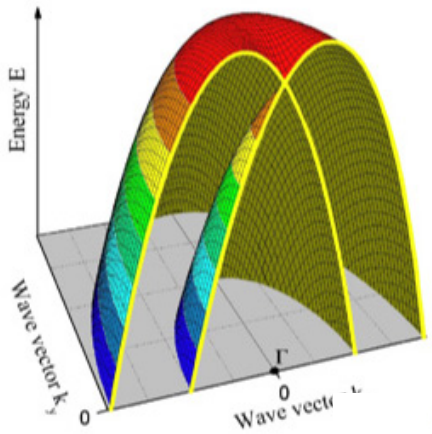
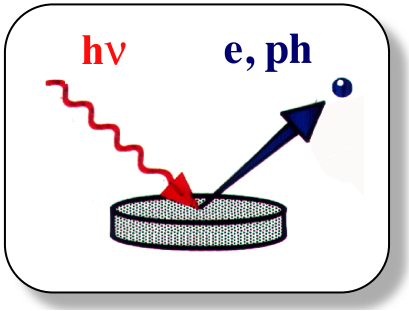
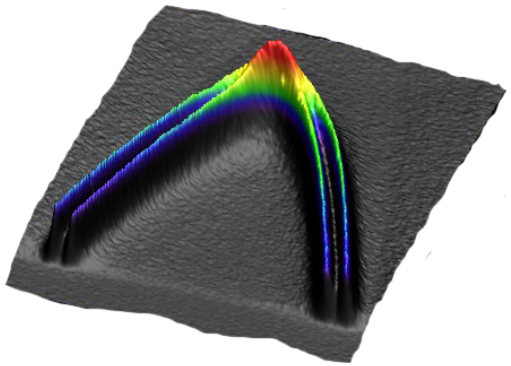
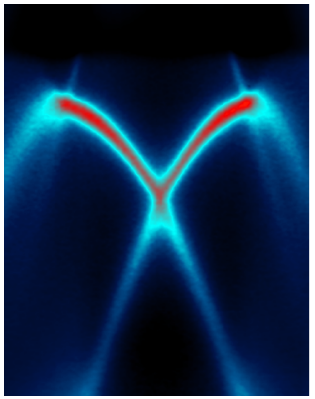
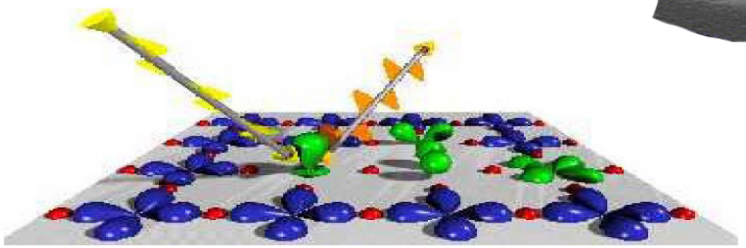
Spin-orbit and spectroscopies from atoms to solids











Marco Grioni
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ÉCOLE POLYTECHNIQUE
FÉDÉRALE DE LAUSANNE

Plan of the lectures

Lecture 1

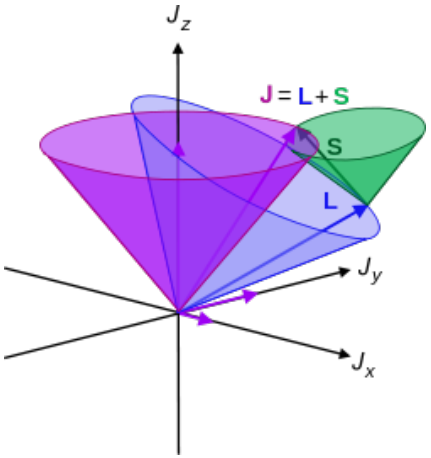
- Generalities on SOI
- Techniques: XAS, PES, RIXS
- Polarized electrons: XMCD and SP-PES
- Exemples

Lecture 2

- The Rashba effect
- From Rasba to TI's
- SOI and RIXS

General consideration

Spin-orbit: where from?



From Dirac to Schrödinger up to $(v/c)^2$ Extra terms

$$H = H_0 - \frac{\mathbf{P}^4}{8m_e^3c^2} + \frac{1}{2m_e^2c^2}\frac{1}{r}\frac{dV(r)}{dr}\vec{\mathbf{L}}\cdot\vec{\mathbf{S}} + \frac{\hbar^2}{8m_e^2c^2}\nabla^2V(r) + \ldots$$

Mass-velocity **Spin-orbit** **Darwin**

$$\frac{H_{MV}}{H_0} \simeq \frac{H_{SO}}{H_0} \simeq \frac{H_D}{H_0} \simeq \alpha^2 \simeq \frac{1}{(137)^2}$$

Spin-orbit: hydrogen atom

A magnetic field appears in the electron's rest frame:

$$\vec{B} = -\frac{1}{c^2}\vec{v}\times\vec{E} = \frac{1}{m_e c^2}\vec{p}\times\frac{1}{q}\frac{dV(r)}{dr}\frac{\vec{r}}{r} = -\frac{1}{qm_e c^2}\vec{r}\times\vec{p}\frac{1}{r}\frac{dV(r)}{dr} = \frac{1}{qm_e c^2}\frac{1}{r}\frac{dV(r)}{dr}\vec{L}\ ,$$

Which entails the interaction term

(Thomas's precession yields the extra 1/2):

$$E_{SO} = -\frac{1}{2}\vec{M}\cdot\vec{B} = -\frac{q}{m_e}\vec{S}\cdot\vec{B} \quad\rightarrow\quad H_{SO} = \frac{1}{m^2{}_e c^2}\frac{1}{r}\frac{dV(r)}{dr}\vec{\mathbf{L}}\cdot\vec{\mathbf{S}}$$

$$V = -\frac{Z e^2}{r}\ ;\quad \alpha = \frac{e^2}{\hbar c} = \frac{1}{137}\ ;\qquad H_{SO} = \frac{Z\hbar^2\alpha^2}{2m_e^2 e^2}\frac{1}{r^3}\vec{\mathbf{L}}\cdot\vec{\mathbf{S}} = \xi(r)\,\vec{\mathbf{L}}\cdot\vec{\mathbf{S}}$$

$$\vec{\mathbf{L}}\cdot\vec{\mathbf{S}} = \frac{1}{2}(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2)$$

Spin-orbit: hydrogen(oid) atom (Z protons, 1 electron)

Without spin-orbit: $\mathbf{L}^2\,;\mathbf{L}_z\,;\mathbf{S}^2\,;\mathbf{S}_z\,;\mathbf{J}^2\,;\mathbf{J}_z$ **commute. Eigenstates:**

$$|n;l;m_l;\pm\rangle \;\;;\qquad j=l\pm\frac{1}{2}$$

With spin-orbit: $\mathbf{H}_{SO}\,;\mathbf{J}_z\,;\mathbf{J}^2$ **commute. The eigenstates** $|n;j;m_j\rangle$ **are appropriate combinations of the** $|n;l;m_l;\pm\rangle$

angular **radial**

$$E_{nlj}=\langle jm_j\,|\,H_{SO}\,|\,jm_j\rangle=\frac{Z\hbar^2\alpha^2}{2m_e^2\,e^2}\langle\frac{1}{r^3}\rangle\langle jm_j\,|\,\vec{\boldsymbol{S}}\cdot\vec{\boldsymbol{L}}\,|\,jm_j\rangle=\qquad\zeta_{nl}\langle jm_j\,|\,\vec{\boldsymbol{S}}\cdot\vec{\boldsymbol{L}}\,|\,jm_j\rangle$$

$$E_{nlj}=\frac{\zeta_{nl}}{2}\left\{\begin{array}{ll} l & (j=l+1/2)\\ -(l+1) & (j=l-1/2)\end{array}\right\}$$

$$\Delta E_{SO}=\frac{(2l+1)}{2}\zeta_{nl}=\frac{|E_n|Z^2\alpha^2}{nl(l+1)}\approx\frac{Z^2}{n^2}\frac{Z^2\alpha^2}{nl(l+1)}\approx\frac{Z^4}{n^3}$$

Textbook example: the *2p* states of hydrogen

$$H_{so} = \frac{\hbar^2 \zeta_{nl}}{2}$$

m_j	3/2	1/2	−1/2	−3/2
3/2	1	0	0	0
1/2	0	−1	$\sqrt{2}$	0
−1/2	0	$\sqrt{2}$	0	0
−3/2	0	0	0	1

$$|m_l; m_s\rangle$$

$|1;+\rangle \qquad m_j = 3/2$

$|1;-\rangle\,|0;+\rangle \qquad m_j = 1/2$

$|0;-\rangle\,|-1;+\rangle \qquad m_j = -1/2$

$|-1;-\rangle \qquad m_j = -3/2$

$$\vec{\mathbf{S}}\cdot\vec{\mathbf{L}} = \mathbf{S}_z\mathbf{L}_z + \frac{1}{2}(\mathbf{S}^+\mathbf{L}^- + \mathbf{S}^-\mathbf{L}^+)$$

$$H_{so} = \frac{\hbar^2 \zeta_{nl}}{2}$$

j	3/2				1/2	
3/2	1	0	0	0	0	0
1/2	0	1	0	0	0	0
−1/2	0	0	1	0	0	0
−3/2	0	0	0	1	0	0
1/2	0	0	0	0	−2	0
−1/2	0	0	0	0	0	−2

$$|\tfrac{3}{2};\tfrac{3}{2}\rangle = |1;+\rangle \;; \quad |-\tfrac{3}{2};-\tfrac{3}{2}\rangle = |-1;-\rangle$$

$$|\tfrac{3}{2};\tfrac{1}{2}\rangle = \sqrt{\tfrac{2}{3}}\,|0;+\rangle + \sqrt{\tfrac{1}{3}}\,|1;-\rangle \qquad \langle \mathbf{S}_z\rangle = \frac{\hbar}{6}\;;\; \langle \mathbf{L}_z\rangle = \frac{\hbar}{3}$$

$$|\tfrac{3}{2};-\tfrac{1}{2}\rangle = \sqrt{\tfrac{1}{3}}\,|-1;+\rangle + \sqrt{\tfrac{2}{3}}\,|0;-\rangle \qquad \langle \mathbf{S}_z\rangle = -\frac{\hbar}{6}\;;\; \langle \mathbf{L}_z\rangle = -\frac{\hbar}{3}$$

$$|\tfrac{1}{2};\tfrac{1}{2}\rangle = \sqrt{\tfrac{2}{3}}\,|1;-\rangle - \sqrt{\tfrac{1}{3}}\,|0;+\rangle \qquad \langle \mathbf{S}_z\rangle = -\frac{\hbar}{6}\;;\; \langle \mathbf{L}_z\rangle = \frac{2\hbar}{3}$$

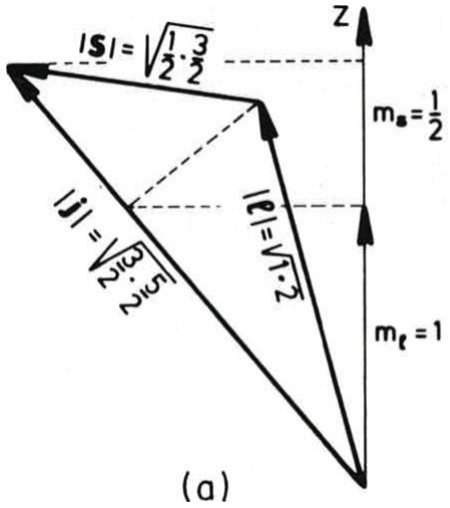
$$|\tfrac{1}{2};-\tfrac{1}{2}\rangle = \sqrt{\tfrac{1}{3}}\,|0;-\rangle - \sqrt{\tfrac{2}{3}}\,|-1;+\rangle \qquad \langle \mathbf{S}_z\rangle = \frac{\hbar}{6}\;;\; \langle \mathbf{L}_z\rangle = -\frac{2\hbar}{3}$$

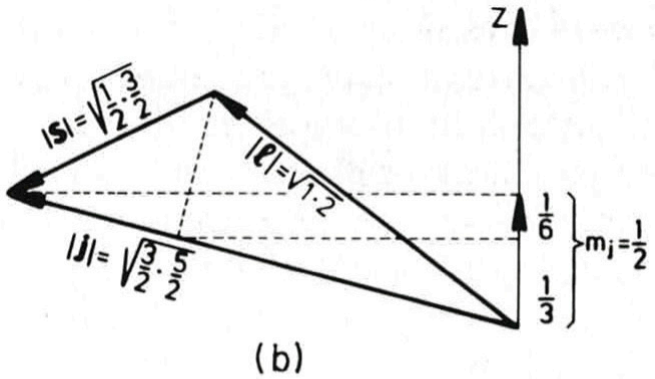
Textbook example: the *2p* states of hydrogen

VECTOR MODEL

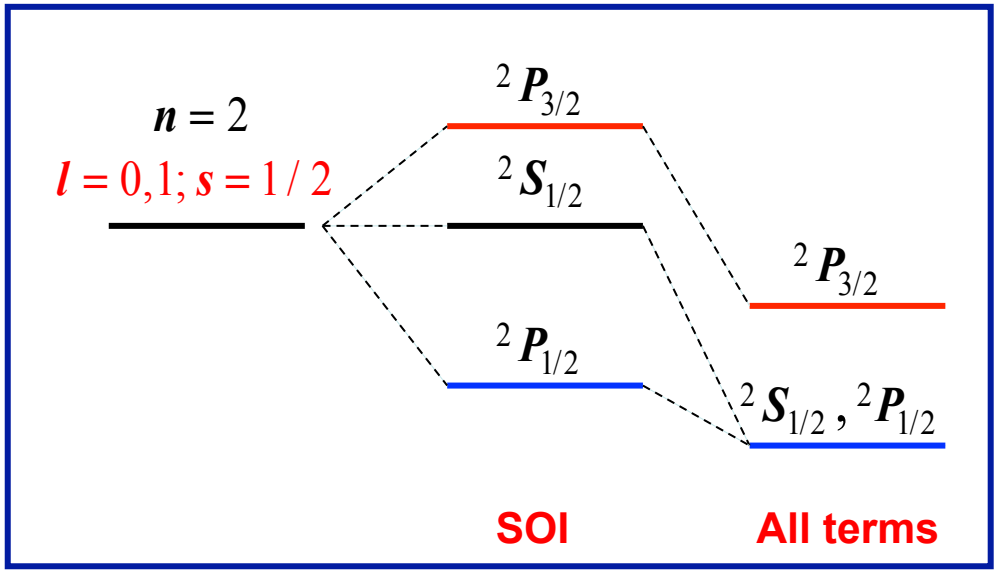
$|\, j\,;\, m_j \rangle$

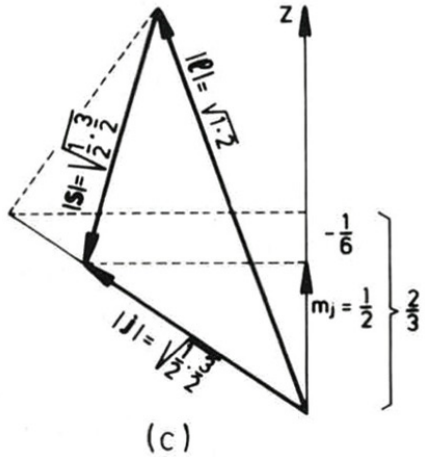
$|\frac{3}{2};\frac{3}{2}\rangle$





$|\frac{3}{2};\frac{1}{2}\rangle$





$|\frac{1}{2};\frac{1}{2}\rangle$

Preliminary considerations

The SOI couples the orientation of the magnetic moments to the crystal directions

→ **magnetic anisotropy, new quantum states…**

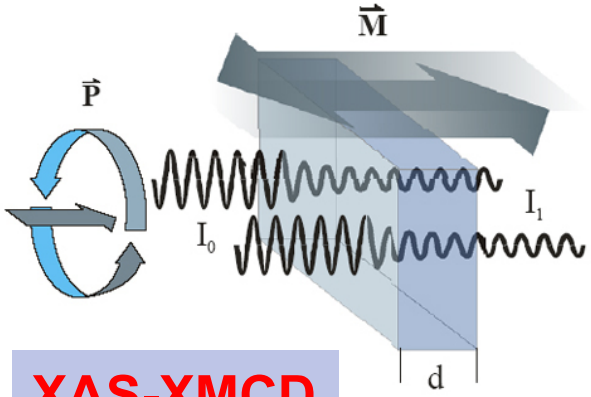
Moreover, e.m. waves interact with L, not with S. **However**

SOI couples L and S, so that we can probe S with light!

→ **Circular magnetic dichroism: absorption (XMCD); photoemission (SP-PES)**

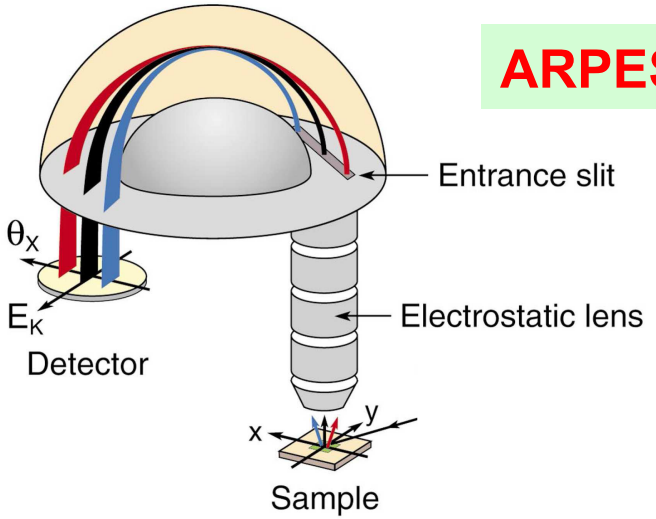
→ **Resonant inelastic x-ray scattering**

Spectroscopic probes

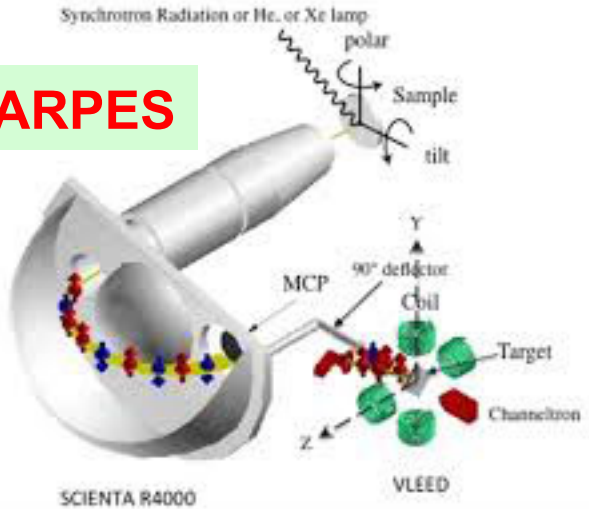


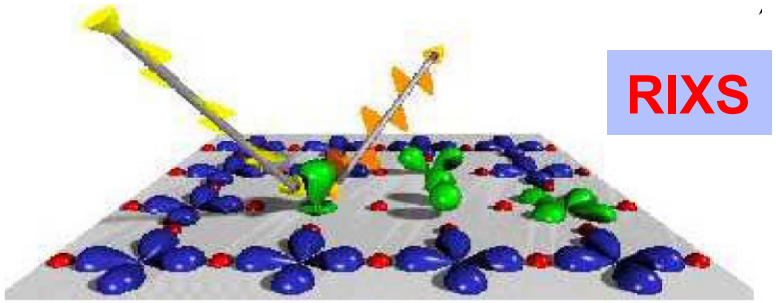
XAS-XMCD

ARPES



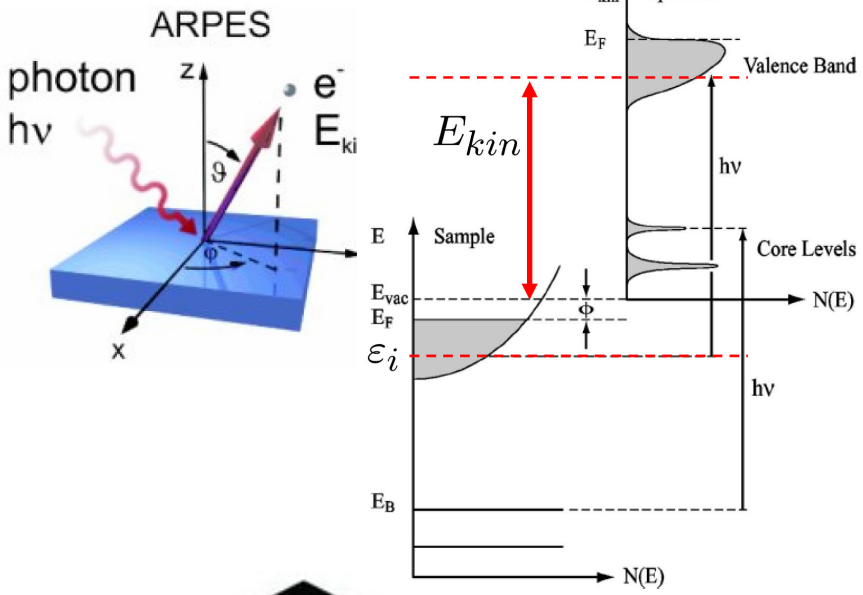
SP-ARPES

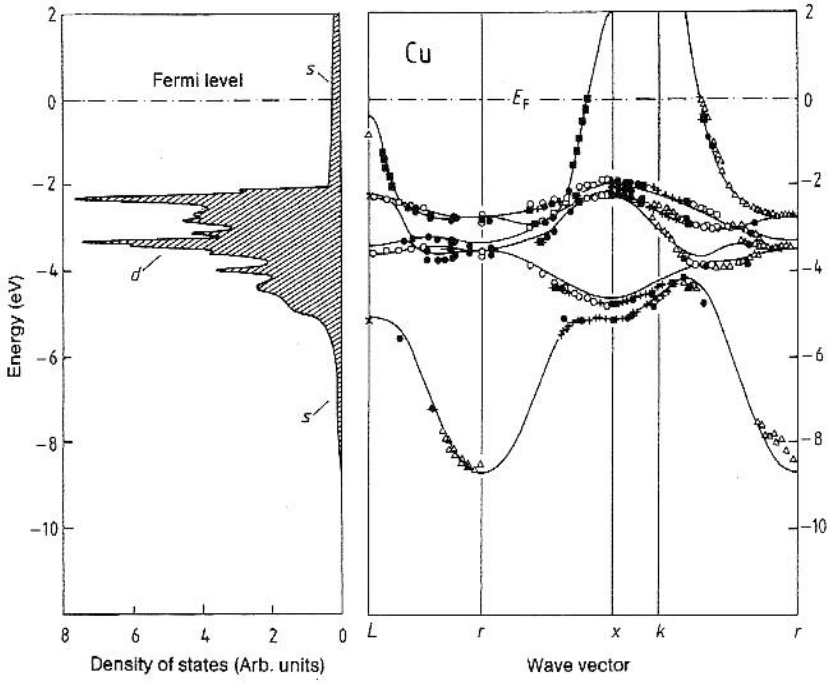




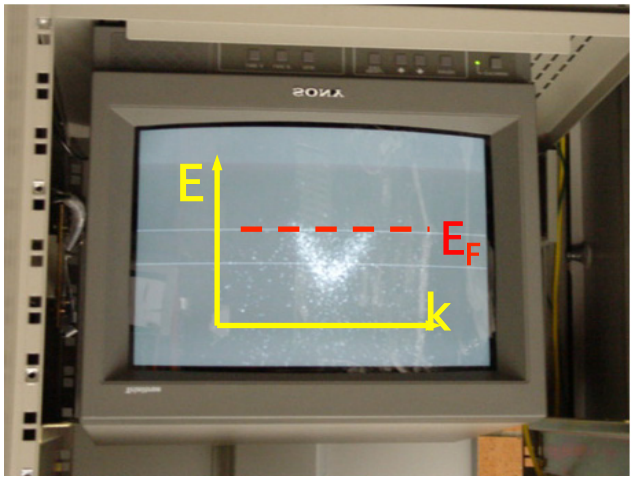
RIXS

PES – ARPES – SP-ARPES



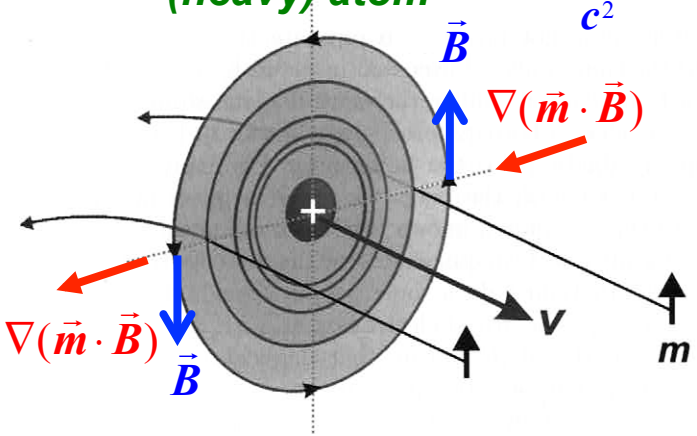


ARPES:
k-resolution



The Mott polarimeter – spin-orbit, again !

(heavy) atom $\vec{B} = -\frac{1}{c^2}\vec{v}\times\vec{E}; \quad \vec{F} = \nabla(\vec{m}\cdot\vec{B})$

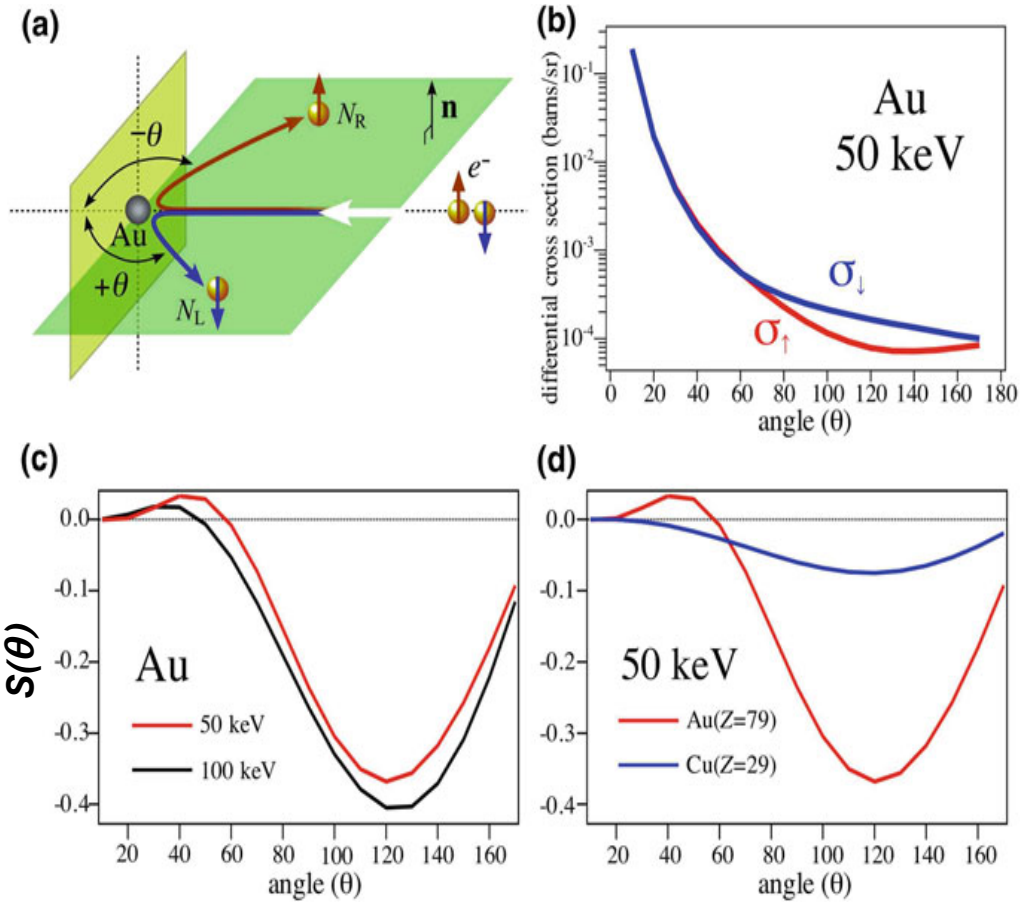


In the electron's rest frame

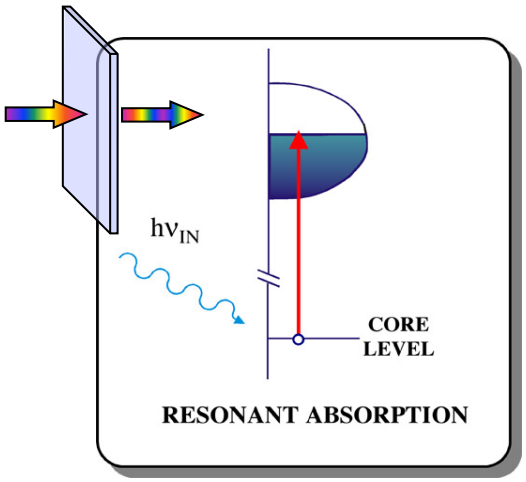
$$\sigma(\theta) = \sigma_0(1 + S(\theta)\vec{P}\cdot\vec{n})$$

$\vec{P}$ **Spin polarization**

S **Sherman function**

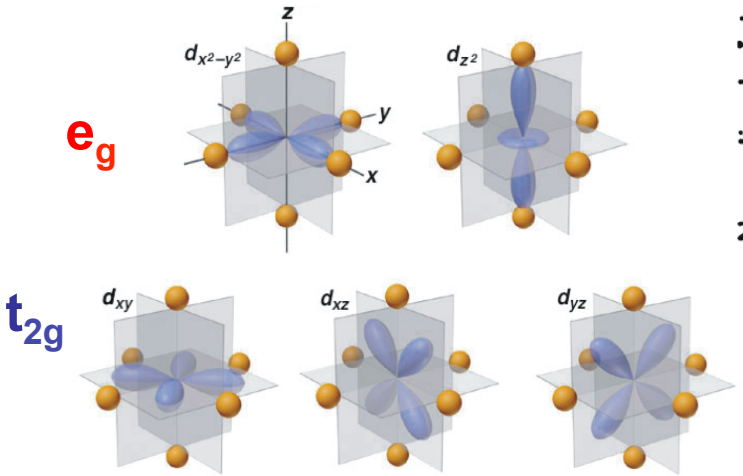


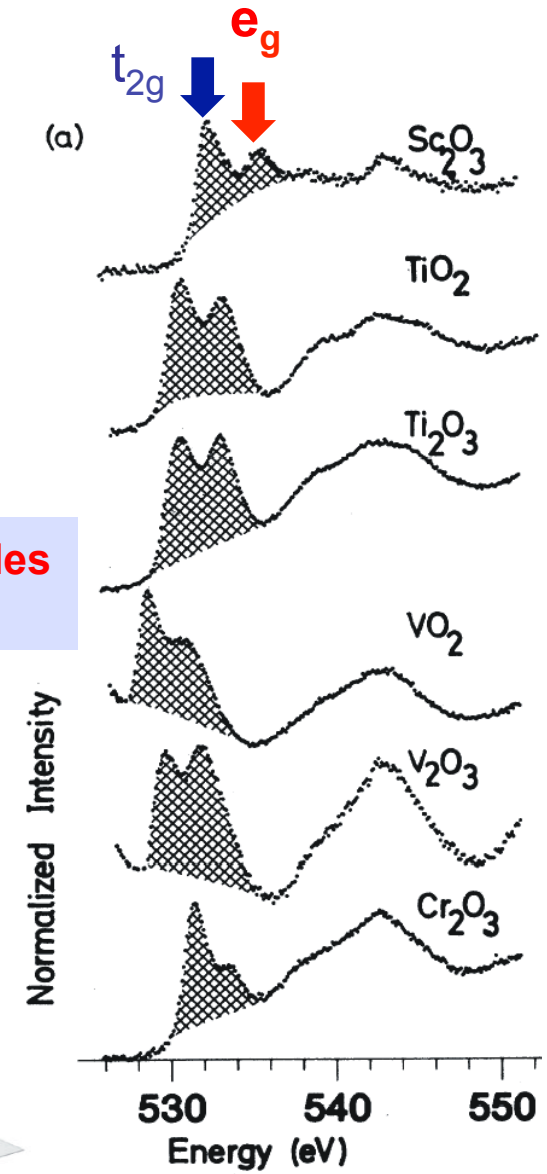
XAS: unoccupied states



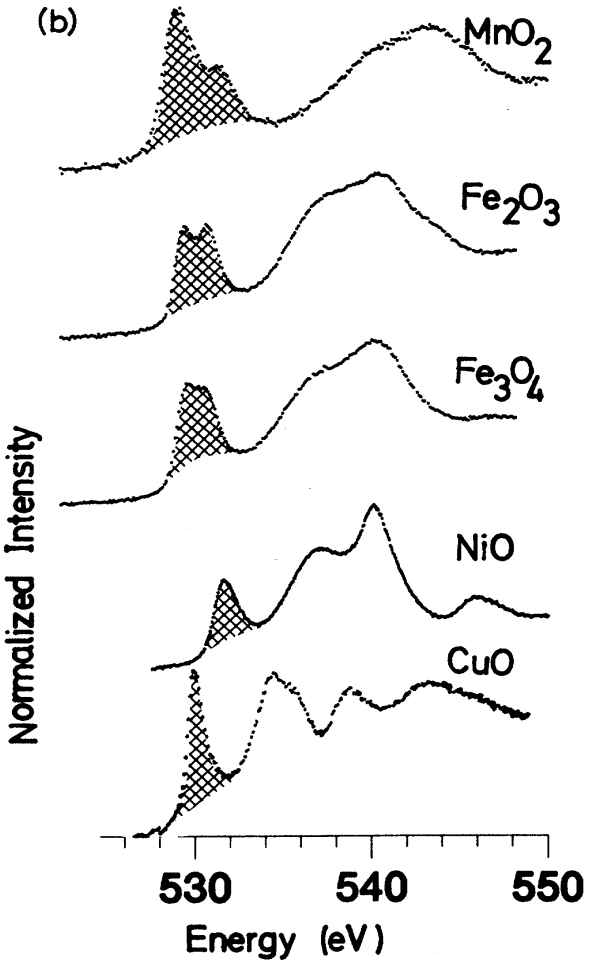
Core hole and dipole selection rules ($\Delta l=\pm1$) select the final states

TM *3d* – O *2p* hybrid states





The O K edge (1s → εp) of 3d TM oxides

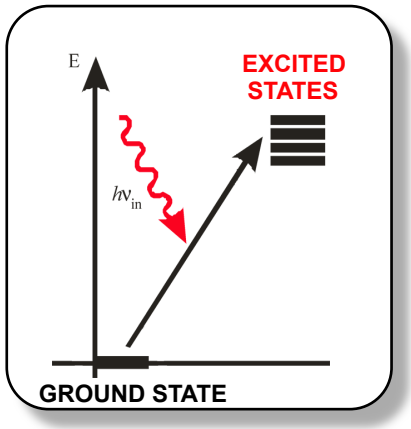


F.M.F. de Groot et al., PRB (1989)

Beyond the single particle picture

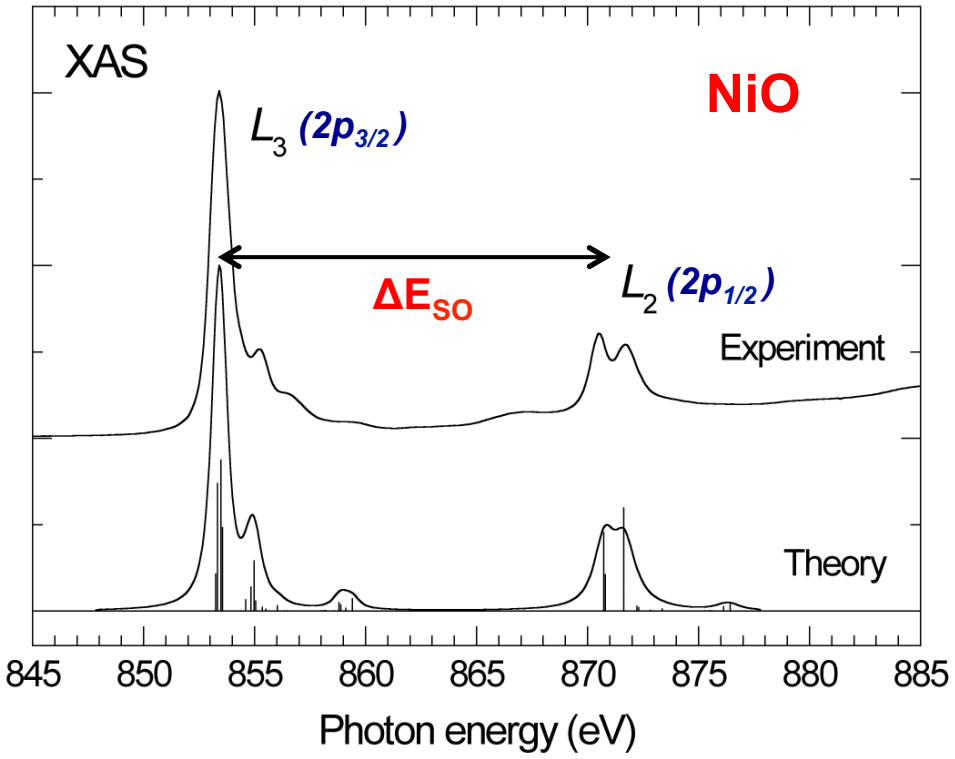
The XAS~DOS picture breaks down when the final states are strongly correlated: TM 3d states

Total energy diagram



$\Delta E_{SO}(2p)$ large
J is the good quantum number
$\Delta J=0,\pm1$ (no $0\rightarrow0$)

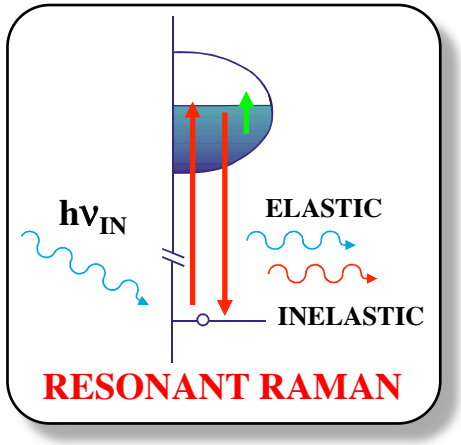
3d TM $L_{2,3}$ edges: $3d^N \rightarrow 2p^5 3d^{N+1}$

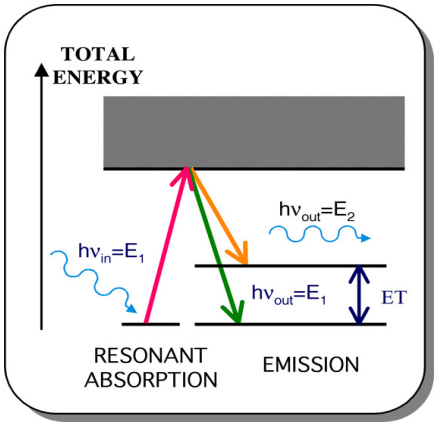


The atomic-like multiplet structure is a fingerprint of the *ground state* configuration…

Photons do it all: resonant inelastic x-ray spectroscopy (RIXS)

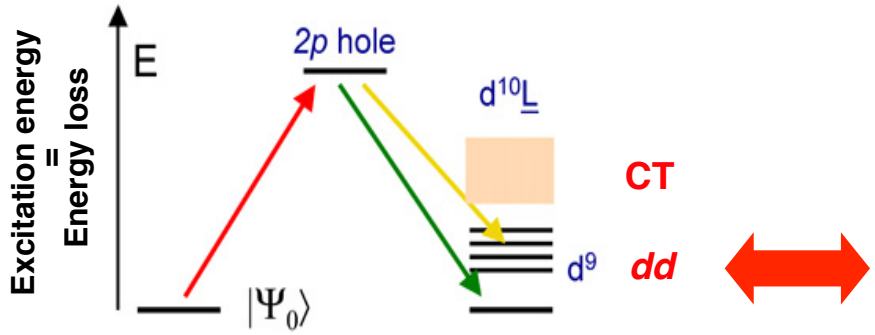
Threshold excitation of a core state

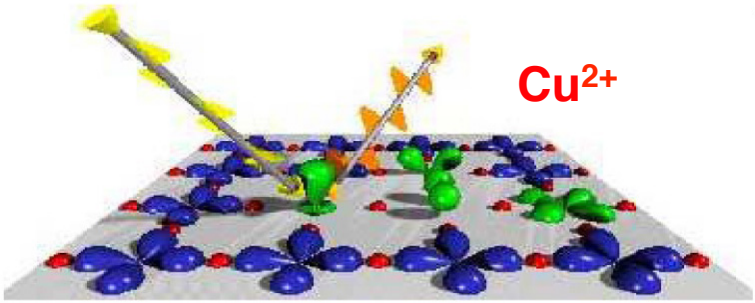




Energy loss (energy transfer)

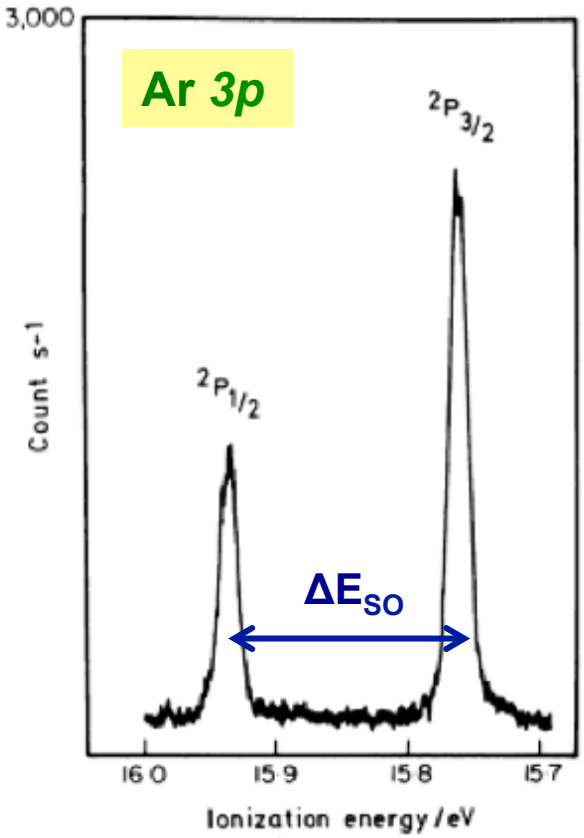
Example - Cu L3 RIXS: $3d^9 \rightarrow 2p^5 3d^{10} \rightarrow 3d^9$



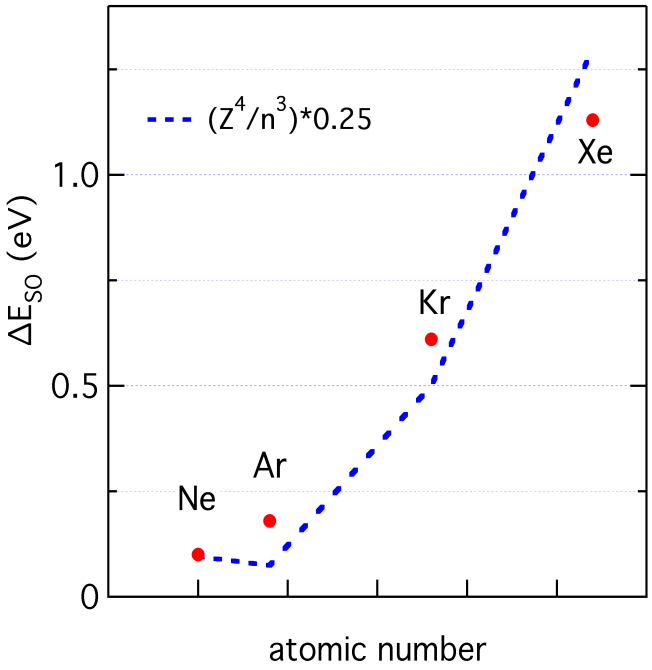


Spin-orbit: rare gases

Photoemission



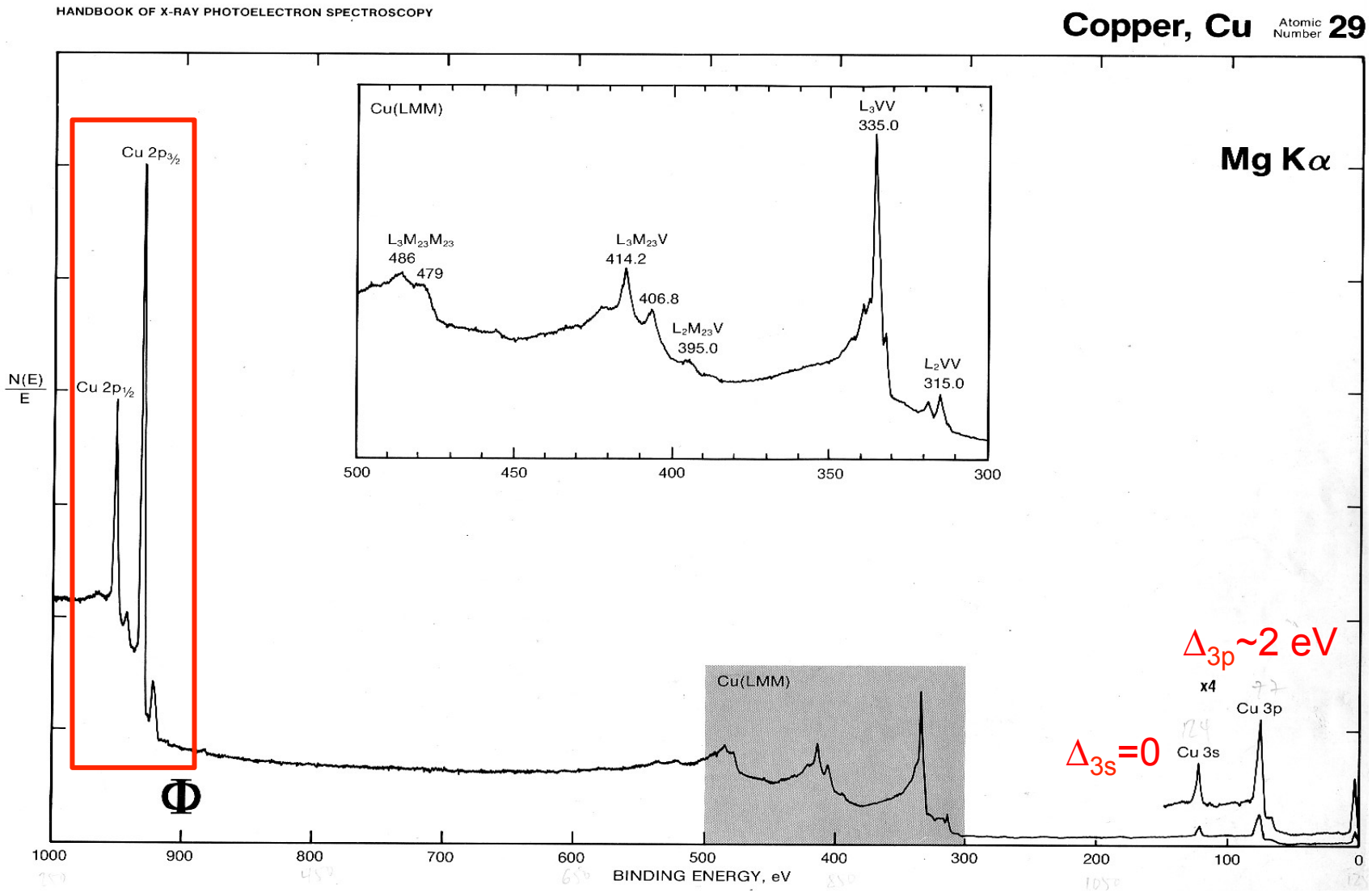
Rare gases - *np*



Semi-empirical:

$\zeta_{n,p}=0.405\ Z^{2.33}/(E_n)^{1.5}$

Solids: core levels - PES



Δ_{3p}~2 eV

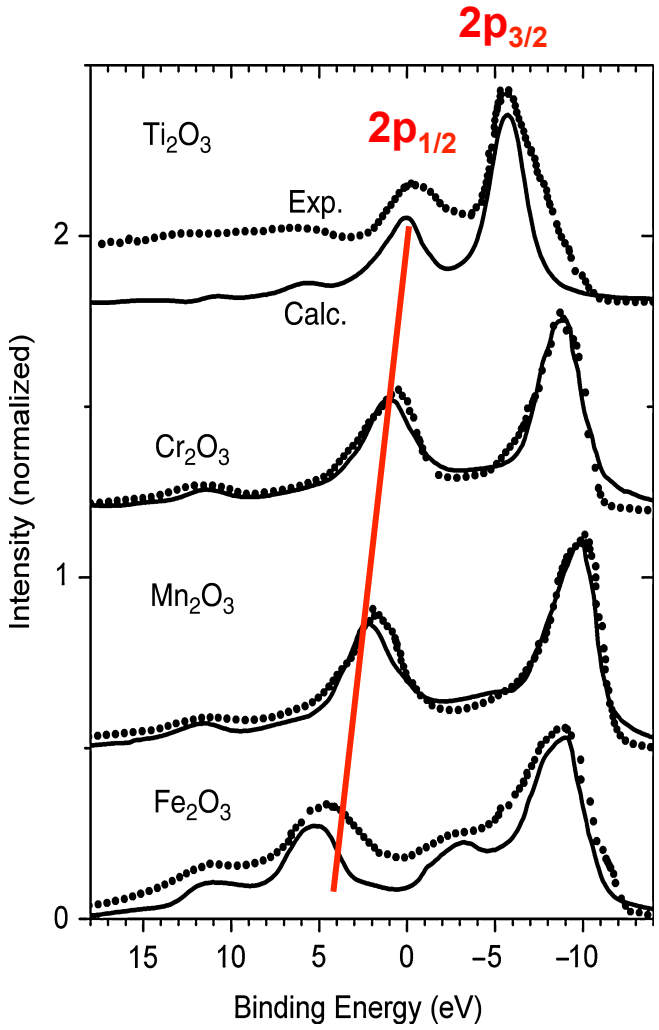
Δ_{3s}=0

Δ_{2p}~20 eV

Solids: core levels - PES

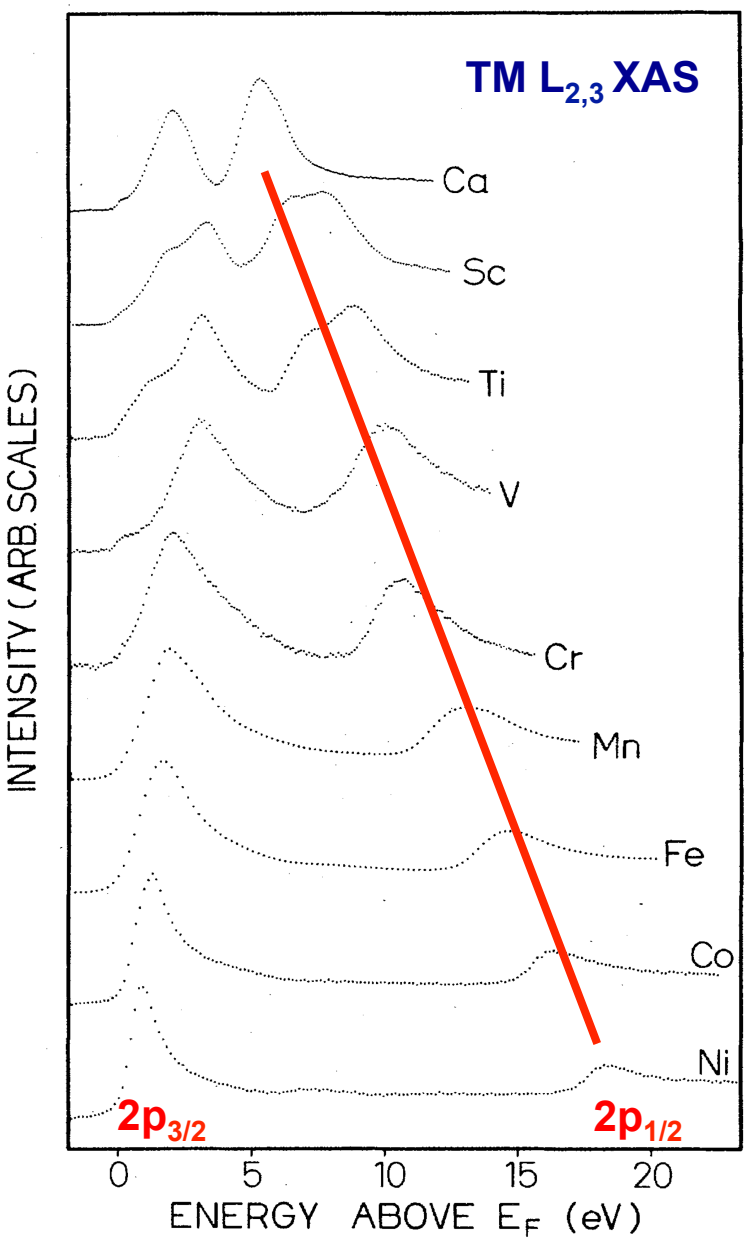
Early 3d TM oxides:

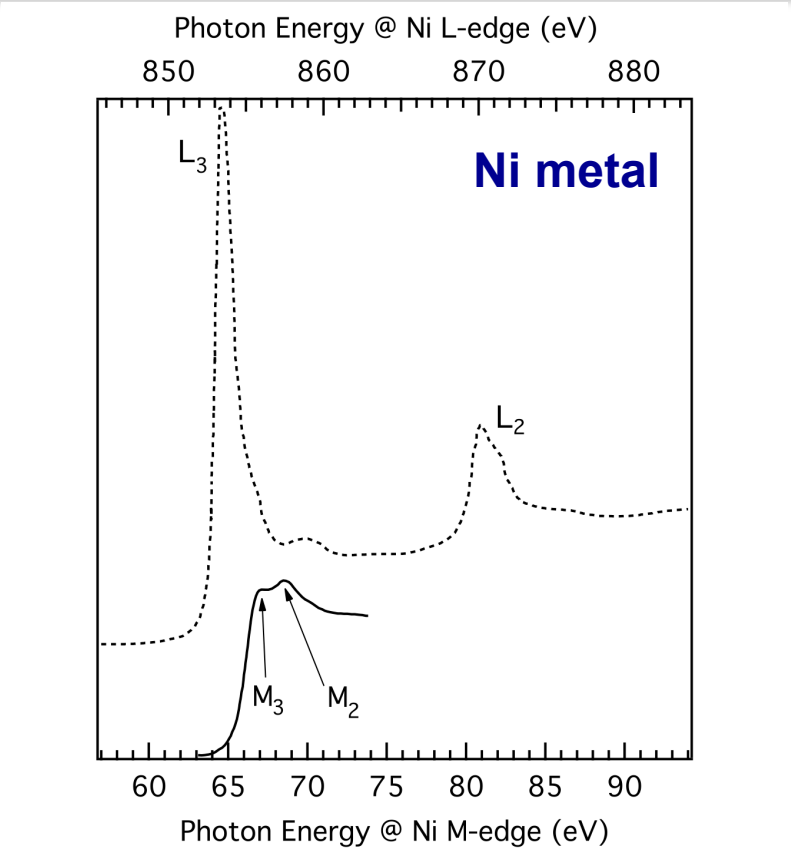
TM 2p PES



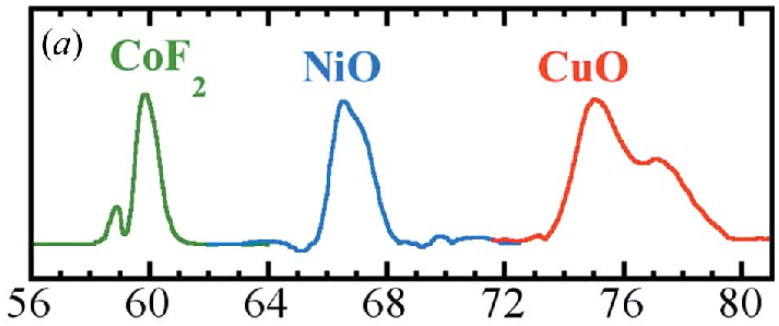
De Groot and Kontani (2008)

Solids: core levels - XAS



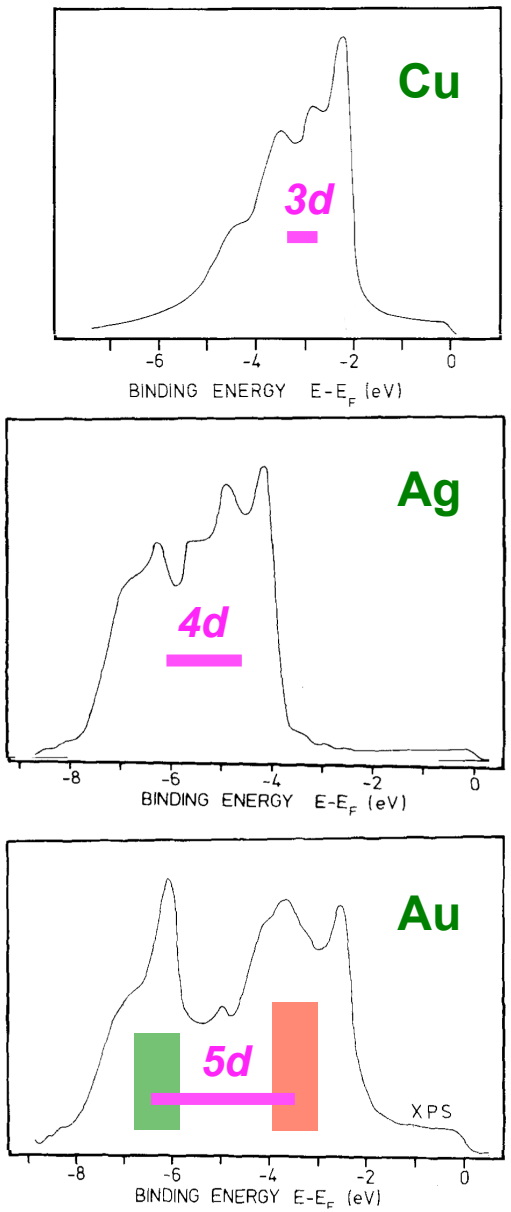


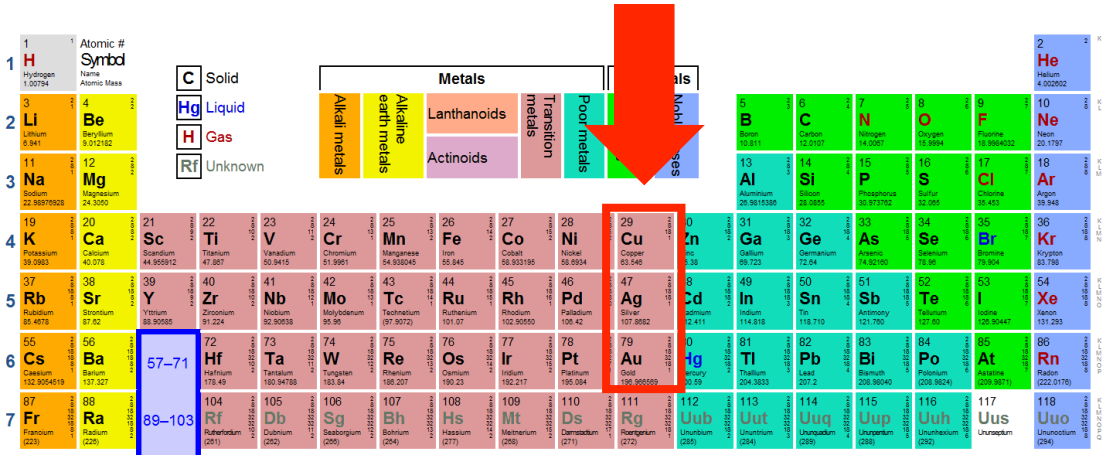
M_{23} (3p→3d) edges



Solids: valence bands - PES

PES – noble metals





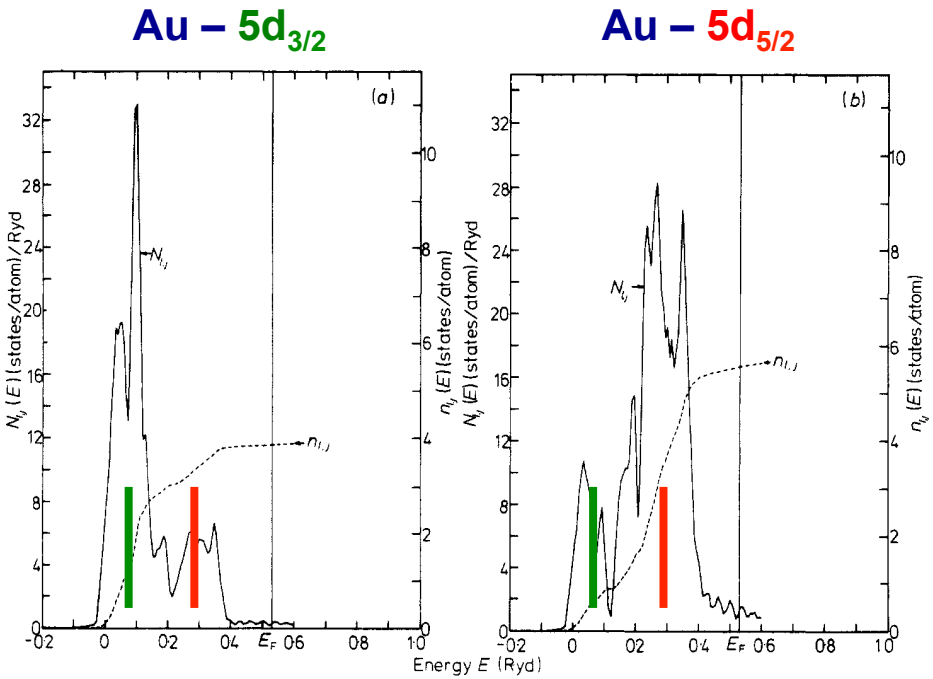
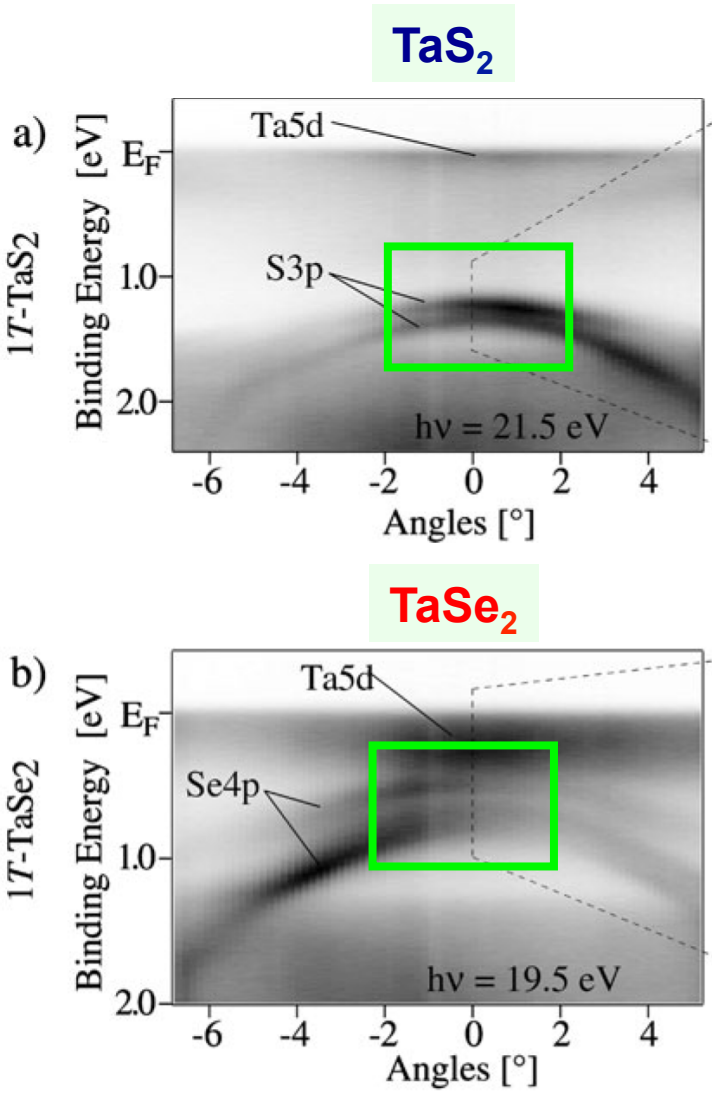
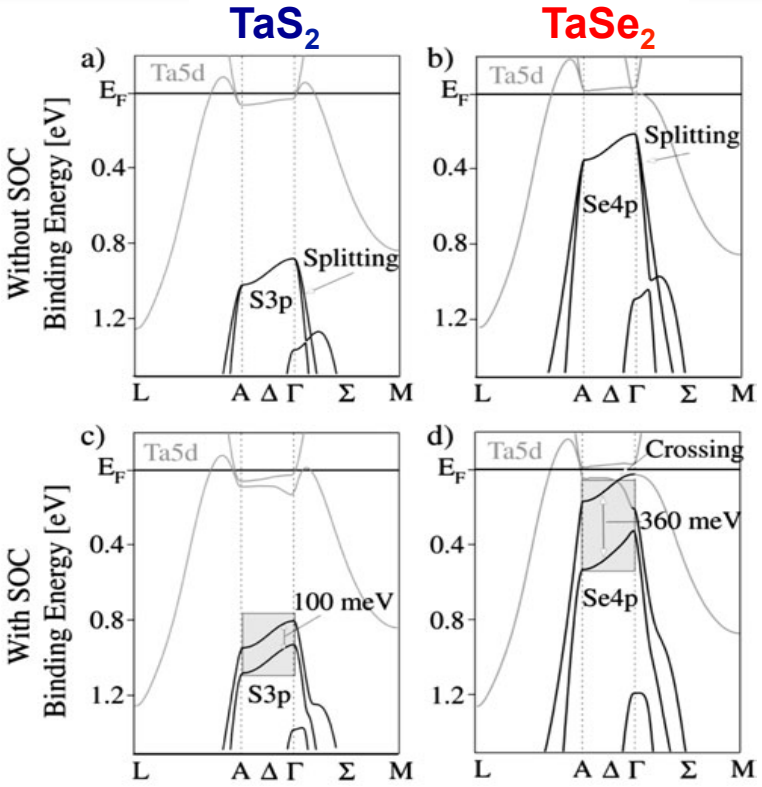


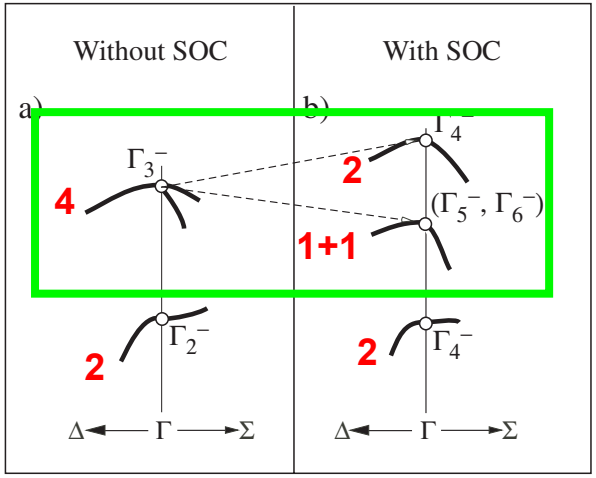
Figure 2. Spin–orbit projected densities of states $N_{l,j}$ for gold, $l = 2$: (*a*), $j = 3/2$ and (*b*), $j = 5/2$ (curves shown with a full line). The broken curves represent the integrated partial DOS functions.

Solids: valence bands - ARPES



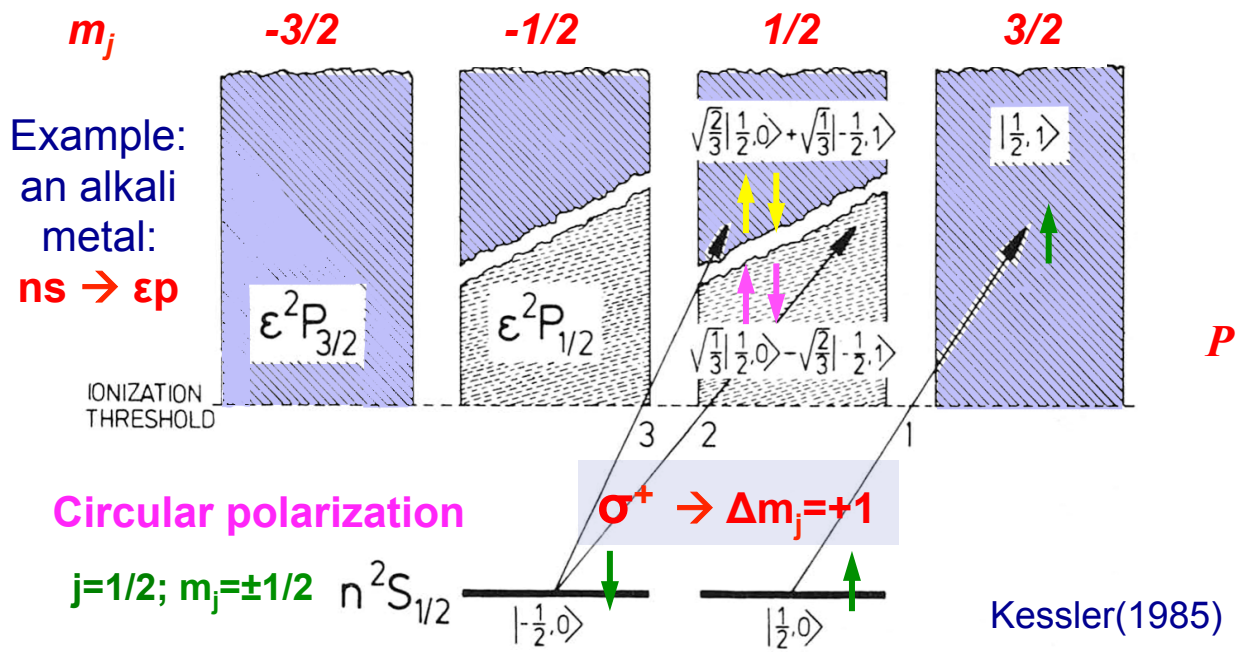
F. Clerc et al., JPCM (2004)





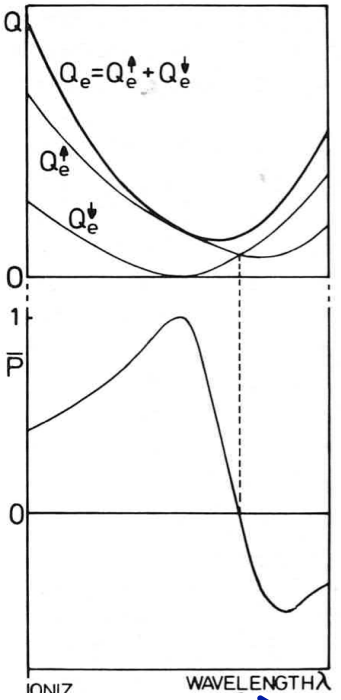
The Fano effect: polarized electrons from unpolarized atoms

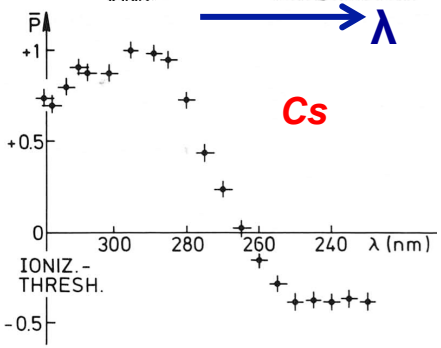
photon angular momentum → dipole selection rules
→ electron orbital momentum → spin-orbit interaction → electron spin
No SO → no spin-flip!!



Kessler(1985)

$$P=\frac{Q_e^{\uparrow}-Q_e^{\downarrow}}{Q_e^{\uparrow}+Q_e^{\downarrow}}$$





Angle-integrated:

$$\frac{Q_e^{\uparrow}}{Q_e^{\downarrow}}=\frac{9R_3^2+2(R_3-R_1)^2}{(2R_1+R_3)^2}\;;\quad R_{1,3}=\langle R_{n,0}\,|\,r\,|\,R_{\varepsilon,1,m_j=1/2;3/2}\rangle$$

No spin-orbit → $R_1=R_3\;;\;\frac{Q_e^{\uparrow}}{Q_e^{\downarrow}}=1\;;\;P=0$

Exploiting the spin polarization: circular dichroism in XAS/PES

Goal(s): to determine separately the spin- and orbital moments (and the expectation values of other observables)

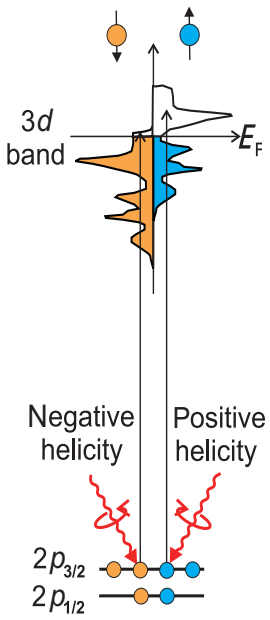
XAS: Transitions into low-lying (localized) correlated final states, polarized by an external field or because of magnetic order

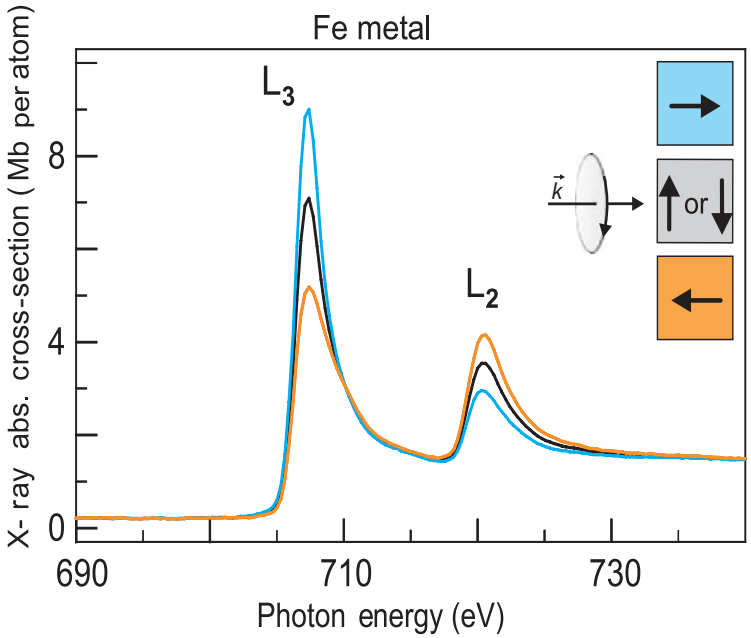
- The Pauli principle enforces spin anisotropy

PES: Transitions to free-electron final states, weakly correlated and non-polarized

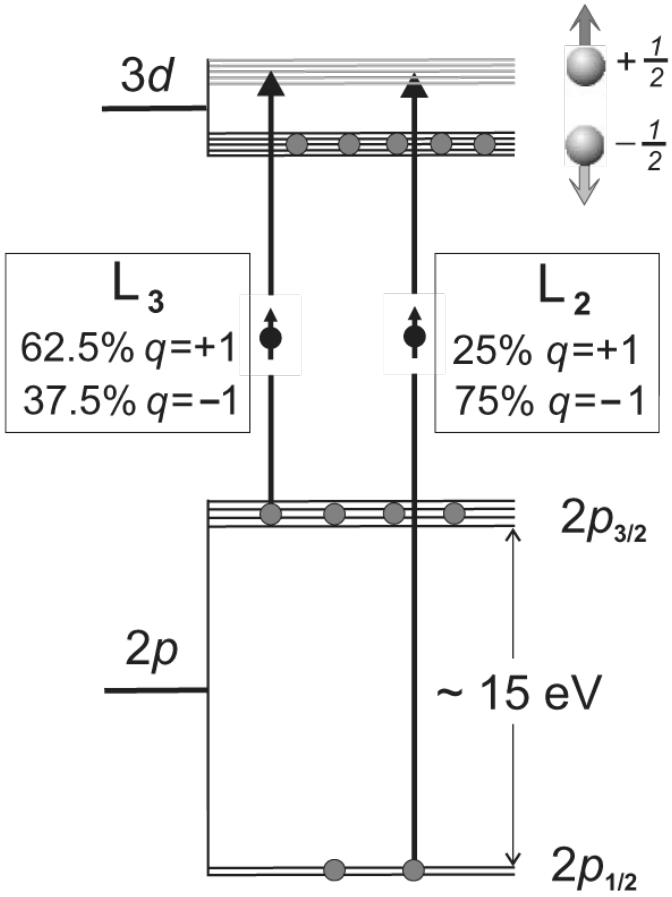
- No need for macroscopic magnetization
- typically needs spin detection

Dichroism in XAS





Simple case: fully polarized 3d band

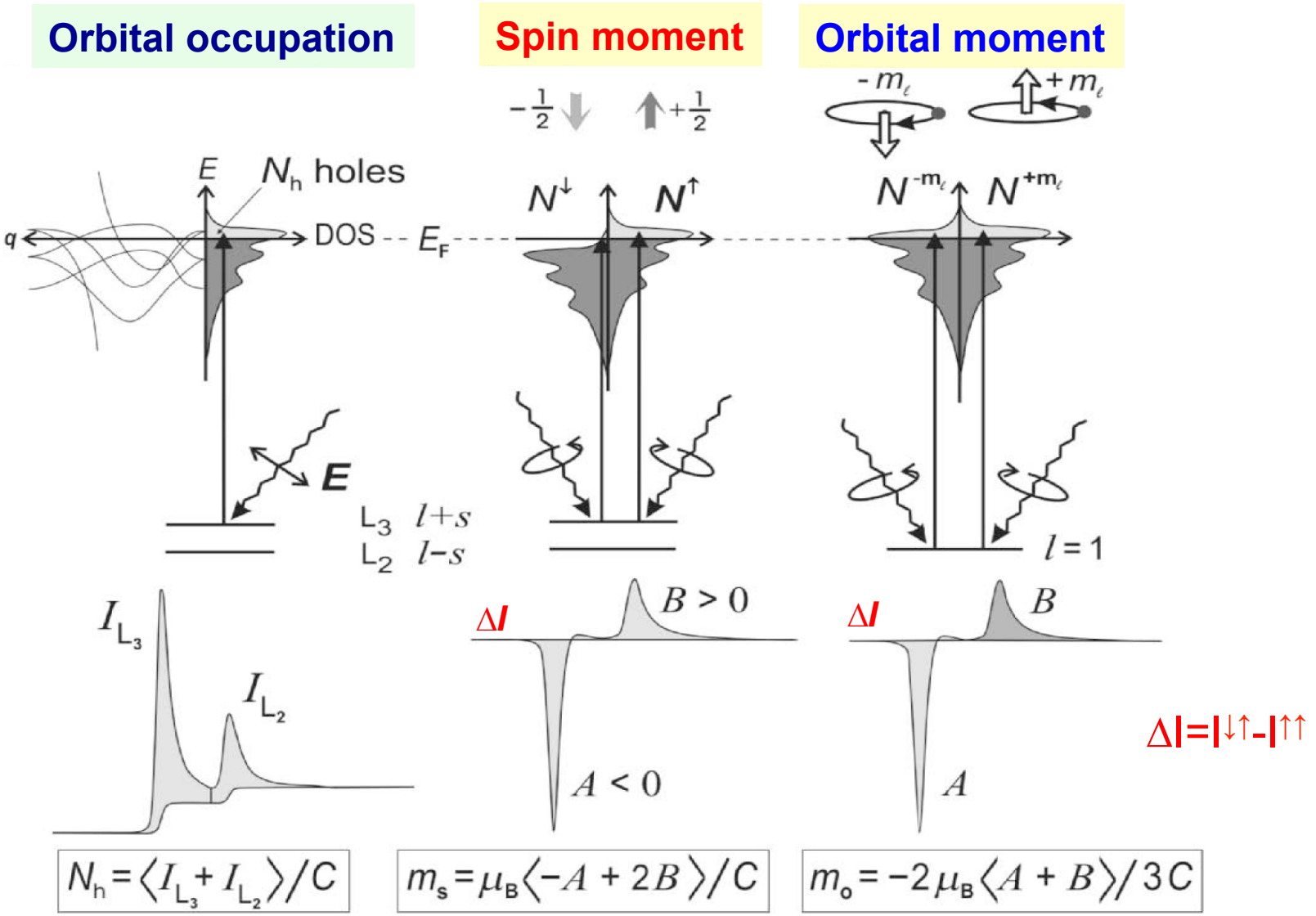


The absorption depends on the
photon polarization
and on the
spin orientation

An atomic model

Stöhr and Siegmann

XMCD sum rules: quantitative determination of m_{orb} e m_{spin}



Photoemission – Polarization and spin detection

TABLE I. The six fundamental photoemission spectra I^{xy}, which are linear combinations of the primitive spin-polarized spectra. $x=0,1,2$ denotes isotropically, circularly, and linearly polarized radiation, respectively. $y=0,1$ denotes without and with spin-polarization measurement, respectively. In the column labeled z, a value 1, 2, or 3 denotes that $\langle M\rangle$, $\langle M^2-\frac{1}{3}J(J+1)\rangle$, or $\langle M^3-\frac{3}{5}M[J(J+1)-\frac{1}{3}]\rangle$ in the ground state has to be nonzero to obtain the spectrum; $z=0$ denotes the value of the monopole, which is always unity.

I^{xy}	Combination of primitive spectra	z	Significance
I^{00}	$I_{1\uparrow}+I_{0\uparrow}+I_{-1\uparrow}+I_{1\downarrow}+I_{0\downarrow}+I_{-1\downarrow}$	0	Isotropic spectrum
I^{01}	$I_{1\uparrow}+I_{0\uparrow}+I_{-1\uparrow}-I_{1\downarrow}-I_{0\downarrow}-I_{-1\downarrow}$	1	Spin spectrum
I^{10}	$I_{1\uparrow}-I_{-1\uparrow}+I_{1\downarrow}-I_{-1\downarrow}$	1	Orbit spectrum (MCD)
I^{11}	$I_{1\uparrow}-I_{-1\uparrow}-I_{1\downarrow}+I_{-1\downarrow}$	0,2	Spin-orbit spectrum
I^{20}	$I_{1\uparrow}-2I_{0\uparrow}+I_{-1\uparrow}+I_{1\downarrow}-2I_{0\downarrow}+I_{-1\downarrow}$	2	Anisotropic spectrum (MLD)
I^{21}	$I_{1\uparrow}-2I_{0\uparrow}+I_{-1\uparrow}-I_{1\downarrow}+2I_{0\downarrow}-I_{-1\downarrow}$	1,3	Anisotropic spin magnetic spectrum

Thole and van der Laan (1991)

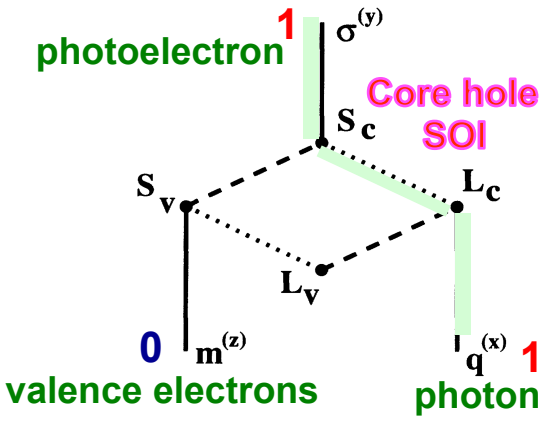
Core level photoemission

FUNDAMENTAL SPECTRA

Pol. — spin detection — moment

Photoemission spectrum	x	y	z	s.o.	U_{cv}
Isotropic spectrum	0	0	0	0	0
Spin spectrum	0	1	1	0	1
Orbit spectrum (MCD)	1	0	1	1	1
Spin-orbit spectrum	1	1	0	1	0
Spin-orbit magnetic quadrupole spectrum	1	1	2	1	1
Anisotropic spectrum (MLD)	2	0	2	1	1
Anisotropic spin magnetic dipole spectrum	2	1	1	1	1
Anisotropic spin magnetic octupole spectrum	2	1	3	1	1

$$I^{11} = I_{1\uparrow} + I_{-1\downarrow} - (I_{1\downarrow} + I_{-1\uparrow})$$

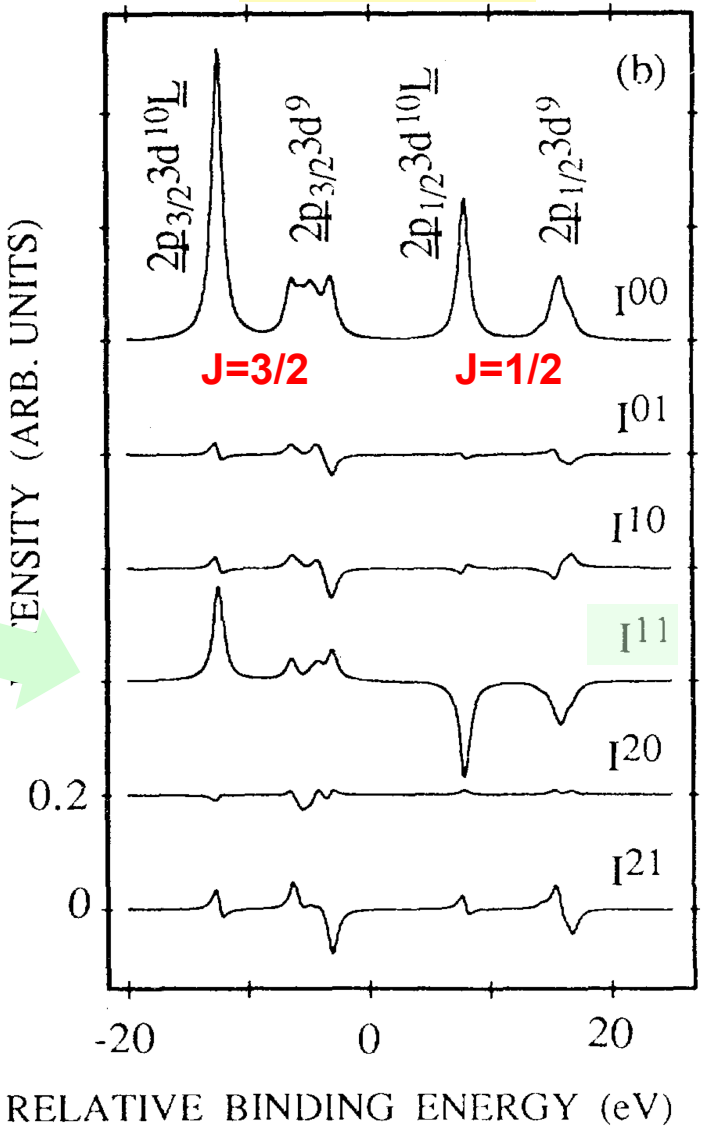


Integrated

$$\approx \langle L_z S_z \rangle = 0$$

(closed shell)

Cu^{II} , Cu 2p

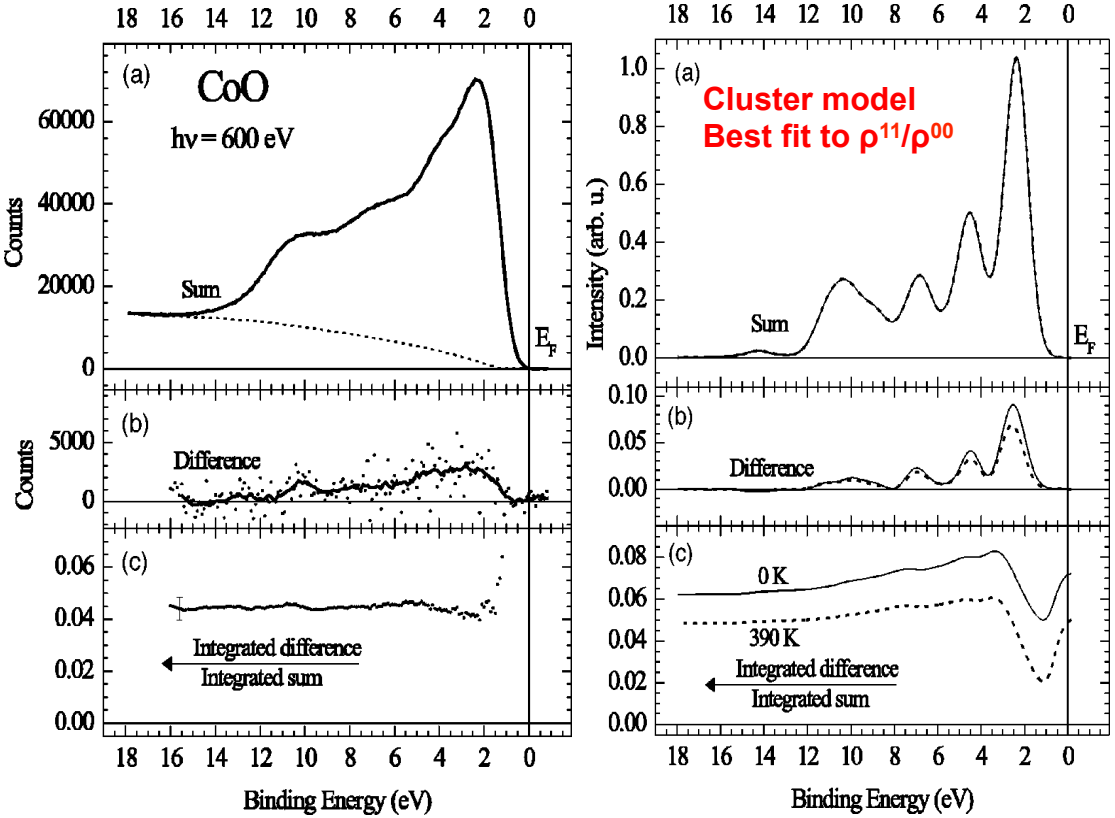


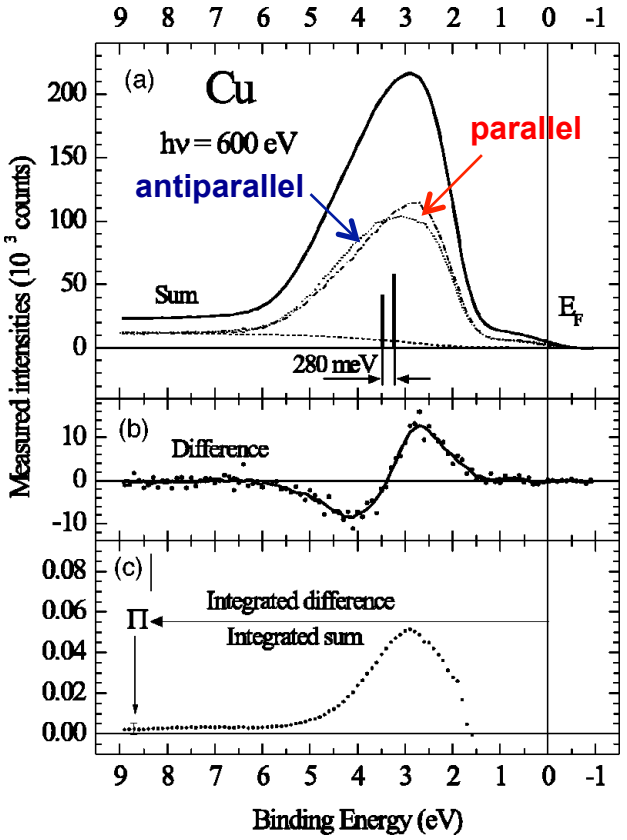
Valence band: Integrated spin-orbit spectrum

$$\frac{\rho^{11}}{\rho^{00}} = \frac{2A_1}{A_0}\frac{\left\langle \sum_i l_{zi}\, s_{zi} \right\rangle}{\langle n \rangle} = \frac{2A_1}{A_0}\frac{\left\langle \sum_i \boldsymbol{l}_i \cdot \boldsymbol{s}_i \right\rangle}{3\langle n \rangle} \quad \textit{if} \quad \langle M \rangle = 0$$

ρ = integrated spectra
z = spin quantization axis, // k_{photon}

Unlike XMCD or XMLD SP-PES does not require FM or AFM order





$$\left\langle \sum_i l_{zi}\, s_{zi} \right\rangle = -0.33 \pm 0.04\ \hbar^2$$

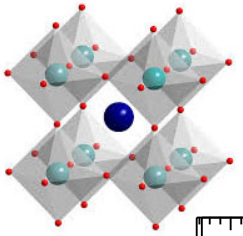
G. Ghiringhelli (2002)

Theory: $\langle L_z \rangle / 2\langle S_z \rangle = 0.57$

Exp.: $m = 3.98\,\mu_B \rightarrow \langle L_z \rangle = 1.36\hbar\ ;\ \langle S_z \rangle = 1.31\hbar$

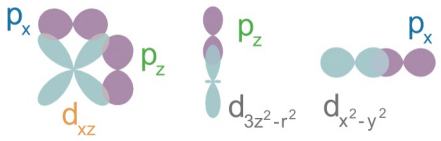
$$\left\langle \sum_i l_{zi}\, s_{zi} \right\rangle = 0$$

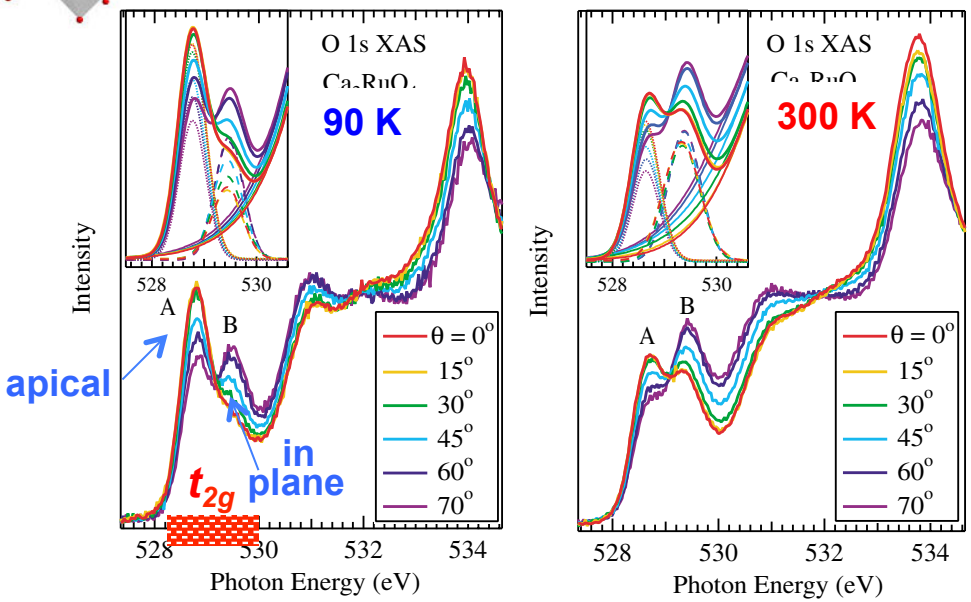
Ca_2RuO_4: an AFM (T_N=110K) Mott insulator

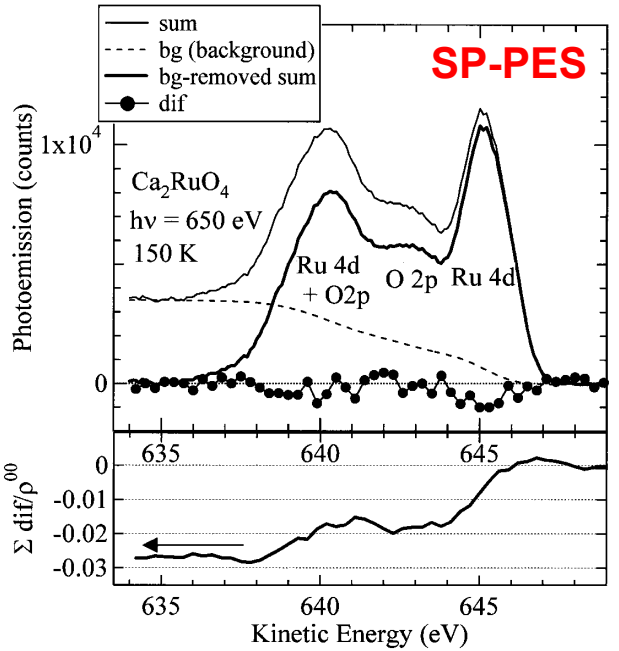


$Ru^{4+}(4d^4; t_{2g}^4)$

O K-edge XAS







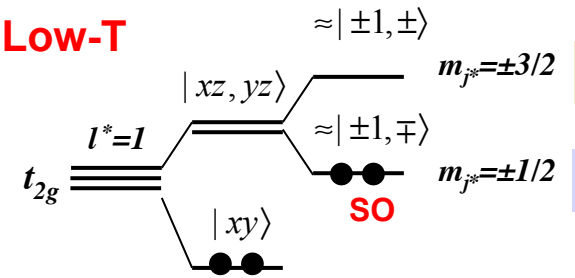
$\left\langle \sum_i l_{zi}\, s_{zi} \right\rangle = -0.28 \pm 0.07\ \hbar^2$

L *not quenched*

t_{2g}: strong angular dependence
(→ O p_{xyz} orbitals / in-plane, out-of-plane)

strong temperature dependence
(Tetragonal distortion → variable orbital occupancy)
300 K: n_{xy}:$n_{yz/xz}$=1:1 ; 90 K: n_{xy}:$n_{yz/xz}$=1/2:3/2

Low-T



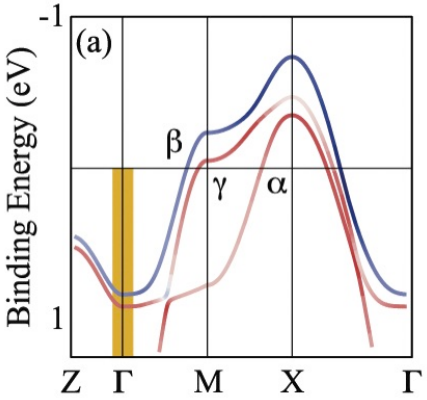
par

anti-

T. Mizokawa et al., PRL (2001)

SO mixes and splits d_{xz} and d_{yz} : $d_{xz} + i\,d_{yz} \approx |-1\rangle$; $d_{xz} - i\,d_{yz} \approx |1\rangle$

SP-ARPES - Sr_2RuO_4 : a spin-triplet superconductor?



SO mixes and splits d_{xz} and d_{yz} :

→ $d_{xz} + i\,d_{yz} \approx |-1\rangle$; $d_{xz} - i\,d_{yz} \approx |1\rangle$

$|\psi_{par}\rangle \approx |-1,\downarrow\rangle$; $|1,\uparrow\rangle$ $m_{j*}=\pm 3/2$

$|\psi_{antipar}\rangle \approx |-1,\uparrow\rangle$; $|1,\downarrow\rangle$ $m_{j*}=\pm 1/2$

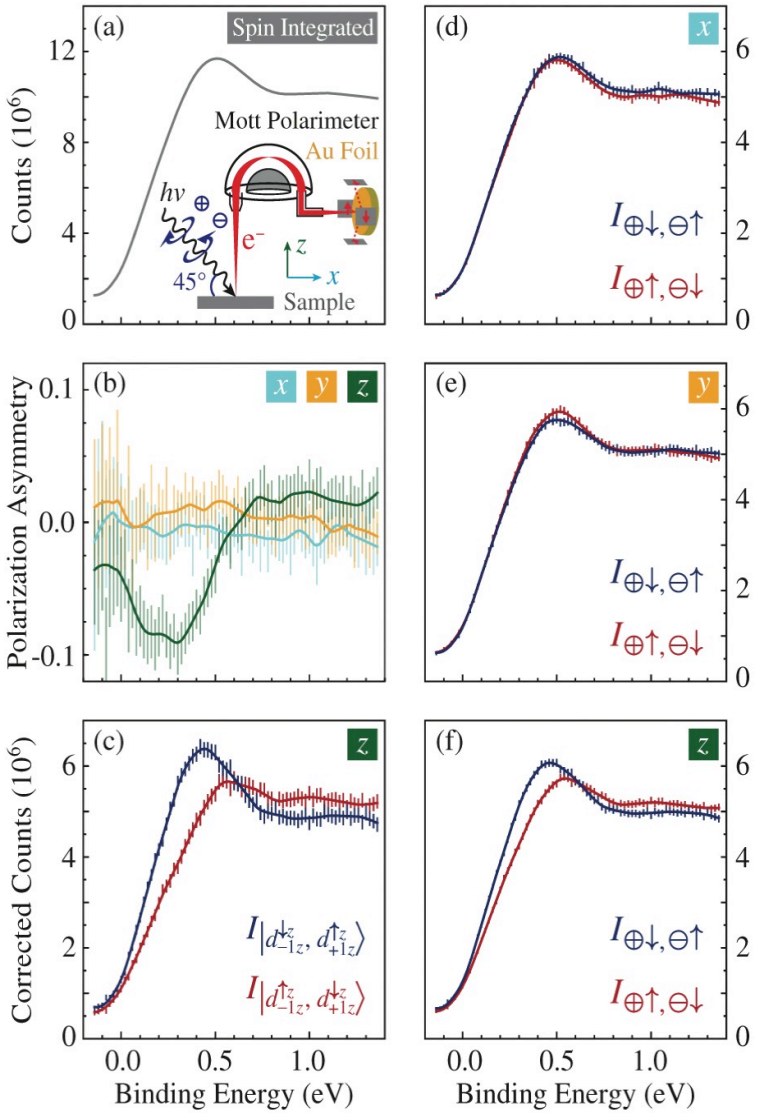
Selection rules: (mainly) $\Delta l = -1$ (d→p) ; $\Delta m_l = \pm 1$

(but $|m_l|<2$ for p states!)

$|\psi_{par}\rangle \approx |-1,\downarrow\rangle$ $|1,\uparrow\rangle$; $|\psi_{antipar}\rangle \approx |-1,\uparrow\rangle$ $|1,\downarrow\rangle$

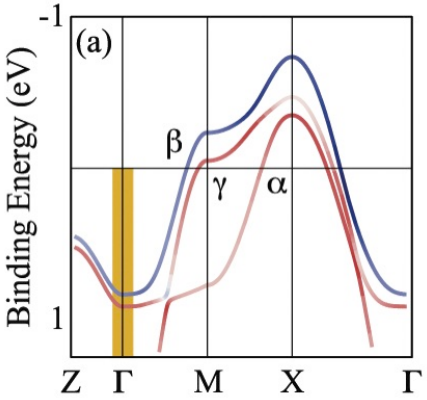
(+) pol (−) pol (+) pol (−) pol

Spin DOWN Spin UP Spin UP Spin DOWN



C.N. Veenstra et al., PRL (2014)

SP-ARPES - Sr_2RuO_4: a spin-triplet superconductor?

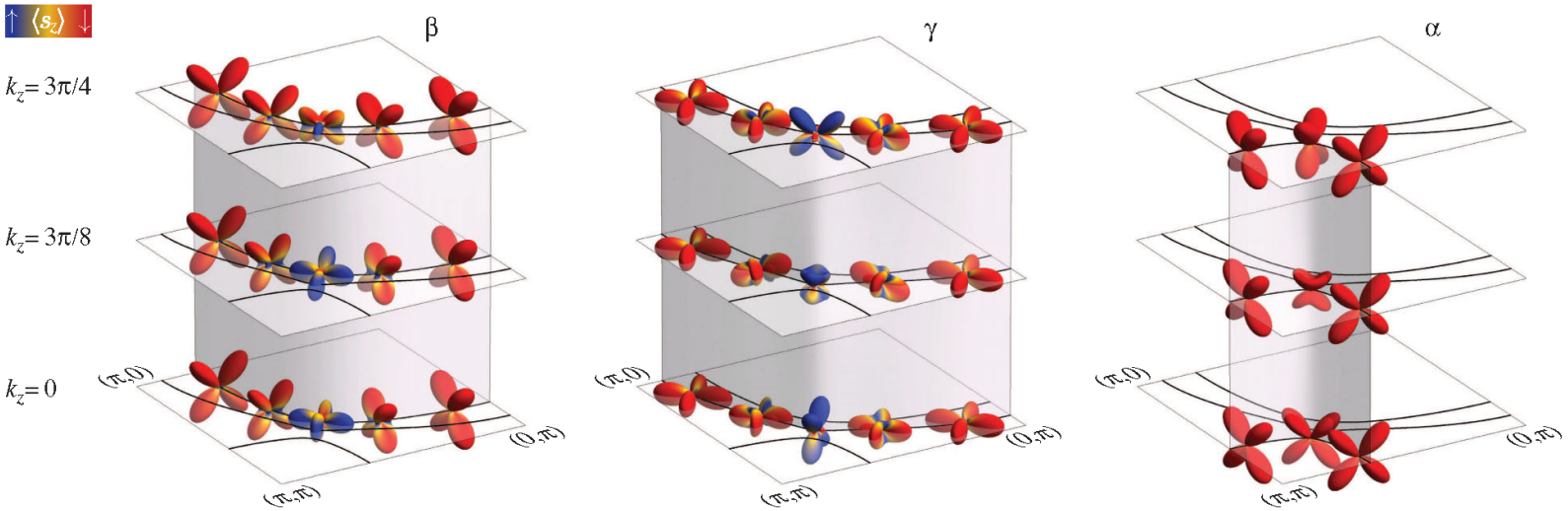


SO is large (~130 meV); $|m_l, m_s\rangle$ and $|-m_l, -m_s\rangle$ states are degenerate and mixed

$$|\psi_{par}\rangle \approx a|-1,\downarrow\rangle + b|1,\uparrow\rangle$$
$$|\psi_{antipar}\rangle \approx c|-1,\uparrow\rangle + d|1,\downarrow\rangle$$

Local description: orbital and spin moments are entangled

In the solid (one Kramers' partner):

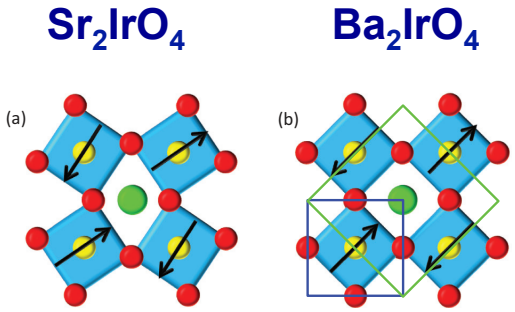


It is not possible to associate a well-defined spin value to a state at the Fermi surface.

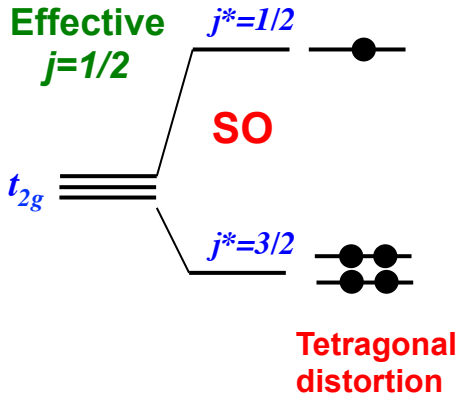
Cooper pairs cannot be simply described as "singlets" or "triplets"

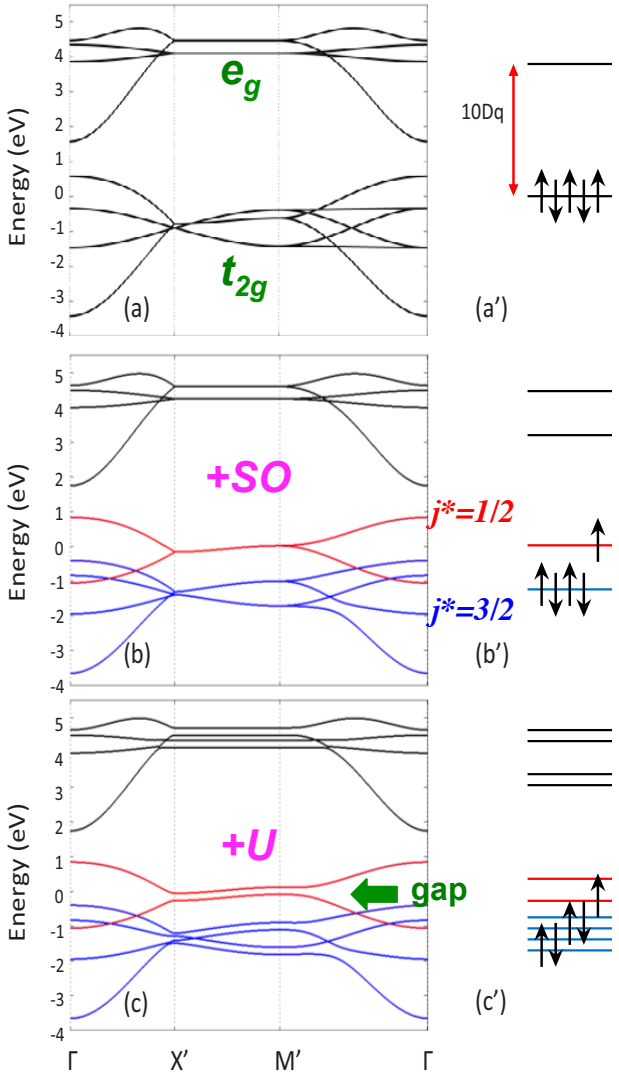
C.N. Veenstra et al., PRL (2014)

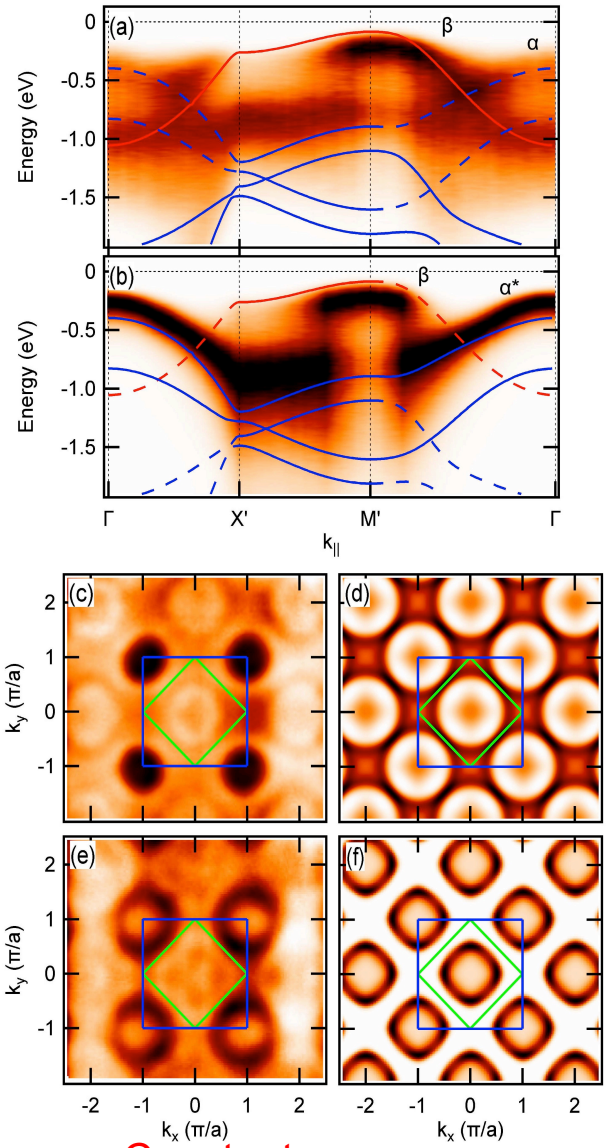
Strong SOI in 5d TM compounds: the iridates



Ir^{4+}; t_{2g}^5







Constant energy maps

Moser et al., NJP (2014)