Water Splitting

Research in the Pantazis group focuses on the study of natural and artificial photosynthetic systems, with an emphasis on reactions that lead to the production of solar fuels from water. We are particularly interested in understanding the fundamental principles that govern the complicated mechanisms of water splitting into hydrogen. To this end we develop and apply quantum chemical methods that allow us to probe the details of the electronic structure and to predict a wide range of spectroscopic properties of polymetallic (bio)inorganic systems, with a view towards understanding the properties of existing catalysts and of developing viable molecular and heterogeneous synthetic systems.

Natural and artificial photosynthesis

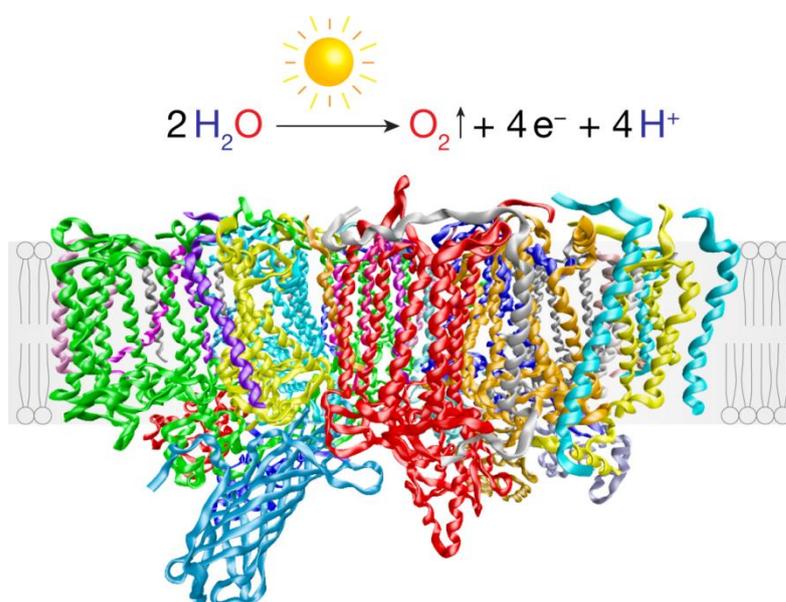$$2\,H_2O \longrightarrow O_2\uparrow + 4\,e^- + 4\,H^+$$

Figure 1

Photosynthetic organisms capture the energy of sunlight and store it in the chemical bonds of carbohydrates. Photosynthesis, the most important biochemical process on Earth, defines life as we know it by providing the building blocks of most living organisms and producing atmospheric oxygen. The main engine of the photosynthetic apparatus is the enzyme Photosystem II, where solar energy splits water into molecular oxygen, protons and electrons, providing the reducing equivalents subsequently employed in carbon fixation. At the heart of PS-II is the oxygen-evolving complex (OEC), the Mn_4O_5Ca functional unit that catalyzes the oxidation of water. Elucidating the chemistry that takes place at the OEC is central for efforts toward artificial photosynthesis, potentially enabling sustainable solar-driven hydrogen production from water.

Our research addresses foremost the problem of establishing firm correlations between structural features and spectroscopic properties. Accurate calculations of spectroscopic properties for potential structural models allow meaningful comparisons with data obtained, for example, from EPR/ENDOR and XAS experiments. To this end we develop methods for the calculation of spectroscopic observables and apply them in the study of the properties and reactivity of catalytic models that range in scale from small clusters to enzymes to surfaces, using a whole range of methods from ab initio and DFT to QM/MM and MD. The safe understanding of structure-property relationships forms the basis for deciphering (and subsequently controlling) catalytic reactivity. For these reasons a topic of special focus is to understand in detail how the various levels of description and interpretation correlate and give rise to a certain phenomenology.
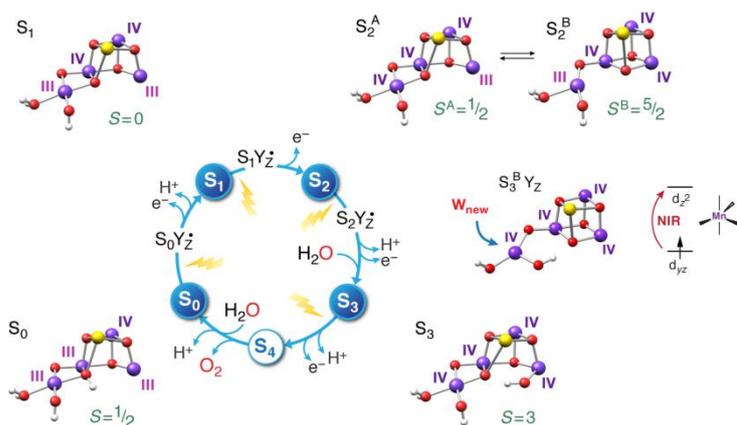
Figure 2

Among the theoretical developments achieved so far are methodologies relevant to the calculation of EPR parameters such as hyperfine coupling constants (HFCs) for oligonuclear metal clusters of arbitrary shape and nuclearity. We have employed these methods in evaluations of models of the S_2 state of the OEC, considering structural variations such as the bonding and connectivity within the inorganic Mn_4O_5Ca part of the OEC, the ligation modes of coordinating aminoacids, and the protonation states of Mn- and Ca-coordinated water molecules and oxo bridges. Given the wealth of state-selective information obtained on the OEC by modern spectroscopic methods, this approach has led to the definition of the topology of the OEC with unprecedented accuracy that is not achievable by methods such as protein crystallography.
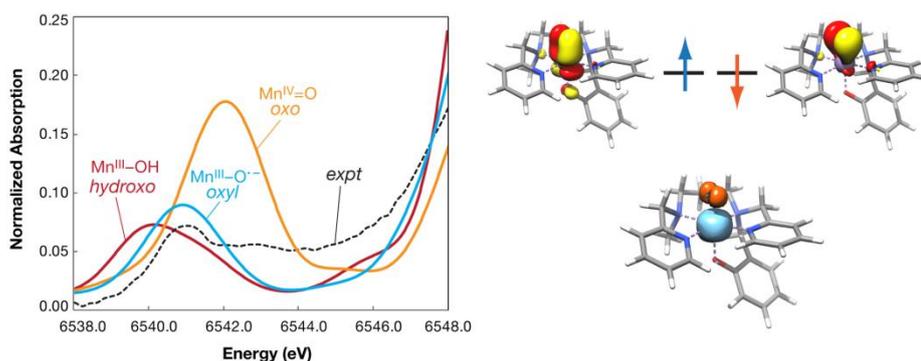

Figure 3

Another example of how the interplay of computational and experimental spectroscopy can lead to firm conclusions regarding the electronic structure and chemical reactivity of an unknown species is the elucidation of the nature of a Mn complex resulting from activation of water. In that case the reference experimental information was the Mn pre-edge X-ray absorption spectrum (**XAS**) that contains information about the valence electronic structure of the metal. Calculations of the XAS pre-edge spectra enabled us to distinguish between protonated and unprotonated adducts and electromeric forms such as oxo and oxyl. These calculations are possible thanks to a recently calibrated TD-DFT protocol, while more recent theoretical advances include an RO-CIS approach.

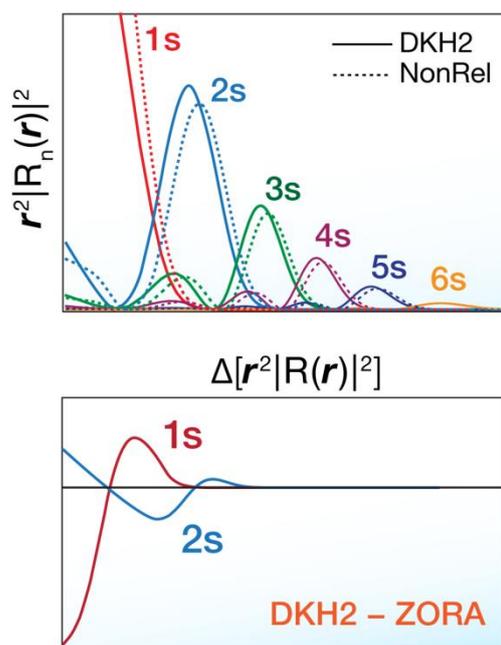# Development of all-electron scalar relativistic basis sets

Figure 4

Routine computational investigations of chemical systems containing elements beyond Kr are dominated by the use of effective core potentials (ECPs) because they reduce the size of the computational task while providing an easy, if approximate, way to account for the most important relativistic effects. However, they have their drawbacks and limitations, for example when there is a need to model a property that depends on the electron density near the nucleus or for topological analysis of electron densities. Therefore, either for validating the use of ECPs or for circumventing their inherent limitations, it is necessary to have all-electron basis sets that allow efficient calculations with the popular scalar relativistic Hamiltonians, such as the Zeroth Order Regular Approximation (**ZORA**), and the Douglas-Kroll-Hess (**DKH**) approach.

An answer to this need is the family of *Segmented All-electron Relativistically Contracted* (**SARC**) basis sets, constructed specifically for DFT treatments in conjunction with the DKH2 and ZORA Hamiltonians. The SARC basis sets are segmented CGTO sets of polarized triple-zeta quality. They present an efficient alternative to ECPs for routine DFT studies of large molecules and their performance has been benchmarked for both atomic and molecular properties.

Exponents are derived from relatively simple rules, using the radial expectation values from accurate atomic calculations as generator quantities. In contrast to non-relativistic basis sets, the SARC basis sets are flexible in the core region, with high exponents required by relativistic Hamiltonians. Polarization functions are added with the requirements of DFT in mind, building flexibility to the chemical valence space without introducing redundant angular momentum (correlation) functions.

Contraction coefficients are optimized separately for the DKH2 and ZORA Hamiltonians, because these two scalar relativistic approximations produce quite different shapes for the orbitals close to the nucleus. From the differences of DKH2 and ZORA radial distribution functions (figure shows differences for the Hg atom), it is readily seen that the ZORA potential is more attractive than DKH2. This issue is explicitly addressed with individually adapted contractions.

Typical applications of SARC basis sets include

- Benchmarking effective core potentials before employing them in extended projects.
- Molecular properties that depend on the density near the nucleus: NMR, Mössbauer, EPR, XAS, etc.
- Topological analysis of electron densities with AIM and ELF.
- Magnetic interactions in f-element-containing molecules, e.g. in 3d-4f single-molecule magnets.
- Processes in lanthanide and actinide chemistry that involve electrons in f-orbitals (e.g. luminescence).

SARC basis sets are available for the third-row transition metals (5d series, Hf-Hg), the 6p elements (Tl-Rn), the lanthanides (4f series, La-Lu), and the actinides (5f series, Ac-Lr). All SARC basis sets for Z > 54 (along with corresponding auxiliary basis sets) are included in the ORCA program package, which also contains scalar relativistic recontractions of the Karlsruhe basis sets up to Xe.