Structural Properties of Aluminum Doped with Zinc Oxide (ZnO) Nanoparticle Theoretical study by Gaussian 09 program

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Abstract. In this research paper study effect of adding aluminum to Zinc Oxide (ZnO) nanoparticle various properties of the ground and excited electronic state of ZnO nanoparticle delve into theoretical methods of time-dependent on the density functional theory (TDDFT) was calculated from the Lee-Yang-Parr (B3LYP) by the Gaussian 09 programs. The structural and spectral characteristics enumerated of zinc oxide nanoparticle and a nanocomposite through additive the concentration of aluminum particles such as (ionization potential, electron affinity, electronegativity, hardness, and the electrophilic, density of states, IR spectra, and Raman spectra that showed a strong E2 mode a peak at nearly 323 cm⁻¹ spectroscopy each calculated results by Gaussian 09 program which approximately with experimental results.

Keywords: Structural properties, electronic properties, (IR and NMR) spectral, Gaussian 09 program

1. Introduction
Zinc oxide nanoparticle significant materials this consequence of natural materials, non-toxic, environmentally, easily synthesis and cheap. All these characteristics made it a significant role in the enormous field of physics, chemistry and materials science. There are several types of metal oxide nanoparticles such as (ZnO) Zinc oxide nanoparticles that have diameters less than 100 nanometers. They have a large surface area relative to their size and high catalytic activity and exhibit chemical-thermal stability characteristics. Today, nanotechnology operates in various field's life, for instance, nanoparticles are used as efficient nano adsorbents, also, that employ important roles in electroanalysis to detect the biomolecules [1,2]. Then ZnO is discriminated against and has been higher electrified resisted, these characteristics are decreasing with adding atoms such as Al³⁺ [3]. These ions ensure added electrons and betterment each of the optics, electrical, thermal, and magnetic characteristics of ZnO nanoparticles. Al³⁺ ions extinguished by a small ionic radius. This research contains the theoretic calculations of ZnO nanoparticles and the effects of adding aluminum as impurities for use to study each electronic and thermal properties and compared these results with experimental results for use as gas sensors.

2. Theoretical study
Present work deals with the electronic structure of zinc oxide (ZnO) nanoparticles without adding aluminum, and with additive aluminum. The electron's characteristics which be calculated be used the Koopmans theorem. The exciting energy and electronic transitions are carried out by using the time-dependent TD density functional theory [4-8]. Methods that be used in the present work " density functional theory (DFT) considered as the best available basis set with 6-311G**. The mode of vibration and their conjunction calculated through the Gaussian 09 program are used for studying ZnO nanoparticle and ZnO doped with (Al) aluminum atom's properties. The energies of orbital some extent with the potential of ionization calculated in experimental work [9]. As well as the bandgap described the different energy between the highest occupied molecular
orbital, and the unoccupied molecular orbital's [10]. The potential of ionization and the affinities of electrons calculated by using the Koopmans' theorem to calculate it by the equation (1), (2) respectively [11,12].

\[ \text{IP} = -E_{\text{HOMO}} \quad \text{(1)} \]
\[ \text{EA} = -E_{\text{LUMO}} \quad \text{(2)} \]

While the electronegativity value (\( \chi \)) calculated by equation (3) [15].

\[ \chi = -\frac{(\text{IP}+\text{EA})}{2} \quad \text{(3)} \]

Whereas the hardness (\( \eta \)) calculated using equation (4) (12).

\[ \eta = \frac{(\text{IP}-\text{EA})}{2} \quad \text{(4)} \]

The softness (S) and electrophillic (W) by the following equations [12].

\[ S = \frac{1}{2} \eta \quad \text{(5)} \]
\[ W = \frac{\chi^2}{2\eta} \quad \text{(6)} \]

3. Results and Discussion
The exact basis set of valence electrons in the bond gives calculations accuracy. Besides, this model is treated with the distortion and the polarity of the ZnO molecules. For this behavior, The structural optimization illustrated in figure 1(a) Whereas van der Waals interaction of aluminum atoms which additives to ZnO nanoparticles in figure 1(b).

3.1 The Chemical Quantum Feature
The standard quantum- chemical factors calculated for instance the valance bands orbits (\( E_{\text{HOMO}} \)), and conduction bands (\( E_{\text{LUMO}} \)), the energy gap values and the total energy are obtained in figure (2,3).

Figure 1. Optimize the structure of (a) ZnO purity, (b)ZnO with Al
From figure (2) and (3) The HOMO levels, LUMO levels, and energy gap values (Eg) ZnO nanoparticle (3.1 eV), but this energy gap when it doped with aluminum (2.88 eV) values units, this result rather consistency with [13]. The X-ray which calculated by Gaussian 09 in the table (1).

Table 1. X-ray of ZnO and ZnO: Al

| ZnO nanoarticle          | Lattice constant | D (nm) | ZnO nanoparticles with Al | Lattice constant | D (nm) |
|--------------------------|------------------|--------|--------------------------|------------------|--------|
|                          | a,b( Å)          | c(Å)   | c/a                      | a,b( Å)          | c(Å)   | c/a |
|                          | 3.57             | 5.74   | 1.608                    | 3.57             | 5.74   | 1.608 |
|                          | 20.3             |        |                          | 17.8             |        |

From table (1) the lattice constant and particle size of ZnO nanoparticles and ZnO with Al, additives showed that lattice parameter similarity, but the coordinates of lattice factors few changing as well as nanoparticle with addition Al caused decreases in the size compared with the ZnO solely this referred to a radius of aluminum that added insufficiency compared with ZnO nanoparticles radius this results in good agreement with [14].

We conclude that the present results are in the right direction of decreasing gaps as required by quantum confinement theory [16]. Energy gap as a function of the combined number of Al and ZnO atoms. Relativistic corrections are incorporated in the present calculated values of the gap given in figure (4).
Figure 5 illustrations density of states of ZnO nanoparticles atoms doped Al. From these figures one can determine the energy gap, width of the valence and conduction bands, the position of the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO).

3.2 The Electronic Characteristics
That all affinity of electrons, the potential of ionization, and electronegativity have been given in the table (2), through these results showed that when adding aluminum atoms with ZnO leads to increase all of these electronic characteristics.

| IP (eV) | X     | D    | X    | W    | S    | EA (eV) | Lumo | Homo   |
|--------|-------|------|------|------|------|---------|------|--------|
| 6.54   | -4.99 | 1.55 | -3.77| 8.032| 0.323| 3.44    | -3.44| -6.54  |
| 8.5    | 7.06  | 1.44 | -7.06| 17.31| 0.347| 5.62    | -5.62| -8.5   | ZnO :Al
3.3 FTIR Spectra

The spectrum can be used to identify and study chemical substances and stretched type of vibrational so that the chemical connection between each of Zn and O atoms, illustrated in figure (6) FTIR spectrum, and table (3). From the results, note theoretical data as well as with experimental results Despite the inconsiderable variance between them this refers to impurities in environmental conditions[15,16].

| Experimental results[15,16] | Theoretical result | Functional group | Vibration types of PMMA |
|---------------------------|--------------------|------------------|-------------------------|
| 185                       | 187                | COO-             | A Symmetric Stretch     |
| 154                       | 154                | COO-             | Symmetric Stretch       |
| 290                       | 292                | C-H              | Stretch alkane          |
| 370,450                   | 370,450            | O-H              | Stretch                 |

**Figure 6.** FTIR of (a) ZnO purity, (b) ZnO with Al

From figure (6) illustrated that it FTIR identical because it did not have chemical interactions, but physical interaction

3.4 Raman scattering

Measures frequency shift(Δω=ωphonon) which is the differences between incident light frequency (ωinc) the peak 323 cm⁻¹ is assigned to A1 transverse mode and seems for the anisotropic of the natural force constant, figure (7) showed the results of the Raman spectrum. About the result of Raman spectra of the ZnO nanoparticles showed peaks in (257, 440 and 547) cm⁻¹ so that theoretical results using the Gaussian 09. The program appeared the approximates with experimental results [14,16].
4. Conclusion
Zinc oxide (ZnO) nanoparticle without and with added aluminum are discussed in the work utilization Gaussian 09 program. These molecules show good convergence properties as their X-ray calculation this leads to a decrease in nanoparticle size on aluminum atoms addition. These results include energy gap, X-ray, vibrational properties and NMR spectra, so it imminent with experimental results. Density of states is sharper and higher

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