Project Title: Development of a protocol for simulating transient XANES spectroscopy based on multi-reference electronic structure methods for investigating ultrafast internal conversion in transition metal complexes

Research Project: Transition metal complexes (TMC) are ubiquitous in nature and pose remarkable electronic properties that have found use in artificial photosynthesis, photovoltaics, phototherapy and molecular electronics. Many of these applications are based on the interaction of TMC with light. Optical excitation triggers an electronic population relaxation cascade which could span several eV on the time scale of a few tens of femtoseconds (1 fs = 10^{-15} s). It involves many transient intermediates accessible via competing channels in which the electron density oscillates between the central metal and the ligands. **These primary steps after the interaction with light are of key importance as they determine the response of the system, but so far they have hardly been explored due to the lack of experimental tools with enough time resolution and accurate theoretical methods**.

Femtosecond, and very recently attosecond, spectroscopies intend to follow real-time ultrafast nuclear and electron dynamics. Among them, transient absorption spectroscopy (TAS) is very powerful due to its versatility and applicability over a wide range of frequencies. TAS in the visible range has provided an enormous amount of information on photoinduced dynamical processes but, in spite of its potential, this spectroscopy is able to probe only valence transitions which in some cases give rise to mixing signals difficult to interpret. Experimentally, this bottleneck is resolved by time-resolved x-ray absorption near-edge structure (tr-XANES) spectroscopy, which allows for molecular-site sensitive measurements.

From the theoretical point of view, the reliable description of the electronic structure of TMC poses great challenges due to: a) high density of states of different spin multiplicities; b) strong vibronic and spin-orbit couplings resulting in competitive ultrafast decay pathways; c) high-dimensionality and low-symmetry. Quantum dynamics (QD) with the multiconfigurational time dependent Hartree (MCTDH) method on vibronically coupled (LVC) harmonic potential energy surfaces parametrized at the time-dependent Density functional theory (TD-DFT) level is the de facto standard in the field. A fundamental problem at the core of the state-of-the-art protocol are the limitations of TD-DFT in treating the electronic diversity of the excited states and the lack of a recipe for systematic improvement of the accuracy.

Multi-reference (MR) electronic structure methods overcome these limitations. Yet applications to the electronic structure of TMC have been scarce owing to their unfavorable scaling and conceptual complexity. The recent developments in the field of MR techniques offer exciting opportunities for computational transition metal and coordination chemistry. As a consequence, studies at the restricted active space self-consistent field (RASSCF), stochastic complete active space self-consistent field (CASSCF) and density matrix renormalization group (DMRG) levels of theory are slowly filling the void. Guidelines regarding the composition of the active space – the core construct of MR methods – need to be established. Applications of these methods to photoinduced dynamics and transient spectroscopy of TMC are rare. The high density of strongly coupled electronic states requires rigorous parametrization of the LVC Hamiltonian whereas the interplay of tens if not hundreds of nuclear and electronic degrees of freedom (DOFs) calls for advanced dynamics protocols such as multi-layer MCTDH. Simulations of tr-XANES relying solely on ab-initio input require protocols for the core-excited electronic structure of TMC.

The aim of the project is to develop of a protocol for simulation of tr-XANES of TMC on top of short-time multidimensional QD driven by Hamiltonians parametrized with novel MR methods, therefore overcoming the weaknesses of TDDFT based simulations. This protocol will facilitate TAS simulations with probe pulses ranging from the Visible to the hard X-ray regime, allowing for an unambiguous interpretation of the experimental data. The protocol will be applied to study the ultrafast (sub-100 fs) internal conversion in metallo porphyrins and iridium complexes.

Activity plan:

1. MR electronic structure calculations will be performed to obtain the valence manifolds of hemin and Ir(ppy)$_3$. The emphasis will be on the cost efficient construction of the AS capable of describing metal- and ligand-centered, as well as metal↔ligand CT states in the desired energy rage. The RASSCF/RASPT2, stochastic CASSCF/CASPT2 and DMRG/NEVPT2 schemes will be compared.
2. The RASSCF/RASPT2 protocol will be used to compute the core-excited (*3p→4d* for Fe *5p→5d* for Ir) excited structure.
3. Preliminary QD simulations will evaluate the optimal balance between number of electronic states, DOFs and nuclear wave function representation in (ML)-MCTDH.
4. LVC Hamiltonians for hemin and Ir(ppy)3 will be parametrized with the optimal MR method identified in Task 1. QD simulations will be initiated at various experimental excitation wavelengths. Insights on the relaxation mechanism will be gained by QD run with intra-state, inter-state and spin-orbit couplings selectively turned on/off.
5. An MCTDH-based implementation of the transient spectroscopy protocol in the limit of δ-pulses will be applied to hemin and Ir(ppy)$_3$.