A DFT study about the effects of exchange-correlation functional on the structural and electronic properties of Anatase

I A González Ramírez¹, L A Alcalá Varilla², and J A Montoya³

¹ Departamento de Química, Universidad de Córdoba, Montería, Colombia
² Departamento de Física y Electrónica, Universidad de Córdoba, Montería, Colombia
³ Grupo de Modelado Computacional, Universidad de Cartagena, Cartagena, Colombia

E-mail: ismhaelgi19@gmail.com

Abstract. A comparative study is presented, based on Density Functional Theory, of the influence that the different approximations of the exchange-correlation functional have on the structural and electronic properties of titanium dioxide in the anatase phase. In this work, the method of plane waves and pseudopotentials, as implemented in the Quantum Espresso package was used. The approximations to the correlation-exchange functional that were considered are the local density approximation, the generalized gradient approximation in the form of Perdew-Burke-Ernzerhof, the Perdew-Burke-Ernzerhof for solids, and the Perdew-Wang 91. For each case, the effects due to the inclusion of spin (spin polarization), and the correction of Hubbard (U=4.2 eV for Ti) were also studied. We found that the Perdew-Burke-Ernzerhof for solids functional offers the best results for the calculation of the lattice parameters and bond lengths, followed by the local density approximation with the Hubbard correction included. For the bond angles, the best description was obtained with the local density approximation. The inclusion of the U term increases the errors associated with the mentioned structural parameters when the following functionals are used: Perdew-Burke-Ernzerhof, Perdew-Burke-Ernzerhof for solids and Perdew-Wang 91. The Perdew-Burke-Ernzerhof and Perdew-Wang 91 functionals show the largest errors when the Hubbard correction is used; while the local density approximation shows significant improvement when the Hubbard correction is included. Regarding the energy gap, we found that the introduction of the U term improves the estimation of this property for all the approximations included in this work.

1. Introduction

Applications of titanium dioxide in catalysis, photocatalysis, and photoelectrochemistry [1–4], have cataloged it as one of the most promising materials in recent years. TiO₂ has had an impact also at an industrial level; due to its low cost, high stability and non-toxicity. TiO₂ presents polymorphism; therefore, we can find it in nature mainly in three crystalline phases: rutile, anatase and brookite; of the three polymorphs, the rutile and anatase phases are the most stable and have been widely studied and synthesized [5–12]; instead, the information of the brookite phase is limited due to its rarity and limited possibilities of preparation. The anatase phase has gained greater interest due to its high photoreactivity [13], for that reason, it is used in heterogeneous and homogeneous catalysis [14,15], for the degradation of organic and inorganic contaminants.
The information related to the theoretical study of TiO$_2$ in the anatase phase is wide; however these studies show very variable results [12, 16–20]; mainly because the exchange-correlation functionals are not exact and the scientists recur to approximations in order to describe them.

In this paper, we are interested in doing a comparative study about the effects that the exchange-correlation functional has over both structural and electronic properties of anatase bulk, using first-principles calculations. The results presented here include fully optimized structures.

2. Computational methods
The calculations were carried out employing the PWscf code included in the Quantum-Espresso package [21] and are based on density functional theory (DFT). The exchange-correlation functional effects were studied using: the local density approximation (LDA) [22], the generalized gradient approximation (GGA) of Perdew-Burke-Emzerhof (PBE) [23], Perdew-Burke-Emzerhof for solids (PBEsol) [24] and Perdew-Wang 91 (PW91) [25]. Due to the strong correlation of the 3d orbitals in the transition metals, the Hubbard correction (DFT+U) [26] was included with a value of $U=4.2$ eV for titanium, which is typically used in other studies about anatase [16]. The ion-electron interactions were described by Vanderbilt ultra-soft pseudopotentials [27] with valence states Ti (3d, 4s) and O (2p, 2s).

The optimization of the titanium dioxide bulk in the anatase phase was obtained as is described in [16]; convergence studies of cutoff kinetic energy were performed for the wave functions and k-points, where a kinetic energy of 45 Ry was established for the cutoff, and we determined a 4x4x2 k-point mesh by method of Monkhorst and Pack [28] in the first Brillouin zone. On the other hand, the cutoff energy for the real-space charge density was taken equal to ten times the kinetic energy cutoff, i.e., 450 Ry [16]. After the optimization of the anatase bulk, the grid of k-points was increased to 8x8x4 in order to calculate the density of states, and this was done for each one of the approximations used in this work.

3. Results and discussion
3.1. Structural properties
Figure 1(a) shows the unit cell of the titanium dioxide in the anatase phase, and the structural parameters measured. As it is observed there, the configuration of the titanium dioxide in this phase can be defined by four parameters: two lengths of bond Ti-O$_z$ and Ti-O$_{x,y}$, an angle of bond 2$\theta$ formed by Ti-O-Ti and another smaller $\gamma$ composed by O-Ti-O; also the (a and c) lattice parameters are observed from Figure 1(a).

Table 1 summarizes the results obtained in this work, compared with the experimental values in [29, 30] and others theoretical results reported in [12, 16–20]. We observe the LDA approach tends to underestimate the experimental values of the (a and c) lattice parameters and the (Ti-O$_2$ and Ti-O$_{x,y}$) atomic distances, in agreement with others DFT studies [12, 18–20], while the PBE and PW91 parameterizations for the generalized gradient approximation (GGA) tend to overestimate these values, in agreement with others DFT studies [12, 16, 18, 20]. On the other hand, the angle 2$\theta$ is underestimated by PBE, PBEsol, PW91 and overestimated by the LDA; while the $\gamma$ bond angle is overestimated by the PBE, PBEsol, PW91 functionals and is underestimated by the LDA, these results are compared in Table 1 with the experimental and theoretical values reported.

The deviation of the results with respect to the experimental values for a, c, Ti-O$_2$ and Ti-O$_{x,y}$, $2\theta$, and $\gamma$ are shown in Table 1. From there, we can observe that the best description of the lattice parameters and atomic distances were obtained with the PBEsol functional in the generalized gradient approximation (GGA). For the $2\theta$ and $\gamma$ bond angles, the best description was obtained with the LDA approximation. On the other hand, when the U term is included we can see an increase in the errors associated with the mentioned parameters for the PBEsol,
PBE, and PW91 functionals; while the LDA+U shows significant improvement with respect to LDA, PBEsol+U, PBE, PBE+U, PW91, and PW91+U, but it is not better than PBEsol.

![Figure 1](image.png)

**Figure 1.** (a) Unit cell of Anatase Bulk, the oxygen atoms are in red, the titanium atoms are in gray and (b) Density of states of Anatase Bulk.

3.2. **Electronic properties**

Figure 1(b) shows the density of states (DOS) and the projections of the orbitals (3d, 4s) and (2s, 2p) of the Ti and O atoms respectively. The Fermi level was arbitrarily chosen as the origin of the energy. The orbitals that contribute mostly to the density of states are the atomic orbitals Ti (3d) and O (2p), with the 2p orbital being the main contribution to the valence band, while for the conduction band the 3d atomic orbital of titanium atom has a more significant contribution.

The analysis of the density of states of the different approximations used in this work is also shown in Table 1, from there, it is observed that the results of the band gap are very close to each other, approximately 2.1 eV for the LDA, PBE, PBEsol and PW91 approximations, which are in agreement with previous studies reported in [12, 16, 17, 19, 20]. It is also seen that the inclusion of the term of Hubbard (U=4.2 eV for the Ti), significantly improves the band gap, thus giving an approximate value of 2.5 eV for the LDA+U, PBE+U, PBEsol+U and PW91+U approximations; but due to the failures of the DFT and DFT+U to describe the exchange-correlation functional, these results are still far from the experimental value $E_g = 3.23$ eV [30]. Finally, the inclusion of the spin did not have a significant influence on the structural and electronic properties, measured with the different approximations, which was to be expected because the titanium dioxide is a non-magnetic material.
Table 1. Lattice parameters, interatomic distances, and bandgap energy observed and calculated for TiO\textsubscript{2} bulk in the anatase phase by different levels of approximations.

| ExCF     | \(a\) (Å) | \(c\) (Å) | Ti-O\(_{x,y}\) (Å) | Ti-O\(_z\) (Å) | \(\theta\) (°) | \(\gamma\) (°) | Gap (eV) |
|----------|-----------|-----------|-----------------|----------------|----------------|----------------|----------|
| Exp [29,30] |           |           |                 |                |                |                |          |
| PBE      | 3.784     | 9.515     | 1.934           | 1.980          | 156.200        | 101.800        | 3.230    |
| PBEsol   | 3.771     | 9.533     | 1.928           | 1.982          | 155.985        | 102.007        | 3.212    |
| SP-PBE   | 3.800     | 9.636     | 1.945           | 1.993          | 155.281        | 102.360        | 2.905    |
| PBEsol+U | 3.834     | 9.759     | 1.964           | 2.011          | 154.803        | 102.599        | 2.471    |
| SP-PBE+U | 3.834     | 9.759     | 1.964           | 2.011          | 154.803        | 102.599        | 2.471    |
| PW91     | 3.819     | 9.612     | 1.950           | 2.003          | 156.200        | 101.800        | 2.905    |
| SP-PW91  | 3.821     | 9.712     | 1.972           | 2.000          | 155.535        | 102.341        | 2.471    |
| SP-PW91+U| 3.800     | 9.641     | 1.972           | 2.000          | 155.535        | 102.341        | 2.471    |
| LDA      | 3.743     | 9.426     | 1.912           | 1.967          | 156.461        | 101.769        | 2.096    |
| SP-LDA   | 3.743     | 9.426     | 1.912           | 1.967          | 156.461        | 101.769        | 2.096    |
| LDA+U    | 3.769     | 9.519     | 1.928           | 1.977          | 155.854        | 102.073        | 2.438    |
| SP-LDA+U | 3.769     | 9.508     | 1.927           | 1.975          | 155.941        | 102.073        | 2.438    |
| 2016 [16] |           |           |                 |                |                |                |          |
| SP-PP-PBE | 3.874     | 9.626     | 1.996           | 1.935          | 155.384        | 102.341        | 2.471    |
| PBE-GGA  | 3.798     | 9.852     | 1.948           | 2.013          | 154.234        | 102.073        | 2.179    |
| HF-LCAO  | 3.771     | 9.688     | 1.937           | 1.976          | 153.20         | ---            | 12.17    |
| LDA-LCAO | 3.735     | 9.580     | 1.914           | 1.973          | 153.50         | ---            | 2.33     |
| LDA-PW91 | 3.786     | 9.867     | 1.946           | 2.006          | 155.941        | 102.073        | 2.36     |
| 2013 [12] |           |           |                 |                |                |                |          |
| PBE-GGA  | 3.798     | 9.852     | 1.948           | 2.013          | 154.234        | 102.073        | 2.179    |
| B3LYP-LCAO | 3.783    | 9.905     | 1.945           | 2.000          | 153.21         | ---            | 3.98     |
| LDA-LCAO | 3.748     | 9.495     | 1.916           | 1.974          | 155.91         | ---            | 1.96     |
| 2007 [18] |           |           |                 |                |                |                |          |
| PBE-LCAO | 3.802     | 9.774     | 1.948           | 2.008          | 154.79         | 102.073        | 2.08     |
| LDA-PAW  | 3.748     | 9.495     | 1.916           | 1.974          | 155.91         | ---            | 1.96     |
| 2004 [19] |           |           |                 |                |                |                |          |
| FP-LAPW  | 3.823     | 9.612     | 1.954           | 1.995          | 155.92         | 102.073        | 2.13     |
| 2000 [20] |           |           |                 |                |                |                |          |
| LDA-FLAPW | 3.782    | 1.563     | 1.979           | 1.979          | 155.92         | 102.073        | 2.00     |

This work (0.407%) (1.606%) (0.548%) (1.035%) (-0.564%) (0.531%) (-33.690%)
4. Conclusions
We conducted a comparative study using first principles (DFT) to determine the effects of the exchange-correlation functional on the structural and electronic properties of Anatase. We found that, among the different functionals used in this work, the PBEsol functional provides the best results for the calculation of lattice parameters and bond lengths, followed by the LDA+U and PBEsol+U. The PBE+U and PW91+U functionals give the highest errors in the structural parameters. For the $2\theta$ and $\gamma$ bond angles, the best description was obtained with the LDA approximation.

The term of Hubbard significantly improves the band gap for all functionals but increases the errors associated with the values of lattice parameters, lengths, and bond angles; except for LDA+U which gives proper structural parameters. The results for the band gaps when the U term is included are very similar to each other, approximately 2.5 eV, that is in good agreement with other DFT studies reported in the literature. In general, the inclusion of electronic spin did not have a significant impact on the results.

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