Core-level spectroscopy:
Basics of XAS, XES, XMCD and alike

Ondřej Šipr

Institute of Physics
Academy of Sciences of the Czech Republic
Prague

Introduction to the application of ab-initio method in spectroscopy

EUSpec Hands-on course

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Outline

Spectroscopy: Light and matter

The zoology of x-ray spectroscopies

How big theory enters the business

When spectroscopy may benefit from calculations: case study

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Why x-ray spectroscopy (one of many why's . . .)

Only indirect methods are available if you want to study interiour of a material: blackbox techniques.

Spectroscopy:
Way to investigate ground state of a system by studying its response to a perturbation

Why x-rays?
Dimensions of the probe have to be comparable to the dimensions of the investigated system.

X-rays are useful for a local view.

Emission and absorption of light quanta

- System is described by a Hamiltonian H_{el}. Consider its two eigenstates $|\psi_i\rangle$ and $|\psi_f\rangle$ (i.e., stationary states).
- The system is perturbed by a Hamiltonian H_{int} which represents the interaction between electrons and photons,

$$H_{\mathrm{int}} = -\frac{e}{m}\mathbf{A}(\mathbf{x})\cdot\mathbf{p} \quad .$$

$\mathbf{A}(\mathbf{x})$	vector potential — quantized electromagnetic field
$\mathbf{p}$	momentum operator acting on electron states

The above Hamiltonian neglects terms proportional to $|\mathbf{A}|^2$, meaning that we cannot describe two-photon transitions in this way.

Fermi's Golden Rule

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

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

("$+$" for absorption of photons, "-" for emission of photons).

(First order time-dependent perturbation theory.)

Transition matrix element:

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

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

Some definitions and manipulations

Absorption coefficient:

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

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

- Initial and final states $|\psi_i\rangle$ and $|\psi_f\rangle$ are in the absence of the interaction with the electromagnetic radiation but in the presence of electron-electron interaction.
- Hamiltonian H_{el} is the full many-body Hamiltonian, including all electron-electron interactions.
  - Often we can go away with describing the electron-electron interaction just on the LDA level.

Matrix elements: dipole approximation

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

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

If the quantum system is localised within a characteristic length a (i.e, processes occur at this length scale),

$$\frac{1}{\hbar} q a \ll 1 \;\Leftrightarrow\; a \ll \frac{c}{\omega} \;\Leftrightarrow\; a \ll \frac{\lambda}{2\pi} \;,$$

then $\frac{\mathrm{i}}{\hbar} \mathbf{q} \cdot \mathbf{x}$ 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.

Other forms of matrix elements

"Primordial form" of the dipole matrix element:

$$M_{fi} \approx \boldsymbol{\epsilon} \cdot \langle \psi_f | \mathbf{p} | \psi_i \rangle \quad .$$

Using the coordinate-momentum commutation relations (and few other tricks), the matrix element can be re-written as

$$M_{fi} \approx \boldsymbol{\epsilon} \cdot \langle \psi_f | \mathbf{p} | \psi_i \rangle = \mathrm{i} m \omega \boldsymbol{\epsilon} \cdot \langle \psi_f | \mathbf{r} | \psi_i \rangle = \frac{\mathrm{i}}{\omega} \boldsymbol{\epsilon} \cdot \langle \psi_f | \nabla V | \psi_i \rangle$$

In most situations, all these forms are equivalent.

(Dipole) selection rules: where do they come from?

Dipole transition matrix element is an integral: $\boldsymbol{\epsilon} \cdot \langle \psi_f \left| \mathbf{r} \right| \psi_i \rangle$

Analogy:
Integral of a product of an even and an odd functions will be identically zero.

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

Transitions for which $\langle \psi_f \left| \mathbf{r} \right| \psi_i \rangle$ is zero are called forbidden transitions.

Transitions forbidden by the dipole selection rule are accessible via higher-order terms in the $\exp(\pm \frac{\mathrm{i}}{\hbar} \mathbf{q} \cdot \mathbf{x})$ expansion, their intensity is usually much smaller than intensity of the dipole-allowed transitions.

Density of states: powerful tool for intuition

Density of states (DOS) describes how many electron states are there at certain energy ε.

$$n(\varepsilon) = \sum_n \int_{1\mathrm{BZ}} \frac{\mathrm{d}\mathbf{k}}{4\pi} \delta(\varepsilon - \varepsilon_{\mathbf{k}}^n) \ .$$

Knowing the DOS for a solid is analogous to knowing the energy levels for an atom.

How DOS enters spectroscopy

Probability of a radiative transition:

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

Recall: $n(\varepsilon) \;=\; \sum_n \int_{(1\mathrm{BZ})} \frac{\mathrm{d}\mathbf{k}}{4\pi}\,\delta(\varepsilon - \varepsilon_{\mathbf{k}}^n)$.

In spectroscopy, we will integrate over i's or f's.

We are interested in a probability that as a results of interaction with electromagnetic radiation, either a specific final state is created out of all possible initial states or that a specific initial state is transferred in any final state.

If the matrix elements do not depend on i or f, we get

$$[I(\omega)]\;/\;[\mu(\omega)]\;/\;[\ldots] \quad\approx\quad \frac{2\pi}{\hbar}\,|M_{fi}|^2\;n(\pm E_{[f,i]} \,\pm\, \hbar\omega)\;\;.$$

The spectra reflect the DOS weighted by transition matrix elements M_{fi}.

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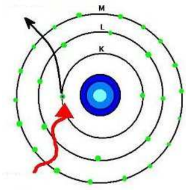
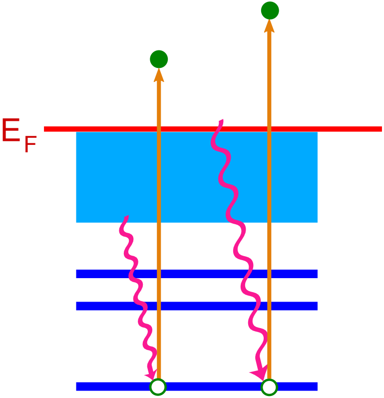
X-ray Absorption Spectroscopy (XAS)

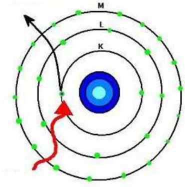
- X-rays go in, x-rays go out, absorption coefficient is measured as a function the energy of the incoming x-rays.

- Most of the absorption goes on account of the photoelectric effect on core electrons.



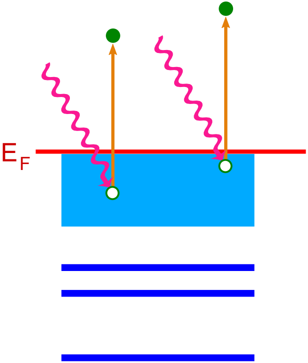
XAS probes density of unoccupied states

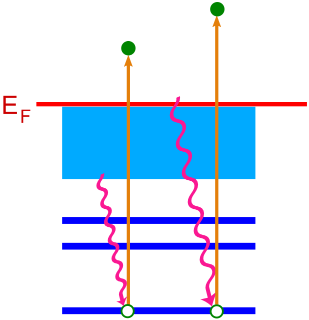




Core hole is left behind the ejected (photo)electron.

Comparing photoemission with x-ray absorption





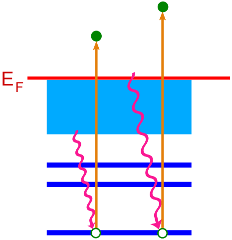
PES: from the valence band to vacuum.

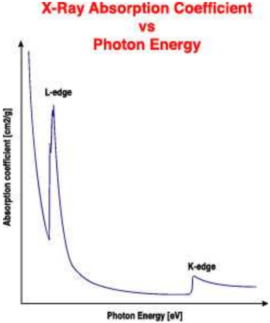
XPS (X-ray photoemission spectroscopy): from core levels.

XAS: from core levels to the conduction band.

XAS is angle-integrated XPS.

Chemical selectivity





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

- Generally, absorption coefficient decreases if x-ray energy increases.
- If incoming x-rays energy is large enough to excite another core electron, the absorption coefficient increases by a jump.
  - Transitions of electrons from one core level only dominate the spectrum close to this jump.

Angular momentum selectivity

Dipole approximation (recall slides on the matrix element):

$$M_{fi} \approx \boldsymbol{\epsilon} \cdot \langle \psi_f \left| \mathbf{r} \right| \psi_i \rangle \quad .$$

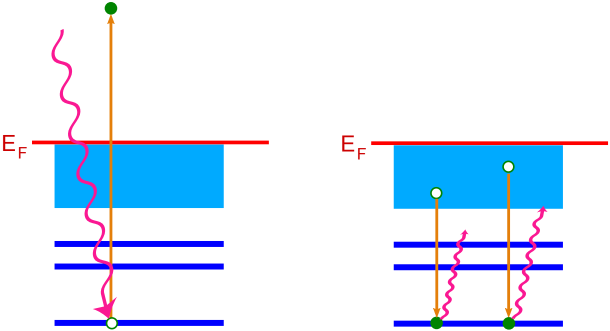
If wave functions $|\psi_i\rangle$ and $|\psi_f\rangle$ have certain symmetries, the (dipole) matrix element will be identically zero.

Only transitions between states with their angular momentum quantum number differing by one are allowed:

$$\ell_f = \ell_i \pm 1$$

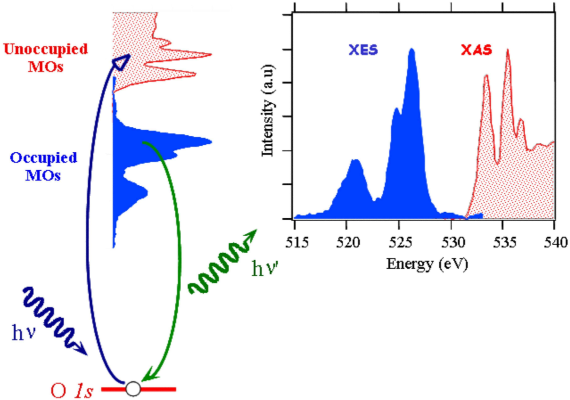
XAS probes angular-momentum selected DOS as seen from a chemically specific site.

X-ray emission spectroscopy (XES)



1. Prepare the conditions: create a hole in the core.
2. Measure the intensity of x-rays which are emitted when electrons from valence band fill this hole.
   (Steady-state situation, *not* a pump-probe experiment.)

XES – XAS complementarity



- XAS probes density of unoccupied states
- XES probes density of occupied states

Information from XES (in comparison to PES)

- Unlike in photoemission, no information about **k**-vector. Only DOS is accessible.

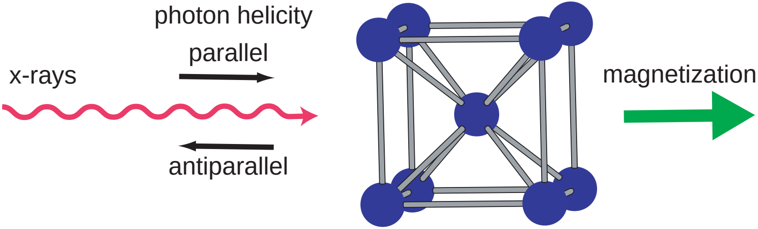
- However, we know which DOS we are probing:
  - Chemically specific.
  - Angular-momentum-specific.

- Calculations: similar formula as in XAS.
  - The core hole is in the initial state, not in the final state. For final state, there is a valence band hole, which is usually well screened.

XMCD = XAS − XAS + magnetization + SOC

XMCD (**X**-ray **M**agnetic **C**ircular **D**ichroism):

Sample is magnetized, measure the difference between absorption of left and right circularly polarized x-rays.



$$\mu_{\mathrm{XMCD}} = \mu^{(+)} - \mu^{(-)}$$

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Electron-electron interaction in spectroscopy

In many (if not most) circumstances, the electron-electron interaction in solids can be handeled within the LDA.

However:

- Spectroscopy: dynamic highly non-uniform situation.
- Core hole is a localized perturbation, strong Coulomb interaction with the excited photoelectron.
- Also other electrons are affected. This may be often downfolded to
  - finite core hole lifetime,
  - finite photoelectron lifetime.

- Some beyond-LDA interactions may be present among the valence and/or conduction electrons which whould be there even without the spectroscopic process
  See earlier talks of Gian-Marco Rignanese, Jürgen Braun, . . .
  Example of LDA+DMFT in PRB **84**, 115102 (2011)

Core hole: take it seriously or not?

Calculating the spectrum fully accounting for all the ingredients is often impossible.

To account for the core hole requires many-body calculations. Such calculations can be done for atoms but not for solids.
(Everything is possible *in principle* but . . .)

The choice is yours:

- You may include many-body effects associated with the core hole but then you cannot include the solid-state-like effects (influence of other atoms apart from the photoabsorbing one).

- You can fully account for the influence of other atoms (hybridization) but then you cannot include the core hole in a truly many-body fashion.

Tailor your approach according to the problem

- If the process is delocalized, hybridization is more important than the core hole interaction. Use LDA and standard solid-state-like approaches.
  E.g. case of K edge of metals [J. Synchr. Rad. **10**, 26 (2003)].

- If the process is localized, core hole dominates over the hybridization. Use atomic-like approach (model crystal field Hamiltonian, multiplets).
  E.g. case of $L_{2,3}$ edges of $3d$ elements in oxides [Micron **41**, 687 (2010)].

What if. . .

If both core hole and hybridization have to be properly accounted for, then you have a problem.

- Time-dependent DFT within the linear response theory [PRL **80**, 4586 (1998); PRB **67**, 115120 (2003); PRB **21**, 215502 (2012)].
- Multi-channel multiple scattering [PRB **42**, 1944 (1990); PRB **70**, 245120 (2004); JPCM **24**, 365501 (2012)].
- Bethe-Salpeter equation [PRB **64**, 165112 (2001); JPCM **21**, 104205 (2009); PRB **82**, 205104 (2010)].
- More sophisticated Hamiltonians with parameters chosen so that the relevant hybridization and interaction is described [Coord. Chem. Rev. **253**, 526 (2009); talk of Maurits Haverkort].
- ???

Simple treatment of the core hole

If the core hole interaction is not too strong, its effect can be described within the final state rule [PRB **25**, 5150 (1982)].

Final state rule:
Take LDA wave functions calculated for a system in the final state of the spectroscopic process.

- XAS: calculate it with the core hole.
- XES: calculate it without the core hole.

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.

Calculational method: embedded impurity (Green's function formalism), supercell (band-structure formalism)

"Relaxed and screened model."

Useful many-body cheats (1)

- “Diffuse” interaction of the core hole with other electrons results in finite core hole lifetime. Broaden the spectrum using FWHM from the tables [At. Data Nucl. Data Tables **77**, 1 (2001)].

- “Diffuse” interaction of the excited photoelectron with other electrons results in finite photoelectron lifetime. Broaden the spectrum employing the universal curve for inelastic mean free path [SSC 42, 365 (1982); Surf. Interface Anal. **1**, 2, 1979].

- LDA-like effects beyond the LDA result in energy-dependent exchange-correlation potential:
  - Hedin-Lundquist,
  - Dirac-Hara.

  [PRB **35**, 2604 (1987); PRB **51**, 13015 (1995)]

Useful many-body cheats (2)

Beware:
these are cheats, do not hang to tabulated values too literally [J. Synchr. Rad. **6**, 236 (1999); PRB **52**, 6349 (1995); J. Synchr. Rad. **10**, 51 (2003); PRB **76**, 104411 (2007)].

However, encouraging attempts to do *real* calculations in many of these respect were done [PRB **65**, 064107 (2002); PRB **76**, 195116 (2007)].

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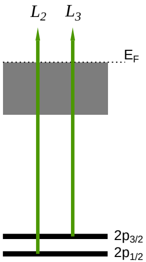
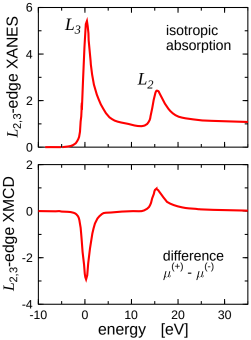
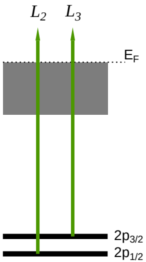
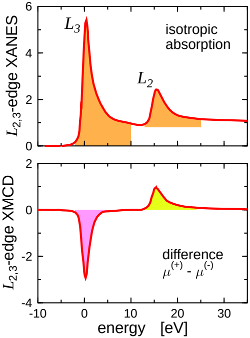
$L_{2,3}$ edge of magnetic systems (transition metals)





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





XMCD sum rules:

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

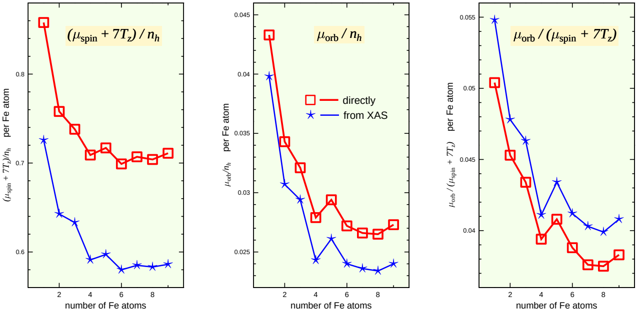
$$\int (\Delta\mu_{L_3} - 2\Delta\mu_{L_2})\, dE \;\sim\; \frac{\mu_{\text{spin}}^{(d)} + 7T_z^{(d)}}{3n_h^{(d)}}$$

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

What can XMCD do for us?

- Through the sum rules, XMCD can inform about μ_{spin} and μ_{orb} separately
- For compounds, magnetic state of each element can be explored separately
- Employing sum rules on experimental data may require substantial theoretical input

Validity of sum rules



Fe_N / Ni(001)

- Trends of the "effective moments" $(\mu_{\rm spin} + 7T_z)/n_h$ and $\mu_{\rm orb}/n_h$ are reproduced well enough
- Applying sum rules to supported clusters *in principle* makes sense

T_z term: A feature, not a bug !

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

I_A	integrated isotropic absorption spectrum
μ_spin	*d* component of the local spin magnetic moment
n_h	number of holes in the *d* band
T_z	*d* component of magnetic dipole operator

$$T_z = \left\langle \hat{T}_z \right\rangle = \left\langle \tfrac{1}{2}\left[\sigma - 3\hat{\mathbf{r}}(\hat{\mathbf{r}}\cdot\sigma)\right]_z \right\rangle$$

T_z is a measure of the *asphericity of spin magnetization*

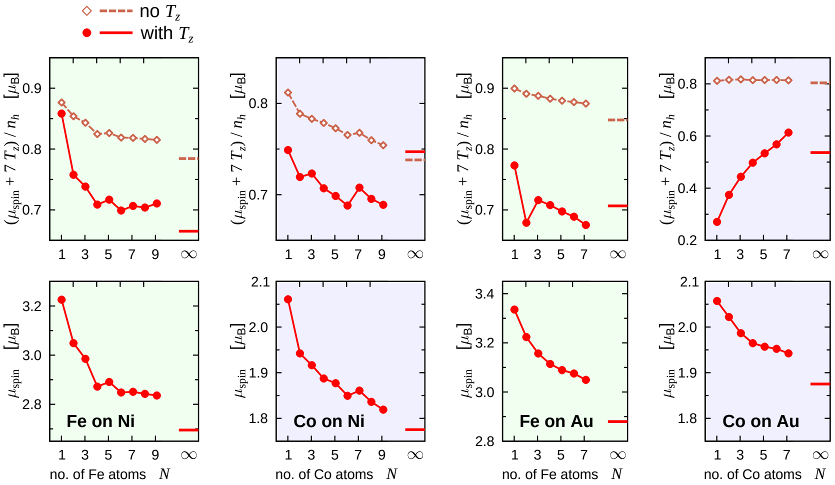
μ_spin can be obtained only in combination with $7T_z$!

Does T_z term really matter ?

- For bulk systems it is usually negligible
- For surfaces, monolayers or wires, absolute value of $7T_z$ is about 20 % of $\mu_{\rm spin}$
- For investigating trends of $\mu_{\rm spin}$ within a series of systems, what matters is how T_z varies from one system to another
  - If variations in T_z are small, neglect of T_z causes just an overall shift of the deduced $\mu_{\rm spin}$
  - Could T_z vary in such a way that the overall trends of $\mu_{\rm spin}+7T_z$ and $\mu_{\rm spin}$ would be quite different ?

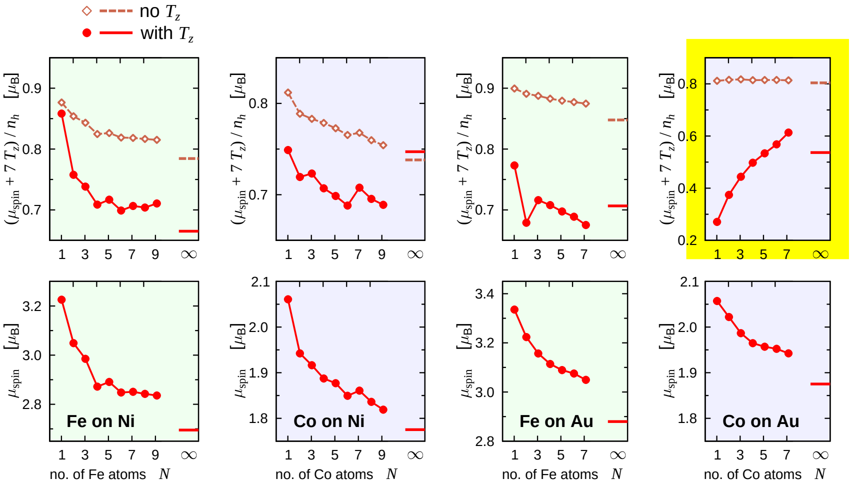
EPL **87**, 67007 (2009)

Results: μ_{spin} and $[\mu_{\text{spin}} + 7\,T_z]/n_h$



$\text{Fe}_N/\text{Ni}(001)$ $\text{Co}_N/\text{Ni}(001)$ $\text{Fe}_N/\text{Au}(111)$ $\text{Co}_N/\text{Au}(111)$

Results: μ_{spin} and $[\mu_{\text{spin}} + 7T_z]/n_h$



$Fe_N/Ni(001)$ $Co_N/Ni(001)$ $Fe_N/Au(111)$ $Co_N/Au(111)$

For $Co_N/Au(111)$, the T_z changes the picture completely!

Conclusion

Spectroscopy can be very useful but you have to know what you are doing.