

Metal-ligand delocalization and spin density in CuCl₂ and (CuCl₄)²⁻: some insights from WFT

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- 1 Why worrying about the SD ?
- 2 CuCl₂ as a prototype of troublemaker
- 3 (CuCl₄)²⁻
- 4 Conclusions and perspectives

Definition of the spin density (SD)

A lot of possible definitions, but mainly :

$$\Delta\rho(\mathbf{r}) = \rho_{\alpha}(\mathbf{r}) - \rho_{\beta}(\mathbf{r})$$

In open shell systems :

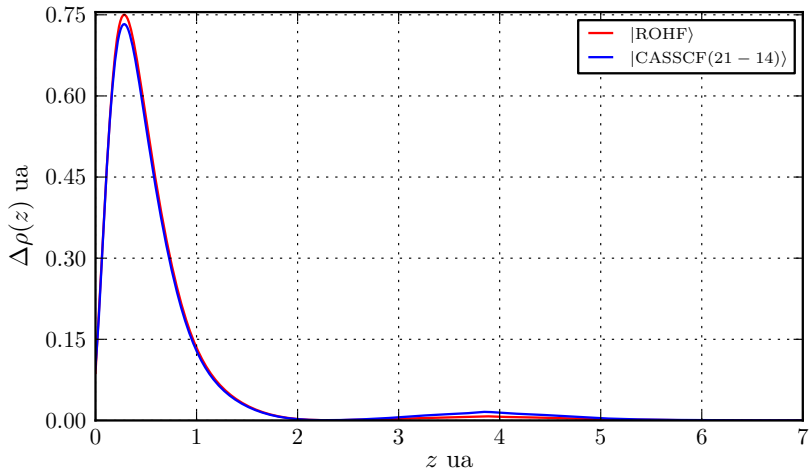
- Distribution of the **unpaired electrons**
- Metal-ligand delocalization
- Calibration of DFT models

The importance of the SD

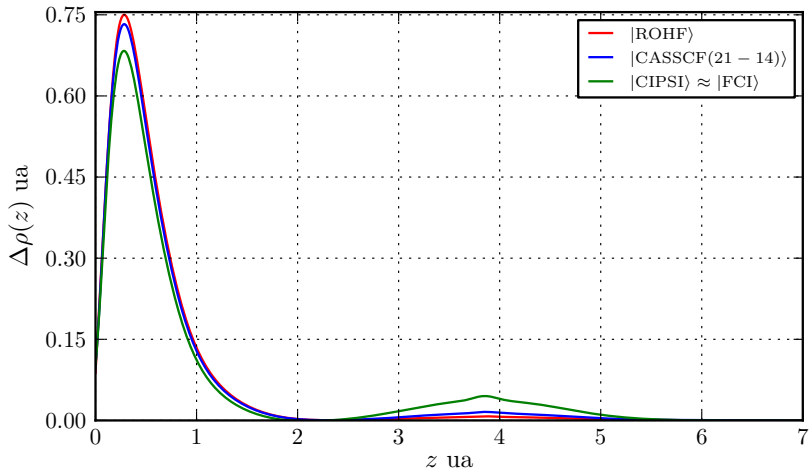
Bad SD can affect :

- one body DM
- bonding analysis
- **SO** treatment ?
- spin coupling

Global shape of $\Delta\rho(z)$ in 6-31G for CuCl₂



Global shape of $\Delta\rho(z)$ in 6-31G for CuCl_2



Analysis of the near-FCI wave function

ROHF \approx **Cl⁻ Cu²⁺ Cl⁻** : unpaired electron on the copper

After that, the most important is a **single excitation** :

- This single excitation is a **LMCT** !

$$|\text{LMCT}\rangle \equiv a_{\beta}^{\dagger} \text{ SOMO } a_{\beta} b_{2g(p_x)} |\text{ROHF}\rangle$$

- $|\text{LMCT}\rangle \approx$ resonance of **ClCu⁺Cl⁻** and **Cl⁻Cu⁺Cl**
 \Rightarrow unpaired electron on the chlorines

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$$\frac{c_{\text{LMCT}}}{c_{\text{ROHF}}} = -\mathbf{0.195}$$

- **Very important for $\Delta\rho(z)$!**

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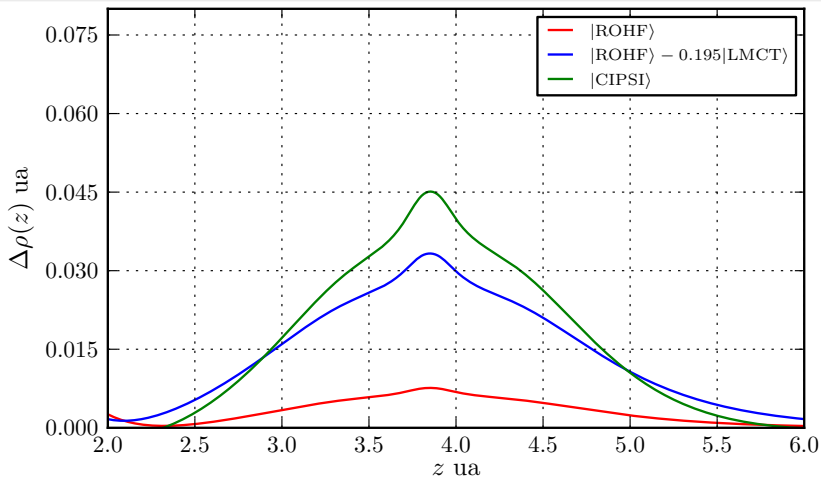
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Importance of the LMCT determinant for the SD



Strange things ...

Large coefficient for a single is weird because :

- **Brillouin theorem** : $\langle \text{LMCT} | H | \text{ROHF} \rangle = 0$
no interaction with the dominant determinant ...
- **Very high in energy** $\Delta E \approx 11.1 \text{ eV}$
No near degeneracy effects!

Where does it come from ? !

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The singles on the LMCT configuration

Largest interaction $\langle \text{LMCT} | H | D \rangle$:

Double which are **single excitations on top of** $|\text{LMCT}\rangle$:

$$|D\rangle = a_r^\dagger a_i |\text{LMCT}\rangle$$

$\langle \text{LMCT} | H | D \rangle$ up to 7 eV !!

⇒ suggest strong orbital relaxation for $|\text{LMCT}\rangle$

copper goes from Cu²⁺ to Cu⁺ ⇒ Response of the 3d orbitals

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First order breathing orbitals CI (FOBO-CI)

Need to relax the orbitals of |LMCT⟩

FOBO-CI wave function :

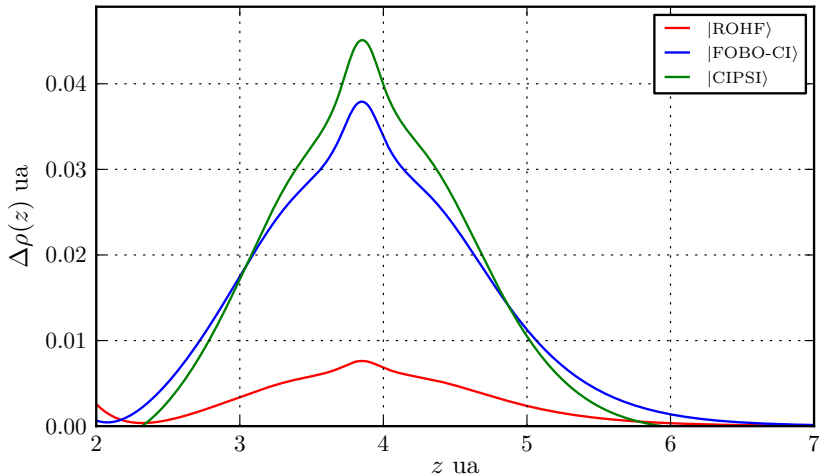
- |ROHF⟩
- |LMCT⟩
- All the singles on top of |LMCT⟩
⇒ many of them are double excitations!

In such wave function :

- |ROHF⟩ is optimal (...)
- |LMCT⟩ is optimal to first order !

Includes charge polarization !

First order breathing orbitals CI (FOBO-CI)



Rafinements : including the **Spin polarization**

What about the **Spin polarization** ?

Including the singles excitations on top of |ROHF⟩ !

$$\begin{aligned} |\text{FOBO-CI} + \text{SP}\rangle &= c_{\text{ROHF}} |\text{ROHF}\rangle + c_{\text{LMCT}} |\text{LMCT}\rangle \\ &+ \sum_{i,r} c_{ir}^{\text{LMCT}} a_r^\dagger a_i |\text{LMCT}\rangle \\ &+ \sum_{i,r} c_{ir}^{\text{ROHF}} a_r^\dagger a_i |\text{ROHF}\rangle \end{aligned}$$

Here |FOBO-CI + SP⟩ contains **216 determinants**.

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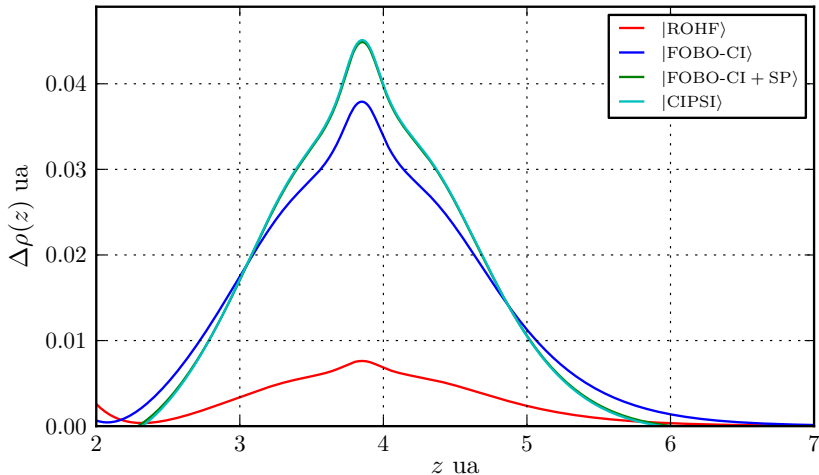
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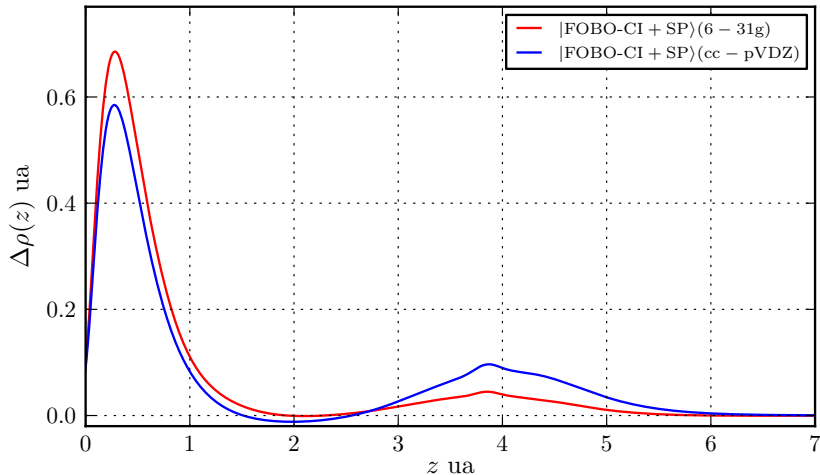
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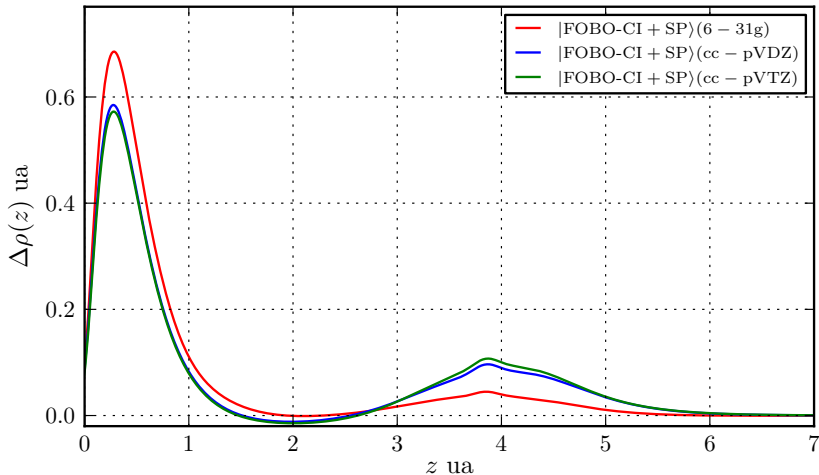
The FOBO-CI+SP spin density



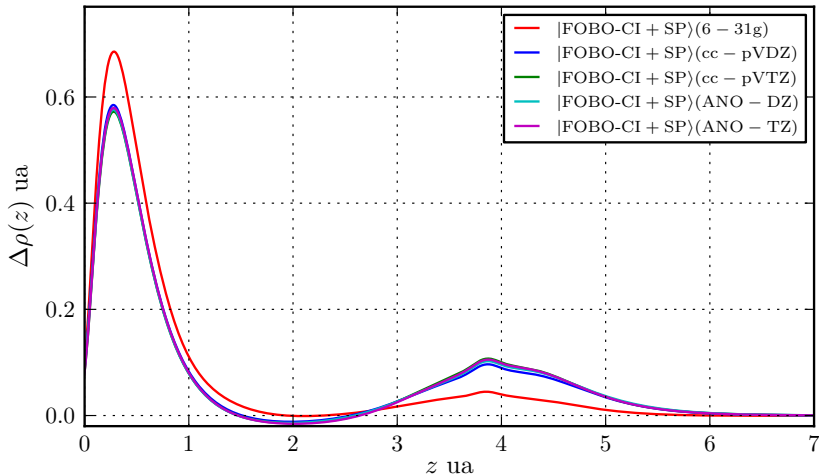
Use of bigger basis set for CuCl_2



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Application of the FOBO-CI to $(\text{CuCl}_4)^{2-}$

Mulliken spin density on the copper atom			
Basis set	ROHF	FOBO-CI+SP	B3LYP
6-31G	0.93	0.81	0.70
cc-pVDZ	0.92	0.63	0.55
cc-pVTZ	0.92	0.66	0.55
aug-ANO-DZ	0.92	0.65	
Experimental 0.62(2)			

metal-ligand delocalization ?

What about

- Don't trust mean-field
- LMCTs determinants are important
- Need to include orbital relaxation for LMCTs
- Then, spin polarization plays a role

Delocalization appears at correlated level :
huge impact of the breathing orbitals for the LMCT !

Results supported also by Non Orthogonal Valence Bond
calculations ...

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The FOBO-CI+SP

Minimal CI space to obtain very accurate SD

Advantages :

- contains most of the physics of delocalization
- modest computational cost (\propto CIS)

Perspectives

Methodological :

- generalize the approach :
How to find the |LMCT⟩ in a general system ?
- MRCC formalism to go beyond 1st order

Applications : use of the natural orbitals of |FOBO-CI + SP⟩

- spin coupling at NEVPT2/CASPT2 cost :
⇒ Inorganic/organic magnets
- spin anisotropy at minimal CI cost :
⇒ **g** and **D** tensors

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Advertising

All the methods employed have been implemented (with love) in the ***Quantum Package*** program developed by :

A. Scemama, T. Applencourt, M. Caffarel, myself, and anybody interested (open source!)

Thank you for the attention !!

What about the **Generalized FOBO-CI** ?

Very general method without **any knowledge on the system** :

- **Loop** on all the holes
- Independent diagonalization of **FOBO-CI**
 - ⇒ Small diagonalization (\propto CIS)
 - ⇒ Fully parallel
- Accumulation of non redundant **differential one body DM**
 - ⇒ No big memory storing

At the end of the day :

- Good approximation of the **DDCI one body DM**
 - One body properties
 - **Natural orbitals**

Last results : **Generalized FOBO-CI**

In few words :

- Independent **FOBO-CI** for each hole
- Accumulation of **differential one body DM**
- approximation of the **DDCI one body DM**

Implemented, tested and it is working for :

- inorganic systems :
CuCl₂, (CuCl₄)²⁻ and (Cu[NH₃]₄)²⁺
- organic systems :
Metaxylilene, dimetil-naphtalene

Results on organic compounds

Atom	ROHF	Generalized FOBO-CI Nat. Orb	CAS(Full- π) Nat. Orb.
SD on the Metaxylilene carbons			
C1	0.7764	0.560	0.559
C2	0.1499	0.310	0.312
C3	0.1233	0.250	0.251
C4	0.1064	0.087	0.084
C5	0.0670	0.013	0.009
SD on dimetil-naphtalene carbons			
C1	0.838	0.614	0.642
C2	0.089	0.217	0.200
C3	0.042	0.131	0.118
C4	0.031	0.069	0.066
C5	0.004	0.014	0.013
C6	0.004	0.011	0.009
C7	0.001	0.004	0.003

Perspectives of the Generalized FOBO-CI

One body DM : properties

- Large organic molecules
- Comparison with experimental SD
- Any suggestion ?

Generalized FOBO-CI natural orbitals :

- Spin coupling
 - NEVPT2 study
 - Poly center of copper
 - Organic radicals
- calculation of g tensors
- Any suggestion ?

Guess ...

Why the SCF optimization fails to reproduce the SD ?

- One VB structure is predominant
- VB structures can not be described with one set of MOs
- Mixing them would be energetically unfavourable for both
- Minimization of the variational energy
- ClCu⁺Cl⁻ and Cl⁻Cu⁺Cl are sacrificed !

Why such success of the FOBO-CI wf?

Physical ingredients of the **FOBO-CI** wf :

- |ROHF⟩ and |LMCT⟩ :
allows the **delocalization**
- All the singles on |LMCT⟩ :
 - allows **orbital relaxation** for |LMCT⟩
 - correlate the |ROHF⟩
- All the singles on |ROHF⟩ :
exactly the same correlation effect for |ROHF⟩ and |LMCT⟩
- All the doubles have a mono excitation in common :
No repeatability ⇒ no **size consistency** error !

very balanced treatment of the |ROHF⟩ and |LMCT⟩ !!

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Intermediate effective Hamiltonian

Taking the effect of the $|D\rangle$ **at second order in PT** :

Intermediate effective Hamiltonian with Epstein-Nesbet H_0 (in eV)

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$$H^{(eff)} = \begin{array}{c} \langle \text{ROHF} | \\ \langle \text{LMCT} | \end{array} \begin{array}{cc} | \text{ROHF} \rangle & | \text{LMCT} \rangle \\ \left(\begin{array}{cc} -0.16 & 1.24 \\ 1.24 & 1.50 \end{array} \right) \end{array}$$

Strong **differential effect** for the effective energies !

The mono on top of $|\text{LMCT}\rangle$ play the role of **orbital relaxation** !

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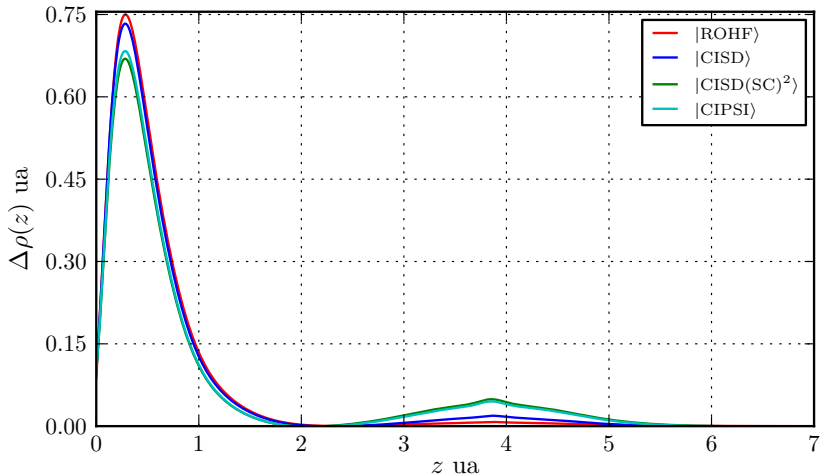
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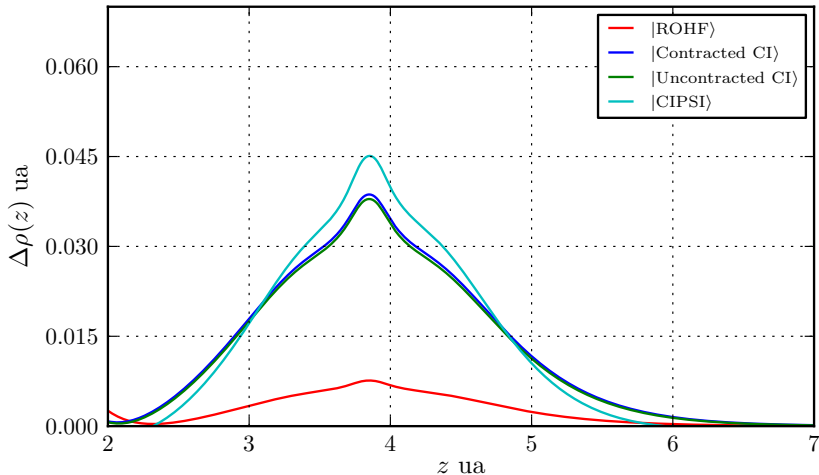
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CISD and CISD(SC)²



Contracted/Uncontracted CI



Basis set	SD (Cu) ROHF	SD (Cu) FOBO-Cl+SP	B3LYP
6-31G	0.942	0.880	0.703
cc-pVDZ	0.970	0.685	0.496
cc-pVTZ	0.970	0.665	0.495
aug-cc-pVDZ	0.971	0.675	0.511
aug-cc-pVTZ	0.971	0.680	0.499
aug-ANO-DZ	0.970	0.672	–
aug-ANO-TZ	0.971	0.688	–

TABLE: Values of the spin density on the Copper (CuCl_2) atom using MPA with the ROHF and FOBO-Cl+SP wave functions in various basis sets.

convergence of the energy

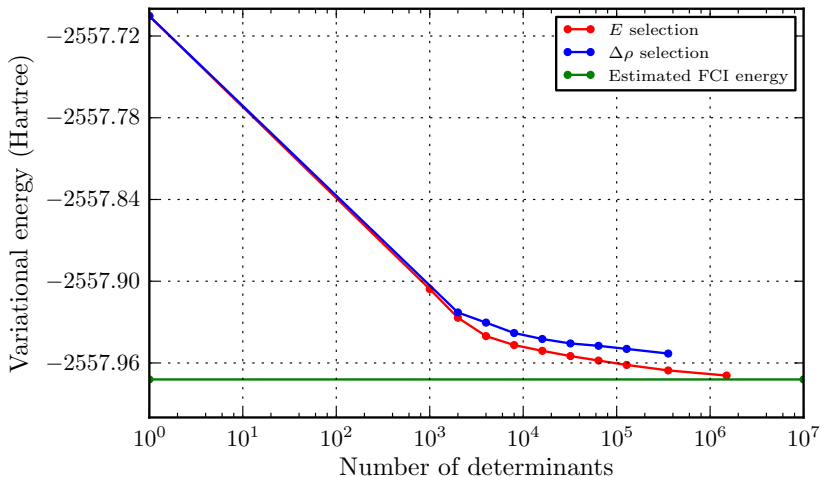


FIGURE: Convergence of the variational energy (Hartree) for the CIPSI

convergence of $\Delta\rho(z)$

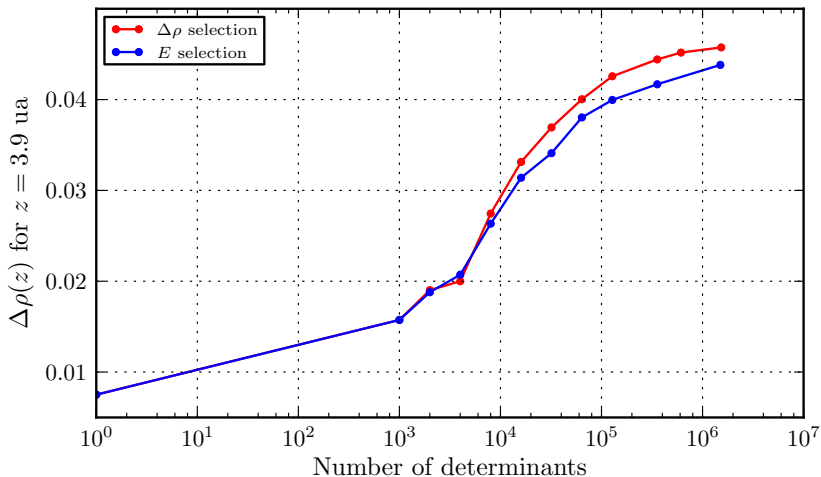


FIGURE: Convergence of the value of $\Delta\rho(z)$ for $z = 3.9 \text{ \AA}$ calculated SD in CuCl₂ and (CuCl₄)²⁻

Non Orthogonal VB calculations

Thanks to the XMVB-2.0 program we have shown that :

- VBSCF on Cl⁻Cu²⁺Cl⁻
⇒ ROHF energy and SD (0.98 on Cu)
- VBSCF on Cl⁻Cu²⁺Cl⁻, ClCu⁺Cl⁻ and Cl⁻Cu⁺Cl
 - No weights on the LMCT VB structures
 - Orbitals optimal for Cl⁻Cu²⁺Cl⁻ !!
 - No change in energy or SD
 - First excited state is at 11.07 eV
- Breathing Orbital VB on the 3 VB structures :
 - Significant weights on the LMCT VB structures
 - 1 eV of lowering in the total energy
 - 3 set of orbitals are different
 - SD goes to 0.85, the FOBO-Cl gives 0.87
 - First excited state at 5 eV

Some remarks ...

In this case :

- FOBO-CI space : **sub space** of CISD ...
- the FOBO-CI **works** ...
- but the CISD **fails** ...
- and the CISD(SC)² **works** ...

FOBO-CI and CISD(SC)² are **both size consistent** !

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Changes in Hamiltonian matrix

One can map the diagonalization to a 2×2 matrix

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The spin polarization with the hands

In open shell system : More α than β

- The unpaired electrons create an "exchange field"
- Only the α will feel it
- The orbitals for α and β will be polarized by this field
- Can be taken into account by single excitations

Global shape of $\Delta\rho(z)$ in 6-31G for CuCl_2

