Effects of exchange, correlation, and numerical approximations on the computed properties of the rutile TiO_2 (100) surface

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(Received 22 July 1998)

We present fully converged, all-electron, *ab initio* calculations of the structural relaxation at the TiO_2 (100)-(1 $\times$ 1) surface. The effects of electron exchange, correlation, and various numerical approximations are isolated and quantified. We find that the predicted relaxations are insensitive to the treatment of exchange and correlation, but do depend on numerical approximations. The results of previous *ab initio* calculations are discussed in the light of these findings. [S0163-1829(99)05003-1]

I. INTRODUCTION

The structural and related chemical properties of metal oxide surfaces, and in particular those of titanium dioxide continue to be the focus of a large number of experimental and theoretical studies. This interest is in part due to the important applications of TiO_2 as a pigment and as a catalyst support.¹⁻³ TiO_2 is also a model transition-metal oxide and its relatively simple structure allows an array of first-principles (*ab initio*) methods to be used in the calculation of its bulk and surface properties. Of the low-index surfaces, the greatest amount of effort has been concentrated on the two most stable surfaces, the (110) and the (100). The (100)-(1 $\times$ 3) surface reconstruction has been observed experimentally⁴⁻⁹ and studied using a variety of theoretical methods.¹⁰⁻¹³ However the stoichiometric (100)-(1 $\times$ 1) surface has not been as extensively studied by experiment. Although it was first seen using low energy electron diffraction,¹⁴ it was not confirmed as having a bulk-terminated structure until a recent scanning tunnelling microscopy study was performed.¹⁵

The increased sophistication of *ab initio* methods coupled with a growth in computer power means that it is now possible to model rather complex physical and chemical processes at surfaces. The insight gained from such simulations is often invaluable.¹⁶⁻¹⁸ The development of surface x-ray diffraction as a noninvasive probe of oxide surface structures has provided a new test for *ab initio* theories of these systems as reliable and accurate structural data for the surface region is obtained.^{9,19} The *ab initio* theories applied to these systems differ in their treatment of electron exchange and correlation effects as well as in the numerical approximations made. Most are based on either Hartree-Fock (HF) theory, in which exchange is treated exactly and correlation effects neglected, or density-functional theory (DFT), in which both exchange and correlation are approximated. The level of accuracy and applicability of these theories has been quantified for several materials, usually in the stoichiometric bulk phase.²⁰⁻²³ To date there has been no systematic evaluation of the effects of these approximations on the surface relaxations of a metal oxide. Such evaluations are vital to establish the accuracy and reliability of simulations of surface properties.

A number of studies of the relaxation of the (100)-(1 $\times$ 1) surface have been performed within the local-density approximation (LDA) to DFT using the plane-wave pseudopotential technique^{12,24} (PW-LDA) and also within the HF approximation²⁵ using an all-electron local basis set formalism. The results of these calculations are, at best, in qualitative agreement. At the present time the experimental determination of the relaxation at the clean (100) surface has not been performed. In the current article we present the first unconstrained, fully converged all-electron calculations of the relaxation of this surface. The effects of exchange, correlation, and various numerical approximations on the structural, electronic, and energetic properties of the surface are isolated and evaluated.

II. METHOD

All calculations have been performed using the CRYSTAL95 software package.²⁶ The crystalline orbitals are expanded as a linear combination of a basis set consisting of atom centred Gaussian orbitals with *s*, *p*, or *d* symmetry. Both pseudopotential and all-electron calculations were performed in which there is no shape approximation to the potential or density. A variety of treatments of exchange and correlation were used; exact exchange neglecting correlation (HF), the LDA to DFT (Refs. 27 and 28) and the generalized gradient approximation (GGA) (Ref. 29) to DFT.

In order to quantify the effects of using a finite basis set we have used a hierarchy of all-electron Gaussian basis sets of increasing sophistication. These basis sets have been developed and optimized for use in rutile TiO_2 bulk and surface studies^{30,31} and are available elsewhere.³² The basis sets have identical descriptions for the core functions but differ in their description of the valence functions. The double valence basis set (DVAE) employs two independent radial functions to describe the valence electrons while the triple valence (TVAE) uses three radial functions. These are further augmented with *d*-symmetry polarization functions on the oxygen ions (TVAE* basis set) and additional *d* functions on the titanium ions (TVAE** basis set).^{32,33}

The effects of the pseudopotential approximation were explored by using small core (SC) and large core (LC) pseudopotentials. In Ti the SC pseudopotential replaces the 1*s*, 2*s*, and 2*p* electrons while the LC also incorporates the

FIG. 1. A section through a (100) surface viewed in the $[00\bar{1}]$ direction. The symmetry inequivalent ions are labeled.

$3s$ and $3p$ electrons.³⁴ For O both SC and LC pseudopotentials replace the $1s$ electrons.³⁵

In the present study the surface is modeled as a two-dimensional slab periodic in the $[010]$ and $[001]$ directions but finite in the $[100]$ direction (Fig. 1). This obviates the need to converge calculations with respect to the interslab vacuum distance introduced in the three-dimensional supercell models of surface structures.^{12,24} The thickness of the slab used to model the surface is an important approximation. We have used slabs of at least nine atomic layer thickness (three TiO_2 units). Thicker slabs were used to determine convergence.

The sampling of k space is also an important approximation. A Pack-Monkhurst grid^{26,36} of shrinking parameter four was used which yields nine symmetry inequivalent k points in the irreducible Brillouin zone of a nine-layer (100) slab. Sampling grids with four irreducible k points were also used to check for convergence.

A further approximation in the present study is related to the use of local basis functions. The truncation of the direct space summations of the Coulomb and exchange series are controlled by five Gaussian overlap criteria. The control of these approximations is described in detail elsewhere.^{26,37} The values used in this study ($10^{-6}, 10^{-6}, 10^{-6}, 10^{-6}$, and

10^{-12}) result in a numerical error of less than 0.1 mHa in the relative energies of different structures.²¹

All surface unit cells were based on bulk lattice parameters optimized using identical computational conditions and with the same treatment of exchange and correlation. The structural optimizations were converged to a displacement of less than $0.01 \text{ \AA}$ or an energy difference of less than 10^{-6} Ha using a Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimisation algorithm.³⁸

III. RESULTS

The rutile TiO_2 structure belongs to the $P4_2/mnm$ tetragonal space group where the unit cell is defined by the lattice parameters, a and c . The Ti ion is located at $(0,0,0)$ and the O at $(u,u,0)$. As a prerequisite to surface studies, the bulk lattice was relaxed with respect to a , c , and the fractional coordinate u . We find that the lattice parameters systematically converge as the basis set is improved. The optimal parameters obtained with the TVAE** basis set for various treatments of exchange and correlation are presented in Table I. The tendency for HF theory to overestimate and the LDA to underestimate the cell volumes of ionic crystals is well known^{21–23,39} and is reproduced in the current results. There is reasonable agreement (0.5% in the cell volume) between the LDA results presented here and those of the PW-LDA studies of Ramamoorthy *et al.*²⁴ However, there is poor agreement with the PW-LDA study of Lindan *et al.*,¹² which reported a cell volume 3.7% larger than that found here and indeed 0.7% larger than experiment, which is not the expected behavior for LDA theory. The reasons for this discrepancy will be explored further below. The displacements in the relaxation of the (100) surface are presented in Table II. These were computed using the TVAE** basis set and a nine-layer slab. The displacements are fully converged with respect to slab thickness (see Sec. IV). The atomic labels refer to Fig. 1. The most striking feature of these results is that the effects of different treatments of exchange and correlation on the surface structure are very small (not more than $0.02 \text{ \AA}$ for any displacement). The convergence of surface geometry with basis set is rapid. A maximum difference of $0.04 \text{ \AA}$ between geometries computed with the DVAE, TVAE, TVAE*, and TVAE** basis sets is observed irrespective of the treatment of exchange and correlation interactions (Fig. 2). There is qualitative agreement between our results and those of the PW-LDA studies. The direction of the displacements is the same in all studies as is the rapid decay in the magnitude of the displacements in the first four

TABLE I. The computed structural parameters of TiO_2 . Values in parentheses indicate the percentage deviation from experimental data (Ref. 44). HF, LDA, and GGA results are from the present study using a TVAE** basis set. Data from previous studies; PW-LDA-1 (Ref. 24), and PW-LDA-2 (Ref. 12) are also presented.

	a ($\text{\AA}$)		c ($\text{\AA}$)		u	Volume ($\text{\AA}^3$)	
HF	4.579	(-0.33)	2.989	(1.05)	0.306	(0.33)	62.671 (0.39)
LDA	4.548	(-1.00)	2.944	(-0.47)	0.305	(0.00)	60.895 (-2.46)
GGA	4.623	(0.63)	2.987	(0.98)	0.306	(0.33)	63.839 (2.26)
PW-LDA-1	4.567	(-0.59)	2.932	(-0.88)	0.305	(0.00)	61.161 (-2.03)
PW-LDA-2	4.638	(0.96)	2.923	(-1.18)	0.305	(0.00)	62.858 (0.69)
Expt.	4.594		2.958		0.305		62.428

TABLE II. The displacement of ions ($\text{\AA}$) relative to a bulk terminated structure of the TiO_2 (100) 1×1 surface. HF, LDA, and GGA are from the present study using a TVAE** basis set. Data from previous studies; PW-LDA-1 (Ref. 24), and PW-LDA-2 (Ref. 12) are also presented.

Label	HF		LDA		GGA		PW-LDA-1		PW-LDA-2	
	[010]	[100]	[010]	[100]	[010]	[100]	[010]	[100]	[010]	[100]
1	-0.32	0.04	-0.31	0.06	-0.31	0.06	-0.18	0.01	-0.15	0.01
2	0.09	-0.03	0.10	-0.04	0.11	-0.04	0.17	-0.07	0.13	-0.04
3	-0.15	0.04	-0.14	0.04	-0.13	0.02	-0.12	0.02	-0.09	0.05
4	-0.05	-0.01	-0.04	0.00	-0.03	0.00	-0.03	0.02	0.00	-0.02

layers. The subsurface relaxations are in quantitative agreement with only minor discrepancies ($<0.03 \text{ \AA}$). However, there is a larger discrepancy in the predicted displacement of the surface oxygen ion along the [010] direction with previous studies yielding a displacement at least $0.1 \text{ \AA}$ smaller than the current results.

We note that a recent study using HF theory on a nine layer (100) slab found the displacement of the surface oxygen to be $-0.39 \text{ \AA}$ in the [010] direction and $0.04 \text{ \AA}$ along the [100] direction.²⁵ In this study only the surface oxygen plane was relaxed. Repeating our relaxation (using the TVAE basis set) but fixing the positions of all the atoms except for the surface oxygen layer, we find similar displacements of $-0.39 \text{ \AA}$ along the [010] direction and $0.06 \text{ \AA}$ in the [100] direction. We conclude that an accurate treatment of the surface geometry requires the relaxation of the subsurface layers.

The computed surface formation energies for relaxed and bulk-terminated (unrelaxed) surfaces are presented in Table

III. The approximation of the exchange and correlation potential has a significant effect on the surface energies. The HF and LDA predictions are similar but the GGA result is some 30% lower than the LDA result. To our knowledge, there is no other determination of the surface energy using GGA functionals for the (100) surface but the tendency of GGA functionals to predict lower surface energies for the TiO_2 (110) surface has been reported recently.²³ The LDA surface energy calculated in the present study agrees (to within 10%) with that reported in the recent PW-LDA studies.^{12,24}

The relaxation energy (the difference in surface energy between relaxed and bulk-terminated surfaces) is somewhat higher for HF theory (1.0 J m^{-2}) than for either LDA or GGA theory (0.7 J m^{-2}). The relaxation energies reported previously are 0.8 (Ref. 24) and 0.4 (Ref. 12) J m^{-2} .

The surface energy is more sensitive to the basis set approximation than the surface structure. For the HF calculations, the relaxed surface energy falls from 2.47 J m^{-2} for the DVAE basis set to 1.21 J m^{-2} for the TVAE** basis set (Fig. 3) with similar trends observed when using the LDA and GGA functionals. It is apparent that the extra flexibility of the polarization functions is important in describing the surface electronic structure. Studies using even larger basis sets would be required to establish the convergence of the surface energy fully.

IV. DISCUSSION

We have found that the biggest ionic displacements as a result of relaxation of the (100) surface are in the top three layers of the surface. The most striking feature is the large ($-0.3 \text{ \AA}$) displacement of the surface oxygen (labeled 1) parallel to the surface (along the [010] direction). The titanium ion directly beneath the surface oxygen (labeled 2) is displaced by $0.1 \text{ \AA}$ along [010] in the opposite direction. The net effect of these displacements is to increase the effective

FIG. 2. The effect of the basis set on the displacements of the surface ions ($\text{\AA}$) along the [100] direction (upper panel) and [010] direction (lower panel) computed within the HF approximation. Atomic labels refer to Fig. 1.

TABLE III. The surface formation energy (J m^{-2}) of the TiO_2 (100) relaxed and unrelaxed geometries. HF, LDA, and GGA are from the present study using the TVAE** basis set. Data from previous studies; PW-LDA-1 (Ref. 24), and PW-LDA-2 (Ref. 12) are also presented.

Surface	HF	LDA	GGA	PW-LDA-1	PW-LDA-2
100 unrelaxed	2.22	2.02	1.57	1.93	1.81
100 relaxed	1.21	1.30	0.83	1.12	1.38

FIG. 3. The convergence of the surface formation energy calculated within the HF approximation with respect to the basis set.

coordination of the fivefold-coordinated Ti ion at the surface (Fig. 1).

The magnitude of the displacements computed in the current study are significantly different from those calculated in the PW-LDA studies. Most notably the displacement of the surface oxygen was reported to be -0.18 Å (Ref. 24) and -0.15 Å.¹² While the details of the LDA functionals used in these studies are not identical to those used here, we would not expect this to produce a significantly different geometry. Numerical errors are estimated in the current study to be less than 0.02 Å and were estimated in previous work to be 0.05 Å (Refs. 12 and 40) and thus do not explain the discrepancy. As we wish to make quantitative comparison with experimental measurements at oxide surfaces (not yet available for this surface) we have explored some of the possible reasons for the discrepancy in some detail.

We have shown above that approximations for exchange and correlation have a small influence on surface geometry (<0.02 Å) and also that the calculations are converged with respect to the local basis set. The discrepancies due to using basis sets of varying quality are not more than 0.04 Å and typically in the region of $0.01 - 0.02$ Å. The remaining major approximation is the use of effective core pseudopotentials in the PW-LDA studies. We have therefore performed calculations to estimate the effects of this approximation. The pseudopotentials we have used are somewhat different in construction to those used in PW-LDA studies but are of sufficiently similar character to yield information about the nature of the approximation. We classify the pseudopotentials used as small core (SC) and large core (LC) as described in Sec. II. We find that the following points hold true irrespective of the exchange and correlation approximation or the basis set used.

First, the use of SC pseudopotentials does not significantly affect the predicted surface geometry. Variations with respect to the all-electron results of less than 0.02 Å are observed. The surface energies are 0.1 J m⁻² lower than the all-electron (AE) case for both the relaxed and unrelaxed surfaces with the relaxation energy in excellent agreement with the AE results. Second, the results of calculations using LC pseudopotentials are in generally poor agreement with the AE results. Variation in the $[010]$ displacement of the surface oxygen ion is at least 0.05 Å. The predicted surface energy is as much as 1 J m⁻² higher than the AE results and the relaxation energies are no longer reproduced reliably.

The reason for the poor performance of the LC pseudopotential approximation lies in the importance of an accurate description of the variation in the semicore Ti $3s$ and $3p$ orbitals at the surface. In the SC approximation these are treated as valence electrons but in the LC approximation are incorporated in the core pseudopotential. The Mulliken populations of Ti ions in the bulk crystal and at the unrelaxed and relaxed (100) surface are presented in Table IV. The populations for core orbitals ($1s$ and $2s+2p$) of ions at the surface are the same as those in the bulk. However, the population of the semicore $3s$ and $3p$ orbitals do change at the surface by $0.03|e|$. It seems likely that the polarization of the $3s$ and $3p$ orbitals on the Ti site, which is neglected in the LC pseudopotential approximation, is responsible for the discrepancy in bulk and surface structures with the work of Lindan *et al.*¹² We note that such polarization of semicore orbitals can be taken into account using nonlinear core corrections.⁴¹ The effects of the LC pseudopotential do not explain the remaining discrepancy in surface structures with respect to the work of Ramamoorthy *et al.*²⁴ as these authors used a SC pseudopotential.

The thickness of the slab model used to study the surface can also be a significant approximation. In order to investigate this, full relaxations of the surface geometry for slabs containing 12 and 15 atomic layers were performed using the TVAE basis set within the HF approximation. The resultant variation in surface geometry is presented in Fig. 4. The surface relaxation is converged to better than 0.03 Å for slabs of nine layers. The slabs relaxed using LDA and GGA show similar behavior. The convergence of the surface energy with respect to slab thickness is presented in Fig. 5. For unrelaxed slabs the surface energy is converged to better than 0.01 J m⁻² at a thickness of nine layers. For relaxed slabs the surface energy is slower to converge. The nine layer slab is converged, with respect to the 15-layer slab, to 0.05 J m⁻² for HF theory and 0.1 J m⁻² for LDA and GGA.

It is interesting to see how the charge distribution within the slabs varies with respect to the slab thickness. In Table V the Mulliken charge populations of the surface and central layers are presented. As the slab thickness is increased, the

TABLE IV. The Mulliken population analysis of the charge distribution at the surface Ti ion at the relaxed and unrelaxed (100) surface compared to that of Ti in the bulk crystal.

System	1s	2s+2p	3s+3p	4s+4p	5s+5p	3d
Bulk	2.00	8.05	2.70	4.37	1.12	.94
100 unrelaxed	2.00	8.05	2.67	4.37	1.16	1.04
100 relaxed	2.00	8.05	2.67	4.36	1.17	1.10

FIG. 4. The effect of slab thickness on the displacements of the surface ions ($\text{\AA}$) along the $[100]$ direction (upper panel) and $[010]$ direction (lower panel) computed within the HF approximation. Atomic labels refer to Fig. 1.

charges on the ions at the surface relative to the bulk converge to $0.25|e|$ and $-0.20|e|$ for the O and Ti ions, respectively whereas the ions at the center become bulklike. At a thickness of nine layers, the charge distribution is almost converged. Whilst the charge of the central ions differs from that of the bulk by up to $0.03|e|$, it must be noted that this difference is spread over all the valence shells and is a much less significant effect than the polarization of the Ti $3p$ orbital discussed previously. There is some oscillatory behav-

FIG. 5. The effect of slab thickness on the relaxed and unrelaxed surface formation energy (J m^{-2}) computed within the HF approximation.

TABLE V. The effect of increasing slab thickness on the charge transfer at the center and surface of the slab.

No. of layers	Ionic charge relative to bulk $\text{TiO}_2(e)$			
	Central O	Central Ti	Surface O	Surface Ti
3	0.11	-0.22	0.11	-0.22
6	0.00	-0.23	0.23	-0.23
9	0.02	-0.03	0.24	-0.19
12	0.00	-0.03	0.25	-0.20
15	-0.01	-0.00	0.25	-0.20

ior in the Mulliken populations between odd- and even-layered slabs, due to the packing of the layers, which mirrors the trends seen for the surface energy. With respect to surface geometry, formation energy, and charge transfer the nine-layer slab is well converged for the purposes of the present study.

The finite sampling of k space is also an important approximation. The calculations described above used a Pack-Monkhorst grid with nine k points in the irreducible Brillouin zone. Calculations based on a grid with four k points yielded insignificant variations in the bulk lattice constants, and variations in the surface relaxation of no more than $0.01 \text{ \AA}$.

Finally, the effects of truncating the direct space summations of the Coulomb and exchange series were evaluated. Computing the energy of the nine-layer slab using very high numerical tolerances ($10^{-8}, 10^{-8}, 10^{-8}, 10^{-8}$, and 10^{-16} as described in Sec. II) with the TVAE** basis set we find absolute energy differences of order 1 mHa for HF theory and 0.1 mHa for the LDA and GGA. The computed surface energies vary by 0.03 J m^{-2} for HF and 0.01 J m^{-2} for LDA and GGA. The slightly greater sensitivity of the HF surface energies is to be expected as the nonlocal exact exchange interaction is rather long ranged. No significant differences in the surface geometry were obtained.

It is apparent that the discrepancy with previous PW-LDA calculations cannot be attributed to any numerical approximations in the current work. We note that a recent study of the detailed behavior of the pseudopotential approximation in PW-GGA calculations on TiO_2 concluded that predicted geometries and energies varied significantly with the choice of the local component in the pseudopotential.⁴² A closer examination of these approximations in surface studies may be of value.

V. CONCLUSIONS

We have performed a detailed investigation of the effects of the various approximations that are commonly used when performing *ab initio* calculations on surfaces in the context of the TiO_2 (100) surface. We find that different treatments of electron exchange and correlation have a small influence on the surface geometry. There are larger effects on the surface formation energy with HF and LDA predictions in close agreement but somewhat higher (by 30%) than the GGA result. We expect that similar trends will be observed in other oxides.

The calculations are demonstrated to be fully converged with respect to k space sampling, slab thickness and the numerical tolerances controlling the summations of the direct

space Coulomb and exchange series.

Surface structures are insensitive to the local basis set if sets of at least double valence quality are used. The computed surface energy is more sensitive to basis set and requires the use of polarization functions on both cation and anion for convergence to within 0.1 J m^{-2} .

The bulk structure is in excellent agreement with PW-LDA calculations, which used small core pseudopotentials.²⁴ Predicted surface energies at the LDA level are also in excellent agreement with the PW-LDA calculations based on the pseudopotential approximation. The surface structure is in qualitatively good agreement with the previous calculations but with a significant quantitative difference in the predicted relaxation of the surface oxygen layer. A detailed examination of the pseudopotential approximation indicates that treatment of the titanium $3s$ and $3p$ orbitals as core states without using nonlinear core corrections is an unacceptable approximation if accurate geometries and surface energies are required.

Although we can understand the discrepancy in bulk and

surface structure with previous work based on large core pseudopotentials¹² the quantitative difference in surface structure with small core PW-LDA calculations²⁴ is unresolved. Our studies point to the need for a investigation into the approximations made when performing pseudopotential PW-LDA calculations on oxide surfaces.

We anticipate that surface x-ray diffraction will be used to determine the surface structure in the near future and the results compared to the predictions of the current work.

ACKNOWLEDGMENTS

J.M. would like to thank the EPSRC for support under Grant No. 95563789. The calculations were performed on a 16-processor IBM SP2 computer and a Silicon Graphics Indigo-2 workstation. The authors would like to thank P.J.D. Lindan for useful discussions. The DL-Visualize software (Ref. 43) was used to produce three-dimensional images of surface structures.

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