Magnetism of free Rh clusters via ab-initio calculations: which intuitive concepts can or cannot be used

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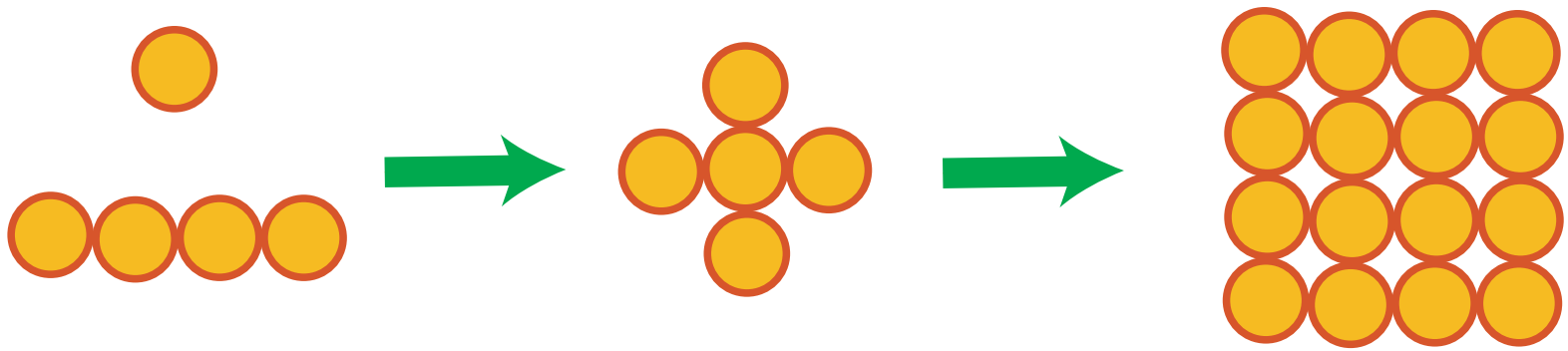
Outline

- Clusters: what to expect?
- $3d$ reference: review of free Fe clusters
- Rh clusters: issues to deal with
- Results: trends and non-trends of magnetism for free Rh clusters
- Executive summary

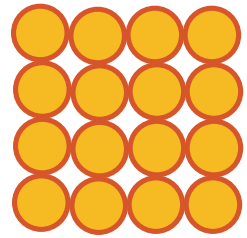
What can we expect from clusters?

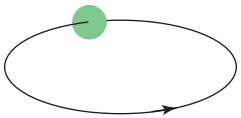
- Clusters mark the transition between atoms, surfaces and bulk systems



Starting point: magnetism of Fe





	atom	surface	bulk
	$\mu_{\text{spin}} = 4\ \mu_B$	$\mu_{\text{spin}} = 2.5\text{–}3.0\ \mu_B$	$\mu_{\text{spin}} = 2.2\ \mu_B$
	$\mu_{\text{orb}} = 2\ \mu_B$	$\mu_{\text{orb}} = 0.07\text{–}0.12\ \mu_B$	$\mu_{\text{orb}} = 0.05\ \mu_B$

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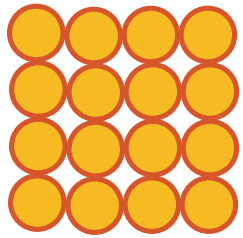

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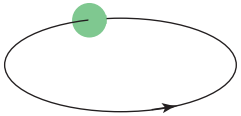
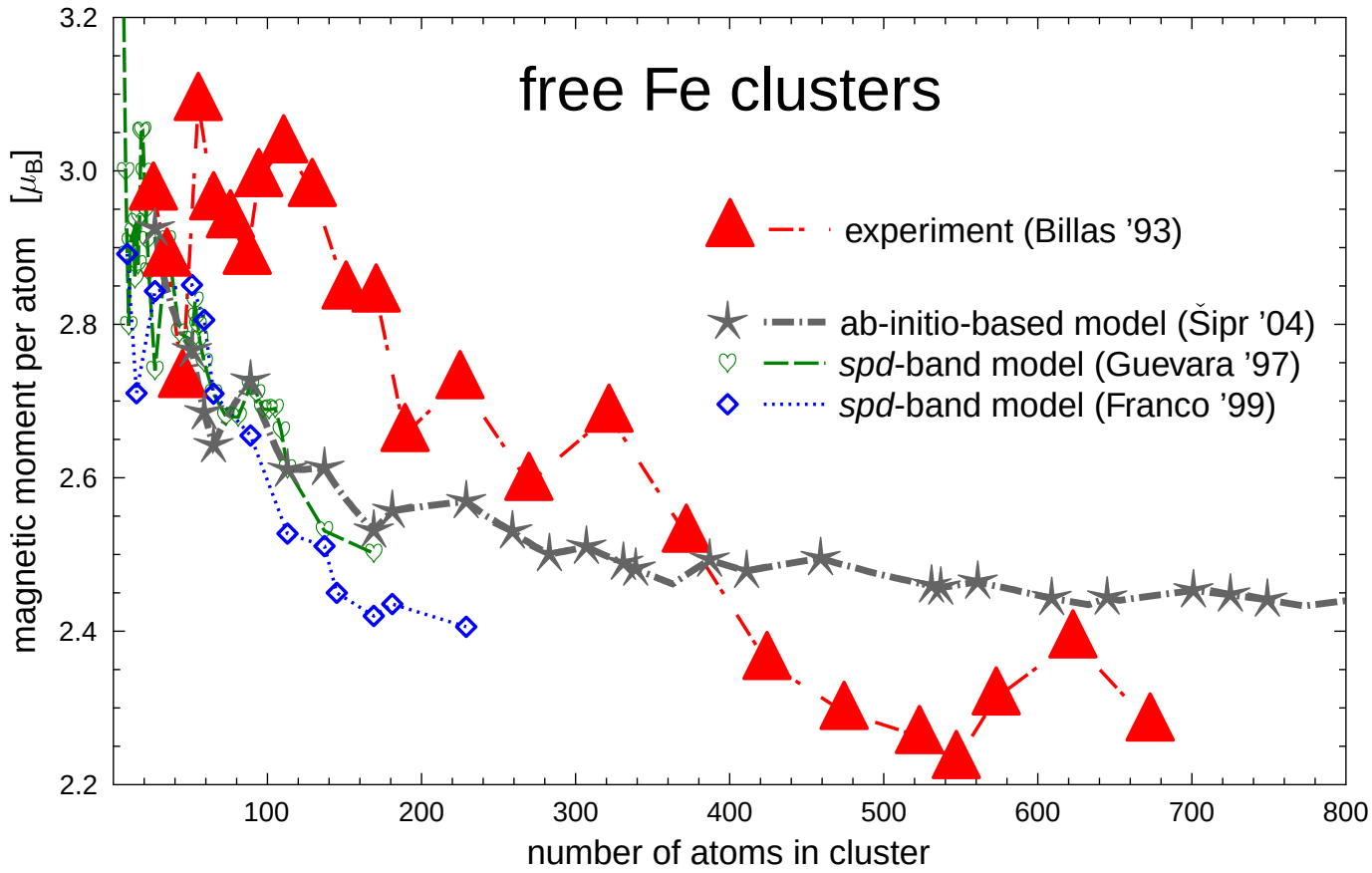
	$\mu_{\mathrm{orb}} = 2\ \mu_B$	$\mu_{\mathrm{orb}} = 0.07\text{–}0.12\ \mu_B$	$\mu_{\mathrm{orb}} = 0.05\ \mu_B$

clusters enter here

Magnetic moments of Fe clusters



- μ_{spin} decrease with cluster size in a quasi-oscillatory way.
- Theory describes this trend (at least to some extent).

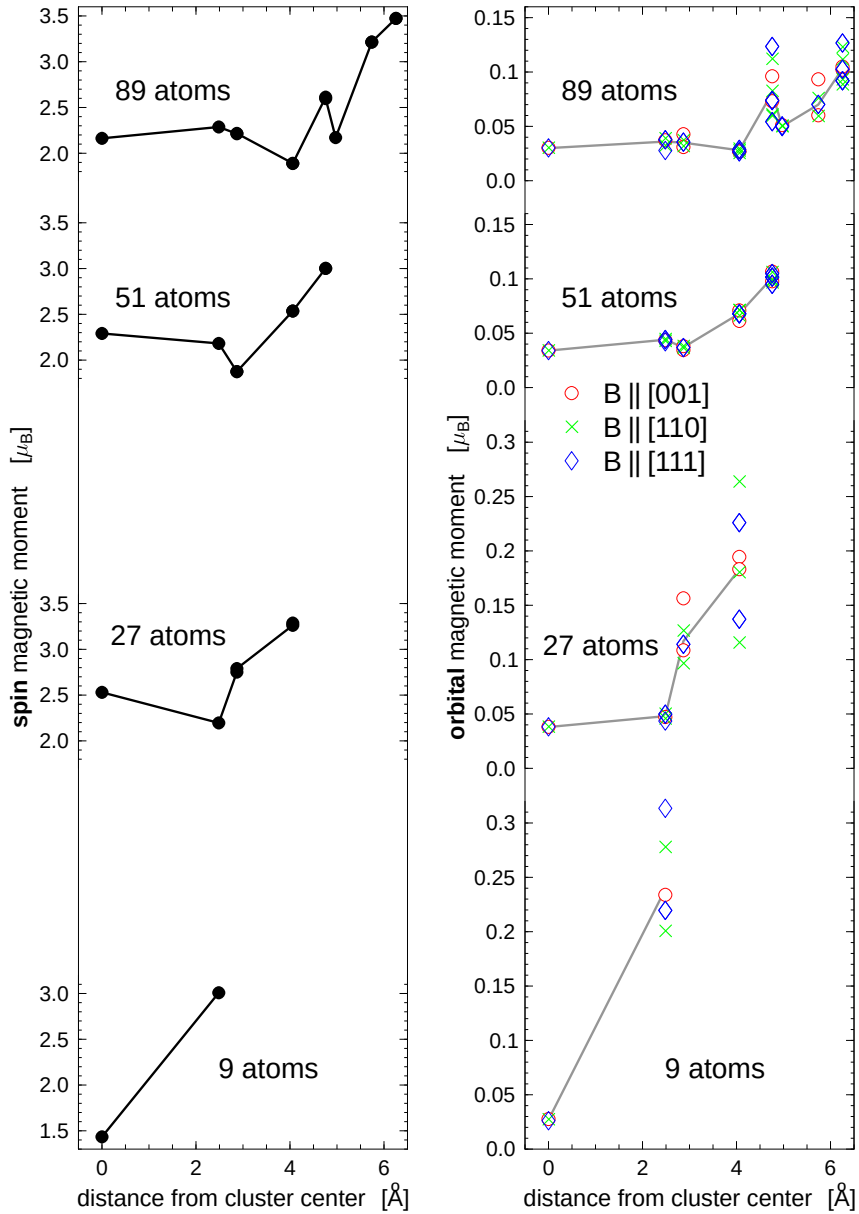
Magnetic profiles for free Fe clusters

μ_{spin} and μ_{orb} increase when going from the center outwards.

Technical reminder:

Relativity decreases the symmetry, therefore atoms belonging to the same shell need not have the same μ_{orb}.

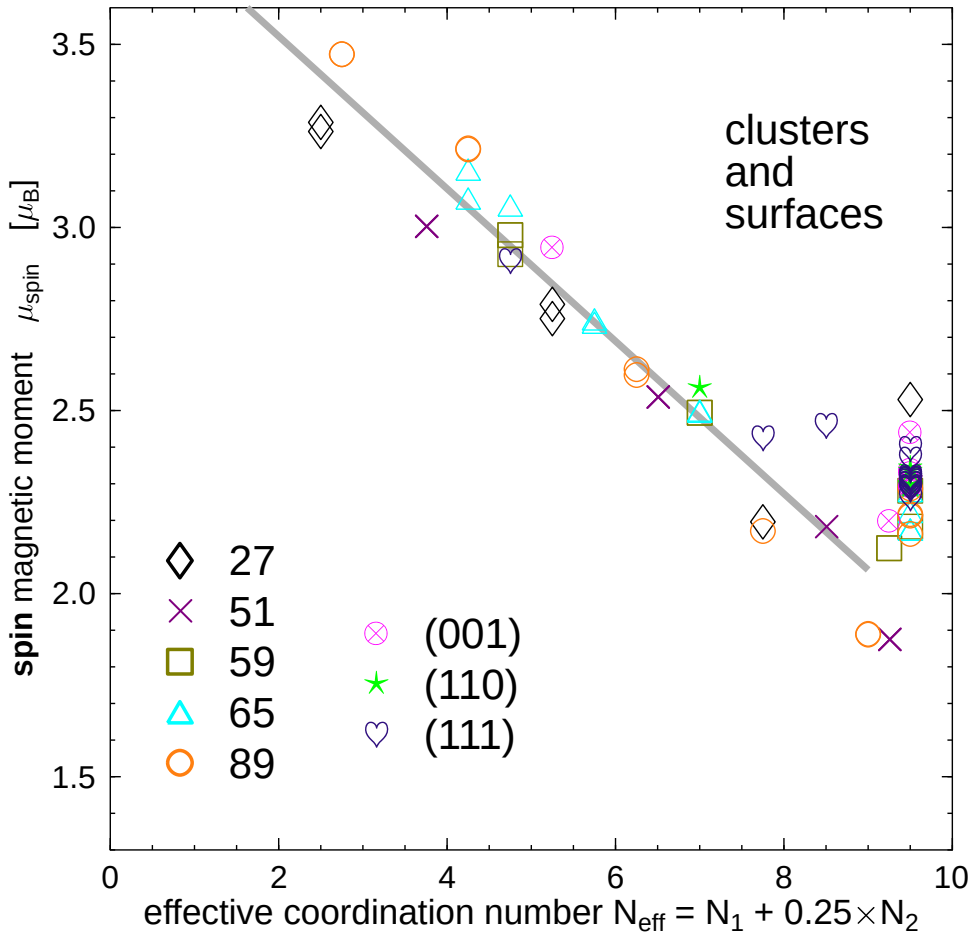
Šipr *et al.* PRB 2004



Dependence of μ_{spin} on the coordination number

Magnetic moment decreases with the coordination number linearly.

Šipr *et al.* PRB 2004



Main points for magnetism of free 3*d* clusters

- μ_{spin} and μ_{orb} are enhanced at atoms close to the cluster surface.

- μ_{spin} depends linearly on the coordination number.
  - This is a universal feature of most 3*d* clusters, both free and supported
    [Šipr *et al.* 2004, Mavropoulos *et al.* 2006, Šipr *et al.* 2007, Bornemann *et al.* 2012].

What to expect for 4*d* clusters?

4*d* electrons are less localized than 3*d* electrons

$r_{3d} = |\langle\psi_{3d}| r |\psi_{3d}\rangle|$ ∼20% of interatomic distance in bulk Co

$r_{4d} = |\langle\psi_{4d}| r |\psi_{4d}\rangle|$ ∼30% of interatomic distance in bulk Rh

Spin-orbit coupling (SOC) is stronger for 4*d* elements than for 3*d* elements

$\xi_{\mathrm{Co}} = 85$ meV

$\xi_{\mathrm{Rh}} = 204$ meV

Rh clusters: controversial results by experiment

- Stern-Gerlach-type experiment: free Rh clusters have magnetic moments which decrease with cluster size (to zero at 60–100 atoms), in a non-monotonous way [Cox *et al.* 1994].

- X-ray magnetic circular dichroism (XMCD): quasi-free Rh clusters of few tens of atoms in a Xe matrix on Ag(100) are magnetic, with $\mu_{\mathrm{orb}}/\mu_{\mathrm{spin}}$ ratio about 40% [Sessi *et al.* 2010].

- XMCD: Rh clusters of about 220 atoms embedded in a Al_2O_3 matrix are paramagnetic, with $\mu_{\mathrm{orb}}/\mu_{\mathrm{spin}}$ ratio less than 2% [Barthem *et al.* 2012].

Rh clusters: controversial results by theory

- Different DFT implementations predict different structures and spin configurations [Beltrán *et al.* 2013].
- Existence of more competing configurations is typical, sometimes the configurations differ only little in energies but considerably in magnetic moments [Jinlong *et al.* 1994, Lee 1997, Kumar *et al.* 2003, Futschek *et al.* 2005].
- Technical note: Most *ab initio* studies focused on clusters of less than 20 atoms.

Questions to be asked

Situation is messy $\Rightarrow$ let us downgrade the question, to get at least some reliable answers.

Focus not on properties of individual clusters but on common trends prevailing over an ensemble of cluster sizes.

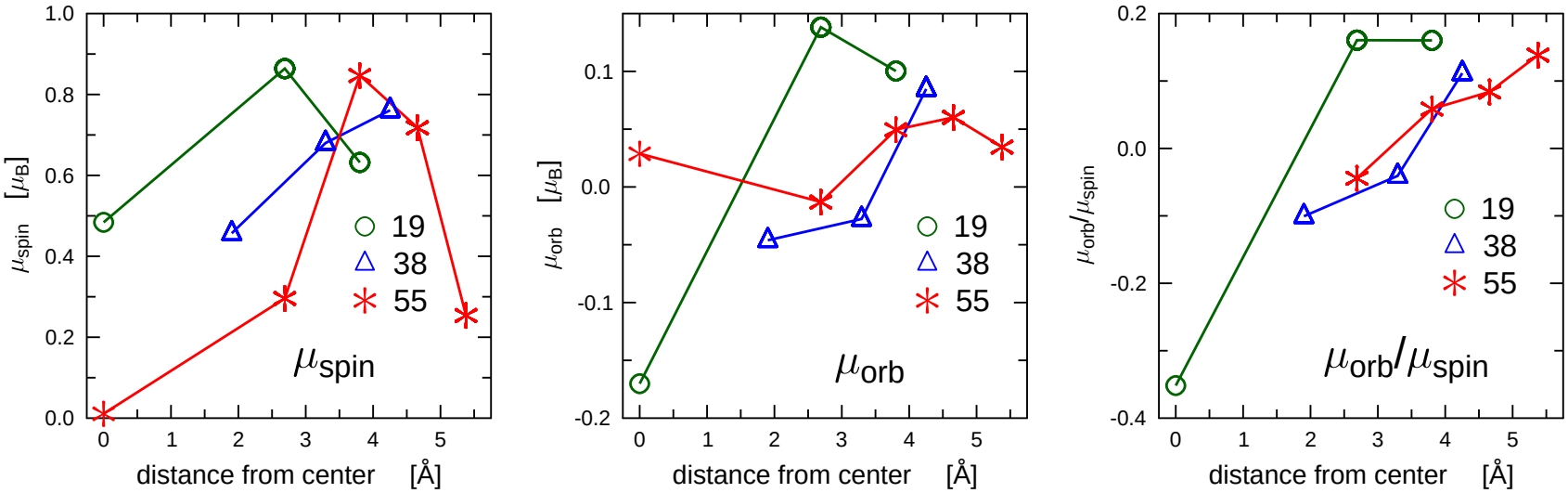
- Is there any systematic relation between local magnetic moments and coordination numbers (as in $3d$)?
- If not, is there another common trend to guide our intuition?

Methodology

- Spherical-like Rh clusters of 13–135 atoms, with fcc geometry as if cut from the bulk.
  - Technical note: Results for large Rh clusters are not very sensitive to whether the structural relaxation has been performed or not [Guirado-Lopez *et al.* 2000, Aguilera-Granja *et al.* 2002].

- Fully-relativistic KKR Green's function formalism as implemented in the SPRKKR code [Ebert *et al.* Rep. Prog. Phys. 2011].

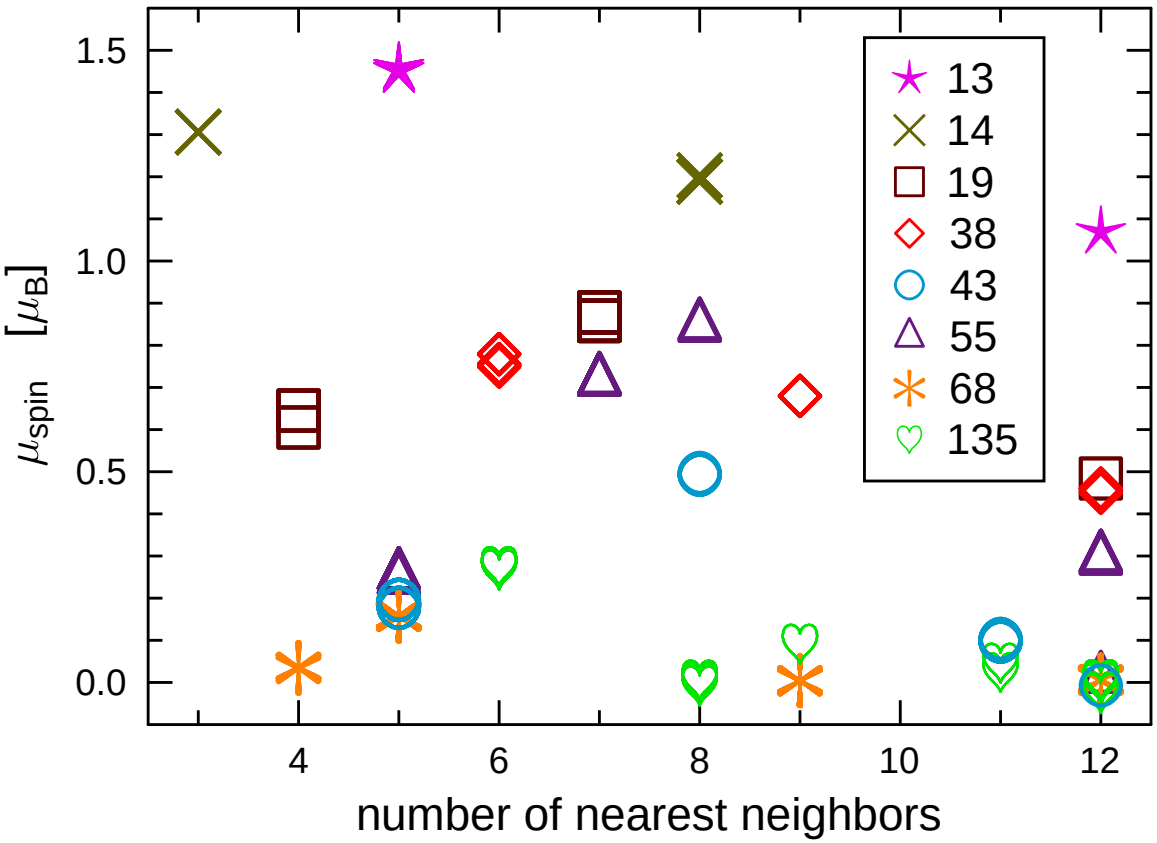
Magnetic profiles for free Rh clusters



- Representative results shown (clusters of 19, 38, and 55 atoms).
- No clear trend for enhancement of magnetic moments towards the surface.
- Note the opposite orientation of μ_{spin} and μ_{orb} for the centermost atoms in 19-atoms and 38-atoms clusters.

(Non-)dependence of μ_{spin} on coordination number

Local μ_{spin} in free Rh clusters as a function of the coordination number for atoms in clusters of 13–135 atoms:



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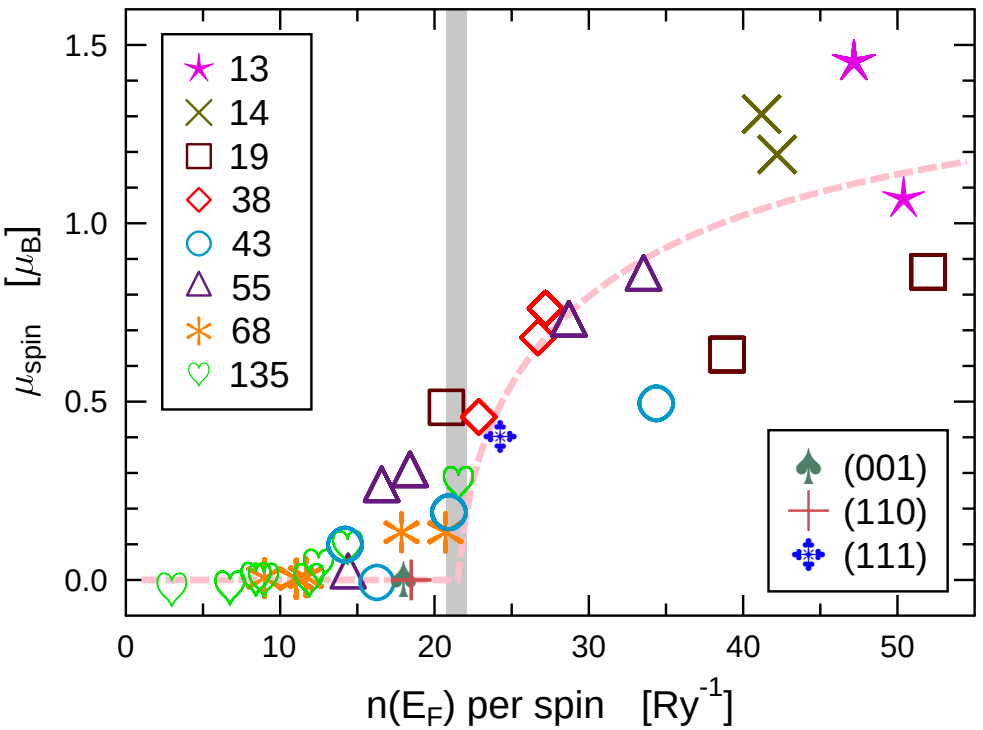
Stoner criterion applied locally



I_s exchange integral practically the same for all Rh systems

$n(E_F)$ DOS at E_F differs from site to site, from system to system

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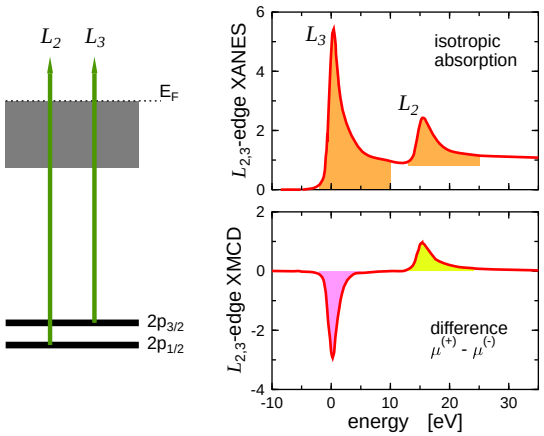
$$\mu_{\mathrm{spin}} \sim \sqrt{1 - \frac{1}{I_s\, n(E_F)}} \quad \Leftrightarrow \quad n(E_F) > \frac{1}{I_s}$$

$$\mu_{\mathrm{spin}} = 0 \quad \Leftrightarrow \quad n(E_F) < \frac{1}{I_s}$$

Can T_z explain the differences in XMCD experiments?



XMCD spin moment sum rule:

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

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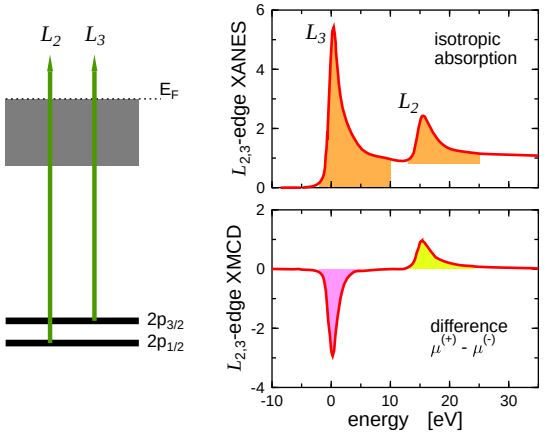

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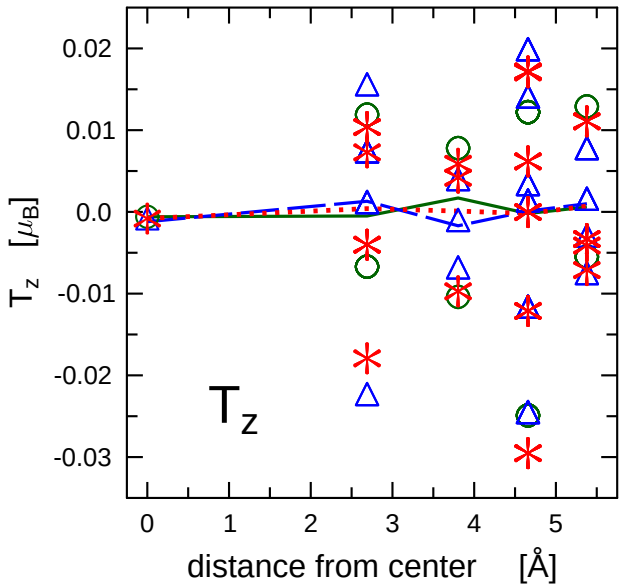

The intra-atomic T_z term can be quite large at certain sites but as a whole it is unlikely to affect the interpretation of XMCD experiments based on the sum rules.

Šipr *et al.* JPCM 2015

Conclusions

Some intuitive concepts that proved to be useful in magnetism of $3d$ clusters are not applicable to magnetism of $4d$ clusters.

- No systematic relation between local magnetic moments and coordination numbers.
- There can be large μ_{orb} antiparallel to μ_{spin} for some atoms in some clusters.
- Stoner model describes even local aspect of Rh magnetism quite well.
- T_z term cannot be used to explain differences between theory and XMCD experiment (or between different XMCD experiments).

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