

## THEORETICAL STUDIES OF NANOSILVER AND PMMA-AGNANOCOMPOSITES BY GAUSSIAN 09 PROGRAM

K. J. KADHIM<sup>1</sup>, H. L. ABDULLAH<sup>2</sup> & I. H. HILAL<sup>3</sup>

<sup>1</sup>Department of Physics, College of Science, Al- Mustansiriah University, Baghdad, Iraq

<sup>2</sup>Department of Chemical, College of Science, Al- Mustansiriah University, Baghdad, Iraq

<sup>3</sup>Regenerated Energies, Technology & Researches Directorate, Al-Ministry of Science & Technology, Baghdad, Iraq

### ABSTRACT

The theoretical studies of Nanosilver molecules and Ag-PMMA nanocomposites by DFT calculations have been performed using Gaussian 09 program with GUI (Graphical User Interface), called Gauss view 5.08. The characterization of programs are such as, optimized geometrical parameters, vibrational frequencies, total energy, dipole moments, frontier orbital energies [HOMO and LUMO], energy gaps etc. From the results, it is found that the values of energy gaps decrease with increasing additives ratio, and are in agreement with experimental results. Also, the theoretical properties of all spectral properties (UV-VIS & FTIR) of nanosilver and nanocomposites results are in good agreement with the experimental results.

**KEYWORDS:** Silver Nano Particles, Nano Composites & Gaussian 09 Program

### INTRODUCTION

Quantum mechanics is a mathematical description of electrons' behavior, which can harbingers the molecules or atoms in their individual position and precisely in the single electron system. The quantum mechanics developed by Schrodinger and Heisenberg stated that all chemical computers and methods depend on the solved value again (Schrodinger [1, 2]).

In 1926, Austrian physicist Erwin Schrodinger formulated an equation to use to describe, how the quantum state of a wave function changes in time [3]? As well as Gaussian 09 program Methods; a modeling program used to elucidate the electronic structure by chemists, chemical engineers, biochemists, physicists and others for research in established and emerging areas of chemical interest. Starting from the basic laws of quantum mechanics, the development of quantum mechanical methods, such as Gaussian is a new approach based on both experiments and molecular modeling techniques [4, 5]. It calculates all of Polarizability ( $\alpha$ ) describes the molecule's ability for polarization, so it determines the linear response of the electron density, in the presence of an infinite seminal electric field F, and stands for a second order variation in the energy. [6]

$$\alpha = - \left( \frac{\partial^2 E}{\partial F_a \partial F_b} \right)_{a,b} = x, y, z \quad (1)$$

The mean polarizability is evaluated by using the equation:

$$\langle \alpha \rangle = \frac{1}{2} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (2)$$

Where  $\alpha_{xx}$ ,  $\alpha$ ,  $\alpha_{zz}$  are the eigen values of the polarizability tensor

While, the total energy of a system is the sum of total kinetic and potential energy at the optimized structure that the total energy of the molecule must be at the lowest value, because, the molecule is at the equilibrium point; this means that the resultant of the effective forces is zero.

The ionization potential (IP) for a molecule is the amount of energy required to remove an electron from an isolated atom or molecule, and expressed as the energy difference between the positive charged energy  $E (+)$  and the neutral  $E_{(n)}$  according to the following relation [7,8]:

$$IP = E_{(+)} - E_{(n)} \quad (3)$$

The electron affinity (EA) of a molecule or atom is the energy change, when an electron added to the neutral atom to form a negative ion, and expressed as the energy difference between the neutral energy  $E (n)$  and the negative charged energy  $E (-)$ , according to the following relation [9].

$$EA = E_{(n)} - E_{(-)} \quad (4)$$

In molecular orbital (MO) theory within the limitation of Koopman theorem, the orbital energies of the frontier orbitals are given by:

$$IP = -\epsilon_{\text{HOMO}} \quad (5)$$

$$EA = -\epsilon_{\text{LUMO}} \quad (6)$$

Where  $\epsilon_{\text{HOMO}}$  is the energy of the highest occupied molecular orbital, and  $\epsilon_{\text{LUMO}}$  is the energy of lowest unoccupied molecular orbital. A molecule with high chemical potential will accept electrons from a molecule with lower chemical potential. Electronic chemical potential  $K$ , defined as [7, 9].

$$K = \left( \frac{\partial E}{\partial N} \right)_V \quad (7)$$

Where,  $v$  is the potential due to nuclei.

Electronic chemical potential, related experimentally, to two known quantities, ionization potential IP and electron affinity EA, as in the relationship [9].

$$K \approx -\chi \approx (IP + EA) / 2 \quad (8)$$

The electronic and chemical potential is the quantity, which measures the escaping tendency of electrons from a species in its ground state. A molecule with high chemical potential will accept electrons from a molecule with lower chemical potential.

The hardness  $\eta$  is defined as a measurement of molecule resistance to the change or deformation [10].

$$\eta = \frac{1}{2} \left( \frac{\partial K}{\partial N} \right)_V \quad (9)$$

In terms of ionization potentials, IP and electron affinities EA, the hardness is half of the energy gap between two frontier orbital's [7, 10].

$$\eta = \frac{|IP - EA|}{2} \quad (10)$$

The hard molecule has a large energy gap and the soft molecule has a small energy gap. In quantum theory,

changes in the electron density of the system result from the mixing of suitable excited state wave functions with the ground state wave function.

A small energy gap means small excitation energies to the manifold of excited states. Therefore, soft molecules with small energy gaps and their electron density change more easily than a hard molecule, and due to that, soft molecules will be more reactive than hard molecules

The difference between HOMO and LUMO known as energy gap, which is given in equation [11, 12]

$$E_{\text{gap}} = E_{\text{HOMO}} - E_{\text{LUMO}} \quad (11)$$

So, it indicates the capability of electronic transitions from occupied orbital's to unoccupied ones. The energy gap is a parameter to determine the molecular electrical transport property, because it is a measure of electron conductivity.

### Experimental Works

Running Gauss views, it is easy to build molecular structures. The first and principle condition of any electronic structure calculation is to obtain the optimized geometry of the sample; all calculations are used Opt. Option and then Freq i.e. Option for vibrational frequency. The method tab provides to set either ground state calculation or excited state calculation. The Vibrational frequency calculation requires setting ground state calculation. Once the DFT method is set, then additional field appeared to select DFT functional, by default, the B3LYP functional.

## RESULTS AND DISCUSSIONS

### HOMO/LUMO

Study of molecular orbitals can provide much useful information about electronic structures, and is widely used in the analysis of chemical reactions. The frontier molecular orbital energies were obtained using the B3LYP/6-311G (d, p) level for Density Functional Theory (DFT) method, with standard split-valence B3LYP/6-311G (d, p) basis set, using Gaussian 09 [13] program package with no imperative on the geometry.

The optimized molecular structure, HOMO and LUMO are important in determining such properties as molecular reactivity and the ability of a molecule to absorb light. The figure (1) shows HOMO and LUMO for AgNPs, whilst the table (1) shows the total energy, dipole moment, and the silver nanoparticles molecular orbital

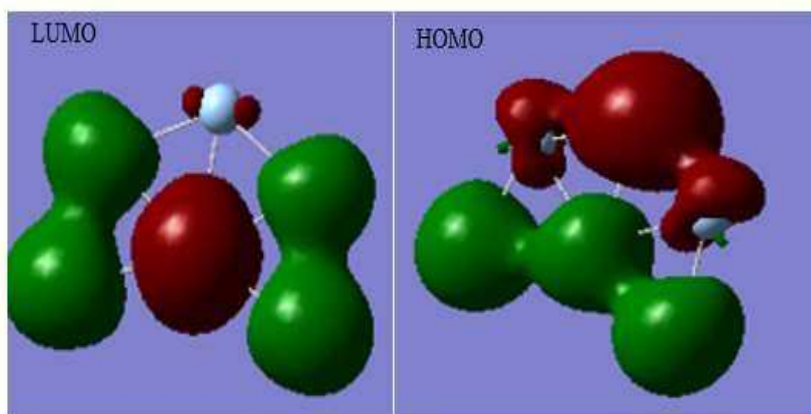


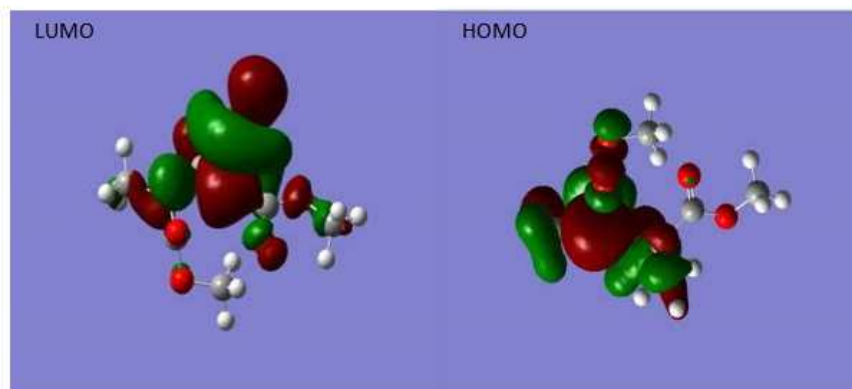
Figure 1: HOMO and LUMO for AgNPS

**Table 1: The Total Energy, Dipole Moment, and the Silver Nanoparticles Molecular Orbital Obtained by using B3LYP/6-311G (D, P)**

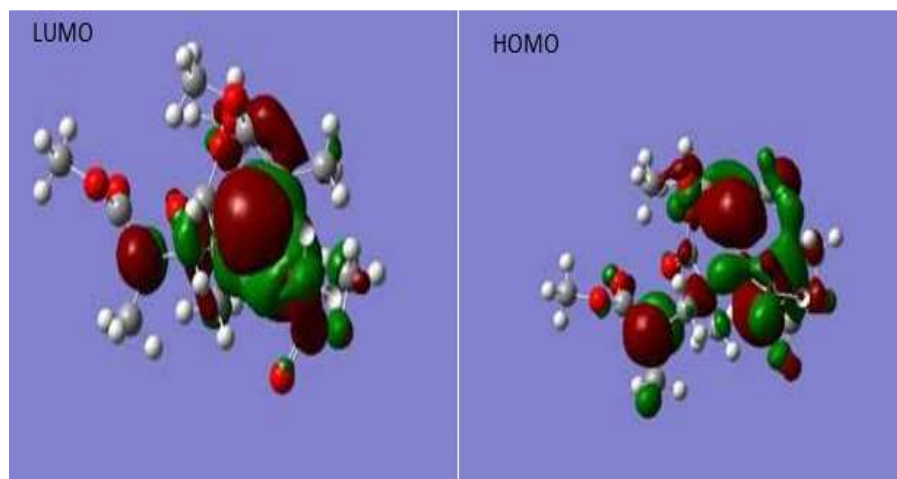
Property	Agnps
Total energy (a.u)	-31058.054
$E_{\text{HOMO}}$ (eV)	4.294598
$E_{\text{LUMO}}$ (eV)	-2.25914
Dipole moment (D)	0.1396
$\Delta E = E_{\text{HOMO}} - E_{\text{LUMO}}$ (eV)	2.04

The HOMO and LUMO energies give values of energy gaps of AgNPs. The theoretical calculation by Gaussian 09 programs obtained  $E_g$  (2.04 eV) and these results are in good agreements with the results of researcher [14, 15] where they obtained  $E_g$  (2.06 eV).

Whilst the figure (2) to (6) shows HOMO and LUMO for different concentration of nanosilver doped with PMMA polymer, whilst the table (2) shows the energy gap values.



**Figure 2: HOMO and LUMO Levels for Ag-PMMA (5%) Molecules from B3LYP Density Functional Theory**



**Figure 3: HOMO and LUMO Levels for Ag-PMMA (10%) Molecules from B3LYP Density Functional Theory**

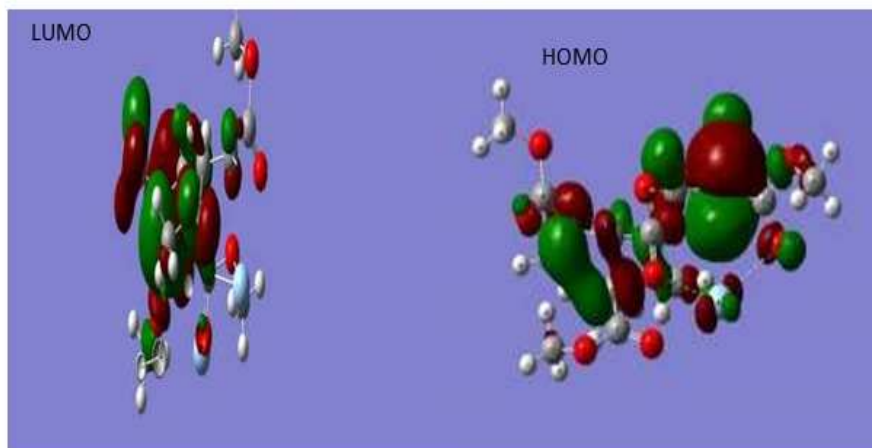


Figure 4: HOMO and LUMO Levels for Ag-PMMA (15%) Molecules from B3LYP Density Functional Theory

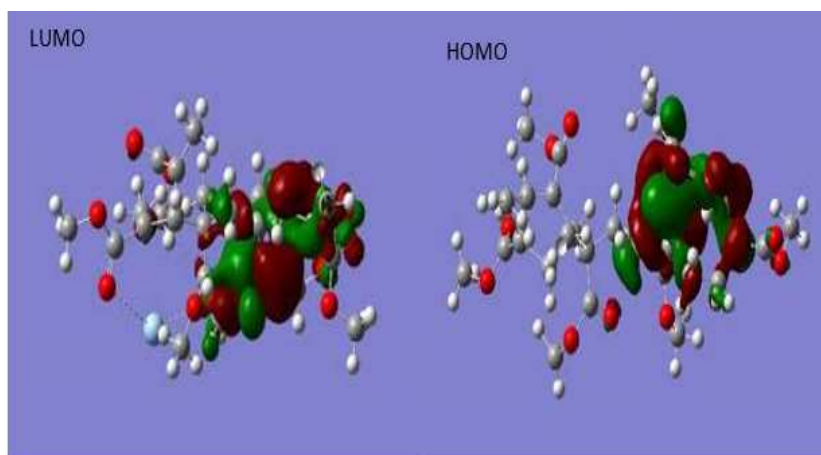


Figure 5: HOMO and LUMO Levels for Ag-PMMA (20%) Molecules from B3LYP Density Functional Theory

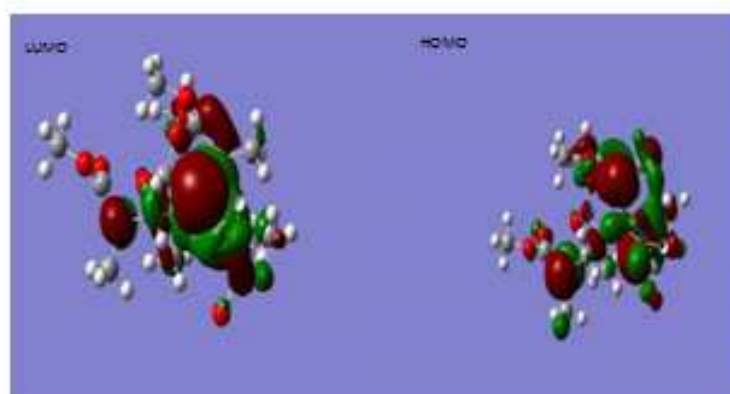


Figure 6: HOMO and LUMO Levels for Ag-PMMA (25%) Molecules from B3LYP Density Functional Theory

Table 2: The Total Energy, HOMO, LUMO Energies, and Energy Gap of Nano Composite at the DFT/B3LYP Method with 6-311G (D, P) Level

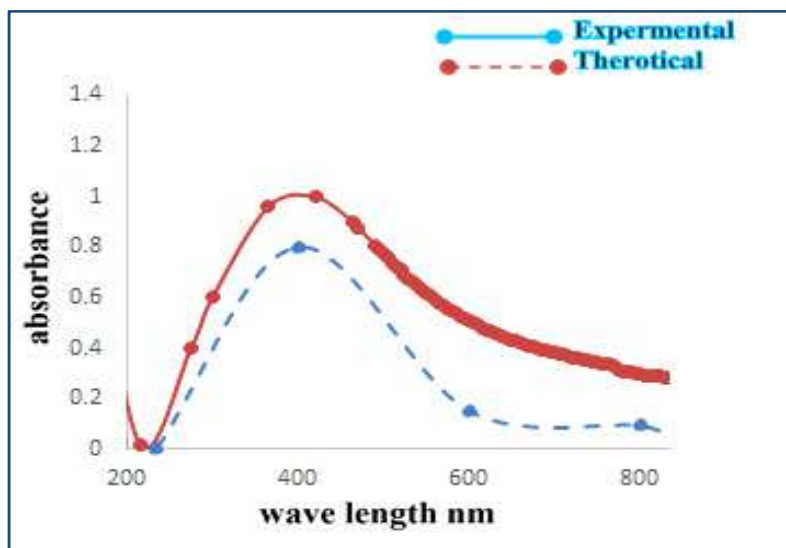
HOMO	LUMO	Theoretical $E_g$	No .of Molecular
-5.1526	-0.1374	5.02	0%

-4.25	-0.4783	3.77	5%
-4.584	-0.9732	3.611	10%
-3.436	-0.0303	3.41	15%
-3.3605	-0.1265	3.23	20%
-4.613	-1.6664	2.95	25%

Table (2) shows, the energy band gap for (Ag -PMMA) nanocomposites was decreased from 5.29 eV, with the increasing percentage weight of the nanosilver to 2.95 eV. These results are considered as having good agreement with the experiment [15].

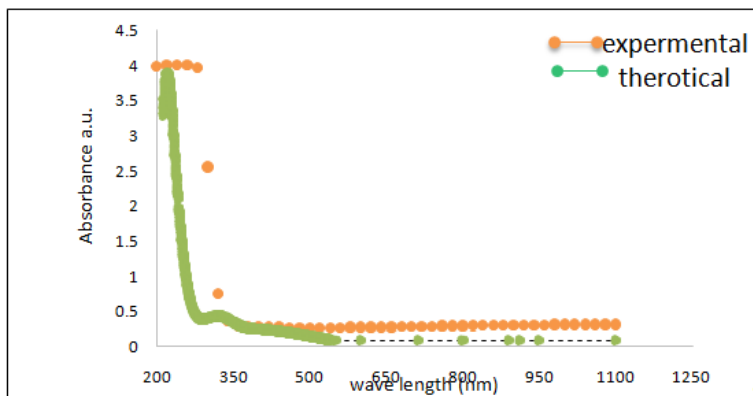
### UV-Visible Spectrum

The chemical quantum computations were done with electronic property inquiry. The DFT / B3LYP method using a basic set 6-311G (d, p), was used to determine the first three low-lying excited states for investigating the UV-Vis absorption spectra of the title compound at TD-DFT (C-PCM) / 6-311G (d, p). The calculated results wavelength is carried out and compared with observed experimental wavelength. The figure (7) showed UV-Visible experimental and theoretical curve of AgNPs



**Figure 7: Experimental and Theoretical Electronic Spectra for AgNPs**

From the figure (7), the theoretical calculation of AgNPs predicts one peak in 400 nm, which is considered as excellent agreements with experimental results, as the peaks appear in 403 nm. While the experimental UV-Vis spectrum has been observed in PMMA and nanocomposites as shown in figure (8), the theoretical calculations were performed for adding nanosilver percentage in PMMA polymers, leading to much smaller red shift. The experimental and theoretical UV-Vis spectra use Gaussian 09 programs, because, it gives better results agreement, in comparison with experimental results. One of the reasons the difference between the experimental values and the theoretical predictions may be, the TD-DFT calculations do not evaluate the spin-orbit splitting; the values are averaged [16, 17].

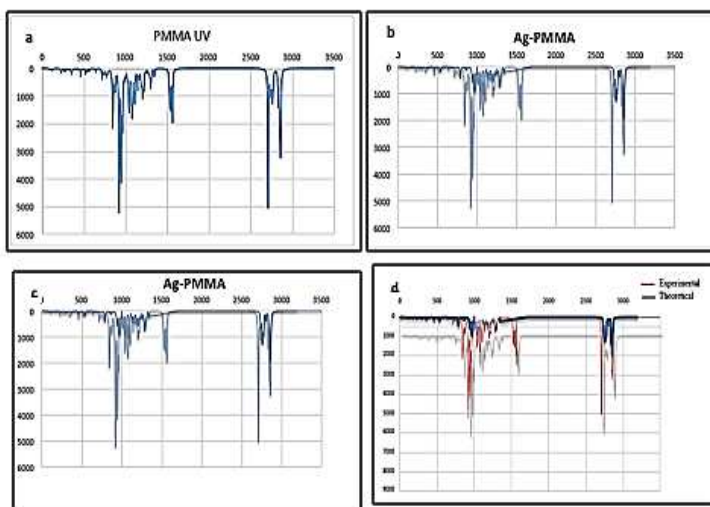


**Figure 8: The Theoretical and Experimental Absorption Spectrum**

**IR Spectra**

The observed and calculated vibrational frequencies alongside relative intensities, probability assignments at B3LYP/6-311G (d, p) level of the title compound are given in Table (3). Vibrational frequencies simulated for PMMA and AgNPS-PMMA compound with the unscaled B3LYP/6-311G (d, p) force field are slightly greater than the observed values, as shown in figures (9-a), (9-b), (9-c) and (9-d).

These differences can be rectified by scaling the simulated wave numbers with appropriate factor. It is necessary to scale down the calculated harmonic frequencies to improve the calculated values, in agreement with experimental values. The different scale factors can be used in different regions of vibrations to obtain a better agreement between the experimental and computed frequencies. The vibrational frequencies were calculated at B3LYP/6-311G (d, p) with the molecule when coupled with the deployment of the measured frequencies. E. B. Wilson was the work of Wilson (70) the appropriate theory to calculate the vibration frequencies



**Figure 9: Theoretical FTIR Spectrum and Experimental of Agnps and Ag-PMMA**

**Table 3: Theoretical and Experimental FTIR Results of PMMA and Ag-PMMA Nanocomposites**

Vibration types of PMMA		Functional group	Theoretical results	Experimental result	Research results
Stretching vibration	Model molecules rang cm <sup>-1</sup>	_CH_, _CH_	2862.3	2924.83	
		_CH <sub>3</sub>	2832.14	2949.91, 2994.81	
		_C=O	1565.09, 1720.97	1721.87, 1677.31	
Bending vibration	Model molecules rang cm-l	_C_O	968.79, 948.434, 997.95, 1022, 1105, 1238.92	986.18, 1062.43, 1239.77	
		_CH <sub>2</sub>	720.393, 774.327	749.48, 1480	
Vibration types of Ag-PMMA		Functional group	Theoretical results	Experimental result	Research results
Stretching vibration	Model molecules rang cm-l	_CH_, _CH <sub>2</sub>	2869.29, 2853.48	2994.81, 2949.91	2925, 2933
		_CH <sub>3</sub>	2850.21, 2776.86	2924.83, 2851.64	2938, 2990
		_C=O	1565.97	1677.31, 1721.87, 1239.77, 1269.45	1700, 1750
Bending vibration	Model molecules rang cm-l	_C_O	1105.24, 1124.29, 994.682, 1222.6	986.18, 1062.43, 1239.77	970-1300
		_CH <sub>2</sub>	727.37, 772.361, 1356.6, 1393.76, 1449.96	749.48, 1434.66	720-770, 1350, 1353, 1368, 1439

The FTIR spectra of PMMA and nanocomposites have two types of vibration stretching and bending.

The bonds CH, CH<sub>3</sub> and C=O had stretched vibration modes, while bending vibration appears in the C-H and C-O. From the results, it can be noted that the theoretical data comparable with experimental data are compatible with results of literature [17, 15, 13].

### Some Electronic Properties

In this section, we calculate some electronic properties for polymer and nanocomposites molecules group, using DFT methods. These properties included the ionization potential IP, electron affinity EA, electro negativity  $\chi$ , chemical hardness  $\eta$ , softness  $S$  and electrophilic index  $\omega$ . The table (4) shows some electronic properties of the nanocomposite studied.

**Table 4: Shows Some Electronic Properties of the Nanocomposite which Studied**

No. of molecular	$I_p$ (eV)	$E_a$ (eV)	$\kappa$ (eV)	$\eta$ (eV)	$S$ (eV)	$\omega$ (eV)
0%	5.1526	0.137	-2.50759	2.645	0.1994	1.395
5%	4.25	0.4783	-2.36415	1.886	0.265	1.482
10%	4.584	0.9732	-2.24332	1.805	0.277	2.138
15%	3.436	0.030	-1.73317	1.703	0.294	0.882
20%	3.361	0.127	-1.61699	1.617	0.309	0.939
25%	4.613	1.666	-3.1397	1.473	0.339	3.346

### Dipole Moments and Polarizability

Table (5) shows the values of the total dipole moment, and average polarizability for nanocomposites molecules



group, calculated by DFT - B3LYP/6-311G (d, p) methods

The reactivity of the molecule, therefore, the nanosilver molecules group is more reactive than PMMA has the largest value of average polarizability, and it is more reactive with small energy gap than the others i.e Dipole moment and average polarizability.

**Table 5: Calculated Dipole Moment M (Debye), Component Of Ai ( I = Xx, Yy, Zz ) and Average Polarizability <A> in Atomic Unites for Nanocomposites Molecules**

B3LYP/6-31G(p,d)					
No. of Molecules	< $\alpha$ >	$\mu_x$	$\mu_y$	$\mu_z$	$\mu_{total}$
0%	7.4793	5.9104	6.0486	-2.7924	8.9059
5%	11.3992	-6.5082	-1.2795	-0.1182	6.6338
10%	8.1364	-3.8670	16.0237	-2.2721	16.6396
15%	4.6130	1.8813	4.2320	-3.0346	5.5369
20%	5.6448	-1.0955	-9.6048	-1.5206	9.785
25%	9.561	0.1749	-7.0971	0.0834	7.0998

## CONCLUSIONS

- The Density Functional Theory (DFT) method with B3LYP/6311G (d, p) level presented a good result in the calculation of geometrical parameters, fundamental vibrational frequencies and exciting energies in comparison with experimental data.
- The HOMO and LUMO energies gave values of energy gaps of AgNPs, the theoretical calculation by Gaussian 09 programs obtained  $E_g$  (2.04 EV).
- HOMO and LUMO for different concentration of nanosilver doped with PMMA polymer, using DFT methods showed the energy band gap for (Ag -PMMA) nanocomposites were decreased from 5.02 eV, with the increasing percentage weight of the nanosilver to 2.95 EV. These results considered as a good agreement with experimental results.
- The UV-VIS and FTIR results using DFT methods find good agreements with experimental results.

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