

# Auxiliary-field quantum Monte Carlo calculations in solids<sup>†</sup>

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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<sup>2</sup>.

In the second development, we formulate a many-body approach for quasi-particle band structure calculations in solids using AFQMC. An orbital orthogonalization constraint is introduced<sup>3</sup> 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.

<sup>†</sup> Supported by NSF and DOE.

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# 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  $\nu_\mu$  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  $\nu_0$  is positive in this case, while at least one of  $\nu_i$  is negative. In a strong topological insulator,  $\nu_0$  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,<sup>1,2</sup> 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  $\text{Bi}_2\text{Se}_3$  and trivial insulator  $\text{Sb}_2\text{Se}_3$ , again confirming that this approach correctly identifies the topological phases.

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# 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.

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# 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.

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# 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<sup>1</sup> 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;<sup>2</sup> iii) the band offset at semiconducting interfaces<sup>3</sup> 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.

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# 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<sup>†</sup>

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The chromium dimer ( $\text{Cr}_2$ ) 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  $\text{Cr}_2$  molecule using the auxiliary-field quantum Monte Carlo (AFQMC) method. We use the phaseless AFQMC (ph-AFQMC) method<sup>1</sup> to calculate the ground-state properties of  $\text{Cr}_2$  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  $\text{Cr}_2$  molecule are in good agreement with the experimental results.

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## 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  $\text{NbFe}_2$ , 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  $I4/mmm$   $\text{Th}_2\text{NiC}_2$  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  $m_z^* \rightarrow \infty$  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.

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# 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<sup>1</sup> 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.

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## **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<sub>3</sub> 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  $\alpha$ -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<sub>7</sub>H<sub>6</sub>OS and four of C<sub>7</sub>H<sub>6</sub>S<sub>2</sub>. Trends similar to that occurring in the C<sub>7</sub>H<sub>6</sub>O<sub>2</sub> system were found.

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# 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<sub>3</sub> (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<sub>3</sub> 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<sub>3</sub> 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 ( $\text{CaCO}_3$ ) 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  $-\text{COOH}$  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  $\text{COOH}$ -terminated molecules interact with calcite surface stands for a real need of investigation. In this work the inhibiting effects of protonated  $-\text{COOH}$  and deprotonated  $-\text{COO}^-$  headgroups on top 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.

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# 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-Stratonovich 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, MoS<sub>2</sub>, ZnO, NbSe<sub>2</sub>, 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.

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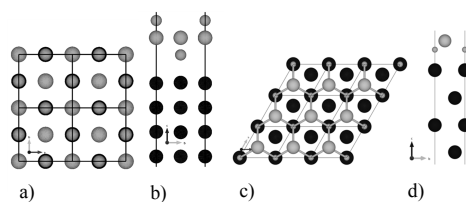


Figure 1: a-b) Top & side view of 2-D tetragonal AlP adsorbed on Pd (100) surface. c-d) Top & side view of 2-D hexagonal InN adsorbed on Ho (111) surface.



# Ab initio studies of ionization potentials of hydrated hydroxide and hydronium

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Solvated hydroxide ( $\text{OH}^-$ ) and hydronium ( $\text{H}_3\text{O}^+$ ) are important solutions of water defects. In a recent state-of-the-art photoelectron spectroscopy (PES) experiment<sup>1</sup>, 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<sup>2,3</sup>, in which the molecular solvation structures are generated by ab initio molecular dynamics (AIMD). The resulting  $\text{OH}^-$  and  $\text{H}_3\text{O}^+$  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  $\text{OH}^-$  ( $\text{H}_3\text{O}^+$ ) molecular excitations. These excitations are further strongly distorted by the surrounding water molecules, mainly in the first solvation shell, in which the  $\text{OH}^-$  and  $\text{H}_3\text{O}^+$  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.

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# 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  ${}^2\text{Co}$  ( $3d^94s^0$ ) and high-spin  ${}^4\text{Co}$  ( $3d^84s^1$ ), 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.

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# 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<sup>[1]</sup> and scanning tunneling spectroscopy<sup>[2]</sup> come from the Ag substrate and not from silicene.<sup>[3]</sup>

Further, we obtained results of electron transport across Ag-silicene-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.

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## 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 ( $\pm 2 \times 10^{20}/\text{cm}^3$  for a 216-atom supercell) that occur when adding and removing one electron from a finite-sized supercell.

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# 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  $\alpha$  including both electronic and ionic (i.e., lattice-mediated) contributions.<sup>1</sup> In several materials, the dominant contribution to the ME response has been shown to be the ionic term  $\alpha_{\text{ion}}$ , which is proportional to both the Born dynamical electric charge  $Z^e$  and its analogue, the dynamical magnetic charge  $Z^m$ .<sup>2</sup> The dynamical magnetic charge also has contribution to other magnetic properties, e.g. piezomagnetism and magnetic susceptibility. Here we present a theoretical study whose ultimate goal is to understand the mechanisms that would enhance the magnetic charge  $Z^m$ . 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  $Z^m$  for both Cr and O atoms in  $\text{Cr}_2\text{O}_3$ , and discuss how these contribute to the ME response and other magnetic properties in this material.

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# 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  $^3\text{He}$ , 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<sub>2</sub>Si

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Mg<sub>2</sub>Si is a promising thermoelectric material since both of the elements Mg and Si are abundant and environmentally friendly. However, its thermoelectric figure of merit ( $ZT \sim 0.5$  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<sub>2</sub>Si. To compute thermal conductivity, we have developed Mg-Si potential based on modified embedded atom method so that thermal conductivity of Mg<sub>2</sub>Si 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<sub>2</sub>Si 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<sub>2</sub>Si.

# $J_{\text{eff}} = \frac{1}{2}$ 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  $J_{\text{eff}} = \frac{1}{2}$  insulating phase found in  $\text{Sr}_2\text{IrO}_4$  [1], which can be regarded as the  $n=1$  member of the Ruddlesden-Popper series  $\text{Sr}_{n+1}\text{Ir}_n\text{O}_{3n+1}$  with parent perovskite ( $n=\infty$ )  $\text{SrIrO}_3$ . We investigated the electronic structures of three members of this series with  $n=1, 2,$  and  $\infty$ . 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  $\text{Sr}_2\text{IrO}_4$  and  $\text{Sr}_3\text{Ir}_2\text{O}_7$  are in the  $J_{\text{eff}} = \frac{1}{2}$  insulating phase, with gaps of 400 and 250 meV respectively.  $\text{SrIrO}_3$  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  $\text{Sr}_2\text{IrO}_4$ , 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  $0.43 \mu_B$  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].

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# 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  $\text{PbTiO}_3/\text{SrTiO}_3$  (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 and 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<sub>2</sub>, 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.

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