

# 35th Workshop on Recent Developments in Electronic Structure Methods

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University of California, Merced

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## Presentation Abstracts

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Invited Talks

Virtual Poster Presentations

In-Person Poster Presentations



# Invited Speaker Abstracts

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## Invited Speaker Abstracts

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Speaker No.	Name	Institution	Title
1	Peter Oppeneer	Uppsala University	A first-principles approach to orbital accumulation and orbital transport
2	Sayantani Ghosh	University of California, Merced	The role of nanostructured metal halide perovskite materials in solar energy harvesting
3	Sanghamitra Neogi	University of Colorado Boulder	Machine Learning Models to Assist Designing Atomic Environments in Semiconductor Heterostructures and Complex Alloys
4	Trevor Rhone	Rensselaer Polytechnic Institute	Artificial intelligence guided materials discovery of two-dimensional magnets
5	Emmanuel Fromager	Université de Strasbourg	Ensemble density functional theory of electrons and nuclei
6	Henrik Larsson	University of California, Merced	Tensor network states for computing vibrational and electronic states
7	Yuan Ping	UW Madison and UC Santa Cruz	Spin relaxation, dephasing and diffusion in solids from ab-initio density-matrix dynamics
8	Carsten Ullrich	University of Missouri	(TD)DFT for noncollinear spins: orbital functionals, semilocal approximations, and xc torques
9	Jennifer Cano	Stony Brook University	Engineering topological phases with a superlattice potential
10	Marco Govoni	Argonne National Laboratory	<i>TBD</i>
11	John Bonini	Flatiron Institute	Lattice dynamics with broken time reversal symmetry
12	Marco Bernardi	California Institute of Technology	Frontiers of First-Principles Electron-Phonon Interactions: Spinful, Data-Driven, and Parsimonious
13	Siyuan Chen	College of William & Mary	Forces, stress, and geometry optimization with auxiliary-field quantum Monte Carlo
14	Lenz Fiedler	CASUS	Demonstrating temperature transferability of neural network models replacing density functional theory
15	Isaac Tamblyn	University of Ottawa	A powerful yet inadequate tool - ML for electronic structure
16	Boris Kozinsky	Harvard University	Machine learning models of many-body atomic and electronic interactions
17	Mit Naik	University of California, Berkeley	Bethe Salpeter equation calculations in moiré superlattices with thousands of atoms in the unit-cell
18	Emmanuel Gull	University of Michigan	Electronic Structure – a view from finite-temperature field theory
19	Marcus Eisenbach	Oak Ridge National Laboratory	Scalable First Principles Calculations for Alloys
20	Xavier Andrade	Lawrence Livermore National Laboratory	The INQ code: reinventing the electronic-structure code

# A first-principles approach to orbital accumulation and orbital transport

Peter M. Oppeneer

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Recent first-principles calculations have predicted that, apart from the electrically induced spin currents and spin polarization, there are in fact much larger orbital angular momentum currents and induced orbital polarizations. A huge orbital Hall effect (OHE) was predicted to exist in 3d metals [1] and a huge orbital Rashba-Edelstein effect (OREE) was predicted for the symmetry-broken antiferromagnets CuMnAs and Mn<sub>2</sub>Au [2]. Both effects do not require spin-orbit interaction (SOI) and large effects can be obtained for materials containing light atoms. This provides a new perspective for future utilization of orbital angular momentum, instead of spin, as information carrier in the emerging field *orbitronics*.

I will discuss our recent first-principles linear-response theory calculations for the electrically induced out-of-equilibrium spin and orbital currents in bulk 3d ferromagnets as well as in Pt/3d-metal bilayer films [3,4]. For bulk 3d ferromagnets as Fe, Co and Ni, we show that there exists a conventional spin Hall effect (SHE), and an OHE, as well as a magnetic spin Hall effect (MSHE) and a magnetic orbital Hall effect (MOHE) [3]. The former two effects are time-reversal even, whereas the MSHE and MOHE are time-reversal odd and exist in ferromagnetic materials. These induce an unusual transverse spin or orbital current with spin/orbital polarization along the applied electric field. The MSHE is strongly electron lifetime dependent, but in general, it is of the same size of the SHE and cannot be neglected. The OHE is the largest quantity as it doesn't require SOI, but the SHE, MSHE, and MOHE all require SOI to be non-zero. We also predict values for the thermal counterparts, namely, the spin Nernst effect, and for the as-yet unobserved orbital Nernst effect (ONE) and the magnetic spin Nernst effect and magnetic orbital Nernst effect.

For the Pt/3d-metal (Co, Ni, Cu) bilayer systems we compute both the spin and orbital currents as well as the spin/orbital accumulation on the sides of the bilayer. The electrically induced transverse orbital current is larger than the spin current and present even without SOI. This underlines that also in the Pt/3d-metal bilayers the electrically induced orbital effects (OREE and OHE) are the primary responses, whereas the SREE and SHE are generated from these through SOI. We further compute atom-resolved response quantities that allow us to identify the induced spin-polarizations that lead to fieldlike (FL) SOTs and dampinglike (DL) SOTs and compare their relative magnitude, dependence on the magnetization direction, as well as their Pt-layer thickness dependence.

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## **The role of nanostructured metal halide perovskite materials in solar energy harvesting**

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Research in nanostructured devices for solar energy harvesting and storage are driven primarily by the design and development of new materials. In my group, we focus on investigating the ramifications of different active materials and architectures on photovoltaic (PV) performance, especially device efficiency and stability. In the past decade, organic–inorganic metal halide perovskites (MHPs) have emerged as the most prominent new PV material, combining a very competitive power conversion efficiency that rivals crystalline silicon with the added benefits of solution processability, high specific power, and excellent defect tolerance. However, without significant and complicated structural and chemical modifications, MHPs degrade under ambient humidity and long-term photo exposure. Here, I will discuss two specific applications of nanostructured MHPs which allow circumventing of these problematic issues. The leverages MHPs' stable performance in vacuum under AMO solar radiation and as part of a collaboration with the National Aeronautics and Space Administration (NASA), demonstrates the long-term viability of using MHP PVs in space, following a 10-month flight on the International Space Station. The second, leading from some findings in the first study, focuses on the interaction between MHP thin films and metal halide perovskite quantum dots (PQDs). Mapping static and dynamic MHP emission as functions of temperature, excitation energy, and excitation power revealed that a low density of PQDs improved thin film properties, while increasing PQD density further had detrimental effects. This complex modulation of MHP properties by PQDs indicate an intricate interplay between different factors that need to be considered in optimizing such heterostructures for optoelectronic applications.

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# Machine Learning Models to Assist Designing Atomic Environments in Semiconductor Heterostructures and Complex Alloys

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## ABSTRACT

Following empirical, theoretical, and computational eras of material development, machine learning (ML)-based materials design and discovery research has emerged as the fourth paradigm of materials science. In my research group at the University of Colorado at Boulder, we leverage ML models to design and discover new materials to realize future technologies. Additionally, we discover materials design strategies that will optimize properties of nanoscale materials. In this talk, I will present an overview of activities of my research group, with particular focus on our use of ML models to predict electronic properties of two classes of materials: (1) semiconductor heterostructures and (2) complex multicomponent alloys.

Over the past few decades, semiconductor heterostructures have emerged as key enabling materials for essential technologies, including telecommunication systems, light-emitting diodes, or high-electron-mobility transistors used in high-frequency devices. The heterostructures are strongly affected by the growth processes. It remains a challenge to explore the vast structural parameter space of ‘real’ heterostructures using first-principles modeling techniques, due to high computational costs. In particular, the calculations of electronic transport coefficients (such as, thermopower or conductivity) require large number of individual energy calculations and computational costs can accrue quickly. In this talk, I will discuss how the use of ML models can assist us in extending the applicability of these *ab initio* techniques to ‘real’ heterostructures. I will discuss a forward ML-model that can predict the Seebeck coefficients of fabricated semiconductor heterostructures of thickness upto  $\sim 12$  nm [1]. Additionally, I will present an inverse approach that predicts the atomic-scale features of a given heterostructure that will result in target electronic band structures [2].

In recent years, a new alloying strategy that aimed to stabilize (near) equimolar mixtures of multiple elements by maximizing the configurational entropy has revealed unprecedented opportunities for materials discovery. The alloy mixtures became known as high-entropy materials. The alloys exhibit unprecedented combinations of mechanical and functional properties, even at extreme environments, making them attractive for energy and aerospace applications. The vast compositional space offers enormous possibilities to engineer lattice and electronics structures and tune the properties. However, the ‘needle in a haystack’ scenario puts targeted alloy design to its hardest test: new materials with exceptional properties can hide in practically infinite and vastly unexplored composition space. I will discuss a ML-based approach that can guide the design and discovery process of novel alloys and compounds.

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2. A. K. Pimachev and S. Neogi. “Deep Learning Model for Inverse Design of Semiconductor Heterostructures with Desired Electronic Band Structures.” arXiv preprint arXiv:2302.00261 (2023).

# Artificial intelligence guided materials discovery of two-dimensional magnets

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The discovery of van der Waals (vdW) materials with intrinsic magnetic order in 2017 has given rise to new avenues for the study of emergent phenomena in two dimensions. In particular, monolayer  $\text{CrI}_3$  was found to be ferromagnet. Other vdW transition metal halides were later found to have different magnetic properties. How many vdW magnetic materials exist in nature? What are their properties? How do these properties change with the number of layers? A conservative estimate for the number of candidate vdW materials (including monolayers, bilayers and trilayers) exceeds  $\sim 10^6$ . A recent study showed that artificial intelligence (AI) can be harnessed to discover new vdW Heisenberg ferromagnets based on  $\text{Cr}_2\text{Ge}_2\text{Te}_6$  [1,2]. In this talk, we will harness AI to efficiently explore the large chemical space of vdW transition metal halides and to guide the discovery of magnetic vdW materials with desirable spin properties. That is, we investigate crystal structures based on monolayer  $\text{Cr}_2\text{I}_6$  of the form  $\text{A}_2\text{X}_6$ , which are studied using density functional theory (DFT) calculations and AI. Magnetic properties, such as the magnetic moment are determined. The formation energy is also calculated and used as a proxy for the chemical stability. We show that AI, combined with DFT, can provide a computationally efficient means to predict the thermodynamic and magnetic properties of vdW materials [3]. This study paves the way for the rapid discovery of chemically stable magnetic vdW materials with applications in spintronics and data storage.

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# Ensemble density functional theory of electrons and nuclei

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I will briefly review in this presentation a recent unified and in-principle-exact extension of density functional theory (DFT) to both charged and neutral electronic excitations [1]. The approach is based on the so-called  $N$ -centered ensemble formalism [2-4]. I will particularly focus on exchange-correlation derivative discontinuities associated to neutral excitation processes [1,5-8]. In a second part, I will discuss the derivation of an exact ensemble DFT of electrons and nuclei, starting from the Born-Huang expansion of the molecular wave function, with a particular focus on the description of non-adiabatic couplings [9]. This work is a first step towards the rationalization of computational non-adiabatic nuclear dynamics studies using electronic density-functional ensembles.

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## Tensor network states for computing vibrational and electronic states

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Mostly independently from each other, the fields of electronic structure and vibrational quantum dynamics developed powerful methods in order to accurately solve the Schrödinger equation. In particular, methods that decompose the high-dimensional wavefunction as a complicated contraction over smaller dimensional functions have attracted much attention. They have led to impressive applications for challenging quantum systems in both fields. While the underlying wavefunction representations, tensor network states, are very similar, the algorithms used to solve the Schrödinger equation for electronic and vibrational motions are very different. A systematic comparison of the strengths and weaknesses of the different approaches is missing but would allow for a better understanding and useful cross-fertilization of ideas. Here, first attempts in this direction are made.

In the first part of my talk, I will show how to use a method from electronic structure theory, the density matrix renormalization group (DMRG), for vibrational simulations.<sup>1</sup> I will compare the DMRG to an algorithm used for vibrational dynamics, the multi-layer multi-configuration time-dependent Hartree (ML-MCTDH) method. I will apply these algorithms to the vibrational spectra simulation the Zundel ion,  $\text{H}_5\text{O}_2^+$ , where a proton is sandwiched between two water units, a challenging system exhibiting large amplitude motion and Fermi resonances. For this system, I will show how the DMRG method can compute eigenstates at least an order of magnitude faster than the ML-MCTDH method. By computing 1000 eigenstates to high accuracy, I will show how subtle energetic effects will lead to a vastly different infrared spectrum of the Zundel ion.<sup>2</sup>

In the second part of my talk, I will show how a technique widely used for MCTDH can allow for faster electronic structure DMRG calculations whenever many virtual orbitals with few electronic excitations are involved.<sup>3</sup> With a combination of this and existing methods, I will then show how to compute a very accurate potential energy curve (PEC) of the chromium dimer, a grand challenge problem of small molecule spectroscopy, where theory and experiment have been at odds for decades. The computed PEC allows for a new analysis of the existing experimental data and hints at a new assignment of the vibrational levels of the chromium dimer.<sup>4</sup>

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# Spin relaxation, dephasing and diffusion in solids from ab-initio density-matrix dynamics

Yuan Ping<sup>1,2</sup>

1. University of Wisconsin, Madison
2. University of California, Santa Cruz

Spin relaxation, dephasing and diffusion are at the heart of spin-based information technology. Accurate theoretical approaches to simulate spin lifetimes ( $\tau_s$ ), i.e. how fast the spin polarization and phase information will be lost, are important to the understandings of underlying mechanism, and invaluable to search for promising spintronic material candidate. Recently, we develop the first-principles real-time density-matrix (FPDM) approach to simulate spin dynamics for general solid-state systems [1,2]. Through the complete first-principles' descriptions of light-matter interaction and scattering processes including electron-phonon, electron-impurity and electron-electron scatterings with self-consistent spin-orbit coupling, as well as *ab-initio* Land'e  $g$ -factor[3], our method can predict  $\tau_s$ , regardless of crystal symmetry, as a function of carrier density and temperature, under electric and magnetic fields[2,3].

By employing this method, we successfully reproduce experimental results of spin lifetime and ultrafast Kerr rotation of disparate materials, and identify the key factors affecting spin relaxation, dephasing, and diffusion[4] in different materials. Specifically, we predict that germanene has long  $\tau_s$  ( $\sim 100$  ns at 50 K), a giant spin lifetime anisotropy and spin-valley locking effect under electric fields[4], making it advantageous for spin-valleytronic applications. Based on our theoretical derivations and *ab-initio* simulations, we propose a new useful electronic quantity, named spin-flip angle  $\theta_{\uparrow\downarrow}$ , for the understanding of spin relaxation through intervalley spin-flip scattering processes[5]. We then show how  $g$  factor fluctuations lead to spin dephasing in halide perovskites under external magnetic field. Our method can be further applied to other emerging materials and extended to simulate exciton spin dynamics and steady-state photocurrents due to photogalvanic effect.

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# **(TD)DFT for noncollinear spins: orbital functionals, semilocal approximations, and xc torques**

**Carsten A. Ullrich**  
**University of Missouri**

Most commonly used approximations in (TD)DFT for noncollinear magnetism are based on reference systems with collinear spins and fail to capture exchange-correlation (xc) torque effects. We present a semilocal exchange-correlation energy functional for noncollinear spin density functional theory based on short-range expansions of the spin-resolved exchange hole and the two-body density matrix [1]. Our functional is explicitly derived for noncollinear magnetism, is U(1) and SU(2) gauge invariant, and gives rise to nonvanishing xc torques. Testing the functional for the ground state of frustrated antiferromagnetic chromium clusters, a delicate interplay between exchange and correlation torques is uncovered. We then consider small Hubbard clusters, including spin-orbit coupling induced geometric spin frustrations, and find that xc torques make a significant contribution to the noncollinear spin dynamics [2].

This work was supported by DOE Grant No. DE-SC0019109.

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Title: Engineering topological phases with a superlattice potential  
Speaker: Jennifer Cano

Abstract: We propose an externally imposed superlattice potential as a platform for manipulating topological phases, which has both advantages and disadvantages compared to a moiré superlattice. In the first example, we apply the superlattice potential to the 2D surface of a 3D topological insulator. The superlattice potential creates tunable van Hove singularities, which, when combined with strong spin-orbit coupling and Coulomb repulsion give rise to a topological meron lattice spin texture. Thus, the superlattice potential provides a new route to the long sought-after goal of realizing spontaneous magnetic order on the surface of a 3D TI. In the second example, we show that a superlattice potential applied to Bernal-stacked bilayer graphene can generate flat Chern bands, similar to in twisted bilayer graphene, whose bandwidth can be as small as a few meV. The superlattice potential offers flexibility in both lattice size and geometry, making it a promising alternative to achieve designer flat bands without a moiré heterostructure.

**Marco Govoni**

Argonne National Laboratory

***TBD***

# Lattice dynamics with broken time reversal symmetry

John Bonini

The dynamics of atoms in molecules and solids are conventionally formulated in terms of forces which are a function of nuclear positions; this results in equations of motion which are symmetric under time reversal symmetry. In magnetically ordered systems such a formulation will not correctly reflect the physical vibration mode degeneracies which are determined by the magnetic symmetry group. The absence of time reversal symmetry can lead to chiral phonon modes where excitations involving “clockwise” and “counterclockwise” atomic trajectories occur at distinct energies. In this talk I will present and compare first principles methods for computing phonon spectra which go beyond the conventional interatomic force matrix approach to incorporate time reversal symmetry breaking effects. The first method, based on an adiabatic separation between electronic and nuclear degrees of freedom, includes the first order changes in forces with atomic velocities[1]. The second method goes beyond this adiabatic assumption and treats phonons and spin excitations on the same footing [2]. While both approaches yield vibration modes which correctly reflect the degeneracies of the magnetic symmetry group, we demonstrate that in systems such as the ferromagnetic insulator  $\text{CrI}_3$  the adiabatic approach yields qualitatively incorrect spectra as the relevant spin degrees of freedom are not “fast” with respect to phonon excitations.

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## **Frontiers of First-Principles Electron-Phonon Interactions: Spinful, Data-Driven, and Parsimonious**

**Marco Bernardi**

*Department of Applied Physics and Materials Science, and Department of Physics,  
California Institute of Technology*

Electron-phonon (e-ph) interactions have become a pillar of first-principles electronic structure calculations. In this talk, I will introduce relevant theory and computational workflows, and then I will highlight two emerging frontiers of e-ph calculations: (i) Precise calculations of spin-phonon interactions and spin relaxation; (ii) data-driven methods to compress e-ph interactions, significantly speed-up their computation, and achieve parsimonious / Pareto-optimal models. To conclude I will discuss advances in our open source code, PERTURBO, which makes these new computational methods available to the community.

Siyuan Chen  
College of William & Mary

## **Forces, stress, and geometry optimization with auxiliary-field quantum Monte Carlo**

Determining the accurate structure of a material is a critical step in understanding its physics. Predictive computations in correlated materials remain a major challenge. We have successfully formulated and implemented a direct, ab initio computation of forces and stresses [1] with auxiliary-field quantum Monte Carlo (AFQMC) using plane wave basis and multiple projector pseudopotentials. Our method potentially allows determination of the potential energy surface at a much higher efficiency than an approach based on total energies alone. In addition, we propose a fast and robust structural optimization algorithm [2] for optimizations when the forces or gradients are statistically noisy. Applying this algorithm in combination with forces and stresses computed by AFQMC, we demonstrate efficient, accurate, and full degrees-of-freedom optimizations in solids. Direct computations of charge densities [3], phonon spectra, and Berry phases in solids with AFQMC will also be discussed.

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# Demonstrating temperature transferability of neural network models replacing modern density functional theory

– *Lenz Fiedler<sup>[1]</sup>, Kyle D. Miller<sup>[2]</sup>, Normand A. Modine<sup>[2]</sup>, Attila Cangi<sup>[1]</sup>*

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Due to its balance between accuracy and computational cost, Density Functional Theory (DFT) is one of the most important computational methods within materials science and chemistry. However, current research efforts such as the modeling of matter under extreme conditions demand the application of DFT to larger length scales as well as higher temperatures. Such investigations are currently prohibited due to the computational scaling of DFT.

We have recently introduced a machine-learning workflow that replaces modern DFT calculations [1,2,3]. This workflow uses neural networks to predict the electronic structure locally. We show that by employing such an approach, models can be trained to predict the electronic structure of matter across temperature ranges. This paves the way for large-scale simulations of thermodynamically sampled observables relevant to modeling technologically important phenomena such as radiation damage in fusion reactor walls.

# A powerful yet inadequate tool - ML for electronic structure

Isaac Tamblyn

Acting as a surrogate model, machine learning (ML) models such as deep neural networks have the ability to estimate the output of expensive electronic structure calculations at a fraction of the computational cost. When trained properly, they are capable of scaling to much larger system sizes, operating at length scales which were previously thought inaccessible. Unfortunately, these advantages have come at a high price - supervised ML models provide little intuition or explanation about *how* they arrived at a particular prediction. As a result, it is difficult for ML practitioners to obtain transferable insight. Each problem feels like a new one.

I will discuss some of the recent successes and failures of ML and provide examples which attempt to provide generalized insight.

Boris Kozinsky, Harvard University

### **Machine learning models of many-body atomic and electronic interactions**

To advance the capability of density functional theory (DFT) we introduce non-local charge density descriptors that satisfy exact scaling constraints and learn exchange functionals called CIDER, that are orders of magnitude faster to evaluate than hybrid functionals but similar in accuracy [1]. To accelerate molecular dynamics, we use machine learning to capture the potential energy surfaces obtained from quantum calculations. We developed NequIP [2] and Allegro [3], the first deep equivariant neural network interatomic potential models, whose symmetry-preserving layer architecture achieves state-of-the-art data efficiency and accuracy for simulating dynamics. To enable autonomous active learning of reactive systems, we developed the FLARE [4] algorithm that constructs accurate and uncertainty-aware Bayesian force fields on-the-fly from a molecular dynamics simulation, using Gaussian process regression.

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Mit H. Naik  
University of California, Berkeley

**Title:** Bethe Salpeter equation calculations in moiré superlattices with thousands of atoms in the unit-cell

**Abstract:**

Recent experimental measurements have demonstrated signatures of novel exciton states in the moiré superlattices of transition metal dichalcogenide bilayer heterostructures. However, the microscopic nature of these moiré excitons was not well understood, and previous studies relied often on empirically fit models. Brute force first-principles *GW*-Bethe Salpeter equation (GW-BSE) calculations are computationally intractable due to thousands of atoms in the reconstructed moiré unit-cell. We present a novel computational approach, the pristine unit-cell matrix projection (PUMP) method [1] which makes it possible to accurately study excitons in large-area transition metal dichalcogenide moiré superlattices. Through these calculations, we discovered a rich diversity of excitonic states. In rotationally aligned WSe<sub>2</sub>/WS<sub>2</sub> moiré superlattice, we find some excitons of a modulated Wannier character and others of a previously unidentified intralayer charge-transfer character [1]. In 57.7° twisted bilayer WS<sub>2</sub>, we discover layer-hybridized excitons with in-plane charge transfer character. These characteristics originate from the strong modulation of electron wavefunctions due to atomic reconstructions of the superlattice. Experimental reflection contrast [1], electron energy loss spectroscopy [2] and scanning tunneling spectroscopy measurements confirm these predictions. The PUMP approach can also be extended to study optical spectrum of shallow defects in materials, which also require large supercell calculations.

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Emanuel Gull  
University of Michigan

## Electronic Structure – a view from finite-temperature field theory

Electronic structure problems are commonly solved in a density functional or in a mean field approach. Lattice model systems, in contrast, are often investigated from the complementary 'diagrammatic' perspective of finite-temperature field theory. While field theory provides straightforward access to statistical properties at finite temperature and to correlation physics, there are substantial technical challenges in adapting the approach to electronic structure. This talk will give an overview of recent progress in this field, emphasizing in particular work on thermodynamic and spectral quantities.

# Scalable First Principles Calculations for Alloys

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The effect of disorder in materials is of great fundamental and technological interest. Here I will present our implementation of multiple scattering theory for first principles density functional calculations. This approach directly obtains the single particle Green's function of the Kohn-Sham equation, either in reciprocal space (Korringa-Kohn-Rostocker i.e. KKR) or real space (Locally-Selfconsistent Multiple Scattering i.e. LSMS). The KKR method allows an efficient description of random solid solution alloys using the Coherent Potential Approximation (CPA), while our LSMS code allows for scalable large scale first principles density functional calculations of materials. A fundamental science driver for scalable, large scale, first principles calculations of materials is the need to understand states beyond periodic crystalline lattices. For large simulation cells, needed to describe extended electronic and magnetic orderings, defect states or disorder in alloys, the cubic scaling of traditional first principles methods have prevented direct calculations. The linear scaling nature of the LSMS ab initio code enables the treatment of extremely large disordered systems from the first principles using the largest parallel supercomputers available, such as calculations for O(10,000 - 100,000) atoms on current high performance computing architectures. For exascale systems, we have extended the use of accelerators to enable the efficient calculation for embedding methods and forces. Currently ongoing work focuses on the calculation of electric conductivity in the presence of disorder and defects.

While DFT calculations have proven to be a useful tool in the study of ground state properties of many materials, we will go beyond the ground state by describing an approach to utilize machine learning methods to combine first principles density functional calculations with classical Monte-Carlo simulations to investigating the statistical mechanics of materials. The investigation of finite temperature properties relies on the possibility of a large number of evaluations of the system's Hamiltonian that are required to sample the phase space needed to obtain physical observables. We have demonstrated a solution to this problem that harnesses the computational power of large massively parallel computers by combining classical Monte-Carlo calculations with our first principles multiple scattering electronic structure code (LSMS) by employing Machine Learning techniques.

The combination of LSMS with a machine learning workflow, that can consider both classical interaction models and artificial neural network based models, allows us to investigate alloy ordering transitions for increased simulation cell sizes. Our approach is able to sample both magnetic or chemical order, allowing the first principles calculation of order/disorder phase transitions and phase separations in alloys.

These computational capabilities are available in our Multiple Scattering Theory suite (MuST)  
[<https://github.com/mstsuite>]

This work was supported in part by the Office of Science of the Department of Energy and by the Laboratory Directed Research and Development (LDRD) Program of Oak Ridge National Laboratory. This research used resources of the Oak Ridge Leadership Computing Facility, which is supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC05-00OR22725.

**Xavier Andrade-Valencia, Lawrence Livermore National Laboratory**

***The INQ code: reinventing the electronic-structure code***

Electronic structure codes are a fundamental tool for the computational study of matter in the ground and the excited states. They are complex pieces of software that need to be accurate, reliable, and implement a wide array of functionalities and features. On top of that, given the costly nature of first principles simulations, they need to be computationally efficient and take advantage of modern high-performance computing (HPC) platform. Many existing codes have been in development for decades and are very large, some of them have several hundred thousand lines of code. This makes them very difficult to maintain, optimize and adapt to new platforms. This last point is particularly critical as in the last few years we have seen a radical change in the design of HPC systems. Graphical processing units (GPUs) have become the standard computational element in supercomputers and clusters. However, many electronic structure codes cannot use GPUs efficiently, especially when running in parallel. At the same time, new ideas have appeared in software engineering that have revolutionized code development. These new approaches not only involve how to write the code, but also how to design it, develop it collaboratively, debug it, test it, and maintain it. We apply these principles to the electronic structure problem in a new software package called INQ, that is currently in development at Lawrence Livermore National Laboratory.

INQ is a compact code that implements density functional theory (DFT) and time-dependent functional theory (TDDFT). It uses modern code design features and techniques that make the development fast and simple, and ensure the quality of the program. By designing the code around algorithms, rather than against specific implementations and numerical libraries, we provide a concise and modular code that is simple to understand, flexible, and extensible. The core code is accompanied by a large set of tests that check the individual components and the program as a whole. This ensures that the program always works correctly as it is developed and that it gives reliable results.

INQ is based on the plane wave approach and can simulate both finite and (partially) periodic systems. It implements the standard DFT semi-local functionals as well as hybrid functionals. Hybrids are applied using the adaptively compressed exchange (ACE) approach to make the calculations computationally affordable. Its current focus is the simulations of the excited state of large systems using real-time TDDFT. However, it is a general code that can calculate ground state properties as well. INQ was designed from the scratch to run in parallel on multiple GPUs. In TDDFT simulations on GPU-based supercomputers INQ achieves excellent performance. It can handle hundreds and thousands of atoms, with simulation times of a second or less per time-step, and scale to thousands of GPUs. The code is open source and it is freely accessible at <http://gitlab.com/npneq/inq>

The work was supported by the Center for Non-Perturbative Studies of Functional Materials Under Non-Equilibrium Conditions (NPNEQ) funded by the Computational Materials Sciences Program of the US Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division. Work by X.A, T.O and A.C was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. C.D.P was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, under Contract No. DE-AC02-76SF00515 at SLAC. Computing support for this work came from the Lawrence Livermore National Laboratory Institutional Computing Grand Challenge program.

# Poster Presentation Abstracts

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## Poster Presentation Abstracts

Name	Institution	Poster Title	Poster No.
Mesfin Asfaw Afrassa	Adama Science and Technology University	DFT study of Zn (1-x) Fe x Se: Electronic structure, and magnetic properties	7
Brianna Aguilar-Solis	University of California, Merced	Approximating excited electronic states with spin-corrected self-consistent field methods	15
Bradford Barker	University of California, Merced	Dependence of magnetocrystalline anisotropy energies on the local crystal-field environment of magnetic dopants in ferroelectric oxides	27
Tunna Baruah	The University of Texas at El Paso	Self-Interaction Correction : Applications to Molecular Properties	29
Chance Baxter	University of New Mexico	Revisiting embedding functions for reactive charge-transfer systems	30
Tathagata Biswas	Arizona State University	Predicting quasiparticle and excitonic properties of materials using Machine Learning	12
Yueqing Chang	Rutgers University	Learning emergent models from ab initio many-body calculations	19
Rafael Del Grande	University of California, Merced	Excited-state force calculations from GW/BSE and DFPT: development and application to organic metal halide perovskites	6
Rachel Gorelik	Arizona State University	Developing a High-Throughput Ab Initio-Kinetic Model for the Prediction of Material Passivation	5
Adway Gupta	Arizona State University	Charge transition levels of nitrogen vacancies in w-AlN computed within the DFT+GW formalism	16
Kishwar-E Hasin	UC Merced	Competing structural phases and piezoelectricity in Ruddlesden-Popper Li <sub>2</sub> SrNb <sub>2</sub> O <sub>7</sub> from first principles	24
Md Kamal Hossain	University of California Merced	Exploring novel strain states in freestanding ferroelectric oxide membranes	21
Chen Hu	UC Berkeley	Excitonic interactions and mechanism for ultrafast interlayer photoexcited response in van der Waals heterostructures	40
Xuance Jiang	Stony Brook University	Manipulating Topological Properties in Bi <sub>2</sub> Se <sub>3</sub> /BiSe/TMDC Heterostructures with Interface Dipole	22
Youngkuk Kim	Sungkyunkwan University	Velocity inverted Dirac points and Weyl nodal lines in noncentrosymmetric hexagonal NaZnSb	8
Eunja Kim	UTEP	Rare-Earths, Critical Materials, and Hexagonal Motifs: Methods and Applications to Energy Systems	13
Alina Kononov	Sandia National Laboratories	Predictions of novel features in x-ray scattering spectra for thermometry	31
Priyanka Kumari	Indian Institute of Technology Jodhpur	Ion Transport and Glass Transition in pectin loaded [BMIM][PF <sub>6</sub> ] Battery Electrolytes	32
Remi Leano	UC Merced	Approaching Periodic Systems in Ensemble Density Functional Theory through 1D Model Studies in the Thermodynamic Limit	36
Daisy Lopez	University of Texas at El Paso	Sodium-containing layered oxides for replacing Li battery cathodes: Defect control to enhance ionic conductivity	10
Subhasish Mandal	West Virginia University	Beyond-DFT database of spectral functions for quantum materials	39

Juan Marmolejo-Tejada	Montana State University	Paraelectric phases and magnetoelectric multiferroics on twisted van der Waals bilayers	14
Vincent Martinetto	University of California, Merced	Predicting Kohn-Sham Potentials with Physics-Informed Neural Nets	17
Luis Martinez-Gomez	Emory University	Topological advantages for adsorbate chemisorption on conjugated chains	37
Md Mehdi Masud	University of California, Merced	Electronic phase transitions, pressure ionization, and electrider-like behavior of solids under extreme compression: A first-principles study	25
Cody Milne	Arizona State University	Electronic and Piezoelectric Properties of Wurtzite $BxAl_{1-x}N$ Alloys	4
Normand Modine	Sandia National Laboratories	Insight into the Role of Excited States in Carrier Capture by Semiconductor Defects	35
Christopher Myers	UC Merced	The Interplay Between Solute-Solvent Interactions for Spectral Lineshapes of the Cresyl Violet Chromophore	23
Drake Niedzielski	Cornell University	The ab initio prediction of ARPES signatures for extended systems without translational symmetry	33
Uday Panta	UC Merced	Perturbative Ensemble Density Functional Theory in real space	38
Vasilios Passias	University of Illinois at Urbana-Champaign.	First Principles and accurate TB model investigation of Fermi Arcs in $Na_3Bi$ .	Virtual
Nabaraj Pokhrel	University of California, Merced	Ferroelectric switching pathways, domain structure, and domain wall vortex in $SrBi_2(Ta,Nb)_2O_9$	42
Babu Baijnath Prasad	National Taiwan University & Academia Sinica, Taipei, Taiwan	Helicity-tunable spin Hall and spin Nernst effects in multifold chiral fermion semimetals $XY$ ( $X=Co, Rh$ ; $Y=Si, Ge$ )	1
Shang Ren	Rutgers University	Zone-center chiral phonons from broken time reversal symmetry	9
Jiawei Ruan	UC Berkeley	Optically controlled single-valley exciton doublet states with tunable internal spin structures and spin magnetization generation	41
Daniel Seleznev	Rutgers University	Theory of surface orbital magnetization	2
Arabi Seshappan	UC Merced	Optical excitation energies and spin studies of charged $Co@S$ defect of $WS_2$ computed with the spin-flip Bethe-Salpeter equation approach	34
Monirul Shaikh	University of Nebraska at Kearney	First principles studies of magnetic adatoms on ferroelectric surfaces	44
Elsa Vazquez	UC Merced	Characterizing Mechanisms and Structure of 2D Sliding in Ni-doped $MoS_2$	28
Abraham Molla Wagaye	Hawassa University	Structure and molecular interactions in 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide ionic liquid, ethylene carbonate and dimethyl carbonate blends for applications in next-generation Li-ion battery electrolytes — combined DFT and molecular dynamics study.	Virtual
Imam Wahyutama	University of California Merced	Attosecond molecular charge migration simulations using the density matrix renormalization group	11

Tyler Wu	Cornell University	A Truncated Green's Function Approach in Plane Wave Density Functional Theory For Free Electron Scattering in Slab Geometries	18
Sameen Yunus	University of California, Merced	Average Atom Models for Warm Dense Matter as a DFT Embedding Theory Problem	26
Shimin Zhang	University of California, Santa Cruz	Advanced Simulations of Spin defect in hBN: Strain and substrate effect, ODMR and Quantum Embedding theory	43
Tobias Zier	UC Merced	Energy flow in laser-excited hBN-graphene heterostructures	3
Rajendra Zope	University of Texas at El Paso	Self-interaction-error free density functional calculations using a locally scaled self-interaction-correction method	20

Poster Title: First Principles and accurate TB model investigation of Fermi Arcs in Na<sub>3</sub>Bi.

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Abstract: Na<sub>3</sub>Bi is a topological Dirac semimetal [1] initially thought to have double surface Fermi arcs on facets with momentum separated surface projected Dirac points [1,2,3]. However, it was shown that bulk symmetry preserving terms that leave the Dirac points unchanged can deform the double surface Fermi arcs into a closed Fermi contour that does not connect to the Dirac points [4]. Angle resolved photoemission spectroscopy (ARPES) measurements on Na<sub>3</sub>Bi's (100) facet [5] are not clear enough to definitively show whether the two surface states connect to the Dirac points with a characteristic cusp at the connection point [2]. To check the existence of Na<sub>3</sub>Bi's double Fermi arcs, we construct a first-principles based tight binding model using pseudo-atomic orbitals [6]. This tight binding model allows us to construct very thick Na<sub>3</sub>Bi (100) slabs and explicitly evaluate whether the arcs form in more realistic models of these slabs.

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[3] E. V. Gorbar et al., *Dirac semimetals A<sub>3</sub>Bi (A= Na, K, Rb) as  $\mathbb{Z}_2$  Weyl semimetals*. Physical Review B, 91(12):121101, March 2015. Publisher: American Physical Society.

[4] Kargarian, M., Randeria, M. & Lu, Y.-M. *Are the surface Fermi arcs in Dirac semimetals topologically protected?* Proc. Natl. Acad. Sci. 113, 8648 (2016).

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## Structure and molecular interactions in 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide ionic liquid, ethylene carbonate and dimethyl carbonate blends for applications in next-generation Li-ion battery electrolytes — combined DFT and molecular dynamics study.

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### Abstract

Both density functional theory (DFT) and molecular dynamics (MD) based on classical force field were used to provide both structural and electronic insight into the multifold interactions occurring in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquid in the presence of ethylene carbonate and dimethyl carbonate co-solvent mixtures which are currently being targeted for applications in next-generation Li-ion battery electrolytes. In order to give a visual understanding of the molecular interactions, the structures of cations, anions, and cation - anion ion pairs were systematically studied using DFT calculations. The nature of hydrogen bond interactions in a series of ion pair conformers have been thoroughly discussed by analyzing the interaction energies, stabilization energies and natural orbital analysis of the ion pair conformers. Multiple but weak C–H---O/N hydrogen bonds and anion donor  $\pi^*_{C-N}$  interactions have been observed. Charge transfer occurs mainly from the lone pairs of oxygen and nitrogen atom to the  $\sigma$ -type anti-bonding orbital of the C–H bonds and  $\pi$ -type anti-bonding orbitals of N–C bonds. According to the MD study, the addition of carbonate co-solvents into the pure ionic liquid creates a more structured system than the pure ionic liquid. The coordination of the O/N atoms of the bis(trifluoromethylsulfonyl)imide anion to the most acidic H atom of 1-ethyl-3-methylimidazolium cation showed a marked decrease with increase in carbonate concentration indicating that the C–H---O/N hydrogen bond interaction is reduced by the presence of high carbonate content. Furthermore, in the pure ionic liquid, adjacent cations are almost exclusively located on top and below the ring cation, whereas the anions mainly coordinate to the cation within the ring plane. The addition of large amount of carbonate co-solvents disturb the original near ordering which is found in the pure ionic liquid.

Key words: electrolyte, Li-ion, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, ethylene carbonate, dimethyl carbonate.

## Helicity-tunable spin Hall and spin Nernst effects in multifold chiral fermion semimetals XY (X=Co, Rh; Y=Si, Ge)

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Transition metal monosilicides CoSi, CoGe, RhSi and RhGe in the chiral cubic B20 structure with space group  $P2_13$  have recently been found to host multifold chiral fermions beyond spin-1/2 Weyl fermions, and also exhibit exotic physical phenomena such as long Fermi arc surface states, gyrotropic magnetic effect and quantized CPGE. Thus, exploring novel spin-related transports in these unconventional chiral fermion semimetals may open a new door for spintronics and spin caloritronics. In this work, we study the spin Hall effect (SHE) and spin Nernst effect (SNE) in the CoSi family based on *ab initio* relativistic band structure calculations. First, we find that unlike nonchiral cubic metals, the CoSi family have two independent nonzero SHC (SNC) tensor elements, namely,  $\sigma_{xy}^z$  and  $\sigma_{xz}^y$  ( $\alpha_{xy}^z$  and  $\alpha_{xz}^y$ ). Further, SHCs and helicity of the chiral structure are found to be correlated, thus enabling SHE detection of structural helicity and hence chiral fermion chirality. Second, the intrinsic SHE and SNE in some of these considered compounds are large. In particular, the calculated SHC of RhGe is as large as  $-140$  ( $\hbar/e$ )(S/cm). The calculated SNC of CoGe is also large, being  $-1.3$  ( $\hbar/e$ )(A/m K) at room temperature. Due to their semimetallic nature with low electrical conductivity, these topological semimetals may have large spin Hall and spin Nernst angles, being comparable to that of Pt metal. Third, the SHC and SNC of these compounds can also be increased by raising or lowering  $\mu$  to, e.g., the topological nodes, via either chemical doping or electrical gating. Our findings thus suggest that the CoSi family could be interesting materials for creating better spintronic and spin caloritronic devices, as well as a platform for investigating novel spin-transport and exotic phenomena in unconventional chiral fermion semimetals.

[1] Ting-Yun Hsieh, Babu Baijnath Prasad and Guang-Yu Guo, Helicity-tunable spin Hall and spin Nernst effects in unconventional chiral fermion semimetals XY (X=Co, Rh; Y=Si, Ge), Phys. Rev. B **106**, 165102 (2022).

## Theory of surface orbital magnetization

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The theory of bulk orbital magnetization has been formulated both in reciprocal space based on Berry curvature and related quantities, and in real space in terms of the spatial average of a quantum mechanical local marker. Here we consider a three-dimensional antiferromagnetic material having a vanishing bulk but a nonzero surface orbital magnetization. We ask whether the surface-normal component of the surface magnetization is well defined, and if so, how to compute it. As the physical observable corresponding to this quantity, we identify the macroscopic current running along a hinge shared by two facets. However, the hinge current only constrains the difference of the surface magnetizations on the adjoining facets, leaving a potential ambiguity. By performing a symmetry analysis, we find that only crystals exhibiting a pseudoscalar symmetry admit well-defined magnetizations at their surfaces at the classical level. We then explore the possibility of computing surface magnetization via a coarse-graining procedure applied to a quantum local marker. We show that multiple expressions for the local marker exist, and apply constraints to filter out potentially meaningful candidates. Using several tight-binding models as our theoretical test bed and several potential markers, we compute surface magnetizations for slab geometries and compare their predictions with explicit calculations of the macroscopic hinge currents of rod geometries. We find that only a particular form of the marker consistently predicts the correct hinge currents.

This work was supported by NSF Grants No. DMR-1954856 and No. DGE-1842213.

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- [1] D. Seleznev and D. Vanderbilt, Towards a theory of surface orbital magnetization, *Phys. Rev. B* **107**, 115102 (2023).

# Energy flow in laser-excited hBN-graphene heterostructures

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Inter-material correlations of electrons and phonons in vdW heterostructures, like hBN-graphene open interaction and energy diffusion channels that are not present in either of the single materials. Recent research showed, e.g., out-of-plane heat transfer by electron-hyperbolic phonon coupling [1] or ultrafast relaxation of hot phonons [2]. Here, we studied how laser-deposited energy is distributed within and between the layers of the heterostructure. Therefore, we performed ab initio calculations of mono-layer hBN-graphene and many-layer hBN-graphite heterostructures excited by femtosecond-laser pulses with a central wavelength of 800 nm. Note that hBN is transparent for that wavelength: it does not absorb laser-pulse energy, whereas graphene does. By comparing our simulation results to our experimentally obtained time-resolved electron diffraction data we gain insights on the energy flow from excited graphene to the connected hBN layer within a 2D heterostructure on an atomistic level and ultrashort timescale.

[1] Klaas-Jan Tielrooj, et al., Nature Nanotechnology 13, 41–46 (2018)

[2] Dheeraj Golla, et al., APL Mat. 5, 056101 (2017)



## Electronic and Piezoelectric Properties of Wurtzite $B_xAl_{1-x}N$ Alloys

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Boron aluminum nitride ( $B_xAl_{1-x}N$ ) alloys are ultra-wide bandgap materials with a wide range of electronic applications, such as high-temperature electronics and optoelectronics. In this poster, we present a comprehensive study of the electronic properties of  $B_xAl_{1-x}N$  based on first-principles calculations. Structural configurations of  $B_xAl_{1-x}N$  were predicted through the method of cluster expansions, and the band gaps and band structures of  $B_xAl_{1-x}N$  were investigated using excited state *GW* calculations. Additionally, we report spontaneous polarization values, dielectric constants, breakdown fields, and piezoelectric properties of  $B_xAl_{1-x}N$ , and provide insights into their dependence on the material's structural properties. Our results reveal that  $B_xAl_{1-x}N$  possesses a wide range of electronic properties, including a ultra-wide bandgap, high spontaneous polarization, and high piezoelectric coefficients which increase with boron fraction. These properties make  $B_xAl_{1-x}N$  a promising candidate for high *k* dielectric and ferroelectric devices, such as high temperature ferroelectric memory devices. Additionally, their high band gaps reduce leakage current in devices. Overall, our study provides a deeper understanding of the electronic properties of  $B_xAl_{1-x}N$  and lays the foundation for its potential use in future electronic devices.

## Developing a High-Throughput *Ab Initio*-Kinetic Model for the Prediction of Material Passivation

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With corrosion remaining a significant economic issue, the ability to *a priori* predict the kinetics of material corrosion in a high-throughput manner remains an important consideration in a wide range of applications that require corrosion resistance in aqueous environments. To address this challenge, we have developed an *ab initio*-kinetic framework for predicting material stability by combining electronic structure and atomistic methods with a kinetic passivation model called the Point Defect Model (PDM). This non-empirical framework can predict the growth rate of passivation films in any elemental material without prior experimental knowledge. After developing this workflow, we have evaluated its performance through a common metal case study and compared it with available experimental literature. Finally, we have evaluated the viability of extending this framework to the more than 700 elemental materials which are currently available in the Materials Project database.

# **Excited-state force calculations from GW/BSE and DFPT: development and application to organic metal halide perovskites**

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While absorption of light has been long studied in electronic structure, the interactions of the resulting excited states with the lattice that cause light-induced structural changes remain hard to handle. This is an underlying phenomenon for photodegradation, Stokes shifts, exciton transport, and other photophysics, which can be studied via excited-state forces. Ismail-Beigi and Louie [Phys. Rev. Lett. 90, 076401 (2003)] developed an approximate theory combining quasiparticle and excitonic effects from GW and Bethe-Salpeter Equation (BSE) with electron-phonon interactions from Density Functional Perturbation Theory, but this approach has been little used. We revisit this theory, with improvements to the underlying approximations, and implement it in a practical workflow for BerkeleyGW. We make detailed tests of the validity of these approximations and demonstrate favorable convergence properties that make the forces less time-consuming than ordinary GW/BSE. Then we explore some applications to methylammonium lead iodide perovskites, whose use in solar cells is limited by photodegradation. We study the equilibrium structures of the excited states, and coupling between different excitons due to the phonons, to give insight into the photophysics of perovskites.

**Title: DFT study of  $\text{Zn}_{(1-x)}\text{Fe}_x\text{Se}$ : Electronic structure, and magnetic properties**

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In this document, we present the electronic structure, and magnetic properties of  $\text{Zn}_{(1-x)}\text{Fe}_x\text{Se}$  (for  $x = 0\%$ ,  $6.25\%$ ,  $12.5\%$ ,  $25\%$ , and  $50\%$ ) using DFT. We examined using the generalized gradient approximation (GGA) and with Hubbard correction (GGA + U), where U is a Hubbard parameter. The calculated lattice parameter is  $5.65 \text{ \AA}$ , which is quite close to the experimental lattice parameter of ZnSe,  $5.66 \text{ \AA}$ . In this study, the GGA+U provides a better bandgap approximation ( $E_g = 1.3708 \text{ eV}$ ) than the GGA ( $E_g = 1.229 \text{ eV}$ ), which is consistent with experimental results and values previously reported. According to our results, the iron-doped zinc selenide exhibits antiferromagnetic coupling for a percentage of substitution greater than  $12.5\%$ . In addition, for an iron substitution of  $12.5\%$  with the distance between dopant atoms exceeding  $5.6364 \text{ \AA}$ , it tends to exhibit ferromagnetic properties. Therefore, the iron-doped zinc selenide manifests the dilute magnetic semiconductor and can be considered to enhance its applications in the field of spintronics and magneto-optical devices based on further experimental results.

# Velocity inverted Dirac points and Weyl nodal lines in noncentrosymmetric hexagonal NaZnSb

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Here we employ first-principles calculations to examine the nodal structure and related topological properties featured in the electronic energy bands of NaZnBi, a polar hexagonal ABC compound with a noncentrosymmetric stuffed wurtzite crystal structure. We show that band inversion at  $\Gamma$  drives four-fold-degenerate Dirac points and three pairs of intersecting nodal circles. The Dirac points with four-fold degeneracy and linear dispersion exhibit unconventional three-dimensional dispersion, in which the radial group velocities are inverted between the conduction and valence bands as the angular coordinate varies. In addition, the band structure exhibits glide mirror-symmetry-protected Weyl nodal lines, which intersect at the Dirac points. We topologically characterize the Weyl line nodes by calculating the Berry phase polarization. The Berry phase polarization is  $\mathbb{Z}_2$  quantized due to the two-fold rotation and time-reversal symmetries, and its physical manifestation is demonstrated by calculating the surface energy spectrum. Our results suggest the potential for experimental exploration of topological states in these materials.

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Title:

Zone-center chiral phonons from broken time reversal symmetry

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Abstract body:

In conventional *ab initio* methodologies, phonons are calculated by solving equations of motion involving static interatomic force constants and atomic masses. However, this approach does not fully account for the effects of broken time-reversal symmetry in systems with magnetic order. Recent attempts to rectify this involve the inclusion of the velocity dependence of the interatomic forces in the equations of motion, which is given by the nuclear Berry curvature. This can result in “chiral” phonon modes with non-zero angular momentum, even at the zone center. We show, via a novel density-functional theory methodology based on finite displacements, that the main contribution to this nuclear Berry curvature is from the spin rotations caused by the phonons. This requires spin and phonon degrees of freedom (DOF) to be treated on the same footing. We propose a method involving Hessian matrices and Berry curvature tensors in terms of both spin and phonon DOF, and develop a first-principles methodology to calculate them. By combining group theory analysis with *ab initio* calculations, we investigate chiral phonon modes in both ferromagnetic and antiferromagnetic materials, and the implication for energy splitting of chiral phonon modes is also discussed.

Reference:

- [1] J. Bonini, S. Ren, D. Vanderbilt, M. Stengel, C.E. Dreyer, and S. Coh, “Frequency splitting of chiral phonons from broken time reversal symmetry in CrI<sub>3</sub>,” *Phys. Rev. Lett.* 130, 086701 (2023)
- [2] S. Ren, J. Bonini, M. Stengel, S. Coh, C.E. Dreyer, and D. Vanderbilt, “Zone-center chiral phonons from broken time reversal symmetry”, *in preparation*

**Sodium-containing Layered Oxides for Replacing Li Battery Cathodes: Defect Control to Enhance Ionic Conductivity.**

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**Abstract:** The goal of this project is to develop sodium-containing novel layered honeycomb oxides for solid state battery cathodes. A combined experimental and theoretical effort is being undertaken by our team to discover alternatives to replace critical elements like lithium (Li) and cobalt (Co) which are currently routinely used in solid state secondary batteries for energy storage. An economically and environmentally viable solution is to use sodium (Na) or other alkalis to replace the critical elements. We will explore the family of compounds  $A_2M_2\text{TeO}_6$  ( $A$  = alkali,  $M$  = transition metal) in this project. Our preliminary results include successful synthesis of several  $\text{Na}_2\text{Ni}_2\text{TeO}_6$ -derived compounds with varying Na content (i.e. cationic vacancies) and substitutions (ex. Zn replacing Na). The motivation for the chemical tuning is the close connection between defect structure and ionic conductivity in the proposed compounds. We are working on the quantification of the optimal Na-content for highest ionic conductivity in the proposed compounds. A related goal is to understand the role played by hexagonal layers of Ni in the ionic conductivity of Na. To test this hypothesis, we have synthesized  $A_2M_2\text{TeO}_6$  variants with chemical substitutions at the Ni site. Density functional theory (DFT) calculations are underway to calculate the most favorable chemical coordination around Na ions which supports optimal ionic conduction. Our preliminary DFT result shows good agreement between calculated and measured lattice constants, predicting the bulk modulus to be 98 GPa and 97 GPa for  $\text{Na}_2\text{Ni}_2\text{TeO}_6$  and  $\text{Na}_3\text{Ni}_2\text{TeO}_6$ , respectively. Further investigation to determine the bulk modulus of  $\text{Na}_2\text{Ni}_2\text{TeO}_6$  is needed experimentally.

## Attosecond molecular charge migration simulations using the density matrix renormalization group 11

The charge migration process resulting from ultrafast ionization of a molecule happens on an attosecond timescale. Attosecond dynamics, however, is challenging to describe because the remaining electrons form complicated, correlated states that cannot be described by mean-field methods. For such dynamical purposes, post-mean-field methods such as multiconfigurational methods offer a much better accuracy. However, they have a steep scaling of the computational cost, which limits their use for large molecules. The density matrix renormalization group (DMRG) provides a more favorable method in terms of both accuracy and efficiency. In this work, we show how to efficiently simulate attosecond dynamics using a time-dependent variant of the DMRG. We showcase our simulation framework using the dynamics upon sudden removal of a valence electron of H<sub>2</sub>O. We observe that the charge response to such a sudden ionization happens primarily within the first ~200-300 as, followed by an asymptotic period where the charge motion is negligible. While the DMRG in an electronic structure setting is very costly due to the required large basis sizes (bond dimension) of more than 1000, we show here that the H<sub>2</sub>O attosecond dynamics can be efficiently captured using a bond dimension of only 50, and simulating the dynamics spanning 2 fs only takes less than 2 minutes on a desktop computer. Thus, simulations of larger molecules are within reach and we plan to apply the DMRG not only to larger systems but also to the more challenging application of directly simulating electron ejection from the molecule by a strong laser field.



Title: Predicting quasiparticle and excitonic properties using machine learning

Authors: Tathagata Biswas and Arunima K. Singh

Affiliation: Arizona State University

Abstract:

In recent years, GW-BSE has been proven to be extremely successful in studying the quasiparticle (QP) bandstructures and excitonic effects in the optical properties of materials. However, the massive computational cost associated with such calculations restricts their applicability in high-throughput material discovery studies. These studies are capable of unearthing future generations of promising photocatalysts, photovoltaics, and many more materials suitable for diverse photoabsorption-related applications. We have developed python workflow package *pyGWBSE* [1] to perform high-throughput GW-BSE simulations. Using *pyGWBSE* we have created a database of various QP properties as well as BSE absorption spectra of ~500 materials. These materials were selected from the Materials Project database and have up to 4 atoms per unit cell. Multiple supervised machine learning methods were then employed on this dataset to investigate the applicability of the methods in predicting the quasiparticle and excitonic properties. We have shown that it is possible to apply machine learning to identify materials that are suitable for various photoabsorption related applications. Our machine-learning model has identified ~100 materials for visible light and ~200 materials for UV light applications based on their excitonic and optical properties.

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## Rare-Earths, Critical Materials, and Hexagonal Motifs: Methods and Applications to Energy Systems

T. Baruah, Z. Hooshmand, M.F. Islam, T. Lombard, K. Withanage, Y. Yamamoto, E. Kim, M. R. Pederson

University of Texas at El Paso, Dept. of Physics

This project improves methods for computational design of energy systems constructed from low-density critical-element systems. We design hexagonal surface templates paired with magnetic adsorbates, improve quantum descriptions of atoms when relativity is important, and work jointly with experimentalists to validate theory.

The nG-hBN/Rh(111), synthesized at large scale by Kuster *et al*, allows for superlattices with chemical potentials that are controlled by graphene-nanoflake concentration. This provides possibilities for trapping rare-earth metals on or in the corrugated regions of the superlattice where variations in chemical potential trap, separate, and/or immobilize rare-earth-elemental systems. Such superlattices can may selectively adsorb rare-earth containing molecular magnets and serve as initiators of hexagonal arrays of such systems that ensure the desired magnetic attributes and allow the molecular magnets to participate in template formation. For example, motivated by experimental developments on a molecular magnetic building block, we demonstrate that such strong magnetic molecule, with less than one percent critical elements can be adsorbed on a hexagonal lattice and conform to the desired structure and symmetry.

**Density Functional Theory (DFT) for Insights on Hexagonal and Monoclinic CePO<sub>4</sub>:** The primary compound found in monazite is CePO<sub>4</sub>, from which cerium is extracted for industrial use. Because of CePO<sub>4</sub>'s dimorphic nature (Mooney et al. 1950), experimental studies observed both hexagonal and monoclinic phases of CePO<sub>4</sub>. More computational work is needed to better understand formation of the hexagonal phase of CePO<sub>4</sub> since monazite may be energetically favorable. We performed DFT calculations on four different structures including monoclinic and hexagonal phases and compared their relative energetics. XRD patterns were simulated, from DFT, using the best structures for hexagonal and monoclinic phases. A close comparison between simulation and experiment confirms the formation of the hexagonal phase. Although the monoclinic phase can be derived by heating up the hexagonal phase suggesting that all monoclinic phases may have once been hexagonal, an f-electron Hubbard Correction shows the monoclinic phase is more favorable. Without such corrections, the two have a similar energy per molecule. Since monoclinic is accepted as the more energetically favorable form, it can be concluded that a Hubbard f-correction is necessary to accurately calculate the electronic properties of CePO<sub>4</sub>.

**Relativistic Improvements in DFT:** Relativistic effects are crucial for heavy elements such as actinides and lanthanides. We implement relativistic DFT methods into the FLOSIC electronic structure software. The FLOSIC code is a software package for DFT calculations with and without the Fermi-Lowdin self-interaction correction method using the Gaussian-type orbitals. Our implementation for relativity is based on the zeroth-order regular approximation (ZORA) or scalar relativity. This is a popular means for approximating the Dirac equation. The Gaussian basis set all electron implementation of ZORA allows for calculation on properties related to core electrons. Scaled ZORA energy and Laikov model potential are also implemented for comparisons. A comparison on the ZORA calculations with DFA potential as well as model potentials are compared. Moreover, the relativistic effects on the total energies and eigenvalues of atoms and molecules are studied.

Drs. Baruah, Kim, and Pederson gratefully acknowledge support from the Department of Energy and ISSR grant.

## Paraelectric phases and magnetoelectric multiferroics on twisted van der Waals bilayers

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Nanometer-thick ferroic and multiferroic systems are being investigated for low-power optoelectronic applications. Recent theoretical and experimental works on few-layer van der Waals structures have explored symmetry breaking phenomena to enable ferroic properties in two-dimensional (2D) systems that could be controlled with small electric fields. Here, we explore the relative rotations of van der Waals bilayers that break inversion symmetry and induce an intrinsic electric dipole. First, we study the ferroelectric properties of rotated (R-stacked) transition metal dichalcogenide (TMD) bilayers by combining density functional theory (DFT) and machine-learned algorithmic training for the generation of moment-tensor potentials (MTPs). This enables molecular dynamics (MD) simulations of large systems during long simulation time frames that are useful to understand their ferroelectric to paraelectric transition, as recently observed in R-stacked WSe<sub>2</sub> bilayers. Secondly, we explore ferromagnetically (FM) coupled rotated CrI<sub>3</sub> bilayers whose lack of inversion symmetry produces an imbalance of nearest neighbors among layers that enhances the out-of-plane intrinsic electric dipole. The observed in-plane atomic displacements also give rise to in-plane intrinsic dipoles that could yield new magnetoelectric coupled multiferroics.

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## Approximating excited electronic states with spin-corrected self-consistent field methods

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The practical treatment of systems with unpaired/localized electron spins remains a challenge in electronic structure theory. Typically, such calculations require computationally expensive multi-determinantal methods. The alternative use of more efficient, single-determinant methods like unrestricted Hartree-Fock and Kohn-Sham density functional theory for approximating excited-state calculations often leads to spontaneous spin symmetry breaking. This project explores the effectiveness of a model for correcting the resulting spin contamination in open-shell, excited state calculations. The proposed methodology hypothesizes that excited-state energies can be calculated at mean-field cost, yet still have comparable results to more sophisticated and computationally involved approaches. Preliminary results support this hypothesis by showing a significant correction in the potential energy curves for a test set of small-molecule excited states.

**Title:** Charge transition levels of nitrogen vacancies in w-AIN computed within the DFT+GW formalism

**Authors:** Adway Gupta, Tathagata Biswas, Arunima K. Singh

**Affiliation:** Department of Physics, Arizona State University, Tempe, Arizona 85287-1504

**Abstract:** Defects in solid state materials have a huge impact on optical and transport properties of a material and can be the foundation for robust qubit systems for quantum information, defect mediated photocatalysis and next generation solar energy applications. The electronic structure of point defects can be modeled using *ab-initio* techniques like density functional theory(DFT). However this ground state theory cannot capture the excited state effects of defects leading to major disagreement between theoretical and experimental values of defect formation energies and subsequently charge transition levels (CTLs). Inclusion of exact exchange-correlation using hybrid functionals leads to a better agreement with experiments, however, the fraction of exact exchange becomes a variable factor limiting the predictability of the method.

In this work we use a DFT+GW formalism[1] to determine defect formation energies and CTLs of nitrogen vacancies in wurtzite-AIN. CTLs for charged N vacancies in wurtzite-AIN have been shown to emit in the far blue region, with robust defect states, driving their potential applications in solid state qubit systems. We isolate the structural and electronic contributions to the CTLs, compute the former using DFT, while the latter is determined using the excited state GW method. Our results are within reasonable agreement with experimental values, as well as show significant improvement over previous theoretical methods to compute the defect formation energies and CTLs of N vacancies in wurtzite-AIN.

**References:**

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# Predicting Kohn-Sham Potentials with Physics-Informed Neural Nets

Vincent Martinetto

May 18, 2023

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Kohn-Sham density functional theory is one of the most successful electronic structure methods for molecules and materials, and density-to-potential inversions can provide insights into the exact formalism underlying this approach. This work looks to circumvent normal inversion schemes by employing Physics Informed Neural Nets (PINNs) in their place. PINNs help to improve predictive transferability and reduce the requisite amount of data to properly train a neural network. The structure of a simple convolutional network and its application to three small datasets in 1D will be presented. Next steps for improving the network will be discussed.

# A Truncated Green's Function Approach in Plane Wave Density Functional Theory For Free Electron Scattering in Slab Geometries

Tyler Wu and Tomás Arias  
*Cornell University*

Johannes Kevin Nangoi  
*University of California, Santa Barbara and  
Cornell University*  
(Dated: May 19, 2023)

Plane wave density functional theory (DFT) has proven to be a powerful tool in modern computational physics for calculations involving crystalline systems. A substantial drawback for systems with finite spatial extent in at least one direction is the interaction of long-range functions with periodic images. While Coulomb truncation methods limit simple image effects, electronic interactions between images become a major source of error when calculating scattering, vacuum-propagating, states. As highlighted in this poster, we will use a truncated Green's Function approach to break periodicity in the  $Z$  direction in such a way that is still compatible within plane wave DFT pseudopotential ( $V_{ps}$ ) codes. Using this approach, we will show both transmission/reflection and photoemission predictions for a variety of 2D materials including transition metal dichalcogenides (TMDs).

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A crucial step for understanding emergent physics of correlated systems is determining whether a particular model is emergent from ultraviolet physics. So far, a systematic way of detecting emergent behavior from *ab initio* calculations has yet to be available in the state-of-the-art model derivation procedures. In this study, we propose that low-energy emergent physics forms disjoint clusters in an extended descriptor space beyond just energy cutoffs. Working from highly-accurate many-body quantum Monte Carlo calculations of the *ab initio* hydrogen chains, we show that a cluster-based classification algorithm can detect a Heisenberg-like emergent subspace using a set of descriptors of the energy eigenstates. We established explicitly the one-to-one mapping between the *ab initio* low-energy Hilbert space and the model Hilbert space by matching the local correlations, and thus the renormalization of the model is directly read off. As a result, the *ab initio* dynamics is nearly exactly reproduced by the renormalized model.

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## **Self-consistent implementation of locally scaled self-interaction-correction method**

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We have recently proposed a local self-interaction correction (LSIC) method [Zope, R. R. et al., J. Chem. Phys. 151, 214108 (2019)] which is a one-electron self-interaction-correction (SIC) method that uses an iso-orbital indicator to apply the SIC at each point in space by scaling the exchange-correlation and Coulomb energy densities. The LSIC method is exact for the one-electron densities, also recovers the uniform electron gas limit of the uncorrected density functional approximation, and reduces to the well-known Perdew-Zunger SIC (PZSIC) method as a special case. We present a self-consistent implementation of LSIC within the FLOSIC scheme. The atomic forces as well as the forces on the Fermi-Lowdin orbital descriptors are also implemented for the LSIC energy functional. Results show that LSIC with the simplest local spin density functional predicts atomization energies of AE6 dataset better than some of the most widely used GGA functional (e.g. PBE) and barrier heights of BH6 database better than some of the most widely used hybrid functionals (e.g. PBE0 and B3LYP). This work shows that accurate results can be obtained from the simplest local density functional by removing the self-interaction errors using an appropriately designed SIC method.

This work was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, as part of the Computational Chemical Sciences Program under Award No. DE-SC0018331

## Electronic Structure Workshop 2023

**Poster title:** Exploring novel strain states in freestanding ferroelectric oxide membranes

**Authors:** Md Kamal Hossain, Elizabeth Nowadnick  
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### Abstract

Recent advances in materials synthesis techniques have enabled the production of oxide materials in freestanding two-dimensional membrane form. These freestanding membranes can display properties distinct from their thin-film counterparts constrained by substrates. For example, recent experiments have shown that ferroelectric oxide membranes, compared to bulk materials, display faster switching times and lower switching energies. However, the underlying mechanisms and strategies for further optimizing these properties remain largely unexplored. Furthermore, the application of mechanical strain has long been employed to modify the properties of ferroelectrics, but the introduction of membranes presents unexplored opportunities to design novel strain states with different symmetries. In this work, we use density functional theory calculations to explore prototypical ferroelectric  $\text{BaTiO}_3$  in freestanding membrane form. In particular, we systematically explore uniaxial, biaxial, and multidirectional strain states and explore how tuning the strain can optimize their ferroelectric behavior. These results advance understanding of strain-mediated tuning of ferroelectric properties in oxide membranes, providing valuable insights for the design and development of next-generation low-power electronic devices.

## Manipulating Topological Properties in $\text{Bi}_2\text{Se}_3/\text{BiSe}/\text{TMDC}$ Heterostructures with Interface Dipole

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The heterostructures of topological insulator  $\text{Bi}_2\text{Se}_3$  on transition metal dichalcogenides (TMDCs) possess rich topological properties, with potential applications as topological superconductors and Chern insulators. Mechanisms to further manipulate the topological states of this class of materials are important for their potential applications. Recent studies demonstrated the growth of a cubic BiSe buffer layer between  $\text{Bi}_2\text{Se}_3$  and the metallic TMDCs substrate. We consider four different metallic TMDC substrates (1T phase  $\text{VSe}_2$ ,  $\text{MoSe}_2$ ,  $\text{TiSe}_2$ , and 2H phase  $\text{NbSe}_2$ ), and study the topological properties of  $\text{Bi}_2\text{Se}_3/\text{BiSe}/\text{TMDC}$  Heterostructures through first-principles density functional theory calculations. We analyze the effects of TMDC work function and strain on the charge transfer at the BiSe/TMDC and BiSe/ $\text{Bi}_2\text{Se}_3$  interfaces. Our findings reveal that the interface dipole at the BiSe/ $\text{Bi}_2\text{Se}_3$  interface induces a strong Rashba spin-orbit coupling and band splitting in  $\text{Bi}_2\text{Se}_3$ . The strong electric field of the interface dipole breaks the inversion symmetry in  $\text{Bi}_2\text{Se}_3$ , leading to the recovery of Dirac surface states at few quintuple layers which otherwise only occurs in thick  $\text{Bi}_2\text{Se}_3$  layered samples. Our study presents a promising avenue for tunable topological properties in this class of heterostructures, allowing for potential applications in quantum devices.

## The Interplay Between Solute-Solvent Interactions for Spectral Lineshapes of the Cresyl Violet Chromophore

Christopher A. Myers,<sup>1</sup> Shao-Yu Lu,<sup>1</sup> Sapana Shedge,<sup>1</sup> Arthur Pyuskulyan<sup>1</sup>, Liang Shi,<sup>1</sup> and Christine M. Isborn<sup>1</sup>

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Molecular dynamics (MD) simulations with explicit solvent, when combined with a trajectory-based approach for determining spectroscopic properties, have been shown to accurately describe the complex coupling between the chromophore's vibrations, electronic excitations, and the influence from the solvent environment. While classical force fields offer a promising route to circumvent the computational complexity of simulating on *ab initio* potential energy surfaces, the extent to which particular chromophore-solvent interactions dictate spectral lineshapes must first be uncovered with electronic structure methods. In the work presented here, we demonstrate how a molecular mechanics (MM) force-field, when parameterized using explicit solute-solvent interactions, can produce similar spectral properties as those obtained using QM/MM simulations at the CAM-B3LYP/6-31G\* level of theory. For the cresyl violet chromophore in methanol, analysis of the solvent environment via TDDFT computations reveal which intermolecular interactions are important for reproducing experimental spectral lineshapes and how such information can in turn be used to further improve force field parameters.

## Competing structural phases and piezoelectricity in Ruddlesden-Popper $\text{Li}_2\text{SrNb}_2\text{O}_7$ from first principles

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### Abstract:

Layered perovskite oxides such as the  $\text{A}_3\text{B}_2\text{O}_7$   $n=2$  Ruddlesden-Popper family have generated significant recent interest because they host a variety of novel properties such as hybrid improper ferroelectricity, competing structural phases, and complex domain structures. A closely related family of materials are the Li-based layered perovskites  $\text{Li}_2\text{AB}_2\text{O}_7$ , with crystal structures characterized by alternating perovskite and lithium oxide layers. Recent experiments have reported a competition between ferroelectric and non-polar phases in  $\text{Li}_2\text{SrNb}_2\text{O}_7$ , mediated by coupled octahedral rotation distortions, polarization, and antipolar distortions. In this work, we use density functional theory along with group theoretical analysis to explore the competing structural phases in  $\text{Li}_2\text{SrNb}_2\text{O}_7$ , as well as the impact of epitaxial strain on controlling these phases. We furthermore use density functional perturbation theory to calculate the piezoelectric coefficients of the material. Interestingly, we find an unusual negative longitudinal piezoelectric coefficient. In order to understand the origin of this result, we explore how changes to the octahedral rotation amplitudes impact the piezoelectric coefficients. Our results advance fundamental understanding of phase competition and piezoelectricity in  $\text{Li}_2\text{SrNb}_2\text{O}_7$ .

## Electronic phase transitions, pressure ionization, and electrider-like behavior of solids under extreme compression: A first-principles study

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Pressure ionization is a fundamental process in plasmas in which electrons are liberated from ions with increasing pressure, which is closely related to ionization potential depression, in which pressure makes it easier to remove electrons from ions. Do these phenomena exist in solids as well as plasmas? We investigated this question with plane-wave density-functional calculations on two elemental solids, diamond-structure silicon and hcp cobalt. The Kohn-Sham potential shows a reduction in depth from maximum to minimum, like in plasmas. With increasing compression, we have observed a reentrant semimetallicity (semiconducting  $\rightarrow$  semimetallic  $\rightarrow$  metallic  $\rightarrow$  semimetallic electronic phase transition) in silicon. On the other hand, hcp cobalt undergoes metallic (ferromagnetic)  $\rightarrow$  semimetallic (paramagnetic)  $\rightarrow$  semiconducting (paramagnetic) phase transitions at high compression (in Mbar regime). An analog of pressure ionization is known to occur in simple metals such as sodium, which become electrides (ionic-like insulators) in association with structural changes at high compression. We found that solids can show signatures of electrider formation at extreme compression even while retaining their initial structures. This investigation gives insight about electronic phase transitions of these two solids at extreme compressions ( $\sim 100$  Mbar), which resemble pressure ionization in plasmas.

## Average Atom Models for Warm Dense Matter as a DFT Embedding Theory Problem

Sameen F. S. Yunus, David A. Strubbe

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Warm Dense Matter (WDM) is a dense state of matter occurring in the interiors of giant planets, dense stars, and in the pathways to generating nuclear fusion. It is of interest to develop computationally efficient and accurate models for WDM to predict equations of state and optical properties of such dense plasmas — typical electronic structure methods tend to be computationally expensive and have poor scaling with higher temperatures, and sampling the ionic degrees of freedom is particularly time-consuming. Average Atom Models (AAM) are a mean-field approach to the ionic many-body problem; they constitute a simplified picture of the interacting problem by averaging over different local environments or charge states and building the constituent system with spherically symmetric averaged atomic densities and potentials. DFT-based AAMs provide a computationally inexpensive and fairly accurate picture for a system with negligible interactions such as hot ideal plasmas. However, in strongly correlated systems such as Warm Dense Matter (WDM) where even core atomic orbitals can overlap, AAMs tend to fall short of providing an accurate model of the interactions. Typical approaches introduce physical boundary conditions imposed at cell boundaries to govern interactions; other schemes use closure relations from plasma physics to model ion-ion correlations (two-component plasma TCP-AAM). We propose a DFT embedding theory approach to handle interactions in the AAM in which we consider the average atom embedded in a background plasma described by an ion pair correlation function, e.g. as calculated from TCP-AAM and full quantum mechanical treatments such as quantum molecular dynamics (QMD) for modelling a dense hydrogen plasma. The connection between the embedded atom and background plasma subsystems is made by the nonadditive kinetic potential  $V^{\text{NAD}}$  which can be calculated either from analytical inversion [M. Banafsheh et al., *Phys. Rev. A* 106, 042812 (2022)] or from simple kinetic energy functionals such as the Thomas-Fermi and von Weizsäcker kinetic energy functionals. The ion pair correlation functions generated from our scheme provide a benchmark comparison to validate our approach against existing AAMs and QMD.

Title:

"Dependence of magnetocrystalline anisotropy energies on the local crystal-field environment of magnetic dopants in ferroelectric oxides"

Authors:

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Abstract:

With the addition of a magnetic dopant defect in a ferroelectric oxide, the magnetic properties of this defect may be controlled by the interaction between the external electric field and the polarization field of the ferroelectric host, allowing for nanoscale technological applications. These magnetic properties are coupled to the local crystal field environment of the magnetic defect through the spin-orbit interaction, and changing the polarization direction changes the crystal field environment. Presently, there is no clear understanding of which crystal field environments will allow for favorable magnetic properties, such as a 180-degree reversal of the spin easy-axis with a 180-degree reversal of the electric polarization, or high magnetocrystalline anisotropy energies (MCAE). To address this and to work towards the formulation of design principles to optimize electronic control of single spin sites in ferroelectric oxide hosts, we seek to understand how the MCAE surfaces for these systems depend on crystalline symmetries and electronic structure through first-principles density functional theory (DFT) calculations to simulate these properties for the tetragonal, rhombohedral, and orthorhombic phases of prototypical ferroelectric oxide BaTiO<sub>3</sub>.



## Characterizing Mechanisms and Structure of 2D Sliding in Ni-doped MoS<sub>2</sub>

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In 2D materials, the interplay of Van der Waals forces between layers and covalent bonding within layers plays a key role in dry film lubrication and the formation of out-of-plane heterostructures and moiré bilayers. These forces have not yet received much attention in the case of doped materials. In this study, we extended our previous 1D investigation ([arXiv:2209.15629](https://arxiv.org/abs/2209.15629)) of Ni-doped MoS<sub>2</sub> in bulk and bilayer forms and employed density-functional theory to examine the 2D sliding landscape. Four meta-stable doped structures were identified in earlier work and are utilized here: two are doped via the substitution of Mo/S, and two through octahedral/tetrahedral intercalations. The potential energy surfaces (PES) of Ni-doped MoS<sub>2</sub> have extrema at high-symmetry stackings, similar to the well-established stacking modes of pristine MoS<sub>2</sub>. Notably, Mo-substituted and octahedral intercalated structures demonstrate hysteresis through sliding. By utilizing the nudged elastic band method, we identify transition states on the pathway to lower energy phases. The introduction of dopants in the structures leads to symmetry breaking, resulting in increased registry mismatch between layers. We investigate contributions to the PES in terms of the Registry Index and explore the generalization of the Registry Index to doped materials. These findings enhance our comprehension of the structure and underlying mechanisms of sliding in Ni-doped MoS<sub>2</sub>.

This work was supported with funding from the National Aeronautics and Space Administration (NASA) grant NNX15AQ01 and by a Cottrell Scholar Award from the Research Corporation for Science Advancement, No. 26921. It used computing resources from the Multi-Environment Computer for Exploration and Discovery (MERCED) and Pinnacles clusters (NSF awards OAC-1429783 and OAC-2019144) at the University of California, Merced.

## Self-Interaction Correction : Applications to Molecular Properties

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The self-interaction error (SIE) in density functional approximations (DFA) is responsible for density delocalization and results in systematic errors in the calculation of many properties such as polarizability, reaction barrier heights, magnetic exchange coupling (J) constants, dissociation of molecules, binding of electrons etc. Using the Fermi-Loewdin self-interaction correction scheme[1] we have investigated the role of SIE in DFAs belonging to the lowest three rungs of Jacob's ladder of functionals, (namely, the local spin density approximation, Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA), and the SCAN meta-GGA functionals). The correction is carried in an orbital-by-orbital manner as given by Perdew and Zunger [2]. The properties of interest include vertical detachment energies of water and ammonia clusters anions [3] where the extra electron is weakly bound, dipole polarizabilities of polycenes [4] which are long planar molecules, magnetic coupling constants J [4], and chemical reaction barrier heights [5]. We show that local scaling of SIC is generally needed to counter the over-correcting tendency of Perdew-Zunger self-interaction correction.

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## Revisiting embedding functions for reactive charge-transfer systems

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The *ensemble charge transfer embedded atom method* (ECT-EAM)<sup>1</sup> is a first-principles, physics-based interaction potential designed for atomistic simulations of molecules and materials in reactive environments exhibiting significant charge redistribution and charge transfer. The method builds upon the embedded atom method (EAM) for metals and metal alloys<sup>2</sup> by introducing dynamically-evolving *pseudoatoms* that embody quantum mechanical knowledge of bond formation and breaking through ionic and covalent interactions. A DFT-based coupling between electronic and atomic length scales is accomplished by extending the original EAM to include DFT statistical ensembles of charged and excited state atomic densities, with corresponding ensemble embedding functions and electrostatic interaction terms. Each pseudoatom consists of a weighted superposition of isolated atomic and ionic densities. Each embedding function describes the energy change induced by embedding an individual, isolated atom or ion in an effective background density due to neighboring pseudoatoms. The net embedding contribution of a given pseudoatom to the total interaction energy is the weighted sum (ensemble) of these embedding terms.

The implementation of the ECT-EAM requires the extension of ground state, neutral-density embedding models to excited and charge-transfer atomic species. We compared three established approaches to the construction of EAM embedding functions: (i) effective medium theory (EMT)<sup>3</sup>, which motivated the development of the original EAM<sup>2</sup>; (ii) the seminal work of Daw<sup>4</sup> in deriving the EAM from Hohenberg-Kohn (HK) DFT, and its application to Ni metal using LDA + von Weizsäcker energy density functionals; and (iii) the modified embedded atom (MEAM)  $\rho \ln \rho$  functional form proposed by Baskes,<sup>5</sup> motivated by Pauling's bond order–bond length correlation picture of chemical interactions. We report an unexpected concordance among the three models for a series of neutral atoms. We further show how the particular concordance between the HK-DFT and Baskes  $\rho \ln \rho$  forms suggests a systematic method for constructing embedding functions for excited states and ions, as required by ECT-EAM. By iteratively optimizing the two approaches using isolated-atom ionic and excited state densities, a general embedding functional is proposed, with unique features corresponding to the physical parameters of the embedded species.

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## Predictions of novel features in x-ray scattering spectra for thermometry

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Design and interpretation of inertial confinement fusion experiments rely on accurate models of material properties far from ambient temperatures and densities. Validation of these models with data from focused experiments is in turn limited by uncertainties in measured sample conditions. In particular, electronic temperatures in the warm dense matter regime are typically inferred from detailed balance of plasmon features in x-ray Thomson scattering spectra, but this approach loses sensitivity for thermal energies above the plasmon energy. Using real-time time-dependent density functional theory, we predict that spectral features arising from scattering into thermally depleted core orbitals can be used as alternative diagnostics at higher temperatures. Our first-principles calculations for aluminum and iron heated to 1 eV and 20 eV validate a simpler average-atom model modified to capture behavior near solid densities. Furthermore, we uncover subtle signatures of atomic order at comparable energy transfers, offering opportunities for simultaneous inference of ionic and electronic temperatures which may be out of equilibrium during e.g., laser heating. This work advances characterization techniques critical for understanding the performance of materials in extreme environments.

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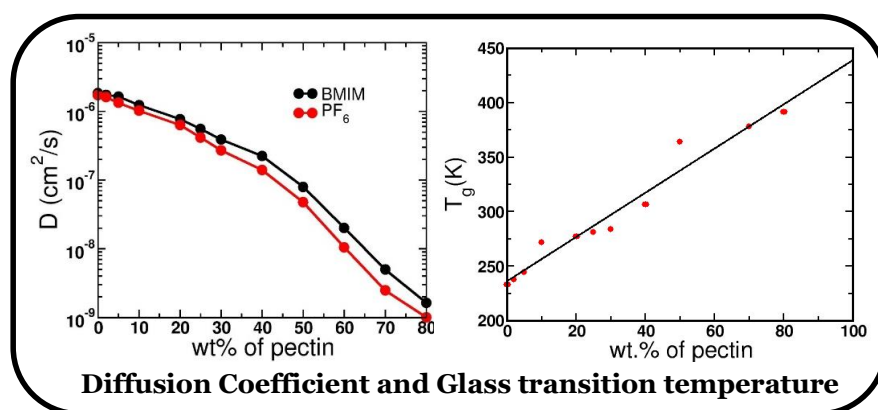
## Ion Transport and Glass Transition in Pectin-loaded [BMIM][PF<sub>6</sub>] Electrolytes

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### Abstract:

There is a growing demand for advanced battery electrolytes which possess higher ionic conductivity, higher mechanical stability, and biodegradability. In this work, we study the effect of pectin loading on the ion transport and glass transition temperature of 1-n-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF<sub>6</sub>] ionic liquid using molecular dynamics simulations. We observed a decrease in the mean squared displacements and diffusion coefficients of both cations and anions with pectin loading. Interestingly, the coordination number and ion association probability (of finding anions around the cations, and vice-versa) decreases with pectin loading implying a higher tendency for the formation of smaller ionic clusters over the large clusters. These characteristics favor improved ionic conducting behavior of pectin-loaded [BMIM][PF<sub>6</sub>] electrolytes. The glass transition temperature also increases with pectin loadings indicating higher mechanical stability of battery electrolytes.



**Keywords:** Molecular dynamics simulations, Ionic liquid [BMIM][PF<sub>6</sub>], Ion diffusivity, Coordination number, Ion association probability, Glass transition temperature.

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## The *ab initio* prediction of ARPES signatures for extended systems without translational symmetry

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The misfit rare earth rock-salt/transition metal dichalcogenide (TMD) layered heterostructures are an interesting family of quantum materials, but their incommensurate structure resists *ab initio* study in conventional supercells. Recent Angle Resolved Photo Emission Spectroscopy (ARPES) experiments on these materials present their data via a mapping to the Brillouin Zone (BZ) of the TMD layer. However, without periodicity the BZ is not well defined. To understand the experiments we note that ARPES measures, essentially, a momentum resolved density of states. To compute this quantity, we build on our previously introduced Mismatched INterface Theory (MINT) by introducing the concept of an infinite sequence of prototype periodic supercells that converges to the misfit structure. We show how to extract the ARPES signature from this sequence and how to accelerate its convergence. We find excellent agreement between our ARPES predictions and measurements. Interestingly, we find that the apparent charge transfer corresponding to the observed shift in fermi-level crossing Niobium-d bands is an order of magnitude greater than our computed interlayer charge transfer. We present a careful analysis of the movement of charge during bonding, finding that changes in valence band hybridization corresponding to re-arranged covalent bonds cause this large apparent doping.

Title: Optical excitation energies and spin studies of charged Co@S defect of WS<sub>2</sub> computed with the spin-flip Bethe-Salpeter equation approach

Authors: Arabi Seshappan, Bradford A Barker, Nolan Kelly, David A Strubbe

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Text: Defected transition metal dichalcogenides are exciting materials as potential single photon emitters, quantum light sources, and room-temperature solid-state qubits. Accurate calculations of the exciton interactions in these materials is imperative to understanding these applications. Charged, monolayer cobalt-at-sulfur-site substituted WS<sub>2</sub> (Co@S:WS<sub>2</sub>)<sup>+1</sup> has an open-shell electronic structure due to the spin of the cobalt atom, as found from our DFT calculations of magnetism and Jahn-Teller distortions in this system. While quasi-particle energies for open-shell systems have been calculated previously—and are known to have multiplet solutions—there is at present no similar approach available for the Bethe-Salpeter equation in open-shell systems. Instead, we investigate the vertical excitation energies through the Spin-Flip Bethe-Salpeter equation approach [arXiv:2207.04549], which allows for the simultaneous calculation of ground- and excited-state energies for multiconfigurational open-shell systems. Previously, this approach has been used to calculate excitation energies for defected bulk semiconductors, and we now leverage methodological development for the calculation of optical excitations in 2D systems to calculate excitation energies for (Co@S:WS<sub>2</sub>)<sup>+1</sup>. Further, we plan to investigate <S<sub>2</sub>> of this system.

## Insight into the Role of Excited States in Carrier Capture by Semiconductor Defects

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Sandia National Laboratories

Semiconductor defects with multiple charge states can capture carriers from the band-edges of the host material. In the 1970s, Lang and Henry explained carrier capture into deep defect levels by developing the theory of multi-phonon emission (MPE). In MPE, thermal fluctuations and/or ionic tunneling allow the system to reach an ionic configuration in which energy can be conserved during an electronic transition that is first-order in the electron-phonon interaction. Many phonons can then be emitted as the system relaxes on the new potential energy surface. More recently, a couple of groups have developed approaches that use density functional theory calculations to predict carrier capture rates. During recent work aimed at implementing these approaches, we noticed that the final state of the electronic transition is often an excited state. Several years ago, we developed an algorithm to find the lowest energy ionic configuration where energy can be conserved during a transition into the electronic ground state, and this new observation explains the failure of this algorithm to predict experimental results. Therefore, we need an approach to calculate the electronic excited states of semiconductor defects (and preferably also the associated forces), and we invite suggestions from ES23 attendees.

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## Approaching Periodic Systems in Ensemble Density Functional Theory through 1D Model Studies in the Thermodynamic Limit

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Ensemble Density Functional Theory (EDFT) is a generalization of ground-state Density Functional Theory (DFT), based on an exact formal theory of finite collections of a system's ground and excited states. EDFT offers a variational (non-perturbative) alternative to Time-Dependent DFT (TDDFT), which can more easily treat multiple and charge-transfer excitations. 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. Using the open-source real-space code Octopus, we extend the application of EDFT toward periodic systems by estimating the thermodynamic limit with increasingly large finite model systems. Beginning with a 1D system whose Kohn-Sham potential is a "particle in a box" system of length  $L$  with  $N$  electrons, we construct ensembles in the Gross-Oliveira-Kohn (GOK-I) weighting scheme and take numerical derivatives of the total Kohn-Sham energy with respect to the GOK-I weight,  $w$ . We examine the limit as  $N$  and  $L$  increase, for electron density  $n$  fixed at one electron per Å, to study properties of the ensemble in the thermodynamic limit. We will compare our results to the free-electron gas with the same electron density  $n$ , representing the infinite limit. The resulting data set will be useful in benchmarking EDFT approximations for periodic systems.

## **Controlling molecular electronic properties with topological phases of matter**

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Due to their novel and unique electronic properties, topological phases of matter hold great promise for future applications in quantum information, spintronics, and thermoelectrics. However, surface interactions of topological insulators and molecules have yet to be harnessed for chemical catalysis, and the underlying question of whether these new phases of matter can be employed to achieve efficient and selective synthesis remains open. In the present work, we study the electron occupancy and electronic friction of the LUMO of a molecule adsorbed on a polyacetylene chain in the trivial, metallic, and topological phases. We find characteristic signatures of the topological phase transition and show that the topological material has a significant advantage and robustness over the metallic phase for electron donation into the molecular system. In addition, the topological phase provides significant advantages and robustness over the metallic for electron donation into the molecular system. This work supports the perspective that topological matter offers a promising direction for future applications on surface reactions and chemisorption.

2023 Electronic Structure Workshop, UC Merced

**Title: Perturbative Ensemble Density Functional Theory approaches in real space**

**Authors: Uday Panta, David Strubbe**

**Affiliation: UC Merced**

**Abstract:**

Ensemble density functional theory (EDFT) is promising as an alternative to time-dependent density functional theory (TDDFT) for low-cost prediction of excitation energies and can handle double excitations more naturally. The Ensemble “HOMO-LUMO gap” (or pEDFT), which has been benchmarked on small molecules [Gould et al., Phys. Chem. Lett. 13, 2452-2458 (2022)], has been shown to provide results similar to TDDFT. To assess how this method handles more complicated systems, we implemented it in the real-space Octopus code, which allows calculations of not only bigger systems, but also small model systems for comparison. Octopus has support for different theory levels and a variety of exchange correlation functionals. We calculate excited states in real-space from pEDFT for various benchmark systems, and we also calculate the potential energy surface of the ethylene molecule under torsion and compare results to other standard excited-state approaches.

## Beyond-DFT database of spectral functions for quantum materials

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The first step in data-science-driven materials discovery is to generate databases of the electronic structure of materials. Many existing materials databases rely almost exclusively upon density functional theory (DFT) engines and often make incorrect predictions for quantum materials, especially in those that harbor electron correlation. Because qualitative predictions of excited-state properties usually require beyond-DFT methods, various advanced methods such as meta-GGAs, hybrid functionals, GW, and dynamical mean-field theory (DMFT) have been developed to describe the electronic structure of correlated materials. However, the expected accuracy of these methods when applied to a given class of materials remains unclear. It is thus of pressing interest to compare their accuracy for different types of materials, and at the same time, to build a broad publicly available database of the results of beyond-DFT calculations [1-3]. In this talk, I will discuss some of the challenges involved in generating such a beyond-DFT database using high-throughput computations and show how we have overcome these challenges in our systematic study of these methods on various training sets of moderately and strongly correlated materials.

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# Excitonic interactions and mechanism for ultrafast interlayer photoexcited response in van der Waals heterostructures

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Optical dynamics in van der Waals heterobilayers is of fundamental scientific interest and importance for potential optoelectronics applications. Despite much progress in experiments, their theoretical interpretations remain to be fully understood. A full understanding of this phenomenon requires accurate descriptions of both nonequilibrium dynamics and excitonic physics. In this work, based on our first-principles time-dependent adiabatic  $GW$  approach, we discover a new many-electron (excitonic) channel for converting photoexcited intralayer to interlayer excitations and the associated ultrafast optical responses in heterobilayers, which is conceptually different from the conventional single-particle picture. We find that, in the ultrafast time regime, strong electron-hole interactions drive the dynamics and enhance the pump-probe optical responses by an order of magnitude with a rise time  $\sim 300$  femtoseconds in  $\text{MoSe}_2/\text{WSe}_2$  heterobilayers, in good agreement with experiment.

**Titles:**

Optically controlled single-valley exciton doublet states with tunable internal spin structures and spin magnetization generation

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**Abstract:**

Manipulating quantum states through light-matter interactions has been actively pursued in two-dimensional (2D) materials research. Significant progress has been made towards the optical control of the valley degrees of freedom in semiconducting monolayer transition-metal dichalcogenides (TMD), based on doubly degenerate excitons from their two distinct valleys in reciprocal space. Here, we introduce a novel kind of optically controllable doubly degenerate exciton states that come from a single valley, dubbed as single-valley exciton doublet (SVXD) states. They are unique in that their constituent holes originate from the same valence band, making possible the direct optical control of the spin structure of the excited constituent electrons. Combining *ab initio* *GW* plus Bethe-Salpeter equation (*GW*-BSE) calculations and a newly developed theoretical analysis method, we demonstrate such novel SVXD in substrate-supported monolayer bismuthene – which has been successfully grown using molecular beam epitaxy. In each of the two distinct valleys in the Brillouin zone, strong spin-orbit coupling and  $C_{3v}$  symmetry lead to a pair of degenerate 1s exciton states (the SVXD states) with opposite spin configurations. Any coherent linear combinations of the SVXD in a single valley can be excited by light with a specific polarization, enabling full manipulation of their internal spin configurations. In particular, a controllable net spin magnetization can be generated through light excitation. Our findings open new routes to control quantum degrees of freedom, paving the way for applications in spintronics and quantum information science.

**Acknowledgment**

\*This work is supported by the U.S. Department of Energy and the National Science Foundation. Computational resources were provided by NERSC, ACCESS and TACC Frontera.

**Title:** Ferroelectric switching pathways, domain structure, and domain wall vortex in  $\text{SrBi}_2(\text{Ta,Nb})_2\text{O}_9$

**Authors:** Nabaraj Pokhrel<sup>1</sup> and Elizabeth A. Nowadnick<sup>2</sup>

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2. Department of Materials Science and Engineering, University of California, Merced, California 95343, USA

**Abstract:** Aurivillius-phase oxides  $\text{SrBi}_2B_2\text{O}_9$  ( $B=\text{Ta, Nb}$ ) are room temperature ferroelectrics which are well known for their fatigue resistance, low coercive fields, and potential application in ferroelectric random-access memory. Previous work has shown that the trilinear coupling between the electrical polarization and two octahedral rotation distortions of different symmetries plays a key role in the structural phase transition sequence and stabilization of the ferroelectric phase in  $\text{SrBi}_2\text{Ta}_2\text{O}_9$ . However, the implications of the trilinear coupling on the ferroelectric switching mechanism in these materials remain to be understood. In this work, we use the group theoretic analysis and density functional theory calculations to enumerate and explore the energetics of ferroelectric switching paths in  $\text{SrBi}_2B_2\text{O}_9$  and identify several low-energy one- and two-step ferroelectric switching pathways. Moreover, we show how the relative energy barriers of these switching paths can provide the insight into the domain structure of these oxides. In particular, our findings indicate that three-fold domain wall vortices are energetically favorable in  $\text{SrBi}_2B_2\text{O}_9$  which corroborates experimental reports of the domain structure in  $\text{SrBi}_2\text{Ta}_2\text{O}_9$ . This work advances our fundamental understanding of the technologically important family Aurivillius oxides.

**Acknowledgement:** This material is based upon research supported by the U.S. Office of Naval Research under award number N00014-21-1-2957.

## **Advanced Simulations of Spin defect in hBN: Strain and substrate effect, ODMR and Quantum Embedding theory**

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University of California, Santa Cruz

Spin defects in hexagonal boron nitride (hBN) have been proposed as promising spin qubits, which are fundamental components for quantum information technologies. We have applied advanced simulation methodologies to explore the optoelectronic properties of these defects. In first part we study the impact of strain and substrate on optoelectronic properties of single-photon emitters (SPEs) in hBN. The second part focuses on the spin-photon interface, where we have developed a methodology for simulating Optically Detected Magnetic Resonance (ODMR) processes, specifically the ODMR contrast. In the third part, we apply the advanced Quantum Defect Embedding Theory (QDET) to simulate the correlated excited state of spin defects. Our research on these three important aspects of the spin defects provides critical guidelines for the future experimental investigation in the field of quantum spin defects.



## First principles studies of magnetic adatoms on ferroelectric surfaces

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### Abstract

Magnetic adatoms on surfaces may function as single atom magnets with significant magnetization and coercivity at low temperatures [1]. Such systems can have potential applications in high-density magnetic memory and quantum information science technologies as long as adatom magnetization can be reliably controlled and detected. In this work we employ first principles electronic structure calculations to investigate structural, electronic, and magnetic properties of Fe atoms adsorbed on a surface of two-dimensional ferroelectric  $\alpha$ -In<sub>2</sub>Se<sub>3</sub> [2]. We identify preferred adsorption sites and study the dependence of binding energies on the adatom concentration. Further, we explore the possibility of controlling adatom properties by switching electric polarization of the In<sub>2</sub>Se<sub>3</sub> layer.

### Acknowledgment

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