Systematic trends of magnetic moments in clusters and solids: Getting the insight

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Outline

Methodology

Free Fe clusters and free Rh clusters: $3d$ vers. $4d$

Comparing free and supported Fe and Co clusters

$3d$-$5d$ system: Can SOC be induced from one atom to another?

Role of Madelung potential for alloy magnetism

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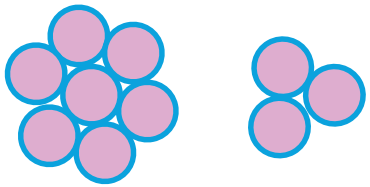
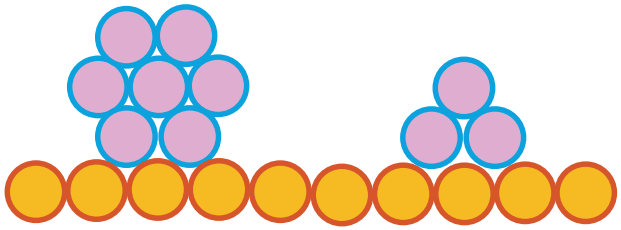
Outline

Clusters nomenclature



Free clusters:

- Electron states less hybridized (more atomic-like)



Supported clusters:

- Electron states more hybridized (less atomic-like)

Theoretical formalism

- Ab-initio, DFT, L(S)DA
- Fully-relativistic spin-polarized multiple-scattering technique, Dirac equation, SPRKKR code (Ebert).
  - Spherical ASA (avoidable but often practical and useful).
- Collinear magnetic moments only.
- Fixed (mostly spherical-like) geometry of clusters taken from the bulk.
- Free clusters: real space calculations.
  - *Empty spheres* put around free clusters in order to account for spilling of the electron charge into vacuum

Dealing with supported supported clusters

Impurity Green function method

- Calculate electronic structure of the "host" system (clean surface).
  - Crystal surfaces treated as 2D finite slabs (mostly; true semi-infinite system sometimes).
  - Tight-binding a.k.a. screened KKR.
- Supported clusters treated as a perturbation to the clean surface.
  - Green's function of the new system (cluster plus substrate) is obtained by solving the Dyson equation.

SPRKKR code: Ebert *et al.* Rep. Prog. Phys. 2011

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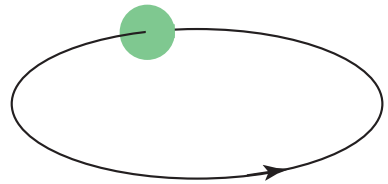
Magnetic moments nomenclature

Spin magnetic moment:

$$\mu^{(z)}_{\mathrm{spin}} = -\frac{\mu_B}{\pi}\,\mathrm{Im\,Tr}\int_{-\infty}^{E_F}\mathrm{d}E\int \mathrm{d}^3 r\beta\,\sigma_z\,G(\mathbf{r},\mathbf{r},E)$$

Orbital magnetic moment:

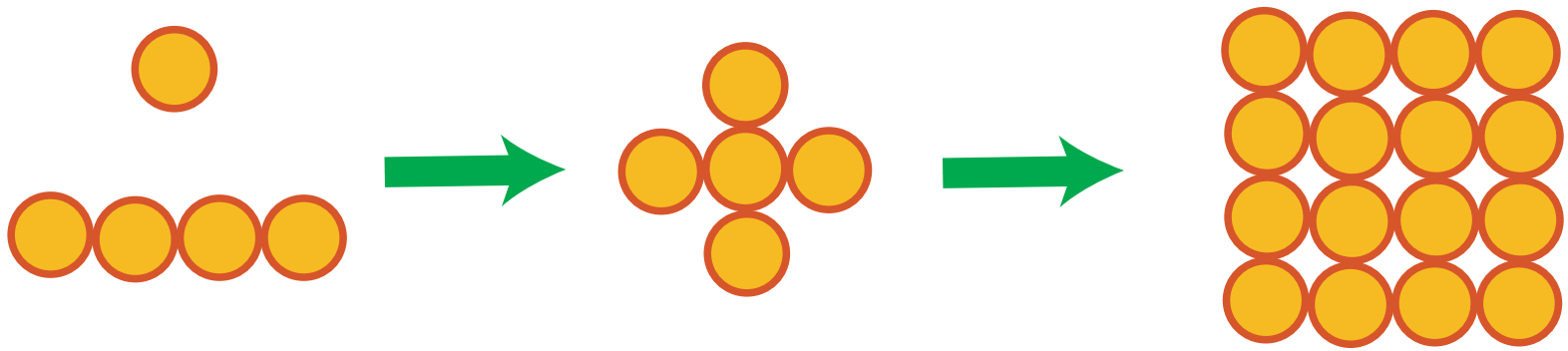


$$\mu^{(z)}_{\mathrm{orb}} = -\frac{\mu_B}{\pi}\mathrm{Im\,Tr}\int_{-\infty}^{E_F}\mathrm{d}E\int \mathrm{d}^3 r\beta\,L_z\,G(\mathbf{r},\mathbf{r};E)$$

In bulk cubic systems, μ_{orb} would be zero if it were not for the spin-orbit coupling.

What can we expect from clusters?

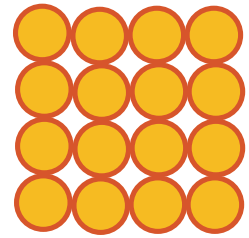
Clusters mark the transition between atoms, surfaces and bulk systems.

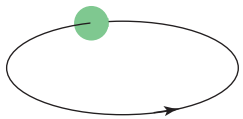


- Rule of thumb for magnetism of clusters:
  small number of atoms
  $\Rightarrow$ less hybridization
  $\Rightarrow$ larger magnetic moments

Example: Magnetism of Fe in different environment





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

clusters enter here

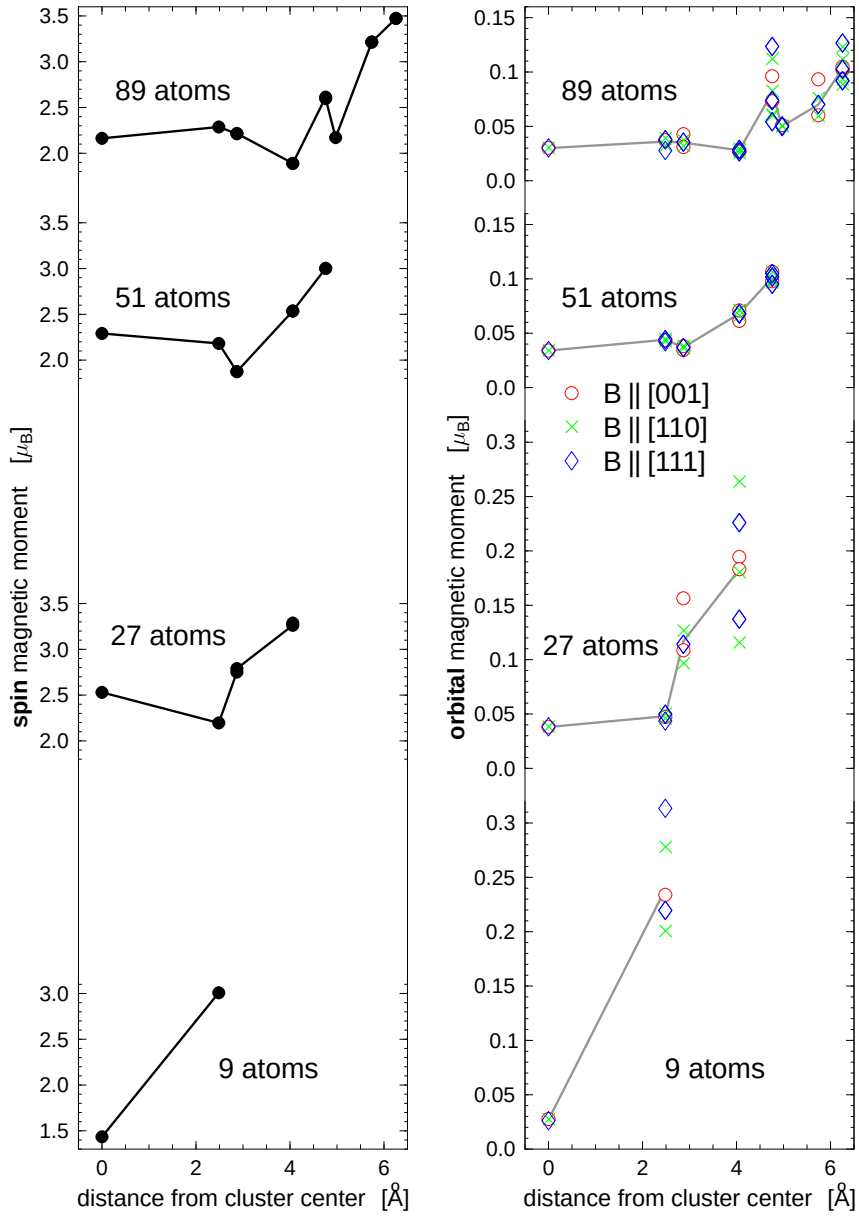
Outline

Magnetic profiles for free Fe clusters

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

Technical reminder:

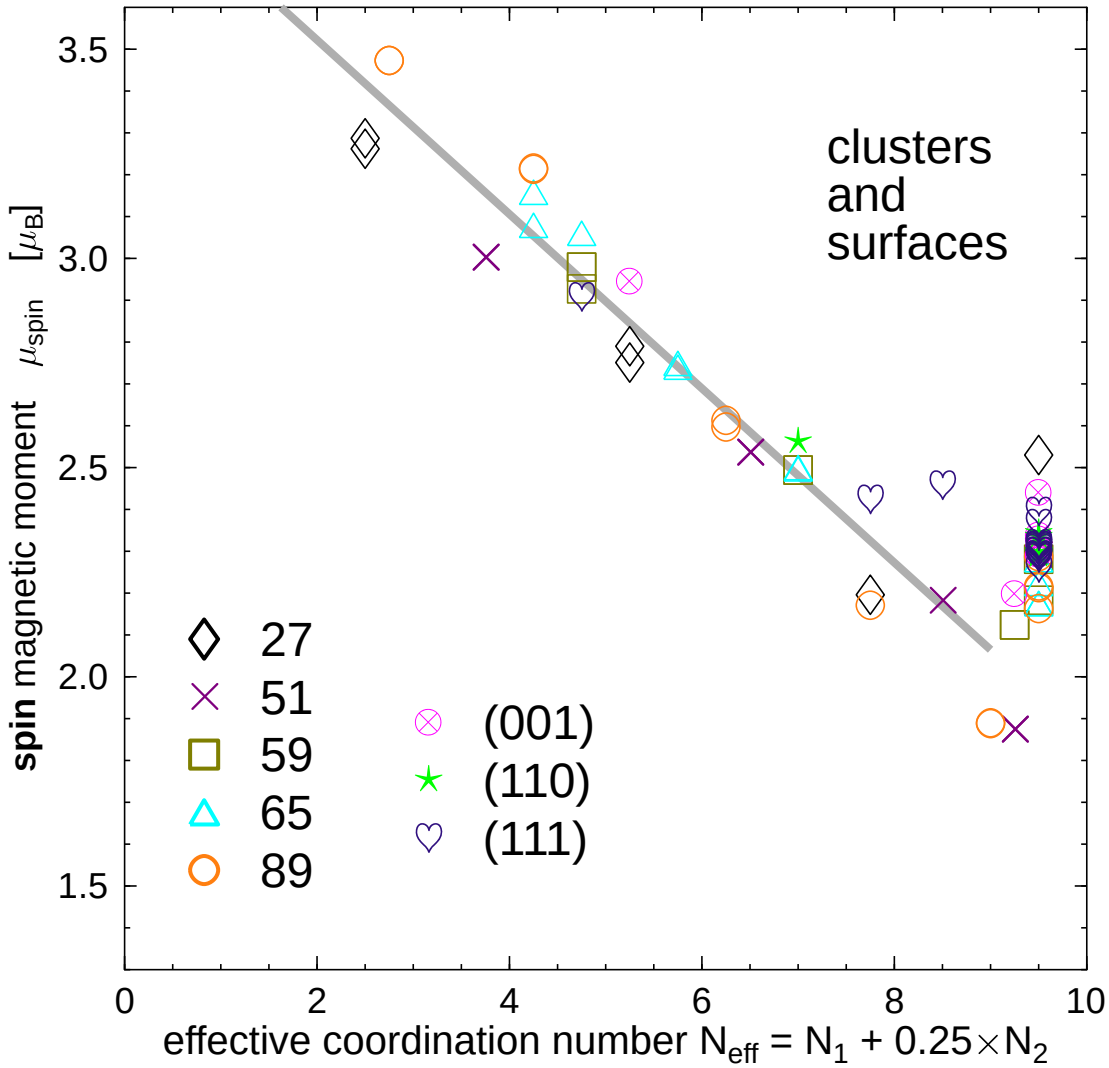
Relativity decreases the symmetry, therefore atoms belonging to the same shell need not have the same μ_{orb}.



Šipr *et al.* PRB **70**, 174423 (2004)

Dependence of μ_{spin} for Fe on the coordination

Magnetic moment decreases with the coordination number linearly.



Šipr *et al.* PRB **70**, 174423 (2004)

Main trends concerning magnetism of free 3*d* clusters

General rules of thumb for free Fe 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.* PRB **70**, 174423 (2004), Mavropoulos *et al.* Appl. Phys. A **82**, 103 (2006), Šipr *et al.* JPCM **19**, 096203 (2007), Bornemann *et al.* PRB **86**, 104436 (2012)].

What to expect for 4d clusters?

4d electrons are less localized than 3d 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 4d elements than for 3d elements

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

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

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Questions to be asked

Bottom line:
Situation with magnetism of Rh clusters is a bit messy.

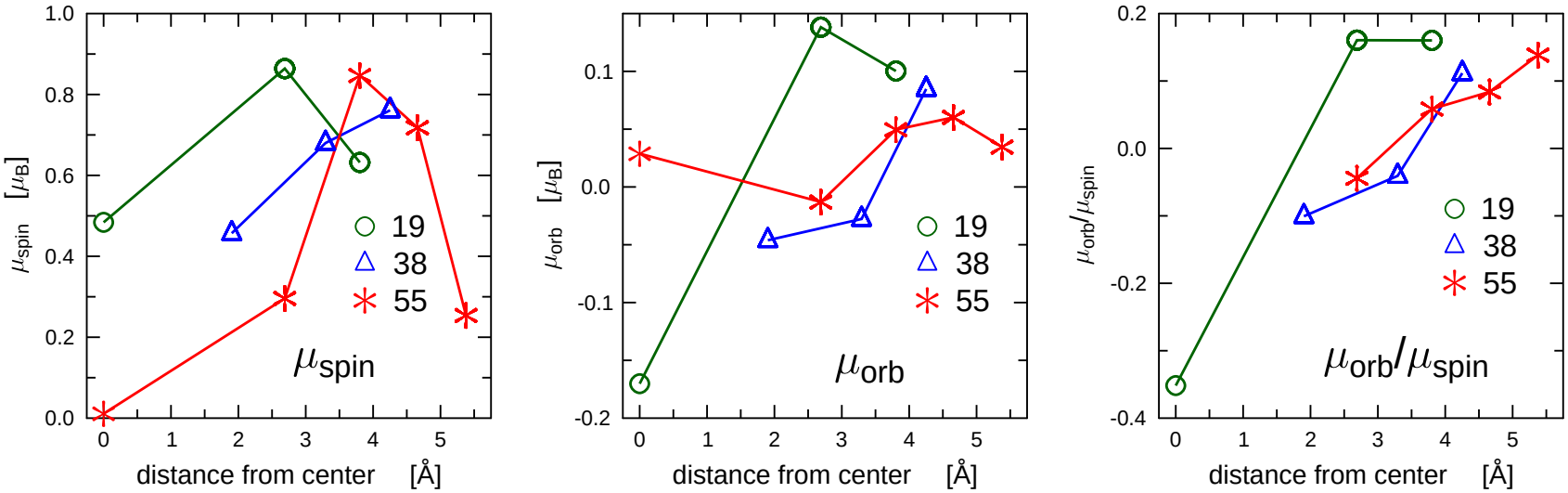
Controversion results by experiment [Cox *et al.* PRB **49**, 12295 (1994), Sessi *et al.* PRB **82**, 184413 (2010), Barthem *et al.* PRL **109**, 197204 (2012)].

Controversial results by theory [Jinlong *et al.* PRB **50**, 7915 (1994), Lee Z. Phys. D **40**, 164 (1997), Kumar *et al.* EPJ D **24**, 81 (2003), Futschek *et al.* JPCM **17**, 5927 (2005), Beltrán *et al.* EPJ D **67**, 1 (2013)].

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?

Magnetic profiles for free Rh clusters

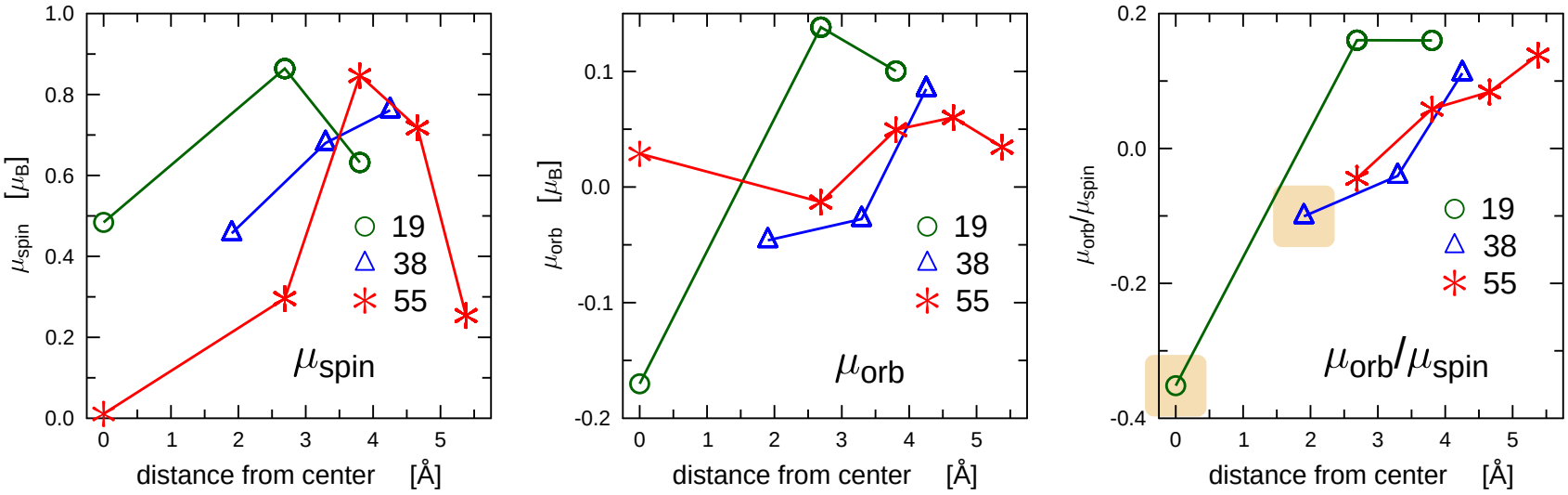


Representative results shown for clusters of 19, 38, and 55 atoms.

- No clear trend for enhancement of magnetic moments towards the surface.

Šipr *et al.* JPCM **27**, 056004 (2015)

Magnetic profiles for free Rh clusters



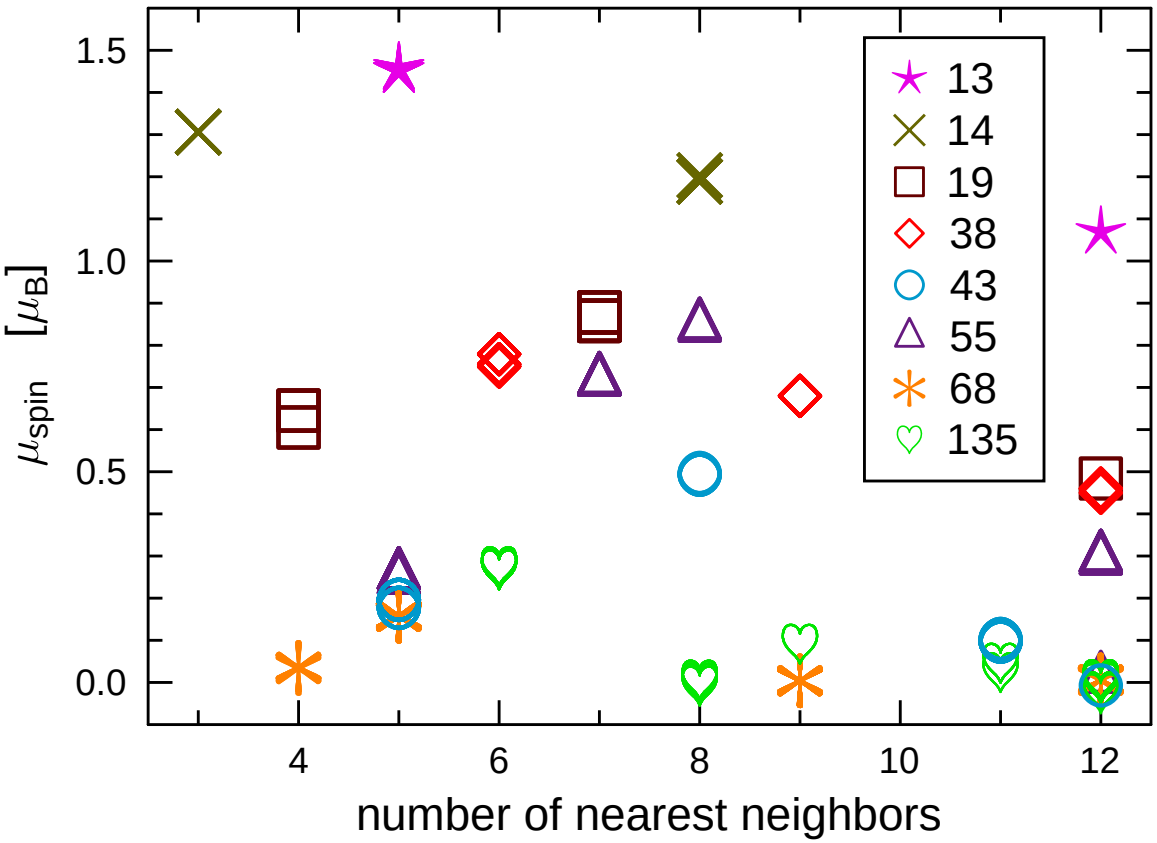
Representative results shown for clusters of 19, 38, and 55 atoms.

- 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.

Šipr *et al.* JPCM **27**, 056004 (2015)

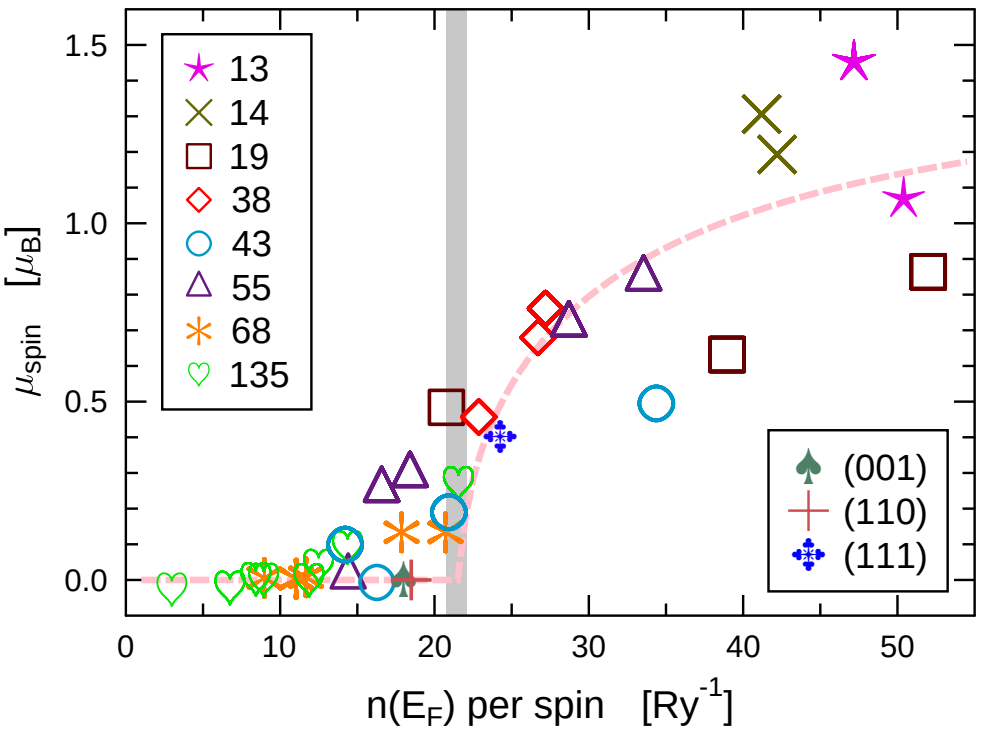
(Non-)dependence of μ_{spin} on coordination number

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



Šipr *et al.* JPCM **27**, 056004 (2015)

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

Šipr *et al.* JPCM **27**, 056004 (2015)

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

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

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Verdict on magnetism of free Rh clusters

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.

Outline

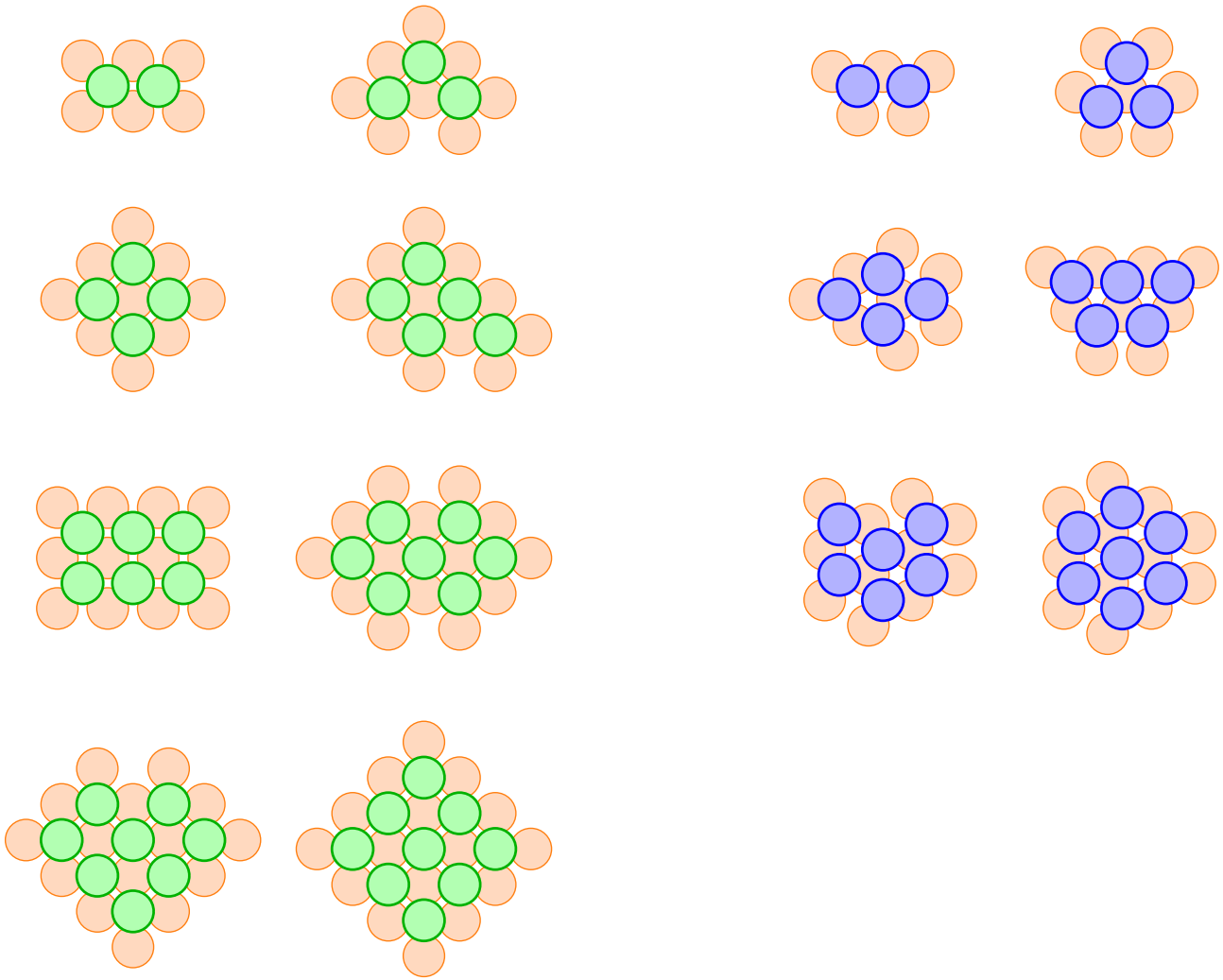
Goals and methods

- How do the magnetic properties change if clusters are deposited on a substrate?
- Take analogous systems (identical sizes, identical geometries) and have a look!
- Focus rather on the trends than on particular values.

Shapes of clusters (free or supported)

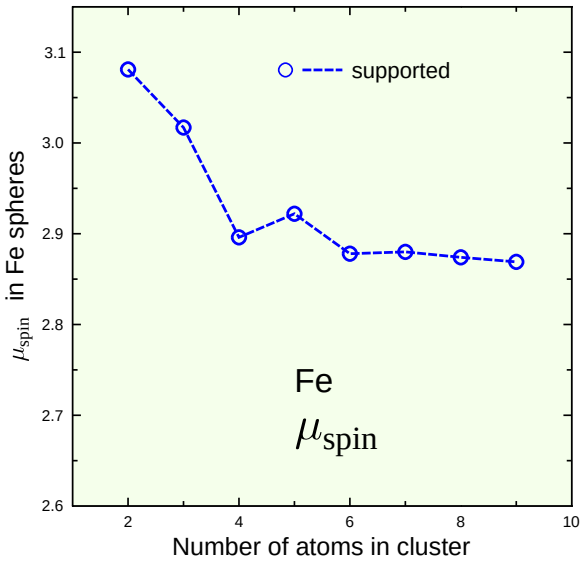
Fe_N / Ni(001)

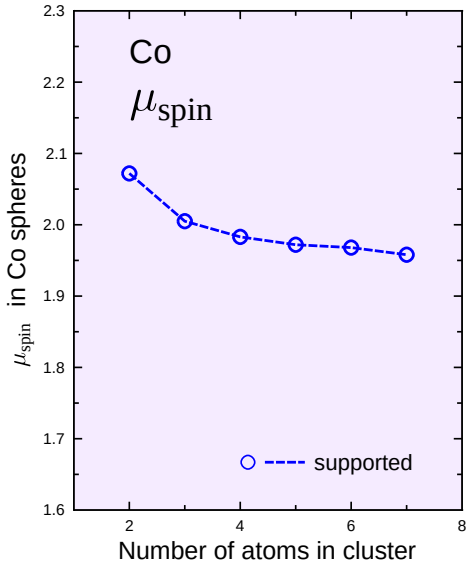
Co_N / Au(111)

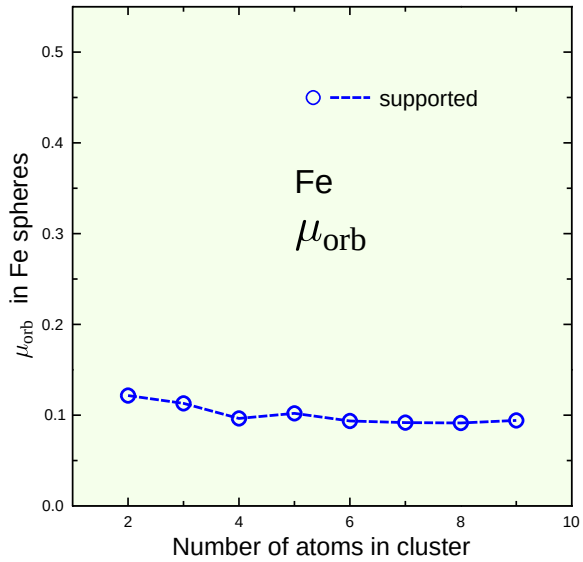


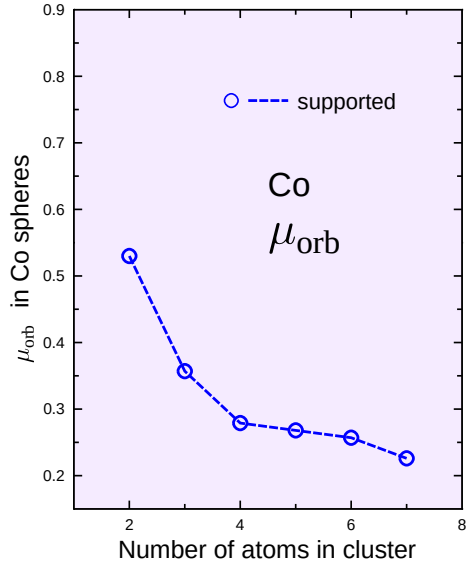
(Only nearest-neighbor substrate atoms are shown.)

Average magnetic moments



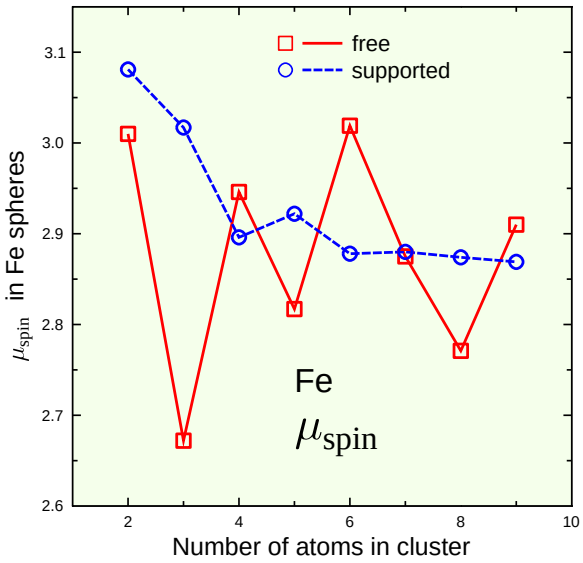


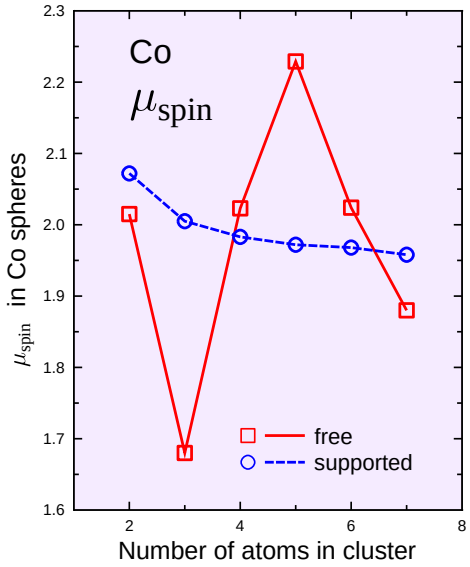


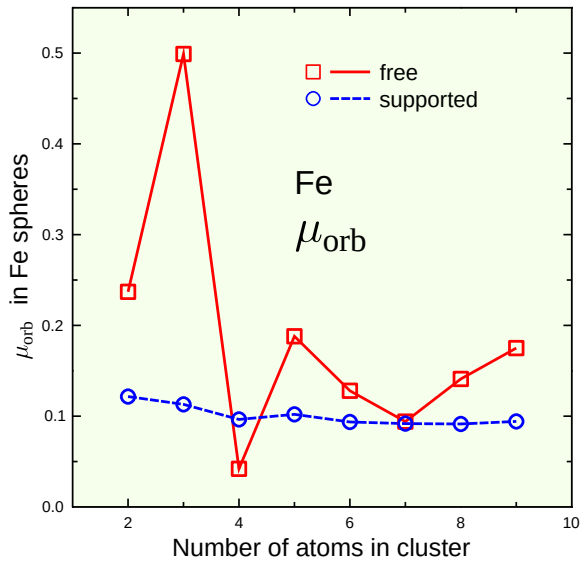


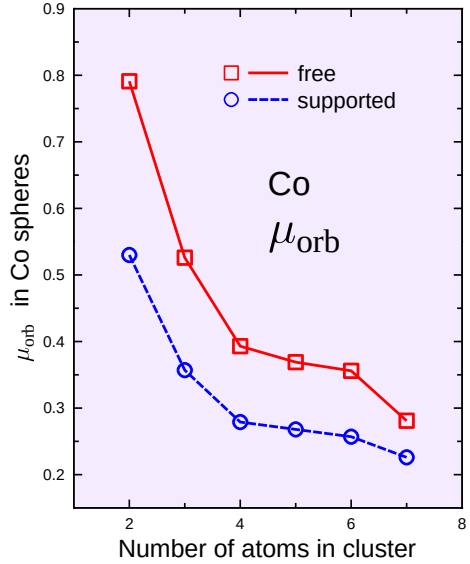
- Supported clusters: nearly monotonous decay of μ_{spin} and μ_{orb} with N.

Average magnetic moments



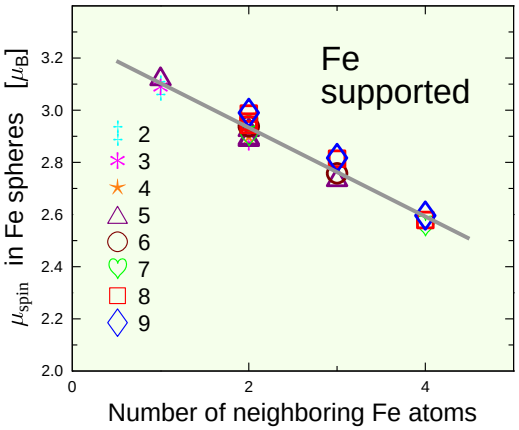


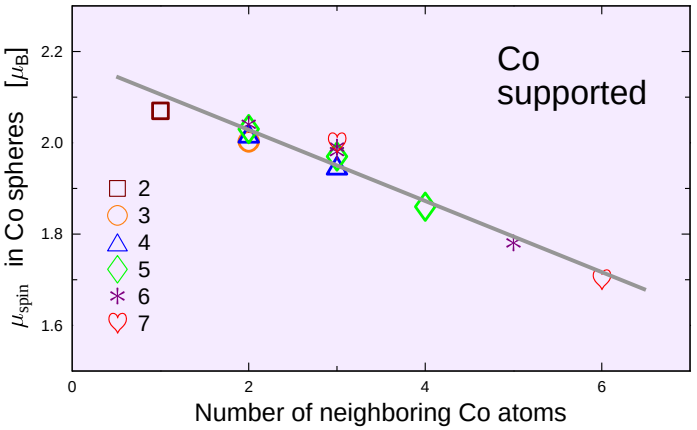




- Supported clusters: nearly monotonous decay of μ_{spin} and μ_{orb} with N.
- Free clusters: quasi-oscillations, quite large amplitides.
- μ_{orb} of free Co clusters does not follow the herd — it does not oscillate.

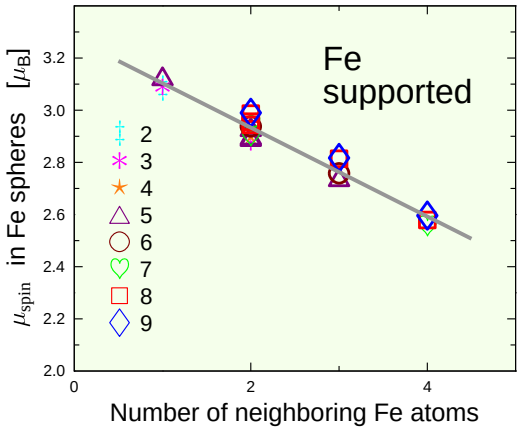
Effect of coordination on μ_{spin}

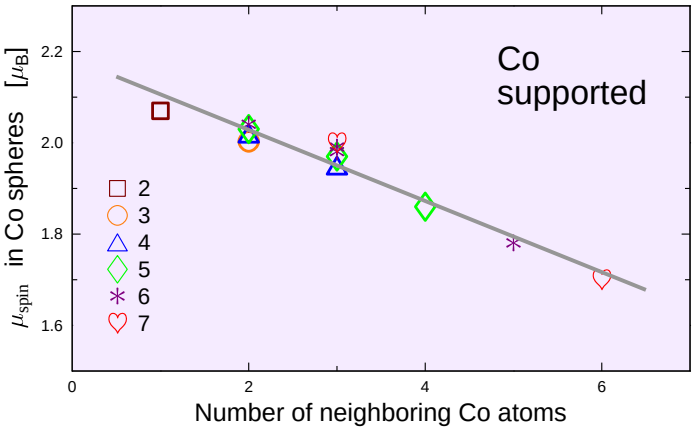


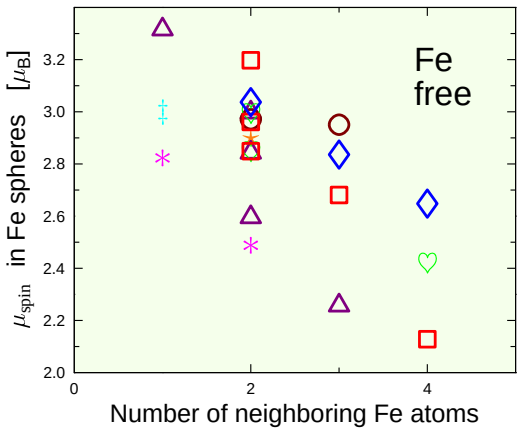


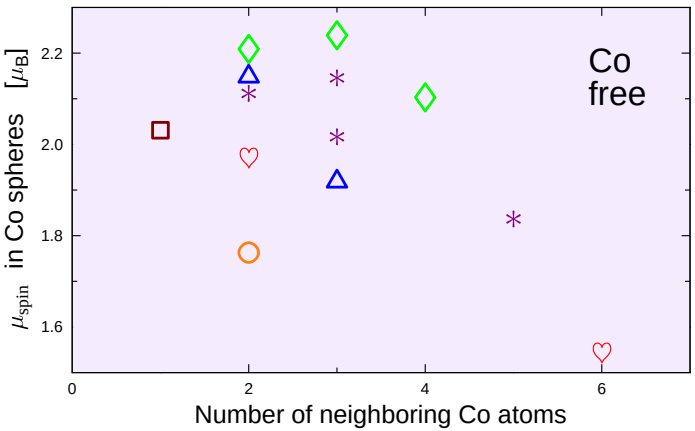
- μ_{spin} decreases if coordination number increases

Effect of coordination on μ_{spin}









- μ_{spin} decreases if coordination number increases
- Big scatter around the linear dependence for small *planar* free clusters

Comparison between free and supported clusters: summary

Substrate acts as an "adult supervisor" for the free clusters.

- Substrate suppresses the tendency of magnetic moments to oscillate with cluster size.
- Substrate makes μ_{spin} to depend on the coordination number linearly, with very little scatter around.
  - For free clusters, this trend appears only for spherical and/or larger clusters

Further reading:
Šipr *et al.* JPCM **19**, 096203 (2007)
Šipr *et al.* Cent. Eur. J. Phys. **7**, 257 (2009)

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Outline

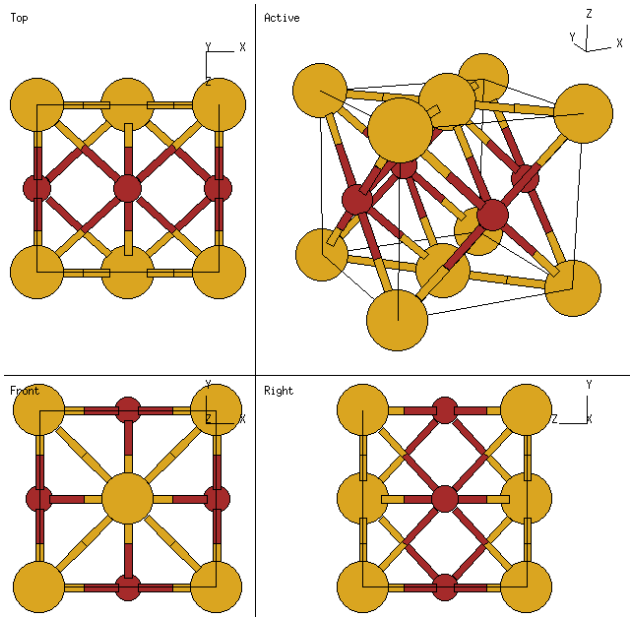
Inducing spin-orbit coupling (SOC) ?

Complex $3d$-$5d$ systems (such as CoPt, FePt) are becoming trendy in research directed towards spintronics: the hope is on inducing large spin-orbit coupling (SOC) of the non-magnetic $5d$ constituent to the magnetic $3d$ constituent.

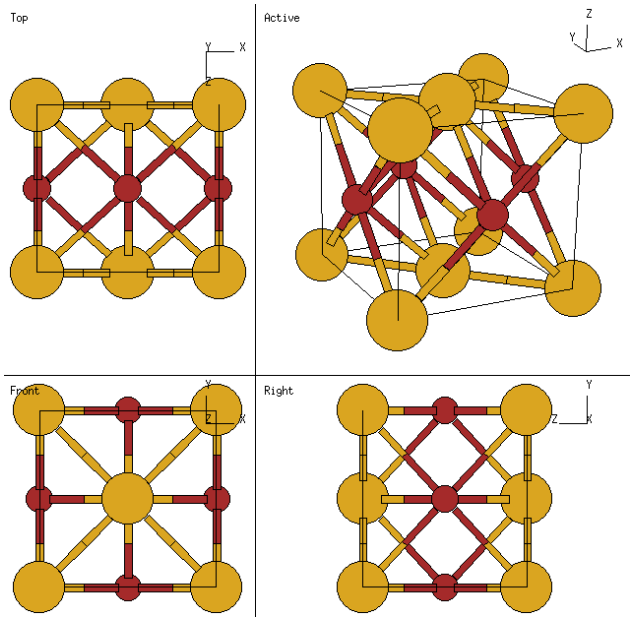
Simple test ("feasibility study"):
If the content of Pt in Co-Pt systems increases, will it enhance the role of SOC in magnetism of Co atoms?

Specific task:
Explore the dependence of μ_{orb} at Co on Pt concentration for Co-Pt systems.

Sequence of ordered Co-Pt systems



CoPt (50 % of Pt): $L1_0$ structure



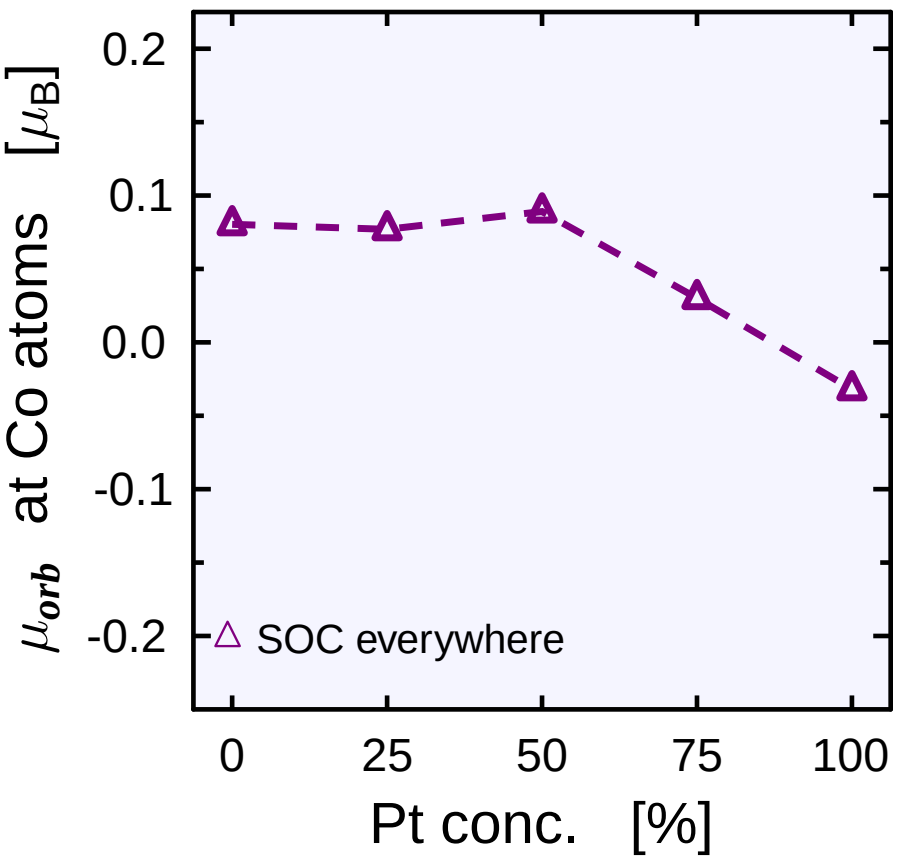
Co_3Pt (25 % of Pt), $CoPt_3$ (75 % of Pt): $L1_2$ structure

Study also the extreme cases:

fcc Co: (0 % of Pt)

Co impurity in fcc Pt: (100 % of Pt)

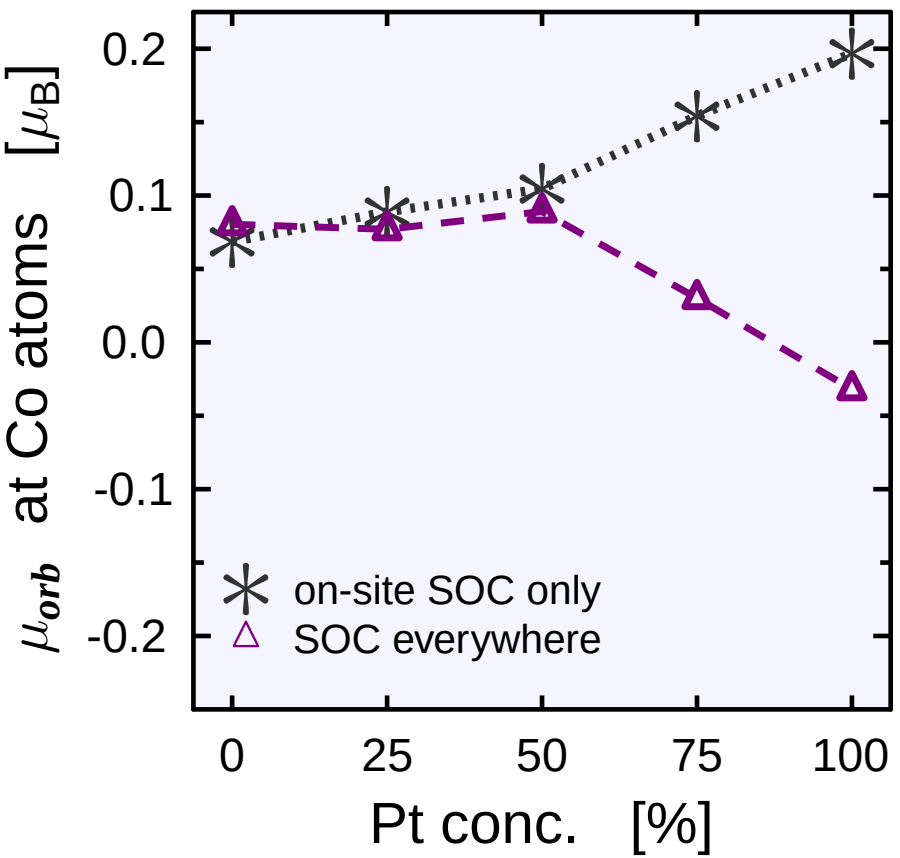
Magnetism of $Co_{1-x}Pt_x$: Influence of spin-orbit coupling



The orbital moment μ_{orb} at the Co atoms in ordered $Co_{1-x}Pt_x$ systems:

Šipr *et al.* PRB **78**, 144403 (2008)

Magnetism of $Co_{1-x}Pt_x$: Influence of spin-orbit coupling



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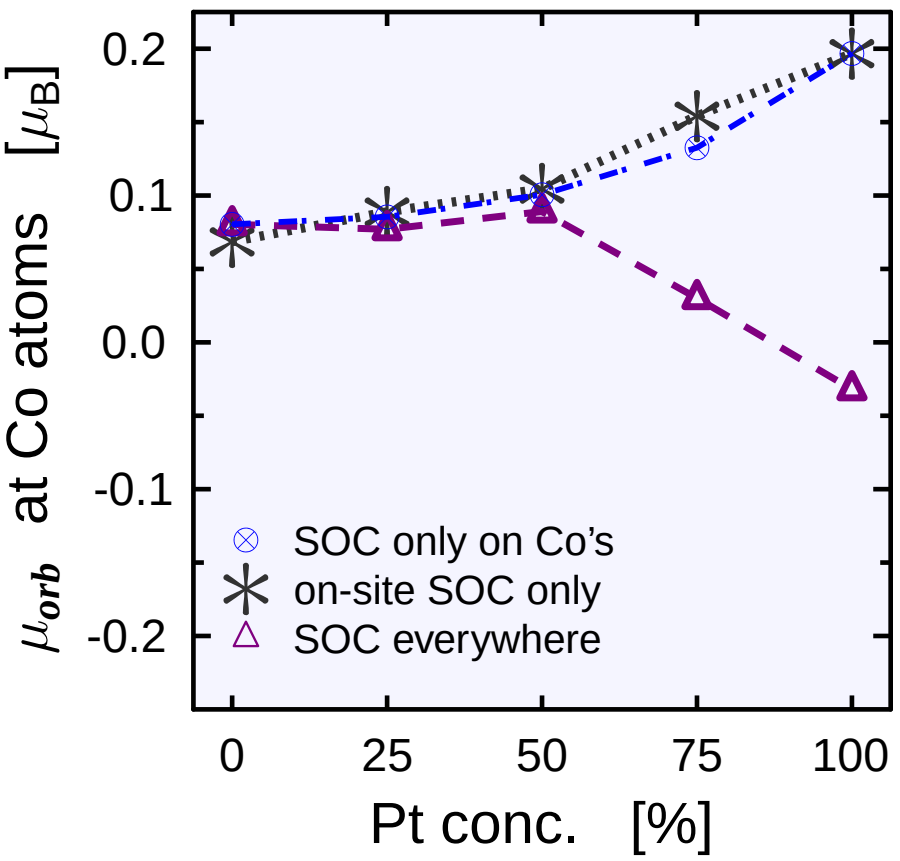

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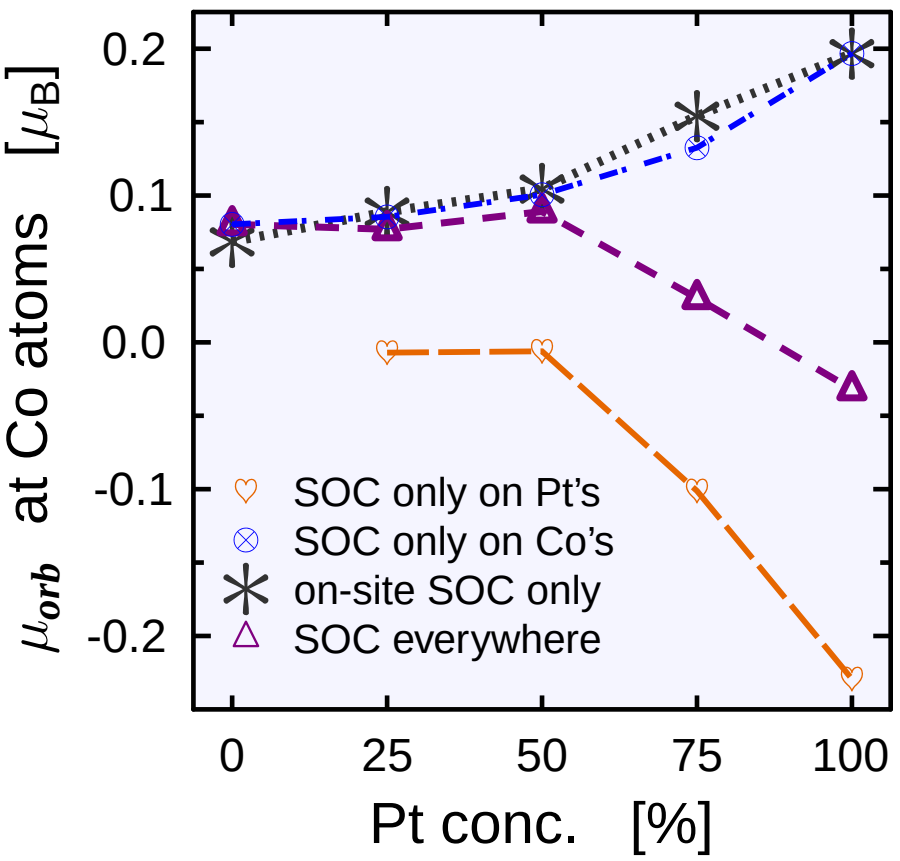


The orbital moment μ_{orb} at the Co atoms in ordered $Co_{1-x}Pt_x$ systems:

SOC is included at one single Co atom (black, asterisks), at all atoms (purple, triangles), at wll Co atoms (blue, crossed circles), at all Pt atoms (orange, hearts).

Increasing the SOC strength at the neighbors decreases μ_{orb} at Co atoms.

Šipr *et al.* PRB **78**, 144403 (2008)

Why increasing SOC does not increase μ_{orb}?

Inducing spin-orbit coupling from Pt to Co does not seem to work!

SOC at Pt atoms actually decreases μ_{orb} at Co atoms.

Because of the presence of Pt atoms, the SOC cannot be considered a weak local perturbation in Co-Pt systems. Moreover, it is off-site as concerns Co. SOC at Pt atoms contributes to disrupting the "spherical" symmetry around Co atoms, decreasing thereby μ_{orb}.

Similar situation elsewhere:

- μ_{orb} at V atom in VAu_4 [Galanakis *et al.* PRB **63**, 172405 (2001)].
- Magneto-optical Kerr rotation angle θ_K in FePt [Ebert *et al.* PRB **56**, 9454 (1997)].

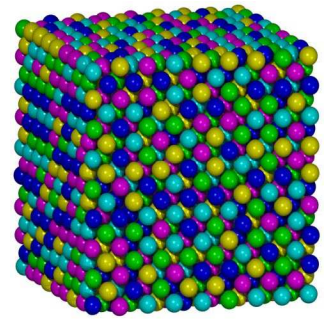
Šipr *et al.* PRB **78**, 144403 (2008)

Outline

Dealing with substitutional alloys

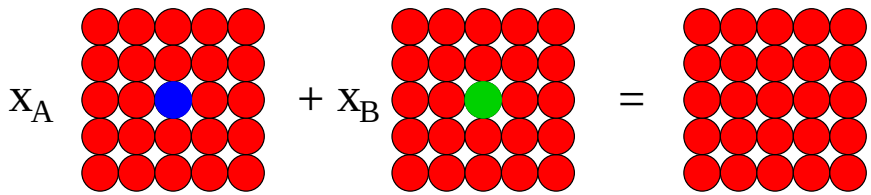
1. Simulating random occupation of sites via supercells

   Exact result if the supercell is large enough.



Special quasirandom structures (SQS's):
Periodic structures created so that they have the same correlation functions as random alloys up to a certain coordination shell.

2. Coherent potential approximation (CPA)



Effective medium approach, all atoms equivalent, no long-range Coulombic (Madelung) contribution to the potential.

Madelung contribution to the potential

Coherent potential approximation (CPA) is an effective medium approach, all atoms are of the same type, therefore there is no "excess charge" on them and consequently there is no longe-range Coulombic a.k.a. Madelung contribution to the potential.

Efforts to tackle this issue: Typically, one tries to ascribe a charge to an atom in an alloy based on some physical assumptions (screened impurity model).

Important advances been made in this respect [Johnson & Pinski PRB **48**, 11553 (1993), Faulkner *et al.* PRB **52**, 17106 (1995), Abrikosov & Johansson PRB **57**, 14164 (1998), Bruno *et al.* PRB **66**, 245107 (2002), Ruban & Skriver PRB **66**, 024202 (2002), ...]

Situation is still murky and controversial.

Does the Madelung potential matter for magnetism?
Case study of disordered FePt.

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CPA and supercells yield different magnetic moments

Average moments for Fe and Pt atoms in disordered FePt:

		$\langle \mu_{\text{spin}} \rangle$	$\langle \mu_{\text{orb}} \rangle$
SQS-4	Fe	2.843	0.043
	Pt	0.253	0.027
SQS-8	Fe	2.821	0.069
	Pt	0.286	0.051
SQS-16	Fe	2.823	0.066
	Pt	0.263	0.042
SQS-32	Fe	2.816	0.073
	Pt	0.264	0.043
$\langle$SQS-4,8,16,32$\rangle$	Fe	2.821	0.069
	Pt	0.266	0.043
CPA	Fe	2.903	0.070
	Pt	0.239	0.039

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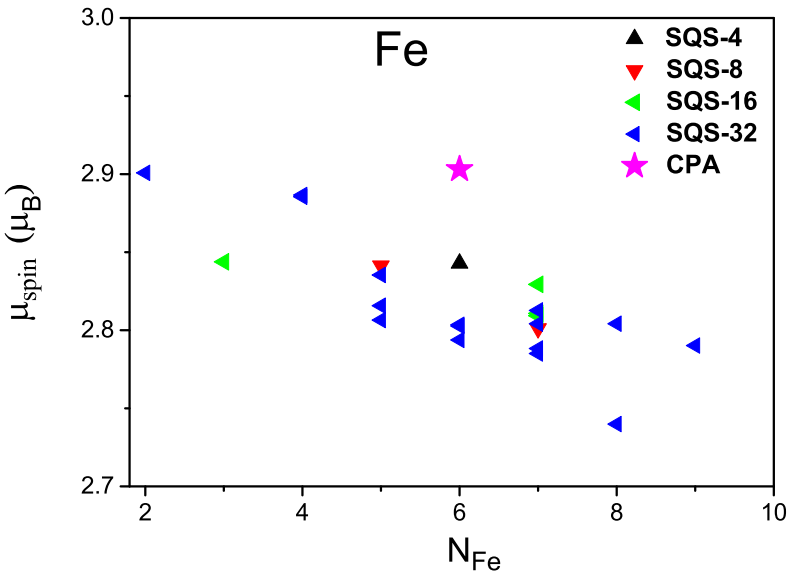
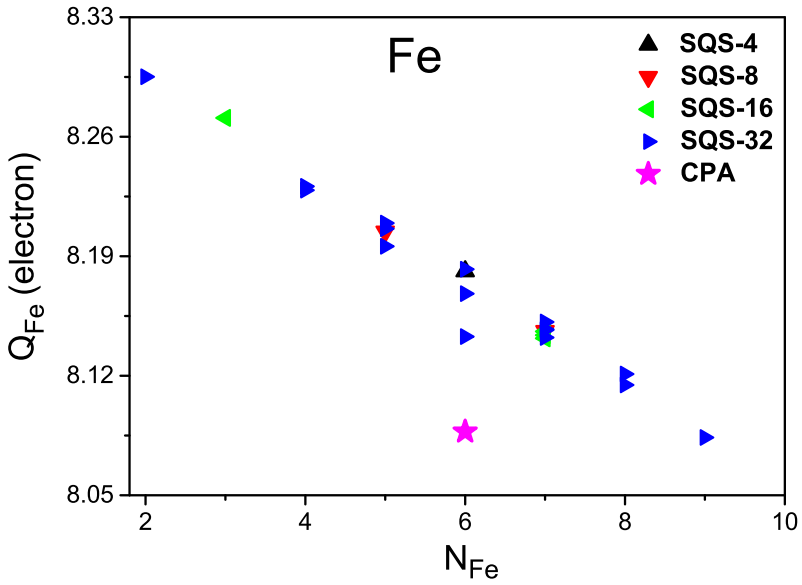
Even for the largest supercell, a small but distinct difference in magnetic moments obtained via the supercells and via the CPA remains!

Trends of μ_{spin} and Q_{Fe} for supercells and for CPA



Dependence of μ_{spin} at Fe sites on the number of Fe atoms in the first coordination shell N_{Fe}.

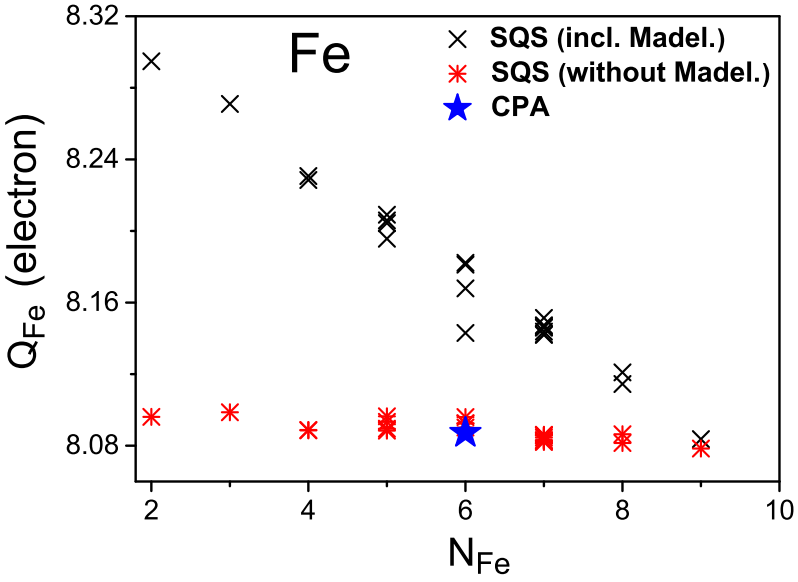


Dependence of electronic charge Q_{Fe} at Fe sites on N_{Fe}.

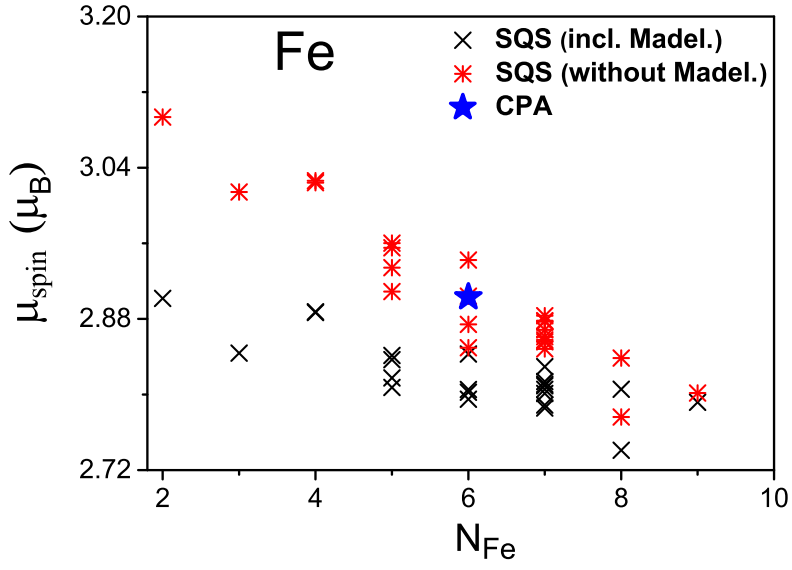
Results of CPA do not follow the same trend as results for supercells.

Effect of the Madelung potential

Compare results of supercell calculations with the Madelung potential with results obtained without it.
See where the CPA results will stand.



Dependence of the electronic charge at Fe sites on the coordination number N_{Fe}. The CPA result shown for comparison.



Dependence of μ_{spin} at Fe sites on coordination number N_{Fe}. Analogous to the figure on the left.

Q and μ_{spin} with or without the Madelung potential

Charges Q and magnetic moments μ_{spin} obtained by averaging over all sites in all four supercells (SQS's), obtained either with the Madelung potential or without it.

	Fe		Pt	
	Q_{Fe}	μ_{spin}	Q_{Pt}	μ_{spin}
$\langle$SQS$\rangle$ (incl. Madel.)	8.174	2.821	9.825	0.266
$\langle$SQS$\rangle$ (no Madel.)	8.088	2.907	9.912	0.245
CPA	8.087	2.903	9.913	0.239

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The difference between CPA and supercells is just the Madelung potential.

Conclusion

If you look on a set of your theoretical data instead of on a single result, you do not need to be *that* accurate to get some useful information from what you have calculated.

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