Final Report for DE-FG02-06ER45795

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2. Institution: Ohio State University, Office of Sponsored Research
1960 Kenny Road, Columbus, OH 43210
3. Project title: Modeling Dynamically and Spatially Complex Materials
4. PI: John W. Wilkins
5. Period covered by report: 1/1/2011 - 12/31/2015
6. Research accomplishments:

Developing new materials and engineering their novel properties have always been the driving force behind many revolutionary modern technologies. In recent decades, computational power has substantially increased due to advances in hardware and software. The confluence of available computing resources has enabled the development of computer simulations and models of unprecedented fidelity. The emerging capabilities in predictive modeling and simulation can accelerate the discovery, development, and deployment of new technologies, and have created an opportunity to implement the "materials-by-design" paradigm with wide-ranging benefits in technological innovation and scientific discovery.

The research supported by this grant focuses on atomistic studies of defects, phase transitions, electronic and magnetic properties, and mechanical behaviors of materials. We have been studying novel properties of various emerging nanoscale materials on multiple levels of length and time scales, and have made accurate predictions on many technologically important properties. A significant part of our research has been devoted to exploring properties of novel nano-scale materials by pushing the limit of quantum mechanical simulations, and development of a rigorous scheme to design accurate classical inter-atomic potentials for larger scale atomistic simulations for many technologically important metals and metal alloys.

The study of two-dimensional (2D) materials has seen tremendous progress in the last few years, starting with isolation and characterization of graphene, and followed by search for 2D analogues of 3D materials with technological importance. One such interesting material is hexagonal boron nitride (h-BN), an insulating material that serves as an excellent dielectric substrate for graphene electronics. Based on extensive density functional theory (DFT), a computational methodology rooted in quantum mechanics, we demonstrated that single-layer carbon-doped hexagonal boron nitride (h-BN) has extraordinary properties with many possible applications. The interactions mediated by the impurity states pertaining to substitutional C atoms in h-BN dictate the electronic structure and properties in these 2D materials. Hence, an accurate description of these impurity states is essential to obtain insights into and engineer properties of this emerging class of 2D materials. Our results open a new venue for the study of complex magnetic and optical phenomena in these 2D crystals.

We also performed a comprehensive and systematic density functional theory study of magnetism in graphene containing substitutional nitrogen atoms, with an aim to investigate its suitability for spintronic devices. The symmetry of the two sub-lattices of the 2D honeycomb lattice is intertwined with the spin states and governs fundamental properties of nitrogen-doped graphene. Our results reveal that the interacting substitutional atoms residing on the same sublattice favor the ferromagnetic spin-alignment for their local unpaired electrons, and substitution-induced impurity states predominantly disturb the spin-polarized pi-orbital of the sublattice where the substitutional atoms

belong. The final result is an asymmetric electron transport for the different spin states. Such asymmetric electron transport and the possibility of achieving complete spin-polarization for the transport carrier may hold the key to the feasibility of spin-based devices.

Experimental observations of magnetism on individual atoms absorbed on surfaces and their potential applications for spintronic devices and quantum computing inspired us to investigate the magnetic properties of Fe atoms and chains on Cu_2N/Cu(100) surface. We performed density functional calculations including spin-orbit effects and observed that a significant structural rearrangement occurs when an Fe atoms sits directly atop a Cu site. Our calculated magnetic anisotropy energies were in good agreement with experiments. We also confirmed that the antiferromagnetic state is the ground state for Fe chains and superexchange mediated by the nonmagnetic N atoms is the predominant mechanism of magnetic interaction in this system.

Besides employing DFT with standard functionals, our group had just explored the new hybrid exchange-correlation functional HSE for the calculation of properties where standard DFT could not be applied accurately: (a) band gaps of semiconductor alloys, (b) valence and conduction band offsets for a variety of technologically relevant semiconductor heterostructures, (c) direct-indirect band gap crossover composition to within 0.10 atomic concentration as compared to experimental values. To add to these successes, another study involving this new hybrid functional was performed to study electronic properties of (Hg,Cd)Te systems that show topological insulating behaviour. The calculated band structures using HSE showed better band gaps and band ordering compared with experiment than standard DFT for bulk HgTe and CdTe. Our results also confirmed the accuracy of HSE in reproducing the semimetal-to-semiconductor transition in the HgCdTe alloy and a valence band offset in strong agreement with recent experimental values for HgTe/CdTe interface.

A standard tool for calculations in condensed matter physics, material science, and chemistry is density functional theory. While DFT calculations are usually highly accurate and reliable, they are computationally expensive and therefore limited to studies of small systems over short times. On the other hand, molecular dynamics (MD) simulations based on classical inter-atomic potentials are much less computationally demanding, greatly extending materials simulations beyond the reach of DFT. Classical MD simulations are capable of studying diverse phenomena including plasticity, deformation under shock, atomic diffusion, and phase transformations. Vital to the success of MD simulations are high-quality potentials capable of mimicking the quantum mechanical interactions between atoms. Force-matching provides a bridge between accurate DFT and classical potentials by optimizing the potential parameters to forces, energies, and stresses computed by DFT for representative atomic configurations. Our potentials are constructed using the force-matching method and a fitting database containing a large number of forces from DFT-based MD simulations, as well as many DFT-computed physical properties. A significant amount of effort has been devoted to develop a systematic scheme that can produce accurate and reliable inter-atomic potentials. A cubic-spline-based modified embedded-atom method potential was developed for pure Ti that accurately describes martensitic phase transformations between the hcp (alpha) , bcc (beta) , and hexagonal (omega) phases. We also developed an embedded-atom method potential for pure Nb and a modified embedded-atom method potential for Mo that accurately models a large variety of behavior, including structural and elastic properties, surface energies and relaxations, and melting.

7. Published papers/theses acknowledging DOE support:

1. *Comparison of polynomial approximations to speed up planewave-based quantum Monte Carlo calculations,*
Parker, William D.; Umrigar, C. J.; Alfe, Dario; et al.
JOURNAL OF COMPUTATIONAL PHYSICS, Volume:287, Pages: 77-87, Published: APR 15 2015

2. *Spin-polarized electronic current induced by sublattice engineering of graphene sheets with boron/nitrogen,*
Park, Hyoungki; Wadehra, Amita; Wilkins, John W.; et al.
PHYSICAL REVIEW B, Volume:87, Issue:8, Article Number: 085441, Published: FEB 27 2013

3. *Ab initio based empirical potential used to study the mechanical properties of molybdenum,*
Park, Hyoungki; Fellinger, Michael R.; Lenosky, Thomas J.; et al.
PHYSICAL REVIEW B, Volume: 85, Issue: 21, Article Number: 214121, Published: JUN 21 2012

4. *Magnetic states and optical properties of single-layer carbon-doped hexagonal boron nitride,*
Park, Hyoungki; Wadehra, Amita; Wilkins, John W.; et al.
APPLIED PHYSICS LETTERS, Volume: 100, Issue: 25, Article Number: 253115, Published: JUN 18 2012

5. *Magnetic properties of Fe chains on Cu2N/Cu(100): A density functional theory study,*
Nicklas, Jeremy W.; Wadehra, Amita; Wilkins, John W.
JOURNAL OF APPLIED PHYSICS, Volume: 110, Issue: 12, Article Number: 123915, Published: DEC 15 2011

6. *Accurate electronic properties for (Hg,Cd)Te systems using hybrid density functional theory,*
Nicklas, Jeremy W.; Wilkins, John W.
PHYSICAL REVIEW B, Volume: 84, Issue: 12, Article Number: 121308, Published: SEP 27 2011

7. *Energy landscape of silicon tetra-interstitials using an optimized classical potential,*
Du, Yaojun A.; Lenosky, Thomas J.; Hennig, Richard G.; et al.
PHYSICA STATUS SOLIDI B-BASIC SOLID STATE PHYSICS, Volume: 248, Issue: 9, Pages: 2050-2055, Published: SEP 2011

8. *A topological point defect regulates the evolution of extended defects in irradiated silicon,*
Park, Hyoungki; Wilkins, John W.
APPLIED PHYSICS LETTERS, Volume: 98, Issue: 17, Article Number: 171915, Published: APR 25 2011

9. *Accuracy of quantum Monte Carlo methods for point defects in solids,*
Parker, William D.; Wilkins, John W.; Hennig, Richard G.
PHYSICA STATUS SOLIDI B-BASIC SOLID STATE PHYSICS, Volume: 248, Issue: 2, Pages: 267-274, Published: FEB 2011

10. *First-Principles based interatomic potentials for modeling the body-centered cubic metals V, Nb, Mo and W*
Fellinger, Michael R. Dissertation submitted to The Ohio State University, 2013

11. *Methods for accurately modeling complex materials,*
Nicklas, Jeremy W. C.
Dissertation submitted to The Ohio State University, 2013