Mathematical modeling of the electronic structure of Titanium dioxide $(TiO_2)_6$ nanoparticles

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Abstract

The calculation of the number of atoms of the given dimensional nanoparticle, composed of different type atoms has been researched in this work. The calculations have been carried out for nanoparticles of titanium dioxide. Theoretical visual models have been configured, and quantum – mechanical calculations have been carried out for $(TiO_2)_6$ nanoparticle. The calculations for titanium dioxide nanoparticle have been carried out on the basis of Gaussian atomic orbitals. Besides, Gaussian functions have been used as atomic orbitals. The numerical values of unknown coefficients of the linear combination of atomic orbitals of the atoms of the titanium nanoparticle have been found from the solution of Hartree–Fock–Roothaan (HFR) equations.The values of orbital energies, ionization potential, and the total electronic energy of titanium dioxide nanoparticles have been determined . The calculations show that, titanium dioxide nanoparticle is tough, electrophile, and stable dielectric, material. The effective charge of atoms have been calculated, and the theoretical visual mode of titanium dioxide nanopartical have been constructed.

Keywords: nanotechnology, quantum-mechanical calculation, computer models, Hartree–Fock–Roothaan method.

1.Introduction

Titanium dioxide nanoparticle material is a wide class of material used in electronics, optoelectronics,and piezo technic. For this possibility of application , it has a great importance to investigate electronic structure of titanium dioxide by quantum mechanical methods [1,9,10,12,14]. In this work, electronic structure and properties of Titanium dioxide nanoparticle have been studied by Hartree-Fock-Roothaan (HFR) method. As HFR method, the state of electron in the molecule is represented with one-electronic wave functions called U_i– molecular orbitals. U_i is represented as linear combinations of $\mathcal{X}_q$ atomic orbitals of atoms of molecules [4,5,8,12,14], with :

$$U_i = \sum_q c_{qi}\mathcal{X}_q \qquad (1)$$

$\mathcal{X}_q$ orbitals are considered as known. Unknown coefficients C_{qi} are found from the solution of HFR equations. We can express these equations in matrix form as following:

$$FC=\varepsilon SC \qquad (2)$$

Here, ε- orbital energies of electrons, S- overlap matrix elements between $\mathcal{X}_P$ and $\mathcal{X}_q$ atomic orbitals, C- matrix of unknown coefficients. F is matrix elements of Fock operator, it depends on the C unknown coefficients. By unitary conversion method (2), it is possible to converse generalized eigenvalues equations to ordinary eigenvalues equations. As a result of calculations ε_i-orbital energies, and values of coefficients C_{qi} have been found. On the basis of values of coefficients C_{qi} ,the analytical expression of molecular orbitals can be obtained. This allows to calculate some parameters of nanostructures, such as effective charge of atoms. On the basis of the values of ε_i it is possible to calculate the total energy, the values of ionization potential, electric conductivity, and strength and other properties of Titanium dioxide nanoparticle .During calculations as $\mathcal{X}_q$ atomic orbitals, 1s-, 2s-, $2p_x$-, $2p_y$-, $2p_z$-, 3s-, $3p_x$-, $3p_y$-, $3p_z$-, $3d_{x2}$-, $3d_{y2}$-, $3d_{z2}$-,

$3d_{xy}$-, $3d_{xy}$-, $3d_{xz}$-, $3d_{yz}$-, 4s-, $4p_x$-, $4p_y$-, $4p_z$- atomic orbitals of titanium atoms, 1s-, 2s-, $2p_x$-, $2p_y$-, $2p_z$- atomic orbitals of oxygen atoms have been used .Gaussian functions have been used as atomic orbitals.

2.Theoretical methodology

The properties of nanoparticles depend on their dimensions, and the number of atoms of nanoparticles. The following formula is used for defining the number of atoms of composed same type atoms, and given dimensional nanoparticle[1,3,6,12,15]:

$$N = \frac{\pi \rho D^3 N a}{6M} \qquad (3)$$

Here, nanoparticle is considered as 'dense packing' sphere. N – The number of atoms, ρ – density of material, D – diameter of sphere formed nanoparticle, N_A = Avogadro's number, molar mass. It is not possible to use (3) for nanostructures, composed with different atoms. In literature, various ways are suggested to define dimensions, and number of atoms in such nanostructures. These ways are complicated, and are hard to make calculations with them. In this work, when the dimensions of such nanostructures are known, some ways are suggested to find out the number of atoms of nanostructure. Nanoparticles is considered as sphere form. the dimension of spherical formed TiO_2 (*fig*.1) compound, the calculation of $(TiO_2)_6$ nanoparticle can be found by :

$$r_h = \frac{AC}{2} = \frac{\sqrt{(AD)^2 + (DC)^2}}{2}$$

$AD = 4 \cdot r_0$, and $DC = 2 \cdot (r_0 + r_{Ti})$, r_0, and r_{Ti} are covalent radiuses of oxygen and titanium atoms: $r_0 = 0.073$ nm, $r_{Ti} = 0.132$nm.

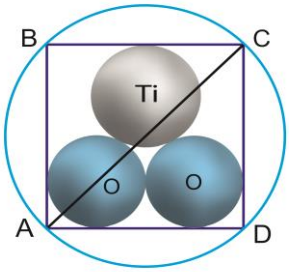

*fig*1. The model of TiO_2 compound

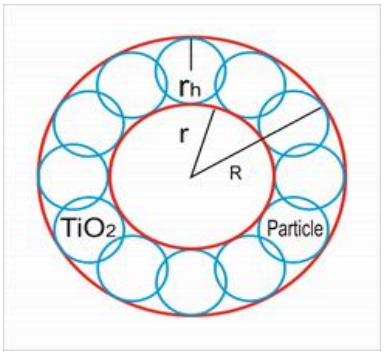

fig. 2. The model of $(TiO_2)_n$ nanoparticle

It is considered that, $(TiO_2)_n$ molecules is located on the surface of empty sphere with r radius (*fig*. 2). Then, the formula for, n, nanoparticles with radius R can be calculated as:

$$n = \frac{R^3 - r^3}{r_h^3} \qquad (4)$$

Here, $r = R - 2r_h$. The calculations are carried out for nanoparticle with radius R= 0.46 nm, and n ≈ 6. The number of atoms in nanoparticle are N=18. The theoretical visual model of $(TiO)_2$ nanoparticle (*fig*. 3) is configured [2,3,4,12] and quantum mechanical calculations are carried out.

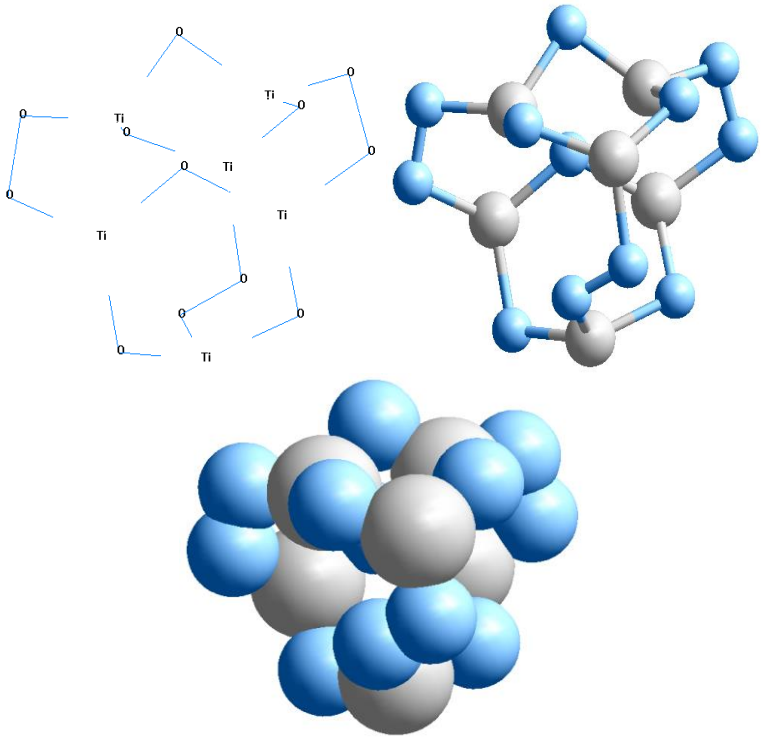

fig. 3. The theoretical visual model of $(TiO_2)_6$ nanoparticle

3.Result and Discussion:

Calculations of $(TiO_2)_6$ nanoparticles have been carried out by Hartree-Fock-Roothaan (HFR) method. As basis atomic orbitals,1s-, 2s-, $2p_x$-, $2p_y$-, $2p_z$-, 3s-, $3p_x$-, $3p_y$-, $3p_z$-, $3d_{x2}$-, $3d_{y2}$-, $3d_{z2}$-, $3d_{xy}$-, $3d_{xy}$-, $3d_{xz}$-, $3d_{yz}$-, 4s-, $4p_x$-, $4p_y$-, $4p_z$- atomic orbitals of titanium atoms, 1s-, 2s-, $2p_x$-, $2p_y$-, $2p_z$- atomic orbitals of oxygen atoms have been used. Gaussian functions have been used as atomic orbitals. Molecular orbitals have been represented as linear combination of mentioned atomic orbitals [2] . While calculating, computer programs have been used . As a result of this calculations the values of orbital energies, ionization potential, and the total electronic energy of titanium dioxide nanoparticle have been determined(TableS1and 2) .

The result of calculations for $(TiO_2)_6$ nanoparticle have been given as follows :

Total energy = -5926.024383 (a.u.)

Ionization potential I_P = 2.19959 *eV*

Table (1) Orbital energies (eV) of $(TiO_2)_6$ nanoparticles

-26.546509	-26.543426	-26.932308	-26.922387	-26.911095
-26.902167	-25.938090	-25.928790	-25.917011	-25.896701
-25.876007	-25.121018	-24.997230	-24.592330	-24.470018
-24.457809	-24.367210	-24.196711	-24.178012	-24.101090
-24.090991	-22.910990	-22.890432	-22.788610	-22.758900
-22.699902	-22.634088	-22.622679	-22.612090	-22.601002
-22.590421	-22.450981	-19.990547	-19.001267	-18.909227
-18.891339	-18.791437	-18.610070	-18.455760	-18.445300
-18.401995	-18.390890	-18.289430	-18.112745	-18.010099
-17.970091	-17.801126	-17.798012	-17.780909	-15.760071
-15.360077	-15.289011	-15.225720	-15.210329	-15.109675
-15.008970	-14.990117	-14.871080	-14.790815	-14.785400
-14.767099	-14.546032	-14.290012	-14.271398	-14.109001
-13.709812	-13.100493	-12.965401	-12.890015	-12.561132
-11.790780	-11.522101	-11.411545	-11.378090	-11.209543
-10.990166	-10.954320	-10.910988	-10.903210	-10.890845
-10.707994	-10.687112	-10.609810	-10.490012	-10.254095
-10.995409	-10.971098	-9.891878	-9.767089	-9.682905
-8.990287	-8.7091398	-8.6906732	-8.3096120	-8.247450
-8.165309	-7.5932190	-7.0787210	-7.023459	-6.845081
-6.754870	-6.7309876	-6.7217600	-6.451900	-6.347438
-5.496018	-5.489126	-5.4359001	-5.426893	-2.199590
-2.001678	-1.874428	-1.5991377	-1.101765	-1.0068430
0.216650	0.612573	0.876321	1.005533	1.998036
2.126409	2.990515	4.767432	6.860980	6.897726
6.923464	8.125875	8.890047	10.035859	10.170929
10.193270	10.267589	10.767090	10.909945	11.250890
11.926027	11.949800	11.950087	11.967901	11.976087
11.984935	14.465505	14.543204	14.876540	14.911765
18.119878	20.163679	20.896217	20.948711	24.976109
24.985871	25.457800	27.678912	29.980122	30.676262
30.895828	33.990543	34.169670	34.606819	36.834678
40.628746	40.845921	41.932082	41.941987	42.309324
44.817115	44.919972	50.837795	50.979410	56.050380
57.879783	58.679800	59.944714	59.956838	60.743010
60.899713	63.239871	63.781129	64.878634	64.911097

Table (2) : The effective charge and coordinates (with Angstrom) of atoms

No of Atom	Z	Effective charge	X	Y	Z
1	22	5.876012	-2.91231905	-1.15894233	0.03974580
2	22	5.949105	-1.91038764	1.62399671	0.36081220
3	22	-5.323890	1.76190435	-0.93254922	-1.86262479
4	22	6.289041	1.28498109	0.67910245	-1.80976270
5	22	-5.890911	1.00964178	-0.90115396	-1.97001126
6	22	5.114760	-1.41769011	-0.92349220	-1.91872440
7	8	-1.548910	0.67813400	0.54963701	-1.13652109
8	8	-1.780980	-1.06987873	0.01827743	-0.16512098
9	8	-0.328719	0.79482716	-4.75493618	1.21098717
10	8	-0.318708	-0.26816769	-3.31396849	1.22432890
11	8	-1.891173	-0.23658907	-1.35609219	1.41209872
12	8	-0.780909	0.85781064	-4.98326549	1.46197300
13	8	-2.192852	-0.09164610	1.76598100	1.47392276
14	8	-3.920149	-.001965130	1.32769400	0.51374608
15	8	1.546107	-0.16710983	2.72518070	0.52609176
16	8	-0.971608	1.21098347	-3.43684300	0.53987091
17	8	2.0921018	-0.66237791	-3.10985231	0.63721108
18	8	-3.1067951	-3.00820911	-1.98432780	0.568120499

In Table(3),we compared the accuracy of result of the titanium dioxide nanoparticle on the basis of HFR(GTO·s) theory with the results which we previously had when we studied for (Au_{16}),(Ag_{12}),and$(CdS)_9$ on the basis of WH(STO·s) method [3,10,11,12,14].

Table3. Results of the computer calculations for (Au_{16}),(Ag_{12}),and$(CdS)_9$,by WH(STO·s) method

No.	**Nanoparticles**	**E (a.u)**	**ΔE(a.u.)**	**I_p**	**$\varepsilon_{LUMO} - \varepsilon_{HOMO}$ (eV)**	**Number of electrons using in calculation**	**Methods**
1	Au_{16}	-6.339366	-0.26367	3.7033899	0.4675225	16	WH(STO·s)
2	Ag_{12}	-61797.168985	-2.26925	2.464504	4.194947	12	WH(STO·s)
3	$(CdS)_9$	-39.103686	-0.650808	9.858220	0.099839	72	WH(STO·s)
4	$(TiO_2)_6$	-5926.024383	-4.557863	2.199590	3.227303	228	HFR(GTO·s)

The result of Table(3) indicates a variety on the calculations accuracy. these varieties of the calculations accuracy because of the type of the basic functions, and the variety of number of electrons which were used in the calculations in each compound.

Interpretation of the results for $(TiO_2)_6$ nanoparticle:

Starting from the lowest energy level 228 electrons of $(TiO_2)_6$ nanoparticles are placed in level two by two levels. The value of band gap can be calculated as $E_g = \varepsilon_{LUMO} - \varepsilon_{HOMO}$. Here, ε_{LUMO} is the energy of the lowest empty molecular orbital, and $\varepsilon_{HOMO}$is the highest energy of molecular orbital occupied by electrons.

$\varepsilon_{LUMO} = \varepsilon_{115} = -5.426893\, eV$,$\varepsilon_{HOMO} = \varepsilon_{114} = -2.199590 eV$,

$\varepsilon_{LUMO} - \varepsilon_{HOMO} = \varepsilon_{115} - \varepsilon_{114} = -2.199590 - (-5.426893) = 3.227303 eV$.

This shows that,(TiO_2) nanoparticle is dielectrical material. The energy of the highest level, occupied by electrons, is equal to the value of ionization potential with negative sign.

$I_p = -\varepsilon_{HOMO} = -\varepsilon_{114} = 2.199590\ eV.$

Strength can be calculated by the formula; $\eta = \frac{1}{2}(\varepsilon_{LUMO} - \varepsilon_{HOMO})$. Consequently, $\eta = 1.6136515eV$, $\eta > 1eV$, then $(TiO_2)_6$ nanoparticle is considered as tough material.$(TiO_2)_6$ nanoparticleis electrophile, as ε_{LUMO} has negative sign. The stability of ($TiO_2)_6$ nanoparticle is calculated by the following formula:

$\Delta E(Fe_8) = E_{Fe_8} - 4 \cdot E_{Fe_2}$. $\Delta E((TiO_2)_6) = E_{(TiO_2)_6} - 6E_{TiO_2}$

When $\Delta E((\mathrm{TiO}_2)_6) > 0$, the material is considered as unstable material, when $\Delta E((\mathrm{TiO}_2)_6) < 0$, the material considered stable. $E_{(\mathrm{TiO}_2)_6}$ is the calculated total energy of $(TiO_2)_6$ nanoparticle, E_{TiO_2} is the calculated total energy of TiO_2 nanoparticle.

As $E_{(\mathrm{TiO}_2)_6} = -5926.024383 a.u.,$

$E_{TiO_2} = -986.4303 a.u.,$

$\Delta E((TiO_2)_6) = E_{(TiO_2)_6} - 6E_{TiO_2} = -5926.024383 - 6(-986.4303) = -4.557863 a.u.,$

Then $(TiO_2)_6$ nanoparticle is stable, because $\Delta E((\mathrm{TiO}_2)_6) < 0$

5.Conclusion:

Titanium dioxide nanoparticle have been investigated by HFR method. Orbital energies, ionization potential, values of total electron energies, and effective charges of atoms of titanium dioxide nanoparticle have been calculated. The results of calculations show that titanium dioxide nanoparticle is tough, electrophile and stable dielectric material.

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النمذجة الرياضية للتركيب الإلكتروني لجسيمات ثاني أكسيد التيتانيوم $(TiO_2)_6$ النانوية

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الملخص

في هذه الدراسة، تم حساب عدد ذرات الجسيمات النانوية ذات الأبعاد المحددة، والمتكونة من ذرات من أنواع مختلفة. أجريت العمليات الحسابية على جسيمات ثاني أكسيد التيتانيوم النانوية. تم في هذا البحث تصميم النماذج البصرية النظرية، وتم إجراء الحسابات الكمية لجسيمات ثاني أكسيد التيتانيوم النانوية. أجريت العمليات الحسابية لجسيمات ثاني أكسيد التيتانيوم النانوية أستنادًا لمدارات جاوس الذرية، إلى جانب استخدام دوال جاوس كمدارات ذرية. تمكنا من أيجاد القيم العددية للمعاملات المجهولة للتوافق الخطي لمدارات الذرة لجسيمات التيتانيوم النانوية من خلال حل معادلات(HFR). من خلال نتائج هذه الحسابات، استطعنا تحديد قيم الطاقات المدارية، جهد التأين، والطاقة الإلكترونية الكلية لجسيمات ثاني أكسيد التيتانيوم النانوية. بينت الحسابات أن جسيمات ثاني أكسيد التيتانيوم النانوية عبارة عن مواد متينة(صلبة)، مستقبلة لثنائي الالكترون (جاذبة للإلكترونات، electrophile)، ثابتة، وعازلة. كما عملنا على حساب الشحنة الفعالة للذرات، كما تم بناء النموذج البصري النظري لثاني أكسيد التيتانيوم.

الكلمات المفتاحية: تقنية النانو، الحسابات الكمية، نماذج الكمبيوتر، طريقة هارتر-فوك-روثان.