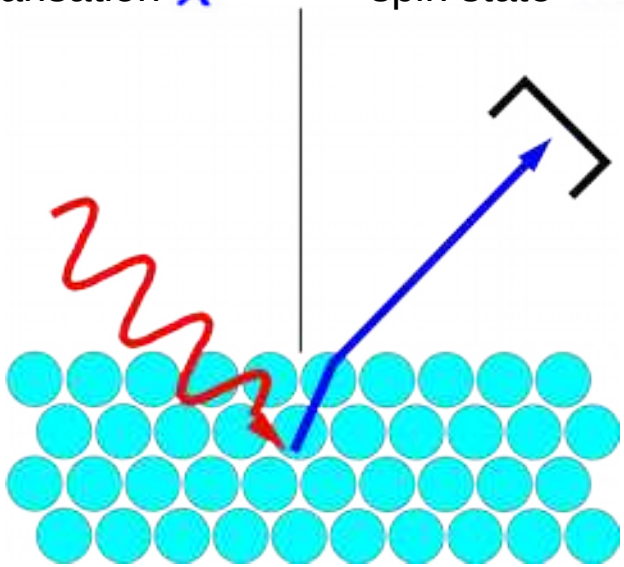
Nice feature:
Simple generalization
(CPA, DMFT, Dirac ...)

(Pendry, Feder, Braun ...)

One-step model of photo-emission I

radiation source
wave vector $\vec{q}$
polarisation λ

photo electron detector
wave vector $\vec{k}$
spin state m_s



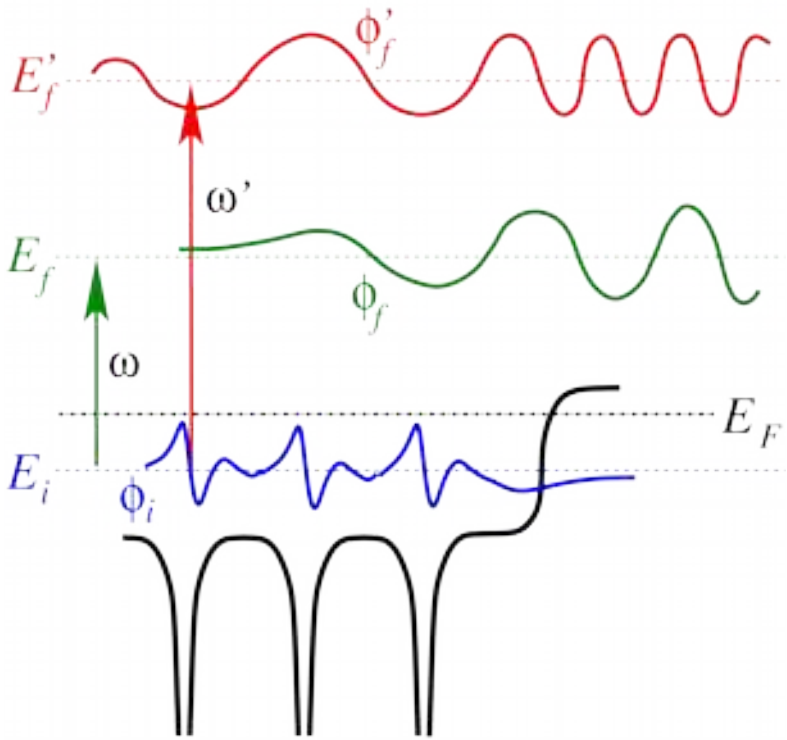


photo-current (Fermi's golden rule)

$$j \propto \sum_i |\langle \phi_f | \hat{\mathcal{H}}_{rad}^{\vec{q}\lambda} | \phi_i \rangle|^2 \delta(E_f - E_i - \omega)$$

with final state $\phi_f = \mathcal{T}_R \phi^{LEED}$ — time reversed LEED state

One-step model of photo-emission II

photo current

$$j \propto \sum_i \langle \phi_f | \hat{\mathcal{H}}^{\vec{q}\lambda}_{rad} | \phi_i \rangle \langle \phi_i | \hat{\mathcal{H}}^{\vec{q}\lambda\,\dagger}_{rad} | \phi_f \rangle \; \delta(E_f - E_i - \omega)$$

$$\propto \langle \phi_f | \hat{\mathcal{H}}^{\vec{q}\lambda}_{rad} | \Im \, G_i | \hat{\mathcal{H}}^{\vec{q}\lambda\,\dagger}_{rad} | \phi_f \rangle$$

initial state Green's function (from KKR):

$$G^+(\vec{r},\vec{r}',E) = G^{+,\mathrm{irr}}_{nn}(\vec{r},\vec{r}',E) + \sum_{\Lambda\Lambda'} Z^n_\Lambda(\vec{r},E)\, \tau^{nm}_{\Lambda\Lambda'}(E)\, Z^{m\times}_{\Lambda'}(\vec{r}',E)$$

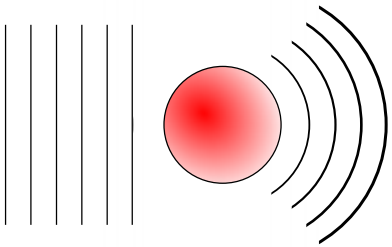
final state (Time reversed LEED):

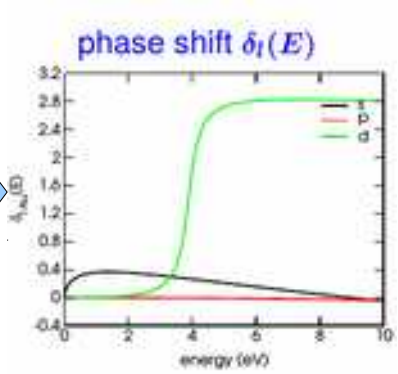
$$\phi_f = \mathcal{T}_R \phi^{LEED}$$

$$= \mathcal{T}_R \left[e^{i\vec{k}_f\vec{r}} + \int d^3r' G(\vec{r},\vec{r}',E_f)\, V(\vec{r}')\, e^{i\vec{k}_f\vec{r}'} \right]$$

e.g. Caroli et al. (1973), Feibelmann and Eastman (1974)

Numerical calculations: 1-st step





Developments:

Fully relativistic: Dirac

Full potential

Correlation effects
LDA+U, LDA+DMFT

$$\psi = \psi_0 + \psi_{st}$$

Lippmann-Schwinger Eq.

$$\psi(\vec{r}, E) = e^{i\vec{k}\vec{r}} + \int_{\Omega_n} d^3r'\, G_0(\vec{r}, \vec{r}', E)\, V^n(\vec{r})\, \psi(\vec{r}, E)$$

$$= e^{i\vec{k}\vec{r}} + \int_{\Omega_n} d^3r' \int_{\Omega_n} d^3r''\, G_0(\vec{r}, \vec{r}', E)\, t^n(\vec{r}', \vec{r}'', E)\, e^{i\vec{k}\vec{r}''}$$

Meaning of **t**
(angular momentum expansion)

$$t_l(E) = -\frac{1}{k} \sin\left(\delta_l(E)\right) e^{i\delta_l(E)}$$

Single site Green's function

Numerical calculations: Multiple scattering (MST)

Single site scattering

2D MST inside one layer

MST between two layers

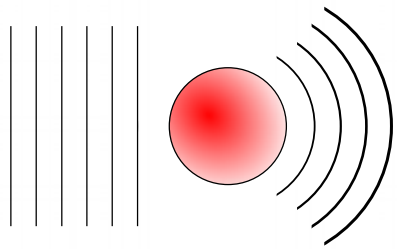
MST semi-infinite surface

Single site t-matrix
Radial wave functions Z, J

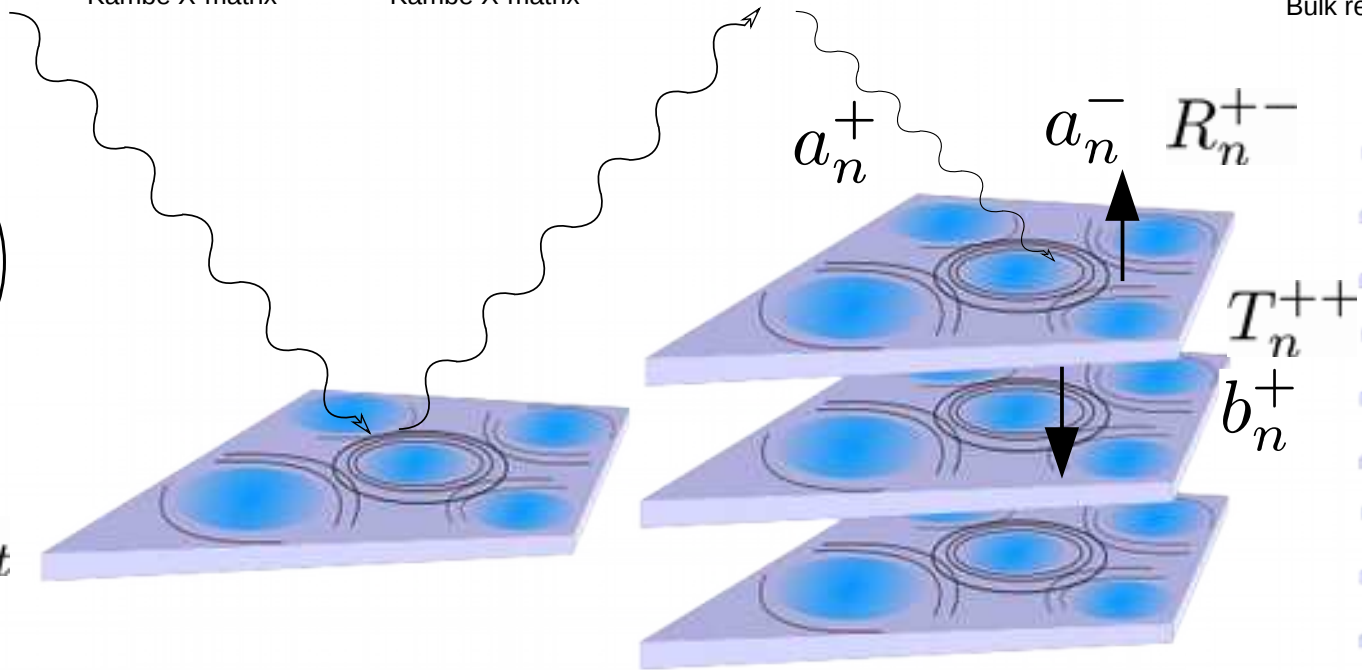
Kambe X-matrix

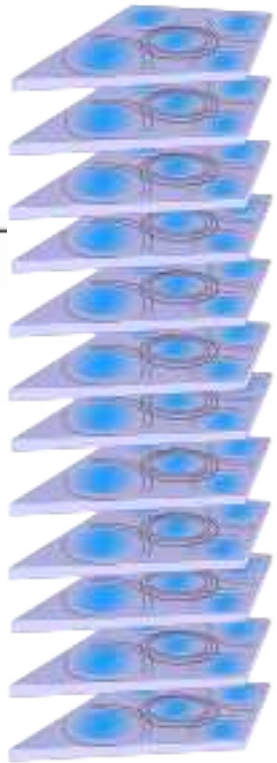
Kambe X-matrix

Bulk reflection matrix



$$\Phi = \Phi_0 + \Phi_{st}$$





Transmitted current $b_n^+ = T_n^{++} a_n^+ + R_n^{-+} a_n^-$

Layer doubling

Layer doubling $a_n^+ = \boxed{M_n^{+-}} a_n^-$ ← All scattering events ← $\boxed{I_{trans} \to 0}$

Numerical calculations: Multiple scattering (MST)

Single site scattering

2D MST inside one layer

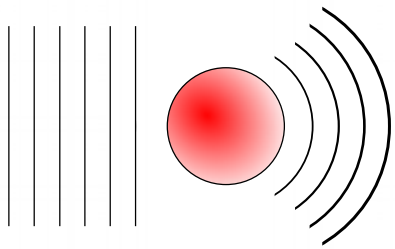
MST between two layers

MST semi-infinite surface

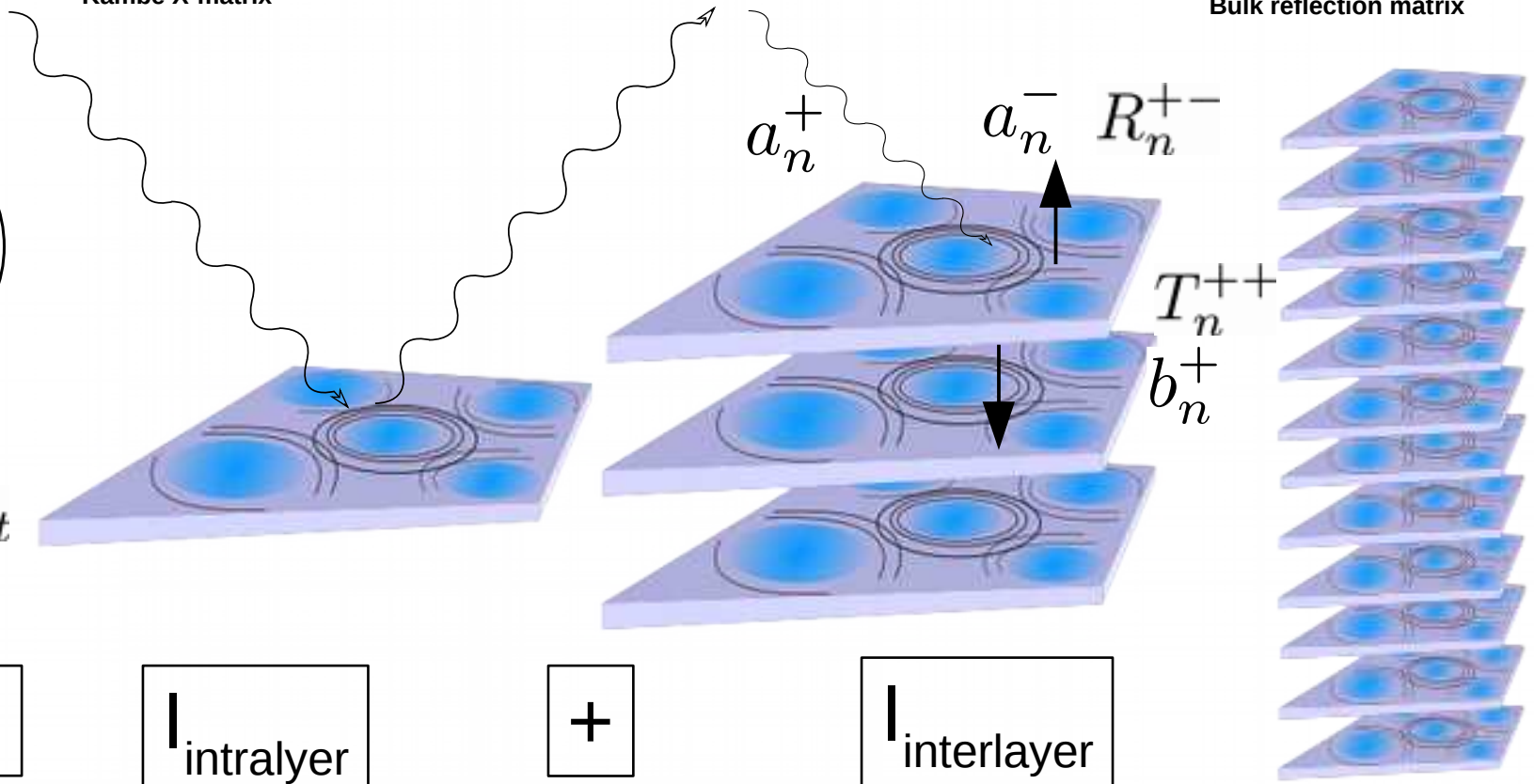
Single site t-matrix
Radial wave functions Z, J

Kambe X-matrix

Bulk reflection matrix



$$\Phi = \Phi_0 + \Phi_{st}$$



I_{atomic} + $I_{intralyer}$ + $I_{interlayer}$

= $I_{photo\ current}$

Numerical calculations:Configurational avarage

Single site scattering

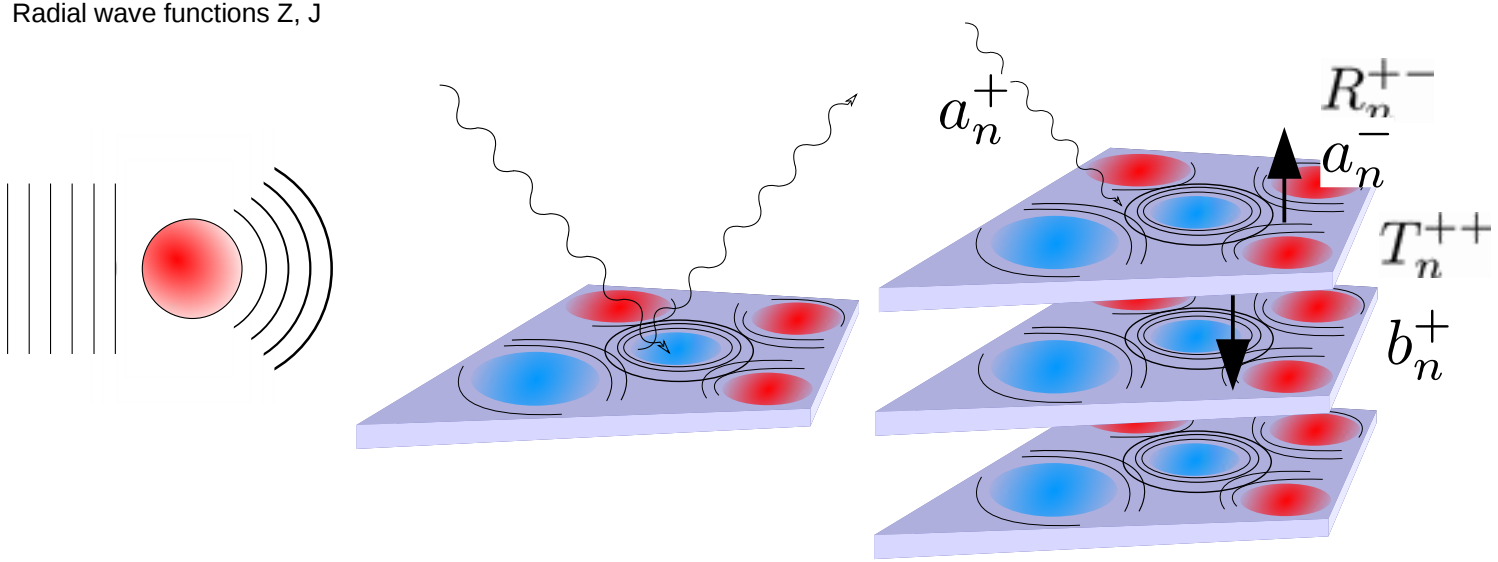
Single site t-matrix
Radial wave functions Z, J

2D MST inside one layer

Kambe X-matrix

MST between two layers

Kambe X-matrix



Developments:

Adsorbates, relaxations …: rumpled layers

Disordered sytems: CPA

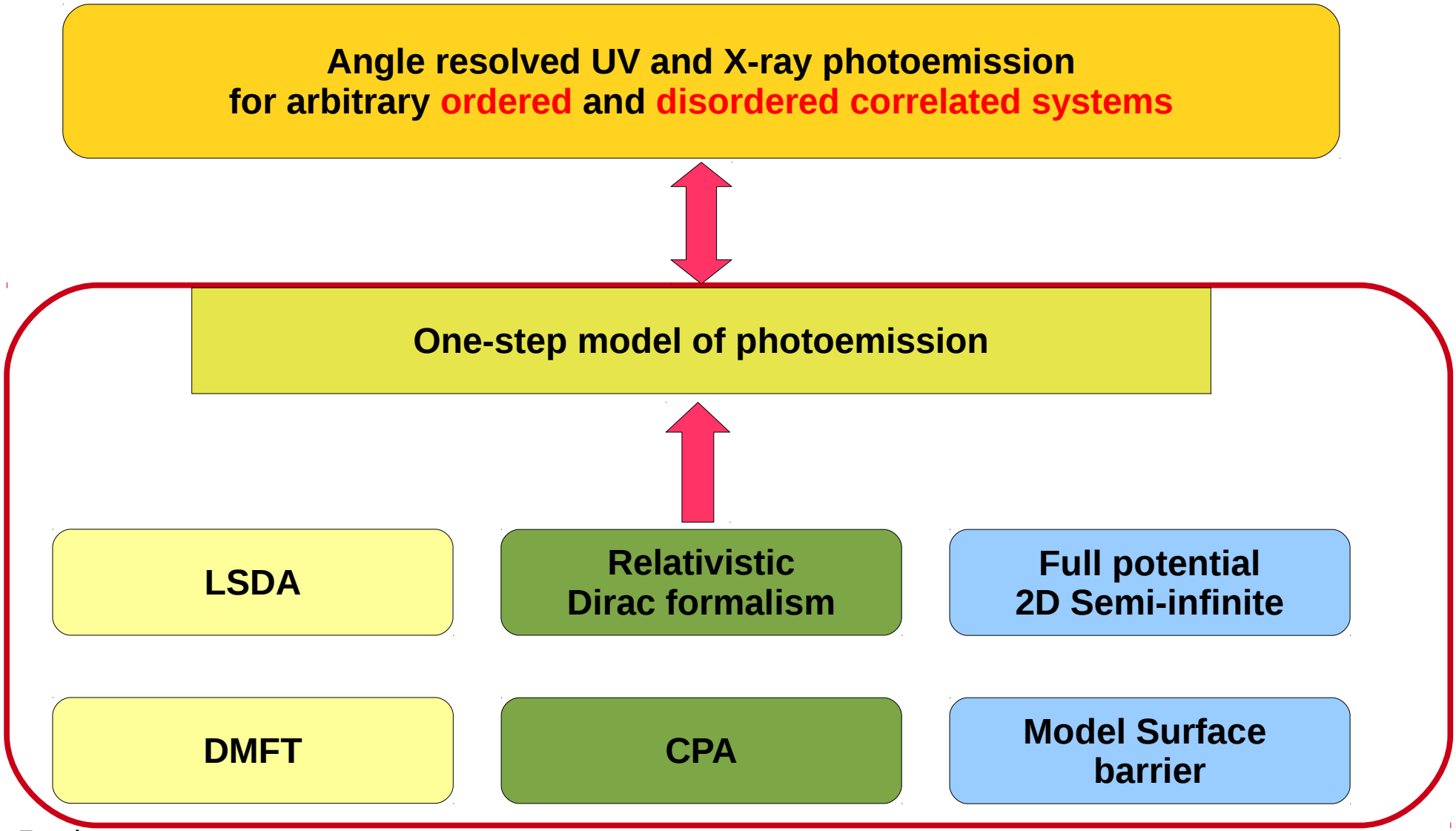
Lattice vibrations

Non-local correlations (El. Phonon coupling)

Spin fluctuations

$\langle I_{atomic} \rangle + \langle I_{intralyer} \rangle + \langle I_{interlayer} \rangle + I_{incoherent} = I_{photo\ current}$

Main Goal: SPRKKR method + One step model



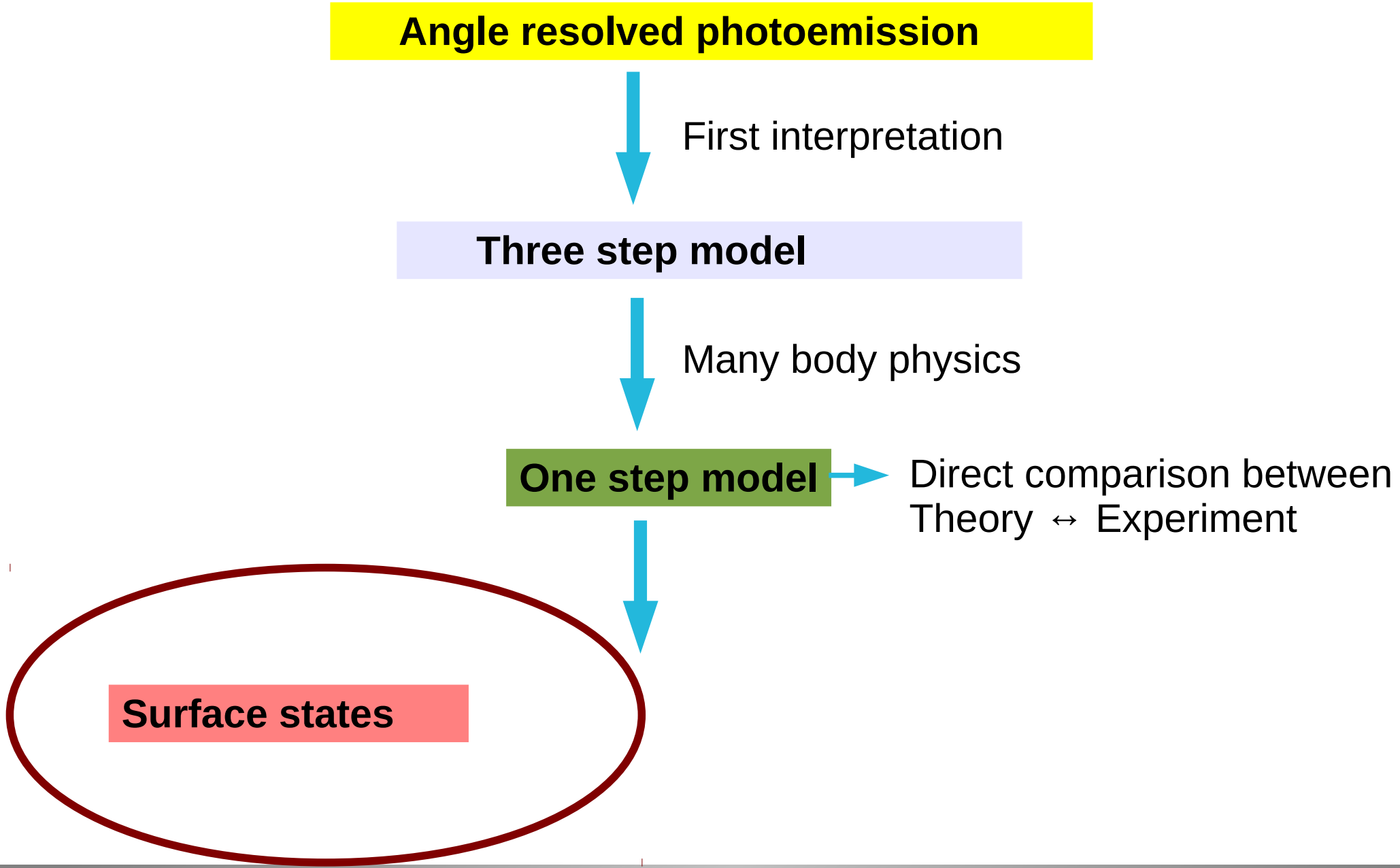
Reviews:

KKR: Ebert, Ködderitzsch, Minar, Rep. Prog. Phys. **74**, 096501 (2011)

KKR+DMFT: Minar, JPCM Topical Review **23**, 253201 (2011)

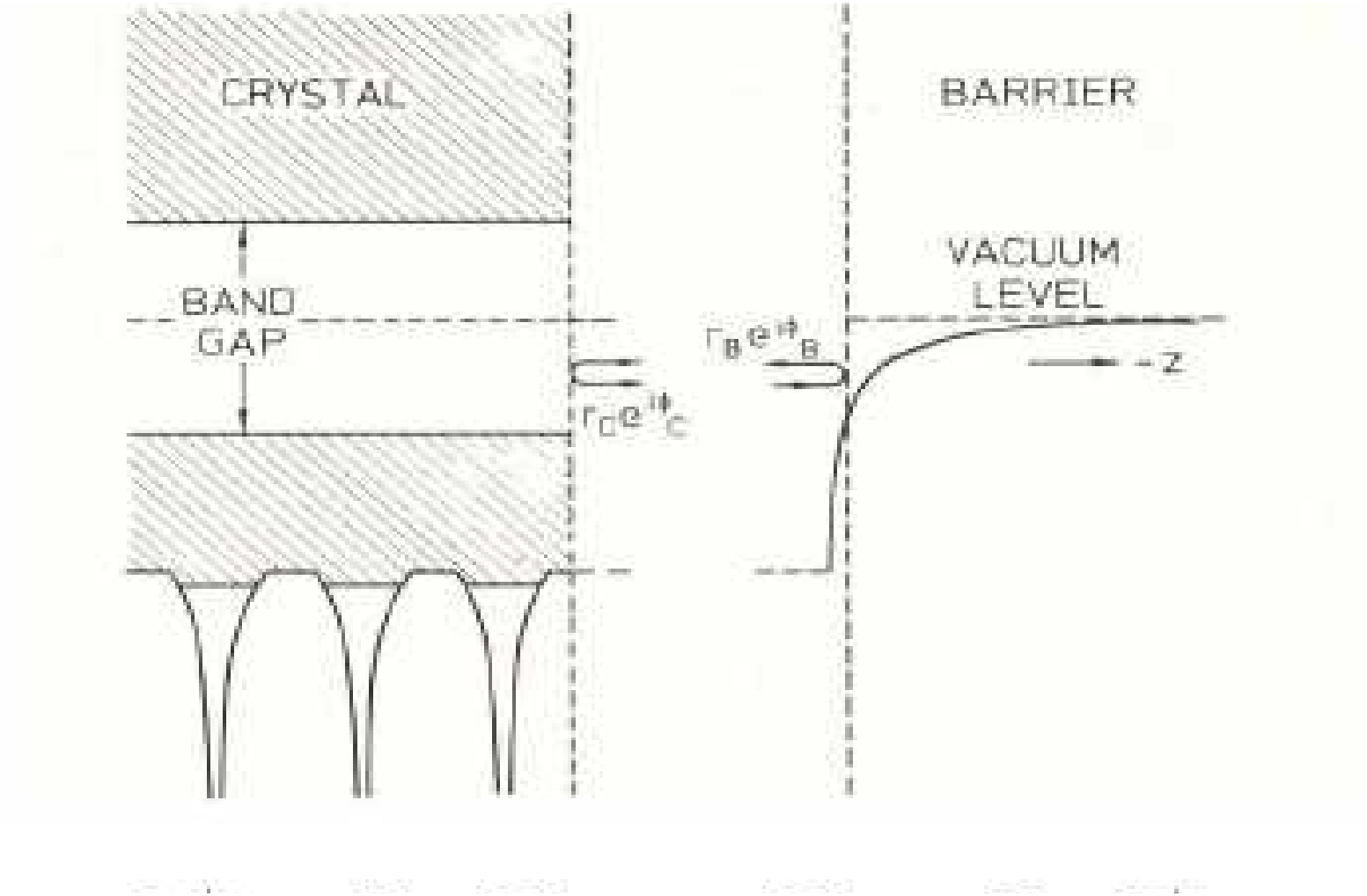
KKR+One step model: Minar, Braun et al., JESRP **184**, 91(2011)

Outline

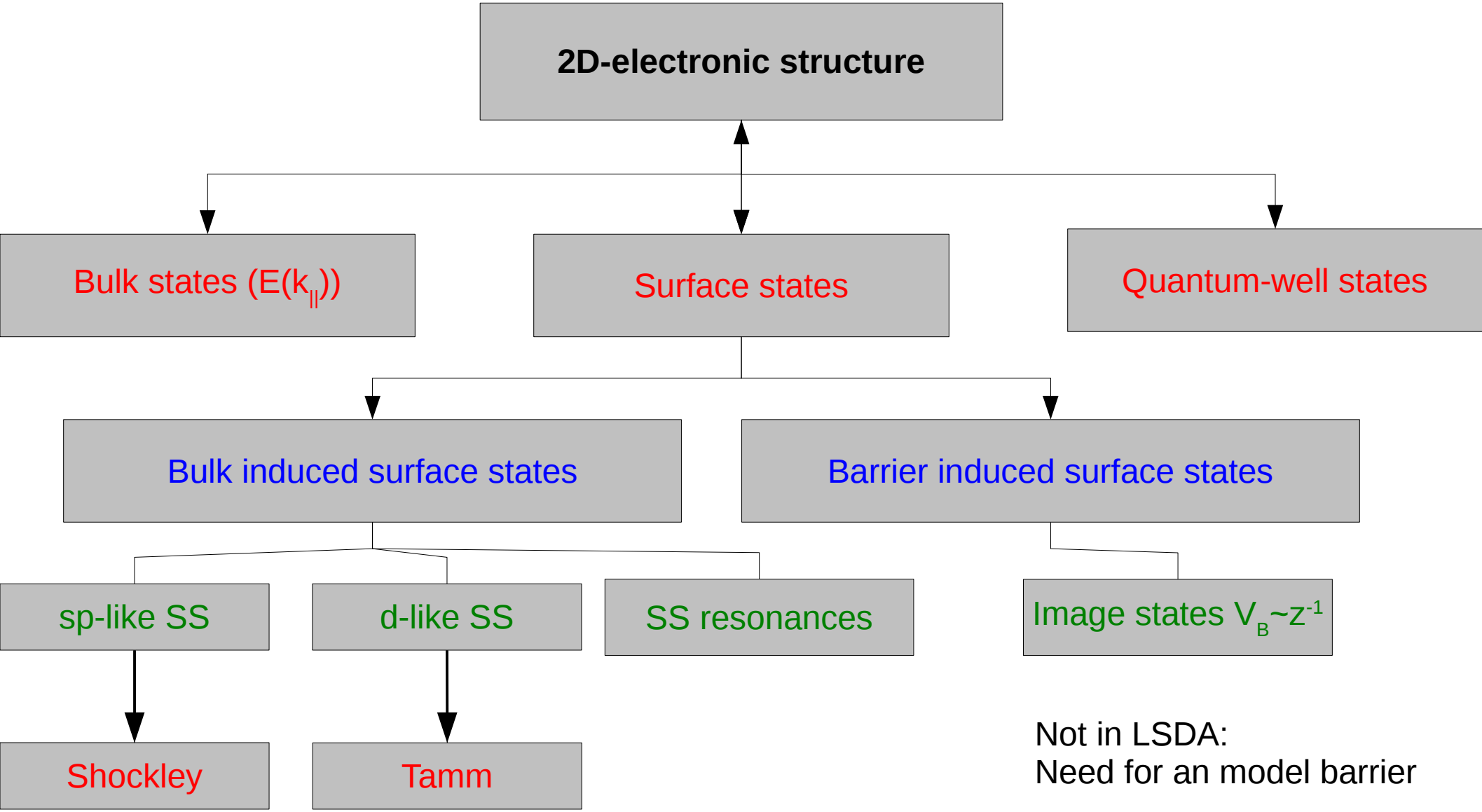

Angle resolved photoemission
First interpretation
Three step model
Many body physics
One step model
Direct comparison between
Theory ↔ Experiment
Surface states

Surface potential

Surface potential



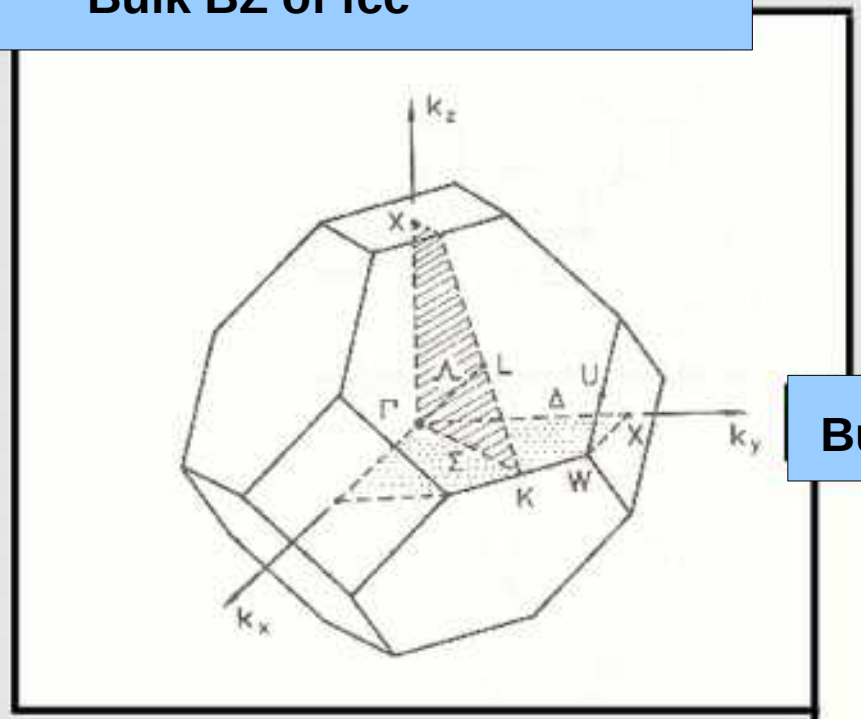
Electronic structure of surface



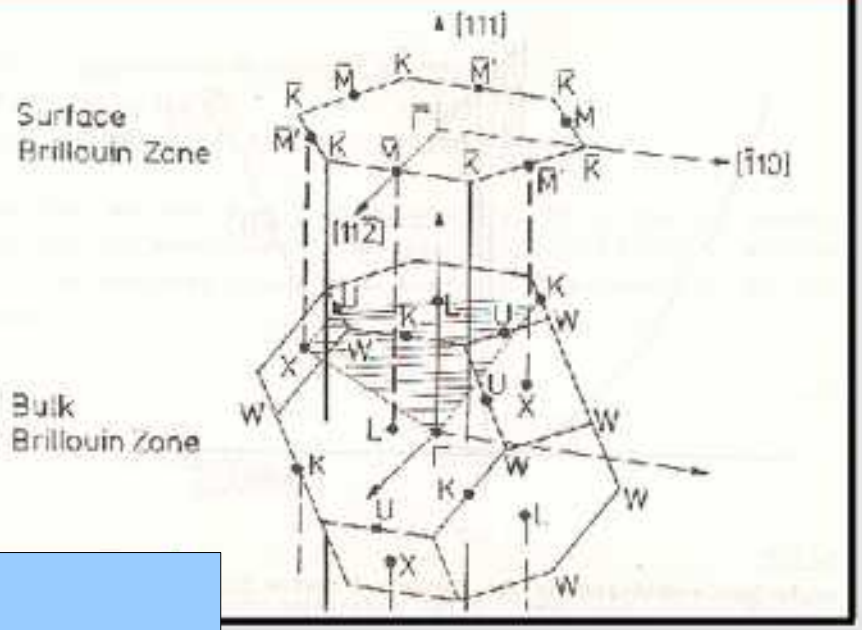
Not in LSDA:
Need for an model barrier

Surface Brillouin Zone

Bulk BZ of fcc



Bulk BZ and Surfcace BZ

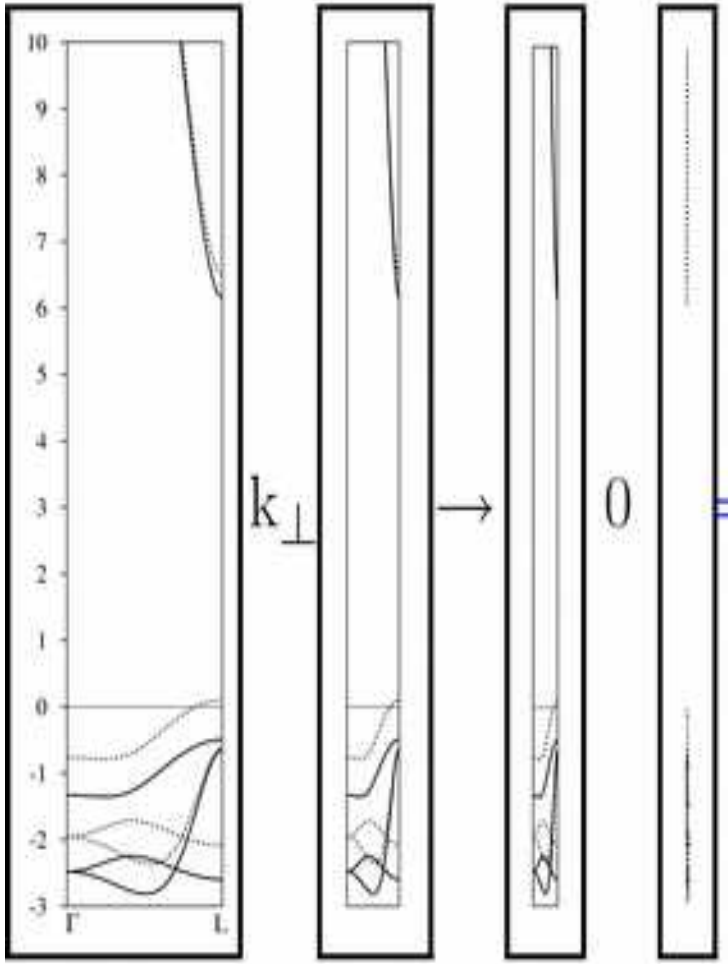


Surface BZ of fcc(111)

Ni(111): 2D-Brillouin zone

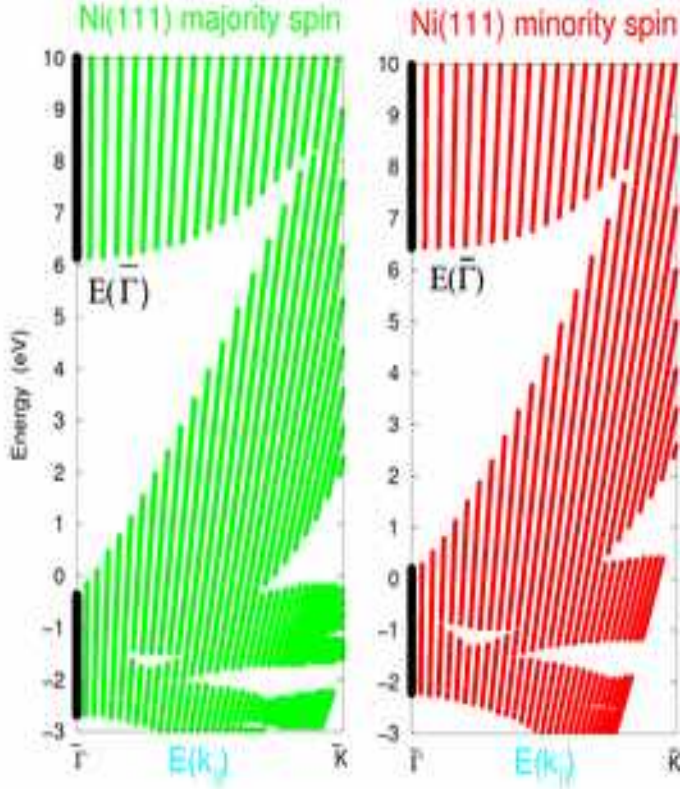
$E(k_\perp) \rightarrow E(\mathbf{k}_\parallel)$ for Ni(111)

Majority (–) and minority (...) bandstructures for ($k_\perp \parallel [111]$)



$k_\perp \rightarrow 0 \Rightarrow E(\mathbf{k}_\parallel = 0)$

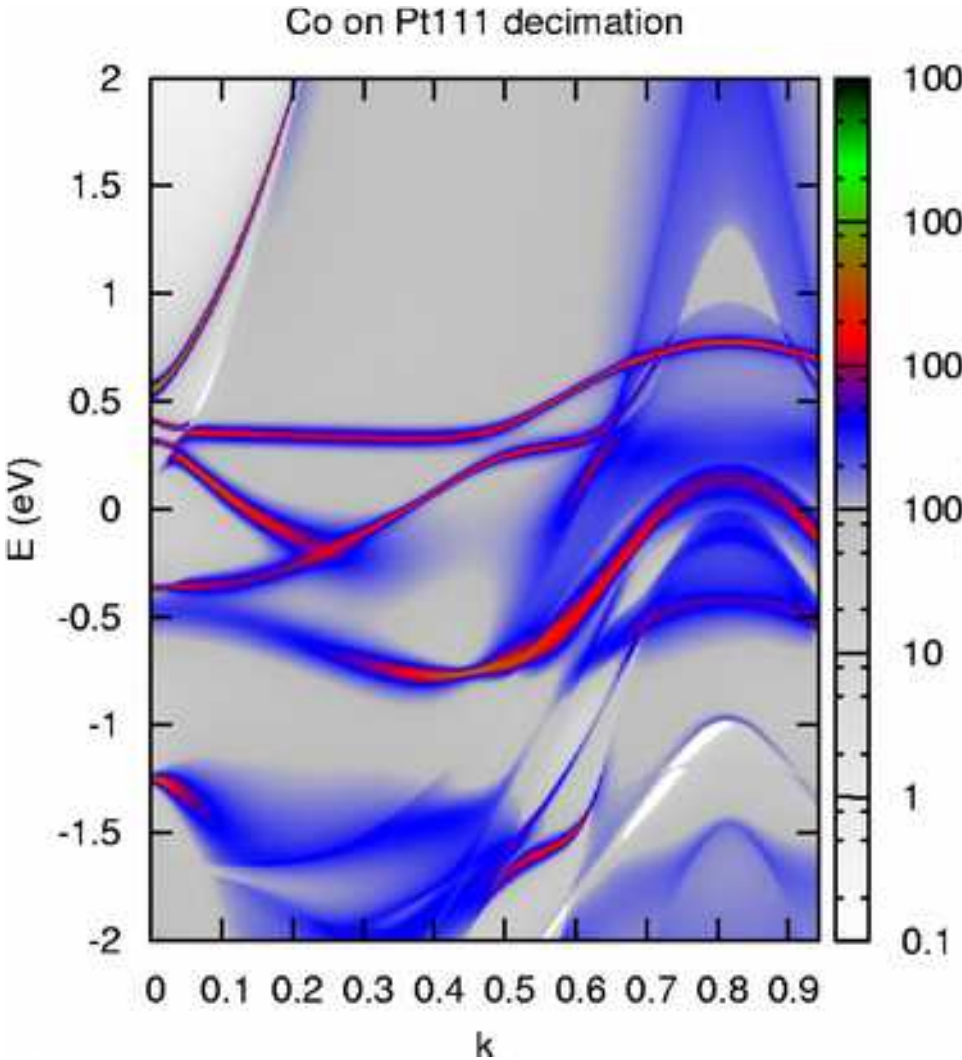
$\equiv E(\bar{\Gamma})$



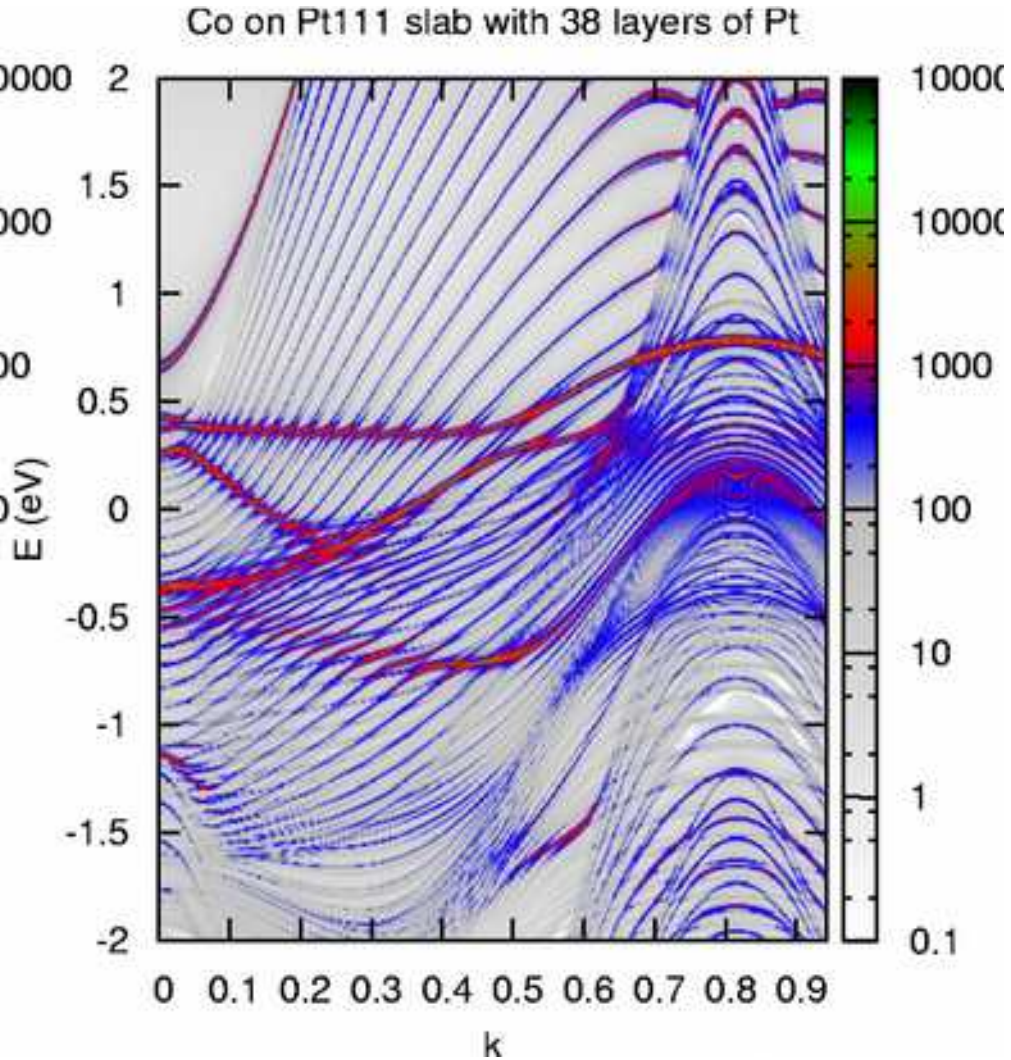
$|\mathbf{k}_\parallel| \propto \sqrt{E}\,\sin\theta$

Electronic structure of surfaces

Half-space calculation



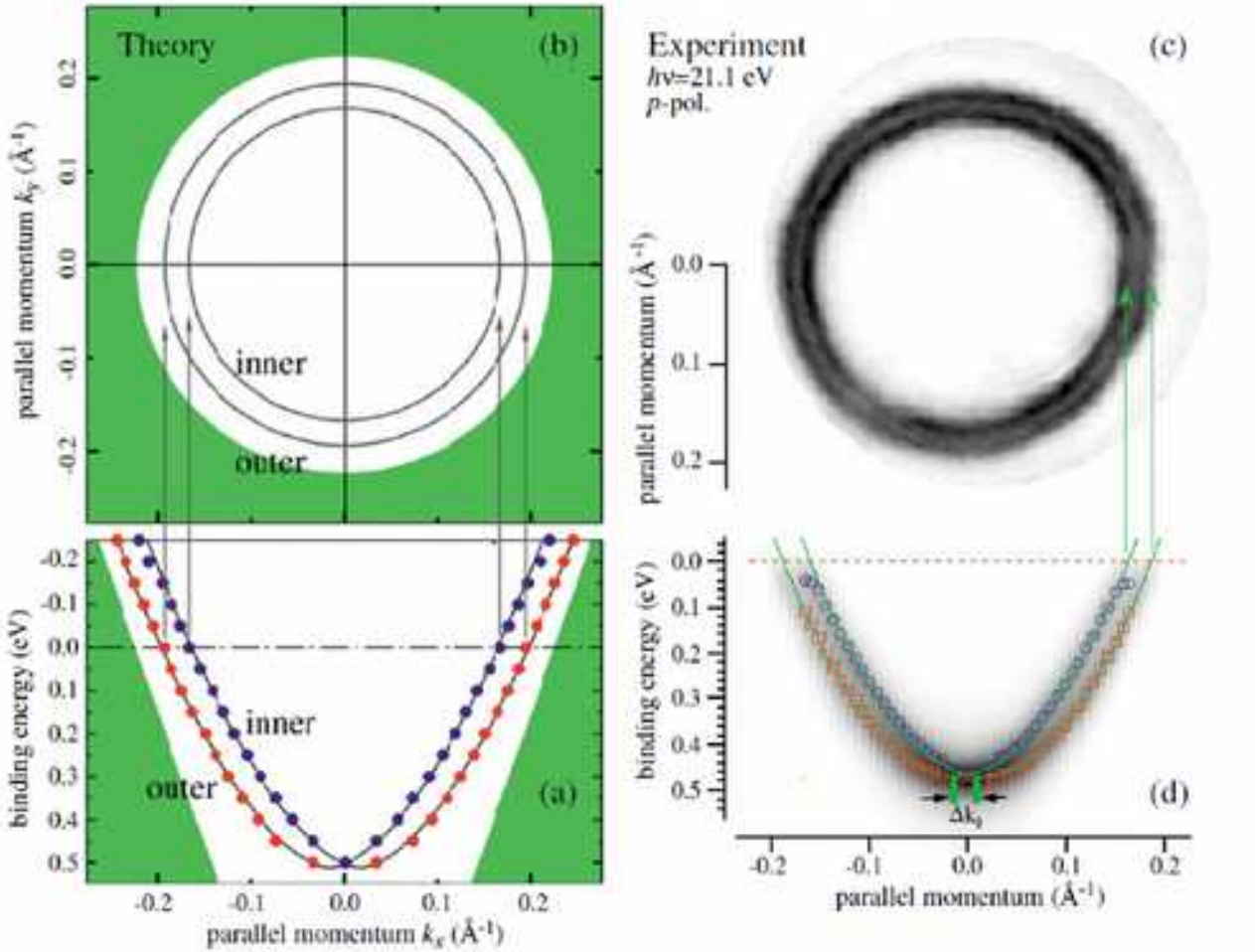
Slab calculation



Surface barrier

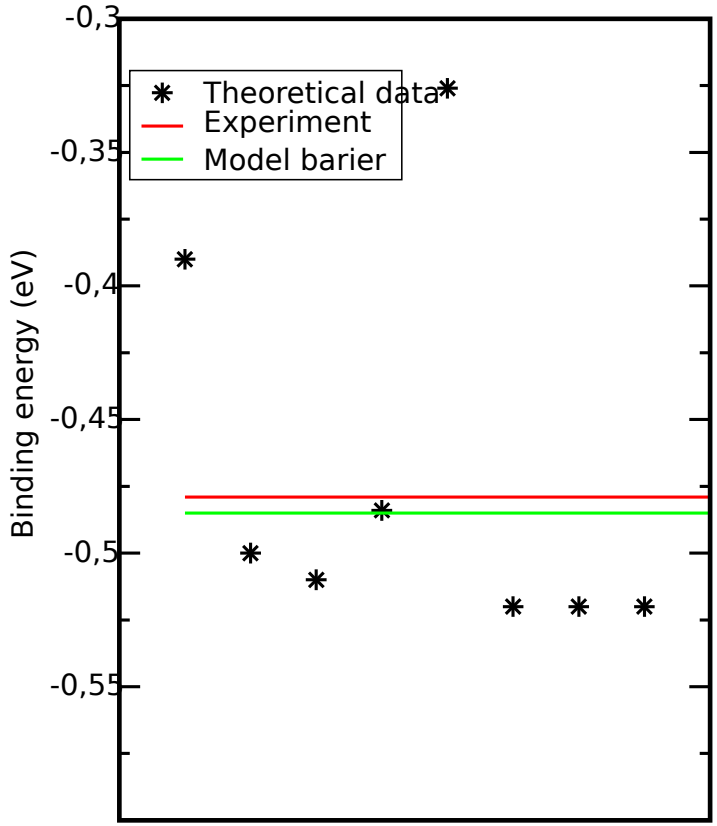
Rashba effect in Au(111) Shockley surface state

$$E_{\pm}(\vec{k}) = E_0 + \frac{\hbar^2 k^2}{2m^*} \pm \alpha_R |k|$$



J Henk et al, JPCM **16,** 7581 (2004)

Binding energy from various calculations

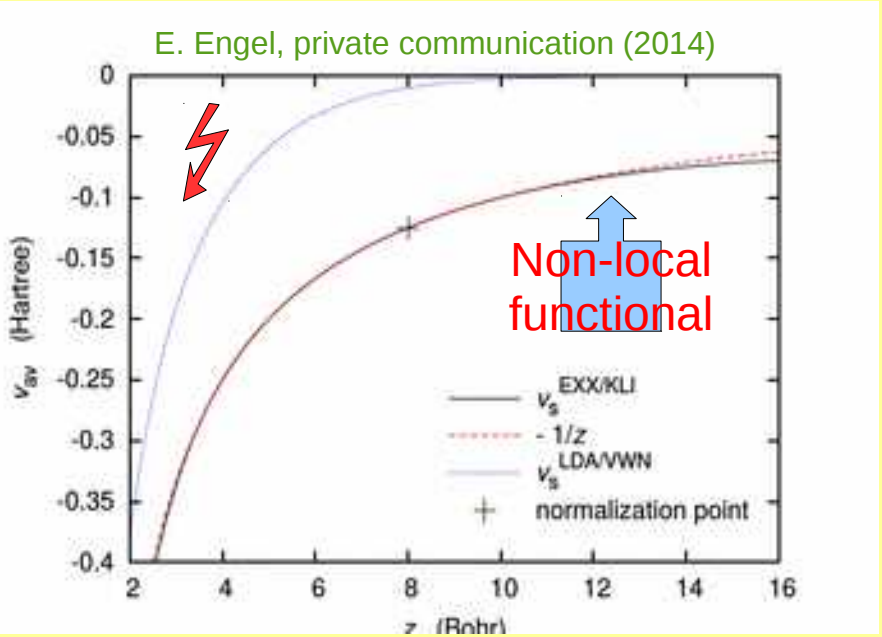


M. James and S. Crampin, PRB B **81**, 155439 (2010)
A. Nuber et al, PRB **83**, 165401 (2011)

Models of surface barrier

Asymptotic behavior of DFT functionals

E. Engel, private communication (2014)



- Transparent surface barrier
- one step barrier
- polynomial 2. order (Read, Price, Jennings)
- polynomial 3. order (Rundgren, Malmström)
- Universal barrier model (JJJ-Model, Jones, Jennings, Jesper)

$$V_B(z) = \begin{cases} \frac{1}{4}(z - z_{im})^{-1} & z < z_A < z_{im} \\ s_0 + s_1(z - z_A) + s_2(z - z_A)^2 + s_3(z - z_A)^3 & z_A < z < z_E \\ V_{or} & z > z_E \end{cases}$$

Solved by Multiple scattering

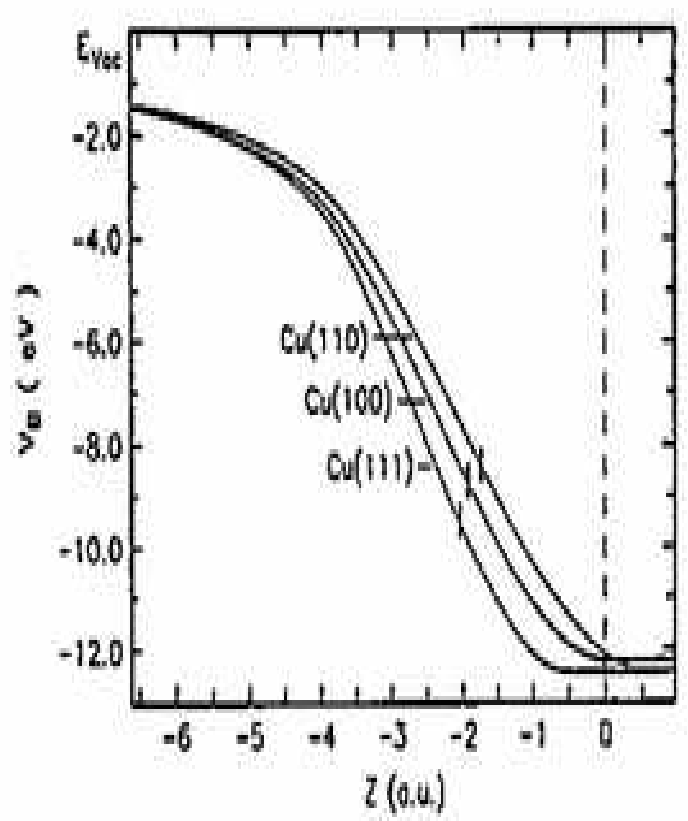
Surface contribution to photocurrent

$I_{surface}$

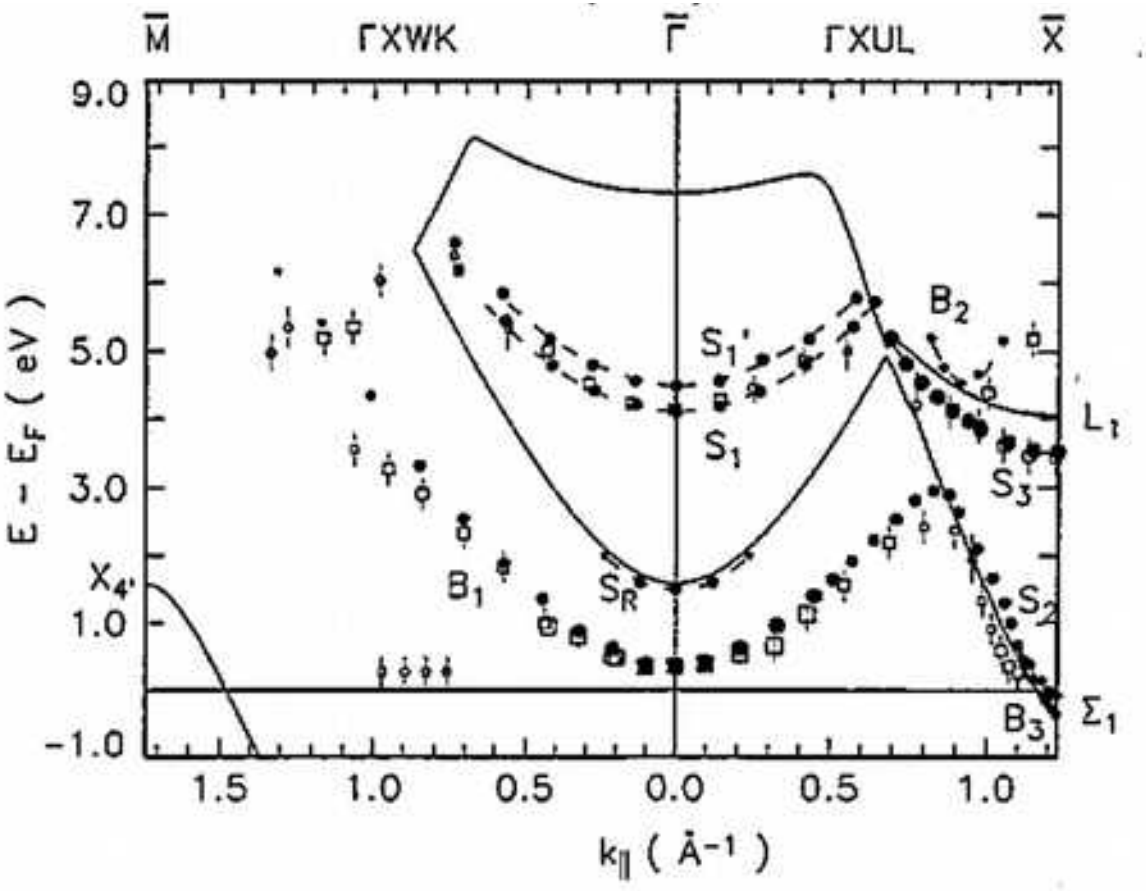
Grass et al., JPCM **5** 599 (1993)

Rydberg states (image states) in Cu

Barrier potentials for Cu surfaces



Inverse PES of Cu(001)

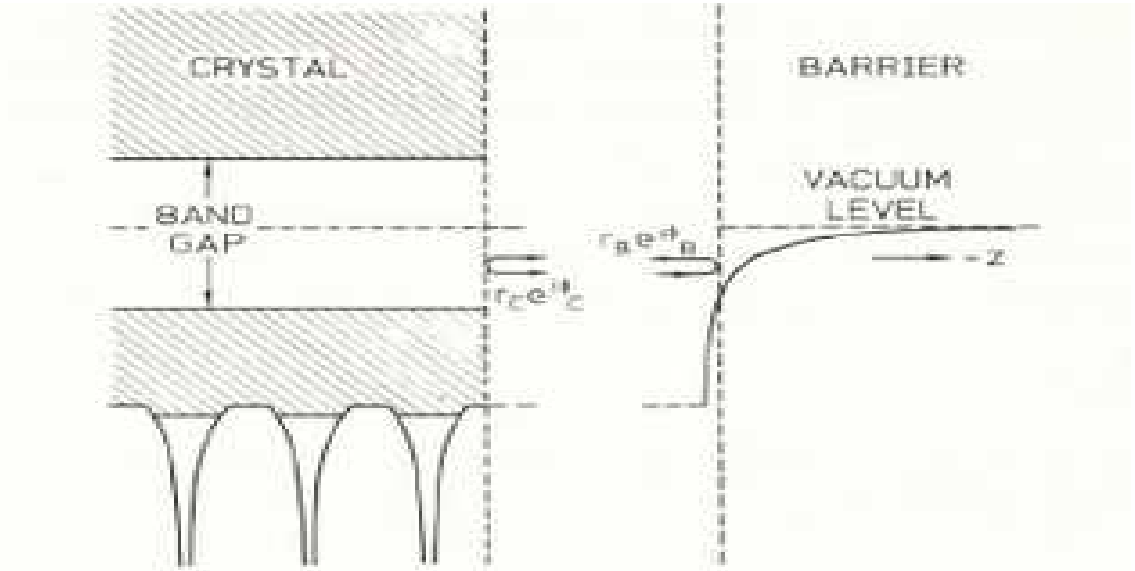


- Rydberg states:
  only possible to calculate if we have proper asymptotics
- Nowadays important because of 2PPE and ultrafast TD-PES of correlated materials

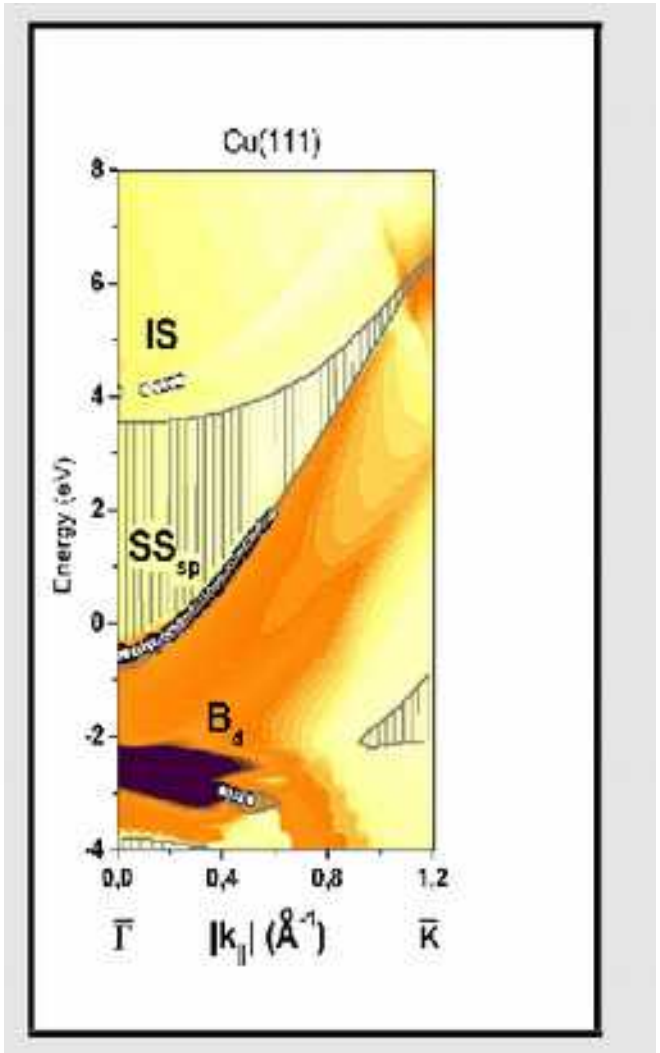
Grass et al., JPCM **5** 599 (1993)

Classification of surface states

Surface potential



$$\mathbf{b}^+ = \mathbf{R}_B\,\mathbf{b}^- \qquad \mathbf{b}^- = \mathbf{R}_C\,\mathbf{b}^+$$



Criteria for surface states in (inverse) photoemission

$$\mathbf{b}^+ = \mathbf{R}_B\mathbf{R}_C\,\mathbf{b}^+ \equiv (\mathbf{1} - \mathbf{R}_B\mathbf{R}_C)\,\mathbf{b}^+ = 0$$

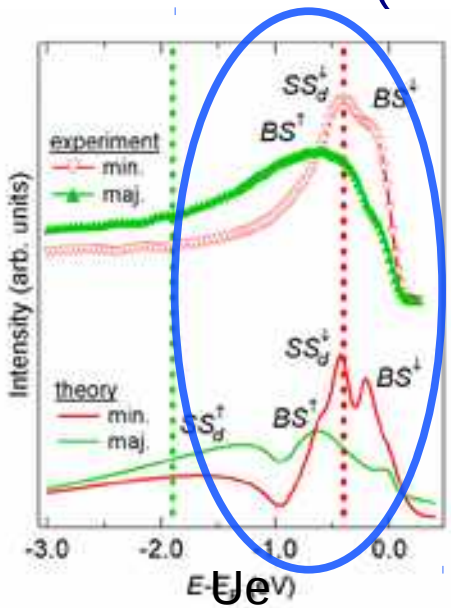
$\det|\mathbf{1} - \mathbf{R}_B\mathbf{R}_C| = 0 \Rightarrow$ Surface State

$\det|\mathbf{1} - \mathbf{R}_B\mathbf{R}_C| = \min \Rightarrow$ Surface Resonance

P. M. Echenique, J.B. Pendry, JPC: Solid State Phys. **11,** 2065 (1978)
E. G. McRae, Rev. Mod. Phys. **51**, 541 (1979)
J. Braun, M. Donath, JPCM 16 (2004) S2539–S2556

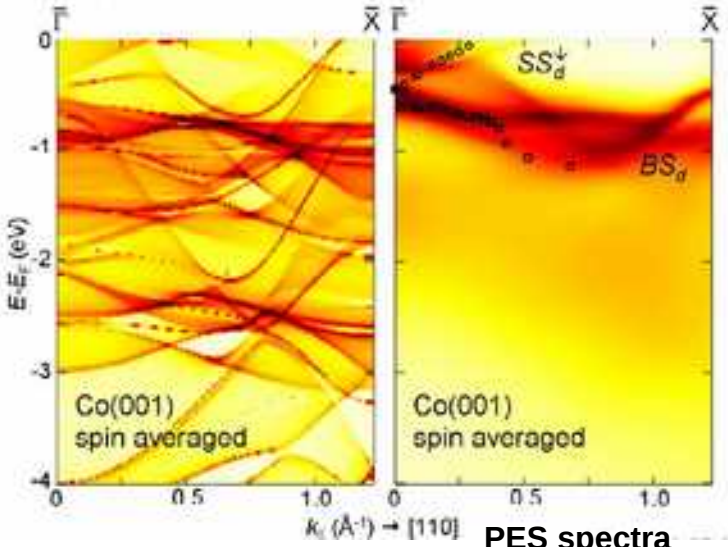
Surface resonances in ground state calculations?

Tamm surface resonance in PES of fcc Co(001)



LSDA+DMFT
U_{Co}= 2.3eV

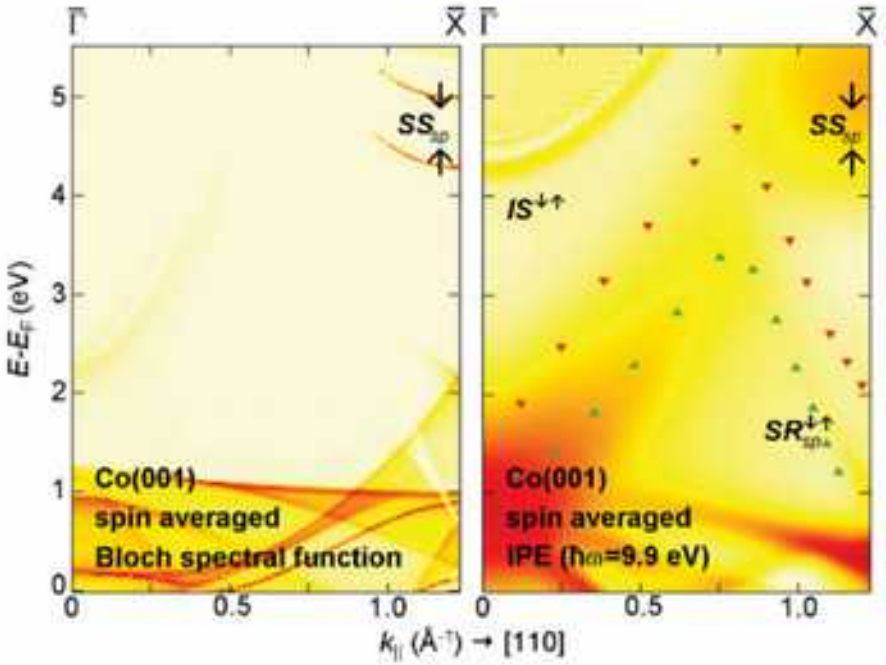
Ue



Spectral function

PES spectra (E_{phot}=21.eV)

Inverse Photoemission



- Surface resonances:
  difficult to identify in ground state calculations

  K Miyamoto et al. New Journal of Physics 10 (2008) 125032

- d-like Tamm surface resonance
  - Due to correlation effects shift in binding energy
    LSDA: -0.7eV, LSDA+DMFT: -0.4eV

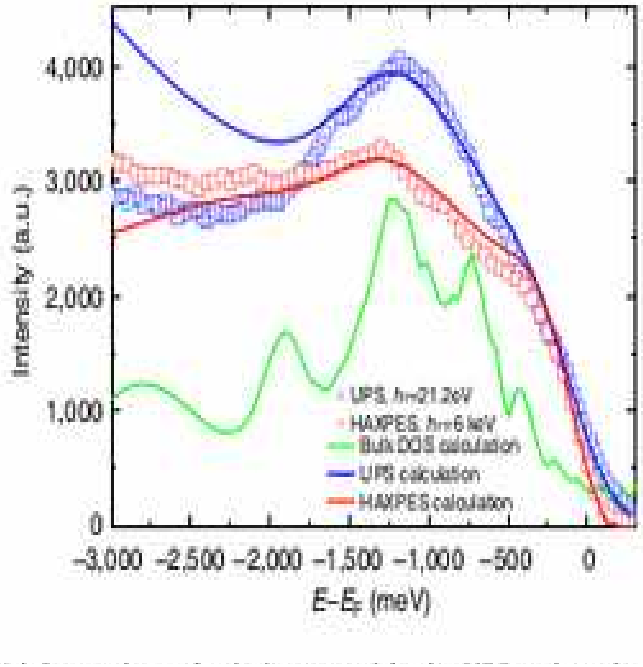
Pickel et al, PRL **101,** 066402 (2008)
Allmers et al, PRB **84,** 245426 (2011)

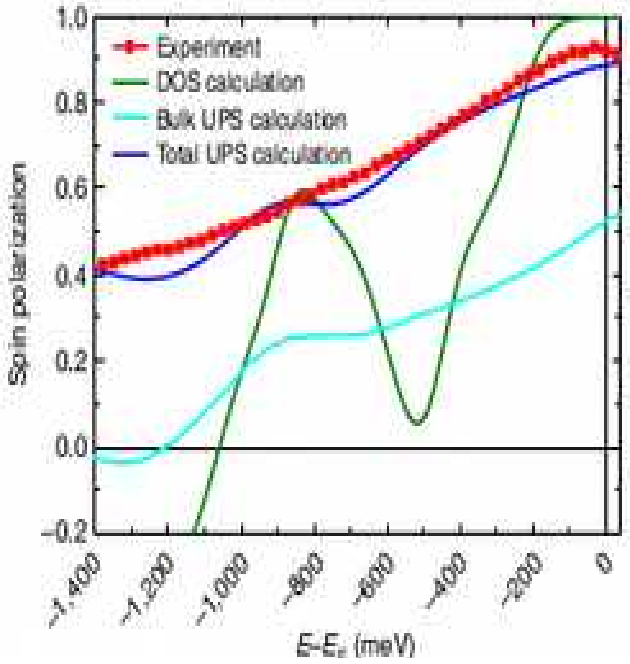
Angle integrated HAXPES: Spintronic materials

ARTICLE
Received 10 Feb 2014 | Accepted 28 Apr 2014 | Published 30 May 2014 DOI: 10.1038/ncomms4974 OPEN

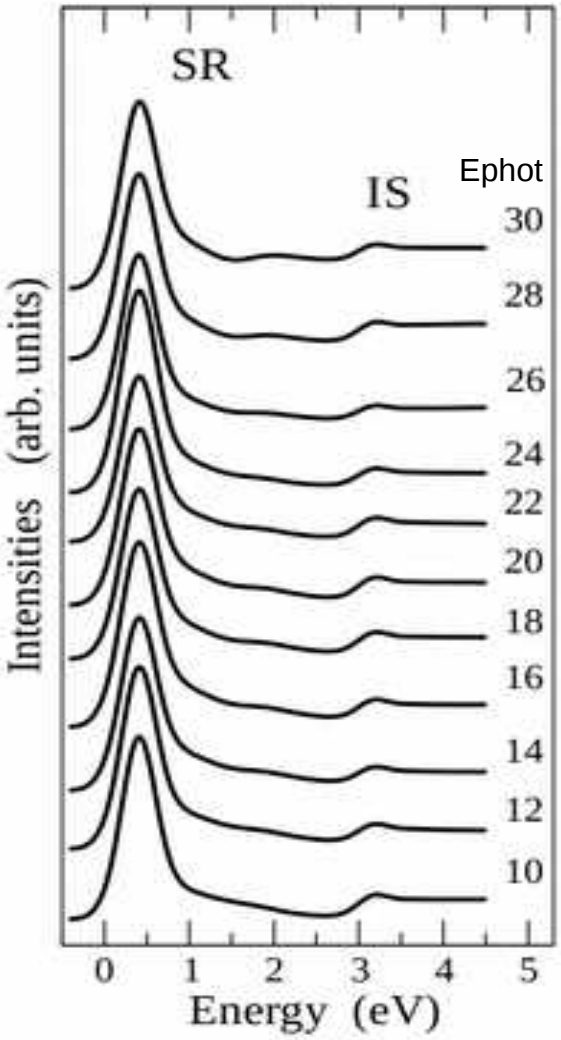
Direct observation of half-metallicity in the Heusler compound Co_2MnSi

M. Jourdan[1], J. Minár[2,3], J. Braun[2], A. Kronenberg[1], S. Chadov[4], B. Balke[5], A. Gloskovskii[6], M. Kolbe[1], H.J. Elmers[1], G. Schönhense[1], H. Ebert[2], C. Felser[4,5] & M. Kläui[1]





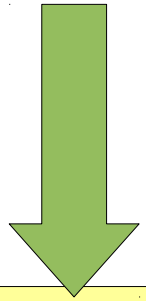
Normal emission



- Spin polarisation of 93% observed
- LSDA+DMFT (U_{Mn}=3.0eV, J_{Mn}=0.9eV)
- Correlation effects lead to increase of band gap
- Spin polarised bulk-like surface resonance

M. Jourdan et al. Nature Comm., 4974 (2014)

Interesting properties of surface resonances

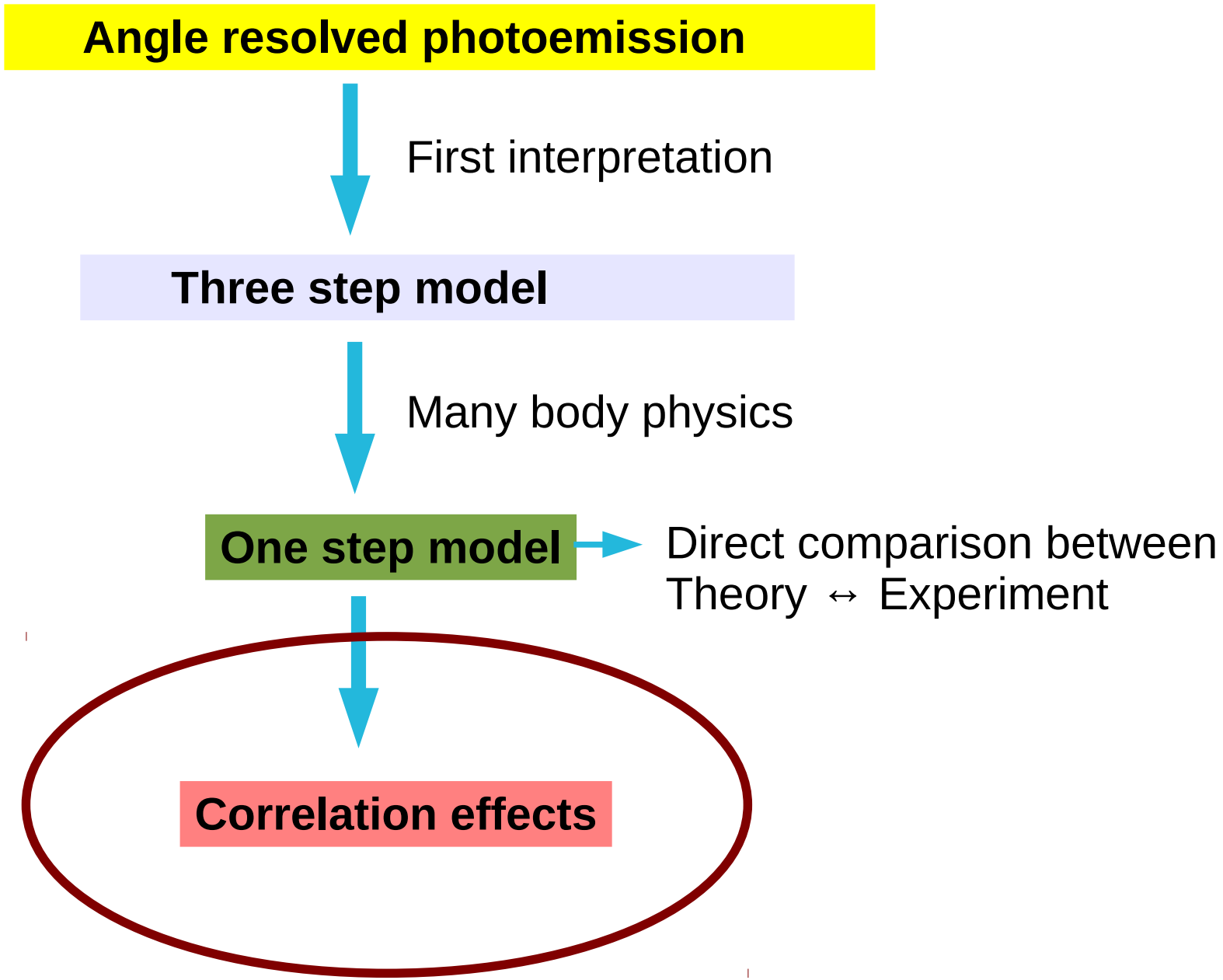


Behaves as “bulk” like:

k_z dispersion
can be seen in ARPES even
after modification of surface
see even in Bulk sensitive methods (HAXPES)

Careful interpretation of measured data

Outline


Angle resolved photoemission
First interpretation
Three step model
Many body physics
One step model
Direct comparison between
Theory ↔ Experiment
Correlation effects

Implementation of LSDA+DMFT using KKR

Dyson equation:

$$G(\vec{r},\vec{r}\,',E) = G_0(\vec{r},\vec{r}\,',E) + \int \mathrm{d}^3r'' \int \mathrm{d}^3r''' G_0(\vec{r},\vec{r}\,'',E) \left[V_{\mathrm{LSDA}}(\vec{r}\,'')\delta(\vec{r}\,''-\vec{r}\,''') + \Sigma(\vec{r}\,'',\vec{r}\,''',E)\right] G(\vec{r}\,''',\vec{r}\,',E)$$

with $\Sigma(\vec{r},\vec{r}\,',E)$ *on-site* self-energy.

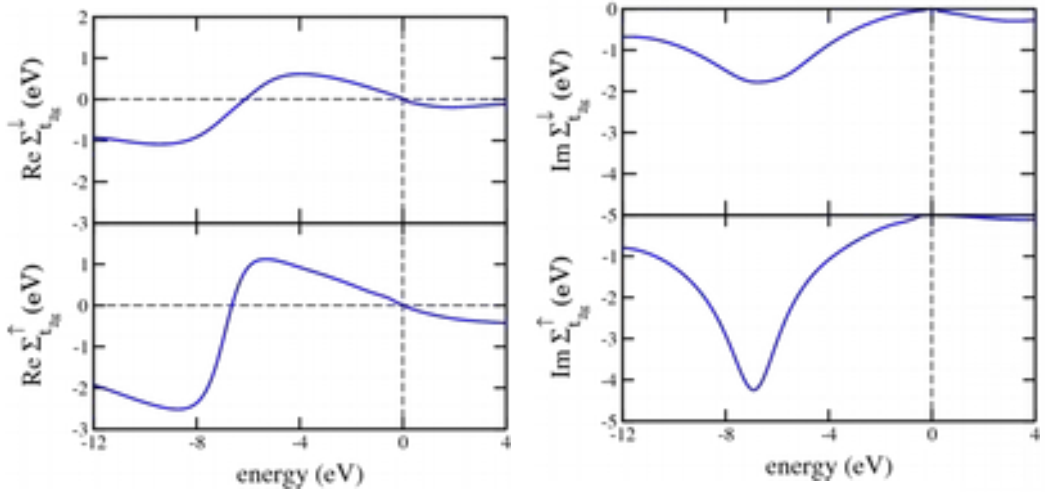
Multiple scattering Implementation of LSDA+DMFT

Dyson equation:

$$G(\vec{r},\vec{r}\,',E) = G_0(\vec{r},\vec{r}\,',E) + \int \mathrm{d}^3r'' \int \mathrm{d}^3r''' G_0(\vec{r},\vec{r}\,'',E) \left[V_{\mathrm{LSDA}}(\vec{r}\,'')\delta(\vec{r}\,''-\vec{r}\,''') + \Sigma(\vec{r}\,'',\vec{r}\,''',E)\right] G(\vec{r}\,''',\vec{r}\,',E)$$

with $\Sigma(\vec{r},\vec{r}\,',E)$ *on-site* self-energy.

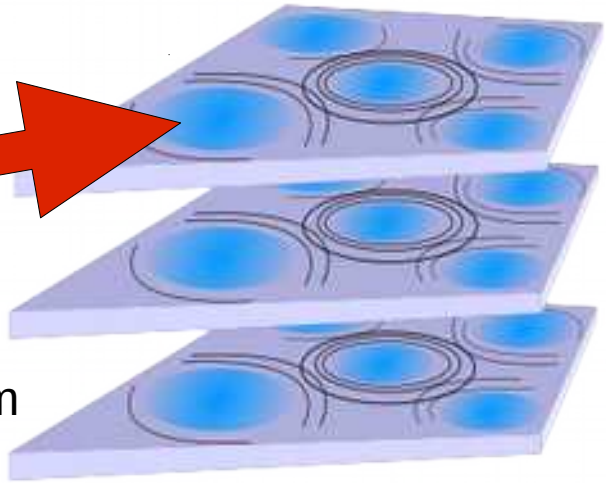
Spin dependent self energy of Ni for d-states



Real part

Imaginary part

Included in the single site scattering problem



KKR single-site problem

$$[-\nabla^2 + V^\sigma(r) - E]\Psi(\vec{r}) + \int \Sigma^\sigma(\vec{r},\vec{r}',E)\Psi(\vec{r}')d^3r = 0$$

Ansatz: $\Psi(\vec{r}) = \sum_L \Psi_L(\vec{r})$

$$\left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - V(r) + E\right]\Psi_L(r,E) =$$

$$\sum_{L''} \int r'^2 dr' \Sigma_{LL''}(E)\,\phi_l(r)\phi_{l''}(r')\Psi_L(r',E)$$

Approximation for the self-energy:

$$\sum_L \int d^3r' \phi^\dagger_{L'}(\vec{r})\Sigma_{L'L}(E)\phi_L(\vec{r}\,')\Psi_L(\vec{r}\,',E) \approx \sum_L \Sigma_{L'L}(E)\Psi_L(\vec{r},E)$$

Pure differential equation:

$$\left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - V(r) + E\right]\Psi_L(r,E) = \sum_{L'} \Sigma_{LL'}(E)\,\Psi_{L'}(r,E)$$

KKR Green's function matrix

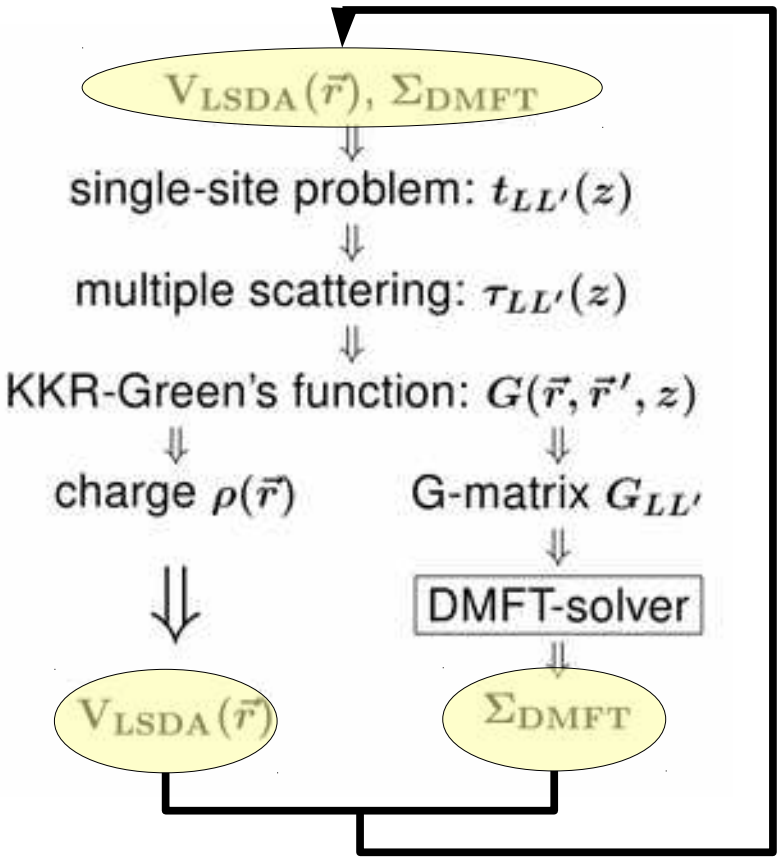
Green's function matrix $G^{nm}_{LL'}$ within KKR-formalism

$$G^{nm}_{LL'}(E) = \sum_{L_1,L_2} \langle \phi_L \mid Z_{L_1} \rangle \tau^{nm}_{LL'}(E) \langle Z^{\times}_{L_2} \mid \phi_{L'} \rangle - \delta_{nm} \sum_{L_1} \langle \phi_L \mid Z_{L_1}(\mathrm{r}_<, E) J^{\times}_{L_1}(\mathrm{r}_>, E) \mid \phi_{L'} \rangle$$

$G^{nn}_{LL'}$ — input for the many-body effective impurity problem

$\phi_L(\vec{r})$ — **“Local”** basis function solution of the Schrödinger equation for spherical LSDA non-magnetic potential

Implementation of LSDA+DMFT using KKR



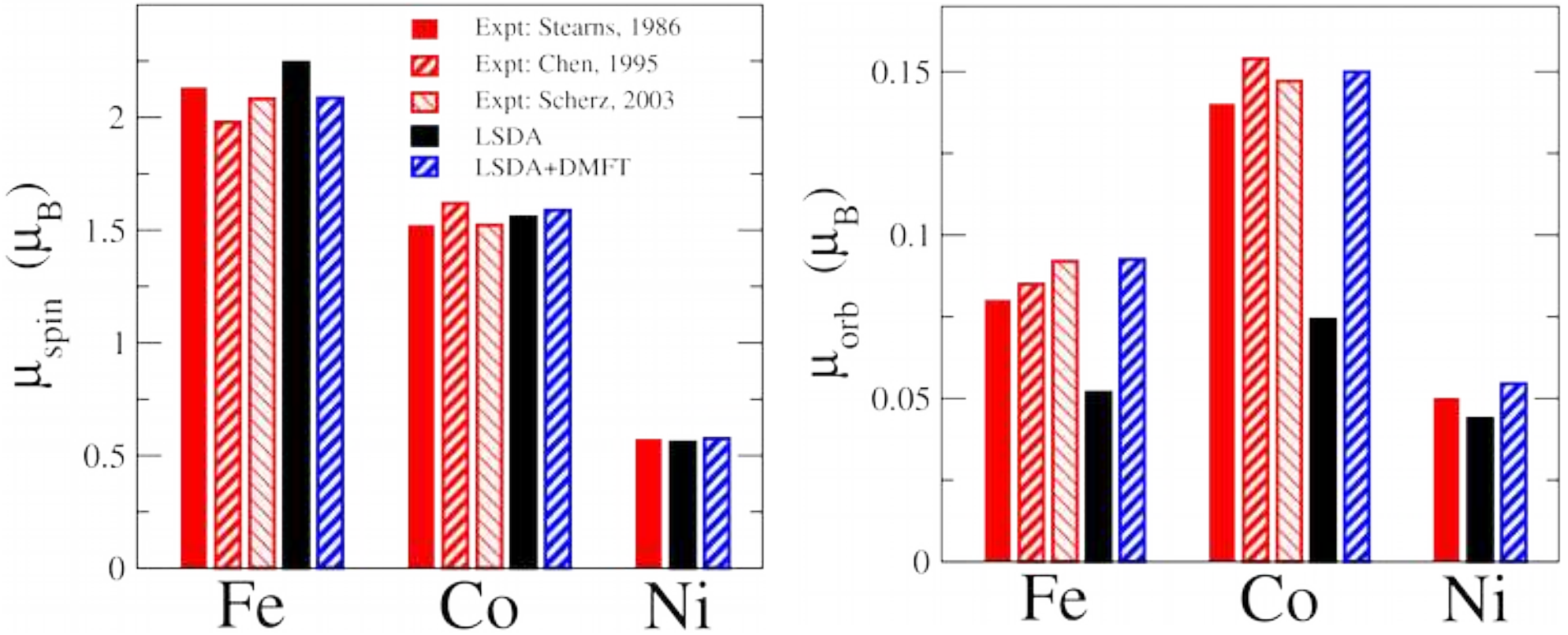
- Fully self-consistent (charge + Σ_{DMFT})
- Fully relativistic (Dirac eq.)
- Σ_{DMFT} solvers:
  SPTF (I. Di Marco el al.)
  ED (I. Di Marco and J. Kolorenc)
  TMA (Chadov et al.)
- Effects of Σ_{DMFT} on wave functions
- Disordered alloys: CPA+DMFT and 2D semi-infinite surfaces
- Spectroscopies + DMFT:
  ARPES, XAS, XMCD,MOKE …

J. Minar, et al, PRB **72**, 045125 (2005),
J. Minar, JPCM Topical review **23,** 253201 (2011)

Magnetic properties of Fe, Co and Ni

Spin magnetic moments

Orbital magnetic moments



Expt: XMCD - Chen et al. (1995), Wende et al. (2003)

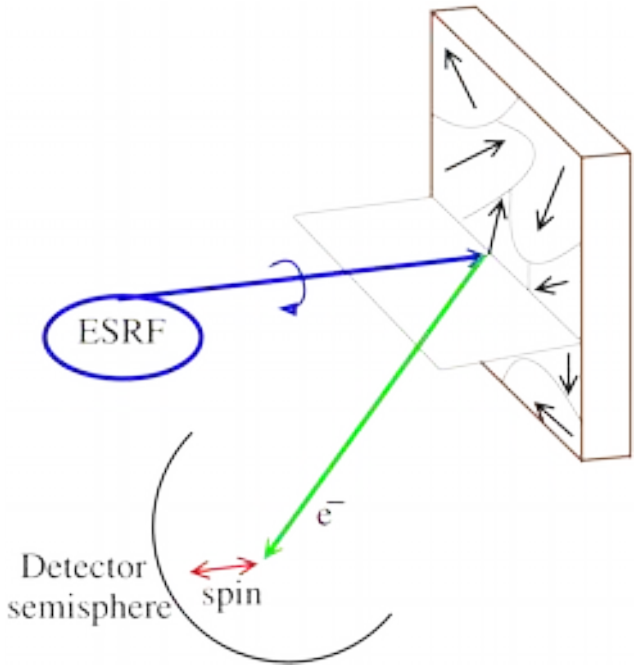
Chadov, Minar et al, EPL **82**, 37001 (2008)
Sipr et al., PRB **84,** 115102 (2011)

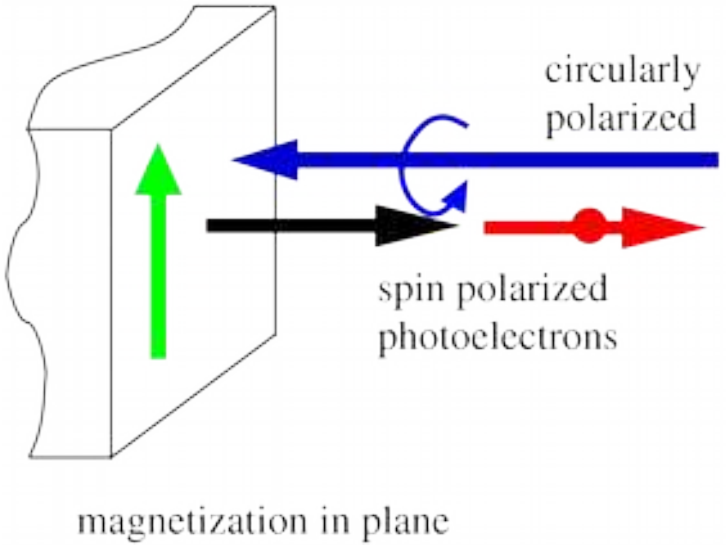
Fano effect in VB-photoemission

Spin polarisation of photo electrons
due to spin-orbit coupling

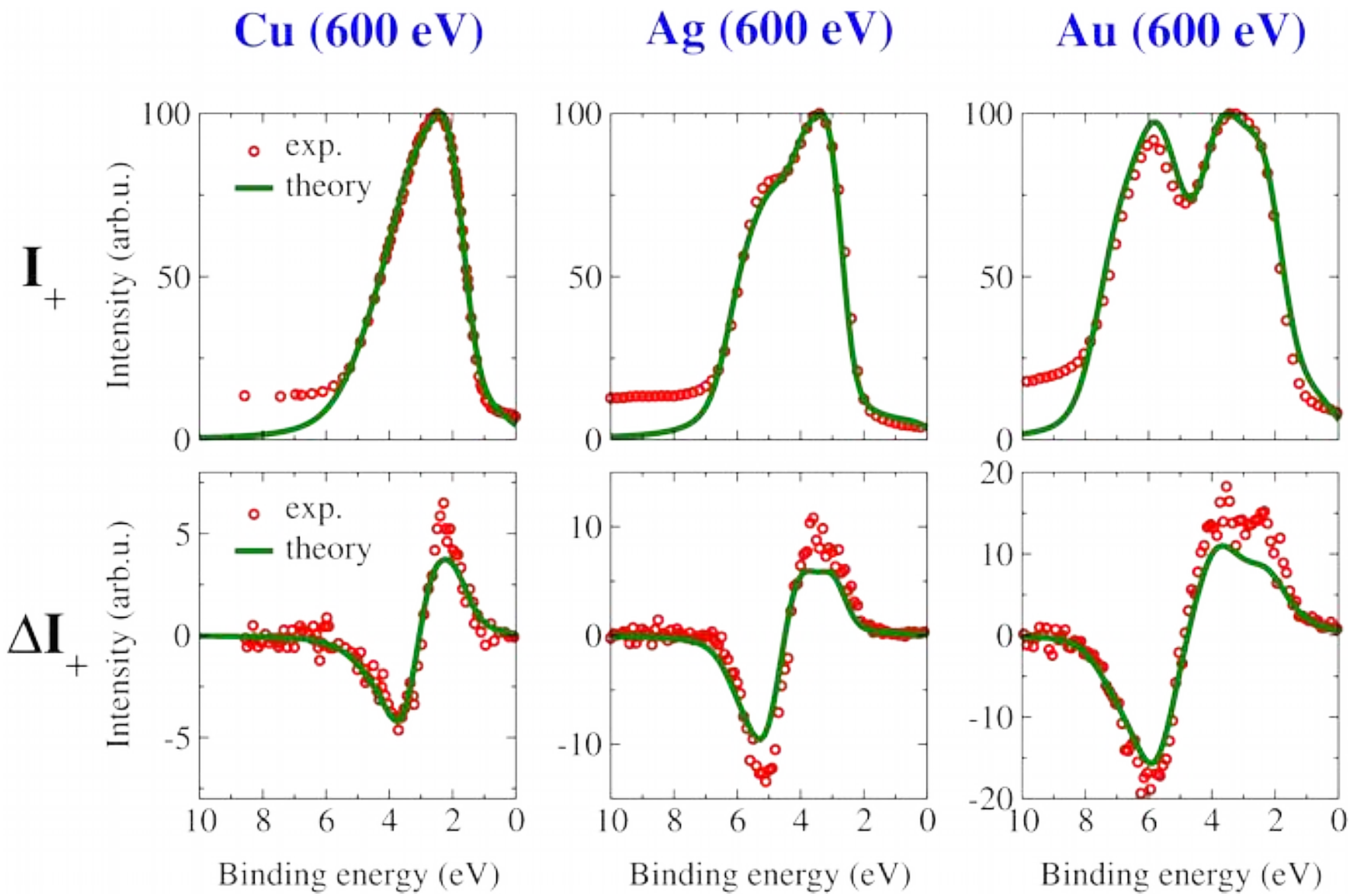
spin-resolved angle-integrated photoemission experiment

ferromagnetic systems





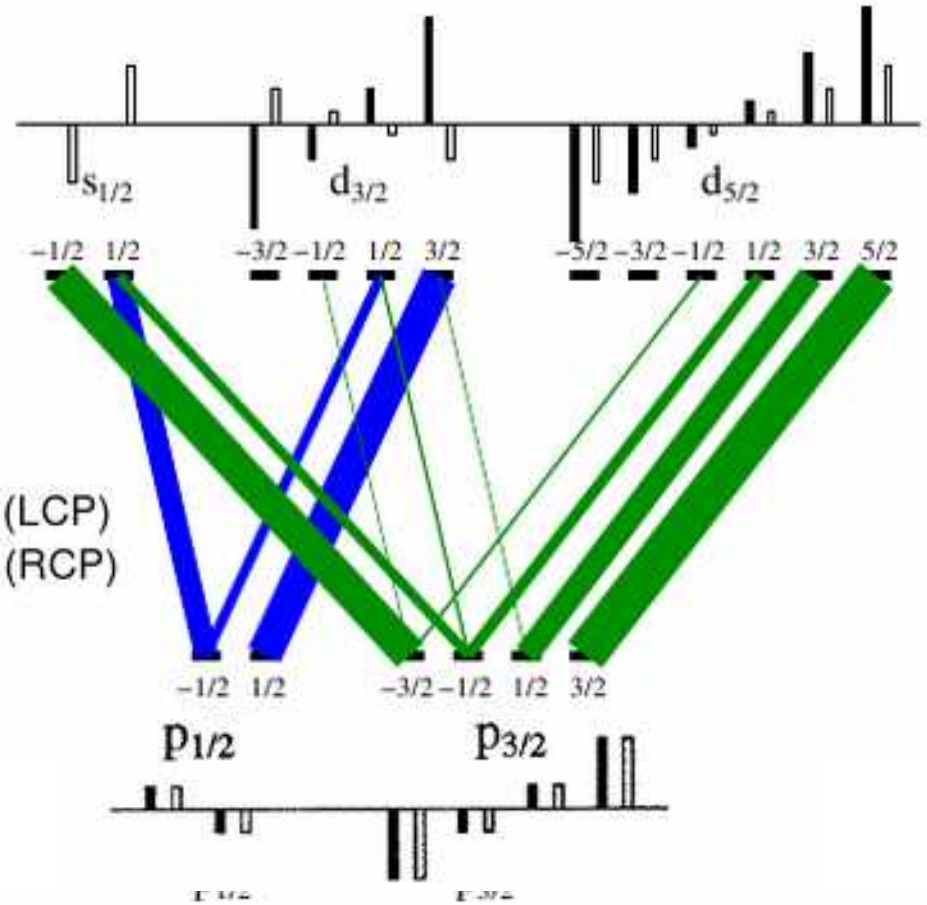
Spin-resolved VB-XPS of Cu, Ag and Au



Origin of the XMCD in magnetic solids

Oscillator strengths due to the angular matrix element

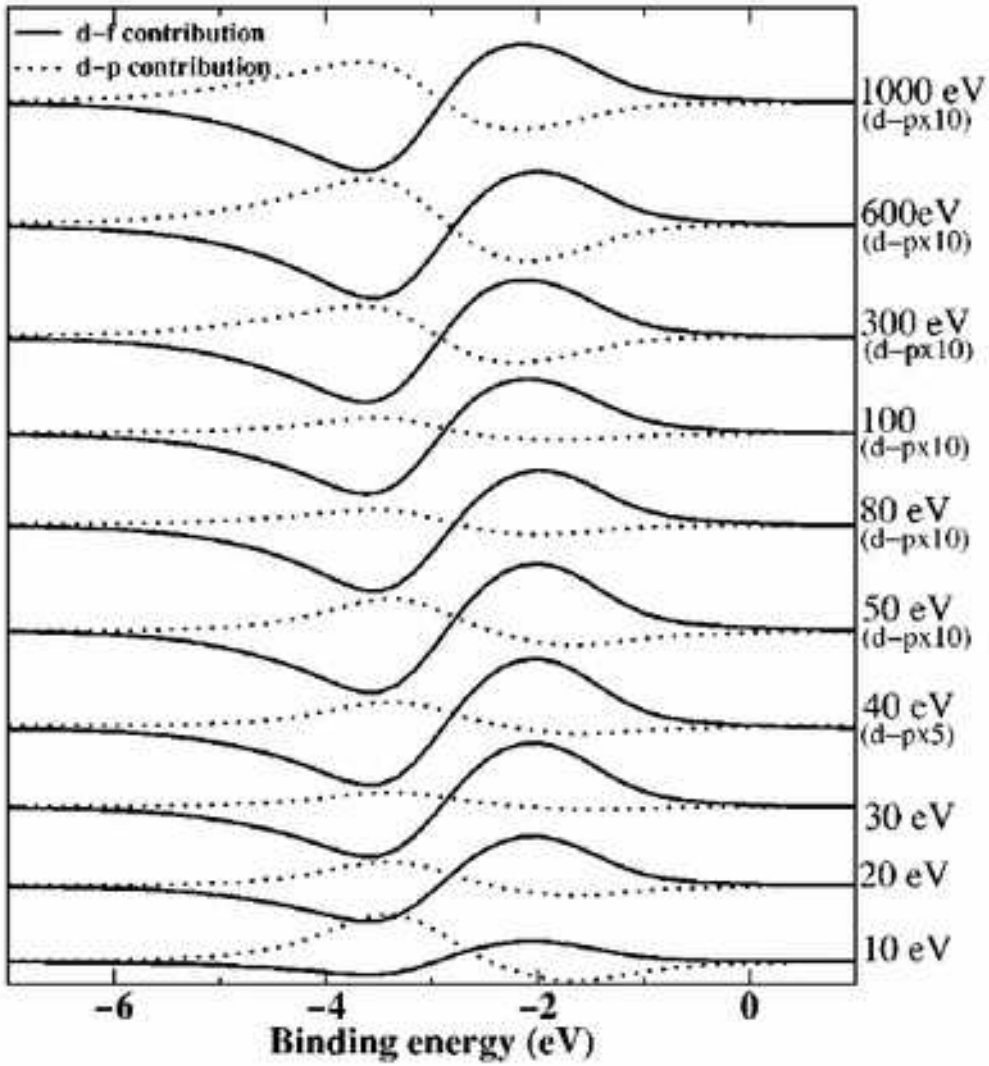
$A^{\lambda}_{\Lambda\Lambda'} = \langle \chi_\Lambda | \hat{r}_\lambda | \chi_{\Lambda'} \rangle$ for left circularly polarised light



$$\mu - \mu_i = \begin{cases} +1 & \text{for } \lambda = +1 \quad \text{(LCP)} \\ -1 & \text{for } \lambda = -1 \quad \text{(RCP)} \end{cases}$$

- light bars: spin matrix element $\langle \chi_\Lambda | \sigma_z | \chi_{\Lambda'} \rangle$
- full bars: orbital matrix elements $\langle \chi_\Lambda | l_z | \chi_{\Lambda'} \rangle$

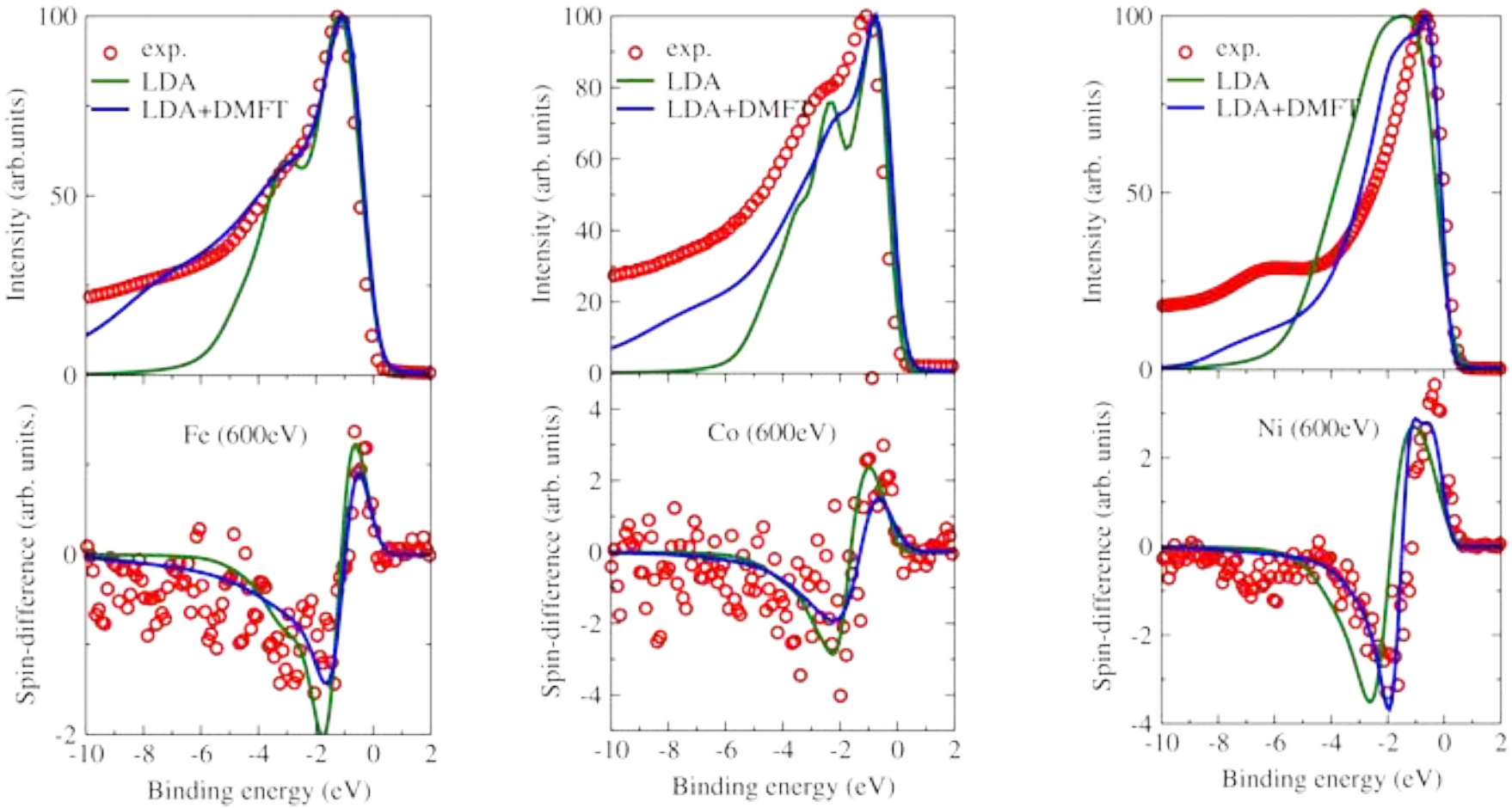
Energy dependence of the matrix elements



Fano effect in VB-XPS of ferromagnets

Photocurrent and spin-difference $E_{phot} = 600$ eV

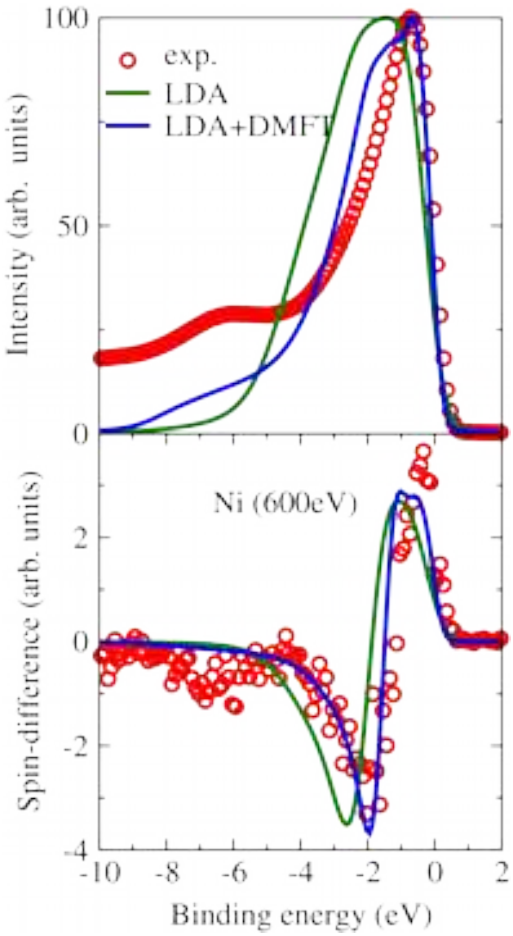
Fe **Co** **Ni**

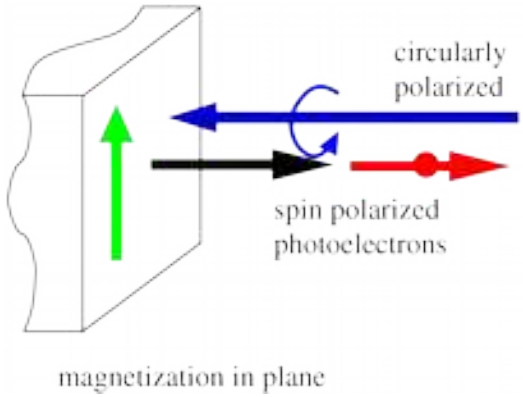


Minár *et al*., PRL **95**, 166401 (2005) - Experiments - N. Brookes *et al*., ESRF

Nickel: Long standing problem

Fano effect
Angle integrated PES



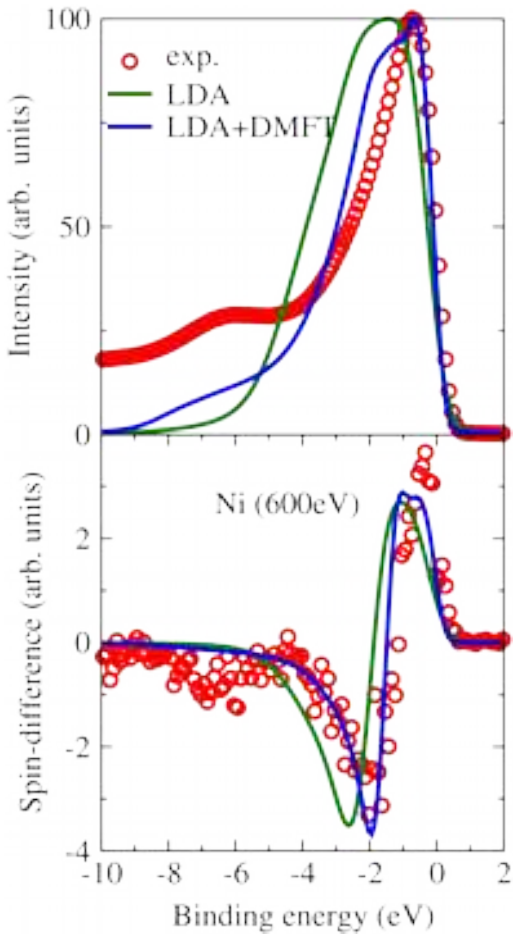


Minar et al,
PRL **95**, 166401 (2005)

U=3.0eV, J=0.9eV

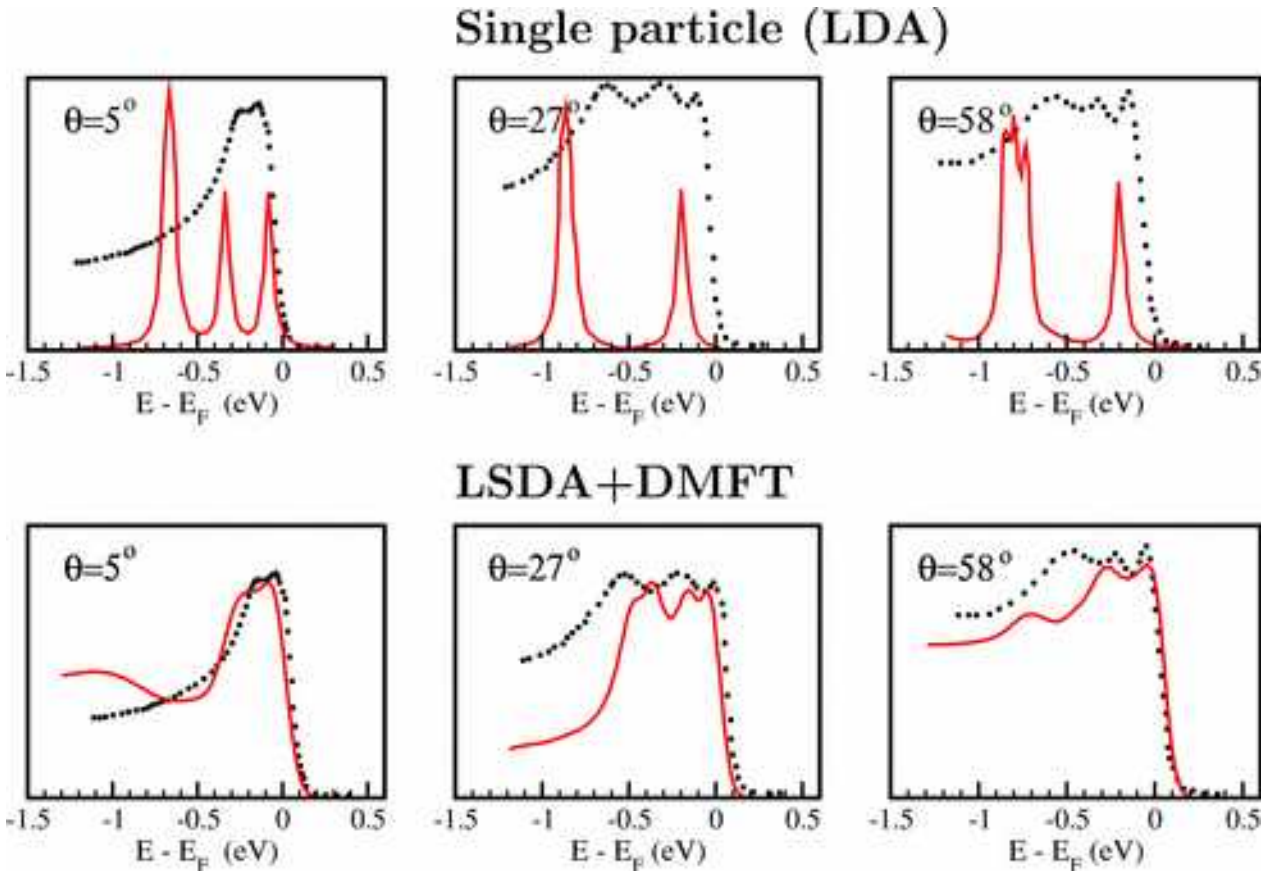
Ni(011): electronic structure and photoemission

Fano effect
Angle integrated PES



Minar et al,
PRL **95**, 166401 (2005)

Comparison between Experiment and theory



J. Braun, J. Minar et al., PRL **97** (2006)

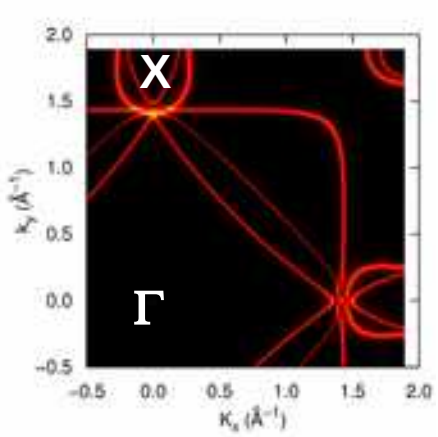
U=3.0eV, J=0.9eV

Exp.: Osterwalder et al

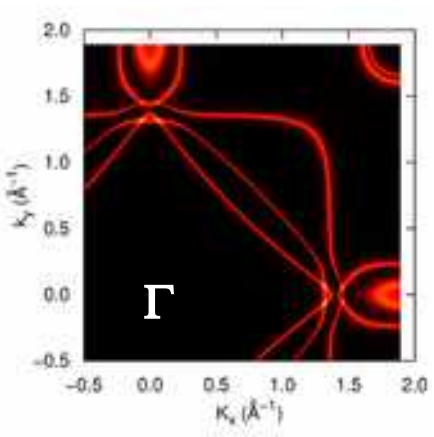
Typical problems of LSDA in case of Ni

Fermi Surface

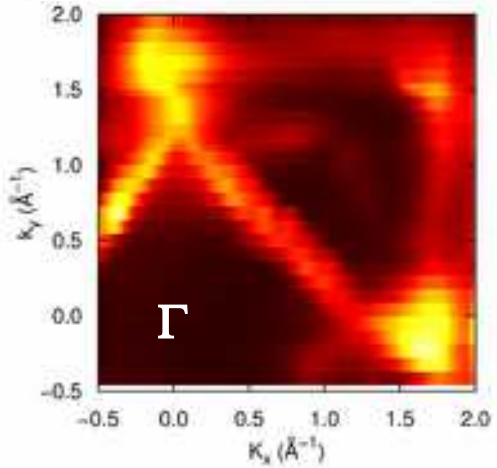
LSDA



LSDA+DMFT

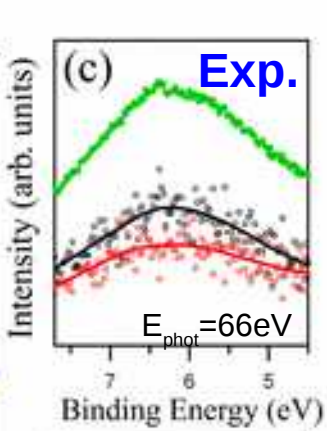


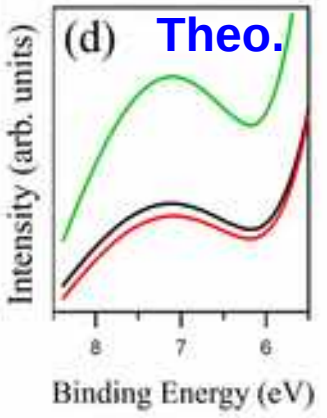
Exp.

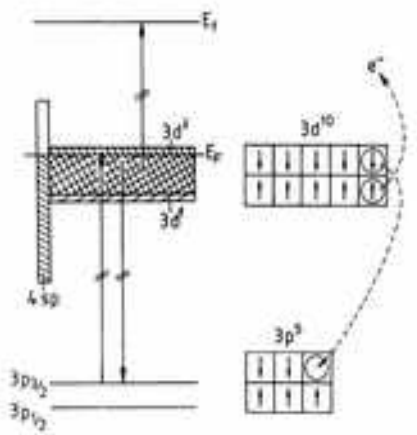


- Electron-hole pocket at X point

6eV satellite in normal emission





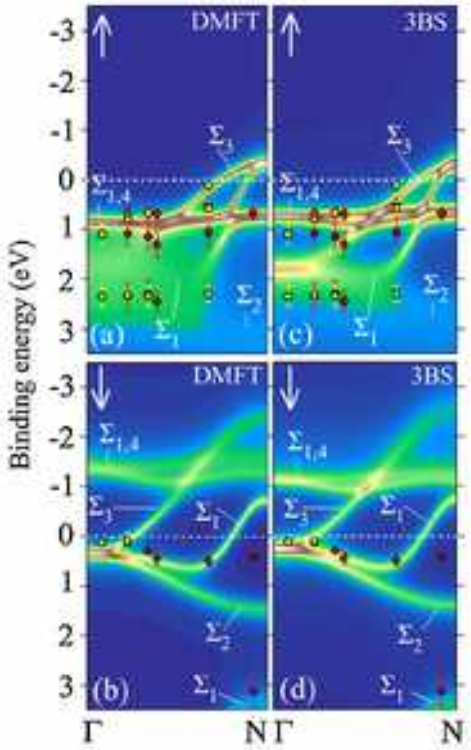


- LSDA+DMFT ==> Spin-polarised satellite
- Hole-Hole interaction

Barriga, Minar et al., PRL **103**, 267203 (2009)
PRB **82,** 104414**,** PRB **85**, 205109 (2012),

Electronic structure and ARUPS of Fe(110)

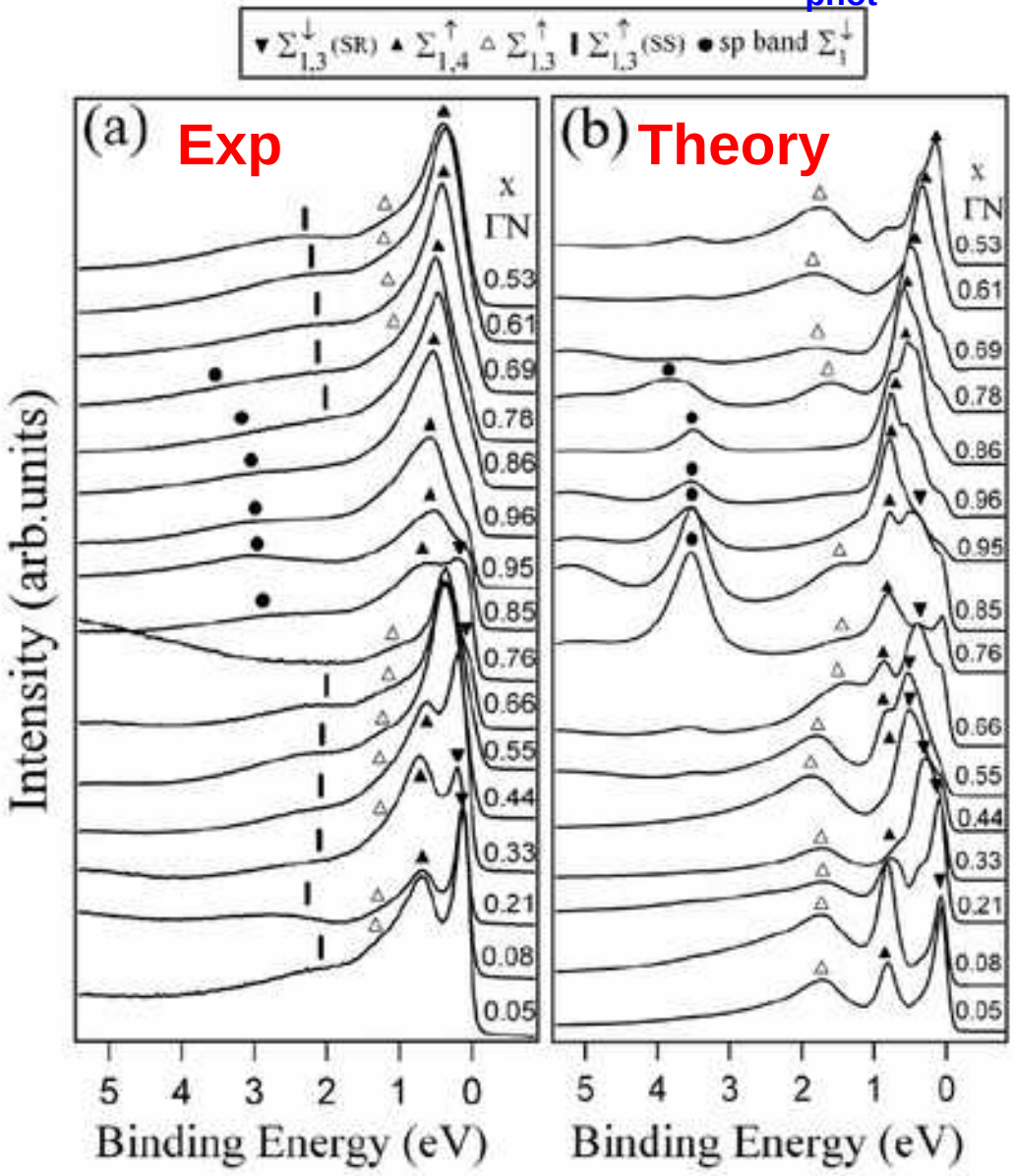
Bloch spectral functions



- U=1.5eV, J=0.9eV
- Agreement between

  3BS (F. Manghi) and DMFT
- Tamm resonance (close to E_F)
- Quantitative agreement for complete BZ along ΓN

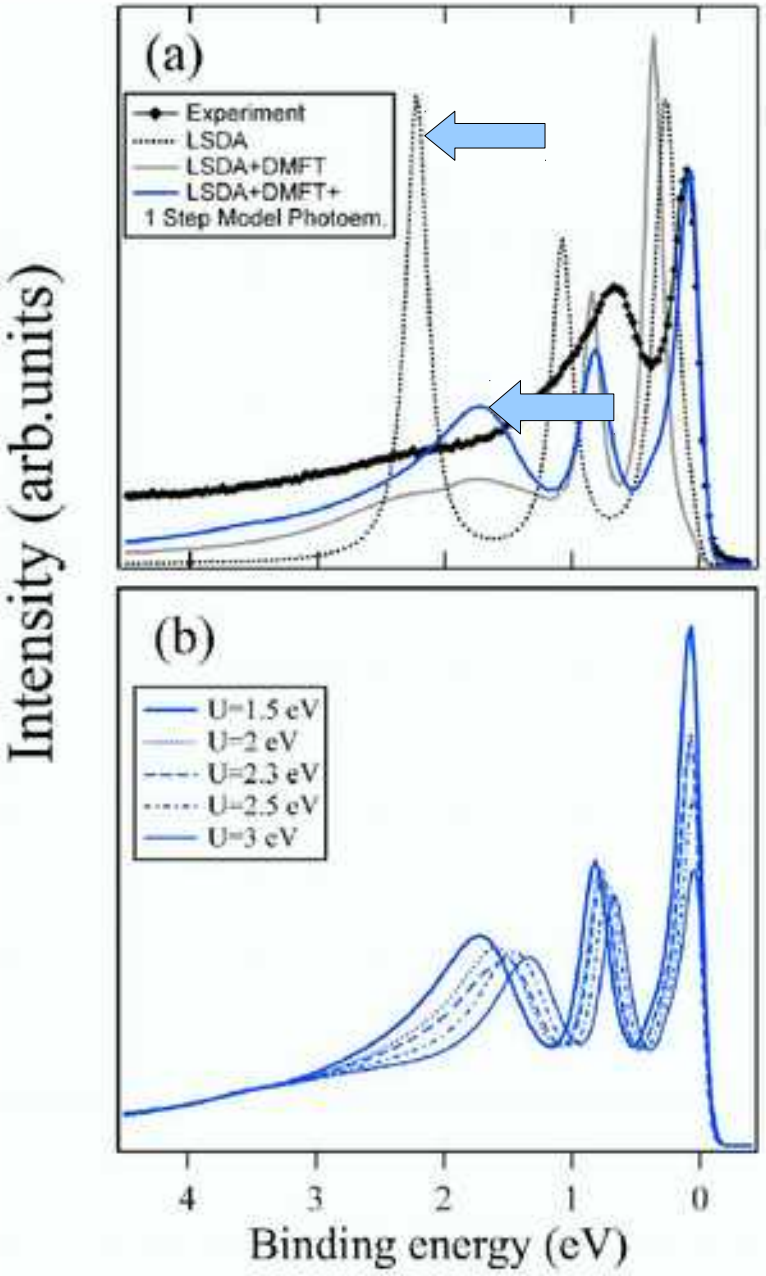
Normal emission along ΓN (E_{phot}=26-80eV)



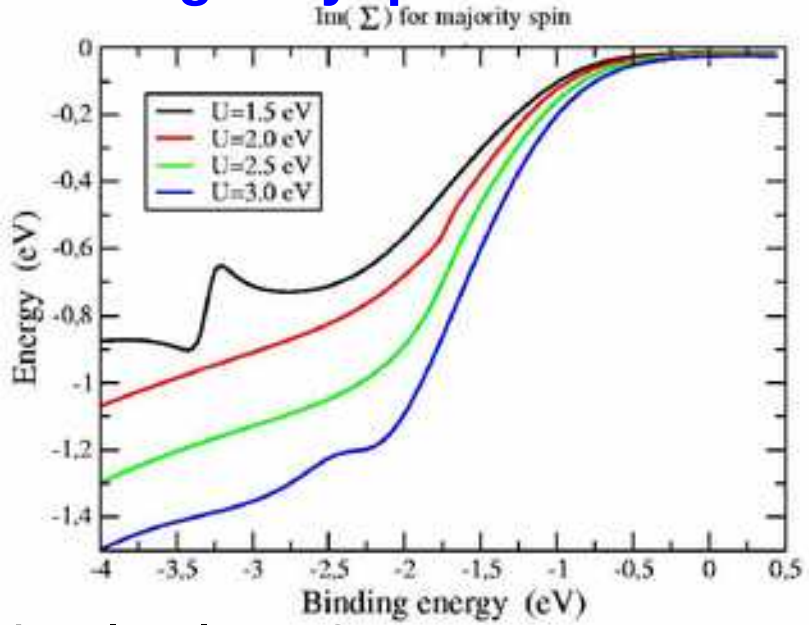
J.S. Barriga, Minar et al. PRL 103, 267203 (2009)

Electronic structure and ARUPS of Fe(110)

Spin-integrated spectra at Γ point



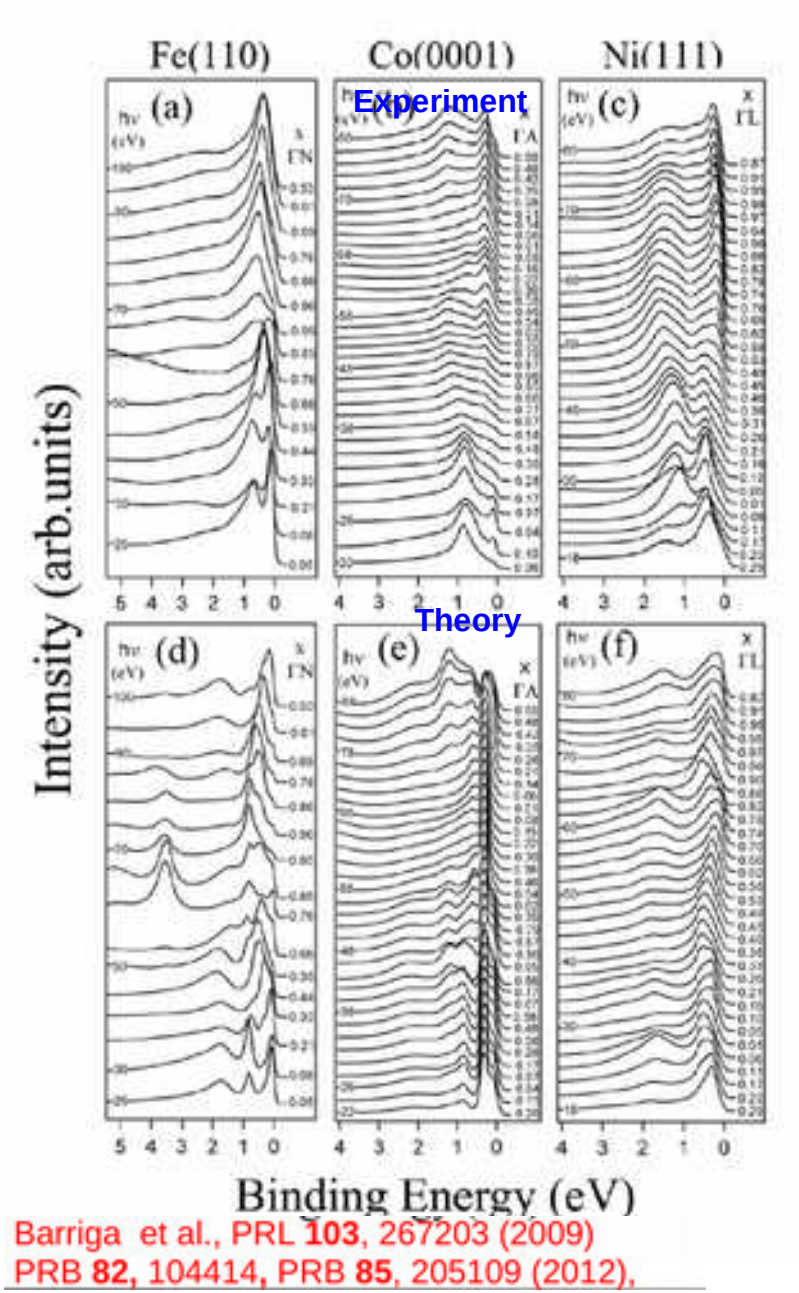
Imaginary part of self energy

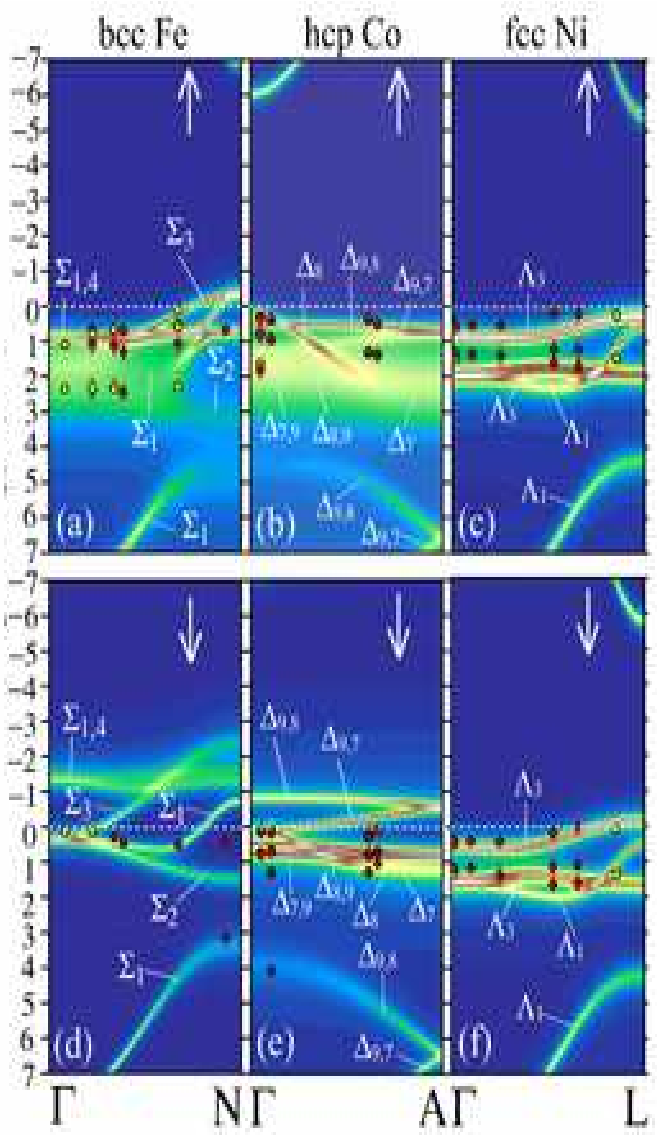


- Optimal value of U=1.5 eV J=0.9 eV
- Even with very high exp. Resolution – broad spectrum
- Physical mechanism: electron-hole decay
- Non-local correlations important for Fe
  - Improved non-local theories

J.S. Barriga et al. PRL 103, 267203 (2009)

Spin integrated spectra for Fe, Co and Ni





Barriga et al., PRL **103**, 267203 (2009)
PRB **82**, 104414, PRB **85**, 205109 (2012),

Fe Co Ni

Averaged U

Non-local correlations

- LSDA+DMFT: improved description of spectroscopic data from 3d-ferromagnets
- Normal emission, p-pol light
- U_{Fe}= 1.5 eV, U_{co}= 2.5 eV, U_{ni}= 2.8 eV
- Need for non-local correlations

Why is LDA+DMFT useful for one-step model

$$A_{m,m'}(E_n)\,\frac{2}{\hbar}\sum_s \; <\Psi_N^0|\mathrm{a}_m^\dagger|\Psi_{N-1}^s>\delta(E_N-E_{N-1}-\hbar\omega)<\Psi_{N-1}^s|\mathrm{a}_{m'}|\Psi_N^0>$$

LDA+DMFT
Single site approach

Correlation effects of "ground state"

Ψ_0^N

Simulation of excited state

Ψ_S^{N-1}

See e.g. 6eV Satellite in Ni

Outline

Angle resolved photoemission

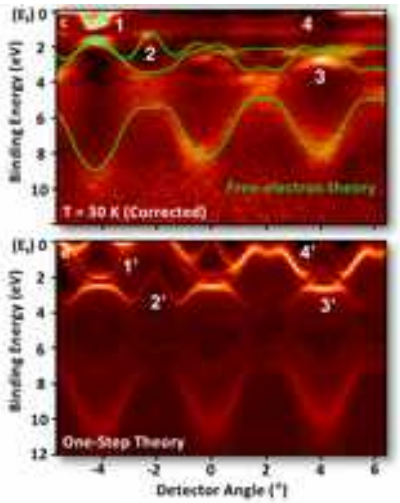
↓ First interpretation

Three step model

↓ Many body physics

One step model → Direct comparison between Theory ↔ Experiment

↓

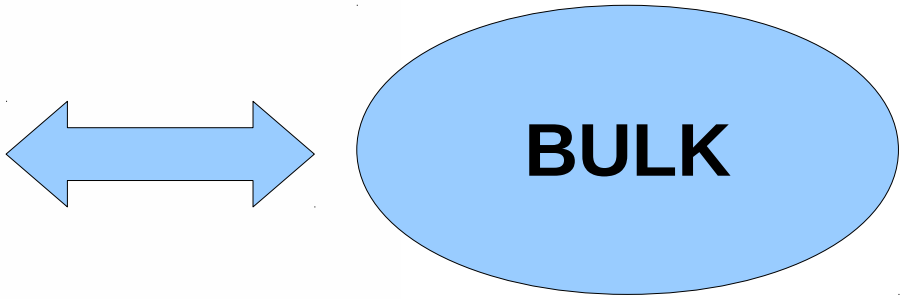


Surface states | **Correlation effects** | **Bulk sensitive ARPES**

Bulk sensitivity is it useful?

Correlated electron materials have unusual properties

- huge resistivity changes
- gigantic volume anomalies
- colossal magnetoresistance
- high-T_c superconductivity
- metallic behavior at interfaces of insulators



With potential for technological applications:

- sensors, switches, Mottronics
- spintronics
- thermoelectrics
- high-T_c superconductors
- functional materials: oxide heterostructures ...

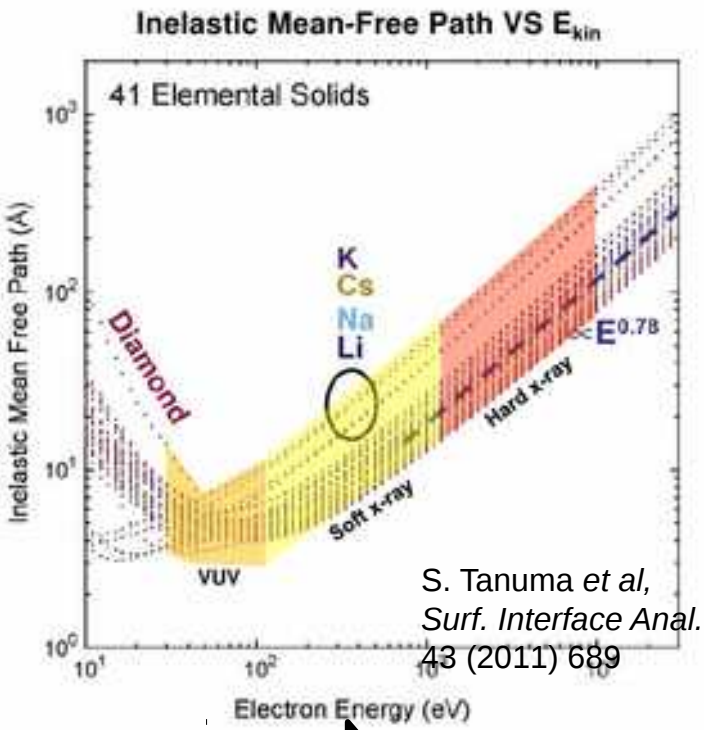
How to study correlated systems theoretically?

Reproduced from D. Vollhardt

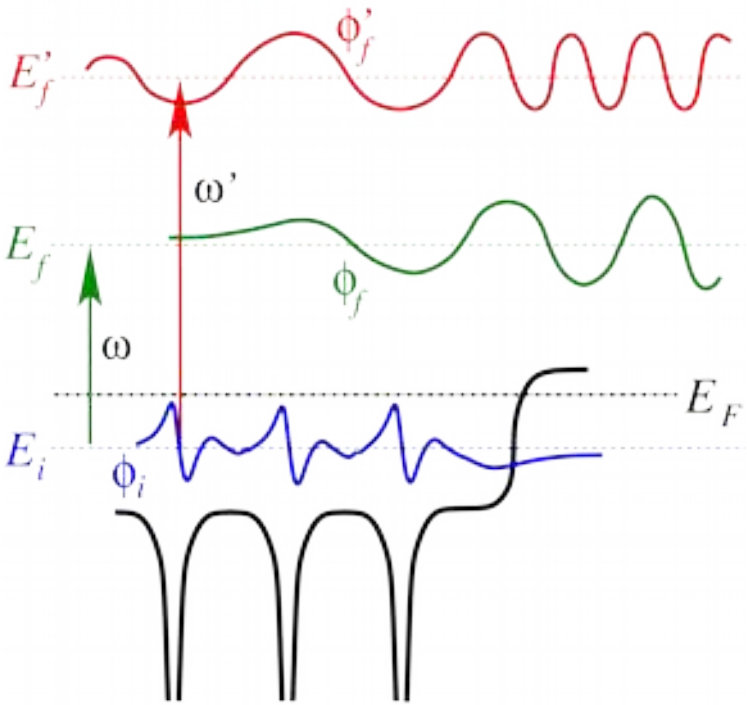
High energy photo emission - HAXPES

- Photoemission with soft and hard X-rays

enhanced bulk sensitivity



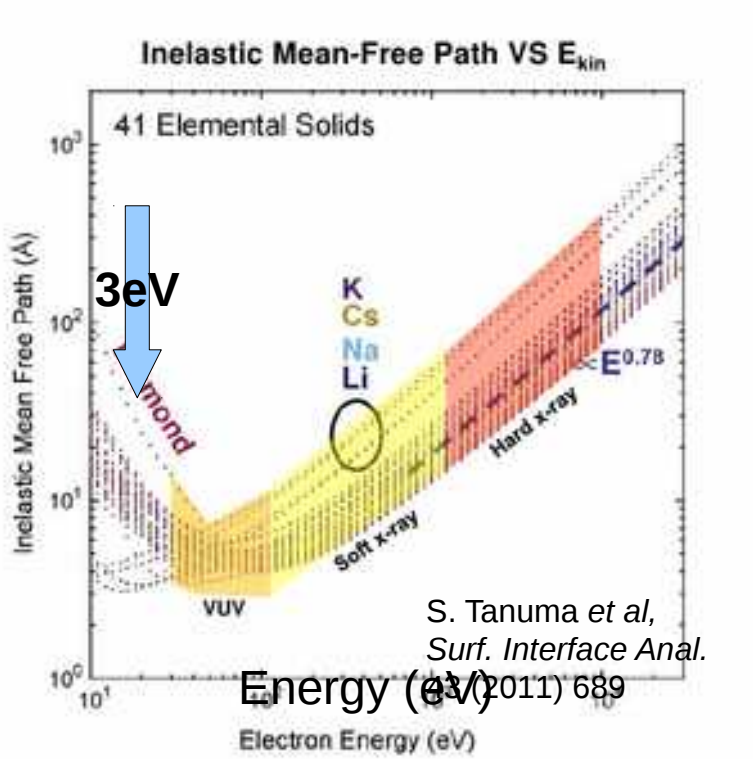
S. Tanuma *et al*, *Surf. Interface Anal.* 43 (2011) 689



- **Important aspects**
  - thermal vibrations
  - band mapping: free electron like final state?
  - photon momentum, sample tilt
  - recoil effects

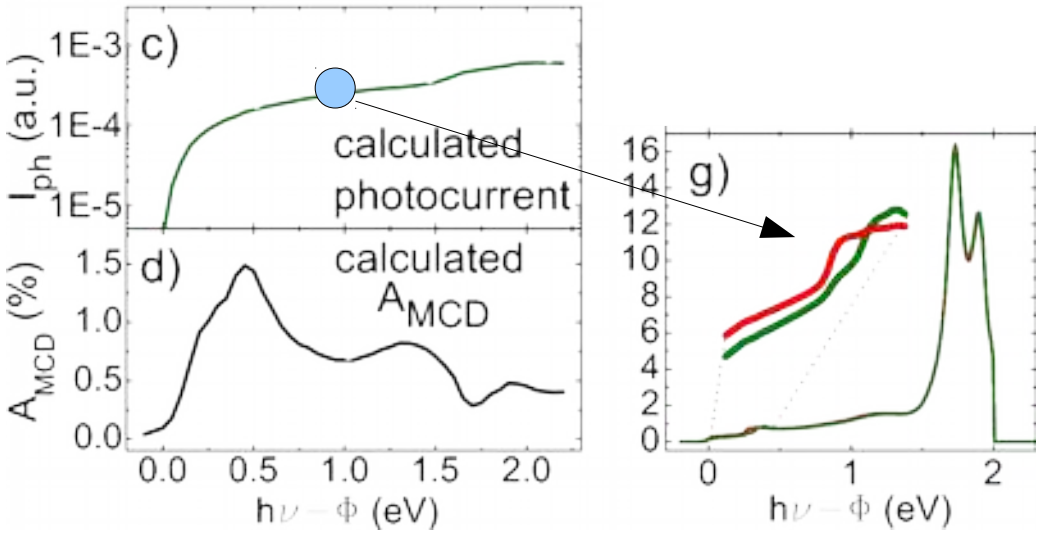
Threshold and Hard-X-ray PES: Bulk sensitivity?

Mean free path



S. Tanuma *et al*, *Surf. Interface Anal.* 43 (2011) 689

Magnetic circular dichroism: Ni thin films on Cu(001)



Kronseder et al, PRB 83, 132404 (2011)

- Photon energy of 3 eV
- LSDA+DMFT calculations

LSDA+DMFT Surface spin polarization of Co2MnSi (E= 5.9 eV)

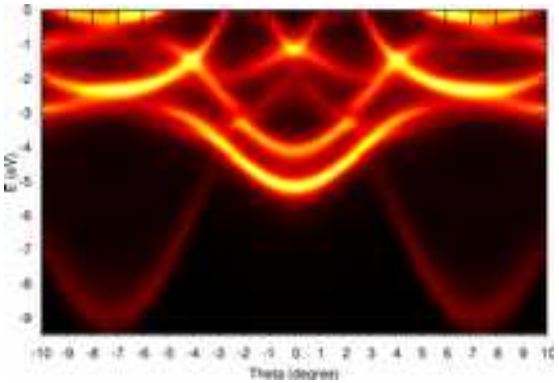
Wüstenberg et al, PRB 85, 064407 (2012)

- Photoemission with visible laser light (use of PEEM)
- Hope enhanced bulk sensitivity?

Surface sensitivity for high photon energies

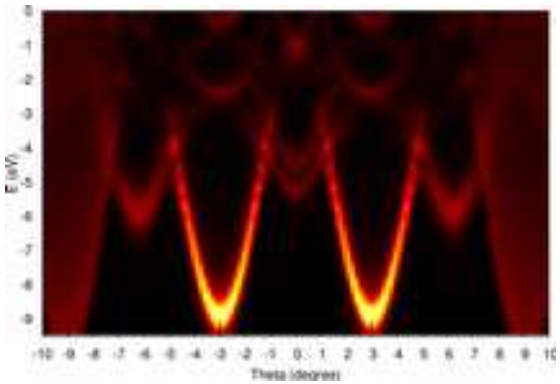
calculated ARPES intensities $I(E, \Theta)$

Fe(001)



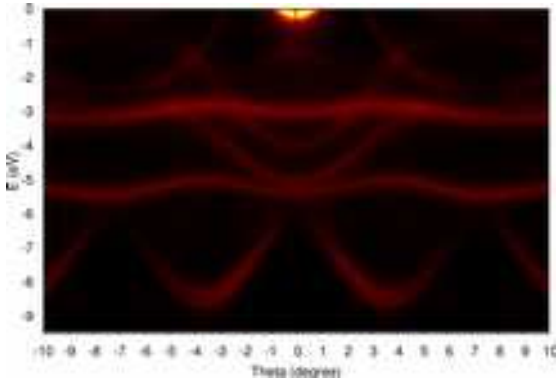
$E_{\text{phot}} = 1000$ eV

Fe(001)

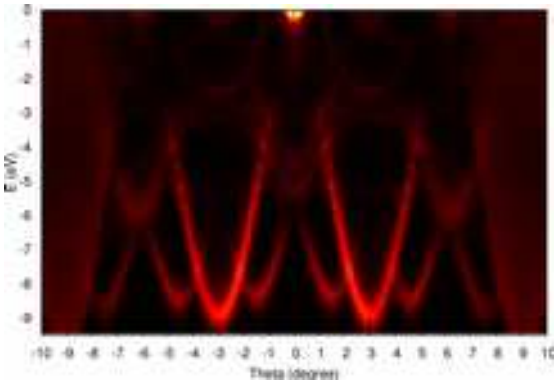


$E_{\text{phot}} = 6000$ eV

8 ML MgO/Fe(001)



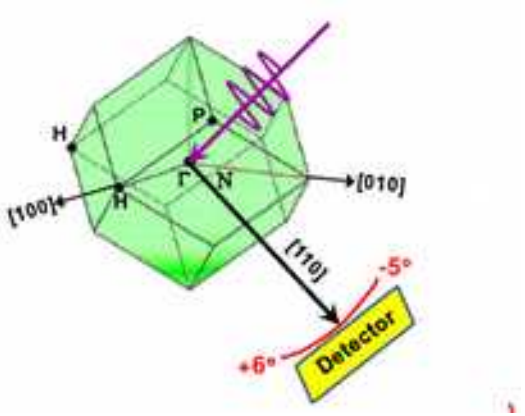
8 ML MgO/Fe(001)

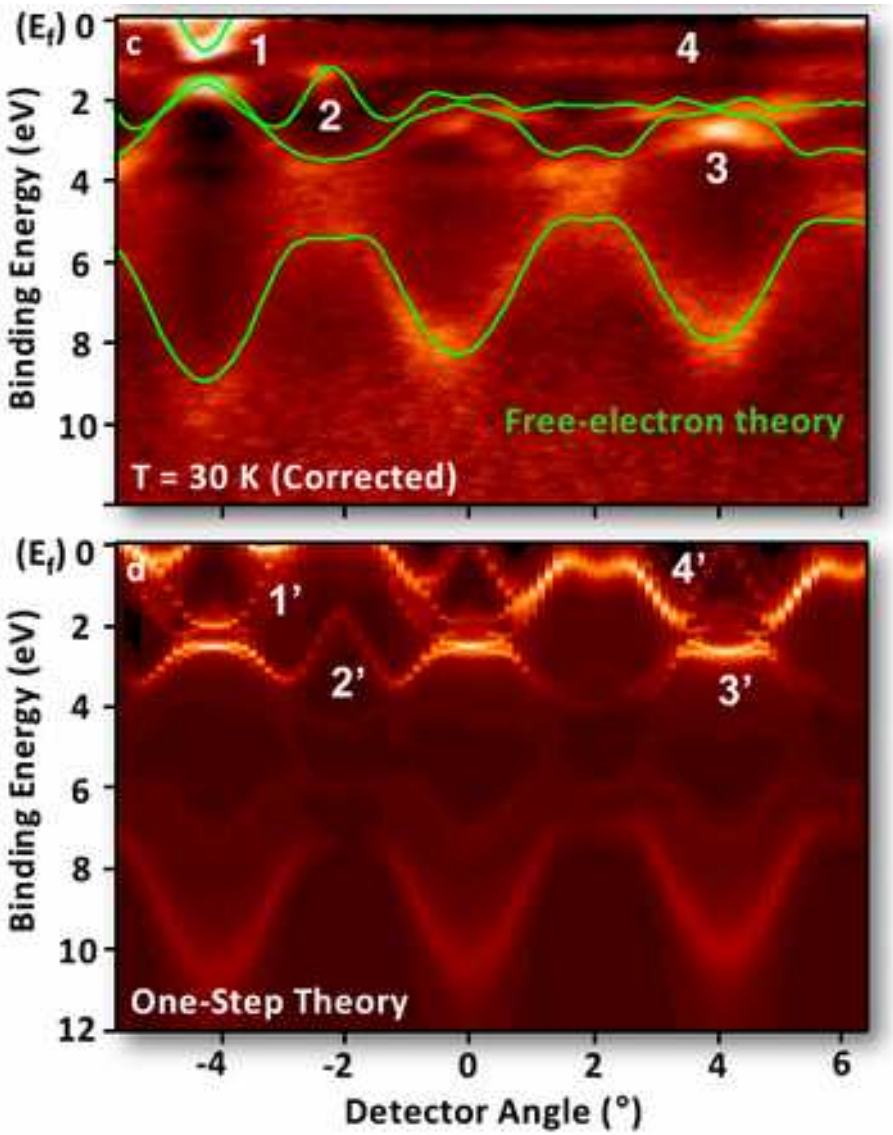


$\Rightarrow$ Fe-related features recovered for high photon energies
access to burried interfaces

Minar et al., JESRP 184, 91 (2011)

Angle resolved HAXPES of W(110) at 5954eV



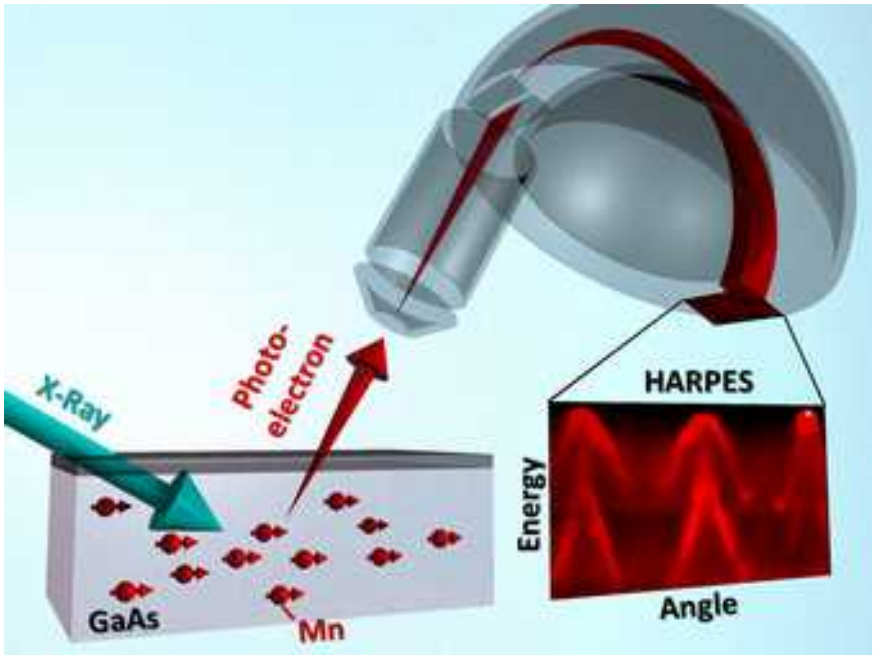


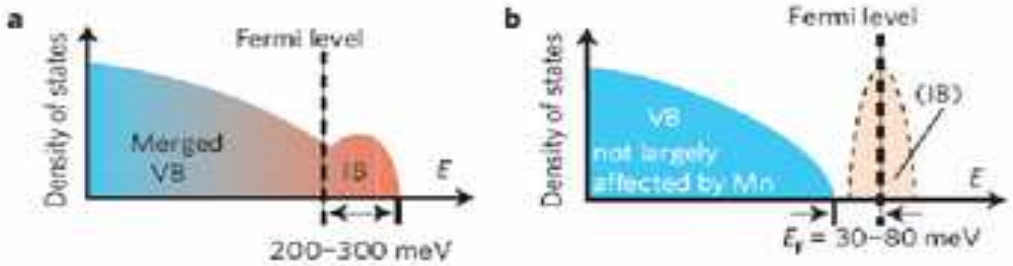
Experiment

Theory

A. Gray, J. Minar, Ch. Fadley et al,, Nature Materials, **10**, 1038/nmat3089 (2011)
(Nat. Mat.: News and Views : D. Feng, Photoemission spectroscopy: deep into the bulk)

HAXPES on technologically relevant materials: Mn doped GaAs





S. Ohya et al., Nature Physics 7, 342 (2011)

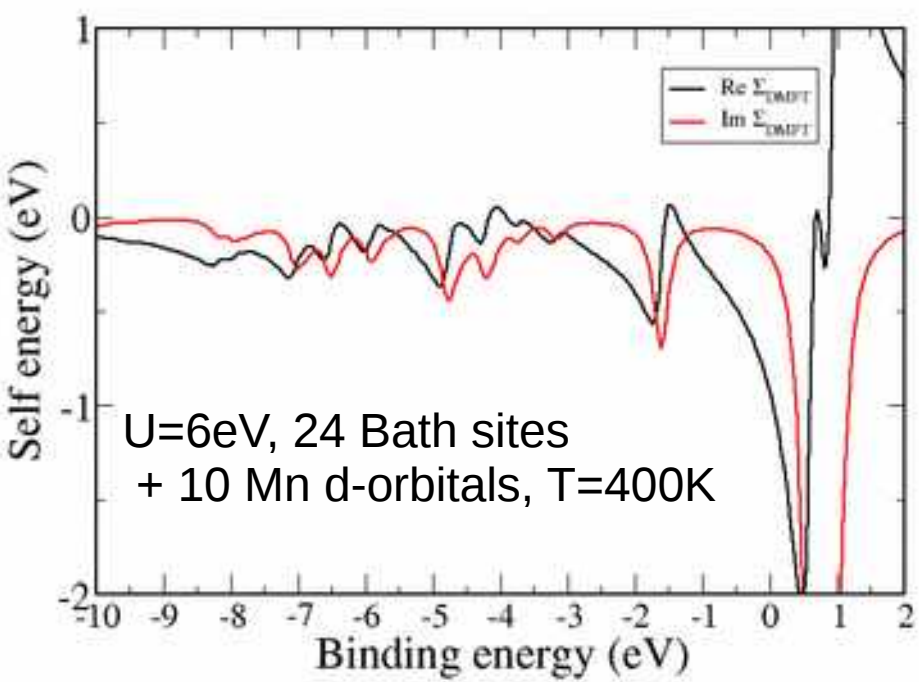
Until recently there were missing reliable photoemission measurements:

Surface sensitivity ⟷ Sample preparation with well defined surface → New technique: HAXPES

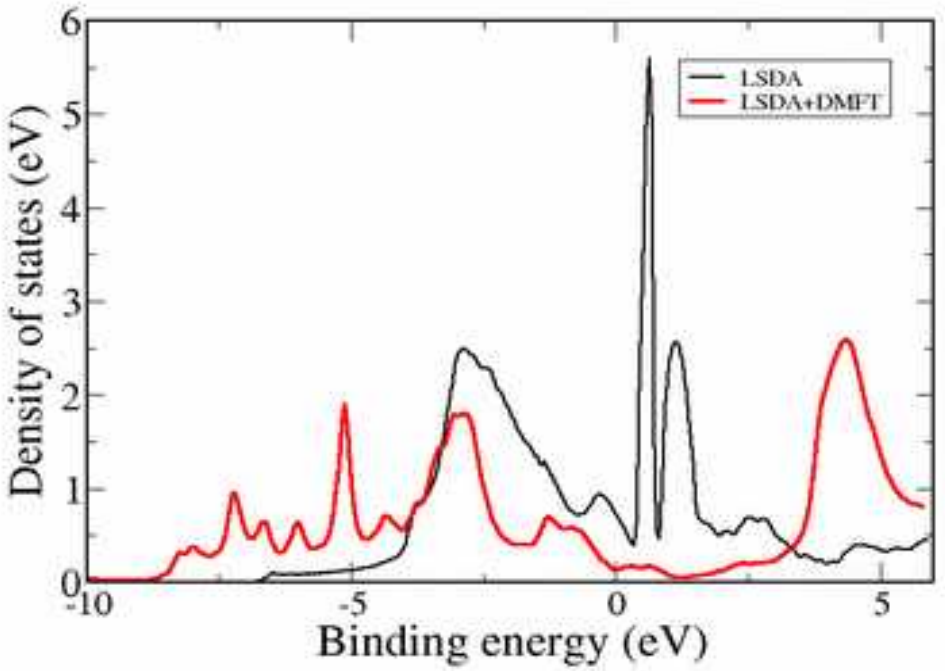
Correlation effects in $Ga_{0.87}Mn_{0.13}As$

Is the standard DFT-LDA approach suitable for this material?

Exact diagonalisation self energy



Density of states



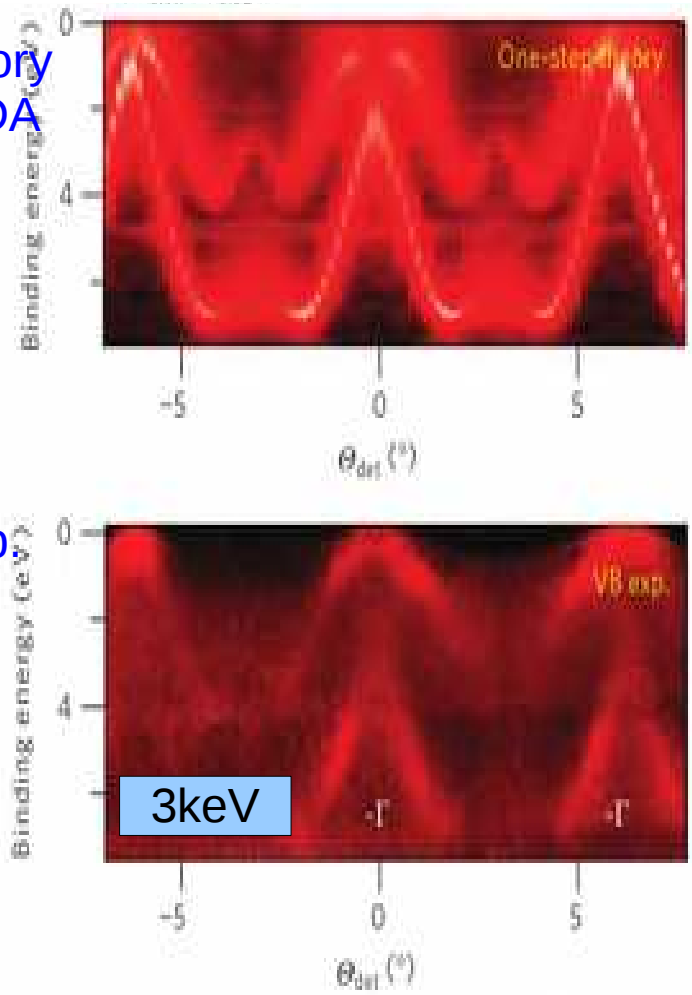
- Exact diagonalisation
  DMFT solver implemented within KKR in combination with CPA
- LSDA+DMFT improved description of the states at higher binding energies
- Local correlations, hybridisation with GaAs states and disorder treated on same level
- Satellite like features at higher binding energies
  (see Di Marco et al., Nat. Comm. 4, 2645 (2013))

HAXPES of GaMnAs

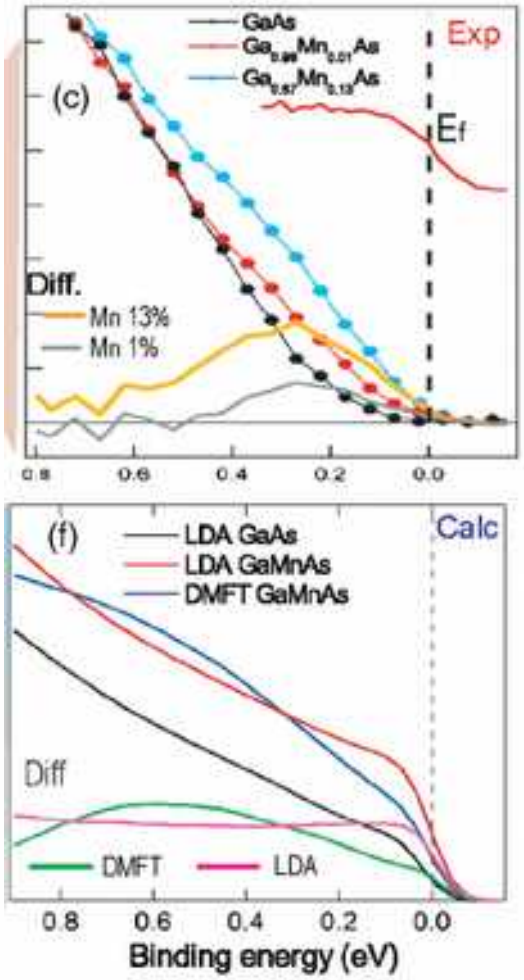
Angle resolved HAXPES of $Ga_{0.97}Mn_{0.03}As$

Theory LSDA

Exp.



Angle integrated HAXPES at 6keV

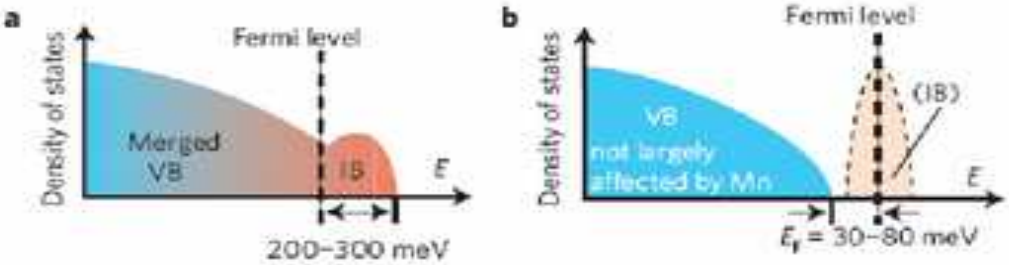


- Mn d-states merged with GaAs derived states
- Maximum at about 250 meV
- LSDA shows Mn states directly at Fermi level
- There is a need to include correlations effects within LSDA+DMFT

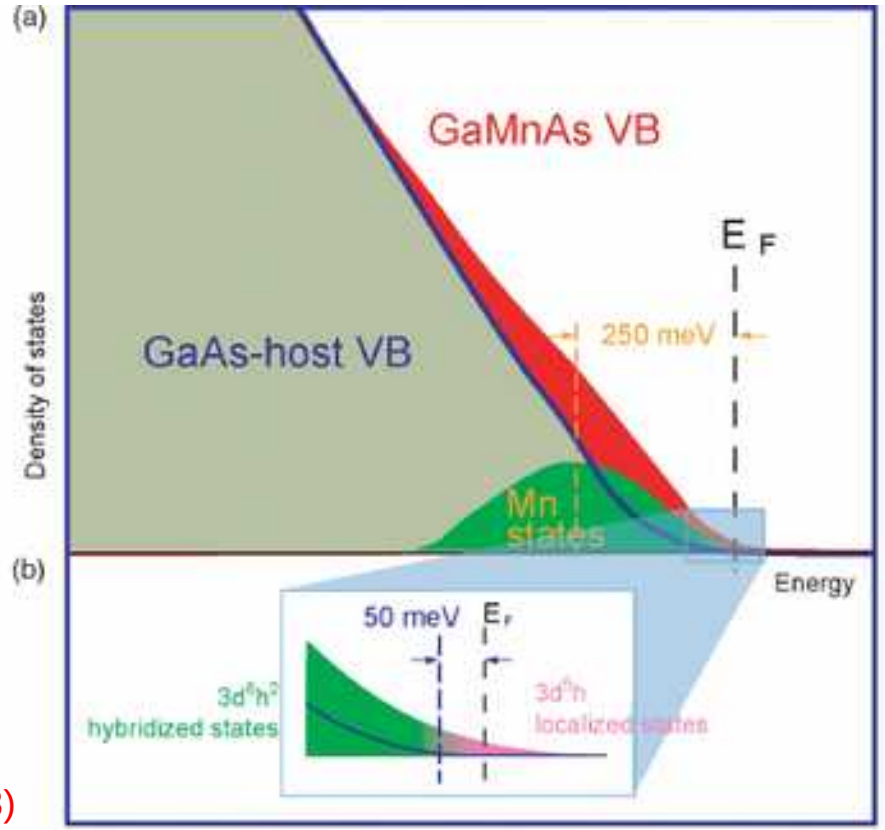
A. Gray, J. Minar et al., Nat. Mat. **11**, 957 (2012)

J. Fujii et al., PRL **111**, 097201, (2013)

HAXPES on technologically relevant materials: Mn doped GaAs



S. Ohya et al., Nature Physics 7, 342 (2011)



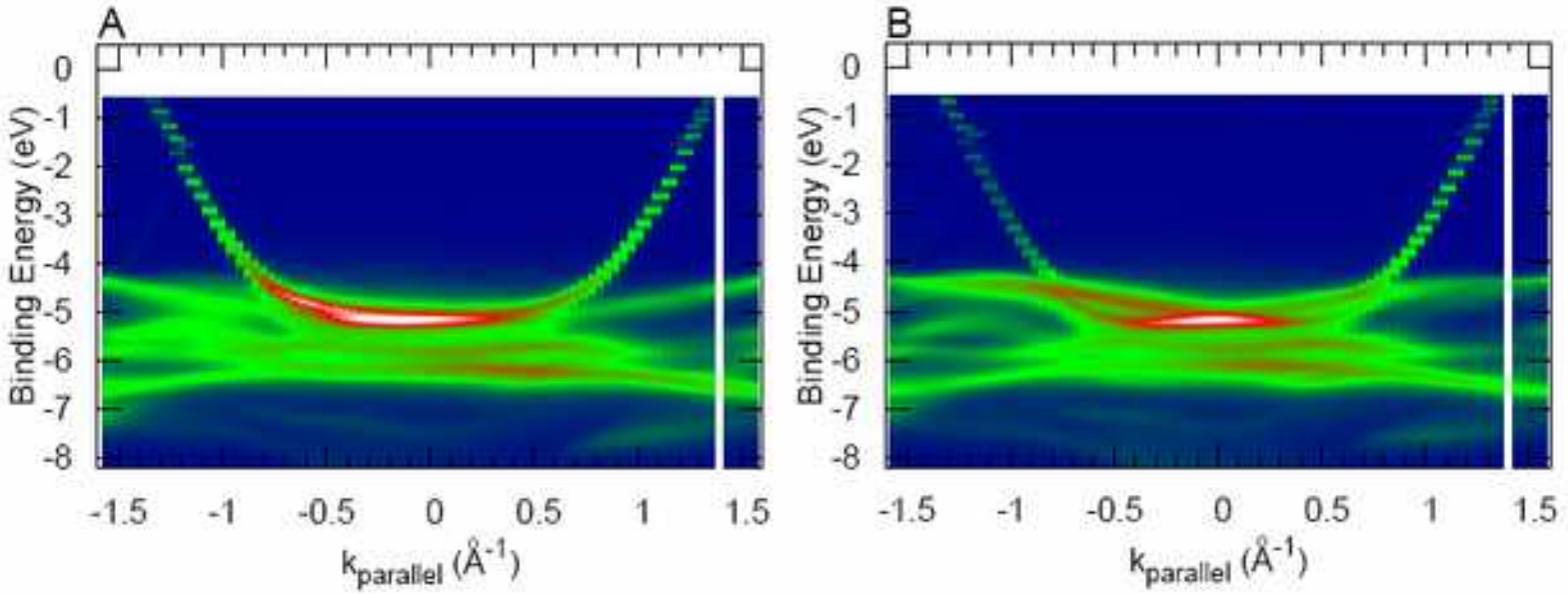
J. Fujii et al., PRL **111**, 097201, (2013)

A. Gray, J. Minar et al., Nat. Mat. **11**, 957 (2012)

Photon momentum
Band mapping
matrix elements and k-dependence

Photon momentum effects on Ag(001)

Ag(001) photoemission intensities along ΓK with LCP-light at hν=552 eV



$\mathbf{q}_{\text{photon}}$ ignored

$$\mathbf{k}_i = (\mathbf{k}_{||} + \mathbf{g}, \sqrt{2(E - iV_{i1}) - |\mathbf{k}_{||} + \mathbf{g}|^2})$$

$$\mathbf{k}_f = (\mathbf{k}_{||} + \mathbf{g}, \sqrt{2(E + \omega - iV_{i2}) - |\mathbf{k}_{||} + \mathbf{g}|^2})$$

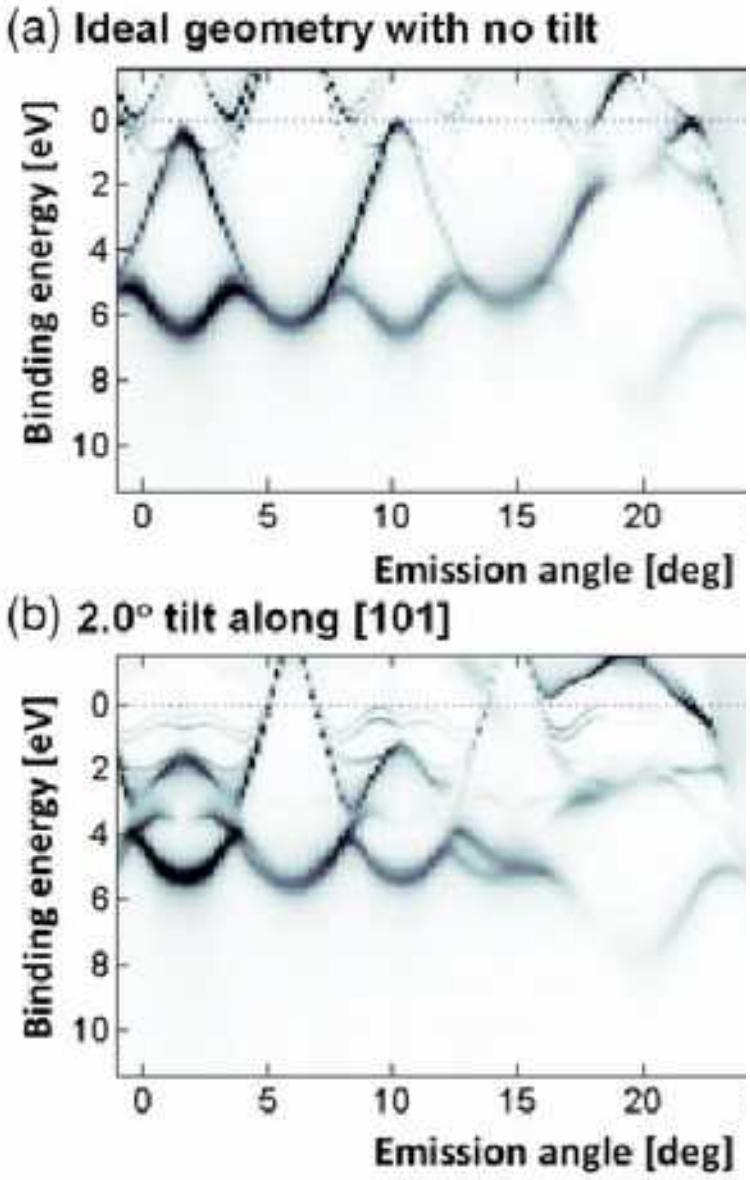
$\mathbf{q}_{\text{photon}}$ included

$$\mathbf{k}_i = (\mathbf{k}_{||} - \mathbf{q}_{||} + \mathbf{g}, \sqrt{2(E - iV_{i1}) - |\mathbf{k}_{||} - \mathbf{q}_{||} + \mathbf{g}|^2})$$

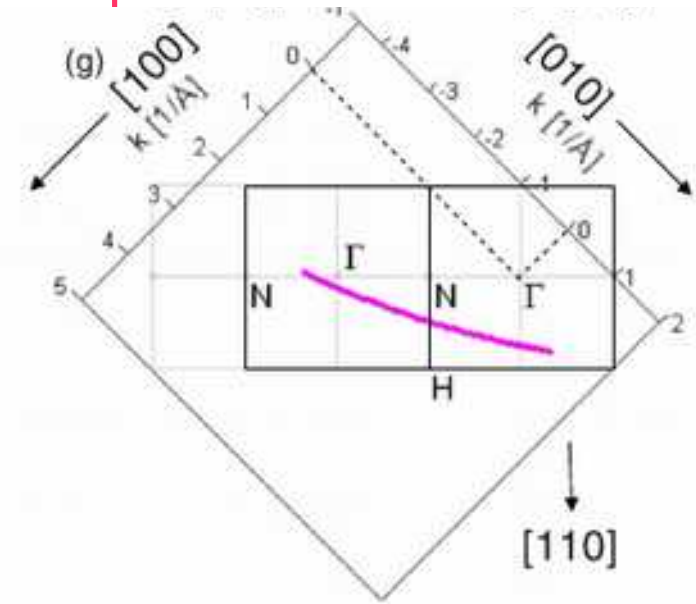
$$\mathbf{k}_f = (\mathbf{k}_{||} + \mathbf{g}, \sqrt{2(E + \omega - iV_{i2}) - |\mathbf{k}_{||} + \mathbf{g}|^2})$$

Venturini et al. PRB **77**, 045126 (2008)

Effect of sample tilt: ARPES of W(110)



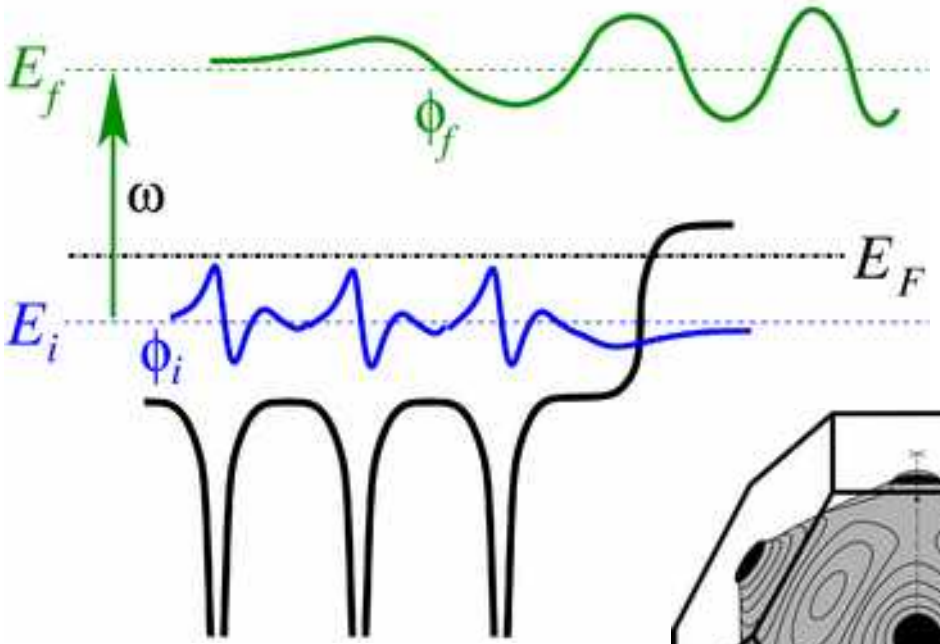
- ARPES of W(110) at 1.25keV
- Laboratory source
- Tilt: normal emission not parallel to the surface normal
- Even small tilt can lead to pronounced deviations in spectra



C. Papp, J. Minar et al. PRB **84**, 045433 (2011)

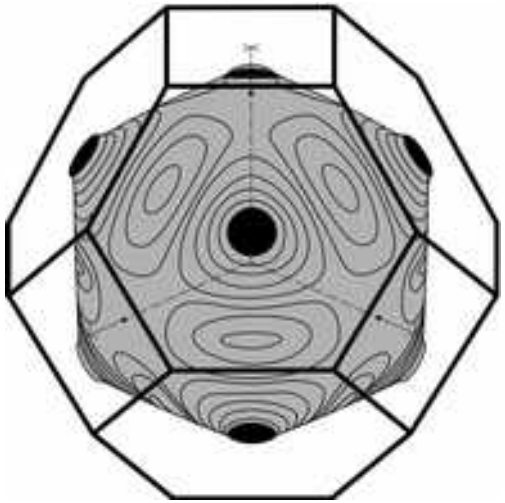
k-perpendicular (k_z-scan)

$\Delta z \sim \lambda$

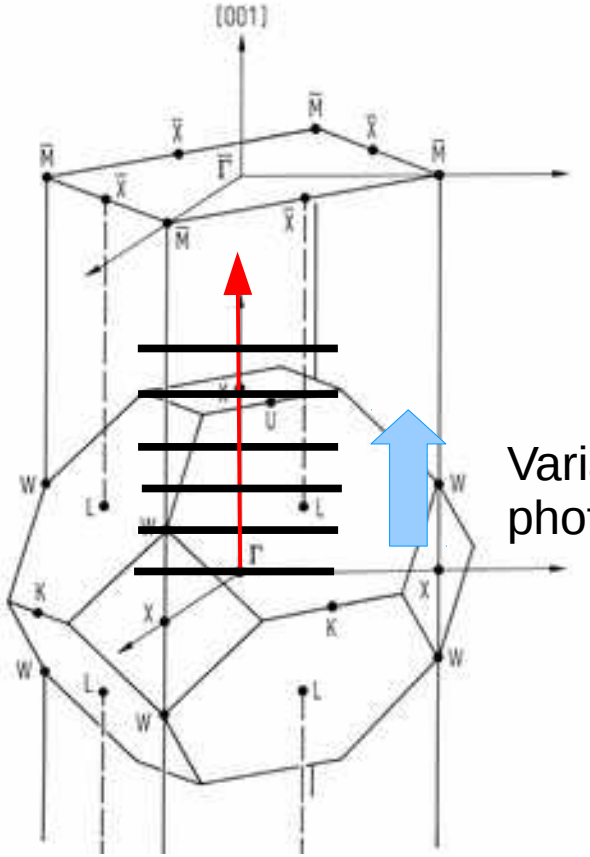


$\Delta k_z \sim \lambda^{-1}$

- reduction of kz broadening
- sharply defined 3D k-vector



Fermi surface of Ag



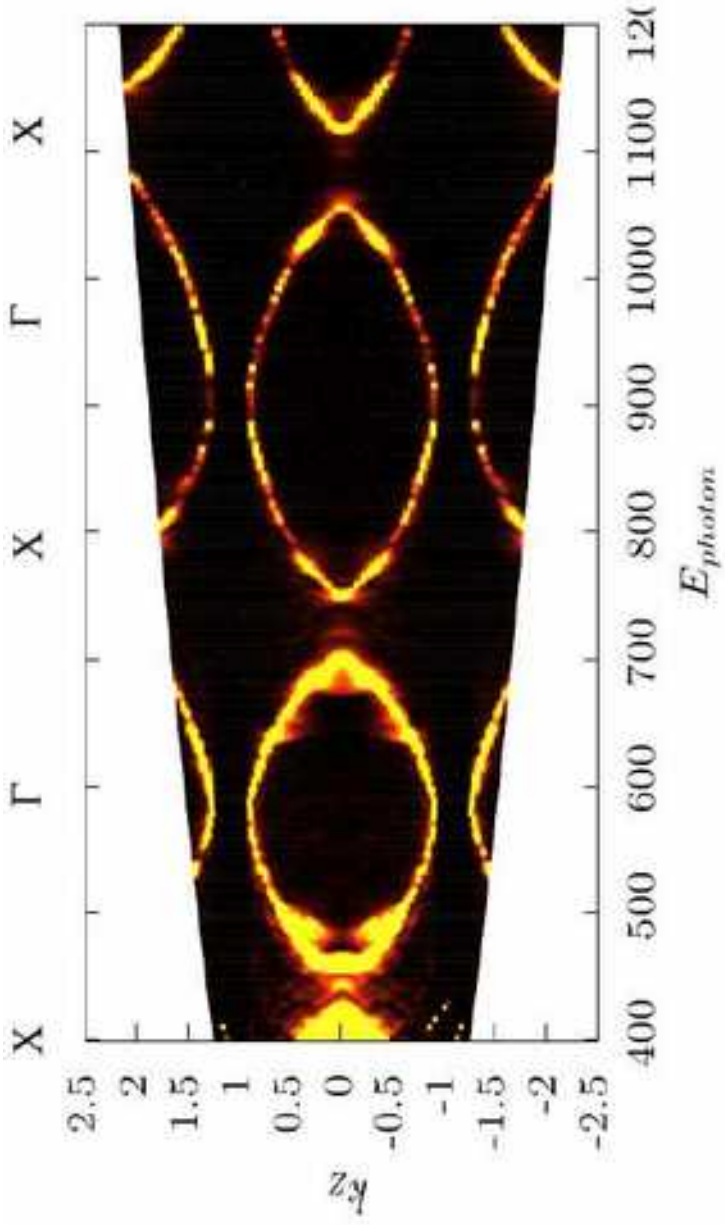
Variation of photon energy

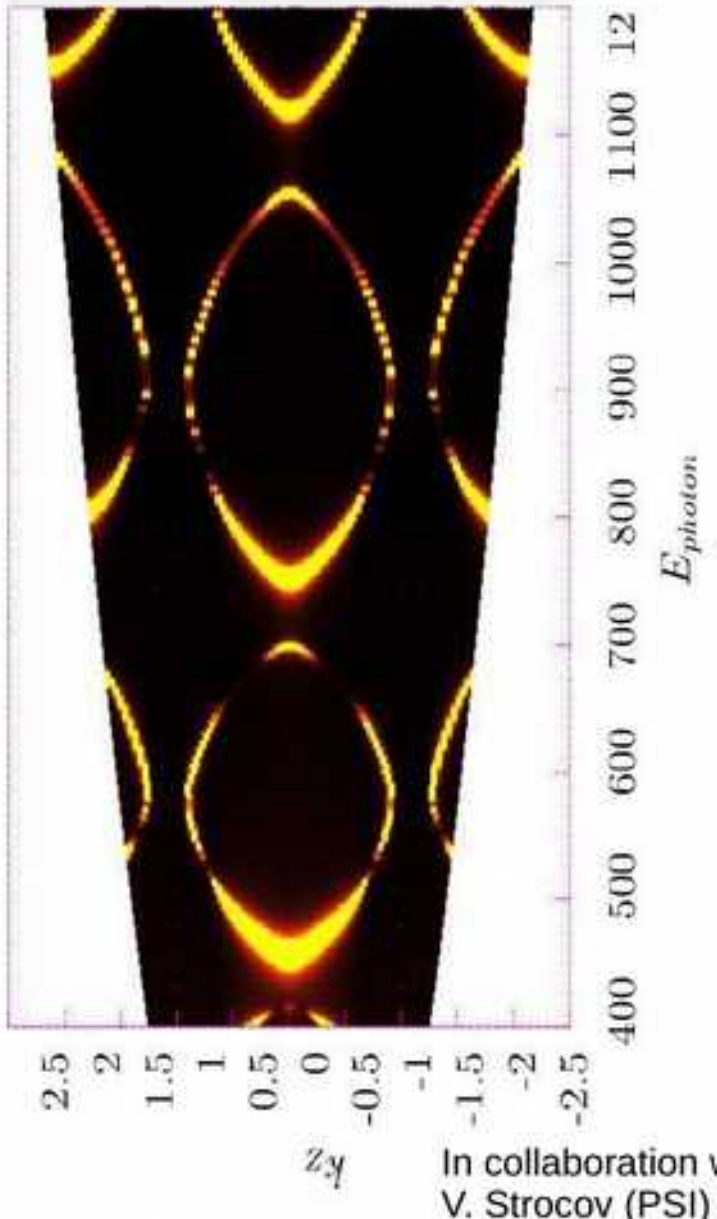
k_z-scan for Ag(001) and final state effects

Experiment

Theory: TR-LEED state

Free electron like final state





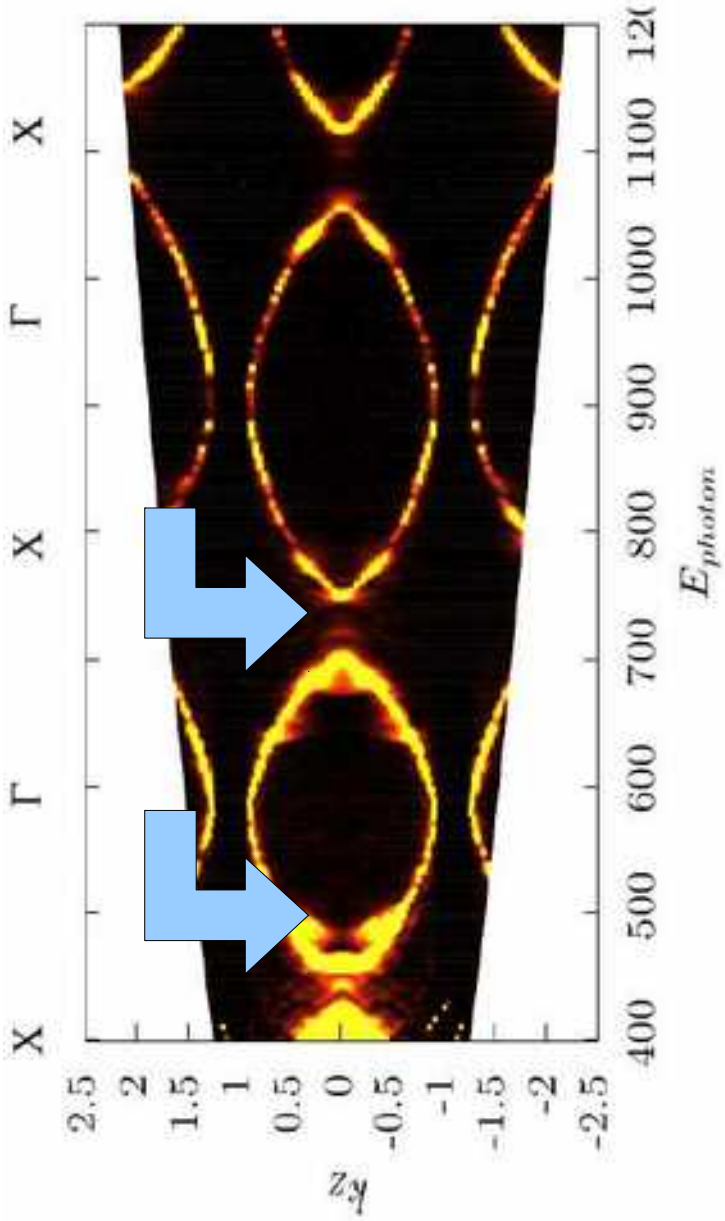
In collaboration with V. Strocov (PSI)

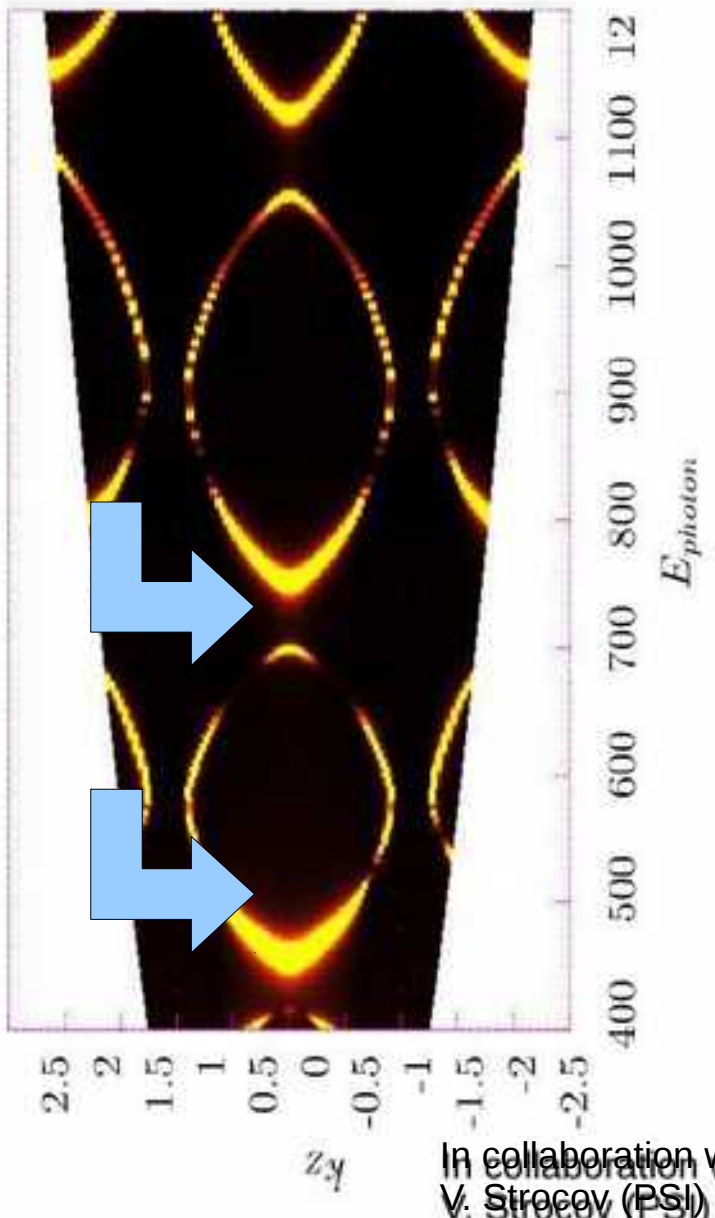
k_z-scan for Ag(001) and final state effects

Experiment

Theory: TR-LEED state

Free electron like final state





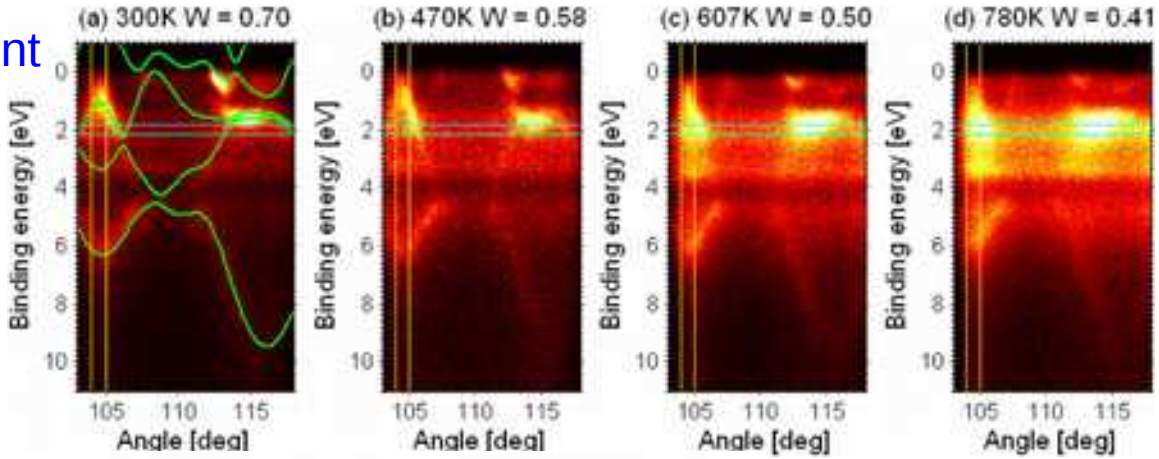
In collaboration with V. Strocov (PSI)

Temperature effects and XPS limit

Thermal effect: W(110) at 870eV

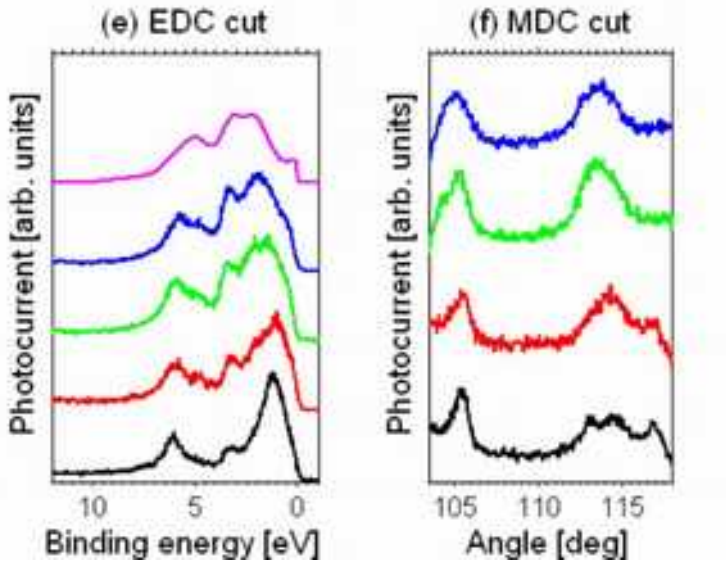
Increasing temperature

Experiment



DOS limit

T



L. Plucinski, J. Minár et al.,
PRB **84**, 195427 (2011)
PRB **78**, 035108 (2008)

Phonon effects in photo emission

- Phonon excitations define fundamental limit to band mapping as energy or temperature is raised because of full BZ averaging Shevchik (1977)

- Photo current can be roughly divided into two contributions:

$$I(E,T) = W(T) I_{DT}(E) + (1 - W(T)) I_{NDT}(E)$$

- Debeye-Waller Factor $W(T) \propto e^{-\Delta k^2 u^2}$

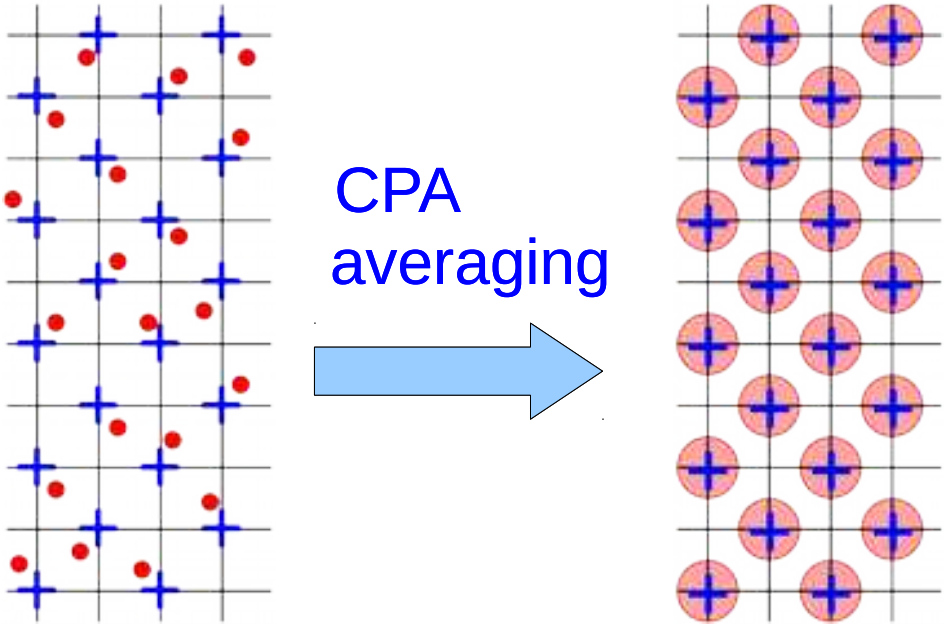
- Actual situation: $I(E,T) = W(T) I_{DT}(E)$ via t(T) (Larson and Pendry, Feder)

- Improved treatment of phonon effects on LEED state – cluster implementation: Zampieri *et al.* (1996)

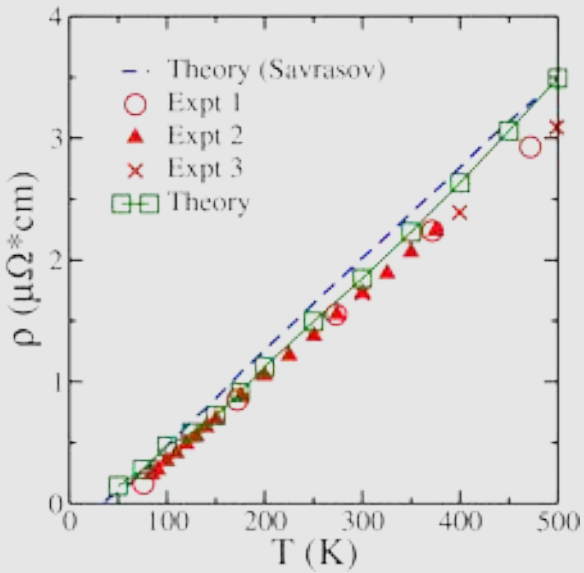
- Proper formulation for solids within multiple scattering formalism for high energy regime: Fujikawa and Arai (2009)

Finite temperature – first principles approach

Scattering theory for **displaced atoms**



fcc Cu – *T* dependent resistivity



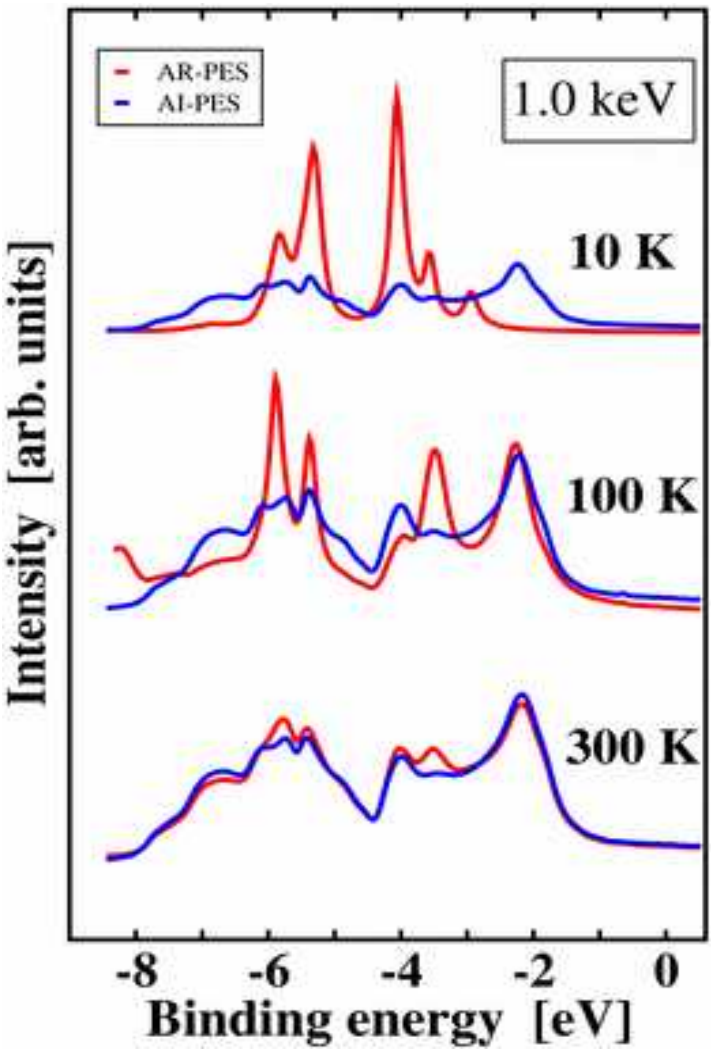
- Assumption: atomic vibrations are uncorrelated

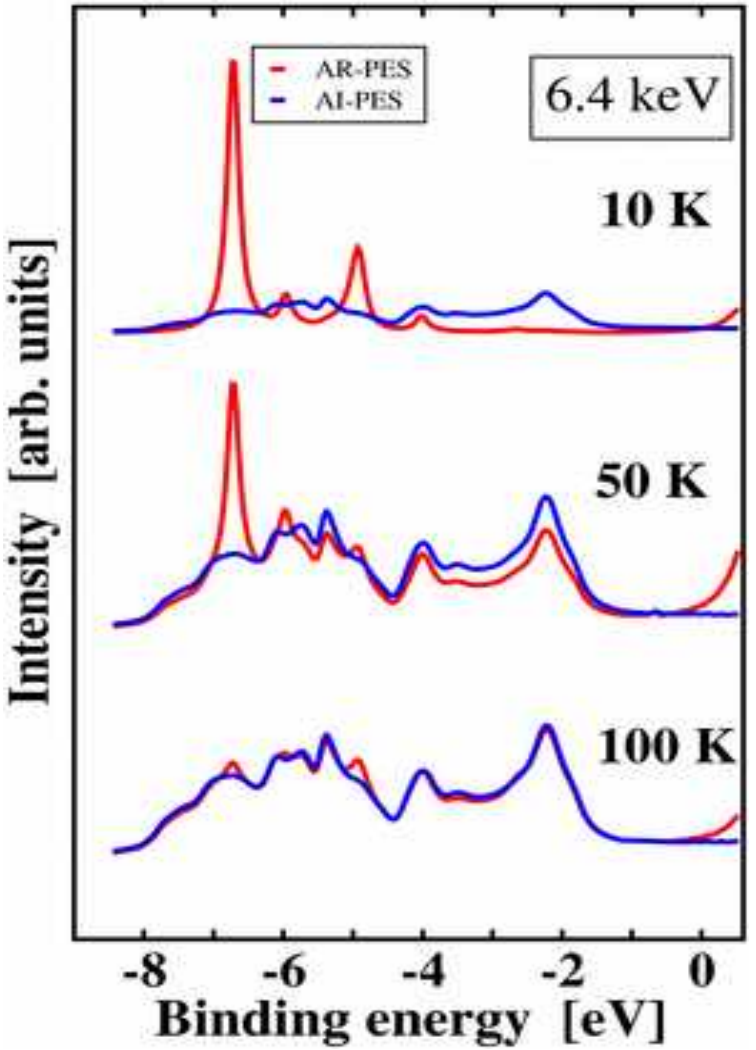
Ebert et al., PRL 107, 066603 (2011)

- Atomic displacements $\Delta\vec{R}_n$ depend on temperature *T* with probability $P(\Delta\vec{R}_n, T)$
- Configurational average - using CPA alloy theory → proper G(T)

NB: Random displacements (no phonons) – Application range: moderate/high temperatures

XPS-limit: Au(111)



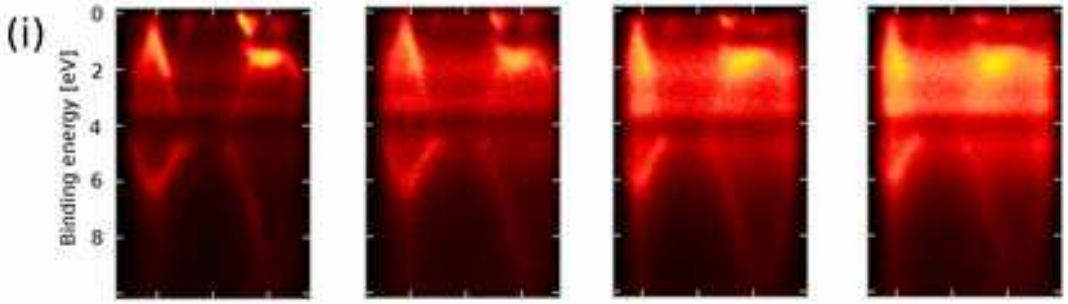


J. Braun et al. PRB **88**, 205409 (2013)

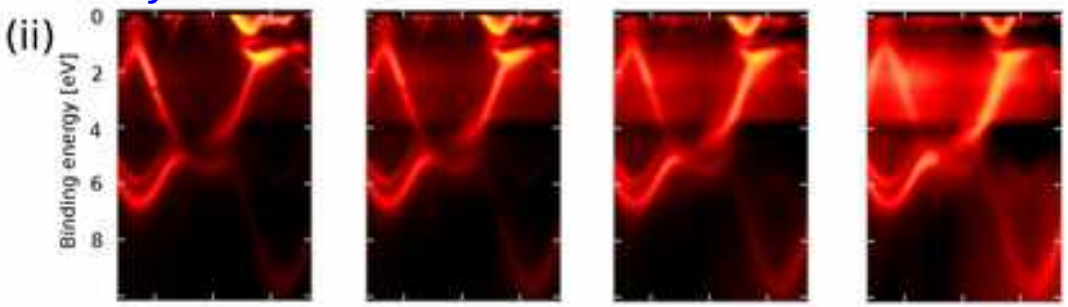
Experiment and theory: W(110)

300 K 470 K 607 K 780 K

Experiment

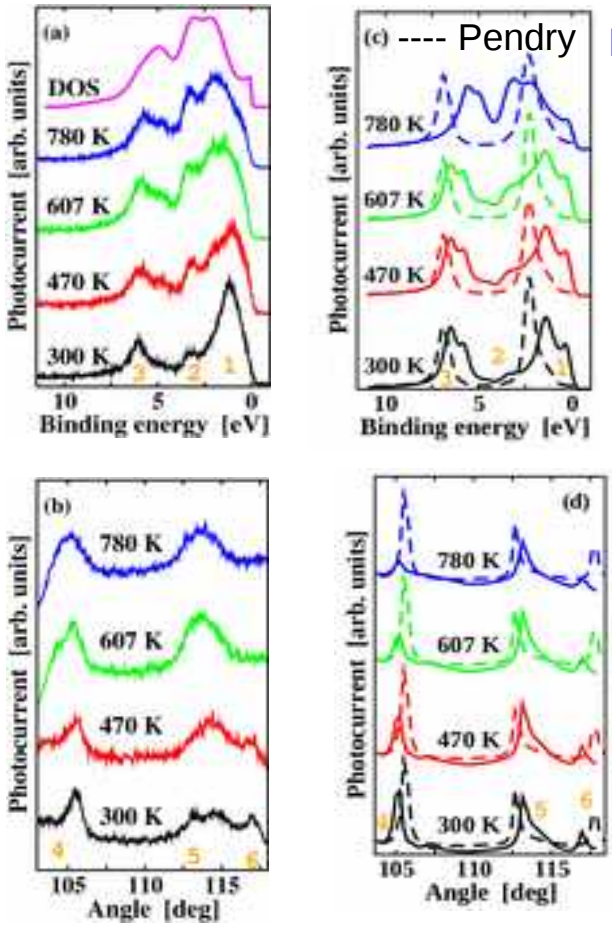


Theory



- DOS Limit
- XPD Diffraction
- Temperature-dependent matrix elements (dipol selection rules not valid)

Exp. **Theory**



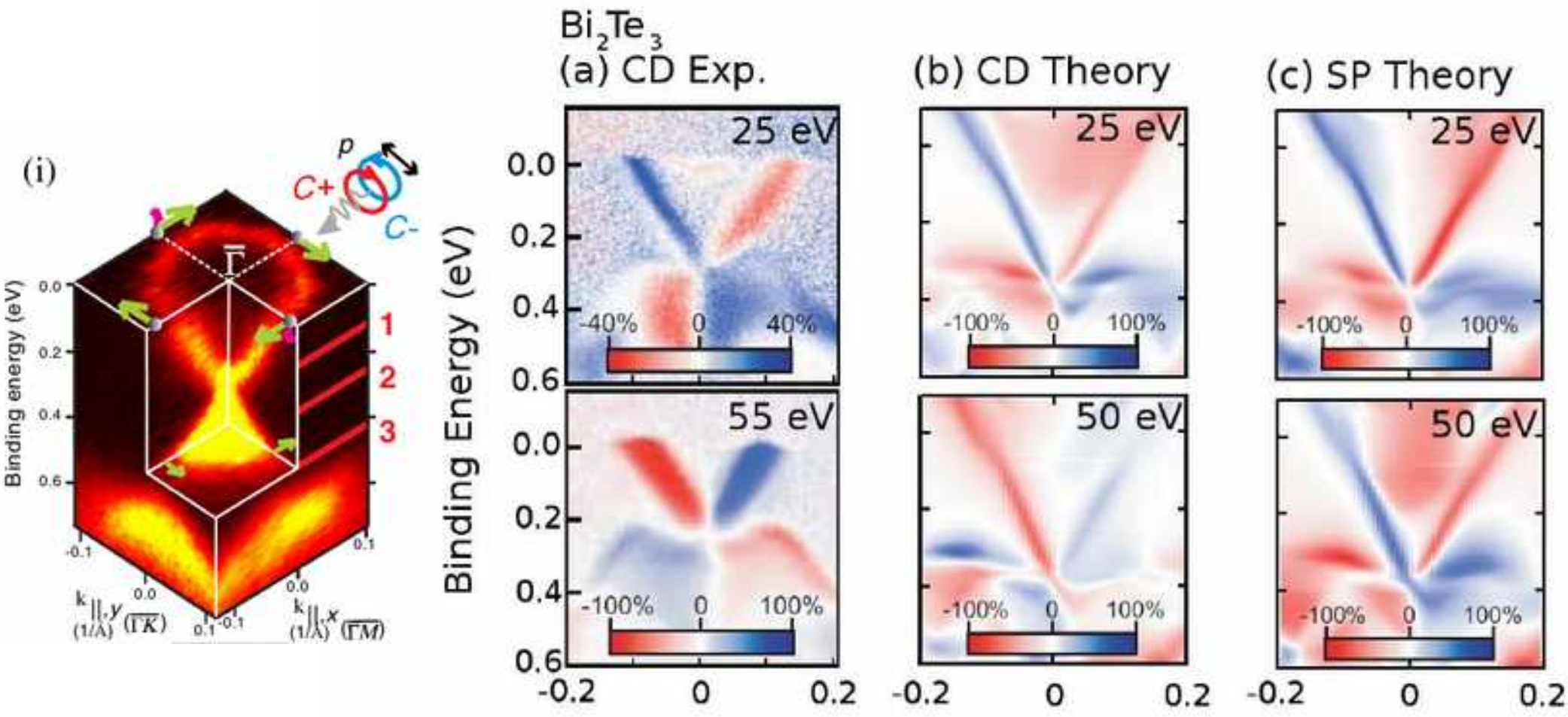
ECD's

MCD's

J. Braun, J. Minár, C. S. Fadley, H. Ebert et al., PRB **88**, 205409 (2013)

Surface features in soft- and hard x-ray PES

Topological surface state (TSS) in Bi_2Te_3

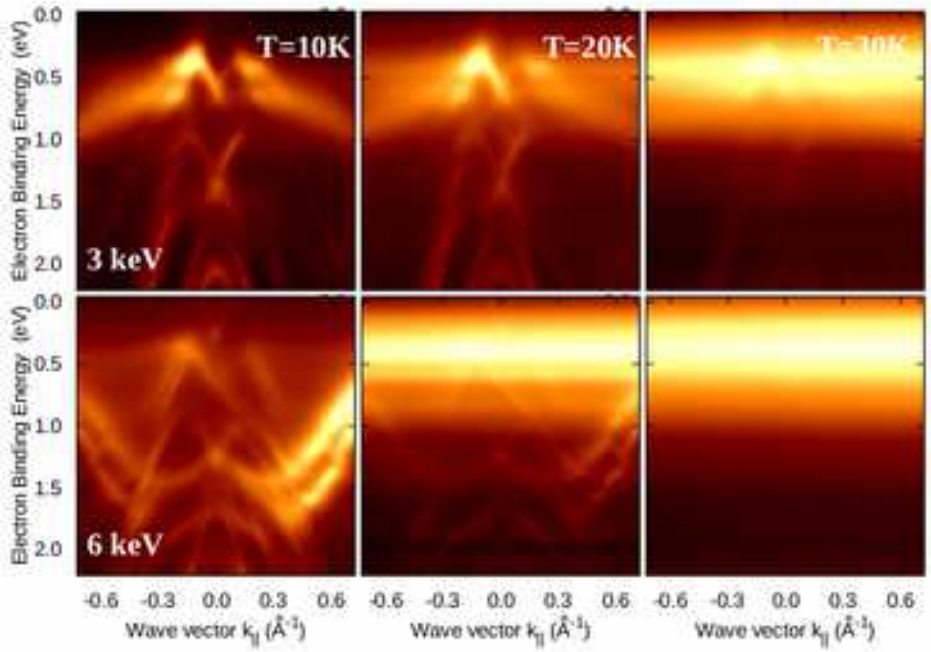


- Circular dichroism: Changes as a function of photon energy
- Final state effect
- Spin density matrix formalism $\overline{\rho}^{\mathrm{PES}}_{ss'}(\mathbf{k}_{||}, \epsilon_f) = \langle s, \epsilon_f, \mathbf{k}_{\parallel} | G_2^+ \Delta G_1^+ \Delta^\dagger G_2^- | \epsilon_f, \mathbf{k}_{||}, s' \rangle$

M. Scholz et al, PRL **110**, 216801 (2013) and PRX 4, 011046 (2014)

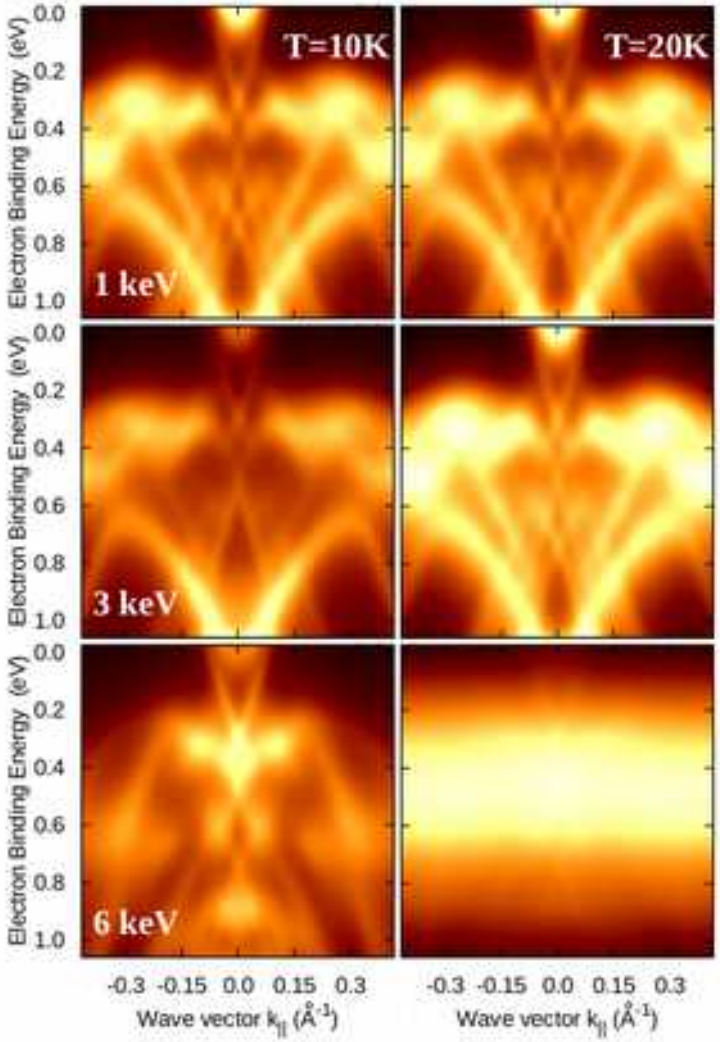
HAXPES from Bi_2Se_3 and Bi_2Te_3

Intensity plots as a function of temperature and excitation energy



Bi_2Se_3

T_{Debye} = 160 K



Bi_2Te_3

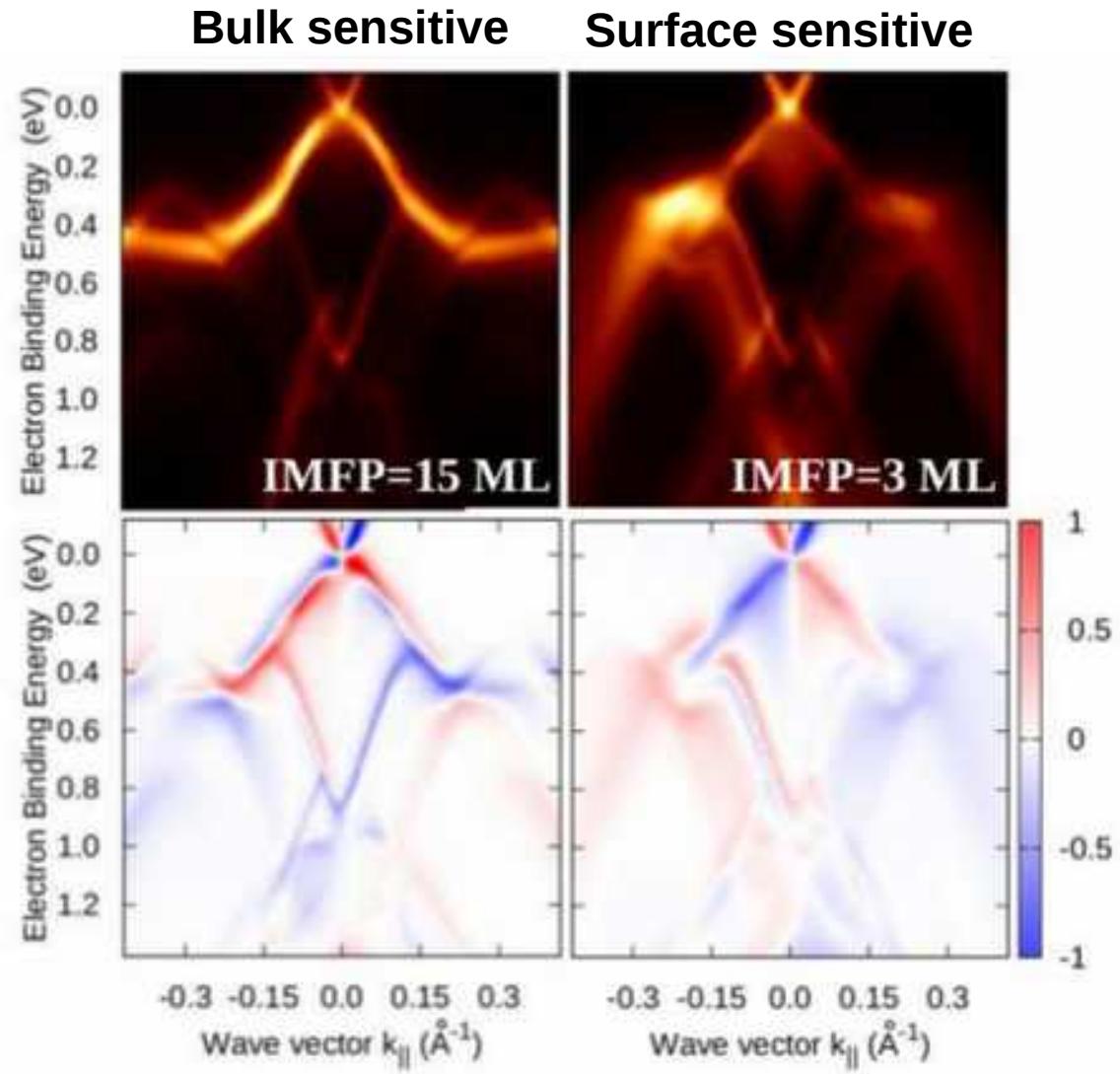
T_{Debye} = 155 K

J. Braun, H. Ebert and J. Minar, PRL, submitted (2014)

Sb_2Te_3: Simulated inelastic mean free path

Simulation of different inelastic mean free path by variation of the inverse life-time of the final state

3 ML = 20 eV
15 ML = 3 keV



J. Braun, H. Ebert and J. Minar, PRL, submitted (2014)

Summary

The **one-step model of photo emission**

supplies a

unified description of ARPES

and allows to deal coherently with:

- Surface effects
- Correlation effects
- Spin-obit induced phenomena
- Magnetic circular and linear dichroism
- Chemical disorder
- Electron-phonon interaction
- High energy spectroscopy (HAXPES)

Acknowledgements

- J. Braun, St. Borek,
- H. Volfova, G. Derondeau, M. Hess

AK Prof. Ebert

Experiments

- K. Hricovini (Cergy)
- Ch. Fadley (UC Davis)
- C. M. Schneider (Jülich)
- C. Felser (Dresden),
- H. Wende (Duisburg)
- K. Kern (Stuttgart), H. Brune (Lausane)
- H. Tjeng (Dresden)
- O. Rader (BESSY)
- C. Back (Regensburg)
- V. Strocov, J. Krempasky, H Dil (Villingen)
- And many many others

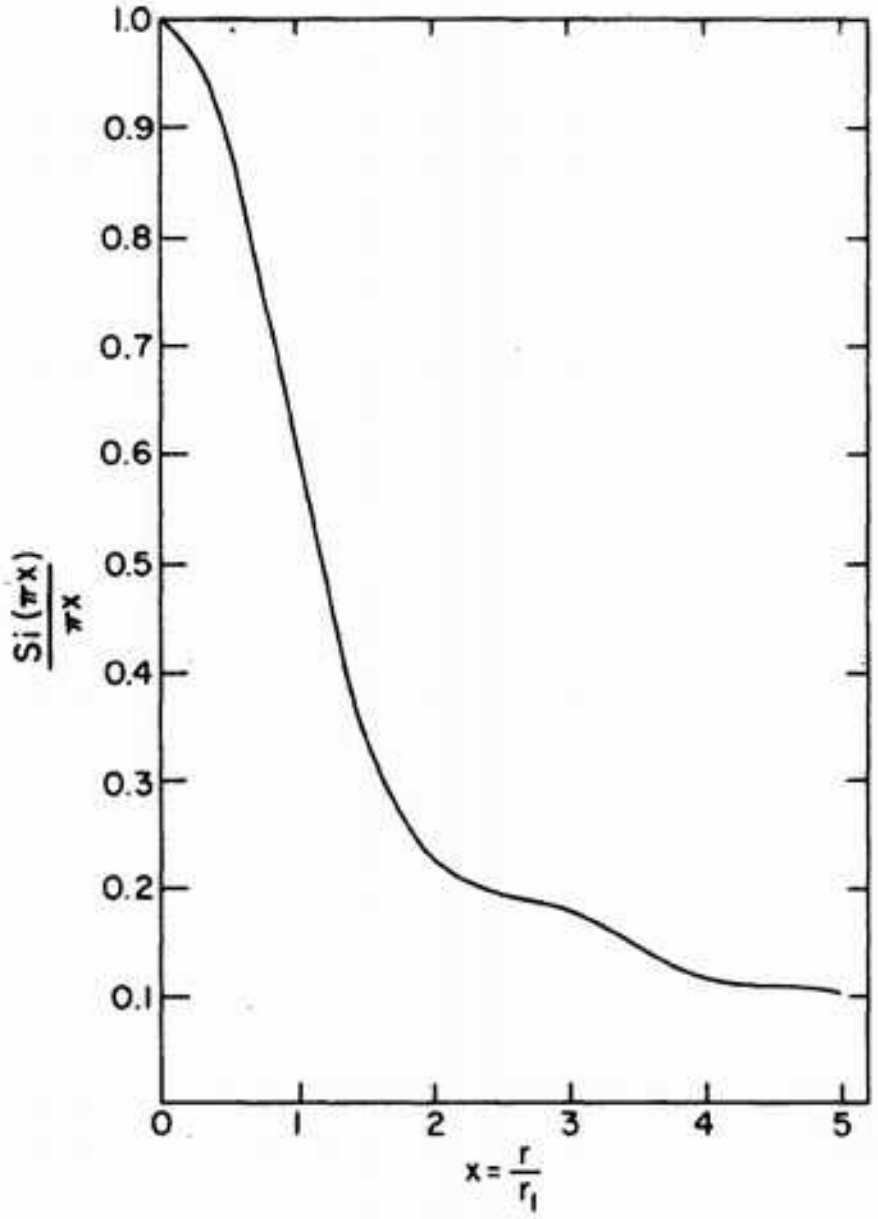
Correlations and spectroscopy: HOC 2015

- 3-4 Days Course
- HOC Course of various packages
  (e.g. SPR-KKR, Ab-init+GW, Multiplets)
- End of February 2015, Pilsen Czech Rep.
- For official announcement and registration see:
  www.euspec.eu

EUSpec
COST Action MP1306:
Modern Tools for
Spectroscopy on Advanced Materials

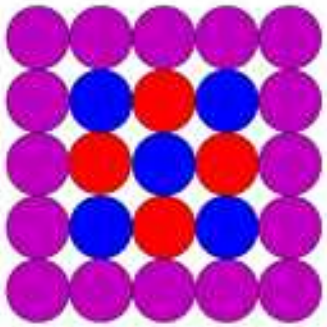
$$\hat{G}^{\pm} = \sum_i \frac{|\psi_i\rangle\langle\psi_i|}{E - E_i \pm i\delta}$$

cost


1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
$\frac{Si(\pi x)}{\pi x}$
0
1
2
3
4
5
$x = \frac{r}{r_1}$

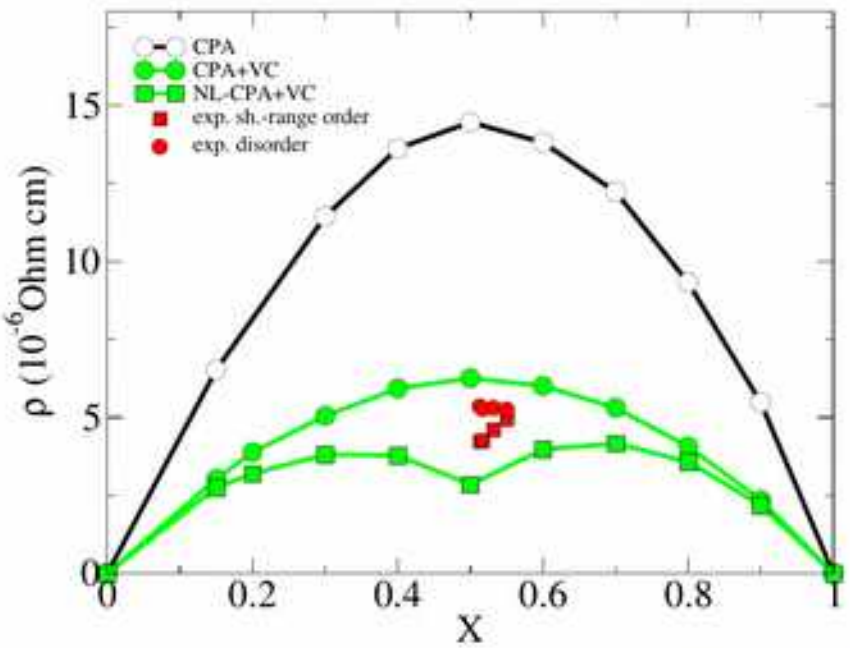
Typical problems of CPA

Certain short-range order

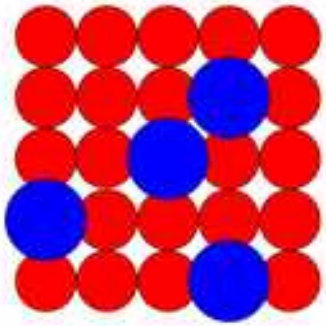


Solution: NL-CPA

Residual resistivity /S. Lowitzer, PhD thesis, 2010/



Atom radii are too different



Relativistic version of KKR-LSDA+DMFT

On-site Green's function calculated via multiple scattering theory:

$$G(\vec{r},\vec{r}',E) = \sum_{\Lambda\Lambda'} Z_\Lambda(\vec{r},E)\tau_{\Lambda\Lambda'}(E)Z^\times_{\Lambda'}(\vec{r}',E) - \sum_\Lambda \left[Z_\Lambda(\vec{r},E)J^\times_\Lambda(\vec{r}',E)\Theta(r'-r) + J_\Lambda(\vec{r},E)Z^\times_\Lambda(\vec{r}',E)\Theta(r-r') \right]$$

Dirac Equation within LSDA+DMFT: solving single site problem:

$$\left[\frac{\hbar}{i}c\vec{\alpha}\cdot\vec{\nabla} + \beta mc^2 + V_{eff}(\vec{r}) + \int d^3r'\Sigma(\vec{r},\vec{r}',E)\right]\phi_i(\vec{r}) = \epsilon_i\phi_i(\vec{r})$$

with $V_{eff}(\vec{r}) = \bar{V}(\vec{r}) + \beta\vec{\sigma}\vec{B}_{eff}(\vec{r})$

Greens function matrix – input for DMFT:

$$G_{\Lambda\Lambda'}(E) = \sum_{\Lambda_1,\Lambda_2}\langle\phi_\Lambda \mid Z_{\Lambda_1}\rangle\tau_{\Lambda\Lambda'}(E)\langle Z^\times_{\Lambda_2} \mid \phi_{\Lambda'}\rangle - \sum_{\Lambda_1}\langle\phi_\Lambda \mid Z_{\Lambda_1}(\mathrm{r}_<,E)J^\times_{\Lambda_1}(\mathrm{r}_>,E) \mid \phi_{\Lambda'}\rangle$$

$|\phi_\Lambda>$ set of *localised* orbitals

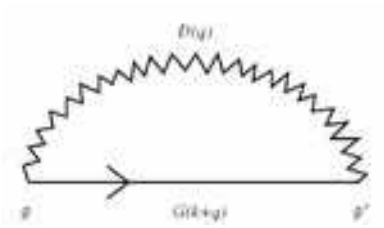
Non-local correlations

Here:

- Electron-phonon coupling
- Can we include k-dependent self energy into KKR and PES?
- Rigid sphere approximation → outlook: linear response (following Savrasov)

Renormalisation of electronic structure

$$\tilde{G}(E) = \frac{1}{E - E_k^0 - \tilde{\Sigma}_k(E)}$$



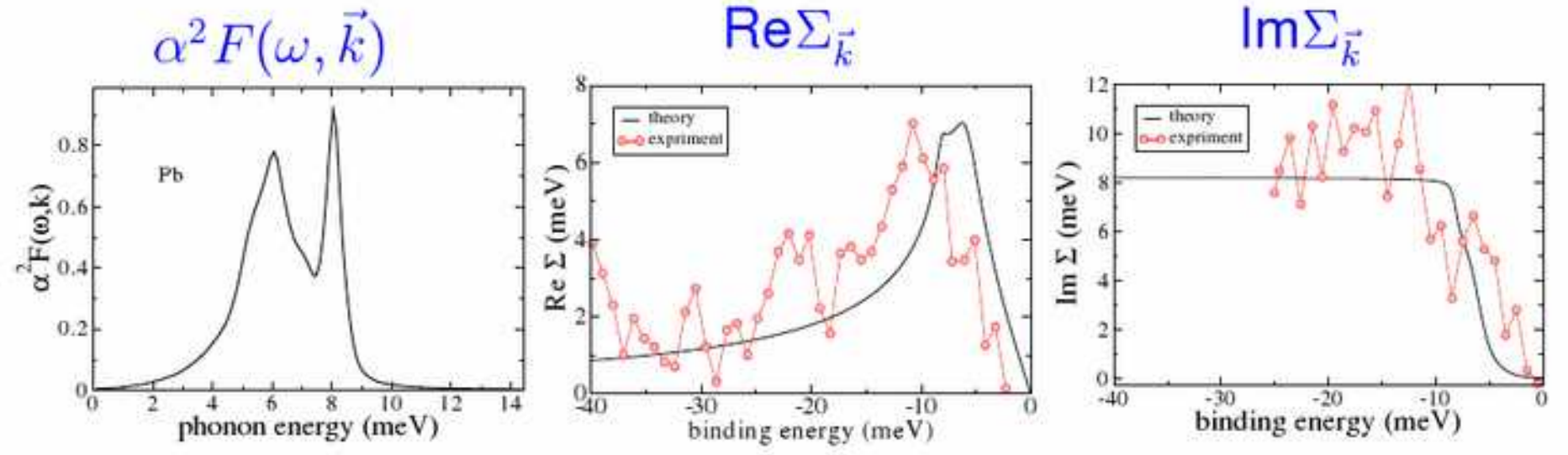
Selfenergy

$$\tilde{\Sigma}_k(E) = 2\int \Sigma^{Einst}(E,\omega)\alpha^2 F_k(\omega)d\omega$$

Eliashberg function

$$\alpha^2 F_k(\omega) = \sum_{\vec{q},\lambda} |g^{\lambda}_{\vec{k},\vec{k}-\vec{q}}|^2 \delta(\omega - \omega^{\lambda}_{\vec{q}})\delta(E_{\vec{k}} - E_F)\delta(E_{\vec{k}-\vec{q}} - E_F)$$

Example of fcc Pb



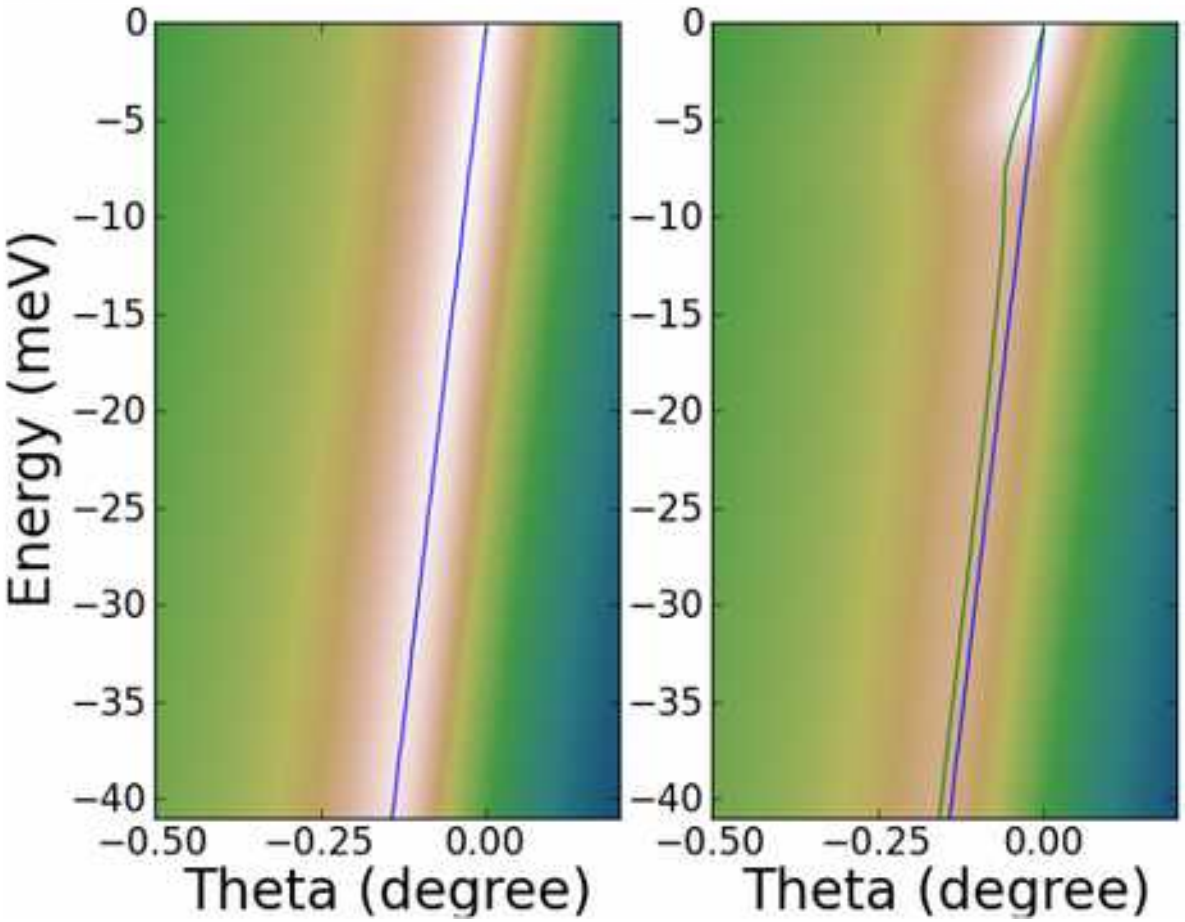
- Rigid sphere approximation
- High resolved ARPES possible to measure El. - phonon coupling
- Experiments: Reinert et al, PRL (2003)
- Quantitative agreement with experiment

Minar et al., JESRP 184, 91 (2011)

ARPES from Pb(110)

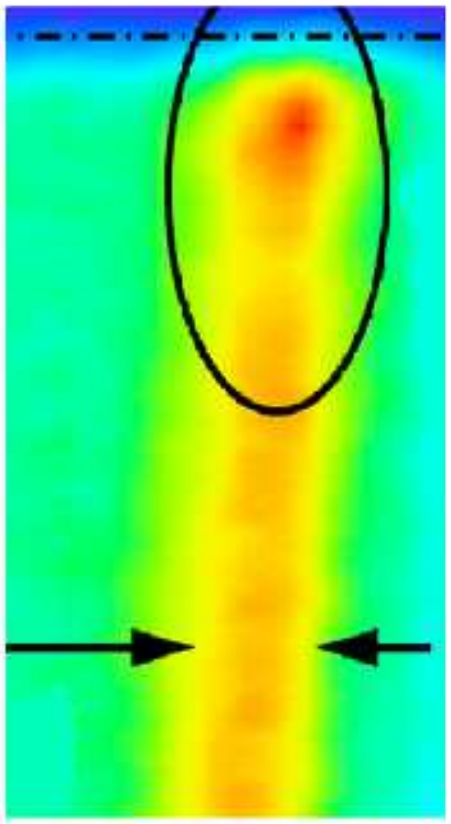
Calculated ARPES spectra

Without SE



Including SE

Experiment



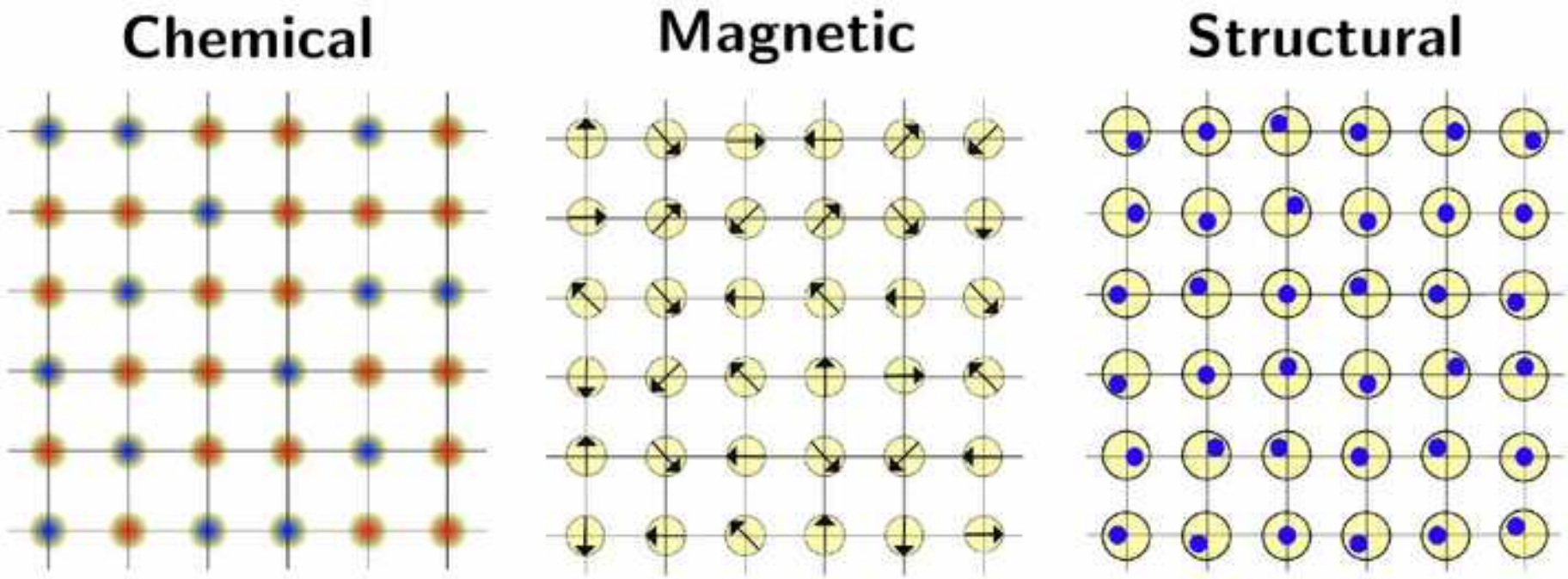
Minar et al., JESRP 184, 91 (2011)

$E_{h\nu}$ = 21.1 eV

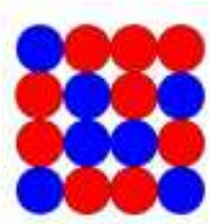
Expt: F. Reinert et al.
PRL, **91**, 186406 (2003)

Treatment of substitutional disorder

Random disorder in solids
(how to avoid super-cells?)

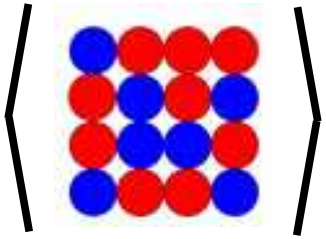


Alloy problem



A-B-Alloy – A und B atoms randomly distributed over the lattice

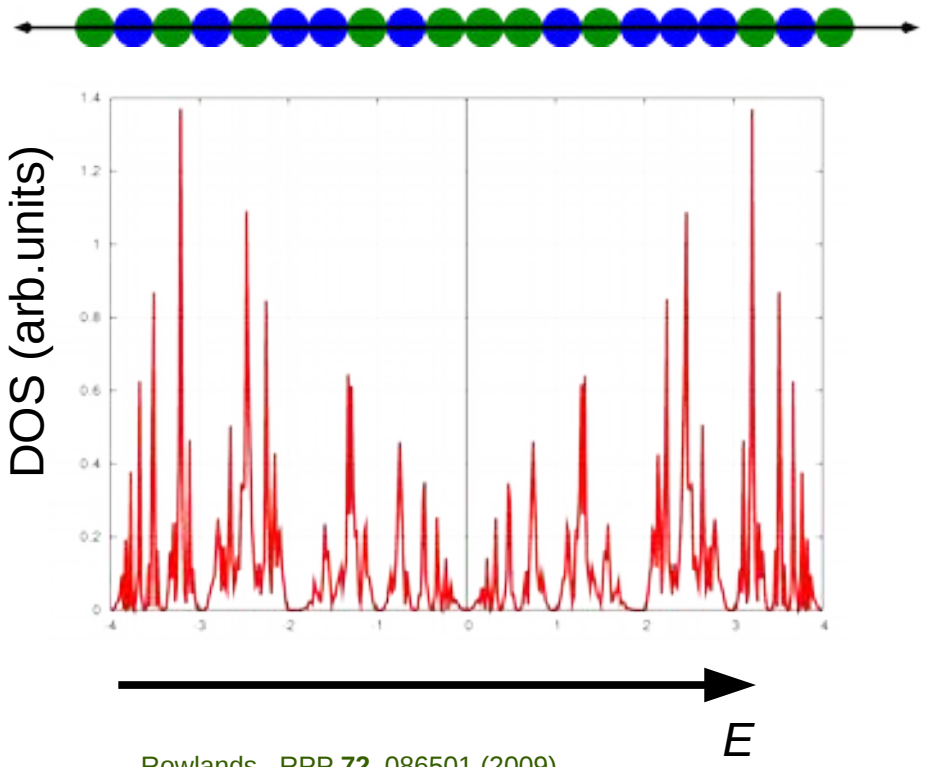
Alloy problem



Statistical average over all
Possible configurations

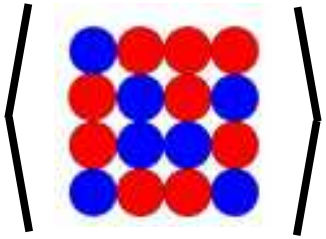
Example

Exact solution for 1D lattice (TB-model)



Rowlands., RPP **72**, 086501 (2009)

Alloy problem



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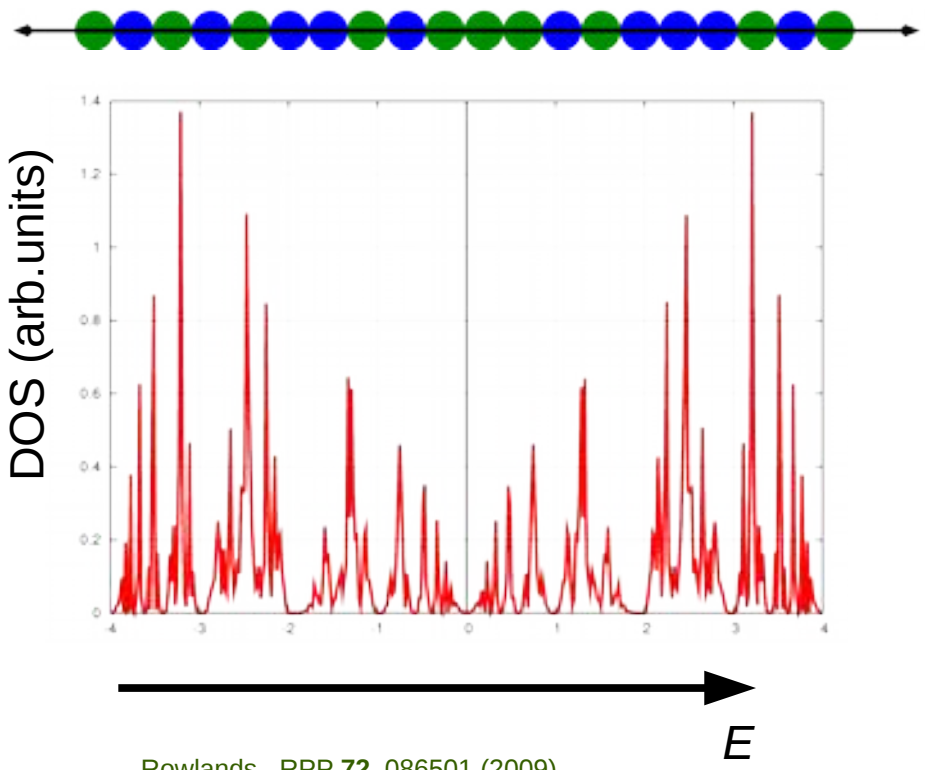
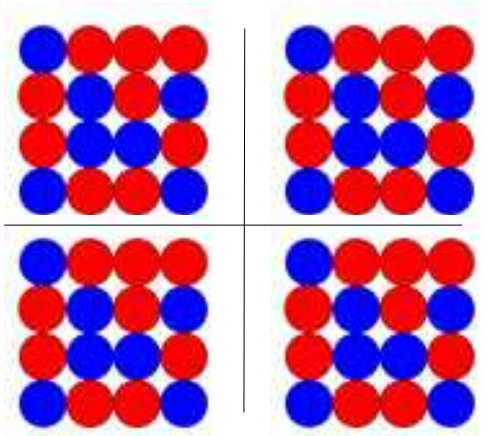


Rowlands., RPP **72**, 086501 (2009)

Not possible for ralistic systems → **Theories of effective medium**

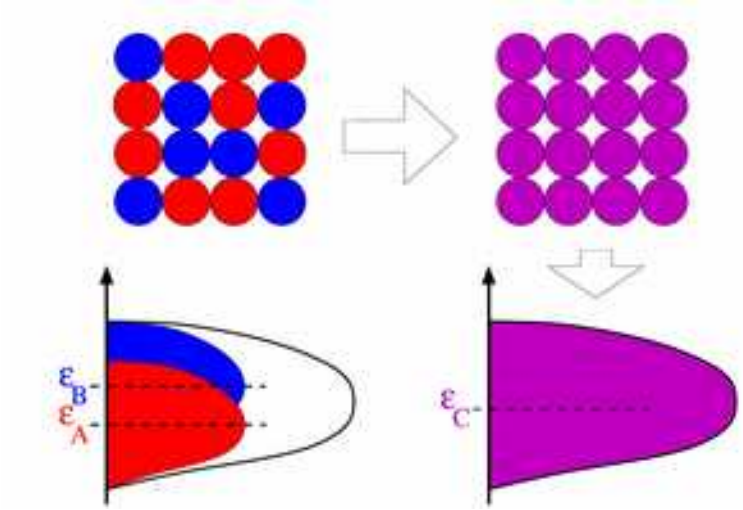
Overview of methods to deal with disorder

Supercell approach



- Applicable to any band structure method (Bloch theorem)
- Disadvantage: need for many calculations of big supercells
- “Up”-folding scheme (see eg. W. Ku, V. Popescu, A, Zunger)
- Advantage: Relaxation around impurities

Mean field approaches

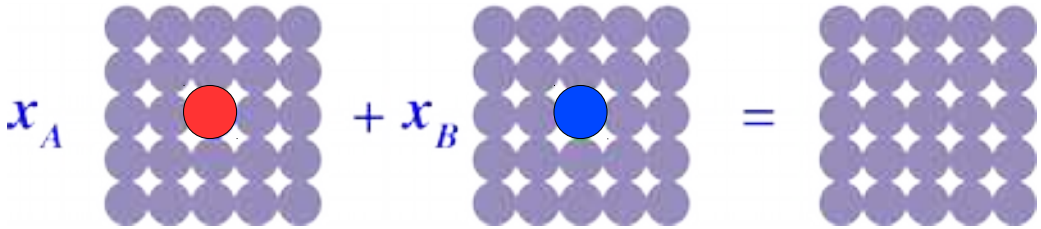


- Virtual crystal approximation (rigid band shift)
  - Implemented in most codes
  - Only applicable for systems having atoms with similar scattering properties
  - No finite life time broadening
  - No access to partial quantities –> as seen by core level spectroscopies
- Averaged t-matrix approximation (ATA)
- Coherent potential approximation (CPA): Averaging of Greens functions

Coherent potential approximation

Best Single site theory: $G_{AB} \approx xG_A + (1-x)G_B = G_C$

Coherent potetnial approximation (**CPA**)



$$x_A \underline{\tau}^{nn,A} + x_B \underline{\tau}^{nn,B} = \underline{\tau}^{nn,CPA}$$

$$\underline{\tau}^{nn,\alpha} = \underline{\tau}^{nn,CPA} \left[1 + \left(\underline{t}_\alpha^{-1} - \underline{t}_{CPA}^{-1} \right) \underline{\tau}^{nn,CPA} \right]^{-1}$$

Self constituent construction of the mean field medium

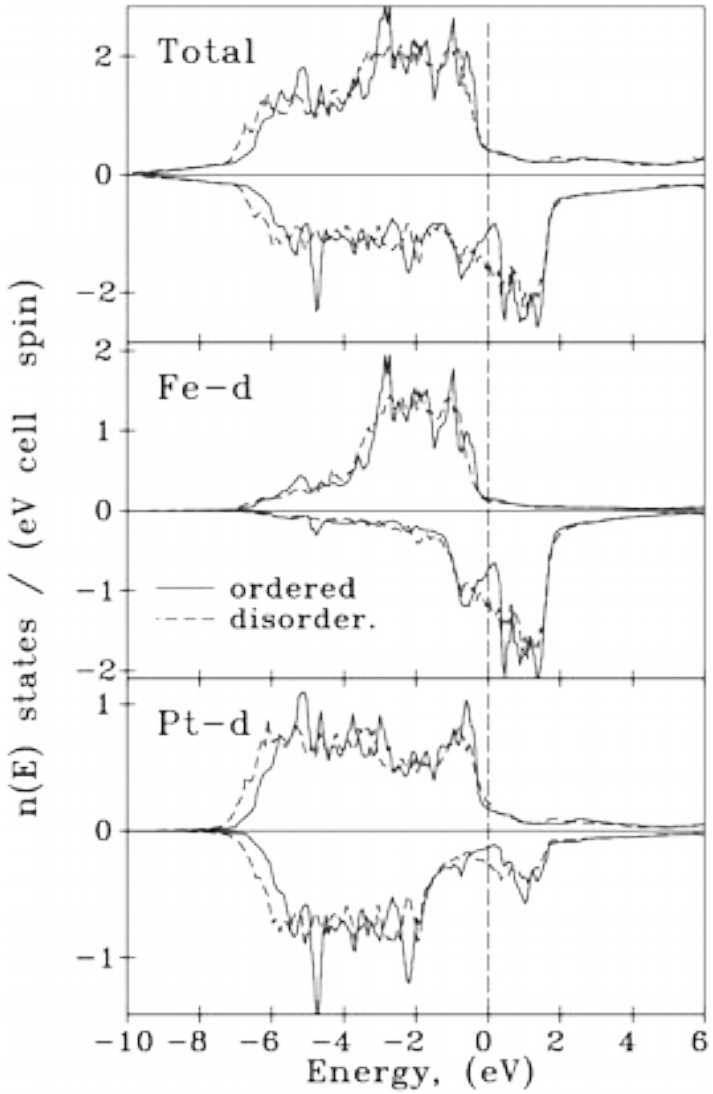
Embedding of an A- or B-atom into the CPA-medium
- in the average - should not give rise to additional scattering

Soven, Physical Review **156**, 809 (1967)

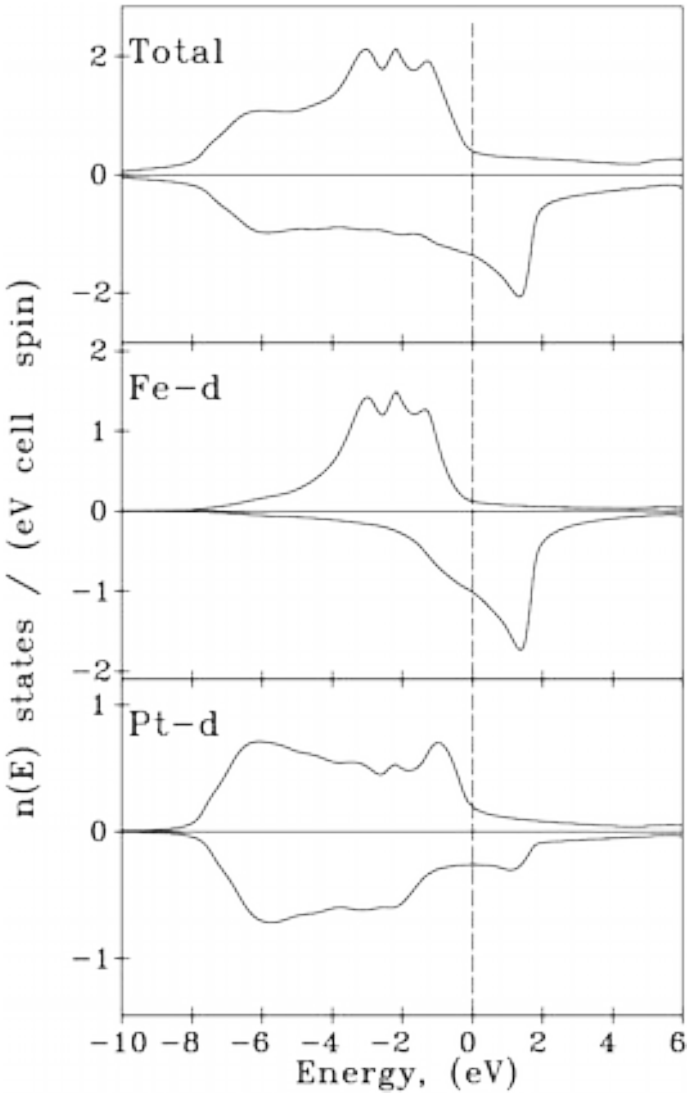
Super cell vs. CPA approach applied to FePt

Disordered fcc-$Fe_{0.5}Pt_{0.5}$

super cell approach



KKR-CPA



A. Perlov, *et al.,* Solid State Commun. **105**, 273 (1998)

Electron photon interaction

- In the relativistic case

$$\begin{aligned} X_{\vec{q}\lambda}(\vec{r}) &= -\frac{1}{c}\vec{j}_{el}\cdot\vec{A}_{\vec{q}\lambda}(\vec{r}) \\ &= -\frac{1}{c}\vec{j}_{el}\cdot\hat{\vec{a}}_{\lambda}Ae^{i\vec{q}\vec{r}} \end{aligned}$$

- With $\vec{j}_{el}$ the electronic current density operator

$$\vec{j}_{el} = -ec\vec{\alpha}$$

- Polarisation vector $\hat{\vec{a}}_{\lambda}$ for circularly polarisation light

$$\hat{\vec{a}}_{\pm} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ \pm i \\ 0 \end{pmatrix}$$

Matrix elements

One has to deal with matrix elements of the form

$$M_{fi}^{\vec{q}\lambda} = \langle \Phi_f | X_{\vec{q}\lambda} | \Phi_i \rangle$$

Electon photon interaction:

$$X_{\vec{q}\lambda}(\vec{r}) = -\frac{1}{c}\vec{j}_{el} \cdot \vec{A}_{\vec{q}\lambda}(\vec{r}) = -\frac{1}{c}\vec{j}_{el} \cdot \hat{\vec{a}}_\lambda A e^{i\vec{q}\vec{r}}$$

$$\vec{j}_{el} = -ec\vec{\alpha}$$

expanding $e^{i\vec{q}\vec{r}}$

$$e^{i\vec{q}\vec{r}} = 1 + i\vec{q}\vec{r} - \frac{1}{1}(\vec{q}\vec{r})^2 + \dots$$

within the dipole approximation the matrix elements:

$$M_{fi}^{\vec{q}\lambda} = \langle \Phi_f | \vec{\alpha} \cdot \hat{\vec{a}}_\lambda | \Phi_i \rangle$$