Final Scientific/Technical Report

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INTRODUCTION AND OVERVIEW

Rapid advances in energy applications require new theory and computational models to provide guidance for interpretation of experimental results and mechanistic understanding. New theory development is necessary to treat systems of increasing complexity, size, and relevance to real applications. Functional transition metal compounds, including molecules, clusters, nanoparticles, surfaces, and solids, provide particular promise for magnetic, optical, and catalytic applications. However, such systems can be exceptionally challenging to model. To make progress in understanding and designing transition metal compounds for energy applications, theory must be able to simulate such systems in complex environments, as well as simulate the spectra of such complex systems to provide direct connections with experiment. Leveraging the independent expertise of the team's members, this project aimed to make inroads to the theoretical and computational challenges associated with studying transition metal compounds, their reaction chemistry, photophysics and photochemistry, and response to spectroscopic interrogation.

The project was organized into three themes, each involving multiple PIs and their research groups. Theme 1 centered on the development of efficient ground and excited state models. Theme 2 sought new methods for treating charge transfer within complex environments. Theme 3 focused on improved methods and theory for simulating non-destructive ultrafast spectroscopies. Importantly, this project supported synergistic scientific efforts involving five groups working in chemical computation and theory that span a broad range of sub-specialties within the field. The project initiated a Center for Chemical Computation and Theory (ccCAT) at UC Merced, which has led to broader synergistic scientific research between PIs and their groups.

CONCLUSIONS

Progress was made in all three aims of the project. Theme 1 resulted in the development, validation, and benchmarking of new models for studying open-shell systems. More specifically, the work from Theme 1 yielded a new so-called spin-flip approach to the GW/Bethe-Salpeter model and implementation, taking advantage of a similar structure of the equations to (linear response) time-dependent density functional theory (TDDFT). Critical issues of spin contamination and convergence with number of states in the Bethe-Salpeter method have been assessed. Another model explored for studying excited

states builds on the Δ-self-consistent-field approach. Specifically, we have implemented a projection-based initial maximum overlap method (PIMOM) approach that significantly improves the robustness of such models. A spin-projection model has been incorporated with PIMOM and the results show that this is an excellent model for studying energies, geometries, and vibrational frequencies of electronic excited state for molecular systems. Theme 2 aimed to develop new models for effective treatment of charge transfer in complex environments. The team reported a reliable and computationally efficient protocol to assign partial atomic charges of water molecules in condensed phases based on quantum chemistry calculations and described initial applications. Theme 3 advanced new methods for simulating and understanding nonlinear spectroscopies. Specifically, the team developed new approaches that minimize the number of cost of full quantum chemistry calculations needed to accurately simulate nonlinear spectroscopic signatures. Finally, this award provided support that encouraged and enhanced synergy and collaboration through a number of intentional efforts to build community among the project's research groups. These efforts included a bi-annual one-day ccCAT retreat, bi-weekly student/postdoc run Joint Computational and Theory Club (JCTC) meetings, jointly mentored students and post-docs, and frequent multi-PI/postdoc/student meetings. Such coordinated effort strongly supported the goals of this project and prepared the team for future research efforts relevant to the CTC Program and other BES/DOE initiatives. Taken together, the project yielded several advancements that will support expanded application spaces for studies involving functional transition metal systems, including those in complex environments.

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