HL 88: Frontiers of Electronic Structure Theory: Focus on Topology and Transport V

Time: Thursday 15:00–18:15   Location: H24

HL 88.1   Thu 15:00   H24

Zero-point renormalization of the electronic structure: trends across chemical and structural space — •Honghui Shang[1], Christian Carbogno[1], Patrick Rinke[1,2], and Matthias Scheffler[1] — [1]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin — [2]Aalto University, Helsinki, Finland

The importance of the renormalization of the electronic structure due to the zero-point nuclear motion (ZPR) has been discussed since long [1,2], but only recent advances in the first-principles treatment of electron-phonon coupling (EPC) enabled an accurate assessment of this effect for simple, prototypical materials, e.g., diamond [3] and Si [4]. However, it is largely unknown how chemical and structural properties affect the ZPR. To shed light on this question, we compute the EPC and ZPR for the octet binaries in both the zincblende and NaCl structure. Computationally, this is achieved by exploiting our recent implementation of density-functional perturbation theory in real-space, which provides considerable computational advantages with respect to numerical costs, parallelization, and especially scalability with respect to the number of atoms. We demonstrate the validity of our implementation by comparing with existing studies and finite difference results, investigate the trends across chemical/structural space, and critically discuss the role of the exchange-correlation functional.

[1] P. B. Allen and V. Heine, J. Phys. C **9**, 2305 (1976).
[2] M. Cardona, Solid State Commun. **133**,3 (2005).
[3] F. Giustino,*et.al.* Phys. Rev. Lett. **105**, 265501 (2010).
[4] S. Poncé, *et.al.* J. Chem. Phys. **143**, 102813 (2015).

HL 88.2   Thu 15:15   H24

All-Electron Many-Body Approach to X-Ray Absorption Spectroscopy — •Christian Vorwerk, Caterina Cocchi, and Claudia Draxl — Institut für Physik, Humboldt-Universität zu Berlin, 12489 Berlin, Germany

We present an all-electron approach of the many-body perturbation theory to describe X-ray absorption spectroscopy (XAS) in solid-state materials. In this formalism, the electron-hole interaction is explicitly included by solving the Bethe-Salpeter equation. A fully relativistic description of core states, as implemented in the all-electron full-potential code `exciting`[1], enables the explicit treatment of the effects of spin-orbit coupling in the spectra. We investigate the XAS for prototypical systems, such as TiO_2 and MgO, considering excitations from oxygen K and metal L edges. Our results, in good agreement with experiments, allow us to gain insight into the nature of the core-level excitations of these materials.

[1] A. Gulans et al., J. Phys. Condens. Matter 26, 363202 (2014).

HL 88.3   Thu 15:30   H24

Cohesive properties from all-electron RPA total energies — •Markus Betzinger[1], Christoph Friedrich[1], Andreas Görling[2], and Stefan Blügel[1] — [1]Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, Germany — [2]Lehrstuhl für Theoretische Chemie, Universität Erlangen-Nürnberg, Germany

We present an all-electron implementation of the RPA total energy within the full-potential linearized augmented plane-wave (FLAPW) method. An incomplete basis-set correction (IBC) [1] is employed to improve the convergence of the total energy with respect to the basis-set and the number of unoccupied states. To some extent the IBC incorporates an infinite number of bands and enables a virtually exact treatment of the core electrons.

We demonstrate that the core electrons give rise to a sizeable contribution to the RPA total energy. Their individual contribution is comparable to that of the valence electrons. All-electron RPA lattice constants and bulk moduli are shown for a set of prototype materials and compared to experimental results. An excellent agreement with experiment is observed.

[1] M. Betzinger *et al.*, Phys. Rev. B (accepted, 2015); **88**, 075130 (2013); **85**, 245124 (2012).

HL 88.4   Thu 15:45   H24

Explicitly correlated self consistent field theory — •Christian Lasar and Thorsten Klüner — Universität Oldenburg

Explicitly correlated correlation methods are an interesting field of current research since they are able to drastically improve the otherwise slow basis set convergence of conventional correlation methods. Therefore, chemical accuracy can be achieved with rather small basis sets.[1] The new correlation method presented in this contribution has already been developed for two-electron systems a long time ago[2]. We present the generalization of this ansatz to N-electron systems.

The basic idea is to augment a single slater-determinant with an explicitly correlated prefactor which then takes care of the correlation effects and the basis set convergence. Another interpretation of this ansatz would be a contracted CISD with orbital optimization in a complete basis set. The contraction is achieved by the explicitly correlated prefactor whose choice therefore defines the possible accuracy of the method. In principle, the generalization to any pair method i.e. CCSD and MP2 will be possible.

The big advantage of this kind of ansatz for the wave function is the drastic reduction of matrix elements needed for the optimization of the wave function. As a result, the presented method will be applicable to large molecules.

[1] Chem. Rev. 112, p. 4 (2012) [2] J. Chem. Phys. 99, p. 8830 (1993)

HL 88.5   Thu 16:00   H24

Representing energy landscapes by combining neural networks and the empirical valence bond method — •Sinja Klees[1], Ramona Ufer[2], Volodymyr Sergiievskyi[2], Eckhard Spohr[2], and Jörg Behler[1] — [1]Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany — [2]Lehrstuhl für Theoretische Chemie, Universität Duisburg-Essen, D-45141 Essen, Germany

In recent years, artificial neural networks (NNs) have become a powerful method to develop reactive interatomic potentials for large systems. However, the construction of NN potentials can become computationally very demanding due to the high dimensionality of the configuration space, which needs to be mapped by reference electronic structure calculations. Combining NN potentials with the empirical valence bond (EVB) method offers a promising approach to derive the potential energy of complex systems with substantially reduced effort, since the size of the reference structures can be strongly decreased. Preliminary results will be discussed and compared to density functional theory data.

HL 88.6   Thu 16:15   H24

CELL: a python package for cluster expansions with large parent cells — •Santiago Rigamonti[1], Maria Troppenz[1], Christopher Sutton[2], Luca M. Ghiringhelli[2], and Claudia Draxl[1] — [1]Humboldt-Universität zu Berlin — [2]Fritz-Haber-Institut der Max-Planck-Gesellschaft

The discovery of new materials for applications in areas such as energy harvesting, relies more and more on the accurate theoretical description of complex structures with large unit cells. The properties of interest are often tuned by substitutional dopants. Due to the vast configurational dopant space, a wide-spread approach is the cluster expansion (CE) technique. Most available CE codes are designed for alloys based on small parent cells, with usually 1 to 4 atoms. For the many important materials with much larger parent cells such approaches can't be applied. We devise an iterative scheme, based on efficient samplings of the configurational space, avoiding full structure enumerations. CELL consists of several modules that can be used independently, enabling to design CEs for specific purposes. Various CE schemes are available, offering ℓ_2 and ℓ_1 norms as penalization terms and different cross-validation strategies. Methods such as LASSO and split Bregman iteration are available for dealing with the ℓ_1 norm (compressive sensing). Access to finite-temperature properties and the characterization of phase transitions is possible through the Wang-Landau and diffusive nested sampling modules. Examples are presented for type-I thermoelectric clathrates, with 46 sites in the parent cell.

HL 88.7   Thu 16:30   H24

Structural and electronic properties of the thermoelectric clathrates $Ba_8Al_xSi_{46-x}$ and $Sr_8Al_xSi_{46-x}$ — •Maria Troppenz, Santiago Rigamonti, and Claudia Draxl — Humboldt-Universität zu Berlin

Clathrate compounds are promising candidates for high-efficiency thermoelectric applications. Their cage-like structure containing guest atoms allows for exploiting the idea of the phonon-glass electron-crystal and reaching a large figure of merit. We study $Ba_8Al_xSi_{46-x}$ and $Sr_8Al_xSi_{46-x}$ ($6 \leq x \leq 16$), where optimal electronic properties are expected close to the Zintl composition ($x = 16$). Cluster expansions on various quantities are performed, thus having access to ground-state as well as finite-temperature properties. A linear increase of the lattice constant with the number of Al substituents is obtained (0.019 Å per Al addition) confirming experimental observations (0.02 Å). The calculated bond distances between high-symmetry sites agree well with experiment for the full compositional range [1,2]. We find a close correlation between bond distances and fractional Al occupancies. This helps improving models used by experimentalists to estimate fractional occupancies. The substitutional configurations present an order-disorder transition around $600 - 900$ K, which is further analyzed applying the Wang-Landau method. An important finding is the semiconducting behavior of the low-temperature ordered phase at the Zintl composition, which points out the technological relevance of these compounds.

[1] J. H. Roudebush *et al.*; *Inorg. Chem.* **51**, 4161 (2012)
[2] M. Bobnar *et al.*; *Dalton Trans.* **44**, 12680 (2015)

HL 88.8   Thu 16:45   H24

***Ab-initio* calculation of Raman spectra of graphene-based materials** — •Albin Hertrich, Caterina Cocchi, Pasquale Pavone, and Claudia Draxl — Department of Physics, Humboldt-Universität zu Berlin, Germany

Raman scattering is an important non-destructive method for characterizing carbon-based materials. The main features of experimental Raman spectra of pristine graphene and graphite are the first-order G-band at ≈ 1580 cm^{-1} and the dispersive second-order 2D-band at ≈ 2700 cm^{-1}. We calculate first- and second-order Raman spectra fully *ab-initio* using the full-potential all-electron DFT package `exciting` [1], which allows for the calculation of both phonon dispersion, within the frozen-phonon approximation, and frequency-dependent dielectric tensors, from time-dependent DFT and the Bethe-Salpeter equation. In our approach [2], we expand the dielectric tensor with respect to the phonon normal coordinates. By taking its derivatives and by computing vibrational matrix elements, we calculate Raman scattering intensities. Applying this scheme to monolayer graphene, bilayer graphene, and graphite, we obtain the G-band in good agreement with experiment [3]. Furthermore, we explore the influence of both the stacking sequence and the laser energy on the 2D-band.

[1] A. Gulans *et al.*, J. Phys.: Condens. Matter **26**, 363202 (2014).
[2] C. Ambrosch-Draxl *et al.*, Phys. Rev. B **65**, 064501 (2002).
[3] A. C. Ferrari *et al.*, Phys. Rev. Lett. **97**, 187401 (2006).

HL 88.9   Thu 17:00   H24

Exciton dispersion in layered and 2D systems — •Francesco Sottile[1,2], Giorgia Fugallo[1,2], Pierluigi Cudazzo[1,2], and Matteo Gatti[1,2,3] — [1]Laboratoire des Solides Irradiés, École Polytechnique, CNRS, CEA-IRAMIS, Université Paris-Saclay, F-91128 Palaiseau, France — [2]European Theoretical Spectroscopy Facility — [3]Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, Boîte Postale 48, F-91192 Gif-sur-Yvette, France

The study of the exciton dispersion is of paramount importance for all applications involving light harvesting, beside providing fundamental knowledge about exciton mobility and migration. Using state-of-the-art ab initio many-body approach, like the Bethe-Salpeter equation [1], we present a first principle study of exciton dispersions in layered materials and 2D systems. Results for the former systems (on the prototypical hBN and MoS2) have been recently confirmed by experiments carried out at the Synchrotron ESRF [2]. For the latter (2D) systems we investigate exciton dispersion in graphane and hBN. From our results we provide a general picture of the mechanisms governing the dispersion of neutral excitations in 2D systems, and of the role played by the confinement of the electronic charge in setting the exciton binding energy. In particular we found that due to the strongly reduced screening of the Coulomb interaction in low- dimensional materials, the binding energy of both Wannier and Frenkel excitons in the optical spectra is large and comparable in size[3]. [1] M. Gatti et al., Phys. Rev. B 88, 155113 (2013) [2] G. Fugallo et al. Phys. Rev. B 92, 165122 (2015) [3] P. Cudazzo et al. submitted to Phys. Rev. Lett.

HL 88.10   Thu 17:15   H24

Electronic structure of selected superheavy elements (Z>104) — •Hana Cencarikova[1] and Dominik Legut[2] — [1]Institute of Experimental Physics, SAS, Kosice, Slovakia — [2]IT4Innovations Center, VSB-TU Ostrava, CZ 708 33 Ostrava, Czech Republic

The electronic structure of selected super-heavy elements (Z>104) have been determined from the first-principle calculations based on the density functional method. To determine the ground-state structure we have calculated number of basic phases including the face-centered cubic, body-centered cubic, simple cubic as well as hexagonal closed packed structures. Our results were obtained using local density approximation for the exchange and correlation effects and without and with the spin-orbit interaction for the band states. The analysis has been focused on the determination of the electronic density of states, electronic band structure dispersion relation, mechanical properties (elastic constants) and selected thermodynamical properties.

HL 88.11   Thu 17:30   H24

Layer-resolved calculated vibrations at gold surfaces — •Andrei Postnikov[1] and Kamil Moldosanov[2] — [1]Université de Lorraine, LCP-A2MC, Metz, France — [2]Kyrgyz-Russian Slavic University, Bishkek, Kyrgyzstan

Vibration modes at (001), (011) and (111) surface of gold are calculated from first principles, using the Siesta method [1] and the frozen phonon approach. Calculations are done on thick slabs of moderate lateral size – (2×2) for (001), (2×3) for (011), (3×3) for (111). This allows to resolve the vibration patterns layer by layer into the depth, in dependence on the in-plane wavevector component, and discriminating the polarisation of vibration modes. One notes the softening of modes at the surface, and an appearance of specifically surfacial modes. The bulk behaviour is largely recovered from the 5th or 6th layer downwards.

This study was driven by an intention to grasp the properties of longitudinal acoustic modes propagating at some depth under the surface of gold nanoparticles, which were an important element of our recent work related to the mechanism of radiofrequency absorption and hence resulting heating of nanoparticles of $\gtrsim 5$ nm size [2]. Since it is difficult to meaningfully incorporate the diversity of the nanoparticles' shapes in a practical calculation, the vibrations beneath the most common facets occurring at the nanoparticles' surface were studied instead.

1. The Siesta method, `http://departments.icmab.es/leem/siesta/`.
2. A. Postnikov and K. Moldosanov, `http://arxiv.org/abs/1508.00735`.

HL 88.12   Thu 17:45   H24

Electronic structure, mechanical and thermodynamic properties of Actinium from first-principles — •Zuzana Grosmanova[1] and Dominik Legut[2] — [1]Nanotechnology, VSB-TU Ostrava, CZ 708 33 Ostrava, Czech Republic — [2]IT4Innovations Center, VSB-TU Ostrava, CZ 708 33 Ostrava, Czech Republic

In this work, the mechanical (elastic constants) and thermodynamic properties of actinium were investigated using first-principle calculations. Our results were obtained using density functional theory employing local density and general gradient approximation for the electronic exchange-correlation effects and including the spin-orbit interaction for the band states. The ground-state structure were determined among simple phases like the face-centered cubic, body-centered cubic, simple cubic as well as hexagonal closed packed structures.

HL 88.13   Thu 18:00   H24

Interaction of Tritium and Chlorine 36 with defects in Graphite: Insights from Theory — •Christoph Lechner[1], Philippe Baranek[1], and Holger Vach[2] — [1]EDF Lab Les Renardières, Avenue des Renardieres, F-77818 Moret-sur-Loing Cedex, France — [2]CNRS-LPICM, Ecole Polytechnique, F-91128 Palaiseau Cedex, France

In order to optimize the waste management of nuclear graphite used in power plants, it is important to understand the properties of the activated impurities it contains, such as tritium and chlorine 36. Therefore, a computational study of the interaction of tritium and chlorine 36 with defects in graphite has been achieved at the density functional theory (DFT) level by using the functionals PBE and PBE0 with Grimme's D3 dispersion correction. The physisorption and chemisorption of atomic and molecular hydrogen or chlorine on graphite surfaces, (001), (100), and (110) with or without mono- and divacancies, have been investigated. The stabilities of the formed complexes are interpreted in terms of the formation energy. To obtain insight into the nature of the bonding a population analysis of the systems has been performed. While the bonding of hydrogen is mostly covalent for

chemisorption and van der Waals for physisorption, the behavior of chlorine is much more complex. Depending on the defect site, both, dominantly covalent and dominantly charge transfer bonding, is ob-served. Raman spectra for selected structures have been investigated, in order to evaluate, if the experimentally observed defect bands can be reproduced.