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Ab initio calculations of electronic structure of anatase TiO_2*

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This paper presents the results of the self-consistent calculations on the electronic structure of anatase phase of TiO_2. The calculations were performed using the full potential-linearized augmented plane wave method (FP-LAPW) in the framework of the density functional theory (DFT) with the generalized gradient approximation (GGA). The fully optimized structure, obtained by minimizing the total energy and atomic forces, is in good agreement with experiment. We also calculated the band structure and the density of states. In particular, the calculated band structure prefers an indirect transition between valence and conduction bands of anatase TiO_2, which may be helpful for clarifying the ambiguity in other theoretical works.

Keywords: DFT, FP-LAPW, anatase, TiO_2, electronic properties
PACC: 7115A, 7115M, 7125P, 6170T

1. Introduction

There has been an increasing interest in the study of titanium dioxide (TiO_2) for many years. Accurate experimental data and comprehensive theoretical studies are still desirable in view of the potential applications of the system in a considerably wide range.[1] Anatase is a TiO_2 polymorph which is less stable than rutile, but more efficient than rutile for several applications, such as chemical catalysis, photocatalysis, and, especially, dye-sensitized solar cells.[2] In the last decades many theoretical studies on TiO_2 have been performed, using methods such as pseudopotential Hartree–Fock (PHF), the orthogonalized linear-combination of atomic-orbitals (OLCAO), the full-potential linearized augmented plane-wave (FP-LAPW), etc.[3−16] Most of them, however, were carried out on the rutile phase, or the results still remain somewhat ambiguous. For example, there is significant disagreement in the band structures given by those works.

This paper presents the *ab initio* calculations of TiO_2 in the anatase structure using FP-LAPW method. The results include the fully-optimized ground-state structure obtained with total energy and atomic forces, band structure, charge densities and densities of states, which are more reliable and in better agreement with experimental data than early works. The article is organized as follows: the computing model systems and methods are described in Section 2, the results are reported and discussed in Section 3, a short section of conclusions closes the paper.

2. Calculation models and methods

Anatase is one of the two most common and widely used polymorphs of TiO_2. Its structure can be described in terms of chains of TiO_6 octahedra. In the anatase structure each octahedron is in contact with eight neighbours (four sharing an edge and four sharing a corner).[17] The conventional unit cell of TiO_2 in the anatase structure is shown in Fig.1. The space group of anatase is $(I4_1/amd)$, and the local symmetry is D_{2d}. The structure is defined by three crystallographic parameters: two lattice parameters, a, c, and the internal parameter, $u = d_{ap}/c$, where d_{ap} is the apical Ti–O bond length.[8]

The atomic configuration of titanium is [Ar] $3d^2$, $4s^2$ while that for oxygen is [He] $2s^2$, $2p^4$. In many cases it is desirable to distinguish between the three types of electronic states, namely, core, semi-core and

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valence states. In our work we treat the Ti 1s, 2s and 2p states together with the O 1s as core states. The semi-core states are Ti 3s, 3p and O 2s. This leaves the Ti 3d, 4s and O 2p as valence states.

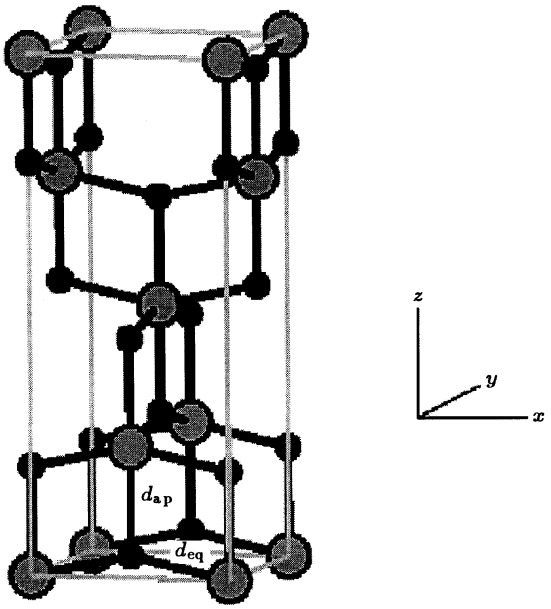


Fig.1. The conventional unit cell of anatase TiO_2. Dark gray and black balls correspond to titanium and oxygen atoms, respectively.

The FP-LAPW method that we employ treats all electrons and has no shape approximations for the potential and charge density.[18] The implementation of the FP-LAPW method includes total energy[19] and atomic-force calculations,[20] which allow structure optimization.[21] The optimized structure of anatase for a set of V and c/a was decided when the total energy was minimized and the force on each atom was smaller than 1mRy/au. The calculations were carried out by means of FP-LAPW method within the scope of density-functional theory (DFT).[22−24] In this method, the unit cell is divided into two regions: non-overlapping atomic spheres with radii and an interstitial region. Taking the structure optimization into account, the atomic sphere radii adopted for Ti and O were 0.095nm and 0.085nm, respectively. We took for the parameter $RK_{\max}$ the value of 7. The basis sets consist of 2367 LAPW functions. We also introduced local orbitals (LO) to include Ti 3s, 3p and O 2s orbitals. Integration in the reciprocal space was performed by the tetrahedron method taking 99 k-points in the irreducible Brillouin zone (IBZ). The calculation was carried out self-consistently and stopped by the force convergence criterion of 1mRy/au. All results in this work were obtained under these conditions.

3. Results and discussion

To calculate the optimized structure of anatase TiO_2, we take the following steps:

(i) Volume optimization: begin with the experimental ratio of c/a, calculate the total energy as the function of the unit cell volume, and obtain the lattice parameters corresponding to the lowest energy.

(ii) Geometry minimization: upon the structure obtained above, perform movements of the atomic positions according to the calculated forces. The iteration was stopped when the force on each atom was smaller than 0.5 mRy/au, and repeat step (i).

(iii) c/a optimization: on the basis of (i) and (ii), calculate the total energy with various ratios of c/a, and find the optimized structure corresponding to the lowest energy.

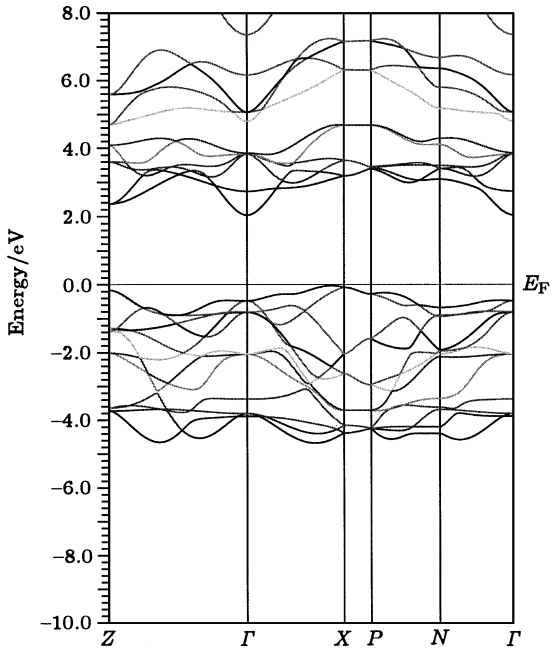


Fig.2. Band structure of the anatase TiO_2 with the optimized structure as described in text obtained using GGA-96. The top of the valence band is taken as the zero of energy.

In Table 1, we present our calculated optimized structure and compare it with experiments and other theoretical results. In general, the agreement of the calculated structures with experiment is good. In particular, our results are in better agreement with experiment for d_{eq}, c/a, u and 2θ than other theoretical outcomes. With the optimized structure, we investigated the band structure of the anatase TiO_2 using GGA-96.[25] The calculated band structure along the high-symmetry direction of the BZ is presented

in Fig.2. The origin of the energy scale is set at the Fermi level. The band structure is similar to that of rutile and is very flat as expected for a mostly ionic compound. The present calculations is found to be similar to that of the B3LYP calculations,[15] while that of the TM calculations[1] is not consistent with ours in the range of Z to Γ. It is noteworthy that the previous theoretical calculations reported in literature educed different conclusions with respect to the type of the transition. In general, the calculated band gap of the B3LYP[15] was indirect, while that of the LDA[8] was direct. In the LDA calculations, Asahi *et al* obtained direct transition when the optimized structure was used, while for the system with the experimental lattice parameters, the indirect band gap was found. They believed, therefore, that whether the band gap is direct or indirect is sensitive to the crystal configuration.[8] In the OLCAO calculations, the band gap for anatase is indirect with a value of 2.04eV, but the energy at Γ is only 0.18eV lower than the top of the valence band (VB). So Mo *et al* regarded anatase as a direct-gap insulator.[16] Compared with the above conclusions, we obtained indirect band gap of the anatase TiO_2 whenever the experimental lattice parameters or the optimized structure was used. With the optimized structure, our calculation yields in the anatase an indirect transition of 2.13eV from the top of the VB near X to the conduction band (CB) at Γ. The calculated results on the band structure for the anatase TiO_2 and the comparison with experimental or other theoretical results are summarized in Table 2. It can be seen that there is an improvement in the band gap with the GGA than that with the LDA, but the improvement is not obvious, due to the well-known shortcoming of the LDA [28] and the GGA.[29]

Table 1. Optimized structural parameters for anatase TiO_2 compared to experiments and other theoretical results. The Exp.1a [26] is obtained at 295K, while the Exp.1b [26] is at 15K (Exp. is the abbreviation for Experiment). The italic values are derived from the experimental data.

	a/0.1nm	c/0.1nm	d_{ap}/0.1nm	d_{eq}/0.1nm	c/a	u	$2\theta/(^\circ)$
This work	3.823	9.612	1.995	1.954	2.514	0.208	155.92
LDA[8]	3.692	9.471	1.948	1.893	2.566	0.206	154.40
PHF[7]	3.763	9.851	1.995	1.939	2.618	0.202	152.10
B3LYP[15]	3.7923	9.8240	*1.9972*	*1.9509*	2.590	0.2033	*152.80*
TM[1]	3.744	9.497	*1.967*	*1.916*	2.536	0.2071	*155.44*
Exp.1a[26]	3.78479(3)	9.51237(12)	1.9799(5)	1.9338(1)	2.51332	0.2081	156.23(3)
Exp.1b[26]	3.78216(3)	9.50226(12)	1.9788(4)	1.9322(1)	2.51239	0.2082	156.30(2)
Exp.2[27]	3.7842(13)	9.5146(15)	1.9797(23)	1.9338(5)	2.5143	0.2081	156.24

To identify the contributions from various orbitals we also calculated the total and partial densities of states (DOS), as shown in Fig.3. The lower VB located 17.85eV below the CB minimum, which are mainly composed by O 2s character, and have a width of 1.77eV, compared with the OLCAO [16] result of 1.76eV. The upper states of VB correspond mainly to the O 2p orbitals and have a contribution from Ti 3d orbitals, and have a width of 4.71eV, which agrees with the XPS [31] result of 4.70 ± 0.05eV excellently, in comparison with 5.05eV from LDA, [8] 5.15eV from B3LYP [15] and 5.17eV from OLCAO.[16] The conduction bands below 7.33eV consist mainly of Ti 3d states with a smaller contribution from O 2p states, which show two distinct structures, below and above 4.75eV.

In the Fig.4, we present the 3D and 2D plots of electron densities of the TiO_2 anatase perfect crystal in different lattice planes, which are very illustrative and useful for analyzing the electron distribution and bond characters.

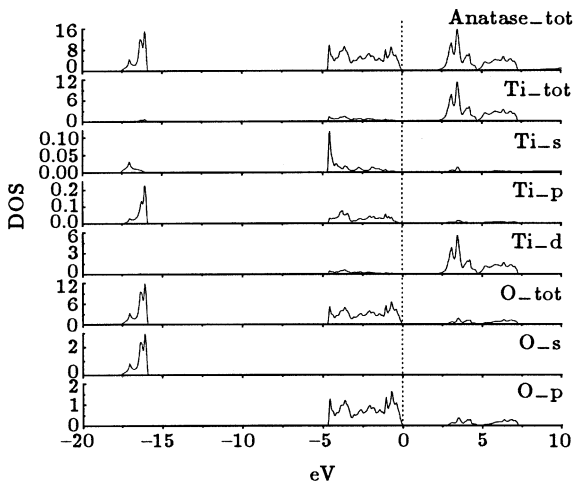
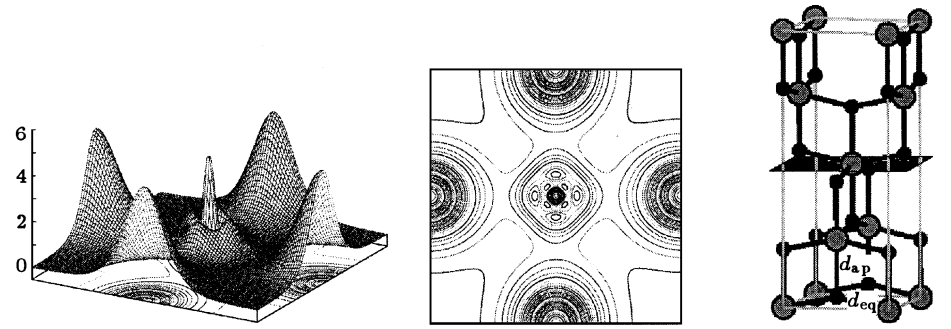
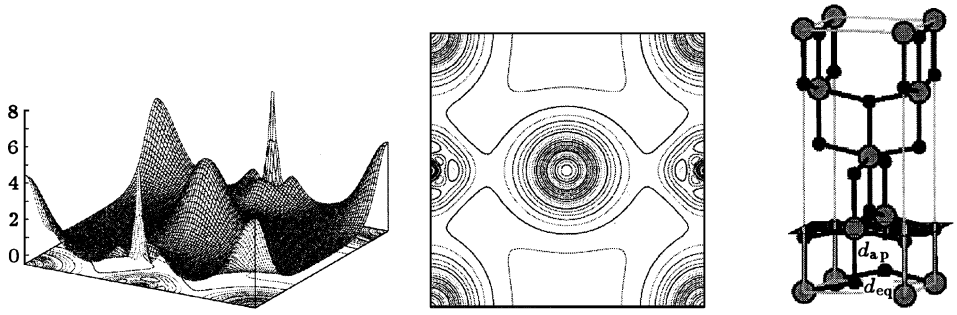


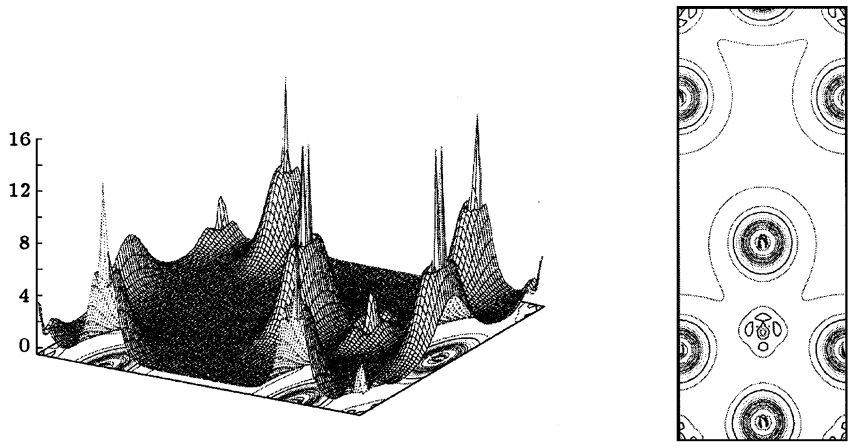
Fig.3. Total and projected DOS for the anatase TiO_2 perfect crystal. The origin of the energy scale is taken at the Fermi level, as the vertical dotted line indicates.



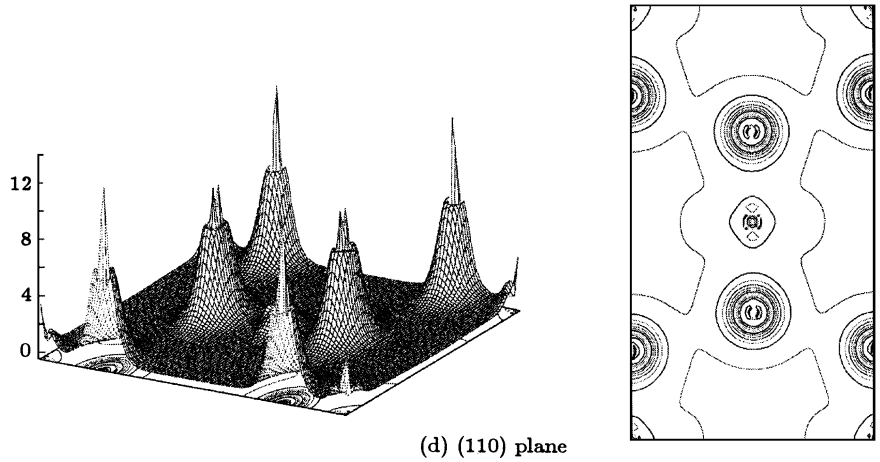
(a) (002) plane



(b) (004) plane



(c) (010) plane



(d) (110) plane

Fig.4. 3D and 2D plots of electron densities of anatase TiO_2.

Table 2. Comparison of the band gap and band width (in eV) of anatase TiO_2. D: Direct gap. ID: Indirect gap.

	This work	Experiment	LDA[8]	OLCAO[16]	B3LYP[15]
Band gap	2.13(ID)	3.2[a]	2.0(D)	2.04(ID)	3.7(ID)
				2.22(D)	4.0(D)
Upper VB width	4.71	4.70 ± 0.05[b]	5.05	5.17	5.15
O_{2s} band width	1.77			1.76	
Gap between O_{2s} bands					
and Minimum of CB	17.85			17.88	

[a]Reference[30], [b]Reference[31].

4. Conclusion

We have presented an *ab initio* study of the electronic structure of anatase TiO_2 using the highly precise FP-LAPW with the exchange-correlation functional of GGA.

The work can be summarized as follows:

(i) The fully optimized structure was obtained by minimization of the energy and atomic forces. Very good agreement with experiment for the d_{eq}, c/a, u and Ti-O-Ti angle demonstrates the high accuracy of our approach.

(ii) With the optimized structure, a number of important electronic parameters such as band-width, band gap with indirect transition of 2.13eV, density of states and electron density have been obtained. The width of upper states of VB is in excellent agreement with XPS results. There is also an improvement in the band gap width with the GGA than that with the LDA, but the improvement is not obvious.

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