Band structure engineered layered metals for low-loss plasmonics

Plasmonics currently faces the problem of seemingly inevitable optical losses occurring in the metallic components that challenges the implementation of essentially any application. In this work, we show that Ohmic losses are reduced in certain layered metals, such as the transition metal dichalcogenide TaS2, due to an extraordinarily small density of states for scattering in the near-IR originating from their special electronic band structure. On the basis of this observation, we propose a new class of band structure engineered van der Waals layered metals composed of hexagonal transition metal chalcogenide-halide layers with greatly suppressed intrinsic losses. Using first-principles calculations, we show that the suppression of optical losses lead to improved performance for thin-film waveguiding and transformation optics.
Band structure engineering in van der Waals heterostructures via dielectric screening: the GΔW method

The idea of combining different two-dimensional (2D) crystals in van der Waals heterostructures (vdWHs) has led to a new paradigm for band structure engineering with atomic precision. Due to the weak interlayer couplings, the band structures of the individual 2D crystals are largely preserved upon formation of the heterostructure. However, regardless of the details of the interlayer hybridisation, the size of the 2D crystal band gaps are always reduced due to the enhanced dielectric screening provided by the surrounding layers. The effect can be significant (on the order of electron volts) but its precise magnitude is non-trivial to predict because of the non-local nature of the screening in quasi-2D crystals. Moreover, the effect is not captured by effective single-particle methods such as density functional theory. Here we present an efficient and general method for calculating the band gap renormalization of a 2D material embedded in an arbitrary vdWH. The method evaluates the change in the GW self-energy of the 2D material from the change in the screened Coulomb interaction. The latter is obtained using the quantum-electrostatic heterostructure (QEH) model. We benchmark the GΔW method against full first-principles GW calculations and use it to unravel the importance of screening-induced band structure renormalisation in various vdWHs. A main result is the observation that the size of the band gap reduction of a given 2D material when inserted into a heterostructure scales inversely with the polarisability of the 2D material. Our work demonstrates that dielectric engineering via van der Waals heterostructuring represents a promising strategy for tailoring the band structure of 2D materials.
Calculating excitons, plasmons, and quasiparticles in 2D materials and van der Waals heterostructures: Topical Review

Atomically thin two-dimensional (2D) materials host a rich set of electronic states that differ substantially from those of their bulk counterparts due to quantum confinement and enhanced many-body effects. This Topical Review focuses on the theory and computation of excitons, plasmons and quasiparticle band structures in 2D materials and their heterostructures. The general theory is illustrated by applications to various types of 2D materials including transition metal dichalcogenides, graphene, phosphorene, and hexagonal boron nitride. The weak and highly non-local dielectric function of atomically thin crystals is shown to be responsible for many of the unique properties exhibited by the 2D materials such as the formation of strongly bound, non-Hydrogenic excitons, large band gap renormalization effects, and the different signatures of excitons and plasmons in electron energy loss spectroscopy (EELS). Among other topics covered are spin-orbit coupling, trions, interlayer excitons, exciton dissociation, and environmental screening. Technical issues associated with the application of the many-body GW method and the Bethe-Salpeter equation (BSE) to 2D materials are also discussed. A combined quantum/classical method is introduced and used throughout to account for dielectric screening and self-energy effects from substrates and van der Waals heterostructures including the difficult case of non-matching lattices.
hBN layers, finding excellent agreement with experimental photoluminescence spectra. A comparison to density functional theory calculations demonstrates the crucial role of self-energy and electron-hole interaction effects.
The Atomic Simulation Environment - A Python library for working with atoms

The Atomic Simulation Environment (ASE) is a software package written in the Python programming language with the aim of setting up, steering, and analyzing atomistic simulations. In ASE, tasks are fully scripted in Python. The powerful syntax of Python combined with the NumPy array library make it possible to perform very complex simulation tasks. For example, a sequence of calculations may be performed with the use of a simple "for-loop" construction. Calculations of energy, forces, stresses and other quantities are performed through interfaces to many external electronic structure codes or force fields using a uniform interface. On top of this calculator interface, ASE provides modules for performing many standard simulation tasks such as structure optimization, molecular dynamics, handling of constraints and performing nudged elastic band calculations.

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Two-Dimensional MXenes as Catalysts for Electrochemical Hydrogen Evolution: A Computational Screening Study

We use density functional theory calculations to explore different polymorphs of a new class of 2D materials commonly known as MXenes, which are primarily carbides and nitrides of transition metals. The stability of the $M_2X$, $M_3X_2$, and $M_4X_3$ polymorphs in their bare and functionalized forms is assessed via the calculated standard heat of formation. We find that most of the MXenes are metallic, and we investigate their performance as electrocatalysts for the hydrogen evolution reaction (HER) using the free energy of hydrogen adsorption at equilibrium coverage as an activity descriptor. For a given type of metal, we find that the hydrogen adsorption energy can vary by up to 0.5 eV depending on the number of metal layers in the structure, suggesting that the catalytic activity of MXenes can be tuned by controlling the layer thickness. On the basis of a combined stability and activity analysis of 72 different MXenes, we identify several new promising nonprecious HER electrocatalysts.
Atomically Thin Ordered Alloys of Transition Metal Dichalcogenides: Stability and Band Structures

We explore the possibility of modulating the electronic band edges of the transition metal dichalcogenides (TMD) via alloying of different semiconductors within the same group (intra-group alloying). The stability of the ordered alloys is assessed from the calculated mixing enthalpy which is found to be close to zero for several alloys and below 20 meV/atom for all the alloys. We explore to what extent the electronic properties like the band gap and band edge positions of the alloy can be evaluated by taking the weighted average of the corresponding properties of the pristine systems. In general, this approach works well with the only exception being Cr containing compounds. Because the calculated properties of the alloys are very similar to the weighted averages, we expect that the trends observed for the ordered alloys will also hold
for more realistic disordered alloys

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Atomic-scale Modelling of Electro-catalytic Surfaces and Dynamic Electrochemical Interfaces

This dissertation addresses numerical calculations on the atomic scale to study catalytic surfaces for electrochemistry. The first half of the thesis deals with calculations on the properties of catalytic surfaces, using well-known methodology, whereas the second half of the thesis deals with the development of new methodology to explicitly include the electrolyte in the atomic scale calculations.

Chapter 3 presents calculations on contracted and reconstructed platinum surfaces, which are relevant for development of catalysts for proton exchange membrane fuel cells. Correlation of the results with experimental observations show that there is a natural limit to how far the reactivity of the catalysts can be fine-tuned, exclusively using the strain effect, that is imposed by alloying with lanthanides.

In chapter 4, calculations are presented for several newly discovered catalysts for the hydrogen evolution reaction. The results show that molybdenum carbides and borides have reactive surfaces, which is not in consistency with their high catalytic activity. A possible active facet is suggested for the molybdenum boride. It is likely, however, that other unexplored active sites, surface terminations or phases are responsible for the observed catalytic activities. For nickel diphosphide, which is another recently discovered catalyst for the hydrogen evolution reaction, it was possible to determine several facets and active sites, which have advantageous catalytic properties.

Chapter 5 presents the new methodology to calculate the structure of the electrolyte in the electrochemical interface. The strength of this methodology is that it makes fewer assumptions on the physics of the interface, while it takes a fundamental statistical mechanics approach. Large datasets of states for the electrolyte in contact with the surfaces of gold (111) and platinum (111) were calculated. Analysis methods were developed for determining the structure of the electrolyte as averages, which depend on pH and the electrode potential of the metal. The methodology remains under development, and it is expected that it will contribute with new insight to how pH and ionic chemical potentials affect the structure of the interface, to the benefit of future fundamental research in electrochemistry.

Band Gap Tuning and Defect Tolerance of Atomically Thin Two-Dimensional Organic-Inorganic Halide Perovskites

Organic–inorganic halide perovskites have proven highly successful for photovoltaics but suffer from low stability, which deteriorates their performance over time. Recent experiments have demonstrated that low dimensional phases of the hybrid perovskites may exhibit improved stability. Here we report first-principles calculations for isolated monolayers of the organometallic halide perovskites (C2H5NH3)2MX2Y2, where M = Pb, Ge, Sn and X,Y = Cl, Br, I. The band gaps computed using the GLLB-SC functional are found to be in excellent agreement with experimental photoluminescence data for the already synthesized perovskites. Finally, we study the effect of different defects on the band structure. We find that the most common defects only introduce shallow or no states in the band gap, indicating that these atomically thin 2D perovskites are likely to be defect tolerant.
Defect-Tolerant Monolayer Transition Metal Dichalcogenides
Localized electronic states formed inside the band gap of a semiconductor due to crystal defects can be detrimental to the material's optoelectronic properties. Semiconductors with a lower tendency to form defect induced deep gap states are termed defect-tolerant. Here we provide a systematic first-principles investigation of defect tolerance in 29 monolayer transition metal dichalcogenides (TMDs) of interest for nanoscale optoelectronics. We find that the TMDs based on group VI and X metals form deep gap states upon creation of a chalcogen (S, Se, Te) vacancy, while the TMDs based on group IV metals form only shallow defect levels and are thus predicted to be defect-tolerant. Interestingly, all the defect sensitive TMDs have valence and conduction bands with a very similar orbital composition. This indicates a bonding/antibonding
nature of the gap, which in turn suggests that dangling bonds will fall inside the gap. These ideas are made quantitative by introducing a descriptor that measures the degree of similarity of the conduction and valence band manifolds. Finally, the study is generalized to nonpolar nanoribbons of the TMDs where we find that only the defect sensitive materials form edge states within the band gap.

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Efficient many-body calculations for two-dimensional materials using exact limits for the screened potential: Band gaps of MoS$_2$, h-BN, and phosphorene

Calculating the quasiparticle (QP) band structure of two-dimensional (2D) materials within the GW self-energy approximation has proven to be a rather demanding computational task. The main reason is the strong q dependence of the 2D dielectric function around q = 0 that calls for a much denser sampling of the Brillouin zone (BZ) than is necessary for similar three-dimensional solids. Here, we use an analytical expression for the small q limit of the 2D response function to perform the BZ integral over the critical region around q = 0. This drastically reduces the requirements on the q-point mesh and implies a significant computational speedup. For example, in the case of monolayer MoS$_2$, convergence of the G$_0$W$_0$ band gap to within similar to 0.1 eV is achieved with 12 x 12 q points rather than the 36 x 36 mesh required with discrete BZ sampling techniques. We perform a critical assessment of the band gap of the three prototypical 2D semiconductors, MoS$_2$, h-BN, and phosphorene, including the effect of self-consistency at the GW$_0$ level. The method is implemented in the open source code GPAW.
Exciton ionization in multilayer transition-metal dichalcogenides

Photodetectors and solar cells based on materials with strongly bound excitons rely crucially on field-assisted exciton ionization. We study the ionization process in multilayer transition-metal dichalcogenides (TMDs) within the Mott-Wannier model incorporating fully the pronounced anisotropy of these materials. Using complex scaling, we show that the field-dependence of the ionization process is strongly dependent on orientation. Also, we find that direct and indirect excitons behave qualitatively differently as a result of opposite effective anisotropy of these states. Based on first-principles material parameters, an analysis of several important TMDs reveals WSe₂ and MoSe₂ to be superior for applications relying on ionization of direct and indirect excitons, respectively.
Excitons in van der Waals Heterostructures: A theoretical study

Van der Waals heterostructures (vdWHs) represent a novel and largely unexplored class of materials. Since 2013, when Geim and Grigorieva first conceived the stacking of 2D (two-dimensional) materials to create artificial layered structures with tailored properties, a number of promising (opto)electronics devices, e.g. light emitting diodes, solar cells, ultra-fast photodetectors, transistors etc., have been successfully fabricated. It is well established that for isolated 2D semiconductors and vdWHs the optical response is governed by excitonic effects. While it is understood that the reduced amount of electronic screening in freestanding 2D materials is the main origin of extraordinarily strongly bound excitons, a theoretical understanding of excitonic effects and of how the electronic screening is affected for the more complex case of multi-layer structures is still lacking due to the computational limitations of standard ab-initio methods.

In this thesis first-principles models that overcome the limitations of standard ab-initio techniques are developed for the description of dielectric, electronic and excitonic properties in isolated 2D materials and vdWHs. The main contribution is a multi-scale method that seemingly connects the excitonic effects in the monolayer limit to the more challenging case of multi-layered structures. The method is based on the analogy between vdWHs and the popular construction toy Lego. This analogy is much deeper than one would first expect: it is possible to predict the dielectric properties of a vdWH from the dielectric functions of the individual 2D layers, which represent the dielectric genome of the heterostructure. From the vdWH dielectric properties one evaluates the screened interaction between the electron and hole forming the exciton which can then be used in a generalized hydrogenic model to compute exciton binding energies in isolated, supported,
encapsulated 2D semiconductors. The non-locality of the dielectric screening is inherently included in our method and we can successfully describe the non-hydrogenic Rydberg series of low-dimensional systems. This multi-scale method also proves successful when combined with many-body perturbation techniques for accurate prediction of electronic band structure or with complex scaling techniques for exciton dissociation rates in vdWHs. The validity of our techniques is demonstrated through numerous comparison to experimental results.

Ultimately this thesis puts forth a first-principles methodology that allows us to address scientific questions that are beyond the capability of existing state of the art techniques and enables 2D materials researcher to predict and design dielectric, electronic and excitonic properties of general vdWHs.

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Finite Bias Calculations to Model Interface Dipoles in Electrochemical Cells at the Atomic Scale
The structure of an electrochemical interface is not determined by any external electrostatic field, but rather by external chemical potentials. This paper demonstrates that the electric double layer should be understood fundamentally as an internal electric field set up by the atomic structure to satisfy the thermodynamic constraints imposed by the environment. This is captured by the generalized computational hydrogen electrode model, which enables us to make efficient first-principles calculations of atomic scale properties of the electrochemical interface.

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First Principles Calculations of Electronic Excitations in 2D Materials

Since the first reported synthesis of graphene - an atomically thin carbon material - in 2004 there has been a surge of research in discovering other novel two-dimensional materials. The reason is clear: two-dimensional materials are thought to be able to lead to new fast and low-power ultra-thin electronics and high efficiency solar cells. Contrary to many other nano-materials, methods for large scale fabrication and patterning have already been demonstrated and the first real technological applications have already been showcased. Still the technology is very young and the number of well-studied 2D materials are few. However as the list of 2D materials is growing it is necessary to investigate their fundamental structural, electronic and optical properties. These are determined by the atomic and electronic structure of the materials that can quite accurately predicted by computational quantum mechanics methods.

One of these methods, Density Functional Theory (DFT), has been very successful at determining structural properties of 2D materials. It is however well-known that it less accurate when it comes to predicting the energy levels of excited states that are important in order to determine electronic transport, optical and chemical properties. On the other hand it has shown to be a great starting point for a systematic perturbation theory approach to obtain the so-called quasiparticle spectrum. In the GW approximation one considers the considering the potential from a charged excitation as if it is being screened by the electrons in the material. This method has been very successful for calculating quasiparticle energies of bulk materials but results have been more varying for 2D materials. The reason is that the 2D confined electrons are less able to screen the added charge and some of the numerical methods that are efficient for bulk systems become invalid.

In this thesis I describe the study of a set of novel 2D materials and establish their electronic and optical properties using DFT and the GW approximation while taking the reduced screening properly into account as well as taking regard to other numerical problems that have often been neglected. Secondly I show how one can efficiently take the 2D nature into account in the GW approximation and thereby make future calculations require much less computational resources.
Hubbard-U corrected Hamiltonians for non-self-consistent random-phase approximation total-energy calculations: A study of ZnS, TiO$_2$, and NiO

In non-self-consistent calculations of the total energy within the random-phase approximation (RPA) for electronic correlation, it is necessary to choose a single-particle Hamiltonian whose solutions are used to construct the electronic density and noninteracting response function. Here we investigate the effect of including a Hubbard-U term in this single-particle Hamiltonian, to better describe the on-site correlation of 3d electrons in the transitionmetal compounds ZnS, TiO$_2$, and NiO. We find that the RPA lattice constants are essentially independent of U, despite large changes in the underlying electronic structure. We further demonstrate that the non-selfconsistent RPA total energies of these materials have minima at nonzero U. Our RPA calculations find the rutile phase of TiO$_2$ to be more stable than anatase independent of U, a result which is consistent with experiments and qualitatively different from that found from calculations employing U-corrected (semi)local functionals. However we also find that the+U term cannot be used to correct the RPA’s poor description of the heat of formation of NiO.
Light-matter interaction in low-dimensional materials. A theoretical study
In this thesis we have investigated the optical properties of layered and two-dimensional materials for application in the field of plasmonics and metamaterials using Density Functional Theory (DFT). Both of these fields, if successful in their goals, promise new technologies for small scale photonics beyond the diffraction limit. A technological breakthrough of such a caliber would have far reaching consequences such as enabling a practical interface to nano scale integrated electronic circuits or enable the construction of novel devices like a superlens with resolution well beyond diffraction limit. However, the progress of these fields is currently inhibited by large losses that can only be resolved through the discovery of new materials.

Using linear response time-dependent DFT we calculate the optical properties of several experimentally known layered transition metal dichalcogenides (TMDs) with the chemical formula of MX2 where M is a transition metal and X is a chalcogen atom (S, Se, Te). The TMDs constitute an interesting class of materials due to their diverse range of properties including both metals and semi-conductors. We find that the TMDs with group 5 transition metal atoms in the H monolayer
exhibit a special bandstructure in which metallic bands are separated from other valence and conduction bands by finite energy gaps which has the potential to minimize the optical losses by reducing the density of states for scattering. The size of the energy gaps are, however, not sufficiently large to completely eliminate optical losses. We therefore propose a new class of layered materials with the chemical formula 2H-MXY where M is a group 4 transition metal atom, X is a chalcogen atom, and Y is a halogen atom (Cl, Br, I) which increases the size of the energy gaps and significantly reduces optical losses. This entails improved plasmonic normalized propagation lengths and superior lifetimes compared to the best plasmonic material, namely, silver.

We show that all of the TMDs are natural hyperbolic materials, which means that they exhibit a strongly anisotropic dielectric response reflected by a sign-difference in their dielectric tensor resulting in hyperbolic isofrequency contours. Hyperbolic metamaterials obtain their anisotropic response from an artificial sub-wavelength structuring and are limited in their performance by the period of the structuring - the smaller, the better. In contrast, natural hyperbolic materials suffer no such limitation due to their lack of artificial structuring, and indeed, we find a much greater performance for all applications of hyperbolic materials.

The possibility of stacking individual two-dimensional materials into so-called van der Waals heterostructures is perhaps one of the most interesting technological developments in the field of two-dimensional materials. We show that effective medium theory for the dielectric properties of graphene and hexagonal boron nitride heterostructures, which treat the heterostructure as a continuous medium, break down for atomically thin layers due to quantum mechanical effects but also for thick components due to multiple reflection effects. We propose an extended version of effective medium theory to account for the interface layers and show that the effective medium description is improved.

The determination of the quality of materials for application within plasmonics and metamaterials requires an accurate calculation of the optical properties of materials which can be computationally demanding. To reduce the computational costs, the linear tetrahedron method and the employment of symmetries have been implemented which in some cases can reduce the computational costs by a factor of 200.
Making the most of materials computations

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Simple Screened Hydrogen Model of Excitons in Two-Dimensional Materials

We present a generalized hydrogen model for the binding energies (EB) and radii of excitons in two-dimensional (2D) materials that sheds light on the fundamental differences between excitons in two and three dimensions. In contrast to the well-known hydrogen model of three-dimensional (3D) excitons, the description of 2D excitons is complicated by the fact that the screening cannot be assumed to be local. We show that one can consistently define an effective 2D dielectric constant by averaging the screening over the extent of the exciton. For an ideal 2D semiconductor this leads to a simple expression for EB that only depends on the excitonic mass and the 2D polarizability \( \alpha \). The model is shown to produce accurate results for 51 transition metal dichalcogenides. Remarkably, over a wide range of polarizabilities the binding energy becomes independent of the mass and we obtain \( E_{2DB} \approx 3/(4\pi \alpha) \), which explains the recently observed linear scaling of exciton binding energies with band gap. It is also shown that the model accurately reproduces the nonhydrogenic Rydberg series in WS2 and can account for screening from the environment.

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Efficient conversion of photons into electrical current in two-dimensional semiconductors requires, as a first step, the dissociation of the strongly bound excitons into free electrons and holes. Here we calculate the dissociation rates and energy shift of excitons in monolayer MoS$_2$ as a function of an applied in-plane electric field. The dissociation rates are...
obtained as the inverse lifetime of the resonant states of a two-dimensional hydrogenic Hamiltonian which describes the exciton within the Mott-Wannier model. The resonances are computed using complex scaling, and the effective masses and screened electron-hole interaction defining the hydrogenic Hamiltonian are computed from first principles. For field strengths above 0.1 V/nm the dissociation lifetime is shorter than 1 ps, which is below the lifetime associated with competing decay mechanisms. Interestingly, encapsulation of the MoS$_2$ layer in just two layers of hexagonal boron nitride (hBN), enhances the dissociation rate by around one order of magnitude due to the increased screening. This shows that dielectric engineering is an effective way to control exciton lifetimes in two-dimensional materials.

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Adiabatic-connection fluctuation-dissipation DFT for the structural properties of solids - The renormalized ALDA and electron gas kernels

We present calculations of the correlation energies of crystalline solids and isolated systems within the adiabatic-connection fluctuation-dissipation formulation of density-functional theory. We perform a quantitative comparison of a set of model exchange-correlation kernels originally derived for the homogeneous electron gas (HEG), including the recently introduced renormalized adiabatic local-density approximation (rALDA) and also kernels which (a) satisfy known exact limits of the HEG, (b) carry a frequency dependence, or (c) display a $1/k^2$ divergence for small wavevectors. After generalizing the kernels to inhomogeneous systems through a reciprocal-space averaging procedure, we calculate the lattice constants and bulk moduli of a test set of 10 solids consisting of tetrahedrally bonded semiconductors (C, Si, SiC), ionic compounds (MgO, LiCl, LiF), and metals (Al, Na, Cu, Pd). We also consider the atomization energy of the H$_2$ molecule. We compare the results calculated with different kernels to those obtained from the random-phase approximation (RPA) and to experimental measurements. We demonstrate that the model kernels correct the RPA's tendency to overestimate the magnitude of the correlation energy whilst maintaining a high-accuracy description of structural properties.
Amongst the X(Sn,Pb)Y₃ perovskites currently under scrutiny for their photovoltaic applications, the cubic B−α phase of CsSnI₃ is arguably the best characterized experimentally. Yet, according to the standard harmonic theory of phonons, this deceptively simple phase should not exist at all due to rotational instabilities of the SnI₆ octahedra. Here, employing self-consistent phonon theory, we show that these soft modes are stabilized at experimental conditions through anharmonic phonon-phonon interactions between the Cs ions and their iodine cages. We further calculate the renormalization of the electronic energies due to vibrations and find an unusual opening of the band gap, estimated as 0.24 and 0.11 eV at 500 and 300 K, which we attribute to the stretching of Sn-I bonds. Our work demonstrates the important role of temperature in accurately describing these materials.
Band-gap engineering of functional perovskites through quantum confinement and tunneling

An optimal band gap that allows for a high solar-to-fuel energy conversion efficiency is one of the key factors to achieve sustainability. We investigate computationally the band gaps and optical spectra of functional perovskites composed of layers of the two cubic perovskite semiconductors BaSnO$_3$ and BaTaO$_2$N. Starting from an indirect gap of around 3.3 eV for BaSnO$_3$ and a direct gap of 1.8 eV for BaTaO$_2$N, different layerings can be used to design a direct gap of the functional perovskite between 2.3 and 1.2 eV. The variations of the band gap can be understood in terms of quantum confinement and tunneling. We also calculate the light absorption of the different heterostructures and demonstrate a large sensitivity to the detailed layering.
Calculated optical absorption of different perovskite phases
We present calculations of the optical properties of a set of around 80 oxides, oxynitrides, and organometal halide cubic and layered perovskites (Ruddlesden-Popper and Dion-Jacobson phases) with a bandgap in the visible part of the solar spectrum. The calculations show that for different classes of perovskites the solar light absorption efficiency varies greatly depending not only on bandgap size and character (direct/indirect) but also on the dipole matrix elements. The oxides exhibit generally a fairly weak absorption efficiency due to indirect bandgaps while the most efficient absorbers are found in the classes of oxynitride and organometal halide perovskites with strong direct transitions.
We present a comprehensive first-principles study of the electronic structure of 51 semiconducting monolayer transition-metal dichalcogenides and -oxides in the 2H and 1T hexagonal phases. The quasiparticle (QP) band structures with spin-orbit coupling are calculated in the G(0)W(0) approximation, and comparison is made with different density functional theory descriptions. Pitfalls related to the convergence of GW calculations for two-dimensional (2D) materials are discussed together with possible solutions. The monolayer band edge positions relative to vacuum are used to estimate the band alignment at various heterostructure interfaces. The sensitivity of the band structures to the in-plane lattice constant is analyzed and rationalized in terms of the electronic structure. Finally, the q-dependent dielectric functions and effective electron and hole masses are obtained from the QP band structure and used as input to a 2D hydrogenic model to estimate exciton binding energies. Throughout the paper we focus on trends and correlations in the electronic structure rather than detailed analysis of specific materials. All the computed data is available in an open database.

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Computational design of molecules for dye sensitized solar cells and nano electronics

The huge increase in computational power has enabled the use of high-throughput computational screening methods for many purposes. In combination with more detailed computational studies, this provides a powerful tool in the search for new materials and molecules useful for e.g. photovoltaics. This is illustrated in this thesis, where a high-throughput Density Functional Theory study of a total of 5145 porphyrin based dye molecules is presented. Initially, the structures of the dyes are optimized and the frontier energy orbital energies calculated. Following this, the dyes are scored for use in a dye sensitized solar cell (DSSC) in terms of a loss-less level alignment quality. This scoring only takes into account a simplified absorption spectrum of the dye in combination with the alignment between the molecular levels, the semi-conductor conduction band edge and the redox mediator. To improve on this, the effect of the free energy barrier associated with the dye regeneration reaction is included through extensive molecular dynamics simulations for a simple model dye, followed by an extrapolation of the result to the 5145 porphyrins. This model succeeds in rediscovering high efficiency dyes and
suggests that the next generation of high efficiency porphyrin dyes may utilize a titanium metal center. Furthermore, the large internal reorganization energies calculated for the octahedral cobalt complexes, used as redox mediators, lead to the requirement of a large driving force for the regeneration reaction. Hence, using redox mediators with a lower internal reorganization energy would allow for a less constrained choice of dye, possibly boosting the efficiency. The obtained data is furthermore used to search for suitable pairs of porphyrins for a novel type of DSSC schemes, using two dyes in a molecular two-photon tandem approach. Here, a high current is sacrificed for a larger voltage. As a smaller current is however often associated with a better fill-factor, the proposed scheme may lead to an increase in the efficiency. Specific candidates for the different schemes are identified and the resulting setups have theoretically obtainable open-circuit voltages exceeding 1.5 V.

Creating a metal-molecule-metal junction allows tuning the conductance through the junction by manipulating the molecular energy levels. In this thesis a computational approach to model the conductance as a function of the applied bias voltage, shifting the molecular levels, for a redox active molecule is presented and compared to experimental results. Here, it is shown that shifting the molecular energy levels in and out of resonance with the Fermi level of the electrodes, allows for a standard tuning of the conductance. In addition to this, reversibly changing the redox state, allows for switching quantum interference on and off, shifting the conductance by an order of magnitude. The simple computational model used is furthermore qualitatively found to be in very good agreement with experiments. A different way of tuning the conductance through a molecular junction, is by controlling the junction geometry. This is achieved by designing a molecule with two sets of anchor groups, which bind to gold with significantly different strengths. Hence, it is proposed that the geometry can be controlled by chemical passivisation of one type of anchor group. Using a simple computational model, this experimental hypothesis is verified and the change in conductance upon changing junction geometry is reproduced.

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Computational Discovery of Sustainable Energy Materials

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Computational Screening of Energy Materials
The current energy consumption of the world’s population relies heavily on fossil fuels. Unfortunately, the consumption of fossil fuels not only results in the emission of greenhouse gases which have deleterious effect on the environment but also the fossil fuel reserve is limited. Therefore, it is the need of the hour to search for environmentally benign renewable energy resources. The biggest source of the renewable energy is our sun and the immense energy it provides can be used to power the whole planet. However, an efficient way to harvest the solar energy to meet all the energy demand has not been realized yet.
A promising way to utilize the solar energy is the photon assisted water splitting. The process involves the absorption of sunlight with a semiconducting material (or a photoabsorber) and the generated electron-hole pair can be used to produce hydrogen by splitting the water. However, a single material cannot accomplish the whole process of the hydrogen evolution. In order do so, a material should be able to absorb the sunlight and generate the electronhole pairs and evolve hydrogen at the cathode and oxygen at anode using the generated electron and hole respectively.

This thesis using first-principle calculations explores materials for the light absorption with the bandgap, band edge positions and the stability in aqueous conditions as descriptors. This strategy results in a handful of materials which can act as good photoabsorbers for the water splitting reaction. Additionally, strategies to tune the bandgap for different applications is also explored. To carry out the cathode reaction, two-dimensional metal dichalcogenides and oxides are explored with a suggestion of few potential candidates for the hydrogen evolution reaction.

The thermodynamics of all the above process requires an accurate description of the energies with the first-principle calculations. Therefore, along this line the accuracy and predictability of the Meta-Generalized Gradient Approximation functional with Bayesian error estimation is also assessed.

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**Controlling Electrical Conductance through a π-Conjugated Cruciform Molecule by Selective Anchoring to Gold Electrodes**

Tuning charge transport at the single-molecule level plays a crucial role in the construction of molecular electronic devices. Introduced herein is a promising and operationally simple approach to tune two distinct charge-transport pathways through a cruciform molecule. Upon in situ cleavage of triisopropylsilyl groups, complete conversion from one junction type to another is achieved with a conductance increase by more than one order of magnitude, and it is consistent with predictions from ab initio transport calculations. Although molecules are well known to conduct through different orbitals (either HOMO or LUMO), the present study represents the first experimental realization of switching between HOMO- and LUMO-dominated transport within the same molecule.

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Controlling Electrical Conductance through a π-Conjugated Cruciform Molecule by Selective Anchoring to Gold Electrodes

Tuning charge transport at the single-molecule level plays a crucial role in the construction of molecular electronic devices. Introduced herein is a promising and operationally simple approach to tune two distinct charge-transport pathways through a cruciform molecule. Upon in situ cleavage of trisopropylsilyl groups, complete conversion from one junction type to another is achieved with a conductance increase by more than one order of magnitude, and it is consistent with predictions from ab initio transport calculations. Although molecules are well known to conduct through different orbitals (either HOMO or LUMO), the present study represents the first experimental realization of switching between HOMO- and LUMO-dominated transport within the same molecule.
Design of two-photon molecular tandem architectures for solar cells by ab initio theory

An extensive database of spectroscopic properties of molecules from ab initio calculations is used to design molecular complexes for use in tandem solar cells that convert two photons into a single electron–hole pair, thereby increasing the output voltage while covering a wider spectral range. Three different architectures are considered: the first two involve a complex consisting of two dye molecules with appropriately matched frontier orbitals, connected by a molecular diode. Optimized combinations of dye molecules are determined by taking advantage of our computational database of the structural and energetic properties of several thousand porphyrin dyes. The third design is a molecular analogy of the intermediate band solar cell, and involves a single dye molecule with strong intersystem crossing to ensure a long lifetime of the intermediate state. Based on the calculated energy levels and molecular orbitals, energy diagrams are presented for the individual steps in the operation of such tandem solar cells. We find that theoretical open circuit voltages of up to 1.8 V can be achieved using these tandem designs. Questions about the practical implementation of prototypical devices, such as the synthesis of the tandem molecules and potential loss mechanisms, are addressed.
This thesis addresses the electron transport in molecular junctions, focusing on the energy level alignment and correlation effects. Various levels of theory have been applied to study the structural and electronic effects in different molecular junctions, starting from the single particle density functional theory (DFT) description over the semi-empirical DFT+$\Sigma$, to the sophisticated fully self-consistent GW approach. We find that in order to obtain a quantitative description of the conductance and the thermopower, it is necessary to go beyond the single particle description.

The effect of side groups on the benzene-diamine (BDA) molecule has furthermore been studied and it is found that the correct energy level alignment for the BDA molecule in Au contacts is only captured by the GW approach. Consequently, the GW approach provides an accurate description for the conductance change resulting from the side groups. The failure of the DFT based description is due to the strong energy level pinning when the BDA molecule is in contact with Au contacts.

The effect of contact geometries on the conductance and the thermopower has also been addressed. It is found that both GW and the DFT+$\Sigma$ with a certain image charge position are in quantitative agreement with the experiments, while pure DFT is not. This is the consequence of the accurate energy level alignment, where the DFT+$\Sigma$ method corrects the self-interaction error in the standard DFT functional and uses a static image charge model to include the image charge effect on the energy level renormalization.

Additionally, the gating of the 4,4′-bipyridine (44BP) molecule contacted to either Ni or Au electrodes has been investigated. Here it is found that the gating mechanism is conceptually different between two cases. In the case of Ni contacts where the lowest unoccupied molecular level (LUMO) of the 44BP molecule hybridizes strongly with Ni 3d orbitals, the gating is auxiliary by the so-called spinterface.
Finally, the correlation effect of the image charge beyond the energy level renormalization has been studied. It is shown that the finite response time of the electrodes to form image charge can suppress the conductance by a factor of 2. This correlation effect is only captured in the GW approach.

Excitons in van der Waals heterostructures: The important role of dielectric screening
The existence of strongly bound excitons is one of the hallmarks of the newly discovered atomically thin semiconductors. While it is understood that the large binding energy is mainly due to the weak dielectric screening in two dimensions, a systematic investigation of the role of screening on two-dimensional (2D) excitons is still lacking. Here we provide a critical assessment of a widely used 2D hydrogenic exciton model, which assumes a dielectric function of the form \( \varepsilon(q) = 1 + 2 \pi \alpha \), and we develop a quasi-2D model with a much broader applicability. Within the quasi-2D picture, electrons and holes are described as in-plane point charges with a finite extension in the perpendicular direction, and their interaction is screened by a dielectric function with a nonlinear q dependence which is computed ab initio. The screened interaction is used in a generalized Mott-Wannier model to calculate exciton binding energies in both isolated and supported 2D materials. For isolated 2D materials, the quasi-2D treatment yields results almost identical to those of the strict 2D model, and both are in good agreement with ab initio many-body calculations. On the other hand, for more complex structures such as supported layers or layers embedded in a van der Waals heterostructure, the size of the exciton in reciprocal space extends well beyond the linear regime of the dielectric function, and a quasi-2D description has to replace the 2D one. Our methodology has the merit of providing a seamless connection between the strict 2D limit of isolated monolayer materials and the more bulk-like screening characteristics of supported 2D materials or van der Waals heterostructures.
Importance of the Reorganization Energy Barrier in Computational Design of Porphyrin-Based Solar Cells with Cobalt-Based Redox Mediators

The shift from iodide-based redox mediators in dye-sensitized solar cells toward octahedral cobalt complexes has led to a significant increase in the efficiency. However, due to the nature of this type of complexes the driving force required for the regeneration of the dye is very high, and this limits the achievable efficiency. Here we show that the large driving force is a direct consequence of the large reorganization energy of the dye regeneration reaction. The reorganization energies for charge transfer between a simple zinc porphyrin dye and two popular cobalt-based redox mediators is calculated using ab
initio molecular dynamics with explicit solvent. These results are then combined with a Marcus-based extrapolation scheme to obtain the reorganization energies of more than 5000 porphyrin-based dyes. We propose a scheme for scoring the performance of the porphyrin dyes, which is able to identify already known high-performance dyes in addition to a number of even better candidates. Our analysis shows that the large internal reorganization energy of the Co-based redox mediators is an obstacle for achieving higher efficiencies.

**General information**

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Scopus rating (2008): SJR 1.856 SNIP 1.033
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Improved description of metal oxide stability: Beyond the random phase approximation with renormalized kernels

The renormalized adiabatic PBE (rAPBE) method has recently been shown to comprise a significant improvement over the random phase approximation (RPA) for total energy calculations of simple solids and molecules. Here we consider the formation energies of 19 group I and II metal oxides and a few transition-metal oxides. The mean absolute error relative to experiments is 0.21 eV and 0.38 eV per oxygen atom for rAPBE and RPA, respectively, and thus the rAPBE method greatly improves the description of metal-oxygen bonds across a wide range of oxides. The failure of the RPA can be partly attributed to the lack of error cancellation between the correlation energy of the oxide on the one hand and the bulk metal and oxygen molecule on the other hand, which are all separately predicted much too negative by the RPA. We ascribe the improved performance of the rAPBE to its significantly better description of absolute correlation energies which reduces the need for error cancellation. The rAPBE is just one out of an entire class of renormalized exchange-correlation kernels which should be further investigated.
Plasmonic eigenmodes in individual and bow-tie graphene nanotriangles

In classical electrodynamics, nanostructured graphene is commonly modeled by the computationally demanding problem of a three-dimensional conducting film of atomic-scale thickness. Here, we propose an efficient alternative two-dimensional electrostatic approach where all calculation procedures are restricted to the graphene sheet. Furthermore, to explore possible quantum effects, we perform tight-binding calculations, adopting a random-phase approximation. We investigate multiple plasmon modes in 20 nm equilateral triangles of graphene, treating the optical response classically as well as quantum mechanically. Compared to the classical plasmonic spectrum which is "blind" to the edge termination, we find that the quantum plasmon frequencies exhibit blueshifts in the case of armchair edge termination of the underlying atomic lattice, while redshifts are found for zigzag edges. Furthermore, we find spectral features in the zigzag case which are associated with electronic edge states not present for armchair termination. Merging pairs of triangles into dimers, plasmon hybridization leads to energy splitting that appears strongest in classical calculations while splitting is lower for armchair edges and even more reduced for zigzag edges. Our various results illustrate a surprising phenomenon: Even 20 nm large graphene structures clearly exhibit quantum plasmonic features due to atomic-scale details in the edge.
Quantum theory of plasmons in nanostructures

In this thesis, ab initio quantum-mechanical calculations are used to study the properties of plasmons in nanostructures that involve atomic length-scales. The plasmon is an electronic excitation that corresponds to oscillations in the electron charge density in metals, often visualized as water ripples in a pond where the water represents a sea of free electrons. Plasmons on metal surfaces and in nanostructured materials, such as metal nanoparticles and atomically thin two-dimensional materials, have several technological applications due to their ability to confine light on nanoscale. For a theoretical description of plasmon in such materials, where the electrons are heavily confined in one or more directions, a quantum mechanical description of the electrons in the material is necessary. In this thesis, the ab initio methods Density functional theory (DFT) and linear response time-dependent DFT are applied to calculate the properties of plasmons in nanostructures in different dimensions. In order to identify and visualize localized plasmon modes, a method for calculating plasmon eigenmodes within the ab initio framework has been developed. In the studied materials, quantum mechanical effects such as coupling to single-electronic transitions, electron spill-out from the surface, tunneling,
and spatial non-locality, are shown to alter the plasmon excitations. The studied systems include two-dimensional materials, such as thin metal films, monolayer transition metal dichalcogenides, and graphene. Here, also van der Waals heterostructures (vdWh), which are stacks of different twodimensional materials, are considered. A new multi-scale approach for calculating the dielectric-function of vdWh, which extends \textit{ab initio} accuracy to the description of hundreds of atomic layers, is presented. Also, one-dimensional plasmons are studied in the case of atomically thin nanowires and edge-states of MoS$_2$. 

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**Single-Molecule Electrochemical Transistor Utilizing a Nickel-Pyridyl Spinterface**

Using a scanning tunnelling microscope break-junction technique, we produce 4,4′-bipyridine (44BP) single-molecule junctions with Ni and Au contacts. Electrochemical control is used to prevent Ni oxidation and to modulate the conductance of the devices via nonredox gating - the first time this has been shown using non-Au contacts. Remarkably the conductance and gain of the resulting Ni-44BP-Ni electrochemical transistors is significantly higher than analogous Au-based devices. Ab-initio calculations reveal that this behavior arises because charge transport is mediated by spin-polarized Ni d-electrons, which hybridize strongly with molecular orbitals to form a "spinterface". Our results highlight the important role of the contact material for single-molecule devices and show that it can be varied to provide control of charge and spin transport.

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Strain sensitivity of band gaps of Sn-containing semiconductors

Tuning of band gaps of semiconductors is a way to optimize materials for applications within photovoltaics or as photocatalysts. One way to achieve this is through applying strain to the materials. We investigate the effect of strain on a range of Sn-containing semiconductors using density functional theory and many-body perturbation theory calculations. We find that the band gaps of bulk Sn oxides with SnO$_6$ octahedra are highly sensitive to volumetric strain. By applying a small isotropic strain of 2% (-2%), a decrease (increase) of band gaps as large as 0.8 to 1.0 eV are obtained. We attribute the ultrahigh strain sensitivity to the pure Sn s-state character of the conduction-band edges. Other Sn-containing compounds may show both increasing and decreasing gaps under tensile strain and we show that the behavior can be understood by analyzing the role of the Sn s states in both the valence and the conduction bands.
The dielectric genome of van der Waals heterostructures

Vertical stacking of two-dimensional (2D) crystals, such as graphene and hexagonal boron nitride, has recently lead to a new class of materials known as van der Waals heterostructures (vdWHs) with unique and highly tunable electronic properties. Ab-initio calculations should in principle provide a powerful tool for modeling and guiding the design of vdWHs, but in their traditional, form such calculations are only feasible for commensurable structures with a few layers. Here we show that the dielectric properties of realistic, incommensurable vdWHs comprising hundreds of layers can be calculated with ab-initio accuracy using a multi-scale approach where the dielectric functions of the individual layers (the dielectric building blocks) are coupled simply via their long-range Coulomb interaction. We use the method to illustrate the 2D-3D dielectric transition in multi-layer MoS$_2$ crystals, the hybridization of quantum plasmons in large graphene/hBN heterostructures, and to demonstrate the intricate effect of substrate screening on the non-Rydberg exciton series in supported WS$_2$. The dielectric building blocks for a variety of 2D crystals are available in an open database together with the software for solving the coupled electrodynamics equations.
Tuning the Schottky Barrier at the Graphene/MoS2 Interface by Electron Doping: Density Functional Theory and Many-Body Calculations

Using ab initio calculations we investigate the energy level alignment at the graphene/MoS2 heterostructure and the use of electron doping as a strategy to lower the Schottky barrier and achieve a low-resistance Ohmic contact. For the neutral heterostructure, density functional theory (DFT) with a generalized gradient approximation predicts a Schottky barrier height of 0.18 eV, whereas the G0W0 method increases this value to 0.60 eV. While the DFT band gap of MoS2 does not change when the heterostructure is formed, the G0W0 gap is reduced by 0.30 eV as a result of the enhanced screening by the graphene layer. In contrast to the case of metal substrates, where the band alignment is governed by Pauli repulsion-induced interface dipoles, the graphene/MoS2 heterostructure shows only a negligible interface dipole. As a consequence, the band alignment at the neutral heterostructure is not changed when the two layers are brought into contact. We systematically follow the band alignment as a function of doping concentration and find that the Fermi level of the graphene crosses the MoS2 conduction band at a doping concentration of around $10^{12}$ cm$^{-2}$. The variation of the energy levels with doping concentration is shown to be mainly governed by the electrostatic potential resulting from the doping charge.

General information
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Organisations: Center for Atomic-scale Materials Design, Department of Physics, Center for Nanostructured Graphene
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Scopus rating (2014): SJR 2.027 SNIP 1.448 CiteScore 5.08
Web of Science (2014): Indexed yes
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Scopus rating (2013): SJR 2.134 SNIP 1.439 CiteScore 5.14
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We explore the possibilities of hydrogen evolution by basal planes of 2D metal dichalcogenides and oxides in the 2H and 1T class of structures using the hydrogen binding energy as a computational activity descriptor. For some groups of systems like the Ti, Zr, and Hf dichalcogenides the hydrogen bonding to the 2H structure is stronger than that to the 1T structure, while for the Cr, Mo, and W dichalcogenides the behavior is opposite. This is rationalized by investigating shifts in the chalcogenide p levels comparing the two structures. We find that usually for a given material only at most one of the two phases will be active for the hydrogen evolution reaction; however, in most cases the two phases are very close in formation energy, opening up the possibility for stabilizing the active phase. The study points to many new possible 2D HER materials beyond the few that are already known.
Accurate Ground-State Energies of Solids and Molecules from Time-Dependent Density-Functional Theory

We demonstrate that ground-state energies approaching chemical accuracy can be obtained by combining the adiabatic-connection fluctuation-dissipation theorem with time-dependent density-functional theory. The key ingredient is a renormalization scheme, which eliminates the divergence of the correlation hole characteristic of any local kernel. This new class of renormalized kernels gives a significantly better description of the short-range correlations in covalent bonds compared to the random phase approximation (RPA) and yields a fourfold improvement of RPA binding energies in both molecules and solids. We also consider examples of barrier heights in chemical reactions, molecular adsorption, and graphene interacting with metal surfaces, which are three examples where the RPA has been successful. In these cases, the renormalized kernel provides results that are of equal quality or even slightly better than the RPA, with a similar computational cost.

General information
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Bandgap calculations and trends of organometal halide perovskites

Energy production from the Sun requires a stable efficient light absorber. Promising candidates in this respect are organometal perovskites (ABX₃), which have been intensely investigated during the last years. Here, we have performed electronic structure calculations of 240 perovskites composed of Cs, CH₃NH₃, and HC(NH₂)₂ as A-cation, Sn and Pb as B-ion, and a combination of Cl, Br, and I as anions. The calculated gaps span over a region from 0.5 to 5.0 eV. In addition, the trends over bandgaps have been investigated: the bandgap increases with an increase of the electronegativities of the constituent species, while it reduces with an increase of the lattice constants of the system.

Calculated Pourbaix Diagrams of Cubic Perovskites for Water Splitting: Stability Against Corrosion

We use density functional theory calculations to investigate the stability of cubic perovskites for photo-electrochemical water splitting taking both materials in their bulk crystal structure and dissolved phases into account. The method is validated through a detailed comparison of the calculated and experimental Pourbaix diagrams for TiO₂ and ZnO. For a class of 23 oxides, oxynitrides, and oxyfluorides, which were recently proposed as candidates for one-photon water splitting, our calculations predict most of the materials to be stable at potentials around the water red-ox level. The oxides
become less stable at lower potentials, while the oxynitrides become unstable at higher potentials. We discuss the implications of these findings for the problem of photo-corrosion of water splitting electrodes.
Cross-conjugation and quantum interference: a general correlation?
We discuss the relationship between the pi-conjugation pattern, molecular length, and charge transport properties of molecular wires, both from an experimental and a theoretical viewpoint. Specifically, we focus on the role of quantum interference in the conductance properties of cross-conjugated molecules. For this, we compare experiments on two series of dithiolated wires. The first set we synthesized consists of three dithiolated oligo(phenylene ethynylene) (OPE) benchmark compounds with increasing length. The second series synthesized comprises three molecules with different pi-conjugation patterns, but identical lengths, i.e., an anthracene (linear conjugation), an anthraquinone (cross-conjugation), and a dihydroanthracene (broken conjugation) derivative. To benchmark reliable trends, conductance experiments on these series have been performed by various techniques. Here, we compare data obtained by conductive-probe atomic force microscopy (CP-AFM) for self-assembled monolayers (SAMs) with single-molecule break junction and multi-molecule EGaIn data from other groups. For the benchmark OPE-series, we consistently find an exponential decay of the conductance with molecular length characterized by beta = 0.37 +/- 0.03 angstrom(-1) (CP-AFM). Remarkably, for the second series, we do not only find that the linearly conjugated anthracene-containing wire is the most conductive, but also that the cross-conjugated anthraquinone-containing wire is less conductive than the broken-conjugated derivative. We attribute the low conductance values for the cross-conjugated species to quantum interference effects. Moreover, by theoretical modeling, we show that destructive quantum interference is a robust feature for cross-conjugated structures and that the energy at which complete destructive interference occurs can be tuned by the choice of side group. The latter provides an outlook for future devices in this fascinating field connecting chemistry and physics.
Development and testing of new exchange correlation functionals

Catalysts are used in 90% of the world's chemical processes to produce 60% of its chemical products, and they are thus very important to our modern society. We therefore seek to better understand current catalytic materials, so that we can find alternatives that will improve the energy efficiency, selectivity or similar of current chemical processes, or to make new technologies economical feasible. Kohn-Sham density functional theory (KS-DFT) has proven to be a powerful theory to find trends in current catalytic materials, which can empower a more informed search for better alternatives. KS-DFT relies...
on accurate and efficient approximations to the exchange correlation functional, yet these functional approximations have lacked a systematic way to estimate the underlying uncertainties. A Bayesian error estimation approach provides a mechanism for calculating approximative uncertainties, and so accurate, computationally feasible exchange-correlation approximations that incorporate it have been called for. This thesis presents significant steps forwards towards providing general applicable exchange-correlation functional approximations with Bayesian error estimation capabilities. A semi-empirical approach was used with a machine learning toolset to improve accuracy and transferability of the functional approximations. The toolset includes Tikhonov regularization of smoothness in a transformed model space, for ensuring sensible model solutions; an explicit model compromise with a geometric mean loss function, for ensuring generally applicable models; a robust MM-estimator loss function, for ensuring resistance to outliers in data; and a hierarchical bootstrap resampling estimating prediction error validation method, for selecting the model complexity that provide best transferability outside the training data. Three new semi-empirical functional approximations have been made: BEEF-vdW, mBEEF, and mBEEFvdW. It is shown that these functionals are able balance the accuracy of predicting energetics of covalent and non-covalent chemistry better than any comparative functional that we have tested, and they could therefore become the functional approximations of choice for understanding chemical processes at the solid-gas and solid-liquid interfaces.

General information
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Dynamical image-charge effect in molecular tunnel junctions: Beyond energy level alignment
When an electron tunnels between two metal contacts it temporarily induces an image charge (IC) in the electrodes which acts back on the tunneling electron. It is usually assumed that the IC forms instantaneously such that a static model for the image potential applies. Here we investigate how the finite IC formation time affects charge transport through a molecule suspended between two electrodes. For a single-level model, an analytical treatment shows that the conductance is suppressed by a factor $Z(2)$, where $Z$ is the quasiparticle renormalization factor, compared to the static IC approximation. We show that $Z$ can be expressed either in terms of the plasma frequency of the electrode or as the overlap between electrode wave functions corresponding to an empty and filled level, respectively. First-principles GW calculations for benzene-diamine connected to gold electrodes show that the dynamical corrections can reduce the conductance by more than a factor of two when compared to static GW or density functional theory where the molecular energy levels have been shifted to match the exact quasiparticle levels.

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Electrochemical Control of Single-Molecule Conductance by Fermi-Level Tuning and Conjugation Switching

Controlling charge transport through a single molecule connected to metallic electrodes remains one of the most fundamental challenges of nanoelectronics. Here we use electrochemical gating to reversibly tune the conductance of two different organic molecules, both containing anthraquinone (AQ) centers, over >1 order of magnitude. For electrode potentials outside the redox-active region, the effect of the gate is simply to shift the molecular energy levels relative to the metal Fermi level. At the redox potential, the conductance changes abruptly as the AQ unit is oxidized/reduced with an accompanying change in the conjugation pattern between linear and cross conjugation. The most significant change in conductance is observed when the electron pathway connecting the two electrodes is via the AQ unit. This is consistent with the expected occurrence of destructive quantum interference in that case. The experimental results are supported by an excellent agreement with ab initio transport calculations.
New Light-Harvesting Materials Using Accurate and Efficient Bandgap Calculations

Electronic bandgap calculations are presented for 2400 experimentally known materials from the Materials Project database and the bandgaps, obtained with different types of functionals within density functional theory and (partial) self-consistent GW approximation, are compared for 20 randomly chosen compounds forming an unconventional set of ternary and quaternary materials. It is shown that the computationally cheap GLLB-SC potential gives results in good agreement (around 15%) with the more advanced and demanding eigenvalue-self-consistent GW. This allows for a high-throughput screening of materials for different applications where the bandgaps are used as descriptors for the efficiency of a photoelectrochemical device. Here, new light harvesting materials are proposed to be used in a one-photon photoelectrochemical device for water splitting by combining the estimation of the bandgaps with the stability analysis using Pourbaix diagrams and with the evaluation of the position of the band edges. Using this methodology, 25 candidate materials are obtained and 5 of them appear to have a realistic possibility of being used as photocatalyst in a one-photon water splitting device. © 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

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Optimizing porphyrins for dye sensitized solar cells using large-scale ab initio calculations

In the search for sustainable energy sources, dye sensitized solar cells (DSSCs) represent an attractive solution due to their low cost, relatively high efficiencies, and flexible design. Porphyrin-based dyes are characterized by strong absorption in the visible part of the spectrum and easy customization allowing their electronic properties to be controlled by structural variations. Here we present a computational screening study of more than 5000 porphyrin-based dyes obtained by modifying the porphyrin backbone (metal center and axial ligands), substituting hydrogen by fluorine, and adding different side and anchoring groups. Based on the calculated frontier orbital energies and optical gaps we quantify the energy level alignment with the TiO2 conduction band and different redox mediators. An analysis of the energy level-structure relationship reveals a significant structural diversity among the dyes with the highest level alignment quality, demonstrating the large degree of flexibility in porphyrin dye design. As a specific example of dye optimization, we show that the level alignment of the high efficiency record dye YD2-o-C8 [Yella et al., Science, 2011, 334, 629-634] can be significantly improved by modest structural variations. All the presented data have been stored in a publicly available database.
Plasmons on the edge of MoS$_2$ nanostructures

Using ab initio calculations we predict the existence of one-dimensional (1D), atomically confined plasmons at the edges of a zigzag MoS$_2$ nanoribbon. The strongest plasmon originates from a metallic edge state localized on the sulfur dimers.
decorating the Mo edge of the ribbon. A detailed analysis of the dielectric function reveals that the observed deviations from the ideal 1D plasmon behavior result from single-particle transitions between the metallic edge state and the valence and conduction bands of the MoS$_2$ sheet. The Mo and S edges of the ribbon are clearly distinguishable in calculated spatially resolved electron energy loss spectrum owing to the different plasmonic properties of the two edges. The edge plasmons could potentially be utilized for tuning the photocatalytic activity of MoS$_2$ nanoparticles.

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Scopus rating (2016): CiteScore 3.16
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 2
Scopus rating (2015): SJR 1.933 SNIP 0.94 CiteScore 2.8
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 2
Scopus rating (2014): SJR 2.667 SNIP 1.262 CiteScore 3.3
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 2
Scopus rating (2013): SJR 2.785 SNIP 1.339 CiteScore 3.55
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 2
Scopus rating (2012): SJR 3.206 SNIP 1.394 CiteScore 3.57
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BFI (2011): BFI-level 2
Scopus rating (2011): SJR 3.382 SNIP 1.438 CiteScore 3.61
ISI indexed (2011): ISI indexed yes
Web of Science (2011): Indexed yes
BFI (2010): BFI-level 2
Scopus rating (2010): SJR 3.417 SNIP 1.451
Web of Science (2010): Indexed yes
BFI (2009): BFI-level 2
Scopus rating (2009): SJR 3.109 SNIP 1.474
Web of Science (2009): Indexed yes
BFI (2008): BFI-level 1
Scopus rating (2008): SJR 2.982 SNIP 1.524
Web of Science (2008): Indexed yes
Scopus rating (2007): SJR 2.923 SNIP 1.546
Web of Science (2007): Indexed yes
Scopus rating (2006): SJR 2.796 SNIP 1.56
Web of Science (2006): Indexed yes
Simultaneous description of conductance and thermopower in single-molecule junctions from many-body ab initio calculations

We investigate the electronic conductance and thermopower of a single-molecule junction consisting of bis-(4-aminophenyl) acetylene (B4APA) connected to gold electrodes. We use nonequilibrium Green's function methods in combination with density-functional theory (DFT) and the many-body GW approximation. To simulate recent break junction experiments, we calculate the transport properties of the junction as it is pulled apart. For all junction configurations, DFT with a standard semilocal functional overestimates the conductance by almost an order of magnitude, while the thermopower is underestimated by up to a factor of 3, except for the most highly stretched junction configurations. In contrast, the GW results for both conductance and thermopower are in excellent agreement with experiments for a wide range of electrode separations. We show that the GW self-energy not only renormalizes the molecular energy levels but also the coupling strength. The latter is a consequence of the finite response time associated with the electronic screening in the metal electrodes.
Static correlation beyond the random phase approximation: Dissociating H2 with the Bethe-Salpeter equation and time-dependent GW

We investigate various approximations to the correlation energy of a H2 molecule in the dissociation limit, where the ground state is poorly described by a single Slater determinant. The correlation energies are derived from the density response function and it is shown that response functions derived from Hedin's equations (Random Phase Approximation (RPA), Time-dependent Hartree-Fock (TDHF), Bethe-Salpeter equation (BSE), and Time-Dependent GW) all reproduce the correct dissociation limit. We also show that the BSE improves the correlation energies obtained within RPA and TDHF significantly for intermediate binding distances. A Hubbard model for the dimer allows us to obtain exact analytical results for the various approximations, which is readily compared with the exact diagonalization of the model. Moreover, the model is shown to reproduce all the qualitative results from the ab initio calculations and confirms that BSE greatly improves the RPA and TDHF results despite the fact that the BSE excitation spectrum breaks down in the dissociation limit. In contrast, second order screened exchange gives a poor description of the dissociation limit, which can be attributed to the fact that it cannot be derived from an irreducible response function. (C) 2014 AIP Publishing LLC.
Temperature effects on quantum interference in molecular junctions

A number of experiments have demonstrated that destructive quantum interference (QI) effects in molecular junctions lead to very low conductances even at room temperature. On the other hand, another recent experiment showed increasing conductance with temperature which was attributed to decoherence effects destroying QI at finite temperatures. Here we study the influence of finite temperatures and electron-phonon interactions on QI in molecular junctions. Two different models leading to two inherently different types of QI effects are considered. Each model is exemplified by specific molecules and studied using first-principles calculations. We find that the molecules exhibiting QI show a much stronger temperature dependence of the conductance compared to molecules without QI. However, the large QI-induced suppression of the conductance remains, showing that QI effects are indeed robust against finite temperatures and inelastic scattering.

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Authors: Markussen, T. (Intern), Thygesen, K. S. (Intern)
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Scopus rating (2016): CiteScore 3.16
Acoustic phonon limited mobility in two-dimensional semiconductors: Deformation potential and piezoelectric scattering in monolayer MoS$_2$ from first principles

We theoretically study the acoustic phonon limited mobility in n-doped two-dimensional MoS$_2$ for temperatures $T<100$ K and high carrier densities using the Boltzmann equation and first-principles calculations of the acoustic electron-phonon (el-ph) interaction. In combination with a continuum elastic model, analytic expressions and the coupling strengths for the deformation potential and piezoelectric interactions are established. We furthermore show that the deformation potential interaction has contributions from both normal and umklapp processes and that the latter contribution is only weakly affected by carrier screening. Consequently, the calculated mobilities show a transition from a high-temperature $\mu \sim T^{-1}$ behavior to a stronger $\mu \sim T^{-4}$ behavior in the low-temperature Bloch-Grüneisen regime characteristic of unscreened deformation potential scattering. Intrinsic mobilities in excess of $10^5$ cm$^2$ V$^{-1}$ s$^{-1}$ are predicted at $T<10$ K and high carrier densities ($n\gtrsim 10^{11}$ cm$^{-2}$). At 100 K, the mobility does not exceed $\sim 7 \times 10^3$ cm$^2$ V$^{-1}$ s$^{-1}$. Our findings provide new and important understanding of the acoustic el-ph interaction and its screening by free carriers, and is of high relevance for the understanding of acoustic phonon-limited mobilities in general.

General information
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Organisations: Department of Physics, Theoretical Atomic-scale Physics, Center for Atomic-scale Materials Design, Department of Micro- and Nanotechnology, Nanointegration, Theoretical Nanotechnology, Center for Nanostructured Graphene, Tel Aviv University
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BFI (2015): BFI-level 2
Scopus rating (2015): SJR 1.933 SNIP 0.94 CiteScore 2.8
Web of Science (2015): Indexed yes
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Scopus rating (2011): SJR 3.382 SNIP 1.438 CiteScore 3.61
ISI indexed (2011): ISI indexed yes
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BFI (2010): BFI-level 2
Scopus rating (2010): SJR 3.417 SNIP 1.451
Web of Science (2010): Indexed yes
Avoiding pitfalls in the modeling of electrochemical interfaces

Alignment of metal and molecular electronic energy levels at electrode-electrolyte interfaces is investigated using density functional theory. Three different regimes exhibiting qualitatively different energy level alignments are observed. The regimes are roughly defined by the size of the metal work function relative to the ionization potential and/or electron affinity of the electrolyte. It is demonstrated that proper matching of these quantities is essential for successful ab initio modeling of electrochemical interfaces and it is further discussed how such matching can be obtained by careful tailoring of the interfacial atomic structure.

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BFI (2016): BFI-level 1
Scopus rating (2016): CiteScore 1.71 SJR 0.726 SNIP 0.721
Bandgap Engineering of Double Perovskites for One- and Two-photon Water Splitting

Computational screening is becoming increasingly useful in the search for new materials. We are interested in the design of new semiconductors to be used for light harvesting in a photoelectrochemical cell. In the present paper, we study the double perovskite structures obtained by combining 46 stable cubic perovskites which was found to have a finite bandgap in a previous screening-study. The four-metal double perovskite space is too large to be investigated completely. For this reason we propose a method for combining different metals to obtain a desired bandgap. We derive some bandgap
design rules on how to combine two cubic perovskites to generate a new combination with a larger or smaller bandgap compared with the constituent structures. Those rules are based on the type of orbitals involved in the conduction bands and on the size of the two cubic bandgaps. We also see that a change in the volume has an effect on the size of the bandgap. In addition, we suggest some new candidate materials that can be used as photocatalysts in one- and two-photon water splitting devices.

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BFI (2015): BFI-level 1
Scopus rating (2015): SJR 0.141 SNIP 0.085 CiteScore 0.09
BFI (2014): BFI-level 1
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BFI (2013): BFI-level 1
Scopus rating (2013): SJR 0.141 SNIP 0.093 CiteScore 0.07
ISI indexed (2013): ISI indexed no
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Scopus rating (2012): SJR 0.146 SNIP 0.11 CiteScore 0.07
ISI indexed (2012): ISI indexed no
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Scopus rating (2011): SJR 0.142 SNIP 0.096 CiteScore 0.06
ISI indexed (2011): ISI indexed no
BFI (2010): BFI-level 1
Scopus rating (2010): SJR 0.162 SNIP 0.111
BFI (2009): BFI-level 1
Scopus rating (2009): SJR 0.159 SNIP 0.106
BFI (2008): BFI-level 1
Scopus rating (2008): SJR 0.156 SNIP 0.103
Scopus rating (2007): SJR 0.169 SNIP 0.119
Scopus rating (2006): SJR 0.188 SNIP 0.152
Scopus rating (2005): SJR 0.199 SNIP 0.152
Scopus rating (2004): SJR 0.213 SNIP 0.156
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Scopus rating (2003): SJR 0.24 SNIP 0.188
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Beyond the random phase approximation: Improved description of short-range correlation by a renormalized adiabatic local density approximation

We assess the performance of a recently proposed renormalized adiabatic local density approximation (rALDA) for ab initio calculations of electronic correlation energies in solids and molecules. The method is an extension of the random phase approximation (RPA) derived from time-dependent density functional theory and the adiabatic connection fluctuation-dissipation theorem and contains no fitted parameters. The new kernel is shown to preserve the accurate description of dispersive interactions from RPA while significantly improving the description of short-range correlation in molecules, insulators, and metals. For molecular atomization energies, the rALDA is a factor of 7 better than RPA and a factor of 4 better than the Perdew-Burke-Ernzerhof (PBE) functional when compared to experiments, and a factor of 3 (1.5) better than RPA (PBE) for cohesive energies of solids. For transition metals, the inclusion of full shell semicore states is found to be crucial for both RPA and rALDA calculations and can improve the cohesive energies by up to 0.8 eV. Finally, we discuss straightforward generalizations of the method, which might improve results even further.

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Carbon nanotubes as heat dissipaters in microelectronics

We review our recent modelling work of carbon nanotubes as potential candidates for heat dissipation in microelectronics cooling. In the first part, we analyze the impact of nanotube defects on their thermal transport properties. In the second part, we investigate the loss of thermal properties of nanotubes in presence of an interface with various substances, including air and water. Comparison with previous works is established whenever is possible.

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Organisations: Department of Physics, Center for Atomic-scale Materials Design, University of the Basque Country
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Computational Approach to Electron Charge Transfer Reactions

The step from ab initio atomic and molecular properties to thermodynamic - or macroscopic - properties requires the combination of several theoretical tools. This dissertation presents constant temperature molecular dynamics with bond length constraints, a hybrid quantum mechanics-molecular mechanics scheme, and tools to analyse statistical data and generate relative free energies and free energy surfaces. The methodology is applied to several charge transfer species and reactions in chemical environments - chemical in the sense that solvent, counter ions and substrate surfaces are taken in to account - which directly influence the reactants and resulting reaction through both physical and chemical interactions. All methods are though general and can be applied to different types of chemistry. First, the basis of the various theoretical tools is presented and applied to several test systems to show general (or expected) properties.
Properties such as in the physical and (semi-)chemical interface between classical and quantum systems and the effects of molecular bond length constraints on the temperature during simulations. As a second step the methodology is applied to the symmetric and asymmetric charge transfer reactions between several first-row transition metals in water. The results are compared to experiments and rationalised with classical analytic expressions. Shortcomings of the methods are accounted for with clear steps towards improved accuracy. Later the analysis is extended to more complex systems composed of a larger osmium complex in solution and at the solute-substrate interfaces, where in particular the redox state of the complex is controlled through chemical means. The efficiency of the hybrid-classical and quantum mechanics method is used to generate adequate statistics and a simple post-sampling scheme used to generate free energy surfaces - which compare to full ab initio calculations. In the last part both the molecular dynamics and hybrid classical and quantum mechanics method are used to generate a vast data set for the accurate analysis of dynamical structure modes. This is for a large iridium-iridium dimer complex which shows a dramatic structural (and vibrational) change upon electronic excitation.

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**Computational screening of functionalized zinc porphyrins for dye sensitized solar cells**
An efficient dye sensitized solar cell (DSSC) is one possible solution to meet the world's rapidly increasing energy demands and associated climate challenges. This requires inexpensive and stable dyes with well-positioned frontier energy levels for maximal solar absorption, efficient charge separation, and high output voltage. Here we demonstrate an extensive computational screening of zinc porphyrins functionalized with electron donating side groups and electron accepting anchoring groups. The trends in frontier energy levels versus side groups are analyzed and a no-loss DSSC level alignment quality is estimated. Out of the initial 1029 molecules, we find around 50 candidates with level alignment qualities within 5% of the optimal limit. We show that the level alignment of five zinc porphyrin dyes which were recently used in DSSCs with high efficiencies can be further improved by simple side group substitutions. All frontier energy levels, gaps and level alignment quality values are stored in a database publicly available.

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Computational Screening of Materials for Water Splitting Applications

Design new materials for energy production in a photoelectrochemical cell, where water is split into hydrogen and oxygen by solar light, is one possible solution to the problem of increasing energy demand and storage. A screening procedure based on ab-initio density functional theory calculations has been applied to guide the search for new materials. The main descriptors of the properties relevant for the screening are: heat of formation, electronic bandgap, and positions of the band edges with respect to the red-ox levels of water. A recently implemented exchange-correlation functional, called
GLLB-SC, has been used for the estimation of the bandgaps. Firstly, a screening procedure has been applied to 19000 cubic perovskite structures. These are obtained by combining 52 metals together with oxygen, nitrogen, sulfur and fluorine as anions. 32 promising materials have been found for visible light harvesting, 20 for the one-photon and 12 for the two-photon water splitting process. In addition, 16 candidates were suggested for the transparent shielding of the photocatalyst. The problem of corrosion has been addressed for the candidates for the one-photon scheme using Pourbaix diagrams.

Later on, the screening has been extended to more complex structures, like double and layered perovskites and new compounds of interest for the light harvesting problem were found. In addition, the trends in the bandgaps have been studied. The bandgaps can be tuned by an opportune combination of the metal atoms in the B-ion position in the double perovskite, and of the B-metal ion with the thickness of the octahedra in the layered perovskite structure. In the first part, the crystal structure has been kept fixed. Later, the calculations were done using the structures provided by the Materials Project database, which is based on the experimental ICSD database, and the bandgaps were calculated with focus on finding materials with potential as light harvesters. 24 materials have been proposed for the one-photon water splitting and 23 for the two-photon mechanism. Another method to obtain energy from Sun is using a photovoltaic cell that converts solar light into electricity. The absorption spectra of 70 experimentally known compounds, that are expected to be useful for light-to-electricity generation, have been calculated. 17 materials have been predicted to be promising for a single-layer solar cell and 11 for a double-layer device.

**DFT+U study of polaronic conduction in Li$_2$O$_2$ and Li$_2$CO$_3$: Implications for Li-air batteries**

The main discharge products formed at the cathode of nonaqueous Li-air batteries are known to be Li$_2$O$_2$ and residual Li$_2$CO$_3$. Recent experiments indicate that the charge transport through these materials is the main limiting factor for the battery performance. It has been also shown that the performance of the battery decreases drastically when the amount of Li$_2$CO$_3$ at the cathode increases with respect to Li$_2$O$_2$. In this work, we study the formation and transport of hole and electron polarons in Li$_2$O$_2$ and Li$_2$CO$_3$ using density functional theory (DFT) within the PBE+U approximation. For both materials, we find that the formation of polarons (both hole and electron) is stabilized with respect to the delocalized states for all physically relevant values of U. We find a much higher mobility for hole polarons than for the electron polarons, and we show that the poor charge transport in Li$_2$CO$_3$ compared to Li$_2$O$_2$ can be understood through a polaronic model for the conduction. Furthermore, the hole polaronic model in Li$_2$O$_2$ provides a possible explanation for the experimentally observed preferential growth direction of the films. Our results also suggest that doping is unlikely to be a viable route for improving the transport properties of Li$_2$O$_2$ or Li$_2$CO$_3$. 
Direct measurement and modulation of single-molecule coordinative bonding forces in a transition metal complex.

Coordination chemistry has been a consistently active branch of chemistry since Werner’s seminal theory of coordination compounds inaugurated in 1893, with the central focus on transition metal complexes. However, control and measurement of metal-ligand interactions at the single-molecule level remain a daunting challenge. Here we demonstrate an interdisciplinary and systematic approach that enables measurement and modulation of the coordinative bonding forces in a transition metal complex. Terpyridine is derived with a thiol linker, facilitating covalent attachment of this ligand on both gold substrate surfaces and gold-coated atomic force microscopy tips. The coordination and bond breaking between terpyridine and osmium are followed in situ by electrochemically controlled atomic force microscopy at the single-molecule level. The redox state of the central metal atom is found to have a significant impact on the metal-ligand interactions. The present approach represents a major advancement in unravelling the nature of metal-ligand interactions and could have broad implications in coordination chemistry.

General information
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Electrochemical CO\textsubscript{2} and CO reduction on metal-functionalized porphyrin-like graphene

Porphyrin-like metal-functionalized graphene structures have been investigated as possible catalysts for CO\textsubscript{2} and CO reduction to methane or methanol. The late transition metals (Cu, Ag, Au, Ni, Pd, Pt, Co, Rh, Ir, Fe, Ru, Os) and some p (B, Al, Ga) and s (Mg) metals comprised the center of the porphyrin ring. A clear difference in catalytic properties compared to extended metal surfaces was observed owing to a different electronic nature of the active site. The preference to bind hydrogen, however, becomes a major obstacle in the reaction path. A possible solution to this problem is to reduce CO instead of CO\textsubscript{2}. Volcano plots were constructed on the basis of scaling relations of reaction intermediates, and from these plots the reaction steps with the highest overpotentials were deduced. The Rh-porphyrin-like functionalized graphene was identified as the most active catalyst for producing methanol from CO, featuring an overpotential of 0.22 V. Additionally, we have also examined the hydrogen evolution and oxidation reaction, and in their case, too, Rh-porphyrin turned out to be the best catalyst with an overpotential of 0.15 V. © 2013 American Chemical Society.
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Energy level alignment and quantum conductance of functionalized metal-molecule junctions: Density functional theory versus GW calculations

We study the effect of functional groups (CH3*, OCH3, CH3, Cl, CN, F*4) on the electronic transport properties of 1,4-benzenediamine molecular junctions using the non-equilibrium Green function method. Exchange and correlation effects are included at various levels of theory, namely density functional theory (DFT), energy level-corrected DFT (DFT+Σ), Hartree-Fock and the many-body GW approximation. All methods reproduce the expected trends for the energy of the frontier orbitals according to the electron donating or withdrawing character of the substituent group. However, only the GW method predicts the correct ordering of the conductance amongst the molecules. The absolute GW (DFT) conductance is within a factor of two (three) of the experimental values. Correcting the DFT orbital energies by a simple physically motivated scissors operator, Σ, can bring the DFT conductances close to experiments, but does not improve on the relative ordering. We ascribe this to a too strong pinning of the molecular energy levels to the metal Fermi level by DFT which suppresses the variation in orbital energy with functional group.

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Scopus rating (2010): SJR 1.73 SNIP 1.052
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How dielectric screening in two-dimensional crystals affects the convergence of excited-state calculations: Monolayer MoS$_2$

We present first-principles many-body calculations of the dielectric constant, quasiparticle band structure, and optical absorption spectrum of monolayer MoS$_2$ using a supercell approach. As the separation between the periodically repeated layers is increased, the dielectric function of the layer develops a strong q dependence around q = 0. This implies that denser k-point grids are required to converge the band gap and exciton binding energies when large supercells are used. In the limit of infinite layer separation, here obtained using a truncated Coulomb interaction, a $45 \times 45$ k-point grid is needed to converge the G(0)W(0) band gap and exciton energy to within 0.1 eV. We provide an extensive comparison with previous studies and explain agreement and variations in the results. It is demonstrated that too coarse k-point sampling and the interactions between the repeated layers have opposite effects on the band gap and exciton energy, leading to a fortuitous error cancellation in the previously published results.
Plasmons in metallic monolayer and bilayer transition metal dichalcogenides

We study the collective electronic excitations in metallic single-layer and bilayer transition metal dichalcogenides (TMDCs) using time dependent density functional theory in the random phase approximation. For very small momentum transfers (below $q \approx 0.02$ Å$^{-1}$), the plasmon dispersion follows the $\sqrt{q}$ behavior expected for free electrons in two dimensions. For larger momentum transfer, the plasmon energy is significantly redshifted due to screening by interband transitions. At around $q \approx 0.1$ Å$^{-1}$, the plasmon enters the dissipative electron-hole continuum and the plasmon dispersions flatten out at an energy around 0.6–1.1 eV, depending on the material. Using bilayer NbSe$_2$ as example, we show that the plasmon modes of a bilayer structure take the form of symmetric and antisymmetric hybrids of the single-layer modes. The spatially antisymmetric mode is rather weak with a linear dispersion tending to zero for $q=0$, while the energy of the symmetric mode follows the single-layer mode dispersion with a slight blue shift.

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Scopus rating (2009): SJR 3.109 SNIP 1.474
Thermopower measurements of molecular junctions have recently gained interest as a characterization technique that supplements the more traditional conductance measurements. Here we investigate the electronic conductance and thermopower of benzenediamine (BDA) and benzenedicarbonitrile (BDCN) connected to gold electrodes using first-principles calculations. We find excellent agreement with experiments for both molecules when exchange–correlation effects are described by the many-body GW approximation. In contrast, results from standard density functional theory (DFT) deviate from experiments by up to two orders of magnitude. The failure of DFT is particularly pronounced for the n-type BDCN junction due to the severe underestimation of the lowest unoccupied molecular orbital (LUMO). The quality of the DFT results can be improved by correcting the molecular energy levels for self-interaction errors and image charge effects. Finally, we show that the conductance and thermopower of the considered junctions are relatively insensitive to the metal–molecule bonding geometry. Our results demonstrate that electronic and thermoelectric properties of molecular junctions can be predicted from first-principles calculations when exchange–correlation effects are taken properly into account.
Quasiparticle GW calculations for solids, molecules, and two-dimensional materials

We present a plane-wave implementation of the GW approximation within the projector augmented wave method code GPAW. The computed band gaps of ten bulk semiconductors and insulators deviate on average by 0.2eV (~5%) from the experimental values, the only exception being ZnO where the calculated band gap is around 1eV too low. Similar relative deviations are found for the ionization potentials of a test set of 32 small molecules. The importance of substrate screening...
for a correct description of quasiparticle energies and Fermi velocities in supported two-dimensional (2D) materials is illustrated by the case of graphene/h-BN interfaces. Due to the long-range Coulomb interaction between periodically repeated images, the use of a truncated interaction is found to be essential for obtaining converged results for 2D materials. For all systems studied, a plasmon-pole approximation is found to reproduce the full frequency results to within 0.2eV with a significant gain in computational speed. Throughout, we compare the GW results with different exact exchange-based approximations. For completeness, we provide a mathematically rigorous and physically transparent introduction to the notion of quasiparticle states.

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Quasiparticle GW calculations within the GPAW electronic structure code

The GPAW electronic structure code, developed at the physics department at the Technical University of Denmark, is used today by researchers all over the world to model the structural, electronic, optical and chemical properties of materials. They address fundamental questions in material science and use their knowledge to design new materials for a vast range of applications. Today’s hottest topics are, amongst many others, better materials for energy conversion (e.g. solar cells), energy storage (batteries) and catalysts for the removal of environmentally dangerous exhausts. The mentioned properties are to a large extent governed by the physics on the atomic scale, that means pure quantum mechanics. For many decades, Density Functional Theory has been the computational method of choice, since it provides a fairly easy and yet accurate way of determining electronic structures and related properties. However, it has several drawbacks. A conceptual problem is the difficulty of interpreting the calculated results with respect to experimentally measured quantities, resulting in, for example, the “band gap problem” in semiconductors. A practical issue is the necessity of adapting the method with respect to the system one wants to investigate by choosing a certain functional or by tuning parameters. A successful alternative is the so-called GW approximation. It is mathematically precise and gives a physically well-founded description of the complicated electron interactions in terms of screening. It provides a direct link to experimental observables through the concept of quasiparticles. Furthermore, it is parameter-free and thereby equally applicable to different kinds of systems. Its downside lies in its immense computational costs that limit its use in practice. Often, only the G0W0 approach is considered, which can be regarded as the lowest level of the GW approximation. This thesis documents the implementation of the G0W0 approximation in GPAW. It serves two purposes: First, it can be read as a manual by anyone who is interested in doing GW calculations with GPAW. All features and requirements are explained in detail and many examples are given. This provides a full understanding of how the code works and how the outcome should be interpreted. Secondly, it gives an extensive discussion of calculated results for the electronic structure of 3-dimensional, 2-dimensional and finite systems and comparison with other implementations, methods and experiments. It shows that bandstructures, band gaps and ionization potentials can be obtained accurately with G0W0 for many different materials. But also exceptions are pointed out, where higher levels of the GW approximation might be necessary.
Random phase approximation applied to solids, molecules, and graphene-metal interfaces: From van der Waals to covalent bonding

The random phase approximation (RPA) is attracting renewed interest as a universal and accurate method for first-principles total energy calculations. The RPA naturally accounts for long-range dispersive forces without compromising accuracy for short-range interactions making the RPA superior to semilocal and hybrid functionals in systems dominated by weak van der Waals or mixed covalent-dispersive interactions. In this work, we present plane-wave-based RPA calculations for a broad collection of systems with bond types ranging from strong covalent to van der Waals. Our main result is the RPA potential energy surfaces of graphene on the Cu(111), Ni(111), Co(0001), Pd(111), Pt(111), Ag(111), Au(111), and Al(111) metal surfaces, which represent archetypical examples of metal-organic interfaces. Comparison with semilocal density approximations and a nonlocal van der Waals functional show that only the RPA captures both the weak covalent and dispersive forces, which are equally important for these systems. We benchmark our implementation in the GPAW electronic structure code by calculating cohesive energies of graphite and a range of covalently bonded solids and molecules as well as the dissociation curves of H2 and H2+. These results show that the RPA with orbitals from the local density approximation suffers from delocalization errors and systematically underestimates covalent bond energies yielding similar or lower accuracy than the Perdew-Burke-Ernzerhof (PBE) functional for molecules and solids, respectively.
Stability and bandgaps of layered perovskites for one- and two-photon water splitting

Direct production of hydrogen from water and sunlight requires stable and abundantly available semiconductors with well positioned band edges relative to the water red-ox potentials. We have used density functional theory (DFT) calculations to investigate 300 oxides and oxynitrides in the Ruddlesden–Popper phase of the layered perovskite structure. Based on screening criteria for the stability, bandgaps and band edge positions, we suggest 20 new materials for the light harvesting photo-electrode of a one-photon water splitting device and 5 anode materials for a two-photon device with silicon as photo-cathode. In addition, we explore a simple rule relating the bandgap of the perovskite to the number of octahedra in the layered structure and the B-metal ion. Finally, the quality of the GLLB-SC potential used to obtain the bandgaps, including the derivative discontinuity, is validated against G0W0@LDA gaps for 20 previously identified oxides and oxynitrides in the cubic perovskite structure.
Ratings:
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BFI (2016): BFI-level 2
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Scopus rating (2014): SJR 2.806 SNIP 1.307 CiteScore 2.89
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Scopus rating (2012): SJR 3.352 SNIP 1.533 CiteScore 3.4
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BFI (2010): BFI-level 2
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Scopus rating (2009): SJR 3.215 SNIP 1.503
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BFI (2008): BFI-level 2
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Scopus rating (1999): SJR 0.737 SNIP 0.26
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Visualizing hybridized quantum plasmons in coupled nanowires: From classical to tunneling regime

We present full quantum-mechanical calculations of the hybridized plasmon modes of two nanowires at small separation, providing real-space visualization of the modes in the transition from the classical to the quantum tunneling regime. The plasmon modes are obtained as certain eigenfunctions of the dynamical dielectric function, which is computed using time-dependent density functional theory (TDDFT). For freestanding wires, the energy of both surface and bulk plasmon modes deviate from the classical result for low wire radii and high momentum transfer due to effects of electron spill-out, nonlocal response, and coupling to single-particle transitions. For the wire dimer, the shape of the hybridized plasmon modes are continuously altered with decreasing separation, and below 6 Å, the energy dispersion of the modes deviate from classical results due to the onset of weak tunneling. Below 2-3 Å separation, this mode is replaced by a charge-transfer plasmon, which blue shifts with decreasing separation in agreement with experiment and marks the onset of the strong tunneling regime.
Ab initio nonequilibrium quantum transport and forces with the real-space projector augmented wave method

We present an efficient implementation of a nonequilibrium Green's function method for self-consistent calculations of electron transport and forces in nanostructured materials. The electronic structure is described at the level of density functional theory using the projector augmented wave method to describe the ionic cores and an atomic orbital basis set for the valence electrons. External bias and gate voltages are treated in a self-consistent manner and the Poisson equation with appropriate boundary conditions is solved in real space. Contour integration of the Green’s function and parallelization over k points and real space makes the code highly efficient and applicable to systems containing several hundreds of atoms. The method is applied to a number of different systems, demonstrating the effects of bias and gate voltages, multiterminal setups, nonequilibrium forces, and spin transport.

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Organisations: Department of Physics, Theoretical Atomic-scale Physics
Authors: Chen, J. (Intern), Thygesen, K. S. (Intern), Jacobsen, K. W. (Intern)
Pages: 155140
Publication date: 2012
Main Research Area: Technical/natural sciences

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Original language: English
Physics, Molecular electronic devices, Single, Conductance, Junctions, Graphene, Circuits, State

Electronic versions:
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Computational screening of perovskite metal oxides for optimal solar light capture

One of the possible solutions to the world’s rapidly increasing energy demand is the development of new photoelectrochemical cells with improved light absorption. This requires development of semiconductor materials which have appropriate bandgaps to absorb a large part of the solar spectrum at the same time as being stable in aqueous environments. Here we demonstrate an efficient, computational screening of relevant oxide and oxynitride materials based on electronic structure calculations resulting in the reduction of a vast space of 5400 different materials to only 15 promising candidates. The screening is based on an efficient and reliable way of calculating semiconductor band gaps. The outcome of the screening includes all already known successful materials of the types investigated plus some new ones which warrant further experimental investigation.
Conventional and acoustic surface plasmons on noble metal surfaces: a time-dependent density functional theory study

First-principles calculations of the conventional and acoustic surface plasmons (CSPs and ASPs) on the (111) surfaces of Cu, Ag, and Au are presented. The effect of s-d interband transitions on both types of plasmons is investigated by comparing results from the local density approximation and an orbital-dependent exchange-correlation (xc) potential that improves the position and width of the d bands. The plasmon dispersions calculated with the latter xc potential agree well with electron energy loss spectroscopy (EELS) experiments. For both the CSP and ASP, the same trend of Cu < Au < Ag is found for the plasmon energies and is attributed to the reduced screening by interband transitions from Cu, to Au and Ag. This trend for the ASP, however, contradicts a previous model prediction. While the ASP is seen as a weak feature in the EELS, it can be clearly identified in the static and dynamic dielectric band structure.
Extending the random-phase approximation for electronic correlation energies: the renormalized adiabatic local density approximation

The adiabatic connection fluctuation-dissipation theorem with the random phase approximation (RPA) has recently been applied with success to obtain correlation energies of a variety of chemical and solid state systems. The main merit of this approach is the improved description of dispersive forces while chemical bond strengths and absolute correlation energies are systematically underestimated. In this work we extend the RPA by including a parameter-free renormalized version of the adiabatic local-density (ALDA) exchange-correlation kernel. The renormalization consists of a (local) truncation of the ALDA kernel for wave vectors \( q > 2k_F \), which is found to yield excellent results for the homogeneous electron gas. In addition, the kernel significantly improves both the absolute correlation energies and atomization energies of small molecules over RPA and ALDA. The renormalization can be straightforwardly applied to other adiabatic local kernels.
First-principles quantum transport modeling of thermoelectricity in single-molecule nanojunctions with graphene nanoribbon electrodes

We overview the nonequilibrium Green function combined with density functional theory (NEGF-DFT) approach to modeling of independent electronic and phononic quantum transport in nanoscale thermoelectrics with examples focused on a new class of devices where a single organic molecule is attached to two metallic zigzag graphene nanoribbons (ZGNRs) via highly transparent contacts. Such contacts make possible injection of evanescent wavefunctions from the ZGNR electrodes, so that their overlap within the molecular region generates a peak in the electronic transmission around the Fermi energy of the device. Additionally, the spatial symmetry properties of the transverse propagating states in the semi-infinite ZGNR electrodes suppress hole-like contributions to the thermopower. Thus optimized thermopower, together with diminished phonon thermal conductance in a ZGNR|molecule|ZGNR inhomogeneous heterojunctions, yields the thermoelectric figure of merit $ZT$ parts per thousand integral $0.4$ at room temperature with maximum $ZT$ parts per thousand integral $3$ reached at very low temperatures $T_a$ parts per thousand integral $10$ K (so that the latter feature could be exploited for thermoelectric cooling of, e.g., infrared sensors). The reliance on evanescent mode transport and symmetry of propagating states in the electrodes makes the electronic-transport-determined power factor in this class of devices largely insensitive to the type of sufficiently short organic molecule, which we demonstrate by showing that both 18-annulene and C10 molecule sandwiched by the two ZGNR electrodes yield similar thermopower. Thus, one can search for molecules that will further reduce the phonon thermal conductance (in the denominator of $ZT$) while keeping the electronic power factor (in the nominator of $ZT$) optimized. We also show how the often employed Brenner empirical interatomic potential for hydrocarbon systems fails to describe phonon transport in our single-molecule nanojunctions when contrasted with first-principles results obtained via NEGF-DFT methodology.
Image-charge-induced localization of molecular orbitals at metal-molecule interfaces: Self-consistent GW calculations

Quasiparticle (QP) wave functions, also known as Dyson orbitals, extend the concept of single-particle states to interacting electron systems. Here we employ many-body perturbation theory in the GW approximation to calculate the QP wave functions for a semiempirical model describing a π-conjugated molecular wire in contact with a metal surface. We find that image charge effects pull the frontier molecular orbitals toward the metal surface, while orbitals with higher or lower energy are pushed away. This affects both the size of the energetic image charge shifts and the coupling of the individual orbitals to the metal substrate. Full diagonalization of the QP equation and, to some extent, self-consistency in the GW self-energy, is important to describe the effect, which is not captured by standard density functional theory or Hartree-Fock. These results should be important for the understanding and theoretical modeling of electron transport across metal-molecule interfaces.
Magnetoresistance and negative differential resistance in Ni/graphene/Ni vertical heterostructures driven by finite bias voltage: a first-principles study

Using the nonequilibrium Green's function formalism combined with density functional theory, we study finite bias quantum transport in Ni/Gr/Ni vertical heterostructures where n graphene layers are sandwiched between two semi-infinite Ni(111) electrodes. We find that the recently predicted "pessimistic" magnetoresistance of 100% for n≥5 junctions at zero bias voltage Vb→0 persists up to Vb≃0.4 V, which makes such devices promising for spin-torque-based device applications. In addition, for parallel orientations of the Ni magnetizations, the n=5 junction exhibits a pronounced negative differential resistance as the bias voltage is increased from Vb=0 V to Vb≃0.5 V. We confirm that both of these nonequilibrium transport effects hold for different types of bonding of Gr on the Ni(111) surface while maintaining Bernal stacking between individual Gr layers.

General information
State: Published
New cubic perovskites for one- and two-photon water splitting using the computational materials repository

A new efficient photoelectrochemical cell (PEC) is one of the possible solutions to the energy and climate problems of our time. Such a device requires development of new semiconducting materials with tailored properties with respect to stability and light absorption. Here we perform computational screening of around 19,000 oxides, oxynitrides, oxysulfides, oxyfluorides, and oxyfluoronitrides in the cubic perovskite structure with PEC applications in mind. We address three main applications: light absorbers for one- and two-photon water splitting and high-stability transparent shields to protect against corrosion. We end up with 20, 12, and 15 different combinations of oxides, oxynitrides and oxyfluorides, respectively, inviting further experimental investigation.

General information
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Organisations: Department of Physics, Theoretical Atomic-scale Physics, Center for Atomic-scale Materials Design, Experimental Surface and Nanomaterials Physics, Center for Individual Nanoparticle Functionality, Stanford University
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Scopus rating (2014): SJR 7.792 SNIP 4.034 CiteScore 19.28
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Scopus rating (2013): SJR 6.02 SNIP 3.011 CiteScore 14.81
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Observation of quantum interference in molecular charge transport
As the dimensions of a conductor approach the nanoscale, quantum effects begin to dominate, and it becomes possible to control the conductance through direct manipulation of the electron wavefunction. Such control has been demonstrated in various mesoscopic devices at cryogenic temperatures(1-4), but it has proved to be difficult to exert control over the wavefunction at higher temperatures. Molecules have typical energy level spacings (similar to eV) that are much larger than the thermal energy at 300 K (similar to 25 meV), and are therefore natural candidates for such experiments. Previously, phenomena such as giant magnetoresistance(5), Kondo effects(6) and conductance switching(7-11) have been observed in single molecules, and theorists have predicted that it should also be possible to observe quantum interference in molecular conductors(12-18), but until now all the evidence for such behaviour has been indirect. Here, we report the observation of destructive quantum interference in charge transport through two-terminal molecular junctions at room temperature. We studied five different rigid p-conjugated molecular wires, all of which form self-assembled monolayers on a gold surface, and find that the degree of interference can be controlled by simple chemical modifications of the molecular wire.

General information
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Organisations: Department of Physics, Theoretical Atomic-scale Physics, Leiden University, University of Groningen
Authors: Guedon, C. M. (Ekstern), Valkenier, H. (Ekstern), Markussen, T. (Intern), Thygesen, K. S. (Intern), Hummelen, J. C. (Ekstern), van der Molen, S. J. (Ekstern)
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BFI (2014): BFI-level 2
Scopus rating (2014): SJR 17.133 SNIP 8.221 CiteScore 21.76
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 2
Scopus rating (2013): SJR 16.647 SNIP 7.835 CiteScore 21.94
We present an efficient implementation of the Bethe-Salpeter equation (BSE) for optical properties of materials in the projector augmented wave method Grid-based projector-augmented wave method (GPAW). Single-particle energies and wave functions are obtained from the Gritsenko, Leeuwen, Lenthe, and Baerends potential [Phys. Rev. A51, 1944 (1995)] with the modifications from Kuisma et al. [Phys. Rev. B82, 115106 (2010)] GLLBSC functional which explicitly includes the derivative discontinuity, is computationally inexpensive, and yields excellent fundamental gaps. Electron-hole interactions are included through the BSE using the statically screened interaction evaluated in the random phase approximation. For a representative set of semiconductors and insulators we find excellent agreement with experiments for the dielectric functions, onset of absorption, and lowest excitonic features. For the two-dimensional systems of graphene and hexagonal boron-nitride (h-BN) we find good agreement with previous many-body calculations. For the graphene/h-BN interface we find that the fundamental and optical gaps of the h-BN layer are reduced by 2.0 and 0.7 eV, respectively, compared to freestanding h-BN. This reduction is due to image charge screening which shows up in the GLLBSC calculation as a reduction (vanishing) of the derivative discontinuity.

Optical properties of bulk semiconductors and graphene/boron nitride: the Bethe-Salpeter equation with derivative discontinuity-corrected density functional energies

We present an efficient implementation of the Bethe-Salpeter equation (BSE) for optical properties of materials in the projector augmented wave method Grid-based projector-augmented wave method (GPAW). Single-particle energies and wave functions are obtained from the Gritsenko, Leeuwen, Lenthe, and Baerends potential [Phys. Rev. A51, 1944 (1995)] with the modifications from Kuisma et al. [Phys. Rev. B82, 115106 (2010)] GLLBSC functional which explicitly includes the derivative discontinuity, is computationally inexpensive, and yields excellent fundamental gaps. Electron-hole interactions are included through the BSE using the statically screened interaction evaluated in the random phase approximation. For a representative set of semiconductors and insulators we find excellent agreement with experiments for the dielectric functions, onset of absorption, and lowest excitonic features. For the two-dimensional systems of graphene and hexagonal boron-nitride (h-BN) we find good agreement with previous many-body calculations. For the graphene/h-BN interface we find that the fundamental and optical gaps of the h-BN layer are reduced by 2.0 and 0.7 eV, respectively, compared to freestanding h-BN. This reduction is due to image charge screening which shows up in the GLLBSC calculation as a reduction (vanishing) of the derivative discontinuity.

General information
State: Published
Organisations: Department of Physics, Theoretical Atomic-scale Physics, Center for Nanostructured Graphene
Authors: Yan, J. (Intern), Jacobsen, K. W. (Intern), Thygesen, K. S. (Intern)
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Publication date: 2012
Main Research Area: Technical/natural sciences

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Phonon-limited mobility in n-type single-layer MoS2 from first principles

We study the phonon-limited mobility in intrinsic n-type single-layer MoS2 for temperatures $T > 100$ K. The materials properties including the electron-phonon interaction are calculated from first principles and the deformation potentials and Frohlich interaction in single-layer MoS2 are established. The calculated room-temperature mobility of similar to 410 cm$^2$/V$\cdot$s is found to be dominated by optical phonon scattering via intra and intervalley deformation potential couplings and the Frohlich interaction. The mobility is weakly dependent on the carrier density and follows a $\mu \sim T^{\gamma}$ temperature dependence with $\gamma = 1.69$ at room temperature. It is shown that a quenching of the characteristic homopolar mode, which is likely to occur in top-gated samples, increases the mobility with similar to 70 cm$^2$/V$\cdot$s and can be observed as a decrease in the exponent $\gamma = 1.52$. In comparison to recent experimental findings for the mobility in single-layer MoS2 (similar to 200 cm$^2$/V$\cdot$s), our results indicate that mobilities close to the intrinsic phonon-limited mobility can be achieved in two-dimensional materials via dielectric engineering that effectively screens static Coulomb scattering on, e.g., charged impurities.
Spatially resolved quantum plasmon modes in metallic nano-films from first-principles

Electron energy loss spectroscopy (EELS) can be used to probe plasmon excitations in nanostructured materials with atomic-scale spatial resolution. For structures smaller than a few nanometers, quantum effects are expected to be important, limiting the validity of widely used semiclassical response models. Here we present a method to identify and compute spatially resolved plasmon modes from first-principles based on a spectral analysis of the dynamical dielectric function. As an example we calculate the plasmon modes of 0.5 to 4 nm thick Na films and find that they can be classified as (conventional) surface modes, subsurface modes, and a discrete set of bulk modes resembling standing waves across the film. We find clear effects of both quantum confinement and nonlocal response. The quantum plasmon modes provide an intuitive picture of collective excitations of confined electron systems and offer a clear interpretation of spatially resolved EELS spectra.
Unraveling the acoustic electron-phonon interaction in graphene

Using a first-principles approach we calculate the electron-phonon couplings in graphene for the transverse and longitudinal acoustic phonons. Analytic forms of the coupling matrix elements valid in the long-wavelength limit are found to give an almost quantitative description of the first-principles matrix elements even at shorter wavelengths. Using the analytic forms of the coupling matrix elements, we study the acoustic phonon-limited carrier mobility and quasiparticle lifetime observable in photoemission spectroscopy for temperatures 0-200 K and high carrier densities of 1012-1013 cm-2. We find that the intrinsic effective acoustic deformation potential of graphene is Ξ_{eff}=6.8 eV and that the temperature dependence of the mobility μ~T^-α in the Bloch-Gruneisen regime increases beyond an α=4 dependence even in the absence of screening when the true coupling matrix elements are considered. The α>4 temperature dependence of the mobility is found to originate in a similar temperature dependence of the relaxation time at the Fermi level. The large disagreement between our calculated deformation potential and those extracted from experimental measurements (18-29 eV) indicates that additional or modified acoustic phonon-scattering mechanisms are at play in experimental situations.
Ab Initio Calculations of the Electronic Properties of Polypyridine Transition Metal Complexes and Their Adsorption on Metal Surfaces in the Presence of Solvent and Counterions

Os(II)/(III) and Co(II)/(III) polypyridine complexes in aqueous solution are robust molecular entities both in freely solute state and adsorbed on Au(111)- and Pt(111)-electrode surfaces. This class of robust coordination chemical compounds have recently been characterized by electrochemical scanning tunneling microscopy (in situ STM). The Os-complexes were found to display strong tunneling spectroscopic (STS) features at the level of resolution of the single molecule while STS features of the Co complexes, although clear, were much weaker. The data was framed by concise but phenomenological theory of interfacial electrochemical electron transfer extended to the electrochemical in situ STM configuration. With a view on first-principle insight into the in situ STM behavior of robust redox (as opposed to nonredox) molecules, we present in this report a density functional theory (DFT) study of the complexes in both free and adsorbate state, in either state exposed to both stoichiometric counterions and a large assembly of solvent water molecules. The oxidation states of the complexes were controlled, first by introducing chlorine counter atoms followed by spontaneous attraction of electrons from the complexes, also at first in electrostatically neutral form. Second, the solvent is found to provide strong dielectric screening of this charge transfer process and to be crucial for achieving the full chemically meaningful charge separated ionic oxidation states. The molecular charge and structure of the complexes in the presence of the solvent, are conserved upon adsorption, whereas the structural features of the different oxidation states are completely lost upon adsorption under vacuum conditions. Detailed microscopic insight such as offered by the present study will be important in molecular-based approaches to “smart” redox molecules enclosed in in situ STM or other nanoscale and single-molecules scale configurations in condensed matter environments.

General information
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The band structure and optical absorption spectrum of lithium peroxide (Li₂O₂) is calculated from first-principles using the G0W0 approximation and the Bethe-Salpeter equation, respectively. A strongly localized (Frenkel type) exciton corresponding to the π*→σ* transition on the O₂⁻² peroxide ion gives rise to a narrow absorption peak around 1.2 eV below the calculated bandgap of 4.8 eV. In the excited state, the internal O₂⁻² bond is significantly weakened due to the population of the σ* orbital. As a consequence, the bond is elongated by almost 0.5 Å leading to an extreme Stokes shift of 2.6 eV. The strong vibronic coupling entails significant broadening of the excitonic absorption peak in good agreement with diffuse reflectance data on Li₂O₂ which shows a rather featureless spectrum with an absorption onset around 3.0 eV. These results should be important for understanding the origin of the high potential losses and low current densities, which are presently limiting the performance of Li-air batteries.
Dispersive and Covalent Interactions between Graphene and Metal Surfaces from the Random Phase Approximation

We calculate the potential energy surfaces for graphene adsorbed on Cu(111), Ni(111), and Co(0001) using density functional theory and the random phase approximation (RPA). For these adsorption systems covalent and dispersive interactions are equally important and while commonly used approximations for exchange-correlation functionals give inadequate descriptions of either van der Waals or chemical bonds, RPA accounts accurately for both. It is found that the adsorption is a delicate competition between a weak chemisorption minimum close to the surface and a physisorption minimum further from the surface.
Efficient electronic structure methods applied to metal nanoparticles

Nano-scale structures are increasingly applied in the design of catalysts and electronic devices. A theoretical understanding of the basic properties of such systems is enabled through modern electronic structure methods such as density functional theory. This thesis describes the development of efficient approaches to density functional theory and the application of these methods to metal nanoparticles.

We describe the formalism and implementation of localized atom-centered basis sets within the projector augmented wave method. Basis sets allow for a dramatic increase in performance compared to plane-wave or real-space methods, but sacrifice accuracy in doing so. This approach is implemented in the GPAW code where it complements the existing real-space approach. For both the real-space and basis set methods we implement parallel code to adapt GPAW for large-scale calculations on the BlueGene/P architecture. Real-space calculations are performed to investigate the convergence of chemical properties of Au and Pt clusters toward the bulk limit. Specifically we study chemisorption of O and CO on cuboctahedral clusters up to 1415 atoms using up to 65536 CPU cores. Small clusters almost universally bind more strongly than large ones. This can be understood mostly as a geometric effect. Convergence of chemisorption energies within 0.1 eV of bulk values happens at about 200 atoms for Pt and 600 atoms for Au. Particularly for O on Au, large variations due to electronic effects are seen for smaller clusters. The basis set method is used to study the electronic effects for the contiguous range of clusters up to several hundred atoms. The s-electrons hybridize to form electronic shells consistent with the jellium model, leading to electronic magic numbers for clusters with full shells. Large electronic gaps and jumps in Fermi level near magic numbers can lead to alkali-like or halogen-like behaviour when main-group atoms adsorb onto gold clusters. A non-self-consistent Newns-Anderson model is used to more closely study the chemisorption of main-group atoms on magic-number Au clusters. The behaviour at magic numbers can be understood from the location of adsorbate-induced states relative to the Fermi level. The relationship between geometric and electronic effects in Au is studied by rough first-principles simulated annealings with up to 150 atoms. Non-magic clusters are found to deform considerably, reducing the total energy through the creation of gaps. Clusters larger than 100 atoms can elongate systematically by up to 15%. This demonstrates a complex interdependence between electronic and geometric structure in a size regime which in most cases has been studied semieperimentally.

Electrical conductivity in Li2O2 and its role in determining capacity limitations in non-aqueous Li-O2 batteries

Non-aqueous Li-air or Li-O2 cells show considerable promise as a very high energy density battery couple. Such cells, however, show sudden death at capacities far below their theoretical capacity and this, among other problems, limits their practicality. In this paper, we show that this sudden death arises from limited charge transport through the growing Li 2O2 film to the Li2O2-electrolyte interface, and this limitation defines a critical film thickness, above which it is not possible to support electrochemistry at the Li2O2 2-electrolyte interface. We report both electrochemical experiments using a reversible internal redox couple and a first principles metal-insulator-metal charge transport model to probe the electrical conductivity through Li2O2 films produced during Li-O2 discharge. Both experiment and theory show a sudden death in charge transport when film thickness is ~8 to 10 nm. The theoretical model shows that this occurs when the tunneling current
through the film can no longer support the electrochemical current. Thus, engineering charge transport through Li2O2 is a serious challenge if Li-O2 batteries are ever to reach their potential. © 2011 American Institute of Physics.

**General information**

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**Organisations:** Theoretical Atomic-scale Physics, Department of Physics, Stanford University, SLAC National Accelerator Laboratory, IBM Research GmbH

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Electronic shell structure and chemisorption on gold nanoparticles

We use density functional theory (DFT) to investigate the electronic structure and chemical properties of gold nanoparticles. Different structural families of clusters are compared. For up to 60 atoms we optimize structures using DFT-based simulated annealing. Cluster geometries are found to distort considerably, creating large band gaps at the Fermi level. For up to 200 atoms we consider structures generated with a simple EMT potential and clusters based on cuboctahedra and icosahedra. All types of cluster geometry exhibit jelliumlike electronic shell structure. We calculate adsorption energies of several atoms on the cuboctahedral clusters. Adsorption energies are found to vary abruptly at magic numbers. Using a Newns-Anderson model we find that the effect of magic numbers on adsorption energy can be understood from the location of adsorbate-induced states with respect to the cluster Fermi level.
Finite Size Effects in Chemical Bonding: From Small Clusters to Solids

We address the fundamental question of which size a metallic nano-particle needs to have before its surface chemical properties can be considered to be those of a solid, rather than those of a large molecule. Calculations of adsorption
energies for carbon monoxide and oxygen on a series of gold nanoparticles ranging from 13 to 1,415 atoms, or 0.8–3.7 nm, have been made possible by exploiting massively parallel computing on up to 32,768 cores on the Blue Gene/P computer at Argonne National Laboratory. We show that bulk surface properties are obtained for clusters larger than ca. 560 atoms (2.7 nm). Below that critical size, finite-size effects can be observed, and we show those to be related to variations in the local atomic structure augmented by quantum size effects for the smallest clusters.
Finite-size effects in surface chemistry of gold nanoparticles

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First-principles study of surface plasmons on Ag(111) and H/Ag(111)
Linear-response time-dependent density functional theory is used to investigate the relation between molecular bonding and surface plasmons for the model system H/Ag(111). We employ an orbital-dependent exchange-correlation functional to obtain a correct description of the Ag 3d band, which is crucial to avoid overscreening the plasmon by the s-d interband transitions. For the clean surface, this approach reproduces the experimental plasmon energies and dispersion to within 0.15 eV. Adsorption of hydrogen shifts and damps the Ag(111) surface plasmon and induces a new peak in the loss function at 0.6 eV below the Ag(111) plasmon peak. This feature originates from interband transitions between states located on the hydrogen atoms and states on the Ag surface atoms.

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Quantum interference (QI) in molecular transport junctions can lead to dramatic reductions of the electron transmission at certain energies. In a recent work [Markussen et al., Nano Lett., 2010, 10, 4260] we showed how the presence of such transmission nodes near the Fermi energy can be predicted solely from the structure of a conjugated molecule when the energies of the atomic pz orbitals do not vary too much. Here we relax the assumption of equal on-site energies and generalize the graphical scheme to molecules containing different atomic species. We use this diagrammatic scheme together with tight-binding and density functional theory calculations to investigate QI in linear molecular chains and aromatic molecules with different side groups. For the molecular chains we find a linear relation between the position of the transmission nodes and the side group π orbital energy. In contrast, the transmission functions of functionalized aromatic molecules generally display a rather complex nodal structure due to the interplay between molecular topology and the energy of the side group orbital.
Improving transition voltage spectroscopy of molecular junctions

Transition voltage spectroscopy (TVS) is a promising spectroscopic tool for molecular junctions. The principles in TVS is to find the minimum on a Fowler-Nordheim plot where \( \ln(I/V^2) \) is plotted against \( 1/V \) and relate the voltage at the minimum \( V_{\text{min}} \) to the closest molecular level. Importantly, \( V_{\text{min}} \) is approximately half the voltage required to see a peak in the \( dI/dV \) curve. Information about the molecular level position can thus be obtained at relatively low voltages. In this work we show that the molecular level position can be determined at even lower voltages, \( V_{\text{min}}(\alpha) \), by finding the minimum of \( \ln(I/V^\alpha) \) with \( \alpha \).
Linear density response function in the projector augmented wave method: Applications to solids, surfaces, and interfaces

We present an implementation of the linear density response function within the projector-augmented wave method with applications to the linear optical and dielectric properties of both solids, surfaces, and interfaces. The response function is represented in plane waves while the single-particle eigenstates can be expanded on a real space grid or in atomic-orbital basis for increased efficiency. The exchange-correlation kernel is treated at the level of the adiabatic local density approximation (ALDA) and crystal local field effects are included. The calculated static and dynamical dielectric functions of Si, C, SiC, AlP, and GaAs compare well with previous calculations. While optical properties of semiconductors, in particular excitonic effects, are generally not well described by ALDA, we obtain excellent agreement with experiments for the surface loss function of graphene and the Mg(0001) surface with plasmon energies deviating by less than 0.2 eV. Finally, the method is applied to study the influence of substrates on the plasmon excitations in graphene.

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Multiterminal single-molecule-graphene-nanoribbon junctions with the thermoelectric figure of merit optimized via evanescent mode transport and gate voltage

We propose thermoelectric devices where a single molecule is connected to two metallic zigzag graphene nanoribbons (ZGNRs) via highly transparent contacts that allow the injection of evanescent wave functions from ZGNRs. Their overlap generates a peak in the electronic transmission that is largely insensitive to the type of the short conjugated molecule, while ZGNRs additionally suppress hole-like contributions to the thermopower. Thus optimized thermopower, together with suppression of phonon transport through a ZGNR-molecule-ZGNR structure, yields the thermoelectric figure of merit ZT similar to 0.5 at room temperature and 0.5 <ZT <2.5 below liquid nitrogen temperature. Using density functional theory combined with the nonequilibrium Green's function formalism for multiterminal devices, we show how the transmission resonance can be manipulated by the voltage applied to a third ZGNR top-gate electrode covering the molecule to further tune the value of ZT.
Nonlocal Screening of Plasmons in Graphene by Semiconducting and Metallic Substrates: First-Principles Calculations

We investigate the role of substrates on the collective excitations of graphene by using a first-principles implementation of the density response function within the random-phase approximation. Specifically, we consider graphene adsorbed on SiC(0001) and Al(111) as representative examples of a semiconducting and metallic substrate. On SiC(0001), the long wavelength π plasmons are significantly damped although their energies remain almost unaltered. On Al(111), the long wavelength π plasmons are completely quenched due to the coupling to the metal surface plasmon. The strong damping of the plasmon excitations occurs despite the fact that the single-particle band structure of graphene is completely unaffected by the substrates illustrating the nonlocal nature of the effect.
Renormalization of Optical Excitations in Molecules near a Metal Surface

The lowest electronic excitations of benzene and a set of donor-acceptor molecular complexes are calculated for the gas phase and on the Al(111) surface using the many-body Bethe-Salpeter equation. The energy of the charge-transfer excitations obtained for the gas phase complexes are found to be around 10% lower than the experimental values. When the molecules are placed outside the surface, the enhanced screening from the metal reduces the exciton binding energies by several eVs and the transition energies by up to 1 eV depending on the size of the transition-generated dipole. As a striking consequence we find that close to the metal surface the optical gap of benzene can exceed its quasiparticle gap. A classical image charge model for the screened Coulomb interaction can account for all these effects which, on the other hand, are completely missed by standard time-dependent density functional theory.
Robust conductance of dumbbell molecular junctions with fullerene anchoring groups

The conductance of a molecular wire connected to metallic electrodes is known to be sensitive to the atomic structure of the molecule-metal contact. This contact is to a large extent determined by the anchoring group linking the molecular wire to the metal. It has been found experimentally that a dumbbell construction with C60 molecules acting as anchors yields more well-defined conductances as compared to the widely used thiol anchoring groups. Here, we use density functional theory to investigate the electronic properties of this dumbbell construction. The conductance is found to be stable against variations in the detailed bonding geometry and in good agreement with the experimental value of G = 3 × 10^{-4}G_0.

Electron tunneling across the molecular bridge occurs via the lowest unoccupied orbitals of C60 which are pinned close to the Fermi energy due to partial charge transfer. Our findings support the original motivation to achieve conductance values more stable towards changes in the structure of the molecule-metal contact leading to larger reproducibility in experiments. © 2011 American Institute of Physics.
Self-consistent GW calculations of electronic transport in thiol- and amine-linked molecular junctions

The electronic conductance of a benzene molecule connected to gold electrodes via thiol, thiolate, or amino anchoring groups is calculated using nonequilibrium Green functions in combination with the fully self-consistent GW approximation for exchange and correlation. The calculated conductance of benzenedithiol and benzenediamine is one-fifth that predicted by standard density functional theory (DFT), in very good agreement with experiments. In contrast, the widely studied benzenedithiolate structure is found to have a significantly higher conductance due to the unsaturated sulfur bonds. These findings suggest that more complex gold-thiolate structures where the thiolate anchors are chemically passivated by Au adatoms are responsible for the measured conductance. Analysis of the energy level alignment obtained with DFT, Hartree-Fock, and GW reveals the importance of self-interaction corrections (exchange) on the molecule and dynamical screening at the metal-molecule interface. The main effect of the GW self-energy is to renormalize the level positions; however, its influence on the shape of molecular resonances also affects the conductance. Non-self-consistent $G(0)W(0)$ calculations, starting from either DFT or Hartree-Fock, yield conductance values within 50% of the self-consistent GW results.
The role of transition metal interfaces on the electronic transport in lithium–air batteries

Low electronic conduction is expected to be a main limiting factor in the performance of reversible lithium–air, Li–O2, batteries. Here, we apply density functional theory and non-equilibrium Green's function calculations to determine the electronic transport through lithium peroxide, Li2O2, formed at the cathode during battery discharge. We find the transport to depend on the orientation and lattice matching of the insulator–metal interface in the presence of Au and Pt catalysts. Bulk lithium vacancies are found to be available and mobile under battery charging conditions, and found to pin the Fermi level at the top of the anti bonding peroxide π*(2px) and π*(2py) levels in the Li2O2 valence band. Under an applied bias, this can result in a reduced transmission, since the anti bonding σ*(2pz) level in the Li2O2 conduction band is found to couple strongly to the metal substrate and create localized interface states with poor coupling to the Li2O2 bulk states. These observations provide a possible explanation for the higher overpotential observed for charging than discharge.
Towards quantitative accuracy in first-principles transport calculations: The GW method applied to alkane/gold junctions

The calculation of the electronic conductance of nanoscale junctions from first principles is a long-standing problem in the field of charge transport. Here we demonstrate excellent agreement with experiments for the transport properties of the gold/alkanediamine benchmark system when electron-electron interactions are described by the many-body GW approximation. The conductance follows an exponential length dependence: \( G_n = G_c \exp(-\beta n) \). The main difference from standard density functional theory (DFT) calculations is a significant reduction of the contact conductance, \( G_c \), due to an improved alignment of the molecular energy levels with the metal Fermi energy. The molecular orbitals involved in the tunneling process comprise states delocalized over the carbon backbone and states localized on the amine end groups. We find that dynamic screening effects renormalize the two types of states in qualitatively different ways when the molecule is inserted in the junction. Consequently, the GW transport results cannot be mimicked by DFT calculations employing a simple scissors operator. © 2011 Strange and Thygesen; licensee Beilstein-Institut.
Trends in Metal Oxide Stability for Nanorods, Nanotubes, and Surfaces

The formation energies of nanostructures play an important role in determining their properties, including their catalytic activity. For the case of 15 different rutile and 8 different perovskite metal oxides, we used density functional theory (DFT) to calculate the formation energies of (2,2) nanorods, (3,3) nanotubes, and the (110) and (100) surfaces. These formation energies can be described semiquantitatively (mean absolute error = 0.12 eV) by the fraction of metal–oxygen bonds broken and the metal d-band and p-band centers in the bulk metal oxide.

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Benchmarking GW against exact diagonalization for semiempirical models

We calculate ground-state total energies and single-particle excitation energies of seven pi-conjugated molecules described with the semiempirical Pariser-Parr-Pople model using self-consistent many-body perturbation theory at the GW level and exact diagonalization. For the total energies GW captures around 65% of the ground-state correlation energy. The lowest lying excitations are overscreened by GW leading to an underestimation of electron affinities and ionization potentials by 0.15 eV on average corresponding to ~3%. One-shot G0W0 calculations starting from Hartree-Fock reduce the screening and improve the low-lying excitation energies. The effect of the GW self-energy on the molecular excitation energies is shown to be similar to the inclusion of final-state relaxations in Hartree-Fock theory. We discuss the breakdown of the GW approximation in systems with short-range interactions (Hubbard models) where correlation effects dominate over screening/relaxation effects. Finally we illustrate the important role of the derivative discontinuity of the true exchange-correlation functional by computing the exact Kohn-Sham levels of benzene.
Communications: Elementary oxygen electrode reactions in the aprotic Li-air battery

We discuss the electrochemical reactions at the oxygen electrode of an aprotic Li-air battery. Using density functional theory to estimate the free energy of intermediates during the discharge and charge of the battery, we introduce a reaction free energy diagram and identify possible origins of the overpotential for both processes. We also address the question of electron conductivity through the Li2O2 electrode and show that in the presence of Li vacancies Li2O2 becomes a conductor.
Batteries and carbon-free energy storage, Materials and energy storage

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Designing multifunctional chemical sensors using Ni and Cu doped carbon nanotubes
We demonstrate a "bottom up" approach to the computational design of a multifunctional chemical sensor. General techniques are employed for describing the adsorption coverage and resistance properties of the sensor based on density functional theory and non-equilibrium Green's function methodologies, respectively. Specifically, we show how Ni and Cu doped metallic (6,6) single-walled carbon nanotubes may work as effective multifunctional sensors for both CO and NH3.
Electrochemical control of quantum interference in anthraquinone-based molecular switches

Using first-principles calculations we analyze the electronic transport properties of a recently proposed anthraquinone-based electrochemical switch. Robust conductance on/off ratios of several orders of magnitude are observed due to destructive quantum interference present in the anthraquinone but absent in the hydroquinone molecular bridge. A simple explanation of the interference effect is achieved by transforming the frontier molecular orbitals into localized molecular orbitals thereby obtaining a minimal tight-binding model describing the transport in the relevant energy range in terms of hopping via the localized orbitals. The topology of the tight-binding model, which is dictated by the symmetries of the molecular orbitals, determines the amount of quantum interference.
Electronic structure calculations with GPAW: a real-space implementation of the projector augmented-wave method

Electronic structure calculations have become an indispensable tool in many areas of materials science and quantum chemistry. Even though the Kohn-Sham formulation of the density-functional theory (DFT) simplifies the many-body problem significantly, one is still confronted with several numerical challenges. In this article we present the projector augmented-wave (PAW) method as implemented in the GPAW program package (https://wiki.fysik.dtu.dk/gpaw) using a uniform real-space grid representation of the electronic wavefunctions. Compared to more traditional plane wave or localized basis set approaches, real-space grids offer several advantages, most notably good computational scalability and systematic convergence properties. However, as a unique feature GPAW also facilitates a localized atomic-orbital basis set in addition to the grid. The efficient atomic basis set is complementary to the more accurate grid, and the possibility to seamlessly switch between the two representations provides great flexibility. While DFT allows one to study ground state properties, time-dependent density-functional theory (TDDFT) provides access to the excited states. We have implemented the two common formulations of TDDFT, namely the linear-response and the time propagation schemes. Electron transport calculations under finite-bias conditions can be performed with GPAW using non-equilibrium Green functions and the localized basis set. In addition to the basic features of the real-space PAW method, we also describe the implementation of selected exchange-correlation functionals, parallelization schemes, Delta SCF-method, x-ray absorption spectra, and maximally localized Wannier orbitals.
First-principles calculations of graphene nanoribbons in gaseous environments: Structural and electronic properties

The stability of graphene nanoribbons in the presence of typical atmospheric molecules is systematically investigated by means of density-functional theory. We calculate the edge formation free energy of five different edge configurations passivated by H, H-2, O, O-2, N-2, CO, CO2, and H2O, respectively. In addition to the well known hydrogen passivated armchair and zigzag edges, we find the edges saturated by oxygen atoms to be particularly stable under atmospheric conditions. Saturation of the zigzag edge by oxygen leads to the formation of metallic states strictly localized on the oxygen atoms. Finally, the vibrational spectrum of the hydrogen- and oxygen-passivated ribbons are calculated and compared.

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First-principles modelling of scanning tunneling microscopy using non-equilibrium Green's functions

The investigation of electron transport processes in nano-scale architectures plays a crucial role in the development of surface chemistry and nano-technology. Experimentally, an important driving force within this research area has been the concurrent refinements of scanning tunneling microscopy (STM) techniques. The theoretical treatment of the STM operation has traditionally been based on the Bardeen and Tersoff-Hamann methods which take as input the single-particle wave functions and eigenvalues obtained from finite cluster or slabs models of the surface-tip interface. Here, we present a novel STM simulation scheme based on non-equilibrium Green's functions (NEGF) and Wannier functions which is both accurate and very efficient. The main novelty of the scheme compared to the Bardeen and Tersoff-Hamann approaches is that the coupling to the infinite (macroscopic) electrodes is taken into account. As an illustrating example we apply the NEGF-STM method to the Si(001)(2x1):H surface with sub-surface P doping and discuss the results in comparison to the Bardeen and Tersoff-Hamann methods.

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Fully self-consistent GW calculations for molecules
We calculate single-particle excitation energies for a series of 34 molecules using fully self-consistent GW, one-shot G0W0, Hartree-Fock (HF), and hybrid density-functional theory (DFT). All calculations are performed within the projector-augmented wave method using a basis set of Wannier functions augmented by numerical atomic orbitals. The GW self-energy is calculated on the real frequency axis including its full frequency dependence and off-diagonal matrix elements. The mean absolute error of the ionization potential (IP) with respect to experiment is found to be 4.4, 2.6, 0.8, 0.4, and 0.5 eV for DFT-PBE, DFT-PBE0, HF, G0W0[HF], and self-consistent GW, respectively. This shows that although electronic screening is weak in molecular systems, its inclusion at the GW level reduces the error in the IP by up to 50% relative to unscreened HF. In general GW overscreens the HF energies leading to underestimation of the IPs. The best IPs are obtained from one-shot G0W0 calculations based on HF since this reduces the overscreening. Finally, we find that the inclusion of core-valence exchange is important and can affect the excitation energies by as much as 1 eV.
Graphene on metals: A van der Waals density functional study

We use density functional theory (DFT) with a recently developed van der Waals density functional (vdW-DF) to study the adsorption of graphene on Co, Ni, Pd, Ag, Au, Cu, Pt, and Al(111) surfaces. In contrast to the local-density approximation (LDA) which predicts relatively strong binding for Ni, Co, and Pd, the vdW-DF predicts weak binding for all metals and metal-graphene distances in the range 3.40–3.72 Å. At these distances the graphene band structure as calculated with DFT and the many-body G0W0 method is basically unaffected by the substrate, in particular there is no opening of a band gap at the K point.

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We use computational screening to systematically investigate the use of transition-metal-doped carbon nanotubes for chemical-gas sensing. For a set of relevant target molecules (CO, NH₃, and H₂S) and the main components of air (N₂, O₂, and H₂O), we calculate the binding energy and change in conductance upon adsorption on a metal atom occupying a vacancy of a (6,6) carbon nanotube. Based on these descriptors, we identify the most promising dopant candidates for detection of a given target molecule. From the fractional coverage of the metal sites in thermal equilibrium with air, we estimate the change in the nanotube resistance per doping site as a function of the target molecule concentration assuming charge transport in the diffusive regime. Our analysis points to Ni-doped nanotubes as candidates for CO sensors working under typical atmospheric conditions.
Quantifying transition voltage spectroscopy of molecular junctions: Ab initio calculations

Transition voltage spectroscopy (TVS) has recently been introduced as a spectroscopic tool for molecular junctions where it offers the possibility to probe molecular level energies at relatively low bias voltages. In this work we perform extensive ab initio calculations of the nonlinear current-voltage relations for a broad class of single-molecule transport junctions in order to assess the applicability and limitations of TVS. We find, that in order to fully utilize TVS as a quantitative spectroscopic tool, it is important to consider asymmetries in the coupling of the molecule to the two electrodes. When this is taken properly into account, the relation between the transition voltage and the energy of the molecular orbital closest to the Fermi level closely follows the trend expected from a simple, analytical model.
Quantum interference (QI) of electron pathways has recently attracted increased interest as an enabling tool for single-molecule electronic devices. Although various molecular systems have been shown to exhibit QI effects and a number of methods have been proposed for its analysis, simple guidelines linking the molecular structure to QI effects in the phase-coherent transport regime have until now been lacking. In the present work we demonstrate that QI in aromatic molecules is intimately related to the topology of the molecule’s π system and establish a simple graphical scheme to predict the existence of QI-induced transmission antiresonances. The generality of the scheme, which is exact for a certain class of tight-binding models, is proved by a comparison to first-principles transport calculations for 10 different configurations of anthraquinone as well as a set of cross-conjugated molecular wires.

The Relation between Structure and Quantum Interference in Single Molecule Junctions

Quantum interference (QI) of electron pathways has recently attracted increased interest as an enabling tool for single-molecule electronic devices. Although various molecular systems have been shown to exhibit QI effects and a number of methods have been proposed for its analysis, simple guidelines linking the molecular structure to QI effects in the phase-coherent transport regime have until now been lacking. In the present work we demonstrate that QI in aromatic molecules is intimately related to the topology of the molecule’s π system and establish a simple graphical scheme to predict the existence of QI-induced transmission antiresonances. The generality of the scheme, which is exact for a certain class of tight-binding models, is proved by a comparison to first-principles transport calculations for 10 different configurations of anthraquinone as well as a set of cross-conjugated molecular wires.

General information
State: Published
Organisations: Theoretical Atomic-scale Physics, Department of Physics, University of Vienna
Authors: Markussen, T. (Intern), Stadler, R. (Ekstern), Thygesen, K. S. (Intern)
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The conductance of π-conjugated molecular wires bonded to gold electrodes at zero bias is studied using density functional theory combined with nonequilibrium Green’s function method. For all systems considered, we find that the...
conductance length dependence follows the simple exponential law characteristic of tunneling through a barrier, \( G = G_c \exp(-\beta L) \). For thiophene, pyrrole, and phenyl wires with thiol end-groups, we calculate decay constants (\( \beta \)) of 0.211, 0.257, and 0.264 Å\(^{-1} \), respectively, and contact conductances (\( G_c \)) of 1.25, 2.90, and 1.22\( G_0 \), where \( G_0 = 2e^2/h \) is the conductance quantum. In comparison, the corresponding values for amine-terminated thiophene are calculated to be \( \beta = 0.160 \) Å\(^{-1} \) and \( G_c = 0.038G_0 \). These results show that (1) the contact resistance is mainly determined by the anchoring group and (2) the decay constant, which determines the conductance in the long wire limit, is not solely determined by the intrinsic band gap of the molecular wire but also depends on the anchoring group. This is because the alignment of the metal Fermi level with respect to the molecular levels is controlled by charge transfer and interface dipoles which in turn are determined by the local chemistry at the interface. Analysis of the charge transfer at the interface shows that the thiol-bonded molecules receive electrons from the Au electrodes while the amine-bonded molecules donate electrons to the Au electrodes.
Density functional theory based screening of ternary alkali-transition metal borohydrides: A computational material design project

We present a computational screening study of ternary metal borohydrides for reversible hydrogen storage based on density functional theory. We investigate the stability and decomposition of alloys containing 1 alkali metal atom, Li, Na, or K (M1); and 1 alkaline earth or 3d/4d transition metal atom (M2) plus two to five (BH4)− groups, i.e., M1M2(BH4)2–5, using a number of model structures with trigonal, tetrahedral, octahedral, and free coordination of the metal borohydride complexes. Of the over 700 investigated structures, about 20 were predicted to form potentially stable alloys with promising decomposition energies. The M1(Al/Mn/Fe)(BH4)4, (Li/Na)Zn(BH4)3, and (Na/K)(Ni/Co)(BH4)3 alloys are found to be the most promising, followed by selected M1(Nb/Rh)(BH4)4 alloys.
Using time-evolution time-dependent density functional theory (TDDFT) within the adiabatic local-density approximation, we study the interactions between single electrons and molecular resonances at surfaces. Our system is a nitrogen molecule adsorbed on a ruthenium surface. The surface is modeled at two levels of approximation, first as a simple external potential and later as a 20-atom cluster. We perform a number of calculations on an electron hitting the adsorbed molecule from inside the surface and establish a picture, where the resonance is being probed by the hot electron. This enables us to extract the position of the resonance energy through a fitting procedure. It is demonstrated that with the model we can extract several properties of the system, such as the presence of resonance peaks, the time electrons stay on the molecule before returning to the surface when hitting a molecular resonance and the lowering of the resonance energy due to an image charge effect. Finally we apply the TDDFT procedure to only consider the decay of molecular excitations and find that it agrees quite well with the width of the projected density of Kohn-Sham states.

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Organisations: Experimental Surface and Nanomaterials Physics, Department of Physics, Theoretical Atomic-scale Physics, Center for Individual Nanoparticle Functionality, Center for Nanoteknologi, Universidad del Pais Vasco
Authors: Gavnholt, J. (Intern), Rubio, A. (Ekstern), Olsen, T. (Intern), Thygesen, K. S. (Intern), Schiøtz, J. (Intern)
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Scopus rating (2013): SJR 2.785 SNIP 1.339 CiteScore 3.55
Inelastic scattering in metal-H$_2$-metal junctions

We present first-principles calculations of the $dI/dV$ characteristics of an H$_2$ molecule sandwiched between Au and Pt electrodes in the presence of electron-phonon interactions. The conductance is found to decrease by a few percentages at threshold voltages corresponding to the excitation energy of longitudinal vibrations of the H$_2$ molecule. In the case of Pt electrodes, the transverse vibrations can mediate transport through otherwise nontransmitting Pt d channels leading to an increase in the differential conductance even though the hydrogen junction is characterized predominately by a single...
almost fully open transport channel. In the case of Au, the transverse modes do not affect the $dI/dV$ because the Au d states are too far below the Fermi level. A simple explanation of the first-principles results is given using scattering theory. Finally, we compare and discuss our results in relation to experimental data.

**General information**

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Organisations: Theoretical Atomic-scale Physics, Department of Physics, Technical University of Denmark
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BFI (2009): BFI-level 2
Scopus rating (2009): SJR 3.109 SNIP 1.474
Web of Science (2009): Indexed yes
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Web of Science (2005): Indexed yes
Scopus rating (2004): SJR 2.742 SNIP 1.606
Influence of O-2 and N-2 on the conductivity of carbon nanotube networks

We have performed experiments on single-wall carbon nanotube (SWNT) networks and compared with density-functional theory (DFT) calculations to identify the microscopic origin of the observed sensitivity of the network conductivity to physisorbed O-2 and N-2. Previous DFT calculations of the transmission function for isolated pristine SWNTs have found physisorbed molecules have little influence on their conductivity. However, by calculating the four-terminal transmission function of crossed SWNT junctions, we show that physisorbed O-2 and N-2 do affect the junctions' conductance. This may be understood as an increase in tunneling probability due to hopping via molecular orbitals. We find the effect is substantially larger for O-2 than for N-2, and for semiconducting rather than metallic SWNTs junctions, in agreement with experiment.
Localized atomic basis set in the projector augmented wave method

We present an implementation of localized atomic-orbital basis sets in the projector augmented wave (PAW) formalism within the density-functional theory. The implementation in the real-space GPAW code provides a complementary basis
set to the accurate but computationally more demanding grid representation. The possibility to switch seamlessly between
the two representations implies that simulations employing the local basis can be fine tuned at the end of the calculation
by switching to the grid, thereby combining the strength of the two representations for optimal performance. The
implementation is tested by calculating atomization energies and equilibrium bulk properties of a variety of molecules and
solids, comparing to the grid results. Finally, it is demonstrated how a grid-quality structure optimization can be performed
with significantly reduced computational effort by switching between the grid and basis representations.

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Scopus rating (2007): SJR 2.923 SNIP 1.546

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Scopus rating (2006): SJR 2.796 SNIP 1.56
Polarization-induced renormalization of molecular levels at metallic and semiconducting surfaces

On the basis of first-principles G0W0 calculations we systematically study how the electronic levels of a benzene molecule are renormalized by substrate polarization when physisorbed on different metallic and semiconducting surfaces. The polarization-induced reduction in the energy gap between occupied and unoccupied molecular levels is found to scale with the substrate density of states at the Fermi level (for metals) and substrate band gap (for semiconductors). These conclusions are further supported by self-consistent GW calculations on simple lattice models. By expressing the electron self-energy in terms of the substrate’s joint density of states we relate the level shift to the surface electronic structure, thus providing a microscopic explanation of the trends in the GW and G0W0 calculations. While image charge effects are not captured by semilocal and hybrid exchange-correlation functionals, we find that error cancellations lead to remarkably good agreement between the G0W0 and Kohn-Sham energies for the occupied orbitals of the adsorbed molecule.
Renormalization of Molecular Quasiparticle Levels at Metal-Molecule Interfaces: Trends across Binding Regimes

When an electron or a hole is added into an orbital of an adsorbed molecule the substrate electrons will rearrange in order to screen the added charge. This polarization effect reduces the electron addition and removal energies of the adsorbed molecule relative to those of the free molecule. Using a microscopic model of the metal-molecule interface, we illustrate the basic features of this renormalization mechanism through systematic GW, Hartree-Fock, and Kohn-Sham calculations for the molecular energy levels as function of the model parameters. We identify two different polarization mechanisms: (i) polarization of the metal (image charge formation) and (ii) polarization of the molecule via charge transfer across the interface. The importance of (i) and (ii) is found to increase with the metal density of states at the Fermi level and metal-molecule coupling strength, respectively.

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Organisations: Theoretical Atomic-scale Physics, Department of Physics, Center for Nanoteknologi, Universidad del Pais Vasco
Authors: Thygesen, K. S. (Intern), Rubio, A. (Ekstern)
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Scopus rating (2014): SJR 5.027 SNIP 2.646 CiteScore 6.62
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BFI (2011): BFI-level 2
Scopus rating (2011): SJR 6.252 SNIP 2.886 CiteScore 7.02
ISI indexed (2011): ISI indexed yes
Web of Science (2011): Indexed yes
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Scopus rating (2010): SJR 6.418 SNIP 2.764
Web of Science (2010): Indexed yes
BFI (2009): BFI-level 2
Scopus rating (2009): SJR 6.342 SNIP 2.94
Web of Science (2009): Indexed yes
BFI (2008): BFI-level 2
Scopus rating (2008): SJR 6.223 SNIP 2.854
Stability and Electronic Properties of TiO2 Nanostructures With and Without B and N Doping

We address one of the main challenges to TiO2 photocatalysis, namely band gap narrowing, by combining nanostructural changes with doping. With this aim we compare TiO2's electronic properties for small 0D clusters, 1D nanorods and nanotubes, 2D layers, and 3D surface and bulk phases using different approximations within density functional theory and GW calculations. In particular, we propose very small (R ≤ 5 Å) but surprisingly stable nanotubes with promising properties. The nanotubes are initially formed from TiO2 layers with the PtO2 structure, with the smallest (2,2) nanotube relaxing to a rutile nanorod structure. We find that quantum confinement effects, as expected, generally lead to a widening of the energy gap. However, substitutional doping with boron or nitrogen is found to give rise to (meta-)stable structures and the introduction of dopant and midgap states which effectively reduce the band gap. Boron is seen to always give rise to n-type doping while depending on the local bonding geometry, nitrogen may give rise to n-type or p-type doping. For undercoordinated TiO2 surface structures found in clusters, nanorods, nanotubes, layers and surfaces nitrogen gives rise to acceptor states while for larger clusters and bulk structures donor states are introduced.
Structure and transport properties of atomic chains and molecules

The work presented in this thesis is based on density functional theory (DFT) applied mainly to calculate conductance properties of nano-scale systems. A full characterization of Ag-oxygen chains between Ag contacts has been performed. Using spin DFT the electronic and magnetic properties of atomically thin, suspended chains containing silver and oxygen atoms in an alternating sequence have been studied. The conductances of the chains exhibit weak even-odd oscillations around an anomalously low value of $0.1G_0$ ($G_0 = 2e^2/h$) in agreement with experiments [1] in the long chain limit. These unusual conductance properties are explained in terms of a resonating-chain model, which takes the reflection probability and phase-shift of a single bulk-chain interface as the only input. The stability of silver-oxygen chains was studied with a thermodynamic model. This model has been developed in this work to describe tip-suspended atomically thin chains.
between macroscopic size electrodes. It has been tested with the use of DFT calculations on metal chains for which good agreement with experiments was obtained. To ensure the correctness of the DFT based transport calculations presented here, and in more general in the literature, a set of benchmark calculations for the Kohn-Sham elastic transmission function of representative single-molecule junctions has been performed. The transmission functions are calculated using two different density functional theory methods, namely an ultrasoft pseudopotential plane-wave code Dacapo [2] in combination with maximally localized Wannier functions and the norm-conserving pseudopotential code Siesta [3] which applies an atomic orbital basis set. For the systems studied we find that the Siesta transmission functions converge toward the plane-wave result as the Siesta basis is enlarged. Overall, we find that a double zeta polarized atomic basis is generally sufficient, and in some cases necessary, to ensure quantitative agreement with the plane-wave calculation. In a detailed DFT study of the carbon monoxide molecule between Pt electrodes, a particularly stable tilted bridge configuration is found, with a conductance of 0.5G0 over a wide range of electrode displacements. This is in agreement with the observed peak at 0.5G0 in the experimentally obtained conductance histogram for Pt/CO [4]. Also, for homogenous Pt point contacts and short chains good agreement with experiments is obtained. A study of CO in Au, Cu and Ni reveals that the conductance for CO in the tilted bridge configuration for Ni is 0.5G0, in agreement with experiments [5]. For Au/CO and Cu/CO we find the effect of CO compared to the homogenous metal contacts is much smaller, in qualitative agreement with the experimental findings [5]. The observed conductance properties of Metal/CO are shown to be determined by the local d-band at the Metal apex atoms. For carbon nanotubes it is shown that the conductance may be controlled by site selective adsorption of molecules. A model to explain this behavior is verified by direct visualization of Kohn-Sham eigenchannel states. The possibility of non-carbon based nanotubes is also discussed. Both calculations of the strain energy of infinite PtO2 nanotubes that this material could be a candidate for non-carbon based nanotubes, as was recently suggested [6].

General information
State: Published
Organisations: Theoretical Atomic-scale Physics, Department of Physics, Center for Nanoteknologi
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Anomalous conductance oscillations and half-metallicity in atomic Ag-O chains
Using spin density functional theory, we study the electronic and magnetic properties of atomically thin, suspended chains containing silver and oxygen atoms in an alternating sequence. Chains longer than 4 atoms develop a half-metallic ground state implying fully spin-polarized charge carriers. The conductances of the chains exhibit weak even-odd oscillations around an anomalously low value of 0.1G(0) (G(0) = 2e(2)/h) which coincide with the averaged experimental conductance in the long chain limit. The unusual conductance properties are explained in terms of a resonating-chain model, which takes the reflection probability and phase shift of a single bulk-chain interface as the only input. The model also explains the conductance oscillations for other metallic chains.

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Organisations: Theoretical Atomic-scale Physics, Department of Physics, Center for Nanoteknologi
Authors: Strange, M. (Intern), Thygesen, K. S. (Intern), Sethna, J. P. (Ekstern), Jacobsen, K. W. (Intern)
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Anomalous conductance oscillations and half-metallicity in atomic Ag-O chains
Using spin density functional theory, we study the electronic and magnetic properties of atomically thin, suspended chains containing silver and oxygen atoms in an alternating sequence. Chains longer than 4 atoms develop a half-metallic ground state implying fully spin-polarized charge carriers. The conductances of the chains exhibit weak even-odd oscillations around an anomalously low value of 0.1G(0) (G(0) = 2e(2)/h) which coincide with the averaged experimental conductance in the long chain limit. The unusual conductance properties are explained in terms of a resonating-chain model, which takes the reflection probability and phase shift of a single bulk-chain interface as the only input. The model also explains the conductance oscillations for other metallic chains.
Benchmark density functional theory calculations for nanoscale conductance

We present a set of benchmark calculations for the Kohn-Sham elastic transmission function of five representative single-molecule junctions. The transmission functions are calculated using two different density functional theory methods, namely an ultrasoft pseudopotential plane-wave code in combination with maximally localized Wannier functions and the norm-conserving pseudopotential code SIESTA which applies an atomic orbital basis set. All calculations have been converged with respect to the supercell size and the number of k(parallel to) points in the surface plane. For all systems we find that the SIESTA transmission functions converge toward the plane-wave result as the SIESTA basis is enlarged. Overall, we find that an atomic basis with double zeta and polarization is sufficient (and in some cases, even necessary) to ensure quantitative agreement with the plane-wave calculation. We observe a systematic downshift of the SIESTA transmission functions relative to the plane-wave results. The effect diminishes as the atomic orbital basis is enlarged; however, the convergence can be rather slow.

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Authors: Strange, M. (Intern), Bækgaard, I. S. B. (Intern), Thygesen, K. S. (Intern), Jacobsen, K. W. (Intern)
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ISI indexed (2011): ISI indexed yes
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Scopus rating (2010): SJR 1.73 SNIP 1.052
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BFI (2009): BFI-level 2
Comparative study of anchoring groups for molecular electronics: structure and conductance of Au-S-Au and Au-NH2-Au junctions

The electrical properties of single-molecule junctions, consisting of an organic molecule coupled to metal electrodes, are sensitive to the detailed atomic structure of the molecule-metal contact. This, in turn, is determined by the anchoring group linking the molecule to the metal. With the aim of identifying and comparing the intrinsic properties of two commonly used anchoring groups, namely thiol and amine groups, we have calculated the atomic structure and conductance traces of different Au-S-Au and Au-NH2-Au nanojunctions using density functional theory (DFT). Whereas NH2 shows a strong structural selectivity towards atop-gold configurations, S shows large variability in its bonding geometries. As a result, the conductance of the Au-NH2-Au junction is less sensitive to the structure of the gold contacts than the Au-S-Au junction. These findings support recent experiments which show that amine-bonded molecules exhibit more well-defined conductance properties than do thiol-bonded molecules.
Conductance of Sidewall-Functionalized Carbon Nanotubes: Universal Dependence on Adsorption Sites

We use density functional theory to study the effect of molecular adsorbates on the conductance of metallic carbon nanotubes (CNT). The five molecules considered (NO$_2$, NH$_2$, H, COOH, OH) lead to very similar scattering of the electrons. The adsorption of a single molecule suppresses one of the two available transport channels at the Fermi level while the other is left undisturbed. If more molecules are adsorbed on the same sublattice, the remaining open channel may or may not be blocked, depending on the relative position of the adsorbates. If the relative positions satisfy a simple geometric condition, this channel remains fully open independently of the number of adsorbed molecules.

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Journal: Physical Review Letters
Volume: 101
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Ratings:
BFI (2017): BFI-level 2
Web of Science (2017): Indexed Yes
BFI (2016): BFI-level 2
Scopus rating (2016): CiteScore 6.33 SJR 3.56 SNIP 2.133
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 2
Scopus rating (2015): SJR 3.823 SNIP 2.205 CiteScore 5.76
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 2
Scopus rating (2014): SJR 5.027 SNIP 2.646 CiteScore 6.62
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 2
Scopus rating (2013): SJR 5.674 SNIP 2.796 CiteScore 7.46
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 2
Scopus rating (2012): SJR 6.243 SNIP 2.845 CiteScore 7.19
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 2
Scopus rating (2011): SJR 6.252 SNIP 2.886 CiteScore 7.02
ISI indexed (2011): ISI indexed yes
Web of Science (2011): Indexed yes
BFI (2010): BFI-level 2
Scopus rating (2010): SJR 6.418 SNIP 2.764
Web of Science (2010): Indexed yes
BFI (2009): BFI-level 2
Scopus rating (2009): SJR 6.342 SNIP 2.94
Web of Science (2009): Indexed yes
BFI (2008): BFI-level 2
Conserving GW scheme for nonequilibrium quantum transport in molecular contacts

We give a detailed presentation of our recent scheme to include correlation effects in molecular transport calculations using the nonequilibrium Keldysh formalism. The scheme is general and can be used with any quasiparticle self-energy, but for practical reasons, we mainly specialize to the so-called GW self-energy, widely used to describe the quasiparticle band structures and spectroscopic properties of extended and low-dimensional systems. We restrict the GW self-energy to a finite, central region containing the molecule, and we describe the leads by density functional theory (DFT). A minimal basis of maximally localized Wannier functions is applied both in the central GW region and the leads. The importance of using a conserving, i.e., fully self-consistent, GW self-energy is demonstrated both analytically and numerically. We introduce an effective spin-dependent interaction which automatically reduces self-interaction errors to all orders in the interaction. The scheme is applied to the Anderson model in and out of equilibrium. In equilibrium at zero temperature, we find that GW describes the Kondo resonance fairly well for intermediate interaction strengths. Out of equilibrium, we demonstrate that the one-shot G(0)W(0) approximation can produce severe errors, in particular, at high bias. Finally, we consider a benzene molecule between featureless leads. It is found that the molecule’s highest occupied molecular orbital-lowest unoccupied molecular orbital gap as calculated in GW is significantly reduced as the coupling to the leads is increased, reflecting the more efficient screening in the strongly coupled junction. For the I-V characteristics of the junction, we find that Hartree-Fock (HF) and G(0)W(0) [G(HF)] yield results closer to GW than does DFT and G(0)W(0)[G(DFT)]. This is explained in terms of self-interaction effects and lifetime reduction due to electron-electron interactions.
Main Research Area: Technical/natural sciences

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Ratings:
BFI (2017): BFI-level 2
Web of Science (2017): Indexed Yes
BFI (2016): BFI-level 2
Scopus rating (2016): CiteScore 3.16
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 2
Scopus rating (2015): SJR 1.933 SNIP 0.94 CiteScore 2.8
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 2
Scopus rating (2014): SJR 2.667 SNIP 1.262 CiteScore 3.3
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 2
Scopus rating (2013): SJR 2.785 SNIP 1.339 CiteScore 3.55
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 2
Scopus rating (2012): SJR 3.206 SNIP 1.394 CiteScore 3.57
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 2
Scopus rating (2011): SJR 3.382 SNIP 1.438 CiteScore 3.61
ISI indexed (2011): ISI indexed yes
Web of Science (2011): Indexed yes
BFI (2010): BFI-level 2
Scopus rating (2010): SJR 3.417 SNIP 1.451
Web of Science (2010): Indexed yes
BFI (2009): BFI-level 2
Scopus rating (2009): SJR 3.109 SNIP 1.474
Web of Science (2009): Indexed yes
BFI (2008): BFI-level 1
Scopus rating (2008): SJR 2.982 SNIP 1.524
Web of Science (2008): Indexed yes
Scopus rating (2007): SJR 2.923 SNIP 1.546
Web of Science (2007): Indexed yes
Scopus rating (2006): SJR 2.796 SNIP 1.56
Web of Science (2006): Indexed yes
Scopus rating (2005): SJR 2.763 SNIP 1.607
Web of Science (2005): Indexed yes
Scopus rating (2004): SJR 2.742 SNIP 1.606
Web of Science (2004): Indexed yes
Scopus rating (2003): SJR 2.75 SNIP 1.536
Web of Science (2003): Indexed yes
Scopus rating (2002): SJR 2.788 SNIP 1.706
Web of Science (2002): Indexed yes
Scopus rating (2001): SJR 2.946 SNIP 1.635
Web of Science (2001): Indexed yes
Scopus rating (2000): SJR 2.986 SNIP 1.631
Impact of exchange-correlation effects on the IV characteristics of a molecular junction

The role of exchange-correlation effects in nonequilibrium quantum transport through molecular junctions is assessed by analyzing the IV curve of a generic two-level model using self-consistent many-body perturbation theory (second Born and GW approximations) on the Keldysh contour. It is demonstrated how the variation of the molecule's energy levels with the bias voltage can produce anomalous peaks in the dI/dV curve. This effect is suppressed by electronic self-interactions and is therefore underestimated in standard transport calculations based on density functional theory. Inclusion of dynamic correlations introduces quasiparticle (QP) scattering which in turn broadens the molecular resonances. The broadening increases strongly with bias and can have a large impact on the calculated IV characteristic.
Influence of functional groups on charge transport in molecular junctions

Using density functional theory (DFT), we analyze the influence of five classes of functional groups, as exemplified by NO2, OCH3, CH3, CCl3, and I, on the transport properties of a 1,4-benzenedithiolate (BDT) and 1,4-benzenediamine (BDA) molecular junction with gold electrodes. Our analysis demonstrates how ideas from functional group chemistry may be used to engineer a molecule's transport properties, as was shown experimentally and using a semiempirical model for BDA [Nano Lett. 7, 502 (2007)]. In particular, we show that the qualitative change in conductance due to a given functional group can be predicted from its known electronic effect (whether it is sigma/pi donating/withdrawing). However, the influence of functional groups on a molecule's conductance is very weak, as was also found in the BDA experiments. The calculated DFT conductances for the BDA species are five times larger than the experimental values, but good agreement is obtained after correcting for self-interaction and image charge effects. (c) 2008 American Institute of Physics.
Quantum conductance of 4,4-bipyridine molecular junctions: Role of electrode work function and local d band

We present density-functional theory calculations for the geometry and conductance of 4,4-bipyridine (BPD) nanojunctions with Au and Pt electrodes. The fact that transport takes place via bipyridine's lowest unoccupied molecular orbital (LUMO) suggests that the Au-BPD junction should have larger conductance than the Pt-BPD junction due to the smaller work function of Au as compared to Pt. On the other hand, coupling to the local d band is stronger in the case of Pt and this broadens the LUMO resonance. We find that these effects largely outbalance each other leading to conductances of 0.01G(0) and 0.02G(0) for the Au and Pt contacts, respectively (G(0)=2ε(2)/h is the conductance quantum). The effect of coupling to the electrodes is investigated by means of the group orbital which makes precise the concept of the local band. The construction allows us to explain and rationalize the first-principles results within a simple single-level model.
Nonequilibrium G\textit{W} approach to quantum transport in nano-scale contacts

General information
State: Published
Organisations: University of the Basque Country, Freie Universität Berlin
Authors: Thygesen, K. S. (Intern), Rubio, A. (Ekstern)
Pages: 091101
Publication date: 2007
Main Research Area: Technical/natural sciences

Publication information
Journal: Journal of Chemical Physics
Volume: 126
Issue number: 9
ISSN (Print): 0021-9606
Ratings:
BFI (2017): BFI-level 2
Web of Science (2017): Indexed Yes
BFI (2016): BFI-level 2
Scopus rating (2016): SJR 1.073 SNIP 0.755 CiteScore 2.13
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 2
Scopus rating (2015): SJR 0.953 SNIP 0.767 CiteScore 1.98
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 2
Scopus rating (2014): SJR 1.386 SNIP 0.989 CiteScore 2.54
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 2
Scopus rating (2013): SJR 1.532 SNIP 1.17 CiteScore 2.95
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 2
Scopus rating (2012): SJR 1.787 SNIP 1.118 CiteScore 2.86
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 2
Scopus rating (2011): SJR 1.805 SNIP 1.207 CiteScore 3.07
ISI indexed (2011): ISI indexed yes
Web of Science (2011): Indexed yes
BFI (2010): BFI-level 2
Scopus rating (2010): SJR 1.73 SNIP 1.052
Web of Science (2010): Indexed yes
BFI (2009): BFI-level 2
Scopus rating (2009): SJR 2.003 SNIP 1.104
Web of Science (2009): Indexed yes
Electron transport in a Pt-CO-Pt nanocontact: Density functional theory calculations

We have performed first-principles calculations for the mechanic and electric properties of pure Pt nanocontacts and a Pt contact with a single CO molecule adsorbed. For the pure Pt contacts we see a clear difference between point contacts and short chains in good agreement with experiments. We identify a tilted bridge configuration for the Pt-CO-Pt contact, which is stable and has a conductance close to 0.5$G(0)$ ($G(0)=2\,e^2/h$), and we propose that this structure is responsible for an observed peak at 0.5$G(0)$ in the conductance histogram for Pt exposed to a CO gas. We explain the main features of the transmission function for the Pt-CO-Pt contact, and show that the conductance is largely determined by the local d band at the Pt apex atoms.

General information

State: Published
Organisations: Department of Physics, Theoretical Atomic-scale Physics, Center for Nanoteknologi
Authors: Strange, M. (Intern), Thygesen, K. S. (Intern), Jacobsen, K. W. (Intern)
Pages: 125424
Publication date: 2006
Main Research Area: Technical/natural sciences

Publication information

Volume: 73
Issue number: 12
ISSN (Print): 1098-0121
Ratings:
BFI (2017): BFI-level 2
Web of Science (2017): Indexed Yes
BFI (2016): BFI-level 2
Scopus rating (2016): CiteScore 3.16
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 2
Scopus rating (2015): SJR 1.933 SNIP 0.94 CiteScore 2.8
Web of Science (2015): Indexed yes
An ab initio study of electron transport through nitrobenzene: The influence of leads and contacts

**General information**
State: Published
Organisations: Department of Physics
Authors: Stadler, R. (Intern), Thygesen, K. S. (Intern), Jacobsen, K. W. (Intern)
Pages: S155-S160
Publication date: 2005
Main Research Area: Technical/natural sciences

**Publication information**
Journal: Nanotechnology
Volume: 16
ISSN (Print): 0957-4484
Ratings:
BFI (2017): BFI-level 2
Web of Science (2017): Indexed Yes
BFI (2016): BFI-level 2
Scopus rating (2016): CiteScore 2.87 SJR 1.096 SNIP 0.814
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 2
Scopus rating (2015): SJR 1.18 SNIP 0.966 CiteScore 3.07
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 2
Scopus rating (2014): SJR 1.465 SNIP 1.258 CiteScore 3.09
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 2
Scopus rating (2013): SJR 1.585 SNIP 1.244 CiteScore 2.74
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 2
Scopus rating (2012): SJR 1.846 SNIP 1.306 CiteScore 3.34
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 1
Scopus rating (2011): SJR 1.892 SNIP 1.461 CiteScore 3.86
ISI indexed (2011): ISI indexed yes
Web of Science (2011): Indexed yes
BFI (2010): BFI-level 1
Scopus rating (2010): SJR 1.844 SNIP 1.259
Web of Science (2010): Indexed yes
BFI (2009): BFI-level 1
Scopus rating (2009): SJR 1.819 SNIP 1.28
Web of Science (2009): Indexed yes
BFI (2008): BFI-level 1
Scopus rating (2008): SJR 1.875 SNIP 1.333
Web of Science (2008): Indexed yes
Scopus rating (2007): SJR 1.91 SNIP 1.36
Web of Science (2007): Indexed yes
Scopus rating (2006): SJR 1.934 SNIP 1.378
Web of Science (2006): Indexed yes
Scopus rating (2005): SJR 1.925 SNIP 1.445
Web of Science (2005): Indexed yes
Scopus rating (2004): SJR 1.849 SNIP 1.477
Conduction Mechanism in a Molecular Hydrogen Contact

We present first principles calculations for the conductance of a hydrogen molecule bridging a pair of Pt electrodes. The transmission function has a wide plateau with $T \approx 1$ which extends across the Fermi level and indicates the existence of a single, robust conductance channel with nearly perfect transmission. Through a detailed Wannier function analysis we show that the H-2 bonding state is not involved in the transport and that the plateau forms due to strong hybridization between the H-2 antibonding state and states on the adjacent Pt atoms. The Wannier functions furthermore allow us to derive a resonant-level model for the system with all parameters determined from the fully self-consistent Kohn-Sham Hamiltonian.
Forces and conductances in a single-molecule bipyridine junction

Inspired by recent measurements of forces and conductances of bipyridine nanojunctions, we have performed density functional theory calculations of structure and electron transport in a bipyridine molecule attached between gold electrodes for seven different contact geometries. The calculations show that both the bonding force and the conductance are sensitive to the surface structure, and that both properties are in good agreement with experiment for contact geometries characterized by intermediate coordination of the metal atoms corresponding to a stepped surface. The conductance is mediated by the lowest unoccupied molecular orbital, which can be illustrated by a quantitative comparison with a one-level model. Implications for the interpretation of the experimentally determined force and conductance distributions are discussed.
We present a systematic study of interference and k-point sampling effects in the supercell approach to phase-coherent electron transport. We use a representative tight-binding model to show that interference between the repeated images is a small effect compared to the error introduced by using only the Gamma-point for a supercell containing (3,3) sites in the transverse plane. An insufficient k-point sampling can introduce strong but unphysical features in the transmission function which can be traced to the presence of van Hove singularities in the lead. We present a first-principles calculation of the transmission through a Pt contact which shows that the k-point sampling is also important for realistic systems.
Molecular transport calculations with Wannier Functions

We present a scheme for calculating coherent electron transport in atomic-scale contacts. The method combines a formally exact Green's function formalism with a mean-field description of the electronic structure based on the Kohn-Sham scheme of density functional theory. We use an accurate plane-wave electronic structure method to calculate the eigenstates which are subsequently transformed into a set of localized Wannier functions (WFs). The WFs provide a highly efficient basis set which at the same time is well suited for analysis due to the chemical information contained in the WFs. The method is applied to a hydrogen molecule in an infinite Pt wire and a benzene-dithiol (BDT) molecule between Au(111) surfaces. We show that the transmission function of BDT in a wide energy window around the Fermi level can be completely accounted for by only two molecular orbitals. (c) 2005 Elsevier B.V. All rights reserved.
Partly occupied Wannier functions

We introduce a scheme for constructing partly occupied, maximally localized Wannier functions (WFs) for both molecular and periodic systems. Compared to the traditional occupied WFs the partly occupied WFs possess improved symmetry and localization properties achieved through a bonding-antibonding closing procedure. We demonstrate the equivalence between bonding-antibonding closure and the minimization of the average spread of the WFs in the case of a benzene molecule and a linear chain of Pt atoms. The general applicability of the method is demonstrated through the calculation of WFs for a metallic system with an impurity: a Pt wire with a hydrogen molecular bridge.
Partly occupied Wannier functions: Construction and applications

We have developed a practical scheme to construct partly occupied, maximally localized Wannier functions (WFs) for a wide range of systems. We explain and demonstrate how the inclusion of selected unoccupied states in the definition of the WFs can improve both their localization and symmetry properties. A systematic selection of the relevant unoccupied states is achieved by minimizing the spread of the resulting WFs. The method is applied to a silicon cluster, a copper crystal, and a Cu(100) surface with nitrogen adsorbed. In all cases we demonstrate the existence of a set of WFs with particularly good localization and symmetry properties, and we show that this set of WFs is characterized by a maximal average localization.
Stretching dependence of the vibration modes of a single-molecule Pt-H-2-Pt bridge

A conducting bridge of a single hydrogen molecule between Pt electrodes is formed in a break junction experiment. It has a conductance near the quantum unit, \( G(0)=2e^2/h \), carried by a single channel. Using point-contact spectroscopy three vibration modes are observed and their variation upon isotope substitution is obtained. The stretching dependence for each of the modes allows uniquely classifying them as longitudinal or transversal modes. The interpretation of the experiment in terms of a Pt-H-2-Pt bridge is verified by density-functional theory calculations for the stability, vibrational modes, and conductance of the structure.
Conductance calculations with a wavelet basis set

We present a method based on density functional theory (DFT) for calculating the conductance of a phase-coherent system. The metallic contacts and the central region where the electron scattering occurs, are treated on the same footing taking their full atomic and electronic structure into account. The linear-response conductance is calculated from the Green's function which is represented in terms of a system-independent basis set containing wavelets with compact support. This allows us to rigorously separate the central region from the contacts and to test for convergence in a systematic way. The method supports the use of both norm-conserving and ultrasoft pseudopotentials. We use the method to study the effect of adsorbates on the conductance of an infinitely long, atomically thin Al wire, and find that hydrogen and oxygen effectively reduce the conductance of the wire by one and two conductance quanta, respectively.
Four-atom period in the conductance of monatomic Al wires

We present first-principles calculations based on density functional theory for the conductance of monatomic Al wires between Al(111) electrodes. In contrast to the even-odd oscillations observed in other metallic wires, the conductance of the Al wires is found to oscillate with a period of four atoms as the length of the wire is varied. Although local charge neutrality can account for the observed period, it leads to an incorrect phase. We explain the conductance behavior using a resonant transport model based on the electronic structure of the infinite wire.
Period: 15/07/2017 → 14/07/2020
Number of participants: 3
Phd Student:
Riis-Jensen, Anders Christian (Intern)
Supervisor:
Jacobsen, Karsten Wedel (Intern)
Main Supervisor:
Thygesen, Kristian Sommer (Intern)

Financing sources
Source: Internal funding (public)
Name of research programme: Institut stipendie (DTU)
Project: PhD

Spin-valley physics and quantum transport in 2D materials
Department of Micro- and Nanotechnology
Period: 01/02/2017 → 31/01/2020
Number of participants: 4
Phd Student:
Handberg Juul Martiny, Johannes (Intern)
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Kaasbjerg, Kristen (Intern)
Thygesen, Kristian Sommer (Intern)
Main Supervisor:
Jauho, Antti-Pekka (Intern)

Financing sources
Source: Internal funding (public)
Name of research programme: Samfinansieret - Andet
Project: PhD

Ultrafast electronic and coupled electronic-nuclear dynamics of solvated metal complexes
Department of Physics
Period: 01/09/2016 → 31/08/2019
Number of participants: 4
Phd Student:
Zederkof, Diana Bregenholt (Intern)
Supervisor:
Nielsen, Martin Meedom (Intern)
Thygesen, Kristian Sommer (Intern)
Main Supervisor:
Haldrup, Kristoffer (Intern)

Financing sources
Source: Internal funding (public)
Name of research programme: Institut stipendie (DTU)
Project: PhD

Atomic-scale modelling of interfaces in electronic devices
Department of Physics
Period: 01/06/2016 → 03/02/2021
Number of participants: 5
Phd Student:
Jelver, Line (Intern)
Supervisor:
Stokbro, Kurt (Intern)
Stradi, Daniele (Intern)
Thygesen, Kristian Sommer (Intern)
Main Supervisor:  
Jacobsen, Karsten Wedel (Intern)

**Financing sources**  
Source: Internal funding (public)  
Name of research programme: Industrial PhD  
Project: PhD

**Atomic-scale modelling of carrier dynamics in photo-excited semi-conductors**  
Department of Physics  
Period: 01/10/2015 → 30/09/2018  
Number of participants: 3  
Phd Student:  
Haastrup, Sten (Intern)  
Supervisor:  
Jacobsen, Karsten Wedel (Intern)  
Main Supervisor:  
T Hughesen, Kristian Sommer (Intern)

**Financing sources**  
Source: Internal funding (public)  
Name of research programme: Institut stipendie (DTU)  
Project: PhD

**Computational screening of new inorganic materials for high-efficiency solar cells**  
Department of Physics  
Period: 01/11/2014 → 31/10/2017  
Number of participants: 3  
Phd Student:  
Kuhar, Korina (Intern)  
Supervisor:  
T Hughesen, Kristian Sommer (Intern)  
Main Supervisor:  
Jacobsen, Karsten Wedel (Intern)

**Financing sources**  
Source: Internal funding (public)  
Name of research programme: Institut stipendie (DTU)  
Project: PhD

**Advanced methods for total energy calculations of complex materials**  
Department of Physics  
Period: 01/09/2014 → 31/08/2017  
Number of participants: 2  
Phd Student:  
Schmidt, Per Simmendefeldt (Intern)  
Main Supervisor:  
T Hughesen, Kristian Sommer (Intern)

**Financing sources**  
Source: Internal funding (public)  
Name of research programme: Institut stipendie (DTU)  
Project: PhD

**Electronic Properties of Transition Metal Dichalcogenide Heterostructures**  
Department of Physics  
Period: 15/09/2013 → 12/12/2016  
Number of participants: 5
Phd Student:
Latini, Simone (Intern)
Main Supervisor:
Thygesen, Kristian Sommer (Intern)
Examiner:
Jacobsen, Karsten Wedel (Intern)
Gatti, Matteo (Ekstern)
Wehling, Tim Oliver (Ekstern)

**Financing sources**
Source: Internal funding (public)
Name of research programme: Grundforskningsfonden

**Relations**
Publications:
Excitons in van der Waals Heterostructures: A theoretical study
Project: PhD

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First-principles theory of Light-matter interaction in Low-dimensional Materials

Department of Physics
Period: 01/09/2013 → 15/03/2017
Number of participants: 5
Phd Student:
Gjerding, Morten Niklas (Intern)
Main Supervisor:
Thygesen, Kristian Sommer (Intern)
Examiner:
Andersen, Ulrik Lund (Intern)
Peres, Nuno M. R. (Ekstern)
Wirtz, Ludger (Ekstern)

**Financing sources**
Source: Internal funding (public)
Name of research programme: Institut stipendie (DTU)

**Relations**
Publications:
Light-matter interaction in low-dimensional materials. A theoretical study
Project: PhD

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X-ray Tracking of Atomic Motion During Chemical Reactions Using Free Electron Lasers

Department of Physics
Period: 01/09/2013 → 12/12/2016
Number of participants: 7
Phd Student:
Biasin, Elisa (Intern)
Supervisor:
Christensen, Morten (Intern)
Haldrup, Kristoffer (Intern)
Main Supervisor:
Nielsen, Martin Meedom (Intern)
Examiner:
Thygesen, Kristian Sommer (Intern)
Milne, Christopher J. (Ekstern)
Nilsson, Anders (Ekstern)

**Financing sources**
Source: Internal funding (public)
Name of research programme: Institut, samfinansiering
Relations
Publications:
Structural dynamics of solvated metal complexes with anisotropy-enhanced X-ray scattering
Project: PhD

DFT-Simulations of low temperature fuel cells catalysis
Department of Physics
Period: 15/05/2013 → 25/08/2016
Number of participants: 6
Phd Student:
Hansen, Martin Hangaard (Intern)
Supervisor:
Rossmeisl, Jan (Intern)
Main Supervisor:
Thygesen, Kristian Sommer (Intern)
Examiner:
Jacobsen, Karsten Wedel (Intern)
Groß, Axel (Ekstern)
Koper, Marcus Theodorus Maria (Ekstern)

Financing sources
Source: Internal funding (public)
Name of research programme: Forskningsrådsfinansiering

Relations
Publications:
Quantum and field effects of oxide heterostructures
Project: PhD

Quantum and field effects of oxide heterostructures
Department of Energy Conversion and Storage
Period: 01/03/2013 → 30/09/2016
Number of participants: 7
Phd Student:
Trier, Felix (Intern)
Supervisor:
Chen, Yunzhong (Intern)
Jespersen, Thomas Sand (Ekstern)
Main Supervisor:
Pryds, Nini (Intern)
Examiner:
Thygesen, Kristian Sommer (Intern)
Gabay, Marc (Ekstern)
Granozio, Fabio Miletto (Ekstern)

Financing sources
Source: Internal funding (public)
Name of research programme: Institut/centerfinansieret

Relations
Publications:
Nanomodulated graphene devices
Project: PhD

Nanomodulated graphene devices
Department of Micro- and Nanotechnology
Period: 15/11/2012 → 07/12/2016
Number of participants: 6
Phd Student:
Jessen, Bjarke Sørensen (Intern)
Supervisor:
Brandbyge, Mads (Intern)
Main Supervisor:
Bøggild, Peter (Intern)
Examiner:
Thygesen, Kristian Sommer (Intern)
Eroms, Jonathan (Ekstern)
Gorbachev, Roman (Ekstern)

Financing sources
Source: Internal funding (public)
Name of research programme: Grundforskningsfonden

Relations
Publications:
Two-Dimensional Heterostructures: Fabrication & Characterization
Project: PhD

Ab-initio modelling of electronic excitations in nano-structured graphene
Department of Physics
Period: 15/10/2012 → 31/03/2016
Number of participants: 5
Phd Student:
Rasmussen, Filip Anselm (Intern)
Main Supervisor:
Thygesen, Kristian Sommer (Intern)
Examiner:
Brandbyge, Mads (Intern)
Draxl, Claudia (Ekstern)
Hofmann, Philip (Ekstern)

Financing sources
Source: Internal funding (public)
Name of research programme: Grundforskningsfonden

Relations
Publications:
First Principles Calculations of Electronic Excitations in 2D Materials
Project: PhD

Computational Screening of Energy Materials
Department of Physics
Period: 01/08/2012 → 30/09/2015
Number of participants: 6
Phd Student:
Pandey, Mohnish (Intern)
Supervisor:
Thygesen, Kristian Sommer (Intern)
Main Supervisor:
Jacobsen, Karsten Wedel (Intern)
Examiner:
Schiøtz, Jakob (Intern)
Jónsson, Hannes (Ekstern)
Wahnström, Göran (Ekstern)

Financing sources
Source: Internal funding (public)
Name of research programme: 1/3 FUU, 1/3 inst 1/3 Andet
Project: PhD

**Computationel tools and studies of Graphene Nanostructures**
Department of Micro- and Nanotechnology
Period: 01/08/2012 → 20/04/2016
Number of participants: 5
Phd Student:
Papior, Nick Rüburner (Intern)
Main Supervisor:
Brandbyge, Mads (Intern)
Examiner:
Thygesen, Kristian Sommer (Intern)
Pecchia, Alessandro (Ekstern)
Stokbro, Kurt (Intern)

**Financing sources**
Source: Internal funding (public)
Name of research programme: Grundforskningsfonden
Project: PhD

**Modeling of level alignment and charge separation at donor/acceptor interfaces**
Department of Physics
Period: 01/08/2012 → 23/10/2015
Number of participants: 6
Phd Student:
Ømso, Kristian Baruël (Intern)
Supervisor:
Jacobsen, Karsten Wedel (Intern)
Main Supervisor:
Thygesen, Kristian Sommer (Intern)
Examiner:
Vegge, Tejs (Intern)
Boschloo, Gerrit Klaas (Ekstern)
Troisi, Alessandro (Ekstern)

**Financing sources**
Source: Internal funding (public)
Name of research programme: Forskningsrådsfinansiering
Project: PhD

**Computational modelling of electron transport at metal-organic interfaces**
Department of Physics
Period: 15/02/2012 → 21/09/2015
Number of participants: 5
Phd Student:
Jin, Chengjun (Intern)
Main Supervisor:
Thygesen, Kristian Sommer (Intern)
Examiner:
Jacobsen, Karsten Wedel (Intern)
Pauly, Fabian (Ekstern)
Ratner, Mark A. (Ekstern)

**Financing sources**
Source: Internal funding (public)
Name of research programme: Forskningsrådsfinansiering
Project: PhD
Theoretical Investigation of Plasmonic Materials using Electronic Structure Methods

Department of Physics
Period: 01/09/2011 → 13/08/2015
Number of participants: 6
Phd Student:
Winther, Kirsten Trøstrup (Intern)
Supervisor:
Jacobsen, Karsten Wedel (Intern)
Main Supervisor:
Thygesen, Kristian Sommer (Intern)
Examiner:
Schiøtz, Jakob (Intern)
García de Abajo, Francisco J. (Ekstern)
Puska, Martti Juhani (Ekstern)

Financing sources
Source: Internal funding (public)
Name of research programme: Institut stipendie (DTU)
Project: PhD

Development and testing of new exchange-correlation functionals

Department of Physics
Period: 01/02/2011 → 20/03/2014
Number of participants: 6
Phd Student:
Lundgård, Keld Troen (Intern)
Supervisor:
Thygesen, Kristian Sommer (Intern)
Main Supervisor:
Jacobsen, Karsten Wedel (Intern)
Examiner:
Schiøtz, Jakob (Intern)
Moses, Poul Georg (Intern)
Tkatchenko, Alexandre (Ekstern)

Financing sources
Source: Internal funding (public)
Name of research programme: Institut stipendie (DTU)
Project: PhD

X-ray studies og dynamical effects in liquids and at interfaces

Department of Physics
Period: 01/01/2011 → 26/08/2014
Number of participants: 5
Phd Student:
Brandt van Driel, Tim (Intern)
Main Supervisor:
Nielsen, Martin Meedom (Intern)
Examiner:
Thygesen, Kristian Sommer (Intern)
Anders, Madsen (Ekstern)
Collet, Eric (Ekstern)

Financing sources
Source: Internal funding (public)
Name of research programme: Grundforskningsfonden
Project: PhD
Electronic-structure simulations of photo-absorptin properties in extended systems

Department of Physics  
Period: 01/11/2010 → 24/01/2014  
Number of participants: 6  
Phd Student:  
Hüser, Falco Jonas (Intern)  
Supervisor:  
Schietz, Jakob (Intern)  
Main Supervisor:  
Thygesen, Kristian Sommer (Intern)  
Examiner:  
Rossmeisl, Jan (Intern)  
Aryasetiawan, Ferdi (Ekstern)  
Rinke, Patrick (Ekstern)  

Financing sources  
Source: Internal funding (public)  
Name of research programme: Forskningsrådsfinansiering  
Project: PhD

Interfacial Electron Transfer of Large Transition Metal Complexes in Condensed Matter Environments

Department of Physics  
Period: 01/10/2010 → 25/04/2014  
Number of participants: 7  
Phd Student:  
Jónsson, Elvar Örn (Intern)  
Supervisor:  
Thygesen, Kristian Sommer (Intern)  
Ulstrup, Jens (Intern)  
Main Supervisor:  
Jacobsen, Karsten Wedel (Intern)  
Examiner:  
Rossmeisl, Jan (Intern)  
Jónsson, Hannes (Ekstern)  
Sprik, Michiel (Ekstern)  

Financing sources  
Source: Internal funding (public)  
Name of research programme: Institut stipendie (DTU)  
Project: PhD

Molecular Dynamics of Nano-Conductors in the Presence of Electronic Current

Department of Micro- and Nanotechnology  
Period: 01/10/2010 → 11/12/2013  
Number of participants: 5  
Phd Student:  
Gunst, Tue (Intern)  
Main Supervisor:  
Brandbyge, Mads (Intern)  
Examiner:  
Thygesen, Kristian Sommer (Intern)  
Nikolic, Branislav K. (Ekstern)  
Stokbro, Kurt (Intern)  

Financing sources  
Source: Internal funding (public)
Computational search for new light harvesting materials for solar-to-fuel energy conversion

Department of Physics
Period: 01/06/2010 → 26/09/2013
Number of participants: 6
Phd Student:
Castelli, Ivano Eligio (Intern)
Supervisor:
Thygesen, Kristian Sommer (Intern)
Main Supervisor:
Jacobsen, Karsten Wedel (Intern)
Examiner:
Schiøtz, Jakob (Intern)
Marzari, Nicola (Ekstern)
Pedersen, Thomas Garm (Intern)

Financing sources
Source: Internal funding (public)
Name of research programme: Forskningsrådsfinansiering
Project: PhD

Time dependent density functional theory applied to molecular electronics

Department of Physics
Period: 01/10/2009 → 28/02/2013
Number of participants: 3
Phd Student:
Glinsvad, Christian (Intern)
Supervisor:
Thygesen, Kristian Sommer (Intern)
Main Supervisor:
Schiøtz, Jakob (Intern)

Financing sources
Source: Internal funding (public)
Name of research programme: Forskningsrådsfinansiering
Project: PhD

Quantum theory of plasmonic excitations in metallic nanostructures

Department of Photonics Engineering
Period: 01/09/2009 → 04/04/2013
Number of participants: 7
Phd Student:
Toscano, Giuseppe (Intern)
Supervisor:
Jauho, Antti-Pekka (Intern)
Wubs, Martijn (Intern)
Main Supervisor:
Mortensen, N. Asger (Intern)
Examiner:
Thygesen, Kristian Sommer (Intern)
García de Abajo, Francisco J. (Ekstern)
Nordlander, Peter Jan Arne (Ekstern)

Financing sources
Source: Internal funding (public)
Name of research programme: Institut stipendie (DTU)
**In-situ TEM observation of growth and properties of group-IV doped and SiGe heterostructure nanowires**

Department of Physics  
Period: 01/01/2009 → 30/04/2012  
Number of participants: 8  
Phd Student:  
Pennington, Robert Scott (Intern)  
Supervisor:  
Boothroyd, Chris (Intern)  
Dunin-Borkowski, Rafał E. (Intern)  
Wagner, Jakob Birkedal (Intern)  
Main Supervisor:  
Hansen, Jørn Otto Bindslev (Intern)  
Examiner:  
Thygesen, Kristian Sommer (Intern)  
Rosenauer, Andreas (Ekstern)  
Rouvière, Jean-Luc (Ekstern)

**Financing sources**  
Source: Internal funding (public)  
Name of research programme: Institut/centerfinansieret  
Project: PhD

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**Electron Transport and Chemistry of Graphene**

Department of Physics  
Period: 01/09/2008 → 30/09/2011  
Number of participants: 6  
Phd Student:  
Vanin, Marco (Intern)  
Supervisor:  
Jacobsen, Karsten Wedel (Intern)  
Main Supervisor:  
Thygesen, Kristian Sommer (Intern)  
Examiner:  
Brandbyge, Mads (Intern)  
Brocks, Geert H. L. A. (Ekstern)  
Hornekær, Liv (Ekstern)

**Financing sources**  
Source: Internal funding (public)  
Name of research programme: Institut stipendie (DTU)  
Project: PhD

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**Katalytiske og elektroniske egenskaber af metalnanopartikler**

Department of Physics  
Period: 01/09/2008 → 20/01/2012  
Number of participants: 6  
Phd Student:  
Larsen, Ask Hjorth (Intern)  
Supervisor:  
Thygesen, Kristian Sommer (Intern)  
Main Supervisor:  
Jacobsen, Karsten Wedel (Intern)  
Examiner:  
Rossmeisl, Jan (Intern)  
Grönbeck, Henrik (Ekstern)
Manninen, Matti Jussi (Ekstern)

**Financing sources**
- Source: Internal funding (public)
- Name of research programme: Institut stipendie (DTU) Samf.
- Project: PhD

**Theoretical study of Photo-Catalytic oxygen evolution**
- Department of Physics
- Period: 01/03/2008 → 01/06/2011
- Number of participants: 5
- Phd Student: Man, Isabela Costinela (Intern)
- Main Supervisor: Rossmeisl, Jan (Intern)
- Examiner: Thygesen, Kristian Sommer (Intern)
- Hellman, Anders (Ekstern)
- Krtil, Petr (Ekstern)

**Financing sources**
- Source: Internal funding (public)
- Name of research programme: Marie Curie (EU-stipendium)
- Project: PhD

**Direct NO decomposition over non-transition metal surfaces**
- Department of Physics
- Period: 01/10/2007 → 20/04/2011
- Number of participants: 5
- Phd Student: Jiang, Tao (Intern)
- Main Supervisor: Bligaard, Thomas (Intern)
- Examiner: Thygesen, Kristian Sommer (Intern)
- Lopez, Nuria (Intern)
- Jónsson, Hannes (Ekstern)

**Financing sources**
- Source: Internal funding (public)
- Name of research programme: Forskningsrådsfinansiering
- Project: PhD

**Theoretical study of ammonia synthesis under ambient conditions**
- Department of Physics
- Period: 01/04/2007 → 02/03/2011
- Number of participants: 7
- Phd Student: Petzold, Vivien Gabriele (Intern)
- Supervisor: Bligaard, Thomas (Intern)
- Nørskov, Jens Kehlet (Intern)
- Main Supervisor: Jacobsen, Karsten Wedel (Intern)
- Examiner: Thygesen, Kristian Sommer (Intern)
- Hyldgaard, Per (Ekstern)
Financing sources
Source: Internal funding (public)
Name of research programme: DTU-lønnet stipendie
Project: PhD

Elektrontransport i Nanostrukturer
Department of Physics
Period: 15/08/2006 → 10/02/2010
Number of participants: 6
Phd Student:
Rostgaard, Carsten (Intern)
Supervisor:
Thygesen, Kristian Sommer (Intern)
Main Supervisor:
Jacobsen, Karsten Wedel (Intern)
Examiner:
Bligaard, Thomas (Intern)
Gao, Shiwu (Ekstern)
van Leeuwen, Robert (Ekstern)

Financing sources
Source: Internal funding (public)
Name of research programme: DTU-lønnet stipendie
Project: PhD

Nye funktionelle nanorør
Department of Physics
Period: 15/06/2005 → 03/09/2008
Number of participants: 6
Phd Student:
Strange, Mikkel (Intern)
Supervisor:
Thygesen, Kristian Sommer (Intern)
Main Supervisor:
Jacobsen, Karsten Wedel (Intern)
Examiner:
Schiøtz, Jakob (Intern)
Puska, Martti Juhani (Ekstern)
Stokbro, Kurt (Intern)

Financing sources
Source: Internal funding (public)
Name of research programme: Programbevilling
Project: PhD

Molekylære kontakters struktur, dynamik og transport
Department of Physics
Period: 01/03/2005 → 16/12/2009
Number of participants: 6
Phd Student:
Bækgaard, Iben Sig Buur (Intern)
Supervisor:
Thygesen, Kristian Sommer (Intern)
Main Supervisor:
Jacobsen, Karsten Wedel (Intern)
Examiner:
Schiøtz, Jakob (Intern)
Stokbro, Kurt (Intern)
Todorov, Tchavdar N. (Ekstern)

Financing sources
Source: Internal funding (public)
Name of research programme: DTU-lønnet stipendie
Project: PhD

Nanostruktureres opbygning, dynamik og transportegenskaber

Department of Physics
Period: 01/02/2002 → 06/06/2005
Number of participants: 5
PhD Student:
Thygesen, Kristian Sommer (Intern)

Main Supervisor:
Jacobsen, Karsten Wedel (Intern)

Examiner:
Nørskov, Jens Kehlet (Intern)
Gonze, Xavier (Ekstern)
Stokbro, Kurt (Intern)

Financing sources
Source: Internal funding (public)
Name of research programme: DTU-lønnet stipendie
Project: PhD