X-ray spectroscopy with SPR-KKR

What to take care of

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Outline

Fundamentals of x-ray absorption spectroscopy

Basic theory

Tips and tricks

X-ray magnetic circular dichroism

Non-collinear systems: tasting via a case study
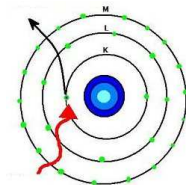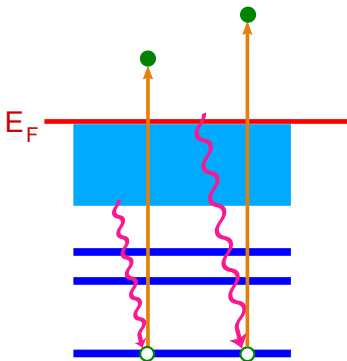
Outline

X-ray absorption spectroscopy

▶ X-rays go in, x-rays go out, absorption coefficient is measured as a function the energy of incoming x-rays.

▶ Focusing on energies where most of the absorption (or rather most of its variation with the energy) goes on account of the photoelectric effect on core electrons.
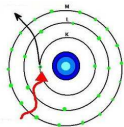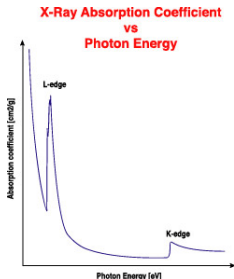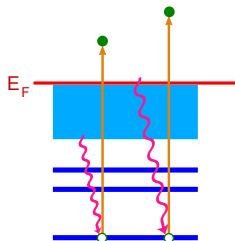
Absorption via core electron excitation

X-ray absorption spectrum (XAS) probes the unoccupied states as seen from a certain well-defined location.

Chemical selectivity

X-Ray Absorption Coefficient
vs
Photon Energy

absorption edge	core level
K	1s
L_1	2s
L_2	$2p_{1/2}$
L_3	$2p_{3/2}$

If the energy of incoming x-rays is large enough to excite another core electron, the absorption coefficient suddenly increases.

▶ Close to this jump, photoelectric effect on electrons arising from just one core level will dominate.

▶ Chemical sensitivity of XAS originates from the same mechanism as the characteristic spectrum.

Energy ranges: EXAFS, XANES
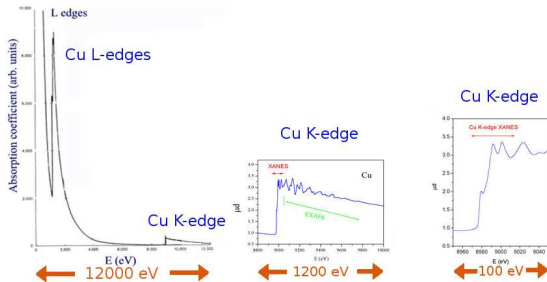
- High photoelectron energies (100–500 eV)
  EXAFS (Extended X-ray Absorption Fine Structure)
  DL_EXCURVE, FEFF, GNXAS, MSSPEC, . . .

- Low photoelectron energies (0–50 eV)
  XANES (X-ray Absorption Near Edge Structure)
  FDMNES, WIEN2K FEFF, QUANTUMESPRESSO, . . .

Absorption edges

X-Ray Absorption Coefficient
vs
Photon Energy
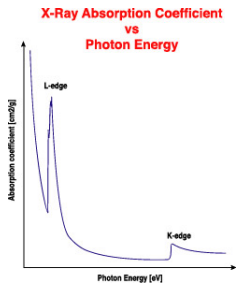
absorption edge	core level
K	1s
L_1	2s
L_2	$2p_{1/2}$
L_3	$2p_{3/2}$

K-edge for element defined by type `IT=1`

TASK   XAS   `IT=1`   `CL=1s`

$L_{2,3}$-edge for element defined by type `IT=3`

TASK   XAS   `IT=3`   `CL=2p`

K-edge and L_1 edge: two core s states

$(\kappa,\mu) = (-1,-1/2), (-1,+1/2)$

Snippet of the `dataset.rat` file containing results of XAS calculation:

```
ICST  N  L  KAP  MUE  IKM     NORM       E(Ry)       E(eV)    <SIGMA_z>  I0
  1   1  0  -1  -1/2   1    1.000000   -511.9138   -6964.942   -0.9884   683
  2   1  0  -1   1/2   2    1.000000   -511.9147   -6964.955    0.9884   683

number of energies  600
output format IFMT    2     1
VUC          185.70117362

  0.70508697 0.0100000 RYD  0.0000 EV (REL EF)
1 1  0.47082232E-02-0.91846464E-07 -0.23882780E-03 0.46589739E-08   0.44693954E-02-0.87187490E-07(+)
1 2  0.49445742E-02-0.96457123E-07 -0.23911991E-03 0.46646723E-08   0.47054543E-02-0.91792451E-07(-)
1 3  0.40792122E-02-0.79575925E-07 -0.50217570E-03 0.97962778E-08   0.35770365E-02-0.69779647E-07(z)
2 1  0.29399541E-02-0.57351550E-07 -0.20937191E-03 0.40843508E-08   0.27305822E-02-0.53267200E-07(+)
2 2  0.35654869E-02-0.69554217E-07 -0.18687122E-03 0.36454154E-08   0.33786157E-02-0.65908801E-07(-)
2 3  0.48878456E-02-0.95350308E-07 -0.11307319E-03 0.22057906E-08   0.47747724E-02-0.93144517E-07(z)
```

$L_{2,3}$ edge: six core p states

$$(\kappa,\mu) \quad = \quad (1, -1/2), (1, +1/2) \qquad\qquad L_2 \quad p_{1/2}$$
$$(-2, -3/2), (-2, -1/2), (-2, +1/2), (-2, +3/2) \quad L_3 \quad p_{3/2}$$

ICST	N	L	KAP	MUE	IKM	NORM	E(Ry)	E(eV)	<SIGMA_z>	I0
1	2	1	1	-1/2	3	0.997779	-48.2396	-656.333	0.4185	719
					6	0.002221				
2	2	1	1	1/2	4	0.997452	-48.2124	-655.964	-0.2348	719
					7	0.002548				
3	2	1	-2	-3/2	5	1.000000	-47.3840	-644.692	-0.9976	719
4	2	1	-2	-1/2	6	0.997779	-47.4101	-645.047	-0.4197	719
					3	0.002221				
5	2	1	-2	1/2	7	0.997452	-47.4379	-645.426	0.2360	719
					4	0.002548				
6	2	1	-2	3/2	8	1.000000	-47.4679	-645.833	0.9976	719

```
 0.87296273 0.00300000 RYD 11.8773 EV (REL EF)
1 1  0.10522392E+01-0.64275171E-04  0.00000000E+00 0.00000000E+00   0.10522392E+01-0.64275171E-04(+)
1 2  0.62233090E+00-0.38014573E-04  0.00000000E+00 0.00000000E+00   0.62233090E+00-0.38014573E-04(-)
1 3  0.12721742E+00-0.77709718E-04  0.00000000E+00 0.00000000E+00   0.12721742E+00-0.77709718E-04(z)
2 1  0.66768178E+00-0.40807350E-04  0.00000000E+00 0.00000000E+00   0.66768178E+00-0.40807350E-04(+)
2 2  0.32912732E+01-0.20115591E-03  0.00000000E+00 0.00000000E+00   0.32912732E+01-0.20115591E-03(-)
2 3  0.13155348E+01-0.80402806E-04  0.00000000E+00 0.00000000E+00   0.13155348E+01-0.80402806E-04(z)
3 1  0.48953521E+01-0.30433046E-03  0.00000000E+00 0.00000000E+00   0.48953521E+01-0.30433046E-03(+)
3 2  0.91444636E+00-0.56848593E-04  0.00000000E+00 0.00000000E+00   0.91444636E+00-0.56848593E-04(-)
3 3  0.18473922E+01-0.11484725E-03  0.00000000E+00 0.00000000E+00   0.18473922E+01-0.11484725E-03(z)
4 1  0.16053261E+01-0.99744662E-04  0.00000000E+00 0.00000000E+00   0.16053261E+01-0.99744662E-04(+)
4 2  0.14289690E+01-0.88786966E-04  0.00000000E+00 0.00000000E+00   0.14289690E+01-0.88786966E-04(-)
4 3  0.28677395E+01-0.17818293E-03  0.00000000E+00 0.00000000E+00   0.28677395E+01-0.17818293E-03(z)
5 1  0.65600632E+00-0.40736536E-04  0.00000000E+00 0.00000000E+00   0.65600632E+00-0.40736536E-04(+)
5 2  0.23873203E+01-0.14824729E-03  0.00000000E+00 0.00000000E+00   0.23873203E+01-0.14824729E-03(-)
5 3  0.11523408E+01-0.71557804E-04  0.00000000E+00 0.00000000E+00   0.11523408E+01-0.71557804E-04(z)
6 1  0.15909865E+00-0.98735531E-05  0.00000000E+00 0.00000000E+00   0.15909865E+00-0.98735531E-05(+)
6 2  0.90750819E+00-0.56319337E-04  0.00000000E+00 0.00000000E+00   0.90750819E+00-0.56319337E-04(-)
6 3  0.44521277E+00-0.27629600E-04  0.00000000E+00 0.00000000E+00   0.44521277E+00-0.27629600E-04(z)
```

Outline

Fermi's Golden Rule

Probability per unit time that a perturbation H_{int} causes
a transition between eigenstates $|\psi_i\rangle$ and $|\psi_f\rangle$ of the unperturbed
Hamiltonian:

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

"+" for absorption of photons, "-" for emission of photons.

Transition matrix element:

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

$\mathbf{q}$ is the photon wave vector ($cq = \hbar\omega$),
$\boldsymbol{\epsilon}$ is the polarization vector of the radiation.

Enter the Green function $G^{(+)}$

Absorption coefficient:

$$\mu(\omega) = \sum_f w_{fi} = \sum_f \frac{2\pi}{\hbar} |\langle \psi_f | H_{\mathrm{int}} | \psi_i \rangle|^2 \, \delta(E_f - E_i + \hbar\omega)$$

$$\mu(\omega) = -\frac{2}{\hbar} \operatorname{Im} \left\langle \psi_i \left| H_{\mathrm{int}}^\dagger \frac{1}{E_i - \hbar\omega - H_{\mathrm{el}} + \mathrm{i}\varepsilon} H_{\mathrm{int}} \right| \psi_i \right\rangle$$

$$\mu(\omega) = -\frac{2}{\hbar} \operatorname{Im} \left\langle \psi_i \left| H_{\mathrm{int}}^\dagger \, G^{(+)}(E_i - \hbar\omega) \, H_{\mathrm{int}} \right| \psi_i \right\rangle$$

Enter scattering path operator τ

Absorption coefficient:

$$\mu(\omega) = -\frac{2\pi^2 m^2}{\hbar^5 k^2} \Im \sum_{LL'} M_L^* \, \tau_{LL'}^{00} \, M_{L'} \ ,$$

$k = \sqrt{2m(\hbar\omega - E_0)/\hbar^2}$ photoelectron wave vector,

M_L *atomic-like* transition matrix element.

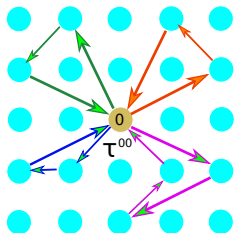$\tau_{LL'}^{00}$ is scattering-path operator associated with photoabsorbing site 0,

$$\tau_{LL'}^{00} = t_L^0 \delta_{LL'} + \sum_p \sum_{L''} t_L^0 \, G_{LL''}^{0p} \, \tau_{L''L'}^{p0} \ ,$$

t_L^0 single-site scattering matrix,

$G_{LL''}^{0p}$ free-electron propagator (Green function).

Scattering path operator τ^{00}

Amplitude of scattering process where electron begins at site 0 with angular momentum L and ends at site 0 with angular momentum L', taking into account all possible multiple scattering paths.

$$\tau^{00}_{LL'} = t^0_L \delta_{LL'} + \sum_p \sum_{L''} t^0_L \, G^{0p}_{LL''} \, \tau^{p0}_{L''L'} \ .$$

t^j_L single-site scattering matrix at site j

$G^{ij}_{LL''}$ free-electron propagator between sites i and j

0 photoabsorbing site

Multiple-scattering expansion:

$$\tau^{00} = t^0 + \sum_p t^0 \, G^{0p} \, t^p \, G^{p0} \, t^0 + \sum_{pq} t^0 \, G^{0p} \, t^p \, G^{pq} \, t^q \, G^{q0} \, t^0 + \dots$$

Real space approach to τ^{00}
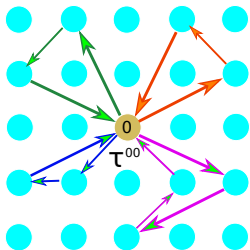
SPRKKR code always employs full multiple scattering.

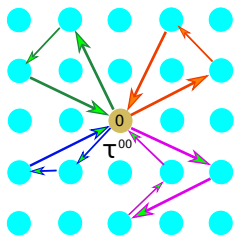$$\tau = t + t\,G\,\tau\,,$$

$$\tau = \left(t^{-1} - G\right)^{-1}$$

TAU   CLUSTER   IQCNTR=1   CLURAD=1.55

IQCNTR=1   photoabsorbing atom is at site IQ=1

CLURAD=1.55   atoms within cluster of radius $1.55 \times$ALAT
                around site IQCNTR taken into account

Reciprocal space approach to τ^{00}

Lattice Fourier transform for crystals:

$$G(\boldsymbol{k}, E) = \frac{1}{N} \sum_{mn} \mathrm{e}^{-\mathrm{i}\boldsymbol{k}(\boldsymbol{R}_m - \boldsymbol{R}_n)} G^{mn}(E)$$

$$\tau^{00}(E) = \frac{1}{\Omega_{\mathrm{BZ}}} \int_{\mathrm{BZ}} \mathrm{d}\boldsymbol{k} \, \left[t^{-1}(\boldsymbol{k}, E) - G(\boldsymbol{k}, E) \right]^{-1}$$

TAU   BZINT=POINTS   NKTAB=800

STRCONST   ETA=1.2   RMAX=6.0   GMAX=6.0

Evaluating $G(\boldsymbol{k}, E)$ requires Ewald summation, because the real-space $G^{mn}(E)$ does not fall off fast enough with $|\boldsymbol{R}_m - \boldsymbol{R}_n|$.

When calculating XAS, attention has to be paid especially to ETA. Otherwise the spectrum will "die out" for large energies.
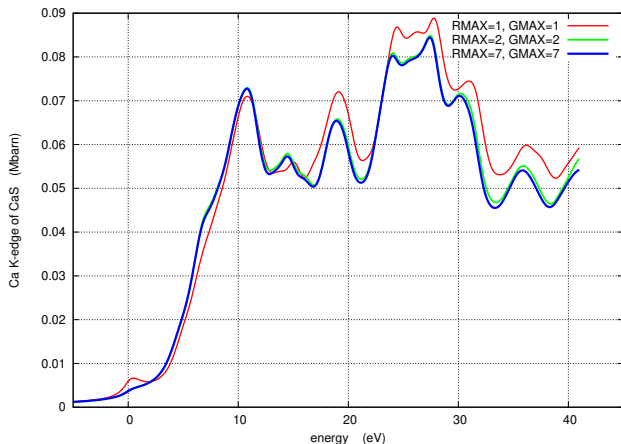
Calculating XAS via SPRKKR: watch out for ETA
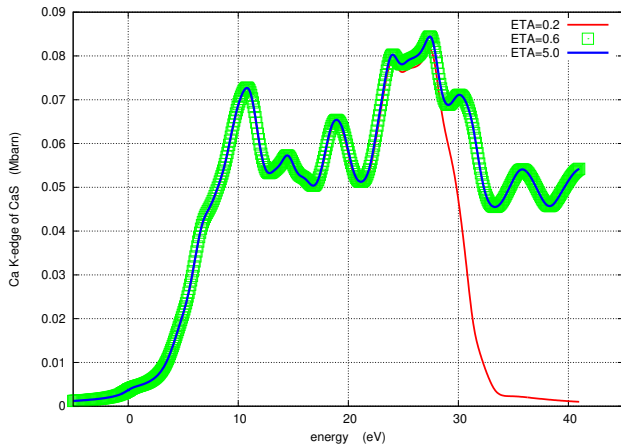
STRCONST   ETA=???   RMAX=6.0   GMAX=6.0

Calculating XAS via SPRKKR: watch out for RMAX, GMAX
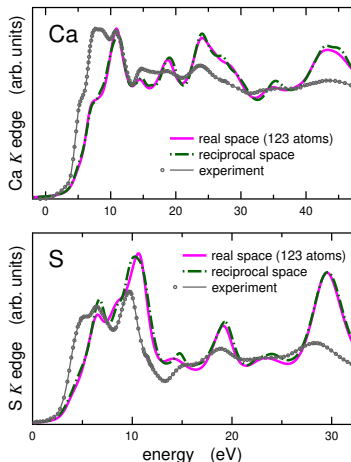

STRCONST   ETA=1.2   RMAX=???   GMAX=???

Comparing real space and reciprocal space calculation

Ca *K*-edge and S *K*-edge of CaS (rock salt structure).

Reciprocal space calculation implicitly involves the whole infinite crystal.

Real space calculation done for a cluster of 123 atoms.

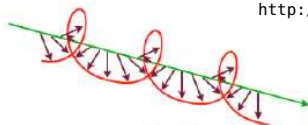Convergence with respect to the size of the cluster should be checked.

Typically, around 70 atoms will be sufficient.

X-ray polarization vectors

$$\boldsymbol{A}(\boldsymbol{r}, t) \;=\; \boldsymbol{A_0}\, \mathrm{e}^{\mathrm{i}\,(\boldsymbol{q}\,\boldsymbol{r}\,-\,\omega\,t)} \qquad \boldsymbol{A_0} \perp \boldsymbol{q}$$

$\boldsymbol{q}$ x-rays wave vector ("the direction where the light comes from")
$\boldsymbol{A_0}$ amplitude of the x-rays (specifies the polarization vector $\boldsymbol{\epsilon}$)
ω frequency of the x-ray wave $(E = \hbar\omega,\ cq = \hbar\omega)$

Linear polarization

http://www.spring8.or.jp

Circular polarization

$$\boldsymbol{A} \;=\; \hat{\boldsymbol{\epsilon}}\, A_0\, \mathrm{e}^{\mathrm{i}\,(\boldsymbol{q}\,\boldsymbol{r}\,-\,\omega\,t)} \qquad\qquad \boldsymbol{A} \;=\; \frac{1}{\sqrt{2}}\,(\hat{\boldsymbol{\epsilon}}_x \pm \mathrm{i}\,\hat{\boldsymbol{\epsilon}}_y)\, A_0\, \mathrm{e}^{\mathrm{i}\,(\boldsymbol{q}\,\boldsymbol{r}\,-\,\omega\,t)}$$

(in case that $\boldsymbol{q} \| \hat{\boldsymbol{z}}$)

Matrix elements: dipole approximation

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

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

If processes are localized (mostly they are), then $\frac{i}{\hbar} \mathbf{q} \cdot \mathbf{x}$ and higher order terms can be neglected.

We thus have just $M_{fi} \approx \boldsymbol{\epsilon} \cdot \langle \psi_f | \mathbf{p} | \psi_i \rangle$.

This is called the dipole approximation.

Intensity of dipole transitions depends on the direction of the polarization vector $\boldsymbol{\epsilon}$, *not* on the direction of the incoming x-rays.

Polarization matters

drawing G. Waychunas

By varying the direction of the x-rays' polarization vector ϵ, one probes the local environment in different directions.

X-ray **L**inear **D**ichroism: $\text{XLD} = \mu(\epsilon_1) - \mu(\epsilon_2)$

$\sigma(\epsilon)$ is the absorption coefficient for photon polarization ϵ.

Usually $\epsilon_1 \perp \epsilon_2$.

Dealing with polarized spectra (i.e., with both XAS and XLD) means that we have got more data to analyze.

Polarization vector ϵ in SPRKKR

Default: polarization vector ϵ is parallel to the z direction.

Direction of ϵ can be specified in the input file:

$\epsilon \| x \quad (\theta = 90°, \phi = 0°)$

```
TASK       XAS   IT=2   CL=1s
           FRAMETET=90   FRAMEPHI=0
```

$\epsilon \| y \quad (\theta = 90°, \phi = 90°)$

```
TASK       XAS   IT=2   CL=1s
           FRAMETET=90   FRAMEPHI=90
```

Polarization: $(+)$, $(-)$, (z)

Snippet of the `dataset.rat` file containing results of XAS calculation:

```
ICST  N  L  KAP  MUE  IKM    NORM      E(Ry)        E(eV)    <SIGMA_z>  I0
  1   1  0  -1  -1/2   1   1.000000  -511.9138   -6964.942    -0.9884  683
  2   1  0  -1   1/2   2   1.000000  -511.9147   -6964.955     0.9884  683

 number of energies  600
 output format IFMT    2    1
VUC          185.70117362

  0.70508697 0.01000000 RYD  0.0000 EV (REL EF)
1 1  0.47082232E-02-0.91846464E-07 -0.23882780E-03 0.46589739E-08    0.44693954E-02-0.87187490E-07(+)
1 2  0.49445742E-02-0.96457123E-07 -0.23911991E-03 0.46646723E-08    0.47054543E-02-0.91792451E-07(-)
1 3  0.40792122E-02-0.79575925E-07 -0.50217570E-03 0.97962778E-08    0.35770365E-02-0.69779647E-07(z)
2 1  0.29399541E-02-0.57351550E-07 -0.20937191E-03 0.40843508E-08    0.27305822E-02-0.53267200E-07(+)
2 2  0.35654869E-02-0.69554217E-07 -0.18687122E-03 0.36454154E-08    0.33786157E-02-0.65908801E-07(-)
2 3  0.48878456E-02-0.95350308E-07 -0.11307319E-03 0.22057906E-08    0.47747724E-02-0.93144517E-07(z)
```

The $(+)$, $(-)$ components correspond to circular polarization, $\boldsymbol{\epsilon} = \hat{\boldsymbol{x}} + \mathrm{i}\hat{\boldsymbol{y}}$, $\boldsymbol{\epsilon} = \hat{\boldsymbol{x}} - \mathrm{i}\hat{\boldsymbol{y}}$.
Needed for x-ray magnetic circular polarization (XMCD).

The (z) component corresponds to linear polarization, $\boldsymbol{\epsilon} = \hat{\boldsymbol{z}}$.

Angular momentum selectivity

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

Dipole approximation: $M_{fi} \approx \epsilon \cdot \langle \psi_f \, | \mathbf{p} | \, \psi_i \rangle$.

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

Only transitions between states with their orbital quantum numbers differing by one are allowed for dipole transitions:

$$\ell_f \;=\; \ell_i \pm 1 \ .$$

K and L_1 spectra (from $1s$ or $2s$ core levels) probe p states.
L_2 and L_3 spectra (from $2p_{1/2}$ or $2p_{3/2}$ core levels) probe d states.

Calculating XAS: convergence with ℓ_{max}=NL-1

Large energy E needs larger ℓ_{max}.
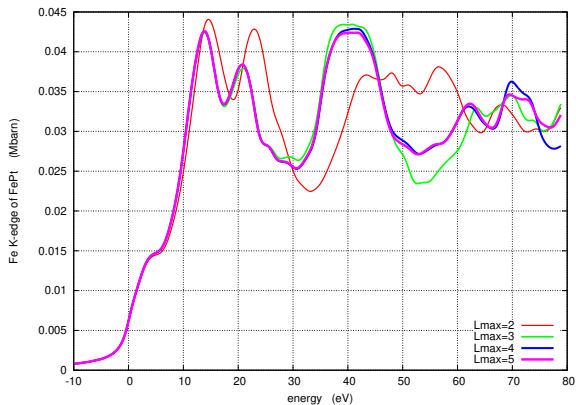
SITES   NL=???   Note: $\text{NL} = \ell_{max} + 1$.

Outline

Finite core hole lifetime
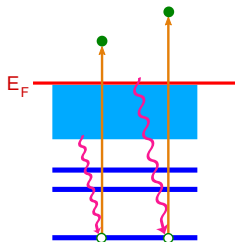
A hole in the core level is left by the ejected photoelectron.

The core hole will be eventually filled $\Rightarrow$ its lifetime is finite.

Intuitive view (though formally wrong): $\Delta E \cdot \Delta t > \hbar/2$.

It can be honestly shown by perturbation theory that the core hole decay is exponential and that the line shape is Lorentzian

[Messiah: Quantum Mechanics, vol. 2, chap. XXI].

Finite core hole width
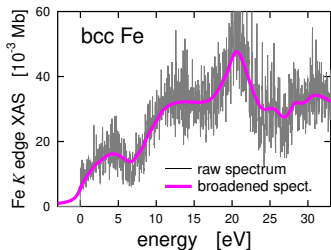
Spectra calculated within an effectively one-electron approach have to be broadened with a Lorentzian.

$$L(E) = \frac{1}{\pi} \frac{\Gamma/2}{E^2 + (\Gamma/2)^2}$$

Use Lorentzian with a **f**ull **w**idth at **h**alf **m**aximum (FWHM) Γ taken from tables.

E.g., Campbell & Papp, At. Data Nucl. Data Tables **77**, 1 (2001).

One has to perform the calculations on sometimes much finer energy mesh than actually needed.

Influence of the energy grid on XANES

Case study: B K-edge of calciborite CaB_2O_4

XANES of calciborite: convoluted and raw 'as calculated'
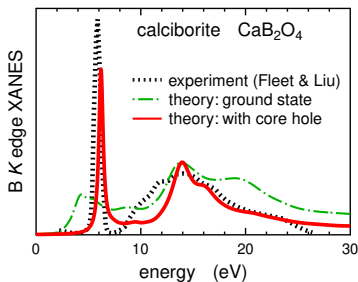
J. Synchrotron Rad. **17**, 367 (2010)
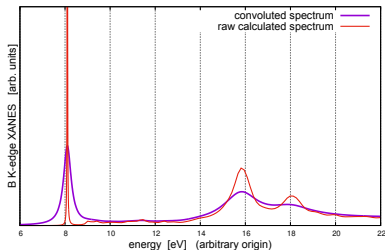
Technical details of how the energy mesh points are distributed around the resonance strongly influence the final convoluted spectrum. 🙁

Doing the convolution via PLOT and/or XBAND

Plot XAS spectra using the `plot` utility, which is accessible via xband.

Default FWHM values are taken from Campbell & Papp, At. Data Nucl. Data Tables (2001).

To tailor the broadening to suit your needs, edit the `*.pin` file.

```
plot < dataset.pin
```

DATASET	dataset.rat	
OUTPUT	TABLE	
BROADEN	WL={1.54}	K edge
BROADEN	WL={0.35,0.15}	L_2 edge, L_3 edge

Alternative: add a small imaginary part to the energy

Lorentzian with FWHM of Γ: $L(E) = \frac{1}{\pi} \frac{\Gamma/2}{E^2 + (\Gamma/2)^2}$.

XAS with the influence of the finite core hole lifetime included:

$$\sigma_{\text{broaden}}(E) = \int_{E_F}^{\infty} dE' \, \sigma_{\text{raw}}(E') \, L(E - E')$$

If the cut-off below E_F is ignored, convolution with a Lorentzian is equivalent to evaluating the spectrum for energies with added imaginary component $\Gamma/2$,

$$\int_{-\infty}^{\infty} dE' \, \sigma_{\text{raw}}(E') \, L(E - E') = \sigma_{\text{raw}}(E + i\Gamma/2) .$$

XAS with the influence of finite core lifetime included:

$$\sigma_{\text{broaden}}(E) \approx \sigma_{\text{raw}}(E + i\Gamma/2) .$$

Benefits and risks of using ImE

ENERGY   GRID={6}   NE=300
         EMIN=0.45   EMAX=3.5   ImE=0.01

Energy mesh can be relatively coarse because the spectrum has already been pre-smeared: $\Gamma = 2\,\text{Im}E$.

Energy step in XAS calculation should be about ImE.

Combine smearing by adding ImE to the energy and by convoluting the spectrum with a Lorentzian of width Γ:

$$2\,\text{Im}E + \Gamma = \Gamma_{\text{total}} \,.$$

Beware: Because of replacing $\int_{E_F}^{\infty} \mathrm{d}E$ with $\int_{-\infty}^{\infty} \mathrm{d}E$, there may be issues close to the edge.

Special care needed for XMCD spectra: ImE should be about ten times smaller than Γ_{core}. [J. Synchrotron Rad. **25**, 525 (2018)]

Finite photoelectron lifetime

Interaction of the excited photoelectron with other electrons results in finite photoelectron mean free path and finite photoelectron lifetime.
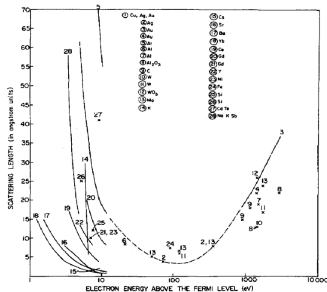
Lindau J. Electron Spect. Relat. Phenom. (1974)
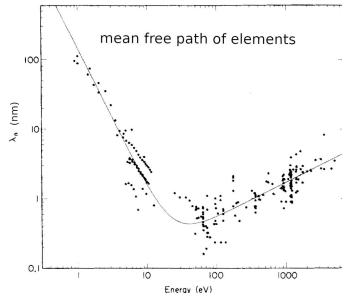
Seah & Dench, Surf. Interface Anal. (1979)

Beware: "Universal curve" is not truly universal.

Broadening due to photoelectron lifetime
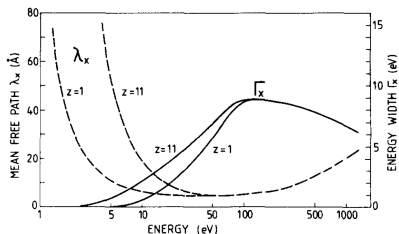
PLOT utility default:

The photoelectron mean free path depends on the number of valence electrons, set by interpolating between two "standard" curves NVAL=1 and NVAL=11

Müller *et al.* Solid State Commun. (1982).

Sometimes the automatically set `NVAL` yields too large broadening.

You may set it be hand in the `*.pin` file.

```
plot < dataset.pin
```

BROADEN   NVAL=4 WL={1.54}

BROADEN   NVAL=0 WL={0.35,0.15}

Core hole
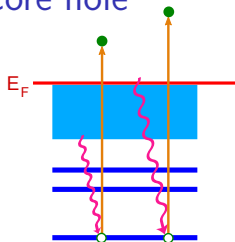
The presence of the core hole affects the behaviour of the photoelectron.

Dealing with this issue exactly requires many-body physics, often beyond what is feasible for solids.

The influence of the core hole on XAS is a "stand-along discipline", not covered by this talk.

- If you focus on the core hole, you have to cheat on the solid-state-like effects: the influence of other atoms apart from the photoabsorbing one is treated as a perturbation.

- If you focus on solid-state-like effects (hybridization), you have to simplify the core hole treatment.
  This is the option available with SPRKKR.

Initial state approximation

A.k.a. frozen orbital approximation.

Calculations done for the ground state potential.

The relaxation of the "passive" electrons to the core hole is neglected.

XAS is more-or-less proportional to the density of unoccupied states.

This approach is often used, because it is very simple (any band structure code can be manage) and the resulting spectra are in fact often quite good. Or, at least, not very bad.

Especially convenient for metals where the screening of the core hole is efficient and its effect is thus small.

Final state approximation: general formulation

The spectra are calculated for the potential of the final state of the x-ray process, i.e., with the core hole for x-ray absorption.

The screening of the core hole is usually modeled by adding an extra electron to the valence band ("complete screening picture").

Technically, this means treating the photoabsorbing atom as an impurity. The photoelectron is removed from the core level and put into the top of the valence band.

"Relaxed and screened model."

Other electrons will screen the hole, so its effect will not be *so* big.

Final state approximation: technicalities

Band-structure codes: supercells.

Green function formalism: embedded impurity.

Available with SPRKKR but not really for novices.

Simpler approach with SPRKKR code: Treat the atom with missing electron within the single-site CPA.

With single-site CPA the influence of the core hole is limited to the photoabsorbing atom.

Single-site CPA calculation of XAS via SPRKKR

1. Add another atomic type to the system at the photoabsorbing site.

2. SCF calculation: the core hole is at the additional atomic type, with zero concentration.

   ```
   SCF     ITHOLE=3  NQNHOLE=1  LQNHOLE=0
   ```

3. XAS calculation: change concentration to 0.001 and multiply result by 1000 (because for zero concentration you get zero absorption "by definition").

   ```
   OCCUPATION
   IQ   IREFQ  IMQ  NOQ  ITOQ    CONC
   1      1     1    2    1     0.99900  3   0.00100
   2      2     2    1    2     1.00000
   TYPES

   IT   TXT_T   ZT   NCORT   NVALT   NSEMCORSHLT
   1     Ca     20    12       8          0
   2     S      16    10       6          0
   3    Ca_ch   20    12       9          0
   ```

Example: Core hole vers. ground state
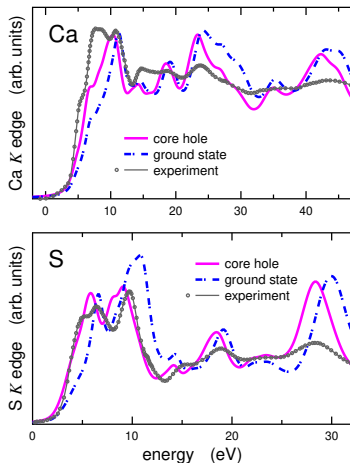
Ca K-edge and S K-edge of CaS (rock salt structure).

ASA

Core hole accounted for within the final state rule.

Ground state potential: core hole ignored.

Example: Two implementations of final-state rule
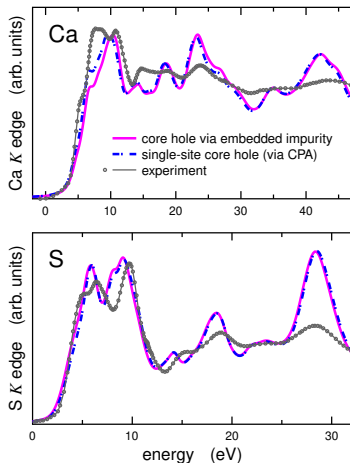
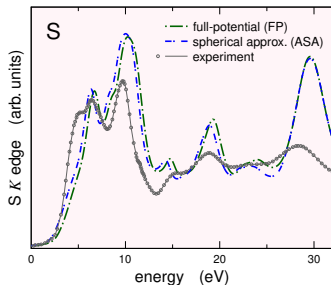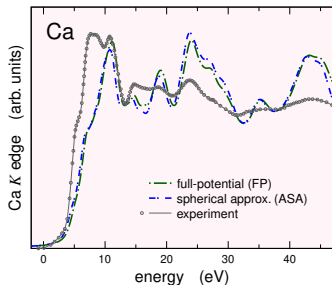Ca K-edge and S K-edge of CaS (rock salt structure).

ASA

Embedded cluster: Core hole on the photoabsorbing atom affects potential on 19 neighboring atoms.

Single-site CPA: Core hole on the photoabsorbing atom does not affect the neighboring atoms.

Full-potential vers. spherical approximation

For close packed systems and/or further from the edge, ASA is usually sufficiently accurate.

Theoretical Ca K-edge (left) and S K-edge (right) XAS of CaS (rock salt structure) obtained in the full-potential (FP) mode and using a spherical potential (ASA).

Outline

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EUROPEAN UNION
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XMCD = XAS − XAS + magnetization + SOC

X-ray **M**agnetic **C**ircular **D**ichroism: $\qquad \sigma_{\mathrm{XMCD}} = \sigma_{\mathrm{XAS}}^{(+)} - \sigma_{\mathrm{XAS}}^{(-)}$

Difference between absorption of left- and right-circularly polarized x-rays in a magnetic sample.
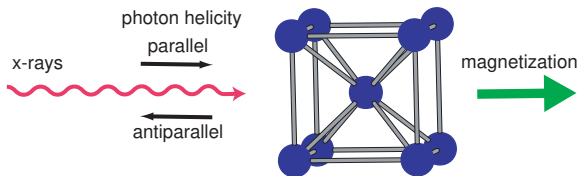
Spin-orbit coupling (SOC) is necessary for XMCD.

Origin of XMCD
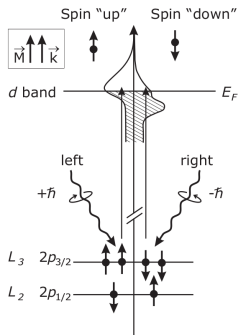
Sorg, PhD thesis (2005)

1. Angular momentum of the photon interacts with the spin of the electron by means of the SOC (Fano effect).

   ▶ Right- and left-circularly polarized photons carry opposite momentum ⇒ there is a spin imbalance in the photocurrent produced by the right- and left-circularly polarized x-rays.

2. Valence band acts as a spin detector for the (spin-imbalanced) photocurrent.

To get XMCD, you need SOC and magnetism.

Anatomy of an XMCD spectrum
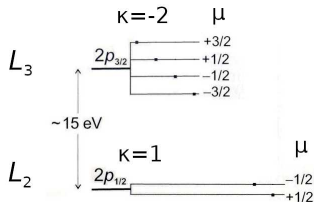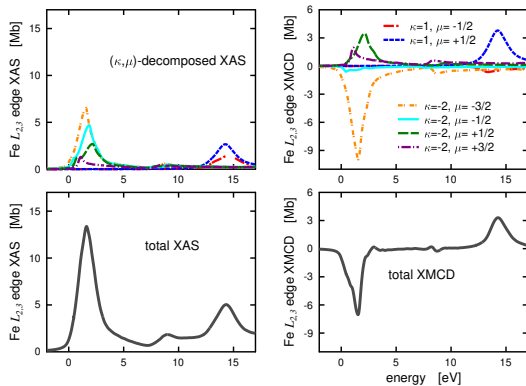
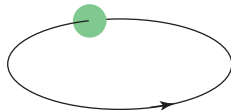- ▶ SOC splitting is between states with different κ (L_2 and L_3 edges).
- ▶ Exchange splitting is between states with same κ but different μ.

Spin and orbital magnetic moments of electron

- Spinning: μ_{spin}

  usually large, $\sim$2.2 μ_B for Fe
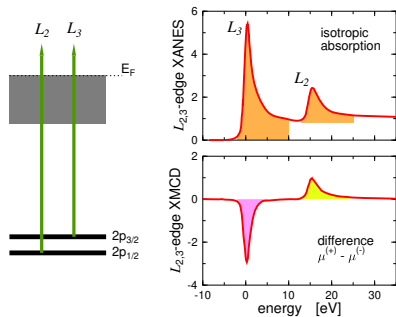
  its magnitude does not depend on the direction

- Orbiting: μ_{orb}

  usually small, $\sim$0.1 μ_B for Fe

  its magnitude depends on the direction

μ_{orb} is small but important, among others, because of its links to magnetocrystalline anisotropy.

Recall the Bruno formula: $E_{\mathrm{MCA}} \sim \mu_{\mathrm{orb}}^{\parallel} - \mu_{\mathrm{orb}}^{\perp}$.

XMCD sum rules

XMCD sum rules:

By adding, subtracting and dividing the peak areas, chemically-specific μ_{spin}, μ_{orb}, and $\mu_{\text{orb}}/\mu_{\text{spin}}$ can be obtained

$$\int \left(\Delta\sigma_{L_3} - 2\Delta\sigma_{L_2} \right) \, \mathrm{d}E \quad \sim \quad \frac{\mu_{\text{spin}}^{(d)} + 7T_z^{(d)}}{3n_h^{(d)}}$$

$$\int \left(\Delta\sigma_{L_3} + \Delta\sigma_{L_2} \right) \, \mathrm{d}E \quad \sim \quad \frac{\mu_{\text{orb}}^{(d)}}{2n_h^{(d)}}$$

$n_h^{(d)}$ number of holes in the d band

T_z magnetic dipole term (see below)

μ_{spin} comes only in combination with $7\,T_z$

XMCD sum rule for the $L_{2,3}$-edge spectra:

$$\frac{\mu_{\text{spin}} + 7\,T_z}{n_h} \sim \int \left(\Delta\sigma_{L_3} - 2\Delta\sigma_{L_2} \right) \, \mathrm{d}E$$

Magnetic dipole term: $\quad T_z = \left\langle \hat{T}_z \right\rangle = \left\langle \frac{1}{2}\left[\boldsymbol{\sigma} - 3\hat{\mathbf{r}}(\hat{\mathbf{r}} \cdot \boldsymbol{\sigma})\right]_z \right\rangle$

Magnetic dipole term depends on the orientation of the magnetization (therefore "$T_{\boldsymbol{\alpha}}$"):

If magnetic field is oriented along the x axis or the y axis:

$$T_x = \left\langle \hat{T}_x \right\rangle = \left\langle \frac{1}{2}\left[\boldsymbol{\sigma} - 3\hat{\mathbf{r}}(\hat{\mathbf{r}} \cdot \boldsymbol{\sigma})\right]_x \right\rangle$$

$$T_y = \left\langle \hat{T}_y \right\rangle = \left\langle \frac{1}{2}\left[\boldsymbol{\sigma} - 3\hat{\mathbf{r}}(\hat{\mathbf{r}} \cdot \boldsymbol{\sigma})\right]_y \right\rangle$$

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T_z-related issues can be handled with SPRKKR

Ignoring the T_z term can cause that for monolayers μ_{spin} appears to be dependent on the orientation of magnetization even if it is not.

Ignoring the T_z term can cause that for clusters μ_{spin} per atom appears to decrease with cluster even if it actually increases.

You can get T_z from SPRKKR output. Use kkrgen.

CONTROL   PRINT=1
ENERGY   GRID={5}   NE={32}   EMIN=-0.7 Ry   ImE=0.0 Ry

```
---------------------------------------------------------------------

 33 E= 0.4784 0.0000          IT=  20  Co
       DOS      NOS      P_spin    m_spin    P_orb     m_orb     B_val       B_core
  s    1.5802   0.5461   -0.2004   0.0324    0.00001   0.00000   197.27 s    -232.99
  p    0.5178   0.2188    0.1768   0.0177    0.01200  -0.00133    -0.43 ns      0.90
  d  109.0353   7.6220 -106.4458   2.0695   -1.11175   0.45265   229.62 cor -232.09
 sum 111.1332   8.3870 -106.4694   2.1197   -1.09974   0.45132   426.47 v+c  194.38
                        P(T_z)    T_z
  s                     0.0000    0.0000
  p                    -0.0161   -0.0011
  d                     2.6197    0.1027
 sum                    2.6036    0.1017
```
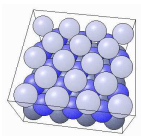
Outline

Magnetic structure of a Mn monolayer on W(110)
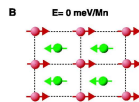
atomic structure of bcc(110):

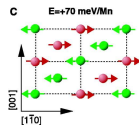magnetic structures:
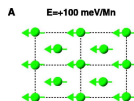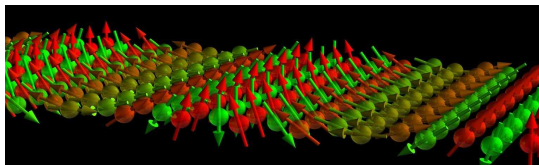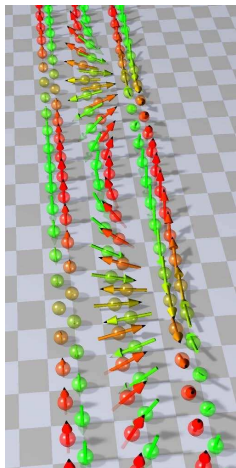

ferromagnetic (FM)

antiferromagnetic (AFM) c(2×2)

AFM p(2×1)

- ▶ Early STM and ab-initio theoretical studies suggested antiferromagnetic (AFM) order

  [Heinze *et al.* Science 2000, Dennler & Hafner PRB 2005].

Antiferromagnetic cycloidal spin spiral

- ► Later studies: a more complicated magnetic structure.

- ► Options: spin density wave (SDW), helical spin spiral (hSS), cycloidal spin spiral (cSS).

- ► Experiment and model calculations suggested that the most probable option is a cycloidal spin spiral [Bode *et al.* Nature 2007, Haze *et al.* Sci. Rep. 2017].

SDW   hSS   cSS

STM may not provide the whole story

- ▶ STM probes a small part of the sample, it may not be quite representative [especially when dealing with terraced surfaces such as W(110)].

- ▶ STM informs about projections of magnetic moments, not about their more complex structure.
  - ▶ Spin density wave?
  - ▶ Helical spin spiral?
  - ▶ Cycloidal spin spiral?

- ▶ Performing an STM measurement takes time, the system may change in between: thermal depinning of spin spirals.

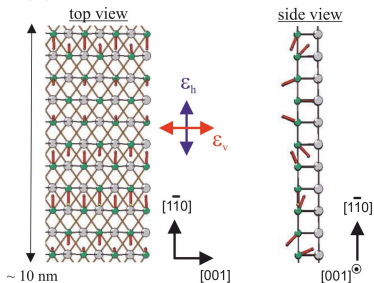# Mn monolayer on W(110)

(a) Step-flow growth of Mn on W(110)

(b) Mn / W(110) surface

top view

side view

ϵ_h

ϵ_v

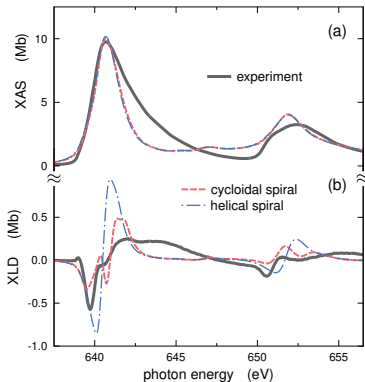[1̄10]

[1̄10]

[001]

[001]

~ 10 nm
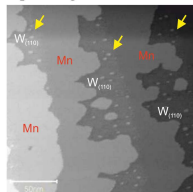
LEED orientation W(110) substrate

$\phi = 0°$

(a) STM image of the Mn/W(110) surface with a Mn coverage of about 80% of a monolayer.

(b) Schematic depiction of the surface atomic configuration and respective orientation of ϵ_h and ϵ_v photon polarization vectors. Magnetic moments are represented by red rods.

Mn/W(110): Comparing experiment and theory

Honolka *et al.* PRB **103**, 174419 (2021)

- ▶ Experimental and theoretical Mn $L_{2,3}$-edge spectra:
  - (a) X-ray absorption (XAS)
  - (b) X-ray linear dichroism
    XLD $= \sigma(\epsilon_v) - \sigma(\epsilon_h)$

- ▶ Theory: Cycloidal and helical spin spirals give rise to significantly different XLD signals.

- ▶ X-ray absorption spectroscopy confirms that the magnetic ground state of Mn/W(110) is an AFM cycloidal spin spiral.

XLD in the presence of magnetism.

Magnetism is not a mere "perturbation"
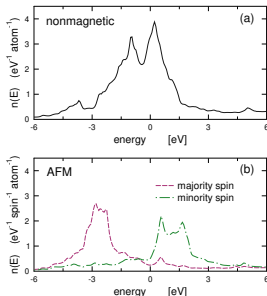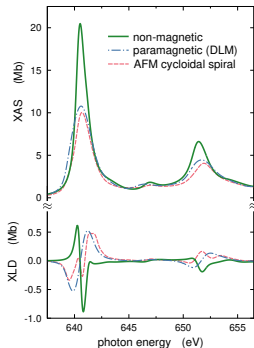
Honolka *et al.* PRB **103**, 174419 (2021)

- ▶ XAS and XLD for the same structure in a *non-magnetic* state and in a *paramagnetic* state differ a lot.
- ▶ DOS for the same structure in a *non-magnetic* state and in an *antiferromagnetic* state differ a lot.
- ▶ Changing the magnetic state is like taking a different element from the periodic table.

Spin-orbit coupling (SOC) matters
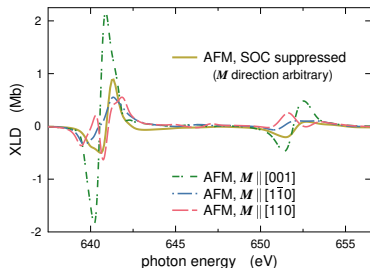
The direction of the magnetic moments (linked to the structure via SOC) has a significant impact on Mn $L_{2,3}$-edge XLD of a Mn monolayer on W(110).

Honolka *et al.* PRB **103**, 174419 (2021)

Mn $L_{2,3}$-edge XLD spectra for Mn/W(110) calculated for collinear AFM configurations, assuming that the direction of the magnetic moments is parallel to one of three mutually perpendicular directions.

Technical note: Non-relativistic mode simulated by (i) suppressing the SOC in the valence band and (ii) suppressing the relativistic exchange splitting of the 2p core levels pertaining to the same relativistic quantum number κ.

Comparative advantage of using SPRKKR for XAS

- ▶ Real-space and reciprocal-space calculation aavailable, on the same footing.

- ▶ SCF potentials naturally, by "default". Full potential available.

- ▶ Disordered systems: CPA, temperature.

- ▶ Magnetic systems: XMCD, XMLD, non-collinear magnetic order.

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