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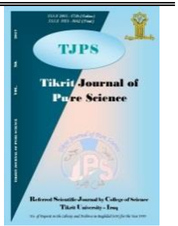

Study of Rutile TiO_2 band structures and optical properties using Density functional theory (DFT)

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ABSTRACT

In this article, a theoretical analysis to measure the band composition, optical properties and density of states (DOS) of rutile titanium dioxide was conducted via the castep simulation program. Calculations of the first principles were carried out using the super cell (1x1x1) process. The first computation of TiO_2 concepts was studied by density functional theory (DFT) with a generalized gradient approximation from Perdew-Wang's 1991 (GGA-PW91), local density approximation (LDA) for exchange-correlation energy functional, and (LDA)+U method, implementation of coulomb interactions btween U_d of (Ti_{3d}) atom and U_p of (O_{2p}) atom.All experimental values are agreed with our results. The results for LDA and GGA-Pw91 indicated weaknesses in the estimation and far from the experimental results for the properties of the TiO_2 rutile under analysis, except for the energy band difference, although the estimation data (LDA) + U was in accordance with the experimental values. The optical properties of rutile TiO_2 was obtained using several methods of exchange correlations, well in accordance with experimental findings and other theoretical evidence.

1. Introduction

TiO_2 is a wide bandgap semiconductor, with three common shapes; Rutile, anatase, and brooket [1] Titanium dioxide TiO_2 is considered one of the important industrial materials, and it has various wide uses such as synthetic fibers and plastics, due to its distinct physical and chemical properties of high chemical and physical stability, non-toxicity and low cost [2]. In addition, it has a strong potential for use as nonlinear optical material [3], in dye-sensitized solar cells [4], gas sensors [5] and complex random access memories [6]. For TiO_2 the most amportant phases are the rutile and anisate structures. Their structural, electrical and optical properties have been experimentally measured using various methods [7-9] and their electronic structures and optical properties have been theoretically studied in the context of powerful density functional-theory (DFT) approaches. [10-12] it is apparent that electronic structures need to be measured specifically since they are the starting point for the first-principle measurement of other physical and chemical properties. However, their energy differences, including that of other semiconductors and insulators, are underestimated by local density approximation (LDA) and generalized gradient approximation (GGA) [13, 14,15] relative to experimental values. Further approximations, for example scissor approximations, are also important in order to adjust differences in order to equate measured results to experimental results. In the other hand, even advanced approaches, such as GW, sometimes overestimate energy gaps [16, 17]. It is however highly desirable or essential to consider the electronic structures and physical properties of TiO_2 and related materials in terms of a nuclear-free, secure DFT approach [18].

2. Theoretical Details

2.1 Density functional theory (DFT)

In comparison to the electronic form of structure based on the wave function, it is understood that the DFT approach is based on the density principle. Owing to its imperfect existence, several improvements were made to this hypothesis. Centered on the approximation of born-oppenheimer and of Hartree-Fock theories [HF] and variational theorems, the DFT-theory was introduced. The Hohenberg-Kuhn scientist theory [HK] [19] which allows for the density of the energy of any electronic device to be expressed:

$$E = E(\rho) \quad .... (1)$$

Where is ρ the electron density.

This approach emerged because of a significant error in the Hartree-Fock system, which in principle ignored the contrary spin effect. Instead of the wave function, the electronic density function is used which transforms from a multi-particle system dilemma into a monopoly system and the number of variables accessing the quantitative equations is diminished. The major purpose of (DFT) calculating the energy association between atoms on the basis of the principles of quantum mechanics [20] in 1927, the fundamental theory (DFT) emerged in the hands of two physicists (Thomas and Fermi) who mostly worked on a mathematical model to estimate the electric distribution of atoms. Through this, the experiment demonstrated the ability to measure the kinetic energy of a device that approximates the electric distribution. Therefore, this model yielded bad results and remained unused until the scientist (Kohn) came along and produced an application for it [21].

2.2 The Local Density Approximation (LDA)

It is considered one of the most commonly used approximations in solid state physics because of the inability of the (kohl-sham) method to provide an unknown function for the relationship of exchange-correlation, and because there is no expression for this concept, several approximations such as LDA have been put in order to solve this problem. The two scientists (kohl-sham) presented this approximation in 1965, according to which this approximation treats the heterogeneous electron system as a locally homogeneous system. The energy correlation equation is given as follows [22].

$$E_{xc}^{LDA}(\rho) = \int \rho(r)\, \varepsilon_{xc}^{LDA}(\rho(r))\, \mathrm{dr}^3 \quad ... (2)$$

Where, ε_{xc}^{LDA} is the XC energy per particle of homogeneous electron gas of density $\rho(r)$.

The exchange-correlation energy is written using the spin theory as

$$E_{xc}^{LSDA}(\rho\uparrow, \rho\downarrow) = \int \rho(r) \varepsilon_{xc}\left(\rho\uparrow(r), \rho\downarrow(r)\right) dr^3 \quad .... (3)$$

Knowing that there are two parts of the energy exchange-correlation

$$\varepsilon_{xc} = \varepsilon_{x(\rho)} + \varepsilon_{c(\rho)} \quad .... (4)$$

Where energy exchange is $\varepsilon_{x(\rho)}$ and the correlation energy is $\varepsilon_{c(\rho)}$

Dirac concluded that the energy density of exchange [23] is $\varepsilon_{x(\rho)}$

Where

$$\varepsilon_{x(\rho)} = \frac{-0.4582}{r_s}\, au \quad ...(5)$$

$$\varepsilon_{c(\rho)} = \frac{-0.44}{r_s + 7.8} \quad .... (6)$$

$$\rho = \left(\frac{4\pi r_s{}^3}{3}\right)^{-1} \quad ... (7)$$

The density, in particular, is expressed in the form of the least quantitative dimension $\boldsymbol{r_s}$ which is the radius of the sphere known as the Wigner-Seitz radius, which is an electron's average orbital.

2.3 The Generalized Gradient Approximation (GGA)

The precision of the LDA effects in the condensed content is reasonable, but it fails in situations where the density is subject to sudden changes as in the particles. The GGA approximation is a correction of the LDA and exceeds it in precision taking into account the density gradations [24, 25] in which the word energy is written in the form

$$E_{xc}^{GGA}(\rho\uparrow(r), \rho\downarrow(r)) = \int f_{xc}^{GGA}(\rho(r) \quad \Delta\rho(r)) \quad dr^3 \quad ....(8)$$

2.4 Hubbard-U scheme

The Hubbard-U method is known to be one of the commonly used methods for the treatment of errors resulting from LDA and GGA measurements, developed by Asimov and others[26] Based on this method the term coulomb repulsion energy was used in the LDA + U method of exchange-correlation [27,28].

$$E_{LDA+U}[\rho(r)] = E_{LDA}[\rho(r)] + E_u[\rho(r)] - E_{cd} \quad ...(9)$$

The first term $E_{LDA}[\rho(r)]$ applies to standard LDA energy, the second term $E_u[\rho(r)]$ reflects energy from Hubbard and the last component E_{cd} is double count correction energy based on Castep's simulation program [29]. There would be a double miscalculation for the related cases owing to Hubbard's additional term; thus, the term "double counting" E_{cd} must be subtracted from the total energy LDA representing electronic interactions using a mean field process.

3. Results and Discussion

In this study, several local approximations have been used, such as GGA-Pw91, LDA, and it is understood that the energy gap is reduced inside these approximations, that the calculation of DFT + U made the value of the energy gap more appropriate compared to others, and what the results showed is proof of that and the explanation is due to U energy. The initial parameters used to design tetragonal rutile TiO_2 geometry are a = b = 4.594 A^0 and c = 2.959 A^0 [30], respectively. For geometry optimization, to achieve a system with minimal total energy. Using the Broyden-Fletcher-Goldfarb-Shenno (BFGS) algorithm, the cutoff energy 400 eV and Monk horst-Pack (MP) grid of size 4x4x3 is used to research the electronic properties of rutile TiO_2; Ultra soft pseudo-potential has been used for several benefits accounts as it is a modified formula for pseudo-potential conservation of Norm. Table.1.tabulates the lattice parameter values determined using LDA, GGA + Pw91 and LDA + U.

Table 1: Band gap Energy and Lattice rutile TiO_2 parameters determined by LDA, GGA-Pw91, LDA+U and compared with experimental parameters [30, 31].

Functional		**a(A°)**	**c(A°)**	**c/a**	**V($A^{\circ 3}$)**	**Band gap E_g(eV)**
Present work	LDA-PZ	4.54319	2.930081	0.645	60.474859	**1.817 eV**
	GGA-Pw91	4.631908	2.973321	0.642	63.791335	**1.826 eV**
	LDA+ U Ud = 8eV , Up =3eV	4.505345	3.049550	0.676	62.010144	**3.297eV**
LDA [32]		4.535	2.9090	0.641		**1.800 eV**
LDA [33]		4.563	2.9140	0.637		**1.7 eV**
GGA-Pw91[34]		.6558	2.9674	0.638		**1.64 eV**
GGA-PBE[35]		4.65	2.9713	0.639		**1.77eV**
LDA+U [36]		4.574	3.004	0.657		**2.58 eV**
Expt [30,31]		4.594	2.959	0.644	62.449	**3.1eV**

The band differences of rutile TiO_2 for LDA-CA-PZ, GGA-Pw91, and LDA+U Are respectively 1.817, 1.826, and 3.297 eV. The value of GGA-Pw91 and LDA is reduced because of the energy of correlation [37]. However, the outcome is the same as for [38].The findings of the LDA + U accounts were consistent with the results of the experimental accounts [31].Table.2 these figures are compatible with experimental and other statistical values with a slight percentage difference. Calculated average bond lengths between titanium (Ti) and oxygen (O) atoms of rutile TiO_2 are reported in Table 2. The lattice parameters from LDA + U results tend to be more compatible with experimental findings[30] than others, which are less than 1 percent error compared to LDA and GGA-Pw91, Different lengths of Ti-O bonds are possible with ranges from 1.93281 to 1.99824 A^0,The experimental Ti – O bonds in the rutile TiO_2 process range from 1.95 to 1.98 A^0 [39]. As opposed to the experimental values, the equilibrium bonds resulting from our measurements are in hasty agreement. The equilibrium Ti – O bonds in rutile TiO_2 recline in the range between 1.94865 and 1.96530 A^0 according to our DFT + U calculations.

Table 2: Interatomic distances and Milliken population of LDA, GGA-Pw91 and LDA+U measured as opposed to experimental rutile TiO_2[39].

functional	**LDA**		**GGA-Pw91**		**LDA+U Ud=8eV , Up=3eV**		**Exp[56]**
band	Length (A°)	population	Length (A°)	population	Length (A°)	population	**Length (A°)**
O4—Ti1	1.93281	0.76	1.95983	0.77	1.96530	0.77	**1.9561**
O3—Ti1	1.93281	0.76	1.95983	0.77	1.96530	0.77	**1.9561**
O1—Ti2	1.93281	0.76	1.95983	0.77	1.96530	0.77	**1.9561**
O2—Ti2	1.93281	0.76	1.95983	0.77	1.96530	0.77	**1.9561**
O1—Ti1	1.95180	0.26	1.99824	0.25	1.94865	0.31	**1.9561**
O4—Ti2	1.95180	0.26	1.99824	0.25	1.94865	0.31	**1.9561**
O3__Ti2	1.95180	0.26	1.99824	0.25	1.94865	0.31	**1.9561**
O2__Ti1	1.95180	0.26	1.99824	0.25	1.94865	0.31	**1.9561**

The determined band configurations of rutile TiO_2 along the BZ rutile symmetry lines are shown in fig.1.The band difference measured by the LDA and GGA is 1,817 and 1,826 eV, respectively as shown in Fig.1.are directly at G and are smaller than the experimental energy gap[31] but similar to other recent calculations[40,41].We have not observed a substantial difference in the structure obtained by implementing the LDA or GGA methods, both of which is less than the reality of the band gap by around 44%, and this is predicted from the LDA and GGA measurements that minimize the experimental energy gap for insulators and semiconductors in general. Estimate in the LDA+U method allows us to better understand the effects of both Up, Ud is consistent with LDA+(Ud+Up) measurements, Where Ud is set to 8 eV and Up is between 3 and 9 eV. The Fermi amount is determined to zero and when we set the values of Up = 3 eV, Ud = 8eV we obtained the results of Erg = 3.297eV in accordance with the experimental findings [31] as seen in Fig.1.

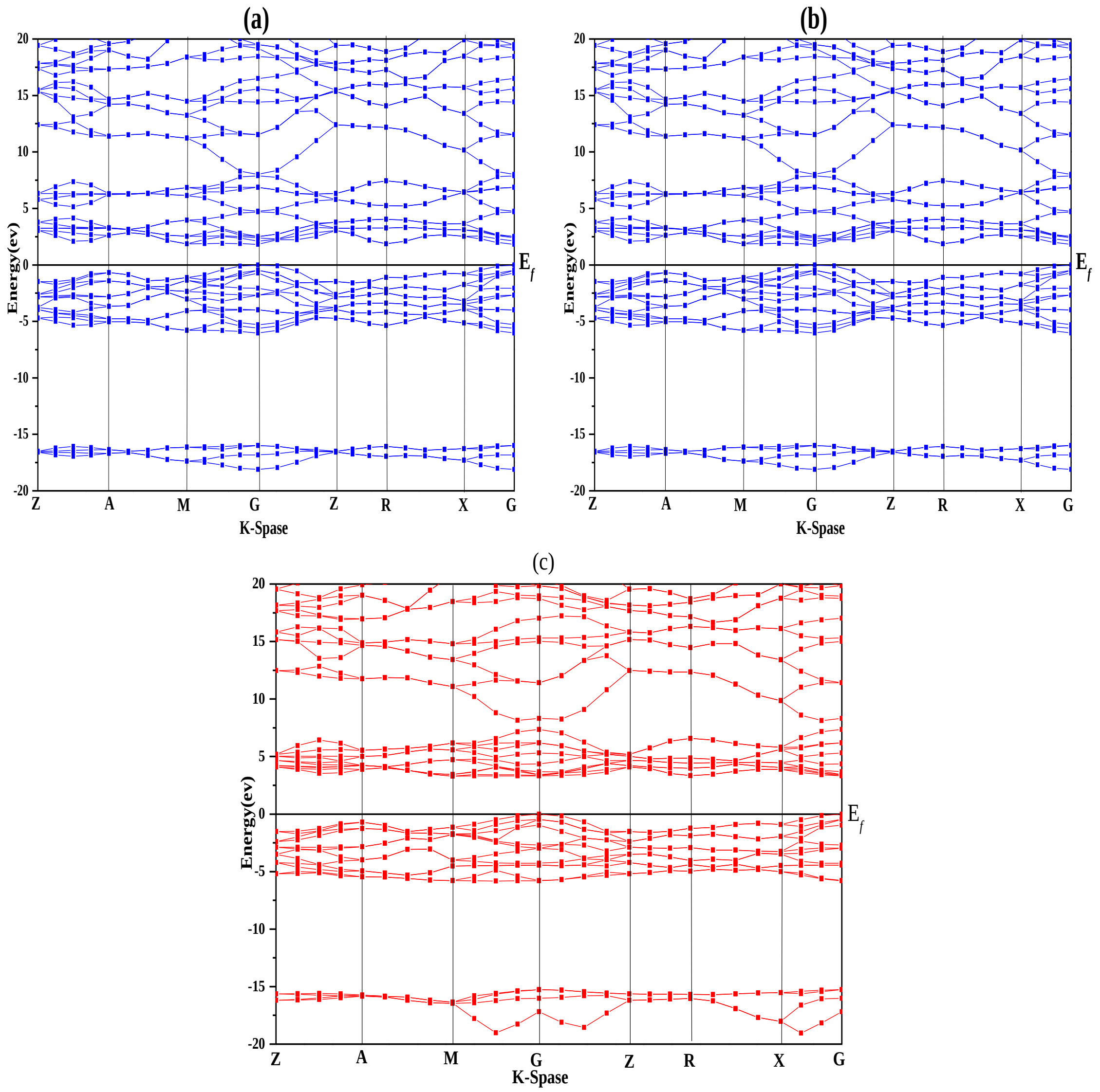

Fig. 1: Structure of the energy band computed by (a) GGA-Pw91 (b) LDA(c) LDA+ (Ud=8eV+Up=3eV).

The PDOS of the TiO_2 rutile is given in Fig.2. (Fermi energy is set at zero energy, (E_f= 0 eV) As we all know, the Valence Band (VB) and the Conduction Band (CB) are both O_{2p}states and Ti_{3d} states in rutileTiO_2. We can see that $3d$ states of Tiadd as much as possible to the CB bottom where the VB edge has the prominent O_{2p} character in the PDOS of pure rutile TiO_2.The PDOS of pure rutile TiO2 in the dicated distribution of electrons should be highly local, but due to the combination between Ti_{3d} and O_{2p} as we can see from the PDOS. The Ti–O bond shows primarily ion bond with some Covalent bond properties. The VB has a bandwidth of 6.0 eV Compatible with the 5.4eV experiment [42].Chart.3. Displays the complete state density (TDOS) and the partial state density (PDOS) obtained for the rutile TiO_2 The Fermi (E_f) amount is 0 eV. By and wide the valence band consists of four major regions, the deep region is mostly originated from the state of O_{2s}, the middle region is mostly derived from the state of Ti_{3p} and the state of O_{2s}, and the shallow region is mostly developed from the state of O_{2p}. The conductor band is governed by the condition of Ti_{3d} .Table 2. Display these areas in more depth, Fig .2. Plays TDOS and PDOS of Rutile TiO_2 using LDA, GGA+Pw91 and LDA+U methods.

Table 3: Contribution of the PDOS to the sum obtained from the Density functional theory of the rutile TiO_2.

Functional	Valence band peak			Conduction band
	Deep region	Middle region	Shallow region	
LDA	-56.4 to – 55.8 eV Mainly originated form Ti_{3s}	-33.1 to -32.1 eV and -18.2 to-15.5 eV Mainly originated from Ti_{3p} ,O_{2s} respectvely	-6.1 to 0 eV Mainly originated from O_{2p}	Dominted by states of $\boldsymbol{Ti_{3d}}$
GGA	-57.55 to -56.2 eV Mainly originated form Ti_{3s}	-33.95 to-32.35 eV and -18.3 to -15.7 eV Mainly originated form Ti_{3p},O_{2s} respectively	-5.9 to 0 eV originated form O_{2p}	Dominted by states of $\boldsymbol{Ti_{3d}}$
LDA+ U(Ti_8 +O_3)	-58.1 to -56.3 eV Mainly originated from Ti_{3s}	-34.25 to-33.5 eV and -19.2 to -14.8 eV Mainly originated form Ti_{3p},O_{2s} respectively	-6 to 0 eV Mainly originated form O_{2p}	Dominted by states of $\boldsymbol{Ti_{3d}}$

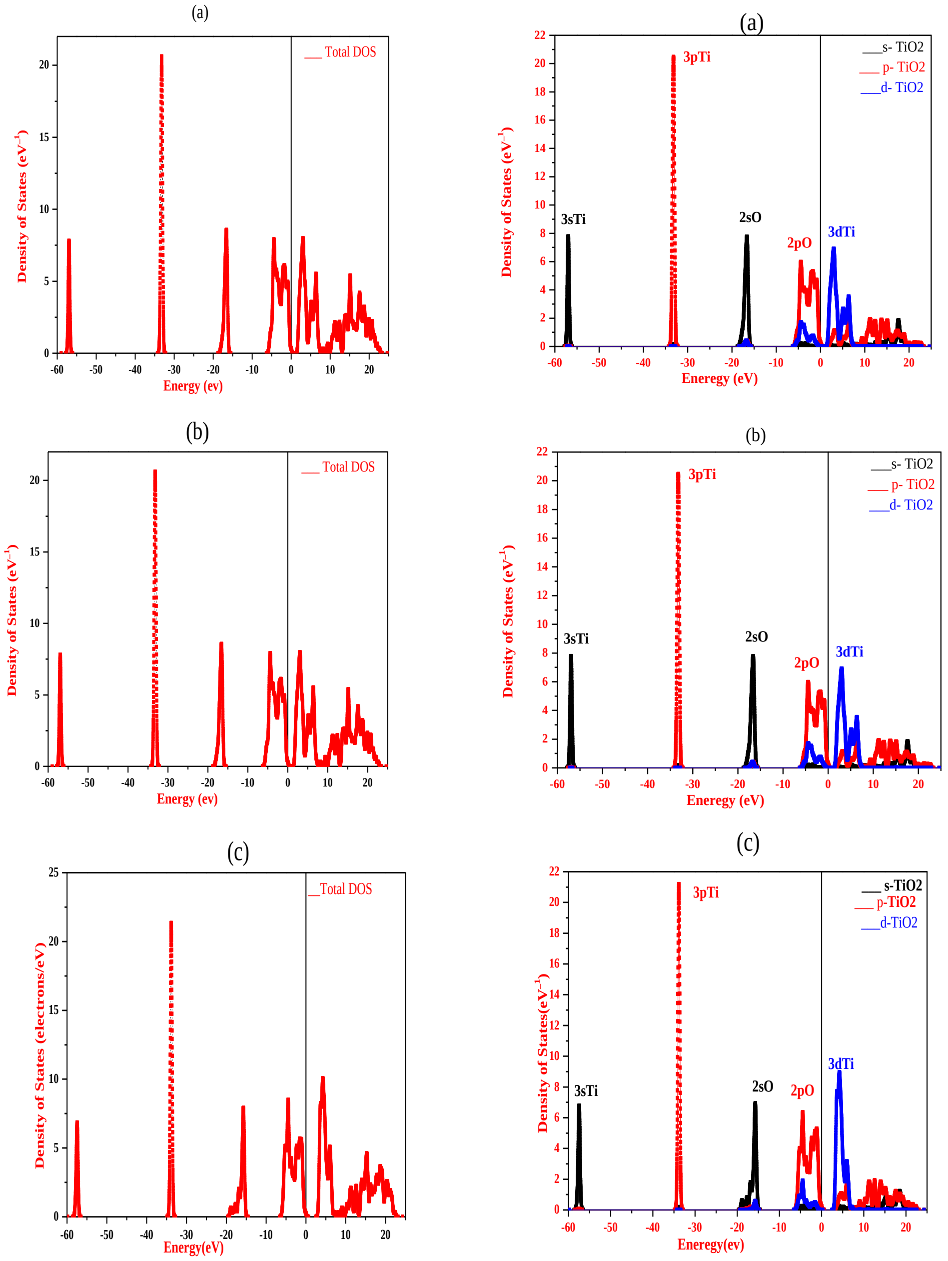

Fig 2: The calculated (a) total density of state, (b) combined partial density of state, using functional LDA, GGA-pw91, LDA+U.

3.2 Optical properties

Using the Density Theory System (DFT), the optical properties of the rutile TiO_2 were investigated using the LDA, GGA-Pw91 and LDA + U functions Fig.3. Illustrating the absorption peaks at which the absorption peaks are located away from the visible region, meaning that the rutile absorbs the visible and catalytic low. Low light, the major absorption rate of these functions ranges from 36 eV to 38 eV.

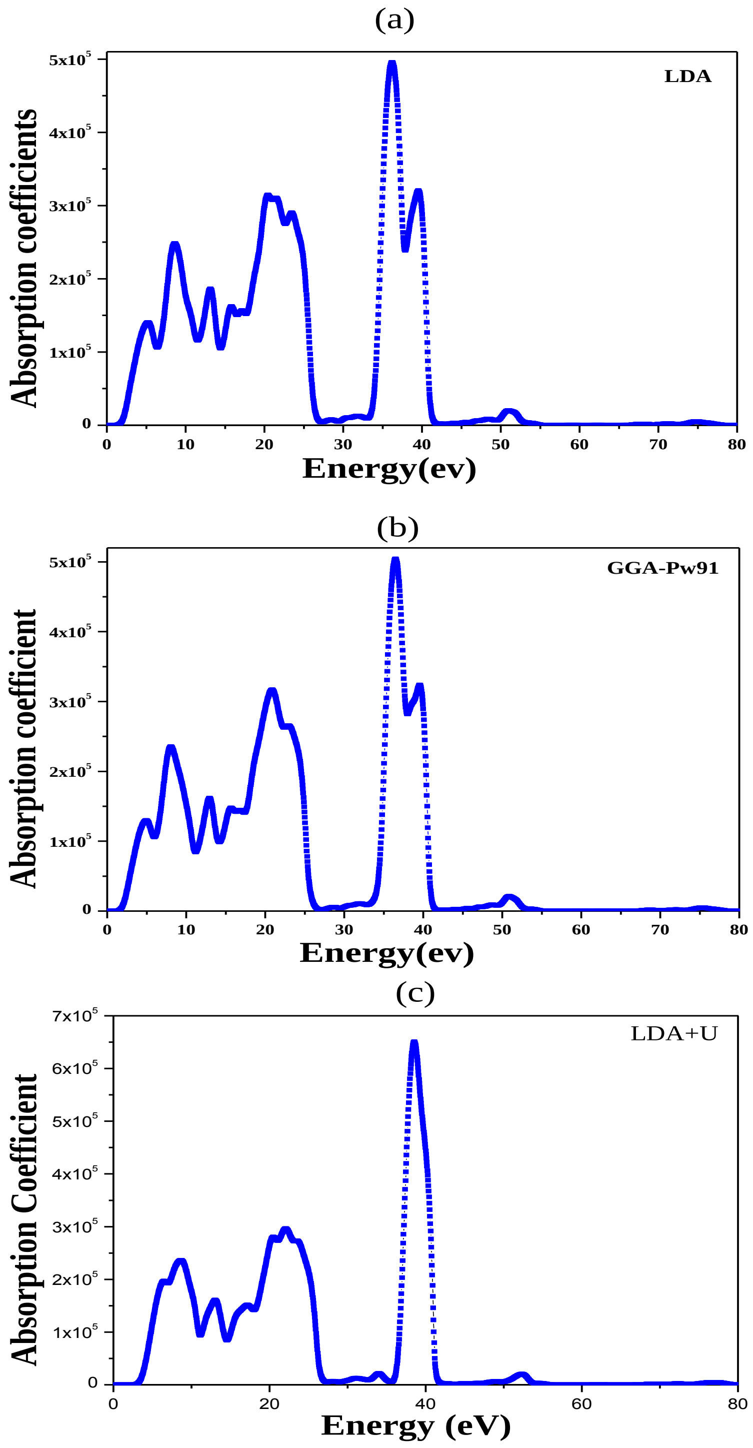

Fig 3: Absorption coefficients of rutile TiO2 using (a) LDA, (b) GGA-Pw91, (c) LDA+U.

Table 4: computation absorption coefficient edge and main absorption peak of the rutile TiO_2 that result through the use of various exchange –correlations.

functionality	Optical edge absorption (eV)	Large absorption peak (eV)	Other Ref
LDA	1.817	36	**present work**
GGA-Pw91	1.826	38	
LDA+U	3.297	37	
LDA	1.773	37	**[43]**
GGA-PBE	1.861	37.5	**[44]**
LDA	1.854	36.5	**[45]**

5. Conclusions

In this paper, we studied the crystal structure, optical properties and energy band gap of the rutile TiO_2 compound and performed the first principle study. These investigations were performed using the functional density theory in the LDA, GGA-PW91 approximations and the LDA + U estimate. where the ultra-soft pseudo potentials was one Good methods for describing the electronic and optical properties of the rutile TiO_2 were the results extracted for the range gaps calculated from the application of these functions (0.1817, 0.1826 and 3.297) eV respectively, and among these results it was found that the evaluation (LDA + U) is consistent with the experimental results More than other methods were used, but for the rutile TiO2 Lattice constants, the results for the functions (LDA, GGA + Pw91 and LDA + U) used were close to each other and consistent with the experimental results at a very low error rate, for total density of states The partial density of states of the rutile TiO_2 was verified and it turned out that the valence band was formed from the orbitals Ti_{3s}, Ti_{3p}, O_{2s}, O_{2p} where the O_{2p} orbital state of oxygen was controlling the top of the valence band, but on the other side of Fermi Level in conduction band, it was observed that the state of the Ti_{3d} orbital state of titanium was dominant. The last part of this study that has been studied, and which relates to the optical properties called absorption through the obtained results. The absorption starts from the ultraviolet light region (3.1eV) and peaks at (37eV) where the energy loss function is the lowest.

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دراسة التركيب الكتروني والخصائص البصرية TiO2 Rutile باستخدام نظرية الكثافة الوظيفية (DFT)

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الملخص

في هذه المقالة ، تم إجراء تحليل نظري لقياس التركيب الحزمي والخصائص البصرية وكثافات الحالات (DOS) لثنائي أوكسيد التيتانيوم الروتيل عبر برنامج محاكاة .Castep تم إجراء حسابات المبادئ الأولى باستخدام عملية الخلية الفائقة (1x1x1). تمت دراسة الحساب الأول لمفاهيم TiO2 بواسطة نظرية الكثافة الوظيفية (DFT) باستعمال تقريب التدرج المعمم (GGA-PW91) Perdew-Wang's 1991 وتقريب الكثافة المحلية (LDA) لوظيفة الطاقة ذات العلاقة المتبادلة, و طريقة (LDA+U) تنفيذ تفاعلات كولوم على مدارات ثلاثية الأبعاد من تياتوم Ti (U_d) ولذرة O(U_P) وكانت هناك توافق جيد النتائج بين جميع القيم التجريبية مع نتائجنا. ولكن نتائج LDA و GGA-Pw91 غير متوافقة مع النتائج التجريبية لخصائص الروتيل TiO2 قيد التحليل ، باستثناء فجوة الطاقة ، على الرغم من أن القيم ل (LDA + U) كانت متوافقة مع القيم التجريبية. تم الحصول على الخصائص البصرية لـ TiO2 Rutile باستخدام العديد من طرق الارتباطات والتبادل ، بشكل جيد وفقًا للنتائج التجريبية والأدلة النظرية الأخرى.