

# A Construction Set with Just Atomic Nuclei and Electrons

Scientists from the Theory Department at the **FRITZ HABER INSTITUTE** in Berlin are simulating chemical processes at surfaces and the structure and stability of biomolecules. Their calculations are based on "first principles", i.e. on natural constants alone. In order to carry out this work, they must develop sophisticated computer programmes – but the effort is certainly worthwhile: their research results are accurate and enable them to achieve a highly reliable predictability.

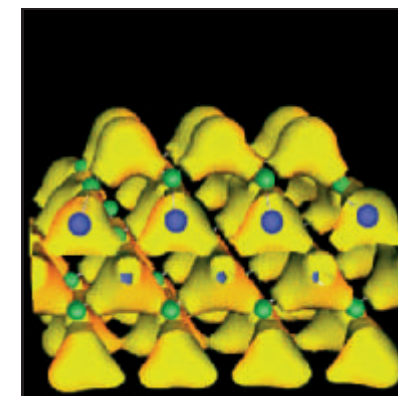
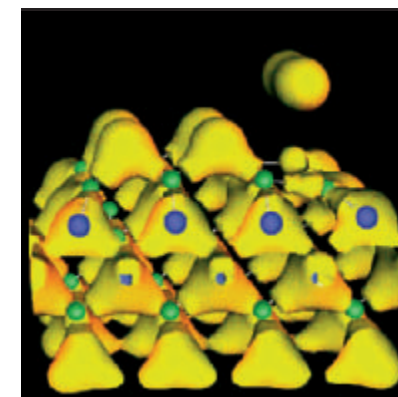
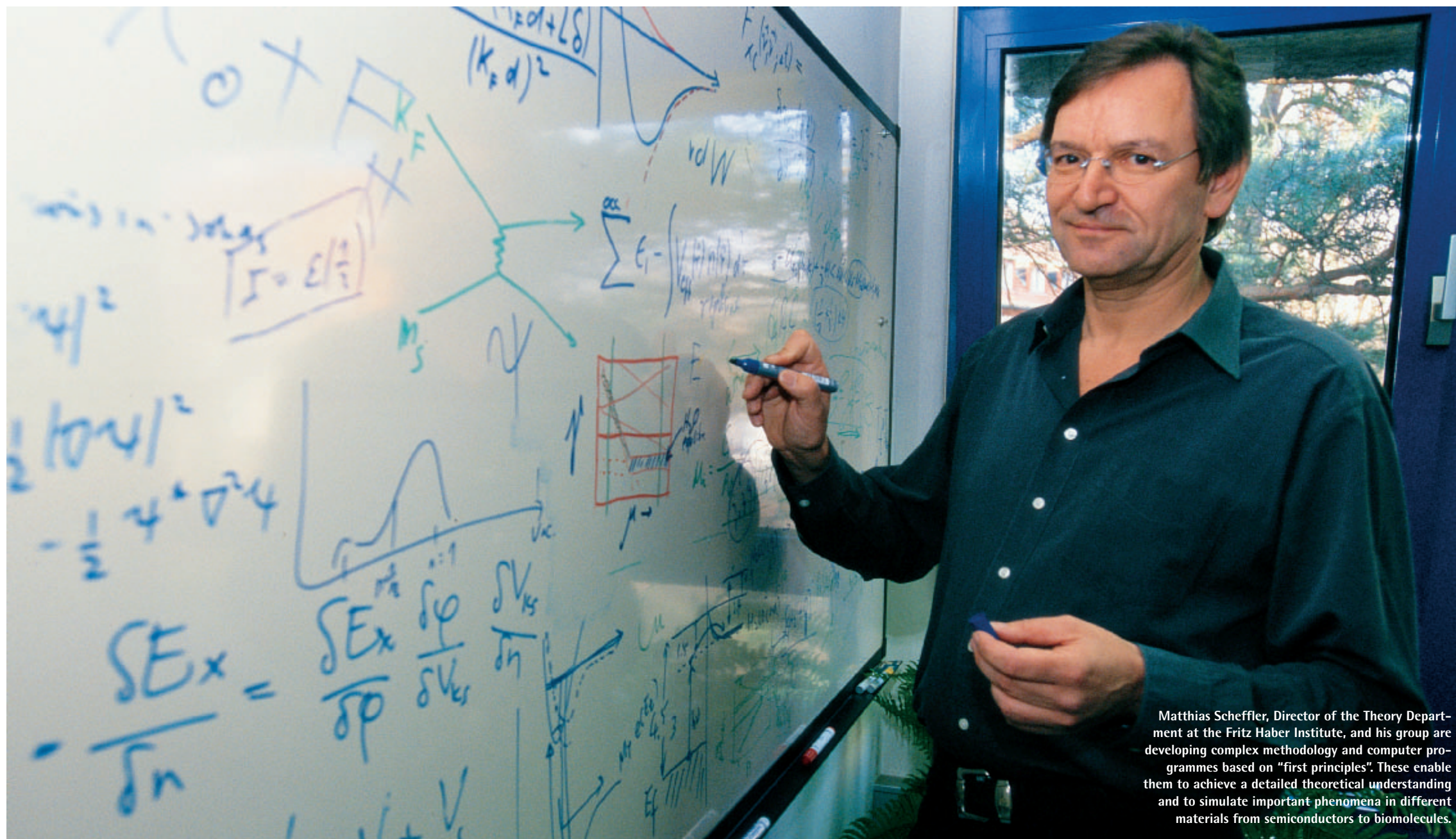


Fig. 1 top: a molecule made up of two As atoms ("dumbbells" consisting of two yellow spheres) approaches a GaAs surface. The electron density of the As atoms is shown in yellow, the blue spheres mark the nuclei of some As atoms, and the green spheres the nuclei of the Ga atoms. Below: the As molecule is fully incorporated; the electrons of the As atoms have formed bonds with the neighbouring Ga atoms.



Matthias Scheffler, Director of the Theory Department at the Fritz Haber Institute, and his group are developing complex methodology and computer programmes based on "first principles". These enable them to achieve a detailed theoretical understanding and to simulate important phenomena in different materials from semiconductors to biomolecules.

ALL PHOTOS: WOLFGANG FISLER / FIG.: FHI OF MPS

**“T**he essential feature of our work is that we do not use empirical parameters, but calculate everything from ‘first principles’”, says Matthias Scheffler, Director of the Theory Department at the Fritz Haber Institute (FHI) of the Max Planck Society in Berlin and recipient of the “Max Planck Research Prize 2001”. For their computer simulations, the researchers in his department are using only the fundamental physical laws and theories. Their building blocks are atomic nuclei and electrons which in a typical Berlin simulation can exist in their thousands. “Many-body quantum theory” and “statistical mechanics” provide the rules for their interactions and concerted interplay. In



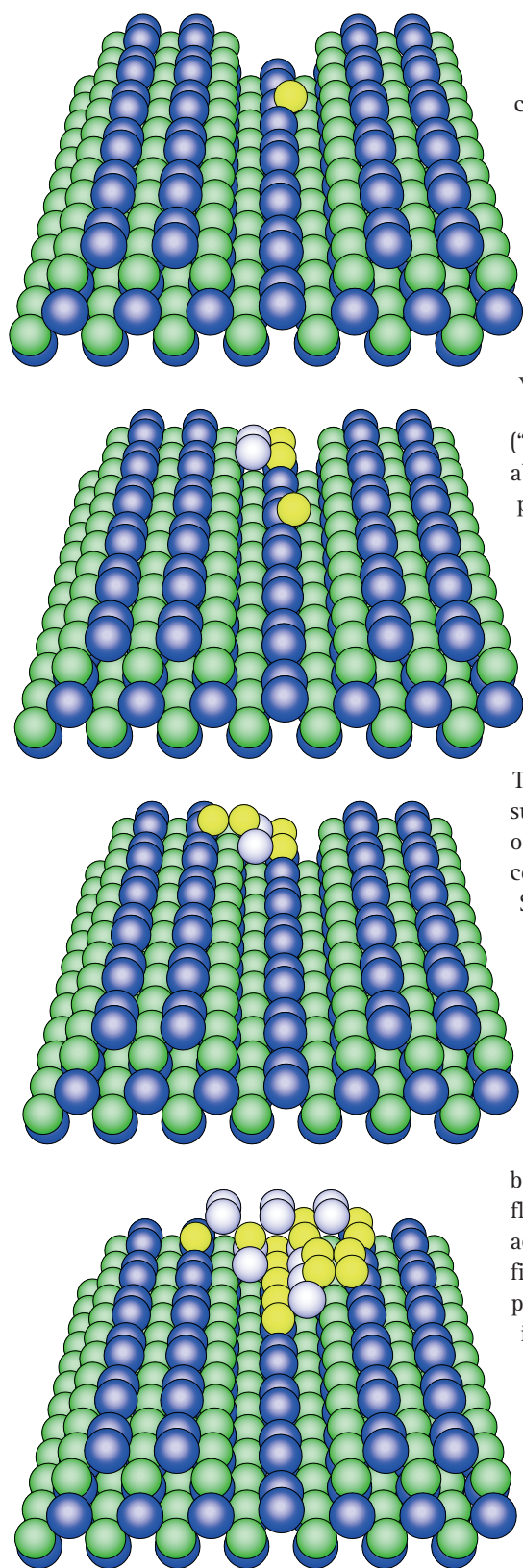


Fig. 2: The sequence of images shows how deposited As molecules (white) and Ga atoms (yellow) locally fill a trench of a GaAs surface. The atoms of the initial GaAs surface are coloured violet (As) and green (Ga). The deposited (new) atoms build an island.

contrast to this, most other simulation approaches are based on empirical data taken from experiments carried out on a highly specialized system. Their relevance is therefore restricted to this system, and physical conditions, such as pressure and temperature, are only allowed to vary within a narrow range.

Theories based on first principles (“ab initio theories”) are more reliable and more general. However, in practice, they have to overcome enormous hurdles: the objects under examination are almost always highly complex multiparticle systems. These include, for example, the chemical processes that take place at surfaces, or the forces that form and maintain the shape of biomolecules. This ab initio modelling pushes even supercomputers such as the Cray T3E or the NEC vector computer at the computing centre of the Max Planck Society in Garching to their processing limits.

If the Berlin scientists succeed in achieving their ab initio theoretical modelling, then this would enable a precise, microscopic understanding to be gained on an atomic scale, and it would also allow predictions to be made on similar systems. Scheffler’s department is working to achieve this research dream in the fields of nanosciences and biophysics. Peter Kratzer is collaborating with Matthias Scheffler on a deeper understanding and reliable description of growth processes at the surfaces of semiconductors. They are seeking to realistically model the way in which individual atoms behave at these surfaces. Whilst both these Max Planck scientists are pursuing fundamental research, these processes are also of interest to the semiconductor industry. Scientists involved in chip development will only achieve the miniaturization step to-

wards nanotechnology when they know how individual atoms move, interact, perform concerted actions, and possibly build precise nanostructures (“self-assembly”). Kratzer and Scheffler are working closely with all three Berlin universities and with other institutes: “The synergy effect is considerable”, says Scheffler.

The components of the Berlin “construction set” are just atomic nuclei and electrons. Kratzer uses these to build virtual gallium arsenide (GaAs), for example, on the computer. GaAs is a semiconductor used, amongst other things, in light-emitting diodes, diode lasers, and high-frequency circuits. A GaAs crystal has a relatively simple structure. However, up until now, experiments had not been able to reveal how the individual atoms behave at surfaces and grow nanostructures. The ab initio computer simulations carried out by the Berlin group are now providing insight, for the very first time, into the concerted motion of these atoms.

#### MASTER OF THE ISLANDS

“One problem is caused by the different time scales,” says Peter Kratzer, “the crucial processes occur very rarely. The atoms often only hop forwards and backwards between neighbouring positions, and for a long time not much is happening. For this reason, it is necessary to examine billions of individual steps.” Kratzer’s programme must therefore simulate this incredibly vast quantity of fruitless events in order to hit the “jackpot”: those rare moments when several atoms bump into each other and possibly form a stable “island” on the surface. This can only be achieved using the very latest methodology along with proper and cautious approximations, otherwise even a supercomputer would have to concede defeat.

“The size of the simulated area of the surface is 300 x 300 atoms,” ex-

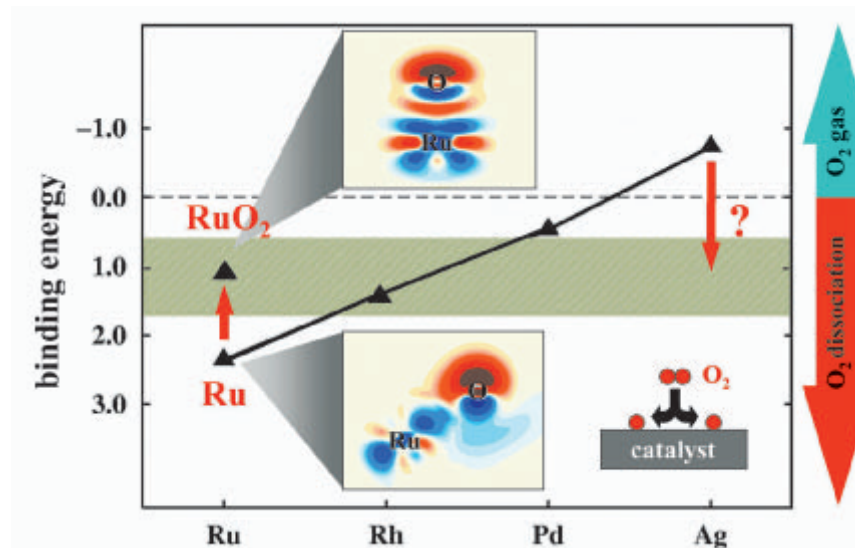


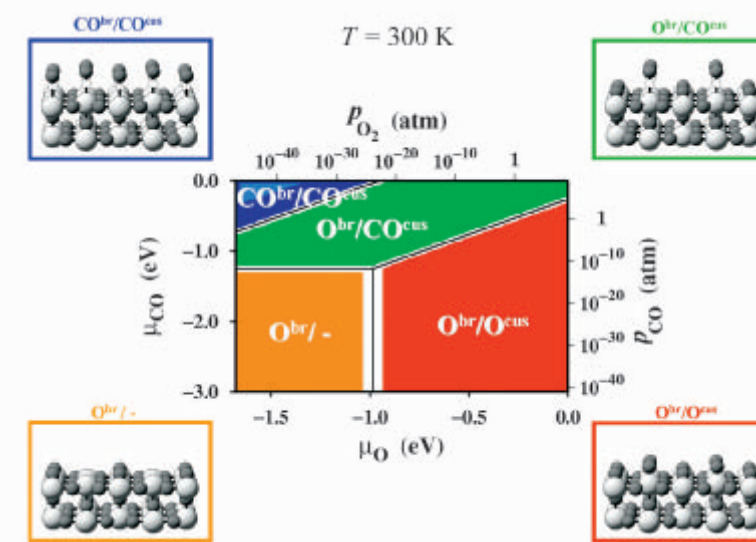
Fig. 3: An illustration of the Sabatier principle: this diagram shows how strongly oxygen binds at the surface of a transition metal (Ru, Rh, Pd and Ag) which is already covered with oxygen. If this energy is positive, then the O<sub>2</sub> molecule will dissociate (inset below right). According to the Sabatier principle, those metals that form a medium-strength bond with the oxygen would be particularly catalytically active (area shaded green).

quantum computers. The research of Karsten Reuter and Matthias Scheffler focuses on chemical processes at surfaces, particularly “oxidation catalysis”. Catalysts are substances whose presence enables (or significantly enhances) specific chemical processes to take place, with practically no wear and tear of the catalyst itself. At the surfaces of oxidation catalysts, an oxidation reaction takes place that is, in principle, very straightforward. A simple example, which is of considerable economic and ecological importance, is  $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$ : the catalyst breaks down an O<sub>2</sub> oxygen molecule into two O atoms, which then convert the

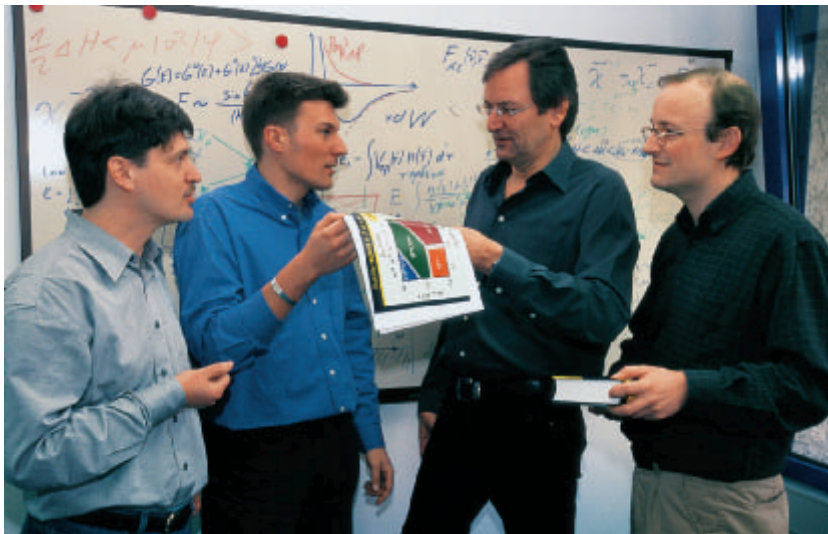
plains Kratzer. In order to be able to realistically simulate the behaviour of this 90,000-atom collective, the researchers developed a two-stage procedure. The first stage calculates how each atom involved makes or breaks chemical bonds with its neighbouring atoms. The FHI researchers are then already in the position to use this information to perform successful simulations of how a molecule consisting of two arsenic atoms can be incorporated in a newly created GaAs layer. Figure 1 outlines the process in two diagrams. A video on this subject can also be seen on the Internet (see page 26, “Videos on the Web”). The Cray T3E then carries out an atom-by-atom calculation of all physically relevant situations that can be encountered at the surface. The results are entered into a large database. The second stage combines the individual steps with the more complex processes at the surface. For each step, the computer accesses the database containing the atomic interactions. A physical time and a temperature, which is above absolute zero, are not introduced until this second stage. The researchers can now successfully simulate how deposited arsenic molecules and gallium atoms fill up an initially existing trench at the GaAs surface and how an island is then formed (Fig. 2 and “Videos on the Web”).

“We can learn from these simulations how individual atoms behave during growth processes at surfaces and we recognise how important concerted actions are,” summarises Kratzer. Above all, both Peter Kratzer and Matthias Scheffler see this as an ideal tool for modelling the growth of nanostructures such as “quantum dots”. Quantum dots are nano-islands consisting of around 10,000 atoms; here, electrons become localized, and this enforces on them a quantum behaviour which is similar to that of electrons of isolated atoms. In the future, quantum dots could be used, for example, in nano-chips for lasers, single-electron transistors, or

Fig. 4: Centre of diagram: Depending on the pressure and mixture of the gas that surrounds a RuO<sub>2</sub> catalyst surface, O atoms and CO molecules occupy this surface in different ways. The small boxes show the molecular structures that they can build in each case. The O atoms are dark coloured, the Ru metal atoms large and grey, the C atoms small and white.







Jörg Neugebauer, Karsten Reuter, Matthias Scheffler and Peter Kratzer (from left to right) discuss new results on the RuO<sub>2</sub> system.

poisonous carbon monoxide (CO) into non-poisonous carbon dioxide (CO<sub>2</sub>). This process takes place, for example, in the catalytic converters used in our cars. Oxidation catalysis is also of great industrial significance and this extends far beyond the realms of exhaust emission control.

However, the precise processes taking place in catalysis still remain largely unexplained on an atomic or molecular scale. Several established models have recently been shown to be incorrect or at least inadequate. Reuter: "The key step in oxidation catalysis is the 1/2 O<sub>2</sub>." If an oxygen molecule approaches the catalyst surface, then it will form a chemical bond with it and divide ("dissociate") itself into two O atoms. The individual O atoms are "adsorbed" on the surface, i.e. form a bond with the surface. The reaction partner, for ex-

ample the CO, also bonds with the surface. Here it reacts with an O atom to produce the end product CO<sub>2</sub>. The end product then separates itself from the catalyst surface and flies away, thereby clearing the way for a new reaction.

A good catalyst must therefore be able to crack the O<sub>2</sub> molecule, but should only bind the O atoms to its surface with no more than medium strength. Otherwise the O atoms become inactive. This rule had already been discovered around 1900 by the French chemist and Nobel Prize winner Paul Sabatier. It was shown that certain "transition metals" in the periodic table fulfil the criteria of good oxidation catalysts, for example rhodium, palladium and platinum. If we move on from these transition metals to neighbouring elements in the periodic table, which have a higher or lower atomic number, we notice that these elements become less and less suitable as oxidation catalysts. Figure 3 shows the Sabatier principle using the example of ruthenium (Ru), rhodium (Rh), palladium (Pd), and silver (Ag). The left axis represents the binding energy of oxygen in relation to the free O<sub>2</sub> molecule: if it is positive then the oxygen molecule will dissociate. If the binding energy lies in the central area shaded green, then according to

the Sabatier principle the element would be a good oxidation catalyst. Indeed, Rh or Pd catalysts are very efficient.

According to this diagram, Ru would be unsuitable as it forms much too strong a bond with oxygen. However, this is not in fact correct, i.e., it is known from experiments that Ru is an excellent oxidation catalyst under realistic pressure and temperature conditions. The failure of this theory indicates that other previously "underestimated" materials could also be excellent catalysts. A discovery made by scientists working with Herbert Over at the FHI, in collaboration with physicists from Vienna, generated a great deal of excitement in the year 2000: it was shown that not the Ru metal, but the oxide RuO<sub>2</sub>, which develops on its surface, is the catalytically active material in the oxidation reaction (illustrated on the left in Fig. 3). Figure 4 shows how the oxygen atoms and CO molecules occupy the RuO<sub>2</sub> surface at room temperature. Their behaviour is determined by the pressure and mixture of the gases that surround the catalyst.

#### COMPUTERS STUDY THE ANTICS OF ATOMS

The simulations carried out by Reuter and Scheffler demonstrate – in the most realistic manner possible – the way in which the oxidation of a material, such as Ru, changes its chemical activity. The researchers are also particularly interested in how pressure and temperature influence the avidity of the atoms and molecules adsorbed on the surface. One problem is the more complex crystalline structure of the oxide (Fig. 4), as this makes the simulations expensive. "I would actually need a computer with two orders of magnitude higher capacity for my simulations", says Reuter – even though the Cray and the NEC are not exactly pocket calculators. However, the efforts of the team have

paid off: researchers were able to analyze the antics of the atoms at high temperature and high gas pressures. Reuter concludes: "Future catalysis research will certainly focus more on oxide formation at the surfaces of metals and on systematic investigations of pressure and temperature effects."

Jörg Neugebauer heads an "Independent Junior Research Group" at the Fritz Haber Institute. In collaboration with Matthias Scheffler and biochemists from Mexico City, the scientists have opened up a whole new world: the world of biomolecules. The long chains of proteins fold in a complicated, yet highly specific manner. The folded structure (the "conformation") controls their characteristics such as, for example, water solubility. Only a chain that has the correct conformation develops the desired biological function. Viewed on the smallest scale, the conformation consists of certain "secondary structures": in certain places the long chain forms a "β-sheet", or in other sections the chain crimps itself, forming an "α-helix".

Which forces actuate and stabilize the folding of proteins? This is an important question for the field of modern biochemistry. If researchers can find the answer, then they will succeed in making considerable progress in understanding how proteins function. One example of this is provided by the infamous prions. The lethal form of this protein differs from the healthy form in just one aspect: one section of the molecule forms a β-sheet instead of a short α-helix. But what makes the prion assume this lethal defective fold?

"A characteristic interaction in biomolecules is the hydrogen bond", explains Jörg Neugebauer. The hydrogen bond develops between a Y atom and an X atom, when a hydrogen atom H is sitting between them. X and Y can be part of different sections of the same molecule chain, or they may belong to two different

molecules. In addition, X and Y must be electronegative, i.e. "hungry" for electrons. Typically, one of these atoms, for instance the X atom, pulls the "electron cloud" of the hydrogen atom H towards itself. This creates an electrostatic field that holds all three atoms together. The hydrogen bond is much weaker than the usual "glue" that binds atoms in molecules, the "covalent" bond.

#### WHAT KEEPS AN α-HELIX IN SHAPE?

Interestingly, if there are many hydrogen bonds in an α-helix, then these will be able to reinforce each other. "This effect is called cooperativity", explains Neugebauer. The Berlin theorists then discovered that this cooperativity contributes decisively to the stability of an α-helix. For their simulation they chose polyalanin, which is an ideal model system. It is the simplest protein chain that forms an α-helix. As a single hydrogen bond corresponds to a very small energy contribution, it is particularly important to achieve a high accuracy. "In particular, it is necessary to accurately determine the electronic structure", says Neugebauer, hereby alluding to the fact that even the smallest detail in the electron distribution in the molecule can affect the final result. Using the vast capacity of the Cray T3E, the Berlin theorists succeeded in making the breakthrough: Figure 5a) shows a simulation of an α-helix made from polyalanin. The researchers discovered that the cooperativity in this helix strengthens each hydrogen bond by more than 200 percent compared to the strength of an isolated hydrogen bond. Previous estimates had suggested a maximum of just 50 percent.

This enormous reinforcement has crucial consequences. Neugebauer's team was able to calculate that without this reinforcement the α-helix would unravel and take on the form illustrated in Figure 5b). This corre-

sponds with the experimental findings: short polyalanin chains are actually found in an extended structure. This discovery enabled the researchers to take an important step forward towards understanding some protein conformation, i.e., it provides a clue to the reason why proteins can be unstable. Neugebauer makes reference to the prions: "The BSE-inducing change that is brought about by transforming a short α-helix into a β-sheet structure resembles the behaviour that we find for our polyalanin model system."

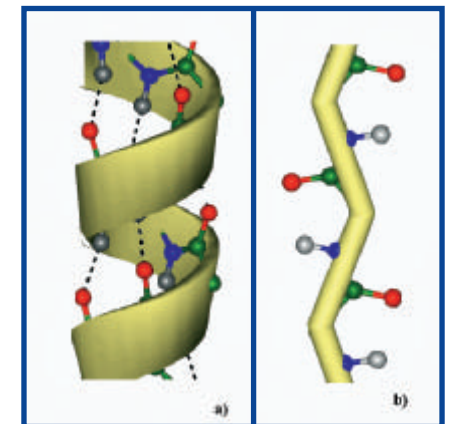


Fig. 5: a) A simulated α-helix made from polyalanin. The hydrogen bonds are depicted as dotted lines. The yellow band denotes the backbone of the molecule. The grey spheres are hydrogen atoms, the blue nitrogen and the green carbon. b) shows the extended structure of the polyalanin molecule.

The challenges for simulating complex systems on the basis of first principle theories are enormous. Nevertheless, the Theory Department at the FHI has demonstrated impressive success in this area. For very good reasons, Matthias Scheffler is optimistic about the future: "I am convinced that in the coming years the methodology of ab initio statistical mechanics will increasingly dominate the field of 'Computational Sciences and Engineering'".

ROLAND WENGENMAYR

#### VIDEOS ON THE WEB

Simulation video on the incorporation of an As<sub>2</sub> molecule into a GaAs layer (Fig. 1): [www.fhi-berlin.mpg.de/th/publications/img/ie-as2-alpha.gif](http://www.fhi-berlin.mpg.de/th/publications/img/ie-as2-alpha.gif) (150 Kbyte file).  
Videos on the process shown in Fig 2: [ftp://ftp.aip.org/epaps/phys\\_rev\\_lett/E-PRLTAO-87-031152/isl-gaas-front.mpg](ftp://ftp.aip.org/epaps/phys_rev_lett/E-PRLTAO-87-031152/isl-gaas-front.mpg) lateral view and [ftp://ftp.aip.org/epaps/phys\\_rev\\_lett/E-PRLTAO-87-031152/isl-gaas-top.mpg](ftp://ftp.aip.org/epaps/phys_rev_lett/E-PRLTAO-87-031152/isl-gaas-top.mpg) view from above. (Each file is almost 5 Mbytes.)