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Summary of workshop ‘Theory Meets Industry’—the impact of *ab initio* solid state calculations on industrial materials research

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Abstract

A workshop, ‘Theory Meets Industry’, was held on 12–14 June 2007 in Vienna, Austria, attended by a well balanced number of academic and industrial scientists from America, Europe, and Japan. The focus was on advances in *ab initio* solid state calculations and their practical use in industry. The theoretical papers addressed three dominant themes, namely (i) more accurate total energies and electronic excitations, (ii) more complex systems, and (iii) more diverse and accurate materials properties. Hybrid functionals give some improvements in energies, but encounter difficulties for metallic systems. Quantum Monte Carlo methods are progressing, but no clear breakthrough is on the horizon. Progress in order- N methods is steady, as is the case for efficient methods for exploring complex energy hypersurfaces and large numbers of structural configurations. The industrial applications were dominated by materials issues in energy conversion systems, the quest for hydrogen storage materials, improvements of electronic and optical properties of microelectronic and display materials, and the simulation of reactions on heterogeneous catalysts. The workshop is a clear testimony that *ab initio* computations have become an industrial practice with increasingly recognized impact.

1. Introduction

Organized by the Center for Computational Materials Science and the Erwin-Schrödinger-Institute for Mathematical Physics in Vienna, Austria, a workshop, ‘Theory Meets Industry’, was held between 12 and 14 June 2007. The enthusiastic feedback from the participants is perhaps the best indicator of the timeliness of this event. Nine years earlier, a workshop under the same title had taken place also in Vienna. The difference between these two events is striking. The 2007 workshop was remarkably balanced between participants from academic research organizations and leading industrial laboratories from the USA, Japan, and Europe. There was a clear sense of a common cause, a common language, and the feeling that we are witnessing the beginning of a new era. In the workshop nine years earlier, the contributions were dominated by

academic researchers, while industrial scientists and engineers were mostly listening and formulating their needs. Today, the exchange between these two groups has become symmetric.

Computational materials science and in particular *ab initio* solid state theory have made the transition from an exciting fundamental research field into an industrial activity of recognized value. This transition did not happen at one specific time in one particular laboratory. Rather, it was a process that started many decades ago with industrial laboratories such as those of the IBM corporation in Yorktown Heights, San Jose, and Rüschlikon (Switzerland), Bell Laboratories of then AT&T in Murray Hills, the Palo Alto Research Center of Xerox, the NEC laboratory in Tsukuba (Japan) and others. However, it is probably fair to say that in the 1970s and 1980s the theoretical/computational work in these industrial laboratories had the character of fundamental research, which was not too

different from academic research being pursued at that time in universities. The present workshop revealed a very different aspect. Solid state *ab initio* computations are now used to help solve urgent technological problems of direct engineering impact. This is a qualitative change from the pioneering days several decades ago. In this process European universities and research groups have achieved a globally recognized leadership position in *ab initio* solid state computational methods. In fact, the resulting computer programs are becoming worldwide industry standards. One of the pillars of this development is the Psi-k network, which is fostering the exchange between researchers and disseminating the knowledge and experience by reaching out to students and young scientists.

In this context, the present conference summary tries to place the individual contributions into a common framework so that the current status, the impact, and future trends may become clearer. The workshop was characterized by an impressively high quality in a large variety of fields of science and technology, and a short synopsis cannot do full justice to each contribution, so let me apologize upfront if one or another important point made in the lectures is not mentioned in this article or if my personal views of the field give impressions which deviate too much from the original authors' view and intentions.

If we try to distil the essential theoretical aspects addressed in this workshop, we find three major themes, namely

- more accurate total energies and electronic excitations;
- more complex systems and more configurations (i.e. statistical ensembles);
- more diverse and accurate materials properties.

On the industrial side four major technology sectors were represented, namely

- energy;
- automotive engineering;
- information technologies;
- catalysis and chemical processing.

It is probably not an exaggeration to say that these four industrial sectors are pillars of modern civilization. Other fundamental areas, namely food, health, housing, and civil engineering, depend critically on the four sectors represented in the workshop by industrial participants.

Each of these four industrial sectors faces unique challenges, which are connected with topics within the scope of computational materials science and *ab initio* theory. In the *energy sector* the major driving forces are the replacement of fossil fuels by sustainable and environmentally responsible sources. Nuclear energy is one of the options, and is being thoroughly re-evaluated worldwide. The highest safety standards combined with the need for increased efficiency by new reactor designs require an unprecedented depth of understanding of thermomechanical and chemical properties of materials. Related to the higher efficiency are innovative energy conversion systems such as thermophotovoltaic devices.

The *automotive industry* is in the early stages of a major transition from combustion engines to electric propulsion

powered by fuel cells. One of the decisive factors for the viability of this technology is the development of efficient, safe, and economic materials for hydrogen storage. At the same time, the optimization of the entire vehicle remains a major objective in the highly competitive automotive industry. This includes the replacement of steel by light metal alloys such as those based on aluminum. Related to transportation is the need to meet the increasingly stringent environmental regulations such as reduction of sulfur in diesel fuels and the removal of nitrous oxides from the exhaust of combustion engines. This requires removal of sulfur from the fuels and improved after-treatment using catalytic materials. In all of the above areas, computational approaches based on *ab initio* theory play a key role in the determination of structural, thermodynamic, and chemical properties of existing and newly designed materials.

Information technology faces several very severe challenges. In the area of microprocessors, the continuing miniaturization has driven the size of the features into the nano-scale. In MOS transistors the insulating layer of the gate oxide requires a switch from silicon dioxide to materials with a higher dielectric constant. Materials such as hafnium oxide are emerging as solutions, but they necessitate the introduction of other new materials, in particular the gate metals. All of a sudden the microelectronics industry is confronted with a range of new materials and intermetallic phases, which need to be controlled at an unprecedented level of purity and miniaturization. At the same time, revolutionary new semiconducting devices such as those based on carbon nanotubes are emerging as potential future technologies. All major microelectronics companies are involved in these developments.

Another major area of significant potential for change is display technology. Within a remarkably short period of time, flat-panel displays have replaced cathode ray tubes. However, their low energy efficiency, poor performance in sunlight, and degradation are obvious signs of the shortcomings of present technological solutions. Active devices such as organic (polymeric) light-emitting diodes offer promising industrial perspectives, but there is ample room for a better control of their optoelectronic and chemical properties. Batteries are a third area related to information technology and transportation, where improvements in performance, reliability, and durability are urgently needed. Magnetic recording is another area where progress is driven by innovations on the level of materials.

The *chemical process industry* remains a basis of any industrial activity. The shift from metals to light-weight composite materials is a major need of the transportation industry and an attractive opportunity for the chemical process industry. However, the rising cost of raw materials (oil and gas) combined with environmental concerns are putting enormous pressure on the chemical industry to implement more efficient and cleaner processes. Often, this amounts to the need for better catalysts. Furthermore, the chemical industry is the major supplier of materials for the microelectronics industry and for display technology. Thus, the chemical industry is pushing its products towards high-value-added materials, which in turn requires in-depth understanding of the structural and functional properties of these materials.

With these general remarks as a framework, let us now review the individual contributions including both oral and poster presentations, and place them in an overall context. On the theoretical side, three major themes stand out, namely (i) improvements of the accuracy in calculating total energies, (ii) treatment of more complex systems, namely systems with a larger number of atoms and/or more configurations of a given system (i.e. consideration of entropy and free energy), and (iii) calculation of more materials properties. These three themes reflect the major challenges of present *ab initio* electronic structure calculations.

2. Theoretical and computational developments

2.1. More accurate energies

The main thrust of the work reported by *Marsman* is a thorough assessment of the performance of current functionals. Before this can be done one needs to be very careful in assuring that algorithmic and numerical errors are significantly smaller than any deviations between experiment and theory due to a particular Hamiltonian. To this end, *Marsman* demonstrated the convergence in computed bond distances and atomization energies using two very different approaches, namely the projector augmented plane wave method as implemented in VASP [1] and contracted Gaussian basis sets as employed in the Gaussian program [2]. Furthermore, results obtained with the VASP program tend to be very close to those computed with the all-electron full-potential linearized augmented plane wave (FLAPW) method, which was designed to solve the Kohn–Sham equations as precisely as possible [3]. This remarkable consistency of different algorithmic and numerical approaches solving the same equations gives confidence that we are indeed in a good position to assess the performance of current functionals. The study shows that hybrid functionals such as the PBE0 [4] and HSE03 [5] are an improvement over standard semi-local functionals based on the generalized gradient approximation (GGA) for molecules, insulators and semiconductors, but not for metallic systems. The B3LYP commonly used for organic molecules turns out to be unsatisfactory for all types of solid state systems, in particular metals.

Besides wavefunction-based approaches of quantum chemistry and density functional approaches originating from solid state physics, quantum Monte Carlo provides a third approach to solving the quantum mechanical many-electron problem. In his contribution, *Needs* demonstrated some clear progress of this approach, but the overall accuracy is not substantially better than those achieved with hybrid functionals or, in the case of small molecules, with traditional quantum chemical methods. It is thus fair to say that the quest for highly accurate total energies remains an extremely challenging topic and we are far from a definitive solution.

On the other hand, we have witnessed significant improvements in the practical calculation of accurate band gaps and other electronic excitation energies in solids. In his contribution *Kresse* discussed various methods beyond GGA-DFT for the calculation of energy band gaps in

semiconductors. The methods range from the use of hybrid functionals all the way to self-consistent GW calculations including electron–hole interactions. The computed excitation energies are gradually reaching a level of accuracy which is comparable to experiment. This is a significant achievement as it enables band gap engineering, for example for advanced microelectronic devices. In particular, this approach provides accurate values for the energy separation of impurity levels from the band edges.

We are presently witnessing the confluence of density functional theory and many-body theory in the form of dynamical mean-field theory, thus leading to an approach called LDA + DMFT. This approach provides a bridge between standard DFT and DFT + U , which are applicable for the extreme cases of weak and very strong correlations, respectively. The contribution by *Held* illustrated the capabilities of this combined approach for the case of compounds such as LaMnO_3 . It has been known for a number of years that local or semi-local potentials encounter serious difficulties with so-called strongly correlated systems such as compounds containing partially occupied $3d$ or $4f$ orbitals. The LDA + DMFT is clearly a significant step forward in dealing with this type of systems, leading to reasonable descriptions of the insulating and magnetic properties of such materials. Since this approach aspires to an accurate description of the electronic correlation effects, it will be necessary to use methods such as GW rather than LDA. Necessarily, this leads to computationally very demanding schemes and major efforts will have to be made to develop general, efficient, and robust implementations and computer programs so that industry can benefit from these exciting and promising developments.

2.2. Larger systems, more configurations

The second major theoretical thrust is the *ab initio* treatment of more complex materials, i.e. systems requiring models with a large number of atoms. By increasing the number of atoms in a model, the number of configurations increases combinatorially. In fact, this configurational complexity is one of the most severe obstacles in building the bridge between atomistic models and macroscopic properties. In other words, the concepts of statistical thermodynamics need to be connected with quantum mechanical calculations on solids. For these reasons it may not be a coincidence that the largest number of theoretical contributions in the present workshop addressed this aspect in one way or another.

In his presentation *VandeVondele* gave a very interesting analysis of the interaction between a polar liquid and an ionic surface, namely acetonitrile (CH_3CN) on an anatase (TiO_2) surface. The challenge arises from the long timescales of the motions of the acetonitrile molecules in the presence of strong local electric fields near the surface. The practical computational solution is the combination of *ab initio* molecular dynamics and a quasi-classical force-field approach with the force-field parameters being calibrated with *ab initio* structures and forces.

The prediction of crystal structures with only the chemical composition as input remains a major challenge of critical

importance to materials design. The work presented by *Oganov* demonstrated an evolutionary approach using an *ab initio* energy as fitness criterion. One of the requirements for the success of this approach is a high robustness of the underlying *ab initio* program, which needs to converge the self-consistency cycles and the geometry optimizations for a large variety of atomic arrangements. This was demonstrated by *Oganov* for cases such as new high-pressure phases of CaCO_3 and metallic structures such as Al_{12}C and Al_{13}K using VASP as the source of optimized structures and energies.

The prediction of chemical reaction rates requires efficient navigation on energy surfaces. This is a difficult problem due to (i) the complexity and possible roughness of energy surfaces and (ii) the requirement for very accurate free energies of transition states. In this context, *Bucko* reported the exploration of the free-energy surface by using two techniques based on *ab initio* molecular dynamics, namely (1) a thermodynamic integration following a given reaction coordinate and (2) metadynamics, i.e. molecular dynamics in which the past trajectory is gradually filled with repulsive ‘Gaussian hills’. These two methods are illustrated for the case of the prototypical bimolecular nucleophilic substitution ($\text{S}_{\text{N}}2$ reaction) $\text{Cl}^- + \text{CH}_3\text{Cl} \rightarrow \text{ClCH}_3 + \text{Cl}$. The first method allows the estimation of statistical errors, but requires knowledge of the reaction path. The second method can be very useful in exploring reaction pathways where transition states are unknown. However, in this case a reliable estimation of the errors is not available.

For several decades there have been significant efforts to develop so-called order- N methods, which exhibit a linear scaling in computational effort with the number of atoms in the model. As illustrated in the contribution by *Artacho*, the SIESTA code [6] offers one of the successful implementations of such algorithms. With this type of approach, non-metallic systems with thousands of atoms have come within the reach of *ab initio* calculations. As pointed out by *Artacho*, the major challenge is the sampling of the large number of configurations in such models. This requires linear scaling methods with small ‘prefactors’. To this end, the use of compact localized basis sets and grid-based methods is appealing. However, it is delicate to find a good balance between accuracy and computational efficiency, as has been known for a number of years from earlier work using numerical localized basis sets [7].

The exploration of novel ideas to treat more complex systems is obviously facilitated by a standardized development platform. This was pointed out in the contribution by *Verstraete*, who reported on the recent progress achieved with the ABINIT code [8]. This program is pursued in the form of a large collaborative effort using an open-source paradigm.

An impressive demonstration of the performance of order- N methods is the work reported by *Skylaris* using their recently developed *ONETEP* program [9]. This investigation includes an *ab initio* calculation of the binding energy of a staurosporine molecule to a protein, which was modeled by fragments containing up to about 1000 atoms.

The quest for larger and more complex structures is also pursued with *ab initio* methods such as the FLAPW

method [3], which are known to give highly accurate solutions of the DFT equations. In their implementation and extension of this method in the Wien2k package [10], the paper presented by *Laskowski* showed the treatment of boron nitride nanomeshes on rhodium surfaces, revealing the limitations of an earlier force-field treatment.

Silhelníková presented the work on 38-atom gold clusters passivated by thio-organic molecules. This work uses localized Slater-type orbitals and numerical integrations as implemented in the ADF program [11]. This implementation is related to the approach implemented in the DMol program [7] and SIESTA [6].

2.3. More materials properties

The third thrust in theoretical and computational developments is aimed at the calculation of more materials properties with increasingly better accuracy. Of course, the work discussed in the previous section also implicitly addresses this aspect. For example, the work reported by *Kresse* using GW methods is aimed at a better description of optical properties. Underlying these calculations is an accurate total electronic energy, which is of course one of the most fundamental properties of quantum mechanics.

For a long time, electronic structure theory had the reputation of being confined to the ‘ $T = 0$ prison’. Conceptually, this veil was pierced with the pioneering work of *Car* and *Parrinello* in the mid-1980s by combining *ab initio* theory with molecular dynamics. In practice, *ab initio* MD simulations have great difficulties in generating sufficiently long trajectories to allow reliable statistical sampling. A quasi-harmonic phonon approach is a realistic alternative to compute thermodynamic functions for solids for temperatures about two-thirds of the melting point. This approach was impressively illustrated in the work from the group of *Tanaka*, who computed free energies of ceramic compounds by a combination of first-principles phonon calculations and statistical approaches. Thus these researchers predict the phase stability of polymorphs of compounds such as Ga_2O_3 and the temperature-dependent occupancy of cationic sites in Mg–Al oxides as a function of temperature. Notwithstanding the limitations in the electronic part of the free energy, this type of free-energy calculations is most useful in domains such as ceramics, where often experimental data are lacking, especially in the high-temperature and high-pressure regimes.

Information technology, which has become so essential for our society, hinges on electron transport. In fact, the very limitations of present metal–oxide semiconductor devices are imposed by electron transport phenomena such as the leakage current. The solution to these fundamental problems can be found in novel materials and designs such as molecular conductors, nanoclusters, and nanotubes. Hence the modeling of electron transport on the nano-scale is of utmost interest. This aspect is treated in the paper presented by *Stokbro*. To this end, a non-equilibrium Green’s function formalism provides a promising theoretical framework. Its application is demonstrated by calculating the I – V characteristics of a single molecule connected with gold electrodes as well as

spin-dependent electron transport through a magneto-tunnel junction consisting of MgO layers sandwiched between Fe electrodes. The practical success of this approach hinges on the ability to simulate complex structures. In principle this should be possible since the present Green's function method scales linearly with the number of atoms.

A fascinating and important property was addressed in the contribution by *Nordström* by demonstrating the calculation of magnetic properties and in particular the magnetic anisotropy energy. It is a remarkable success of today's *ab initio* electronic structure methods that one is able to compute extremely subtle magnetic effects such as the magnetic anisotropy energy with impressively high accuracy. In the same contribution, these authors demonstrate an approach to compute the Curie temperature, which still remains as a formidable challenge.

Another illustration of the capabilities of today's electronic structure method as applied to magnetic phenomena is given in the work presented by *Ahuja*. In addition to the structural and magnetic properties, this work also addresses the mechanical properties of the so-called MAX phases, which consist of layers of transition metal carbides or nitrides with mono-atomic layers of elements such as Al. *Ab initio* calculations provide an excellent vehicle to explore the structure, stability, and mechanical properties of a large number of potential candidates, thus helping to interpret and focus experimental efforts.

The interplay between soft phonon modes, structural stability, and magnetic properties in shape memory alloys such as Ni₂MnGa was shown in the work presented by *Hickel*. One of the main objectives of this study is the elucidation of the reaction pathways involved in the phase transformations of these materials.

The work discussed by *Wröbel* illustrates the use of the *ab initio* phonon approach to investigate the phase stability of ZnO polymorphs under high pressure. This type of study shows the power of *ab initio* techniques to explore systems under extreme conditions, where experiments are difficult if not impossible.

Finally, the examples presented by *Friak* on Ti-based alloys for human implants opens the view on the potential usefulness of *ab initio* theory in cross-disciplinary areas such as materials science and medicine.

3. Industrial applications

3.1. Energy

Safe, sustainable, and environmentally responsible energy is one of the major needs of our societies. The generation of electricity from nuclear energy is a viable route, provided that the design and the management of the plants and the fuel cycles are carefully controlled. Of particular concern from a materials science point of view is the structural evolution of materials used as fuels, in the cladding, and in the reactor vessel under radiation. Experiments under these conditions are difficult, costly, and lengthy, thus limiting the introduction of novel and potentially better materials. Hence, simulations can play a major role provided that they are realistic and

reliable. In this context, the presentation by *Domain* from the research laboratories of Electricité de France (EDF) showed the systematic investigation of the structure and energetic of defects in nuclear materials using an *ab initio* approach. The results provide a detailed understanding of the energetics of alloying elements and impurity atoms such as their tendency to form clusters and to migrate to other defects, grain boundaries, and surfaces. The detailed information obtained from these *ab initio* calculations serves as input for simulations on larger length and timescales, thus enabling a multi-scale modeling approach based on consistent materials property data.

The use of *ab initio* modeling in the development of efficient thermophotovoltaic devices was convincingly illustrated in the contribution by *Geller* from the Bechtel Bettis Laboratory in Pennsylvania, USA. In such devices, photons from the infrared, i.e. with energies around 0.5 eV, are used to generate electron-hole pairs in narrow-band-gap semiconductors. The control of the mobility of the carriers and potential decay mechanisms such as Auger recombination play a critical role in the performance of these devices. *Ab initio* calculations using post-DFT methods such as screened exchange as implemented in the FLAPW method offer sufficient accuracy to guide the selection of materials and to provide property data including accurate energy differences between local minima in the conduction band and effective masses of electrons and holes [12].

A third illustration of the use of *ab initio* techniques in the development of energy-related materials was given in the contribution by *Cheng*. This work investigates the usefulness of carbon-based materials for hydrogen storage and in particular the role of the so-called spillover effect. The present *ab initio* calculations provide detailed insight into the process of dissociation of molecular hydrogen and the diffusion of hydrogen atoms. The study reveals fundamental difficulties in using carbon-based materials as hydrogen storage materials, thus providing useful guidance in the choice of suitable materials.

Photovoltaic materials for solar energy continue to be a topic of great interest and general popularity. Thus, a large number of research and development projects are pursued in this domain. The work presented by *Olsson* involving the French energy utility company EDF describes a particularly intriguing system, namely Mn-doped AIP. The magnetic dopants induce energy levels in the band gap, which allow absorption of photons with an energy below that of the fundamental gap. The magnetic character reduces the recombination rate, thus leading to potentially very high efficiencies. Electronic structure calculations play an instrumental role in establishing the local structure around the dopants and in finding the corresponding dopant levels.

3.2. Automotive engineering

The research laboratories of leading automotive companies have embraced *ab initio* quantum mechanical approaches as a viable part of their R&D efforts. In his contribution, *Asahi* from Toyota Central R&D Laboratories in Japan showed two recent applications, namely (1) the development of improved

photocatalysts for the decomposition of unwanted or toxic molecules and (2) the design of thermoelectric materials. In the first case the result is higher safety and comfort due to photocatalytic removal of hydrophobic layers on glass surfaces (e.g. rear mirrors) and better air quality inside a vehicle. In the second case the aim is improved fuel efficiency of vehicles due to re-use of waste heat via thermoelectric devices. Low thermal conductivity is one of the requirements for effective thermoelectric materials. *Ab initio* calculations turn out to be well suited to predict this property, thus helping in the design and selection of the most promising materials.

Fuel cells using hydrogen promise a major improvement of the energy efficiency of cars. Given the enormous geo-economic importance of fossil fuels and the role of cars in our societies, a change from gasoline and diesel fuels to hydrogen would be a dramatic transformation. At present we are in a very early stage and there are many fundamental technological problems yet to be resolved. Storage of hydrogen is one of the big road blocks. These issues and the opportunities for *ab initio* modeling were comprehensively exposed in the contribution by *Wolverton* from Northwestern University and previously at Ford Motor Company in the USA. *Ab initio* methods are useful in three aspects, namely (i) the determination of the thermodynamic properties of the materials involved in the decomposition of hydrides, (ii) the prediction of crystal structures of novel hydride phases, and (iii) the prediction of the decomposition pathways. Despite the limitations of present *ab initio* methods, the approaches are sufficiently accurate, robust, and powerful to be of true industrial value.

Along the same lines, the contribution from *Siegel* from the Ford Motor Company reinforced the value of *ab initio* calculations in the development of hydrogen storage materials. An obvious but nevertheless crucial point was made in this contribution: the success of *ab initio* modeling in an industrial research program depends critically on the tight coupling with experimental efforts. Successful hydrogen storage materials need to have the proper thermodynamic properties, but also have to allow sufficiently fast kinetics, especially in the fueling steps. Consequently, there is an urgent need for efficient computational tools to investigate reaction pathways.

Hector from the R&D Center of General Motors near Detroit, USA, stressed the importance of a full thermodynamic analysis based on *ab initio* phonon calculations to predict the structural and energetic properties of hydrides. Such an approach was carried out in detail for the alkaline earth hydrides [13]. Furthermore, *Hector* showed the calculation of mechanical properties (e.g. Young's modulus) of hydrides. In fact, computations provide sometimes the only available data for this fairly important materials property. The uncertainties due to the approximations in the exchange-correlation potentials remain an Achilles heel, but again the present accuracy has proven to be already extremely valuable. In concert with the other speakers from industry, *Hector* stressed the critical importance of a close collaboration between computational scientists and experimentalists.

3.3. Information technologies

Since the discovery of the transistor in 1947 we have seen a whirlwind of technological progress in microelectronics and information technology. However, one aspect has remained the same from the very beginning of electronic solid state devices, namely the struggle with the purity of the materials. Today, the semiconductor industry is facing again major challenges related to materials. In the constant striving for higher integration and lower power consumption, we are reaching the limits of SiO₂ gate oxides and new materials such as high-*k* dielectrics and the corresponding gate metals are determining competitive advantages. Furthermore, optoelectronic devices especially for flat-panel displays are of great interest. For example, anybody who has used the display of a digital camera in bright sunlight will agree that there is ample room for improvements.

In his contribution, *Van de Walle* discussed the use of LDA + *U* in the understanding of point defects in a fascinating and versatile wide-band-gap semiconductor, namely ZnO. The high purity and crystalline quality required for many optoelectronic materials is an enormous challenge for synthesis and an opportunity for accurate atomistic modeling using *ab initio* techniques. The present work shows that electronic structure methods are now capable of calculating the thermodynamics of defect concentration, ionization energies, and the migration energies of defects such as Zn interstitials. In fact, *ab initio* calculations are probably the most accurate and versatile approach available today to gain such detailed insight into the behavior of point defects and to explain technologically important properties such as unintentional conductivity in wide-band-gap semiconductors.

Related to information technology is the paper by *Mannstadt* from the German specialty glass company Schott. His contribution focused on thermo-mechanical properties of oxides with high stiffness and on optical properties of calcium fluoride used in photolithography of microelectronic circuits. Computed elastic properties of oxides were found to be of similar accuracy and consistency as measured data. For CaF₂ post-DFT calculations using a screened-exchange FLAPW approach together with standard DFT for the structure and energetics of point defects provide valuable new insight into this material. The quasi-harmonic approximation with *ab initio* phonon calculations gives very encouraging results for the coefficient of thermal expansion, thus allowing the prediction of temperature effects on these materials.

The paper by *Gosálvez* from the Helsinki University of Technology introduced the connection of three tools for the simulation of anisotropic etching of silicon substrates, namely density functional theory (DFT), kinetic Monte Carlo (KMC), and continuous cellular automaton (CCA) methods combined under a common graphical user interface. The trend to integrate a range of simulation methods in a common platform reflects the reality of industrial research and development that a single tool is rarely the solution, but high practical value is achieved from the integration of complementary tools.

An informative presentation by *Zempe* from the research laboratory of Sumitomo Chemical in Tsukuba, Japan, illustrated the use of time-dependent density functional theory

(TDDFT) in the understanding of polymer light-emitting diodes (PLEDs). These materials have great industrial potential in the next generation of flat-panel displays by improving the brightness and efficiency of these devices over the current liquid crystal displays, which are energetically inefficient due to the use of color filters rather than active light-emitting materials. While present TDDFT simulations are limited to relatively small fragments of a polymer, the results are sufficiently relevant and valuable as to guide the development of new materials.

The fourth contribution in this category related to information technology was given by *Shankar* from the Intel Corporation in Santa Clara, California. This paper made it very clear that the microelectronics industry is facing tremendous materials challenges as the device features are pushed to smaller and smaller dimensions on the nano-scale. At the same time there is the need to introduce new and more complex materials such as high-*k* dielectrics containing a range of transition metals. With the increasing number of different materials in a device such as a PMOS or NMOS stacks combined with the reduction in size, interfaces are starting to become a dominant features requiring better and more detailed control. This opens fascinating opportunities for atomic-scale simulations using *ab initio* methods. The integration of a range of different simulation methods and tools is perceived to be crucial for the further success of materials modeling in the microelectronics industry.

3.4. Catalysis and chemical processing

The fourth group of industrial application comprises catalysis and chemical processing. Undeniably, the chemical and petrochemical industry is of fundamental importance to modern civilization as it touches almost all aspects of our lives, including the most essential needs such as clothing, food, housing, health, and transportation. A large number of chemical reactions of vital importance rely on catalytic reactions, the most famous being the Haber–Bosch synthesis of ammonia. For these reasons, the detailed understanding of surface reactions has attracted the interest of many researchers in the field of *ab initio* theory. In fact, the limitations of Hartree–Fock-based quantum chemistry methods in treating transition metals, which play such a crucial role in catalysis, have been one of the factors stimulating the extension of density functional methods into the realm of chemistry. In the 1980s and perhaps well into the 1990s this happened not without a certain initial skepticism and resistance by the quantum chemists working with wavefunction-based methods. Today, the virtues and limitations of both wavefunction-based methods and density functional methods are quite well understood and we are actually seeing a confluence of the two types of electronic structure methods.

In her contribution, *Opalka* from the United Technologies Research Center in Hartford, Connecticut, focused on the water gas shift reaction, which plays a fundamental role in large-scale production of hydrogen. Requirements for a catalyst operating at low temperature and with high turnover have led to a combined experimental and computational

effort at this industrial research laboratory in search of more efficient catalytic materials. In this project, *ab initio* calculations using VASP allowed a detailed understanding of the effect of transition metal dopants on the surface reactivity of cubic ceria–zirconia, thus providing a rational basis for improvements of this catalyst.

The performance of industrial catalysts depends to a significant extent on the support of the active catalytic particles. This intriguing question was addressed by *Raybaud* from the Institut Français du Pétrole using an *ab initio* approach to describe the state of hydroxylation and wetting properties of surfaces of γ -alumina (Al_2O_3) and anatase (TiO_2). The work offers detailed insight into the relationship between the surface state of the catalyst support, the binding of the active particles to the support, and the resulting reactivity of the system.

The effect of the environment on the reactivity of catalytic surfaces was developed in the presentation by *Rogal* (Fritz-Haber Institut, Berlin) for the prototypical case of CO oxidation on a Pd surface. This work represents a multi-scale approach combining *ab initio* quantum mechanics, statistical mechanics, and kinetics.

A fairly difficult problem comparing homogeneous and heterogeneous catalytic processes was discussed in the paper by *Coussens* from DSM in the Netherlands. The aim of this study is the elucidation of the factors which govern the hydrogen sensitivity of olefin polymerization catalysts. To this end, model calculations are performed and a correlation is found with the strength of complexation of hydrogen versus ethene with the metal centers and the hydrogen sensitivity of the catalysts.

A detailed study of the reaction sites of the important CoMoS and NiMoS hydrogendesulfurization catalysts was presented by *Hinnemann* from the Haldor Topsøe company in Denmark. In this work, the combination of atom-resolved scanning tunneling microscopy experiments with DFT calculations on models of the edge structures of the catalytically active nanoparticles enables a unique insight into the catalytic mechanisms.

The so-called Hägg Fe carbide (Fe_5C_2) is considered to be the active catalyst in the Fischer–Tropsch synthesis, which is central to the conversion of coal to liquid fuels. In this context, the work of *Steynberg* from Sasol Technology in South Africa provided a detailed analysis of the structure and surface composition of the energetically most stable surfaces of this catalytic material. Thus valuable information is gained where experimental data are currently lacking.

In heterogeneous catalysis, the large number of possible active surfaces and surface structures present a tantalizing challenge for *ab initio* approaches. One way out of this difficulty is the reduction of complex systems to simpler models, which retain the dominant trends while being computationally accessible. In his contribution, *Bligaard* from the Technical University of Denmark illustrated the application of such a concept to the design of alloy catalysts for the methanation reaction ($\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$), resulting in a surprisingly simple scaling relation.

Catalytic processes play a critical role in hydrogen storage systems. In this context the work presented by *Zuliani* (Vrije

Universiteit Amsterdam) elucidated the catalytic role of Ti in the bonding of H₂ molecules to carbon nanotubes or benzene molecules.

A nagging problem in the DFT treatment of CO adsorption on metal surfaces is the distinction between top and hollow sites. The work shown by *Stroppa* from the University of Vienna demonstrated that the use of hybrid functionals removes the discrepancy between experiment and calculations for the cases of CO on Cu and Rh, but still fails for Pt.

Finally, the work by *Seriani*, also from the University of Vienna, provided an impressive example of the use of *ab initio* calculations in mapping out the formation of various oxide films on the catalytic surfaces of Rh, Pd, and Pt as a function of the partial pressure and temperature (i.e. chemical potential) of oxygen in the gas phase. The study reveals a great richness of different surface oxides, thus influencing the adsorption and reaction of CO as well as desorption of CO₂.

4. Assessment and perspectives

Ab initio density functional computations of condensed matter have made the step from academic research to industrial practice. The present workshop is a clear testimonial of this fact. The industrial value of such simulations is threefold, namely (i) a better *understanding* of the fundamental mechanisms determining the performance of materials, (ii) a clearer *interpretation* of experimental results, and (iii) the *prediction* of materials property data with ease and consistency. This success has become possible by the confluence of the following achievements.

- Density functional theory has proven to be a general, efficient, and sufficiently accurate many-body approach.
- There exist now highly efficient and robust computer programs.
- Results for a large number of systems give confidence in the validity and reliability of the computations.
- Industrial research laboratories have built teams including computational experts.
- Computer hardware has become powerful and cost effective.

The dramatic challenges in the domains of energy, transportation, information technology, and chemical process industries are driving the leading companies in the world to adopt innovative R&D strategies. Computational modeling and simulations have proven to be tremendously valuable in the macroscopic domains such as structural analysis with finite element methods, computational fluid dynamics, electronic device simulations, and the optimization of chemical processes. The industrial acceptance of these macroscopic simulation techniques has occurred during the past three or four decades and these techniques are now an integral part of industrial practice. Essentially, these methods are based on classical mechanics, electrodynamics, and thermodynamics with some of the theoretical foundations reaching back several centuries. The simulation programs in these domains are well developed and they are commercially supported by well established and successful companies.

The field of atomistic simulations is in a much earlier stage, but carries the potential of a more profound industrial impact. The reason is the following. The macroscopic simulations mentioned above rely on experimental materials property data as input. Thus the design space is determined by the properties and performance of known materials. Computational materials science based on quantum mechanical theory has the potential to lead to entirely new materials with novel properties, thus initiating disruptive technologies. The development of novel hydrogen storage materials for the automotive industry may very well be such a case. In fact, the present workshop offered a glimpse of the industrial activities in this area, especially in the USA.

The study of catalytic reactions occupied a significant part of the workshop. This reflects the importance of catalytic processes in the chemical and petrochemical industry as well as for on-board systems in the transportation industry. In this context it may be useful to recall that one of the first industrial applications of quantum mechanical methods occurred in the chemical industry in the 1980s. *Ab initio* calculations of Dixon and co-workers at the Experimental Station of DuPont in Delaware, USA, resulted in systematic datasets for the molecular heat of formation with the data being subsequently used in the selection of molecules and the design of reactors [14]. The key factors for this early success was the ability to perform automatic geometry optimization of industrially relevant molecules such as chlorofluorocarbon (CFC) replacements, to compute reliable total energies, and to evaluate their vibrational spectrum and hence the vibrational enthalpy and entropy as a function of temperature. At that time, molecular *ab initio* calculations were basically limited to main group elements. Full geometry optimizations and the computation of thermodynamic properties of organometallic complexes such as metallocenes used for homogeneous olefin polymerization or reactions on transition metal surfaces were out of reach. Today, about 20 years later, we are in a position to perform such calculations on a routine basis. We are now also able to compute the structure and thermodynamic properties of solids and surfaces including transition metals and to investigate surface properties at an unprecedented level of detail. In fact, the advances in surface science during the past decades were due to a remarkable synergy between advances in theory and experiment. A gratifying reflection of this Golden Age of surface science is the award of the 2007 Nobel Prize in Chemistry to Gerhard Ertl ‘for his studies of chemical processes on solid surfaces’.

Despite these achievements, a realistic assessment of the current situation shows that atomistic modeling of heterogeneous catalysts struggles with the lack of detailed information of the actual surface structures at the reactive site under operating conditions. In contrast, the realm of microelectronics—or perhaps better called nanoelectronics—deals with very pure and often better defined materials. The present workshop showed very impressively how electronic structure calculations provide unrivaled insight into the structure and energetics of semiconductors, the role of dopants, and the effect of impurities. It is reasonable to expect that this field of technology will increasingly benefit from

quantum mechanical simulations, especially as the drive for even smaller feature sizes requires the use of new compounds and materials such as hafnium oxide, hitherto unknown to the microelectronics industry. Display technologies will continue to be an area of intense R&D. In particular, the introduction of organic polymeric materials will generate numerous challenges for atomistic simulations, which will require the combination of statistical methods for simulating polymers with quantum mechanical methods for molecules and solids, and to address processes on interfaces between the electrodes and the optically active layers. Besides microelectronic devices and display technologies, efficient energy conversion systems such as photovoltaics and thermophotovoltaics will require accurate simulations methods including accurate treatment of excited states and electron transport phenomena.

This brings us back to the fundamental challenges for theory, which were a common thread throughout the workshop, namely more accurate total energies, more complex systems, and more materials properties. The most difficult of these is perhaps the quest for more accurate energies. At present, there is no obvious solution. Hybrid functionals mixing non-local exchange and correlation operators with DFT are an improvement, especially for non-metallic systems, but fall short in delivering ‘chemical accuracy’. Furthermore, these approaches do not address the issue of weak interactions, which play such an important role in liquids, polymers, and biomolecular systems. There is progress in quantum Monte Carlo methods, but no obvious breakthrough is on the horizon. Wavefunction-based quantum chemistry methods achieve remarkable accuracy for small benchmark systems, but the scaling of their computational effort with system size remains prohibitive. Hence, the quest for higher accuracy in the electronic energy will require innovative ideas as well as diligent and hard work with the present tools and approaches. Progress on this front is of fundamental importance!

The quest for the treatment of larger systems is fueled by the continuous development of computer hardware. Progress in order- N methods is encouraging, but this should not distract from the tantalizing problem of the configurational space combined with the need for extremely accurate free energies in capturing chemical processes. It is impressive that we can treat an organic molecule binding to an active site of a protein using a fully quantum mechanical approach, but we need to keep the following in mind. The difference between an industrially successful drug (i.e. a pharmaceutical product which generates more than one billion dollars in sales per year) and an abysmal failure can be a difference of 1 kcal mol^{-1} in the free energy of binding. Furthermore, for the majority of pharmaceutical agents, the detailed structure of the biological

targets is not known. While there are clearly most fascinating research topics in molecular biology awaiting the use of rigorous quantum mechanical methods, the gap between actual and desired capabilities remains rather large.

Compared with the extremely complex and subtle issues faced by the pharmaceutical industry, the industrial part of the present workshop focused on structural and functional materials for applications such as hydrogen storage and heterogeneous catalysis, where the relationship between composition, structure, and function is conceptually much better defined than in the pharmaceutical world. But even in these areas of inorganic materials, the challenge of the configuration space remains intimidating. Nevertheless, the combination of approaches such as evolutionary algorithms, robust DFT solvers, sophisticated software environments, and the sheer power and number of compute nodes offers truly exciting perspectives for applying theory to the practical solution of industrial problems.

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