

# Ab-initio Electronic Structure Calculations for Aluminum Arsenide Nanocrystals using Hartree-Fock Method Coupling with Large Unit Cell Method

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**Abstract:** The simulation of the electronic structure of aluminum arsenide nanocrystals (nc<sub>s</sub>) by means of Ab-initio restricted Hartree-Fock (HF) method within the large unit cell (LUC) formalism has been carried out in the present work. Gaussian 03 package is used to study the AlAs nc<sub>s</sub> with 8, 16, 54, 64 and 128 core atoms in the wavelength range (0.229-0.274) μm. Results shows the dependency of the number of core atoms on the structural and electronic properties of the AlAs nc<sub>s</sub>. The no. of core atoms is proportional to cohesive energy, the density of states and the energy gap. Other properties such as total energy, lattice constant and the ionicity inversely depends of the no. of core atoms. More stability values for both energy gap and lattice constant was found beyond 64 core atoms.

**Keywords:** AlAs nc<sub>s</sub>, Ab-initio, Hartree-Fock, (LUC)

## 1. Introduction

Semiconductor III-IV compound such as AlAs, GaAs, etc., and their alloys recently got a great technological activity as well as experimental interest. AlAs is used as electronic and optoelectronic material because of its frequent incorporation into GaAs-based heterostructures [1]. Special attention attracted to AlAs/AIP superlattices due to their potential applications such as mobiles, laptops and computers because they are expected to become direct band gap materials [2]. There have been many theoretical studies, mostly by pseudopotential methods [3-8] of the electronic structure of pure AlAs and GaAs compounds and their superlattices. There have been numerous calculations of the structural and electronic properties of AlAs and AIP compounds were investigated using the full potential linearized augment plane wave plus local orbitals (FP-LAPW+LO) [9-11].

In this work the structural and electronic properties have been investigated for AlAs nanocrystals for 8, 16, 54, 64 and 128 core atoms using Ab-initio restricted Hartree-Fock calculations with frame work of large unit cell approximation employing the commercial package called Gaussian 03 software [12].

## 2. Theoretical back ground

It is impossible to solve the Schrödinger equation exactly for many-particle system, so we should use some approximations. One of the most important approximations is the Hartree-Fock method. The main focus is on Hartree-Fock method coupled with large unit cell (LUC) and applying generalized gradient approximation (GGA) level.

A stationary electronic state (for n electrons) can be described by a wavefunction

$\Psi(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N, \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n)$  fulfilling the many-body Schrödinger equation:

$$\hat{H} \Psi(R_1, R_2, \dots, R_N, r_1, r_2, \dots, r_n) = E \Psi(R_1, R_2, \dots, R_N, r_1, r_2, \dots, r_n) \quad (1)$$

The non-relativistic Hamiltonian for a system consisting n electrons and N nuclei is given by (all equations are expressed in atomic units)

The Schrödinger equation can be written in compact form as [12]:

$$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_{eN} + \hat{V}_{NN} + \hat{V}_{ee} \quad (2)$$

introducing Born-Oppenheimer approximation assuming that the nuclei are much more massive than the electrons, which means that the nuclei are nearly fixed with respect to electron motion [13]



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$$\hat{H}^{el} = -\frac{1}{2} \sum_i^n \nabla_i^2 - \sum_i^n \sum_l^N \frac{Z_l}{r_{li}} + \sum_{i < j}^n \frac{1}{r_{ij}} \quad (3)$$

Now the expectation value of Hamiltonian operator due to the Hartree-Fock representation is given by [14]:

$$E_{HF} = \langle \psi_{HF} | \hat{H} | \psi_{HF} \rangle = \sum_{i=1}^N H_i + \frac{1}{2} \sum_{i,j=1}^N (J_{ij} - K_{ij}) \quad (4)$$

the coulomb integrals  $J_{ij}$  is given by

$$J_{ij} = \iint \psi_i(\bar{x}_1) \psi_i^*(\bar{x}_1) \frac{1}{r_{12}} \psi_j^*(\bar{x}_2) \psi_j(\bar{x}_2) d\bar{x}_1 d\bar{x}_2 \quad (5)$$

And the exchange integrals  $K_{ij}$  is

$$K_{ij} = \iint \psi_i^*(\bar{x}_1) \psi_j(\bar{x}_1) \frac{1}{r_{12}} \psi_i(\bar{x}_2) \psi_j^*(\bar{x}_2) d\bar{x}_1 d\bar{x}_2 \quad (6)$$

All these integrals are real, and  $J_{ij} \geq K_{ij} \geq 0$ .

The unrestricted Hartree-Fock is based upon the use of a single determinant total wavefunction in which orbitals of the same  $n$ ,  $l$ , and  $m_l$  values but different  $m_s$  values are regarded as being independent [15]. This method is the most common molecular orbitals method for open shell molecules where the number of electrons of each spin is not equal. It is an extremely convenient method because it is a very natural extension of the conventional Hartree-Fock method, and the many-electron wave function is written in the form of a single determinant so that calculations are relatively easy.

However, because the unrestricted Hartree-Fock method allows the  $\alpha$  and  $\beta$  spins to have different wave functions the total wave function obtained is not an eigen- functions of  $S^2$  and hence the validity of the method must be questioned. It has been suggested that [16,17] this objection may be overcome by determining the one-electron functions by the unrestricted Hartree-Fock method and then eliminating by means of the appropriate projection operators those parts of the function corresponding to the unwanted values of  $S^2$ .

### 3. Results and discussion

The calculations presented in this work were performed using the Ab-initio restricted Hartree-Fock method within the framework of large unit cell (LUC) formalism to study the electronic structure and some other properties of AIAs nanocrystal utilizing the code named Gaussian 03.

The optimized lattice constant for 8, 16, 54, 64 and 128 zinc blend AIAs nanocrystals has been reached by minimizing the total energy at a specific lattice constant. Figure (1) shows the total energy as a function of lattice constant of AIAs 8 core atoms  $nc_s$ . The energy decreases till it reaches a minimum value then it starts to increase at a critical and optimized lattice point. This minimum value means that equilibrium state lattice constant is reached which indicate that forces, the attractive and the repulsive are equal. Increasing the distance between atoms increases the total energy, and the repulsion forces become the dominant at short distance between the atoms. Annane *et al* found the lattice constant [18] for the optimized lattice constant for 8 core atoms using WIEN2k code to be { 5.731 Å° (PBE\_GGA), 5.726Å° (PW-GGA) and 6.039Å° 9EV-GGA) and in other works for theoretical value was (5.74 Å°) [19], and for experimental value was 5.66Å° [20], in this work we found the lattice constant of AIAs  $nc_s$  (5.55 Å°).

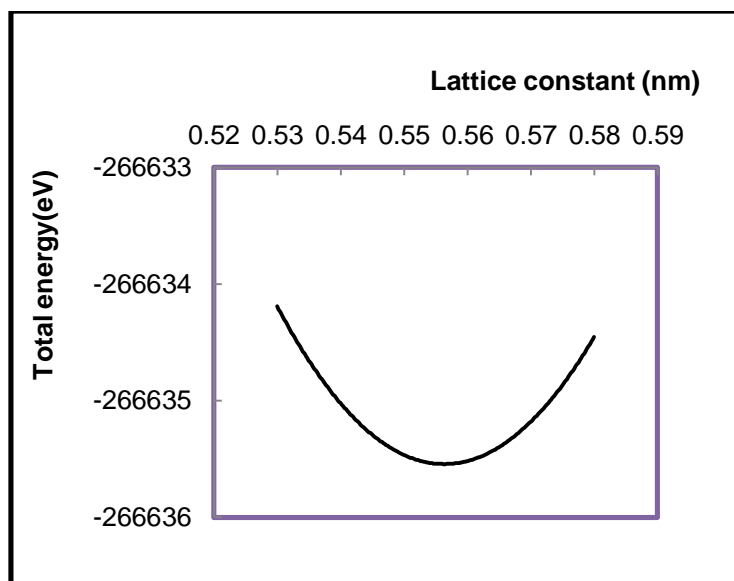


Fig. 1 The total energy Vs lattice constant for AlAs nanocrystal 8 core atoms

The total energy as a function of number of core atoms is shown in fig.(2), the total energy is linearly increasing with decreasing the number of core atoms.

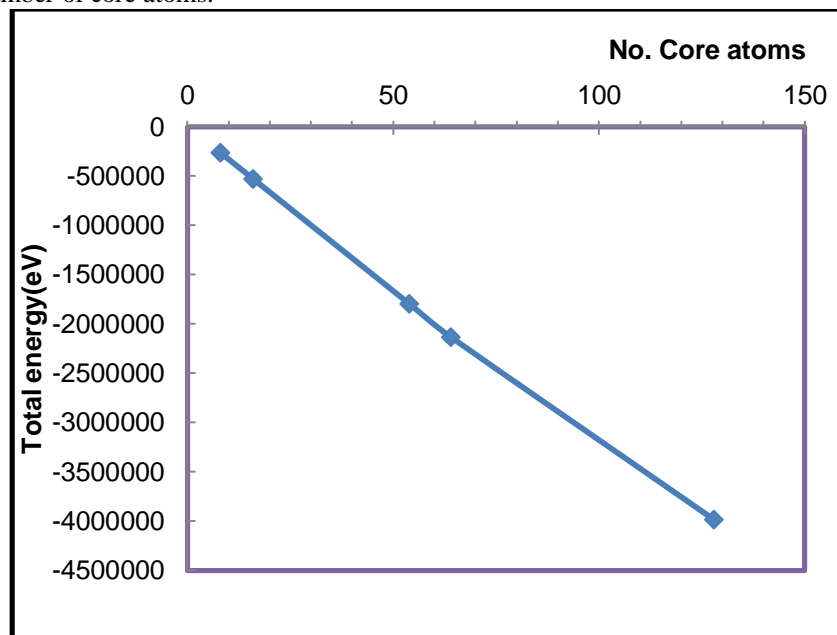


Fig. 2 The total energy Vs No. of core atoms for AlAs nc\_s

The cohesive energy dependency on the number of core atoms is shown in fig.

(3). The cohesive energy is given by [21]

$$E_{\text{coh.}} = E_T/n - E_{\text{Free}} - E_0$$

Where  $E_{\text{Free}}$  is the free atom energy, the cohesive energy must be corrected to the zero-point motion

of the nuclei, but in this work we neglect  $E_0$  due to its small rate of correction compared with the total energy value. The cohesive energy increases with the increasing of number of core atoms and it tends to be more stable after 64 atoms in the LUC. The cohesive energy value is in good agreement with results found by Flude [22].

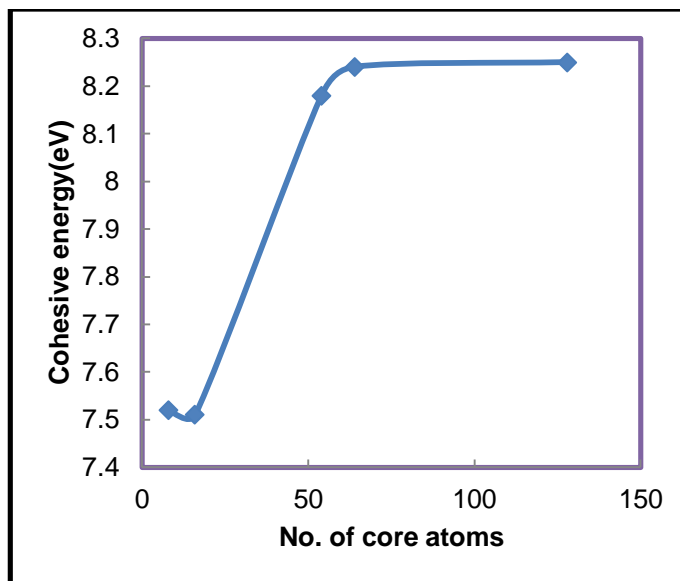


Fig. 3 Shows the relationship between the cohesive energy and the No. of core atoms for AlAs (nc<sub>s</sub>)

The energy gap as a function of core atoms is shown in Fig. (4), also the AlAs nanocrystals shows an increment in band gap with increasing the LUC atoms. The energy gap for bulk AlAs is 2.32eV [23], while F. Annane *et al* [18] and M. Briki *et al* [19] found it to be 2.486eV and 1.65eV respectively. Experimental value of the AlAs energy gap (3.13 eV) was found by

Thompson *et al* [24]. The energy gap value has been increased in comparison with the bulk AlAs to reach a value of (4.527 eV) for AlAs 8 atoms per LUC. Increasing in the energy gap is due to the finite size of nanocrystals, the continuous bands of the bulk crystal transforms into discrete states resulting in widening of the effective energy gap given by [25]:

$$E_g = \frac{h^2}{8m^*} \left( \frac{\pi}{L} \right)^2$$

Where  $m_c^*$  and  $m_v^*$  are conduction and valence band effective mass respectively.  $\Omega_x, \Omega_y, \Omega_z$  are the three-dimensional box.

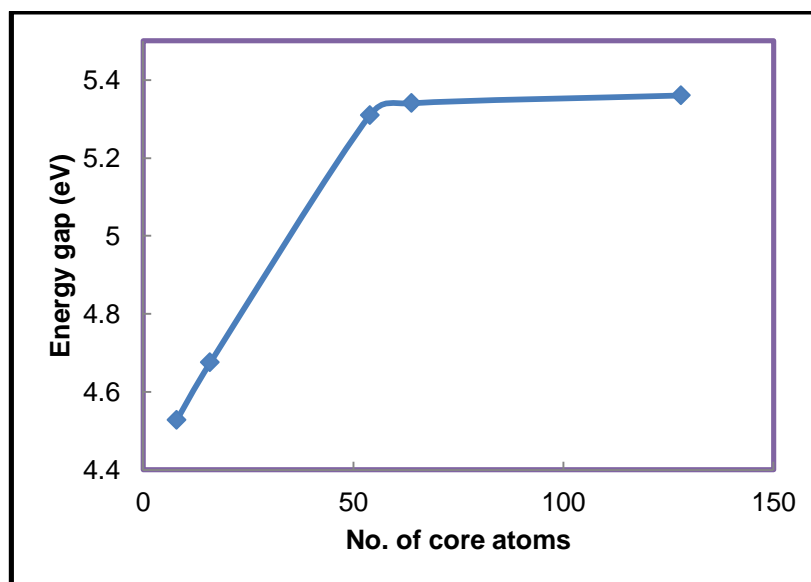


Fig. 4 Shows the energy gap Vs the No. of core atoms for AlAs nc<sub>s</sub>

The relationship between the lattice constant and the number of core atoms shows an convergence to some value as the nanocrystal grow up in size, this value is at lattice constant (5.45 Å) see fig. 5.

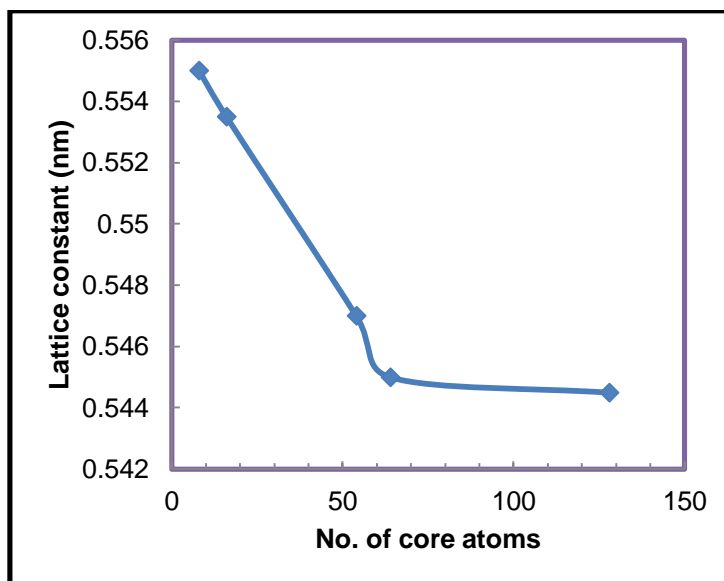


Fig. 5 The lattice constant Vs the No. of core atoms for AlAs Nanocrystals

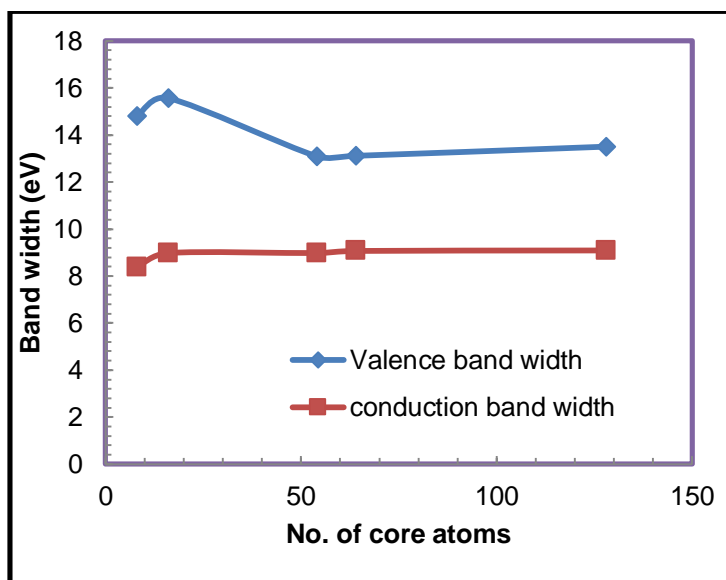


Fig. 6 Conduction and valance bands depth with number of core atoms of AlAs  $nc_s$

The band width (valence and conduction band) as a function of No. of core atoms is shown in fig. 6, the fluctuation of both band widths depending on the geometry of the nanocrystal core. Figure 7 shows the

inverse dependency between the ionicity and the No. of core atoms. The density of states increases with the number of core atoms (see fig. 8); more core atoms mean more electron states.

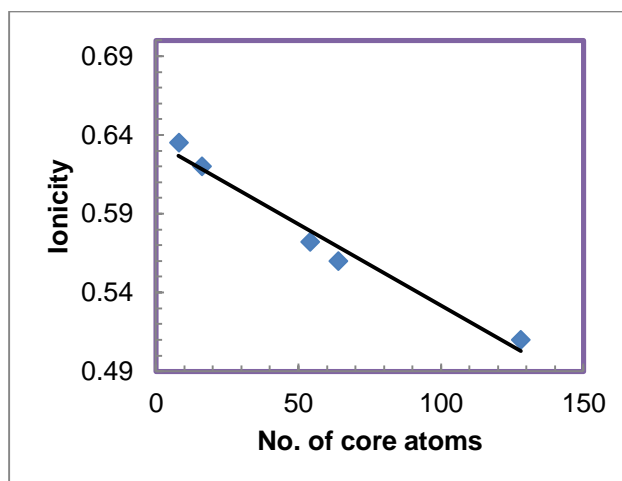


Fig. 7 shows the relationship between the ionicity and the No. of core atoms

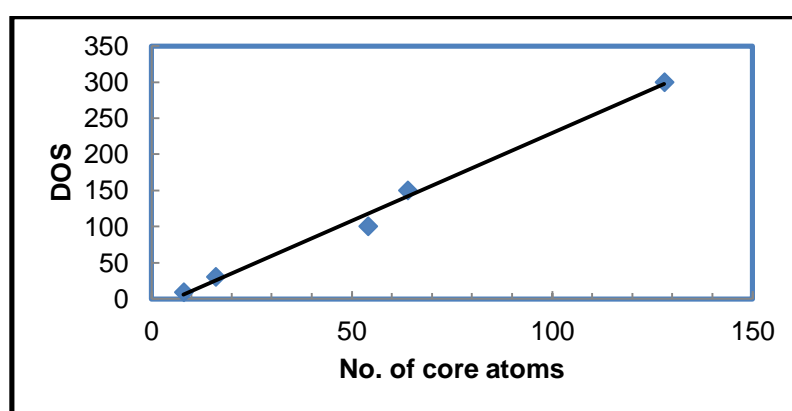


Fig. 8 Density of states variation with the No. of core atoms of AlAs nc<sub>s</sub>

#### 4. Conclusion

In this work, we present a theoretical analysis of the structural and electronic properties of AlAs nc<sub>s</sub> compound using Ab-initio restricted Hartree-Fock method. Calculations shows an important dependency between the number of core atoms and the structural and electronic properties such as lattice constant, energy gap, cohesive energy, ....etc.

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