TT 28: Focussed Session: Frontiers of Electronic Structure Theory - Non-Equilibrium Phenomena at the Nano-Scale II (organized by O)

Time: Monday 16:00–18:45 Location: TRE Ma

Topical Talk TT 28.1 Mon 16:00 TRE Ma

Simulating heat transport: from large scale molecular dynamics to first-principles calculations — •Davide Donadio — Max Planck Institute for Polymer Research, Mainz, Germany

The necessity to design materials and devices able to harness thermal energy, and possibly convert it into more amenable energy forms, has stimulated a major effort in the scientific community to understand heat transport at the mesoscale and the nanoscale. In this talk I will discuss different atomistic approaches to simulate nanoscale heat transport, ranging from large scale molecular dynamics simulations with classical empirical potentials at equilibrium and non-equilibrium conditions, to lattice dynamics calculations with force-constants computed by first principles. Applications will include silicon and carbon nanostructures, phase-change materials and molecular junctions.

TT 28.2 Mon 16:30 TRE Ma

First principles study of thermal conductivity cross-over in nano-structured Zinc-Chalcogenides — •Ankita Katre[1], Atsushi Togo[2], Ralf Drautz[1], and Georg K. H. Madsen[1] — [1]ICAMS, Ruhr-Universität Bochum, 44801 Bochum, Germany — [2]ESISM, Kyoto University, Sakyo, Kyoto 606-8501, Japan

Nano-structured Zinc-Chalcogenides are interesting for thermoelectric applications due to their low thermal conductivity.[1] A simple model study has reported how the thermal conductivity of ZnS, ZnSe and ZnTe can potentially show a cross-over as a function of the maximal mean free path of the phonons.[2] We have applied the Boltzmann transport equation in the relaxation time approximation to verify this. We find that thermal conductivity of ZnS crosses ZnSe and ZnTe and explain this in terms of the different contributions of phonon modes in these materials. Furthermore, the cross-over is found to be strongly influenced by isotope scattering. The calculated thermal conductivity is found to be strongly dependent on the volume and we explain the observed differences between LDA and GGA calculations. We compare further calculated thermal properties, such as the thermal expansion coefficient, to experiment to validate our approach.

[1] L.Zhen, S.Qiao, D.Y.Xiang, H.Z.Zhong, and Q.L.Gao, J. Mater. Chem. 22, 22821 (2012). [2] N.Mingo and D.Broido, Phys. Rev. Lett. 93, 246106 (2004).

TT 28.3 Mon 16:45 TRE Ma

Density-functional perturbation theory for lattice dynamics with numeric atom-centered orbitals — •Honghui Shang, Christian Carbogno, Patrick Rinke, and Matthias Scheffler — Fritz-Haber-Institut der MPG, Berlin

The response of the electronic structure to atomic displacements gives rise to a variety of interesting physical phenomena, which can be probed by experimental techniques such as infrared or Raman spectroscopy or neutron diffraction. The response can be conveniently computed from first principles by means of density-functional perturbation theory (DFPT). Here we present our implementation in the all-electron atom-centered numeric orbital code FHI-aims [1]. Our approach combines the accuracy of an all-electron full-potential treatment with the computationally efficiency of localised atom-centered basis sets that is necessary to study large and complex systems. We verified the accuracy of our DFPT implementation by comparing the vibrational frequencies to finite-difference reference calculations and literature values. Due to the atom-centered nature of the integration grids in FHI-aims, the portion of the grid that belongs to a certain atom also moves when this atom is displaced. Here we demonstrate that, unlike for first derivatives (i.e. forces) [2], this moving-grid-effect plays an important role for second derivatives (i.e. vibrational frequencies). Further analysis reveals that predominantly diagonal force constant terms are affected, which can be bypassed efficiently by invoking translational symmetry.

[1] V. Blum et al. Comp. Phys. Comm. 180, 2175 (2009)

[2] B. Delley, J. Chem. Phys. 94, 7245 (1991).

TT 28.4 Mon 17:00 TRE Ma

Breakdown of Fourier law in layered materials — •Andrea Cepellotti[1], Giorgia Fugallo[2], Francesco Mauri[3], and Nicola Marzari[1] — [1]THEOS, École Polytechnique Fédérale, Lausanne — [2]IMPMC, Universite Pierre et Marie Curie, Paris — [3]LSI, École Polytechnique, Paris

We compute the thermal conductivity in crystalline layered materials by solving the Boltzmann Transport Equation (BTE) for phonons [1], with the phonon-phonon collision rates obtained from density-functional perturbation theory. We find that in 2D materials, such as graphene and related compounds, and even in 3D layered materials, like bulk graphite, the single-mode relaxation time approximation (SMRTA) cannot describe heat transport correctly, underestimating by one order of magnitude or more thermal conductivities and phonons' mean free paths. Instead, we show that the exact self-consistent solution of the BTE provides results in excellent agreement with experimental measurements [2]. The shortcomings of the SMRTA lie in the assumption that heat flow is transferred only by individual phonon excitations, whereas in layered materials the transport can only be explained in terms of collective phonon excitations. The characteristic length of these collective excitations is often comparable with that of the experimental sample - as a result, Fourier's law become questionable, since its statistical nature makes it applicable only to systems larger than a few mean free paths.

[1] G. Fugallo et al., Phys. Rev. B, **88**, 045430 (2013).

[2] A. A. Balandin, Nat. Mater. **10**, 569 (2011).

TT 28.5 Mon 17:15 TRE Ma

High Temperature Thermal Conductivity from First Principles — •Christian Carbogno[1], Rampi Ramprasad[2], and Matthias Scheffler[1] — [1]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin — [2]Chemical, Materials & Biomolecular Engineering, University of Connecticut, Storrs, USA

In spite of significant research efforts, a first principles determination of the thermal conductivity at high temperatures has remained elusive. Under such conditions, Boltzmann transport techniques [1] that include anharmonic effects only perturbatively become inaccurate or even inapplicable. In this work, we overcome this limitation by performing first-principles Green-Kubo simulations [2], in which all orders of anharmonicity are incorporated by the means of *ab initio* molecular dynamics. The thermal conductivity is then assessed from the autocorrelation function of the heat flux in thermodynamic equilibrium. We discuss the details of our implementation and the definition of our heat flux that is based on the virial theorem. We validate our approach by presenting calculations for ZrO_2 that also showcase the importance of higher order anharmonic effects in materials with low thermal conductivities. Eventually, we discuss how our technique can be coupled to multi-scale models to achieve a computationally efficient and accurate description of the thermal conductivity at the nanoscale.

[1] D. A. Broido *et al.*, *Appl. Phys. Lett.* **91**, 231922 (2007).

[2] R. Kubo, M. Yokota, S. Nakajima, *J. Phys. Soc. Jpn.* **12**, 1203 (1957).

TT 28.6 Mon 17:30 TRE Ma

Accurate Modelling of the Polymorphism and Elastic Response of Molecular Materials from First Principles — •Anthony Reilly and Alexandre Tkatchenko — Fritz-Haber-Institut der MPG, Berlin, Germany

Molecular materials are of great fundamental and applied importance in science and industry, with numerous applications in pharmaceuticals, electronics, sensing, and catalysis. A key challenge for theory has been the prediction of their stability, polymorphism and response to perturbations. While pairwise models of van der Waals (vdW) interactions have improved the ability of density functional theory (DFT) to model these systems, quantitative and even qualitative failures often remain. Here, we show how a many-body description of vdW interactions can dramatically improve the accuracy of DFT for molecular materials, yielding quantitative description of stabilities and polymorphism for these challenging systems. Moreover, the role of many-body vdW interactions goes beyond stabilities to response properties. In particular, we have studied the elastic properties of a series of molecular crystals, finding that many-body vdW interactions can account for up to 30% of the elastic response, leading to quantitative and qualitative changes in elastic behavior. We will illustrate these crucial effects with the challenging case of the polymorphs of aspirin, leading to a better understanding of the conflicting experimental and theoretical studies of this system.

TT 28.7 Mon 17:45 TRE Ma

Surface chemistry on nanostructured oxides: do we have to go beyond hybrid DFT? — •Daniel Berger, Harald Oberhofer, and Karsten Reuter — Technische Universität München, Germany

Nanostructured oxide surfaces are promising candidates for a wide range of energy and catalysis applications. For first-principles modeling of corresponding surface chemical reactions the current state-of-the-art is generally defined by hybrid-level density-functional theory (DFT). Systematic work assessing the achieved accuracy at this level is nevertheless scarce, also owing to the fact that higher-level reference methods are often not available for standard periodic boundary condition supercell calculations. To this end, we present a study benchmarking semi-local and hybrid DFT against (renormalized) second-order perturbation theory (MP2,rPT2) as recently implemented in the FHI-aims package [1]. We make the efficient usage of the latter theories for oxide surfaces possible through a solid-state embedding framework, in which a central cluster region is described quantum mechanically, the long-range electrostatic interactions in the oxide are accounted for through a polarizable monopole field, and a shell of norm-conserving pseudopotentials correctly connects the two regions. We illustrate the performance of the various levels of theories using the water-splitting reaction at ideal and defected $TiO_2(110)$ surfaces as showcase. [1] X. Ren *et al.*, Phys. Rev. B **88**, 035120 (2013)

TT 28.8 Mon 18:00 TRE Ma

Atoms-in-solids perspective on polarizabilities and van der Waals coefficients in semiconductors — •Guo-Xu Zhang, Anthony M. Reilly, Alexandre Tkatchenko, and Matthias Scheffler — Fritz-Haber-Institut der MPG, Berlin, Germany

The calculation of response properties of solids including their polarizabilities and van der Waals (vdW) coefficients usually requires the knowledge of the full electronic bandstructure. For non-covalently bound solids, such as noble-gas and ionic crystals, atoms-in-solids model can be successfully utilized to define their polarizabilities. Here we critically assess the atoms-in-solids model for covalently-bound solids, ranging from wide-gap (10 eV) to narrow-gap (below 1 eV) semiconductors. We model their response by assigning a single quantum harmonic oscillator to every atom, where the parameters of the oscillators are defined as functionals of the electron density, following the Tkatchenko-Scheffler method [1]. The response function is then calculated by solving self-consistent screening equations of classical electrodynamics, without any explicit information about the electronic bandstructure [2]. The calculated polarizabilities and vdW coefficients for 23 semiconductors are compared with TDDFT and experimental benchmark data, revealing an overall agreement within 10%. The efficiency of our method and the accuracy of the calculated vdW parameters allows us to demonstrate the crucial role of vdW interactions in the cohesive properties of the 23 semiconductors. [1] Tkatchenko and Scheffler, PRL (2009); [2] Tkatchenko, DiStasio, Car, Scheffler, PRL (2012).

TT 28.9 Mon 18:15 TRE Ma

Adsorption at semiconductor surfaces - an energy analysis method — •Ralf Tonner and Marc Raupach — Fachbereich Chemie & Materials Sciences Centre, Philipps-Universität Marburg, Germany

The chemical bond is one of the most fundamental concepts in chemistry. Classifications such as covalent, ionic or metallic bonding are central in discussing trends in different compounds and predicting new reactivity. Several very helpful concepts and methods were developed to understand the chemical bond at surfaces.[1] The question about energetic contributions to surface chemical bonds on the other hand did not receive great attention although energy changes are the ultimate driving force in bond formation.

Starting from preliminary work by Philippsen and Baerends,[2] we implemented all terms of an Energy Decomposition Analysis (EDA) to obtain quantitative data about energetic contributions to chemical bonding in periodic systems. This periodic EDA method was applied to questions of chemisorption of organic molecules at semiconductor surfaces where it can shed light on the nature of the surface-adsorbate bonds.

[1] a) A. Nilsson, L. G. M. Pettersson, J. Nørskov, Chemical Bonding at Surfaces and Interfaces, Elsevier, Amsterdam, 2007; b) A. Groß, Theoretical Surface Science, Springer, Berlin, Heidelberg, 2009. [2] P. H. T. Philipsen, E. J. Baerends J. Phys. Chem. B 2006, 110, 12470.

TT 28.10 Mon 18:30 TRE Ma

Non-local density functionals meet many-body dispersion: A hybrid approach for van der Waals interactions — •Jan Hermann, Matthias Scheffler, and Alexandre Tkatchenko — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

Different approaches to treating van der Waals (vdW) interactions in density-functional theory can be loosely divided into the atom-based and the ones based on non-local functionals. The first type comprises a range of methods from atom-pairwise additive schemes by Grimme to many-body dispersion (MBD) approach of Tkatchenko et al. Usually, these methods require precalculated atomic parameters and thus rely on information not explicitly contained in the electron density. The other category consists of nonlocal functionals either of the Langreth and Lundquist or the Vydrov and van Voorhis (VV) type. In these approaches, the vdW interaction is obtained as a functional of the electron density and at most a few tuning parameters are needed.

Here, we show that these two contrasting approaches can be synergistically combined. We use the polarizability from the nonlocal functional of VV within the MBD method of Tkatchenko et al. Such a combination is worthy for several reasons. First, it is an atom-centered approach with no atomic parameters. Second, it puts aside the problem of partitioning electron density between atoms, which can be problematic in some cases. Third, it enables more direct comparison of so far unrelated methods. Fourth, it highlights the idea of combining working elements from different approaches.