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Theoretical analysis of STM experiments at rutile TiO_2 surfaces

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Abstract

A first-principles atomic orbital-based electronic structure method is used to investigate the low index surfaces of rutile titanium dioxide (TiO_2). The method is relatively cheap in computational terms, making it attractive for the study of oxide surfaces, many of which undergo large reconstructions, and may be governed by the presence of oxygen vacancy defects. Calculated surface charge densities are presented for low-index surfaces of TiO_2 , and the relation of these results to experimental scanning tunnelling microscopy images is discussed. Atomic resolution images at these surfaces tend to be produced at positive bias, probing states which largely consist of unoccupied Ti 3d bands, with a small contribution from O 2p. These experiments are particularly interesting since the O atoms tend to sit up to 1 Å above the Ti atoms, so providing a play-off between electronic and geometric structure in image formation.

Keywords: Ab initio quantum chemical methods and calculations; Low index single crystal surfaces; Scanning tunnelling microscopy; Surface structure, morphology, roughness, and topography; Titanium oxide

1. Introduction

There has been considerable interest in recent years in using scanning probe microscopy to investigate the surfaces of transition metal oxides. These materials, frequently used in technological applications in which surface properties are crucial, are obvious candidates for study by methods which potentially offer atomic resolution; even a low-index “clean” surface may undergo considerable structural relaxation, and may have its electronic and structural properties dominated by localised (O-vacancy) defects. For the semiconducting oxides, such as rutile TiO_2 and SnO_2 , scanning tunnelling microscopy (STM) may be used. The aim of our work is to use computational modelling

to aid understanding of atomic resolution STM experiments at oxide surfaces using $\text{TiO}_2(110)$ in particular as a model surface. At least three groups have published atomic resolution images at this surface [1–6], whose structure appears to be heavily influenced by local stoichiometry. Issues to be addressed include identification of the atoms responsible for features seen in positive-bias images, and the extent to which we expect STM to distinguish between the various structural models proposed for the surface.

Unfortunately, the problems associated with modelling the full STM experiment are considerable. The breaking of translational symmetry caused even by a simple bulk-terminated surface make quantitative atom-based calculations very compute expensive. The addition of a scanning tip, not even periodic in the plane of the surface,

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and its associated electric fields, compounds the problem, as does the extension to systems with reconstructions, defects and adsorbates.

Perhaps the most successful computational methods for modelling surfaces are those based on *ab initio* plane-wave pseudopotential calculations. These have been performed for low-index TiO_2 surfaces [6–9]. Their principal drawback is that atomic oxygen is particularly difficult to pseudise, due to the lack of core p orbitals. The same problem occurs for the first-row transition elements, lacking a core d orbital. Pseudopotential calculations involving these atoms are therefore rather expensive. We are engaged in a programme of research using less rigorous, but far cheaper, computational methods to model transition metal oxides. The ability of our method to reproduce a reasonable account of the physics of these surfaces has been investigated through a series of benchmarking exercises, reported elsewhere [10]. Though the results presented here are for relatively simple, isolated surfaces, we feel they already make a contribution to the understanding of STM experiments at these surfaces. Further, we are confident that it will be possible to model realistic systems, including tips, on a moderate workstation.

The rest of the paper is organised as follows. Section 2 contains a brief outline of the computational method employed. In Section 3 we present calculated densities of states (DOS) for bulk rutile TiO_2 , from which it might be assumed that positive bias experiments only ever image Ti atoms, and computed local-DOS (equivalent to the “perfect tip” approximation to STM imaging [11]) which show that this is not necessarily the case. Our conclusions are drawn in Section 4.

2. Method

The calculations were carried out in a first-principles atomic-orbital based scheme [12]. The basis set comprised the valence orbitals for Ti (4s, 4p and 3d) and O (2s and 2p). The numerical atomic orbitals were generated using a standard local-density approximation for exchange and correlation, and the potential in the solid was calculated by superposing neutral-atom charge densities.

The Schrödinger equation was then solved for the electronic structure of TiO_2 slabs with a thickness of six to 12 atomic layers (sufficient to prevent substantial interaction between the two surfaces). Self-consistency was included only to the extent that the energy of the Ti 3d state was made consistent with that in a neutral atom with the same d-occupancy; this leads to an occupancy of 1.85 d electrons per Ti atom in bulk TiO_2 , with small variations from this value at the surface. The method has previously been used to study the electronic structure of various TiO_2 surfaces [13,14]. Although this approach is crude compared to fully self-consistent calculations, the advantage of the method is its simplicity which allows it to be easily applied to the local electronic structure in complicated geometries such as defective TiO_2 surfaces.

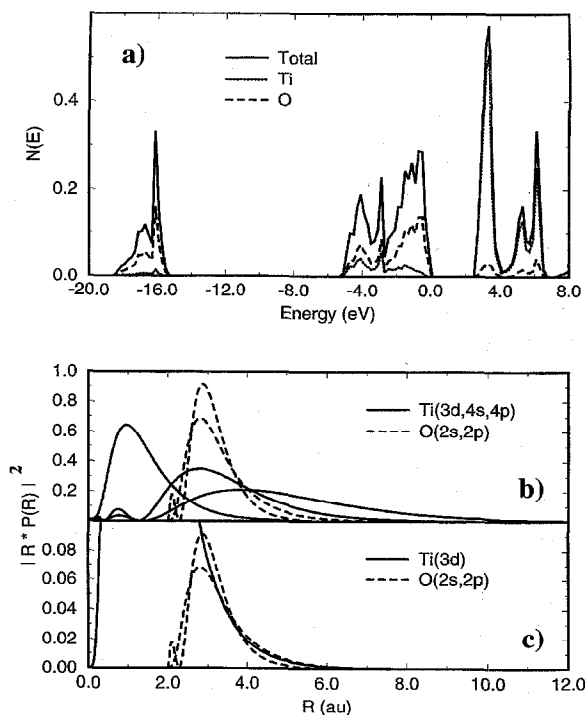


Fig. 1. (a) Computed density of states for bulk rutile TiO_2 . (b) Radial wavefunctions, multiplied by radius and squared, of the self-consistent atomic basis states of neutral titanium and oxygen. (c) Some of the same states replotted to show how the charge density at a surface depends on the relative heights and occupancy of contributing orbitals. See text for details.

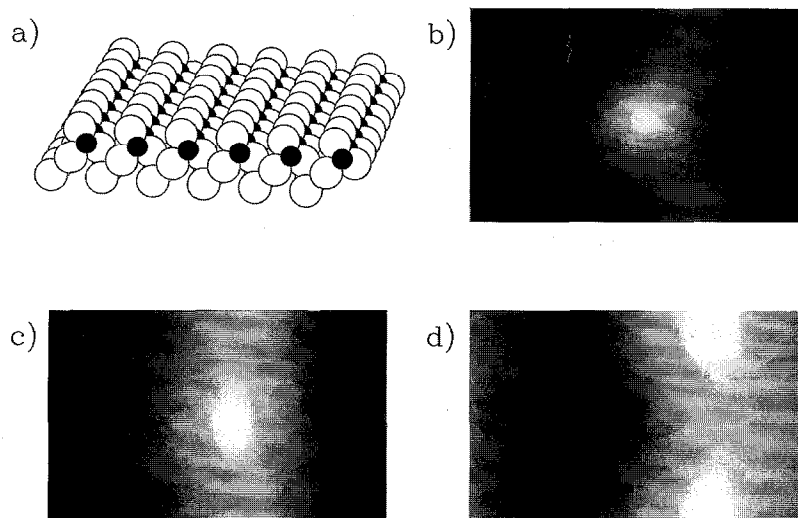


Fig. 2. (a) The unrelaxed stoichiometric (100) surface of TiO_2 . Filled circles represent Ti atoms. (b–d) Constant height charge densities including only conduction band states at Γ within 1.5 eV of the conduction band edge at heights of 1, 2 and 4 Å, respectively, above the uppermost O atoms, which sit below the centre of each figure. In each case, a single surface unit cell is shown. In all greyscale images white shows higher charge.

3. Results

The calculated DOS of bulk rutile TiO_2 is presented in Fig. 1. The total DOS is resolved in terms of atomic Ti and O contributions. TiO_2 is a direct-gap semiconducting material. Our calculations yield a fundamental gap of 2.85 eV; the experimental value is 3.0 eV [15]. The character of the valence band is mainly O 2p, with rather less Ti 3d. The unoccupied, conduction band is formed by Ti 3d orbitals with a small contribution from O 2p states.

Scanning tunnelling microscopy experiments with atomic resolution at TiO_2 surfaces are achieved with a positive tip bias [1–5, 16, 17] which means the tunnelling occurs into empty conduction band states. Because of the mainly Ti 3d character of these states, it is expected from the electronic point of view that Ti atoms will be imaged. However, at the unrelaxed (100) and (110) surfaces, the uppermost O atoms are approximately 1 Å above the Ti atoms. Since the tails of the radial wavefunctions are decaying exponentially, the contribution of O atoms to the STM images may be appreciable because of this height difference. Radial wavefunctions of the relevant O and

Ti atomic orbitals are shown in Fig. 1b. In Fig. 1c the wavefunctions are re-plotted to give an approximate indication of the interplay between electronic structure and geometry. The O wavefunctions are shifted 1 Å to the right of those of Ti to take into account the height difference and are scaled by 0.1 since the O contribution to the DOS is $\sim 10\%$ of the Ti contribution for the conduction band states shown. This plot would suggest that both O and Ti may contribute to constant height images, with O dominating out to ~ 3 Å and Ti further out.

This simple analysis agrees well with the computed constant height (z) charge densities $\rho(x, y)$, shown in Fig. 2 for the unrelaxed, stoichiometric $\text{TiO}_2(100)-(1 \times 1)$ surface. The charge densities consist of the sum of all states at Γ within 1.5 eV of the conduction band edge. Assuming the Fermi level is pinned at or close to the conduction band edge, this figure represents the crudest, perfect delta-function tip, estimate of a constant-height STM image at +1.5 V bias. At the smallest height $z = 1$ Å (measured from the uppermost surface O) $\rho(x, y)$ shows a peak close to the surface O atom position, as seen in Fig. 2b. At $z = 2$ Å $\rho(x, y)$ is more uniform along the 001 direction. Further away from the surface at $z = 4$ Å a peak appears

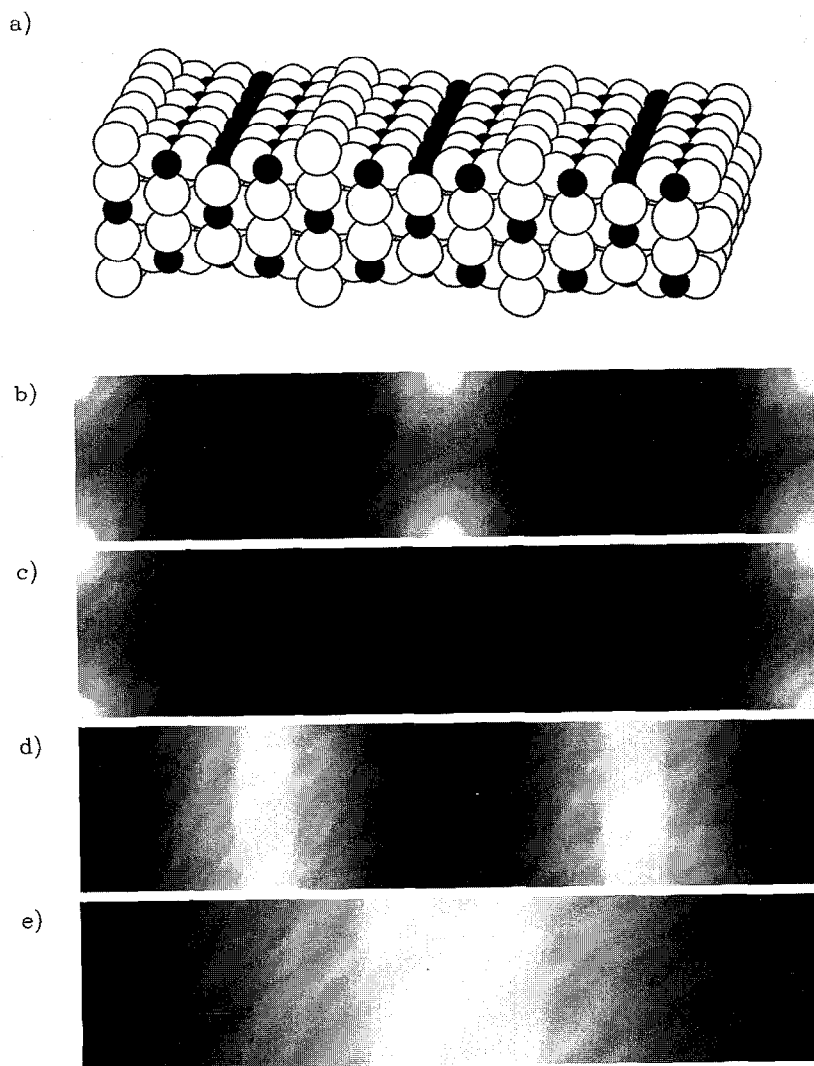


Fig. 3. (a) The unrelaxed missing O-row model of $\text{TiO}_2(110)-(1 \times 2)$, in which alternate bridging O rows are removed from the stoichiometric 1×1 termination. (b) Constant height charge density at 2 \AA above the bridging O atoms for two surface units cells of stoichiometric $\text{TiO}_2(110)-(1 \times 1)$. (c) Constant height charge density 2 \AA above the bridging O atoms for a single surface unit cell of the 1×2 surface shown in (a). (d), (e) The same as (b) and (c), respectively, except at a height of 4 \AA . All $\rho(x, y)$ consist of the sum of conduction band states at Γ within 1.5 eV of the conduction band edge. In (b)–(e) each corner of the figure sits above a bridging O atom. In all greyscale images white shows higher charge.

close to the Ti atom positions (Fig. 2d). By 6 \AA our calculations suggest that lateral structure has all but disappeared. This may give a qualitative explanation as to why the 1×1 surface has never been imaged with atomic resolution in STM.

Atomically resolved STM images have been reported both for the 1×1 and 1×2 phases of

$\text{TiO}_2(110)$ [1–5]. One of the proposed models for the 1×2 surface is a missing row reconstruction, in which every second bridging O row is removed (Fig. 3a). This reduction results in a surface state just below the bottom of the conduction band. Computed constant-height charge densities $\rho(x, y)$ for the unrelaxed 1×1 and unrelaxed missing row

1×2 surfaces are shown in Fig. 3 at heights of 2 and 4 Å. Again, only states at Γ within 1.5 eV of the conduction band edge have been included. Two surface units cells of the 1×1 surface are plotted for easy comparison with the 1×2 surface. At 2 Å the charge comes mainly from a state having the character of O 2p and two Ti 3d orbitals. The mixing of all these results in a peak over the bridging O atom. Thus the difference between the 1×1 (b) and 1×2 (c) plots is merely that half the bridging oxygens are missing in the latter.

At $z=4$ Å the charge density has switched, as in the (100) case, to being associated in position with surface Ti atoms [18], though there is little to suggest much resolution of individual atoms within rows lying along the [001] direction. At the 1×1 surface, the rows are centred over the fivefold-coordinated Ti atoms which sit halfway between the rows of bridging oxygen atoms. At the 1×2 surface, there is a single, much wider row, centred over the fourfold-coordinated Ti atoms exposed on the removal of the O rows. These results, including the relative register of the main features in the two phases, are in broad agreement with experimental STM images of $\text{TiO}_2(110)$.

4. Conclusions

We have presented the results of computationally cheap atomic-orbital based calculations at low-index TiO_2 surfaces which show broad agreement with published experimental STM images. Despite the problems inherent to any attempt to model STM, we are encouraged that even the simplest calculations of charge density at the surfaces of TiO_2 yield results which make sense in terms of published STM images and yield information, relating to orbital content of observed features, which may be of use in interpretation. The constant height charge densities $\rho(x, y)$ at TiO_2 surfaces are affected by both geometrical structure, as the surface oxygen atoms sit ~ 1 Å above the next plane, and electronic structure, in that the conduction band is mainly formed by

Ti 3d orbitals but mixing of orbitals shift the peak positions. The next stage at the $\text{TiO}_2(110)-(1 \times 2)$ surface is to investigate the sensitivity of the computed charge densities (integrated over the surface Brillouin zone) to the geometry of various proposed structures. The inclusion of a tip, and consideration of other oxide surfaces are obvious extensions on which we are currently working.

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