

# **CORE-CM SEMINAR**

## **Michigan State University — Department of Chemistry and Department of Physics and Astronomy**

**Piotr Piecuch, Department of Chemistry and Department of Physics and  
Astronomy, Michigan State University**

### **Understanding Photochemistry, Multi-photon Ionization, and Photoelectron Spectra with the Equation-of-Motion Coupled-Cluster Theory**

#### **Abstract**

Understanding electronic excitation, multi-photon ionization, and photoelectron spectra, particularly those involving strongly correlated and dark states or transition metal nanoparticles, poses a significant challenge for theory and experiment. The existing experimental techniques may not be powerful enough to provide definitive information on their own, whereas an accurate treatment of the relevant many-electron correlation effects required in theoretical analyses is not always obvious. This talk will demonstrate that extensions of coupled-cluster (CC) theory to excited states via the equation-of-motion (EOM) CC formalism and its particle-non-conserving EA/IP, DEA/DIP, etc. counterparts designed to handle open-shell systems obtained by attaching electrons to or removing electrons from the corresponding closed-shell cores offer computationally attractive alternatives to other quantum chemistry techniques that aim at a highly accurate description of molecular electronic spectra. This is especially true when the completely renormalized and active-space EOMCC approaches, their merger in the form of the so-called CC( $P;Q$ ) methodology, and the active-space extensions of the EA/IP- and DEA/DIP-EOMCC approaches, all developed by our group, are exploited. All of these methods rely on the easy-to-use single-reference EOMCC ideas, modified to allow one to handle excited-state potential energy surfaces along bond breaking coordinates and one- as well as two-electron transitions without resorting to complex multi-reference wave functions. All of the formal concepts will be illustrated with a wide range of benchmark computations and realistic applications to interesting problems in areas of photochemistry and multi-photon ionization and photoelectron spectroscopies, including examples where the original EOMCC ideas and computer codes developed by our group have played a transformative role in understanding the previously unexplained experiments and phenomena involving electronically excited states. Among the examples in the latter category, we will discuss our discovery of the doubly excited state of azulene, located below the ionization threshold, mediating the  $1 + 2'$  multi-photon ionization that leads to clear Rydberg fingerprint spectra, using the completely renormalized EOMCC approach, abbreviated as  $\delta$ -CR-EOMCC(2,3), and the scalar relativistic IP-EOMCC calculations correlating valence and semi-core electrons and including up to 3-hole-2-particle excitations for the  $\text{Au}_3^-$  nanoparticle, which have enabled us to provide an accurate assignment of peaks and shoulders in the experimental photoelectron spectrum of  $\text{Au}_3^-$  for the first time.

**Thursday, September 10, 2015**

**12:00 PM**

**Room 1400 – BPS**

**Professor – Ben Levine**