Calculation of STM spectra:

Co-Phthalocyanine on metallic surfaces

Institute of Theoretical Physics I TU Bergakademie Freiberg
Leipziger Str. 23 I 09599 Freiberg I tbrumme@gmx.de

Overview

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- Motivation
- Theoretical background and computational methods
- Co-Phthalocyanine on metallic surfaces
  - Cu(111)
  - Co(111)
- Summary and outlook

Motivation

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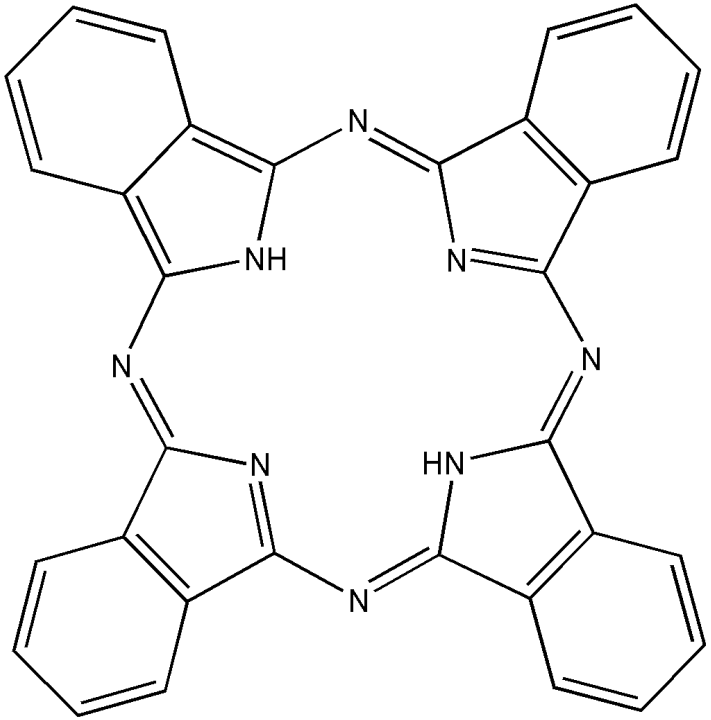
- Application of phthalocyanines
  - Dye in paper and plastics industry
  - Sensors, fuel cells, medicine
  - Model compound for biological important metallo-porphyrins
  - Organic electronics, e.g. OLEDs
- Nearly all Me-Phthalocyanines have a magnetic moment
  => possible application in spintronics and in storage devices



Phthalocyanine

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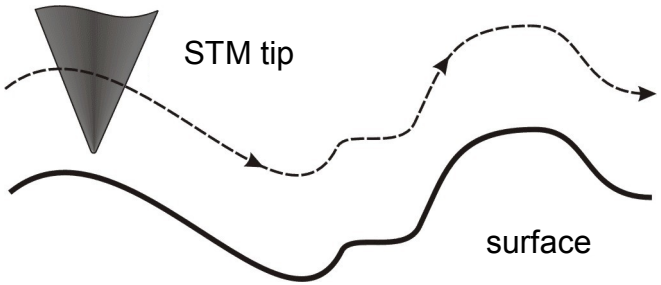
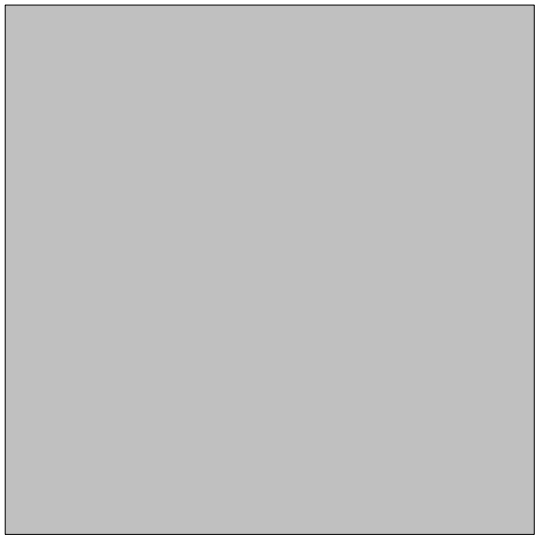
Motivation

- Metal-Molecule-Interaction
- Investigation of surfaces
  (with adsorbed substances)
  - Scanning Tunneling Microscope (STM)
  - SP-STM (Spin Polarized)
  - Constant-Current-Mode





- STS-mode (Scanning Tunneling Spectroscopy)
  - Measurement of dI/dV
  => differential conductance

Theoretical Background

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- Ground state of a quantum mechanical many-electron system
- => Density functional theory
- Calculation of STM- and STS-images by means of the Tersoff-Hamann-approximation [1]

$$I(\boldsymbol{R}) \propto \sum_{E_n > E_F - e\,V_{bias}}^{E_n < E_F} |\psi(\boldsymbol{R}, E_n)|^2 =: n(\boldsymbol{R}, V_{bias})$$

- Used codes / programs: PWscf, XCrysDen

[1] J. Tersoff and D.R. Hamann, Phys. Rev. B, 31(2) (1985).

Co-Phthalocyanine

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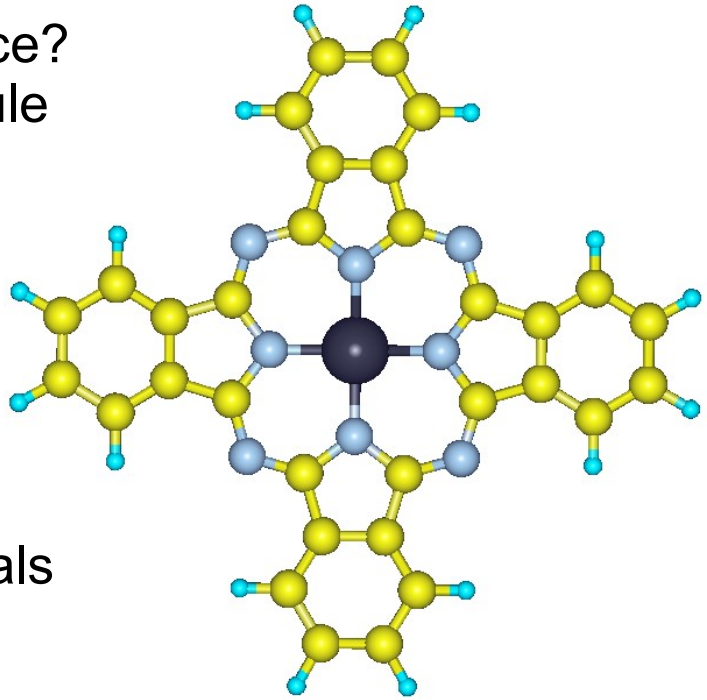
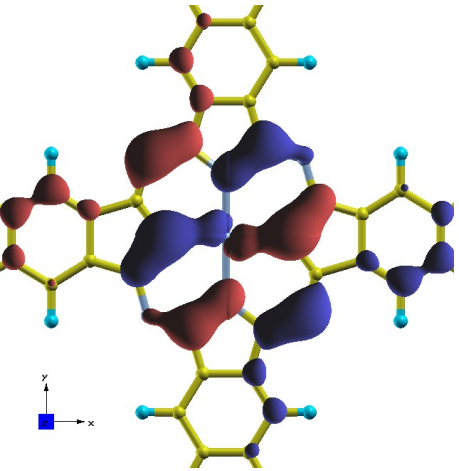
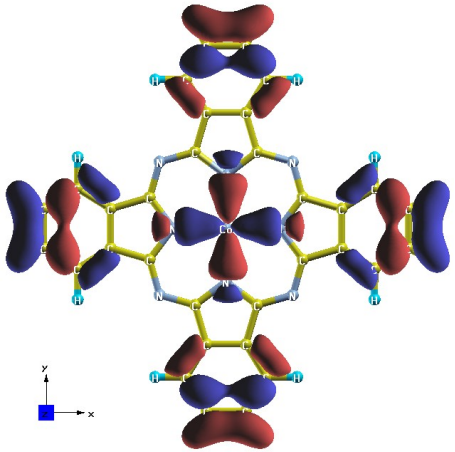
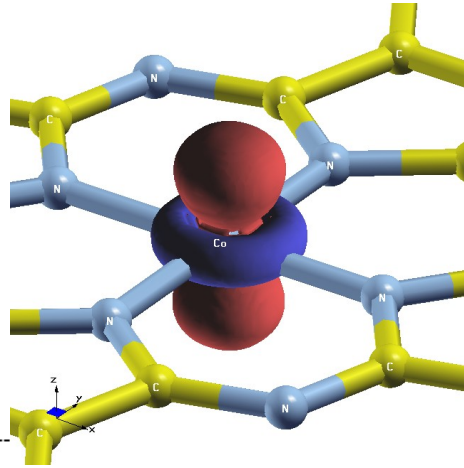
- How is the molecule bonded to the surface?
  => Electronic structure of the free molecule important
- Bond between cobalt d-orbitals and phthalocyanine-ligand
- Strongest bond between Co $d_{x^2-y^2}$ and nitrogen
- Bonds between degenerated d_{xz}/d_{yz}-orbitals and two different ligand-orbitals

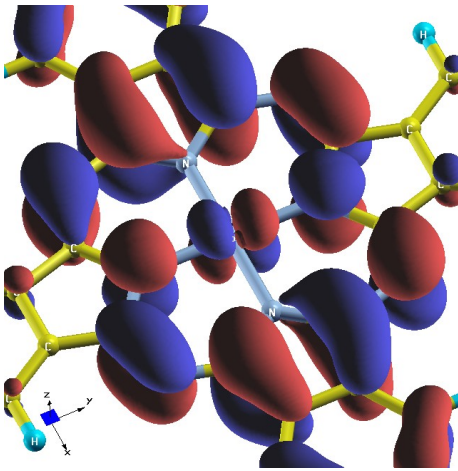


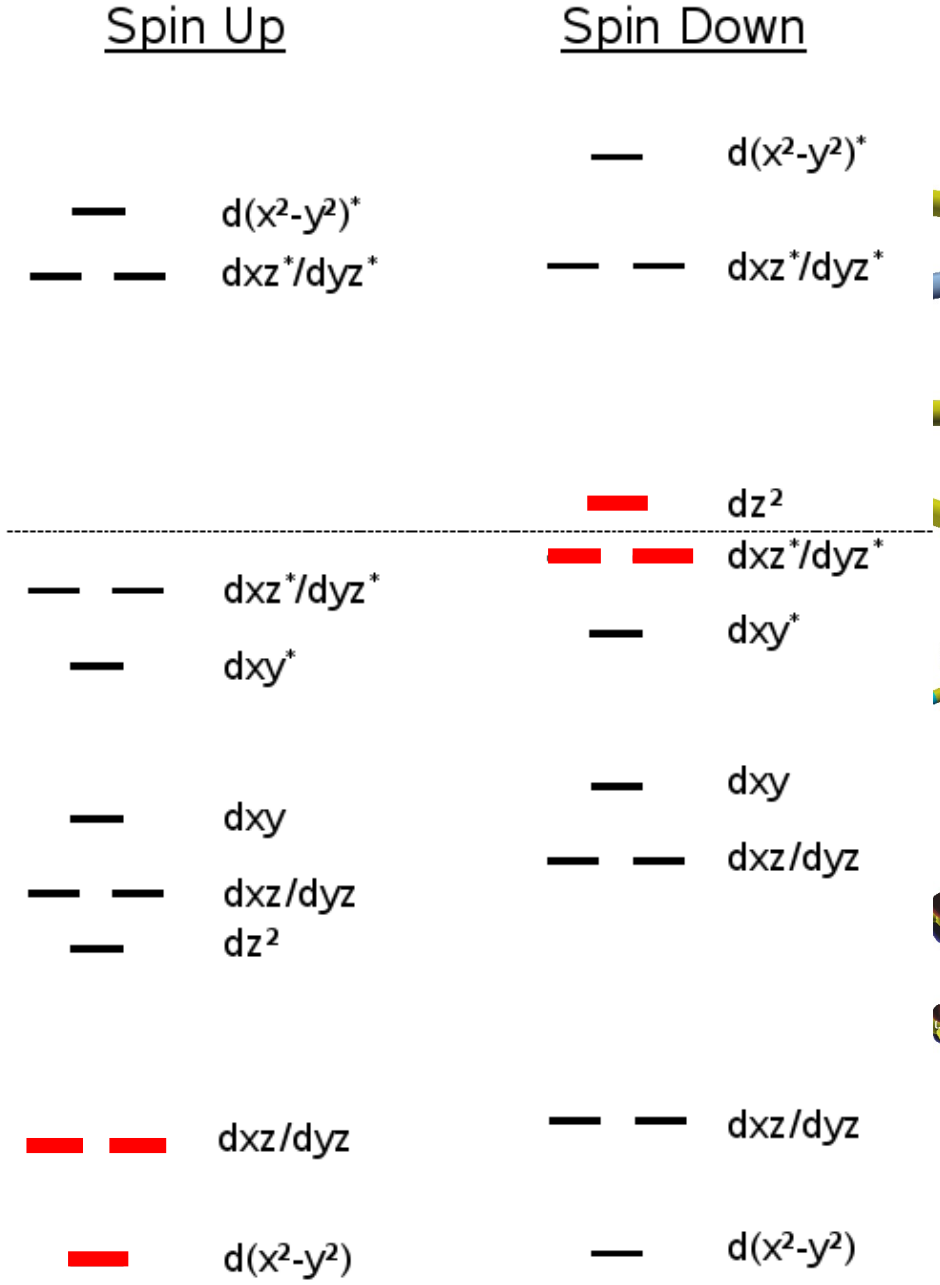
CoPc











Calculated energy-level diagram of the central cobalt of CoPc.

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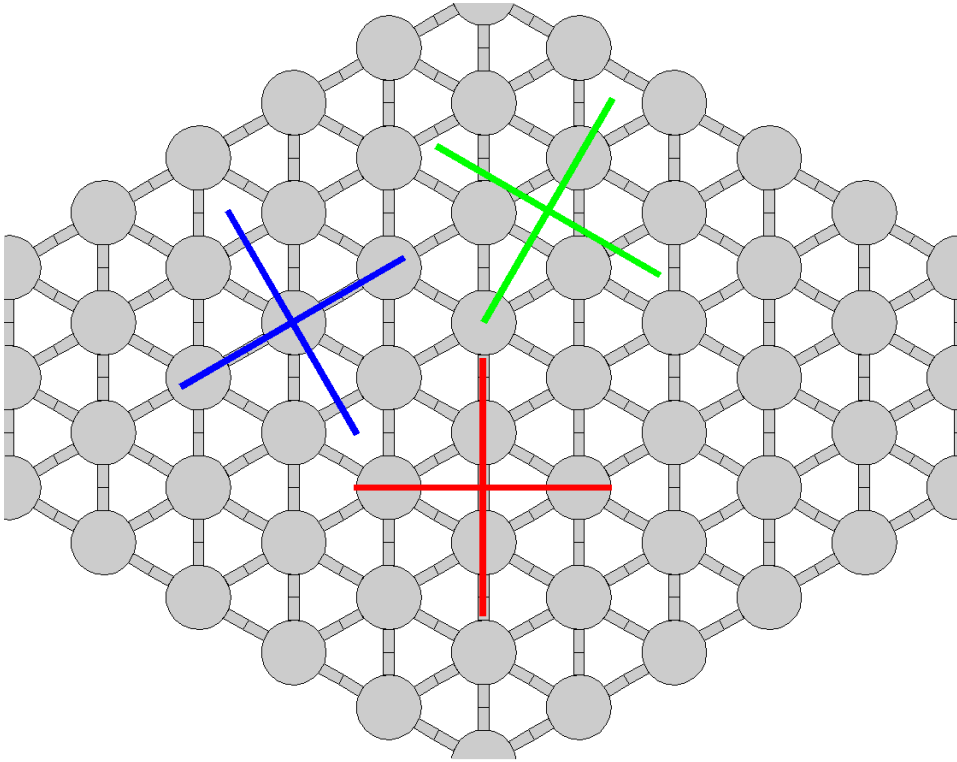
Co-Phthalocyanine

- Investigated surfaces: Cu(111), Cu(001), Co(111)
- Bridge-position always energetically preferred, hollow-position unfavorable
- Reasons:
  - Ligand-surface-interaction
  - Symmetry
- x- / y-direction not degenerated anymore



Different positions of CoPc on surfaces.

Co-Phthalocyanine – Cu(111)

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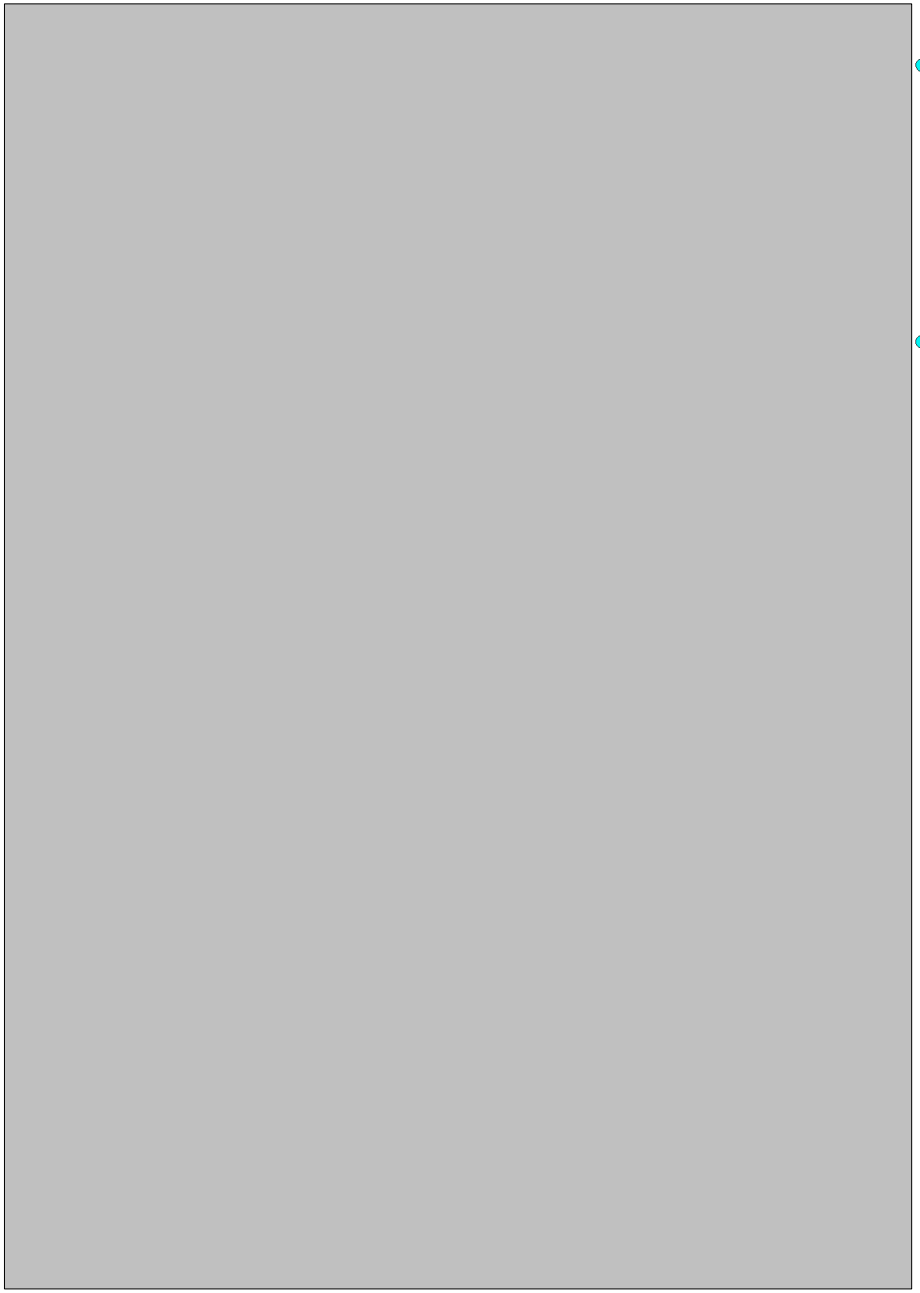
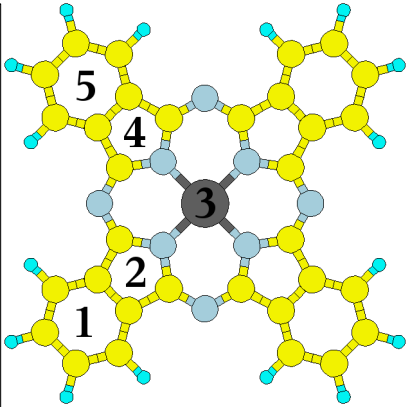
- Axis, defined by the bridge atoms, is preferred one.
- Direct bond between central cobalt and surface copper results in zero magnetization.
- Most intense signal in STM-images above the cobalt, because of the weakly bonded d-electrons.
- Considering that the cobalt LUMO (Lowest Unoccupied Molecular Orbital) is partly occupied yields good agreement between theory and experiment.



STS above different positions of the CoPc



- Resonances from lowest to highest sample bias:
  - Co d_{xy} (HOMO*1 – 1 of the free molecule)
  - Bond tween Co d_{π} – N p – OF Cu
  - Co d_{z^2} and d_{π}
  - Broad peak at -0.5eV – 0eV (experiment) and the 2 peaks (theory) –> Ligand HOMO
  - Ligand LUMO
  - Bond tween Co $d^*_{x^2-y^2}$ and ligand

*1 Highest Occupied Molecular Orbital

Co-Phthalocyanine – Co(111)

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- Cobalt is magnetic at low temperatures
- Stronger interaction between CoPc and surface
- Significant differences between Spin Up and Spin Down
- Cobalt LUMO (d_{z^2}) again partly occupied
  => reduced magnetic moment
- At E_F mainly minority-states
- The CoPc is coupled ferromagnetically to the surface
  => – 2. Goodenough-Kanamori rule for direct exchange
  – Superexchange through the inner nitrogen

Summary

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- Significant differences between magnetic and non-magnetic surfaces
- Differences between the various positions on a surface smaller
- “How” and “Where” the molecule is adsorbed is determined by the ligand
- Good agreement between theory and experiment

Outlook

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- More (magnetic) surfaces
- Different metals in MePc
- Other molecules
- Transport through molecules on surfaces
- But: comparison between theory and experiment is important

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Special thanks go to:

– Jean-Pierre Bucher, Laurent Limot
Institut de Physique et Chimie des Matériaux de Strasbourg

Accepted for publication in PRL
“Visualizing the Spin of Individual Cobalt-Phthalocyanine Molecules”

http://arxiv.org/abs/0805.0485

– ZIH Dresden

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Thank you for your attention!

Co-Phthalocyanine - Cu(111)

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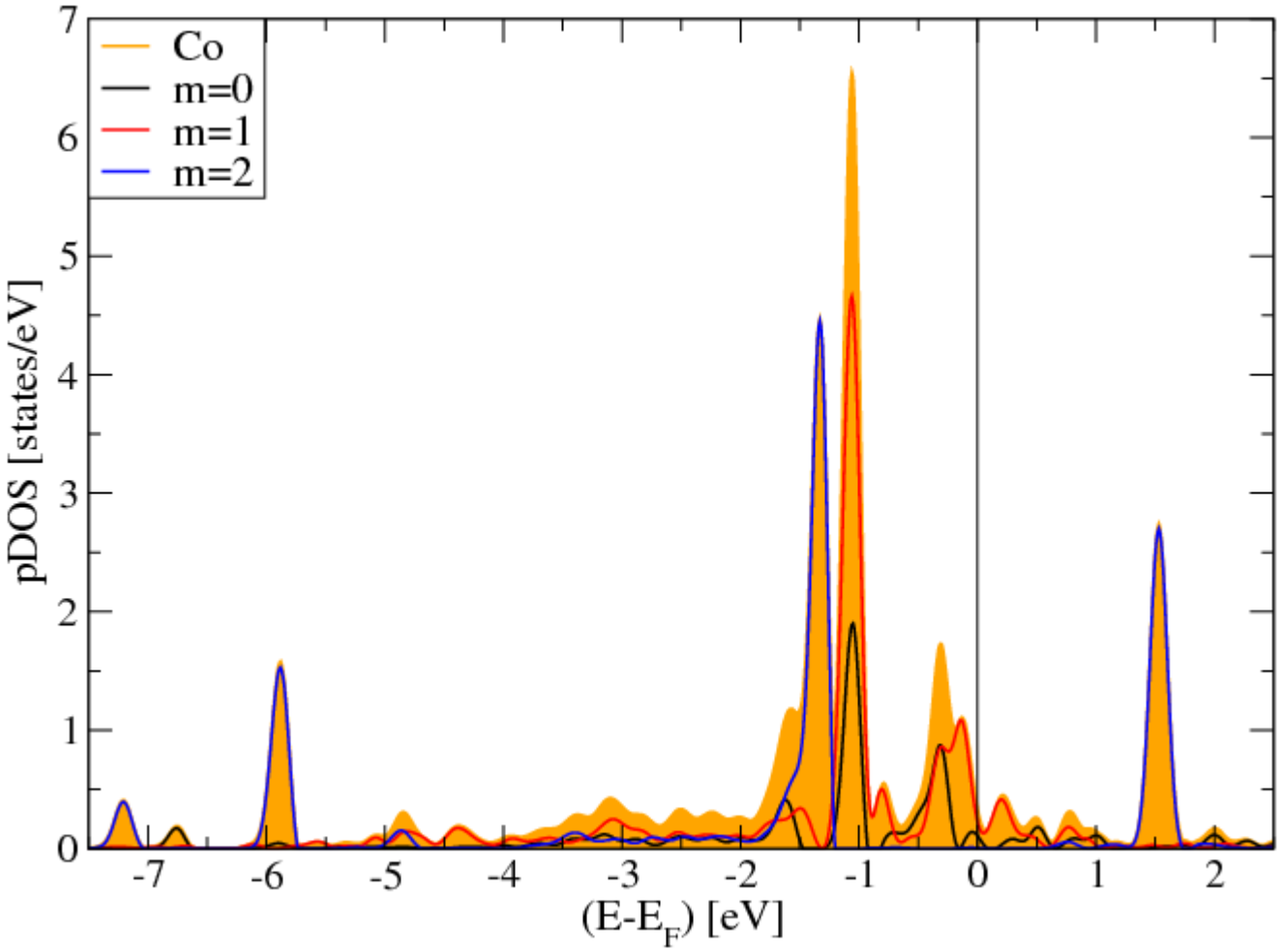

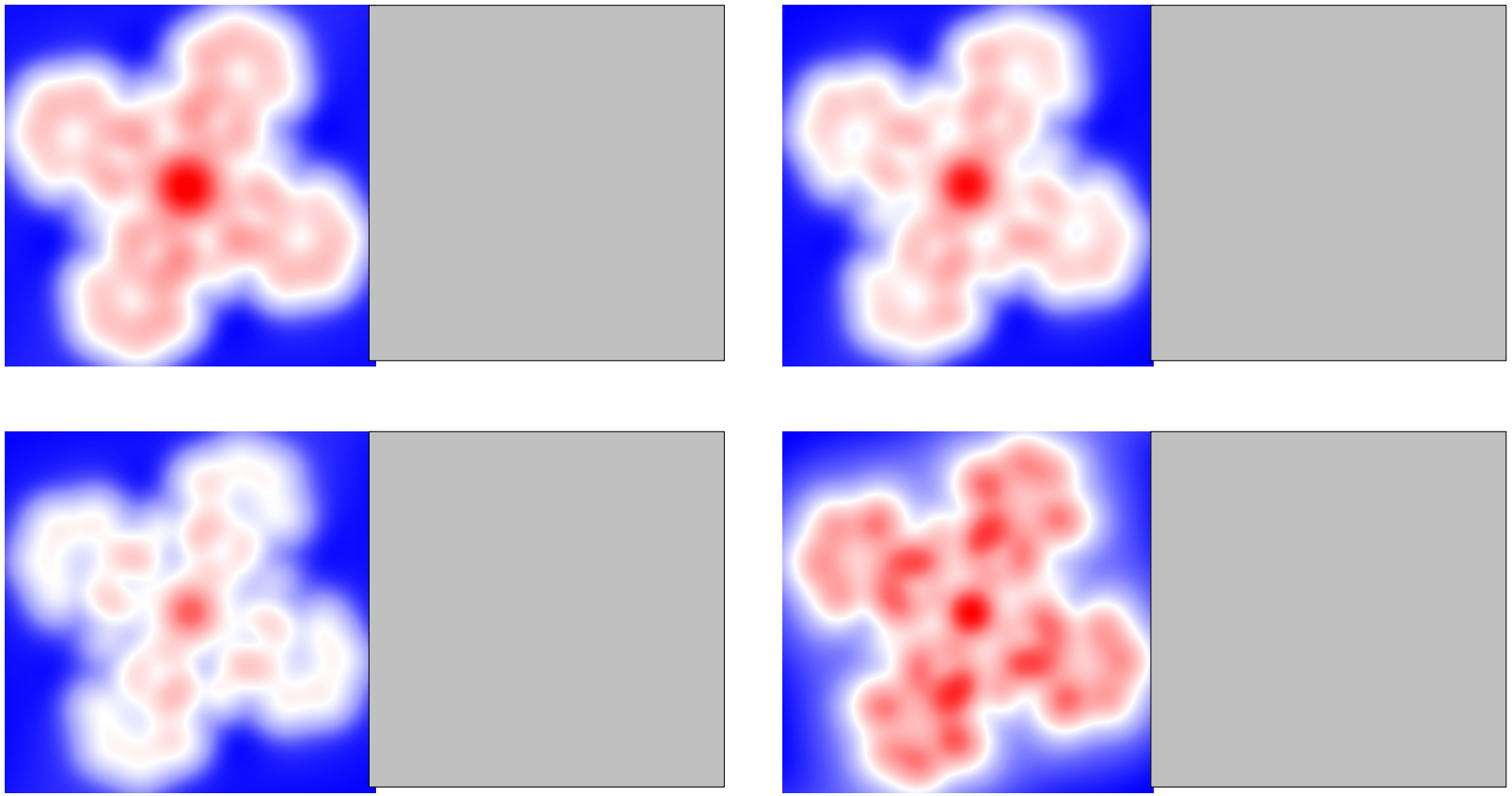

Comparison between calculated (blue-red) and measured (black-green) STM-images at different bias-voltages. Upper left (right) -1.4eV (-0.5eV), lower left (right) -0.1eV (1.5eV).

Co-Phthalocyanine - Cu(001)

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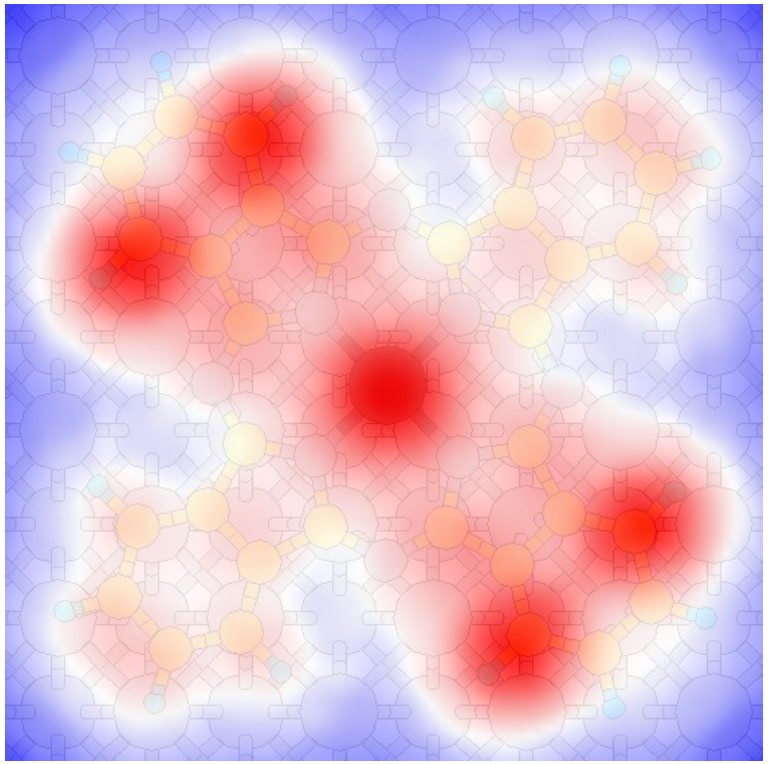

Structure of CoPc on Cu(001),
superimposed: STM-image at 1.57 eV.

Co-Phthalocyanine - Co(111)

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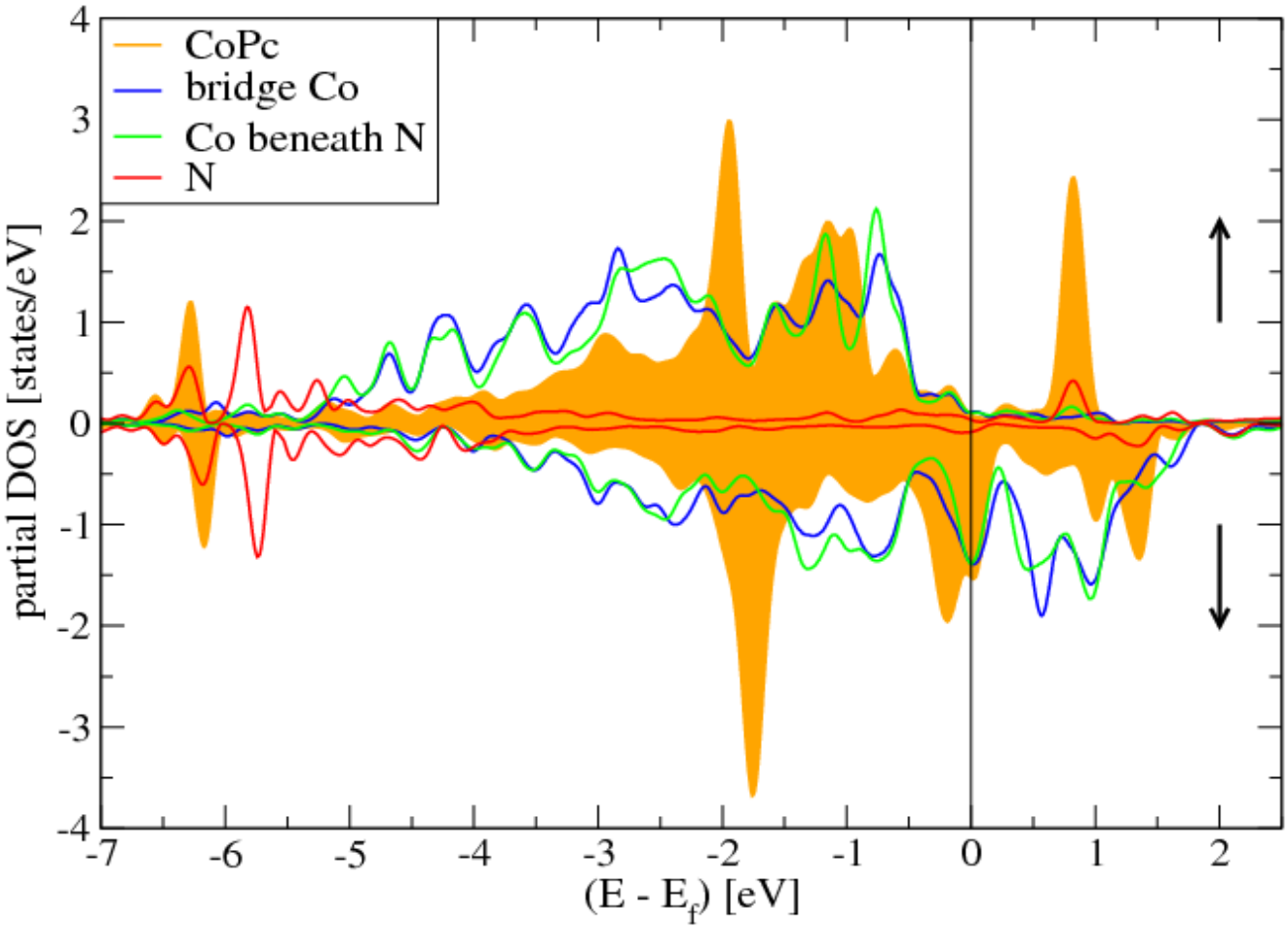

Co-Phthalocyanine – Co(111)

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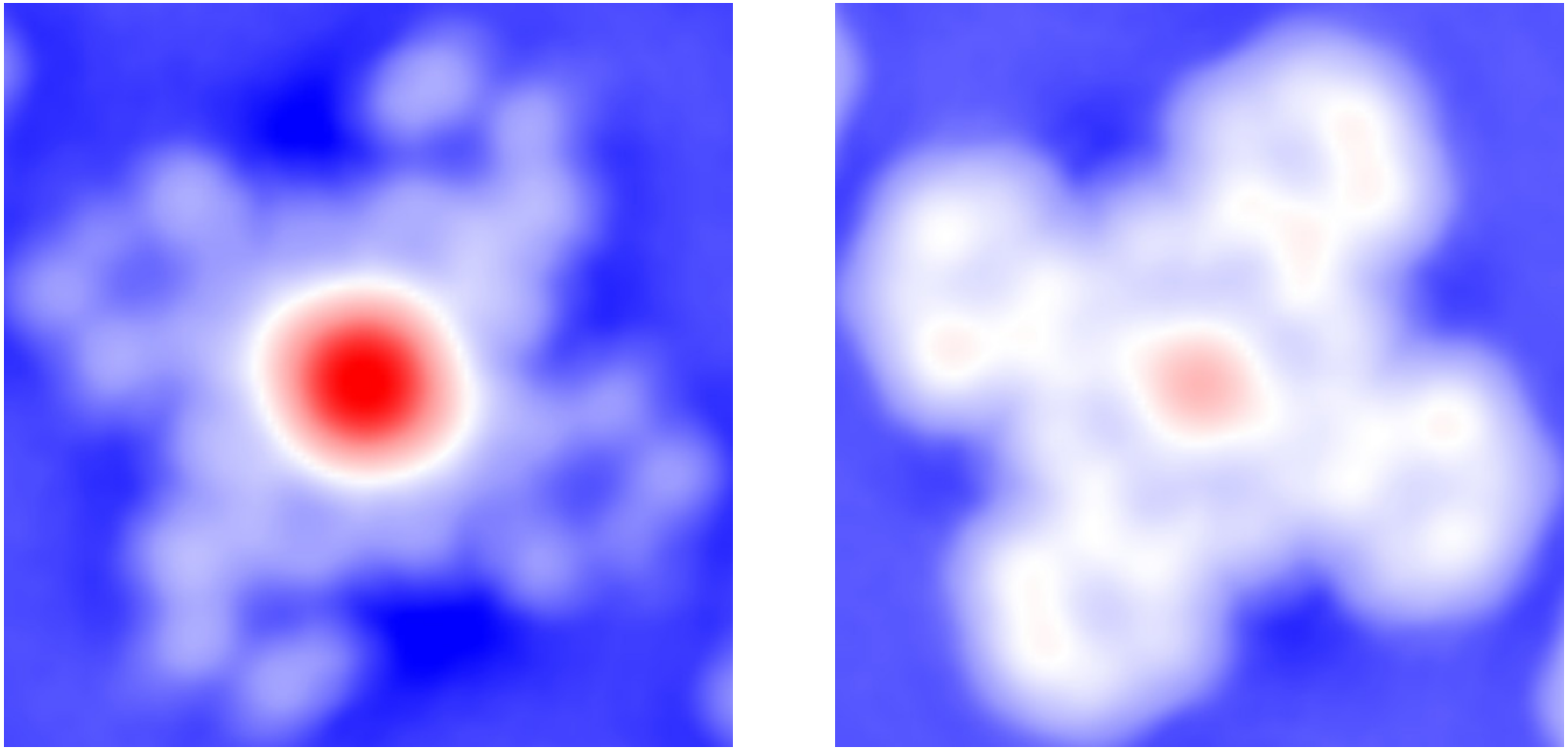

SP-STM of CoPc on Co(111) at V_{bias}=0.51 eV, left Spin Down, right Spin Up.

Fe-Phthalocyanine - Co(111)

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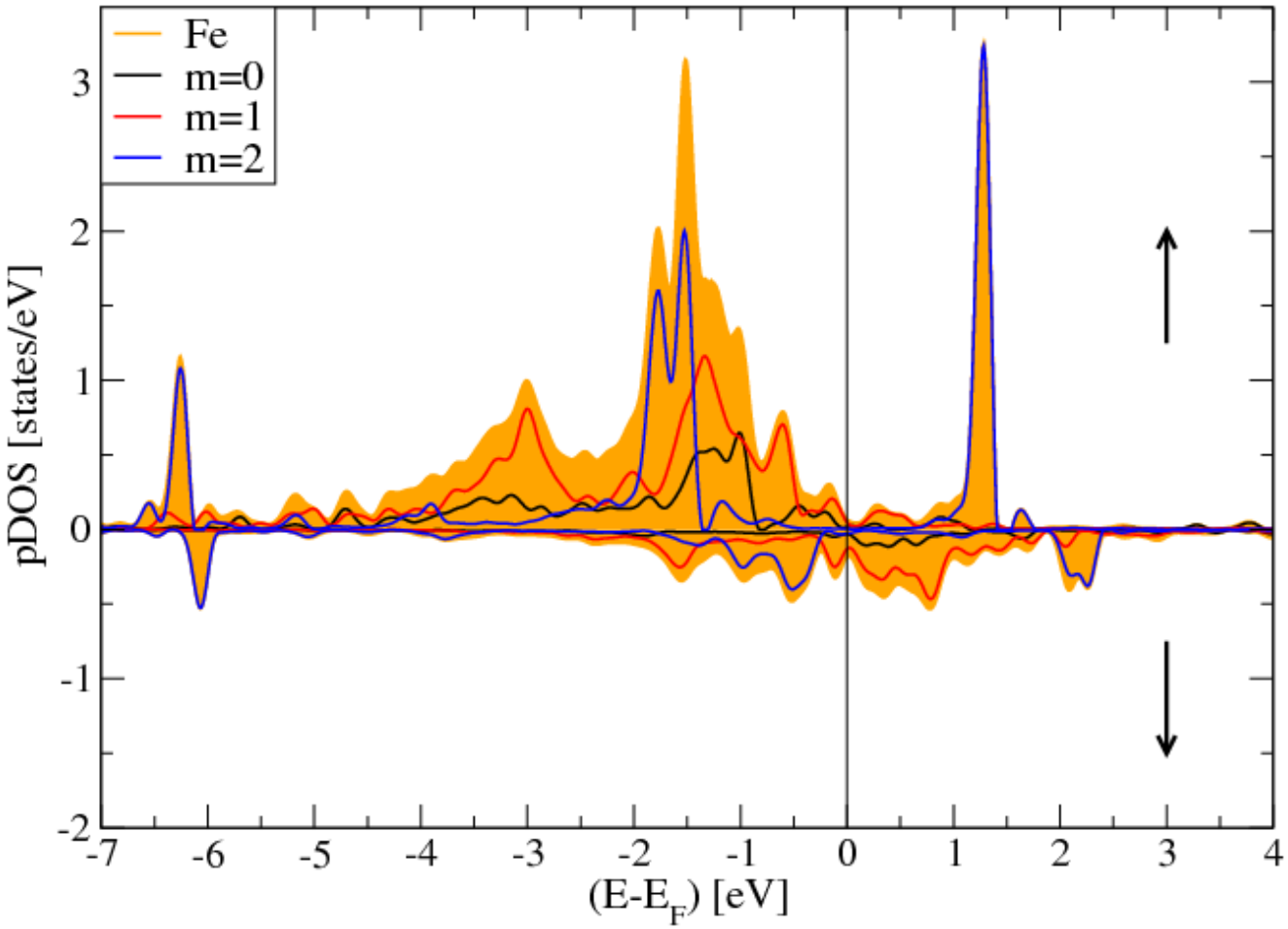

Magnetic interactions

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- Magnetic interactions between an adsorbed molecule and a magnetic surface
  - Classical dipole-dipole-interaction
  - Double exchange, anisotropic exchange
  - In metals: RKKY-exchange
  - Direct / indirect exchange => Goodenough-Kanamori rules

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