Induced magnetic moments make MAE calculation fun or nightmare

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Outline

Issues with MAE calculations

Varying the thickness of the substrate slab

Varying the size of the surface supercell

What went wrong ?

Lessons to be taken

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Magnetic Anisotropy Energy (MAE)

- Difference between total energies of a magnetic material for different orientations of the magnetization **M**

$$\mathrm{MAE} = E_x - E_z$$

- Magnetocrystalline contribution to MAE is linked to the spin-orbit coupling.

- Calculations of MAE for 0-, 1- and 2-dimensional transition metal systems done in the past.

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Calculating the MAE

- Calculating the magnetocrystalline contribution to MAE is demanding.
- Sources of errors explored in the past:
  - numerical issues (e.g., number of the $\mathbf{k}_{\|}$ points) [Gay & Richter PRL 1986, Solovyev *et al.* PRB 1995],
  - many-body effects beyond the LSDA [Nonas *et al.* PRL 2001, Shick *et al.* JAP 2009, Błoński & Hafner JPCM 2009],
  - geometry relaxation [Mosca Conte *et al.* PRB 2008, Błoński & Hafner JPCM 2009].
- Still deviations of ∼30–100% with respect to experiment.

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Going back to basics

Issues not really addressed so far:

- Semi-infinite substrate represented by a thin slab.
- Isolated ad-atom substituted by a array of atoms located in surface supercells.

Our aim:

Explore how the calculated MAE depends

1. on the thickness of the slab representing the substrate,
2. on the size of the surface supercell which simulates the isolated ad-atom.

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HOW

- Spin polarized fully relativistic Green's-function KKR formalism.
- Magnetocrystalline contribution to the MAE calculated by evaluating the torque.
- Potentials treated within the atomic sphere approximation (ASA), angular momentum cut-off $\ell_{\max}=2$.

WHAT

- Fe and Co ad-atoms, monolayers and surface superstructures on Pt(111).
- Fe–Pt and Co–Pt interlayer distances estimated from earlier calculations of other authors
  [Wu *et al.* 1991, Meier *et al.* 2006, Sabiryanov *et al.* 2003, Tsujikawa *et al.* 2007,Balashov *et al.* 2009, Błoński & Hafner 2009].

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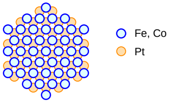
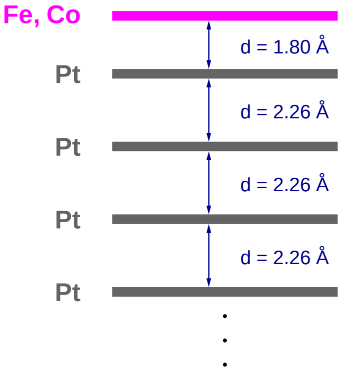
Dependence on the slab thickness



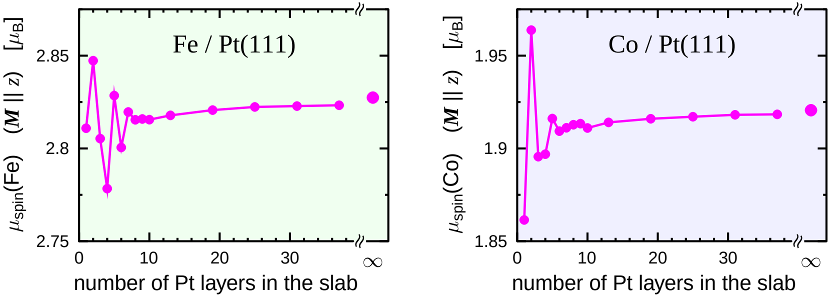
- Full (111) monolayer coverage by Fe or Co atoms

- Varying thickness of the underlying Pt slab (1–38 layers)

  Semi-infinite substrate added as the end-point of the sequence



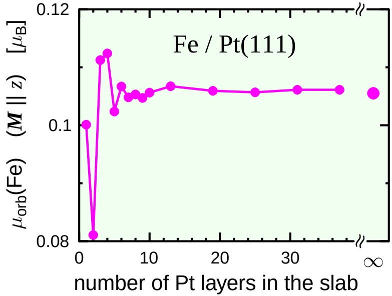
Spin magnetic moment μ_{spin}

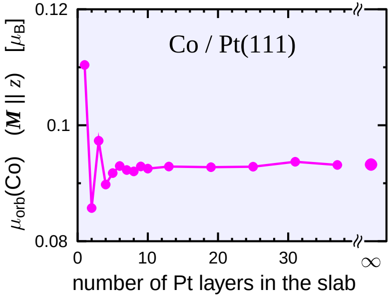


Magnitude of quasi-oscillations in μ_{spin}:

2% **3%**

Orbital magnetic moment μ_{orb}

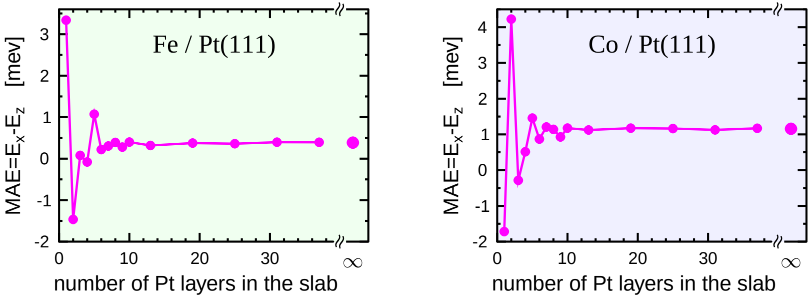




Magnitude of quasi-oscillations in μ_{orb}:

9% **10%**

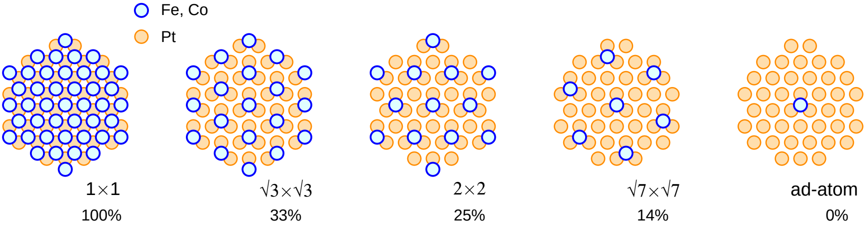
Magnetocrystalline anisotropy energy



Magnitude of quasi-oscillations in MAE: **~50–100%**

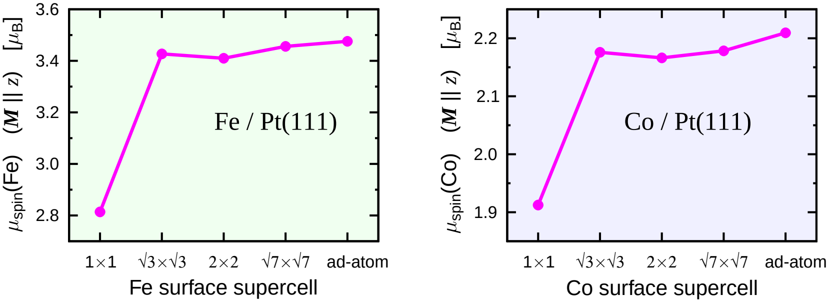
MAE stabilizes only after ≈10 layers thickness.

Dependence on the density of ad-atoms



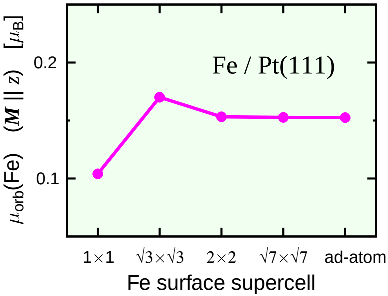
Increasing the size of the surface supercell which approximates the isolated ad-atom

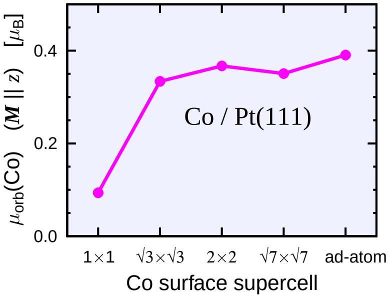
Spin magnetic moment μ_{spin}



Same μ_{spin} for the $\sqrt{3} \times \sqrt{3}$ supercell as for the ad-atom with an accuracy of **1%**.

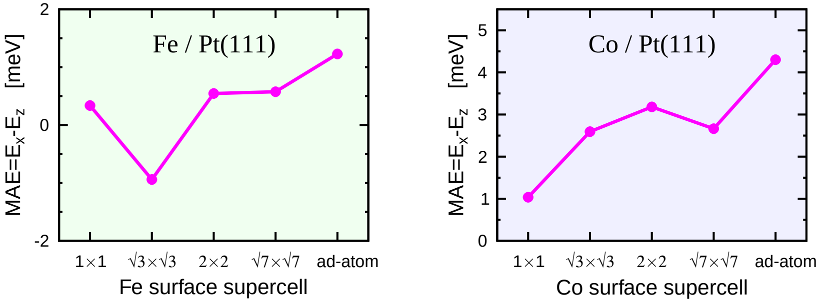
Orbital magnetic moment μ_{orb}





Same μ_{orb} for the $\sqrt{3} \times \sqrt{3}$ supercell as for the ad-atom with an accuracy **10–15%**.

Magnetocrystalline anisotropy energy



50–100% deviation from the $\sqrt{7} \times \sqrt{7}$ supercell to the ad-atom !

Non-monotonous behaviour (on top of that).

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This cannot be true. . .

- Common experience with *ab-initio* surface science:
  Only first few layers below the surface matter.

- Claiming that you need a slab of 10 layers or more to model the substrate is outrageous !
  We all know that MAE is a delicate thing but. . .

- Let us make a comparison with another system !

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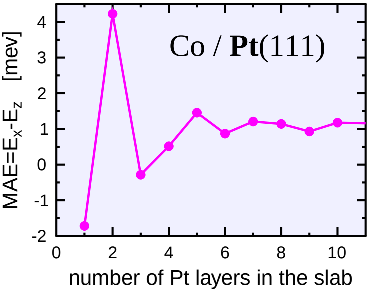
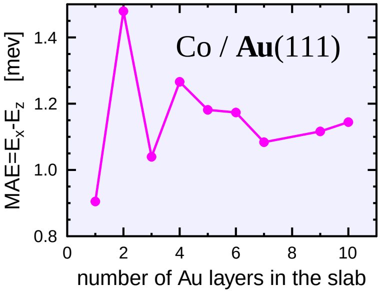
Thickness-dependence of MAE for Pt and Au substrates





Look on the numbers:

variations of $\sim$**100%** variations of $\lesssim$**20%**

What is the difference between Pt and Au ?

- Au is difficult to polarize.
- Pt is highly polarizable (close to “ferromagnetic instability”).
- Polarization cloud around magnetic ad-atom on Pt(111) spreads far away and contributes the MAE significantly.

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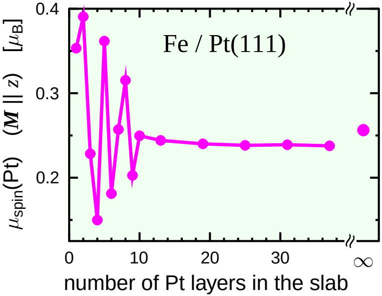
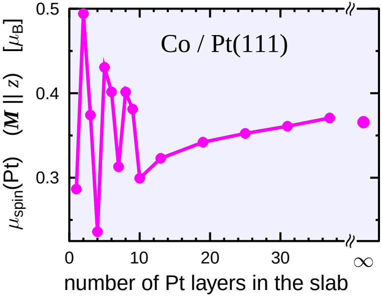
Total μ_{spin} induced in the Pt substrate

Fe or Co monolayer on Pt(111), varying the thickness of the slab:





Magnitude of quasi-oscillations:

90% **50%**

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A note to the skeptics

- The approximations we used limit the accuracy of the calculated MAE.

  The "true" values of MAE will probably differ from the values shown here.

- However, fact that calculated MAE may be substantially affected by the thickness of the substrate slab and by the size of the surface supercell is here to stay.

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Message to the mankind

- MAE is much more sensitive to the thickness of the slab representing the substrate and to the interaction between the ad-atoms than $\mu_{\rm spin}$ or $\mu_{\rm orb}$.
- For polarizable substrates (Pt, Pd, V, ...), reliable values of MAE cannot be obtained if the substrate is modeled by a slab of $\lesssim$10 atomic layers.
- If a surface superstructure is meant to represent an ad-atom, then decoupling has to be ensured by using very large supercells.

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Outlook (1)

To have a truly predictive MAE calculation for ad-atoms, one has to include

- polarization cloud in the substrate,
- structural relaxation,
- full potential,
- many-body effects beyond the LSDA,
- sufficiently large basis (high enough ℓ_{max}),
- god-knows-what-else.

None of the studies published so far includes all the ingredients. Agreement with experiment may be due to a lucky coincidence.

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Outlook (2)

There is still a lot of work out there waiting for us !