Summary of

Fourth edition of QBtopIC, September 29th, 16:30-18:00 CEST

Classification and Analysis of Excited-state Wavefunctions in Transition Metal Complexes

The fourth QBtopIC took place as an online discussion on Wednesday, September 29th. Felix Plasser was joined by Ilaria Ciofini and Sebastian Mai for a discussion about excited-state wavefunctions in transition metal complexes. Different strategies for analysing wavefunctions produced in quantum chemistry computations and for assigning their character were outlined.

Felix started the discussion by introducing the different traditional types of excited states in transition metal complexes – metal-centred (MC), ligand-centred (LC), metal-to-ligand charge transfer (MLCT) etc – highlighting that excited-state character has immediate consequences on spectroscopic properties. He continued by outlining that the traditional way of assigning excited state character via frontier orbitals has formal as well as practical problems. To solve the problem, he suggested a fragment-based numerical analysis of excited-state character[1,2] and illustrated its application to transition metal complexes.[3,4]

Ilaria continued focusing on approaches based on the analysis of difference density matrix allowing to quantitatively assess the charge transfer extent and eventually its directional character. Limitations of the original implementation[5] as well as recent developments allowing to overcome more relevant problems[6,7] were exposed together with the possible use of these descriptors to diagnostic and correct for the presence of ghost and spurious states in Time Dependent Density Functional calculations.[8]

Sebastian then presented three applications of the fragment-based charge transfer analysis, with the first one being concerned with the excited states of a tetra-manganese cubane water oxidation catalyst.[9] The second example showed the dynamics of different charge transfer states in a Re-complex-sensitized azurin.[10] The third application focused on the dynamics of an Fe complex with MLCT and MC states, where an automatic fragmentation procedure[4] was shown to lead to additional insights.

The open discussion covered a variety of questions around the above topics. We discussed the importance of defining fragments for the above-mentioned decomposition, the possibility of automatic fragment definitions, and the question if and when the transition metal atom should sit in its own fragment. Differences between Mulliken and Lowdin type decompositions were discussed. We highlighted that with different computational methods and, in particular, density functionals one can find strong differences not only in excitation energies but also in the computed wavefunction descriptors.[11,12] Possibilities for analysing other types of states, in particular $n\pi^*$ and $\pi\pi^*$ states, were mentioned. We contrasted analyses of unrelaxed and relaxed densities.

The discussion illustrated that the topic of excited-state wavefunction analysis has gained quite some prominence in the recent years, serving as a powerful tool for gaining new insight into physical processes and for tackling methodological issues.

References

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