CHEMISTRY & CHEMICAL BIOLOGY COLLOQUIUM:

The Pursuit of Free Energies and Free Energy Relationships

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Date:

10/23/2020

Time:

1:30 PM-2:50 PM

Link:

Please email snsgradstaff@ucmerced.edu for Zoom link and passcode

About The Speaker:

Shaama Mallikarjun Sharada's research interests span the development of algorithms to enhance the reliability of quantum chemistry-based reaction rate predictions and their application towards the design of viable catalysts for sustainable chemistry transformations. Dr. Sharada received her Bachelors and Masters in Chemical Engineering from the Indian Institute of Technology, Bombay (India) where she was awarded the Institute Gold Medal. She received her PhD in Chemical Engineering from UC Berkeley in 2015 for her work on the development of efficient reaction path search and wavefunction stability algorithms for catalysis applications. As a postdoctoral researcher at Stanford University, her work spanned the development of machine learning density functionals, construction of databases for benchmarking functional accuracies for surface chemistry, and design of electrocatalytic systems for ammonia synthesis. Since 2017, Prof. Sharada is the WiSE Gabilan Assistant Professor in the Mork Family Department of Chemical Engineering and Materials Science and Assistant Professor (by Courtesy) in the Department of Chemistry at the University of Southern California. She is a recipient of the 2020 ACS Petroleum Research Fund Doctoral New Investigator Award and is a 2020 Scialog Fellow for the Negative Emissions Science initiative.

Abstract:

Chemical reactions lie at the heart of processes designed to meet our growing energy and material needs. The first step towards designing and optimizing chemical reactions involves identification of underlying mechanisms and quantification of rates. Quantum chemistry methods along with theories such as transition state theory (TST) are indispensable for this purpose and have played a pivotal role in elucidating mechanisms in recent decades. While widely successful, conventional TST is relatively simplistic and can lead to inaccurate rates for many classes of reactions. Alternative, more accurate rate theories such as variational transition state theory (VTST) are well-established but incur exceptionally high computational costs which limits their widespread use. Our goal is to lower these costs, thereby enhancing the reliability of rate predictions, by adapting algorithms typically used in signal processing and information recovery. I will discuss our algorithm that leverages matrix completion methods, widely used to recover signals from noisy, incomplete data, to recover otherwise expensive second derivatives of energy for points on the minimum energy path of a reaction.

The second step is to utilize mechanistic and rate information to develop a design framework for catalysts. Hammett and Taft equations emerged as powerful tools in organic chemistry to quantify the sensitivity of reaction kinetics and equilibria to substituent electronic and size/steric properties. Extending these principles to transition metal chemistry with molecular catalysts can be challenging, owing to synthetic difficulties, poor understanding of underlying mechanisms, and ligand, solvent, and counterion effects that are challenging to quantify. By using density functional theory and energy decomposition analysis with the activation strain model, our group is developing linear free energy relationships (LFERs) that quantify the sensitivity of reaction mechanisms to electronic and steric effects of ligands coordinated to the active center. I will present our progress towards developing computational Hammett plots and strain LFERs for methane activation with copper-oxygen complexes. I will also discuss salient features and challenges associated with transferability of these principles for transition metal chemistry.

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