

O 28: Focused Session: Frontiers of Electronic Structure Theory III (jointly with HL and TT)

Time: Tuesday 10:30–13:15

Location: H36

Topical Talk

O 28.1 Tue 10:30 H36
Materials for Alternative Energies: Computational Materials Discovery and Crystal Structure Prediction — ●CHRIS WOLVERTON — Northwestern University, Evanston, IL, USA

Many of the key technological problems associated with alternative energies may be traced back to the lack of suitable materials. The materials discovery process may be greatly aided by the use of computational methods, particular those atomistic methods based on density functional theory. In this talk, we present an overview of recent work on energy-related materials from density-functional based approaches. We have developed novel computational tools which enable accurate prediction of crystal structures for new materials (using both Monte Carlo and Genetic Algorithm based approaches), materials discovery via high-throughput, data mining techniques, and automated phase diagram calculations. We highlight applications in the area of Li battery materials and hydrogen storage materials.

O 28.2 Tue 11:00 H36
Doping at the Si-SiO₂ interface — FABIANO CORSETTI¹ and ●ARASH MOSTOFI² — ¹CIC nanoGUNE Consolider, Donostia-San Sebastian, Spain — ²Dept. of Materials & the Thomas Young Centre for Theory and Simulation of Materials, Imperial College London, UK

The Si-SiO₂ interface is a common feature in modern silicon-based CMOS technology for the fabrication of integrated circuits. The ongoing miniaturisation drive for such devices makes it increasingly important to understand the effect of the interface on the dopant distribution and properties. Indeed, in some cases channel lengths can be a few tens of nanometres, with the device properties being determined by only about 100 dopant atoms.

We have investigated the properties of arsenic dopants at the Si-SiO₂ interface. We use a large supercell to simulate both ordered (α -cristobalite) and disordered silica interfaces with crystalline Si. The disordered interface is generated using a multiscale approach in which a Monte Carlo method, parametrised with density-functional theory (DFT) calculations, is used to access the long time scales required for amorphising the oxide. The segregation of arsenic dopants in silicon at the interface is then studied using DFT.

We are able to accurately characterise the long-range quantum confinement effect due to the interface, which is found to result in a small energy barrier for segregation. We also investigate the effect of the local stress at the defect site on its segregation energy, and show that a simple ‘particle in a box’ model can be used to explain the calculated segregation energies at all substitutional silicon sites.

O 28.3 Tue 11:15 H36
Pressure-induced structural transformations in nanomaterials: a linear-scaling DFT investigation — ●NICCOLO CORSINI¹, PETER HAYNES¹, CARLA MOLTENI², and NICHOLAS HINE¹ — ¹Imperial College, London, UK — ²King’s College, London, UK

Semiconductor nanomaterials, including nanocrystals, nanorods and tetrapods, display a number of peculiar and tunable properties that distinguish them from their bulk counterparts and make them versatile materials for use as e.g. effective optical probes in medical diagnostics or photovoltaic devices. Of particular interest is their response to applied pressure, as they transform from one crystalline or amorphous structure to another. Accurate simulations are important for understanding finite size effects in the atomistic mechanisms of phase transformations (difficult to observe clearly in macroscopic experiments), for the opportunity to uncover novel metastable phases stabilized in finite systems, and for potentially innovative applications of nanomaterials. First-principles methods are essential to accurately describe the bond breaking/making in phase transformations and the realistic description of surfaces (often covered by complex surfactants). However the computational cost limits both the length- and time-scales attainable. We have combined an order-N density functional theory code for large systems and an electronic-enthalpy method to apply pressure to finite systems to model with quantum mechanical precision processes induced by pressure in nanomaterials (including their surfaces) under realistic conditions. The focus is on Si, CdSe and CdS nanocrystals that are currently favoured for technological applications.

O 28.4 Tue 11:30 H36

Density functional / molecular dynamics simulations of nucleus-driven crystallization of amorphous Ge₂Sb₂Te₅ — ●JAAKKO AKOLA^{1,2,3}, JANNE KALIKKA⁴, JULEN LARRUCEA⁴, and ROBERT O. JONES³ — ¹Department of Physics, Tampere University of Technology, Finland — ²COMP Centre of Excellence, Department of Applied Physics, Aalto University, Finland — ³GRSS and PGI-1, Forschungszentrum Jülich, Germany — ⁴Nanoscience Center, Department of Physics, University of Jyväskylä, Finland

Early stages of nucleus-driven crystallization of the prototype phase change material Ge₂Sb₂Te₅ have been studied by massively-parallel density functional/molecular dynamics simulations for amorphous samples (460 and 648 atoms) at 500, 600, and 700 K [1]. All systems assumed a fixed cubic seed of 58 atoms and 6 vacancies in order to achieve sub-nanosecond phase transition. Crystallization occurs within 600 ps for the 460-atom system at 600 and 700 K, and signs of crystallization (nucleus growth, percolation) are present in the others. Crystallization is accompanied by an increase in the number of ABAB squares (A: Ge, Sb, B: Te) [2,3], and atoms of all elements move significantly. The evolution of cavities/vacancies is closely monitored. The existence of Te-Te, Ge-Ge, and Sb-Sb (wrong) bonds is an inevitable consequence of rapid crystallization.

[1] J. Kalikka, J. Akola, J. Larrucea, and R. O. Jones, *Physical Review B* 86, 144113 (2012). [2] J. Akola and R. O. Jones, *Phys. Rev. B* 76, 235201 (2007). [3] J. Akola and R. O. Jones, *Phys. Rev. Lett.* 100, 205502 (2008).

O 28.5 Tue 11:45 H36
Large-Scale Moiré Patterns of hexagonal Boron Nitride on Cu(111): DFT Studies of Structural and Electronic Properties — ●RALPH KOITZ, ARI P SEITSONEN, MARCELLA IANNUZZI, and JÜRIG HUTTER — Institute of Physical Chemistry, University of Zurich, Switzerland

Hexagonal boron nitride (*h*-BN) adsorbed on metal surfaces shows great promise for applications in nanoscience. Interesting structural and electronic properties have been found, e.g. for *h*-BN on Rh(111) and Ru(0001), where the overlayer is strongly corrugated. Recent experiments with *h*-BN on Cu(111) indicate that the difference in lattice constants and a rotation of the monolayer lead to moiré patterns with periodicities greater than 5 nm. To thoroughly understand this system, however, further insight is needed at the atomic level.

In this contribution we present an in-depth DFT study of a moiré pattern of a rotated 24×24 *h*-BN sheet on a 23×23 Cu(111) slab. The periodic pattern extends over 6 nm, making this simulation the largest of its kind so far reported. We study the gradual change of adsorption registry of the monolayer, and its influence on the electronic structure. Both B and N occupy the entire range of *top*, *hcp*, *fcc*, and bridging positions. This modulation over the unit cell is reflected in the projected DOS, the electrostatic potential, and the contrast in simulated STM images. Contrary to other *h*-BN/metal systems, only minute structural changes occur upon adsorption. Our results show that the observed corrugation is chiefly electronic in nature and strongly related to the lateral variation of adsorption registries.

O 28.6 Tue 12:00 H36
A computational perspective for the development of electronic excited-states calculations — ●XAVIER ANDRADE — Department of Chemistry and Chemical Biology, Harvard University, Cambridge, United States

In this talk I present different aspects of my work, focused on improving electronic structure theory for excited states with the aim of making it suitable for current computer architectures.

First, I will present an approach to approximate the exchange and correlation (XC) term in density functional theory. In this approach the XC potential is considered as an electrostatic potential. Based on this representation we develop a scheme that fixes the asymptotic behavior of an approximated XC potential. Additionally, from the procedure it is possible to extract the derivative discontinuity of the XC potential to directly obtain the gap of atoms and molecules.

Real-time methods like molecular dynamics and real-time time-dependent density functional theory are a good alternative for computing response properties. However, long propagation times are needed to obtain resolved properties. As a second topic of this talk, we ad-

dress this problem by using a state-of-the-art signal-analysis technique: compressed sensing. By using this method instead of a Fourier transform, we find that the total propagation time required for resolved spectra can be reduced by a factor of five.

Finally, I will discuss my work on electronic structure calculations on graphical processing units (GPU) and the strategies to profit from the data parallelism available in the density functional formalism.

O 28.7 Tue 12:15 H36

Nuclear quantum effects in first principles molecular dynamics by colored-noise thermostats — ●MICHELE CERIOTTI — University of Oxford, United Kingdom

Oftentimes atomistic computer simulations treat atomic nuclei as purely classical particles, even when the electronic structure problem is treated quantum mechanically. This is a very good approximation when the system contains only heavy atoms. However, lighter nuclei such as hydrogen exhibit a strong quantum behavior, which manifests itself as sizable zero-point energy, tunnelling, isotope effects, etc.

Path integral methods are the state-of-the-art technique to model quantum nuclei, but they are computationally very demanding. Here I will discuss how a correlated-noise Langevin dynamics can be used to approximate nuclear quantum effects inexpensively, and how it can reduce by an order of magnitude the cost of quantitatively accurate path integral molecular dynamics. I will also present applications to the simulation of nuclear quantum effects in hydrogen-bonded materials by ab initio molecular dynamics.

O 28.8 Tue 12:30 H36

Semiconductor and Metal-Oxide Nanocrystal Simulations with Linear-Scaling PAW DFT — ●NICHOLAS HINE — Department of Materials, Imperial College London, Exhibition Road, London SW7 2AZ, United Kingdom — Cavendish Laboratory, J. J. Thomson Avenue, Cambridge CB3 0HE, United Kingdom

Nanocrystals enable tuning of material properties by varying attributes not available in bulk crystals, such as size, shape and surface termination, and such systems have innumerable applications in the field of energy materials, particularly in photovoltaics and photocatalysis. While whole nanocrystals are too large to be studied with traditional cubic-scaling first-principles methods, linear-scaling formulations of density functional theory (LS-DFT) enable the study of systems of many thousands of atoms. This allows nanocrystal simulations to make contact with the realistic size regime of 5-10nm, thus overlapping with the feasible scale of experimental characterisation and control. I will discuss recent developments in the ONETEP LS-DFT code that enable these large-scale, high-accuracy simulations, including the Projector Augmented Wave method, and recent applications to TiO₂ nanocrystals, pressure-induced phase transformations in II-VI semiconductor nanocrystals, and wurtzite-structure III-V semiconductor nanorods. I will discuss the origin of the large dipole moments which can be observed in such structures, and show how an effect akin to Fermi-level pinning can have a determining influence on the overall polarisation, explaining its variation with size, shape, surface chemistry and com-

position.

O 28.9 Tue 12:45 H36

Many-body effects on the carrier dynamics of graphene — ●CHEOL HWAN PARK — Department of Physics and Astronomy, Seoul National University, Seoul, Korea

It is very important to understand how a charge carrier in real materials interacts with other charge carriers or with the lattice vibration. In this presentation, I will explain that the measured carrier scattering rate versus energy behavior in graphene can be quantitatively described from first-principles calculations considering electron-electron interactions within the GW approximation and electron-phonon interactions within the Migdal approximation [1]. Then, I will show that our calculation can also explain (i) the mismatch between the extrapolations of the upper and lower Dirac cones in heavily doped graphene [2] and (ii) the significant deviation from linear energy dispersion in extremely low-doped graphene [3]. Last, I will show that first-principles calculations on the intrinsic electrical resistivity of graphene arising from electron-phonon interactions [4] can quantitatively explain the transport experiments on heavily doped graphene [5].

[1] C.-H. Park, F. Giustino, M. L. Cohen, and S. G. Louie, *Phys. Rev. Lett.* 99, 086804 (2007).

[2] C.-H. Park, F. Giustino, C. D. Spataru, M. L. Cohen, and S. G. Louie, *Nano Lett.* 9, 4234 (2009).

[3] D. A. Siegel, C.-H. Park, C. Hwang, J. Deslippe, A. V. Fedorov, S. G. Louie, and A. Lanzara, *Proc. Nat. Acad. Sci.* 108, 11365 (2011).

[4] C.-H. Park et al., in preparation.

[5] D. K. Efetov and P. Kim, *Phys. Rev. Lett.* 105, 256805 (2010).

O 28.10 Tue 13:00 H36

Theory of nanomagnetic and graphene hybrid systems: adatoms and multiorbital Kondo physics — ●TIM WEHLING — Institute for Theoretical Physics and BCCMS, University of Bremen, D-28359 Bremen, Germany

Graphene combines chemical inertness with a distinctly symmetric low energy electronic structure. Here, we show based on first-principles calculations that these two characteristics largely determine its interaction with adatoms. We find that covalent bonds to first row elements cause midgap states which can control electron transport [1] and the dielectric properties [2] of graphene based systems. The special nature of the Dirac electrons furthermore governs the coupling of magnetic adatoms to graphene by orbital selection rules and leads to peculiar multiorbital Kondo physics [3,4]. Finally, it is shown how multiorbital effects control the physics of magnetic transition metal atoms coupled to normal metals [5] and topological insulators [6].

[1] T. O. Wehling et al., *Phys. Rev. Lett.* 105, 056802 (2010).

[2] S. Yuan et al., *Phys. Rev. Lett.* 109, 156601 (2012).

[3] T. O. Wehling et al., *Phys. Rev. B* 84, 235110 (2011).

[4] T. O. Wehling et al., *Phys. Rev. B* 81, 115427 (2010).

[5] B. Surer et al., *Phys. Rev. B* 85, 085114 (2012).

[6] J. Honolka et al., *Phys. Rev. Lett.* 108, 256811 (2012).