Illustrative view on the role of spin-orbit coupling in magnetocrystalline anisotropy of adatoms

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30. November 2016 / CZ-IL workshop on strong electron correlations in nano-materials

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Outline

- MAE: What is it about?
- SOC-induced splitting of DOS:
  How to do it
- SOC-induced splitting of DOS:
  Ab-initio results
- SOC-induced splitting of DOS:
  Model Hamiltonian results
- Summary

Magnetic Anisotropy Energy (MAE)

- Difference between total energies for two orientations of the magnetization $\hat{\mathbf{M}}$ with respect to the crystal lattice:

$$E_{\mathrm{MAE}} = E(\hat{\mathbf{M}}_1) - E(\hat{\mathbf{M}}_2)$$

- Magnetocrystalline contribution to MAE is due to the spin orbit coupling (SOC).

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- Magnetocrystalline contribution to MAE is due to the spin orbit coupling (SOC).
  - What is the specific mechanism that gives rise to the MAE for a concrete system?
  - Can we see a signature of MAE in the electronic structure?
  - People strive to understand MAE to make it as high as possible [Jesche *et al.* Nature Comm. (2014), Rau *et al.* Science (2014), Khajetoorians & Wiebe Science (2014), Antropov & Antonov PRB (2014), Antropov *et al.* SSC (2014)].

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Total energies and single-particle (band) energies

- Total energy within the DFT framework:

$$E_{\text{tot}} = \sum_{i}^{\text{occ}} E_i - \frac{1}{2}\int \mathrm{d}\mathbf{r}\int \mathrm{d}\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{\text{xc}}[n] - \int \mathrm{d}\mathbf{r}\, n(\mathbf{r})v_{\text{xc}}[n](\mathbf{r})$$

- Kohn-Sham functional is extremal $\Rightarrow$ differences in E_{tot} can be approximated by differences in single-particle or "band" energies:

$$E_{\text{MAE}} \approx \sum_{i}^{\text{occ}} E_i(\hat{\mathbf{M}}_1) - \sum_{i}^{\text{occ}} E_i(\hat{\mathbf{M}}_2)$$

Issue to be addressed:

How are the band energies affected by the spin-orbit coupling?

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Change of band energy upon inclusion of SOC

- SOC-perturbed Hamiltonian:

$$H = H_0 + H_{\mathrm{SOC}} = H_0 + \xi(r)\,\boldsymbol{\sigma}\cdot\mathbf{L}$$

- Lowest-order non-vanishing correction to the ground state is the second-order term:

$$\delta E^{(2)} = \sum_{j\neq 0} \frac{\left|\langle\psi_0|\, H_{\mathrm{SOC}}\,|\psi_j\rangle\right|^2}{E_0 - E_j}$$

However:
There may be contributions to the MAE which *cannot* be described within perturbation theory (e.g., if SOC is large or if degenerate states are important).

If the perturbation theory cannot be used. . .

- Inspiration:

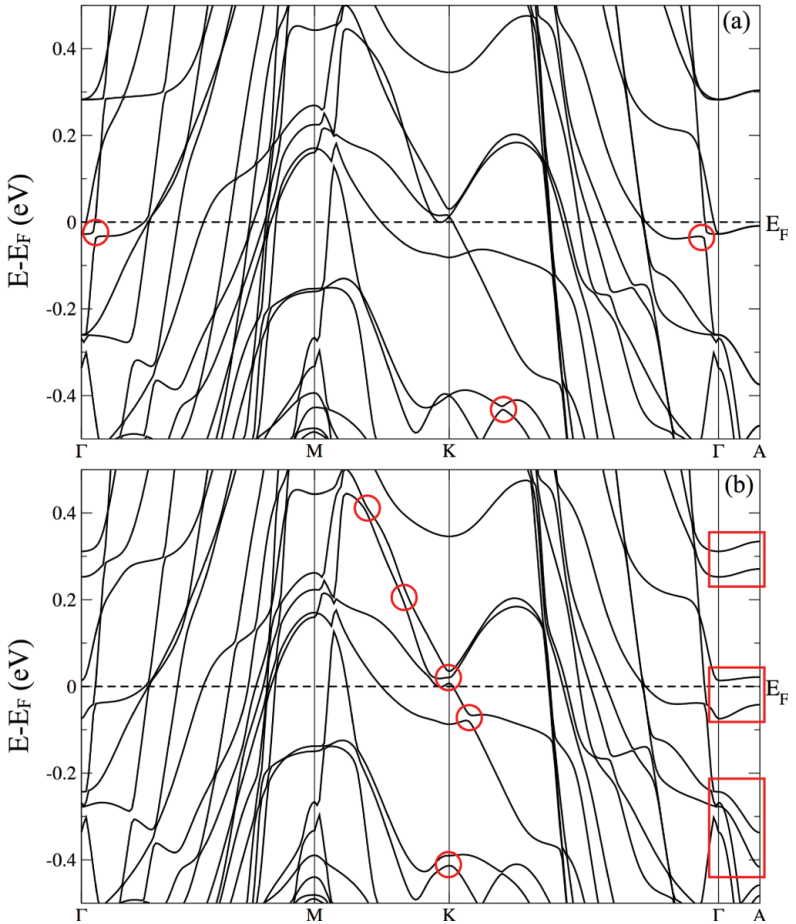
  For free atoms, SOC splits the originally degenerate states by

  $$\sim m_\ell \, \lambda \, \cos\theta \ ,$$

  m_ℓ is the (orbital) magnetic quantum number,
  λ is the SOC scaling factor,
  θ is the angle between $\hat{\boldsymbol{M}}$ and the spin quantization axis.

- If the degenerate states are near the Fermi level, the SOC-induced splitting may push some levels above E_F, lowering thus the energy [Daalderop *et al.* (1990,1991,1994), Wang *et al.* (1993), Ravindran *et al.* (2001)].

Contributions due to degenerate states: Important?



Gimbert & Calmels PRB (2012)

- For extended systems, the degeneracy is limited only to a small part of the Brillouin zone, hence its influence on the MAE is limited.

  [Lessard *et al.* (1997), Gimbert & Calmels (2012)]

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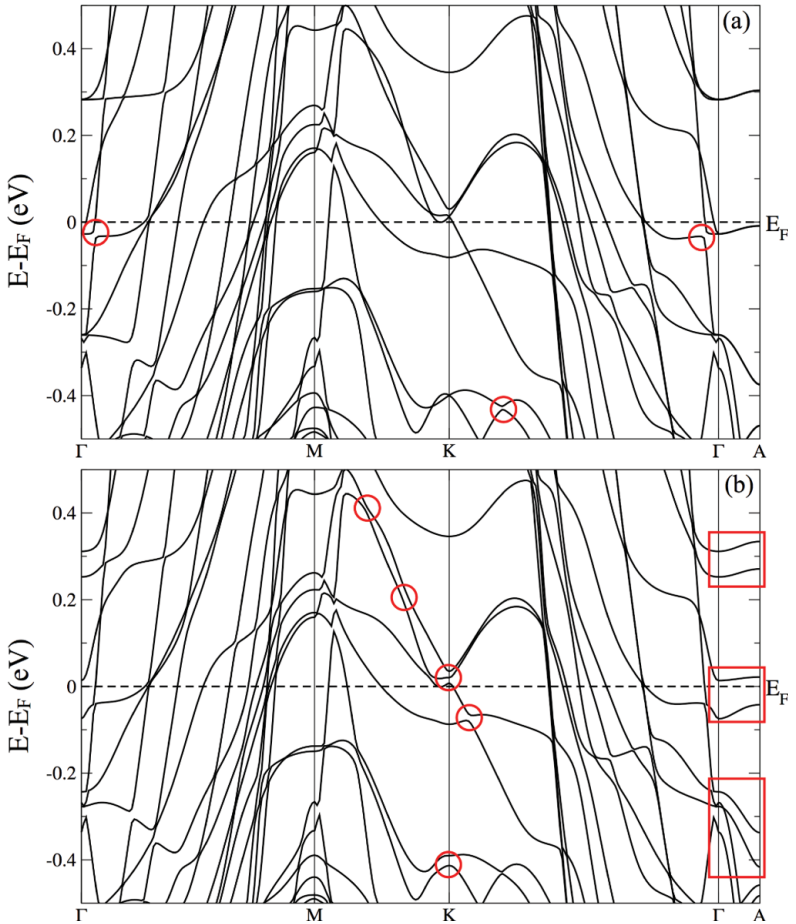

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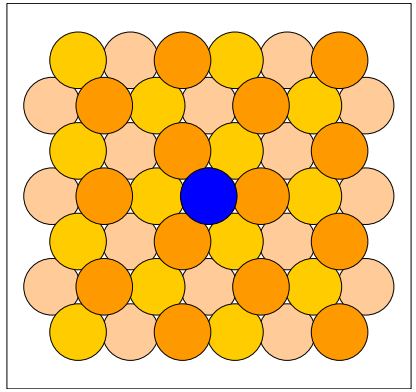
- What if the **k**-dependence is suppressed (as in the case of adatoms)?

  Let us have a look...

Calculate MAE for adatoms

Fe, Co, and Ni adatoms
on Au(111) surface



- Fully relativistic Green's-function KKR formalism, solving the Dirac equation
  [Ebert, Ködderitzsch and Minár RPP (2011)]
- MAE evaluated via the torque
  - Definition: $E_{\mathrm{MAE}} \equiv E^{(x)} - E^{(z)}$
    $E_{\mathrm{MAE}} > 0 \Leftrightarrow$ easy axis is normal to the surface
- Plain LDA, potential is subject to the ASA
- Adatoms geometry taken from VASP calculations

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Results for E_{MAE} and magnetic moments

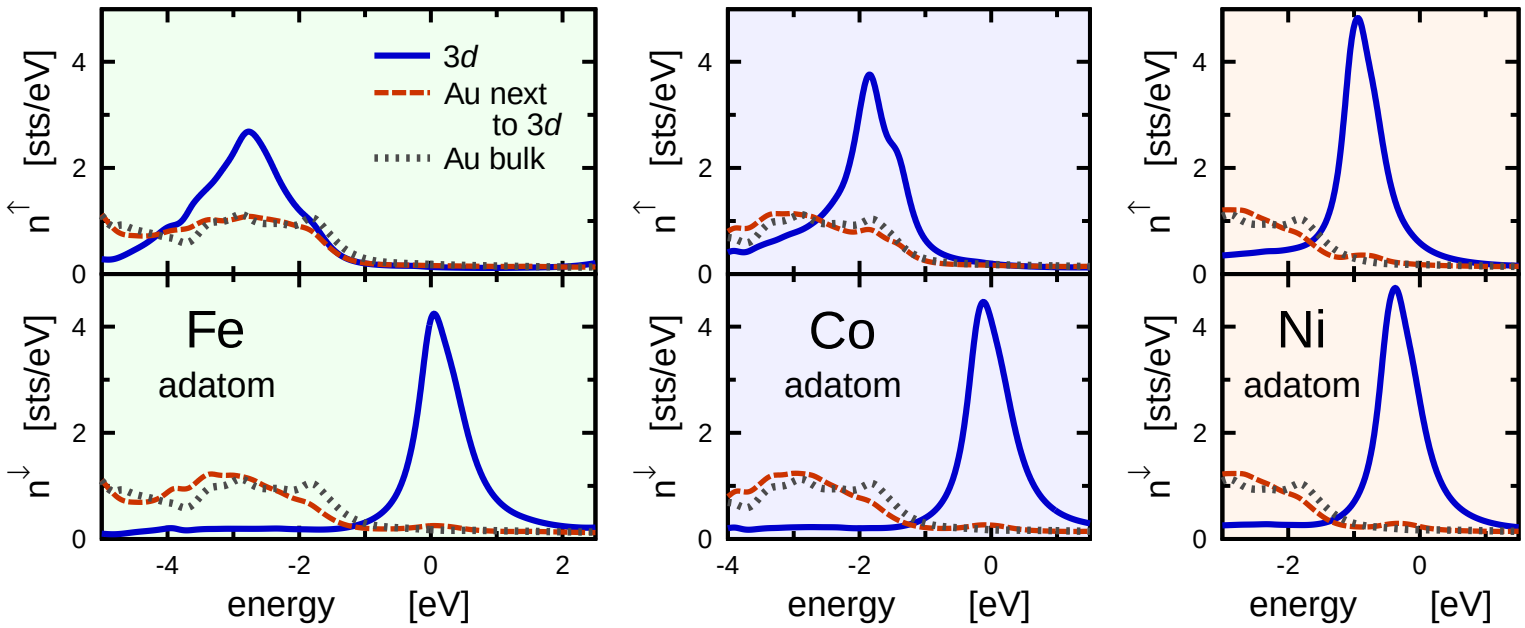
		E_{MAE} (meV)	$\mu^{(z)}_{\mathrm{spin}}$ (μ_{B})	$\mu^{(z)}_{\mathrm{orb}}$ (μ_{B})	$\mu^{(x)}_{\mathrm{orb}}$ (μ_{B})
Fe	adatom	4.07	3.40	0.536	0.062
Co	adatom	4.42	2.13	0.218	0.206
Ni	adatom	-1.63	0.67	0.063	0.158

Numbers may be interesting but they are not our focus.

Besides, the particular values could be affected by approximations we have made.

See, e.g., Khan *et al.* PRB **94** 144436 (2016) to learn more.

DOS for Fe, Co and Ni adatoms on Au(111)



Magnetization perpendicular to the surface $\boldsymbol{M} \| \boldsymbol{z}$ (but it does not matter at this scale).

Let us focus on for the minority-spin states, where the most interesting stuff happens.

Šipr *et al.* PRB **93**, 174409 (2016)

What to do

Plan:
Have a look at the spin-polarized orbitally-resolved DOS and monitor how it changes upon rotation of the magnetization.

Problem:
That's easier said than done.

Spin-resolved and m-resolved DOS for $\boldsymbol{M} \nparallel \hat{\boldsymbol{z}}$

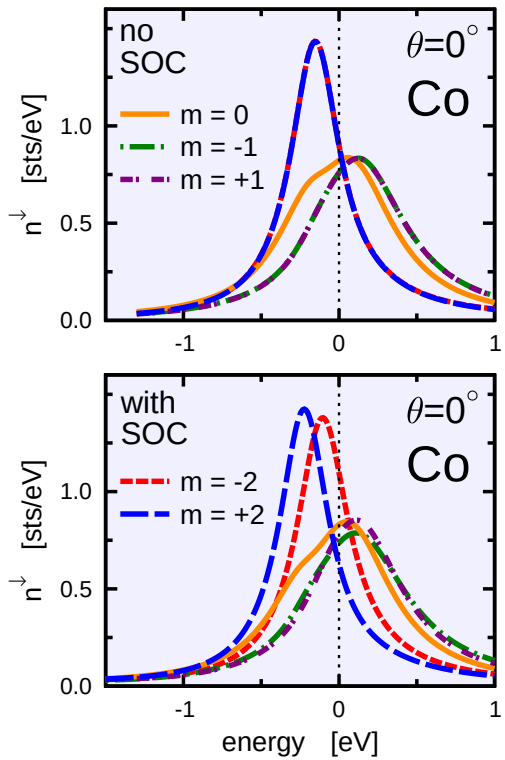
The way the DOS components $n_{\ell m}$ are defined depends on the reference frame.

Spherical harmonics $Y_{\ell m}$ can be defined in a global reference frame (fixed to the crystal lattice) or in a local reference frame chosen so that the $z^{(\mathrm{loc})}$ axis is parallel to $\boldsymbol{M}$.

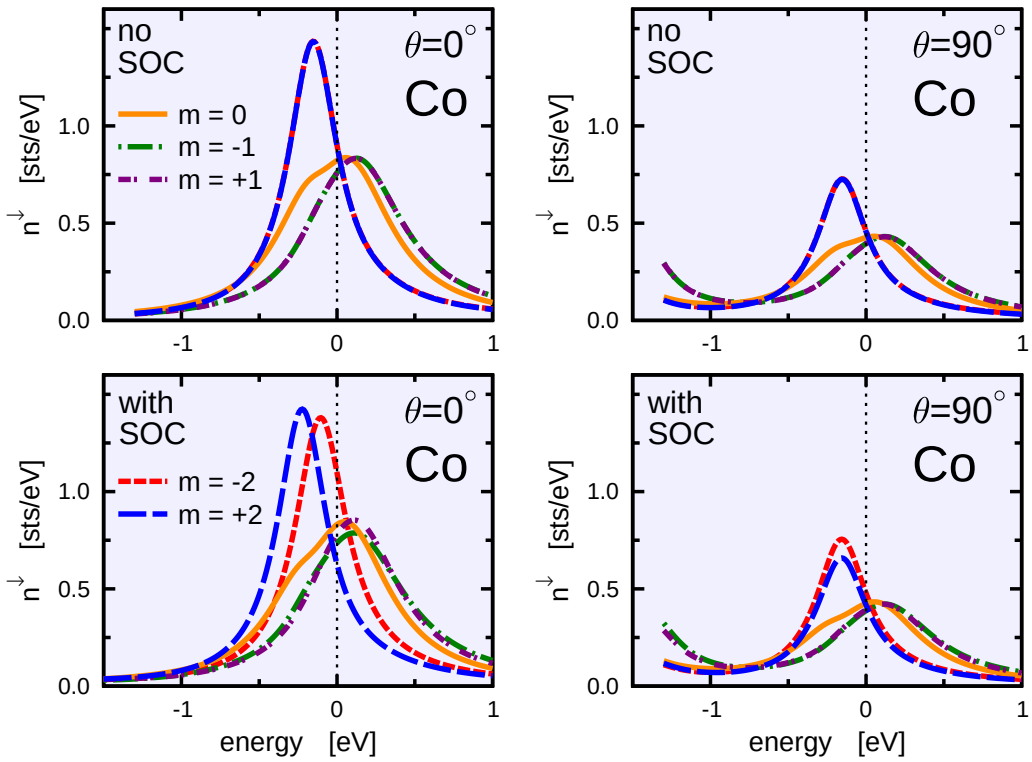
$$
\begin{aligned}
n_{\ell m}^{(\mathrm{glo})}(E) &= -\frac{1}{\pi} \Im \langle Y_{\ell m}^{(\mathrm{glo})} | \, G(E) \, | Y_{\ell m}^{(\mathrm{glo})} \rangle \\
n_{\ell m}^{(\mathrm{loc})}(E) &= -\frac{1}{\pi} \Im \langle Y_{\ell m}^{(\mathrm{loc})} | \, G(E) \, | Y_{\ell m}^{(\mathrm{loc})} \rangle
\end{aligned}
$$

☹ If $\boldsymbol{M} \nparallel \hat{\boldsymbol{z}}$, projecting the DOS in a global reference frame mixes the spin components because the spin quantization axis is no longer parallel to $\boldsymbol{M}$.

Spin-resolved and *m*-resolved DOS for Co adatom



Spin-resolved and *m*-resolved DOS for Co adatom



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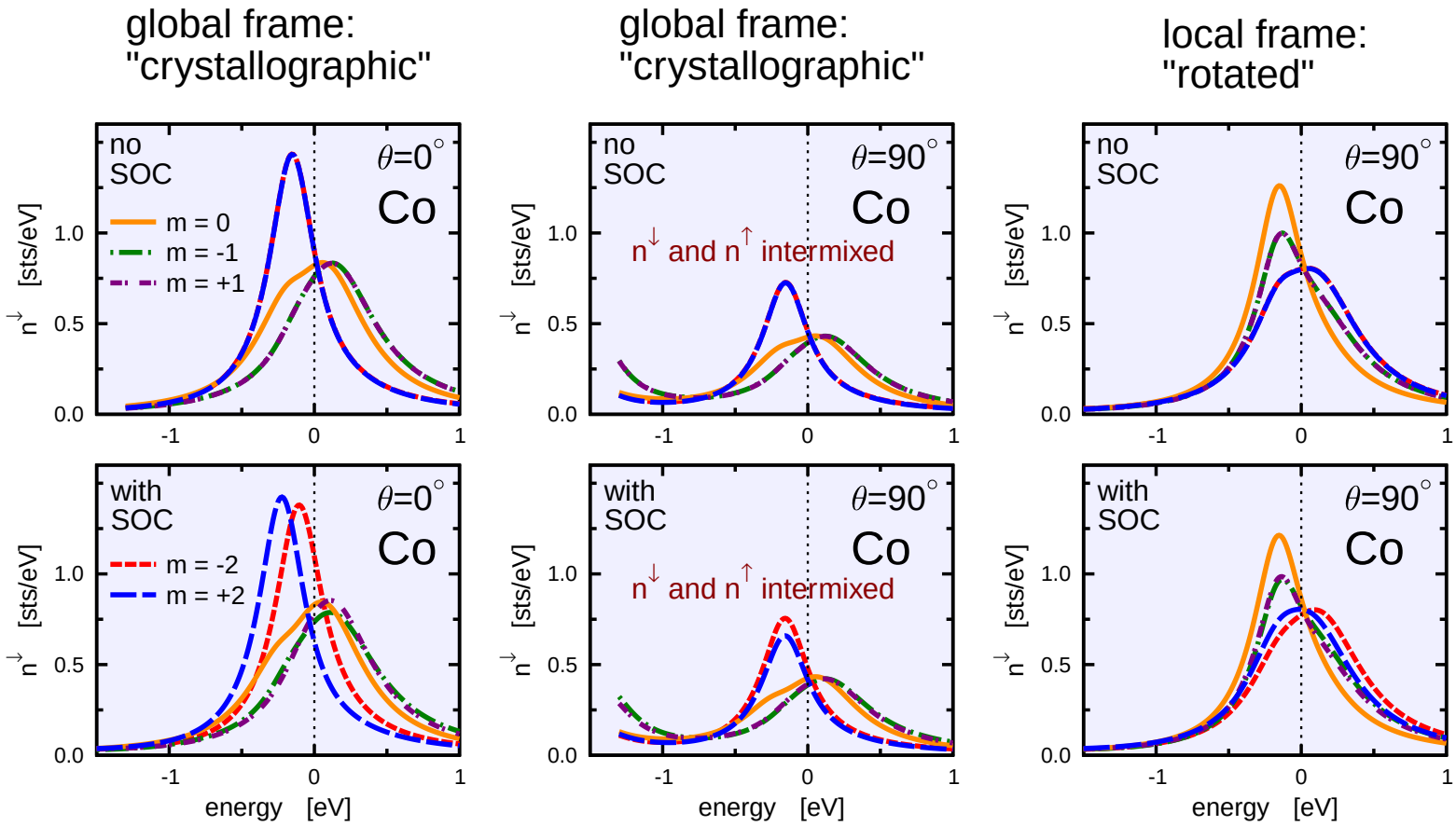
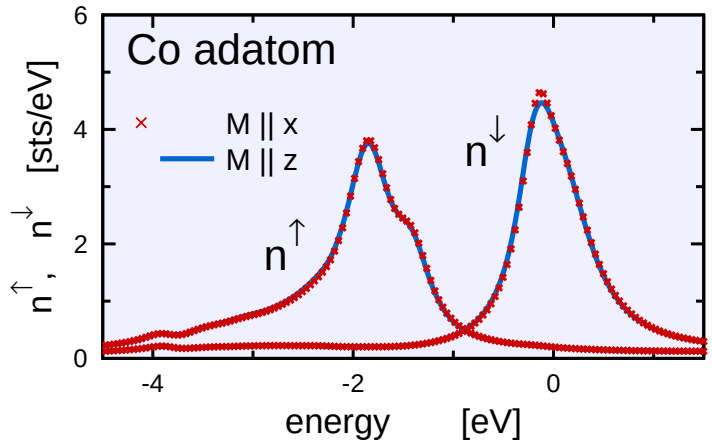


If $\boldsymbol{M} \nparallel \hat{\boldsymbol{z}}$, then $n_{\ell m}^{(\mathrm{glo})\uparrow}(E)$ and $n_{\ell m}^{(\mathrm{glo})\downarrow}(E)$ are identical.

How to maintain spin separation even if $\boldsymbol{M} \nparallel \hat{\boldsymbol{z}}$

Resolving the spin can be done *(with a good accuracy)* once and for all, in any reference frame where it can be done.



- Start by resolving the DOS according to the spin in the local reference frame, where $\boldsymbol{M} \| \hat{\boldsymbol{z}}^{(\mathrm{loc})}$ (without resolving the DOS into the m-components).
- Assume that the separation of spin components is maintained through subsequent transformation.
  - All the further manipulations will be applied to minority-spin DOS and to majority-spin DOS separately.

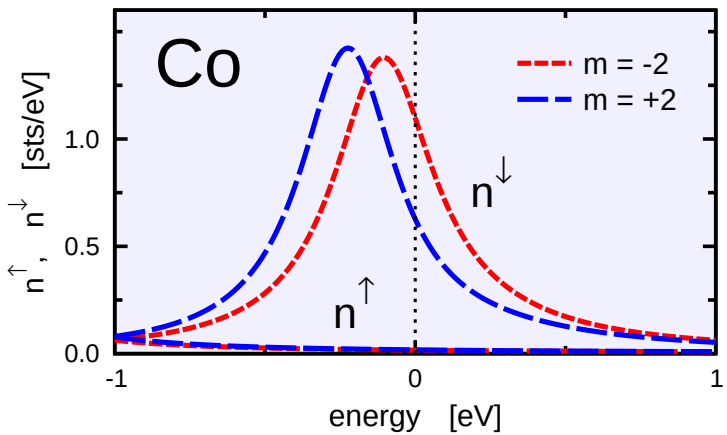
Transforming $n_{\ell m}$ between global and local frames

Transformation between $n_L^{(\mathrm{loc})}$ and $n_L^{(\mathrm{glo})}$ generally not possible.
Only the Green's function $G(E)$ can be properly transformed.

The transformation of the DOS can be done if $G(E)$ is diagonal in the global reference frame.
This is often the case.

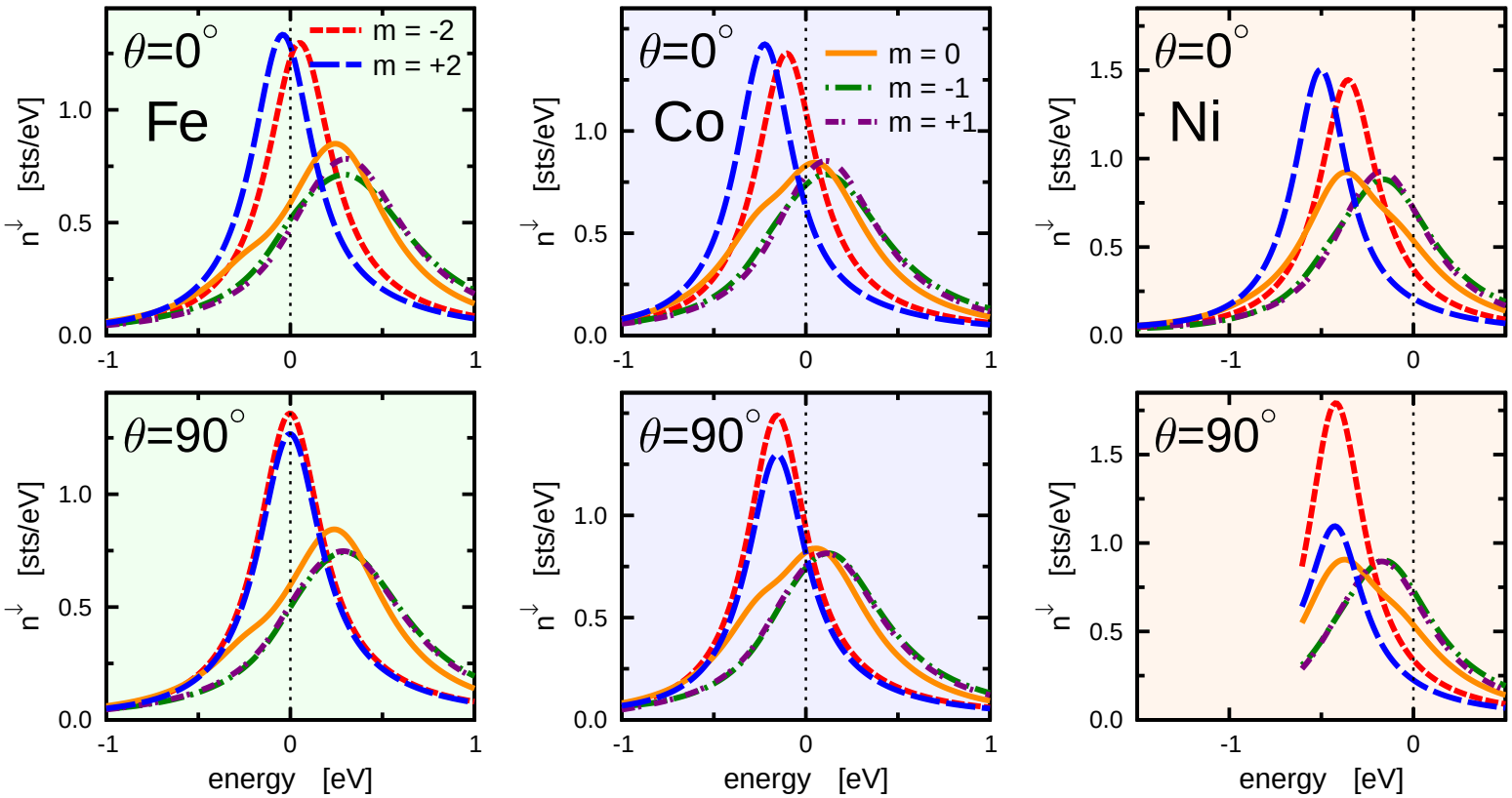
Assume further:

$$n_{|m|}^{(\mathrm{glo})} = n_{-|m|}^{(\mathrm{glo})}$$
$$n_{|m|}^{(\mathrm{loc})} = n_{-|m|}^{(\mathrm{loc})}$$



Then a tranformation between $n_L^{(\mathrm{loc})}$ and $n_L^{(\mathrm{glo})}$ can be performed.

Change of DOS upon rotation of magnetization M



- The influence of the SOC is significantly larger for θ=0° than for θ=90°.
- For θ=0° the SOC splits the m=±2 peak into two and shifts their positions in different directions.

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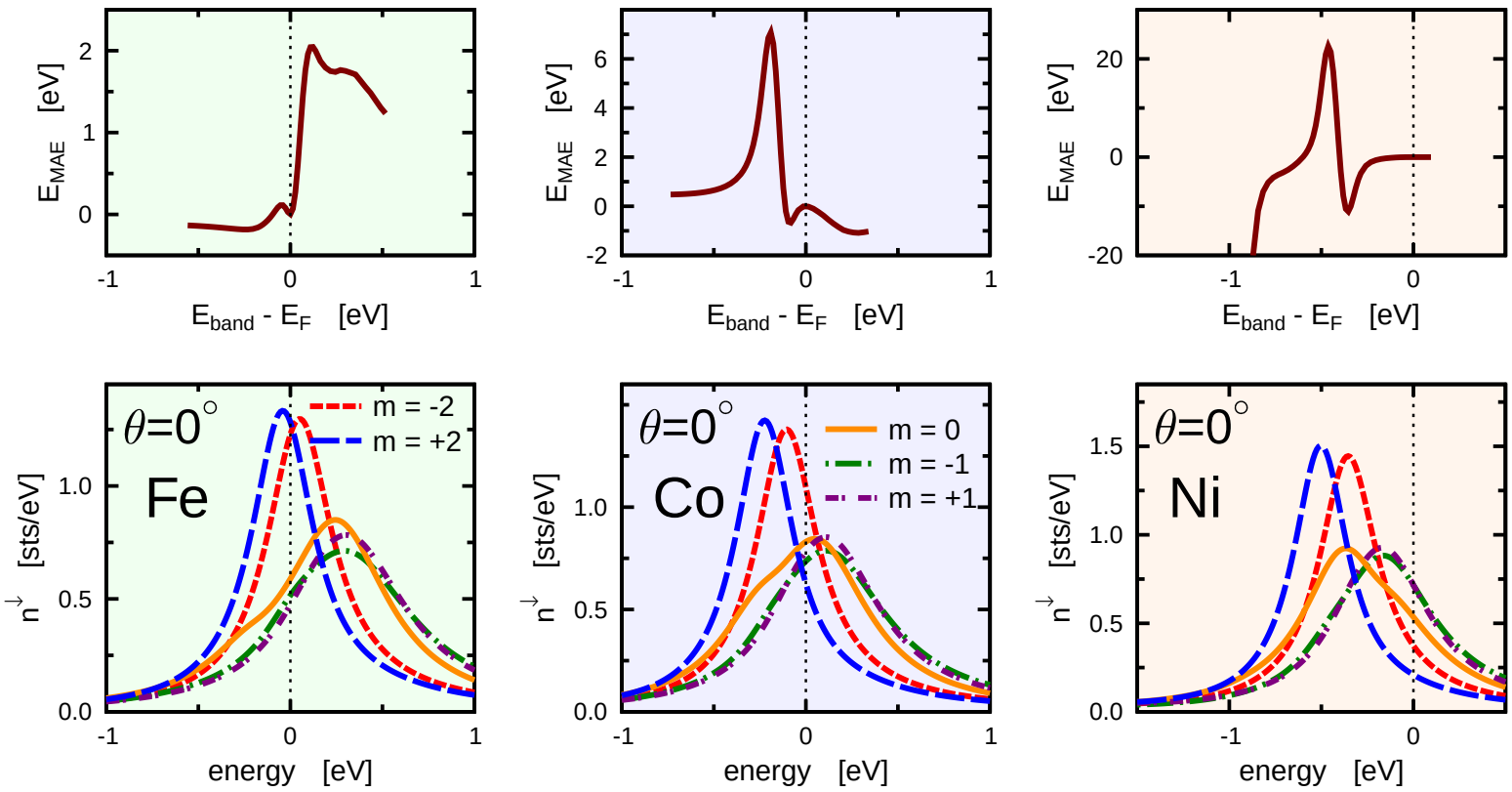
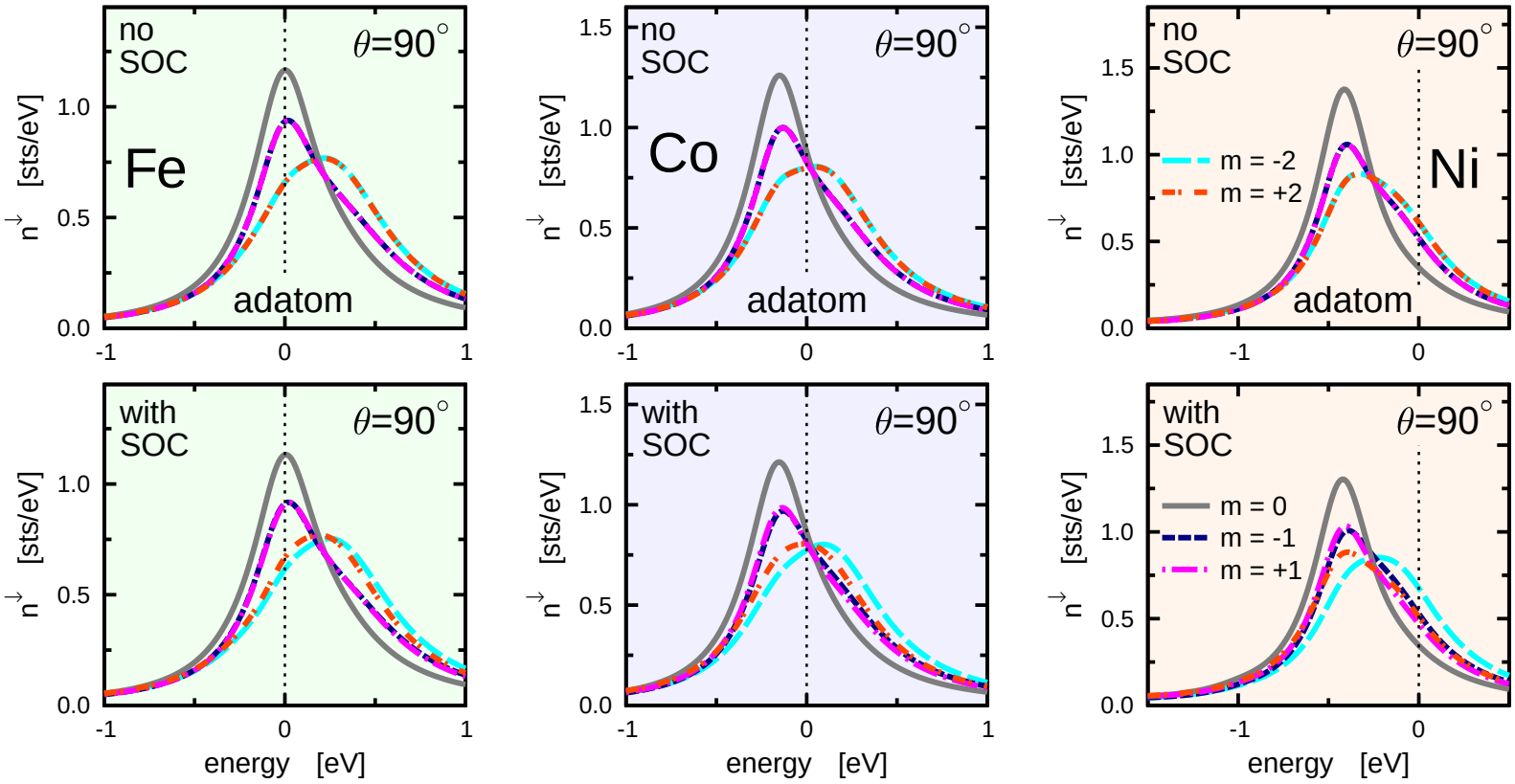
Dependence of MAE on the position of the Fermi energy



- A sharp peak in the MAE at the energy where there is a peak for the $|m|$=2 component.
- For the Fe adatom this is overshadowed by the fact that, in this case, also the $|m|$=1 states are affected by SOC.

DOS for inplane magnetization in a local frame



- The θ=90° case cannot be directly compared the θ=0° case because the definitions of the m-components differ.
- Effect of SOC for θ=90° is less than for θ=0°.

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Model Hamiltonian

Simple model with only the crystal-field effects taken into account: Electron feels only the Coulombic field generated by charges located at the positions of the nuclei.

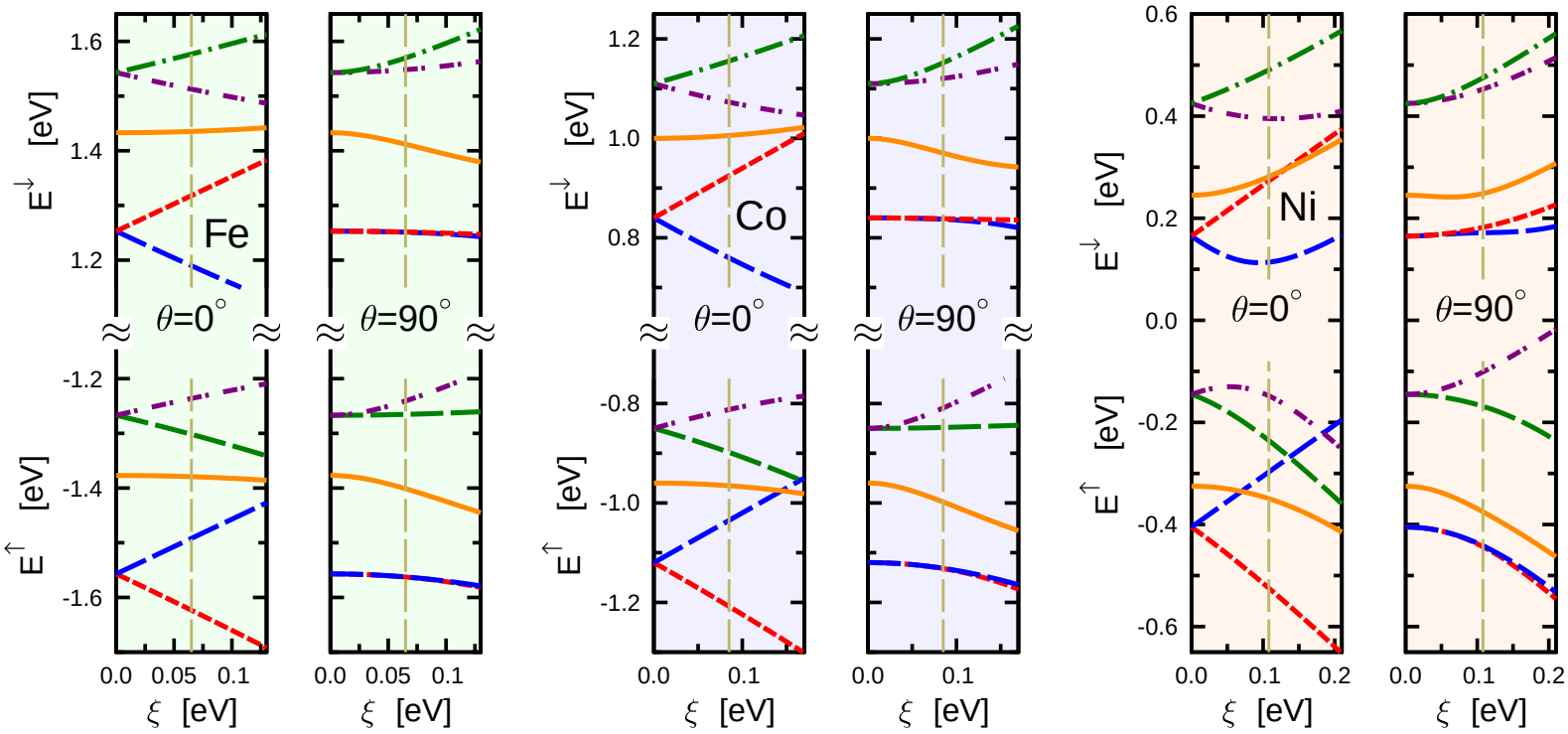
Restrict to d electrons in an axial field (corresponding to D_{4d}, i.e., antiprism symmetry).

$$H = H^{(\mathrm{cry})} + H^{(\mathrm{ex})} + H^{(\mathrm{SOC})}$$

- $H^{(\mathrm{cry})}_{ms,m's'}$ is determined by two parameters, resulting in three spin-degenerate energy levels.
- To distinguish between two orientations of the magnetization, we keep the spin quantization axis fixed (parallel to z) and vary the Hamiltonian $H^{(\mathrm{ex})}$.
- $H^{(\mathrm{SOC})} = \xi \boldsymbol{L} \cdot \boldsymbol{S}$

Energy levels for model Hamiltonian

Dependence of eigen-energies of the model Hamiltonian on the SOC strength ξ for two orientations of $\boldsymbol{M}$.



Thin dashed lines mark ξ values appropriate for each element.

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Conclusions

- The effect of SOC on adatoms that only weakly hybridize with a substrate consists in splitting atomic-like levels that would be degenerate otherwise.
  - The splitting is much larger if the magnetization is oriented perpendicular to the surface than if it is oriented parallel to the surface.
  - The splitting is a combined result of crystal field, exchange splitting and spin-orbit coupling.
- If the originally degenerate level is close to the Fermi level, one of the peaks can be pushed above it, decreasing thereby the energy of the system.
  - This results in a significant contribution to the magnetocrystalline anisotropy of adatoms.