Magnetocrystalline anisotropy of adatoms: How to make it big?

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Outline

- MAE: What is it about?
- Scaling of MAE with SOC: case of adatoms
- SOC-induced splitting of DOS as a marker of MAE
- Message to the mankind

Magnetic Anisotropy Energy (MAE)

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

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

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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?
  - The way the MAE scales with the SOC tells us something about its mechanism.
    - People still strive to understand how to make MAE as high as possible [Jesche *et al.* Nature Comm. (2014), Rau *et al.* Science (2014), Khajetoorians & Wiebe Science (2014), Antropov *et al.* arXiv (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 (SOC is scaled by λ):

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

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

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

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  - $\delta E^{(2)}$ scales as $\lambda^2 \Rightarrow$ MAE scales with SOC **quadratically**.
  - 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

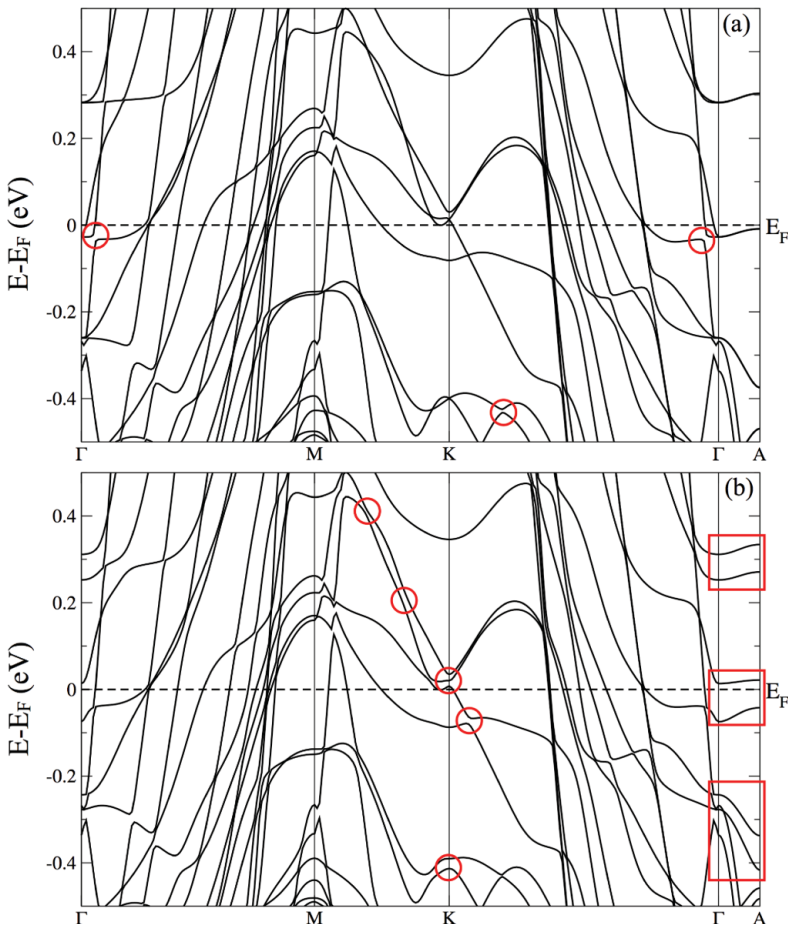
  $$\sim m_\ell \, \lambda \, \cos\theta \ ,$$

  m_ℓ is the (orbital) magnetic quantum number,
  λ is the SOC scaling factor,
  θ is the angle between $\hat{\mathbf{M}}$ 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 this effect could scale linearly with the SOC strength λ but the situation is more complicated... [Lessard *et al.* (1997), Gimbert & Calmels (2012)]

SOC-scaling of contribution due to degenerate states



Gimbert & Calmels PRB (2012)

- ☹ For extended systems, the degeneracy is limited only to a small part of the Brillouin zone, hence it does not affect the overall quadratic scaling of the MAE with the SOC.

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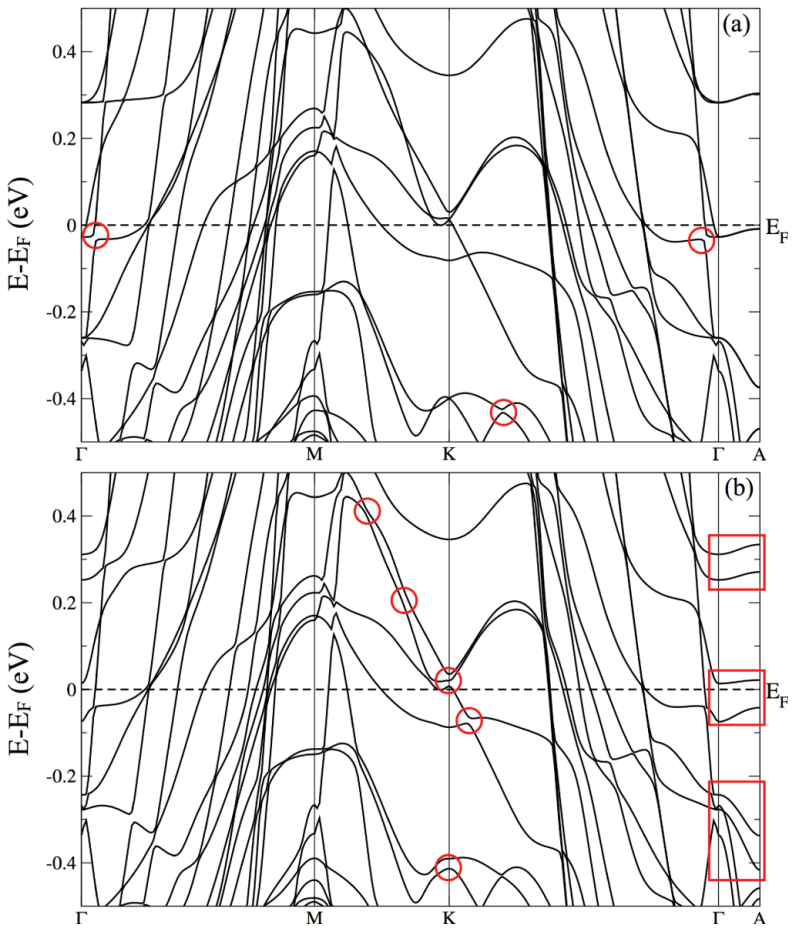

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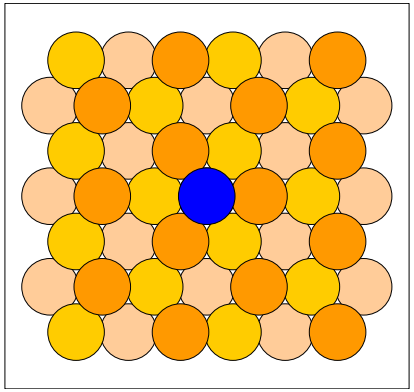
- What if the **k**-dependence is suppressed (as in the case of adatoms)?

  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 [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
- Scaling of the SOC done via identifying the SOC-related term by means of an approximate Dirac equation [Ebert *et al.* PRB **53**, 7721 (1996) extending the scheme of Koelling & Harmon (1977) and MacLarren & Victora (1994)]

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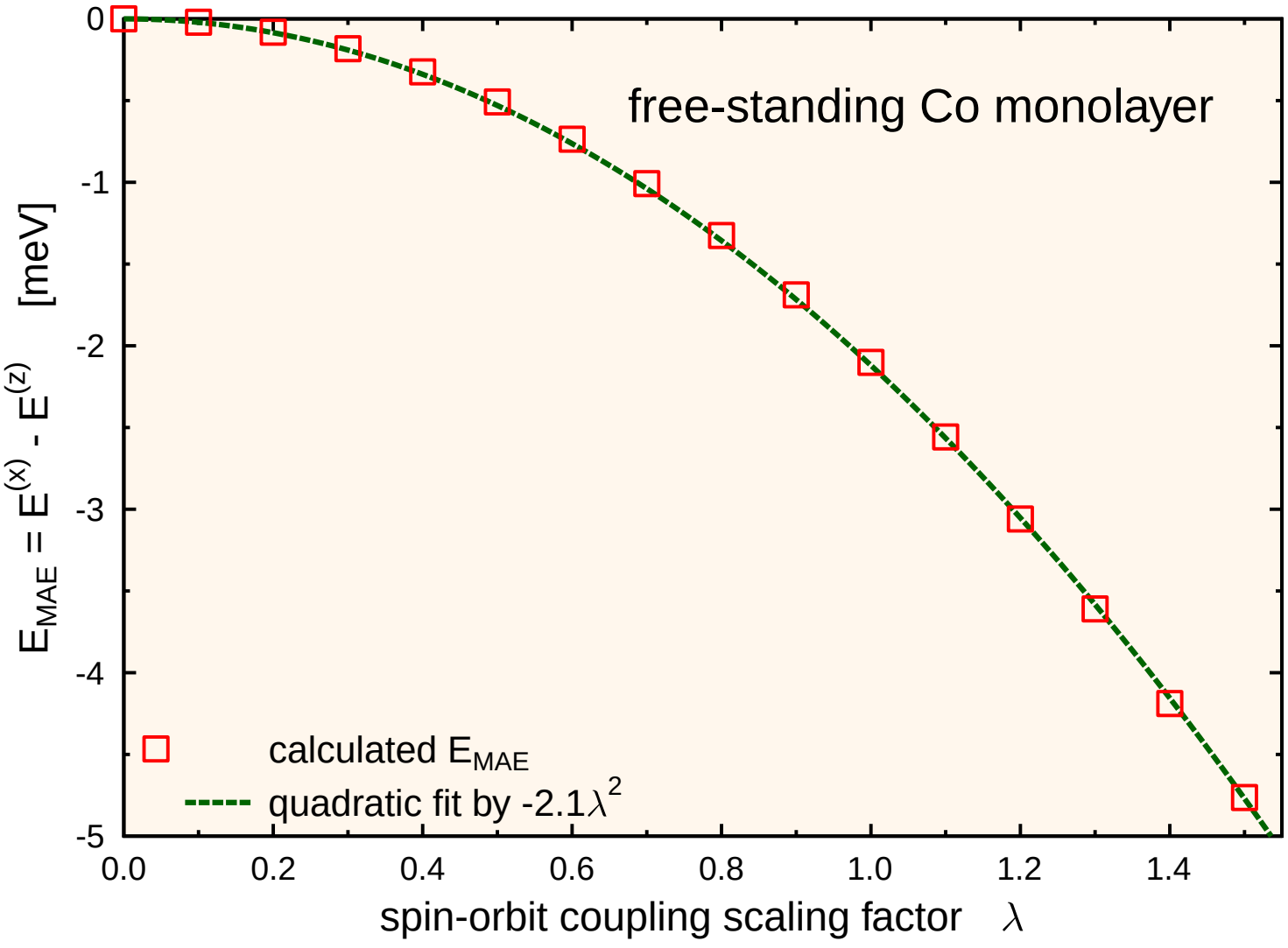
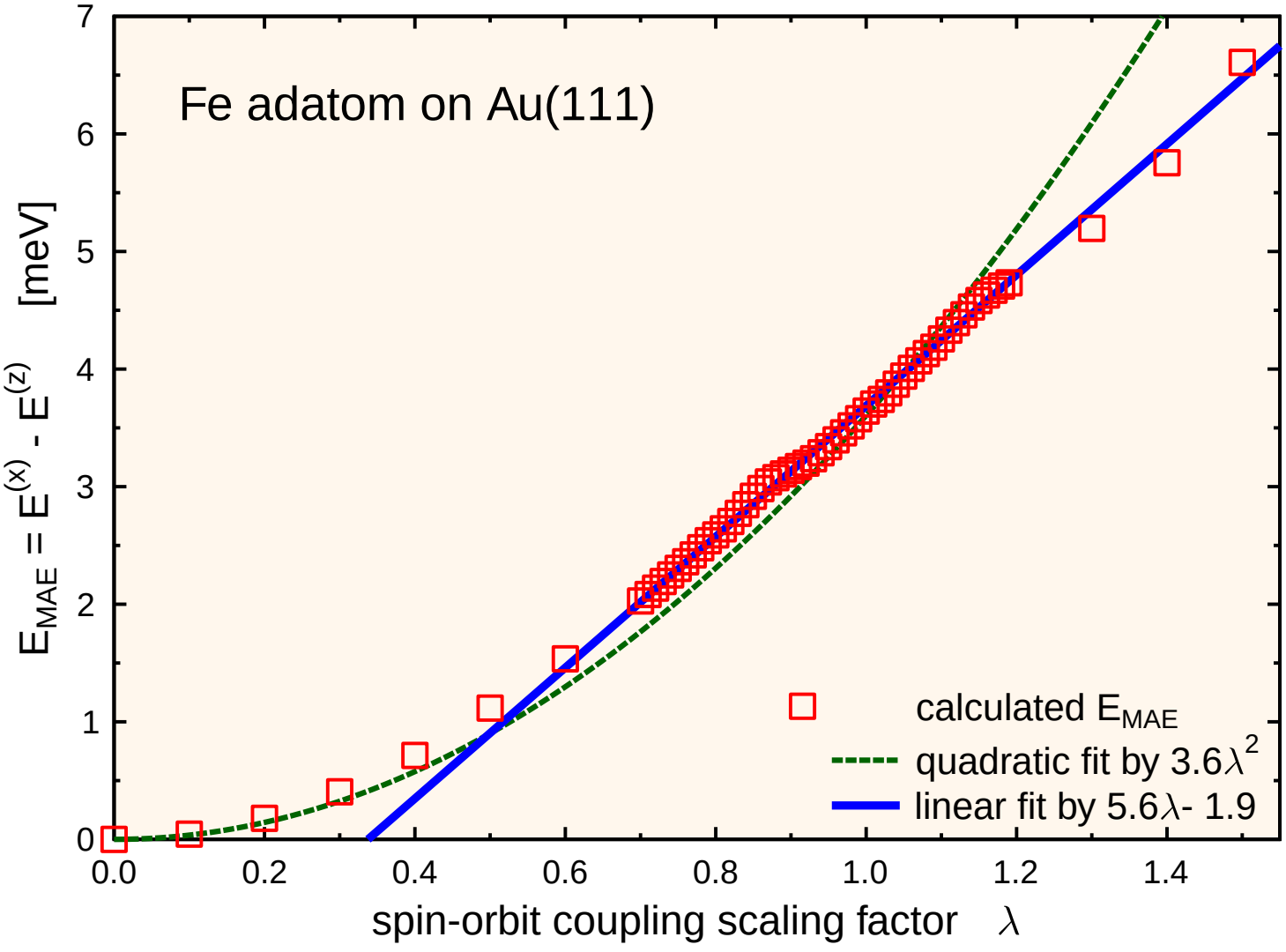
When things work: Free-standing monolayers



MAE as function of SOC: Fe adatom



Fits sought within the range λ=0.8–1.2, i.e., for realistic SOC values.

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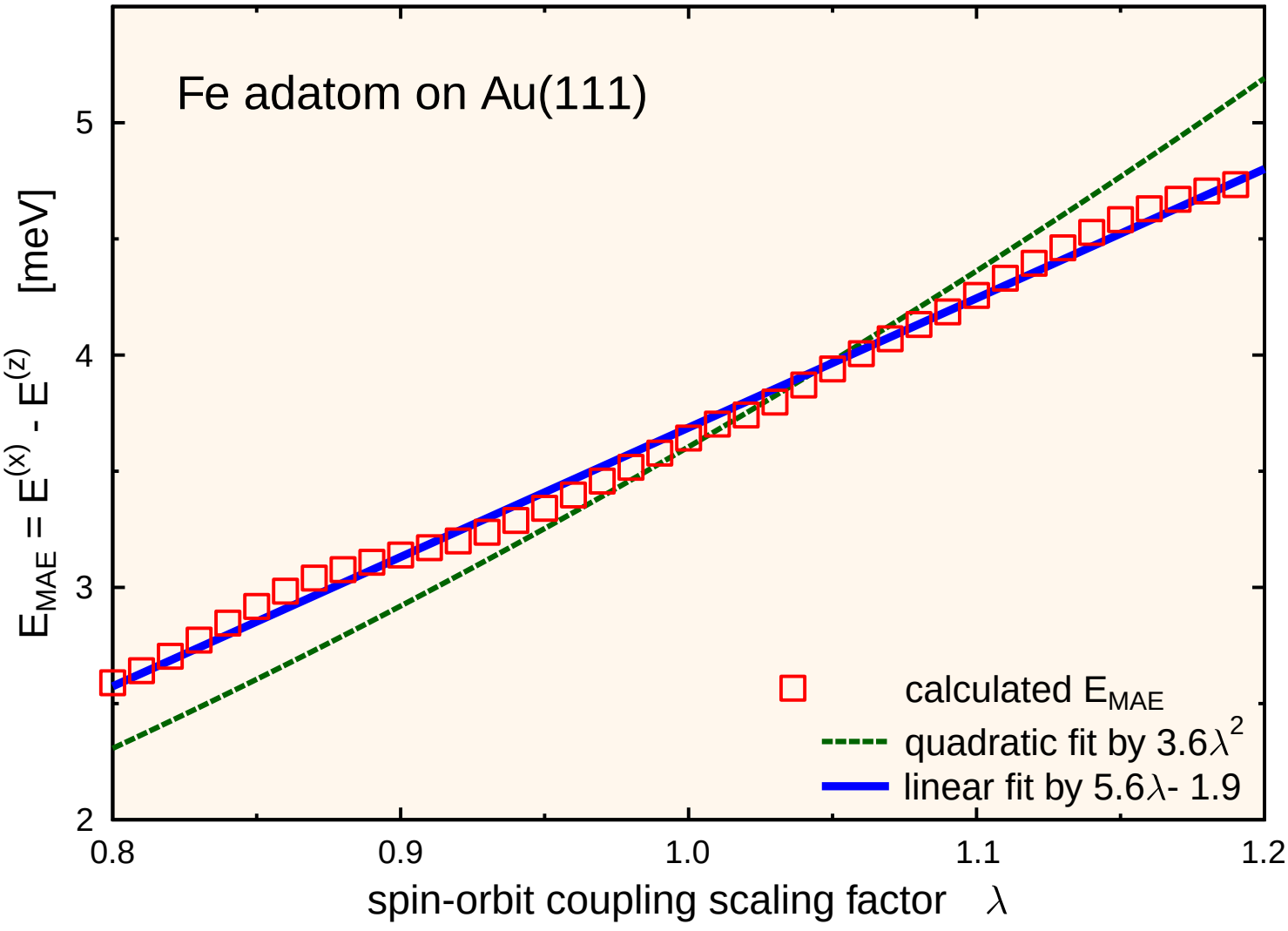

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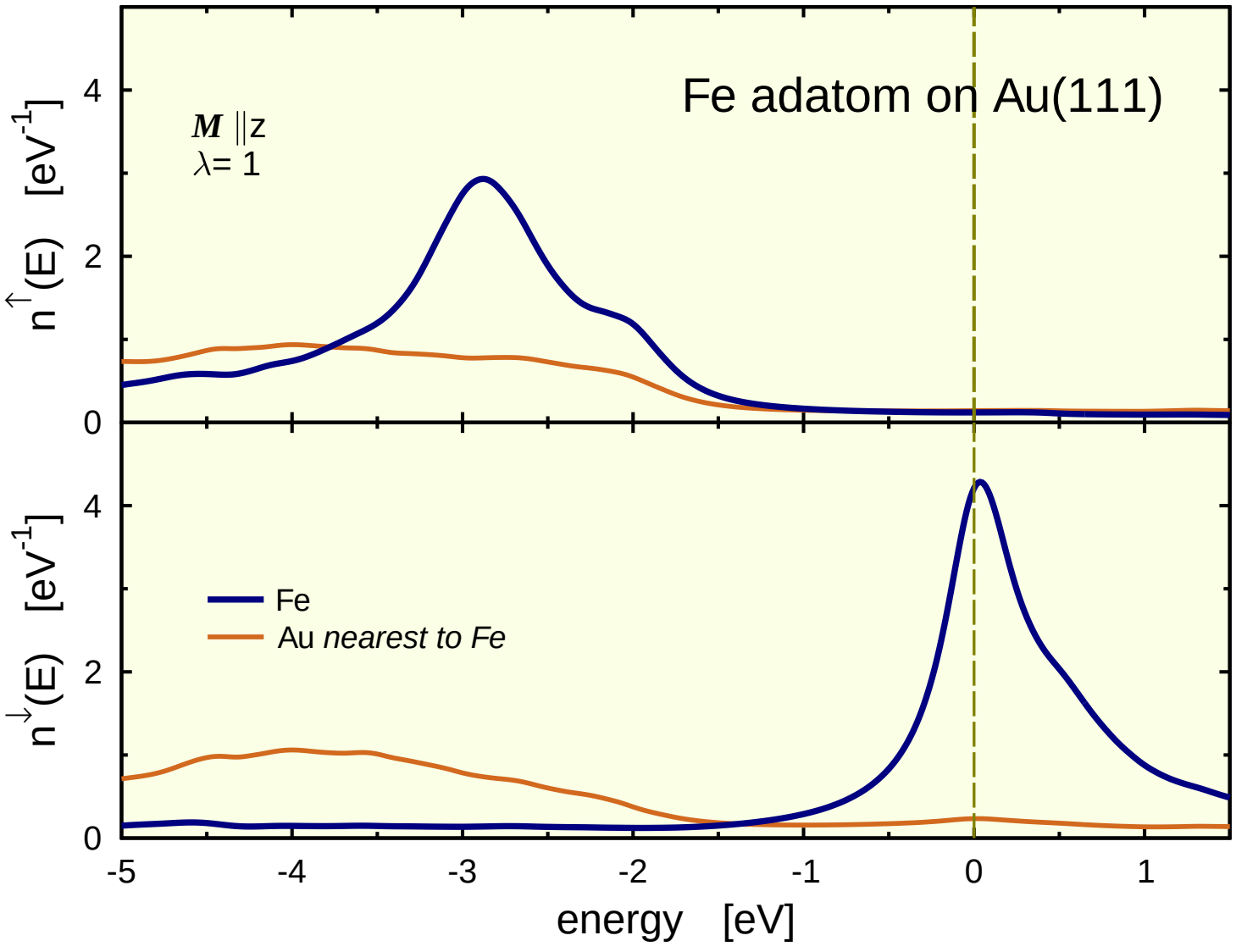
SOC-scaling of MAE: verdict for adatoms

For $3d$ adatoms on Au(111), the MAE does not scale with the SOC quadratically (in the range of realistic SOC values).

Rather, this scaling is quasi-linear.

$\Rightarrow$ For realistic SOC values, we are in the regime where the MAE cannot be described by a perturbation theory.

DOS for Fe adatom



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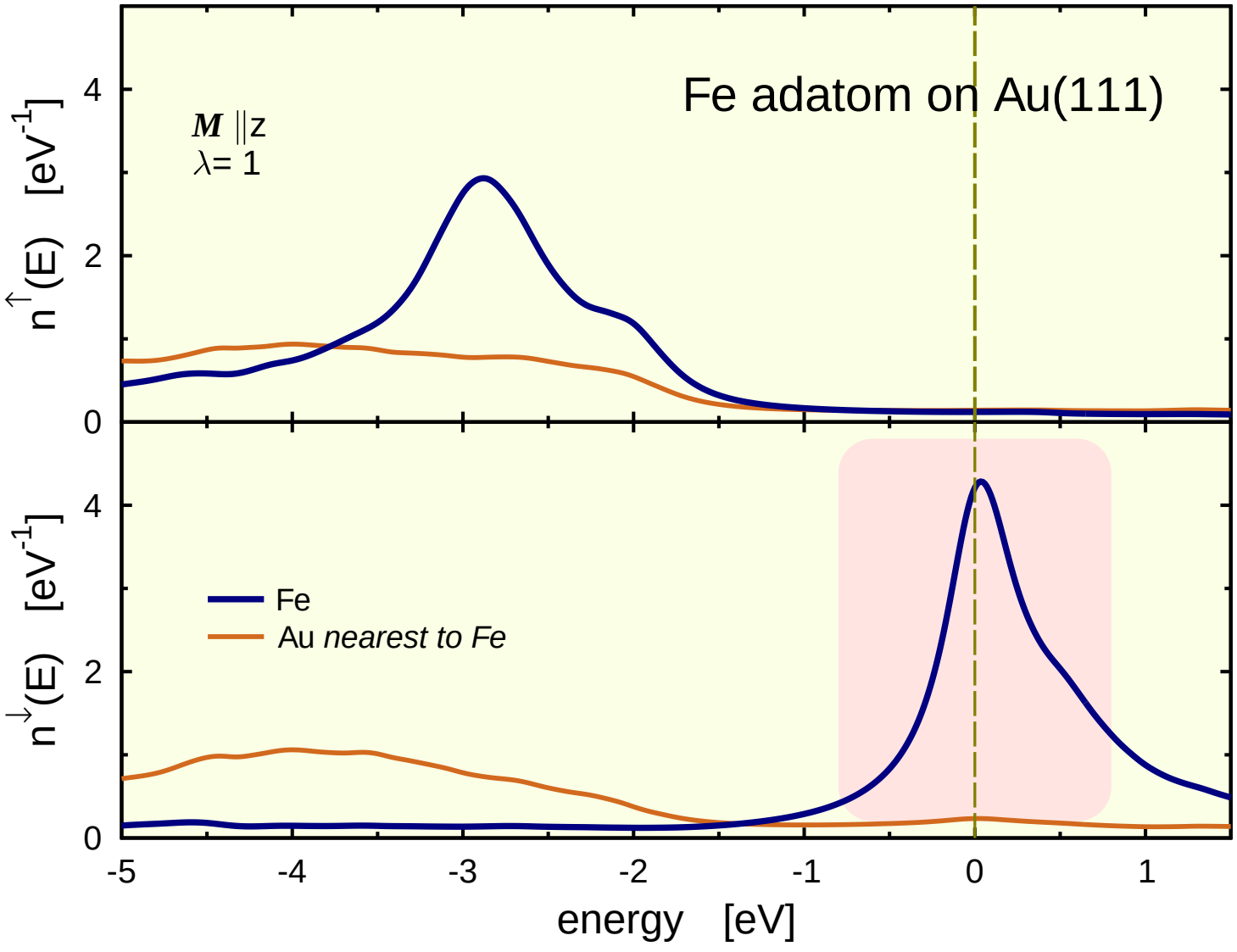
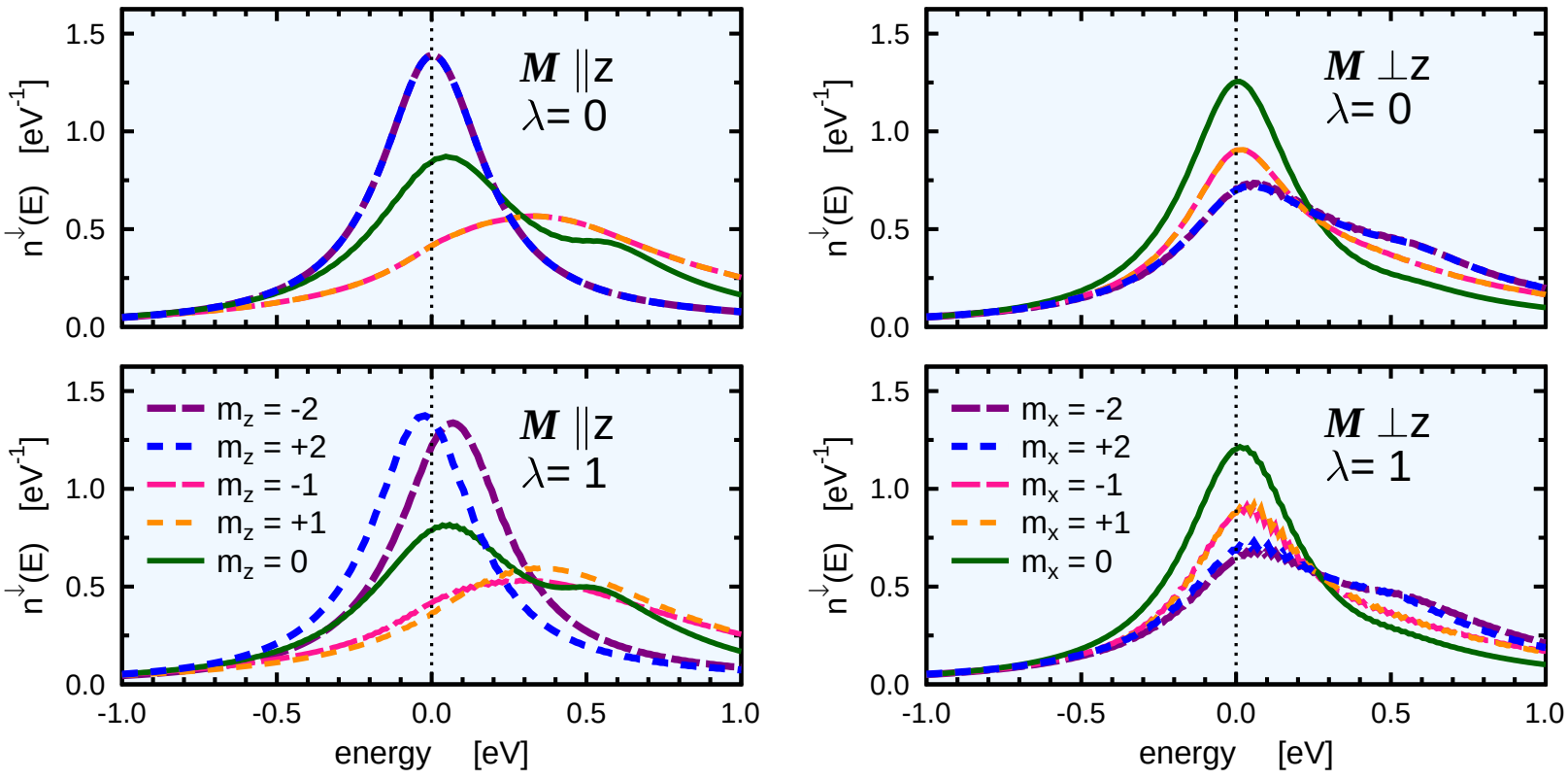


Effect of SOC on m_ℓ-resolved DOS: Fe adatom



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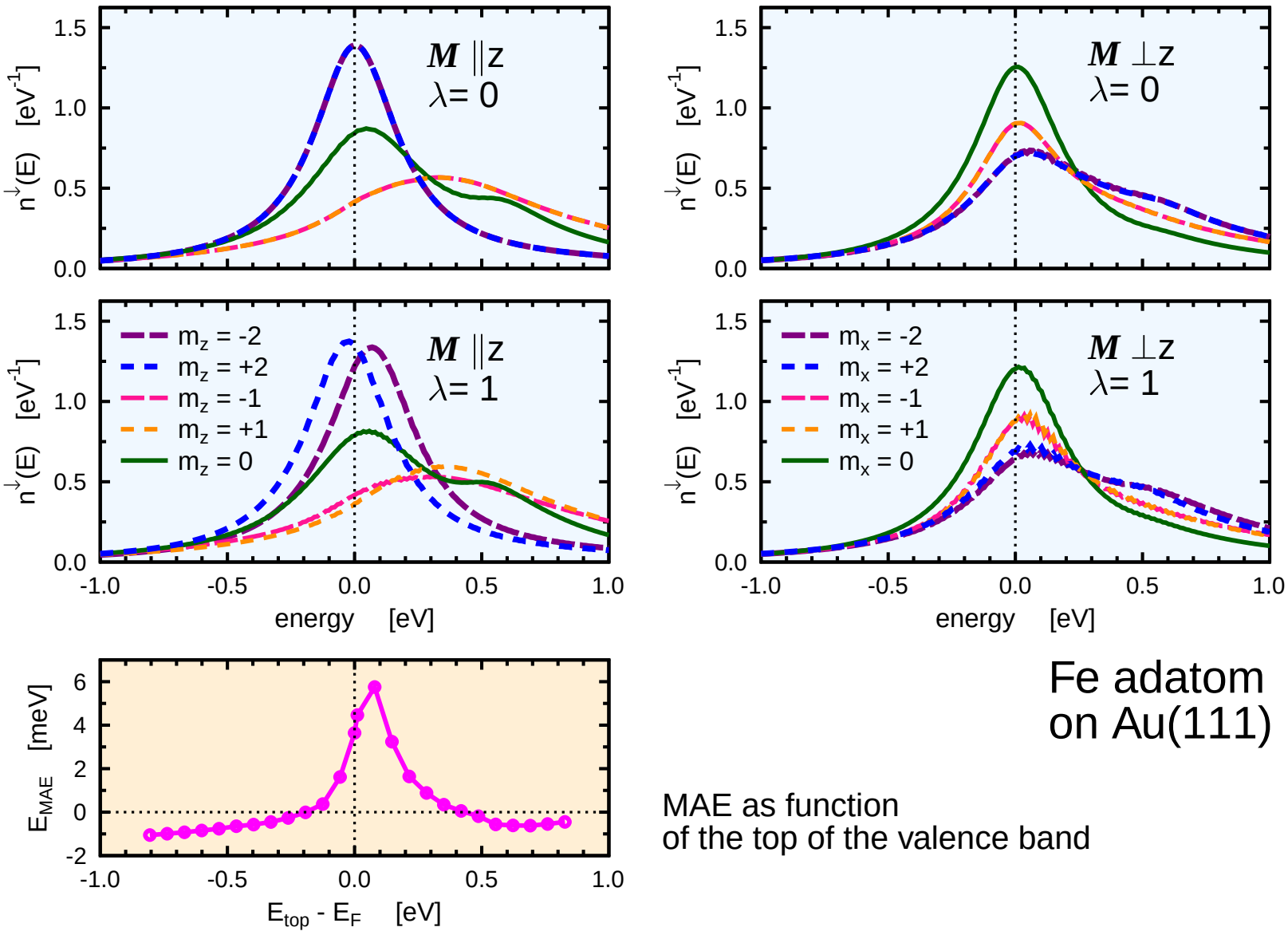

Fe adatom
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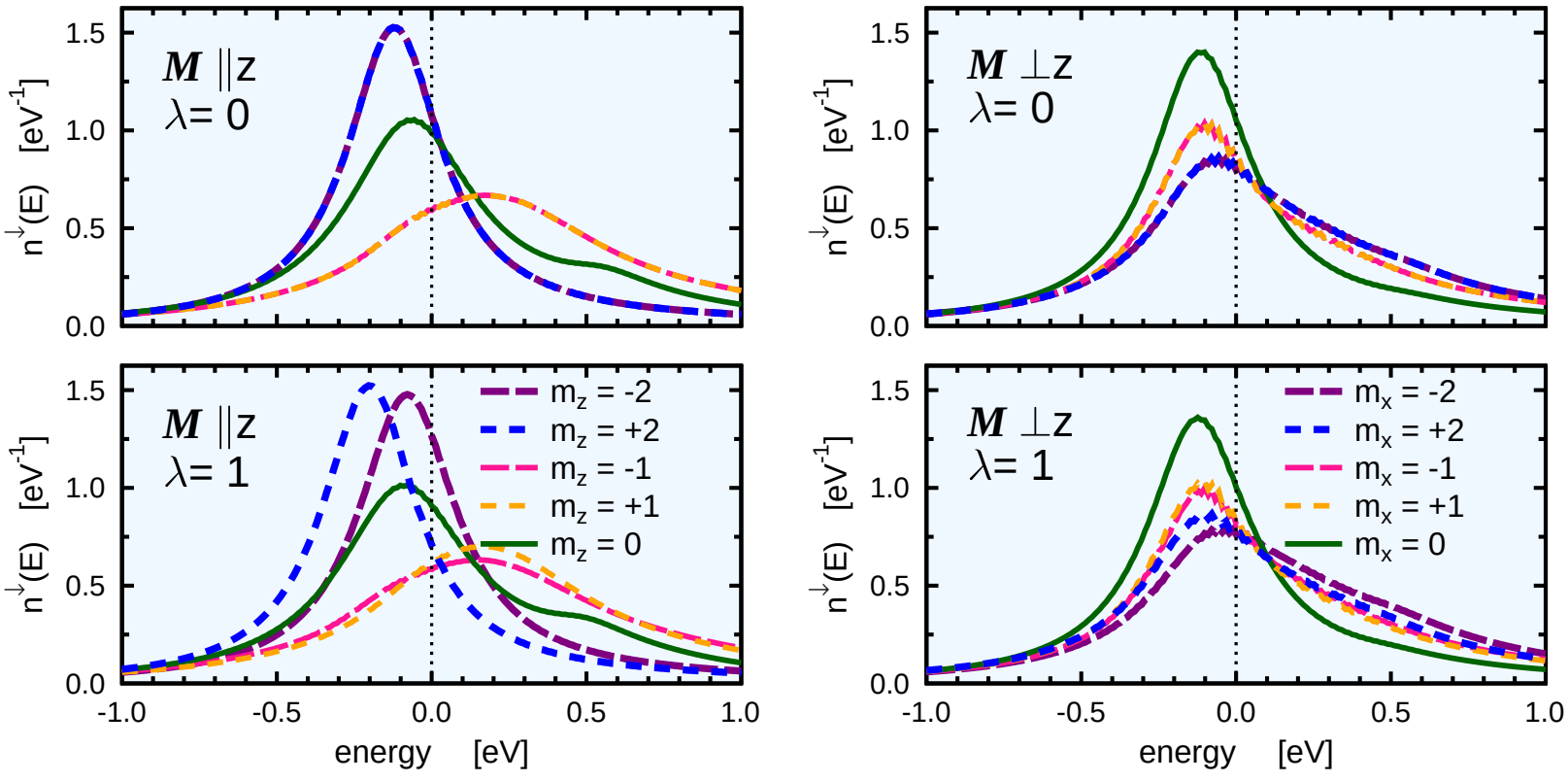
MAE as function
of the top of the valence band

Effect of SOC on m_ℓ-resolved DOS: Co adatom



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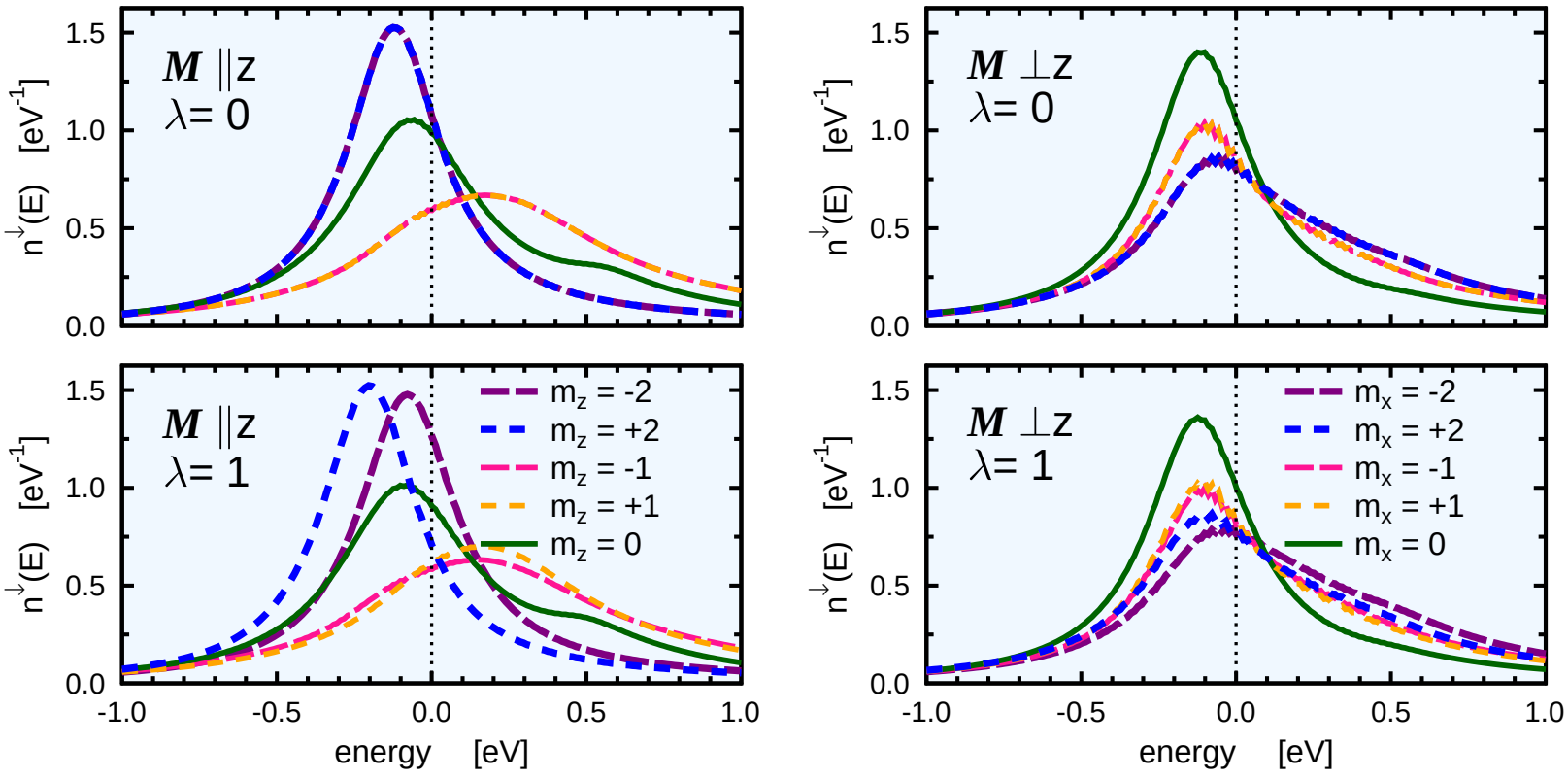

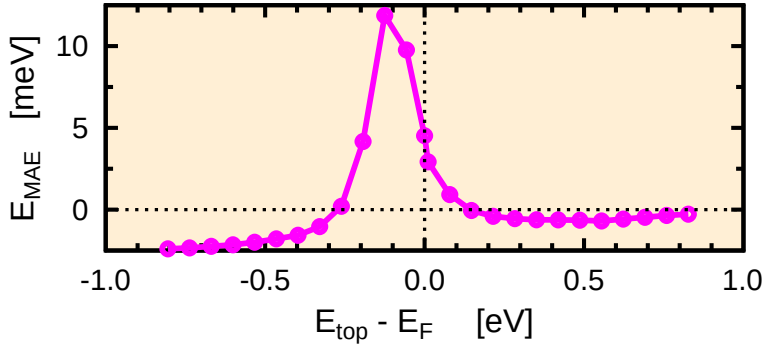

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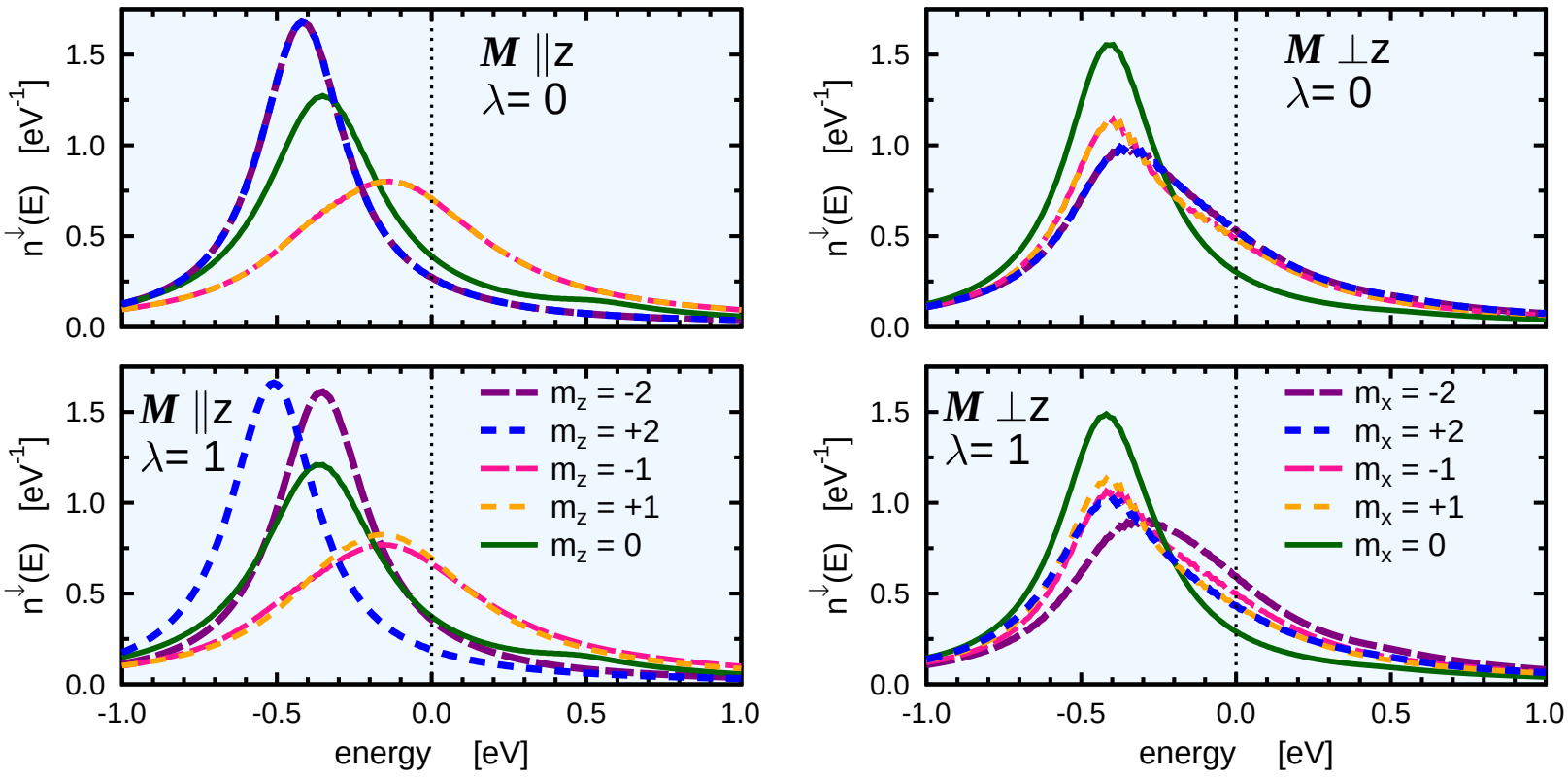
Effect of SOC on m_ℓ-resolved DOS: Ni adatom



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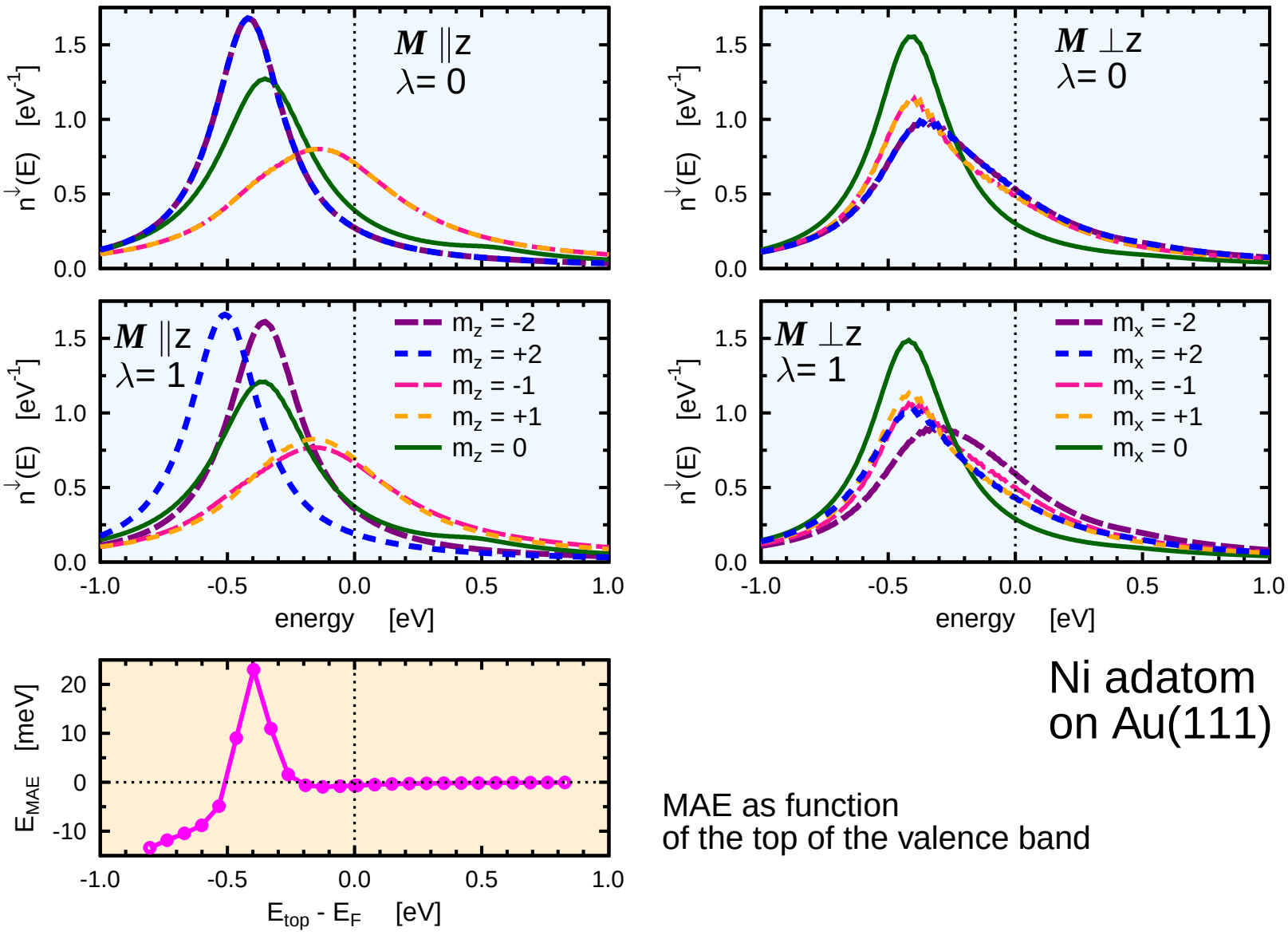

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Conclusions

- For adatoms, if there is a degeneracy between states of different m_ℓ, it is not restricted only to a small region of the **k**-space and hence it affects the DOS.

- Because of this, a significant contribution to the MAE appears which cannot be described within the perturbation theory (it does not scale quadratically with the SOC...)

- In such a case, the mechanism behind the (large) MAE is the pushing of one of the m_ℓ-resolved DOS components above the Fermi level.

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Thank you!

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