Research Article

Ab–initio method with Density Functional Theory using to Study of the electronic structure and mechanical properties of BN Nanocrystals

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Abstract

Using first principles density functional theory calculations, we systematically studied the electronic and mechanical properties of boron nitride nanocrystals with the range $(0 \pm 50)GPa$. The calculated properties include lattice constant, conduction and valence bands width, energy of the highest occupied orbital, energy of the lowest unoccupied orbital, energy gap, density of states , bulk modulus and speed of sound ...etc for (8 , 16 , 54 and 64) atom. It is found that shape effect on the energy gap , conduction and valance bands. Moreover the lattice constant decrease with increase number of core while bulk modulus and speed of sound increases. The effect of pressure increase the bulk modulus and plasmon energy.

Keywords: Ab-initio method , DFT , electronic structure and mechanical properties

Introduction

The size-dependent properties of semiconductor nanocrystals have attracted considerable interest from physicists and chemists both because of the scientific questions they raise and because of their potential technological applications (T. Vossmeyer *et al*, 1994). As the investigation of size-dependent properties progresses, experimental techniques for nanocrystal synthesis and analysis continue to improve (A. Ekimov *et al*, 1993). At the same time, theoretical methods for computing nanocrystal properties develop increasing accuracy.

Pervious theoretical studies of electronic and structural properties have included effective mass calculations, tight binding calculations, band-structure discretization, and other approaches (L. M. Ramaniah and S. V. Nair, 1993; A. Franceschetti and A. Zunger, 1997) . Such varied schemes have been suggested because semiconductor nanocrystals are in a difficult size regime: they are generally too big for molecular techniques but too small for a bulk computation that ignores the nanocrystal surface.

BN$_{cub}$ (Zinc blende modification , also known as cubic or sphalerite or □-BN) was first synthesized in 1957 using the technique similar to that used for diamond growth. Now crystals with a few millimeter sizes are commercially available. The present work will be involved in calculating electronic properties of BN nanocrystals as the size and shape of these

nanocrystals change. Cubic boron nitride (CBN or c-BN) is widely used as an abrasive (D. Golberg *et al*, 2007). Boron nitride binds well with metals, due to formation of interlayers of metal borides or nitrides. Materials with cubic boron nitride crystals are often used in the tool bits of cutting tools. For grinding applications, softer binders, e.g. resin, porous ceramics, and soft metals, are used (Jochen Greim and Karl A. Schwetz, 2005).

We were used density functional theory at the generalized-gradient approximation level (Perdew, Burke, and Ernzerhof PBE approximation) coupled with large unit cell method (LUC- DFT) to simulate the electronic structure of BN which is a well developed theory that had been applied repeatedly for the nanocrystals electronic structure (M. T. Hussein *et al*, 2013; M. A. Abdulsattar, 2010; M. A. Abdulsattar, 2009.

Theory

The large unit cell method (LUC) which can be used to simulate systems of periodical symmetry such as the bulk or surfaces of ordinary crystals. The LUC is adopted for the simulation of the electronic structure of nanocrystals in conjunction with the k = 0 approximation (k is the reciprocal wave vector). This approximation is used to drop sums of contributions from other points in k space except the origin (N. H. Aysa *et al*,2011; Mohammed T. Hussien *et al*, 2013; H. M. Abduljalil *et al*, 2011).

This is translated in nanocrystals structure by saying that we have a limited translational symmetry

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in the inside core of the nanocrystal only. Since the inside core of the nanocrystal has a well-defined 3D symmetry structure such as in the present zincblende structure, we optimize the structure by optimizing the lattice constant of the inner core only. This method can be used to simulate nanocrystals surfaces by adopting the **k** = 0 approximation but with more elaborate optimization procedure. Density functional theory at the generalized gradient approximation level coupled with large unit cell method (LUC-DFT) is used to simulate the electronic structure of zincblende cadmium sulfide nanocrystals. Four LUC cores are considered in the present work 8, 16, 54, and 64 atoms (M. A. Abdulsattar, 2011).

The bulk modulus is calculated by Cohen empirical formula (J.Zheng *et al*, 1999):

$$B_o = \frac{(1970 - 200I)}{d^{3.5}} \tag{1}$$

Where I is the ionicity factor which equals 0, 1 and 2 for IV, III-V and II-V groups respectively (J.Zheng *et al*, 1999), *d* is the intera-tomic distance (S. Q. Wang and H. Q. Ye, 2002).

$$d = \frac{\sqrt{3}}{4} a_o \tag{2}$$

Where a_0 lattice constant at zero temperature (t) and pressure (P)

And speed of sound equal to:

$$v_o = \sqrt{\frac{B_o}{\rho}} \tag{3}$$

Where v_o the speed of sound , ρ density equal to 3.45 g/cm³ to Boron Nitride (Soma T. *et al*,1974) .

The lattice constant (a) at any pressure:

$$a = a_o \exp(-P/3B_o) \tag{4}$$

According to (Kuma V. and Sastry B.S.R. 2001) the plasmon energy (*Epl*) is defined as:

$$Ep = \left(\frac{d}{15.3}\right)^{-3/2} \tag{5}$$

In order to simulate zincblende nanocrystals electronic structure using LUC method two kinds of cells are available: primitive and Bravais cell multiplets (Fig. 1 and 2 respectively). The main difference between these two kinds of cells is the shape and its associated surfaces. Primitive cells are parallelograms while Bravais cells are cubic in shape (H. M. Abduljalil *et al,* 2011). This difference in shape results in many fluctuations in the electronic structure of zinc-blende

structured materials (M. A. Abdulsattar, 2009; N. H. Aysa *et al*, 2011; Mohammed T. Hussien *et al*,2013; H. M. Abduljalil *et al*, 2011).

However, the present fluctuations are the strongest between the investigated materials. Two primitive cell multiplet cores are investigated namely: 16, 54 atoms. Two Bravais cell multiplet cores are investigated namely 8 and 64 atoms.
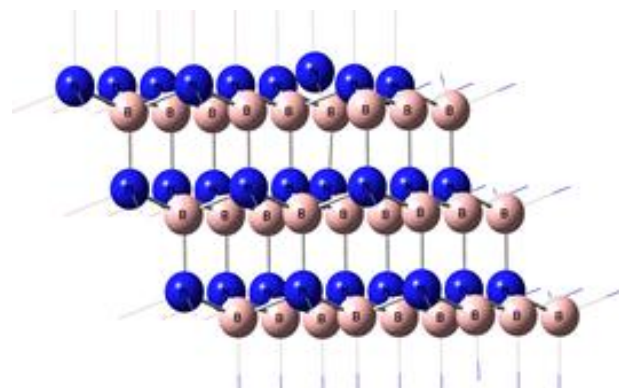

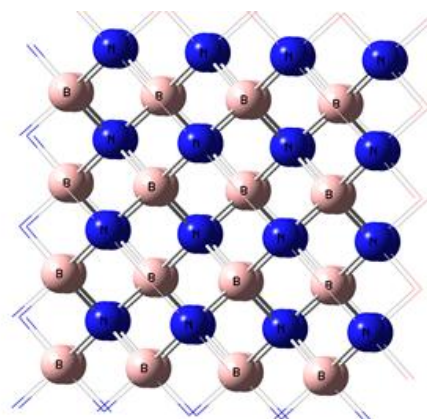**Fig. 1:** (color online) BN 54 atoms core LUC (parallelepiped shape primitive cell multiplet)

Fig. 2: (color online) BN 64 atoms core LUC (cubic Bravais cell multiplet)

Results and Discussions

To optimize core structure the lattice constant is needed to be optimized. In the optimization procedure we pick the minimum energy structure for every investigated LUC. From the set of minimum structures we can draw the following figures for the core part : Figs.3 and 4 show the total energy for 54, 64 atoms respectively of BN nanocrystal as a function of lattice constant from which we obtained the equilibrium lattice constant. This behavior is due to the attraction forces that take place at the large distance between atoms. The stability of the nanocrystal at the equilibrium when lattice constant equal to (0.37 and 3.68) nm or 54 and 64 atom respectively, while the attraction forces between the atoms equal to the repulsion (M. A. Abdulsattar,2010).
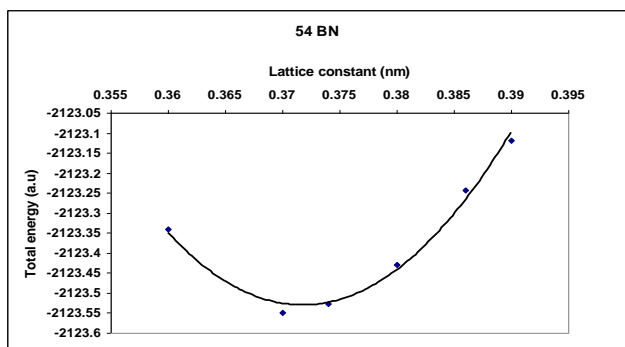
Fig.3: Total energy of 54 atoms of BN nanocrystal core as a function of lattice constant
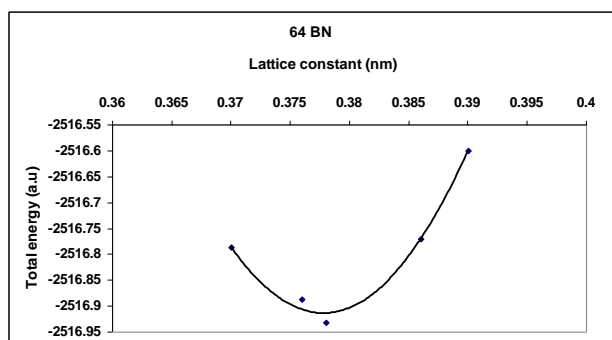

Fig.4: Total energy of 64 atoms of BN nanocrystal core as a function of lattice constant

In Fig. 5 the lattice constant of BN nanocrystals core shows a decreasing trend as the number of core atoms increase. The value of lattice constant decreases from the value 0.37nm and converges to 0.377nm. A similar behaviour is observed in previous studies (N. A. Nama *et al*, 2010; J. P. Perdew and Y. Wang,1992; S.J. Sque *et al*, 2006; J. B. Foresman and A.E. Frisch,1996).
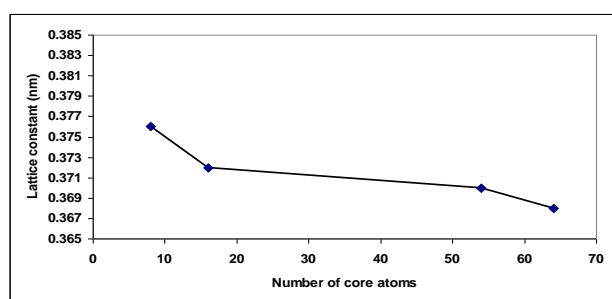

Fig. 5: Lattice constant variation with the number of core LUC atoms of BN nanocrystals

Fig. (6) shows the variation of the energy gap as a function of the variation of the number of core atoms, the energy gap of 8 atom LUC core is nearer to the value of energy gap of 64 atom core which is also the case between 16 atom, 54 atom and 128 atom core. Both 8 and 64 atom core cells are cubic Bravais multiples while 16, 54 and 128 atom cores are parallelepiped primitive cell multiples. Although this shape effect was found in previous literature (M. A. Abdulsattar, 2010; M. A. Abdulsattar,2009).
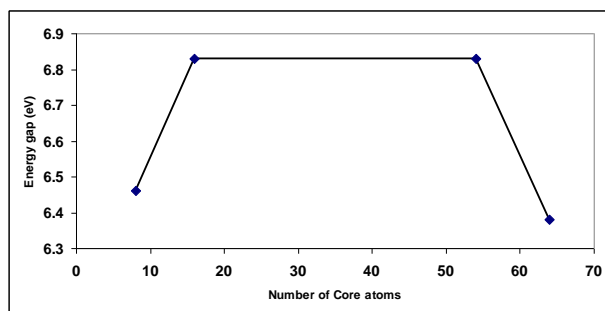

Fig. 6: Energy gap variation with the number of core LUC atoms of BN nanocrystals

Valence and conduction bands in Figs. 7 and 8 are show the same trend of shape effects. Cubic cells (8, 64 atoms) have wider bands than parallelepiped cells. This effect was also recognized but with less obvious shape effects in previous studies (M. A. Abdulsattar, 2009; N. H. Aysa *et al*,2011). The same is true in Fig. 8 for the HOMO and LUMO orbital energies. HOMO and LUMO orbitals do not only show shape effects, but also continues to fluctuated indefinitely due to the formation of different surfaces in larger nanocrystals (N. H. Aysa *et al*,2011). Other quantities that can be derived from HOMO and LUMO orbital energies include affinity, ionization energy and Fermi level. Affinity and ionization potential is connected approximately by a negative sign to LUMO and HOMO energies respectively (Soma T., 1974). Fermi level is the average of LUMO and HOMO energies (S. M. Sze and K. K. Ng, 2007). As a result of these relations, these three quantities also have the same shape effect that affect HOMO and LUMO energies.
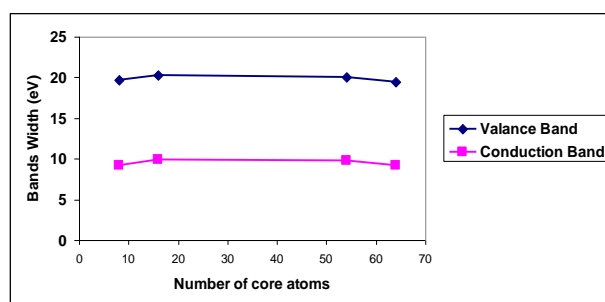

Fig. 7: Valence and conduction bands variation with the number of core LUC atoms of BN nanocrystals
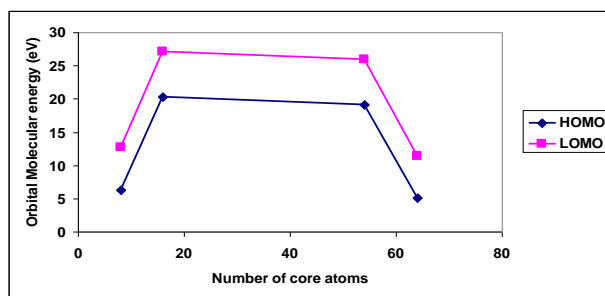

Fig. 8: Energy of the LUMO and HOMO levels variation with the number of core LUC atoms of BN nanocrystals.

Figures (9a,9b) summarizes the physics of many of the previous figures. Degeneracy of states of 54 and 64 atom LUCs show the above valence and conduction band widths variation between primitive and Bravais cells. The variation of the energy of HOMO and LUMO movements are also obvious in this figure. The highest degeneracy of primitive cells is higher than that of Bravais cells. This shows that symmetry of primitive cells is more definite than Bravais cells.
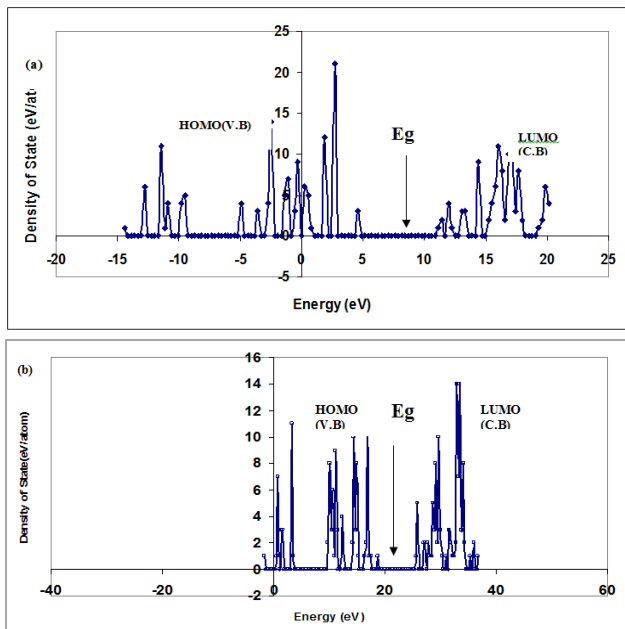

Fig. 9: Degeneracy of states of 54 and 64 atom LUCs (a and b respectively) as a function of energy levels are shown in this figure.

Bulk modulus of BN nanocrystal as a function of number of atoms in the core is shown in Figure (10). 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) . And this relation shows in Fig.(11) for speed of sound with number of core atoms, while the speed of sound depends on the atoms arrangement (T. Iitaka and T. Ebisuzaki, 2001) .
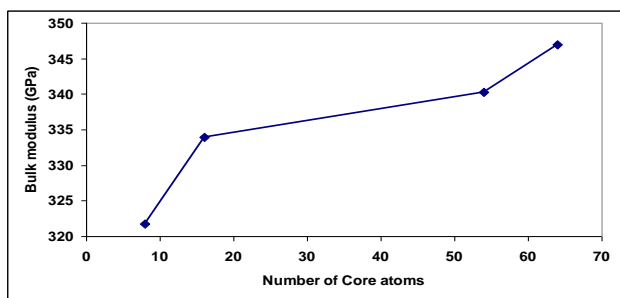

Fig.10: Bulk modulus as a function of the number of core atoms for BN nanocrystals
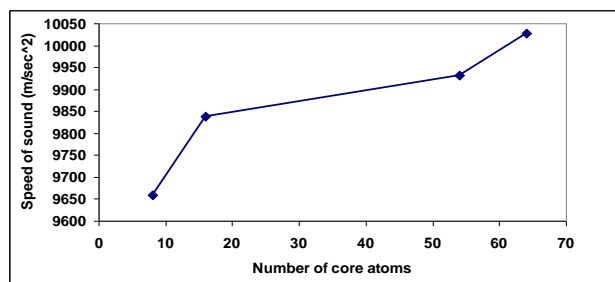

Fig.11: Speed of sound as a function of the number of core atoms for BN

The compression stress increases the density and decreases volume due to the shrinkage of orbitals (J. P. Connerade *et al*, 2000) as shown in Figure (12), and the distance between atoms (S. M. Sze, 1990), which entails an increment in the bond strength (J. Z. Jiang *et al* , 2002) and bulk modulus (M. P. D'Evelyn and T. Taniguchi, 1998) Figure (13) because the bulk modulus depends upon the density directly, and the young modulus which depends upon the bulk modulus (B. T. Wang *et al*, 2010), and vice verse for the tensile stress.
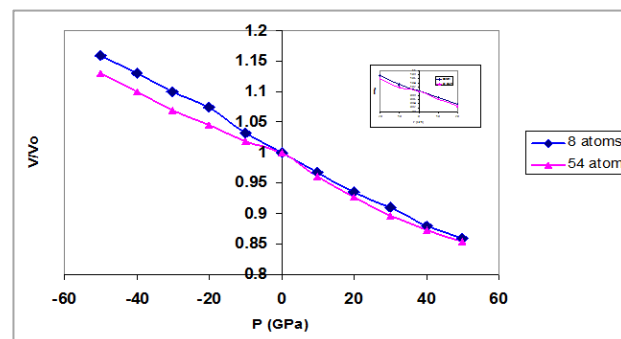

Fig.12: The variation of volume with pressure

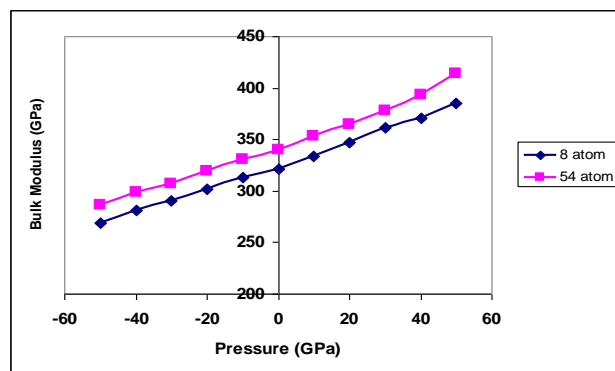**Fig.13:** The variation of Bulk modulus with pressure

Figure (14) shows the variation of plasmon energy with compression. Kornyushin has showed that the plasma affects the charge distribution and so the sound wave (L. C. M. Miranda and D. Ter Haar, 1972). On the other hand, the phonon frequency affects the effective charge (J. A. Sanjurjo, 1983) which depends upon the charge distribution and determines the plasma

frequency (E. Burstein, 1968).   The vibrational energy depends upon the behavior of the total energy which increases with stresses due to repulsion and attraction forces (J. N. Murrel, 1982).
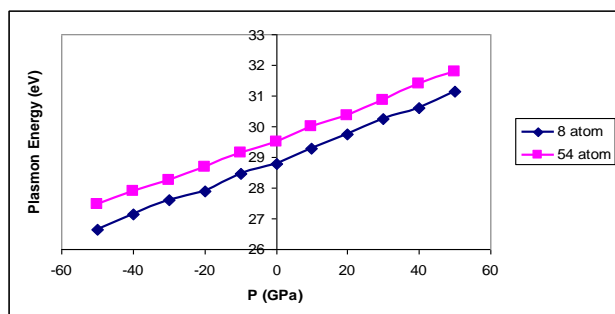

Fig.14: The variation of plasmon energy with pressure

Conclusions

Ab – initio DFT is preferred for wide range of calculations such as lattice constant , energy gap, conduction and valance bands , bulk modulus , speed of sound , plasmon energy . It is found that energy gap , valence band, conduction band, energy of the HOMO and LUMO orbitals all show shape effects. Degeneracy of states as a function of energy show a summary of the above mentioned shape properties. Moreover the bulk modulus and plasmon energy increases with the pressure.

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