THE ROLE OF DFT IN CHARACTERIZATION OF COORDINATION COMPOUNDS: OPPORTUNITIES AND CHALLENGES

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In the last two decades, considerable theoretical efforts have been made to develop suitable methods for predicting and rationalizing the complicated electronic structure of TM compounds. However, the matter remains open and calculations on molecules with TM centers are still far from being straightforward. The main reason is that these calculations require a balanced treatment of both static and dynamic correlations. Furthermore, it is necessary to understand the influences of coordination number, molecular symmetry, ligand field strength, spin-orbit coupling, spin and oxidation states, redox potential, spin and charge localization, electronic degeneracies, etc. Finally, a complete understanding of the electronic structure of TM compounds and their properties requires investigations that go beyond the ground states alone, i.e., the consideration of excited states.

In this talk we will present our efforts to understand and control metal-ligand bonding based on density functional calculations, considering all its limitations. A fundamental understanding of all factors influencing the properties of a molecule is inherently related to its electronic structure. In the case of a transition metal (TM) complex, the electronic structure is determined by the number, geometry, and character (e.g., σ-donating or π*-backdonating) of its metal-ligand bonds. In addition, a variety of examples will show how experimental results and properties of coordination compounds can be rationalized using DFT calculations.

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