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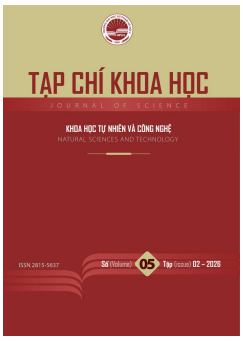

Article type: Research article

A first-principles study on the structural and electronic properties of ZnO clusters

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Abstract

This work presents a first-principles study of the structural, energetic, and electronic properties of $(ZnO)_n$ clusters with n =1 ÷ 10. Various low-energy isomers were constructed and fully optimized using density functional theory within the DMol3 framework with the GGA–PBE functional. The most stable geometries were identified based on total energy calculations. The results reveal a clear size-dependent structural evolution: small clusters ($n \leq 7$) favor planar or ring-like geometries, while larger clusters ($n \geq 8$) adopt compact three-dimensional configurations with higher symmetry. The calculated average binding energy increases with cluster size, indicating enhanced stability and a tendency for cluster growth. Electronic structure analysis shows that the valence band is mainly contributed by O-2p states, whereas the conduction band is primarily derived from Zn orbitals, confirming the semiconducting nature of the clusters. Charge density difference analysis indicates electron transfer from Zn to O atoms, suggesting strong Zn–O bonding with significant covalent character in these clusters.

Keywords: ZnO clusters, ab-initio calculation, stable structures, binding energy, electronic structures

1. Introduction

Zinc oxide (ZnO) is an interesting semiconductor material due to its novel physical and chemical properties such as wide and direct bandgap, high refractive index, high thermal conductivity, high electron mobility [1]. These properties have enabled the successful synthesis of ZnO nanomaterial to be prepared via different synthetic strategies, including sol–gel [2] and hydrothermal methods [3], leading to their use in food processing, medicine and more [4]–[7]. Recently, ZnO has attracted increasing interest in environmental applications to degrade organic compounds such as methyl orange (MO) [8] or methylene blue (MB) [9], [10].

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https://doi.org/10.56764/hpu2.jos.2026.5.2.84-93

Received date: 26-02-2026 ; Revised date: 07-6-2026 ; Accepted date: 07-8-2026

However, the large band-gap value of ZnO limits its photocatalytic behaviour under visible light irradiation. Common strategies to enhance the photocatalytic activities of ZnO include doping with suitable elements [11], [12] and forming composites with specific materials [13], [14]. Although effective, these approaches are often costly and involve time-consuming preparation procedures. Density functional theory (DFT) can be used as a cost-effective way to predict the electronic properties and photocatalytic activity of modified ZnO prior to synthesis.

Models of ZnO doped with other elements have been developed and calculated by many research groups worldwide, while composite material models between ZnO and other materials have not been extensively studied. To elucidate the effect of composite materials on the physical and chemical properties of ZnO, it is necessary to develop and select fundamental building blocks to serve as the basis for the composite material models, and the choice is (ZnO)n clusters. These clusters have been created and studied by various software such as SIESTA [15], Gaussian98 [16], FHI-aims [17] or MHM [18] and more [19]. Cheng et al. [16] reported that for small clusters with $\boldsymbol{n} \leq 5$, the ring-shaped structures are energetically favored, whereas for larger clusters with $\boldsymbol{n} \geq 6$, the three-dimensional structures are more stable, in good agreement with Sarsari et al. [17]. Zhao et al. [20], using DMol3 to investigate the stability of (ZnO)n clusters ($\boldsymbol{n}$ = 2 ÷ 18) and obtained similar results. In contrast, Balasaheb et al. [21] prove that the ring-shapes are stable for all (ZnO)n clusters with $\boldsymbol{n} \leq 8$.

These inconsistent conclusions regarding the most stable geometries of small ZnO clusters make it difficult to select appropriate cluster models for further investigations, particularly for time-dependent DFT (TDDFT) calculations of optical and photocatalytic properties. Therefore, a systematic and consistent study of the structural stability of small (ZnO)n clusters is necessary.

In this work, all (ZnO)n clusters with n = 2 ÷ 10 are systematically investigated using the DMol3 package. The most stable geometrical configurations are identified based on total energy calculations. The obtained stable cluster models provide a reliable structural foundation for subsequent TDDFT calculations aimed at predicting the optical response and photocatalytic activity of modified ZnO-based nanomaterials.

2. Computational Methods

First-principles calculations were carried out using the DMol3 [22] computational package, which is based on density functional theory (DFT) and employs numerical atomic basis sets to describe the electronic wave functions. The exchange–correlation potential was treated within the generalized gradient approximation (GGA) as implemented in the Perdew–Burke–Ernzerhof (PBE) functional [23], which has been widely applied in the investigation of metal oxide nanostructures.

To represent valence electrons - ionic cores interactions, the density functional semi-core pseudopotential (DSPP) method [24] was adopted. In the present calculations, the valence electron configurations were taken as 4s2 for Zn atoms and 2p4 for O atoms. The Brillouin zone integration was performed using a Monkhorst–Pack [25] k-point grid of 2×2×1.

Geometry optimizations were conducted without imposing symmetry constraints, allowing all atoms to relax freely around their original positions until the convergence criteria were satisfied. The convergence threshold for self-consistent field calculations was set at 10−6 eV. During the structural relaxation process, the change in maximum force, maximum atomic displacement, and energy change were set to 1×10−5 Ha/atom, 2×10−3 Ha/Å, and 5×10−3 Å, respectively.

These computational settings ensure reliable optimization of the cluster geometries and provide accurate evaluations of the geometrical shapes and electronic properties of the investigated $(ZnO)_n$ systems.

3. Results and discussion

3.1. Structural Properties

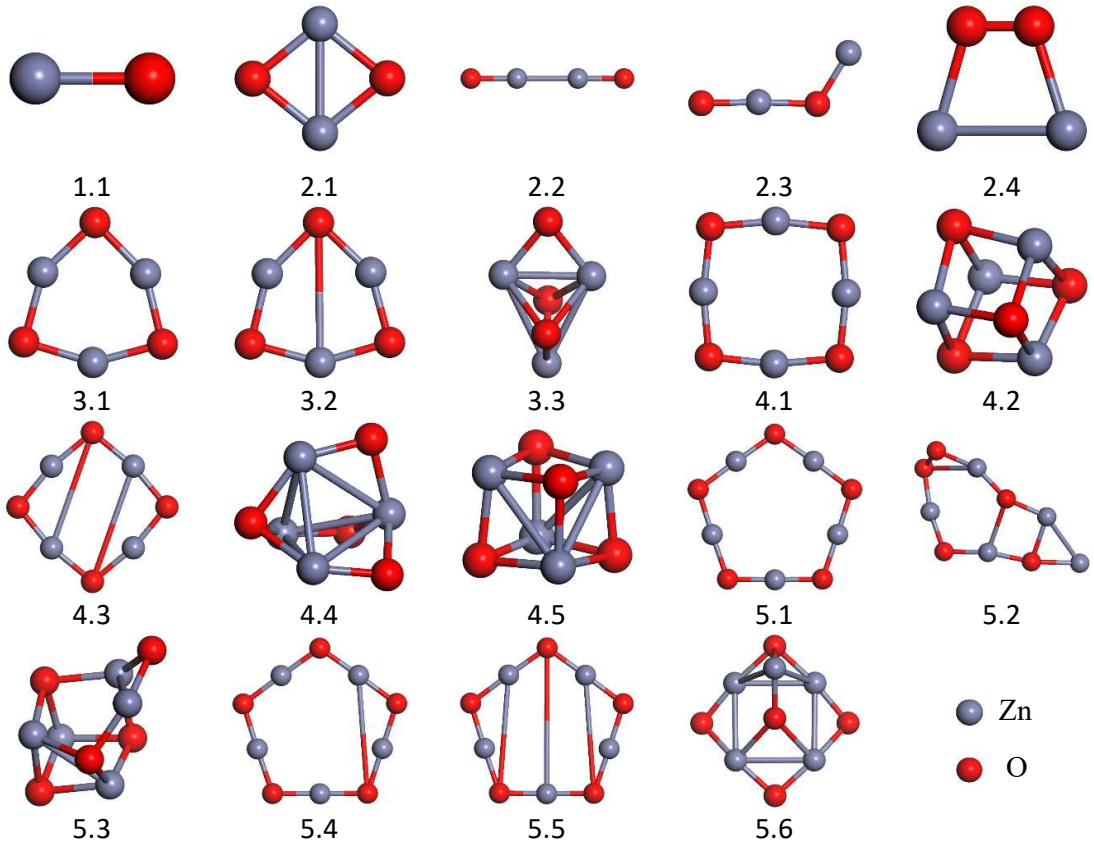

Figure 1. Optimized considered structures of (ZnO)n clusters with n = 1÷5.

A systematic and exhaustive structural investigation was performed to find all plausible low-energy isomers of $(ZnO)_n$ clusters with n = 1÷10. For small clusters with n ≤ 5, a total of 19 structures were created and optimized, as shown in Figure 1, including one structure for n = 1, four for n = 2, three for n = 3, five for n = 4, and six for n = 5.

For larger clusters with n = 6÷10, the total number of isomers was extended to 24, their geometrical structures are presented in Figure 2. The number of considered structures is five for n = 6, four for n = 7, six for n = 8, four for n = 9, and five for n = 10. All clusters were subjected to full geometry optimization, and their relative stabilities were evaluated based on total energy comparisons to reliably identify the most stable configurations for each cluster size.

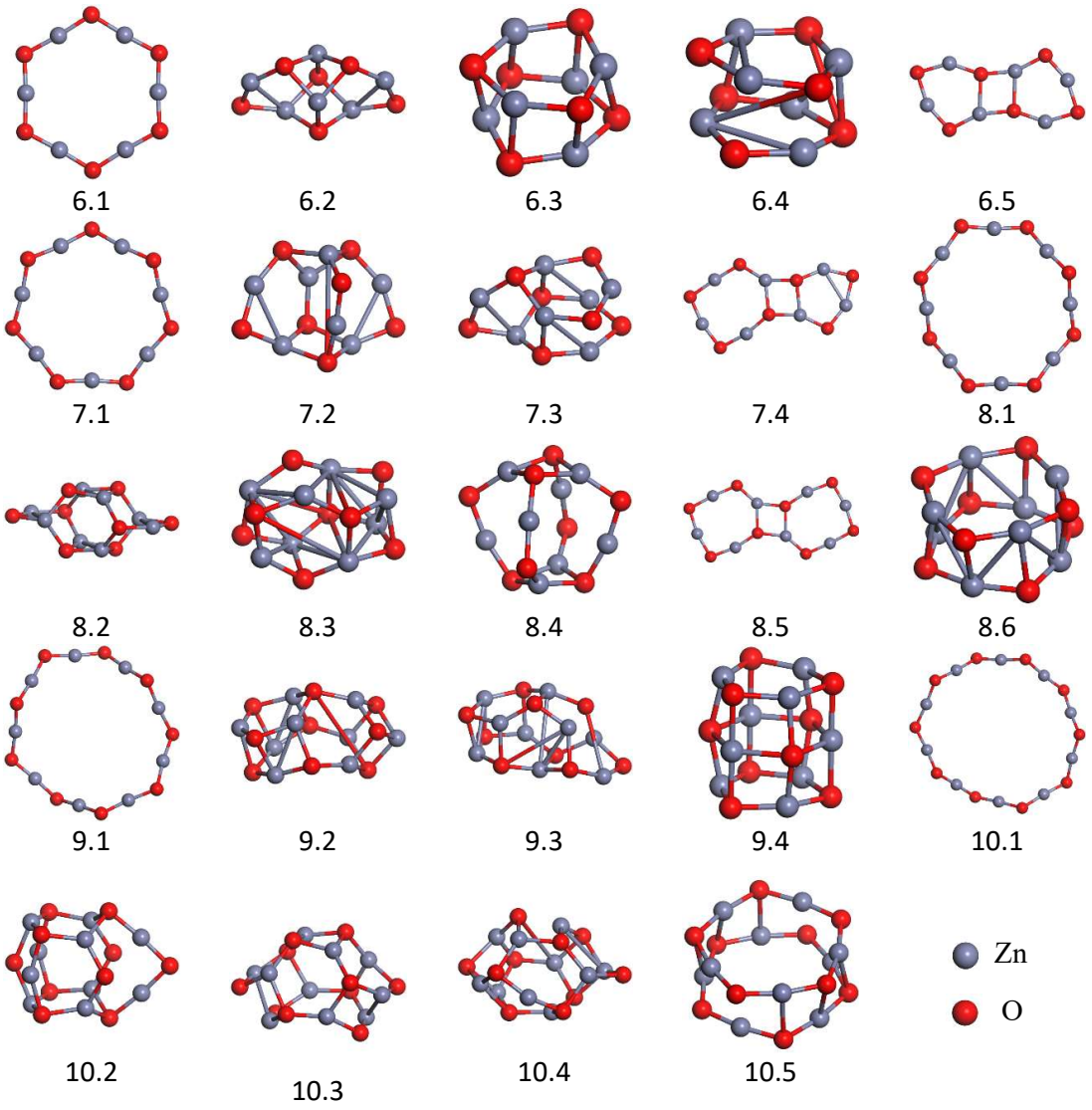

Figure 2. Optimized considered structures s of $(ZnO)_n$ clusters with $\boldsymbol{n}$ = 6÷10.

To distinguish the stable structures for each cluster size $\boldsymbol{n}$, the total energies of all considered $(ZnO)_n$ clusters were calculated using DMol3, the results were shown in Figure 3. For n = 3, 4 and 5, more than one structure exhibits very small total energy differences, and the one with lowest total energy and highest symmetry was chosen, as marked by red dash circles in Figure 3. For $n \leq 7$, the most stable structures have the ring-like shapes, whereas for $n \geq 8$, the stable configurations become more complex 3-dimensional forms, which is consistent with previous studies [21]. All selected isomers, as shown in Figure 4, generally possess higher symmetry compared to other isomers. This trend can be used as a guideline for predicting stable geometries of larger $(ZnO)_n$ clusters.

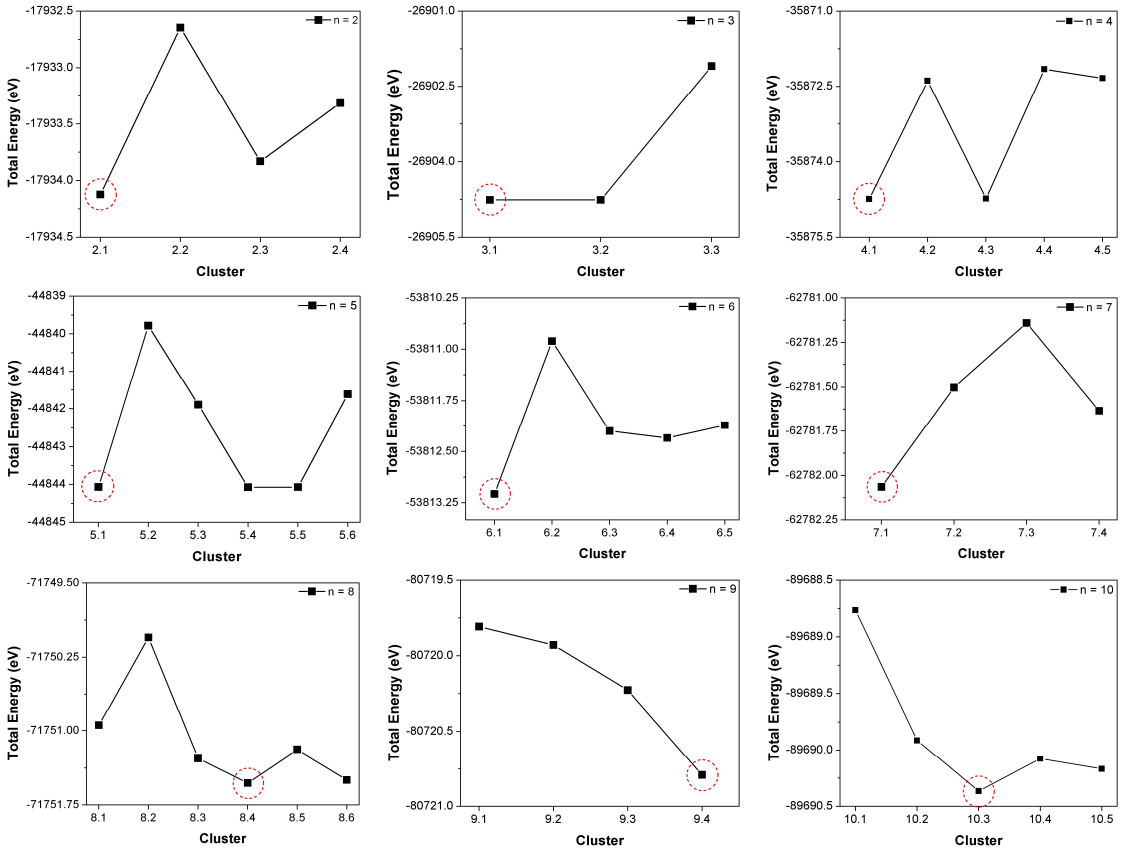

Figure 3. Calculated total energies of $(ZnO)_n$ clusters with $\boldsymbol{n}$ = 1÷10 and the most stable models (marked by red dash circles).

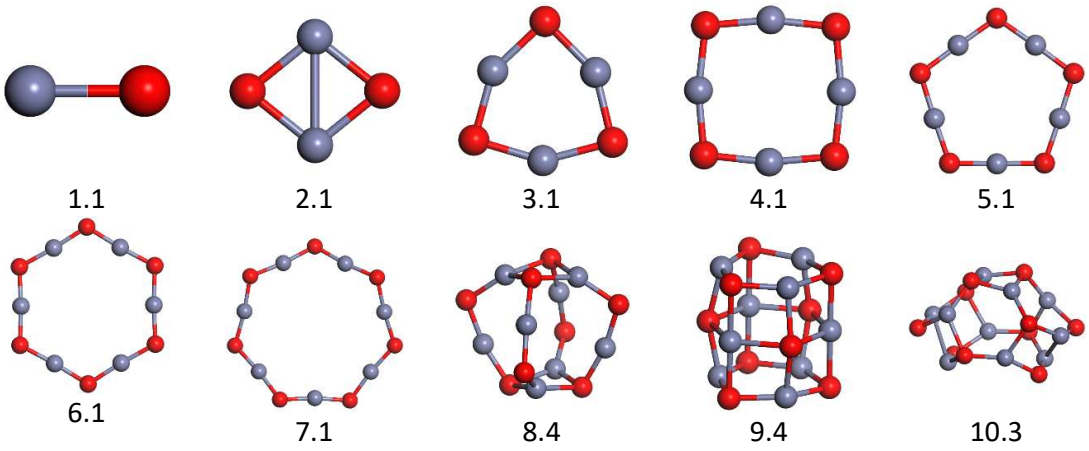

Figure 4. The most stable configurations of $(ZnO)_n$ clusters with $\boldsymbol{n}$ = 1÷10.

3.2. Binding Energies of ZnO Clusters

The calculated data presented in Figure 3 show the lowest total energy structures of ZnO clusters for each cluster size *n* from 1 to 10. To clarify the formation trend of ZnO clusters, the average binding energy of the most favorable $(ZnO)_n$ cluster with n = 1÷10 was evaluated using following expression [26]

$$BE(n) = \frac{nE_{Zn} + nE_O - E_n}{n} \quad (1)$$

where E_{Zn} is the energy of a free Zn atom in the bulk form, E_O represents the energy of a single oxygen atom derived from the total energy of an isolated O_2 molecule and E_n corresponds to the total energy of the considered cluster, was calculated and presented in Figure 3. The reference energy E_{Zn} was calculated from a single Zn atom in bulk Zn, while E_O was derived from the total energy of a free O_2 molecule. The resulting reference energies are −6923.1410 eV and -2048.4620 eV for Zn and O, respectively.

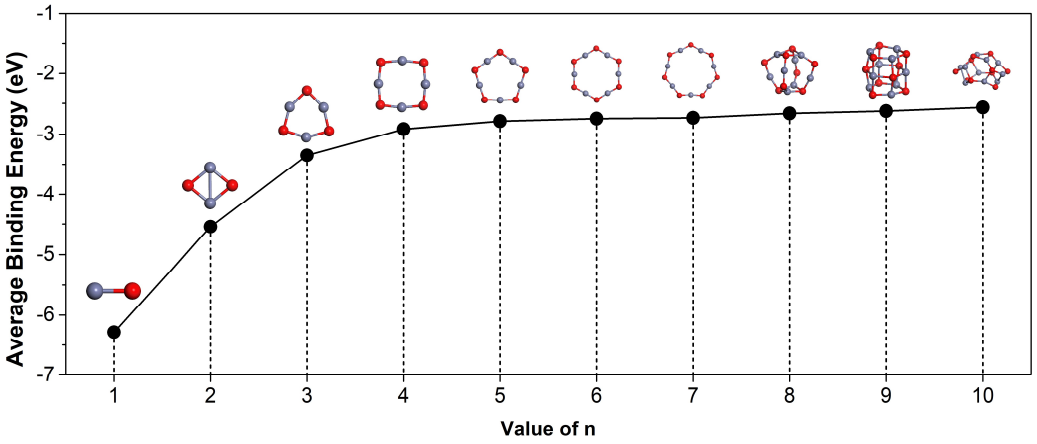

Figure 5. The average binding energies of ZnO clusters (***n*** = 1÷10) and corresponding stable structures.

Figure 5 shows the variation of the average binding energy per formula unit as a function of cluster size *n* for the most stable $(ZnO)_n$ clusters. The average binding energy increases rapidly from n = 1 to n = 3, indicating a significant enhancement in structural stability with increasing cluster size. This behavior can be attributed to the increasing number of Zn–O bonds and improved atomic coordination as the clusters grow.

For n ≥ 4, the increase in average binding energy becomes more gradual and tends to saturate, suggesting that the clusters are approaching a high stable bonding form and exhibiting bulk-like characteristics. This trend is consistent with the structural evolution observed in Figure 4, whereas small clusters with n ≤ 7 favor ring-like geometries, and larger clusters (n ≥ 8) have more complex three-dimensional structures. The increase in average binding energy with cluster size n confirms that larger $(ZnO)_n$ configurations are more energetically stable than smaller clusters, suggesting the appropriate cluster size selection for future simulations of composite ZnO materials.

3.3. Electronic Structures

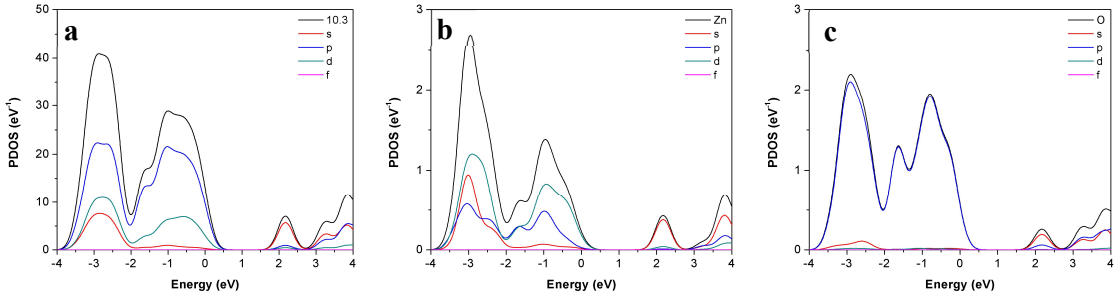

Figure 6. (a) Total density of states and (b,c) projected density of states Zn and O atoms in $(ZnO)_{10}$ clusters.

Figure 6 presents the total density of states (TDOS) and the projected density of states (PDOS) of Zn and O atoms for the stable $(ZnO)_{10}$ cluster, indicating a close relation with the structural stability and energetic trends discussed above. As shown in Figures 3 and 4, the $(ZnO)_{10}$ cluster has a highly symmetric and compact three-dimensional geometry, which was identified as the most stable configuration among the considered isomers. The structural stability of this cluster is confirmed by its high average bond energy value as shown in Figure 5.

The high symmetry and increased atomic coordination in the $(ZnO)_{10}$ cluster lead to strong orbital hybridization between Zn and O atoms, as evidenced by the PDOS analysis in Figure 6. In particular, the dominant contribution of O-2p states to the valence band and Zn-3d states at lower energies reflects strong Zn–O bonding, which is consistent with the monotonic increase in binding energy with cluster size. Meanwhile, the Zn-4s and Zn-4p states forming the conduction band indicate that the electronic structure is mainly governed by Zn states at higher energies.

Moreover, the absence of states at the Fermi level confirms the semiconducting nature of the cluster, suggesting that the enhanced energetic stability of larger clusters ($n \geq 8$) is accompanied by the opening of a clear energy gap. This behavior can be attributed to the transition from ring-like to more compact three-dimensional structures, which reduces structural distortions and stabilizes the electronic states.

Furthermore, the absence of Fermi-level states indicates that $(ZnO)_{10}$ exhibits semiconducting properties, suggesting that the overall energy stability of large clusters ($n \geqslant 8$) leads to the formation of band-gaps in their energy range. This may be due to a transition from a ring-like structure to a more compact three-dimensional structure, which minimizes structural distortion and stabilizes electronic states.

Overall, the density of states analysis results provides clear evidence for the support of electronic structure for the energy and structure transformation trends discussed in previous sections, demonstrating that the increased stability of larger $(ZnO)_n$ clusters stems from both geometric optimization and enhanced Zn–O bonding.

3.4. Charge Distribution in ZnO Clusters

To gain inside into the Zn-O bonding characteristics in ZnO clusters, the charge density differences of each $(ZnO)_n$ clusters were calculated using the following expression.

$$\Delta\rho = \rho_c - \rho_{Zn} - \rho_O \tag{2}$$

where $\Delta\rho$ is the charge difference; ρ_c, ρ_{Zn} and ρ_O are the charge density of ZnO clusters, Zn atoms and O atoms, respectively.

The calculated charge density difference maps are shown in Figure 7, where the red regions represent charge accumulation and the blues indicate charge depletion. It can be seen that electron densities around Zn atoms decrease, whereas it increases around O atoms, indicating a charge transfer from Zn to O atoms and the formation of Zn-O covalence bonds. In particular, for the $(ZnO)_1$ cluster, the spatial distributions of the depletion and accumulation regions resemble the Zn 4s and O 2p orbitals, respectively, suggesting that electrons are transferred from the Zn 4s orbital to the O 2p orbital during bond formation.

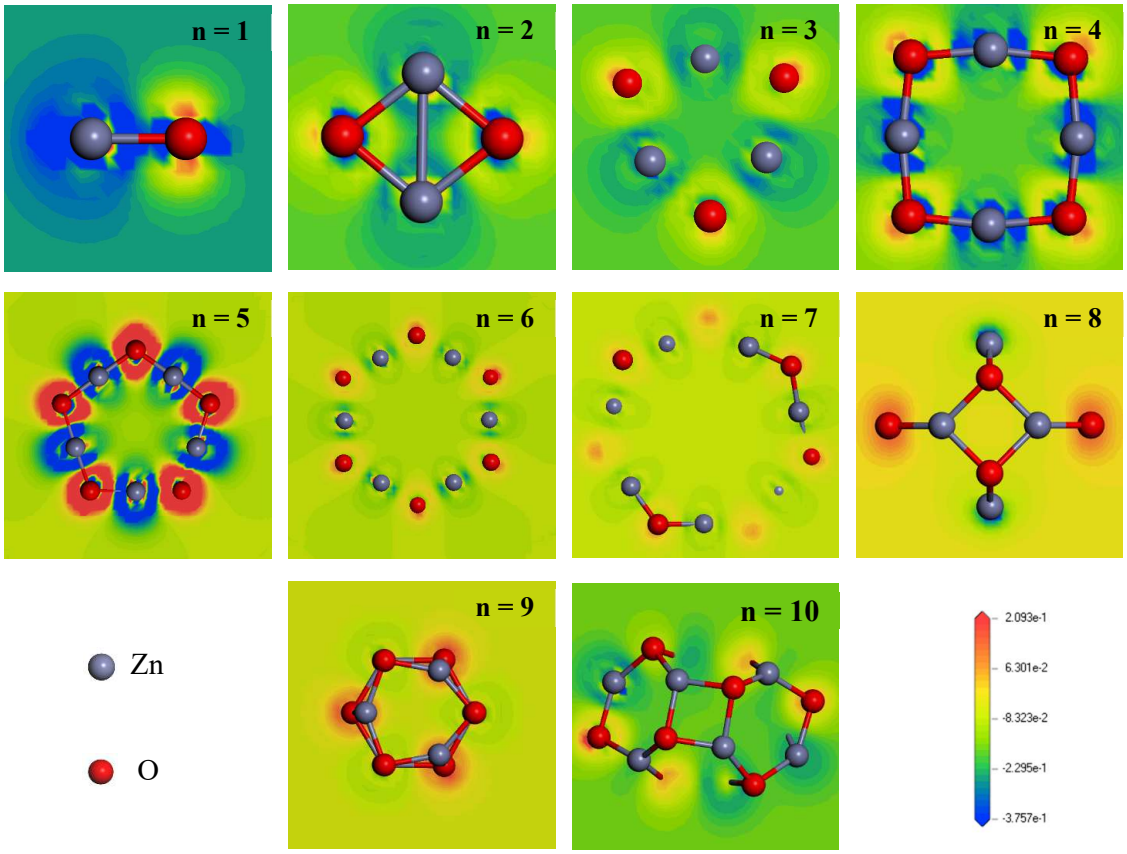

Figure 7. Charge density difference of stable $(ZnO)_n$ clusters.

4. Conclusion

In this work, a systematic ab-initio investigation of $(ZnO)_n$ clusters (n = 1÷10) has been carried out to interpret the dependence of structural, energetic, and electronic properties on their size. The results reveal a clear transition in structure of clusters, from planar or ring-like geometries for small clusters ($n \leq 7$) to more compact three-dimensional configurations for larger clusters ($n \geq 8$), accompanied by enhanced symmetry and stability. This structural evolution leads to a gradual decrease in total energy and a corresponding increase in average binding energy with increasing cluster size. All stable clusters exhibit semiconducting behavior, with valence bands dominated by O-2p states and conduction bands mainly derived from Zn orbitals. Charge density difference analyses confirm a significant charge transfer from Zn to O and an increase in charge redistribution in larger clusters, indicating strengthened Zn–O bonding when the cluster's size increases. Overall, the enhanced stability of larger $(ZnO)_n$ clusters originates from the combination of three different effects: geometric optimization, increased atomic coordination, and reinforced Zn–O interactions, providing valuable insights for understanding the evolution of ZnO nanostructures from molecular clusters toward the bulk limit.

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