Localization
of magnetocrystalline anisotropy energy:
Answering the Unanswerable

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Outline

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Magnetic Anisotropy Energy (MAE)

- Difference between total energies of a magnetic material for different orientations of the magnetization with respect to the crystal lattice:

$$E_{\mathsf{MAE}} \; = \; E_x - E_z \;\; .$$

- Especially interesting
  - for layered composite systems (such as FePd or CoPt),
  - for adatoms, monolayers and generally nanostructures supported by non-magnetic substrates.

- Not only interesting but also relevant:
  For nanostructures, MAE is much larger than for bulk systems and could be significantly influenced by manipulating just few atoms.

Mechanism behind MAE

General fact: Magnetocrystalline contribution to MAE is due to the spin orbit coupling (SOC).

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Specific questions:

- For composite materials:
  What is the role of non-magnetic atoms?

- For supported nanostructures:
  What is the role of the substrate?

    - Does MAE come only from the magnetic nanostructure (cluster, monolayer) or is there also a significant contribution from the substrate?

Where does the MAE come from? (1)

Relying on "technical means", one can split MAE into adsorbate
and substrate parts.

- By decomposing the spatial integral in the expression for total
  energy into parts coming from different cells:

$$E_{\text{total}} = \int d\mathbf{r} \sum_n \Psi_n^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m}\Delta \right) \Psi_n(\mathbf{r}) + \int d\mathbf{r}\, n(\mathbf{r})\, V_{\text{nucl}}(\mathbf{r}) + \dots$$

Tsujiwaka *et al.* PRL **102**, 247203 (2009): Fe on Pt(001), FePt

Where does the MAE come from? (2)

Relying on "technical means", one can split MAE into adsorbate and substrate parts.

- ▶ By assigning sum of band-energies to individual sites by decomposing the density of states into atom-resolved quantities:

$$E_{\text{MAE}} = \sum_j \int_{-\infty}^{E_F} \mathrm{d}E\ E\ [n_j(E; \hat{\mathbf{e}}_1) - n_j(E; \hat{\mathbf{e}}_2)]\ .$$

Nordstrom *et al.* JPCM **4**, 3261 (1992): bulk YCo$_5$

Burkert *et al.* PRB **71**, 134411 (2005): bulk FePt, Fe$_{1-x}$Mn$_x$Pt

Where does the MAE come from? (3)

Relying on "technical means", one can split MAE into adsorbate and substrate parts.

- By relying on the Bruno formula, looking for anisotropies of orbital magnetic moments for each site:

$$E_{\text{MAE}} = \sum_j \left[\mu_{\text{orb}}^{(j),\parallel} - \mu_{\text{orb}}^{(j),\perp} \right] .$$

Duan *et al.* PRL **101**, 137201 (2008): metallic films

Gimbert *et al.* PRB **86**, 184407 (2012): Co/Ni (111) superlattices

Where does the MAE come from? (4)

Relying on "technical means", one can split MAE into adsorbate and substrate parts.

- ▶ By comparing terms assignable to each site in the torque formula:

$$E_{\text{MAE}} = \sum_j T_j^{(45°)} .$$

Schick *et al.* PRB **78**, 054413 (2008): Mn monolayer on W(001)

Khmelevskyi *et al.* PRB **83**, 224419 (2011): Mn{Ni,Pd,Rh,Ir}

Bornemann *et al.* PRB **86**, 104436 (2012): adatoms on Ir, Pt, Au

Aas *et al.* JPCM **24**, 406001 (2012): Pt monolayer inside Co

Is there some hard-line physics in such a separation?

☹ Energy cannot be localized

- Energy is not an extensive quantity.
  - Energy of a system cannot be decomposed into sum of energies of its parts.

- Asking whether the MAE comes from the magnetic adsorbate or from the substrate is not well-defined,
  it has no exact meaning $\Rightarrow$ it cannot be answered!

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  it has no exact meaning $\Rightarrow$ it cannot be answered!

- This solves the problem but does not satisfy our curiosity...
  - We are not going to stop asking a question just because it cannot be answered.

Outline

Way forward: Make the question answerable!

- The only option left: amend the question so that it becomes well-defined and can be answered.
  - If you cannot make the people to change, make them to change the question they are asking.

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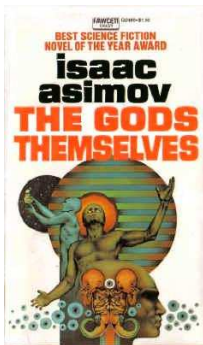
Wanted:

An internally consistent formulation of the question about the localization of MAE.

Switch SOC and B_{ex} in the substrate on and off

- To get MAE, one must have spin-orbit coupling (SOC) and magnetism, which is enhanced by the exchange field B_{ex} ($B_{ex} = V_\uparrow - V_\downarrow$).

- We can selectively switch the SOC and B_{ex} on and off in the substrate only, thereby assessing their influence on MAE of the whole system.

- If manipulating the substrate SOC and/or B_{ex} does not change the calculated MAE, one can say that the substrate does not directly contribute the MAE.

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Credit where it is due. . .

We are not the first to play with SOC.

In some works, influence of SOC is also investigated (even though not in a systematic way):

Wang *et al.* PRB **48**, 15886 (1993): Pd/Co/Pd sandwich

Daalderop *et al.* PRB **50**, 9989 (1994): Co/Pd multilayer

Ravindran *et al.* PRB **63**, 144409 (2001): {Fe,Mn}{Ni,Pd,Pt}

Burkert *et al.* PRB **71**, 134411 (2005): bulk FePt, $Fe_{1-x}Mn_xPt$

Baud *et al.* PRB **73**, 104427 (2006): Co wires on steps of Pt(111)

Subkow *et al.* PRB **84**, 054443 (2011): Fe surfaces

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Our playground

Co monolayers and Co adatoms
on Cu, Ag, Au, Pd, Pt (111) surfaces

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Co monolayers and Co adatoms
on Cu, Ag, Au, Pd, Pt (111) surfaces
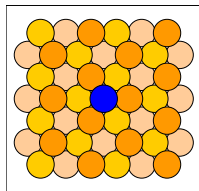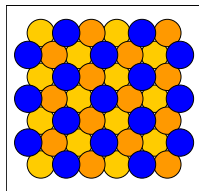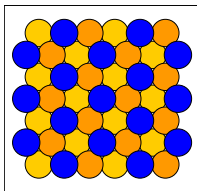
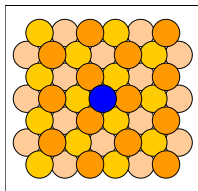Low polarizability:
Cu, Ag, Au
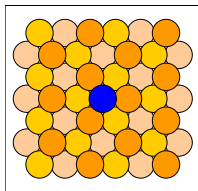
High polarizability:
Pd, Pt

Our playground

Co monolayers and Co adatoms
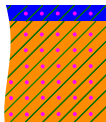on Cu, Ag, Au, Pd, Pt (111) surfaces
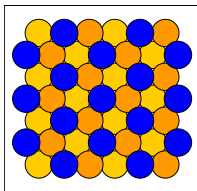
Low polarizability:
Cu, Ag, Au

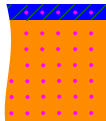High polarizability:
Pd, Pt
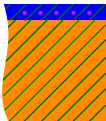
Small SOC:
Cu

Large SOC:
Pt, Au

SOC $\neq 0$
$B_{\text{ex}} \neq 0$

SOC $\neq 0$
$B_{\text{ex}} = 0$

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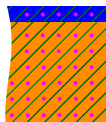
SOC $= 0$
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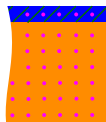# Computational framework

- Spin polarized fully relativistic Green's-function KKR formalism

- Manipulate SOC and B_{ex} for the substrate only

- MAE evaluated via torque

- ASA potentials, bulk-like geometry

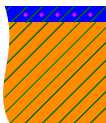- Ebert, Ködderitzsch and Minár RPP **74**, 096501 (2011) for more
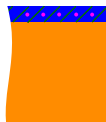
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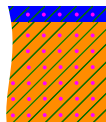
SOC $= 0$
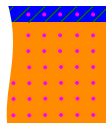$B_{ex} \neq 0$

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Computational framework

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Definition: $E_{MAE} \equiv E_\parallel - E_\perp$
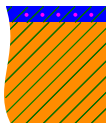$E_{MAE} > 0 \Leftrightarrow$ easy axis $\perp$ to surface

SOC $\neq 0$
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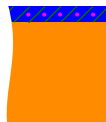
SOC $= 0$
$B_{ex} \neq 0$

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Outline

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What to expect?

MAE needs for its existence SOC and magnetism.

Conjecture:

1. Suppressing SOC in the substrate will decrease MAE.

2. Suppressing B_{ex} in the substrate will decrease MAE.

3. For substrates with large SOC and/or B_{ex}, the role of the substrate will be more important.

4. For adatoms, the role of the substrate will be more important than for monolayers (more substrate atom per magnetic atom than for monolayers).

Results: MAE for Co **adatoms** [meV]

	Cu
	13.2

Pd	Ag
6.6	**15.9**

Pt	Au
8.7	**14.7**

SOC $\neq 0$
$B_{\text{ex}} \neq 0$

	Cu
	13.2

Pd	Ag
6.5	15.9

Pt	Au
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SOC $\neq 0$
$B_{\text{ex}} = 0$

	Cu
	12.4

Pd	Ag
4.7	14.5

Pt	Au
5.7	10.1

SOC $= 0$
$B_{\text{ex}} \neq 0$

	Cu
	12.5

Pd	Ag
4.6	14.5

Pt	Au
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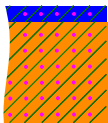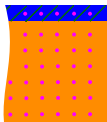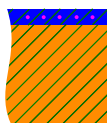
SOC $= 0$
$B_{\text{ex}} = 0$

Results: MAE for Co **monoloayers** [meV]

	Cu		
	-0.69		

Pd	Ag		
0.20	**-1.59**		

Pt	Au
0.08	**-0.62**

SOC $\neq 0$
$B_{\text{ex}} \neq 0$

	Cu
	-0.69

Pd	Ag
0.15	-1.62

Pt	Au
-0.24	-0.63

SOC $\neq 0$
$B_{\text{ex}} = 0$

	Cu
	-0.83

Pd	Ag
-0.27	-1.90

Pt	Au
-0.21	-1.51

SOC $= 0$
$B_{\text{ex}} \neq 0$

	Cu
	-0.83

Pd	Ag
-0.34	-1.90

Pt	Au
-0.26	-1.51
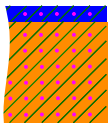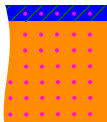
SOC $= 0$
$B_{\text{ex}} = 0$

Pragmatist's view: Contributions to the torque

When MAE is evaluated via the torque, one adds contributions which can be "mechanically" assigned to individual atoms: $E_{\text{MAE}} = \sum_j T_j^{(45°)}$.

It is possible to see *mechanistically* which portion of the sum comes from substrate atoms (it is not a well-defined procedure but...):

Co adatom

	Cu
	0.02%

Pd	Ag
0.7%	0.01%

Pt	Au
0.1%	0.01%

Co monolayer

	Cu
	-0.1%

Pd	Ag
25%	-0.1%

Pt	Au
191%	-0.4%

Torque vers. SOC and B_{ex} manipulation

Role of the substrate in generating MAE for Co adatoms and monolayers on noble metals as assessed by SOC and B_{ex} manipulation and as assessed by comparing individual terms in the torque evaluation:

adatoms

	SOC and B_{ex}	T_i terms
Cu	5.1%	0.02%
Ag	8.4%	0.00%
Au	31.1%	0.01%
Pd	30.7%	0.67%
Pt	34.8%	0.14%

monolayers

	SOC and B_{ex}	T_i terms
Cu	-20.4%	-0.10%
Ag	-19.3%	-0.06%
Au	-142.5%	-0.39%
Pd	265.5%	24.7%
Pt	422.5%	190.9%

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Outline

Things to remember

- Substrate contribution to MAE of supported nanostructures can be isolated by manipulating SOC and B_{ex} for the substrate.

- For adatoms, substrate contribution is relatively small.
  For monolayers, substrate contribution can be essential.

- Contribution from SOC is more important than contribution from the exchange field B_{ex}.

  - For adatoms, B_{ex} has negligible effect even for highly-polarized hosts such as Pd or Pt (not so for monolayers...)

  - If SOC and B_{ex} in the substrate are large, their effect is non-linear.

- For all five substrates, their contribution to MAE is in-plane.

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