Excitonic Coupled-cluster Theory for Large-scale Electronic Structure Calculations

Anthony Dutoi
Department of Chemistry
Univeristy of the Pacific

Date: **9/21/18**
Time: **3:00 PM**
Location: **COB1 267**

For more information contact:
**Vivian Saephan,
vsaephan@ucmerced.edu**

ABSTRACT

Many chemical problems contain electrons that are doing something interesting. This includes bond breaking, which is at the heart of chemistry, as well as electrons being excited or transferred in photophysical processes. Sometimes the need for high energetic accuracy alone motivates detailed descriptions of electronic wavefunctions. For all of these reasons, and in spite of the apparent obstacles to doing so, the electronic structure community still seeks methods that can be systematically improved to arbitrary accuracy, and which are applicable to large systems. This talk will present work on a fresh approach to this problem, which is showing a lot of promise in initial tests. The well-worn motif of dividing a super-system into chemically meaningful fragments is adopted. However, a shortcoming of existing fragment-based methods is that electron correlation (if included) is modeled at the level of individual electrons, effectively recomputing local many-body fluctuations for each separate inter-fragment interaction. We show that, without approximation, the ab initio Hamiltonian may be rewritten in terms of sub-system fluctuations between locally correlated electronic states (the excitonic basis). This not only reduces the computational cost of conventional highly correlated electronic structure methods, but also the scaling. Using this foundation, we developed a working excitonic coupled-cluster (X-CC) code. We have acquired promising results on test systems of chains of Be atoms (the dimer is already a notoriously difficult multiconfigurational, semicovalent problem). In a toy 6-31G basis, our pilot code can handle 100 Be atoms (200 active electrons) in about 11 minutes, achieving a total dissociation energy comparable to conventional CCSD (coupled-cluster with single and double substitutions). A calculation of this size is challenging to even complete with existing production-level CCSD codes. Upcoming real-world applications and extensions of this work will be discussed alongside the conceptual aspects of the theory.

BIO:

I obtained my BS in Chemistry with highest honors from Saint Louis University, where I worked with Ronald See on varied computational projects. I undertook a year of independent study as a Fulbright Scholar in Göttingen, taking on a research project in vibrational spectroscopy with Peter Botschwina. I completed my PhD under the supervision of Martin Head-Gordon at the University of California, Berkeley, researching novel approaches to solving the electronic Schrödinger equation for molecules. I took a postdoctoral position with Tamar Seideman at Northwestern University, looking into the electron dynamics underlying high-order harmonic generation. I then moved to Heidelberg, Germany, with a Humboldt Fellowship to research correlated electron dynamics with Lorenz Cederbaum. Since 2012, I have been an Assistant Professor at the University of the Pacific.