Comparative study of the effect of the exchange-correlation functional on the structural and electronic properties of rutile

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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 rutile phase. In this work, the method of plane waves and pseudopotentials, as implemented in the Quantum Espresso package was used. The approximations to the exchange-correlation 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 Perdew-Burke-Ernzerhof and Perdew-Wang 91. For the bond angles, the best description was obtained with the Perdew-Burke-Ernzerhof and Perdew-Wang 91 approximations. The density analysis of states showed that the functional PW91 and PBE, better describe the band gap compared with the functional PBEsol and LDA when the Hubbard correction it is not been included, however, when this is included all the functional show the same deviation with respect to the experimental value (E\text{gap} = 3.0 eV). With and without the Hubbard correction (U = 4.2), all functionals underestimate the band gap.

1. Introduction

Due to the environmental deterioration caused by the pollution of the environment, scientists have increased their interest in semiconductor materials [1, 2], which can be used in the remediation of water and air, in addition to the generation of clean energy. Titanium dioxide (TiO\textsubscript{2}) has proven to be an ideal material, due to its many applications, such as chemical catalysis, photocatalysis, and, especially, dye-sensitized solar cells [2-6]. The dioxide of titanio phases (TiO\textsubscript{2}) found in nature are: rutile, anatase and brookite, the rutile and anatase phases are the most stable and have been widely studied and synthesized [5-12]. However, due to its large band gap, ∼ 3.0 –3.2 eV (for rutile and anatase phases respectively), titanium dioxide lacks sensitivity to visible light which is necessary for high performance under solar illumination [7]. Titanium dioxide has different polymorphs, industrially the most common and used are anatase and rutile. The rutile phase is the most stable and used in dye-sensitized solar cells due to...
its lower band gap with respect to anatase, and is the most studied phase. Many theoretical studies on titanium dioxide in rutile phase have been carried out using first principles density functional theory (DFT), however, these studies show very variable results [7–12], because we humans have been unable to find the exact form of the exchange-correlation functional; and this is why scientists resort to the use of approximations to describe it. In this paper, we present a comparative study about the effects that the exchange-correlation functional have over both structural and electronic properties of rutile bulk, using first-principles calculations.

2. Computational methods

For the study of the structural and electronic properties of the titanium dioxide bulk in the rutile phase, the structures were optimized by calculations of first principles DFT, using the PWscf (Plane-Wave Self-Consistent Field) code included in the Quantum-Espresso package [13]. The effects of exchange-correlation were described by following approximations: the local density approximation (LDA) [14], the generalized gradient approximation (GGA) of Perdew-Burke-Emzerhof (PBE) [15], Perdew-Burke-Emzerhof for solids (PBEsol) [16] and Perdew-Wang 91 (PW91) [17]. Electron-ion interactions were described by Vanderbilt ultra-soft pseudopotentials [18], with valence electrons Ti (3d, 4s) and O (2p, 2s) explicitly included in the calculations. The Hubbard correction [19] was included due to the strong correlation of the 3d orbitals of the titanium atom, (U = 4.2 for Ti), as Araujo.et.al described in [20], and a kinetic cutoff energy of 45 Ry was established for the wave functions. The integration reciprocal-space, in the cases of structural optimization, was performed by sampling the Brillouin zone with a 3x3x6 k-point mesh by method of Monkhorst and Pack [21]. After the structural optimization of the titanium dioxide bulk in rutile phase for each functionals, the grid of k-points was increased to 6x6x12 in order to calculate the density of states.

3. Results and discussion

3.1. Structural properties

The rutile phase has a tetragonal geometry as shown in Figure 1(a), which is determined by the measurement of three fundamental parameters: the lattice parameters a and c, the $d_{ax}$ and $d_{eq}$ bond distances and two bond angles ($2\theta$ and $\alpha$); $2\theta$ higher than $\alpha$, the results of these measurements for each functional are shown in Table 1 with their respective error percentages.

![Figure 1](image-url)

Figure 1. (a) Unit cell of rutile bulk, the oxygen atoms are in red, the titanium atoms are in gray and (b) density of states of rutile bulk.
Table 1. Lattice parameters, interatomic distances, and band gap energy observed and calculated for TiO$_2$ bulk in the rutile phase by different levels of approximations.

| Ref.  | ExCF   | $a$ (Å) | $c$ (Å) | $d_{eq}$ (Å) | $d_{ax}$ (Å) | $2\theta$ (°) | $\gamma$ (°) | Gap (eV) |
|-------|--------|---------|---------|-------------|-------------|-------------|-------------|---------|
| Exp.  | [23,24] | 4.587   | 2.9541  | 1.9486      | 1.9796      | 98.7900     | 81.2100     | 3.0000  |
| PBEsol|        | 4.585   | 2.943   | 1.955       | 1.972       | 98.391      | 81.509      | 1.800   |
| sp-PBEsol |      | (-0.027%) | (-0.388%) | (0.232%) | (-0.364%) | (-0.404%) | (0.368%) | (-40.00%) |
| PBEsol+U|        | 4.593   | 2.996   | 1.964      | 1.980       | 99.550      | 80.446      | 2.200   |
| sp-PBEsol+U |   | (0.127%) | (1.416%) | (0.790%) | (0.040%) | (0.769%) | (-0.941%) | (-26.667%) |
| PBE   |        | 4.633   | 2.967   | 1.974      | 1.996       | 98.433      | 81.411      | 1.537   |
| sp-PBE |        | 4.630   | 2.967   | 1.9139     | 1.939       | 98.413      | 81.396      | 1.800   |
| sp-PBEsol |     | (-0.090%) | (0.428%) | (1.319%) | (0.849%) | (-0.361%) | (0.248%) | (-36.667%) |
| sp-PBEsol+U |   | (-0.090%) | (0.428%) | (1.555%) | (0.849%) | (-0.382%) | (0.239%) | (-36.667%) |
| PBE+U |        | 4.639   | 3.023   | 1.979      | 1.998       | 99.614      | 80.388      | 2.200   |
| sp-PBE+U |      | (0.127%) | (1.416%) | (0.790%) | (0.051%) | (0.777%) | (-0.959%) | (-26.667%) |
| This work |              | 4.640   | 3.023   | 1.979      | 1.998       | 99.605      | 80.394      | 2.200   |
| PW91  |        | 4.613   | 2.956   | 1.966      | 1.987       | 98.401      | 81.448      | 2.000   |
| sp-PW91 |      | (0.592%) | (0.052%) | (0.908%) | (0.389%) | (-0.394%) | (0.342%) | (-36.667%) |
| PW91+U |        | 4.628   | 3.019   | 1.977      | 1.998       | 99.565      | 80.358      | 2.200   |
| sp-PW91+U |     | (0.893%) | (2.198%) | (1.437%) | (0.919%) | (0.877%) | (-1.049%) | (-26.667%) |
| LDA   |        | 4.547   | 2.922   | 1.941      | 1.953       | 98.348      | 81.556      | 1.700   |
| sp-LDA |      | (-0.669%) | (-1.086%) | (-0.416%) | (-1.339%) | (-0.447%) | (0.426%) | (-43.333%) |
| PW91  |        | 4.614   | 2.956   | 1.970      | 1.988       | 98.389      | 81.529      | 1.900   |
| sp-PW91 |     | (0.592%) | (0.052%) | (1.093%) | (0.399%) | (-0.406%) | (0.393%) | (-36.667%) |
| PW91+U |        | 4.628   | 3.019   | 1.977      | 1.998       | 99.664      | 80.365      | 2.200   |
| sp-PW91+U |     | (0.893%) | (2.198%) | (1.437%) | (0.919%) | (0.866%) | (-1.041%) | (-26.667%) |
| LDA   |        | 4.554   | 2.972   | 1.949      | 1.961       | 99.476      | 80.497      | 2.100   |
| sp-LDA+U |     | (-0.730%) | (0.614%) | (-0.021%) | (-0.940%) | (0.696%) | (-0.878%) | (-30.000%) |
| 2017  | [8]    | 4.565   | 2.926   | 1.937      | 1.959       | 98.110      | 81.880      | 1.562   |
| LDA   |        | 4.565   | 2.926   | 1.937      | 1.959       | 98.110      | 81.880      | 1.562   |
| PBE   |        | 4.648   | 2.967   | 1.963      | 2.001       | 98.200      | 81.810      | 1.537   |
| PW91  |        | 4.643   | 2.967   | 1.962      | 1.999       | 98.230      | 81.770      | 1.532   |
| sp-PW91 |     | (1.228%) | (0.438%) | (0.688%) | (0.980%) | (0.437%) | (0.478%) | (-43.333%) |
| TPSS  |        | 4.682   | 2.981   | 1.972      | 2.020       | 98.210      | 81.780      | 1.578   |
| RTPSS |        | 4.624   | 2.961   | 1.957      | 1.989       | 98.250      | 81.750      | ——      |
| 2010  | [11]   | 4.656   | 2.967   | 1.960      | 2.010       | 98.200      | 80.910      | 3.530   |
| PW91  |        | 4.656   | 2.967   | 1.960      | 2.010       | 98.200      | 80.910      | 3.530   |

Acronyms used are: spin polarized (sp), Perdew, Burke y Ernzerhof (PBE), Hubbard term, all values are in eV (U), Revised Perdew-Burke-Ernzerhof functional (RPBE), Becke, three-parameter Lee-Yang-Parr exchange-correlation functional (B3LYP), Perdew Wang exchange and correlation functional (PW91), Hybrid functional (PBE0), Generalized gradient approximation (GGA), Local density approximation (LDA), aproximación de gradiente meta-generalizado (meta-GGA) de Tao-Perdew-Staroverov-Scuseria (TPSS) revised-TPSS (RPBSS). Numbers in parenthesis indicate the percentage of the deviation calculated as $D_{cv} = \left(\frac{V_{cal} - V_{ref}}{V_{ref}}\right) * 100$. 
Table 1, it is observed that the LDA approach tends to underestimate the experimental values of the \((a\) and \(c\)) lattice parameters and the \((d_{ax}\) and \(d_{eq}\)) atomic distances, in accordance with others DFT studies [8,12], while the PBE and PW91 parameterizations for the generalized gradient approximation (GGA) tend to overestimate these values, in agreement with other DFT studies [8,11]. PBEsol functional tends to underestimate the experimental values of the \((a\) and \(c\)) lattice parameters and the \(d_{ax}\) atomic distance, and overestimate \(d_{eq}\) in accord with [8,22].

The 2\(\theta\) angle is underestimated by all the functionals, when the Hubbard correction it is not been included, being the PBE and PW91 the functionals that best describe this parameter, followed by the PBEsol and LDA functionals. The \(\alpha\) angle is overestimated by all the functionals, when the Hubbard correction has not been included, being the PBE and PW91 functionals that best describe this parameter, followed by the PBEsol and LDA functionals.

On the other hand, when the U term is included it can seen 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 PBEsol+U, PBE+U and PW91+U, but it is not better than PBEsol, PW91, PBE and LDA. Generally, in Table 1, it was observed that for the study of structural properties the best description was obtained with the functional PBEsol, followed by the functional PW91.

3.2. Electronic properties

Figure 1(b) shows the density graph of state, where the projections and contributions of the (3d and 4s) orbitals of the titanium atom and the (3p and 2s) orbitals for the oxygen atom, for the Spin-up and Spin-down are observed; this symmetrical contribution for both spin-up and spin-down indicates that the material does not exhibit magnetic properties. The Fermi level was arbitrarily chosen as the origin of the energy. In Figure 1(b), it is shown that the orbitals that most contribute to the valence band are the 3p orbitals of oxygen, followed by the 3d orbitals of titanium, on the other hand, this relationship is reversed in the conduction band, for this case, the 3d orbitals of the titanium atom present a higher contribution, followed by the 3p oxygen orbitals. The results obtained for the state density analysis with the different approximations are shown in Table 1, the associated error percentages; it shows that the PW91 and PBE approximations when the Hubbard correction it is not included, give the lowest error percentages (-33.667%) in both cases, followed by the PBEsol (40%) and LDA (43%) approximations; results that are in concordance with other studies reported in the literature [8, 11, 12]. When the Hubbard correction is included, the value of the gap improves significantly for all the functionals, but compared with experimental value (\(E_{\text{gap}} = 3.0\) eV) [24], 2.2 eV is still very small. In general, the inclusion of electronic spin did not have a significant impact on the results.

4. Conclusions

We carried out a DFT study of the structural and electronic properties of the titanium dioxide bulk in the rutile phase, using different approaches to describe the exchange-correlation functional. In this comparative study, the best description of the structural properties was obtained with the PBEsol functional, followed by the PW91 functional. For the 2\(\theta\) and \(\alpha\) angles, the best description was obtained with the PBE and PW91 approximations. The term of Hubbard significantly improves the band gap for all functionals but increases the errors associated with the values of lattice parameters, bond lengths and bond angles; except for the LDA+U that shows significant improvement with respect to PBEsol+U, PBE+U and PW91+U. The results obtained for the state density analysis with the different approximations show that the PW91 and PBE functionals when the Hubbard correction is not included give the lowest error percentages (-33.667%) in both cases, followed by the PBEsol (40%) and LDA
(43%) approximation. When the Hubbard correction is included, the value of the gap improves significantly for all the functional ones, but with a value of 2.2 eV it is still very small compared with the experimental value ($E_{\text{gap}} = 3.0$ eV ). In general, the inclusion of electronic spin did not have a significant impact on the results.

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