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Electronic Properties And Molecular Structure For AsGe Nanoclusters

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***Abstract*—Some electronical properties for Arsenic Germanium nanoclusters have been studied by using density functional theory at the ground state, B3LYP level and 3-21G basis set by applying sophisticated algorithms in Gaussian 09 package. Molecular structure, density of states, infrared spectra, polarizability, binding energy, total energy, energy gap and electronic states have been investigated for As_4, As_6, Ge_4, Ge_6, As_4Ge_4, As_6Ge_4, As_4Ge_6 and As_6Ge_6 nanoclusters. The study shows that the nanocluster As_4 has non-zero energy gap, but the other nanoclusters have semiconductor properties, and this property very useful in electronic devices as solar cells. Non-bonding orbitals will generate in mixed nanclusters. The nanocluster As_4Ge_6 has the highest valuebinding energy. Arsenic nanoclsters stand for acceptors, but Germanium nanoclusters represent donors. New orbitals will originate in band gap diagram. The nanocluster As_4Ge_6 the most reactivity nanocluster. New bonds generate in Arsenic Germanium nanoclusters.**

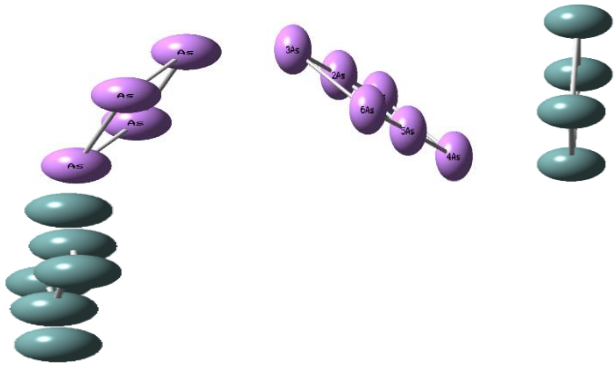
Keywords—DFT, Binding energy, Polarizability, DOS, Infrared spectra.

1. Introduction:

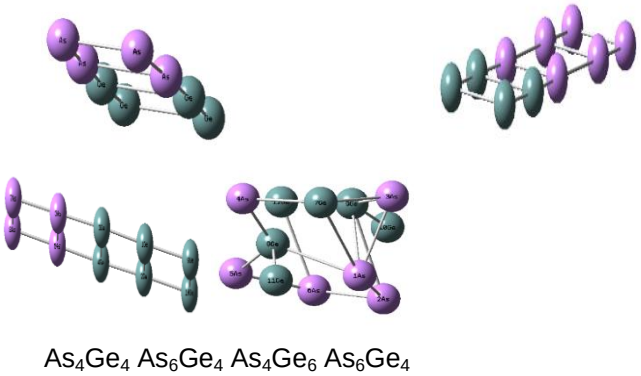
Density functional theory (DFT) is one of the methods that are used to investigate molecular structure, electronic properties, contours and surfaces to individual atoms, molecules and nanoclusters[1]. This method is used largely in material science and solid state physics [2]. DFT deals with the electron density instead of the wave function. It proposes that the electron density depend only on spatial coordinates without consideration how the electrons are existed in the system [3]. But the wave function assume 3N spatial variables and one coordinate for the spin, in which the positions of the nuclei fixed [4]. Density functional theory is regarded one of the popular methods in computational physics and chemistry [5]. One can define DFT with a simplified form that it is a method to find an approximately solution to Schrodinger equation for many particle system [6]. In solid state physics mostly the theoretical calculations agree satisfactory with the experimental data [7]. The name density functional theory came from using the electron density in the calculations [8]. Density functional theory has been introduced in 1960's in two seminal papers by Hohenberg-Kohn in 1964 and Kohn-Sham in 1965. The predecessor of density functional theory is Thomas-Fermi model in 1927[9]. DFT employs some approximations like Generalized Gradient Approximation (GGA), Local Density Approximation (LDA) and Local Density Spin Approximation (LDSA) [10]. Density functional theory has been submitted throughout geometrical optimization procedure by applying sophisticated algorithms in Gaussian09 program. In DFT need to implement appropriate basis sets [11]. The geometrical optimization stops when stationary point is found on the potential surface, this means it can be find configuration to the minimum energy when the resultant force on the atoms is zero[12].

2. Molecular Geometry:

The molecular structure has been investigated for As_4, As_6, Ge_4, Ge_6, As_4Ge_4, As_6Ge_4, As_4Ge_6 and As_6Ge_6 by using density functional theory at the level B3LYP and 3-21G basis set with Gaussian09 program. The following figures stand for the molecular structure for the samples under study.



Ag_4 Ag_6 Ge_4 Ge_6



As_4Ge_4 As_6Ge_4 As_4Ge_6 As_6Ge_4

Figure (1):The molecular structure for As_4, As_6, Ge_4, Ge_6, As_4Ge_4, As_6Ge_4, As_4Ge_6 and As_6Ge_6 nanoclusters.

3. Calculations:

3.1. Total Energy:

The total energy of the nanocluster in density functional theory can be divided to the following parts in the equation below [13]:

$$E = E_T + E_v + E_J + E_{XC} \ .(1)$$

Where E stands for the total energy, E_T is the electronic kinetic energy, E_v stands for the electronuclear interaction energy, E_J indicates to the electron-electron repulsion energy, E_{XC} denotes to the exchange correlation term.

Table (1): Total energy for As4, As_6, Ge_4, Ge_6, As_4Ge_4, As_6Ge_4, As_4Ge_6 and As_6Ge_6 nanoclusters.

System	Total Energy(a.u)	Total Energy(eV)
As_4	-8900.625316	-242186.0149
As_6	-13350.95768	-363279.5586
Ge_4	-8268.009177	-224972.5297
Ge_6	-12402.03688	-337459.4235
As_4Ge_4	-17168.68115	-467159.8141
As_6Ge_4	-21619.00049	-588253.0034
As_4Ge_6	-21302.66529	-579645.5225
As_6Ge_6	-25753.24958	-700745.921

3.2. Binding energy:

The binding energy of the nanocluster is amount describe how the atoms bind in the nanoclusters. Binding energy can calculate from the relation [14]:

$$E_{Binding} = n\,E_x + m\,E_y - E(x_n, y_m) \ .(2)$$

$E_{Binding}$ represent the binding energy, E_x is the energy of the molecule x, E_y is the energy of the molecule y, n is the number of atoms of the molecule x, m is the number of atoms of the molecule y and E (x_n,y_m) stands for the energy of the molecule (x_n y_m).

Table (2): Binding energy for As_4, As_6, Ge_4, Ge_6, As_4Ge_4, As_6Ge_4, As_4Ge_6 and As_6Ge_6 nanoclusters.

System	Binding Energy(eV)
As_4Ge_4	1.26953697
As_6Ge_4	0.91515393
As_4Ge_6	0.08418774
As_6Ge_6	6.9390942

3.3. Energy gap(Eg):

Energy gap is the quantity that refers to the energy which the electron need to cross from valence band to the conduction band [15]. Through the value of the energy gap one can knows if the material conductor or insulator or semiconductor. In density functional theory the energy gap can calculate from the equation [16]:

$$E_g = E_{LUMO} - E_{HOMO} \ .(3)$$

Table (3): Energy gap (E_g) for As_4, As_6, Ge_4, Ge_6, As_4Ge_4, As_6Ge_4, As_4Ge_6 and As_6Ge_6 nanoclusters.

System	Energy gap(eV)
As_4	0.188293
As_6	0.76188
Ge_4	2.240744
Ge_6	2.286184
As_4Ge_4	1.783888
As_6Ge_4	1.427709
As_4Ge_6	0.996702
As_6Ge_6	1.973813

3.4. Electronic states:

HOMO and LUMO energies stand for the electronic states. In which HOMO means high occupied molecular orbital, but LUMO means low unoccupied molecular orbital [17]. From HOMO and LUMO values one can predict if the element will behave as donor or acceptor [18].

Table (4): Electronic states for As_4, As_6, Ge_4, Ge_6, As_4Ge_4, As_6Ge_4, As_4Ge_6 and As_6Ge_6 nanoclusters.

System	HOMO(eV)	LUMO(eV)
As_4	-5.2858146	-5.0975214
As_6	-5.3056779	-4.5437979
Ge_4	-5.8098792	-3.5691357
Ge_6	-5.5824036	-3.2962194
As_4Ge_4	-5.5225416	-3.738654
As_6Ge_4	-5.5883898	-4.1606811
As_4Ge_6	-4.982151	-3.9854487
As_6Ge_6	-5.3802333	-3.4064199

3.5. Polarizability:

Polarizability is a quantity describe the capability of the molecule to polarization. Also polarizability determines the linear response of the electron density with existence of seminal electric field. It gives sight about the internal structure of the molecules. Polarizability stands for variation with second order according to the equation [19]:

$$\alpha = -\left(\frac{\partial^2 E}{\partial F_a \partial F_b}\right)_{a,b} = x, y, z \ .(4)$$

The average of polarizability $< \alpha >$ in density functional theory can be given by the relation [20]:

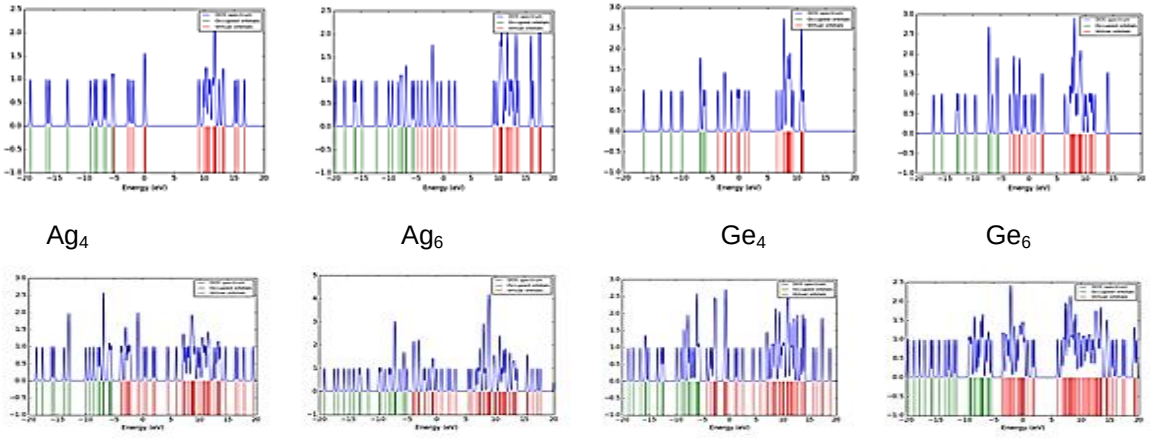
$$< \alpha > = \frac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right) .(5)$$

Table (5): Polarizability and the average polarizability for As_4, As_6, Ge_4, Ge_6, As_4Ge_4, As_6Ge_4, As_4Ge_6 and As_6Ge_6 nanoclusters.

System	α_{xx}	α_{yy}	α_{zz}	< α >
As_4	40.837	137.255	157.721	111.9376667
As_6	310.707	191.907	63.514	188.7093333
Ge_4	61.838	148.373	213.667	141.2926667
Ge_6	316.1	296.097	84.028	232.075
As_4Ge_4	87.75	273.251	598.708	319.903
As_6Ge_4	111.412	334.371	757.792	401.1916667
As_4Ge_6	107.736	339.443	987.797	478.3253333
As_6Ge_6	511.697	364.604	311.179	395.8266667

3.6. Density of states (DOS):

In solid state physics density of state can be defined as the number of permitted states of the energy level that can be occupied [21]. In quantum physics the waves and particles that like waves can occupy modes or states with specific wavelengths, and the propagation direction determine by the system [22]. Mostly, there is certain allowed states, this denotes to number of certain allowed wavelengths with certain energy levels [23]. Density of states can be investigate for electrons, photons and phonons according to quantum mechanics. Density of state is very important property in solid state physics and quantum physics [24].



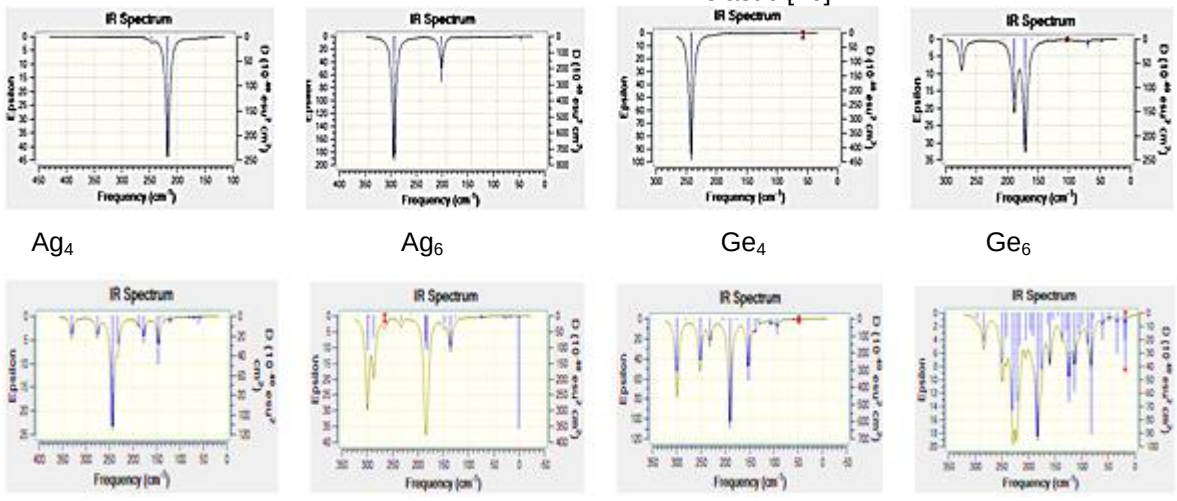
Ag_4 Ag_6 Ge_4 Ge_6

As_4Ge_4 As_6Ge_4 As_4Ge_6 As_6Ge_4

Figure (2):Density of states As_4, As_6, Ge_4, Ge_6, As_4Ge_4, As_6Ge_4, As_4Ge_6 and As_6Ge_6 nanoclusters.

3.7. Infrared Spectra:

There are two kinds of stretching vibrations, symmetric and asymmetric. When the atoms vibrate in the same phase the stretching oscillation happen. Non-stretching vibrations take place when the atoms oscillate with different phases [25]. Infrared spectra provides with harmonic vibrational frequencies. The number of modes depends on the number of atoms in the nanocluster. Each value or range stands for vibration mode. The vibration mode either elastic or inelastic [26].



Ag_4 Ag_6 Ge_4 Ge_6

As_4Ge_4 As_6Ge_4 As_4Ge_6 As_6Ge_4

Figure (3) Infrared spectra for As_4, As_6, Ge_4, Ge_6, As_4Ge_4, As_6Ge_4, As_4Ge_6 and As_6Ge_6 nanoclusters.

4. Results and Discussion:

Table (1) summarize the total energy for all nanoclusters under study. The total energy of the nanocluster As_4Ge_4 is greater than the total energy for sum of the total energy of As_4 plus Ge_4, hence non-bonding orbitals will originate between Arsenic atoms and Germanium atoms. Also the total energy of As_6Ge_6 is greater than the total energy of sum of sum of the total energy of As_6 adding to the total energy of Ge_6, this explain that the orbital which emerge between Arsenic atoms and Germanium atoms will be non-bonding [27].

From table(2)one can say the nanocluster As_4Ge_6 is more binding nanocluster because of the minimum value of the binding energy among the nanoclusters under study, so this nanocluster need less amount of energy to enter binding state. But the nanocluster As_4Ge_4 is less binding nanocluster because it has the maximum value of binding energy. One can consider the nanocluster As_4Ge_6 will be more stable nanocluster, but the nanocluster As_4Ge_4 will be less stable nanocluster. Binding energy is very important property in physics because this quantity denotes to existence of the system [28].

Table (3) appears that some nanoclusters have value close to the energy gap of semiconductors, but the other nanoclusters have energy gap close to the energy gap of semi-metallic. For example As_4 has value of energy gap equal to (0.188293 eV), hence this nanocluster has semi-metallic property while the nanocuster As_4Ge_6 has value of energy gap (0.996702 eV), so this nanoclster can be considered semiconductor. One can see adding As_4 to Ge_6 nanocluster lessened the value of energy gap, this indicates to improvement the electronic properties of the nanoclusters[29].

Table (4) gives HOMO and LUMO energies for all nanoclusters. HOMO energy of the nanocluster Ge_4 is larger than HOMO energy of the nanocluster As_4, one can say Ge_4 will behave as an acceptor in the nancluster As_4Ge_4, but As_4 will behave as donor, hence the electrons will release to the unoccupied orbitals. Also from observation of HOMO energies values one can see HOMO energy of individual Germanium nanoclusters is greater than HOMO energy of individual Arsenic nanoclusters, therefore when Germanium nanoclusters interact with Arsenic nanoclusters Germanium stands for acceptor, but Arsenic represents the donor[30].

In table (5) some can see the nanocluster As_4Ge_6 has the highest value of the average polarizability among all nanoclusters under study, therefore As_4Ge_6 is more reactivity nanocluster. But the nanocluster As_4Ge_4 is the lowest reactivity nanocluster because it has the lowest value of the polarizability. Polarizability is very important property in physics because it gives sight about the internal geometry of the nanoclusters[31].

Figure (2) show density of state to the nanoclusters. When the density of state at certain level equal to zero this means there is no state to occupy. If the density of states (DOS) equal to zero, the local density of states may be not zero because of local vibrations which cause distortion in the original system, another factor effects on local density of states is the local potential. Density of state increase as the electron energy increase. Topological properties and symmetry also influences on the density of states. In the figures one can see adding Ge_4 to the nanocluster As_4 tend to change in band gap, this means new levels or new states can be occupied. Hence new non-bonding orbitals will generate, and the electrons can occupy this orbitals with consideration some quantum conditions [32].

Figure (3) demonstrates infrared spectra diagrams. The nanocluster As_4 has only one clear peak, when Ge_4 adds to As_4 the new nanocluster As_4Ge_4 will have five clear peaks, hence new bonds generate in the new nanocluster. In general adding new atoms to the nanocluster effects on the number of peaks in the nanocluster, and the difference in the number of peaks refers to new bonds originate between atoms. Hence one can say (As-Ge bonds) generate in the mixed nanoclusters. When someone makes a comparisons between figures can conclude new bonds will generate after the interaction [33].

Conclusions:

All hybrid nanoclusters under study have non-bonding orbitals because of the interference between their atomic orbitals according to molecular orbital theory. The nanocluster As_4Ge_6 is the highest binding nanocluster, it has binding energy ($E_{Binding}$ = 0.08418774 eV), this value stands for the lowest value of binding energy among all nanoclusters under study, hence this nanocluster need less amount of energy to enter binding state. As_6 nanoclster has energy gap close to the energy gap of Gallium Arsenide ($EgAs_6$ = 0.76188eV), one can conclude this property is very important in electronic species and solar cells. As_4 has semi-metallic properties, but As_4Ge_6 has semiconductor energy gap. As_4 and As_6 stand for acceptors, but Ge_4 and Ge_6 represent donors throughout the interactions according to HOMO and LUMO energies. The nanocluster As_4Ge_6 has the largest value of polarizability (478.3253333 eV), therefore this nanocluster is the highest reactivity. There are new states or new energy level originate when the interaction between Germanium and Arsenic happen and this is very clear through the structure of band gap. The new peaks in hybrid nanoclusters refers to new (As-Ge) bonds generate after interaction.

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