Egyptian Journal of Chemistry
http://ejchem.journals.ekb.eg/

The Quantum-Chemistry Calculations of Electronic Structure of Boron Nitride Nanocrystals with Density Functional Theory Realization

Dilshod D. Nematov[1], Amondullo S. Burhonzoda[1], Mirzoaziz A. Khusenov[1], Kholmirzo T. Kholmurodov[2,3], Hanan Elhaes[4] and Medhat A. Ibrahim[5*]

[1]*Tajik Technical University named after academician M. S. Osimi.*
[2]*Joint Institute for Nuclear Research,141980, Dubna, Moscow Region, Russian Federation.*
[3]*Dubna State University, 141980, Dubna, Moscow Region, Russian Federation.*
[4] *Physics Department, Faculty of Women for Arts, Science and Education, Ain Shams University, 11757 Cairo, Egypt*
[5]*Spectroscopy Department, National Research Centre, 33 El-Bohouth St., 12622, Dokki, Giza, Egypt.*

WITHIN the framework of the density functional theory (DFT), a theoretical study of the structural features of nanocrystals doped by an atom of foreign elements was carried out. Nanotubes of boron nitride (BN (3.3)) and carbon nanotubes (CNT (3.3)) were chosen as the objects of a current comparative study. Based on quantum chemical calculations using the WIEN2k code, the band gap theory and density of states for BN (3.3) and CNT (3.3) are determined according to the theory of DFT. Further, with the substitution of one Zr atom in the BN (3.3) and CNT (3.3) lattice, the band structure of the BN (3.3) + Zr and CNT (3.3) + Zr systems as well as the changes occurring in them are investigated.

Keywords: Comparative analysis, Boron nitride nanotube (BN), Carbon nanotube (CNT), Doping elements, Electron density, Density functional theory (DFT).

Introduction

Computational methods based on quantum mechanical calculation show significant contribution for studying many systems and molecules [1-3].

It is now widely applied in many systems and interactions [4-6]. The field of applications is ranged from chemistry, biology, and physics to emerging materials whereas such computational work could provide structural, chemical and biological properties of the studied systems and interactions [7-10]. The main application of computational methods is to assign and describe certain experimental phenomena and/or start certain phenomena in which the experimental resources are limited or unavailable [11-13].

Using the density functional theory (DFT) method [14] and the multi-purpose software package WIEN2k [15], a quantum chemical study of the electronic structure of BN (3.3) and CNT (3.3) was carried out. The goal of quantum chemical calculations using the DFT method was to determine such important BANT characteristics as the band gap and the density of states before and after doping.

Currently, quantum chemical calculations within the framework of the density functional theory (DFT) are used to study a wide range of theoretical and applied problems in condensed matter physics, biochemistry and nanotechnology. The essence of the density functional theory is that the energy of the ground state of a system of interacting particles in a given external field

*Corresponding author e-mail: medahmed6@yahoo.com
Received 28/2/2019; Accepted 19/5/2019
DOI: 10.21608/EJCHEM.2019.12879.1805

is represented as a single-valued functional that depends only on the particle density $\rho(r)$. In other words, all properties of the electronic structure of a system in a nondegenerate ground state are completely determined by its electronic density. The electron density functional theory is based on the theorem of and Kohn [16], according to which all properties of the ground state of a nonhomogeneous interacting electron gas can be described by introducing some functional of electron density $\rho(r)$. Instead of the usual Hamiltonian of the system, a functional of the following structure is introduced in equation (1):

$$E[\rho] = \int d\ \rho(r) v_{ext}(r) + \int drdr' \frac{\rho(r)\rho(r')}{|r - r'|} + G[\rho]$$

where $v_{ext}(r)$ is the external field which includes the field of nuclei. The $G[\rho]$ functional includes the kinetic and exchange-correlation energy of electrons. In the work of Sham and Cohn [16], it was proposed in the form:

$$G[\rho] = T[\rho] + E_x[\rho]$$

Here $T[\rho]$ is the kinetic energy of a system of no interacting electrons of density ρ (r); the $E_x[\rho]$ functional contains many electron effects - exchange and correlation.The total energy of the system coincides with the extreme of the functional.

$$\delta E[\rho]_{\rho=\rho_0}(r) = 0$$

where ρ_0 is the electron charge distribution.

Thus, in order to find the total energy of the system ***E***, it is not necessary to know the wave $E[\rho]$ functions of all electrons; it is enough just to determine a certain functional and find its minimum. In this case, the functional $G[\rho]$ is universal and does not depend on the external field.

Materials and Methods

Calculation methods and Structures

The WIEN2k package makes it possible to implement DFT to solve physical problems, such as computing the electronic structure and total energy of the system, determining atomic parameters of force fields, spin-polarized bonds and antiferromagnetic effects, spin-orbit interactions, charge density, etc. [17].

Structural characteristics of BN (3.3):

The boron atoms and nitrogen in BANT are linked by ionic bonds, where the bond length between the boron and nitrogen atoms is about 1.471 Å. The crystal constants for non-doped BANT have the following meanings: a = 7.59240Å, b = 7. 59240Å, c = 7.53360Å, with angles α = β = γ = 90 ° and the space group 11_P2 / m, and for the doped BANT a = 7.59240Å, b = 7. 59240Å, c = 12.75500 Å, with angles α = β = γ = 90 and space group 6Pm. Fig. 1 shows the structure of BN (3,3) - nanotubes before and after doping with zirconium.

As part of the DFT and the WIEN2k package, each atom is surrounded by a muffin sphere (Mufftin; MT). In this case, the common space is divided into two areas (Fig. 1). One area consists of the inside of these non-overlapping spheres, and the second part of the space has the form of an intermediate area. The radii of the MT spheres are, respectively, $1.31a_0$ for B, $1.45a_0$ for N, where a_0 is the Bohr radius. For the BN + Zr system, the radii of the MT - spheres are $1.31a_0$ for B, $1.45a_0$ for N, and $1.3\ a_0$ for Zr, where a_0 is the Bohr radius.

Structural characteristics of CNT (3.3)

The carbon atoms in CNTs (3.3) are linked by chemical bonds, where the length of the C – C bond is about 1.421Å. The crystal constants for undoped CNT have the following values: a = 7.47620Å, b = 7.47620Å, c = 7.39290Å, with angles α = β = γ = 90 ° and the space group 11_P2 / m. For doped CNTs (3.3): a = 7.47620 Å, b = 47620 Å, c = 12.32150 Å, with angles α = β = γ = 90 ° and space group 6_(Pm).

The radii of the MT spheres for the CNT system (3.3) are $1.33\ a_0$, where a_0 is the Bohr radius. For a CNT system (3.3) + Zr, the radii of the MT-spheres are $1.33\ a_0$ for C and $1.3\ a_0$ for Zr, where a_0 is the Bohr radius. Fig. 2 shows the structure of CNT (3.3) before and after doping with Zr.

Below, atomic geometry optimization for BN (3.3) and CNT (3.3) is performed at the k-point of the Brillouin zone, generated by uniform grid parameters 1 × 1 × 1, and for the BN system (3.3) and CNT (3, 3) doped Zr is 1 × 1 × 5.

Results and Discussion

The results of calculating the electronic band structures for the BN (3.3) and CNT (3.3) systems before and after doping are expressed in terms of the density of states (DOS) before and after doping. The effects of exchange correlation are described

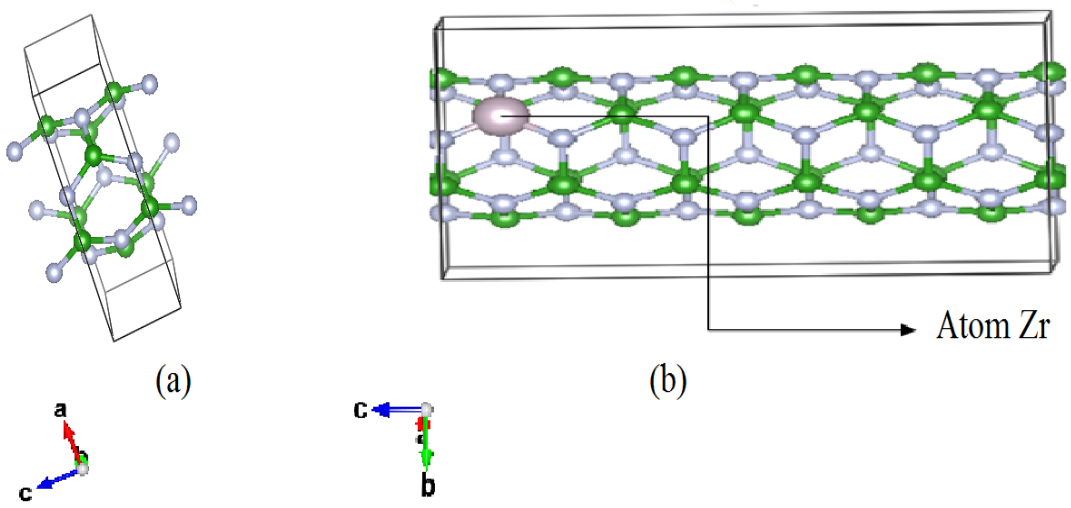

Fig. 1. Structures of (a) boron nitride nanotubes BN (3,3),(b) BN (3,3) with doped Zr atom.

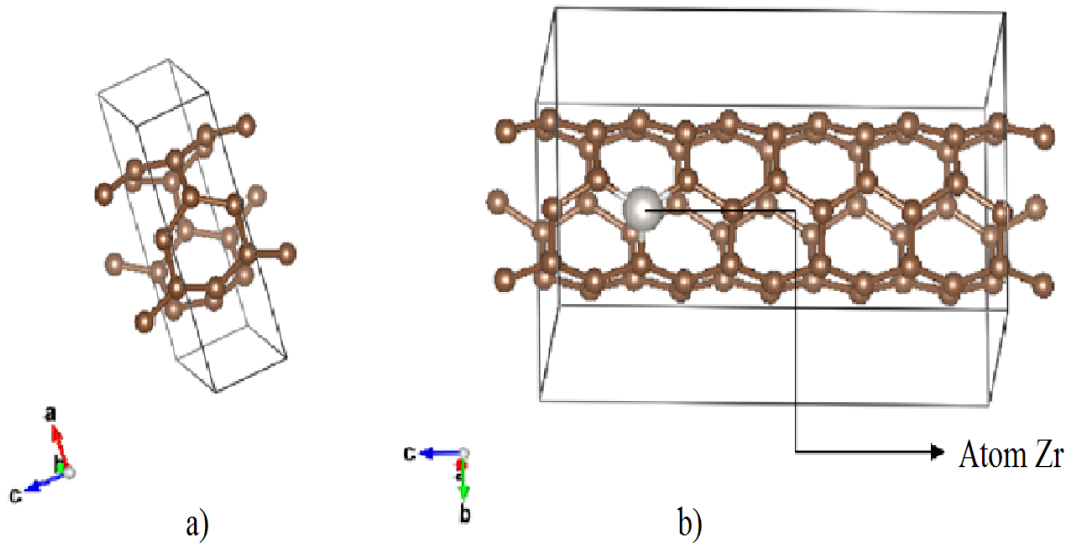

Fig. 2. Structures of (a) CNT (3,3), (b) CNT(3,3) with doped Zr atom.

by the generalized gradient approximation (GGA) proposed by Perdew - Burke - Ernzerhof (PBE [18]).

Calculation results for the BN (3.3) system

Below, using the DFT method and the WIEN2k package, we present the results of studying the electronic structure of BN (3.3), where the band gap and the density of states are determined.

The band gap for a BN nanotube (3.3) calculated in the local density approximation (PBE) using the GGA method is 4.25 eV. After doping of Zr, the band gap decreases to 0.6 eV.

The results of calculations in the framework of PBE, by definition, the band gap of BN (3.3) before and after doping are given with the help of Fig. 3 (a, b). Dotted lines correspond to Fermi levels.

Thus, the study shows that the doping of Zr in BN (3.3) has a significant effect on the modification of their electronic properties, that is, the BN system (3.3) after doping dominates the semiconductor property. In addition, after doping, a new gap appears in the region with negative energy values near the Fermi level.

Calculation results for CNT (3.3) system

The results of the calculation of electronic characteristics in the framework of WIEN2k-DFT, using the GGA method, completely confirm

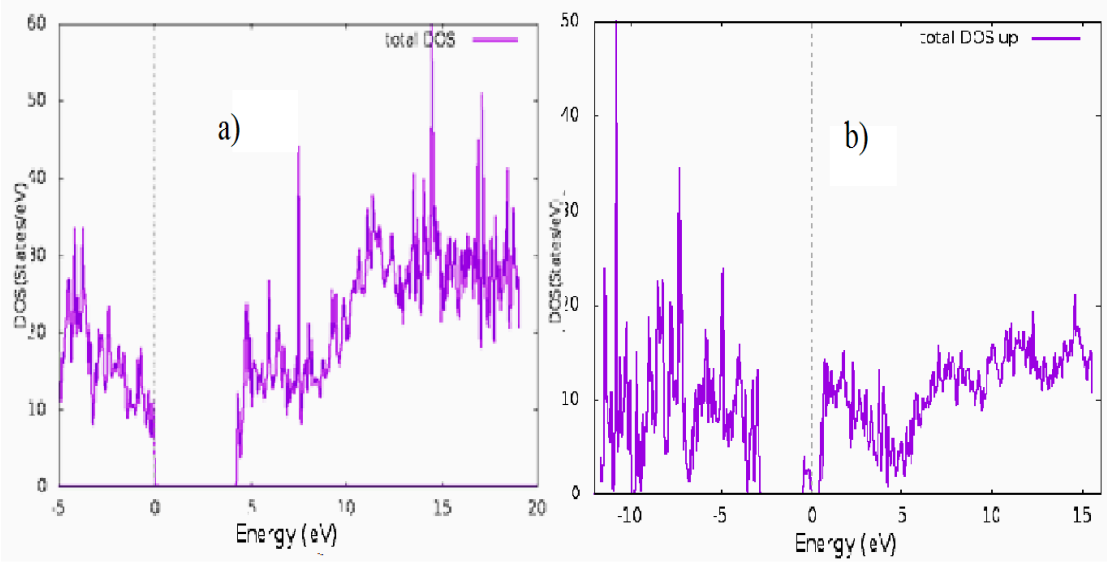

Fig. 3. Total electron density of states for: (a) undoped BN (3,3) (b) BN (3,3) nanotube doped with Zr atom.

that CNT (3.3) is a material with zero bandgap, which is explained by the metallic nature of CNT (3.3).

After doping with Zr atoms, the band structure of the CNT system (3.3) changes, that is, the doping process has a significant effect on the band structure of CNT (3.3). As a result, a gap appears with values of 0.5 eV (Fig. 4).

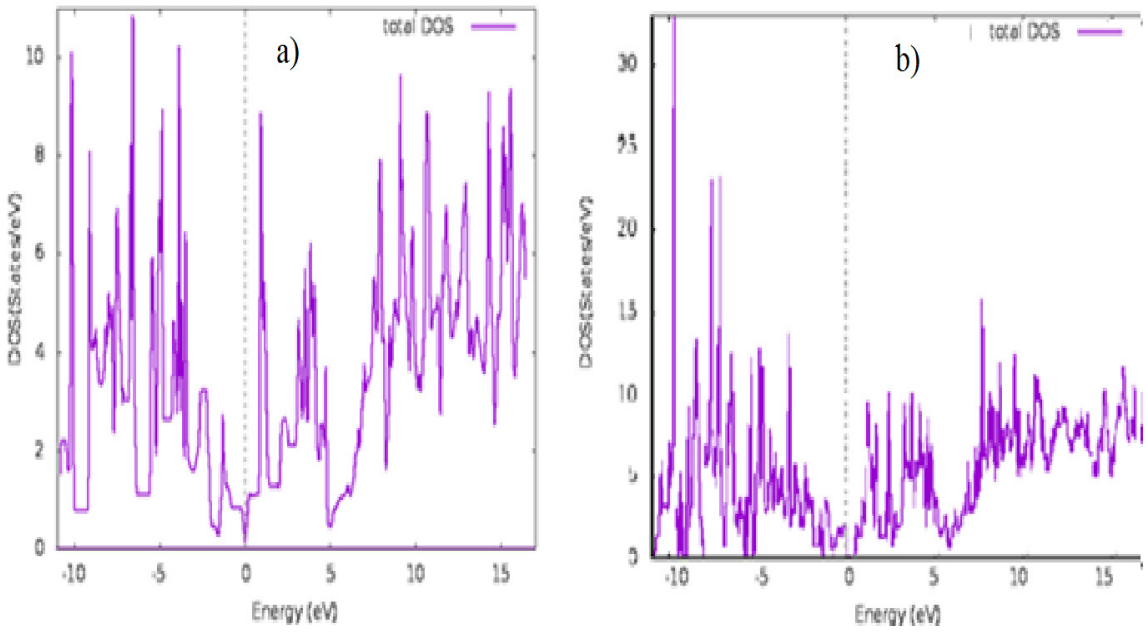

Fig. 4. Total electron density of states for: (a) undoped CNT (3,3) (b) CNT (3,3) nanotube doped with Zr atom.

As can be seen from Fig. 4 (a, b), the doping process significantly affects the electronic structure of the CNT (3.3), that is, the metal CNT (3.3) after doping is also dominated by the semiconductor property.

Comparison of the results of the band structure of BN (3.3) and CNT (3.3)

The results of calculations with the help of the WIEN2k package using the DFT theory and the GGA method show that the forbidden zone for undoped BN (3.3) is too large, which is explained by its dielectric nature. However, after doping, a sharp decrease in the band gap in the BN (3.3) + Zr system is observed. As a result, the system dominates the semiconductor properties.

The results of the calculation of the electronic characteristics of CNT (3.3) using the GGA method completely confirm the metallic properties of CNT (3.3). After doping foreign atoms in the CNT system (3.3), semiconductor properties are dominant. Below is a table of the results of calculating the band gap for the BN (3.3) and CNT (3.3) systems before and after doping of foreign atoms.

TABLE. The band gap for the system BN (3.3) and CNT (3.3) before and after doping Zr.

System	BN (3,3)	BN (3,3) +Zr	УНТ (3,3)	УНТ (3,3)+ Zr
Band gap (eV)	4.25	0.6	0	0.5

Based on the data of the electronic properties of BN (3.3) and CNT (3.3), in the future it is possible to study the multiscale dynamic and structural properties of other materials and their proposal for use in various fields. As it became clear to us, alien atoms have a strong effect on the electrical conductivity of nanocrystals.

Conclusion

This paper presents the results of quantum-mechanical calculations using DFT and using the WIEN2k software package of the electronic state BN (3.3) and CNT (3.3) with the aim of studying the effect of Zr on their electronic properties. The results showed that Zr has a strong influence on the possibility of increasing the conductivity of BN (3.3) and vice versa reducing the conductivity of CNT (3.3). This study will serve as the basis for further work that will lead to an understanding of the role of substitution atoms (like Zr) on the electronic properties of BN (3.3) and CNT (3.3), which are used in modern semiconductor technology, nanomedicine, nanoelectronics, in field emission devices, etc. This study, on the one hand, indicates the possibility of changing the properties of nanocrystals, on the other hand, it indicates the difficulties of technology in the manufacture of semiconductor materials with desired characteristics.

The results can be used to verify theoretical and experimental data for the further development of BN (3.3) and CNT (3.3) for such important aspects as containers for the delivery of biomolecules and drugs in living cells [19].

Acknowledgements

We appreciate very much the collaboration support provided by Prof. Tomoyuki Yamamoto of Waseda University, Japan,on using the WIEN2k package with DFT realization.This work in part is supported by the IGSF (International Fund for Humanitarian Cooperation), based in JINR, Dubna, ISTC (International Innovative Nanotechnology Center) of the CIS. This work in part is supported by JINR-ASRT (ARE) grant "Molecular Modeling Analysis of the Effect of Nano-Metal Oxides on Biological Molecules". The work in part is supported bya collaborative research program under Indo-Russian Joint Research-2016 (DST-RFBR), grant No.17-52-45062"Studies of the molecular orientation and radiation damage of DNA adsorbed on Zirconia".

References

1. Boukhvalov D.W., Moehlecke S., da Silva R.R., Kopelevich Y.; Effect of oxygen adsorption on magnetic properties of graphite, *Phys. Rev. B*, **83**, 233408 (2011).

2. Maddah M., Maddah M., Peyvandi K.;Molecular Dynamics Simulation of Methane Hydrate Formation in Presence and Absence of Amino Acid Inhibitors, *J. Mol. Liq.*, **269**, 721-732

3. Essa A.H., Al-Masoudi N.A.; SAR and DFT Studies on Some Analogues of 3-Azido-2-dideoxythymidine (AZT), *J. Comput. Theor.*

Nanoscience, **5**, 2210–2215 (2008).

4. Foresman J.B., Frisch A., *Exploring Chemistry with Electronic Structure Methods,* 2nded., Gaussian Inc., Pittsburgh, PA (1996).
5. Welsh W.J., Tong W., Georgopoulos P.G., In *Computational Toxicology: Risk Assessment for Pharmaceutical and Environmental Chemicals;* Ekins S, Ed.; John Wiley & Sons: Canada, pp. 153-175 (2007).
6. Novoselov K.S., Geim A.K., Morozov S.V., Jiang D.,Katsnelson M.I.,Grigorieva I.V.,Dubonos S.V.,Firsov A.A.; Two-dimensional gas of massless Dirac fermions in graphene, *Nature*, **438**, 197-200 (2005).
7. Kubinyi H.; QSAR and 3D QSAR in drug design. Part 1: methodology, Drug Discov. *Today*, **2**, 457-467 (1997).
8. Abdelsalam H.,Teleb N.H., Yahia I.S., Zahran H.Y.,Elhaes H., Ibrahim M.A,; First principles study of the adsorption of hydrated heavy metals on graphene quantum dots, *J. Phys. Chem. Solid*s, **130**, 32-40 (2019).
9. Youness R.A., Taha M.A., Ibrahim M.A.; Effect of Sintering Temperatures on the In Vitro Bioactivity, Molecular Structure and Mechanical Properties of Titanium/Carbonated Hydroxyapatite Nanobiocomposites, *J. Mol. Struct.*, **1150**, 188-195(2017).
10. Abdelsalam H.,Elhaes H., Ibrahim M.A.; First principles study of edge carboxylated graphene quantum dots, *Physica B*, **537**, 77-86 (2018).
11. Grenni, P., Caracciolo A.B., Mariani L., Cardoni M., Riccucci C., Elhaes H., Ibrahim M.A.; Effectiveness of a new green technology for metal removal from contaminated water, *Microchem. J.*, **147**, 1010-1020(2019).
12. Galal A.M.F., Atta D., Abouelsayed A., Ibrahim M.A., Hanna A.G.; Configuration and Molecular Structure of 5-Chloro-N-(4-sulfamoylbenzyl) Salicylamide Derivatives, *Spectrochim. Acta A.*,**214**, 476–486(2019).
13. Ibrahim M., Kholmurodov K.T., Fadeikina I.N., Morzhuhina S.V., Popova E.S., Elhaes H., Mahmoud A-A; On the Molecular Modelling Structure of the Egyptian Soil/Sediment in River Nile Delta Region, *J. Comput. Theor. Nanosci.*, **14** (8), 4133–4136 (2017).
14. Parr R.G., Yang W.; *Density-Functional Theory of Atoms and Molecules,* Oxford University Press, New York (1989).
15. Schwarz K., Blaha P.; Solid state calculations using WIEN2k, *Comp. Mater. Sci.*, **28**(2), 259-273 (2003).
16. Kohn W., Sham L.; Self-Consistent Equations Including Exchange and Correlation Effects, *Phys. Rev.*, **140**, A1133 (1965).
17. Nematov D.D., Burkhonzoda A.S., Husenov M.A., Kholmurodov Kh.T.; Quantum- mechanical calculation of the electronic structure of nanotubes of boron nitride doped with titanium by the density functional method, *Bulletin of The Tajik National University, Series of Natural Sciences* ISNN 2413-452X, **No. 1**, 107-112 (2019).
18. Perdew J.P., Burke K., Ernzerhof M.; Generalized Gradient Approximation Made Simple, *Phys. Rev. Lett.*, **77**(18), 3865 (1996).
19. Hilder, T.A., Hill J.M.; Carbon nanotubes as drug delivery nanocapsules, *Curr. Appl. Phys.*, **8**, 258–261 (2008).

دراسه الخواص الالكترونية لكريستالات نيتريد البورون النانومترية باستخدام حسابات كثافة الدالة الوظيفية

ديلشوت نعمتوف[1] أموندللو بروتذودا[1]، ميرزوعزيز كيزونزوف[1]، كولميرزو كولميردوف[2-3] ،
حنان الحايس[4] و مدحت ابراهيم[5]
[1] جامعه الطاجيك التقنية- طاجيكستان.
[2] المركز الدولي للفيزياء النووية - دوبنا- الاتحاد الروسي.
[3] جامعه دوبنا- دوبنا- الاتحاد الروسي.
[4] قسم الفيزياء- كلية البنات للأداب والعلوم والتربية- جامعة عين شمس- 11757 القاهرة- مصر.
[5] قسم الطيف- المركز القومى للبحوث- 33 شارع البحوث- 12622 الدقى- الجيزة- مصر.

تتميز طرق الحسابات باستخدام ميكانيكا الكم بالقدرة علي استنباط العديد من الصفات الفيزيقية والتركيبية للكثير من المواد، كما ازدادت اهميه هذه الطرق الحسابية في الدراسات المتعلقة بتطبيقات المواد النانومترية. لذلك يتم في هذا العمل اعداد نموذج جزيئي باستخدام نظرية الكثافة الوظيفية (DFT) لكريستالات نانومترية مطعمة بنيتريد البورون.
أيضا يتم اجراء دراسة مقارنة بين الانابيب النانومترية المطعمة ب ذرات انابيب الكربون النانومترية (CNT) و نيتريد البورون (BN) اعتمادا على نظرية الكثافة الوظيفية، كما تم عمل بعض الحسابات التي تتضمن حسابات فجوة الطاقة و كثافة مستويات الطاقة لكلا من (3.3) BN و (3.3) CNT).
علاوة على ذلك فانه باستبدال ذرة Zr للمركبين (3.3) BN و (3.3) CNT) فانه يتم دراسة التركيب الاكترونى للمركبين BN (3.3) + Zr و CNT (3.3) + Zr كما يتم ملاحظة التغيرات في الخواص الالكترونية التى تحدث عليه.