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Surface Science 500 (2002) 347–367

SURFACE SCIENCE

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The virtual chemistry lab for reactions at surfaces: Is it possible? Will it be useful?

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Received 5 July 2000; accepted for publication 27 April 2001

Abstract

Ab initio total-energy calculations based on electronic structure theory have tremendously enlarged our knowledge about the geometrical and electronic structure of clean and adsorbate-covered low-index surfaces and reactions on these surfaces. In technological applications, however, extended flat surfaces are very rarely used. Hence the applicability of the theoretical results for the technological surfaces are indeed questionable. In this review I will reflect on the question whether ab initio calculations of reactions at surfaces can contribute to the development of, e.g., better catalysts. Simulations alone will not be able to lead to new products but it will be demonstrated that they can contribute enormously to the development process. Thus the virtual chemistry lab is indeed possible and helpful. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ab initio quantum chemical methods and calculations; Atomistic dynamics; Computer simulations; Density functional calculations; Models of surface chemical reactions; Catalysis; Sticking; Surface chemical reaction

1. Introduction

It has always been the goal of theoretical surface science to understand the fundamental principles that govern the geometric and electronic structure of surfaces and the processes occurring on these surfaces like gas-surface scattering, reactions at surfaces or growth of surface layers [1]. Processes on surfaces play an enormously important technological role. We are all surrounded by the effects of these processes on surfaces in our daily life. Some are rather obvious to us like rust and corrosion. These are reactions that we would rather like to avoid. Less obvious are surface reactions that are indeed very advantageous. Many chemical reactions are promoted tremendously if they take place on a surface that acts as a catalyst. Actually most reactions employed in the chemical industry are performed in the presence of a catalyst. Catalysts are not only used to increase the output of a chemical reaction but also to convert hazardous waste into less harmful products. The most prominent example is the car exhaust catalyst. The enormous technological relevance of catalysts is also reflected by the large worldwide demand of catalysts which, e.g., amounted to 6.4 billion dollars in 1996. More than 90% of the chemical manufacturing processes employed throughout the world utilize catalysts in one form or another [2]. And since in total chemicals worth more than

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PII: S0039-6028(01)01526-6

1,000 billion dollars are produced annually, the economic importance of catalyst development is obvious.

Traditionally catalysts have been designed and improved by a trial and error approach. For example, before the iron-based catalyst for the ammonia synthesis was found, about 10,000 different catalysts had been tried by A. Mittasch in the first decade of the century [3]. This trial and error approach is still employed nowadays. A modern version of this approach is used in Combinatorial Chemistry [4–6] where the search is automated so that a huge number of different systems can be checked within a short period of time.

Now the question arises whether theoretical surface science can contribute to technological advances in the field of processes at surfaces. In the last decade there had been a tremendous progress as far as the accurate and reliable theoretical description of the geometric and electronic structure of surfaces and the interaction of atoms and molecules with surfaces is concerned. This progress was caused partially by the improvement in computer power, but also to a large extent by the improvement of programs based on ab initio electronic structure calculations [7–11] and other methods that use information coming from electronic total-energy calculations as an input.

The information obtained by electronic structure calculations is complete and detailed enough in order to construct whole potential energy surfaces (PESs) which allows to perform dynamical simulations of the reactions. The great advantage of such calculations compared to the experiment is that the calculations can shed light on the underlying electronic factors that determine bond making and breaking processes at surfaces; in addition, one can follow the microscopic steps of a reaction while in the experiment usually only the initial reactants and final products can be determined. Using some examples I will illustrate what has been learned in recent years by modern computational simulations about reactions at surfaces.

There is one basic question for any scientific research with the claim to contribute to the technological progress. Is it better to study and discover fundamental principles and mechanisms that will in the long run be beneficial for the overall progress, or should one concentrate on the development of particular products? In my opinion there is no definite answer to this question. Often the lines are even blurred between the two approaches so that this clear distinction between a more basic and a more applied approach cannot be made. But I will show that ab initio based calculations of properties and processes at surfaces have not only tremendously enlarged our knowledge about basic mechanisms, but that they are also now accepted as a very valuable tool for the development of particular products.

Quantum chemistry methods based on Hartree–Fock theory have been an integral part of research and development in the chemical and pharmaceutical industry for more than 20 years. These methods that are based on representations of the electronic many-body wave function have also significantly contributed to our understanding of processes at surfaces (see, e.g., Refs. [12,13]). Unfortunately, wave function based methods are limited to rather small systems. Electronic structure algorithms based on density functional theory (DFT) can be applied to larger systems. The theoretical chemistry community has long been reluctant to accept DFT methods because they considered them as not accurate enough, but now DFT becomes more and more accepted due to some fundamental developments in the formulation of DFT algorithms that greatly improved the accuracy of the DFT calculations. And now even material science related industries such as catalyst manufacturers and semiconductor industries begin to realize the potential of electronic structure calculations.

The theoretical description of reactions is often much less expensive than carrying out many different experiments. Hence besides satisfying the curiosity of a scientist there is actually an economic need for the quantitative description of reaction pathways at surfaces. The computational tools are now reliable enough for a sufficiently accurate determination of chemical interactions at surfaces for many systems. I will show that the surface science approach is not only an intellectual endeavor, but that even industrially used catalysts have been developed by a combination of

theoretical and experimental surface science techniques.

In this review I will first introduce basic theoretical concepts necessary to treat processes at surfaces. Although electronic structure theory calculations based on Hartree–Fock theory continue to contribute to the field of theoretical surface science, I will concentrate on DFT because of its widespread use in the theoretical treatment of surface processes. I will give some examples of successful applications of ab initio calculations in the fields of both basic and applied research. The list of examples does not claim at all to be complete. The selection is certainly biased through my personal view, but I am convinced that the studies presented will show that a virtual chemistry lab of reactions at surfaces is indeed possible and helpful.

However, we are still far away from the development of technological products solely on a theoretical basis. It is even rather likely that this will never become possible. It is fair to say that most quantitative simulations of reactions at surfaces are still limited to rather simple systems like molecular dissociation on close-packed metal surfaces. There is plenty of room for the theoretical description of more complicated systems like reactions on structured substrates. The determination of the reaction pathways for these more complicated reactions and their dynamical simulation even may require the improvement of the theoretical tools. I will sketch the theoretical challenges that are still lying ahead for a quantitative description of reaction pathways, but also the opportunities that open up once these problems have been solved.

2. Brief sketch of electronic structure theory

The theoretical treatment of reactions at surfaces requires in principle the solution of the quantum mechanical many-body problem including all electronic and ionic degrees of freedom. In practice, this solution is not possible in closed form. However, in many chemical reactions the electrons follow the motion of the nuclei almost adiabatically due to the large mass difference. We will concentrate on reactions of this type in this review, i.e., we will assume that the Born–Oppenheimer approximation [14] is valid. This means that we can break up the theoretical description of a chemical reaction. First the electronic problem for a particular configuration of the nuclei will be solved, and only then the motion of the nuclei has to be considered.

Still the solution of the electronic problem represents a formidable task. Of central importance for the progress in the theoretical description of processes at surfaces are the recent developments in electronic structure theory. There are two main different approaches to electronic structure calculations, based on either Hartree–Fock theory or DFT. Both approaches are called first-principles or ab initio theories because in principle they do not require any empirical parameter, i.e. they are derived *from first principles*.

Electronic structure calculations based on Hartree–Fock theory determine the many-body wave function by directly solving the Schrödinger equation. They are also called wave function based methods. As far as these methods are concerned, I refer to the excellent "non-mathematical" review by Head-Gordon [7] and references therein. Wave function based methods usually describe the electrons by a localized basis set derived from atomic orbitals. Within this localized description the surface is modeled by a finite cluster. Since the computational effort scales very unfavorably with the system size in wave function based methods, these calculations are limited to a rather small number of atoms, typically about 10–20. This is often not sufficient to model an extended substrate. Cluster calculations can still yield qualitative trends, but they are "often best used for explanatory rather than predictive purposes" [7].

Electronic structure calculations based on DFT allow the treatment of larger systems. Since I focus on calculations using DFT, I will briefly sketch some fundamentals of DFT. As the name DFT already suggests, the electron density is the basic quantity in DFT [15]. The Hohenberg–Kohn theorem [16] states that the ground state expectation value of the total energy is a unique functional of the ground state electron density. Even more important is the existence of a variational principle for the energy functional, namely that the exact

ground state density and energy can be determined by the minimization of this energy functional.

This still sounds rather technical. But instead of using the many-body quantum wave function which depends on many coordinates now we only have a function of three coordinates which has to be varied. In practice, however, no direct variation of the density is performed. The density is rather expressed as a sum over single-particle states. These states are obtained by self-consistently solving effective single-particle equations, the Kohn–Sham equations [17], where the quantum mechanical many-body effects are contained in the so-called exchange-correlation potential. In principle the solution of the single-particle equation still requires the diagonalization of a rather large matrix. This diagonalization is avoided in almost all modern DFT algorithms by using the fact that the diagonalization can be regarded as a minimization problem for which many efficient algorithms exist.

The exchange-correlation potential is an universal functional of the electron density, i.e., it does not depend on any particular system. Unfortunately this non-local functional is not known; probably it is even impossible to determine it exactly in a closed form. What is known is the exchange-correlation potential for the homogeneous electron gas, i.e. for a system with a constant electron density [18]. In the so-called local density approximation (LDA), the exchange-correlation potential for the homogeneous electron gas is also used for non-homogeneous situations. At any point this local potential is used for the corresponding density, ignoring the non-locality of the true potential. Surprisingly, for many solid state systems the LDA yields rather satisfying results in good agreement with experiment. This is still not fully understood but probably due to a cancellation of opposing errors in the LDA. For chemical reactions in the gas phase and at surfaces the LDA results are not sufficiently accurate. That is the reason why many theoretical chemists were rather reluctant to use DFT for a long time. Only with the advent of exchange-correlation functionals in the generalized gradient approximation (GGA) [19–23] this situation has changed. In the GGA the gradient of the density is also included in the exchange-correlation functional, but the dependence on the gradient is modified in such a way as to satisfy important sum rules. DFT calculations in the GGA arrive at chemical accuracy (error $\leqslant 0.1$ eV) for many chemical reactions. Still there are important exceptions where the GGA also does not yield sufficient accuracy. The development of more accurate expressions for the exchange-correlation functional is certainly not finished yet.

In most molecules and materials the chemical interaction is governed by the valence electrons while the core electrons are hardly involved in the binding process. This fact is used in the pseudopotential concept [24] in which the influence of the core electrons on the other electrons is represented by an effective potential, the pseudopotential. This approach reduces the number of electrons dramatically that have to be taken into account explicitly in the calculations. Most modern DFT studies presented in this review employ the pseudopotential concept, and many large-scale computations would be impossible without the use of pseudopotentials.

There are very efficient DFT algorithms based on a plane-wave expansion of the Kohn–Sham single-particle states. These programs often originate from solid-state applications. However, they usually require a three-dimensional periodicity of the considered system. In the so-called supercell approach surfaces are modeled by periodically repeated slabs with a sufficient vacuum layer between them in order to avoid any interaction between the slabs. Furthermore, the slabs have to be thick enough to reproduce the correct electronic structure. Such a supercell geometry is shown in Fig. 1. In this approach the extended nature of the surfaces in the lateral direction is taken into account. Using this technique, modern efficient DFT algorithms can treat more than 100 [25] or even 300 [36] atoms per supercell.

3. The potential energy surface

In Section 2 we have described how the electronic structure problem can be solved for a particular configuration of the nuclei. To describe a chemical reaction, we need to know the potential energy of the system as a function of the coordi-

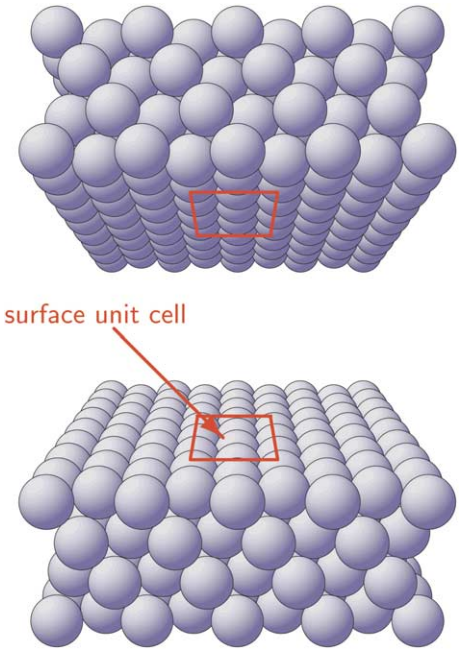

Fig. 1. Supercell approach to model surfaces: the surface is represented by a periodic stack of slabs with a sufficient layer of vacuum between them. The surface unit cell is indicated by the boxes on the surface.

nates of the reactants. This defines the PES. The PES is the central quantity in any theoretical description because all chemical processes are governed by the underlying PES.

One important concept in the discussion of chemical reactions is the reaction path which is usually defined as the minimum energy path combining the region of reactants with the region of products in the PES. A plot of the potential energy along this path reveals, e.g., the minimum energy barrier hindering a reaction. This concept is usually very helpful for understanding the thermodynamics and kinetics of a certain reaction. Furthermore, qualitative concepts can thus be explained. This is demonstrated in Fig. 2 where the concept of catalysis is illustrated for a certain reaction $A + B \rightarrow AB$. This reaction might be hindered in the gas phase by a large barrier. In the presence of the catalyst the barrier is strongly reduced so that the reaction proceeds much more efficiently.

However, simple one-dimensional representations of the energetics are often oversimplifying

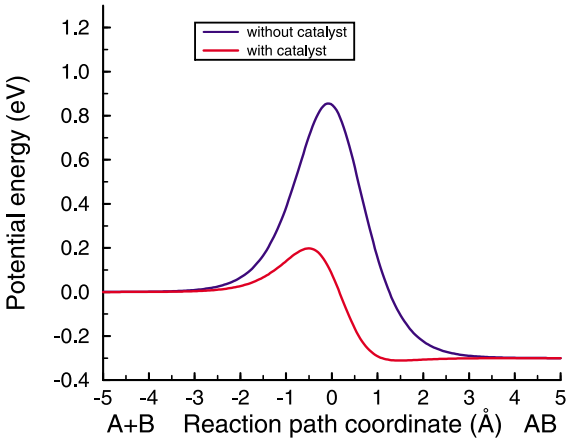

Fig. 2. Schematic drawing of the energetics along the reaction path for the reaction $A + B \rightarrow AB$ without and in the presence of a catalyst.

the reaction mechanism and can be rather misleading. For example, Fig. 2 suggests that the presence of a catalyst simply leads to a reduction of the reaction barrier, nothing else. However, most often the reduction of the barrier is achieved through some additional intermediate reaction steps like the adsorption of the reactants on the catalyst. In a pictorial way one could say that the presence of the catalyst makes a detour in the multidimensional PES possible that has smaller barriers than the direct route.

Hence for a proper discussion of a chemical reaction the multidimensionality of the relevant PES has to be taken into account. One example of the multidimensionality of the PES is shown in Fig. 3. These two-dimensional cuts through the PES are derived from DFT calculation of the adsorption of O_2/Pt(1 1 1) by Eichler and Hafner [27]. The notation above the figures characterizes the dissociation path. For example, top–bridge–top orientation means that the center-of-mass is fixed over the bridge site and the two O atoms are oriented towards the top sites. The dissociation path is also illustrated in the insets in Fig. 3. These figures do not, however, correspond to the number of atoms considered in the calculations. As mentioned in the last section most DFT algorithms used nowadays for surface science studies employ a plane-wave basis set which requires a

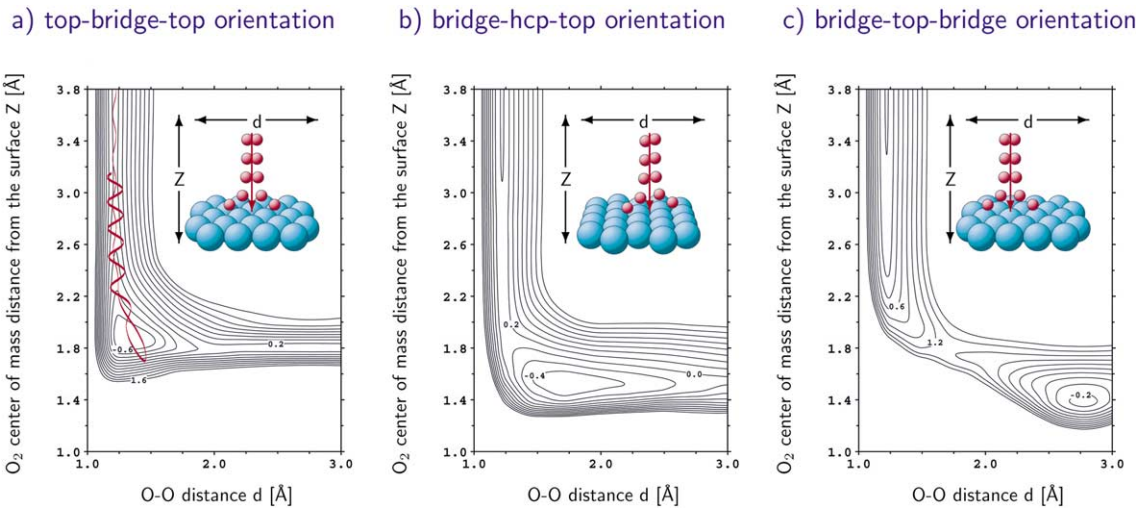

Fig. 3. PES of the dissociation of O_2/Pt(1 1 1). The coordinates in the figure are the O_2 center-of-mass distance from the surface Z and the O–O interatomic distance d. The insets illustrate the orientation of the molecular axis and the lateral O_2 center-of-mass coordinates. For the notation above the figures see the text. Energies are in eV per O_2 molecule. The contour spacing is 0.2 eV. The contour plots are derived from DFT calculations by Eichler and Hafner [27]. In (a) a trajectory of an O_2 molecule scattered at Pt(1 1 1) is also plotted.

three-dimensional periodicity of the calculated structures. In supercell calculations typically slabs are used that are between three and 10 layers thick while the periodic surface unit cell contains usually less than 10 atoms.

Even for a rather simple reaction like molecular adsorption and dissociation on a close-packed metal surface, the PES shows a strong dependence on the lateral coordinates of the molecular center-of-mass. While molecular adsorption above the bridge and the three-fold hollow sites is non-activated, above the top site the molecular adsorption is hindered by a barrier of more than 1.2 eV. What is not illustrated in Fig. 3 is the anisotropy of the PES. In the upright orientation the O_2 molecule cannot adsorb, i.e., the PES is repulsive.

Although the PES is an abstract object, the movement of the corresponding reactants on a PES can be understood and analyzed in very simple terms. An illustration is shown in Fig. 3a where also a trajectory of an O_2 molecule is plotted. This molecule is initially non-vibrating, but after the scattering process it is vibrationally excited. This can be inferred from the oscillating trajectory which corresponds to the molecular vibration. Furthermore, it is rather obvious that if the molecule is already initially vibrating, i.e., if it is oscillating back and forth in the d-direction, then it will be easier for the molecule "to make it around the curve" and enter the dissociation channel. This is called vibrationally enhanced dissociation [28] and was already realized 30 years ago [29].

One note of caution should be added. Total-energy calculations only yield a finite number of potential energies. Hence plotted PESs like in Fig. 3 always involve an interpolation scheme between the actual calculated points. If the grid of ab initio points is rather sparse then large regions of the PES are actually determined by the interpolation scheme and not by the actual calculations. Sometimes different interpolation schemes can give surprisingly varying results. In principle always the grid of the calculated ab initio points and the interpolation scheme should be reported, however, this is hardly ever done. The PES in Fig. 3 has actually been calculated by a tight-binding interpolation scheme [30], and the tick marks at the axes correspond to the chosen grid.

If many degrees of freedom are involved, PESs are often too complex to be mapped out in detail. Furthermore, for kinetic simulations not the whole

PES is of interest but rather the minimum energy barrier hindering a certain transition or reaction. In such a situation the saddle points in the multidimensional PES yield the relevant information. Once these saddle points are located, transition rates can be approximated via transition state theory [31]. There is no unique way to find a saddle point between two minima of the PES. However, powerful methods have been developed for climbing up the PES from minima to saddle points (see, e.g., Refs. [32,33]). These methods are often already part of standard ab initio electronic structure packages.

Another complimentary way of illustrating a reaction path obtained by ab initio calculations is to plot some atomic positions along this path. This is shown for the case of the CO oxidation on Ru(0 0 0 1) in Fig. 4 [34]. The sequence of snapshots shows how the CO axis is tilted and the atoms are lifted during the oxidation process. However, these snapshots do not yield any information about the energetics along the reaction path.

For a deeper understanding of a particular reaction the knowledge of the PES alone is usually not sufficient. One should rather analyze the electronic and geometric factors that lead to the specific topology of a PES. Fortunately total energy calculations also yield information on the electronic density and structure. Charge density plots are a good tool to analyze the interaction and hybridization of the chemical bonds between the reactants. We will show an example in Section 4.

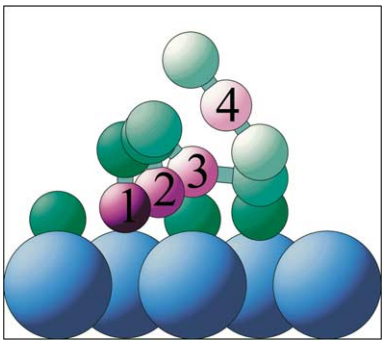

Fig. 4. Atomic positions along the reaction path of the CO oxidation on Ru(0 0 0 1). The blue, purple and green circles denote the Ru, C and O atoms, respectively (from Ref. [34]).

Furthermore, an analysis of the density of states (DOS) for different configurations is also very helpful in understanding the reasons for the specific topology of a PES, for example, why and where energetic barriers in bond breaking or making processes are formed. However, the interpretation of a DOS evaluated from the Kohn–Sham eigenvalues of DFT calculations does not rest on firm theoretical grounds. The Kohn–Sham one-particle energies enter the theory as Lagrange multipliers ensuring the normalization of the wave functions; thus they correspond to quasiparticles with no specific physical meaning except for the highest occupied state [15]. Still it is almost always taken for granted that the Kohn–Sham eigenenergies can be interpreted, apart from a rigid shift, as the correct electronic one-particle energies. This is justified by the success since the Kohn–Sham eigenenergy spectrum indeed very often gives meaningful physical results, as will be shown later in this review.

4. Applications of first-principles calculations to reactions at surfaces

In this section I will illustrate the contribution that first-principles calculations have made to our understanding of reactions and processes at surfaces. First I will focus on fundamental studies in the field of theoretical surface science. Then I will show that nowadays first-principles studies, in particular DFT calculations, are advanced enough to even contribute to the development of technological products.

First I will review the situation in the early nineties and report on some of the first spectacular results of ab initio studies of hydrogen dissociation on clean flat surfaces. I will then proceed to some very recent examples of fundamental studies in which surface imperfections like steps and adatoms are considered. These studies represent the cutting edge of modern research. They show how far applications of electronic structure calculations can go, and at the same time they demonstrate what is just possible with modern algorithms and computers. Hence these examples can be regarded

as an outlook; they also indicate the direction further ab initio investigations will take.

4.1. Basic research

In the early 1990s the computer power and the development of efficient electronic structure algorithms had been improved enough so that for example hundreds of DFT calculations with a few tens of atoms in a repeated supercell structure (see Fig. 1) became feasible on workstations. This made the calculation of the PES of simple reactions like the dissociative adsorption of hydrogen on metal surfaces possible [35–40]. In these calculations the surface is represented by a repeated slab structure separated by a sufficiently wide region of vacuum between the surfaces so that there is no interaction between the slabs. The first ab initio studies of molecular dissociation at surfaces mainly focused on hydrogen dissociation, the main reason being that the interaction of hydrogen with surfaces can be well-studied experimentally as well as theoretically [28,41]. This established the role of hydrogen adsorption as a model system where a fruitful interaction between theory and experiment has been possible.

One of the surprising results of these studies was that the PES of hydrogen dissociation on close-packed metal surfaces is highly corrugated. Before, it was anticipated that the PES depends only very weakly on the location of the molecule in the surface unit cell since the electron density in front of metal surfaces is rather smeared out [42,43]. This picture of a flat, structureless surface was seemingly confirmed by the experimentally found normal energy scaling of the sticking probability [44–46], i.e., the parallel component of the incident kinetic energy seemed to have no influence on the sticking. However, the bond-breaking process during the dissociative adsorption involves the hybridization of chemical bonds which has a rather localized nature.

The results of the ab initio calculations motivated new efforts in the dynamical simulation of processes at surfaces. These simulations have to be done quantum mechanically due to the light mass of hydrogen. For the dissociation of hydrogen on close-packed metal surfaces the recoil of the substrate atoms is usually negligible due to the large mass mismatch between the impinging hydrogen molecule and the metal atoms. Hence the hydrogen dissociative adsorption can be simulated within a six-dimensional PES corresponding to the six molecular degrees of freedom and fixed substrate atoms. Taking into account all hydrogen degrees of freedom quantum mechanically in a dynamics calculations was until recently still considered to be computationally impractical [47,48]. In the first studies the dynamics calculations were still performed in a restricted geometry, but the PES used in these simulations had features derived from electronic structure calculations [49–51]. One of the first successes of dynamics calculations based on a PES derived from ab initio calculations was the reconciliation of normal energy scaling with strong corrugation. Darling and Holloway showed [49] that for a special form of corrugation termed "balanced" corrugation [28] where the higher barriers are further away from the surface than the lower ones the effects of the corrugation for non-normal incidence of the impinging molecular beam effectively cancel. These features are indeed present in the calculated PES of H_2/Cu [35,36].

In 1995, the first dynamical study of hydrogen dissociative adsorption was performed in which all hydrogen degrees of freedom were treated quantum mechanically [52] using a time-independent coupled-channel scheme [53]. This study not only represented a technical achievement, but it also led to a new qualitative picture of hydrogen dissociation at reactive transition metal surfaces. In these systems the hydrogen sticking probability often shows an initial decrease as a function of the kinetic energy of the impinging molecules. Such a behavior is typical for molecular adsorption, i.e. non-dissociative sticking, because molecular adsorption is determined by the energy transfer to the surface which becomes less efficient at higher kinetic energies. Hence the canonic interpretation of a decreasing sticking probability in *dissociative adsorption* was a *precursor model*: before dissociation the molecule has to be trapped in a molecular adsorption state, the precursor to dissociation, and it is the trapping probability that determines the overall sticking probability.

The system chosen for the first six-dimensional quantum dynamical study, H_2/Pd(1 0 0), indeed showed an initially decreasing sticking probability in the experiment [54]. However, the ab initio PES [37] on which the dynamical study was based did not exhibit any indication of a molecular precursor state. Still the dynamical calculations reproduced the experimentally observed trend of the sticking probability as a function of the initial kinetic energy of the hydrogen molecules.

The advantage of a computer simulation compared to an experiment is that the simulation is performed under well-defined conditions and can be analyzed at any point of the simulation. This analysis showed that the initially decreasing sticking probability is caused by a dynamical process which had been proposed before [55] but whose efficiency had been grossly underestimated: dynamical steering. This process can only be understood if one takes the multidimensionality of the PES into account. The PES of H_2/Pd(1 0 0) shows purely attractive paths toward dissociative adsorption, but the majority of reaction paths for different molecular orientation and impact points exhibits energetic barriers hindering the dissociation. This coexistence of activated and non-activated paths is similar to the situation in the system O_2/Pt(1 1 1) plotted in Fig. 3.

At very low kinetic energies the particles are so slow that they can be very efficiently steered to a favorable configuration for dissociation. This leads to a very high dissociation probability. Since this mechanism becomes less effective at higher kinetic energies, the reaction probability decreases. This scenario is illustrated in Fig. 5 where snapshots of two classical molecular dynamics runs of H_2/Pd(1 0 0) on the PES based upon the ab initio results [37] are shown. The trajectories have the same initial conditions except for the kinetic energy. The initially non-rotating molecules approach the surface in an almost upright orientation in which the interaction with the surface is purely repulsive. However, in Fig. 5(a) the molecule is so slow ($E_{kin} = 0.01$ eV) that the torque acting upon the molecule is able to turn the molecule in a parallel orientation so that the molecule can directly dissociate. If the molecule is much faster as in Fig. 5(b) ($E_{kin} = 0.12$ eV), the rotation to the favorable parallel orientation cannot be completed, the molecule hits the repulsive wall of the potential and is scattered back to the gas phase.

The efficiency of the steering effect was also confirmed in an independent theoretical study [56]. Furthermore, predictions of the dependence of the reaction probability on the molecular rotation and

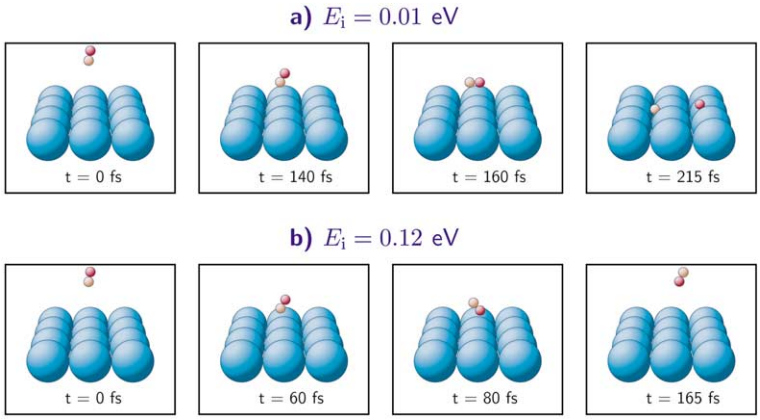

Fig. 5. Illustration of the steering effect. The figures show snapshots of classical molecular dynamics runs of H_2/Pd(1 0 0) on a PES based upon ab initio results. Both trajectories have the same initial conditions except for the kinetic energy which is 0.01 eV in (a) and 0.12 eV in (b). Initially the molecules are not rotating. The slower molecule is turned to a parallel orientation which is favorable for dissociation while the faster molecule hits the repulsive wall of the potential before the re-orientation is completed and is scattered back into the gas phase.

orientation based on the ab initio dynamics calculations [52] have later been confirmed experimentally [57–59]. In the meantime, hydrogen dissociation in the activated systems H_2/Cu(1 0 0) [60,61] and H_2/(2 × 2)S/Pd(1 0 0) [62] has also been treated with six-dimensional quantum dynamics calculations on PESs derived from DFT calculations.

Calculations of the reaction dynamics based upon PESs derived from DFT calculations are not only important for a deeper understanding of the reaction mechanism. In fact they also serve as a check of the accuracy of the DFT calculations. The information obtained from static total energies is often not sufficient to really judge the quality of the calculated PES. In the experiment the PES is never directly measured but the consequences of the PES on reaction rates and probabilities. For a true comparison with experiment also reaction rates and probabilities have to be derived from the calculated PESs. For a more detailed discussion of the theoretical treatment of reaction dynamics see the contribution by Bonn et al. in this volume [63].

In contrast to close-packed metal surfaces, semiconductor surfaces show a strong surface rearrangement upon hydrogen adsorption. This is caused by the covalent nature of the bonding in semiconductors where an additional chemisorbed adsorbate strongly perturbs the bonding situation of the substrate. Hydrogen on silicon has become the model system for the study of adsorption on semiconductor surfaces [1,64]. This system is not only interesting from a fundamental point of view, but also because of its technological relevance. Hydrogen desorption is the rate determining step in the growth of silicon wafers from the chemical vapor deposition (CVD) of silane. We will address this system also in the next section. Here we focus on fundamental aspects of the adsorption and desorption process of hydrogen on Si(1 0 0).

The so-called barrier puzzle has caused a great interest for this system: While the sticking coefficient of molecular hydrogen on Si surfaces is very small [65,66] indicating a high barrier to adsorption, the low mean kinetic energy of desorbed molecules [67] suggests a small adsorption barrier. This puzzle was assumed to be caused by the strong surface rearrangement of Si upon hydrogen adsorption [67]: The hydrogen molecules impinging on the Si substrate from the gas phase typically encounter a Si configuration which is unfavorable for dissociation, while desorbing hydrogen molecules leave the surface from a rearranged Si configuration with a low barrier.

It was immediately realized that the large influence of the dissociation barrier on the substrate configuration should cause a strong surface temperature dependence of the hydrogen dissociation probability on Si [68]. This predicted strong dependence was indeed confirmed experimentally [66,69,70]. Still it turned out later that the solution of the barrier puzzle involves a much more complex scenario taking into account surface structure and coverage effects, as will be shown below.

As for the ab initio calculations, H_2/Si(1 0 0) is a system that initially was studied extensively by quantum chemical methods in which the extended substrate was modeled by a finite cluster [71–73]. Due to the localized nature of the covalent bonds in semiconductors it was believed that the cluster description for a Si surface might be appropriate. These cluster studies could not reproduce the experimentally observed activation energy for H_2 adsorption from Si(1 0 0) for a clean surface. Therefore defect-mediated desorption mechanisms had been proposed [71,73,74]. DFT calculations based on the slab approach, however, were in good agreement with experiment, as far as the desorption energy was concerned [75–77]. There were speculations whether the difference between cluster and slab calculations was due to the different treatment of the electron exchange-correlation [78]. A later study showed [79] that one has to use rather large clusters to appropriately model the extended Si substrate. The slab approach is more efficient for representing semiconductor surfaces and consequently becomes more and more accepted [80]. However, all GGA functionals used nowadays have limitations as far as their accuracy is concerned [78]. Hence the development of improved exchange-correlation functionals still represents a very active area of research (see below).

The situation was not only confusing from the theoretical side, but also experiments of the adsorption of H_2/Si(1 0 0) showed large quantitative differences [65,70]. However, slowly a consistent picture of the interaction of hydrogen with Si(1 0 0) is emerging that is able to explain even the sometimes seemingly contradictory results [81,82]. This progress in the understanding has been achieved in a close collaboration between experiment and electronic structure calculations. It was realized that it is very important to determine the exact surface structure. At surface imperfections like steps the reactivity of a surface can be extremely altered. Indeed it was found experimentally on vicinal Si(1 0 0) surfaces that the sticking coefficient at steps is up to six orders of magnitude higher than on the flat terraces [83]. This finding was supported by DFT studies which showed that non-activated dissociation of H_2 on the so-called rebonded D_B steps on Si(1 0 0) is possible [25,83], while on the flat Si(1 0 0) terraces the dissociative adsorption is hindered by a barrier of 0.4 eV [77].

Indeed adsorbates can have a similar effect on the dissociation probability as steps since the electronic structure of the dangling bonds is perturbed in a similar way by both steps and adsorbates [81]. Recent scanning tunneling microscope experiments demonstrated that predosing the Si(1 0 0) surface by *atomic* hydrogen creates active sites at which the H_2 adsorption is considerably facilitated [84]. Actually the predosing of atomic hydrogen makes the adsorption of H_2 in an *interdimer* configuration possible, an adsorption configuration that is energetically unfavorable on the clean Si(1 0 0) surface compared to the *intradimer* pathway [85] (recent DFT calculations using large surface unit cells to avoid elastic strain, however, obtain the opposite result [81]).

Electronic structure calculations cannot only yield information on the energetics of a particular configuration or reaction pathway, but they can also provide an analysis of the underlying electronic structure that contributes to the PES. This is illustrated in Fig. 6 for the H_2 interdimer adsorption path on the Si(1 0 0) surface where one additional H atom acts as spectator. In order to understand the influence of this additional atom, charge density isosurfaces for single bands are plotted. The isosurfaces correspond to a density of 0.005 electrons/bohr^3, and the states are characterized by their eigenenergies.

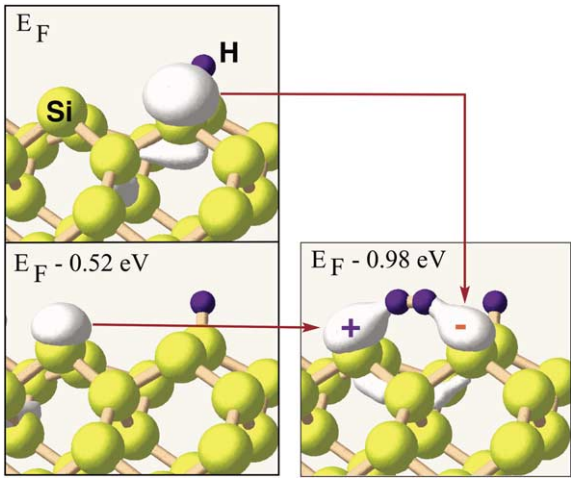

Fig. 6. Charge density isosurfaces of single bands illustrating the H_2 dissociation mechanism on a Si(1 0 0) surface along the interdimer reaction path where one adsorbed H atom on one of the Si dimers acts as a spectator. Left panel: clean surface before H_2 adsorption; right panel: at the transition state geometry (courtesy of E. Pehlke).

The left panel shows the dangling bond states of the interdimer Si atoms before the adsorption of the H_2 molecule. These states are at the Fermi energy and 0.5 eV below the Fermi energy. The right panel of Fig. 6 exhibits the charge distribution of the state 1.0 eV below the Fermi energy at the transition state to dissociation where the H–H bond breaks. The phase relation between both dangling bonds is indicated by the + and − sign. By a representation like this the chemical nature of bonds that are broken respectively formed during a dissociation process at a surface can be nicely analyzed.

Not only on semiconductor surfaces, but also on metal surfaces, surface imperfections can modify the reactivity enormously. Some of these surface imperfections are illustrated in Fig. 7. This scenario corresponds to a snapshot of different molecules in front of a close-packed surface with a straight step. In addition, atoms of another sort are incorporated substitutionally into the surface. These additional atoms may form an ordered alloy

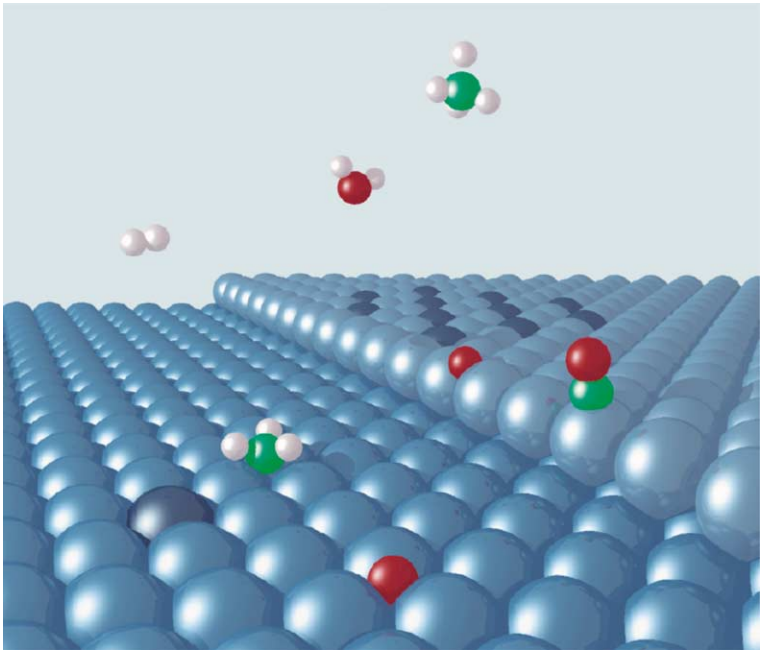

Fig. 7. Schematic scenario of different kinds of molecules in front of a surface with surface imperfections like steps or substitutionally incorporated adsorbates (courtesy of B. Hammer).

structure (see the dark atoms on the upper terrace in Fig. 7).

While most surface science studies deal with well-characterized low-index surface planes, real catalysts are usually highly dispersed as small particles in order to increase the active surface area. This is commonly called the "structure gap". The catalyst is often microcrystalline, the surface is not well ordered but consists of microfacets with a lot of surface imperfections. Thus, ab initio investigations of active sites at non-perfect surfaces are already rather close to applied research since they contribute to close the structure gap.

Later in this review I will give an example of the effect of alloying on the activity of a catalyst. Here I focus on the influence of steps. A DFT study of the NO dissociation at corrugated Ru(0 0 0 1) [86] has demonstrated the tremendous effect of steps on the reactivity at surfaces. Atoms at steps have a lower coordination number than at terraces. At transition metal surfaces this leads to an upward shift of the metal d states and causes a stronger bonding to NO-2π orbitals [86]. Thus the NO molecular chemisorption is stabilized at the Ru steps with respect to the flat Ru surface by about 0.4 eV. Even much more dramatic is the effect of the Ru steps on the NO dissociation. While the dissociation of NO on flat Ru(0 0 0 1) is hindered by a barrier of 1.3 eV, on a corrugated surface with steps along the $[1\,0\,\bar{1}\,0]$ direction the barrier is reduced to 0.15 eV. Assuming an Arrhenius behavior of the reaction, this corresponds to an increase in the reaction rate by 20 orders of magnitude at room temperature. At a surface with even a small amount of steps the dissociation on the steps will dominate the overall reactivity. Consequently, the diffusion to the step which is hindered by energy barriers of about 0.5 eV will be the rate limiting step.

Note that the calculations reported in Ref. [86] did not correspond to the geometry shown in Fig. 7. The terraces used in these calculations were actually only four atom rows wide. This is, however, sufficient to differentiate between dissociation on the terraces and the steps. Electronic structure calculations do not only yield numbers, they also help to understand the particular reason for this

strong reduction in the barrier height. The energy of the barrier can be decomposed into an interaction energy between the two reactants N and O and the bonding energy of the reactants alone. By this decomposition it was shown that it is mainly the increase in the bonding energy of the atomic fragments that causes the dramatic reduction in barrier height [86]. Additionally, at the steps the dissociating atoms do not share nearest neighbor surface atoms. This reduces the repulsion between the reaction products and further reduces the dissociation barrier.

In recent years the focus of ab initio studies of reactions on surfaces has shifted from hydrogen dissociation to reactions involving oxygen [34,87–90]. These important class of reactions is technologically very important, for example in the context of the car exhaust catalyst. Since these reactions are covered by another contribution in this volume [91], I will not discuss them here any further.

4.2. Applied research

The examples shown in this review so far have been devoted to the study of fundamental processes at surfaces. The number of atoms that were considered in these studies per periodic cell were well below 100. Unfortunately, almost no technical device exhibits perfect structures on a large length scale. Therefore the question arises whether electronic structure calculations for periodic structures have any relevance for the development of real products?

Indeed there are already companies that prosper by applying combinatorial technologies to discover and develop new materials for the chemical and electronic industry [6]. In this approach a vast number of microscale quantities of compounds is created and automatically tested. However, the preparation and performance of new materials can often not be tested with microscale quantities. For example, a new lubricant still has to be tested under realistic conditions in an engine. An excellent discussion of this issue has been given by Wimmer et al. [3]. They demonstrate that for the development of a catalyst that contains five elements one could end up with about 50,000 combinations. If one additionally considers different preparation methods and performance conditions, easily about one million experiments have to be carried out. This is a formidable task, even with modern automated synthesis and screening methods. Hence computational methods that at least noticeably reduce the number of experiments which have to be performed can have a sizable economic impact. Thus the goal of the computations is not to create a new product theoretically from the scratch, but much more humble, namely "to add more relevant information" [3] for the research and development process.

The authors of the cited article [3] were actually employed by a company that offers computational software; hence they might be slightly biased as far as the quality and impact of their products is concerned. Still they give very convincing examples of the contribution that calculations can make (although they are faced with the problem of confidentiality that always comes up when industrial products are involved). The first example they give is concerned with an iron-oxide based catalyst. In this catalyst Cr had to be replaced because under production conditions it was oxidized to Cr(VI) which is rather poisonous. In electronic structure calculations the influence of Cr on the oxidation state of the Fe atoms in the iron oxide catalyst material was studied. This helped to establish a ranking among possible Cr substitutes that were then tested in experiment thus providing an efficient strategy for the testing.

Another example of applied research using ab initio methods was actually performed by scientists employed by the electronic industry [92]. The materials for electronic devices are rather well characterized which is a great advantage for the application of electronic structure methods. As we have already learned in the last section, hydrogen desorption is often the rate limiting step in the CVD growth of semiconductor devices. Currently there has been growing interest in SiGe alloys as a material for high speed electronic devices. It has been observed experimentally that already small amounts of Ge incorporated into a Si surface significantly enhance the deposition during CVD growth. This is caused by the fact that the presence of Ge facilitates the desorption of hydrogen which then creates additional surface sites for deposition.

Hydrogen on pure Ge is less strongly bound than on pure Si. However, it was not clear whether the presence of Ge in the SiGe alloys globally lowers the barriers for hydrogen desorption or whether hydrogen desorbs locally from the Ge sites so that first hydrogen diffusion to these sites is required. Using clusters with 35 Si and/or Ge atoms, barriers for hydrogen diffusion and desorption were determined by DFT calculations [92]. It was found that the barriers for diffusion from Si to Ge are indeed smaller than the barriers for hydrogen desorption from the Si sites. Thus the surface diffusion on mixed SiGe surfaces leads to an enhanced desorption via Ge surface sites. The calculated barrier heights were then implemented into a kinetic reactor model [92]. The computed growth rates were in rather good agreement with experiments. The authors of this article conclude that ab initio electronic structure calculations "provide access to data where measurements would be much more time consuming, expensive, and sometimes basically not possible".

Ab initio calculations have also been performed in the industry in order to determine the electronic structure of compact low pressure discharge fluorescent lamps [93]. The fluorescent lamp cathode surfaces consist of tungsten because of its high melting point. It is usually coated by some alkaline earth-metal oxide in order to reduce the work function. The emitter material has to exhibit a good thermal stability due to the high operation temperatures of 1000–1500 K. Because of these severe constraints, it is very important to understand the oxide–substrate interaction for further cathode development.

The researchers at the company that manufactures the fluorescent lamps chose the BaO/W(001) system to study this interaction. They performed DFT slab calculations in the $c(2 \times 2)$ geometry using a five layers thick tungsten slab. This geometry is shown in Fig. 8, the box in the top view of Fig. 8(B) indicates the surface unit cell.

This study demonstrates the ability of DFT calculations for analyzing the electronic structure of a particular system. The DOS for the clean and BaO covered tungsten surface is plotted in Fig. 8(C). As already mentioned in Section 2, there is no firm theoretical justification for interpreting the Kohn–Sham eigenvalues as the electronic one-particle energies that can be measured for example by photoemission studies. However, the peaks in the Kohn–Sham DOS of the clean surface in Fig. 8(C) at -0.8 and -4.2 eV can be identified with surface resonances obtained in photoemission experiments [94]. An agreement like this lends credibility to the analysis of the DOS from DFT calculations.

As Fig. 8(C) shows, these surface resonances are strongly perturbed by the presence of BaO. A state-resolved analysis of the DOS shows [93] that the large increase in the DOS between -5 and -3 eV is mainly due to oxygen 2p states that interact with the W surface resonance at -4.2 eV. Furthermore, the Ba d states which are unoccupied in the free Ba atom are shifted down and partially occupied. They strongly hybridize with the W d states leading to a covalent bond. This transfers electronic charge into the interface between the adlayer and the substrate atoms and induces a dipole moment that causes the reduction of the work function. At the same time it stabilizes the surface–adsorbate bonding leading to the high thermal stability of the BaO coating. Insights like these in the microscopic origins of the work function reduction and high thermal stability of adlayers will be very helpful for the future cathode materials development.

Finally I like to turn to a celebrated success story [95] which is one of the first examples where a close collaboration between fundamental academic research, both experimental and theoretical, and industrial development has led to the design of a successful catalyst for the steam-reforming process. This impressive success will be reviewed elsewhere in this volume [96]. Besides, just recently a very detailed review about this subject has been published [97]. Here I will focus on the contribution of electronic structure calculations [95,98] to the design of the catalyst.

In the steam-reforming process, hydrocarbon molecules (mainly CH_4) and water are converted into H_2 and CO. This is a very important process since it is the first step for several large scale chemical processes as ammonia synthesis, methanol production or reactions that need H_2 [97]. The catalysts usually used for this reaction are based

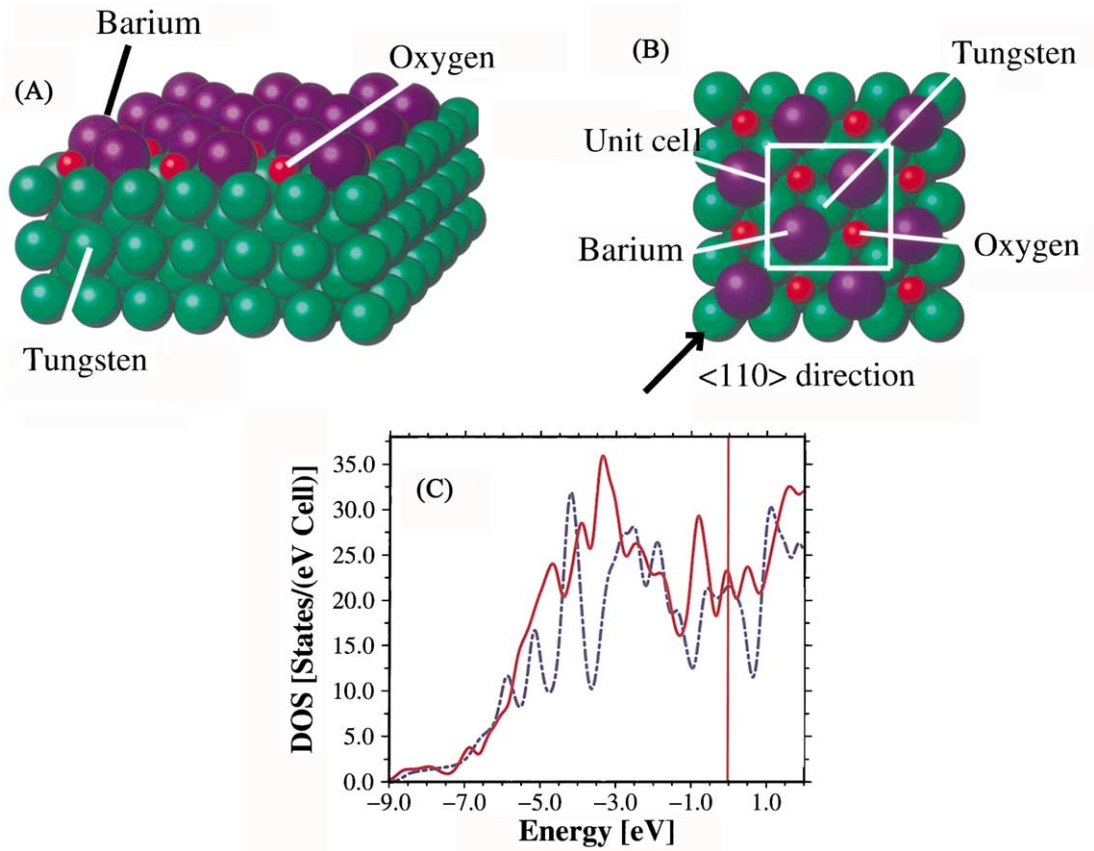

Fig. 8. Atomic geometry and electronic structure of c(2 × 2)-BaO/W(0 0 1): (A) Side view and (B) top view of the atomic geometry used in DFT calculations [93]. The box in (B) indicates the surface unit cell. (C) Calculated DOS of the clean (dashed blue line) and the BaO covered (solid red line) W(0 0 1) surface. The vertical red line indicates the Fermi energy (after [93]).

on Ni. However, during the catalyzed reaction also an unwanted by-product, namely graphite, is formed. A graphite overlayer on the Ni surface leads to a poisoning of the reaction, i.e., it lowers the activity of the catalyst. Such poisoning processes are very costly since they reduce the time the catalyst can be used and require a more frequent maintenance of the reactor unit in the chemical plant.

One way of changing the reactivity of metal surfaces is to modify their chemical composition by alloying them with other metals. Some metals that are immiscible in the bulk may still be able to form alloys at the surface. Au and Ni is such a system. The rate limiting process in the steam-reforming process on Ni is the dissociation of CH_4 into CH_3 and H. DFT calculations by Kratzer et al. showed that this process is hindered by a relatively high barrier of 1.1 eV on Ni(1 1 1) [98]. If a Ni atom on the (1 1 1) surface has one or two Au atoms as neighbors, this barrier is even increased by 165 and 330 meV, respectively. Due to the fact that Au is a noble metal, the CH_4 dissociation barrier over the Au atom is even much higher [95]. An analysis of the calculated electronic structure revealed that the presence of neighboring Au atoms leads to a downshift of the d states at the Ni atom which reduces the reactivity at the Ni atoms [99]. Hence alloying a Ni surface with Au atoms leads to a reduced activity of the catalyst. However, DFT calculations also demonstrated [95] that the presence of the Au atoms lowers

the chemisorption energy considerably for C atoms on Ni. If carbon is less strongly bound to the surface, the formation of CO becomes more likely which prevents the building up of a graphite layer.

Altogether, the DFT calculations showed that the lowering of the C chemisorption energy by alloying Ni with Au is much more effective than the increase of the CH_4 dissociation barrier. Hence one ends up with a catalyst that is slightly less reactive but much more robust and stable due to its higher resistance to graphite formation. These fundamental theoretical results together with experimental studies have led to the design of a new catalyst that is now patented [97].

5. Conclusions and outlook

The two preceding sections about basic and applied research have been devoted to examples of successful theoretical surface science studies. They have indicated the deep insight that can be gained into surface processes by electronic structure calculations based on DFT. Such methods are not only used by academic researchers but become more and more accepted by industrial researchers as a valuable and versatile tool in the research and development process.

However, not all materials and systems can be addressed with the same level of accuracy by electronic structure methods; there are still severe problems and strong limitations associated, in particular with DFT calculations. In the following I will sketch some of the problems. These problems represent very challenging tasks where still a lot of work is to do. But they also offer many opportunities for ambitious projects that might be very rewarding.

As already mentioned in Section 3, usually well below 100 atoms are considered either in the periodic supercells or in the finite clusters representing surfaces in electronic structure calculations. Consequently, most studies are still concerned with highly ordered structures. For example, in calculations of stepped surfaces the distance between the steps is usually two to four atom rows [86,100]. Since the stress field of line defects vanishes only logarithmically with distance and also electronic perturbations can be rather long ranged [26,101], there is still an interaction present between the steps in these studies. Furthermore, nanotechnology is one of the most exciting research fields nowadays. But the supercells are still not large enough to model "real" nanostructures since the dimensions of the surface unit cell are in general <10 Å. One very active experimental research subject is the study of supported model catalysts where the active sites are metal particles grown by vapor deposition on clean and well-defined oxide surfaces. The size dependence of the electronic structure and reactivity of these clusters is hardly understood yet [102,103]. There is certainly a demand for theoretical support. However, electronic structure calculations of supported clusters so far have been limited to very small clusters of less than ten atoms that are not really relevant for metal catalysts [102]. One very demanding, but important technological field is the development of sensors where only first applications of electronic structure theory have been performed [104].

In order to be able to address larger systems with first-principles calculations one can either wait for faster computers or try to improve the algorithms. One example of a very successful improvement is the development of ultrasoft pseudopotentials by Vanderbilt [105] which made it possible to use much smaller energy cutoffs, i.e. much smaller plane-wave basis sets, in the supercell calculations. Many DFT studies including transition metals which have rather localized d states actually use these ultrasoft pseudopotentials [27,86,88,100].

Another possibility to make the calculations faster is to run them in a massively parallel fashion on many processors. Usually the communication, i.e. the exchange of data, between different processors is the computational bottleneck in massively parallel implementations. In this context so-called O(N) (order N) methods are rather well suited [106]. These methods take advantage of the localization properties of the fundamental interactions in materials [107]. Thus they are able to exhibit linear scaling with respect to the size of the system. Due to the locality of the algorithm only little communication is needed between the

processors which treat each some localized region of the system. However, O(N) applications so far have mainly used tight binding [108] or semiempirical methods. This is due to the fact that O(N) methods which use DFT still have certain shortcomings that require some algorithmic progress [106]. Another way to address larger systems is to use multiscale modeling techniques in which different aspects of a certain system are treated within different levels of microscopic accuracy. Such multiscale approaches are presented elsewhere in this volume [91,109].

Progress is also still needed as far as the exchange-correlation functionals used in DFT calculations are concerned. While quantum chemists using DFT prefer exchange-correlation functionals that are fitted to a number of reference reactions in the gas phase [19,20], physicists rather rely on functionals that are derived without any adjustment of parameters [21,22]. However, Hammer et al. [23] have shown that within the construction of the widely used PBE functional [22] there is a certain freedom in the interpolation scheme. Results obtained with different GGA functionals that follow the same construction can have discrepancies by up to 0.5 eV as far as chemisorption and dissociation energies are concerned [23]. This is certainly a very unsatisfying situation. There are attempts to improve the accuracy of the functionals, for example by constructing so-called meta-GGAs [110]. But they require a second order gradient expansion which makes them computationally less efficient so that they have not found a wide-spread recognition. Particularly problematic for present GGA functionals are oxygen systems. For example, the binding energy of O_2 comes out wrong in DFT pseudopotential calculations by more than 0.4 eV [23].

All examples of ab initio studies presented in this review so far were devoted to electronic ground state properties; consequently the Born–Oppenheimer approximation was used for dynamical simulations. But very interesting physics and chemistry is concerned with processes involving electronic excitations [111]. Ordinary DFT methods, for example, are not well suited to address electronically excited states. Here wave function based calculations are the method of choice at the moment [112]. One very promising approach to treat excited states is based on time-dependent DFT [113], other attempts employ the so-called GW approximation [114,115]. However, the algorithms based on these approaches are still not mature enough to allow a complete detailed description of reactions at surfaces with electronic excitations. This means that there is plenty of room for further research.

A problem closely related to the treatment of excited states is the fact that band gaps are grossly underestimated in DFT calculations based on LDA. In the LDA, the Si band gap is only half the experimental value while Ge even turns out to be metallic instead of being a semiconductor. This is a severe limitation for, e.g., the study of optoelectronic materials where an accurate description of optical excitation energies is needed [3]. There have been several attempts to tackle this problem like the screened-exchange LDA approach [116,117] or pseudopotentials incorporating the so-called self-interaction correction [118]. These approaches are often only well suited for particular problems and not universally applicable.

An important materials class that has not been discussed so far are the actinides and lanthinides where the f-shell is in most cases only partially filled so that the f electrons are essential for understanding most properties of these elements. Because of the strong electronic localization in these heavy elements, which is associated with high electronic kinetic energies, these systems have to be treated relativistically. This strong localization also renders the use of pseudopotentials very ineffective. One method to treat these systems with strong electron correlation is the LDA + U method where the non-local and energy dependent self energy is approximated by a non-local screened Coulomb potential [119]. This method is still a mean-field approximation, hence it is not really suited for strongly correlated metals and often only gives qualitative information.

This list of problems associated with electronic structure algorithms is certainly not complete. These obstacles have prevented the use of ab initio methods for certain material classes. But alternative methods are either not accurate or not efficient enough. However, once any of these particular

problems is solved, an almost "virgin" research field for calculations and simulations opens up with all its exciting opportunities. The examples presented in this review show what kind of contribution electronic structure theory can make to a research field. A similar impact is to be expected in other research fields. There is every reason to believe that the theoretical study of processes on surfaces based on ab initio electronic structure methods will also prosper in the future. It will provide further exciting insights into fundamental mechanisms but it will also become a very valuable tool in the research and development process.

Acknowledgements

Scientific work is almost never done alone. I have profited enormously from the close collaborations and fruitful discussions with, among others, Wilhelm Brenig, Matthias Scheffler, Bjørk Hammer, Steffen Wilke, Eckhard Pehlke, Dimitrios Papaconstantopoulos, Peter Kratzer, Andreas Eichler, and Jürgen Hafner. I like to thank them all for the insights they have shared with me. As for this article, I like to thank in particular Bjørk Hammer, Eckhard Pehlke and Jürgen Almanstötter for providing me with nice illustrations. Furthermore, I am grateful to again Eckhard Pehlke and Markus Lischka for a careful proofreading of the manuscript.

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