Short description of the project for general public

Transition metal ions (e.g., iron, manganese, or cobalt) coordinated by suitable ligands in complexes as well as in active sites of enzymes or other catalytic systems (zeolites, metal-organic frameworks), may exhibit an interesting phenomenon of spin-state isomerism. This is due to the existence of several close-lying spin states (i.e., electronic states with different number of unpaired electrons). It turns out that the spin state of a metallic center is important not only for its physical (e.g., magnetic) properties, but also may affects its chemical reactivity and propensity to activate the adsorbed ligands. The change of spin state occurring in some reactions may have important consequences for the kinetics, thermodynamics and selectivity of such processes. The key determinants in theoretical description are *spin-state energetics* (i.e., energy differences between the alternative spin states; they determine the preferred ground state and possibility of its change in the course of a chemical transformation).

It turns out that reliable prediction of spin-state energetics is a grand challenge for computational methods of quantum chemistry, now widely used in the field of molecular modeling. The results obtained from popular DFT (density functional theory) methods are usually strongly dependent on the choice of, so called, exchange-correlation functional, and thus may be inconclusive. There are currently high hopes of improvement by the use of more advanced (thus potentially more reliable) wave function theory methods, such like multireference CASPT2 method or coupled cluster CCSD(T) method. These methods are, however, computationally more expensive than DFT methods, and little is known in practice about their actual accuracy when applied to the problem of spin-state energetics of transition metal complexes. The lack of sufficiently reliable and solid comparison with the experimental data is a major issue. Moreover, many studies performed so far neglected possible effects of the environment (solution, crystalline phase) on relative energies of spin states. Preliminary studies revealed that intermolecular interactions with the environment may significantly affect the spin-state energetics; therefore, such effects should always be taken into account when comparing theory with experiment. It also seems that similar environmental effect may play a role in biological systems and for spin-crossover materials.

The main objective of this project is to thoroughly investigate of how reliable are various quantum-chemical methods in prediction of spin-state energetics for transition metal complexes. We will try to determine probable "error bars" characterizing the results obtained using different methods. To facilitate systematic benchmarking of the computational methods we would like to devise a database containing reliable and quantitative experimental data of spin-state energetics for a representative set of complexes. The experimental data for comparison with theory will be corrected for the environmental effects. In addition, simplified model systems will be studied; their small size will allow us to compare with the results of exceptionally accurate computational methods and thus to better understand the phenomenon of electron correlation in transition metal complexes.

This project is a theoretical study situated at the interface of (bio)inorganic and quantum chemistry. Its successful implementation will contribute to the understanding of basis issues relevant to quantum-chemical description of transition metal complexes as well as to the development of new computational protocols, which may be found useful in future molecular modeling research on enzymatic active sites and other catalytic systems. An important goal of the project will be also to gain better understanding of how intermolecular interactions may lead to selective stabilization of spin states in a condensed phase.