Theoretical analysis of the structures of titanium dioxide crystals

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This paper presents results of pseudopotential Hartree-Fock calculations on the titanium dioxide crystals. The optimized structures are in good agreement with experimental data. Both anatase and rutile structures have a large ionic character. The distortions from the undistorted crystals made of regular octahedra are discussed and qualitative trends for the distortions are justified by semiempirical calculations (extended Hückel theory). When correlation is taken into account, a large part of the binding energy is recovered and the rutile structure is found to be more stable than the anatase one.

I. INTRODUCTION

Titanium dioxide has been the subject of considerable interest. Many experimental[1-15] and theoretical[16-22] studies have been performed. Using extended Hückel tight-binding calculations (EHT),[23] Burdett studied the electronic structure of anatase and rutile.[6,16] The most stable crystal structures are rutile ($P4_2/mmm$ space group) and anatase ($I4_1/amd$ space group). Rutile structure is more stable than anatase structure by 1.2–2.8 kcal mol^{-1}.[24,25] This paper presents a qualitative analysis of both structures and explains the importance of the distortions relative to regular crystal lattices, made of undistorted octahedra. It shows that the main difference between the stability of the two phases is the angular distortion. Anatase is less dense and also found to be less stable. Next, this paper presents results of pseudopotential periodic Hartree-Fock calculations on the anatase structure and compares them with results on the rutile structure already calculated by one of us[22] (Table I).

II. THE TiO$_2$ STRUCTURES

Formally, the TiO$_2$ oxides are made of d^0 titanium ions ($+IV$) at the center of octahedra of six O^{2-} ions. Each oxygen atom has three titanium neighbors and therefore belongs to three different octahedra. The two structures differ by the distortion inside each octahedron and by their assemblage.

The rutile structure is defined by three crystallographic parameters, the two lattice parameters a, c, and the oxygen fractional coordinate u. Alternatively, three parameters can be chosen, as shown in Fig. 1: the Ti-O bond lengths, d_{ap} and d_{eq}, and one angle. The local symmetry is D_{2h}. There are two apical and four equatorial oxygen

atoms. The OTi$_3$ pattern has a planar Y shape. Let us call 2θ the smallest Ti-O-Ti angle (the smallest O-Ti-O angle which concerns two equatorial Ti-O bonds is $\alpha = \pi - 2\theta$). The neighboring octahedra share opposite edges in the equatorial plane. Extending this pattern plane leads to a linear chain. Conversion from our parameters to the crystallographic ones are the following:

$$a = \sqrt{2}(d_{ap} + d_{eq}\cos\theta) = 4.593 \text{ Å} ,$$

$$c = 2d_{eq}\sin\theta = 2.959 \text{ Å} ,$$

$$u = \frac{d_{ap}}{2(d_{ap} + d_{eq}\cos\theta)} = 0.305 .$$

The cell volume (2 TiO$_2$ units) is

$$V = a^2c = 4(d_{ap} + d_{eq}\cos\theta)^2 d_{eq}\sin\theta .$$

In the undistorted structure, the θ angle is 45° and $d_{ap} = d_{eq}$ so that locally the building block around the titanium atom is a regular octahedron.

Similarly, for the anatase structure, we can define three parameters (Fig. 2): the two Ti-O bond lengths and the angle 2θ (the largest Ti-O-Ti angle; the smallest O-Ti-O angle which concerns one apical and one equatorial Ti-O bond is $\alpha = \theta$). The local symmetry is D_{2d}. There are two apical and four equatorial oxygen atoms. The OTi$_3$

TABLE I. Enthalpies and entropies of TiO$_2$ (Ref. 24).

298.15 K (25 °C)	Rutile	Anatase
ΔH_f^0 (kcal mol^{-1})	225.8	224.6
ΔG_f^0 (kcal mol^{-1})	212.6	211.4
S^0 (cal/deg mol)	12.03	11.93

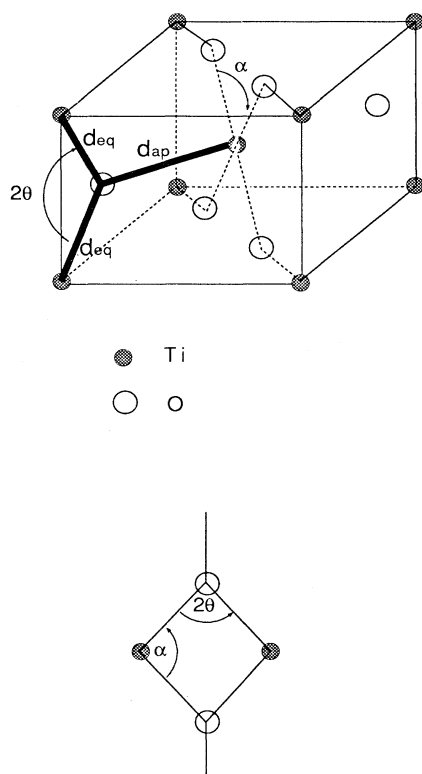FIG. 1. Definition of parameters in rutile structure.

FIG. 2. Definition of parameters in anatase structure.

pattern has a planar T shape. The neighboring octahedra share adjacent edges. Extending this pattern leads to a zigzag chain with a screw axis. Conversion from our parameters to the crystallographic ones are the following:

$$a = 2d_{eq}\sin\theta = 3.784 \text{ Å} ,$$

$$c = 4(d_{ap} + d_{eq}\cos\theta) = 9.515 \text{ Å} ,$$

$$u = \frac{d_{ap}}{4(d_{ap} + d_{eq}\cos\theta)} = 0.208 .$$

The unit-cell volume (which contains two TiO_2 units; half of the quadratic cell) is

$$V = \frac{a^2 c}{2} = 8(d_{ap} + d_{eq}\cos\theta)d_{eq}^2\sin^2\theta .$$

In the undistorted structure, the θ angle is 90° and $d_{ap} = d_{eq}$ so that locally the octahedra are not distorted (Table II).

III. THE ANGULAR DISTORTION

A. The volume expansion

Assuming $d_{ap} = d_{eq} = d$ (where d is the average Ti-O distance in the observed structures, $d = 1.95$ Å) allows us to study the angular distortion. The crystal cohesion arises from the Ti-O bonds. Keeping the d value constant and increasing the crystal volume mainly minimizes
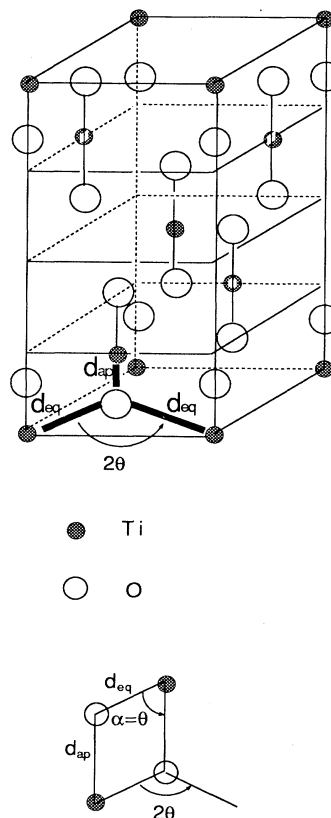
the repulsion between "unbounded atoms," the Coulomb repulsion between the oxygen ions. Hence, the search for the largest volume within these constraints should lead to the most stable geometry. Previously O'Keeffe[26] had the general statement that the ionic solids adopted, under such a constraint, the structure with the maximum volume.

For the rutile structure, the cell volume may be simplified as $V = 8d^3(1+\cos\theta)^2\sin\theta$, which has a maximum value for $2\theta = 96.52°$, a value which is very close to the experimental value 98.88°. The cell volume is $8.282d^3$.

For the anatase structure, the cell volume may be simplified as $V = 4d^3(1+\cos\theta)\sin^2\theta$, which has a maximum value for $2\theta = 140.2°$, a value which is again close to the experimental value 156°. The cell volume is $9.481d^3$.

TABLE II. The experimental (Refs. 2 and 3) structural parameters.

	Rutile	Anatase
Equatorial Ti-O bond	1.947 Å	1.934 Å
Apical Ti-O bond	1.982 Å	1.980 Å
O-Ti-O $= \alpha$	81.12°	78.10°
Ti-O-Ti $= 2\theta$	98.88°	156.20°
Volume (Å^3)	62.420	68.154

With these assumptions, the anatase volume is larger than the rutile volume by a factor 1.145 (experimental 1.092). This agreement contrasts with the value 0.97 calculated for the undistorted structures; the anatase structure has the smallest volume ($8d^3$ vs $8.242d^3$).

The search for the maximum volume leads to angular distortions that are close to the experimental values. In the next subsection, we will examine whether or not the Coulomb repulsion is the driving force for that volume expansion.

It is tempting to try similar arguments to check whether the difference between the axial and the equatorial distance is also reproduced, assuming for instance the average Ti-O distance as a frozen parameter. Changing the bond length of each Ti-O bond from the optimal value implies a destabilization which requires the expression of some energetic terms. Pure geometrical arguments therefore cannot do well.

B. The Coulomb repulsion

In the two structures, the O-Ti-O angle α (Figs. 1 and 2) between the two bridging oxygen ligands is smaller than 90°. The different explanations for this reduction are a repulsion between the titanium atoms, a repulsion between the oxygen atoms, and a compromise between the hybridization around each atom.

Referring to the undistorted structure (with regular octahedra), the square Ti-O-Ti-O formed by two titanium atoms and two bridging ligands becomes a rhombus with a long Ti-Ti diagonal and a short O-O diagonal. Therefore, the first explanation for the angular distortion would be a decrease of the repulsions between the titanium atoms; however, this is not the driving force. Indeed, EHT calculations predict the correct distortion despite the lack of any electrostatic repulsion between positive charges (empty orbitals). The only repulsions result from the population of crystal orbitals with a Ti-Ti out-of-phase contribution. The resulting overlap population is found to be small because (i) all the occupied orbitals have small coefficients on the titanium atoms, (ii) not all of them are Ti-Ti out of phase, (iii) the overlap between titanium atoms is small. Calculated Ti-Ti overlap populations using the CRYSTAL program[27,28] are negligible (-0.002).

Repulsions between the oxygen atoms are important. The overlap population from the CRYSTAL calculation is -0.017. The O_{eq}-O_{eq} distance (the shortest one) is 2.532 Å in rutile, which is a short distance for two oxygen atoms. Burdett[16] has shown that the repulsion between oxygens raised quickly below 2.8 Å, faster than the usual $1/r$ repulsion.

At first sight, the repulsion between the two oxygen bridging ligands would lead to an increase in the α angle and therefore cannot explain the experimental angular distortion that is opposite. A variation of that angle does not affect the distance between the two bridging oxygen atoms only; it also affects all the other oxygen-oxygen distances and could increase their repulsions. Taking into account all the first O-O nearest neighbors, however, again leads to the same conclusion. A decrease of the α

angle brings closer the equatorial bridging ligands but moves away the other pairs of equatorial ligands; the resulting averaged O_{eq}-O_{eq} distance is $d_{eq}[\sin(\alpha/2)+\cos(\alpha/2)]/2$, which is maximum for $\alpha = 90°$ (the undistorted crystal). Neither the O_{ap}-O_{eq} distance ($d\sqrt{2}$) nor the distance between second neighbors ($2d$) changes with the α angle.

In conclusion, repulsion between oxygen atoms cannot explain the decrease of the α angle. A decrease of the α angle increases the cell volume without noticeable lengthening of the O-O distances. It has consequently no immediate effect on the Coulomb repulsion. The maximization of the cell volume does not significantly decrease the repulsion between the oxygen atoms.

C. The hybridization

The consideration of regular octahedra fixes the 2θ value for the Ti-O-Ti angle at 90° and 180° in the rutile and anatase structures, respectively. Such a point of view privileges the environment around the titanium atom. Let us now consider the local symmetry around the oxygen atoms. OTi_3 pattern has a Y shape in rutile and a T shape in anatase. Optimal coordination would lead to three equivalent 120° angles for the trigonal planar system (Burdett[16] has shown that the planarity was imposed by the π conjugation). In the rutile structure, 2θ is increased from 90° to 98.88°, while in anatase 2θ is decreased from 180° to 156.16°. In both cases, this angle gets closer to 120°. The α angle is not independent and is reduced in both cases. The angular distortion therefore results from a compromise between the optimal coordination modes for the titanium and the oxygen atoms. The increase of volume follows; it is not due to the Coulomb repulsion.

IV. THE LONG d_{ap} AND SHORT d_{eq} DISTANCES

Distances are a compromise between the Ti-O bonding which would be increased by shrinking the structure and O-O repulsion which prevent that. The overlap populations reveal the Ti-O bonding term. EHT is not good for the distance optimizations; it underestimates the repulsions. The optimization of the Ti($+IV$)-O^{2-} distance would nearly collapse and that of the O^{2-}-O^{2-} optimization requires the use of diffuse Slater exponents. However, EHT greatly helps us to analyze the factors that influence the geometry. Let us try the two following cluster models that focus on the coordination of each atom. It will be shown that the difference between the Ti-O bond lengths mostly results from the minimization of the repulsion between oxygen atoms.

A. The OTi_3^{10+} model

The OTi_3^{10+} model, which represents the oxygen coordination, is the simplest cluster that contains the apical and the equatorial distances. As mentioned by Burdett,[6,16] the consideration of the Ti-O EHT overlap populations of the OTi_3^{10+} model for rutile structure ($2\theta < 120°$) leads to the wrong prediction whereas similar

arguments for the anatase structure $(2\theta > 120°)$ lead to the correct prediction. If we fix the titanium atoms and move the oxygen atom along the C_2 axis of the cluster, energy is won for the motion which shortens the equatorial bonds and elongates the apical bond for the rutile model, a correct prediction. Unfortunately, the result is incorrect on the anatase model. The main reason is that these motions involve implicit angular distortions which are the dominant factors.

B. The TiO$_6^{8-}$ octahedron model

In the rutile structure in each octahedron, there are four O_{eq}-O_{eq} distances vs eight O_{ap}-O_{eq}. Clearly enlarging d_{ap} and reducing d_{eq} leads to a decrease in eight repulsions while only four are increased. In Fig. 3 we report the result of EHT calculations for the TiO$_6^{8-}$ octahedron. To be sure to take into account the O-O repulsion, a diffuse Slater exponent has been given to the oxygen orbitals $(\xi = 1.9)$. This allows us to optimize the Ti-O distance in the ideal octahedron. The result is 1.876 Å. Next we vary the distance assuming that the crystal volume remains constant as in an undistorted rutile with $d = 1.876$ Å,

$$d_{eq}\left[d_{ap} + \frac{d_{eq}}{\sqrt{2}}\right]^2 = 19.24 \text{ Å}^3 .$$

Results of the calculations are shown for Ti-O distances larger than 1.8 Å from $(d_{ap} = 1.8$ Å, $d_{eq} = 1.925$ Å) to $(d_{ap} = 2$ Å, $d_{eq} = 1.8$ Å). In this region the energy decreases from the symmetric situation to an optimum $(d_{ap} = 1.965$ Å, $d_{eq} = 1.82$ Å). This clearly shows that *the difference between the Ti-O bonds is due to a reduction of the oxygen-oxygen repulsions*. Similarly, for the model of the anatase structure, the volume constraint $d_{ap}d_{eq}^2 = 6.6$ Å^3 leads to a stabilization of 0.04 eV for $d_{ap} = 2.0$ Å and $d_{eq} = 1.817$ Å.
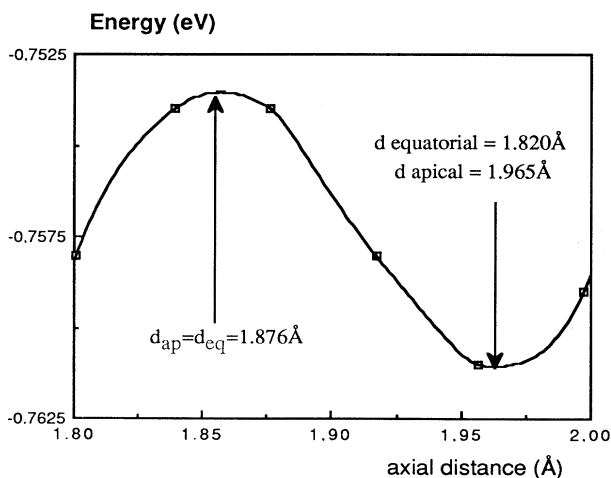

FIG. 3. EHT optimization of Ti-O distance in ideal octahedron TiO$_6^{8-}$.

V. THE EHT RESULTS

Many calculations have been performed assuming $d_{ap} = d_{eq} = 1.95$ Å, clusters such as the sequence of three octahedra Ti$_3$O$_{14}^{16-}$ and chains. Each time, one geometry is close to that of rutile and the other to that of anatase. The number of atoms and the number of Ti-O bonds are equivalent in both structures. In the undistorted structures $(2\theta = 90°)$, the difference in energy between the two structures is very small and not significant. The differences are increased when the angle 2θ is optimized and the rutile structure is then found to be more stable than the anatase structure. For the Ti$_3$O$_{14}^{16-}$ cluster it increases from -0.0065 (a minus sign means that anatase structure is more stable than the rutile one) to 0.18 eV; for the chain, from 0.035 to 0.078 eV. These differences in energies per TiO$_2$ are, respectively, 1.38 kcal mol^{-1} for the cluster and 0.9 kcal mol^{-1} for the chain. The published experimental values are between 1.2 (Ref. 24) and 2.8 (Ref. 25) kcal mol^{-1} per TiO$_2$.

The sequence of the octahedra (linear or zigzag) does not induce important changes in energies. As far as octahedra are regular, the permutation of the ligands is not really important. This also concerns the sequence of octahedra. On the contrary, the angular distortion has drastic consequences on the energies. As it is related to the hybridization of the oxygen atoms, it requires for the cluster calculations that the model is taken large enough to include oxygen atoms with at least two ligands. For the cluster and the chain, the calculated 2θ angles are, respectively, 95.73° and 98.67° for the rutile structure and 172.06° and 164.37° for the anatase structure. The undistorted bulk structure of rutile is much more stable than that of anatase (by 0.308 eV; 7.11 kcal mol^{-1} per TiO$_2$). The main reason seems to be the difference between the repulsion between the oxygen atoms. In the anatase structure, each oxygen atom has 12 neighbors at $d\sqrt{2}$ whereas in the rutile structure, their are only 11 neighbors at the same distance. The Madelung constants for the two structures are very close.[29] This difference is reduced to 0.137 eV (3.17 kcal mol^{-1}) when the angle is optimized which leads to a value closer to experiment. As often, provided that the parametrization remains reasonable, the EHT method which is supposed to emphasize a qualitative comparison between topologically different structures also leads to reasonable quantitative energy differences. The calculated 2θ angle is 93.33° for the rutile structure and 165.74° for the anatase structure. These values imply that the deviation from the undistorted structure is more pronounced for the anatase than for the rutile structure: the change is double for the reduction of the α angle (7.13° vs 3.33°); it is considerable for the cell volume increase (10.68% vs 0.37%). The increase of the volume mostly stabilizes the anatase structure and reduces the energy difference between the two structures.

VI. THE PSEUDOPOTENTIAL HARTREE-FOCK RESULTS

Recently, the rutile structure has been calculated[22] by using the CRYSTAL program. The optimized structure

was in good agreement with experiment. In this section, we present the results of the calculation for the anatase structure and the influence of the correlation on the energies for the two structures.

A. Structure optimization

The optimized structure has been calculated by minimizing the unit-cell energy with respect to the internal coordinates previously defined. The geometric parameters are given in Table III. The overall agreement with experimental data is very good: the accuracy on bond lengths and the bond angles is better than 0.02 Å and 2°, respectively. These results are consistent with both experience on molecular calculations and with the results previously obtained on the rutile modification by the same technique.[22] They constitute a noticeable improvement with respect to the best previous set of calculations[18] with the modified electron-gas theory which works within the electron-gas approximation and assumes a purely ionic description of the oxide.

B. Binding energy

The total energy per TiO_2 at the optimized structure, 34.895 04 a.u., is larger than that reported for the rutile phase, 34.894 09 a.u. The small difference, 0.6 kcal mol^{-1} per TiO_2, is spuriously in favor of the anatase structure. We checked that this difference remained by varying the basis sets or improving the number of k points or the various thresholds determining the cutoff of the Coulomb and exchange expansions. Results are only inverted when correlation is taken into account. Correlation effects are more important on the rutile structure which is denser than the anatase one. The rutile structure is found more stable by, respectively, 2.75 and 0.7 kcal mol^{-1} per TiO_2 when the Perdew[30] and Colle-Salvetti[31] correlation density functionals are used in a post-SCF (self-consistent field) step. For both functionals the relative stability of anatase with respect to rutile is in correct agreement with experiment.

The "experimental" binding energy of TiO_2 can be roughly estimated from the standard heat of formation and from the heats of atomization,[24] neglecting zero-point motion and specific-heat contributions, one finds 449.58 kcal mol^{-1} (per TiO_2) for rutile. The Hartree-Fock binding energy, 207.53 kcal mol^{-1}, accounts for

TABLE III. CRYSTAL calculated and experimental (Ref. 3) structural parameters for anatase.

	Calculated	Experimental
d_{eq} (Å)	1.9388	1.9338
d_{ap} (Å)	1.9946	1.9797
θ	76.03	78.08
a (Å)	3.763	3.784
c (Å)	9.851	9.515
u	0.202	0.208
c/a	2.618	2.515
V (Å^3) per 4TiO$_2$	139.48	136.24

TABLE IV. CRYSTAL correlation energy per TiO_2, charges and overlap populations.

	Anatase	Rutile
HF energy	−34.895 04	−34.894 09
Perdew	−35.523 26	−35.527 64
Colle-Salvetti	−35.454 52	−35.455 62
Net charge on O	−1.305	−1.302
Net charge on Ti	+2.610	+2.604
Overlap Pop., apical	0.085	0.080
Overlap Pop., equatorial	0.090	0.096

only 46% of the experimental one. The large difference, 242.04 kcal mol^{-1}, has been interpreted as an effect of the change of the correlation energy between a neutral oxygen atom and O^{2-}. The Perdew and Colle-Salvetti functionals yield correlation contributions of 226.51 and 183.22 kcal mol^{-1}, respectively. In both cases the calculated and experimental binding energies are very close and at least 87% of the experimental binding energy is recovered.

C. Population analysis and electron density

The Mulliken net charges and overlap populations quoted in Table IV are very close in the two structures. The total valence electron density along the two unequivalent Ti-O bonds and in a cutting plane in which they are contained are displayed in Figs. 4–6. The density around the oxygen centers is almost spherical with bulges in the cation directions. In contrast, around the Ti cations the density is very anisotropic: the 0.75 e^- Å^{-3} isoline presents four maxima pointing to-
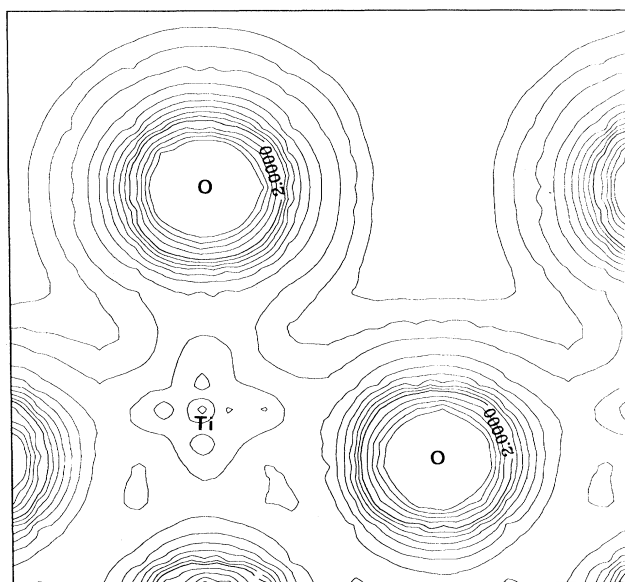

FIG. 4. Total valence electron density along the two unequivalent Ti-O bonds.
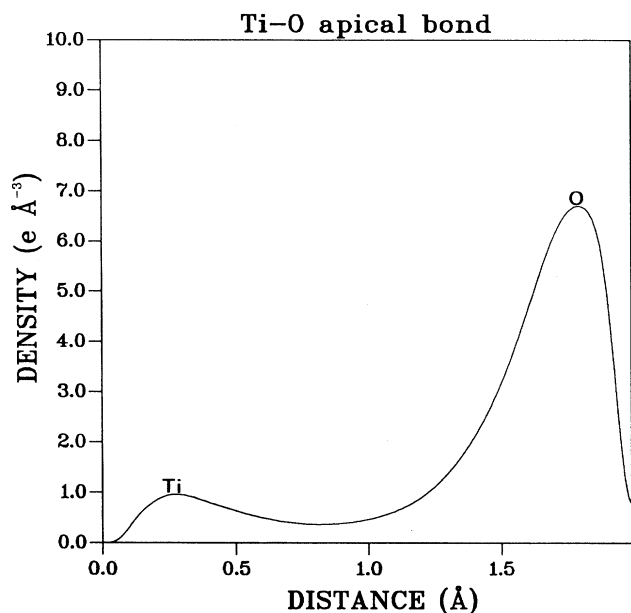
Ti—O apical bond

FIG. 5. Density curve along the apical Ti-O bond.

wards the oxygens which indicate a partial covalent character of the bonds. The density curves along the apical and equatorial Ti-O bonds are very similar and they both present maxima near the O centers. These curves provide of an upper bound to the electron density around the Ti atoms which can be used to estimate upper bounds of the atomic effective electron charge. These curves can be
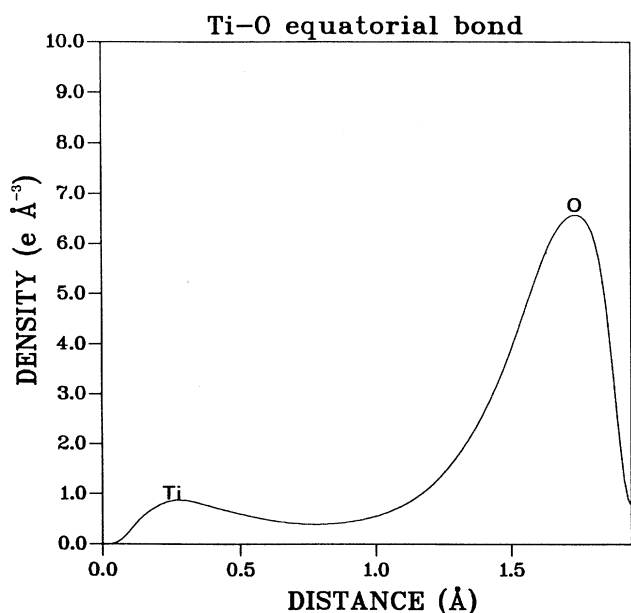
Ti—O equatorial bond

FIG. 6. Density curve along the equatorial TiO bond.

used to perform an approximate Bader analysis of the charge density[32] in which we assume spherical densities around the Ti centers, in order to get a realistic upper bound to the titanium net charge. The result of this analysis shows that $1.05e^-$ corresponds to an ionicity of 75%, which is larger than that one can derive from the Mulliken population analysis.

D. Band structure and density of states

The band structure along the high-symmetry lines of the Brillouin zone is presented in Fig. 7. The topmost states of the valence band correspond to the oxygen $2p$ states, whereas the lowest states are essentially due to the $2s$ oxygen orbitals. The topology of the band structure is very similar to that of rutile and is very flat as expected for a mostly ionic compound. The band gap between the top of the valence and conduction band is of the order of 10 eV and therefore anatase is calculated to be an insulator. For titanium dioxide, the experimental gap is about 3.0–3.5 eV.[33] It is well known that Hartree-Fock calculations overestimate this quantity. In fact the variational calculation is performed for the ground state, the unoccupied bands correspond to orbitals which have not been subjected to optimization, the only requirement being that they must be orthogonal to the occupied ones. Moreover, a straightforward vertical excitation neglects Coulomb and exchange contributions which account for the change in the interelectronic repulsion upon excitation and which, in the case of molecular calculations, lower the excitation energies.

The total and projected density of states are presented in Fig. 8. It confirms the assignment of the band structure made in the previous paragraph. In addition, it indicates a noticeable contribution of the titanium $3d$ orbitals to both $2s$ and $2p$ oxygen bonding states which is another proof of the partial covalent character of the Ti-O bonds. The density of states of the rutile and anatase modifications of TiO_2 are very similar.
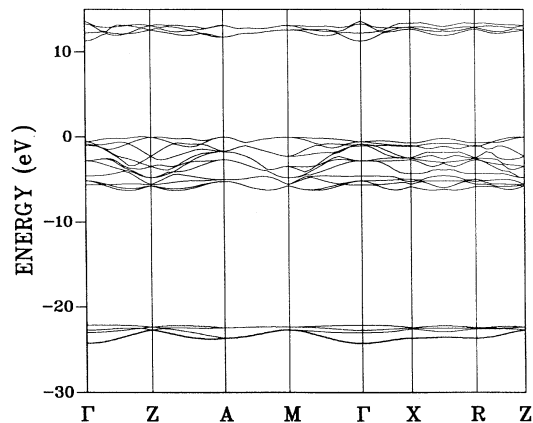

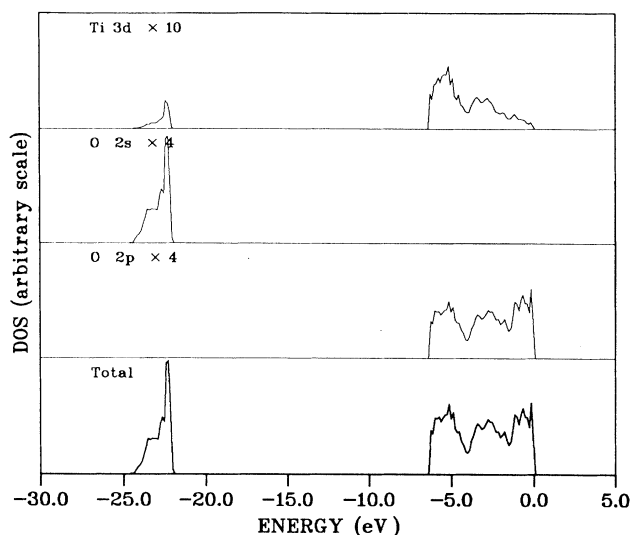FIG. 7. Band structure of anatase. The origin of the energy scale is taken at the Fermi level.

FIG. 8. Total and projected density of states. The origin of the energy scale is taken at the Fermi level.

VII. PARAMETERS AND BASIS SETS USED

A. CRYSTAL calculation

The basis sets for the CRYSTAL calculation are the same as in Ref. 22. A PS-31G basis set is used for the oxygen atom.[34] As the $4s$ atomic orbitals are not populated, a smaller basis set is used for the titanium atom. It consists of the d functions contracted to a (4/1) basis set and a single $4sp$ shell with an exponent of 0.484 for polariza-

tion purposes. Results are not affected by this reduction. Similarly, the pseudopotentials are those from Durand-Barthelat.[35]

B. The EHT method and parameters

In the EHT calculations[23] the periodic system is defined by a set of valence orbitals contained in a unit cell and by three translation vectors. These atomic orbitals are described by Slater wave functions. Parameters are taken from Ref. 16. Then, one can form a set of Bloch sums. The crystal orbitals are linear combinations of the Bloch sums. The variational theorem leads to a generation of the secular determinant $|H_{\mu v}(k) - e(k)S_{\mu v}(k)|$ where the interaction element, $H_{\mu v}(k)$ and the overlap integrals $S_{\mu v}(k)$ are defined in terms of Bloch sums. $e(k)$ is the energy associated with a crystal orbital for a given k point. In the EHT theory, the $H_{\mu v}(k)$ are derived from the $S_{\mu v}(k)$ terms and from the atomic energy levels $H_{\mu\mu}$ and H_{vv} given in Ref. 16. In the section concerning the difference between d_{ap} and d_{eq} the Slater exponent for the oxygen atom has been modified to 1.9.

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