Interplay of electronic correlation and metal-ligand delocalization in the spectroscopy of planar Cu^{2+} compounds

Emmanuel Giner, David Tew, Yan Garniron, Ali Alavi

The main subject of this talk is to unravel the main physical effects at work in the ground state and low lying excited states of planar Cu^{2+} complexes and how they impact the quantitative prediction of the spectroscopy.

Thanks to the use of selected CI, we could obtain near FCI energies and wave functions for the ground and two low lying excited states of a series of three medium-size systems, namely the $[CuCl_4]^{2-}$, $[Cu(NH_3)_4]^{2+}$ and $[CuH_2O_4]^{2+}$ molecules. We found that the correlation effects are larger in the ground states and strongly impact the value of the electronic transitions. Then, we analyze both the chemical and mathematical structures of the near FCI wave functions using Valence Bond type analysis and perturbation theory. We find that the introduction of a very specific type of electronic correlation effect necessary induces the rising of charge transfer (CT) components in all ground wave functions, whether such an effect is much smaller in excited states wave functions. Then, we mathematically and numerically demonstrate how such an effect is mandatory for an accurate description of the electronic transitions.

Based on such analysis, we investigate how single and multi-reference wave function methods perform and explain their successes and failures. We show that all Coupled Cluster based methods are systematically able to reproduce near FCI values, and how the choice of the active space in CASSCF calculations drastically impacts the quality of the results.

Finally, by using strongly localized molecular orbitals we explain the difference found between the three ligands used here, and show that the CT play a very important role in the magnitude of the electronic transition.

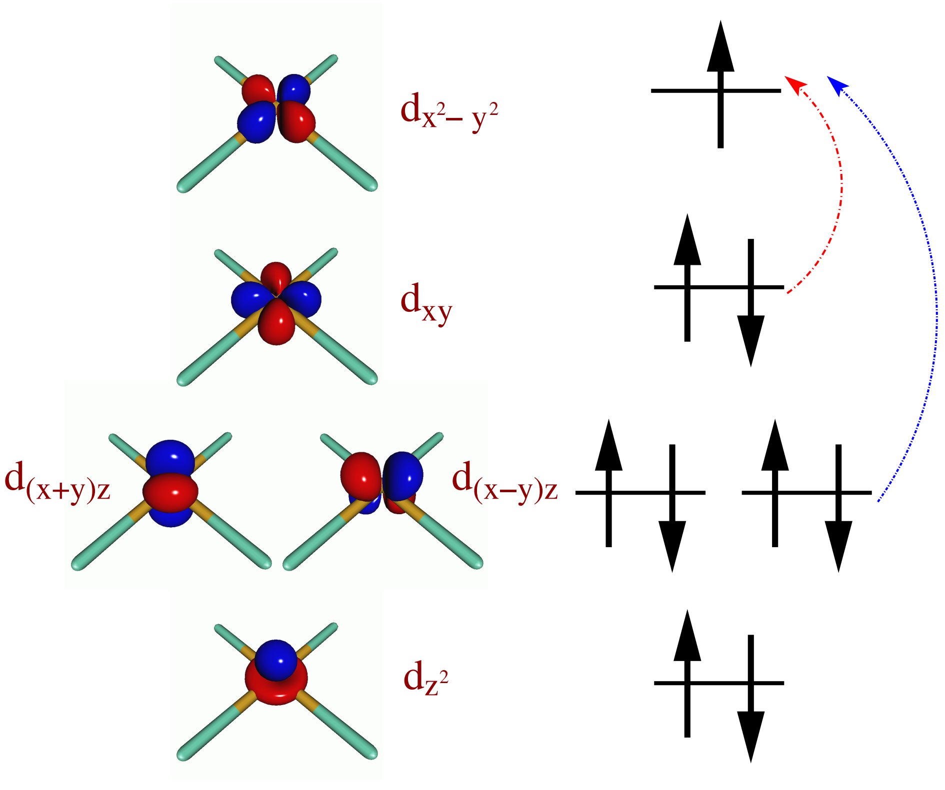

Figure 1: Schematic representation of the ordering of the orbitals according to the ligand-field theory and of the first (red arrow) and second (blue arrow) low lying $d-d$ electronic transitions.