

ABSTRACTS OF TALKS

Rational Design of Functional Nanomaterials: Theory and Experiment Working in Tandem

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In one or two lectures I will attend to recent efforts in utilizing novel properties of 2D materials for broad applications. The approach falls under the general umbrella of the Materials Genome Initiative (MGI) in which theory, experiments, and simulations work in a feedback loop with information from one used to better the other, taking us closer to our goal of rational material design. One objective is to obtain the descriptors for desirable characteristics of these functional materials for their accelerated discovery, sparing us the costly tradition of trial and error. My focus will be on characteristics of single-layer transition metal dichalcogenides (TMDC) which appear to be promising materials for next generation applications (optoelectronic and catalysis), because of their low-dimensionality and intrinsic direct band-gap which typically lies in the visible spectrum. Several experimental groups have already reported novel electronic and transport properties which place these materials beyond graphene for device applications. MoS₂ is also known to be a leading hydrodesulphurization catalyst. Efforts are underway to further tune these optoelectronic and catalytic properties through alloying, defects, doping, coupling to a substrate, and formation of bilayer stacks (homo- and hetero-structures). The large binding energies of excitons, trion, and biexcitons also suggest important applications. In these lectures, I will focus on possible ways to manipulate the chemical and optical properties of these materials and also on their ultrafast charge dynamics. In terms of chemical properties, I will also provide examples of our work on defect-laden h-BN which appears to be a promising non-metal catalyst for hydrogenation reactions.

Multiscale View of Crystal Structure and Growth: From Lattice Gas Models to Continuum Shapes

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This talk focuses on some fundamental aspects that produce and characterize the structure of surfaces, nanostructures, and macroscopic crystals. We begin with the lattice gas model, discussing its uses and limitations. Next we deal with the various interactions between atoms, which produce superstructures and modify diffusion rates. In addition to the familiar pairwise interactions, there can be trio (three-atom non-pairwise) interactions and even multisite interactions, especially as one tries to model actual rather than “toy” systems. Sophisticated methods may well be needed to obtain optimal fits, as we found for Cu on Cu(110).

Next we discuss how to compute surface and step energies, crucial ingredients in determining the equilibrium crystal shape (ECS) and catalytic enhancements. Stepped surfaces occur in rough orientations of the ECS and have useful properties for growth. In a multiscale perspective, such surfaces can be viewed at the atomic, step-continuum, and full-continuum scales. Step properties can be characterized in terms of basic parameters such as step stiffness and repulsion strength. Analysis and extraction of physical parameters is enhanced by use of a simple formula that applies to a broad range of fluctuating systems. We discuss applications to metallic and semiconductor surfaces. Advances in producing curved crystals promise significant experimental advances.

Time permitting; we will discuss how edge decoration can be used to tune shapes. With kinetic Monte Carlo we have also studied how impurities can alter some effects in growth.

Patterns on Surfaces and Distributions of Size-Related Properties: Applications from Nanoscale to Societal Scales

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Organic molecules can form more intricate structures on surfaces than can atoms. In particular, networks of empty cells can arise. The cells can host small molecules and alter chemical reaction rates. A specially intriguing example is anthracenequinone (AQ) on Cu(111), the close-packed surface. We discuss the electronic underpinnings of this structure and some possible applications. Recent experiments show that on Au(111) find that the overlayer structures are remarkably different; we discuss why this is not unexpected.

On the other hand, molecules on deposited onto surfaces tend to form islands. Small ones decay but islands larger than some critical size are stable. We show how the same distribution used to characterize step spacings also describes these islands and their "capture zones" and complements data concerning the scaling of number of islands vs. deposition flux. Physical experiments and Monte Carlo simulations illustrate this behavior. On a completely different scale, we show how such distributions can be applied to societal situations such the distributions of subway stations in Paris, Tokyo, Mexico City, and Moscow as well as to the areas of secondary administrative units such as counties or districts. However, in a minority of countries, such as the Netherlands and Turkey, a lognormal distribution provides a better fit, because of multiple resizings. (Likewise, vacancy clusters for AQ on Au(111) have this behavior.) Preliminary analysis suggests that Pakistan is also in this group.

Electrically Controlled Surface Magnetism and Energy Savings in Solid State Electronics

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The problems faced by the increasing power density and decreasing device size in semiconductor technologies will be reviewed and an effort is made to motivate why spintronics may lead to energy savings in solid state electronics. The inherent non-volatility of long-range ordered magnetism adds functionality over today's random access memory (RAM) elements. The latter require refresh power during operation and the information is lost when power is lost, not true of the nonvolatile magneto-electric device. Manipulation of magnetically ordered states by electrical means (the magneto-electric effect) is among the most promising approaches towards novel spintronic devices [1-4]. Indeed, voltage control of magnetism is a grand challenge of spintronics. The reasons that magnetoelectric devices lead to energy savings are simple enough: voltage control of a nonvolatile magnetic state virtually eliminates the need for large current densities, the accompanying power consumption, and detrimental Joule heating on writing and potentially also on reading. In this talk, the magneto-electron phenomena is reviewed. Exchange bias is reviewed. The interplay between band structure and boundary polarization has considerable significance in devices that rely on the magneto-electric phenomena and this too is reviewed. Here I discuss the influences, by boundary polarization, in an experimental context. The context for this discussion is that one can then utilize the electrically switchable and nonvolatile boundary magnetization of magneto-electric antiferromagnets, such as chromia, to generate a voltage-controlled exchange field, which determines the carrier spin in the conducting channel or can be used to reverse magnetization or an adjacent ferromagnet. Such devices can actually "beat" silicon technologies in terms of energy cost.

A competitive magnetoelectric device needs to fulfill a minimal set of necessary prerequisites. In the presence of a stationary magnetic field H , the magnetoelectric coercive voltage, or voltage applied to the device, must be small so as to be practical and the product, EH , of electric field, E , and magnetic field, H , must be sufficient to switch the magneto-electric spintronic device on and off. This switching must be achieved with sufficient speed, at least in the range of several GHz, to be competitive with silicon technology. Is this possible? Will it save energy?

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Tutorial on the Fundamentals of Electron Spectroscopies: Photoemission, Inverse Photoemission and X-Ray Absorption

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The basic principles of photoemission and inverse photoemission are discussed, and a brief description of some of the instrumentation that one might use in different regimes. This includes a discussion of work function and examples. The examples included things like characterization of semiconductor to metal contacts, the difference between n-type and p-type semiconductors. Photoemission is also very surface sensitive and surface composition may sometimes be extracted from angle resolved photoemission by exploiting the limited mean free path of the electron. How this is done is reviewed. By extension, the techniques and approaches to this type of quantitative surface analysis will be discussed. Making use of the chemical shift to extract chemical changes at the surface will also be touched upon. Complications from photoelectron diffraction and forward scattering discussed if time is available.

Tutorial on Symmetry and Band Structure: the Experimental Situation Versus Theory

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This is a brief review of the successes of perturbation Hamiltonian quantum mechanics and symmetry. Photoemission can be used to identify initial state symmetries - what are the details of the quantum state you see in photoemission? This is presented in the context of the application of very basic perturbation Hamiltonian quantum mechanics to electron spectroscopies (photoemission, inverse photoemission). Some very basic ways photoemission can be used to identify symmetry are reviewed. There is a side note that state symmetry does show up in other experiments like scanning tunneling microscopy. Examples included ordered molecular overlayers on surfaces. This view of basic quantum is then expanded to include a very, very basic review of band structure, then how it is measured in photoemission electronic structure. The role of symmetry in band structure is also touched upon. Examples of band structure in single crystals, 2D materials like the transition metal dichalcogenides are reviewed and a comparison with theory is made. Time permitting, surface states that differ from the bulk will be discussed and some description of their origin.

Rational Design Methodology Applied to the Oxygen-Reduction Reaction in Hydrogen Fuel Cells: Insights from Density Functional Theory

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Designing cost-effective, highly active and thermodynamically as well as electro-chemically stable electro-catalysts for the oxygen reduction reaction (ORR) on hydrogen fuel cell cathodes is of great importance to address the pressing need of renewable and sustainable energy resources. This talk focuses on the rational design of such electro-catalysts and how the latter is supported by Density-Functional-Theory (DFT) computations. I will discuss the key factors determining the thermodynamic/electrochemical stability and catalytic activity of tailored catalysts such as single or double overlayers on suitable substrates. The rational selection of overlayers and substrates requires understanding the link between four aspects: *composition, electronic structure, binding energies of the ORR intermediates and activity toward ORR*. DFT calculations are by excellence a means to analyze these four aspects but it is up to us to understand their correlation. From our point of view, the least known link in the above chained dependence is the relation between *electronic structure* and *binding energy*. A number of models rationalizing that link (*d*-band center model, linear scaling between binding energies of different ORR intermediates, relation between surface strain and its reactivity) have been proved to be insufficiently accurate to predict surface reactivity. Moreover, the electrochemical and thermodynamic stability of the tailored structures strongly depend on their electronic structure. In this chapter, based on the wealth of information available from two decades of research, we will discuss the paths to design cost-effective, highly active and thermodynamically as well as electro-chemically stable ORR electro-catalysts. Our rational design approach to find them is implemented in the following manner: (a) using the existing knowledge on the mentioned-above relations to preselect promising candidates for the ORR catalysts (a dozen, not hundreds or thousands); (b) performing DFT calculations to confirm and quantify the properties in question (in particular, thermodynamic and electrochemical stability and activity toward ORR) and narrow down the selection; (c) testing experimentally the systems found to be most promising in steps (a) and (b). I will use our recent results to illustrate the efficacy of this approach.

Fully Relativistic Density-Functional-Theory Calculations Applied to Investigate how Symmetry Constraints and the Spin-Orbit Coupling Shape the Electronic Structure of Bi(111)

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The remarkable electronic properties of Bi and its Bi(111) surface are tightly related to (1) its crystal structure – the so-called A7 or α As structure – and (2) the strong spin-orbit coupling energy shift even its valence electronic states undergo because of bismuth's large atomic mass number. In order to capture how the spin-orbit coupling shapes Bi and Bi(111) electronic properties, fully relativistic density-functional-theory calculations are in order. I will show that the calculated electronic band-structure of a ~15-nm (111) film satisfactorily reproduce three independent measurements obtained for macroscopic samples. Our results (1) confirm the existence of surface states within the spin-orbit-coupling-induced gaps that lie *inside* the valence band, and (2) indicate that the two split surface-state metallic branches along the ΓM direction do not overlap with the bulk band at the Brillouin zone boundary but lie within the conduction-valence band gap (which is induced by the A7-distortion of bulk Bi with respect to a simple cubic structure). I will show that (1) neither the existence of the metallic surface states nor their observed splitting is related to inversion *asymmetry* and (2) the spin texture observed in such states cannot be attached to the lifting of the Kramers degeneracy. Thus, such splitting is not of the Rashba-type. I will hence provide grounds to identify the large splitting of the metallic branches as a “ $m_j = \pm 1/2$ – $m_j = \pm 3/2$ splitting”, as expected from the strong spin-orbit coupling. Moreover, I will show that the degeneracy at the M -point of the SBZ of Bi(111) – implied by the translational symmetry of the surface (which is apparently not satisfied under the assumption that the two split metallic branches are two singlets of opposite magnetic quantum number) – is satisfied irrespectively of the presence of inversion symmetry centers, even if not detectable by measurements. I will also show that the apparent magnetic-moment discontinuity at the M point – also implied by the assumption that the translational symmetry is not satisfied – does not exist, which also explain why the measured spin-polarization of the metallic branches vanishes near M . Furthermore, I will present the Rashba-splitting on the band structure of Bi(111) due to three different types of structural/electronic perturbations to reveal the actual lifting of the Kramers degeneracy. Finally, I will discuss that depending on the magnitude of the perturbation imposed on a film, the magnitude of the splitting and the localization of the Rashba-split states may change dramatically.

Functional Characterization Toolbox for Nanoscale Systems

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Nanoscale systems drive a substantial number of processes for renewable energies. Understanding these processes requires probing the local behavior of complex systems - such as heterogeneous catalysts, active layers of photovoltaic materials or the deconstruction of plant cell walls for biofuel productions. This can be challenging with standard analytical methods as they lack sensitivity and spatial resolution. For direct measurements revealing the interplay between morphology, composition and functionality of the material, it is critical to develop tools capable of detecting more than the morphology of the materials surface. In addition, the dynamic nature of some of the reactions taking place in the systems implies that the functional information should be collected over time.

Here, we will discuss the state-of-the-art developments of nanoscale functional imaging based on Atomic Force Microscopy. We will introduce the premises of the technique, and how it is adapted to study mechanical and electrical properties locally. We will also present recent advances in the field, making it possible to achieve infrared spectroscopy with nanoscale lateral resolution.

To illustrate the capabilities of the techniques presented, we will present some applications based on the study energy-related systems including 2D materials for optoelectronics, hybrid 2D material for catalytic reactions and the effect of catalytic reaction in biofuel production. We show how a combination of several techniques is required to draw connections between the local fundamental properties of the materials and their performance in large scale devices.

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Predictive Modeling of Metal-Organic Chain with Active Metal Site

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Creation, stabilization, characterization and control of single atom transition metal (TM) sites may lead to significant advancement of the next-generation catalyst. We have performed density functional theory based calculations of TM-dipyridyltetrazine (DT) chains in which TM atoms are stabilized and separated by the DT molecules. Our calculations show that the formation energies of the chains are high (~ 2.0 to 7.9 eV), suggesting that these chains can be synthesized and stabilized. We investigated the oxidation state of these metal centers using core level shift and compared the results with the reported XPS data. Mo and Cr has an oxidation state +6, Fe shows +3 oxidation state, while Pt and V shows +2 oxidation state. Moreover, by calculating the adsorption energies of CO, O₂ and O atom on the metal atom sites of the chains we found that these molecules/atoms strongly bond to TM atoms Mo, Cr, Fe, V and Co occupying these sites, suggesting that these TM-DT chains are potential candidates for CO oxidation catalyst. The adsorption energies of CO and O₂ on these metal centers ranges from 1.0 to 4.0 eV. The O₂ molecule undergoes dissociation while adsorption on V center and causes strong distortion to V-DT chain. Our adsorption barrier calculations show that CO and O₂ spontaneously adsorb having no adsorption barrier on these metal centers.

Two Dimensional Transition Metal Dichalcogenides and their Heterostructures

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Structural, electronic, and optical properties of out-of-plane and in-plane heterostructures of transition metal dichalcogenides (MX_2 ($\text{M}=\text{Mo}, \text{W}$, $\text{X}=\text{S}, \text{Se}, \text{Te}$)) are investigated by (hybrid) first principles calculations. The out-of-plane heterostructures are found to be indirect band gap semi-conductors with type-II band alignment. Direct band gaps can be achieved by moderate tensile strain in specific cases. The excitonic peaks show blue shifts as compared to the parent monolayer systems, whereas redshifts occur when the chalcogen atoms are exchanged along the series S-Se-Te. Strong absorption from infrared to visible light can be achieved. Furthermore, the stability of the systems under study is confirmed by performing phonon spectrum calculations.

Towards Understanding CO₂ Hydrogenation on Defect-Laden Hexagonal Boron Nitride*

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Employing density functional theory (DFT) with the inclusion of van der Waals interaction, we have studied the elementary steps in CO₂ hydrogenation on defect-laden single layer hexagonal boron nitride (dh-BN) [with N vacancy (V_N) or N substitution by B (B_N)]. We first examine the adsorption properties of small molecules (H₂, CO₂, CO, HCOOH) on both types of dh-BN to find that, except for H₂, the molecules chemisorb molecularly. The adsorption energy, optimized geometry, and the electron density distribution provide detailed microscopic information about the chemisorption characteristics of the latter three molecules. We find that CO and CO₂ adsorb more strongly on dh-BN with V_N defect than on that with B_N . On the basis of the energetic profile, showing the downhill potential energy for the overall reaction, we conclude that dh-BN with V_N offer good catalytic activity towards the CO₂ hydrogenation to yield formic acid (HCOOH) as the intermediate specie, which undergoes decomposition to form CO and H₂O. Efforts are underway to corroborate these findings with experimental data from Blair and Tetard laboratories.