

Theory Department

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Recent work done in the *Theory Department* is displayed on 24 posters. All posters are displayed in building T and the poster site is given below (left column). The superscript ^E marks work of A. Tkatchenko's ERC group.

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Advanced Electronic Structure Approaches in FHI-Aims

Igor Ying Zhang, Xinguo Ren^(*), Arvid Ihrig, Wael Chibani, Sergey Levchenko,
Patrick Rinke, Volker Blum^(†), and Matthias Scheffler

Advanced electronic-structure methods (AESM) ideally combine accuracy and tractability with transferability across different chemical environments and dimensionalities and overcome the shortcomings of traditional (semi) local density-functional theory (DFT). We here present significant new developments in the all-electron electronic structure code FHI-aims: 1) *Double-hybrid DFT* semi-empirically adds the second-order perturbation energy to a hybrid density functional, which provides both accurate covalent-bond and van der Waals interactions [1]. 2) *Renormalized second-order perturbation theory (rPT2)* [2], on the other hand, systematically combines the random-phase approximation (RPA), second-order screened exchange (SOSEX), and renormalized single excitations, which all contain infinite summations of diagrams. rPT2 presents a considerable overall improvement over the standard RPA approach [2]. The SOSEX irreducible self-energy correction also improves the related *GW* approach, which has been the method of choice for charged excitations. 3) *A self-consistent dynamical embedding scheme* treats the physically important part of a system with AESMs, whereas the rest of the periodic system is treated with computationally less demanding approaches in a self-consistent manner. The embedding is based on the concept of dynamical mean-field theory using Green's function techniques. The 4) *full configuration interaction* scheme within the quantum Monte Carlo framework delivers ultimate benchmarks for our AESMs [3]. The numerical efficiency of these methods is facilitated by 5) *numeric atom-centered orbital (NAO) valence correlation-consistent (VCC) basis sets* and 6) *the localized resolution of identity (RI-LVL)*. NAO basis sets are efficient, compact, and transferable, but the basis set convergence for AESMs is slow due to the difficulty in describing the electron-electron cusp in the Coulomb interaction. We have developed basis sets that combine the concept of VCC with the compactness of NAOs, enabling an efficient extrapolation of the valence-correlation energy to the complete-basis-set limit. RI-LVL, on the other hand, allows us to remove the expensive four-center integrals occurring for AESMs. In RI-LVL, a product of basis functions is expanded in a rigorously justified, systematically converging subset of auxiliary basis functions, that gives efficient memory usage and linear scaling with system size.

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Self-Consistent Density Functional with Non-Local van der Waals Interactions

Nicola Ferri, Robert A. DiStasio Jr.^(*), Alberto Ambrosetti, Roberto Car^(*),
Alexandre Tkatchenko, and Matthias Scheffler

Van der Waals (vdW) interactions are significant for a wide variety of systems, from simple noble-gas dimers to complex hybrid organic/inorganic interfaces. The long-range vdW energy is a tiny fraction ($\sim 0.001\%$) of the total energy, hence it is typically assumed that it has no visible influence on the electronic properties. Although the Langreth/Lundqvist vdW-DF functional includes the effect of non-local correlation energy on the electronic structure [1,2], the influence of “true” vdW interactions is difficult to assess since a significant part of vdW-DF energy arises from short distances.

Here, we present a fully self-consistent (SC) implementation of the Tkatchenko-Scheffler DFA+vdW functional [3], where DFA stands for an approximate semi-local exchange-correlation density functional. The analysis of SC effects for atomic and molecular dimers allows us to establish a link between Feynman’s view on vdW binding arising from purely electrostatic interactions between perturbed electron densities [4] with the more traditional electrodynamic model based on non-local fluctuations and employed in practical calculations.

The effect of DFA+vdW^{SC} on electronic densities of molecular dimers is assessed, finding quantitative agreement with correlated densities obtained from “gold standard” coupled-cluster quantum-chemical calculations. In agreement with previous work [2], we find a very small overall contribution from self-consistency in the structure and stability of vdW-bound molecular complexes. However, non-local vdW interactions turn out to significantly affect electronic properties of coinage metal (111) surfaces, leading to an increase of up to 0.3 eV in their workfunction. Furthermore, vdW interactions are also found to visibly influence workfunctions and charge transfer in hybrid organic/metal systems.

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Accurate Thermoelectric Transport Coefficients up to the Melting Point

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The need for a sustainable energy economy has revamped interest in the development of thermoelectric materials, which have the potential to recover significant amounts of otherwise wasted heat. Research along these lines requires an accurate theoretical assessment of the transport coefficients that determine the thermoelectric efficiency, i.e., the electrical conductivity σ , the Seebeck coefficient S , as well as the electronic and vibrational heat conductivities κ_{el} and κ_{vib} . To date, methods based on the Boltzmann transport equation (BTE) [1,2] are the most widespread approaches to estimate these quantities. At elevated temperatures, however, these techniques become inaccurate, since they rely on the validity of the harmonic approximation (and small perturbations thereof). In particular, the relevant scattering processes that stem from the phonon-phonon [2] and the electron-phonon [3] interaction are only accounted for to lowest order.

In this work, we overcome the severe limitations of the BTE by the newly developed/implemented *ab initio* Green-Kubo [4] and Kubo-Greenwood [5] approach, in which *all* transport coefficients are determined from the correlation functions of the heat and charge fluxes [5]. Thereby, electron-phonon and phonon-phonon scattering is accounted for to all orders by evaluating the electronic and vibrational contributions to these fluxes by first-principles molecular dynamics. We discuss the details of our implementation as well as future extensions to account for ionic transport and validate our approach by investigating insulators (ZrO_2), metals (Al) as well as direct and indirect band gap semiconductors (Si, InP). First, our calculations reveal that higher-order anharmonic effects are extremely effective in lowering κ_{vib} . Second, the electron-phonon interaction leads to a thermal renormalization of the electronic structure that significantly affects σ , S , and κ_{el} at elevated temperatures. Both these mechanisms can thus not be neglected in the simulation of thermoelectric materials. The presented techniques are the only parameter-free, truly first-principles options available to date that account for these effects and that hence allow an accurate assessment of the thermoelectric transport coefficients up to the melting point.

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Exploring the GW Ground State – the Self-Consistent GW Approach Applied to Molecules

Fabio Caruso, Patrick Rinke, Xinguo Ren^(*), Angel Rubio^(†), and Matthias Scheffler

Many-body Green's function theory holds the promise of a universal electronic structure approach, because it provides both ground and excited state properties in a single framework. In this context, the GW approach has become the method of choice for the description of charged excitations in solids, and its application to molecules and nanosystems is steadily increasing. However, with few exceptions the ground state properties of GW have not been explored yet.

We have implemented a fully self-consistent GW scheme (sc- GW) – based on the iterative solution of the Dyson equation – in the all-electron code FHI-aims [1,2,3]. Unlike in the more common perturbative GW schemes (G_0W_0), sc- GW is independent from the reference state. This provides a well defined total energy, which we calculate by means of the Galitskii-Migdal formula. Our results for a diverse set of (organic) molecules show that the sc- GW quasi-particle energies are in good agreement with experiment and more accurate than G_0W_0 based on Hartree-Fock or density-functional theory (DFT) with local or semi-local exchange-correlation functionals [2,3]. To assess the sc- GW ground state, we calculated bond lengths, binding energies, and vibrational frequencies for a set of diatomic molecules. The accuracy of sc- GW is comparable to exact-exchange plus correlation in the random-phase approximation (EX+cRPA), which is, however, not as good as that of renormalized second-order perturbation theory (rPT2) [4]. Since EX+cRPA is an advanced DFT functional that is on the same quantum mechanical level as GW , we address the question if the DFT and the Green's function framework are in fact equal. Inspecting the dissociation curve of H_2 , we find that sc- GW and EX+cRPA are indeed very close around the equilibrium bond distance, but when it comes to bond breaking DFT outperforms Green's function theory [5]. Finally, for prototypical donor/acceptor molecules we demonstrate that sc- GW – due to its synergetic description of ground- and excited-state properties – is a promising method for charge-transfer systems, in which the electron density depends on the relative alignment of the molecular orbitals of the donor and the acceptor.

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Exact Hohenberg-Kohn Functional for a Lattice Model

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Standard local exchange-correlation and semi-local functionals in ground-state density functional theory are known for their shortcomings in describing correct charge transfer, dissociation energies of molecular ions, and barriers of chemical reactions [1,2]. One major reason for these shortcomings is the delocalization error of commonly used approximations. The mentioned functionals violate the derivative discontinuity of the exact Kohn-Sham potential and hence, underestimate ground-state energies for fractional particle numbers, as in the stretched limit of molecules [2,3]. Some of these shortcomings are partially resolved by ensemble density functional theory [4], logarithmically diverging enhancement factors in GGA functionals [5], or the particle-particle random-phase approximation [6]. To understand the failures of approximate functionals, to gain insight into the behavior of the exact functional, and to devise new approximations, we investigate the exact solution of the many-body Schrödinger equation in Fock space for a lattice model with a softened Coulomb interaction term. Using quadratic optimization with quadratic constraints, or alternatively exact diagonalization, we explicitly construct the *exact* Hohenberg-Kohn functional and the mapping from densities to wavefunctions. The exact functional exhibits softened *intra-system derivative discontinuities* in the low-density limit that resemble the inter-system derivative discontinuity widely discussed in the density-functional community [3]. Besides the energy expectation value also the configuration-interaction coefficients of the wavefunction can be regarded as functional of the density. We show that also the configuration-interaction coefficients exhibit a softened intra-system derivative discontinuity which directly affects expectation values of general operators. Using exact many-body densities, we compute exact Kohn-Sham potentials by inverting the Kohn-Sham equations. The exact potentials exhibit clear steps and peaks and we observe the same softened intra-system derivative discontinuity in the low-density limit. We discuss how such effects can be incorporated on top of simple exchange-correlation functionals. The description of many physical phenomena linked to charge-transfer processes (both in the static and dynamical regimes) require a proper account of those "intra-system derivative discontinuities".

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Correlated Light-Matter Interactions in Cavity QED

Johannes Flick, René Jestädt, Heiko Appel, and Angel Rubio^(*)

Many chemical reactions are mediated through the interaction between light and matter. Important examples include photosynthesis, the vision process, photo-chemical reactions, solar cells, and nanoplasmonics based on metamaterials. To better understand these complex processes, experimentalists in the field of cavity quantum electrodynamics (QED) have developed methods to study quantum systems at the single-photon interaction limit (Nobel prize 2012). Further recent developments in this field are Fabry-Perot resonators with optical high-quality (high-Q) factors, circuit QED [1] and optomechanics [2].

In the electronic structure community, the quantized nature of the electrons is usually (approximately) incorporated, whereas the electromagnetic field is mostly treated classically. In contrast, in quantum optics, matter is typically simplified to models with a few levels, while the quantized nature of light is fully explored. In this work, we aim at treating both, matter and light, on an equal quantized footing.

To incorporate arbitrary geometries and matter distributions, we reformulate Maxwell's equations, by using the Riemann-Silberstein vector into a matrix spinor representation similar to the Dirac equation. In the stationary limit, its eigenvalues and eigenmodes are the essential input for a quantized description of the electromagnetic field. Using this input, we present exact solutions for fully quantized prototype systems consisting of atoms or molecules placed in optical one-dimensional high-Q cavities and coupled to the quantized electromagnetic modes in the dipole or quadrupole coupling regime. We focus on spontaneous emission, atomic revivals, strong-coupling phenomena, dipole-dipole couplings including van-der-Waals interactions, and Förster resonance energy transfer (FRET), all beyond the rotating wave approximation. Further, we compare to a propagation of coupled Maxwell-Schrödinger systems, using the matrix spinor representation on a real-space grid.

This work has implications for a future development of a time-dependent density functional theory formulation of QED [3,4] and further allows to study modifications to the classical Maxwell's equations for correlated multi-photon configurations. In the future, both may be used for the new field of correlated spectroscopy [5].

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Electronic Decoherence in Molecules

Ignacio Franco^(*), Heiko Appel, and Angel Rubio^(†)

Electronic decoherence in molecules is a basic feature of the time evolution that accompanies photoexcitation, passage through conical intersections, electron transfer, or any other dynamical process that creates electronic superposition states. Understanding electronic decoherence is central to our description of fundamental processes such as photosynthesis and vision, and is also vital in the development of approximation schemes to the full vibronic evolution of molecules.

Here we present three basic contributions toward the understanding of electronic decoherence in molecules: First, we introduce a hierarchy of measures of decoherence for many-electron systems that is based on the purity and the hierarchy of reduced electronic density matrices [1]. Usual measures of decoherence are of limited applicability in molecules because they are based on the many-body electronic density matrix and this quantity is generally not available. By contrast, the reduced purities introduced here can be used to characterize electronic decoherence in the common case when only reduced information about the electronic subsystem is available.

Second, using the reduced purities and related measures we investigate decoherence dynamics in a model molecular system: the Su-Schrieffer-Heeger model of trans-polyacetylene [1,2]. The decoherence is modeled by following the coupled dynamics of electronic and vibrational degrees of freedom explicitly albeit approximately in an Ehrenfest mixed quantum-classical approximation. The simulations reveal the basic structure expected for the decoherence dynamics in molecules, provide insights into the main mechanisms for coherence loss, and illustrate how the decoherence dynamics changes with system size and initial state. Last, in this context, we identify a long-lived coherent-like phenomenon termed VIBRET [3]. In it, via vibronic interactions, the decay of an electron in the manifold of π^* -states resonantly excites an electron in the manifold of π states, and vice versa, leading to oscillatory exchange of electronic population between two distinct electronic states that lives for up to tens of picoseconds. The oscillatory structure is reminiscent of quantum beating patterns and is suggestive of the presence of a long-lived molecular electronic coherence. Significantly, however, a detailed analysis of the electronic coherence properties through the reduced purities shows that the VIBRET arises from a purely incoherent process.

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Graphene Engineering: Stability of Epitaxial Graphene and the Surface Reconstructions of 3C-SiC

Lydia Nemeč, Florian Lazarević, Volker Blum^(*), Patrick Rinke,
and Matthias Scheffler

Graphene films grown by Si sublimation on SiC are promising material combinations for future graphene applications based on existing semiconductor technologies [1]. To refine the growth quality and the resulting electronic character, it is important to understand the atomic and electronic structure of the interface. However, electronic-structure calculations are a challenge since the unit cells observed in experiment are large, requiring thousand(s) of atoms for a converged slab treatment. In this work, we present first-principles thermodynamic predictions for graphene and its precursor phases on SiC in their experimentally observable unit cell.

We performed a density-functional theory study on the Si-side of the polar 3C-SiC(111) surface using the all-electron electronic structure code FHI-aims, including $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ zero-layer graphene (ZLG), monolayer (MLG), bilayer (BLG), and three-layer graphene (3LG). The formation energies of different reconstructions are presented as functions of the chemical potential of C. This (i) reveals a C-rich chemical-potential range for which ZLG is stable, in agreement with experiment [2], and (ii) indicates an even more C-rich stability range for MLG [2]. Thus, the calculations suggest that, by tuning the chemical potential (in experiment, e.g., by varying the temperature and background pressure of C or Si reservoir gases) it should be possible to grow high quality interfaces and graphene phases on the Si side.

The experimental situation on the C face of SiC is very different. Although few-layer graphene films with promising electronic structure can be grown [3], growing monolayer graphene films is difficult. A phase mixture of different surface phases is observed when surface graphitization sets in. However, the atomic structure of some of the competing surface phases and of the SiC-graphene interface is unknown. In our calculations, we compare the surface energies of the known (2×2) phase with several structural models of the (3×3) phase proposed in the literature. This shows that all the previously suggested (3×3) models are higher in energy than the known (2×2) phase. We present a new model for the (3×3) reconstruction. Its formation energy crosses that of the (2×2) phase at the carbon rich limit of the chemical potential, explaining the observed phase mixture.

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Sub-Monolayer Water Adsorption on Alkaline Earth Metal Oxide Surfaces: A First-Principles Genetic Algorithm Study

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and Matthias Scheffler

Distribution of adsorbed water molecules, OH groups, and protons on surfaces sensitively depends on the interactions between adsorbed species, and between the adsorbed species and the substrate, in particular at initial stages of wetting (in the sub-monolayer regime). In the present work, we predict atomic structures of adsorbed complexes that should appear on alkaline earth metal oxide (001) terraces in thermodynamic equilibrium with water and oxygen gases. Density-functional theory with the hybrid exchange-correlation functional HSE06, combined with the self-consistent many-body dispersion approach [1], is used to calculate total energies. The choice of this functional is validated by renormalized second-order perturbation theory [2]. An unbiased search for global minima on the potential-energy surface for H_xO_y adsorption in the sub-monolayer regime is performed using a first-principles genetic algorithm for periodic models. x and y as a function of temperature and pressure are determined using *ab initio* atomistic thermodynamics.

Recently, one-dimensional structures have been observed with scanning tunneling microscopy on CaO(001) in the presence of H_2O (X. Shao, N. Nilius, Y. Fujimori, M. Sterrer, and H.-J. Freund, Department of Chemical Physics, FHI). In agreement with the experimental results, we find a range of H_2O chemical potentials around the experimental conditions ($T = 300$ K, $p_{H_2O} = 10^{-10}$ atm) where one-dimensional adsorbed water structures are most stable on CaO(001). The structures are found to retain the 2H:1O stoichiometry at realistic conditions. On MgO(001), one-dimensional structures are metastable, while on SrO(001) long-range ordered structures are not found. Using molecular dynamics simulations, we also predict finite-temperature anharmonic vibrational spectra of the one-dimensional adsorbed structures, and demonstrate that the anharmonicity has a significant effect on the calculated spectra. Based on the analysis of energetics and bonding, we explain the formation of the one-dimensional structures by the balance between water-water and water-oxide interactions.

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O vacancy or O interstitial at Corners of MgO Surfaces?

Saswata Bhattacharya, Sergey V. Levchenko, Luca M. Ghiringhelli,
and Matthias Scheffler

Defects such as oxygen vacancies are believed to play the key role in catalysis at oxide surfaces [1]. However, significant controversy still exists regarding their formation energy, charge state and stability. Theory can provide an invaluable support for understanding the role of defects in the catalytic function of oxides. Extensive literature exists about the atomic and electronic structure of point defects in the bulk and at surfaces of oxides. Surprisingly, we found no theoretical studies that would carefully explore both the configurational *and* the compositional space of an oxide surface at realistic conditions, in particular for surfaces with structural defects such as steps and corners. Recently, we have shown [2] that the interplay between atomic structure and composition can be counter-intuitive, by finding that small *neutral* Mg_MO_x clusters ($1 \leq M \leq 15$) form thermodynamically stable non-stoichiometric “nano-oxides” (i.e, with $x > M$).

In this work, we explore the intermediate region between extended surfaces with structural defects and the “nano-oxides”. We calculate the relative stability of medium-size parallelepipedal $[(\text{MgO})_N]^q$ clusters at various charge states q ($N = 18, 24, 32$; $q = -2, -1, 0, 1, 2$) as function of T , p_{O_2} , and doping conditions, using DFT with the HSE06 hybrid exchange-correlation functional and *ab initio* atomistic thermodynamics. At this stage, the doping is considered only as a way to fix the chemical potential of electrons (μ_e). The global-minimum structures of such clusters are found via our massively-parallel cascade genetic algorithm implementation (see also TH12). We find that at realistic temperatures and pressures (e.g., $T = 300$ K, $p_{\text{O}_2} \sim 1$ atm) O_2 or O interstitial states at the oxygen corners of pristine $[(\text{MgO})_N]^q$ clusters are favored for *all* studied charge states, over a wide range of μ_e . In fact, the interstitials are stable even at some values of μ_e for which oxygen vacancies are preferred at flat (001) surfaces of doped MgO [3]. Strikingly, this behavior is confirmed when the clusters are embedded in a point-charge array, in order to mimic a corner defect (intersection of two step ridges) on an extended surface.

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Importance of Space-Charge Effects for the Concentration of Defects at Metal-Oxide Surfaces

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Doping, either intentional or unintentional, can affect the charge state, the concentration, and the distribution of defects in a material. However, the different mechanisms and relative significance of these effects have not been studied properly so far. Experiments measuring defect concentrations as a function of thermodynamic variables (temperature, pressure, doping) are scarce. On the other hand, previous theoretical approaches have aimed at a description of isolated defects, or, more recently, dopant-defect complexes. In this work, we consider the charge-carrier conductivity induced by doping as a thermodynamic factor influencing defect concentrations. Our results show that in addition to the local contributions to the free energy of defect formation, such as breaking or making of bonds and local lattice distortions, there can be a significant global contribution at realistic conditions due to the overall electrostatic energy of the system.

As a technologically relevant example, we study surface oxygen vacancies (F centers) in MgO, which is widely used as a catalyst or catalyst support. The standard methodology for calculating defect formation energies is extended to include the electrostatic free energy. Defect formation energies are determined using *ab initio* atomistic thermodynamics in combination with hybrid density-functional theory (DFT), with parameters of the exchange-correlation functional optimized according to a condition on DFT ionization energies. Formation energies for neutral defects are validated by coupled-cluster CCSD(T) calculations for embedded clusters. The virtual-crystal approximation [1] is used for a realistic modeling of doping. We find that at catalytically relevant conditions charge transfer between surface defects and bulk dopants leads to formation of a macroscopically extended space-charge region. The concentration of F_s^{2+} centers at the (100) terrace of *p*-type MgO can be as high as 1%, while F_s^+ and F_s^0 concentrations are negligible [2].

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Stability and Metastability of Clusters in a Reactive Atmosphere: Theoretical Evidence for Unexpected Stoichiometries of Mg_MO_x

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The quest for new materials demands the accurate description of *all* their (meta) stable structures under realistic conditions. In particular, in heterogeneous catalysis, materials function at finite temperature and in an atmosphere of reactive molecules at finite pressure. As a first step towards understanding the catalytic behavior of metal-oxide clusters, we study the (T, p) dependence of the composition, structure, and stability of the various isomers for each size M of Mg_MO_x clusters in an oxygen atmosphere. The calculations are performed via a massively parallel genetic algorithm in a cascade approach. With the term “cascade”, we identify a multistep procedure in which successive steps employ higher levels of theory, with each next level using information obtained at the lower level.

Our results [1] show that phase diagrams of Mg_MO_x clusters calculated via DFT with a hybrid exchange-correlation (xc) functional agree with the benchmark at the rPT2 level. Neither a force field as flexible as reaxFF [2] (whose range of validity is found to be quite narrow for the studied class of systems) nor DFT with semilocal xc functionals are sufficient for even a qualitative prediction of the phase diagrams of the studied cluster sizes. The failure of the semilocal functionals is explained by the underestimation of the energy cost for the electron delocalization over excess oxygen atoms due to the self-interaction error. In contrast to bulk MgO, an interplay of ionic (Mg-O) and covalent (O-O) bonding in small Mg_MO_x clusters ($M \leq 5$) favors $x > M$ at realistic T and p_{O_2} (e.g, $T \leq 800$ K for $p_{\text{O}_2} \sim 1$ atm). As a result of this interplay, O_2 and O_3 moieties appear as structural elements of the non-stoichiometric clusters. At the same (T, p_{O_2}) conditions, for bigger clusters there is a competition/coexistence between stoichiometric ($M = x$) and non-stoichiometric ($x > M$) compositions. Non-stoichiometric Mg_MO_x clusters with $x > M$ are found to be paramagnetic, due to the localization of the spin density at the O_2 and O_3 moieties. Stoichiometric clusters are all diamagnetic. At most of the sizes, we observe a peculiar (T, p_{O_2}) -dependent paramagnetic to diamagnetic transition, suggesting the possibility of tuning magnetic properties by changing environmental conditions.

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Ferroelastic Stabilization and Toughening of Doped Zirconia

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Thermal barrier coatings (TBCs) are widely used to protect superalloys from extreme temperatures. They increase durability, enable higher operational temperatures, and hence improve the fuel efficiency in power and propulsion turbines [1]. Due to its low thermal conductivity, high phase stability, and remarkable toughness, yttria stabilized zirconia (YSZ) is presently the material of choice for TBCs – but only in a narrow compositional range ($\sim 7\text{-}8$ mol-% $\text{YO}_{1.5}$). On the one hand, the addition of yttria stabilizes the tetragonal (and cubic) phase by suppressing the disruptive monoclinic transformation active in pristine ZrO_2 ; on the other hand, it degrades the toughness [1]. Conversely, co-doping YSZ with titania (TiYSZ) recently resulted in superior phase stability *and* toughness [2]. This is particularly surprising, since previous theoretical investigations had rationalized the stabilization mechanism in YSZ solely in terms of F^{2+} oxygen vacancies [3], which are introduced by aliovalent Y^{3+} doping, but not by isovalent Ti^{4+} .

We use density-functional theory to investigate the dynamics and the stability of the monoclinic, tetragonal, and cubic phases of pristine and doped ZrO_2 . Our *generalized solid-state nudged elastic band* [4] and molecular dynamics calculations show that the minimum-energy path for the tetragonal-to-cubic phase transformation differs significantly from the path that has been discussed in the literature so far [3]. In particular, we show that the correct minimum-energy path involves *ferroelastic switches*, i.e., the realignment of the tetragonal distortions along a different cartesian direction. This finding thus sheds light on the atomistic mechanism that determines these *ferroelastic switches*, which are generally considered to be the primary toughening mechanism in these compounds [1]. Furthermore, we discuss how various (co-)dopants affect this minimum-energy path and the associated *ferroelastic switches* and are thereby able to explain both the stabilization of the tetragonal phase *and* the controversial reduction/increase of toughness found in YSZ and TiYSZ, respectively. Accordingly, our calculations reveal that cation (co-)doping is essential to understand and control the toughness and thus the longevity of TBCs.

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Role of Vacancies in Thermoelectric Clathrates

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For the development of novel and improved thermoelectrics, one promising material class may be clathrates, i.e., semiconducting host lattices that can encapsulate guest atoms and molecules. In particular, the electronic and phononic transport coefficients that determine the thermoelectric efficiency of such clathrates can be granularly tuned by independently varying the composition of the host and guest lattice [1]. Even in the simplest clathrates, such as the type-I Si_{46} and Ge_{46} structures, the introduction of guests can result in surprising electronic and structural changes that go well beyond a simple filling of the cages. In the case of a Si-host for instance, synthesis under addition of K results in a K_8Si_{46} clathrate that exhibits metallic behavior due to the electrons donated by the guests [2]. Conversely, Ge-based clathrates retain their semiconducting character [3], since two spontaneously generated tetravalent vacancies \square balance the surplus electrons stemming from the potassium in $\text{K}_8\text{Ge}_{44}\square_2$. But even more intriguingly, filling the Ge-clathrate with divalent barium does not generate *four*, but *three* vacancies, whereby the resulting $\text{Ba}_8\text{Ge}_{43}\square_3$ exhibits a curious metal-semiconductor transition at ~ 280 K [4].

In this work, we use density-functional theory to investigate these puzzling effects. Foremost, we validate our approach by comparing the outcome of calculations performed at different (semi-)local and hybrid levels of theory, e.g., by discussing the impact of the chosen treatment for exchange and correlation on the structural parameters and on the formation energies of diluted defects in type-I clathrates. In a second step, we compute the formation energies for vacancies and vacancy complexes in Si- and Ge-hosts as function of the filling with K and Ba, whereby we take into account structural disorder as well as geometric and lattice relaxations. These calculations unravel the puzzling mechanism that drives/suppresses the spontaneous occurrence of vacancies and thus confirm the experimentally found vacancy concentrations and the associated electronic character of K_8Si_{46} , $\text{K}_8\text{Ge}_{44}\square_2$ and $\text{Ba}_8\text{Ge}_{43}\square_3$. Eventually, we use the *harmonic* approximation as well as *ab initio* molecular dynamics to study the temperature dependent changes of the electronic and vibrational structure in these compounds. In the light of our collaboration with the experimental group of J. Grin at the MPI for Chemical Physics of Solids, we discuss the implications of our findings for the synthesis of novel thermoelectric materials.

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Role of van der Waals Interactions in the Stability and Mobility of Point Defects in Semiconductors

Wang Gao and Alexandre Tkatchenko

Point defects are abundant in essentially all real-world materials, and they often significantly modify the electronic, optical, and magnetic properties of solids. However, our understanding of the stability and mobility of point defects even in prototypical semiconductors (Si, Ge, GaAs) remains incomplete, despite decades of intensive work on the subject. The formation energy and diffusion barriers of point defects in semiconductors can be estimated from experimental measurements, however it is often hard to deconvolute the contributions from interstitial and vacancy diffusion [1]. Calculations based on many-body *GW* and quantum Monte Carlo (QMC) methods can be used to accurately determine defect energetics, but these calculations are often impractical due to the rather large unit cells required to accurately model defect energetics. In the framework of DFT, semi-local functionals underestimate formation energies of defects by more than 0.7 eV due to the electron self-interaction error [2], while hybrid functionals such as Heyd-Scuseria-Ernzerhof (HSE) yield defect formation energies in better agreement with *GW* and QMC calculations, but often overestimates migration barriers by up to 0.4 eV [3].

Here we focus on understanding the interplay between electronic structure and nonlocal van der Waals interactions for defects in bulk Si and heavier semiconductors. Specifically, we use the HSE functional, coupled with the recently developed method for screened long-range vdW interactions [4,5]. We find that HSE+vdW resolves the underestimation of Perdew-Burke-Ernzerhof (PBE) functional on defect formation energies and the overestimation of HSE on defect migration barriers. The inclusion of vdW interactions significantly changes the transition state geometries, and brings migration barrier heights into close agreement with experimental values for six different defects. For multiatom vacancies in Si, and point defects in heavier and more polarizable semiconductors such as Ge, GaAs, InP, and InAs, vdW interactions are shown to play an increasingly larger role. These results suggest that the HSE+vdW method can improve our understanding of materials where the correct description of electronic structure and the non-local electron correlation is essential [6].

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Evidence for a β -Peptide Equivalent of the α -Helix

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Compared to the natural α -peptides, the backbone of a β -peptide contains one additional methylene group per residue. Research of such non-natural peptides is driven by the aim to find secondary-structure elements analogous to the ones in natural peptides. Various helical structures have been identified in β -peptides already [1]. However, a safe identification of the most prominent helix type, the α -helix, was still lacking despite hints from diffraction experiments on nylon-3 polymers [2].

We compare the structure space of β -peptides and α -peptides with specific focus on helical conformations. The polyalanine-based peptide series Ac-Ala_{*n*}-Lys(H⁺), $n \simeq 6 - 19$, has been designed to form α -helices in the gas phase [3-5], i.e., an environment where experiment and our theoretical results can be compared on equal footing. We concentrate on a comparison between isolated Ac-Ala₆-Lys(H⁺) versus its related β -peptide Ac- β^2 hAla₆-Lys(H⁺). For this, we employ density-functional theory (DFT) with the PBE functional corrected for van der Waals interactions and compare our results to ion-mobility mass-spectrometry and infrared multiphoton dissociation measurements. Our conformational search for Ac- β^2 hAla₆-Lys(H⁺) is based on replica-exchange molecular dynamics (REMD). First, a large conformational pool is generated by force-field (FF) REMD simulations (OPLS-AA), which is then refined locally by DFT-based REMD runs for the lowest-energy helical structures that yielded even lower-energy helical conformations.

Ac-Ala₆-Lys(H⁺) is found to be mostly α -helical at room temperature [5]. After sorting all 14,000 DFT structures for Ac- β^2 hAla₆-Lys(H⁺) (energy window about 1.6 eV) into families according to their H-bond network, free energy corrections at 300 K are considered in the harmonic approximation. We find both helical and non-helical conformers in the low-energy regime. Notably, the helical conformations are stabilized by vibrational free energy. The combination of theory and experimental fingerprints identifies a helical structure with a hydrogen-bond pattern analogous to the α -helix as the most likely structure candidate – we here provide the first evidence for a β -peptide equivalent of the α -helix.

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The Peptide-Water Interaction: Accurate Description from First Principles and Nuclear Quantum Effects

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The function and stability of polypeptides and proteins rely on a delicate balance of various types of interactions. These comprise intramolecular and intermolecular interactions of the peptide with its environment. We here identify the importance of energetic contributions coming from the electronic structure and present the first steps towards the inclusion of nuclear quantum effects (NQE). We investigate isolated and microsolvated peptides large enough to form secondary structure, and isolated water clusters. We use density-functional theory including van der Waals dispersion (vdW) effects, as implemented in the all electron code FHI-aims [1].

Previously, we have shown that for the Ac-Ala_n-LysH⁺, $n=4-8$ peptide series, an interplay of H-bonds, vdW interactions, and vibrational entropy act to stabilize helical motifs at finite temperatures [2]. We here study the conformational preferences and water binding sites of $n=5$ (non-helical) and 8 (helical). From conformational searches involving relaxations of thousands of microsolvated conformers with the PBE+vdW functional, we find the low energy structure candidates. For both molecules, the most favorable single water adsorption sites break intramolecular H-bonds associated with the LysH⁺ ammonium group, in contrast to earlier suggestions. Our Gibbs free energies and equilibrium constants for the adsorption reaction are in excellent agreement with experiments. We trace a drop in the adsorption propensity from $n=5$ to $n=8$ to subtle changes in zero-point and vibrational free energy [3], which point to a clear importance of NQE in these systems.

We thus present our efforts to capture NQE in large systems realistically. We first study protonated water hexamers where NQE favor open clusters already at low temperatures, and compare their IR spectra to low temperature, conformer-selective experimental data [4]. We also discuss improvements, based on recently published techniques [5], in path integral and analytical continuation methods to approximate real time correlation functions that can be treated using *ab initio* potentials.

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Space Charge Transfer in Inorganic/Organic Hybrids

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Hybrid inorganic/organic systems (HIOS) have opened up new opportunities for the development of (opto)electronic and photovoltaic devices due to their potential of achieving synergy by combining the best features of two distinct material classes. From a quantum mechanical first-principles point of view, this combination is particularly challenging, because hard materials with a preference for band transport come in contact with soft, often disordered and van-der-Waals-bonded matter with a prevalence for localized states and polaron formation. An aspect that has so far been overlooked, however, is the build-up of a space-charge region at the inorganic/organic interface and the influence it has on the interface properties, although space-charge layers are a common occurrence in inorganic semiconductors and insulators.

We here present a quantum mechanical first-principles approach that introduces excess charge in the unit cell by means of the virtual crystal approximation with fractionally charged nuclei [1] to simulate bulk doping and that includes the energy contribution of the space-charge layer explicitly. For the bulk terminated ZnO(000-1) surface covered with half a monolayer of hydrogen (2x1-H), we demonstrate that electrons from bulk dopants can stabilize deviations from this half monolayer coverage at low hydrogen pressures [2]. Ambient hydrogen background pressures are therefore more conducive than ultra high vacuum conditions to form the defect free 2x1-H surface, which would be a more controlled substrate in HIOS [2]. For the interface between ZnO(000-1) 2x1-H and monolayers of tetrafluoro-tetracyanoquinodimethane (F4TCNQ), a strong acceptor that is frequently used for interface modifications, we show that the adsorption energy and the charge transfer to the molecules depend strongly on the bulk dopant concentration. While the build-up of a space-charge layer is not unexpected, the magnitude of its effect is astounding: the adsorption energy of F4TCNQ changes by more than 2 eV and more than doubles from low to high doping. In the limit of low bulk doping concentrations, charge transfer becomes vanishingly small in agreement with photoemission data [3], while the F4TCNQ induced work function change remains unaffected and large. The bulk doping concentration and the associated build-up of a space-charge layer therefore provide an additional way to tune the interface properties in HIOS.

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Charge Transfer and Localization at Inorganic/Organic Heterojunctions

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A reliable theoretical description of the level alignment and the charge-transfer at heterointerfaces is of fundamental importance for a variety of fields, including organic photovoltaics and electronics. The quantum mechanical method of choice for such systems is density-functional theory. However, the predictive power of the commonly used local and semi-local functionals is limited, mainly because of their inherent self interaction error. Subsequently, unoccupied orbitals appear too low and occupied orbitals too high in energy, which could result in spurious charge transfer. This deficiency can be reduced by employing hybrid functionals, that include a fraction α of exact (Hartree-Fock) exchange. However, the α required for an optimal description is material dependent and may differ strongly for organic and inorganic materials. We address this conundrum and investigate how the description of different organic acceptors adsorbed on metal surfaces is affected by the transition from semi-local to hybrid functionals using the functional family of Heyd, Scuseria, and Ernzerhof [1].

For adsorbates which strongly hybridize with an Ag(111) surface, only quantitative changes are observed. We find that the contribution to the interface dipole arising from covalent interactions is barely affected by hybrid functionals, while the total charge transfer systematically increases with α . Comparing to experimental work-function data, we report for $\alpha \approx 0.25$ a notable but small improvement over (semi)-local functionals for the interface dipole. Coincidentally, also the density of states agrees well with the photoelectron spectra (although Kohn-Sham eigenvalues are only approximate representations of ionization energies). Increasing α to values for which the energy of the highest occupied molecular orbital of the negatively charged adsorbate matches its experimental electron affinity in the gas phase worsens both the interface dipole and the density of states.

In contrast, qualitative differences appear when the hybridization between metal and adsorbate is prevented by a NaCl spacer layer. In this case, semi-local functionals predict a fractional electron transfer resulting in equally charged molecules. Hybrid functionals, on the other hand, are able to break the translation symmetry and produce integer charging of only a fraction of the adsorbate layer, when using supercells with sufficiently many organic molecules. Both situations give qualitatively different core-level shifts, electrostatic potentials in the vicinity of the surface, and a different coverage dependence of the adsorption-induced work-function change that should be observable in experiment.

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Concerted Effects of Covalent Bonding and van der Waals Interactions in Organic/Metal Interfaces

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The adsorption of aromatic molecules at transition-metal surfaces is important for fundamental and applied surface science studies. These systems are also promising in numerous applications including light-emitting diodes, transistors, sensors, and solar cells [1]. The understanding of electronic properties of organic/metal interfaces requires an accurate method for the prediction of their structure and stability. However, reliable treatment of both weakly and strongly adsorbed systems is a challenge for density-functional theory (DFT), due to the well-known fact that the accurate description of van der Waals (vdW) interactions is a difficult task for commonly used functionals. Recently, several promising vdW-inclusive DFT methods have shown remarkable accuracy for intermolecular interactions. However, none of these approaches accounts for non-local (inhomogeneous) collective electron response in the vdW energy tail, an effect that is particularly important in metals.

We developed the so-called DFT+vdW^{surf} method [2] to accurately model adsorbates on surfaces, by a synergetic linkage of the DFT+vdW method [3] for intermolecular interactions with the Lifshitz-Zaremba-Kohn theory for the dielectric screening within the substrate surface. This method is demonstrated to achieve *quantitative* accuracy for 9 molecules adsorbed on 8 metals (25 systems in total), leading to a performance of 0.1 Å in adsorption heights and 0.1 eV in binding energies with respect to state-of-the-art microcalorimetry experiments, and the revised interpretation of temperature-programmed desorption data by Campbell's group [4,5]. Using the DFT+vdW^{surf} method also enables us to obtain new *qualitative* findings. For example, our calculations predict the existence of an incipient precursor state for benzene/Pt(111) in agreement with experiments [4,6]. Finally, to demonstrate the predictive power of the DFT+vdW^{surf} method, we design a novel type of single-molecule push-button switch, by carefully controlling the stability and activation barrier between a chemically bound state and a physically bound state for benzene derivatives adsorbed on metal surfaces [7].

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Reliable Modelling of Stabilities, Polymorphism, and Response Properties in Organic Materials

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Organic materials are of great fundamental and applied importance, with numerous applications in pharmaceuticals, food science, electronics, sensing, and catalysis. A key challenge for theory has been the prediction of their stabilities, polymorphism, and response to external perturbations. In recent years, there has been substantial progress in the modeling of organic materials with semi-local approximations to density functional theory (DFT) coupled with pairwise descriptions of dispersion interactions [1]. However, the majority of studies neglect the contribution of many-body dispersion (MBD) and also the self-interaction error (SIE) present in widely used density functionals. As a result, many quantitative and even qualitative failures remain [2].

To categorically understand the importance of MBD contributions and SIE we have studied two databases of gas-phase and solid-state intermolecular interactions [3,4]. While pairwise dispersion methods perform remarkably well for simple dimers, they substantially overestimate molecular-crystal lattice energies. Correctly accounting for electrodynamic response and many-body energy contributions using the MBD method [5] yields substantial improvements. The application of a hybrid functional (PBE0) also gives noticeable improvements, particularly for hydrogen-bonded solids. Overall, the PBE0+MBD method is capable of reaching accuracies of a few kJ/mol for both crystalline and gaseous phases compared to high-level theoretical and experimental stabilities [3,4], giving a systematic method for modeling both gas-phase and condensed molecular materials.

The accuracy achieved by PBE0+MBD enables us to account for the correct polymorphic ordering of a number of challenging systems, such as glycine, for the first time [6]. However, the importance of dispersion goes far beyond energetic stabilities. Many response properties show even larger contributions from many-body dispersion interactions. In particular, we have studied the elastic properties of a series of molecular crystals, finding that MBD contributions can account for up to 25% of the elastic constants.

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Strain Derivatives for Localized-Orbital Based Electronic-Structure Theory and their Application to Polyacetylene

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The electronic properties of semiconductors such as band gaps and effective masses typically exhibit a significant dependence on the strain [1]. In turn, the strain imposed during fabrication depends distinctly on the growth conditions, e.g., on the pressure in the case of organic [2] and on the stress in the case of inorganic [1] semiconductors. These effects are a crucial ingredient to simulate, to understand, and to optimize the performance of (opto-)electronic devices.

To investigate the intricate dependence of the electronic structure on the applied stress (viz. strain and pressure), we have implemented the analytical strain derivatives of the total energy, i.e., the stress tensor, in the numeric, atom-centered orbitals based all-electron electronic structure code FHI-aims. Both the contributions that arise at the LDA/GGA level of theory and the contributions associated with the Fock matrix, i.e., the terms that arise in the case of non-local hybrid functionals, are accounted for in our implementation. Furthermore, we include the strain derivatives of a common van der Waals correction term [3] as well. We discuss the accuracy and the efficiency of our implementation by presenting extensive benchmark calculations for a variety of different crystal systems.

The implementation described above is applied to the crystalline organic semiconductor trans-polyacetylene. We show how geometry and electronic properties depend on the exchange-correlation functional and the van der Waals corrections for this particular system. Furthermore, the fraction of Hartree-Fock exchange used in hybrid functionals critically affects the resulting dimerization and band gap. We validate our findings by comparing to high-level CCSD(T) calculations [4], and also investigate the changes in the electronic band structure as a function of the applied external pressure. Thereby, we are able to qualitatively reproduce and explain the pressure dependence of the band gap found in experiments [5,6].

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Is Cerium Unique? Rare Earth Metals in Density-Functional Theory

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The rare earth elements are the Wild West of the natural elements. They were discovered relatively recently, but already have applications in several fields including medicine, communication technology and catalysis. Yet they remain enigmatic, because the simultaneous presence of itinerant *spd*-states and localized, partially occupied *f*-states and their mutual interaction gives rise to a plethora of physical phenomena. One prominent example is the isostructural α - γ phase transition in cerium (Ce) – the first element with an *f*-electron in the lanthanide series – and the associated volume collapse of 15% at room temperature and ambient pressure [1]. We have shown that density-functional theory (DFT) captures the volume collapse in Ce at zero temperature, but only if advanced density functionals such as exact exchange plus correlation in the random-phase approximation (EX+cRPA) are used [2]. Adding entropic contributions, the experimental phase transition line at finite temperature is reproduced. Inspection of the electron density reveals that the *f*-electrons are delocalized in the α -phase and localized in the γ -phase. For the first time, we were thus able to directly visualize the concept of *localization-delocalization* that is commonly invoked to describe the lanthanides.

The question then arises, *is cerium unique?* In fact, several of the rare earth metals exhibit a volume collapse, but only in cerium is the phase transition isostructural [1]. We addressed this puzzle by applying DFT also to lanthanum (La), praseodymium (Pr) and neodymium (Nd). Out of these three, only Pr exhibits a volume collapse. Lanthanum has no *f*-electrons and we subsequently only find one phase in our DFT calculations. For Pr and Nd, on the other hand, our calculations produce more than one stable solution in the fcc crystal structure. But unlike in Ce, for which two separate minima emerged in the energy vs volume curve, the curves are nested and thus only yield one minimum. Experimentally, Pr and Nd undergo a series of structural changes from the fcc structure, to distorted-fcc to α -uranium [1]. These transitions are already captured at a lower level of DFT (i.e. with (semi)-local functionals) and we therefore conclude that *f*-electrons are not the driving force for the phase transitions in Pr and Nd.

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Strengthening Gold-Gold Bonds by Complexing Gold Clusters with Noble Gases

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In the great majority of molecular systems that contain rare-gas (RG) atoms, the bonding with RG can be explained as mainly due to either van-der-Waals interaction or electrostatics. In the latter case, the RG atoms can be simply polarized by multipole moments of the attached fragment. The few compounds where this is *not* the case always present a puzzling and fascinating challenge for the physical understanding of the bonding. In this work, we study a practically important case of RG-involving compounds: *neutral* $Au_N \cdot RG$ complexes, where both isolated fragments have zero charge and zero or very small electric dipole moment. Knowing the atomic and electronic structure of gold clusters is important for understanding their catalytic activity. Rare gases can be exploited as “messengers” in experiments where infrared spectroscopy in combination with theoretical analysis is used to determine the atomic structure of metal clusters in the gas phase. The atomic and electronic structure of the complexes is calculated using various methods, from density-functional theory with semi-local exchange-correlation functionals to coupled-cluster theory with single, double, and perturbative triple substitutions (CCSD(T)). Our theoretical analysis reveals a relatively strong bonding of RG atoms to very small Au clusters. For example, the binding energy of Kr to Au_2 is 0.2 eV. Attaching Kr (as well as Ar and Xe) to Au_2 results in the shortening of the Au-Au bond and the blue shift of the corresponding stretching vibrational mode. Similarly, adsorption of Kr to Au_3 induces the shortening of *one* Au-Au bond and the blue shift of the corresponding stretching vibrational mode. These results are qualitatively independent of the level of theory employed. Finite-temperature vibrational spectra (i.e., including anharmonic effects) are calculated using *ab initio* molecular dynamics simulations. The calculated spectra for $Au_3 \cdot Kr$ are in good agreement with measured far-infrared multi-photon dissociation (FIR-MPD) spectra [1] ($Au_2 \cdot Kr$ is invisible to the experiment due to too high ionization potential).

Analysis of the electronic structure of the complexes reveals that the unusual bonding is due to the overlap of the $4p$ orbitals of Kr with d orbitals of the gold clusters, which leads to the depletion of the electron density in the region between the gold atoms. This reduces the electron-electron repulsion between the gold atoms and effectively strengthens the Au-Au bonds.

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