

# Study of the Geometrical Optimization and Energy Gap of AIAs Diamondoids

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## Abstract

The electronic structure of zinc blend AIAs diamondoids was investigated using density functional theory at the local spin density approximation with double zeta functions that include polarization functions (LSDA/6-31G+(d,p)). Different sizes of diamondoids are investigated. The investigated properties include geometrical optimization, comparison between the bond length in the different structures, density of bonds, total energy,  $E_{HOMO}$ ,  $E_{LUMO}$  and energy gap. The results showed that the energy gap of these structures was mostly reduced with increasing the number of Al and As atoms. This result is in good agreement with experimental results.

**Keywords:** Diamondoids, Band Structure, Ab initio, DFT.

## الخلاصة

تم في هذا البحث دراسة التركيب الإلكتروني لبورات أرسنايد الألمنيوم الماسية (AIAs) زنك بلند بأحجام مختلفة باستعمال نظرية دالية الكثافة DFT عند تقريب كثافة اليرم الموضعي واستخدام تمثيل الدالة LSDA/ 6-31G+(d,p) ان الخواص التي تم بحثها تضمنت الامثلية الهندسية وكثافة الاواصر ومقارنتها لكافة التراكيب التي درست والطاقة الكلية وفجوة الطاقة واعلى مستوى طاقة محجوز بالإلكترونات واقل مستوى طاقة غير محجوز. تبين من النتائج التي تم التوصل اليها ان فجوة الطاقة للتراكيب المدروسة تقل بشكل عام مع زيادة العدد الكلي لذرات الألمنيوم والأرسنايد المضافة للتركيب وتقترب من فجوة الطاقة للمادة في الحالة الصلبة وتتوافق بشكل جيد مع النتائج العملية.

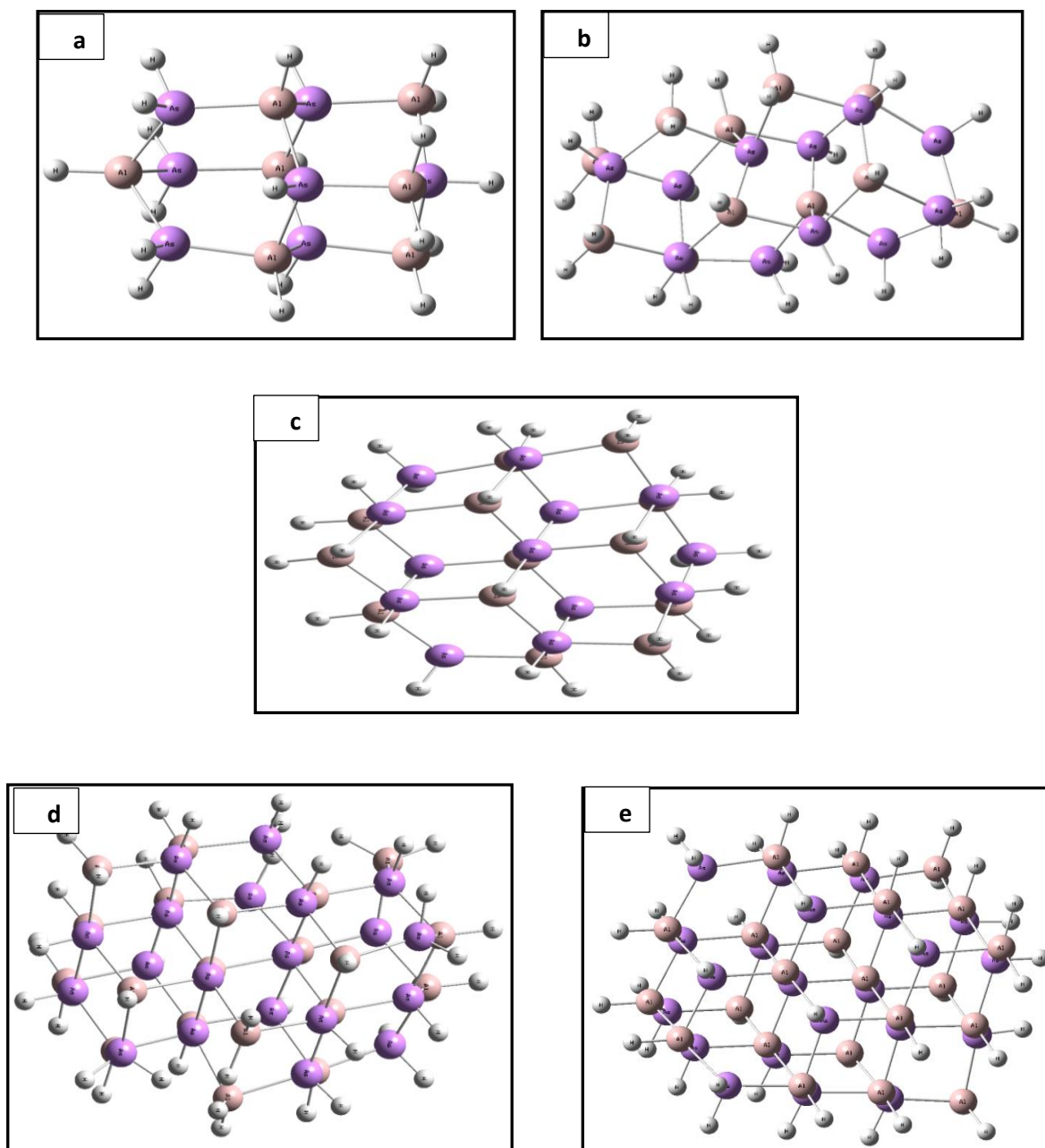
الكلمات المفتاحية: تركيب ماسي، التركيب الحزمي، طريقة كمية تامة، نظرية دالية الكثافة.

## Introduction

The group III-V zinc blende type binary compounds have attracted much attention for their potential application in electronic industry. In the recent past decades, number of experimental and theoretical investigations were carried out on electronic, optical, mechanical and thermodynamic properties of these compounds [Reshak and Auluck, 2007; Salehi, 2014; Ameri, *et al.*, 2012].

Diamondoids are a class of molecules and nanocrystals that are fractions of nano synthesizing procedures of diamond and zinc blende structure materials. However, these molecules need to be separated from other kinds of molecules which is the case for carbon diamondoids separated from petroleum, [Dahl, *et al.*, 2003, De Araujo, *et al.*, 2012]. Diamondoids have the shape of cages that are added together to form nanocrystals and bulk. Present trend in molecular electronics is to manufacture single molecules that should be the ultimate smallest possible electronic component. These molecules should have exceptional stability that can endure applied electrical or magnetic fields that are applied due to electronic signals. AIAs applications in present day electronics [Sze and Ng, 2007] give us the feeling that it will have promising future in molecular electronics, [Alanis, *et al.*, 2008, Nishizawa and Kurabayashi, 2002]. AIAs diamondoids have not been explored before. These diamondoids have exceptional stability with respect to other molecules or AIAs nano structures. In Figure (1) some AIAs diamondoids are shown. From this Figure we can note that all of surface Al and As atoms are bond to either one or two hydrogen atoms from a total of four bonds for each atom. This means every atom is bonded to the core of AIAs diamondoid by at least two bonds. As a result, removal of Al or As atoms

from the surface of the molecule requires breaking at least two bonds. Other classes of AIAs nanocrystals or molecules (other than diamondoids) might have Al or As surface atoms that are bonded to the nanocrystals (molecule) by one bond only. These non-diamondoid molecules are relatively easier to break leading to deterioration of the molecule or nanocrystals. Aluminum arsenide (AIAs) is a compound semiconductor with an indirect band gap and it has a zinc-blend (zb) structure, [Grundmann.2010]. AIAs is one of the most technologically important compound semiconductor materials, where it has many optoelectronics and photovoltaic applications in space solar cells, telecommunication and data communication networks, mobiles, telephones, laptop computers, compact disc players, etc, [Mohammad, 2005]. Therefore, aluminum arsenide has been intensively investigated in the recent years, where Bouarissa and Boucenna [Hehre, *et al.*, 1986], studied the electronic, optical and mechanical properties of AIAs and they showed that the results are in agreement with the available experimental and theoretical data. Chimata[Chimata, 2010] studied theoretically the electronic structure of aluminum arsenide crystal, and they found that the band gap value obtained is in good agreement with the experimental value. Shimazaki and Asai, [Chimata. 2010], studied the energy band structure of Si, AlP, AIAs, GaP and GaAs using screened Hartree–Fock exchange method, and they found that the direct and indirect band gaps don't agree with experimental values. AIAs semiconductor belong to this group. These materials are one of the important electronic and optical materials and they are used in the field of electronic device fabrication[Bouarissa and Boucenna, 2009]. In the present work have investigated the electronic structure properties of titled compounds using DFT method within Local Spin Density Approximation.



**Figure 1. Geometrically optimized a- AlAs-diamantine b- AlAs-tetramantane c- AlAs-hexamantane d- AlAs octamantane e- AlAs-decamantane diamondoids using LSDA / 6-31G+(d,p) theory and basis.**

### Theory

Diamondoids are cage shaped structures discovered in petroleum. These cages are stable and strong since all the constituting atoms (except hydrogen atoms) are connected to bulk of molecule by two or more bonds. Nomenclature of diamondoids follows the number of cages in each diamondoid. As an example, diamantine contains two cages while decamantane contains ten cages Figure (1). To keep the number of Al atoms equal to As atoms, only even numbers of cages are discussed here that have nearly equiaxed dimensions. To clearly manifest size effects, we added two other small molecules i.e.  $\text{AlAsH}_6$  and  $\text{Al}_3\text{As}_3\text{H}_{12}$  that are not diamondoids. All-electron density functional theory (DFT) at Local spin density approximation, is used. 6-31G+(d,p) basis set that contains polarization and diffuse functions are incorporated

in present calculations, [NIST, 2014]. All calculations are performed using Gaussian 09 Program, [Frisch, *et al.*, 2003].

One of the key quantum mechanical methods used in physics and chemistry to investigate the electronic structure of many-electron systems is density functional theory, in particular molecules based on a strategy of modeling electron correlation via general functional of the electron density. DFT is widely used by physicists and chemists to investigate the ground-state properties of interacting many-particles systems such as atoms, molecules and crystals. DFT transforms the many-body system into one of non-interacting fermions in an effective field. In other words, the electrical properties of many interacting particles system can be described as a functional of the ground-state density of the system [Parr and Weitao, 1994].

The local density approximation (LDA) is the simplest approximation to  $E_{xc}[\rho(\vec{r})]$ , which assumes the system is a homogenous electron gas and  $E_{xc}[\rho(\vec{r})]$  depends only on the local value of electron density. Therefore  $E_{xc}[\rho(\vec{r})]$  can be written in a simple form [Young, 2001, Mueller, 2001].

To compared LDA, LSDA, defines the exchange correlation potential in terms of the density of  $\alpha$  and  $\beta$  spins (i.e. spin up and spin down respectively) and was developed for calculating the properties of open-shell systems [Cramer, 2008]:

$$E_{xc}^{LSDA}[\rho_{\alpha}, \rho_{\beta}] = \int \rho(\vec{r}) \varepsilon_{xc}(\rho(\vec{r})_{\alpha}, \rho(\vec{r})_{\beta}) d\vec{r} \quad \dots (1)$$

Where  $\varepsilon_{xc}$  is the exchange-correlation energy per particle. The LSD approximation provides better results than (HF) for certain properties such as equilibrium structures, vibrational frequencies and dipole moments, however, it cannot determine the highly accurate energy data as desired by many computational chemists. In general, the LSDA provides reliable information for those systems that closely resemble a uniform electron gas, namely those in which the density varies slowly with position. However in reality, atomic and molecular system do not possess uniform electron densities and thus more sophisticated models are required.

## Results and discussion

Table 1 shows the results of the relaxation of the structures under study, included the bond length Al-As(max-min) and the lattice constant of each structure. The value of the distance between two neighboring atoms ( $r_{nn}$ ) in diamond structure is

$$\text{given by [Van Camp, 1988]: } r_{nn} = \frac{\sqrt{3}}{4} a \quad \dots (2)$$

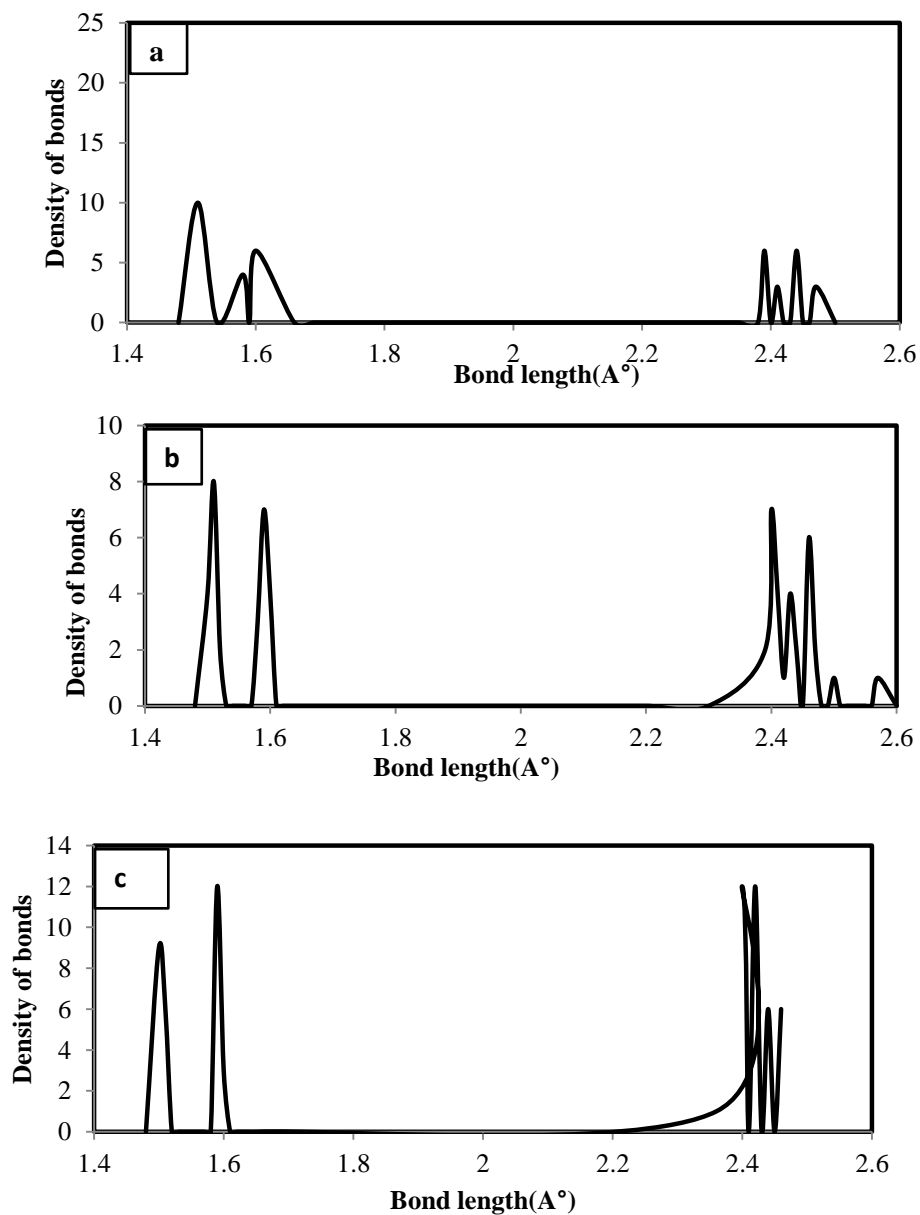
where ( $a$ ) is a lattice constant.

**Table 1: The geometrical parameters from the relaxation of the studied structures**

Molecular structure	Bond Length (Å)		Lattice constant (Å)
	Min	Max	
$\text{Al}_7\text{As}_7\text{H}_{20}$	2.394	2.47	5.6
$\text{Al}_{11}\text{As}_{11}\text{H}_{28}$	2.399	2.57	5.63
$\text{Al}_{13}\text{As}_{13}\text{H}_{30}$	2.363	2.46	5.59
$\text{Al}_{20}\text{As}_{20}\text{H}_{42}$	2.35	2.47	5.58
$\text{Al}_{22}\text{As}_{22}\text{H}_{42}$	2.34	2.470	5.54

In Figure 2 the bond length of AlAs diamondoids is shown. The shortest bonds are As-H and Al-H respectively. The small number of bonds in AlAs diamantane does not allow the true features of these bonds. From AlAs tetramantane to decamantane the As-H is a sharp high peak while that of Al-H is wide low height peak. The reason for this is that (As) is a nonmetal that strongly localizes electrons in its bonds. On the contrary (Al) is a metal that has relatively more delocalized electrons in its bonds. The Al-As bond has several peaks depending on the number of hydrogen atoms attached to Al and As atoms.

In AlAs-diamantane (Figure 2a) the smallest value of this bond is when both Al and As connected to single hydrogen atom having the value 2.39 Å which is the highest peak for diamantane. The longest bond is at 2.47 Å near the far ends of diamantane molecule in which one of the atoms is connected to two hydrogen atom. The position of the molecule affects their values that explain the several peaks for AlAs tetramantane and hexamantane. AlAs octamantane and decamantane on the other hand have different situation since some inner Al-As are formed which are not connected to any hydrogen atoms. This results in smaller bonds that reach 2.35 Å. For the same reason bigger nanoparticles have usually smaller average bond length than small nanoparticles. The spectrum of bonds in the case of AlAs octamantane has the range 2.35-2.47 Å with the highest peak at 2.41 Å and the spectrum of bonds for AlAs decamantane is the range 2.34-2.47 Å with the highest peak at the 2.4 Å.



**Figure 2 : Density of bonds as a function of bonds length in AIAs (a) diamantane (b) tetramantane (c) hexamantane (d) octamantane (e) decamantane using LSDA/6-31G+(d,p) basis set.**

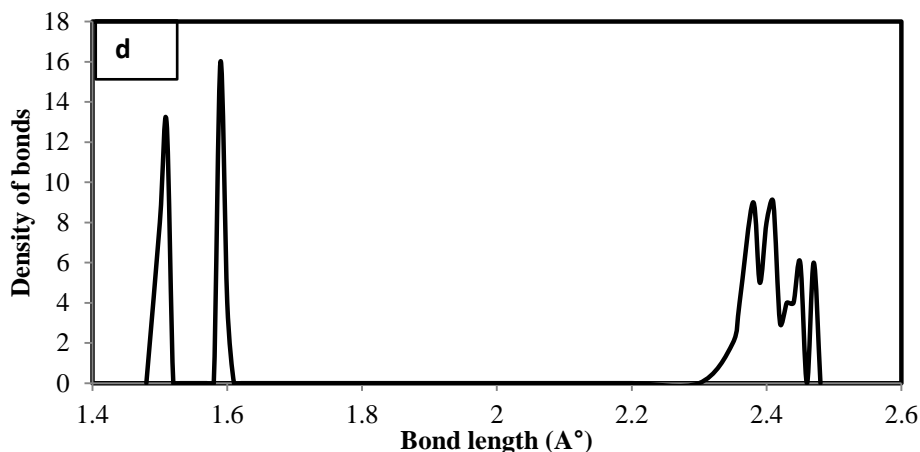
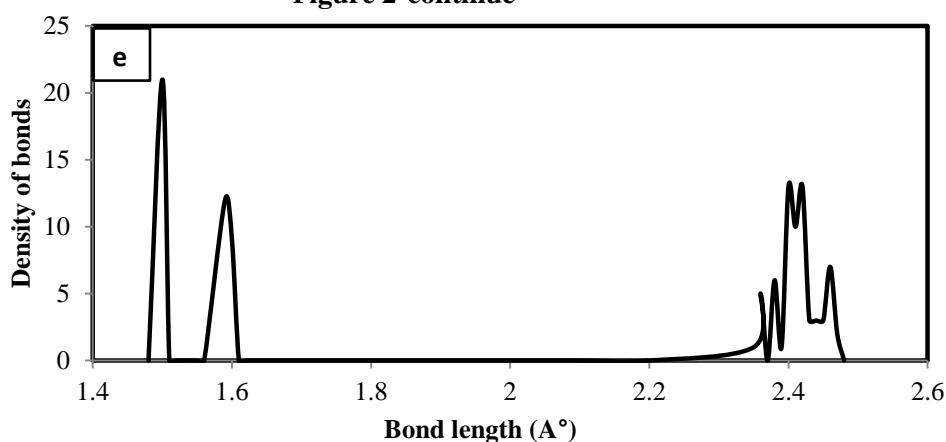


Figure 2 continue



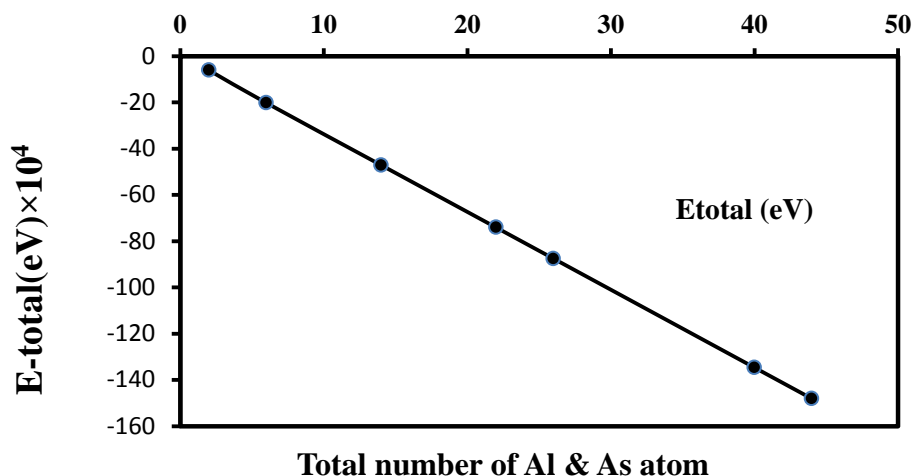
It is found from Figure 2 and Table 2, that the value of density of bonds is increased with increasing the number of Al and As atoms.

**Table 2: The density of bonds and bond length of the AlAs diamondoids under study**

LSDA 6-31G+(d,p) basis set	As-H		Al-H		Al-As highest peak		Al-As lowest peak	
	Bond Length (Å°)	Density of bonds	Bond Length (Å°)	Density Of bonds	Bond Length (Å°)	Density of bonds	Bond Length (Å°)	Density Of Bonds
Diamantane	1.51	10	1.6	6	2.39	6	2.41	3
tetramantane	1.51	8	1.59	7	2.4	7	2.5	1
hexamantane	1.5	9	1.59	12	2.4	12	2.36	1
octamantane	1.51	13	1.59	16	2.41	9	2.36	2
decamantane	1.51	21	1.59	12	2.4	13	2.39	1

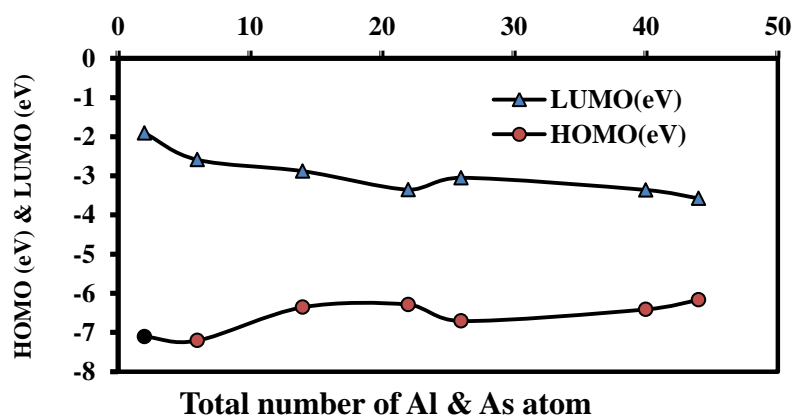
The total energy for all studied molecules as a linear function of Al& As atoms number adding to the ring and the final total energy of the product is the collection of total energy of all small molecules. Figure 3 shows the total energy in eV of the diamondoids under study, from the relationship between the total energy and the total number of Al and As atoms we showed that the structure goes to more stable with

increasing the Al and As atoms. On the scale shown in this Figure, the size dependence of the energy is linear inversely proportional.



**Figure 3 : The total energy in eV of the diamondoids under study**

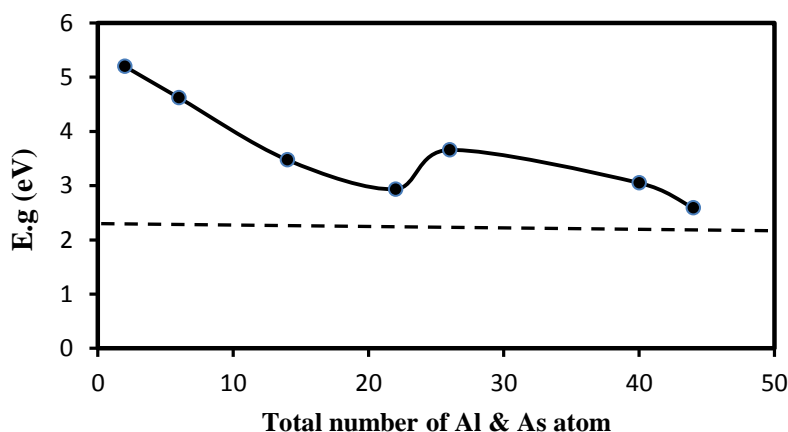
The Local spin density approximation LSDA has shown to be highly successful for determination of properties such as HOMO energy, LUMO energy. Figure 4 illustrates the effect of increasing the number of Al and As atoms on the high occupied molecular orbital energy  $E_{HOMO}$  and the lower unoccupied molecular orbital energy  $E_{LUMO}$  of the structures under study. From this figure, increasing the number of Al and As atoms has an effect on both  $E_{HOMO}$  and  $E_{LUMO}$ , approximately, the HOMO energy was increased and LUMO energy was decreased, this behavior comes from the linear combination of atomic orbitals to construct the molecular orbitals. The last structure decamantane ( $Al_{22}As_{22}H_{42}$ ) has the largest value of HOMO energy and the smallest value of LUMO energy.



**Figure 4: The  $E_{HOMO}$  and  $E_{LUMO}$  of the structures under study**

The results showed that the energy gap of the diamondoids under study decreases with the addition of Al and As atoms. All new structures have energy gap smaller than that of the original, but the least is at the last structure  $Al_{22}As_{22}H_{42}$ . Figure 5 shows the variation mode of the energy gap, this variation indicates that the energy gap of diamondoids will be soft with adding the Al and As atoms and depends on the shape of the diamondoids under study.





**Figure 5: The energy gap of the structures under study. The dashed line represent the experimental bulk value 2.25 eV.**

## Conclusions

From the above results we conclude that, the increasing of the total number of Al and As atoms in the diamondoids structures decreases the total energy of the structure, the structure becomes more stable than the reference structure. All new structures have energy gap smaller than that of the original, but the least is at the last structure  $\text{Al}_{22}\text{As}_{22}\text{H}_{42}$ . Increasing the number of Al and As atoms in diamondoid structures leads to soft and efficient electronic properties. These results are global properties in which the new structures are more active in donating or accepting electrons than the original structure. It was noted that the AlAs tetramantane is the best structure among all structure under study. This is an indication to construct low dimensional structures that have efficient properties in which the lower lattice constant structure has the larger number of atoms and the smaller value of energy gap.

## References

- Bouarissa N. and Boucenna M, "**Band parameters for AlAs, InAs and their ternary mixed crystals**", Phys. Scr, 79, 2009.
- Camacho-Alanis, F. ; L. Wu, G. Zangari, and N. Swami, J. Mater. Chem. 18, 5459 (2008).
- Chimata R, "**Optical Properties of Materials Calculated from First Principles Theory**", (Department of Information Technology, 2010).
- Cramer, C.J. "**Essentials of Computational Chemistry: Theories and Models**", 2<sup>nd</sup> ed., John Wiley & Sons Ltd., The Atrium, Southern Gate, Chichester, England, 2004.
- Dahl, J. E.; S. G. Liu, and R. M. K. Carlson, Sci. 299, 96, 2003.
- de Araujo, P.L.B.; G.A. Mansoori, and E. S. de Araujo, Int. J. Oil Gas Coal Technol. 5, 316, 2012.
- Frisch, M.J.; G.W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J.

- Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian 03, Revision B.01, Gaussian, Inc., Pittsburgh PA, 2003.
- Fulde P., "**Solids with Weak and Strong Electron Correlations**", (Max-Planck-Institut für Physik komplexer Systeme, 2008.
- Grundmann M.: "**The Physics of Semiconductors**" (Springer-Verlag Berlin Heidelberg, , 2<sup>nd</sup> ed., 2010
- Hehre W, Random L, Schleyer P, and Pople J, "**Ab-initio Molecular Orbital Theory**", John Wiley and Sons,1986.
- Komsa H. and Pasquarello A.: "**Dangling bond charge transition levels in AlAs, GaAs, and InAs**", J. Applied Physics Letters, 2010.
- Mohammad R, "**The Electronic Band Structure of III (In, Al, Ga)-V (N, As, Sb) Compounds and Ternary Alloys**", M.Sc. Thesis, Middle East Technical University, 2005.
- Mohammed Ameri, Fatima Boufadi, Amina Touia, Meriem Faudil, Djelloul Hachemane, Keltouma Boudia, Amel Slamani, Adjadj Aze-Eddine, "**Ab Initio Calculations Study of Structural and Electronic Properties of Ternary Alloy Al<sub>x</sub>In<sub>1-x</sub>As**", Materials science and applications. Vol. 3, pp. 674-683, 2012.
- Mueller M. "**Fundamentals of Quantum Chemistry: Molecular spectroscopy and Modern Electronic Structure Computations**", Kluwer Academic/plenum publishers, New York, 2001.
- Nishizawa, J.; P. Plotka, and T. Kurabayashi, IEEE Trans. Electron Devices 49, 2002.
- NIST Computational chemistry comparison and benchmark database, release 15b, 2011. <http://cccbdb.nist.gov/> accessed July 1, 2014 .
- Reshak A. H. and S. Auluck, Physica B, Vol. 395, pp. 143-150, 2007.
- Salehi, H.; Mat. Sci. in Semi. Pro. Vol. 26, pp. 477-490, 2014.
- Van Camp, P.; V. Van Doren, and J. Devreese, Phys. Rev. B 38, 1988.
- Young, D. "**Computational Chemistry: A practical Guide for Applying Techniques to Real- World Problems**", NY: John Wiley & Sons, Inc., New York, 2001.