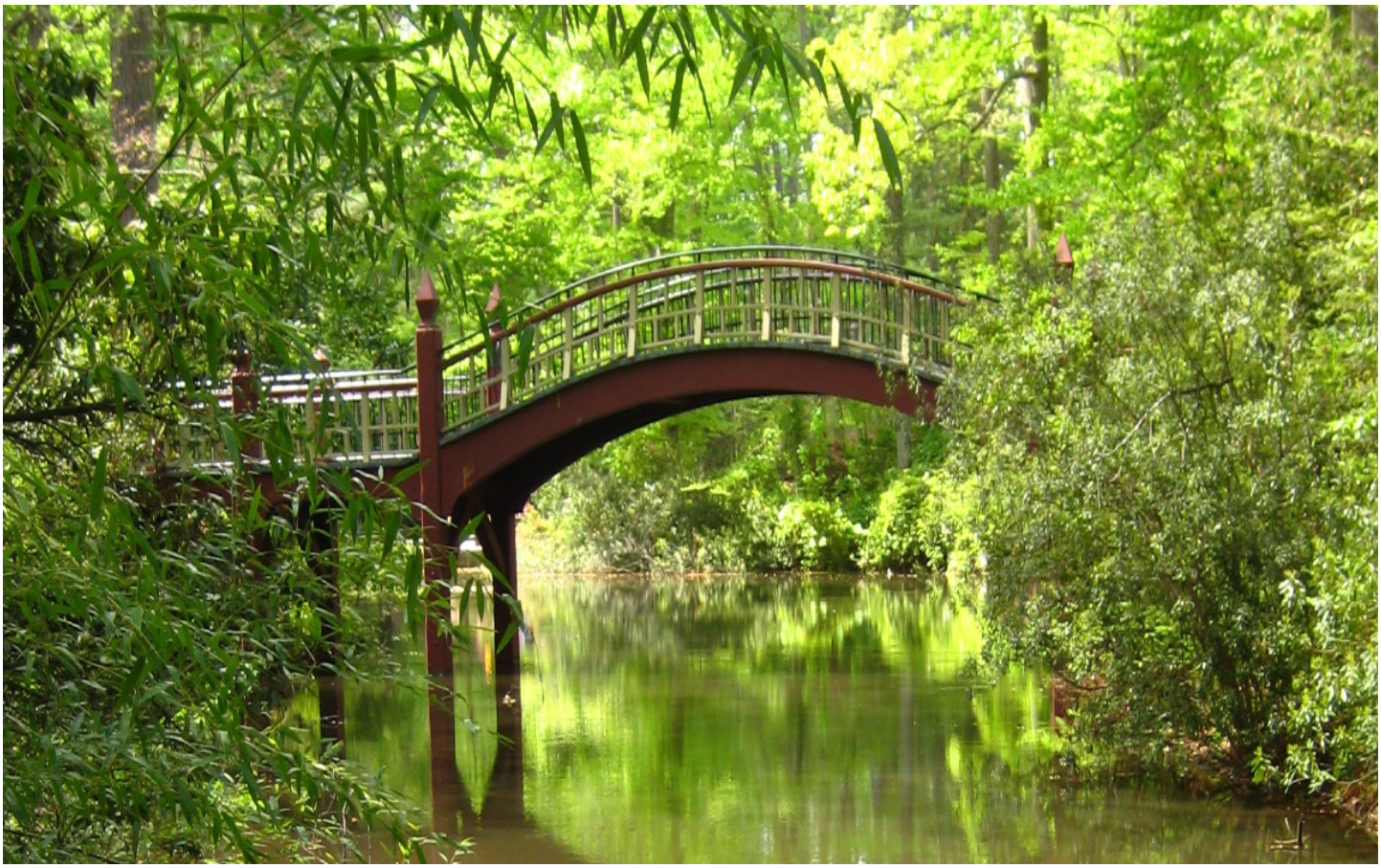
ES2013: The 25th Annual Workshop on Recent Developments in Electronic Structure Methods

June 11-14, 2013

College of William and Mary
Williamsburg, VA 23187, USA



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ES2013: The 25th Annual Workshop on Recent Developments in Electronic Structure Methods

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25th Annual Workshop on Recent Developments in Electronic Structure Methods (ES2013)
College of William & Mary
Williamsburg, Virginia
June 11-14, 2013

Schedule of Events

Tuesday, June 11

3:00 PM	7:00 PM	DORM CHECK-IN and REGISTRATION (Dupont Hall)
6:00 PM	8:00 PM	RECEPTION (Dupont Hall)

Wednesday, June 12

8:00 AM	8:50 AM	REGISTRATION - CONTINENTAL BREAKFAST (Miller Hall, Brinkley room)
8:50 AM	9:00 AM	OPENING REMARKS: **Dennis Manos**, Vice Provost for Research and Graduate/Professional Studies

SCIENTIFIC PROGRAM (Miller Hall, Brinkley room)

GW and Beyond / Session Chair: David Ceperley		
9:00 AM	9:35 AM	**Steven Louie**, *Electronic Excitations in Solids and Nanostructures: GW, GW-BSE, and Beyond*
9:35 AM	10:10 AM	**Brian Kolb**, *The Bandgap of Pyrite: Bandgap Oscillations on an Ultrafast Timescale*
10:10 AM	10:40 AM	COFFEE BREAK
Comples Oxides / Session Chair: Mei-Yin Chou		
10:40 AM	11:15 AM	**Chris van de Walle**, *Complex Oxide Interfaces*
11:15 AM	11:50 AM	**Nicole Benedek**, *Exploring the Structure and Properties of Complex Oxides: New Ideas and Insights from Theory and Simulation*
11:50 AM	1:10 PM	LUNCH (Miller Hall, Brinkley room)
New Methods / Session Chair: Stefano Baroni		
1:10 PM	1:45 PM	**Roberto Car**, *Correlated electron calculations with Hartree-Fock scaling*
1:45 PM	2:20 PM	**Jiawang Hong**, *Beyond Piezoelectrics: First-Principles Theory and Calculation of Flexoelectricity*
2:20 PM	3:50 PM	POSTER SESSION I - COFFEE (Miller Hall, Brinkley room)
Quantum Monte Carlo / Session Chair: Jeongnim Kim		
3:50 PM	4:25 PM	**Cyrus Umrigar**, *Semistochastic Quantum Monte Carlo -- A Hybrid of Exact Diagonalization and QMC Methods*
4:25 PM	5:00 PM	**Saverio Moroni**, *Forces and Response Functions in QMC*
6:30 PM	7:00 PM	COCKTAILS (Sadler Center, Tidewater A&B)
7:00 PM	9:30 PM	CONFERENCE BANQUET (Sadler Center, Tidewater A&B)

Thursday, June 13

8:00 AM	9:00 AM	REGISTRATION - CONTINENTAL BREAKFAST (Miller Hall)

SCIENTIFIC PROGRAM (Miller Hall, Brinkley room)

Topological Insulators / Session Chair: Enrico Rossi		
9:00 AM	9:35 AM	**Ruqian Wu**, *Generating Topological Insulator Gap in Graphene with Heavy Adatoms*
9:35 AM	10:10 AM	**Kevin Garrity**, *Heavy Adatoms on Magnetic Surfaces: A Search for Chern Insulators*
10:10 AM	10:40 AM	COFFEE BREAK
Many-body / Session Chair: Andrew Rappe		
10:40 AM	11:15 AM	**Markus Holzmann**, *Momentum Distribution and Effective Mass of Jellium and Simple Metals*
11:15 AM	11:50 AM	**Abhijit Mehta**, *Zigzag Phase Transition in Quantum Wires*
11:50 AM	1:20 PM	LUNCH (Miller Hall, Brinkley room)
Strong Correlation / Session Chair: Paul Kent		
1:20 PM	1:55 PM	**Sandro Sorella**, *Spin Liquid Phases in Strongly Correlated Lattice Models*
1:55 PM	2:30 PM	**Emanuel Gull**, *Energetics of Superconductivity in the Two Dimensional Hubbard Model*
2:30 PM	4:00 PM	POSTER SESSION II - COFFEE (Miller Hall, Brinkley room)
DMFT, Fe Pnictides / Session Chair: David Vanderbilt		
4:00 PM	4:35 PM	**Zhiping Yin**, *DFT+DMFT to Correlated Electronic Structures: Recent Developments and Applications to Iron-based Superconductors*
4:35 PM	5:10 PM	**Michele Casula**, *Dynamical Screening Effects from First Principles: Implications for Low-Energy Models and Application to the Iron Pnictides*
6:30 PM	9:00 PM	DINNER (Miller Hall)

Friday, June 14

8:00 AM	9:00 AM	CONTINENTAL BREAKFAST (Sadler Center, Tidewater A&B)

SCIENTIFIC PROGRAM (Sadler Center, Tidewater A&B)

9:00 AM	9:15 AM	**Poster Awards**
Large scale / Session Chair: Jerry Bernholc		
9:15 AM	9:50 AM	**Ravishankar Sundararaman**, *Nonlocal Polarizable Continuum Models from Joint Density-Functional Theory*
9:50 AM	10:25 AM	**Emil Briggs**, *Electronic Structure Calculations on Thousands of CPUs and GPUs*
10:25 AM	10:50 AM	COFFEE BREAK
Materials Design / Session Chair: Natalie Holzwarth		
10:50 AM	11:25 AM	**Xingao Gong**, *Computational Design of Multinary Alloys for Solar Energy Absorber*
11:25 AM	12:00 PM	**Stefano Curtarolo**, *The Quest for Descriptors in High-Throughput Searches: Thermoelectrics and Topological Insulators*
12:00 PM	12:10 PM	*Closing Remarks*
12:10 PM	1:10 PM	LUNCH (Sadler Center, Tidewater A&B)

END

Invited Talk Abstracts

(in alphabetical order of speaker last name)

Exploring the Structures and Properties of Complex Oxides: New Ideas and Insights from Theory and Simulation

Nicole A. Benedek

Materials Science and Engineering Program, The University of Texas at Austin

Austin, Texas, USA

Perovskite oxides are perhaps the most widely studied and technologically important of all the ABO_3 phases. The remarkable versatility of the perovskite structure (the A and B site can accommodate nearly every element of the periodic table) leads to a huge range of properties, including (but not limited to) ferroelectricity, ferromagnetism and colossal magnetoresistance, piezoelectricity, multiferroicity and metal-insulator transitions. One reason for this is that nearly all cubic perovskites are unstable to energy-lowering structural distortions and hence typically have rich structural phase diagrams. The most common distortions are those that give rise to ferroelectricity (usually an off-centering of the B-site cation) and tilts or rotations of the BO_6 octahedra. We have explored the interaction between these distortions in perovskites using symmetry principles, crystal chemistry arguments and first-principles calculations. Our results revealed some counter-intuitive surprises, including that rotations by themselves do not generally suppress ferroelectricity in perovskites, as is commonly assumed. I will discuss how the knowledge and new insights gained in the course of our investigations can be used to search for and design new functional materials.

Electronic Structure Calculations on Thousands of CPUs and GPUs

J. Bernholc, W. Lu, M. Hodak and Emil Briggs

Department of Physics, North Carolina State University
Raleigh, NC, USA

The latest generation of supercomputers is capable of multi-petaflop peak performance. These results are achieved by using thousands of multi-core CPU's, often coupled with thousands of GPU accelerators. However, efficient utilization of this computing power for electronic structure calculations presents significant challenges. Previous parallelization schemes based on one MPI process per CPU core have worked well on prior generations of supercomputers, but current state-of-the-art machines typically have hundreds of thousands of CPU cores distributed over thousands of network nodes. Using one MPI process per core in these situations leads to an unacceptably large performance degradation and also affects scalability.

We describe an alternative parallelization strategy adopted in the Real-Space Multigrid (RMG) code, which dramatically improves scalability and performance. Specifically, we employ a hybrid approach with one MPI process per node, rather than per core, and achieve intra-node parallelization by using POSIX threads and OpenMP. The advantages of this approach are: (i) the number of MPI processes is reduced by an order of magnitude, and (ii) shared memory is used within a node, dramatically reducing the ratio of communication to computation.

Turning to supercomputers with GPU accelerators, a large fraction of their peak performance is usually provided by the accelerators. However, adapting a code originally designed for CPU's to GPU accelerators is not always straightforward. GPU's perform well on vector-type operations, but they have much lower scalar performance than CPU's and a markedly different programming model. Furthermore, the current generation of accelerators utilizes a separate memory space and data transfer between the CPU and GPU memories is costly.

In our case, optimizing RMG for GPU utilization required significant restructuring of code. When combined with our MPI/Posix threads/OpenMP parallelization, we have obtained large performance increases and excellent scalability to over 100,000 CPU cores on the Cray XE6, as well as more than threefold performance improvement on the Cray XK7 system, in which the XE6 nodes with two multi-core CPUs are replaced with XK7 (CPU-GPU) nodes.

Correlated electron calculations with Hartree-Fock scaling*

Roberto Car, Princeton University, USA

Due to its simplicity and numerical efficiency, density functional theory (DFT) is the most popular approach for calculating the electronic structure of large molecules and materials. Nevertheless, the accuracy of DFT is not always satisfactory and the search for improved approximations that avoid self-interaction and capture strong electron correlations faces severe difficulties. In this talk I will present an alternative approach in which the one- and two-particle density matrices needed to compute the ground-state energy, are explicit functionals of the natural spin orbital states and their joint occupation probabilities. The scheme is parameter-free and not affected by self-interaction error. In its simplest formulation, restricted to the seniority zero sector of the many-particle Hilbert space, it has the same scaling of Hartree-Fock theory. Yet, it describes strong correlations as demonstrated by the calculated dissociation energy curves of diatomic molecules and linear chains of hydrogen atoms. Improved approximations with a higher polynomial cost but not restricted to seniority zero will be discussed.

(*) Work in collaboration with Ralph Gebauer (ICTP, Trieste, Italy) and Morrel H. Cohen (Rutgers and Princeton University)

Dynamical screening effects from first principles: implications for low-energy models and application to the iron pnictides

Michele Casula*, Ph. Werner, F. Aryasetiawan, T. Miyake, L. Vaugier, A. Rubtsov, A. J. Millis, and S. Biermann

*CNRS and Institut de Minéralogie et de Physique des Milieux Condensés, Université Pierre et Marie Curie

Paris, France

The discovery, in 2008, of superconductivity above 50K in the iron pnictides has opened a new playground in condensed matter physics. The theoretical description of their electronic properties, even in the normal phase, poses a challenge to theory, emphasizing the need of determining many-body models entirely from first principles. A proper ab-initio derivation of low-energy correlated Hamiltonians, based on the constrained RPA method, produces a frequency dependent Coulomb interaction U, as it is dynamically screened by the higher-energy degrees of freedom. We present new methods to include these screening effects in an extended dynamical mean field theory (DMFT) framework[1,2]. We demonstrate that the frequency dependence of U brings in additional features, such as the correlation satellites seen in photoemission spectroscopy together with a renormalization of the low-energy properties[3]. Our first application of the dynamically screened U to the iron pnictides indicates that $BaFe_2As_2$ is a strongly correlated compound with strongly doping- and temperature-dependent properties. In the hole-overdoped region an incoherent metal is found, whereas Fermi-liquid behaviour is recovered in the undoped compound[4]. In the intermediate-doping regime, a fractional power-law behavior of the self energy is observed for the first time in a realistic modelization of materials. The resulting spectral function is in an overall agreement with the most recent ARPES data, and provides a theoretical support to their interpretation.

[1] Ph. Werner, and A. J. Millis, Phys. Rev. Lett. **104**, 146401 (2010).

[2] M. Casula, A. Rubtsov, S. Biermann, Phys. Rev. B **85**, 035115 (2012).

[3] M. Casula, Ph. Werner, L. Vaugier, F. Aryasetiawan, T. Miyake, A. J. Millis, S. Biermann, Phys. Rev. Lett. **109**, 126408 (2012).

[4] Ph. Werner, M. Casula, T. Miyake, F. Aryasetiawan, A. J. Millis, and S. Biermann, Nature Physics **8**, 331 (2012).

The quest for descriptors in high-throughput searches: thermoelectrics and topological insulators

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High-throughput computational materials design is an emerging area of materials science [1]. By combining advanced thermodynamic and electronic-structure methods with intelligent data mining and database construction, and exploiting the power of current supercomputer architectures, scientists generate, manage and analyze enormous data repositories for the discovery of novel materials [2].
The key for discovering new materials is the availability of descriptors. These are physically sound empirical quantities, not necessarily observables, connecting the calculated microscopic parameters to macroscopic properties of the materials. In other words, the descriptor is the language with which the researcher speaks to the database, the heart of any effective HT implementation.
In this talk **(i)** we provide a current snapshot of this rapidly evolving field (e.g. catalysis [3], thermodynamics [4], battery materials [5], thermoelectricity [6,7], topological insulators [8], photovoltaics [9], water splitting [10,11], nuclear detection [12], nuclear detection, and so on), **(ii)** we highlight the challenges and opportunities that lie ahead, and **(iii)** we illustrate the needs and goals of the communities involved: open and free repositories with widely accepted standards [13].

[1] Nature Mater, **12**, 191 (2013). [2] http://aflowlib.org - http://materialsproject.org [3] Nature Mater. **5**, 909 (2006). [4] Comp. Mat. Sci. **58**, 227 (2012). [5] Mater. Res. Soc. Bull. **35**, 693 (2010). [6] Phys. Rev. X **1**, 021012 (2011). [7] Carrete, Li, Mingo, Wang, Curtarolo, "*Finding unprecedentedly low thermal conductivity compounds via HT materials modeling*", (2013). [8] Nature Materials **11**(7), 614 (2012). [9] Phys. Rev. Lett. **108**, 068701 (2012). [10] Energy Environ. Sci. **5**, 5814 (2012). [11] Energy Environ. Sci. **6**, 157 (2013). [12] ACS Comb. Sci. **13**, 382 (2011). [13] "*Fuelling discovery by sharing*", Nature Mater. **12**, 173 (2013).

Chern insulators from heavy atoms on magnetic substrates

Kevin F. Garrity and David Vanerbilt

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Piscataway, NJ, USA

Since the work of Haldane[1] twenty-five years ago, it has been known that two-dimensional insulating systems with spontaneously-broken time reversal symmetry and spin-orbit coupling can have non-zero Chern numbers. Recently, there has been a renewed theoretical and experimental interest in finding an experimentally realizable example of such a Chern insulator, which would display much of the physics of the Quantum Hall effect without requiring large magnetic fields or low temperatures. We propose a new strategy for constructing Chern insulators, which consists of depositing atomic layers of elements with large spin-orbit coupling (e.g., Bi) on the surface of a magnetic insulator. We argue that such systems will typically have isolated surface bands with non-zero Chern numbers. If these overlap in energy, a metallic surface with large anomalous Hall conductivity (AHC) will result; if not, a Chern-insulator state will typically occur. Thus, our search strategy reduces to looking for examples having the Fermi level in a global gap extending across the entire Brillouin zone. We verify this search strategy and identify several candidate systems by using first-principles calculations to compute the Chern number and AHC of a large number of such systems on MnTe, MnSe, and EuS surfaces. Our search reveals several promising Chern insulators with gaps of up to 140 meV.

[1] F.D.M. Haldane, Phys. Rev. Lett. **61**, 2015 (1988).

Computational Design of Multinary Alloys for Solar Energy Absorber

X. G. Gong
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Shanghai,200433, China

Cu_2ZnSnS_4 is one of the most promising absorber materials for thin-film solar cells, since it is a low-cost material with the optimal band gap 1.5 eV for single-junction solar cells and a high adsorption coefficient. Although the synthesize of such compound could be almost 50 years, due to the complicity of quaternary compound, the properties are not well understood, which are crucial for improving the solar cell performance.

In this talk, I will show that Cu_2ZnSnS_4 can be derived from the binary zinc-blende semiconductor through sequential cation cross-substitution, and present our theoretical investigation on the structural and electronic properties evolution from the binary, to ternary and to quaternary chalcogenide compounds. We found that the low energy crystal structure obeys the octet rule, and predicted the ground state structure of Cu_2ZnSnS_4 to be kesterite. The dominant defect in CZTS will be *p*-type Cu_{Zn} antisite, which has an acceptor level deeper than the Cu vacancy. We proposed that $Cu_{Zn}+Sn_{Zn}$ and $2Cu_{Zn}+Sn_{Zn}$ defect complex could be detrimental to efficiency, with a small Voc. I will show that Si_3AlP, which can be derived from Si with AlP, is another possible new solar energy absorber. As an example, I will also present the results of direct gap Si obtained by the inverse design.

This work is closely collaborated with S.Y. Chen, Hongjun Xiang, A. Walsh and S.H. Wei

Energetics of Superconductivity in the Two Dimensional Hubbard Model

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Recently developed numerical methods have enabled the explicit construction of the superconducting state of the Hubbard model of strongly correlated electrons in parameter regimes where the model also exhibits a pseudogap and a Mott insulating phase. $d_{x^2-y^2}$ symmetry superconductivity is found to occur in proximity to the Mott insulator, but separated from it by a pseudogapped nonsuperconducting phase. The superconducting transition temperature and order parameter amplitude are found to be maximal at the onset of the normal-state pseudogap. The emergence of superconductivity from the normal state pseudogap leads to a decrease in the excitation gap. All of these features are consistent with the observed behavior of the copper-oxide superconductors.

Momentum Distribution and Effective Mass of Jellium and Simple Metals

Markus Holzmann

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I will present results of Quantum Monte Carlo calculations of the simplest spectral properties of metals: momentum distribution and effective mass. Since QMC calculations are limited to rather small system sizes, extrapolation to the thermodynamic limit remains one of the major obstacles. I will discuss strategies how to improve convergency in certain cases and compare theoretical results for the momentum distribution to experimental measurements on crystaline sodium.

Beyond Piezoelectrics: First-Principles Theory and Calculation of Flexoelectricity

Jiawang Hong, and David Vanderbilt

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Flexoelectricity, which is the linear response of polarization to a strain gradient, can have a significant effect on the functional properties of dielectric nanostructures. Despite growing experimental interest, there have been relatively few theoretical studies of flexoelectricity, especially in the context of first-principles calculations. Previous theories have tended to focus either on the lattice or the electronic contribution, and have involved some approximations or limitations. Here we develop a general and unified first-principles theory of the piezoelectric and flexoelectric tensors, formulated in such a way that the tensor elements can be computed directly in the context of density-functional calculations. We demonstrate a supercell method for calculating the flexoelectric coefficients using first-principles methods, including lattice and electronic contributions. In order to obtain the longitudinal elements of the flexoelectric tensor, we carry out calculations on supercells extended along different orientations, taking special care to carry out conversions between objects calculated under fixed $\mathcal{E}$ or fixed D electric boundary conditions in different parts of the procedure. In this way, the longitudinal elements of both the electronic and lattice contributions to the flexoelectric tensor are determined.

The bandgap of pyrite: Bandgap oscillations on an ultrafast timescale

Brian Kolb and Alexie Kolpak

Department of Mechanical Engineering, Massachusetts Institute of Technology

Cambridge, MA, USA

Iron pyrite (fool's gold) has attracted attention as a potential solar cell material because of its good bandgap, high absorption, low cost, abundance, and environmentally benign components. Despite its high promise, photoelectrochemical cells made from pyrite typically exhibit poor performance. Although much work has been undertaken to understand the properties of pyrite, little attention has been paid to its dynamical properties. The conduction band minimum of pyrite is comprised of sulphur p σ^* anti-bonding orbitals so its energy depends critically on the sulphur-sulphur distance. As there are a number of phonon modes that dynamically change this distance, the bandgap of pyrite is a dynamical quantity. In particular, there is a mode at 347 cm^{-1} that consists of sulphur atoms oscillating with respect to one another. This sets up bandgap oscillations on a 100 fs timescale. The magnitude of these oscillations is temperature dependent but they can be extremely wide, taking the material from a near metal to a wide bandgap semiconductor with even a modest change in the sulphur-sulphur distance. In this work, we use fully self-consistent GW calculations to elucidate the band structure of pyrite and to track its changes upon excitation of phonons in the material.

Electronic excitations in solids and nanostructures: GW, GW-BSE, and beyond

Steven G. Louie

Department of Physics, University of California at Berkeley, and Materials Sciences Division, Lawrence Berkeley National Laboratory

In this talk, we discuss some recent progress in the use of the GW approach and its extensions to electronic excitations and related spectroscopic properties of materials and nanostructures. Inclusion of electron-hole interactions allows further *ab initio* study of optical properties. Several topics are discussed. We present results on excitonic effects in the optical spectra of graphene, in the form of a strong resonant exciton, and show how the prominent exciton features are altered by carrier doping and quasiparticle lifetime. We describe how calculations of electronic multiplet splittings are possible within the GW approximation. Finally, we show that the *ab initio* GW approximation overestimates the quasiparticle-satellite separation significantly in photoemission spectra and falsely predicts a plasmaron excitation. By including significant vertex corrections via the *ab initio* GW+cumulant approach, we demonstrate that the plasmon satellites may be accurately computed, explaining recent angle-resolved photoemission measurements, e.g., on graphene. Comparisons with experiments for all three cases are presented.

Quasi-1D Electron Gas: Zigzag Phase Transition in Quantum Wires and Localization in Constrictions

Abhijit C. Mehta

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The interplay between interactions, reduced dimensionality, and inhomogeneity drives a rich variety of phenomena in mesoscopic physics. We use quantum Monte Carlo (QMC) methods to study two situations where these themes play an important role—the quantum phase transition from a linear one-dimensional (1D) electron system to a quasi-1D zigzag arrangement, and electron localization in quantum point contacts (QPC's).

I will discuss the quantum phase transition of interacting electrons in quantum wires from a 1D linear configuration to a quasi-1D zigzag arrangement. As the density increases from its lowest values, first, the electrons form a linear Wigner crystal; then, the symmetry about the axis of the wire is broken as the electrons order in a quasi-1D zigzag phase; and, finally, the electrons form a disordered liquid-like phase. We show that the linear to zigzag phase transition is not destroyed by the strong quantum fluctuations present in narrow wires; it has characteristics which are qualitatively different from the classical transition.[1]

Second, I will discuss electron localization in QPC's. We show that electrons form a Wigner crystal in a 1D constriction.[2] For sharp constriction potentials, the localized electrons are separated from the leads by a gap in the density, while for smoother potentials, the Wigner crystal is smoothly connected to the leads. Isolated bound states can also form in smooth constrictions if they are sufficiently long. We thus show that localization can occur in QPC's for a variety of potential shapes and at a variety of electron densities, which is consistent with experimental evidence for bound states in QPC's.[3]

[1] Abhijit C. Mehta, C. J. Umrigar, Julia S. Meyer, and Harold U. Baranger. to be published in Phys. Rev. Lett. (2013). arXiv:1302.5429

[2] A. D. Güçlü, C. J. Umrigar, Hong Jiang, and Harold U. Baranger, Phys. Rev. B **80**, 201302(R) (2009).

[3] Abhijit C. Mehta, A.D. Güçlü, C.J. Umrigar, H.U. Baranger, unpublished

Forces and Response Functions in QMC

Saverio Moroni

International School for Advanced Studies and Democritos IOM-CNR
Trieste, Italy

We will discuss two different subjects, physically related but very far from each other in terms of technical development in quantum Monte Carlo (QMC).

One is a Nudged Elastic Band (NEB) calculation of minimum energy paths for a few chemical reactions between small molecules –a structural optimization problem which is carried out using QMC forces. It is aimed at showing that routine use of forces is becoming feasible in QMC. Interestingly, the accuracy on the transition states' geometries and energies is much better than using DFT with GGA functionals (adopted in the vast majority of NEB calculations for catalysis problems), and even slightly better than using DFT with highly parameterized hybrid functionals (which include the studied reactions in their learning data sets).

The other one, a more explorative effort, is an attempt at exploiting imaginary-time correlation functions for spectral properties of Fermions. We will show (i) an example in liquid 3He where the nodal constraint used in QMC to avoid the sign problem can be in part relaxed to good effect, and (ii) an assessment of accuracy for the imaginary time evolution for the jellium model, obtained by Auxiliary Field Monte Carlo in the phaseless approximation.

Spin liquid phases in strongly correlated lattice models

Sandro Sorella[1,2,3]

1 SISSA – International School for Advanced Studies, Via Bonomea 265, 34136 Trieste, Italy,
2 Democritos Simulation Center, CNR – IOM Instituto Officina dei Materiali, 34151 Trieste, Italy,
3 Computational Materials Science Research Team, RIKEN AICS, Kobe, Hyogo 650-0047, Japan

In the last few years an enormous progress in computer performances and a significative advance in computational techniques are opening a new frontier for the solution of fundamental problems in the physics of strongly correlated systems, that has been lacking for too many decades. We report recent calculations for the Hubbard model on the honeycomb lattice at half filling, for cluster sizes containing up to 2500 sites, much larger than previous simulations[1], ruling out possible spin liquid phases. We instead show that in a spin model with frustrating interactions a gapless spin liquid phase naturally emerges as the variational ansatz is systematically improved by means of few Lanczos steps[2].

[1] S. Sorella, Y. Otsuka and S. Yunoki, Nature, Scientific Reports Scientific Reports **2**, 992 (2012) doi:10.1038/srep00992.

[2] W. Hu, F. Becca, A. Parola and S. Sorella, arXiv:1304.2630 (2013).

Nonlocal polarizable continuum models from joint density-functional theory

Ravishankar Sundararaman, Kendra Letchworth-Weaver, Deniz Gunceler, Kathleen Schwarz and T.A. Arias

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Ithaca, NY 14853, USA

Ab initio calculations provide useful insights into the structure of matter and processes at the atomic scale. Delivering these benefits to the study of surface structures and reactions in solution is complicated by the need for thermodynamic phase-space sampling of the liquid environment. Continuum solvation models avoid the prohibitive cost of molecular dynamics methods and efficiently treat solvent effects, but typically at the price of empiricism.

Joint density functional theory (JDFT) provides a rigorous, in-principle exact framework for combining classical density functional theories of liquids with electronic density functional theory for a subsystem of interest. We briefly review practical approximations to JDFT that occupy the middle ground between molecular dynamics and traditional continuum solvation models, in rigor as well as in computational efficiency. We then derive a solvation model as a limit of JDFT, which includes nonlocal solvent response and matches the accuracy and efficiency of traditional polarizable continuum models without the empiricism. Finally, we demonstrate the capability of this theory to study chemistry in solution with a model electrochemical system.

Semistochastic Quantum Monte Carlo – A hybrid of of Exact Diagonalization and QMC methods

Cyrus J. Umrigar

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, NY 14853

This talk will provide a pedagogic and unified overview of various zero-temperature QMC methods, discuss their advantages and disadvantages, and the nature of the infamous "Sign Problem". Then the recently developed Semistochastic Quantum Monte Carlo method [1], which combines some of the advantages of Exact Diagonalization with those of the FCIQMC [2, 3] method will be discussed.

References

[1] F. R. Petruzielo, A. A. Holmes, Hitesh J. Changlani, M. P. Nightingale and C. J. Umrigar, Phys. Rev. Lett., **109**, 230201, (2012).

[2] George H Booth, Alex Thom and Ali Alavi, J. Chem. Phys., **131**, 054106 (2009).

[3] Deidre Cleland, George H Booth, and Ali Alavi, J. Chem. Phys., **132**, 041103 (2010).

Complex oxide interfaces

Chris G. Van de Walle

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The formation of a two-dimensional electron gas (2DEG) at the interface between two insulators, $SrTiO_3$ (STO) and $LaAlO_3$ (LAO), has sparked huge interest in oxide electronics. In spite of almost a decade of research, the mechanisms that determine the density of this 2DEG have not yet been unravelled. The polar discontinuity at the STO/LAO interface can in principle sustain an electron density of 3.3×10^{14} cm^{-2} (0.5 electrons per unit cell). However, experimentally observed densities are more than an order of magnitude lower.

We have investigated the issue using first-principles calculations based on DFT+U, as well as using a hybrid functional. We have analyzed the nature of the heterostructures, in particular whether it is possible or not to form a second LAO/STO interface that does not act as a sink for electrons.[1] The effects of different terminations of the LAO surface are examined.

Our results apply to oxide interfaces in general, and explain why the $SrTiO_3$/$GdTiO_3$(GTO) interface has been found to exhibit the full density of 0.5 electrons per unit cell.[2] We have also investigated the effects of strain on the band structure of STO,[3] with the goal of guiding strain engineering to enhance the mobility in the 2DEG. Explicit first-principles calculations for both STO/LAO and STO/GTO heterostructures will be discussed.

Work performed in collaboration with L. Bjaalie, L. Gordon, B. Himmetoglu, K. Krishnaswamy, and A. Janotti, and supported by ARO, ONR, and NSF.

[1] A. Janotti, L. Bjaalie, L. Gordon, and C. G. Van de Walle, Phys. Rev. B **86**, 241108(R) (2012).

[2] P. Moetakef, T. A. Cain, D. G. Ouellette, J. Y. Zhang, D. O. Klenov, A. Janotti, C. G. Van de Walle, S. Rajan, S. J. Allen, and S. Stemmer, Appl. Phys. Lett. **99**, 232116 (2011).

[3] A. Janotti, D. Steiauf, and C. G. Van de Walle, Phys. Rev. B **84**, 201304(R) (2011).

Generating topological insulator gap in graphene with heavy adatoms

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Graphene was the first material predicted to realize a topological insulator (TI) in seminal work by Kane and Mele, though unfortunately the gap is unobservably small due to carbon's exceedingly weak spin-orbit coupling. It is hence important to search appropriate adatoms and/or substrates to expand the spin-orbit coupling gap through hybridization. We found that heavy In or Tl adatoms may dramatically enhance the gap to 7 or 20 meV. These gaps are large enough for the realization of quantum spin Hall effect in graphene in most experimental conditions.

We also have a new proposal for generating a two-dimensional spin-orbit coupling gap with impurity bands arising from heavy adatoms that are mediated through graphene. First principles calculations predict that spin-orbit coupling induced gaps as large as 200 meV can be generated by placing Re, Os and Ir adatoms on graphene over a broad range of coverage. Furthermore, tuning the Fermi level is not required to enter the TI state. The mechanism at work is expected to be rather general and may open the door to designing new two-dimensional TI phases in many materials.

DFT+DMFT to correlated electronic structures: Recent developments and applications to iron-based superconductors

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Dynamical mean field theory (DMFT) has been widely used to study correlated systems which have open d or f shell and require treatment of correlation effects beyond static mean field theories such as the density functional theory (DFT). In this talk, I will first discuss recent developments in our group of a fully charge self-consistent implementation of DMFT into a full-potential all-electron DFT code, so-called DFT+DMFT, where the impurity problem is solved by a highly accurate continuous-time quantum Monte-Carlo solver. Then I will show some applications of our implementation of DFT+DMFT, taking the iron-based superconductors as examples, to compute various physical properties such as photo-emission spectroscopy, optical conductivity, spin and charge susceptibility, valence fluctuations, and so on. In the meantime, I will demonstrate that our DFT+DMFT provides a much better description of many experimental observable in comparison to the DFT. Hence the DFT+DMFT is a very promising tool to help us understand and design correlated functional materials.

Poster Abstracts I

Wednesday session

(in alphabetical order of submitting author)

FEAST real-time propagation scheme for TDDFT with study of CNT's plasmonic effects

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We have developed a robust and accurate real-time and real-space all-electron-TDDFT simulator capable to obtain the excited states of molecules and small nanostructures with direct comparisons with experimental data. Using the standard formalism of dipole time-response from short-polarized impulses [1], the time propagations are then performed using a spectral based approach making efficient use of the FEAST eigenvalue software [2,3] (i.e. direct integration of the evolution operator at each time step). FEAST transforms the eigenvalue problem into solving a set of independent linear systems, and it then relies on a subspace-iteration procedure where convergence is reached in a single iteration at each step of the time propagation. In comparison with a Crank-Nicolson scheme where small time intervals are needed and the linear systems need to be solved one after another, our spectral approach allows for larger time intervals and requires only one linear system to be solved by interval using a parallel implementation of FEAST. Similarly to the linear response theory, extended states need to be computed for performing the spectral decomposition at each time step. Within the real-space and real-time framework, however, the system matrices are sparse and linear parallel scalability can easily be obtained using multiple search intervals for FEAST and an appropriate parallel computing power. Several numerical results on molecules will be presented including the optical response of short CNTs. We have obtained the plasmonic excitations including some evidence of a 1-D Luttinger plasmon excitation peak from which the plasmon velocity can be calculated.

[1] K. Yabana, T. Nakatsukasa, J.-I. Iwata, and G. F. Bertsch, *Real-time, real-space implementation of the linear response time-dependent density-functional theory.* Phys. Stat. Sol. (b) 243,No. 5 , pp11211138 (2006).

[2] E.Polizzi, *Density-Matrix-Based Algorithms for Solving Eigenvalue Problems*, Phys. Rev. B. Vol 79, 115112 (2009)

[3] FEAST solver, *http://www.ecs.umass.edu/∼polizzi/feast*,

Coprecipitation of Cd(II) aqua-ion on calcite surface: a first principles study

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Coprecipitation is the incorporation of metal ions into a mineral structure by substituting for lattice atoms. This complex uptake mechanism occurs during crystal growth mostly in aqueous environment. Calcite, the most stable form of calcium carbonate, has the ability of trapping heavy metals and it is a good candidate to be used in water decontamination. As discussed in a recent document of the Environmental Protection Agency [1], calcite is effective as a natural site-specific remediation, the so called "monitored natural attenuation". To this end, it is essential to know how the surface of calcite interacts with metals in the presence of water. Despite the large body of experimental and theoretical results the details of the interfacial properties are yet to be fully elucidated. In this work the interaction between an hydrated Cd(II) complex, $[Cd(H_2O)_6]^{2+}$, known as aqua-ion, and two stepped calcite surfaces, namely the $\{318\}$ and the $\{3\bar{1}16\}$, is investigated by means of ab initio DFT-GGA simulations. Favored adsorption sites are located and the adsorption energy calculated accordingly. Relaxation calculations show the presence of a water layer between the cation and the calcite surface. The detailed electronic structure of the interacting system is described.

[1] Richard T. Wilkin, *Metal Attenuation Processes at Mining Sites*, EPA, (2007).

Effect of interfaces on electron transport properties of MoS_2 - Au Contacts

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Single layer MoS_2 is a promising material for future electronic devices such as transistors since it has good transport characteristics with mobility greater than 200 $cm^{-1}\ V^{-1}\ S^{-1}$ (comparable to the mobility achieved in thin silicon lms or graphene nanoribbons) and on-off current ratios up to 10^8 [1]. However, before MoS_2 can become a mainstream electronic material for the semiconductor industry, the design of low resistive metal-semiconductor junctions as contacts of the electronic devices needs to be addressed and studied systematically. We have examined the effect of Au contacts on the electronic transport properties of single layer MoS_2 by using density functional theory in combination with the non-equilibrium Greens function method. Charge density analysis shows the charge transfer from MoS_2 to Au contacts. The Schottky barrier between Au contact and MoS_2, transmission spectra, and I-V curves will be reported and discussed as a function of MoS_2 and Au interfaces of varying geometry. We will discuss our results in the light of recent experimental findings.

[1] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti and A. Kis, Nature Nanotechnology **6**, 147 - 150 (2011).

Density-Functional Theory Study of the Equilibrium Shape of Gold-Copper Nanoalloys

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Heterogeneous catalytic chemical reactions are at the core of many energy and environment related challenges. The shape of catalyst particles determines the accessible surfaces, and thus has a significant influence on the catalytic activity. Understanding this structure-reactivity relationship is crucial for the optimization of industrial catalysts.

Recently, Shao-Horn and coworkers have shown that gold-copper (Au/Cu) nanoparticles are stable and efficient electrocatalysts for the reduction of CO_2 to methane [1]. Our goal is to understand the structures of the Au/Cu nanoalloy at the atomic scale for further investigations of the mechanism of the catalytic reaction. Using density-functional theory, we report the equilibrium shape of Au/Cu clusters for different alloy compositions and under varying catalytic conditions.

[1] Z. Xu, E. Lai, Y. Shao-Horn, and K. Hamand-Schifferli, Chem. Commun. **48**, 5626 - 2528 (2012).

Deconstructing Densities

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We state and prove a density functional theorem for the celebrated atom-in-molecule problem, demonstrating that given an arbitrary molecular structure and corresponding electronic density, the Hohenberg-Kohn theorem induces an approximate but unique spatial density deconstruction into atomic-like components. The decomposition is expressed as an *ensemble-of ensembles*, a weighted double sum over ionic and excited state densities. The relative contributions of the ensemble states reflect the subtle interplay between the ionic charge transfer and covalent charge distortions characteristic of chemical bonding. The theorem is illustrated for canonical diatomic molecular systems, and we show that computed atom-in-molecule effective charges are in good accord with chemical intuition, and remarkably consistent with the traditional quantum chemical definitions of Mulliken and Löwdin. Implications for the construction of atomistic interaction potentials and correlated energy density functionals are discussed.

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Simulating Electron Energy Loss Spectroscopy in Large Systems

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The EELS and IXS cross sections in extended systems are proportional to the imaginary part of the diagonal of the inverse dielectric matrix, which can be computed using Time-Dependent (TD) Density Functional Theory (DFT). Current TDDFT-based approaches to dynamical screening involve the computation of a large number of single-particle unoccupied states and the manipulation (multiplication, inversion) of large matrices, two tasks that make them unfit to address systems larger than a handful of atoms. We present a new method, based on TDDFT linear response, that avoids these difficulties by adopting a Lanczos recursion scheme and a representation of the response orbitals borrowed from density-functional perturbation theory [1]. The resulting algorithm allows to compute the EELS and IXS cross sections for a same transferred mometum and in an entire, wide, frequency range with a numerical workload comparable to that of a single ground-state DFT calculation. We have implemented our method in the QUANTUM ESPRESSO distribution of computer codes [2], and successfully benchmarked it on the prototypical examples of bulk silicon and aluminum. The EELS/IXS angle-resolved cross sections in bismuth have been calculated for the first time. Details of the work being presented can be found in Ref. [3].

[1] D. Rocca, R. Gebauer, Y. Saad, and S. Baroni, J. Chem. Phys. 128, 154105. http://dx.doi.org/10.1063/1.2899649

[2] P. Giannozzi, S. Baroni et al., J. Phys.: Cond. Matt. 21, 395502 (2009). http://dx.doi.org/10.1088/0953-8984/21/39/395502

[3] I. Timrov, N. Vast, R. Gebauer, and S. Baroni, arXiv:1305.6233 [cond-mat.mtrl-sci] http://arxiv.org/abs/1305.6233

First-principles calculations of the improper s-wave symmetry for the electronic pairing in iron-based superconductors

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By means of space-group symmetry arguments, we argue that the electronic pairing in iron-based high temperature superconductors shows a structure which is a linear combination of *planar* s-wave and d-wave symmetry channels, both preserving the 3-dimensional A_{1g} irreducible representation of the corresponding crystal point-group. We demonstrate that the s- and d-wave channels are determined by the parity under reflection of the electronic orbitals through the iron planes, and by improper rotations around the iron sites. We provide evidence of these general properties by performing accurate quantum Monte Carlo ab-initio calculations of the pairing function, for a FeSe lattice with tetragonal experimental geometry at ambient pressure. We find that this picture survives even in the FeSe under pressure and at low temperatures, when the tetragonal point-group symmetry is slightly broken. Our theory can rationalize and explain a series of contradictory experimental findings, such as the observation of twofold symmetry in the FeSe superconducting phase, the anomalous drop of T_c with Co-impurity in $LaFeAsO_{(1-x)}F_x$, the s-to-d-wave gap transition in $BaFe_2As_2$ under K doping, and the nodes appearing in the LiFeAs superconducting gap upon P isovalent substitution.

Semistochastic Quantum Monte Carlo with the use of spatial and time reversal symmetries

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Exact Diagonalization of a Hamiltonian relies on the ability to perform sparse matrix vector multiplications, and Quantum Monte Carlo performs the same operations stochastically at the cost of the infamous sign problem. To mitigate deficiencies with either method, we have recently proposed a hybrid method, namely semistochastic Quantum Monte Carlo [Petruzielo et al., Phys. Rev. Lett. 109, 230201]. The method is semistochastic in that the matrix multiplication is partially implemented numerically exactly and partially stochastically with respect to expectation values only. Though the idea is quite general, we use elements from the recently proposed Full Configuration Interaction Quantum Monte Carlo (FCIQMC) method [Booth et al. J. Chem. Phys., 131 , 054106, (2009)] to demonstrate that its semistochastic version significantly reduces the computational time required to obtain the eigenvalue to a specified statistical uncertainty. This is demonstrated by the application of the semistochastic quantum Monte Carlo method to systems with a sign problem: the fermion Hubbard model and the carbon dimer. In addition, we show how we can make these calculations more efficient with the use of symmetries of the Hamiltonian. We use spatial (and time reversal) symmetries for the square lattice Hubbard model and time reversal symmetry for singlet ground states of quantum chemical Hamiltonians.

High magnetocrystalline anisotropy in oxides with near cubic local environments

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We investigate magnetic coercivity in double perovskite related oxides, based on first principles calculations of the magnetic properties and magnetocrystalline anisotropy. The Re-based materials studied have large magnetic moments on Re (nearly 1 μ_B in Sr_2CrReO_6) and relatively large magnetocrystalline anisotropy energies. This is unexpected considering the octahedral coordination. Based on this, we studied an intergrowth of double perovskite Sr_2CrReO_6-like and $SrTiO_3$-like blocks. We obtain a very high predicted coercive field in excess of 90 T. This shows that it is possible to have large coercive fields arising from magnetocrystalline anisotropy associated with transition elements in nearly cubic local environments.

Phases of attractive spin-imbalanced fermions in square optical lattices

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We determine the relative stability of different ground-state phases of spin-imbalanced populations of attractive fermions in square lattices. The phases are systematically characterized by the symmetry of the order parameter and the real- and momentum-space structures using Hartree- Fock-Bogoliubov theory. We find several type of unidirectional Larkin-Ovchinikov-type phases. We discuss the effect of commensuration between the ordering wave vector and the density imbalance, and describe the mechanism of Fermi surface reconstruction and pairing for various orders. A robust supersolid phase is shown to exist when the ordering wave vector is diagonally directed.

Orbital engineering of carrier mobilities and densities at oxide interfaces

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Emergent phenomena at ABO_3 oxide interfaces, e.g. two dimensional electron gases (2DEGs)[1] are paramount to understanding critical behavior arising from electron confinement; like metal-insulator transitions,[2] novel magnetic effects[3] and superconductivity.[4,5] In this presentation we review our recent efforts to exploit the local chemistry and physics at oxide interfaces in order to enhance the fundamental properties at the interfaces. For this purpose, the chemically intuitive δ-doped system is used as a model system for exploring the physics at these interfaces. We explore three design concepts for manipulating the wavefunction and thus electronic configuration at oxides interfaces: (i) charge balance, (ii) dopant concentration and (iii) interlayer wavefunction overlap. Our results highlight the importance of relative population of the strongly localized d_{xy} orbital versus the more dispersive d_{xz} and d_{yz} orbitals; where increases in the fraction of the latter result in significant enhancements in carrier mobilities.[6] In addition, we show that an increase in charge imbalance at an interface, e.g. in $KXO_3/LaXO_3$ systems, can both decrease band effective masses (possibly enhancing mobility) and significantly increase the charge density at an interface.[7] Our results also suggest that by modulating the thicknessof the $SrTiO_3$ layers in La δ-doped systems that it is possible to achieve 3D conductivity; again possibly higher mobilities may be attainable in these materials due to changes in relative orbital populations. Together, these studies present routes toward enhancing 2DEG carrier mobilities and/or densities; thus having significance for exploring interfacial physics with consequences for novel device applications.

[1]Ohtomo, A., Muller, D. A., Grazul, J. L., Hwang, H. Y., *Nature* **419**, 378, (2002)
[2]Thiel, S., et al., *Science*, **313**, 1942 (2006)
[3]Brinkman, A., et al., *Nat. Mater.* **6**, 493 (2007).
[4]v. Klitzing, K., Dorda, G., Pepper, M. *Phys. Rev. Lett.*, **45**, (1980)
[5]Ando, T., *Rev. Mod. Phys.* **54**, 437 (1982).
[6]Choi, W. S., Lee, S., Cooper, V. R., Lee, H. N., *Nano Lett.* **12**, 4590 (2012).
[7]Cooper, V. R., *Phys. Rev. B* **85**, 235109 (2012).

$ZnAl_2O4$ spinel : electronic structure and formation energy of native defects

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$ZnAl_2O_4$ (Gahnite) is a ceramic which is considered as a possible transparent conducting oxide (TCO) due to its wide band gap and transparency for UV. The key physical properties of TCO material are the band gap, which determines the optical transparency and the band mass, that controlls the mobility of the charge carriers. Defects play an important role in controlling the conductivity of a TCO material along with the dopant - which is the main source of conductivity in an otherwise insulating oxide. We discuss the band gap anomaly observed for this spinel and present the band gap calculated using the state of the art GW approximation[1]. Further, a comprehensive first-principles density functional theory study for point defects in $ZnAl_2O_4$ spinel is also presented using the HSE06 hybrid functional. We have investigated the formation energies of intrinsic defects which include the Zn, Al and O vacancy, and the antisite defects: Zn at Al site (Zn_{Al}) and Al at Zn site (Al_{Zn}). The antisite defect Al_{Zn} has the lowest formation energy and acts as a shallow donor, indicating possible n-type conductivity in $ZnAl_2O_4$ spinel by Al doping[2].

[1] H. Dixit, N. Tandon, S. Cottenier, R. Saniz, D. Lamoen, B. Partoens, V. Van Speybroeck and M. Waroquier, New Journal of Physics, **13**, 063002 (2011).

[2] H. Dixit, N. Tandon, S. Cottenier, R. Saniz, D. Lamoen and B. Partoens, Phys Rev. B, **87**, 174101 (2013)

Ab initio study of the $BaTiO_3$/Ge interface

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Growing thin films of crystalline metal oxides on silicon or germanium has been of great research interest for decades because of the possible applications of such systems in electronic devices. Being ferroelectric in the bulk, $BaTiO_3$ on a semiconductor points to a chance to realize e.g. non-volatile transistors. In such a system, the state is encoded in the ferroelectric polarization direction of the oxide, which directly modifies the transport properties of the semiconductor under it.

Thanks to recent advances in epitaxial growth methods, one can explore such interfaces in parallel with the experiment. Here, we use density functional theory to study the interface between $BaTiO_3$ and Ge. We describe how the structure of the interface depends on the oxygen content of the interface and compare to X-ray diffraction results for fabricated interfaces. We show how the polarization of the $BaTiO_3$ thin film changes when compared to the bulk. We analyze the electronic structure of the interface and illustrate how valence and conductance bands are alligned. We explore the energetics of oxygen vacancies in $BaTiO_3$ both in terms of positional and concentration dependence and try to explain the results with simple lattice models of vacancy-vacancy interactions.

Absolute surface energies of polar and non-polar planes in GaN

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Growth of high quality single crystals and epitaxial layers of GaN is critical for producing optoelectronic and power electronic devices that reach the full potential of this material system. One of the fundamental material properties that govern growth of single crystals is the absolute surface energy of the crystallographic planes. Knowledge of these energies is required to understand and optimize growth rates of different facets in GaN, which determine bulk and selective area growth morphologies. In addition, surface energies provide brittle fracture toughnesses of the crystal, which determine the propensity for cracks to form in different crystallographic directions. By means of hybrid functional calculations, we have determined absolute surface energies for the non-polar {11-20} *a* and {10-10} *m* and polar (0001) +*c* and (000-1) -*c* planes in wurtzite GaN. Since polar surface energies are ill defined due to the low symmetry in the *c* direction of the wurtzite structure, we approximate their values using the zinc-blende phase. For all surfaces, we consider low-energy bare and hydrogenated reconstructions under a variety of conditions relevant to experimental growth techniques. We find that the energies of the *m* and *a* planes are similar, and constant over the range of conditions studied. In contrast, the energies of the polar planes are strongly condition dependent. Even so, we find that the +*c* polar plane is systematically lower in energy than the -*c* plane.

This work was supported by the Center for Energy Efficient Materials (an EFRC funded by DOE), by NSF, and by the UCSB Solid State Lighting and Energy Center.

The role of long-range order and local sublattice symmetry breaking in defected graphene

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Previous work[1,2,3] has shown that certain periodic structural modifications on graphene can change graphene from a semimetal to a semiconductor without breaking A- and B-sublattice symmetry. However, there is still no understanding of such a mechanism based on fundamental considerations. We have developed a simple perturbative tight-binding model[4], which correctly predicts the analytic relation between bandgap opening and the supercell periodicity of the defected graphene without breaking the C_3 symmetry. Here, we generalize this model to investigate periodic defects violating the C_3 symmetry, employing a model Hamiltonian based on the virtual crystal approximation. In addition, non-Bravais superlattices are considered by including structure factors for each defect position in a unit cell. These predictions obtained from analytical modeling agree very well with first-principles electronic structure computations for partially H-passivated and BN doped graphene. This work was supported by DOE Early Career Award (No. DE-SC0006433).

[1] J. A. Furst, J. G. Pedersen, C. Flindt, N. A. Mortensen, M. Brandbyge, T. G. Pedersen, and A.-P. Jauho, New J. of Phys. **11**, 095020 (2009).

[2] R. Zhao, J.Wang, M. Yang, Z. Liu, and Z. Liu, J. Phys. Chem. C **116**, 21098 (2012).

[3] W. Oswald and Z. Wu, Phys. Rev. B **85**, 115431 (2012).

[4] M. Dvorak and Z. Wu, submitted to Scientific Reports.

Pseudopotentials for high-throughput DFT calculations

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The increasing use of high-throughput density-functional theory (DFT) calculations in the computational design and optimization of materials requires a systematic approach to designing and testing a comprehensive set of soft and transferable pseudopotentials. Here we present design criteria and testing results for a new open-source "GBRV" ultrasoft pseudopotential library that has been optimized for use in high-throughput DFT calculations. We benchmark the GBRV potentials, as well as two other pseudopotential sets available in the literature, to all-electron calculations in order to validate their accuracy. The results allow us to draw conclusions about the accuracy of modern pseudopotentials in a variety of chemical environments. Potential files compatible with either QUANTUM ESPRESSO or ABINIT are available at http://physics.rutgers.edu/gbrv.

What energy loss spectra tell us about interfacial structure

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Advanced transmission electron microscopy (TEM) combined with electron energy loss spectroscopy (EELS) are cutting edge experimental methods that provide information on the atomic geometry and electronic states with atomic resolution in cross section. However, interpreting the EELS spectra is non-trivial as one needs theoretical guidance to match spectral features to particular features of the electronic structure. For bulk perovskite manganites such as $La_xSr_{1-x}MnO_3$ or $La_xCa_{1-x}MnO_3$, the relationship between the oxygen K-edge (O-K) EELS spectra and the A-site doping level of the manganite has been well established [1]. However, such an understanding is lacking for interfacial systems where the charge state, magnetic structure, and bonding topology of the material is distorted. Here, we focus on ferroelectric/manganite interface between $La_xSr_{1-x}MnO_3$ and $PbZr_xTi_{1-x}O_3$ where the dynamic switching of the ferroelectric polarization changes the electronic properties of the interfacial Mn significantly. We use density functional theory based methods to elucidate and separate the various contributions to the interfacial O-K EELS spectra (e.g., electron density on Mn sites, distortions of bond lengths around the Mn due to the ferroelectric polarization, etc.)

[1] Weidung Luo, Maria Varela, Jing Tao, Stephen J. Pennycook and Sokrates T. Pantelides, Phys. Rev. B **79**, 052405 (2009).

Correlation between band gap and electronegativity of substituted atoms in the TiO_2 crystalline structure

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The electronic structure of TiO_2 has been extensively studied through a variety of experimental and computational methods. Its properties range from thin film photovoltaic cells to optics. TiO_2 provides an excellent model to study computationally due to the wealth of experimental data and its inexpensive computational cost. Our hypothesis is that the electronegativity of a substituent changes the band gap of crystalline TiO_2. Atoms of different electronegativities were selected for substitution into the three polymorphic forms of TiO_2, which are rutile, anatase, and brookite. Our computational approach utilizes the linearized-augmented plane-wave approach of density functional theory in the WIEN2k computational software, and includes the incorporation of the modified Becke-Johnson potential, to determine the band gap and density of states for each case. Initial results showed that fluorine substitution in a 2x2x2 rutile supercell resulted in a slight decrease in the band gap.

Nonlinear continuum model for solvated electronic structure

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May 31, 2013

Abstract

Density functional theory, coupled to a polarizable continuum model (PCM), can accurately describe electronic structure of molecules and metallic surfaces in a liquid. However, due to the linear reponse assumption in PCMs, it fails to be as successful when microscopic electric fields are strong. For example, this is the case when ions or ionic surfaces are solvated in a liquid. We formulate a nonlinear generalization of polarizable continuum models within the framework of joint density-functional theory, in which dielectric saturation effects, critical for highly polar systems, are included naturally. We also discuss applications of this theory to the calculation of electron enegy-loss and optical excitation spectrum of solvated ions.

First principles modeling of the interface between a solid state lithium thiophosphate electrolyte and a lithium metal anode

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Recently, there has been progress in improving the conductivity and stability of solid electrolytes such as Li_3PS_4.[1] For a variety of interface configurations, computer modeling studies show that Li_3PS_4 surfaces are structurally and chemically altered by the presence of Li metal. On the other hand, experiments have shown [1] that an electrochemical cell of $Li/Li_3PS_4/Li$ can be cycled many times. One possible explanation of the apparent stability of the Li_3PS_4 electrolyte/Li metal interface, is that a stable thin buffer layer is formed during the first few cycles. In order to computationally explore this possibility, we modeled a thin film buffer layer of Li_2S on a surface of Li_3PS_4. Using first principles techniques described in previous work,[2] stable electrolyte-buffer layer configurations were found. Results for the idealized configurations indicate that a thin film of Li_2S can provide a protective buffer layer to stabilize the interface between the Li_3PS_4 electrolytes and Li metal anodes.

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Bibliography:

[1] Z. Liu, W. Fu, E. A. Payzant, X. Yu, Z. Wu. N. J. Dudney, J. Kiggans, K. Hong, A. J. Rondinone, and C. Liang, ***J. Am. Chem. Soc.*** **135**, 975-978 (2013).

[2] N. A. W. Holzwarth, N. D. Lepley, and Y. A. Du, ***J. Power Sources*** **196**, 6870-6876 (2011).

Density-functional Study of the Kinetics of Chemical Transformation of Cobalt to Cobalt Oxides

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Transition metal oxides are particularly interesting materials because they exhibit unique magnetic, optical and chemical properties. Cobalt oxides, in particular, have recently received increased attention due to their catalytic properties and potential as a promising anode material in Li-ion batteries.[1] Even though we know a lot about the structure, synthesis techniques, and properties of these oxides, very little is known about the mechanisms and kinetics of the reactions that occur as cobalt is oxidized.

Here, we present a study of the chemical transformation of ε-Co metal into CoO and Co_3O_4, using density functional theory.[2] The goal of our study is to determine (i) the kinetics of the nanoscale transformation, (ii) the diffusion processes during chemical conversion, and (iii) the structural and morphological changes that occur during the reaction.

We combine our computational results with experimental characterization data to elucidate the dominant diffusion mechanism in these reactions. We come across an interesting indirect-exchange mechanism for the diffusion of O in ε-Co that has a lower energy than simple vacancy and interstitial diffusion mechanisms. The results of the activation energies of diffusion of Co and O in the oxides explain the occurrence of the nanoscale Kirkendall effect which leads to hollowing of the nanoparticles.

[1] D.-H. Ha, M. A. Islam, and R. D. Robinson, Binder-Free and Carbon-Free Nanoparticle Batteries: A Method for Nanoparticle Electrodes without Polymeric Binders or Carbon Black. *Nano Lett* **12**, 5122–5130 (2012).

[2] D.-H. Ha, L. M. Moreau, S. Honrao, R. G. Hennig, and R. D. Robinson, The Oxidation of Cobalt Nanoparticles into Kirkendall-Hollowed CoO and Co_3O_4: The Diffusion Mechanisms and Atomic Structural Transformations. *J. Phys. Chem. C*, in print (2013).

CdSe quantum dot/carbon nanotube hybrid photovolatic systems

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CdSe quantum dot/cabon nanotube (QD/CNT) heterojunctions are one approach to creating hybrid organic/inorganic photovoltaics which combines the tunable band gap of the QDs with the high carrier mobility of CNTs. The QDs are grown in solution and capped with the ligand oelic acid. Recent edge X-ray absorption fine structure data indicate that ultrasonication of oleic acid capped QDs with acid treated multi-wall CNTs leads to strong binding of the QDs to CNTs [1]. Our first principle calculations describe the binding geometries and mechanisms involved. A strong defect enhanced binding of the QDs to CNTs via -COOH ligands is found. The enhancement is an indirect effect where structural rearrangements in the defect region of the CNTs enhances the binding energy. In terms of electronic structure, due to a negligible band gap in MWNTs with a large diameter, both the highest occupied state and lowest unoccpuied state of the QDs sit in CNT bands and overlap energetically with CNT states. The question is then if one can actually use this system for a photovoltaic device: only if the tunneling rates of electrons and holes form the QD to the CNT are significantly different can one effect charge separation, and we discuss our present findings from first principles simulations.

[1] S. Azoz et al. (to be published).

Multigap Semiconducting ferroelectric perovskites

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The energy conversion efficiency of a solar cell is directly related to the band gap of the material [1]. By doping ferroelectric perovskites with Bi^{5+} on the B-site, we propose low band-gap materials suitable for bulk photovoltaic effect and related solar applications.Our DFT calculations indicate that the low-lying $6s$ empty states of the electronegative Bi atom produce empty isolated bands in the gap of the parent materials, effectively lowering the band gap by 1$\sim$2eV in various perovskites. Ferroelectricity (and therefore inversion symmetry breaking) weakens but survives upon doping, which enables the "shift current" mechanism [2] for photocurrent generation, while the decreased band gap helps absorb low energy photons in the visible range. Furthermore, the existence of multiple band gaps allows for solar conversion devices with efficiency beyond the traditional Shockly-Queisser limit, in which successive photon excitations result in carriers with higher energy than a single-step excitation would achieve [3].

[1] W. Shockley and H. Queisser, J. Appl. Phys. **32**, 510 (1961).

[2] G. Dalba, Y. Soldo, F. Rocca, V. M. Fridkin, and P. Sainctavit, Phys. Rev. Lett. **74**, 988 (1995).

[3] A. Luque and A. Martí, Phys. Rev. Lett. **78**, 5014 (1997).

A Potentially New Window towards Catalysis: Polarization Dependent Chemistry on Ferroelectric Surfaces

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The fact that a bulk material has an order parameter raises an interesting question as to how its surface chemistry can be affected by the order parameter. We use DFT methods to explore the possibility of flippable surface chemistry by switching the polarization of a ferroelectric substrate. One specific practical application is to potentially use ferroelectric surfaces for effective reduction of NO_x molecules (which are environmental pollutants) in oxygen rich environments. The difficulty of catalyzing NO_x reduction is a key problem with current automotive catalysts which force lower oxygen content and thus lower fuel efficiency.

In addition to exploring the effect of order parameter of the substrate, we show how depositing a monolayer of an active transition metal oxide, in this case RuO_2, can enhance desirable chemical reactions on the surface. This approach provides an additional degree of freedom in controlling surface chemistry which can be exploited to expand the types of transition metals that can be used as effective catalysts.

We present results for polarization dependent binding and dissociation energies of N_2, O_2, and NO molecules, atomic N and O, and we describe how this leads to new types of proposed catalytic pathways for NO_x reduction.

Direct Determination of the Chemical Bonding of Individual Impurities in Graphene.

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Abstract

Using a combination of Z-contrast imaging and atomically resolved electron energy-loss spectroscopy on a scanning transmission electron microscope, we show that the chemical bonding of individual impurity atoms can be deduced experimentally. We find that when a Si atom is bonded with four atoms at a double-vacancy site in graphene, Si 3d orbitals contribute significantly to the bonding, resulting in a planar sp^2d-like hybridization, whereas threefold coordinated Si in graphene adopts the preferred sp^3 hybridization. The conclusions are confirmed by first-principles calculations as implemented in the Vienna Ab initio Simulation Package and demonstrate that chemical bonding of two-dimensional materials can now be explored at the single impurity level[1].

Acknowledgment

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[1] Wu Zhou, Myron D. Kapetanakis, Micah P. Prange, Sokrates T. Pantelides, Stephen J. Pennycook, Juan-Carlos Idrobo, *Phys Rev Lett*, **109**, 206803 (2012).

FEAST Eigensolver for non-Hermitian Problems in Quantum Mechanics

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One can identify several instances of non-Hermitian problems in quantum mechanics. The perfectly matched layer (PML) technique or complex absorbing potentials can be used to approximate open boundary conditions for electron transport and nanoelectronics modeling. Complex band structure calculations give rise to non-Hermitian system matrices. A complex scaled Hamiltonian has also recently been proposed to compute quantum resonant states [1]. Currently these problems have few robust options for computing the eigen-decomposition.

Here, we propose to extend the capabilities of the FEAST eigenvalue algorithm and solver [2,3] for addressing the non-symmetric problem. The main computation behind the eigenvalue problem is transformed into solving a set of linear systems along a complex contour. Non-symmetric FEAST is capable of obtaining the imaginary eigenvalues in any given region of the complex plane as well as the right and left eigenvectors forming a bi-orthonormal basis [4,5]. This algorithm retains all computational benefits of the original Hermitian algorithm including parallelism and scalability.

[1] A. Cerioni, L. Genovese, I. Duchemin, T. Deutsch, *Accurate Complex Scaling of Three Dimensional Numerical Potentials*, arXiv:1303.6439 (2013)

[2] E. Polizzi, *Density-Matrix-Based Algorithms for Solving Eigenvalue Problems*, Phys. Rev. B. Vol 79, 115112 (2009)

[3] FEAST solver, *http://www.ecs.umass.edu/∼polizzi/feast*,

[4] S.E. Laux, *Solving complex band structure problems with the FEAST eigenvalue algorithm*, Phys. Rev. B 86, 075103 (2012)

[5] P. Tang, J. Kestyn, E. Polizzi *Subspace Iteration on Steroids A New Highly Parallel Non-Hermitian Eigensolver*, Submitted (2013).

Fully-optimized study of the electronic structure of FeSe

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We have performed density functional theory (DFT) calculations using the linearized augmented plane wave method (LAPW) with both the generalized gradient approximation (GGA) and local density approximation (LDA) functionals, to study the electronic structure of the iron-based superconductor, Iron-Selenium (FeSe). In our study, we have performed a most comprehensive set of calculations involving structural, atomic and spin configurations. All calculations were performed using the tetragonal lead-oxide (tetra-PbO) structure, with various volumes, c/a ratios and internal parameters. Furthermore, we investigated the spin polarization using the LDA and GGA to assess ferromagnetism in this material. The GGA calculations find the equilibrium configuration of FeSe for the tetra-PbO structure to have a volume of ~576au^3 with a c/a ratio of 1.70 and internal parameter of 0.22, with the ferromagnetic having slightly lower energy than the paramagnetic. For LDA, the equilibrium configuration for FeSe for the tetra-PbO structure is found to have a volume of ~464au^3 with a c/a ratio of 1.50 and internal parameter of 0.26, with the ferromagnetic also having slightly lower energy than the paramagnetic. In addition, we have started fitting the LAPW results on a tight-binding (TB) basis and obtained indications that the resulting TB Hamiltonian will be robust to use for applications such as molecular dynamics, vacancy formation energies, and even exploring properties beyond the DFT capabilities.

First-order metal-insulator transitions in vanadates from first principles

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Materials that exhibit first-order metal-insulator transitions, with the accompanying abrupt change in the conductivity, have potential applications as switches in future electronic devices. Identification of materials and exploration of the atomic-scale mechanisms for switching between the two electronic states is a focus of current research. In this work, we search for first-order metal-insulator transitions in transition metal compounds, with a particular focus on d^1 and d^2 systems, by using first principles calculations to screen for an alternative low-energy energy state having not only a electronic character opposite to that of the ground state, but a distinct structure and/or magnetic ordering which would permit switching by an applied field or stress. We will present the results of our investigation of the perovskite compounds $SrVO_3$, $LaVO_3$, $CaVO_3$, YVO_3, $LaTiO_3$ and related layered phase, including superlattices and Ruddlesden-Popper phases. While the pure compounds do not satisfy the search criteria, the layered phases show promising results.

Predicting In-Situ X-ray Diffraction for the $SrTiO_3$/Liquid Interface from First Principles

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Recent advances in experimental techniques, such as *in-situ* surface x-ray diffraction, allow researchers to probe the structure of the solid-liquid interface in electrochemical systems under operating conditions. These advances offer an unprecedented opportunity for theory to predict the properties of electrode materials in aqueous environments and inform the design of energy conversion and storage devices. To make contact with experimental measurements, these theoretical studies require a method which captures microscopic details of the liquid structure at the electrode surface.

Joint Density Functional Theory (JDFT)[1,2], a computationally efficient alternative to molecular dynamics simulations which replaces thermal sampling of the liquid with a single variational principle for the free energy of the full system, employs a liquid water functional which captures microscopic structure over the entire phase diagram of the liquid. We present a JDFT exploration of the (001) surface of $SrTiO_3$, which has been shown to catalyze solar-driven water splitting, in an electrochemical environment. We predict the geometry of the polar $SrTiO_3$ surface and the equlibrium structure of the contacting liquid, as well as the influence of the liquid upon the electronic structure of the surface. Using this detailed information about the atomic structure of the solid-liquid interface, we calculate the effect of the fluid environment on x-ray crystal truncation rod (CTR) diffraction patterns and compare our predictions to *in-situ* experimental x-ray diffraction measurements performed at the Cornell High-Energy Synchotron Source (CHESS).

[1] S.A. Petrosyan, A.A. Rigos, and T.A. Arias, J. Phys. Chem. B **109**,15436 (2005).

[2] R. Sundararaman, K. Letchworth-Weaver, and T.A. Arias, "JDFTx," `http://jdftx.sourceforge.net` (2012).

Mechanistic Aspects of Nitrogen Cycle: the Action of Copper-Containing Nitrite Reductase

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The nitrogen cycle is a natural process in which nitrogen is converted between biological and non-biological forms. Nitrogen fixation and nitrification convert nitrogen gas into nitrate, while denitrification converts nitrate back into nitrogen gas. The balance between nitrification and denitrification has been altered by human activities of using synthetic fertilizers since the discovery of the Haber-Bosch process. As a result, the excess nitrogen in biosphere has caused many environmental problems such as eutrophication and harmful algal bloom. Denitrification is currently the only proven nitrogen removing process, which is catalyzed by complex metalloenzymes with transition metal cofactors. Copper-containing nitrite reductase (CuNiR) performs a key step in denitrification by catalyzing the reduction of NO_2^- to NO. Experimental X-ray data have provided valuable insight into the overall function of CuNiR. However, many important questions remain unanswered. We have performed a computational study of the enzymatic mechanism of CuNiR based on density functional theory. Our results determine the minimum energy pathways, transition states and the activation energy barriers of each step in the reaction. A critical residue Asp^{98} is found to stabilize the initial attachment of nitrite. It also contributes to stability of a previously reported "side-on" coordination of the nitrosyl intermediate, although this geometry does not occur during the reaction. We also find that the transformation of the O- to N-attachment is achieved by an electron transfer from Type I copper.

First-principles-guided design of classical interatomic potential for oxides

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We developed a new type of interatomic potential for oxides based on the principles of bond-valence and bond-valence vector conservation. [1] The relationship between the bond-valence model and the bond-order potential is derived analytically in the framework of a tight-binding model. We showed that the bond-valence energy can be rewritten into the form of the well-known Finnis-Sinclair potential. The model potentials for two ferroelectric materials, $PbTiO_3$ and $BiFeO_3$, have been parametrized based on first-principles results. [2,3] The optimized potential is accurate for both canonical ensemble and grand canonical ensemble molecular dynamics (MD) simulations and sufficiently efficient for studying large systems ($\sim$1,000,000 atoms). We expect that this bond-valence model can be applied to a broad range of inorganic materials.

[1] I. D. Brown, Chem. Rev. **109**, 6858 (2009).

[2] S. Liu, H. Takenaka, T. Qi, I. Grinberg, and A. M. Rappe, arXiv:1211.5166 (2012).

[3] S. Liu, I. Grinberg, and A. M. Rappe, J. Phys. Cond. Matt. **25**, 102202 (1-6) (2013).

Topological phase transitions in $(Bi_{1-x}In_x)_2Se_3$ and $(Bi_{1-x}Sb_x)_2Se_3$

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We study the phase transition from a topological to a normal insulator with concentration x in $(Bi_{1-x}In_x)_2Se_3$ and $(Bi_{1-x}Sb_x)_2Se_3$ in the Bi_2Se_3 crystal structure. We carry out first-principles calculations on small supercells, using this information to build Wannierized effective Hamiltonians for a more realistic treatment of disorder. The intrinsic spin-orbital coupling (SOC) strength is similar in In and Sb, with similar atomic numbers, so that if the topological transitions in $(Bi_{1-x}In_x)_2Se_3$ and $(Bi_{1-x}Sb_x)_2Se_3$ are purely driven by the decrease of SOC strength, one would expect to see similar critical concentrations x_c in the two systems. However, based on our supercell calculations, x_c in $(Bi_{1-x}In_x)_2Se_3$ is expected to be slightly below 12.5%. This is much lower than that of $(Bi_{1-x}Sb_x)_2Se_3$, which is above 87.5% based on supercell calculations and around 65% based on the virtual crystal approximation. More accurate results are obtained from realistic disordered calculations, where the topological properties of the disordered systems are understood from a statistical point of view. Based on these calculations, x_c is around 17% for $(Bi_{1-x}In_x)_2Se_3$, but as high as $78\% - 83\%$ for $(Bi_{1-x}Sb_x)_2Se_3$. In $(Bi_{1-x}Sb_x)_2Se_3$, we find that the phase transition is mostly dominated by the decrease of SOC. However, for $(Bi_{1-x}In_x)_2Se_3$, the In $5s$ orbitals suppress the topological band inversion at low impurity concentration, therefore accelerating the phase transition. In $(Bi_{1-x}In_x)_2Se_3$, we also find a tendency of In atoms to segregate.

Environment-dependent U for CeO_x from first principles

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DFT+U method has been widely used to describe localized electrons in strongly correlated materials, where a Hubbard U is introduced in the model Hamiltonian to account for the on-site screened Coulomb energy. In practice, the value of U is often obtained empirically by fitting to experimental data for reference systems, and may vary significantly depending the specific quantity used in the fitting. To reduce the degree of empiricism, in this work, we calculated U from *ab initio* theory using the linear response method (*Phys. Rev. B* **71**, 035105, 2005). Results for Ce oxides in different forms, e.g., crystal, surface and molecule, were analyzed, and trend that relates U to Ce valence states and the local chemical environment was discussed.

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Poster Abstracts II

Thursday *session*

(in alphabetical order of submitting author)

Auxiliary-field quantum Monte Carlo calculations in solids[†]

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We present two recent developments in ab initio auxiliary-field quantum Monte Carlo (AFQMC) calculations of solid systems: down-folded Hamiltonians and the treatment of excited states. In the first, we derive simplified many-body Hamiltonians using truncated basis sets of Kohn-Sham orbitals obtained from the best possible density-functional calculations. AFQMC calculations are then performed on the down-folded Hamiltonians. The approach allows many-body calculations to treat a much simpler Hamiltonian while retaining material-specific properties. The Hamiltonians are systematically improvable and allow one to dial, in principle, between the simplest model and the full Hamiltonian. Test applications to typical semiconductors (Si and diamond), an ionic insulator (NaCl), and metallic systems (Na and Al) are presented. As a by-product of this approach, pseudopotential-free QMC calculations can be performed for solids[2].

In the second development, we formulate a many-body approach for quasiparticle band structure calculations in solids using AFQMC. An orbital orthogonalization constraint is introduced[3] to prevent collapse of the stochastic Slater determinants in the imaginary-time propagation. Detailed band structures can be calculated. Results for standard semiconductors are in good agreement with experiments. For the challenging ZnO wurtzite structure, we obtain a fundamental band gap of 3.26(16) eV, consistent with experiments.

[†] Supported by NSF and DOE.

[1] S. Zhang and H. Krakauer, Phys. Rev. Lett. **90**, 136401 (2003)

[2] W. Purwanto, S. Zhang, and H. Krakauer, in preparation.

[3] F. Ma, S. Zhang, H. Krakauer, arXiv:1211.4635

Wannier Charge Center Sheets in Topologically Non-trivial 3D Band Insulators

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The electronic ground state in a periodic crystalline insulator can be described by hybrid Wannier functions $|W_{nl_z}(k_x, k_y)\rangle$ which are maximally localized in one direction and Bloch-like in the other two. The sheets of Wannier charge centers (WCCs), defined as $\bar{z}_n(k_x, k_y) = \langle W_{n0}(k_x, k_y)|\hat{z}|W_{n0}(k_x, k_y)\rangle$, have distinct behaviors in different topological phases. In a 3D time-reversal (TR) invariant insulator, pairs of WCC sheets touch at the TR-invariant points in the 2D Brillouin zone. The Z_2 topological invariants $[\nu_0, \nu_1, \nu_2, \nu_3]$ can be determined by the way in which these TR-invariant points are connected by the WCC sheets. In a topologically trivial insulator, pairs of WCC sheets are well separated from each other, which means the four ν_μ are all positive. In a topological non-trivial insulator, however, a WCC sheet touches two different WCC sheets at different TR-invariant points. In a weak topological insulator, which can be thought of as a stack of 2D spin-Hall insulators, it is always possible to find a direction along which the WCC sheets pair up as in a trivial insulator, while they have a non-trivial behavior along the other two directions. The strong Z_2 index ν_0 is positive in this case, while at least one of ν_i is negative. In a strong topological insulator, ν_0 is negative and the WCC sheets have a topologically non-trivial behavior in any chosen direction. This distinct behavior is illustrated for different topological phases in the 3-D Kane-Mele model,[1,2] which is a four-band tight-binding model of s states on a diamond lattice with spin-orbit interaction. By varying the relative strength of a nearest-neighbor bond in one direction, the system can be switched between trivial, weak, and strong topological insulating phases. We also present the WCC sheets computed from first principles for the occupied states of the strong Z_2 insulator Bi_2Se_3 and trivial insulator Sb_2Se_3, again confirming that this approach correctly identifies the topological phases.

[1] L. Fu, C.L. Kane, and E Mele, Phys. Rev. Lett **98**, 106803 (2007).

[2] A. Essin, J. Moore, D. Vanderbilt, Phys. Rev. Lett. **102**, 146805 (2009).

Representing the Thermal State in Time-Dependent Density Functional Theory

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Classical molecular dynamics (MD) provides a widely used approach to determining thermodynamic properties by integrating the classical equations of motion of a system of atoms. Time-Dependent Density Functional Theory (TDDFT) provides a powerful approach to integrating the quantum equations of motion of a system of electrons. In analogy to MD, one could imagine obtaining the thermodynamic properties of an electronic system from a TDDFT simulation. For a variety of systems (e.g., many metals), the electronic subsystem reaches an effective state of internal equilibrium on a time scale that is short compared to electron-phonon equilibration. During the initial time-evolution of such systems, electron-phonon interactions should be negligible, and therefore, TDDFT should be able to capture the thermalization of the electronic subsystem. However, it is unclear how TDDFT represents the resulting thermal state. The thermal state is usually represented in quantum statistical mechanics as a mixed state, while TDDFT simulates the unitary evolution of a many-electron pure state, which is mapped by the TDDFT formalism into a fictitious non-interacting system. We work to address this puzzle by: (A) Reformulating quantum statistical mechanics to evaluate thermodynamic expectations as an unweighted average over a set of many-body pure states, and (B) Constructing a family of non-interacting (single determinant) states that approximate the required many-body states.

This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. Sandia National Laboratories is a multiprogram laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

A pedagogical program in MATLAB for auxiliary-field quantum Monte Carlo

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We describe `CPMC-m`, a pedagogical MATLAB program for learning the constrained-path and phase-free auxiliary-field Monte Carlo methods [1]. The package illustrates the constrained-path Monte Carlo method for the Hubbard model in any dimensions, with a graphical interface. The ground-state energy is calculated using importance sampling and implementing the algorithmic details of a total energy calculation. This tool allows users to experiment with various model and run parameters and visualize the results. It provides a direct and interactive environment to learn the method and study the code with minimal overhead for setup.

† Supported by NSF (REU) and DOE (SciDAC and CMCSN).

[1] S. Zhang, J. Carlson and J. E. Gubernatis, Phys. Rev. B 55, (12) (1997); S. Zhang and H. Krakauer, Phys. Rev. Lett. **90**, 136401 (2003)

GW calculations using a spectral decomposition of the dielectric matrix: applications to nanostructures, solids and liquids

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Abstract

We recently developed a GW approach[1] that avoids costly summations over empty electronic states and does not require the use of plasmon-pole models. We present various applications of the method, encompassing calculations of i) vertical ionization energies of molecules, band structures of crystalline and amorphous semiconductors; ii) the relative position of energy levels of anions and water in hydrated sulfate clusters and of the solvated chloride anion in aqueous solution;[2] iii) the band offset at semiconducting interfaces[3] and (iv) the electronic properties of liquid water, including the positions of the conduction band maximum and valence band minimum with respect to the vacuum level. The efficiency of our approach allowed us to compute quasiparticle energies of multiple configurations of liquid water, using samples with 64 molecules, selected over trajectories generated by ab initio molecular dynamics simulations.

[1] T. Anh Pham, H. Viet Nguyen, D. Rocca and G. Galli, Phys. Rev. B **87**, 155148 (2013);

H. Viet Nguyen, T. Anh Pham, D. Rocca and G. Galli, Phys. Rev. B **85**, 081101(R) (2012)

[2] C. Zhang, T. Anh Pham, F. Gygi and G. Galli, J. Chem. Phys. **138**, 181102 (2013)

[3] T. Anh Pham, T. Li, H. Viet Nguyen, S. Shankar, F. Gygi and G. Galli, Appl. Phys. Lett. (accepted)

Accurate total energy derivatives from correlated sampling diffusion Monte Carlo calculations

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Quantum Monte Carlo (QMC) methods are powerful techniques for calculating the electronic structure of atoms, molecules and solids with an accuracy comparable to the standard ab initio methods of quantum chemistry. The two most commonly used methods, variational Monte Carlo (VMC) and fixed-node diffusion Monte Carlo (DMC), rely on the statistical sampling of an accurate many-body wave function with a computational cost that scales favourably when compared to post-Hartree-Fock methods such as configuration interaction and coupled cluster calculations. This makes the QMC approach the ideal tool for computing the total energies of large collections of interacting quantum particles where conventional density functional theory methods fail to capture the role of dispersion interactions or electronic correlation.

Despite a number of advances in the area, the extraction of total energy derivatives, required for force calculations, remains problematic. This poster presents a method for correlating DMC simulations performed on two similar systems, which leads to a large reduction in the error of the energy difference between the systems when compared to independently obtained results. Accurate energy differences form the basis for finite difference estimates of total energy derivatives, where it is shown that for increasingly small displacements the stochastic error in the energy gradient remains constant. Results are presented for atomic force calculations on the water molecule and pressure calculations of solid hydrogen phases.

An auxiliary-field quantum Monte Carlo study of the chromium dimer†

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The chromium dimer (Cr_2) has become a challenging test case for many-body electronic structure methods because of its strong correlations and complicated nature of the binding. The ground state is highly multiconfigurational; in addition, accurate treatment of the dynamic correlation is essential to describe its weak binding. The quest for a scalable many-body method that is capable of treating this system properly is still ongoing despite many years of efforts. We will present results from an ongoing study of Cr_2 molecule using the auxiliary-field quantum Monte Carlo (AFQMC) method. We use the phaseless AFQMC (ph-AFQMC) method[1] to calculate the ground-state properties of Cr_2 using large, realistic basis sets. In parallel, we perform unconstrained (exact) AFQMC calculations for smaller basis sets to systematically improve the ph-AFQMC results. The calculated spectroscopic properties of the Cr_2 molecule are in good agreement with the experimental results.

† This research work is supported by DOE and NSF. Computing is provided by NCSA Blue Waters, CPD, and W&M SciClone.

[1] Zhang and Krakauer, Phys. Rev. Lett. **90**, 136401 (2003)

Fine structures in electronic structure calculations

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Fine structure in the electronic structure at the Fermi level E_F can give rise to unusual behavior. A recent example is provided by $NbFe_2$, where a highly unusual $(\delta k)^3$ wiggle near E_F correlates perfectly with the small doping level at which a quantum phase transition occurs, accompanied by non-Fermi liquid behavior in the vicinity at low temperature. Another example is the the fine structure in the electronic spectrum of the recently reported nickel carbide superconductor, body-centered tetragonal $I4/mmm$ Th_2NiC_2 with $T_c = 8$ K. The filled Ni $3d$ band complex is hybridized with C $2p$ and Th character to and through the Fermi level, and a sharply structured density of states arises only when spin-orbit coupling is included, which splits a zone-center degeneracy leaving a very flat band portion centered at the Fermi level. The flat part of the band corresponds to an effective mass $m_z^* \to \infty$ with very large and negative $m_x^* = m_y^*$. Although the region over which the effective mass characterization applies is less than 1% of the zone volume, it yet supplies of the order of half the states at the Fermi level.

[1] A J S Machado et al 2012 Supercond. Sci. Technol. 25 045010

High-throughput database search of antiferroelectric materials in ABX_2

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We use a first-principles rational design approach to identify a previously unrecognized class of antiferroelectric materials in the ABX_2 family of compounds. We perform a high-throughput scan of a large number of ABX_2 compounds in the ICSD[1] database, testing for dielectric and structural conditions leading to antiferroelectricity. The *Pnma* $SrCN_2$ structure type can be described in terms of antipolar distortions of the nonpolar *Immm* $NaNO_2$ structure type, present in the ferroelectric compound $NaNO_2$. We find members of the *Pnma* $SrCN_2$ structure type close in energy to the related polar *Imm2* $NaNO_2$ structure type, which includes members we predict to be ferroelectric. We calculate structural parameters and relative energies for all three structure types, both for reported and hypothetical representatives of this class. Our results provide guidance for experimental realizations and further investigation of high-performance materials suitable for practical applications.

[1] A. Belsky, M. Hellenbrandt, V. L. Karen, and P. Luksch, Acta Crystallogr. Sect. B **58**, 364 (2002).

Ground state of double layer graphene heterostructures in the presence of charged impurities.

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A graphene double layer heterostructure is formed by two sheets of graphene separated by a thin dielectric film. Using the Thomas-Fermi-Dirac theory we have studied the carrier density profile in the presence of charged impurities. In this talk I will present our results for the case of heterostructures formed by two sheets of single-layer-graphene (SLG) and two sheets of bilayer-graphene (BLG). As for isolated layers, we find that the presence of charged impurities induces strong carrier density inhomogeneities, especially at low dopings where the density landscape breaks up in electron-hole puddles. We find that the amplitude of the carrier density inhomogeneities in double layers can be much lower than in isolated layers due to the better screening properties of double layer systems. I will then present results for the case of "hybrid" structures formed by one sheet of SLG and one sheet of BLG.

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Understanding Electronic Structure with Constrained DFT: Pu and Pu Compounds

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Imposing crystal and magnetic structures on Pu and Pu compounds in density functional theory (DFT) calculations constrains these materials in ways that provide insight into their electronic structure. Constrained DFT also provides insight into the limitations of DFT calculations' description of strongly correlated materials. Systematic constrained DFT applied to Pu, Pu hydrides, and $PuGa_3$ reveals relations between their experimentally observed crystal structures. Furthermore, the results suggest that the effectiveness of using magnetic structure to simulate correlation effects depends critically on both the magnetic and the crystal structure.

Computational Study of Tautomerism and Aromaticity in Tropolone and its Sulphur Substituted Analogues

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Tautomerism of the *keto-enol* variety occurs in aliphatic carbonyl compounds when there are α-hydrogens relative to the carbonyl group. In such systems the *keto* isomer is typically favoured. This is in contrast to cyclic conjugated ketones, where the *enol* form predominates, and which is attributed to resonance stabilization. In this study we report results of tautomeric equilibrium constants obtained from full geometry optimizations of tropolone (2-hydroxy-2,4,6-cycloheptatrien-1-one) and 3,5- and 3,6-cycloheptadiene-1,2-dione. This was accomplished by employing the B3LYP/6-311++G** model chemistry for optimizations in the gas phase, with the effects of an aqueous solvent examined using the Self-Consistent Reaction Field-Polarizable Continuum Model (SCRF-PCM) at the same theoretical level. pK values for tropolone relative to the two *keto* structures were 13.75 (g), 15.78 (g), and 13.05 (aq) and 13.45 (aq), respectively [1]. The extent of aromaticity, or otherwise, present in these compounds was understood using Hückel theory and supported by Nucleus Independent Chemical Shifts (NICS) [2] computations, confirming that tropolone is aromatic, while the other two tautomers are not. The influence of sulphur on relative stability was studied by performing the same calculations on mono- and di-thio substituted compounds of tropolone and its structural isomers [3]. This comprised seven isomers of C_7H_6OS and four of $C_7H_6S_2$. Trends similar to that occurring in the $C_7H_6O_2$ system were found.

[1] S. W. Paine and A. Salam, *Chem. Phys*. **331**, 61 (2006).

[2] H. Falleh-Bager-Shaidei, C. S. Wannere, C. Corminbeouf, R. Puchta and P. v. R. Schleyer, *Org*. *Lett*. **8**, 863 (2006).

[3] S. W. Paine and A. Salam, *Int. J. Quant. Chem.* **113**, 1245 (2013).

Carrier Density Modulation in the Graphene/Ferroelectric Interface

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Atomic and electronic structure insights of the graphene/ferroelectric interface via density functional theory (DFT) calculations elucidate the yet unexplored theoretically anticipated strong coupling between graphene transport properties and the exposed ferroelectric polarization. A model system consisting of ferroelectric $LiNbO_3$ (0001) slab with graphene facing both up- and down-polarized surfaces has been constructed to investigate the nature of the interfacial interaction. Our DFT calculations predict that the electronic structure of graphene facing either polar surface is preserved with neat Dirac cones at the K points in the Brillouin zone. We observed that the Dirac cone of the graphene in close contact with the up-polarized (down-polarized) $LiNbO_3$ surface is shifted below (above) the Fermi energy. Here, we demonstrate that the doping levels of graphene can be modulated based on the ferroelectric polarization leading to n-doped and p-doped graphene for up-polarized and down-polarized $LiNbO_3$ surfaces, respectively.

Carboxyl groups on hydrated calcite from first principles

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Understanding the mechanisms that rule the interaction between minerals and the biosphere is crucial for predicting both the stability and the reactivity of minerals. In particular, calcium carbonate ($CaCO_3$) is here considered in the form of calcite, as calcium-bearing minerals are the most abundant among all biominerals, with applications in geosciences, material science, bioengineering, and medical sciences. In order to understand and control the chemical processes occurring during biomineralization, functionalized headgroups on self-assembled monolayers are widely used as growth templates. More specifically, some experiments [1] show that -COOH moieties used to induce a controlled crystallization enabled the growth of several nucleating planes of calcite with the exclusion of the {10.4}. A detailed knowledge of the reactivity of the calcite surface and the exact mechanism of how COOH-terminated molecules interact with calcite surface stands for a real need of investigation. In this work the inhibiting effects of protonated -COOH and deprotonated -COO^- headgroups ontop of the {10.4} hydrated surface of calcium carbonate are investigated by means of ab initio DFT-GGA simulations. The interfacial properties and the trend of adsorption energies for different coverages are given in details and show that the adsorption is favored by the presence of water.

[1] A.B. Han, T. Y.-J.; Aizenberg, J. Chemistry of Materials, **20** 1064 (2008).

Recent developments in auxiliary-field quantum Monte Carlo: symmetry and constraint release

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We discuss the use of symmetry properties to increase the accuracy and efficiency in auxiliary-field quantum Monte Carlo (AFQMC) calculations of electronic systems. With the Hubbard model as an example, we study the effect of preserving symmetry in two aspects of ground-state AFQMC calculations, the Hubbard-Straonovich transformation and the form of the initial trial wave function. It is shown that significant improvement over state-of-the-art calculations can be achieved. In calculations with constraints, the use of symmetry can greatly reduce the systematic error. In calculations in which the constraint is released, the implementation of symmetry often leads to shorter convergence time and much smaller statistical errors, thereby alleviating the sign problem. Moreover, certain excited states become possible to calculate which are otherwise beyond reach. We also discuss the use of the energy variance to help monitor and accelerate convergence in ground-state projections. Detailed comparisons are made with exact results from direct diagonalization in smaller systems. Near-exact ground-state energies can be obtained with our method for systems with 100 lattice sites (basis functions).

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Computational synthesis of single-layer III-V materials

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Graphene has been of great interest since its discovery in 2005. The importance of graphene is not only that it has unique properties but also that it has promoted the interest in the isolation and synthesis of other 2-D materials, e.g. BN, MoS2, ZnO, NbSe2, with a variety of interesting properties, from insulators to metal, from mechanically strong to soft, and chemically active to chemically inert. In our recent work [1], using a first principles design approach, we have identified a previously unrecognized large family of mono layer group III-V materials. Three different structures that are energetically and dynamically stable in various materials of this family have been identified, namely a planar honeycomb hexagonal structure, a buckled hexagonal structure, and a surprising low-energy tetragonal structure. In this poster we show, using density functional theory, a synthesis approach for these as-yet hypothetical novel 2-D materials. We have identified several lattice-matched and symmetry-matched metallic substrates for the synthesis of these 2-D materials. These substrates stabilize the 2-D III-V materials by reducing the formation energies of the 2-D materials in comparison to their bulk counterparts. The 2-D III-V materials range from semiconductors to metals and from mechanically stiff to very soft. The predicted suitable substrates enable the tuning of the electronic properties of these 2-D materials. Our results provide guidance for experimental synthesis and an engineering methodology for the electronic properties of these novel 2-D III-V materials.

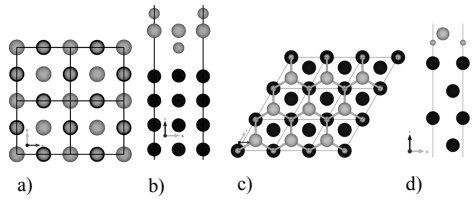

Figure 1: a-b) Top & side view of 2-D tetragonal AlP adsorbed on Pd (100) surface. c-d) Top & side view of 2-D hexagonal InN adsorbed on Ho (111) surface.

[1] H. L. Zhuang, A. K. Singh, and R. G. Hennig, Computational discovery of single-layer III-V materials, Phys. Rev. B, 87, 165415 (2013).

*A*b initio studies of ionization potentials of hydrated hydroxide and hydronium

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Solvated hydroxide (OH^-) and hydronium (H_3O^+) are important solutions of water defects. In a recent state-of-the-art photoelectron spectroscopy (PES) experiment[1], the ionization potentials of these water defects have been measured. Theoretically, we show that the photoelectron spectroscopy can be accurately computed based on a GW quasi-particle excitation theory[2,3], in which the molecular solvation structures are generated by ab initio molecular dynamics (AIMD). The resulting OH^- and H_3O^+ ionization potential distributions are centered at $\sim$ 10 eV and $\sim$ 19 eV respectively, which are closely consistent with the recent PES experimental values of 9.2 eV and 20 eV. A close inspection reveals that the defect orbitals can be associated with the $1b_1$-like ($1b_2$-like) states of the OH^- (H_3O^+) molecular excitations. These excitations are further strongly distorted by the surrounding water molecules, mainly in the first solvation shell, in which the OH^- and H_3O^+ excitations are clearly localized on the stable solvation complexes for the respective ions. Electron excitations are more delocalized during proton transfer which changes the excitation energies and distributions for both hydrated ions. As a result, the ionization potentials of the hydrated ions are broadened and shift into the main features of the bulk water PES spectrum.

[1] W. Chen, X. Wu, and R. Car, Phys. Rev. Lett. **105**, 017802 (2010).

[2] M. S. Hybertsen and S. G. Louie, Phys. Rev. B **86**, 134203 (2012).

[3] B. Winter, M. Faubel, I. Hertel, C. Pettenkofer, S. Bradforth, B. Jagoda-Cwiklik, L. Cwiklik, and P. Jungwirth, J. Am. Chem. Soc. **128**, 3864 (2006).

Periodic Density Functional Theory Solver using Multiresolution Analysis with MADNESS

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We describe the first implementation of the all-electron Kohn-Sham density functional periodic solver (DFT) using multi-wavelets and fast integral equations using MADNESS (multiresolution adaptive numerical environment for scientific simulation; http://code.google.com/p/m-a-d-n-e-s-s). The multiresolution nature of a multi-wavelet basis allows for fast computation with guaranteed precision. By reformulating the Kohn-Sham eigenvalue equation into the Lippmann-Schwinger equation, we can avoid using the derivative operator which allows better control of overall precision for the all-electron problem. Other highlights include the development of periodic integral operators with low-rank separation, an adaptable model potential for nuclear potential, and an implementation for Hartree Fock exchange.

Screening and Collective Modes of Gapped Bilayer Graphene

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We study the static and dynamic screening of gapped AB-stacked bilayer graphene. Unlike previous works we use the full 4-band model instead of the simplified 2-band model. We find that there are important qualitative differences between the dielectric screening function obtained using the simplified 2-band model and the 4-band model. In particular, within the 4-band model, in the presence of a band gap, the static screening exhibits Kohn anomalies that are absent within the simplified 2-band model. Moreover, using the 4-band model, we examine the effect of trigonal warping on the screening properties of bilayer graphene. We also find that the plasmon modes have a qualitatively different character in the 4-band model compared to the ones obtained using the simplified 2-band model.

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Ab initio many-body study of cobalt adatoms adsorbed on graphene

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Research interest in the adsorption of transition metal adatoms on graphene has grown rapidly because of their possible use in spintronic applications. Single Co atoms on graphene have been extensively studied recently [1–3], and possible Kondo effects have been considered [4]. Calculations of Co/graphene systems have largely been done at the density functional theory (DFT) level with local or semi-local functionals, or with an empirical Hubbard on-site repulsion U (DFT+U). These calculations show significantly varying results on the bonding nature of Co/graphene system. We use auxiliary-field quantum Monte Carlo (AFQMC) and a size-correction embedding scheme to accurately calculate the binding energy of Co/graphene [5]. We find that as a function of the distance h between the Co atom and the six-fold hollow site, there are two states that provide binding and exhibit a double-well feature with nearly equal binding energy of 0.4 eV at $h = 1.51$ and $h = 1.65$ Å, corresponding to low-spin ^{2}Co ($3d^9 4s^0$) and high-spin ^{4}Co ($3d^8 4s^1$), respectively. A recent experimental study [6] reported good agreement with DFT+U in predicting the adsorption site of Co/graphene. We systematically investigate the accuracy of DFT+U calculations for this system with near-exact AFQMC calculations.

This work is funded by the DOE, ONR, and NSF. The computing support was provided by INCITE, Blue Waters, and CPD.

[1] T. O. Wehling, A. V. Balatsky, M. I. Katsnelson, A. I. Lichtenstein, and A. Rosch, Phys. Rev. B **81**, 115427 (2010).

[2] D. Jacob and G. Kotliar, Phys. Rev. B **82**, 085423 (2010).

[3] T. O. Wehling, A. I. Lichtenstein, and M. I. Katsnelson, Phys. Rev. B **84**, 235110 (2011).

[4] V. W. Brar *et al.*, Nat. Phys. **7**, 43 (2011).

[5] Y. Virgus, W. Purwanto, H. Krakauer, and S. Zhang, Phys. Rev. B **86**, 241406(R) (2012).

[6] T. Eelbo *et al.*, Phys. Rev. Lett. **110**, 136804 (2013)

Electronic Structure and Transport at Silicene-Ag Interface

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We have investigated electronic properties of silicene-Ag(111) interfaces using first-principles calculations based on density functional theory. By unfolding the band structure in the Brillouin zone of a supercell to that of a primitive cell, followed by projecting onto Ag and silicene subsystems, we demonstrated that the Dirac cone at the Fermi level in silicene on Ag(111) is destroyed. Our results clearly indicate that the linear dispersions observed in both angular-resolved photoemission spectroscopy[1] and scanning tunneling spectroscopy[2] come from the Ag substrate and not from silicene.[3]

Further, we obtained results of electron transport across Ag-silicence-Ag junctions, which have not been previously reported. To address this issue properly, we developed and implemented a generalized Fisher-Lee relation that bridges the non-equilibrium Green's function (NEGF) techniques, scattering theory, and Boltzmann transport theory. Within this hybrid quantum-classical two-scale framework, we calculated transmission and reflection coefficients of monolayer and bilayer silicene junctions using NEGF in conjunction with density functional theory, derived and calculated group velocities, and computed conductance using the semi-classical Boltzmann equation. We found that resistances of silicene junctions are $\sim$0.08 $f\Omega m^2$ for monolayer silicene and $\sim$0.3 $f\Omega m^2$ for bilayer, corresponding to resistance 8 and 2 times smaller than the Sharvin resistance estimated via the Landauer formalism.

[1] P. Vogt, P. D. Padova, C. Quaresima, J. Avila, E. Frantzeskakis, M. C. Asensio, A. Resta, B. Ealet, and G. L. Lay, *Phys. Rev. Lett.* **108**, 155501 (2012).

[2] L. Chen, C. Liu, B. Feng, X. He, P. Cheng, Z. Ding, S. Meng, Y. Yao, and K. Wu, *Phys. Rev. Lett.* **109** 056804 (2012).

[3] Y.-P. Wang and H.-P. Cheng, Arxiv:1302.5759.

Correlation matrix renormalization method for correlated-electron systems

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We developed a correlation matrix renormalization (CMR) method which extends the commonly adopted Gutzwiller approximation for the evaluation of the one particle density matrix to treat the evaluation of the two-particle correlation matrix of strongly correlated-electron systems. This approach allows the expectation value of the many-electron Hamiltonian with a variational many-body wave function of the Gutzwiller form to be evaluated with reduced computational complexity. We have applied the method to the study of dissociation behavior of Hydrogen clusters with single correlated orbital and Nitrogen clusters with multiple-correlated orbitals. The results compare favorably with sophisticated quantum chemical calculations. We believe our approach can serve as an alternative starting point for building up the exchange-correlation energy functional for an improved density functional theory description of systems with strong electron correlations.

Insights into why the DFT band-gap problem does not limit the range of energy levels computed for point defects in semiconductors

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Point defects in semiconductors are largely characterized by their levels, which are defined as the Fermi levels at which the equilibrium charge state of the defect changes. Kohn-Sham density-functional theory (DFT) has successfully predicted defect levels for a wide variety of semiconductors and, surprisingly, these levels are often found to span an energy range significantly larger than the DFT gap. One reason for this result is that the range of levels computed using a finite-sized supercell are not limited by the DFT gap, which is defined as the difference in the energies to add and remove one electron to and from infinite bulk, but rather by the energy difference to add and remove one electron to and from the finite-sized bulk supercell corresponding to the one in which the defect calculations are performed. This supercell size-dependent gap is larger than the DFT gap for the same physical reasons that the measured gap in a degenerately doped semiconductor is larger than the measured gap in an undoped semiconductor, namely Moss-Burstein (band filling) effects arising from the large changes in the electron density ($\pm 2\times 10^{20}/\mathrm{cm}^3$ for a 216-atom supercell) that occur when adding and removing one electron from a finite-sized supercell.

This work was supported, in part, by Sandia's Solid-State Lighting Science Energy Frontier Research Center, sponsored by the U.S. Department of Energy, Office of Basic Energy Sciences. This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

Coupled Dirac Fermions and Neutrino-like Oscillations in Twisted Bilayer Graphene

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The low-energy quasiparticles in graphene can be described by a Dirac-Weyl Hamiltonian for massless fermions, hence graphene has been proposed to be an effective medium to study exotic phenomena originally predicted for relativistic particle physics, such as Klein tunneling and Zitterbewegung. In this work, we show that another important particle-physics phenomenon - the neutrino oscillation can be studied and observed in a particular graphene system, namely, twisted bilayer graphene. It has been found that graphene layers grown epitaxially on SiC or by the chemical vapor deposition (CVD) method on metal substrates display a stacking pattern with adjacent layers rotated by an angle with respect to each other. The quasiparticle states in two distinct graphene layers act as neutrinos with two flavors, and the interlayer interaction between them induces an appreciable coupling between these two flavors of massless fermions, leading to neutrino-like oscillations. In addition, our calculation shows that anisotropic transport properties manifest in a specific energy window, which is accessible experimentally in twisted bilayer graphene. Combining two graphene layers enables us to probe the rich physics involving multiple coupled Dirac fermions.

Quasiparticle energy and band offsets of monolayer of molybdenum and tungsten chalcogenides

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We employ the first-principles single-shot G_0W_0 approach to calculate the quasiparticle energy of monolayer of molybdenum and tungsten dichalcogenides, MX_2 (M=Mo, W; X=S, Se, Te). Beyond calculating bandgaps, we manage to achieve converged absolute band energies relative to the vacuum level. Compared with the results from density functional theory and hybrid functional theory, enhanced many-electron interactions result in substantially larger bandgaps and different absolute band energies. Interestingly, our fully-converged quasiparticle energies ratify the band-gap-center approximation, making it a convenient way to estimate the band offsets of monolayer dichalcogenides. The absolute band energies and corresponding band offsets obtained in this work are important for designing heterojunction devices and chemical catalysts based on monolayer dichalcogenides.

General efficient Gutzwiller solver with interfaces to model Hamiltonian and DFT calculations

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We developed a general efficient Gutzwiller solver to treat electron correlation effects with Gutzwiller approximation (GA). Interfaces of the Gutzwiller solver with tight-binding model Hamiltonians or standard DFT packages within DFT+GA framework for electronic structure and total energy calculations have also been developed. Applications of the solver to d and f-electron systems will be reported.

First-principles study of the dynamical magnetic charge tensor

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Magnetoelectric (ME) materials are of fundamental interest and are investigated for their broad potential for technological applications. The search for, and eventually the theoretical design of, materials with large ME couplings present challenging issues. First-principles methods have only recently been developed to calculate the full ME response tensor α including both electronic and ionic (i.e., lattice-mediated) contributions.[1] In several materials, the dominant contribution to the ME response has been shown to be the ionic term $\alpha_{\rm ion}$, which is proportional to both the Born dynamical electric charge $Z^{\rm e}$ and its analogue, the dynamical magnetic charge $Z^{\rm m}$.[2] The dynamical magnetic charge also has contribution to other magnetic properties, e.g. piezomagntism and magnetic susceptibility. Here we present a theoretical study whose ultimate goal is to understand the mechanisms that would enhance the magnetic charge $Z^{\rm m}$. Using first-principles density-functional methods within a relativistic framework with the inclusion of the spin-orbit interaction, we calculate the atomic magnetic charge tensors $Z^{\rm m}$ for both Cr and O atoms in Cr_2O_3, and discuss how these contribute to the ME response and other magnetic properties in this material.

[1] A. Malashevich et al., Phys. Rev. B, **86**, 094430 (2012).
[2] J. Íñiguez, Phys. Rev. Lett. **101**, 117201 (2008).

Chiral superfluid states in hybrid graphene heterostructures

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We study the "hybrid" heterostructure formed by one sheet of single layer graphene (SLG) and one sheet of bilayer graphene (BLG) separated by a thin film of dielectric material. In general it is expected that interlayer interactions can drive the system to a spontaneously broken symmetry state characterized by interlayer phase coherence. The peculiarity of the SLG-BLG heterostructure is that the electrons in the two layers have different chiralities. We find that this difference causes the spontaneously broken symmetry state to be N-fold degenerate. Moreover, we find that some of the degenerate states are chiral superfluid states, topologically distinct from the usual layer-ferromagnetism. The chiral nature of the ground state opens the possibility to realize protected midgap states. The N-fold degeneracy of the ground state makes the physics of SLG-BLG hybrid systems analogous to the physics of ^{3}He, in particular given the recent discovery of chiral superfluid states in this system.

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Theoretical and experimental investigation on thermoelectric properties of Mg_2Si

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Mg_2Si is a promising thermoelectric material since both of the elements Mg and Si are abundant and environmentally friendly. However, its thermoelectric figure of merit (ZT ~ 0.5 at 700K) is not yet high enough to efficiently convert heat energy into electricity. In this work, we use a theoretical approach to investigate the impact of intrinsic defects (*e.g.* interstitials, vacancies) and nano-clusters on thermoelectric properties of Mg_2Si. To compute thermal conductivity, we have developed Mg-Si potential based on modified embedded atom method so that thermal conductivity of Mg_2Si can be calculated from non-equilibrium molecular dynamics simulation method. Based on first principle methods, the other transport properties, such as electron conductivity, Seebeck coefficient and thermal conductivity from electron contribution, can be determined with Boltzmann transport theory. In parallel to the theoretical work, we also have done experiments to synthesis Mg_2Si thin film and characterize its thermoelectric properties. This combined theoretical and experimental work can provide more insights on the contributing factors in ZT enhancement for Mg_2Si.

$\mathbf{J_{eff} = \frac{1}{2}}$ insulating state in Ruddlesden-Popper iridates: An LDA+DMFT study

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The competition between strong spin-orbit coupling (SOC) and electron correlations in $5d$ compounds gives rise to many interesting phenomena. One particularly interesting case is the $J_{\rm eff} = \frac{1}{2}$ insulating phase found in Sr_2IrO_4 [1], which can be regarded as the n=1 member of the Ruddlesden-Popper series $Sr_{n+1}Ir_nO_{3n+1}$ with parent perovskite (n=∞) $SrIrO_3$. We investigated the electronic structures of three members of this series with n=1, 2, and ∞. Our calculations were carried out using the dynamical mean field theory (DMFT) method [2], where both spin-orbit coupling and electron-electron correlations are considered consistently at the first principles level. We demonstrated that Sr_2IrO_4 and $Sr_3Ir_2O_7$ are in the $J_{\rm eff} = \frac{1}{2}$ insulating phase, with gaps of 400 and 250 meV respectively. $SrIrO_3$ is shown to be a correlated metal, with strongly renormalized bands of effective mass about $6{\sim}8\,m_e$ around the Fermi energy. The electronic structures we obtained are in good agreement with recent ARPES measurements [3-5]. Moreover, for Sr_2IrO_4, a detailed analysis of the electronic structures reveals that it is difficult to get the correct spin and orbital moments by performing LDA+U+SOC calculations, while our DMFT calculations give a total magnetic moment of 0.43 μ_B per Ir ion, with the ratio between spin and orbital moments being close to 1:2. Finally, we calculated the optical conductivity of all three compounds, and found good agreement with experimental results [6].

[1] B.J. Kim, H. Jin, *et al.*, Phys. Rev. Lett. **101** 076402 (2008).

[2] K. Haule, C.-H. Yee, and K. Kim, Phys. Rev. B **81** 195107 (2010).

[3] B.M. Wojek, *et al.*, J. Phys.: Condens. Matter **24** 415602 (2012).

[4] B.J. Kim, private communication.

[5] Y. Nie, P. King, and K. Shen, private communication.

[6] S.J. Moon, *et al.*, Phys. Rev. Lett. **101**, 226402 (2008).

Ground state structure searching in perovskite superlattices

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Determination the crystal structure is the essential first step in the first-principle calculations of electronic properties. The ground state structure is not always straightforward to measure experimentally in cases of epitaxial superlattices and thin films, mostly because the small thickness. In this work, we propose a novel strategy for first-principle calculations to search for the ground state and low-energy structures in perovskite superlattices. Our approach bases on the assumption that the inner parts of superlattices tend to have similar distortions with their low-energy bulk states. Using 2:2 $PbTiO_3$/$SrTiO_3$ (PTO/STO) superlattice as an example, we first compute the low-energy states structures in pure PTO and STO perovskites, and then construct superlattice by stacking low-energy structures of PTO ans STO, where the atomic positions in interfacial layers are linear superpositions of the two components. Results recover the low-energy structures in previous work. In addition, we find another low-energy structure complementary to previous "ground-state" structure for 0% epitaxial strain, with negligible energy difference, suggesting a "flat" energy surface near the ground-state structure in 2:2 PTO/STO superlattice. The success in the complex PTO/STO system shows the possibility of generalization our approach to other perovskite systems as well as future high-throughput studies.

Single-Layer Group-III Monochalcogenide Photocatalysts for Water Splitting

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The recent synthesis of single-layer GaS and GaSe opens the question of stability for other single-layer group-III monochalcogenides (MX, M = Ga and In, X = S, Se, and Te) and how the dimension reduction affects the properties of these materials. Using a first-principles design approach, we determine that the single-layer group-III monochalcogenides exhibit low formation energies and are suitable for photocatalytic water splitting. First, density-functional calculations using a van der Waals functional reveal that the monochalcogenides have formation energies similar to that of single-layer MoS_2, implying the ease of mechanically extracting single-layer monochalcogenides from their layered bulk counterparts. Next, calculations using a hybrid density functional and the quasiparticle many-body G_0W_0 approximation determine the conduction and valence band edge positions. Comparing the band edge positions with the redox potentials of water, shows that single-layer monochalcogenides are potential photocatalysts for water splitting. Moreover, the bandgaps, band edge positions, and the optical absorption of the single-layer monochalcogenides can be tuned by biaxial strain to increase the efficiency of solar energy conversion. Finally, our qualitative assessment of the solubility of single-layer monochalcogenides suggests their stability in solution.

[1] H. L. Zhuang and R. G. Hennig, submitted to Chemistry of Materials (2013).

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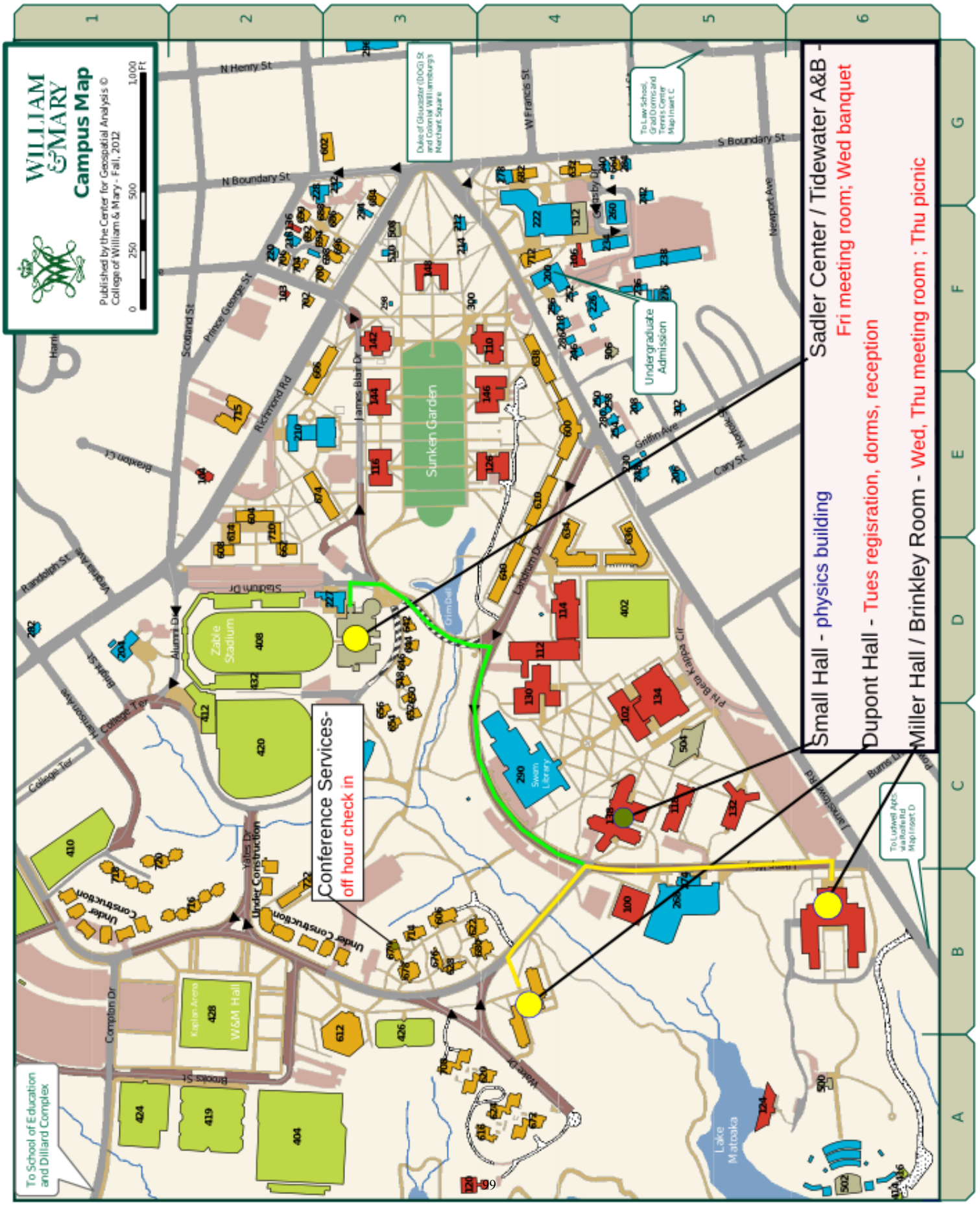
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0 250 500 1,000 Ft
Small Hall - physics building
Sadler Center / Tidewater A&B - Fri meeting room; Wed banquet
Dupont Hall - Tues regisration, dorms, reception
Miller Hall / Brinkley Room - Wed, Thu meeting room ; Thu picnic
Conference Services- off hour check in
Sunken Garden
Zable Stadium
W&M Hall
Undergraduate Admission
Lake Matoaka
To School of Education and Dillard Complex
To Law School, Grad Dorms and Tennis Center Map Insert C
To Ludwell Apts via Rolfe Rd Map Insert D
Duke of Gloucester (DOG) St and Colonial Williamsburg's Merchant Square
N Henry St
N Boundary St
S Boundary St
W Francis St
Newport Ave
Scotland St
Prince George St
Richmond Rd
James Blair Dr
Griffin Ave
Cary St
Nicholas St
Landrum Dr
Pitt Beck Knapps Cir
Jamestown Rd
Stadium Dr
Alumni Dr
Ukpeagvik Hall
Randolph St
Boswell Ave
Boundary St
College Ter
Hansbrough Rd
Yates Dr
Under Construction
Compton Dr
Brooks St
Ukpeagvik Hall
Swem Library
Kaplan Arena