I1

Materials design and development of functional materials for industry

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It is now well-recognized that we are witnessing a golden age of innovation with novel materials, with discoveries important for both basic science and industry. With development of theory along with computing power, quantum materials design—synthesis of materials with desired properties in a controlled way via materials engineering on the atomic scale—becomes a major component of materials research. Computational prediction based on first-principles calculations has helped to find an efficient way to develop materials even much needed for industry, as we have already seen in successful development of a visible-light sensitized photocatalyst [1] that is now commercialized.

The load placed on our environment has grown tremendously in recent years, because of increased resource and energy consumption fueled by entrenched socioeconomic activities based on mass production, mass consumption and mass waste. Thermoelectric energy conversion has attracted considerable interest for tackling global environmental issues, which has renewed attention for the past decade stimulated by several new findings of thermoelectric materials. To find guiding principles for high thermoelectric materials, we have investigated two systems: one is Al-Re-Si 1/1-1/1-1/1 approximant that shows a low thermal conductivity (~1 W/mK) as explained by first-principles phonon calculations [2], and another is half-Heusler TiNiSn compound where pair-wise doping is designed with computations to improve thermoelectric performance. The essentials for success will continue to be the close collaboration between theory and experiment.

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I2

Large scale simulations with CP2K: investigating electron transfer at a solid/liquid interface

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Electron transfer (ET) reactions play a crucial role in a number of processes of biological and technological importance. Well-known examples include cell respiration, photosynthesis, corrosion, fuel cell catalysis and photovoltaics. The efficiency of these processes can be optimized by tuning the ET properties of electron-donor and –acceptor or the pathway between them. Recently, significant progress has been made in computing the rate of electron transfer from atomistic simulations and desity functional theory. In particular, all parameters in the Marcus expression for the rate of electron transfer – the reaction free energy, the solvent re-organization energy, and the quantum coupling matrix elements – can now be computed from density functional theory, which we will illustrate with applications of biological interest. [1]

Our approach to compute these properties is based on DFT and employs an atomistic description of the full system, i.e. redox active sites and their environment (100s to 1000s of atoms). Furthermore, an extensive sampling of configurations representative of a finite temperature ensemble is required. These two aspects combined make the calculations computationally demanding. However, we will describe how these calculations can be performed efficiently and accurately using the linear scaling Gaussian and Plane Waves scheme as implemented in CP2K/Quickstep. [2,3] Finally, we will present results on the TiO2/acetonitrile solid/liquid interface, which is important in dye sensitized solar cells.

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http://dx.doi.org/10.1016/j.cpc.2004.12.014

I3

Discovery of novel hydrogen storage materials: An atomic scale computational approach

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Practical hydrogen storage for mobile applications requires materials that contain large amounts of hydrogen, have low decomposition temperatures, and fast kinetics for absorption and desorption. Unfortunately, no reversible materials are currently known that possess all of these attributes. We present here results from an effort we have been developing over the past few years directed a predicting novel hydrogen storage materials from a computational first-principles approach. Such an approach requires several key capabilities: (i) Accurate prediction of decomposition thermodynamics, (ii) Prediction of crystal structures for unknown hydrides, and (iii) Prediction of preferred decomposition pathways. We show examples of progress we've made in these three areas: (i) prediction of hydriding enthalpies and free energies across a wide range of hydride materials, (ii) prediction of crystal structures for multivalent alanates and borohydrides, [such as Ca(AlH4)2 and Ca(BH4)2], and (iii) predicted decomposition pathways for Li4BN3H10 and destabilized systems based on combinations of LiBH4, Ca(BH4)2 and metal hydrides. These capabilites have led to the prediction of several novel high-density hydrogen storage materials and reactions.

I4

Hybrid functionals applied to extended systems

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Hybrid functionals, i.e. functionals that admix a fraction of non-local fock exchange to a local or semi-local density functional, yield more accurate formation energies for molecules than conventional density functionals using the generalized gradient approximation (GGA). Recent studies suggest that these improvements might carry over to extended systems, but only few calculations have yet been reported. Three hybrid functionals, PBE0 (Perdew-Burke-Ernzerhof), HSE03 (Heyd-Scuseria-Ernzerhof), and B3LYP are currently implemented in the Vienna ab initio simulation Package (VASP), within the plane wave projector augmented wave (PAW) formalism [1,2].

We present a rigorous benchmark of our implementation by performing geometry optimizations and calculations of the atomization energies of the G2-1 quantum chemical test set (55 molecules). Excellent agreement with Gaussian03 calculations is achieved, and the agreement with experiment is indeed improved compared to conventional semi-local density functionals.

For extended systems, we have evaluated the structural (lattice constants and bulk moduli) and thermochemical (atomization energies and heats of formation) properties of 20 bulk materials including insulators, semiconductors and metals [2,3]. The PBE0 and HSE03 description of the lattice constants and bulk moduli shows a substantial improvement over conventional semi-local density functionals. PBE0 and HSE03 atomization energies and heats of formation agree well with experiment, except for *d*-metal systems. The B3LYP description of the structural properties is comparable to the performance of a conventional GGA density functional (PBE).

B3LYP atomization energies are drastically worse than those obtained with the PBE0 and HSE03 functionals. The latter can be traced back to the lack of a proper description of 'free electron like' systems with itinerant character (metals, small gap semiconductors).

Finally we report on hybrid functional (HSE03) calculations of the chemisorption of CO on Pt(111), Rh(111) and Cu(111) surfaces. In all three cases, GGA functionals predict the wrong site preference (hollow instead of top). Unfortunately the hybrid functionals hardly improve the situation, and in addition seriously overestimate the adsorption energies.

Generally, one may conclude that hybrid functionals improve the overall description of semiconductors and insulators, but are not applicable yet to metallic systems.

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I5

Density functional calculations on structural materials for nuclear energy and functional materials for photovoltaic energy

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Ab initio DFT calculations are carried out in order to predict the evolution of structural materials under aggressive working conditions such as corrosion and irradiation, as well as to predict and investigate the properties of functional materials for photovoltaic energy.
Structural metallic materials used in nuclear facilities are submitted to irradiation which induce the creation of large amounts of point defects. These defects interact with each other as well as with the different elements constituting the alloys, which leads to modifications of the microstructure and the mechanical properties. VASP has been used to determine the properties of point defect clusters and also those of extended defects such as dislocations. The resulting quantities, such as interaction energies, migration energies, etc, are used in larger scale simulation methods in order to build predictive tools.
For photovoltaic energy applications, ab initio calculations are used in order to search for new semiconductors and possible element substitutions in existing ones in order to improve their efficiency.

I6

Quantum Monte Carlo - electron correlation from random numbers

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Fixed-node diffusion quantum Monte Carlo (DMC) is the most accurate method known for calculating the energies of large many-particle quantum systems. The key element of the method is the development of accurate trial many-body wave functions which control the statistical efficiency of the calculations and the accuracy obtained. Accurate wave functions can be obtained by building correlation effects on top of mean field descriptions such as density functional theory. The wave functions can be improved by introducing multi-determinants, pairing functions, and backflow transformations. The calculations are expensive, but the method scales well with systems size and calculations on 1000 particles are possible. Some recent applications of the DMC method to atoms, molecules and solids will be presented.

I7

Design of water gas shift catalysts for H_2 production in membrane reactors

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The conversion of easily stored and handled fossil or biofuels' liquids to hydrogen in compact fuel processing systems typically involves either catalytic steam reforming, autothermal reforming or catalytic partial oxidation to produce a H_2 + CO mixture known as reformate. Reformate is reacted with steam in the water gas shift (WGS) reaction, $H_2O + CO \Leftrightarrow H_2 + CO_2$ ($\Delta G = - 41$ kJ/mole), to yield a $2H_2 + CO_2$ mixture. As hydrogen production is favored by low temperatures there is a need for high volumetric activity, low temperature WGS

catalysts. One of the most active, robust and non-pyrophoric catalyst families is the Pt-alloy/$Ce_{[1-(x+y)]}Zr_xDp_yO_2$. This catalytic system was developed through coordinated atomistic modeling, syntheses, structural characterization, kinetic performance tests, and micro-kinetic analyses. VASP density functional simulations were used to predict the impact transition metal dopants in the nano-crystallites had on the surface chemistry of cubic ceria-zirconia. The VASP results suggested that the undoped catalyst WGS activity would be limited by the strong binding of CO intermediates, blocking the reoxidation of the reduced oxide by water. These predictions were confirmed by in-situ cylindrical internal reflection-Fourier transform infrared spectroscopy and by micro-kinetic analyses of the micro-reactor results. VASP predicted that dopants like Mo or Ta dopant would increase the oxide surface affinity for water and thus increase the turnover rate of the catalyst. The efficacy of Mo-doped ceria-zirconia compositions were confirmed in replicated catalyst synthesis-reactor studies. The Mo-doped catalyst supports exhibited lower apparent activation energies compared to the undoped material. This work has been extended to guide an advanced water gas shift membrane reactor project for the large scale production of high purity hydrogen from coal.

I8

Controlling the conductivity of wide-band-gap semiconductors (nitrides and oxides)

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The ability to control *n*-type and *p*-type conductivity is essential for design and fabrication of electronic and optoelectronic devices. Such conductivity control has traditionally been very difficult in wide-band-gap semiconductors, and native point defects have often been invoked to explain these problems. Using examples from our recent work on GaN and ZnO, I will show how state-of-the-art first-principles calculations based on density-functional theory (DFT) can be used to elucidate these issues. We have developed an approach (based on the "LDA+*U*" method) for overcoming the DFT band-gap problem, allowing us to more accurately compare and predict defect levels.

Zinc oxide and other metal oxides have numerous device applications, but progress is still hampered by the fact that these oxides are typically unintentionally *n*-type, the cause of which has been widely debated. Our investigations reveal that the prevailing *n*-type conductivity can *not* be attributed to native defects [1,2]; it must thus be caused by impurities that are unintentionally incorporated. I will show that hydrogen is an excellent candidate for such an impurity. While hydrogen in other semiconductors is *amphoteric*, always assuming a charge state that *counteracts* the prevailing doping, hydrogen in ZnO behaves exclusively as a donor, and strongly *dopes* the material [3,4]. We find that substitutional hydrogen (i.e., hydrogen on an oxygen site) is consistent with all experimental observations of unintentional *n*-type doping: it acts as a shallow donor, it is stable up to 500-600°C, and it exhibits the same dependence on partial pressure as oxygen vacancies. In addition, the substitutional hydrogen configuration displays an unexpected type of chemical bonding, in which hydrogen forms a *multicenter bond* with the surrounding metal atoms. I will also discuss results for other oxides, comparisons with experiment, and prospects for *p*-type doping.

This work is performed in collaboration with A. Janotti, D. Segev, A. Singh, and S. Limpijumnong, and is supported in part by NSF.

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I9

First-principles computation as a guide to the design of new hydrogen storage materials

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The potential of emerging technologies such as fuel cells (FCs) and photovoltaics for environmentally-benign power generation has sparked renewed interest in the development of novel materials for high density energy storage. For mobile applications such as in the transportation sector, the demands placed upon energy storage media are especially stringent, as the candidates for replacing fossil-fuel-powered internal combustion engines (ICEs) --- proton exchange membrane FCs and hydrogen-powered ICEs --- utilize hydrogen as a fuel. Although hydrogen has about three times the energy density of gasoline by weight, its volumetric energy density (even when pressurized to 700 bar) is roughly six times less than that of gasoline. Consequently, the efficient storage of hydrogen has been identified as one of the key scientific obstacles to realizing a transition to H2-powered vehicles. This talk will present an overview of recent first-principles computational efforts at Ford aimed at developing new materials for reversible, solid state hydrogen storage. A tight coupling between computation and experiments has greatly accelerated our materials discovery efforts: for example, computation has been used both to complement experimental materials characterization and to guide experiments towards materials with promising thermodynamic properties. While appropriate thermodynamics are a necessary condition for any viable H2-storage material, the (generally slow) kinetics of the storage reaction must also be considered. Thus, a mechanism for identifying and moderating kinetic barriers from first principles would be of great value.

I10

Evolutionary crystal structure prediction: a novel approach to materials design

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Crystal structure prediction (i.e. finding the stable crystal structure, at given *P-T* conditions, given only the chemical composition) is a central problem in condensed matter physics and materials design. However, this problem was believed to be of extreme complexity [1] and numerous attempts to solve it have generally been unsuccessful, as evidenced by the results of "blind tests" of crystal structure prediction [2].

To solve this problem, one needs to find the global minimum on the free energy surface. The main obstacles are the multidimensionality of the problem and the rugged energy landscape characterized by an astronomic number of local minima. In 2004-2006, we developed a new approach merging *ab initio* total energy calculations and a specifically developed evolutionary algorithm USPEX [3-5]. About 70 tests demonstrated the efficiency and reliability of this algorithm, which for systems containing up to ~30 atoms in the unit cell shows a practically perfect success rate and has been successful in tests on systems containing up to 128 atoms/cell. The algorithm has been described exhaustively in [4,5]; its main ingredients are:

1. Representation of crystal structures: lattice vectors and atomic fractional coordinates. The use of fractional coordinates (which are scale-invariant) enables to cross-breed structures with different lattice types.
2. Random initialization of the first generation of structures.
3. Fitness function: *ab initio* total energy, enthalpy or free energy. All produced structures are locally optimized and then ranked. The use of local optimization is crucial for the success of the algorithm.
4. Selection: a given percentage of the best structures in each generation produce the next generation, through variation operators.
5. Variation operators: heredity (daughter structures are obtained by fitting together slices of the parents), lattice mutation (random distortion of the cell) and permutation (swaps of pairs of atoms). A newly generated structure is discarded if it has too short interatomic distances or too small unit cell lengths or pathological (<<60˚ or >>120˚) unit cell angles.
6. Survival of the fittest: the best structures (one or several) of the previous generation are carried over into the next generation.

We will demonstrate results of several applications of the USPEX method, including the discovery and prediction of several new interesting materials. Further developments of the method and possible collaborations with the industry will be outlined.

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I 11

Computational material science aided design of glass ceramics and crystal properties

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Today's high-tech materials have in many cases highly specialized properties and designed functionalities. Materials parameters like high temperature stability, high stiffness or certain optical properties have to be optimized and in many cases an adaptation to given processes is necessary. Many materials are compounds or layered structures. Thus surface and interface properties need to be considered as well. At the same time to some extend only a few atomic layers determine sometimes the properties of the material, well known in semiconductor industries and other thin film technologies. Therefore a detailed understanding of the materials properties at the atomic scale becomes more and more important. In addition many high-tech materials have to be of high purity or selective dopant concentrations have to be adjust to fulfil the desired functionality. Modern materials development access successfully computational material science for that purpose. Improved software tools and continuously growing computational power allow to predict macroscopic properties of materials based on microscopic/atomic ab intio simulation approaches.

At Schott specialty materials are produced for a variety of applications, in particular glasses and glass ceramics. In a glass ceramic all the above mentioned difficulties for materials development arise. The properties of a glass ceramic are determined by the interplay of crystalline phases embedded in an amorphous glass matrix. For a materials development the understanding of crystal structures and their properties, surfaces and interface phenomenons and amorphous systems are necessary likewise. Each of them by itself already a challenging problem. Many crystal phases that are grown within the glass matrix do not exist as single crystals or are difficult to grow in a reasonable amount for experimental investigations. The only way to obtain these properties of the crystalline phases is by ‘ab initio’ simulations in the computer.

In this presentation results of Density Functional Theory (DFT) calculations of various crystal structures, mainly oxides are discussed. The focus is on the thermo-mechanical and optical properties. We present elastic properties and the anisotropic Youngs’s modulus of spinel structures, pyrosilicates and further oxides like Rutil. Their influence on the stiffness of a resulting glass ceramic is discussed. The thermal expansion of glass ceramics is an important feature and is strongly dependant on the coefficient of thermal expansion (CTE) of the crystalline phases. For selective oxides the calculation of the CTE in the harmonic approximation is presented and a comparison with experiments is given.

Optical devices for microlithography use CaF_2 crystals as lens material. The optical properties and the influence of certain impurities in CaF_2 are crucial for the performance of such devices. ‘Ab initio’ simulation helps here to estimate the formation of defects and color centers. LDA-sx calculations for the optical properties of CaF_2 are present as well as DFT simulation results for impurities and defects.

I12

Ab-initio calculations of free-energy reaction barriers

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Theoretical description of chemical reactions was limited to the 'static' approach until recently.In this approach, reaction parameters such as the free-energy barrier and the rate constant are deduced on the basis of the local topology of potential energy surface close to minima and transition states. Such an approach has, however, serious limitations. The growing computational power allows now to use advanced simulation techniques to determine entropic effects for medium-sized systems at ab initio level accurately. In my contribution I will present free-energy simulation techniques based on the molecular dynamics, recently implementend into the periodic DFT code VASP. The advantages and limitations connected with the practical use of these techniques will be discussed. The methodology will be demonstrated on example of chemical reaction - proton exchange

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between small hydrocarbons and acidic zeolite. In this reaction, the experimentally observed regioselectivity between different functional groups of isobutane cannot be explained on the basis of a potential-energy analysis alone. I will show that accurate treatment of the entropic effect is necessary to reproduce experimental data.

I13

Gearing for complexity: Recent developments around linear-scaling materials calculations and the SIESTA program

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The SIESTA method and program [1] originated from the methodological developments that gave rise to the first linear-scaling density-functional-theory (DFT) method [2]. Linear-scaling was considered (and is) the way to face ever larger system sizes, since the computational expense (in both time and memory) scales like the number of atoms in the system, unlike more established approaches, in which the scaling is quadratic or cubic (by increasing the computer power by an order of magnitude, the sizes attainable merely double). Several linear-scaling methods and programs of different kinds have been developed since then, suited for different needs and different computer architectures: not only the size-scaling matters, but also its pre-factor, on one hand, and the scaling with parallelisation for high-performance computers, on the other. SIESTA has proven to be a flexible and efficient method for a large variety of systems, on extremely varied computer platforms [3], with both academic and industrial users, working on nano, bio, geo, materials, chemical or physical sciences. Based on the SIESTA core, more recent developments have gone beyond electronic ground-state properties, most notably into ballistic electronic transport (exploiting the locality of Siesta's basis sets) and time-dependent DFT. The latter will be illustrated with an account of recent developments and results in the study of the effects of electronic heating in radiation-damage processes in materials, of interest to the semiconductor and nuclear industries. Other developments have faced the problems posed by the increasing complexity characteristic of large system sizes: multiple minima, complex energy landscapes, long time scales, all of them of relevance to bio/pharmaceutical industries.

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I14

Industrial supported catalysts in working states: DFT insights beyond all expectations

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Ever stronger environmental concerns prompt the research in the area of heterogeneous catalysis to play an ever more crucial role to produce ever cleaner fuel from the refining of petroleum effluents. The catalytic active phase is often used in a dispersed state over a well defined oxide materials.

This paper puts forward recent progresses brought by periodic density functional theory (DFT) calculations in the area of relevant industrial supported catalysts. We focus on two important supports used in the refining industry: anatase-TiO_2 and γ-alumina. According to the various reaction conditions, the presence of H_2O, H_2 and H_2S, may change the working surface states of the support. Especially, it is crucial to know and control the hydroxlation state as a function of temperature and partial pressure of reactants (H_2O, H_2, H_2S) [1]. A fruitful comparison with available experimental data on the spectroscopic characterization of support's surfaces will be given.

The support effects on the catalytic active phases are presented for the Co promoted MoS_2 particles, used in hydrotreating catalysts [2], and Pd particles, used in hydrogenation catalysts [3,4]. It is shown how the wetting property and equilibrium morphology of the active phase depend on the support. A discussion on the impact for catalytic activities will be provided.

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I15

Catalytic oxidation at surfaces: Insight from first-principles statistical mechanics

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To accomplish a first-principles modeling of heterogeneous catalysis that allows for a quantitative description of the catalytic activity over a wide range of relevant environmental conditions (e.g. elevated temperatures and ambient pressures) poses an enormous challenge. Detailed insight into the elementary processes taking place on a microscopic level can nowadays often be obtained by employing *ab initio* electronic structure theory calculations. The statistical interplay between these processes, however, which is decisive for the functionality of a material only evolves in the meso- to macroscopic regime.

Here we apply a multiscale modeling approach to achieve a predictive modeling of macroscopic material properties on the basis of a microscopic understanding. Within this approach we use density-functional theory to accurately describe the elementary processes in the microscopic regime and we then suitable combine these results with concepts from thermodynamacs and statistical mechanics to obtain an appropriate linking to the meso- and macroscopic regime.

Employing this approach to the field of heterogeneous catalysis we investigate the CO oxidation over the Pd(100) surface as an example, particularly focusing on the relevance of the surrounding gas phase as well as the reaction kinetics on the structure and composition of the catalyst surface.

I16

A systematic computational study of electronic effects on hydrogen sensitivity of olefin polymerisation catalysts

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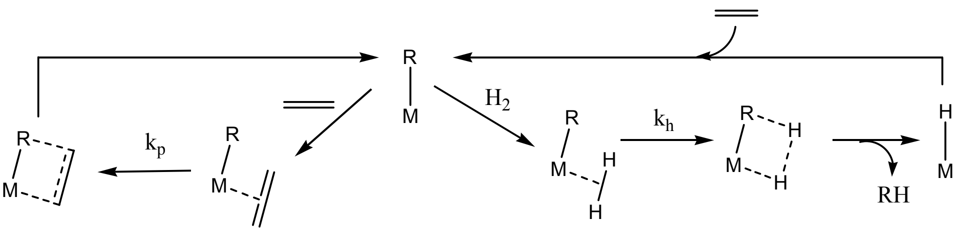
One of the important product parameters of polyolefins is their molecular weight (distribution). A common way to control this parameter is to add molecular hydrogen during the polymerization, which then acts as a chain transfer agent.

The factors governing the hydrogen sensitivity of olefin polymerization catalysts are poorly understood and have attracted little attention from computational chemists. To explore the electronic factors determining hydrogen sensitivity we performed density functional calculations on a wide range of simple model systems including some metallocenes and a few basic models of heterogeneous catalysts. As a quantitative measure for hydrogen sensitivity we used the ratio of the rate constant for chain transfer to hydrogen towards the rate constant for ethene insertion, k_h/k_p (see the scheme below). As a measure of electrophilicity we used the complexation energy to the probe molecule ammonia.



For isolated species in the gas phase, complexation energies appear to dominate the chemistry. Ethene complexes more strongly than hydrogen and with increasing electrophilicity of the metal centre this difference grows; the hydrogen sensitivity decreases accordingly. Although many factors (like catalyst dormancy and deactivation issues) complicate the comparison with experiment, this result seems to agree both in broad terms with the experimental lower hydrogen sensitivity of heterogeneous catalysts, and more specifically with the increased hydrogen sensitivity of highly alkylated or fused metallocenes. The opposite conclusion reached by Blom (see Blom et al., *Macromol. Chem. Phys.* **2002**, *203*, 381-387) is due to the use of a very different measure of electrophilicity, rather than to different experimental data.

I17

Accurate band gaps and dielectric properties from one electron theories

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For semiconductor modeling, a major shortcoming of density functional theory is that the predicted band gaps are usually significantly too small. It is generally argued that this shortcoming is related to the fact that density functional theory is a groundstate theory, and as such, it is not allowed to associate the one electron energies with the energy of quasi particles. Although this fundamental objection is certainly true, the modeling of the position of donor and acceptor levels in semiconductors faces serious limitations with present density functionals.

Several cures to this problem have been suggested. A particular attractive and fairly simple one is the inclusion of a small fraction of the non-local exchange in the Hamiltonian (hybrid functionals). This approach leads to sensible band gaps for most semiconductors, but fails for ionic solids. A more reliable approach is via many-electron Greens function techniques, which have made tremendous advances in recent years. Here GW calculations in various flavors are presented for small gap and large gap systems, comprising typical semiconductors (Si, SiC, GaAs, GaN, ZnO, ZnS, CdS and AlP), small gap semiconductors (PbS, PbSe, PbTe), insulators (C, BN, MgO, LiF) and noble gas solids (Ar, Ne). The general finding is that single shot G0W0 calculations based on wavefunctions obtained by conventional density functional theory yield too small band gaps, whereas G0W0 calculations following hybrid functional calculations tend to overestimate the band gaps by roughly the same amount. This is at first sight astonishing, since the hybrid functionals yield very good band gaps themselves. The contradiction is resolved showing that the inclusion of the attractive electron-hole interactions (excitonic effects) are required to obtain good static and dynamic dielectric functions using hybrid functionals. The corrections are usually incorporated in GW using "vertex corrections", and in fact inclusion of these vertex corrections rectifies the predicted band gaps.

Finally, in order to remove the dependency on the initial wavefunctions, selfconsistent GW calculations are presented, again including an approximate treatment of vertex corrections. The results are in excellent agreement with experiment, with a few percent deviation for all considered materials. We conclude that predictive band gap engineering is now possible with the theoretical description approaching experimental accuracy.

I18

Theoretical and experimental studies of MoS_2, CoMoS and NiMoS hydrotreating catalysts

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In this talk I will give an overview of our recent theoretical and experimental studies of hydrodesulphurization (HDS) catalysts. We have performed density functional theory (DFT) calculations of the HDS reaction of thiophene over different MoS_2 edge structures, which are predominantly present under HDS conditions. We find that the hydrogenation pathway, where thiophene is hydrogenated before the sulphur-carbon bond is broken, preferentially occurs on different edge structures than the direct desulphurization pathway, where the sulphur-carbon bond is broken after only one hydrogenation.

It is well established that the promoters Co and Ni increase the activity of MoS_2 and WS_2 catalysts, and the commercial HDS catalysts are typically CoMoS and NiMoS-based. We have studied the structure and morphology of CoMoS and NiMoS particles using DFT and scanning tunneling miscroscopy (STM). By combining atom-resolved STM images of CoMoS and NiMoS particles supported on a gold surfaces with DFT calculations, we obtain information about the location of the promoter atoms and about the induced change in stability of the Mo edge $(10\bar{1}0)$ and the S edge $(\bar{1}010)$ as well as higher-indexed edges. We also discuss recent results on promoted MoS_2- and WS_2-based nanostructures supported on graphite, which we have obtained using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). We can relate the structural changes induced by the promoter atoms Co and Ni to their enhancement of the HDS reaction, and in this way gain further insight into their action on an atomic scale.

I19

First principles calculations for ceramic science and engineering

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Ceramic materials are widely used in modern technology. They are used for energy conversion devices such as fuel cells and lithium batteries, photoemission devices for information technology, catalysis for environmental issues just to mention a few examples. Compared to metallic alloys such as aluminum and copper alloys forming simple close-packed structures, ceramic crystals often form more complicated open structures having multiple atomic sites with different local environments. They are therefore more difficult to be examined by theoretical methods. Moreover, less experimental information is available for ceramic crystals as compared to the common metals. In the authors' group, efforts to combine experimental works and first principles calculations in order to reveal fundamental structure-property relationships in ceramics materials have been made. Some recent topics will be covered in our talk which includes some of the followings:

1) Stability and structures of complex oxides

Free energy of compounds and their temperature/pressure dependence are the most valuable information in materials science and engineering. Phonon contribution can be computed accurately by the modern first principles tools. Solid state phase transformations of perovskite compounds [1], ZrO_2 [2] and other oxides have been examined using this method. Configurational contribution can be evaluated by combining a large set of first principles calculations with cluster expansion and Monte Carlo simulations. Employing these methods, thermodynamic stability as well as structures of ceramic alloys and compounds can be precisely computed. Typical examples done in our group are the MgO-ZnO phase diagram [3], the order-disorder transition of AB_2O_4 spinels [4,5], non-stoichiometric compounds of rutile oxides [6].

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2) XANES and ELNES for ceramic science

Both XANES (x-ray absorption near edge structures) and ELNES (electron energy loss near edge structures) are important tools in ceramic science offering information on local environment of selected elements not only in crystals but also in amorphous materials. Recent technological progress enables measurements of XANES of ppm-level dopants using modern synchrotron facilities[7]. Combined with transmission electron microscopy, ELNES can be used to analyze the local structures with sub-nanometer spatial resolution. First principles methods to reproduce and interpret the spectra have been established just recently. When a core-hole is adequately taken into account, most of *K*-edge spectra can be well reproduced using a modern band-structure method within one-electron approximation [8,9]. However, multi-electron calculations are mandatory to reproduce $L_{2,3}$-edge spectra of 3*d* transition-metal elements because of strong correlations among 3d electrons and a 2p hole. We have developed a novel DFT-CI method applied for model clusters to obtain the theoretical $L_{2,3}$-edge spectra in a first principles manner[10], which is successful in reproducing experimental XANES/ELNES systematically.

I20

DFT analysis of bulk and selected surfaces of Hägg Fe-Carbide (Fe_5C_2)

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Iron-based catalysts are widely used in Fischer-Tropsch synthesis (FTS) processes for the industrial production of liquid fuels from synthesis gas (CO and H_2). During pre-treatment, and also during FTS, Fe-based catalysts proceed through several phase transformations. In particular, during the activation process hematite (α-Fe_2O_3) first transforms to magnetite (Fe_3O_4), followed by the formation of iron carbide phases upon exposure to synthesis gas, including ε-Fe_2C, ε'-$Fe_{2.2}C$, χ-$Fe_{2.5}C$ and θ-Fe_3C. The predominant phases present during FTS is Hägg Fe-carbide (χ-$Fe_{2.5}C$, also referred to as Fe_5C_2) and cementite (θ-Fe_3C), of which Hägg Fe-carbide is generally accepted to constitutes the active phase for FTS.

In the present paper a DFT analysis of both the bulk and selected surfaces of Hägg Fe-carbide is presented. A spin-polarized plane-wave quantum mechanical methodology was followed to analyze bulk properties of Fe_5C_2, including lattice parameters, bulk modulus and magnetic data. These analyses were used to establish the most relevant theoretical parameters, e.g. exchange-correlation functionals, evaluated by comparison with available experimental data for bulk Fe_5C_2. In particular, insight is gained on the formal characterization of the bulk crystal structure as monoclinic (C2/c) or triclinic ($P\bar{1}$), an aspect which is currently under debate from power diffraction XRD studies.

A comprehensive surface analysis of Hägg Fe-carbide was performed by cleaving a series of low Miller index surfaces from the bulk structure. Careful analysis of relative surface energies yielded insight into relative stabilities of the selected surfaces. From this data insight into the composition and structure of relatively stable surfaces could be established, which in turn provided relevant models for analysis of additional surface properties of Hägg Fe-carbide. These theoretical studies provide insight into the surface characteristics of Hägg Fe-carbide, an area for which experimental data is currently lacking.

I21

First-principles computation of the electronic and dynamical properties of solids and nanostructures with ABINIT

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The field of first-principles simulation of materials and nanosytems has seen an amazing development in the past twenty years. Using the density-functional theory and complementary approaches, like many-body perturbation theory, it is now possible to compute both basic quantities, like crystalline lattice parameters, as well as more involved properties like optical or phonon spectra. New and improved concepts, approximations, algorithms, and numerical techniques appear every year.

In order to cope with the increasing software complexity, it became apparent over a decade ago that software engineering techniques and a group collaborative effort would be major ingredients of a successful first-principles project. The open source ABINIT project was launched in 1997; as of now, there are more than 1000 members in the main mailing list, over 40 active contributors, and more than 200 articles have been published in international journals using ABINIT.

I will present the overall structure of the package, and its main and most exciting capabilities. Specific recent examples of projects will demonstrate some of the full palette of features in ABINIT. These projects are often carried out in close collaboration with experimentalists, and ABINIT is also used by or for a number of industrial partners.

I22

First principles modelling of electron transport across interfaces

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The dimension of electronic devices is rapidly scaling down, and the ratio between the number of surface and bulk atoms is therefore increasing. This has the consequence that the interfaces between different parts of the device start to have a strong effect on the device performance. The Atomistix Tool Kit (ATK) from Atomistix[1] allows for accurate modelling of the electrical properties of interfaces between metals, oxides and semiconductors, and for instance investigating the effects of defects on the electrical properties of the different interfaces. The calculations are based on a state of art Non-Equilibrium Green's Functions (NEGF) implementation of Density Functional Theory (DFT)[2].

I this talk I will present the background of the NEGF-DFT theory and present results for the electrical properties of transport across Fe-MgO-Fe, Si-SiO2-Si, and organic-metal interfaces. The Fe-MgO-Fe system has recently gained a lot of interest, due to the ability of the MgO layers to function as a spin filter[3]. I will present new calculations for the spin transport in this system, and from the calculations we have gained new insight to the physical mechanisms underlying the spin-filtering effects in the system. I will also discuss calculations for the electrical properties of Si-SiO2-Si, and organic-metal interfaces.

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I23

Calculation of technologically important aspects of magnetism: Anisotropy, critical temperatures and spin dependent transport

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Magnetic materials, i.e. where the moments arising from the electron spins are ordered, have many potential applications of technological relevance. For instance, in recent years a lot of focus has been on spintronics, a future technology where not only the electron's charge but also its spin will be utilized.

In this presentation we will deal with a few of these applications from a microscopic theoretical view. The discussion is based on calculations of the electronic structure often within (spin) density functional methods.

A large magnetic anisotropy, the fact that there are considerable energy differences between different magnetization direction, have considerable importance for e.g. magnetic storage and permanent magnet applications. We will here discuss how to calculate this quantity, which is exemplified by both a bulk system and a layered material, and the calculational accuracy and the method's predictability.

One example of spin dependent transport is the so-called spin transfer torque, the fact that a current through a magnetic layer can rotate its magnetization. We will review its physical origin and present some recent calculations on naturally magnetic layered materials, so-called helical spin density waves.

A crucial quantity for applications of the various spectacular magnetic effects is the Curie temperature, the temperature above which the magnetic order disappear. Many systems are limited by low Curie temperatures. A route to calculations of this quantity is described, and with the help of a few calculations we try to generalize what is needed to achieve significant magnetic ordering temperatures.

I24

Multiscale modeling of nanophase materials and devices for magnetic data storage

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Magnetic data storage has become the mainstream technology during past three decades for mass storage solutions in recording and archiving personal, audio, video, and software content data. The continuous demand for ever-higher storage density and faster data transfer prompts to reevaluate basic materials and device physics used so far. In this presentation we provide a brief introduction to basic material and device physics of a prototypical magnetic storage device, and illustrate new modeling challenges which may arise in the future. The latter is done with particular emphasis on nano-phase materials and device physics. We consider L10 FePt as a particular material set to illustrate the multi-scale nature of the modeling problems. First, we focus on a larger scale device physics aspects arising from the response of multiple grains with a distribution of easy axis orientation [1]. Then we consider a single grain of L10 FePt as a vivid example of magnetic 3d-5d(4d) nano-alloy [2,3]. We discuss examples showing importance of atomic scale finite size effects and correspondingly a need to develop a quantitative model of magnetic interactions. The proposed microscopic model of the magnetic interactions generally applicable for 3d-5d(4d) alloys [2,3] is tested against measurements of the temperature dependent magnetic [2] and switching properties of nano-particulate and granular FePt thin films [1]. We discuss strategy for a multi-scale modeling combining relevant microscopic model of magnetic interactions with statistical modeling/theory [2,3] and micro-magnetic techniques [1]. We illustrate how multi-scale modeling may enable seamless description of both a-thermal and thermal magnetization processes at different length scales. We conclude by highlighting the importance of bridging the physics over length scales spanning many orders of magnitude for modeling future magnetic data storage devices.

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I25

Electronic structure modeling in an engineering context

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From 1994 through 2005 the US Department of Energy developed advanced thermophotovoltaic devices with world's record energy conversion efficiency. I discuss my role as a materials physicist and electronic structure modeler embedded in this engineering development effort, in which I supported device design improvements throughout the project. I then generalize from these and other experiences to discuss the critical interfaces needed between potential electronic structure tool users in engineering organizations in industry and government, and electronic structure tool developers in academia.

I26

The ONETEP program for linear-scaling density functional calculations with plane waves: applications and recent developments

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I will present an overview of the ONETEP (Order-N Electronic Total Energy Package) code [1] for Density Functional Calculations with computational cost that increases linearly with the number of atoms. ONETEP exploits the locality of the single-particle density matrix inherent in non-metallic materials by optimising directly nonorthogonal generalised Wannier functions (NGWFs) expressed in terms of periodic cardinal sine (PSINC) basis functions [2]. The PSINC basis is equivalent to a plane wave basis set, and near-complete basis accuracy can be achieved by improving it systematically via a single parameter. Its properties make it ideal for imposing localisation in real space with linear-scaling cost. ONETEP has been developed as a parallel code [3] able to run on an arbitrary number of processors, allowing plane wave calculations with thousands of atoms to be performed. Recent developments and results of applying the method to nanostructures [4] and biomolecules [5] will be presented.

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I27

Density functional theory and beyond: Opportunities for quantum methods in materials modeling for semiconductor technology

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In the semiconductor industry, use of new materials has been increasing with the advent of nanotechnology. Traditionally, application of *ab initio* techniques have been confined to electronic structure and band gaps of bulk materials which are further used in coarse-grained models such as mesoscopic and continuum models. Density functional theory is the most widely used *ab initio* technique which has been successfully extended to several applications. However, with the critical dimension decreasing and the number of materials increasing, the interactions of these heterogeneous materials and processing are continuing to be difficult. These challenges are due to presence of nanodomains in materials and the increasing role of interfaces in smaller structures. The paper consists of three parts; background of semiconductor processing, specific applications of density functional theory, opportunities for extension of ab initio techniques in nanotechnology.

I28

Computational alloy catalyst design

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Electronic structure calculations based on density functional theory have reached a level of maturity where they can accurately describe complete catalytic reactions on transition metal surfaces. This gives unprecedented insights into heterogeneous catalytic reactions, and it allows pinpointing the origin of catalytic activity of metals in terms of their electronic structure. The use of electronic structure theory as a tool for designing or searching for new heterogeneous catalysts has, however, so-far been extremely limited. The complexity of the design problem arises to a smaller extent from the high computational cost of the electronic structure calculations and to a larger extent from the enormous number of surfaces and geometries that needs to be considered. In some fortunate cases, reactivity trends determined from density functional calculations can be applied to reduce the complexity of the catalyst design procedure.

Results will be presented on the computational design of a new alloy catalyst for the methanation reaction. The method utilizes the underlying reactivity trends for the reaction intermediates, and the applicability of the design procedure for other reactions is suggested through the identification and analysis of a range of new reactivity trends for intermediates. By correlating the reactivity of a range of simple atomic and molecular adsorbates over different transition metal surfaces, we find a simple set of “empiric” rules that can be used as guide lines in a rough computational screening of new catalysts for various reactions. A surprising observation from the trends is that a range of seemingly very different hydrogenation and dehydrogenation reactions can all be described on a simple common footing through simple scaling relations.

I29

Ab initio simulations of hydrogen storage materials at General Motors R&D Center: An overview of light and heavy metal hydride property predictions

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In 2003, the U.S. congress was challenged to a $1.2 billion national commitment to take hydrogen fuel cell vehicles from the laboratory to the showroom. The intervening years have been witness to an impressive growth in hydrogen storage materials research as motivated by U.S. Department of Energy requirements for vehicular hydrogen storage requirements. The developments and application of first principles simulation methodologies continue to play an increasing important role in hydrogen storage material property prediction in both academia and industry.

This lecture will provide an overview of hydrogen storage material property prediction at General Motors R&D Center using first principles methodologies.We will begin by reviewing a series of recent thermodynamic, vibrational and mechanical property predictions of selected solid state hydrides and how some of these predictions are being used to support experiments. We will first focus on binary, tertiary and quaternary "light metal" hydrides, and then examine ab initio results from simulations of selected metallich hydrides. The importance of continual benchmarking of theoretical predictions with physical experiments will be emphasized. Finally, a perspective on future applications of ab initio methodologies to hydride structure and property prediction will be offered.

I30

Band structure meets many-body theory: the LDA+DMFT method

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The calculation of electronic properties of materials is an important task of solid state theory, albeit particularly difficult if electronic correlations are strong, as for example in transition metals, their oxides and in f-electron systems. A consequence of strong correlation is the emergence of "colossal" responses to small changes of external parameters such as pressure, temperature, or magnetic fields, which make these materials interesting for technical applications.

Encouraged by the success of dynamical mean field theory (DMFT) in dealing with strongly correlated model Hamiltonians, physicists from the bandstructure and the many-body community have recently joined forces and developed a combined LDA+DMFT method for the (ab initio) calculation of materials with strong electronic correlations. Depending on the strength of electronic correlations, this new approach yields a weakly correlated metal as in LDA, a strongly correlated metal, or a Mott insulator.

In my talk, I will give an introduction to the LDA+DMFT method and, as an example for its application, present results for manganites, showing the "colossal" magnetoresistance.

I31

Unraveling the structure of the BN/Rh(111) nanomesh with ab-initio calculations

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The search for nanostructured new materials, in particular, when formed by self-assembly, is of great importance and thus a very active field of research. Recently, such a self-assemling structure was detected when borazine is thermally decomposed on a Rh(111)surface[?]. Boron nitride forms a highly regular h-BN/Rh(111) nanomesh with a periodicity of about 3.2 nanometers. A hexagonal unit cell consisting of a 12×12 Rh substrate, on which a 13×13 h-BN forms, was deduced from LEED patterns, surface x-ray diffraction, and STM pictures. A periodic hole structure of about 2 nm diameter was observed within this unit cell. Based on the STM images and on ultraviolet photo-electron spectroscopy (UPS) data, which showed a splitting of the BN-σ bands, an atomic model was suggested which consists of two (partially) incomplete) boron nitride (BN) layers.

Here, using the ab-initio methodology as implemented in the Wien2k package, we invalidate the former model and propose an alternative understanding of the h-BN/Rh(111) nanomesh. The new model provides an understanding of the h-BN interaction with Rh surfaces, which extends to a wider class of systems like BN/Ru(001), BN/Pt(111) or C/Ir(111). The proposed structure consists of only a single layer of h-BN, which however, is highly corrugated. The theoretically predicted corrugation is consistent with both, the observed splitting of the BN-bands as well as with the experimental STM images.

I32

A mechanistic study on hydrogen spillover onto carbon-based materials

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Recent studies on hydrogen storage have shown significant storage capacities in several carbon-based materials, including graphite nanofibers, carbon nanotubes and some metal-organic framework compounds. The unusually large hydrogen uptake in these materials, reportedly up to 5.5wt.%, was attributed to the so-called "hydrogen spillover" phenomena, in which dihydrogen molecules first undergo dissociative chemisorption upon interacting with platinum catalysts and subsequently hydrogen atoms are spilled over onto the carbon substrates via an adsorption process. To achieve the reported high storage capacity, it is essential that the adsorbed hydrogen atoms be nearly free to move to other adsorption sites far from where the catalysts reside. Using density functional theory under the generalized gradient approximation, we systematically investigated the possible hydrogen spillover mechanisms. We first calculated the sequential H desorption energies in a selected Pt cluster and identified the threshold energy required for H atoms to desorb from the catalyst. Subsequently, we evaluated the thermochemical energies and barriers of "spillover" process at the catalyst-substrate interface. The substrates selected in the present study include MoO_3 solid, which is a well-known hydrogen reservoir upon hydrogen spillover, and several carbon-based materials. Detailed H-diffusion pathways in the lattices were examined. We will show that hydrogen spillover at ambient conditions in MoO_3 is energetically feasible. However, spillover in carbon-based materials was found to be difficult to proceed at ambient conditions due to the high energy barriers for H diffusion. The implications to hydrogen storage will be discussed.

I33

Materials design from *ab initio* calculations: Nanolayered MAX phases

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The advancement in new materials processing and fabrication techniques has made it possible to better control the atomistic level of structures in a way, which was not feasible only a decade ago. If one can couple this atomic control with a good understanding of the relationship between structure and properties, this will in the future lead to a significant contribution to the synthesizing of tailor-made materials. In this paper we have focused on, the structurally related nanolayered ternary compounds $M_{N+1}AX_N$, (MAX) where N = 1, 2 or 3, M is an early transition metal, A is an A-group (mostly IIIA and IVA) element, and X is either C and/or N, which has attracted increasing interest owing to their unique properties. These ternary carbides and nitrides combine unusual properties of both metals and ceramics. Like metals, they are good thermal and electrical conductors with electrical and thermal conductivities ranging from 0.5 to $14\times10^6\ \Omega^{-1}m^{-1}$, and from 10 to 40 W/m·K, respectively. They are relatively soft with Vickers hardness of about 2-5 GPa. Like ceramics, they are elastically stiff, some of them like Ti_3SiC_2, Ti_3AlC_2 and Ti_4AlN_3 also exhibit excellent high temperature mechanical properties. They are resistant to thermal shock and unusually damage tolerant, and exhibit excellent corrosion resistance. Above all, unlike conventional carbides or nitrides, they can be machined by conventional tools without lubricant, which is of great technological importance for the application of the $M_{N+1}AX_N$ phases. In present talk, the general relations between the electronic structure and materials properties of MAX phases have been elaborated based on *ab initio* calculations.

I34

VisualTAPAS: an example of DFT-assisted understanding and simulation of anisotropic etching

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VisualTAPAS is a self-contained, user-friendly, Graphical User Interface (GUI) based simulator of wet etching and Deep Reactive Ion Etching (DRIE) with multi-masking capabilities, built upon an octree representation of the silicon substrate (www.fyslab.hut.fi/~mag/VisualTAPAS/Home.html). The program allows the use of a wide range of Kinetic Monte Carlo (KMC) and Cellular Automata (CA) time-evolution algorithms, including a fast octree search algorithm for the KMC simulations. 'VisualTAPAS' stands for 'Visual Three-dimensional Anisotropic Processing at All Scales'. The use of the term 'Visual' stresses the interactive visual capabilities of the program.

In this talk, a brief history of the evolution of VisualTAPAS as a research tool will be presented. From the initial efforts, explaining the anisotropy of wet etching as a result of steric hindrance using a combination of Density Functional Theory (DFT) and KMC simulations, to the most recent implementation focusing on the propagation of the etch front for engineering applications by making use of the analytical solution of the Continous Cellular Automaton (CCA) method. In between, a recent example of DFT-assisted understanding of the effects of metal impurities on the surface morphology of the etched surfaces will be presented.

The talk tries to bridge togetheer three complementary simulation tools, namely, DFT, KMC and CCA. Our experience with the use of the three methods for the simulation of anisotropic etching shows that DFT is very useful and, many times, an unavoidable approach. Similarly, KMC is the method of choice for understanding the large variety of etched surface morphologies while CCA is an outstanding tool for the simulation of the process at an engineering level.

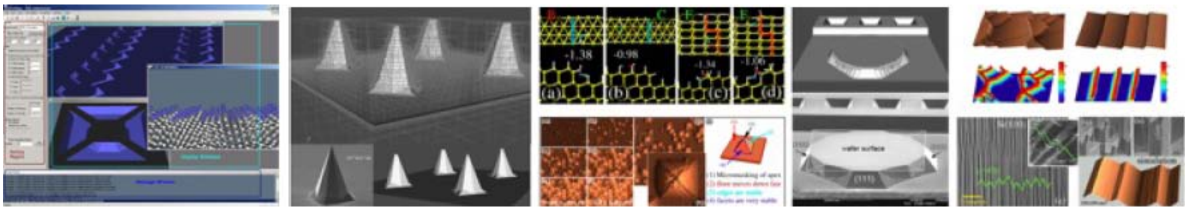

Figure 1: Graphical User Interface and examples of simulations using VisualTAPAS

I35

Practical application of computational materials science in the development of optical materials

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Recent technical innovations in IT-related material along with the popularization of Internet accelerate the development in communication technologies. In particular, the development of flat panel display is remarkable, which is widely used for PC's, cellular telephones and TV's. Consequently, many optical materials have been newly developed as well. For these material developments, the computer technology and its application are the driving force undoubtedly.

In computational materials science, meanwhile, many improvements are introduced to DFT as advanced techniques. As one of these improvements, Time Dependent Density Functional Theory (TDDFT) has been a focus of attention recently, which is also introduced in our materials research. Our TDDFT is quite simple, which is based on the real-space and real-time scheme instead of the conventional basis-expansion techniques. This simplicity meets processing capabilities of recent computers, and it works. Many results are effectively utilized and fed back to the material development.

We have been applying this technique to the practical research of light emitting materials as in polymer light emitting diodes, and dielectric responses in semiconductors. In the presentation, we will introduce our TDDFT and its application together with some examples of our results, and the feed back of the material developments.

P1

Titanium addition as a potential catalyst for high-capacity hydrogen storage medium

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In recent years there has been an increased interest in the characterization of Titanium as catalyst for high-capacity hydrogen storage materials. A first-principle study demonstrated [1] that a single Ti atom coated on single-walled nanotube (SWNT) binds up to four hydrogen

molecules. The bonding was claimed to be an "unusual combination of chemisorption and physisorption".
We report an *ab-initio* study by means of ADF program, which provides a complete insight into the donation/backdonation mechanism characterizing the bond between the Ti atom and the four H_2 molecules, and a full understanding of the catalytic role played by the Ti atom.
In addition, we found that the same amount of adsorbed hydrogen can be stored using benzene support for Ti in place of SWNT, due to the dominant local contribution of the hexagonal carbon ring surrounding the Ti atom. The benzene-Ti-H_2 bonding is discussed on the basis of molecular orbital interaction schemes as provided by ADF.
This result advances our insight into the role of the titanium as a catalysts and suggests new routes to better storage through different combinations of supports and catalysts.

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P2

Elucidation of Au-S bond in a passivated gold cluster through DFT calculations

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Gold clusters are of increasing interest due to a number of its already established as well as new potential application in different fields of nanotechnology. The use of gold nanoparticles can be significantly extended by surface modification, sulfidation being the most popular. The identification of preferred adsorption geometries, bond formation, and binding energies are helpful tools for understanding the properties of these particles.
This study is focused on 38-atom gold cluster passivated by 3-hydroxypropanthiolate linkers. Starting from the re-optimized global minimum structure of bare 38-atom gold cluster [1] and aiming at description the passivated particle, DFT calculations (within the framework of Amsterdam density functional calculation package; ADF 2006.01 [2]) were performed at the level of GGA of Perdew-Wang 1991, with triple-zeta Slater basis sets plus p- and f-polarization functions (TZ2P) for 33 outermost electrons of each gold atom, and considering scalar relativistic effects. Using this methodology, the space around the gold cluster (distance of S of the thiolate from the gold cluster surface in range 2.3- 2.6 Å) was examined to identify the most favourable absorption site for the thiolate linker. As a result, a 3D map was created and low-energy areas corresponding to potential most favourable site for one 3-hydroxypropanthiolate linker on the gold cluster localized. Structures representing these areas were further optimized and consequently analysed using Mulliken population analysis to compare charge distribution over the tested structures, Mayer bond order analysis as well as ELF/ELI bond formation analysis.
The obtained results will be presented in comparison to available studies of other research groups.

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P3

Towards improved photovoltaic conversion using dilute magnetic semiconductors

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Present photovoltaic devices, based on p/n junctions, are limited from first principles to maximal efficiencies of 31% (respectively 40% under full solar concentration) [1]. However, more innovative schemes may overcome the Schockley-Queisser limit since the theoretical maximal efficiency of solar energy conversion is higher than 85% [2]. To date, the only practical realisation of such an innovative scheme has been multi-junction devices, which presently hold the world record efficiency of nearly 41% at significant solar concentration [3]. It has been proposed to make use of the solar spectrum in much the same way as the multi-junction devices does but in a single cell, using impurity induced intermediate levels to create gaps of different sizes. This intermediate level semiconductor (ILSC) concept [4,5] has a maximal efficiency similar to that of multi-junction devices but suffers from prohibitively large non-radiative recombination rates.

We here propose to use a ferromagnetic impurity scheme in order to reduce the non-radiative recombination rates while maintaining the high theoretical maximum efficiency of the ILSC scheme, that is about 46%. Using density functional theory calculations, the electronic and energetic properties of transition metal impurities in a wide range of semiconductors has been analysed. Out of the several hundred compounds studied, only a few fulfil the design criteria we here present. As an example, the wide gap AlP is one of the most promising compounds. It was found that inclusion of significant amounts of Mn in AlP induces band-structures providing conversion efficiences potentially close to the theoretical maximum, with an estimated Curie temperature reaching above 100K.

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P4

Determination of symmetry reduced structures by a soft-phonon analysis in magnetic shape memory alloys

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Ni_2MnGa is a typical example of a Heusler alloy that undergoes a martensitic transformation. In the high-temperature austenitic phase it has a cubic $L2_1$ structure, whereas below 200 K the symmetry is reduced by an orthorhombic distortion. Despite lattice deformations of more than 6% and large strains connected to this change, it is completely reversible. Therefore, Ni_2MnGa serves as a shape memory compound. The fact that Ni_2MnGa additionally orders ferromagnetically below 360 K makes the material particularly attractive for applications as actuators and sensors. Nevertheless, its structural details in the martensitic phase are still a subject of much debate. Several shuffling structures have been observed experimentally. The temperature and magnetic field dependent transformations between these structures need to be understood for an improvement of the magnetic switching (e.g. operation with higher reliability and smaller magnetic fields).

Our tool to identify the stable structures and the low energy transition paths is the calculation of free energy surfaces as function of key reaction coordinates (e.g. c/a-ratio) in DFT. (The GGA xc-functional and the PAW approach implemented in VASP were used in these investigations.) The different variants of the low symmetry orthorhombic structures lead to characteristic minima at this surface. However, the ab initio determination of the experimentally observed shuffling structures is challenging, due to the large phase space of possible atomic positions and the small shuffling formation energies of only a few meV per unit cell. Hence, we used the quasiharmonic approximation in order to compute and analyze phonon spectra. Starting with the symmetric structure of the austenite, the TA_2 phonon dispersion shows a phonon softening along the [110] direction. We were able to extract detailed information about the kind of this lattice instability from the eigenvectors of the unstable phonon modes. By setting up the corresponding modulated harmonics in supercell calculations, we systematically and efficiently identified stable shuffling structures. The resulting structural phases (austenite, martensite, pre-martensite) allow to assign and to interpret the experimental observations.

P5

Phase stability of ZnO from first-principles calculations

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First principles calculations of the phonon dispersion relations and the phonon density of states for ZnO polymorphs: wurzite-, zinc-blende-, rocksalt-structures, and yet experimentally undiscovered CsCl-structure are presented. All the phases were exposed to pressures ranging from 0 to 20 Gpa. The pressure-temperature phase diagram of ZnO was constructed and compared to experimental data, where available.

P6

CO adsorption on metal surfaces: a hybrid density functional study with plane wave basis set

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We present a detailed study of the adsorption of CO on Cu, Rh, and Pt (111) surfaces in top and hollow sites. The study has been performed with a gradient corrected functional (PBE) and PBE0 and HSE03 hybrid Hartree-Fock density functionals within the framework of generalized Kohn-Sham density functional theory using a plane-wave basis set.

As expected, the gradient corrected functional shows the tendency to favor the hollow sites, at variance with experimental findings that give the top site as the most stable adsorption site.

The PBE0 and HSE03 functionals reduce this tendency. Indeed, they predict the correct adsorption site for Cu and Rh but fail for Pt. But even in this case, the hybrid functional destabilizes the hollow site by 50 meV compared to the GGA description. This suggests that, in general, hybrid functionals still do not predict the correct adsorption site.

P7

Transition metal surfaces under oxygen-rich conditions

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The catalytic oxidation activity of transition metal particles in automobile catalysts is influenced by the superficial oxide phases which form under oxygen-rich reaction conditions. Here we study the thermodynamic stability of ultrathin oxide films on low-index surfaces of transition metals by means of first principles atomistic thermodynamics calculations based on density fundtional theory. On Pd(111) a surface oxide with Pd_5O_4 stoichiometry is stable which does not correspond to any bulk structure. At the same time, a variety of metastable structures form. On Pd(100) a PdO(101) trilayer is the stable surface oxide. All structures display two-oxygen and four-oxygen coordinated Pd atoms, the difference lying in the spatial arrangement of these basic structural elements. On rhodium surfaces a Rh oxide trilayer forms that corresponds to a bulk oxide structure. On the Pt(111) surface the most stable superficial oxide phase is found to be a thin layer of α-PtO_2, which appears not to be reactive towards either methane dissociation or carbon monoxide adsorption. On Pt(100) an α-PtO_2 layer is thermodynamically most stable, even if Pt_3O_4 films could grow coherent and stress-free. Bulk Pt_3O_4 is found to be thermodynamically stable in a region around 900 K at atmospheric pressure. The enthalpy barrier for the adsorption of CO molecules on oxygen atoms of this surface is as low as 0.34 eV, and desorption of CO_2 is obsserved to occur without any appreciable energy barrier in molecular dynamics simulations.

P8

Theory-guided design of Ti-based binaries for human implants

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State-of-the-art ab initio methods constitute a solid basis of modern materials science and materials design. The theoretical research is nowadays increasingly combined with meso- and macro-scale approaches as well as advanced experimental techniques in order to address complex multi-scale and finite-temperature phenomena. The applicability of such a interdisciplinary methodology will be exemplified by our development of novel alloys for human implants, particularly the improvement of hip transplants. The progress in this field is severely hampered by a lack of suitable materials which are biocompatible in terms of non-toxicity and mechanical properties. The aim of our research has been therefore to identify metallurgical trends for non-poisonous Ti-based alloys employing quantum-mechanical calculations. Guided by the theoretical calculations of phase stability and elastic properties, selected alloys were actually melted, cast, and heat treated to a homogeneous state. The samples have been experimentally characterized by X-ray methods, electron microscopy including crystallographic and chemical analysis, and mechanically tested using ultrasound measurements. The experimental data obtained in these experiments are in excellent agreement with theoretical predictions.

P9

Interatomic bonding and mechanical properties of trialuminides: An ab-initio study for Al3(Sc,Ti,V)

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On the basis of ab-initio density-functional calculations we have analyzed the character of the interatomic bonding in the intermetallic compounds Al3(Sc,Ti,V) with the D022 and L12 structures. In all structures we found an enhanced charge density along the Al-transition-metal(TM) bonds, a characteristic feature of covalent bonding. The series Al3Sc to Al3V corresponds to the gradually d-band filling and leads to a gradual increase of bond-strength and covalent bond formation. In this series, the tensile anisotropy in the elastic limit have been investigated and a trend towards an increased anisotropy of the elastic constants and Young modulus has been observed. Additionally we performed a study of the response of trialuminides to uniaxial tensile deformation along the [110] direction. This direction is known to be the weak direction of fcc materials under tensile strain, and it is generally accepted that their deformation path is characterized by a "flip strain" instability which restores the fcc structure after full relaxation by interchanging the [110] and [100] directions. The structures of trialuminides have a close structural relationship with face-centered cubic (fcc) metals. We found the L12-type trialuminides response to tension along [110] direction in another way as fcc metals and the "flip strain" mechanism is not active here. Their deformation path is strongly affected by TM--TM interaction acting along the [001] direction. Contrary, the D022-type trialuminides react in the same way as the fcc metals and regenerate with the same "flip strain" mechanism.