Tackling challenging electronic structure problems: from transition metal complexes to photoinduced reactions

Elvira Sayfutyarova, Yale University

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Miller Room, 328 Havemeyer

First-principles calculations have become indispensable in interpreting experimental spectra, understanding the reactivity of compounds, and characterizing various molecular properties. But despite many advances in theoretical and computational chemistry, there remain challenges, which arise especially in the chemical modelling of transition metal complexes and chromophores with conjugated \( \pi \)-bonds, both of which are widely represented in biomolecules. Their electronic structure featuring multiple near-degenerate electronic states cannot be accurately described by density-functional theory (DFT) based approaches and requires multireference methods. However, multireference methods do not operate as “black-box” routines — they require selecting the so-called “active space”, a set of frontier orbitals for constructing important electronic configurations. Traditionally active space is selected manually based on chemical intuition and detailed inspection of orbitals. This way of selecting an active space appears to be impractical or impossible in the case of large and complex systems, such as occurring in biomolecules, or in the study of potential energy surfaces. Thus, automated and more systematic approaches are desirable. I will present two automatic algorithms for the active space selection, one targeted at transition metals and one at large \( \pi \)-conjugated systems, which can be combined in practical applications. I then will demonstrate their performance for variety of different problems. These range from excitation energies of transition metal complexes over the homolytic dissociation of hydrogen peroxide catalyzed by aqueous ferrous ion in Fenton chemistry, to the scanning potential energy surface along double proton transfer pathways in photoreceptor BLUF proteins.

Plenty of pizza will be provided.