

Recent Developments in the Theory Department

Director: Matthias Scheffler

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I. General Remarks

The year 2013 marked the 25th anniversary of the foundation of the FHI *Theory Department*. Since the very beginning, research in the Department has been concerned with fundamental aspects of the chemical and physical properties of surfaces, interfaces, clusters, and nanostructures. Obviously, this theme is sufficiently general and covers such a wide range of topics, that there has been no need for a change, even when some years ago we added a group working in biophysics.

A significant part of our work concerns the development of new and advanced methods and their coding for high-performance computers. More specifically, validation of the electronic-structure base and linking it with methods from thermodynamics and statistical mechanics has always played a significant role in the *Theory Department*. While in the eighties, we developed the “*ab initio* atomistic thermodynamics” approach for defects in bulk semiconductors and at interfaces (together with Carl Michael Weinert and Jarek Dabrowski), in the nineties we complemented the *ab initio* molecular dynamics approach of Car and Parrinello by “*ab initio* kinetic Monte Carlo (kMC)” methods in order to reach the time scales relevant for crystal growth (together with Paolo Ruggerone, Christian Ratsch, Kristen Fichthorn, and Peter Kratzer). Then, in 2004 an “*ab initio* kMC” approach for heterogeneous catalysis was introduced (together with Karsten Reuter). Karsten continued this development by linking it to the proper description of gas-phase or fluid dynamics, in order to include mass and heat transport (he has been at the TU Munich since 2010). Recent developments in the Department have concentrated on techniques like basin hopping and a genetic algorithm for mapping out the enormous configuration space of larger molecules and clusters (Luca Ghiringhelli and Saswata Bhattacharya).

Progress in this field has been considerable in the last few years, and here, we briefly highlight some outstanding achievements. A more complete discussion of the breadth of the work of the Department is sketched in Sections IV and V.

- *Van der Waals interactions* — In 2008 Alexandre Tkatchenko joined the Department, shortly after he had finished his PhD in physical chemistry at the Universidad Autonoma Metropolitana (UAM-I), Mexico. In February 2009, the paper on “Accurate Molecular van der Waals Interactions from Ground-State Electron Density and Free-Atom Reference Data” appeared (A. Tkatchenko and M. Scheffler, *Phys. Rev. Lett.* **102**, 073005 (2009)), which by the end of 2013 had been cited already more than 500 times. Since then Alexandre has

made several advances based on the initial idea, some are described below (Section IV). In 2011 he was awarded an ERC Starting Grant.

- *Renormalized perturbation theory, second order (rPT2)* — Another breakthrough concerns the development of advanced DFT functionals, in particular the “exact exchange plus correlation in the random-phase approximation (RPA)” approach. Identifying two contributions, which in many-body perturbation theory appear at the same level of approximation as the RPA, have yielded what we call “renormalized perturbation theory, second order (rPT2)”. This approach treats electron correlation in terms of the RPA plus renormalized single excitations (rSE) plus second-order screened exchange (SOSEX): $rPT2 = RPA + rSE + SOSEX$. (X. Ren, P. Rinke, G.E. Scuseria, and M. Scheffler: *Renormalized Second-order Perturbation Theory for the Electron Correlation Energy: Concept, Implementation, and Benchmarks*. *Phys. Rev. B* **88**, 035120 (2013)).
- *Space-charge layer* — Work on defects at surfaces of MgO and parallel studies of the adsorption of organic molecules at ZnO surfaces showed that for charge transfer situations the build-up of a space charge layer not only gives rise to band bending, but also represents a significant energy cost. The latter had been neglected so far, largely because of technical reasons that prevented a proper theoretical description. Our developments and results have shown that the space-charge layer changes the concentration of charged defects or the amount of charge transfer at the surface significantly. It implies that carrier doping of the substrate bulk may be used for tuning defect or adsorbates concentrations and properties. (N.A. Richter, S. Siculo, S.V. Levchenko, J. Sauer, and M. Scheffler: *Concentration of Vacancies at Metal Oxide Surfaces: Case Study of MgO (100)*. *Phys. Rev. Lett.* **111**, 045502 (published July 2013), and Y. Xu, O.T. Hofmann, R. Schlesinger, S. Winkler, J. Frisch, J. Niederhausen, A. Vollmer, S. Blumstengel, F. Henneberger, N. Koch, P. Rinke, and M. Scheffler: *Space Charge Transfer in Hybrid Inorganic-Organic Systems*. *Phys. Rev. Lett.* **111**, 226802 (published November 2013)).
- *FHI-aims code* — The development of the FHI-aims code, which combined many of the earlier ideas and concepts developed in the Department (and even earlier), has been a great success. This applies to the daily computations in the Department, but also to the worldwide distribution of the code. FHI-aims was released in 2009 (V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter, and M. Scheffler: *Ab initio molecular simulations with numeric atom-centered orbitals*. *Comp. Phys. Comm.* **180**, 2175 (2009)). By the

end of 2013 the paper had been cited about 250 times. Recent developments are significant and briefly sketched out in Section IV below.

The following Section describes organizational developments and Section III personnel and related matters. Subsequently, Sections IV and V briefly outline some of the work performed in the *Theory Department*: Section IV describes conceptual, methodological, and technical developments, which enable us to study new types of problems and/or to improve the accuracy of calculations. Finally, in Section V, the main applications studied in the *Theory Department* are outlined and some recent results presented.

To keep things short, the presentation focusses on a description of progress achieved during the last two years. Nevertheless, a few studies from the last six years are also mentioned.

II. Organizational

We simply summarize the various aspects of the present situation in bullet form.

- The collaboration with the University of California Santa Barbara (UCSB, College of Engineering and College of Mathematical, Life and Physical Sciences) has been very fruitful. Since 2005 Matthias Scheffler spends about three months per year at the UCSB, although in the past two years this has been reduced to two months. The exchange of postdocs and PhD students between the institutes has turned out to be stimulating and very successful.
- The so-called “UCSB-MPS program” supports joint activities and exchange of students and postdocs between scientists working in Materials Science in the entire Max Planck Society (MPS) and the University of California Santa Barbara since 2005. For the MPS, the program is coordinated by Matthias Scheffler. The program will terminate in 2015.
- We are also part of a “Partnership for International Research and Education: Electron Chemistry and Catalysis at Interfaces” (PIRE-ecci). This activity, managed by Susannah Scott at UCSB, helps to intensify collaborations through the exchange of graduate students with chemical-physics institutes in China, in particular the Dalian Institute for Chemical Physics of the Chinese Academy of Sciences. In 2010 we added a German component to this activity by officially including the FHI, and in 2011, also the University of Göttingen.
- In 2009 the MPS decided to create “Max Planck Centers” at high-ranking universities outside Germany. The *Theory Department* is part of the “MPS-UBC Centre for Quantum Materials” which was established in October 2010 at the University of British Columbia

(UBC) in Vancouver. The Center is directed by George Sawatzky and Bernhard Keimer who chair a Scientific Board comprised of three Max-Planck directors, currently Bernhard Keimer, Hao Tjeng, and Matthias Scheffler, and three UBC professors, currently George Sawatzky, Andrea Damascelli, and Ian Affleck.

- At the École Polytechnique Fédérale de Lausanne (EPFL) the “Max Planck - EPFL Center for Molecular Nanoscience and Technology” has been initiated by Klaus Kern (MPI Stuttgart), together with Benoit Deveaud-Plédran (EPFL), Jeffrey Hubbell (EPFL), Thomas Rizzo (EPFL), Matthias Scheffler, and Alec Wodtke (Göttingen). The official start was January 1st, 2013. Several PhD students will jointly work with us and colleagues in Lausanne, receiving their PhD from EPFL.

As of December 1st, 2013 the FHI *Theory Department* is structured into 7 research groups. Nevertheless most of the work in the Department typically involves more than one of these groups. The groups and their leaders are:

- Unifying Concepts in Catalysis, headed by **Sergey Levchenko**
- *Ab Initio* Statistical Mechanics of Cluster Catalysis and Corrosion, headed by **Luca M. Ghiringhelli**
- Heat and Charge Transport, headed by **Matthias Scheffler**
- *Ab Initio* Biomolecular Simulations, headed by **Carsten Baldauf**
- Many Body Electronic Structure Theory, headed by **Patrick Rinke**
- Theoretical Spectroscopy, headed by **Angel Rubio**
- ERC group on Organic Functional Materials and Molecular Interactions, headed by **Alexandre Tkatchenko**
- In addition we host Emeritus **Alex Bradshaw** (since January 2009) who is working on photoionization in molecules and clusters as well as on questions of energy supply and resources in the context of the sustainability debate

Together with Martin Vingron (director at the MPI for Molecular Genetics) Matthias Scheffler is responsible for the *Joint Network Center* (Gemeinsames Netzwerkzentrum, GNZ) of the Berlin-Brandenburg Max Planck activities. This is a regional IT competence center, serving 8 MPIs and 5 additional institutions. It focusses on networking, backup, virtualiza-

tion, and security services. It is headed by Gerd Schnapka and more information is given on p. 45.

III. Personnel and Related Matters

Since the last visit of the *Fachbeirat* in November 2011 the following noteworthy developments have taken place:

- In summer 2013 **Volker Blum** moved to his new post as Associate Professor in the *Department of Mechanical Engineering and Materials Science at Duke University*, North Carolina, USA. The department continues to collaborate with him on several projects and, together with Matthias Scheffler, he will remain coordinator of the FHI-aims developments.
- **Ignacio Franco** assumed the position Assistant Professor at the *Department of Chemistry at University of Rochester*, New York, USA in summer 2013.
- On January 1st, 2013 **Xinguo Ren** started his professorship at the *Key Laboratory of Quantum Information at the University of Science and Technology of China (USTC)* in Hefei, China. He remains one of the key developers and coordinators of the “beyond RPA” and *GW* components of the FHI-aims code.

Looking back at the last five years, 12 former members of the *Theory Department* have been appointed to lecturerships or professorships. In addition to the above, these are:

- Bothina Hamad, University of Jordan Amman, Jordan - since 2012
- Ville Havu, Aalto University School of Science, Espoo, Finland - since 2013
- Hong Jiang, Peking University, Beijing, China - since 2009
- Suljo Linic, University of Michigan, Ann Arbor, USA - since 2010
- Angelos Michaelides, University College London, London, UK - since 2009
- Rossitza Pentcheva, Universität Duisburg-Essen, Duisburg, Germany - from 2014
- Karsten Reuter, Technische Universität München, München, Germany - since 2009
- Aloysius Soon, College of Engineering Yonsei University, Seoul, South Korea - since 2010
- Hua Wu, Fudan University, Shanghai, China - since 2011

We are also proud to report that Mariana Rossi received the Otto Hahn Medal and the Otto Hahn Award in 2012. The latter awards the best PhD work concluded in the whole MPS (Sections for Humanities, for Biology and Medicine, and for Chemistry, Physics, and Technology) during the period from fall 2011 to fall 2012. About 900 PhD students finished their PhD during this period, and one of them, namely Dr. Rossi, was bestowed with the Otto Hahn Award. This gives her the opportunity to establish a small group at a Max Planck Institute of her choice when coming back to Germany after her postdoc stay abroad.

Members of the *Theory Department* take part in various national, European (EU and ESF) and international programs. The list of these activities is as follows:

- Einstein Foundation Berlin – Einstein Research Project ETERNAL: Exploring Thermoelectric Properties of Novel Materials, K.-R. Müller, C. Draxl, M. Scheffler - since April 2013.
- ERC – European Research Council, Starting Grant: Van der Waals Interactions in Complex Materials; A. Tkatchenko - since 2011.
- EU – European Commission, Marie Curie Actions, Initial Training Network (ITN): Surfaces for Molecular Recognition at the Atomic Level (SMALL), coordinator: J.N. O’Shea; M. Scheffler - since October 2010.
- DFG – German Research Foundation, Cluster of Excellence 314: Unifying Concepts in Catalysis (UniCat), coordinator: M. Driess; M. Scheffler - first funding period November 2007 - October 2012, new funding period until October 2017.
- DFG – German Research Foundation, SFB 951: Hybrid Inorganic/Organic Systems for Opto-Electronics (HIOS), spokesman: F. Henneberger; project B4: A. Knorr, P. Rinke, M. Scheffler - since July 2011.
- DFG – German Research Foundation, FOR 1543: Shear-flow regulation of Hemostasis (SHENC), spokesman: R. Schneppenheim; subgroup C1: F. Gräter, C. Baldauf - since June 2011.
- NSF – The National Science Foundation, Partnership for International Research and Education (PIRE): Electron Chemistry and Catalysis, director: S. Scott; M. Scheffler - since 2005.

- UCSB – University of California, Santa Barbara, College of Engineering and College of Mathematical, Life & Physical Sciences; M. Scheffler (distinguished visiting professor) - since 2005.
- Max Planck - EPFL Center for Molecular Nanoscience and Technology - Max Planck Society and the École Polytechnique Fédérale de Lausanne, directors: K. Kern, T. Rizzo; board members: B. Deveaud-Plédran, J. Hubbel, A. Wodtke, M. Scheffler - since 2013.
- MPS-UBC Center – Max-Planck-Gesellschaft – University of British Columbia Center for Quantum Materials, directors: B. Keimer, G.A. Sawatzky; board members: A. Damascelli, L.H. Tjeng, I. Affleck, M. Scheffler - since 2010.
- INCITE – US Department of Energy, Innovative and Novel Computational Impact on Theory and Experiment, computer allocation grant for 100 million CPU hours per year: Non-Covalent Bonding in Complex Molecular Systems with Quantum Monte Carlo, Oak Ridge/Argonne Labs, PI: D. Alfè; M. Gillan, K. Jordan, A. Michaelides, A. Tkatchenko, M. Towler, O.A. von Lilienfeld - since 2012.
- CNMS – Center for Nanophase Materials Sciences, user project, CNMS2012-287, computer allocation grant for 450,000 CPU-hours: Finger Printing Protein Secondary Structure Motifs from First Principles: Computational Spectroscopy, Oak Ridge National Laboratory, PI: V. Blum - since 2012.
- PRACE – Partnership for Advanced Computing in Europe, PRACE-DECI-11 computer allocation grant for 14,700,000 standardized CPU-hours: Graphene Precursor Phase and Graphene-SiC(000-1) Interface by First Principles Thermodynamics and a Massively Parallel Structure Search (GraSiC-1), PI: V. Blum - since November 2013.
- Vetenskapsrådet – Swedish Research Council: “Catalysis on the atomic scale”, organizer: E. Lundgren; S. Levchenko, M. Scheffler - since 2011.

Since Professor Claudia Draxl was appointed to the Chair of Theoretical Solid State Physics at the Humboldt University Berlin in November 2011, some research of the *Theory Department* is being performed together with her and her group. In particular this concerns research on thermoelectric materials and the development of novel tools for the scientific analysis of *Big Data* that are now being generated on nearly every aspect in materials science (Christian Carbogno, Sergey Levchenko, Luca Ghiringhelli). A proposal for appointing Claudia “Max

Planck Fellow”, as discussed at the last meeting of the Fachbeirat, had been put on hold by the MPS President’s Office, because of a budget crises of the MPS that turned up in summer 2012.

Over the last twelve years we have strongly supported CECAM, a high-level European organization devoted to the promotion of fundamental research on advanced computational methods and their application to important problems in frontier areas of science and engineering. In particular, CECAM organizes scientific workshops and tutorials on computational molecular and materials science. It is financed by European research organizations. The Max Planck Society became a member in 2008. Since 2008 the CECAM headquarters is at the EPFL Lausanne, and “CECAM nodes” have been established in several member states. In Germany Matthias Scheffler was influential in creating a joint node, “cecam-MM1P.de”, which focuses on multi-scale modeling from first principles (MM1P) with emphasis on methods and applications to materials and biophysics. The board of directors of the MM1P.de node consists of Thomas Frauenheim (University of Bremen), Eberhard K.U. Gross (MPI Halle), Matthias Scheffler, and Björn Winkler (Goethe University Frankfurt). Recently, the CECAM council endorsed the renewal of the Node agreement which will apply until 2018.

In the field of *ab initio* calculations of complex processes in materials CECAM has informal contacts to the Psi-k network. This is the umbrella organization for the electronic-structure community in Europe and beyond. Four years ago Psi-k was granted charitable status, and Matthias Scheffler is a member of the board of trustees. For example, Psi-k organizes a large Psi-k-conference every 5 years, one of the international key meetings in the field. The next one will be organized in 2015 by Angel Rubio.

Scientists of the *Theory Department* were involved in various services to the surface science and electronic-structure communities worldwide. For example, they lecture at the *Free University* and the *Technical University Berlin* as well as at the *International Max Planck Research School*. They organized or co-organized conferences, workshops, tutorials, and summer schools on topics in electronic-structure theory, multi-scale modeling, surface science, and biophysics, impacting upon the careers of numerous students of theoretical material science. This list of activities in the last two years includes:

- Conference on “SMALL is Beautiful: Theory Meets Experiment”, November 9-12, 2011, Berlin, Germany; organizers: A. Tkatchenko and G. Held (University of Reading, UK)

- Symposium on “Frontiers of Electronic Structure Theory: Strong Correlations from First-Principles”, March 25-30, 2012 at DPG Spring Meeting, Berlin, Germany; organizers: S. Biermann (Centre de Physique Théorique, Palaiseau Cedex, France) and M. Scheffler
- 12th Einstein Lecture – David J. Gross - “Einstein's dream of unification - then and now”, June 29, 2012, Berlin, Germany; organizer: L. Wöste (Freie Universität Berlin, Germany) and M. Scheffler
- International Workshop on “Frontiers in Computational Material Science” July 18-21, 2012, Ringberg Castle, Germany; organizers: P. Rinke and M. Scheffler
- FHI-aims Developers' and Users' Meeting on “Density Functional Theory and Beyond with Numeric Atom-Centered Orbitals”, August 28-31, 2012, Berlin, Germany; organizers: V. Blum, M. Rossi, and M. Scheffler
- Workshop on “Towards First-Principles Description of van der Waals Interactions in Complex Materials”, October 15-19, 2012, Lausanne, Switzerland; organizers: A. Tkatchenko, A. Rubio, and M. Scheffler
- Workshop on “Vibrational coupling: most important, often ignored, and a challenge for *ab-initio* theory”, November 6-9, 2012, Lausanne, Switzerland; organizers: H. Appel, C. Carbogno, C. Draxl (Humboldt-Universität zu Berlin, Germany), and M. Scheffler
- Symposium on “Frontiers of Electronic Structure Theory: Discovery of Novel Functional Materials”, March 10-15, 2013 at DPG Spring Meeting, Regensburg, Germany; organizers: N. Marzari (École Polytechnique Fédérale de Lausanne, Switzerland), R. Drautz (Ruhr-Universität Bochum, Germany), and M. Scheffler
- International Summer School on “Basic Concepts and First-Principles Computations for Surface Science: Applications in Chemical Energy Conversion and Storage”, July 21-26, 2013, Norderney, Germany; organizers: K. Reuter (Technische Universität München, Germany) and M. Scheffler
- School on “Density-functional theory and beyond: Computational materials science for real materials”, August 6-15, 2013, Trieste, Italy; organizers: V. Blum, C. Baldauf, M. Scheffler, and R. Gebauer (International Centre for Theoretical Physics, Trieste, Italy)
- Symposium on “New Theoretical Concepts and Directions in Catalysis”, August 27-30, 2013, Santa Barbara, CA, USA; organizers: H. Metiu (University of California, Santa Barbara, USA) and M. Scheffler

- CECAM/Psi-k Research Conference on “Multi-scale Modeling from First-Principles”, September 8-13, 2013, Cap Roig, Spain; organizers: M. Mareschal (Zaragoza Scientific Center for Advanced Modeling, Zaragoza, Spain) and M. Scheffler
- IPAM (Institute of Pure and Applied Mathematics) long program on “Materials for a Sustainable Energy Future”, September 9 - December 13, 2013, IPAM/UCLA, Los Angeles, USA; organizing committee: M. Bazant (MIT, Cambridge, USA), G. Galli (University of California, Davis, USA), G. Henkelman (University of Texas, Austin, USA), K. Promislow (Michigan State University, East Lansing, USA), and M. Scheffler
- Workshop on “Fuels from Sunlight”, October 14-18, 2013, IPAM/UCLA, Los Angeles, USA; organizing committee: R. Klein (Freie Universität Berlin, Germany), J. Nørskov (Stanford University, USA), and M. Scheffler
- Workshop on “Energy Conservation and Waste Heat Recovery”, November 18-22, 2013, IPAM/UCLA, Los Angeles, USA; organizing committee: G. Galli (University of California, Davis, USA), R. James (University of Minnesota, Twin Cities, USA), J. Lukes (University of Pennsylvania, Philadelphia, USA), and M. Scheffler

One event that should be stressed was the “hands-on tutorial” in August 2013. This successful ten-day school (with 112 participants) was organized by Volker Blum, Carsten Baldauf, Matthias Scheffler, and Ralf Gebauer (ICTP). The tutorial was well received and there was very positive feedback from the participants, as can be seen in the report by the ICTP (http://www.ictp.it/about-ictp/media-centre/news/2013/9/dft_workshop.aspx).

Alex Bradshaw has served on several committees of the National Academy of Sciences (Leopoldina), National Academy of Engineering (acatech), and the Royal Society in the UK. He is currently member of an inter-academy study group on the prioritization of the various governmental and administrative measures associated with the transformation of the German energy supply system (*Energiewende*). He has also given evidence to parliamentary committees on sustainability questions and on open access.

IV. New Concepts, Methods and Techniques

A full description of the developments in the department during the last six years would exceed the space available for this summary. The 14 items below therefore give only an over-

view of the main highlights. We focus on the work done since summer 2011 and mention earlier work only in a few exceptional cases.

IV.1 Beyond the Random-Phase Approximation for Correlation

This work started in 2009 when we demonstrated that, and explained why, exact exchange plus correlation in the random-phase approximation (in short RPA) solves the “CO adsorption puzzle”. Previous to our work it had been realized that standard exchange-correlation (XC) functionals often predict the wrong (adsorption) geometries; sometimes they even turn out to be qualitatively incorrect. The reason for this failure had not been fully understood, nor was a computationally tractable approach known that would provide a robust and reliable treatment. Our subsequent work on RPA-based methods contributed significantly to the resurgence of RPA in electronic-structure theory. A deeper analysis of RPA performance revealed that some of its shortcomings can be overcome by adding renormalized single excitations (rSE) and second-order screened exchange (SOSEX) terms. Both contributions emerge from a systematic diagrammatic expansion in many-body perturbation theory. We refer to the combined scheme of RPA+rSE+SOSEX as renormalized perturbation theory second order (rPT2), because it can be viewed as a renormalization of all second order diagrams. Systematic benchmarks show that the performance of rPT2 is well balanced across different quantities and systems e.g. atomization energies, energy barriers, and non-covalent interactions. For this reason, we are now using rPT2 as reference when assessing the accuracy of standard XC functions, such as PBE. Current and future work now addresses a) ways to go even beyond rPT2, b) to make RPA and rPT2 computationally more efficient, c) to develop new and compact basis sets that systematically approach the complete basis set limit, and d) to derive forces (Igor Zhang, Xinguo Ren, Volker Blum, Patrick Rinke).

IV.2 Self-Consistent *GW* Approach

The *GW* Green function 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*) that is based on the iterative solution of the Dyson equation into the FHI-aims code. Unlike in the more common, perturbative *GW* schemes (G_0W_0), sc*GW* is independent of the reference state. This

provides a well-defined total energy, which we calculate by means of the Galitskii-Migdal formula. To assess the scGW ground state, we calculated bond lengths, binding energies, and vibrational frequencies for a set of diatomic molecules. The accuracy of scGW is comparable to RPA, which is, however, not as good as that of rPT2. A detailed analysis of H₂ dissociation reveals that scGW and RPA are close around the equilibrium bond distance, but when it comes to bond breaking the DFT-based RPA outperforms Green-function theory. For prototypical donor/acceptor molecules, we demonstrate that scGW - 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 (Fabio Caruso, Patrick Rinke, Xinguo Ren, Angel Rubio).

IV.3 Full CI Quantum Monte Carlo

In quantum chemistry so called test sets have been developed, with which highest level calculations were performed for a selection of molecules. G2, HTBH38, S22, and ISO34 are well known examples of such test sets for covalent-bond interactions, reaction barrier heights, bio-oriented weak interactions, and isomerization energies, respectively. The importance of test sets is that approximations, e.g. of the XC treatment or the basis set, can be benchmarked against the almost exact results, providing a validation and error estimates of the approximate methods. Due to the lack of reliable electronic structure methods, such a test set does not exist so far for materials science.

With the mid-term goal of establishing a “test set for materials science and engineering” we are presently implementing the full configuration interaction quantum Monte Carlo (FCI-QMC) approach into the FHI-code with the aid of the post-SCF NECI code maintained by A. Alavi's group. For clusters this development has been largely completed, but for solids and surfaces significant developments are still needed. Parallel to the FCI-QMC approach we are also implementing coupled-cluster theory and double hybrid functionals (Igor Zhang).

IV.4 Consistent Combination of Hybrid Density Functionals and Quasiparticle Energy Calculations

To overcome the self-interaction error and the band-gap problem of density-functional theory (DFT), we combine hybrid density functionals with the G_0W_0 approach for quasiparticle excitations. We exploit the formally exact condition of exact DFT that the energy of the highest

occupied molecular orbital (HOMO) corresponds to the ionization potential (IP) of a finite system. The α -value that controls the amount of exact exchange, and therefore the self-interaction error in the hybrid functional, is then optimized to obey this condition as closely as possible for our hybrid functional/ G_0W_0 combination. This combined approach is essential for describing electron transfer (as exemplified by the TTF/TCNQ complex) and yields the vertical ionization potentials of the G2 set with a mean absolute percentage error of only $\sim 3\%$. For MgO clusters, the formation energy of the optimal hybrid functional is in good agreement with coupled cluster reference calculations at the singles, doubles, and perturbative triples level (CCSD(T)). This validation then facilitated the description of oxygen vacancies at the MgO surfaces (see also **V.1 e**) (Viktor Atalla, Norina Richter, Sergey V. Levchenko, Patrick Rinke).

IV.5 Practical and Accurate Treatment of van der Waals Interactions

Van der Waals (vdW) interactions are ubiquitous in nature, playing a major role in defining the structure, stability, and function for a wide variety of molecules and materials. Our recent developments in methods for vdW interactions go beyond the pairwise Tkatchenko-Scheffler method that we introduced in 2009. We have developed the so-called many-body dispersion (MBD) method that determines the full many-body vdW energy in the dipole approximation for non-metallic systems (Alexandre Tkatchenko, Robert A. DiStasio Jr. and Roberto Car (Princeton University)). The efficiency of the method has been demonstrated by calculations on systems with more than 10,000 atoms (Alexandre Tkatchenko and Vivekanand Gobre) and the accuracy of DFT+MBD calculations has been thoroughly assessed for molecular materials (molecules, supramolecular systems, molecular crystals) and semiconductors (Alexandre Tkatchenko, Anthony M. Reilly, Noa Marom (Tulane University), Alberto Ambrosetti, Wang Gao, Guo-Xu Zhang). In all of these cases, the MBD method coupled with non-empirical PBE and PBE0 xc functionals is able to achieve the elusive “chemical accuracy” of 1 kcal/mol in the binding and cohesive energies. Further developments of the MBD method are ongoing in order to extend its applicability to highly polarizable materials (layered nanostructures) and metals. Our final goal is to systematically connect the MBD approach which depends exclusively on the electron density with RPA calculations based on Kohn-Sham DFT orbitals. Our recent demonstration that the MBD energy expression is equivalent to RPA for a model system of localized dipoles suggests that a seamless connection between MBD and RPA is eventually possible to achieve.

IV.6 Influence of van der Waals Interactions on Electronic Properties

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 direct influence on the electronic properties of molecules and solids. To assess the reliability of this “conventional wisdom”, we recently implemented a fully self-consistent version of the Tkatchenko-Scheffler DFA+vdW functional, where DFA stands for an approximate semi-local exchange-correlation density functional (Alexandre Tkatchenko, Nicola Ferri, Robert A. DiStasio Jr. and Roberto Car (Princeton University)). In agreement with previous work, 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, bringing it in agreement with experiments. Furthermore, vdW interactions are also found to noticeably affect workfunctions and charge transfer in hybrid organic/metal systems.

IV.7 Heat Transport by Phonons

An accurate first-principles determination of (vibrational) thermal conductivity has remained elusive: State-of-the-art techniques treat deviations from the harmonic approximations perturbatively and thus become questionable at elevated temperatures, e.g., above 70% of the melting temperature, at which the dynamics of the nuclei is significantly affected by anharmonic interactions. To overcome this limitation, we have implemented a variant of the *Green-Kubo* method that accounts for the full anharmonicity via molecular dynamics. The new and crucial step is the reformulation of the heat flux, which is required for assessing the thermal conductivity, within a *first-principles* framework. Starting from an *energy density* formalism, we have shown that the virial theorem allows the heat flux to be defined in terms of the *stress tensor*. In contrast to the energy density, this formulation is independent of the periodic boundary conditions and thereby alleviates the strong finite size artifacts that appear in the small supercells that are treatable from first principles. Whereas excellent results could be achieved with this method in the case of strong anharmonicity (low thermal conductivity), the description of good heat conductors (low anharmonicity) is still challenging due to the long time and large length scales required to achieve convergence in such cases. Currently, strategies to bridge these scales are being implemented and tested, e.g. the separation of time and

length scales and the extrapolation via harmonic and quasi-harmonic potentials (Christian Carbogno, Ramamurthy Ramprasad (University of Connecticut)).

IV.8 Electronic Transport (Charge and Heat)

Many efforts have been undertaken to accurately describe the interactions (electron-phonon and electron-electron scattering) that drive electronic charge and heat transport on different time and length scales. For macroscopic transport, we have followed the lines of Sec. IV.7 and have implemented the *Greenwood-Kubo* method, in which the electronic transport coefficients are assessed from the electron-phonon scattering that arises in molecular dynamics. To bridge the necessary time and length scales, an implementation of the Boltzmann Transport formalism is used (Karsten Rasim, Christian Carbogno). On the microscopic, molecular scale, the group of Ferdinand Evers at the Karlsruhe Institute for Technology (KIT) has developed a *non-equilibrium Green-functions* module for FHI-aims that performs the calculation of transmission functions as well as charge and heat conductances (Alexei Bagrets and Ferdinand Evers (KIT)).

IV.9 Time-Dependent Density-Functional Theory for Quantum Electrodynamics - Bridging Materials Science and Quantum Optics

R.P. Feynman called Quantum Electrodynamics (QED) “the jewel of physics” for its extremely accurate predictions of quantities like the Lamb shift or the anomalous magnetic moment of the electron. It is the underlying theory for the non-relativistic Hamiltonian in Coulomb gauge that is often used as starting point for modern electronic-structure theory. Recently, we went back to the foundations of QED and, starting from the full QED-Lagrangian, have developed a time-dependent density-functional theory for QED. We have addressed how this new theory translates into lower levels of theory from the non-relativistic approximation to the Maxwell description of the photon field. Such an approach has the advantage that the quantization of the radiation field can be treated explicitly and in this way a more microscopic perspective on optical excitations which appear in photosynthesis, the vision process, solar cells, etc. can be gained. As starting point for our studies, we have constructed numerically exact solutions for QED model systems with entangled photons. Using an iterative fixed-point scheme, these exact solutions can be inverted to extract the exact Kohn-Sham potentials for our multicomponent TDDFT/QED approach. This provides an explicit route to find corrections to the clas-

sical Maxwell equations which incorporate the quantized nature of the electromagnetic field. We also have started to use our numerically exact QED solutions for the emerging field of correlated spectroscopy where, in contrast to normal spectroscopy, entangled photons are used to probe matter (Johannes Flick, Rene Jestädt, Heiko Appel, Angel Rubio).

IV.10 Electronic Decoherence in Molecules and Other Vibronically Coupled Systems

In the past two years, we have investigated electronic decoherence effects in molecules. Understanding electronic decoherence is vital to the development of approximation schemes to the full vibronic evolution of molecules and is central to our description of fundamental non-equilibrium processes such as photosynthesis and vision. Three basic contributions have been developed: 1.) We have introduced a hierarchy of measures of decoherence, termed “reduced purities”, that can be used to characterize decoherence in many-electron systems. While usual measures of decoherence are based on the full many-body electronic density matrix and are thus not of general applicability, the reduced purities are based on the few-body electronic density matrix and can be used to characterize decoherence in the common case when only reduced information about the electrons is available. 2.) Using the reduced purities and related measures, we have investigated the basic electronic decoherence dynamics for the Su-Schrieffer-Heeger model of trans-polyacetylene by following the vibronic dynamics explicitly in a mixed quantum-classical Ehrenfest approximation. The simulations reveal the basic structure of the decoherence dynamics and illustrate the influence of system size and the nature of the initial state on the decoherence. 3.) Finally, in this context, we have identified a remarkable vibronic process that we call VIBRET in which the decay of an electron in the conduction band to a further inner state resonantly excites an electron in the valence band, leading to an oscillatory exchange of population between two distinct electronic states that lives for up to tens of picoseconds. Such oscillatory behavior suggests the presence of a long-lived electronic coherence. Interestingly, however, through the reduced purities VIBRET is shown to arise from a purely incoherent process (Ignacio Franco, Heiko Appel).

IV.11 Genetic Algorithm and the Cascade of Increasing Accuracy

Finding the global minimum of a given potential-energy surface (PES) is a formidable problem that cannot be solved either analytically or via grid-based methods, unless only a few

degrees of freedom are involved. Only stochastic methods offer a viable alternative. The genetic algorithms (GA) form a class of stochastic global optimizers which are based on the principles of natural evolution. When applied to atomic structures and when a search for the global energy minimum is made, a GA is in practice designed to randomly select low-energy structures and combine them into a new test structure, which is then locally optimized. The accurate knowledge of the PES is one of the critical aspects of any global search. In order to avoid wasting accurate energy and force evaluations on high-energy and already-known structures, a “cascade” scheme was designed: A multi-stepped procedure in which successive steps employ higher levels of theory, with each next level using information obtained at the lower level. High-energy and already-known structures are discarded in one of the low-level steps (Luca M. Ghiringhelli, Saswata Bhattacharya).

IV.12 Simulating the Global Effects of Charge-Carrier Doping by the Virtual-Crystal Approximation

Introducing atomically dispersed extrinsic species into a material, called doping, can have diverse effects on the material's properties. In particular, it can promote or suppress formation of intrinsic defects. Theoretical description of the effects of doping have so far remained focused on local effects, namely on changes in geometric and electronic structure and formation energies of an isolated intrinsic defect in the vicinity of a dopant. However, doping usually also changes electron or hole conductivity of a material, providing new pathways for charge transfer and compensation on macroscopic length scales. The relative importance of these global effects of doping for defect formation and surface chemistry has not been assessed so far.

In order to address this problem, we developed an approach based on the virtual-crystal approximation (VCA). In this approach, instead of explicitly introducing dopants, we modify native species in the material in such a way that delocalized partially occupied states are introduced with only a slight perturbation of the valence states of the host system. This simulates the dopant-induced states responsible for changes in conductivity. In an all-electron framework, this is achieved by modifying charges of all or of a selected subgroup of atomic nuclei in the system. The advantage of this approach is that the density of the “virtual dopant” states, i.e. the dopant concentration, can be varied independently of the size of the unit cell.

This allows low dopant concentrations to be modeled using smaller unit cell sizes in periodic models (Norina Richter, Sergey V. Levchenko).

IV.13 Sensitivity Analysis in Heterogeneous Catalysis

The kinetics of heterogeneous catalysis is affected by various processes. On surfaces with steps and defects their number can reach well over a hundred. Using the (first-principles) kinetic Monte Carlo approach, we modify the rate of each process and measure the resulting change of the turnover frequency. Such a sensitivity analysis (also called “degree of rate control”) identifies the key processes (typically more than one but less than ten). It is particularly important for finding (causal) descriptors for a “Big Data Analysis” of different catalyst materials (Karsten Reuter, Hakim Meskine and Sebastian Matera (TU Munich), Horia Metiu (UCSB)).

IV.14 The Atom-Centered Numeric Basis-Set Code “FHI-aims”

The FHI-aims all-electron code continues to expand as a strong base for the implementation and application of electronic structure methods developed in the department and elsewhere. Since 2011, the code has seen two major releases as well as continuous upgrades in the development branch. The number of developers that have contributed to the code in a noteworthy way now exceeds 50, most of them located in Berlin, but with several strong contributions from groups in Munich (Karsten Reuter), Helsinki (Ville Havu), Hefei (Xinguo Ren), London, and elsewhere. The key methodological choice behind the code are numeric atom-centered basis functions, allowing us to reach a computational accuracy on par with, e.g., the full-potential LAPW approach, but roughly at the same cost as plane-wave pseudopotential calculations. Several significant methodological additions to the code have been mentioned in the above sections, including: Correlation methods beyond the random-phase approximation; numeric atom-centered basis sets with valence correlation consistency for H-Ar, to obtain basis-set converged total energies for correlated methods directly; self-consistent *GW*; many-body perturbation inspired approaches to van der Waals dispersion interactions in DFT. Further important improvements include:

- Completed implementation of non-periodic and periodic hybrid functionals in an $O(N)$ scaling approach based on a localized version of resolution of the identity (RI) and enhanced aux-

iliary RI basis sets (Sergey V. Levchenko, Jürgen Wieferink, Arvid Ihrig, Xinguo Ren, Patrick Rinke, Matti Ropo, Volker Blum)

- Stress tensor and unit cell relaxation for local and semilocal DFT, hybrid functionals, and pairwise van der Waals contributions (Christian Carbogno, Franz Knuth, Viktor Atalla, Jürgen Wieferink, Volker Blum)

- Initial implementation of linear-response time-dependent density-functional theory for molecular optical spectra (Jan Kloppenburg, Heiko Appel, Volker Blum)

- Initial implementation of periodic *GW* and RPA methods in reciprocal-space and real-space frameworks (Xinguo Ren, Sergey V. Levchenko, Mark Glaß)

- QM/MM Embedding infrastructure for surface models as clusters by repulsive pseudopotentials and point charges (Daniel Berger and Karsten Reuter (TU Munich), Volker Blum)

- Connection to i-pi infrastructure (Michele Ceriotti and coworkers) for nuclear quantum effects modelled by path-integral Monte Carlo (Mariana Rossi)

- “aimsChain” infrastructure to compute transition states: currently, nudged elastic band and the string method (Yingyu Yao, Luca M. Ghiringhelli)

- Linear macroscopic dielectric tensor (Björn Bieniek, Christian Carbogno) and Kubo-Greenwood transport (Christian Carbogno, Karsten Rasim)

- Connection to “aitranss” infrastructure (Evers group, KIT) for molecular transport based on the Landau-Büttiker formalism (Alexei Bagrets (KIT))

- Generalized Langevin Equation colored-noise thermostat to include nuclear quantum effects (Mariana Rossi)

V. Applications – Some Highlights

This Section briefly summarizes some computational studies, results, and insights from the various research fields and topics studied in the *Theory Department* during the last six years. The selection criteria for the examples presented were their visibility or expected impact. To keep this Section to a reasonable length, emphasis is put on the last two years.

V.1 Surfaces, Adsorption, and Heterogeneous Catalysis

V.1 a Benzene Adsorbed on Transition-Metal Surfaces: Structure and Adsorption Mechanism

The adsorption of aromatic molecules on metal surfaces plays a key role in condensed matter physics, catalysis, and functional materials. We systematically studied the adsorption of benzene on transition-metal surfaces, demonstrating that our recently developed DFT+vdW^{surf} method allows quantitative treatment of both weak and strong adsorption on metal surfaces, thus extending the already excellent performance found for molecules in the gas phase. Notably, we found that van der Waals forces contribute more to the binding of covalently bonded benzene than they do when benzene is physisorbed (Alexandre Tkatchenko, Wei Liu, Victor G. Ruiz, Guo-Xu Zhang, Biswajit Santra, Xinguo Ren).

V.1 b Graphene Engineering: Stability of Epitaxial Graphene and the Surface Reconstructions of 3C-SiC

SiC is an important material for growing graphene films directly on a semiconducting substrate. The underlying process is Si sublimation. Several experimental groups claim 'wafer-scale' high-quality monolayer graphene films on the Si side of SiC, and first devices are being made by groups at IBM, U Erlangen, and elsewhere. We have shown that these films in fact grow due to the establishment of specific equilibrium, or very-near equilibrium conditions, and are not just necessary kinetic intermediates during Si sublimation. This result will help focus future growth efforts on the C side (where the same growth mode is not possible) and probably also on other substrates (Volker Blum, Lydia Nemeč, Florian Lazarević, Patrick Rinke).

V.1 c Ultrathin Oxides: Bulk Oxide-Like Model Surfaces or Unique Films?

On the nanoscale, materials often reveal new and unexpected features. Ultrathin silica films on Mo(112), for example, differ significantly from the surfaces of bulk SiO₂ and should therefore be considered as new materials with interesting and novel properties of their own. The same is true for monolayer ZnO films on the (111) surfaces of Ag, Cu, Pd, and Pt. Thicker films, on the other hand, approach the structure of the bulk ZnO surface and might potentially

serve as model surfaces in catalysis or for the study of hybrid inorganic/organic systems (Patrick Rinke, Christoph Freysoldt, Björn Bieniek).

V.1 d Importance of Many-body Effects and Self-interaction Corrections in the Adsorption Puzzle of CO on Metal Surfaces

Since the adsorption of CO on metals requires a good description for systems that are as diverse as metal surfaces and small molecules, it has become an important benchmark system for electronic-structure methods. We have demonstrated that RPA outperforms the common density functionals, because it combines exact exchange, which removes the self-interaction error, with a correlation energy based on the renormalized (screened) Coulomb potential that is finite for metallic systems and yields the right decay behavior outside a metal surface (Patrick Rinke and Xinguo Ren).

V.1 e Importance of Space-Charge Effects for the Concentration of Defects at Metal-Oxide Surfaces

We have calculated the concentration of oxygen vacancies at the (100) surface of doped MgO as a function of temperature, oxygen pressure, and dopant concentration, using *ab initio* atomistic thermodynamics. The global electrostatic energy of the charge separation generated by the electron transfer from the vacancies to the dopant-induced states is considered as part of the free energy of the system. We find that a space-charge layer with a thickness up to hundred nanometers forms under the surface at realistic conditions solely due to the formation of charged oxygen vacancies at the surface (Norina Richter and Sergey V. Levchenko, Sabrina Siculo and Joachim Sauer (HU Berlin)).

V.1 f Stability and Metastability of Clusters in a Reactive Atmosphere: Unexpected Stoichiometries of Mg_MO_x

By applying the cascade genetic algorithm (IV.11) and *ab initio* atomistic thermodynamics, we identify the stable and metastable compositions and structures of Mg_MO_x clusters at realistic temperatures and oxygen pressures. Small clusters ($M < 5$) are found to be in thermodynamic equilibrium when $x > M$. The non-stoichiometric clusters exhibit peculiar magnetic behavior, suggesting the possibility of tuning magnetic properties by changing environmental

pressure and temperature conditions (Luca M. Ghiringhelli, Saswata Bhattacharya, Sergey V. Levchenko).

V.1 g Critical Assessment of Li/MgO-Based Catalysts for the Oxidative Coupling of Methane

We have used *ab initio* atomistic thermodynamics to analyze stability of different types of defects on the Li-doped MgO(100) surface. The Li substitutional defects, as well as their complexes with oxygen vacancies, are predicted to segregate from the bulk to the surface. There they form islands which are rich in Li substitutional defects and oxygen vacancies. These findings have helped to explain recent experimental observations, and prompted a critical re-assessment of the relevance of a large number of previous theoretical and experimental studies on the practical application of Li-MgO as a catalyst for the oxidative coupling of methane (Sergey V. Levchenko).

V.1 h Sub-Monolayer Water Adsorption on Alkaline Earth Metal Oxide Surfaces: A First-Principles Cascade Genetic Algorithm Study

Using *ab initio* atomistic thermodynamics and the cascade genetic algorithm (IV.11), we have studied trends in the stability of adsorbed water structures on alkaline earth metal-oxide surfaces. We find a range of H₂O chemical potentials where one-dimensional adsorbed water structures are thermodynamically stable on CaO(001). On MgO(001) and SrO(001) such structures are not found. The formation of the one-dimensional structures is explained by the balance between water-water and water-surface interactions (Xunhua Zhao, Saswata Bhattacharya, Luca M. Ghiringhelli, Sergey V. Levchenko).

V.1 i Unexpected Stability of O-Interstitial on Rough MgO Surfaces

In order to model the thermodynamic stability of rough metal oxide surfaces in a reactive atmosphere, we calculate, by combining *ab initio* atomistic thermodynamics and the cascade genetic algorithm (IV.11), the relative stability of medium-size parallelepipedal [(MgO)_N]^q clusters ($N = 18, 24, 32, 108$), isolated or embedded in a point-charge matrix, at various charge states q as function of T , p_{O_2} , and doping conditions (accounted for by the chemical potential of the electrons, μ_e). We find that, at realistic temperatures, pressures, and μ_e , O₂ or

O₃ interstitial states at the oxygen corners of pristine clusters are favored for *all* studied charge states (Saswata Bhattacharya, Sergey V. Levchenko, Luca M. Ghiringhelli).

V.1 j Towards Catalysis by Free Gold Clusters

Using constrained *ab initio* atomistic thermodynamics we have studied free gold clusters in contact with an atmosphere composed of O₂ and CO. The approach enables us to account for spin, temperature, and pressure effects. The results suggest that the adsorption of an incoming O₂ molecule drives the system from the singlet to the triplet spin state, and vice versa, and the oxidation reactions then occur on either the $S=0$ or the $S=1$ potential-energy surface (Elizabeth C. Beret, Merel M. van Wijk, Luca M. Ghiringhelli).

V.2 Defects in Bulk Semiconductors and Insulators

V.2 a First-Principles Optical Spectra for F Centers in MgO

The study of the oxygen vacancy in MgO has been aggravated by the fact that the positively charged and the neutral vacancy absorb at practically identical energies in the optical spectrum. We apply the Bethe-Salpeter approach on top of a newly developed scheme for defect formation energies in the G_0W_0 approach and obtain optical spectra in unprecedented agreement with experiment. Our calculations reveal that not only the absorption but also the emission spectra of different charge states peak at the same energy, which leads to a reinterpretation of the optical properties of the F center. (Patrick Rinke, André Schleife (University of Illinois at Urbana-Champaign), Emmanouil Kioupakis (University of Michigan), Anderson Janotti and Chris Van de Walle (UCSB) and Claudia Rödl and Friedhelm Bechstedt (University of Jena)).

V.2 b Ferroelastic Switching in the Dynamics of Y- and Ti-stabilized ZrO₂

Using *ab initio* molecular dynamics and the *generalized solid state-nudged elastic band* method, which accounts for the unit-cell degrees of freedom, we have studied the thermodynamic properties of ZrO₂ based ceramics. By investigating extended supercells we have identified a novel phase stabilization mechanism for the high-temperature cubic phase. This particular dynamics, which can be controlled via cation doping, involves the realignment of the lattice vectors along different cartesian directions (Christian Carbogno, Carlos Levi (UCSB)).

V.2 c Electronic Structure and van der Waals Interactions in the Stability and Mobility of Point Defects in Semiconductors

Defects are abundant in real-world materials where they significantly modify the electronic, optical, and magnetic properties. Density functional theory calculations with hybrid functionals are essential to achieve a reasonable description of defect electronic levels and defect formation energies. However, these functionals significantly overestimate the experimental migration barriers. Notably, the inclusion of screened van der Waals interactions on top of hybrid functionals significantly improves the description of defect formation energies and brings migration barrier heights into close agreement with experimental values (Wang Gao, Alexandre Tkatchenko).

V.3 Biophysics

V.3 a Building Blocks of Proteins

Secondary structure (helices, sheets, turns, etc.) are the key conceptual building blocks used to understand structure formation (and ultimately, function) in peptides and proteins. Our goal has been to quantify the contributions that determine the stability of helices and turns. Regarding helices, direct comparisons to gas phase experiments enabled us to show that especially the vibrational entropy can tip the balance towards this structure, avoiding the formation of less organized, more compact “blobs”. On the other hand, we showed that specific ion-peptide interactions can in fact disrupt the neutral, organized secondary structure, using turn-forming tetrapeptides as an example. A key question that must be asked, however, is whether first-principles methods are worth the effort for solving such questions - i.e., what is the accuracy needed to match what experiment can resolve. We have addressed this question for a set of benchmark experiments of a helical peptide from the Rizzo group, showing that indeed, a hybrid functional and many-body dispersion interactions are needed to capture this 100-atom chain (Mariana Rossi, Franziska Schubert, Carsten Baldauf, Sucismita Chutia, Matti Ropo, Volker Blum, Gert von Helden (MP Department)).

V.3 b Critical Role of Van der Waals Interactions for Polypeptide Secondary Structures

Folding and unfolding processes are important for the functional capability of polypeptides and proteins. We have employed both the pairwise and many-body methods for vdW interactions to show that their accurate inclusion is essential for understanding the stability of peptides *in vacuo*. VdW interactions qualitatively change the conformational landscape of alanine polypeptides, and greatly enhance the thermal stability of helical structures, in agreement with gas-phase experiments. Many-body effects in the vdW energy increase in importance for larger and structurally more complex peptides (Mariana Rossi, Volker Blum, Alexandre Tkatchenko, Joel Ireta Moreno (Metropolitan Autonomous University, México)).

V.3 c Formation of the Protein α -Helix Motif in the Chemically Homologous Class of β -Peptides

The β -peptide backbone compensates the limitations of natural peptides for a potential use as drugs, namely by increasing lifetime, enlarging chemical space, and improving folding behavior. We have demonstrated here the potential of β -peptides to imitate the most-prominent structural motif of natural proteins, the α -helix. A first-principles conformational search served as the basis for simulations of vibrational spectra and the computation of molecular shapes (collision cross sections) which were then compared with the corresponding experimental values (Franziska Schubert, Kevin Pagel (MP Department), Volker Blum, Carsten Baldauf).

V.3 d Water-Peptide Interaction

Perhaps the most frequently emphasized question in the peptide structure area concerns the interaction with water. Here, too, a critical first step is to understand the interaction between peptides and individual water molecules quantitatively, including adsorption energies, adsorption trends, and conformational preferences. Based on a series of measured equilibrium constants from the Jarrold and Bowers groups, we showed that DFT-PBE+vdW predictions yield excellent agreement with experiments for lysine-terminated polyalanine chains, including a surprising sensitivity to peptide chain length which is traced to the vibrational contribution. This can be addressed in the harmonic approximation, but it is clear that this approach will be of limited value in future. Real (anharmonic) “nuclear quantum effects” are needed, especially

for protons. We have therefore connected our approach to path integral dynamics methods, initially for small water clusters. We are continuing to work towards an incorporation of such effects in a way that is effective for larger peptide molecules and electronic structure theory (Mariana Rossi, Sucismita Chutia, Michele Ceriotti (EPFL), David Manolopoulos (University of Oxford), Volker Blum).

V.3 e Force Regulation of von Willebrand Factor (VWF) Activity

VWF is a large multimeric blood protein. Its maximal length of up to 40 μ m makes it sensitive to shear-flow, which acts as a trigger to regulate blood clotting mediated by cross-linking injured vessel walls and blood platelets. In this project, we perform force field simulations at the level of protein domains and have been able to elucidate a force-dependent auto-inhibition mechanism that regulates the VWF interaction with a platelet receptor and collagen. Thus, we are beginning not only to understand physiology in atomistic detail, but also to discover new drug targets to potentially intervene in threatening diseases like strokes (Camilo Aponte-Santamaría and Frauke Gräter (Heidelberg Institute for Theoretical Studies (HITS), Carsten Baldauf).

V.4 Organic Materials and Interfaces

V.4 a Reliable Modelling of Stabilities, Polymorphism, and Response Properties in Organic Materials

Organic materials are of great fundamental and applied importance. We have demonstrated that the recently developed DFT+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, giving a systematic and seamless method for modeling both gas-phase and condensed molecular materials. The importance of accurate treatment of dispersion goes far beyond energetic stabilities. Many response properties show even larger contributions from many-body dispersion interactions (Anthony M. Reilly, Alberto Ambrosetti, Alexandre Tkatchenko).

V.4 b Effects of Stress and Strain on the Electronic Structure of Organic Semiconductors

Stress, strain, and pressure are key determinants of the stability, mechanical and electronic properties of any material, but are particularly important in semiconductors. Being able to predict the effects of stress / strain on the electronic structure accurately, however, involves non-trivial decisions, including the electronic structure method itself, a quantitative treatment of stress in periodic systems, and the question of the impact of nuclear effects (electron-phonon interaction) on the eventual results. We have completed a full implementation of the stress tensor for numeric atom-centered basis sets in the FHI-aims code. For the prototypical organic semiconductor polyacetylene, we show that the effect of pressure on the band gap is correctly captured *if* a hybrid functional with a sufficiently high exact exchange contribution is used (HSE06 with a fraction 0.5 of exact exchange or higher). This is closely connected to the chain dimerization in the electronic ground state, i.e., the electronic gap itself can be described by a static symmetry-broken arrangement at the Born-Oppenheimer surface (Franz Knuth, Viktor Atalla, Volker Blum, Christian Carbogno).

V.4 c Reliable Description of van der Waals Interactions for Inorganic/Organic Systems

Reliable modeling of the structure, stability, and electronic properties of complex adsorption systems remains a daunting task for modern electronic structure calculations. Our recently developed DFT+vdW^{surf} method extends the applicability of semi-local DFT to organic/metal systems and leads to a few surprising findings: (1) The vdW energy can contribute more to the binding of covalently bonded systems than it does for that of physisorbed molecules; (2) the physically bound precursor state for aromatics on Pt(111) can be more stable than the corresponding chemisorbed state; (3) many-body vdW interactions lead to a binding energy for a fullerene molecule adsorbed on multi-layered graphene that *decreases* as a function of the number of underlying graphene layers (Wei Liu, Victor G. Ruiz, Sergey Filimonov, Javier Carrasco, Alexandre Tkatchenko).

V.4 d Charge Transfer and Charge Localization at Organic/Metal Interfaces

For organic adsorbates that strongly hybridize with a metal surface, we find that semi-local density functionals provide an adequate description of charge transfer and the associated

work-function change compared to experimental data. When the hybridization between metal and adsorbate is prevented by a NaCl spacer layer, semi-local functionals predict a fractional electron transfer resulting in equally charged molecules, while hybrid functionals, are able to break the translation symmetry and produce integer charging of only a fraction of the adsorbate layer (Oliver T. Hofmann, Viktor Atalla, Patrick Rinke).

V.4 e Space-Charge Transfer in Hybrid Inorganic-Organic Systems

For the hybrid inorganic-organic system tetrafluoro-tetracyanoquinodimethane (F4TCNQ) on the ZnO(000-1) surface we have shown that the adsorption energy and the electron transfer depend strongly on the bulk doping concentration of ZnO. The associated work-function changes are large, for which the formation of space-charge layers is the main driving force. Our prediction of a large work-function change at vanishing charge transfer is in agreement with photoemission experiments on the same system (Yong Xu, Oliver T. Hofmann, Patrick Rinke, Raphael Schlesinger, Sylke Blumstengel, Fritz Henneberger and Norbert Koch (HU Berlin), Antje Vollmer (Helmholtz-Zentrum Berlin)).

V.5 And More...

V.5 a The *f*-Electron Challenge: Lanthanides and Lanthanide Oxides in Density-Functional and Many-Body Perturbation Theory

We challenge the notion that classifies the *f*-electron lanthanides as strongly correlated. We find that, unlike conventional density functionals, the advanced RPA functional predicts a pressure-induced isostructural α to γ phase transition in cerium with a transition pressure in good agreement with the experimental extrapolation to 0 K. The similarly good agreement between photoemission spectra and G_0W_0 calculations for the lanthanide sesquioxides unveils that the variation of the band gaps across the series can be explained in terms of the *f*-electron filling (Marco Casadei and Patrick Rinke, Hong Jiang (Peking University), Xinguo Ren (University of Science and Technology of China), Angel Rubio).

V.5 b Van der Waals Interactions in Ionic and Semiconductor Solids

How much do van der Waals interactions contribute to the cohesive properties of ionic and semiconductor solids? The answer to this fundamental question has remained elusive for a

long time. We have developed an efficient method to determine vdW parameters for “atoms” in solids, and have assessed the relative contribution of vdW interactions to the lattice constant, cohesive energy, and bulk modulus for a wide variety of solids. While the vdW energy is clearly not the most relevant contribution in many solids, its accurate inclusion in semi-local and hybrid DFT functionals leads to significantly improved performance of these functionals when comparing to reliable experimental data for the cohesive properties of solids (Guo-Xu Zhang, Alexandre Tkatchenko).

V.5 c Consistent Set of Band Parameters and Deformation Potentials for the Group-III Nitrides and Group-II Oxides

We have derived consistent sets of band parameters and strain deformation potentials for the group-III nitrides (AlN, GaN and InN) and the group-II oxides (MgO, ZnO and CdO) in the wurtzite phase. Consistency is achieved by using the HSE hybrid density functional for the deformation potentials and the G_0W_0 approach for the band structures. It is verified by computing selected deformation potentials in G_0W_0 and vice versa. The parameters are in good agreement with available experiments and can now be used in device simulations and to interpret experiments (Patrick Rinke, Qimin Yan, Anderson Janotti and Chris Van de Walle (UCSB), Manfred Winkelkemper, and Dieter Bimberg (TU Berlin), Abdallah Qteish (Yarmouk University, Jordan), Jörg Neugebauer (MPI Düsseldorf)).

V.5 d Polymorphism in Ice at Ambient and High Pressures

It has long been recognized that water molecules interact with each other through a combination of electrostatic dipoles, hydrogen bonding, and vdW forces. However, the way in which the interplay of such interactions leads to the rich and complex phase diagram of ice remains far from being understood. Using diffusion quantum Monte Carlo (DMC), accurate lattice energies of several ice phases have been obtained. Then, employing the DFT+vdW approach, we show that the vdW contribution to the lattice energy increases monotonically from the ambient to the high pressure phases of ice. Conversely, the strength of the hydrogen bonds between the water molecules decreases as the pressure increases. This results in the finding that in the highest pressure phase one quarter of the entire lattice energy comes from vdW forces (Biswajit Santra, Alexandre Tkatchenko, Jiří Klimeš, Dario Alfè, Ben Slater, Angelos Michaelides (UCL), Roberto Car (Princeton University)).

V.5 e Gold Clusters at Finite Temperatures

Typical theoretical studies of clusters address the $T=0$ K structures and then focus on the lowest-energy isomer(s). We have performed, however, unbiased sampling of the free-energy landscape of Au_N clusters ($3 \leq N \leq 20$) by means of DFT (PBE+vdW)-based replica-exchange molecular dynamics. For many sizes of pristine as well as complexed gold clusters we find a fluxional, and for some sizes, even a liquid character at room temperature. The calculations also reveal that anharmonicity as well as the presence of adsorbed noble gas atoms can have significant effects on IR spectra. The bonding between rare gas (RG) atoms and small gold clusters has been analyzed and found to be due to an overlap of the p orbitals of the RG with s - 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 (their length is shortened and the stretching vibrational frequency is increased) (Luca M. Ghiringhelli, Sergey V. Levchenko, Phillipp Gruene, Jonathan T. Lyon, André Fielicke, and Gerard Meijer (MP Department)).

V.5 f Sustainability and Resource Depletion

The transformation of the energy system in Germany (known as the *Energiewende*) involves a substantial increase in the generation of renewable energy. It is also expected to create a strong demand for many raw materials, some of which are already regarded as scarce. Examples are lithium and cobalt for batteries, rare earth elements for wind turbines, as well as cadmium, tellurium and indium for solar cells. Does this mean that regenerative energy systems are not necessarily sustainable? And what does “sustainable” actually mean when applied to mineral resources? Within the framework of the project we examine the concept of “sustainability” in general and the possible role played by resource depletion. Particular emphasis is given to raw materials required for the new energy economy and for electric vehicles. (Alex M. Bradshaw, Benjamin Reuter and Thomas Hamacher (TU Munich)).

V.5 g History of Quantum Field Theoretical Methods in Many-Body Physics: The Story of RPA

In the two decades after World War II, the quantum theory of many-body systems underwent a major transformation by extending concepts and techniques originating from quantum electrodynamics (QED) to the study of solids and nuclei. Since the late 1950s, quantum field the-

oretical techniques (in particular Feynman-Dyson diagrammatic perturbation theory) have become commonplace in condensed-matter theory. In order to gain a better understanding of this process of knowledge transfer, we contextualize a particular thread of this development: the story of the random-phase approximation (RPA), a perturbative technique which is of particular importance even today (Alexander S. Blum (MPIWG), Christian Joas (LMU Munich)).

