

University of Louisville
Department of Chemistry

Emily Kempfer-Robertson

Research Seminar

When: February 17, 2022

Time: 12:00 p.m.

Location: CB LL-16

Excited State Methodologies for Modeling Multistate Chemical Processes

Abstract:

It is widely understood that the theoretical methods used for studying electronic excited states are extremely limiting yet many prominent areas of technological advancements rely on exploiting the photochemical response of molecules.¹⁻³ An application that has been of particular interest to our research group is the control of molecular switches through a combination of different external stimuli (light, electric field, deprotonation).^{4,5} However, despite significant advances in theoretical approaches⁶ and numerous cases of successful application of theory,⁷ simulating photochemical reactions remains a computational challenge. Theoretical methods for describing excited states can broadly be divided into two categories: single-reference response methods and multireference methods. Single reference methods provide reliable semiquantitative results for single excitations in molecules with a well-defined set of Aufbau occupied orbitals in the ground state. However, these methods cannot describe double excited states, Rydberg states, charge transfer states, systems with strongly correlated ground states, or regions of the potential energy surface with degeneracies between electronic states. Multireference methods are alternatives for studying excited states and can provide accurate and general results. However, multireference methods require significant technical and chemical insight, and become extremely computationally costly as the system size increases. In this talk, I will discuss our work applying various types of excited state methods for understanding the electric field control of azobenzene isomerization. Due to the size and complexity of the π structure in azobenzene, I will highlight the limits of the current excited state methodologies that prevent researchers from studying larger and more complex systems. As a result, I will then turn to discuss our new method developments in projected double-hybrid density functional theory, which seeks to overcome several of the problems of single reference excited state models.^{8,9} I will illustrate the underlying ideas motivating the development of the method, the performance of the model compared to established theories. Finally, I will discuss the planned work for improving the methodology in order to resolve sources of error that remain and increase the performance.

References:

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