One step model of photoemission

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Theory and experiments

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

Brain extension

Approximations

Results?

Exp.

Theory
Synchrotron radiation based techniques

New light sources
Synchrotron radiation based techniques

New light sources

Strong need of Theoretical support

Interpretation

Old

Solid state spectroscopies
Photoemission data as measured

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)

Chemical shift

U. Starke, PRB (2011)

Angle integrated (XPS)


Total density of states

Band structure spectral function


Angle resolved PES (ARPES)


Graphene: U. Starke, PRB (2011)
Fermi surface of Fe-based HTC superconductor

Bloch Spectral Functions

\[ \text{BaFe}_2\text{As}_2 \]

Experiment

at 900 eV, p-pol light

\[ \text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2 \]

**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

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
\[
\left(-\frac{1}{2} \nabla^2 + V + V_{xc}\right) \phi_i = \epsilon_i \phi_i
\]

Variational:

\[
\phi_i = \sum_n C_{n}^{i} \phi_n
\]

Localized:

- OPW
- Pseudo Pot.
- PAW

Augmented:

- LCAO
- FPLO

Augmented KKR:

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

Linearized:

- APW
- MTO

- LAPW
- LMTO

Scattering:
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

\[
\left[ \hat{H}_k^j (E) - E_{j\vec{k}} \hat{O}_{\vec{k}}^j (E) \right] \psi_{j\vec{k}} = 0
\]

Energy dependent eigenvalue problem

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

Idea: Taylor expand energy dependence of radial wave functions

\[ \phi_n(E, r) \approx \phi_n(E_v, r) + \phi_n(E_v, r)(E - E_v) \]

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

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

⇒ KKR ≡ multiple scattering theory

e.g. J. Rehr, FEFF code
Multiple scattering and Green function $G$

Lippmann-Schwinger equation

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

$t$ – Matrix Operator

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

Green function without barrier (potential)

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

Iterate (*)

$$\hat{t} \Rightarrow |\psi\rangle \Rightarrow \text{Reflexion } R \quad \text{Transmission } T$$

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 $\mathcal{A}$)

$$\langle \mathcal{A} \rangle = -\frac{1}{\pi} \text{Im} \int_{-\infty}^{\infty} f_{FD}(E) \mathcal{A} \hat{G}(E)$$
Green function of total system

\[ \hat{G} = \hat{G}_0 + \hat{G}_0 \hat{V} \hat{G} \]
Multiple scattering and Green function $G$

\[ \hat{G} = \hat{G}_0 + \hat{G}_0 \hat{V} \hat{G} \]
\[ = \hat{G}_0 + \hat{G}_0 \hat{T} \hat{G}_0 \]

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

\[ = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4 \]
\[ = \sum_{mn} \hat{\tau}^{mn} \]

scattering path operator
Multiple scattering and Green function $G$

\[
\hat{G} = \hat{G}_0 + \hat{G}_0 \hat{V} \hat{G} = \hat{G}_0 + \hat{G}_0 \hat{T} \hat{G}_0
\]

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

\[
= \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4
\]

\[
= \sum_{mn} \hat{t}^{mn}
\]

scattering path operator
Multiple scattering representation of $G$ in KKR

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

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

Muffin-Tin-Potential

scattering path operator

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

\[ \hat{G} = \hat{G}_0 + \hat{G}_0 \hat{V} \hat{G} \]

\[ \hat{H} = \hat{H}_0 + V \]
Dyson–Equation

\[
\hat{G} = \hat{G}_0 + \hat{G}_0 \hat{V} \hat{G}
\]

\[
\hat{H} = \hat{H}_0 + V
\]

- 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)

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

Lounis et al,
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:

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

- 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 potential approximation (CPA)

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)
Example: Cu – Ni alloy: pure Cu
Example: Cu – Ni alloy: 5% Ni
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
Example: Cu – Ni alloy: 50% Ni
Coherent Potential Approximation

Example: Cu – Ni alloy: 60% Ni
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
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
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, Feibelman, ...
      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 ...

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
II Transmission to surface
I Excitation

\[ I \sim \tilde{D}(E, \omega) \sum_{nn'} \int d^3 k \ T(E, \vec{k}) \ |\langle n'\vec{k}|\vec{p}|n\vec{k}\rangle|^2 \]
\[ \times \delta(E - E_{n\vec{k}} - \omega) \delta(E_{n'\vec{k}} - E) \Theta(E - E_F) \Theta(E_F + \omega - E) \]
PES calculations based on three-step model

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

Theory: Janak et al. (1975)  
Expt: Eastman and Grobman

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

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

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

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

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

\[
\Gamma = -\frac{2\pi}{\hbar} |\langle \psi_F | \Delta | \psi_I \rangle|^2 \delta(E_F - E_I - \epsilon_{ph})
\]

Fermi’s Golden Rule

\[
\Delta^{PES} = \sum_{e,k} M^P_{e,k} a^+_e a_k
\]

\[
\Delta^{IPE} = \sum_{e,k} M^P_{k,e} a^+_k a_e
\]

Sudden approximation

The interaction of the photoelectron with the rest system is neglected

PES:

\[
|\psi_I > = |\psi^N_0 >
\]

IPE:

\[
|\psi_I > = a^+_e |\psi^N_0 >
\]

PES:

\[
|\psi_F > = a^+_e |\psi^{N-1}_S >
\]

\[
a^*_e |\psi^N_0 > = 0
\]

IPE:

\[
|\psi_F > = |\psi^{N+1}_S >
\]

General theory of photoemission

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

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

\[
T^{\text{PES}} = \sum_k M_{e,k}^P a_k
\]

\[
T^{\text{IPE}} = \sum_k M_{e,k}^P a_k^\dagger
\]

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

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

$$T^{PES} = \sum_k M_{e,k}^P a_k$$

$$T^{IPE} = \sum_k M_{e,k}^P a_k^\dagger$$

$$A_{m,m'}(E_N) \frac{2}{\hbar} \sum_s < \Psi_N^0 | a_{m'}^\dagger | \Psi_{N-1}^s > \delta(E_N - E_{N-1} - \hbar\omega) < \Psi_{N-1}^s | a_m | \Psi_N^0 >$$

One step model of photoemission

$$I(\epsilon_e, k_\parallel) = \int dr \int dr' \Psi_e^\dagger(r) \alpha A_0 \cdot A^{(1)}(r, r', E) (\alpha A_0)^\dagger \Psi_e(r')$$

$\alpha \cdot A_0$: relativistic form of electron-photon interaction

Practical calculations of Photocurrent

One step model of photoemission

\[ I(k_{||}, \epsilon_f) = -\frac{1}{\pi} \text{Im} \langle k_{||}, \epsilon_f | G_2^+ \Delta G_1^+ \Delta_1^\dagger G_2^- | \epsilon_f, k_{||} \rangle \]

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 ...)

DFT (e.g. N-1 → N)

Pendry
One-step model of photo-emission I

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

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

photo-current (Fermi's golden rule)

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

with final state $\phi_f = \mathcal{T}_R \phi^{LEED}$ — time reversed LEED state
One-step model of photo-emission II

photo current

\[ j \propto \sum_i \left\langle \phi_f | \hat{H}_\text{rad}^\lambda | \phi_i \right\rangle \left\langle \phi_i | \hat{H}_\text{rad}^\lambda \dagger | \phi_f \right\rangle \delta(E_f - E_i - \omega) \]

\[ \propto \left\langle \phi_f | \hat{H}_\text{rad}^\lambda | \mathcal{S} G_i | \hat{H}_\text{rad}^\lambda \dagger | \phi_f \right\rangle \]

initial state Green's function (from KKR):

\[ G^+ (\vec{r}, \vec{r}', E) = G_{nn}^+ (\vec{r}, \vec{r}', E) + \sum_{\Lambda \Lambda'} Z_{\Lambda}^n (\vec{r}, E) \tau_{\Lambda \Lambda'}^{nm} (E) Z_{\Lambda'}^m (\vec{r}', E) \]

final state (Time reversed LEED):

\[ \phi_f = \mathcal{T}_R \phi^{LEED} \]

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

e.g. Caroli et al. (1973), Feibelmann and Eastman (1974)
Numerical calculations: 1-st step

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)

\[ t_l(E) = -\frac{1}{k} \sin(\delta_l(E)) e^{i\delta_l(E)} \]

Developments:
- Fully relativistic: Dirac
- Full potential
- Correlation effects
- LDA+U, LDA+DMFT

Single site Green's function
Numerical calculations: Multiple scattering (MST)

- 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

- MST semi-infinite surface
  - Bulk reflection matrix

Mathematical expressions:

\[ \Phi = \Phi_0 + \Phi_{st} \]

Transmitted current:

\[ b_n^+ = T_{n}^{++} a_n^+ + R_{n}^{--} a_n^- \]

Layer doubling:

\[ a_n^+ = M_{n}^{++} a_n^- \]

Layer doubling:

\[ I_{trans} \rightarrow 0 \]
Numerical calculations: Multiple scattering (MST)

Single site scattering
Single site t-matrix
Radial wave functions Z, J

2D MST inside one layer
Kambe X-matrix

MST between two layers

MST semi-infinite surface
Bulk reflection matrix

\[ \Phi = \Phi_0 + \Phi_{st} \]

\[ I_{\text{atomic}} + I_{\text{intralayer}} + I_{\text{interlayer}} = I_{\text{photo current}} \]
Numerical calculations: Configurational average

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 systems: CPA
- Lattice vibrations
- Non-local correlations (El. Phonon coupling)
- Spin fluctuations

\[
\langle I_{\text{atomic}} \rangle + \langle I_{\text{intralyer}} \rangle + \langle I_{\text{interlayer}} \rangle + \langle I_{\text{incoherent}} \rangle = \langle I_{\text{photo current}} \rangle
\]
Main Goal: SPRKKR method + One step model

Angle resolved UV and X-ray photoemission for arbitrary ordered and disordered correlated systems

One-step model of photoemission

- LSDA
- Relativistic Dirac formalism
- CPA
- DMFT
- Full potential 2D Semi-infinite
- Model Surface barrier

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
Electronic structure of surface

2D-electronic structure

- Bulk states ($E(k_{||})$)
- Surface states
  - Bulk induced surface states
    - sp-like SS
      - Shockley
    - d-like SS
      - Tamm
  - Barrier induced surface states
    - SS resonances
    - Image states $V_B \sim z^{-1}$

Not in LSDA: Need for a model barrier
Surface Brillouin Zone

Bulk BZ of fcc

Bulk BZ and Surface BZ

Surface BZ of fcc(111)
Ni(111): 2D-Brillouin zone
Electronic structure of surfaces

Half-space calculation

Slab calculation
Surface barrier

Rashba effect in Au(111) Shockley surface state

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

-0.55
-0.5
-0.45
-0.4
-0.35
-0.3
-0.2
-0.1
0.1
0.2
0.3
0.4
0.5

Binding energy (eV)


M. James and S. Crampin, PRB B 81, 155439 (2010)

A. Nuber et al, PRB 83, 165401 (2011)

Theoretical data
Experiment
Model barrier

Binding energy from various calculations
Models of surface barrier

Asymptotic behavior of DFT functionals

- 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)

Solved by Multiple scattering

Surface contribution to photocurrent

\[ I_{\text{surface}} \]

Grass et al., JPCM 5 599 (1993)
Rydberg states (image states) in Cu

- 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

Criteria for surface states in (inverse) photoemission

\[ b^+ = R_B b^- \]
\[ b^- = R_C b^+ \]

\[ \det |1 - R_B R_C| = 0 \Rightarrow \text{Surface State} \]
\[ \det |1 - R_B R_C| = \min \Rightarrow \text{Surface Resonance} \]

E. G. McRae, Rev. Mod. Phys. 51, 541 (1979)
Surface resonances in ground state calculations?

Tamm surface resonance in PES of fcc Co(001)

- LSDA+DMFT
  \[ U_{\text{Co}} = 2.3 \text{eV} \]

- Spectral function
- PES spectra \( (E_{\text{phot}} = 21.\text{eV}) \)

Inverse Photoemission

- Surface resonances:
  difficult to identify in ground state calculations

- d-like Tamm surface resonance
  - Due to correlation effects shift in binding energy
    LSDA: -0.7eV, LSDA+DMFT: -0.4eV
  Allmers et al, PRB 84, 245426 (2011)
Angle integrated HAXPES: Spintronic materials

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

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
Dyson equation:

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

with \( \Sigma(\vec{r}, \vec{r}', E) \) on-site self-energy.
Multiple scattering Implementation of LSDA+DMFT

Dyson equation:

\[ G(\vec{r}, \vec{r}', E) = G_0(\vec{r}, \vec{r}', E) + \int d^3r'' \int d^3r''' G_0(\vec{r}, \vec{r}'', E) \]

\[ \left[ V_{\text{LSDA}}(\vec{r}'') \delta(\vec{r}'' - \vec{r}''') + \Sigma(\vec{r}'', \vec{r'''}, E) \right] \]

\[ G(\vec{r'''}, \vec{r}', E) \]

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

Spin dependent self energy of Ni for d-states

Included in the single site scattering problem

Real part

Imaginary part
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: \(\Psi(\vec{r}) = \sum_L \Psi_L(\vec{r})\)

\[\frac{d^2}{dr^2} - \frac{l(l + 1)}{r^2} - V(r) + E \] \(\Psi_L(r, E) = \sum_{L''} \int r'^2 d r' \Sigma_{LL''}(E) \phi_l(r) \phi_{l''}(r') \Psi_L(r', E)\)

Approximation for the self-energy:

\[\sum_L \int d^3 r' \phi_L^\dagger(\vec{r}) \Sigma_{LL'}(E) \phi_L(\vec{r}') \Psi_L(\vec{r}', E) \approx \sum_L \Sigma_{LL'}(E) \Psi_L(\vec{r}, E)\]

Pure differential equation:

\[\frac{d^2}{dr^2} - \frac{l(l + 1)}{r^2} - V(r) + E \] \(\Psi_L(r, E) = \sum_{L'} \Sigma_{LL'}(E) \Psi_L(\vec{r}, E)\)
Green's function matrix $G_{LL'}^{nm}$ within KKR-formalism

$$G_{LL'}^{nm}(E) = \sum_{L_1,L_2} \langle \phi_L | Z_{L_1} \rangle \tau_{LL'}^{nm}(E) \langle Z_{L_2}^\times | \phi_{L'} \rangle$$

$$- \delta_{nm} \sum_{L_1} \langle \phi_L | Z_{L_1}(r<,E)J_{L_1}^\times(r>,E) | \phi_{L'} \rangle$$

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

$\phi_L(r)$ — "Local" basis function solution of the Schrödinger equation for spherical LSDA non-magnetic potential
Implementation of LSDA+DMFT using KKR

- Fully self-consistent (charge + $\Sigma_{DMFT}$)
- Fully relativistic (Dirac eq.)
- $\Sigma_{DMFT}$ solvers:
  - SPTF (I. Di Marco el al.)
  - ED (I. Di Marco and J. Kolorenc)
  - TMA (Chadov et al.)
- Effects of $\Sigma_{DMFT}$ 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

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

$$\mu - \mu_i = \begin{cases} 
+1 & \text{for } \lambda = +1 \\
-1 & \text{for } \lambda = -1
\end{cases}$$

(LCP)

(RCP)

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 \( E_{\text{phot}} = 600 \text{ eV} \)

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

Comparison between Experiment and theory


U=3.0eV, J=0.9eV
Exp.: Osterwalder et al

Minar et al,
PRL 95, 166401 (2005)
Typical problems of LSDA in case of Ni

- Electron-hole pocket at X point
- 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 $\Gamma N$

Normal emission along $\Gamma N$ ($E_{\text{phot}}$=26-80eV)

Exp

Theory

J.S. Barriga, Minar et al. PRL 103, 267203 (2009)
Electronic structure and ARUPS of Fe(110)

- Optimal value of $U=1.5 \text{ eV}$ $J=0.9 \text{ eV}$
- 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

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

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

LDA+DMFT
Single site approach

Correlation effects of "ground state"
\[ \Psi^0_N \]

Simulation of excited state
\[ \Psi^{N-1}_S \]
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

Exp.

Theory
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
- 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?

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

Mean free path

- Energy (eV)
- Inelastic Mean-Free Path VS $E_{\text{kin}}$
- 3 eV

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)
Surface sensitivity for high photon energies

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

Fe(001)  |  8 ML MgO/Fe(001)

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

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

Fe-related features recovered for high photon energies

$\Rightarrow$ access to buried interfaces

Minar et al., JESRP 184, 91 (2011)
Angle resolved HAXPES of W(110) at 5954eV

HAXPES on technologically relevant materials: Mn doped GaAs

Until recently there were missing reliable photoemission measurements:

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

S. Ohya et al., Nature Physics 7, 342 (2011)
Correlation effects in \( \text{Ga}_{0.87}\text{Mn}_{0.13}\text{As} \)

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))

U=6eV, 24 Bath sites
+ 10 Mn d-orbitals, T=400K
HAXPES of GaMnAs

Angle resolved HAXPES of Ga$_{0.97}$Mn$_{0.03}$As

- 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

Angle integrated HAXPES at 6keV

- Exp: 3keV


J. Fujii et al., PRL **111**, 097201, (2013)
HAXPES on technologically relevant materials: Mn doped GaAs

A. Gray, J. Minar et al., Nat. Mat. 11, 957 (2012)
J. Fujii et al., PRL 111, 097201, (2013)
Photon momentum
Band mapping
matrix elements and k-dependence
Photon momentum effects on Ag(001)

Ag(001) photoemission intensities along \( \Gamma K \) with LCP-light at \( h\nu = 552 \text{ eV} \)

**q\text{photon} \text{ ignored}**

\begin{align*}
  k_i &= (k_\parallel + g, \sqrt{2(E - iV_{11}) - |k_\parallel + g|^2}) \\
  k_f &= (k_\parallel + g, \sqrt{2(E + \omega - iV_{12}) - |k_\parallel + g|^2})
\end{align*}

**q\text{photon} \text{ included}**

\begin{align*}
  k_i &= (k_\parallel - q_\parallel + g, \sqrt{2(E - iV_{11}) - |k_\parallel - q_\parallel + g|^2}) \\
  k_f &= (k_\parallel + g, \sqrt{2(E + \omega - iV_{12}) - |k_\parallel + g|^2})
\end{align*}

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 \((k_z\text{-scan})\)

\[\Delta z \sim \lambda\]

\[\Delta k_z \sim \lambda^{-1}\]

- reduction of \(k_z\) 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**
$k_z$-scan for Ag(001) and final state effects

Experiment

Theory: TR-LEED state

Free electron like final state
Temperature effects and XPS limit
Thermal effect: W(110) at 870eV

Increasing temperature

Experiment

DOS limit

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

- Assumption: atomic vibrations are uncorrelated
- 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

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

- 300 K
- 470 K
- 607 K
- 780 K

**Theory**

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

---

Surface features in soft- and hard x-ray PES
Topological surface state (TSS) in $\text{Bi}_2\text{Te}_3$

- Circular dichroism: Changes as a function of photon energy
- Final state effect
- Spin density matrix formalism

$\rho_{ss'}^{\text{PES}}(k_\parallel, \varepsilon_f) = \langle s, \varepsilon_f, k_\parallel | G_2^+ \Delta G_1^+ \Delta^+ G_2^- | \epsilon_f, k_\parallel, s' \rangle$

M. Scholz et al, PRL 110, 216801 (2013) and PRX 4, 011046 (2014)
HAXPES from $\text{Bi}_2\text{Se}_3$ and $\text{Bi}_2\text{Te}_3$

Intensity plots as a function of temperature and excitation energy

$\text{Bi}_2\text{Se}_3$

$T_{\text{Debye}} = 160 \text{ K}$

$\text{Bi}_2\text{Te}_3$

$T_{\text{Debye}} = 155 \text{ K}$

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

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)
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- 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)
- For official announcement and registration see: www.euspec.eu
Typical problems of CPA

Certain short-range order

Solution: NL-CPA

Atom radii are too different
Relativistic version of KKR-LSDA+DMFT

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

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

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

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

with

\[
V_{\text{eff}}(\vec{r}) = \tilde{V}(\vec{r}) + \beta \mathbf{\sigma} \tilde{B}_{\text{eff}}(\vec{r})
\]

Greens function matrix – input for DMFT:

\[
G_{\Lambda \Lambda'}(E) = \sum_{\Lambda_1, \Lambda_2} \langle \phi_{\Lambda} | Z_{\Lambda_1}(E) \tau_{\Lambda \Lambda'}(E) Z_{\Lambda_2}^\times | \phi_{\Lambda'} \rangle \\
- \sum_{\Lambda_1} \langle \phi_{\Lambda} | Z_{\Lambda_1}(r_\text{<}, E) J_{\Lambda_1}^\times (r_\text{>, E}) | \phi_{\Lambda'} \rangle
\]

| \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

\[ \alpha^2 F_k(\omega) = \sum_{q, \lambda} |g_{k, \bar{k}-\bar{q}}^{\lambda}|^2 \delta(\omega - \omega_{\bar{q}}^{\lambda}) \delta(E_{\bar{k}} - E_F) \delta(E_{\bar{k}-\bar{q}} - E_F) \]
Example of fcc Pb

- Rigid sphere approximation
- High resolved ARPES possible to measure El. - phonon coupling
- 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)

$E_{hv} = 21.1 \text{ eV}$

Expt: F. Reinert et al.  
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

Exact solution for 1D lattice (TB-model)

Statistical average over all Possible configurations

Example

Rowlands., RPP 72, 086501 (2009)
Alloy problem

Exact solution for 1D lattice (TB-model)

Example

Statistical average over all Possible configurations

Not possible for realistic systems

Theories of effective medium

Rowlands., RPP 72, 086501 (2009)
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 potential approximation (CPA)

\[ x_A \tau_{nn,A} + x_B \tau_{nn,B} = \tau_{nn,CPA} \]

\[ \tau_{nn,\alpha} = \frac{1}{\tau_{nn,CPA} \left[ 1 + \left( \frac{1}{t_{\alpha}} - \frac{1}{t_{CPA}} \right) \tau_{nn,CPA} \right]^{-1}} \]

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$_{0.5}$

Electron photon interaction

- In the relativistic case

\[ X_{\vec{q}\lambda}(\vec{r}) = \frac{1}{c} \vec{j}_{el} \cdot \vec{A}_{\vec{q}\lambda}(\vec{r}) \]

\[ = \frac{1}{c} \vec{j}_{el} \cdot \hat{a}_\lambda A e^{i\vec{q}\vec{r}} \]

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

\[ \vec{j}_{el} = -e c \vec{a} \]

- Polarisation vector \( \hat{a}_\lambda \) for circularly polarisation light

\[ \hat{a}_\pm = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm i \\ 0 \end{pmatrix} \]
One has to deal with matrix elements of the form

\[ M_{fi}^{q\lambda} = \langle \Phi_f | X_{q\lambda} | \Phi_i \rangle \]

Electron photon interaction:

\[ X_{q\lambda}(\vec{r}) = -\frac{1}{c} \vec{j}_{el} \cdot \vec{A}_{q\lambda}(\vec{r}) \]

\[ = -\frac{1}{c} \vec{j}_{el} \cdot \hat{a}_{\lambda} A e^{i\vec{q}\vec{r}} \]

expanding \( e^{i\vec{q}\vec{r}} \)

\[ e^{i\vec{q}\vec{r}} = 1 + i\vec{q}\vec{r} - \frac{1}{1} (\vec{q}\vec{r})^2 + \ldots \]

within the dipole approximation the matrix elements:

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