Magnetism and spectroscopy of clusters

What the SPRKKR package is good for

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Outline

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Introduction: Clusters and magnetism

- Primer on clusters
- Magnetism — basic concepts

Free Fe clusters — ground-state magnetic properties

- Magnetism of clusters — intuitive expectations
- Clusters - DOS, μ_{spin}, μ_{orb}
- Comparing Fe clusters and Fe surfaces

Magnetism of free and supported clusters

Magnetism of clusters for $T \neq 0$

- Finite temperature magnetism HOWTO
- Free Fe clusters: exchange coupling
- Free Fe clusters: magnetization

X-ray absorption spectroscopy of clusters

- Primer on x-ray absorption spectroscopy
- XAS and XMCD of free Fe clusters
- Verification of XMCD sum rules for Fe_N/Ni(001)

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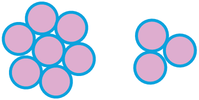

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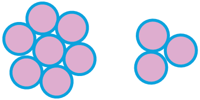
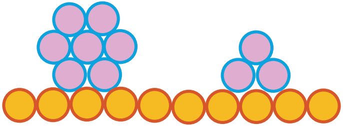
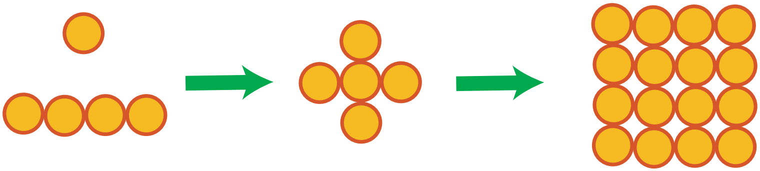


- Supported clusters — adsorbed on a surface



Clusters: What can we expect ?

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



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- Our main focus will be on their *magnetic* properties

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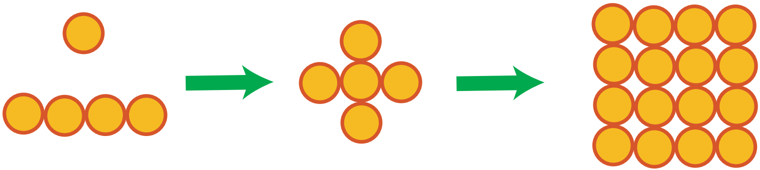

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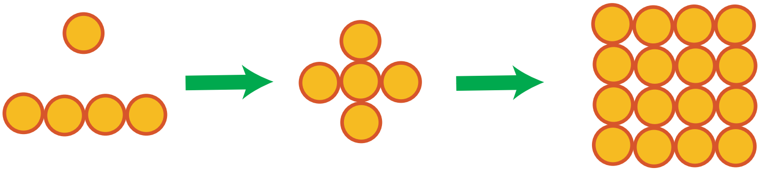

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Where does magnetism come from?

- Classically: Magnetic field is *something* produced by moving electric charges that affects other moving charges

- Special relativity: Magnetism is a *fictitious force* needed to guarantee Lorentz invariance when charges move

- Dealing with magnetism in the framework of Dirac equation is ideologically simple
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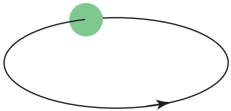
Two ways of moving an electron

(A quick and dirty introduction to magnetism)

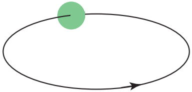
- Orbiting



- Spinning

Orbital magnetic moment (1)

Classical expression for magnetic moment:



$$\boldsymbol{\mu}_{\rm orb} = I\,\mathbf{S} \quad\Longrightarrow\quad \boldsymbol{\mu}_{\rm orb} = -\,\mu_B\,\mathbf{L}$$

where μ_B is Bohr magneton

$$\mu_B \equiv \frac{e}{2m_e}\,\hbar$$

and $\mathbf{L}$ is angular momentum devided by $\hbar$.

For electron orbiting *around an atom*, the z-component of orbital magnetic moment is thus

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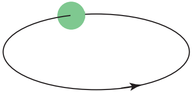

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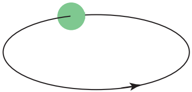
Orbital magnetic moment (2)

Practical evaluation of orbital magnetic moment of electrons in a solid:



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

β is Dirac matrix
L_z is the z-component of a 4×4 matrix vector $I_4 \otimes \mathbf{L}$
$G(\mathbf{r},\mathbf{r};E)$ is a 4×4 Green function matrix.

Even more practical *evaluation of* μ_{orb}*:*
Find it in the output of the SPRKKR *program.*

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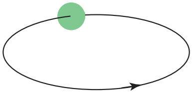

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Spin magnetic moment (1)

Electron spin: Picture of a rotating charged sphere fails. . .

$$\boldsymbol{\mu}_{\text{orb}} = -\,\mu_B\,\mathbf{L} \quad \textit{vers.} \quad \boldsymbol{\mu}_{\text{spin}} = -\,2\,\mu_B\,\mathbf{S}$$

L is angular momentum connected with *orbital* motion
S is angular momentum connected with "*spinning*"

For electron *around an atom*, the z-component of spin-related angular momentum is

$$S^{(z)} = \pm\frac{1}{2}\hbar \ ,$$

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Free Fe clusters — ground-state magnetic properties

Magnetism of Fe atom

Magnetic properties of atoms are governed by Hund rules

Electron configuration: $3d^6 4s^2$

- Spin magnetic moment: $\mu_{\text{spin}} = 4\,\mu_B$
  - First Hund rule: Total atomic spin quantum number $S = \sum m_s$ is maximum (as long as it is compatible with Pauli exclusion principle)
- Orbital magnetic moment: $\mu_{\text{orb}} = 2\,\mu_B$
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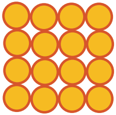
Magnetism of bulk Fe crystal



- Generally: Magnetism is suppressed in the bulk (with respect to atomic case)
  - Spin magnetic moment is $\mu_{\mathrm{spin}} \approx 2.2\ \mu_B$ per atom
  - Orbital magnetic moment is quenched (outright zero in non-relativistic case)
    - Intuitively: Electron are not free to orbit around atoms
    - Relativistic effect: The quenched orbital moment is partially restored by LS coupling ($\mu_{\mathrm{orb}} \approx 0.05 \mu_B$ per atom)

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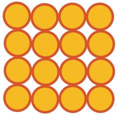

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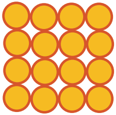

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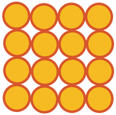

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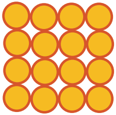

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Surfaces are magnetism-friendly

- Atoms at surfaces exhibit some atomic-like characteristics
  - Spin magnetic moment is larger than in bulk; for Fe it is $\mu_{\rm spin} \approx 2.5$–$3.0\ \mu_B$ per atom
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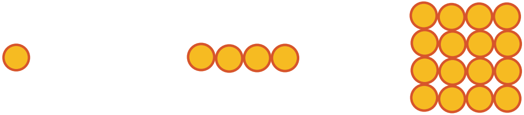
Magnetism of iron: summary



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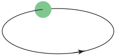	$\mu_{\text{orb}} = 2\ \mu_B$	$\mu_{\text{orb}} = 0.07\text{–}0.12\ \mu_B$	$\mu_{\text{orb}} = 0.05\ \mu_B$

(clusters go in between)

Properties of clusters should display traces of surface and bulk trends

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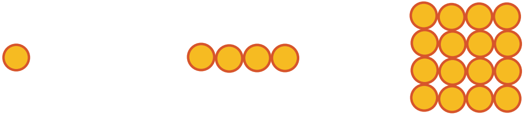

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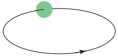	$\mu_{\text{orb}} = 2\ \mu_B$	$\mu_{\text{orb}} = 0.07–0.12\ \mu_B$	$\mu_{\text{orb}} = 0.05\ \mu_B$

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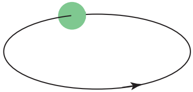
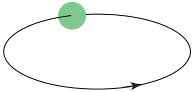
Why all the fuss with μ_{orb} ?



- μ_{orb} is small

Why all the fuss with $\mu_{\rm orb}$?



- $\mu_{\rm orb}$ is small *but important !*
  - It is a manifestation of spin-orbit coupling, which is the mechanism behind the magnetocrystalline anisotropy
  - Under certain assumptions, magnetocrystalline anisotropy energy (MAE) can be estimated as

$$\Delta E_{\mathrm{M}AE} \; = \; \text{const} \times \left(\boldsymbol{\mu}^{\parallel}_{\rm orb} \; - \; \boldsymbol{\mu}^{\perp}_{\rm orb} \right)$$

where $\boldsymbol{\mu}^{\parallel}_{\rm orb}$ and $\boldsymbol{\mu}^{\perp}_{\rm orb}$ are orbital magnetic moments for two perpendicular directions of the magnetization **M**

System we study

- Free spherical-like Fe clusters with geometry taken as if cut from a bulk *bcc* Fe crystal

System we study

- Free spherical-like Fe clusters with geometry taken as if cut from a bulk *bcc* Fe crystal
- Cluster size between 9 atoms (1 coordination shell) and 89 atoms (7 coordinations shells)

shells	atoms	radius [Å]
1	9	2.49
2	15	2.87
3	27	4.06
4	51	4.76
5	59	4.97
6	65	5.74
7	89	6.25

Lowering of symmetry

- Magnetization and spin-orbit coupling lower the symmetry of our systems
- Atoms belonging to the same coordination shell may be inequivalent
- Classes of equivalent atoms depend on the direction of magnetization **M**

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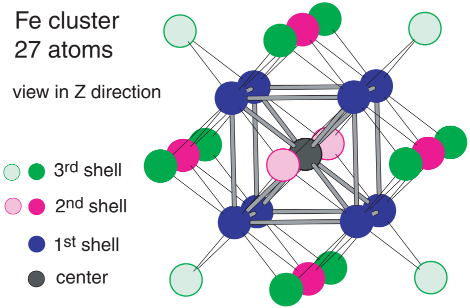

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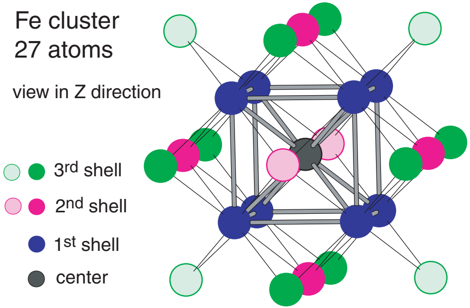

Theoretical formalism

- L(S)DA scheme
- cluster calculations done in real space via a fully-relativistic spin-polarized multiple-scattering technique
- crystal surfaces treated as 2D finite slabs (fully-relativistic spin-polarized TB-KKR method)
- spherical ASA approximation
- *empty spheres* put around the clusters in order to account for spilling of the electron charge into vacuum

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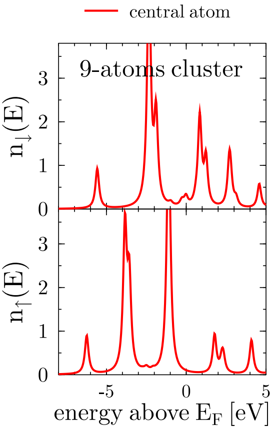
DOS in clusters and in bulk

- Atomic-like features present in DOS of clusters



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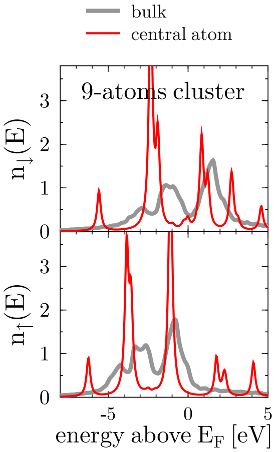

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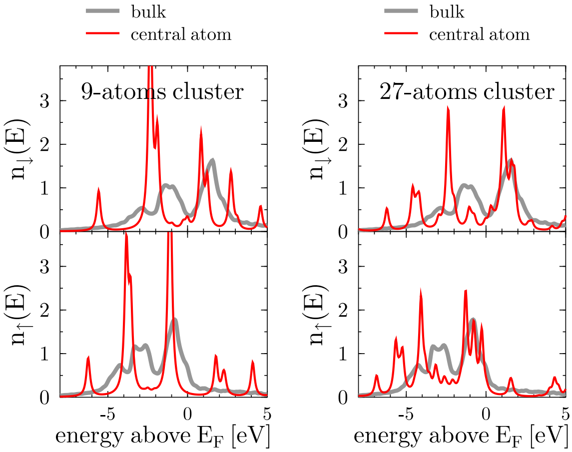
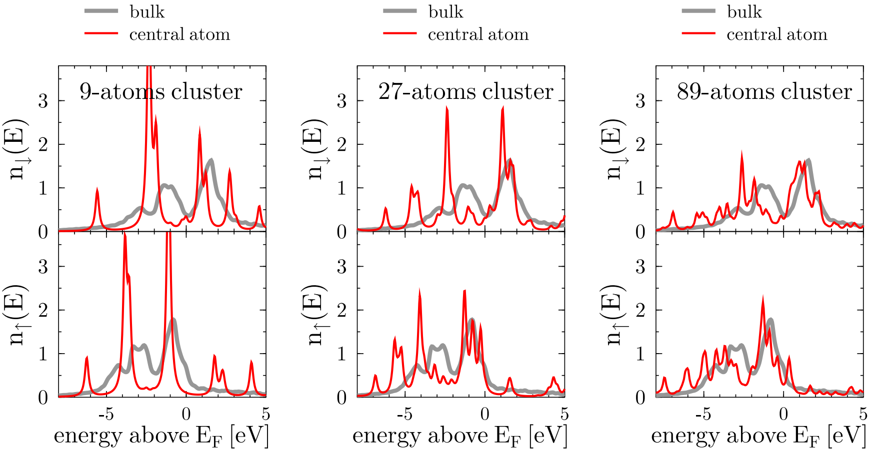


DOS in clusters and in bulk

- Atomic-like features present in DOS of clusters
- DOS in the center of clusters approaches the bulk quite slowly



Magnetic profiles of clusters

What do we mean by that

Local magnetic moments:

μ_{spin} and μ_{orb} can be attributed to individual sites

Magnetic profiles of clusters

What do we mean by that

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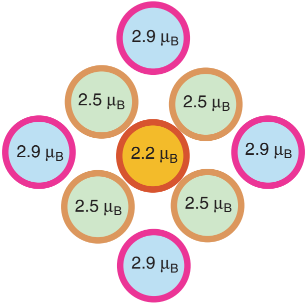

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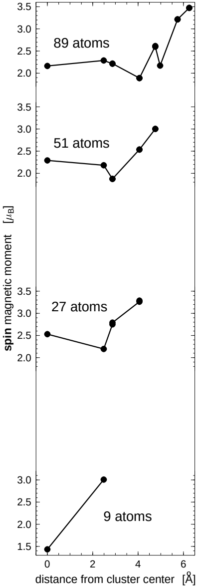
Free Fe clusters: magnetic profiles

- Enhancements and oscillations all around
- μ_{spin} does not depend on the direction of **M**
- μ_{orb} depends on the direction of **M**
  - for *inequivalent atoms* of the same coordination sphere μ_{orb} differs
- μ_{orb} averaged over coordination spheres does not depend on the direction of **M**



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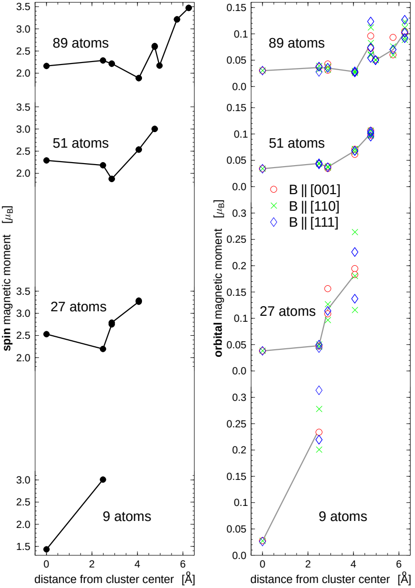

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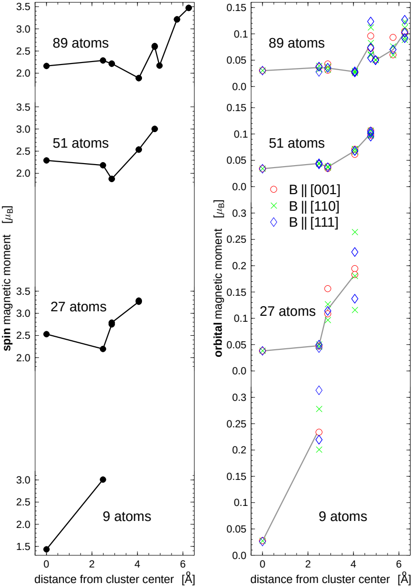

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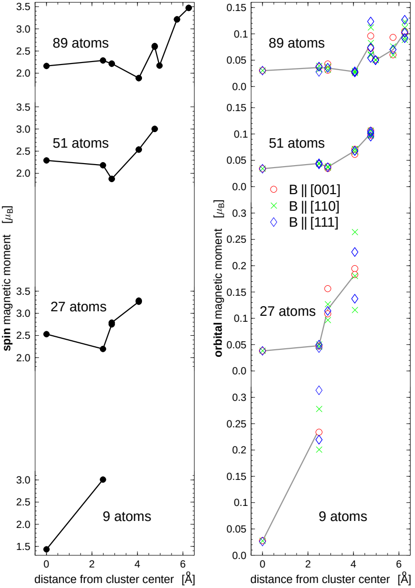
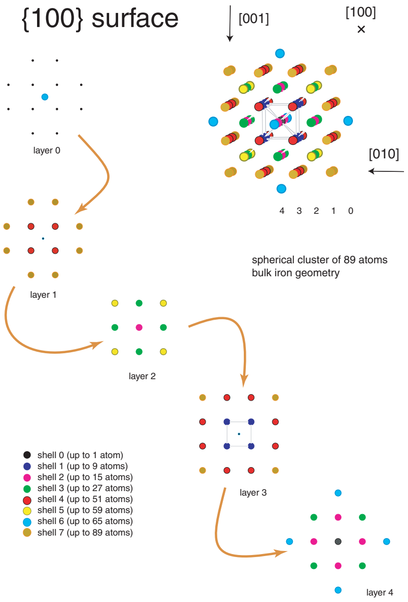


Clusters vers. surfaces: HOWTO

- take free iron cluster of 89 atoms
- drill a hole into this cluster
- inspect μ_{spin} and μ_{orb} around you and compare them with what you see beneath a crystal surface
- explore various "crystallographic directions"



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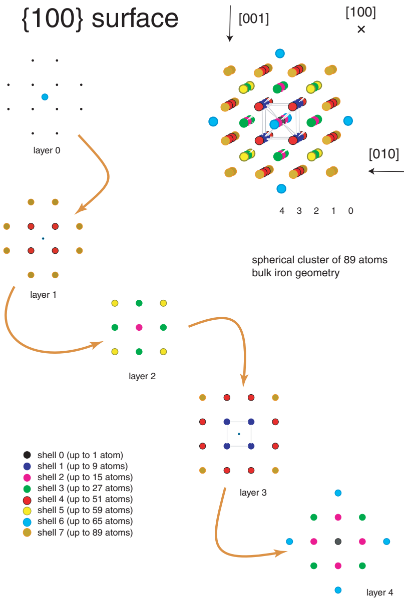

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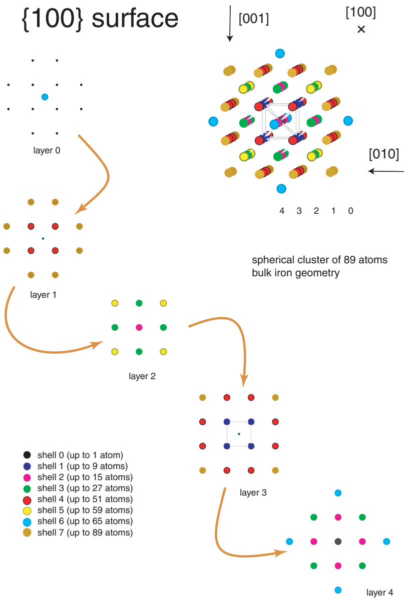

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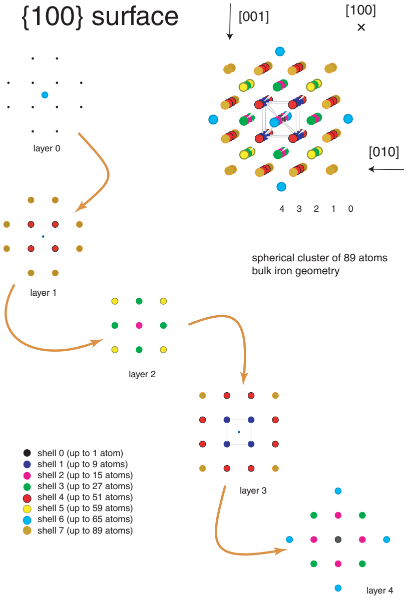

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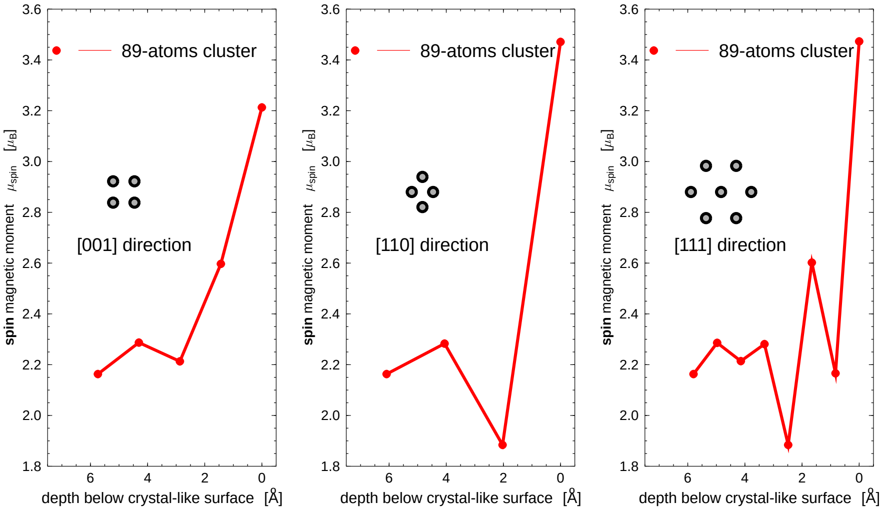

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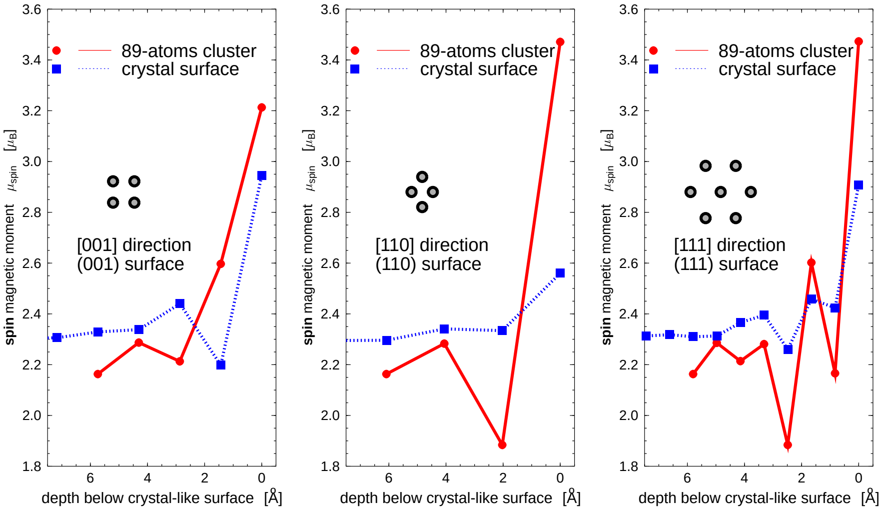

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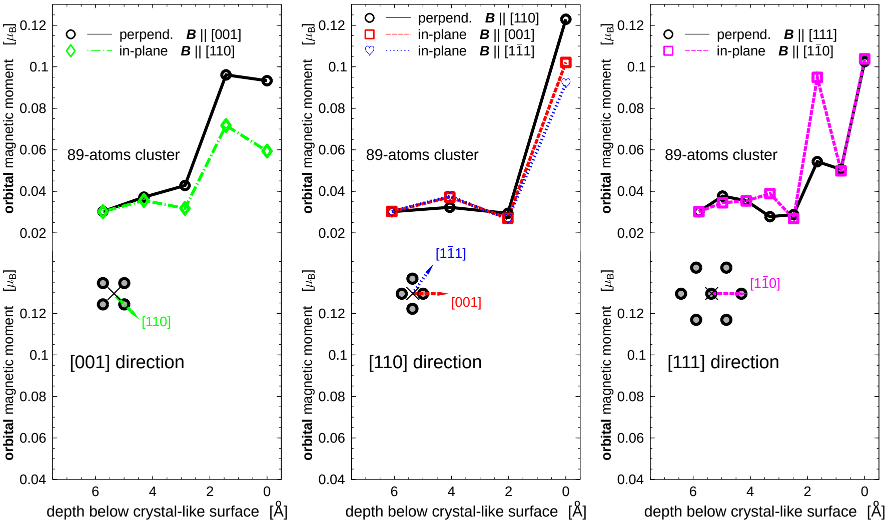

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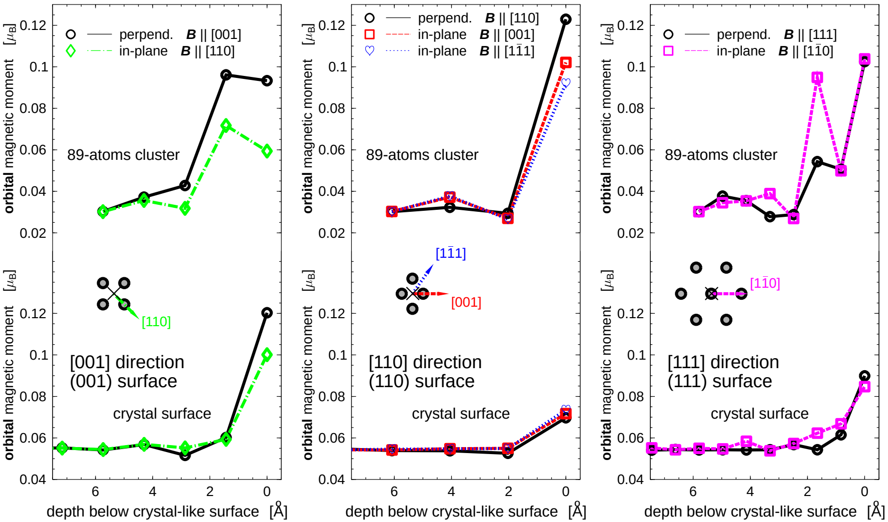

Dependence of $\mu_{\rm spin}$ on $N_{\rm eff}$

Effective coordination number:
for a *bcc* crystal one defines

$$N_{\rm eff} = N_1 + 0.25 \times N_2,$$

where N_1 is number of 1^{st} neighbors and N_2 is number of 2^{nd} neighbors.

[D. Tománek *et al.* (1983); J. Zhao *et al.* (1995)]

For orbital moment $\mu_{\rm orb}$, a similar dependence can be observed but with much larger "fluctuations".

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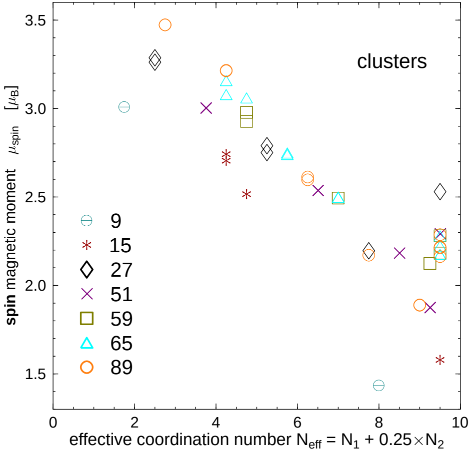

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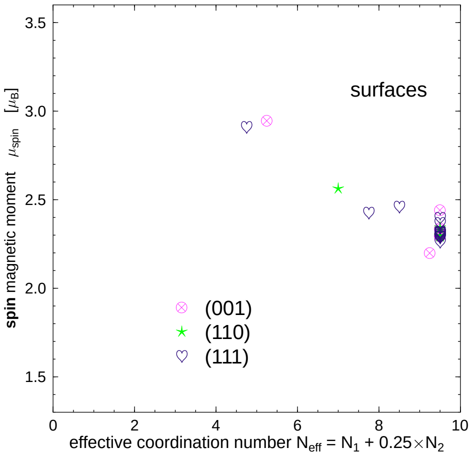

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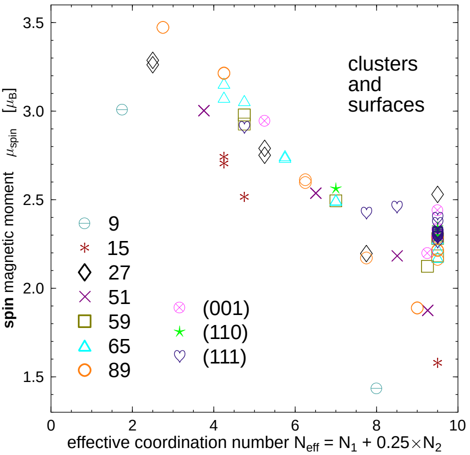

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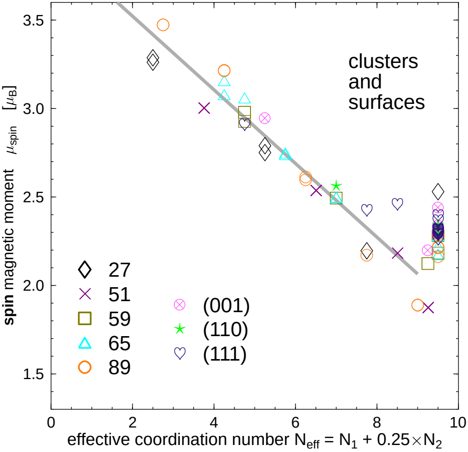

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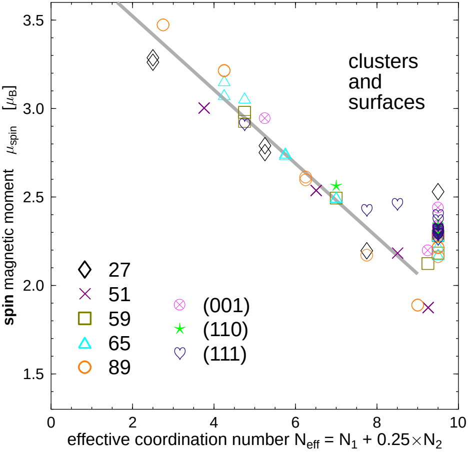

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Magnetism free clusters: summary

- In free clusters, $\mu_{\rm spin}$ and $\mu_{\rm orb}$ are enhanced at atoms close to the cluster surface
- Oscillations both in $\mu_{\rm spin}$ and in $\mu_{\rm orb}$ are a general feature of magnetic profiles.
  These oscillations are more pronounced in clusters than at crystal surfaces.
- $\mu_{\rm orb}$ at *individual* atoms strongly depends on the direction of **M**
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Magnetism of free and supported clusters

Free and supported clusters

- 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

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Calculational procedure for supported clusters

Impurity Green function method

- Calculate electronic structure of the "host" system (clean surface)
  - Tight-binding or screened KKR
- Supported clusters are treated as a perturbation to the clean surface and the
  - Green's function of the new system (cluster plus substrate) is obtained by solving the Dyson equation.
- Atomic sphere approximation (ASA), $\ell_{\max}=2$
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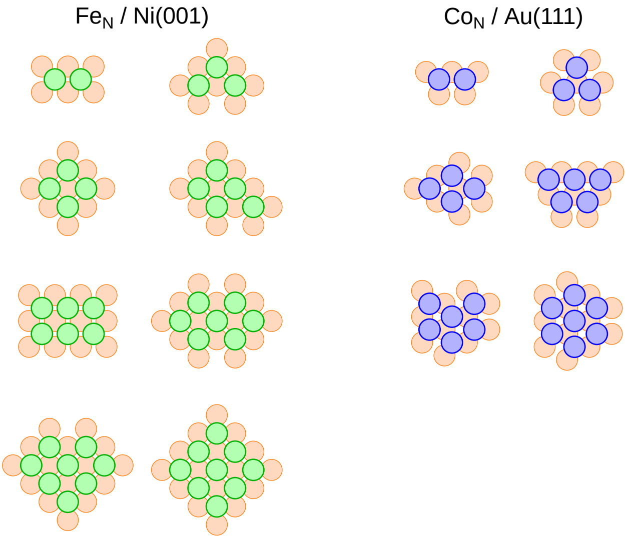
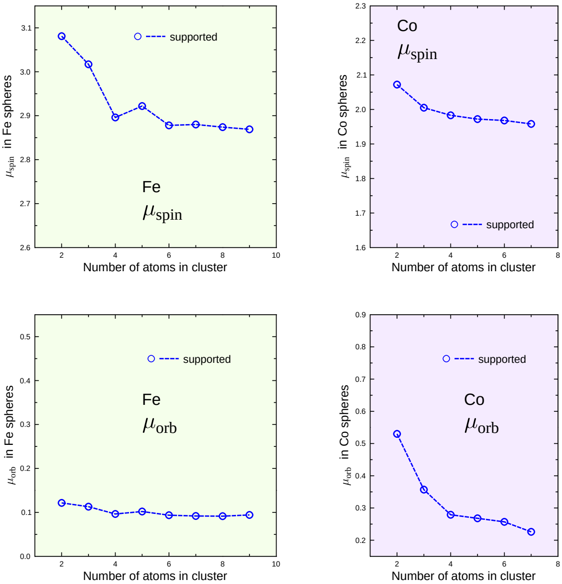
Shapes of clusters (free or supported)



Only nearest-neighbor substrate atoms are shown.

Average magnetic moments



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

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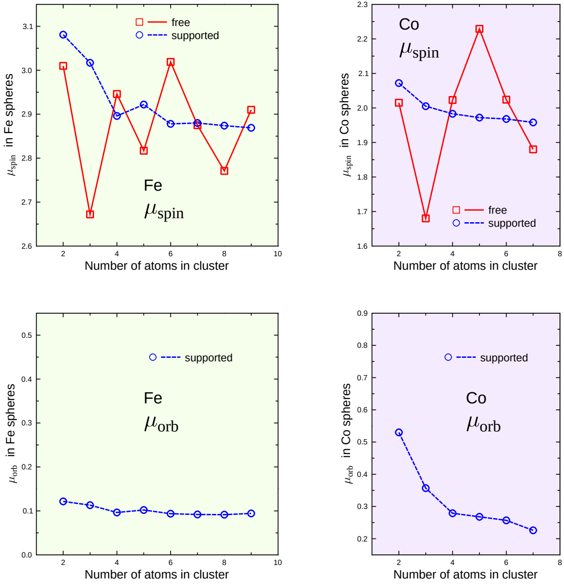

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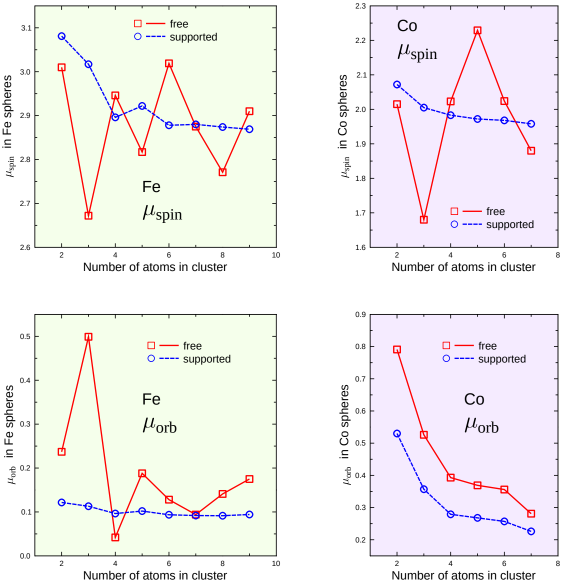

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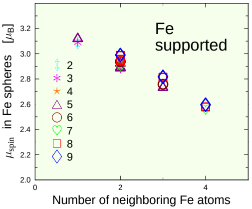
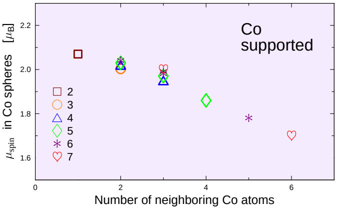
- μ_{orb} of free Co clusters does not follow the herd

Effect of coordination on μ_{spin}





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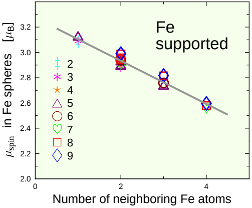

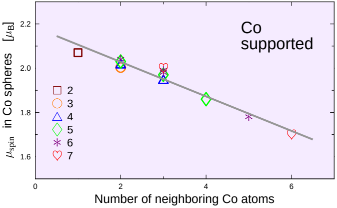

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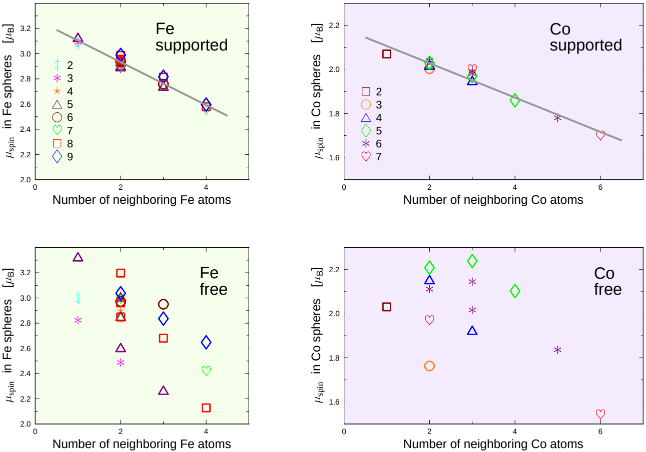

- μ_{spin} decreases if coordination number increases
- Big scatter around the linear dependence for small planar free clusters

Comparison between free and supported clusters: summary

- Substrate acts as an adult supervisor for the free clusters
  - It suppresses the tendency of magnetic moments to oscillate with cluster size
- It makes μ_{spin} to depend linearly on the coordination number
  - For free clusters, this trend appears only for spherical and/or larger clusters

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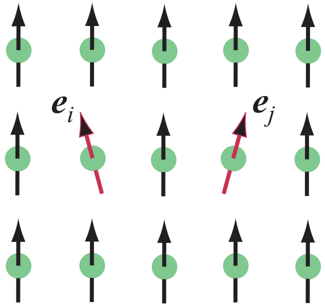
Magnetism of clusters for $T \neq 0$

Finite temperature magnetism

For localized moments, finite temperature magnetism can be described by a classical Heisenberg hamiltonian

$$H_{\mathrm{eff}} = -\sum_{i \neq j} J_{ij}\, \mathsf{e}_i \cdot \mathsf{e}_j$$



Mapping DFT onto Heisenberg

Comparing energy associated with infinitesimal rotations of local magnetic moments $\Longrightarrow$

$$J_{ij} = -\frac{1}{4\pi} \mathrm{Im} \int^{E_F} \mathrm{d}E \, \mathrm{Tr} \left[(t_{i\uparrow}^{-1} - t_{i\downarrow}^{-1}) \, \tau_{\uparrow}^{ij} \, (t_{j\uparrow}^{-1} - t_{j\downarrow}^{-1}) \, \tau_{\downarrow}^{ji} \right]$$

[Liechtenstein *et al.* (1986)]

Valid only if magnetism can be described by localized magnetic moments (fine for Fe)

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From J_{ij} to $M(T)$

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$$M(T) = \frac{\sum_k M_k \, \exp(-\frac{E_k}{k_B T})}{\sum_k \exp(-\frac{E_k}{k_B T})}$$

M_k is the magnetization of the system for a particular configuration k of the directions of spins

E_k is the energy of configuration k

- Practical evaluation: Monte Carlo method with the importance sampling Metropolis algorithm

- For bulk Fe, this procedure yields finite-temperature results that are in a good agreement with experiment [Pajda *et al.* (2001)]

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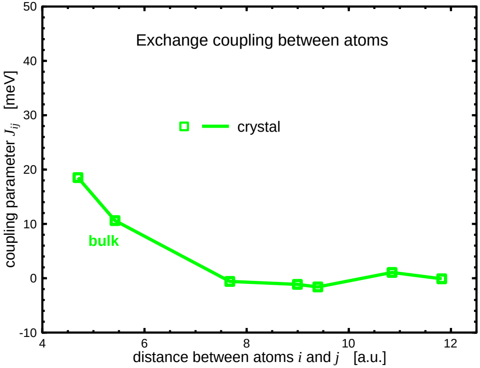
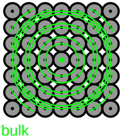
J_{ij} in bulk and in clusters

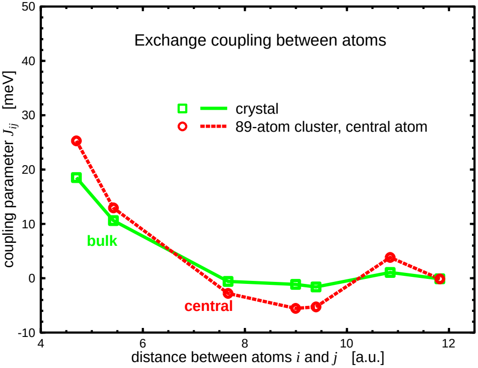


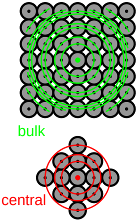


Atom i is fixed, atom j scans coordination shells around i

- Oscillatory decay of J_{ij} with distance
- J_{ij} for a given distance differs a lot between clusters and crystals

J_{ij} in bulk and in clusters





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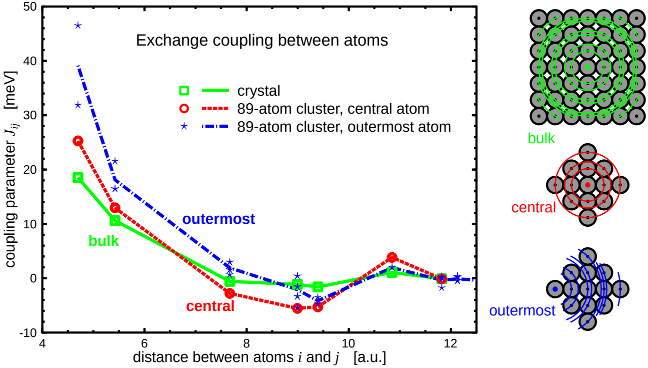

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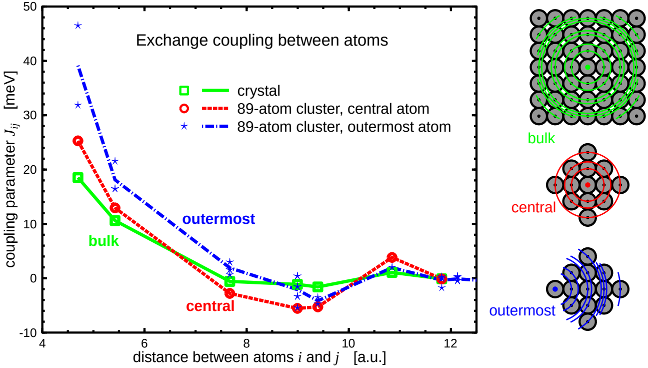

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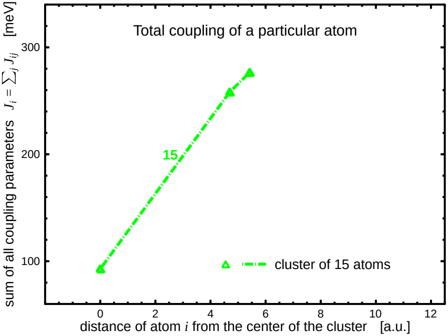
Site-dependence of $\sum_j J_{ij}$

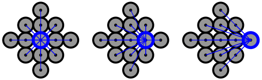
Total strength with which one spin (at site i) is held in its direction:

Energy needed to flip the spin of atom i while keeping all the remaining spins collinear:

$$J_i = \sum_{j \neq i} J_{ij}$$

Site-dependence of $\sum_j J_{ij}$





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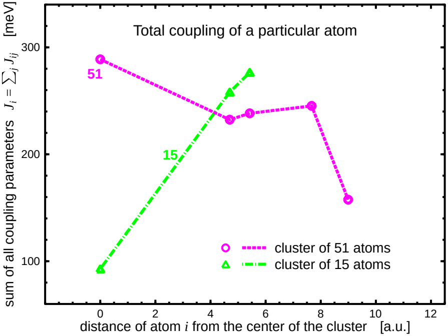

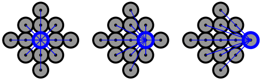

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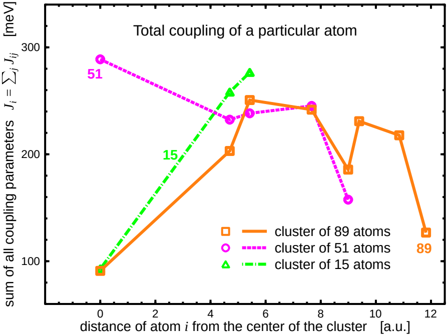

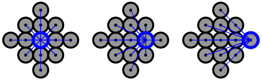

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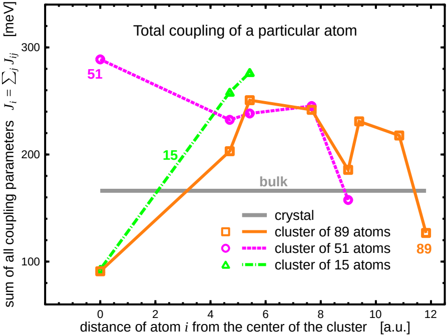

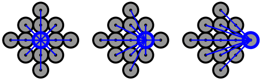

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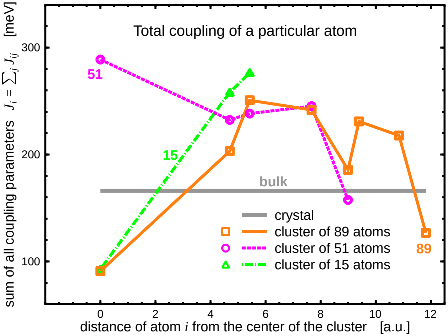

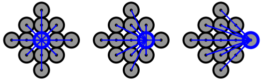

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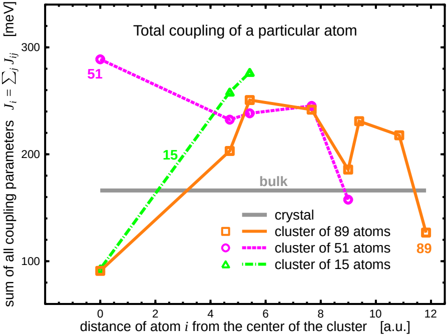

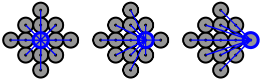

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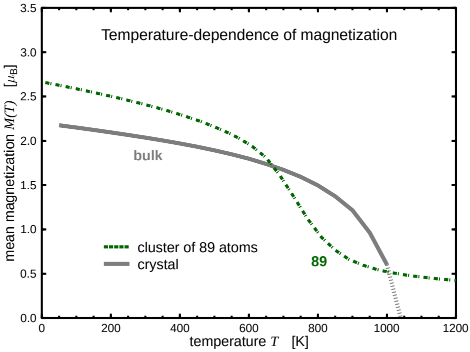
Decay of magnetization with T



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- $M(T)$ curves are more shallow in clusters than in bulk

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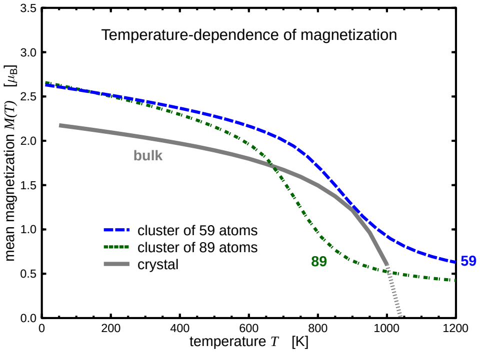

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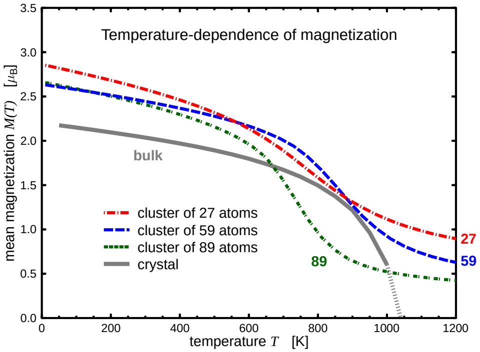

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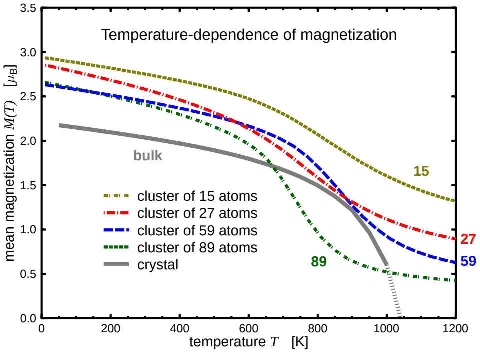

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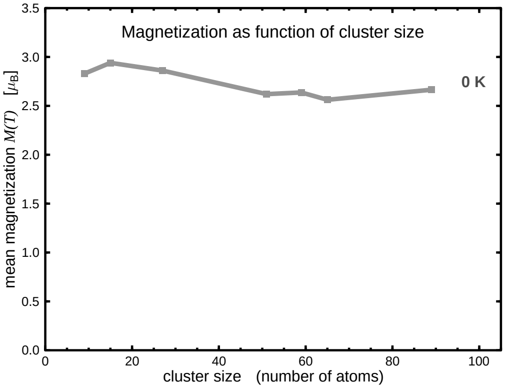

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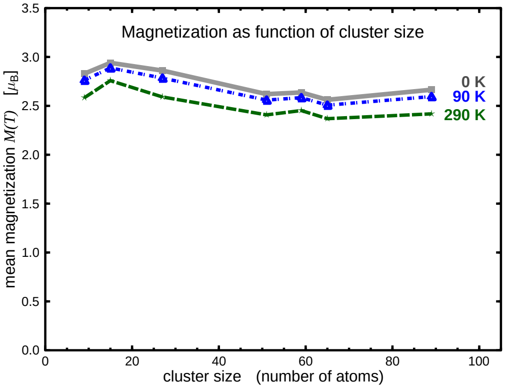

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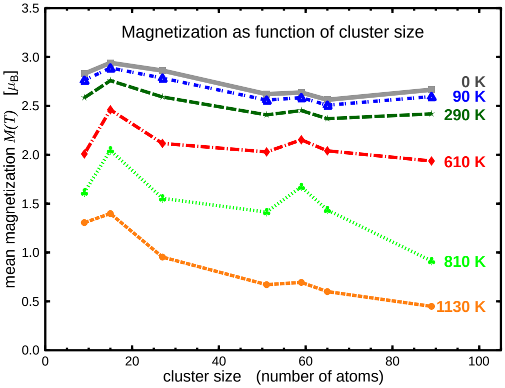
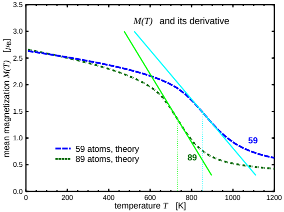


- Dependence of M on cluster size does not really vary with T for low ("experimental") temperatures
- For large T, magnetization of large clusters is significantly reduced

Dependence of T_c on cluster size



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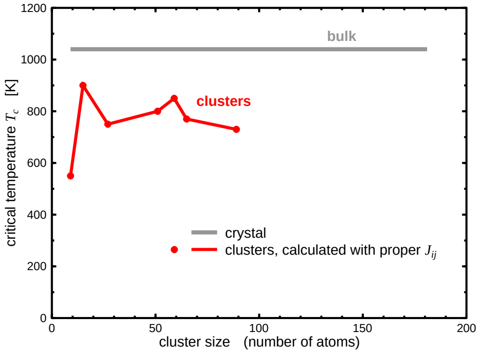

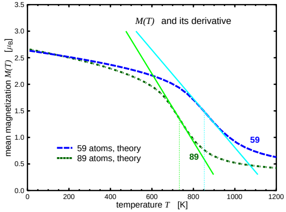

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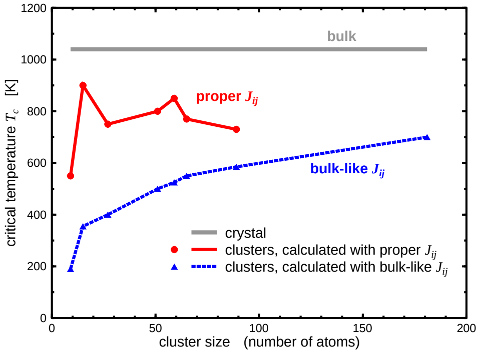

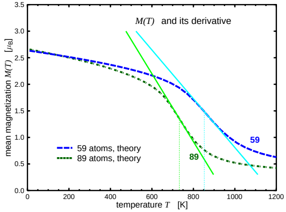

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- T_c oscillates with cluster size
- Proper cluster-adjusted J_{ij} have to be taken into account

Shell-resolved magnetization

Expectations:

outer shells have smaller coordination numbers than inner shells

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$\Rightarrow$ M in outer shells should decay more quickly with T than M of inner shells

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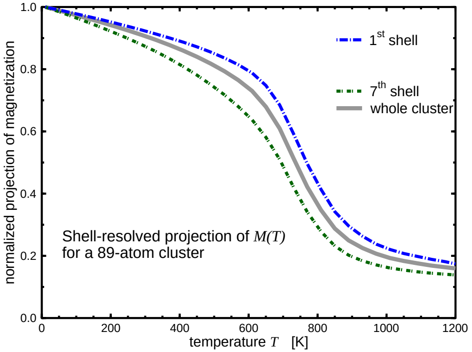

Projecting M of a shell onto the direction of the total M of the 89-atom cluster

(Projections are normalized to $T = 0$)

- Not monotonous in order of shells
- Although M of outer shells *usually* decays faster than M of inner shells, no systematics can be found.

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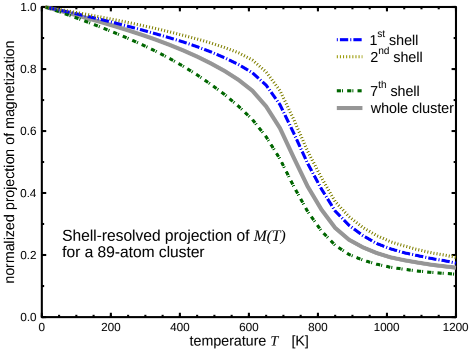

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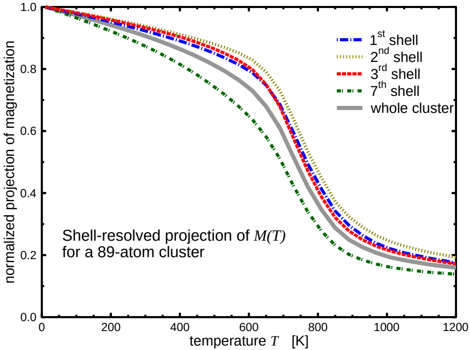

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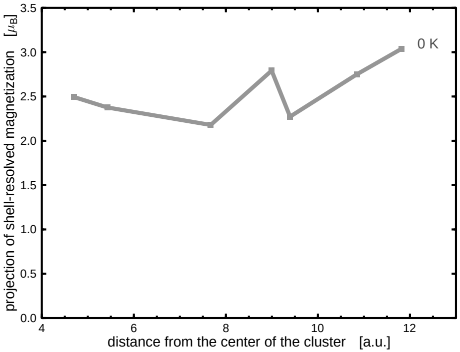

Cluster of 89 atoms
(7 coordination shells)

- Magnetic profile gets more flat if temperature increases
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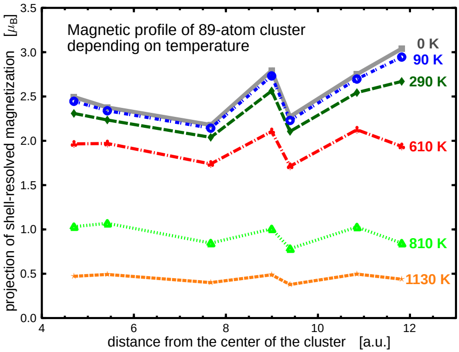

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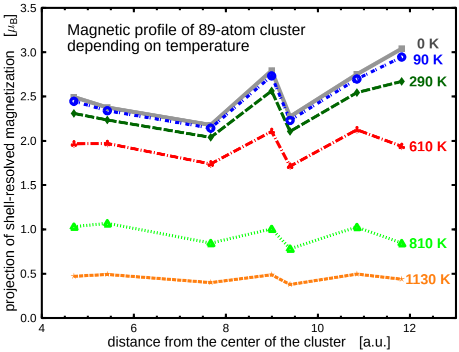

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Further reading:
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X-ray absorption spectroscopy of clusters

X-ray absorption spectroscopy HOWTO

- 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
- By tuning the energy of incoming x-rays, electrons from one core level only participate
  - Chemical selectivity
- Dipole selection rule
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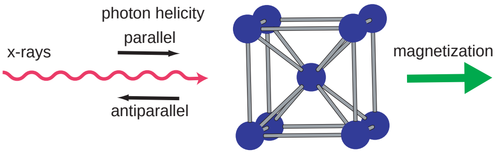

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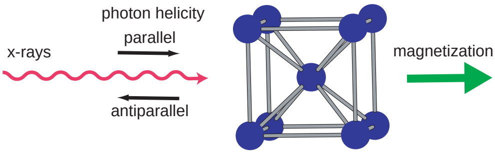

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What can XMCD do for us?

- XMCD spectroscopy probes the magnetic properties of materials
- Through the sum rules, XMCD can inform about $\mu_{\rm spin}$ and $\mu_{\rm orb}$ separately
  - $L_{2,3}$ edge: sum rules give access to the d components of $\mu_{\rm spin}$ and $\mu_{\rm orb}$ (for transition metals, that's what we want)
  - K edge: sum rule gives access to the p component of $\mu_{\rm orb}$
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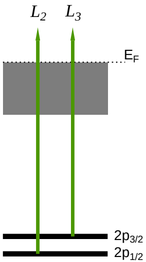
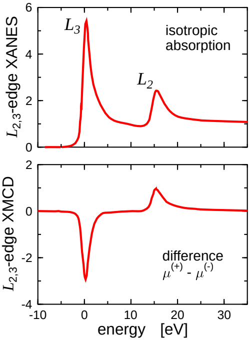
$L_{2,3}$ edge of magnetic TM systems





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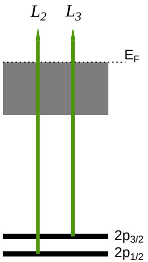

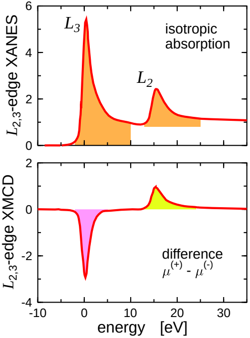

XMCD sum rules:

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

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

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

Some more details

- Spectrum of cluster is a superposition of spectra at edges of individual atoms
- The spectra do not depend on the direction of **M**
  - magnetic anisotropy in bcc-like Fe clusters is practically negligible
  - average of μ_{orb} over all atoms does not depend on **M** either
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$L_{2,3}$ edge XAS of clusters

- No significant variation with cluster size
  - Fine structure just after the L_3 white line — presence of truly discrete states (vaccum level is 5–8 eV above E_F)
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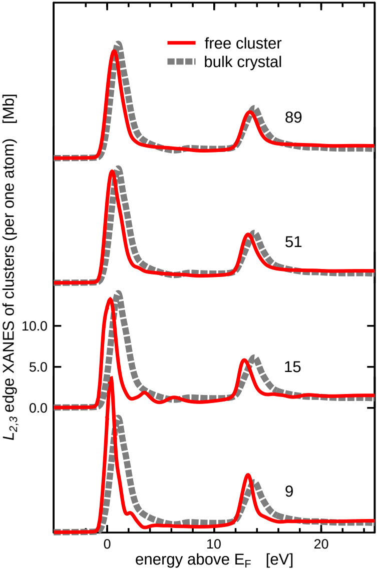

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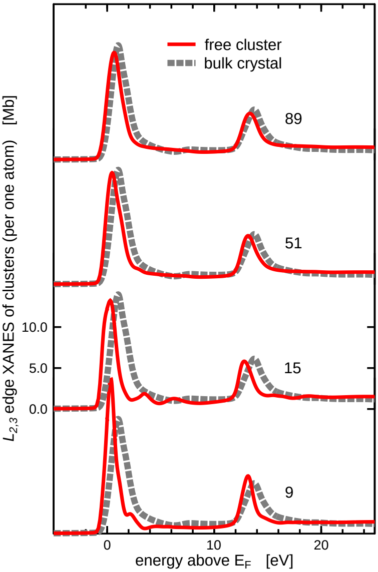

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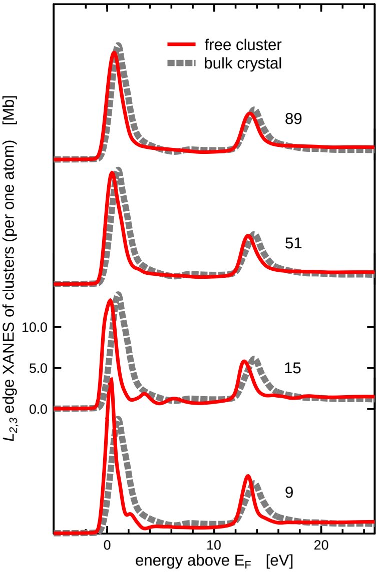

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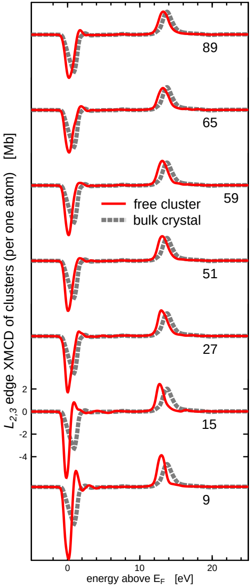

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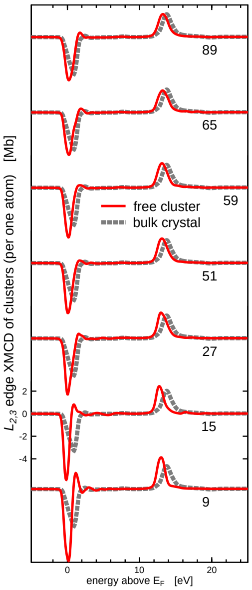

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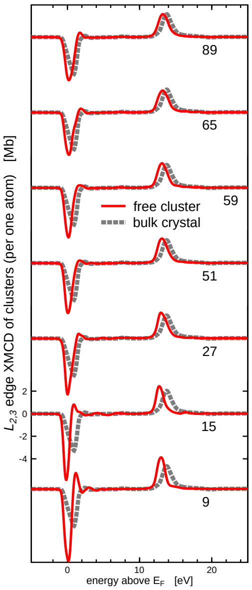

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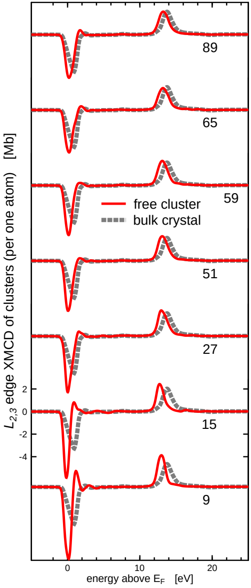
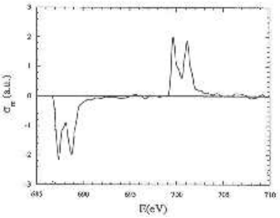
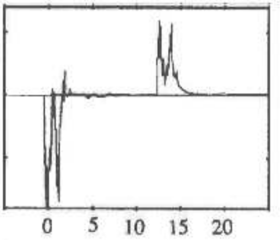




Fe(001) surface

[Wu et al. PRL 71, 3581 (1993)]



Fe_2Cu_6 (001) multilayer

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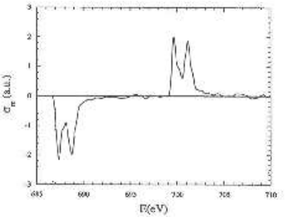

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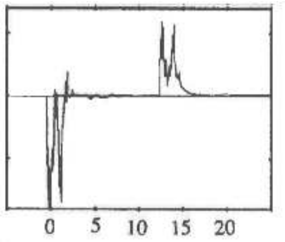

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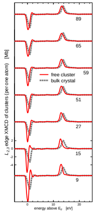

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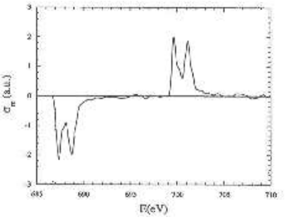

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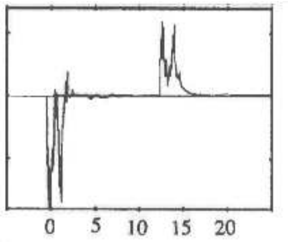

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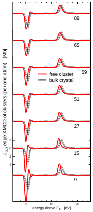

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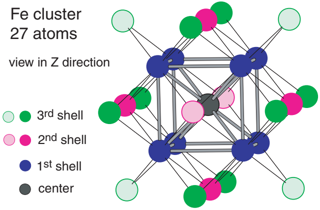
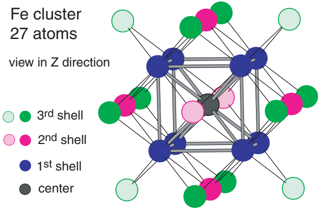


Spectrum of the whole cluster is a superposition of signals from all individual atoms



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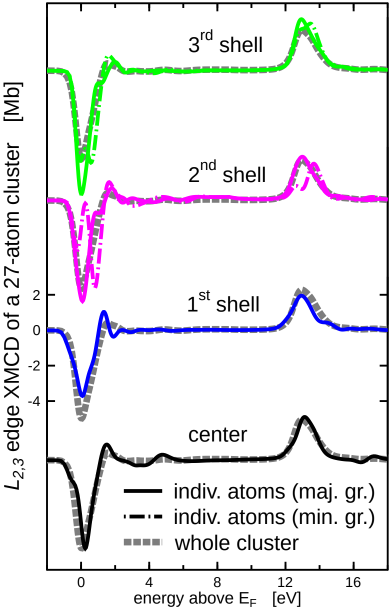
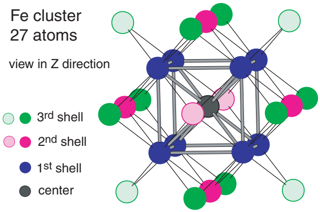


The wiggles in XMCD mutually cancel !



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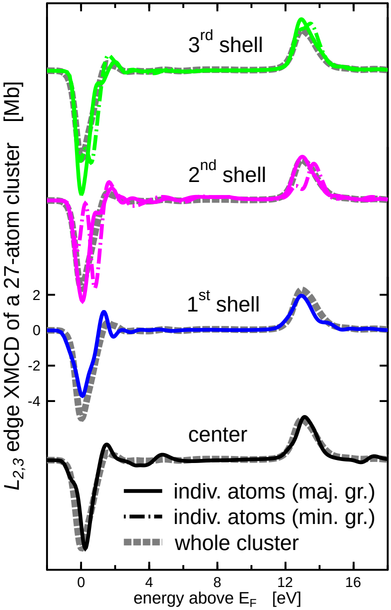
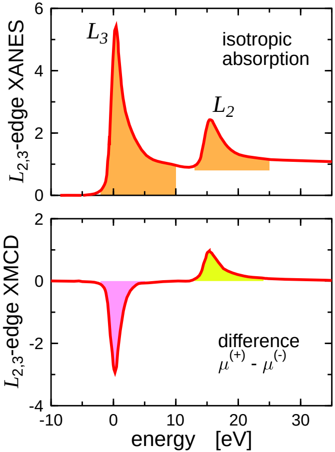


Sum rules can be checked



- Calculate the spectra theoretically
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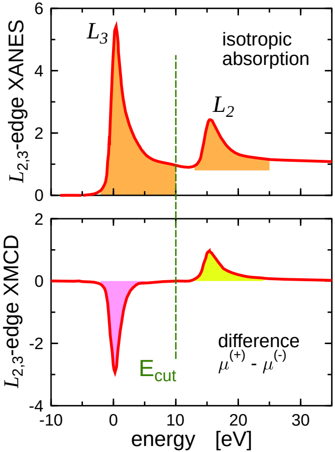

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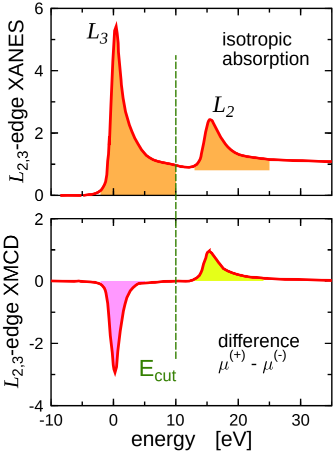

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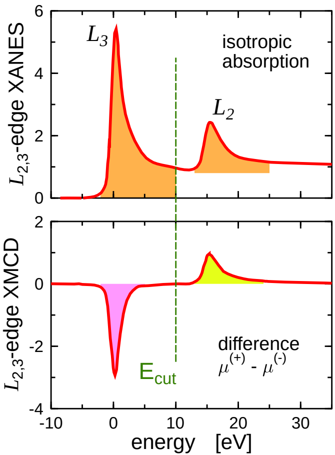

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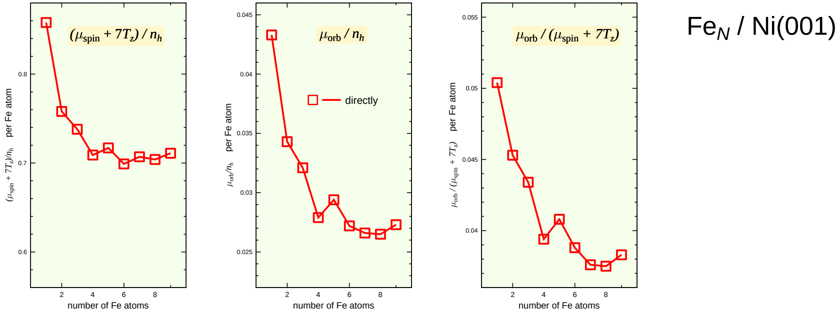

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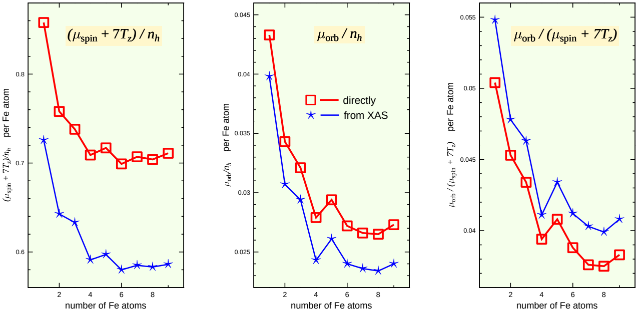

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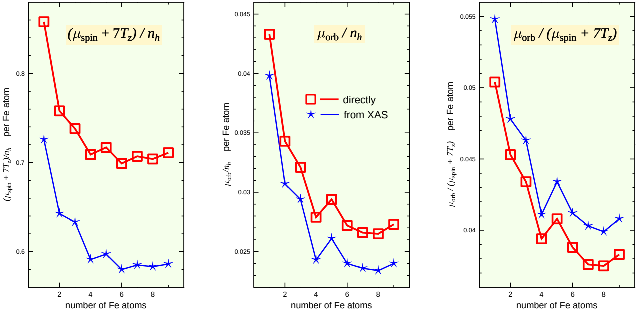

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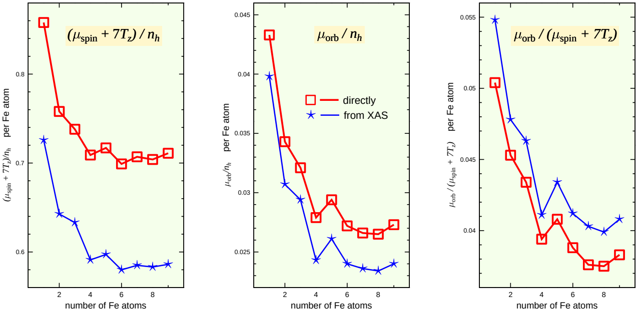

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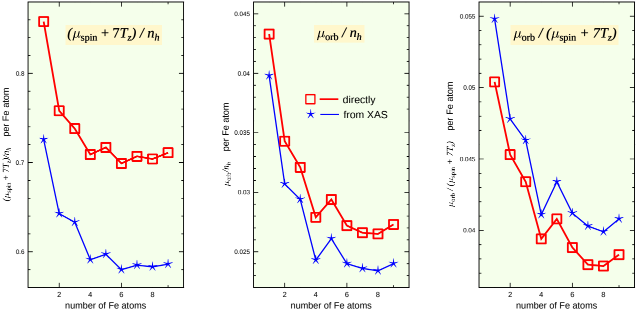

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