MAKERERE UNIVERSITY

PHYSICS DEPARTMENT

ELECTRONIC AND STRUCTURAL PROPERTIES OF TITANIUM OXIDE.

By;

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PROJECT REPORT SUBMITTED TO THE DEPARTMENT OF PHYSICS IN PARTIAL FULFILLMENT OF AWARD OF BACHELOR OF SCIENCE IN PHYSICS OF MAKERERE UNIVERSIY

OCTOBER 2022

Declaration.

I ARINDA JIMMY, declare that this report is my original work and has not been submitted to any University for the purpose of awarding a degree.

Referencing has been made where work from other authors has been used.

Signature.....

Date.....10th/Nov/2023.....

APPROVAL

This is to certify that this project study has been done under the supervision of my supervisor, and has been submitted for examination with the approval from my supervisor.

Signature.....

Date.....18/12/2023.....

Dr. Alex OKELLO

ABSTRACT.

Titanium oxide, $TiO_{2,}$ also known as titania is an inorganic compound with the chemical formula $TiO_{2,}$ white in color, water insoluble with a melting point of about 1843^{o}C, density of 4.23g/cm3, boiling point of 2992^{o}C, molar mass of 79.866 g/mol, chemically stable and highly versatile.

The world health organization has come to a conclusion that multiple people in the world don't have safe water for drinking and other uses so they've found need to provide a cheaper way of providing water to people, and titanium would be a better option due to its abundancy and its ability to be applied in processes such as photocatalytic treatment of water, but its large band gap has limited its efficiency in this process and thus various studies have been made to understand its band structure so as to find a way of reducing its band gap so as to improve its efficiency.

In this study I'll aim at obtaining the structural properties of titanium oxide that partially enable it to ably operate in the photocatalytic treatment of water and photovoltaics through the determination of its lattice constants, lattice structure that is bond angles, its constituent components, its bond angles, bond length through use of various automatic software such as Xcrysden, Xmgrace among others.

In tis study we'll be able to show how total energy varies with various parameters such lattice constants, plane wave cutoff and the K-points also known Brillouin sampling.

In this study I employed the density functional theory DFT zwhich is a computational tool that is essential in analyzing and predicting the properties of metals. DFT is built on the Kohn Shann theory

ACKNOWLEDGEMENTS.

I take this opportunity to thank the Almighty GOD who has enabled me to finish this project and the program Bachelor of science with Education. He's guided me through the ups and downs and has helped endure through the whole process.

I'm also profoundly grateful to my supervisor Dr. Alex OKELLO who has guided and helped me all through the process of conducting this project work starting from getting the project topic to this point of writing the final report about the project. He's corrected me when I went wrong, always been around to make sure everything I needed for the progress of my project is available, even when I seemed hard to advise, he still didn't give up on me. Honestly the success of this report greatly relies on him and I have nothing much to offer but to pray that the Almighty GOD guides him in all his endeavors, blesses him and grants him what he desires most.

Not forgetting the course facilitator Dr. Annet ZAWEDDE, who has supported, guiding in far as the unit is concerned, I'm really humbled. And to every lecturer at the physics department whose comments made during our presentation guided me, I'm grateful.

I would also love to unconditionally acknowledge my parents Mr. Rukundo BENARD and Mrs. Leonida RUKUNDO.K., who have made my academic life a success through the support and guidance they've provided all through, my

academic career up to this point, through paying my school dues, advising me and making sure I get all I needed for my success, I'm grateful and may GOD continue providing and blessing the work of their hands.

Lastly, I would wish to extend my regards to my project partners Sinzabakwira ABDALAH and Wajja.K. ALOYSIUS with whom we've managed to take on this project and have come this far as one. I'm so thankful for their support and co-operation. And for every one that has been part of my journey, I'm thankful.

MAY GOD BLESS YOU ALL ABUNDANTLY.

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CHAPTER ONE:

INTRODUCTION:

1.0 Background of the study.

According to the world health organization, about 1.1 billion people don't have access to safe and clean water despite it being considered the most important natural resource since it forms about 70% of the earth's surface

This has been brought about by the continued industrialization, urbanization and improper disposal of wastes that contaminate the water, it is therefore preferred that each and every person has access to safe and clean water to use in their daily life.

Due to this, various ways of treating water have been improvised such as use of chlorine to purify water, use of machines to filter water though all these have proved costly thus a new kind of water treatment that is cheaper has been devised and that is photocatalytic treatment of water and this has called for the use of Titanium oxide since it's cheap and occurs in adequate amounts.

During photocatalysis, Titanium oxide absorbs ultra violet light from sunlight, to form Hydrogen gas and Hydroxyl radical (OH). Hydroxyl radical is an extremely powerful oxidation agent. With the strong oxidation strength of hydroxyl radicals, photocatalytic oxidation can effectively disinfect and purify water thus cleaning it.

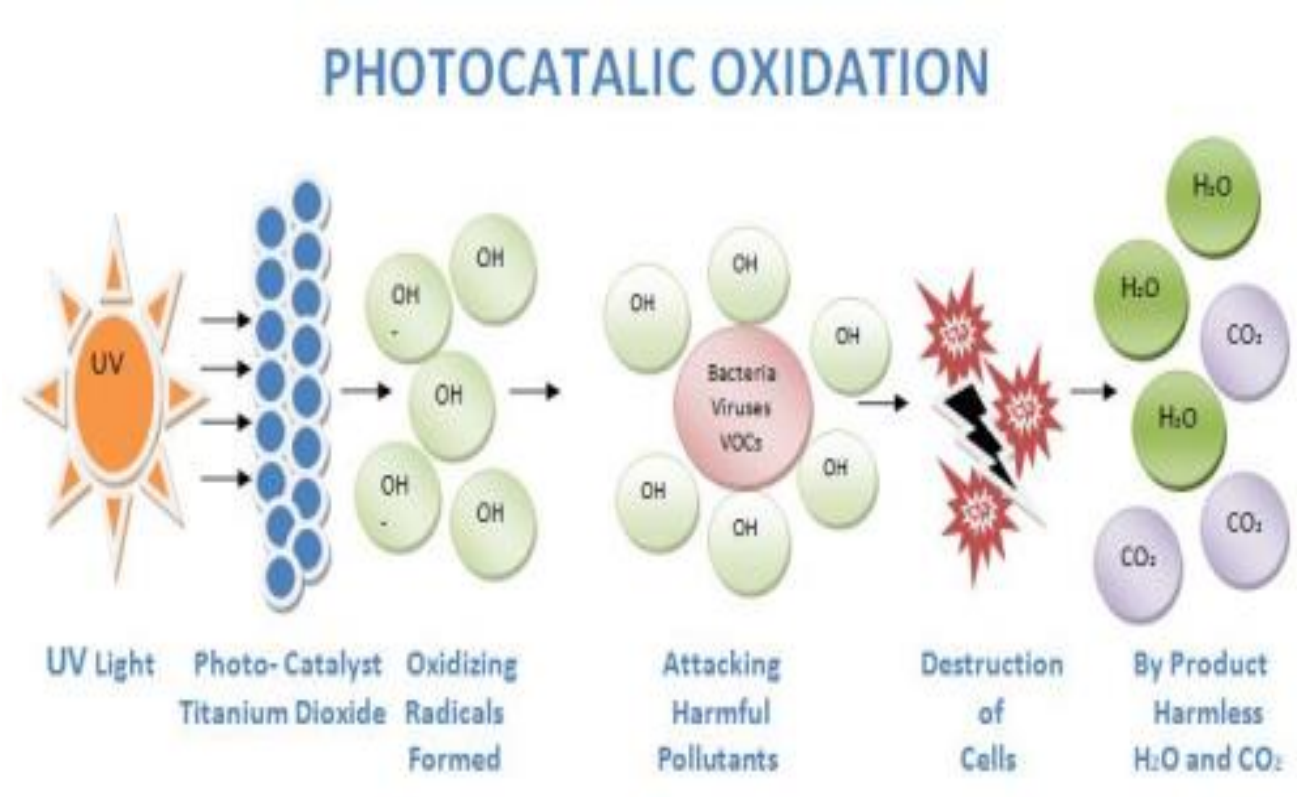

Figure 1 The process of photocatalytic action

In addition, there has been an increased shortage of power and energy in various regions of the world due to the increased prices attached to accessing electricity and low distribution levels of power in some areas thus people have resorted to the use of solar energy since it's associated with the sun which is in abundance. Titanium oxide has been vastly used as an electron transport layer in the solar cells because it is highly versatile. Because of its large band gap of about 3.2-3.8 eV, titanium oxide is only able to absorb about 4% of the solar energy radiated by the sun, to increase on the absorption rate of Titanium oxide, it's been proposed that it should be doped (introduce some impurities to it) as this would help reduce on its band gap thus increasing the absorption rate of Titanium oxide and the efficiency of the solar cells.

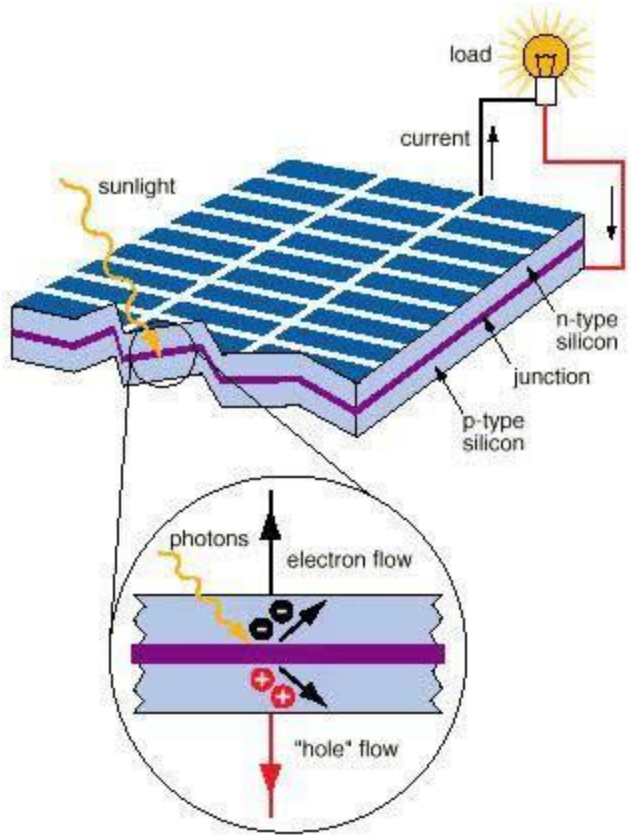

Figure 2 The process of photovoltaic action

In this project, we employed the Density Functional Theory to investigate the electronic and structural properties of Titanium oxide.

1.1 Problem statement.

Titanium oxide is used in photoactivity, it's been observed that it's only able to absorb about 4% of the solar energy radiated and this is attributed to the large band gaps of 3.2-3.8eV, these are too large to absorb visible light there by presenting us with the need of reducing these band gaps so as more visible light can be absorbed. Thus, the need to understand the electronic and structural properties of titanium oxide.

1.2 Aims and objectives

1.3 Major objective;

To investigate the structural and electronic properties of titanium oxide using Density functional theory.

1.4 Specific objectives.

a) To determine the lattice constants of titanium oxide.

b) To determine the structure of titanium oxide.

1.5Significance of the study.

This study helps us describe the structural properties of titanium oxide such and the bond angles, bond length, lattice parameters and the arrangement of atoms in titanium oxide that enable its application in the photocatalytic and photovoltaic processes.

CHAPTER TWO

LITERATURE REVIEW.

2.0 Introduction.

This chapter gives a summary of the material properties of titanium oxide, what has been done and what hasn't been done about titanium. This chapter also talks about the theories that have been developed about titanium oxide and the studies that have been made.

Finally, it gives a brief introduction to the DFT on which this study is based.

2.1 Material properties

In this section, I tried to elaborate more about our desired results. Determining the structural and electronic structure of titanium oxide being our main objective, in this section, I give more light on the fundamental knowledge about structural and electronic properties of titanium oxide.

2.2 Structural properties.

When we talk about structure of an object, things like its dimensions in this project referred to as lattice constant, band length, bond angles are essential characteristics of the object and must obtained. The lattice constant helps us determine how far lattice points are from each other. Bond length helps us determine how strong the bond is that is the longer the bond length, the weaker the bond and vice versa. Then the bond angles determine the arrangement of atoms along the whole volume of the material and all this helps us determine whether the material is a simple cubic, body centered cubic, a face centered cubic or any other structure.

2.3Literature review.

Titanium oxide has various applications and photovoltaics, but its efficiency is limited by the large bandgap that it has, its band gap ranges from 3,2-3,8 which is too large to absorb visible light, thus visible studies have been made to facilitate reduction of the band gap to a smaller range that absorbs visible light and this has been done by trying to understand its structural and electronic properties.

In this study, I aimed mainly at studying the structural properties. In this study we are provided with an input file as attached in chapter three of this report, this file contains various information about titanium oxide such as lattice parameters, plane wave cutoff (Ecutoff), number of Bravais lattices, number of atom types, initial K-points, atomic species, atomic positions among others.

In this study, I used various software such as Xcrysden to visualize the structure of titanium oxide, Xmgrace to plot graphs of various results obtained among others.

To obtain the various results, I ran self-consistent field calculations (SCF) under the DFT since they depend on the electronic density and are the simplest levels of quantum chemical models. This method is an iterative method that involves selecting an appropriate Hamiltonian solving the Schrodinger equation to obtain a more accurate set of orbitals and then solving the Schrodinger equation again with these until the result converges.

Depending on the parameters in the input file such as 2.50000+01 for Ecutwfc, 6 6 6 0 0 0 for the initial K-points, 2.96991e+00 and 4.65178e+00 for lattice constants, we select relative values that I will consider while running the SCF calculations, I edit the input file using the ‘gedit’ command and then run the SCF calculations to obtain the converged values for Ecutwfc, K-points and lattice constants. The obtained converged values are the used to run further SCF calculations to obtain the electronic structure of titanium oxide.

For Ecutwfc I chose my values to range from 22-27, for K-points I chose values ranging from 5 5 5 0 0 0 to 11 11 11 0 0 0 and then for lattice constants I chose to use values ranging from 4.0 - 5.0 and 2.4 – 3.4 and the ran the SCF calculations for each of the above steps to obtain a converged value.

2.4Density Functional Theory. (DFT)

In this study, we embarked on the use of DFT on which this work is based, I was able to determine the structural and electronic properties of titanium oxide.

DFT is a computational tool that is essential in analyzing and predicting the properties of metals such as titanium oxide. DFT is built on the Kohn and sham theorems (Burke, 2007; Sholl and Steckel, 2011) that state that;

a) The ground-state energy from the Schrödinger equation is a unique function of the electron density.
b) The electron density that corresponds to the complete solution of the Schrödinger equation is the true electron density that minimizes the energy of the overall function.

CHAPTER THREE

MATERIALS AND METHODS

3.0 Introduction.

This chapter provides details on how the structural properties of Titanium oxide TiO_2 were obtained. Density Functional Theory was used to study the properties of the TiO_2

3.1 Input file;

3.3&CONTROL

4.3 calculation = 'scf'

5.3 max_seconds = 8.64000e+04

6.3 pseudo_dir = './pseudo'

7.3 outdir='./tmp'

8.3/

9.3

10.3 &SYSTEM

11.3 a = 4.65178e+00

12.3 c = 2.96991e+00

13.3 degauss = 1.00000e-02

14.3 ecutrho = 2.25000e+02

15.3 ecutwfc = 2.50000e+01

16.3 ibrav = 6

17.3 nat = 6

18.3 nspin = 2

19.3 ntyp = 2

20.3 occupations = "smearing"

21.3 smearing = "gaussian"

22.3 starting_magnetization(1) = 2.00000e-01

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23.3          starting_magnetization(2) =  0.00000e+00
24.3
25.3       /
26.3
27.3       &ELECTRONS
28.3          mixing_mode = 'plain'
29.3          mixing_beta = 0.3
30.3
31.3       /
32.3
33.3       K_POINTS {automatic}
34.3        6  6  6  0 0 0
35.3
36.3       ATOMIC_SPECIES
37.3       Ti     47.86700  Ti.pbe-sp-van_ak.UPF
38.3       O      15.99940  O.pbe-rrkjus.UPF
39.3
40.3       ATOMIC_POSITIONS {angstrom}
41.3       Ti      2.325892   2.325892   1.484957
42.3       Ti      0.000000   0.000000   0.000000
43.3       O       3.233404   3.233404   0.000000
44.3       O       0.907512   3.744272   1.484957
45.3       O       1.418380   1.418380   0.000000
46.3       O       3.744272   0.907512   1.484957
```

3.2 Determination of lattice constants of titanium oxide

Having been provided with the input file as shown in chapter three, I opened it using the Linux software and using the Xcrysden software I was able to obtain the visualized structure of titanium oxide.

Having obtained the visualized structure, I then highlighted two titanium atoms and then using Xcrysden I calculated the distance between them and that was the lattice constant.

Titanium oxide being rectangular based, I had to calculate for two sides to obtain the two lattice constants a and c

3.3Determination of the structure of titanium oxide.

From the visualized structure, I was able to obtain the bind angles between the titanium atoms and the titanium-oxygen bond. I was able to do so by highlighting three titanium atoms and obtained the angle between them using the Xcrysden software and then highlighted two titanium atoms and one oxygen atom to obtain the bond angle between them

Then after using the command “gedit” I was able to edit the input file so as to create a new file that would allow me vary the planewave cutoff, K-points, and the lattice constants so as to obtain how total energy varies with these parameters.

Then using Xmgrace software, I was able to obtain various plots of how total energy varies with the above-named parameters and the minimum energy of each graph was read.

CHAPTER 4

RESULTS AND DISCUSSION OF RESULTS.

4.0 Introduction.

In this chapter, we discuss the results obtained from the calculations and processes conducted for the structural and electronic properties of titanium oxide TiO_2.

First, we talk about the structural properties and the geometry of titanium.

Then we talk about how the total energy of titanium oxide varies with its lattice parameters, various K-points and the plane wave cutoff ecutoff.

4.1Structural properties.

After using Xcrysden, I obtained the following results TiO_2 has a rectangular base with dimensions 8.7906 Bohr as the length and 5.6123 Bohr as the width with 8.7096 Bohr as the height. This implies that titanium oxide has lattice parameters a=b≠c where a=b=8.7906 Bohr/ 4.6518 angstrom and c = 5.6123 Bohr/ 2.9699 angstrom and the calculated bond angles are 131.94° and 90°with the separation between oxygen and titanium oxide = 3.7090 Bohr/ 1.9627 angstrom

4.2Structural visualization.

Titanium oxide is tetragonal in shape with 15 atoms that is 9 titanium atoms and 6 oxygen atoms as viewed using Xcrysden.

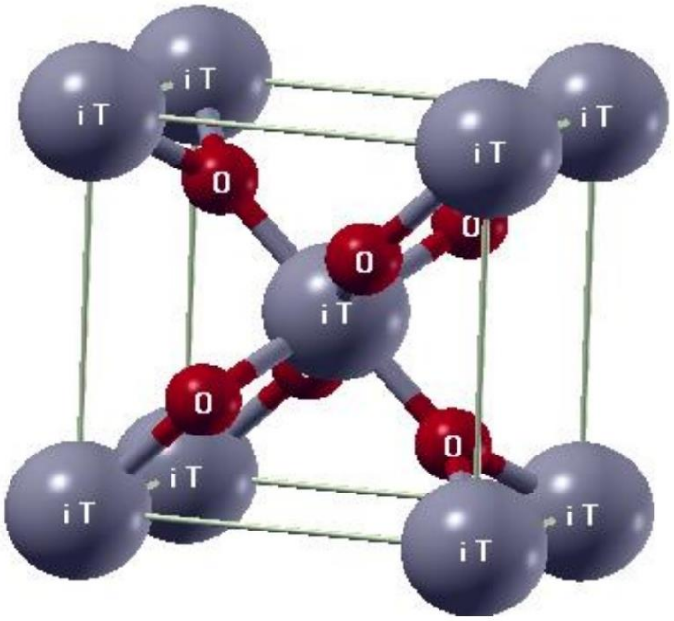

Figure 3 Structure of titanium oxide

Table 1 : output for how total energy varies with k-pints

K-POINT	TOTAL ENERGY
5	-361.60995214
6	-361.60995625
7	-361.60991632
8	-361.61013717
9	-361.61011268
10	-361.61024861
11	-361.61014300

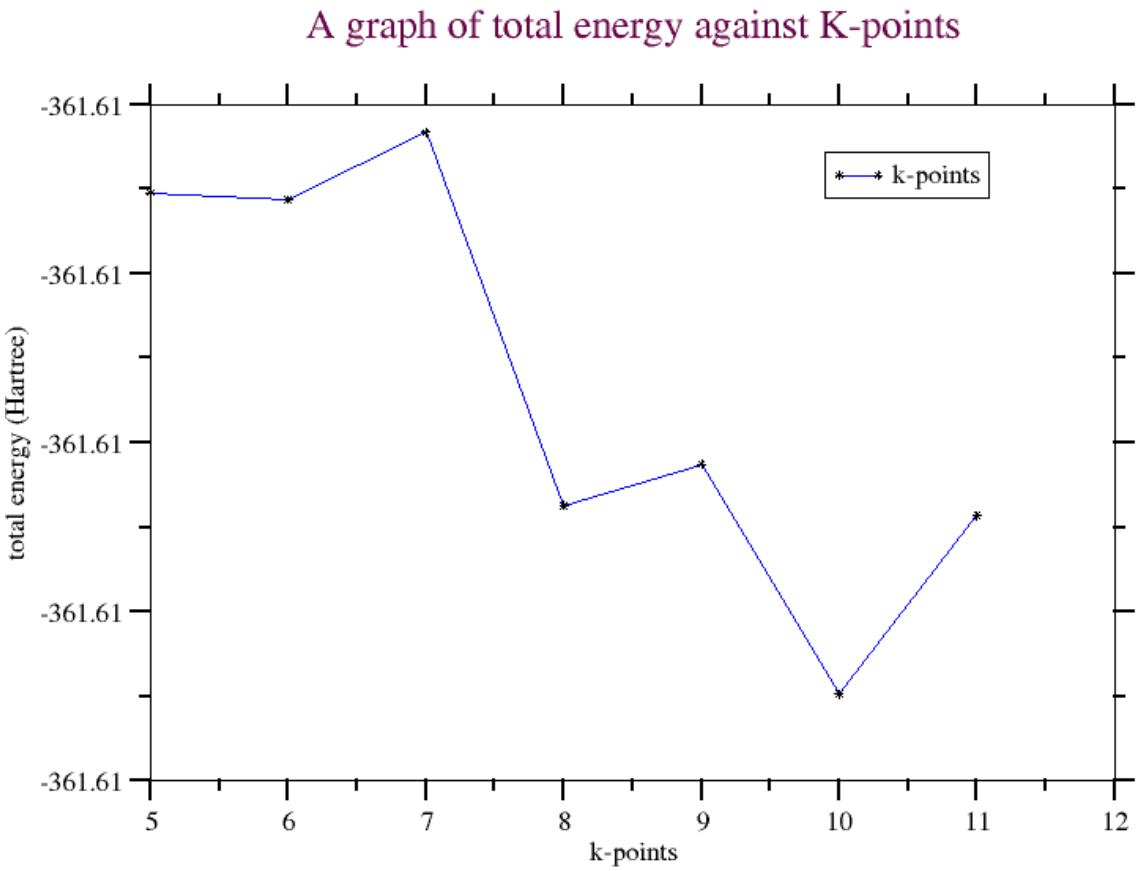

Figure 4 Graph of total energy against k-points.

Table 2 Output file for how total energy against varies with Ecut.

Ecut (Hartree)	Total energy (Hartree)
22	361.46189158
23	361.53071567
24	361.57791490
25	361.60995625
26	361.63212027
27	361.64655805

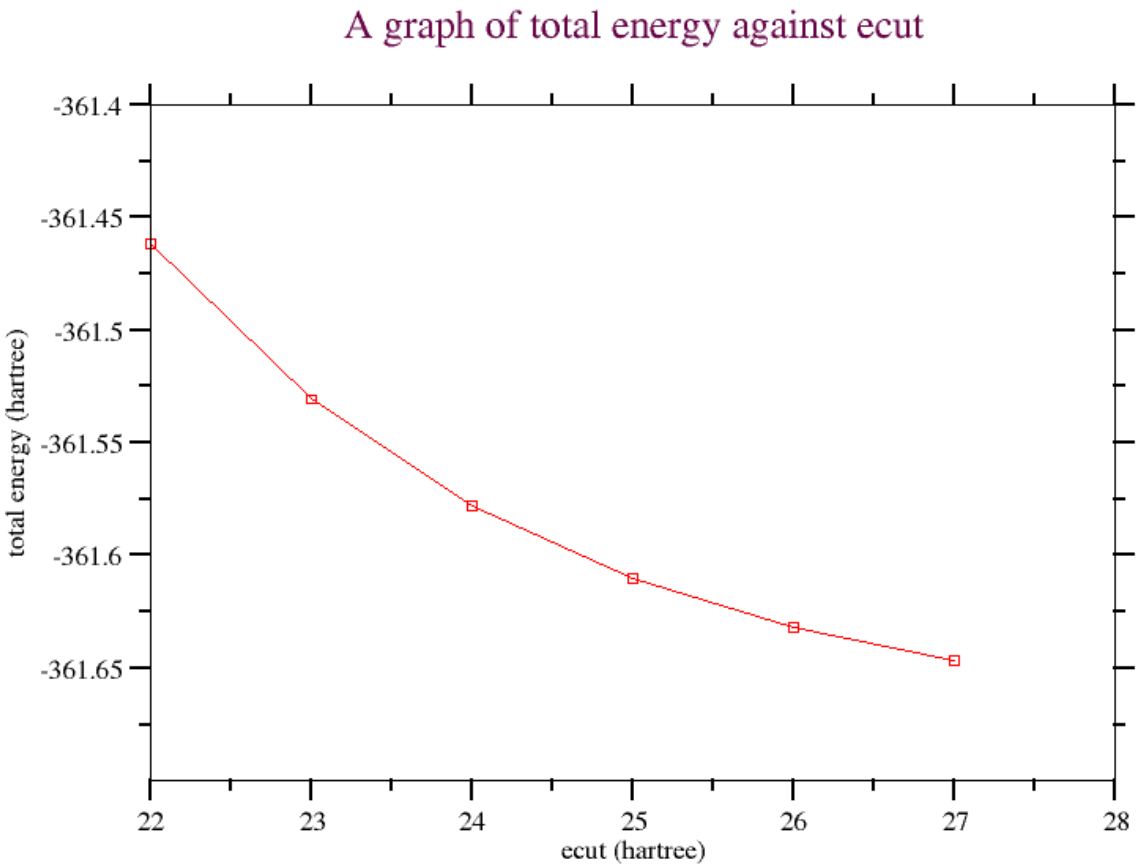

Figure 5: Graph of total energy against Ecut.

Table 3 Output file of how total energy varies with lattice parameter a

Lattice parameter a	Total energy (Hartree)
4.0	359.17509628
4.2	360.93463305
4.4	361.47919418
4.6	361.60785521
4.8	361.58052614
5.0	361.61024861

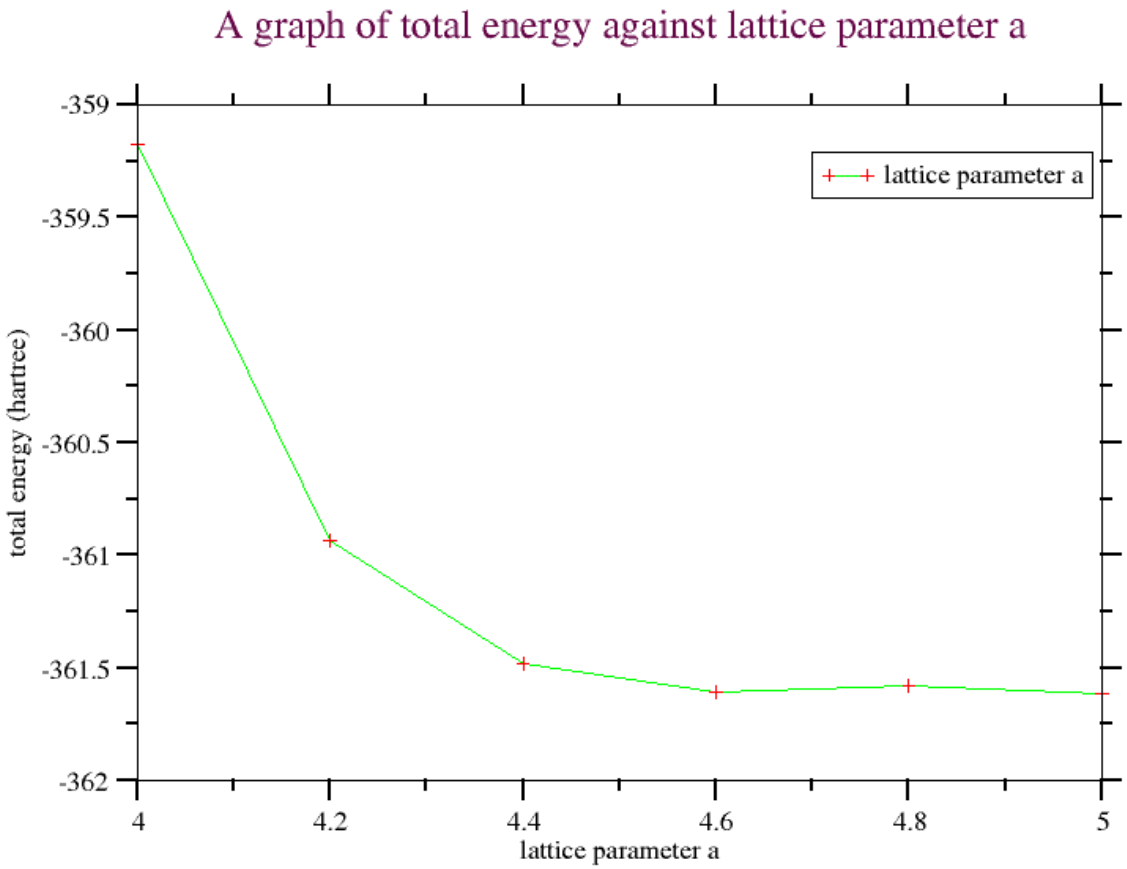

Figure 6: Graph of total energy against lattice parameter a

Table 4 Output file for how total energy varies with lattice parameter c

Lattice parameter c	Total energy (Hartree)
2.2	361.07093261
2.4	361.43806733
2.8	361.58505356
3.0	361.60851933
3.2	361.57134653
3.4	361.51027721

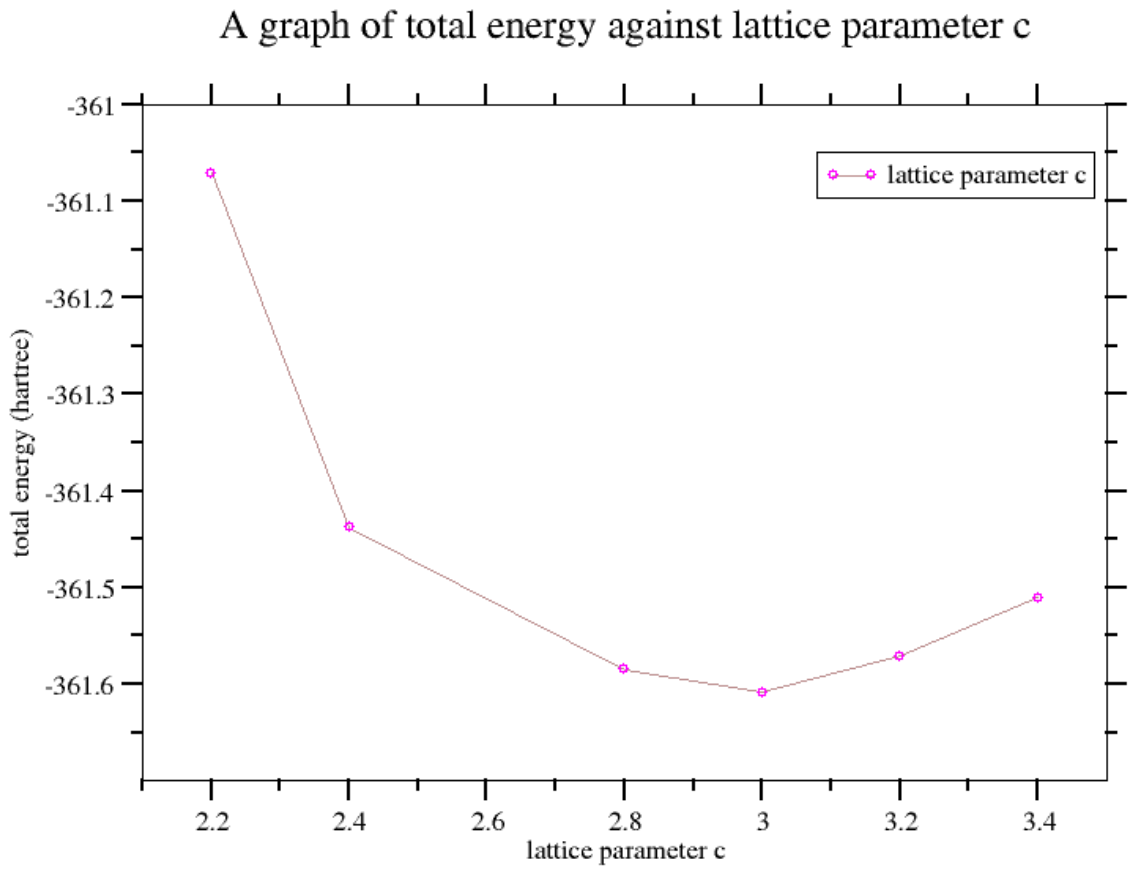

Figure 4: Graph pf total energy against lattice parameter c

The above plots are obtained by plotting the respective results shown in the tables above which are obtained by running automatic SCF calculations, through the use of Xmgrace.

From the above plots, I obtained: the converged value of total energy with respect to the plane wave cutoff and the value of the plane wave at which it occurs, the equilibrium lattice parameters and then noted the value of total energy at the equilibrium lattice parameters, lastly the converged value of total energy with respect to K-points and the K-point at which it occurs.

I obtained the converged value of the total energy with respect to the planewave cutoff as -361.647 Harterees and it happens at planewave cutoff value of 27.

I also obtained the equilibrium lattice parameters as 3 and 4.6 with the correspondent energy of -361.612 Hartrees and -361.613 Hartrees respectively.

I then obtained the converged value of the total energy with respect to K-points as -361.61 Hartrees and it happens at K-point 10.

The obtained value of total energy are then used to run SCF calculations which help us calculate the band structure, density of states and the extract charge density of titanium oxide thus the electronic properties of titanium oxide.

CHAPTER 5:

CONCLUSION AND RECOMMENDATIONS.

5.0Conclusion

The results for the structural properties and part of the work needed to obtain the electronic properties with DFT have been obtained in this study. This study showed that titanium oxide has different lattice parameters and it is tetragonal in shape. The study further shows that TiO_2 has a composition of two elements that is titanium and oxygen having 9 titanium atoms and 6 oxygen atoms.

This study further more predicts the way total energy of titanium oxide varies with K-points, lattice parameters and the plane wave cutoff (Ecut).

5.1Recommendations

In this study, I dwelled mostly on the structural properties but titanium oxide TiO_2 has other properties such as the electronic properties which haven't been well investigated in this study though the study provides the basis of investigating these properties so it would be interesting for someone to build on and investigate these properties.

This study also provides an insight on the various applications of TiO_2 in photocatalysis and photovoltaics which would be of great help in solving day to day problems such as high electricity bills, lack of clean water among others, thus I hope is can be used extensively.

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