POSTER SESSION

Monday, June 5th 7:00pm to 9:00pm

Vishikh Athavale	University of Pennsylvania
Sarah Bard	Princeton
Paul Bailey	University of Utah
Isaac Brown	University of Utah
Junhuan Chen	University of Pennsylvania
Renai Chen	Los Alamos National Lab
Moshe Chesler	University of Arizona
Megan Davis	Los Alamos National Lab
Nikita Fedik	Los Alamos National Lab
Aaron Forde	Los Alamos National Lab
Harshad Gajapathy	Ohio State University
Suresh Gnawali	Georgia State University
Jeffrey Gorman	MIT
Sarah Grefe	Los Alamos National Lab
Donghyo Hahm	Los Alamos National Lab
Guiying He	CUNY
Sheng He	Emory
Giyang. Hu	University of Hong Kong
Maksim Kulichenko	Los Alamos National Lab
Jason Kusznski	Florida State University
Deseree Lai	North Seattle College
Thanh Hai Le	Los Alamos National Lab
Hao Li	University of Houston
Xinyang Li	Los Alamos National Lab

Tuesday June 6th 7:00pm to 9:00pm

Clement Livache	Los Alamos National Lab
Sam May	University of Pennsylvania
Declan McCarthy	UC, Boulder
Carlos Mora-Perez	University of Southern Cali.
Aiswarya Mohanpatra	UC, Boulder
Yeonsig Nam	UC, Irvine
Thabassum Nattikallungal	USC
Daniel Nikiforov	University of Utah
Catrina Oberg	Princeton
Connor Orrison	Los Alamos National Lab
Yamuna Paudel	City University of New York
Gabriel Phun	Los Alamos National Lab
Valerio Pinchetti	Los Alamos National Lab
Varunprasaath Selvaraju	UC, Boulder
Marvin Schumaker	UC, Boulder
Syed Shah	Los Alamos National Lab
Mohammad Shakiba	Univeristy of Buffalo
Vidushi Sharma	Los Alamos National Lab
Colette Sullivan	Florida State University
Yanze Wu	University of Pennsylvania
Mingbin Yuan	Los Alamos National Lab
Hao Zhang	Rice University
Qingxin Zhang	University of Buffalo

TDDFT-1D: A Novel Path in Photophysical Studies

Vishikh Athavale

University of Pennsylvania

vishikh@sas.penn.edu

Investigating photophysical and photochemical processes in solvent environments presents a challenge in computational chemistry. A crucial component for accurate modelling of these processes is the development of efficient and precise electronic structure methods for the quantum description of the subsystem of interest. In this study, we introduce the TDDFT-1D method, which employs fictitious DFT/TDDFT wave functions within a larger configuration interaction Hamiltonian framework, incorporating one doubly excited state. This innovative approach allows for the generation of physically meaningful potential energy surfaces in the vicinity of avoided crossings and conical intersections between the singlet ground state (S_0) and excited states (S_n).

To further enhance our understanding of these processes in complex environments, we adopt multiscale approaches, such as the mixed quantum mechanics/molecular mechanics (QM/MM) method. By applying nonadiabatic dynamics to the prototypical photoswitch model system of 1,3-cyclohexadiene, we are able to observe the electronic relaxation process from an electronically excited state. We then extend our investigation to explore more intricate processes, such as ultrafast charge transfer in donor-acceptor species.

Our findings highlight the potential of the TDDFT-1D method and multiscale approaches for providing insights into photophysical and photochemical processes in solvent environments, ultimately paving the way for the development of more efficient and accurate computational models in theoretical chemistry.

Resolving the Effects of Thin Film Annealing on Molecular Polaritons and Cavity Absorption

Sarah Bard

Princeton

sbard@princeton.edu

Molecular polaritons form from the strong, collective coupling of molecular electronic transitions to a common photon mode in an optical cavity. We aim to illuminate how the preparation of the organic thin film in the cavity impacts polariton formation and subsequent cavity absorption. Experimentally, we varied the post-deposition annealing of the cavity sample layer containing PDI-DPP-PDI, a molecule that is susceptible to annealing-based reorientation while maintaining its main electronic excitation. Through comparison of experimental and simulated cavity absorption spectra for each annealing type, we found that annealing and consequently the mesoscale changes in the film resulted in a slowing of the molecular dephasing timescale. We concluded that this homogenous broadening, as opposed to inhomogeneous, static disorder, was the main contributor to differences in the polariton linewidths over the various annealing types. Furthermore, the reorientation of PDI-DPP-PDI upon certain annealing conditions resulted in additional, non-dominant excited state species coupling to the cavity photon mode off-resonantly. While the cavities were fabricated identically with the same molecule, the sole variation of film preparation through annealing showed significant effects on molecular properties, polariton formation, and cavity absorption.

Time-of-flight Carrier Mobilities of Hybrid Organic-Inorganic Perovskites

Paul Bailey

University of Utah

u0972040@utah.edu

Hybrid organic-inorganic perovskites (HOIPs) are of interest because of their favorable optoelectronic properties—such as their wide absorption range, long carrier diffusion length, and low exciton binding energy—relevant to semiconductor devices such as photovoltaics, photodetectors, and light-emitting diodes. We study the carrier mobilities of HOIP single crystal photodiode devices using the time-of-flight (TOF) method. TOF involves exciting carriers at one electrode using a pulsed laser. After which, an applied bias pulls carriers through the device and we measure the corresponding photocurrent. We show that the charge transport is dispersive in HOIPs, leading to a field and thickness dependent carrier mobility.

Excited State Absorption of the Rashba Band in Metal Halide Perovskites

Isaac Brown

University of Utah

Isaac.brownh@gmail.com

Two-dimensional (2D) layered hybrid organic-inorganic perovskites can form natural “multiple quantum wells” that have strong spin-orbit coupling due to the heavy elements they contain. This may lead to “Rashba splitting” close to the extrema in the electron bands. We have measured ultrafast transient photoinduced absorption. In the excited state pumped by a 400 nm pulse, we then use mid-infrared absorption to probe the energy of these Rashba bands directly in thin films of 2D perovskite, namely, (C6H5C2H4NH3)2PbI4, or PEPI. From this, we obtain a Rashba energy splitting of (20 ± 5) meV and Rashba parameter of(1.6 ± 0.1) eV·Å. This finding shows that 2D hybrid perovskites have great promise for potential applications in spintronics. Additionally, the study of n=2 PEPI reveals the structural dependence of this Rashba splitting.

Nonadiabatic Potential Energy Surfaces For A Molecule on a Surface as Found by Constrained Complete Active Space Theory

Junhan Chen

University of Pennsylvania

chenjunh@sas.upenn.edu

In order to study electron-transfer mediated chemical processes on a metal surface, one requires not one but two potential energy surfaces (one ground state and one excited state) as in Marcus theory. In this letter, we report that a novel, dynamically-weighted, state-averaged constrained CASSCF(2,2) (DW- SA-cCASSCF(2,2)) can produce such surfaces for the Anderson Impurity model. Both ground and excited state potentials are smooth, they incorporate states with a charge transfer character, and the accuracy of the ground state surface can be verified for some model problems by renormalization group theory. Future development of gradients and nonadiabatic derivative couplings should allow for the study of non-adiabatic dynamics for molecules near metal surfaces.

Phononic heat current manipulation at the molecular-level using temperature modulations

Renai Chen

Los Alamos National Laboratory

renaic@lanl.gov

In recent years, nanoscale heat transfer has gained significant attention, particularly in the context of molecular heat conduction. Advances in molecular synthesis techniques have made it possible to fabricate a broad range of molecular structures that could potentially be used to advance the field of phononics. One promising approach is to manipulate the heat current through the device by modulating its temperature. This has been demonstrated experimentally in macroscale systems, and we extend this mechanism to the nanoscale by applying a stochastic Langevin framework to describe the energy transport properties of a particle connecting two heat baths with different temperatures, where the temperature difference between baths is oscillating in time. Our theoretical framework includes Langevin dynamics and Nonequilibrium Green's function approaches. Using stochastic molecular dynamics simulations, we confirm the validity of our theoretical approach for examining thermal transport in driven systems. Analytical expressions for the energy flux of each heat bath and for the system itself are derived for the case of a free particle and a particle in a harmonic potential. Our results indicate that controlling molecular heat currents using time-periodic temperature modulations could be used to advance the design of molecule-based thermal devices, and could be a potential route to control energy storage and release in nanosystems.

Exciton basis MRSDCI calculations of electronic structure of intramolecular singlet fission molecules

Moshe Chesler

University of Arizona

mchesler@arizona.edu

Singlet Fission (SF) is a spin-allowed multichromophore process in which a singlet exciton reached optically undergoes internal conversion to a bound triplet-triplet spin biexciton, which may further dissociate into two free triplets, each of which may contribute to the photoconductivity of an organic solar cell. In order to achieve a quantitatively accurate description of the relevant excited states of SF systems, one must perform high order calculations that capture the contributions of the multiple excitations characterizing these states. While doing so is possible within the standard molecule orbital theory, the results give little to no intuition about the physical nature of these states in SF candidate materials. We thus investigate relevant materials within the so-called exciton basis, a hybrid between molecular orbital theory and configuration space, which gives a pictorial description that allows clear identification of how the individual monomers within an oligomer contribute to the relevant excitations. We present results of these calculations on various materials which demonstrate the necessity of retaining high order excitations in gaining a clear picture of the relevant SF states and the utility of the exciton basis in yielding pictorial results which are easy to interpret physically.

F12+EOM Quartic Force Fields for Rovibrational Predictions of Electronically Excited States

Megan Davis

Los Alamos National Laboratory

megand@lanl.gov

Quartic force fields (QFFs) constructed using a sum of ground-state CCSD(T)-F12b energies with EOM-CCSD excitation energies are proposed for computation of spectroscopic properties of electronically excited states. This is dubbed the F12+EOM approach and is shown to provide similar accuracy to previous methodologies at lower computational cost. Using explicitly correlated F12 approaches instead of canonical CCSD(T), as in the corresponding (T)+EOM approach, allows for 70-fold improvement in computational time. The mean percent difference between the two methods for anharmonic vibrational frequencies is only 0.10%. A similar approach is also developed herein which accounts for core correlation and scalar relativistic effects, named F12cCR+EOM. The F12+EOM and F12cCR+EOM approaches both match to within 2.5% mean absolute error of experimental fundamental frequencies. These new methods should help in clarifying astronomical spectra by assigning features to vibronic and vibrational transitions of small astromolecules when such data is not available experimentally.

Synergy of Semiempirical Quantum Mechanics and Machine Learning

Nikita Fedik

Los Alamos National Laboratory

nfedik@lanl.gov

Pure machine learning approaches have achieved remarkable success in chemistry and material science, but their performance often decreases when applied to new regions of chemical space. Models such as interatomic potentials lack electronic structure information, hindering their transferability. To overcome these limitations, our group has been focusing on the development of PYSEQM (Pytorch-based Semiempirical Quantum Mechanics), differentiable physics model that combine domain knowledge of quantum mechanics with machine learning as a corrective tool. Work in progress includes development of the excited states capability based in CIS and RPA approaches solved in a reduced space through Davidson diagonalization routine.

Non-Equilibrium and Equilibrium Charge-Transfer Excited-States in Molecules and Materials

Aaron Forde

Los Alamos National Laboratory

aforde@lanl.gov

Charge-transfer states arise at interfaces which are important in a variety of scenarios, such as charge-separation in the reaction centers of photosynthetic systems and at donor-acceptor regions in opto-electronic devices. Charge-transfer excited-states are elusive to capture accurately with *ab Initio* electronic structure as they require inclusion of long-range electronic exchange interactions as well as inclusion of dynamic changes in solvent degrees of freedom describing dielectric relaxation. For molecular systems, to illustrate the distinction between non- equilibrium and equilibrium solvation we explore a recent class of donor-acceptor dyads. They are based on the fluorescent BODIPY functionalized with triphenylamine (TPA) which shows the peculiar property of dual fluorescence. We use time-dependent density functional theory to characterize the energetic alignment of excitonic and charge-transfer states in a BODIPY-TPA molecular complex. We observe that using a long-range exchange corrected functional in combination with state- specific solvation scheme, as opposed to linear-response solvation, gives a qualitatively correct alignment of the exciton and charge-transfer states with an enhancement in oscillator strength for the equilibrium solvated charge-transfer state, in agreement with experiment.[1] For materials, we investigate the role of non-equilibrium charge-transfer excitations in A_2PbBr_4(A=PEA,NEA) Ruddleson-Popper lead halide perovskite for sensitizing naphthalene (NEA) accepting units. Excited-states are computed using the Bethe-Salpeter equation using GW computed electronic structure. We identify the lowest-excited state as having charge-transfer character, indicating that sensitization occurs via 2-step charge transfer as opposed to triplet energy transfer. These methods of electronic structure provide pathways to describe non-adiabatic excited-states involving charge-separation and charge-transfer recombination pathways.

(1) Forde, A.; Freixas, V. M.; Fernandez-Alberti, S.; Neukirch, A. J.; Tretiak, S. Charge-Transfer Luminescence in a Molecular Donor–Acceptor Complex: Computational Insights. *The Journal of Physical Chemistry Letters* **2022**, *13* (37), 8755-8760. DOI: 10.1021/acs.jpclett.2c02479.

Observing Transient Magnetic Oxidation States with Magnetic Circular Dichroism Spectroscopy

Harshad Gajapathy

Ohio State University

gajapathy.1@buckeyemail.osu.edu

Hydrogen is considered a clean fuel for vehicles and electricity generation. Photocatalytic water splitting provides hydrogen from clean and renewable resources. Although metal-based electrocatalysts have been studied for electrochemical water splitting, metal oxides with properly aligned band gaps provide the possibility for direct solar-to-chemical energy conversion by photocatalytic water splitting. It has been shown that catalysts with spin-polarized charge carriers favor the production of triplet oxygen over competing peroxide during water-splitting, but controlling spin polarization at semiconductor photoelectrodes remains a challenge due to the lack of methods available to directly probe the underlying electron spin dynamics. In this talk, I will discuss recent measurements of electrons and spin in Yttrium Iron Garnet ($Y_3Fe_5O_{12}$, YIG) using time-resolved extreme ultraviolet reflection-absorption and magnetic circular dichroism spectroscopy. This method provides direct observation of electron and magnetic moment dynamics at the surfaces with element and spin state resolution. YIG is a ferrimagnetic semiconductor with two different lattices of tetrahedral and octahedral Fe(III) atoms with opposite spins. The measurements on YIG show lattice-dependent electron dynamics upon photoexcitation. When excited above the bandgap, a charge transfer occurs from oxygen to iron atoms. Depending on the lattice of iron where the electron is excited, the dynamics of these charge transfer electrons vary. The electrons in the octahedral iron form a small polaron at the surface. The tetrahedral electrons are more mobile and diffuse from surface to bulk forming a natural spin filter. This filtering of spin depending on the lattice causes the surface to be spin-polarized. The surface polarization can be observed through XUV magnetic circular dichroism experiment. This surface spin accumulation results in spin-polarized photocatalysis in YIG.

Optical Nonlinearities in Graphene Quantum Dots: High Harmonic Generation

Suresh Gnawali

Georgia State University

sgnawali1@gsu.edu

Graphene quantum dots (GQDs), the graphene nanoparticles of a few nanometers excited by an ultrafast optical pulse of a few femtoseconds, exhibit several optical nonlinearities, including residual population and high harmonic generation (HHG). By introducing dephasing, we addressed nonlinearity, namely HHG in GQDs placed in a short linearly polarized optical pulse. At short finite dephasing times, the ultrafast electron dynamics show significant irreversibility with a large residual population of the excited quantum dot levels. When dephasing time increases, intensities correspond to a low-frequency boost, while the cutoff energy decreases regarding the high harmonic spectra. The cutoff energy's dependence on the optical pulse's amplitude is also sensitive to the frequency of the pulse. This dependence is almost linear when the optical pulse frequency is much less than the quantum dot band gap. However, when the pulse frequency is comparable to the band gap, the cutoff energy shows saturation behavior at a large field amplitude, >0.4 V/Å. In triangular graphene quantum dots with zigzag edges, the intensities of high harmonics show a strong dependence on the initial electron population of the edge states of the quantum dot. If a zigzag triangular quantum dot possesses an even number of edge states, then, even high harmonics are strongly suppressed when half of the edge states of the quantum dots are populated before the pulse. For any other populations of the edge states, the odd and even harmonics are of comparable intensities.

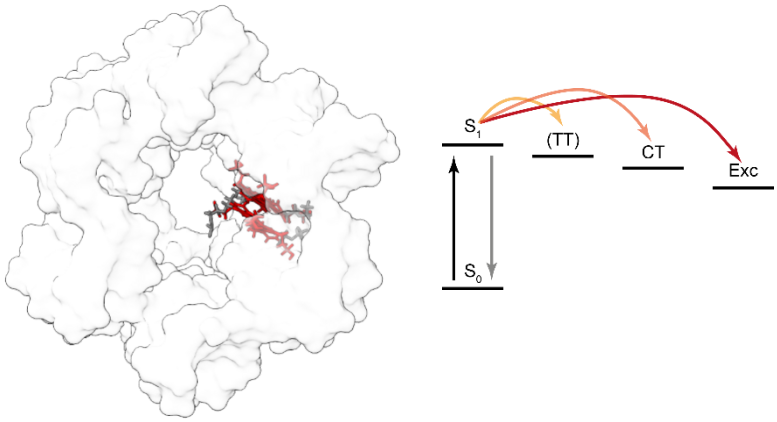
Probing the exciton dynamics of strongly-coupled chromophores using DNA origami libraries

Jeffery Gorman

Massachusetts Institute of Technology

jegorman@mit.edu

Molecular aggregates mediate many photophysical processes in optoelectronic devices. Exciton theory shows the spatial relationships between dyes are critical to the transport and conversion of absorbed energy and electrons. Whilst models successfully predict the behaviour of excitons through aggregates, our ability to synthetically generate molecular networks with the prescribed nanoscale structure is lacking. To address this, we study the exciton evolution between strongly coupled perylene diimide (PDI) pairs scaffolded in DNA. PDIs are exemplar molecular aggregates as they produce a range of photoinduced excited states, including Frenkel excitons, symmetry-broken charge-transfer states, excimers, and singlet-fission borne triplets, depending on the spatial organization. To study how we can map a specific excited-state pathway to a PDI structure, we exploited the molecular precision of DNA base-pairing and nanoscale rigidity of DNA origami to generate a library of PDI-DNA origami constructs. Using ultrafast spectroscopy, we identified constructs that gave rise to different photoinduced species, including excimers and charge-transfer states, which are often implicated in tuning singlet fission pathways. Then, computational modelling allowed us to pinpoint geometrical features that can be linked to a specific excited-state pathway. Our synthetic DNA platform offers the ability to rapidly survey the structure-property of molecular aggregates and identify optimized structures that can be useful for applications in excitonic devices, including solar conversion and quantum information.



Comparing Nonlinear Optical Responses of Topology and Correlations

Sarah E. Grefe

Los Alamos National Laboratory

seg@lanl.gov

In addition to many-body properties (such as charge dynamics) associated with strong correlations, high-harmonic generation via high-intensity pulse probes have been recently proposed to detect nontrivial topology through Berry curvature contributions to the second harmonic. Despite this, determining which and how higher order harmonic spectral features correspond to band structure properties has been challenging, calling for suitable platforms that can explore the signatures of strong correlation physics and topology. The Weyl-Kondo semimetal presents an elegant solution: the experimental material $Ce_3Bi_4Pd_3$[1-3] and the concurrently developed theoretical model[4-5] display strong-correlation-driven topology. The Weyl-Kondo semimetal model can be tuned from Kondo to valence regime, and from topological semimetal to trivial insulator phases, independently. We therefore study the high-harmonic generation of the Weyl-Kondo semimetal model, using a Peierls-substituted noncentrosymmetric periodic Anderson model including spin orbit coupling. We study the response of the Weyl-Kondo semimetal phase in contrast with a topologically trivial Kondo insulator, and compare to the response of their uncorrelated, itinerant-electron-only counterpart models. We further uncover the significance of features of high-harmonic generation spectra to many-body dynamics through analyzing the nonequilibrium spectral function and band topology by detection of nontrivial Berry curvature-originated second harmonic response.

[1]S. Dzsaber et al., PRL 118, 246601 2017
[2]S. Dzsaber et al., PNAS 118, 8 2021
[3]S. Dzsaber et al., Nat Commun 13, 5729 2022
[4]H.-H Lai, S. E. Grefe, S. Paschen, & Q. Si: PNAS 115, 93 2018
[5]S. E. Grefe, H.-H Lai, S. Paschen, & Q. Si: PRB 101, 075138 2020; arXiv:2012.15841; JPS Conf. Proc. 30, 011013 2020
*This work was supported by the U.S. DOE NNSA under Contract No. 89233218CNA000001 through the LANL LDRD Program, DOE Office of Science Energy Frontier Research Center for the Advancement of Topological Semimetals, and the Center for Integrated Nanotechnologies, a DOE BES user facility.
LA-UR-23-25393

Bright and fast trion-based single-photon emitters using charged colloidal QDs in a current-focusing LED

Donghyo Hahm

Los Alamos National Laboratory

donghyohahm@lanl.gov

Extensive research has been conducted on single-photon sources for their applications in photonic quantum information technologies. However, there is still a need to develop stable, room temperature single-photon sources that can be excited electrically. In this presentation, we will share new and unpublished findings on a background-free, non-blinking, narrowband, and stable single-photon electroluminescence achieved at room temperature. The photon repetition rates obtained are comparable to the radiative rate. This achievement is made possible by using continuously-graded quantum dots (QDs) with a robust structure that allows for high current densities at the individual QD level. We analyze our results using a current focusing model and a detailed carrier dynamics model, solved through a 22-state rate equation matrix. The excellent agreement between our experimental results and the models validates our findings.

Direct Exciton Harvesting from a Bound Triplet Pair

Guiying He

CUNY

ghe@gn.cuny.edu

Singlet fission (SF) has received considerable attention because of its potential to overcome the Shockley-Queisser limit on the power conversion efficiency (PCE) of solar cells. SF is a multiexciton generation process, in which two triplet excitons form from a single absorbed photon. However, ambiguities within this definition arise due to the complexity of the various double triplet states that exist in SF chromophores and corresponding interconversion processes. To clarify this process, singlet fission is frequently depicted as sequential two-step conversion in which a singlet exciton decays into a bound triplet pair biexciton state which dissociates into two "free" triplet excitons. However, this model discounts the potential for direct harvesting from the coupled biexciton state. Recently, intramolecular SF (iSF) in covalent dimers and oligomers are widely studied because of their well-controlled morphology and electronic coupling. The bound triplet pair state of the isolated covalent system in solution does not dissociate readily, allowing for more thorough studies of the multiexciton state, but is a disadvantage for triplet harvesting. Since the limit of geometry, more than half of triplet state will be lost in a dephasing process. We demonstrate that individual triplet excitons can be extracted directly from a bound triplet pair prior to dephasing. Due to the requirement for geminate triplet-triplet annihilation in iSF compounds, unique spectral and kinetic signatures can be used to quantify triplet pair harvesting yields. We achieve an internal quantum efficiency for triplet exciton transfer from the triplet pair of greater than 50%, limited only by the solubility of the compounds. The harvesting process is not dependent on the net multiplicity of the triplet pair state, suggesting that an explicit dissociation step is not a requirement for using triplet pairs to do chemical or electrical work.

Ultrafast Laser-Pulse-Controlled Tunneling Currents in Scanning Tunneling Microscopy

Ziyang Hu

University of Hong Kong

qiyanghu@yangtzee.hku.hk

Controlling and detecting electron transfer processes in their intrinsic timescale is a goal pursued by nano scientists. Scanning tunneling microscopy (STM) can probe electron densities with sub-Angstrom spatial resolution. By introducing ultrafast lasers with specific profiles, the tunneling currents in STM can be precisely controlled. With two pump-probe pulses, the temporal information of electron transfer can be captured by the pump-probe interval. Recording integrated currents at different spatial sites with varying intervals can thus reveal the electron transfer process in real space and time.

Using non-equilibrium Green's function formalism, we showed theoretically that the integrated tunneling currents induced by a laser pulse with stable carrier envelope phase (CEP) can be controlled by tuning the duration and CEP of the pulse. The experimentally observed phase shift between the integrated current and the electric field is mainly caused by the third-order response. When the full-width half maximum (fwhm) is large enough, the third-order signal vanishes, thus the integrated current will be independent of the CEP. [1]

We then demonstrated that using two CEP-stable pump-probe pulses, the electron transfer between modeled sites can be tracked in real space and time. Large fwhm (20 fs) is adopted to eliminate the influence of the CEP. Real-time NEGF simulations showed that the fourth-order integrated current with pump-probe interval Δt is related to the occupation of electrons at the time Δt after the initial excitation. This observation pushes the temporal resolution from the limitation of electronics to the delay time of two pulses on a femtosecond timescale. [2]

[1] Carrier-Envelope-Phase Modulated Currents in Scanning Tunneling Microscopy, Z. Hu, Y. H. Kwok, G. H. Chen, and S. Mukamel, *Nano Lett.*, 2021, **21**, 6569.
[2] STM Imaging of Electron Migration in Real Space and Time: A Simulation Study, Y. H. Kwok, G. H. Chen, and S. Mukamel, *Nano Lett.*, 2019, **19**, 7006.

Semi-Empirical Shadow Molecular Dynamics: A PyTorch Implementation

Maksim Kulichenko

Los Alamos National Laboratory

maxim@lanl.gov

Direct Born-Oppenheimer molecular dynamics (BOMD) requires an expensive iterative SCF optimization of density matrix which hinders long-scale simulations of large systems. We present the most recent formulation of Extended Lagrangian Born–Oppenheimer Molecular Dynamics (XL-BOMD) which avoids SCF optimization and propagates electronic degrees of freedom along with ionic motion, implemented in the semiempirical PyTorch-based software PySeQM. The implementation includes finite electronic temperatures, canonical density matrix perturbation theory, and an adaptive Krylov subspace approximation for the integration of the electronic equations of motion within the XL-BOMB approach (KSA-XL-BOMD). The PyTorch implementation leverages the use of GPU and machine learning hardware accelerators for the simulations. The new XL-BOMD formulation allows studying challenging chemical systems with charge instabilities and low electronic energy gaps. Applied to molecular dynamics, simulation of 840 carbon atoms, one integration time step executes in 4 s on a single Nvidia RTX A6000 GPU.

A Schematic for Plasmon-Induced Hot Carrier Excited-State Dynamics in Semicondcutor Nanocrystals

Jason Kuszynski

Florida State University

jkuszynski@fsu.edu

WO_{3-x} is investigated as a model plasmonic wide bandgap semiconductor nanocrystal system to temporally profile the relaxation of hot carriers after direct excitation of the plasmon in the femtosecond to nanosecond regime. It is found that hot carriers generated from plasmon excitation relax through the electronic band structure of the semiconductor through both inter- and intraband pathways. Additionally, this work shows that the plasmon is a resonance state where hot carriers are only generated from direct excitation with the plasmon and cannot be accessed through relaxation pathways of the electronic structure alone. These results are generalizable for n-type, plasmonic transparent conducting oxide nanocrystals and address the UV-Vis-NIR range of femtosecond transient absorption features that are observed from LSPR excitation and contrasted directly with optical band gap pump experiments as a control.

Organic Photovoltaics: Undergraduate Synthesis of Poly(3-Hexylthiophene)

Deseeree Lai

North Seattle College

deseree.lai@hotmail.com

Organic photovoltaic (OPV) solar cells present promising solutions in photovoltaic technology due to their lower cost and the abundance of materials compared to earlier solar technologies. As energy costs rise, OPV's are increasingly of interest as a source of energy. The development of new curricula using a socio-scientific issues (SSI) framework can encourage students to consider careers in organic chemistry to fill these critical needs in global energy. The SSI framework also allows students in the developing stages of their STEM pathway to engage more deeply in traditionally 'weed-out' coursework and develop skills which will allow them to persist through STEM. We have designed a laboratory experiment using a SSI framework to allow undergraduate organic chemistry students to explore OPV's current energy. Students synthesize poly(3-hexylthiophene) (P3HT), the active layer of an OPV cell and a promising polymer in OPV technology due to its stability and scalability. Undergraduates also build and strengthen skills of fundamental processes of organic chemistry using Grignard monomer formation and gain insight into the benefits and current challenges of organic solar cells, increasing their scientific literacy. Synthesis is conducted without the use of an inert atmosphere, lowering the barrier to implementation in under-resourced learning environments. This laboratory protocol exposes students early in their STEM careers to SSI-based learning in OPV technology and allows them to see connections in coursework to broader global issues.

Expanding the interface engineering toolbox for bright, efficient, and stable Green-Light-Emitting Diodes

Thanh Hai Le

Los Alamos National Laboratory

thanhhai@lanl.gov

Lead halide perovskite polycrystals are considered highly promising for next-generation ultrahigh-definition displays due to their ability to deliver vivid and pure colors, along with a wide color gamut. However, the practical implementation of these materials faces a major obstacle: poor stability caused by the migration of halide ions at the grain boundaries of perovskite polycrystal thin films. This persistent issue presents a significant challenge that needs to be addressed. In this study, we propose an interface engineering strategy using small molecules to mitigate detrimental halide ion migration and stabilize perovskite polycrystals. We employed a tetraoctylammonium bromide solution processed through a direct-treatment method to efficiently passivate three-dimensional perovskites. Our results demonstrate that tetraoctylammonium ions effectively inhibit bromide ion migration in lead halide perovskite polycrystal thin films. Through surface passivation, the polycrystal thin film exhibited a high absolute photoluminescence quantum yield (PLQY) of approximately 100% and excellent stability during air storage. These findings suggest that the synthesized materials have the potential to be used in the fabrication of bright, efficient, and stable Green-Light-Emitting Diodes.

A non-stationary stochastic approach to spectral line shapes in 2D perovskites

Hao Li

University of Houston

hli36@central.uh.edu

Stochastic models have a long and important history in optical spectroscopy, particularly for spectral line broadening. Here, we developed a stochastic many-body approach that describes the exciton dynamics in the presence of a non-stationary and co-evolving background population of excitations, which is appropriate for cases using broadband laser pulses. Starting from a field theory description for interacting bosonic excitons, we derive a reduced model in which bright excitons are coupled to an incoherent background of dark excitons. The latter can be described as a Heisenberg-Langevin equation and hence be solved as an Ornstein-Uhlenbeck process. The model is applied to interpret the evolution of 2D line shapes observed in 2D metal-halide perovskite derivatives. We further generalize the stochastic approach by including the exchange coupling to the bath, and showcase its distinct spectral features.

Predicting Excited-State Properties with Hierarchically Interacting Particle Neural Network

Xinyang Li

Los Alamos National Laboratory

lix@lanl.gov

When molecules are coupled to an optical cavity, a new light-matter hybrid state, called polaritons, is formed. Recent experiments have shown that polariton chemistry can be used to manipulate chemical reactivities. However, simulating an ensemble of molecules in the excited state coupled to a cavity mode is both theoretically and computationally challenging. Recent advances in machine learning techniques have shown great potential in modeling chemical systems in the ground state. In this work, we present a general protocol to predict excited-state properties, such as energies, transition dipoles, and non-adiabatic coupling vectors with the hierarchically interacting particle neural network, and applying these predictions to excited-state polariton chemistry potential energy surfaces and spectra in the collective coupling regime.

Towards a colloidal quantum dot laser diode: gain/loss engineering in an LED device

Clement Livache

Los Alamos National Laboratory

livache@lanl.gov

Laser diodes based on solution-processable materials can benefit numerous technologies including integrated electronics and photonics, telecommunications, and medical diagnostics. An attractive system for implementing these devices is colloidal semiconductor quantum dots (QDs). The progress towards a QD laser diode has been hampered by rapid nonradiative Auger decay of optical-gain-active multicarrier states, fast device degradation at high current densities required for laser action, and unfavorable competition between optical gain and optical losses in a multicomponent device stack. Here we resolve some of these challenges and demonstrate optically excited lasing from fully functional high-current density electroluminescent (EL) devices with an integrated optical resonator. This advance has become possible due to excellent optical gain properties of continuously graded QDs and a refined device architecture, which allows for highly efficient light amplification in a thin, EL-active QD layer.

Spin-Orbit versus Hyperfine Coupling-Mediated Intersystem Crossing in a Radical Pair

Sam May

University of Pennsylvania

samrmay@sas.upenn.edu

While spin–orbit coupling (SOC) is typically the dominant interaction that couples singlet and triplet states within individual chromophores, hyperfine coupling (HFC) becomes important in multichromophoric systems, particularly in relation to the radical pair mechanism. Here, we use TD-DFT to calculate the spin–orbit coupling and hyperfine coupling between the first singlet and triplet charge transfer states of the radical pair ^{2}Pyrene^{-} and ^{2}*N*,*N*-dimethylaniline^{+}. We show that, as the intermolecular donor–acceptor distance grows, SOC decays to zero (as one would expect) because singlet and triplet states are characterized by identical orbitals in space, while the HFC remains comparatively constant. The switching region occurs around 4 Å, beyond which HFC dominates over SOC as far as defining the rate of intersystem crossing (ISC).

A crosslinkable and n-dopable electron transporting copolymer for perovskite solar cells

Declan McCarthy

University of Colorado, Boulder

declan.mccarthy@colorado.edu

We synthesize a photo-crosslinkable naphthalene diimide (NDI) copolymer with a cinnamate pendant moiety as a crosslinkable electron transporting layer (ETL) for solution processed n-i-p perovskite solar cells. The crosslinked ETL exhibits high transparency over 90% in the visible region, higher thermal stability (>300 °C) and lower surface energy compared to its non-crosslinked counterparts. We measure a lower function of ITO with photo-crosslinkable naphthalene diimide (NDI) copolymer. Our solar cell device results show that the crosslinked NDI polymer gives higher open-circuit voltage (V_{OC}), fill factor (FF), power conversion efficiency (PCE), and less hysteresis than its non-crosslinked counterpart. The average of V_{OC} is enhanced to ~1.08 V from ~ 1.05 V with PCE increasing to 15.10% from 13.31%, followed by the enhancement of FF to 64.43% on average from 58.77%. We ascribe the improved performance to decreased work function of NDI-CL modified ITO, reduced nonradiative recombination and higher shunt resistance with crosslinked NDI polymer-based perovskite solar cells.

Hot-Electron Cooling in Lead-Halide Perovskite Nanomaterials

Carlos Mora-Perez

University of Southern California

morapere@usc.edu

The hot phonon bottleneck effect has been the subject of rigorous investigation within perovskite research. Despite wide acceptance of its existence, an increasing body of evidence suggests potential disruption of these phonon bottlenecks. Applying state-resolved pump/probe spectroscopy (SRPP) and time-resolved photoluminescence spectroscopy (t-PL) has been instrumental in examining hot exciton relaxation dynamics in perovskites. Recent t-PL experiments conducted on perovskite nanocrystals presented definitive evidence contradicting the presence of a hot phonon bottleneck, thereby deepening our understanding of these materials. We have employed ab initio quantum dynamics simulations to investigate the underlying processes further. Our research focuses on the effects of Auger and electron-vibrational relaxation processes on electron cooling in $CsPbBr_3$ and $FAPbBr_3$ perovskites. The Auger mechanism posits that excess energy from a hot electron can be transferred to a cold hole. Interestingly, when both processes (Auger and electron-vibrational relaxation) are modeled concurrently, the Auger mechanism predominates, resulting in sub-100 fs relaxation time scales. Our study provides pivotal insights into the role of the Auger mechanism within the broader context of perovskite nanocrystal relaxation dynamics. Additionally, I will present work for applying machine learning to chiral molecules for identifying structural features, such as molecular conformation, from their electronic and vibrational circular dichroism spectra.

Protocol for Sequential n-doping of Photo-Crosslinkable Naphthalene Diimide (NDI) Polymer

Aiswaya Abhisek Mohapatra

Colorado State University, Boulder

aimo2902@colorado.edu

To enable solution processability of the subsequent layers and improve chemical stability of the devices, crosslinking of semiconducting polymeric interlayers has been one of the employed strategies. Chemical doping of the interlayers is routinely used to enhance conductivity and achieve desirable energetic alignment with the active layer components. We attempt to immobilize the n-dopants in the interlayer matrix by simultaneous crosslinking that can potentially reduce the ion migration and help in stability. Co-mixing of the dopants and crosslinkers with the naphthalene diimide based side chain polymer resulted in low film retention due to a competitive reduction pathway between the polymer and crosslinker, because of their close lying reduction potential. Whereas sequential treatment of the photo-crosslinked polymer film with dopant solution resulted in n-doping as evident from the polaronic signatures in the visible spectrum. This resulted in more than 3 orders of magnitude increase in the conductivity of the doped and crosslinked film as compared to the undoped. The crosslinked polymer film exhibited better thermal stability, transparency in visible region and helped improve the performance of the n-i-p perovskite cells from 13.31 % to 15.1%.

Real-time monitoring of vibronic coherences and aromaticity in photoexcited cyclooctatetraene with X-ray Probe

Yeonsig Nam

University of California, Irvine

yeonsign@uci.edu

Understanding conical intersection (CI) dynamics and aromaticity changes is key for exploring and controlling photo-reactions in aromatic ring molecules. Real-time monitoring of their relaxation pathways remains a formidable experimental challenge. We simulate the photoinduced S_3 to S_1 non-adiabatic dynamics of cyclooctatetraene (COT), involving multiple CIs with relaxation times in excellent agreement with experiment. We directly probe the CI passages in COT by off-resonant X-ray Raman spectroscopy (TRUECARS) and time-resolved X-ray diffraction (TRXD). We find that these signals sensitively monitor the emergence of vibronic coherence and geometric conformation change, respectively, during the ultrafast dynamics. First, we distinguish two CIs by using TRUECARS signals with their appearances at different Raman shifts. Second, we demonstrate that TRXD, where X-ray photons scatter off electron densities, can resolve ultrafast changes in the aromaticity of COT. It can further distinguish between planar and non-planar geometries explored during the dynamics, as e.g. two different tetraradical-type CIs. The knowledge gained from these measurements can give unique insight into fundamental chemical properties that dynamically change during non-adiabatic passages.

References

Y. Nam et al., Chem. Sci. 2023, 14, 2971-2982

Intra- and Inter-Molecular Charge Transfer Dynamics of Carbene-Metal-Amide Photosensitizers

Thabassum Nattikallungal

University of Southern California

tnk@usc.edu

The detrimental environmental impacts of fossil fuels and increasing energy demand insist on continuing the search for new eco-friendly and sustainable alternatives. Here, we studied a series of carbene-metal-amide (cMa) complexes, where M = Cu and Au, that could be used as sustainable photosensitizers for electrocatalytic reactions. The photophysics is elucidated by employing a set of steady-state and time-resolved spectroscopies. Using ps-to-ns and ns-to-ms transient absorption spectroscopies (psTA and nsTA, respectively), the excited state kinetics from light absorption is elucidated. Ultrafast intersystem crossing (ISC) rates for these compounds were obtained from time-correlated single photon counting (TCSPC) experiments utilizing a thermally activated delayed fluorescence (TADF) model, leading to $\sim 3 - 20 \cdot 10^{!} s^{"}$ rate constants for ISC ($S \rightarrow T$). Further, it's observed that ISC is insensitive to solvent and amide variations whereas ISC varies significantly with metals and carbene ligands. The psTA additionally abstracted an early time ($0.2 - 0.8 \cdot 10^{\#\$} s^{"\#}$) relaxation rate attributed to solvent relaxation and vibrational cooling. The singlet-triplet energy gap ranges from 80-90 meV for Cu to 110 meV for gold-based complexes. The nsTA experiments for a gold-based cMa complex demonstrated efficient intermolecular charge transfer from the excited cMa to either an electron acceptor or donor.

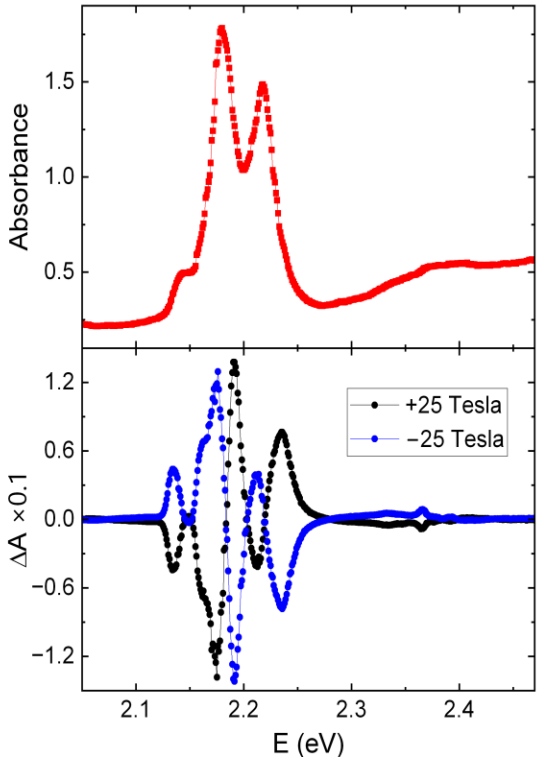
Magnetic Circular Dichroism Spectroscopy in 2D (PEA)2(MA)n-1PbnI3n+1 n=2 films at high field

Daniel Nikiforov

University of Utah

sdanielniki@gmail.com

We have studied films of two-dimensional (2D) (Phenethylammonium)$_2$ (Methyl- ammonium)$_{n-1}$Pb$_n$I$_{3n+1}$ (PEPI) n=2, which is a prototype 2D hybrid organic inorganic perovskite using magneto-circular- dichroism (MCD) and field-induced circularly polarized (FICPO) emission in the Faraday configuration at high magnetic fields (up to 25 Tesla) at liquid- He temperature. Particular attention was given to the exciton fine structure and phonon side bands including the exciton Landé g_{eff}-values. We found evidence for dark and bright exciton sub states and estimated an electron (g_e≈2.1) and a hole (g_h≈−1.1) g-values.



Chirped Laser Pulse Control of Vibronic Wavepackets and Energy Transfer in PC645

Catrina Oberg

Princeton

coberg@princeton.edu

Photosynthetic organisms use light-harvesting antenna complexes to capture solar photons and rapidly funnel the excitation energy to the reaction center. Recent ultrafast spectroscopic studies have revealed that efficient (sub-ps) energy transfer is mediated by vibronic coherence in phycobiliprotein phycocyanin 645 (PC645). Here, we employed broadband pump-probe spectroscopy with linearly chirped excitation pulses to further investigate the relationship between vibronic state preparation and energy transfer dynamics in PC645. Negatively chirped pulse excitation is found to enhance a high-frequency mode (1580 cm^{-1}) that is proposed to bridge the donor-acceptor energy gap, while positively chirped pulses suppress these oscillatory features. Global analysis reveals a slowdown of the first energy transfer event using positively chirped excitation pulses, which suggests that the 1580 cm^{-1} vibronic mode is important to efficient energy transfer on a sub-ps timescale.

Magnetic impurities turn quantum dots into emitters of free electrons

Connor Orrison, Jungchul Noh

Los Alamos National Laboratory

orrison_c@lanl.gov jungchul@lanl.gov

Auger recombination is a non-radiative process wherein an 'energy-donor' electron recombines with a hole, while another 'energy-acceptor' electron captures the released energy and whereby is excited to a higher energy state. This process can be exploited as an up-conversion process through which carrier energies can be increased at the expense of their number. The efficiency of this pathway is limited by intraband relaxation of hot carriers, which can be quantified in terms of an energy gain/loss-rate ratio. In a typical CQD, the Auger lifetime is on the order of tens of ps, while energy losses due to phonon emission occur on a sub-ps time scale. As a result, the energy losses outcompete the energy gains by a factor ~3. Using Mn-doped CdSe CQDs, we demonstrate that the Auger process can be accelerated *circa* 100-fold, thanks to spin-exchange processes between the CdSe excitons and Mn dopant states. These Mn-assisted spin-exchange Auger interactions are due to the formation of hybrid multiexciton states, where the excitonic population is split between CdSe band-edge and Mn ions, owing to ultrafast (<100 fs) spin-exchange exciton transfer. In these doped CQDs, Auger lifetimes are of ~200 - 300 fs, which allow for the energy gain rates to outpace the energy loss rates by a factor of ~7. As a result, a band-edge electron can experience multiple steps of uphill Auger re-excitation and thereby reach a vacuum state outside the dot. We practically demonstrate high efficiency photoemission via two-step spin-exchange Auger recombination using band-edge excitation with visible light pulses. Further, we take advantage of this ionization pathway to achieve high-yield generation of reactive solvated electrons (free electrons stabilized by water molecules) with unprecedented internal quantum efficiency of >3%. These results demonstrate great utility of the discovered effects in practical photoemission and photoconversion technologies.

Gallium Arsenide semiconductor metasurface for the enhancement of photocatalytic activity for chemical energy

Yamuna Paudel

City University of New York

ypaudel@gradcenter.cuny.edu

Solar energy is a continuous renewable source of energy. Utilization of the enormous amount of available solar energy as clean alternative to fossil fuels is extremely important. Besides the most common application of solar cells to produce electricity, there is also potential to use solar energy for hydrogen gas production and industrial waste utilization such as methane and carbon reduction. Although extensive research has been reported in these fields, only a limited fraction of the total energy from the sun can currently be used due to the limitations of today's technology. To this end, a question emerges: Are there suitable earth abundant materials and appropriate ways to utilize the energy from sun more effectively and therefore develop more efficient solar harvesting devices. We purpose to enhance absorption of light in gallium arsenide (GaAs) by patterning a surface with nano pillars to create what is known as meta-surface. Our aim is to design and fabricate ultrathin (~ 150 nm height) structures which exhibit perfect absorption, near zero reflection. Recently we have minimized the optical reflectivity (< 10 %) using above designed method and we also intend to optimize the surface properties, DC conductivity, and carrier dynamics. Finally, we will use the solar energy captured by these enhanced surfaces for hydrogen production by water splitting and other electrochemical process.

Constructing the Mechanism of Dinoflagellate Luciferin Bioluminescence Using Computation

Gabriel Phun

Los Alamos National Laboratory

gphun@uci.edu

Dinoflagellate luciferin bioluminescence is unique since it does not rely on decarboxylation but poorly understood compared to that of firefly, bacteria, and coelenterata luciferins. Here we computationally investigate possible protonation states, stereoisomers, a chemical mechanism, and the dynamics of the bioluminscence intermediate that is re- sponsible for chemiexcitation. Using semiempirical dynamics, time-dependent density functional theory static calculations, and a correlation diagram, we find that the intermediate's functional group that is likely responsible for chemiexcitation is a 4-member ring, a dioxetanol, that undergoes [2π + 2π] cycloreversion and the biolumiphore is the cleaved structure. The simulated emission spectra and luciferase-dependent absorbance spectra agree with the experimental data—giving support to our proposed mechanism and biolumiphore. We also compute circular dichroism spectra of the intermediate's four stereoisomers to guide future experiments in differentiating them.

Unusual optical gain properties of continuously graded quantum dots with strongly suppressed Auger recombination

Valerio Pinchetti

Los Alamos National Laboratory

vpinchetti@lanl.gov

A multi-fold degeneracy of the band-edge states and very fast, non-radiative Auger recombination of multiexcitons hinder the realization of light amplification and lasing with colloidal quantum dots (QDs). Recent advancements in understanding of Auger effects have resulted in the development of QDs with suppressed Auger decay. One such approach entails controlled compositional grading of the QD interior implemented with CdSe/$Cd_{1-x}Zn_xSe$ core/shell structures. Such continuously graded QDs (cg-QDs) exhibit long biexciton Auger lifetimes (>2 ns) and correspondingly high biexciton emission quantum yields (>40%). These characteristics are beneficial for applications in light emitting diodes and lasers. We present a detailed study of the optical gain properties of cg-QDs conducted using femtosecond transient absorption (TA) measurements of both solution samples and solid-state films. Because of strong Auger decay suppression, the cg-QDs exhibit an unprecedented optical-gain bandwidth spanning four excitonic transitions ($1S_{HH}$, $1S_{LH}$, 1P and 1D) from 2.1 to 2.4 eV. In addition, optical gain extends into the sub-bandgap region due to a new mechanism of Auger-assisted stimulated emission ($1S_A$) involving a virtual intra-gap state. To test the practical utility of the observed effects, we combine the cg-QDs with second-order distributed feedback resonators and use these devices to demonstrate multi-color lasing (at 2.04, 2.065, 2.08, 2.10, and 2.27 eV) achieved with the same QD sample.

Electrochromism: Decoupling redox and color in rhodamine-based systems

Varunprasaath Ramasamy Selvaraju

University of Colorado, Boulder

Varunprasaath.ramasamySelvaraju@colorado.edu

Electrochromic materials refer to the ability of the material to reversibly change color upon a redox process. Oxidation/reduction of these materials leads to charged states whose spectral absorption is different from the charge-neutral state. These materials have wide applications in the field of smart windows[1], sensors[2], visors[3] and electronic displays[4]. A particular section of electrochromism is the interconversion between a colorless state and a brightly colored state which is necessary for applications in high-contrast displays. In our study, we propose to design alternative approaches to design systems in which the redox and color can be decoupled. We plan to achieve this by coupling pH-indicator based chromophores and electrophores in such a way that the redox process of the electrophore is coupled to the color of the indicator. We aim to have a better understanding of the mechanism in which electrophore and chromophore are coupled to develop a robust high-contrast electrochromic system that can cleanly and reversibly switch between a transparent and a brightly colored state. Here in this work, we synthesized a lactam derivative of rhodamine-ferrocene and studied its electrochemical properties of it. We observed ring-opening of the dye upon oxidation of the ferrocene unit. The kinetic studies indicated that the rate of ring-opening (bond-breaking) is slower than that of electrochemical oxidation. The rate can be enhanced by the addition of a mild lewis acid species like $LiPF_6$. The ring-opened state is highly stable and has potential applications in bistable devices. The reversibility of the system, both electrochemical and chemical, is currently being explored.

1. C.G Granqvist, A Azens, A Hjelm, L Kullman, G.A Niklasson, D Rönnow, M Strømme Mattsson, M Veszelei, G Vaivars, Recent advances in electrochromics for smart windows applications, *Solar Energy*, **1998**, *63*, 199-216
2. Klymchenko, A. S.; Demchenko, A. P. Electrochromic Modulation of Excited-State Intramolecular Proton Transfer: The New Principle in Design of Fluorescence Sensors. *J. Am. Chem. Soc.* **2002**, *124*, 12372−12379
3. Österholm, A. M., et al., Four Shades of Brown: Tuning of Electrochromic Polymer Blends Toward High-Contrast Eyewear, *ACS Appl. Mater. Interfaces*, **2015**, *7*, 1413-1421
4. Mortimer R. J., Dyer, A. L., Reynolds, J. R., Electrochromic organic and polymeric materials for display applications, Displays, **2006**, *1*, 2-18

A Marvel of Chiral Squaraine Aggregates: Chiroptical Spectra beyond the Exciton Model

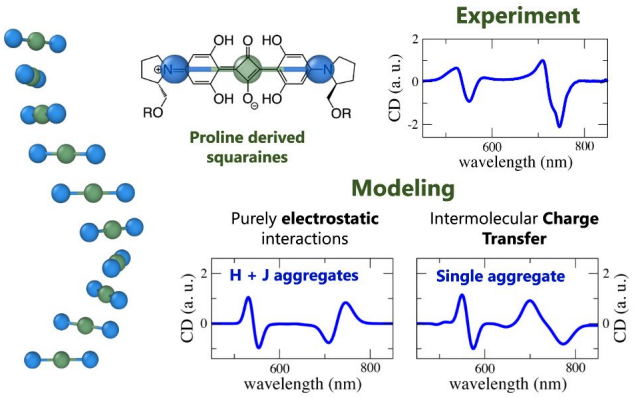
Marvin Schumaker

University of Colorado, Boulder

marvin.schumacher@uni-bonn.de

Squaraines are quadrupolar molecular dyes forming aggregates with remarkable structure-correlated excitonic properties within the visible to near-infrared spectral range. Upon chiral functionalization a chiroptical response such as circular dichroism acts as an additional spectroscopic feature. We provide a combined experimental and theoretical survey on chiral aggregates dispersed in solution of proline derived anilino squaraines (ProSQs) with varying terminal alkyl chain length (C3 to C12 and C16) directing the aggregation. Different aggregation scenarios with characteristic spectroscopic features appear, intricately depending on the alkyl chain length: Concomitant blue- and red-shifted spectroscopic signature both within the linear and circular absorption for intermediate chain length, and a scenario with dominating, blue-shifted signatures for shorter and longer alkyl chain length. Molecular Dynamic (MD) simulations on the aggregate structure return the opposite handedness suggesting a kinetic control for the experiments. Two modified essential state models (ESM) are applied to calculate the optical spectra with prescribed geometric parameters: A model accounting for just electrostatic intermolecular interactions (ESM-ES) suggests two concomitant aggregates to explain the simultaneous blue- and red-shifted spectral signatures while a model including intermolecular charge transfer (ESM-CT) returns both features for a single aggregate. Due to the complexity of calculation this is the first time an explicit expression for calculating circular dichroism including intermolcular charge transfer is rendered. However, the ESM-CT model is yet limited to tetramers so that finite size effects such as disorder are not fully captured.

D. Giavazzi et al., *J. Mater. Chem. C,* **2023***, Accepted Manuscript*, DOI: 10.1039/D2TC05555D.



n/a

Syed Alamdar Hussain Shah

Los Alamos National Laboratory

shah@lanl.gov

Nonadiabatic molecular dynamics simulations in large scale nanomaterials and periodic solids

Mohammad Shakiba

University of Buffalo

mshakiba.kerman.iran@gmail.com

Photophysics and photochemistry processes in solar-energy materials can be described using nonadiabatic molecular dynamics (NA-MD) simulations. The electronic structure calculations used in NA-MD often rely on expensive methods such as density functional theory (DFT). Nevertheless, the computational cost of such calculations for structures close to those observed in experimental studies can be quite expensive. Therefore, modeling NA-MD is often conducted for small and medium sized structures with few hundreds of atoms which can lead to overestimation of the charge carrier concentration and nonrealistic relaxation or recombination dynamics. Tight-binding and semiempirical approaches have been utilized to extend the size of the structures in NA-MD simulations but there are only limited parametrizations available for few elements in the periodic table. Recently, extended tight-binding (xTB) method has been proposed that provides parametrization for a wide range of atoms and can be utilized for electronic structure calculations in inorganic materials such as quantum dots and metal organic frameworks.

In this presentation, I will first highlight our most recent xTB/NA-MD approach, implemented in the open-source Libra software package, which can be utilized for modeling excited states dynamics in large structures with thousands of atoms. Then, I will show the application of this method in studying hot electron relaxation dynamics in silicon quantum dots and the role of charge carrier concentration in electron-hole recombination dynamics in carbon nitride monolayers. As the first application, I will show how one can explain the non-monotonic dependence of the hot electron relaxation dynamics on nanocluster size by performing NA-MD simulations in silicon quantum dots with sizes up to 3.5 nm. Then, I will show the dependence of the electron-hole recombination dynamics on charge carrier concentration in carbon nitride monolayers where a variety of supercell sizes are considered ranging from 2.84 nm x 2.46 nm (224 atoms) to 14.24 nm x 12.33 nm (5600 atoms). The largest supercell size in this application is one of the largest solid-state system where direct NA-MD calculations have been conducted for. I will also explain the role of various trajectory surface hopping methods and decoherence schemes in each of these applications.

A Mixed Stochastic-Deterministic Subsystem DFT Approach For Simulating Large Nanostructures

Vidushi Sharma

Los Alamos National Laboratory

vidushi@lanl.gov

In quantum materials modeling, Kohn-Sham density functional theory (KS-DFT) has emerged as a powerful tool for studying systems ranging from just a few molecules to much more condensed phases. However, the cubic computational complexity of the traditional KS-DFT algorithm (O(*N*^3)) prevents its application to truly large systems. Linear-scaling DFT approaches have targeted this niche of large-*N* systems wherein the modeling of the underlying physical and chemical processes merits a quantum-mechanical representation. I will describe one such linear-scaling method that applies stochastic techniques to the KS-DFT framework. I will further illustrate a novel proposal for a mixed DFT (mDFT) formalism that combines the stochastic and deterministic algorithms of KS-DFT with the objective of improving computational complexity while retaining KS- accuracy. Recently, mDFT was successfully applied to model the ground-state and dynamic properties of warm-dense systems ($T \geq E_F$). We now apply mDFT to study nonequilibrium dynamics in aqueous-solvated nanostructures in the subsystem DFT approach. This affords us another parameter for controlling the level of precision in different regions of the system.

Influencing Perovskite-Sensitized TTA-UC through Solvent Treatment and Annihilator Substitution

Colette Sullivan

Florida State University

cmsullivan@fsu.edu

Photon upconversion via triplet-triplet annihilation (TTA-UC) has the potential to efficiently generate higher energy photons from low energy incident photons at low relative fluences. Recently, bulk metal halide perovskites have offered promise in efficiently sensitizing molecular triplet states in the solid state through a charge transfer mechanism. To understand the underlying charge transfer processes at the perovskite/organic interface and increase the yield of TTA-UC, surface treatments using various organic solvents are explored. Scanning tunneling spectroscopy reveals differences in the Fermi energy, where both n- and p-type terminated perovskite surfaces are observed dependent upon the solvent used. Our results indicate that n-type perovskite sensitizers feature higher TTA-UC efficiencies due to favorable band bending resulting in efficient hole-mediated triplet formation. Additionally, until this work reported herein, rubrene has been the sole annihilator used for bulk metal halide perovskite sensitized TTA-UC, limiting its applications due to the limited achievable apparent anti-Stokes shift. We demonstrate successful sensitization of the triplet state of 1-chloro-9,10-bis(phenylethynyl)anthracene using the established formamidinium methylammonium lead triiodide perovskite $FA_{0.85}MA_{0.15}PbI_3$, resulting in upconverted emission at 550 nm under 780 nm excitation demonstrating that this approach of triplet sensitization is universal and not restricted to rubrene.

Spin Dependent Nonadiabatic Dynamics and Its Modeling by Phase-Space Surface Hopping

Yanze Wu

University of Pennsylvania

wuyanze@sas.upenn.edu

Nonadiabatic dynamics plays a crucial role in various chemical relaxation phenomena, including photochemistry and electron transfer processes. In recent years, interest arises in the nonadiabatic dynamics with spin interaction (including by spin-orbit couplings (SOC), hyperfine interaction or external magnetic field), and the discovery of chiral induced spin selectivity (CISS) hints an important role of spin direction in chemical processes. In recent studies, we found that in the presence of a strong SOC, the nuclear motion and electronic spin direction are entangled by geometric effects, which could lead to spin-controlled reaction pathways. However, such coupled spin-nuclear dynamics cannot be described by the standard trajectory surface hopping (TSH) approach. To solve this issue, we develop a variant of surface hopping, namely the phase-space surface hopping (PSSH), that can successfully describe the coupled spin-nuclear motion in our model systems.

Photoinduced Isomerization of Lanthanide Nitrogen Complex: Competition in the Bonding Interactions of N2 with 4f Element

Mingbin Yuan

Los Alamos National Laboratory

myuan@lanl.gov

The reduction chemistry of N_2 is a crucial component in many biological and industrial processes, and it has been actively studied in the field of sustainable energy. Upon reacting with N_2, monometallic and bimetallic dinitrogen complexes can be formed. Compared to the widely used transition metal catalysts, 4f elements have gained more focus recently due to their higher selectivity in the process of dinitrogen reduction. Unlike transition metals, rare-earth (4f elements) mainly form bimetallic bridging dinitrogen (N=N) complexes $[L_xM]_2[\mu\text{-}\eta^y\text{:}\eta^y\text{-}N_2]$ in end-on (y = 1) and side-on (y = 2) binding modes. However, side-on to end-on isomerization of the (N=N) moiety has only been reported for a limited set of lanthanide systems in specific reaction conditions. In this vein, we studied the mechanism of a novel photoinduced isomerization from side-on to end- on binding mode of N_2 bridge in the Lu dinitrogen complex using density functional theory (DFT). The simulated results (e.g., Raman and UV-vis spectra) revealed mechanistic details that explained the experimental data. Furthermore, the coordination of the chelating solvent molecules (THF) was found to influence the spectroscopic properties in a non-negligible way. These findings are expected to improve the understanding of the bonding and spectroscopic properties of 4f element dinitrogen complexes, as well as shed light on the dynamic transformation processes of side-on and end-on binding mode of the bridging dinitrogen moiety.

Visualizing ultrafast relaxation of lattice distortion in two-dimensional perovskites

Hao Zhang

Rice University

hz64@rice.edu

Direct visualization of ultrafast coupling between charge carriers and lattice degrees of freedom in photoexcited semiconductors has remained a long-standing challenge and is critical for understanding the light-induced physical behavior of materials under extreme non-equilibrium conditions. Here we obtain a direct visualization of the structural dynamics in monocrystalline 2D perovskites. We achieve this by monitoring the evolution of wavevector-resolved ultrafast electron diffraction intensity following above-bandgap high-density photoexcitation. Our analysis reveals a light-induced ultrafast reduction in antiferro-distortion resulting from a strong interaction between the electron–hole plasma and perovskite lattice, which induces an in-plane octahedra rotation towards a more symmetric phase. Correlated ultrafast spectroscopy performed at the same carrier density as ultrafast electron diffraction reveals that the creation of a dense electron–hole plasma triggers the relaxation of lattice distortion at shorter timescales by modulating the crystal cohesive energy. Finally, we show that the interaction between carrier gas and lattice can be altered by tailoring the rigidity of the 2D perovskite by choosing an appropriate organic spacer layer.

Exploring non-adiabatic dynamic reaction mechanisms in organic semiconductors using eQE and pyUNIxMD

Qingxin Zhang

University of Buffalo

qingxinz@buffalo.edu

Organic solar cells use organic semiconductors as the active material to achieve solar photoconversion. Compared to inorganic solar cells, they have the advantages of lower cost, thinner thickness, lighter weight, a simpler manufacturing process, and can be made into large-area flexible devices, making them highly promising for development and application. In the last decade, the power conversion efficiency (PCE) of organic solar cells has reached 17.4% (as reported by the National Renewable Energy Laboratory). In my research, fullerene and pentacene were used as representatives to study the material properties of organic semiconductors. Both materials mentioned above are based on non-adiabatic dynamics to study their properties.

In this presentation, I will discuss the utilization of eQE (short for enhanced Quantum Espresso) in computing various fragments of pentacene and its implications. Unlike Quantum Espresso, eQE offers the capability to calculate multiple fragments and define parameters for cell cutting, providing a fresh perspective on material properties. The pertinent computational data can be acquired from three sets of cells: 1x1x1, 2x2x1, and 3x3x1 system fragments, along with cutting parameter data. The utilization of sDFT (subsystem Density Functional Theory) is crucial in completing the eQE calculations. The advantages of eQE are demonstrated through factors such as calculation time, band gap, and DOS (Density of States) diagrams. Furthermore, an essential aspect of finalizing the eQE calculations involves discussing script usage and software format conversions to generate cuttable input files.