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Dissertation Defense

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**Excited State Methodologies with Application to Controlled
Azobenzene Isomerization**

ABSTRACT:

Many prominent areas of technological development rely on exploiting the photochemical response of molecules. 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). However, despite significant advances in theoretical approaches and numerous cases of successful application of theory, simulating photochemical reactions remains a computational challenge. Theoretical methods for describing excited states can be broadly 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 computationally costly as the system size increases. Here, I will discuss my 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 limitations of the current excited state methodologies that prevent researchers from studying larger and more complex systems. I will then turn to discuss new methodological developments in projected double-hybrid density functional theory, which seeks to overcome several of the problems of single reference excited state models. I will illustrate the underlying ideas motivating the development of the method and its performance compared to more established theories. Despite its success, projected double-hybrid density functional theory is unable to account for 'multiple correlation mechanisms'. As a result, I will also introduce concepts in multiple correlation mechanisms and how they can be exploited to perform nonorthogonal active space decomposition, along with applications and paths for future improvements.

REFERENCES:

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3. Kempfer-Robertson, E. M., Haase, M. N., Berrson, J. S., Avdic, I. & Thompson, L. M. Role of Exact Exchange in Difference Projected Double-Hybrid Density Functional Theory for Treatment of Local, Charge Transfer, and Rydberg Excitations. *J Phys Chem* **126**, 8058–8069 (2022).
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