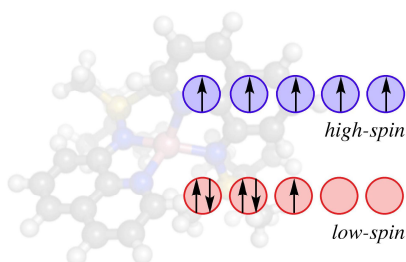


# Spin States in Biochemistry and Inorganic Chemistry



**September 18, 2012 - September 21, 2012**  
**University of Zaragoza, Spain**

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*Another contemplating visitor of Zaragoza (photo: M. Swart)*

# 1 Description

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The electrons surrounding the nuclei of all matter around and within us can be in two different states, denoted the electron spin. This effect, although being purely quantum-chemical, has profound implications for real-world, large-scale systems like, for example, living tissue. In most cases, electrons of different spin pair up, effectively cancelling the spin-effect. In some cases, however, electrons prefer not to pair up, which leads to an excess of one type of electrons in a system. Depending on the exact conditions and surroundings, the number of these unpaired electrons can vary, leading to different spin-states not only for the individual electrons, but for much larger molecular species. In many cases, the spin-state has been found to be a key factor governing the behaviour of the system. Elucidating the role and effect of different spin states on the properties of a system, even deciding which spin-state occurs naturally, is presently one of the most challenging endeavours both from an experimental and theoretical point-of-view.

Reactivity patterns in organometallic and bioinorganic chemistry often depend critically on the spin state, e.g., on the spin-state preferences of reactants, products, intermediates and transition states [1,2]. For heme-proteins, this has been acknowledged for decades [3], and recently, spin-state controlled reactions have been proposed to be important also outside the realm of biomolecules, that is, in industrial catalysis [4]. As a specific, intriguing example of this, merely one of a myriad, we consider the catalytic cycle of cytochrome P450cam that catalyzes the hydroxylation of R-camphor to 5-exo camphorol [5]. In the catalytic cycle [6], a low-spin doublet is observed for the resting state which goes to a high-spin sextet after substrate binding [7-12]. This spin-flip in the first step seems to be determined primarily by the presence or absence of water molecules in the active site, and is vital for the specificity of the reaction taking place. Another key factor is a tyrosine residue that serves as an anchor for the natural substrate (R-camphor) and prepares it maximally for the subsequent hydroxylation [13-15]. For instance, a previous study [13] showed that upon binding to Tyr96, the substrate is found to be distorted, especially at the atom (C5) where the reaction takes place. The replacement of the Tyr96 residue by phenylalanine indeed reduces the regio- and stereo-specificity dramatically [16].

Another intriguing aspect of the catalytic cycle of P450cam is related to the step after the substrate has entered the active site [5]. The cycle continues with an electron transfer from a reducing agent, in the natural system putidaredoxin [17,18], to give a quintet state after the transfer. This electron transfer takes place only when substrate is present, that is, only for the high spin state. Moreover, it seems that only when the electron transfer has taken place, that dioxygen can enter the active site. In this process of dioxygen binding, there is a second spin-flip present. The paramagnetic dioxygen molecule (with a triplet ground-state) on its own already induces a change of the spin-state, which would have lead to a triplet. Instead, it goes to a singlet state. The subsequent steps to product formation probably follow a rebound mechanism involving "Compound I", but there are also studies that suggest other mechanisms [19-23].

In order to help understand these subtleties and explain the missing steps in the reaction mechanism that occur too fast for experiments to follow, theoretical chemistry can play an important role. However, theory is not without its own problems (see State of the art section). At present, the situation is such that it is advisable to always include the results from a number of different quantum-chemical methods, to ensure the results are consistent. In practice, when large molecular systems are of interest, the density functional theory (DFT) approach is the only viable alternative. There are, however, many different functionals that are proposed by different research groups (B3LYP\*, TPSSH, OPBE/OLYP, SSB-D, M06-L, B3LYP, B2PLYP, ...), without a clear consensus on which should be used (and why). The motivation for proposing this workshop is to be able to get together important players in the field and discuss this unfortunate situation thoroughly. The aim is to reach consensus on the current situation at hand, and more importantly, discuss best practices on how to deal with the problem in future scientific research.

The focus of the workshop will not be limited only to theory; many of the assumptions about spin-state preferences are based on experimental data, which may not be not conclusive in each and every case. For instance, different complications may occur in the experiments, such as dimerization, ligand exchange, or disproportionation, which make that the system studied theoretically does not correspond to the one for which experimental data are observed. Likewise, there may be metal impurities present in the sample that might interfere with the observation of magnetic moments. Recent examples of "failures" of DFT in our research group in Girona turned out to be most likely due to inconsistencies in the experiments (e.g., disproportionation as described in refs. [24,25]). In order to

resolve this, and get a clear discussion about these effects, we have also invited several experimentalists (Mayer, Que, Ghosh, Costas) to share their experiences and insights on this.

The most popular method for studying (bio)inorganic catalysis is presented by Density Functional Theory (DFT) [26-28], due to its efficiency that enables to treat large systems of up to several hundreds, even thousands of atoms in a reasonable time. Also wave-function based methods can be used (for example, CASPT2), such as done by, e.g., de Graaf or Pierloot, with the significant draw-back that only much smaller systems can be treated. Almost all DFT studies in the literature so far have either used the B3LYP [29,30] or BP86 [31-32] functionals, which for most simple cases both give good results. This is no longer true when spin-states with energy levels in close proximity are involved [33,34], that is, when a transition metal like chrome, manganese, iron, cobalt or nickel is present. Previous studies [35-37] have shown that both of these functionals are unable to correctly predict the spin ground-state of these transition-metal complexes. Early GGA functionals like BP86 tend to overstabilize the low-spin state, while hybrid functionals like B3LYP tend to overstabilize the high-spin state (due to the inclusion of a portion of Hartree-Fock exchange) [34, 38]. Several remedies have been proposed, such as lowering the amount of Hartree-Fock exchange in B3LYP to 15% (B3LYP\*) [35], mixing the Becke88 and PW91x [39,40] exchange functionals (XLYP, X3LYP) [41], or introducing a Hubbard U parameter [42], but none one of these was really satisfactory for all situations. In fact, it was suggested to always calculate the spin-state energies with a number of functionals. An important step forward was made by the application of Handy and Cohen's optimized exchange (OPTX) functional (abbreviated as O in combination with other functionals, as in OPBE or OLYP) [43]. Previous validation studies have shown the validity of the OPBE [33, 44] and OLYP [45-51] functional for the spin-state splittings of iron complexes. While for the vertical spin-state splittings a number of DFT functionals could be trusted to give the correct spin ground-state [33], this picture changed for relaxed splittings [25, 34]. The experience with the OPBE and PBE functionals for spin-states and ( $S_N2$ ) reaction barriers has led to the development of an improved GGA functional (SSB-D), which like OPBE works well for spin states. Other groups have advocated other functionals such as B3LYP\* (Reiher, Siegbahn), OLYP (Ghosh), TPSSh (Jensen), or B2PLYP (Neese).

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## 2 Program

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### Day 1 – Tuesday, September 18, 2012

#### ***Session Ia – Chairperson: Mikael Johansson***

- 15:00 to 15:30 – Welcome
- 15:30 to 16:00 - **Marcel Swart**  
Origins of Workshop
- 16:00 to 16:30 - **Kasper P. Kepp**  
Consistent Descriptions of Spin-Crossover in Inorganic Chemistry
- 16:30 to 16:45 - **Daniel Escudero**  
RASPT2/MM Studies on the Spin State Energetics of Cpd I
- 16:45 to 17:00 - **Mariusz Radoń**  
Spin State Energetics of Heme-Related Models From DFT and *ab initio* Calculations
- 17:00 to 17:15 – Discussion
  
- 17:15 to 17:45 - Coffee Break

#### ***Session Ib – Chairperson: Sam de Visser***

- 17:45 to 18:15 - **Rob Deeth**  
Molecular Discovery and Spin Crossover
- 18:15 to 18:45 - **Coen de Graaf**  
Ultrafast Deactivation Mechanism of the Excited Singlet in the Light Induced Spin Crossover of  $[\text{Fe}(\text{bipy})_3]^{2+}$
- 18:45 to 19:00 – Discussion

## Day 2 – Wednesday, September 19, 2012 (morning)

### *Session IIa – Chair: Kara Bren*

- 9:00 to 9:30 – **Victor Guallar**  
QM/MM Methods: Following Electrons in Complex System
- 9:30 to 10:00 - **W. Robert Scheidt**  
All High-Spin ( $S = 2$ ) Iron(II) Porphyrinates are NOT Alike
- 10:00 to 10:30 - **Per E. M. Siegbahn**  
Spin States and Mechanisms for Natural Water Oxidation
- 10:30 to 11:00 – Discussion
- 11:00 to 11:30 - Coffee Break

### *Session IIb – Chair: Paola Belanzoni*

- 11:30 to 11:45 - **Alexandra T. P. Carvalho**  
Molecular Dynamics of Complex II Within a Lipid Membrane: Parameterization of the Iron-Sulfur Clusters
- 11:45 to 12:00 - **Oliver Krahe**  
Interplay of Theory and Spectroscopy: Study of an Fe<sup>V</sup>-Nitride Complex and its Photolytic Formation
- 12:00 to 12:30 - **Shengfa Ye**  
Elucidation of the Reaction Mechanism of Nonheme Iron Enzymes by a Combined Theoretical and Experimental Approach
- 12:30 to 13:00 - **Jeremy Harvey**  
Spin-State Changes in Thermal Reactions: What Can We Learn from Computational Chemistry?
- 13:00 to 13:30 – Discussion

### **Lunch**

13:30 to 15:30 – Lunch

## Day 2 – Wednesday, September 19, 2012 (afternoon)

### *Session IIIa – Chair: Rob Deeth*

- 15:30 to 16:00 - **Paola Belanzoni**  
How to Make the Iron-Oxo Group an Effective Catalyst in the Oxidation of C–H Bonds and Water
- 16:00 to 16:30 - **Lawrence Que, Jr.**  
Spin State Effects on C–H Bond Cleavage by High-Valent Iron-Oxo Complexes
- 16:30 to 16:45 - **Puneet Gupta**  
Biomimetic Hydroxylation of Non-Activated C–H Bonds in a Bis-( $\mu$ -Oxo)Dicopper Complex: An Evaluation of DFT for Mechanistic Studies
- 16:45 to 17:00 - **Prokopis Andrikopoulos**  
Oxidation of Alkanes: In Silico Catalyst Design
- 17:00 to 17:15 – Discussion
- 17:15 to 17:45 - Coffee Break

### *Session IIIb – Chair: Kasper Kepp*

- 17:45 to 18:15 - **Kallol Ray**  
Lewis-Acid Trapping of an Elusive Copper-Tosylnitrene Intermediate Using Scandium Triflate
- 18:15 to 18:45 - **Sam de Visser**  
Cysteine Dioxygenase: Enzymatic Reaction Mechanism and Biomimetic Models
- 18:45 to 19:00 – Discussion

### **Conference dinner**

- 21:00 to 23:30 - Social Dinner (Restaurante La Bastilla, C/ Coso 177)



## Day 3 – Thursday, September 20, 2012 (morning)

### *Session IVa – Chair: Lubomír Rulíšek*

- 9:00 to 9:30 - **Martin Kaupp**  
Challenges and Means to Obtain Correct Spin-Density Distributions by DFT
- 9:30 to 10:00 - **Markus Reiher**  
Spin States, Spin Density and Local Spin in DFT
- 10:00 to 10:30 - **Rongzhen Liao**  
Why is the Oxidation State of Iron Crucial for the Activity of Heme-Dependent Aldoxime Dehydratase? A QM/MM Study
- 10:30 to 11:00 – Discussion
  
- 11:00 to 11:30 - Coffee Break

### *Session IVb – Chair: Marc-Etienne Moret*

- 11:30 to 12:00 - **Kara Bren**  
The Influence of Heme Conformation and Second-Sphere Interactions on Spin State and Spin Density Distribution in Cytochromes *c*
- 12:00 to 12:30 - **Dage Sundholm**  
The Gauge Including Magnetically Induced Current Method
  
- 12:30 to 13:00 - **Eckard Münck**  
Mössbauer, EPR and DFT Studies of High-Valent Diiron TPA Complexes: Spin Transitions at an Fe(IV)-Oxo Site Induced by Superexchange Interactions
  
- 13:00 to 13:30 – Discussion

## Lunch

13:30 to 15:30 – Lunch

## Day 3 – Thursday, September 20, 2012 (afternoon)

### *Session Va – Chair: Coen de Graaf*

- 15:30 to 16:00 - **Cecilia Sánchez-Hanke**  
Magnetic Circular Dichroism and Other Synchrotron Techniques Sensitive to Spin States
- 16:00 to 16:30 - **Ulf Ryde**  
Accurate Calculations of Geometry and Spin-Splitting Energies for Active-Site Models of [Ni, Fe] Hydrogenase
- 16:30 to 16:45 - **Lucian Constantin**  
Improving Atomization Energies of Molecules and Solids with a Spin-Dependent Gradient Correction from One-Electron Densities Paradigms
- 16:45 to 17:00 - **Julianna Oláh**  
The Peculiar Role of the Iron-Oxo Species in the Catalytic Cycle of the Human Aromatase Enzyme
- 17:00 to 17:15 – Discussion
- 17:15 to 17:45 - Coffee Break

### *Session Vb – Chair: Markus Reiher*

- 17:45 to 18:15 - **Lubomír Rulíšek**  
Calculations of Spectroscopic Parameters of Open-Shell Bioinorganic Systems: Need for Accurate Treatment of Multiple Spin States
- 18:15 to 18:45 – **Kristine Pierloot**  
Coordination of NO to Metal Heme and Heme-Related Systems Studied with Multiconfigurational Perturbation Theory
- 18:45 to 19:00 – Discussion

## Day 4 – Friday, September 21, 2012

### *Session VIa – Chair: Kallol Ray*

- 9:00 to 9:30 - **Miquel Costas**  
Biologically Relevant Oxidation Catalysis with Non-Heme Fe Complexes with N-Based Scaffolds that Provide Strong Ligand Fields
- 9:30 to 10:00 - **Kazunari Yoshizawa**  
Spin-Crossover Phenomena in Electronic Properties and Chemical Reactions Mediated by Transition Metals
- 10:00 to 10:30 - **Marc-Etienne Moret**  
Dinitrogen Functionalization at Iron Metallaboratranes
- 10:30 to 11:00 – Discussion
- 11:00 to 11:30 - Coffee Break

### *Session VIb– Chair: Ulf Ryde*

- 11:30 to 11:45 – **W. M. Chamil Sameera**  
Nitrene Insertion Reactions: Concomitant Involvement of the Singlet and Triplet Pathways
- 11:45 to 12:00 - **Pablo Campomanes**  
Assignment of Zero-Field Splitting Parameters for the Mn(II) Centers in Oxalate Decarboxylase
- 12:00 to 13:00 - General Discussion and Conclusion

### **Lunch**

13:15 to 14:15 – Lunch

### **Departure**

14:15 to 14:45 – Departure, with bus to RENFE train station, then hotel

## 3 Abstracts

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### Origins of Workshop

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Here I will show my personal experiences from the past with spin states. It all started back in 2003 when I was postdoc in the Center for Complex Molecules (CCM) at the VU University Amsterdam. At that time I was working on cytochrome P450cam and how the enzyme environment influences the catalytic cycle of it [1]. After a German conference, we found out that my favourite functional until that time (BP86) was unable to describe correctly the spin states of iron complexes. Soon after we discovered that instead OPBE works very well [2,3], and works well for  $S_N2$  barriers [4,5], but not weak interactions [6,7].

Later on we studied the basis set [8,9], made a new density functional (SSB-D) [10], and applied these to different systems [11-16]: metallocenes, metalloporphyrins, trispyrazolylborates and trispyrazolylmethanes, minimum polarizability principle, spin-crossover, and polymerization mechanisms. These and other studies have been reviewed in a book chapter [17] and a recent Perspective [18].

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## **Consistent Descriptions of Spin-Crossover in Inorganic Chemistry**

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Density functional theory (DFT) is today the unchallenged tool for routinely obtaining information on electronic structure, chemical stability, and reactivity across the Periodic Table. The presentation will discuss the methodological considerations necessary for state-of-the-art accurate calculations of enthalpies or free energies of inorganic systems, with a particular focus on spin cross-over. Physical effects and ingredients in functionals, their systematic errors, and approaches to deal with them are discussed, in order to identify which functionals that provide the right answers for the right reasons.

## RASPT2/MM Studies on the Spin State Energetics of Cpd I

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Cytochrome P450 enzymes catalyze a variety of reactions involving the insertion of molecular oxygen into organic molecules, such as C-H oxidations [1]. The ultimate active species in the catalytic cycle of these P450 enzymes is Compound I (Cpd I), an iron-oxo porphyrin complex, that is responsible for activating the otherwise inert C-H bonds.

In this contribution, we present a benchmark study on Cpd I using second-order Restricted Active Space Self-Consistent-Field Perturbation Theory (RASPT2) for the active center combined with a Molecular Mechanics (MM) treatment for the environment. Single-point RASPT2/MM energies have been computed at the important stationary points along the C-H abstraction reaction catalyzed by Cpd I. High-valent iron-oxo porphyrin complexes are particularly difficult to treat with single-reference quantum chemical methods due to the presence of densely lying electronic states of different multiplicities. While Density Functional Theory (DFT) provides a reasonable performance on reactivity patterns of P450 enzymes, there are certain discrepancies in the spin state energetics depending on the chosen exchange-correlation (xc) functional. Therefore, the use of *ab initio* multiconfigurational methods is preferred for these compounds [2]. We address the optimal partitioning of the RAS subspaces (RAS1, RAS2 and RAS3) as well as the effect of including orbitals involved in specific correlation effects into the active space. In particular, we examine the influence of 3s/3p(Fe) intershell orbitals and 4f(Fe) double-shell orbitals on the spin state energetics. Finally, we consider the effects of spin-orbit coupling along the reaction profile.

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# Spin State Energetics of Heme-Related Models from DFT and *ab initio* Calculations

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Correct description of the iron spin state energetics in heme complexes remains challenging for DFT and *ab initio* methods. Likewise for many other transition metal species, the relative energies of their spin states are highly variable from one functional to another. However, a more detailed analysis indicates that this dependence is pronounced only for the spin transitions involving a change in occupancy of the orbital(s) with antibonding metal–ligand character, *i.e.*, those transitions which modulate the amount of nondynamical correlation connected to the metal–ligand bonding. It is highly desirable to perform correlated *ab initio* calculations in order to resolve the doubts from DFT and to pick the best functionals. To this end, DFT and *ab initio* calculations are compared for selected heme and heme-related models, including Fe(II), Fe(III), Co(II), and Mn(II) complexes. Apart from multireference CASPT2 method, which has already been applied to some of these systems [1–3] the present contribution is focused on CCSD(T) calculations on suitably chosen small models in which the porphyrin ring is mimicked by smaller *N*-chelating ligands—following an approach used, *e.g.*, by Harvey *et al.* [4] and by Johansson and Sundholm [5]. Although the fully-sized heme models are too large for high-quality coupled cluster treatment, much information about their spin state energetics can be inferred from the results obtained for the corresponding small mimics. The role of basis set, extrapolation procedure, and treatment of semicore correlation in such CCSD(T) calculations is systematically investigated with aim of providing the benchmark quality results.

This research has been supported by the Polish Ministry of Science and Higher Education (grant no IP2011 044471) and by the Foundation for Polish Science (START program). This scholarly work was made thanks to POWIEW project. The POWIEW project is co-funded by the European Regional Development Fund (ERDF) as a part of the Innovative Economy program.

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## Molecular Discovery and Spin Crossover

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Spin crossover (SCO) in coordination complexes represents a delicate balance between high- and low-spin states. Seemingly tiny variations in ligand and/or packing may have a significant impact on transition temperatures and hysteresis. Consequently, experimental investigations have had to be extremely conservative and 50 years on from the serendipitous discovery of the first Fe(II) SCO system,  $[\text{Fe}(\text{phen})_2(\text{NCE})_2]$  ( $E = \text{S}, \text{Se}$ ) the vast majority of 'new' SCO complexes remain locked in the original  $\text{FeN}_6$  paradigm. Discovering novel SCO systems requires a knowledge of *both* spin states and thus computational chemistry can – and should – play a crucial role, assuming suitable methods are available. Quantum chemistry (QC) is capable of reaching the required precision but the discovery process represents millions of individual calculations rendering QC impractical. A much faster method is required. Thus, we have extended molecular mechanics by adding two explicit terms to deal with the d-electron effects necessary to treat SCO: (1) the d electron stabilisation energy and (2) the d-d interelectron repulsion. The former favours low spin while the latter favours high spin. By harnessing QC, and experiment, we can generate training data for our ligand field molecular mechanics (LFMM) method which, in conjunction with powerful machine-learning optimisation techniques, enables us to rapidly generate bespoke force fields for any desired metal-ligand combination and thence explore large libraries of complexes for potential SCO behaviour. The process will be illustrated for metal-a(m)mine complexes of the first transition series.



# Ultrafast Deactivation Mechanism of the Excited Singlet in the Light Induced Spin Crossover of $[\text{Fe}(\text{bipy})_3]^{2+}$

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The mechanism of the light-induced spin crossover of the  $[\text{Fe}(\text{bipy})_3]^{2+}$  complex (bipy = 2,2'-bipyridine) is studied by combining accurate electronic structure calculations and time-dependent approaches to calculate intersystem crossing rates [1]. We investigate how the initially excited metal-to-ligand charge transfer (MLCT) singlet state deactivates to the final metastable high spin state. Although ultrafast x-ray free electron spectroscopy have established that the total time scale of this process is on the order of a few tenths of a picosecond [2], the details of the mechanisms still remain unclear. We determine all the intermediate electronic states along the pathway from low-spin to high-spin and give estimates for the deactivation times of the different stages. The calculations result in a total deactivation time on the same order of magnitude as the experimental determined rate and indicate that the complex can reach the final high spin state via different deactivation channels. The initially populated excited singlet state rapidly decays to a triplet state with an  $\text{Fe}-d^6 t_{2g}^5 e_g^1$  configuration either directly or via a triplet MLCT state. This triplet ligand field could in principle decay to the final high spin, but a much faster channel is provided by the internal conversion to a lower lying triplet state and subsequent intersystem crossing to the quintet high spin state. The deactivation rate from this triplet state to the low-spin ground state is much smaller, in line with the large quantum yield reported for the process.

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## **QM/MM Methods: Following Electrons in Complex System**

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Combining quantum chemistry with molecular mechanics one can track now spin densities and follow the electron transfer pathway in complex enzymatic systems. The journey for our group started about 10 years ago with the electron delocalization for Cytochrome P450's compound I. Now quantitative rate constants for complex protein-protein electron transfer can be assessed. We will review these studies and present new data on Cytochrome C Oxidase.

## All High-Spin ( $S = 2$ ) Iron(II) Porphyrinates are NOT Alike

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The first hint of the title's correctness was the observation that the active heme site in hydroxylamine oxidoreductase had an anomalously large value of the quadrupole splitting (QS) in the Mössbauer spectrum compared to hemes such as that in myoglobin. Similar large values of the QS were subsequently found for an iron(II) chloride. An important observation was that the five-coordinate, imidazole complex completely changed character when the imidazole was deprotonated to yield the imidazolate complex. Experimental differences between the two species include Mössbauer (both magnitude and sign of the QS), molecular structure differences, MCD and even-spin EPR. The Mössbauer spectral differences are consistent only with different  $d$  electron configurations, DFT calculations confirm the conclusions reached from the experimental data. It is now clear that this pattern is very general and high-spin iron(II) porphyrinates are strongly segregated into two classes. There is possible biological significance.

## Spin States and Mechanisms for Natural Water Oxidation

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The water oxidation catalyst in photosystem II is a  $Mn_4Ca$  complex with high-spin states on each manganese. The mechanism for water oxidation will be used to exemplify how spin enters in different situations. Ferro- and antiferromagnetic couplings are of concern in the different S-state intermediates. In  $S_4$ , which is the highest S-state, the O-O bond is formed, and has in all mechanisms investigated been found to contain an oxyl radical. Rather surprisingly, a low barrier is found only if a new type of spin-requirement is fulfilled with alternating spins on two manganese and two oxygens, where the two manganese spins are anti-ferromagnetically coupled. This also leads to the requirement that two manganese have to be directly involved in the O-O bond formation, and that their spins are antiferromagnetically coupled. Previous suggestions with a water attack on the oxyl radical, were all built on the assumption that only one manganese was directly active. That mechanism has been found to have a much higher barrier than the present direct coupling of two oxo ligands, of which one is the oxyl radical.

# Molecular Dynamics of Complex II within a Lipid Membrane: Parameterization of the Iron-Sulfur Clusters

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Aerobic respiration, the same process that allows most life to exist, as we know it, also promotes aging and eventually death because of the formation of reactive oxygen species (ROS).

There is now scientific evidence that complex II acts as major source of electrons for ROS production under many highly relevant physiological states relating to disease scenarios such as cancers or oxidative-stress-associated tissue damage in stroke, cardiac arrest, or related conditions.

Here we will present molecular dynamics simulations of complex II embedded within a lipid membrane with the substrate and all the required cofactors. Particularly emphasis will be given to how the parameterization of the three iron-sulfur clusters was achieved. The enzyme has a [Fe<sub>2</sub>S<sub>2</sub>], a [Fe<sub>3</sub>S<sub>4</sub>] and a [Fe<sub>4</sub>S<sub>4</sub>] clusters coordinated to 4, 3 and 4 cysteinyl ligands, respectively. We have carried a detailed analysis of all the possible spin-states for the oxidized and reduced metal clusters using density functional approaches. Calculation of the bond and angle force constants was made resorting to the Seminario *et al.* method.

# Interplay of Theory and Spectroscopy: Study of an Fe<sup>V</sup>-Nitride Complex and its Photolytic Formation

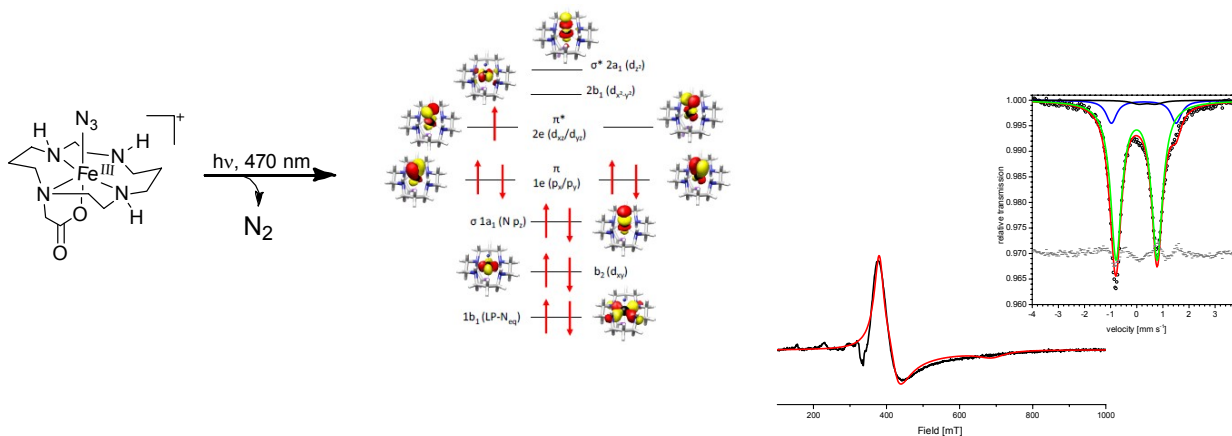
Oliver Krahe, Eckhard Bill, Taras Petrenko, Frank Neese

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In bioinorganic chemistry a wide range of highly developed spectroscopic methods have been used in the study of bio-relevant complexes and over the last two decades, computational chemistry has gained prominence as a powerful tool to provide insight into, *e.g.*, bio-relevant reactions from an additional perspective. DFT is of course the most frequently used method, but with contemporary computers and software it is possible to handle bio-relevant systems with higher level theory, such as correlated single- and multi reference methods.

Both fields, spectroscopy and theory, are individually very powerful, but a combination of both can facilitate the interpretation of data and permits an even more detailed understanding of the studied systems. The ORCA software package developed in our group features all common standard functionality, but is particularly well suited for the calculation of spectroscopic parameters [1]. Therefore we can experimentally verify our calculated electronic structures and confirm or rule out proposed intermediates by comparing calculated and experimental parameters.

For my PhD-thesis I am interested in iron nitrides, which are believed to be key intermediates in the industrial and biological fixation of N<sub>2</sub> [2]. Given the difficulties in isolating and characterizing transient intermediates, model complexes of low molecular weight are synthesized and studied and the results have a high impact on the understanding of real biological systems.



The nitridoiron model system we have chosen to focus upon is a six coordinated Fe<sup>V</sup>-nitride supported by a cyclam derived ligand which is formed by photolysis of its Fe<sup>III</sup>-azide counterpart in frozen solution with 470nm light [3]. Combining spectroscopy and theory we have been investigating the formation process of Fe<sup>V</sup> by N<sub>2</sub> elimination and the electronic structure of the resulting high-valent iron complex. Using DFT we are able to accurately model the measured Mössbauer parameters, but a more sophisticated insight in the electronic structure was obtained by multi-reference calculations (CASSCF/NEVPT2), which also made it possible to reproduce the measured g-values accurately. To map the processes that accompany photo excitation, resonance Raman spectroscopy is a very applicable method, with DFT once again very useful in band assignment.

The presentation will demonstrate how theory and spectroscopy was combined in the study of an Fe<sup>V</sup>-nitride complex.

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# **Elucidation of the Reaction Mechanism of Nonheme Iron Enzymes by a Combined Theoretical and Experimental Approach**

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A range of nonheme iron enzymes utilize high spin ferrous centers to activate oxygen to functionalize the substrates. The catalytic mechanism of Fe(II)/ $\alpha$ -ketoglutarate dependent dioxygenases was investigated by a combined theoretical and experimental approach. Comparison of the reaction energetics among the feasible spin multiplicities reveals that the oxygen activation may proceed either on the quintet and septet surfaces, while the triplet reaction channel is catalytically irrelevant. Moreover, for the septet mechanism, only one step is needed. By contrast, the quintet reaction features a multistep pathway. For the subsequent C-H bond oxidation step by the ferryl intermediate, the calculations show that the quintet species is much more aggressive oxidant than its triplet counterpart. In the second part, we will try to rationalize the theoretical prediction that the quintet species is much more aggressive oxidant than its triplet counterpart.

# Spin-State Changes in Thermal Reactions: What Can We Learn from Computational Chemistry?

Jeremy Harvey

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In this presentation, I will review recent work from my group concerning the effect of spin-state change on the mechanism and rate of thermal reactions (*i.e.*, not photochemical processes).

The talk will cover some simple organometallic reaction steps, *e.g.*, ligand addition to  $\text{Fe}(\text{CO})_4$  [1], as well as some more complex organometallic reaction steps [2] and proton-coupled electron transfer [3]. I will also present unpublished results relating to spin-state changes in catalytic processes.

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# How to Make the Iron-Oxo Group an Effective Catalyst in the Oxidation of C-H Bonds and Water

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Ligand field considerations and density functional calculations indicate the EDTAH<sub>4</sub> complex of the iron-oxo group to be a singularly effective intermediary both in the H abstraction step from C-H bonds in the hydroxylation reaction mechanism and in a catalytic cycle for the water oxidation reaction. Water oxidation may occur either by direct O-O coupling of the oxo group with O(water), or by H abstraction from water, analogous to the H abstraction from C-H bonds by the same iron-oxo group. We can understand the high reactivity of the quintet state of the iron-oxo group from a number of factors that work together. One of them is the stabilizing exchange field of the quintet state with four up spin electrons. But the factors that make the quintet state preferred (weak donors as ligands) already make the  $\sigma^* \alpha$  (antibonding Fe- $d_{z^2}$  – O- $p_z$ ) orbital low-lying to begin with.

## Spin State Effects on C–H Bond Cleavage by High-Valent Iron-Oxo Complexes

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USA

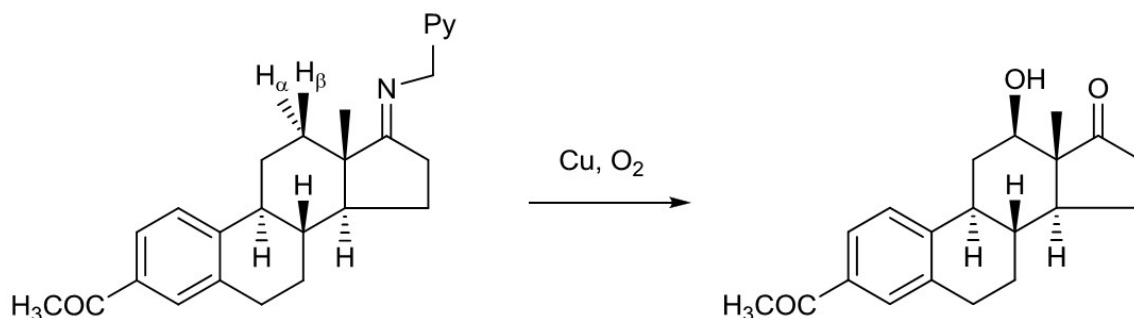
The activation of dioxygen by iron enzymes generally involves the formation of a high-valent iron oxidant. For heme enzymes, this oxidant is formally an iron(V) species but is best described as an  $S = 1$  oxoiron(IV) unit that is coordinated to a porphyrin radical cation. For mononuclear nonheme iron enzymes, the high-valent oxidant is characterized as an  $S = 2$  oxoiron(IV) unit coordinated to histidine and carboxylate ligands. An important goal of our research effort has been to synthesize and characterize oxoiron(IV) complexes of both spin states in nonheme ligand environments. Such molecules can help us gain insight into the factors that govern the ability of the Fe=O unit to cleave C-H bonds. Crystallographically characterized examples of both types are now available. In addition, an Fe=O unit supported by the same ligand has been obtained in both spin states. These intriguing results and other recent developments will be presented.

# Biomimetic Hydroxylation of Non-Activated C-H Bonds in a Bis-( $\mu$ -Oxo)Dicopper Complex: An Evaluation of DFT for Mechanistic Studies

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Bioinorganic research has demonstrated impressively that small synthetic complexes containing a  $[\text{Cu}_2\text{O}_2]$  core can mediate the selective hydroxylation of aliphatic and aromatic C-H bonds, mimicking the function of metalloenzymes like tyrosinase or D $\beta$ H. We have studied the mechanistic scenario underlying the regio- and stereoselectivity of the aliphatic C-H $_{\beta}$  bond hydroxylation in Schönecker's system [1] (Fig. 1) by DFT.



**Figure 1.** The C-H $_{\beta}$  bond hydroxylation through a bis-( $\mu$ -oxo) dicopper complex

Prior to the aliphatic C-H bond activation a peroxo/bis-( $\mu$ -oxo) core-isomerization occurs [2], which represents a notorious problem for DFT [3]. Several authors have put forward differing recommendations as to the choice of functionals for related systems [3] and in this context it remains an open question whether or not to apply a broken-symmetry approach for the peroxo-isomer with its coupled copper(II) ions.

In a careful benchmark study we tested various flavors of DFT and relativistic schemes against experimental reference data obtained by Stack and coworkers, who studied the core isomerization and subsequent aliphatic C-H bond activation for a representative set of systems [4]. We find that the BLYP-D functional provides the most balanced description for the systems at hand, if used in combination with a triple- $\zeta$  basis set and a Stuttgart-Dresden effective core potential. Its use for evaluating the reaction mechanism in Schönecker's system provides a convincing mechanistic picture in line with all available experimental data.

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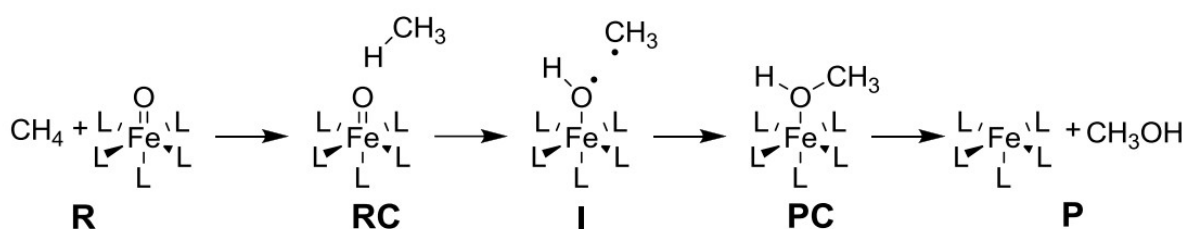
## Oxidation of Alkanes: In Silico Catalyst Design

Prokopis Andrikopoulos<sup>1</sup>, Carine Michel<sup>1</sup>, Sandra Chouzier<sup>2</sup>, Philippe Sautet<sup>1</sup>

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Alkane C-H activation, and in particular, selective oxidation under mild conditions has been an enduring challenge in catalysis. In an effort to match the *in vivo* effectiveness of metallo-enzymes such as cytochrome P-450, much attention has been drawn to metal-oxo systems that can mimic their reactivity [1]. The selective oxidation of alkanes into various oxidized products employing a transition metal catalyst together with the oxidative agent (i.e., hydrogen peroxide in Fenton chemistry processes) has been thoroughly investigated by computational means [2]. Various metal-centred catalysts have been proposed for the above functionalization with a documented large dependence on the choice of the transition metal and the ligand environment. These range from  $[\text{FeO}(\text{H}_2\text{O})_5]^{2+}$  and the ammonia substituted equivalent [2,3] to Mn-heme containing systems [4]. A plausible mechanism that governs the C-H bond activation is the oxygen rebound mechanism [5], shown in Figure 1, which applies to remarkably diverse systems.



**Figure 1.** H-abstraction/O-rebound mechanism scheme for the methane to methanol conversion. **R** signifies the reactants, **RC** the reactant complex, **I** is the intermediate, while **PC** stands for the product complex and **P** for the product. (Illustration taken from [2b])

Theory can assist in tailoring an efficient catalyst, finding the optimum compromise between a fast H-abstraction/O-rebound step but also a facile regeneration of the iron-oxo active site. The latter part of the catalytic cycle is often neglected in the literature but represents a determining factor for the functionality of the catalyst. In the present DFT study, the complete catalytic cycle is considered, so that complexes that are known to perform well in the H-abstraction/O-rebound step are also assessed at the regeneration step. Heme and non-heme containing systems such as the ones mentioned above are included in the study. Furthermore, the effect of the equatorial or axial position of the ligands on the spin state and reactivity of the species is also taken into account, throughout the catalytic cycle.

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## Lewis-Acid Trapping of an Elusive Copper-Tosylnitrene Intermediate Using Scandium Triflate

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High-valent copper nitrene intermediates have long been proposed to play a role in copper catalyzed aziridination and amination reactions. However, such intermediates have eluded detection for decades, which prevents the unambiguous assignments of mechanisms. Moreover, the electronic structure of the proposed copper-nitrene intermediates has also been controversially discussed in the literature. Both singlet ( $S=0$ ) and triplet ( $S=1$ ) spins have been considered as possible ground states. These mechanistic questions and controversy have provided tremendous motivation for probing the accessibility and reactivity of  $\text{Cu}^{\text{III}}\text{-NR}/\text{Cu}^{\text{II}}\text{N}^{\bullet}\text{R}$  species. In this paper we report a breakthrough in this field by trapping a transient copper-tosylnitrene species in presence of scandium triflate. Sufficient stability of the metastable intermediate at  $-90\text{ }^{\circ}\text{C}$  enabled its characterization with optical, resonance Raman, nuclear magnetic resonance, and x-ray absorption near edge (XANES) spectroscopies, which helped to establish its electronic structure as  $S=0\text{ Cu}^{\text{II}}\text{N}^{\bullet}\text{Ts}$  ( $\text{Ts}$  = tosyl group) and not  $\text{Cu}^{\text{III}}\text{NTs}$ . The intermediate can initiate tosyl-amination of cyclohexane, thereby suggesting  $\text{Cu}^{\text{II}}\text{N}^{\bullet}\text{Ts}$  cores as viable reactants in oxidation catalysis.

# **Cysteine Dioxygenase: Enzymatic Reaction Mechanism and Biomimetic Models**

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Cysteine dioxygenase are vital enzymes for human health involved in the metabolism and biodegradation of toxic cysteine. They utilize molecular oxygen on a non-heme iron center that is linked to the protein via three histidine ligands. Recent crystallographic studies led to a controversy regarding the catalytic mechanism of cysteine dioxygenase enzymes and implicated a persulfenate intermediate in the catalytic cycle. We performed a quantum mechanics/molecular mechanics study into the mechanism of oxygen activation and the formation of cysteine sulfinic acid products using the Turbomole (QM) and ChemShell/CHARMM (MM) software packages on a selection of snapshots and models. We predict the persulfenate structure to be high in energy and find a lower energy mechanism that involved attack of superoxo on the cysteinate group followed by dioxygen bond cleavage to form cysteine sulfoxide. An internal rotation followed by the second oxygen atom transfer then gives cysteine sulfinic acid products. Our study shows that the reaction takes place on multiple spin state surfaces. Further studies investigated biomimetic cysteine dioxygenase model complexes and compared their electronic properties and reactivities with enzymatic systems.

# Challenges and Means to Obtain Correct Spin-Density Distributions by DFT

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It is well known that approximate DFT does not always give correct spin-density distributions. Examples for such cases will be discussed, and some more or less pragmatic recipes for obtaining improved spin-density distributions or the closely related magnetic-resonance parameters will be discussed, with examples from the following areas: *a)* The localization/delocalization in mixed-valence compounds will be addressed using non-standard hybrid functionals and solvent models up to the D-COSMO-RS approach [1]. *b)* The spin contamination/spin polarization dilemma in transition-metal complexes [2] will be discussed. *c)* The extraction of EPR parameters from broken-symmetry DFT calculations on spin-coupled multinuclear manganese systems (with emphasis on the oxygen-evolving complex of photosystem II) requires sophisticated spin-projection techniques [3]. *d)* Spin-orbit induced spin polarization effects can lead to large effects on NMR chemical shifts of diamagnetic compounds [4]. We show how giant spin-orbit shifts lead to unprecedented spectral ranges for uranium(VI) complexes, opening the door to the characterization of new compound classes [5].

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## Spin States, Spin Density and Local Spin in DFT

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The description of electronic spin in first-principles theories is central to the development of predictive tools for transition metal chemistry [1]. In this talk, I will review our early work on spin state splittings [2] and local spin [3] and then discuss our recent results for the calculation of spin densities within a density functional theory (DFT) framework and their comparison to accurate *ab initio* reference spin densities [4]. A review on the thorough embedding of these concepts into relativistic and nonrelativistic DFT will also be provided [5].

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# Why is the Oxidation State of Iron Crucial for the Activity of Heme-Dependent Aldoxime Dehydratase? A QM/MM Study

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Aldoxime dehydratase is a heme-containing enzyme that utilizes the ferrous rather than the ferric ion to catalyze the synthesis of nitriles by dehydration of the substrate [1]. We present DFT and QM/MM [2] calculations of this enzyme aimed at elucidating its catalytic mechanism and understanding this oxidation state preference ( $\text{Fe}^{2+}$  vs.  $\text{Fe}^{3+}$ ). The uncatalyzed reaction assisted by three and four water molecules was studied by DFT and coupled cluster methods, as a reference for assessing the rate enhancement of the enzyme. QM/MM calculations were performed for the whole solvated enzyme using large QM region (103 QM atoms) and covering both the ferrous and ferric form of the heme, with all possible spin states. The oxidation state of iron is confirmed to be crucial for the enzyme activity. The calculations yield feasible barriers for the ferrous form and confirm that it is active, while the ferric form of the enzyme is found to be inactive.

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## The Influence of Heme Conformation and Second-Sphere Interactions on Spin State and Spin Density Distribution in Cytochromes *c*

Kara Bren

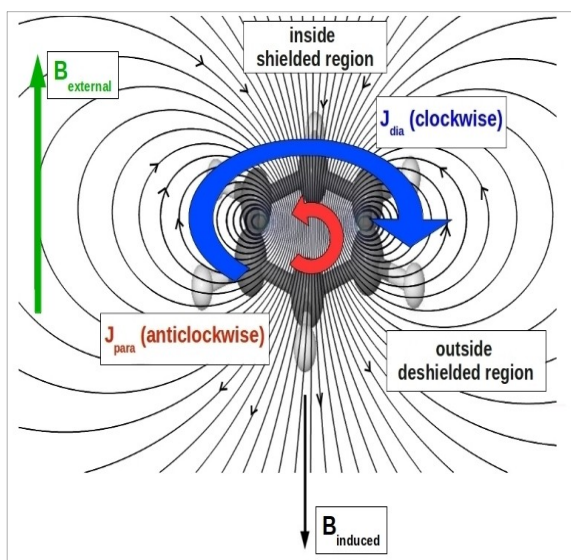
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Heme electronic structure is controlled by many factors. Two areas receiving increased attention are the coupling of the propionates to the porphyrin macrocycle and the conformation of the heme. To probe the influence of hydrogen bonding to propionates on spin density distribution in low-spin ferric heme, we have performed NMR analyses of two variants of human mitochondrial cytochrome *c* with altered hydrogen-bonding to the propionates. One of these variants, G41S cytochrome *c*, is the only known naturally-occurring mutant of human cytochrome *c*, and the only variant known to have enhanced pro-apoptotic activity. Analysis of experimental hyperfine shifts of G41S reveals an increased amount of spin density on heme pyrrole C, the pyrrole that is exposed to solvent in folded mitochondrial cytochromes *c* and the site where electron-transfer partners dock. Notably, the G41S mutant has a faster electron self-exchange electron transfer rate than wild-type, consistent with greater electronic coupling to electron transfer partners. A related mutant, K39Q, has decreased hydrogen bonding to propionate-7, decreased spin density at pyrrole C, and slower electron-self exchange rates in comparison with wild-type. In studies of heme conformation, we have examined the relationship between porphyrin ruffling and ligand-field strength using the axial Met-to-Ala mutant of *H. thermophilus* cytochrome *c*552. Although the mutant is predominantly high-spin, it exhibits a low-spin component as observed by NMR, EPR, and resonance Raman spectroscopy. Introducing mutations that increase heme ruffling increase the population of the low-spin component, demonstrating that ruffling raises ligand-field strength. Proposals regarding the functional roles of heme ruffling will be presented.

# The Gauge Including Magnetically Induced Current Method

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Molecules exposed to external magnetic fields sustain currents in the electron density. The magnetically induced currents strengths provide information about molecular electron and spin transport properties, which can be used as a quantitative aromaticity indicator. An overview of applications of the gauge including magnetically induced current method (GIMIC) is presented [1,2]. The GIMIC method is used for calculating magnetically induced current and spin-current densities in molecules. The currents flow across bonds and around molecular rings. The current densities provide detailed information about electron delocalization, degree of aromaticity, and electron-current and spin-current pathways in molecules [3]. The method has been employed in aromaticity studies on hydrocarbons, complex multi-ring organic nanorings, Möbius twisted molecules [4], inorganic and all-metal molecular rings, and open-shell species [5,6]. Recent studies on hydrogen-bonded molecules indicate that GIMIC can also be used to estimate hydrogen-bond strengths without fragmentation of the system [7]. GIMIC can thus be

employed as a non-invasive tool for determining the strength of internal hydrogen-bonds in, *e.g.*, proteins, DNA, and other complex hydrogen-bonded structures.

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# Mössbauer, EPR and DFT Studies of High-Valent Diiron TPA Complexes: Spin Transitions at an Fe(IV)-Oxo Site Induced by Superexchange Interactions

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Together with the group of L. Que, Jr. we have studied with Mössbauer and EPR spectroscopy as well as with DFT a variety of  $\text{Fe}^{\text{IV}}\text{Fe}^{\text{IV}}$  and  $\text{Fe}^{\text{IV}}\text{Fe}^{\text{III}}$  complexes based on the TPA ligand. The states studied include four diiron(IV) complexes having either open or closed (diamond) cores: (a)  $\text{O}=\text{Fe}^{\text{IV}}-\text{O}-\text{Fe}^{\text{IV}}=\text{O}$  (two conformers with different local spins), (b)  $\text{O}=\text{Fe}^{\text{IV}}-\text{O}-\text{Fe}^{\text{IV}}-\text{OH}$ , (c)  $\text{Fe}^{\text{IV}}(\mu\text{-O})_2\text{Fe}^{\text{IV}}$ ; and in addition (d)  $\text{O}=\text{Fe}^{\text{IV}}-\text{O}-\text{Fe}^{\text{III}}-\text{OH}$  and (e)  $\text{Fe}^{\text{IV}}(\mu\text{-O})_2\text{Fe}^{\text{III}}$  (valence delocalized). In (b) the  $\text{Fe}^{\text{IV}}=\text{O}$  site has  $S=1$  whereas the same site has  $S=2$  in (d). This spin transition is driven by superexchange interactions between the two Fe sites. The change in spin at the  $\text{Fe}^{\text{IV}}=\text{O}$  site is associated with a 1000-fold increase in C-H bond cleavage reactivity. One of the conformers of (a) has local  $S = 2$  sites with Mössbauer parameters matching those of methane monooxygenase diiron(IV) intermediate **Q**.

# **Magnetic Circular Dichroism and Other Synchrotron Techniques Sensitive to Spin States**

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The large number of Storage Rings in the World provides the scientific community with synchrotron radiation, an excellent tool that can be used either in spectroscopy, diffraction, imaging or time resolved experiments (or combinations of them) for the study and understanding of materials properties. The intense photon beams provided by these sources have an extended energy range, (infrared, visible, vacuum ultraviolet, soft and hard x-rays) that provides element specificity to these studies. At these sources it is possible control the polarization and in some of them the time structure. In the newest sources the brightness is the most enhanced characteristic. These different qualities combined makes synchrotron Sources a very versatile tool to perform different type of experiments. All these characteristics opens the possibility to look for small signals associated to minority effects, such as induced magnetic moments, the detection of dopands, impurities or defects in materials that affect or control the functionality of devices or change and/or enhance the materials behavior, as is the case in magnetic diluted materials, or allow us to study the influence of interfaces in multilayered structures.

I am going to provide a fast overview of work done at synchrotron sources focusing on the results obtained at X13A at NSLS, a soft x-ray beamline (260 eV to 1.6 keV) that provides elliptically polarized radiation, switching its handiness with 22 Hz. This is a World class beamline were it is possible to perform magnetic circular dichroism (MCD) and quantify the magnetic moment on the samples separating the orbital moment from the spin moment especially in magnetic materials. The beamline is also being used in scattering experiments allowing one to separate the magnetic from the charge signal in a single scan.

# Meta-GGA: Beyond the Generalized Gradient Approximation

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On the ladder of density functional approximations for the exchange-correlation energy, the lowest rung is the local spin density approximation (LSDA), which constructs the exchange-correlation energy density at a point from the electron spin densities there. The second rung is the generalized gradient approximation (GGA), which adds the gradients of the spin densities. While GGA is typically more accurate than LSDA, it may be too simple to provide a good simultaneous description of the more slowly varying densities of solids and surfaces and of the more rapidly-varying densities of atoms and small molecules. The third rung or meta-GGA, which adds the Kohn-Sham orbital kinetic energy densities as a third ingredient at little additional computational cost, can satisfy more constraints appropriate to both limits and so provide a better simultaneous description of both. In particular, the non-empirical revised Tao-Perdew-Staroverov-Scuseria (revTPSS) meta-GGA [1] can accurately predict lattice constants and surface energies on the one hand and molecular atomization and desorption energies on the other [1-3]. The space of possible meta-GGAs is large, and may permit further formal and practical improvements, including the possibility of an improved description of spin states. I will also discuss why Kohn-Sham determinants, unlike true wavefunctions, do not have to be common eigenfunctions of  $S^2$  and  $S_z$

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# Accurate Calculations of Geometry and Spin-Splitting Energies for Active-Site Models of [Ni, Fe] Hydrogenase

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We have studied how well various theoretical methods reproduce the geometry and single-triplet energy splitting of three simple Ni<sup>2+</sup> models of the active site in [NiFe] hydrogenase. We compare various density functional theory methods with multiconfigurational second-order perturbation theory on a complete or restricted active-space wavefunction (CASPT2 or RASPT2) and coupled-cluster calculations with single, double and (perturbatively treated) triple excitations (CCSD(T)).

# Improving Atomization Energies of Molecules and Solids with a Spin-Dependent Gradient Correction from One-Electron Densities Paradigms

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We propose a spin-dependent correction to generalized gradient approximation (GGA) and meta-GGA correlation functionals of the density functional theory. It is derived from a simple statistical constraint on one-electron densities analysis, which we found to be linearly related to atomization-energy errors, and is based on a reduced gradient density parameter of the form  $v \sim |\nabla n|/n^{10/9}$ , found from one-electron densities analysis.

The spin-dependent correction is constructed to be important only in the rapidly-varying spin-dependent density regimes (*i.e.*, spin-polarized valence and tail regions), vanishing for all other cases (as slowly-varying density regimes, and any spin-unpolarized regions).

We found that this spin correction solves one of the main drawbacks of the GGA functionals optimized for the solid-state, *i.e.*, atomization energies of molecules and solids, fully preserving their accuracy for geometries and other (spin-dependent) properties.

In particular, the corrected PBEsol GGA (named zvPBEsol) significantly improves the cohesive energies of molecules and solids over the original PBEsol, keeping unchanged the high accuracy of PBEsol for paramagnetic solids. We also present the zvPBEint GGA, that is a spin-corrected functional with a broad applicability, being accurate for energetical and structural properties of molecules, hybrid interfaces (*i.e.*, interaction between molecules and metallic surfaces), metallic clusters, solids and surfaces.

This spin-dependent correction is also applied to meta-GGA dynamical correlation functionals combined with exact-exchange; in this case a significant (about 30%) improvement in atomization energies of small molecules is found.



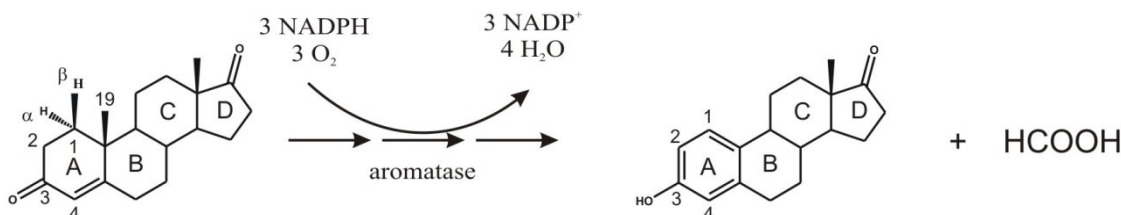
# The Peculiar Role of the Iron-Oxo Species in the Catalytic Cycle of the Human Aromatase Enzyme

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Estrogens are key steroid hormones involved in the proper functioning of the human body. Long exposure to estrogens either via early menarche or late menopause or via hormone-replacement therapy has been shown to be directly linked to development of breast cancer [1]. Understanding the formation and metabolism of estrogens could help in the development of strategies to prevent and treat estrogen-sensitive cancers. Aromatase [2], a member of the cytochrome P450 superfamily and an attractive target in drug research against breast cancer, carries out the last step of estrogen biosynthesis. It catalyzes the aromatization of androgens to estrogens in three oxidative steps, all of which require a single mole of molecular oxygen and NADPH:



In order for the third oxidative step to occur it has been suggested [3] that the enolization of the substrate is required, but the mechanism is still unknown. In this work we present our results obtained by molecular dynamics simulations, cluster model QM and QM/MM calculations on the mechanism of the enolization step. We show that the ferric peroxo complex occurring in the catalytic cycle of P450s can efficiently catalyze this process and investigate the role of the Asp309 and Thr310 residues. Furthermore we examine whether Asp309 is essential for the process or water molecules could also act as potential hydrogen-donors. By applying various reaction coordinates in the QM/MM adiabatic mapping calculations we study the dependence of the reaction mechanism on the choice of reaction coordinate.

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# Calculations of Spectroscopic Parameters of Open-Shell Bioinorganic Systems: Need for Accurate Treatment of Multiple Spin States

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Quantum chemical calculations and experimental spectroscopic techniques represent two complementary tools providing an invaluable source of information about the structure and function of bioinorganic systems, most notably metalloproteins. In our attempts to understand reaction mechanisms of metalloproteins containing open-shell transition metal ions in their active sites, such as multi-copper oxidases (MCO) [1], non-heme biferrous  $\Delta^9$ -desaturase ( $\Delta^9$ D) [2], and manganese superoxide dismutase (MnSOD), we correlated theoretical calculations with experimental spectroscopic data to obtain comprehensive and unambiguous picture about the structures of the key intermediates in catalytic cycles of these enzymes [3,4,5]. It is shown that high-level multireference methods, such as CASPT2 and MR-CI are often needed to obtain at least semiquantitatively correct results. These include low-lying electronic transitions [6] and  $g$ -tensors of  $(\text{Cu})_3$  spin-frustrated core in MCO [7] which still present a major challenge for contemporary quantum chemical methods. Multi-reference methods were also shown to be of a key importance for describing correctly the superoxide disproportionation in MnSOD, where the reaction barriers are actually represented by the transition between two electronic states with different spin multiplicity [5]. On the other hand, it is possible to obtain at least qualitative trends in the calculated spectroscopic parameters (optical, CD, vibrational, Mössbauer) for systems with complicated electronic structure, such as biferrous active site of  $\Delta^9$ D, using much cheaper DFT and TD-DFT methods [4]. In this contribution, the critical assessments of the method performance for the spectroscopy of bioinorganic systems (often relying of the accurate treatment of multiple spin states) will be made.

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## **Coordination of NO to Metal Heme and Heme-Related Systems Studied with Multiconfigurational Perturbation Theory**

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Due to its non-innocent character, NO binding to a transition metal center is inherently a multiconfigurational problem. In this lecture, the results of a systematic theoretical study of the bonding of NO to a series of transition metal ( $M = \text{Mn(II)}, \text{Fe(II)}, \text{Co(II)}$ ) systems surrounded by a macrocyclic or a Schiff base ligand (L) will be presented, making use of multiconfigurational perturbation theory, RASPT2. This study involves (a) the investigation of the relative energies of low-lying electronic states with different spins, both for the ML as for ML-NO complexes; (b) a comparison of the M-NO bond strength dependence on the metal and its surrounding ligand; (c) an analysis of the electronic structure in terms of contributions from  $M^{\text{II}}-\text{NO}^0$ ,  $M^{\text{I}}-\text{NO}^+$ ,  $M^{\text{III}}-\text{NO}^-$  resonance structures. Advantages, disadvantages and complementarities with respect to the more popular density functional theory will also be shortly discussed.

## Biologically Relevant Oxidation Catalysis with Non-Heme Fe Complexes with N-based Scaffolds that Provide Strong Ligand Fields

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The formation and cleavage of the O-O bond is arguably the most important reaction in living organisms [1,2]. In both oxidative and respiration enzymes, metal ions adopting high oxidation states result from reductive O-O cleavage reactions while in PSII they are responsible for O-O bond formation [3]. Selected coordination complexes catalyze analogous reactions, and some of these complexes have turned into very attractive tools for organic synthesis [4]. The study of the mechanisms of action of these catalysts has shed light into the molecular details of enzymatic systems. Iron complexes in Nitrogen rich strong ligand field environments are shown as excellent scaffolds to sustain iron high oxidation states and efficient catalytic activity in for challenging oxidation reactions such as the selective oxidation of alkyl C-H bonds [5], the cis-dihydroxylation of alkenes [6], stereoselective epoxidation [7], and the oxidation of water [8].

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# Spin-Crossover Phenomena in Electronic Properties and Chemical Reactions Mediated by Transition Metals

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In this talk our studies of various spin-crossover phenomena in the electronic properties and chemical reactions mediated by transition-metal complexes are presented. Since the high-spin and low-spin states of transition-metal complexes are closely lying in energy, the two or more potential energy surfaces are crossed by external perturbations. Spin-crossover effects in transition-metal complexes that involve, for example, iron and cobalt are an extensively studied example for molecular bistability upon external perturbation. The spin transition can be triggered by changing temperature and pressure and by light irradiation; as a result, the magnetic properties of transition-metal complexes are dramatically changed. Another example of spin-crossover phenomena is chemical reactions catalyzed by transition-metal complexes. Biochemical reactions are often mediated by metalloenzymes that involve transition metals such as manganese, iron, nickel, and copper at the active sites. Spin-crossover effects play important roles in such enzymatic and catalytic reactions. For example, high-spin and low-spin potential energy surfaces are crossed in the course of C-H bond activation catalyzed by transition-metal oxides, which are used in oxygenation enzymes such as cytochrome P450 and methane monooxygenase. The energy barrier for the cleavage of C-H bond is lowered upon spin crossover. We have theoretically studied such interesting spin-crossover phenomena using quantum chemical calculations and orbital interaction analyses.

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[4] Y. Shiota, D. Sato, G. Juhász, and K. Yoshizawa, *J. Phys. Chem. A*, **114**, 5862 (2010).

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## Dinitrogen Functionalization at Iron Metallaboratranes

Marc-Etienne Moret

Organic Chemistry and Catalysis Group, University of Utrecht

This presentation will focus on the iron chemistry of triphosphine-borane (TPB) ligands in relation with the activation and functionalization of dinitrogen. Owing to the flexibility of the Fe-B bond, the (TPB)Fe platform is able to stabilize both terminal iron-dinitrogen complexes and multiply bonded imidoiron compounds. This flexibility allows for the functionalization of the Fe-bound  $N_2$  ligand to yield silyldiazenido (Fe-NNSiMe<sub>3</sub>) and 2,2-disilylhydrazido(2-) (FeNN(SiMe<sub>3</sub>)<sub>2</sub>) compounds. These compounds (and others) will be discussed in the context of mechanistic hypotheses for biological nitrogen fixation.

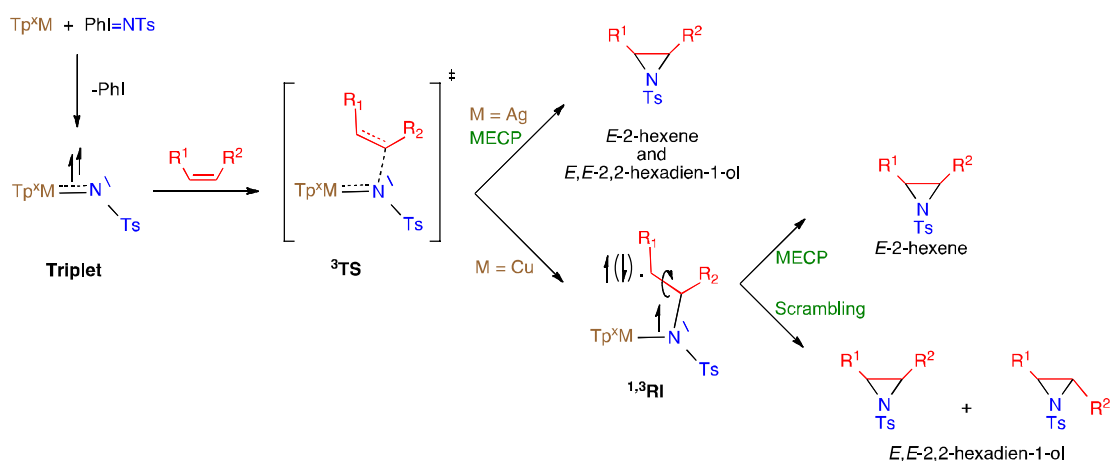
# Nitrene Insertion Reactions: Concomitant Involvement of the Singlet and Triplet Pathways

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Nitrogen atom transfer reactions constitute an important area of research in bioinorganic and organic chemistry. Transition metal-mediated aziridination of olefins is a promising route for nitrogen atom transfer processes [1], and undergoes highly regio- and stereoselective transformations. Pérez, Castellón and co-workers have previously reported  $Tp^xM$  complexes ( $Tp^x$  = homoscorpionate ligand;  $M = Ag, Cu$ ) as effective catalysts for the aziridination of olefins using PhINTs (Ts = 4-toluene-sulfonyl) as the nitrene source [1]. We present herein a mechanistic proposal on the basis of the information that we collected from experimental and theoretical studies.



The reaction starts with the formation of a triplet metal-nitrene species that interacts with the olefin, and aziridination reaction proceeds on the triplet surface. The silver-based systems show a minimum energy crossing point (MECP) between the triplet and closed-shell singlet surfaces that induce the direct formation of the aziridines, and therefore stereochemistry of the olefin is retained. In case of the copper-based systems, a radical intermediate can be formed, and is the starting point for the competing pathways: ring closure towards the product and bond rotation towards the scrambling. Overall, current mechanistic proposal explains the correlation between the reaction stereoselectivity and the nature of substrates and catalysts.

[1] J. Llaveria, Á. Beltrán, M. M. Díaz-Requejo, M. I. Matheu, S. Castellón, P. J. Pérez, *Angew. Chem.* 2010, 122, 7246-7249.

## Assignment of Zero-Field Splitting Parameters for the Mn(II) Centers in Oxalate Decarboxylase

Pablo Campomanes

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Oxalate decarboxylase (OxDC) catalyzes the Mn-dependent conversion of the oxalate monoanion into CO<sub>2</sub> and formate. EPR-based strategies for investigating the catalytic mechanism of oxalate decarboxylation have been complicated by the difficulty of assigning the signals associated with the Mn(II) centers in the two domains of the enzyme. In this talk, it will be discussed how a combined strategy based on the calculation of fine structure parameters employing static *ab initio* methodologies upon appropriate sampling using classical and QM/MM molecular dynamics techniques can permit the unambiguous assignment of the zero-field splitting parameters determined from high-field EPR spectroscopy to each of the two Mn(II) centers in OxDC, therefore demonstrating the utility of applying this kind of combined strategies *(i)* to delineate the fine-structure parameters for protein-bound Mn(II) ions, even when these metals have very similar coordination, and *(ii)* set the stage for future EPR work on the electronic properties of the Mn(II) centers in both OxDC and other Mn-dependent enzymes.



## 4 Participant List

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## 5 Short Biographies and Selected Publications

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### Organisers

#### Mikael Johansson

Under the patient guidance of Profs Dage Sundholm and Mårten Wikström, I received my PhD in 2007 from the University of Helsinki for the thesis entitled “A quantum chemical investigation of the metal centres in cytochrome *c* oxidase”. The thesis work earned the first annual Ruth and Nils-Erik Stenbäck Foundation prize for a young researcher, awarded by The Finnish Society of Sciences and Letters. After the dissertation, two years were spent at the University of Århus, under the supervision of Prof Poul Jørgensen. Currently, I am working as a Juan de la Cierva research fellow in the group of Prof Marcel Swart, University of Girona. Since 2010, I am also a docent (adjunct professor) of physical chemistry at the University of Helsinki. My research interests include applications of computational (quantum) chemistry on metalloproteins, clusters and aesthetically pleasing new species, as well as the concept of aromaticity. The phenomenon of spin has been a fascination ever since I learned of its existence.

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- [5] “Autoxidation of Conjugated Linoleic Acid Methyl Ester in the Presence of  $\alpha$ -Tocopherol: The Hydroperoxide Pathway”, T.I. Pajunen, M.P. Johansson, T. Hase, A. Hopia, *Lipids* **43** (2008) 599–610. DOI: <http://dx.doi.org/10.1007/s11745-008-3195-0>
- [6] “The chemistry of the Cu<sub>B</sub> site in cytochrome *c* oxidase and the importance of its unique His–Tyr bond”, V.R.I. Kaila, M.P. Johansson, D. Sundholm, L. Laakkonen, M. Wikström, *Biochim. Biophys. Acta – Bioenergetics* **1787** (2009) 221–233. DOI: <http://dx.doi.org/10.1016/j.bbabi.2009.01.002>
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- [8] “Subtle effects control the polymerisation mechanism in  $\alpha$ -diimine iron catalysts”, M.P. Johansson, M. Swart, *Dalton Trans.* **40** (2011) 8419–8428. DOI: <http://dx.doi.org/10.1039/C1DT10045A>
- [9] “Quantum chemical studies of the ground states of the metal centres in haem-copper oxidases” (mini-review), M.P. Johansson, *Curr. Inorg. Chem.* **2** (2012) 316–324.
- [10] “Density functional study on UV/VIS spectra of copper-protein active sites: The effect of mutations”, M. Swart, M.P. Johansson, *Chem. Biodiversity* **9** (2012) 1728–1738. DOI: <http://dx.doi.org/10.1002/cbdv.201200058>

#### Marcel Swart

Prof. Swart has published >90 papers in peer-reviewed scientific journals that have been cited more than 1800 times, with a corresponding *h*-index of 24. He has been invited to give seminars at several international scientific conferences, workshops, and visits to scientific groups. He has acted as chairman at several international scientific meetings, and has been invited for a series of lectures in Japan. He has been awarded the Young Scientist 2005 award by ICCMSE, and has been selected as one of the promising young inorganic chemists of “The next generation” that were invited to contribute to a special issue of *Inorganica Chimica Acta* in 2007, and to a special issue of *Polyhedron* in 2010. He has been invited to form part of tribunals for Master and PhD ceremonies in The Netherlands and in Spain. He has received funding from both the Spanish government for starting his own research group from 2009 onwards, as well as additional funding from a collaboration with the company Lucta for studying molecular interactions related to taste perception (GPCR receptors). He has been successful in attracting promising young scientists to join his group with a Spanish three-year post-doc position (Mikael Johansson, Juan de la Cierva), or with a PhD scholarship. In the summer of 2009, he was promoted to ICREA Research Professor. In the summer of 2011, his funding from MICINN was renewed including a PhD-student (starting end 2012). In 2012, he was awarded the MGMS Silver Jubilee Prize for his development of new computational chemistry programs, design of new research tools and application to (bio)chemical systems that are highly relevant for society and science. Competition for the prize was very strong this year, but Prof. Swart's submission was truly outstanding.

## Participants

### Prokopis Andrikopoulos

Prokopis Andrikopoulos was born in Corfu, Greece. He graduated from the Department of Chemistry of the Aristotle University of Thessaloniki on 2001. He obtained his PhD in the University of Strathclyde, Glasgow under the supervision of Dr. D.R. Armstrong and Professor E.W. Smith. His PhD thesis involved the computational study of benzotriazole systems and synergic Na, Mg mixed compounds. From 2008-2011 he held a postdoctoral position in the J. Heyrovsky Institute of Physical Chemistry in Prague, focusing on the N<sub>2</sub>O decomposition over various zeolite frameworks. In 2012 he joined the theoretical chemistry lab at Ecole Normale Supérieure of Lyon, under Professor Philippe Sautet. His current research project involves the design, in silico, of a catalyst for the oxidation of alkanes, in collaboration with the chemical company Rhodia.

### Paola Belanzoni

Paola Belanzoni is Associate Professor of Inorganic Chemistry and Bioinorganic Chemistry at the University of Perugia, Italy. Her research activity has covered several aspects of the Theoretical Inorganic Chemistry area: electronic structure, bonding and magnetic properties of transition metal containing systems, of both material science and catalytic interest, as well as reactivity and chemical processes involving bioinorganic molecules, and silicon surfaces properties by Density Functional Theory (DFT). Her interests have been also addressed to the four-component and two-component relativistic approach to heavy-metal containing systems. She has had frequent collaborations with academic centers (Vrije Universiteit, Amsterdam; Pohang University of Science and Technology, South Korea; School of Chemistry, University of Melbourne; University of Milano-Bicocca, Milan) and industry (STMicroelectronics).

### Kara Bren

Kara Bren is a native of Minneapolis, Minnesota, USA. She earned her B.A. in chemistry (1991) at Carleton College (Northfield, Minnesota) where she did research on conformations of carbohydrates. She attended graduate school at Caltech (Pasadena, California) where she earned her Ph.D. (1996) performing research on ligand binding to engineered cytochromes in the group of Harry Gray. She did part of her thesis work in the lab of Ivano Bertini (Florence, Italy) where she performed NMR studies of paramagnetic cytochromes. After a postdoc in the lab of Gerd LaMar on NMR of ferredoxins, she began her independent career at the University of Rochester, NY, in the Department of Chemistry. Kara currently is a Professor of Chemistry.

- [1] "Modulation of the Ligand-field Anisotropy in a Series of Ferric Low Spin Cytochrome c Mutants Derived from *Pseudomonas aeruginosa* Cytochrome c-551 and *Nitrosomonas europaea* Cytochrome c-552. An EPR and NMR Study", G. Zoppellaro, E. Harbitz, R. Kaur, A. A. Ensign, K. L. Bren, and K. K. Andersson, *J. Am. Chem. Soc.*, **2008**, 130, 15348-15360. DOI: <http://dx.doi.org/10.1021/ja8033312>
- [2] "Studies of Ferric Heme Proteins with Highly Anisotropic/Highly Axial Low Spin ( $S=1/2$ ) Electron Paramagnetic Resonance Signals with Two Histidines or Histidine and Methionine Axial Fe Coordination", G. Zoppellaro, K. L. Bren, A. A. Ensign, E. Harbitz, R. Kaur, H.-P. Hersleth, U. Ryde, L. Hederstedt, and K. K. Andersson, *Biopolymers* **2009**, 91, 1064-1082. DOI: <http://dx.doi.org/10.1002/bip.21267>
- [3] "NMR and DFT Investigation of Heme Ruffling: Functional Implications for Cytochrome c", M. D. Liptak, X. Wen, and K. L. Bren, *J. Am. Chem. Soc.* **2010**, 132, 9753-9763. DOI: <http://dx.doi.org/10.1021/ja102098p>
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- [5] "The Proapoptotic G41S Mutation to Human Cytochrome c Alters the Heme Electronic Structure and Increases the Electron Self-Exchange Rate", M. D. Liptak, R. D. Fagerlund, E. C. Ledgerwood, S. M. Wilbanks, and K. L. Bren, *J. Am. Chem. Soc.*, **2011**, 133, 1153-1155. DOI: <http://dx.doi.org/10.1021/ja106328k>
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## Pablo Campomanes

Pablo Campomanes received his Ph.D. in Physical Chemistry from the University of Oviedo (Spain) under the guidance of Prof. Tomas L. Sordo. Subsequently, he moved to Switzerland and joined Prof. Ursula Rothlisberger's group at the Ecole Polytechnique Fédérale Lausanne (EPFL), where he is currently working as a Research Fellow. His research interests focus on the application of hybrid DFT-based Quantum Mechanical/Molecular Mechanical (QM/MM) and classical molecular dynamics (MD) methodologies to characterize and get a deeper understanding of the molecular interactions that drive biologically relevant processes.

- [1] "Studies of Glutathione Transferase P1-1 Bound to a Platinum(IV)-Based Anticancer Compound Reveal the Molecular Basis of Its Activation", Parker, L. J., Italiano, L. C., Morton, C. J., Hancock, N. C., Ascher, D. B., Aitken, J. B., Harris, H. H., Campomanes, P., Rothlisberger, U., De Luca, A., Lo Bello, M., Ang, W. H., Dyson, P. J., and Parker, M. W., *Chem. Eur. J.*, **17**(28):7806-7816. **2011**. DOI: <http://dx.doi.org/10.1002/chem.201100586>
- [2] "Reactions of Alkynes with [RuCl(cyclopentadienyl)] Complexes: The Important First Steps", Dutta, B., F. E. Curchod, B., Campomanes, P., Solari, E., Scopelliti, R., Rothlisberger, U., and Severin, K., *Chem. Eur. J.*, **16**(28):8400-8409. **2010**. DOI: <http://dx.doi.org/10.1002/chem.201000855>
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- [4] "A Theoretical Proposal for the Synthesis of Carbapenems from 4-(2-Propynyl)azetidinones Promoted by [W(CO)<sub>5</sub>] as an Alternative to the Ag<sup>+</sup>-Assisted Process", Campomanes, P., Menéndez, M. I., and Sordo, Tomás L., *Chem. Eur. J.*, **12**(30):7929-7934. **2006**. DOI: <http://dx.doi.org/10.1002/chem.200501219>
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## Alexandra Carvalho

Alexandra Carvalho has a bachelor in Biochemistry and PhD in Computational Chemistry. The title of her thesis was "Computational enzymatic studies by the determination of chemical properties" and it was obtained under the supervision of Prof. Maria João Ramos at Universidade do Porto. She complemented her PhD with research visits to Universidad Complutense (Madrid), Edinburgh University and Vrije University (Amsterdam). Afterwards, she started a post-doc in Porto where she studied DNA and RNA enzymes structure and function. During that period, as a guest researcher, she also worked with Prof. Carlos Simmerling at the Stony Brook University, NY. She is currently working in Universitat de Girona in the Group of Prof. Marcel Swart.

## Lucian Constantin

Team leader at the Italian Institute of Technology.

## Miquel Costas

Miquel Costas graduated in Chemistry at the University of Girona (UdG) in 1994, where he also pursued PhD studies. After defending the PhD dissertation, he moved to the group of Prof. Lawrence Que, Jr, at the University of Minnesota. In September 2002 he returned to Girona with a Ramon I Cajal Fellowship, and become professor in April 2003. His research interests involve the fundamental understanding of the mechanisms of O<sub>2</sub> activation and/or substrate oxidation taking place at transition metal ions that have biological relevance, specially Fe, Cu and Mn, and application of this knowledge to the development of bioinspired oxidation catalysts to carry out selective oxidation reactions under environmentally benign conditions. In 2008 he was awarded with the ICREA Academia Award from the Generalitat de Catalunya.

### **Coen de Graaf**

ICREA Research Professor at URV (Universitat Rovira i Virgili). Experimental Sciences & Mathematics. Graduated in Chemistry in 1993 at the University of Amsterdam. PhD student at the University of Groningen, the Netherlands from 1994 to 1998 (supervisors: Prof. Wim Nieuwpoort and Prof. Ria Broer). Post-Doc in the group of Prof. Francesc Illas of the University of Barcelona with a Marie Curie fellowship from 1998-2000 (subject: magnetism in low-dimensional Heisenberg systems). Post-Doc in the Quantum Chemistry group of the University Rovira i Virgili (2000-2005) with a Ramón y Cajal fellowship. Presently ICREA Research Professor in the same group.

### **Sam de Visser**

Sam de Visser did a PhD in Organic Mass Spectrometry from the University of Amsterdam (the Netherlands) and obtained postdoctoral experience in computational chemistry on biochemical systems from work with Mike Robb (King's College London, UK) and Sason Shaik (Hebrew University of Jerusalem, Israel). He has been an independent researcher at the University of Manchester (UK) since 2004, where he currently holds a senior lectureship in biophysics. His research interests include mechanism and function of nonheme iron enzymes and biomimetic model complexes. He has published well over 130 scientific publications and currently has an *h*-index of 36.

### **Robert Deeth**

Rob Deeth was born in Tasmania some time before man landed on the moon. He completed his BSc (Honours) degree at the University of Tasmania before winning a Commonwealth Scholarship to undertake a PhD at Cambridge University under the supervision of Malcolm Gerloch. The thesis, entitled 'Redirected Ligand Field Analysis', was submitted in 1985. He then took up an Australian National Research Fellowship with Brian Figgis at the University of Western Australia where he was first exposed to polarised neutron diffraction and DFT. In 1989, he returned to Cambridge as a postdoctoral fellow in the Cambridge Crystallographic Data Centre where he was responsible for integrating the new version of the Cambridge Structural Database into Tripos's SYBYL version 5.0. In 1988, he took up a lectureship in Inorganic Chemistry at Bath University before moving in 1995 to Warwick University as a Warwick University Research Fellow. He proceeded to climb the greasy pole and was promoted to Full Professor in 2009. His research focuses on the application and development of computational methods for modelling systems containing transition metal centres with over 130 publications in refereed journals.

### **Daniel Escudero Masa**

Daniel Escudero was born in 1984 in Palma de Mallorca, Spain. He earned his degree in Chemistry with honors at the University of the Balearic Islands, Spain. He obtained his Ph.D in 2011 from the Friedrich-Schiller Universität Jena with the grade "*summa cum laude*", working in the group of Prof. L. González. Since November 2011 he is a postdoctoral researcher in the group of Prof. W. Thiel at the Max-Planck Institut für Kohlenforschung, Mülheim an der Ruhr. His research interests are non-covalent interactions and the spectroscopy and photochemistry of transition metal complexes and organic compounds. Currently he is involved in the study of spin-states in bioinorganic systems, as, *e.g.*, P450cam.

### **Victor Guallar**

Bachelor in Physical Chemistry at the University Autonomus of Barcelona. PhD in theoretical Chemistry at the University Autonomus of Barcelona and University of California at Berkeley. Postdoctoral education at Columbia University. Assistant Professor from 2003 to 2006 in the Biochemistry & Molecular Biophysics department at the Washington University School of Medicine. 2006 to present ICREA professor at the Barcelona Supercomputing Center.

### Puneet Gupta

Puneet Gupta was born and brought up in Kanpur, India and received his M.S. degree in chemistry from the Indian Institute of Technology (IIT), Kanpur, in the laboratory of Prof. Rabindranath Mukherjee. There, he was involved in the synthesis and characterization of copper complexes containing multidentate N-donor ligands. At present, he is pursuing his PhD degree in the group of Prof. Max. C. Holthausen at the University of Frankfurt, Germany. His work is focused on quantum chemical calculations of transition metal complexes containing non-innocent ligands.

### Jeremy Harvey

JNH was born in the UK in 1969 but grew up in Belgium, where he studied chemistry, obtaining a PhD in organic chemistry in 1995. His supervisor was Heinz Viehe, and his thesis was about reaction mechanisms in organo-sulfur chemistry. He was then a postdoc and Alexander von Humboldt fellow with Helmut Schwarz at the TU Berlin, studying gas-phase ion chemistry using experiment and computation, and a postdoc studying theoretical chemistry with Benny Gerber, in Jerusalem. In 1999, he became a lecturer in Bristol, and was promoted to Professor in 2008. His work focuses on using computation to understand reaction mechanisms and dynamics, and he was awarded the 2009 Dirac Medal of the World Association of Theoretical and Computational Chemists for this work.

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### Martin Kaupp

Martin Kaupp carried out PhD work with P.v.R. Schleyer at the Institut für Organische Chemie at Universität Erlangen-Nürnberg. The thesis (1992) covered *ab initio* calculations on compounds containing heavy elements. Martin Kaupp then joined the group of H. G. von Schnering (Max-Planck-Institut für Festkörperforschung, Stuttgart). A postdoctorate at Université de Montréal (Canada) with D. R. Salahub from 1993-1994 brought him into contact with density functional theory, and he started an ongoing collaboration with Vladimir and Olga Malkin on the quantum chemical calculation of NMR and EPR parameters for heavy-element compounds. The Habilitation in Theoretical Chemistry was completed in spring 1997 at Universität Stuttgart, followed by an appointment to Privatdozent. Since November 1999, Martin Kaupp was a professor of Chemistry at Universität Würzburg, where he headed the quantum chemistry group at the Institut für Anorganische Chemie. As of 2010, the group has moved to the newly founded Institut für Physikalische und Theoretische Chemie. Martin Kaupp's wide research interests include development and applications of quantum chemical methods to calculate NMR and EPR parameters, density functional theory, (*e.g.*, the new class of local hybrid functionals), relativistic effects, biradicals, and various aspects of computational bioinorganic, inorganic, and organometallic chemistry. Prof Kaupp was awarded the 2001 Dirac Medal of the World Association of Theoretical and Computational Chemists (WATOC).

### Kasper Planeta Kepp

Kasper Planeta Kepp is Associate Professor at the Technical University of Denmark, DTU Chemistry. He received his Ph.D. from Lund University under the supervision of Professor Ulf Ryde and has been a postdoctoral associate at Yale University and Stanford University, working with Professor William L. Jorgensen and Edward I. Solomon, respectively. His research at DTU centers around the theoretical description of metalloproteins. He has published about 40 internationally reviewed papers and was recently awarded the Danish National Young Elite Researcher Prize.

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### Oliver Krahe

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### Rongzhen Liao

Rongzhen Liao was born in Hubei, China, in 1983. He received his B.Sc. degree in chemistry from Beijing Normal University (China) in 2005 and his Ph.D. degree in organic chemistry from Stockholm University (Sweden) in 2010, under the supervision of Prof. Fahmi Himo. Since then he has been working with Prof. Walter Thiel at the Max Planck Institute für Kohlenforschung (Germany) as a postdoctoral fellow until now. His main research interests are QM-only and QM/MM studies of enzymatic reactions.

### Marc-Etienne Moret

Marc-Etienne Moret was born in Lausanne, Switzerland. In 2005 he obtained his master's degree in chemistry from the Ecole Polytechnique Fédérale de Lausanne (EPFL). During his undergraduate time at EPFL he acquired research experience in organometallic synthesis and computational chemistry, working on the synthesis of organochromium(0) ionic liquids in the group of Prof. Paul Dyson and subsequently writing his master thesis on QM/MM simulations of aqueous [Ru(bpy)<sub>3</sub>]<sup>2+</sup> in the group of Prof. Ursula Rothlisberger. Marc-Etienne then moved to the Eidgenössische Technische Hochschule Zürich (ETHZ) where he obtained his PhD under the supervision of Prof. Peter Chen. His graduate work focused on the study of reaction mechanisms in organoplatinum chemistry by mass spectrometric methods, as well as on platinum-copper heterobimetallic compounds and their reactions. Following graduation in 2009, Marc-Etienne moved to the California Institute of Technology (Caltech) for two-years of postdoctoral research in the group of Prof. Jonas C. Peters on the activation of N<sub>2</sub> by synthetic iron complexes, for which he was awarded a fellowship for prospective researchers and a fellowship for advanced researchers from the Swiss National Science Foundation (SNF). Marc-Etienne then accepted a position as assistant professor in the Organic Chemistry and Catalysis group at the University of Utrecht starting in August 2012.



## Eckard Münck

1967, PhD in physics, Technical University Darmstadt, Germany

1968-1974, postdoc and Research Asst. Prof, U. of Illinois

1974-78, Assoc. Prof. of Biochemistry, U. of Minnesota

1978-90, Prof. of Biochemistry, U. of Minnesota

1990-present, Prof. of Chemistry, Carnegie Mellon University

Throughout my career I have focused on studying nitrogen fixation, oxygen activation and magneto-chemistry with Mössbauer and EPR spectroscopy. These studies include proteins as well as synthetic complexes.

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## Julianna Oláh

Julianna Oláh received her MSc in 2002 in bioengineering from the Budapest University of Technology and Economics, (BUTE, Hungary), where she obtained her PhD in chemistry in 2006. After a short period in the Drug Discovery Laboratory of the pharmaceutical company Richter Gedeon Plc, she was a Marie Curie post-doctoral research fellow at the University of Bristol (UK) under the supervision of Jeremy Harvey between 2007 and 2009. In Bristol she studied iron-porphyrin systems and modelled cytochrome P450 enzymes using QM/MM calculations. Presently, she is a senior research fellow in Budapest at BUTE, and her work is focussed on modeling enzyme catalyzed reactions.

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## John Perdew

John Perdew's research in the density-functional theory of electronic structure has helped to establish this theory as the most widely-used method to predict the properties of atoms, molecules, and solids, from the principles of quantum mechanics. His work is now cited 10,000 times per year. He is a Fellow of the American Physical Society and a member of the International Academy of Quantum Molecular Science and the National Academy of Sciences. In 2012, he was selected to receive the second annual Materials Theory Award of the Materials Research Society. Perdew received a B.S. from Gettysburg College in 1965 and a Ph.D. in Physics from Cornell University in 1971. After postdoctoral work at the University of Toronto and Rutgers University, in 1977 he joined Tulane University, where he is a Professor of Physics.

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## Kristine Pierloot

Kristine Pierloot is a professor at the University of Leuven (since 2001). She is the head of the division "Quantum and Physical Chemistry" at the Department of Chemistry, and leads the research group "Computational Coordination Chemistry", performing research focused on the electronic structure and reactivity of transition metals( $d^n$ ) and heavier metals( $f^n$ ) in a variety of coordination environments, with special emphasis on electronic spectroscopy, and using both density functional theory (DFT) and multiconfigurational wave function methods. She is co-author of more than 100 scientific articles published in SCI journals (average citation/paper > 32; two papers with > 400 citations;  $h$ -index = 30) and of several book chapters. She teaches several courses in computational chemistry, both in the Master of Chemistry and the European Master of Theoretical Chemistry and Computational Modelling. She is the chairman of the expert panel W&T4 (Science and Technology 4: Chemistry) of the Fund of Scientific Research-Flanders FWO (2010-2013).

## Lawrence Que, Jr.

Larry Que received his Ph. D. in chemistry in 1973 from the University of Minnesota and carried out postdoctoral work with Prof. Richard Holm at MIT and Prof. Eckard Münck at the University of Minnesota. He started his independent career at Cornell University in 1977 and then returned to the University of Minnesota in 1983 where he is now Regents Professor and 3M/Alumni Distinguished Professor of Chemistry. He has had a long-term interest in how biological nonheme iron centers activate dioxygen and, more recently, has pioneered the synthesis and characterization of nonheme oxoiron(IV) complexes that serve to model high-valent iron intermediates in enzymes. He has received the Alfred Bader Award in Bioorganic or Bioinorganic Chemistry in 2008 from the American Chemical Society and the Inorganic Reaction Mechanisms Award in 2011 from the Royal Society of Chemistry.

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### Kallol Ray

Dr. Kallol Ray was born in Kolkata, India. He received his B.Sc. and MSc degrees in India. He moved to the Max-Planck Institute for Bio-Inorganic Chemistry, Mülheim, Germany, as a PhD student in 2002, and joined the research group of Prof. Dr Karl Wieghardt. During his PhD he was involved in the spectroscopic and density functional characterization of transition metal complexes involving non-innocent ligands. He completed his PhD on Jan 25th 2005. After spending three years as a post-doctoral associate in the University of Minnesota under the supervision of Prof. Lawrence Que Jr, he started his independent academic career in the Humboldt University Berlin in 2009. Current research in his group encompasses synthetic bioinorganic and organometallic chemistry.

- [1] "The Electronic Structure of the Isoelectronic, Square Planar Complexes, [Fe<sup>II</sup>(L)<sub>2</sub>]<sup>2-</sup> and [Co<sup>III</sup>(L<sup>Bu</sup>)<sub>2</sub>]<sup>-</sup> (L<sup>2-</sup> and (L<sup>Bu</sup>)<sup>2-</sup> = benzene-1,2-dithiolates): an Experimental and Density Functional Theoretical Studies", K. Ray, A. Begum, T. Weyhermüller, S. Piligkos, J. van Slageren, F. Neese, and K. Wieghardt, *J. Am. Chem. Soc.* **2005**, 127, 4403-4415. DOI: <http://dx.doi.org/10.1021/ja042803i>
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## Markus Reiher

Born in Paderborn (Westphalia) in 1971, diploma in chemistry from the University of Bielefeld in 1995, PhD in theoretical chemistry from the same University with Professor Juergen Hinze in 1998, habilitation in theoretical chemistry at the University of Erlangen-Nuremberg with Professor Bernd Artur Hess from 1999 to 2002, 'venia legendi' in summer 2003, Oct. 2003 - Mar. 2005 Privatdozent at the University of Bonn, during this time representative (Lehrstuhlvertreter) of the Chair of Theoretical Chemistry at Erlangen (2003/2004) and of the Chair of Theoretical Chemistry at Bonn (2004/2005), Dec. 2004 offer of a position 'full professor in theoretical chemistry' at the University of Groningen, Apr. 2005 - Jan. 2006 Professor for Physical Chemistry (designation: Theory) at the University of Jena, since Feb. 2006 Professor for Theoretical Chemistry at ETH Zurich (Laboratory of Physical Chemistry from 2006 to 2011 as ausserordentlicher Professor and since 2011 as ordentlicher Professor); Markus Reiher served as head of the Laboratory of Physical Chemistry from 2009 to 2010; research fellow during short-time research stays in Tel Aviv (2000), Budapest (2001), Tromsø (2003/2004), Lund (2006), and Singapore (2009); awards include the 2004 Award of the 'Arbeitsgemeinschaft Deutscher Universitaetsprofessoren fuer Chemie' (ADUC Jahrespreis 2004), the Emmy-Noether-Habilitationspreis 2003 of the University of Erlangen-Nuremberg, in 2005 the Dozentenstipendium of the Fonds der Chemischen Industrie, and in 2010 the OYGA award of the Lise-Meitner-Minerva Center for Computational Chemistry Jerusalem and the Golden Owl of the students of ETH Zurich.

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## Lubomír Rulíšek

Lubomír Rulíšek received his Master's Degree from the Faculty of Science, Charles University, Prague, in 1995 and his Doctorate from the Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic (IOCB) in 2001. He spent two years as the postdoctoral fellow at the Lund University (2002-2004), working in the group of Prof. Ulf Ryde. In 2007, he has been appointed as the Junior Research Group Leader at IOCB. His interests include application of quantum chemical methods and QM/MM modelling in studying the structure and reactivity of bioinorganic systems, chemical reactivity and catalysis, calculations of spectroscopic and physico-chemical properties of transition metal-containing systems, theoretical aspects of metal ion complexation in biomolecules and design of novel metal-binding sites.

## Ulf Ryde

Ulf Ryde was born in 1963 and obtained a PhD in biochemistry (enzyme kinetics and control theory) at Lund University, Sweden, 1991, under the supervision of Prof. Gösta Pettersson. As a postdoctoral fellow, he moved to the department of Theoretical Chemistry at the same university, where he was appointed as docent 1996 and professor 2004. He studies the relation between the structure and function of proteins with all types of theoretical methods and their combinations with experimental data. He has studied many different proteins, *e.g.*, alcohol dehydrogenase, blue copper proteins, hydrogenases, superoxide dismutases, multi-copper oxidases, as well as haem and other tetrapyrrole proteins. The latest years he has also been involved in the development of methods to study ligand binding to protein.

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## W. M. Chamil Sameera

W. M. C. Sameera is a postdoctoral fellow in the Professor Feliu Maseras group, Institute of Chemical Research of Catalonia (Spain). Sameera's research interest focuses on Quantum Mechanics/ Molecular Mechanics method developments and applications of computational methods for homogeneous catalysis and redox-active transition metal clusters. He received a BSc honours degree in Chemistry from the University of Sri Jayawardenapura (Sri Lanka). In 2005, he was awarded a WestCHEM PhD fellowship from the School of Chemistry, University of Glasgow (United Kingdom). Soon after his graduation in 2009, Sameera joined the Professor John E. McGrady group, Inorganic Chemistry laboratory, University of Oxford (United Kingdom) as an Engineering and Physical Sciences Research Council (EPSRC) postdoctoral fellow. In 2012, he was awarded a Marie Curie FP7 ITN (LASSIE) experienced researcher position, and Sameera will continue his research at the Professor Gunnar Nyman group, University of Gothenburg (Sweden) from the beginning of 2013.

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## Cecilia Sánchez-Hanke

Dr. Sánchez-Hanke transferred to NSLS-II from the Light Source on June 1, 2009 as Group Leader of the Soft X-ray Scattering Beamline. As the group leader, Cecilia will work closely with the user community to define the scientific mission and technical requirements for a soft x-ray beamline and for its design, construction, and commissioning. She will also be responsible for developing and managing the scientific research program.

While holding the position of Group Leader, Dr. Sánchez-Hanke will continue to work on the development of new synchrotron radiation techniques to study magnetism and characterize magnetic materials. Cecilia is the spokesperson and scientist at the X13A NSLS beamline. The main focus of her research is on the exploration of new experimental techniques and the use of a unique insertion device, the Elliptically Polarized Wiggler.

After completing her PhD in Physics from University Autónoma of Madrid, Spain, Dr. Sánchez-Hanke secured a position as an Associate Professor. In 1998, she joined BNL as a postdoctoral research associate at the NSLS and has progressed through the scientific ranks to her current position as Physicist.

## Bob Scheidt

W. Robert Scheidt was born near St. Louis Missouri USA and attended the University of Missouri, Columbia, where he received a BS in Chemistry. He then received a Ph.D. in chemistry at the University of Michigan, Ann Arbor. After a two year postdoctoral position with Prof. J. L. Hoard at Cornell University, he joined the Chemistry and Biochemistry faculty at the University of Notre Dame. He became the Wm K. Warren Professor of Chemistry and Biochemistry in 2012. He has served on the editorial boards of Chemical Reviews and Inorganic Chemistry and as a member of NIH study sections. He received the Hans Fischer Career Award in Porphyrin Chemistry in 2008 for his extensive work on the physical properties and molecular structures of metallporphyrins, especially that of iron.

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## Per Siegbahn

I am a professor at the Department of Physics of Stockholm University. My main research interest is in theoretical biochemistry, in particular reaction mechanisms of metalloenzymes. In our group we use the tools of theoretical chemistry, mainly the hybrid-DFT methods, to study the reaction mechanism of various metalloenzymes. The main emphasis is on the systems with redox active transition metals, which among others include photosystem II, cytochrome *c* oxidase, methane monooxygenase, ribonucleotide reductase, manganese catalase, nickel-iron hydrogenase, heme peroxidase, copper amine oxidase, isopenicillin *n* synthase, galactose oxidase, thermolysin and orotidine decarboxylase.

## Dage Sundholm

Professor Dage Sundholm is professor in Computational and Theoretical Chemistry at the Department of Chemistry, University of Helsinki. His research interests comprise computational studies of magnetic and optical properties of molecules. He has developed a computational method to calculate gauge-independent magnetically induced current densities in molecules at *ab initio* and density functional theory levels. He studies molecular excited states of large molecules using time-dependent density functional theory and coupled cluster calculations. He also develops numerical methods for electronic structure studies of molecules.

## Shengfa Ye

In 2005, I obtained Ph.D in the field of physical inorganic chemistry at the University of Stuttgart. After that I worked as a postdoc scholar with Prof. Dr. Frank Neese at the University of Bonn. In 2011, I was appointed as a staff scientist at the Max-Planck institute for Chemical Energy Conversion (previously Max-Planck Institute for Bioinorganic Chemistry).

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## Kazunari Yoshizawa

Kazunari Yoshizawa received his Bachelor, Master, and Ph.D. degrees at Kyoto University under the direction of Kenichi Fukui and Tokio Yamabe. After spending one year (1994-1995) at Cornell University as a postdoctoral associate with Roald Hoffmann, he joined the faculty of Kyoto University, where he became an assistant and associate professor. In 2001 he moved as a full professor to Kyushu University, where his research interests are extended to enzymatic and catalytic reactions and electronic properties of molecules and solids.

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