

# Quantum Mechanical Investigations into Thermochemistry Properties and Electronic, Structural of Nanocrystals

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Article Info	Abstract
Received 11/10/2018	<p>This paper presents quantum mechanical investigations that is into electronic and thermochemistry properties of Gallium phosphide. It also investigates diamondoids and nanocrystals using the density functional theory. This is done at the generalized gradient approximation of Perdew et al basis set. This has been used to create Gaussian 09 program auxiliary by Gaussian view. In order to full investigate the ionization potential, affinity, valance bond, conduction bond, zero point energy and thermochemistry properties. The result GaP diamondoids. Electron affinity and conduction band, decreases as a function of the total number of Ga and P atoms in most of the investigated range. Ionization energies zero point and valance bands increased with the number of Ga and P atoms but there are fluctuations in tetramantane and hexamantane In fact, since the present diamondoids are built from nearly cubic cages. Thermochemistry entails calculation of frequency which also includes thermochemical analysis of actual system comprising of thermal energy correction, heat capacity and entropy.</p> <p>Keywords: Gallium Phosphide, Nanocrystals, Thermochemistry, Diamondoids, Quantum, tetramantane and hexamantane</p> <p><b>الخلاصة</b></p> <p>في هذا البحث تم دراسة الخواص الميكانيكية الكمية وهي الخصائص الإلكترونية والكيميائية الحرارية للكاليوم فوسفيد ( GaP). باستخدام تراكيب diamondoids للبلورات النانوية واستخدام نظرية الكثافة الحالات. ويتم ذلك عند تقريب التدرج العام لمجموعة Perdew. وقد تم تحقيق هذا العمل باستخدام برنامج Gaussian 09 ومساعدته برنامج عرض Gaussian من أجل حساب طاقة التأيين، والألفة الإلكترونية، حزمة التكافؤ، حزمة التوصيل، طاقة نقطة الصفر وخصائص الكيمياء الحرارية. وكانت النتائج GaP diamondoids نقصان في الألفة الإلكترون و حزمة التوصيل بزيادة عدد ذرات Ga و P في معظم الحالات المدروسة. وهناك زيادة في طاقات التأيين، نقطة الصفر وحزمة التكافؤ مع زيادة عدد الذرات Ga و P ولكن هناك تقلبات في tetramantane و hexamantane. وذلك لان بنية diamondoids على شكل أقفاص تكاد تكون مكعبة. اما الخواص الكيميائية الحرارية تم حسابها لكل الترددات وتم دراسة تصحيح الطاقة الحرارية والسعة الحرارية والإنتروبييا.</p>
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## Introduction

Gauss rate is classified to be a program that is used for the analysis reactants, products as well as state of transmission of chemical reactions especially when it's for direct dynamics calculation of a state known as variational state theory. This is also done with rate constants as well as multi-dimensional semi classical tunnelling probabilities with the usage of electronic structure methods in the Gaussian [1]. Representation of potential energy using packages of interaction as its first and second derivative whenever needed is reflected in the paper as it is presents investigations in

mechanical quantum into electronic, structural and thermochemistry properties of diamondoids. The use of density functional theory at the PBE/6-31(d) level includes polarization functions as well as part of the used Gaussian program. Density-functional theory is widely accepted as a framework for the study of the electronic ground-state properties of molecules and solids.

The realization of both molecular bond energies as well as thermochemistry properties [2] is been long. Matter, in theoretical description, coupled with physical, chemical as well as biological processes, requires more

accurate methods especially when it comes to description of atomic and molecular-scale interactions. Quantum mechanical approaches are many but over the past 2 to 4 decades, one functional theory that has established itself as theoretical method of choice for this task is the Kohn-Sham density functional theory (DFT). It has also undergone what is.

## Materials and Methods

### Theory

Quantum mechanical calculations are based on the famous Schrödinger wave equation

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + \phi(x)\psi(x, t) \equiv \hat{H}\psi(x, t) \quad (1)$$

Here:  $\hbar = h/(2\pi)$  also known as Planck's constant,  $\Psi$  = wave function,  $t$  = time,  $m$  = mass,  $x$  = position,  $\hat{H}$  = Hamiltonian and  $\phi$  = potential energy.

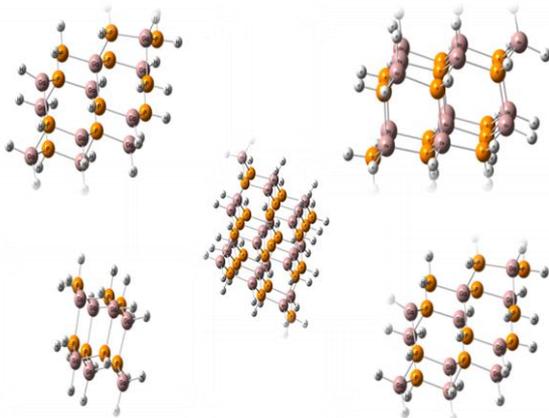


Figure (1): Geometrically optimized GaP-diamondoids

The equation above is regarded as fundamental equation and its role in quantum mechanics is to describe time – dependence of the wave function  $\Psi$  in quantum mechanical systems as analogous to Newton's law of classical mechanics which happens to be the second law. Atom and molecule characterization is an application of Schrödinger equation in which atoms and molecule's inner system which is made up of fundamental particles can be associated to the complex Hilbert space. Hilbert space is used to generalize Euclidean vector algebra using finite or infinite number of dimensions. Each instantaneous state of the quantum mechanical system is described by a unit vector. Each time dependent unit vector

encodes the probability probabilities for the outcomes of all possible measurements applied to the system [4]. In this study used Solutions of the time-independent Schrödinger equation represent various stationary states of the molecule (corresponding to stable electronic configurations).

$$\hat{H}\Psi = E\Psi \quad (2)$$

$\Psi$  is the wave function. This is function of positions pertaining to all fundamental particles in the system [5].  $\hat{H}$  is the Hamiltonian operator. This operator is usually linked with observable energy.  $E$  is the total energy of the system. It is a scalar (number).

$$H^{\wedge} = T^{\wedge} + V^{\wedge} \quad (3)$$

Is the kinetic energy operator:

$$T^{\wedge} = T_e^{\wedge} + T_n^{\wedge} \quad (4)$$

$$T_e^{\wedge} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^{\wedge} \quad (5)$$

$$T_n^{\wedge} = -\frac{1}{2M_A} \sum_A \nabla_A^{\wedge} \quad (6)$$

$\nabla^{\wedge}$  is the Laplacian given by [6]:

$$\nabla^{\wedge} = \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2} \quad (7)$$

$V^{\wedge}$  is the potential energy operator:

$$V^{\wedge} = V_{nn}^{\wedge} + V_{ne}^{\wedge} + V_{ee}^{\wedge} \quad (8)$$

$V_{nn}^{\wedge}$  is the nuclear-nuclear repulsion term:

$$V_{nn}^{\wedge} = \sum_{A < B} \frac{Z_A Z_B}{R_{AB}} \quad (9)$$

$V_{ne}^{\wedge}$  is the nuclear-electron attraction term:

$$V_{ne}^{\wedge} = -\sum_{iA} \frac{Z_A}{R_{iA}} \quad (10)$$

$V_{ee}^{\wedge}$  is the electron-electron repulsion term:

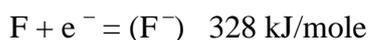
$$V_{ee}^{\wedge} = \sum_{i < j} \frac{1}{r_{ij}} \quad (11)$$

And  $E$  is the total energy of the molecule. The various stationary states of a molecule are a representation of solutions of time-independent Schrödinger equation. The wave function  $\psi$

that satisfy equation (1) are its Eigen functions, and the energies of the molecule,  $E$ , in each stationary state are its eigenvalues. The ground state is the lowest energy stationary state.

### Results and Discussion

The study can be computer electron affinity. Electron Affinity is described as the energy that is released or required o adds an electron in gaseous state. Units: (electron Volt) or kilo Joule/mole.



Energy released = positive value of electron Affinity  
Energy required = negative value of electron affinity

#### Periodic table tendencies

The periodic table shows electron affinity increase from left to right (both with a few exceptions) [8]. Table (1) shows the diamondoids Electron Affinity. Diamondoids has several the cages nature of like as Diamantane, Tetramantane, Hexamantane, Octamantane and Decamantane. The electron affinity computes by electron Volt. Figure (2) it can be noted the electron affinity, decreases as a function of the total number of Ga and P atoms in most of the investigated range. The exceptions are between GaP-tetramantane and GaP-hexamantane. The deviation is as a result of GaP diamondoids shape. Diamondoids studied here have unequal lengths in the three dimensions. Diamondoids do not have spherical shapes; the implication of this is that law of quantum confinement is not applicable to the current case. This becomes more interesting because the present diamondoids are built using cubic cages. These results can be of one, two or three dimensional structures.

Table 1 shows the diamondoids electron affinity (eV)

Diamondoids	Affinity (A.U)	Total Energy (A.U)	Total Energy - Affinity	*27.211e V
1- Diamantane	- 15858.706008 2	- 15856.945 4	1.761	47.918
2-	-	-	0.6045	16.4490

Tetramantane	24918.895835 2	24918.291 3		
3- Hexamantane	- 29447.937239 4	- 29447.284 8	0.6524	17.7524
4- Octamantane	- 45302.178805 0	- 45302.148 7	0.301	0.8190
5- Decamantane	- 49830.032298 7	- 49829.564 4	0.4678	12.729

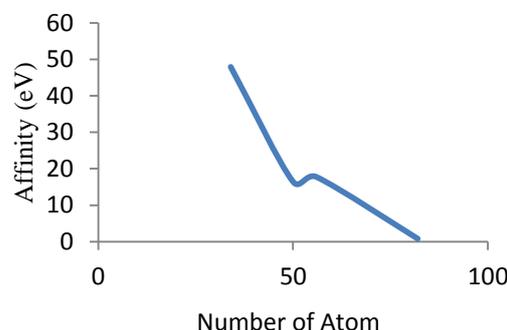


Figure (2). Diamondoids electron affinity as a function of the total number of Ga and P atoms in most of the investigated range.

Figure (3) it can be noted the ionization energy. The minimum energy that is required which removes an electron from an atom is referred to as ionization energy ( $E_I$ ), with (KJ/mol) as its unit. Values and tendencies in the periodic table. Ionization energy can described as first: is the energy required when gaseous atom/ion loses an electron which makes it form gaseous +1 valence ion. Subsequently, it can also be described as second: is energy required when gaseous +1 valence ion lose electron which forms gaseous +2 valences. The general consensus is that second ionization energy is always higher than first ionization of an element.

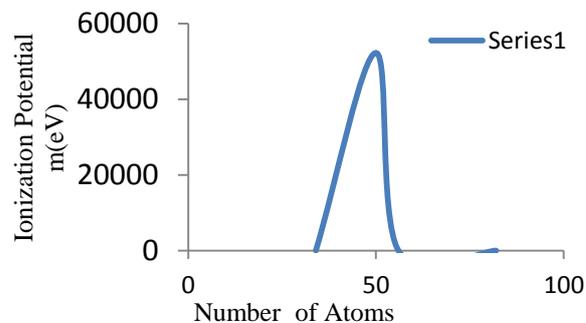


Figure (3): the ionization energies as a function of the total number of Ga and P atoms

According to the elements of main group, the first ionization energies generally decrease from top to bottom across the periodic table [10]. In this figure the ionization energies increased as a function of the total number of Ga and P atoms in most of the investigated range accepted hexamantane.

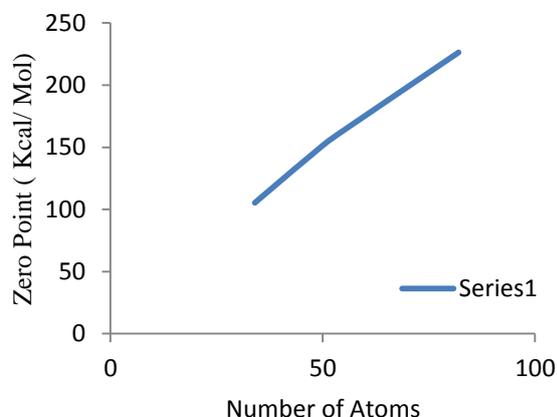


Figure (4): zero point as a function of the total number of Ga and P atoms.

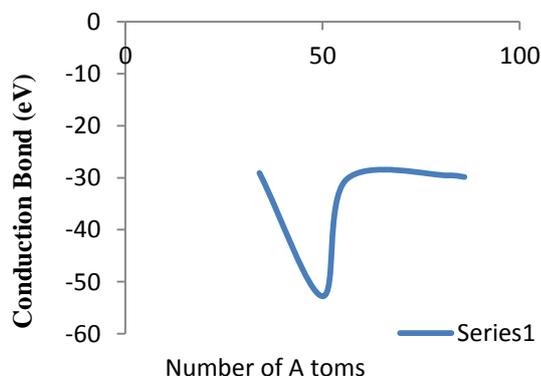


Figure (5): conduction band as a function of the total number of Ga and P atoms.

The reason mention above Figure (4) illustrates zero point energy, the existence of an underlying sea known as Zero Point Energy which is at every point in the universe is predicted by Quantum physics. This is totally different to the concept of cosmic microwave background. It is seen as the lowest state and can be referred to as “electromagnetic quantum vacuum”.

The enormity of the energy cannot be overemphasizing which made most physicists believe Zero-Point Energy seems to be an inescapable consequence of elementary quantum theory. The implication of this is that

there might be a possibility of tapping the source of power which will generate propulsive force for space travel, provided the Zero Point Energy is real. In this figure the Zero point increased as a function of the total number of Ga and P atoms in most of the investigated range. This means whenever increasing the numbers of atoms are approaching the bulk any more stable. Figure (5) shows the conduction band as a function of the total number of Ga and P atoms.

Figure (6) Shows valance band increases with the number of Ga and P atoms but there are fluctuations in tetramantane and hexamantane In fact, since the present diamondoids are built from nearly cubic cages.

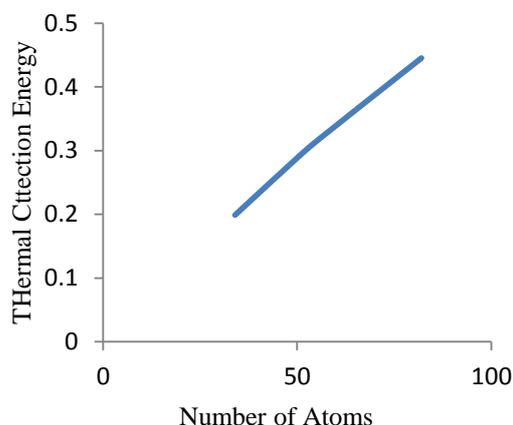


Figure (6): valance band as a function of the total number of Ga and P atoms.

Table (2) shows the Thermochemistry, all frequency calculations include thermochemical analysis of the system. The analysis was carried out at K and 1 atmosphere of pressure, as default. This was also based on the principle of isotope for each type of element. This marks the start of the thermochemistry output for formaldehyde [13]. Gaussian predicts various important thermodynamic quantities at the specified temperature and pressure, including the thermal energy correction, heat capacity and entropy. These items are broken down into their source components in the output [14]. The number of Ga and P atoms was also based on the principle of isotope for each type of element. This marks the start of the thermochemistry output for formaldehyde [13]. Gaussian predicts various important

thermodynamic quantities at the specified temperature and pressure, including the thermal energy correction, heat capacity and entropy.

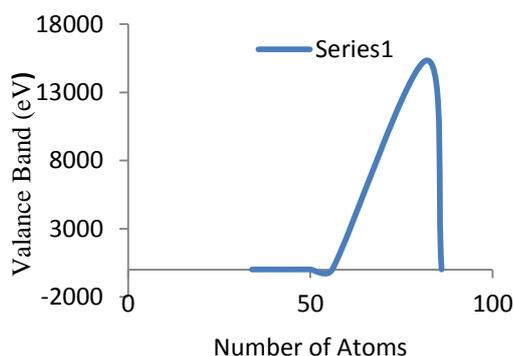


Figure (7): Thermal correction energy as a function of the total number of Ga and P atoms.

Table (2): the Thermochemistry.

Diamondoids	Number of Atoms	thermal energy	heat capacity	entropy
1-Diamantane	34	124.805	111.971	197.426
2-Tetramantane	50	181.089	169.534	271.973
3-Hexamantane	56	200.701	197.8	306.101
4-Octamantane	82	279.352	300.949	441.126

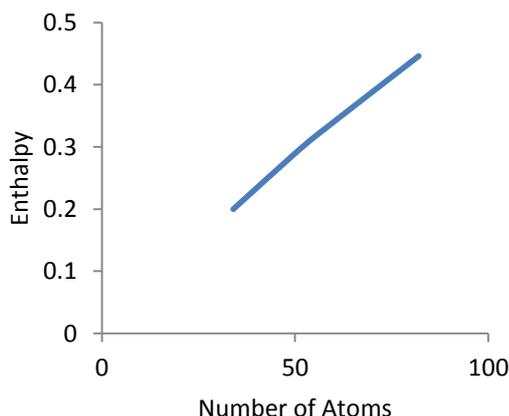


Figure (8): Thermal enthalpy as a function of the total.

## Conclusions

1. This semiconductor has an allotropic zinc blende (cubic) or wurtzite phases [14].
2. Electron affinity, decreases as a function of the total number of Ga and P atoms in most of the investigated range. The exceptions

are between GaP-tetramantane and GaP-hexamantane.

3. Ionization energies increased as a function of the total number of Ga and P atoms.
4. Zero point increased as a function of the total number of Ga and P atoms in most of the investigated range. This means whenever increasing the numbers of atoms are approaching the bulk any more stable.
5. Conduction band decreases with increasing the number of GaP atoms using PBE/6-31G (d) basis sets. Diamondoids size dependence of the energy is linear inversely proportional.

Valance band increases with the number of Ga and P atoms but there are fluctuations in tetramantane and hexamantane. In fact, since the present diamondoids are built from nearly cubic cages.

Thermochemistry, all frequency calculations include thermochemical analysis of the system. Including the thermal energy correction, heat capacity and entropy.

Thermal correction to energy and thermal enthalpy energy increased with increased number of atoms Ga and P.

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