Theory Department

Poster List

Recent work done in the Theory Department is displayed on 22 posters.

All posters are displayed in building T and the poster site is given below.

The superscript[ERC] marks the work of A. Tkatchenko's ERC group.

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New Concepts, Methods, and Techniques	
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TH 2	**Real-Time Propagation of Coupled Light-Matter Systems** Uliana Mordovina, René Jestädt, Heiko Appel, and Angel Rubio
TH 3	**Time-Evolution of Tensor Networks in Quantum Electrodynamics** Teresa Reinhard, Wilhelm Bender, Heiko Appel, and Angel Rubio
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TH 5	**Tailored Cascade Genetic Algorithms for the Study of the Thermodynamical Stability of Metal-Oxide Clusters and their Structure-Property Relationships** Saswata Bhattacharya, Daniel Berger, Karsten Reuter, Noa Marom, Sergey V. Levchenko, Matthias Scheffler, and Luca M. Ghiringhelli
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Victor G. Ruiz López, Fairoja Cheenicode Kabeer, Wei Liu, and Alexandre Tkatchenko

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Xunhua Zhao, Sergey V. Levchenko, and Matthias Scheffler

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Oliver T. Hofmann, Patrick Rinke, Georg Heimel, and Matthias Scheffler

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TH 16 **Towards a Quantitative Description of the Energetics of Peptide-Cation Interactions**

Markus Schneider, Matti Ropo, Volker Blum, Carsten Baldauf, and Matthias Scheffler

TH 17 **Reduced Molecular Potential-Energy Surfaces from First Principles**

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TH 18 **Anomalous Electron-Phonon Coupling in Thermoelectric Clathrates and Skutterudites**

Amrita Bhattacharya, Susmita Basak, Maria Troppenz, Santiago Rigamonti, Christian Carbogno, Claudia Draxl, and Matthias Scheffler

TH 19 **The FHI-aims Project**

Volker Blum and Matthias Scheffler; Martin Andersen, Daniel Berger, Christian Carbogno, Lukas Gallandi, Mark Glass, Vivekanand V. Gobre, Jan Hermann, William Huhn, Arvid C. Ihrig, Thomas Körzdörfer, Björn Lange, Hermann Lederer, Sergey V. Levchenko, Xiangyue Liu, Andrew Logsdail, Andreas Marek, Florian Merz, Harald Oberhofer, Xinguo Ren, Karsten Reuter, Stefan Ringe, Patrick Rinke, Adrienn Ruzsinszky, Christoph Schober, Honghui Shang, Tonghao Shen, Markus Sinstein, Kurt Stokbro, Alexandre Tkatchenko, and Igor Ying Zhang

TH 20 **Big Data of Materials Science: Critical Role of the Descriptor**

Luca M. Ghiringhelli, Jan Vybiral, Sergey V. Levchenko,
Claudia Draxl, and Matthias Scheffler

TH 21 **Test Set for Materials Science and Engineering**

Igor Ying Zhang, Norina A. Richter, Xiangyue Liu, Sergey V. Levchenko,
Luca M. Ghiringhelli, and Matthias Scheffler

TH 22 **The Novel Materials Discovery (NOMAD) Center of Excellence: Big-Data Storage, Search, and Analysis**

Luca M. Ghiringhelli, Fawzi Mohamed, Christian Carbogno,
Lorenzo Pardini, Pasquale Pavone, Johann-Christoph Freytag,
Thomas Zastrow, Binyam Gebrekidan Gebre, Raphael Ritz,
Hermann Lederer, Stefan Heinzel, Alessandro De Vita, Daan Frenkel,
Francesc Illas, Risto Nieminen, Angel Rubio, Kristian Sommer Thygesen,
Claudia Draxl, and Matthias Scheffler

Kohn-Sham Approach to Quantum Electrodynamics

Johannes Flick, Christian Schäfer[a], Camilla Pellegrini[b], Heiko Appel,
Michael Ruggenthaler[a], Ilya V. Tokatly[c], and Angel Rubio[a,b]

Time-dependent density-functional theory (TDDFT) has been successfully applied to a large variety of problems, such as calculations of absorption spectra, excitation energies, or dynamics in strong laser fields. On the other side, many-body perturbation theory (MBPT) opens the possibility to construct approximations to every desired order of a 'weak' interacting system. Here, the drawback is an in general non-local interaction in space and time, and it is therefore a demanding task to apply it to 'real' systems. In the framework of quantum electrodynamics (QED), we have recently generalized TDDFT to also describe electron-photon systems (QED-TDDFT)[1,2]. In this approach matter and light are treated on an equal quantized footing.

The optimized effective potential (OEP), derived by inversion of the Sham-Schlüter equation, is a natural connection between local density functional theory and MBPT. In principle, this variationally best local potential reduces the problem to solving a simple system of Kohn-Sham equations combined with the solution of the OEP integral equation. However, converging the full set of OEP equations is quite challenging and is in practice rarely tackled. The Krieger-Li-Iafrate (KLI) approximation reduces the integral equation to an analytically solvable one via a dominant orbital approximation.

In this work, we present the first numerical calculations in the framework of QED-TDDFT. We show exact solutions for fully quantized prototype systems placed in optical high-Q cavities and coupled to quantized electromagnetic modes, both for model systems heavily used in Quantum Optics, as well as for 1D soft-Coulomb systems in real-space. We focus on the electron-photon exchange-correlation contribution by calculating exact Kohn-Sham potentials in real-space using fixed-point inversions and present the performance of the first approximated exchange-correlation potential based on an optimized effective potential approach for a Jaynes-Cummings-Hubbard Dimer[3]. Furthermore, we extend the OEP and KLI approaches to the case of electron-photon interactions in quantum optics and quantum electrodynamics. Here an effective electronic interaction is transmitted via transversal photons. We present first static and time-dependent results for the OEP[3] and KLI approximations of the Rabi and 1D-hydrogen model and compare with the exact configuration-interaction solution and the corresponding exact Kohn-Sham potentials[2].

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Real-Time Propagation of Coupled Light-Matter Systems

Uliana Mordovina[a], René Jestädt, Heiko Appel, and Angel Rubio[a,b]

Modern free electron x-ray lasers (XFEL) produce pulses on a timescale of femtoseconds and wavelengths of few nanometers. This experimental progress opens new frontiers for understanding the dynamics of molecules under extreme conditions. A particular challenge for theorists is the development of new theoretical and computational tools for the investigation of non-equilibrium dynamics of large coupled light-matter systems under such conditions. Here, the quantum nature of both the electronic and the photonic part cannot be omitted.

By solving the full relativistic quantum electrodynamics (QED) on a non-pertubative level as a lattice-field theory, we investigate real-time dynamics of coupled electron-photon-systems. In the current work we present our first numerical results in this framework. Using Dirac spinors and the Riemann-Silberstein vector[1], we study the wave-packet dynamics for electrons and photons and investigate effects such as pair annihilation and Compton scattering in real-time. These solutions serve as exact numerical reference calculations for the construction of novel exchange and correlation functionals to the recently established density-functional theory for QED[2].

In the non-relativistic limit, we present the first steps towards the implementation of the coupled Maxwell's and time dependent Kohn-Sham equations. The Riemann-Silberstein vector of the electromagnetic field allows us to write Maxwell's equations in a symplectic spinor representation similar to the Dirac equation. This spinor representation allows us to use standard unitary propagation techniques[3] developed for the solution of the Schrödinger equation.

Our implementation in the real-space real-time code octopus[4] allows to propagate the Maxwell and Kohn-Sham systems with electrical dipole, magnetic dipole, and electrical quadrupole couplings. As first application, we investigate dipole radiation and electromagnetic near-field effects for jellium spheres[5].

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Time-Evolution of Tensor Networks in Quantum Electrodynamics

Teresa Reinhard[a], Wilhelm Bender[a], Heiko Appel, and Angel Rubio[a,b]

Due to the high intensities and small wavelengths in modern light sources such as free electron lasers, a non-pertubative and beyond-dipole description of the coupling of electrons and photons is necessary. To describe the dynamics in such coupled quantum systems, time-dependent density-functional theory was recently extended to include quantum-electrodynamical effects (QEDFT)[1].

Like all density-functional approaches, this description is formally exact. However, for current approximate QEDFT functionals, no error bars for the deviation from the exact solution of the Schrödinger equation are known. In order to develop such error bars, we construct systematically improvable approximations for the wavefunction of lattice quantum-electrodynamics. In our work, we expand the many-body wavefunction in terms of a tensor network[2]. For quantum electrodynamics this naturally leads to two different strategies.

First, we employ the Lanczos algorithm in order to compute the dynamical evolution of the system in terms of generalized matrix-product states. If all the symmetries of the Hamiltonian and of the initial state are exploited, we find from our analysis that only a few possible states have to be retained to describe the whole dynamics of the system.

Second, we consider a tensor network in discrete space and time variables. Globally optimizing this tensor network according to the the McLachlan variational principle[3], we detemine states which are equivalent to stationary solutions of the action principle of quantum electrodynamics.

In both cases, we analyze the entanglement of the involved states and compare our approach to QEDFT. The amount of entanglement is the only approximation that is inherent in the tensor networks that we consider. Since this quantity can be converged by increasing the bond dimension of the network, we can assess the deviation from the exact solution of the problem with an asymptotic analysis.

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Correlation Consistent Basis Sets and Explicitely Correlated Wavefunctions in a Numerical Atom-Centered Framework

Salih Akbudak[a], Arvid C. Ihrig, Volker Blum[b], Patrick Rinke[c], Igor Ying Zhang, and Matthias Scheffler

Methods like second-order Møller-Plesset perturbation theory (MP2) and the random-phase approximation (RPA) suffer from a slow basis set convergence due to the inaccurate modeling of the inter-electronic cusp. One popular strategy to alleviate this problem are complete basis set (CBS) extrapolation schemes as e.g. Dunning's correlation consistent (CC) Gaussian type orbital (GTO) basis sets[1]. Compared to Gaussian or plane-wave basis sets, numeric atom-centered orbitals (NAO) are more compact and transferable, thus they are appealing for the CC basis-set construction, as we have already demonstrated for light elements from H to Ar[2]. However, finding efficient and accurate CC basis sets for transition metals remains an open challenge for both GTOs and NAOs.

The RPA correlation of the 3*d* transition metals exhibits a significantly different convergence behavior compared to light elements. Based on this observation, we develop new CC basis sets for copper and several other 3*d* transition metals. The quality of CC strategies can be assessed by the energy difference from the counterpoise corrected and bare extrapolation, because the superposition error vanishes in the CBS limit. For the copper dimer, our new basis set yields an energy difference of about 10 meV, while the best available but considerably more expensive GTO basis set has a discrepancy of 91 meV.

Another approach is the introduction of an explicit dependence on the inter-electronic distance into the wave-function (F12 strategies[3]). However, the explicit dependence on inter-electronic distances gives rise to new matrix elements, which yield computationally expensive three and more electron integrals. We present an efficient evaluation scheme for these integrals in the NAO-framework using our recently developed maximally localized variant of the resolution of identity technique[4]. For the example of MP2 we demonstrate the improved convergence with the basis set size. In combination with CC basis sets, the F12 approach yields the prospect of reaching CBS-converged total energies for transitions metals with computationally affordable basis sets.

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Tailored Cascade Genetic Algorithms for the Study of the Thermodynamical Stability of Metal-Oxide Clusters and their Structure-Property Relationships

Saswata Bhattacharya[a], Daniel Berger[b], Karsten Reuter[b], Noa Marom[c], Sergey V. Levchenko, Matthias Scheffler, and Luca M. Ghiringhelli

Materials at nanoscale size show unusual properties that have prompted extensive studies of clusters and that are generally attributed to the presence of undercoordinated atoms. However, in the presence of a reactive atmosphere, clusters can adsorb species from the gas phase, changing their stoichiometry. Thus, in order to understand the functional properties of clusters and in general nanostructures in a reactive atmosphere, it is important to know which structures and stoichiometries are energetically accessible.

We introduce a robust first-principles methodology[1] for the determination of (meta)stable structures at realistic environmental conditions. First, the *ab initio* potential-energy surface is scanned by means of a global-optimization technique, i.e., a massive-parallel cascade genetic algorithm (cGA) for which the choice of all settings is validated against higher-level methods. In particular, we validate (a) the criteria for selection and combination of structures used for the assemblage of new candidate structures, and (b) the choice of the exchange-correlation functional. In the second step, the low-energy structures are analyzed by means of *ab initio* atomistic thermodynamics in order to determine compositions and structures that minimize the Gibbs free energy at the temperature and pressure of the reactive atmosphere.

We demonstrate our cGA by exploring O-vacancy and O/O_2-ad-species defects at steps and corners at MgO surface. The defects are modeled using MgO clusters, described at the hybrid-functional level and embedded into a field of norm-conserving pseudopotentials and point charges. The long-range response of the oxide to the charge carriers trapped at the defects is taken into account using a polarizable force field. Unexpectedly, we find that O-ad-species rather than O-vacancies are dominating defects at realistic conditions. The stability of the O-ad-species over O-vacancies and pristine corners is explained by an interplay between bond-breaking, bond-making, and charge-carrier trapping.

Furthermore, we extend the cGA by including the optimization of properties different form energy, in order to allow for the understanding of the structure-property relationship of desired properties of (nano)materials, e.g., large electron affinity (EA) and small ionization potential (IP). This extension is demonstrated by applying it to $(TiO_2)_n$ clusters (n = 3−10, 15, 20), where we identify correlations between electronic properties (large EA, small IP) and structural features (number and distribution of dangling-O atoms)[2]. A tailored cGA can provide insight for the understanding of "design rules" of targeted metastable materials, in experiments and practical applications where quantities other than energy can be optimized (e.g., selection of clusters having a large EA in photoemission spectroscopy experiments).

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Wavelike Nature of van der Waals Interactions at the Nanoscale

Jan Hermann, Alberto Ambrosetti[a], Vivekanand V. Gobre, Mausumi Chattopadhyaya, and Alexandre Tkatchenko

Van der Waals (vdW) interactions crucially influence the structure and properties of molecular clusters, soft-matter solids and heterogeneous material interfaces, thus driving applications from drug design to electronics to catalysis. With the increasing focus on supramolecular chemistry and nanostructured materials, vdW interactions are being employed and probed at increasingly larger scales and decreasing dimensionality. However, our current understanding of these interactions is largely based on small model systems and idealized, mostly pairwise-additive London dispersion picture. As a result of this inconsistency, predictions of both static and dynamic properties of nanoscale structures may fail in quantitative and sometimes even qualitative manner[1,2].

Here, we demonstrate that in supramolecular complexes and low-dimensional nanostructures, vdW correlations are more naturally described in terms of coupling between fluctuating dipole waves. This wavelike nature stems from the coupling between initially localized fluctuations, which lose their individuality due to strong interatomic interactions. This leads to several nontrivial effects in vdW interactions that cannot be explained by perturbative dispersion corrections and non-local functionals based on the electron density, but that are correctly captured by the infinite-order many-body dispersion (MBD) model[3,4]. In linear chain structures and 2D materials, the interaction energy is described by a combination of power laws that can vary widely between pairwise insulating and delocalized metallic limits. For molecules interacting through nanostructures, we observe a regime in which their interaction energy *increases*, instead of decreasing as naively expected from the conventional dielectric screening model. Further application to carbon-based supramolecular complexes demonstrates that omitting wavelike vdW fluctuations leads to differences in association constants of up to five orders of magnitude where there should be degeneracy according to high-level quantum Monte Carlo calculations.

Taken together, our findings indicate that the wavelike nature of vdW interactions provides a hitherto unexplored avenue that could be used for tailoring the assembly of complex polarizable systems at the nanoscale.

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First-Principles Simulations of Polarons in Oxides: Insights and Challenges

Sebastian Kokott, Honghui Shang, Christian Carbogno, Sergey V. Levchenko, Patrick Rinke[a], and Matthias Scheffler

The formation and migration of polarons plays an important role for many properties of functional materials, e.g., optical spectra and electrical conductivity[1,2]. However, a systematic first-principles assessment of the underlying electron-phonon (e-ph) coupling still faces severe challenges – especially in the case of oxides[3,4] such as ZnO, MgO, and TiO_2.

Foremost, we demonstrate that the e-ph interaction can be very sensitive to errors associated with the use of approximate exchange-correlation (XC) functionals in density-functional theory (DFT). Our results show that the stability of polarons can be decisively affected by small changes in parameters, e.g., the fraction of exact exchange included in hybrid functionals such as PBE0 and HSE06. We discuss how these uncertainties can be reduced by enforcing the XC functional to satisfy certain constraints that an exact functional would fulfill[5]. We investigate how the approach depends on the finite size of the employed supercell and the type of the lattice distortion (from small atomic displacements to O and cation vacancies).

Furthermore, we show that obtaining the correct atomic distortions of polarons proves to be more challenging than naively expected. On the one hand, strong e-ph coupling can result in small polarons that are localized within a few unit cells and that can therefore be treated in a supercell approach. Several types of small polarons with different atomic displacements but similar energies can co-exist, depending on the point group of the perfect crystal. On the other hand, weak e-ph coupling can result in large polarons that span several thousand atoms, defying a supercell treatment. In this case, analytic but approximate models can be used to estimate the polaron formation energies, e.g., by evaluating the renormalization of the band edges due to the zero-point motion of the atoms from first-principles[6] or by estimating the interactions in the elastic limit with the Fröhlich model[7]. We critically review and compare the available techniques, and investigate to which extent they allow us to bridge the gap between the localized and delocalized states. In particular, we show that in the intermediate coupling-strength regime neither of the first-principles techniques is able to achieve qualitatively correct results[1].

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Modeling Quantum Nuclei with Perturbed Path Integral Molecular Dynamics

Igor Poltavsky and Alexandre Tkatchenko

The quantum nature of nuclear motions can play an important role in the structure, stability, and thermodynamics of molecules and materials. Whenever interatomic forces are strong, nuclear quantum fluctuations (NQF) can be fairly pronounced at room temperature and even above it. The standard approach to model NQF in chemical and biological systems is path-integral molecular dynamics (PIMD). Unfortunately, conventional PIMD simulations can have exceedingly large computational cost due to the need of employing an excessive number of coupled classical subsystems (beads) for quantitative accuracy. More sophisticated approaches have been developed[1,2,3], but they either require extensive parameterization or inadequately sample the phase space, which limits their applicability to realistic molecules and materials. Hence, the development of a parameter free method for NQF that is both accurate and efficient would be desirable.

To achieve this challenging goal we combine perturbation theory[4] with the Feynman-Kac imaginary-time path integral approach[5] to quantum mechanics and derive improved non-empirical partition function and estimators to calculate converged quantum observables. Our *perturbed path-integral* (PPI) method requires the same ingredients as conventional approaches, but increases the efficiency of path integral simulations by an order of magnitude. Any kind of phase sampling technique and any thermostat or barostat can be utilized. The *converged* observables can be obtained either *on-the-fly* or *a posteriori* from conventional PIMD simulations, which form the base of the developed PPI approach.

Applications are presented for the thermodynamics of the quantum harmonic oscillator and the double-wall potential, empirical water model containing 256 water molecules within periodic boundary conditions, *ab initio* simulations of nitrogen and benzene molecules, and graphene. For all of these examples, our PPI approach with 4 to 8 classical beads recovers the nuclear quantum contribution to the total energy and heat capacity at room temperature within 3% accuracy, paving the way toward accurate modeling of nuclear quantum fluctuations in realistic molecules and materials.

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Machine Learning of Quantum Mechanical Properties of Materials

Matthias Rupp[a], Saswata Bhattacharya[b], Luca M. Ghiringhelli, and Matthias Scheffler

Systematic computational design and study of materials requires rigorous, unbiased, and accurate theoretical treatment at the atomic scale. While numerical approximations to the many-electron problem are available, their prohibitive computational cost severely limits their applicability to large systems, long timescales, or large numbers of systems. Based on the reasoning that electronic-structure calculations of similar systems contain redundant information, machine learning models have been developed that interpolate between a computationally feasible number of *ab initio* reference calculations to predict properties of new similar systems[1]. This Ansatz of mapping the problem of solving the electronic Schrödinger equation onto a non-linear statistical regression problem has led to computational savings of up to several orders of magnitude for molecules, with accuracy on par with the reference method.

We present machine-learning models for properties of atoms in molecules and materials. To establish proof of principle, we predicted quantum mechanical observables such as proton and carbon nuclear chemical shifts, atomic core level excitations, and forces on atoms for a diverse set of 9 k small organic molecules, reaching accuracies close to the employed density-functional theory reference method (DFT/PBE0/def2TZVP). In these models, locality is exploited within non-linear regression via local atom-centered coordinate systems. This enables both computational linear scaling with low prefactor and extrapolation to larger systems locally similar to the reference systems, which we demonstrated for saturated polymers (linear polyethylene doped with NH and O for chemical variety) with up to sub-mesoscale lengths[2].

Metal-oxide clusters constitute a more challenging class of systems due to their larger flexibility of bonding compared to the small organic molecules. For a dataset of 3000 MgO clusters, Mulliken and Hirshfeld partial charges were predicted with a relative root mean squared error of 2.1–3.1 %. In addition, other properties of atoms in their environments were investigated, such as core level ionization energies, forces, and Fermi contact interactions (proportional to the electron density at the atomic nucleus and relevant for electron paramagnetic resonance spectroscopy). Similar investigations were carried out for TiO_2 and CrMgO clusters. Part of the data are available via the NOMAD data repository[3]. Our aim is to further develop these models to enable treatment of both more and larger systems in areas such as thermoelectric materials, photovoltaics, and heterogeneous catalysis.

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Thermal Conductivities in Solids from First Principles: Accurate Computations, Qualitative Insights, Rapid Estimates

Christian Carbogno and Matthias Scheffler

The development of materials with suitable thermal conductivity is crucial for a variety of applications, e.g., for the optimization of thermoelectric elements or for the design of novel thermal barrier coatings for gas and airplane turbines[1]. Since an assessment of vibrational heat transport in solids requires detailed knowledge of the anharmonic dynamics on macroscopic time and length scales, an accurate calculation of thermal conductivities is conceptionally and computationally challenging: On the one hand, approaches based on the *Boltzmann Transport Equation* (BTE) allow a computational efficient assessment in reciprocal space by utilizing the phonon properties (dispersions, group velocities, etc.) valid in the harmonic approximation at zero Kelvin. However, these approaches fail at elevated temperatures and/or for strongly anharmonic systems, since the anharmonicity is only accounted for perturbatively in terms of phonon lifetimes. On the other hand, molecular dynamics (MD) techniques using the *Green-Kubo* formalism[2] naturally capture the full anharmonic dynamics in real space. For the exact same reason, however, they can become prohibitively costly to converge in time and size – even when numerically rapid force fields are used to approximately model the inter-atomic interactions[3].

In this work, we developed a formalism that seamlessly bridges the gap between these two approaches so that both the BTE and the GK formalism can be evaluated via MD simulations. For this purpose, we determine the *effective* quasi-harmonic potential the atoms experience during the MD simulation[4], the associated temperature-dependent phonon properties, and the respective fluctuations in the phonon occupation numbers from the MD trajectory[5]. Besides facilitating a systematic quantitative comparison of the BTE and MD approach, this enables to extrapolate MD calculations to macroscopic time and size scales by applying interpolation techniques in reciprocal space. This accelerates such *Green-Kubo* simulations by several orders of magnitude and thus enables an accurate assessment of thermal conductivities within the limited time and length scales accessible in *ab initio* MD. For both force-field and *ab initio* MD, we carefully validate and critically discuss the involved conceptional and numerical approaches by investigating heat transport in silicon and zirconia, two materials known for their particularly harmonic and anharmonic character.

Eventually, we show how the developed techniques facilitate reasonable estimates of thermal conductivities from existing phonon or MD calculations at virtually no additional computational cost, how they enable qualitative insights in the mechanisms and properties promoting/hindering heat transport[6], and how they lay the founding for systematic data-mining approaches in this field.

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Essential Role of van der Waals Interactions in the Structure, Stability, and Catalytic Processes for Molecules at Surfaces

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Hybrid inorganic/organic systems (HIOS) often possess collective electronic, optical, vibrational, and catalytic properties that the separate components forming the interface do not exhibit. These novel interface properties stem from a subtle interplay of covalent and non-covalent interactions. In particular, van der Waals (vdW) dispersion interactions play an essential role in many properties of HIOS, including their structure and stability, and sometimes even their electronic properties and reactivity[1,2].

Here, we summarize our systematic efforts in developing efficient first-principles methods that enable quantitative modeling and new qualitative insights into the structure and stability of HIOS. Our DFT+vdW^{surf} method[3] synergistically combines Lifshitz-Zaremba-Kohn theory with intermolecular perturbation techniques, demonstrating that the collective response of the substrate electrons can modify vdW coefficients in HIOS by up to an order of magnitude. Calculations using this method have shown that the inclusion of collective vdW effects is essential to cover a wide range of interactions in the adsorption of molecules on surfaces. The critical role of screened vdW interactions in the structure and stability of HIOS has implications in catalysis, as demonstrated by the relative stability of reactive intermediates in oxygen-assisted reactions in catalytic systems such as amides, isopropoxys, thiolates, and acetylides on the Au(111) surface[2].

Further gain in accuracy and conceptual understanding of HIOS is possible by applying the recently developed many-body dispersion (MBD) method[4]. This method allows us to capture anisotropic polarization effects in HIOS and demonstrate strong non-additivity in vdW interactions for atoms, molecular assemblies, and nanostructures adsorbed on metal surfaces[5,6,7]. The application of the MBD method enables us to go beyond single molecules on surfaces and efficiently address many-body interactions in dense adsorbed molecular layers, which is necessary to understand the assembly of complex nanostructures on surfaces.

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Electronic Properties of Molecules, Surfaces, and Interfaces with a Self-Consistent Interatomic van der Waals Density Functional

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Long-range van der Waals (vdW) interactions play a fundamental role in the structure and stability of a wide range of systems, ranging from small dimers to complex hybrid inorganic/organic interfaces (HIOS). However, how strong is the effect of vdW interactions on the electronic properties of molecules and extended systems? It is often argued that the vdW energy has a small, or even negligible, influence on the electron density, $n(\mathbf{r})$, and derived electronic properties, since the vdW energy represents only a tiny fraction (0.001%) of the total electronic energy.

To answer the question posed above, we derived a fully self-consistent (SC) implementation of the density-dependent interatomic vdW functional of Tkatchenko and Scheffler[1] and its extension to surfaces[2]. Not surprisingly, vdW self-consistency leads to tiny modifications of the structure, stability, and electronic properties of molecular dimers and crystals. However, unexpectedly large effects are found in the binding energies, distances and electrostatic moments of highly polarizable alkali metal dimers. Most importantly, vdW interactions produced complex and sizable electronic charge redistribution in the vicinity of metallic surfaces and at organic/metal interfaces. As a result, for several coinage metal (111) surfaces, self-consistency induces modifications in the surface dipole, leading to an increase of up to 0.30 eV in the computed workfunctions. Furthermore, in the case of HIOS, SC vdW entails modifications of up to 0.22 eV in the shift of the interface workfunction, a property induced by molecular adsorption. The underlying mechanism responsible for the workfunction modifications stems from an interplay between two effects driven by SC vdW interactions: (i) the modification of the interface dipole, and (ii) a reduction in the charge transfer between the molecule and the surface.

In conclusion, the analysis of SC vdW effects performed in this work demonstrates the importance of vdW interactions on the electronic properties of different classes of systems, with self-consistency systematically improving the agreement between the theoretical predictions and the experimental measurements. Our study reveals a nontrivial connection between electrostatics and long-range electron correlation effects[3].

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Adsorbate-Adsorbate Interactions at Realistic Conditions: Cluster Formation of Adsorbates and Coverage-Dependent Chemistry

Xunhua Zhao, Sergey V. Levchenko, and Matthias Scheffler

Adsorbate-adsorbate interactions play an important role in adsorption and chemical reactions on metal and metal oxide surfaces, even at low coverage. In particular, such interactions can lead to the formation of dense adsorbate structures or networks. Inside such structures, the chemical properties of adsorbates are determined by both adsorbate-adsorbate and adsorbate-substrate interactions. A high coverage of co-adsorbed species will also affect the reaction barriers.

The first part of our work focuses on the atomic structure of adsorbed complexes that appear on alkaline-earth metal-oxide (001) surfaces in thermodynamic equilibrium with water and oxygen gases. Density-functional theory with the HSE06 hybrid functional[1] combined with the self-consistent many-body dispersion approach[2] is used to calculate total energies. The most stable adsorbed water structures are obtained using a first-principles genetic algorithm. Thermodynamically stable adsorbed water phases are then determined using *ab initio* atomistic thermodynamics. We find a range of H_2O chemical potentials where ordered one-dimensional (1D) adsorbed water structures are thermodynamically stable on CaO(001). This result is in agreement with scanning tunneling microscopy and infrared spectroscopy studies of CaO films exposed to water vapor[3]. On MgO(001) and SrO(001), thermodynamically stable 1D adsorbed water structures are not found. We show that the formation of the 1D structures on CaO(001) is due to a balance between adsorbate-adsorbate and adsorbate-surface interactions, which is largely determined by the substrate lattice constant.

In the second part of our work, we investigated effects of hydrogen co-adsorption on the adsorption and reactions of CH_x (x = 0-4) species on Ru(0001) at realistic temperatures and hydrogen pressures. We find that co-adsorbed hydrogen qualitatively changes the preferred site and the stability of CH_2 species, which is crucial for understanding the mechanism of Fischer-Tropsch synthesis. Our results explain the recent observation of CH_2 species on methane-dosed Ru(0001) surface[4]. Moreover, hydrogen co-adsorption is found to have a profound influence on the C-C coupling reactions: While it generally reduces all the coupling reaction barriers, some reaction paths become more favored in the presence of the co-adsorbed hydrogen. Our study of the hydrocarbon chemistry on Ru(0001) surface at realistic conditions both explains the new observations[4] and resolves some of the controversies between existing theoretical and experimental studies.

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Controlling the Localization of Charge at Interfaces between Organic Molecules and Passivated Metals or Semiconductors

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At inorganic/organic interfaces, the concept of electrons moving in extended bands collides with the notion of electrons localized in molecular orbitals. The interaction between the organic and the inorganic part then determines which of the two scenarios will manifest at an actual interface. When for example electron acceptors are adsorbed on a weakly reactive metal, such as Cu, they often form laterally homogenous layers that result in fractionally filled bands. Conversely, if the acceptors are adsorbed on passivated metals or on semiconductors, such as ZnO, charge localizes sponanteously, yielding a laterally inhomogenous layer consisting of completely uncharged and fully charged molecules. This situation is known as "integer charge transfer" (ICT). Until now the detailed mechanism that leads to ICT remained elusive, due to a lack of theoretical studies which we attribute in part to the failure of state-of-the-art, semilocal density functionals to localize charge.

In our work, we find that the absence of ICT in many density functionals is caused by the self-interaction error. Hybrid functionals that overcome this error yield a spontaneous breaking of the translational symmetry and a coexistence of differently charged moieties on the surface. Signatures of the charge-transfer mechanism are then clearly seen in several observables, such as valence and core level spectra and the bond length distribution of the individual molecules. Applying these hybrid functionals to a prototypical interface of tetracyanoethene adsorbed on a NaCl-passivated Cu(100)-surface, we find that the amount of charge transfer across the interface, as well as its spatial distribution, depends of course on the electron affinity of the adsorbate, but also on the interface geometry, in particular the adsorption distance and packing density of the organic layer[1].

In addition, we extend our studies to the adsorption on the wide-bandgap, n-type doped semiconductor ZnO. Here, the substrate-adsorbate interaction is two-fold: The molecules donate charge to the substrate by forming covalent bonds, while simultaneously accepting charge, forming ionic bonds. The charge donation originates from the hybridization of cyano-group (σ-)orbitals with the ZnO valence band, yielding homogenous fractional charging, while the back-transfer of electrons from the substrate's Fermi-level to the molecular LUMO exhibits the aforementioned ICT. Now the bulk-doping concentration of ZnO permits us to switch between different charge transfer mechanisms. At low ZnO bulk-doping concentrations, this leads to the counterintuitive situation that on the surface most of the strongly electron accepting molecules are, in fact, *positively* charged.

Our results indicate that the bulk doping concentration is not only an important control parameter for the amount of charge transfer to a hybrid interface[2], but also determines the spatial charge distribution at the interface. We expect these insights to have far reaching implications for hybrid interfaces.

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Pressure Dependent Electronic Properties of Organic Semiconductors from First Principles

Franz Knuth, Christian Carbogno, Volker Blum[a], and Matthias Scheffler

The electronic properties of organic semiconductors such as band gaps, effective masses, and conductivities typically exhibit a significant dependence on the strain, stress, and pressure, i.e., on the growth conditions during fabrication[1,2]. As shown in this work for two prototypical examples (anthracene, *trans*-polyacetylene), assessing these effects within density-functional theory (DFT) is challenging. First, DFT calculations at a semi-local level of theory suffer from a self-interaction error and from missing long-range, non-local van der Waals interactions. Both these shortcomings can critically affect the properties of organic systems, so that the employed description of exchange and correlation has to be carefully validated with respect to higher levels of theory. Second, the strain derivatives of the total energy, i.e., the stress tensor, are needed in order to investigate materials under pressure. We have implemented[3] these derivatives – including the terms that stem from van der Waals corrections and the exact exchange used in hybrid functionals – in the numeric atom-centered orbitals based all-electron electronic structure code FHI-aims[4].

We find that incorporating van der Waals corrections is pivotal for anthracene, a molecular organic semiconductor, since these interactions determine the binding between the constituent molecules and their arrangement in the crystal. In turn, this critically influences the electronic band structure, since the intermolecular interactions lead to a splitting of the valence and conduction bands that increases under pressure. In the case of *trans*-polyacetylene, we find again that van der Waals interactions are most influential for the binding between the individual polymer chains. Furthermore, the structure of the chains itself is critically affected by the self-interaction error. While semi-local functionals fail to reproduce its broken symmetry ground state, hybrid functionals yield the qualitatively right geometry. Quantitatively, however, the properties of *trans*-polyacetylene critically depend on the fraction α of exact exchange included in the calculations. Again, this is qualitatively consistent with previous high-level quantum chemical studies (CCSD(T)) of one isolated chain[5]. Our calculations reveal that the geometry, the electronic band structure, and the band gap of crystalline *trans*-polyacetylene do not only depend on α and on the symmetry breaking in the individual chains, but are at least as much influenced by interchain interactions, which lead to a pressure-dependent splitting of valence and conduction band as in the case of anthracene.

Eventually, we compute the pressure-dependent charge carrier concentrations and electronic transport coefficients for both organic semiconductors using the Boltzmann transport equation in the constant relaxation time approximation and point out how these macroscopic thermodynamic properties of intrinsic and doped systems are affected by changes in the band structure under pressure.

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Towards a Quantitative Description of the Energetics of Peptide-Cation Interactions

Markus Schneider, Matti Ropo[a], Volker Blum[b], Carsten Baldauf, and Matthias Scheffler

Metal cations are essential to life by shaping the three-dimensional structure of proteins or in the active centers of nature's catalysts. One-third of the proteins in the human body require a metal cofactor for biological function[1,2]. Peptides in complex with cations undergo significant conformational changes that may alter important properties, e.g. binding sites, catalytic properties, and biological functions. On the negative side, it is hypothesized that metal cations promote protein misfolding of Aβ-amyloid peptides into aggregated senile plaques inside the human brain of Alzheimer patients[3]. Importantly, however, the accuracy of ion-peptide interactions in empirical simulation frameworks ("force fields") is anything but clear and, in fact, can be grossly misleading. Accurate electronic structure based validation data are thus a critical need, but here, too, the accuracy of a given method must be comprehensively established.

From a large-scale structure search effort, we present a structural data set[4] of 20 proteinogenic amino acids and their amino-methylated and acetylated (capped) dipeptides with and without divalent cations (Ca^{2+}, Ba^{2+}, Sr^{2+}, Cd^{2+}, Pb^{2+}, and Hg^{2+}). Different protonation states of the backbone as well as varied side chain protonation states were considered. All systems were calculated on equal first-principles footing, applying the PBE generalized gradient density-functional approximation (DFA) corrected for long-range van der Waals interactions with the pairwise Tkatchenko-Scheffler scheme (DFT-PBE+TS). The database covers the conformational hierarchies of 280 systems in a wide relative energy range of up to 4 eV (390 kJ/mol), providing a total of more than 45k stationary points on the respective potential-energy surfaces. Experimentally established gas-phase relative ion binding propensities correlate well with DFT-PBE+TS energies. Given the vast space of conformations covered, the data base is thus a solid foundation for future validation work of higher-level electronic structure methods and lower-level force fields alike. We use examples from our curated data[4] and of Zn^{2+}-histidine complexes to first assess the performance of DFAs *vs.* CCSD(T) for a wide range of amino acids and cations. Secondly we also compare classical (OPLS-AA, Amber99, and Charmm22) and advanced polarizable (Amoeba-Bio-2009) force fields. Force fields fail to accurately describe the peculiarities of the test systems, indicated by large errors of relative energies of conformers compared to coupled-cluster calculations. The use of DFAs substantially reduces these errors, but a quantitative description requires the use of hybrid functionals, e.g. PBE0, in conjunction with a van der Waals correction.

In future steps, the foundation established here will enable us to suggest modifications to force fields for bare peptide-cation interactions. If successful, the overall effort can fundamentally enhance a critical piece of biomolecular simulation infrastructure and represent a key simulation tool to accurately study health-relevant processes at atomic resolution.

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Reduced Molecular Potential-Energy Surfaces from First Principles

Adriana Supady, Mateusz Marianski, Matthias Scheffler, and Carsten Baldauf

Flexible organic molecules and biomolecules can adopt a variety of energetically favorable conformations. We propose a method to construct a reduced potential-energy surface from low-energy local minima and selected transition states. It is computationally efficient enough to be used with first-principles energy functions in order to study the dynamics of conformational ensembles.

First, we assessed a genetic algorithm-based search with Fafoom (Flexible algorithm for optimization of molecules, available from https://github.com/adrianasupady/fafoom)[1] to sample the molecular conformational space. The algorithm was designed to work with first-principles methods, facilitated by the incorporation of local optimization and by blacklisting conformers to prevent repeated evaluations of very similar structures. Conformational transitions of molecules happen via bond rotations. The orientation of minima in structure space relative to each other can be resolved by estimating their distance by means of the root-mean-square deviation of torsion angles (tRMSD). We assume that short distances in torsion angle space are a characteristic of direct transitions between pairs of minima and consequently apply a tRMSD threshold to select direct transitions. With this, we build a network where the nodes represent conformers and the edges the tRMSD between adjacent minima. For each edge in the network connecting a pair of conformers, we suggest a transition path that is subsequently optimized by the aimsChain routine developed by Y. Yao and L. M. Ghiringhelli. With the identified transition states and the local minima, barrier trees[2] can be drawn for the investigated systems.

For the peptide Ac-Ala$_3$-NMe we use the force field Amber99sb as energy function and compare a barrier tree of the reduced potential-energy surface to a free-energy surface representation (Markov-chain model) constructed from long molecular dynamics simulations. The main features of the converged free-energy surface are already present in the potential-energy surface barrier tree. We investigate another system, a well-characterized synthetic peptide[3], exclusively with first principles (PBE+MBD*) and present a potential-energy surface that matches the experimental results.

Our approach provides a reduced, and thereby understandable, representation of the potential-energy surface. The sampling for stationary points (minima and transition states) can be performed with first-principles methods and can be fully automated. The outcome represents an ideal starting point to investigate free energy by, for example, constructing stochastic models or performing biased MD simulations along the known transitions.

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Anomalous Electron-Phonon Coupling in Thermoelectric Clathrates and Skutterudites

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Over the last decades, inclusion compounds have attracted considerable interest in different fields, since their electronic and vibrational properties can be tuned by doping the host and/or by filling the cages with guest atoms. For these reasons, clathrates and skutterudites have been identified as particularly promising materials for thermoelectric applications[1]. In this work, we use first-principles calculations to elucidate how electron-phonon (e-ph) coupling affects the thermodynamic properties of these compounds.

For clathrates, we find fundamentally different formation energies and distortions for (charged) vacancies in Si_{46} and Ge_{46} – in spite of their isoelectronicity. While an anomalous e-ph coupling suppresses vacancy $\square$ formation in Si, it favors it in Ge. For the exact same reason, these clathrates also behave differently upon addition of guests: While the Si host framework remains intact upon filling with K or Ba, the most favorable phases for fully filled Ge clathrates are $K_8Ge_{44}\square_2$ and $Ba_8Ge_{43}\square_3$, featuring two and three vacancies $\square$, respectively. Accordingly, controversial experimental discussions regarding the vacancy formation in these compounds and the underlying mechanism are resolved by our calculations.

Furthermore, we have extended these investigations to ternary clathrates such as $(Sr, Ba)_8Al_xSi_{46-x}$ by developing a cluster-expansion code capable of treating such large unit cells (> 40 atoms). This enables studies of the thermodynamic stability with respect to competing phases, which sheds light onto the narrow ($x \simeq 10$) and wide ($x < 15$) stability range found for Sr and Ba guests, respectively[2].

For $CoSb_3$ and $CoAs_3$ skutterudites, we perform a systematic analysis of the vibrational properties depending on the type of guest (Ga, In, Sn, etc.) and its concentration. In this case, an anomalously strong e-ph coupling translates into a sensible dependence of the electronic properties on the geometries[3]. This gives rise to drastically different vibrational dynamics for different guests, ranging from coherent phonon modes to the formation of localized polarons.

In all cases, we validate the choice of the exchange-correlation functional (semi-local and hybrid functionals), in particular in view of the e-ph coupling strength. Furthermore, we use the *harmonic* approximation and *ab initio molecular dynamics* to investigate the temperature-dependent changes in the electronic and vibrational structure. We confront our findings with experimental results from our collaborators, the group of J. Grin at the MPI for Chemical Physics of Solids, and we discuss the implications of our findings for the synthesis of novel thermoelectric materials with improved transport properties.

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The FHI-aims Project

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The FHI-aims all-electron code, based on numeric atom-centered basis sets, is the flagship of code developments in the FHI theory department. Begun over ten years ago at the FHI, FHI-aims has developed into a key platform for new developments in and applications of electronic structure theory at the FHI and in many other groups around the globe. The core strength of FHI-aims is its ability to supply accurate, numerically converged calculations without hard-wired *a priori* approximations. This is feasible for both traditional and advanced electronic structure algorithms, for large systems, and exploiting massively parallel computer architectures efficiently where necessary. FHI-aims has proven itself as a high-accuracy framework on par with the best available benchmark codes in numerous past applications, most recently in the community-wide "Delta test" benchmark of solid $E(V)$ curves[1]. Here, FHI-aims provides essentially the same accuracy as benchmark (linearized) augmented plane wave codes such as Wien2k or exciting, the "gold standard" of accuracy for DFT. However, FHI-aims is significantly faster than the latter class of all-electron codes and offers far greater flexibility in terms of system types and methods beyond DFT. In terms of usability, FHI-aims is essentially as easy to use as pseudopotential codes due to the availability of a predefined hierarchy of basis sets and reliable numerical settings.

This contribution highlights recent achievements and future directions in FHI-aims. With the continued evolution of its community, the FHI-aims development has now diversified into numerous active centers outside the FHI, including Duke University (Blum), Munich (Reuter, Lederer), Hefei (Ren), Helsinki (Rinke, Havu), London (Catlow group), and many others. We highlight important new developments including: Periodic all-electron random-phase approximation (RPA), second-order Møller-Plesset perturbation theory (M- P2), and G_0W_0 for electronic excitations; a screened second-order exchange correction to GW; spin-orbit coupling, essential for electronic levels in any material beyond light elements; new metaGGA based and orbital-dependent level-5 density functionals; many-body dispersion method[2]; "embedding" localized regions into explicit (atomistic)[3] or implicit (continuum-like) electrostatic environments; density-functional perturbation theory, e.g., for phonons; efficient, localized "resolution of identity" treatment of the Coulomb operator for heavy elements and "beyond-DFT" approaches such as MP2 and RPA[4]; and range-separated hybrid functionals for molecular electronic properties.

Not least, FHI-aims now features a strong connection to QuantumWise's (Copenhagen) graphical and python based interface "Virtual NanoLab"[5]. This combination provides a foundation for easy integration of FHI-aims into industrial workflows, where electronic structure theory is playing an increasingly important role.

Important next steps to chemical accuracy in FHI-aims are thus implemented both based on the DFT paradigm and based on quantum chemical approaches. MP2 reference results for solids are obtained based on an efficient memory-distribution strategy with near-perfect parallelization efficiency and are available online. On the DFT side, the new *strongly constrained and appropriately normed (SCAN) meta-GGA*[6], constructed by satisfying all 17 known possible exact constraints, is implemented in FHI-aims. Likewise, a non-empirical *screened* second-order correlation functional based on the *Bethe-Goldstone equation (BGE), termed sBGE2* is available, offering accurate descriptions of significant problem cases such as H_2^+ and H_2 dissociation. The sBGE2 functional is used as a building block to construct a non-empirical doubly-hybrid functional termed ZRS0. This functional distinguishes itself by a satisfactory description of particularly challenging dissociation cases such as N_2 or C_2.

In short, FHI-aims is now an active and vibrant platform with a high degree of technical maturity, emerging as a source of a broad range new developments for electronic structure theory in general. We foresee that this trend will only accelerate in the next few years.

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Big Data of Materials Science: Critical Role of the Descriptor

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Statistical learning of materials properties or functions so far starts with a largely silent, nonchallenged step: the introduction of a set of descriptive parameter (a multidimensional descriptor). However, when the scientific relationship of the descriptor to the actuating mechanisms is unclear, causality of the learned descriptorproperty relation is uncertain. Thus, scientific advancement, trustful prediction of new promising materials and identification of anomalies is doubtful. We discuss and analyze this issue and define requirements for a descriptor that is suited for statistical learning of materials properties and functions.

Compressed sensing is a method[1,2], originally developed for signal processing, that finds sparse solutions of systems of linear equations which are in general undetermined, i.e., the number of descriptive parameters (the input information, that builds the feature space) is (much) smaller than the number of data (sampling) points. In practise, with compressed sensing a (small) subset of the input parameters is identified as a stable input set for the linear mapping from the descriptor to the sampled property. The size of the selected subset is controlled by the desired accuracy in the mapping

Here, we show how a meaningful descriptor can be found systematically, by means of compressed sensing techniques, which allow for an unbiased and robust model selection among many competing descriptive models.

These concepts are demonstrated for solving problems in materials science: i) prediction of the relative stability of zincblende/wurtzite vs. rocksalt octet binary semiconductors[3], and ii) prediction of their band gaps, by using simple atomic input and/or simple binding models (e.g., tight binding) for building the descriptor, and iii) prediction of other mechanical and elastic properties.

The causal character and predictive capability of the found descriptor(s) are discussed in terms of the robustness of the learned model with respect to perturbation applied to the data and cross validation.

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Test Set for Materials Science and Engineering

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Representative test sets with accurate reference data are crucial for developing simulation techniques in diverse fields of computational science. In quantum chemistry, a variety of such test sets has been well established, which plays an instrumental role in the development of hierarchical electronic-structure approximations for both wavefunction and density-functional theory. In particular, they are needed for validating the numerical implementation, investigating the basis-set convergence, and benchmarking the intrinsic limitations of these quantum chemistry methods.

In computational materials science, however, such test sets are still lacking. This is because the periodic boundary conditions, needed for studying periodic materials, increase both the complexity of the algorithms for the implementation of advanced electronic-structure methods and the computational demand for their application.

Here, we fill the gap by presenting a test set for materials science and engineering (MSE). At this point and as a first step, our MSE test set contains results for first- and second-row elements and their binary compounds spanning diverse cubic crystal structures and bonding characters, allowing for systematic benchmarking of various chemical interactions. In a later stage, also heavy elements and non-cubic crystalline structures, defects, surfaces, etc. will be included in our MSE test set, aiming at establishing it as a representative selection of systems of main interest in MSE.

In the present MSE test set, we consider cohesive energy, lattice constant, bulk modulus, electronic and phononic band structures, and more. We employ a hierarchy of electronic-structure methods, from the local-density approximation to the state-of-the-art many-body perturbation theory methods MP2 and RPA, implemented in our all-electron, full-potential FHI-aims code[1]. For each method, a strong effort was made to achieve full convergence with respect to basis set[2] and k-mesh, so that the only approximation for the presented quantities is the exchange-correlation treatment.

To guarantee the accessibility of our MSE test set, we presented all selected reference data for the systems on the web page (http://mse.fhi-berlin.mpg.de). In addition, the crystal structure and the electronic and phononic band structures and density of states can be visualized, and the plots can be downloaded in print quality.

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The Novel Materials Discovery (NOMAD) Center of Excellence: Big-Data Storage, Search, and Analysis

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The development of modern commercial products may it be from the health and environment, clean energy, heavy industry, information or communication technology sector depends strongly on the development and design of new and improved materials. However, identifying the best materials for a particular application is a significant challenge. Of key importance are the characteristics of the materials at the atomic and molecular levels, which determine their properties and behavior at the macro scale.

Computational materials science uses computers to investigate, characterise, and predict materials at the atomic level, and thus to provide insight into materials properties and functions and into the design and development of new materials to meet specific requirements. A huge number of materials has been and is being investigated using computational materials science methods employing either quantum mechanics (solving the Schrödinger equation for the electrons of the material) or a classical description via force fields or combination of both.

Since many years, the materials science community has been producing an enormous amount of data by CPU-intensive calculations. However, most of this data is not used in our target-oriented research and way of publishing. For optimal exploitation of the significant information content inherently inside all materials data, we need the willingness of the community to share, and we need repositories that allow for the long-term storage and access of all data.

Following this spirit, the NOMAD (Novel Materials Discovery) Repository[1] has been established, promoting the idea of storing open-access data, sharing, and enabling data reuse and repurposing. Open access implies that data can be used by anyone, not just by the experts who develop or run advanced codes. These include computer scientists, applied mathematicians, analytic condensed matter scientists, and more. Therefore, the future reuse of the stored data may be unpredictable, probably through the employment of tools that the present computational materials community does not even know. At present, we support major community codes, like ABINIT, CASTEP, CRYSTAL, exciting, FHI-aims, GAUSSIAN, octopus, Quantum ESPRESSO, VASP, and WIEN2k; this list is still increasing in order to incorporate more important electronic-structure codes and soon including also the force-field based codes.

The NOMAD Repository stores raw data, as they are output by the supported codes. Data can be retained private for up to 3 years after their upload to the repository, then they are made open access. Of course, they can be made open access earlier by the owner of the data. Simple searches for chemical composition, electronic structure code, basis set, exchange-correlation treatment, authors, and DOI help locate the desired entry in the repository, that can be downloaded even without registration.

The NOMAD Repository is a solid basis for the NOMAD Center of Excellence (CoE)[2], a unique collaboration between eight computational materials science groups and four high-performance computer centers. The goal of this CoE is to get scientific insight into the vast amount of existing data by extracting (often hidden) information in various ways.

In a first step, a code-agnostic (-independent) database will be created, where all data will be stored in a uniform, robust, and extensible representation. This will allow for making data as computed by different methods and codes comparable. This is achieved by implementing a *translation layer*, that transforms the data from the raw output contained in the repository into a code-agnostic format that uses HDF5 and json file formats. The HDF5 file format uses a flexible classification system that can be easily extended, to describe the data stored. In this way, scalar quantities as energies, vectors like forces and positions, functions like electronic or phonon density of states, and scalar fields like electronic densities and wavefunctions can be efficiently stored and searched.

Building on the database, a *Materials Encyclopedia* will be developed, based on Apache Flink[3] (a fast large-scale data-processing engine). This will be used to efficiently perform queries on the extracted data, allowing for either a comprehensive characterization of a material or trends across a class of materials or even all materials in the database. Besides this *Materials Encyclopedia*, an infrastructure will be established to develop advanced *big-data analytics* tools aiming at finding correlations between materials, their properties, and functions. The queries can be simple, e.g., a search for a material that has the band gap within a certain range while having a specific weight below a given threshold. They can be more complex, i.e. involving machine-learning algorithms. For example, pattern recognition (similarity among atomic structures, band structures, type of defects, etc.), identification of outliers, and more.

Illustrative examples of the queries and data analytics enabled by the developed infrastructure, and in particular of their scalability, are demonstrated.

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