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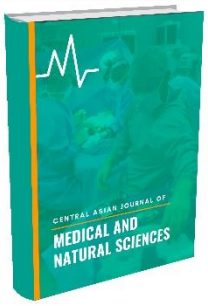

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STUDY OF STRUCTURAL AND ELECTRONIC PROPERTIES OF (ZnO)n (n=10÷30) NANOCLUSTERS USING QUANTUM CHEMICAL METHODS

Usmonova H.[1], Uzokov J.R.[1], Mukhamadiev N.Q.[1], Mukhamadiev A.N.[1]

EMAIL:
hilolausmonova82@gmail.com

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[1]Samarkand state university, Uzbekistan.

ABSTRACT: Quantities such as the structural stability of (ZnO)n (n = 1035) clusters of different geometric configuration, charge transfer effect, electron density distribution in the molecule, distance between atoms and bond angles, and electrophilic index of clusters were calculated. According to it, when the number of atoms in (ZnO)n nanoclusters is increased from 10 to 35, the bond energy (Eb) increases from 40.273 kcal/mol to 71.823 kcal/mol, and the electrophilic index (ώ) increases from 5.16 eV to 7.48 eV. Also, when changing from n = 10 to n = 35 in cluster isomers with different geometric structures, the energy value of the highly occupied region HUMO and the empty molecular region LUMO decreases from 4.42 eV to 3.70 eV, and the width of the forbidden region between them is found to increase from 0.29 nm to 0.68 nm.

KEYWORDS: Nanocluster, (ZnO)n, DFT, basis set, B3LYP/DZVP2, molecular orbital, forbidden region.

INTRODUCTION

Metal oxide clusters and nanomaterials prepared on their basis have seen a significant increase in their fields of application over the last ten years [1-2]. Clusters, quantum dots, and quantum dots of this type have unique physical and chemical properties due to the occurrence of size effects due to factors such as the number of particles, their size, and the interaction between atoms [3-8]. Today, metal oxide nanoclusters with superparamagnetic, high adsorption and photocatalytic activity, semiconducting, and piezoelectric properties are the main object in biomedicine, electronics, energy, and other such fields [9]. Among metal oxide nanoclusters, ZnO has a high potential for making optoelectronic, photoluminescent, diluted magnetic semiconductors, laser diodes, high-efficiency and thin-film transistors, as well as compounds in the field of counter-energetics [10]. Also, most conformational isomers of ZnO nanoclusters have a band gap of 3.36 eV and a high binding exciton gap of 60 meV, making them active in the field of

UB [11–12]. Therefore, clusters of this type are promising for obtaining n-type conductive and laser diodes in the field of optoelectronics. Therefore, determining their properties in (ZnO)n nanoclusters using quantum chemical calculations helps to realize their targeted synthesis [13].

It is known that theoretical calculations were performed on $(ZnO)_n$ nanoclusters with some conformational structures. According to calculations, fullurene-like structures are stable in small molecular mass clusters, and wurtzite conformation structures are stable in high molecular mass clusters. For example, for the $(ZnO)_{34}$ cluster, the frame-core structure, $(ZnO)_2$ square, and $(ZnO)_3$ hexagonal isomers were found to be the most stable. In $(ZnO)_{60}$ clusters, it was determined that the hexagonal hollow sadolite configuration is energetically preferable. These indicators are usually estimated based on calculations of bond energies between atoms in different geometrical structures of $(ZnO)_n$ nanoclusters [14–18].

The purpose of the work is to study the structural and electronic properties of $(ZnO)_n$ (n = 10–30) nanoclusters using quantum chemical methods.

CALCULATION METHODS

The Gaussian 09 and HyperChem programs were used for quantum chemical evaluation of the physical and chemical characteristics of $(ZnO)_n$ (n = 10-35) clusters. Optimization of the geometric structure of clusters and various physical Chemical properties were evaluated using the B3LYP (Lee-Yang-Parr) hybrid functional basis set with the LANL2DZ set of density functional theory (TDDFT). Also, the linear combination of atomic orbitals (LCAO) was used in the calculations in the systematic study of molecular orbitals of nanoclusters.

RESULTS AND DISCUSSION

In the quantum chemical calculations of single-layer structures of (ZnO)n (n = 10-35) clusters, molecular geometry optimization and energy calculation were performed using the B3LYP/DZVP2 method. Because the minimum energy of clusters using CCSD(T) can be calculated using semi-quantitative methods, calculations using the B3LYP method can calculate 2D structures with an accuracy of 5-6 kJ/mol when compared to 3D structured clusters. Therefore, the B3LYP method is acceptable for calculating the minimum energy of relatively polyatomic clusters. The optimized geometric structures of $(ZnO)_n$ (n = 10–35) clusters were determined (Fig. 1). Also, various geometrical parameters of stable structural isomers of clusters (bond length, bond angle, bond energy) were calculated (Table 1).

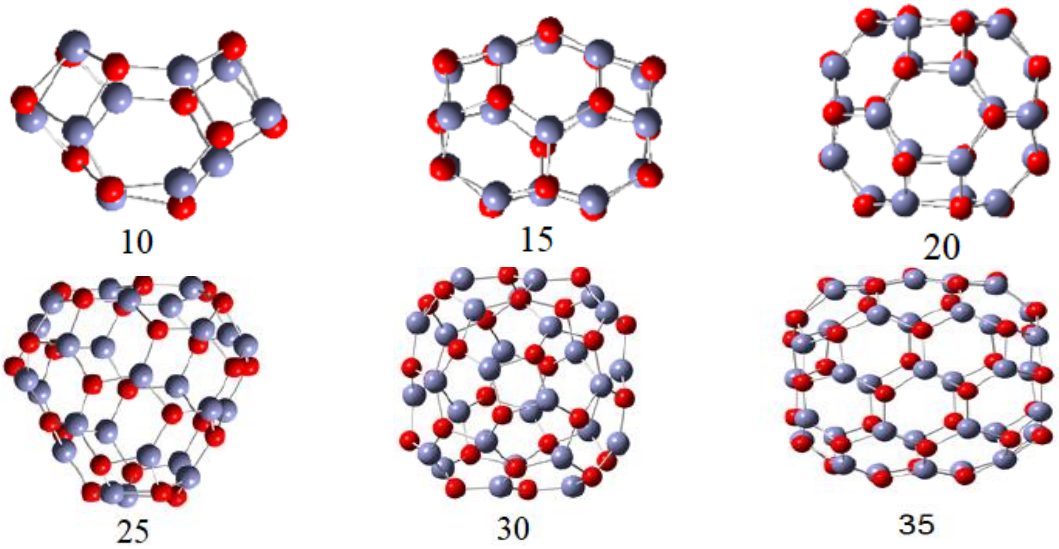

Figure 1. Geometric structures of optimized $(ZnO)_n$ (n = 10–35) nanoclusters

Table 1

The value obtained by quantum chemical calculation of various physical quantities in $(ZnO)_n$ (n = 10-35) clusters

n	Zn-O bond length (A°)	The corner of connections		The energy of connection (kcal mol)	Dipole moments (D)
		< O-Zn-O	< Zn-O-Zn		
10	1,824 ÷ 2,138	90,2÷143,8	82,2÷115,6	40,273	7,412
15	1,883 ÷ 2,064	88,8÷134,9	86,6÷108,2	48,129	7,854
20	1,886 ÷ 1,993	89,1÷157,5	83,9÷113,3	52,416	7,215
25	1,936 ÷ 1,959	90,7÷133,8	86,5÷112,5	59,358	8,042
30	1,881 ÷ 2,045	91,9÷131,2	82,5÷121,9	65,414	8,148
35	1,877 ÷ 1,993	90,7÷134,7	85,6÷116,4	71,823	6,896

According to the results of quantum chemical calculations, it was found that the one-layer hollow tetragonal structural isomer of the $(ZnO)_{10}$ cluster is stable. In this isomer, it was determined that the total bond energy value is E = 40,273 kcal/mol, the Zn-O bond length is 2,138, and the O-Zn-O bond angle is 90.2°. Also, the fullurin structural, i.e., hexagonal isomers, in $(ZnO)_{15}$ and $(ZnO)_{20}$ clusters are energetically stable, and the Zn-O bond length in the $(ZnO)_{15}$ cluster is 1.883 A°, and the O-Zn-O bond angle is 88.8° was determined to have value. It was discovered that isomers of $(ZnO)_{25}$, $(ZnO)_{30}$, and $(ZnO)_{35}$ clusters with one-layer octahedral and one-layer decagonal structures are stable. In the $(ZnO)_{35}$ nanocluster, the Zn-O bond length is 1.877 and the bond energy is 71.823 kcal/mol. From this, it can be observed that with an increasing number of atoms in $(ZnO)_n$ clusters, stable structural isomers are formed.

In addition, the chemical potential (μ), electrophilic index (ώ), ionization potential (σ), and total energy (E) of the $(ZnO)_n$ nanoclusters were calculated using the DFT/B3LYP/6-31G**(p, d)) method (2-table).

Table 2

Energy sizes of $(ZnO)_n$ (n = 10-35) clusters

n	μ (eV)	ώ (eV)	σ (eV)	E (eV)
10	-3,345±0,25	1,92±0,24	0,462±0,01	5,16
15	-5,816±0,19	1,90±0,12	0,206±0,04	5,78
20	-10,44±0,45	1,84±0,14	0,186±0,09	6,12
25	-2,565±0,38	1,76±0,10	0,513±0,05	6,24
30	-6,420±0,84	1,62±0,18	0,196±0,05	6,84
35	-8,48±0,23	1,33±0,12	0,173±0,07	7,48

An increase in the number of atoms in clusters with different morphologies led to an increase in the electrophilic index. The increase in the electrophilic index indicates the high reactivity of $(ZnO)_{30}$ and $(ZnO)_{35}$ clusters.

In order to characterize the forbidden zone (energy gap) of electronic and molecular orbitals in clusters, it is important to determine the energy ranges where no electronic states exist [19–23]. This is related to the energy of the ground and excited the atoms in the cluster's highly occupied state (HUMO) and unoccupied molecular orbital (LUMO) [24-27]. Therefore, the UV-VIS absorption spectra of ZnO

clusters appear due to electrons excited from the HUMO to the high-energy LUMO. Figure 2 depicts the electronic states HUMO and LUMO orbital energies for $(ZnO)_n$ (n = 10-35) clusters.

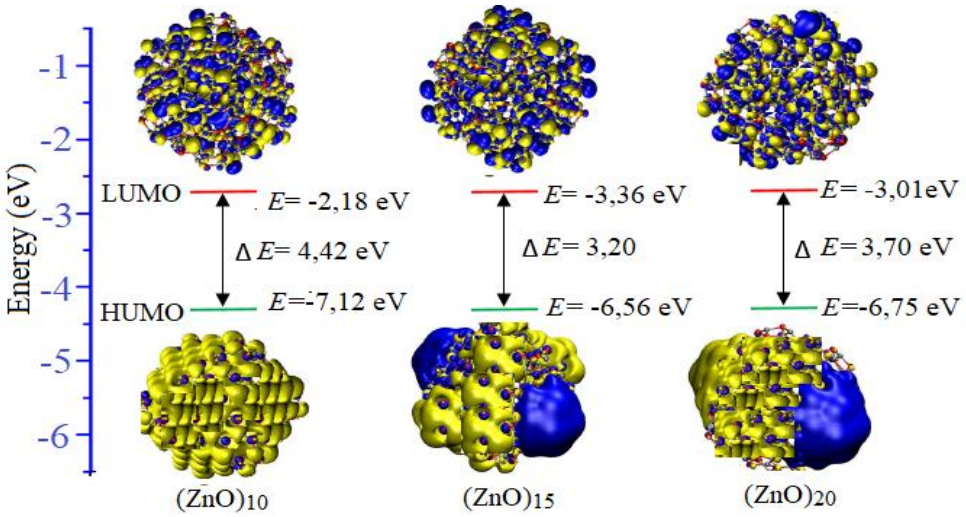

Figure 2. Values of LUMO and HUMO MOs in $(ZnO)_{10}$, $(ZnO)_{15}$, and $(ZnO)_{20}$ clusters calculated by the B3LYP/DZVP2 program

The gap energy between these orbitals changes as the number of atoms changes. When changing from n = 10 to n = 35 in cluster isomers with different geometrical structures, the forbidden region energy changes from 4.42 eV to 3.22 eV due to the 3d orbitals of Zn atoms, and 2p orbitals of O atoms, and the energy change in the conduction bands from 3.256 eV to 4.158 eV is due to Zn; it was determined that it is created due to the 4s, 2s, and 2r orbitals of O atoms.

It is clear that the energy difference between HUMO and LUMO (EHUMO-ELUMO) gives the energy of the forbidden region between them. When n=10, for example, the HOMO energy is E = - 0.166 a. u. and the LUMO energy is E = - 0.33 a, with a free energy of 0.167 a. $_U$. X 27.211 = 4.5 eV.

Also, it was found that the width of the forbidden zone, which describes the surface energy and optical properties, increases with the increase in the number of atoms in $(ZnO)_n$ nanoclusters calculated by the B3LYP/DZVP2 density functional method. It was found that the width of the forbidden zone is 0.293 nm depending on the variation of the width of the valence region and conduction regions with a tetragonal geometric structure $(ZnO)_{35}$, and this value increases to 0.687 nm, i.e. 2.4 times, in the isomer of $(ZnO)_{35}$ with an octahedral structure (Fig. 3).

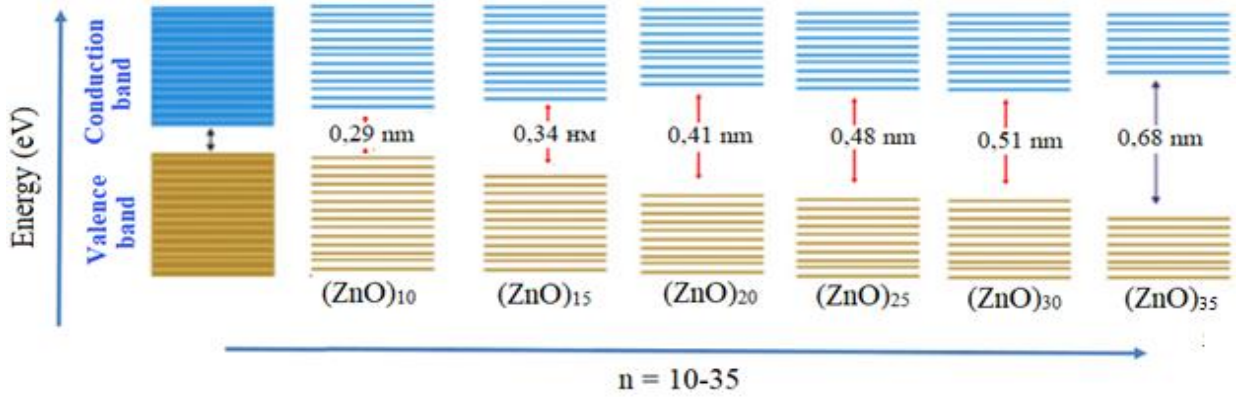

Figure 3: Band gap width values in $(ZnO)_n$ clusters

It can be seen from the three-dimensional graph in Fig. 4 that with the increase in the number of atoms in $(ZnO)_n$ clusters with different geometric structures, the energy of their valence regions increases, which leads to an increase in the width of the forbidden region.

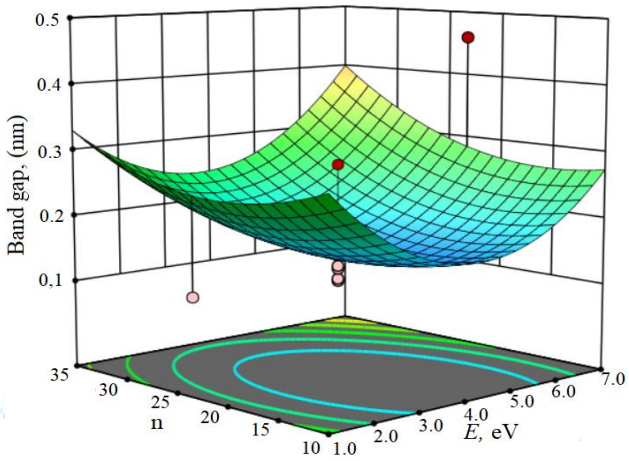

Figure 4: Band-gap energy in $(ZnO)_n$ clusters dependence on the number of cluster atoms

From the figure, it can be observed that with the increase in the number of atoms in the clusters, the energy of frontier molecular orbitals, i.e., HUMO and LUMO, decreases and the width of the forbidden region between them increases.

SUMMARY

1. Quantum chemical calculations were performed on $(ZnO)_n$ nanoclusters with different geometric structures using the Gaussian software package using the density functional theory (TDDFT) method using the B3LYP/DZVP2 hybrid basis set.
2. When the number of atoms is increased from 10 to 35, the bond energy (E_b) increases from 40.273 kcal/mol to 71.823 kcal/mol, and the electrophilic index () increases from 5.16 eV to 7.48 eV.
3. When changing from n = 10 to n = 35 in cluster isomers with different geometric structures, the energy value of the highly occupied region HUMO and the empty molecular region LUMO decreases from 4.42 eV to 3.70 eV, and the width of the forbidden zone between them is found to increase from 0.29 nm to 0.68 nm..

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