Intuitive view on the magnetic dipole term Tz occurring in the XMCD sum rules

Case study of a failed intuition

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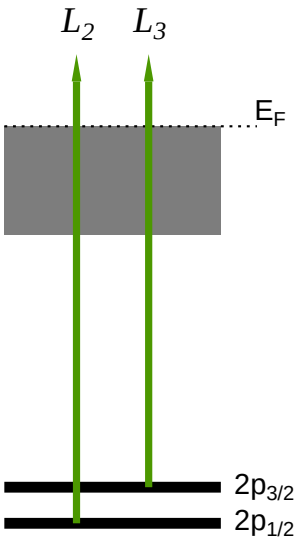
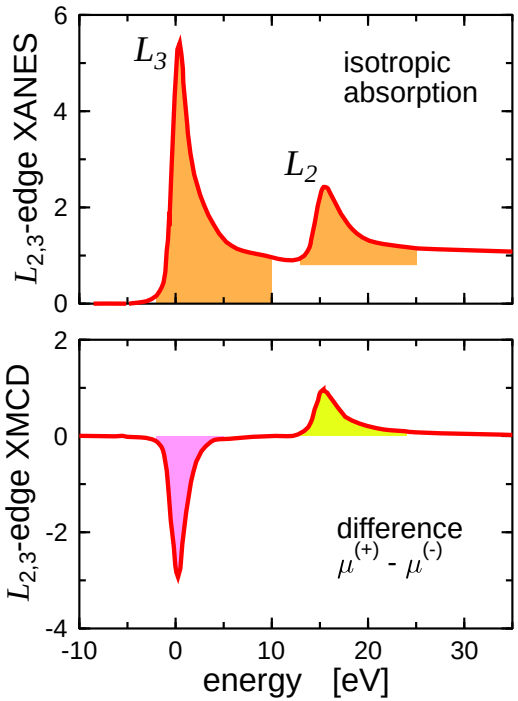
$L_{2,3}$ edge of magnetic systems (transition metals)





XMCD sum rules:

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

$$\int (\Delta\mu_{L_3} - 2\Delta\mu_{L_2})\, dE \sim \frac{\mu_{\mathrm{spin}}^{(d)} + 7T_z^{(d)}}{3n_h^{(d)}}$$

$$\int (\Delta\mu_{L_3} + \Delta\mu_{L_2})\, dE \sim \frac{\mu_{\mathrm{orb}}^{(d)}}{2n_h^{(d)}}$$

Outline

- Why to care about the magnetic dipole T_z term
- What to look for, what to expect: Focus on the spin-orbit coupling (SOC).
- Results: When things works as expected and when they do not
- Practical lessons?

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

Spin magnetic moment XMCD sum rule for the $L_{2,3}$ edge:

$$\frac{\mu_{\mathrm{spin}} + 7T_z}{n_h} = \frac{3}{I_A}\int (\Delta\mu_{L_3} - 2\Delta\mu_{L_2})\,\mathrm{d}E$$

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

Magnetic dipole term depends on the orientation of the magnetization **M** (therefore "T_α" from now on):

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

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

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

What to think about T_α ?

- Its existence and importance is universally acknowledged but it is not clear how to "visualize" it.
- Often quoted statement: T_α is a measure of the intra-atomic spin asphericity (see below on what this really means).
- For bulk systems T_α is usually negligible.
- For surfaces, monolayers or wires, absolute value of $7\,T_\alpha$ is about 20 % of μ_{spin}.
  $\Rightarrow$ T_α matters for low-dimensional systems.

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T_α changes apparent dependence of μ_{spin} on cluster size

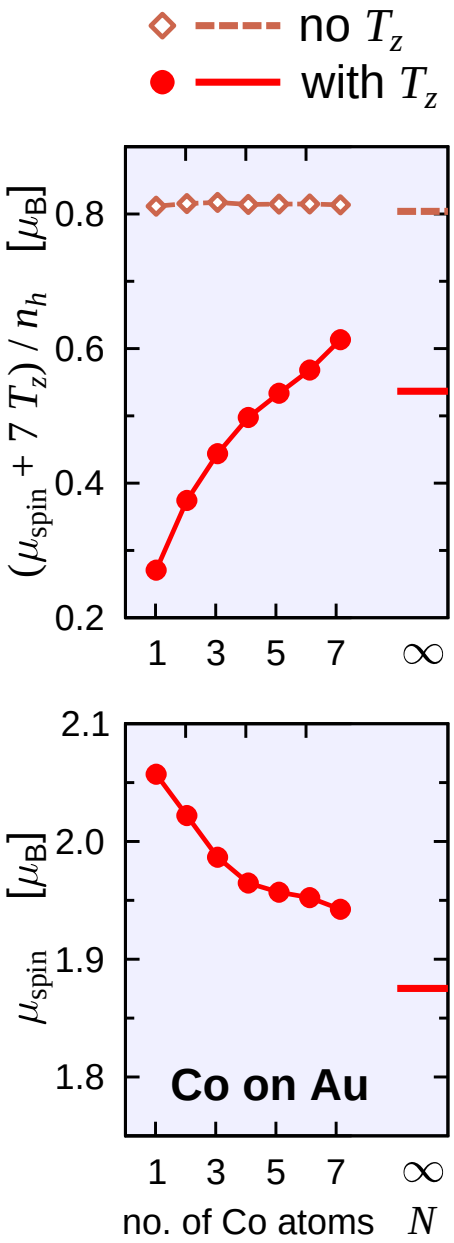


Illustration:
Ab-initio calculation for Co_N clusters of 1–7 atoms supported by Au(111)

The T_z term changes the picture completely:

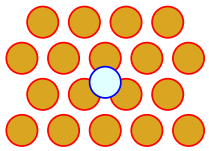
While the "true" μ_{spin} decreases with the cluster size, the "apparent XMCD-derived" μ_{spin} determined by $\mu_{\mathrm{spin}} + 7T_z$ increases with the cluster size.

O. Šipr *et al.* EPL **87**, 67007 (2009)

T_α makes μ_{spin} to falsely appear to be anisotropic

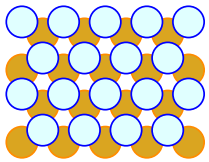
Co ad-atom and Co monolayer on Pd(111) surface,
varying the direction of the magnetization **M**.

ad-atom



	μ_{spin} $[\mu_B]$	$\mu_{\mathrm{spin}} + 7T_\alpha$ $[\mu_B]$
$\mathbf{M} \parallel xy$	2.47	2.65
$\mathbf{M} \parallel z$	2.47	2.11

monolayer



	μ_{spin} $[\mu_B]$	$\mu_{\mathrm{spin}} + 7T_\alpha$ $[\mu_B]$
$\mathbf{M} \parallel xy$	2.02	2.26
$\mathbf{M} \parallel z$	2.02	1.56

O. Šipr *et al.* PRB **88**, 064411 (2013)

Intuition can be obtained via approximations

Start with exact equation: $T_\alpha = -\frac{\mu_B}{\hbar} \left\langle \sum_\beta Q_{\alpha\beta} S_\beta \right\rangle$,

$Q_{\alpha\beta} = \delta_{\alpha\beta} - 3 r^0_\alpha r^0_\beta$ is the quadrupole moment, S_α is the spin.

If the spin-orbit coupling (SOC) is neglected, one gets

$$T_\alpha = \frac{1}{2}(-\mu_B) \sum_{mm'} \left[N^{\uparrow}_{mm'} - N^{\downarrow}_{mm'} \right] \langle Y_{2m} | \hat{Q}_{\alpha\alpha} | Y_{2m'} \rangle \ ,$$

where $N^{(s)}_{mm'}$ is a spin-dependent "number of states" matrix.

[Stöhr & König PRL **75**, 3748 (1995), Stöhr JMMM **200**, 470 (1999)]

Linking T_α to m-resolved components of μ_{spin}

Neglecting components not diagonal in m, one gets

$$T_\alpha = \sum_m \frac{1}{2} \langle Y_{2m} | \hat{Q}_{\alpha\alpha} | Y_{2m} \rangle \, \mu_{\mathrm{spin}}^{(m)} \ ,$$

where $\mu_{\mathrm{spin}}^{(m)}$ are m-resolved components of μ_{spin}.

Non-zero $\langle Y_{2m} | \hat{Q}_{\alpha\alpha} | Y_{2m} \rangle$ components:

	Q_{xx}	Q_{yy}	Q_{zz}
$\langle Y_{xy} \lvert \hat{Q}_{\alpha\alpha} \rvert Y_{xy} \rangle$	$-\frac{2}{7}$	$-\frac{2}{7}$	$\frac{4}{7}$
$\langle Y_{yz} \lvert \hat{Q}_{\alpha\alpha} \rvert Y_{yz} \rangle$	$\frac{4}{7}$	$-\frac{2}{7}$	$-\frac{2}{7}$
$\langle Y_{3z^2-r^2} \lvert \hat{Q}_{\alpha\alpha} \rvert Y_{3z^2-r^2} \rangle$	$\frac{2}{7}$	$\frac{2}{7}$	$-\frac{4}{7}$
$\langle Y_{xz} \lvert \hat{Q}_{\alpha\alpha} \rvert Y_{xz} \rangle$	$-\frac{2}{7}$	$\frac{4}{7}$	$-\frac{2}{7}$
$\langle Y_{x^2-y^2} \lvert \hat{Q}_{\alpha\alpha} \rvert Y_{x^2-y^2} \rangle$	$-\frac{2}{7}$	$-\frac{2}{7}$	$\frac{4}{7}$
$\langle Y_{x^2-y^2} \lvert \hat{Q}_{\alpha\alpha} \rvert Y_{3z^2-r^2} \rangle$	$\frac{2\sqrt{3}}{7}$	$-\frac{2\sqrt{3}}{7}$	0

[Stöhr & König PRL **75**, 3748 (1995), Crocombette *et al.* JPCM **8**, 4095 (1995), Stöhr JMMM **200**, 470 (1999), Šipr *et al.* PRB **88**, 064411 (2013)]

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How to view the elusive T_α term

If the spin-orbit coupling (SOC) can be neglected:

T_α term arises due to differences in m-resolved components of μ_{spin}.

In this respect one can indeed say that T_α is a measure of deviations of μ_{spin} from spherical symmetry.

Technical view:

Magnetic dipole term T_α for magnetization parallel to the α axis is generated via a competition between those m-components of μ_{spin} which contain the α coordinate and those which do not.

Quest for a T_α-free XMCD measurement

It makes sense to ask whether the SOC can be neglected in T_α.

- If the SOC is neglected, average of T_α is zero, $T_x + T_y + T_z = 0$.
- If the SOC is neglected, the dependence of T_α on the magnetization direction goes as $T(\theta) \sim 3\cos^2\theta - 1$, so T_α vanishes at the magic angle $\theta = 54^\circ$.

[König & Stöhr PRL **75**, 3748 (1995), Stöhr JMMM **200**, 470 (1999)]

Can the effect of SOC on T_α be neglected?

A tell-tale sign that the SOC cannot be neglected is breakdown of the $T_x + T_y + T_z = 0$ equation.

- Many-body effects beyond the LDA violate the $T_x + T_y + T_z = 0$ condition for low-dimensional systems such as free-standing $3d$ wires.
  [Ederer *et al.* JESRP **130**, 97 (2003)]

- Experimental evidence that SOC matters: deviations from the $T_x + T_y + T_z = 0$ rule observed for magnetite nanoparticles in the monoclinic low-temperature phase.
  [Schmitz *et al.* Sci. Rep. **4**, 5760 (2014)]

Our mission

Verify validity of following relations:

1. $T_\alpha = \sum_m \frac{1}{2} \langle Y_{2m} | \hat{Q}_{\alpha\alpha} | Y_{2m} \rangle \mu_{\text{spin}}^{(m)}$
2. $T_x + T_y + T_z = 0$

- Make a systematic study over a range of systems.
- Monitor the validity of the relations above if we go from small-SOC materials to large-SOC materials.
  - For supported magnetic nanostructures, the SOC of the substrate may be more important than SOC of the nanostructure itself.
- Fully-relativistic ab-initio calculations as implemented in the KKR-Green's function SPRKKR code [Ebert *et al.* Rep. Prog. Phys. 2011].
  - Rely on LDA (no orbital polarization).

Results: Co monolayers on noble metals (1)

	Co/Cu(111)		Co/Ag(111)		Co/Au(111)	
	exact	approx	exact	approx	exact	approx
μ_{spin}	1.710		1.961		1.976	
T_x	0.020	0.021	0.025	0.024	0.032	0.032
T_y	0.020	0.021	0.025	0.024	0.032	0.032
T_z	-0.037	-0.042	-0.043	-0.048	-0.061	-0.064
$\frac{\sum_\alpha 7T_\alpha}{\mu_{\mathrm{spin}}}$	0.011		0.021		0.009	

exact: $T_\alpha = -\frac{\mu_B}{\hbar} \left\langle \sum_\beta Q_{\alpha\beta} S_\beta \right\rangle$

approximative: $T_\alpha = \sum_m \frac{1}{2} \langle Y_{2m} | \hat{Q}_{\alpha\alpha} | Y_{2m} \rangle \mu_{\mathrm{spin}}^{(m)}$

Results: Co monolayers on noble metals (2)

	Co/Pd(111)		Co/Pt(111)	
	exact	approx	exact	approx
μ_{spin}	2.018		2.004	
T_x	0.028	0.027	0.028	0.027
T_y	0.028	0.027	0.028	0.027
T_z	-0.051	-0.054	-0.053	-0.054
$\frac{\sum_\alpha 7 T_\alpha}{\mu_{\mathrm{spin}}}$	0.015		0.008	

exact: $T_\alpha = -\frac{\mu_B}{\hbar} \left\langle \sum_\beta Q_{\alpha\beta} S_\beta \right\rangle$

approximative: $T_\alpha = \sum_m \frac{1}{2} \langle Y_{2m} | \hat{Q}_{\alpha\alpha} | Y_{2m} \rangle \mu_{\mathrm{spin}}^{(m)}$

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Results: Co ad-atoms on noble metals (1)

	Co/Cu(111)		Co/Ag(111)		Co/Au(111)	
	exact	approx	exact	approx	exact	approx
μ_{spin}	2.086		2.164		2.257	
T_x	0.057	0.031	0.059	0.008	0.080	0.040
T_y	0.057	0.031	0.059	0.008	0.080	0.040
T_z	-0.052	-0.061	-0.004	-0.016	-0.068	-0.080
$\frac{\sum_\alpha 7 T_\alpha}{\mu_{\mathrm{spin}}}$	0.206		0.372		0.284	

exact: $T_\alpha = -\frac{\mu_B}{\hbar} \left\langle \sum_\beta Q_{\alpha\beta} S_\beta \right\rangle$

approximative: $T_\alpha = \sum_m \frac{1}{2} \langle Y_{2m} | \hat{Q}_{\alpha\alpha} | Y_{2m} \rangle \mu_{\mathrm{spin}}^{(m)}$

Results: Co ad-atoms on noble metals (2)

	Co/Pd(111)		Co/Pt(111)	
	exact	approx	exact	approx
μ_{spin}	2.290		2.331	
T_x	0.098	0.093	0.109	0.098
T_y	0.098	0.093	0.109	0.098
T_z	-0.173	-0.186	-0.185	-0.196
$\frac{\sum_\alpha 7 T_\alpha}{\mu_{\mathrm{spin}}}$	0.072		0.098	

exact: $T_\alpha = -\frac{\mu_B}{\hbar} \left\langle \sum_\beta Q_{\alpha\beta} S_\beta \right\rangle$

approximative: $T_\alpha = \sum_m \frac{1}{2} \langle Y_{2m} | \hat{Q}_{\alpha\alpha} | Y_{2m} \rangle \mu_{\mathrm{spin}}^{(m)}$

Results: $T_x + T_y + T_z = 0$ criterion "all-on-one"

Compare the $\frac{\sum_\alpha 7T_\alpha}{\mu_{\mathrm{spin}}}$ quantity for different systems:

	monolayer	ad-atom
Co/Cu(111)	0.011	0.206
Co/Pd(111)	0.015	0.072
Co/Ag(111)	0.021	0.372
Co/Pt(111)	0.008	0.098
Co/Au(111)	0.009	0.284

SOC is *nominally* small!

Dimensionality seems to be more important than SOC of the substrate.

SOC strength ξ is to be compared to crystal field splitting Δ_{CF}.

Results: Effect of dimensionality

Monitor how $\frac{\sum_\alpha 7T_\alpha}{\mu_{\mathrm{spin}}}$ varies for Co systems of difference sizes supported by Au(111).

	$\frac{\sum_\alpha 7T_\alpha}{\mu_{\mathrm{spin}}}$	
Co adatom	0.284	
Co wire	0.058	
Co biwire	0.020 / 0.009	(two inequivalent Co atoms)
Co monolayer	0.009	

Summary:

Effect of SOC on T_α can be neglected for two-dimensional systems but it cannot be neglected for clusters.

Does it matter that SOC cannot be neglected?

For a class of materials where employing XMCD is especially conveniently, approximative relations for T_α and the whole the intuitive concept of "asphericity of spin density" cannot be used.

However, intuition might be in troubles also for other reasons:

T_z of low-dimensional systems crucially depends in the position of the Fermi level E_F, meaning that its value will be difficult to guess anyway.

[Komelj *et al.* PRB **66**, 140407 (2002), Ederer *et al.* JESRP **130**, 97 (2003), Šipr *et al.* EPL **87**, 67007 (2009)].

So we have just another reason why intuitive thinking about T_z term would fail.

Conclusions

- For small supported systems such as ad-atoms and clusters, the intuitively plausible relation

$$T_\alpha = \sum_m \frac{1}{2} \langle Y_{2m} | \hat{Q}_{\alpha\alpha} | Y_{2m} \rangle \, \mu_{\text{spin}}^{(m)}$$

  cannot be used (not even for purely $3d$ systems).

- Likewise, T_z-free XMCD measurement by means of exploiting the magic angle $\theta = 54^\circ$ cannot be employed for such systems.

- Is intuition doomed to fail for T_α term in nanostructures?

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Thank you!

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