

Spin and charge distribution in iron porphyrin models: DFT vs CC2

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Introduction

- **Density Functional Theory** is the method of choice for quantum chemical studies of, among other things, large systems.
- Approximate DFT, however, suffers from the lack of a systematic method of checking the accuracy of a given calculated property.
- Desirable to **check DFT results with wave function methods**, especially when new combinations of properties and systems are studied.
- Here, two effects for **iron porphyrins**, previously studied with DFT, are checked with the coupled cluster RI-CC2 method:

1. The molecular spin polarisation

- We recently performed a thorough DFT examination of the **molecular spin polarisation** for low-spin iron porphyrins [1].
- The **gross spin density**, or, the sum of unpaired α and β density, is significantly **larger than unity**, about 1.3.
- This reconciled two seemingly contradictory experimental views of the spin density distribution, based on ESR and NMR spectra.

2. The charge delocalisation

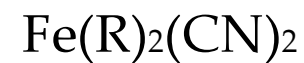
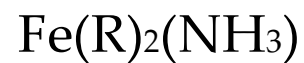
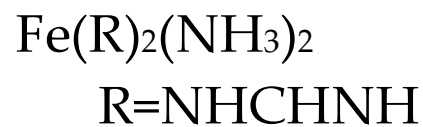
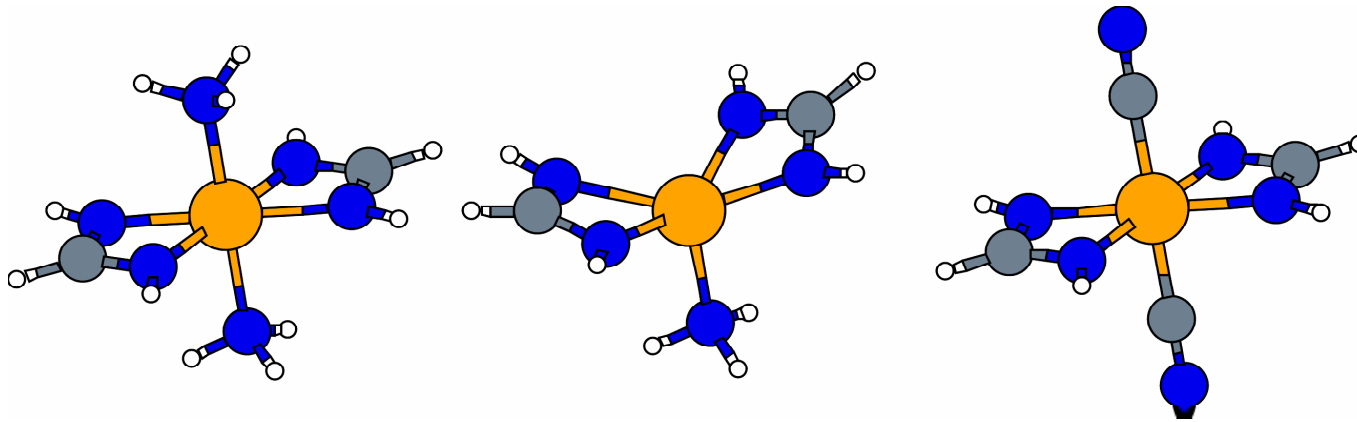
- In another work [2] the charge delocalisation upon reduction of haems (iron porphyrins in general) was found to be quite extensive.

- This "dilution" of the added unit charge is crucial for the accommodation of the haem in the protein, and favours the *edge-to-edge* electron transfer mechanism between haems.

Motivation

- Both properties above are *potentially badly described by DFT*:
 1. The molecular spin polarisation could be a manifestation of one of the recently discussed caveats in the definition of Spin-DFT:
 - a) The external potential is not unambiguously defined [3].
 - b) $\rho(\alpha) - \rho(\beta)$ could describe something else than the spin density [4].
 2. DFT might not be well suited for describing electron (de)localisation in charged species.

- Therefore, a **second opinion** provided by traditional wave function methods is of interest.
- Here, we present coupled cluster calculations on small five- and six-coordinated FeP-models, which reproduce both the spin polarisation and charge delocalisation effects:



Computational methods

Level

- **Structures** were optimised with the semi-local functionals **BLYP** and **PBE**, as well as with **LDA**.
- **Electron densities** were calculated with DFT and the approximate singles and doubles coupled cluster method, CC2.
- Augmented triple-zeta basis sets were used. (aug-TZVPP and aug-cc-pVTZ)
- The density fitting resolution of the identity (RI) approximation was employed at both DFT and CC2 levels.
- The RI-DFT [5] and RI-CC2 [6] methods reduce the computational cost significantly, without noticeable loss of accuracy.

Electron density calculations

- The **spin density** is obtained as the difference between α and β electron-densities.
- The **gross spin density** is defined as the sum of unpaired α and β spin densities.
- The **charge density** difference is obtained as the difference in total electron density between the oxidised and reduced forms.
- The electron densities were studied by evaluating them in equidistant Cartesian grid points.
- Direct numerical integrations of the electron densities were performed.

The accumulated electron density inside a sphere of radius r is defined by:

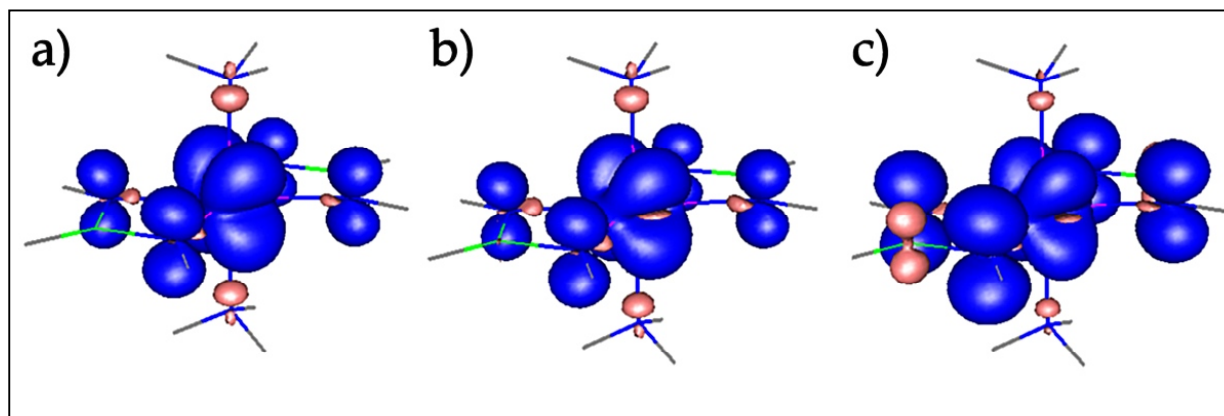
$$\rho_{el}(r) = \frac{1}{N(r)} \frac{4}{3} \pi r^3 \sum_i^{N(r)} \rho_{el,i}$$

where $N(r)$ is the number of integration points and i runs over all three Cartesian coordinates.

- The **core orbitals were left out** of the integration; $1s$ of C and N, as well as $1s$, $2s$, and $2p$ of Fe were ignored. This actually improves the numerical accuracy.
- The CC2 electron densities were obtained from the CC2 natural orbitals and their occupation numbers.
- To dissect the contributions from exchange and correlation, exchange- and correlation-only functionals were employed.
- All calculations were performed using the **TURBOMOLE** package [7], version 5.6.

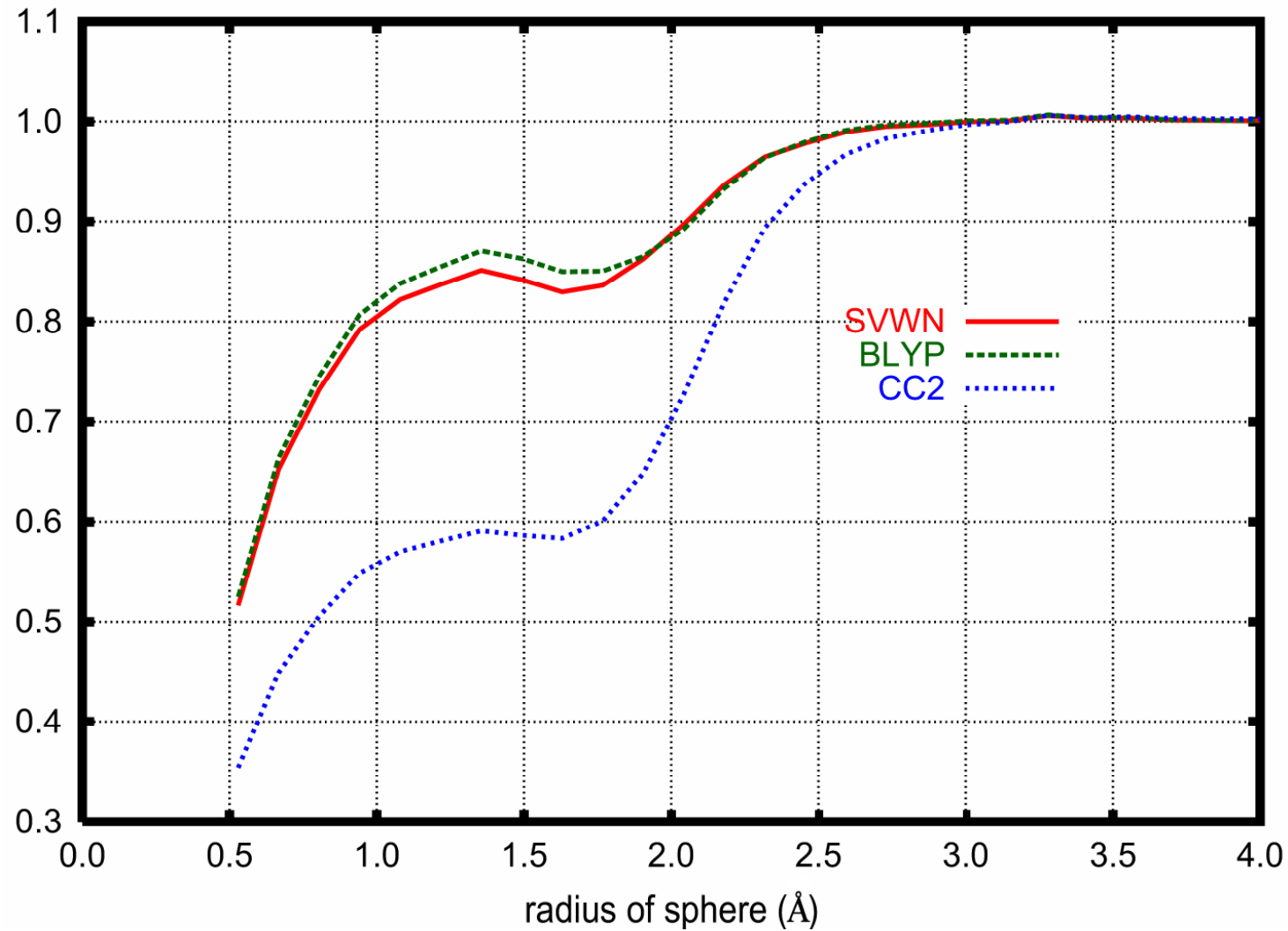
Results

Spin densities, low-spin case



- The figure shows the spin density distribution for the **cationic model** system, $[\text{Fe}(\text{R})_2(\text{NH}_3)_2]^+$. **Blue** represents excess α -spin, and **red** excess β -spin. a) LDA, b) BLYP, c) CC2.
- All methods give similar spin density distributions, although some differences between DFT and CC2 can be noted.

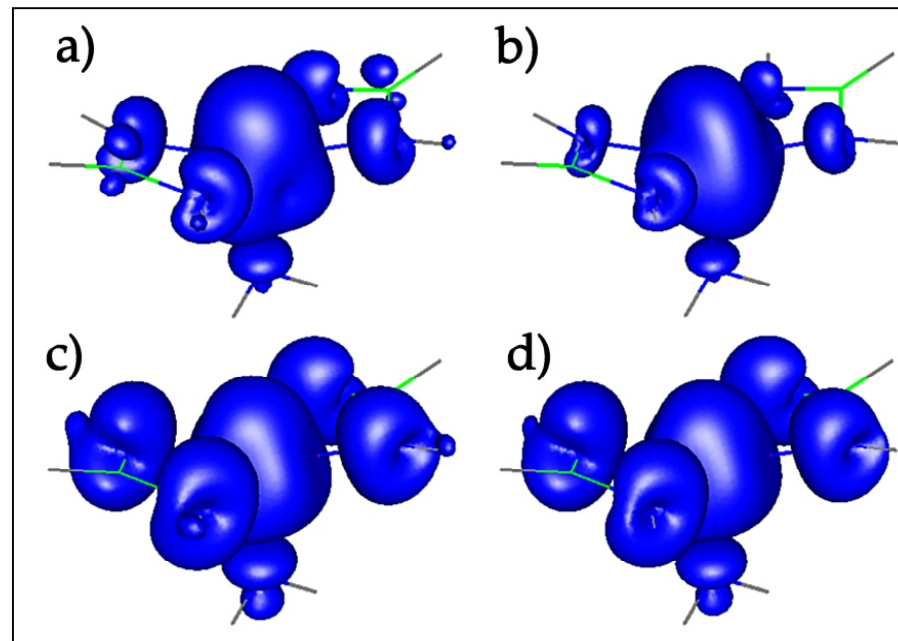
- The biggest difference is found for the spin density concentration around iron:



- The CC2 method has a much lower Fe spin density. The system has high **multiconfiguration character**, so DFT is probably more correct.
- Within the covalent radius of Fe, 1.2 Å, CC2 has less than 0.6 unpaired electrons, whereas DFT gives 0.85.
- The **gross spin densities** were however found to be of comparable magnitude:
 - SVWN: 1.18 electrons
 - BLYP: 1.20
 - PBE: 1.20
 - CC2: 1.24
 - HF: 1.50
- The spin density in the **anionic model**, $[\text{Fe}(\text{R})_2(\text{CN})_2]^-$, was very similar to the cationic, gross spin densities of 1.23 (BLYP) and 1.28 (CC2) were obtained.

Spin densities, high-spin case

- For the high-spin model, $\text{Fe}(\text{R})_2(\text{NH}_3)$, the spin density for both the oxidised and the reduced forms were studied



a) BLYP / $S=2$

b) CC2 / $S=2$

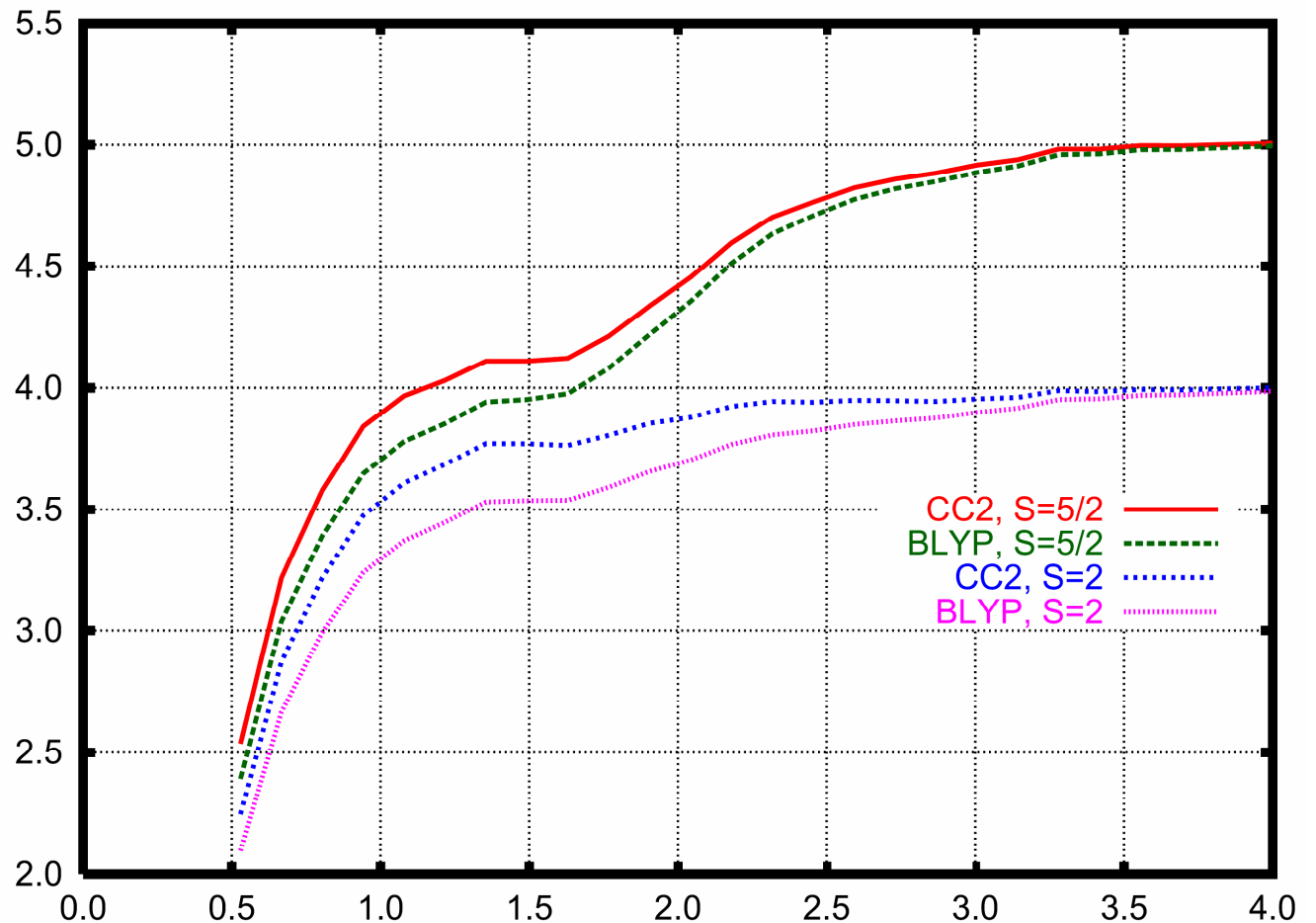
c) BLYP / $S=5/2$

d) CC2 / $S=5/2$

- Very similar distributions are seen

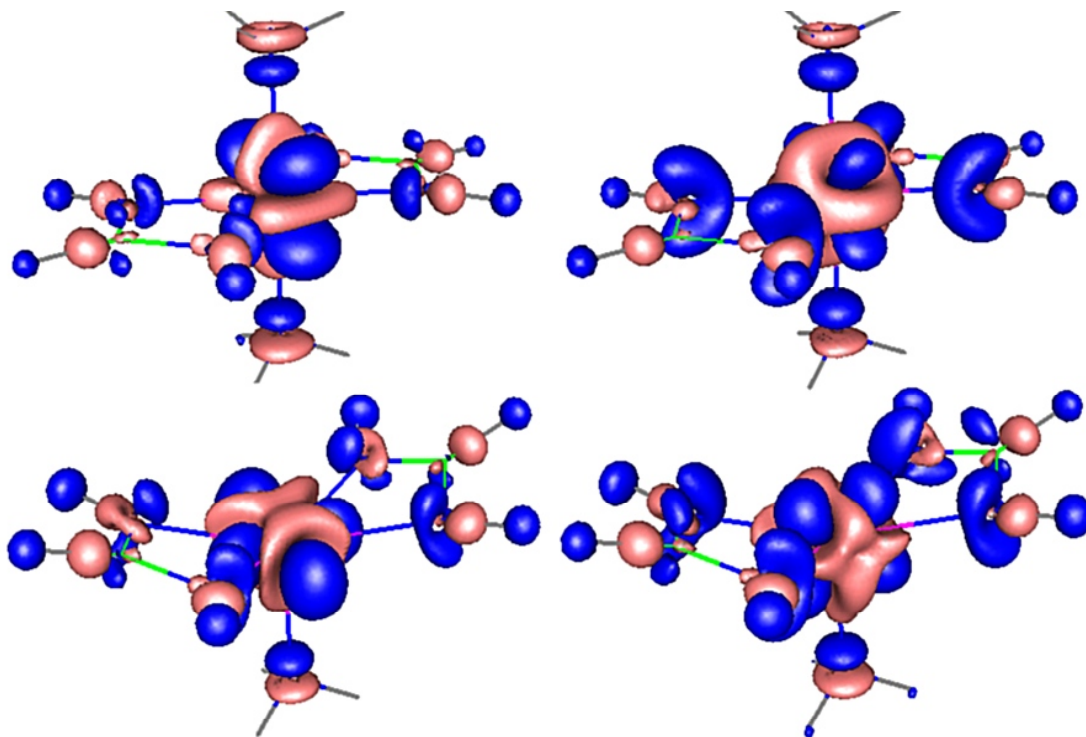
- Small difference in the ferrous, $S=2$ case: C spin density of opposite sign, different d -orbital occupation.
- **Gross spin densities** very near the net spin density
 - ferrous: 4.06 (BLYP) and 4.09 (CC2)
 - ferric: 5.03 (BLYP) and 5.06 (CC2)

- Now DFT and CC2 curves almost overlap.
- **Large delocalisation of the spin density**
- For the oxidised system with 5 unpaired electrons, the iron holds only 4. A preference for a d -orbital occupation of 6.



Change in electron density upon reduction

- The changes in total electron density upon reduction of the low- and high-spin models were studied
- The **degree of delocalisation** was found to be **very similar at DFT and CC2 levels**.
- CC2 actually delocalises the added electron more than BLYP.
- **Within a sphere of 2 Ångström** around Fe, touching the ligating nitrogens, all methods show **less than 0.2 electrons more** for the reduced system compared with the oxidised.
- Generally, electron density upon reduction is added to regions where the oxidised model has **higher spin density**:



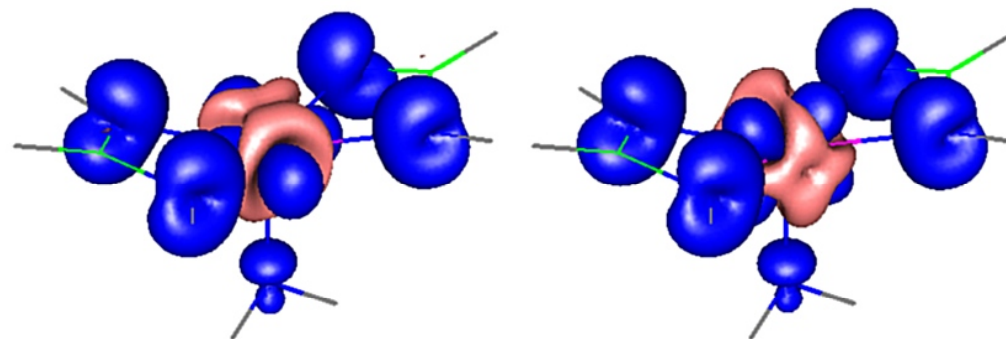
change in total electron density on reduction.

blue = more electrons in the reduced form,

red = more electrons in the oxidised form

change in absolute spin density on reduction

blue = more unpaired electrons in the oxidised form.



Conclusion

- The wave function based CC2 method corroborates the DFT results. **DFT works. [9].**

Acknowledgements

The nice molecular plots were made using the **gOpenMol** package [8], while the curves were obtained with **gnuplot**. CSC – Scientific Computing Ltd. is acknowledged for continuous extension of computational quota.

References

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