MATHEMATICAL MODELLING OF THE ELECTRON STRUCTURE OF SiO_2 NANOPARTICLE

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The electronic structure of $(SiO_2)_n$ nanoparticles were investigated by non-empirical method. This method is a variant of the molecular orbitals method. Molecular orbitals are represented as a linear combination of atomic orbital's of the atoms of the nanoparticle. The numerical values of the unknown coefficients of the linear combination are found by solution of equations of molecular orbitals. The orbital energies, potential ionization, the total electronic energy of $(SiO_2)_n$ nanoparticles were calculated. The results show that in case of n=1, 2, 3, 4, 6 then the $(SiO_2)_n$ nanoparticles are dialectical, and in case of n=7, 8, 10 и 12 the ones are semi conductive hard, nucleophile and stabile materials.

Key words: computer modeling, nanotechnology, quantum mechanical calculations, non-empirical method.
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INTRODUCTION

$(SiO_2)_n$ nanoparticles due to its properties have been applyed on wide range [1-4], for example, in electronic industry in planar processess for forming electron plates, in military industry for making hard guard covers etc. So, it is very important to investigate of the electron structure of $(SiO_2)_n$ nanoparticle by quantum mechanics method.

From the point of view of electrophysical properties as opposed to volumetric materials the quantum effects play much part in nanosistems, becouse wave functions have hard constraints. In this time the electronic structure of nanoparticles are qualitatively similar to electronic structure of molecules and is consisted of the assembly of discrete states.

Usually, the nanoparticles' electronic structure is differed from the volumetric materials' one, especially near of the range of Fermi level. The metal conductivity materials can turn into the dielectric and semiconductive materials, and the dielectrics can turn into the metals.

During modelling of nanoparticles and nanosystems, first of all, its equilibrium atom structure and form are determined. At this stage it is determined how change of the form and the structure when the volume of nanoparticles is changed. If we know this, then we can simulate an assemblage of nanoparticles and nanosystems. The common method of this procedure is calculation of total energy of the system and searching its minimum.

In our last works [5-8] we have constructed theoretical models of the electronic structures of nanoparticles and nanocomposites.

In [5] the theoretical visual model was constructed for the silver nanoparticles and their nano-composites. These models were investigated by Hartree-Fock-Roothan method. The results of the calculations show that the silver nanoparticles and their PP+Ag_5 and PVDF+Ag_5 nano-composites are tough, nucleophile and stable dielectric materials.

In [6] the electronic structure of the cadmium sulfur CdS nanoparticles were investigated by semi-empirical Wolfsberg – Helmholz method. Molecular orbitals are represented as a linear combination of valence atomic orbitals of the atoms of the nanoparticle. The orbital energies, potential ionization, the total electronic energy and effective charge of atoms of cadmium sulfur nanoparticles were calculated.

By the same method in [7] for Au and in [8] for Ag nanoparticles the electronic structures were investigated. Here, the calculations have been carried out on the basis of Slater functions.

Now, in given paper the electronic structure and properties of the $(SiO_2)_n$ nanoparticle were investigated by non-empirical method [9]. It is implied that this method is most informative and so it is most suitable.

THEORETICAL METHODOLOGY

It is known, that the structure and properties of nanoparticles are determined by number and size of atoms inside one [3]. There are various methods for determination of atom number. Knowing the covalent radius of *Si* and O atoms (r_{Si}=0,111 nm, r_O=0,073 nm – see periodic table [10]) it is possible to determine the approximate radius of sphere where there is one Si and two O atoms. For this, let us use theoretical models of SiO_2 molecule and $(SiO_2)_n$ nanoparticle (fig. 1).

The radius r_h of adopted as sphere form of SiO_2 molecule is determined from ΔACD triangle (or ΔABC)

$$r_h = AC/2 \quad (\text{or } r_h = AB/2)$$

In this right triangle we have

$$AC = \sqrt{AD^2 + CD^2}$$

and

$$AD = 4r_O$$

and

$$CD \approx 2(r_{Si} + r_O)$$

So, $r_h \approx 0{,}24$ nm.

The number of atom in the nanoparticle can be calculated by approximate formula [6]

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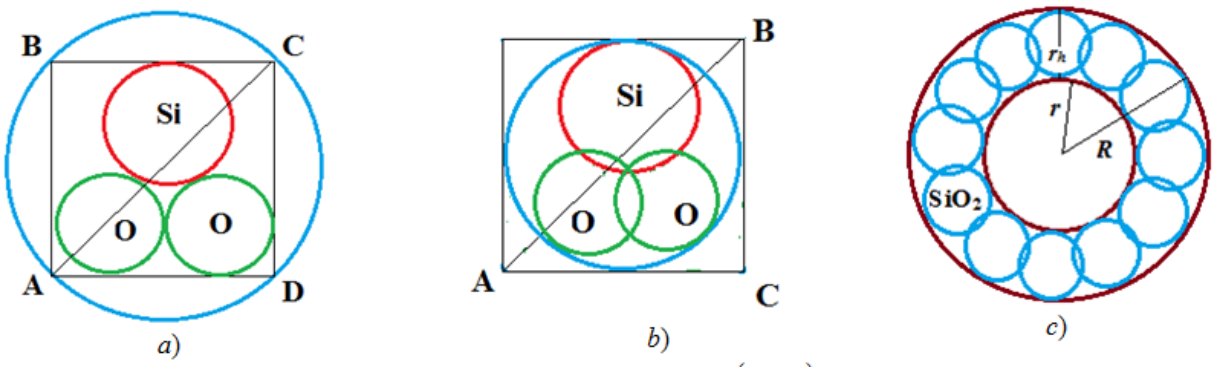

Fig. 1. Theoretical models of SiO_2 molecule (*a* and *b*) and $(SiO_2)_n$ nanoparticle (*c*).

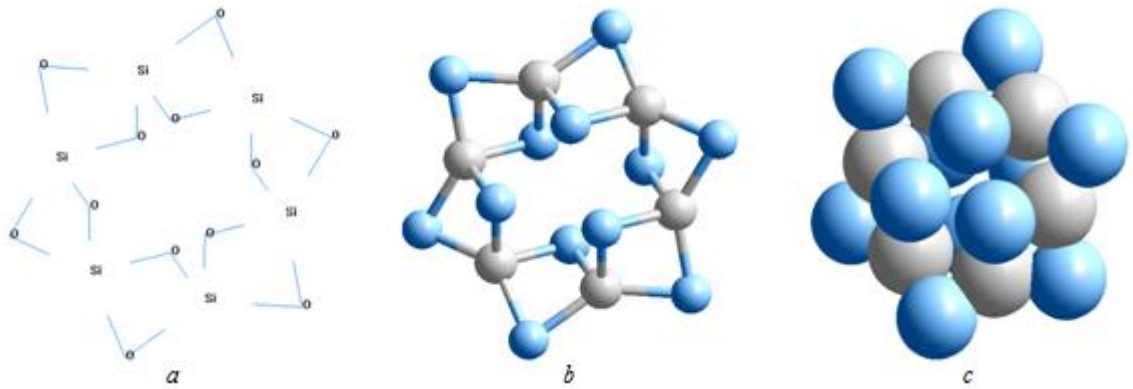

Fig. 2. Various forms models of $(SiO_2)_n$ nanoparticle (n=6, N=18): lines (*a*), lines and spheres (*b*), sphreres (*c*).

$$n = \frac{R^3 - r^3}{r_h^3}$$

Here, r is inter radius of nanoparticle.
If we accept that $r \approx 0$, then

$$n = \left(\frac{R}{r_h}\right)^3$$

Here, R is a radius of adopted as sphere form of (SiO_2) nanoparticle.

If R=0,43 nm then we have n=6. The total number of silicium and oxygen atoms is N=18. Then, the theoretical models of $(SiO_2)_n$ nanoparticle can be constructed by various forms in depended on n (figure 2.). The non-empirical or Hartree-Fock-Roothan (HFR) method is a one of the quantum-mechanical methods used for investigation of quantom levels of nanosystems [5,11,12]. The main idea of this method is that inside a nanosystem the nanoparticle interaction with each other is substituted for some $V(r)$ potential. So, the quantum-mechanical multiparticles' task is substituted for one particle's task and below HFR equations are used for investigation of quantom levels of nanosystems:

$$\sum_{q=1}^{m}(F_{i,pq} - \varepsilon_i S_{pq})c_{qi} = 0, \quad (p = \overline{1,m}) \tag{1}$$

here

$$F_{i,pq} = f_i H_{pq} + \sum_{jk\ell}\sum_{rs} c^*_{rk} c_{s\ell}(2A_{ij,k\ell} J_{prqs} - B_{ij,k\ell} J_{prsq})$$

$$S_{pq} = \int \chi_p \chi_q dV$$

Here: ε_i is orbital energy of the i electron, f_i is a degree of fill of the i level by electrons, c_{qi} are unknown factors, χ_p are basis functions, S_{pq} is overlapping matrix, H_{pq} are one electron matrix elements of Hamilton operator, J_{prqs} and

J_{prsq} are two electron matrix elements, $A_{ij,kl}$ and $B_{ij,kl}$ are the given 4 dimensional matrixes. (1) equations are called HFR ones. The total energy of system is calculated by next formula:

$$E = 2\sum_{ipq} c_{pi}^{*} c_{qi} f_i H_{pq} + \sum_{ijk\ell}\sum_{prqs} c_{pi}^{*} c_{rk}^{*} c_{qj} c_{s\ell} (2A_{ij,k\ell} J_{prqs} - B_{ij,k\ell} J_{prsq})$$

For find of unknown factors c_{qi} we should solve non-linear uniform algebraic equations (1). In this time we adopt that the basis functions χ_p are known. These functions describe electron's states inside the atom. And so, we adopt that the numerical values of S_{pq}, H_{pq}, J_{prqs}, J_{prsq}, $A_{ij,k\ell}$ and $B_{ij,k\ell}$ matrix elements in these equations are known. $F_{i,pq}$ quantities are non-linearly depended on c_{qi} unknown quantities and so, (1) equations' system is a non-linear algebraic one and below these equations' system can be written as matrix form:

$$F \cdot C = E \cdot S \cdot C \qquad (2)$$

Here: E – is a vector of orbital energy of electrons, S is an overlapping matrix, C is a matrix of unknown factors, F is a Fock matrix depended on the matrix elements of unknown C factors. (2) is an equation of generalized eigenvalues.

Using unitary transformation the generalized eigenvalues equation (2) can be transformed to common eigenvalues equation. For this we use V unitary matrix which transforms S matrix to I unit matrix

$$V^T \cdot S \cdot V = I$$

Then

$$X = V^{-1} \cdot C$$

and

$$F' = V^T \cdot F \cdot V$$

Finaly, we obtain eigenvalues equation

$$F' \cdot X = E \cdot X \qquad (3)$$

For solving equation (3) we use method of F' Fock matrix diagonalization. As result, we determine the values of ε_i orbital energies and c_{qi} factors. Now, knowing calculated ε_i and c_{qi} values we can determine total electron energy of system, ionization potential, effective charge of atoms etc.

Should be note, that non-empirical method is one of the molecular orbitals (MO) methods. It is adopted that in MO method each electron in molecule moves in certaine effective field created by atoms and electrons of molecules not depended on other electrons. The electron's state in molecula is described by one electron wave function (molecule orbital). These functions are multicentered ones. That is, its expressions include a distance of electrons from nucleuse of various atoms.

There are various variants of seaching of the molecule's orbites. The MO LCAO method [13,14,15] of the seaching of U_i molecule orbits as the atom's orbits linear combination is one of them:

$$U_i = \sum_{q=1}^{m} c_{qi} \chi_q \qquad (4)$$

Here: c_{qi} are unknown factors, χ_q are atoms' orbits as basis functions.

In (4) equation Gauss functions were used as χ_q atom's orbits [9]. Orbits energies ε_i were calculated for each n. For n=6 state the orbits energies are presented in table 1.

By using ε_i values $(SiO_2)_n$ nanoparticles total electron energy and ionization potential can be calculated, mechanical, electrical, magnetical properties etc. can be investigated.

For calculations we have used Mathcad and HyperChem 7.5 proqrams (free version).

CALCULATIONS FOR $(SiO_2)_n$ NANOPARTICLE AND ANALYSIS

The results of calculations of the orbits energies, ionization potential and total electron energies of $(SiO_2)_n$ nanoparticle are presented in table 2. The electrons of $(SiO_2)_n$ nanoparticle are located on two-two levels beginning on the lowest energy level. The capture by electrons upperst molecul's orbits energy ε_{HOMO} and lowest empty molecul's orbit energy ε_{LUMO} have been determined. Ionization potential of nanoparticle I_p = - ε_{HOMO} and band-gap energy $E_g = \varepsilon_{LUMO} - \varepsilon_{HOMO}$ have been calculated. As seen from table 2, for $(SiO_2)_n$ nanoparticle the minimum value of stabilization parameter is obtained at n=6. In this case, the value of band-gap energy is $E_g = 12{,}890254 eV$. At n=6 it indicates that $(SiO_2)_n$ nanoparticle is a dielectric material. From scientific publications there is E_g = 8-9 eV for SiO_2 [16].

The solidity and radiated photon wave lenght of nanoparticle can be calculated by below formules, respectively [5-8]

$$\eta = \frac{1}{2} E_g \text{ and } \lambda = \frac{c \cdot h}{1{,}6 \cdot E_g} \cdot 10^{28}\ nm.$$

Here: h is Planck's constant, c is a light speed in vacuum. When $\eta < 1eV$ the material is soft, when $\eta > 1eV$ the material is solid. If n=6 then $\eta > 1eV$ and $(SiO_2)_n$ nanoparticle is a solid dielectric material. $(SiO_2)_n$ nanopaerticle is nucleophil because the

lowest empty molecule orbit energy has a positive sign. The stability of $(SiO_2)_n$ nanoparticle is calculated by below formula [5-8]

$$\Delta E\left((\mathrm{SiO}_2)_n\right) = E_{(\mathrm{SiO}_2)_n} - n\cdot\left(E_{Si} + 2E_O\right)$$

If $\Delta E\left((\mathrm{SiO}_2)_n\right) > 0$ then the material is non-stabile, if $\Delta E\left((\mathrm{SiO}_2)_n\right) < 0$ then the material is stable. $(SiO_2)_n$ nanoparticles are non-stable at n = 4, 9, 11 and are stable at n=1, 2, 3, 5, 6, 7, 8, 10, 12. The results are presented in table 2.

Table 1.

The values of *i* orbits energies (*eV*) for $(\mathrm{SiO}_2)_6$ nanoparticle

$i = 1,2,\ldots,30$	$i = 31,32,\ldots,60$	$i = 61,62,\ldots,90$	$i = 91,92,\ldots,114$
-1852.60252	-111.224844	-14.497279	5.449863
-1852.60231	-111.201595	-13.196862	6.559509
-1852.60123	-111.200924	-13.196764	6.560208
-1852.60003	-111.172931	-12.894042	7.942687
-1852.59893	-111.172104	-12.891976	7.944644
-1852.59815	-111.161577	-12.684754	8.507430
-550.261493	-111.150486	-12.398353	8.706767
-550.260576	-111.144948	-12.396422	9.576916
-550.258934	-111.144168	-12.181360	10.545444
-550.258179	-111.122919	-11.187507	10.548156
-550.257061	-111.121919	-11.186590	10.924087
-550.255843	-111.112633	-10.663999	10.928117
-548.973874	-35.017569	-10.567299	12.064183
-548.972954	-34.096239	-10.478238	12.064934
-548.968453	-34.093681	-10.224824	12.751561
-548.967345	-33.272679	-10.222495	12.902745
-548.964483	-33.271238	-9.830077	12.906865
-548.958380	-33.060528	-9.828017	13.089263
-164.977808	-32.424266	-9.732331	16.800189
-164.965241	-32.421465	-9.730517	16.804941
-164.964113	-31.884290	-9.540998	17.134486
-164.942126	-31.881379	-9.287795	18.512019
-164.941026	-31.659088	-9.252553	18.516079
-164.930328	-31.655735	-8.935980	19.950982
-111.304568	-17.167922	-8.932199	
-111.283740	-17.165280	-8.500290	
-111.282658	-16.698655	-8.194362	
-111.250171	-16.695127	-8.190613	
-111.249198	-16.662022	-7.444088	
-111.228622	-16.462190	-7.440391	

Table 2.

The results obtained for $(SiO_2)_n$ nanoparticle

N	Objekt	ε_{HOMO}	ε_{LUMO}	Total energy E (a.u.)	Stable parameter ΔE (a.u.)	Ionizing potential I_p (eV)	Band-gap energy E_g (eV)	Solid parameter η (eV)	Photon wavelength λ (nm)
1	SiO2	-7.46791	5.536341	-433.3548767	-1.642570853	7.46791	13.004251	6.5021255	95.594
2	$(SiO2)_2$	-5.447256	1.681954	-866.4987541	-0.98804751	5.447256	7.12921	3.564605	174.371
3	$(SiO2)_3$	-6.219263	0.466485	-1299.908631	-1.642570853	6.219263	6.685748	3.342874	185.937
4	$(SiO2)_4$	-3.576335	3.535457	-1730.039457	0.981955843	3.576335	7.111792	3.555896	174.798
5	$(SiO2)_5$	-2.687114	1.931155	-2166.265703	-2.488936726	2.687114	4.618269	2.3091345	269.176
6	$(SiO2)_6$	-7.440391	5.449863	-2600.645508	-4.113388277	7.440391	12.890254	6.445127	96.439
7	$(SiO2)_7$	-0.812659	2.463377	-3033.426918	-4.139445511	0.812659	3.276036	1.638018	379.460
8	$(SiO2)_8$	-3.396007	1.618684	-3463.449217	-1.40639056	3.396007	5.014691	2.5073455	247.897
9	$(SiO2)_9$	-2.787062	2.885106	-3893.920946	0.877233848	2.787062	5.672168	2.836084	219.162
10	$(SiO2)_{10}$	-2.040018	2.950686	-4330.165495	-2.611962388	2.040018	4.990704	2.495352	249.088
11	$(SiO2)_{11}$	-3.336001	2.489439	-4757.267161	3.041725181	3.336001	5.82544	2.91272	213.396
12	$(SiO2)_{12}$	-1.228955	2.587575	-5200.237772	-7.17353312	1.228955	3.81653	1.908265	325.721

CONCLUSION

So, the electronic structure of the $(SiO_2)_n$ nanoparticles were investigated by non-empirical method. The results of calculations show that $(SiO_2)_n$ nanioparticle is solid, nucleophil, dielectric material at n=1, 2, 3, 4, 6 and is solid, nucleophil, semiconductive material at n=5, 7, 8, 9, 10, 11, 12. $(SiO_2)_n$ nanoparticles are non-stable at n = 4, 9, 11 and are stable at n=1, 2, 3, 5, 6, 7, 8, 10, 12. These materials can be applied for making various electronic plates and for military covering materials.

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