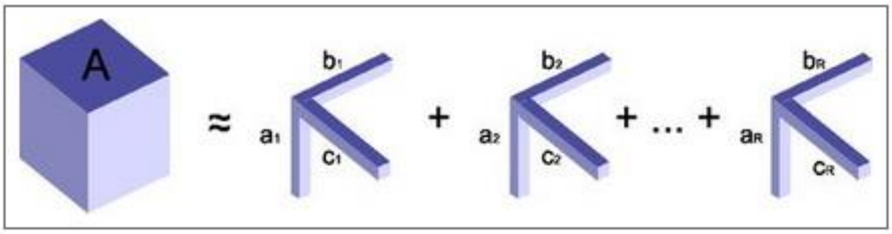
Method development - new algorithms and approximations for post HF Methods

The great advantage of high level ab-initio methods like from Coupled Cluster theory is that they can be improved systematically within a hierarchy of methods, their limitations are well known and often indications can be found if the methods break down. Furthermore, at levels of theory like CCSD(T) or better results for molecular properties fall within the experimental error bars. Besides the high accuracy of the results, these methods can be used as black box tools that require little knowledge on the system in advance.

All these benefits come at a price - computational time. Traditionally, high-level ab-initio calculations were only feasible for small systems and these methods could only be applied for benchmark studies in order to estimate the errors more cost-efficient methods another approach are various further approximations that reduce the computational effort of these methods. With the development of local correlation methods this has changed dramatically, and using modern approximations, high level calculations can be carried out routinely for systems that before could only be treated at the DFT level of theory.

However, if the exact limit of solving the Schrödinger equation is the goal, local correlation methods are of little help, as they do reduce the computational cost with system size for methods like CCSD or CCSD(T) but do not offer a solution for the systematic improvement of the correlation treatment towards FCI. While methods like FCI-MC or DMRG offer solutions to this problem, a robust, accurate and affordable solution is yet to be found.

Exploring Tensor Decomposition techniques for solving the n-electron problem



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The main focus of the methodological work in our group is the application of techniques from applied mathematics to large dimensionality tensors as they occur in Coupled Cluster or CI theory. Here, new ideas brought in from a cooperation with mathematicians might help to develop more general approximation schemes that break the curse of dimensionality for high level post-HF methods.

An approach that is especially promising is investigated in a collaboration with the group of Prof. W. Hackbusch (MPI für Mathematik in den Naturwissenschaften, Leipzig). Tensor decomposition methods are well known tools in mathematics and engineering. However, little is known about their applicability for the truncation of wavefunction parameters. In the framework of this project, the potential of tensor decomposition methods for devising new approximations for electronic structure methods are explored. While we have been able to show, that the application of tensor decomposition techniques should be beneficial for methods like CCSDT, a FCI implementation with subexponential scaling is currently under development.

Method development for post-HF methods: Code Generation

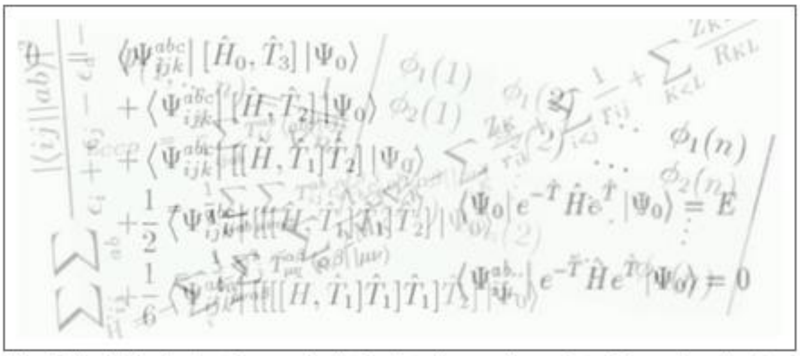

Fig. 2 The high algebraic complexity is often the main problem if novel methods are to be implemented error-free.

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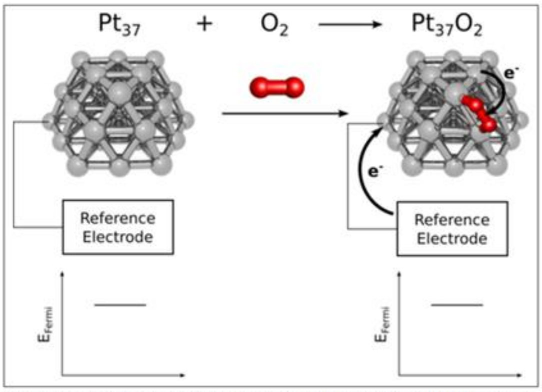
The high complexity of the working equations for approaches like Coupled Cluster or multireference methods in general renders method and development very time demanding and error prone. Often, the time to develop and test new methods is only limited by the large coding effort that has to be invested even for simple test implementations. If new ideas and concepts should be put to work quickly, new tools for the development itself have to be devised. Instead of carrying repetitive and systematic steps out by hand, software tools can be used that convert algebraic expressions or symbolic input into efficient electronic structure code. The right tool for this purpose is Computer aided implementation / automatic code generation.

The basic idea is that starting from an algebraic expression or working equations or even a symbolic representation of an algorithm, all steps to obtain an efficient code can be carried out by script or compiler like software tools. Almost very modern electronic structure code has an interface to a generator tool or provides its own development patform of its kind. Currently, the ORCA developers team is working on a generator tool in order to implement novel and existing multireference-CI methods.

Work in Electrocatalysis



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MAXNET Energy

Our group participates in the MAXNET Energy research initiative and Alexander Auer is the research coordinator of the compound project. For details see the MAXNET Energy homepage.

Method development for modelling electrocatalysis

In contrast to heterogeneous catalysis, electrochemical reactions include flux of electrons from or into the surface. This effect is often modeled by an a-posteriori approach, in which a grand canonical ensemble thermodynamics is constructed on top of calculations which include a fixed number of electrons. In order to go beyond this scheme we are working on the implementation of a constant potential approach, in which the electronic structure is treated for a given electrochemical potential wit variable electron number. While several studies of related approaches exist, a robust and efficient implementation is yet to be devised.

Especially for non-faradaic processes in electrocatalysis this might prove to be a very powerful tool with which theoretical chemistry might be used to gain deep insight in many important electrochemical processes.

Electronic structure calculations of platinum nanoparticles in electrocatalysis

To gain electric energy from the reaction of Oxygen with Hydrogen, proton exchange membranes fuel cells (PEMFC) are the most common technology. The most important part of these devices is the catalyst. In practice Pt nanoparticles on a carbon support are used to catalyze the the Oxygen Reduction Reaction (ORR). Yet these devices are not without shortcomings. This project focuses on several aspects of the catalyst system.

- The performance of low temperature PEMFC is mainly limited by the slow kinetics of the platinum catalyzed ORR on the cathode side. Here, a detailed understanding of the relevant mechanisms can aid to optimize the catalyst. Recent experiments try to gain insight into the mechanism by the decomposition reactions of H2O2 as an intermediate of the ORR (O2+H2 → H2O2 → H2O).
- Promising systems towards more effective and cheaper catalysts are core-shell particles of Pt-Co alloys. Experiments show, that starting from alloyed particles, core shell particles are obtained from an electrochemical or a thermal treatment. This process is enhanced by adsorbed CO. On the other hand, Co is leached during the catalytic process in an oxygen rich environment. Electronic structure calculations based on a cluster model allow to estimate the key influences in these processes.
- The deadhesion of Pt nanoparticles from the supporting carbon materials are a problem for the endurance of PEMFC. Here, a better understanding of the interactions between the particles and the support is needed.
- To further reduce the cost of catalysts it is highly desirable to move away from precious metals to more abundant materials like transition metals or even to carbon-based materials. However, in order to assess novel non-precious metals systems, profound knowledge on

As a model for the nanoparticles we consider small Pt clusters and Pt/Co clusters, respectively. To model the carbon support, polycyclic aromatic hydrocarbons are used. Quantum chemical techniques, namely atomic orbital based DFT methods are applied. They offer several advantages over periodic plane wave calculations, for example in treating charged species and in obtaining chemical insight into orbital interactions and reaction mechanisms.

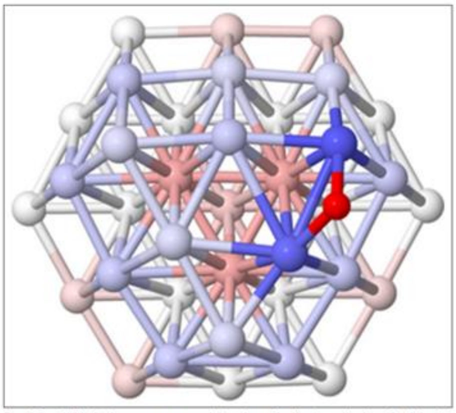

Fig. 4

Fig. 4 Small Pt-clusters serve as model systems for the investigaion of catalyst stability and activity.

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Decomposition of H2O2 - probing mechanistic details of the ORR indirectly

In collaboration with the group of K. Mayrhofer at the MPIE (Düsseldorf), the reactions of H2O2 on Pt nanoparticles were investigated. Experiments showed that decomposition of H2O2 depends on the applied voltage. At low potentials the H2O2 reduction reaction is dominating, while it is the oxidation at high potentials. Calculations show that on a reduced Pt surface (the dominating surface state at low potentials) the reduction of H2O2 (H2O2 → 2OH-) takes place with a negligible barrier. On the other hand the oxidation of H2O2 (H2O2 → O2 + H2O) is the reaction with a negligible barrier at an OH-covered Pt surface at high potentials. These results support the experimental findings of the decomposition of H2O2.

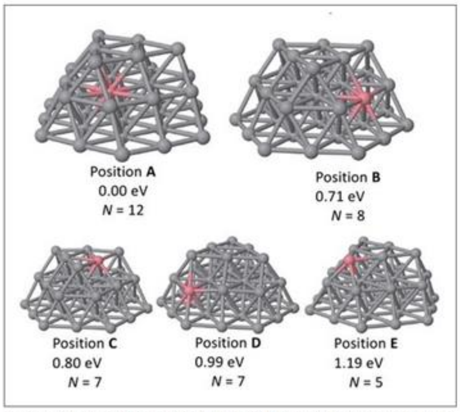

Fig. 5

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Segregation phenomena on Pt/Co-alloy nanoparticles

One approach to increase the catalytic activity of Pt-nanoparticles that has been intensively investigated during recent years is to apply alloy nanoparticles with core-shell structure. In practice, however, these systems are often limited by their stability, as often less noble metals (like Ni or Co) are leeched out of the particles during the electrocatalytic process.

As a model for Pt/Co-alloyed nanoparticles the cluster model with the substitution of several Pt atoms by Co atoms was applied. The calculations show that the preferred configuration of Pt-Co-alloyed particles is the core shell configuration with Co located in the centre of the cluster. Furthermore, it is shown that adsorbed CO is raising the segregation energy, depending of the considered cluster system by ca. 0.5 eV while adsorbed oxygen species lowers it by approximately 0.2 eV. It is also found that adsorbed oxygen leads to a deformation of the cluster, whereby the migration of the cobalt to the surface might be promoted. Studies of the influence of the alloying Co indicate that it is rather an electronic than a geometric influence that leads to the higher catalytic activity of the core-shell-particles.

DFT and DFT-D calculations yield insight in the decisive contributions to the nanoparticle-carbon support interactions.

Nanoparticle-Support-Interactions

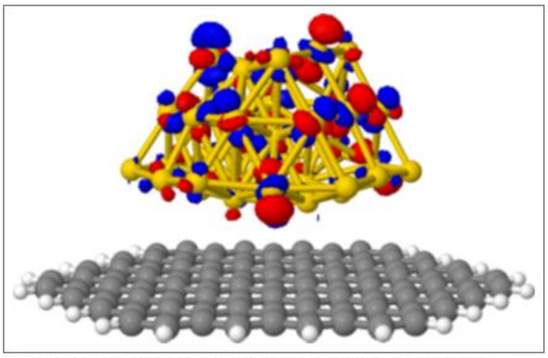
Catalyst systems as applied in fuel cells are typically Pt nanoparticles on a conducting carbon support. In order to prevent catalyst degradation it is essential to understand the basic interaction forces and binding motives of nanoparcles on carbon materials.

Analyses of the interaction between the cluster and the polycyclic aromatic hydrocarbon show that they are of dispersion type on an undoped carbon support. Furthermore, introducing doping elements like N, O or S improve the interactions by introducing a dipole. However, the inclusion of doping atoms or defects comes at the expense of perturbing the structure of the support. This leads to a large decrease of the dispersion type interactions.

This work is supported by the BMWi (Project PtTM-HGS Fachbereich "Wärme-Kraft-Mobilität" ESN4) and the BMBF (Project "Joint Lab GEP").

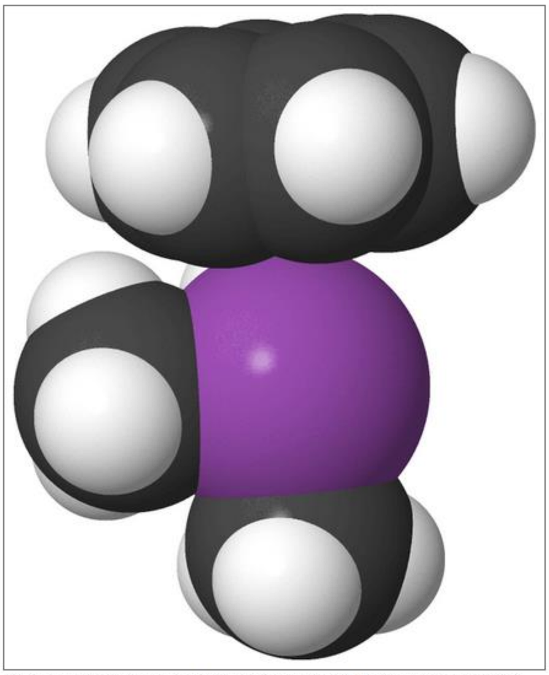
A deeper understanding of protoype compounds like BiR3 - Benzene allows to rationalize and quantify how dispersion and donor-acceptor interactions balance in heavy main group element compounds

Materials Science: Heavy main group elements as dispersion energy donors



DFT and DFT-D calculations yield insight in the decisive contributions to the nanoparticle-carbon support interactions.

Within the framework of the SPP 1807 "Control of London dispersioninteractions in molecular chemistry" our group works on heavy main group elements as dispersion energy donors in inter- and intramolecular interactions. The joined project with Prof. M. Mehring's group at the TU Chemnitz focuses on the rich phenomenology of heavy main group atom interactions in coordination and supramolecular chemistry. While the coordination group in Chemnitz synthesizes and characterizes new structural motifs of, for example, Bismuth, Arsenic and Atimonycompounds, our group carries out computations for the detailed analysis of the balance of donor-acceptor interactions and dispersion forces in these compounds.



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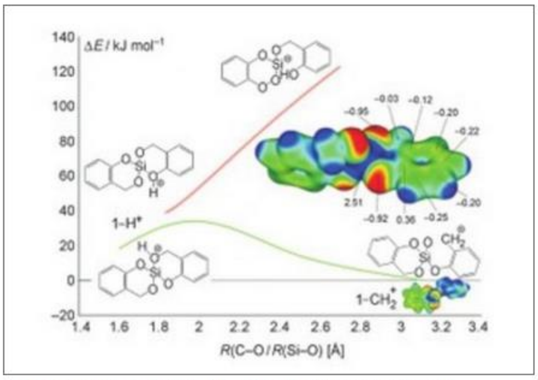

Fig. 7 Calculations on intermediates of the twin polymerization exhibit mechanisms and rate-determining steps of this novel type of polymerisation that yields organi/inorganic nanocomposites.

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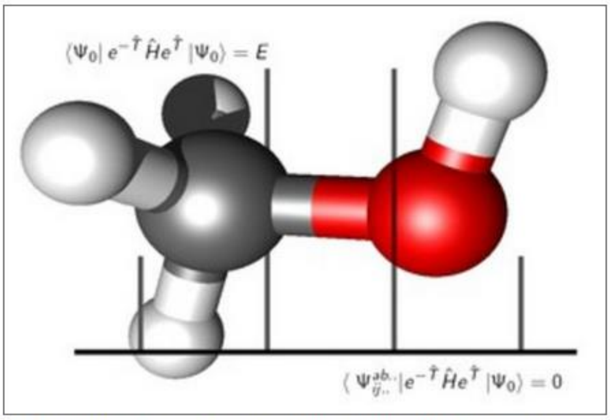
Materials Science: DFT study of the twin polymerization process

The twin polymerization is a novel technique for synthesizing hybrid organic/inorganic polymers with domain sizes in the nm range. These are obtained from a single source monomer in a single step procedure either in the melt or in solution. While a broad variety of monomers and products have been investigated in this context, the mechanistic details and the most important influences on the nanostructure formation of the hybrid polymer are unknown.

A detailed analysis of possible reaction paths exhibits that the unique morphology of the resulting polymer is the result of a very fast formation of the organic phase that impedes separation of the inorganic phase. In our work, we devised a scale bridging approach to simulate the twin polymerization of 2,2'-spirobi (4H-1,3,2-benzodioxasiline). This approach is based on detailed quantum chemical calculations at the DFT level of theory to identify the most important reaction steps and estimate reaction rates.

This work is carried out in close collaboration with experimentalists and theoreticians from the TU Chemnitz in the Framework of the Forschergruppe "organic-inorganic nanocomposites by twin polymerization" (FOR 1497).



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Theory and Spectroscopy - quantitative calculation of NMR chemical shifts

The accurate prediction of chemical shifts is still a great challenge for theoretical chemistry. While, for example, the typical error of SCF 13C chemical shift calculations are about 5-10 ppm, correlated methods can be applied to reduce the error significantly. This way it is possible to predict 13C chemical shift with an accuracy of about 1 ppm deviation from the gas phase experiment. This has been demonstrated in previous benchmark studies, where calculations of 13C chemical shifts for a set of 15 small organic compounds have been carried out. To reach this precision the molecular geometry hat to be optimized at the CCSD(T) or MP2 level using sufficiently large basis set like the Dunning cc-pVTZ or cc-pVQZ basis set. The chemical shifts have to be calculated at CCSD(T) level using large basis sets augmented in the core region like qtz(2p,3d).

Further benchmark studies that have been carried out focus on chemical shifts of oxygen, nitrogen and phosphorus, the inclusion of temperature effects and the comparison to DFT methods. Current work is focused on temperature effects and isotope shifts of NMR shieldings. Here, we have been able to show that secondary isotope effects on NMR chemical shieldings can be predicted using standard electronic structure methods, provided a sufficient treatment of zero-point vibrational effects and temperature corrections.

Prof. Alexander Auer, Method Development and Heterogeneous Reactions, from website MPI CEC 12/2017