Ab initio study of metalorganic coordination complexes

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Outline

Methods

- Classical force field
- All electron *ab initio* molecular dynamics
- Full Potential Linear Augmented Plane Wave (FPLAPW) method
- N-th order Muffin Tin Orbital (NMTO) downfolding

Materials

- Metalorganic coordination polymer Cu(II)-2,5-bis (pyrazol-1-yl)-1,4-dihydroxybenzene ($[Cu(bpydhb)]_n$) with substitutions and ligands.
- Model Fe(II) triazole (Fe(II) with 4-methyl-1,2,4-triazole and F^- counterions, $[Fe(Htrz)_3]F_2$).

Results

- ⋆ $[Cu(bpydhb)]_n$: Control over band structure and Cu(II) ion interactions.
- ⋆ $[Fe(Htrz)_3]F_2$: LS to HS transition as a function of Fe-N distance.

Motivation

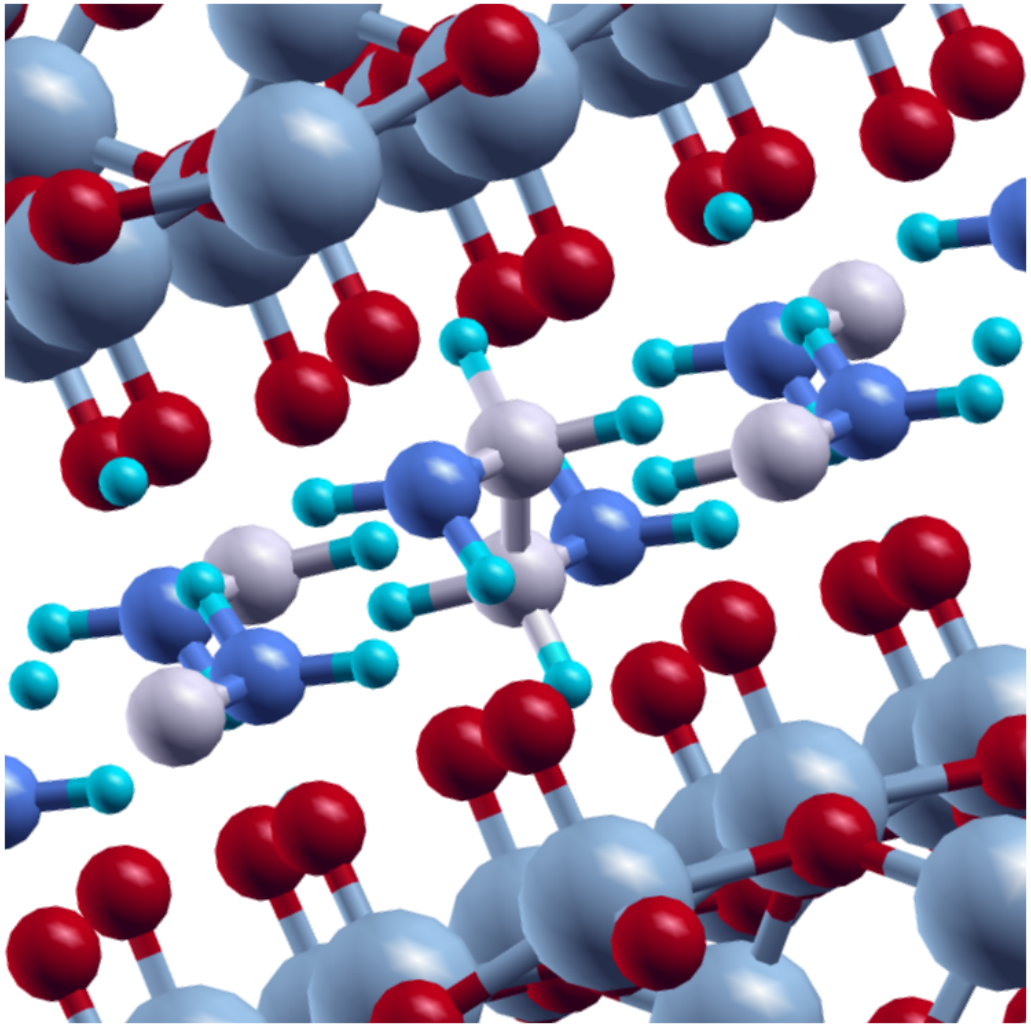
A) Make transition metal compounds with large unit cells accessible to precise DFT calculations

- Problem: Insufficient description of many transition metal complex structures in the literature → precise DFT methods have nothing to work with. (Reasons: low crystallinity, large uncertainties in determination of light atom positions).
- Existing approaches for structure prediction are not enough

B) Design materials with specific electronic and magnetic properties in the computer

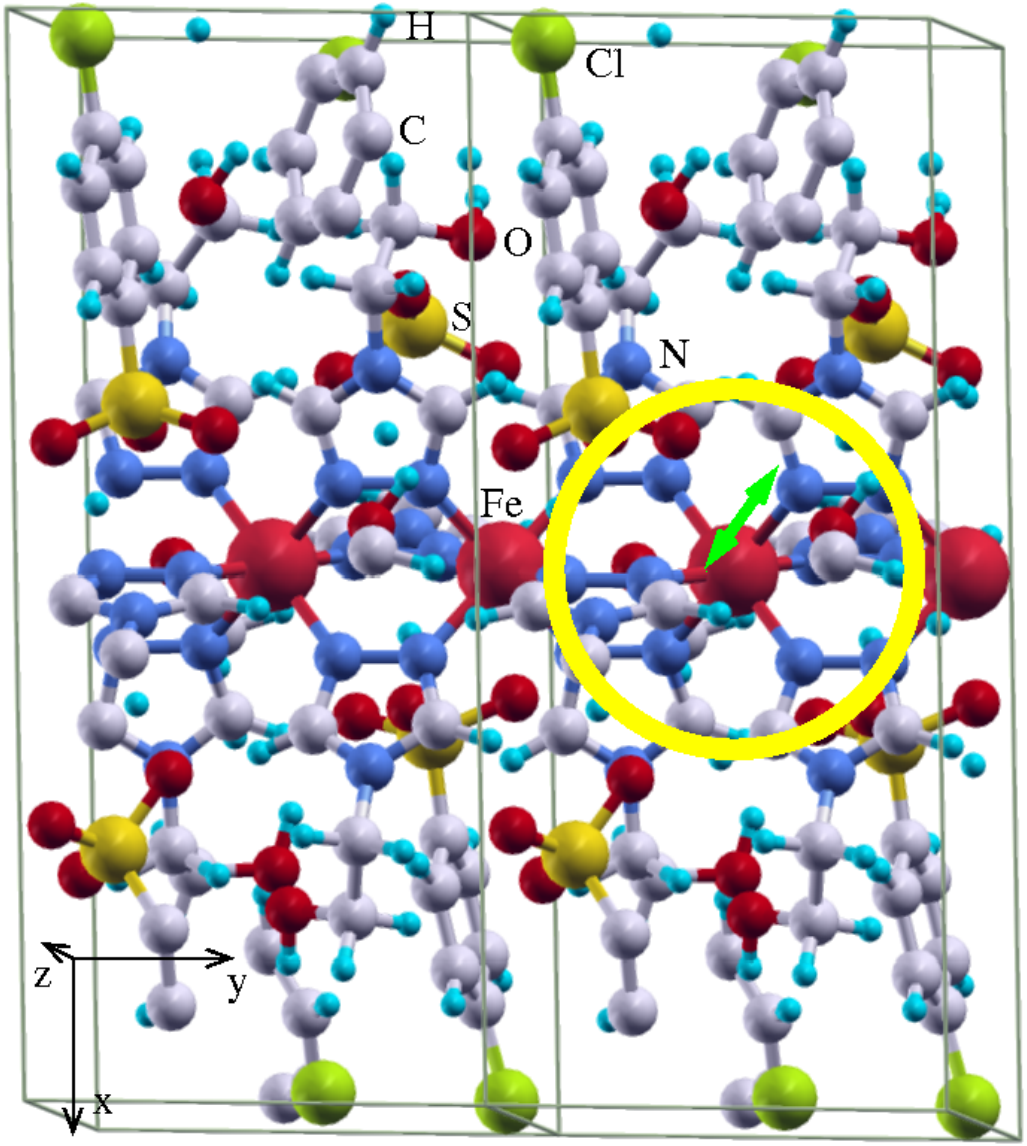
- Learn from success of doping of transition metal oxides
- Modular approach of synthetic chemistry for coordination complexes
- Use subtle changes like substitutions to tune electronic properties (band width, conductivity, dimensionality) and magnetic properties (ground state, frustration, transition temperatures)

Motivation: Layered vanadium oxides with partially published structures



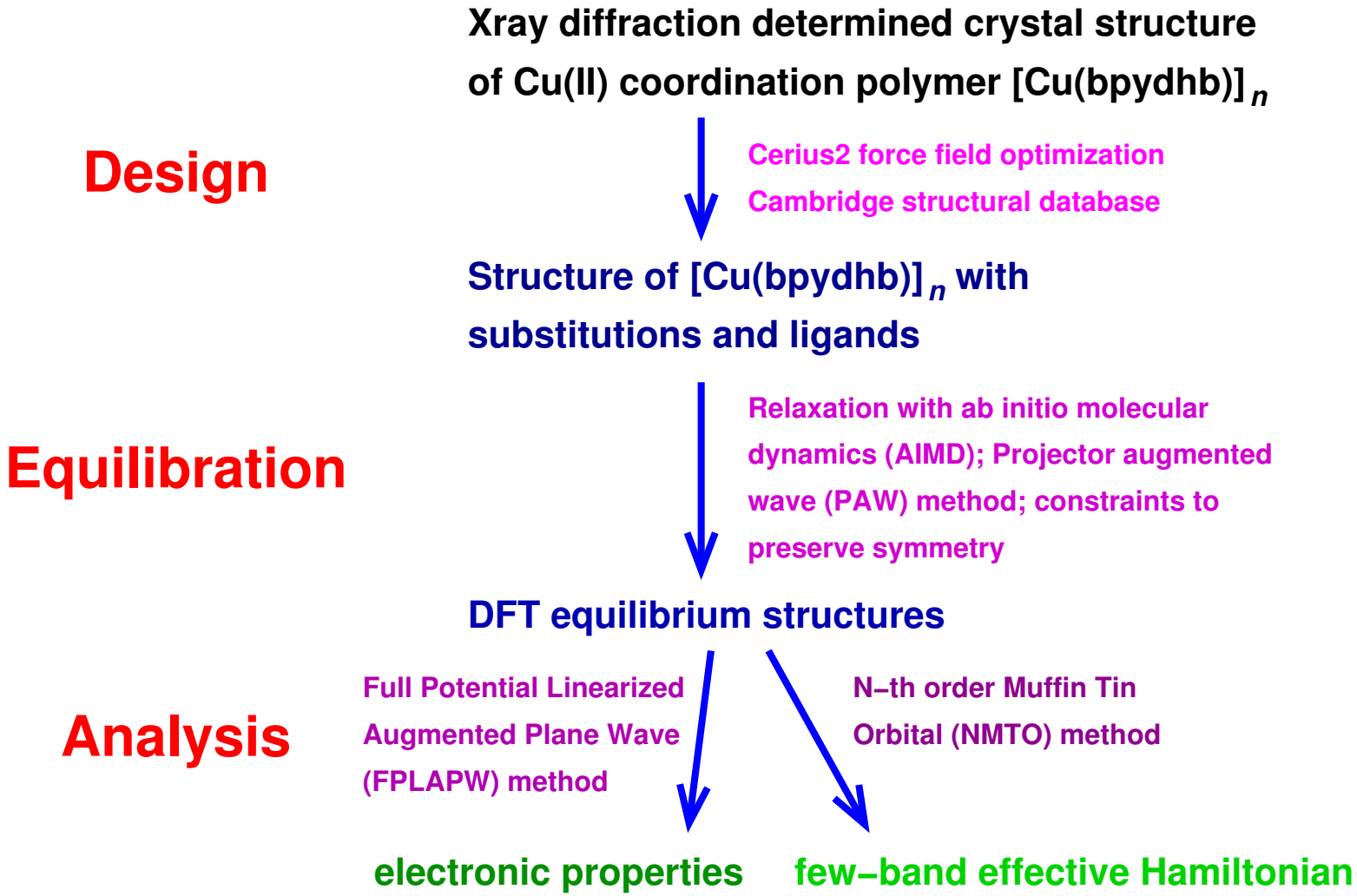
- Layered vanadate (en)V_7O_{16} with ethylenediamine (en) between the layers.
- Structure determined, except for H positions: Wörle, Krumeich, Bieri, Muhr, Nesper, Z. Anorg. Allg. Chem. **628**, 2778 (2002).
- Hydrogen atoms added in likely positions.
- Careful relaxation necessary!
- Next step: $BaV_7O_{16} \cdot nH_2O$ with unknown H positions!

Motivation: Study of a low spin high spin transition



- 1D Fe(II) triazole complex $[Fe(hyetrz)_3](4\text{-chloro-phenylsulfonate})_2 \cdot 3H_2O$, with hyetrz≡ (2'-hydroxy-ethyl)-1,2,4-triazole.
- Possible structure; low crystallinity prevents reliable structure determination.
- $N = 152$ atom unit cell, $P1$ symmetry: this is too big for precise *ab initio* study.
- Need to construct model structure for study of LS-HS mechanism!

Methods for structure design, relaxation, analysis and property prediction



Methods for design and relaxation

Force field:

- Dreiding force field modified for octahedrally coordinated metal ions.
- Classical method allows global optimization.

Ab initio **molecular dynamics**:

- Principle of Car Parrinello method:

$$M_i \ddot{R}_i = -\frac{dE(R, |\Psi\rangle)}{dR_i}$$

$$m_\Psi |\ddot{\Psi}_n\rangle f_n = -\frac{dE(R, |\Psi\rangle)}{d\langle\Psi_n|} + \sum_m |\Psi_m\rangle \Lambda_{m,n}$$

- Projector Augmented Wave (PAW) basis set: Generalization of pseudopotential approach, all electron method
- Constraints to preserve symmetry ($P\bar{1}$ for $[Cu(bpydhb)]_n$, $P21/m$ for $[Fe(Htrz)_3]F_2$),
- Plane wave cutoff of 30 Ryd, $(4 \times 4 \times 4)$ k mesh.

Methods for analysis and property prediction

Full Potential Linearized Augmented Plane Waves (FPLAPW)

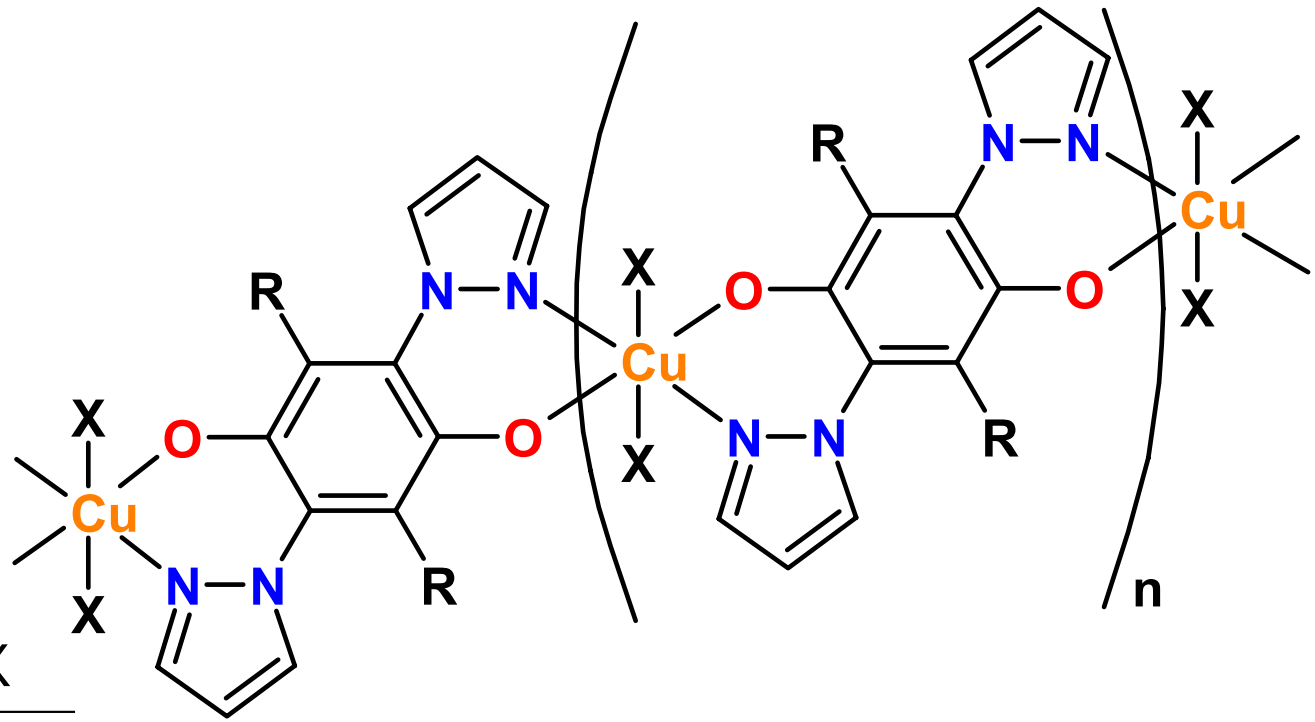
- Analysis of electronic and magnetic properties with WIEN2K.
- k mesh of $(8 \times 6 \times 5)$ in the irreducible Brillouin zone.
- Generalized Gradient Approximation (GGA).

N-th order Muffin Tin Orbital (NMTO) downfolding

- Calculation of few-orbital Hamiltonian $H_{TB} = \sum_{ij} t_{ij}(c_i^\dagger c_j + h.c.)$ by integrating out degrees of freedom that are not of interest.
- Effective hopping t_{ij} between the downfolded Wannier-like, energy-selected, effective orbitals.
- Calibration by comparison of band structure with FPLAPW result.

Cu(II) coordination polymer with substitutions and ligands

Metalorganic coordination polymer Cu(II)-2,5-bis (pyrazol-1-yl)-1,4-dihydroxybenzene ($[Cu(bpydhb)]_n$, CuCCP).

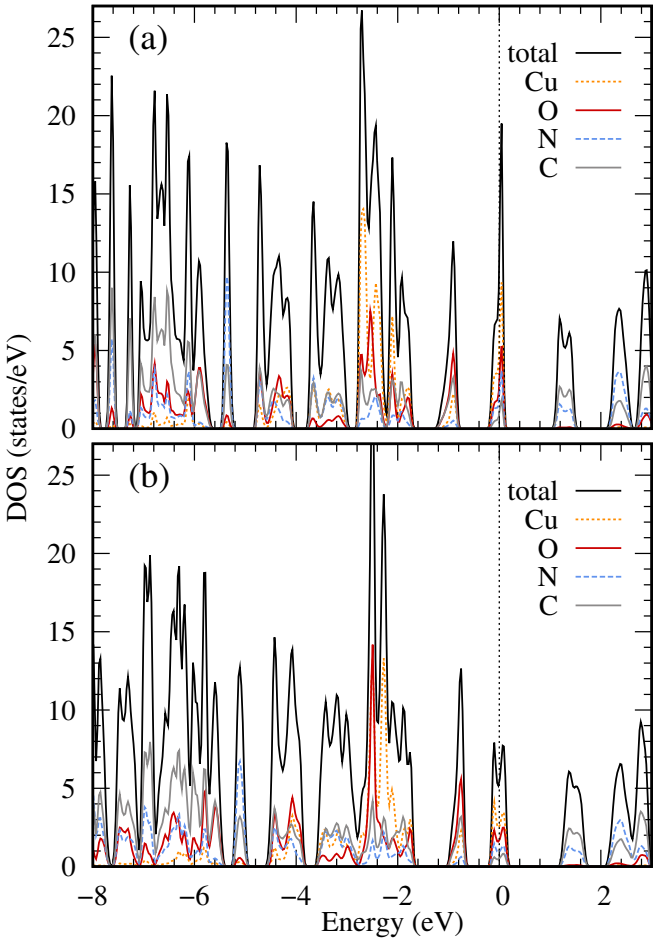


Short name	R	X
CuCCP	H	-
Cu(II)-NH_2	NH_2	-
Cu(II)-CN	CN	-
Cu(II)-H_2O	H	H_2O
Cu(II)-NH_3	H	NH_3

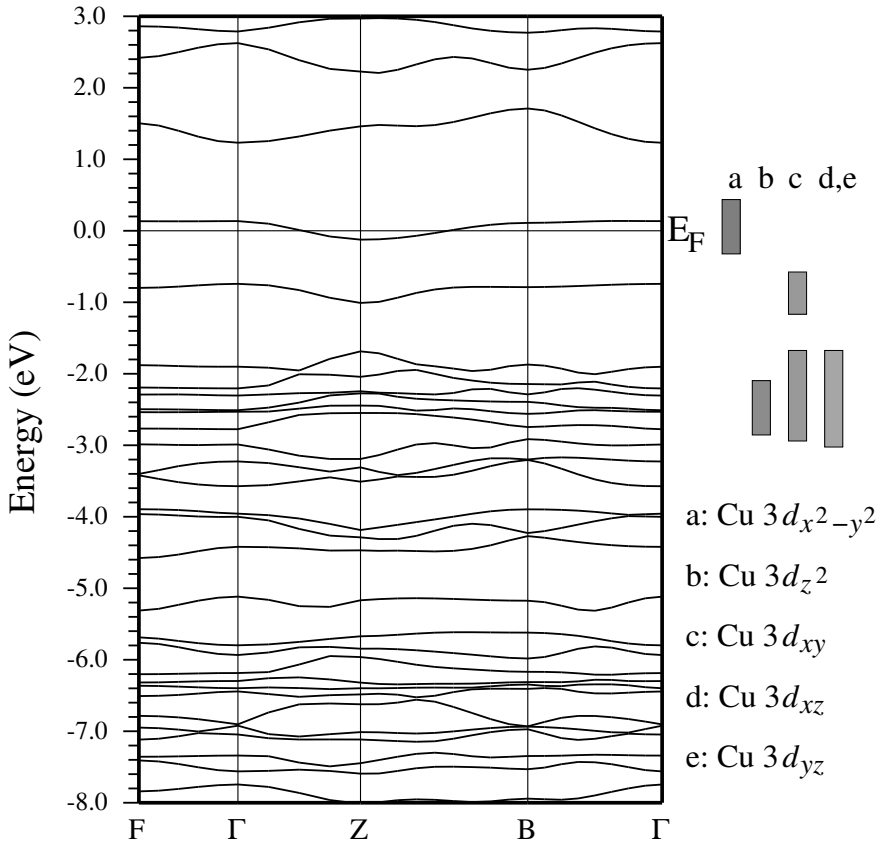
- Substitution R: Electron donating and electron withdrawing group.
- Ligand X: Change of Cu(II) coordination.

Jeschke, Salguero, Valentí, Buchsbaum, Schmidt, Wagner, Comptes Rendus Chimie **10**, 82 (2007), doi:10.1016/j.crci.2006.06.007.

Electronic structure of CuCCP

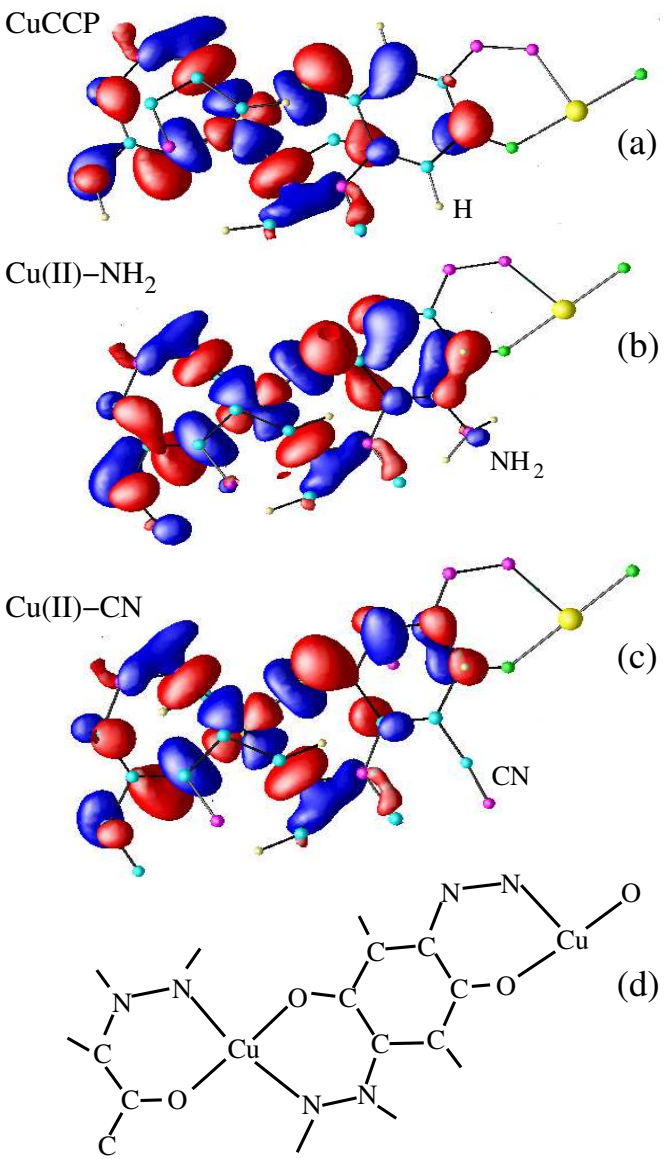


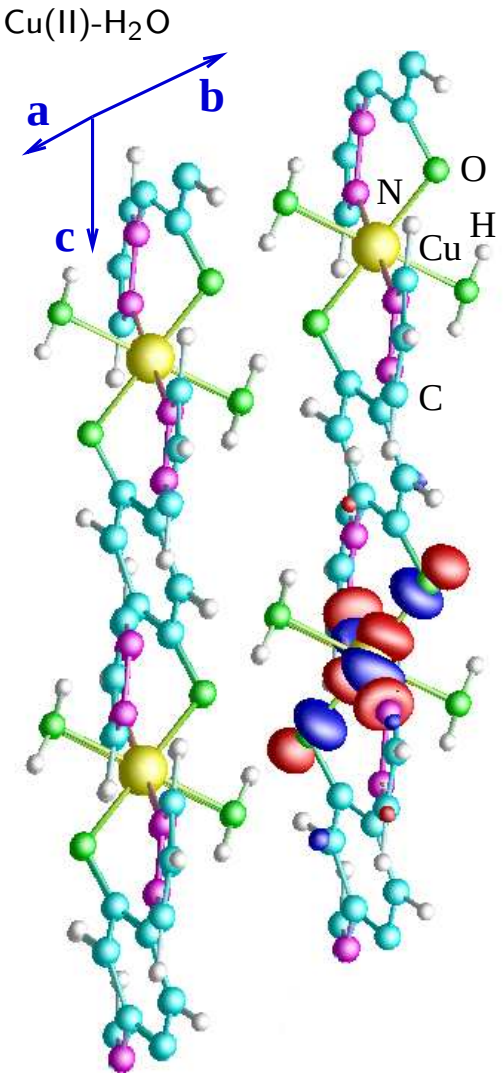
- Experimental structure (a) stabilized (b) by relaxation.

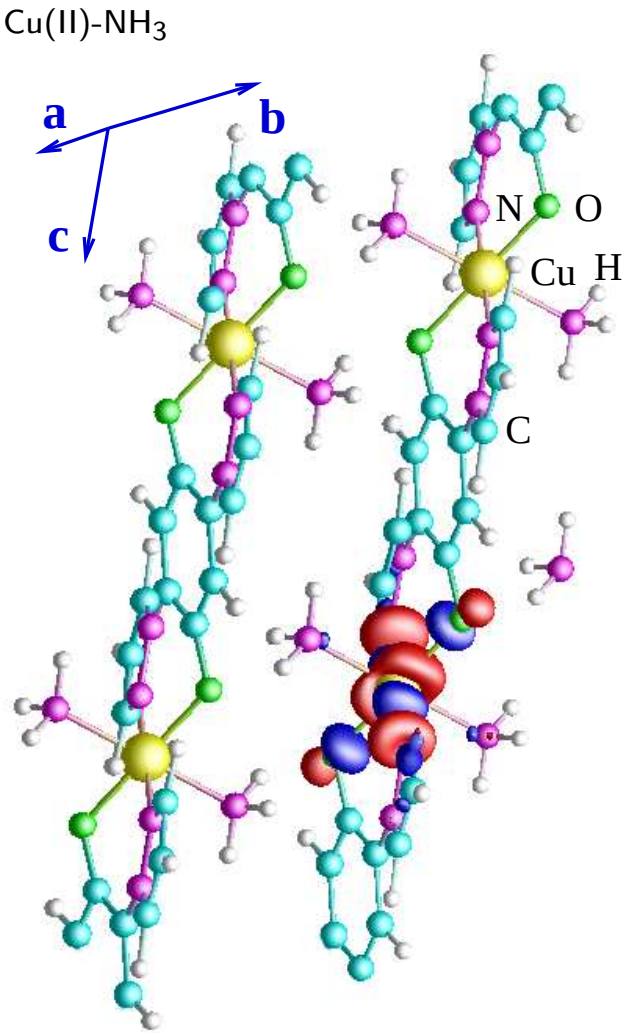


- Antiferromagnetic Heisenberg spin-1/2 chain

Wannier functions from NMTO downfolding





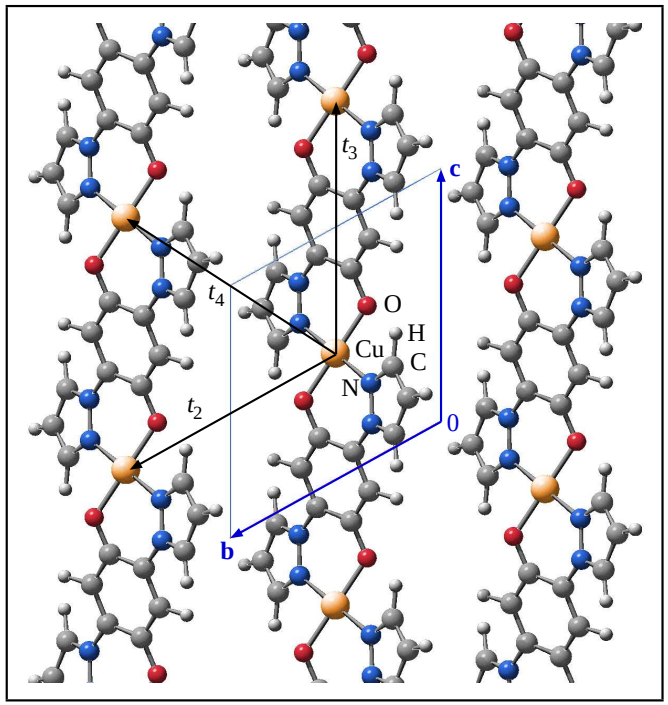


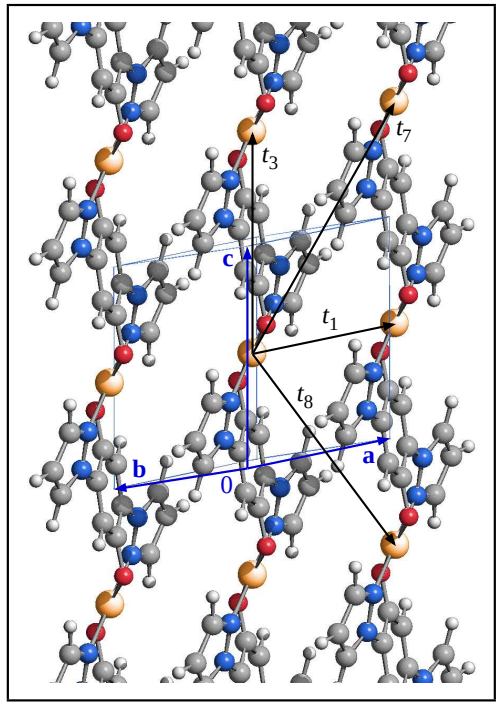
Salguero, Jeschke, Rahaman, Saha-Dasgupta, Buchsbaum, Schmidt, Valentí, New J. Phys. **9**, 26 (2007).

Paths identified by downfolding

Relevant Cu-Cu hopping integrals t_i (in meV) from NMTO downfolding:

t_i	Cu	Cu-NH_2	Cu-CN	Cu-H_2O	Cu-NH_3
t_1	4	9	2	8	11
t_2	8	3	0	7	5
t_3	79	88	68	57	22
t_7	5	1	9	1	1
t_8	3	8	8	0	0
t_{12}	0	0	9	0	0

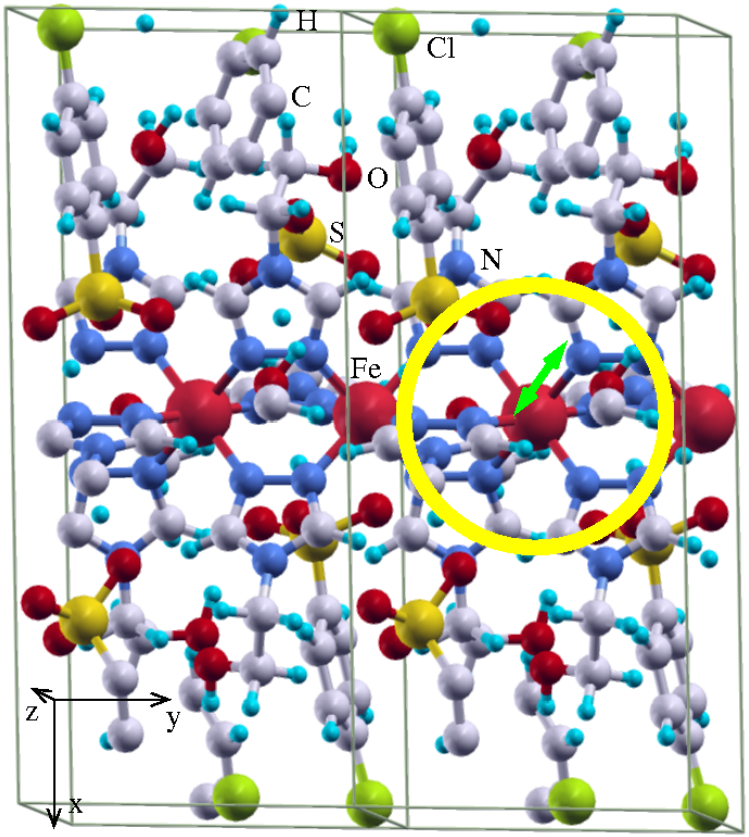




Interpreting t_3 in terms of a superexchange coupling $J_{\mathrm{AFM}} \approx 4t_3^2/U_{\mathrm{eff}}$ with effective Coulomb interaction $U_{\mathrm{eff}} = 5$ eV, gives

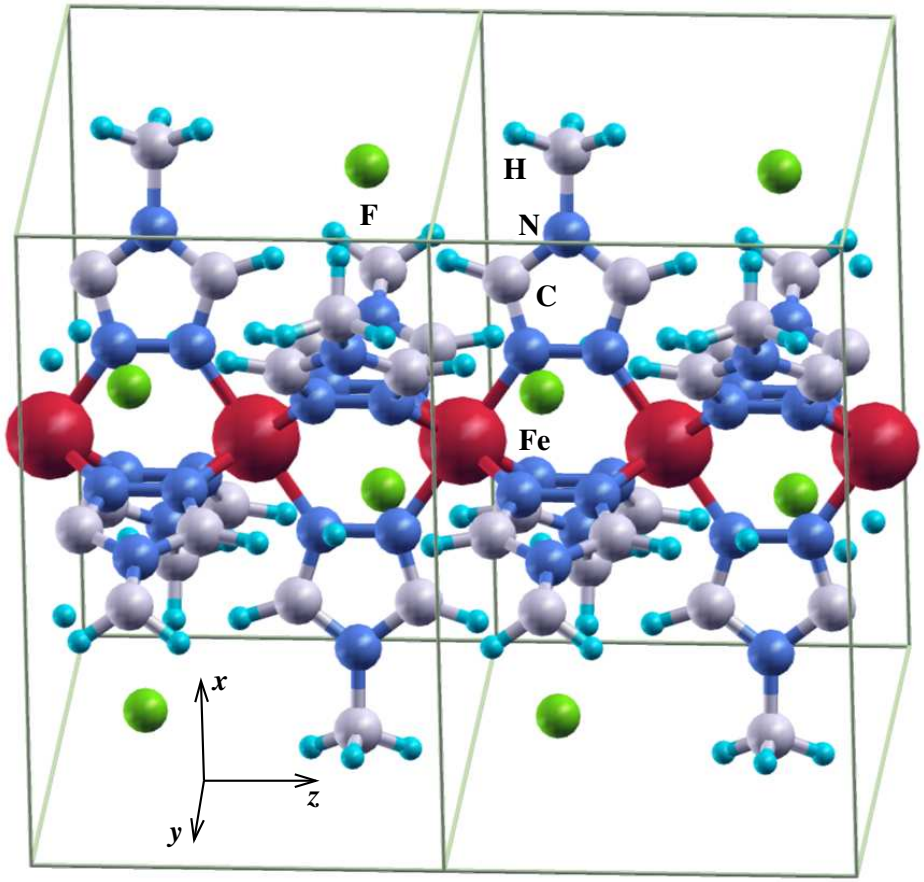
	Cu(II)	Cu(II)-NH_2	Cu(II)-CN	Cu(II)-H_2O	Cu(II)-NH_3
J_{AFM}	58 K	72 K	43 K	30 K	4 K

Construction of a model structure



Simplify Fe(II) triazole complex:
Transition known to be
triggered by Fe-N distance:
2.0 Å → LS, 2.2 Å → HS

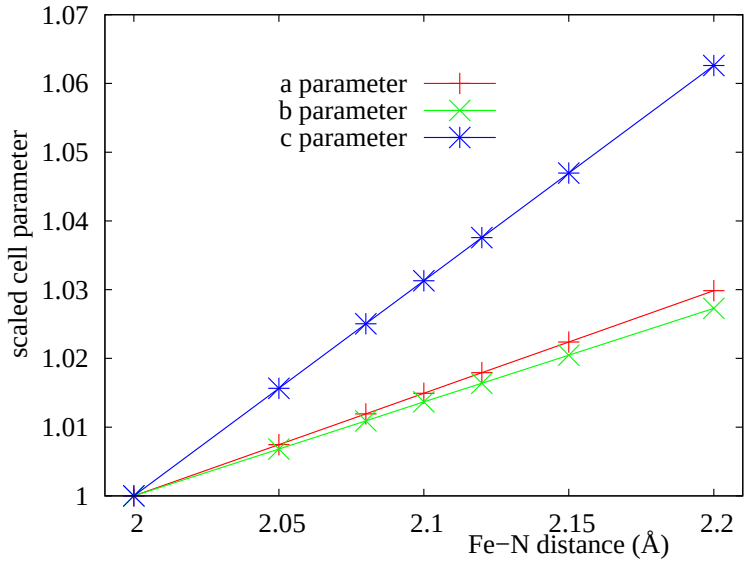
Probably unimportant: chlorophenyl-sulfonate anion, hydroxy-ethyl group.
Simplification: F^- anion, methyl group.



Set of model triazole structures

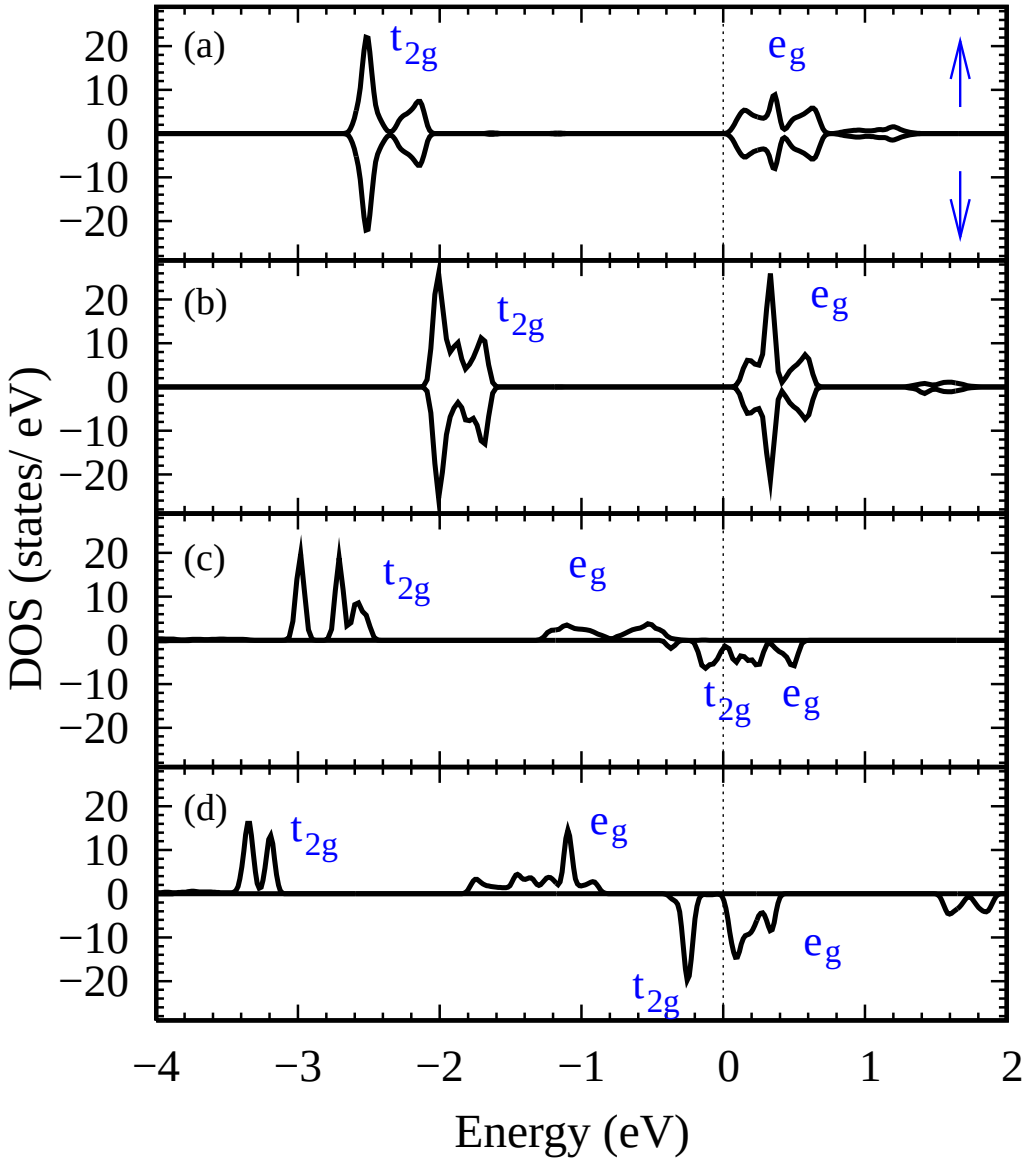
- Principles for construction of model set with Fe-N distances varying across the LS-HS transition:

1. N-N distance constant at 1.38 Å.
2. Therefore, each Fe-N distance requires different unit cell.
3. Perfect octahedral environment of Fe(II).
4. Other atoms except F^- prerelaxed by force field.



- Several days of parallel computation for FPLAPW electronic structure.
- Several weeks of parallel computation for *ab initio* molecular dynamics relaxed structure.
- Without CPMD relaxation no FPLAPW convergence!

Triazole model structures show LS-HS transition



- Contribution of Fe *d* states to the density of states.
- (a) $d_{\text{Fe-N}} = 2.0$ Å and (b) $d_{\text{Fe-N}} = 2.05$ Å are low spin, $S = 0$.
- (c) $d_{\text{Fe-N}} = 2.15$ Å and (d) $d_{\text{Fe-N}} = 2.2$ Å are high spin, $S = 2$!

Conclusions and Outlook

Cu(II) coordination polymer

- Combination of force field and *ab initio* methods makes metalorganic materials accessible to precise analysis.
- Computer design of magnetic properties by substitutions becomes feasible.

1D Fe(II) triazole model polymer

- Careful preparation of model structure allows *ab initio* study of LS-HS transition.

Ongoing and future applications

- Family of vanadates with incomplete coordinates.
- Quantum spin system CuHpCl with badly resolved H positions.
- Charge transfer salts κ-(BEDT-TTF)$_2$X with unknown H positions.

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Publications:

H.O. Jeschke, L.A. Salguero, R. Valentí, C. Buchsbaum, M.U. Schmidt, M. Wagner, *Classical and ab initio preparation of reliable structures for polymeric coordination compounds*, C.R. Chimie **10**, 82 (2007), doi:10.1016/j.crci.2006.06.007

L.A. Salguero, H.O. Jeschke, B. Rahaman, T. Saha-Dasgupta, C. Buchsbaum, M.U. Schmidt, R. Valentí, *Cu-based metalorganic systems: an ab initio study of the electronic structure*, New J. Phys. **9**, 26 (2007).