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.

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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.

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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.

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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.

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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].

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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.

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ZnAl$_2$O4 spinel : electronic structure and formation energy of native defects

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ZnAl$_2$O$_4$ (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$_2$O$_4$ 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$_2$O$_4$ spinel by Al doping[2].

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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.

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).

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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.)

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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.

1

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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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.

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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.

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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∼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].

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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].

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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.

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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).

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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.

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Topological phase transitions in (Bi$_{1-x}$In$_x$)$_2$Se$_3$ and (Bi$_{1-x}$Sb$_x$)$_2$Se$_3$

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We study the phase transition from a topological to a normal insulator with concentration x in (Bi$_{1-x}$In$_x$)$_2$Se$_3$ and (Bi$_{1-x}$Sb$_x$)$_2$Se$_3$ in the Bi$_2$Se$_3$ 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-orbit coupling (SOC) strength is similar in In and Sb, with similar atomic numbers, so that if the topological transitions in (Bi$_{1-x}$In$_x$)$_2$Se$_3$ and (Bi$_{1-x}$Sb$_x$)$_2$Se$_3$ 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$_x$)$_2$Se$_3$ is expected to be slightly below 12.5%. This is much lower than that of (Bi$_{1-x}$Sb$_x$)$_2$Se$_3$, 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$_x$)$_2$Se$_3$, but as high as $78\%-83\%$ for (Bi$_{1-x}$Sb$_x$)$_2$Se$_3$. In (Bi$_{1-x}$Sb$_x$)$_2$Se$_3$, we find that the phase transition is mostly dominated by the decrease of SOC. However, for (Bi$_{1-x}$In$_x$)$_2$Se$_3$, the In $5s$ orbitals suppress the topological band inversion at low impurity concentration, therefore accelerating the phase transition. In (Bi$_{1-x}$In$_x$)$_2$Se$_3$, 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.