Summary of

Six edition of QBtopIC, November 24th, 15:30-17:00 CEST

Excited state dynamics of transition metal complexes

The sixth QBtopIC took place as an online discussion on Wednesday, November the 24th of 2021. Leticia González (University of Vienna) invited Oliver Kühn (University of Rostock) and Patrick Zobel (University of Vienna) for a presentation and discussion about how to run excited state dynamics simulations in transition metal complexes.

Leticia opened the discussion explaining why performing excited state dynamics in transition metal complexes is a challenging problem: basically, the large size and consequently large number of nuclear degrees of freedom, in combination with a large number of coupled electronic excited states which are also not easy to describe with quantum chemical methods, makes it a tough problem. [1] Then, she presented the two strategies that are currently used to deal with this problem: wavepacket dynamics and trajectory surface hopping. She elaborated in the main requirements for both scenarios and discussed the advantages and disadvantages of both approaches. She then illustrated the use of trajectory surface hopping with their home-developed code, SHARC (**s**urface-**h**opping including **ar**bitrary **c**ouplings) [2] that is able to treat internal conversion and intersystem crossing on one footing in two transition metal complexes: $[Ru(bpy)_3]^{2+}$ in gas phase [3] and $[Re(CO)_3Im(phen)]^+$ in water [4].

Patrick continued by introducing the linear vibronic coupling model (LVC), an approach to parametrize potential energy surfaces of coupled electronic states [5], and its use in trajectory surface hopping simulations.[6] He then showcased the computational efficacy of this combination that allows the dynamics simulation of transition metal complexes with hundreds of nuclear degrees of freedom and dozens of electronic states can be performed for thousands of trajectories and tens of picoseconds. This even allows the usage of multi-reference methods to parametrize the potentials, as was exemplary shown for the open-shell d^2-complex $VCl_3(ddpd)$, for which dynamics were simulated on CASSCF-parameterized LVC potentials [7]. Patrick then warned, however, that the full-dimensional study of transition-metal complexes is not always possible, as some LVC potentials can lead certain complexes to non-physical structures due to too large displacements along low-frequency vibrational modes, a problem that can only fixed by excluding such modes from the dynamics [8].

Oliver introduced the multi-configuration time-dependent Hartree (MCTDH) approach to quantum dynamics [9]. In principle, it provides a numerical exact road to perform high-dimensional quantum dynamics simulations on coupled electronic states. In practice, the bottleneck is the availability of respective potential energy surfaces. He showed why the LVC model with its separable form is particularly well-suited to run MCTDH simulations. Pushing the limits of dimensionality becomes possible by using the multilayer extension of standard MCTDH [9]. It yields a tree-like structure of the wave packet with respect to correlated modes. However, the actual numerical effort strongly depends on the choice of the combination of modes in the tree [10]. For the example of $VCl_3(ddpd)$, Oliver illustrated mode combination using the LVC parameters.

The presentations were closed with Leticia showing a graphical overview of the cost per ps in all the simulations of dynamics of transition metal complexes, which again emphasized that LVC models are the most efficient avenue to perform dynamics in such systems. The discussion was then opened to address the questions of the audience. Questions about how and whether vibronic coupling potentials can describe Jahn-Teller effects and double minima were posed. The quality of the potentials, whatever way they are calculated is of prior importance, and the qualities and abilities of different flavors of DFT, with emphasis on range-separated functionals, were discussed. It was highlighted that, unfortunately, there is no single recipe to choose a functional, so benchmarks are needed. Similarly, the accuracy of LVC models cannot be taken for granted. It was highlighted that problems might arise and a case-by-case inspection is necessary before it is possible to run dynamics. The possibility to automatize multi-layer MCTDH trees was discussed. Further, it was discussed what type of experimental information can be obtained nowadays with such simulations and how accurate can it be. It was pointed out that, for instance, the interpretation of transient absorption spectroscopy is challenged by the high density of states of transition metal complexes. Finally, the possibilities for direct quantum dynamics were commented upon, with little optimism to became a real alternative in systems with experimental relevance.

The discussion showed that the main bottleneck to run excited state dynamics in transition metal complexes is still obtaining a reliable and efficient underlying quantum chemistry.

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