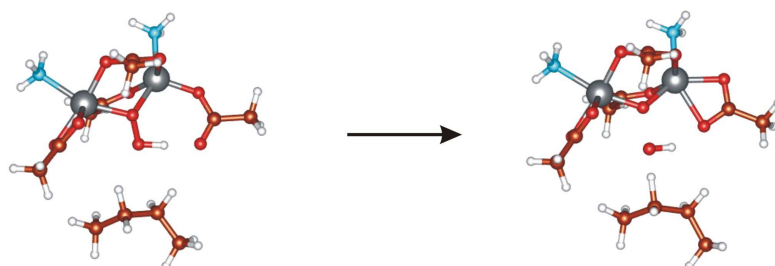


Quantum chemical DMRG study of biological dinuclear metal complexes: Δ^9 desaturase and $\{[\text{Cu}(\text{NH}_3)_3]_2\text{O}_2\}^{2+}$ complex

(Institute for Molecular Science¹) Jakub Chalupský¹, Yuki Kurashige¹, Takeshi Yanai¹

We present quantum chemical study of two biologically relevant dinuclear transition metal complexes based on DMRG-CASSCF and DMRG-CASPT2 calculations. These methods, allowing us to use sufficiently large active spaces for dinuclear complexes, can provide useful information about electronic structure of low-lying states as well as the energetics of studied processes. We address two problems in this poster, barrier height of one of the reactions in catalytic cycle of Δ^9 desaturase and energetics of isomerization of $\{[\text{Cu}(\text{NH}_3)_3]_2\text{O}_2\}^{2+}$ complex.

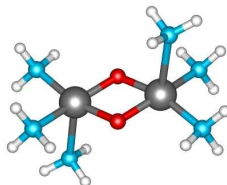
Stearoyl-ACP Δ^9 desaturase is the non-heme iron-containing enzyme involved in fatty-acid metabolism and its regulation in plants, which catalyzes the conversion of the saturated stearic-acid chain into the unsaturated oleic-acid chain. It undergoes multi-step catalytic cycle, whose mechanism is under investigation by the experiments as well as theoretical DFT-based QM/MM calculations. Although several alternatives of its mechanism have been already revealed by theory, reliable prediction of the barrier height for one of the key steps – abstraction of the first hydrogen atom from the saturated stearic-acid chain – seems to be very difficult to make using DFT or conventional CASSCF/CASPT2 approaches. We thus provide a study of height of this barrier based on DMRG-CASSCF/CASPT2 methodology, which allows for qualitatively correct description of the electronic structure of the active site. We have found that this type of calculations is practically feasible even for such a large system (model of active site involves almost 70 atoms), and it provides very important results. Our DMRG-CASPT2 calculations have shown that from the two alternatives of the mechanism studied so far, one (so called “protonated” version of the mechanism, geometry change



during the studied step is shown in the figure) is significantly more favored than the other (water-containing version). Although a lot of work still needs to be done for other alternatives of the mechanism of catalytic cycle of Δ^9 desaturase, already these first obtained results seems to be very promising, and we expect this project to be a highly important application of DMRG approach to biologically relevant chemical problems.

Another interesting problem is the energy of isomerization between bis(μ -oxo) and peroxo forms of $\{[\text{Cu}(\text{NH}_3)_3]_2\text{O}_2\}^{2+}$ complex, which are mimicking structural motives in various copper-containing enzymes, for example tyrosinase. Accurate predictions of the relative energies of these structures have been shown to be extremely difficult to make by nowadays theoretical methods – they seem to require either RASPT2 with the size of active space practically at its limit, or CCSD(T) including corrections for

multiconfigurational character of the reference wave function. We thus consider the problem of energetics of isomerization of $\{[\text{Cu}(\text{NH}_3)_3]_2\text{O}_2\}^{2+}$ complex (in the figure) to be an important case for testing the applicability of DMRG approach on systems, which



require including many orbitals on one center in the active space (Cu 3d and 4d shell – 10 orbitals on a single atom), because it is expected from the principles of DMRG that this type of systems might be problematic to describe correctly. This study thus should provide important information about way of dealing with such systems and possible limitations of DMRG-CASSCF/CASPT2 approach, which could be of high importance to the theoretical chemists in this field.