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General Introduction to Spin States

Marcel Swart^{1,2} and Miquel Costas¹

¹*Institut de Química Computacional i Catàlisi and Departament de Química, Universitat de Girona, Spain*

²*Institució Catalana de Recerca i Estudis Avançats (ICREA), Barcelona, Spain*

1.1 Introduction

Spin is a fundamental property of all elements and molecules, which originates from their unpaired electrons. Spin states have a major role in defining the structure, reactivity, magnetic and spectroscopic properties of a molecule. Furthermore it is possible that more than one spin state is energetically accessible for a given molecule. In such cases, the molecule can accumulate multiple spectroscopic, magnetic and reactivity patterns arising from the different accessible spin states. The ground spin state of most organic molecules is a singlet, that is, they have a closed-shell electronic structure, and other states are energetically not accessible under standard conditions. Important exceptions are carbenes, which can exist as singlet and triplet spin states, and the molecule of dioxygen, whose triplet nature poses kinetic barriers to its thermodynamically favorable reaction with organic matter. The situation is completely reversed when transition metals are present, which makes that different spin states are accessible for the majority of transition metal complexes. This primarily results from the particular nature of d-orbitals of the metals (see Figure 1.1) that are close in energy and which can be occupied in different ways depending on the metal oxidation state, its ligands and its coordination geometry (see Figure 1.1). This picture can be further complicated when ligands are not redox innocent and can have a spin that can also engage in ferro or anti-ferromagnetic interactions with the spin of the metal center.

Spin states play an important role [1, 2] in metalloenzymatic reactions (e.g. cytochrome P450cam), in metal-oxo complexes, in spin-crossover compounds and even in catalysis processes mediated by organometallic compounds where different reactions take place via different spin states [3, 4]. However, computational studies have shown that a correct description of the spin state is not trivial [1, 5, 6], and a combination of different density functionals (DFT) and/or *ab initio* methods may be needed. Experimental studies on

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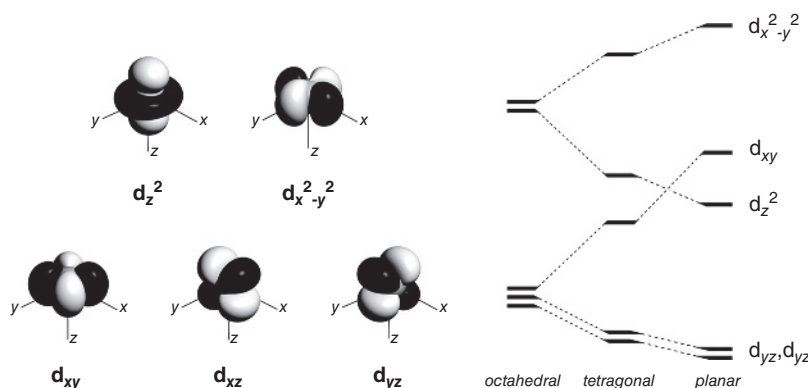


Figure 1.1 Transition metal d-orbitals shape (left) and orbital-level diagram (right).

biomimetic model complexes, enzymes or spin-crossover compounds have added to the complexity, making the spin state a challenging property that is poorly understood [1]. This was the origin for a CECAM/ESF Workshop organized in Zaragoza in September 2012 [7], leading subsequently to a COST Action (CM1305, ECOSTBio).

1.2 Experimental Chemistry: Reactivity, Synthesis and Spectroscopy

Spin states constitute a fundamental aspect of the electronic structure of molecules, and as such spin determines their electronic properties, magnetism and reactivity. Therefore, rationalization of the latter properties in paramagnetic molecules most often requires determination of their spin state. The most important spectroscopic techniques employed to determine spin states in transition metal complexes and proteins have been discussed in Chapter 4, and the use of nuclear magnetic resonance spectroscopy as a tool to shed information on the electronic structure of paramagnetic metal centers, especially those of metalloenzymes, is described in Chapter 16.

Compounds that can exist in multiple spin states open exciting possibilities in a number of fields. An interesting, widely explored case is transition metal centers in octahedral coordination environments with d-electron configurations d^4 to d^7 , which can exist as high spin (HS) and low spin (LS) (see Chapters 5 and 12). Low-spin complexes favor pairing of electrons in t_{2g} orbitals rather than population of e_g orbitals, and the opposite happens for high-spin complexes. The energy difference between both states can be small, and with certain stimulus (light, heat or pressure) one can switch the predominant population of the two states in a reversible manner. In the solid state, cooperative intermolecular interactions may install kinetic barriers to spin interconversion, leading to hysteresis effects. In these cases, the system exhibits a bistability, a property that can potentially find use as memory units in electronic devices. Ongoing and exciting efforts in this field target the manipulation of the electronic spin by taking advantage of the quantum mechanical properties at molecular scale (quantum coherence and entanglement) as the key element for realizing quantum computing.

An important consequence of different spin states for a transition metal complex is that because of the change in occupation from non-bonding (d_{xy} , d_{xz} , d_{yz}) to anti-bonding orbitals (d_{z^2} , $d_{x^2-y^2}$), dramatic changes in spectroscopic properties and the metal–ligand bond distances are observed. For instance, typical $\text{Fe}^{\text{II}}\text{–N}$ distances in low ($S=0$) or intermediate ($S=1$) are of the order of 1.98–2.09 Å, while for the high-spin state

($S=2$) distances of 2.15–2.25 Å are observed [8]. When comparing the geometries of low- and high-spin states for one and the same metal–ligand system, one finds usually mainly a lengthening of the metal–ligand distances. However, a recent study showed [9] that if the ligand is flexible enough with a large number of possible ligating atoms, severe changes in the coordination around the metal can be observed for different spin states. This feature is often observed for different oxidation states of a metal (e.g. Cu^{I} vs Cu^{II}), but is not so common for different spin states of the same metal in the same oxidation state. Translation of spin crossover phenomena in changes in the first coordination sphere of transition metal complexes may allow taking advantage of this property in solution state [10, 11].

The influence of spin states on reactivity can manifest itself in many ways. For example, it is at the basis of the reactions that sustain aerobic life. Spin-forbidden reactions, of, e.g. triplet dioxygen with singlet organic molecules to give singlet-only products, tend to be sluggish, despite being thermodynamically favorable processes. This is altered dramatically by the intermediacy of first-row transition metal ions in low oxidation states (Fe^{II} , Cu^{I}), which reduce the dioxygen molecule and form peroxide species that can oxidize organic functionalities (non-heme iron oxygenases, and models for the oxidizing species that form in their reactions are discussed in Chapters 10 and 15). Intermediacy of transition metals with multiple spin states in close energetic proximity is also used by nature extensively in order to open reaction paths to catalyze many otherwise unfeasible elementary processes. The interplay of multiple spin states in the oxidation reactivity of P450 is recognized as the origin of its chameleonic reactivity nature [12].

Multiple spin states are usually the result of the different possibilities of accommodating valence electrons in d-orbitals, but sometimes ligands are redox non-innocent (see, for example, Chapter 11) and can either offer ligand-based orbitals to accommodate electrons from the metal center or also transfer electrons to d-orbitals. P450 constitutes again a paradigmatic example for this situation. CpI of P450 is best defined as an oxoiron(IV) center with a porphyrin radical ligand. Occupation of the d-orbitals of the iron center and the porphyrin-based radical with the five electrons produces $S=1/2$ and $S=3/2$ systems, close in energy, which exhibit important differences in their reactivity [12].

The idea that the spin state can dramatically influence the reactivity of transition metal centers, including those present in enzymes, is now commonly accepted but was initially recognized in reactions of transition metal ions in the gas phase. The excellent connection between computational and experimental observations for reactions taking place in this phase converts this field in a powerful tool for exploring and understanding the role of spin state in reactivity (see, e.g. Chapter 8). Joint computational and experimental studies have also produced understanding on the role of spin-state-dependent reactivity in organometallic chemistry (Chapter 6). Novel reactivity principles such as the exchange-enhanced reactivity are also emerging to explain the prevalence of high spin states as the most favorable path in reactions that can occur in multiple spin energy surfaces (Chapter 7). Reactivity patterns of transition metal complexes are often difficult to predict, interpret and/or understand, and this complexity is further accentuated in metalloenzymes. Only through a combination of a variety of techniques can one be assured that the interpretation of experimental and/or computational results is plausible. A number of good examples of this are present in the literature on oxidation states and/or spin states. For instance, until a few years ago the iron–molybdenum cofactor of nitrogenase was thought to consist of only Fe/Mo and sulfurs. However, through a series of breakthroughs [13] of X-ray crystallography, X-ray emission spectroscopy and computational chemistry, it was finally determined that there is a central atom present in the cofactor. Moreover, it was clearly determined to be a carbon atom, even though this had been thought to be very unlikely only a few years before. Nevertheless, a second surprising feature of the same enzyme was reported more recently [14], when it was shown that the molybdenum is most likely in the Mo(III) state, a new feature for the use of molybdenum in biology. A detailed understanding of the spin states involved, involving as well a reassignment of oxidation and spin states on iron, was put forward for a number of the intermediate stages of this highly complex catalytic cycle.

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Table 1.1 Systematic effects of computational chemistry ingredients on spin states

Ingredient	Effect on metal–ligand bonds	Favors
HF exchange	Longer/weaker	High spin
Dispersion energy	Shorter/stronger	Low spin
Relativistic effects	Stronger s-bonds, weaker bonds in middle d- and p-blocks	–
Solvation	Shorter metal–ligand bonds	Low spin
Zero-point vibrational energy	“Longer/weaker”	High spin
Entropy	“Longer/weaker”	High spin

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Finally, the editors are sorry that the limited scope of the book could not include other interesting aspects of bioinorganic chemistry [15].

1.3 Computational Chemistry: Quantum Chemistry and Basis Sets

A number of theoretical methods can be used almost straightforwardly, such as density functional theory (DFT) or ligand-field theory based on it, and wavefunction methods such as coupled cluster (CC) theory, multi-reference configuration interaction (MR-CI) or complete active space coupled with second-order perturbation theory (CASPT2). The advantages and drawbacks of each of these classes of methods are described in the first two chapters, and of course these methods have been applied in many studies as described throughout the book.

An important aspect of computational chemistry is the basis set used, which is true in general where more accurate results are obtained with larger basis sets; however, they come at greater (computational) cost. The influence of the basis set on spin state energies is nevertheless an easily overlooked problem. Already in 1977 Hay [16] warned about the use of a double- ζ basis set, which is not flexible enough to properly describe the 3d-orbital manifold, and at least three d-functions were shown to be needed. This was reiterated more recently by Pulay and co-workers [17] who improved the often used 6-31G* basis set (to give m6-31G*) by refitting the exponents to make these more diffuse (but still keeping only two d-functions) or by Swart and co-workers who added an additional third (diffuse) d-function through an even-tempered approach to give the s6-31G* form [18]. Both of these modified basis sets greatly improved the performance for spin states although the convergence towards the infinite basis set results still goes much faster with Slater-type orbital basis sets [19].

A very useful dissection of the importance of different aspects of computational chemistry (inclusion of portion of Hartree–Fock exchange; dispersion energy; relativistic effects; solvation; zero-point vibrational energies; entropy) was recently reported by Kepp (see Table 1.1) [20].

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