Molecular processes on oxide surfaces studied by first-principles calculations

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ABSTRACT

First-principles quantum techniques based on density functional theory (DFT) have made important contributions to the understanding of oxide surfaces over the last four years. Important features of these calculations include: the use of periodic boundary conditions, which avoid the edge effects associated with the cluster approach; plane-wave basis sets, which make the calculation of ionic forces straightforward, so that both static relaxation and dynamical simulation can be done; and the approximate inclusion of electron correlation. A short introduction to DFT techniques is given, and recent work on the structure and energetics of a variety of oxide surfaces is presented. It is shown how the techniques can be used to study molecular and dissociative adsorption of molecules on oxide surfaces, with the emphasis on water and simple organic molecules. The growing importance of dynamical first-principles simulation in the study of surface chemical reactions is illustrated.

Introduction

WHAT are the atomic-scale mechanisms underlying the weathering of rocks? How do water molecules attack mineral surfaces, and what are the reaction pathways leading to surface dissolution? If we were smart enough, we could use fundamental quantum theory to help unravel the complex chemistry of these processes. In fact, weathering is only one example: a large part of geology depends ultimately on what happens at mineral surfaces. The formation as well as the destruction of rocks involves surface processes, and the role of water at surfaces is as important in diagenesis as it is in weathering. The morphology of natural crystals, and the way this is influenced by the chemical environment, also depend on such processes. On a more practical level, the flow of pollutants in the environment depends crucially on surface chemistry. The percolation and trapping of heavy metals such as lead and mercury, or of fertilisers and pesticides, would all be better understood if we knew more about molecular adsorption on mineral surfaces.

The use of quantum mechanical calculations to study surface chemistry is not an idle pipe-dream. There has recently been vigorous movement in this field, and the present article describes how first-principles methods are now combining with experimental techniques to elucidate the structure of both perfect and defective oxide surfaces, as well as the adsorption and reaction of water and other molecules on these surfaces. We will mainly consider oxide surfaces, because there has been a lot of recent work on them, but we will stress that the theoretical methods are equally applicable to more complex materials like silicates and carbonates.

An excellent broad overview of quantum methods and their possible application to geological problems was given by Tossell (1995). But here we limit ourselves to one main theoretical approach: density functional theory (DFT) (Hohenberg and Kohn, 1964; Kohn and Sham, 1965; Jones and Gunnarsson, 1989). This originated from solid-state physics, rather than theoretical chemistry, and over the past twenty

years has grown into the most widely used way of doing (fairly) accurate quantum calculations on condensed-matter systems. Combined with the pseudopotential technique (Heine, 1970; Cohen and Heine, 1970), DFT theory has been extensively used to study a large variety of systems, including metals, insulators, semiconductors and their surfaces, liquids, and materials under high pressures, and it can be used either to determine relaxed equilibrium structures or to do dynamical simulations. We shall also mention work done using the Hartree-Fock approach, which is also proving very powerful for surface studies.

Within either the DFT or Hartree-Fock approaches, a major decision of principle is whether to treat a surface as an infinitely extended periodic structure, or alternatively to approximate it by a finite cluster of atoms. In this article, we will discuss only the periodic approach. (The cluster approach can sometimes be useful, but some of the comparisons with experiment that are becoming important seem to us virtually impossible in this approach.)

A brief description of the periodic DFT-pseudopotential techniques used in most of the oxide surface work to be described will first be given. We shall then concentrate on three main aspects of oxide surfaces. The first of these concerns the relaxed equilibrium structure of the surfaces themselves. This is important because it is the foundation for everything else, and because it offers comparisons with surface structure measurements which allow us to check the reliability of the theoretical methods. The second aspect is defective surfaces, and we shall discuss here first-principles calculations on oxygen removal and addition, which are relevant to surface structure in reducing or oxidising environments. Calculations on topological defects, such as steps, will also be mentioned. The final aspect is molecular adsorption and reactions, and we shall particularly emphasise problems involving water, though we shall also refer to work on organic molecules such as formic acid and methanol. We conclude by pointing to likely developments in the next few years.

First-principles techniques

The basic aim of first-principles calculations is to use quantum mechanics to calculate the total energy E_{tot} and the distribution of electrons for systems containing many atoms. 'First principles' means essentially the same as *ab initio*, namely

that the calculations are free of empirical or adjustable parameters, so that the only experimental input is the values of the electronic mass m and charge e and Planck's constant $\hbar$. In the techniques relevant to this article, the algorithms for calculating E_{tot} also give a simple way of calculating the forces on all the atoms, and this enables one to search for equilibrium relaxed structures. In the context of surface problems, this means that it is technically straightforward to determine the equilibrium structure of a perfect or defective surface, or the stable configurations of adsorbed molecules. The forces can also be used to make dynamical simulations, so that in some cases the pathways by which molecules are adsorbed or dissociate on surfaces can be studied.

The following description of the methods will be brief. A more detailed non-technical discussion can be found in an article by one of the present authors (Gillan, 1997), and full technical details are given in reviews (Jones and Gunnarsson, 1989; Gillan, 1991; Payne et al., 1992). In the following, we summarise the ideas of density functional theory (DFT) and we explain how these ideas can be applied to many-atom systems using the pseudopotential concept and plane-wave basis sets. The accuracy of the methods will be illustrated at the end of this section by some typical results for crystals and molecules.

Density functional theory

We want to know the total ground-state energy of a system of atomic nuclei and electrons, when the nuclei are in certain positions R_I. DFT separates this energy into a number of components:

$$E_{tot} = E_M + E_{kin} + E_c + E_H + E_{xc} \qquad (1)$$

Here, E_M is the Coulomb interaction energy of the nuclei; E_{kin} is the kinetic energy of the electrons; E_c is their interaction energy with the nuclei; E_H is the Hartree energy, i.e. the Coulomb energy of the electron charge distribution; and E_{xc} is the quantum mechanical exchange energy of the electrons plus their correlation energy. The kinetic energy term E_{kin} needs more explanation. When the electrons are in the ground state, they have a certain density distribution $n(r)$ (number of electrons per unit volume at point r). The precise meaning of E_{kin} is that it is the kinetic energy of a fictitious system of non-interacting electrons having the same density distribution $n(r)$ as the real system of interacting electrons. With this definition, E_{kin} as well as E_c and E_H can be

expressed in terms of $n(\mathbf{r})$. DFT makes two exact statements, on which the whole theory rests (Hohenberg and Kohn, 1964; Kohn and Sham, 1965): first, the exact exchange-correlation energy E_{xc} is a function only of $n(\mathbf{r})$; second, the exact ground-state energy is obtained by treating all the energy terms as functions of $n(\mathbf{r})$ and minimising E_{tot} with respect to $n(\mathbf{r})$. The second statement is a form of the usual variational principle of quantum mechanics.

In applying this theory, it is convenient to express $n(\mathbf{r})$ in terms of the wavefunctions $\psi_i(\mathbf{r})$ of the system of non-interacting electrons needed to define E_{kin}:

$$n(\mathbf{r}) = 2 \sum_i |\psi_i(\mathbf{r})|^2 \qquad (2)$$

where the sum goes over occupied orbitals, and the factor 2 accounts for electron spin. It can then be shown that in the ground state these wavefunctions are the solutions to an equation that has exactly the form of the Schrödinger equation:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{eff}(\mathbf{r}) \right)\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}) \qquad (3)$$

where V_{eff} is an 'effective' potential acting on the electrons. This potential comes from the interaction of the electrons with the nuclei and with their own charge distribution, and there is also a contribution from the exchange-correlation energy.

If this theory was applied exactly, it would give exact results for the energetics of real systems. The problem is that we do not have an exact expression for the exchange-correlation energy. Remarkably, it has turned out that a very simple approximation is often very accurate. This is called the local density approximation (LDA) (Kohn and Sham, 1965; Jones and Gunnarsson, 1989), and works by relating E_{xc} of the real system to the exchange-correlation energy of a uniform gas of electrons, sometimes called jellium. The LDA says that:

$$E_{xc} \simeq \int d\mathbf{r}\, n(\mathbf{r})\, \epsilon_{xc}(n(\mathbf{r})) \qquad (4)$$

where $\epsilon_{xc}(n)$ is the exchange-correlation energy per electron in jellium of density n. The LDA generally works well for bulk matter, but it is not adequate for calculating molecular adsorption and dissociation energies, and much of the work to be described is based on 'generalised gradient approximations' (GGAs) (Perdew, 1986; Perdew and Wang, 1986; Becke, 1988; Perdew, 1991; Perdew et al., 1992), which give much improved accuracy.

Pseudopotentials and plane waves

One of the key problems in doing practical calculations is that of representing the wavefunctions ψ_i on a computer. The methods we are emphasising in this article are based on an important set of ideas known as pseudopotential theory (Heine, 1970; Cohen and Heine, 1970).

A guiding idea in this theory is that the electrons in the system can be separated into two groups, which are treated completely differently: core electrons and valence electrons. The tightly bound core electrons are almost unaffected by their environment, and are assumed to be in exactly the same states as in the free atoms. Their wave functions are calculated once and for all from DFT free-atom calculations. The valence electrons govern the energetics of the system, and it is their wavefunctions which have to be calculated for each set of ionic positions $\mathbf{R}_I$. The interactions felt by the valence electrons are of two kinds: (i) their interaction with each other, and (ii) their interaction with the atomic cores.

It was discovered nearly forty years ago (Phillips and Kleinman, 1959) that the strong interaction V_c of the valence electrons with the atomic cores can be replaced by a much weaker 'pseudopotential' V_c^{ps}, and that this can be done in such a way that the energetics of the valence electrons is almost unaffected. This is a very general statement which applies to all elements in the periodic table, and there are now standard techniques for generating pseudopotentials from all-electron DFT calculations on free atoms (Bachelet et al., 1982; Rappe et al., 1990; Lin et al., 1993). The replacement of the true valence-core interaction by an ionic pseudopotential entails the replacement of the true wavefunctions $\psi_i(\mathbf{r})$ by pseudo-wavefunctions $\psi_i^{ps}(\mathbf{r})$. In more detail, the replacement of V_c by V_c^{ps} is done within a cut-off radius of the atomic nucleus, known as the pseudopotential core radius r_c, and V_c^{ps} is a non-local quantity which depends on the angular momentum of the valence electrons about the nucleus. Correspondingly, ψ_i^{ps} differs from the true wavefunction ψ_i only within the core radius.

A key requirement in ensuring the correct energetics, and also in ensuring that the pseudopotential scatters the valence electrons in the same way as the true potential, is that the amounts of electronic charge inside the core radius calculated from ψ_i and ψ_i^{ps} must be the same. This is called the condition of norm conservation (Hamann et al., 1979).

Since the pseudopotential is much weaker than the true potential, the pseudo-wavefunction is much smoother than the true wavefunction, and this means that it is much simpler to represent in terms of basis functions. The most common (though certainly not the only) method is to represent the ψ_i^{ps} in terms of plane waves $\exp(i\mathbf{G} \cdot \mathbf{r})$:

$$\psi_i^{ps}(\mathbf{r}) = \sum_{\mathbf{G}} c_{i\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{r}) \qquad (5)$$

where the summation goes over a set of wavevectors $\mathbf{G}$. This is physically meaningful, because $\exp(i\mathbf{G} \cdot \mathbf{r})$ is the wavefunction of a free electron whose momentum is $\hbar\mathbf{G}$, so that this is an extremely economical representation if the valence electrons are only weakly perturbed by the pseudopotentials. But even if the perturbation is not weak, a plane-wave basis set is always perfectly valid: provided enough wavevectors $\mathbf{G}$ are included in the summation of equation (5), the pseudo-wavefunctions can be represented to any required accuracy.

In this DFT-pseudopotential scheme, a practical calculation consists of expressing all the terms in E_{tot} in terms of the pseudo-wavefunctions and the associated valence electron density, and minimising E_{tot} with respect to the plane-wave coefficients $c_{i\mathbf{G}}$.

Supercells

In most problems involving bulk matter or surfaces, our real need is to treat systems containing an almost infinite number of atoms. Clearly, this is impossible, and some artifice has to be adopted. An extremely effective artifice is the supercell method, in which the calculations are done on a limited number of atoms in a cell which is surrounded on all sides by periodic images of itself. The reason this method works so well is that it completely eliminates all unwanted surfaces and boundaries. It also fits extremely well with plane-wave basis sets. The reason for this is that a plane-wave expansion is mathema-

tically equivalent to a Fourier series, and this is the natural way of representing periodically repeating wavefunctions. In this scheme, the wavevectors $\mathbf{G}$ entering the Fourier series are the reciprocal vectors of the supercell lattice, and the sum in eqn. (5) goes over all $\mathbf{G}$ for which $\hbar^2 G^2/2m < E_{cut}$, where E_{cut} is a chosen plane-wave cut-off energy.

One way of viewing the supercell method is to say that the system is represented as a crystal having a very large and complicated unit cell. This means that all the sophisticated methods developed over many decades for treating crystals can be brought into play. The way the supercell method is applied to surfaces will be outlined below.

Forces, relaxation and dynamics

In treating surface problems, it is essential to be able to calculate the equilibrium positions of the ions, which may differ substantially from the perfect-lattice positions. We also need to calculate the equilibrium configurations of adsorbed molecules. Sometimes, we may want to investigate the dynamical processes involved in molecular adsorption or dissociation. All these things rely on the calculation of the forces $\mathbf{F}_i$ on the ions.

In principle, the calculation of forces is simple, since we know the Coulomb forces exerted on each other by the ionic cores, and DFT gives us the density distribution $n(\mathbf{r})$ of the valence electrons, so that we can calculate the forces exerted by these electrons on the cores. A great advantage of the pseudopotential plane-wave approach is that force calculations are also simple in practice. In fact, the ionic forces require few additional computations beyond those needed to calculate the total energy. The technical simplicity comes mainly from the fact that the basis set itself does not depend on the ionic positions. This allows a direct application of the Hellmann-Feynman theorem (Hellmann, 1937; Feynman, 1939), which ensures that the variation of E_{tot} caused by small ionic displacements is exactly given by the work done on the ionic cores by the forces exerted by the electrons and the other cores.

Given the forces, it is usually quick and automatic to relax all ions in the system to their equilibrium positions, and it can be taken as read that this was done in virtually all the work described in the following sections. An efficient technique for performing this relaxation is the conjugate-gradients method, which uses the

TABLE 1. Calculated and experimental values of lattice parameter a_0, bulk modulus B, and five phonon frequencies of MgO (De Vita *et al.*, 1992). Phonon modes are the transverse-optic mode at the Γ point and the transverse and longitudinal-acoustic and -optic modes at the X point of the Brillouin zone

	Calculated	Experimental
a_0 (Å)	4.17	4.21
B (Mbar)	1.54	1.55−1.62
TO(Γ) (THz)	12.39	12.23
TAX) (THz)	8.65	8.96
LAX) (THz)	12.57	12.65
TOX) (THz)	13.24	13.15
LOX) (THz)	16.36	16.61

forces to search iteratively for the ionic configuration of minimum energy. In some problems, for example the determination of the equilibrium configurations of absorbed molecules, there can be a serious danger that the search will get stuck in a local minimum which is not the most stable configuration. The heuristic solution to this problem is to repeat the search from many different starting points. There are also 'simulated annealing' methods, which have a sounder theoretical foundation, but are more demanding in computer power.

The ionic forces can also be used to perform dynamical first principles simulations (Car and Parrinello, 1985), in which the time evolution of the ionic positions is generated. This used to be regarded as elaborate and expensive, but is becoming increasingly commonplace. The idea is to use Newton's equation of motion:

$$M_I d^2 \mathbf{R}_I / dt^2 = \mathbf{F}_I \qquad (6)$$

to compute the time-dependent trajectories of all the ions in the system. This is done by breaking time up into a sequence of small time-steps and using the positions $\mathbf{R}_I$ and velocities $\mathbf{v}_I$ at each step to generate these quantities at the next step. To do this, the differential equation of motion is replaced by a finite difference approximation, such as Verlet's algorithm (Allen and Tildesley, 1987).

First-principles dynamical simulations of molecular adsorption and dissociation on surfaces were first done several years ago (De Vita *et al.*, 1993), and their application to oxide surface problems will be discussed below.

Crystals

The DFT-pseudopotential technique has been a standard way of calculating the properties of perfect crystals for nearly 20 years. As an illustration of the kind of accuracy that can be expected, we show in Table 1 a comparison between LDA calculations and experiment for the lattice parameter, bulk modulus and selected phonon frequencies of MgO (periclase). As Table 1 illustrates, lattice parameters of oxides are usually reproduced within 1−2%, and elastic constants and vibrational frequencies within about 5%.

Molecules

Since we are interested in molecular processes on surfaces, it is clearly essential that the theoretical techniques correctly describe isolated molecules. The application of DFT to molecules has been standard for several years, and its reliability in predicting equilibrium molecular geometries and vibrational frequencies is well known. It is also well known that LDA is not at all reliable for molecular dissociation energies, but that gradient corrections give a major improvement. With a good GGA such as Perdew-Wang-91 (Perdew, 1991), calculated dissociation energies are generally correct to within a few tenths of an eV. This is not full chemical accuracy, but is certainly good enough for many purposes.

However, the treatment of isolated molecules using plane-wave basis sets is not widely practised. Indeed, plane waves seem at first sight so ill-suited to describing localised molecular wave functions that it might be asked whether this is really a practical procedure at all. Several groups have studied this (Rappe *et al.*, 1992; Andrews *et al.*, 1996), and there is now no possible doubt that plane waves are not only practical, but are actually quite competitive with more traditional basis functions like Gaussians. To illustrate this, we show in Table 2 the calculated equilibrium bond lengths and angles for a number of simple molecules, obtained from pseudopotential plane-wave calculations and from Gaussian all-electron calculations (Andrews *et al.*, 1996), compared with experimental values. It is clear that the quality of the predictions from the two approaches is extremely similar.

The equilibrium structure of oxide surfaces

A good understanding of the relaxed equilibrium structure of perfect stoichiometric surfaces is a

TABLE 2. Equilibrium bond lengths (in Å) and angles (in degrees) for simple molecules from pseudopotential calculations using plane-wave basis sets (PW-PS) and all-electron calculations using high quality Gaussian basis sets (G-AE) (Andrews et al., 1996), compared with experimental values

Molecule	Structure	PW-PS	G-AE	Expt.
H_2O	$r(O-H)$	0.973	0.971	0.958
	$\angle(HOH)$	104.5	105.0	104.5
CO	$r(C-O)$	1.126	1.128	1.128
HCN	$r(C-N)$	1.148	1.151	1.153
	$r(C-H)$	1.082	1.080	1.066
C_6H_6	$r(C-C)$	1.378	1.386	1.399
	$r(C-H)$	1.097	1.094	1.101

sine qua non for at least two reasons. The first is that the relaxed structure may differ greatly from what would be obtained simply by terminating the bulk crystal. Relaxations of surface ions away from their perfect crystal positions are sometimes large, and this can cause a dramatic reduction of surface formation energies. The second reason is that accurate experimental data are now becoming available for the relaxed positions of surface ions, and this provides one of the key ways of testing the reliability of the calculations. We explain next the repeating slab geometry used to study equilibrium surface structure in periodically repeating DFT-pseudopotential calculations. The prediction of relaxed structures and the comparison of the predictions with experiment will then be illustrated for the cases of MgO (001), TiO$_2$ (110) and Al$_2$O$_3$ (0001).

Repeating slab geometry

The ideal system that we have in mind is the unbounded perfect surface of a semi-infinite crystal. Direct calculations on this ideal system are not straightforward. However, the difficulty is not the unbounded extent of the surface. In fact, this is a major simplification. The surface consists of a unit cell periodically repeated, and this fits perfectly with the periodic geometry that we wish to use. The real difficulty is the semi-infinite extent of the ideal system in the direction perpendicular to the surface.

The traditional way round this problem is to replace the semi-infinite crystal by a slab of some chosen thickness L. In principle, there is nothing to

prevent one doing calculations on a single slab in free space, and this is the approach used in the Hartree-Fock code CRYSTAL (Causà et al., 1986). But in DFT-pseudopotential work one usually demands that the system have full three-dimensional periodicity. This can be achieved by working with an infinite stack of slabs, with each slab separated from its neighbours on either side by a vacuum layer of width L' (Fig. 1). With this geometry, we can now apply the standard DFT-pseudopotential technology, including automatic relaxation of all ionic positions, or – if we want to make direct studies of dynamical surface processes – first-principles molecular dynamics simulation.

Repeating slab geometry brings two unwanted artefacts: the slab thickness L and the vacuum width L'. To get back to our ideal, we must let both L and L' tend to infinity. The vacuum width must be big enough so that neighbouring slabs do not interact; the slab thickness must be big enough so that opposite surfaces of each slab do not interact. The values of L and L' needed to achieve this will not be the same for all systems. However, in some cases calculations have been done which demonstrate that L and L' can easily be made large enough to render the results from repeating slab geometry virtually identical to what would be obtained in the ideal semi-infinite system. Examples of this convergence with respect to L and L' will be given below.

The MgO (001) surface

Having emphasised that surface relaxations can sometimes be large, we actually start with a case where they are very small. The (001) surface of periclase (MgO) is one of the simplest oxide surfaces. Without relaxation, all the surface ions lie in the same plane, and it has long been known from LEED measurements that the relaxations consist of small outward movements of the O ions and inward movements of the Mg ions, an effect known as rumpling. The MgO (001) surface is also one of the few oxide surfaces for which a reliable surface energy is known.

It has been shown that MgO (001) is a case where remarkably thin slabs suffice to eliminate the effect of slab thickness on surface properties. To illustrate this, we report in Table 3 values of the rumpling parameter ε_{rum}, the average relaxation ε_{rel} and the relaxed surface energy σ from DFT-pseudopotential calculations on slabs of different thicknesses. The parameters ε_{rum} and ε_{rel} are defined as:
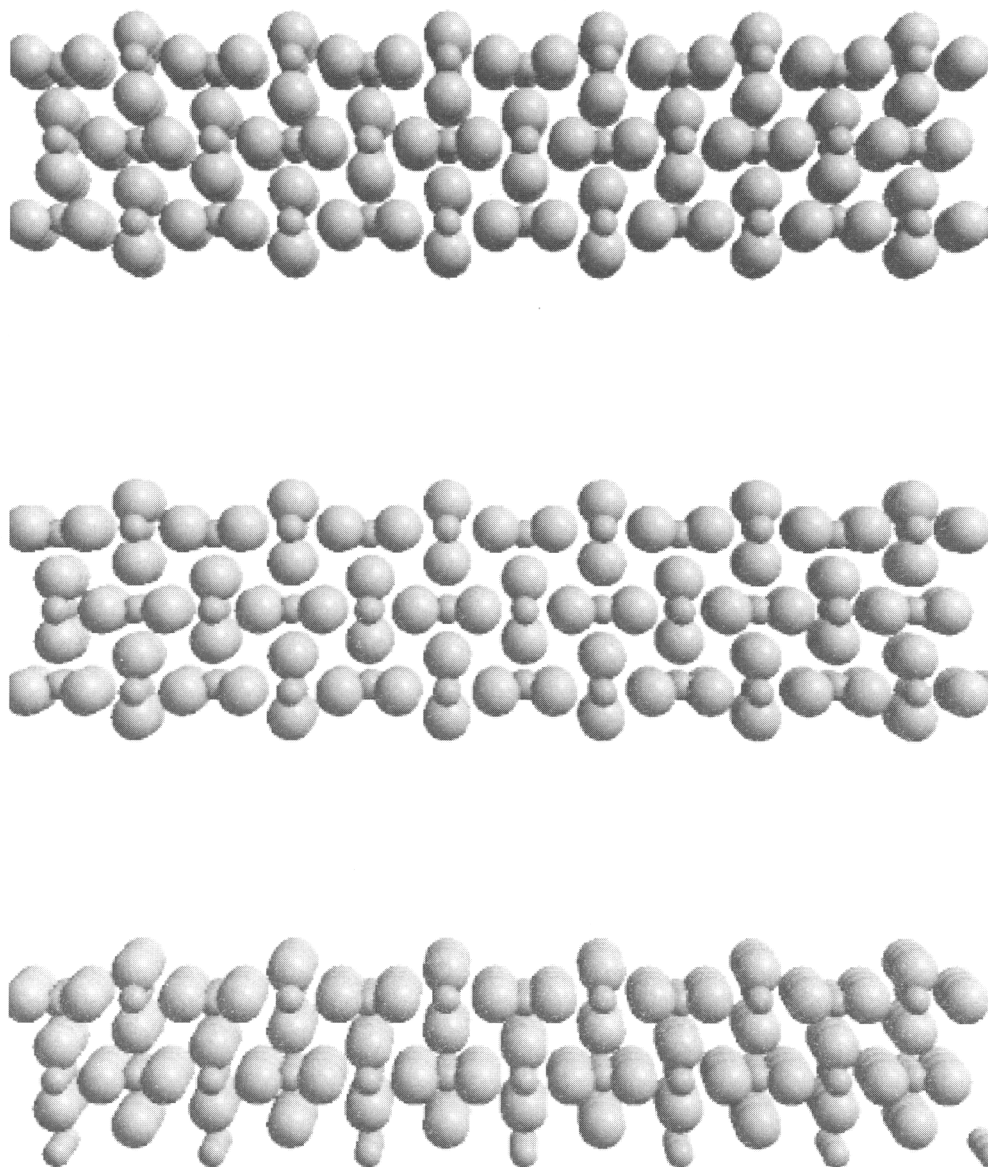
FIG. 1. Repeating slab geometry.

$$\varepsilon_{rum} = (\varepsilon_O - \varepsilon_{Mg})/d \qquad (7)$$
$$\varepsilon_{rel} = (\varepsilon_O + \varepsilon_{Mg})/2d \qquad (8)$$

where ε_{Mg} and ε_O are the displacements of Mg and O ions along the (outward) surface normal, and d is the Mg–O distance in the perfect crystal. The quantity σ is the energy per unit area needed to form the relaxed surface starting from bulk

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TABLE 3. The rumpling parameter ε_{rum}, relaxation parameter ε_{rel}, and surface energy σ for MgO slabs containing different numbers of ionic layers (Pugh, 1996). The rumpling and relaxation parameters are expressed as percentages of the nearest neighbour distance $a_0/2$

Slab thickness	ε_{rum} (%)	ε_{rel} (%)	σ (Jm^{-2})
2 layers	3.8	0.0	0.76
3 layers	3.7	0.0	—
4 layers	3.6	0.0	0.76

crystal. It is clear from Table 3 that for this surface the semi-infinite limit is effectively reached already for slabs containing three layers of ions. This undoubtedly has to do with the electrostatic properties of the rock-salt lattice structure (Zangwill, 1988).

Hartree-Fock calculations on this surface were first done many years ago (Causà et al., 1986), and more recently there have been several DFT studies. All these quantum mechanical calculations predict values for the rumpling and relaxation parameters and the surface energy in reasonable agreement with experiment, as reported in detail elsewhere (Pugh and Gillan, 1994). An interesting technical point has emerged, which is that the replacement of LDA with GGA produces a marked lowering of the surface energy, though it has rather little effect on the relaxation. This effect appears to be rather general, and is found also for the rutile (110) surface (Goniakowski et al., 1996).

The TiO₂ (110) surface

The (110) surface of rutile (TiO$_2$) is particularly interesting, since it is far from flat even when unrelaxed, and relaxation effects are far more significant than for MgO (001). The structures of the perfect crystal and of the perfect stoichiometric surface are shown in Fig. 2. A prominent feature of the surface are the rows of so-called 'bridging' oxygens which stand proud of the surface plane of Ti and O ions. The latter plane contains two kinds of Ti ions: 6-fold coordinated Ti ions lying beneath the bridging oxygens, and exposed 5-fold Ti ions; the O ions in this plane are referred to as in-plane oxygens.

Recently, a detailed study (Bates et al., 1997) has been made on the dependence of the surface

energy and relaxed structure on the slab thickness L and the vacuum width L' in repeating slab calculations for this surface. As an example, we show in Fig. 3 the calculated formation energy σ of the relaxed surface as a function of L and L' from slabs containing from 2 to 7 ionic layers (each layer in the repeating cell contains 6 ions, so that the cells contain from 12 to 42 ions). The results show that the convergence with respect to L' is simple and rapid, but the dependence on L is more complex. The reason for the oscillatory variation of σ turns out to be that for slabs having an even number of layers the relaxations on opposite faces of each slab reinforce each other, whereas for odd numbers they oppose each other. Even so, it is clear that convergence to the limit of infinite slab thickness is quite readily obtained.

First-principles calculations on the relaxed structure of the TiO$_2$ (110) surface were first done by Ramamoorthy et al. (1994a,b), and several other groups have reported DFT (Bates et al., 1997; Vogtenhuber et al., 1994; Lindan et al., 1997) and Hartree-Fock (Fahmi et al., 1993; Reinhardt and Heß, 1994) calculations. Very recently, measurements of the relaxed surface positions by surface X-ray diffraction have been published by Charlton et al. (1997). Encouragingly, the experiments and almost all the calculations (the theoretical results of Vogtenhuber et al. (1994) appear to be anomalous) agree on the main features of the surface relaxations: the 6-fold Ti and in-plane O ions move out of the surface, and the 5-fold Ti and bridging O ions move in.

A comparison of the predictions of Ramamoorthy et al. (1994a,b) and of two of the present authors — both using the DFT-pseudo-potential technique on repeating slabs — with the recent experimental results is given in Table 4. The comparison shows good semi-quantitative agreement both for surface ions and those in sub-surface layers, but with one striking exception: according to experiment, the bridging oxygens relax inward by 0.27 Å, but the calculated values are less than half of this. Other recent calculations (Reinhardt and Heß, 1994; Lindan et al., 1997) not shown in Table 4 suffer from a similar problem. Unless the experiments are at fault, which we have no reason to suspect, this disagreement may be pointing to some deficiency in the treatment of electronic correlation in all the calculations. (The reason for saying this is that, between them, the various calculations appear to have eliminated all other sources of error.) If there
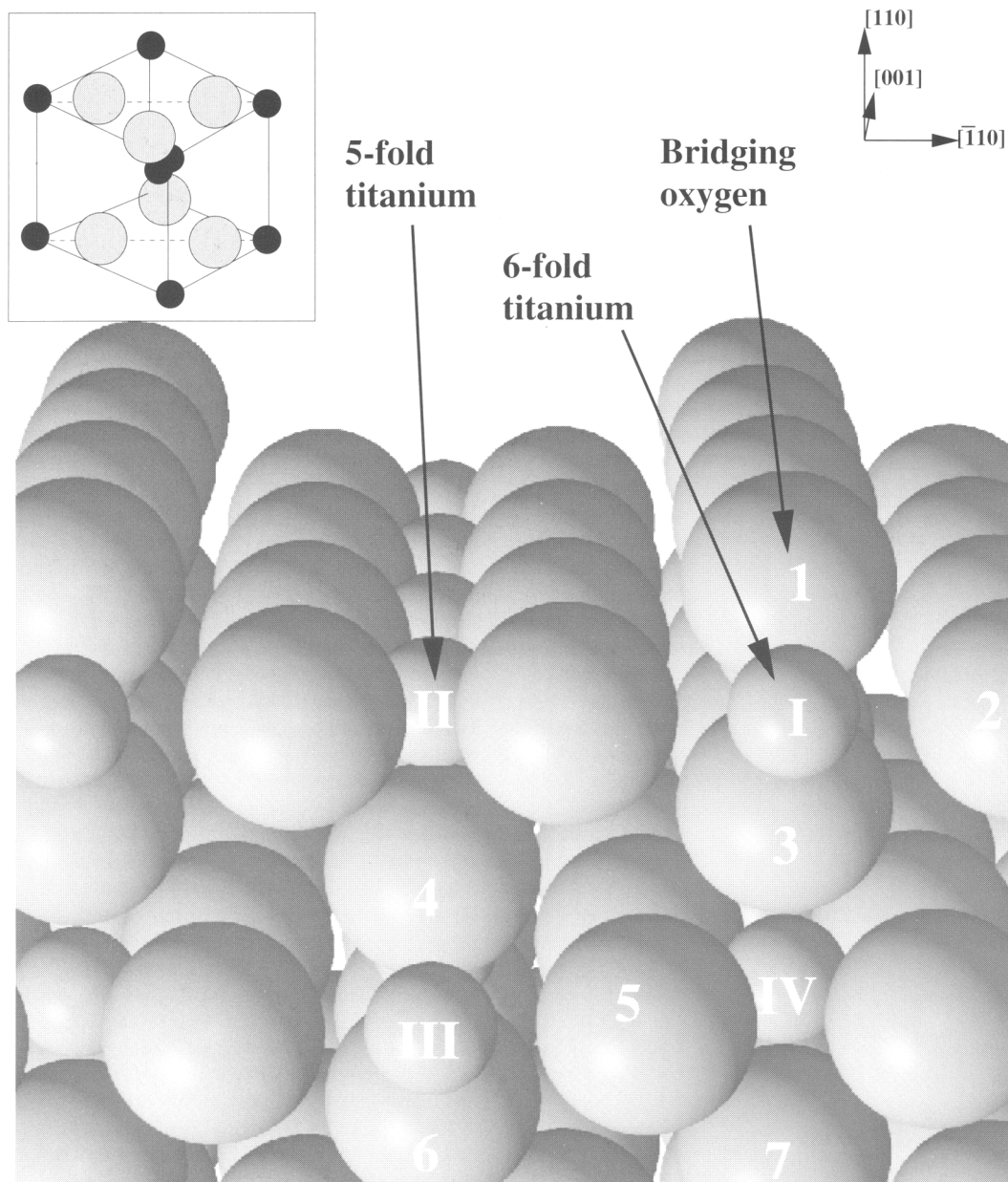
FIG. 2. Structure of the stoichiometric TiO$_2$ (110) surface. Small and large spheres represent Ti and O ions respectively, with numbering of ions corresponding to the notation of Table 4. Inset: the perfect-crystal structure, with small black spheres and large white spheres representing Ti and O ions respectively; diagonal dotted lines on top and bottom square faces mark a {110} plane.

TABLE 4. Atomic displacements along [110] for TiO_2 (110) from recent DFT-pseudopotential calculations (Bates *et al.*, 1997; Ramamoorthy *et al.*, 1994*b*) and from surface X-ray diffraction studies (Charlton *et al.*, 1997). Atom labels refer to Fig. 2 and displacements (in Å) are considered positive out of the surface in the [110] direction

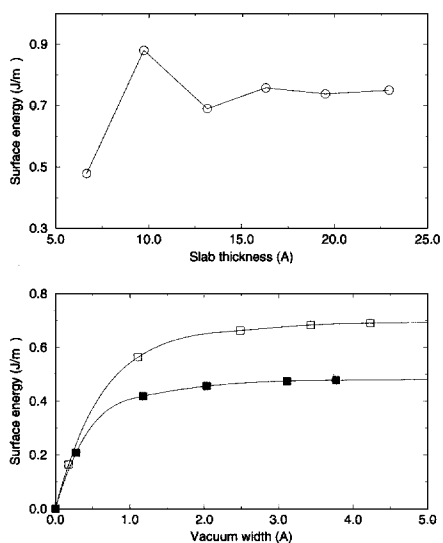| Atom	Bates *et al.*	Ramamoorthy *et al.*	Charlton *et al.*
Ti I	+0.23	+0.13	(+0.12 ± 0.05)
Ti II	−0.11	−0.17	(−0.16 ± 0.05)
Ti III	−0.06	−0.08	(−0.09 ± 0.04)
Ti IV	+0.12	+0.06	(+0.07 ± 0.04)
O 1	−0.02	−0.06	(−0.27 ± 0.08)
O 2	+0.18	+0.13	(+0.05 ± 0.05)
O 3	+0.03	−0.07	(+0.05 ± 0.08)
O 4	+0.03	+0.02	(0.00 ± 0.08)
O 5	0.00	−0.03	(+0.02 ± 0.06)
O 6	+0.03	−0.01	(−0.09 ± 0.08)
O 7	0.00	—	(−0.12 ± 0.07)

FIG. 3. Top panel: calculated surface energy of TiO_2 (110) as a function of slab thickness for a vacuum width of 5 Å. Bottom panel: calculated surface energy as a function of vacuum width for slab thickness of 6.5 Å (filled squares) and 13.0 Å (open squares).

really is a problem of this kind, it will surely reappear in theory-experiment comparisons for other oxide surfaces.

The α-Al_2O_3 (0001) surface

The surfaces of corundum (α-Al_2O_3) were studied several years ago by Hartree-Fock theory (Salasco *et al.*, 1991), and there have been several recent theoretical and experimental papers on their relaxed structure. The crystal structure is trigonal, with 10 ions in the unit cell, and the basal-plane surface (0001) is believed to be the most stable.

Older work (Mackrodt *et al.*, 1987; Tasker, 1988) based on empirical interaction models suggested spectacular ionic relaxations at this surface, and these have been fully confirmed by very recent X-ray measurements (Guénard *et al.*, 1997), and by DFT (Manassidis *et al.*, 1993; Manassidis and Gillan, 1994) and Hartree-Fock (Puchin *et al.*, 1997) work done in the past four years. These all indicate that relaxation causes the spacing between the surface plane of Al ions and the plane of O ions beneath it to decrease by ~60%. DFT calculations (Manassidis and Gillan, 1994) show that some of the other low-index surfaces exhibit equally dramatic relaxations. Effects like these serve to emphasise that *ab initio* and first-principles calculations must include full ionic relaxation if they are to be believable.

Surface defects

In the real world, oxide surfaces (or indeed any surfaces) rarely exist in the perfect form discussed

in the previous section. Atoms can be lost or gained at surface sites to give vacancies or adatoms; in addition, the processes by which the surface was formed generally give rise to topological defects, such as steps and corners, which may act as the initiation sites for chemical attack. First-principles methods are increasingly being used to study surface defects of all kinds, and this section will illustrate what can be done.

Oxygen loss

Many oxides lose oxygen from the surface under reducing conditions or at high temperatures. This is particularly true for oxides of variable-valence metals like Sn and Ti, but surface oxygen vacancies can be produced even on very stable oxide surfaces such as MgO (001). First principles methods have been used to study the reduction of MgO (Kantorovich *et al.*, 1995), TiO$_2$ (Lindan *et al.*, 1997) and SnO$_2$ (Manassidis *et al.*, 1995), and we use the last of these as an illustration.

Stoichiometric SnO$_2$ (cassiterite) is a semiconductor (the bandgap is 3.6 eV) having the rutile structure shown in Fig. 2, and its most stable surface is (110). When the material is heated to about 600 K, bridging oxygen atoms start to leave the surface (Cox *et al.*, 1988). This produces several measurable effects, including the

formation of a broad distribution of electronic states in the band gap, which can be seen in ultraviolet photoelectron spectroscopy (UPS).

First-principles calculations (Manassidis *et al.*, 1995) on perfect stoichiometric SnO$_2$ (110) show that the atomic relaxations are qualitatively similar to those measured on rutile (110), and the electronic density of states shows no states in the gap. On removal of bridging oxygens, the calculations reveal surface gap states very similar to what is seen experimentally. One of the most interesting things that has emerged from the calculations is an exact identification of what these states are. First-principles calculations give complete information about the spatial distribution, not only of the valence electrons as a whole, but of individual valence states. By studying in detail the calculated wavefunctions of the electronic states in the bandgap, one can say precisely what these states are.

For reduced SnO$_2$ (110), the calculations show that the gap states are localised around surface Sn ions (Fig. 4). This is not unexpected, since this ion is readily reduced from the Sn^{4+} to the Sn^{2+} state. What is interesting is that the electron density around reduced surface Sn ions is extremely asymmetric, consisting of a lobe sticking out into the vacuum. A connection can be made here with the strong polarisibility of the
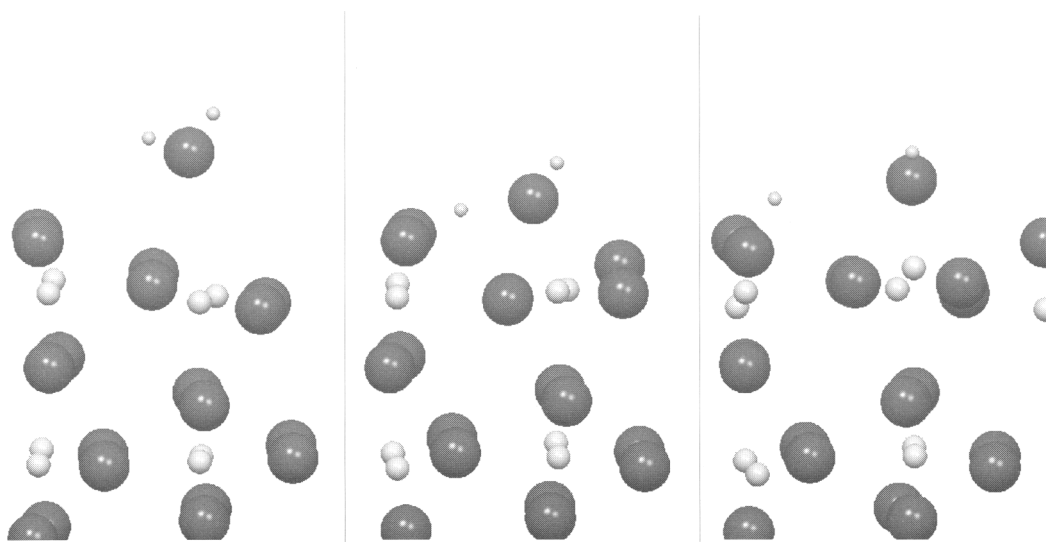

FIG. 4. Three snap-shots from a dynamical simulation of an H$_2$O molecule being dissociatively adsorbed on the TiO$_2$ (110) surface. Large, medium and small spheres represent O, Ti and H atoms respectively. Time proceeds from left to right, with an interval of ~0.2 ps between successive frames.

Sn^{2+} ion, and it has become clear that the easy loss of surface oxygen is intimately connected with the stabilisation coming from the polarisation of this ion.

Bridging oxygen vacancies are also readily formed on the (110) surface of rutile itself (Henrich and Kurtz, 1981), but the large electronic differences between the Sn and Ti ions mean that the vacancies are likely to be very different from those on SnO_2 (110). This is confirmed by recent calculations using both DFT (Lindan *et al.*, 1997) and Hartree-Fock methods (Mackrodt *et al.*, 1997). These show that spin polarisation of Ti^{3+} ions plays a major role in the energetics of surface reduction and in the origin of gap states observed by UPS.

Oxygen addition

The process of oxygen adsorption is enormously important because it is believed to be the first stage in a range of oxidation reactions which are promoted by oxide surfaces. It has been well established for many years that oxygen can be adsorbed in various forms, and there is evidence from electron spin resonance for species such as O^- and O^{2-}. Until fairly recently, however, very little had been done on this problem using first-principles methods. We have recently undertaken (Kantorovich *et al.*, 1996; Kantorovich and Gillan, 1997) a detailed study of atomic and molecular adsorption on the (001) surface of MgO and CaO, and several qualitatively important conclusions have emerged.

Perhaps most important is that atomic oxygen is very strongly adsorbed, but molecular oxygen shows only very small adsorption energies. On the flat MgO (001) surface, it has been shown that there are two main mechanisms for adsorption of atomic O, which involve binding to cation and anion sites respectively. At cation sites, O is most stable with an electron spin of unity (as in the free atom) and the adsorption energy is ~0.8 eV. At anion sites, binding of O leads to formation of surface peroxide (O_2^{2-}) and the adsorption energy is ~2.0 eV. At the CaO (001) surface, the calculated binding energies are even larger, being 1.0 eV at cation sites and 2.9 eV at anion sites. The anion-site adsorption energy is so large that it is energetically favourable for molecular oxygen to dissociate at the CaO (001) surface, combining with two surface lattice oxygens to form a pair of peroxide ions. These findings confirm the general picture suggested by some-

what earlier cluster calculations (Nygren and Pettersson, 1994), though the adsorption energies we find are considerably higher.

Topological defects

In contrast to the situation on metal or semiconductor surfaces, first-principles work on topological defects on oxide surfaces is still in its infancy. Yet it is universally accepted that features such as steps and corners can play a key role in surface reactions.

There is nothing to prevent one studying topological defects with slab geometry. A convenient way of treating the step, for example, is to introduce a regular sequence of steps separated by flat terraces, so that each face of the slab resembles a staircase. Provided the spacing between them is large enough, the steps will behave as though they are isolated. This is the procedure used in the recent first-principles work of Kantorovich *et al.* (1995) on irregular MgO surfaces. The results have provided important confirmation of earlier work (Colbourn *et al.*, 1983) based on simple models for the interaction between the ions. The main qualitative result is that ions at both steps and corners relax away from the perfect lattice sites in a way that tends to smooth out the irregularity. For example, ions at the salient edge of a step relax into the surface, and ions at the re-entrant edge relax outwards. For the monatomic {010} step on MgO (001), the largest of the ionic relaxations is over 10% of the nearest cation–anion distance.

Molecular processes

Over the past four years, there has been major progress in the use of the DFT-pseudopotential method to study the adsorption of simple inorganic and organic molecules on oxide surfaces. The case of water adsorption is particularly important for geology, so we pay particular attention to this problem. We also mention recent results on the adsorption of formic acid and methanol.

Water on MgO

The reaction of water with the surfaces of MgO is a paradigm problem for theory, because the molecule is so simple and because the surfaces themselves are reasonably well understood. All *ab initio* and first-principles calculations done so far

indicate that H_2O adsorbs in molecular form on the non-defective MgO (001) surface, but that it dissociates at steps and corners.

The first major *ab initio* calculations on this problem (Scamehorn *et al.*, 1993, 1994) were based on the Hartree-Fock method and consisted of a survey of several different adsorption geometries of H_2O at a quarter monolayer coverage on MgO (001). It was shown that the energetics of adsorption was governed mainly by electrostatic interactions of the H_2O dipole with the charges on surface ions. The most stable configuration examined had the water hydrogens coordinated to surface oxygen ions, and this gave an adsorption energy of ~0.5 eV after correlation corrections had been added. A number of dissociated configurations were also looked at, but these were all considerably less stable. This work was followed by Hartree-Fock studies of water at corner sites (Scamehorn *et al.*, 1994), and it was demonstrated that dissociative adsorption is then favoured.

These findings have been strongly supported by DFT-pseudopotential work. Recently, the Keele group (Pugh *et al.*, unpublished) has used this approach to study a variety of adsorbed molecular geometries, including some not examined in the Hartree-Fock work. A range of coverages was also looked at. The results indicate that the most stable configuration actually has the molecule lying flat on the surface with the H_2O oxygen coordinated to surface Mg, and with the two H atoms pointing to surface O. A flat configuration is what one would expect from electrostatics, since it enables all three atoms in H_2O to enjoy attractive Coulomb interactions with surface ions. This conclusion does not conflict with the Hartree-Fock work, since the latter looked only at configurations in which the molecular axis is normal to the surface. (In fact, if compared at the same coverage and for the same adsorbed geometries, the two theoretical approaches yielded extremely similar adsorption energies – mostly within 0.1 eV for an adsorption energy of typically 0.4 eV.) The DFT calculations were also used to study dissociated configurations, which all turned out to be less stable than the favoured molecular geometries by typically 0.8 eV.

The role of defects in the reaction of H_2O with MgO has been dramatically shown in dynamical first principles simulations by Langel and Parrinello (1995) on flat and stepped MgO (001) surfaces. In complete agreement with the static calculations we have described, they found that H_2O does not spontaneously dissociate on the flat surface. However, at re-entrant step-sites, dissociation spontaneously occurred within roughly 1 ps. These findings tie in well with experimental evidence that water reacts much more readily with defective than with perfect MgO surfaces.

Experiments (Jones *et al.*, 1984) show that water reacts quite rapidly with the MgO (001) surface provided it is not too perfect, and the growth of the hydroxide phase has been studied in detail. The steps involved in this transformation remain elusive, but an important insight has emerged from recent DFT-pseudopotential work (Refson *et al.*, 1995). This demonstrates that, although the MgO (001) surface is the most stable *in vacuo*, it is not the most stable in the presence of water. The calculations strongly suggest that there is a net stabilisation on going from the (001) surface covered with molecular water to the (111) surface covered with hydroxyl groups. The resulting (111) structure is also commensurate with the crystal structure of $Mg(OH)_2$ (brucite), and there may be a clue here to the growth mechanism of the hydroxide phase. This is an encouraging sign that further theory-experiment collaboration will lead ultimately to a full understanding of this important process.

Water on TiO_2 (110)

Even though H_2O dissociation appears to be energetically unfavourable on the perfect MgO (001) surface, it may be favourable on other oxide surfaces. An important case that has been investigated recently is H_2O adsorption on TiO_2 (110). Earlier rather primitive Hartree-Fock calculations (Fahmi *et al.*, 1993) had indicated that in this instance dissociation gives stabilisation, and semi-empirical calculations also gave this conclusion. This has now been confirmed by detailed DFT-pseudopotential calculations. In the work of Goniakowski and Gillan (1996), a variety of symmetrical and unsymmetrical adsorption geometries were investigated. The results indicate that there is a stabilisation of about 0.3 eV when the molecule is allowed to dissociate. It is worth mentioning that first-principles calculations on water absorption on the geometrically identical SnO_2 (110) surface (Goniakowski and Gillan, 1996) also predict that dissociation is energetically favoured.

The TiO_2 (110) surface is considerably more complicated than MgO (001), and there is always the danger with static calculations that the system may relax to a configuration that is not the most

stable possible. In this kind of situation, dynamical first-principles simulations are extremely valuable, because they allow the system to explore configuration space in much the same way as happens in the real world. Lindan *et al.* (1996) have reported simulations in which an H_2O molecule is sent down onto the TiO_2 (110) surface and the time evolution is observed. These simulations confirm what was found in the static calculations: that water spontaneously dissociates to form surface hydroxyl species (see Fig. 4). Very recently (Lindan *et al.*, 1998), dynamical simulations of this kind have been performed for full coverage of water on TiO_2 (110), and these indicate that under these conditions a mixed state is thermodynamically stable, with half of the water in molecular form and the remainder dissociated.

A further advantage of dynamical simulations is that they allow a rather direct analysis of the vibrations of surface species in thermal equilibrium. This is potentially important, because infra-red and HREELS measurements of vibrational frequencies are a commonly used way of attempting to identify adsorbed species. The simulations of Lindan *et al.* (1996) show that the two kinds of surface hydroxyls produced when H_2O is dissociatively adsorbed on TiO_2 (110) have very different vibrational behaviour, and this may well be relevant to the interpretation of recent HREELS experiments on adsorbed water on this surface (Henderson, 1996*a,b*).

Organic molecules

The study of organic molecules on oxides is still at an early stage, but we mention briefly two examples of recent DFT-pseudopotential work to illustrate the issues that are beginning to be addressed. Since the dissociative adsorption of H_2O on perfect MgO (001) seems to be energetically unfavourable, it is natural to ask whether there are other molecules which would dissociate on this surface. The dissociation $H_2O \rightarrow H^+ + OH^-$ is an acid-base reaction, and this suggests that stronger acids, e.g. formic acid (HCOOH), are likely candidates. In fact, there is experimental evidence that formic acid does dissociate on the surface, even in the absence of defects.

The adsorption of HCOOH on MgO (001) was investigated in the calculations of Szymański and Gillan (1996), who studied a variety of both molecular and dissociated absorbed configurations. As in the case of H_2O adsorption, the binding of the HCOOH molecule to the surface seems to be mainly due to electrostatic attraction, and we found an adsorption energy of about 0.5 eV, which is similar to what was found for H_2O. At low coverage, the most stable molecularly adsorbed geometry that we have found has the acid H and the carbonyl O of HCOOH coordinated to surface O and Mg ions respectively. However, the important finding is that there is virtually no barrier to spontaneous dissociation of this configuration to give the formate ion $HCOO^-$, with the released proton combining with the surface oxygen ion to form a hydroxyl ion. The resulting stabilisation is about 0.3 eV. In the light of the H_2O calculations, one would expect HCOOH to dissociate even more readily at a surface step, but this has not yet been investigated.

Finally, we mention very recent work, in which we have done first-principles calculations on the adsorption of the series of ROH molecules H_2O, CH_3OH, H_2O_2 and HCOOH on TiO_2 (110), with the aim of exploring some of the factors that determine whether adsorption is molecular or dissociative (Bates *et al.*, 1998; Bates and Gillan, 1998). Not surprisingly, we find that the acidity of the molecule plays a major role, with HCOOH dissociating very readily on the surface. But the electrostatic properties and geometry of the surface also turn out to be very important. A third strong factor is interactions between the adsorbed molecules, which are very important in determining the detailed adsorbed geometries.

Outlook

For many years, technical difficulties prevented a satisfactory interaction between theory and experiments on oxide surfaces. We hope we have shown that the tide is now definitely on the turn. The experiment-theory interaction is already becoming fruitful in the area of perfect surfaces, where the gross features of the relaxed structure of several surfaces are now quite firmly established. Theory is also helping to interpret the observed electronic structure of reduced surfaces, as in the cases of SnO_2 and TiO_2. Finally, the energetics, equilibrium geometry and electronic structure associated with adsorption of a range of simple molecules are being studied by first-principles methods, and preliminary comparisons with experimental adsorption energies are encouraging. This recent progress gives good reason for believing that first-principles calculations on oxide surfaces can also be used in a predictive way.

We want to emphasise that the techniques we have described should not be regarded as 'difficult', in terms of either the expertise or the computer power needed to apply them. The DFT-pseudopotential technique is now so well established and robust that it can be routinely applied as a tool by anyone prepared to spend a little time mastering it. Advances in computer power also mean that much can now be done with standard workstations or even PCs. Not everything will be done in this way, of course: the most ambitious calculations, for example dynamical first-principles simulations of complex surface processes, need the power of massively parallel supercomputers. Our simulations (Lindan *et al.*, 1996) of the dynamics of water adsorption on TiO$_2$ (110) are a case in point.

The scene is now set for a major expansion of this kind of work. First-principles calculations are needed on a much wider range of surfaces and adsorbed species. For example, the systematics of molecular versus dissociative adsorption and the role of surface defects in this systematics are very poorly understood. The calculations already done on the adsorption of H$_2$O, HCOOH and other molecules on MgO (001) and TiO$_2$ (110) suggest what is possible, but have not yet given a systematic understanding. What is needed here is a comparison of the adsorption of given molecules on a range of perfect and defective surfaces, or a range of molecules on a given surface. Systematic studies like this should also be invaluable in bringing theory and experiment into closer contact.

Finally, we want to stress that the capabilities already demonstrated for oxide surfaces are directly transferable to a wide range of other materials, some of them of geological interest. An obvious example here is sulphides, such as FeS$_2$ (pyrites). These present no new technical problems, and should if anything be somewhat less computationally demanding than oxides. There has already been quite extensive first-principles and *ab initio* work on silicates and a smaller amount on carbonates. Virtually nothing has yet been done on the surfaces of these materials. There are clearly enormous possibilities for future work.

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