Band Gaps from Hybrid Density Functionals in 1D, 2D, or 3D: The Right Answer for the Right Reason

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Abstract - The fundamental energy gap of a periodic solid distinguishes insulators from metals and characterizes low-energy single-electron excitations. But the gap in the band-structure of the exact multiplicative Kohn-Sham (KS) potential substantially underestimates the fundamental gap, a major limitation of KS density functional theory. Here we give a simple proof of a new theorem: In generalized KS theory (GKS), the band gap of an extended system equals the fundamental gap for the approximate functional if the GKS potential operator is continuous and the density change is delocalized when an electron or hole is added. Our theorem explains how GKS band gaps from meta-generalized gradient approximations (meta-GGAs) and hybrid functionals can be more realistic than those from GGAs or even from the exact KS potential. The theorem also follows from earlier work. The band edges in the GKS one-electron spectrum are also related to measurable energies. A linear chain of hydrogen molecules, solid aluminum arsenide, and solid argon provide numerical illustrations.

Efficient First-Principles Predictions towards Chemical accuracy for Solids Stability

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Abstract - Whether a solid can exist and in what phases are of fundamental and technological interest in condensed matter physics and materials science. Due to various chemical degrees presented, ranging from the configurational difference between phases to the changes of oxidation number and to the chemical bonding characteristics, it is challenging for first-principles methods to tackle the stability problem with reasonable computational cost. We show here that density functional theory (DFT), one of the most widely used first-principles electronic structure theories, has advanced to a point where the stability of main group solids, including the relative stability of competing phases, can be reliably and efficiently predicted, while that of transition metal compounds remains as a challenge though alleviated. It is expected that this development will further accelerate the discovery of materials by computational design and keep DFT as the choice for the study of materials.
**Xifan Wu** - *Electronic origin of spin-phonon coupling effect in transition-metal perovskites* Hongwei Wang1,2, Lixin He1, Hong Jiang3, Cameron C. Steele2, and Xifan Wu1.

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**Abstract** - Spin-phonon coupling effect in transition metal perovskites has been identified by the fact that the low-lying phonon modes, as well as the polar ones, are significantly softened when the spin coupling is changed from being antiferromagnetic to ferromagnetic. We study the electronic origins of spin-phonon coupling effect by using SrMnO3 and BiFeO3 as examples. In particular, we compute the superexchange interactions via the virtual electronic hopping processes by a recently developed extended Kugel-Khomskii model based on maximally localized Wannier functions, in which the electronic screening is considered by constrained random phase approximation. The spin-phonon coupling effect can be understood as the tendency towards the suppressed superexchange interaction under the structural distortion along the phonon mode. However, the electronic structure plays a crucial role in the above. On one hand, phonon modes that effectively change the hybridization between Mn-3d and O-2p are found to have strong spinphonon coupling effect. On the other hand, the rather different details in the virtual hopping processes originating from the distinct electronic configurations in Mn4+ and Fe3+ ions explain the much weaker spin-phonon coupling effect in BiFeO3 than that of SrMnO3. Our results bridge the gap between the Goodenough-Kanamori-Anderson phenomenological rule based on metaloxygen-metal angle only and the electronic structure calculation of materials. Furthermore, it also provides useful guidance to the search for new spin-phonon coupling materials.

**Haowei Peng** - *Redox properties of birnessite for catalysis: A defect perspective*

Haowei Peng, Ian G. McKendry, Ran Ding, Akila C. Thenuwaru, Qing Kang, Samantha L. Shumlas, Daniel R. Strongin, Michael J. Zdilla, and John P. Perdew, Temple University

**Abstract** - Birnessite, a layered-structure MnO2, is an earth-abundant functional material with potential for various energy and environmental applications, such as water oxidation. An important feature of birnessite is the existence of Mn(III) within the MnO2 layers, accompanied by interlayer charge-neutralizing cations. Using first-principles calculations, we reveal the nature of Mn(III) in birnessite with the concept of the small polaron, a special kind of point defect. Further taking into account the effect of the spatial distribution of Mn(III), we propose a theoretical model to explain the structure-performance dependence of birnessite as an oxygen evolution catalyst. We find an internal potential step which leads to the resonance between Mn(III) and Mn(IV) that is critical for enhancing the catalytic activity of birnessite. Finally, we conduct a series of comparative experiments which support our model.

**Adrienne Ruzsinszky** - *Surface energies within the Random Phase Approximation*

Adrienne Ruzsinszky, Jefferson E. Bates, Niladri Sengupta and Niraj Nepal

Temple University

**Abstract** - Metallic and semiconducting surfaces are highly relevant in industrial applications such as catalysis or molecular electronics. Metal surfaces also play a key role as paradigm systems in the development of Kohn-Sham density functional theory. In any application to realistic materials we have to rely on accurate benchmark surface energies. Benchmark surface energies have been available so far for the jellium model of metallic surfaces. Wavefunction methods in electronic structure theory are more accurate than Kohn-Sham density functional theory, however at a much
higher computational price. The Random Phase Approximation (RPA) can be interpreted within the density functional context and has recently become computationally more feasible than it was before. At the same time RPA is a wavefunction-based method and therefore it has the potential to be a benchmark in materials science. We are applying and testing the RPA to various problems relevant to our EFRC Center including surface energies. For the first time we apply the RPA within the Renormalized Perturbation framework with kernel correction and report surface energies for metallic and semiconducting surfaces.

Qimin Yan - Construction of a two-dimensional materials database for functional material discovery and design
Q. Yan, J. Pan, H. Peng, J. Yu, X. Qian, J. P. Perdew, Temple University

Abstract - Single-layer two-dimensional (2D) materials have shown entirely different properties compared with their bulk counterparts, offering great new opportunities for the discovery and design of new functionalities in this largely unexplored compound space. In this work, we construct a comprehensive single-layer 2D materials database based on a stable and efficient data-mining approach. Around 1000 compounds with layered structures have been identified through the data-mining process utilizing the ICSD crystallographic materials database, upon which single-layer structures are constructed. High-throughput first-principles computations based on density functional theory (DFT) with PBE, HSE, and newly developed SCAN functionals are performed to optimize geometric structures. We perform a thorough computational study of magnetic, electronic, and elastic properties of newly identified 2D compounds. Additionally, we identify unique 2D symmetry group and Brillouin zone for each 2D compound and are generating HSE band structures for all the compounds. Key materials properties (including electronic band gaps, band edge energies, formation energies, elastic modulus, magnetic configurations, and so on) are stored in the 2D materials database, which offers the community a great opportunity for the rational design of functional 2D materials for technical applications including solar fuel conversion, topological materials, electronics, and catalysis. The database and related website are under construction and will become public in 2017.

Weitao Yang - Electronic Excitations from Particle-Particle Random Phase Approximation
Weitao Yang, Duke University

Abstract - We developed the particle-particle Random Phase Approximation for determine electronic excitation energies by the differences of two-electron addition/removal energies. This approach can be viewed as combining the accurate many-body description of two-electron subsystems with the DFT description for the remaining (N-2) electrons. It is a seamless embedding in the Fock space. This approach captures many types of interesting excitations: single and double excitations are described accurately, Rydberg excitations are in good agreement with experimental data and CT excitations display correct 1/R dependence. Applications to the singlet-triplet energy gaps of diradicals and poly-acenes and conical intersections will be featured.


SESSION II - TUESDAY MAY 16, 12:40 - 15:00

Arun Bansil - Progress in Modeling and Understanding Properties of Novel Phases of Layered Materials, Northeastern University

Abstract - I will highlight examples drawn from our recent work aimed at modeling novel phases of layered materials and their properties as follows [1-7]. (i) How a new type of tunable and laser-reconfigurable 2D heterocrystal can be obtained by epitaxial stacking of crystallographically incommensurate Bi₂Se₃ and MoS₂ atomic layers. (ii) By considering silicene on Ag (111) surface, we identify the first case of a new type of Dirac Fermion generated through the interaction of two different constituents. (iii) We show the immunity of the Fe-Nₓ-Cᵧ active centers to chloride poisoning, which opens promising avenues for developing affordable and robust oxygen consuming electrodes. (iv) We predict half-fluorinated GaBi honeycomb under tensile strain to harbor a quantum anomalous Hall (QAH) insulator phase. (v) Efficacy of the SCAN meta-GGA functional is demonstrated by considering a number of ‘beyond’ graphene materials as well as for cuprate high-temperature superconductors. (vi) Nature of electronic structure changes induced via interlayer coupling in few-layer MoS₂ were examined to gain an understanding of how layer thickness can be used to control electronic properties in 2D materials. Work supported by the U.S.D.O.E.

Mikko Haataja - Modeling of structural phase transformations in bendable transition metal monolayers, Princeton University

Abstract - In this talk, I will provide an overview of our recent efforts in developing physically-based, first-principles informed continuum models for strain-induced structural phase transformations in bendable transition metal dichalcogenide monolayers, both chemically homogeneous and heterogeneous.

Joel Berry - Analysis and Multi-Scale Modeling of Directly Synthesized 1H-MoS₂ / 1T'-MoTe₂ In-Plane Heterostructures

Joel Berry¹, Songsong Zhou¹, Carl H. Naylor, William M. Parkin, A.T. Charlie Johnson, David J. Srolovitz¹, ¹UPenn

Abstract - Heterostructures of transition metal dichalcogenides (TMDs) are of great interest due to the possibility of combining the physical properties derived from different TMD structures. Here we analyze aspects of heterophase interface structure, composition, and out-of-plane bending in
the first directly synthesized in-plane monolayer 1H-MoS2/1T'-MoTe2 heterostructures. First-principles computations and a first-principles-informed continuum modeling approach are employed to explain origins of three surprising or unique features of the synthesized heterostructures. 1) Significant buckling is observed in the 1H region, which should experience a large tensile rather than compressive strain due to lattice mismatch with the 1T’ region. 2) Despite the large misfit strain between 1H and 1T’ lattices (>8%), the heterophase interface is found to be highly coherent and free of misfit dislocations. 3) Unlike most in-plane heterostructures synthesized to date, these exhibit morphologies with spike-like rather than compact 1T’ domains protruding from triangular 1H islands. We show that this morphology results from 1T’ edge energy anisotropy and elastic misfit strain between the two lattices. This system provides an interesting example of the interplay that can occur between chemical and thermomechanical driving forces in 2D heterostructures, leading to sometimes unexpected consequences for heterophase interface structure, buckling behavior, and growth morphology - all of which ultimately impact the optoelectronic properties of the material system.

Maria Iavarone - Moiré Superlattices and 2D electronic properties in graphite/MoS2 and MoS2/MoS2 heterostructures
M., Iavarone\textsuperscript{3}, D. J., Trainer\textsuperscript{1}, A. V., Putilov\textsuperscript{1}, T., Saari\textsuperscript{2}, B., Wang\textsuperscript{3}, C., Lane\textsuperscript{3}, T.-R., Chang\textsuperscript{5}, H.-Tay Jeng\textsuperscript{6,7}, H., Lin\textsuperscript{4,7}, X., Xi\textsuperscript{1}, J., Nieminen\textsuperscript{2,3}, A., Bansil\textsuperscript{3}
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Abstract - Heterostructures of MoS2 bilayers and graphite/MoS2 display a wide range of lattice registry due to rotational alignment and/or lattice mismatch. Using high resolution scanning tunneling microscopy and spectroscopy (STM/STS) we investigate the electronic properties of these heterostructures as a function of the twist angle between the van der Waals layers. We observe changes in the bandgap of both single MoS2 layers on graphite and MoS2/MoS2 bilayers.

Goran Karapetrov - Dynamics of Defects in MoS2 Monolayer Films
Goran Karapetrov\textsuperscript{1}, Marian Precner\textsuperscript{1}, Tomas Polakovic\textsuperscript{1}, Qiao Qiao\textsuperscript{2,3}, Yimei Zhu\textsuperscript{3}, Daniel J. Trainer\textsuperscript{2} and Maria Iavarone\textsuperscript{2}
\textsuperscript{1}Drexel University, \textsuperscript{2}Temple University, \textsuperscript{3}Brookhaven National Laboratory

Abstract - Advances in fabrication of large area few unit-cell thick MoS2 films could enable the next generation of electronic devices based on this semiconductor. The fundamental understanding of the electronic properties of this material is therefore crucial. We combine Kelvin probe force microscopy, scanning tunneling microscopy and high-resolution transmission electron microscopy to study the evolution of sulfur vacancies in MoS2 monolayer films grown by chemical vapor deposition. We find that the single atom vacancies are mobile at elevated temperatures or under the electron beam irradiation. The experiments show that sulfur vacancies formed after exposure to elevated temperatures diffuse, coalesce, and migrate bringing the system from a metastable to equilibrium ground state. The process is thermally activated with estimated energy barrier for sulfur vacancy migration of 0.6eV in single unit cell MoS2. The results provide initial
estimates of the thermal budgets available for reliable fabrication of MoS$_2$-based integrated electronics and indicate the importance of defect control and passivation.

**SESSION III - WEDNESDAY MAY 17, 9:40 - 12:00**

**Eric Borguet** - *Progress in Synthesis and Characterization of Layered and 2D materials Report on Thrust III activities and plans*

**Mike Zdilla** - *Theory guided transformation of a cheap, poor catalyst into a cheap, great catalyst*

**Abstract** - Nature's selection of manganese as the redox active element in nature's sole water oxidizing catalyst has prompted study of manganese-oxide based materials as synthetic water oxidation catalysts in pursuit of practical water splitting. Among manganese dioxide phases, birnessite, a layered MnO$_2$ with interlayer cations, possesses an intriguing structural similarity to biology's catalyst. Despite this, birnessite is one of the worst known catalysts for water oxidation with an overpotential of about 800 mV. By a combination of experiment and theory, we have uncovered the desirable features that lead to catalysis, and enriched birnessite with these features and have been able to generate a number of modified birnessites with overpotentials as low as 390 mV. Our development of these catalysts, especially insights from theoretical collaborators, will be highlighted.

**Samantha Shumlas** - *Investigations of the birnessite interlayer for water oxidation chemistry*

**Abstract** - Manganese (III) is a key species for water oxidation chemistry to occur in manganese oxides. The location of this species within the structure of birnessite, a layered manganese oxide, differs depending on the phase of birnessite being studied. Experiments were performed by converting triclinic birnessite (sheet manganese (III)) to hexagonal birnessite (interlayer manganese (III)) in pH 3, 5, and 7 DI water with stirring for 18 hrs. Once the conversion was complete, the solid samples were characterized with TEM and X-ray photoelectron spectroscopy (XPS). The resulting hexagonal birnessites from experiment at pH 3, 5, and 7 possessed the same particle morphology and average surface oxidation states within 1% of each other. This observation supported the claim that upon transformation, Mn (III) within the sheet of triclinic birnessite migrated into the interlayer region of the resulting hexagonal birnessite. Furthermore, the migration of Mn(III) into the interlayer and formation of the hexagonal birnessite led to an increased chemical reactivity for water oxidation compared to the bulk. Ceric ammonium nitrate was used to test birnessite for water oxidation reactivity. These experiments showed that the pH 3 birnessite produced the most O$_2$ of all the samples, 8.5 mmol O$_2$/mol Mn, which was ~6 times more than hexagonal birnessite which did not undergo post-synthesis exposure to low pH conditions.

**Yimei Zhu** - *Anisotropic charge density wave in layered 1T-TiSe$_2$*

Qiao Qiao$^1$, Songsong Zhou$^2$, Jing Tao, Jin-Cheng Zheng, Lijun Wu, Maria Iavarone$^3$, David Srolovitz$^2$, Goran Karapetrov$^4$, Yimei Zhu$^1$

$^1$BNL, $^2$UPenn, $^3$Temple University, $^4$Drexel University
Abstract - We present a three-dimensional study on the correlation length of charge density wave (CDW) in 1T-TiSe₂, by means of in-situ atomically resolved electron microscopy at cryogenic temperature in both reciprocal and real spaces. Using coherent nano-electron diffraction, we observed short-range coherence of in-plane CDW component while the long-range coherence of out-of-plane CDW component remains intact at 19K(?), indicating anisotropy of electron-phonon coupling. The in-plane CDW coherence length of ~10 nm and the out-of-plane CDW coherence length of 17.5 nm, as a lower bound, were determined. The electronic origin of the CDW anisotropy observed by diffraction agrees well with electron energy-loss spectroscopy measurements, and confirmed with DFT calculations. Our integrated approach illustrates the electron modulation induced symmetry breaking of a 2D material in three dimensions, providing an opportunity to study the effect of reduced dimensionality in strongly coupled electron-phonon systems.

Rick Remsing - Solvent Effects on Interfacial Electron Transfer Reactions and Implications for Catalysis
Richard C. Remsing¹, Akila C. Thenuwaru¹, Qing Kang¹, Loranne Vernisse², Samantha L. Shumlas³, Ian G. McKendry³, Nuwan H. Attanayake¹, Eric Borguet¹, Michael J. Zdilla¹, Daniel R. Strongin¹, and Michael L. Klein¹
¹Temple University, Temple University, ²Nanoplast Group, University of Poitiers, France

Abstract - Earth abundant materials for affordable renewable energy conversion promise to address growing world energy demands. For example, many mineral surfaces can promote chemical transformations necessary for fuel production. In particular, naturally occurring manganese oxides mimic the oxygen evolving complex of Photosystem II and have been shown to exhibit promising energy conversion and catalytic properties, especially with regard to water oxidation. Despite the immense promise of these materials in artificial photosynthetic technologies, little is known regarding the molecular details governing chemical reactivity at these solid-liquid interfaces. Such an understanding is required to inform the knowledge-based design of novel catalytic materials. In this talk, I will discuss unique properties of water confined between two-dimensional sheets of a layered phase of manganese dioxide. Coupling between interfacial ordering and confinement results in unique solution structures with analogies to classical descriptions of magnetism. I will then describe how the hydration environment impacts solvent fluctuations that control redox reactions and consequently dictates the rate of electron transfer. The generality of our findings is demonstrated through the development of simple models that further the analogy to magnetic systems. Strategies for using the understanding of this solid-liquid interface to inform the design of water oxidation catalysts will be suggested. I will also discuss the complex dynamics surrounding chemical reactions in this system, knowledge of which is crucial to guiding the study of water oxidation and other multistep chemical reactions at this and related catalytic interfaces.

Liping Yu - New Auxetic 2D Materials and bent MoS for water splitting
Liping Yu, Adrienn Ruzsinszky, Qimin Yan

Abstract - Materials with a negative Poisson’s ratio, also known as auxetic materials, exhibit unusual and counterintuitive mechanical behavior – becoming fatter in cross-section when stretched. Such behavior is mostly attributed to some special re-entrant or hinged geometric structures regardless of the chemical composition and electronic structure of a material. Here, using first principles calculations, we report a class of auxetic single-layer two-dimensional materials, namely the 1T-type monolayer crystals of groups 6-7 transition-metal dichalcogenides, MX₂ (M = Mo, W, Tc, Re; X = S, Se, Te). These materials have a crystal structure distinct from all
other known auxetic materials. They exhibit an intrinsic in-plane negative Poisson’s ratio, which is dominated by electronic effects. We attribute the occurrence of such auxetic behavior to the strong coupling between the chalcogen p orbitals and the intermetal t2g-bonding orbitals within the basic triangular pyramid structure unit. The unusual auxetic behavior in combination with other remarkable properties of monolayer two-dimensional materials could lead to novel multifunctionalities.

Linyou Cao - *MoS2 as better and cheaper hydrogen evolution catalyst than Pt*
Guoqing Li¹, Du Zhang², Qiao Qiao³, Yimei Zhu³, Weitao Yang², Linyou Cao¹
¹North Carolina State University, ²Duke University, ³BNL,
Abstract - Developing cost-effective high-performance catalysts for the hydrogen evolution reaction (HER) stands as a key issue for the utilization of hydrogen as a major energy carrier. While Pt may provide the best HER catalysis performance, it is too expensive and rare to be useful for massive production of hydrogen. MoS2 has been widely considered a promising low-cost alternative to Pt, but the catalytic performance of all the MoS2 materials reported to date is way worse than Pt. Here I will show our work on engineering MoS2 to have even better HER catalysis performance than Pt. This includes numerous new fundamental understanding on the HER catalysis of MoS2, including layer-dependence of the catalysis, the catalytic activities of sulfur vacancies, the effect of substrates, and the role of crystallinity. We rationally design the composition and structure as well as substrates of MoS2 following the guidance of the new understanding, and eventually develop MoS2 HER catalysts with an overpotential at 45 meV at 20mA/cm², which is better than that of Pt.

Dan Strongin - *Forum B: Theory and computation focused on the design and understanding of water splitting catalysts*
Abstract - Optimizing catalysts for the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) plays a central role in water splitting chemistry. Forum B uses the theoretical and computational expertise in the CCDM to both guide the design active catalysts and to understand the catalysis of OER and HER on a molecular level. Importantly, the feedback between theory/computation and experiment validates many of the theoretical and computational developments in the CCDM. To illustrate this synergy, this presentation will highlight how the integration of theory, computation, and experiment has led to a new paradigm in the design of water splitting catalysts. It particular, it is shown how this integrated research effort has led to the realization that the confinement of metal ions (active for OER) in the interlayer region of 2D layered materials can promote complex dipolar interactions between the metal cations, water, and 2D material and this can lead to improved OER catalysis.