Orbital Magnetism in Molecules and Solids

Proposal for a Research Grant

Helmut Eschrig,[1] **Gotthard Seifert,**[2] **and Manuel Richter**[1]

[1]IFW Dresden e.V., D-01171 Dresden, Germany

[2]Technische Universität Dresden, D-01062 Dresden, Germany

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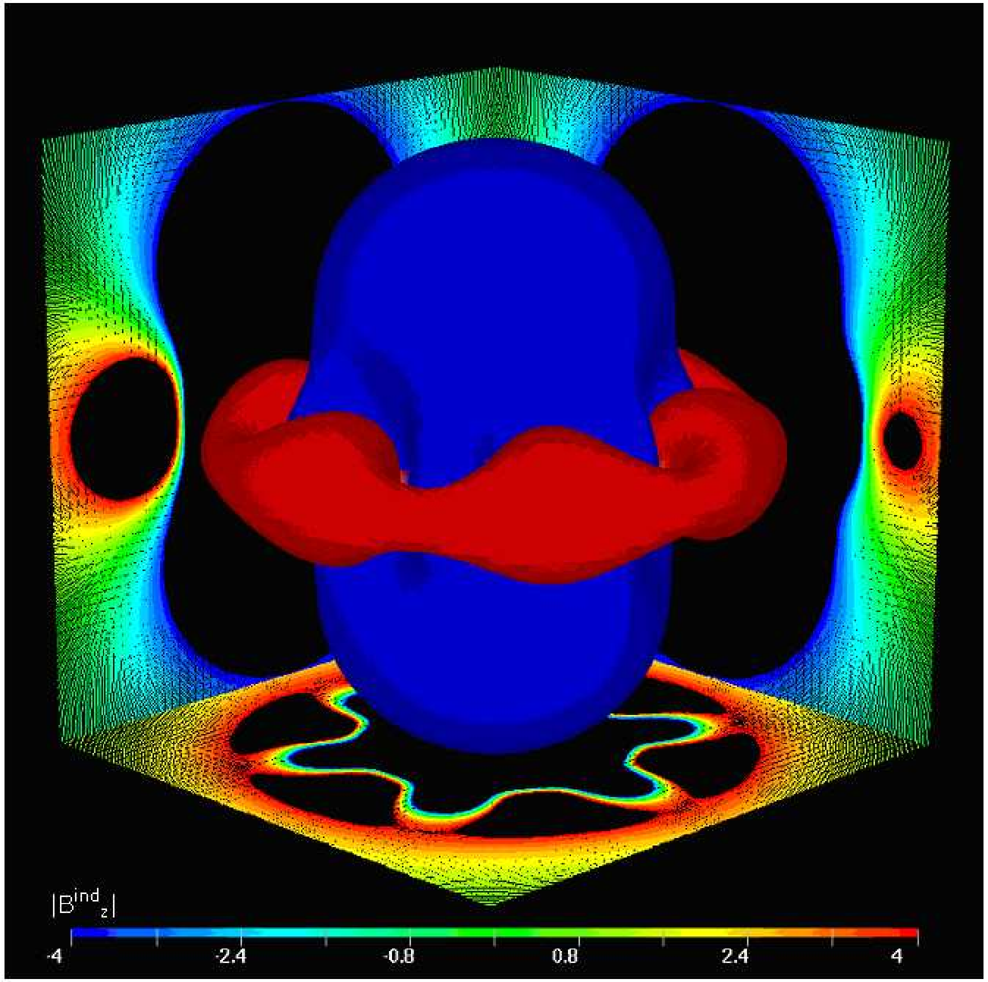
Results: Diamagnetic response in molecules
Results: Orbital magnetism of Co impurities in Au

Orbital magnetism in DFT: state-of-the-art
Derivation of orbital polarization corrections from CDFT

Agenda: Development of numerical tools
Agenda: Physical systems to be investigated

Summary

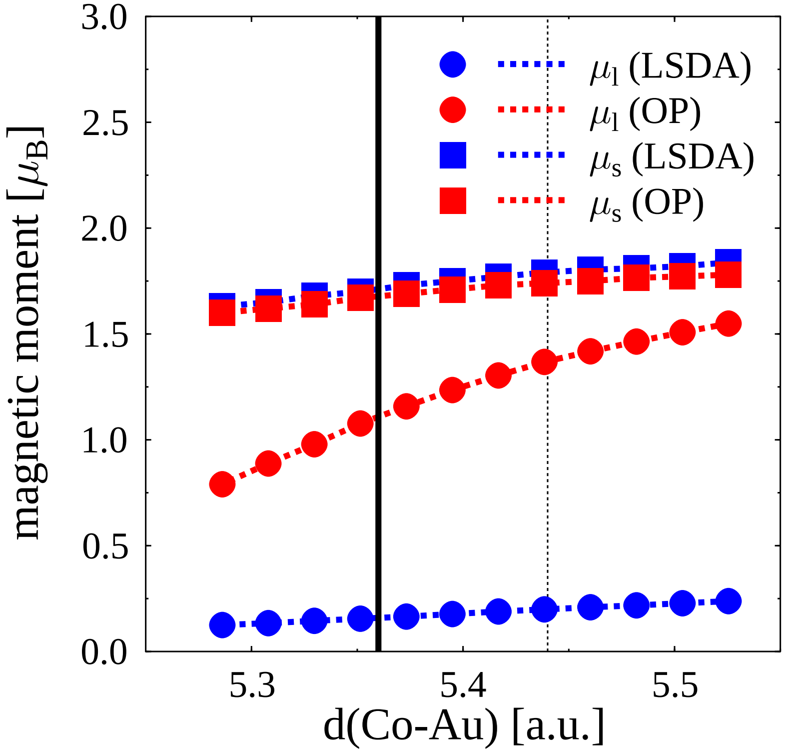
Orbital polarization in diamagnetic in molecules



Induced magnetic field in a benzene molecule.

External field perpendicular to the ring plane.

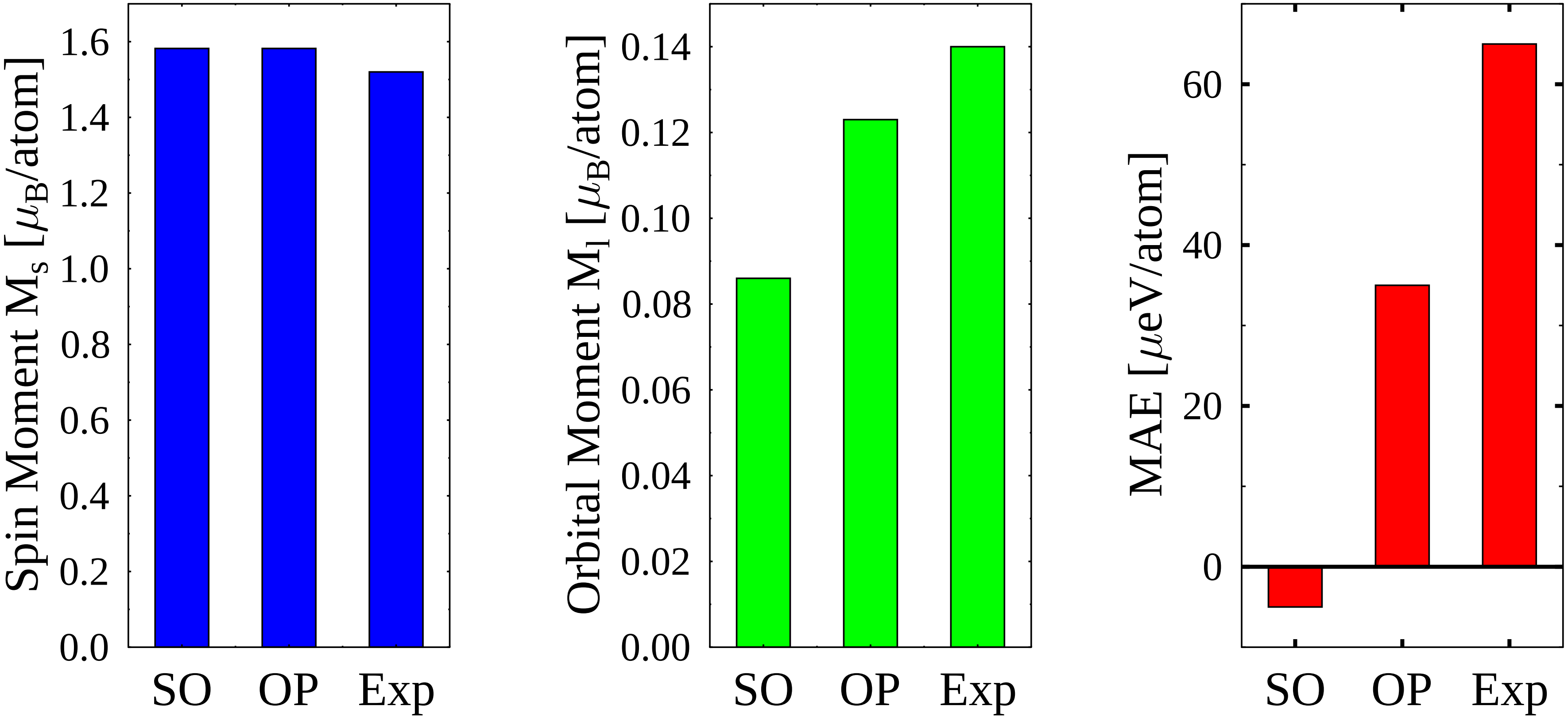
Cobalt impurities in Gold



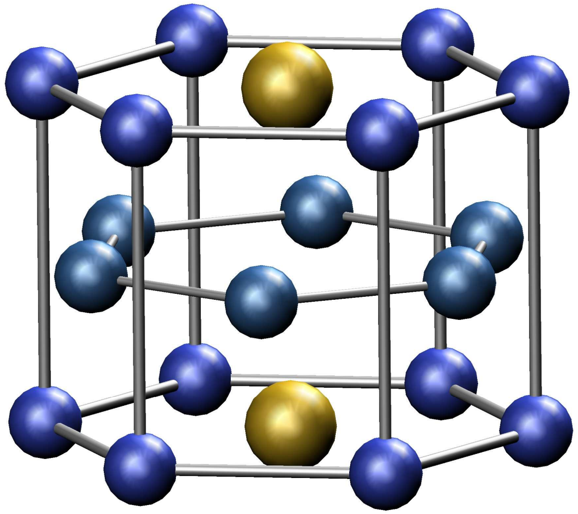
Au$_{31}$Co supercell modell:
influence of NN relaxation

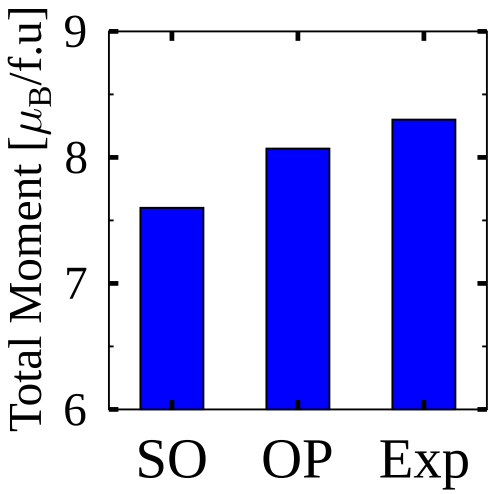
Method	μ_l/μ_s
Experiment (XMCD) Brewer *et al.*, 2004	≈ 0.35
LSDA	≈ 0.07
LSDA+OP	≈ 0.80
LSDA+OP + Relaxation	≈ 0.65

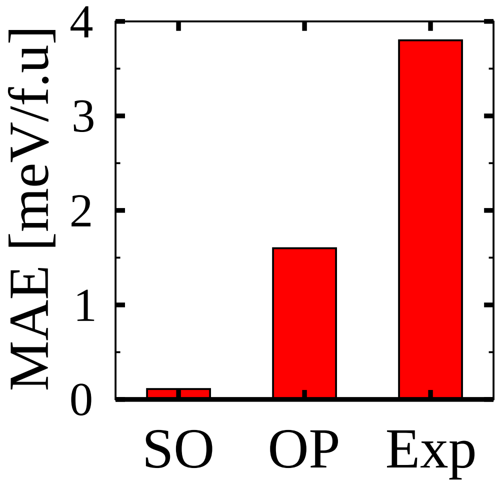
Orbital magnetism in hcp Co: DFT results



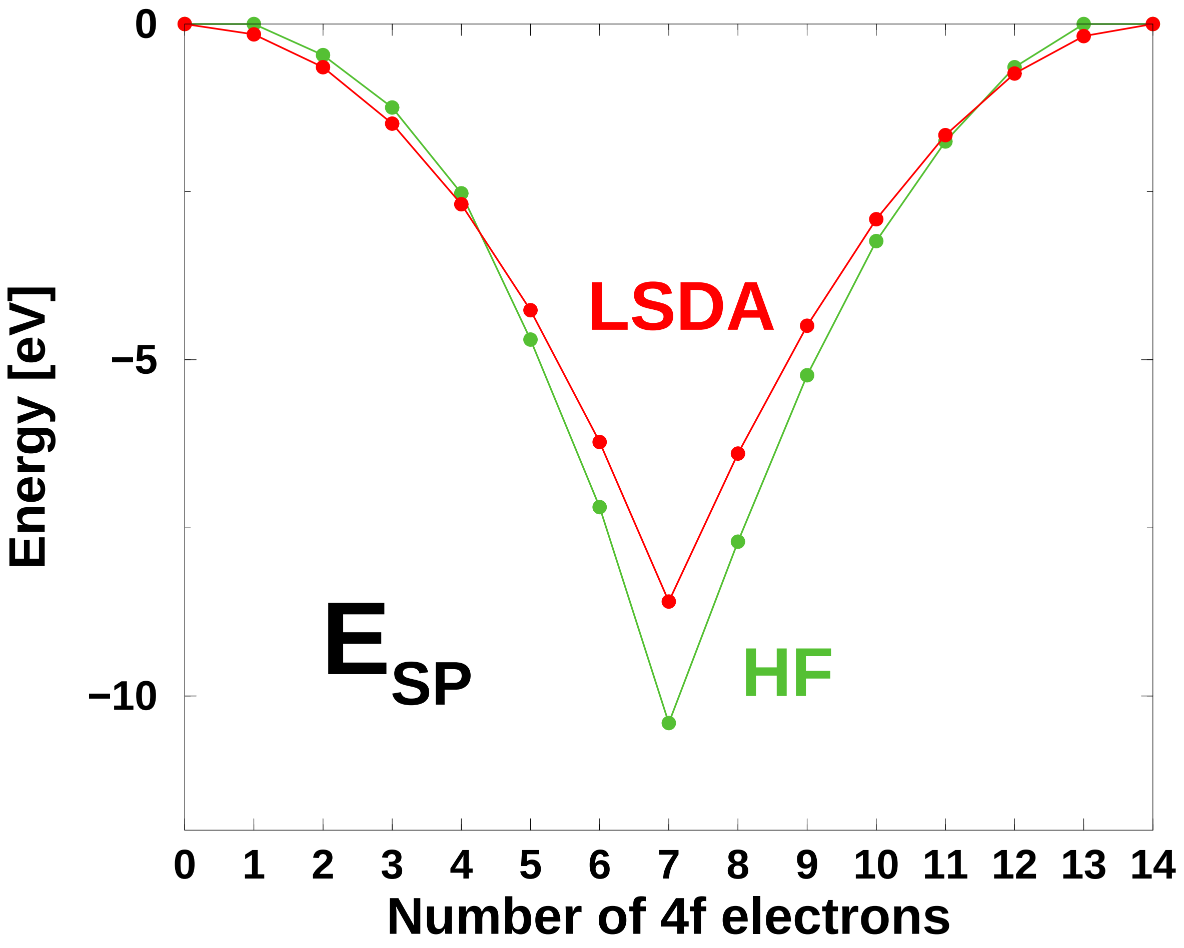
Orbital magnetism in YCo_5: DFT results







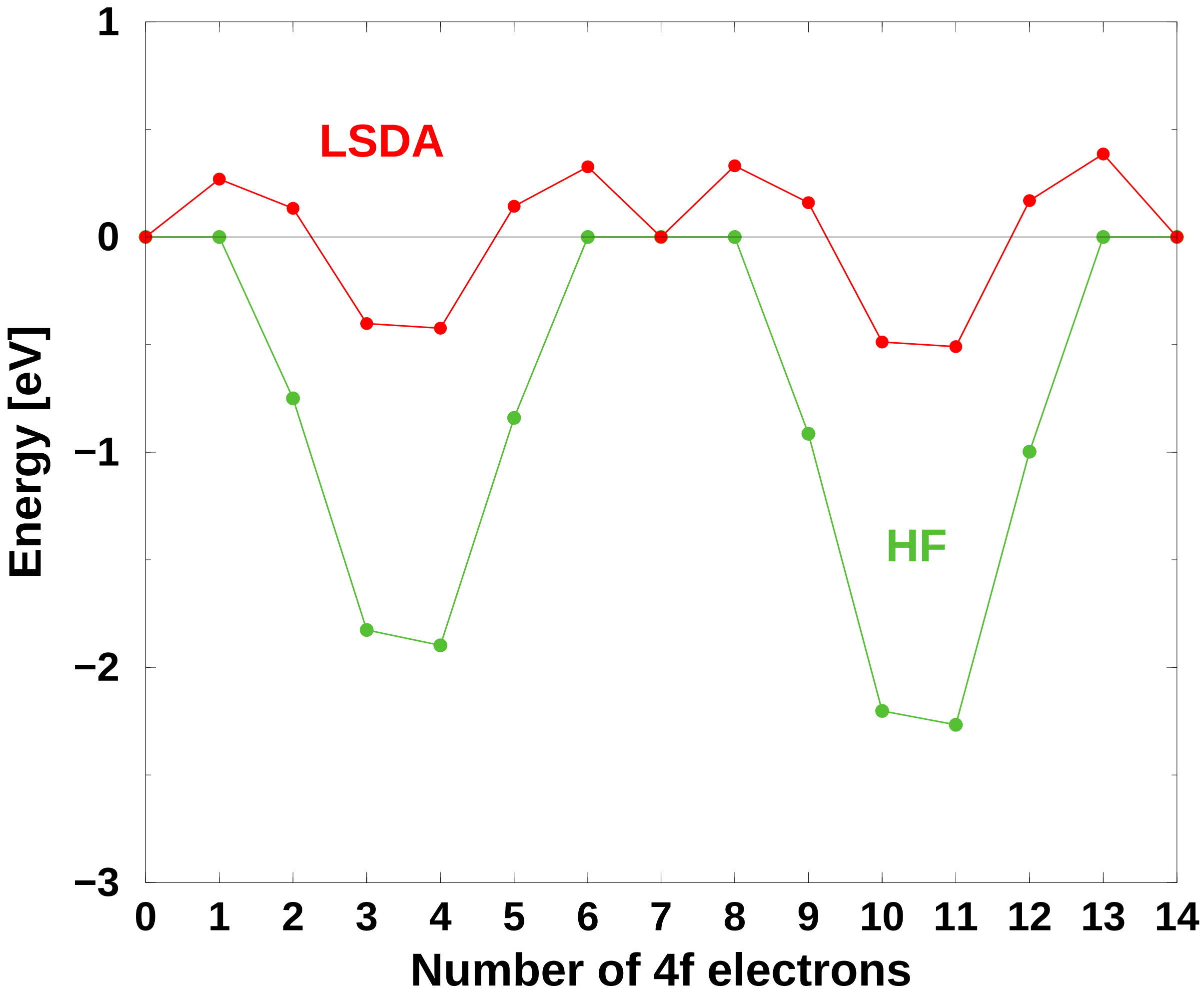
Spin polarization energy of lanthanide ions (Ln^{3+})



HF provides Hund's first rule, see J.C. Slater, Phys. Rev. **165**, 655 (1968).

LSDA provides a maximum spin ground state as well.

Orbital polarization energy of Ln^{3+}-ions

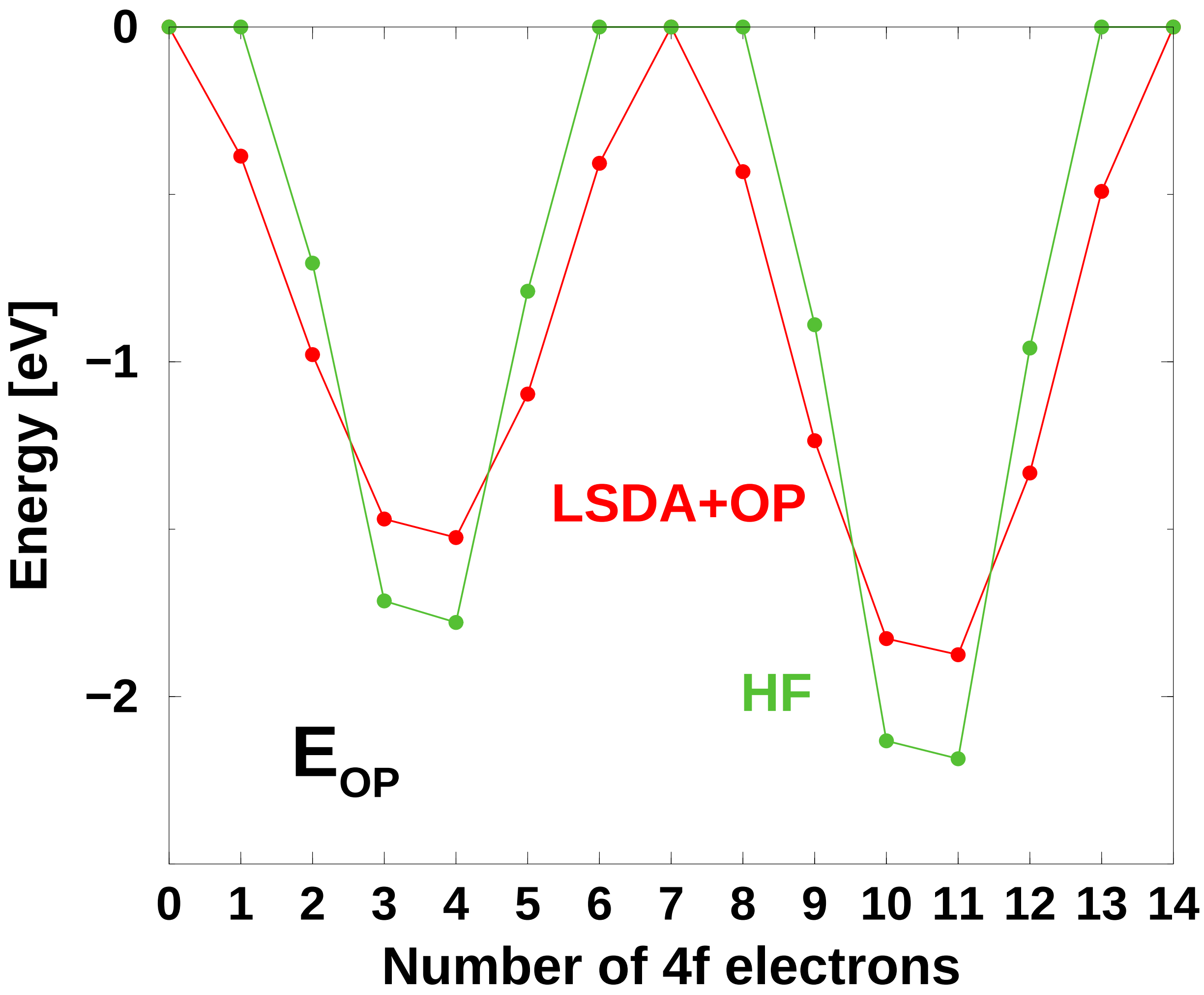


HF provides a maximum angular momentum ground state.

LSDA does in general not provide a maximum angular momentum ground state.

However, full potential LSDA calculations do provide (positive or negative) OP contributions of up to 0.5 eV.

Second Hund rule in LSDA+OP



LSDA+OP provides a maximum angular momentum ground state: $E_{\text{OP}} = -\frac{1}{2} M_L^2 \cdot E^3$.

O. Eriksson *et al.*, PRB **41** (1990) R7311.

The results of LSDA+OP are sensitive to approximations for the effective potential.

Orbital polarization corrections

Authors	Comments
Eriksson *et al.* PRB **41** (1990) R7311	LSDA + OP: $\Delta E_{\mathrm{OP}} = -\frac{1}{2}\, M_L^2 \cdot B$ no correlation, self-interaction, simple
Norman PRB **44** (1991) R1364	HF in a crystal-field basis no correlation, complicated
Severin *et al.* PRL **71** (1993) 3214	Exchange-only with downscaled Slater F's no correlation, self-interaction
Solovyev *et al.* PRL **80** (1998) 5768	relativistic LSDA+U most suited for less correlated metals
Ebert *et al.* EPL **40** (1997) 545	CDFT in local vorticity approximation OP enhancement is to small

Orbital polarization corrections from CDFT

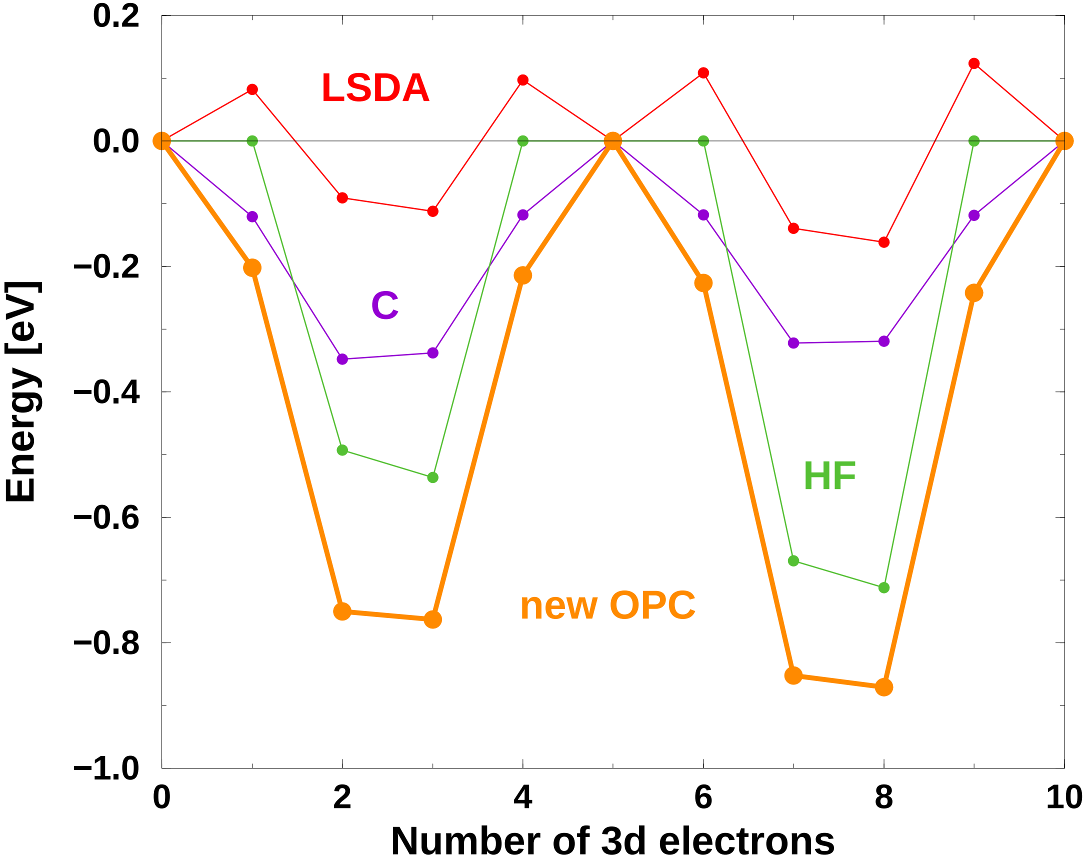
- Separation of the Hartree-Fock operator: $\Delta E_{\mathsf{OP}}^{\mathsf{HF}} + \Delta E^{\mathsf{C}}$
- LSDA-correlation ansatz for the orbital correlation term ΔE^{C}
- Explicit exclusion of spin-orbit terms from the OP correction: $\Delta E^{\mathsf{C,L}}$

Orbital polarization corrected Kohn-Sham-Dirac equation:

$$\left[-ic\boldsymbol{\alpha}\cdot\nabla + \beta c^2 + V_{\mathsf{LSDA}}(\boldsymbol{r}) \;+\; \mu_{\mathsf{Bohr}} H_{\mathsf{LSDA}}(\boldsymbol{r})\beta\Sigma_z\right]\psi_k(\boldsymbol{r}) +$$

$$+\,\beta\sum_m C_m\langle\varphi_m|\psi_k\rangle\varphi_m(\boldsymbol{r}) \;\;=\;\; \psi_k(\boldsymbol{r})\epsilon_k$$

Numerical results: 3d transition metal ions T^{2+}



$$\Delta E_{\text{OP}} = \Delta E_{\text{OP}}^{\text{HF}} + \Delta E^{\text{C,L}} - \Delta E_{\text{OP}}^{\text{LSDA}}$$

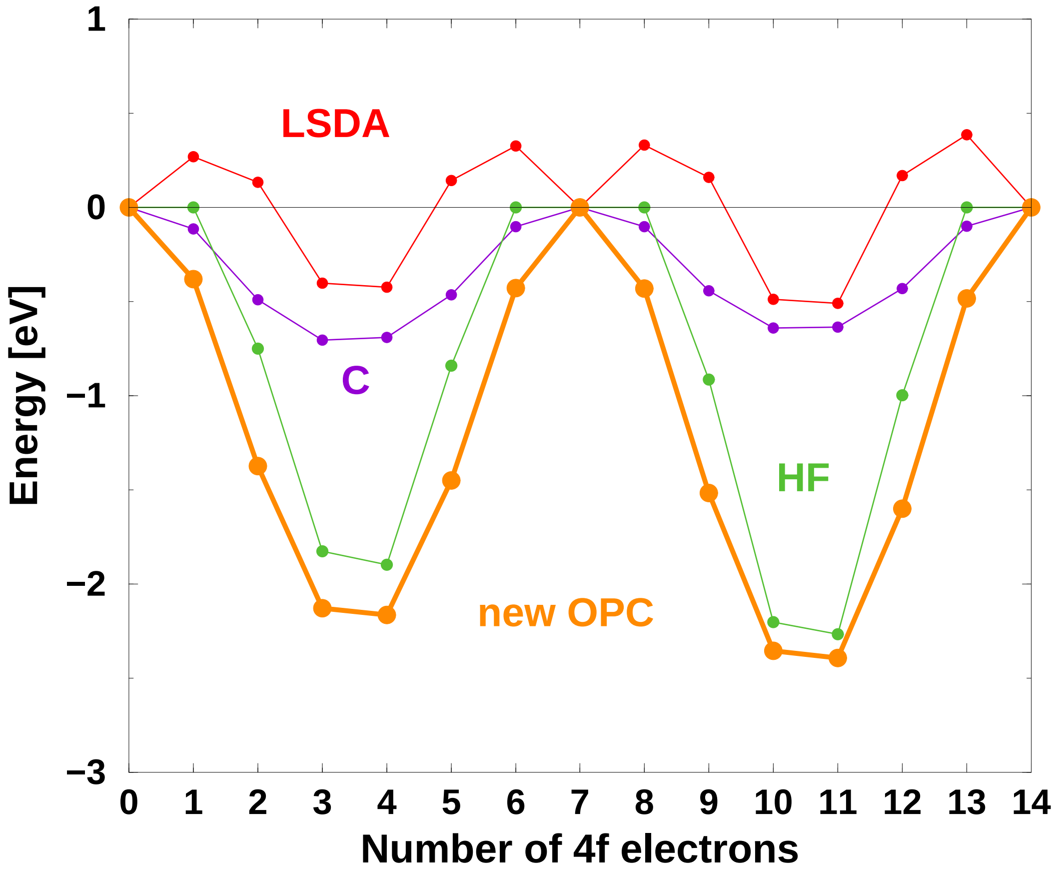
$$\Delta E_{\text{OP}} \approx -\frac{P}{3}|M_L|^3$$

$$M_L = \sum_k n_k \langle \psi_k | \phi_m \rangle m \langle \phi_m | \psi_k \rangle$$

$$C_m = P M_L^2 m$$

$$P_{3d} = (78 \cdots 101)\ \text{meV}$$

Numerical results: 4f ions Ln^{3+}



$$\Delta E_{\mathrm{OP}} = \Delta E^{\mathrm{HF}}_{\mathrm{OP}} + \Delta E^{\mathrm{C,L}} - \Delta E^{\mathrm{LSDA}}_{\mathrm{OP}}$$

$$\Delta E_{\mathrm{OP}} \approx -\frac{P}{3}|M_L|^3$$

$$M_L = \sum_k n_k \langle \psi_k | \phi_m \rangle m \langle \phi_m | \psi_k \rangle$$

$$C_m = P M_L^2 m$$

$$P_{4f} = (30 \cdots 36)\ \mathrm{meV}$$

Advantages of the new OP approximation

- derived from the CDFT
- contains a correlation contribution
- LSDA double counting is removed
- simple expression
- can easily be implemented

Development of numerical tools

The proposed OP approach (and possible further variants with improved description of the correlation contribution) has to be implemented in two existing numerical codes. The implementation has to be cross-checked and tested against alternative OP methods.
Rotational invariant implementation in a later stage.

FPLO code: four-component relativistic local orbital method for extended systems (slab and cluster variants are being developed).
http://www.fplo.de

deMon code: local orbital (Gaussian) method for atoms, molecules, and clusters.
http://www.demon-software.com/public_html/

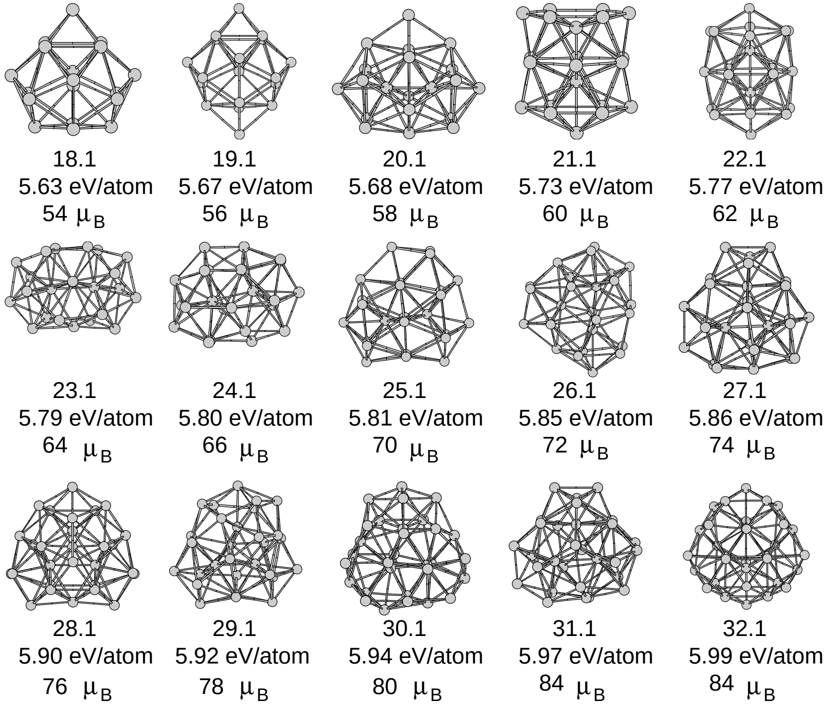
Physical systems/problems to be investigated

Atoms: Evaluation of total and ionization energies of open-shell atoms in current states. In particular, the promotion energies obtained by DFT calculations have partly the wrong sign (s-d promotion in transition metal atoms and d-f promotion in lanthanide atoms), see Forstreuter *et al.* 1997.

Molecules: Spin and orbital magnetism in transition metal clusters, wires, and filled carbon nanotubes.

Solids: Orbital moments and magneto-crystalline anisotropy energy of Co (and other transition metals) in different chemical environments and different geometries (including surface and adatoms).

Problems to be investigated: Example



Lowest energy iron cluster isomers Fe_{18} to Fe_{32}: structures, binding energies and spin magnetic moments (Koehler *et al.* 2005).

Problem: Size of the measured moment ($\approx 3\mu_\mathrm{B}$) is not explained in the spin-only calculations.

→ Orbital contributions?

Summary

- The current status of DFT-derived orbital magnetism is not satisfactory.
- A new OP correction to LSDA has been formally derived from CDFT:

$$\Delta E_{\text{OP}} = -P|M_L|^3/3$$

- This correction includes:
  - Hartree-Fock orbital polarization for the exchange contribution
  - LSDA orbital polarization for the correlation contribution
  - Proper removal of the LSDA double counting
  - very little self-interaction
- The new approach will be implemented in two different codes allowing calculations for solids, molecules, and clusters.
  Calculations on transition metal systems in different geometries are planned.