Spin-fluctuations, theory and planned application to nanostructures

16. April 2014 | Julen Ibañez Azpiroz

Samir Lounis, Manuel dos Santos Dias, Stefan Blügel

Outline

- Motivation
- Introduction: localized vs itinerant electron magnets
- Spin-fluctuations
    - Phenomenological approach
    - Gaussian statistics
    - Zero-point spin-fluctuations
- Goal of the project: calculation of spin-fluctuations in nanostructures
- Conclusions

Motivation

- How well does DFT (+LDA) describe the ground state magnetic properties?

  ✔ Fair description of several systems such as 3-d ferromagnets, Fe, Co; magnetic compounds of transition metals FeNi, NiCr, CoMn,; ...

  ✗ Contradiction with experiments for weak itinerant electron magnets:

Magnetic moments:

	DFT	Experiments
MnSi	0.68	0.27
Ni_3Al	0.7	0.23
$ZrZn_2$	0.5	0.2

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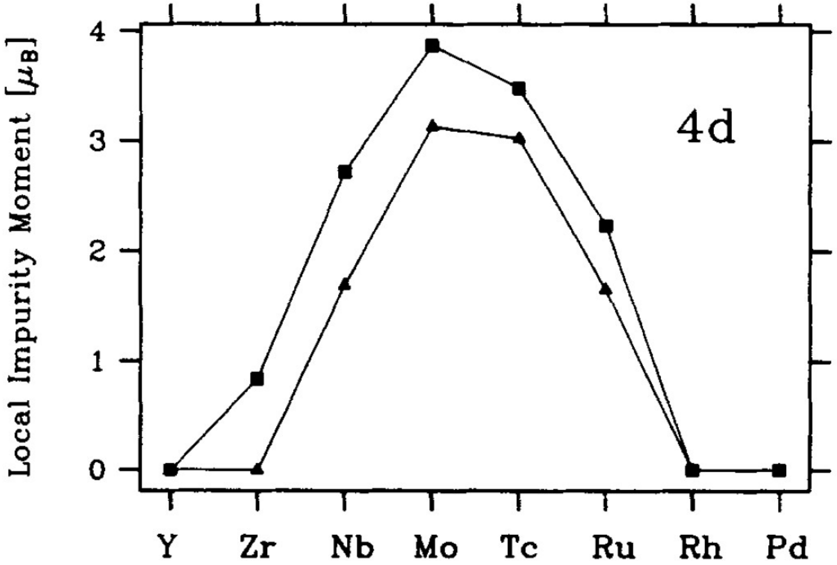
- The DFT (+LDA) description of magnetism is at a mean field level, and **neglects fluctuations:** tendency to overestimate magnetism
- Evidence for large effects of **spin-fluctuations:**
  - Measurements of spin-fluctuations of the **order of Bohr magneton** in $Y_{0.93}Sc_{0.07}Mn_2$ [Shiga etal, JPSP **57**, 3141 (1988)]
  - Spin-fluctuations in Ni_3Ga destabilize the ferromagnetic ground state predicted by DFT [Aguayo etal, PRL **92**, 147201 (2004)]
  - Spin-fluctuations in Ni_3Al can correct the magnetic moment predicted by DFT [Ortenzi etal, PRB **86**, 064437 (2012)]

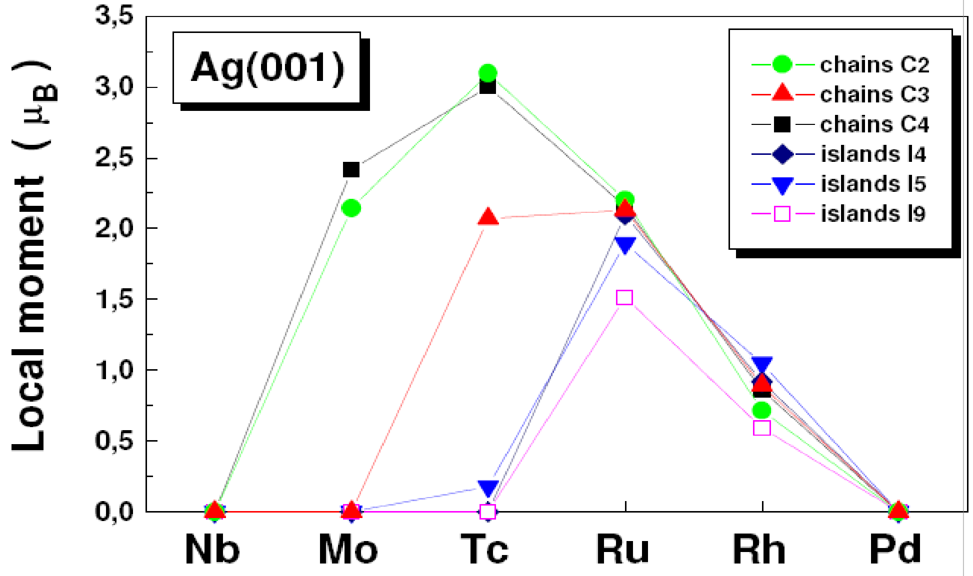
Motivation: nanostructures

Impurities on Ag(100)



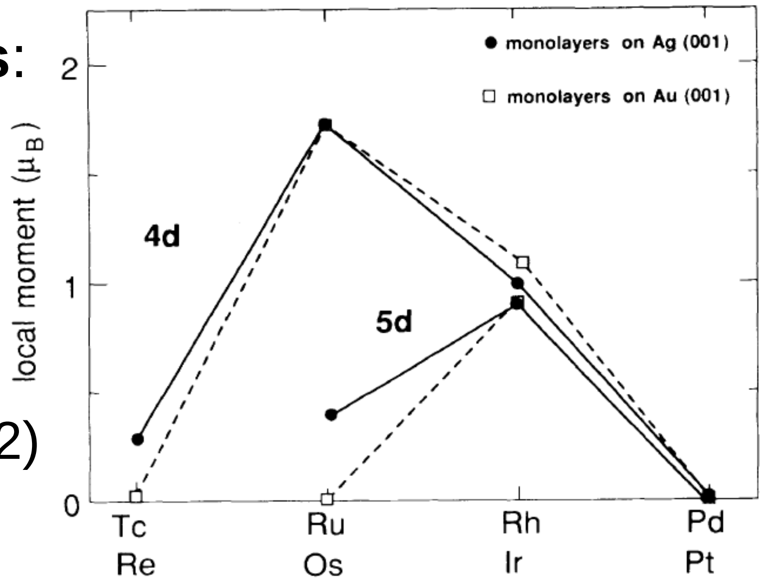
Lang, Stepanyuk, Wildberger, Zeller and Dederichs, SSC **92** 755 (1994)

Chains



Wildberger, Stepanyuk, Lang, Zeller and Dederichs, PRL **75** 509 (1995)

Monolayers:



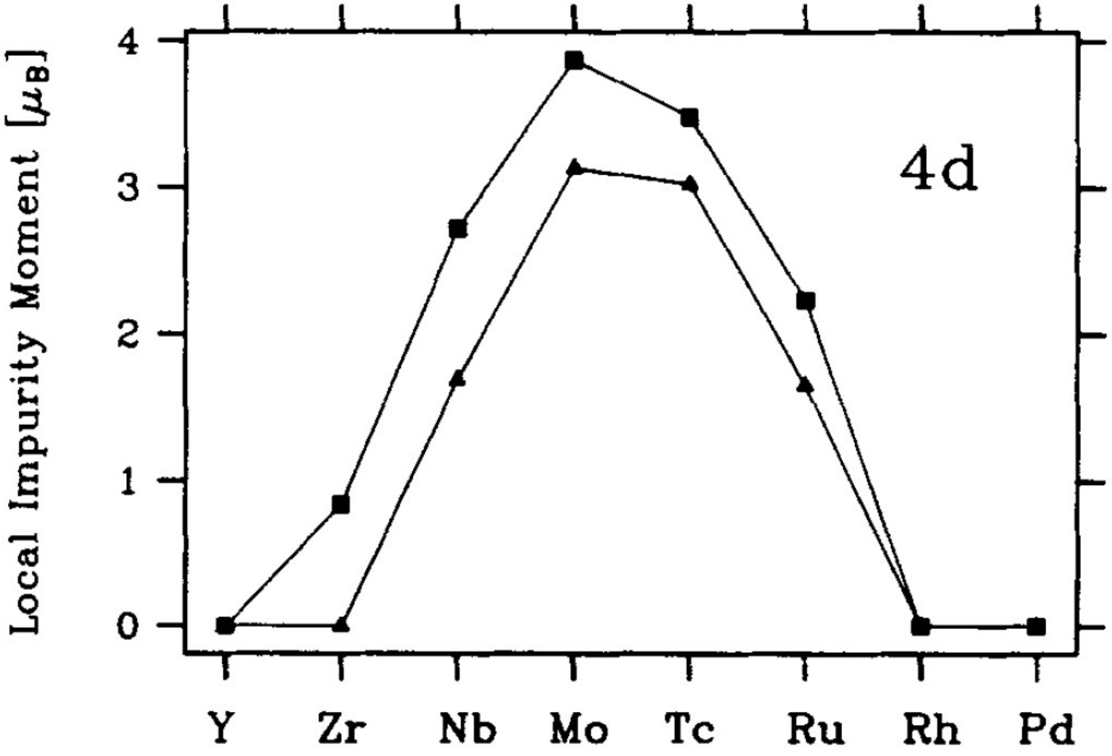
Blügel, PRL **68** 851 (1992)

Motivation: nanostructures

- Nanostructures on non-magnetic metallic substrates

- DFT predicts large local moments (Stoner criterion almost always fulfilled)

- Experimentally, no local moment has been found in these systems [see, for instance, Ru and Rh in Ag(100), Honolka etal, PRB **76**, 144412 (2007)]



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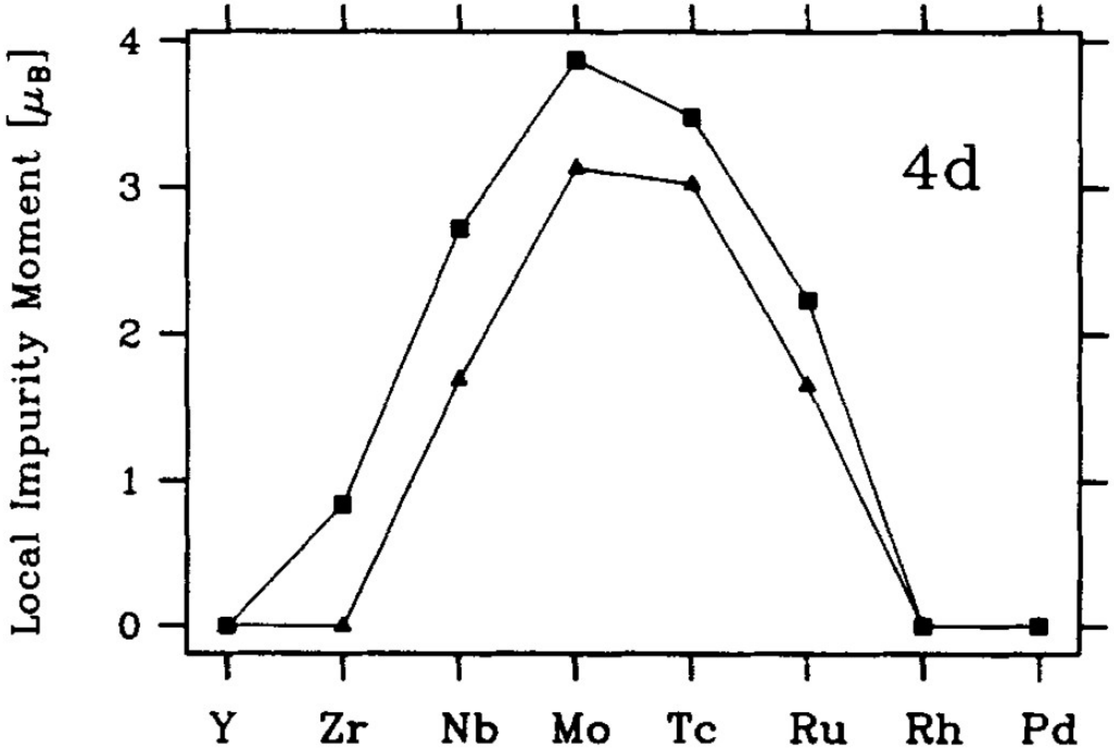

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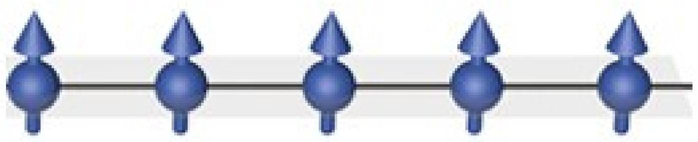
Can spin-fluctuations correct the local magnetic moments predicted by DFT?

Srivastaka etal, JPPM **18**, 9463 (2006)

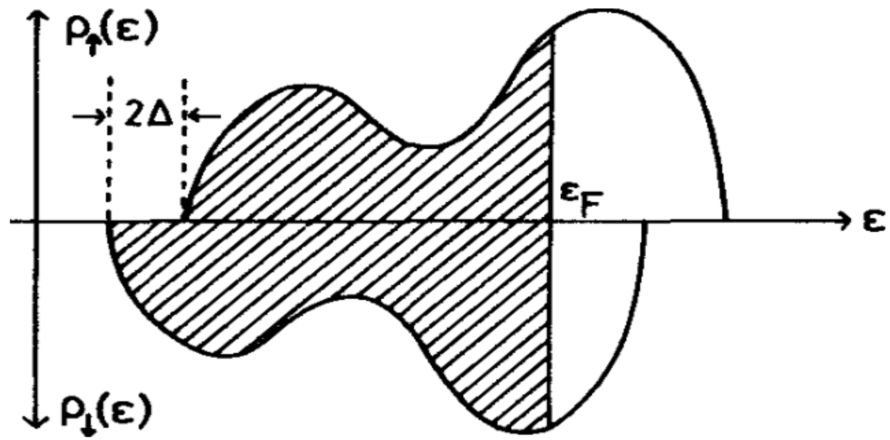
Introduction: opposite views of magnetism

Localized electrons



- Localized in real space
- Magnetic moment: **integer** value (Hund's rule)
- Examples: magnetic insulators, rare earth metals...

Itinerant electrons

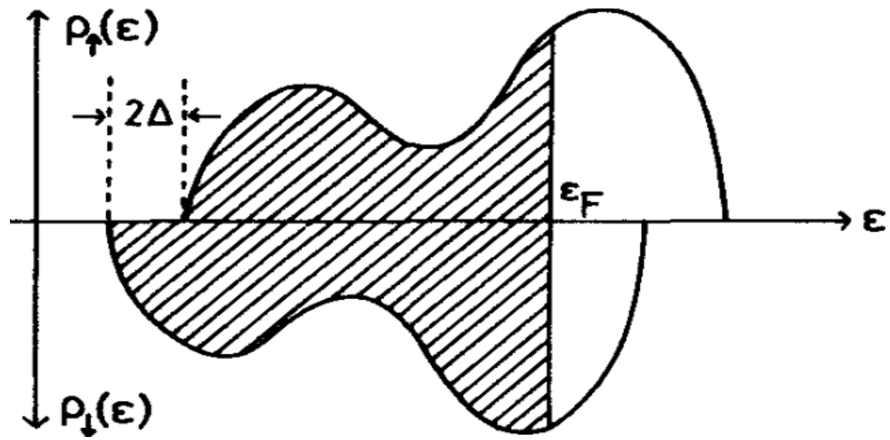


- Localized in momentum space
- Magnetic moment: **rational** value
- Examples: transition metals, weak ferromagnetic compounds...

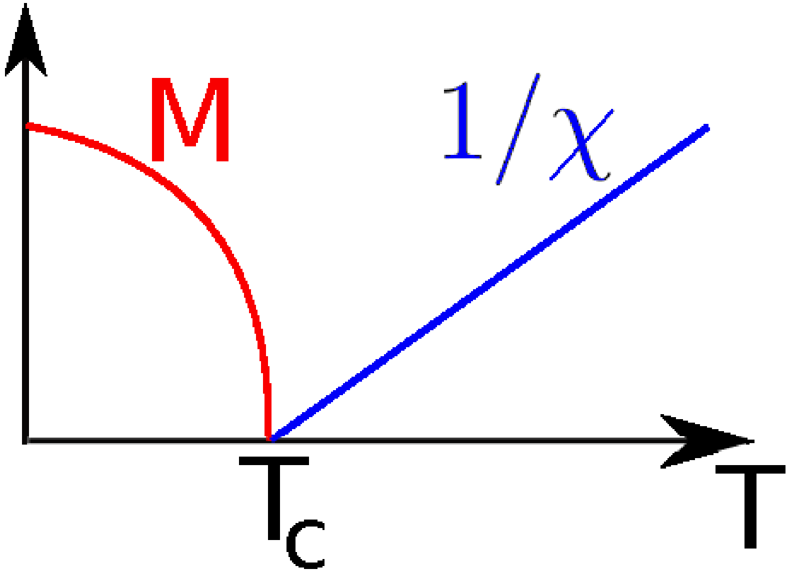
Introduction: opposite views of magnetism

Localized electrons

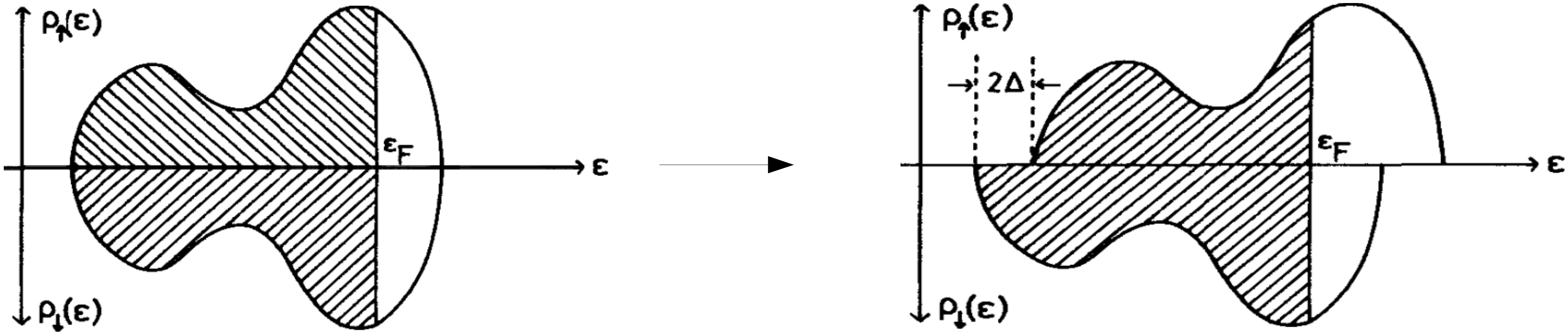
Itinerant electrons



- General common feature: temperature dependence of magnetic moment and inverse susceptibility



Stoner model



- Effects of exchange are treated within a molecular field term: $\mathbf{H} = \pm\Delta\hat{\mathbf{z}}$
- Magnetic susceptibility $\chi = \dfrac{\chi_0}{1 - I_s \rho(\epsilon_F)}$
- Criterion for magnetism provided: $I_s \rho(\epsilon_F) > 1$

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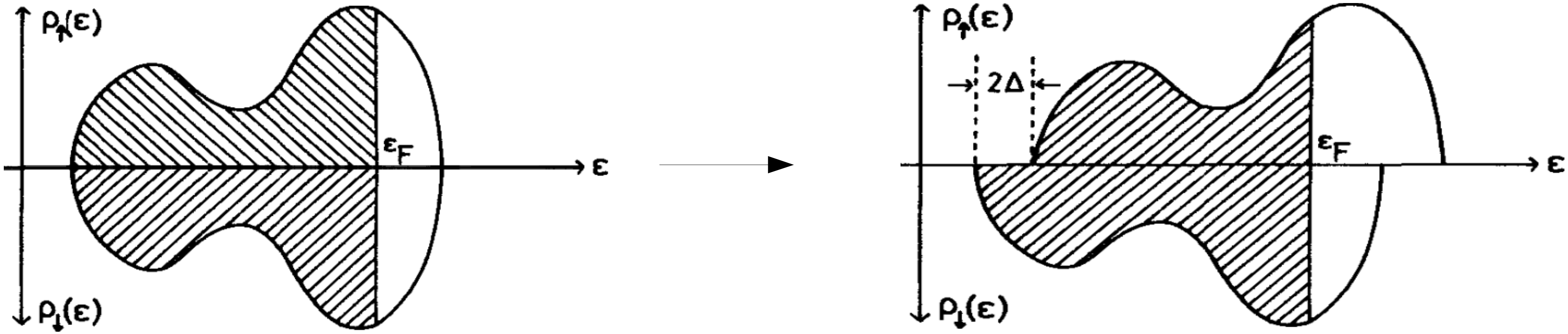

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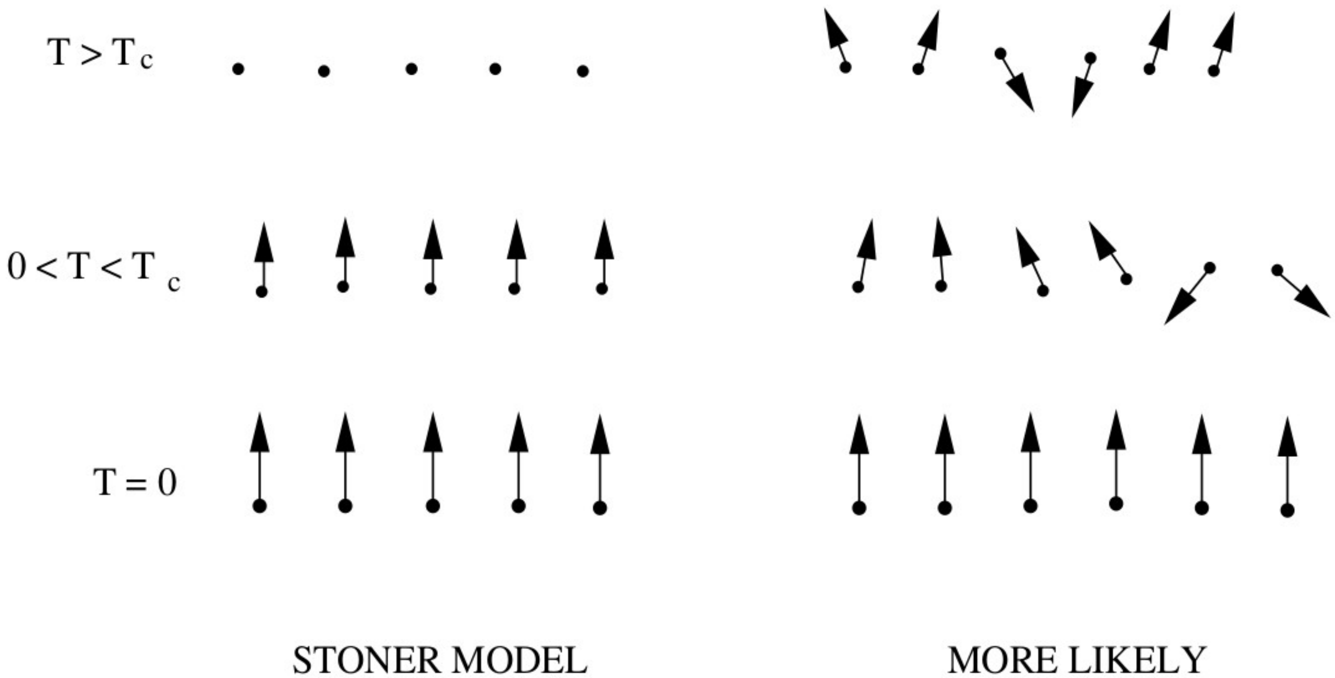
- Main drawback of Stoner theory: extension to **finite temperatures**
  - Temperature enters only through Fermi occupation factors: too weak temperature dependence
  - Wrong analytic behavior of temperature dependent variables as compared to experiments; in particular, **Curie-Weiss law not recovered**

Spin fluctuations

- Moriya and Kawabata, JPSJ **34** 639 (1973); Moriya, JMMM **14** 1 (1979)
- Murata and Doniach, PRL **29** 285 (1972)
- Shimizu, RPP **44** 329 (1981)
- Lonzarich and Taillefer, JPCCM **18** 4339 (1985)
- Mohn and Wohlfart, JPFMP **17** 2421 (1986)
- Takahashi, JPSJ **55** 3553 (1986)
- Solontsov and Wagner, PRB **51** 12410 (1994)
- ...



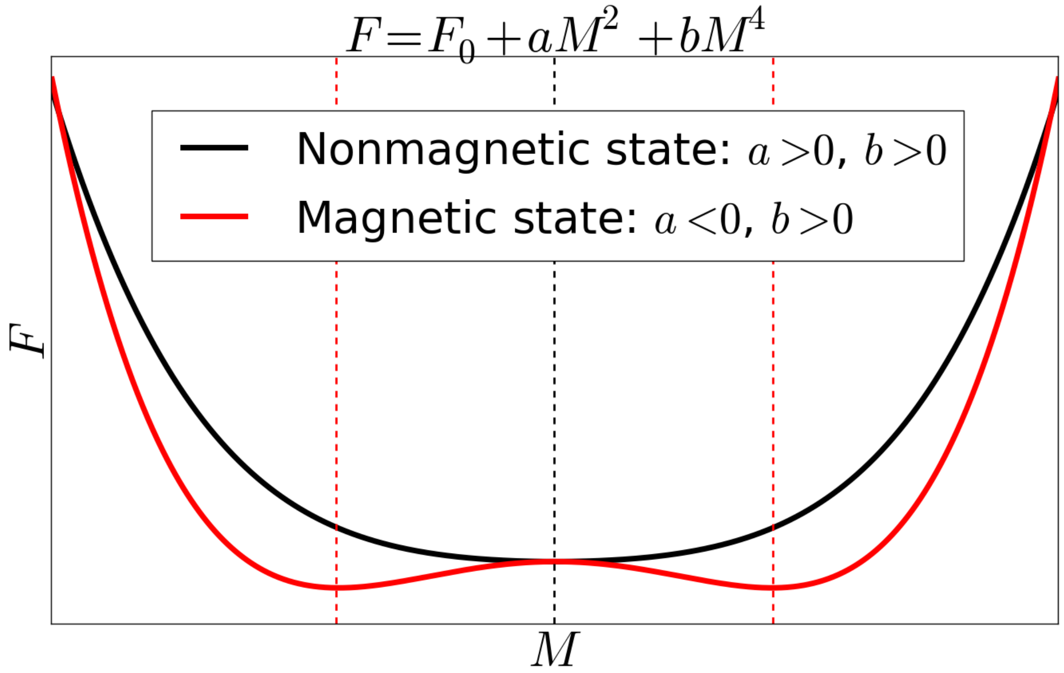
Spin fluctuations
Phenomenological approach

- Phenomenological Landau-Ginzburg method: expansion of free energy with magnetization as the order parameter

$$F = F_0 + aM^2 + bM^4 + \dots$$

With $a \propto \chi^{-1} \propto 1 - I_s \rho(\epsilon_F)$

Stoner criterion, $a < 0 \Leftrightarrow I_s \rho(\epsilon_F) > 1$



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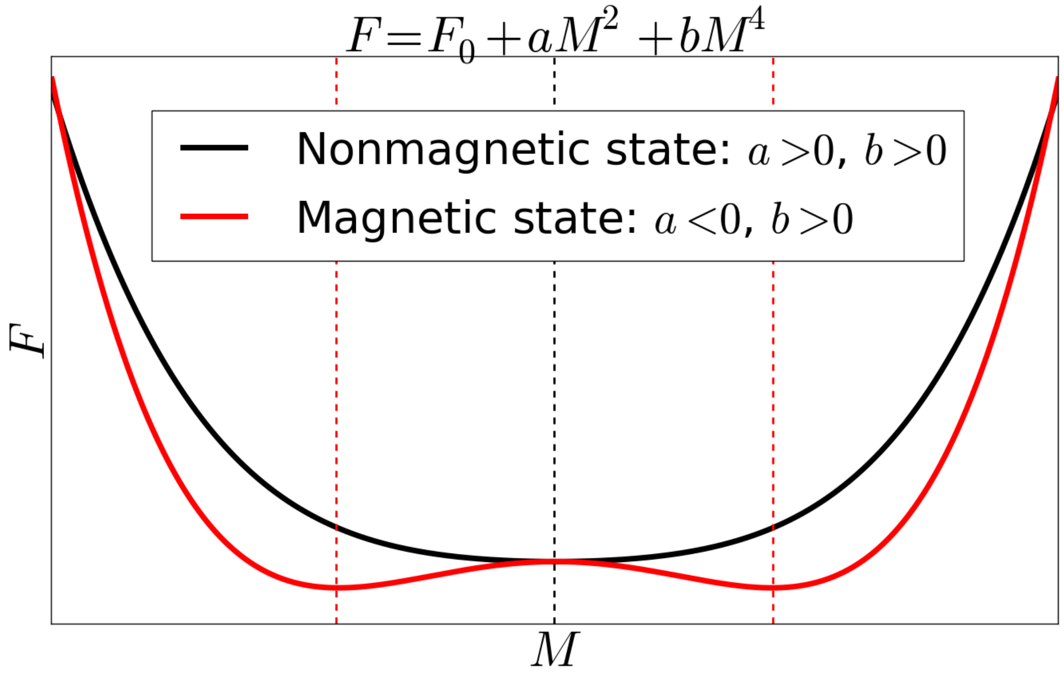

- Including spin-fluctuations (**m**); from scalar to vectorial quantities

$$M^{2n} \rightarrow \left\langle \left(\mathbf{M} + \sum_{i=1}^{3} \mathbf{m}_i \right)^{2n} \right\rangle$$

$$F = F_0 + M^2 \overbrace{\left(a + b(6\langle m_\perp^2 \rangle + 4\langle m_\parallel^2 \rangle)\right)}^{\overline{a}} + M^4 \left(b + \mathcal{O}(cM^6)\right) + \ldots$$

- Spin-fluctuations affect the (main) coefficient responsible for the magnetic order; $\overline{a} = a + b(6\langle m_\perp^2 \rangle + 4\langle m_\parallel^2 \rangle$ → push towards a nonmagnetic state

Spin fluctuations
Gaussian statistics

- Gibbs-Bogoliubov (Peierls-Feynman) inequality:

$$\boxed{F \leqslant F_0 + \langle H - H_0 \rangle_0}$$

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$$H = \int \mathrm{d}\mathbf{r} \left(E\left(\mathbf{M} + \sum_{i=1}^{3} \mathbf{m}_i(\mathbf{r}) \right) + C \sum_{i,j} (\nabla_j m_i(\mathbf{r}))^2 \right)$$

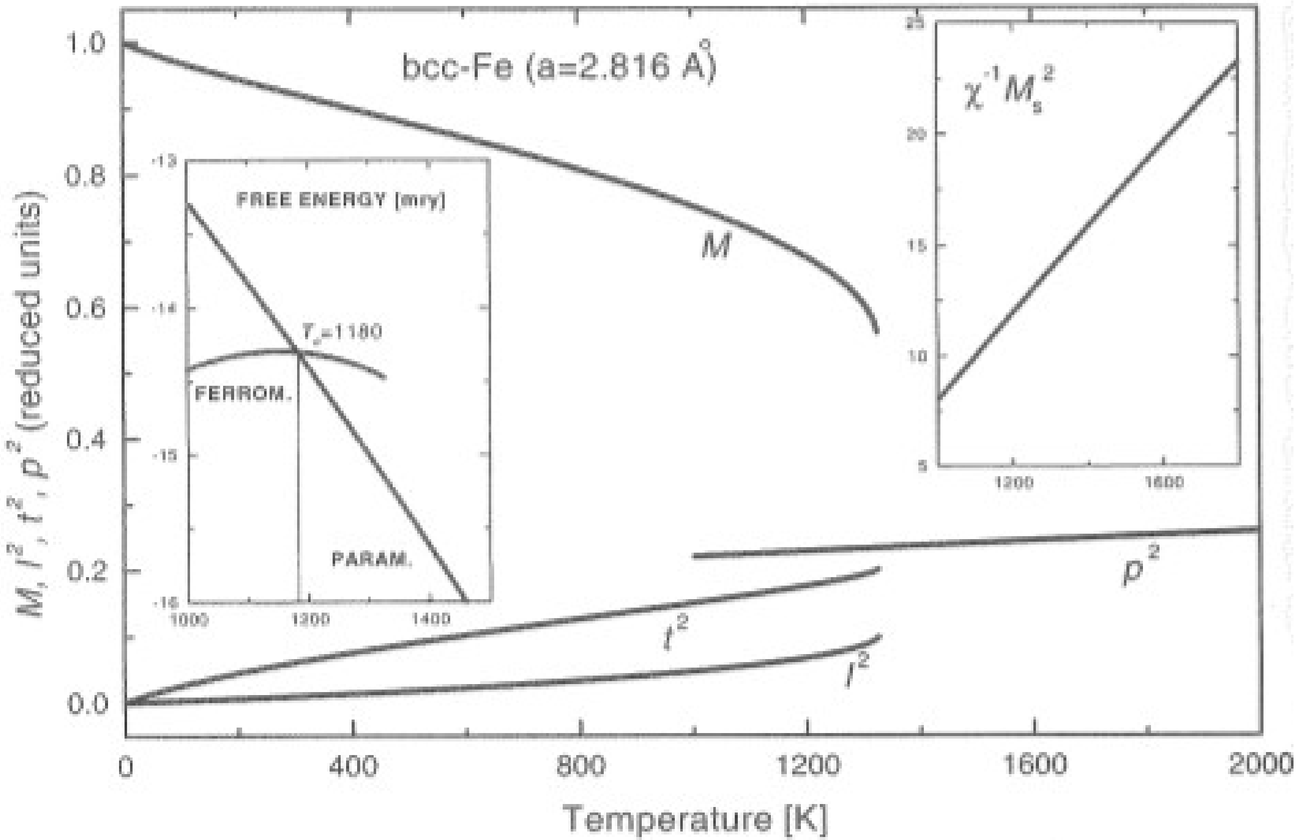
$$H_0 = \sum_{i=1}^{3} \int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \Omega_i(\mathbf{r}-\mathbf{r}') \mathbf{m}_i(\mathbf{r}) \mathbf{m}_i(\mathbf{r}')$$

$\Omega_i(\mathbf{r}-\mathbf{r}')$ are variational parameters to be determined from $\dfrac{\delta F}{\delta \Omega_i} = 0$

- The theory leads to a set of equations to be solved self-consistently to determine (numerically) quantities such as bulk moment, spin-fluctuations or inverse susceptibility at a given temperature T:

$$\langle \mathbf{m}_i^2 \rangle \propto \frac{k_B T}{C} \left(1 - G(\mathbf{m}_i^2, \mathbf{M}^2, T)\right)$$

Spin fluctuations
Gaussian statistics



Kübler, *Theory of Itinerant Electron Magnetism*

- Renormalization of expansion coefficients of free energy by spin-fluctuations

✔ Finite temperatures: deviations of Curie temperature and susceptibility within 15% as compared to experiments: spin-fluctuations seem to cover the essential physics of magnetic coupling

✔ Curie-Weiss law of itinerant electron magnets

✗ Inappropriate discontinuos change of the spontaneous magnetization at Tc

✗ Neglects spin-fluctuations at T=0

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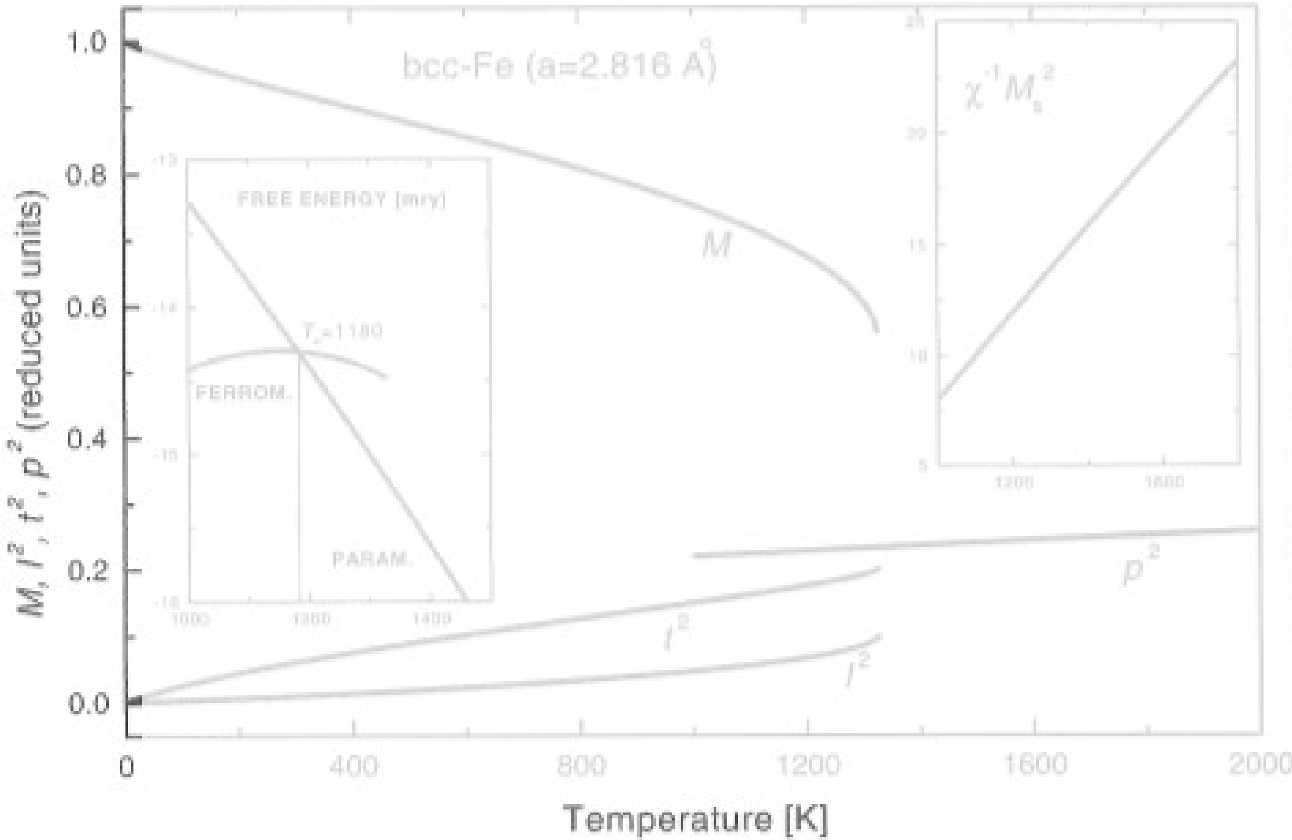

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Spin fluctuations, T=0

- **Fluctuation-dissipation theorem**:

$$\langle m_i^2(\mathbf{q})\rangle = \frac{1}{2\pi}\int_0^\infty \mathrm{d}\omega \big(1 + 2n(\omega,T)\big)\mathrm{Im}\chi_i(\mathbf{q},\omega)$$

with the Bose occupation factor $n(\omega,T) = \big(\exp(\omega/T) - 1)\big)^{-1}$

- **Zero-point** (ZP) spin-fluctuations:

$$\langle m_i^2(\mathbf{q})\rangle_{\mathrm{ZP}} = \frac{1}{2\pi}\int_0^\infty \mathrm{d}\omega \mathrm{Im}\chi_i(\mathbf{q},\omega)$$

Spin fluctuations, T=0

JÜLICH FORSCHUNGSZENTRUM

- Experimental evidence for large **zero-point** spin-fluctuations, $\langle m_i^2(\mathbf{q})\rangle_{\mathrm{ZP}}^{1/2} \sim \mu_B$, [Shiga etal, JPSP **57**, 3141 (1988); Ziebeck etal, PRB **31**, 5884 (1982)]

- [Aguayo etal, PRL **92**, 147201 (2004)] Renormalization of the Stoner criterion by zero-point spin-fluctuations; calculation of approximate susceptibility within DFT+LDA

$$\chi_0(\mathbf{q},\omega) = \rho(\epsilon_F) - Aq^2 + iB\omega/q$$

$$\overline{a} = a + 10b\langle m^2\rangle > 0 \Rightarrow \tilde{I}_s = I_s - 10b\langle m^2\rangle$$

- Correct the magnetic properties of DFT+LDA at T=0 adjusting the exchange-correlation potential taking into account ZP spin-fluctuations [Ortenzi etal, PRB **86**, 064437 (2012)]

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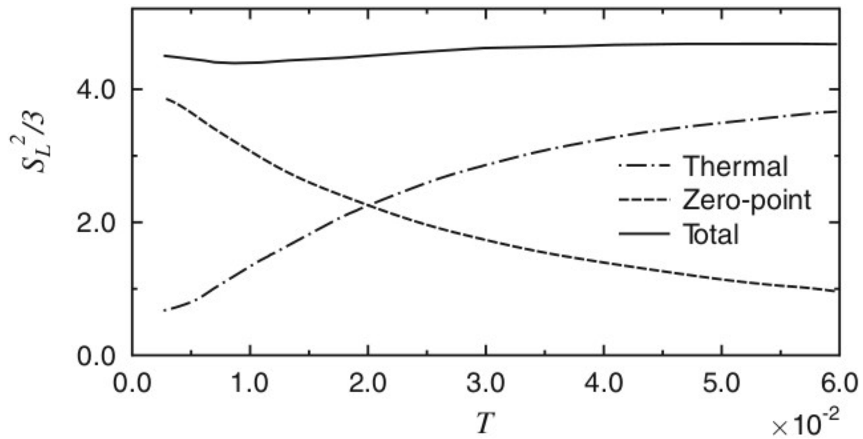
- Effect of ZP spin-fluctuations at finite T? See review by: Takahashi, JPCM 13 6323 (2001) also: Solontsov & Wagner, PRB **51** 12410 (1994)

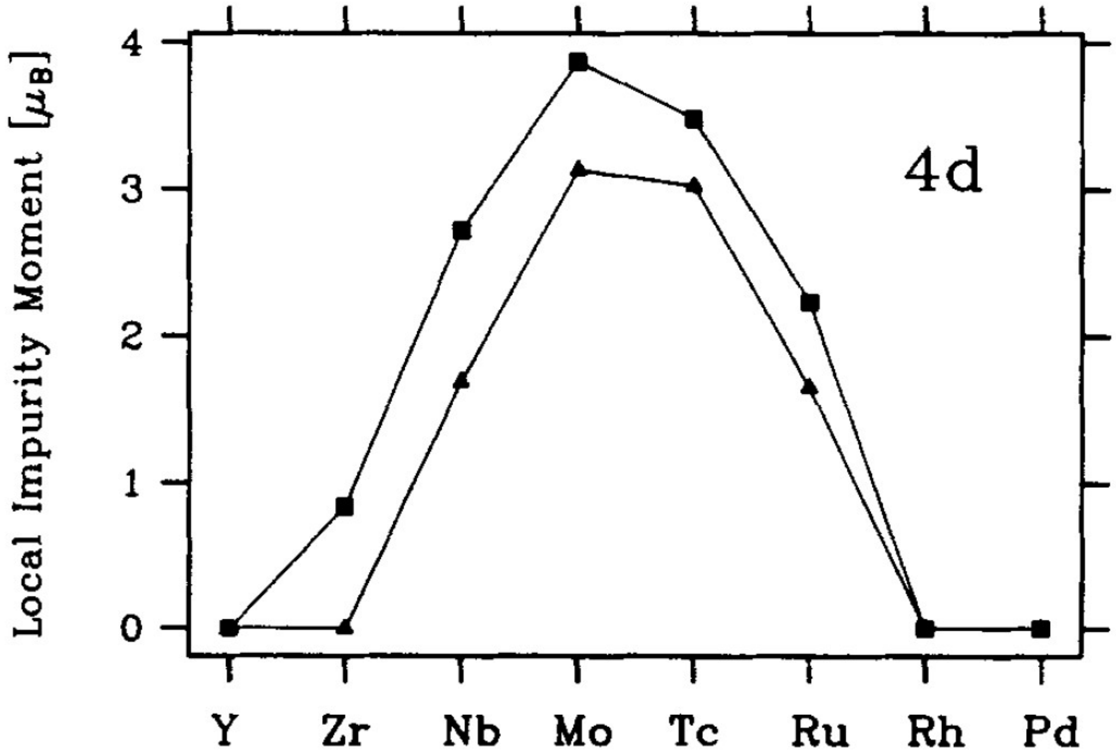
Model calculations in MnSi



Takahashi & Moriya JPSP **54** 1592 (1985)

Goal of the project: nanostructures

Can **zero-point** spin-fluctuations correct the magnetic state predicted by DFT?



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Goal: calculate the zero-point spin-fluctuation from *ab-initio*

- Method: Korringa-Kohn-Rostoker Green function

- Real-space approach for describing the impurity

$$G(\mathbf{r},\mathbf{r}';z) = G_0(\mathbf{r},\mathbf{r}';z) + \int \mathrm{d}\mathbf{r}'' G_0(\mathbf{r},\mathbf{r}'';z)\Delta V(\mathbf{r}'')G(\mathbf{r}'',\mathbf{r}';z)$$

$G_0(\mathbf{r},\mathbf{r}';z)$: Green function of the **unperturbed** system

$G(\mathbf{r},\mathbf{r}';z)$: Green function of the **perturbed** system (impurity)

$\Delta V(\mathbf{r})$: change in the potential induced by the perturbation

- Access to dynamical magnetic susceptibility: $\chi = \chi_0(1 - K_{xc}\chi_0)^{-1}$

$$\chi_0^{ij}(\mathbf{r},\mathbf{r}';\omega) = -\frac{1}{\pi}\int \mathrm{d}z f(z)\left[G_{ij}^{\downarrow}(\mathbf{r},\mathbf{r}';z+\omega)\mathrm{Im}G_{ij}^{\uparrow}(\mathbf{r},\mathbf{r}';z)\right.$$
$$\left.+G_{ij}^{\downarrow}(\mathbf{r},\mathbf{r}';z)\mathrm{Im}G_{ji}^{-\uparrow}(\mathbf{r},\mathbf{r}';z-\omega)\right]$$

Details in Lounis, Costa, Muniz, Mills, PRL **105** 187205 (2010)
Lounis, Costa, Muniz, Mills, PRB **83** 035109 (2011)

Goal of the project: nanostructures

- Technical problem: **frequency integration**

$$\langle m_i^2 \rangle_{\mathrm{ZP}} = \int \mathrm{d}\mathbf{r} \langle m_i^2(\mathbf{r}) \rangle_{\mathrm{ZP}} = \frac{1}{2\pi} \int_0^\infty \mathrm{d}\omega \int \mathrm{d}\mathbf{r} \,\mathrm{Im}\chi_i(\mathbf{r},\mathbf{r};\omega)$$

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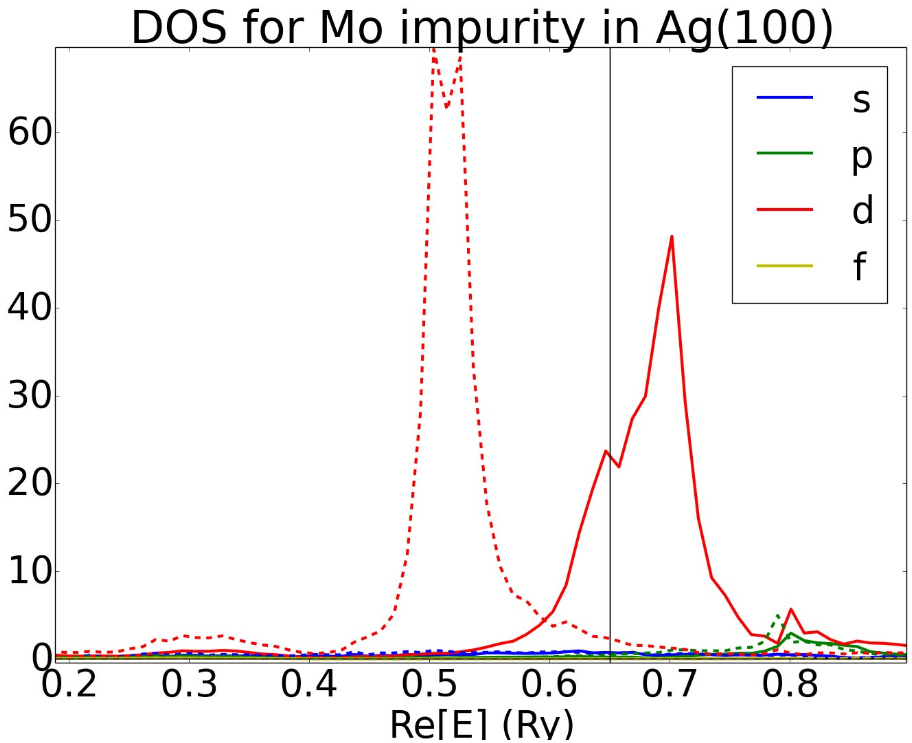

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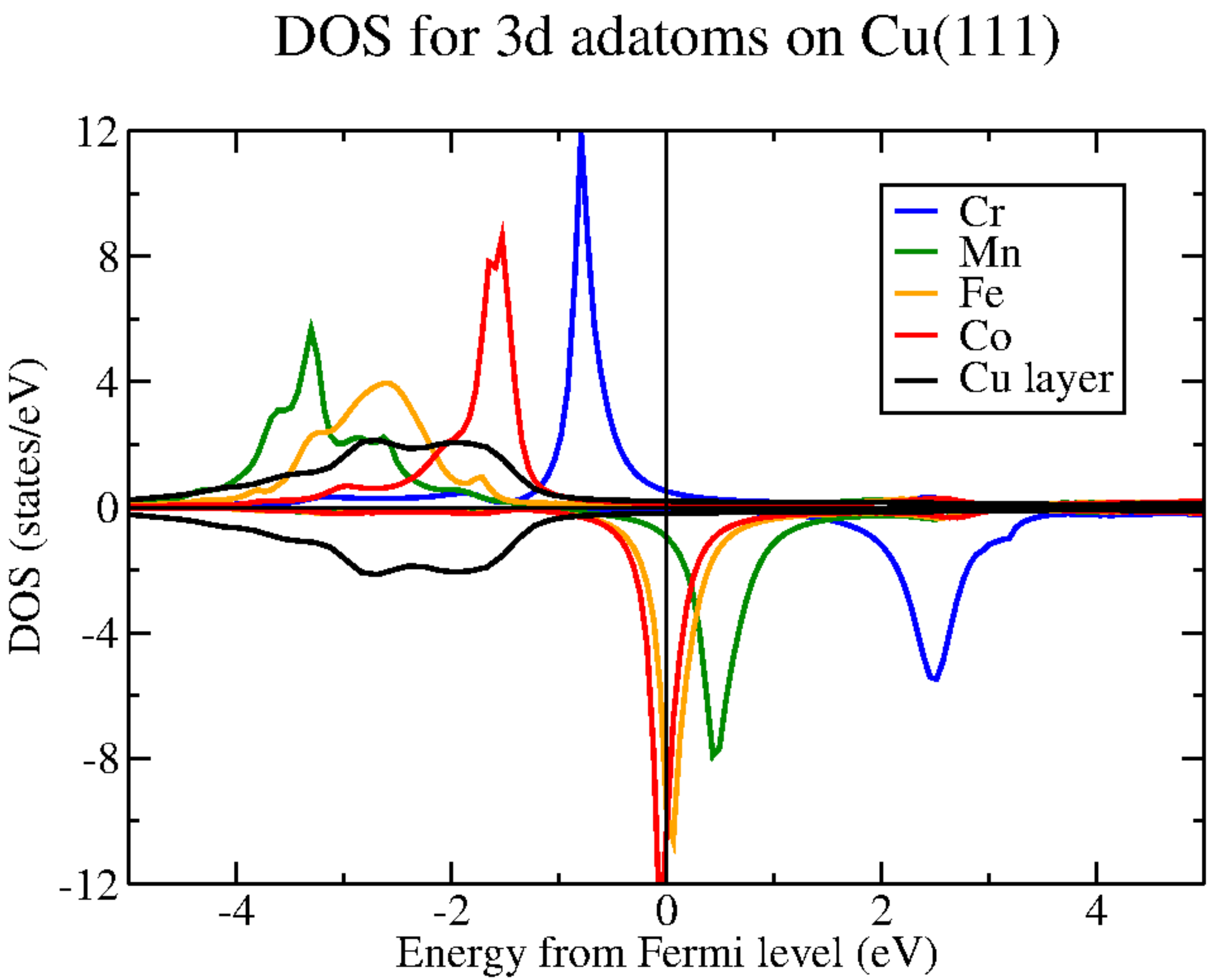
- Frequency integration along the real axis: computationally very heavy
  Possible solution: integrate in complex plane, but...
  - Currently, the method gives access to the susceptibility only along the real axis
  - Green functions are not analytical on the same side of the complex plane

Final remarks

- What is the magnitude of longitudinal spin-fluctuations? (coupling to the charge density)
- Are spin-fluctuations independent of temperature, as suggested by Takahashi?
- Impact of spin-orbit interaction
- Impact of dimensionality: surfaces, thin-films

Thank you



DOS for 3d adatoms on Cu(111)
DOS (states/eV)
Energy from Fermi level (eV)
12
8
4
0
-4
-8
-12
-4
-2
0
2
4
Cr
Mn
Fe
Co
Cu layer