A First principle study of structural and electronic properties of ZnO and ZnS Buckyball structures

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Abstract - The nanostructured ZnO and ZnS in Buckyball form have been optimized using first-principle density functional (DFT) approach. For an improved understanding of the systems, investigation of their structural and electronic properties are performed. Study of Density of states (DOS) and partial density of states (PDOS) are carried out. The system obtained a well near reported values of energy and bond length, done previously. DFT study was found to be very much compatible with the theories of solid-state physics. This study provides a good comparison between the properties of ZnO and ZnS buckyball structures, which is reported for the first time. The study may be useful for group II-VI elements based applications on various fields such as OLEDs, Photovoltaics, sensors, biomedical applications etc.

Keywords: Nanostructure; Buckyball; First principle study; Density functional theory; DOS; PDOS.

1. Introduction

Group II-VI based materials have been investigated for different research works from the past 100 years. These are one of the most prominent materials for application-based research. Due to its large band gap and high electron mobility, it has various optical and electronic applications [1, 2]. Bulk material exhibits a wide direct band gap and high exciton binding energy in case of ZnO and ZnS. While ZnO and ZnS quantum dots display quantum confinement effect due to which bulk properties can be custom-made, which generates its wide-ranging applications in different fields like solar cells, gassensors and biosensors, optoelectronic luminescent materials etc [3].

Fullerene has a wider range of applications in the area of bio-medicines. It has a unique structure, which makes it a desirable candidate for the formation of a conjugate with protein and DNA, which is helpful for the development of anti-cancer treatment. It could be used as a drug delivery tool for the treatment of a particular cell. After the discovery of carbon buckyball structure, there are lots of
development in the field of fullerenes both in experimental ways as well as in theoretical ways by using material modelling [4]. Here we are using material modelling for the examination of ZnO and ZnS buckyball structures and their comparative study is performed for the first time. Valence electrons play a significant role in defining a material. Valence electrons define various structural, electronic, magnetic, optical and transport properties in condensed matter physics. For understanding these properties there are various approaches available, but quantum mechanics has proven to be the best formulation to describe the interacting system of electrons and nuclei. As we know the Schrödinger equation is an essential quantum mechanical equation that defines a system of electrons and nuclei in terms of wave function $\psi$. The DFT based study provides an interpretation for intrinsic properties of a semiconductor.

In this paper, we have presented briefly the approximations to solve the problem of many-body using density functional theory and computational implementation of DFT is done using SIESTA (Spanish Initiative for Electronic Simulations on Thousands of Atoms) code [5].

2. Methodology
Here we performed simulations by using a computational program called Spanish Initiative for Electronic Simulations with thousands of atoms (SIESTA). This is based on density functional theory [6, 7]. The whole system was optimized by following all essential steps like mesh-cutoff, k-point, lattice-optimization etc. For correct results, it is essential that all the atoms remain fully relaxed while performing the optimization. Moreover for exchange and correlation potential; a Generalized Gradient Approximation (GGA) of Perdew–Burke–Ernzerhof is used [8]. As GGA is comparatively more efficient to predict the energy gap of semiconductor than the LDA, so here we used GGA for our study [9]. Core electrons are modelled with Troullier–Martins norm-conserving pseudopotentials [10] the valence electrons functions are expanded in double zeta polarized basis set [11, 12] of localized orbitals and the real space grid is set to be 400 Ry. Until the Hellmann–Feynman forces acting on all components of each atom are smaller than 0.01 eVÅ$^{-1}$, the structure remains relaxed. This yielded a fully optimized ZnO buckyball which contained 24 Zn and 24 O atoms. Similarly, ZnS buckyball structure which contained 24 Zn and 24 S atoms.

3. Results and discussion
3.1 Structural Analysis:
Here the structural analysis of both ZnO and ZnS buckyball structures are done. For which some of the input parameters are set like Mesh-cut off, K-grid, CG steps etc. Some of the parameters are discussed below.

k-grid were acquired by using Monkhorst pack scheme with a value of (5x5x5) arbitrary units, these are among all three axes.

| System used | Mesh-cutoff (Ry) | Fermi energy (eV) | Cell volume (Å$^3$) |
|-------------|-----------------|------------------|-------------------|
| ZnO         | 400             | -5.6007          | 384.077           |
| ZnS         | 400             | -4.6340          | 570.988           |

Table 1. Input parameters of ZnO and ZnS buckyball structure.
Figure 1. a) ZnO Bucky ball structure b) ZnS Bucky ball structure.

Figure 1 (a) and (b) displays the buckyball structure of ZnO and ZnS by a ball and stick model. In Figure 1 (a) the yellow (bigger ball) and red (smaller ball) balls signify zinc and oxygen atoms respectively. While in Figure 1 (b) the brown (bigger ball) and yellow (smaller ball) balls signifies the Zinc and Sulphur atoms respectively. As reported in other papers the most symmetric buckyball structure among all comparing compounds, is the most stable one [13], here we obtained symmetric structures of both. The bond length and bond angles between the atoms are shown in the tables below.

Table 2. Bond lengths of ZnO and ZnS buckyball structures.

| S.no. | Compound Name | Bond Name | Bond Length (Å) |
|-------|---------------|-----------|-----------------|
| 1.    | Zinc Oxide    | Zn-Zn     | 2.99            |
|       |               | Zn-O      | 2.02            |
|       |               | O-O       | 2.85            |
| 2.    | Zinc Sulphide | Zn-Zn     | 3.20            |
|       |               | Zn-S      | 2.41            |
|       |               | S-S       | 3.50            |

Table 3. Bond Angles of ZnO and ZnS buckyball structures.

| S.no. | Compound Name | Angle Name | Angle Value(degrees) |
|-------|---------------|------------|----------------------|
| 1.    | Zinc Oxide    | Zn-O-Zn    | 90.66                |
|       |               | O-Zn-O     | 86.63                |
|       |               | Zn-Zn-Zn   | 60.98                |
|       |               | O-O-O      | Not present          |
| 2.    | Zinc Sulphide | Zn-S-Zn    | 82.25                |
|       |               | S-Zn-S     | 93.58                |
|       |               | Zn-Zn-Zn   | Not present          |
|       |               | S-S-S      | Not present          |
As we know that electronegativity is nothing but a tendency to attract electrons shared in a covalent bond between atoms. Smaller is the atom, more is its electronegativity, this is because the distance between the electron and positively charged nuclei is less in them. Here we obtained that bond length of Zn-S is greater than that of Zn-O. This goes with the fact that Sulphur is less electronegative than oxygen. [14]. Because of the difference between the bond length of ZnS and ZnO, the cell volume of ZnS (570.988 $\text{Å}^3$) is greater than that of ZnO (384.077 $\text{Å}^3$). Which implies that there is a change in energy density due to increased cell volume. Also, it is observed that there is a difference in the Fermi level of the two compounds. ZnO (-5.6007 eV) is having higher fermi energy as compared to ZnS (-4.6340 eV).

3.2 Electronic properties Analysis:

Figure 2 (a) and (b) displays the calculated density of states (DOS) and Figure 3 (a) and (b) displays the projected density of states (PDOS) of ZnO and ZnS molecules. We can define the forbidden energy gap as the difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) which is an essential mechanism to understand conductivity of material [15]. As the charge transport properties of the molecule predominantly depend on the forbidden energy gap, it is important to examine the variations in the molecular orbital energy level and forbidden energy gap. [16–18].

3.2.1. The density of states:

In Figure 2 (a) it could be observed that the forbidden energy gap of ZnO buckyball structure is around 0.4 eV. Whereas in Figure 2 (b), it could be observed that the forbidden energy gap of ZnS buckyball structure obtained is around 2.2 eV, both of these values are quite less than the reported band gaps in its bulk form.

![Figure 2. a) DOS plot of ZnObuckyball structure b) DOS plot of ZnS buckyball structure.](image)

Defect levels are observed in the Valence band region which may contribute to the conductivity. Due to these defects, the band gap is reduced as compared to its bulk structure. This is the reason they are showing metallic behavior in case of ZnO. While in the case of ZnS it is still showing semiconductor properties.

3.2.2. Projected Density of states:

From the PDOS plots, it is obtained that in case of ZnO 3d orbital of Zn atom and 2p orbital of O atom shows maximum contribution in the valence band. 4s orbital in Zn and 2s orbital of O atom shows
equal contribution in both valence band and conduction band. Similarly, in case of ZnS, 3d orbital of Zn atom and 3s orbital of S atom shows maximum contribution in the valence band. While 4s orbital of Zn atom and 3p orbital of S atom shows maximum contribution in conduction band [19].

Figure 3. a) PDOS plot of ZnO structure b) PDOS plot of ZnS structure.

We optimized ZnO and ZnS structures which showed a density of states and partial density of states plots. The band gap of ZnO as evaluated here is 0.4 eV which is less than the reported bulk structure value of 3.37 eV, whereas for ZnS we got 2.2 eV which is also less than the reported band gap for its bulk structure value of 3.54 eV, but it gives way for material modelling to go for some different morphologies of ZnO and ZnS structures and improve its approach for practical use.

4. Conclusions
DFT was used for investigation of two new structures, each of ZnO and ZnS. The result obtained for the new buckyball structures of ZnO and ZnS shows that these two structures have reduced band gap as compared to its bulk structures. As reported in other papers the most symmetric buckyball is the most stable one, here we obtained symmetric structures of both. The molecular dimensions of both buckyballs are less than 100 nanometers. These are the very useful result as buckyball structures are having wide range applications in the fields of solar cells, sensors and biomedicine.

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