

# Advances in Electronic Structure Theory and Dynamics

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**ABSTRACTS**

# Talks

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*SATURDAY, JUNE 6*

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**9:10 AM - 9:45 AM**

## **Coupled Cluster Accuracy at DFT Cost: Interpretable Graph-Network Based Machine Learning Models via Molecular Fragmentation**

*Krishnan Raghavachari\**  
*Indiana University, Bloomington, IN*

The failure of available density functional (DFT) methods to compute accurate electronic structures and energies for complex systems is well documented. While newly developed dispersion corrected and long-range corrected density functionals offer improved results, the errors in thermochemical properties computed with DFT are often greater than 5 kcal/mol for many chemical processes. In this talk, we discuss a new fragmentation-based molecular representation framework designed for delta machine learning ( $\Delta$ -ML) with the central goal of correcting the deficiencies of approximate methods such as DFT to achieve a high level of accuracy that is currently only achievable with sophisticated and computationally intensive methods such as coupled cluster theory.

Our framework is based on a judicious combination of ideas from fragmentation, error cancellation, and a state-of-the-art deep learning architecture. Broadly, we develop a general interpretable framework for molecular machine learning by incorporating the inherent advantages prebuilt into existing error cancellation methods such as the generalized Connectivity-Based Hierarchy. More specifically, we develop an attributed graph representation through a fragmentation-based encoding of local chemical environments. In addition, we incorporate electronic descriptors from DFT calculations in the  $\Delta$ -ML model to achieve high accuracy for the calculation of electronic properties. Our QM/ML framework and its performance for theoretical thermochemistry, redox potentials, pKa calculations, and NMR chemical shifts are analyzed and assessed in this presentation.

**9:45 AM - 10:20 AM**

## **Periodic Wavefunction Methods for Materials: From MP2 to Coupled-Cluster Theory**

*Xiao Wang\**

*University of California, Santa Cruz, Santa Cruz USA*

Accurate and efficient wavefunction-based treatment of extended systems remains a major challenge in theoretical chemistry. In this talk, I will present three recent advances in periodic wavefunction methods with applications to 2D materials and surface chemistry. First, I will introduce a Gaussian-based Laplace-transformed scaled opposite-spin MP2 (SOS-MP2) formulation for periodic systems, which substantially reduces the computational cost of conventional MP2 while preserving accuracy, broadening its applicability to complex materials. Second, I will discuss pyridine adsorption on graphene as a model for graphene functionalization, studied using local natural orbital CCSD(T) (LNO-CCSD(T)). Our results show that common DFT functionals overestimate the binding energy by 0.2-0.3 eV — an error large enough to qualitatively change whether a functional group is predicted to bind to graphene. This underscores the need for high-level wavefunction methods in surface chemistry benchmarking. Third, I will present equation-of-motion CCSD (EOM-CCSD) calculations of optical absorption spectra for transition metal dichalcogenides (TMDs). By developing an EOM-CCSD formalism based on a generalized Hartree-Fock (GHF) reference and incorporating spin-orbit coupling, we successfully reproduce the experimentally observed A/B exciton energy splitting in TMDs, demonstrating the capability of periodic coupled cluster theory to capture relativistic excitonic effects. Together, these developments push the frontier of periodic wavefunction methods toward predictive accuracy for realistic materials systems.

*10:35 AM - 11:10 AM*

## **From Hot Plasmas to Mineralizing Seawater: Electronic Structure for Multiphysics Dynamics**

*Vidushi Sharma\**

*Princeton Plasma Physics Laboratory, Princeton, NJ, USA*

This talk will touch upon two intricately connected themes rooted in electronic structure theory arising in the seemingly disparate arenas of disordered plasmas and electrolytic seawater carbon mineralization. A critical quantity for characterizing electron transport in warm dense plasmas is the effective ionization of an atom ( $Z_{\text{eff}}$ ). However,  $Z_{\text{eff}}$  is poorly defined within common static charge-partitioning schemes because warm dense systems contain many loosely bound and delocalized electrons. In the first part of the talk, I will revisit dynamical Born effective charges using mixed stochastic time-dependent density functional theory (TD-DFT), to derive a novel atomic partitioning scheme of a bulk electron response property that we call the group conductivity. A physically meaningful  $Z_{\text{eff}}$  for disordered metals hinges on the group conductivity, as I will illustrate with mixed liquid metals. In the second part, I will describe a density-based embedding theory in which a system is replaced by an embedded subsystem interacting with its extended environment via a uniquely defined embedding potential at the DFT level. By combining this framework with embedded correlated wavefunction theory, we piecewise-refine the electronic structure description of the chemically important regions and incorporate electron correlation effects inadequately captured by standard density functionals. We apply this multiphysics modeling framework to investigate metal-bicarbonate ion-pairing mechanisms in alkaline aqueous solutions akin to seawater. These ion-pairing mechanisms are a missing microscopic component in the broader picture of electrolytic seawater carbon mineralization.

**11:10 AM - 11:30 AM**

## **Chemical Origins of Non-Bonded Interactions Within and Between Solids**

*Paul J. Robinson\*, Adam Rettig, Hieu Q. Dinh, and Joonho Lee  
Harvard University, Cambridge USA*

Quantum chemical analysis tools help to bridge microscopic electronic structure and chemically intuitive principles. In this work, we generalize the absolutely localized molecular orbital energy decomposition analysis (ALMO-EDA), widely used in molecular quantum chemistry, to study non-covalent interactions within and between solids. We showcase the utility of the new tool at the level of density functional theory in several classes of materials: molecular crystals, moiré heterobilayer materials, and layered perovskite heterostructures. Analysis of aspirin polymorphs and co-crystals reveals existing crystal engineering principles arising naturally from EDA of the lattice energy. EDA of the band gap in moiré heterobilayer MoS<sub>2</sub>/WSe<sub>2</sub> demonstrates distinct characteristics arising in each of the different stacking domains of the electronic superlattice. In a set of layered perovskite heterostructures, EDA of the band structure reveals that the difference in ionic radii between Li<sup>+</sup> and Na<sup>+</sup> determines whether the quantum-well has the electron and hole localized to different layers or the same layer. Our tool dissects lattice-formation energies, interlayer interaction energies, and band structures, and reveals their appropriate chemical origins. Overall, our energy decomposition analysis provides structural insight and enables quantitatively informed design principles in solid-state systems.

*11:30 AM - 12:05 PM*

## **Capturing the quantum dynamics of polaron formation and transport over experimentally relevant system sizes and times**

*Andres Montoya-Castillo\**  
*University of Colorado Boulder*

Small polarons—electronic excitations and the deformation they induce in their environment—are the primary excitation and charge carriers in transition metal oxides, organic crystals, and conjugated polymers—materials with myriad applications in photocatalysis, solar cells, and electronics. Despite their central importance, a theoretical understanding of how the microscopic properties of materials control polaron formation and transport remains incomplete. This is largely due to the absence of scalable quantum dynamics methods capable of simulating systems at experimentally relevant sizes and timescales and *ab initio* descriptions that can directly interface with such quantum dynamics. In this talk, I introduce a new space- and time-local generalized master equation (STL-GME) that enables us to predict the nonequilibrium dynamics of polaron formation and the various phases of its transport across experimentally relevant length and time scales. Our simulations reveal surprisingly long-lived polaron subdiffusion, which emerges as a nonequilibrium response to impulsive excitations, and its asymptotic transformation to diffusive motion. I will conclude by showing how we combine our quantum dynamics simulations with *ab initio* characterization of materials to explain recent experiments on ultrafast polaron formation in transition metal oxides and provide insights into material design for tunable polaron properties.

**1:30 PM - 2:05 PM**

## **Chiroptical Linear Response Properties of Molecules and Materials**

*Marco Caricato\**

*University of Kansas, Lawrence USA*

Molecular and supramolecular chirality has always played an important role in chemistry as life has developed around building blocks of specific handedness (L-amino acids and D-sugars), a phenomenon known as homochirality. This has enormous implications, for instance, in drug design as only one enantiomer of a particular compound will have the desired pharmacological effect. However, in recent years supramolecular chirality has shown tremendous potential for other technological applications, like optoelectronics, sensing, magnetism, information technology, and imaging. The interpretation of experimental data and predictions on new systems require accurate quantum mechanical simulations of the electronic response to external fields, and tools to translate the output of these simulations into insightful chemical concepts. In this contribution, we present the development of new computational strategies to simulate and interpret chiroptical spectra of molecular and solid-state systems. We discuss technical challenges that need to be overcome and how these simulations can help in the interpretation of experiment.

**2:05 PM - 2:40 PM**

## **Energy Decomposition Analysis of Core Binding Energies**

*Afifa Yousaf, Alexis A.A. Delgado, and Devin A. Matthews\**

*Southern Methodist University, Dallas, USA; University of Texas at El Paso, El Paso, USA*

Core electrons in second-row elements, while non-bonding, are subtly affected by chemical environment and can provide sensitive element- and regio-specific probes of electronic structure via soft x-ray spectroscopy (NEXAFS, XPS, RIXS, etc.). In this talk, we consider the effect of hydrogen and halogen bonding on (primarily) oxygen core binding energies (CBEs), in arrangements spanning gas-phase dimers to medium-sized clusters. We perform an energy decomposition analysis of the core orbital energy in various localized bases, which allows for assignment of atom-specific effects as well as an analysis of perturbations to the core orbital shape via the virial theorem. While the primary effects are explained via electrostatic interaction of redistributed charges, cooperative and non-bonded effects are also seen to be very important in emergent non-covalent bonding networks.

*2:40 PM - 3:15 PM*

## **A Kohn-Sham Orbital Approach to Extended Configuration-Interaction Singles with Core/Valence Separation (DFT/XCIS-CVS)**

*Avik Kumar Ojha\* and John M. Herbert  
Ohio State University, Ohio, USA*

Spectroscopic core-to-valence transitions provide a sensitive probe of valence virtual orbitals and are particularly informative for molecules and materials with open-shell ground states, where frontier orbitals are often (quasi-)degenerate. However, open-shell excited states are difficult to tackle at the level of single excitations using standard methods such as time dependent density functional theory, because spin-unrestricted references often lead to severe spin-contamination in both ground and excited states. Extended configuration interaction singles (XCIS), is a simple, variational, and size-consistent wavefunction ansatz that extends the conventional CIS excitation space by a limited set of doubly substituted determinants, producing spin-pure open-shell excited states from a restricted open-shell Hartree-Fock reference. XCIS is less spin-contaminated than ROHF-based CIS and produces improved excitation energies. In earlier work we combined XCIS with the core/valence separation (CVS) approximation, to produce a computationally efficient way to simulate core-to-valence excitations for open-shell systems, through limiting the occupied orbital space. XCIS-CVS calculations for core-to-valence x-ray transitions in a dataset of open shells, such as different 3d transition-metal complexes showed semi quantitative agreement with experiment for K-edge and pre-edge orbital splittings. However, we found that the absence of dynamic correlation can lead to noticeable errors in predicted intensities and splittings. Here, we combine XCIS-CVS with Kohn-Sham-orbitals and with scaling of the two-electron integrals (DFT/XCIS-CVS), while retaining the computational advantages of the XCIS formalism while improving the description of the splittings.

**3:30 PM - 4:05 PM**

## **Low-spin ROHF revisited: A spin-pure framework for open-shell electronic structure**

*Cameron Y. Z. Brown and Hugh G. A. Burton\**  
*University College London*

Accurately predicting open-shell states is essential to understand the electronic structure of molecular radicals, excited states, and transition metal complexes. It has recently been shown that configuration state functions (CSF) with local orbitals can provide good reference states for low-spin open-shell states, capturing a large portion of a multiconfigurational wavefunction without relying on spin-symmetry-breaking or complete active space methods.[1-3] However, converging SCF calculations for low-spin CSFs has been a longstanding challenge due to the lack of a universal Fock operator for open-shell orbitals. Here, I present a robust quasi-Newton SCF procedure that allows arbitrary CSFs to be optimised at mean-field cost.[4] I explore the chemical and mathematical properties of optimal CSF solutions and show how they can be used to qualitatively understand open-shell character in both ground and excited states. Furthermore, I show how multiple CSF solutions can be used to define a spin-pure basis for nonorthogonal configuration interaction to predict excited-state energy surfaces. I will finish with a perspective on the open challenges and opportunities of using low-spin ROHF solutions as a basis for single-reference correlation methods for open-shell chemistry.

[1] G. Li Manni, W. Dobrautz, and A. Alavi, *J. Chem. Theory Comput.* 16, 2202 (2020)

[2] T. Leyser da Costa Gouveia, D. Maganas, and F. Neese, *J. Phys. Chem. A* 128, 5041 (2024)

[3] D. Marti-Dafcik, N. Lee, H. G. A. Burton, D. P. Tew, arxiv:2402.08858 (2024)

[4] H. G. A. Burton, *J. Chem. Theory Comput.* 21, 9444 (2025)

**4:05 PM - 4:25 PM**

## **Advancing nonadiabatic dynamics in the condensed phase**

*Momir Mališ, Tjeerd Futai de Jong, Andrey Sinyavskiy, Eva Vandaele, and Sandra Luber  
University of Zurich, Zürich, Switzerland*

Accurate simulation of nonadiabatic processes in condensed-phase environments remains a significant challenge due to system size, the number of excited electronic states, and the versatility of nonradiative deactivation (NRD) pathways. We present recent advancements within the CP2K software package that enable nonadiabatic molecular dynamics (NAMD) for extended systems (such as liquids) under periodic boundary conditions. Focus will be on the delta self-consistent field ( $\Delta$ SCF) method, trajectory surface hopping, and advancing time-dependent density functional perturbation theory (TDDFPT)-based NAMD (e.g., by inclusion of spin-orbit couplings (SOC)). Notably,  $\Delta$ SCF reduces computational costs to those of the ground-state DFT level, facilitating the study of large-scale solvated systems, while also including SOC. These methodologies were applied to several photoexcited systems in aqueous solution to demonstrate their utility. For cis- and trans-diimide,  $\Delta$ SCF-NAMD shows that explicit solvation significantly extends excited-state lifetimes, particularly for the trans isomer, through stabilized hydrogen bond interactions. In cyclopropanone, while NRD pathways largely mirror the gas phase, its hydrated form undergoes complex photochemistry, producing several photoproducts in reactions between the solute and the solvent molecules. Finally, TDDFPT-NAMD simulations of ortho- and para-nitrophenol, including SOC, identify a solvent-cage effect that restrains molecular flexibility and inhibits intersystem crossing, while a comparative analysis with the QM/MM results shows that only a fully quantum mechanical treatment of the solvent manages to accurately capture the NRD processes. These findings emphasize the importance of explicit quantum-level solvation treatment (ideally with periodic boundary conditions) for realistic modeling of condensed-phase photochemistry.

**4:25 PM - 5:00 PM**

## **Mutual information and mutual correlation: their spin-free formulations and comparison**

*Jiri Pittner\**

*J. Heyrovsky Institute, Czech Academy of Sciences, Praha, Czech Republic*

Orbital entropies, pair entropies, and mutual information have become popular tools for analysis of strongly correlated wave functions.

They can quantitatively measure how strongly an orbital participates in the strong correlation and reveal the correlation pattern between different orbitals.

However, this pattern can become rather complicated and sometimes difficult to interpret for large active spaces and is not invariant with respect to the spin projection component of the spin multiplet state.

We introduce a modified spin-free orbital entropy, pair entropy, and mutual information, which simplify the correlation analysis and are invariant with respect to the spin projection.

By comparison of these quantities with their "original" spin-including counterparts one can distinguish static correlation due to spin couplings from the "genuine" strong correlation due to a multiconfigurational character of the wave function.

Recently, Evangelista introduced mutual correlation computed from the two-body cumulant as an alternative correlation measure, which is easier to compute for some methods.

We present here a spin-free analogue of this quantity and perform a comparison of the entropy-based and cumulant-based correlation measures in both original and spin-free variants.

We illustrate the approaches on iron-sulfur bound complexes with one and two iron atoms.

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*SUNDAY, JUNE 7*

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**9:00 AM - 9:35 AM**

**From molecules to materials: Extending applicability of density-corrected and conditional probability DFT**

*Kieron Burke and friends\**

*University of California, Irvine, Irvine, CA, USA*

I will discuss two very different methodologies that have been developed in molecular contexts and have recently been extended to materials calculations. In collaboration with Professor Eunji Sim of Yonsei University, we have extended DC-DFT to weakly correlated solids[1]. We show that both dispersion and choice of density have significant impact on the results of DFT calculations across a wide range of main group solids and molecular crystals. Several years ago, we developed conditional probability DFT as an alternative to KS DFT that naturally captures some strong correlation effects, such as correct dissociation of H<sub>2</sub> and H chains. In collaboration with Professor Hardy Gross, we extend the methodology of CP DFT to both weakly and strongly correlated materials[2].

[1] DC-DFT for solids. Y. Kim, S. Song, M. Sogal, KB, and E. Sim (2026),  
<https://doi.org/10.26434/chemrxiv.15002348/v1>

[2] Conditional probability density functional theory for solids. Pewei You, Ryan Pederson, Kieron Burke and E.K.U. Gross (2026),  
<https://doi.org/10.48550/arXiv.2605.13226>

**9:35 AM - 10:10 AM**

**Accurately capturing many-body effects in molecular core level spectra through real-time coupled cluster methods**

*Vibin Abraham and Bo Peng\**

*Pacific Northwest National Laboratory, Richland, USA*

Accurately resolving many-body satellite features in molecular core-level spectra requires theoretical approaches that capture electron correlation efficiently and systematically. In this work, we developed a hierarchy of cost-effective approximations to the time-dependent double coupled-cluster (TD-dCC) ansatz, which combines correlation effects from the  $N$ - and  $(N-1)$ -electron sectors but is computationally demanding in its exact form. These approximate TD-dCC ansatzes are derived from truncated Baker–Campbell–Hausdorff expansions, preserving a single-similarity-transformation structure while retaining the key correlation diagrams responsible for satellite formation. We also introduced a component analysis that isolates hole-mediated excitation pathways arising from the coupling between ground-state and ionized-state amplitudes, enabling mechanistic interpretation of quasiparticle and satellite features. Applications to the single-impurity Anderson model, H<sub>2</sub>O, and CH<sub>4</sub> show that the approximate TD-dCC methods efficiently reproduce exact many-body spectral features and quasiparticle weights.

**10:10 AM - 10:30 AM**

## **Mixed-Reference Spin-Flip TDDFT: Energy, Properties, and Density-based Characterization of the Excited States**

*Arnab Chakraborty\*, Zheng Pei, Yihan Shao, and Anna I. Krylov  
University of Southern California, Los Angeles USA; Brandeis University, Waltham USA*

Quantum chemical methods for excited electronic states are essential for understanding photochemistry, chemical reactivity, and molecular materials. While time-dependent density functional theory (TDDFT) is widely used due to its favorable computational cost, it often struggles in systems exhibiting strong static correlation, near-degeneracies, or significant double-excitation character. The spin-flip (SF) approach addresses these challenges by generating low-lying states from a high-spin reference through spin-flip excitations. However, conventional SF formulations suffer from spin contamination arising from an incomplete configuration space, which complicates the characterization of low-lying states.

The mixed-reference spin-flip TDDFT (MRSF-TDDFT) method addresses this limitation by employing a mixed reduced density matrix constructed from the  $M_s=+1$  and  $M_s=-1$  components of the high-spin triplet reference, recovering most of the missing configurations and, thus, making the state assignment unambiguous. We present a new and efficient implementation of MRSF-TDDFT within the Q-Chem electronic structure package. The implementation enables the calculation of excitation energies, properties, and density-based state analyses using the libwfa framework. These analyses include natural orbitals, natural transition orbitals, and natural difference orbitals, providing insight into the electronic structure and character of the multiconfigurational states. The capabilities of the implementation are demonstrated through comparisons with previous SF-TDDFT results and high-level wave function methods, as well as applications to diradicals, linear conjugated systems with strong static correlation and doubly excited states, singlet-triplet gaps in polyacenes, and systems exhibiting conical intersections. The results demonstrate that this implementation provides a robust framework for studying complex excited-state phenomena in molecular systems.

**10:45 AM - 11:20 AM**

## **Nonadiabatic Rate Theories: From Intersystem Crossing to Internal Conversion**

*Sergey Varganov\**

*University of Nevada, Reno, Reno, USA*

Predicting the rates of non-radiative transitions between electronic states is important for understanding the kinetics of many chemical and physical processes, including spin-forbidden reactions, spin-crossovers, intersystem crossings, and internal conversions. First, the different nonadiabatic theories that aim to predict the rate constants for such processes will be discussed. The goal is to make clear connections between Fermi's Golden Rule, Marcus theory, spin-boson model, and different versions of nonadiabatic transition state theory (NA-TST). Second, applications of NA-TST to thermally activated spin-forbidden reactions and photochemical intersystem crossing transitions between electronic states with different spin quantum numbers will be demonstrated. Finally, the NA-TST extension to predict internal conversion rates between electronic states with the same spin will be discussed.

*11:20 AM - 11:55 AM*

**The two component noncollinear exchange correlation (XC) kernel: formulation, implementation and numerical stability.**

*Giovanni Scalmani\* and Michael J. Frisch  
Gaussian, Inc.*

General SCF (GHF/GKS) single determinant wavefunction are required to describe systems of noncollinear spins, frustrated magnetic states, or to include relativistic effects, such as spin-orbit interaction. In this context Density Functional Theory calculations rely on the definition of a small number of space- and spin-rotationally invariant quantities (the functional variables) from a larger number of quantities which are built from density matrices and basis functions (and their derivatives, the density variables). More than one way of defining such functional variables has been proposed, and among them, the definition set forth by us is simple, consistent and physically well motivated. Nevertheless, its robust implementation needs to address numerical instabilities due to the unavoidable presence of square root operations in the definition of spin-rotationally invariant functional variables. In particular, the calculation of the XC kernel has proved to be particularly challenging, with the consequence of limiting the availability and adoption of two component versions of wavefunction stability tests, and one-electron excited states methods like CIS/TDA and TD-DFT.

*1:30 PM - 2:05 PM*

## **Breaking the Quadrillion Determinant Barrier in Numerically Exact Configuration Interaction**

*Xiaosong Li\**

*University of Washington, Seattle, WA USA*

The combinatorial growth of configuration interaction (CI) has long limited this formally exact quantum chemistry method to only the smallest molecules. Here, we report a numerically exact CI calculation exceeding one quadrillion ( $10^{15}$ ) determinants, made possible by a lossless categorical compression strategy within the small-tensor-product distributed active space (STP-DAS) framework. This approach overcomes the traditional memory bottlenecks of CI by a numerically exact compression of the wavefunction representation and reformulating the most computationally demanding matrix-vector operations. Using this method, we performed a fully relativistic CI calculation of the ground state of HBrTe with over  $10^{15}$  complex-valued determinants in just 34.5 h on 1000 computing nodes—the largest CI calculation ever reported. We further achieved fast computation for systems with hundreds of billions of determinants on only a few compute nodes. Extensive benchmarks confirm that the method retains full numerical exactness while cutting memory and computational cost by orders of magnitude. Compared to previous state-of-the-art CI calculations, this work achieves a 1000 times increase in CI space, a  $10^6$ -fold increase in floating-point operations performed, and a  $10^6$ -fold improvement in computational speed.

2:05 PM - 2:25 PM

## Information-Theoretic Appraisal of Electronic Densities

*Abdulrahman Y. Zamani\* and Kevin Carter-Fenk*  
*University of Pittsburgh, Pittsburgh, USA*

The relative performance of density functional approximations (DFAs) depends on specific design principles, such as those motivated by empirical parameterization and strong physical constraints. It is of interest to examine the fidelity of many-electron densities from a variety of DFAs with those calculated from correlated wavefunction and many-body methods. There has been a resurgence of information theory applied to spectral estimation, chemical bonding, molecular similarity, and the more general electron correlation problem in quantum chemistry. We present an information-theoretic assessment of atomic and molecular densities in the ground state and under excitation, confinement, and ensemblization. Comparison of densities obtained from single reference methods is facilitated by means of the Shannon entropy, the Kullback–Leibler information gain, and the  $J$ -divergence—all calculated over position-space. We demonstrate that the entropic distance is a key metric for appraising total densities with respect to coupled cluster and configuration interaction methods. Information spread or delocalization at the orbital level obtained from DFAs are measured against those of Brueckner and Dyson orbitals. We also examine changes in the density information content of multiple self-consistent-field solutions under various symmetry-breaking conditions. Additionally, we explore the relationship between entropic measures of electron delocalization and the accuracy of the dipole moment of CO computed with different methods. Our work offers insights into the selection of optimal reference determinants for a given chemical application and signifies potential benefits of incorporating information entropy concepts in the development of new density functionals.

2:25 PM - 2:45 PM

## Size-consistent Padé Resummed Møller-Plesset Perturbation Theory with Near-Chemical Accuracy

*Kyle Bystrom, Timothy C. Berkelbach, and Diptarka Hait\**  
*Flatiron Institute, New York City, USA; Columbia University & Flatiron Institute, New York City, USA*

Padé resummation is widely used in applied mathematics and physical sciences to obtain better approximants to functions than truncated Taylor series. Unfortunately, naive Padé resummation of many body perturbation theory is not size consistent, leading to limited use in modern quantum chemistry. We present a matrix based approach to size consistent Padé resummed Møller-Plesset perturbation theory, utilizing second and third order contributions to correlation energy. This approach provides near chemical accuracy for the standard datasets used to evaluate single-reference quantum chemical methods. In particular, it yields an RMSE of 1.5 kcal/mol for the non-multireference subset of the W4-17 thermochemistry dataset (vs 12 kcal/mol for CCSD) and other single-reference datasets widely used for assessing quantum chemical methods. Our approach thus appears to represent one of the most accurate  $O(N^6)$  scaling methods for single-reference quantum chemistry, and therefore ought to be broadly applicable in many regimes (including the development of double hybrid functionals and/or new composite methods).

**3:00 PM - 3:35 PM**

## **Nonorthogonal Real-Time Time-Dependent Wavefunction Theories**

*Lee M. Thompson\**

*University of Louisville, Louisville, USA*

There is a growing interest in the nonequilibrium processes of molecules, driven by the development of time-resolved spectroscopic tools. Many of these effects go beyond simple perturbative regimes, rendering standard stationary ab initio methods inadequate for their description. To model techniques such as photoelectron spectroscopy and pump-probe transient absorption spectroscopy, real-time time-dependent (RT-TD) methods are required. A wide range of RT-TD approaches have been proposed over the years, with the most prominent variants based on density functional theory, coupled-cluster theory, and complete active space (CAS) methods. As is well known, many systems require both static and dynamic correlation to be accurately described (e.g., transition metals and lanthanides), which has motivated the development of RT-TD-CAS-based approaches. Our group has been developing a library of nonorthogonal methods aimed at reducing the size of wave-function expansions while maintaining accurate modeling. In this presentation, we introduce a nonorthogonal multiconfigurational self-consistent field propagation scheme capable of recovering both static and dynamic correlation with a substantially smaller expansion than RT-TD-CAS owing to the adaptive internal space that can propagate into new regions of the Hilbert space as variationally required. The properties of this method will be explored using representative molecules, focusing on the breaking of orbital orthogonality, changes in the internal-space metric, and the dependence on the user's initial wave-function choice.

**3:35 PM - 4:10 PM**

## **Computational Simulations of Strong Field Ionization Using Time-Dependent Configuration Interaction with a Complex Absorbing Potential (TDCI-CAP)**

*H. Bernhard Schlegel\**

*Wayne State University, Detroit, Michigan, USA*

Attosecond spectroscopy and strong field ionization of molecules by intense laser pulses are very active fields of research because they can probe the dynamics of electrons on their natural time scale. Strong field ionization can be simulated by time-dependent configuration interaction (TD-CI). The wavefunction is written as a linear combination of time-dependent coefficients with time-independent states of the field-free Hamiltonian. A complex absorbing potential (CAP) is used to remove the outgoing electron, and the ionization rate is obtained from the decrease in the norm squared of the wavefunction. A number recent applications will be presented. TD-CI simulations of the angular dependence of strong field dissociative ionization of vinyl bromide are in good agreement with experiment. The coherent superposition of the X and A states of iodoacetylene cation results in charge migration which has been observed to decay within 10 – 20 fs. Simulations of strong field ionization and wavepacket dynamics on the excited surfaces have been used to model the detection of charge migration and its decay. Modeling excited state potential energy surfaces for wavepacket dynamics can be challenging. HCCX(+), CH<sub>3</sub>X(+), vinyl bromide cation and propiolic acid cation are used to illustrate some of the difficulties that can be encountered. Vibrational frequencies for excited cations have been calculated with CCSD, EOM-CCSD, EOMCC-IP, CASSCF and MC-PDFT.

**4:10 PM - 4:30 PM**

## **Dressed time-dependent density functional theory: Opening and closing a Pandora's box**

*Jack Taylor\* and Neepa Maitra  
Rutgers University, Newark, United States*

The popularity of time-dependent density functional theory (TDDFT) inarguably stems from its attractive trade-off between computational affordability, chemical accuracy and fundamental rigour. However, within the adiabatic approximation, which is almost always used in practice, TDDFT has been plagued by the inability to capture excited states of double-excitation character. Recent efforts have sort to address this problem by extending the original formulation of dressed TDDFT (DTDDFT), so that it reproduces not just excitation energies but also oscillator strengths of such states. Here, we provide an extensive (albeit not exhaustive) test of DTDDFT to predict the excited states of several molecules possessing either “genuine” or “partial” double-excitation character, as characterised in the recent updated work of Kossoski et al. [JCTC, 20, 5655-5678 (2024)]. We consider multiple flavours of DTDDFT to approximate the frequency-dependent exchange-correlation kernel, both with and without invoking the Tamm-Dancoff approximation. Throughout, we highlight a number of operational subtleties left to be ironed out before DTDDFT can be considered fully “black-box” in nature, some of which we provide a novel workaround for.

**4:30 PM - 4:50 PM**

## **Efficient Low-Scaling Electron Correlation Methods: BTD-MP2 and GW-SAPT for Molecular Interactions**

*Yueyang Zhang and Peifeng Su\**  
*Xiamen University, Xiamen, China*

We present recent advances in low-scaling electron correlation methods built upon the block tensor decomposition (BTD) framework. Building on our previous BTD work for Hartree–Fock exchange and SOS-MP2, we have now achieved a formal  $O(N^3)$  algorithm for full MP2 correlation energy evaluation (BTD-MP2). This is realized by integrating BTD with canonical polyadic decomposition (CPD) in a block-wise manner, overcoming the  $O(N^4)$  bottleneck of conventional THC kernel construction. The resulting method combines the dual-grid efficiency of BTD with the compact tensor format of CPD, enabling accurate MP2 calculations for large molecular systems with significantly reduced computational cost.

Furthermore, we extend the BTD formalism to develop GW-based symmetry-adapted perturbation theory, called SAPT(GW). This new method provides a rigorous many-body decomposition of intermolecular interaction energies. By leveraging the low-scaling BTD-GW engine, SAPT(GW) achieves near-cubic scaling and is applicable to large non-covalent complexes.

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*TUESDAY, JUNE 9*

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**8:30 AM - 9:05 AM**

**Highly accurate, size-extensive, divergence free energies at linear scaling cost from AFQMC**

*Sandeep Sharma\* and Yichi Zhang*

*California Institute of Technology, Pasadena; University of Colorado, Boulder*

In this talk, I will present recent developments from my group aimed at improving the auxiliary-field quantum Monte Carlo (AFQMC) method. These advances enhance its accuracy (often exceeding that of CCSD(T) even for main-group systems), ensure size extensivity, and eliminate divergences in challenging regimes such as near degeneracies arising from strong electron correlation or band-gap closure in metals at large system sizes. Furthermore, when combined with a local natural orbital approximation, the method achieves linear scaling with system size. I will illustrate these developments through applications to challenging electronic structure problems.

**9:05 AM - 9:40 AM**

## **Strong Correlation from Single Reference Perturbation Theory**

*Paul A. Johnson\**

*Université Laval, Québec, Canada*

Weakly correlated systems are well-described as individual electrons. The physical behaviour is described by a Slater determinant of occupied orbitals upon which one could add cheap approximate corrections (density functional theory) or hierarchical systematic corrections (coupled cluster theory). This is not the case for strongly correlated systems: many Slater determinants are required which makes the physical picture unclear. Multi-reference methods are in general difficult.

**9:40 AM - 10:15 AM**

## **Systematically Deriving Effective Hamiltonians with Density Matrix Downfolding**

*Elvira R. Sayfutyarova\**

*Pennsylvania State University, University Park, USA*

Effective Hamiltonians provide a convenient framework for reducing complex many-electron quantum problems to simpler models with a small number of, usually physically interpretable, parameters. That is often useful: For example, a variety of model Hamiltonians (e.g., Hubbard and Heisenberg models) are widely used to interpret physical phenomena and to connect experimental observations with the underlying interactions in strongly correlated systems. However, not all observations easily map to existing model Hamiltonians. That issue can be approached with the recently introduced Density Matrix Downfolding (DMD) method: it enables the derivation of model Hamiltonians, of arbitrary form, in a systematically improvable manner. Thereby DMD offers the opportunity to not only refine existing models, but also to construct new, accurate effective physical models which are tailored to specific systems of interest. In this talk, I will present our work on revising established model Hamiltonians and developing new ones for antiferromagnetically coupled spin centers in polynuclear transition-metal complexes using DMD. I will also discuss the use of non-eigenstates of the ab initio Hamiltonian in the downfolding procedure and demonstrate the performance of these approaches for selected chemical systems.

**10:30 AM - 11:05 AM**

## **Locality in Aufbau Suppressed Coupled Cluster and Hartree Fock**

*Harrison Tuckman, Trine Quady, Qasim Javed, Conor Bready, and Eric Neuscamman\**  
*Caltech; UC Berkeley*

Aufbau suppressed coupled cluster theory is a state-specific approach designed to tackle difficult excited state predictions, such as the energetics of charge transfer and double excitations. Although it can be highly accurate for these, the approach suffers from the same high cost scaling as ground state coupled cluster (its cost roughly mirrors that of CCSD). In this talk, we will discuss how the corresponding second order perturbation theory can be used to automatically identify which electrons are strongly affected by an excitation, at which point the coupled cluster treatment can be limited to those electrons only. The result is a method with the asymptotic scaling of MP2 but the accuracy of excited-state-specific coupled cluster.

Of course, in many applications, even the cost of the Hartree Fock calculation that precedes coupled cluster can be a problem. Thanks to local correlation methods, this is increasingly an issue for very large molecules, but it can also be a concern when a small or medium sized molecule has its energy evaluated many times, as when performing on-the-fly dynamics or training a data-driven potential energy model. This challenge in mind, we will discuss recent work that investigates an aggressively local approximation to Hartree Fock theory. Thanks to by-design cancellation of error, the approach maintains the parent method's energetics (e.g., producing MP2 reaction energies within 1 kcal/mol of standard MP2) while achieving an early cost crossover relative to resolution-of-the-identity Hartree Fock.

*11:05 AM - 11:40 AM*

## **Recent Advances in the CC(P;Q) Methodology: CIPSI-Driven and Adaptive Approaches**

*Piotr Piecuch\*, Karthik Gururangan, Swati S. Priyadarsini, and Jun Shen  
Michigan State University, East Lansing, Michigan, USA*

It is well established that the exponential wave function ansatz of coupled-cluster (CC) theory and its extensions to excited, open-shell, and multireference states are among the most efficient ways of incorporating many-electron correlation effects in molecular applications. In this talk, we will focus on novel ways of obtaining accurate energetics equivalent to high-level CC and equation-of-motion (EOM) CC calculations, such as CCSDT, CCSDTQ, and EOMCCSDT, at small fractions of the computational costs, even when electronic quasi-degeneracies become large and higher-than-two-body components of the cluster and excitation operators become nonperturbative, which result from the moment expansions defining the CC(P;Q) formalism. For this formalism to be most effective, an efficient method must be developed to identify the leading higher-than-doubly excited determinants for inclusion in the subspace of the many-electron Hilbert space used in the iterative steps of the CC(P;Q) algorithm. This can be done with the help of active orbitals, configuration interaction (CI) and CC Quantum Monte Carlo approaches, selected CI schemes, such as CIPSI, and the adaptive, self-improving, CC(P;Q) framework. In this presentation, we will discuss our most recent progress in the CC(P;Q) methodology, especially in the CIPSI-driven and adaptive CC(P;Q) algorithms and their excited-state extensions. The usefulness of the CIPSI-driven and adaptive CC(P;Q) approaches will be illustrated by chemical bond dissociations and reaction pathways, singlet-triplet gaps in biradicals, and excited states including one- as well as many-electron transitions. Information about the CC(P;Q) methods in our open-source CCpy package on GitHub will be provided as well.

**2:45 PM - 3:20 PM**

## **Dualities for Taming Strong Electron Correlation**

*Gustavo E. Scuseria\**

*Rice University, Houston, Texas, USA*

Dualities establish exact equivalences between different formulations of the same problem. For example, the Jordan-Wigner (JW) transformation connects spinless fermions with spin  $\frac{1}{2}$  qubits. Hamiltonians written in these different representations have identical spectra, but approximations differ: simple uncorrelated wave functions in one representation can become sophisticated correlated ansatzes in the other [1]. Indeed, we have recently proven that the Hartree-Fock state obtained for the JW-mapped  $su(2)$  seniority-conserving part of the electronic Hamiltonian is equivalent to variational pair-CCD in the physical representation [2]. Working in the dual frame is not exempt from challenges: JW strings must be generalized to restore permutational invariance in Hartree-Fock, and allowing  $S_z$  symmetry to break before mapping yields fermionic Hamiltonians that break number-parity, requiring special Bogoliubov transformations and attention to overlaps. In this talk, I will present the conceptual framework behind these ideas and proof-of-principle applications to strongly correlated spin and electronic systems.

References:

[1] Strong-weak duality via Jordan-Wigner transformation: using fermionic methods for strongly correlated  $su(2)$  spin systems, T. M. Henderson, G. P. Chen, and G. E. Scuseria, *J. Chem. Phys.* 157, 194114 (2022).

[2] Jordan-Wigner Transformation for the Description of Strong Correlation in Fermionic Systems, T. M. Henderson, G. P. Chen, and G. E. Scuseria, *J. Chem. Theory Comput.* 22, 2324 (2026).

**3:20 PM - 3:55 PM**

## **Stochastic tensor contraction for quantum chemistry**

*Jiace Sun\* and Garnet K. Chan  
California Institute of Technology*

Many computational methods in ab initio quantum chemistry are formulated in terms of high-order tensor contractions, whose cost determines the size of system that can be studied. We introduce stochastic tensor contraction to perform such operations with greatly reduced cost, and present its application to the gold-standard quantum chemistry method, coupled cluster theory with up to perturbative triples. For total energy errors more stringent than chemical accuracy, we reduce the computational scaling to that of mean-field theory, while starting to approach the mean-field absolute cost, thereby challenging the existing cost-to-accuracy landscape. Benchmarks against state-of-the-art local correlation approximations further show that we achieve an order-of-magnitude improvement in both total computation time and error, with significantly reduced sensitivity to system dimensionality and electron delocalization. We conclude that stochastic tensor contraction is a powerful computational primitive to accelerate a wide range of quantum chemistry.

3:55 PM - 4:30 PM

## Localized Active Space Modeling of Multimetallic Molecules With Dense Quasidegenerate Electronic Spectra

*Matthew R Hermes\*, Laura Gagliardi, Yi Deng, and Valay Agarawal  
University of Chicago, Chicago IL, USA*

Multimetallic molecules often have electronic wave functions which are challenging to model theoretically because each metal atom typically has an open shell of d or f atomic orbitals, resulting in large numbers of nearly degenerate electronic states. Even multireference methods such as DMRG or CASSCF, which in principle can model these states accurately, do not escape the consequences: many quasidegenerate electronic states corresponds to many nearby local minima in variational energy functions, promoting ubiquitous “orbital rotation” and related active-space difficulties. We have found that the localized active space (LAS) approach to modeling multireference wave functions furnishes a powerful tool for overcoming these difficulties. In LAS calculations, each atom with an open frontier orbital shell is assigned an active space consisting of its own d orbitals and some hybridized ligand orbitals, and each fragment can be assigned a particular unambiguous local charge and spin quantum number. Orbitals and wave functions thus characterized can be robustly optimized with less risk than conventional CASSCF or DMRG of “hopping” to adjacent “local minima”. We show how this technique is used to systematically explore the wave function space of a series of aluminum-substituted metal oxides, leading to unambiguous assignment of the ground state structure and successful theoretical reproduction of the heretofore uncharacterized experimentally determined IRPD spectra. We also show how LAS calculations with GPU acceleration provide a platform for unprecedented multi-state multireference electronic structure modeling of the famous  $[4\text{Fe-4S}]^{2-}$  iron-sulfur cluster, showing for the first time discernable spin-manifold structure in its low-energy electronic spectra.

**4:30 PM - 5:05 PM**

## **Quantum Embedding for Coupled-Cluster Band Structures and Metal-Surface Adsorption**

*Tianyu Zhu\**

*Yale University, New Haven, USA*

Accurate many-body predictions for extended systems remain challenging because they require a balanced treatment of local and nonlocal electron correlation in the thermodynamic limit. In this talk, I will present two ab initio quantum embedding frameworks that address these challenges in complementary settings. First, I will introduce a Green's function embedding approach, interacting-bath dynamical embedding theory, for equation-of-motion coupled-cluster (EOM-CC) calculations of band structures in solids. This framework enables substantially denser k-point sampling than previous studies and controlled convergence toward the thermodynamic limit, providing a practical route to benchmark band gaps or bandwidths in semiconductors, insulators, and simple metals at the EOM-CCSD level. Second, I will present a density-matrix-based embedding framework for molecular adsorption on metallic surfaces, designed to make coupled-cluster calculations feasible for molecule-metal interfaces with fractional occupancies. I will show how this approach accelerates convergence toward the full-system limit and opens the door to systematically improvable studies of adsorption energetics at neutral and charged metal surfaces. Together, these developments illustrate how quantum embedding extends high-level electronic structure theory to challenging problems in materials science and catalysis.

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**WEDNESDAY, JUNE 9**

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**9:00 AM - 9:35 AM**

## **Where (Time-Dependent) Wave Functions meet Kohn Sham Theory**

*Paul Zimmerman\**

*University of Michigan, Ann Arbor, MI*

Wave function theory (WFT) and density functional theory (DFT) have held their places as key electronic structure strategies due to their respective traits of systematic improvability (WFT) and low cost-to-accuracy ratios (DFT). It is highly plausible that a better understanding of the relationships between WFT and DFT could lead to important new concepts that benefit both areas. In this talk, we will outline our procedure—which can make use of Gaussian or Slater atomic orbital basis sets—to translate full configuration interaction wave functions into Kohn- Sham (KS) potentials and exchange-correlation energies. In particular, we will discuss an accelerated method that makes computation of Exc more routine, with the possibility of generating benchmark sets of this quantity alongside accurate KS densities. This talk will also cover inversion of time-dependent KS states, using input from TD-CI wave functions. Features that are nonlocal in space and time will emerge, showing the challenges that need to be overcome in order to describe memory effects in nonadiabatic KS functionals.

9:35 AM - 10:10 AM

## Advancing linear-scaling energies, parallel forces, and protein embedding for CCSD(T)-level machine-learning dynamics and biochemistry

Peter Nagy\*

*Budapest University Of Technology And Economics, Budapest, Hungary*

Our linear-scaling local natural orbital (LNO) CCSD(T) method provide state-of-the-art accuracy-over-cost performance, as reviewed recently[1]. Current LNO developments in the MRCC package include optimized closed- and open-shell MP2, CCSD(T), and general-order LNO-CC as well as density and floating orbital based CBS convergence acceleration.[1] Systematic convergence and error estimates of LNO-CCSD(T)/CBS are broadly affordable for a few 100 atoms and uniquely scale up to 1000-atom proteins.

Thus, we can now use rigorous LNO-CCSD(T)/CBS for unprecedented biochemical and pharma applications. We reported the first CCSD(T)/CBS-level interaction energy datasets for binding of the most common cations and real-life drug molecules to (model and then) full-sized protein pockets (up to 300 atoms)[2]. For enzyme catalysis, we developed a practical multi-layer approach: LNO-CCSD(T)/MM energy corrections to locality accelerated, hybrid DFT-in-GGA/MM Huzinaga (projector) embedding based dynamics.[3] The latter enables hybrid DFT/MM quality forces for 200+ QM atoms in complicated enzymes, with a speed suitable for enhanced sampling and reactive FES computations. Extending LNO-CCSD(T) for molecular crystals provided experiment-quality polymorph free energies for so far inaccessible-sized and DFT error-prone pharmaceuticals[4].

We extended our highly-optimized and MPI/OpenMP parallel CCSD(T) algorithms to analytical forces[4], achieving ~10x speedup over the next best implementation and surpassing 1000 orbitals for the first time. This enabled 1000s of CCSD(T)/CBS force computations, hence CCSD(T)-MLFF development for molecules of 20-30 atoms, i.e., ~1.5-2x larger than possible before.

[1] Chemical Science 15, 14556(2024), MRCC package [www.mrcc.hu](http://www.mrcc.hu)

[2] Nature Communications 16, 8583(2025), Science Advances 12, eadz8521(2026)

[3] JCTC: 21, 9573(2025) & 22, 3415(2026)

[4] JPCA 129, 2086(2025)

**10:10 AM - 10:45 AM**

## **Recent Advances in Brillouin-Wigner Perturbation Theory: Practical New Tools for Describing Electron Correlation**

*Martin Head-Gordon\**

*University of California, Berkeley, USA*

Rayleigh-Schrodinger perturbation theory with the Moller-Plesset (MP) partitioning has been tremendously useful in quantum chemistry, especially at low order as MP2 theory. However, while MP theory is size-consistent, it fails to be regular, which makes it poor for systems with small gaps or strong correlations. Brillouin-Wigner PT is an alternative that is regular but is seldom used because it fails to be size-consistent with MP partitioning. I will discuss the size-consistent formulation of BW-PT, which uses non-MP partitioning to achieve the best properties of both MP-PT and BW-PT. Based on formal properties and numerical results, at second order, BWs2 is a strong candidate to replace MP2 theory in both wavefunction theory and double hybrid DFT. At third order, replacement of MP3 and comparison with CCD is the focus.

# Posters

# 1. Towards an Atomistic Understanding of Quantum Dot Optical Properties: Predicting Urbach Tails and Exciton-Phonon Coupling

*Alexandra Alexiu\**, *Carina Luo*, and *Prof. Troy Van Voorhis*  
*Massachusetts Institute of Technology*

Explicit treatments of exciton-phonon coupling (EPC) and ensemble averaging are often neglected in the computational studies of realistic nanocrystals. Here, we present a simple harmonic approximation framework for predicting temperature-dependent UV-Vis absorption spectra of II-VI quantum dots (QDs) from first principles, at a fraction of the computational cost of the conventional nuclear ensemble approach. Two variants are introduced: the equilibrium harmonic approximation, which captures homogeneous broadening, and the averaged variant, which additionally accounts for configurational sampling and band gap renormalization. Application to II-VI QD model systems demonstrates nearly quantitative agreement with experiment, additionally revealing that the Urbach tail originates predominantly from surface-to-bulk excitations associated with hole trap states.

Building on this foundation, we compute Huang-Rhys factors across the excited state manifold, as a measure of EPC. Using the vertical gradient approximation, we find that dark, surface-localized trap states couple strongly to key acoustic and surface optical vibrational modes. Therefore, effective passivation schemes should not only reduce the number of trap states, but also their spatial overlap with phonons.

Collectively, these results establish that accurate prediction of QD optical properties requires an *ab initio* treatment of the electronic structure, alongside explicit thermal and ensemble effects. By resolving individual exciton-phonon couplings, we establish a comprehensive toolkit for the atomistic analysis of trap states, allowing for the rapid screening of passivation strategies.

## **2. Efficient simulation of optical spectra via machine learning and physical decomposition of environmental effects**

*Andrew Snider\*, Michael S. Chen, and Thomas E. Markland  
University of California Merced; New York University; Stanford University*

Simulations of optical spectra can provide key insights to aid experimental interpretation of electronic excitation phenomena. For chromophores in the condensed phase, these spectra, which incorporate the coupling between electronic excitation and molecular and solvent nuclear motions, can be simulated using excitation energies obtained from molecular dynamics simulations of the chromophore and solvent. Here, we present a hybrid scheme that exploits machine learning and physically informed spectral densities to show that as few as 25 ground and excited state energetic gradient calculations can be used to construct models that accurately predict environment-influenced vibronic coupling in optical spectra. We demonstrate our approach for the green fluorescent protein chromophore in water and the cresyl violet chromophore in methanol. We show that our hybrid approach, employing a machine learning model for the high-frequency spectral density and an ab initio parameterized Debye spectral density for the low-frequency, results in a systematic improvement of the optical absorption lineshape, leading to a simple machine learning scheme that can be used for the simulation of spectral densities and optical spectra.

### **3. Time-dependent Kohn-Sham potential for quantum electrodynamical density functional theory: Insights from exact factorization**

*Anna Baranova\* and Neepa T. Maitra*  
*Rutgers University - Newark*

Quantum electrodynamical density functional theory (QEDFT) is a promising ab initio method for solving large and complex problems of polaritonic chemistry, where properties of matter in optical confinement are modified due to strong light-matter coupling. Recent developments in ground-state and linear-response QEDFT already provide an accurate description of various cavity-induced phenomena (e.g., polaritonic Rabi splitting, photon-mediated long-range interactions, and many-body dispersion). However, few approximations exist for the dynamics of systems driven to excited states, in particular, lower and upper polaritons - central in polaritonic chemistry. The choice of photon-electron exchange-correlation potential for QED time-dependent Kohn-Sham (KS) equations is limited to ground-state and mean-field approximations. In this work, we explore the features of the time-dependent light-matter correlation potential using the exact factorization (XF) approach. We analyze the properties of the exact KS potential for a simple single-electron system coupled to a cavity mode, and derive an approximation for the time-dependent light-matter correlation from XF.

## 4. Inversions of Thermal Systems in Density Functional Theory

*Anthony Osborne\* and Aurora Pribram-Jones*  
*University of California, Merced*

Warm dense matter is an important area of study for many fields, from astrophysics to clean energy, one that has been supported by density functional theory--based computations for experimental design, interpretation of results, and theoretical investigations. Density-to-potential inversions can be used to obtain the exact Kohn-sham potential, from which we can extract the exact exchange-correlation potential. Inversions of finite-temperature densities can expose the temperature dependence of the exchange-correlation potential, which can inform construction and analysis of finite-temperature exchange-correlation approximations. In this work, I will present results from inverting finite-temperature densities for model systems using the thermal analogue to the Wang-Parr inversion method to show the temperature dependence of the exchange-correlation potential. Additionally, I will present results showing the influence of the local density approximation on the zero-temperature approximation, in which one uses a zero-temperature exchange-correlation approximation in a finite-temperature calculation.

## **5. Axial Solvent Control of the Ultrafast Dynamic Stokes Shift Decay and the Spectral Broadening in Two-Dimensional Electronic Spectroscopy and Transient Absorption**

*Arthur Pyuskulyan\**, Christopher Myers, Shao-Yu Lu, Sapana Shedge, Liang Shi, and Christine Isborn  
*University of California, Merced*

The dynamic Stokes shift captures time-dependent changes in electronic energy gaps arising from solvent reorganization and vibrational relaxation, providing insight into solvation and excited-state dynamics. Fitting the dynamic Stokes shift enables the prediction of both ultrafast and slow relaxation times. We model the dynamic Stokes shift directly from the energy gap correlation function and also follow an experimental approach that extracts the dynamic Stokes shift stimulated emission from projecting the Two-dimensional Electronic Spectrum (2DES). We use cresyl violet as our model chromophore in explicit methanol solvent and demonstrate that the closest axial solvent molecules directly above and below the plane of the chromophore are responsible for the majority of the ultrafast dynamic Stokes shift decay and for the broadening in the 2DES and transient absorption.

## 6. Projected Hartree Fock as a Compact Trial for Phaseless Auxiliary-Field Quantum Monte Carlo

*Brad Ganoë\*, Don Danilov, and James Shee  
Rice University*

Phaseless Auxiliary-Field Quantum Monte Carlo (ph-AFQMC) has gained traction as a general tool for the description of correlated electronic systems. While some clarity has emerged around the pragmatic and sufficient qualities that make for excellent trial wavefunctions in weakly correlated regimes, the requisite features in the context of strongly correlated systems (especially among polynomial-scaling wavefunctions) has remained nebulous. One fruitful avenue of exploration has been in introducing and managing spin contaminants via the breaking and restoration of constants of motion, with prior studies pursuing both spin symmetry restrictions on walkers in the ph-AFQMC machinery and by explicit introduction of spin-projected trial wavefunctions, especially in the context of model Hamiltonians. We here investigate the use of polynomial-scaling Projected Hartree Fock (PHF) trial wavefunctions, with a focus on a test set of small strongly correlated molecular systems. Through this evaluation, we aim to establish the efficacy of PHF trials in reducing errors in the strongly correlated limit. We report the ph-AFQMC-PHF energy results against various ground-state energy methods relative to their error from Full Configuration Interaction. In elaborating the work, we further comment on hierarchies of spin contamination/restoration and what this may imply about the symmetry features which construct ideal ph-AFQMC trials.

## 7. Thermalized LDA Correction to Zero-Temperature Exchange-Correlation Energy

*Brianna Aguilar-Solis\*, Brittany P. Harding, and Aurora Pribram-Jones  
University of California Merced*

Developing accurate thermalized exchange-correlation free energy functionals is essential for studying systems under extreme temperatures and pressures, such as warm dense matter. Common approximations, like the zero-temperature approximation, incorporate implicit temperature dependence via Fermi-weighted densities. As such, this neglects explicit temperature dependence and exchange-correlation entropy contributions to the overall exchange-correlation free energy. This work introduces a local density approximation-like correction for the exchange-correlation entropy, that is applied in a similar way to the zero-temperature approximation. Results using this method and comparisons with the zero-temperature approximation will be presented.

## 8. Extracting Exchange-Correlation Behavior Using Physics-Informed Neural Operator Inversion Tools

*Bridget Sprecher\*, Vincent Martinetto, Karan Shah, Mani Lokamani, Attila Cangi, and Aurora Pribram-Jones*

*University of California, Merced; Center for Advanced Systems Understanding*

A vital component to managing the energy crisis is the development of photovoltaics, technologies which are driven by electron behavior. These behaviors can be modeled with computational simulation methods, the most widely used method being density functional theory (DFT). Unfortunately, current implementations of time-dependent DFT used to simulate the excited states of light harnessing processes cannot fully describe the double excitations, charge transfer, or temperature effects common in these technologies, necessitating further development of ensemble and thermal variants of DFT. Careful approximation of the electron-electron interaction is central to these improvements. Inversions in Kohn-Sham (KS) DFT, which take a density and return the exchange-correlation potential, can be used as a method of analysis and improvement. Additionally, continued advancements in machine-learning techniques like the use of neural operators, function-to-function mappings on infinite-dimensional function spaces, are also opening new pathways to these approximations. This work has begun by constructing a library of ground-state molecular system training data for building the first real-space physics-informed neural operator (PINO)-based density-to-potential inverter. The PINO has been applied to model test systems of the one-dimensional hydrogen molecule, establishing familiarity with the machine-learning architecture and a hyperparameter optimization framework. Initial steps toward the ultimate goal of expanding the application of the PINO inversion method to ensemble density functional theory are underway and will be discussed.

## 9. A compact spin-adapted basis for state-specific electronic structure using $\Delta$ CSF

*Cameron Brown\* and Hugh G. A. Burton*  
*University College London*

Current excited state methods based on linear response theory or state averaging struggle to accurately simulate excited states with significant orbital rearrangements. Alternatively, state-specific methods predict excited states as higher-lying stationary points on the electronic energy landscape. By incorporating bespoke orbital relaxation, state-specific methods can provide a balanced description of excited states and yield improved energies for challenging excitations.<sup>(1)</sup> However, the success of state-specific methods depends critically on the choice of approximate wavefunctions. Unrestricted mean-field methods provide low computational scaling but break spin symmetry for open-shell states, while multiconfigurational methods have redundancies that lead to an over-abundance of stationary points on the energy landscape.<sup>(2)</sup> These difficulties create practical challenges in the interpretation of stationary points and the selection of relevant excited state solutions. Here we investigate the energy landscape of configuration state functions (CSFs) as compact, spin-adapted mean-field approximations for excited states. Importantly, CSFs preserve spin purity for open-shell systems while avoiding the redundancy present in multiconfigurational approaches. We examine the properties of  $\Delta$ CSF solutions and assess their suitability as a basis for nonorthogonal configuration interaction (NOCI). We demonstrate this approach for the excited-state potential energy surfaces of formaldehyde C-O bond breaking and the torsion of ethylene. We find that  $\Delta$ CSF successfully avoids redundancy issues and yields qualitative excitation energies after CSF-NOCI. This highlights  $\Delta$ CSF as a source of physically interpretable basis functions for correlated excited state methods. As with other state-specific methods,<sup>(3)</sup> the coalescence of solutions remains a challenge, emphasising the need for further methodological development.

[1] Hait, D.; Head-Gordon M. Orbital Optimized Density Functional Theory for Electronic Excited States. *J. Phys. Chem. Lett.* 2021, 12, 4517–4529

[2] Marie A.; Burton H. G. A. Excited States, Symmetry Breaking, and Unphysical Solutions in State-Specific CASSCF Theory. *J. Phys. Chem. A* 2023, 127, 4538–4552

[3] Saade S.; Burton H. G. A. Excited State-Specific CASSCF Theory for the Torsion of Ethylene. *J. Chem. Theory Comput.* 2024, 20, 5105–5114

## 10. Transition Partial Atomic Charges: A Comparison of ESP-based and Population Analysis Methods

*Carolynn Mendoza\*, Sayan Adhikari, and Christine Isborn  
University of California, Merced*

Although they are a popular concept in chemistry, partial atomic charges are not a molecular observable. As such, there exist numerous classes of methods for assigning them, often based on different molecular properties. Some methods fit charges to the electrostatic potential (ESP) generated by the electron density, whereas others are based directly on a decomposition of the electron density. Similar to state specific charges, transition partial atomic charges decompose the change in electron density upon electronic excitation into atomic contributions. Transition charges can be used to understand transition properties and to compute Coulombic couplings between molecules, which are the main contributor to the excitonic couplings that contribute to the optical and energy transfer properties of multi-chromophore systems. This excitonic coupling between chromophores often occurs in a solvent, polymer, or biological environment, but is generally only roughly accounted for at the level of the dielectric constant scaling the coupling. Instead, the modeling of couplings in an explicit environment, e.g. in solvent, may be improved by treating a shell of solvent molecules at the QM level, to the effect of accounting for not only electrostatic but also electronic solvent-chromophore interactions. At large interchromophore separations, excitonic couplings may be approximated based solely on their long-range electrostatic contributions, and therefore by Coulombic couplings from transition charges. To assess their utility in computing couplings, here we compare various ESP-based population analysis approaches to assigning transition charges. Calculations shown here are for the BODIPY (neutral) and Cresyl Violet (+1) systems.

## 11. Delta-SCF for Charge Transfer Excitations

*Cristian Sarabia\*, Andrew Bovill, and Hrant Hratchian  
University of California, Merced*

Computational modeling of electronic excited states is essential for understanding photophysical transitions and photochemical phenomena in dyes, photocatalysts, and optoelectronics. Delta-SCF has recently shown promise as an alternative method for studying excited state geometries and frequencies using maximum overlap methods such as PIMOM. Results for charge transfer (CT) excited states comparing delta-SCF to TD-DFT with different CT character will be discussed. CT distance metrics, difference densities, energies, and oscillator strengths are used to assess LMCT, LLCT, and MLCT on ruthenium, copper, and zirconium complexes, respectively.

## **12. Simulating Non-adiabatic Molecular Dynamics in the Strong Light-Matter Coupling Regime: Excited State Proton Transfer**

*Darwin Martínez\*, Sourav Majumdar, Christopher Myers, and Christine Isborn  
University of California, Merced*

The interplay between strong excitonic light-matter coupling and excited state dynamics provides a promising route to control chemical reactivity. Here, we present our implementation of polaritonic nonadiabatic dynamics and results for simulating nonadiabatic molecular dynamics under strong light matter coupling, focusing on excited state proton transfer in malonaldehyde and aminopropenal. Light matter interactions are described using a Jaynes Cummings Hamiltonian formulated in the adiabatic electronic basis, where electronic energies, transition moments, and nuclear forces are evaluated on-the-fly along ensemble trajectories. The nonadiabatic dynamics are treated using the linearized semiclassical initial value representation (LSC-IVR), enabling a phase-space description of coupled electron-nuclear motion trajectory.

Within this formulation, coupling to a quantized cavity mode gives rise to polaritonic states whose character evolves dynamically with nuclear motion. By analyzing population transfer, we characterize how light matter coupling reshapes reaction pathways and redistributes photonic and electronic character of individual states along the trajectory. This trajectory resolved perspective provides an atomistic understanding of polariton modified chemical reactivity at the single molecule level and establishes a direct connection between nonadiabatic dynamics and polaritonic chemistry frameworks.

### **13. Analyzing Band Gaps in Ensemble Density Functional Theory using Thermodynamic Limits of Finite One-Dimensional Model Systems**

*Gregory G. V. Kenning, Remi J. Leano, and David A. Strubbe\**  
*University of Pittsburgh; University of California, Merced*

Ensemble Density Functional Theory (EDFT) is a promising extension to Density Functional Theory (DFT) for calculating excited states. While Kohn-Sham eigenvalue differences underestimate gaps, EDFT has been shown to provide more accurate excitation energies in atoms, molecules and isolated model systems. However, it is unclear whether EDFT is capable of calculating band gaps of periodic systems – and what an appropriate theoretical formulation would be to describe periodic systems. We explored how EDFT could calculate band gaps by estimating the thermodynamic limit with increasingly wide finite versions of the one-dimensional Kronig-Penney (KP) periodic model. We use Octopus, an ab initio, open-source, real-space DFT code, as in our previous work [R. J. Leano et al., *Electron. Struct.* 6, 035003 (2024)] in which we found with “particle in a box” models that EDFT can provide a reasonable effective mass correction for the homogeneous electron gas. Now, we use a periodic reference that is gapped. We find that the finite systems’ Kohn-Sham gap approaches the same periodic limit for each of three ways of terminating the finite system, though the appropriate states corresponding to the valence band maximum and conduction band minimum have to be carefully identified in each case. Finally, our EDFT results, using a simple ensembled LDA approximation, have a reasonable nonzero correction to the bandgap in the periodic limit. The results indicate that EDFT is promising for periodic systems, to motivate further work on developing a suitable formalism.

## 14. Noncovalent Interaction Energies with Phaseless Auxiliary-Field Quantum Monte Carlo

*Devesh Awasthi\* and James Shee  
Rice University*

Noncovalent interactions are ubiquitous in chemistry and play key roles in drug-protein interactions, secondary-sphere effects in catalysis, molecular crystals, the structure of biomolecules, and the properties of liquids. However, their description with approximate electronic structure models remains a long-standing challenge due to many-body correlation effects, relatively small energy scales, and potentially large system sizes. In this work, we assess phaseless auxiliary-field quantum Monte Carlo (ph-AFQMC) with restricted Hartree-Fock trial wave functions for representative noncovalent interaction test sets, including S66, A24, S22, and X31. Against CCSD(T) reference values, we find that ph-AFQMC gives accuracy consistently better than CCSD and sometimes dramatically better than MP2. Using the water dimer, with available CCSDTQ reference energies, we demonstrate that noncovalent interaction energies calculated with ph-AFQMC-RHF benefit significantly from error cancellation. We further show how a branching correlated sampling scheme can reduce the computational cost of noncovalent interaction energy calculations, paving the way for more tractable ph-AFQMC studies of larger molecules. The talk will also discuss ongoing correlated sampling developments and the canonical transcorrelated (CT) Hamiltonian within the ph-AFQMC framework, implemented in collaboration with Prof. Ed Valeev's group at Virginia Tech, as a route to accelerate convergence toward the complete-basis-set limit at reduced computational cost. Preliminary results on the A24 noncovalent interaction set indicate that CT-AFQMC in a double- $\zeta$  basis can improve upon standard ph-AFQMC in a triple- $\zeta$  basis, while comparisons with larger conventional basis sets and CT-AFQMC in a triple- $\zeta$  basis are under investigation.

## 15. Single Bond Dissociation using Aufbau Suppressed Couple Cluster Theory

*Dylan Fowler\* and Eric Neuscamman*  
*University of California, Berkeley*

Coupled cluster (CC) theory is a highly accurate method for describing weak correlation in electronic structure calculations. However, describing strong correlation using CC has proven challenging. Aufbau suppressed coupled cluster (ASCC) theory is a recently developed method that has proven effective at describing electronically excited state, including those with small contributions from the ground state wave function. We present another application of ASCC, where the multireference character present in a single bond dissociation is described using the de-exciting similarity transformation characteristic of ASCC. This approach preserves many of the important formal properties of CC theory, such as size-extensivity and systematic improvability, while also maintaining the same time complexity. ASCC also preserves spin-symmetry throughout the potential energy surface (PES) of a single bond dissociation, whereas typical CC approaches for bond dissociation do not. In this work, we compare the performance of ASCC in describing single bond dissociations on a test set of small organic molecules to that of commonly-used electronic structure methods including unrestricted CC (UCC), the complete active space self-consistent field method (CASSCF), and complete active space perturbation theory (CASPT).

## 16. Computation of Temperature-Dependent Spectra Using Tensor Network States

*Gino E. Gamboni\* and Henrik R. Larsson*  
*University of California, Merced*

Infrared and UV/VIS spectra of complex molecules such as protonated water clusters and pyrazine have been simulated and studied extensively at the zero temperature limit. It is less understood how observables for such molecules change as they are modulated to finite temperatures. In this work, we simulate such spectra at different temperatures. Our work combines the thermofield formalism, which introduces temperature dependence in a wavefunction through an extended fictitious Hilbert space, and tree tensor networks states (TTNS) together with algorithms based on the density matrix renormalization group (DMRG). This leads to numerically efficient and stable simulations, even for molecules with large vibronic couplings. We showcase this thermofield TTNS-DMRG formalism through temperature-dependent simulations of various systems, including the UV/VIS photoabsorption spectrum of pyrazine and the IR spectrum of the Zundel ion. This formalism opens the door to direct comparisons with experimental spectra and understanding underlying quantum effects at finite temperatures.

## 17. Ground-State Mapping and Electronic Properties of Sulfamethoxazole

*Hannah Blackmon\* and Kristina Closser  
California State University*

Sulfamethoxazole (SMX) is a widely used sulfonamide antibiotic and persistent aquatic contaminant whose photochemical behavior governs its environmental fate. Despite extensive detection in surface waters, the relationship between SMX's conformational landscape and its excited-state behavior remains unclear. This project employs density functional theory and time-dependent density functional theory to investigate the ground- and excited-state properties of SMX in aqueous conditions. Potential energy surface scans around core sulfonamide dihedrals identified one global minimum and three local minima, with consistent energetic ordering across different functionals. Excited-state calculations at the CAM-B3LYP-D3(BJ)/def2-TZVPD level revealed that the dominant low-energy and high-intensity electronic transitions are  $\pi \rightarrow \pi^*$  excitations localized to the aniline ring, which are consistent among conformers. Relative to experimental data, the computed UV-visible absorption spectra exhibit a modest blue shift, consistent with established time-dependent density functional theory tendencies. Solvent effects modeled via the polarizable continuum model indicate that excitation energies and oscillator strengths are largely insensitive to cavity parameters. Excited-state relaxation leads to S1 and S2 state reordering and partial charge-transfer character toward the isoxazole ring, indicating a shift in electronic structure along the relaxation pathway. Natural transition orbital analysis further supports the evolving localization and character of key excitations. While conformational differences have a minimal effect on vertical absorption, the initial geometry appears to have a significant impact on the relaxation pathways. These results provide a molecular-level understanding of SMX photodegradation by linking conformational flexibility to electronic structure and optical properties.

## 18. Improving Optical Properties of III-V Quantum Dots

*Hannah Liu\*, Alexandra Alexiu, and Troy Van Voorhis  
Massachusetts Institute of Technology*

Quantum dots' size-tunable sharp emission makes them valuable for a variety of applications such as lasers and bioimaging. However, the current best performing QDs often contain toxic chemicals and cannot be used in biological applications. On the other hand, III-V QDs have low toxicity, but their emission properties are greatly hindered by defects. As a result, identifying and passivating trap states is crucial for improving their emission properties and widening their applications. In this work, we present results on a variety of III-V QDs with different compositions and geometries. We find that the tetrahedral III-V QDs at equilibrium (0 K) have sharper absorption than their spherical counterparts due to weaker exciton-phonon coupling, suggesting that they are more trap-free. Furthermore, we include finite temperature effects via *ab initio* molecular dynamics (AIMD) simulations to better match our theoretical predictions with experimental results. The GaP QDs are relatively stable in AIMD when passivated with fluoride ligands, while the InP QDs require passivation by heavier halide ligands such as chlorides to help maintain thermal stability. State analysis indicates that tetrahedral structures exhibit weaker exciton-phonon coupling, especially for the GaP QDs, leading to brighter and narrower spectrum. We hope that our results can help experimental synthesis of III-V QDs with improved optical properties.

## 19. Factorized Electron Nuclear Dynamics: Theory Development and Implementation

*Julian Stetzler\*, Sophya Garashchuk, and Vitaly Rassolov  
University of California, Merced; University of South Carolina*

Conventional theoretical and computational approaches to fully coupled quantum molecular dynamics, i.e. when both the electrons and nuclei are treated as quantum-mechanical particles, are impractical for all but the smallest chemical systems. The Factorized Electron Nuclear Dynamics (FENDy) with effective complex potential [*J. Chem. Theory Comput.* **19** (2023), 1393-1408] was developed to provide a scalable theoretical and computational approach to such problems. This method is based on the exact factorization of the molecular wavefunction, with the nuclei evolving under a complex time-dependent potential which captures the key features of dynamics in the nuclear subspace. The imaginary part of the potential ensures that the electronic component satisfies the partial normalization condition. The electronic wavefunction is represented within the standard electronic structure basis sets, but without referencing the electronic eigenstates. The nuclear wavefunction is represented as a quantum-trajectory ensemble, which in principle circumvents the exponential scaling of the numerical cost with the system size. The FENDy formalism is implemented and used to model the photodissociation of  $\text{H}_2^+$  beyond the established framework of the Born-Oppenheimer approximation or Born-Huang expansion of the molecular wavefunction using the standard basis sets of electronic structure. We also observe that the wavefunction propagation becomes unstable when the nuclear wavefunction begins to bifurcate and identify step-like features in the basis function ‘populations’ as the source of the problem. We also note that our current analysis is limited to just a few electronic basis functions, which is far from the intended regime of electronic-nuclear wavepackets.

## 20. Kohn-Sham Hamiltonian Mapping with Machine Learning for Nonadiabatic Molecular Dynamics

*Mohammad Shakiba\* and Alexey Akimov*

*University of California, Merced; University at Buffalo*

In this poster, I will show a conceptually simpler yet novel and general ML strategy from our group for constructing the Kohn-Sham (KS) Hamiltonian matrix at a desired level of theory. We observed that the KS Hamiltonian from a converged charge density maps smoothly from a simple non-self-consistent atomic density guess. Using this, we map an initial guess KS Hamiltonian from one theory level, such as PBE, to a converged KS Hamiltonian at another level, like B3LYP or HSE06. This approach requires fewer training data points, accelerates calculations with high accuracy, and is scalable and applicable to various nanoscale materials. I will also demonstrate how atomic orbital matrices, even when obtained at a low level of theory, can be used as feature vectors, bypassing the need for neural network for feature extraction. Additionally, I will show our implementation of a user-friendly interface in Libra, making this method accessible and practical for a wide range of users. Finally, I will demonstrate how this model, when applied to NA-MD simulations of hot-carrier relaxation dynamics, produces timescales within the error margins of conventional methods.

## 21. Rank-Reduced Equation-of-Motion Coupled Cluster Methods – Affordable Electronic Excitation Energies With Controllable Errors

*Piotr Michalak\* and Michał Lesiuk*  
*University of Warsaw*

An accurate determination of electronic excitation energies is crucial for the description of photochemical phenomena, yet it still poses a challenge for larger systems, especially if the target state has significant doubly-excited character. The source of this challenge is mainly connected with the high computational scaling of accurate methods, such as equation-of-motion coupled cluster family (EOM-CC), which, if the triple amplitudes are approximately (EOM-CC3) or fully (EOM-CCSDT) included, scales as  $N^7$  or  $N^8$  with the system size, respectively. The focus of this presentation is on two newly developed rank-reduced EOM-CC methods, namely RR-EOM-CC3 and RR-EOM-CCSDT for singlet states, which rely on the Tucker decomposition of the triple-excitation excited-state amplitudes tensor and are based on the rank-reduced ground-state implementation. The main advantage of the presented formalism is the reduced computational scaling which for both RR-EOM-CC3 and RR-EOM-CCSDT is  $N^6$ . Although the tensor decomposition scheme introduces an error, it is straightforwardly controllable with a single parameter which determines the size of the projection subspace, with the canonical result restored in the full space. Additionally, for optimal subspace sizes, the obtained errors in electronic excitation energies are several times smaller than the average inherent error of a given method with respect to FCI/TBEs (theoretical best estimates), for states exhibiting singly- and doubly-excited character.

## 22. Multi-symmetry Projected Coupled Cluster Theory

*Ruiheng Song\*, Thomas M. Henderson, and Gustavo E. Scuseria  
University of Maryland; Rice University*

Projected Coupled Cluster (PCC) theory offers a computationally efficient framework for capturing both static and dynamic electron correlation at polynomial cost. In this work, we integrate multiple symmetries—ranging from unitary  $SU(2)$  to anti-unitary time-reversal—to investigate challenging strongly correlated systems. Our multi-symmetry PCC approach demonstrates excellent agreement with Full Configuration Interaction (FCI) benchmarks for model systems and small molecules. Furthermore, we introduce a perturbative triples correction, PCCSD(T), to recover the dynamic correlation missing in the PCCSD treatment. Notably, PCCSD(T) yields qualitatively correct results for the  $Cr_2$  dissociation, showcasing its potential for handling transition metal chemistry.

## 23. The Hydrogen Helix: A Chiral Model to study Dynamics using Time-Dependent Configuration Interaction

*Samantha Piwoni\* and Paul Zimmerman  
University of Michigan - Ann Arbor*

Chiral molecules are essential to innumerable physical, chemical, and biological processes. To truly capture the nature of such processes, we must develop accurate time-dependent modeling capabilities of chiral molecules, the prototypical example of which is a helix. Therefore, we are using Time-Dependent Configuration Interaction (TDCI) to model the dynamics of a simple hydrogen helix system. With our current capabilities, we can represent our system's electronic structure as the field-driven, non-stationary state Hamiltonian matrix in the CI eigenstate basis using Heat-Bath Configuration Interaction. Then, through propagating this Hamiltonian through time, we can simulate the perturbed dynamics of our system and calculate key observables, including the density of states, the electron density, the current density, and the induced magnetic field. We are investigating the impact on electron spin polarization from changing various parameters in our system, including the size and structure of the helix (length, width, number of loops), the electronic structure of the helix (neutral/closed shell vs cationic/open shell), as well as external parameters (applied field strength). Through validating our method on this simpler system, we hope to bridge this study into modeling more complex chiral systems.

## 24. Developing models for solvent and surface interactions on excitonic couplings in chromophore aggregates

*Sayan Adhikari\*, Liang Shi, and Christine Isborn  
University of California, Merced*

Excitonic couplings, which describe the interactions between excited electronic states (excitons) of neighboring chromophores, are central to energy transfer dynamics, optical spectra, and nonlinear optical (NLO) responses in molecular systems. Their magnitude, sign, and distribution govern exciton delocalization, transfer rates, and coherence lengths, while the surrounding environment whether solvent, protein, surface, or neighboring chromophores modifies these couplings through dielectric screening, induced polarization, structural fluctuations, and aggregation motifs. Despite their importance, accurate and physically transparent computational protocols for excitonic couplings in realistic, complex environments remain limited. We aim to address these limitations through three interconnected objectives. First, we develop computational methods that explicitly account for environmental modulation of excitonic couplings. Second, we connect computed couplings to experimentally accessible observables by simulating the absorption spectra of chromophore dimers in solution using molecular dynamics (MD)-based ensemble approaches. By sampling a large number of geometries along MD trajectories, we obtain the full statistical distribution of couplings and their structural and solvent-induced correlations, which are inaccessible to experiment alone. Third, we extend excitonic models to describe the NLO response of organic electro-optic (OEO) materials, where conventional additive models based on single-molecule hyperpolarizabilities neglect the inherently non-additive contributions arising from exciton delocalization and intermolecular electronic polarization. Together, these studies provide both accurate computational protocols and fundamental physical insight into how environmental and intermolecular effects shape excitonic couplings and thereby determine the optical and electro-optic properties of chromophore assemblies.

## 25. Hartree-Fock solver for aggressively local molecular orbitals

*Trine Kay Quady\* and Eric Neuscamman*  
*University of California, Berkeley*

We present a novel route to produce aggressively localized Hartree-Fock-like molecular orbitals that preserve energy differences. Unlike standard HF solvers, we only enforce occupied-occupied and occupied-virtual orthogonality for nearby pairs of molecular orbitals while maximizing locality. As a result, the Fock matrix is only ever constructed in an aggressively localized basis, providing a path to accelerated Fock builds—the main bottleneck in post-HF methods. To demonstrate the accuracy of using these aggressively local HF-like orbitals, we reproduce Hartree-Fock and second-order Møller-Plesset perturbation theory energy differences to sub-mEh accuracy in a set of fully conjugated keto-enol tautomerization reactions.

## 26. LLM-Guided Symbolic Regression for Wavefunction-Informed Exchange-Correlation Functional Development

*Vaibhav Khanna\**, *Haolun Cai*, *Joshua Kammeraad*, and *Paul M. Zimmerman*  
*University of Michigan*

For strongly correlated systems, we have shown that weakly interacting pairs of electrons are a much better starting point. Model systems are available, which yield not a wavefunction ansatz but a complete set of states to work with. One state is a good first approximation and single reference methods converge quickly with modest cost. In particular, the corrections from Epstein-Nesbet perturbation theory are indistinguishable from the corresponding configuration interaction while being cheaper to compute than the original mean-field reference.

## **27. Automatically Assigning Thousands of Vibrational Eigenstates**

*Wolfgang Kern\* and Henrik R. Larsson*

*Department of Physics; Department of Chemistry & Biochemistry*

## **28. Electro-Optic Activity of Organic Chromophores Covalently Bound to SiO<sub>2</sub> Electrode Surface: Toward Rational Design of High-Performance Hybrid EO Materials based on First-Principles Insight.**

*Chamikara Karunasena\**, Sayan Adhikari, Bruce H Robinson, Delwin Elder, Lewis Johnson, Liang Shi, and Christine Isborn  
*University of California Merced; University of Washington; NLM Photonics*

Organic electro-optic chromophores (OEOs) used in hybrid organic–inorganic electro-optic (EO) modulator systems have emerged as a promising materials platform for a broad range of technologies, including radio-frequency photonic links, millimeter-wave wireless backhaul, high-speed analog signal processing, and quantum computing. Owing to their large molecular hyperpolarizabilities ( $\beta$ ) and ultrafast electronic response to applied electric fields, OEOs enable high modulation bandwidth, improved efficiency, and significant reductions in device footprint. Despite these advantages, achieving the theoretical limits of EO performance remain elusive, largely due to poor morphological order, particularly at the organic chromophore–electrode interface. The fundamental structure–property relationships that govern optimal molecular dipole orientations needed for superior molecular hyperpolarizabilities and thereby EO activity remain poorly understood and thus represent significant knowledge gaps in the field. To address these challenges, we develop a multiscale computational modeling and simulation strategy to investigate EO activity as a function of structural properties and chromophore assemblies on silicon electrode surfaces. This approach provides critical first-principles insight into how molecular structure and interfacial organization collectively govern macroscopic electro-optic response, establishing groundwork for a predictive framework for the rational design of high-performance hybrid EO materials.

## 29. A Kohn-Sham Orbital Approach to Extended Configuration-Interaction Singles with Core/Valence Separation (DFT/XCIS-CVS)

*Avik Kumar Ojha\* and John M. Herbert  
Ohio State University*

Spectroscopic core-to-valence transitions provide a sensitive probe of valence virtual orbitals and are particularly informative for molecules and materials with open-shell ground states, where frontier orbitals are often (quasi-)degenerate. However, open-shell excited states are difficult to tackle at the level of single excitations using standard methods such as time dependent density functional theory, because spin-unrestricted references often lead to severe spin-contamination in both ground and excited states. Extended configuration interaction singles (XCIS), is a simple, variational, and size-consistent wavefunction ansatz that extends the conventional CIS excitation space by a limited set of doubly substituted determinants, producing spin-pure open-shell excited states from a restricted open-shell Hartree-Fock reference. XCIS is less spin-contaminated than ROHF-based CIS and produces improved excitation energies. In earlier work we combined XCIS with the core/valence separation (CVS) approximation, to produce a computationally efficient way to simulate core-to-valence excitations for open-shell systems, through limiting the occupied orbital space. XCIS-CVS calculations for core-to-valence x-ray transitions in a dataset of open shells, such as different 3d transition-metal complexes showed semi quantitative agreement with experiment for K-edge and pre-edge orbital splittings. However, we found that the absence of dynamic correlation can lead to noticeable errors in predicted intensities and splittings. Here, we combine XCIS-CVS with Kohn-Sham-orbitals and with scaling of the two-electron integrals (DFT/XCIS-CVS), while retaining the computational advantages of the XCIS formalism while improving the description of the splittings.

### 30. Mixed-Reference Spin-Flip TDDFT: Energy, Properties, and Density-based Characterization of the Excited States

*Arnab Chakraborty\*, Zheng Pei, Yihan Shao, and Anna I. Krylov  
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Quantum chemical methods for excited electronic states are essential for understanding photochemistry, chemical reactivity, and molecular materials. While time-dependent density functional theory (TDDFT) is widely used due to its favorable computational cost, it often struggles in systems exhibiting strong static correlation, near-degeneracies, or significant double-excitation character. The spin-flip (SF) approach addresses these challenges by generating low-lying states from a high-spin reference through spin-flip excitations. However, conventional SF formulations suffer from spin contamination arising from an incomplete configuration space, which complicates the characterization of low-lying states.

The mixed-reference spin-flip TDDFT (MRSF-TDDFT) method addresses this limitation by employing a mixed reduced density matrix constructed from the  $M_s=+1$  and  $M_s=-1$  components of the high-spin triplet reference, recovering most of the missing configurations and, thus, making the state assignment unambiguous. We present a new and efficient implementation of MRSF-TDDFT within the Q-Chem electronic structure package. The implementation enables the calculation of excitation energies, properties, and density-based state analyses using the libwfa framework. These analyses include natural orbitals, natural transition orbitals, and natural difference orbitals, providing insight into the electronic structure and character of the multiconfigurational states. The capabilities of the implementation are demonstrated through comparisons with previous SF-TDDFT results and high-level wave function methods, as well as applications to diradicals, linear conjugated systems with strong static correlation and doubly excited states, singlet–triplet gaps in polyacenes, and systems exhibiting conical intersections. The results demonstrate that this implementation provides a robust framework for studying complex excited-state phenomena in molecular systems.

## 31. Kohn-Sham Density Encoding for Improving Coupled Cluster Accuracy

*Abdulrahman Y. Zamani\**, *Barbaro Zulueta*, *Andrew M. Ricciuti*, *John A. Keith*, and *Kevin Carter-Fenk*  
*University of Pittsburgh*

Improvements to coupled cluster (CC) calculations have been reported when the canonical Hartree-Fock (HF) reference wavefunction is supplanted with one from Kohn-Sham (KS) density functional theory, but the origin of these improvements has remained unclear. We reveal that these improvements arise from differences in the one-particle density matrix that are encoded into the non-canonical Fock matrix—not from the nature of the KS orbitals, as is commonly assumed. Equipped with this insight, KS-CCSD(T) can be leveraged to achieve near-chemical-accuracy for electronic and thermochemical properties of transition-metal dimers and main-group compounds, supporting the prospect of treating strongly correlated systems through simple enhancements to the “gold standard” of quantum chemistry. Whereas HF-CCSD(T) fails for the bond dissociation of Cr<sub>2</sub>, a highlight of our results is the qualitative recovery of the entire Cr<sub>2</sub> potential energy surface at the KS-CCSD(T) level. Additionally, we present a new density difference analysis capable of appraising multireference character in many-electron systems at mean-field cost. This metric can inform the selection of optimal single-reference densities for KS-CC methods and our results on strongly correlation systems hold deep implications for the viability of KS-CC methods in solid-state materials research.

## 32. Development of Valence Bond Methods and Algorithms

*Chen Zhou\**  
*Xiamen University*

Valence bond (VB) theory is inherently a multi-configuration approach, well-suited for treating strongly correlated systems. A VB structure, constructed from nonorthogonal atomic orbitals, directly corresponds to a Lewis structure, providing unique physical insights that align with classical chemical concepts and revealing the intrinsic nature of chemical bonds. Additionally, VB theory is an effective framework for constructing diabatic states. Despite its strengths, the widespread application of VB theory is hindered by its higher computational cost compared to molecular orbital (MO) theory. In this presentation, we focus on our recently developed VB methods and algorithms, which address this limitation:

- (1) Efficient algorithms for VB theory with nonorthogonal orbitals, including biorthogonal transformations, low-rank algorithms for electronic integrals, and analytical energy gradient evaluations.
- (2) The hybrid DFVB method and its multistate extension, which are multireference density functional theory (MRDFT) approaches that incorporate both static and dynamic correlation. The multistate extension allows for the calculation of both adiabatic and diabatic states.

A deep learning framework that integrates VB theory with graph transformers through a chemically interpretable representation of VB structures. The regression model predicts VB structure weights without requiring ab initio calculations, while the classifier model automatically selects the most relevant VB structures for ab initio VB computations.

### 33. Benchmarking $\Delta$ SCF, IP-EOM-CC, and Electron Propagator Theory for Ionization Energies of Open-Shell Species

*Li Ji\*, Abigail O. Gyamfi, Ali Abou Taka, Marco Caricato, and Hrant P. Hratchian  
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Vertical ionization energies (VIEs) are essential quantities for interpreting photoelectron spectra and understanding charge-transfer and ionization processes. Accurate theoretical prediction of VIEs is particularly important for open-shell molecules and radicals, which are reactive and difficult to characterize experimentally. However, modeling open-shell ionization remains challenging because of spin contamination, electron correlation, orbital relaxation, and the computational cost of high-level electronic structure methods. In this work, we assess the performance of several approaches for calculating VIEs of open-shell species, including  $\Delta$ -Self-Consistent Field ( $\Delta$ -SCF) methods, electron propagator theory (UEPT: OVGf-A, P3, and P3+), and an open-shell implementation of ionization-potential equation-of-motion coupled-cluster theory with single and double excitations (IP-EOM-UCCSD). Two complementary datasets, OM-40 and Rad-18, are used to benchmark these methods against high-level  $\Delta$ UCCSD(T) reference values and experimental ionization energies. The results show that IP-EOM-UCCSD provides strong overall performance and generally outperforms the electron propagator methods, while OVGf-A outperforms P3+ among the UEPT approaches.  $\Delta U\omega B97X-D$  also emerges as an appealing and computationally affordable alternative for predicting VIEs of open-shell molecules and radicals. Basis-set analysis further demonstrates that augmented correlation-consistent triple- $\zeta$  basis sets are important for reliable VIE predictions. These findings provide practical guidance for selecting computational methods to model and assign open-shell photoionization spectra.