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FIRST PRINCIPLE STUDY OF STRUCTURAL, ELECTRONIC AND OPTICAL PROPERTIES OF ZnO QUANTUM DOTS

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ABSTRACT

ZnO quantum dots (ZQD) has been simulated and optimized using the First principle Density Functional (DFT) approach and calculations were performed to investigate its structural, electronic and optical properties. Structural bond length, electronic orbital behavior and optical responses were studied to have a better understanding of the system. Density of states (DOS), partial density of states (PDOS) and charge density study were also carried out. The optical properties of ZQD have been investigated, and compared with planar hexagonal structure of ZnO. The ZQD yielded a well near reported values of bond length and energy values done previously. The optical properties helped to understand the UV region emission and simulation is found to be very much compatible with the theories of solid state physics. Optical conduction is observed in the UV region of the absorption characteristics, which point towards its photovoltaic application. The work aims at revealing the optoelectronic properties of ZQDs based on DFT study. It will encourage ZQD related transport studies and luminescent applications.

Keywords: Quantum dots, Electronic structure, Density Functional Theory, Nanostructures

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I. INTRODUCTION

ZnO had been a topic of research and of wide commercial use since last 100 years. ZnO is found to have application in wide range of fields starting from nanowires [1], transparent conducting films[2], to that of optical[3] and luminescence[4], Hao Ming Chen et. al. reported the ZnO Nanowire-Array Photoelectrodes for water splitting[5], gas sensing properties of ZnO quantum dots has been reported[6], ZnO quantum dot based immune-sensors was explained by Baoxian Gu[7], White-LEDs [8] etc. The flexibility of ZnO for application in different fields opens a wide area of interest for the researchers. The simulation based study of ZnO has also pawed a way for the investigation of the intrinsic properties of the semiconductor. LDA and GGA functional based study has been done for ZnO and MgO by John E. Jaffe et. al.[9]. Paul Erhart et. al. investigated the role of band structure, volume relaxation, and finite-size effects for point defects in ZnO[10]. Baolin Wang et. al. made a theoretical study on the Structural Growth Sequences and Electronic Properties of Zinc Oxide Clusters[11]. S.Q. Wang made a comparative first-principles study of ZnS and ZnO in zinc blend structures[12].

Chun Li et. al. studied ZnO nanoclusters with hexagonal prism structures[13], while study on LDA+U functional based study on bonding mechanism of ZnO was made by G.C. Zhou et. al.[14]. M. Topsakal et. al. reported the first-principles study of zinc oxide honeycomb structures[15]. A. Dominguez et. al, studied the anchor groups on ZnO nanowires and surfaces[16].

Bulk ZnO exhibits a wide direct band gap of 3.3 eV with an exciton binding energy of ~60 meV. ZnO quantum dots exhibit quantum confinement effect as a result of which the bulk properties can be tailored to make varied applications in different fields from sensors to optoelectronic luminescent materials[17,18]. One of the theoretical studies also includes DFT based study of ZnO nanostructure adopting Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA) correlation function. So far Density Functional based electronic and optical study of ZnO quantum dots has been scarcely reported, so this kind of work is needed to generate sufficient data in this field and to support further research in this field.

II. COMPUTATIONAL ASPECTS

In this study we have used SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) programme for the simulation and optimization of the ZQD structure. SIESTA is a computer programme to perform efficient electronic calculation and ab-initio molecular dynamics simulation of molecules and solids [19,20]. It adopts density functional method using standard norm-conserving pseudopotenstial and a flexible, numerical linear combination of atomic orbitals basis set, and includes multiple-zeta and polarization orbitals. The interaction are governed by LDA or GGA correlation functions[21]. The whole system was optimized following all essential steps viz mesh-cutoff, k-point, lattice-optimization etc. The norm–conserving pseudo-potentials were constructed for each chemical species using the Troullier and Martins scheme [22,23] . All the atoms were fully relaxed while performing the optimization. We used the generalized gradient approximation (GGA) in the scheme of Perdew–Burke–Eruzerhof (PBE) [24] to describe the exchange and correlation potential since the GGA is found relatively more efficient to predict the energy gap of semiconductor than the LDA[25]. The cutoff of 300 Ry was obtained while k-grid were obtained by using Monkhorst pack scheme with a value of (3x3x3) arbitrary units along the three axes. The volume of 531.441 $Å^3$ is obtained where the whole system was at its lowest energy state which finally led to final-optimization done for several conjugate gradient steps. This yielded a fully optimized ZQD which contained 12 Zn and 12 O atoms. Further, for the comparative study of the effect of morphology on the optical properties of ZnO nano particles, we also optimized planar hexagonal ZnO with the same number of atoms. The mesh cutoff and k-point for hexagonal ZnO was obtained to be 150 Ry, (1x1x8) and the volume of 10 x 2.5 x 11 $Å^3$ along the three perpendicular axes.

III. RESULTS AND DISCUSSION

3.1 Structural Analysis

The optimization values are given in the previous section. The structure of the optimized ZQD can be visualized form figure 1, in which the visible bond length is found to be 1.82 Å while the reported bond length is in the range of 1.87-2.01 Å [26], which reveals the quantum size of the structure. The structure seems to be a hexagonal 2D ZnO chains to form a spherical. As it resembles a hexagonal structure the bond length also is similar to the wurtzite structure of the ZnO[13]. The structural and electronic properties of planar ZnO has been

studied and submitted elsewhere [27] . Here it is given to compare the optical properties only. The equilibrium cohesive energy of the atom/atom-pair in the nanostructure is defined as the difference of total energy of nanostructure per atom/atom-pair with the total energy of constituent atoms individually in similar environment. Here, the equilibrium cohesive energy per Zn-O pair (E_C) is calculated by

$$E_C = E_{tot}(ZnO) – E_{tot}[Zn]- E_{tot}[O] \quad \ldots(1)$$

The cohesive energy per atom pair for ZQD and hexagonal ZnO is found to be 7.3279 and 2.5885 eV respectively. where ZQD seems to be more stable than hexagonal ZnO, while other studied structural parameters are summarized in the table 1.

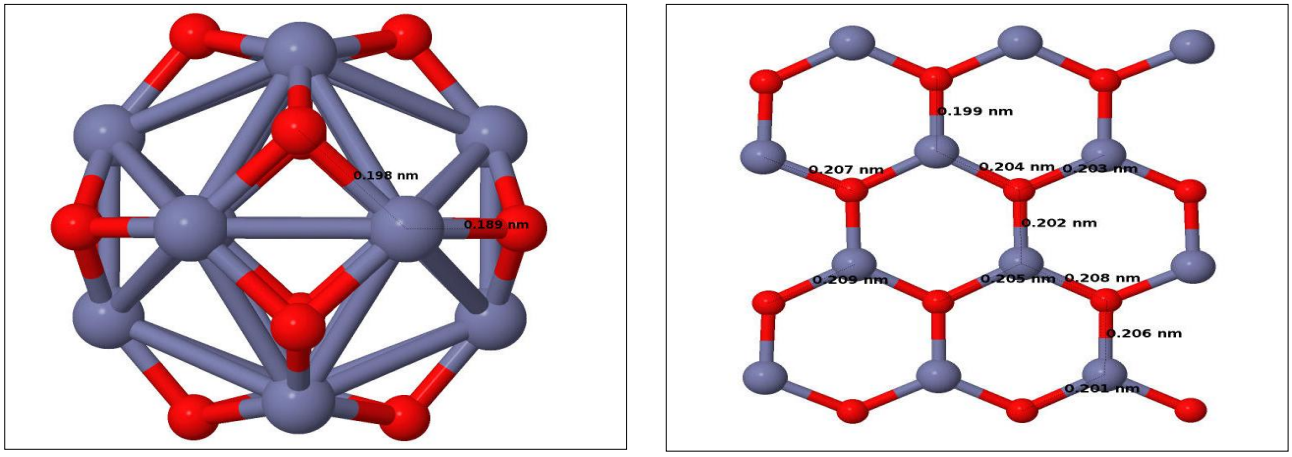

Figure 1: (a) optimized structure of ZQD and (b) planar hexagonal ZnO

3.2 Electronic property analysis

The study of DOS and PDOS is quite helpful in approximating the electronic properties of a system. Figure 2 corresponds the comparative DOS and PDOS of ZQD. The Fermi level is adjusted to match with the zero level of the graph. The empty space in the graph is the HOMO- LUMO gap of ZQD. The HOMO-LUMO gap is found to be 1.60 eV which is nearly equal to earlier reported result of 1.72 eV [25].

Table 1: Structural parameters of ZQD and hexagonal ZnO

Structure	Fermi Energy (eV)	Cohesive Energy (eV/atom-pair)	Bond Length (Å)	Reported Simulated Value of Bond Length(Å)
ZQD	**-5.35**	**7.3279**	**1.89-1.98**	**1.87 to 2.01** [24]
Hexagonal ZnO	**-4.91**	**2.5885**	**1.99-2.09**	**1.96-2.18** [24]

The band gap of ZQD is also equal to ZnO single crystal studied using GGA correlation function [28]. The differed value (from experimental values) may be due to the inherent properties of DFT which underestimates the energy gap (for few hundred meV). On comparing the graphs of DOS with PDOS, the peaks on the valence band are due to Zn-3d orbitals and O-2p orbitals. While higher energy states are contributions of Zn-4s orbitals,

no contributions can be figured out due to the Zn-4p orbital which explains the existence of Zn excited states in the valence band maximum while the ionic nature of ZnO can be assumed for the orbital contribution of Zn and O in the valence and conduction band respectively.

In order to explore the bonding interaction, the charge density has been studied as shown in figure 3. The analysis of charge distribution shows higher density near the atomic sites revealing the ionic-type bonding of ZnO. The finite charge distribution near the atomic site makes a visible indication that apart from ionic bonding there is a dominant covalent

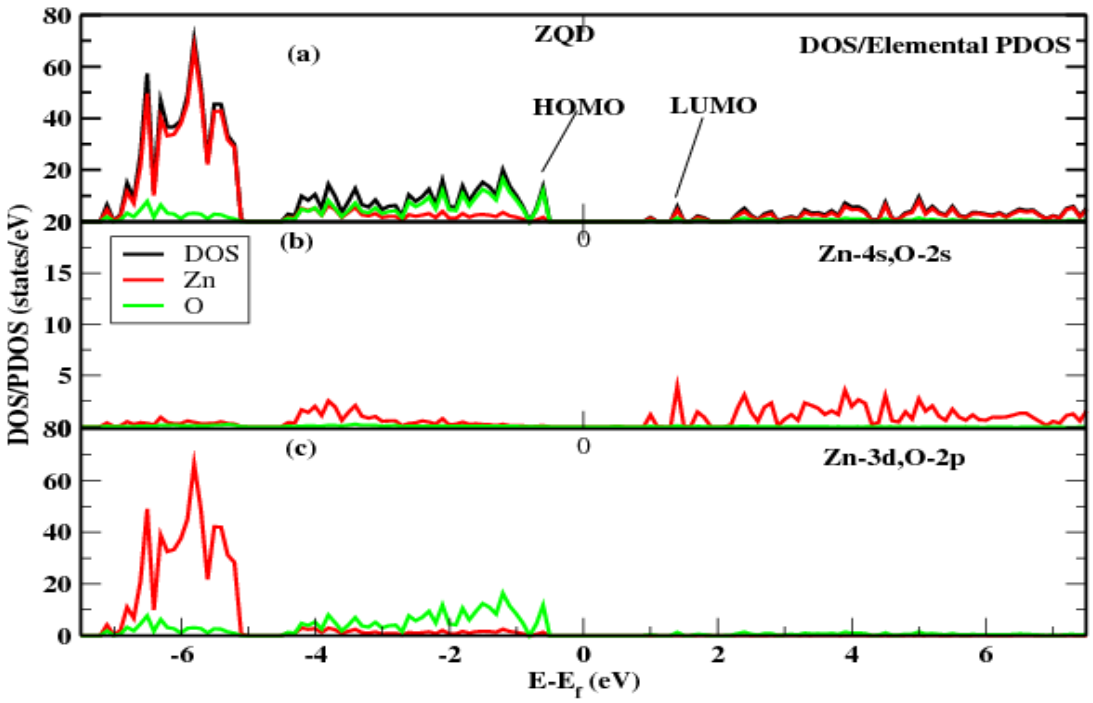

Figure 2: Density of States(DOS) and Partial density of States(PDOS) of ZQD(colors online)

bonding between ZnO which is in agreement with the previous study [29]. The hexagonal section of the ZQD as is visible form figure 3, the plot expresses the bonding nature of the Zn-O which is important for emission of energies in different energy levels. Also the charge distribution is same on both the sections visible from the contour lines around the atoms. The charge densities around the hexagonal section reveals the hybridization between Zn-4s and O-2p orbital electrons.

3.3 Optical Properties Analysis

Optical characterization is an important tool to measure band gap and quantum confinement effects. In this section the optical properties of ZQD are reported at ambient conditions. The optical properties are obtained from the complex dielectric function :

This is mainly connected with the electronic structure. The imaginary part of the dielectric function is calculated from the momentum matrix elements between the occupied and unoccupied wave functions [31] as :

$$\varepsilon_2(\omega) = \frac{Ve^2}{2\pi\hbar m^2\omega^2}\int d^3k\,|\langle K_n \mid p \mid k_{n'}\rangle|^2\; f(k_n)\times(1-f(k_{n'}))\;\delta(Ek_n - Ek_{n'} - \hbar\omega) \qquad \ldots (3)$$

where, *e* is the electronic charge, *V* is the unit cell volume, *p* is the momentum operator, $|k_n\rangle$ is a crystal wave function, $f(k_n)$ is the Fermi distribution function and $\hbar(\omega)$ is the energy of the incident photon. The real part $\varepsilon_1(\omega)$ can be extracted from Kramers - Kroning relationship:

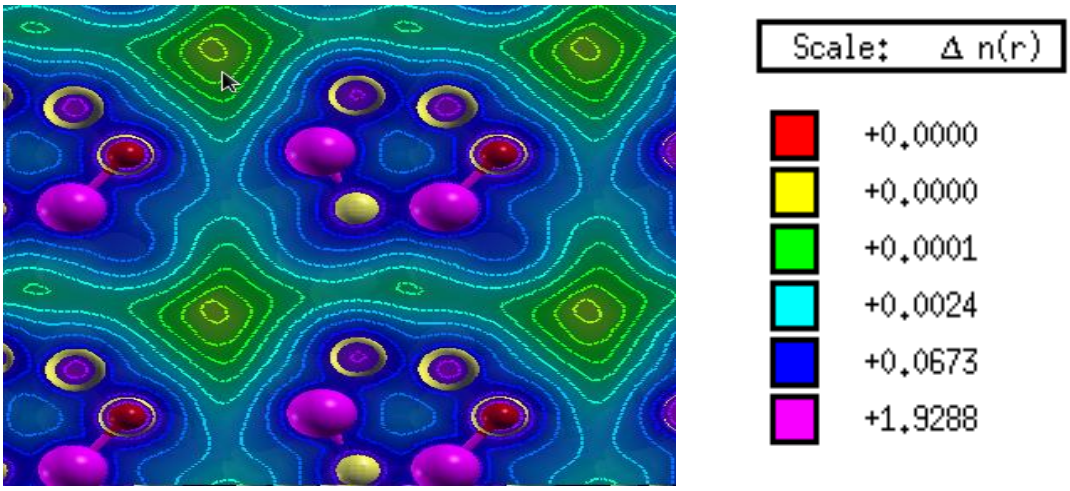

Figure 3: charge density plot for ZQD.

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \quad \text{...(2)}$$

$$\varepsilon_1(\omega) = 1 + \frac{2M}{\pi} \frac{\int_0^\infty \varepsilon_2(\omega')\omega' d\omega}{\omega'^2 - \omega^2} \quad \text{... (4)}$$

where, M is the principal value of the integral. Other optical constants such as refractive index *n(ω)*, extinction coefficient $k(\omega)$, optical reflectivity $R(\omega)$, absorption coefficient $I(\omega)$ and optical conductivity $\sigma(\omega)$ can be computed from the complex dielectric function $\varepsilon(\omega)$, through the following relations [5-8] :

$$\mathrm{n}(\omega) = \sqrt{(|\varepsilon(\omega)| + \varepsilon_1(\omega))} / 2 \quad \text{... (5)}$$

$$\mathrm{k}(\omega) = \sqrt{(|\varepsilon(\omega)| + \varepsilon_1(\omega))} / 2 \quad \text{... (6)}$$

$$R(\omega) = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad \text{... (7)}$$

$$I(\omega) = 2k\omega / c \quad \text{... (8)}$$

The optical response can be studied with SIESTA using different approaches. The approximate dielectric function is calculated using dipolar transition matrix elements between occupied and unoccupied single-electron eigen states using first-order time-dependent pertubation theory [30]. Figure 4 shows the Absorption curve for both ZQD and hexagonal ZnO. The onset of absorption shows a blue shift in case of ZQD as compared to hexagonal ZnO, it was observed at 2.87 eV for ZQD and 5.88 eV for hexagonal ZnO. Secondly, the absorption curve shows a broad peak in case of hexagonal ZnO, where as sharp peaks are observed in case of ZQD. This indicates the characteristic quantum confinement effect observed in QDs, due to which discrete energy levels are obtained, resulting in sharp peaks in emission and absorption spectrum.

Figure 5 shows the optical reflectivity of both ZQD and hexagonal ZnO. The maximum reflectivity is found at 2.80 eV for ZQD and 7.17 eV for hexagonal ZnO. The percentage reflectivity is much higher in case of hexagonal ZnO as compared to ZQD. This can be attributed to the distinct morphologies of the two samples. The reflectance refers interaction of the energy with the surface atoms.

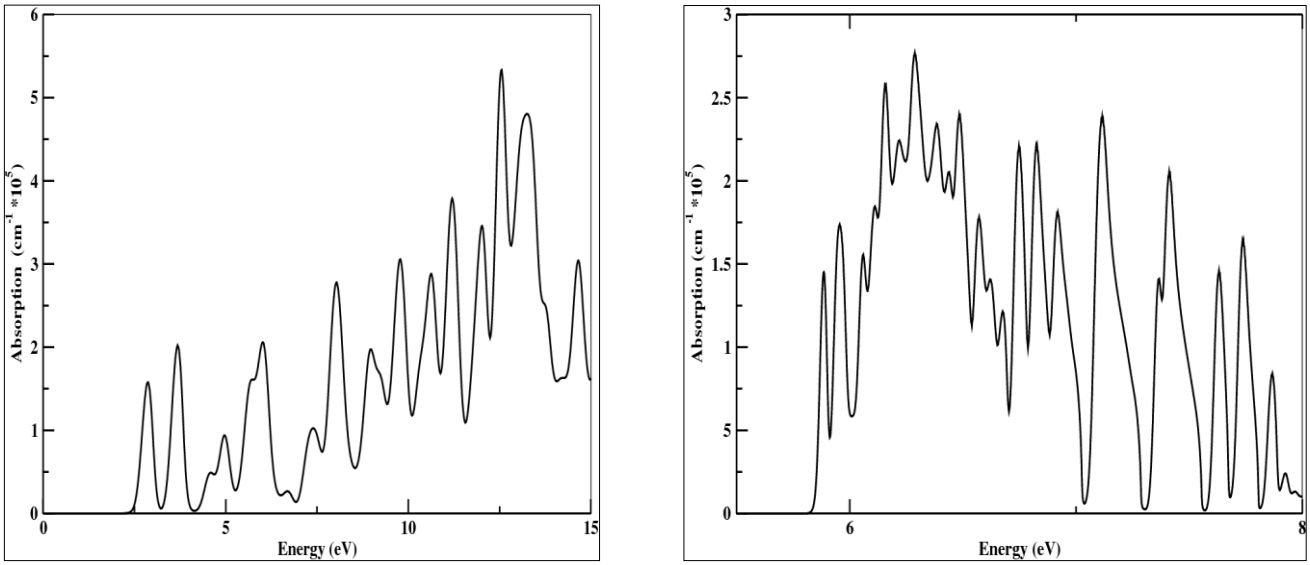

Figure 4 : absorption curve for (a) ZQD and (b) hexagonal ZnO .

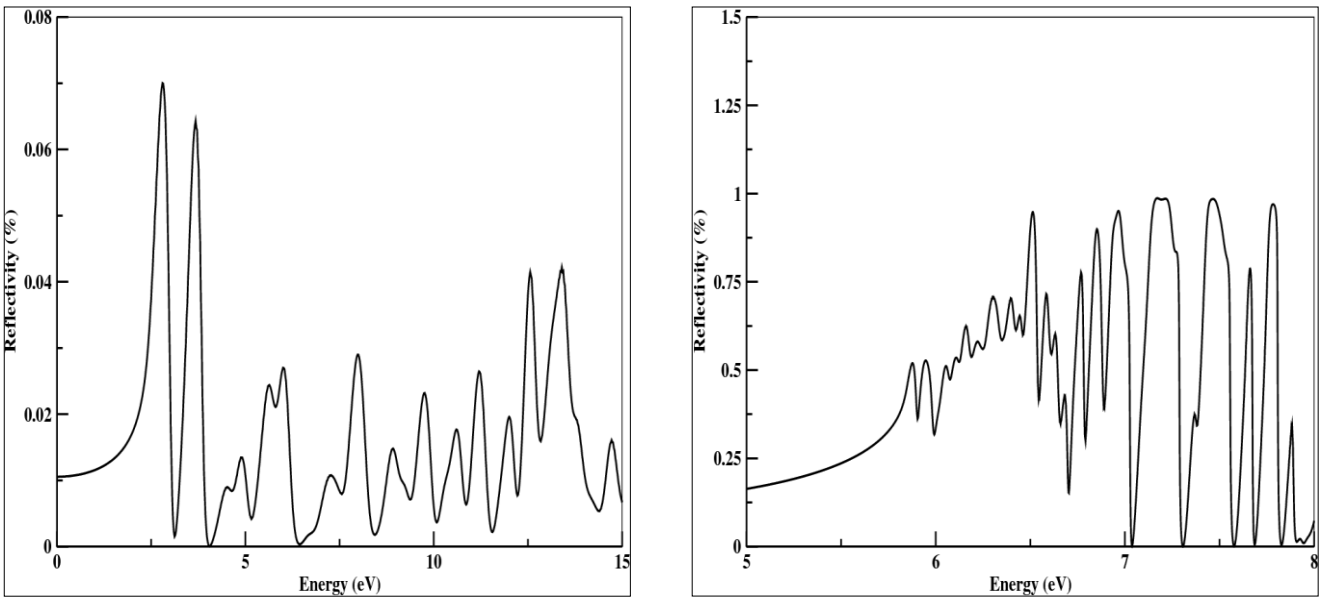

Figure 5: reflectivity curve for (a) ZQD and (b) hexagonal ZnO

IV. CONCLUSIONS

In this work we have studied the structural, electronic and optical properties of ZQDs. we assumed the whole system of 24 atoms to be a quantum dot as the size of a typical quantum dot comes under 5 to 50 nm and the volume of the optimized ZQD in present case was 531.441 Å. The calculated cohesive energy and bond length

nods with experimental results. The electronic structure established an understanding of the band gap which also complied with some earlier reported works. Finally the optical behavior was studied which showed the conducting image of ZQDs. A comparison of the optoelectronic characteristics properties of ZQD with hexagonal ZnO gives an insight into the quantum confinement effect. The absorption characteristics showed conduction in the ultraviolet region for ZQD. It encourages its application in the field of photovoltaics. The study may be helpful to carry out transport studies in ZQDs which can pave the way for the application of ZQD as a good active material as well as electrodes in photovoltaic cells. The effect of doping and transport properties study are under progress in the lab to check its further application.

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