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Ab-initio studies of SrTiO₃(001) surface reconstructions

by

Benjamin David Ringham

A Doctoral Thesis

Submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of Loughborough University

1st October 2007

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Acknowledgments

Firstly I would like to thank my supervisor Dr. Steven Kenny, without whom I would not have begun this PhD. His continued support, patience and, when needed, motivation have ensured that I have reached the end of my research. I would also like to thank Dr. Martin Castell, from the Department of Materials at Oxford University, for his experimental view and suggestions on the subject.

I would like to thank EPSRC and Loughborough University for providing me with the necessary funding and equipment to carry out my research.

I would also like to thank my family for their support both emotionally and financially. Their understanding and encouragement have been invaluable to my completing my research. I especially want to thank my girlfriend, Emma, who has got me through some tough times and has always been there for me at home.

Finally I would like to thank my friends, particularly those in w1.62 (both past and present), for constant distractions and providing a light hearted environment in which to work.
Abstract

A number of SrTiO₃(001) surface reconstructions have been studied using Plato, Package for Linear Combinations of Atomic Type Orbitals, a first principles density functional theory approach. The reconstructions studied are of order (1×1), (2×1) and (\(\sqrt{2} \times \sqrt{2}\)), and include a mixture of previously studied surface reconstructions and new proposals. Also studied are a series of adatom reconstructions, proposed by Kubo and Nozoye, involving (1×1), (2×1), c(2×2), (2×2), \((\sqrt{5} \times \sqrt{5})\)-R26.6° and c(4×4) terminations.

Energy calculations have been performed for each surface reconstruction, and phase diagrams produced for a range of temperatures and pressures. This allows for a measure of relative stability to be achieved, and, where possible, results are compared with those published previously. These phase diagrams have shown that under certain conditions the (1×1) SrO terminated surface, the (2×1) Ti adatom on a (1×1) SrO terminated surface at site 1 and the \((\sqrt{2} \times \sqrt{2})\)R-45° DL-TiO₂ terminated surface are the most stable surface reconstructions.

Scanning Tunneling Microscopy (STM) has been used extensively to study the surface reconstructions of SrTiO₃(001) experimentally. STM images have therefore been simulated by employing the Tersoff-Hamman approach and compared with those images seen experimentally, as well as those previously simulated, to complement the energetic analysis. By comparison of simulated and experimental images, unsuitable surface reconstructions are identified and eliminated from consideration. These images, in conjunction with the phase diagrams, identify likely candidates for those surfaces observed experimentally.
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7.1 The surface excesses for the supercells of the (1x1), c(2x2), (2x2), (\sqrt{5} \times \sqrt{5}) and c(4x4) adatom surface reconstructions. .................................................. 107
SrTiO$_3$ is a perovskite oxide that is of interest for a number of applications because of its dielectric and ferroelectric properties. It has also come to prominence as a lattice matched substrate in the growth of high $T_c$ superconducting thin films [1] and hetero-structures [2]. SrTiO$_3$ is particularly useful for these applications as it does not exhibit a domain structure that influences the topography of the surfaces. Throughout a range of temperatures the simple cubic structure is maintained. However, whilst the atomic structure of SrTiO$_3$ is well known, the surface reconstructions are currently poorly understood, and it is because of this fact that both experimental and theoretical work is being extensively carried out and is the main motivation behind this thesis.

A variety of experimental techniques have been used to study SrTiO$_3$(001), including scanning tunneling microscopy (STM) [3, 4, 5, 6], low energy electron diffraction (LEED) [7, 8, 4], reflection high-energy electron diffraction (RHEED) [9, 10], medium energy ion scattering (MEIS) [11] and room-temperature X-ray diffraction (SXRD) [12]. Numerous surface reconstructions have been observed from these techniques, including (2 x 1) [3, 13, 14], (2 x 2) [14, 15], c(4 x 2) [3, 8], c(6 x 2) [8] and ($\sqrt{5} \times \sqrt{5}$)-R26.6° [5, 6, 16]. Through these experimental processes the periodicity of the surface structure can be determined, however, the underlying surface stoichiometry cannot be resolved. SrTiO$_3$ is a structure made up of alternating layers of its sub-units SrO and TiO$_2$, as shown in figure 2.1. As such it is possible to create many different surface terminations by cleaving layers off to reveal the layer below. These are then annealed to varying temperatures in a UHV environment to create the desired
SrTiO$_3$ has many different surface terminations, and we are interested in examining the energetics of these, as well as the differences between them. It might be expected that an unreconstructed SrTiO$_3$ surface would give rise to both SrO and TiO$_2$ terminations, however all observations show a step height that is one unit cell height, so a mixed termination is not present.

The proposed (2×1) reconstructions in the literature are that of TiO$_2$ and Ti$_2$O$_3$, both suggested by Castell [3], and the double layer TiO$_2$ structure proposed by Erdman et al. [13]. These surface reconstructions have previously been studied by Johnston et al. [17], and they found that none of these reconstructions were stable for realistic temperature and pressure conditions.

Kubo and Nozoye [5] proposed a set of reconstructions where Sr adatoms are situated at the fourfold O site of the underlying (1×1) TiO$_2$ layer. Simulations were performed and simulated STM images displayed that show that for some of these cases the simulated images agree with those gained experimentally. However no calculations of the surface energies were performed, so no conclusions could be drawn as to whether any of these surfaces are energetically stable. Liborio et al. [18] further studied these reconstructions and found that under certain conditions some of the reconstructions were favourable, however, this work did not consider the (2×1) adatom reconstruction.

This work begins with an introduction to both SrTiO$_3$ and experimental STM, a non-intrusive method of surface analysis which maps the surface electronic structure, in Chapter 2. Previous studies on the (1×1) surface reconstructions, both experimental and theoretical, are outlined and comparisons are drawn. Various larger surface reconstructions that have previously been proposed are also presented in this chapter.

The study of surface energy is not a trivial one. Comparison of one surface with another is problematic due to the different numbers of sub-units contained within each structure. To solve this problem the concept of chemical potentials is introduced, however this is not sufficient for all of the surfaces. Non-stoichiometric surfaces provide a different set of problems. A non-stoichiometric surface is one that can not be defined in terms of integer multiples of sub-units. As such the concept of surface excesses is introduced, as well as a formulation of the method required to calculate the energies of these surfaces.
In chapter 3 PLATO (Package for Linear-combination of Atomic Type Orbitals), a program developed by Steven Kenny\(^1\) and Andrew Horsfield\(^2\), is presented. As PLATO is built on a Density Functional Theory framework, the fundamentals of DFT are also outlined. The method of total energy calculation is outlined, and necessary preliminary calculations are presented. The method that shall be used in simulating experimental STM images is also introduced.

The method of computational steering is then introduced in chapter 4, outlining the benefits of such a method and a simple case study is presented. Fully interactive 3-dimensional STM visualisation is also introduced in this chapter.

Experiments into the surface structure of SrTiO\(_3\) have produced some interesting results. The simplest of the surface terminations, that of the (1×1) surfaces, has yet to be imaged experimentally. This is a curious result that presently has two possible explanations, either that the surfaces are too electronically flat to be successfully imaged, or that they are simply unstable in a high vacuum environment. The former shall be addressed within this work in chapter 5, and an explanation of the later and the possible method for analysis shall be presented in chapter 8. Also within this work will be graphical representations of all of the surfaces that we shall study.

This study will initially focus in chapter 5 on the (1×1) and (2×1) surfaces previously proposed in the literature. There has been extensive work carried out on these surfaces, which allows for a good comparison to be made between the results of this work with those already published. This will allow for extensive analysis of our methods, so that in future we can move forward to work on more complex systems with a high degree of confidence. New proposals for (2×1) reconstructions are also presented here, with the motivation behind each outlined. Surface energy calculations are performed for each surface across a range of temperatures and pressures, and simulated STM images are then presented. Within this chapter are energy calculations and simulated STM images for the \((\sqrt{2} \times \sqrt{2})R-45^\circ\) DL-TiO\(_2\) surface reconstruction, a recent proposal by Liborio [19].

Chapter 6 focusses on the (2×1) adatom model proposed by Kubo and Nozoye. Their

\(^1\)S. D. Kenny, Dept. of Mathematical Sciences, Loughborough University
\(^2\)A. P. Horsfield, Department of Materials, Imperial College London
work is expanded to include both Ti and Sr adatoms on both TiO$_2$ and SrO terminated surfaces. This is further extended to consider three different adatom positions for each case. Surface energy calculations and simulated STM images are presented, and the most likely candidates are selected and compared to the surfaces in chapter 5 and experimental work. Special attention should be paid to the (2×1) Ti adatom at site 1 on the SrO terminated surface which has shown to be the stand out result in terms of surface energy calculations, and also proves to be a very good match to the experimental STM imagery.

Some of the additional adatom reconstructions proposed by Kubo and Nozoye are studied in chapter 7. Again their work is extended, however here only the suggested Sr adatom on TiO$_2$ and the equivalent Ti adatom on SrO are considered. Surface energies are then calculated, and graphs are presented to show how these new energies compare with those previously studied. Simulated STM images are then shown and compared with those gained experimentally, and the displacement of atoms during relaxation is shown and compared with that calculated in [5].

Finally in chapter 8, final conclusions are drawn over which of the studied reconstructions are the most energetically favourable and which produce a simulated STM image that corresponds to those gained experimentally. Proposals are then made to further this work to give a more complete picture of SrTiO$_3$. 
Chapter 2

SrTiO$_3$ surface studies

2.1 SrTiO$_3$

Strontium Titanate (SrTiO$_3$) has a cubic perovskite structure with a lattice parameter of 3.905 Å. Its unit cell is composed of distinct layers of SrO and TiO$_2$, with Ti situated at the cube corners, O at the cube edges and Sr in the centre of the cube, as illustrated in figure 2.1. In this image, and all following images of SrTiO$_3$, the grey spheres represent the Sr atoms, the blue spheres the Ti atoms and the red spheres the O atoms. Classically SrTiO$_3$ is considered to be composed of Sr$^{2+}$, Ti$^{4+}$ and O$^{2-}$ ions.

The main interest in studying SrTiO$_3$ surfaces comes from its extensive use as a substrate in the growth of high $T_c$ superconducting thin films. It has also been suggested as a candidate for a crystalline gate dielectric in silicon based devices. However, currently the atomic structure of the surface reconstructions are only poorly understood.
2.2 Scanning Tunneling Microscopy

Scanning Tunneling Microscopy (STM) was developed by Binnig and Rohrer in 1981 [20], and first implemented by Binnig, Rohrer, Gerber and Weibel [21, 22]. Binnig and Rohrer received the Nobel Prize for physics just five years after building their first STM. Figure 2.2 shows the basic layout of an STM, which consists of a probe tip, usually made of W or a Pt-Ir alloy, and three mutually perpendicular piezoelectric transducers. By applying a sawtooth voltage to the x-piezo and a voltage ramp to the y-piezo, the tip can be made to scan over the xy plane. STM gave for the first time images of individual atoms on the surfaces of materials.

It is a non-intrusive technique used to determine the surface structure of solids. STM is not a technique for examining a physical map of the surface, but rather the surface electronic structure. It offers the possibility of direct, real-space determination of surface structures in three dimensions, including non-periodic systems. The real usefulness of STM stems from the fact that it is not just one dimensional but is instead sensitive to the full three-dimensional structure of the surface.
There are two types of modes in which an STM can operate in, constant current and constant height. In both cases the tip is brought close enough to the surface of the substance that the vacuum tunneling resistance between tip and surface is both finite and measurable. The tip and substrate never physically touch, but get to a point where it is possible for electrons to tunnel through the vacuum between them, resulting in a current in the system. A voltage, or bias, is needed to create this current between the tip and surface. The resulting current can then either tunnel from the tip to the surface, this occurs with a positive bias, or from the surface to the tip, in the case of a negative bias. The tip then scans in two dimensions, usually x and y as in figure 2.2. In constant current STM, the height of the tip adjusts to maintain a constant current. It is this height of the tip which is measured and mapped, with respect to the position, that gives the surface electronic structure. In constant height STM, the tip remains at the same distance from the surface throughout, and the value of the current with respect to position is measured. The result is essentially a contour map of the electronic surface of the substance. Within STM, the tunneling current is exponentially dependent on the height, with a 1Å change typically giving a factor of ten difference in the tunneling current. It is this sensitivity to the current that allows for a good
atomic resolution. This means that the tip can be expected to follow the surface height to 0.1 Å or better. All work presented here will be based on constant current mode STM as this is by far the most common mode of operation.

2.3 SrTiO₃ (100) Surface Reconstructions

Previous studies on SrTiO₃ suggest that a (1x1) surface is the most energetically favourable and yet these surfaces have not been successfully imaged experimentally. Currently there are two suggestions as to why this may be. Firstly, it has been proposed that the (1x1) reconstructions are too electronically flat for a STM tip to image any distinct surface features. By producing simulated STM images of these cases it is hoped that it can be seen whether or not this is true. Secondly, in preparing SrTiO₃ for STM imaging, it is annealed within a UHV environment. It has been proposed that the surfaces are susceptible to oxygen defects in this case.

Previous studies have shown that a number of surface reconstructions are more energetically favourable than a surface with an oxygen vacancy. It is suggested that a surface with an oxygen vacancy will reconstruct to a (2x1) reconstruction, and this local (2x1) ordering causes further oxygen vacancies to occur, spreading this (2x1) reconstruction throughout the surface. It is hoped that via simulation of these (2x1) surfaces, suitable candidates can be identified through a combination of relative stability and simulated imagery.

In its stoichiometric form, SrTiO₃ is an insulator, with a band gap of 3.2eV. This band gap will not allow the necessary current to tunnel between the STM tip and the surface, so a dopant is required to add conduction states. Experimentally, Nb⁵⁺ is used as a substitutional dopant for Ti, adding the required states within the band gap and allowing successful imaging to occur. However, it is not yet clear how this affects the surface and the resultant imagery. Additional to this, the interpretation of atomic resolution STM can be very difficult as it is not clear whether what can be seen is purely a result of the electronic structure, or if the surface topology is affecting the results. By simulating the surfaces we can see a much clearer picture of both the surface electronic structure and the underlying topology.

SrTiO₃ is a substance that has constant new proposals for its surface structure. The tra-
ditional surface reconstructions have been well studied both experimentally and theoretically. However, with many new surfaces being proposed it is a substance that still requires a great deal of study. The most well studied surface reconstruction are the (1x1) surfaces. There are only two possible charge neutral (1x1) reconstructions, a TiO₂ terminated surface and a SrO terminated surface, as can be seen in figures 2.3 and 2.4 respectively. Theoretically, these are the surfaces that we would expect to obtain at atmospheric pressure, as these have been shown to be the most energetically stable. However, to date, neither of these surfaces have been successfully imaged in an STM. Martin Castell [3] reports that images showed a rough surface morphology with no distinct terrace formation, and that no atomic resolution images can be obtained from these surfaces, even though the same samples showed crisp (1x1) LEED patterns. He then suggests that this could be down to a C contamination, which would require an anneal temperature of 570°C to remove, increasing the chances that an O defect would occur.

In order to compare results it is necessary to calculate the atomic displacement, \( \delta_z \), the change in interlayer distance between two adjacent slabs, \( \Delta d_{ij} \), and the amplitude of the rumpling of each layer \( \eta_i \). We denote the change in z-position of an atom as \( \delta_z(M) \) and \( \delta_z(O) \) for a metal and oxygen respectively. The change in interlayer distance is the difference of averaged atomic displacements between two layers \( i \) and \( j \) and is defined as

\[
\Delta d_{ij} = \delta_z(M_i) - \delta_z(M_j).
\] (2.1)
Figure 2.4: The (1x1) TiO$_2$ surface reconstruction. The small circles in the top down view represent atoms in the layer below the surface.

Layer rumpling is the amplitude of these displacements, and is defined as

$$\eta_i = \delta_z(O_i) - \delta_z(M_i).$$  \hspace{1cm} (2.2)

In the case of multiple metal or oxygen atoms in a layer, this value $\delta_z(M)$ or $\delta_z(O)$ is taken as the average of the atoms. In each case a positive value represents a displacement towards the vacuum.

There have been a number of experimental studies on the (1x1) structure of SrTiO$_3$(001). Tables 2.1 and 2.2 show results for the TiO$_2$ and SrO terminations respectively. Bickel et al. [7] used low-energy electron diffraction (LEED) to study the (1x1) terminated surfaces of SrTiO$_3$. Their sample was prepared by Argon-ion sputtering at 550 K and 0.2 Pa for 1 hour, with a current of 10 $\mu$A, followed by annealing at 900 K. This sputtering annealing cycle was repeated several times before a final flash to 1400 K with subsequent cycles of annealing in Hydrogen and Oxygen. They varied the interlayer distances $d_{12}$ and $d_{23}$ to find a best fit model, giving them 588 trial structures for each termination. Combining each structure of one termination with each structure of the other meant a total of about $3.5 \times 10^5$ $R$-factor calculations. They calculated a lattice constant of 3.82 $\pm$ 0.15 Å, which compares favourably with the widely accepted value of 3.905 Å. Using the Pendry $R$ factor [24] as a qualitative analysis of their results they performed trial calculations on each of the (1x1) reconstructions, giving a best $R$ factor above 0.63. Performing the calculation assuming a 1:1 mixture of both terminations gave a minimum $R$ factor of 0.529. This value is acceptable, but
it suggests that the structures examined can be refined by additional structural variations. The authors noted that the reconstruction may also extend to layers below the surface and that the assumed 1:1 mixture is only an approximation.

Ikeda et al. [11] and Nisimura et al. [25] investigated the TiO$_2$ terminated surface reconstruction using medium energy ion scattering (MEIS) and reflection high energy electron diffraction (RHEED). Their substrate was prepared by chemical etching using a NH$_4$F-HF buffer solution (pH 3.5-3.8) to remove SrO terminations, gaining 88 ± 2 % TiO$_2$ surface coverage. They observed that this coverage remained constant at temperatures from room temperature to 710 °C whilst annealing in O$_2$. However, after UHV annealing at 710 °C for 1 hour, they found this coverage decreased to 82-83 %, suggesting that the Sr-O bond is more stable against UHV annealing. The authors noted oxygen vacancies created at random sites of the TiO$_2$ termination, with a rearrangement of atomic configuration to minimise the surface energy resulting in a (2x2) ordered structure.

Charlton et al. [12] used room-temperature X-ray diffraction (SXRD) to investigate the surface relaxation of SrTiO$_3$. Like Bickel et al. [7] they prepared their samples with repeated cycles of Ar$^+$ sputtering and annealing to 900 K. A final anneal at 900 K in 10$^{-6}$ mbar O$_2$ to prevent formation of the (2x2) phase noted by Bickel et al. [7]. They fitted their experimental data to theory using a total of 19 fitting parameters, including 10 vertical atomic displacements. The authors found their best fit came with a surface coverage that was 22 % SrO and 78 % TiO$_2$.

Hikita et al. [9] used reflection high energy electron diffraction (RHEED) to study the two (1x1) terminations of SrTiO$_3$. Their sample was cleaned by a Bi deposition/desorption cleaning method, and then oxidation was carried out with NO$_2$ at a pressure of 10$^{-4}$ Pa at 673 K for 1 hour. This resulted in the (1x1) TiO$_2$ terminated surface. The (1x1) SrO termination was then gained from this by depositing a monolayer of SrO onto the TiO$_2$ terminations. These terminations were optimised by altering the interlayer distance to gain the smallest $R$-factors. They gained as best results for the TiO$_2$ and SrO terminations an $R$-factor of 0.26 and 0.28 respectively.

These studies seem to indicate that a (1x1) terminated surface will contain a mixture of TiO$_2$ and SrO terminations.
<table>
<thead>
<tr>
<th></th>
<th>LEED</th>
<th>RHEED</th>
<th>MEIS</th>
<th>SXRD</th>
</tr>
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<tbody>
<tr>
<td><strong>Ref</strong></td>
<td>[7]</td>
<td>[9]</td>
<td>[11]</td>
<td>[12]</td>
</tr>
<tr>
<td><strong>Atomic Displacements (Å)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\delta_z(TO_1)$</td>
<td>-</td>
<td>-</td>
<td>0.02 ± 0.01</td>
<td>0.00 ± 0.03</td>
</tr>
<tr>
<td>$\delta_z(O_1)$</td>
<td>-</td>
<td>-</td>
<td>0.08 ± 0.01</td>
<td>-0.50 ± 0.30</td>
</tr>
<tr>
<td>$\delta_z(Sr_2)$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-0.01 ± 0.01</td>
</tr>
<tr>
<td>$\delta_z(O_2)$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.20 ± 0.10</td>
</tr>
<tr>
<td><strong>Surface Rumbling (Å)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\eta_1$</td>
<td>0.08 ± 0.08</td>
<td>0.10</td>
<td>0.06 ± 0.02</td>
<td>-0.50 ± 0.33</td>
</tr>
<tr>
<td>$\eta_1(%)$</td>
<td>4 ± 4</td>
<td>5.1</td>
<td>3.1 ± 1.0</td>
<td>-26 ± 17</td>
</tr>
<tr>
<td>$\eta_2$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.21 ± 0.11</td>
</tr>
<tr>
<td>$\eta_2(%)$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>11 ± 6</td>
</tr>
<tr>
<td><strong>Change in interlayer spacing</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta d_{12}$</td>
<td>0.04 ± 0.04</td>
<td>0.07</td>
<td>0.02 ± 0.01</td>
<td>0.01 ± 0.04</td>
</tr>
<tr>
<td>$\Delta d_{12}(%)$</td>
<td>2 ± 2</td>
<td>3.6</td>
<td>1 ± 0.5</td>
<td>0.5 ± 2.0</td>
</tr>
<tr>
<td>$\Delta d_{23}$</td>
<td>-0.04 ± 0.04</td>
<td>0.05</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\Delta d_{23}(%)$</td>
<td>-2 ± 2</td>
<td>2.6</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2.1: Experimental atomic displacements, surface rumpling and change in interlayer spacing for the (1x1) TiO$_2$ terminated surface. Positive displacements indicate a displacement towards the vacuum.
The results for the (1x1) TiO$_2$ terminated surface suggest very little atomic displacement for the surface layer metal, with a much larger displacement for surface oxygens. However, the oxygen shows displacement both towards the bulk and towards the vacuum. Again, where results are present, it can be seen that this pattern repeats in the second layer, with a much larger displacement of oxygen. The results gained from LEED [7], RHEED [9] and MEIS [11] all show excellent agreement for rumpling of the surface layer, with the results from SXRD [12] showing a much larger and negative rumpling. All of the results show good agreement of the interlayer distance $\Delta d_{12}$, with all showing a tendency for the first two layers to move apart. The results of Bickel et al. [7] showed that the first SrO layer and second TiO$_2$ layer are actually closer together than their ideal lattice positions.

In contrast with the TiO$_2$ termination, the metal in the surface layer undergoes a much larger displacement in the (1x1) SrO termination, here showing movement towards the bulk. Good agreement can be seen for the results of LEED [7] and RHEED [9] for the surface rumpling, with SXRD [12] again showing much more surface rumpling. The results for the interlayer distances are very varied, with the results from LEED [7] and SXRD [12] both showing the first two layers closer together, but by much different magnitudes. LEED [7] and RHEED [9] show agreement for the second and third layers, with both predicting that these layers will be further apart than their ideal positions, but SXRD [12] shows that they will be much closer together.

There have been a number of different theoretical methods employed to study SrTiO$_3$(001), and in particular the (1x1) surface reconstructions. Tables 2.3 and 2.4 show the results of the methods outlined below.

The results from Padilla and Vanderbilt [26] were obtained using a plane wave basis and the LDA in conjunction with ultrasoft pseudopotentials. As in the work presented here they have used seven atomic layers, but with three vacuum layers. They reported the biggest displacement for the metal atom situated in the surface layer in both cases, with the Ti moving a distance of 0.131Å and the Sr atom moving 0.220Å, both inwards towards the bulk.

Cheng et al. [27] used CASTEP to also perform plane-wave pseudopotential (PWP) calculations. They used eleven atomic layers and four vacuum layers. Their results differ
Table 2.2: Experimental atomic displacements, surface rumpling and change in interlayer spacing for the (1x1) SrO terminated surface. Positive displacements indicate a displacement towards the vacuum.
slightly from that of Vanderbilt [26], with the authors suggesting that this was due to the use of different pseudopotentials. However, the trend observed is the same as that observed by Padilla and Vanderbilt, with the metal atom in the surface layer of each type moving towards the bulk. The main difference is in the Sr atom in the second layer of the TiO₂ termination, which shows the biggest displacement at 0.18Å, although it again is moving towards the vacuum.

Liborio et al. [19] and Zhang et al. [28] utilised SIESTA, which is a pseudopotential code employing a basis of localised atomic orbitals and the LDA. They both used cells consisting of seven atomic layers. Both sets of results show good agreement with each other, and show the same trends as for the plane-wave pseudopotential cases, except in the third layer of the SrO termination where Zhang et al. showed both metal and oxygen to be moving towards the vacuum, whereas previously they had both been shown to be moving towards the bulk.

Johnston et al. [17], [29], used the full-potential linear combination of muffin-tin orbitals (FP-LMTO), a DFT methodology utilising the LDA, and again used seven atomic layers with three vacuum layers. The main difference arising from this technique is in the oxygen atoms in the first two layers of the SrO termination. FP-LMTO shows an inwards displacement, where an outwards displacement is shown in both the PWP and SIESTA cases.

Theoretical work on the TiO₂ terminated surface predicts a displacement towards the bulk of the surface atoms, with the underlying Sr atom showing a tendency to move towards the vacuum. This is in contrast to the experimental work, where both the Ti and O atoms are shown to move towards the vacuum. Larger magnitude displacements are also reported in the theoretical work than have been shown experimentally. However, the surface rumpling shows excellent agreement with that shown experimentally for the surface layer, although the change in interlayer spacing is shown to be much larger here than in table 2.1.

The results for the SrO terminated surface predict a large displacement towards the bulk for the surface Sr atom, and this is also shown to be the case in table 2.2. However, the results for the second layer show opposite trends, with theory predicting a displacement towards the vacuum and experimental work showing a contraction back into the bulk. Again good agreement can be seen in the surface rumpling, and the change in interlayer spacing matches very well with the results from LEED [7].
Table 2.3: Theoretical atomic displacements, surface rumpling and change in interlayer spacing for the (1x1) TiO$_2$ terminated surface. Positive displacements indicate a displacement towards the vacuum.
<table>
<thead>
<tr>
<th></th>
<th>PWP</th>
<th>SIESTA</th>
<th>FP-LMTO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref</td>
<td>[26]</td>
<td>[27]</td>
<td>[19]</td>
</tr>
</tbody>
</table>

### Atomic Displacements (Å)

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta_x(Sr_1)$</td>
<td>-0.220</td>
<td>-0.26</td>
<td>-0.2</td>
</tr>
<tr>
<td>$\delta_x(O_1)$</td>
<td>0.004</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td>$\delta_x(Ti_2)$</td>
<td>0.046</td>
<td>0.07</td>
<td>0.06</td>
</tr>
<tr>
<td>$\delta_x(O_2)$</td>
<td>0.00</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>$\delta_x(Sr_3)$</td>
<td>-0.046</td>
<td>-0.06</td>
<td>-</td>
</tr>
<tr>
<td>$\delta_x(O_3)$</td>
<td>-0.004</td>
<td>0.01</td>
<td>-</td>
</tr>
<tr>
<td>$\delta_x(Ti_4)$</td>
<td>-</td>
<td>0.01</td>
<td>-</td>
</tr>
<tr>
<td>$\delta_x(O_4)$</td>
<td>-</td>
<td>0.00</td>
<td>-</td>
</tr>
</tbody>
</table>

### Surface Rumpling (Å)

| $\eta_1$ | 0.224 | 0.30 | 0.23 | 0.19 | 0.219 |
| $\eta_2$ | -0.046 | -0.06 | -0.02 | -0.04 | -0.043 |
| $\eta_3$ | 0.042 | 0.07 | -    | 0.03 | 0.037 |
| $\eta_4$ | -    | -0.01 | -    | -    | -     |

### Change in interlayer spacing

| $\Delta d_{12}$ | -0.26 | -0.33 | -0.24 | -0.22 | -0.256 |
| $\Delta d_{23}$ | 0.10  | 0.14  | 0.06  | 0.02  | 0.072  |
| $\Delta d_{34}$ | -     | -0.08 | -     | -     | -      |

Table 2.4: Theoretical atomic displacements, surface rumpling and change in interlayer spacing for the (1x1) SrO terminated surface. Positive displacements indicate a displacement towards the vacuum.
The next surface reconstructions to be considered are the (2x1) reconstructions. These reconstructions have been shown to arise when annealing the samples in UHV between 600°C to 800°C. These surfaces have been successfully imaged experimentally, but the images gained are not of sufficient detail to reveal the surface topology underneath. Only the general pattern, one of distinct rows, can be determined. Figure 2.5 shows an experimental image of a (2x1) reconstructed surface generated by Castell [3], and it can be seen that the bright spots of the peaks are much bigger than the dark troughs between them. Through discussions with M. Castell, it was noted that the experimental images he produced showed peaks that were twice the width of the troughs between them. Again, it is difficult to say whether this is purely due to the surface electronic structure, or if this is the result of the surface topology. Through LEED patterns he determined a single cell periodicity along the rows, and noted that step heights of 0.4 nm, which correspond to the bulk unit cell height of 0.39 nm, were always observed meaning that mixed TiO₂ and SrO terminations do not apply to (2x1) terminations. It is of interest to note that a combination of (2x1) and (1x2) patterns were actually formed by the experiment that obtained this picture, but they are not seen on the same image. This suggests that the areas of each reconstruction are at least 50nm, as this is the largest area that can be imaged by STM whilst still maintaining the atomic resolution. SrO terminations have not generally been considered in these surfaces as most experimental data suggests a Ti rich termination.

Castell [3] proposed two (2x1) reconstructions, one with a surface stoichiometry of TiO₂ and the other Ti₂O₃. He states that is is not possible from a qualitative interpretation alone to determine which of these surfaces best matches his simulated image, but using the fact that TiO₂ has Ti⁴⁺ ions and Ti₂O₃ has Ti³⁺ ions, an electronic structure technique should be able to distinguish between the two surfaces. He noted that ultraviolet-photoelectron spectroscopy (UPS) studies on the surface showed a high concentration of surface states that were assigned to O surface defects, and that this would suggest the presence of Ti³⁺ ions, but that it is still unclear whether this is due to the (2x1) Ti₂O₃ termination or random O defects in the (2x1) TiO₂ termination.

To gain the (2x1) TiO₂ surface from a (1x1) reconstruction it is necessary to remove every second [010] row of Ti ions, remove half the O ions, and place the remaining O ions
Figure 2.5: An experimental (2x1) image generated by Castell [3]. The bright spots represent peaks on the surface, and the black spots show troughs.

on top of second layer Sr ions, as shown in fig. 2.6

Figure 2.6: (2x1) TiO$_2$/A surface reconstruction. The small circles in the top down view represent atoms in the layer below the surface.

Recently Liborio [19] proposed a second surface with (2x1) TiO$_2$ stoichiometry. He noted that whilst performing atomistic relaxations on the (2x1) TiO$_2$ reconstruction seen in figure 2.6, the relaxation process led him to the surface geometry shown in figure 2.7, here labelled (2x1) TiO$_2$/B.
Figure 2.7: (2x1) TiO$_2$/B surface reconstruction. The small circles in the top down view represent atoms in the layer below the surface.

Castell's [3] second (2x1) reconstruction is created from a (1x1) reconstruction by removing a [010] row of O ions at two unit cell spacings, giving a Ti$_2$O$_3$ stoichiometry, as seen in figure 2.8.

Figure 2.8: A 2x1 Ti$_2$O$_3$ surface reconstruction. The small circles in the top down view represent atoms in the layer below the surface.

The next reconstruction was proposed by Erdman et al. [13]. The surface has a double layer TiO$_2$ termination, so it will be referred to as the (2x1) DL-TiO$_2$ surface. This surface is interesting because the upper layer of TiO$_2$ does not have the same construction as that of the layer below. The Ti and O atoms form distinct zig-zag patterns, which Erdman et al. [13] have successfully imaged using high resolution electron microscopy. Upon analysis of the surface structure, they were able to determine the surface Ti and O positions, and then performed DFT calculations to refine this model further. The surface structure of this can
be seen in figure 2.9.

Figure 2.9: A 2x1 DL-TiO₂ surface reconstruction. The small circles in the top down view represent atoms in the layer below the surface.

The final (2x1) reconstructions were driven by the results of atomic relaxations carried out in chapter 6. Results suggested a possible TiO termination, but this is not an idea that has had much study. So the following surfaces will be studied here, they all have TiO stoichiometry, but with different symmetry. These surfaces can be seen in figures 2.10-2.13.

Figure 2.10: (2x1) TiO/A surface reconstruction. The small circles in the top down view represent atoms in the layer below the surface.
Figure 2.11: (2x1) TiO/B surface reconstruction. The small circles in the top down view represent atoms in the layer below the surface.

Figure 2.12: (2x1) TiO/C surface reconstruction. The small circles in the top down view represent atoms in the layer below the surface.

Figure 2.13: (2x1) TiO/D surface reconstruction. The small circles in the top down view represent atoms in the layer below the surface.
The most recently proposed surfaces, introduced by Kubo and Nozoye [6], involve Sr adatoms situated on a (1x1) TiO₂ terminated surface. Initially, they proposed a \((\sqrt{5} \times \sqrt{5})\)-R26.6° surface reconstruction [5], which they studied using noncontact atomic force microscopy (NC-AFM). They generated images which clearly show distinct \((\sqrt{5} \times \sqrt{5})\)-R26.6° surface reconstructions. They then extended this work to show (2x1), c(2x2), 2x2, c(4x2), two kinds of c(4x4), 4x4, \((\sqrt{5} \times \sqrt{5})\)-R26.6° and \((\sqrt{13} \times \sqrt{13})\)-R33.7° surfaces using ab-initio total-energy calculations, as can be seen in figure 2.14. They discovered that the Sr adatom model explains the experimental results very well when the adatom is situated at the oxygen fourfold sites of the underlying TiO₂ layer. These surfaces were then studied by Liborio [18] who showed the relative energetic stability of each surface via total energy calculations, and also produced a surface phase diagram. The theory behind these surfaces is that the Sr adatom donates its outermost 5s electrons to the surface, lowering the conduction band.
Figure 2.14: The surface phase diagram as proposed by Kubo and Nozoye [5]. Pictures (a)-(e) show STM images, (f)-(k) show the proposed Sr adatom models and (l)-(n) are models used to explain the structural phase transition.

The suggested model for a (2x1) adatom is one of Sr atoms situated at the fourfold O site of the underlying TiO$_2$ layer. However, we have identified three possible sites for the
adatom to be situated. It is also useful for completeness to examine Ti adatoms on SrO, Ti adatoms on Ti and Sr adatoms on SrO. These sites are illustrated in figure 2.15 where the adatom is to be placed on a SrO layer and in figure 2.16 where the adatom is to be placed on a TiO₂ layer.

![Figure 2.15: (2x1) adatom sites on a SrO reconstructed surface.](image)

(a) Top View  
(b) Side View

The final surface reconstruction to be investigated was first proposed by Liborio [19], and again involves a double layer TiO₂ reconstruction. He proposed a \((\sqrt{2} \times \sqrt{2})\)-R45° reconstruction with TiO₂ stoichiometry, where the Ti atoms are arranged in diagonal rows, as can be seen in figure 2.17. Liborio [19] noted that whilst this surface reconstruction proved to be energetically stable, the simulated STM image produced a very different pattern to the physical surface geometry.
Figure 2.16: (2x1) adatom sites on a TiO$_2$ reconstructed surface. The small circles in the top down view represent atoms in the layer below the surface. Adatom placement sites are labelled 1-3, with the same sites used for both Ti and Sr adatoms.

Figure 2.17: Top down view of the ($\sqrt{2} \times \sqrt{2}$)-R45° DL-TiO$_2$ surface reconstruction. The small circles represent atoms in the layer below the surface.
Chapter 3

Calculations with PLATO

3.1 Density Functional Theory

3.1.1 Schrödinger’s equation

Quantum theory is based upon Schrödinger’s equation, of which the time-independent form is:

\[ H\Psi = E\Psi \]  

This is a many body problem in which electrons are treated as wave-like particles whose nature is represented by a set of wave-functions. The problem with this equation is that it can not be solved exactly for more than the 2 body problem, meaning it can only be solved exactly for Hydrogenic like ions. We have to use an approximation method to solve Schrödinger’s equation for molecular systems, and one such method is density functional theory.

In 1964, Hohenberg and Kohn [30] produced the theorem on which density functional theory (DFT) is based. They showed that there exists within the ground state a one to one mapping from the electron density to the wavefunction of a many particle system, and that this mapping can be reversed. The expectation value of any operator is a unique functional of the ground state charge density.

\[ \langle \hat{O} \rangle = O[p_0] \]  

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So that given a density $\rho(r)$ we can gain a uniquely determined $H$. Consider

$$H = T + V_{\text{ext}} + V$$  \hspace{1cm} (3.3)$$

where $T$ is the kinetic energy, $V_{\text{ext}}$ is the external potential and $V$ is the electron-electron interaction. Applying the theorem of Hohenberg-Kohn to the energy operator $H$ gives

$$E[\rho_0] \equiv \langle \Psi_0(\rho_0) | T + V_{\text{ext}} + V | \Psi_0(\rho_0) \rangle.$$  \hspace{1cm} (3.4)$$

This can be rewritten as

$$E[\rho_0] = F_{HK}[\rho_0] + \int V_{\text{ext}}(r)\rho_0(r) \, dr$$  \hspace{1cm} (3.5)$$

where $F_{HK}$ is the same for all electron-electron systems, and can be written as

$$F_{HK}[\rho_0] = \langle \Psi(\rho_0) | T + V | \Psi(\rho_0) \rangle.$$  \hspace{1cm} (3.6)$$

By doing this we convert the system from one of finding many body wave functions of $3N$ variables to a system containing just three variables. Hohenberg and Kohn’s second theorem showed that the total electronic energy of the system is minimised by the ground state density $\rho_0$.

$$E[\rho] \geq E[\rho_0]$$  \hspace{1cm} (3.7)$$

where $E[\rho]$ is the energy functional. Thus $E_0$, the ground state energy, can be found by varying $\rho$ to minimise $E[\rho]$.

The theorems proposed by Hohenberg and Kohn only stated that this mapping exists, and it was Kohn and Sham [31] that then provided what has become the most common implementation of this theory in 1965, known as the Kohn-Sham equations.

What we need to know is how to approximate $E[\rho]$. If we consider a system of non-interacting electrons with charge density $\rho(r)$, this system is described by the Hamiltonian

$$H_{KS} = T + V_{KS}$$  \hspace{1cm} (3.8)$$

The Hohenberg-Kohn theorem now states that

$$E_{KS}[\rho] = T_{KS}[\rho] + \int V_{KS}(r)\rho(r) \, dr$$  \hspace{1cm} (3.9)$$
Which has the exact wavefunction

\[ \Psi = \hat{A}[\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\ldots\psi_N(\mathbf{r}_N)] \]  

(3.10)

which is a single Slater determinant. Now by writing \( \rho(\mathbf{r}) \) in terms of some trial single particle wavefunctions \( \psi_i \)

\[ \rho(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2 \]  

(3.11)

Then by application of the variational principle combined with norm conversion we can write

\[ \left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{KS}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = E_i \psi_i(\mathbf{r}) \]  

(3.12)

Where \( V_{KS} \) is defined to be

\[ V_{KS} = V_{KS}[\rho] = V_{ext} + V_H[\rho] + V_{xc}[\rho] \]  

(3.13)

\( V_{ext} \) is the external potential, or the Coulomb potential due to the ionic cores, \( V_H \) is the Hartree potential which is the classical potential due to the electrons and \( V_{xc} \) is the Exchange Correlation potential, which is defined to be

\[ V_{xc} = \frac{\partial}{\partial \rho} E_{xc}[\rho] \]  

(3.14)

So the Kohn-Sham equations now read

\[ \left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{KS} + V_H + V_{xc} \right] \psi_i(\mathbf{r}) = E_i \psi_i \]  

(3.15)

This is formally an exact description of the ground state of the many electron system.

### 3.1.2 LDA

We do not know the exact form of \( E_{xc}[\rho] \), so we have to take an approximation to it. There are a number of well known approximations, and the one that we shall use is the Local Density Approximation (LDA). We perform exact many electron calculations in a system of interacting electrons with constant \( \rho \). Hence we can calculate \( e_{xc}(\rho) \), which is the exchange-correlation energy density in this system. The LDA makes the assumption that

\[ E_{xc}^{LDA}[\rho] = \int \rho(\mathbf{r}) e_{xc}(\rho(\mathbf{r})) \, d\mathbf{r} \]  

(3.16)
Within the LDA we divide space into small elements and assume that the exchange-correlation energy contribution in each of these elements is the same as in a homogeneous electron gas with the same $\rho$. The exchange-correlation energy functional within the LDA is assumed to be purely local, and we get a single well defined global minimum for the energy when dealing with a non-spin polarised system of electrons.

### 3.1.3 Pseudopotentials

The valence electrons play a more important role in the bonding of solids than the tightly bound core electrons. We can make use of this fact by introducing pseudopotentials to represent the potential within the core region. In an atom we have spherical symmetry, and so can write

$$H_{KS} \Psi_{l,m} = E_l \Psi_{l,m} \tag{3.17}$$

where

$$\Psi_{l,m} = \frac{U_l}{r} Y_{l,m}(\theta, \phi). \tag{3.18}$$

$U_l$ is the solution of the radial Schrödinger equation. We replace $U_l$ within $r_c$ with a smooth nodeless function that can be chosen to be optimally smooth to gain a semilocal pseudopotential.

$$V_{ps} = V_{loc}(r) + \sum_{i=0}^{l_{max}} \delta V_i p_l \tag{3.19}$$

Within this work we use the relativistic separable dual-space Gaussian pseudopotentials of Hartwigs, Goedecker and Hutter [32]. Within this formalism the local part of the pseudopotential is given by

$$V_{loc}(r) = -\frac{Z_{ion}}{r} \text{erf} \left( \frac{r}{\sqrt{2}r_{loc}} \right) + \exp \left[ -\frac{1}{2} \left( \frac{r}{r_{loc}} \right)^2 \right] \times \left[ C_1 + C_2 \left( \frac{r}{r_{loc}} \right)^2 + C_3 \left( \frac{r}{r_{loc}} \right)^4 + C_6 \left( \frac{r}{r_{loc}} \right)^6 \right] \tag{3.20}$$

where erf denotes the error function. $Z_{ion}$ is the total charge minus the charge from the valence electrons. The non-local contribution is defined as

$$V_l(r, r') = \sum_{i=1}^{3} \sum_{j=1}^{3} \sum_{m=-l}^{l} Y_{l,m}(r) p_i^l(r) h_{ij} p_j^l(r') Y_{l,m}(r') \tag{3.21}$$
where $Y_{l,m}$ are spherical harmonics, $l$ the angular momentum and $p^l(r)$ are Gaussians as defined in [32]. In some atom cases, there is an ambiguous separation of the system into a clearly defined core and valence shell. This problem can be overcome by using semi-core electrons. Use of semi-core electrons does make simulations more computationally expensive as they contain more electrons and a larger basis set is required to accurately describe the localized semi-core wave functions. We utilise semi-core electrons in the cases of Titanium and Strontium to give 12 and 10 valence electrons respectively, whereas Oxygen has 6 valence electrons.
3.1.4 Basis Sets

Traditionally, basis sets for DFT calculations have been comprised of plane waves. These are used because it is possible to obtain complete convergence with respect to the basis set in a stable and straightforward manner. Also the atomic forces are cheap to obtain, and certain algorithms are able to handle systems of 100 or more non-equivalent atoms. However, orthogonalizing the eigenstates results in \( N^3 \) scaling, and plane waves can be computationally expensive in terms of both time and memory when dealing with a large proportion of vacuum, a problem especially relevant when dealing with surfaces. To combat this problem we will use a real-space localized basis set of numerical, fixed energy atomic type orbitals [33]. What we have to generate is a set of orbitals that have enough variational freedom. To do this we perform a self consistent spherical atomic calculation wherein the orbitals are forced to zero at some finite radius. This method is equivalent to confining the atom in an infinite spherical well potential. This can be thought of as atoms in a solid being compressed by the surrounding atoms. The result of this calculation is orbitals that have a discontinuous first derivative at the cutoff radius, \( r_c \), leading to undefined kinetic energy integrals. These discontinuities are smoothed in such a way as to guarantee that the first two derivatives go to zero at \( r_c \), thus giving well defined kinetic energy integrals. The smoothing function used here is performed over a distance \( \sigma \) and is defined as:

\[
s(r) = 1 - \exp \left[ \frac{-(r - r_c)^2}{2\sigma^2} \right]
\]  

(3.22)

The basis sets generated for the work presented here are triple numeric dual polarisation (TNDP), which contains 27, 28 and 22 basis functions for Strontium, Titanium and Oxygen respectively.

3.1.5 Calculations using PLATO

Package for Linear Combinations of Atomic Type Orbitals (PLATO) is an ab-initio code developed by Kenny and Horsfield in [33]. Based on DFT methodology, it expands Kohn-Sham eigenvectors in numeric atomic type orbitals of finite range. Pseudopotentials are utilised to represent the electron-ion interactions, where the local part of the pseudopotential
is combined with the electrostatic potential due to spherical atomic charge density. This produces a short range potential. The pseudopotentials of Hartwigsen, Goedecker and Hutter [32] are used throughout this work. Building matrices within this method is linear with the number of atoms, compared to plane wave methods which go as \((\text{number of atoms})^2\). The memory scales as \((\text{number of atoms} \times \text{number of basis functions})^2\), and the method can be used in conjunction with density matrix schemes to achieve order \(N\) scaling. What we want to evaluate is

\[
E_{\text{tot}} = \sum_i f_i \epsilon_i - \frac{1}{2} \int V_{Ha}[\rho]\rho(r)dr + E_{xc}[\rho] - \int V_{xc}[\rho]\rho(r)dr + \frac{1}{2} \sum_{i \neq j} \frac{Z_i Z_j}{|R_i - R_j|} \tag{3.23}
\]

where the \(\epsilon_i\)’s are the eigenvalues of the Hamiltonian

\[
\hat{H} = \hat{T} + V_{e-Ion}(r, r') + V_{Ha}[\rho] + V_{xc}[\rho] \tag{3.24}
\]

and \(f_i\) is the occupancy of the state \(i\). The Hartree and exchange-correlation potentials are given by

\[
V_{Ha}[\rho] = \int \frac{\rho(r')}{|r - r'|} dr' \tag{3.25a}
\]
\[
V_{xc}[\rho] = \frac{\delta E_{xc}[\rho]}{\delta \rho} \tag{3.25b}
\]

Eigenstates \(|\psi_i\rangle\) are found by expanding in terms of atomic like basis functions \(|\phi_{I\alpha}\rangle\), giving

\[
|\psi_i\rangle = \sum_{I\alpha} C_{I\alpha}^{(i)}|\phi_{I\alpha}\rangle \tag{3.26}
\]

where \(I\) is a site index and \(\alpha\) is an orbital index. This allows us to write \(\hat{H}|\psi_i\rangle = \epsilon_i|\psi_i\rangle\) as

\[
\sum_{I\alpha} C_{I\alpha}^{(i)}\hat{H}|\phi_{I\alpha}\rangle = \epsilon_i \sum_{I\alpha} C_{I\alpha}^{(i)}|\phi_{I\alpha}\rangle \tag{3.27}
\]

Now we define the hamiltonian and overlap matrix elements as

\[
H_{I\alpha, J\beta} = \int \phi_{I\alpha}(r)\hat{T}\phi_{J\beta}(r)dr \\
\quad + \int \int \phi_{I\alpha}(r)V_{e-Ion}(r, r')\phi_{J\beta}(r')drdr' \\
\quad + \int \phi_{I\alpha}(r)V_{Ha}[\rho(r)]\phi_{J\beta}(r)dr \\
\quad + \int \phi_{I\alpha}(r)V_{xc}[\rho(r)]\phi_{J\beta}(r)dr \tag{3.28a}
\]

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\[ S_{\alpha,\beta} = \int \phi_{\alpha}(r)\phi_{\beta}(r)dr \]  
(3.28b)

So the problem of finding the eigenstates reduces to solving the generalised eigenvalue problem

\[ \sum_{\beta} H_{\alpha,\beta} C^{(i)}_{\beta} = \epsilon_i \sum_{\beta} S_{\alpha,\beta} C^{(i)}_{\beta} \]  
(3.29)

Due to the Hartree potential being linear in density, it can be rewritten:

\[ V_{Ha}[\rho] = \sum_{I} V_{Ha}[\rho^{(I)}_a] + V_{Ha}[\Delta \rho] \]  
(3.30)

where \( V_{Ha}[\rho^{(I)}_a] \) is the Hartree potential associated with the atomic electron density on atom I. It is now a case of calculating the Hartree potential at the ground state density and due to the change in density. The ground state density term is spherical, and as such can be combined with the local part of the pseudopotential to give the neutral atom potential:

\[ V_{NA}^{(I)} = V_{Ha}[\rho^{(I)}_a] + V_{loc}^{(I)} \]  
(3.31)

where \( V_{loc} \) is the local part of the pseudopotential. The neutral atom potential \( V_{NA} \) is species dependent, but as we deal with each individual atom term, values of the same species are spatially different. This is a short ranged potential, where the range is defined to be the cutoff radius of the density. Now what needs to be done is to evaluate the integrals. Certain integrals are performed at the start of each calculation, and then interpolated throughout. These integrals are the orbital overlap, the kinetic energy, the one and two centre neutral atom potential terms, the non-local pseudopotential terms and the neutral ion-ion electrostatic interaction. We perform rotations using Slater-Koster tables [34], meaning that we only need to store the ss\( \sigma \), sp\( \sigma \), pp\( \sigma \), pp\( \pi \), sd\( \sigma \), pd\( \sigma \), pd\( \pi \), dd\( \sigma \), dd\( \pi \) and dd\( \delta \) hopping integrals. The three-centre terms \( V_{NA}, V_{xc} \) and \( V_{Ha}[\Delta \rho] \) are dealt with using a mesh. \( V_{NA} \) and \( V_{xc} \) utilise the mesh to perform their respective integrals, and the technique is independent of the mesh used. A relatively coarse grid is used for \( V_{xc} \), and this can be done because \( V_{xc} \) varies slowly. \( V_{Ha}[\Delta \rho] \) is calculated differently depending on which mesh is being used within a simulation. If a uniform mesh is being used then fast Fourier transforms are used to calculate \( V_{Ha}[\Delta \rho] \), but if the mesh is atom centred then an Ewald summation is used.
We then separately deal with the non-local part of the pseudopotential. This is split into two two-centre terms, and this can be done because the non-local pseudopotential is in the form

\[ Y_{i,m}(r)P_{i}^{l}(r)h_{i}^{l}P_{i}^{l}(r')Y_{i,m}(r') \]  

which is separable. The forces in the calculated system are then obtained by simple differentiation of the total energy of the system.

### 3.1.6 Setting up the simulations

Before we could run any simulations it was necessary to perform calculations to test the convergence of the SrTiO₃ system as a function of the parameters. This meant performing a number of single point energy calculations for different parameters. The first parameter that we had to establish whether we were going to use an atom centred grid (ACG) or a uniform mesh to perform our calculations. It was decided that an ACG would be better suited to these calculations, as it produces a finer mesh near the atoms, but a coarser one in the regions between atoms. This gives a better convergence with respect to mesh size than the uniform mesh. ACG has three distinct parameters; the number of radial points, the number of angular points, and the highest angular momentum component in the expansion of the density. We chose to use a Lebedev ACG with parameters of 35, 29 and 4 to perform our calculations, as this gave the best combination of accuracy and speed. This mesh was further optimised by deducing a minimum partition weight, where points with weights below this are discarded. We also reduced the number of mesh points near the atomic core, further reducing our points. This optimisation led to a reduction of 8000 grid points, and a run time of 1700s for a unit cell of SrTiO₃, whereas an equivalently accurate uniform mesh took 4000s. We then had to choose a suitable k-point sampling, which we took to be 6 × 6 × 1 for the (1x1) terminations as this gives good convergence. In creating the cell, we have to specify the amount of vacuum region, we have chosen a thickness equivalent to 9 atomic layers. The substrate was taken to be 7 layers thick. Once we had chosen all of our parameters we ran single point energy calculations on the unit cell of SrTiO₃, for a range of lattice parameters roughly ±10% of the experimental value of 3.905Å. We fitted these
results to Murnaghan's equation of state to get a value for the lattice parameter that we will use throughout this work. We obtained a lattice constant of 3.87 Å, a bulk modulus of 1.95 MBars, which compares favourably with the experimental value of 1.84 MBars, and energy per atom of -54.970 Ry. The graph in fig 3.2 shows the results where the red data points represent the simulations that we ran at different volumes, and the black line is the fit to the Murnaghan equation of state generated by our code.

![Graph showing binding energy curve for bulk SrTiO₃](image)

Figure 3.2: Binding Energy Curve for bulk SrTiO₃ showing the total energy versus the lattice parameter.

### 3.2 Total Energy Calculations

The system we are dealing with has two phases, gas and solid, and three components, SrO, TiO₂ and O. We choose the chemical potential of TiO₂, \( \mu_{TiO_2} \), the partial pressure of oxygen, \( p_{O_2} \), and the temperature, \( T \), to be our degrees of freedom, and an explanation of why we do this can be found in [19]. The surface excess free energy is then calculated as

\[
E(\mu_{TiO_2}, p_{O_2}, T) = \frac{1}{2A} \left( E_{slab} - \sum_i \mu_i N_i \right)
\]  

(3.33)

where \( E_{slab} \) is the Gibbs free energy of the system, \( N_i \) is the number of each component within the system, and \( \mu_i \) is the chemical potential of component \( i \) per formula unit. \( A \) is the surface area of the system, and the factor of a half accounts for there being two surfaces in each system. To deal with the non-stoichiometric systems in particular, we introduce surface excesses. Essentially this is the excess of a particular component on the surface of a
system. We define the excess, $\Gamma_i$, of component $i$ with respect to component $A$ as

$$\Gamma_i = \left( N_i - N_A \frac{N_i^\text{bulk}}{N_A^\text{bulk}} \right)$$  \hspace{1cm} (3.34)$$

By choosing component $A$ to be SrO we can obtain the surface excesses of TiO$_2$ and O, in terms of which the surface free energy is

$$\frac{1}{2A} \left( E_{\text{slab}} - N_{\text{SrO}} E_{\text{SrTiO}_3} - \mu_{\text{TiO}_2} \Gamma_{\text{TiO}_2} - \frac{1}{2} \mu_{\text{O}_2} \Gamma_{\text{O}} \right)$$  \hspace{1cm} (3.35)$$

where $E_{\text{SrTiO}_3}$ is the Gibbs free energy of a bulk formula unit of SrTiO$_3$.

3.2.1 Chemical potential of TiO$_2$

We cannot calculate exactly $\mu_{\text{TiO}_2}$ as this depends on the environment in which a particular surface is created, but we can put bounds on it. To do this we first need to start by defining the Gibbs free energy of formation for one unit of bulk SrTiO$_3$ such that

$$E_f^{\text{SrTiO}_3} = E_f^{\text{SrTiO}_3} - E_f^{\text{SrO}_2} - E_f^{\text{SrO}}$$  \hspace{1cm} (3.36)$$

where $E_f^{\text{SrTiO}_3}$ is the formation energy of a unit cell of bulk SrTiO$_3$, $E_f^{\text{SrTiO}_3}$, $E_f^{\text{SrO}_2}$, $E_f^{\text{SrO}}$ are the free energies of a unit cell of SrTiO$_3$, SrO and TiO$_2$ respectively, and $E_f^{\text{SrTiO}_3} < 0$. We calculated $E_f^{\text{SrTiO}_3}$ to be -0.1132 Ry which compares favourably to the -0.1094 Ry calculated by Johnston et al. [17]. Assuming that the slab is in equilibrium, it can be written that

$$E_{\text{SrTiO}_3} = \mu_{\text{SrO}} + \mu_{\text{TiO}_2}$$  \hspace{1cm} (3.37)$$

and if we neglect temperature dependence and variation of the energy of bulk SrTiO$_3$ due to stoichiometry then we can write $E_{\text{SrTiO}_3} = E^0_{\text{SrTiO}_3}$ and now

$$E^0_{\text{SrTiO}_3} = \mu_{\text{SrO}} + \mu_{\text{TiO}_2}$$  \hspace{1cm} (3.38)$$

Because we do not know the conditions that any surface is created in, we cannot predict either $\mu_{\text{SrO}}$ or $\mu_{\text{TiO}_2}$, but it is known that

$$\mu_{\text{TiO}_2} \leq E^0_{\text{TiO}_2}$$  \hspace{1cm} (3.39)$$

and

$$\mu_{\text{SrO}} \leq E^0_{\text{SrO}}$$  \hspace{1cm} (3.40)$$
Now we can combine these two inequalities with equations 3.36 and 3.38 to gain bounds on one of these chemical potentials, which we choose to be $\mu_{\text{TiO}_2}$.

$$E_{\text{TiO}_2}^0 + E_{J, \text{SrTiO}_3}^0 \leq \mu_{\text{TiO}_2} \leq E_{\text{SrTiO}_3}^0$$  \hfill (3.41)

Therefore at $\mu_{\text{TiO}_2} = E_{\text{TiO}_2}^0$, the system is in equilibrium with TiO$_2$ and SrTiO$_3$ and at $\mu_{\text{TiO}_2} = E_{\text{TiO}_2}^0 + E_{J, \text{SrTiO}_3}^0$, the system is in equilibrium with SrO and SrTiO$_3$.

### 3.2.2 Chemical Potential of Oxygen

The chemical potential of oxygen is defined in terms of the enthalpy and entropy per molecule in the standard state by

$$\mu_{\text{O}_2}(p_{\text{O}_2}^0, T^0) = h_{\text{O}_2}^0 - T^0 s_{\text{O}_2}^0$$  \hfill (3.42)

A value for $h_{\text{O}_2}$ is obtained from the standard enthalpies per molecule of the components in an oxide, for which TiO$_2$ is demonstrated, which are related by

$$h_{\text{TiO}_2}^0 = h_{\text{O}_2}^0 + h_{\text{Ti}}^0 + E_{J, \text{TiO}_2}^0$$  \hfill (3.43)

where $E_{J, \text{TiO}_2}^0$ is the energy of formation of TiO$_2$, which we have obtained from the NIST tables of thermochemical data [35]. The values of $h_{\text{TiO}_2}^0$ and $h_{\text{Ti}}^0$ have been calculated through the use of PLATO. The value of $s_{\text{O}_2}^0$ also comes directly from tables of thermochemical data. In theory it should be irrelevant which oxide is used to calculate $\mu_{\text{O}_2}$, but due to intrinsic errors in the calculation process, a variety of oxides have been used. The experimental structural data for the oxides used here come from [36, 37], with the oxides used being SrO, TiO$_2$, MgO and Ag$_2$O, and results for these can be seen in table 3.1 and figure 3.3.
<table>
<thead>
<tr>
<th>$M_xO_y$</th>
<th>Structure</th>
<th>$a_{exp}$ (Å)</th>
<th>$a_{calc}$ (Å)</th>
<th>$c_{exp}$ (Å)</th>
<th>$c_{calc}$ (Å)</th>
<th>$(c/a)_{exp}$</th>
<th>$(c/a)_{calc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr</td>
<td>FCC</td>
<td>6.085</td>
<td>5.814</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SrO</td>
<td>Rocksalt</td>
<td>5.106</td>
<td>5.062</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ti</td>
<td>HCP</td>
<td>2.950</td>
<td>2.869</td>
<td>4.686</td>
<td>4.555</td>
<td>1.588</td>
<td>1.588</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Rutile</td>
<td>4.594</td>
<td>4.80</td>
<td>2.958</td>
<td>3.079</td>
<td>0.644</td>
<td>0.641</td>
</tr>
<tr>
<td>Mg</td>
<td>HCP</td>
<td>3.209</td>
<td>3.122</td>
<td>5.210</td>
<td>5.022</td>
<td>1.624</td>
<td>1.609</td>
</tr>
<tr>
<td>MgO</td>
<td>Rocksalt</td>
<td>4.211</td>
<td>4.179</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ag</td>
<td>FCC</td>
<td>4.086</td>
<td>4.045</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ag$_2$O</td>
<td>Cuprite</td>
<td>4.72</td>
<td>4.693</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 3.1: Structural parameters for several oxides. $exp$ values are the experimental lattice constants shown in [36, 37] and $calc$ values are the lattice constants obtained using PLATO.

Figure 3.3: $\mu_{O_2}$ calculated for various oxides. The dashed line represents the average of these values and is the value of $\mu_{O_2}$ used here.

Now it is necessary to integrate $\mu_{O_2}^0$ to get to the required $\mu_{O_2}(p, T)$. Firstly, by applying the standard thermodynamic relation to a perfect gas

$$\frac{\partial \mu_{O_2}}{\partial p} |_T = \frac{kT}{p}$$

where $k$ is Boltzmann's constant, we can obtain the well known formula

$$\mu_{O_2}(p_{O_2}, T) = \mu_{O_2}(p_0^0, T) + kT \ln \left( \frac{p_{O_2}}{p_0^0} \right)$$
which deals with the pressure dependence in the system. To gain an expression for the
temperature dependence we use the fact that the Gibbs free energy per mole is equivalent
to the chemical potential. To make use of this it is necessary to refer to experimental data.
The experimental enthalpies, entropies and Gibbs free energies per mole have been fitted to
the following polynomials [35]

\[
H(p^0, T) - H(p^0, T^0) = AT + \frac{1}{2} BT^2 + \frac{1}{3} CT^3 + \frac{1}{4} DT^4 - \frac{E}{T} + F 
\]  

(3.46)

\[
S(p^0, T) = A \ln(10^{-3}T) + BT + \frac{1}{2} CT^2 + \frac{1}{3} DT^3 - \frac{E}{2T^2} + G 
\]  

(3.47)

where the Gibbs free energy per mole is just a combination of the entropy and enthalpy,
given by \( G = H - TS \), so is

\[
G(p^0, T) = A(T - \ln(10^{-3}T)) - \frac{1}{2} BT^2 - \frac{1}{6} CT^3 - \frac{1}{12} DT^4 - \frac{E}{2T} + F - GT 
\]  

(3.48)

The coefficients for the above expressions are given in the following table:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>26.659 \times 10^{-3}</td>
<td>kJ mol(^{-1}) K(^{-1})</td>
</tr>
<tr>
<td>B</td>
<td>6.137261 \times 10^{-6}</td>
<td>kJ mol(^{-1}) K(^{-2})</td>
</tr>
<tr>
<td>C</td>
<td>-1.186521 \times 10^{-9}</td>
<td>kJ mol(^{-1}) K(^{-3})</td>
</tr>
<tr>
<td>D</td>
<td>0.095780 \times 10^{-12}</td>
<td>kJ mol(^{-1}) K(^{-4})</td>
</tr>
<tr>
<td>E</td>
<td>-0.219663 \times 10^{3}</td>
<td>kJ mol(^{-1}) K</td>
</tr>
<tr>
<td>F</td>
<td>-9.861391</td>
<td>kJ mol(^{-1})</td>
</tr>
<tr>
<td>G</td>
<td>237.948 \times 10^{-3}</td>
<td>kJ mol(^{-1}) K(^{-1})</td>
</tr>
</tbody>
</table>

Thus it is possible to gain a final formula for \( \mu_{O_2}(p_{O_2}, T) \)

\[
\mu_{O_2}(p_{O_2}, T) = \mu_{O_2}(p^0, T^0) + G(p^0, T) - G(p^0, T^0) + kT \ln \left( \frac{p_{O_2}}{p^0} \right) 
\]  

(3.49)

3.3 Model of STM

To perform a computational simulation of the STM, we have used the Tersoff-Hamann
model [38]. In this model, the surface is treated exactly, while the tip is modelled as a local
spherically potential well where it approaches nearest the surface. It is necessary to treat the
tip in this manner due to the current poor understanding of the actual microscopic geometry
of the tip, which is prepared in an uncontrolled and non-reproduceable manner. The main
premise of the model is that the current is proportional to the density in an energy window.
The definition of density is
\[ \rho(r) = \sum_i f_i |\psi_i(r)|^2 \]
where \( f_i \) is the occupancy. To simulate the STM it is necessary to calculate the surface local
density of states (at \( E \)) at the point \( r \)
\[ \rho(r, E) = \sum_i |\psi_i(r)|^2 \delta(E_i - E) \]
which is equivalent to the charge per unit energy from states of the surface at \( E \). At constant
current the tip follows a contour of constant \( \rho(r, E) \). To simulate the experiments it is
necessary to specify an energy window within which to calculate the density of states. We
are concerned with the density of states around the Fermi energy, and we want to simulate a
positive bias, so we have to specify a window of energy which is just above the Fermi energy.
There are two methods that we use to do this. Firstly, where the system is not metallic we
treat the lowest unoccupied state as 0V, but where the surface is metallic, we take our value
of 0V to be just above the Fermi energy. This means to simulate a 1V bias we must specify
an energy window from our assigned zero to 1eV above this state, an example of this can be
seen in fig 3.4.

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Figure 3.4: The local density of states for one of our surfaces showing the required energy window for STM simulation

If we wanted to simulate a negative bias, it would be necessary to specify a window with the upper bound defined as the highest occupied state. However, we are only interested in the positive bias as this is the one that is used experimentally. This is because SrTiO$_3$ has an insulating band gap, and as such a dopant, typically Nb, is substituted for certain Ti atoms to add sufficient states below $E_f$ to lower the band gap and allow tunnelling to occur. It is then necessary to integrate the density of states in the specified energy window. We have written a code to do this from Plato wavefunction files. It is then mapped onto a uniform grid to allow us to visualise the STM surface.
Chapter 4

Computational Steering and STM Visualisation

4.1 Steering introduction

4.1.1 Steering motivation

To improve the process of performing computer simulations, we have implemented a steerer into PLATO that has resulted in a more robust method that performs complete relaxations significantly quicker than previously. In performing our simulations there are a number of parameters that we need to change in order for our simulations to be successful. The way that these parameters have been changed in the past has involved stopping the simulation, changing the parameter and then restarting. Whilst this method produces the correct results, it is wasteful of time. This is especially relevant on heavily used computer systems, or ones with queueing systems in place where stopping a simulation can result in a lot of time spent waiting for it to restart. Another problem that we have encountered, especially in our larger systems, is where the surface is metallic. These surfaces have proven to be very sensitive to any change in parameters. As such, changes have needed to be made in a lot of very small increments, something that just would not be practical to do by stopping and restarting the simulation. If the change that has been made is too large, or sometimes when the calculations just take an unexpected step, the simulation can become unstable to the extent that it will
never reach the required tolerance for a self consistent calculation. Without steering this would require another stopping of the simulation, but we can now just increase the tolerance or change the parameter back to the previous value. Added to this, every time that the simulation is restarted the Hamiltonian and overlap matrices have to be rebuilt, and this can take a significant amount of time. The method that we will use to steer our simulations was developed by the Supercomputing, Visualisation and e-Science group at the University of Manchester [39]

4.1.2 Steering fundamentals

We have two types of parameters that are of interest when we want to steer a simulation, monitored and steered. These parameters are not allocated by the steerer itself, but can be chosen to suit any specific simulation by changing the underlying code. Monitored parameters are the quantities from each simulation that either tell us how well the simulations are running or provide useful data that we require in order to successfully steer our simulation. For our simulations, the parameters that we want to monitor are:

- **sequence_num** - how far into the simulation we are
- **cpu_time_per_step** - how long the previous step took in seconds
- **energy** - the total energy (Ry) in the system
- **energy change** - the difference in energy (Ry) from the previous step
- **F** - the force in the system calculated at the end of the last self consistent cycle
- **dRho** - the difference in density from the previous step
- **Filled Bands** - the total number of filled bands in the calculation

The steered parameters are those that we want to change whilst the simulation is running, either to increase the accuracy of the simulation or reduce the time taken per calculation. The following are the parameters that we have chosen to be steerable:

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• **Steering Interval** - how many steps we want to calculate in between communication with the steerer

• **Electron Temperature** - the temperature (Ry) that the electrons in the system are given to smooth the finding of the Fermi level

• **NLoops** - the maximum number of steps we want to allow within a self consistent cycle

• **ResidueTol** - the threshold for dRho, where a value less than this assumes that the density within a self consistent cycle has reached convergence

• **MixFactor** - gives the fraction of the new density mixed with the old density when simple mixing is used

• **MixThreshold** - if dRho is above this value then we employ simple mixing instead of Pulay mixing

• **FTo1** - the threshold for the force, where a value less than this indicates that we have reached our required convergence

• **MaxNSteps** - the maximum number of relaxation steps for the atoms that we want to perform

• **Diagonalisation Method** - which of the seven diagonalisers we want to use

• **NBands** - the maximum number of bands that we want to include in a calculation, this must be bigger than Filled Bands

• **rst file** - the number of self consistent cycles that we want to perform before generating a fail-safe file from which we can restart our simulation

• **rho file** - the number of self consistent cycles that we want to perform before generating a density file

The client that we use to steer our simulations can be seen in figure 4.1, and all of the parameters mentioned above can be seen in the two windows of the client. Multiple
simulations can be steered from the same client via the use of tabs. As you can also see in figure 4.1 we have the ability to pause and restart our simulation, detach the steerer in case we want to steer from a different location, and stop the simulation all together.

Figure 4.1: A snapshot of the steering client in use, showing the monitored and steered parameters that we have in use.

We currently have seven different diagonalisation methods available to us. The first five methods available allow for splitting the data via k-point. Therefore a simulation like the (1x1) surfaces with 18 k-points can be run on 1, 2, 3, 6, 9 or 18 processors. The use of ScaLAPACK for diagonalisation methods 6 and 7 allows for parallel diagonalisation, so our larger jobs can be run on more processors than previously would have been available. The methods that we have implemented are:

1. LAPACK - slow but economical on memory and robust

2. ARPACK
3. LAPACK - divide and conquer

4. LAPACK - expert driver

5. LAPACK unpacked - expert driver

6. ScaLAPACK unpacked - parallel diagonaliser

7. ScaLAPACK unpacked - parallel diagonaliser, factorises overlap upfront

More information on the different methods can be found at [40].

There are two options available to us when we want to steer our simulations, file-based steering and socket based steering. File-based steering is a purely local method, where you can only steer from the machine that the simulation is being run on. This is good in that the communication time between steerer and PLATO is relatively small, but limited in what machines you can actually utilise this on. Socket based steering utilises a central registry to handle the data passing back and forth between the steerer and PLATO. The data is wrapped as Simple Object Access Protocol (SOAP) packets, and transferred using http. This increases the communication time, but allows you to both steer on machines that can not run the steering client and also potentially steer from anywhere in the world. Initially we used a steering registry provided by Manchester, but have recently installed a registry locally with the help of Andrew Porter.

4.2 Steering in practice: (2x1) Si surface

To illustrate the importance of steering we have performed a simulation on a (2x1) Si surface containing 32 atoms. We are not interested here in following the simulation all the way to completion, but rather we want to see how the steerer improves performance over a limited range. We chose to only vary one parameter, with this parameter being the residual tolerance. In the case of the non-steered simulation this is set at 0.0001 electrons/Bohr radii$^3$, and the simulation is run until convergence is obtained. For the steered simulation, this is started at 0.01 and reduced to 0.0001 in two increments, (0.01 → 0.001 → 0.0001). Both calculations are performed on a single 2.5 GHz G5 processor.
The most important parameter when steering our simulations is dRho. This best tells us how the simulation is behaving, and whether or not it is the right time to make a change to any of our steerable parameters. It is possible for the steering client to produce a graph of this parameter so that we can see it more clearly and better judge when the right time for a change is.

Figure 4.2: The difference in the density between successive computational steps for the steered (2x1) Si surface example. Illustrated are the two points where dRho is incrementally dropped during the simulation.

Figure 4.2 shows the difference in the density between successive computational steps in the simulation performed with steering. dRho is first dropped at point 1 to 0.001, and again further at point 2 to 0.0001. These parameter changes occur at times when few steps are taken in each self consistent cycle, indicating that the system is quite stable before the change.

What we are interested about in this simulation is the time taken to reach convergence, and whether each simulation has converged to the same point. The total energy in each case is -253.3167 Ry, so we can say that steering the simulation has not effected the result.
Figure 4.3: Simulation times in seconds for a (2x1) Si surface.

Figure 4.3 shows the time taken for each simulation to reach the required convergence. As can be seen, the steered simulation took about 14% less time to reach the same point as the non-steered simulation. This is a significant saving for what is a very stable calculation. If we wanted to increase the accuracy of this calculation further then we would have to lower the electron temperature whilst also further lowering the residue tol. This would require us to stop the simulation and then restart after making the necessary changes to the input file.

As we have seen in the case of a (2x1) Si surface, steering the simulation provides a significant reduction in the time taken to perform calculations. This is especially of importance when dealing with large systems, where this time saving could take weeks off the total simulation time. As an indication, our (2x2) Ti Adatom on SrO ($\theta = 0.25$) took 32.5 days simulation time to reach convergence. Assuming the same saving as seen here, this job would have taken an additional 5 days to run.

### 4.3 STM Visualisation

Once we have performed a successful relaxation of a surface, the next step that we take is to simulate an STM. We do this from the files that PLATO generates by the method outlined in section 3.3. Previously seen STM simulation images can be difficult to interpret,
consisting mainly of a slice through a substrate and electronic surface. Here we present a fully interactable 3D representation of both the substrate and the electronic surface. The viewer that we use was created in conjunction with Rob Haines at Manchester, and is built on a Java platform utilising the Visualisation Toolkit (VTK) [41]. As with our simulations, we again utilise the steerer to control our viewing allowing us to change parameters on the fly. The variables that we have been steering are:

- **Steering Interval** - sets how regularly the steerer and visualiser communicate
- **Molecule visible?** - boolean variable setting whether or not to render the molecules
- **Bonds visible?** - boolean variable setting whether or not to render the bonds
- **Iso visible** - boolean variable setting whether or not to render the isosurface, where it is possible to render more than one isosurface at a time
- **Iso value** - the value given to the associated isosurface
- **Orthoslice?** - boolean variable setting whether or not to render a slice through the middle of the window
- **Cut-plane?** - boolean variable setting whether or not to render a cut-plane
- **Cut-plane normal** - values setting the direction of the cut-plane
- **Cut-plane centre** - values defining the centre point of the cut plane
- **Elevation Filter** - boolean variable setting whether or not to colour the isosurface
- **Elevation Filter Height** - upper and lower bounds on the colouring, where everything below is coloured red, and everything above is coloured dark blue
- **Duplication** - integer values to set the duplication of the isosurface

These variables are changeable relatively simply, and additional functionality can be added as required. The interface that we use to steer our visualisation is very similar to that we see when performing our relaxations. Figure 4.4 shows the steerer window in use.
4.4 A sample visualisation

The best way to illustrate how we perform our visualisation and to showcase some of the features that we can use is through an example. Here the $2\times1$ TiO$_2$ STM simulation is imaged. Initially the viewer calculates a value for the isosurface, but this is generally too high to produce any useful image so it is the first thing that will be changed, setting to a new value of 0.00001 electrons/Bohr radii$^3$. 

![Figure 4.4: A snapshot of the visualisation steerer interface during a visualisation.](image-url)
Figure 4.5 shows the result of setting the isosurface to $10^{-5}$ electrons/Bohr radii$^3$. As can be seen, we now have a good electronic surface representation, but the surface features are difficult to pick out. Turning the elevation filter on makes any surface features easier to pick out, so that is the next variable to be changed.

Figure 4.6 shows the image gained with elevation filter bounds of 20 and 23. Any part of the isosurface below 20 will be coloured red, with a range of colours above this culminating in a dark blue at 23 and above. This means that now we can see where the highest and lowest points are easily, and that any features are much easier to pick out, such as the bumps to the left and right sides of the image. The problem that we now face is in spotting patterns in the surface, where the single cell that we use is not sufficient to do this.
Figure 4.7: Visualisation of a (2x1) TiO$_2$ STM simulation with isosurface set to $10^{-5}$ electrons/Bohr radii$^3$ and elevation filter switched on with the cell duplicated in both the x and y directions.

Figure 4.7 shows the same features as figure 4.6, but here the cell has been duplicated along both the x and y directions. This makes it easy to now see the rows of peaks and troughs that are present on the surface. We can do this duplication to any size that we want, and if we wanted could just perform the duplication in one direction. This is very useful as actually performing a simulation to this size would be very computationally expensive.

Now that we have got our surface successfully imaged, we can change other parameters to better see what is happening beneath the surface. By setting a cut-plane we can tell the viewer to render only the isosurface in certain areas, leaving the rest blank so that the underlying atoms can be easily seen.

Figure 4.8: Visualisation of a (2x1) TiO$_2$ STM simulation with isosurface set to $10^{-5}$ electrons/Bohr radii$^3$ and elevation filter switched on with the cell duplicated in both the x and y directions and a centred [010] cut-plane.
Figure 4.9: Visualisation of a (2x1) TiO$_2$ STM simulation with isosurface set to $10^{-5}$ electrons/Bohr radii$^3$ and elevation filter switched on with the cell duplicated in both the x and y directions and a centred [100] cut-plane.

Figure 4.10: Visualisation of a (2x1) TiO$_2$ STM simulation with isosurface set to $10^{-5}$ electrons/Bohr radii$^3$ and elevation filter switched on with the cell duplicated in both the x and y directions and a centred [110] cut-plane.

Figures 4.8-4.11 show the effects of applying different cut-planes to the image. The first plane shown in figure 4.8 is centred in the middle of the cell, and is along the (010) direction. As you can see, this shows us easily the underlying TiO$_2$ stoichiometry. Figure 4.9 shows a plane again centred at the middle of the cell, but this time in the (100) direction. Again the underlying surface is clear to see, and knowing that the same structure lies directly under the isosurface makes identifying regions of interest easy. Figure 4.10 shows a cut-plane in direction (110), again centred in the middle of the cell. These cut planes do not always have to be centred in the middle of the cell, as can be seen in figure 4.11 where the (100) cut-plane...
In addition to these features, we have full control over the rendered objects, so that we can orientate them as best fits our needs. This allows us much greater control over what we can see, and makes the interpretation of our results relatively straightforward. Figure 4.12 shows the image in figure 4.7 rotated from a top down view to a side view. As you can see in this image, the bottom surface is coloured red as the elevation filter only effects one surface.
Figure 4.12: Visualisation of a rotated (2x1) TiO$_2$ STM simulation with isosurface set to $10^{-5}$ electrons/Bohr radii$^3$ and elevation filter switched on with the cell duplicated in both the x and y directions.
Chapter 5

(1×1), (2×1) and (\sqrt{2} × \sqrt{2}) Surface Reconstructions

5.1 Simulation Details

For the (1×1), (2×1) and (\sqrt{2} × \sqrt{2}) cases a cell containing seven layers has been employed. The equivalent of 9 layers of vacuum separate the top and bottom surfaces from each other. The basis set and integration mesh are identical to that described previously, with the k-point sampling being scaled according to the simulation cell size. In all cases the force and residual tolerances are set to be 10^{-4} Ry/Bohr radius and 10^{-4} electrons/Bohr radii^3 respectively whilst the electron temperature in each case is 10^{-3} Ry. Electron temperature is introduced into the system via a Fermi-Dirac distribution [42]. The only exception is for (2×1) TiO₂/B which was calculated at an electron temperature of 3×10^{-3} Ry, residual tolerance of 3×10^{-3} electrons/Bohr radii^3 and force tolerance of 10^{-4} Ry/Bohr radius.

5.2 Layer Rumpling and Atomic Displacements

As we are dealing with relaxed systems, atoms will not necessarily be at their ideal lattice positions. This means that there is a certain amount of displacement to be calculated for each system. We define these displacements in such a way as to give an inward relaxation (towards the bulk) a negative displacement. In the case of the (1×1) systems, there is only a
displacement perpendicular to the surface to consider. It is also only necessary to calculate the displacements of half of the layers, as there is a mirror symmetry about the middle layer. To compare our results with those published previously it is going to be necessary to calculate the atomic displacements, $\delta_z$, the change in interlayer distance between two adjacent slabs, $\Delta d_{ij}$, and the amplitude of the rumpling of each layer $\eta_i$. Definitions for $\Delta d_{ij}$ and $\eta_i$ can be seen in equations 2.1 and 2.2 respectively.

Tables 5.1 and 5.2 show the atomic displacements, surface rumpling and the change in the interlayer spacing for both of the (1×1) cases. The tables show the work presented here alongside previously reported results from a variety of methods.

Our results show an excellent agreement with those previously stated, with the biggest displacement in both cases being that of the surface metal atom. We show a displacement of 0.129Å for the Ti atom, and 0.196Å for the Sr atom, both inwards towards the bulk. These are both within the range of values that have previously been witnessed. The biggest difference is in $\delta_z(O_2)$ in table 5.2, where our result is roughly double that of Cheng et al. [27], Liborio et al. [19] and Zhang et al. [28], whereas Johnston et al. [17] shows a negative displacement. We see that, for both terminations, there is an oscillating relaxation pattern. The results of the interlayer spacing are similar in both cases, even though the layer rumpling is quite different. The SrO termination can be seen to have a great deal of rumpling in the surface layer, whereas the TiO$_2$ termination can be seen to have more rumpling in the second layer.

5.3 Surface Studies

5.3.1 Surface Energies

Surface energies were calculated by the method presented in section 3.2 over a range of temperatures from 300K to 1600K. The graphs in figure 5.1 show the surface energies of the (1×1) and (2×1) surfaces at atmospheric pressure at temperatures of 300K, 1000K and 1600K.

Before we can calculate the surface energies of any reconstruction, we have to calculate
Table 5.1: Atomic displacements, surface rumpling and change in interlayer spacing for the (1×1) TiO₂ terminated surface. Positive displacements indicate a displacement towards the vacuum.
Table 5.2: Atomic displacements, surface rumpling and change in interlayer spacing for the 
(1×1) SrO terminated surface. Positive displacements indicate a displacement towards the 
vacuum.

<table>
<thead>
<tr>
<th></th>
<th>PLATO</th>
<th>PWP</th>
<th>SIESTA</th>
<th>FP-LMTO</th>
</tr>
</thead>
<tbody>
<tr>
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<td>[27]</td>
<td>[19]</td>
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<td>-0.26</td>
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<td>0.04</td>
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<td><strong>Surface Rumpling (Å)</strong></td>
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<td>$\eta_4$</td>
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<td>-0.01</td>
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<td><strong>Change in interlayer spacing (Å)</strong></td>
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<td>$\Delta d_{34}$</td>
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<td>-</td>
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</table>
the excesses $\Gamma_{\text{TiO}_2}$ and $\Gamma_O$ that were defined in equation 3.34. These surface excesses are shown in table 5.3, and a negative excess implies that there is a deficiency from bulk.

<table>
<thead>
<tr>
<th>Surface</th>
<th>$\Gamma_{\text{TiO}_2}$</th>
<th>$\Gamma_O$</th>
</tr>
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<tbody>
<tr>
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<td>0</td>
</tr>
<tr>
<td>$(1 \times 1)$TiO$_2$</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>$(2 \times 1)$TiO$_2$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$(2 \times 1)$Ti$_2$O$_3$</td>
<td>2</td>
<td>-2</td>
</tr>
<tr>
<td>$(2 \times 1)$DL-TiO$_2$</td>
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<td>0</td>
</tr>
<tr>
<td>$(2 \times 1)$TiO/A</td>
<td>0</td>
<td>-2</td>
</tr>
<tr>
<td>$(2 \times 1)$TiO/B</td>
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<td>-2</td>
</tr>
<tr>
<td>$(2 \times 1)$TiO/C</td>
<td>0</td>
<td>-2</td>
</tr>
<tr>
<td>$(2 \times 1)$TiO/D</td>
<td>2</td>
<td>-4</td>
</tr>
<tr>
<td>$(\sqrt{2} \times \sqrt{2})$DL-TiO$_2$</td>
<td>6</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 5.3: Surface excesses for the supercells of the $(1 \times 1)$ and $(2 \times 1)$ surface reconstructions.

These graphs show that over all the temperatures considered the $(1 \times 1)$ SrO termination is the most energetically favourable surface reconstruction at atmospheric pressure across most of the range of $\mu_{\text{TiO}_2}$. The $(\sqrt{2} \times \sqrt{2})$ DL-TiO$_2$ termination becomes the most favourable surface reconstruction when the proportion of $E_{f,\text{SrTiO}_3}^0$ in $\mu_{\text{TiO}_2}$ is less than 0.07, where the environment is very TiO$_2$ rich. Of the $(2 \times 1)$ surface reconstructions, the TiO$_2$/B and DL-TiO$_2$ are the most energetically favourable, with the DL-TiO$_2$ having an energy close to that of the $(1 \times 1)$ surfaces only when you move towards a TiO$_2$ rich environment. We can effectively rule the others out of contention at these conditions from their energetics. There is good agreement between the results gained here at 1000K with those in [17].

As STM is carried out under UHV conditions, typically to a pressure of $10^{-10}$ atm, it is necessary to analyse the results over varying pressures. The graphs in figure 5.2 and figure 5.3 show the surface energies calculated over a range of pressures from $10^{-30}$ atm up to atmospheric pressure. Figure 5.2 shows the energies calculated assuming that we are in a TiO$_2$ rich environment, and figure 5.3 shows the energies calculated assuming a SrO rich
Figure 5.1: Graphs of the surface energies of the (1×1), (2×1) and (√2 × √2) surface reconstructions as a function of the chemical potential of TiO₂. All the graphs are at atmospheric pressure, temperatures of 300K, 1000K and 1600K are illustrated.

environment, corresponding with the left and right hand side of the graphs in figure 5.1 respectively. The oxygen boundary refers to the critical pressure where it becomes more favourable for SrTiO₃ to split into its constituent parts.
Figure 5.2: Graphs of the surface energies of the (1 x 1), (2 x 1) and (√2 x √2) surface reconstructions at $\mu_{TiO_2} = E_{TiO_2}^0$ over a pressure range of 10^{-30} to 1 atm, temperatures of 300K, 1000K and 1600K are illustrated.

At 300K it can be seen that the (√2 x √2) DL-TiO_2 reconstruction is the most energetically favourable surface at all relevant pressures, with the TiO_2 and DL-TiO_2 again the most favourable of the (2 x 1) reconstructions. When increasing the temperature to 1000K, a similar pattern follows, only now the (2 x 1) Ti_2O_3 has dropped significantly enough in energy to be close to the most stable surfaces. At 1600K this energy drop continues, with the (2 x 1) Ti_2O_3 surface becoming energetically more favourable than the (√2 x √2) DL-TiO_2 surface at a pressure of 10^{-20} atm. This, however, is still too low to realistically be seen in an experimental STM.
Figure 5.3: Graphs of the surface energies of the (1×1), (2×1) and (√2×√2) surface reconstructions at $\mu_{TiO_2} = E^0_{TiO_2} + E^0_{f,SrTiO_3}$ over a pressure range of $10^{-30}$ to 1 atm, temperatures of 300K, 1000K and 1600K are illustrated.

Over all temperatures and pressure shown in figure 5.3 the (1×1) SrO terminated surface can be seen to be the most energetically favourable surface, with none of the other surfaces becoming energetically favourable before hitting the boundary. The best of the other surface reconstructions is the (2×1) TiO$_2$/B surface, although this is still considerably higher than the (1×1) SrO termination.

The (1×1) surface reconstructions have been shown to be the most energetically favourable surfaces over a range of temperatures and pressure one would expect to find in the process of experimental STM.
5.3.2 Simulated STM images

The proposal that the (1×1) surface reconstructions have not yet been successfully imaged experimentally because they are just too electronically flat can best be examined through simulating the images. The images in figures 5.4 and 5.5 show these simulated images. The systems have been duplicated in both the x and y directions to that of (2x2) to allow us to better see surface patterns.

![Simulated STM images of the (1×1) SrO surface reconstruction.](image)

(a) Side View  
(b) From Above

Figure 5.4: Simulated STM images of the (1×1) SrO surface reconstruction. The surface is coloured according to height from red at the lowest point to dark blue at the highest.

![Simulated STM images of the (1×1) TiO₂ surface reconstruction.](image)

(a) Side View  
(b) From Above

Figure 5.5: Simulated STM images of the (1×1) TiO₂ surface reconstruction. The surface is coloured according to height from red at the lowest point to dark blue at the highest.
These simulated images assume an atomically sharp STM tip, something which is not realistic, so some of these features, like the sharp troughs in figure 5.5(a), will be smoothed over slightly. However, these simulated images still show sufficient corrugation to make them visible experimentally, especially in figure 5.5.

The experimental image of a (2×1) reconstruction gained by Castell and shown in figure 2.5 predicts distinct rows of peaks and troughs, and as such is what we are hoping to see in the simulated (2×1) images. The first reconstruction that we will look at is the (2×1) TiO$_2$/A termination, as shown in figure 5.6. As for the (1×1) surfaces, and all following (2×1) surfaces, the image has been duplicated in both the x and y directions, giving a (4×2) image to better allow patterns to be seen. Distinct rows of peaks and troughs can clearly be seen, so this could be a possible candidate for the reconstruction seen by Castell in figure 2.5. The mini peaks seen visible in figure 5.6(a) would probably not be clearly defined when performing experimental STM.

![Figure 5.6: Simulated STM images of (2×1) TiO$_2$/A. The surface is coloured according to height from red at the lowest point to dark blue at the highest.](image)

Figure 5.6: Simulated STM images of (2×1) TiO$_2$/A. The surface is coloured according to height from red at the lowest point to dark blue at the highest.

The simulated STM image of (2×1) TiO$_2$/B in figure 5.7(a) shows the rows of peaks and troughs that are associated with the experimental (2×1) image in figure 2.5. However, the peaks are not symmetrical, with one steep side and one more gently sloped. This is in agreement with the image generated by Liborio [19].
Figure 5.7: Simulated STM images of (2×1) TiO₂/B. The surface is coloured according to height from red at the lowest point to dark blue at the highest.

Figure 5.8: Simulated STM images of (2×1) Ti₂O₃. The surface is coloured according to height from red at the lowest point to dark blue at the highest.

For the case of the (2×1) Ti₂O₃ reconstruction, seen in figure 5.8, it is not clear whether the images show enough corrugation to be consistent with the experimentally gained (2×1) STM images. In figure 5.8(b) the black lines indicate what could be one of the double width peaks, although this is only very vague. A clearer pattern present is one similar to that of the (1×1) reconstructions, with the peaks showing a distinct 1x1 periodicity. This is not consistent with the experimental (2×1) images generated, and with the (1×1) surface pattern yet to be imaged, it is doubtful that this is a surface seen experimentally.
Figure 5.9: Simulated STM images of (2×1) DL-TiO$_2$. The surface is coloured according to height from red at the lowest point to dark blue at the highest.

The simulated image of the DL-TiO$_2$ is the best case so far to demonstrate the features of STM imagery. Figure 5.9(a) shows that the highest point on the surface does not correspond to the highest atom on the surface. This occurs because empty states are projected out into the vacuum, causing the electronic structure to rise where physically the surface lowers. You can also see from the image in figure 5.9(b) that there is a definite zig-zag pattern to the surface, something that was not seen in the experimental image.

Figure 5.10: Simulated STM images of (2×1) TiO/A. The surface is coloured according to height from red at the lowest point to dark blue at the highest.

The images shown in figures 5.10, 5.11 and 5.12 all show very similar properties. They all have very prominent peaks and troughs that an experimental STM would easily be able to image. The image of (2×1) TiO/A shown in figure 5.10(a) shows similar features to that
of (2×1) TiO$_2$ in figure 5.6(a), with the peak not being a smooth curve, but rather has a little dip in the middle. This is a feature that would likely be missed experimentally as the tip would not be atomically sharp like in these simulated images.

![Simulated STM images of (2×1) TiO/B.](image)

Figure 5.11: Simulated STM images of (2×1) TiO/B. The surface is coloured according to height from red at the lowest point to dark blue at the highest.

(2×1) TiO/B shows a very smooth surface in the x direction, with a series of mini peaks along the y direction. This follows the pattern seen experimentally where there are a series of bright spots along the direction of the peaks. figure 5.11(b) shows a very uniform surface pattern, with the peaks and troughs of the surface being of similar width, and this is not a pattern that is seen experimentally.

![Simulated STM images of (2×1) TiO/C.](image)

Figure 5.12: Simulated STM images of (2×1) TiO/C. The surface is coloured according to height from red at the lowest point to dark blue at the highest.

The images of (2×1) TiO/A in figure 5.10(b) and (2×1) TiO/C in figure 5.12(b) show very wide peaks with relatively narrow troughs, and this is a feature that we see in the
experimental image generated by Castell [3] in figure 2.5. (2×1) TiO/C does not show a symmetrical surface pattern, as you can see in the peaks of the surface in figure 5.12(a). This does not follow the pattern that we expect to see, and is therefore an unlikely candidate for the (2×1) surfaces that are observed.

Figure 5.13: Simulated STM images of (2×1) TiO/D. The surface is coloured according to height from red at the lowest point to dark blue at the highest.

The image of (2×1) TiO/D has features resembling that of (2×1) DL-TiO₂, where again the highest point on the surface does not fall above the highest surface atom. figure 5.13(b) shows that we are seeing the doubly wide peaks, but not in the same manner as we expect. The features of this surface are similar to that of (2×1) DL-TiO₂, only this time it is not a zig-zag pattern that we are seeing, as the lesser peaks are in line with the highest peaks. Again, this is not a pattern that is seen experimentally, as the row of bright spots we are seeing would be replaced by a row of smaller bright spots, with slightly dimmer spots beside.
Figure 5.14: Simulated STM images of \((\sqrt{2} \times \sqrt{2})\) DL-TiO\(_2\). The surface is coloured according to height from red at the lowest point to dark blue at the highest.

The last image in this section is the \((\sqrt{2} \times \sqrt{2})\) DL-TiO\(_2\) termination. The expected rows of peaks and troughs can clearly be seen in figure 5.14. figure 5.14(b) shows these rows of peaks to be roughly double the width of the troughs between, as is seen experimentally. However, there is a faint zig-zag pattern within the peaks which does not correspond with what is expected from the experimental images.
Chapter 6

(2×1) Adatom Reconstructions

In this chapter calculations that have been performed on a series of (2×1) adatom structures are described. These are based upon a structure proposed by Kubo and Nozoye [6], which was one of a series of adatom based structures which aimed at explaining the surface reconstructions observed on SrTiO$_3$. Kubo and Nozoye [6] proposed that Sr adatoms should be placed on a TiO$_2$ terminated surface. Given the earlier results on potential surface reconstructions both Sr and Ti adatoms on the SrO and TiO$_2$ terminated surfaces have been investigated.

6.1 Simulation Details

The simulation cell employed for the (2×1) adatom cases differs from that used previously. A cell containing seven layers with adatoms then placed on both surfaces has been employed. The equivalent of 6 layers of vacuum separate the adatoms. The basis set, integration mesh and k-point sampling are identical to that described previously for the (2×1) surface reconstructions. In all cases the force and residual tolerances are set to be $10^{-4}$ Ry/Bohr radius and $10^{-4}$ electrons/Bohr radii$^3$ respectively whilst the electron temperatures range from $10^{-2}$ to $10^{-3}$ Ry.

Three possible sites for the adatoms on both the SrO and TiO$_2$ terminated surfaces have been considered. These sites are illustrated in figure 6.1. These sites were chosen due to symmetry considerations. These diagrams will be used to refer to all the structures.
Considering all the possible systems that arise from these requires that 12 different adatom cases are studied.

![Candidate adatom placement sites for both the SrO and TiO$_2$ terminated surfaces in order to form a (2×1) reconstruction.](image)

Figure 6.1: Candidate adatom placement sites for both the SrO and TiO$_2$ terminated surfaces in order to form a (2×1) reconstruction. The sites remain the same for both species of Adatom.

### 6.2 Surface Energies

Out of the twelve possible adatom cases to investigate, results are provided here for eleven of the cases. The (2×1) Ti Adatom on SrO situated at site 3 proved to be too unstable to reach a satisfactory convergence. The first thing that needs to be done in order to calculate the surface energies is to calculate the surface excess of TiO$_2$ and O as identified in equation 3.34. Table 6.1 shows the excesses for all of the (2×1) adatom cases.

<table>
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<th>$\Gamma_{\text{TiO}_2}$</th>
<th>$\Gamma_O$</th>
</tr>
</thead>
<tbody>
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<td>-2</td>
</tr>
<tr>
<td>Ti Adatom on SrO</td>
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</tr>
<tr>
<td>Sr Adatom on SrO</td>
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<td>-2</td>
</tr>
<tr>
<td>Ti Adatom on TiO$_2$</td>
<td>4</td>
<td>-4</td>
</tr>
</tbody>
</table>

Table 6.1: The surface excesses for the supercells of the (2×1) adatom surface reconstructions.

From the graphs in figure 6.2 it can be seen that the Sr adatom on TiO$_2$ terminated surface is the most energetically favourable adatom case at the temperatures of 300 and
Figure 6.2: Graphs showing how the surface energies of the (2x1) adatom cases vary as a function of $\mu_{TiO_2}$. All the graphs are at atmospheric pressure, temperatures of 300K, 1000K and 1600K are illustrated.

1000K for most of the range of $\mu_{TiO_2}$. This is the surface proposed by Kubo and Nozoye [6]. In the SrO rich environment at all temperatures the Sr adatom sitting at site 2 on the SrO terminated surface becomes the most favourable. At the temperature of 1600K the Ti adatom on the SrO terminated surface is more favourable for most of the range of $\mu_{TiO_2}$. The Sr adatom at site 2 on the SrO surface is again more favourable in a SrO rich environment.

Based on the calculations performed, the surface energy of the Ti adatom at site 1 on the SrO surface becomes more stable than the Sr adatom at site 1 on the TiO$_2$ surface at about 1125K. This is subject to errors in our calculation of $\mu_O$, as well as our bulk energy and formation energy of SrTiO$_3$. 

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Figure 6.3: Graphs showing how the surface energies of the (2x1) adatom cases vary at $\mu_{TiO_2} = E_{TiO_2}^0$ over a pressure range of $10^{-30}$ to 1 atm, temperatures of 300K, 1000K and 1600K are illustrated.

In figure 6.3 the variation of the surface energies of the adatom cases is shown as a function of the oxygen partial pressure in a TiO$_2$ rich environment. At 300K it can be seen that the most favourable adatom case is that proposed by Kubo and Nozoye [6] for the range of pressures considered here. At 1000K it can be seen that although the Sr adatom at site 1 on the TiO$_2$ terminated surface is favourable at 1 atm, the Ti adatom at site 1 on the SrO terminated surface becomes more stable with a small change in pressure. At 1600K the Ti adatom at site 1 on the SrO terminated surface is the most favourable adatom system at all pressures.
Figure 6.4: Graphs showing how the surface energies of the (2 x 1) adatom cases vary at
\( \mu_{TiO_2} = E_{TiO_2}^0 + E_{j,SrTiO_3}^0 \) over a pressure range of \( 10^{-30} \) to 1 atm, temperatures of 300K, 1000K and 1600K are illustrated.

Figure 6.4 shows the variation of the surface energies as a function of the oxygen partial pressure in a SrO rich environment. At 300K the Sr adatom at site 2 of the SrO terminated surface is the most stable adatom case. At 1000K this adatom case is again the most stable case down to a pressure of \( \sim 10^{-10} \) atm. At this point the Ti adatom at site 1 on the SrO terminated surface becomes more stable. At 1600K the Sr adatom at site 2 of the SrO terminated surface is the most stable case at 1 atm. At \( \sim 10^{-1} \) atm the Ti adatom at site 1 on the SrO terminated surface becomes more energetically favourable.
Figure 6.5: Graphs showing how the surface energies of the most stable cases vary at $\mu_{TiO_2} = E_{TiO_2}^0$ over a pressure range of $10^{-30}$ to 1 atm, temperatures of 300K, 1000K and 1600K are illustrated.

Figure 6.5 shows the variation of the surface energies as a function of the oxygen partial pressure in a TiO$_2$ rich environment for those (2×1) adatom reconstructions that have been shown to be the most stable combined with the most stable surfaces from chapter 5. At 300K it can be seen that the $(\sqrt{2}x\sqrt{2})$DL-TiO$_2$ terminated surface is the most stable reconstruction across the entire pressure range, with both of the (1x1) terminated surfaces slightly higher in energy. At 1000K this is again the case across most of the pressure range, with the Ti adatom at site 1 of the SrO terminated surface becoming more stable at $\sim10^{-25}$ atm. At 1600K the $(\sqrt{2}x\sqrt{2})$DL-TiO$_2$ terminated surface is again the most stable down to a pressure of $\sim10^{-10}$ atm, where the Ti adatom at site 1 of the SrO terminated surface becomes the
most energetically stable reconstruction.

Figure 6.6: Graphs showing how the surface energies of the most stable cases vary at \( \mu_{TiO_2} = E_{TiO_2}^0 + E_{SrTiO_3}^0 \) over a pressure range of \( 10^{-30} \) to 1 atm, temperatures of 300K, 1000K and 1600K are illustrated.

In figure 6.6 the variation of the surface energies of the adatom cases is shown as a function of the oxygen partial pressure in a SrO rich environment for the cases that have been seen to be the most stable of those considered both in this chapter and in chapter 5. At temperatures of 300 and 1000K the (1x1) SrO terminated surface can be seen to be the most energetically stable surface across the entire pressure range. At 1600K the (1x1) terminated surface is again the most stable surface from 1 atm down to \( \sim 10^{-15} \) atm where the Ti adatom at site 1 of the SrO terminated surface becomes the most stable reconstruction.
6.3 STM images

6.3.1 Ti adatom on SrO

Looking at the simulated STM image for the (2×1) Ti adatom on SrO at site 1, seen in figure 6.7, an interesting physical feature can be seen. An oxygen from the underlying SrO layer has migrated to the surface, effectively giving us a (2×1) TiO termination, with an underlying (2×1) Sr₂O stoichiometry. The isosurface that we obtain shows typical (2×1) features, namely that of rows of peaks and troughs, where the peaks are roughly double the width of the troughs. This agrees well with the experimental image generated by Castell [3], shown within this work in figure 2.5, where distinct rows of bright spots separated by half width dark trenches can be seen. Figure 6.7(b) clearly shows a pattern that would correspond to these bright spots. This similarity combined with the calculated energetic stability of the surface suggest that this is an excellent candidate for the (2×1) termination.

Similar simulated STM images can be seen for site 2, figure 6.8, as in site 1, figure 6.7. Site 1 saw significant movement from an underlying oxygen, where here we maintain our Ti adatom termination, with no significant displacement shown for the adatom. The oxygens in the layer below the adatom show some movement towards the vacuum, whilst the Sr atoms can be seen to move towards the bulk from their ideal lattice positions. The isosurface shows
Figure 6.8: Simulated STM images of (2×1) Ti adatom situated at site 2 on a (1x1) SrO surface. The surface is coloured according to height from red at the lowest point to dark blue at the highest. Wide peaks and narrow troughs, with a row of dimples present in the trough, although these would most likely be smoothed over in an experimental STM. However, the energetics of this case suggest that this surface is unlikely to be a viable candidate for a (2×1) reconstruction.

6.3.2 Sr adatom on TiO₂

Figure 6.9: Simulated STM images of (2×1) Sr adatom situated at site 1 on a (1x1) TiO₂ surface. The surface is coloured according to height from red at the lowest point to dark blue at the highest.
This is the adatom reconstruction initially proposed by Kubo and Nozoye [6]. The adatom shows a slight contraction into the bulk, and the underlying TiO$_2$ shows a great deal of displacement. The adatom sits in a bridging site between two oxygens, as can be seen in figure 6.9(a) by the bonds present. The four oxygen atoms surrounding the adatom show a displacement towards the vacuum, with the two oxygen atoms with which the adatom forms a bridge showing the largest displacement. The Ti atoms show a contraction into the bulk along with the oxygen atoms that are furthest from the adatom. The steep troughs that can be seen in figure 6.9(a) are probably too steep to be properly imaged experimentally, and the narrowness of the troughs in relation to the rows of peaks seen in figure 6.9(b) suggest that this is not likely to be the experimentally observed surface.

Figure 6.10: Simulated STM images of (2×1) Sr adatom situated at site 2 on a (1x1) TiO$_2$ surface. The surface is coloured according to height from red at the lowest point to dark blue at the highest.

The images in figure 6.10 are very similar to those in figure 6.9. This is an interesting result as the adatom at site 2 was initially placed directly above an oxygen atom. During relaxation the adatom has undergone significant displacement such that it now sits in the same hole as site 1. This would also explain why the surface energy for sites 1 and 2 in this case are very similar.
The results from the third placing of the Sr adatom on TiO₂ shows a simulated STM image similar to that in figure 6.9 with very steep sided narrow troughs. You can see in the image that the troughs are not smooth, but contain a succession of well defined dimples. You can also see in figure 6.11(a) that the adatoms are a large distance from the underlying layer, and that this topmost layer of TiO₂ shows very little displacement. The adatom displays a significant displacement towards the vacuum, with all of the oxygen atoms in the underlying TiO₂ also showing a displacement towards the vacuum, but of much smaller magnitude. The Ti atom directly below the adatom shows a significant displacement towards the bulk, with the remaining Ti atom showing a slight displacement, also towards the bulk.

6.3.3 Ti adatom on TiO₂

The simulated STM images for the (2x1) Ti adatom situated at site 1 on a (1x1) TiO₂ surface in figure 6.12 shows us that the adatom has moved towards the bulk whilst the underlying layer displays a displacement towards the vacuum, and that there is now a surface stoichiometry of Ti₃O₄. The simulated STM image shows peaks and troughs of roughly equal widths, so not the double width peak that we were looking for. Also, the troughs here are relatively shallow, so they may not be well defined when viewed experimentally. The
Figure 6.12: Simulated STM images of (2×1) Ti adatom situated at site 1 on a (1x1) TiO₂ surface. The surface is coloured according to height from red at the lowest point to dark blue at the highest.

Features of the simulated STM image suggest that this is probably not the surface that is seen experimentally.

Figure 6.13: Simulated STM images of (2×1) Ti adatom situated at site 2 on a (1x1) TiO₂ surface. The surface is coloured according to height from red at the lowest point to dark blue at the highest.

Like in figure 6.12(a) the same Ti₃O₄ stoichiometry can be seen in figure 6.13(a). This, coupled with the surface energy calculations, indicates that these two cases after relaxation form the same surface, and as such the same simulated STM image. Comparing figure
6.12(b) with figure 6.13(b) shows this to be the case, with the two surfaces indistinguishable with each other.

![Side View](attachment:side_view.png) ![From Above](attachment:from_above.png)

Figure 6.14: Simulated STM images of (2×1) Ti adatom situated at site 3 on a (1x1) TiO₂ surface. The surface is coloured according to height from red at the lowest point to dark blue at the highest.

The image generated in figure 6.14(a) shows that there is a TiO surface stoichiometry as an oxygen has displaced towards the vacuum significantly. The adatom also shows a displacement towards the vacuum, and also away from its initial placement. The initial placement of the adatom was directly above another Ti atom, but these atoms have relaxed in opposite x directions whilst maintaining their y positions. The underlying layer now displays a Ti₂O₃ stoichiometry, although this is a different configuration to the (2×1)Ti₂O₃ studied here previously. The electronic surface is very different from the other 2 Ti adatom on TiO₂ cases, with the troughs being narrower than the peaks. It can also be seen in figure 6.14(b) that the peaks contain two separate peaks. If this was imaged experimentally, 2 bright spots within the rows would be seen, although the resolution may not be good enough to separate these.

The surface energies and simulated STM images for the Ti adatom on TiO₂ cases suggest that these are not configurations that we are seeing experimentally.
6.3.4 Sr adatom on SrO

Figure 6.15: Simulated STM images of (2\times1) Sr adatom situated at site 1 on a (1x1) SrO surface. The surface is coloured according to height from red at the lowest point to dark blue at the highest.

Here, like in the case of Sr adatom on TiO$_2$, we see very narrow steep sided troughs. There are very prominent low points within these troughs, although these are a feature we would probably only see theoretically. The patterns displayed here do not agree with those generated experimentally by Castell [31], suggesting that this is not a reconstruction that we see experimentally. The adatom in this case is situated between the two Sr atoms of the layer below, and these Sr atoms display a tendency to move away from the adatom, whilst also contracting into the bulk. The oxygen atoms display differing displacements, with one moving slightly towards the bulk, and the other more significantly towards the vacuum.

Figure 6.16 shows that site 2 follows the pattern seen for site 1. Very narrow troughs are present, but they appear to be shallower than those present when the Sr adatom is at site 1. It can also be seen that the low points within the troughs are not so prominent. The adatom in this case shows a displacement towards the vacuum, along with the oxygen atoms of the underlying layer. The Sr atoms in this layer have contracted slightly into the bulk. Whilst the simulated STM image does not agree with that generated experimentally, the energy graphs in figure 6.4 show that under certain conditions, this is the most stable of the adatom cases.
Figure 6.16: Simulated STM images of (2×1) Sr adatom situated at site 2 on a (1x1) SrO surface. The surface is coloured according to height from red at the lowest point to dark blue at the highest.

The very sharp points within the troughs of figure 6.17 are a feature that would probably only be seen theoretically. Again sharp sided narrow troughs, here much deeper than when the Sr adatom is at site 2, and wider smooth peaks can be seen. The adatom in this case shows a significant displacement towards the vacuum, whilst the Sr atom that this is situated above contracts back into the bulk. There is very little displacement shown from any of the
other atoms. The calculated surface energy and simulated STM image suggest that this is not a reconstruction that we are likely to see experimentally.

6.4 Conclusions

It can be seen from the surface energies calculated in figures 6.2, 6.3 and 6.4 that their are three adatom cases that are most stable under certain conditions. These are the Sr adatom at site 1 of the TiO$_2$ terminated surface, the Ti adatom at site 1 of the SrO terminated surface and the Sr adatom at site 2 on the SrO terminated surface. The Ti adatom at site 1 on the SrO terminated surface looks to be the most likely candidate from the adatom cases, as at 1600K it becomes the most stable at pressures between $\sim 10^{-10}$ and $\sim 10^{-15}$ atm depending on the particular environment, and these are realistic pressures when dealing with STM. Of these three cases, only the Ti adatom at site 1 on the SrO terminated surface produced a simulated STM image that resembles that of the experimental image shown in figure 2.5. This, combined with the calculated surface energies, makes this case an excellent candidate for the (2×1) reconstructions that are seen experimentally. However, examining the relaxation of this case revealed a (2×1) TiO surface stoichiometry, and this was the driving factor behind the (2×1) TiO cases presented in chapter 5.
Chapter 7

Adatom Reconstructions

A number of adatom reconstructions have been proposed by Kubo and Nozoye [6]. These can be seen in figure 2.14, and comprise of Sr adatoms on an underlying (1×1) TiO₂ surface. These are given a value $\mathcal{O}$ referring to the surface coverage of the adatom. The (1×1) ($\mathcal{O} = 1.0$), c(2×2) ($\mathcal{O} = 0.5$), (2×2) ($\mathcal{O} = 0.25$ and 0.75), $(\sqrt{5} \times \sqrt{5})$-R26.6° ($\mathcal{O} = 0.2$) and c(4×4) ($\mathcal{O} = 0.125$ and 0.375) have been studied here. The (4×4) and $(\sqrt{13} \times \sqrt{13})$-R33.7° reconstructions have been omitted due to the computation time required. Due to the results in chapter 6, where the (2x1) Ti adatom situated on a (1x1) terminated surface proved to be an excellent candidate for the (2x1) reconstruction, the Sr adatom models proposed by Kubo at al. [5, 6] have been extended to include Ti adatoms on (1×1) SrO terminated surfaces.

7.1 Simulation Details

As in the case of the (2x1) adatoms, a nine layer cell is employed giving seven alternating layers of SrO and TiO₂ between the adatoms. As periodic boundary conditions are used, six layers of vacuum have been incorporated to separate the surfaces. The basis set and integration mesh are identical to that described previously, with the k-point sampling being scaled according to the simulation cell size. For the larger surface reconstructions of $(\sqrt{5} \times \sqrt{5})$-R26.6° and c(4×4) ScaLAPACK [40], a parallel diagonaliser, has been utilised to allow more processors to be used.
In all cases the force tolerance and residual tolerance are set to be $10^{-4}$ Ry/Bohr radius and $10^{-4}$ electrons/Bohr radius respectively. The electron temperatures of the simulations vary from $10^{-2}$ to $10^{-3}$ Ry.

### 7.2 Surface Energies

The first thing to do in calculating the surface energies is to calculate the surface excess of TiO$_2$ and O, as identified in equation 3.34. Table 7.1 shows the excesses for all of the adatom cases studied.

<table>
<thead>
<tr>
<th>Surface</th>
<th>$\Gamma_{\text{TiO}_2}$</th>
<th>$\Gamma_{\text{O}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1×1) Sr Adatom on TiO$_2$</td>
<td>-1</td>
<td>-2</td>
</tr>
<tr>
<td>(1×1) Ti Adatom on SrO</td>
<td>1</td>
<td>-4</td>
</tr>
<tr>
<td>c(2×2) Sr Adatom on TiO$_2$</td>
<td>0</td>
<td>-2</td>
</tr>
<tr>
<td>c(2×2) Ti Adatom on SrO</td>
<td>0</td>
<td>-4</td>
</tr>
<tr>
<td>(2×2) Sr Adatom on TiO$_2$ ($\varnothing = 0.25$)</td>
<td>2</td>
<td>-2</td>
</tr>
<tr>
<td>(2×2) Sr Adatom on TiO$_2$ ($\varnothing = 0.75$)</td>
<td>-2</td>
<td>-6</td>
</tr>
<tr>
<td>(2×2) Ti Adatom on SrO ($\varnothing = 0.25$)</td>
<td>-2</td>
<td>-4</td>
</tr>
<tr>
<td>(2×2) Ti Adatom on SrO ($\varnothing = 0.75$)</td>
<td>2</td>
<td>-12</td>
</tr>
<tr>
<td>($\sqrt{5} \times \sqrt{5}$)-R26.6° Sr Adatom on TiO$_2$</td>
<td>3</td>
<td>-2</td>
</tr>
<tr>
<td>c(4×4) Sr Adatom on TiO$_2$ ($\varnothing = 0.375$)</td>
<td>2</td>
<td>-6</td>
</tr>
<tr>
<td>c(4×4) Ti Adatom on SrO ($\varnothing = 0.375$)</td>
<td>-2</td>
<td>-12</td>
</tr>
</tbody>
</table>

Table 7.1: The surface excesses for the supercells of the (1×1), c(2×2), (2×2), ($\sqrt{5} \times \sqrt{5}$) and c(4×4) adatom surface reconstructions.

The graphs in figure 7.1 show the variation of surface energy as a function of $\mu_{\text{TiO}_2}$ at temperatures of 300K, 1000K and 1600K. All results are calculated at atmospheric pressure. At all temperatures considered here it can be seen that the ($\sqrt{5} \times \sqrt{5}$) Sr adatom on the TiO$_2$ terminated surface is the most stable across the entire range of $\mu_{\text{TiO}_2}$, with the (2×2) Sr adatom on the TiO$_2$ terminated surface ($\varnothing = 0.25$) only marginally higher in energy.
Figure 7.1: Graphs showing how the surface energies of the (1 x 1), c(2 x 2), (2 x 2), (4 x 4) and c(4 x 4) adatom cases vary as a function of $\mu_{\text{TiO}_2}$. All the graphs are at atmospheric pressure, temperatures of 300K, 1000K and 1600K are illustrated.

The (1 x 1) Ti adatom, the (2 x 2) Ti adatom ($\varnothing = 0.75$) and the c(2 x 2) Ti adatom are, at atmospheric pressure, the least stable of the surfaces considered here.

In the graphs in figure 7.2 the variation of the surface energies of the adatom cases is shown as a function of the oxygen partial pressure in a TiO$_2$ rich environment. It can be seen that, for all temperatures and pressures considered here, the (5 x 5/5) Sr adatom on the TiO$_2$ terminated surface and the (2 x 2) Sr adatom on the TiO$_2$ terminated surface ($\varnothing = 0.25$) are the most stable surfaces. Again it can be seen that the (1 x 1) Ti adatom, the (2 x 2) Ti adatom ($\varnothing = 0.75$) and the c(2 x 2) Ti adatom are the least energetically favourable of the surfaces considered here.
Figure 7.2: Graphs showing how the surface energies of the (1x1), c(2x2), (2x2), (v/5 x v/5) and c(4x4) adatom cases vary at $\mu_{TiO_2} = E^0_{TiO_2}$ over a pressure range of $10^{-30}$ to 1 atm, temperatures of 300K, 1000K and 1600K are illustrated.

The graphs in figure 7.3 show the variation of the surface energies as a function of the oxygen partial pressure in a SrO rich environment. It can be seen that, at 300K and 1000K, the ($\sqrt{5} \times \sqrt{5}$) Sr adatom on the TiO$_2$ terminated surface and the (2x2) Sr adatom on the TiO$_2$ terminated surface ($\varnothing = 0.25$) are the most stable surfaces across the entire pressure range. At 1600K it can be seen that again these two surfaces are the most stable across most of the pressure range considered, but at a pressure of $\sim 10^{-20}$ atm the (2x2) Sr adatom on the TiO$_2$ terminated surface ($\varnothing = 0.75$) becomes the most stable surface, with the (1x1) Sr adatom also very close in energy to it. Pressures below the oxygen boundary are not considered as this is the critical pressure where it becomes more favourable for SrTiO$_3$ to
Figure 7.3: Graphs showing how the surface energies of the (1 x 1), c(2 x 2), (2 x 2), (5 / 5) and c(4 x 4) adatom cases vary at $\mu_{TiO_2} = E_{TiO_2}^0 + E_{f, SrTiO_3}^0$ over a pressure range of $10^{-30}$ to 1 atm, temperatures of 300K, 1000K and 1600K are illustrated.

split into its constituent parts.

Figure 7.4 shows the variation of the surface energies as a function of the oxygen partial pressure in a TiO$_2$ rich environment for the reconstructions that have been shown to be the most stable of those studied in chapters 5 and 6 along with the most stable of the surfaces seen in this chapter. At 300K the $(\sqrt{2} \times \sqrt{2})DL$-TiO$_2$ reconstruction is the most stable surface across the entire pressure range. At 1000K this is again the most stable reconstruction down to a pressure of $\sim 10^{-25}$ atm where the (2x1) Ti adatom at site 1 of the SrO terminated surface becomes the most favourable, however, this pressure is unrealistic for the conditions of STM. These two surfaces are also the most stable at 1600K, with the (2x1) Ti adatom at
Figure 7.4: Graphs showing how the surface energies of the most stable cases vary at $\mu_{TiO_2} = E_{TiO_2}^0$ over a pressure range of $10^{-30}$ to 1 atm, temperatures of 300K, 1000K and 1600K are illustrated.

Figure 7.5 the variation of the surface energies of the adatom cases is shown as a function of the oxygen partial pressure in a SrO rich environment for the cases that have been shown to be the most stable of those studied in chapters 5 and 6 along with the most stable of the surfaces seen in this chapter. At 300K and 1000K it can be seen that the $(1 \times 1)$ SrO reconstruction is the most stable surface across the entire pressure range. At 1600K this surface is again initially the most stable surface down to a pressure of $10^{-15}$ atm where the $(2 \times 1)$ Ti adatom at site 1 of the SrO terminated surface becomes the most energetically
Figure 7.5: Graphs showing how the surface energies of the most stable cases vary at $\mu_{TiO_2} = E^0_{TiO_2} + E^0_{f, SrTiO_3}$ over a pressure range of $10^{-30}$ to 1 atm, temperatures of 300K, 1000K and 1600K are illustrated.
7.3 STM images

7.3.1 (1×1) Adatom

Figure 7.6: Simulated STM images of (1×1) Sr adatom situated on a (1×1) TiO₂ surface. The surface is coloured according to height from red at the lowest point to dark blue at the highest.

The simulated STM image in figure 7.6(a) is very similar to that generated for (1×1) SrO in figure 5.4. There is a very uniform pattern with individual bright spots present. There is a slight contraction of the Sr adatom into the bulk, whilst the O atoms in the underlying layer displace towards the vacuum with almost no movement from the Ti atom.

The simulated STM image for the (1×1) Ti adatom situated on a (1×1) SrO surface in figure 7.7 shows very similar features to the (1×1) Sr adatom situated on a (1×1) TiO₂ surface in figure 7.6. Again distinct bright spots are present in the electronic surface. Both the Ti adatom and the O atom directly below show a displacement towards the vacuum, whilst the Sr atom displays a displacement towards the bulk.
Figure 7.7: Simulated STM images of (1x1) Ti adatom situated on a (1x1) SrO surface. The surface is coloured according to height from red at the lowest point to dark blue at the highest.

7.3.2 \textit{c}(2x2) Adatom

Figure 7.8: Simulated STM images of \textit{c}(2x2) Sr adatom situated on a (1x1) TiO$_2$ surface. The surface is coloured according to height from red at the lowest point to dark blue at the highest.

The simulated images in figure 7.8 shows a distinct and uniform pattern that has peaks at the corner of the cell with a dip in the centre. The Sr adatom and the underlying Ti atoms show a displacement towards the bulk. The O atoms all displace towards the vacuum, and
also show a horizontal displacement towards the adatom.

Figure 7.9: Simulated STM images of c(2×2) Ti adatom situated on a (1×1) SrO surface. The surface is coloured according to height from red at the lowest point to dark blue at the highest.

The pattern generated in the images of figure 7.9 again shows that there are distinct high and low points in the simulated STM image. Here, however, the high points look to be much more prominent than the low points between, and the sides are much steeper than in the previous case. The Ti adatom and the underlying Sr atoms show a displacement towards the bulk. Both O atoms show a displacement towards the vacuum, with the O atom directly below the adatom showing the largest displacement. There is no horizontal displacement present.
Figure 7.10: STM image of a SrTiO$_3$(001)-(2×2) reconstructed surface. The area of the image is 35 x 35 nm$^2$; $V_s = +0.7$ V, $I_t = 0.3$ nA. This image was generated by Silly et al. in [43].

The image in figure 7.10 shows an experimental STM image of a SrTiO$_3$(001) (2×2) reconstructed surface. Uniform bright spots can be identified, but there is no distinct pattern like in the case of (2x1). It appears that there are individual bright spots with dips in the surface electronic structure surrounding each one.

Figure 7.11 shows a very distinctive simulated STM image. The peaks are very wide when compared to the troughs between them, and show very steep sides. The image in figure 7.11(b) shows that the peaks are surrounded by troughs. This is a very similar pattern to that generated by Silly et al. in [43], and shown in figure 7.10. The peaks in the simulated image correspond to an underlying Sr adatom, and where physically it might be expected for the peak to be dominated by troughs, this is not what is seen.
Figure 7.11: Simulated STM images of the (2×2) Sr adatom situated on a (1×1) TiO₂ surface (θ = 0.25). The surface is coloured according to height from red at the lowest point to dark blue at the highest.

Figure 7.12: Top down view of the (2×2) Sr adatom on a (1×1) TiO₂ surface (θ = 0.25). The grey spheres represent Sr atoms, the blue spheres represent Ti atoms and the red spheres represent O atoms, where the largest spheres represent the uppermost layer. The arrows show the direction of displacement during relaxation.

During relaxation, the Sr adatom and the Ti atoms in the underlying layer show a
displacement inwards towards the bulk. The O atoms behave differently dependent upon what atoms are near them. The 4 O atoms that surround the adatom move towards the vacuum, whilst the others displace back into the bulk. Horizontally, the Ti atoms show a tendency to move away from the adatom, with no other horizontal displacement present.

Figure 7.13: Simulated STM images of the (2x2) Sr adatom situated on a (1x1) TiO$_2$ surface ($\theta = 0.75$). The surface is coloured according to height from red at the lowest point to dark blue at the highest.

The simulated STM images for the (2x2) Sr adatom situated on a (1x1) TiO$_2$ surface ($\theta = 0.75$) seen in figure 7.13 show a very distinct surface pattern. The peaks correspond to the Sr adatom underneath, with the "holes" in the surface pattern corresponding to an area with no adatom. Figure 7.13(a) show that these dips are quite pronounced, although some smoothing would occur experimentally.

Figure 7.14 shows the direction of horizontal displacement for the Sr adatom and the underlying layer of TiO$_2$ during the relaxation process. The Ti atoms show a displacement towards the vacant area seen in the top right of the image, whilst the O atoms in this region all move towards an adatom. All of the Sr adatoms and Ti atoms show a vertical displacement towards the bulk, with the Sr adatoms that have a vacant adatom site as their next nearest neighbour displacing a greater distance than the Sr without. All O atoms show a movement towards the vacuum. This agrees with the results gained by Kubo and Nozoye.
Figure 7.14: Top down view of the (2×2) Sr adatom on a (1×1) TiO₂ surface (Ø = 0.75). The grey spheres represent Sr atoms, the blue spheres represent Ti atoms and the red spheres represent O atoms, where the largest spheres represent the uppermost layer. The arrows show the direction of displacement during relaxation.

[6] for this arrangement.

Figure 7.15: Simulated STM images of the (2×2) Ti adatom situated on a (1×1) SrO surface (Ø = 0.25). The surface is coloured according to height from red at the lowest point to dark blue at the highest.
The STM images in figure 7.15 show that there are distinct peaks in the surface electronic structure above each Ti adatom. Figure 7.15(b) shows these peaks to be roughly double the width of the troughs surrounding them. There is a small dip in each of the peaks, although this would not show up experimentally. The peaks correspond to the Ti adatom beneath.

Figure 7.16: Top down view of the (2×2) Ti adatom on a (1×1) SrO surface (Ο = 0.25). The grey spheres represent Sr atoms, the blue spheres represent Ti atoms and the red spheres represent O atoms, where the largest spheres represent the uppermost layer. The arrows show the direction of displacement during relaxation.

The Sr atoms in the underlying layer all show a horizontal displacement away from their nearest Ti adatom, with no other horizontal displacement present. The Ti adatoms and the O atoms directly beneath display a displacement towards the vacuum region, with the O atoms showing a greater magnitude of displacement. The rest of the O atoms and the Sr atoms displace inwards towards the bulk.

The images generated for the (2×2) Ti adatom situated on a (1×1) SrO terminated surface (Ο = 0.75) show a very distinct pattern that is unlike anything seen previously in this work. The peaks in the surface electronic structure are not uniform, with three separate peaks present in one triangular grouping. These appear to occur due to the displacement undergone by the Ti adatoms, as can be seen in figure 7.18. Rather than the uniform troughs
Figure 7.17: Simulated STM images of the (2x2) Ti adatom situated on a (1x1) SrO surface ($\Theta = 0.75$). The surface is coloured according to height from red at the lowest point to dark blue at the highest.

that have been seen previously, there is a very prominent low area at the top right of the simulation cell, as can be seen in figure 7.17(b). This is not the sort of image that was seen by Silly et al. in [43].

The Ti adatom at the corner of the simulation cell displaces downwards during relaxation, whilst those at the side displace towards the vacuum. The Sr atoms in the underlying layer contract back into the bulk, whilst all of the O atoms move out towards the vacuum, with the O atom with no adatom above showing the smallest magnitude of displacement. Horizontally, the Sr atoms show a displacement towards the centre of the cell, whilst the Ti adatoms show a tendency to move towards each other, producing the clumps seen in figure 7.17(b). The O atoms at the corner of the cell displace away from their overhead adatoms in the y direction, but in the same x direction.
Figure 7.18: Top down view of the (2×2) Ti adatom on a (1×1) SrO surface (Ø = 0.75). The grey spheres represent Sr atoms, the blue spheres represent Ti atoms and the red spheres represent O atoms, where the largest spheres represent the uppermost layer. The arrows show the direction of displacement during relaxation.

7.3.4 \( (\sqrt{5} \times \sqrt{5}) \) Adatom

Figure 7.19: Experimental image of a \( (\sqrt{5} \times \sqrt{5}) \) surface reconstruction generated by Newell et al. [44]. The left image shows a \( (\sqrt{5} \times \sqrt{5}) \) domain with a rotation of -26.6°. The sample is imaged with a positive bias and a tunnelling current of 1 nA \( (7.9 \times 7.9 \text{ nm}^2, V_s = +0.5 \text{ V}) \). The right image shows a \( (\sqrt{5} \times \sqrt{5}) \) domain with a rotation of 26.6°. The sample is imaged with a positive bias and a tunnelling current of 2 nA \( (7.9 \times 7.9 \text{ nm}^2, V_s = -0.5 \text{ V}) \).
The images in figure 7.19 show \((\sqrt{5} \times \sqrt{5})\) domains obtained by Newell *et al.* in [44]. Clear bright islands can be seen on the surface, surrounded by darker areas which are the troughs seen in the simulated images. The islands are not spherical in nature, but consist of a cluster of similar bright spots.

![Side View](image1.png) ![From Above](image2.png)

Figure 7.20: Simulated STM images of the \((\sqrt{5} \times \sqrt{5})\) Sr adatom situated on a \((1\times1)\) TiO\(_2\) surface \((\theta = 0.2)\). The surface is coloured according to height from red at the lowest point to dark blue at the highest.

The simulated STM image of the \((\sqrt{5} \times \sqrt{5})\) Sr adatom situated on a \((1\times1)\) TiO\(_2\) terminated surface shows peaks in the surface electronic structure at the corners of the simulation cell, corresponding to the Sr adatom underneath. These peaks are surrounded by low areas that are roughly the same area as the peaks. Within each of the low areas is another mini peak that is about half of the height of the main peaks. This agrees with the image presented by Kubo and Nozoye [5, 6] and seen in figure 2.14 and with the image generated by Newell *et al.* [44], seen in figure 7.19.
Figure 7.21: Top down view of the \((\sqrt{5} \times \sqrt{5})\) Sr adatom on a (1\times1) TiO\(_2\) surface \((\varnothing = 0.2)\). The grey spheres represent Sr atoms, the blue spheres represent Ti atoms and the red spheres represent O atoms, where the largest spheres represent the uppermost layer. The arrows show the direction of displacement during relaxation.

All of the atoms in the top two layers of this simulation cell show a horizontal displacement in the same direction. Vertically, the Sr adatom and all of the Ti atoms displace back towards the bulk. The O atoms at the edge of the cell displace inwards towards the bulk, whilst those closest to an adatom displace towards the vacuum.
7.3.5 c(4×4) Adatom

Figure 7.22: STM images of a SrTiO$_3$(001)-c(4×4) surface. The image in (a) is 131 x 124 nm$^2$ and appears to show disorder. The image is magnified in (b) to show an area 75 x 75 nm$^2$ and shows local c(4×4) ordering. These images were generated by Silly et al. using $V_s = +2.0$ V and $I_t = 0.1$ nA in [43].

The images in figure 7.22 show a SrTiO$_3$(001)-c(4×4) surface. The magnified image clearly shows c(4×4) ordering, where uniform bright spots can be seen. There appears to be no distinct pattern, like the rows of the (2x1) image. The bright spots are distinct from one another and of equal size, and there appears to be darker regions between each bright spot.

It can be seen in figure 7.23 that the simulated STM image shows a series of peaks surrounding a low point in the surface. The peaks are situated above adatoms, with the low point in the surface corresponding to the area with no adatoms present. Where a peak is adjacent to another peak both in the x and y directions, the peak appears to take a spherical shape, whereas those peaks with a dip adjacent show a more elongated shape in the direction of the dips, as is apparent in figure 7.23(b). These images do not agree with the experimental STM images generated by Silly et al. in [43].
Figure 7.23: Simulated STM images of c(4×4) Sr adatom situated on a (1×1) TiO₂ surface (Ω = 0.375). The surface is coloured according to height from red at the lowest point to dark blue at the highest.

Figure 7.24: Top down view of the c(4×4) Sr adatom on a (1×1) TiO₂ surface (Ω = 0.375). The grey spheres represent Sr atoms, the blue spheres represent Ti atoms and the red spheres represent O atoms, where the largest spheres represent the uppermost layer. The arrows show the direction of displacement during relaxation.

It can be seen in figure 7.24 that there is a lot of displacement occurring during relaxation.
The central Ti atoms move away from their nearest adatom, towards the middle of the cell. The outermost O atoms move towards their closest adatom neighbour, whilst the remaining Ti atoms move away from the corners of the cell. The Sr adatoms and the Ti atoms in the underlying layer displace inwards towards the bulk during relaxation, as do the central O atoms. The outer ring of O atoms displace outwards towards the vacuum, bringing them closer to the above adatoms.

![Side View](image1)

![From Above](image2)

(a) Side View

(b) From Above

Figure 7.25: Simulated STM images of c(4×4) Ti adatom situated on a (1×1) SrO surface (O = 0.375). The surface is coloured according to height from red at the lowest point to dark blue at the highest.

The images in figure 7.25 are very similar to those generated in figure 7.23. The main difference in this case appears to be in the peaks. Here, each peak seems to display a slight dimple at its centre. Again the elongated shapes can be seen where a peak has a dip adjacent to it in either the x or y direction. This is not the sort of image we would expect to see when compared to those generated by Silly et al. [43] and shown in figure 7.22.
Figure 7.26: Top down view of the c(4×4) Ti adatom on a (1×1) SrO surface (Ω = 0.375). The grey spheres represent Sr atoms, the blue spheres represent Ti atoms and the red spheres represent O atoms, where the largest spheres represent the uppermost layer. The arrows show the direction of displacement during relaxation.

The Sr atoms surrounding a vacant adatom site show a tendency to move towards the empty space, as do the O atoms. This can be seen in figure 7.26. The remaining Sr atoms move towards the space vacated by these displaced atoms. The Ti adatoms show no horizontal displacement, and only slight displacement towards the vacuum. All Sr atoms show a tendency to contract back into the bulk. The O atoms directly below a Ti adatom show the biggest vertical displacement, and in each case the direction is towards the above adatom. All other O atoms displace slightly towards the vacuum, except for the O atom right of centre, which displays a slight contraction back to the bulk.

7.4 Conclusions

The graphs in figures 7.1, 7.2 and 7.3 seem to suggest that there are three possible candidates from an energetic point of view. These are the (1×1) Sr adatom on a (1×1) TiO₂ surface, the (2×2) Sr adatom on a (1×1) TiO₂ surface (Ω = 0.25) and the (\(\sqrt{5} \times \sqrt{5}\))R26.6° Sr adatom on a (1×1) TiO₂ surface. Of these surfaces, the (\(\sqrt{5} \times \sqrt{5}\))R26.6° Sr adatom on a (1×1)
TiO₂ surface is the most stable surface at atmospheric pressure and when in a TiO₂ rich environment. It can also be seen to be the most stable surface under most conditions when in a SrO environment, with the (1×1) Sr adatom on a (1×1) TiO₂ surface only becoming more stable at 1600K and a pressure of ~10⁻⁰² atm. However when comparing these adatom cases with those surfaces studied in chapters 5 and 6, none are energetically more favourable, as can be seen in figures 7.4 and 7.5. However, experimental work has shown that by following an annealing process, these surfaces are reproducible. Newell et al. [44] suggest that the (\(\sqrt{5} \times \sqrt{5}\)) reconstruction may only be stable as a component of a phase separated system, and may not exist without the coexistence of TiO islands.
Chapter 8

Conclusions

The experimental work on the (001) surface of SrTiO$_3$ shows a variety of different reconstructions are possible under different conditions. However, it is not clear from the work what the particular surface stoichiometry is. It is only possible to determine what the periodicity of the surface reconstruction is. A number of different surface reconstructions have been proposed for each cell periodicity.

Ab-initio calculations have been performed for a variety of different (001) surface reconstructions of SrTiO$_3$ using PLATO. A method of total energy calculation has been outlined that takes into account the differing conditions that exist in the real world.

Simulated STM images of the reconstructions have been produced that show the surface electronic structure for a bias of +1V. Taking those results that have shown to be the most stable, it has been possible to see whether these reconstructions are comparable to those seen experimentally, and hence whether or not these reconstructions are feasible.

8.1 Surface Energies

Surface energy calculations have allowed for a measure of stability of a variety of surface reconstructions to be obtained. From these calculations certain surfaces can be discounted as they are not stable under realistic conditions. This work has shown that the most stable surfaces over a variety of temperatures and pressures to be: both of the (1x1) terminations, (2x1) Ti$_2$O$_3$, the (2x1) Sr adatom situated at site 1 on a (1x1) TiO$_2$ terminated surface, the
(2x1) Ti adatom situated at site 1 on a (1x1) SrO terminated surface, the (2x1) Sr adatom situated at site 2 on a (1x1) SrO terminated surface, (\(\sqrt{2}x\sqrt{2}\))DL-TiO\(_2\) surface, both of the (2x2) Sr adatom on a (1x1) TiO\(_2\) terminated surfaces \((\phi = 0.25 \text{ and } 0.75)\) and the \((\sqrt{5}x\sqrt{5})\) Sr adatom on a (1x1) TiO\(_2\) terminated surface.

Figure 8.1: Graphs showing how the surface energies of the most stable surfaces vary as a function of \(\mu_{\text{TiO}_2}\). All the graphs are at atmospheric pressure, temperatures of 300K, 1000K and 1600K are illustrated.

Figure 8.1 shows that, when at atmospheric pressure, it can be seen that the (1x1) SrO terminated surface is the most stable surface across the range of \(\mu_{\text{TiO}_2}\) and at all temperatures considered. The \((\sqrt{2}x\sqrt{2})\)DL-TiO\(_2\) terminated surface becomes the most stable surface only when approaching a very TiO\(_2\) rich environment.
Figure 8.2: Graphs showing how the surface energies of the most stable cases vary at $\mu_{TiO_2} = E_{TiO_2}^0$ over a pressure range of $10^{-30}$ to 1 atm, temperatures of 300K, 1000K and 1600K are illustrated.

Figure 8.2 shows the variation of the surface energies as a function of the oxygen partial pressure in a TiO$_2$ rich environment for the reconstructions that have been shown to be the most stable. It can be seen that two surfaces are the most stable across the entire feasible pressure range. At low temperatures the $(\sqrt{2}x\sqrt{2})$DL-TiO$_2$ is the most stable surface reconstruction across the pressure range. As the temperature is increased, the (2x1) Ti adatom situated at site 1 on a (1x1) SrO terminated surface becomes the most stable surface when in a low pressure environment.
Figure 8.3: Graphs showing how the surface energies of the most stable cases vary at $\mu_{TiO_2} = E^0_{TiO_2} + E^0_{j, SrTiO_3}$ over a pressure range of $10^{-30}$ to 1 atm, temperatures of 300K, 1000K and 1600K are illustrated.

In figure 7.5 the variation of the surface energies of the adatom cases is shown as a function of the oxygen partial pressure in a SrO rich environment for the cases that have been shown to be the most stable. It can be seen that the (1x1) SrO reconstruction is the most stable surface at low temperatures. Increasing the temperature again shows the (2x1) Ti adatom situated at site 1 on a (1x1) SrO terminated surface becoming the most stable surface when in a low pressure environment.

Of the most stable surfaces, the (2x1) Ti adatom situated at site 1 on a (1x1) SrO terminated surface has shown to be a very stable surface in the environment expected when performing STM, regardless of whether in SrO or TiO$_2$ conditions. From a purely energetic
view the Sr adatom model proposed by Kubo and Nozoye [6] does not appear to answer the question of what surfaces are being seen experimentally, although these surfaces could exist if the system is not in equilibrium.

### 8.2 Simulated STM images

From the total energy calculations a few surfaces stand out as the most stable. However, to match these surfaces with what is seen experimentally the STM images have to be compared. There are no experimental STM images of the (1x1) surfaces to compare with, but the simulated image shows that it is not a case of the surface being too electronically flat to produce a sufficient image.

![Simulated STM Images](image)

Figure 8.4: Simulated STM images of the (1x1) SrO terminated surface. The surface is coloured according to height from red at the lowest point to dark blue at the highest.

Whilst the sharpness of the troughs in the simulated images would be reduced experimentally, there are sufficient features in the simulated STM image to suggest that experimental imagery is possible. However, the energetics calculated in this work support the theory that this surface is not the most stable at pressures involved in experimental STM. It can be seen that this surface reconstruction is stable at lower temperatures, and only when in a very SrO rich environment.
Figure 8.5: Simulated STM images of the (2x1) Ti adatom situated at site 1 on a (1x1) SrO surface. The surface is coloured according to height from red at the lowest point to dark blue at the highest.

The (2x1) Ti adatom situated at site 1 on a (1x1) SrO terminated surface has been seen to be the most stable surface when at high temperatures and in the pressure range associated with STM. The simulated image compares favourably with that generated by Castell [3]. Clearly defined rows of peaks and troughs can be seen in both the experimental and simulated images. The peaks can be seen to be roughly twice the width of the troughs, and again this matches what is expected from the experimental image. This, combined with the energy calculations, have shown this to be an excellent candidate for a (2x1) reconstruction.
Figure 8.6: Simulated STM images of the \( (\sqrt{2}x\sqrt{2}) \) DL-TiO\(_2\) terminated surface. The surface is coloured according to height from red at the lowest point to dark blue at the highest.

The \( (\sqrt{2}x\sqrt{2}) \) DL-TiO\(_2\) image shows a very distinctive pattern. As such, this would be clearly identifiable in any experimental images generated. The energetics of this surface reconstruction suggest that this is a surface that could be stable, although not when at the pressures involved in experimental STM. As of yet nothing has been produced experimentally that matches with this pattern.

8.3 Future Work

SrTiO\(_3\) is an insulating material, and as such the band gap is too large to allow tunneling to occur. So to generate STM images of SrTiO\(_3\) experimentally dopants are used that lower the conduction band by adding states below the Fermi energy. It is not clear, however, what effect if any these dopants have on the images generated and the relative stability of the surface. Simulating these dopants will allow for a clearer understanding of the role of dopants in both the energetics and imagery. In experimental STM contaminants can be present in the equipment, primarily carbon. These contaminants could have adverse effects
on the stability of the surfaces under UHV conditions, as well as altering the images that are produced. Finding a way to simulate these contaminants would bring the simulations closer to the experimental process.

There are a number of larger surfaces that have been proposed, both with and without the use of adatoms. These include c(4x2) [3], c(4x4) [3], (4x4) [6] and (sqrt(13)xsqrt(13))-R33.7° [6]. These larger surfaces usually arise after an annealing process is performed, and clear experimental images have been obtained each of these surface reconstructions, so more theoretical work could help to explain the phase transitions that lead to these surfaces.

Oxygen vacancies are another area of interest. It has been suggested that the (1x1) surfaces are simply not stable enough in UHV conditions, and that this leads to the formation of oxygen vacancies. Calculations have been produced by Johnston et al. [17] that show the energy of a (2x2) oxygen vacancy relative to early surface reconstructions. However, with the use of periodic boundary conditions the oxygen vacancies may be too close together, so a study of larger cells and rotated cells may give a better picture of the energetics involved.

The method of total energy calculations outlined in this work can be further improved. Vibrational contributions to the energy are a factor that have not been considered in this work, but may change the relative stability of any given surface reconstruction. It is thought that vibrations may lead to the instability of surfaces, giving rise to oxygen vacancies and causing other reconstructions to form.
Bibliography


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