Renewal proposal for XSEDE computing time

TITLE: *Ab initio* studies of nanostructured materials
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1   Abstract

The general objective of the proposed research is to use *ab initio* techniques to develop a fundamental understanding of the relationship between the atomic and electronic structure of nanostructured materials and their functional properties. Our research will both expand upon the work performed in the past year using XSEDE resources and embark on the study of important new systems. In particular, we will focus on phenomena in electronically correlated transition metal oxides, controlling surface chemistry on ferroelectric transition metal oxides, ferroelectric/semiconductor interfaces, elastooptic properties of semiconductors, electronic excitations in oxide materials, two-dimensional topological insulators, and benchmarking of metal organic framework materials for hydrogen storage. This research is funded by NSF MRSEC DMR-1119826, NSF ACI-1339804, NSF DMR-0808665 (no cost extension), and Theme 1 of Functional Accelerated nano-Material Engineering (FAME).

2   Introduction

The overarching goal of our research is to understand the micro- and macroscopic properties of real materials systems based on accurate first-principles, quantum mechanical descriptions of their atomic and electronic structure and to use this information to design, study, and understand novel materials systems. We focus on the physical and chemical properties of nanoscale assemblies of matter in many contexts: epitaxial growth, interface dynamics, molecular dynamics for hydrogen storage, correlated electron behavior, thin films and surface effects, nanotubes, inorganic/organic interfaces, etc. The work is interdisciplinary, and we have the privilege and pleasure of directly collaborating with a number of experimental colleagues. Part of the work is under the auspices of Yale's Center for Research on Interface Structures and Phenomena (an NSF MRSEC) where our interdisciplinary team focuses on the phenomena occurring at the interfaces involving transition-metal oxides and the effects that interfacial interactions have on the macroscopic properties of the systems. The work on excited state methods, hydrogen storage material, and optical properties benefits form a SI2-SSI grant that funds software development between Yale, UIUC, and IBM Yorktown Heights.

Our primary tool is density functional theory (DFT) [1, 2] which can yield the ground state atomic geometry and electronic structure of nanoscale systems. DFT computations accurately predict the properties of various bulk materials as well as the characteristics of surfaces and interfaces: the only inputs are the atomic numbers of the constituent atoms [3]. In addition to explaining experimental results, the lack of empirical parameters enables DFT to make accurate predictions of novel materials properties. Both aspects are critical in our close interactions with experimentalists who actively study the materials in which we are interested. In addition to structure, DFT provides information about electronic states such as band energies, band-offsets, Fermi surfaces, energy gaps, or interfacial or surface electronic states. This then permits us to explain other properties such as electronic transport, the effect of interfaces on the dielectric, ferroelectric, magnetic,

and other functional properties of heterostructures, and the thermodynamic stability of nanostructured phases. Finally, we use DFT to design new materials that exhibit novel physics. We aim to increase understanding of the atomic-scale interactions that occur at the interfaces and surfaces of nanostructured materials, the coupling between different order parameters across such interfaces, and our ability to predict how these properties will affect macroscopic behavior.

Below are high-level summaries and motivations for each of our proposed research projects.

Epitaxial oxide/semiconductor interfaces – Thin films of metal oxides grown on semiconductors have been the focus of much research interest because of their use in electronic devices. A multitude of physical phenomena observed in crystalline oxide films open up the possibility of novel technological applications. One example of such a potential application is a non-volatile transistor enabled by ferroelectricity in the oxide thin film. In this system, the state of the device (i.e., the bit) is encoded in the polarization direction of the ferroelectric oxide which controls the transport properties of the semiconductor. One system that we have been studying is $BaTiO_3$ films epitaxially grown on Ge (001). We have analyzed the atomic configurations, interface chemistry and electronic properties of this interface. We have concluded that a significant modification of the interface chemistry is needed in order to induce ferroelectricity in this type of system. For that purpose we have began studying monolayers of ZrO_2 epitaxially grown on Si (001). We have shown that these monolayers have multiple different metastable configurations with differing out-of-plane electrical polarizations. In our next set of studies, we aim to determine whether a monolayer of ZrO_2 induces a variety of differently polarized configurations in thin films of $SrTiO_3$ when it is grown as a buffer layer between Si and $SrTiO_3$.

Separately, we have begun the study of Si-doped HfO_2 films which have recently been discovered to show ferroelectric properties [4]. A thorough theoretical understanding of ferroelectricity in these films is lacking. We will investigate these films when they are grown on Si (001) and attempt to explain some of the experimental observations via *ab initio* theory.

Rare-earth nickelate oxides – Recently, piezoelectronic transistor (PET) devices have been proposed as an alternative to standard field-effect transistors [5]. PET functioning derives from the change of resistance of a material (used as the conducting channel) due to mechanical strain. Materials exhibiting strong dependence of resistance on applied strain (piezoresistive or PR materials) are therefore needed for efficient PET devices. Perovskite rare-earth nickelate oxides $R\text{NiO}_3$, where R is a rare-earth atom, may be suitable candidates for PR elements since they exhibit metal-insulator transitions with changes in resistivity of several orders of magnitude. The transition can be controlled by temperature, strain, and choice of R element. We wish to evaluate the suitability of several $R\text{NiO}_3$ thin film structures, such as $SmNiO_3$ and $NdNiO_3$, for application in PET architectures. To this end, we need to elucidate the precise dependence of crystal, electronic and magnetic structure of these materials on applied strain.

Stanene – Two-dimensional topological insulators have attracted much attention recently because they display unique electronic properties, such as quantum spin Hall (QSH) states [6, 7]. In these systems, gapless edge states are protected by time-reversal symmetry, allowing for nondissipative conductivity. Stanene, a two-dimensional atomically thin analogue of graphene, is composed of tin (Sn) atoms and has been predicted to be a large-gap QSH insulator. However, the presence and stability of QSH states in stanene depends on the choice of substrate, its strain state, its atomic scale structure, and possible defects and adsorbates. In our work, we aim to investigate how various substrates, such as BiTe (111) and Si (111), as well as adsorbates affect

the crystal, electronic and topological band structure of stanene.

Ferroelectric-Based catalysis: A Search for Water Splitting and Partial Methane Oxidation Catalyst – Following our prior work on ferroelectric surface chemistry [8, 9], we have recently proposed that using the ferroelectric polarization dynamically as a switch can lead to surface catalysis beyond the limits of conventional catalysis [10]. The Sabatier principle, which is a cornerstone of catalysis for surfaces with fixed chemical properties (conventional catalysis), dictates that the substrate-molecule interaction should be just right: strong enough for the reactions to proceed but weak enough to release the products [11]. This compromise leads to the ubiquitous presence of "volcano plots" (i.e., maximum catalytic activity for intermediate interaction strength) and scaling relations in catalysis. As discussed in a recent review paper, catalysis using transition metals and their alloys is facing several challenges [12]. Among these challenges are the design of efficient catalysts for water splitting and methane partial oxidation to methanol, both of which are of technological and industrial importance. Current catalysts for these reactions are inefficient in part due to the fundamental limitations of conventional catalysis, one of which is the Sabatier principle. Using our dynamic scheme, which departs from the concept of fixed surface chemical properties, and employing ferroelectric polarization as a switch, we have proposed an efficient cyclic method for direct decomposition of NO_x molecules [10], which has been a challenge for conventional catalysis. By using the same ideas (ferroelectric-based catalysis) and optimizing the choice of specific materials, we hope to extend this method in order to design catalytic cycles for water splitting and partial oxidation of methane into methanol.

Elasto-optic coupling in semiconductors – Elasto-optic coupling (i.e., the photoelastic effect) describes the optical response of a material due to imposed strain. It quantifies the change of material's refractive index due to imposed strain (specifically, the change of dielectric tensor). Elasto-optic coupling can be used in nanostructures to greatly enhance the coupling between photons and acoustic phonons. Therefore, it has many potential applications in the design of phononic devices. Although there have been a number of computational and experimental studies of elasto-optic coupling [13], fundamental physical understanding of this effect is still lacking. For example, Si, Ge and GaAs have very different elasto-optic responses while they are all similar and tetrahedrally coordinated semiconductors. At present, there is no physical picture that predicts the sign and magnitude of the coefficients in the elasto-optic tensor based on basic materials properties (bonding topology, locality of bonds, deformation potentials, etc.). We are in the process of developing such a microscopic physical theory using DFT as our main tool. Once a physical picture is in place, we will use the knowledge to predict and design materials with enhanced or tailored elasto-optic couplings.

Electronic excitations in oxide materials – Electronic excitations are important in the design of new materials for various technological applications such as photovoltaics, photocatalysts, and optoelectronic devices. Calculations of electronically excited states require more advanced theories and calculation methods than standard DFT in order to better describe the modified electronic interactions in excited states. To this end, the GW and Bethe-Salpeter Equation (GW-BSE) many-body methods have been used [14, 15, 16, 17, 18] with much quantitative success in going beyond standard DFT's shortcomings for excitations. However, the GW-BSE approach is computationally challenging and costly which has limited its regular application to relatively small systems compared to the size of the systems that DFT calculations can tackle. As part of our NSF SI2-SSI work, we have been developing new software and algorithms for GW-BSE computations that take advantage of modern massively parallel high performance architectures. To evaluate the perfor-

mance and scaling of our new methods, we will benchmark them on metal oxide systems that are simultaneously potentially useful for photovoltaic and catalytic applications.

H$_2$ storage in Metal-Organic Framework (MOF) – In response to growing power demands, one of the major goals of applied research has been to deliver a source of clean and renewable energy, and hydrogen is a candidate. Finding new H$_2$ storage materials and understanding the H$_2$ diffusion processes in such materials are active and challenging research areas in physics, chemistry, and material science. For example, the DOE 2015 targets for a hydrogen storage system have not yet been reached, e.g., a capacity of 40g H$_2$ per L [19]. Materials with large surface area and low density should be good candidates for hydrogen storage materials. For example, metal-organic framework (MOFs) have been found to adsorb hydrogen at up to 4.5% mass density at low temperature and at modest pressure (20 bar) and exhibit much higher reversible hydrogen uptake than other candidate porous materials [20, 21, 22]. The overall aim of our research is to understand the kinetic and diffusive properties of hydrogen adsorbed in a specific promising MOF, Zn-MOFs, as a function of external fields (i.e., pressure and temperature). Investigating Zn-MOFs using *ab initio* molecular dynamics simulations requires enormous computational resources since the simulation cell contains more than 500 atoms. To this end, we have submitted an INCITE proposal to acquire such resources for 2016. However, much ground work is needed to fully understand and properly simulate such materials. Here, we wish to test and benchmark smaller segments of the Zn-MOF to see if simpler Zn pseudopotentials, Zn being the heaviest and most electron rich element in the MOF, are accurate enough for describing the underling H$_2$ dynamics. If doable, this greatly simplifies further large scale Zn-MOF simulations.

3   Proposed Research

Here we provide a brief description of the scientific questions relevant to each project and the types of computations and numerical experiments envisaged.

Epitaxial oxide/semiconductor interfaces – Our current work on the BaTiO$_3$/Ge interface, and the similar case of SrTiO$_3$/Si interfaces [23], show that the electrical polarization of the thin film oxide is unswitchable (i.e., pinned) by the interfacial chemistry in this class of systems. In order to induce polarization switching, a modification of interfacial chemistry is required. We have began a study of ZrO$_2$ monolayers (ML) on Si in order to explore their potential as switchable (ferroelectric) buffer layers between Si and SrTiO$_3$ that promote ferroelectricity in SrTiO$_3$ thin films grown on top. So far, we have identified several metastable configurations of the ZrO$_2$ ML that have a range of of positive and negative polarizations. We have computed transition barriers between pairs of metastable structures as well as domain wall energies. To understand polarization switching in the actual experimental samples fabricated by Yale collaborators, we wish to begin by computing the energy barriers for the motion of domain boundaries between different polarization phases via the nudged elastic bands (NEB) method [24] for the uncapped ML ZrO$_2$ on Si. We have also begun studying Si-ML ZrO$_2$-SrTiO$_3$ and obtained multiple metastable structures for 1.5 unit cell thick SrTiO$_3$. We will continue exploring this system by simulating thicker SrTiO$_3$ as well as similar candidate monolayers such as HfO$_2$.

A related new project is the study of thin films of Si-doped HfO$_2$. The recent discovery that these materials are ferroelectric under certain conditions has sparked extensive research [4]. The Si doping density and temperature dependence of the ferroelectric behavior has not been fully understood. We will attempt to answer some of these questions by simulating large supercells of these systems. This will allow us to study strain, the inclusion of the Si substrate, as well as various

Si doping patterns and densities in realistic ranges that should closely represent experiment.

Rare-earth nickelate oxides – Our goal is to evaluate whether $NdNiO_3$, $SmNiO_3$, or their alloys $Nd_{1-x}Sm_xNiO_3$ are suitable piezoresistive materials for PET applications. First, we need to carefully benchmark the theoretical apparatus to make sure that we can correctly reproduce the experimentally observed bulk crystal structures and band gaps. For this purpose, we plan to perform DFT+U calculations using several exchange-correlation functionals to select the best choice. Hubbard U effects will be considered for both Ni $3d$ and O $2p$ states. After this necessary benchmarking, we will investigate the effect of various epitaxial strain modes on the electronic properties of $SmNiO_3$ and $NdNiO_3$ and several $Sm_xNd_{1-x}NiO_3$ structures. Specifically, we wish to know the dependence of the band gap on strain and find the epitaxial strain and composition combinations so that the electronic behavior (e.g., band gap) is most sensitive to strain.

Stanene – We wish to investigate the topological electronic properties of stanene and their dependence on the choice of substrate, strain and adsorbates based on non-collinear-spin DFT including spin-orbit coupling. We will begin by calculating the crystal and electronic structure of free standing 2-dimensional stanene and will also consider several structures with applied compressive and tensile strain. Next, we will consider stanene on top of several substrates included explicitly in the calculations. We will focus on BiTe (111) and Si (111). With the substrates present, the crystal structure of stanene may not be trivial or similar to the free standing structure and understanding potential surface reconstructions is important. We will have to consider several large supercells in order to obtain the correct ground state crystal structure. Finally, we will clarify the effect of various adsorbates on the stanene structure and electronic states.

Ferroelectric-Based catalysis: A Search for Water Splitting and Partial Methane Oxidation Catalyst – Using DFT simulations, we have recently shown that by manipulating the ferroelectric polarization in a dynamic manner, one can catalyze reactions that are challenging for conventional catalysis [10]. For example, we have shown that a monolayer of CrO_2 or RuO_2 on ferroelectric $PbTiO_3$ can simultaneously catalyze NO_x direct decomposition and CO oxidation. The specific choices of CrO_2 or RuO_2 were based on an optimization process to achieve the most effective NO_x direct decomposition and CO oxidation. More generally, the choice of transition oxide monolayer (XO_2) on the ferroelectric support may be optimized for any desired reaction.

Switching the polarization alternatively drives the surface into highly reducing or oxidizing limits. For example, the polarization direction can efficiently control the binding energy of oxygen atoms to the surface from strongly bound to weakly bound. In principle, such a system may be optimized to directly oxidize methane to methanol in one polarization state (hole doped surface with weak O binding) and to replenish the lost oxygen supply in the opposite polarization state (electron doped surface which easily dissociates O_2 into strongly bound atomic O). By examining different transition metal oxide surface monolayers (XO_2) and their interaction with CH_4, CH_3OH, O and O_2, we might find the best choice of monolayer that together with the ferroelectric polarization oxidizes methane into methanol. A specific scenario we wish to explore is the required strength of the oxygen binding in the oxidizing surface state such that the surface O combines easily with methane to form methanol but is not mobile enough to find other O atoms to form inert O_2 prior to oxidizing the methane. One question addressable from our computational results for the XO_2 monolayers is the optimized d-band fillings and d-band central energies for the metal oxide that best drive the desired reaction.

Our second project involves water splitting to form hydrogen gas. Again, the ability to drive the surface between oxidizing and reducing states might allow us to efficiently catalyze the hydrogen

production and oxygen evolution on opposite polarizations. Optimization of the surface layer may permit incorporation of these oxidation and reduction processes in a cycle that efficiently splits water into hydrogen and oxygen. This requires simulations of the interaction of different ferroelectric-supported transition metal oxide monolayers with the various molecules and atoms participating in water splitting reaction including H_2O, H_2, O_2, OH, and atomic oxygen and hydrogen.

Elasto-optic coupling in semiconductors – We will be studying the change in the dielectric tensor under various lattice deformations in a number of materials. Our preliminary results show that density functional perturbation theory (DFPT) [25] and the random phase approximation (RPA) are in good agreement with each other when used to compute the dielectric tensor of silicon. They also both agree with the experimental measurements of elasto-optic coefficients (e.g., [13]). The RPA is useful for analysis as it is an analytical formula containing only the band energies, Bloch wave functions, and the interband dipole transition matrix elements. Our examination of the RPA results shows that the change of optical transition matrix elements due to strain dominates the change in dielectric tensor as opposed to the change of band energies (deformation potentials). Unfortunately, the change in optical transition strength is spread throughout the Brillouin zone which strongly suggests that one should abandon the standard approach in wave vector space and move to a real space description. We have developed an *ab initio* method that computes the RPA dielectric tensor based on Maximally Localized Wannier Functions (MLWFs) [26, 27] with no fitting parameters. This approach provides an exact real-space tight-binding method to probe the underlying physical basis of the strain-dependent effects. We wish to use this method to clarify how the optical transitions between local MLWF electronic states contribute to the dielectric tensor and how they determine the sign and magnitude of the elasto-optic coefficients. For this proposed work, we will be focusing primarily on tetrahedrally coordinated semiconductors such as Si, Ge, and GaAs. These materials have very different elasto-optic responses but similar crystal structure and refractive indices. They provide a good test bed for our theoretical approach before we can apply it in order to predict and design materials with desired elasto-optic couplings.

Electronic excitations in oxide materials – In our NSF funded SI2-SSI work, we have focused on developing GW-BSE software and algorithms that tackle several of the major computational bottlenecks for excited state GW-BSE calculations. One major bottleneck is the vast number of fast Fourier transforms (FFTs) that must be performed in the usual plane-wave pseudo potential GW-BSE implementations. We have introduced new algorithms that greatly reduce the number of FFTs and have developed efficient parallelization strategies geared for modern super-computing architectures. We have also implemented effective matrix operation methods such as iterative inversion techniques which accelerate the calculation process. Our GW-BSE methods is in the process of being integrated into an existing *ab initio* molecular dynamics simulation package, OpenAtom [28, 29], which has been developed collaboratively with computer scientists at UIUC. To benchmark the performance of our method with the OpenAtom package, we plan to study TiO_2, MgO, and ZnO, all of which are of interest for photovoltaic and catalytic applications.

H_2 storage in Metal-Organic Framework (MOF) – One of the most popular implementation of *ab initio* molecular dynamics (AIMD) is based on the Car-Parrinello (CP) approach within DFT. We will perform CPAIMD on Zn-MOF systems using the OpenAtom software that scales well on petascale computers. For practically useful hydrogen storage materials, studying the kinetic and diffusive properties of H_2 inside MOFs is important. For that purpose, MD simulations are appropriate. Simulation studies of diffusions of H_2 molecules for various model MOFs are discussed in the literature [20].

We have already carried out preliminary CPAIMD simulations of a Zn-based MOF with 43 H_2 inside. The system consists of 939 Kohn-Sham doubly occupied states, and 512 atoms in the unit cell including hydrogens. We ran the test simulations at 77 K and 300 K. The functional includes van der Walls interactions based on the Grimme II approach [30]. However these calculations did not take the nuclear quantum effect of the hydrogen atoms, which is computationally included via the path integral (bead) method. We have an INCITE proposal under review where we propose to perform path integral CPAIMD simulations at 77 and 300 K. However, we still need to benchmark and understand some basic aspects of the MOF dynamics and energetics prior to any large scale simulations. To that end, a fragment of the MOF (1/8 of the full system) with 63 atoms in the unit cell and 5 H_2 molecules will be studied here. This gives us confidence in the overall approach, might give us a preliminary idea of the quantum effects, and allow us to optimize the computation ahead of time. The most costly contributor to the computation is the presence of Zn in the MOF which leads to a large number of valence electrons and a large plane wave energy cutoff (85 Ry for a norm-conserving pseudo potential compatible with OpenAtom). We would like to be able to test and benchmark simpler Zn pseudopotentials, which will have much lower plane wave cutoffs, to see what accuracy tradeoffs exist for the gain in computational efficiency.

4   Requested XSEDE Resources

This past year, we benefitted greatly from approximately 1.79 million SUs on Gordon. Our progress report shows significant ongoing work and a number of publications based on these resources. We find that the Gordon cluster is very well suited to the types of calculations that we do in our group, and our jobs show good scaling with the number of CPUs from 8 to at least 128 (which is typical in our case). We also benefit from having up to 48 hours of walltime to run our jobs. If possible, we prefer to continue using Gordon in the future. At the time of this submission, our current allocation is almost exhausted. The CPU hours requested below for the next cycle are in units of Gordon SU hours.

Epitaxial oxide/semiconductor interfaces — Typical supercells for the ZrO_2-Si domain migration calculations need (2×1) unit cells, each with about 150 atoms; an NEB simulation over six such "images" requires about 10,000 CPU hours. Since we are going to study a total of 25 of these domain walls, we will need 25×10,000=250,000 CPU hours. Next, we will study (2×1) cells of Si-ML ZrO_2-$SrTiO_3$ with varying $SrTiO_3$ thicknesses. These cells will consist of 50 to 100 atoms. We estimate each relaxation calculation to cost 1,000 to 5,000 CPU hours (3,000 CPU hours on average). Given that there are about 5 metastable configurations for each thickness, and that there are about 10 thicknesses, we will need 10×5×3,000=150,000 CPU hours. Lastly, in our work on Si-doped HfO_2, we will simulate supercells that include up to 100 atoms. Each relaxation requires 5,000 CPU hours. We will study 4 doping densities with 10 initial configurations. So we will need 10×4×5,000=200,000 CPU hours.
The total requested computational time for this project is 600,000 CPU hours.

Rare-earth nickelate oxides — To benchmark DFT+U calculations for bulk nickelate oxides, we will perform 80-atom cell calculations for bulk $NdNiO_3$ and $SmNiO_3$. For each system, we will consider LDA, PBE, and PBEsol exchange-correlation functionals. For each functional, we will use the DFT+U method with the Hubbard $U = 0$ eV and up to three positive U values. Since we

examine Hubbard parameters on Ni $3d$ and O $2p$ states, we need to consider up to 16 combinations of U values (4 values for Ni and 4 values for O). Each relaxation requires on average 1,000 CPU hours. Therefore, for benchmarking stage we will need approximately 2×3×16×1,000=96,000 CPU hours. After identifying the best exchange-correlation approximation and U values, we will consider 5 mixed $Sm_xNd_{1-x}NiO_3$ structures with $x \in [0,1]$. For each structure, we will perform 25 calculations with applied strain (5 calculations for in-plane strain times 5 for out-of-plane strain). This stage will require 5×5×5×1,000=125,000 CPU hours.

The total requested computational time for this project is 220,000 CPU hours.

Stanene — We will perform crystal-structure relaxation calculations of stanene on BeTe (111) and Si (111) surfaces. Due to the explicit inclusion of substrates, each supercell structure will have at least 50 atoms. For each structure, in addition to pristine surfaces, we will consider surfaces with 4 different contaminants: O, OH, F, and Cl. Since we are interested in precise calculations of the topological properties of stanene band structure, we will perform relativistic non-collinear-spin calculations. We estimate each relaxation in this case to take on average 10,000 CPU hours. Therefore, we will need approximately 2×5×10,000=100,000 CPU hours.

Total requested computational time for this project is 100,000 CPU hours.

Ferroelectric-Based catalysis: A Search for Water Splitting and Partial Methane Oxidation Catalyst — We wish to design an optimized catalytic system consisting of a monolayer of transition metal oxide (XO_2) on top of the ferroelectric oxide ($PbTiO_3$) that might be able to partially oxidize methane (CH_4) into methanol (CH_3OH) and water to O_2 and H_2, under cyclic-polarization-change conditions. We need to perform several DFT relaxation simulations for different systems and adsorbed molecules or atoms. A typical direct oxidation process for CH_4 consists of CH_4, CH_3OH, OH, CH_3, O and H species. A typical water splitting process consists of H_2O, O_2, H_2, OH, H and O species. In total, we need to investigate the interactions of 9 species with our surfaces. Since we will be performing an optimization process containing several choices for the transition metal (X) in the XO_2 top monolayer on the ferroelectric, we will be investigating at least 6 different transition metals (e.g., Ti, Cr, Fe, Mn, Ni, Ru) for 2 different choices of ferroelectric polarization state (positive and negative). Since our relaxation algorithms only find the relaxed structures that correspond to local minima and not necessarily the ground state (global minimum) in energy, we plan to perform at least 5 different calculations, for each case of molecular/atomic binding, corresponding to different initial geometric configurations in order to be reasonably sure that we have found the global minimum in energy. We estimate the CPU hour necessary for each single relaxation to be 1,500 CPU hours. The total estimated CPU hours that we need for this project, is thus 9×6×2×5×1,500=810,000.

The total requested computational time for this project is 810,000 CPU hours.

Elasto-optic coupling in semiconductors — We will be primarily working on bulk Si, Ge, and GaAs, which all possess cubic symmetry and have two atoms in one primitive cell (also these will be our simulation cells). We have already found from our RPA calculations that the dielectric tensor computation reaches acceptable convergence for extremely dense k-point grids (i.e. Brillouin zone samplings), typically 24×24×24. This is also the k-point density we will use for our maximally localized Wannier function (MLWF) calculations. The calculation consists of two major steps: (i) we compute the local electronic states for each strain configuration for all three types of materials in terms of MLWFs. We estimate that 2,000 CPU hours will be needed for each

strain configuration, so 30,000 CPU hours are needed for all structures in this step because we have five strain configurations for each of the three kinds of materials; (ii) for every structure, we will compute the dielectric tensor using the local electronic states with our newly developed method. Preliminary tests of our method indicate that the majority of the time is spent on computing optical matrix elements between MLWFs. We will need about 4,000 CPU hours for each structure, which means that approximately 60,000 CPU hours are needed in this second step.

The total requested computational time for this project is 90,000 CPU hours.

Electronic excitations in oxide materials — We will benchmark a number of bulk metal oxide systems and clusters with our new GW software. Our test systems will include TiO_2, MgO, and ZnO. It is well known that a large number of conduction (unoccupied) electronic energy bands is required to obtain converged results for GW calculations, e.g., more than 3000 conduction bands are needed for the primitive unit cell of ZnO. We estimate that we will need approximately 250 processors running for 24 hours for each system, which consumes 6,000 CPU hours. We expect to run ten variations of input parameters for each structure to examine the performance and convergence of our method. We will consider at least three different oxide materials. This requires $30 \times 6,000 = 180,000$ CPU hours of compute time.

The total requested computational time for this project is 180,000 CPU hours.

H_2 storage in Metal-Organic Framework (MOF) — We will perform CPAIMD at two temperatures for a segmental Zn-MOF consisting of 53 atoms with an additional 5 H_2 molecules inside the MOF. We will first benchmark two different "flavors" of psuedopotentials (PP) for Zn. The purpose is to examine which PP reduces computational cost while still providing stable simulation runs for short molecular dynamics time steps. We will be performing standard CPAIMD at 77 K to compute the H_2 dynamics at different binding sites in the MOF; a typical observable that will be computed will be the mean square displacement of the H_2 as a function of simulation time. We will perform these simulations with two different PP to compare and benchmark them. Based on very short runs to date, we estimate that each CPAIMD with a given PP will need 120,000 CPU hours to reach a simulation time of 5 ps which is a short but reasonable simulation length to generate meaningful preliminary results. The CPAIMD simulations with path integral beads are far more expensive and the costs scales linearly with the number of beads (32 in our case). Running a path integral CPAIMD of 5 ps with 32 beads will be beyond the scope of this request; instead we will run the 32 bead system for a very short simulation time to test its stability and scaling while also getting the system to perform its initial thermalization. We estimate that an additional 40,000 CPU hours should be sufficient for this purpose.

The total requested computational time for this project is 280,000 CPU hours.

Total XSEDE request: 2.28 million (2,280,000) Gordon-equivalent CPU hours.

5   Local Computing Environment

Our local computing environment consists of two shared parallel linux clusters within Yale's HPC facilities, and is managed by Yale ITS with a total of about 5000 processors altogether. On each cluster, the group has access to 5% of the aggregate computational time each year, for a total of approximately 2 million CPU hours shared among the 7 group members. In addition, we have

unrestricted access to a low priority background queue on the same clusters whose availability is dependent on the load of the clusters (typically high loads).

6   Other Supercomputer Support

As part of our NSF funded SI2-SSI collaboration (Yale-IBM-UIUC), we have collaborative access via our UIUC collaborators to a number of supercomputers *for non-science computations*: namely, the available CPU hours are strictly for software testing, development, and scaling performance on multiple software grants and not for large scale simulations that generate scientific results. The computers are Mia, Cooley, Vest, Tukey and Cetus (ALCF at Argonne National Laboratory) and Titan and EOS (OLCF at Oak Ridge National Laboratory). The total number of CPU hours over all grants and all computers is large (on the order of 50,000,000 CPU hours) of which we may, with permission, access a small amount for code development, timing and testing and not for scientific computation.

Code Performance and Scaling for Renewal of
"*Ab initio* studies of nanostructured materials"

We compute the ground-state structural and electronic properties of our proposed systems using density functional theory [1, 2] (DFT). In practice, we primarily employ the Quantum ESPRESSO DFT software package [31] (primarily the PWscf module within the package).

DFT reduces the $3N$-dimensional Schrödinger equation describing a system of N electrons to a set of N three-dimensional Schrödinger-like eigenvalue equations which must be solved self-consistently [3]. The self-consistent eigenvalues and eigenfunctions obtained describe the energetics and the quantum mechanical wave functions of the electrons in the system from which numerous physical properties can be computed. Among the most important are the electron density, the total energy, and the gradient of the energy versus atomic positions (i.e., atomic forces). For more details of the physics of DFT, we refer interested readers to available reviews [3].

Computationally, the wavefunctions (eigenfunctions) are expanded in a planewave (Fourier) basis which provides an unbiased representation, and completeness and convergence are naturally obtained in an unbiased and systematic manner by increasing the number of Fourier modes. Each wave function $\psi_n(\mathbf{r})$ for band n is expanded as

$$\psi_n(\mathbf{r}) = \sum_{\mathbf{q}}^{|\mathbf{q}|<q_c} C_{\mathbf{q},n} \frac{e^{i\mathbf{q}\cdot\mathbf{r}}}{\sqrt{\Omega}}. \tag{1}$$

$C_{\mathbf{q},n}$ is a complex-valued matrix of expansion coefficients, the wave vectors $\mathbf{q}$ label the Fourier modes, and Ω is the volume of the simulation cell. (The set of $\mathbf{q}$ vectors is discrete due to periodic boundary conditions.) The cutoff q_c determines the maximum length of $\mathbf{q}$ retained in the basis. Convergence is reached as $q_c \to \infty$, but for a given accuracy, a finite value is sufficient. The converging value of q_c is a materials property determined by the atomic species present in the system. The size of the basis (number of plane waves) N_q scales as $O(\Omega \cdot q_c^3)$.

A further advantage of a plane wave basis is that the calculations can be close to exactly variational for a fixed basis set while sampling or integrating on a uniform and discrete spatial grid: this is simply due to the fact that the product of two Fourier modes is also a Fourier mode. Many other numerical implementations for DFT do not allow products of their functions to be computed easily or integrations to be performed exactly on a discrete numerical grid.

It is of course best to use the smallest number of planewaves possible to reduce computational time. The localized core orbitals (electrons) are difficult to represent without a prohibitively large number of planewaves, but, physically, they are largely irrelevant as they are weakly perturbed away from their configuration in the isolated atoms and do not participate in bonding. Therefore, we employ the pseudopotential approximation [32]. This approximation assumes that the bonding properties are determined primarily by the valence (non-core) electrons. The core orbitals are removed from the calculation and their effect on the valence electrons is replaced by a smooth function (pseudopotential) constructed such that the scattering properties of the valence electrons off the potential are correctly maintained. We often use ultrasoft pseudopotentials [33] which greatly reduce q_c and thus N_q.

In a standard DFT calculation, for a fixed set of nuclear coordinates, an initial guess is made for the electronic wavefunctions and the self-consistent eigenvalue problem is solved via an iterative method. Each self-consistent iteration has two parts. First, the eigenvalue equations are solved for

N_{proc}	total CPU time (sec)	speed-up
1	10,149	1.0
2	5209	0.51
4	3320	0.33
8	2880	0.28
16	1367	0.13
32	668	0.066
64	373	0.037
128	198	0.019

Table 1: Strong scaling on Gordon XSEDE cluster for a 72 atom SiO_2 layered system: CPU times and speed-ups are relative to the serial calculation ($N_{proc} = 1$).

the N_b lowest orthonormal eigenvectors (bands or the index n for ψ_n above) of a given Hamiltonian; PWscf uses an efficient iterative blocked-Davidson algorithm [34]. Second, the Poisson equation is solved to find the resulting potential, providing a new Hamiltonian for the subsequent iteration. The process ends when the input and output Hamiltonians differ by less than a desired tolerance. Then, the forces on the nuclei are computed using the self-consistent electronic information, and the nuclei are moved as determined by the structural optimization algorithm, e.g. conjugate gradients. The entire process then begins anew with the new set of nuclear coordinates until all atomic forces are also below a desired tolerance. The final structure is the desired ground-state in terms of both electronic and nuclear degrees of freedom.

The main computational routines in PWscf involve matrix multiplications, matrix inversions, matrix diagonalizations, and Fast Fourier Transforms (FFTs). The LAPACK and SCALAPACK libraries are used for the former, and the FFTW package [35] or other optimized FFT libraries are used for the latter. The PWscf code is written in FORTRAN 90 and parallelized over the N_q Fourier modes and the N_b bands using MPI. The dominant computational burden scales as $O(N_q \cdot N_b^2)$ which is due to the orthonormalization of the N_b eigenstates. Another subleading but significant contribution is from FFTs performed on each wavefunction that scales as $O(N_b \cdot N_q \cdot \ln N_q)$.

We have tested and timed PWscf on representative nanoscale interfacial problem involving ultrathin SiO_2 in a layered phase. These test calculations were run on the Gordon XSEDE cluster and involved 8 self-consistent field iteration steps of the code (the essential kernel of any computation using this method). Hence, the results are directly indicative of the performance for the actual systems proposed for study. Table 1 shows the strong scaling results for a system of 72 atoms. The Table indicates better performance for larger problems. Tests on our local parallel clusters at Yale show similar performance results with PWscf.

We move to an Amdahl analysis. In this widely used model, the total run time T in terms of parallel and serial components, T_{par} and T_{ser}, which ideally follow the following simple relation:

$$T(N_{\text{proc}}) = T_{\text{ser}} + T_{\text{par}}/N_{\text{proc}}. \tag{2}$$

Fig. 1 shows the total run time $T(N_{\text{proc}})$, normalized to the serial run time $T(1)$, as a function of the inverse number of processors (N_{proc}^{-1}). The behavior in the Figure over the entire processor count range is more complex than this formula as the software internally adjusts its computational mode depending on the processor count. To the best of our understanding, in this specific case when 8 or more processors are used, PWscf switches to a distributed-memory SCALAPACK algorithm. With fewer than 8 processors, a serial LAPACK method is used in conjunction with parallel code in
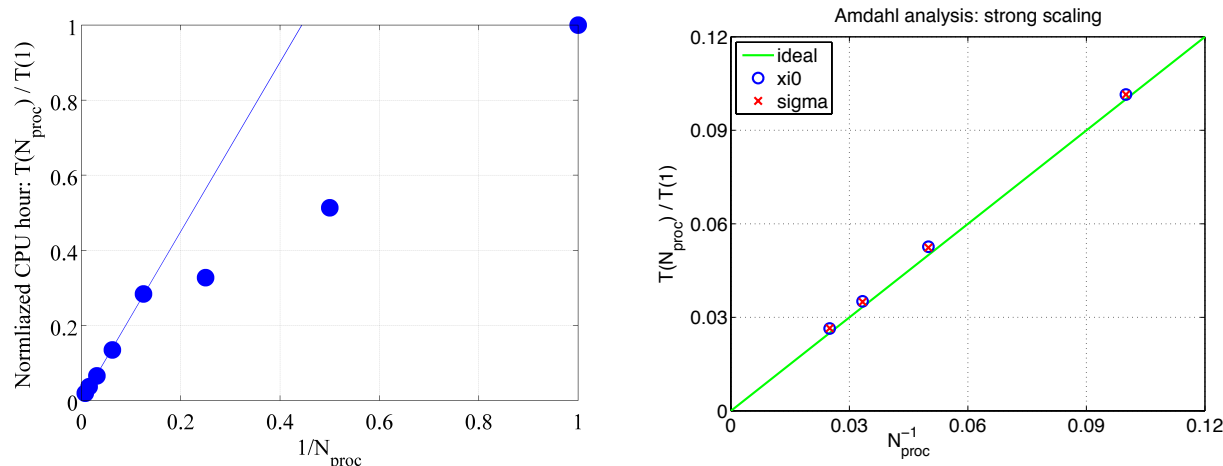
Figure 1: Amdahl analyses. Left: normalized computation time as a function of the inverse number of processors for 72 atom layered SiO_2 DFT calculations on the Gordon cluster (blue circles). The straight line fit shown by the thin line is made against the data with $N_{proc} \geq 8$ as explained in the text. Right: analysis of a standard GW algorithm for a 32 atom GaN system. "xi0" computes the polarizability and "sigma" computes electronic energy level correction to DFT using the polarizability. The green line represents perfect scaling.

other portions of the calculation leading to good run times which are, however, not representative of the typical processor counts we use in practice.

For 8 or more processors, the behavior does fit the model very well as indicated by the straight line fit in the Figure for all data obeying $N_{proc} \geq 8$. The slope of the line (normalizing in this case by the $N_{proc} = 8$ time) is 0.994 and the intercept is smaller than 0.005 (0.5%). Ideal parallelization would give a slope and intercept of 1 and 0, respectively. Since T_{par} is reduced by parallelization, only a small component — less than 0.5% — of the total computation is not parallelized for this problem size. When the two components in Eq. 2 become comparable, it no longer becomes advantageous in terms of optimal CPU usage to further increase the number of processors. The turnover value of N_{proc} for our test calculation is $\sim$200-250. This level of performance and scaling is representative of the systems we propose study in this proposal since the typical unit cells we plan to use have $\sim$50-100 atoms.

In terms of the GW-BSE calculations, the main challenge that our new software developments aim to overcome is the heavy computational load of the calculations which is a distinct question from scaling. To put this in perspective, Fig. 1 shows scaling data for parallel GW calculations using an older version of the BerkeleyGW software package [36, 37] on a 32 atom GaN system run in-house at Yale on a commodity linux Xeon cluster with plain vanilla *gigabit ethernet* interconnects. Despite the modest size of the problem and the modest computer with poor communication infrastructure, the strong scaling behavior is near ideal: the serial component is less than 0.2% of the total. Scaling is excellent and only improves on a superior supercomputer (such as Gordon) and for larger simulation sizes. The point is that despite the excellent scaling, the algorithm is not optimal so the time to solution is poor. Our new methodological improvements aim to reduce the total computation and thus the time to solution without major degradation in scaling.

For an example of what this means, the above conventional implementation of the "xi0" GW
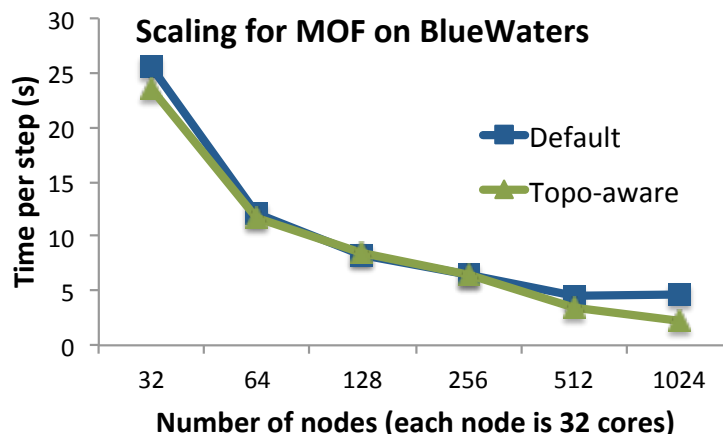
Figure 2: Strong scaling performance of OpenAtom software on a MOF system with 424 atoms on the NCSA BlueWaters supercomputer. The two curves correspond to a default choice of work distribution to the compute nodes compared to a topology aware distribution of work which is optimized for the BlueWaters network architecture. The y-axis is the walltime per molecular dynamics step (i.e., time to solution).

calculation for the electronic polarizability of the 32 atom GaN system spends 73% of its time performing FFTs. Our new approach reduces the number of FFT operations needed for this segment of the GW calculation by a factor of 60. The requested XSEDE resources will help us explicitly demonstrate the resulting improvements and also clarify the scaling behavior of our new software.

Our final scaling data concerns the *ab initio* molecular dynamics software we use for large scale Car-Parrinello *ab initio* molecular dynamics (CPAIMD) simulations. We use the plane-wave pseudopotential OpenAtom electronic structure software [28, 29]. OpenAtom is a massively parallel density functional theory software for large scale molecular dynamics simulations and has been developed in close collaboration with computer scientists with expertise in parallel computing (Kalé group at UIUC who is also our collaborator on our NSF SI2-SSI grant). We refer the reader to the website for the software [29] for publications and comprehensive scaling data. As an example of OpenAtom's scaling for systems of interest in this proposal, Figure 2 displays strong scaling data for OpenAtom's performance on a zinc-containing metal organic framework (MOF) system with over 400 atoms in the simulation cell run on the NCSA BlueWaters supercomputer.

References for Renewal of
"*Ab initio* studies of nanostructured materials"

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Progress Report: *Ab initio* studies of nanostructured materials

This past year, we have used XSEDE computational resources and first principles theory and computation to understand and predict the relationship between atomic-scale structure and the resulting properties of a variety of nanostructured systems. Due to space limitations, we can only highlight selected research projects below.

1   Nickelate interfaces

Interfaces between rare-earth transition-metal perovskite oxides and ferroelectric materials have been shown to exhibit dependence of their functional properties on the polar state of the ferro-electric. In particular, we have shown recently that the (001) interface between an ultrathin layer of metallic $LaNiO_3$ (LNO) and ferroelectric $PbZr_{0.2}Ti_{0.8}O_3$ (PZT) changes its electrical conductivity upon ferroelectric field switching.[1] Our work to date has been focused on the NiO_2/PbO interface for this heterostructure which shows a change in conductivity when the ferroelectric polarization is flipped, and the change in conductivity is driven not by carrier density modulation but instead a change of mobility. The mobility change mechanisms are twofold: (i) a new conducting channel appears in the interfacial PbO layer of the ferroelectric , and (ii) significant polarization-dependent structural distortions at the interface change electronic band widths and effective masses. The two mechanisms partially compete with each other in this field effect device.

We are now focusing on enhancing the conductivity on/off ratio by considering the alternative LaO/TiO_2 interface. We have performed density-functional theory calculations of this system. We find that at the LaO/TiO_2 interface, the interfacial $PbTiO_3$ remains insulating regardless of the polarization state, and the structural distortions at the interface are completely responsible for conductivity modulation. The simulations provide a simple physical picture of how the structural distortions depend on the polar state of the ferroelectric as well as the choice of atomic planes that form the interface. Our semi-classical calculations of the conductivity predict an enhancement of the conductivity on/off ratio for the LaO/TiO_2. These findings have been confirmed by experiment.

2   Ultrathin SiO_2 structures

Atomically-thin 2-dimensional structures draw significant attention because their properties can be dramatically different from their bulk counterparts. Recently, bilayer SiO_2 structures have been grown on metallic substrates. These structures show amorphous or crystalline phases with the Si atoms forming rings of different sizes and arrangements. Hence, bilayer SiO_2 is attractive as an atomically-thin membrane. To understand the key role of the substrate on the SiO_2 structure and morphology, we have simulated several bilayer SiO_2 systems. Total energy calculations of fully-relaxed (unstrained) free-standing SiO_2 bilayers with different motifs (hexagonal and several combinations of 4-, 5-, 6-, and 8-membered Si rings) show that the free-standing hexagonal structures are energetically favored. When uniaxial and biaxial strain is applied to the above structures, we find that strain states representative of a metallic substrate such as Ru can change the energetic ordering of the various possible structures.

3   Oxide/semiconductor interfaces

Much effort has been expended to obtain a ferroelectric material epitaxial directly on a semiconductor because of its many potential applications in electronic devices: e.g., a non-volatile transistor where the state (bit) is encoded in the direction of the ferroelectric polarization which does not

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[1]M. S. J. Marshall, A. Malashevich, A. S. Disa, M. G. Han, H. Chen, Y. Zhu, S. Ismail-Beigi, F. J. Walker, and C. H. Ahn, "Conduction at a Ferroelectric Interface", *Phys. Rev. Applied* **2** 051001 (2014).

require constant application of voltage and thus provides significant energy efficiency compared to traditional CMOS transistors. We have examined epitaxial thin films of $BaTiO_3$ on the (001) surface of Ge (grown and characterized by our Yale NSF MRSEC collaborators). Building on last year's work, we have completed a comprehensive analysis of this system. We find that the interface pins the out-of-plane polarization of the $BaTiO_3$ film in one direction. Once the $BaTiO_3$ is at least three atomic planes thick, there are two stable energy minima, the lower energy one agreeing with X-ray diffraction characterization of the interface. Simulations of the behavior of oxygen vacancies at the interface show that the desired elimination of GeO_2 formation at the interface is due to kinetic trapping of oxygen vacancies at the interface, and we have fully explored the landscape for oxygen vacancies by also computing energy barriers to their motions.

Due to the above polarization pinning, a change in interface chemistry is needed for ferroelectricity to exist in such systems. Our present idea is to use a ferroelectric buffer layer between the semiconductor and oxide to enable ferroelectricity in the oxide thin film. We have begun to explore ZrO_2 monolayers on Si (001) surfaces as potential buffer layers. The monolayer has multiple metastable configurations with differing polarizations (see Fig. 1). Preliminary experiments also show signatures of ferroelectric behavior in these monolayers. The next steps have involved computing the transition energy barriers between the multiple metastable structures as well as the energies of the domain boundaries that must form between the multiple states during potential ferroelectric switching processes. This large database of *ab initio* data permits us to create a 2D lattice model which is being studied in greater depth to understand the thermodynamics and dynamics of these 2D ferroelectric buffer layers. Finally, we are in the process of seeing how the ZrO_2 buffers can control the polarization state of a $SrTiO_3$ film grown on top: initial results are highly encouraging.
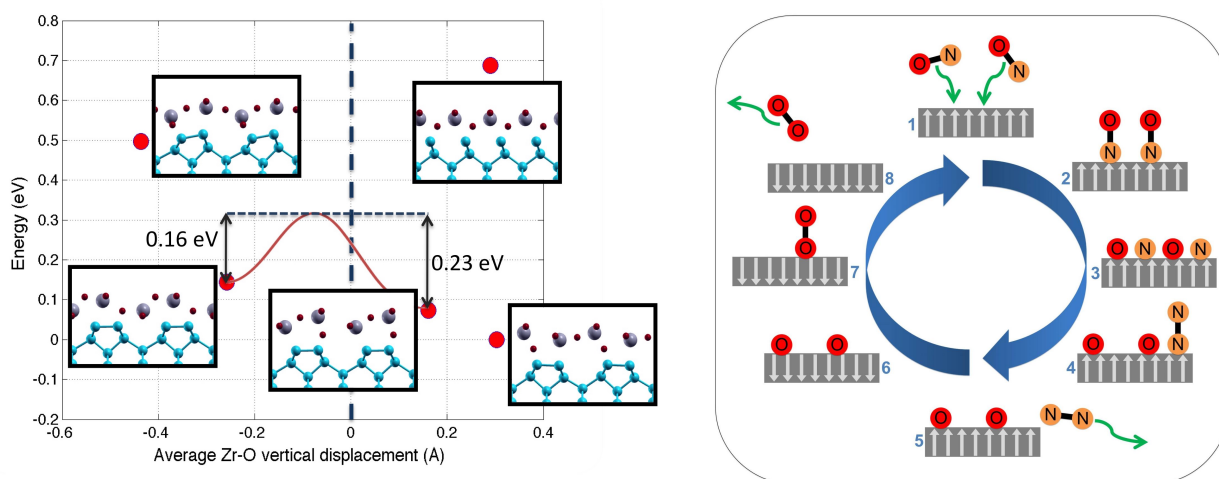

Figure 1: Left: Five lowest-energy metastable configurations of ZrO_2 monolayers on Si (001) surface shown in the boxes: cyan balls are Si, red are O, and gray are Zr. Energies (red dots) are per 2×1 unit cell. Horizontal axis is the average Zr-O vertical displacement. One energy barrier is also shown as an example. Right: Proposed catalytic cycle of a CrO_2 monolayer on $PbTiO_3$ for NO direct decomposition into N_2 and O_2. The polarization direction is indicated by gray arrows. The green arrows show molecular adsorption and desorption. The cycle achieves $2NO \rightarrow N_2 + O_2$.

4 Superconducting Fe-chalcogenide monolayers

The recent discovery of high temperature superconductivity (i.e., above liquid nitrogen temperature) in monolayer (ML) FeSe on (001) $SrTiO_3$ (STO) has drawn much attention.[2] Although the mechanism for electron pairing is under debate, interfacial interactions between FeSe and $SrTiO_3$ must play a crucial role due to the enhancement of superconductivity compared to bulk FeSe.

To date, density functional theory studies were unable to explain a key feature in the Fermi surface topology of the system, namely the absence of a "hole pocket" about the Γ point in the Brillouin zone of the FeSe subsystem. In a combined work with experimental colleagues in the Yale MRSEC, we find that the STO surface termination is not the primitive 1×1 single-layer TiO_2 assumed in almost all work to date but instead a more complex double-layered TiO_2 structure. Experiment and theory show that the double layer facilities the epitaxial growth of the ML FeSe. In addition, we show that we can reproduce the elimination of the Γ hole pocket due to the strong tendency of the double layer to donate electrons to the FeSe when oxygen vacancies are present in the surface TiO_2 layer. Electron doping of ML FeSe is an important known factor in its superconducting behavior. A manuscript will be submitted by the end of October 2015.

5 Ferroelectric surface chemistry

The maximum efficiency of a fixed catalytic surface occurs when the adsorbate-surface interaction strength is optimal as per the Sabatier principle: strong enough to drive the reactions forward but weak enough to permit the products to desorb. Such a compromise can fundamentally limit catalytic activity. One solution is to create a surface with switchable activity between strong binding (rapid dissociation) and weak binding (easy desorption). We have studied catalysts comprising an epitaxial monolayer of a transition metal oxide on an oxide ferroelectric substrate where reversing the ferroelectric polarization state switches the surface activity between these two limits.[3] The initial objective was to design a catalyst that directly dissociates NO_x into N_2 and O_2, an open challenge in conventional automotive catalysis. We show when the ferroelectric polarization of a monolayer of CrO_2 supported on ferroelectric $PbTiO_3$ is periodically switched in a cyclic manner, one can efficiently catalyze the dissociation (see Fig. 1). The first part of the reaction (NO decomposition and N_2 formation and desorption) is driven by one polarization state while the second part (O_2 formation and desorption) takes place for the other polarization. In addition, this system can simultaneously oxidize CO into CO_2, another vital process for the automotive emission control industry. Since the surface periodically goes through an inactive phase, "poisoning" agents (including normally tightly bound oxygen and sulfur) naturally get cleaned off the surface.

Our finding that the polarization can strongly alter oxygen surface binding energies (>2 eV per O_2) motivated us to see if bare ferroelectric $PbTiO_3$ itself can drive partial methane oxidation to methanol. Thermodynamically, we find that it is possible to oxidize methane into methanol for the polarization state with weak oxygen binding, while one can easily replenish the oxygen supply in the opposite polarization which adsorbs and dissociates oxygen molecules with no energy barrier. Further computations uncovered a kinetic problem with this scenario: in the weak oxygen binding state, the molecular oxygen formation barrier is smaller than the methanol formation barrier so the desired reaction should not take place with a significant rate. We are exploring how monolayers of metal oxides may change the energetics and dynamics of this system in a favorable direction.

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Professional Preparation

Institution	Major/Area	Degree and year
Harvard College	Physics	A. B., 1993
Ecole Normale Superieure de Lyon	Statistical Physics and Nonlinear Phenomena	D. E. A., 1994
Massachusetts Institute of Technology	Physics	Ph. D., 2000
University of California at Berkeley	Physics Postdoc.	2000-2003

Appointments

Professor of Applied Physics and Physics, Yale University, September 2007-2015.
Associate Professor of Applied Physics and Physics, Yale University, September 2007-2015.
Assistant Professor of Applied Physics and Physics, Yale University, September 2003-2007.

Five publications most closely related to this proposal

Arvin Kakekhani and Sohrab Ismail-Beigi, "Ferroelectric-Based Catalysis: Switchable Surface Chemistry", *ACS Catalysis* **5**, 4537 (2015).

Kevin Garrity, Arvin Kakekhani, Alexie Kolpak and Sohrab Ismail-Beigi, "Ferroelectric surface chemistry: First-principles study of the $PbTiO_3$ surface", *Physical Review B* **88**, 045401 (2013).

K. Garrity, A. M. Kolpak, S. Ismail-Beigi, and E. I. Altman, "Chemistry of Ferroelectric Surfaces", *Advanced Materials* **22**, 2969-2973 (2010).

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Hanghui Chen, Divine P. Kumah, Ankit S. Disa, Frederick J. Walker, Charles H. Ahn and Sohrab Ismail-Beigi, "Modifying the Electronic Orbitals of Nickelate Heterostructures via Structural Distortions", *Physical Review Letters* **110**, 186402 (2013).

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S. Ismail-Beigi, "Correlation energy functional within the GW-RPA: Exact forms, approximate forms, and challenges", *Physical Review B* **81**, 195126 (2010).

A. M. Kolpak, F. J. Walker, J. W. Reiner, Y. Segal, D. Su, M. S. Sawicki, C. C. Broadbridge, Z. Zhang, Y. Zhu, C. H. Ahn, and S. Ismail-Beigi, "Interface-Induced Polarization and Inhibition of

Ferroelectricity in Epitaxial SrTiO$_3$/Si", *Physical Review Letters* **105**, 217601 (2010).

C. D. Spataru, S. Ismail-Beigi, L. X. Benedict, and S. G. Louie, "Excitonic Effects and Optical Spectra of Single-Walled Carbon Nanotubes", *Physical Review Letters* **92**, 077402 (2004).

Synergistic Activities
Proposals: Reviewer of proposals for various funding agencies (NSF, DOE, DOD, PRF, etc).
Publishing: Reviewer on a regular basis for more than 15 journals.
Undergraduate mentoring: Supervised seven theses and 8 summer students since 2003.
Collaborative software development: Continues development of the DFT++ first-principles density-functional theory software package in collaboration with Arias research group (Cornell): an open-source, object-oriented, fully parallelized code in C++ that is freely available on the web at http://dft.physics.cornell.edu; collaborates with Prof. Leeor Kronik (Weizmann Institute) and developing methods with his group to perform Greens function calculations on half-metallic systems (since spring 2005).
Local Outreach: Develops teaching modules in collaboration with a New Haven Public School science teacher on the role of materials science in modern electronic devices, broadly understood, as appropriate for high school students and teachers in digital web form as well as physical kits for demonstrations; on advisory board of Center for 21st Century Skills; judges in various science fairs in New Haven public middle and high schools. Website is http://volga.eng.yale.edu/pmwiki.php/Main/TeachingResources

Collaborators and Other Affiliations
a) *Collaborators in the past 48 months:*
Charles Ahn (Yale), Eric Altman (Yale), Dario Arena (BNL), Sarbani Basu (Yale), Victor Batista (Yale), Eric Bohm (UIUC), Christine Broadbridge (Southern Connecticut State University), Hanghui Chen (Columbia), Sang-Wook Cheong (Rutgers), Ronald R. Coifman (Yale), Furio Cora (U. College London), Kevin Garrity (NIST), Steven Girvin (Yale), Ricardo Grau-Crespo (U. of Reading), Jung Han (Yale), Victor Henrich (Yale), Jie Jiang (AFRL), Robert Klie (UIC Chicago), Laxmikant Kalé (UIUC), Kim Kisslinger (BNL), Alexie M. Kolpak (MIT), Leeor Kronik (Weizmann Institute), T. P. Ma (Yale), Thomas Mellan (U. College London), Corey O'Hern (Yale), Chinedum Osuji (Yale), Glenn Martyna (IBM), Lisa Pfefferele (Yale), Karen Rabe (Rutgers), James Reiner (Hitachi), Udo Schwarz (Yale), Mitchell Smooke (Yale), Xuan Shen (BNL), Eliot Specht (ORNL), Catalin D. Spataru (Sandia), Dong Su (BNL), Hui Tang (Morgan Stanley), Andre Taylor (Yale), Carlos Vaz (Paul Scherrer Institute), John Tully (Yale), Frederick Walker (Yale), Yimei Zhu (BNL).

b) *Ph.D. Advisor:* Tomás A. Arias, Cornell University, Cornell, NY.

c) *Postdoctoral Advisor:* Steven G. Louie, U. C. Berkeley, CA.

d) *Thesis Advisees and postdoctoral fellows:* Currently, I have four graduate students (Mehmet Dogan, Alexandru Georgescu, Arvin Kakekhani, Xin Liang). My current postdocs are Drs. Minjung Kim, Andrei Malashevich, and Subhsish Mandal. My previous doctoral students are Hanghui Chen (now a postdoc at Columbia with Profs. Marianetti and Millis), Kevin Garrity (now at NIST), and Hui Tang (now at Morgan Stanley, NY). My previous postdocs were Dr. Jie Jiang (Air Force Research Lab, NRC fellow) and Dr. Alexie Kolpak (co-advised with John Tully) and is now a faculty in Mechanical Engineering at MIT.