

# Electronic structure of aluminum arsenide nanocrystals

## Using Ab initio large unit cell method

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### Abstract

The ab initio restricted Hartree-Fock method is used to simulate the electronic structure of aluminum arsenide nanocrystals consists of (216-738 atoms) with sizes ranging up to about 2.5 nm in diameter. The calculations are divided into two parts, surface and core. The oxygenated (001)-(1×1) facet that expands with larger sizes of nanocrystals is investigated to determine the rule of the surface in nanocrystals electronic structure. Results show that lattice constant and ionicity of the core part are decreasing by increasing the size of nanocrystals. The smallest investigated nanocrystal is 1.83% larger in lattice constant and 13.5% larger in ionicity than the converged value of largest investigated nanocrystal. Increasing nanocrystals size also resulted in an increase of core cohesive energy (absolute value), increase of core energy gap, and increase of the core valence bandwidth. The surface states are found mostly non-degenerated because of the effect of surface discontinuity and oxygen atoms. The method shows fluctuations in the converged energy gap, valence bandwidth and cohesive energy of core part of nanocrystals duo to shape variation. The present work suggests the addition of ionicity and lattice constant to the quantities that are affected by quantum confinement phenomenon. The method of the present model has threefold results; it can be used to approach the electronic structure of crystals bulk, surface, and nanocrystals.

### الخلاصة

استعملت طريقة المبادئ الأساسية المحددة لهارترتي-فوك لمحاكاة التركيب الإلكتروني لبلورة فوسفيد الألمنيوم النانوية مكون ما بين 216 و 738 ذرة بقطر يصل إلى 2.5nm. قسمت الحسابات إلى جزئين هما السطح والقلب. وقد درس الوجه المؤكسد (001)-(1×1) والذي يتوسع بزيادة حجم البلورة النانوية لتحديد دور السطح في التركيب الإلكتروني للبلورات النانوية. أظهرت النتائج ان ثابت الشبكة الأيونية للقلب تتناقص بزيادة حجم البلورات النانوية. ان ثابت الشبكة للبلورة النانوية الأصغر قيد الدراسة اكبر بمقدار 1.83% والتأينية اكبر بمقدار 13.5% من قيمهما في البلورة النانوية الأكبر. بينت النتائج أيضا ان زيادة حجم البلورة النانوية في القلب يؤدي إلى زيادة طاقة الترابط ( القيمة المطلقة)، زيادة فجوة الطاقة، و زيادة عرض حزمة التكافؤ. ولقد بينت النتائج أن حالات السطح تكون قليلة التحلل قياسا بالقلب بسبب عدم استمرارية السطح ووجود ذرات الأوكسجين. أظهرت الطريقة تقلبات في تقارب فجوة الطاقة وعرض حزمة التكافؤ وطاقة الترابط للقلب، نتيجة لتغيرات شكل البلورة. العمل الحالي يقترح إضافة الأيونية وثابت الشبكة للكميات التي تتأثر بظاهرة الحصر (التقييد) الكمي. ان طريقة النموذج الحالي لها ثلاث استعمالات ؛ فهي يمكن ان تستعمل للحصول على التركيب الإلكتروني للمادة الصلبة و للسطح و للبلورات النانوية.

## 1 Introduction

Aluminum arsenide (AlAs) is one of the most important electronic and optoelectronic materials because of its frequent incorporation into GaAs-based heterostructures [Vurgaftman et al., 2001; Adachi, 1994]. AlAs is a wide-gap semiconductor with a band structure and crystallize in the zinc blende. Measurements have revealed a camel's back structure near X. The two semiconductors AlAs and AlP form a continuous series of alloys denoted by  $\text{AlAs}_{1-x}\text{P}_x$ , where x is the mole fraction of AlAs in the alloy [Badi et al., 1994], AlAs/AlP superlattices are

attractive due to their potential applications in optoelectronic devices because they are expected to become direct band gap materials [Ohnuma and Nagano, 2000].

AlAs is a subject of extensive theoretical studies ranging from the semiempirical to the first principles methods [Mujica et al., 2003], within the density functional theory framework using both pseudopotential [Mujica et al., 1999], and all-electron approaches. For the bulk properties of AlAs, theoretical calculations based on, the Hartree-Fock [Froyen and Cohen, 1983], and potential model [Jivani et al., 2005] have obtained a very good description of its structural and electronic properties. Recently, Annane et al. [Annane et al., 2010] investigated the structural and electronic properties of AlAs and AlP compounds using the full potential linearized augmented plane wave plus local orbitals method based on density functional theory.

The present work addresses large NCs that have the size range of 216–738 total atoms. These atoms are divided between core and surface. The present lower limit (of atoms) is chosen since it provides the first occurrence of idle core part [nearly ideal zinc blende (ZB) structure] that is far from surface reconstruction by more than three surface layers.

In the present work, we study the electronic structure and physical properties of AlAs NCs core and surface part with different sizes by using an *ab initio* restricted Hartree-Fock (RHF) method coupled with large unit cell method (LUC-RHF). LUC method was formulated and used before for several kinds of bulk materials including diamond and ZB structured materials [Abdulsattar and Al-Bayati, 2007; Harker and Larkins, 1979].

## 2 Computational details

*Ab initio* self-consistent Hartree-Fock (RHF) is used to obtain AlAs NCs molecular orbitals. Correlation corrections are neglected in the present calculations relying on Koopmans theorem [Hehre *et al.*, 1986]. This theorem states that comparisons of Hartree-Fock closed-shell results (which is the case in the present work) with experimental values suggest that in many cases the energetic corrections due to relaxation effects nearly cancel the corrections due to electron correlation. Simple STO-3G basis [Hehre *et al.*, 1969, Collins *et al.*, 1974] is used in the present work to reach higher number of core and surface atoms.

This method uses ( $k=0$ ) approximation, where  $k$  is the wave vector, that is one point in the wave vector space. The LUC method is one kind of supercell methods with the above  $k=0$  restriction. In this method, instead of adding more  $k$  points, the single central cell is expanded to contain more atoms, which are now called core atoms in the present work. The LUC method was first suggested and applied to covalent semiconductors in the 1970s [Dobrotvorskii and Evarestov, 1974]. The method was found suitable for NCs calculations because the  $k=0$  approximation retains only one central cluster of atoms surrounded by other atoms to passivate the outer dangling bonds. The method is used to simulate parts of specific symmetry in the NCs in the same way it is used for bulk materials.

We used 3D PBC (Periodic Boundary Condition) method in GUSSIAN 03 code [Gaussian 03, 2003] to calculate *ab initio* restricted Hartree-Fock electronic structure of AlAs NCs internal core. The 2D PBC calculations are used to simulate oxygenated (001)-(1×1) surface.

In the present work, we divided the work into two parts, core and surface parts which is the traditional method used in microscopic-size solid-state calculations. In LUC core part only the lattice constant is optimized, at the surface part all bond lengths and lattice constant still need to be optimized because of surface

reconstruction. The (001) chosen surfaces are terminated by oxygen atoms to passivated dangling bonds. The width of surface part is set to one conventional lattice that is deduced from AlAs surface bonds calculations. The oxygenated (001)-(1×1) AlAs surface in the oxygen double bonding configuration is investigated to obtain the total electronic structure of the AlAs NCs with (001)-(1×1) facets. The oxygenated (001)-(1×1) AlAs surface is chosen since it is one of the least reconstructed surfaces. Unlike the core part, the bond lengths and lattice constant are not unique and a variation of geometrical parameters is needed. Normally surface effects do not penetrate more than four layers (one lattice constant) from the crystal surface [Kittel, 1976]. On the other hand, short-range  $sp^3$  bonds do not require more than fourth neighbor's interaction range to conduct electronic structure calculations successfully using molecular orbital methods. The upper two identical conditions are applied in the present calculations.

Two kinds of core LUCs are investigated, namely cubic and parallelepiped cells. The cubic cells are multiples of ZB structure Bravais unit cells, while the parallelepiped cells are multiples of primitive ZB structure unit cells [Kittel, 1976]. Cubic core cells include 8, 64 atoms. Parallelepiped cells include 16, 54, 128 atoms.

### 3 Calculations and results

In this section, we present the calculated band structures of aluminum arsenide nanocrystals. Figure (1) shows the total energy for AlAs nanocrystal as a function of lattice constant for 8 core atoms, from which we obtained the equilibrium lattice constant. Figure (2) shows the variation of the lattice constant of AlAs NCs core as a function of number of core atoms. This figure is obtained after minimizing the energy lattice curve of every investigated number of core atoms. From this figure we see that the lattice constant for the core part of the crystal decrease with increasing number of atoms, the lattice constant for AlAs NCs shows decreasing values from 0.555 nm for 8 atoms to 0.545 nm for 64 atoms LUC, then the lattice constant tends to be constant for LUC of atoms number greater than 64. The converged lattice length for a high number of core atoms (0.545nm) is found to be close to the lattice constant values of 0.562 nm for bulk [Zhu and Louie, 1991].

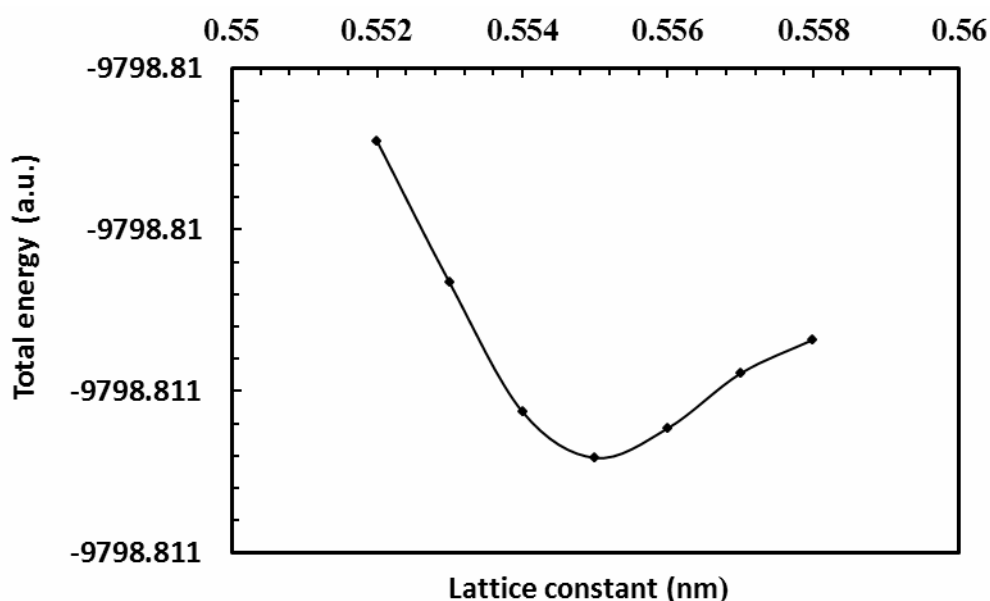


Figure (1): Total energy of 8 AlAs core atoms as a function of lattice constant.

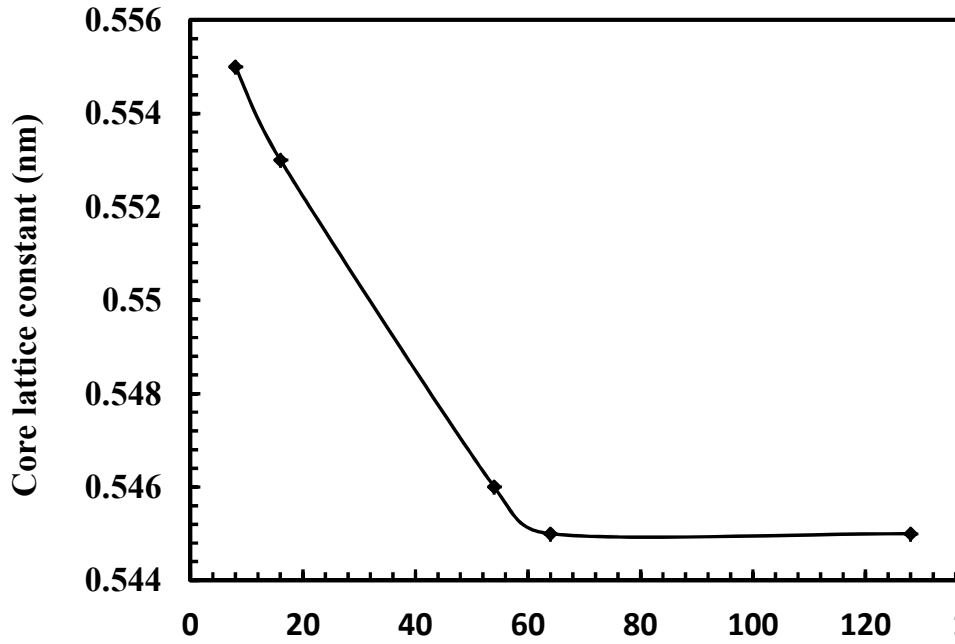


Figure (2). Energetically optimized AlAs core lattice constant as a function of the number of atoms in the core.

The bulk modulus has been calculated from Cohen's theory [Kaxiras, 2003]:

$$B = \frac{N_C (1971 - 220\lambda)}{4 d^{3.5}} \quad (\text{GPa}) \quad (1)$$

where  $N_C$  is the coordination number ( $= 4$ ),  $\lambda$  is a dimensionless number which describes the ionicity: ( $= 0, 1$  and  $2$  for IV, III-V and II-V groups respectively) [Zheng *et al.*, 1999],  $d$  is the first-neighbor distance in Å, i.e., the interatomic distance, for the ZB structure we have [Adachi, 2009]:

$$d = \frac{\sqrt{3}}{4} a \quad (2)$$

Bulk modulus of AlAs nanocrystal as a function of number of atoms in the core is shown in Figure (3). This Figure shows that the bulk modulus increases with the number of atoms in the core. This relation can be simply attributed to the fact that the lattice constant for the core part of the crystal decrease with increasing number of atoms, the latter equation means that the decrease in lattice constant entails a decrease in interatomic distance ( $d$ ) which leads to increasing in the bulk modulus according to equation (1).

We note that the bulk modulus for AlAs nanocrystal of 81.39GPa is in a good agreement with the experimental value of 82 GPa [Hellwege and Madelung, 1982] of the bulk taking into consideration that Hartree-Fock theory always overestimates bulk modulus values [Abdulsattar and Al-Bayati, 2007].