

2024 West Coast Theoretical Chemistry Meeting

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Sponsors

Department of Chemistry and Biochemistry

School of Natural Sciences

Graduate Division



Talk Abstracts

Techniques for Multiscale Simulations of Solid-Solid Interfaces

Nicole Adelstein

San Francisco State University

Solid-solid interfaces impact the performance of most energy storage and conversion devices. Engineering these interfaces demands multiscale information about their composition, structure, and properties. Since experimental characterization of these complex interfaces is challenging, multiscale simulations offer important insights. Atomic scale ab-initio simulations enable predictive calculations of properties and new phases or structures, but are limited in their time and length scales. Thus, machine learning force fields can be employed to simulate more realistic structures at the microscale and phase transitions, which can require longer timescales.

Organic Reactions with Bifurcating Reaction Coordinates - What, Why, Why care?

Dean Tantillo

University of California, Davis

Thermal reactions whose pathways involve post-transition state bifurcations will be discussed, with a focus on transition metal promoted C-H insertion reactions. These reactions were interrogated using a combination of modern theoretical tools – from classic density functional theory on reaction coordinates to ab initio molecular dynamics. The overall aim of this work is to facilitate the prediction of product distributions for reactions that do not conform to the tenets of transition state theory.

From coarse-grained models to conformational ensembles

Grant M. Rotskoff

Stanford University

Nearly half of the proteome is intrinsically disordered, consisting of proteins or motifs that lack a stable secondary structure. Modeling these regions remains challenging, even with tremendous advances in generative models for protein structure prediction. Sampling the conformational ensemble of the intrinsically disordered proteome is out of reach for atomistic molecular dynamics due to the deeply metastable probability distributions over conformational space. In this talk, I will show how generative models with physical latent space dynamics provide a generalizable strategy for robustly sampling conformational ensembles. Furthermore, I will detail how to construct this sampling scheme to ensure asymptotic convergence of the samples to a Boltzmann distribution.

Taking Chemistry Far from Equilibrium

David T. Limmer

University of California, Berkeley

Most of our intuition for how chemical reactions proceed comes from classical mechanics in equilibrium settings. The Arrhenius rate law and the transition state theory that underpins it, conceive of a reaction as the motion across a barrier mediated by thermal environmental fluctuations. Increasingly, systems of current interest violate the equilibrium assumptions built into these theories, either because molecules are manipulated directly or because they evolve in environments that are constantly dissipating energy. In this seminar, I will discuss some recent ideas to extend reaction rate theories away from equilibrium using principles from stochastic thermodynamics so that they can be applied to living and driven systems. Trajectory reweighting principles and a thermodynamic speed limit provide formal results that can be understood with some simple, exactly solvable models. Variational path sampling and nonequilibrium instanton methodologies allow for these formal results to be brought to bear to complex systems. Throughout this talk, I will highlight results related to force spectroscopy of proteins and ion pair dissociation in electrolyte solutions, as well as active matter and driven self-assembly.

What can the MolSSI do for you? Resources, programs, and software from the Molecular Sciences Software Institute

Ashley Ringer McDonald

Cal Poly San Luis Obispo and the Molecular Sciences Software Institute

The Molecular Sciences Software Institute (the MolSSI) is an NSF-funded institute that aims to improve software, education, and training in the computational molecular sciences. This presentation will highlight resources and programs from the MolSSI, including core software solutions, educational resources, and fellowship opportunities that can benefit students and researchers at all levels of their career. Specific software products discussed and demonstrated will include: QCArchive, a program to generate, compile, aggregate, and share quantum chemistry data; the MolSSI Driver interface, an interface to allow fast, on-the-fly communication between different software packages; and SEAMM, a GUI that lets researchers run atomistic simulations for organic molecules, fluids, and materials. The presentation will discuss MolSSI's fellowship programs for grad students, post-docs, and faculty, and it will showcase some of MolSSI's educational resources and workshops that provide training in a wide range of software topics, including fundamental programming, best practices in software development, machine learning, high performance computing, and more.

Periodic wavefunction methods for materials science

Xiao Wang

University of California, Santa Cruz

Wavefunction-based quantum chemistry methods, such as perturbation theory, configuration interaction, and coupled-cluster theory, are most widely used for the study of molecular systems. However, accurate *ab initio* quantum chemical description of solid-state systems remains a theoretical and computational challenge. In recent years, several wavefunction methods have emerged as powerful approaches for the prediction of electronic structure properties of crystalline solids. In this talk, I will present our research development of wavefunction-based techniques that incorporate periodic boundary conditions. Specifically, I will discuss the accuracy of spin-component-scaled second-order Møller-Plesset perturbation theory (SCS-MP2) on ground-state properties of covalent and ionic solids. I will then discuss the development of periodic equation-of-motion coupled-cluster theory with singles and doubles (EOM-CCSD) and demonstrate its accuracy on predicting a wide range of exciton properties, such as optical gaps and absorption spectra, for several insulators, semiconductors, and molecular crystals.

Can Excited States of Radical Ions Act as Photoredox Catalysts?

Diptarka Hait (presenter) and Todd J. Martinez

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It has been recently suggested that electrochemically accessible organic radical ions can act as effective photoredox catalysts, as excited states of radical anions (cations) typically have high energy electrons (low energy holes) that can permit strongly reducing (oxidizing) behavior. However, bimolecular redox catalysis in solution is only feasible if excited states of radical ions persist for at least a nanosecond. Using multireference perturbation theory, we show the existence of conical intersections through which ultrafast internal conversion from excited states to the ground doublet state can occur for representative organic radical ions like dicyanoarene anions and trisaminocyclopropenium dications. The discovered photorelaxation pathways involve geometric changes like bond length alteration, deplanarization of substituents, and charge-transfer inducing twists that are likely to be feasible for most organic radical ions. The computational results furthermore are consistent with transient absorption experiments that indicate picosecond scale radical ion excited state lifetimes. Our work therefore reveals the relative unsuitability of radical ion excited states as bimolecular redox catalysts and suggests that any experimentally observed photoredox catalysis in the presence of radical ions likely involve alternative mechanisms.

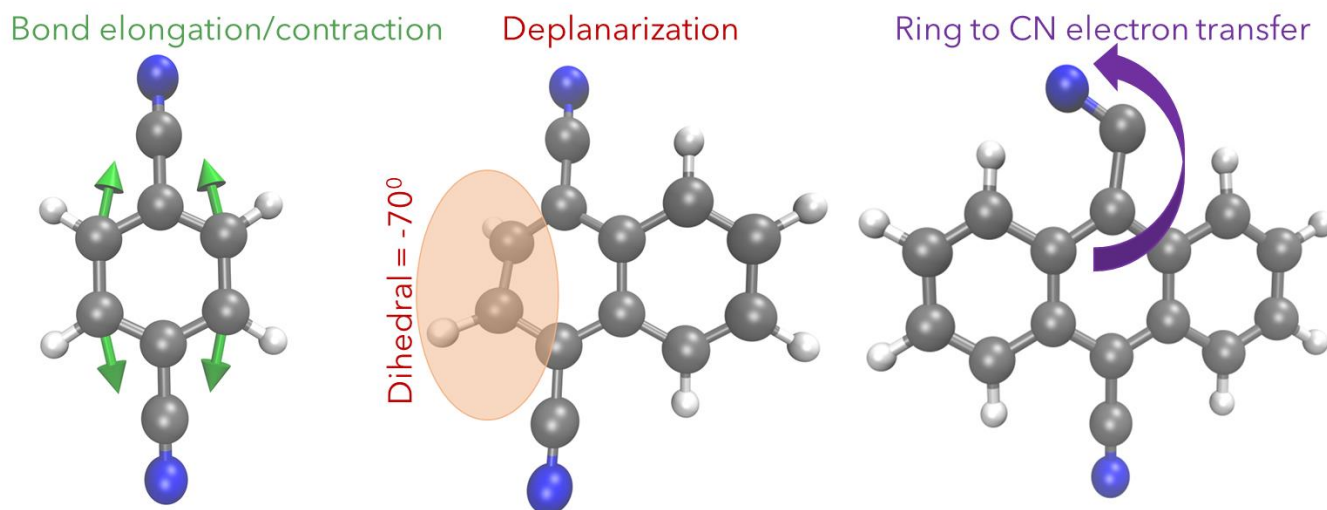


Figure 1. Mechanisms for internal conversion for representative dicyanoacene radical anions.

Simulating photoreactions in biological environments with state averaged CASSCF in AMOEBA polarizable models

Chenchen Song

Department of Chemistry, UC Davis

Many important photoreactions in life, such as vision in animals and photo-perception in plants, take place in solvents or within macromolecules and are affected by their interactions with the environments. Because the excited wavefunction is generally localized on the chromophore, this suggests a natural multi-scale description of the system in which the electronically excited chromophore is treated quantum mechanically and the surroundings are treated classically in a hybrid QM/MM framework. My talk will present recent method development efforts towards rigorous QM/MM simulations of non-adiabatic molecular dynamics with nonequilibrium environment effects. The QM region is described with state averaged (SA)-CASSCF, which provides a balanced treatment between ground and excited states and can properly describe the topology around conical intersections. The environmental effects are described by embedding in AMOEBA polarizable models, a highly accurate polarizable model for solvents and biomolecules. I will discuss algorithms that solve the energies, analytical nuclear gradients and non-adiabatic couplings for SA-CASSCF/AMOEBA, which provide the essential ingredients for non-adiabatic QM/MM molecular dynamics simulations. To demonstrate the performance of the method, I will discuss results from various benchmark studies as well as an application to study the mechanism of a bioluminescence reaction.

References:

- Song, C.C., State averaged CASSCF in AMOEBA polarizable water model for simulating nonadiabatic molecular dynamics with nonequilibrium solvation effects. *J. Chem. Phys.* 158, 014101 (2023)
- Song, C.C., State-averaged CASSCF with polarizable continuum model for studying photoreactions in solvents: Energies, analytical nuclear gradients, and nonadiabatic couplings. *J. Chem. Phys.* 156, 104102 (2022).

Elucidating the Fluxionality and Dynamics of Zeolite-Confined Au Nanoclusters Using Machine Learning Potentials

Siddharth Sonti¹ (Presenter), Chenghan Sun¹, Zekun Chen², Davide Donadio², Surl-Hee Ahn¹, Ambarish R Kulkarni¹

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Sub-nanometric clusters (NCs) of transition metal (TM) atoms, typically consisting of fewer than 15 atoms, have exhibited remarkable catalytic activity in various industrial reactions. However, these NCs are thermodynamically unstable and susceptible to deactivation due to sintering. Previous experiments have proposed zeolites as effective structural scaffolds to stabilize small NCs. However, key physiochemical phenomena such as fluxionality and diffusion properties of such zeolite-confined TM NCs (TM@zeolites) are not well understood. The central challenge is the steep computational cost associated with performing sufficiently long ab initio molecular dynamics (AIMD) simulations. As a step towards addressing this challenge, we developed a self-adaptive workflow that leverages two state-of-the-art machine learning potential (MLP) packages (i.e., SchNetPack and neuroevolution potential) to develop an accurate, robust, and transferable MLP for a prototypical Au@zeolite system. The resulting MLP, which is shown to be transferable across several other zeolites and various temperatures, is used to study the confinement effects and determine the free energy landscape and the corresponding rates for the diffusion of gold NCs in different zeolites.

Conjugation and Symmetry Effects in Ultrafast Charge Migration

Imam Wahyutama (Presenter), Madhumita Rano, and Henrik R. Larsson

Department of Chemistry and Biochemistry

University of California Merced

A central process that happens after ionization in (bio-)molecules is charge migration. This is an electron-correlation-driven process where an electron hole is created during the ionization, which then migrates through the molecule. In this work, we study ultrafast charge migration dynamics in several molecules by employing the time-dependent density matrix renormalization group (TDDMRG) *ab initio* method. We apply TDDMRG to propagate the wave function starting from a state exhibiting a localized hole, which emulates local sudden ionization. The resulting dynamics is studied using intrinsic bond orbitals decomposition analysis of the instantaneous density, which enables a bond-resolved probe of the dynamics. From this analysis, we are able to elucidate the distinction in the dynamical behavior between conjugated and hyperconjugated molecules. In particular, we will show that the hole migrates out of its initial site faster when the molecule is conjugated. Using the aforementioned analysis, we are also able to see that the initial hole symmetry and the local symmetry of the bonds in the molecule dictate which bonds the hole traverses throughout the dynamics. We anticipate that these findings will significantly enhance our understanding of how the hole migrates through the molecule during charge migration.

Poster Abstracts

Møller—Plesset second-order and double-hybrid density functional theory for accurate transition dipole moments and oscillator strengths. A balancing act between dynamic and static correlation

Andrew Bovill

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Modeling oscillator strengths is essential for studying electronic excited states and connecting computational results to experimental spectra. Such calculations can also be used to assess the quality of electronic structure methods used to study electronic transitions. In this presentation, we report on an investigation of transition dipole and oscillator strength calculations using Møller—Plesset second-order perturbation theory (MP2) and double-hybrid density functional theory model chemistries. Incorporating spin-projection with these methods, we aim to balance dynamic and static correlation effects. In addition to comparisons with other models and experiment, details of the theory and implementation will be discussed.

Title: Elucidating the binding mechanism of paramagnetic amyloid ligands to α -synuclein monomer

Hung-Yu Wan

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It is well known that the hallmark of Parkinson's disease (PD) is the accumulation of α -synuclein oligomers (α SOs), which is one of the aggregate forms of α -synuclein. Recently, our collaborator, Prof. John Voss (UC Davis), has found that paramagnetic amyloid ligands (PALs) could potentially inhibit the formation of α SOs. However, the specific mechanism of how PALs interact and block the aggregation is unknown, which is crucial for drug discovery for PD.

In this study, we utilized Ligand Gaussian accelerated Molecular Dynamics (LiGaMD) simulations to examine the interactions between PALs and the α -synuclein monomer. Our findings indicate that a 1 μ s LiGaMD is sufficient for our system, as evidenced by the near-zero auto-correlation values observed after the 1 μ s run. Notably, we discovered that most PALs exhibit the highest molecular dynamics (MD) contact probability within the non-amyloid β component (NAC) region, which spans residues 61 to 94 of the α -synuclein monomer. This suggests that PALs are more likely to bind to the NAC region instead of the N-terminal or C-terminal regions of the α -synuclein monomer. Additionally, our results suggest that PALs may impede the formation of secondary structures, particularly α -helices and β -sheets. Moreover, to identify the most predominant structure within our system, we utilized k-means clustering analysis, which shows that there is not much difference between the bound and unbound states of the α -synuclein monomer.

On-the-fly Semiclassics for Large Systems: Implementation of LSC-IVR with TeraChem

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On-the-fly nonadiabatic molecular dynamics (NAMD) that propagate equations of motion using multiple adiabatic electronic surfaces can be extremely computationally expensive to perform. This is due to both the cost of computing the nonadiabatic couplings between these electronic states, which grows quadratically with the number of surfaces utilized in the system, as well as the number of simulations needed to converge an average over initial conditions. In this poster, we will present our implementation of the Linearized Semiclassical Initial Value Representation (LSC-IVR) approach, an on-the-fly nonadiabatic simulation code, with the GPU accelerated TeraChem software for performing quantum chemistry electronic structure calculations. Originally designed to use CPU-based GAMESS as the electronic engine, we will examine the computational cost of performing NAMD simulations of varying system sizes using TeraChem, and show how they can be parallelized over multiple GPU compute nodes using a server-based communication protocol.

A Computationally Intensive Materials Study for Gas Adsorption: Interweaving Machine Learning with Quantum Mechanical and Statistical Mechanics Methods

Karim Aljamal, Xiao Wang[†]

University of California, Santa Cruz

Advancing computational research to the next frontier requires using a multitude of theoretical approaches and depth within theoretical calculations. This work presents a comprehensive study into the methodology of studying the phenomena of methane adsorption in metal organic frameworks. For this complex phenomenon where traditional experimental research approaches are costly, computational methodologies allow the progression of materials design and characterization, as well as the establishment of innovative workflows for future research endeavors. This work focuses on examining the accuracy and robustness of predictive capabilities in methods such as Density Functional theory and Machine learning methods. DFT methods give insight into the electronic structure of adsorbents, and an understanding into adsorption mechanisms and properties. For machine learning methods, a multi-modal transformer encoder, pre-trained on focused local and global structural descriptors for metal-organic frameworks, is used as a foundation to then create new versatile models with property-specific fine-tuning. In this study three high performing MOFs in methane adsorption: HKUST-1, ZIF-8, and ATC-Cu, are studied and characterized for various adsorption properties. To examine the versatility and constancy of these methods, structure modification of the MOFs in the form of Copper and Zinc respective metal substitutions was carried out through alterations to the crystal structure. In order to benchmark these methods, the trends of adsorptive capability of these MOFs, and affinity to methane was tracked throughout the structure modifications. In comparison of the methods, adsorption energy determined through DFT, as well as uptake and heat of adsorption properties determined through machine learning property prediction. The ability of the methods to track structure modifications with uniform accuracy, indicated through property predictions, show their potential use as individual characterization methods. With work there hopes to be a unification of computational methodologies, interweaving the insightfulness and extensity of electronic structure theory with the rapid learning of machine learning methods.

Microscopic origin of tunable assembly forces in chiral active environments

Clay H. Batton, Grant M. Rotskoff

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Across a variety of spatial scales, from nanoscale biological systems to micron-scale colloidal systems, equilibrium self-assembly is entirely dictated by---and therefore limited by---the thermodynamic properties of the constituent materials. In contrast, nonequilibrium materials, such as self-propelled active matter, expand the possibilities for driving the assemblies that are inaccessible in equilibrium conditions. Recently, a number of works have suggested that active matter drives or accelerates self-organization, but the emergent interactions that arise between solutes immersed in actively driven environments are complex and poorly understood. Here, we analyze and resolve two crucial questions concerning actively driven self-assembly: i) How, mechanistically, do active environments drive self-assembly of passive solutes? ii) Under which conditions is this assembly robust? We employ the framework of odd hydrodynamics to theoretically explain numerical and experimental observations that chiral active matter, i.e., particles driven with a directional torque, produces robust and long-ranged assembly forces. Together, these developments constitute an important step towards a comprehensive theoretical framework for controlling self-assembly in nonequilibrium environments.

Excitonic Renormalization: A novel fragmentation scheme for Modular Large-scale *ab-initio* Electronic-structure Calculations

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Anthony Dutoi

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Fragmentation schemes were explored in many different flavors throughout the history of quantum chemistry. Prominent examples are symmetry-adapted perturbation-theory (SAPT), block correlated (BC) and active space decomposition (ASD) methods, as well as the very successful density-matrix renormalization-group (DMRG). However, BC and ASD methods require explicit orthogonalization for all fragments, SAPT requires tedious derivation for global anti-symmetry and lacks cooperative effects at low orders of perturbation theory, while DMRG lacks in its description of dynamical correlation. A different strategy, proposed by Dutoi and Liu[1], is based on separating local and long-range correlation making use of a biorthogonal framework. The approach allows for methods and basis sets of choice for each fragment separately, allowing for tailored treatment of local correlation. The resulting densities can be truncated to the "relevant" state space. The Hamiltonian is then build from the correlated densities of the single fragments and integrals in the atomic orbital basis between multiple fragments. This Hamiltonian provides a comparably small state space, which already includes intra-fragment correlation, as well as a second quantized formulation, see Figure 1. Deriving a CCSD approach within this framework[2] results in a formal scaling of N^3 with the system size and N^4 with the number of states per fragment, which is massively truncated. Here we show how the Hamiltonian can be build efficiently, by expanding the overlap between non-orthogonal states in orders of orbital rotations, leading to smooth and fast convergence.

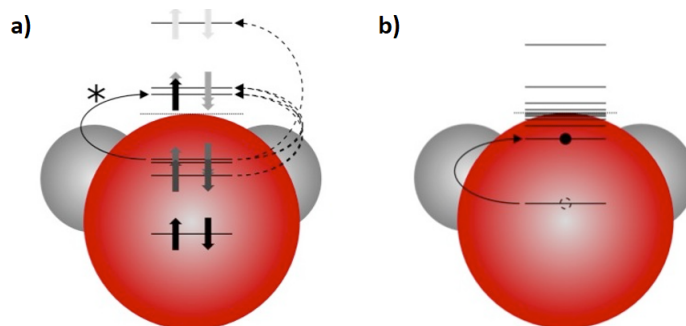


Figure 1: Single excitation in the fluctuation operator basis (a) and the orbital basis (b).

[1]Anthony D. Dutoi, Yuhong Liu, *Molecular Physics* **117:4**, 431-445 (2019).

[2] Yuhong Liu, Anthony D. Dutoi, *Molecular Physics* **117:4**, 446-461 (2019).

Born-Oppenheimer Molecular Dynamics Simulations of Nitrate Anion Photolysis in an Aqueous Solution

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NO_3^- in aerosol particles is an essential sink of NO_x . The photolysis of NO_3^- is a 'renoxification' process, which converts NO_3^- solvated in water or deposited on surfaces back into NO_x to the atmosphere. NO_3^- photolysis under environmental conditions can follow two channels: (1) NO_2 and O^- ; (2) NO_2^- and $\text{O} (^3\text{P})$. Despite the well-studied macroscopic kinetics of the two channels, the microscopic picture of the photolysis still needs to be explored. Furthermore, previous experiments have shown that NO_3^- photolysis in aqueous solutions has a low quantum yield of $\sim 1\%$, leading to a solvation cage effect hypothesis. A previous theoretical study has indicated that the low quantum yield may be due to the direct spin-forbidden absorption of NO_3^- to its triplet state. Here, we employ BOMD simulations at the level of hybrid DFT with enhanced sampling to explore the two channels in an aqueous solution to unravel the atomistic and electronic structure details of the photolysis, as well as investigate the causes of its low quantum yield under a solvation environment. We find that the direct spin-forbidden absorption is viable through spin-orbit coupling and is ~ 20 times weaker than the spin-allowed absorption. A solvation cage complex is identified as a meta-stable state on the free energy surface of the triplet state, which suggests that additional thermal energy is required for the complete dissociation of the N-O bond. This meta-stable state allows the photo-fragments to recombine or deactivate through non-radiative processes. We also observe that the completion of channel (1) requires a more extensive rearrangement of H-bonds than channel (2), which matches the temperature dependence of the two channels observed in experiments. This work provides a novel molecular picture to illustrate the significantly low quantum yield and temperature dependence of NO_3^- photolysis under environmental conditions and a starting point for future studies of environmental nitrate photochemistry.

Transition-point Metadynamics: Accelerating Reaction Discovery through Event Deceleration

Alexander M. Chang, Rui Xu, Todd J. Martinez

Stanford University

Ab initio molecular dynamics (AIMD) has often been used as an approach for discovering chemical reactions from first principles. However, using AIMD for uncovering an entire reaction network, including rare events, is computationally expensive. To address this difficulty, our recently developed *ab initio* nanoreactor uses accelerating forces in AIMD to hasten the exploration of reactants, products, and transition states on the potential energy surface (PES) of a chemical system. The nanoreactor also decouples reaction discovery from the estimation of reaction rates. Within the nanoreactor framework, a reaction path only needs to be discovered once for the construction of a kinetic model. Therefore, it is beneficial for the nanoreactor to effectively traverse the PES of a chemical system and efficiently sample many different reactions. To accomplish this goal, we introduce the transition-point metadynamics methodology. Unlike traditional metadynamics, we start AIMD with gaussian potentials already placed at the highest energetic points of reaction paths that were found during previous AIMD discovery simulations. This shuts off the sampling of those previously discovered paths, allowing other regions of the PES to be explored. We apply this methodology to the previously explored phenyl radical oxidation reaction network, and demonstrate its ability for accelerating reaction discovery in an efficient manner.

When Machine Learning Meets Chemistry: From Thermodynamics of Water and Ice to UV-Vis Absorption of Solvated Aromatic Molecules

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Water is the universal solvent for biological and environmental reactions, including atmospherically relevant photochemical processes. Depending on its state – solid or liquid – water provides different solvation environments that may enhance or hinder chemical reactions. One such case is the photolysis of organic pollutants: Experiments suggest that small aromatic molecules produced in wildfires such as guaiacol and dimethoxybenzenes undergo photolysis at a faster rate when solvated at the air-ice interfaces and in snowpack compared to bulk water. However, these measurements cannot ascertain the microscopic origin of such enhancement and the role of the solvation environment. Molecular modeling can fill the experimental gaps and deliver insights to interpret the mechanisms that lead to faster photodegradation rates of organic pollutants in water. To this scope, it is, however, necessary to model accurately and efficiently the structure and dynamics of the solvated molecules in the specific solvation environment and their molar absorptivity, one of the main drivers of photodissociation. In this poster presentation, I will illustrate how machine learning (ML) can be exploited to realize these goals. The first part of the poster presentation will feature the development of a scalable, first-principles neuroevolution potential (NEP) that accurately captures the thermodynamics and anomalies of water. Eventually, I will then introduce an innovative approach that employs ML models trained on accurate quantum chemical calculations to predict the line shape of the UV-visible absorption band of solvated aromatic molecules, from which we ascertain the atomistic origin of the enhanced photolysis rates.

Quantum Particle Motion: Understanding Quantum Behavior of Protonated Water Clusters

Codin Cheng, Henrik R. Larsson

Department of Chemistry, University of California-Merced

The Zundel ion is significant to investigating the quantum effects on water and how its proton motion coupled with wagging influences pH. Assigning over 130 eigenstates, each with 15 different vibrations, the Larsson Group led by Henrik R. Larsson was able to investigate the quantum behavior of the Zundel ion relative to the Marx potential surface.

Automated, Iterative Force Field Fitting

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Molecular mechanics force fields enable atomistic simulations for complex systems too large for a quantum mechanical treatment. Simulation accuracy depends on the parameters employed in the force field. Every new molecule must have parameters generated for it, either by using a general force field or fitting a custom parameter set for that system. While fitting custom parameter sets can provide superior accuracy to generating parameters by analogy from a general force field, the process of single-molecule force field fitting was often tedious, expensive, and bespoke. We present an automated, iterative procedure for fitting single-molecule force fields. This program optimizes the parameters using a dataset of quantum mechanical (QM) forces and energies, samples conformations via dynamics with the new parameters, computes QM energies and forces on those conformations, adds them to the dataset, and returns to the parameter optimization step. We use a validation set to determine when the iterative optimization should be terminated. An early-stopping criterion (with patience) saves computational effort and identifies the most accurate parameters from a force field optimization for a first-generation donor-acceptor Stenhouse adduct. Boltzmann sampling at 400 K produces an accurate forcefield for a tri-alanine peptide, a system with a rugged potential energy surface. Last, we demonstrate the speed of the cloud-computing backend by refitting the dihedrals for Bacteriochlorophyll-a, a system with 140 atoms, in a single weekend.

Two Ground States of Heme: A Spin-Forbidden Equilibrium

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An incomplete 3d shell of iron in Fe(II)-porphyrins gives rise to the close-lying low-spin (S=0), intermediate-spin (S=1), and high-spin (S=2) states, with the relative energies highly sensitive to the molecular environment. Predicting accurate spin-state energetics in Fe(II)-porphyrins is critical for understanding the biological functions of heme proteins, including myoglobin and cytochrome c, where the interplay between different spin states is a key component of the protein's reactivity. However, the ground state multiplicity of even the simplest unsubstituted Fe(II)-porphyrin (FeP), also known as heme, remains unknown due to the lack of experimental data. Available experimental data pointed to a triplet or a quintet ground state for different four-coordinated Fe(II)-porphyrins. Experimental observations suggest a strong dependence of the ground state multiplicity in four-coordinated Fe(II)-porphyrins on the Fe–N distance. A small adiabatic energy gap between the lowest triplet and quintet states predicted for FeP indicates the possibility of a thermal equilibrium between these states due to small energy barriers for the spin-forbidden reaction in both directions. We investigate a potential nonadiabatic equilibrium between the lowest energy triplet and quintet spin states along the Fe–N distance in FeP using the Density Functional Theory (DFT) and multireference methods. DFT predicts a triplet ground state, however with a negligible adiabatic energy gap. Moreover, spin-forbidden quintet-to-triplet and triplet-to-quintet reactions are expected to be effectively barrierless due to the negligible minimum energy crossing point potential barriers in both directions. Both reactions become barrierless after adiabaticization with a large spin-orbit coupling constant predicted for FeP, resulting in a spin-adiabatic state with a global minimum located at the Fe–N distance in between the equilibrium distances for the triplet and quintet states. The results of the multireference calculations support the hypothesis of a low energy barrier and the existence of the spin-forbidden equilibrium between the two spin states in FeP.

Effect of Extreme Variations of Fundamental Constants on Structure of Molecules

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The fundamental constants (FCs) of physics are promoted to dynamic quantities by modern theories. So far most of the literature focused on small fractional variations in the values of FCs. In this paper, we investigate the novel regime of extreme but transient variations of FCs. We focus on the speed of light c and show that its variation can dramatically change the electronic structure and chemistry of molecules. These changes are induced by increased relativistic effects when c is reduced from its nominal value. To model these changes, we solve the fully relativistic Dirac equation at different values of c . We show that at extreme variations of c , the periodic table is truncated, atoms can change their nominal ground states, water fails to serve as a universal solvent, and the ammonia molecule becomes planar. Our predicted changes in the structure of ammonia, which is one of the most abundant polyatomic molecules in interstellar space, can be potentially used in astrophysical searches for the dark matter clumps.

Exploring ultra-fast dissociation processes in fluorinated hydrocarbons using Ab-initio surface hopping dynamics

Luka Dockx, Dr. Anthony D. Dutoi

University of the Pacific

Obtaining accurate rate constants and thermodynamic properties for the dissociation of halogenated hydrocarbons is crucial for understanding the impacts of these molecules on our atmosphere. In the past, it was thought that these processes could almost always be modeled statistically using transition state and RRKM theory. However, this assumption has been thoroughly disproven over the past decades.

We investigate the case study of the trifluoropropene cation, where high-energy photons in the atmosphere can cause the D_2 to D_5 excited states to rapidly dissociate the molecular cation within tens of femtoseconds on a highly repulsive potential energy surface. Surface-hopping molecular dynamics simulations show the interplay between different excited states causing the rapid dissociation of carbon-fluorine bonds before relaxation to the ground state can occur. Excited states may also facilitate dissociation on the ground-state or non-repulsive excited states by stretching the C-F bond and adding kinetic energy in the dissociation mode before relaxation to the ground state occurs. Moreover, excitations to higher-lying, non-dissociative excited states were shown to ultimately produce an increased number of dissociations compared to direct excitation to the dissociative state through the complex interplay and surface-hopping processes occurring among the excited states.

Capturing hydrogen bonding between organic chromophore and solvent with improved partial atomic charges

Katherine Donahoe (Presenter), Arthur Pyuskulyan, Christopher Myers

University of California, Merced

Christine Isborn, Liang Shi

University of California, Merced

Classical force field molecular dynamics have the advantage of low computational cost, with the drawback of not directly treating electronic structure. This has led to interest in finding ways to parameterize the force field using information derived from quantum mechanical simulations. One promising method is to parameterize the force field in terms of partial charges localized on the atomic centers of the chromophore molecule, as with tools like the QUantum mechanical BEspoke Kit (QUBEKit).

In this work, four sets of partial atomic charges are examined for an organic chromophore, cresyl violet, solvated in methanol: (a) derived from QUBEKit with an implicit solvent model for methanol, (b) generated with explicit solvent, (c) generated by symmetrizing the charges on like molecular moieties, and (d) a "maximally-polarized" variant generated from sampling ab initio molecular dynamics configurations. The resulting force fields with these charge sets are scrutinized against QM/MM simulation. Hydrogen bond statistics and dynamics are characterized for the two amine centers of the chromophore and their effect on spectral density and absorption spectrum is examined.

Improving spin-contamination in potential energy surface exploration using Approximate Projection

Christian J. Dwyer, Hrant P. Hratchian

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The Approximate Projection (AP) method is a widely-used model for correcting spin contamination and correcting energy values in Density Functional Theory (DFT) calculations. A key advantage of the AP model lies in its balanced treatment of different regions of a potential energy surface with either negligible or significant spin contamination. This study explores this feature by calculating Intrinsic Reaction Coordinate (IRC) pathways for a series of reactions involving bond cleavage and formation, where spin contamination varies across the reaction pathway. The effectiveness of spin correction with the AP model across these pathways is examined and discussed.

Automated splitting of reactions paths for minimum energy path optimization

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Abstract:

A primary goal of theoretical chemistry is to predict reaction outcomes from first principles. The Nudged Elastic Band (NEB) algorithm has emerged as a powerful tool for studying the energetics of complex reactions, but its effectiveness is limited by its computational cost, particularly when the reaction pathway involves many intermediates.

We have developed an Automatically-Splitting Nudged Elastic Band (AS-NEB) algorithm in order to efficiently and accurately describe multi-minima reaction pathways. Computational time is reduced by stopping NEB optimizations early when a chain appears to have intermediates, followed by separate NEB optimizations on each minima-to-minima path.

We demonstrate the applicability and performance of AS-NEB on 2D model potentials, as well as for a dataset of 60 reactions. Autosplitting can save the number of gradient calls needed for optimization in some cases, as well as elucidate intermediates along a reaction mechanism.

Quantum Vibrations: Analyzing the Quantum Behavior of Protonated Water Clusters

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Classical mechanics-based molecular behavior should result in water having a pH level of 8.5. However, actual water has a pH level of 7 which indicates that there are quantum mechanical effects at work. While studying the quantum vibrations of protonated water clusters, it has been found to have fifteen degrees of freedom in which to move. Measuring these vibrations using various algorithms like DMRG and the Bowman method, these quantum vibrations can be represented by wavefunctions of discrete eigenvalue energy states. To make it easier to analyze excitations in these states, the fifteen dimensions of movement can be reduced to two and visualized through plots. From these plots, states have been assigned values describing the types of vibrational motion occurring at each eigenstate. Thus so far just over 111 states have been properly assigned and the motion described. With further analysis, the effects of these quantum vibrations on the acidity of water may become clear.

Modeling correlation free energies with temperature-dependent fitting constants

Sage Gorney (Presenter), Brittany Harding

UC Merced

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UC Merced

The uniform electron gas is a key model system for the development of density functional theory. In this model, the Wigner-Seitz radius (r_s) parameter can be adjusted to manipulate the electron probability density. This allows for the investigation of strongly and weakly correlated systems. Multiple expansions for the correlation energy per particle of a uniform electron gas currently exist at zero temperature, both for high and low density. However, less research has been conducted for examining correlation free energies in temperature-dependent systems. Temperature effects are not all captured by traditional, ground-state density functional theory approaches. Thus, we require new methods of approximation. This research aims to test the uses and breaking points of truncated zero-temperature models in thermal density functional theory. This was accomplished through analysis of the temperature and density ranges at which the models were effective at predicting correlation free energies. Topics of interest have been expanded to include dependence on temperature for specific coefficients, as analyzed via their variance.

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Abstract

Electronic Structure and Photodetachment of $Zn_xO_x^{-/0}$ ($x=1-5$) Clusters

Exploring electron detachment processes offers a valuable opportunity to investigate electronic and molecular structures of clusters, particularly those that have complicated electronic states, such as small transition metal oxide clusters in the gas phase. Cluster models have been broadly used in the investigation of bulk and surface properties of crystals. We report new computational results on $Zn_xO_x^{-/0}$ ($x=1-5$) using Natural Orbital Ionization (NIO) model for Δ SCF calculations to describe ionized states and assign photodetachment spectra. The pole strengths have a direct correlation with the experimental cross-sectional measurements observed during photoelectron spectroscopy.

Using the generalized thermal adiabatic connection to analyze and build exchange-correlation free energy approximations

Brittany Harding

Department of Chemistry and Biochemistry, University of California, Merced

Warm dense matter is a highly energetic phase found within planetary cores that exhibits properties of both plasmas and solids. Thermal density functional theory is commonly used to simulate this challenging phase, driving development of temperature-dependent approximations to the exchange-correlation free energy. The generalized thermal adiabatic connection (GTAC) introduces a fictitious temperature parameter in order to connect ground-state approximations to their finite-temperature counterparts. This approach will be demonstrated as an analytical tool and as a means to generate new approximations to entropic and kinetic free energy components.

Advances In Q-Chem 6.2

Shannon Houck (Presenter)

Q-Chem Inc.

The Q-Chem software package continues to provide a comprehensive library of cutting-edge methods for electronic structure modeling, allowing fast, accurate simulations of structures, reactivities, and properties. Our “open teamware” approach, alongside our modular developer environment, provides researchers with a well-tested foundation of code on which to develop new methods, fostering scientific collaboration and innovation while also ensuring long-term sustainability and maintenance of the developed code. This poster will discuss several recent developments from Q-Chem developer groups across the globe, including new methods for modeling X-ray spectroscopy, energy and force decomposition analysis, real-time nuclear-electronic orbital (NEO) methods, and many other new improvements.

Accurate and efficient structure elucidation from routine one-dimensional NMR spectra using multitask machine learning

Frank Hu (Presenter), Michael S. Chen, Grant M. Rotskoff, Matthew W. Kanan, Thomas E. Markland

Department of Chemistry, Stanford University

Accurate rapid structure determination of reaction products can greatly accelerate synthetic workflows across many chemical disciplines. However, elucidating a complete molecular structure using only routine one-dimensional (1D) spectroscopies, such as NMR, remains an extremely challenging problem due to the combinatorial explosion of the number of possible molecules as the number of constituent atoms is increased. Here, we introduce a multitask machine learning framework that predicts the chemical structure (atomic composition and connectivity) of an unknown compound solely based on its one-dimensional ^1H and/or ^{13}C NMR spectra. We demonstrate the effectiveness of this framework on molecules with up to 19 heavy (non-hydrogen) atoms, a size for which there are trillions of possible structures. Without relying on any prior chemical knowledge, we show that our approach predicts the exact molecule 64.4% of the time within the first 15 predictions, reducing the search space by up to nine orders of magnitude. To achieve this, we show how a transformer architecture can be constructed to efficiently solve the task, traditionally performed by chemists, of assembling large numbers of molecular fragments into chemical structures. Integrating this with a convolutional neural network (CNN), we build an end-to-end model for structure elucidation that is fast, accurate, and requires only routinely obtained 1D NMR inputs.

Computational Modeling of the Radical Formation of Pentane as a Plasma Precursor in Low Temperature Plasma

Mackenzie Jackson

California State University, Fresno

Low Temperature Plasma (LTP) modification is an ideal method to change the chemical properties of surfaces, which affects how the materials react with the environment. This project models a specific plasma precursor– Pentane– using computational chemistry. The study uses classical DFT functions and looks at the geometry, frequencies, and energies of the neutral radicals and cations formed during the ionization process. The data is obtained using the quantum chemistry program Q-Chem with the B3LYP method along with two basis sets: 6-311++G** and def2-TZVPPD for comparison. The data was then analyzed to determine the most stable fragments that were subsequently used to predict the types of co-polymers that will most likely be formed. In future work, another precursor– Acrylic Acid– will be analyzed and the data collected from these precursor fragments, in conjunction with experimental surface measurements, will be used to develop a machine learning model to predict the properties of the co-polymers these compounds form. This will help understand key characteristics of the deposition of the thin film via the thickness of the film, deposition rate, and the chemical composition of the film.

Nanoconfinement in metal/ligand electrocatalysts:

how is it created and why does it reduce CO₂ efficiently?

Asmita Jana (Presenter), Ethan Crumlin, and Jin Qian

Lawrence Berkeley National Laboratory

Enhancing the performance of electrocatalysts for applications like carbon conversion is important for making that technology viable. Nanoconfinement is a promising strategy for doing so. Understanding how it is created and why it enhances reaction rates can lead to a better characterization of nanoconfinement—the first step towards smarter nanoconfined catalyst design. A nanoconfined microenvironment is a characteristic feature of the activated silver nanoparticle/ordered ligand interlayer catalyst. This nanoconfined region is hypothesized to facilitate CO₂ electrochemical reduction to CO at selectivities as high as 98% compared to H₂.

We use density functional theory to a) study conditions to create nanoconfinement, b) design systems to create it more energy efficiently, and c) demonstrate why it enhances CO₂ reduction in this catalyst. First, we show that nanoconfinement can only be created at highly negative potentials. As the potential becomes more negative, the surface repels the ligand more strongly, causing it to detach from the surface one bond at a time. At highly negative potentials, the ligand completely detaches, forming a pocket in the metal/ligand interlayer. This is the nanoconfined pocket. Second, we explore ways to create nanoconfinement efficiently by decreasing the magnitude of the potential needed to build it. Since the charge transfer between Au and the ligand is lower than Ag, it is easier to detach the ligand and create nanoconfinement at lower potentials in Au-doped catalysts. The opposite is true for Cu dopants. Further, we show that this phenomenon can be captured by electronegativity differences between the metal and ligand. Finally, we investigate CO₂ reduction reaction rates under nanoconfinement. The reaction intermediates adsorbed on the surface are further stabilized by the hydrogen bonds with the confining ligand. Thus, by stabilizing key intermediates, nanoconfinement enhances overall reaction rates. This series of computational investigations is advancing our understanding of electrochemistry under confinement, offering a new way to improve CO₂RR conversion efficiency.

Elucidating the multidimensional electronic spectroscopy of Nile blue in ethanol using machine learning based molecular dynamics simulations

Joseph Kelly¹ (Presenter), Michael Chen¹, Andrew Snider², Frank Hu¹, Angela Lee³, Andrés Montoya-Castillo⁴, Tim Zuehlsdorff⁵, Christine Isborn², Gabriela Schlau-Cohen³, and Thomas E. Markland¹

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Understanding the way light and matter interact is fundamental to harnessing a wide range of natural phenomena from photosynthesis to photo-induced chemical reactions. Two-dimensional electronic spectroscopy (2DES) allows one to extract rich information about how the electronic states of light-sensitive molecules, proteins and solid-state materials interact with each other and their surrounding environment. I will present our recent work developing a machine learning framework that uses atomistic dynamics and electronic structure to simulate and understand 2DES spectra and apply this to Nile blue in ethanol. This work offers insight into how molecules behave in complex environments and how this manifests in 2DES signals.

Calculating Absorption and Fluorescence Spectra for Chromophores in Solution with Ensemble Franck-Condon Methods

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Accurately modeling absorption and fluorescence spectra for molecules in solution poses a challenge due to the need to incorporate both vibronic and environmental effects, as well as the necessity of accurate excited state electronic structure calculations. Nuclear ensemble approaches capture explicit environmental effects, Franck-Condon methods capture vibronic effects, and recently introduced ensemble-Franck-Condon approaches combine the advantages of both methods. In this study, we present and analyze simulated absorption and fluorescence spectra generated with combined ensemble-Franck-Condon approaches for three chromophore-solvent systems and compare them to standard ensemble and Franck-Condon spectra, as well as to experiment. Employing configurations obtained from ground and excited state ab initio molecular dynamics, three combined ensemble-Franck-Condon approaches are directly compared to each other to assess the accuracy and relative computational time. We find that the approach employing an average finite-temperature Franck-Condon lineshape generates spectra nearly identical to the direct summation of an ensemble of Franck-Condon spectra at one-fourth of the computational cost. We analyze how the spectral simulation method, as well as the level of electronic structure theory, affects spectral lineshapes and associated Stokes shifts for 7-nitrobenz-2-oxa-1,3-diazol-4-yl (NBD) and Nile Red in dimethyl sulfoxide (DMSO), and 7-methoxy coumarin-4-acetic acid (7MC) in methanol. For the first time, our studies showcase the capability of combined ensemble-Franck-Condon methods for both absorption and fluorescence spectroscopy and provide a powerful tool for simulating linear optical spectra.

Mechanomechanistic Changes in Dioxetane Dissociation

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In polymer mechanochemistry, molecules of interest are pulled upon by the transduction of forces from large polymer chains. This leads to (usually designed, constructive) chemical reaction through the use of mechanical energy. However, these reactions may occur through unexpected pathways. 1,2-Dioxetane is a 4-membered ring that chemiluminesces upon thermal or mechanochemical dissociation via what is formally a retro-[2+2]-cycloaddition. In the thermal decomposition of dioxetane, its O–C–C’–O’ dihedral angle increases as the two oxygen atoms rotate away from each other, leading initially to an O–O bond scission to a biradical. This reaction mechanism has been investigated in numerous studies both experimentally and theoretically. It has been suggested that the mechanically activated pathway goes through a very similar mechanism to the thermal pathway. In this work, we show that dioxetane only becomes a mechanophore above a certain threshold force, at which point its dissociation mechanism switches to one in which C–C scission precedes O–O scission. Specifically, we show how the O–O scission pathway is largely unaffected by applied forces, while the C–C scission pathway becomes more energetically accessible as the magnitude of applied forces increases, and how C–C scission first consequently becomes the operative mechanism of dissociation. We further investigate how mechanochemical pulling on different atoms in the molecule to cause different directions of torque reshapes the force-modified potential energy surface of the molecule in different ways.

Dark State Trapping in *o*-Nitrophenol

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Here, we consider *o*-nitrophenol, which has long held the interest of the photochemical community due to its potential implications for atmospheric chemistry and because its simplicity enables its chemical motifs (intramolecular hydrogen bonding, push-pull substituents) to be studied without an assortment of confounding variables. Equation-of-motion coupled cluster singles and doubles (EOM-CCSD) electronic structure calculations reveal a low-lying dark $n \rightarrow \pi^*$ state which results in population trapping, impeding internal conversion and possibly the generation of nitrous acid (HONO). Hole-hole Tamm-Dancoff approximation (hh-TDA) non-adiabatic dynamics simulations predict <50% internal conversion to the ground electronic state within 1 ps, as opposed to ~85% for simulations without the $n \rightarrow \pi^*$ state. We find pathways connecting S_1 to S_0 via both $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ states which are characterized by a rotation of the newly formed HONO group and a small ($\sim 93^\circ$) O-N-O angle, respectively. We compare our results to ultrafast electron diffraction (UED) experiments. We also find no evidence of HONO dissociation on either the singlet or triplet manifold within 1 ps, suggesting that *o*-nitrophenol might be of limited consequence for atmospheric chemistry.

Approaching Periodic Systems in Ensemble Density Functional Theory *via* Finite One-Dimensional Models

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Ensemble Density Functional Theory (EDFT) is a generalization of ground-state Density Functional Theory (GS DFT), which is based on an exact formal theory of finite collections of a system's ground and excited states. EDFT in various forms has been shown to improve the accuracy of calculated energy level differences in isolated model systems, atoms, and molecules, but it is not yet clear how EDFT could be used to calculate band gaps for periodic systems. We extend the application of EDFT toward periodic systems by estimating the thermodynamic limit with increasingly large finite one-dimensional "particle in a box" systems, which approach the uniform electron gas (UEG). Using ensemble-generalized Hartree and Local Spin Density Approximation (LSDA) exchange-correlation functionals, we find that corrections go to zero in the infinite limit, as expected for a metallic system. However, there is a correction to the effective mass, with results from tri-ensembles similar to literature on 2D and 3D UEGs, indicating promise for non-trivial results from EDFT on periodic systems. Singlet excitation energies are found to be positive, but triplet excitation energies are sometimes negative (a triplet instability), pointing to deficiencies of the approximations.

Reference: <http://arxiv.org/abs/2402.17742>

Energy Level Engineering of Molecular Plasmon through Cavity Quantum Electrodynamics Configuration Interaction Theory and Dimer Interaction

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Abstract: Polaritons are hybrid light-matter states arising from the quantum mechanical superposition of photonic states and matter states in a cavity. The photons can hybridize with different type of matter states such as electronic and vibrational excitations, leading to different polaritons. In an optical cavity, the molecular systems interact with the quantized electromagnetic fields. For a certain cavity frequency, the Rabi splitting can be observed between upper polariton (UP) and lower polariton (LP). The degree of splitting was be tuned by changing the cavity strength. In this study, we demonstrated both cavity quantum field and inter-molecule interaction can be used for precise tuning the energy level, while the molecule in cavity can further consider the strong interaction. Naphthalene, the simplest molecule with plasmon-like character, is an ideal structure for understanding the origin of plasmon resonances. From the plasmon hybridization model, the dimers are showing a bright state red shifts with the interparticle distance decrease when the transition dipoles are oriented along interaction axis. While the bright state blue shifts when the transition dipoles are perpendicular to the interaction axis. Therefore, tuning the interparticle distance for dimer system and cavity field can be effective methods for engineering the optical properties.

The Adiabatic Connection for Finite Temperature Strictly Correlated Electrons

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The strictly correlated electron approach is extended to thermal density functional theory, building on well-known work in this area at zero temperature, which gives a description of electron-electron interaction that should inherit the same idiosyncrasies as modern density functional theory with a Kohn-Sham reference system. The finite-temperature upside-down adiabatic connection is an integral expression for the decorrelation free energy, a quantity of interest in simulations of planetary cores and fusion experiments. This approach smoothly connects a thermal ensemble of strictly correlated electrons to one with realistic interaction strength, while requiring that the density of the system remain fixed across all interaction strengths. The asymmetric Hubbard dimer allows for an exact demonstration of finite-temperature adiabatic connections. The properties of the upside-down adiabatic connection in a variety of regimes are presented using this exactly solvable model, along with their extraction from the traditional finite-temperature adiabatic connection formula. The zero-temperature strictly correlated Hubbard dimer is demonstrated and connected to known correlation expansions. A strong dependence on temperature in the curvature of the finite temperature strictly correlated Hubbard dimer's integrand is demonstrated.

Do Solvated Chromophores Have Energy Gaps That Follow Gaussian Statistics

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Understanding the nature of energy fluctuations in different environments is crucial for developing realistic models and predictions. Linear response approximations to modeling dynamics and spectroscopy often assume Gaussian statistics for the energy gaps of molecules in solution. Our study quantifies the energy gap distributions for various solvated molecular systems, assessing how well they adhere to Gaussian statistics. We investigate how molecules behave in different environments when exposed to light or undergoing chemical changes, primarily using a method called density functional theory (DFT) to predict molecular behavior. Density functional theory focuses on where electrons are likely to be found around atoms, aiding our understanding and prediction of electron cloud behavior, which is crucial for how atoms and molecules interact. We evaluated solvated systems in three ways to address the following questions: (1) Does increasing the number of solvent molecules result in fluctuations becoming more Gaussian? (2) Do different strengths of solute-solvent interactions affect the distribution? (3) How does modeling the solvent environment as classical fixed-point charge with molecular mechanics (MM) vs with quantum mechanics (QM) change the distribution? Using the TeraChem computational chemistry software program, we computed excitation energies using the time-dependent density functional theory method with the CAM-B3LYP functional and 6-31+G* basis set. Our solvated systems consisted of four different chromophores - Cresyl Violet, Nile Red, the chromophore of green fluorescent protein, and the chromophore of photoactive yellow protein - surrounded either by methanol or water solvent molecules. Our initial results indicate that as we increase the number of solvent molecules, the fluctuation of energies becomes less Gaussian, challenging current assumptions in the field. Additionally, when changing the solvent model from MM to QM, we observed that the distributions also become less Gaussian.

Acknowledgement

We would like to express our sincere gratitude to the UCOP MRPI for their generous funding through the California Interfacial Science Institute. Additionally, we acknowledge the support provided by the Leaning Aligned Employment Program (LAEP), funded by the California Student Aid Commission. This research was made possible through their financial support, which greatly contributed to the success of our project.

Implementation of Time-dependent Hartree-Fock in the real-space Octopus code

Uday Panta, David A. Strubbe

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Time-dependent Hartree-Fock (TDHF), although an old approach, still finds its place in electronic structure theory because of its relatively cheap cost compared to more accurate post Hartree-Fock methods like higher order Configuration Interaction (CI) or Coupled Cluster. Its version under the Tamm-Dancoff approximation is Configuration Interaction Singles, which is widely used and particularly applicable to big molecules where more accurate methods may be unfeasibly expensive. TDHF also has similar building blocks as compared to other approaches which allows us to implement other approaches using the framework from TDHF. As its application is mostly aimed towards atoms and molecules, TDHF is mostly implemented using Gaussian basis sets. Real-space implementation of TDHF is rarely seen because of the additional cost of solving exchange integrals in grid-based approaches, which is also the case for ground-state Hartree-Fock and hybrid DFT functionals.

We have implemented TDHF in Octopus, a real-space code, and performed a benchmark study of excitation energies from full TDHF and TDHF-TDA on a set of molecules, comparing to a Gaussian implementation [Gould et al., Phys. Chem. Lett. 13, 2452 (2022)] and also to the “Theoretical Best Estimate” of Loos et al., J. Chem. Theory Comput. 14, 4360 (2018)]. We also compare the absorption spectrum from full TDHF to that from real-time TDHF. We show solutions to the difficulties in solving the ground-state HF in real-space, which is the first step to TDHF, in terms of the starting guess for SCF, mixing schemes for faster convergence, and the Adaptively Compressed Exchange (ACE) formalism to calculate the exact exchange.

Reference: <http://arxiv.org/abs/2405.01522>

Recovering dynamic correlation for SA-CASSCF with diabatic shifts: the diabatize-shift-diagonalize method

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Quantitatively accurate simulations of non-adiabatic molecular dynamics require both static and dynamic electron correlation. State-Averaged Complete Active Space Self-Consistent Field (SA-CASSCF) captures static correlation, allowing for qualitatively correct descriptions of potential energy surfaces (PES) and non-adiabatic couplings, but does not effectively treat dynamic correlation. Multi-state perturbation theory (MSPT) on top of SA-CASSCF reference wavefunctions can capture dynamic correlation but adds a significant computational cost. In our work, we demonstrate that by performing a unitary transformation of our reference wavefunctions, the CASSCF diabats, into a set of diabatic electronic states, the correlation energy recovered with MSPT is effectively constant or slowly varies with changes in molecular geometry. We leverage this finding to efficiently recover dynamic correlation in SA-CASSCF dynamics by diabatizing the CASSCF wavefunctions for each geometry, shifting the diagonals of the diabatic Hamiltonian by a constant shift computed for a reference geometry, and then rediagonalizing the resultant Hamiltonian. Applying Boys diabatization to SA-CASSCF wavefunctions, we validate this diabatize-shift-diagonalize (DSD) approach by reproducing the non-adiabatic dynamics of photoexcited ethylene on MS-CASPT2 surfaces.

A Continuum Picture of Absorption Near Liquid-Vapor Interface

Kritanjan Polley (Presenter) and David T. Limmer

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Abstract

The molecular details of the interaction of incoming particles at the liquid-vapor interface are amazingly complex with complicated fluctuations assisting the chemical and physical processes. An explicit molecular dynamics (MD) simulation contains all this information in great detail, often making them too hard to identify. A continuum picture with stochastic differential equations that incorporates some of those molecular details provides us with a better understanding of the interfacial phenomenon. The early time non-equilibrium dynamics of absorption depends strongly on the spatially dependent friction which we propose to compute by combining MD trajectories and stochastic differential equation.

Here we look at the nature of absorption of ozone to an air-water interface containing sodium halide ions. We highlight the computation of mass accommodation coefficient and uptake coefficient (its reaction with iodide) within the continuum framework. The mass accommodation gives us insight about the fraction of incoming solute particles enters the bulk phase through the interfacial region while the uptake coefficient tells us what fraction of ozone is lost to its reaction with iodide compared to desorption to the gas phase. We also investigate the super-Maxwellian nature of helium evaporation from an air-water interface.

Static and Dynamic Condensed Phase Linear and Nonlinear Optical Spectroscopy Through Second-Order-Cumulant-Based Correlation Function and Franck-Condon Methods

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Optical linear and nonlinear spectroscopy are sensitive to environmental and vibronic effects, and both effects must be included for accurate spectroscopic simulations. Explicit solvent environments can be sampled with molecular dynamics trajectories on the ground and excited states. Vertical excitation energies computed along the trajectory can be used to build an energy gap correlation function for use within the 2nd order cumulant approximation to the linear response function for simulation of absorption and emission that account for explicit environment and vibronic coupling. Here we will compare this dynamic 2nd order cumulant approximation to the correlation function approach to the static approaches based on normal modes employing both the 2nd order cumulant approximation and the exact Franck-Condon (FC) solution. With the static approaches, in a frozen solvent environment, we compute the normal modes of both the ground and excited states and map the harmonic potential energy surfaces to compute either the static 2nd order cumulant and FC spectra. In addition, we utilize the recently developed ensemble-FC method by computing a set of FC spectra throughout the trajectory to merge them into a single ensemble-FC spectrum. We compute linear and nonlinear spectra with and without environments, showcasing environmental effects on spectra, while comparing them to experiments.

Renormalization of Exciton Binding by Polar Phonons in 2D Perovskites

Rohit Rana (Presenter), David T. Limmer

University of California, Berkeley

Two-dimensional materials have gained great interest due to the enhanced tunability of optical properties through layer compositions. In accordance with experiment, the ionic character of hybrid organic-inorganic perovskites leads to excitons interacting with a strong polarization generated by optical phonons. To understand the physics of this interaction, a model Hamiltonian was created in which an exciton couples linearly to the lattice polarization. This Hamiltonian was then treated within a path integral Monte Carlo framework. It was found that the quantum and dielectric confinement of these perovskites result in non-trivial trends of charge-phonon coupling as a function of inorganic layer thickness. Furthermore, accounting for charge-phonon interactions in these perovskites brings theoretical exciton binding energies in better agreement with experiment.

Developing efficient targeted eigensolvers for tensor network states

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Interior eigenstates are responsible for many interesting phenomena like core ionization processes, conical intersections, and high-frequency regions of vibrational spectra.[1] However, an accurate description of this part of the eigenspectrum can be extremely challenging, and there are fewer algorithms available for this challenge. The reason is twofold: (a) the high density of states that lead to slow convergence of the optimization procedure and may cause root-flipping problems, and (b) the intrinsic strong correlation of the excited states that requires an appropriate wave function to account for the correlation. We aim to solve part (a) by using the Lanczos method in inaccurate Krylov expansions of the spectrally transformed Hamiltonian by Carrington et. al. (the inexact Lanczos method) and the complex contour integration of Green's function by Polizzi (the FEAST method) to explicitly target interior eigenstates.[2] For part (b), we use tensor network states, which are capable of capturing the higher degrees of correlation and groups of different degrees of correlation.[3] For a test instance of the circular well problem, we have found that the FEAST method works reasonably well, but the inexact Lanczos method is performing by an order of magnitude better. So far, we have seen that the inexact Lanczos method has demonstrated excellent performance in determining the vibrational levels of acetonitrile. Our preliminary findings indicate the potential of targeted eigensolvers for interior eigenstates in conjunction with tensor network states.

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Modeling Magnetic Field Effects on Spin-Dependent Reactions with Nonadiabatic Statistical Theory

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Abstract: The application of an external magnetic field to chemical reactions holds significance as it provides a novel element for controlling the reaction rate, potentially leading to the development of more efficient reactions that rely on magnetic properties of molecules. In this study, we explore a theoretical framework aimed at modeling spin-orbit coupling mediated transitions between electronic states with different spin multiplicities in the presence of an external magnetic field. Our approach incorporates the Zeeman interaction (interaction of electron spin with an external magnetic field) into the spin-dependent kinetics equations, alongside the spin-orbit interaction. The foundational equations of this investigation are derived within the framework of nonadiabatic statistical theory (NAST). We have integrated the external magnetic field effect into our NAST software package. The approach relies on electronic structure calculations to compute the Landau-Zener transition probabilities and the associated rate constants for spin-dependent processes. Our primary focus centers on the application of an external magnetic field to singlet-triplet transitions. We systematically examine the influence of the magnetic field on the spin adiabatic states for various field strengths, covering examples that span different spin-orbit coupling regimes. This comprehensive analysis allows us to gain a deeper understanding of the intricate interplay between the spin-orbit coupling and magnetic field effects in spin-dependent chemical reactions. As an example, we calculate the rate constants for singlet-triplet transitions in $\text{Ni}(\text{dpp})\text{Cl}_2$ (dpp=1,3-bis(diphenylphosphino)propane) in the presence of an external magnetic field.

Title:

Influence Of Explicit Solvent Environments On Band Gap And Excitation Energy Statistics for the Anionic GFP Chromophore

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Abstract:

Optical spectroscopy is sensitive to the condensed phase and interfacial environment of a chromophore and accurate simulation of spectra can connect experiment to molecular level insight. However, simulating optical spectroscopy is often heavily influenced by the quality of the underlying excited state method used to model the ground to excited state transition. Time-Dependent Density Functional Theory (TDDFT) is a common approach, with charge transfer excitations often modeled correctly with long-range corrected hybrid functionals. In recent work, our group has observed a significant deviation in simulated optical spectra for the GFP chromophore in water for TDDFT with CAM-B3LYP and higher level wave function based EOM-CCSD methods, which we believe demonstrates a failure of TD-CAMB3LYP in capturing the response of this anionic chromophore to its aqueous environment, potentially due to under-polarization. Here we present a cursory initial analysis of DFT band gaps and TDDFT excitation energies for the GFP chromophore in water with different methods, which we aim to use as a baseline for the benchmarking and application of novel electronic structure methods.

Adaptive Machine Learning-Assisted Semiempirical Quantum Chemistry

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Understanding the mechanisms that underpin chemical and biological processes under realistic conditions is crucial for the development of novel pharmaceutical and technological applications. Over the past years, machine learning (ML) has revolutionized our approach to gain such insights promising to bypass the prohibitive costs of *ab initio* calculations. However, the lack of general applicability of data-driven ML models can represent a fatal pitfall – especially in the context of dynamics, where a single unphysical prediction can lead to an irreversible simulation breakdown. One computationally-efficient alternative is semiempirical quantum chemistry (SEQC), which constructs effective, reduced-order Hamiltonians from parametric interaction models. Due to the involved approximations, however, SEQC can show poor accuracy outside the domain of its usually fixed, elementwise parametrization. Here, we present a combined formalism of SEQC and ML. In this hybrid approach, we go beyond the limitations of global elementwise parametrizations, introducing environment-dependent atomwise parameters predicted via ML. In particular, we introduce a parameter Delta-learning model, where ML predicts corrections to a reference SEQC parametrization rather than the full parameter set. Using kernel-based learning and uncertainty measures, this allows to leverage the reference parameters as fallback solution in low-confidence regions away from training instances and to avoid fatal generalization errors during dynamics simulations. The ML-based, dynamic atom-typing significantly improves the accuracy and transferability of the model, while the underlying SEQC formalism encodes the fundamental principles of quantum mechanics and provides deeper chemical insights, as well as access to electronic structure properties. We showcase the reliability and data-efficiency of our hybrid approach for hydrocarbons, where we achieve good accuracy in energetics, structure, and electronic properties across a wide range of equilibrium and non-equilibrium conformations with remarkably few training instances. The hybrid ML-SEQC approach is thereby able to capture interactions across scales and can be easily incorporated into well-established quantum chemistry workflows. Combining the best of both worlds, we foresee the synergy of ML and adaptive, semiempirical Hamiltonians to offer a promising route towards the accurate description of practically-relevant systems at realistic length and time scales.

New directions for the Bethe-Salpeter equation: spin flips and forces

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The GW approximation and Bethe-Salpeter equation (GW/BSE) is an approach for electronic energy levels and optical spectra based on Green's functions and many-body perturbation theory. Originally applied to bulk semiconductors, this approach is being increasingly used for molecular systems as well. I will show two ways that ideas from quantum chemistry can be used profitably with GW/BSE.

Open-shell systems, including molecules and defects, are interesting platforms for spin physics and quantum information, but their multi-determinantal states are difficult to handle with conventional first-principles calculations. A solution is the spin-flip approach: the ground and excited states are considered as spin-flipping excitations of a single-determinant high-spin reference state. We introduce spin-flip to the GW/Bethe-Salpeter approach (SF-BSE) for applicability to solids [1]. Through calculations of the S^2 operator on our states [2], we find only small spin contamination in our results.

Excited-state forces or analytic gradients are commonly studied in quantum chemistry but have been rarely considered in GW/BSE. We have developed an accurate and computationally efficient approximation for analytic forces in GW/BSE, based on density-functional perturbation theory. With our implementation with the BerkeleyGW code, we can study phenomena like self-trapped excitons, coherent excitation of vibrations, light-induced degradation, exciton-phonon coupling, and vibronic effects in optical spectra. The approach can be applied to SF-BSE as well.

[1] Bradford A. Barker and David A. Strubbe, "Spin-flip Bethe-Salpeter equation approach for ground and excited states of open-shell molecules and defects in solids," arXiv:2207.04549 (2022).

[2] Bradford A. Barker, Arabi Seshappan, and David A. Strubbe, "Computation of the expectation value of the spin operator S^2 for the Spin-Flip Bethe-Salpeter Equation," arXiv:2402.17719, *Electronic Structure* (under review) (2024).

Biomimetic Modeling of Non-Heme Iron Halogenase Enzymes

Dante Waltonen, Mason Mcanally

CSUS

Dr. Benjamin Gherman

CSUS

Non-heme iron halogenase enzymes are a class of enzymes that catalyze the halogenation of organic compounds in various bio-organic reactions. An understanding of their reactivity provides potential for development of new halogenation catalysts and less toxic routes to halogenation reactions employed in organic chemistry syntheses. Biomimetic modelling has been used to study these enzymes, based on a model by Que et al, $[\text{Fe}^{\text{IV}}(\text{O})(\text{TQA})(\text{Cl}/\text{Br})]^+$ (TQA= tris(quinolyl-2-methyl)amine)), which is the first synthetic model showing chemoselective halogenation reactivity (J. Am. Chem. Soc., 2016, 138, 2484-2487). Prior research done by our lab focused on determining the energetics of the halogenation reaction with the TQA model system using computational chemistry with density functional theory (DFT), cyclohexane and toluene as substrates, and Cl and Br as the halides. Both the high spin (S=2) and low spin (S=1) states for the Fe^{IV} metal center were modeled, as Que et al showed that successful halogenation depended on the spin state. Our current research is focused on a related biomimetic model system employing the ligand TPA=tris(pyridyl-2-methyl)amine, which does not show halogenation reactivity (Inorg. Chem., 2006, 45, 6435-6445). TPA was chosen to compare with the data from TQA in order to understand the chemoselective reactivity seen in the TQA system. The reaction was modeled in two steps: 1) hydrogen atom abstraction by the Fe^{IV} -oxo complex from the substrate produces a substrate radical and iron(III)-hydroxyl complex as intermediates; 2) halogenation or hydroxylation of the substrate radical occurs from recombination of the intermediates. The TPA study similarly included Cl and Br as the halides, cyclohexane and toluene as the substrates, and low and high spin states for the iron center.

Water in Proton Transfer Channels of Respiratory Complex I

Panyue Wang, Alexei Stuchebrukhov

University of California Davis

We study proton pumping mechanism of respiratory complex I. Complex I, or NADH-dehydrogenase, is a redox-driven proton pump in the electron transport chain of aerobic cells that creates proton gradient across the inner mitochondrial membrane, which in turn drives ATP synthesis in cells. Two problems are addressed in the current stage of the project. 1. Finding proton transfer (PT) channels/pathways. 2. Finding water in proton transfer channels.

Water plays an important role in proton transfer in respiratory complex I; therefore, finding water molecules buried inside complex I is key to solve the proton transfer mechanism. Proton channels are predicted by a modified program Caver, which is based on Voronoi's partitioning method in the spatial analysis of protein structure. Thus, a central axis continuous proton transfer channel was identified. To find water molecules along the central axis of complex I, we have developed an improved version of Dowser++ which incorporates Caver, the docking programs Autodock Vina and WaterDock. The position of the calculated water molecules was compared to recent cryo-EM data from *Y. Lipolytica* (7o71).

More efficient *ab initio* methods: GPU-accelerated density fitting and functionals support from libxc DFT functional library

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The density fitting approximation expedites the calculation of Coulomb (J) and Hartree-Fock exchange (K) contributions to the Fock matrix by decomposing four-center, two-electron repulsion integrals (ERIs) into products of two- and three-center integrals through the use of auxiliary basis sets. We have developed GPU-accelerated algorithms for evaluating the relevant integrals and perform tensor-matrix contractions for constructing J and K matrices. Preliminary implementation in the TeraChem software package shows enhanced performance for single-point energy calculations of medium-sized molecules. However, for larger systems, computational bottlenecks arise when computing three-centred center integrals before contraction and storing three-indexed intermediates. Future revisions aim to bypass these limitations by recalculating three-centred center integrals to directly contract with the density matrix for each self-consistent field (SCF) iteration. We also enable usage of meta-generalized gradient approximations in TeraChem through interfacing with the libxc library for density functional approximations. It is therefore possible to perform GPU accelerated calculations with many highly accurate modern density functionals for large chemical systems, providing flexibility to users without compromising computational efficiency.

GPU-Accelerated Integrals for Molecular and Periodic Systems

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TeraChem is a GPU-accelerated electronic structure package that was historically optimized for molecular calculations involving light elements. We have extended TeraChem's applicability to metals and extended materials by implementing support for f-type orbitals and periodic boundary conditions. Support for higher angular momentum basis functions necessitated rewriting of TeraChem's GPU-accelerated electron integral kernels with a SymPy-based metaprogramming code to carry out the McMurchie-Davidson recurrence relation and convert the equations to efficient CUDA algorithms. We use Nvidia Nsight tools to identify the bottlenecks in the integral kernels and fine-tune the generated kernels for new generations of GPU hardware. We also implemented integrals for Γ -point periodic calculations with Gaussian basis functions. Using the Ewald summation scheme, we designed two kernel functions for every electrostatic integral, one for real space and one for reciprocal space. A preliminary implementation shows a 2 – 10 times speedup compared to CPU-based software, and a 10 – 50 times slowdown compared to the molecular calculation on one unit cell.

Post Transition State Surface Intersection in PTAD-Bicyclobutane Cycloaddition

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Abstract. Herein we report an investigation of Post Transition State Surface Intersection between radical and zwitterionic states causing reaction path bifurcation through *ab initio* molecular dynamics with unrestricted density functional theory in Bicyclobutane–Triazolinedione(PTAD) Cycloadditions. We revealed that a single closed-shell transition state can lead to two distinct products connected by Intrinsic Reaction Coordinate (IRC) calculations with the usage of restricted or unrestricted Kohn Sham wavefunction caused by spin symmetry breaking after the transition structure, leading to a diradical intermediate and a ring-opened zwitterionic product. We also show that under different solvent polarity or gas phase, the product ratio could change significantly, presumably through mediation of the early or late onset of spin symmetry breaking, leading to interesting nonstatistical dynamic effects. Our predicted results were corroborated by experiments. This work should lead to helpful insights in terms of control of side product formation for reactions involving diradicals and bicyclobutane chemistry.

Toward an automatic assignment of vibrational eigenstates
in protonated water clusters
Wolfgang Kern, Henrik R. Larsson

Water exhibits quantum effects that are not completely understood. One striking example is the pH value of 7, which would be 8.5 if water were classical. The Zundel ion (H_5O_2^+) is a prototypical building block of acidic water that is useful for studying these quantum effects. The strong anharmonic and fluxional nature of this 15-dimensional system is difficult to simulate, but recently we were able to use novel methods based on Tensor Tree Network States (TTNSs) to obtain more than one thousand vibrational eigenstates of the Zundel ion to high accuracy. By assigning these eigenstates in terms of approximate quantum numbers, we can gain deep insight into the structure of the states and vibrational spectrum. However, assignment of these wavefunctions is cumbersome, as it involves manual inspection and analysis of excitation patterns using plots of wavefunction cuts. Here, we outline three ways to improve and automate this assignment: (1) Apply transformations to different curvilinear coordinates that decouples the vibration to facilitate the classification of excitation patterns. (2) Use natural orbital decompositions in subsets of the 15 available dimensions to facilitate understanding of coupling. (3) Use unsupervised artificial neural networks to cluster visual features of the plots of wavefunction cuts. By employing these improvements, we will be able to more quickly and accurately assign the eigenstate wavefunctions of the Zundel ion. With these assignments, we will be able to improve our understanding of the quantum effects of protonated water clusters. Our proposed techniques are general and can be applied to any vibrational system.

GPU accelerated molecular dynamics via the many-body expansion

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Ab initio methods provide insight into molecular properties but require significant computational resources. Fragmentation techniques alleviate this burden but have historically been limited to small fragmentation sizes. With TeraChem, our GPU-accelerated software, we expand fragment sizes to enable large fragment calculations at the DFT level of theory. Strategies such as ensembling and minimizing fragment contact area reduce errors. We demonstrate proof of principle on water clusters (50-750 molecules) and provide an initial look at dynamics with intent to expand to large protein systems in the future.

Photochemical Ring-Opening Dynamics of Diarylethenes

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Abstract: Diarylethenes (DAEs) are a class of molecular compounds that are building blocks for photomechanical switch materials. These materials can uniquely convert photon energy into macroscopic mechanical work, through light-actuated mechanical deformation. Although DAE holds promise for a wide range of energy harvesting and conversion applications, bulk DAE materials are severely limited in their mechanical behavior, such as their tendency to fracture upon light actuation. Therefore, it is critical to understand the DAE's molecular-level photochemistry and connect its molecular photochemical mechanism to macroscopic material performance. To address this issue, in the current work, we present an *ab initio* molecular dynamics study to discover the photochemical ring-opening reaction of three representative DAE molecules. We leverage *ab initio* multiple spawning (AIMS) for nonadiabatic molecular dynamics and state-averaged complete active-space self-consistent field theory for electronic structure modeling. The AIMS dynamics simulation shows that the three DAE molecules exhibit distinct photo-excited-state lifetimes and different open-ring product yields. Furthermore, we found the yields of open-ring products of the three DAE compounds may correlate with their excited-state lifetimes. Future work will include investigations on the topology of the excited-state potential energy surfaces and consequently, the underlying effects on the photochemical lifetime and product yields of DAE compounds.

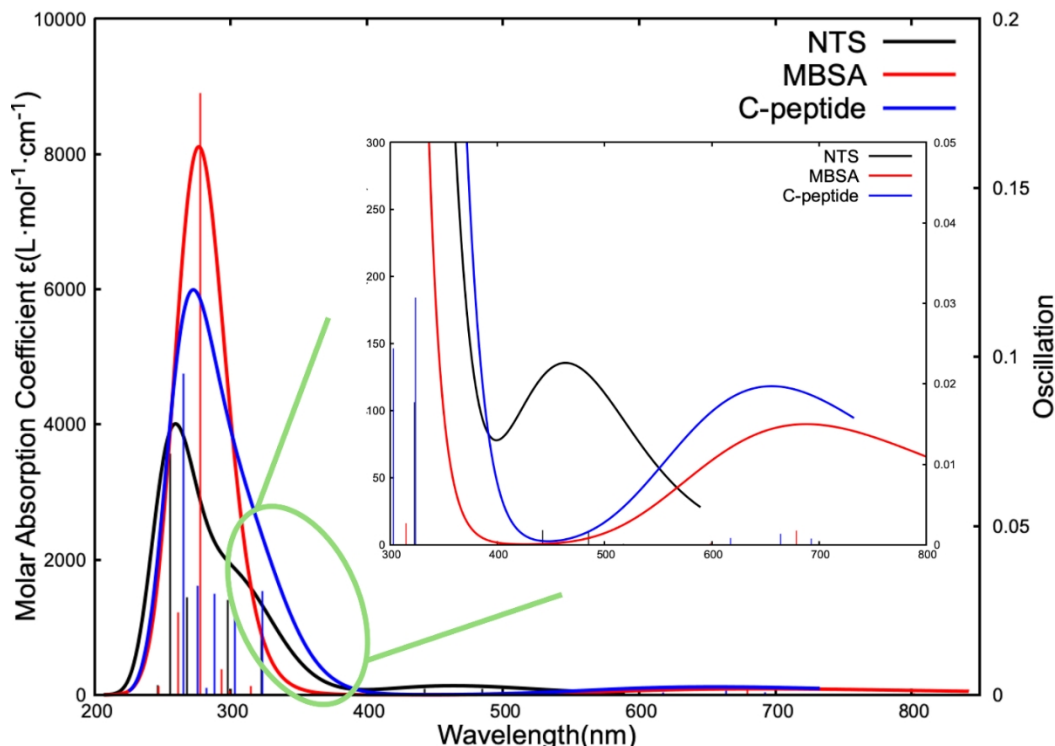
Hypothetical ternary complex with copper, C-peptide, albumin with high UV-Vis absorbance by a state-targeted geometry optimization.

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C-peptide has been identified as an important biomarker involving in insulin production and treatment for various pancreatic diseases. It is also reported to be responsible for Cu(II) delivery in human body cooperating with human serum albumin (HSA). In this study, computational UV-Vis spectra of Cu(II) in complex with C-peptide or HSA is obtained within 0.05 eV difference compared to experiments and also provides additional insight into the possible structures of the ternary complex by proposing several model complexes and comparing their TDDFT-predicted absorption spectra with experiments. A new geometry optimization method tailored to searching structure with high absorption in specific wavelength is proposed. A ternary complex including all three species is found by applying this method with an agreement of experimental high absorbance, which can be considered as a promising ternary structure for further investigation. The following analysis points out that distance between Cu(II) and backbone ligands in this complex have a strong effect in absorbance.

Computational UV-Vis spectrum



Effect of the Protonation States of Titratable Residues on Fluorescent Proteins Dynamics

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Understanding the protonation equilibrium of fluorescent protein residues, especially those that are highly buried and form hydrogen bonds with the chromophore, is crucial for modeling the photochemical properties of fluorescent proteins since these protonation equilibria influence the geometry and the electrostatic environment of the chromophore. Using mCherry as a model, we explore the protonation effects of two ionizable residues located $<4\text{\AA}$ from the chromophore, GLU 215 and LYS 70, on the protein dynamics at pH=7.5 (**Figure 1**). Constant pH molecular dynamics reveal all four microstates exist with different probabilities. GLU 215 protonation depends on its conformation relative to the chromophore imidazole ring and local solvation, while LYS 70 protonation relies more on its salt bridge with GLU 148. These microstates alter the chromophore geometry and hydrogen bonding patterns on the ground state, leading to different accessibility to twisted conical intersections on the excited state S_1 . Clockwise twisting of the imidazole ring of the chromophore on S_1 increases with GLU 215 protonation, leading to a larger non-radiative decay rate, whereas its deprotonation blocks both chromophore rings from twisting on S_1 due to increased hydrogen bond formation at the phenol oxygen (O_P) and less favorable electrostatic environment for twisting around the imidazole ring. These insights aid in designing RFP variants with lower non-radiative decay rates, addressing questions on blocking 'dim' microstate decay channels and stabilizing 'bright' microstates.

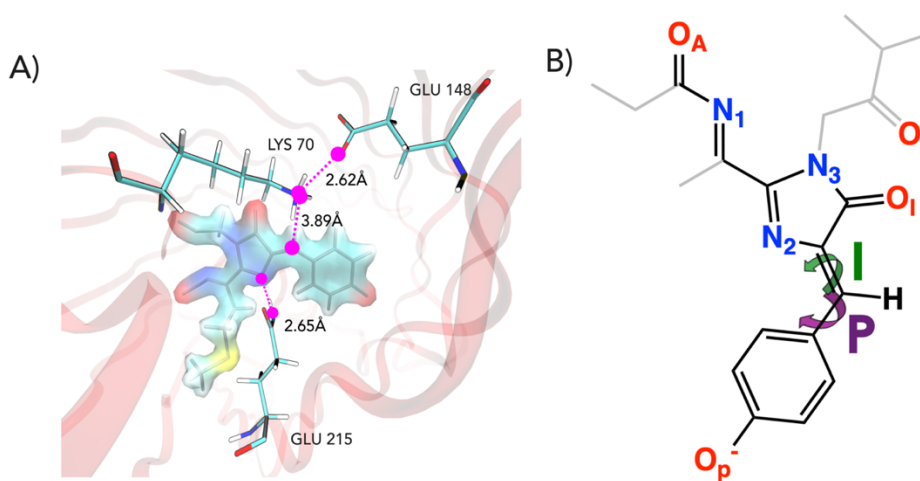


Figure 1. A) The positions of buried ionizable residues (LYS 70, GLU 215, and GLU 148, colored sticks) relative to the chromophore in the crystal structure of mCherry. LYS 70 and GLU 215 are within 4\AA of the chromophore, and GLU 148 can form a salt bridge with LYS 70. B) The detailed structure of the RFP chromophore. The I dihedral and the P dihedral are specified by the green and purple arrows, and the conjugated structure is bolded with black bonds.