

# Comparison between density functional theory and large unit cell theory for GaP nanocrystal

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## ABSTRACT

Comparison between density functional theory and large unit cell (LUC) for Gallium phosphide (GaP) nanocrystals. Density functional theory (DFT) for (GaP) nanocrystals are investigated using DFT at the generalized gradient approximation of Perdew, Burke and Ernzerhof (PBE) /6-31G (d) basis set and LUC have been used in the calculation of the total energy, energy gap, electron affinity (LUMO), ionization potential (HOMO), cohesive energy and density of state for the GaP core LUC part. The result show that DFT more suitable than LUC to study electronic properties in ground state for solid state. small-sized GaP diamondoids is perfect represent bulk or GaP nanocrystals with good levels of accuracy as a result. Gap energy and the lengths of the bond of GaP diamondoids are very close to those of with their massive counterparts. To increase the atoms number the value of cohesive energy reduction in both theories. The density of states increasing with rising of the atoms number.

**KEY WORDS:** Large unit cell (LUC) Diamondoids, Gallium phosphide (GaP), nanocrystal, density functional theory (DFT).

## 1. INTRODUCTION

The current work comparison between ab-initio DFT coupled with LUC and density functional theory (DFT) at the non-specific gradient approximation (GGA), of (PBE) /6-31G (d) basis set for Gallium phosphide (GaP) nanocrystals. (DFT) has established itself as the theoretic way of selection for this task, to be subjected to a meteoric rise in large parts of physics, chemistry, and materials science (Jiri Klimes, 2012). DFT has constantly been suitable than conventional methods to the Schrodinger equation. The hartree fock approximation has disagreeable particularity for zero-gap materials i.e. metals. The standard approximations is the next rational step beyond are meta-GGA, that include the denseness of the kinetic energy as an input and can produce accurate ground state energies simultaneously for molecules, solids, and surfaces (Kieron Burke, 2012). The comparison of electronic structure computations is a popular task in quantum chemistry functioned at different planes of theory. When comparing an inferior method against a top-level benchmark or when testing a newly computationally developed protocol (Felix Plasser, 2016). Specifically for calculations of state, it is substantial to have a fast and reliable method to monitor whether changes in the wave function list occur between computations done by various methods. A popular exercise is to compare the energies and chosen other physical observables derived from the special wave functions. While this is explicit and physically correct approach, it needs a careful selection of the properties to be taken into consideration.

## 2. METHODS & MATERIALS

**Theory:** The LUC alters the form of the primeval unit cell so that the correspondence points in the original Brillouin area at a wave vector  $K$  became equal to the central correspondence point in the new decreased zone. In the LUC method, a unit cell of a multiple of either the Bravais or primitive cell of the zinc blende construction is used to perform the bulk of the crystal (Hehre, 1986). A number of these LUC are given in terms of the 8 atom Bravais unit cell or 2 atom primeval cells. Cells that have essential multiple of latticework constant ( $a$ ) are multiple of Bravais cell (8, 64 atoms), while the others multiples of primeval cell (16, 54 and 128 atoms. It must be indicated that the number of atoms in LUC is not the same of nanocrystals, it is only the number in the core of the nanocrystal that nearly have perfect zinc blende structure. At least these atoms are one lattice constant far from the surface. As a result all the distance between two atoms has exactly the same value. The primitive unit cell can be represented by the following matrix (Kittle, 1979).

$$1/2a \begin{pmatrix} 1 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 1 \end{pmatrix}$$

Where is the lattice constant of the Bravais lattice. In order to choose a LUC, one must multiply the above matrix by a convenient transforming matrix that will result in a new cell with different shape or size. To transform the primitive cell to the Bravais lattice cell the following matrix can be used: (Kittle, 1979).

$$\begin{pmatrix} 1 & 1 & -1 \\ 1 & -1 & 1 \\ -1 & 1 & 1 \end{pmatrix} \quad (1)$$

This will result in the following matrix:

$$1/2a \begin{pmatrix} 2 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix} \quad (2)$$

As can be noted by this matrix, the Bravais lattice is four times the volume of the primitive unit cell and has a different shape from the original primitive cell. The bravais lattice will be used as the LUC in this work. Another feature of the LUC is the applicability of the  $k=0$  approximation. The first Brillouin zone of a given lattice with a lattice constant in the one dimensional case is defined by the wave vector

$$+\pi/a \geq k \geq -\pi/a \quad (3)$$

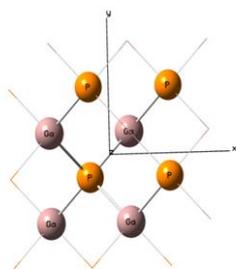
However this zone will become smaller when choosing a LUC lattice with a lattice constant  $2a$  and is defined by the wave vector

$$+\pi/2a \geq k \geq -\pi/2a \quad (4)$$

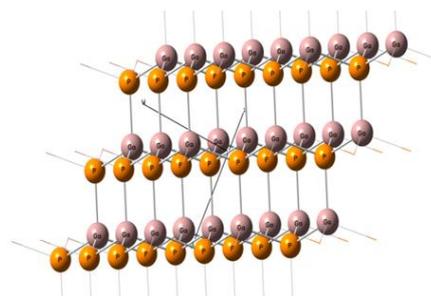
As can be noticed from the above argument that selecting a LUC lattice with a lattice constant big sufficient will make all points in the first Brillouin zone close to the point  $k=0$  in the three-dimensional case. As an outcome the self – consistent equations should be solved only for the points at the origin of the first Brillouin zone. This approximation is called the  $k=0$  and is used much in physics of solid state whenever this large cells are encountered (Johns, 1973). The use of the  $k=0$  approximation will result in a great simplifications of the self – consistent field equations. In LUC model only lattice constant is optimized for the core part the lengths and angles of the surface part bond still need to get optimized in LUC method only latticework constant is optimized for the core part, the essential idea of LUC is computing the construction of electronic of the unity cell extended in special maner at  $k=0$  in the decreased Brillion zone. This equal to the calculation of the band at that  $k$ -point which converts to Brillion zone center on extending the unit cell.

### 3. RESULTS AND DISCUSSION

Figures (1a and 1b) show that the geometrically optimized in LUC of GaP nanocrystals. The (16 and 54) core atoms for the parallelepiped shape primitive cell multiple, but (8 and 64) core atoms cubic shape Bravais cell multiple).

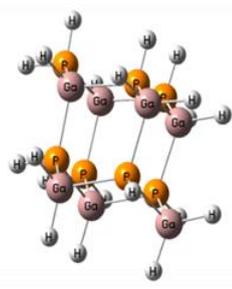


**Figure.1a. (color online) GaP 8 atoms core LUC (parallelepiped shape primitive cell multiple)**

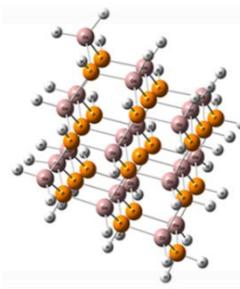


**Figure.1b. (color online) GaP 54 atoms core LUC (cubic shape Bravais cell multiple)**

Figures (2a and 2b) show the geometrically optimized of GaP- diamondoids in DFT diamondoid structure, begin Diamantane, Tetramantane, Hexamantane and Octamantane, depened on simulation electronical structure of GaP nanocrystal. From the Figures it can be noticed that the diamondoids structures are suitable to build the GaP nanocrystals according to Schrodinger equation solution using density functional theory with 6-31g (d) basis set which created using Gaussian 09 program auxiliary by Gaussian view 5.08. The reasons of choice of only these structures of diamondoids to build the nanocrystals of GaP related to that the crystals of the type of atoms (molecule) as our case must be consisted from the accurate number of atoms. So, if we are counted the atoms of Ga as well as P in any structure of nanocrystals, we will exist there are in same numbers which is the condition to get the crystal. We know that the Ga as well as P atoms have zinc blend structure, so the geometrically optimization result in view as shown in (2a and 2b) is the evidence that the diamondoids structures are suitable to study a new materials with explant properties. For the Ga- group as well as P- group in periodic table i.e. III-V elements. And that is agreement with.

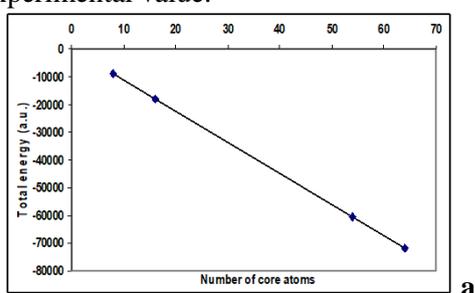


**Figure.2a. Geometrically optimized GaP-decamantane (Ga<sub>22</sub>P<sub>22</sub>H<sub>42</sub>)**

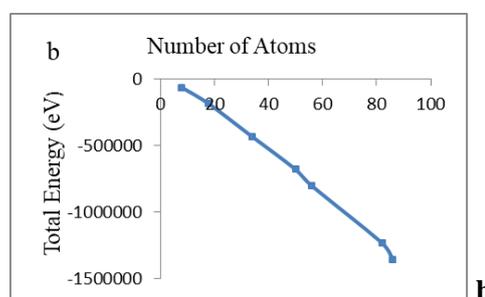


**Figure.2b. Geometrically optimized GaP-diamantane (Ga<sub>7</sub>P<sub>7</sub>H<sub>20</sub>)**

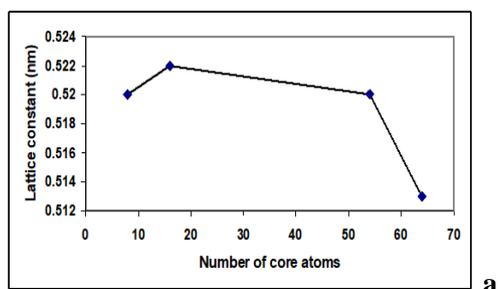
Figure (3a) shows that the whole energy in LUC of GaP nanocrystals as a function of core atoms number. The attractive forces that happen at the large distances among atoms reducing the length between atoms total energy when reducing the distance among atoms. At small distances between atoms, the repulsion forces become controlling and take place to cause the raise of the total energy. The Nanocrystal stability at the equilibrium is due to that the attraction forces equal to the repulsion forces at this dot (Ibtisam Radi, 2007). On the other hand it is illustrated in this figure that the total energy for core part reduced with rising the core atoms number per LUC, where the volume reliance of the energy is linear. The total energy has a high sensitiveness to the potential energy of the crystal. The potential energy of the crystal varies with all for mentioned effects. Figure (3b) shows the total energy in diamondoids DFT reduces with rising the number of GaP atoms using PBE/6-31G (d) basis sets. On the scale illustrated in this shape, where the volume reliance of the energy is linear. The total energy has inversely proportional. In Figure (4a) the lattice constant of GaP nanocrystals core show a reducing as the core atom's number rises. The value of lattice constant reduce from the value 0.522nm and converges to 0.513nm. The converged lattice constant for a higher core atoms is in a good accordance with the reported value of the experimentally (0.54nm) for bulk. Figure (4 - b) shows the allocation lengths of bond in GaP-diamondoids. The dashed line represents the experimental value of GaP bulk bond length at 2.36 Å (Assali, 2013). Figure (4b) shows the process of distributing the lengths of the bond in GaP-decamantane. The chief cause for the nonequivalent lengths of bond in our case is the location of atoms either near or far from the surface, and their bonding with either one or two H atoms. The figure begins with a clearly defined, high value for the number of phosphorus-hydrogen bonds. The distribution of GaP-decamantane is nearly centered on the experimental value.



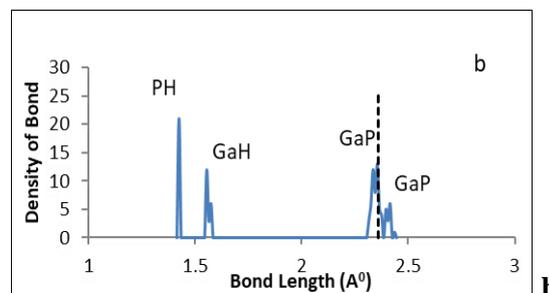
**Figure.3a. Total energy of the core LUC atoms of GaP nanocrystals as a function of the number of core atoms**



**Figure.3b. The total energy in DFT decreases with increasing the number of GaP atoms**

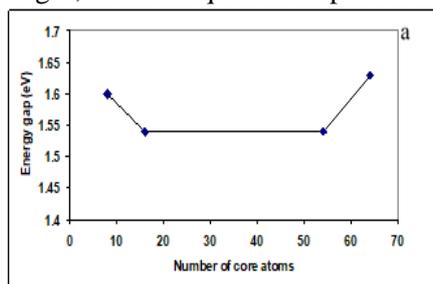


**Figure.4a. Lattice constant as a function of number of core LUC atoms for GaP nanocrystals**

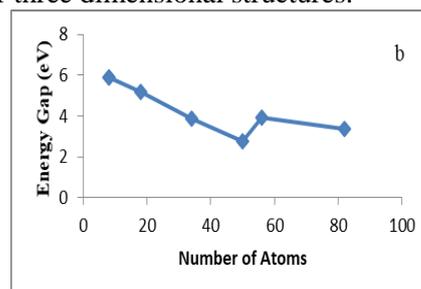


**Figure.4b. Distribution of bond lengths in GaP-diamondoids. The dashed line represents the experimental value of GaP bulk bond length GaP – decamantane**

Figure (5a) shows the gap of the energy with the varying of the core number atoms. Where the gap of energy 8 atom LUC core is closer to the value of gap of energy 64 atom core which is also the case between 16 atom, 54 atom core. Both 8 and 64 atom core cells are cubic Bravais multiples while 16, 54 cores are parallelepiped primitive cell multiples. The shape impact was found in previous literature (Aysa, 2011; Abdulsattar, 2010). This is a clear indicator of geometry impacts on electronic structure of nanocrystals. Parallelepiped cells have minimal values of gap than cubic ones. In Figure (5b) it can be noticed that the gap of the energy reduces as a function of the entire number of Ga and P atoms in most of the investigated range. The exceptions are between GaP-tetramantane and GaP-hexamantane. The cause for the deviation is because of the impact of the form Gap diamondoids. Diamondoids studied here have unequable lengths in the three dimensions. Since the form of these diamondoids is not spherical. The laws of the confinement of the quantum do not apply restrictedly in the present case and that is a good agreement with reference (Lorenz, 1968). In actuality since the present diamondoids are built from close to cubic cages, the consequent nanoparticles can be of one, two or three dimensional structures.

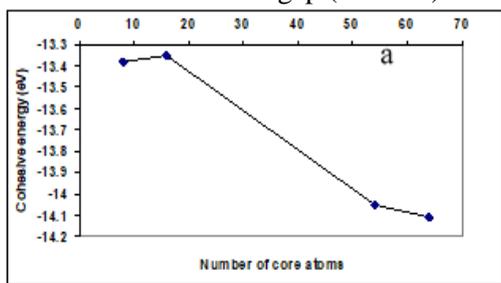


**Figure.5a. Energy gap variation with the number of core LUC atoms of GaP nanocrystals**

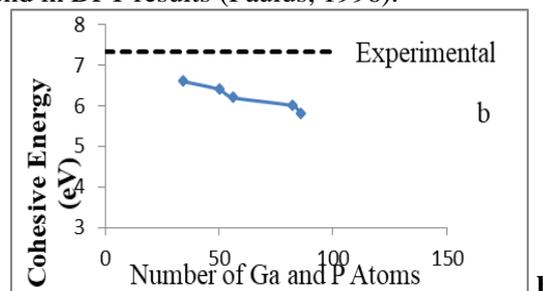


**Figure.5b. Energy gap of geometrically optimized GaP diamondoids as a function of total number of Ga and P atoms. The dashed line represents the experimental value of bulk GaP energy gap**

The connection between the cohesive energy and the number of atoms per LUC is illustrated in figure (6a). It can be noticed that the value of cohesive energy reduces with rising of the number of atoms per LUC be inverted the strong contribution of atoms. The process of increasing the cohesive energy is not linear and the larger crystals sizes rate of change decreases. Figure (6b) shows cohesive energy as a function of the entire number of Ga and P. It can be shown from the figure that the cohesive energy per atom of GaP-diamantane is 6.66 eV. The cohesive energy reduces with heavier diamondoids and it is decreased to 5.87 eV for Gap-decamantane. This value is less than the experimental value of bulk gap (7.34 eV) that is the usual trend in DFT results (Paulus, 1996).

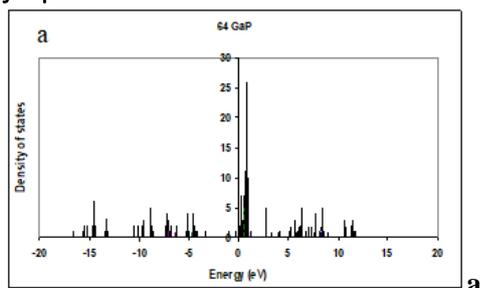


**Figure.6a. Cohesive energy variation with the number of core LUC atoms of GaP nanocrystals**

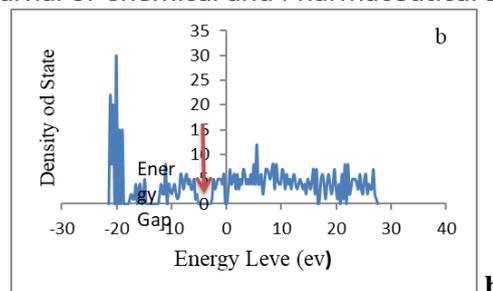


**Figure.6b. Cohesive energy as a function of total number of Ga and P atoms using PBE/6-31G (d) compared with the experimental value 7.34 eV**

Figure (7a) shows the denseness of the states as a function of orbital energy. It shows the degeneracy of states that has maximum (7, 9, 19 and 26) for (8, 16, 54, and 64) atoms respectively. These causes show the denseness of states increasing with the rising of the core LUC number of atoms. The high degenerate states can be seen in the core. This reflects the high symmetry, equal the lengths of the bond and angles in the perfect structure. Figure (7b) shows the denseness of energy states of geometrically optimized GaP-decamantane a function of the level of the energy. The energy levels are nearly discrete in GaP-diamantane. As the number of levels energy increase, the discrete behavior in GaP-diamantane turns to nearly continues band in GaP-decamantane. It can be explained the causes of the state denseness as follow: the denseness of state of degenerate energy levels have been increased by increasing the numbers of diamondoids atoms i.e. by increasing its size. Whereas, for any atoms there are numbers of energy levels which are expanded increasing in a distance. Where there are many numbers of atoms, i.e. furthermore the atoms increase from the diamantane to decamantane, the density of states will be increased with overlapping of these levels, as same for values as well as conduction band.

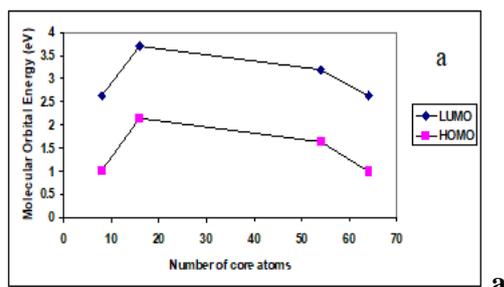


**Figure.7a. Density of states of (64) LUC Core atoms of core part of GaP**

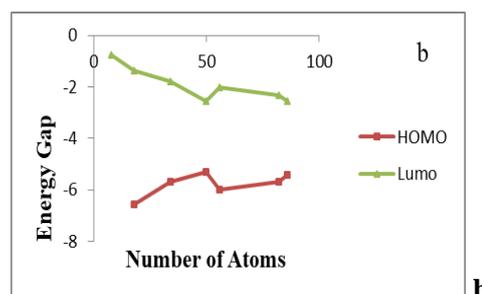


**Figure.7b. Density of energy states of geometrically optimized GaP-diamondoids as a function of energy level, GaP- decamantane**

Figure (8a) notes the difference highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) as the core of nanocrystals grows up in size and changes its shape. This curve strongly fluctuates because of the alteration in size and shape which make various surfaces with different properties (Rahman, 2012). Note the first and fourth data points of the figure are Bravais LUC (8 atoms and 64 atoms) and they have very close to distinct  $t$  constant values that different from the second and third data points, which are primitive LUC (16 atoms and 54 atoms). In Figure (8b) both HOMO and LUMO levels of energy are negative, and sometimes they are used as approximations to electron affinity and ionization energy respectively and that can be compared with the result reported in reference (Nasir, 2012). This shows that neither adding nor removing electrons from GaP diamondoids are energetically favorable. This reflects the high stability and inertness of the present diamondoids structure.



**Figure.8a. Molecular orbital HOMO and LUMO levels variation with the number of core LUC atoms of GaP nanocrystals**



**Figure.8b. HOMO and LUMO of geometrically optimized GaP diamondoids as a function of total number of Ga and P atoms**

#### 4. CONCLUSION

The total energy in LUC of GaP nanocrystals as a function of core number atoms. the core part total energy reduces with the increasing of the core atoms number per LUC, and the total energy in diamondoids DFT reduces with increasing the number of GaP atoms the two theories have same result.

The lattice constant of GaP nanocrystals core show a reducing trend as the number of core atoms increases, and of bond lengths in GaP-diamondoids. The dashed line represents the experimental value of GaP bulk and the lengths of the bond at 2.36 Å. The distribution of GaP-decamantane is nearly centered on the experimental value.

The energy gap variation with the core number variation atoms. Where the gap energy of 8 atom LUC core is closer to the value of gap energy of 64 atom cores that is also the case between 16 atoms, 54 atom cores. That the gap energy reduces as a function of the Ga and P atoms total number in most of the investigated range.

The cohesive energy value reduces with the increasing of the atoms number per LUC reflecting the strong contribution of atoms. Cohesive energy reduces as we proceed to heavier diamondoids.

These results show the states denseness increasing with the increasing of the LUC core number atom. The state denseness of degenerate energy levels has been increased by increasing the numbers of diamondoids atoms.

The variation of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) as the core of nanocrystals grows up in size and changes its shape. Both HOMO and LUMO energy levels are negative, and sometimes they are used as approximations to electron affinity and ionization energy respectively and compared which could be with the result reported in reference (Nasir, 2012).

The result show that DFT more suitable than LUC to study electronic properties in ground state for solid state. As a result, relatively small-sized GaP diamondoids can be used with good levels of accuracy to represent bulk or GaP nanocrystals. Gap energy and the lengths of the bond h of GaP diamondoids are very close to those of their bulk counterparts

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