

materials science & ENGINEERING

1st Symposium on

Computational Materials Research

Advanced Electronic Structure Calculations and Big Data

Thursday **July 27, 2017** 9am - 4pm **IMS 20**, UConn Storrs Campus*

SYMPOSIUM SCOPE

Quantum theory has been at the forefront of materials research as the technology shrinks towards the nanoscale. This has been partly driven by the progress in methodologies that could be pursued within present day high-performance computational capabilities. The state-of-the-art theory goes hand-in-hand with experiments and helps capture the physics of materials. There are examples where new properties predicted by theory have been later validated by experiments. The data mining and the machine learning of the first-principles data adds completely new dimension to designing materials by theory. The goal of the conference is to provide a platform for discussion on the current research trends. The scope also covers some introductory and visionary perspective in materials theory.



S. Pamir Alpay



S. Rajasekharan



Sanjubala Sahoo



Huan Tran



Deya Das



Sanjeev K. Nayak



Lydie Louis



Anand Chandrasekharan



Chiho Kim

SPEAKERS

IMS Members

Keynote Speaker: Prof. S. Rajasekaran, UConn Professor & BECAT Director

TOPICS

- Density Functional Theory (DFT), its Advantage and Limitations
- Wannier Functions and their Applications
- Phonons and their Properties
- Applications of DFT for Physical and Catalytic Properties
- Data Mining and Machine Learning

APPLICABLE FOR

- Graduate students (Materials Science and Engineering, Physics, Chemistry)
- Industry researchers interested in brushing up theory knowledge
- IMS/MSE Postdocs
- Faculty members (IMS, MSE, Physics, Chemistry)





AGENDA

- 9:15am – 9:30am **Introduction**
Prof. S. Pamir Alpay
- 9:30am – 10:00am **A Pragmatic Viewpoint of the Density Functional Theory**
Sanjeev K. Nayak
- 10:00am – 10:30am **First Principles Studies of Diisopropylammonium-Based Molecular-Ferroelectric Crystals**
Lydie Louis
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- 10:30am – 10:45am *Coffee Break*
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- 10:45am – 11:15am **First-Principles Modeling of Ferroelectric Materials**
Anand Chandrasekaran
- 11:15am – 12:00pm **Big Data Technique for Materials Science**
Prof. Sanguthevar Rajasekaran (keynote speaker)
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- 12:00pm – 1:15pm *Lunch Break*
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- 1:15pm – 1:45pm **Reactivity of Graphene-supported Single Transition Metal Atom Catalysts**
Sanjubala Sahoo
- 1:45pm – 2:15pm **Phonons in Solid-State Materials**
Huan D. Tran
-
- 2:15pm – 2:30pm *Coffee Break*
-
- 2:30pm – 3:00pm **Large Dirac Cone Splitting in Graphene/Graphane Heterostructure Under Normal Compressive Strain**
Deya Das
- 3:00pm – 3:30pm **Density Functional Theory and Machine Learning Assisted Selection of Dielectrics Tolerant to Extreme Electric Fields**
Chiho Kim
- 3:30pm – 4:00pm **Panel Discussion**
Moderators: Sanjeev K. Nayak, Huan D. Tran

A Pragmatic Viewpoint of the Density Functional Theory

Sanjeev K. Nayak and S. Pamir Alpay

Department of Materials Science & Engineering, University of Connecticut



Density functional theory (DFT) is one of the most popular theory for materials research at the nanoscale. It brings together a balance between computability of physical properties and the accuracy of results. The exchange-correlation treatment is the most important approximation in the theory. It has been found that DFT is applicable for structural, electronic and magnetic properties of metals. On the other hand, for semiconductors the prediction of the electronic band gap values has been underestimated. DFT is rather valid for systems where the charge density is varying smoothly in space. Thus, it makes complete sense that the physics of s- and p-orbital systems are predicted accurately. The limitations of DFT for systems with charge localization and with orbitals with strong correlation have been investigated with additional tools such as the DFT+U and the hybrid functional methods. Such, methods that are used to overcome the limitations are often called the beyond DFT treatments. In the talk, the strength and limitations of DFT will be discussed and a perspective will be presented that could be valuable for materials researchers.

First-Principles Modeling of Ferroelectric Materials

Anand Chandrasekharan

Institute of Materials Science, University of Connecticut



Ferroelectric oxides, such as lead zirconate titanate, have proved invaluable due to their excellent dielectric and piezoelectric properties. These classes of materials possess a large electric polarization below the Curie temperature. Regions of the crystal lattice having different directions of polarization are separated by nano-scale interfaces known as domain walls. These interfaces, which can be moved by electric and mechanical fields, are not only important for electromechanical properties but they also exhibit unique structural and electronic properties that may be exploited through novel application in nanoelectronics and photovoltaics. In this work, we investigate the origin of the so-called "hard" and "soft" behavior in lead zirconate titanate. The microscopic origin of this phenomena is best investigated using first-principles simulations of the atomistic properties of defects and domain wall in these materials to bring to light novel structural and electronic properties. First, we show that polar defect complexes are likely to exist in both acceptor-doped and undoped PbTiO_3 . These defects and defect associates are attracted to 180 degree domain walls and cause pinning of such

interfaces. A complete study of domain walls in PbTiO_3 also entails looking closer at the properties of the ferroelastic "head-to-tail" 90 degree domain boundary. We show the presence of an asymmetry in the variation of the lattice parameter across the domain wall. This asymmetry is verified using high resolution aberration corrected electron microscopy. We look at the energy landscape of oxygen vacancies in the vicinity of these walls to explain the pinning effect in terms of random-bond and random-field defects. In parallel to the first principles work, we also prepared high quality samples of PZT 50/50 with different concentrations of donor dopant. We characterized the microstructure and hysteresis loops as a function of donor dopant concentration. Based on experimental observations and ab initio calculations we propose ideas on the origins of hardening and softening in PZT.

First Principles Studies of Diisopropylammonium-Based Molecular-Ferroelectric Crystals

Lydie Louis, Krishna Pitike, and Serge M. Nakhmanson

Department of Materials Science & Engineering, University of Connecticut

Shashi Podar and Stephen Ducharme

Department of Physics & Astronomy, and Nebraska Center for Materials & Nanoscience, University of Nebraska-Lincoln



Recent advances in the synthesis of polar organic materials have introduced strategic alternatives to well-known ferroelectric ceramics, such as PbTiO_3 and BaTiO_3 perovskite oxides. In particular, cocrystals formed by combinations of diisopropylammonium (DIPA) molecules with Chlorine and Bromine counterions were shown to possess large room-temperature spontaneous polarization [1,2]. This opens up exciting new avenues for their incorporation in modern all-organic electronic devices, including capacitors, as well as piezoelectric, pyroelectric, and electro-optical sensors.

In this investigation, we present a systematic density-functional theory (DFT) based study of structural, electronic, dielectric and polar properties of the DIPA-X molecular cocrystals, with X representing various halogens, namely, Chlorine, Bromine and Iodine, as well as the polyatomic nitrate anion. For each of the cocrystals, the polar properties for all of the relevant polymorphs were evaluated and decomposed into contributions from individual structural units by computing the charge centers of their maximally localized Wannier functions (MLWFs). Our calculations reveal antipolar dipole moment arrangements present in all of the cocrystals, with non-zero spontaneous polarization emerging as a result of small cantings of the dipole moments. These insights, combined with the elucidated influence of the cofomer/counterion chemical identity on the cocrystal properties, can be used for the design of high-performance flexible-ferroelectric materials for novel all-organic technological applications.

References

1. D.-W. Fu, H.-L. Cai, Y. Liu, Q. Ye, W. Zhang, Y. Zhang, X.-Y. Chen, G. Giovannetti, M. Capone, J. Li, R.-G. Xiong, Diisopropylammonium bromide is a high-temperature molecular ferroelectric crystal, *Science* **339**, 425 (2013).
2. D.-W. Fu, W. Zhang, H.-L. Cai, J.-Z. Ge, Y. Zhang and R.-G. Xiong, Diisopropylammonium Chloride: A Ferroelectric Organic Salt with a High Phase Transition Temperature and Practical Utilization Level of Spontaneous Polarization, *Adv. Mater.* **23**, 5658 (2011).

Big Data Technique for Materials Science

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One of the major challenges faced currently by any science or engineering domain is the lack of adequate data analytics tools to keep pace with the voluminous datasets that are constantly being generated. This is very much true for the Materials Science domain. The Materials Genome (MG) Initiative for Global Competitiveness, inspired by the Human Genome Project, aims to accelerate the discovery, development, manufacturing, and deployment of new and advanced materials. It is generally accepted that the goals of the Materials Genome Initiative can only be successful if the efforts are data-driven.

In this talk we present some challenges existing in processing big data. We also provide an overview of some basic techniques. In particular, we will summarize various data processing and reduction techniques that are relevant for Materials Science.

Phonons in Solid-State Materials

Huan D. Tran

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The phonon spectrum of a solid provides insights, at some certain levels, into its dynamical stability and finite-temperature thermodynamic stability [1]. At the DFT level, it can be computed pretty well, being useful complement to the regular methods in materials science [2,3]. We will discuss the DFT-based methods for calculating the phonon spectrum and accessing the aforementioned characteristics of some solid-state materials.

References

1. T. D. Huan, Evaluation of crystal free energy with lattice dynamics, arXiv:1506.09189 (2015).
2. T. D. Huan, V Sharma, GA Rossetti Jr, R Ramprasad, Pathways towards ferroelectricity in hafnia, Phys. Rev. B **90**, 064111 (2014).
3. H. D. Tran, M. Amsler, S. Botti, M. A. L. Marques, and S. Goedecker, First-principles predicted low-energy structures of NaSc(BH₄)₄, J. Chem. Phys. **140**, 124708 (2014).

Reactivity of Graphene-supported Single Transition Metal Atom Catalysts

Sanjubala Sahoo and S. Pamir Alpay

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Single-atom catalysis is relatively a new concept to enhance catalytic activity of transition metal atoms through proper choice of support. The interest in such systems is due to the fact that both the quantum size effect and support-catalyst interactions may lead to unique electronic structures that may enhance catalytic properties. This allows for the design of materials systems at the atomic scale, tailored for specific reactions. Utilizing this concept, we investigated theoretically free and graphene supported single Cr, Mn, Fe and Co atoms for the activation of methane where we have identified the catalytically active centers. We have employed density functional theory within generalized gradient approximation for the exchange-correlation treatment. Our results show that graphene-supported TM systems have a high binding energy for methane relative to free ones. The binding can be further enhanced by the presence of defects in graphene. Our analysis shows that the TM-C bond interaction, the charge transfer between the

TM-support and the d-density of states play significant role in the catalytic activity.

Density Functional Theory and Machine Learning Assisted Selection of Dielectrics Tolerant to Extreme Electric Fields

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Understanding the behavior of dielectric insulators experiencing extreme electric fields is critical to the operation of present and emerging electrical and electronic devices. Despite its importance, the development of a predictive theory of dielectric breakdown has remained a challenge, owing to the complex multiscale nature of this process. Here, we focus on the intrinsic dielectric breakdown field of insulators - the theoretical limit of breakdown determined purely by the chemistry of the material, i.e., the elements the material is composed of, the atomic-level structure, and the bonding. Starting from a benchmark dataset (generated from laborious first principles computations) of the intrinsic dielectric breakdown field of a variety of model insulators, simple predictive phenomenological models of dielectric breakdown are distilled using advanced statistical or machine learning schemes, revealing key correlations and analytical relationships between the breakdown field and easily accessible material properties. Next, we apply these design rules to a vast chemical space of perovskite materials in order to demonstrate the efficacy, generalizability and true predictive power of our model. Starting from several thousands of compounds, we systematically downselect 209 insulators which are dynamically stable

in a perovskite crystal structure. After making predictions on these compounds using our machine learning model, the intrinsic dielectric breakdown strength was further cross-validated explicitly using first principles computations. Our analysis reveals that several boron-containing compounds are of particular interest, some of which exhibit remarkable intrinsic breakdown strength of about 2 GV/m.

Large Dirac Cone Splitting in Graphene/Graphane Heterostructure Under Normal Compressive Strain

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Graphene is one of the most exciting two-dimensional materials due to its linear band dispersion at the Fermi level. However, the lack of a band gap limits graphene from its application in optical and electronic devices. Using first-principles calculations, we report a large band-gap opening in the van der Waals heterostructure of graphene and graphane (hydrogenated graphene) under normal compressive (NC) strain. In the presence of graphane, interlayer charge transfer from graphene to graphane triggers the intralayer charge redistribution in graphene, which breaks the equivalence of the two sublattices. This symmetry breaking, however, is not strong enough to split the Dirac cone. The application of the NC strain enhances the inter- and intralayer charge transfer leading to a splitting of the Dirac cone. The band gap increases monotonically and attains a maximum of 0.74 eV at 20% strain, which is the largest ever reported splitting of a Dirac cone in graphene. The enhancement of charge transfer from graphene to graphane under NC strain has also been consistently captured through theoretical Raman spectra by red-shift of G peak of graphene. While the large band gap will ensure a high switching ratio, the linear dispersion of Dirac bands will result into high mobility, making

these heterostructures ideal candidates for optoelectronic applications.

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Reference:

D. Das, S. Bhattacharyya, Enrique Muñoz, and A. K. Singh, Strain-induced chiral symmetry breaking leads to large Dirac cone splitting in graphene/graphane heterostructure, *Phys. Rev. B*, **94**, 115438 (2016)