Magnetization probed by spectroscopy

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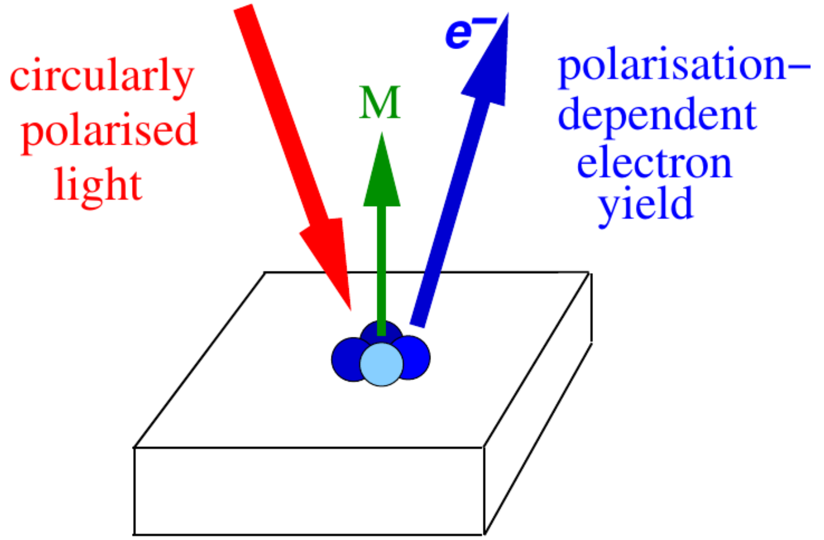
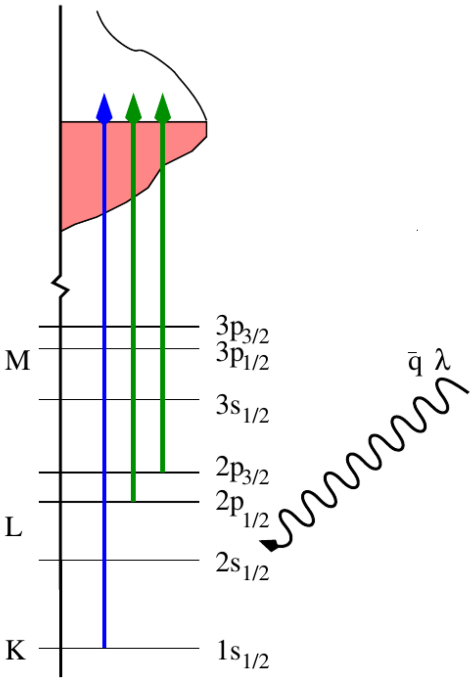
Outline

- Introduction
- Ground state magnetization
  - Magnetic circular dichroism in X-ray absorption (XMCD)
  - Spin and angle resolved photo emission (SAR-PES)
- Out of equilibrium - Steady state situation
- Out of equilibrium - Pump and probe experiments
  - Time-dependence via the Keldysh formalism
  - 2PPE from Ag(100) and pure ferromagnets
- Outlook and summary

J. Braun, J. Minar and H. Ebert, Physics Reports, 740, 1 (2018)

Magnetic circular dichrosim in X-ray absorption (XMCD)





Fermi's golden rule

$$\mu^{\vec{q}\lambda}(\omega) \quad \propto \quad \sum_{\substack{i\ \mathrm{occ}\\ f\ \mathrm{unocc}}} |\langle\Phi_f|X_{\vec{q}\lambda}|\Phi_i\rangle|^2 \delta(\hbar\omega - E_f + E_i)$$

$$\propto \quad \sum_{i\ \mathrm{occ}} \langle\Phi_i|X^{\times}_{\vec{q}\lambda}\, \Im G^{+}(E_f)\, X_{\vec{q}\lambda}|\Phi_i\rangle\theta(E_f - E_{\mathrm{F}})$$

Expressed in terms of retarded single particle Green function

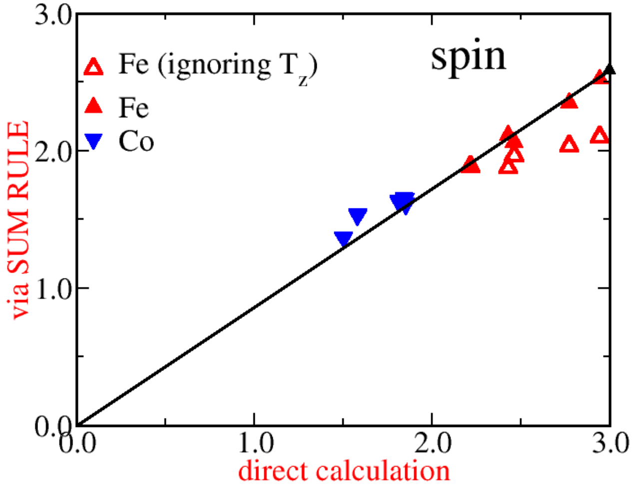
Magnetic circular dichrosim (XMCD) and sum rules

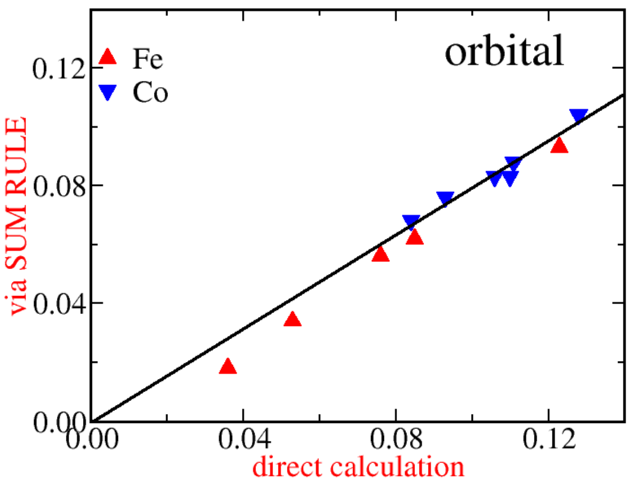
magnetic dichroism $\Delta\mu = \mu^+ - \mu^-$

Spin and
$$\int (\Delta\mu_{L_3} - 2\Delta\mu_{L_2})\, dE = \frac{N}{3N_{h\,d}} (\langle \sigma_z \rangle_d + 7\langle T_z \rangle_d)$$

orbital sum rules
$$\int (\Delta\mu_{L_3} + \Delta\mu_{L_2})\, dE = \frac{N}{2N_{h\,d}} \langle l_z \rangle_d$$

applied to $L_{2,3}$-edge spectra of Fe and Co in various multi layer systems

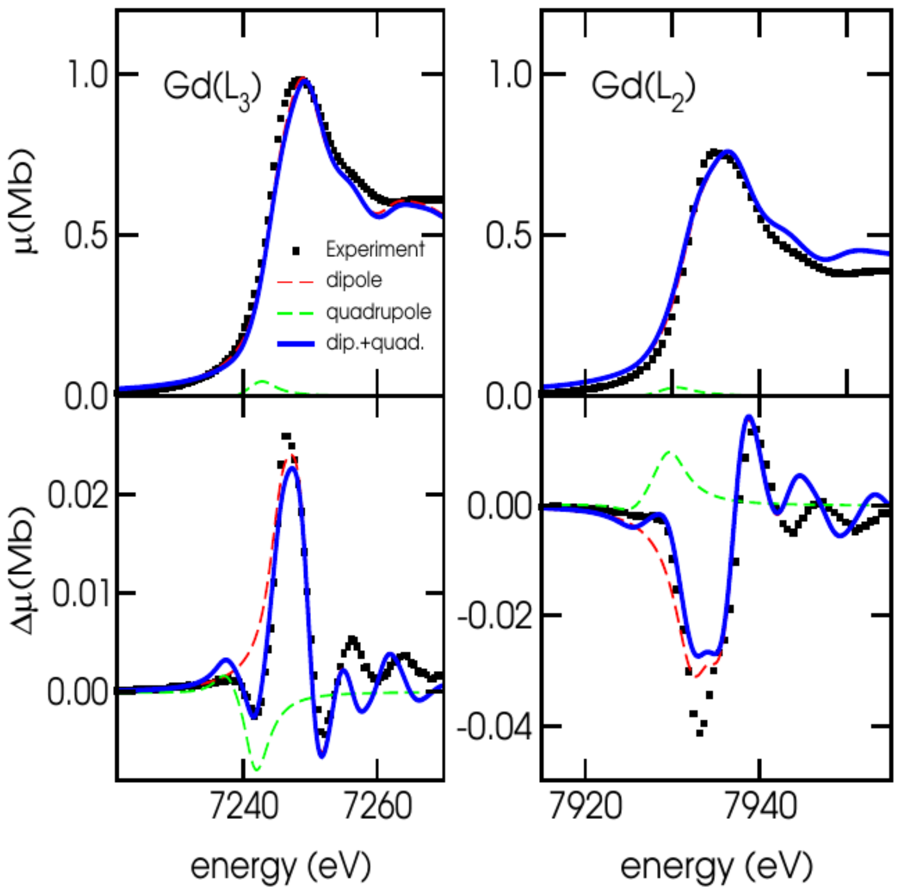




Comparison with experiment

XAS and XMCD

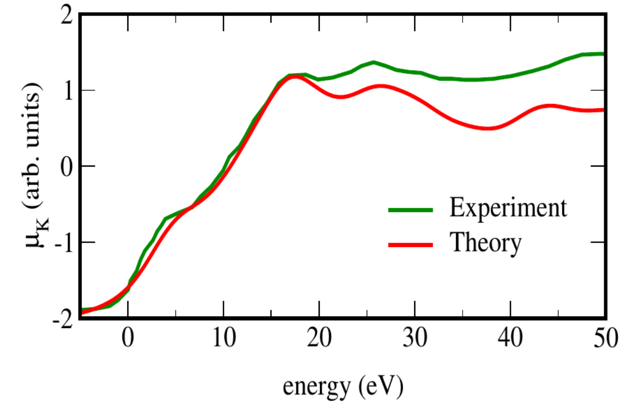
at L_2- and L_3-edges of Gd



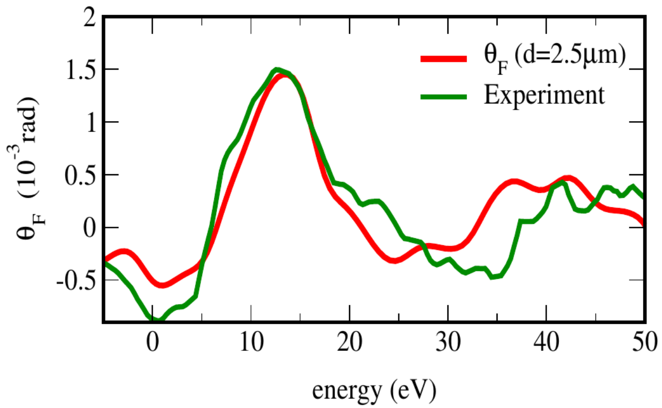
XAS and Faraday rotation

at K-edge of Co

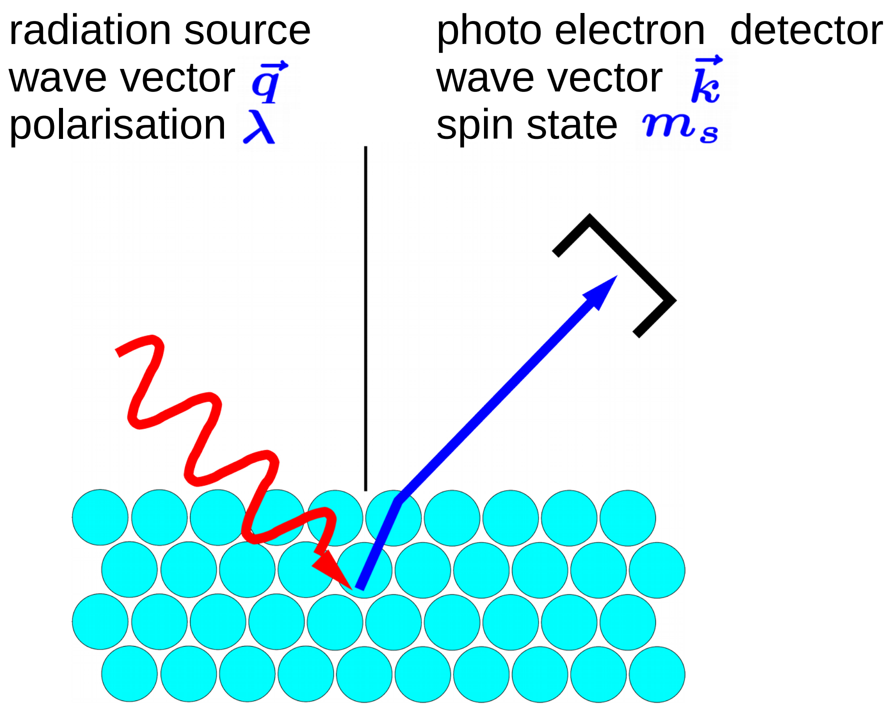
absorption



rotation



One-step model of spin and angle resolved photo emission



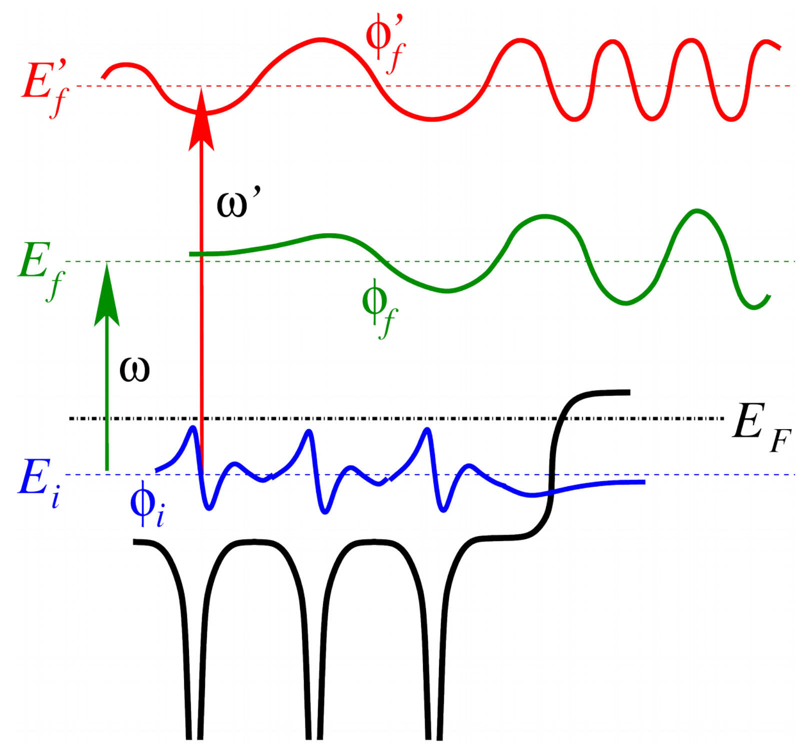


photo current (Fermi's golden rule)

$$I \quad \propto \quad |\langle \Psi_F | \Delta | \Psi_I \rangle|^2 \delta(E_F - E_I - \omega)$$

Many body approach: e.g. Caroli *et al.* (1973), Feibelmann *et al.* (1974)

Pendry: ***replace one-electron by retarded single particle Green function***

One-step model of photo emission

photo current

$$P_k(E_f) \propto \int d^3r' \int d^3r'' \; \phi_k^\dagger(r', E_f) \;\; W \left[G^+(r', r'', E_i) - G^-(r', r'', E_i) \right] W^\dagger \, \phi_k(r'', E_f)$$

Pendry *et al.* (1980)

Electron – photon interaction

$W = \alpha \cdot \mathbf{A}_\lambda$ **with** $\hbar\omega = E_f - E_i$

final state: time-reversed LEED-state

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

retarded Green functions via KKR multiple scattering formalism

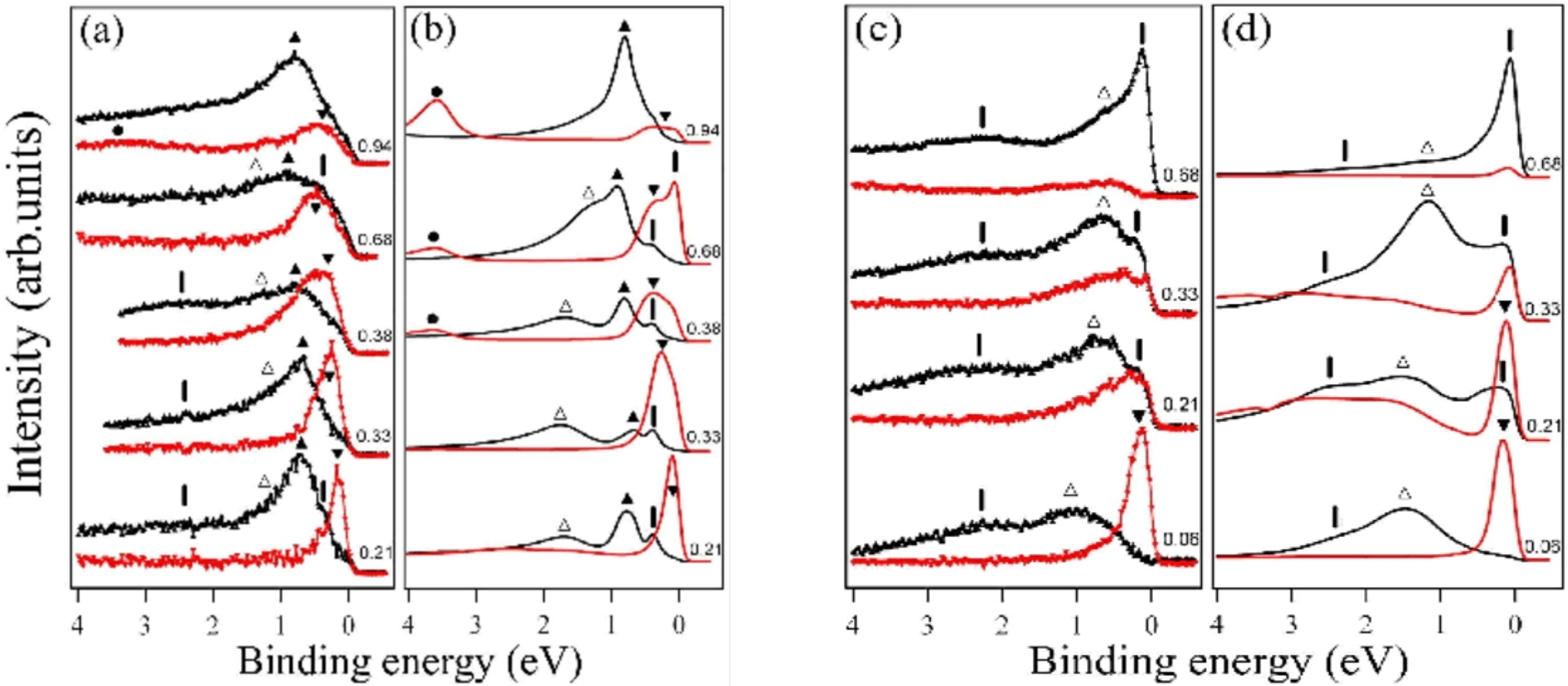
$$G^+(\vec{r}, \vec{r}\,', E) = \sum_{\Lambda\Lambda'} Z_\Lambda(\vec{r}, E) \, \tau^{nm}_{\Lambda\Lambda'}(E) \, Z^\times_{\Lambda}(\vec{r}\,', E) - \delta_{nm} \sum_{\Lambda} Z_\Lambda(\vec{r}_<, E) \, J^\times_\Lambda(\vec{r}_>, E)$$

Spin-resolved ARPES of Fe(110)

Spin-resolved ARPES intensity along $\overline{\Gamma N}$ obtained by one-step calculations

p-polarisation **s-polarisation**

Experiment **Theory** **Experiment** **Theory**



J. Sanchez-Barriga *et al.* PRL **103**, 267203 (2009)

Correlations via LSDA+DMFT

Electric field induced magnetic circular dichroism in X-ray absorption (EFI-XMCD)

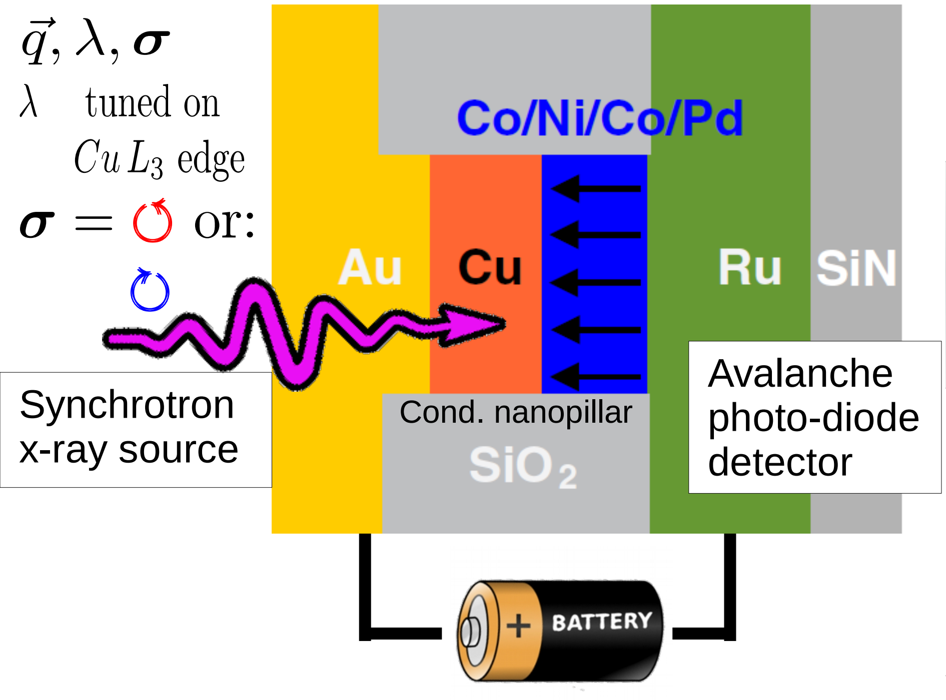
Sample & detector layout:

- Out-of-plane, large Co spin mag. moment;
- X-ray @ Cu L_3 absorption edge i.e. 932.7 [eV];
- Cu nanopillar DC resistance: R = $47\ [\Omega]$
- Cu DC current: $\pm 5[mA]$ i.e. EMF $\simeq \pm 0.235[V]$

$\vec{q}, \lambda, \boldsymbol{\sigma}$

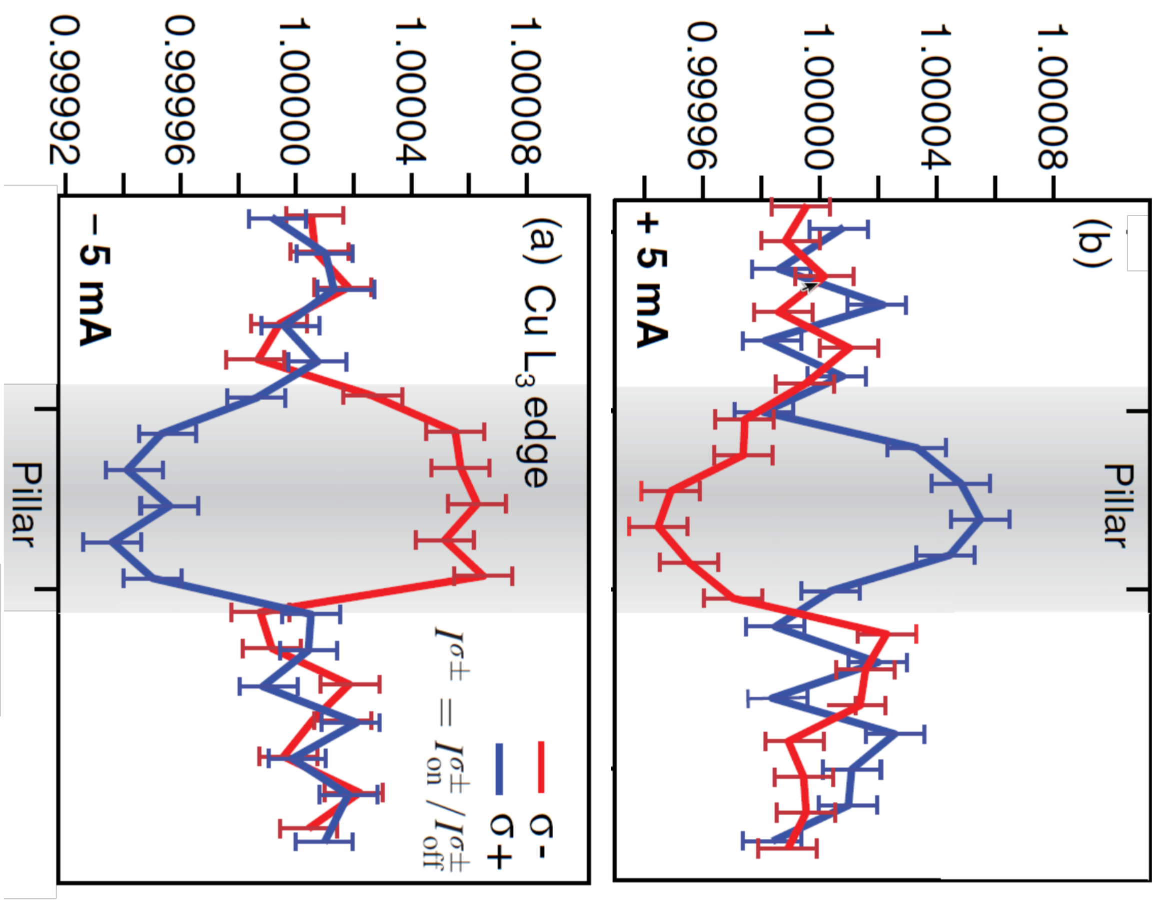
λ tuned on $Cu\, L_3$ edge

$\boldsymbol{\sigma} =$ ⟲ or: ⟳



Measured x-ray intensity: $I^{\sigma\pm} = I^{\sigma\pm}_{\text{on}} / I^{\sigma\pm}_{\text{off}}$

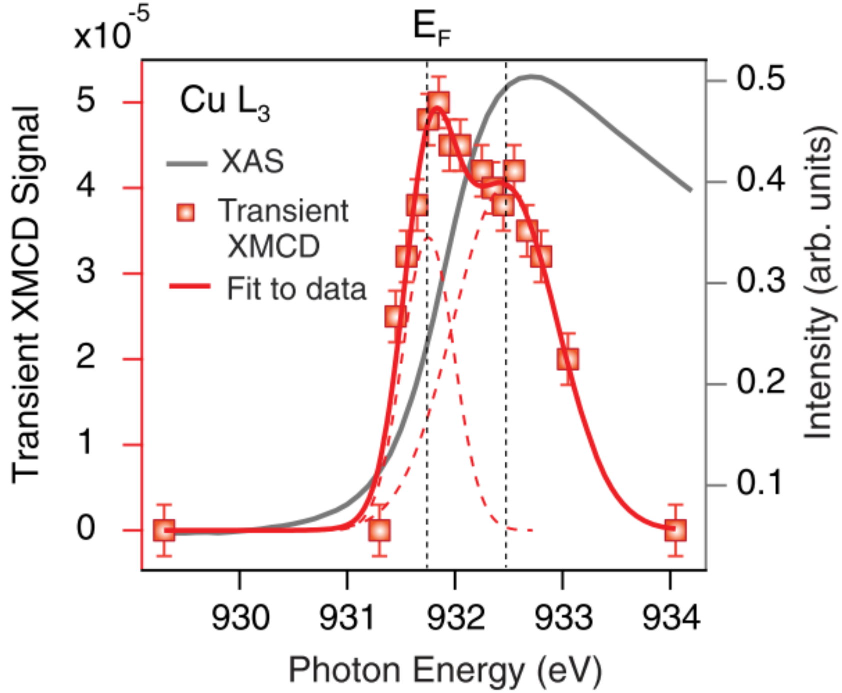
With "negative" DC current / With "positive" DC current



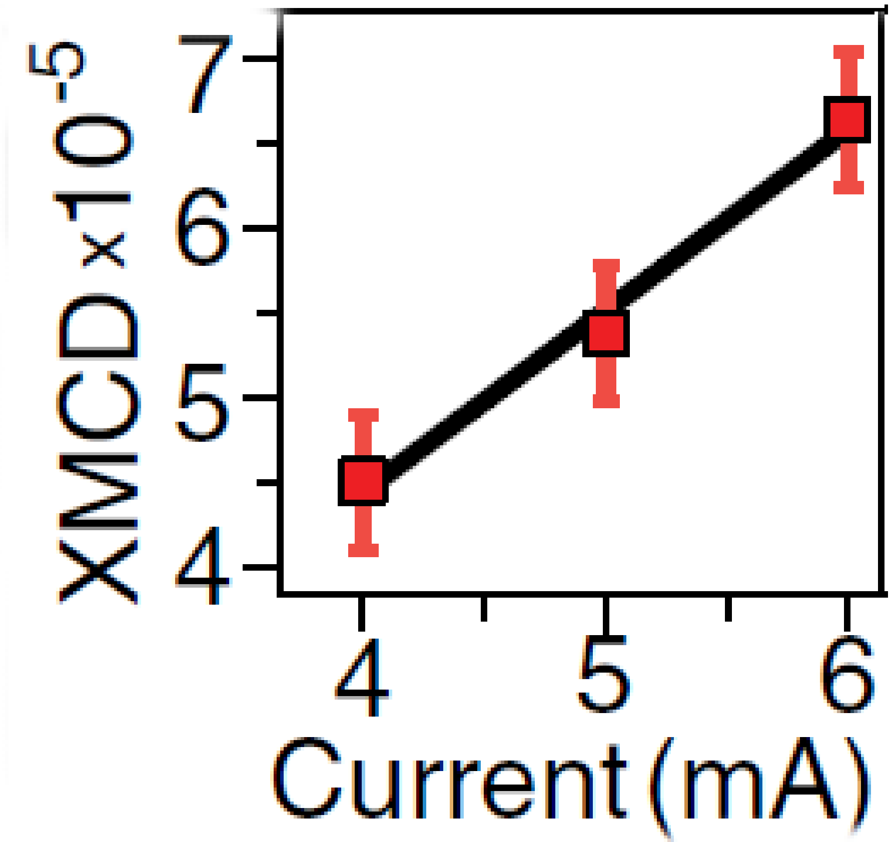
"X-ray Detection of Transient Magnetic Moments Induced by a Spin Current in Cu".
R.Kukreja *et al.*, Phys.Rev.Lett. 115, 096601 (2015)

Electric field induced XMCD of Cu in Co/Cu

Transient i.e. applied EMF -dependent spectral features, next to EFermi:

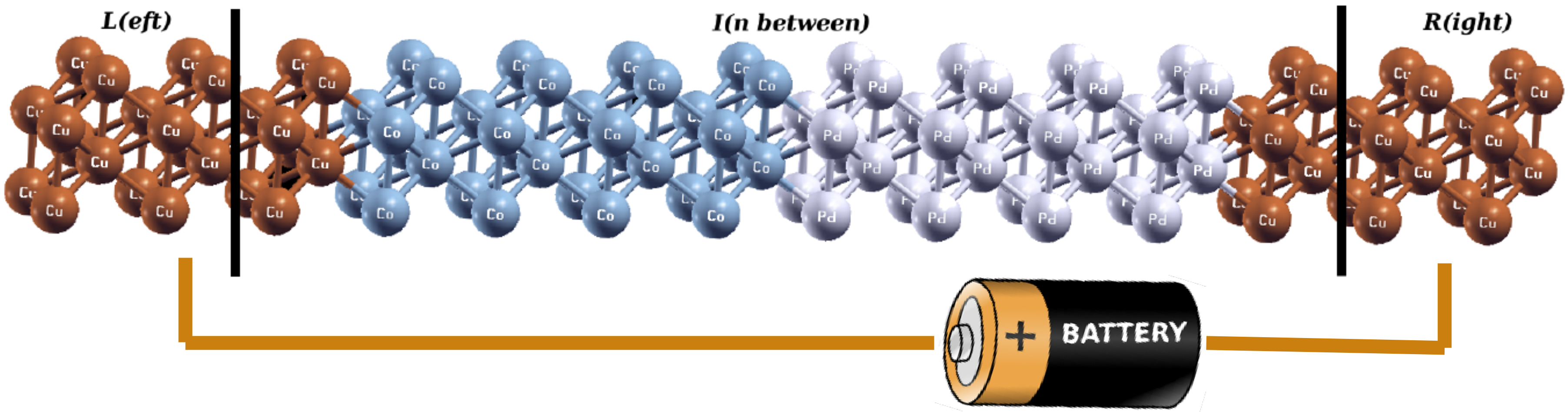


Linearity with voltage:
Ohm's law: EMF $\propto$ DC current

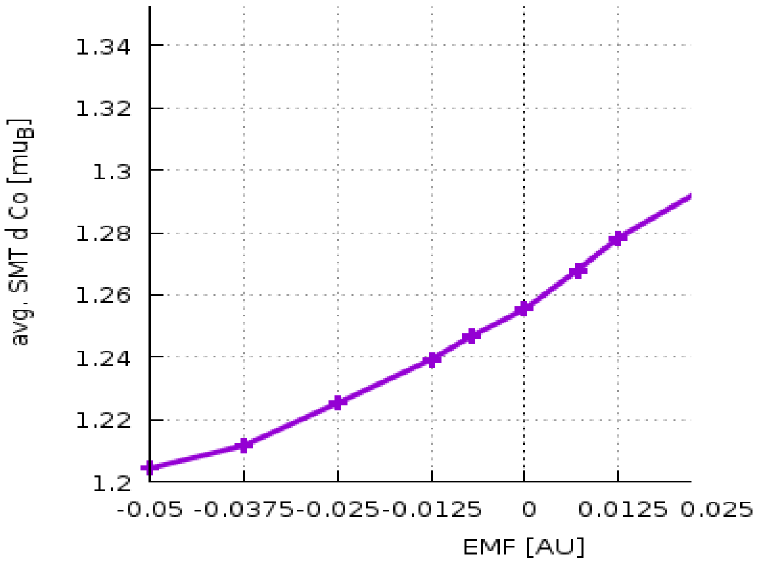


"X-ray Detection of Transient Magnetic Moments Induced by a Spin Current in Cu".
R.Kukreja *et al.*, Phys.Rev.Lett. 115, 096601 (2015)

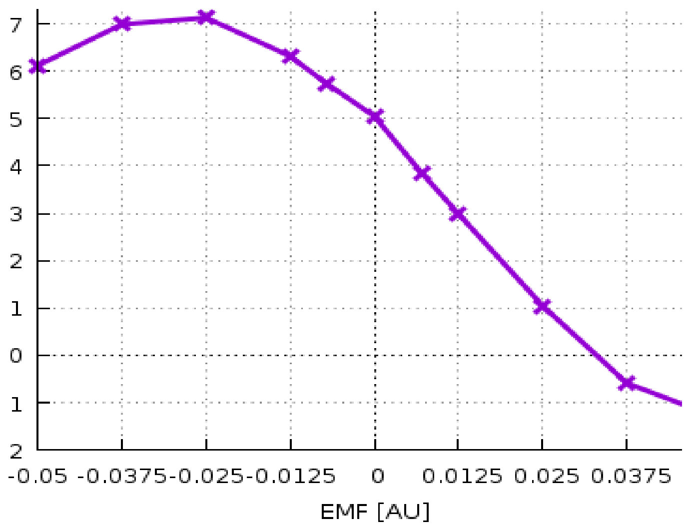
Spin magetic moments at a Co/Pd interface as a function of applied electric field



Cobalt:



Palladium:



Theoretical description of electric field induced (EFI) XMCD

XAS in terms of retarded Green function

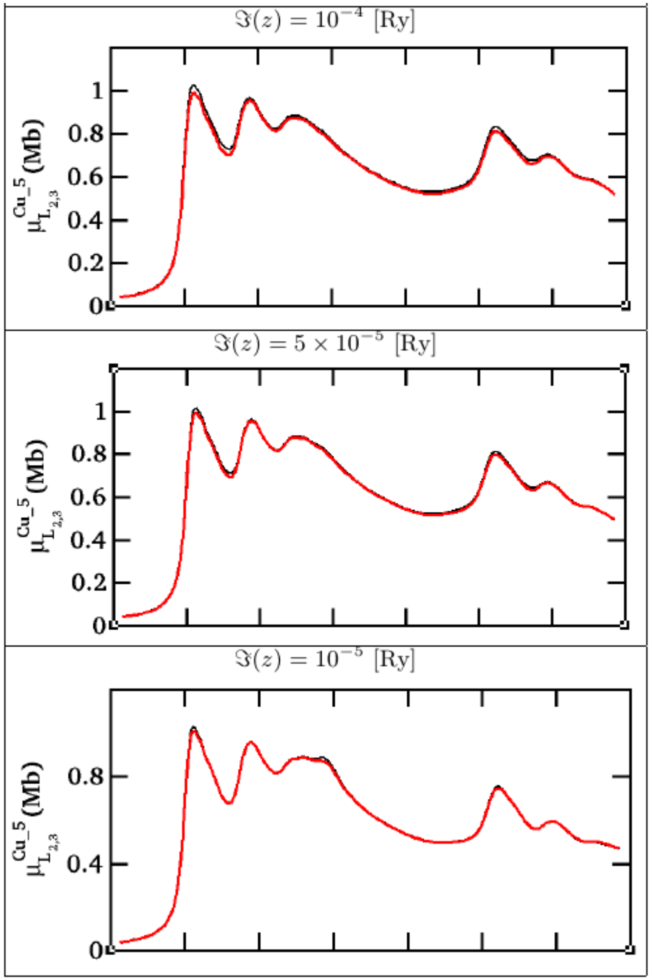
$$\mu^{\vec{q},\lambda}(\omega) \propto \sum_{g\in occ} \langle\Phi_g|X^{\dagger}_{\vec{q},\lambda}\Im\left(G^{+}(E_f)\right)X_{\vec{q},\lambda}|\Phi_g\rangle\theta\left(E_f - E_F\right)$$

XAS in terms of greater Green function

$$\mu^{\vec{q},\lambda}(\omega,\mathcal{V}) \propto \sum_{g\in occ} \langle\Phi_g|X^{\dagger}_{\vec{q},\lambda}G^{>}(E_f,\mathcal{V})X_{\vec{q},\lambda}|\Phi_g\rangle$$

•with static perturbation $\mathcal{V}$

Numerical test:
XAS of Cu calculated via retarded (black) and greater (read) Green function for $\mathcal{V}$=*0*



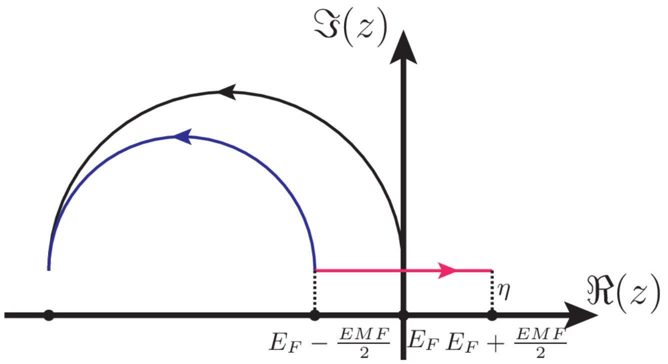
A. Marmodoro, H. Ebert, unpublished (2018)

Spin mag.moment vs. applied voltage EMF

in Spinmagnetic moment via direct calculation and XMCD sum rules

$$m^< = \int_{-\infty}^{+\infty} dE \, \left(n^{<,\uparrow}(E) - n^{<,\downarrow}(E)\right)$$

$$= \int_{-\infty}^{E_F - \frac{EMF}{2}} dz \, \left(n^{r,\uparrow}(z) - n^{r,\downarrow}(z)\right) + + \int_{E_F - \frac{EMF}{2}}^{E_F + \frac{EMF}{2}} dE \, \left(n^{<,\uparrow}(E) - n^{<,\downarrow}(E)\right)$$

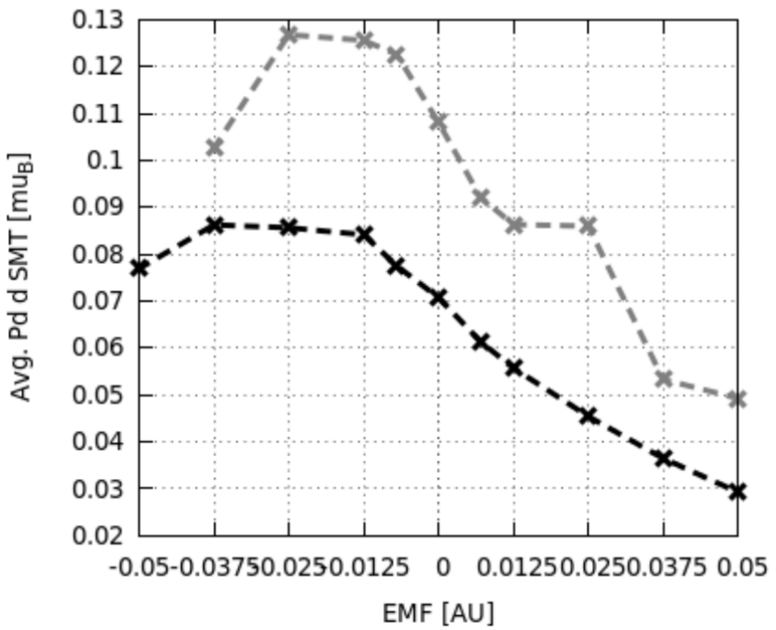


$$\frac{m^d + 7T_z^d}{3N_h^d} = \frac{\int_{E_F}^{E_{cutoff}} d\omega \, \left(\Delta\mu^{L_3}(\omega) - 2\Delta\mu^{L_2}(\omega)\right)}{\int_{E_F}^{E_{cutoff}} d\omega \, \left(\bar{\mu}^{L_3}(\omega) + \bar{\mu}^{L_2}(\omega)\right)}$$

Results for Pd at Co/Pd interface

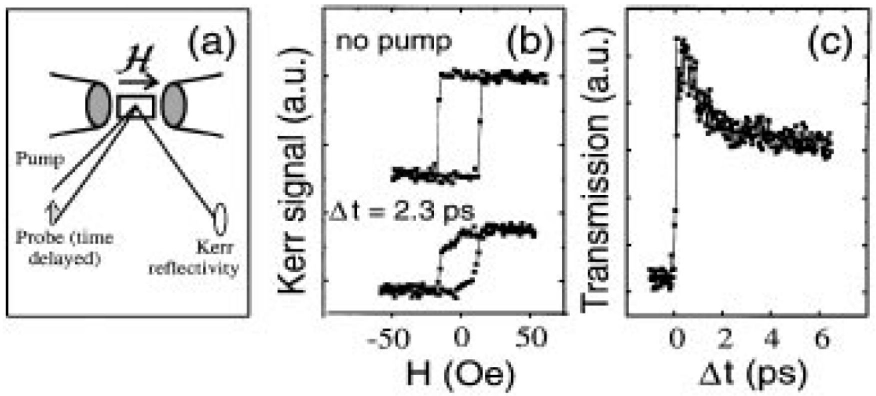
- **Black**: spin moment from lesser Green function
- Gray: XAS/XMCD sum rule from greater Green function

results agree in trend and order of magnitude

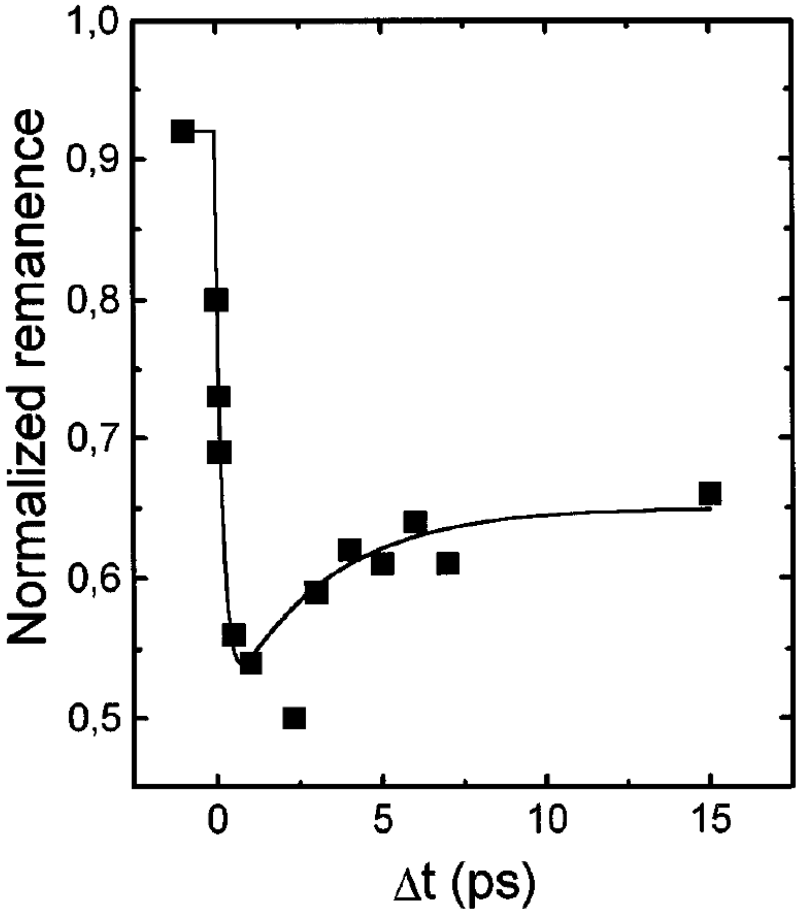


Detection of magnetization M(t) after laser pump pulse via longitudinal MOKE

Transient longitudinal MOKE signal
Ni(20 nm)/MgF2(100 nm) film



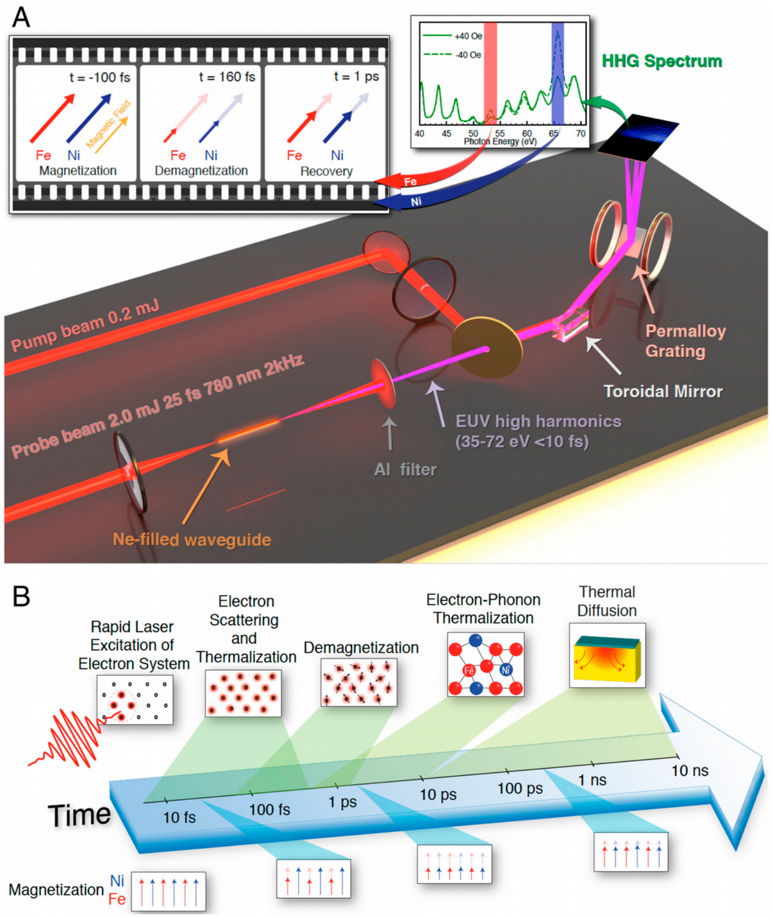
(a) Experimental pump-probe setup
(b) Kerr loop w/o and w/ pump beam with Δt = 2.3 ps
(c) Transient transmissivity



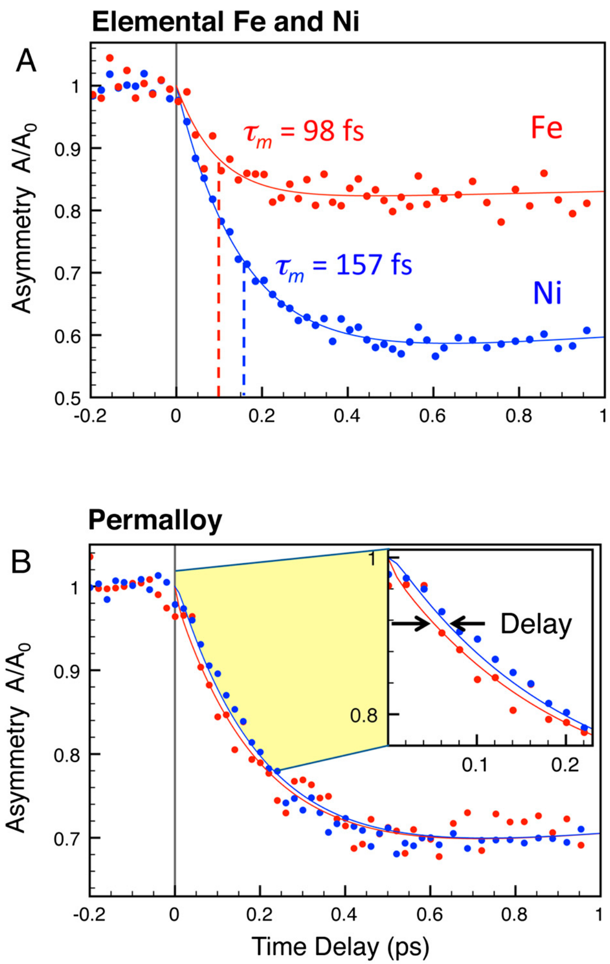
E. Beaurepaire *et al.*, PRL **76** 4250 (1996)

Probing the timescale of the exchange interaction in a ferromagnetic alloy

Element specific magnetization M(t) after laser pump pulse via transverse MOKE



Demagnetization times of Fe and Ni



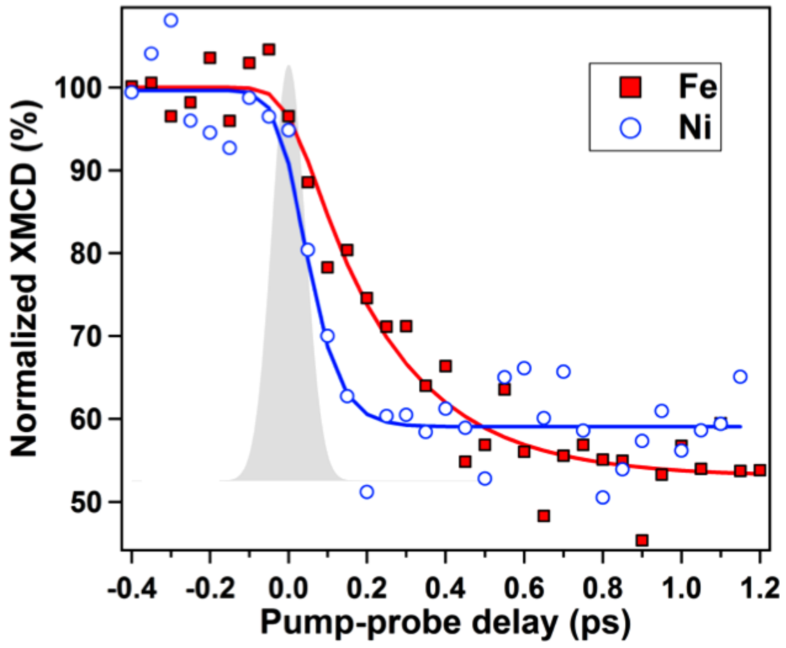
Same demagnetization time for Fe and Ni in permalloy

Mathias *et al.* PNAS **109**, 4792(2012)

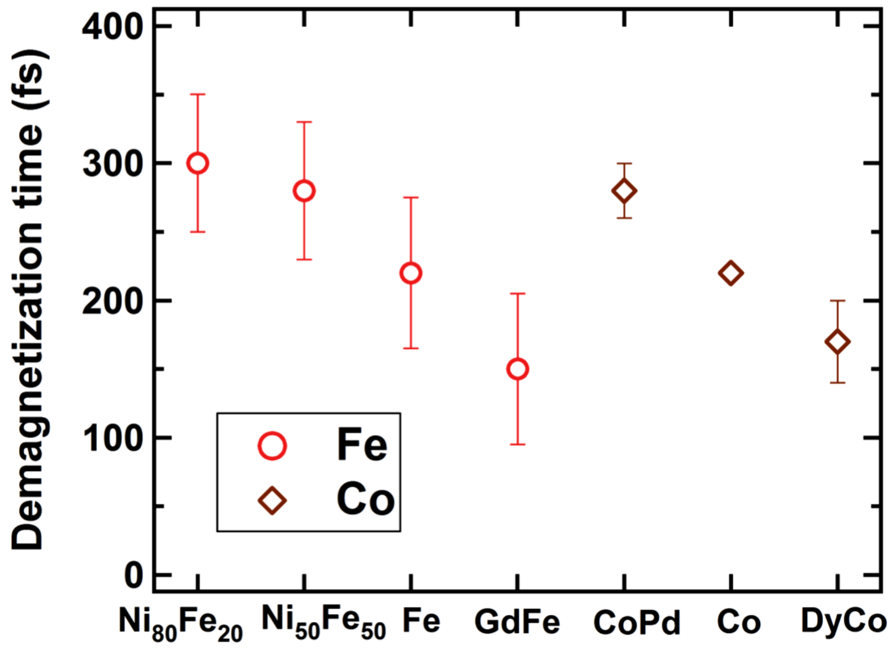
Ultrafast and Distinct Spin Dynamics in Magnetic Alloys

Element specific magnetization M(t) after laser pump pulse via XMCD

Ferromagnetic $Ni_{50}Fe_{50}$ probed at the Fe L_3 and Ni L_3 edges



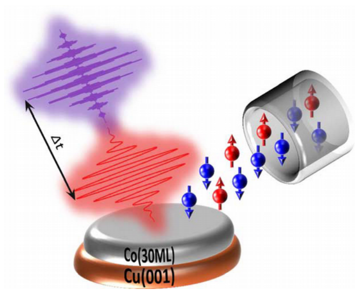
Demagnetization times of Fe and Co for different host alloys



Different demagnetization time for Fe and Ni in $Ni_{50}Fe_{50}$

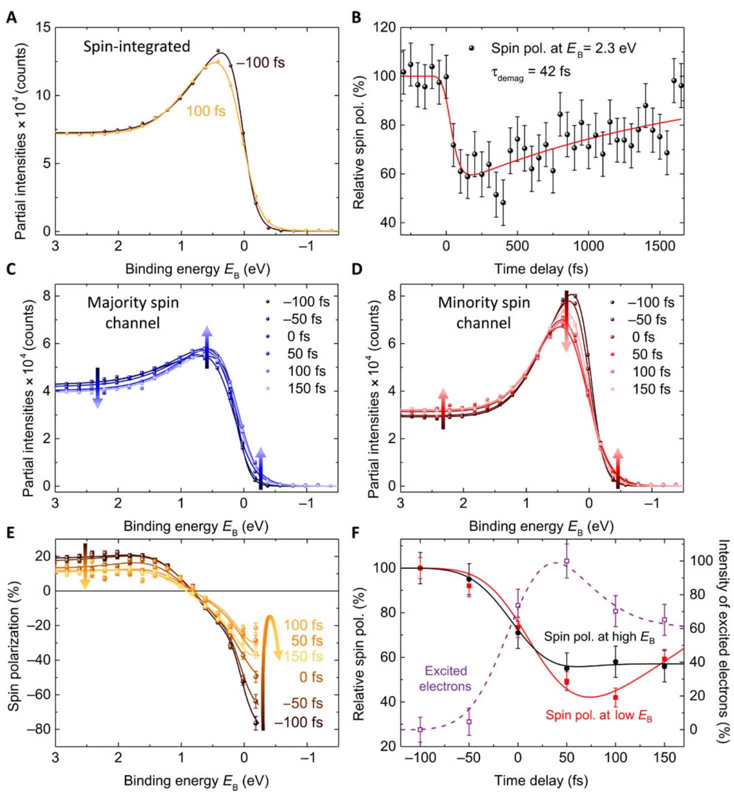
Radu *et al.*, SPIN **5**, 1550004 (2015)

Band structure evolution during the ultrafast ferromagnetic-paramagnetic phase transition in Co

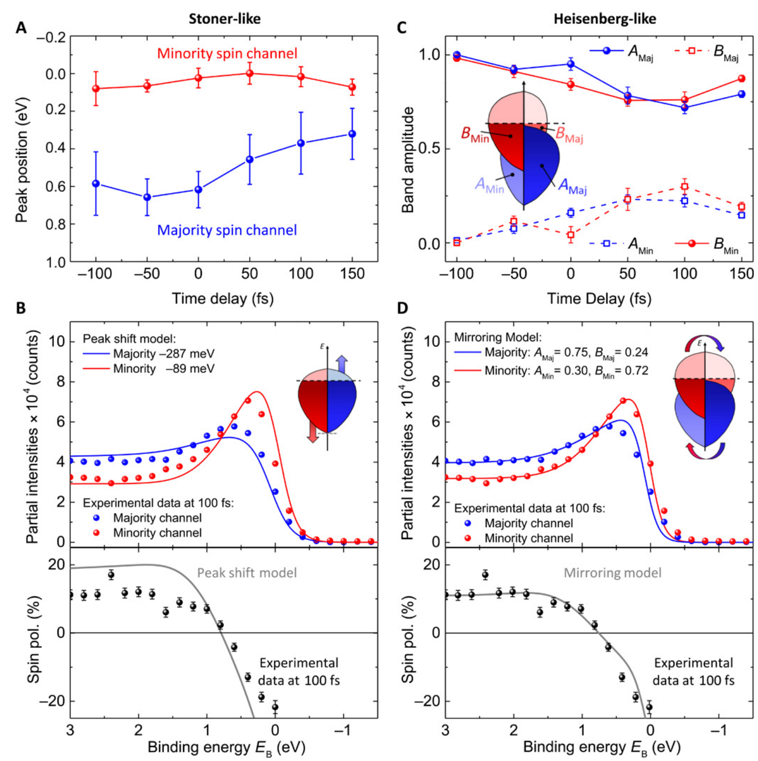


Probing exchange splitting after laser pump via spin- and angle-resolved photoemission

Spin-resolved photoemission spectra



Analysis of possible exchange collapse versus band mirroring



Eich *et al.*, Sci. Adv. **3** e1602094 (2017)

Time-dependent magnetisation reflected by exchange splitting

Very short history of time-resolved PES theory

Theory of pump-probe PES

Eckstein et al., Phys. Rev. B **78**, 245113 (2008)
Freericks et al., Phys. Rev. Lett. **102**, 136401 (2009)
M. Sentef et al., Phys. Rev. X **3**, 041033 (2013)

Two photon photo emission (2PPE) theory

C. Timm and H. Bennemann, J. Phys. Condens. Matter **16**, 661 (2004)
B. Gumhalter et al., Prog. Surf. Sci. **82**, 193 (2007)

Disadvantage: **Full many-body description not appropriate for real systems. Same situation as about 50 years ago with conventional PES**

Follow Pendry and describe initial state by the retarded one particle Green Function G^+

Advantage: **G^+ is accessable via KKR multiple scattering approach**

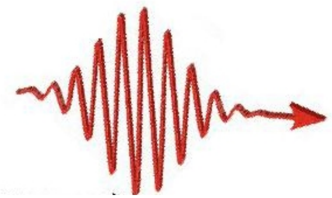
→ **photo current calculations for real systems get possible**

Theory of pump-probe photo emission in a *hazelnut shell*

Transition probability P(t) for a many particle state excited by a ***arbitrarily strong pump pulse***

$$P_k(t) = \sum_{m,n} p_m \, |\langle \Phi_n | a_k | \Psi_m(t) \rangle|^2$$

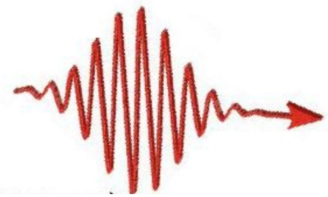
$$\mathcal{V}(t) = \sum_{\alpha\alpha'} V_{\alpha\alpha'}(t) c^\dagger_\alpha c_{\alpha'}$$



Using the ***sudden approximation*** Φ is seen as a many particle state of the rest system excluding the *high energy* electron

Time evolution of the initial state ψ due to subsequent ***probe pulse***

$$\mathcal{W}(t) = s_{\mathcal{W}}(t) \sum_{k,\alpha} M_{k\alpha} a^\dagger_k c_\alpha$$



$$|\Psi_m(t)\rangle = \mathcal{U}_1(t, -\infty) |\Psi_m\rangle$$

with $\mathcal{U}_1(t,t') = \mathcal{T} \exp\left(-i \int_{t'}^{t} d\tau \, [\mathcal{H}_{\rm tot}(\tau) + \mathcal{W}(\tau)] \right)$

First order perturbation theory w.r.t. probe pulse

$$P_k(t) = \sum_{\alpha\beta} M^*_{k\beta} \, M_{k\alpha} \int_{t_0}^{t} dt' s_{\mathcal{W}}(t') \int_{t_0}^{t} dt'' s_{\mathcal{W}}(t'') \, e^{-i\varepsilon(k)(t'-t'')} \underbrace{\left\langle c^\dagger_\beta(t') \, c_\alpha(t'') \right\rangle}_{-iG^<(t',t'')}$$

Lesser Keldysh Green function

Time-dependent pump-probe PES

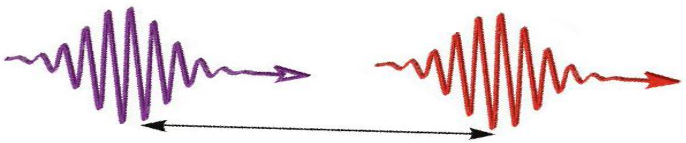
Pump pulse

$$V(r,t) = -s_{\mathcal{V}}(t)\alpha \cdot \mathbf{A}_{0\mathcal{V}}$$

Probe pulse

treated via perturbation theory

$$W(r,t) = W(t) = -s_{\mathcal{W}}(t)\alpha \cdot \mathbf{A}_{0\mathcal{W}}$$



$$\text{delay } \tau$$

Time-dependent transition probability for *arbitrarily strong* pump pulses

$$P_k(t) = \int d^3r' \int d^3r'' \int_{t_0}^{t} dt' \int_{t_0}^{t} dt''\, e^{-i\varepsilon(k)(t'-t'')}\, \phi_k^\dagger(r')\ W(t')\ G^<(r',t',r'',t'')\ W^\dagger(t'')\ \phi_k(r'')$$

J. Braun, R. Rausch, M. Potthoff, J. Minar and H. Ebert, Phys. Rev B **91**, 035119 (2015)
See also: Freericks et al. Phys. Rev. Lett. **102**, 136401 (2009)

Time-dependent pump-probe PES
Relation to conventional one-step model

Pump pulse

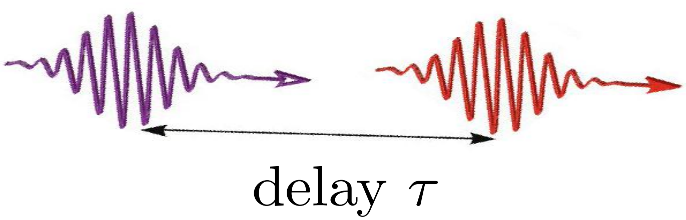
$$V(r,t) = -s_{\mathcal{V}}(t)\alpha \cdot \mathbf{A}_{0\mathcal{V}}$$

Probe pulse

treated via perturbation theory

$$W(r,t) = W(t) = -s_{\mathcal{W}}(t)\alpha \cdot \mathbf{A}_{0\mathcal{W}}$$

$$s_{\mathcal{V}}(t) = 0$$



Time-dependent transition probability for *arbitrarily strong* pump pulses

$$P_k(t) = \int d^3r' \int d^3r'' \int_{t_0}^{t} dt' \int_{t_0}^{t} dt'' \, e^{-i\varepsilon(k)(t'-t'')} \, \phi_k^\dagger(r') \;\; W(t') \;\; G^<(r',t',r'',t'') \;\; W^\dagger(t'') \;\; \phi_k(r'')$$

No pump pulse and CW probe: $s_{\mathcal{V}}(t) = 0 \quad s_{\mathcal{W}}(t) = 1 \quad t_0 \to -\infty \quad t \to +\infty$

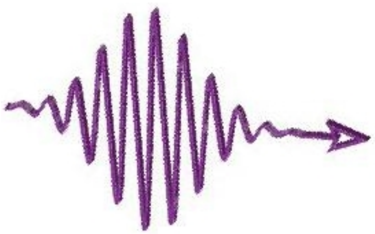
Conventional one-step model of photo emission

$$P_k(E_f) \propto \int d^3r' \int d^3r'' \, \phi_k^\dagger(r', E_f) \;\; W \left[G^+(r',r'',E_i) - G^-(r',r'',E_i) \right] W^\dagger \, \phi_k(r'', E_f)$$

Calculation of the lesser Green function

$G^<$ describes the time evolution of the system in response to the pump pulse

Pump pulse $$V(r,t) = -s_{\mathcal{V}}(t)\alpha \cdot \mathbf{A}_{0\mathcal{V}}$$



Interaction free case

$$G^<(r,t,r',t') = i\int dE\, f_T(E)\int d^3r_1 \int d^3r_2\, G^+(r,t,r_1,t_0)\, \Im G_0^+(r_1,r_2,E)\, G^-(r_2,t_0,r',t')$$

G. Stefanucci and R. van Leuween, Nonequilibrium Many-Body Theory of Quantum Systems (2013)

Dyson equation for the retarded Keldysh Green function

$$G^+(r,t,r',t') = G_0^+(r,t,r',t') - \int_{t'}^{t} dt_1 s_{\mathcal{V}}(t_1) \int d^3r_1\, G_0^+(r,t,r_1,t_1)\, \alpha \cdot \mathbf{A}_{0\mathcal{V}}\, G^+(r_1,t_1,r',t')$$

$$G^-(r,t,r',t') = \left(G^+(r',t',r,t)\right)^\dagger$$

$G^<$ can be traced back to the retarded single particle Green function G^+

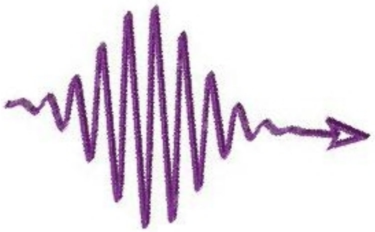
J. Braun, R. Rausch, M. Potthoff, J. Minar and H. Ebert, Phys. Rev B **91**, 035119 (2015)
J. Braun, R. Rausch, M. Potthoff, and H. Ebert, PRB **94,** 125128 (2016)

Calculation of the lesser Green function via KKR multiple scattering formalism

LMU LUDWIG-MAXIMILIANS-UNIVERSITÄT MÜNCHEN

$G^<$ describes the time evolution of the system in response to the pump pulse

Pump pulse $V(r,t) = -s_{\mathcal{V}}(t)\alpha\cdot\mathbf{A}_{0\mathcal{V}}$



Interaction free case

$$G^<(r,t,r',t') = i\int dE\, f_T(E)\int d^3r_1\int d^3r_2\; G^+(r,t,r_1,t_0)\,\boxed{\Im G_0^+(r_1,r_2,E)}\,G^-(r_2,t_0,r',t')$$

Dyson equation for the retarded Keldysh Green function

$$G^+(r,t,r',t') = \boxed{G_0^+(r,t,r',t')} - \int_{t'}^{t} dt_1 s_{\mathcal{V}}(t_1)\int d^3r_1\,\boxed{G_0^+(r,t,r_1,t_1)}\,\alpha\cdot\mathbf{A}_{0\mathcal{V}}\,G^+(r_1,t_1,r',t')$$

KKR representation **of the** **retarded single particle Green function**

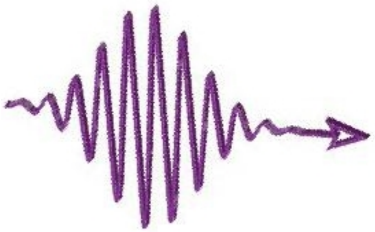
$$\boxed{G_0^+(\vec{r},\vec{r}\,',E)} = \sum_{\Lambda\Lambda'} Z_\Lambda(\vec{r},E)\,\tau^{nm}_{\Lambda\Lambda'}(E)\,Z^\times_{\Lambda}(\vec{r}\,',E) - \delta_{nm}\sum_{\Lambda} Z_\Lambda(\vec{r}_<,E)\,J^\times_\Lambda(\vec{r}_>,E)$$

J. Braun, R. Rausch, M. Potthoff, J. Minar and H. Ebert, Phys. Rev B **91**, 035119 (2015)
J. Braun, R. Rausch, M. Potthoff, and H. Ebert, PRB **94,** 125128 (2016)

Calculation of the lesser Green function
linear approximation for weak pump pulse

$G^<$ describes the time evolution of the system in response to the pump pulse

Pump pulse $V(r,t) = -s_{\mathcal{V}}(t)\alpha \cdot \mathbf{A}_{0\mathcal{V}}$



Interaction free case

$$G^<(r,t,r',t') = i\int dE\, f_T(E) \int d^3r_1 \int d^3r_2\; G^+(r,t,r_1,t_0)\;\; \Im G_0^+(r_1,r_2,E)\;\; G^-(r_2,t_0,r',t')$$

Linear approximation **to Dyson equation for the retarded Keldysh Green function**

$$G^+(r,t,r',t') = G_0^+(r,t,r',t') - \int_{t'}^{t} dt_1 s_{\mathcal{V}}(t_1) \int d^3r_1\, G_0^+(r,t,r_1,t_1)\,\alpha \cdot \mathbf{A}_{0\mathcal{V}}\, G_0^+(r_1,t_1,r',t')$$

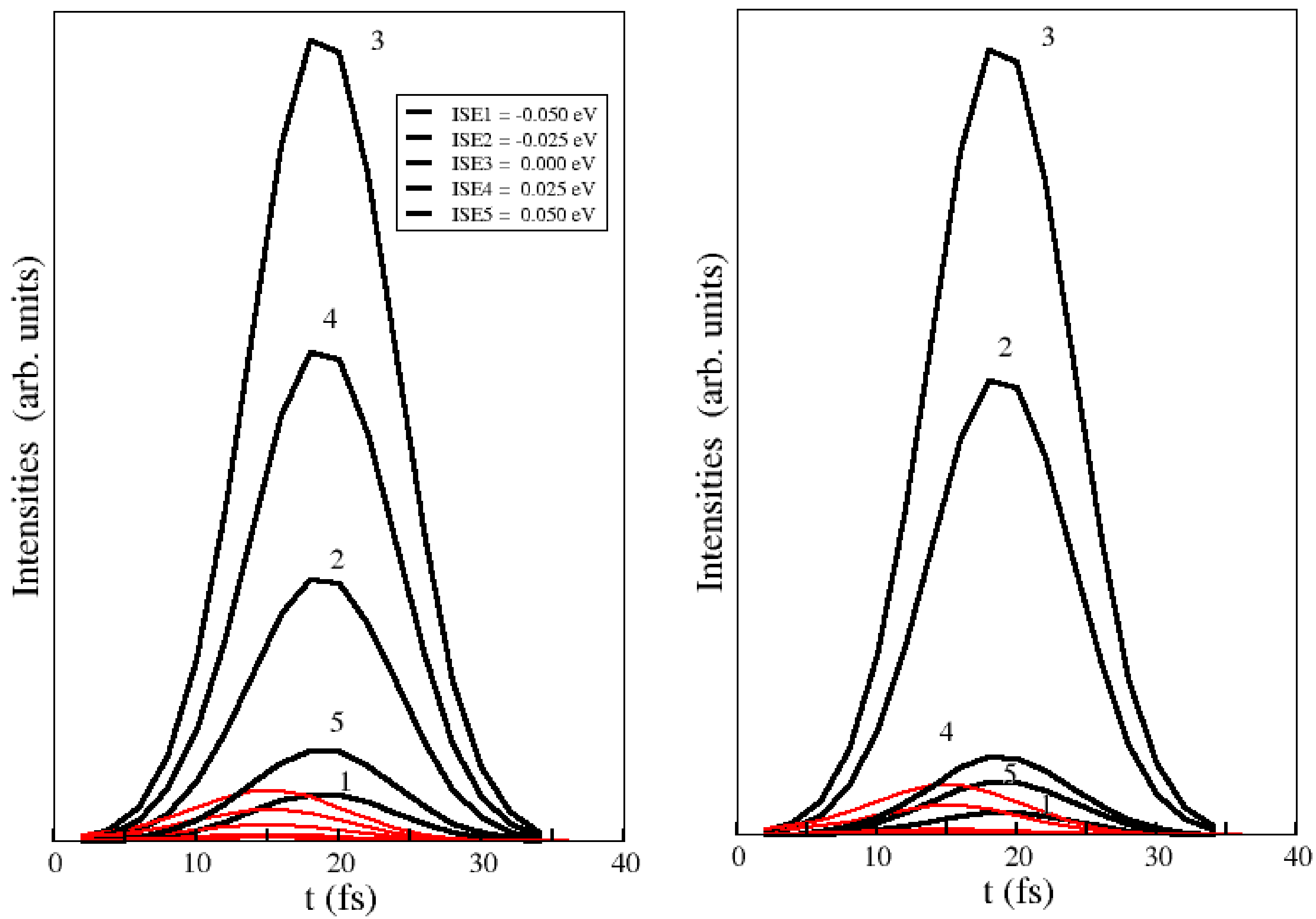
KKR representation of the retarded single particle Green function

$$G_0^+(\vec{r},\vec{r}\,',E) = \sum_{\Lambda\Lambda'} Z_\Lambda(\vec{r},E)\,\tau^{nm}_{\Lambda\Lambda'}(E)\,Z^\times_{\Lambda}(\vec{r}\,',E) - \delta_{nm}\sum_{\Lambda} Z_\Lambda(\vec{r}_<,E)\,J^\times_\Lambda(\vec{r}_>,E)$$

J. Braun, R. Rausch, M. Potthoff, J. Minar and H. Ebert, Phys. Rev B **91**, 035119 (2015)
J. Braun, R. Rausch, M. Potthoff, and H. Ebert, PRB **94,** 125128 (2016)

Time-dependent photo current P(t) at different binding energies of the initial state

Majority spin — Co(100) — Minority spin



Normal emission

$h\nu_{pump}$ = 4.3 eV

$h\nu_{probe}$ = 3.0 eV

Linear p-pol light

Pump pulse with Gaussian profile $FWHM_{pump}$ = 12 fs

Probe pulse with Gaussian profile $FWHM_{probe}$ = 12 fs

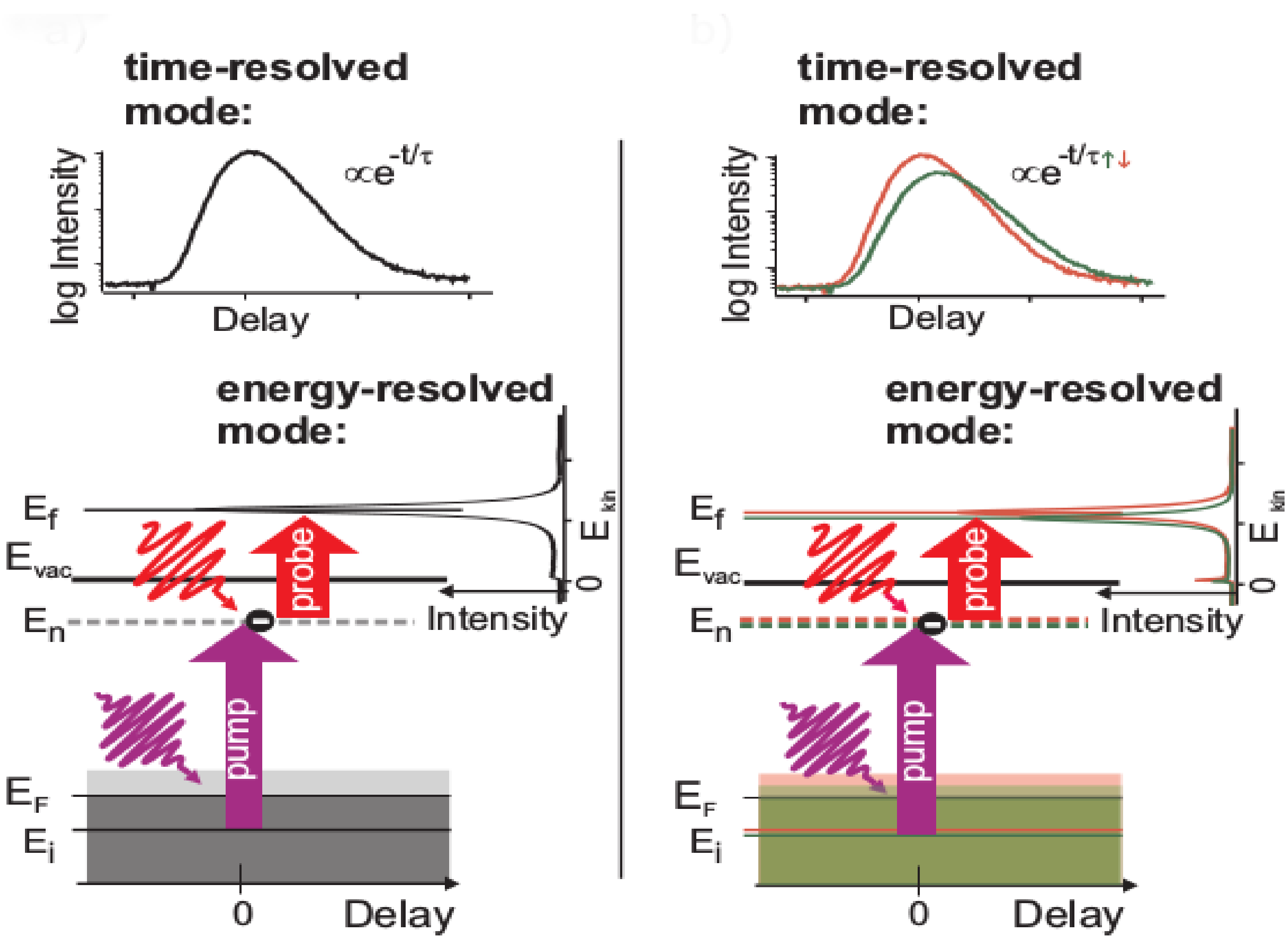
Pump-probe delay is fixed to 12 fs

Black color: PES^0 contribution

Red color: first order perturbation

J. Braun and H. Ebert (2017)

Two Photon Photo emission (2PPE)
excitation scheme and operational modes



M. Pickel, PhD thesis (2007)

Image-potential surface states

Formation and wave functions of image-potential surface states

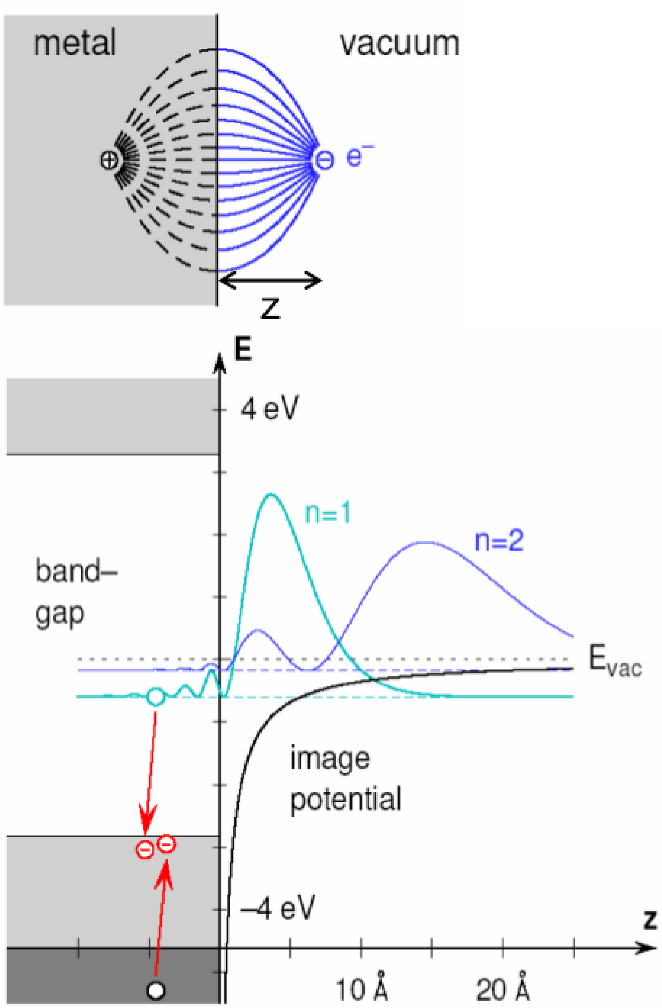
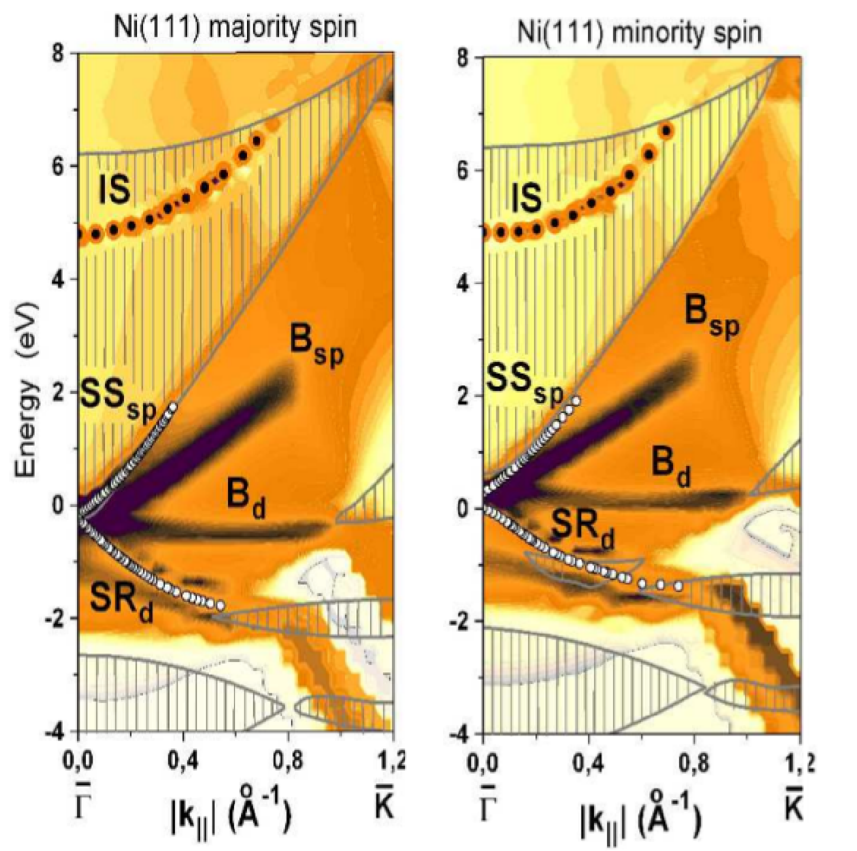


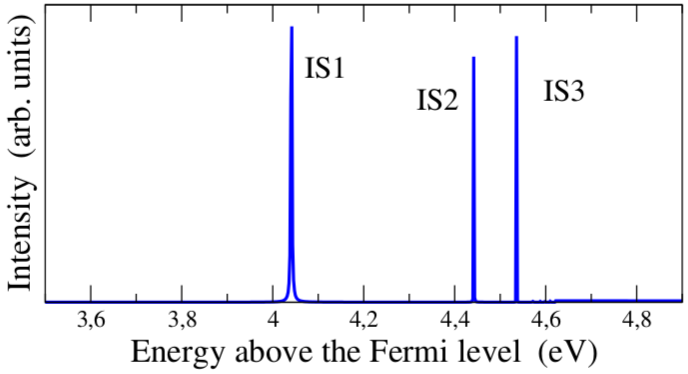
Image-potential states (IS) on Ni(111) in the band gap of the projected band structure



J. Braun and M. Donath, EPL **59**, 592 (2002)

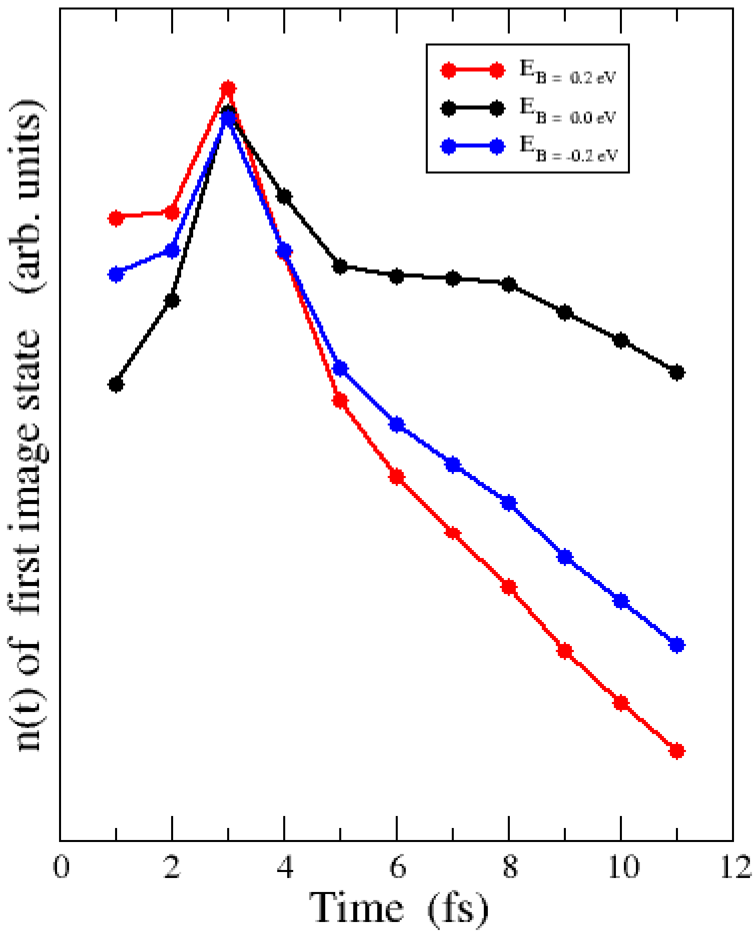
Time-dependent particle number: Ag(100) image states and response to pump pulse

First 3 ***image-potential states*** calculated for Ag(100)



Time-dependent particle number N(t)

$$N(t) = -\frac{1}{\pi}\,\Im\,\mathrm{Trace}\,i\int_{\mathrm{IS}} G^{<}(r,t,r,t)$$



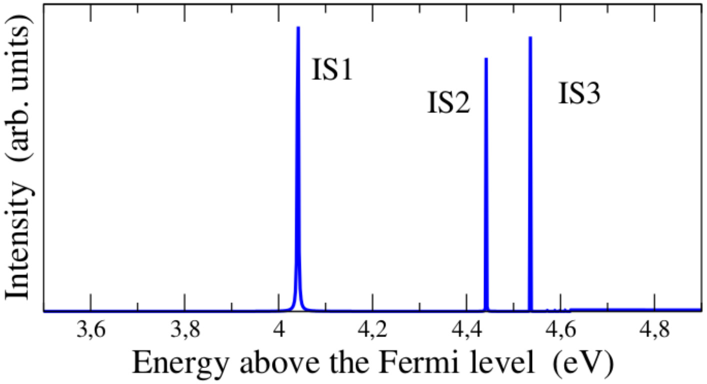
Pump pulse:

Linearly p-polarized
hν = 3 eV
Gaussian profile
with FWHM = 5 fs

Black curve for E_B=0.0 eV
Corresponds in energy to maximum
Population of the first image state

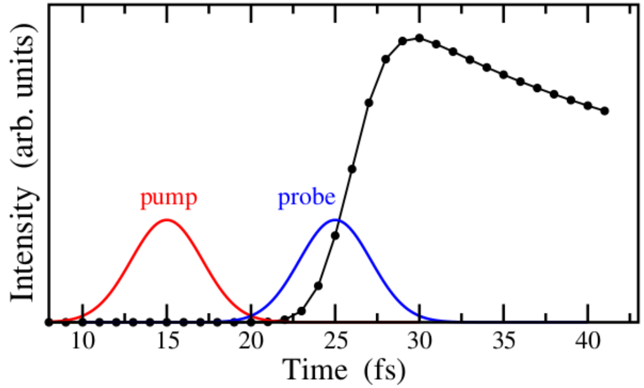
2PPE calculations on Ag(100) time-dependent photo current intensity

Image-potential states



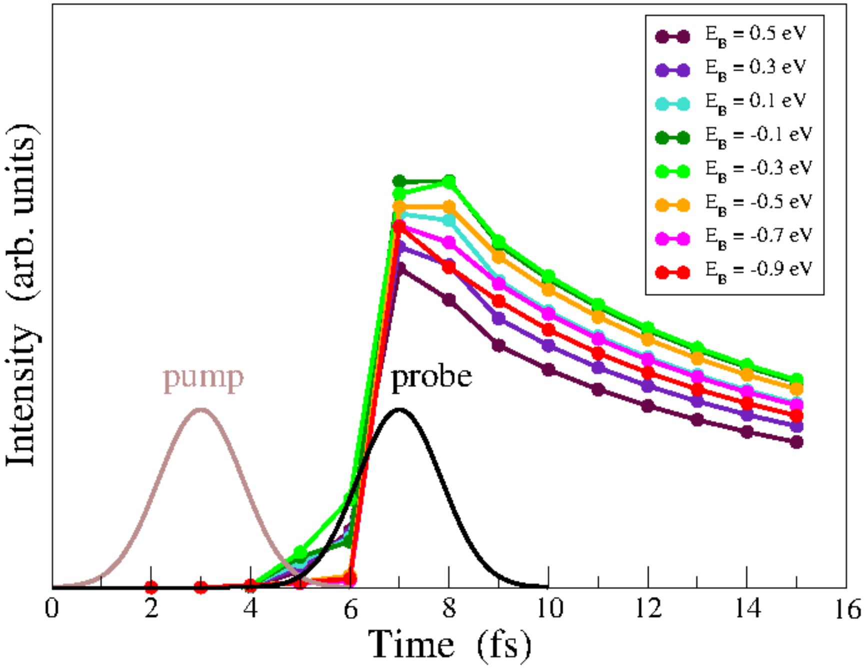
Intensity rate P(t):

Linear p-polarized light
Single pump-probe delay Photon energies of pump and probe pulse hν = 3 eV
Gaussian profiles with FWHM = 5 fs



Intensity rates P(t) for energy-resolved mode as a function of binding energy:

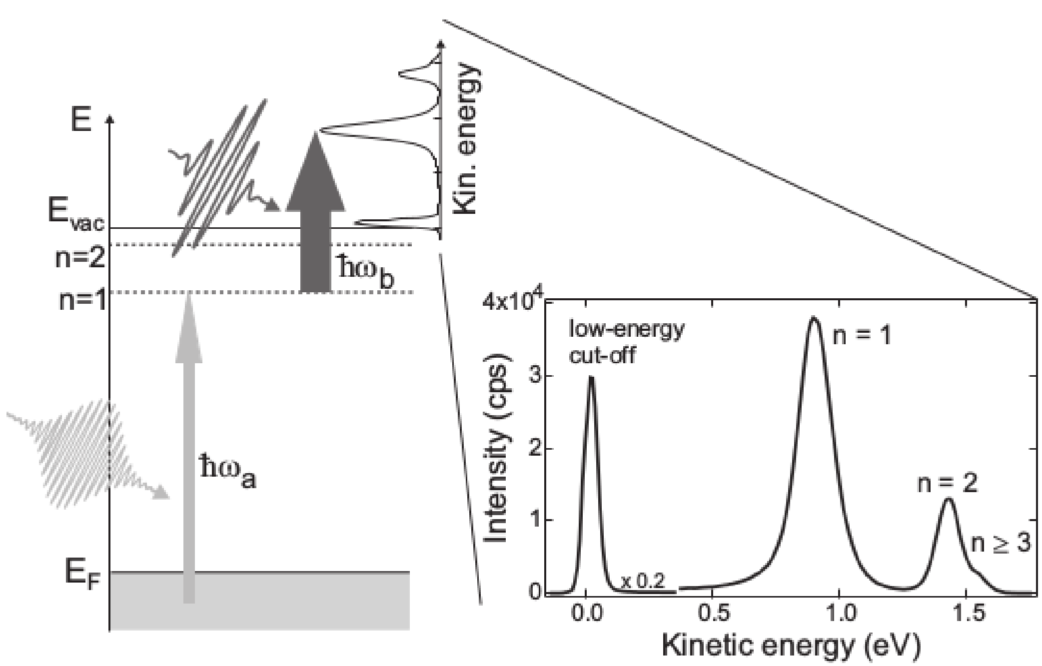
Linear p-polarized light
Pump pulse: hν = 4 eV
Probe pulse: hν = 2 eV
Gaussian profiles with FWHM = 2 fs
Pump-probe delay is fixed to 4 fs



J. Braun, R. Rausch, M. Potthoff, and H. Ebert, PRB **94,** 125128 (2016)

2PPE calculations on Ag(100): energy-resolved mode

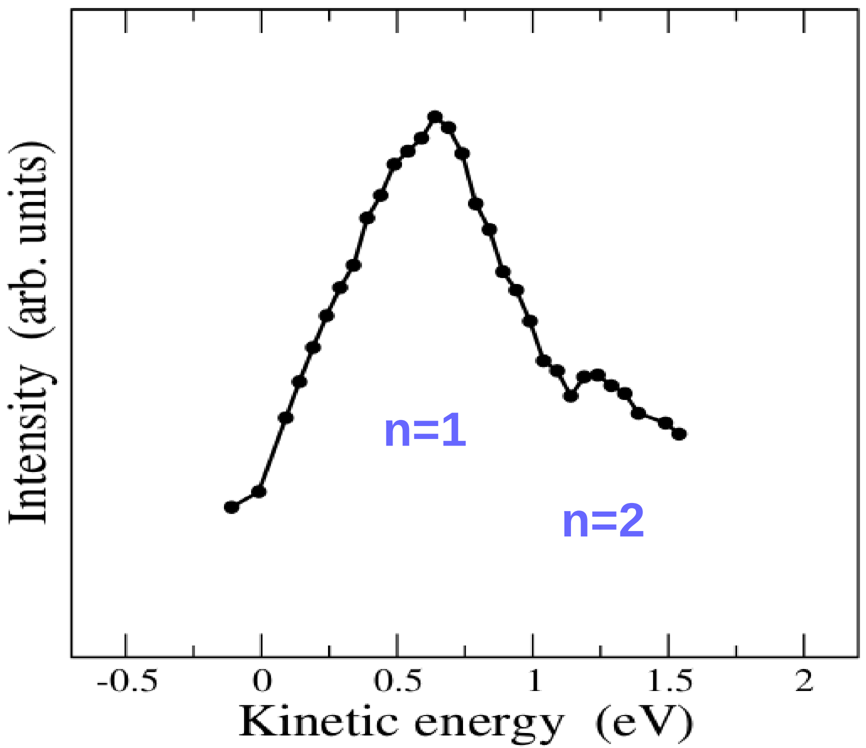
Scheme for of 2PPE in energy-resolved mode



A. B. Schmidt, PhD thesis (2007)

Integrated intensity rate as a function of the binding energy

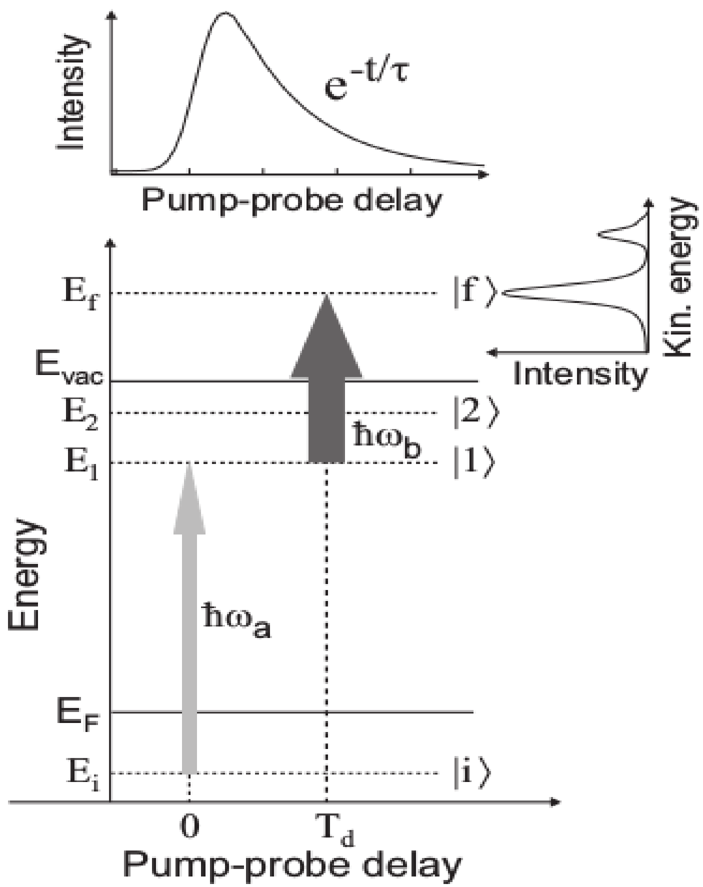
- fixed pump-probe delay of 4 fs



J. Braun, R. Rausch, M. Potthoff, and H. Ebert, PRB **94**, 125128 (2016)

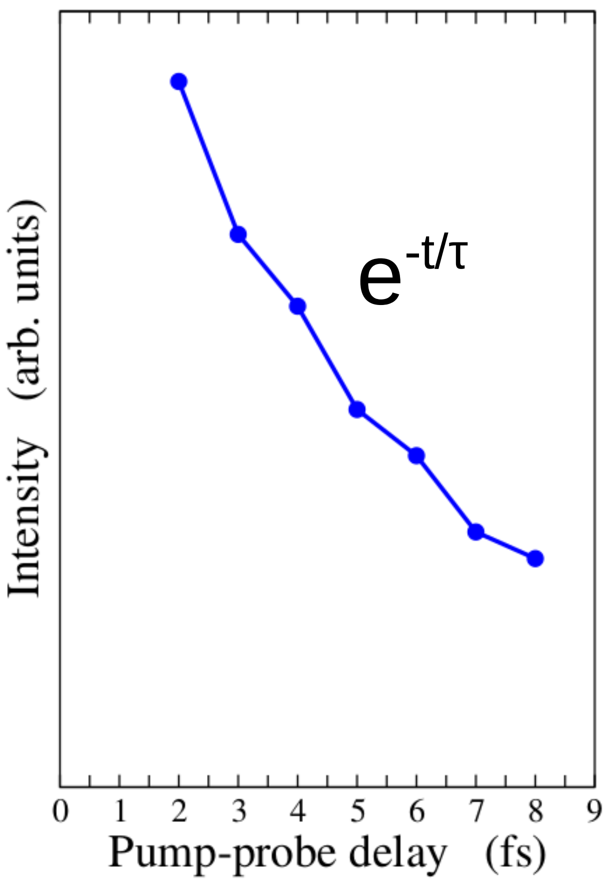
2PPE calculations on Ag(100): pump-probe delay mode

Scheme of 2PPE in pump-probe delay mode
measurement of the decay time τ



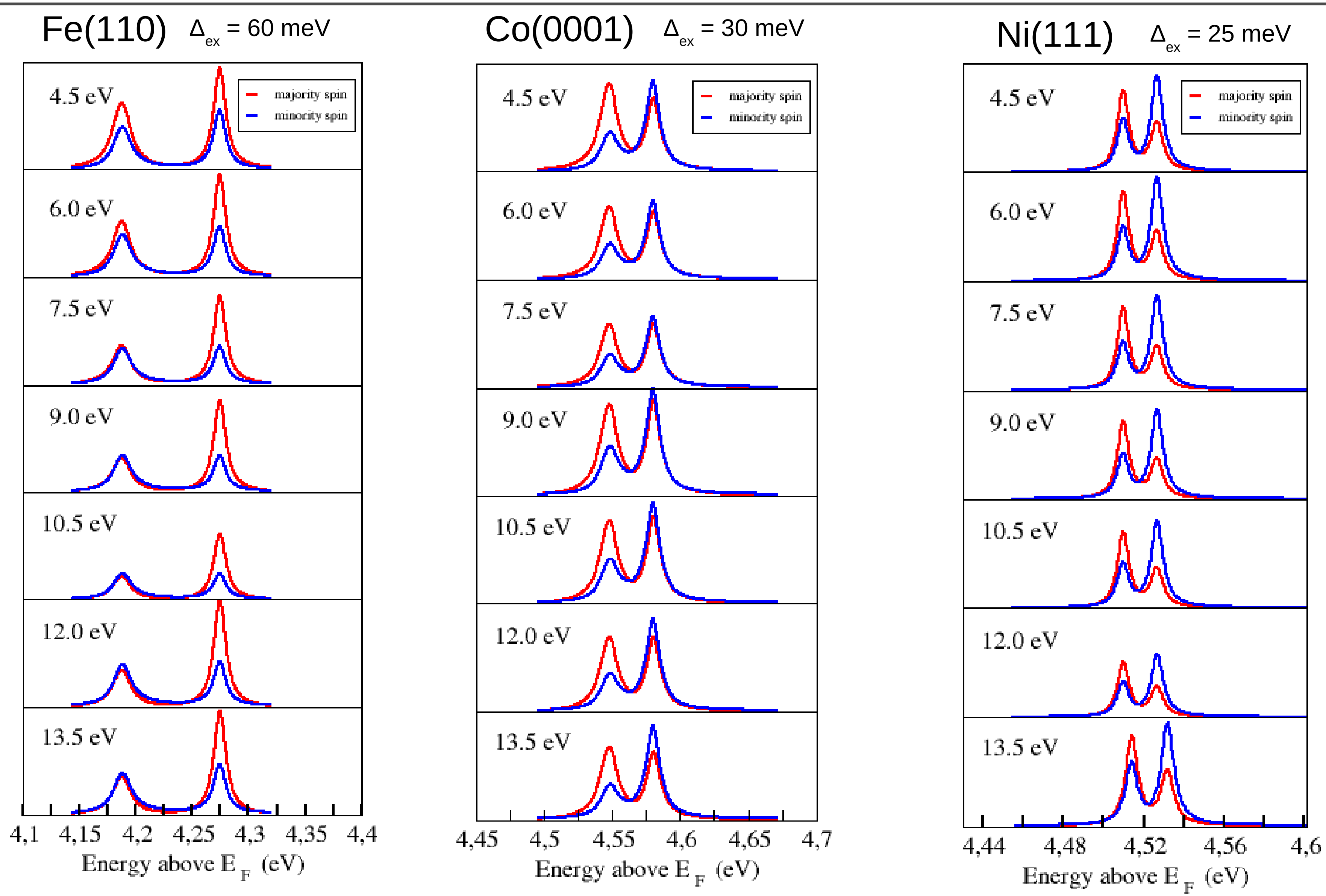
A. B. Schmidt, Ph.D. thesis (2007)

Calculated Intensities for Ag(100) as a function of the time-delay between pump- and probe pulses



J. Braun and H. Ebert (2017)

SP-ARPES in normal emission from the first image states of Fe, Co and Ni as a function of the photon energy

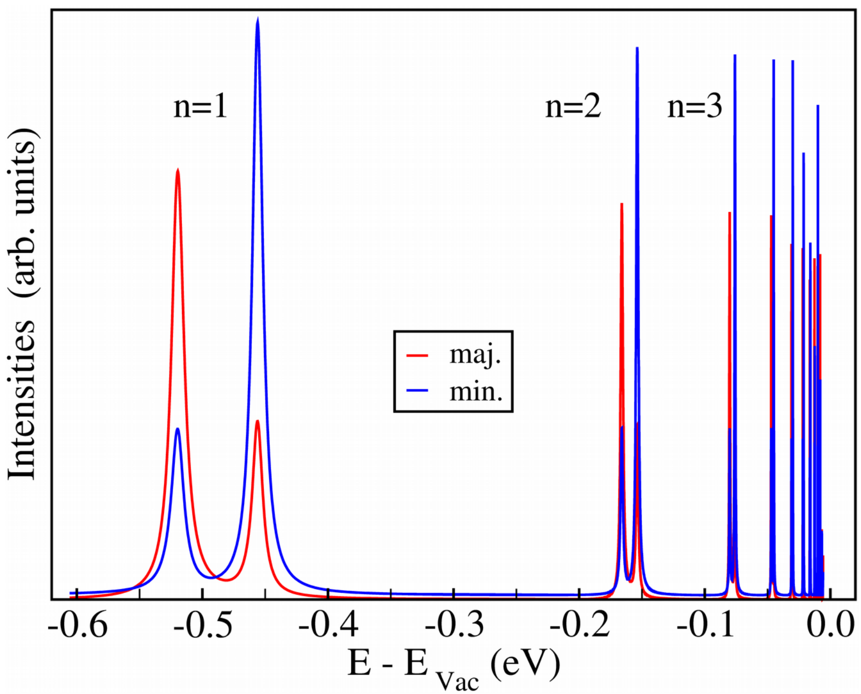


Theory: Incomplete spin-polarization due to SOC Exp.: 100% spin-polarization is assumed

J. Braun and H. Ebert (2019)

IPE and 2PPE on fcc Fe(100): Theory and Experiment

Calculated spin-resolved IPE spectra of image states on fcc Fe(100)



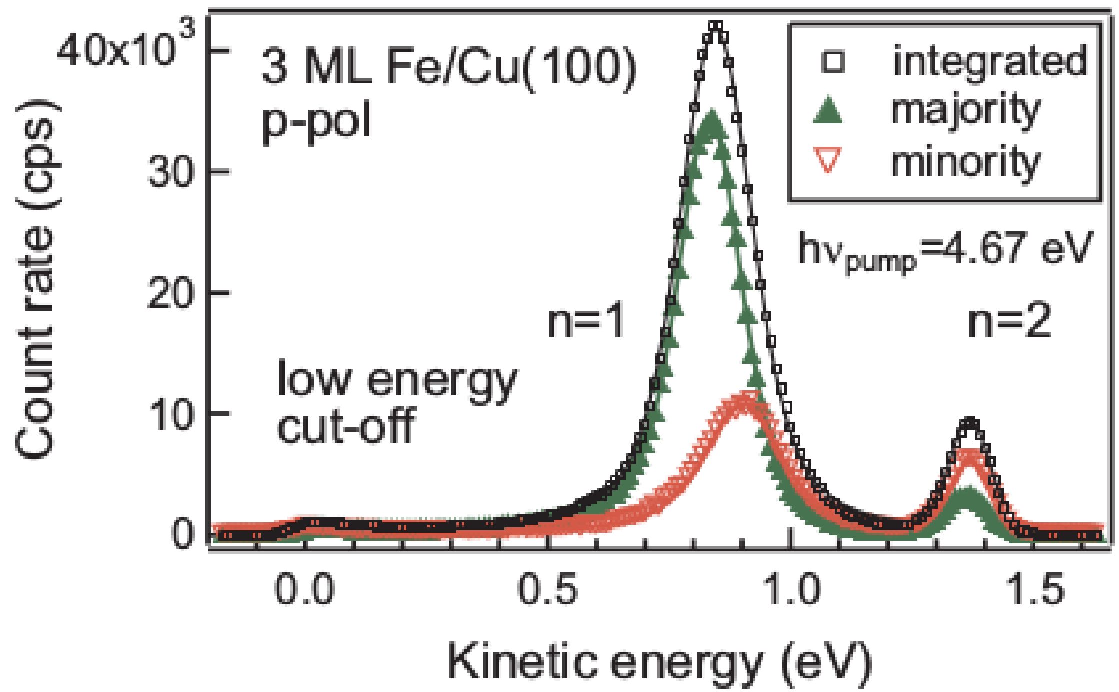
p-pol light
hν = 10.0 eV
normal emission

Δ^1_{ex} **= 64 meV**

Δ^2_{ex} **= 12 meV**

J. Braun, J. Minar and H. Ebert, Physics Reports, 740, 1 (2018)

Measured spin-resolved 2PPE spectra from Fe/Cu(100)

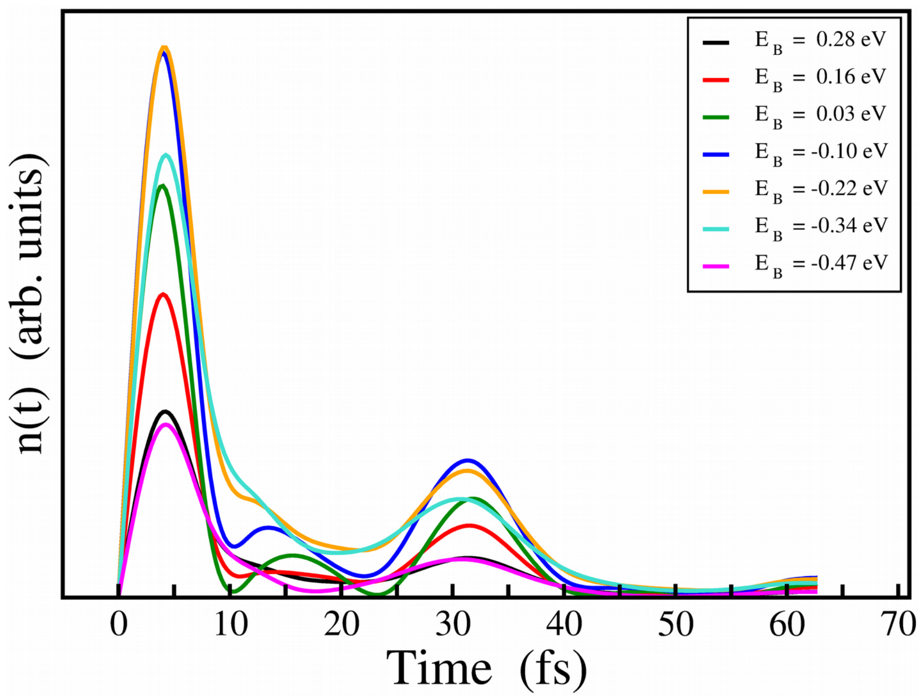


M. Pickel Ph.D. thesis, Berlin (2007)
M. Weinelt et al. Prog. Sci. 82, 388 (2007)

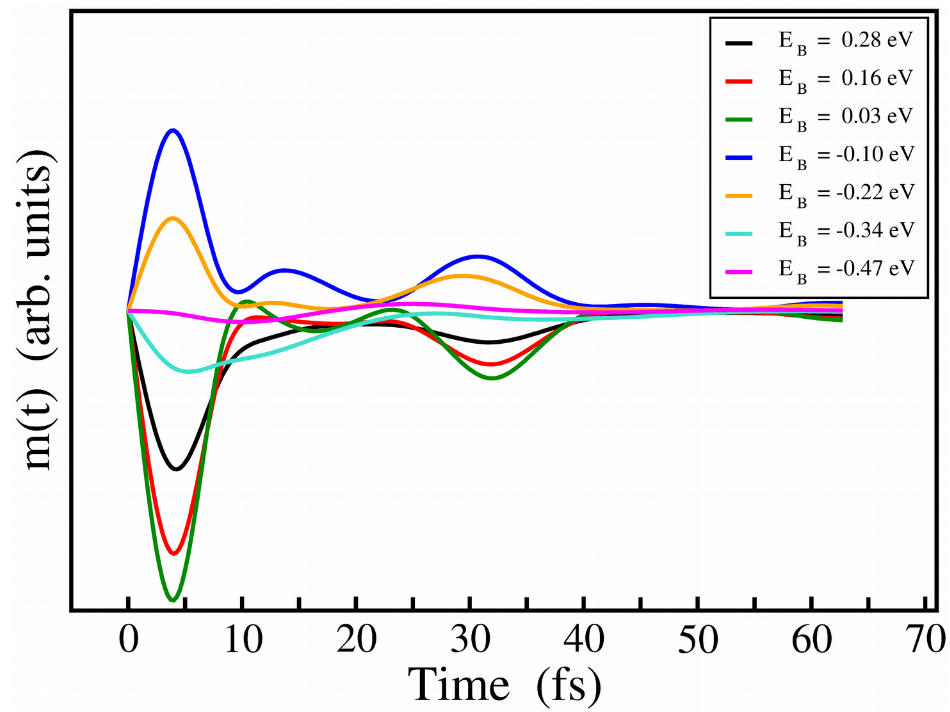
2PPE calculations on fcc Fe(100)

Time-resolved particle number n(t) and magnetic moment m(t) with the binding energy as a parameter

n(t)



m(t)



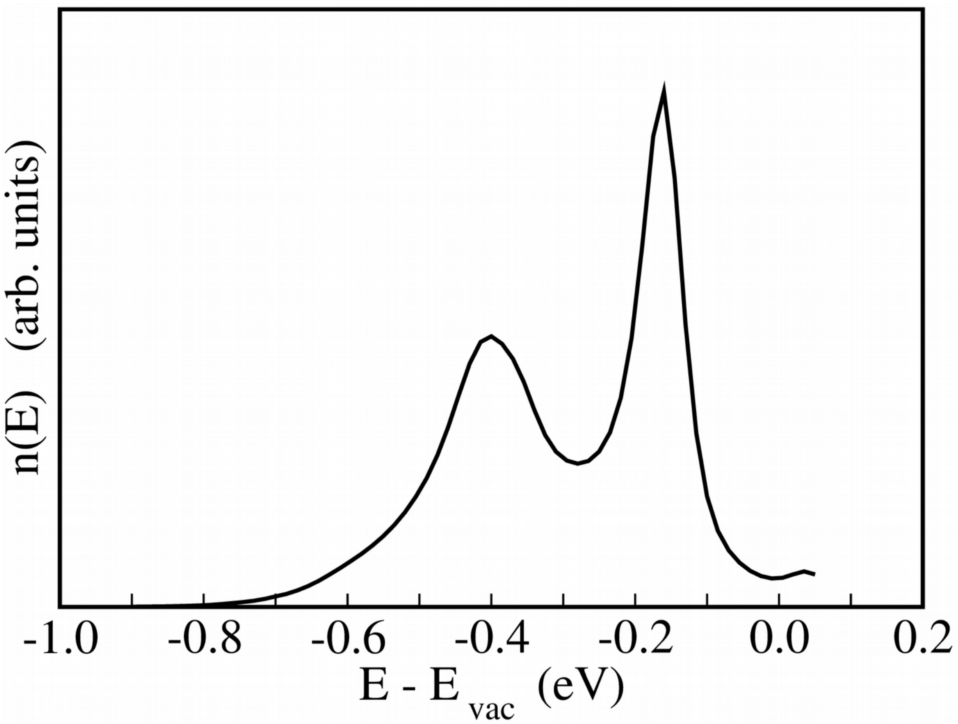
- **Pump pulse: hν = 4.4 eV**
- **Probe pulse: hν = 6.0 eV**
- **Gaussian profiles with FWHM = 8 (12) fs**
- **Pump-probe delay is fixed to 18 fs**
- **Work function ϕ = 4.8 eV**

J. Braun and H. Ebert (2018)

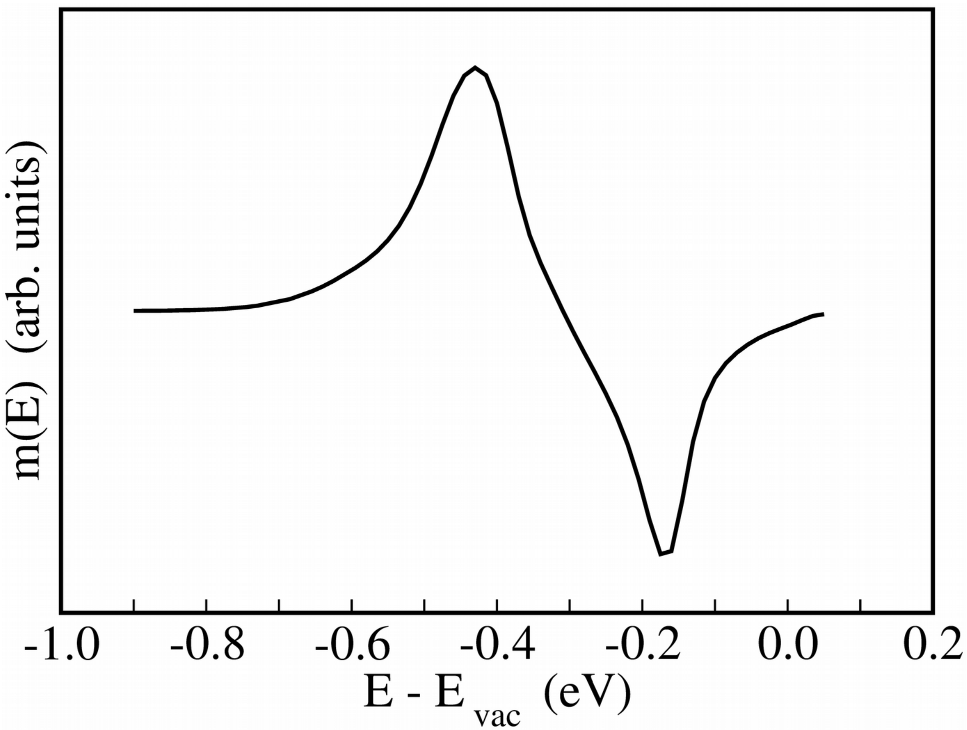
Image-potential states on fcc Fe(100): particle number n(E) and magnetic moment m(E)

Particle number n(E) and magnetic moment m(E)

n(E)



m(E)

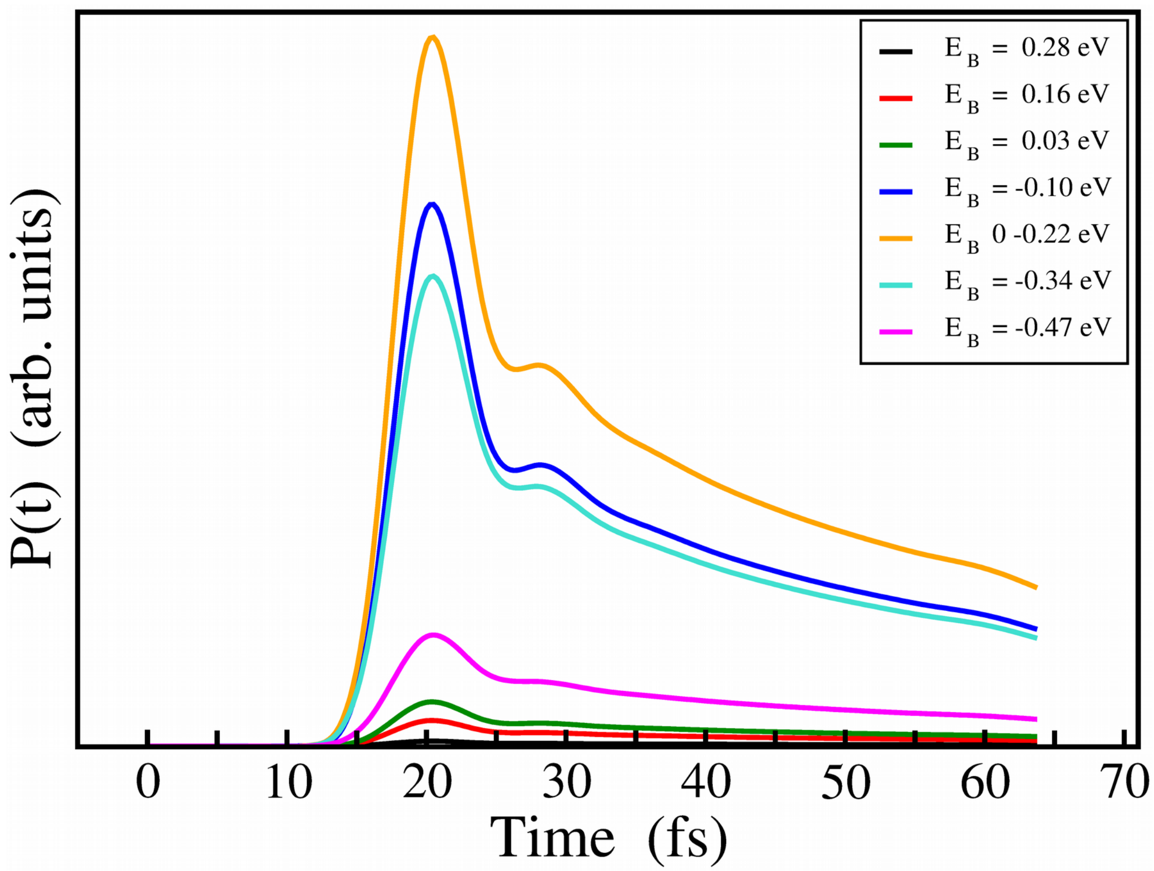


- **Pump pulse: hν = 4.4 eV**
- **Probe pulse: hν = 6.0 eV**
- **Gaussian profiles with FWHM = 8(12) fs**
- **Pump-probe delay is fixed to 18 fs**
- **Work function ϕ = 4.8 eV**

J. Braun and H. Ebert (2018)

2PPE calculations on fcc Fe(100)

Time-resolved photocurrent P(t)



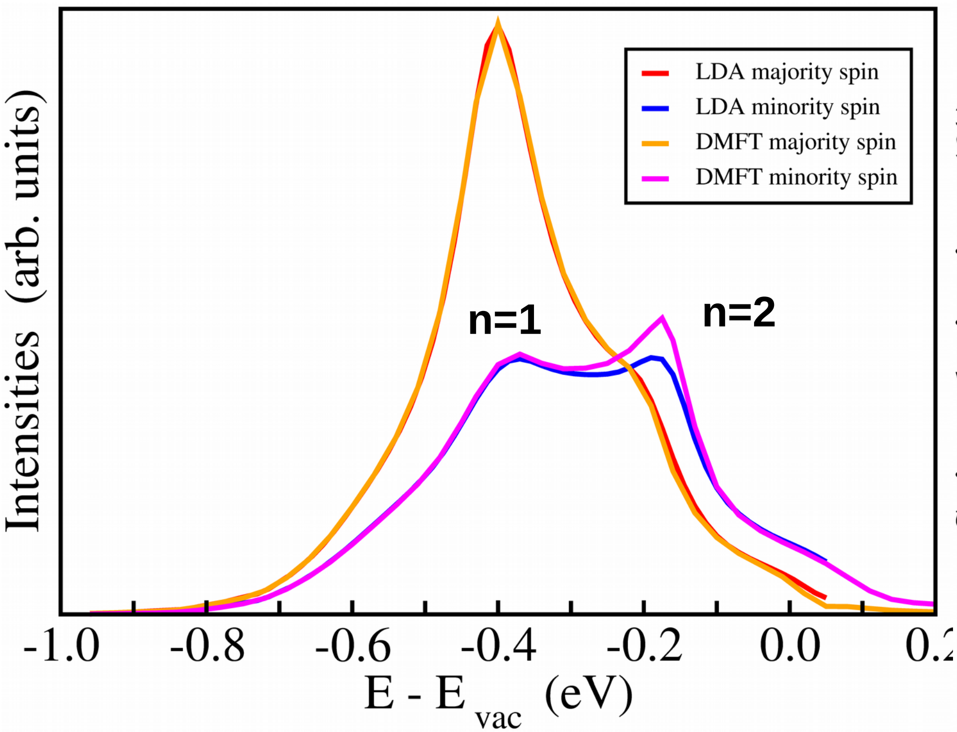
- **Pump pulse: hν = 4.4 eV**
- **Probe pulse: hν = 6.0 eV**
- **Gaussian profiles with FWHM = 8(12) fs**
- **Pump-probe delay is fixed to 18 fs**
- **Work function ϕ = 4.8 eV**

J. Braun and H. Ebert (2018)

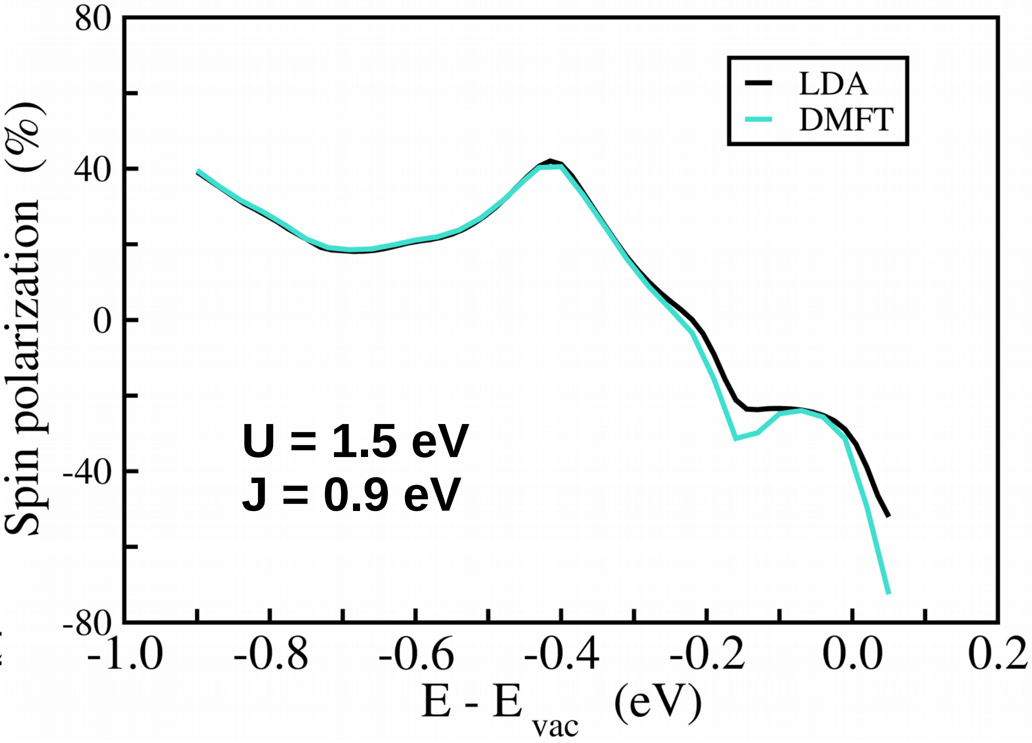
2PPE calculations on fcc Fe(100): LDA versus LDA+DMFT

Photocurrent and spin polarization as functions of E_B

Spin-resolved intensities



Spin polarization



- Pump pulse: hν = 4.4 eV
- Probe pulse: hν = 6.0 eV
- Gaussian profiles with FWHM = 8(12) fs
- Pump-probe delay is fixed to 18 fs
- Work function ϕ = 4.8 eV

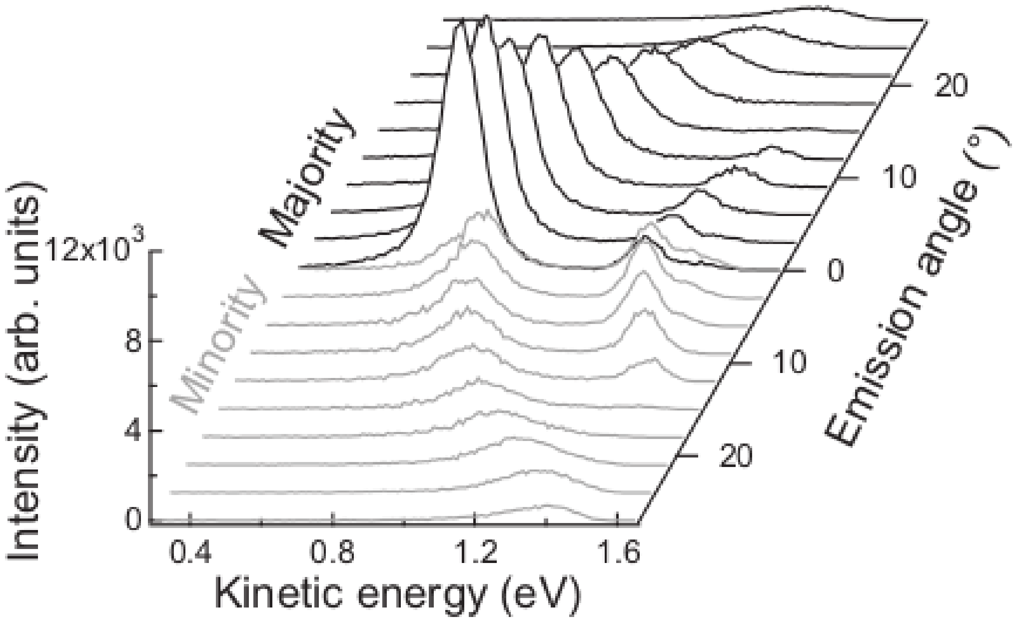
Δ_{ex} = 65 meV W. Wallauer and Th. Fauster PRB 54, 5086 (1996)

Δ_{ex} = 50 meV J. Braun and H. Ebert (2018)

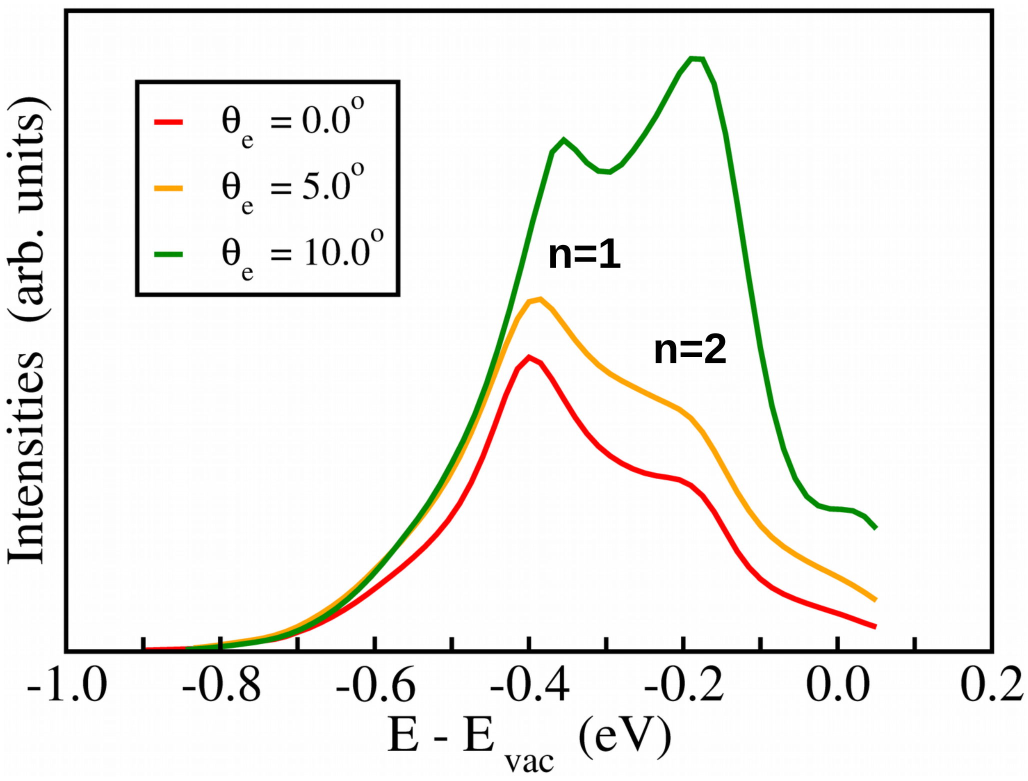
J. Sanchez-Barriga, J. Braun, J. Minar, H. Ebert, H. Dürr et al. PRL 103, 267203 (2009)

Angular-resolved 2PPE calculations on Fe(100)

2PPE spin-resolved intensities for the first and second image state measured for an increasing electron emission angle



2PPE intensities calculated on Fe(100) for different electron escape angles θ_e

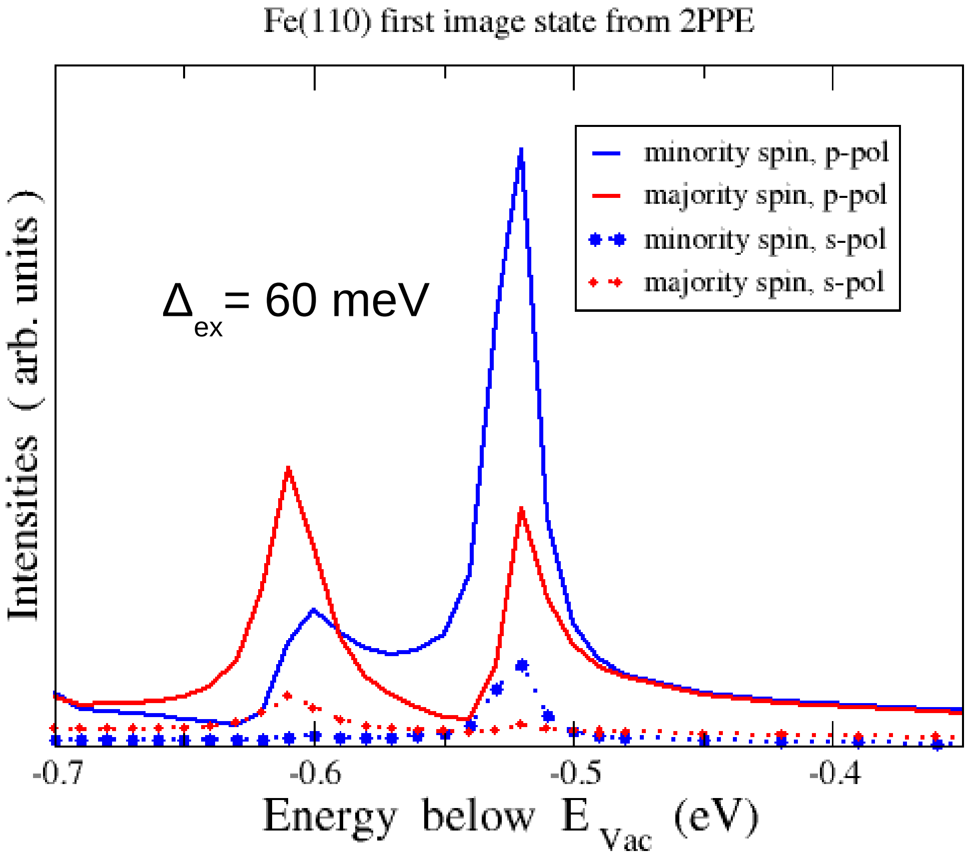


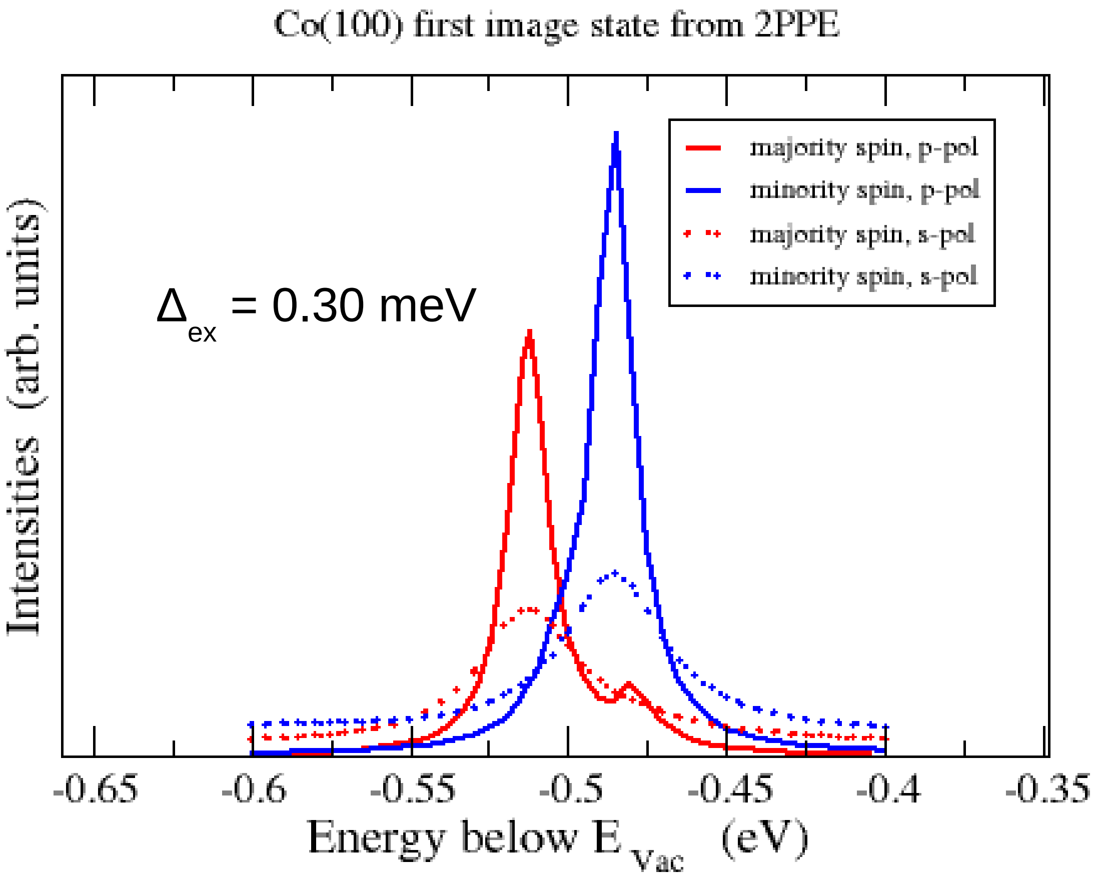
Anke B. Schmidt Ph.D. thesis, Berlin (2007)

J. Braun and H. Ebert (2018)

2PPE on Fe(110) and Co(100) for normal emission

Linear p-pol light versus linear s-pol light





$h\nu_{pump}$ = 4.33 eV

$h\nu_{probe}$ = 6.00 eV

Work function φ=4.7 eV

Gaussian profiles for pump and probe pulses with both FWHM = 12 fs, pump-probe delay is fixed to 12 fs

$h\nu_{pump}$ = 4.3 eV

$h\nu_{probe}$ = 7.0 eV

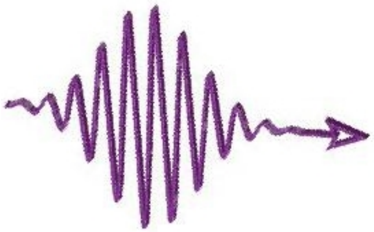
Work function φ=4.8 eV

J. Braun and H. Ebert (2019)

Quasi-static feed back of the system

G< describes the time evolution of the system in response to the pump pulse

Pump pulse $V_0(r,t) = -s_{\mathcal{V}}(t)\alpha \cdot \mathbf{A}_{0\mathcal{V}}$



Interaction free case

$$G^{<}(r,t,r',t') = i\int dE\; f_T(E)\int d^3r_1 \int d^3r_2\, G^{+}(r,t,r_1,t_0)\,\Im G_0^{+}(r_1,r_2,E)\, G^{-}(r_2,t_0,r',t')$$

Dyson equation for the retarded Keldysh Green function

$$G^{+}(r,t,r',t') = G_0^{+}(r,t,r',t') + \int_{t'}^{t} dt_1 \int d^3r_1 G_0^{+}(r,t,r_1,t_1)\; \boxed{V(r_1,t_1)}\; G^{+}(r_1,t_1,r',t')$$

Perturbation due to pump pulse and feed back of the system (e.g. within LDSA)

$$\boxed{V(r,t)} = -s_{\mathcal{V}}(t)\alpha \cdot \mathbf{A}_{0\mathcal{V}} + \Delta\mathcal{H}_{\mathrm{LSDA}}(r,t) + \Sigma(r,t)$$

see for example: de Melo *et al.* PRB, **93**, 155102 (2016)

Laser-Induced Demagnetization at Ultrashort Time Scales: Predictions of TDDFT

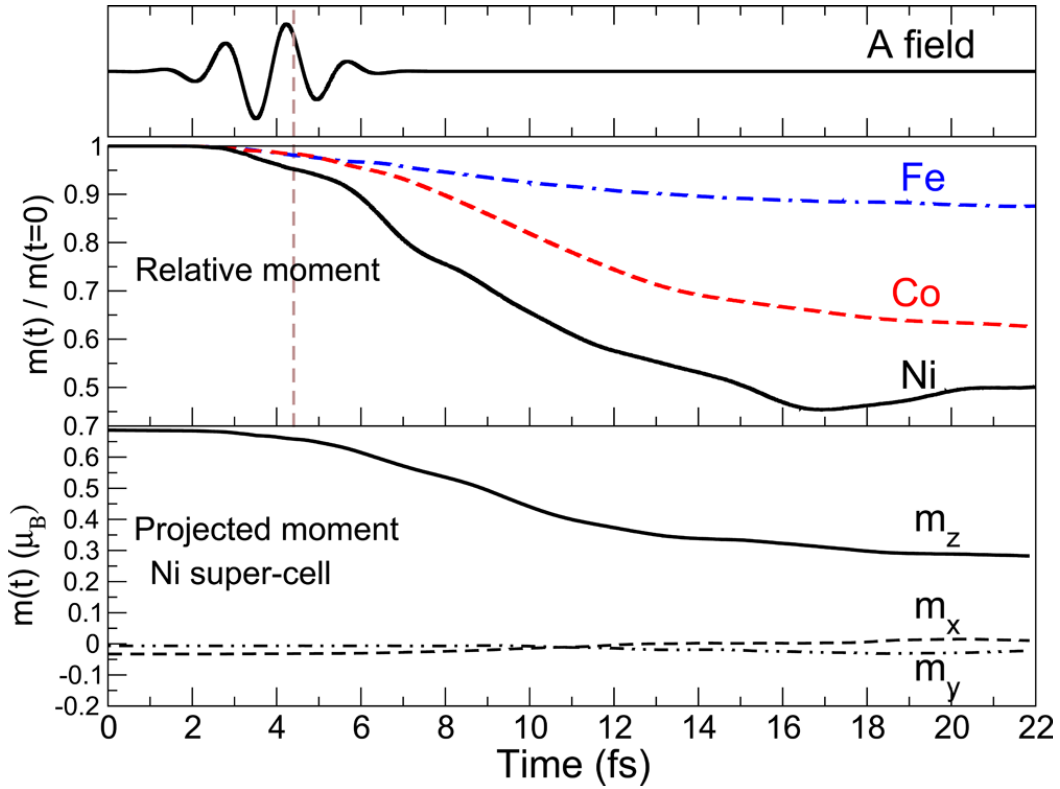
Time-evolution of the electronic system under the influence of an intensive laser pump pulse described within ***time-dependent DFT (TD-DFT)***

$$i\frac{\partial \psi_j(\mathbf{r},t)}{\partial t} = \left[\frac{1}{2}\left(-i\nabla + \frac{1}{c}\mathbf{A}_{\mathrm{ext}}(t)\right)^2 + v_s(\mathbf{r},t) + \frac{1}{2c}\boldsymbol{\sigma}\cdot\mathbf{B}_s(\mathbf{r},t) + \frac{1}{4c^2}\boldsymbol{\sigma}(\nabla v_s(\mathbf{r},t)\times -i\nabla)\right]\psi_j(\mathbf{r},t)$$

The vector potential $A_{ext}(t)$ represents the pump pulse

- Demagetisation only due to ***spin-orbit coupling***
- Relaxation processes missing
- No direct connection to Experiment

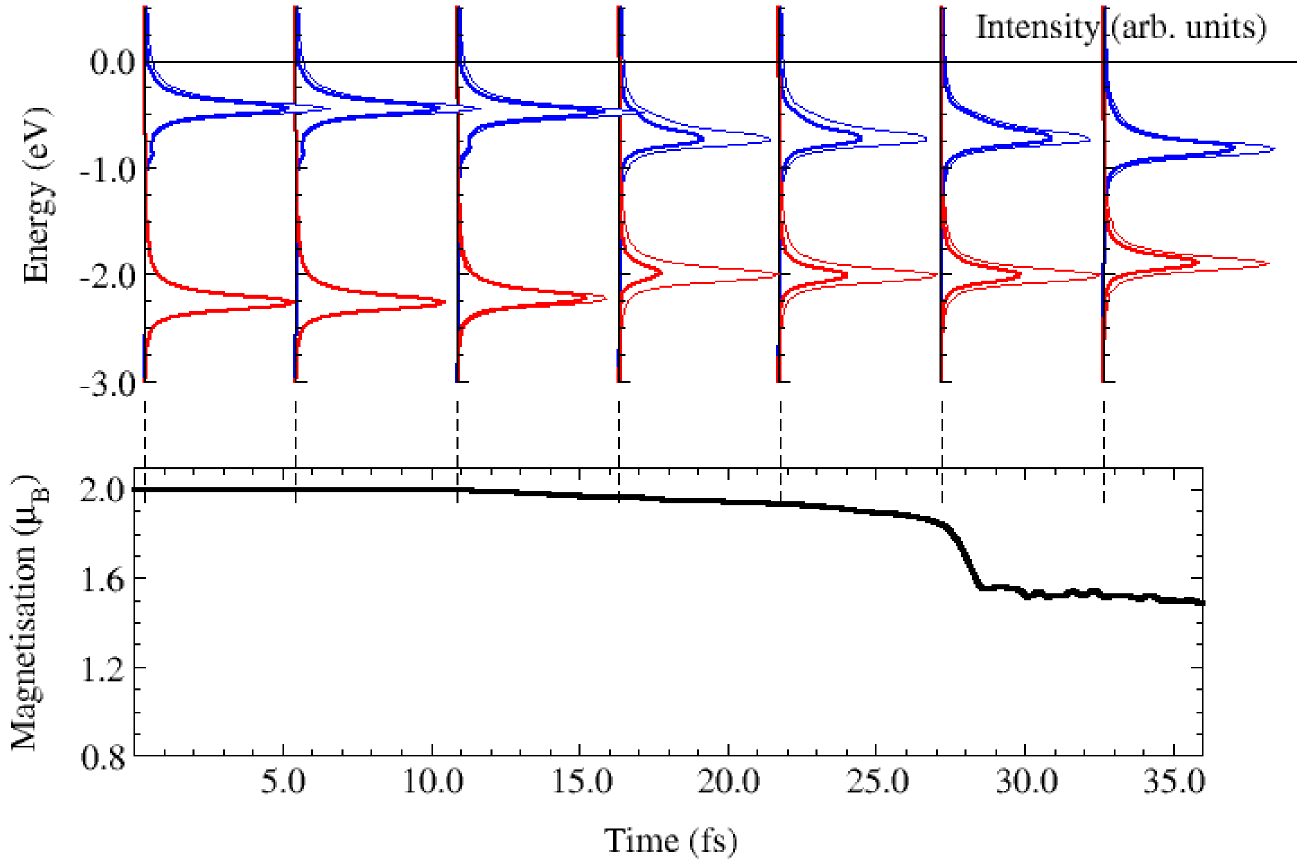
Relative magnetic moment m(t)/m(0) of Fe, Co and Ni after a pump pulse



K. Krieger *et al.,* J. Chem. Theory Comput. **11**, 4870 (2015)

Time-dependent Photoemission of bcc-Fe based on time-dependent DFT (TD-DFT)

- Fe bcc



- Photon energy 60 eV
- Normal emission

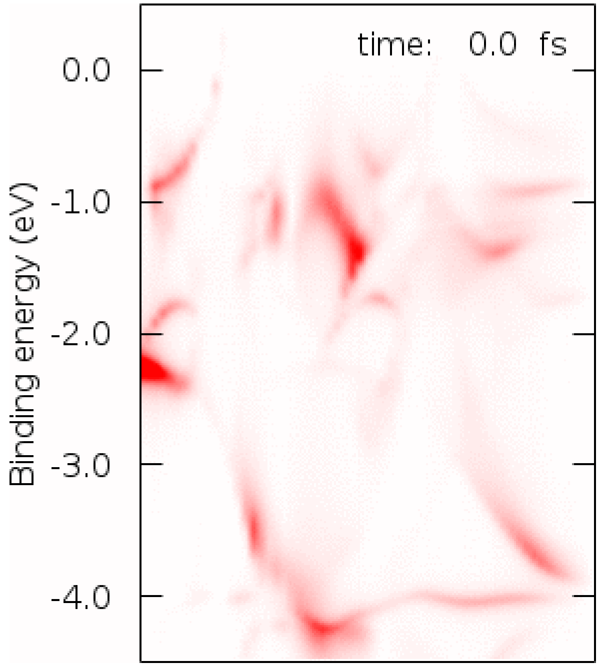
- Time-dependent magnetisation after a laser pulse of 0.816 eV

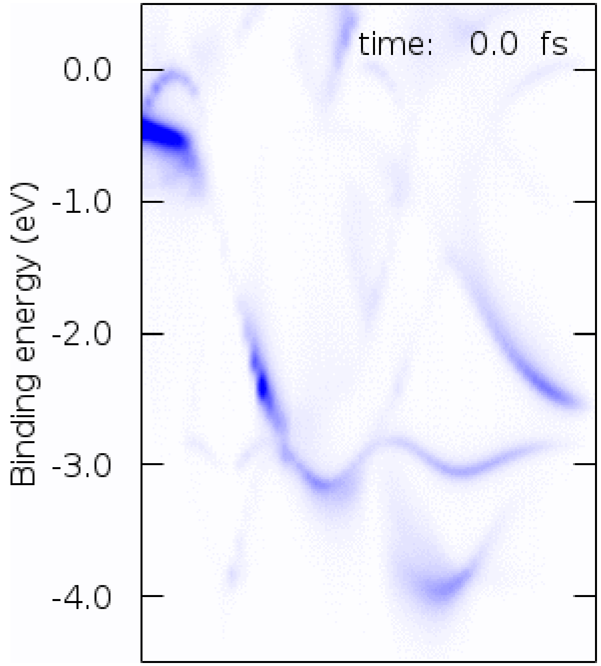
- Comparison of PES without (thin lines) and **with (thick lines)** properly accounting for the **time-dependent** occupation

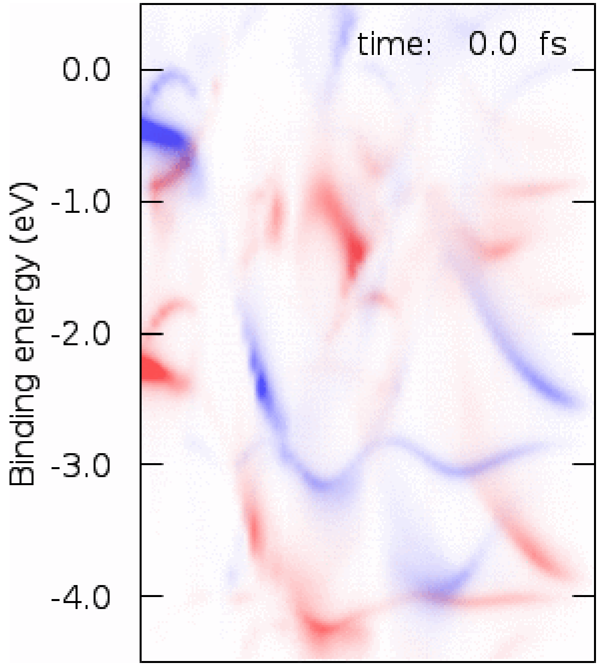
V. Popescu, J. Braun, and H. Ebert, unpublished (2018)

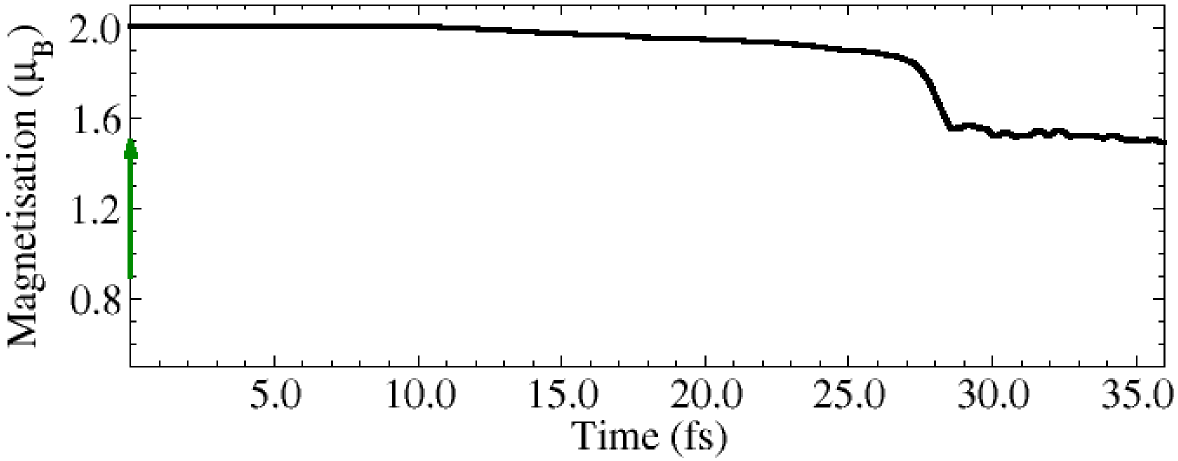
Angle- and spin-resolved TD-PES for Fe bcc

- Majority spin
- Minority spin
- Both spin channels

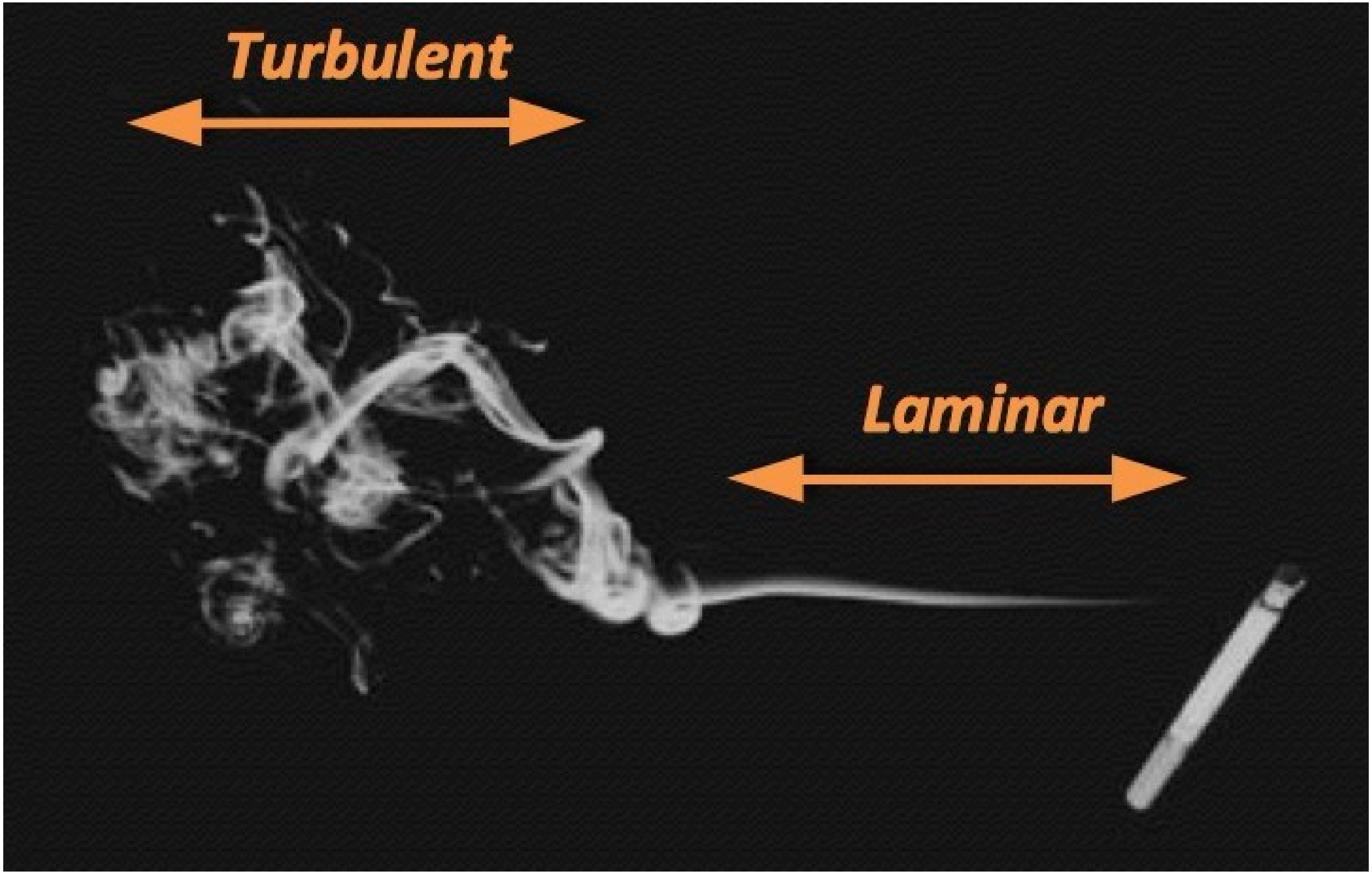








Outlook: Feed back of the system



Outlook: Dynamical correlations - self-energy

$$\boldsymbol{\Sigma^e_{s,2}(z,z') = U(z)\,U(z')\,\int dz''\int dz'''\,G_{s,1}(z,z'')\,G_{s,1}(z'',z''')\,G_{s,1}(z''',z')}$$

Exchange and direct part of the self-enrgy in 2nd order perturbation theory

$$\boldsymbol{\Sigma}^d_{s,2}(z,z') = U(z)\,U(z')\,\boldsymbol{G}_{s,1}(z,z')\,\boldsymbol{G}_{\bar{s},1}(z',z)\,\boldsymbol{G}_{\bar{s},1}(z,z')$$

$$\boldsymbol{C}(z,z') = \boldsymbol{A}(z,z')\,\boldsymbol{B}(z,z') \quad\rightarrow\quad \boldsymbol{C}^<(t,t') = \boldsymbol{A}^<(t,t')\,\boldsymbol{B}^<(t,t')$$
$$\boldsymbol{C}(z,z') = \boldsymbol{A}(z,z')\,\boldsymbol{B}(z',z) \quad\rightarrow\quad \boldsymbol{C}^<(t,t') = \boldsymbol{A}^<(t,t')\,\boldsymbol{B}^>(t',t)$$

Langreth-Wilkins rules

$$\boldsymbol{\Sigma}^{\lessgtr}_{s,2}(t,t') = U^2\,\boldsymbol{G}^{\lessgtr}_{s,1}(t,t')\,\boldsymbol{G}^{\gtrless}_{\bar{s},1}(t',t)\,\boldsymbol{G}^{\lessgtr}_{\bar{s},1}(t,t')$$

$$\begin{aligned}\boldsymbol{\Sigma}^{\pm}_{s,2}(t,t') = U^2\Big(&\boldsymbol{G}^{<}_{s,1}(t,t')\,\boldsymbol{G}^{>}_{\bar{s},1}(t',t)\,\boldsymbol{G}^{\pm}_{\bar{s},1}(t,t') + \boldsymbol{G}^{<}_{s,1}(t,t')\,\boldsymbol{G}^{\mp}_{\bar{s},1}(t',t)\,\boldsymbol{G}^{<}_{\bar{s},1}(t,t')\\ &+\boldsymbol{G}^{\pm}_{s,1}(t,t')\,\boldsymbol{G}^{<}_{\bar{s},1}(t',t)\,\boldsymbol{G}^{<}_{\bar{s},1}(t,t') + \boldsymbol{G}^{<}_{s,1}(t,t')\,\boldsymbol{G}^{\mp}_{\bar{s},1}(t',t)\,\boldsymbol{G}^{\pm}_{\bar{s},1}(t,t')\\ &+\boldsymbol{G}^{\pm}_{s,1}(t,t')\,\boldsymbol{G}^{<}_{\bar{s},1}(t',t)\,\boldsymbol{G}^{\pm}_{\bar{s},1}(t,t')\Big)\,.\end{aligned}$$

Dyson equation

$$\boldsymbol{G}^{\pm}_1(t,t') = \boldsymbol{G}^{\pm}_0(t,t') + \int_{t'}^{t} d\tau\,\boldsymbol{G}^{\pm}_0(t,\tau)\,V(\tau)\,\boldsymbol{G}^{\pm}_1(\tau,t')$$

J. Braun, M. Potthoff and H. Ebert (2017) following Aoki *et al.* RMP **86** 779 (2014)

Outlook: Dynamical correlations - Dyson equation

$$\boldsymbol{G}_1^{<}(t,t') = \frac{1}{2}\boldsymbol{G}_1^{+}(t,t_0)\int dE f_T(E)(\boldsymbol{G}_0^{+}(E) - \boldsymbol{G}_0^{-}(E))\boldsymbol{G}_1^{-}(t_0,t')$$

$$\boldsymbol{G}_1^{>}(t,t') = \frac{1}{2}\boldsymbol{G}_1^{+}(t,t_0)\int dE(1 - f_T(E))(\boldsymbol{G}_0^{+}(E) - \boldsymbol{G}_0^{-}(E))\boldsymbol{G}_1^{-}(t_0,t')$$

Dyson equation for the retarded Green function: ***the interacting case***

$$\boldsymbol{G_2^{\pm}(t,t') = G_1^{\pm}(t,t') + \int d\tau \int d\tau' \, G_1^{\pm}(t,\tau)\,\Sigma_2^{\pm}(\tau,\tau')\,G_2^{\pm}(\tau',t')}$$

Integral expression for the lesser and greater Green functions

$$\boldsymbol{G}_2^{\lessgtr}(t,t') = \left[\left(1 + \boldsymbol{G}_2^{+}\,\boldsymbol{\Sigma}_2^{+}\right)\boldsymbol{G}_1^{\lessgtr}\left(1 + \boldsymbol{\Sigma}_2^{-}\boldsymbol{G}_2^{+}\right)\right](t,t') + \left[\boldsymbol{G}_2^{+}\,\boldsymbol{\Sigma}_2^{\lessgtr}\,\boldsymbol{G}_2^{-}\right](t,t')$$

$$\boldsymbol{\Sigma}_2^{X}(t,t') = \begin{pmatrix} \boldsymbol{\Sigma}_{\uparrow,2}^{X}(t,t') & 0 \\ 0 & \boldsymbol{\Sigma}_{\downarrow,2}^{X}(t,t') \end{pmatrix}$$

J. Braun, M. Potthoff and H. Ebert (2017) following Aoki *et al.* RMP **86** 779 (2014)

Summary and outlook

- A description of X-ray absorption and XMCD for steady state out of equilibrium situation in terms of the lesser Green function has been worked out and applied to Co/Pd interfaces

- A generalisation of the one-step model of photo emission to the time-dependent case was worked out based on the Keldysh Green function approach

- Coherent inclusion of all surface and matrix element effects

- First applications to 2PPE on Ag(001) and ferromagnetic bcc-Fe(001) and fcc-Fe(001) in good agreement with experiment

- Further developments
  - Removal of the linear approximation w.r.t. pump pulse
  - Combination with TD-DFT
  - Inclusion of the time-dependent response of the system, relaxation processes, dynamical correlations …
  - Application to other *time-dependent spectroscopies*

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