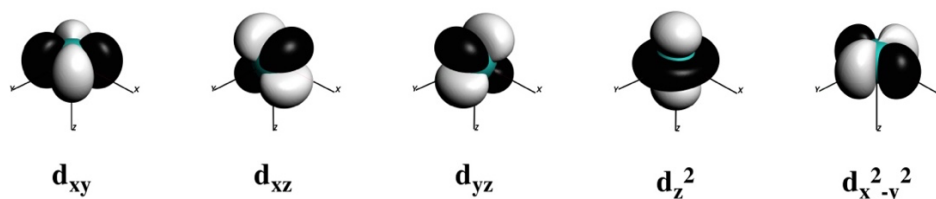


Summary of:  
**First edition of QBtopIC, February 24, 16.30-18.00h**  
**SPIN STATES**

The chemistry of the first-row transition-metals is highly diverse with a multitude of different reactivity and property patterns. This richness results from the partial occupation of the shell of d-orbitals, which leads to different oxidation and spin states. Of course, having a different number of unpaired electrons has a direct effect on the structure, magnetism, and reactivity of molecules. Especially the spin states remain an enigmatic property that has triggered many studies, and recently the first text-book (Swart/Costas, Wiley)<sup>[1]</sup> and COST Action (CM1305) devoted entirely to it appeared.



*Metal d-orbitals leading to different spin states*

The majority of these studies is based on experiment, but computational chemistry plays increasingly an important role, in giving a description of e.g. spectroscopy or transition-state structures to lead to a deeper understanding of reaction mechanisms. Being able to reliably describe the electronic structure of transition-metal complexes through their spin states is a challenge, which affects both wavefunction theory and density functional theory.

The first systematic study on spin states was reported in 2001 by Trautwein and co-workers<sup>[2]</sup> when they studied spin-crossover complexes (low-spin at low temperatures, switching over to high-spin at the transition temperature through cooperative effects), which showed disastrous results for then-available density functional approximations (DFAs): early-GGA and LDA over-stabilize low-spin state, and the B3LYP hybrid already showed high-spin at 0K; in the same year, Reiher and co-workers showed why B3LYP failed.<sup>[3]</sup> Many follow-up studies were published,<sup>[4,5]</sup> among which a series of papers on three Fe(II)-complexes with water, ammonia and bipyridine ligands.<sup>[6-10]</sup> The total spread between LDA on one extreme and Hartree-Fock (HF) at the other end ranges to 125 kcal·mol<sup>-1</sup>; CASPT2 results by Pierloot and co-workers<sup>[6]</sup> match OPBE results<sup>[10]</sup> to within 1 kcal·mol<sup>-1</sup>. The performance for two simple Fe(II) complexes (one low-spin, one high-spin), by ca. 60 DFAs<sup>[11]</sup> confirms the expected preferences of LDA and early-GGA for low-spin, and high-spin for hybrids. Only 9 out of all 60 tested DFAs<sup>[11]</sup> are able to predict both spin-states correctly.

For wavefunction methods, the choice of orbitals is very important, with a preference for using DFT orbitals (M.P. Johansson, WATOC2017) or stochastic CASSCF orbitals.<sup>[12,13]</sup> A systematic investigation of the choices made in coupled cluster (CC) calculations is presented by Feldt and co-workers:<sup>[14]</sup> type of orbitals (HF vs. DFT), unrestricted or restricted orbitals, solving CC equations in restricted or unrestricted fashion, level of coupled cluster method needed, and approximations to canonical CC. Based on these results, characteristic trends of local and DLPNO approximations to CC are observed,<sup>[15,16]</sup> which are discussed later by Neese and co-workers<sup>[17]</sup> and Pantazis and co-workers.<sup>[18]</sup> Radoń with co-workers reported benchmark studies on octahedral iron complexes<sup>[19-21]</sup> and metallocenes<sup>[22]</sup> using reference energies obtained from experimental data. Their results support high accuracy of the CC calculations. Interestingly, the MVS functional,<sup>[23]</sup> advocated as promising by Swart,<sup>[4]</sup> fell short of the expectations for the studied Fe(III) complexes (although it did give encouraging results for Fe(II) complexes),<sup>[19]</sup> while for [Fe(NCH)<sub>6</sub>]<sup>2+</sup> the Diffusion Monte Carlo results by Sim, Burke and co-workers<sup>[24]</sup> gave results that are not consistent with high-level coupled cluster and experimental results for a similar Fe(II) complex.<sup>[19]</sup> The (non-)innocence of nitrosyl ligands when bound to transition-metals was shown to be a complicated situation.<sup>[25-28]</sup>

Panel members:



*invited expert*  
Milica Feldt



*invited expert*  
Mariusz Radoń



*discussion leader*  
Marcel Swart

**References:**

- [1] M. Swart; M. Costas. *Spin States in Biochemistry and Inorganic Chemistry: Influence on Structure and Reactivity*. Wiley: Oxford, **2015**.
- [2] H. Paulsen; L. Duelund; H. Winkler; H. Toftlund; A.X. Trautwein. *Inorg. Chem.* **2001**, *40*, 2201-2203.
- [3] M. Reiher; O. Salomon; B.A. Hess. *Theor. Chem. Acc.* **2001**, *107*, 48-55.
- [4] M. Swart; M. Gruden. *Acc. Chem. Res.* **2016**, *49*, 2690-2697.
- [5] M. Radoń. Chapter Seven - Toward accurate spin-state energetics of transition metal complexes. In *Advances in Inorganic Chemistry*; R. van Eldik, R. Puchta, Eds.; Academic Press, **2019**; Vol. 73; pp 221-264.
- [6] K. Pierloot; S. Vancoillie. *J. Chem. Phys.* **2006**, *125*, 124303.
- [7] A. Fouqueau; S. Mer; M.E. Casida; L.M. Lawson Daku; A. Hauser; T. Mineva; F. Neese. *J. Chem. Phys.* **2004**, *120*, 9473-9486.
- [8] A. Fouqueau; M.E. Casida; L.M. Lawson Daku; A. Hauser; F. Neese. *J. Chem. Phys.* **2005**, *122*, 044110.
- [9] R.J. Deeth; N. Fey. *J. Comput. Chem.* **2004**, *25*, 1840-1848.
- [10] M. Swart. *J. Chem. Theory Comp.* **2008**, *4*, 2057-2066.
- [11] M. Swart. *Chem. Phys. Lett.* **2013**, *580*, 166-171.
- [12] G. Li Manni; A. Alavi. *J. Phys. Chem. A* **2018**, *122*, 4935-4947.
- [13] G. Li Manni; D. Kats; D.P. Tew; A. Alavi. *J. Chem. Theory Comp.* **2019**, *15*, 1492-1497.
- [14] M. Feldt; Q.M. Phung; K. Pierloot; R.A. Mata; J.N. Harvey. *J. Chem. Theory Comp.* **2019**, *15*, 922-937.
- [15] Q.M. Phung; C. Martín-Fernández; J.N. Harvey; M. Feldt. *J. Chem. Theory Comp.* **2019**, *15*, 4297-4304.
- [16] M. Feldt; C. Martín-Fernández; J.N. Harvey. *Phys. Chem. Chem. Phys.* **2020**, *22*, 23908-23919.
- [17] B.M. Flöser; Y. Guo; C. Riplinger; F. Tuczek; F. Neese. *J. Chem. Theory Comp.* **2020**, *16*, 2224-2235.
- [18] S.E. Neale; D.A. Pantazis; S.A. Macgregor. *Dalton Trans.* **2020**, *49*, 6478-6487.
- [19] M. Radoń. *Phys. Chem. Chem. Phys.* **2019**, *21*, 4854-4870.
- [20] M. Radoń; K. Gąssowska; J. Szklarzewicz; E. Broclawik. *J. Chem. Theory Comp.* **2016**, *12*, 1592-1605.
- [21] M. Radoń; G. Drabik. *J. Chem. Theory Comp.* **2018**, *14*, 4010-4027.
- [22] G. Drabik; J. Szklarzewicz; M. Radoń. *Phys. Chem. Chem. Phys.* **2021**, *23*, 151-172.
- [23] J. Sun; J.P. Perdew; A. Ruzsinszky. *Proc. Natl. Acad. Sci. USA* **2015**, *112*, 685-689.
- [24] S. Song; M.-C. Kim; E. Sim; A. Benali; O. Heinonen; K. Burke. *J. Chem. Theory Comp.* **2018**, *14*, 2304-2311.
- [25] A. Stępniewski; M. Radoń; K. Góra-Marek; E. Broclawik. *Phys. Chem. Chem. Phys.* **2016**, *18*, 3716-3729.
- [26] M. Radoń; E. Broclawik; K. Pierloot. *J. Phys. Chem. B* **2010**, *114*, 1518-1528.
- [27] E.I. Solomon; K.D. Sutherlin; M. Srnc. High-Spin and Low-Spin States in {FeNO}<sub>7</sub>, Fe<sup>IV</sup>=O, and Fe<sup>III</sup>-OOH Complexes and Their Correlations to Reactivity. In *Spin states in Biochemistry and inorganic chemistry: Influence on Structure and Reactivity*; M. Swart, M. Costas, Eds.; Wiley: Chichester, UK, **2015**; pp 369-407.
- [28] E. Broclawik; P. Kozyra; M. Mitoraj; M. Radoń; P. Rejmak. *Molecules* **2021**, *26*, 1511.