Industrial Use of Electronic Structure Methods

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8.1   Introduction

It is exciting and satisfying to see that electronic structure methods are becoming an integral part of industrial research. In addition to the intrinsic scientific and intellectual values, this methodology is now creating direct economic benefits. The vision of the founders of computational materials science developed earlier in this century is thus becoming a reality. Of course, such a development occurs gradually and it is probably hard to determine when the industrial acceptance of electronic structure methods actually started. In fact, the chemical and pharmaceutical companies were probably first to employ molecular orbital calculations to help in solving problems of molecular structures and chemical reactivity. Today all major chemical companies in Europe, the US, and Japan are using quantum chemical methods in their daily work.

Except for companies with a long tradition in fundamental research such as Bell Labs, IBM and NEC, the majority of materials science related industries, most notably the microelectronics companies such as Intel, Motorola, and Infineon (Siemens) have started only recently to use electronic structure methods. This applies also to diversified companies and catalyst manufacturers. Hence it is timely to discuss highlights from the use of electronic structure methods in the area of industrial materials science. In trying to do so, however, one is confronted with the problem of confidentiality. Often, important industrial discoveries and inventions become generally known in the form of patents and publications only years after they were made or they are kept as trade secrets and are never publicly disclosed. The authors of this contribution in their work in the private industry are confronted with this problem daily. Therefore, the following discussions and illustrative examples are perhaps in some cases more vague then the reader would like. The authors apologise for this in advance!

Reflecting the major research efforts within the Psi-k Network, the focus of this article is on inorganic solid state materials. Within this field, the following sections present a selection of recent industrial cases where electronic structure methods have been used.

8.2 Improvement of Iron Oxide Catalyst

The use of electronic structure methods in heterogeneous catalysis immediately triggers the thought that the main problem is related to surface reactivity. One thinks of surface structures and surface reactions, of adsorption and dissociation pathways, and the associated energy hypersurface with its local minima, energy barriers, and transition states. Once this information is known, one might conclude, then the problem of catalyst design is essentially solved. In practice, this line of reasoning is flawed in several ways. First, the surface of a real catalyst is not a property which can be determined from knowing just the chemical composition. It depends on the history of the preparation of the catalyst and the conditions within the chemical process including all changes in feedstock and operating variables. Second, even if one could determine the surface structure in each stage (a combination of advanced experimental methods including high-resolution transmission electron microscopy, x-ray photoemission spectroscopy, scanning tunnelling microscopy, and Raman spectroscopy might allow that in principle) and if one had a complete chemical inventory of reactants, intermediates, and products, there would be such a large multitude of possible reactions and intermediate steps that the shear number of systems to be considered would be overwhelming. Third, if one could narrow the number of relevant reactions to only a few, then current electronic structure methods are not accurate enough to determine the energies of an energy barrier of a transition state of a surface reaction with chemical accuracy. An error of 4 kcal/mol in the barrier height (which is not easy to achieve computationally) causes an order of magnitude error in a reaction rate! Given this situation, it is not surprising that technology managers of catalyst manufacturers are highly sceptic about the potential benefits of computational approaches. From a computational materials scientist's point of view, the above reality is challenging indeed.

Nevertheless, the situation is not as bad if one considers the alternatives. If we imagine a discussion between a sceptical technology manager of a catalyst manufacturer and a computational materials scientist eager to show the usefulness of electronic structure methods, the arguments could go as follows. The computational scientist would admit that the theoretical and computational tools are by no means perfect and ask the technology manager, what approaches and tools are currently used to improve existing catalysts or to develop new ones. The answer would be that a large number of experiments are made and evaluated based on the experience present in the companies. In other words, the approach is essentially the same as at the beginning of the century when A. Mittasch developed the catalyst for the ammonia synthesis [2]. The computational scientist would ask how many experiments would be needed and how one would decide which ones to perform first. He could also confirm that the cost of an industrial researcher and

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[2]The catalyst introduced by A. Mittasch and coworkers in 1910 is made from iron oxides and contains Al_2O_3, K_2O and CaO. It is estimated that at least 10 000 experiments, but probably many more (perhaps 70 000) were made to find and optimise this system

engineer in the European chemical industry runs at about 300 000 euros or more per year. Then the technology manager would say that in addition to a range of experimental techniques for materials characterisation there are now wonderful techniques called combinatorial chemistry and high-throughput experimentation which are being applied to catalysis. In fact, companies such as Symyx are receiving industrial contracts valued in the tens of millions of dollars to perform such work. At that point, the computational materials scientist would propose a little analysis: consider a catalyst containing only 5 elements including transition metals, rare-earth atoms, some promoters like alkali atoms, and some main-group elements like Al or Ga. If one would select a total of 12 elements as possible candidates (perhaps based on prior experience) and choose three concentrations for each element, one would end up with about 50 000 combinations. Then one would need to consider a range of possible preparation methods, for example calcination at different temperatures under reductive or oxidative conditions and one would have to test the performance of the catalysts for a range of reaction conditions (e.g. high and low temperature). One could easily end up with about one million experiments. When this is all set and done, which is clearly a major effort even with very sophisticated high-throughput synthesis and screening methods, another practical problem will have to be addressed as well, namely the degradation of the catalyst in the reactor. Thermostability is a critical factor in catalyst technology. One would probably have to address this design requirement through long-term tests once a set of promising candidates has been found. All in all, this represents a formidable task and one begins to appreciate the enormous accomplishments of scientists and technologists that have lead to the present generation of successful catalytic systems. By analysing this problem, one could also come to the conclusion that intuition and serendipity have lead to useful materials but that the majority of materials have never been synthesised or tested. Real treasures may still await their discovery!

Without developing this scenario further, it is clear that the experimental efforts to develop new catalytic systems are enormous and in today's economic conditions are simply becoming too expensive and time consuming if done in a brute-force manner. At this point, the technology manager and computational materials scientists may stop arguing with each other and bring up the real issue. We simply don't understand most of the structure, function, and degradation mechanisms of a catalyst system. Experimental screening guided by experience and vague models provides solutions, but they are very tedious to obtain and even if they work, one still does not have a good way to optimise the system in a rational manner.

Obviously, any approach is welcome that would help to rank possible candidates before any experiments are made, thereby increasing the chances for finding a good solution sooner. It is probably safe to say that computational methods, in particular *ab initio* electronic structure methods, are starting to fill that role and thus are truly valuable. In this sense, computational materials science together with experiment can make a real difference. The aim of computations is not the design of a material solely by simulations, but the goal is much more humble and realistic. Computations simply add more relevant information, they provide insight and understanding, they help in the interpretation of experimental data, assist in asserting or eliminating mechanistic hypotheses, and can help in the design of experimental training sets. With this

in mind, theoretical and computational approaches are making real contributions to industrial research.

As an example, let's take iron-oxide based catalysts. These catalysts are used in the important water-gas shift reaction, which yields hydrogen from carbon monoxide and water. Another major use of iron-based catalysts is the conversion of ethylbenzene to styrene, the precursor of polystyrene. Styrene is a commodity product with an annual world consumption of more than 15 million metric tons representing a commercial value of approximately 20 billion euros. Chemical producers such as BASF, Dow and BP Amoco need to keep the production cost as low as possible in order to compete on the world market while maintaining clean and safe processes. Equipment in the chemical plant is expensive and each unit such as a reactor or separation unit needs to run as long as possible without interruption because of the links to other processes. Any down-time of a reactor is very expensive. If a catalyst manufacturer introduces a new catalyst which gives higher yields and higher selectivity, but needs to be replaced more frequently than the old catalyst, then this may be a disaster for the catalyst producers as well as their users! The introduction of a new catalyst brings another risk: the performance of a catalyst depends on its synthesis. Unless the catalyst can be manufactured with fully reproducible and predictable performance, it cannot be brought to the market. There is yet another threat lurking. If during the life time of the catalyst in the reactor toxic compounds are formed (certain metal compounds can be a serious environmental hazard), then the catalyst user or manufacturer has a nasty problem at hand concerning the safe disposal of the used catalyst.

In fact, a major producer of iron oxide catalysts was faced with the problem of replacing Cr because of environmental issues. During the life time of the catalyst material, Cr was oxidized to Cr(VI). This made the disposal of the used catalyst material very costly and the catalyst manufacturer was asked to replace Cr without altering the other properties of the system too much. Early attempts lead to a system with good catalytic properties, but the material tended to sinter much faster than the original one. This would have reduced the time in the reactor necessitating a more frequent maintenance shut-down of the reactor unit in the chemical plant. Furthermore, the synthesis needed to be better understood in order to ensure reproducible quality and performance of the catalyst. To help with these problems, the particular catalyst manufacturer decided to explore the use of computational methods.

It would have been fairly hopeless trying to simulate the sintering process directly using quantum mechanical and atomistic models. Therefore, a simpler approach was taken. It is reasonable to assume that diffusion of atoms in the bulk and at the surface combined with changes in the local chemical composition are related to sintering. Therefore, it was decided to develop a better understanding of the solubility, diffusion, possible clustering and surface segregation of Cr. The situation was complicated. These catalysts are typically prepared by dissolving metal salts in water and precipitation by alkali hydroxides. The precipitates are filtered, dried, and then calcinated. This leads to the formation of a hematite phase, Fe_2O_3 with elements such as Cr substituting some Fe atoms in the lattice. The reactor is loaded with this form and then the catalyst is activated by reduction with hydrogen to a magnetite phase,

Fe_3O_4. This phase becomes the active catalyst. Total energy calculations revealed that Cr had a tendency towards clustering and formation of super-structures, but the energy difference between the energetically most and least stable Cr distributions was quite small [1]. In contrast, some of the candidates considered for the replacement of Cr either showed tendencies for clustering in the bulk or exhibited surface segregation. By carrying out electronic structure calculations of the original Cr-containing system and possible replacements of Cr, information was gained on the changes in the charge distribution (oxidation state) of the Fe atoms surrounding the substitutional site, which allowed a ranking among possible Cr substitutes. This insight provided a screening tool for the pre-selection of possible candidates, thereby reducing the number of systems that had to be tested experimentally.

In the actual theoretical and computational studies, methods based on empirical potentials were used in conjunction with quantum mechanical methods, since a great number of cases needed to be screened. This use of theoretical and computational methodology is reducing the development time for the Cr-free catalyst and it increases the knowledge-base of the catalyst manufacturer thus benefiting other development projects as well. It was gratifying to see that at the completion of this computational study the catalyst manufacturers announced a new position for a scientist with modelling experience to join their research team.

8.3   CVD reaction mechanisms

In contrast to practical heterogeneous catalysts, which are "dirty" systems, materials for electronic devices are extremely well controlled and characterised. Therefore, microelectronic materials offer interesting possibilities for electronic structure methods. One of the key competitive advantages in the microelectronics industry comes from the rapid introduction of a new generation of microprocessors or memory chips. In practice this means that the manufacturing plant needs to become fully operational as fast as possible. The set-up of a manufacturing plant for devices such as memory chips costs approximately one billion euros. This means that every day lost in getting the production up to full capacity (i.e. achieving a yield of 80 or 90%) causes a shortfall in revenues of several million euros. In addition, markets strongly favour those companies who are able to introduce their products such as a new memory chip first. Therefore, being late in production penalises the producer even further. Needless to say that major efforts are made to shorten the time of developing and tuning the production process. Yet at the same time this industry is very conservative in setting up the production facility. Nobody wants to take high risks by using unproven technologies such as electronic structure calculations in establishing the manufacturing process.

In chemical vapour deposition (CVD), which is the predominant technology used in the production of microelectronic devices such as processors or memory chips, the key operational parameters are reactor geometry, concentrations and flow rates of reactants, and temperature profiles. These parameters need to be selected and tuned such that optimal uniformity is achieved over the entire wafer (300 mm in the new generation). Furthermore, the process conditions have to be chosen such as to ensure robustness of the process with respect to slight variations in any

of the parameters. Another major concern is the control of impurities in the reactants. This is primarily the problem of the CVD gas suppliers such as Air Liquide.

For the above reasons, one needs a reliable and predictive model for the CVD processes. Traditionally, simplified reaction schemes were used and parameterised by control experiments. In many cases, this approach works sufficiently well, at least for the current generation of microelectronic devices. However, if the chemical mechanisms of the deposition process are not properly captured, the model is reliable only in the range for which it has been parameterised. This is dangerous. For this reason there is an urgent need in the microelectronics industry to have tools which can help in the determination of reaction mechanisms. To this end, quantum mechanical methods offer unique capabilities.

An illustrative example has recently been presented by M. Hierlemann from Infineon (the microelectronics company created by Siemens) [2]. In the CVD growth of Si-Ge alloys it has been observed that small amounts of Ge significantly enhance the deposition rate of Si. This is a rather surprising observation and one can easily imagine that a kinetic model would be seriously flawed if it does not properly take this effect into account. Two possible mechanisms were considered as explanation for this effect, namely (i) a collective rearrangement of the surface atoms in the presence of Ge atoms thus leading to enhanced reactivity of the surface Si atoms and (ii) a local change of the surface reactivity near the Ge atoms.

It is well known that the desorption of hydrogen is the rate determining step in the CVD growth of pure Si from dimethylchlorosilane. It is also known that the desorption of molecular hydrogen from a germanium surface has a smaller barrier than for a silicon surface. If this property of Ge is maintained also in the case of Si-Ge alloys, then this property could explain the increased growth rate of Si provided that the lateral diffusion barrier of hydrogen atoms is smaller than the desorption barrier. In this case, hydrogen atoms could diffuse from Si sites to a surface Ge atom, recombine to form molecular hydrogen and desorb. At a finite temperature this diffusion process would free more Si sites from hydrogen thus enabling the faster deposition of fresh Si atoms.

This problem was treated by researchers at Siemens using *ab initio* quantum mechanical methods. As validation of the computational model, the desorption energies of hydrogen from Si and Ge surfaces were determined and the results were found to be in very good agreement with experiment, thus lending credibility to the computational approach. Encouraged by these results, the energetics of lateral diffusion of hydrogen on models of Si and Si-Ge surfaces was investigated. The results clearly demonstrated that the lateral diffusion barriers were lower than the desorption barrier, thus giving strong support for the diffusion mechanism rather than a cooperative surface reconstruction. In fact, earlier studies of molecular adsorption on a (4x2) reconstructed Si(001) surface with its alternating tilted Si surface dimers showed that the structural and electronic changes induced by the adsorption on one dimer did not alter the geometry of the neighbouring dimer [3]. This provides a further indication of the local nature of the surface processes on a Si(001) surface and casts doubts on a cooperative model.

Using this information gained from *ab initio* quantum mechanical calculations, researchers at Siemens developed a kinetic model based on the hydrogen diffusion mechanism, tuned it with available experimental data, and achieved an excellent description of observed deposition rates. This kinetic model thus provides a sound basis for predictions in a parameter space where no experiments are available.

A. Korkin from Motorola and coworkers reported similar studies on CVD growth of silicon nitride [4]. In this case, the situation is complicated by the fact that silicon nitride grows as an amorphous layer. This makes the construction of structural models quite difficult. However, the previous case as well as other studies on covalent semiconductor surfaces show a fairly local nature of the surface reactions. Therefore, a cluster model containing a rather modest number of atoms (about 10 to 30 atoms), with hydrogen atoms terminating bonds towards the bulk is sufficient to capture the major effects of adsorption. Such an approach is valuable, but it is hard to make an assessment of the errors introduced by the structural model. In fact, any engineering application requires first and foremost reliable estimates of errors rather than automatically the highest possible accuracy. However, all factors need to be taken into account which can cause differences between predictions and real systems.

8.4   Optoelectronic materials

The third example is taken from a particular area of optoelectronics, namely thermophoto-voltaics. The technological objective is the direct conversion of heat into electricity. Specifically, one envisions radiation sources emitting predominantly in the infrared with a photon energy of about 0.5 eV. In order to capture this energy by photovoltaic devices, one obviously needs narrow band gap semiconducting materials which absorb in the above energy range. Quaternary III-V materials containing Ga, In, As, and Sb meet this requirement. In order to achieve a long life time of the electron-hole pair one needs to grow device materials with low defect concentrations (e. g. dislocations). This requires a very good epitaxial lattice match with the substrate. In fact, InP is a convenient substrate for this type of III-V semiconductors. By using a quaternary alloy, it is possible to tune the energy band gap independently of the lattice parameter. However, different substrates could be considered if there are good reasons.

III-V alloys containing four or more atomic species can form local ordering on the sub-lattices which can be driven thermodynamically or kinetically. It is known that such effects can have significant impact on the optoelectronic properties.

In order to gain a deeper understanding of the delicate relationship between chemical composition, crystallographic structure, alloy ordering effects, doping, electronic structures and optoelectronic properties, one needs a robust and reliable theoretical and computational approach that can provide structural as well as electronic and energetic information. The key requirements for an appropriate theoretical and computational approach are therefore: (i) accurate prediction of ground state structures of pure, alloyed, and doped III-V semiconductors, (ii) calculation of relative energies accurate enough to predict local ordering effects in alloys, (iii) calculations of

optical excitation energies (band gaps) with an absolute accuracy of a few tenths of one eV, (iv) inclusion of relativistic effects for the accurate description of systems containing heavy elements such as In and Sb, and (v) ability to treat unit cells (super cells) of up to about 30 atoms.

Considering a number of possible options, the choice was made to build on the proven all-electron full-potential linearised augmented plane wave (FLAPW) method. On the LDA level, this method provides very good structural properties as well as relative energies as needed, for example, to investigate local ordering effects in alloys. For the calculation of optical excitation energies, the screened-exchange LDA approach was implemented self-consistently in the FLAPW method [5]. Spin-orbit relativistic effects are included as well thus resulting in a comprehensive methodology to tackle narrow band gap semiconductors meeting the requirements specified above.

The capability of this methodology has been tested on a range of elemental and compound semiconductors with small and large band gaps. Compared with the LDA Kohn-Sham eigenvalues, it is remarkable that the sX-FLAPW approach consistently improves the absolute as well as relative accuracy in computed energy band gaps. In particular, narrow band gap semiconductors such as InSb are well described whereas LDA wrongly predicts these materials to be metallic. The calculated optical absorption spectrum of GaAs demonstrates that this methodology, as applied to III-V semiconductors, achieves "engineering quality". In fact, optical absorption spectra calculated with this methodology are now being used as input into macroscopic device models.

8.5   Perspectives and Conclusions

Electronic structure methods are becoming an integral part of research and development of materials related industries such as catalyst manufacturers and electronics companies. This development is taking place about 10 to 15 years after the chemical and pharmaceutical industries started to adopt electronic structure methodology. The sequence is remarkable as it reflects the pace of methodological developments in the areas of quantum chemistry and solid state physics. The principal theoretical approach for organic molecules is based on Hartree-Fock theory as implemented in programs such as Gaussian, GAMESS and Turbomole. Automatic geometry optimisations and hence the calculation of relative molecular energies based on Hartree-Fock theory with Gaussian-type orbitals were developed around 1970, i.e. about 10 to 15 years earlier than the same capabilities with DFT methods. Since the reliable calculation of structural properties and related energies are critical for most practical applications of *ab initio* methods, this capability appears to have been a key enabling factor. The other factor is the availability and ease of use of electronic structure programs. Programs such as Gaussian and the semiempirical MOPAC program were successful because of these features. In addition, industrial organisations want to use commercially supported programs in order to save the costly time of industrial research scientists. Thus, the introduction of commercial software products is a third factor in the successful industrial deployment of a novel technology. (The same is true for experimental techniques and equipment such as the scanning tunnelling microscope.) At present, commercially supported solid state programs coexist with programs available from academic sources. This

is characteristic for the early phase of a growing field. Experience in other areas of simulation technology such as structural analysis and computational fluid dynamics show that commercial software eventually dominates as particular methodologies mature and academic research focuses on new areas.

The examples discussed in this article give a glimpse on the type of industrial problems where electronic structure methods can make a difference. These cases show that one needs to be very careful in setting expectations. If one positions electronic structure methods as a tool that can make a useful contribution in solving a variety of problems, then success can be achieved. If, on the other hand, the claim is made that this approach will suddenly change industrial research and development and replace experiment, then the harsh economic realities can cause deep disappointment and thus damage the field. Unfortunately, there were cases where this happened and it takes almost a decade to demonstrate the true value of this methodology and to rebuild confidence.

Given the incredible reduction in the cost of computing, the development of reliable and powerful electronic structure programs, and the steady progress on the fundamental theoretical level, it is safe to say that the industrial acceptance and usefulness of this methodology will grow and will become a significant part of industrial research.

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