Modulating Band Gap and HOCO/LUCO Energy of Boron-Nitride Nanotubes under a Uniform External Electric Field

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ABSTRACT: *In this study, spectroscopic properties of the single-walled boron-nitride nanotube (SWBNNT) –a semiconductor channel in molecular diodes and molecular transistors–have been investigated under field-free and various applied electric fields by first principle methods. Our analysis shows that increasing the electric field in boron-nitride nanotube (BNNT) decreases the Highest Occupied Crystal Orbital (HOCO) /Lowest Unoccupied Crystal Orbital (LUCO) gap (HLG) significantly and the nanotube can be a conductor. The observed results suggest that the BNNTs is a useful semiconductor channel as nano-molecular diodes and nano-molecular transistors. Apart from that, the relationship between isotropic chemical shielding as an observable spectroscopic property with atomic charge and magnetizability in the presence and absence of an external electric field was studied. In order to rationalize energy changes, the relationship between the relative energy with the average electron delocalization of nitrogen and boron atoms with a variation of the external electric field is studied.*

KEYWORDS: *Molecular transistor; Nano-trasnsistor; Molecular diode; Nano-diode; Boron-nitride nanotube; PBC.*

INTRODUCTION

In recent years, the concept of using molecules such as carbon nanotubes as active electronic components has received a considerable amount of attention [1-5]. In addition, carbon nanotubes such as molecular components to being smaller, they don't need to be composed of rare earth elements or heavy metals, unlike traditional electronics. Therefore their manufacturer makes them both more environmentally friendly and cheaper to achieve 'Green Chemistry'. In previous efforts, the difficulty of placing such as tiny components into a circuit have been hindered to test possible molecules for this purpose. In these efforts, an electronic transistor made from a single molecular such as carbon nanotube has been placed onto an electronic chip. This sudden and important development could be an important step in the development of smaller, cheaper and greener electronic devices and will simplify the testing of other molecular components. In recent years, interest in devices made of single molecules has been growing [6-13]. Therefore the creating of the first transistor made from a single molecule was succeeded [13].

The Boron Nitride Nanotube (BNNT) as a one-dimensional tubular structure was first predicted in 1994 [14,15]. It was theoretically predicted that BNNTs and BN nano-rings with perfect BNBN alternation, containing a covalent bond between two atoms of N and B in the quasi-borazine rings to be stable [16-21]. Analogous to the formation of a Single-Walled Carbon NanoTube (SWCNT) from a 2D graphite, the tubular structure of BNNT was formed by rolling a 2D hexagonal BN(h-BN) film. The electronic properties of BNNTs are independent of chirality [22], unlike the electronic properties of Carbon NanoTubes (CNTs) which depend upon the chiral indices (m, n). Therefore in contrast to carbon nanotubes, BNNTs have semiconducting properties, with a large, near-constant band gap of ~5.5 eV, which is independent of the diameter and chirality of the nanotube [14].

In the recent years, topological specifications of electron density, respective Critical Points (CP) and atomic properties have been employed for the explanation of many of chemical concepts in the bonding area [8,9,23-29]. Of course, in some cases, it is difficult to describe such local specifications, and some of them triggered disagreement in the chemical community [10, 30-34].

First-principles calculations, as well as experiments, have demonstrated that the geometry and electronic structure of aromatic species might be influenced by means of an External Electric Field (EEF) of appropriate strength [35-42].

Although the effect of the electric field on the band gap and Highest Occupied Crystal Orbital (HOCO)/Lowest Unoccupied Crystal Orbital (LUCO) energy molecules seems to be easy for computing using commercial packages, interpretation of their results needs great attention in the case of their function as a molecular transistor or molecular diode. Indeed, finding an appropriate reference system for comparison of the energy of molecules in the presence of an EEF is a nontrivial task.

In previous studies, it was shown that the band gap of SWCNT [43,44] and SWBNNT [44-46] changes under a transverse EEF by inducing a semiconductor-metal transition. In this contribution, controlling the band gap and HOCO/LUCO Energy of BNNTs under a uniform EEF is studied. It is demonstrated that the BNNTs are useful as semiconductor channels to justify the design and performance of nano-molecular diodes and nano-molecular transistors.

METHODS AND COMPUTATIONS

In the present work the armchair (4,4), (5,5) and (6,6) Single-Walled Boron-Nitride NanoTubes (SWBNNTs) geometry were optimized at field-free as well as various applied electric fields at the framework of Density Functional Theory (DFT) using the three-parameter Becke's exchange [47,48] and Lee-Yang-Parr's correlation non-local functional [49,50], usually known as B3LYP method, combined with 6-31G(d) basis sets based on Periodic Boundary Condition (PBC) approach. The excellent performance of the cited model in producing of reliable molecular properties at an appropriate computational time with non-expensive hardware's was the main criterion for choosing this model.

All calculations were performed by considering the electric field as implemented in the Gaussian 09 suite of programs [51]. The optimization of molecular structures were done by conserving the coordinate origin of nanotubes fixed on their center at different electric field strengths parallel to the long axis of the nanotubes from 0.0005 a.u. in increments of 0.0005 a.u. up to 0.0015 a.u. without any symmetry constraint. Our computations show that for EEF= 0.0013, 0.0014 and 0.0015 a.u. no stationary point found for each nanotube, i.e. the electric field that the SCF (Self Consistent Field) in nanotube was not converged.

The second derivatives of energy with respect to the structural variables (harmonic frequencies) were computed at the same level of theory to verify the nature of stationary points for each nanotube at various applied fields. No imaginary frequency was observed for the systems at various electric fields applied on nanotubes.

The nature of bonding between boron and nitrogen atoms in armchair (4,4) SWBNNTs in the presence of an EEF were analyzed using the Quantum Theory of Atoms in Molecules, QTAIM [52] by dividing the systems into its subsystems [52,53], using the AIMAll [54] suite of programs on wave functions that were obtained from the B3LYP/6-31G(d) computations.WFX files obtained from NMR calculations without PBC approach were on the local minimum structures by the Gauge-Including Atomic Orbital (GIAO) method [55-59] at the aforementioned level of theory were used for assessing atomic energy, charge, localization and delocalization indices, and the second-rank magnetizability tensor. Intra- and inter-atomic magnetize abilities were computed by the Proaim or
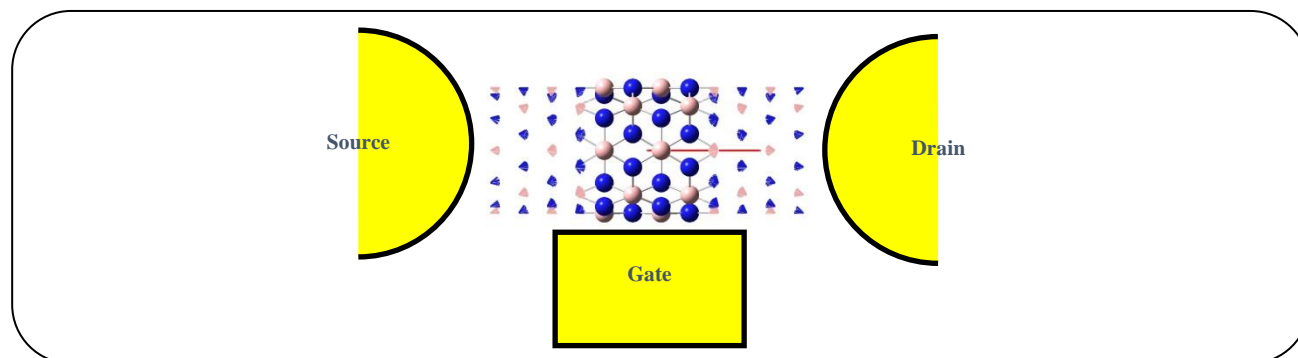
Fig. 1. A molecular transistor based on armchair (4,4) single-walled BNNT.

Promega first-order integration approach as implemented in the AIMAll suite of the program. All obtained magnetize abilities are directly tabulated in the AIMAll output (.sum file). The accuracy of the integration process was guaranteed by keeping the atomic integral of the Laplacian of each atomic basin below 3×10^{-4} atomic units. Furthermore, the sum of the electronic energies and charges of all subsystems in a molecule, i.e., topological atoms, were compared with the total electronic energy and charge of each molecule in order to ensure that errors in the QTAIM related integrations were below the chemical accuracy, e.g., 1 kcal/mol.

RESULTS AND DISCUSSION

In this research, we hypothesize molecular nano-transistors based on the armchair (4,4), (5,5) and (6,6) Boron-Nitride Nanotubes (BNNTs). The geometries of (4,4),(5,5) and (6,6) BNNTs (Fig. 1) have employed to study the relationship between the electronic and magnetic properties of the boron and nitrogen atoms.

The relationship between chemical shielding with atomic charge and atomic magnetizability

The B3LYP method was used to study the relationship between the trace of isotropic shielding tensor for boron and nitrogen atoms in an armchair (4,4) BNNT with atomic magnetizability from zero to 0.0012 a.u. field strength based on one-dimensional periodical systems of the $B_{16}N_{16}$ unit cell under PBC approach.

The results of QTAIM atomic charges, $q(\Omega)$;localization indexes, $\lambda(\Omega)$; trace of isotropic shielding tensors, σ_{iso}; using GIAO approximation and also isotropic intra-atomic, $\chi(\Omega)^{intra}$; interatomic, $\chi(\Omega'|\Omega)$; and total-atomic, $\chi(\Omega)$; magnetize abilities for armchair

(4,4) SWBNNT with B3LYP/6-31G(d) level at zero, 0.0005, 0.0010 and 0.0012 a.u. field strengths applied to the long axis of the nanotube are given in Tables S.1 to S.4 in supplementary data.

Isotropic chemical shielding (σ_{iso}) v.s. QTAIM atomic charge ($q(\Omega)$) and the isotropic total atomic magnetizability ($\chi(\Omega)$) of boron and nitrogen atoms individually for armchair (4,4) SWBNNT without an external electric field, in Fig. 2 and in the presence of 0.0005, 0.0010 and 0.0012 a.u. external electric field are shown in Figs. 3-5 respectively. The linear relationships between isotropic chemical shielding with atomic charge and isotropic total atomic magnetizability in an armchair (4,4) SWBNNT without external electric field (Fig. 2) and in the presence of 0.0005, 0.0010 and 0.0012 a.u. external electric field (Figs. 3-5) are obtained. The obtained linear relationships between isotropic chemical shielding with an atomic charge for boron and nitrogen atoms are inverse each other. As in Figs. 2(a) through 5(a) can be seen, the isotropic chemical shielding in boron atoms directly related to atomic charge, while this relationship is the reverse for nitrogen atoms. This means that with increasing atomic charge to more positive values for boron atoms, chemical shielding is increased, and conversely with decreasing atomic charge to more negative values for nitrogen atoms, chemical shielding is reduced. This result is in contrary to the expectation for the boron atoms and the chemical shielding should be reduced by increasing the amount atomic charges to more positive. Also, the lack of correlation, the discrepancy between the results and/or lack of compliance between chemical shielding and atomic charges has been observed in previous work [8,10].
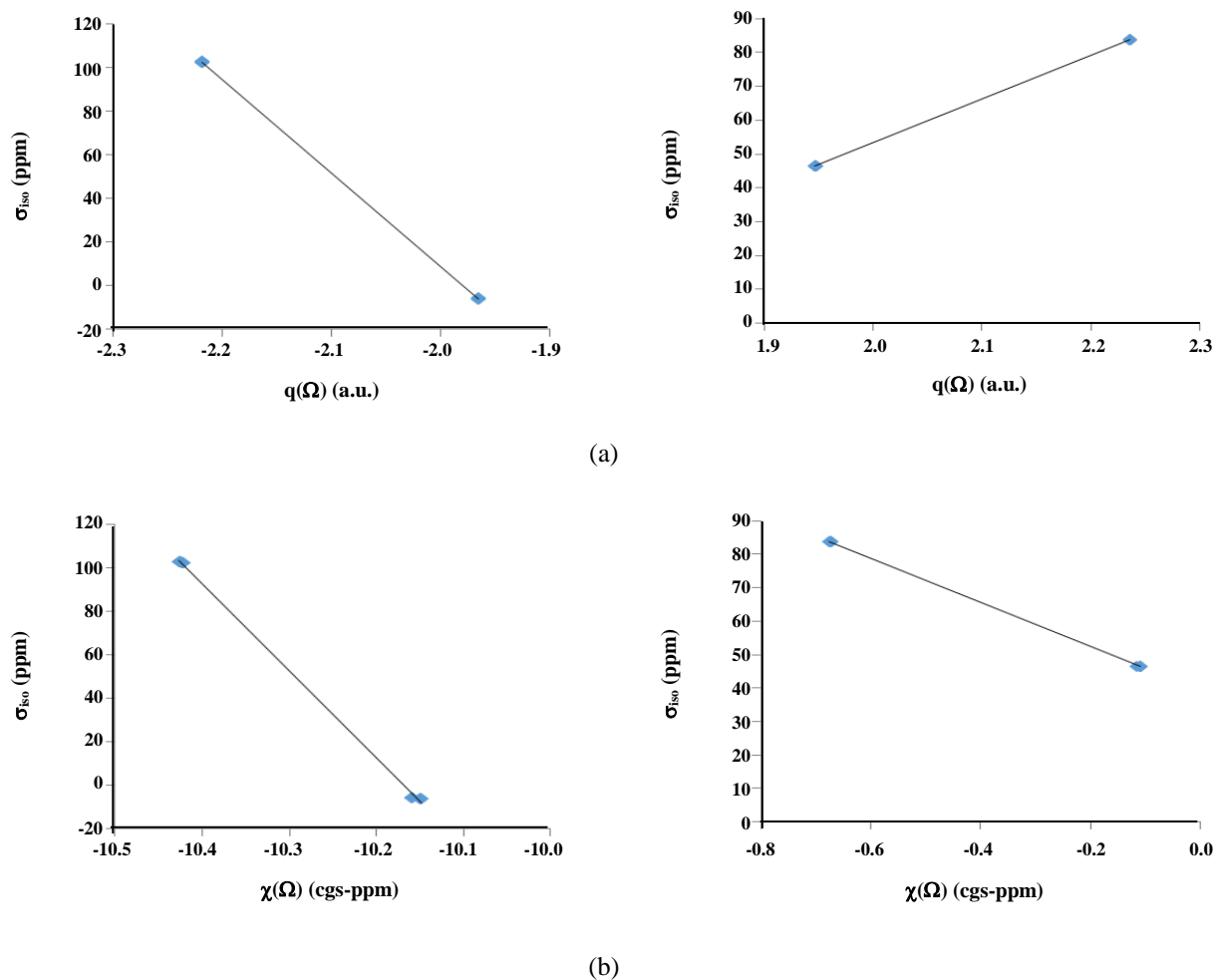
*Fig. 2: Isotropic chemical shielding (σ_{iso}) (a) vs. QTAIM atomic charge (q(Ω)) of boron atoms (right)
and nitrogen atoms (left) and (b) vs. the isotropic total atomic magnetizability ($\chi(\Omega)$) of boron atoms (right) and
nitrogen atoms (left) for armchair (4,4) single-walled BNNT without an external electric field.*

Magnetizability of boron and nitrogen atoms in an armchair (4,4) SWBNNT with periodic boundary condition shows that by increasing the chemical shielding, the isotropic total atomic magnetizability is reduced. The inverse association obtained in the Figs. 2 (b) through 5 (b)shows that the relationship between the magnetic shielding integration with magnetizability as presented in Equation 1, corresponds [60].

An induced magnetic moment ***m*** in a molecule is given by the product of the molecular magnetizability tensor χ and an external magnetic field ***B***. This simple physical interpretation leads to the following relation:

$$\sigma^I m = \nu \chi B \tag{1}$$

Where ***m*** and ***B*** denote the unit magnetic moment and the magnetic field, respectively. The Integrated Magnetic Shielding (IMS) tensor, σ^I has a dimension of a volume (m^3 or $ppmm^3$) that can be obtained by integration of magnetic shielding tensor σ_R at the arbitrary position ***R*** in an atom provides information about shielding properties of an electronic structure at that point, over a whole space ***R*** (Equation 2).

$$\sigma^I = \int \sigma_R (R) dR \tag{2}$$

The strong correlation with regression coefficient close to the one between isotropic total atomic magnetizability ($\chi(\Omega)$) with isotropic chemical shielding
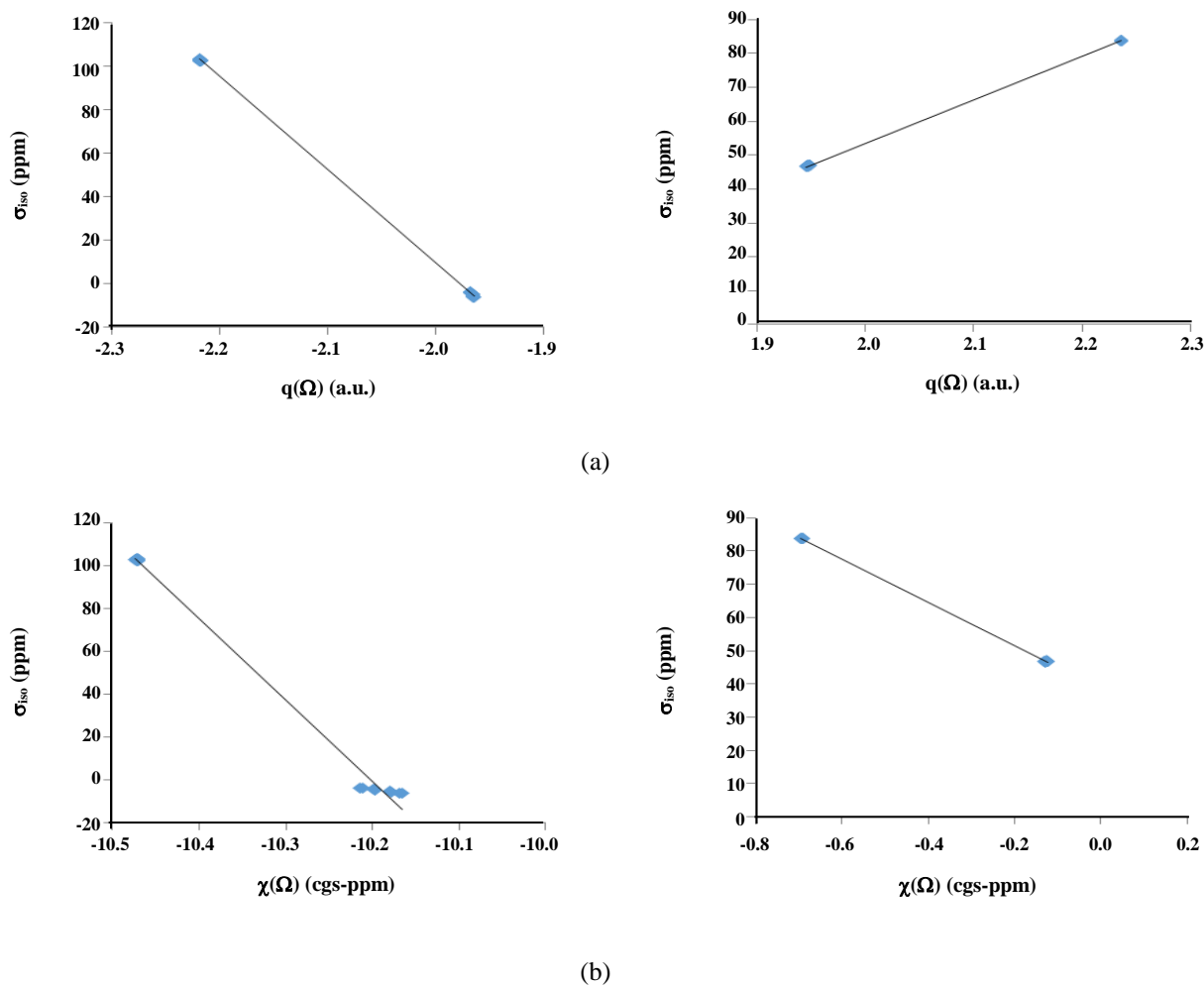
(a)

(b)

Fig. 3: Isotropic chemical shielding (σ_{iso}) (a) vs. QTAIM atomic charge ($q(\Omega)$) of boron atoms (right) and nitrogen atoms (left) and (b) vs. the isotropic total atomic magnetizability ($\chi(\Omega)$) of boron atoms (right) and nitrogen atoms (left) for armchair (4,4) single BNNTin the presence of 0.0005 a.u. external electric field.

(σ_{iso}) in boron and nitrogen atoms observed separately. The results show that there are two kinds of atoms with different properties. The first group of boron and nitrogen atoms that are attached to three of nitrogen and boron atoms respectively and the second boron and nitrogen atoms in the ends of boron nitride nanotube connected to two atoms of nitrogen and boron respectively. The results show that the first group boron and nitrogen atoms have more chemical shielding.

With increasing of the external electric field in the Figs. 2 (b) through 5 (b) respectively, the linear reverse relationship between total isotropic atomic magnetizability ($\chi(\Omega)$) with isotropic chemical shielding (σ_{iso}) in boron atoms are retained, but in the second group of nitrogen atoms that is related to the ends of the nanotube, a new linear

relationship between magnetizability and chemical shielding is observed. This relationship is similar other cases that with increasing of chemical shielding, the total atomic magnetizability is reduced (Fig. 6).

The relationship between relative energy and band gap with electron delocalization

Meanwhile, the relative energy (E_{rel}) and the relative differences in the energy band gap for HOCO and LUCO (LUCO-HOCO) in (4,4), (5,5) and (6,6) BNNTs with the PBC approach without the presence of an external electric field and in the presence of different external electric fields have been studied.

LUCO-HOCO band gap is a distance between Lowest Unoccupied Crystal Orbital (LUCO) and Highest
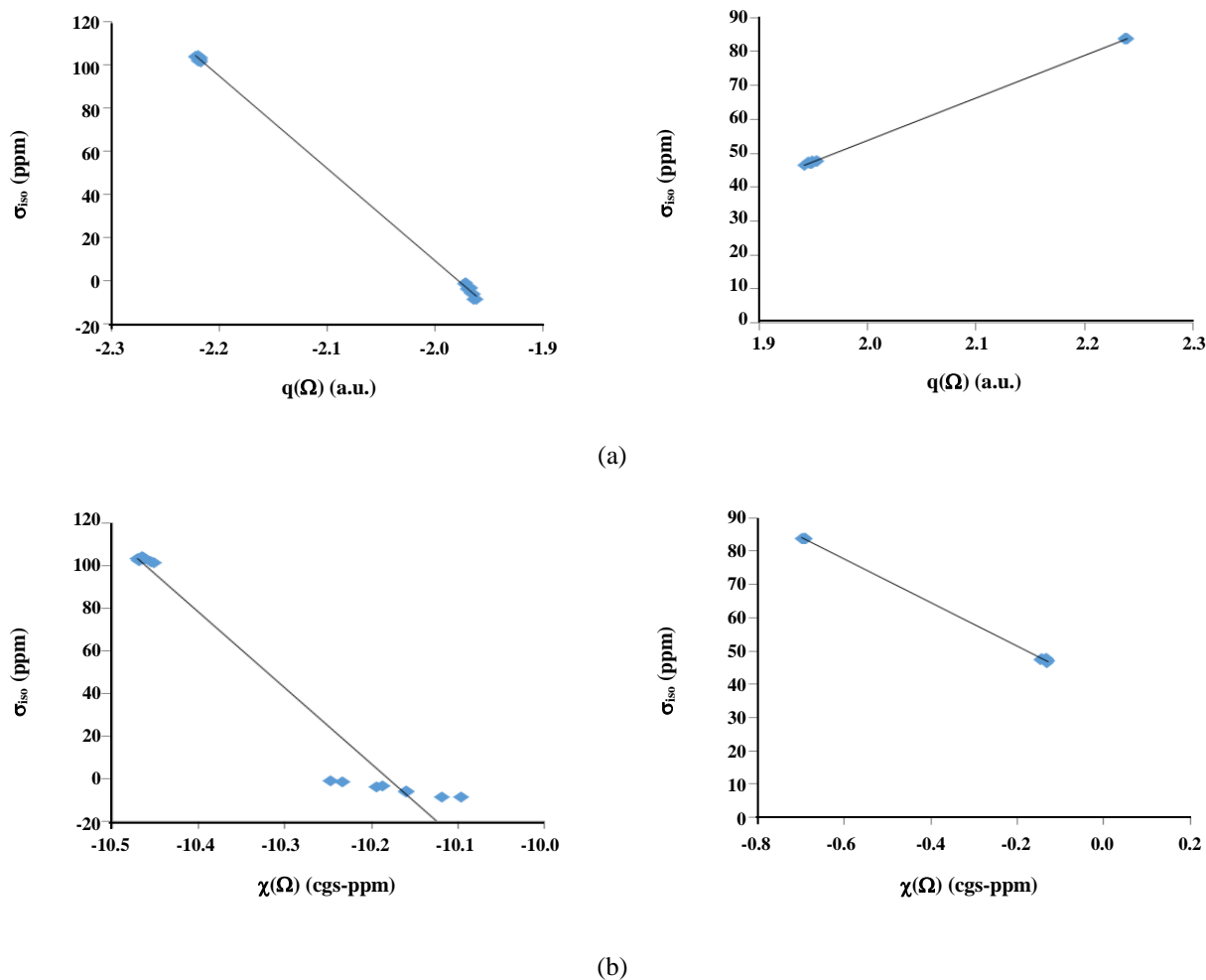
(a)

(b)

Fig. 4: Isotropic chemical shielding (σ_{iso}) (a) vs. QTAIM atomic charge ($q(\Omega)$) of boron atoms (right) and nitrogen atoms (left) and (b) vs. the isotropic total atomic magnetizability ($\chi(\Omega)$) of boron atoms (right) and nitrogen atoms (left) for armchair (4,4) single-walled BNNT in the presence of 0.0010 a.u. external electric field.

Occupied Crystal Orbital (HOCO). Band gap of (4,4), (5,5) and (6,6) BNNTs as the relative differences in HOCO and LUCO energy in the presence of external electric field from zero to 0.0012 a.u. has been reported in Table 1. According to the results obtained in this table, (4,4), (5,5) and (6,6) BNNTs without the presence of an external electric field has a band gap (ΔE) about 6 eV. The large LUMO-HOMO gap is often regarded as a molecule stability criterion. More sophisticated treatment of large gaps is seen to occur for systems with high relative stability [9, 17].

Energy graph of HOCO and LUCO vs. external electric field in(4,4), (5,5) and (6,6) BNNTs has been shown in Fig. 7. Current figures show that by increasing the electric field to 0.0010 a.u., does not change HOCO

and LUCO energy. But from 0.0010 a.u. to maximum electric field operable i.e. 0.0012 a.u., immediately LUCO energy is reduced to zero and LUCO-HOCO gap has done equal to zero and therefore BNNTs have done conductive. The results show that increasing of BNNTs diameter has not a great effect on the usable electric field for conducting of BNNTs and acting of them as semiconductor channels for nano-diodes and nano-transistors.

Energy graph of the relative energy band gap as the difference in energy HOCO and LUCO (LUCO-HOCO) in terms of eV to the external electric field (a.u.) in an armchair (4,4) SWBNNT in Fig. 8 shows that the enhanced electric field from zero to 0.0010 a.u. does not change much band gap energy. But from 0.0010 a.u.
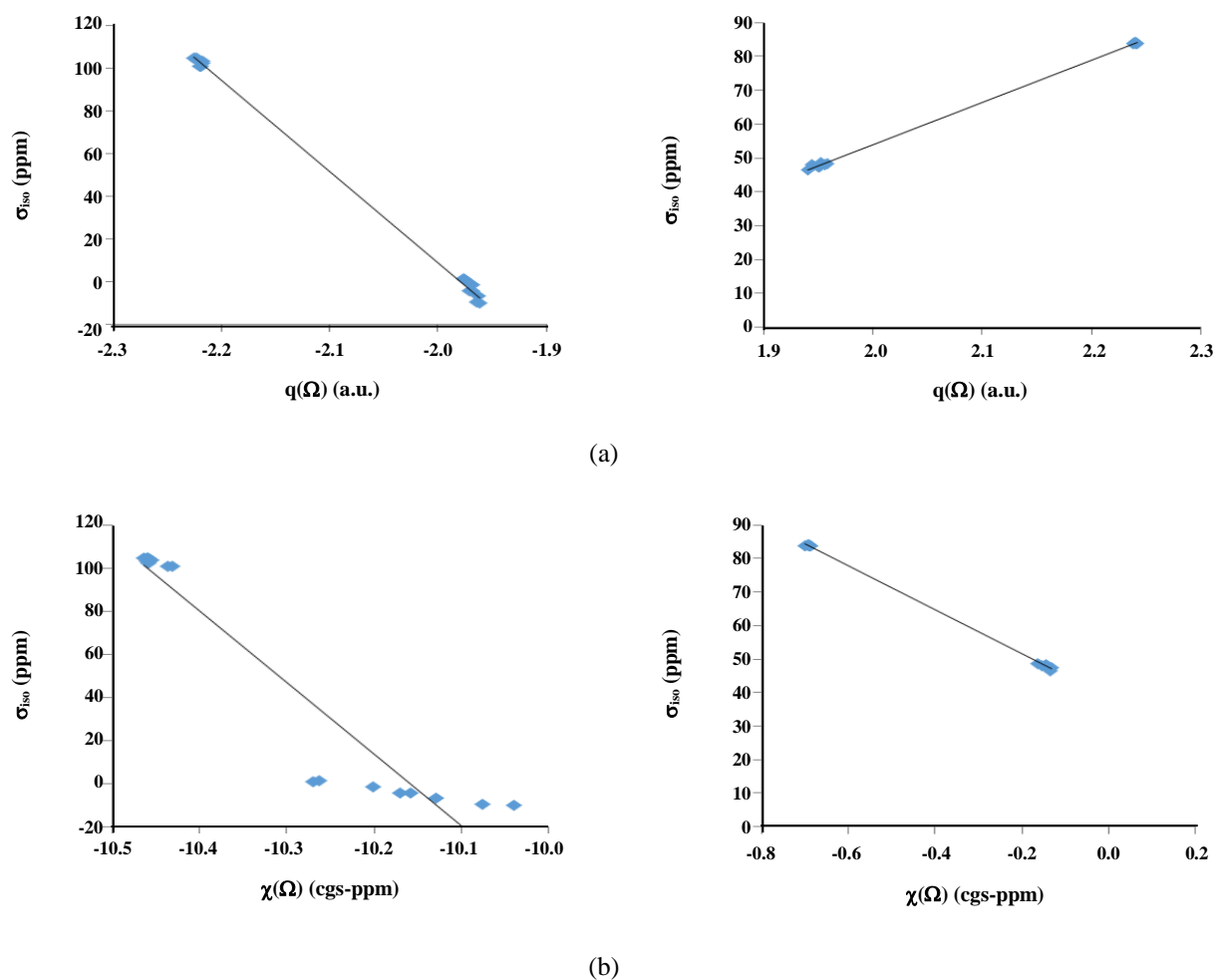
(a)

(b)

Fig. 5: Isotropic chemical shielding (σ_{iso}) (a) vs. QTAIM atomic charge (q(Ω)) of boron atoms (right) and nitrogen atoms (left) and (b) vs. the isotropic total atomic magnetizability ($\chi(\Omega)$) of boron atoms (right) and nitrogen atoms (left) for armchair (4,4) single-walled BNNTin the presence of 0.0012 a.u. external electric field..

electric field to maximum operable electric field i.e. 0.0012 a.u., the band gap energy immediately dropped to the zero and nanotube is conductive.

With results reported in Tables S.1 to S.4 in supplementary data as well as the results listed in Table 1, the total energy (E_{tot}), the relative energy (E_{rel}) in armchair (4,4) SWBNNT and also average electron localization ($\lambda_m(\Omega)$) and average electron delocalization index ($DI_m(\Omega)$) in nitrogen and boron atoms of (4,4) BNNT by changing the external electric field from zero to 0.0012 a.u. have been reported in the Table 2.

The relative energy (E_{rel}) against external electric field, average electron delocalization index of nitrogen atoms ($DI_m(N)$) and average electron delocalization index of boron atoms ($DI_m(B)$) in an armchair (4,4) SWBNNT

by B3LYP/6-31G(d) computational level are shown in Fig. 9.

As shown in Fig. 9 (a), with increasing of the external electric field, the relative energy of BNNT increases. The situation with the reduced energy bandgap corresponded to higher electric fields (Fig. 8). The large LUCO-HOCO gap often occurs for systems with high relative stability [9, 17]. On the other hand Fig. 9 (b) is observed by increasing average electron delocalization index of nitrogen atoms ($DI_m(N)$) to more minus, the relative energy of BNNT is increased, but on the contrary by increasing the average electron delocalization index of boron atoms ($DI_m(B)$) to more positive, the relative energy increases (Fig. 9 (b)).The results show that with the increasing of 0.0016 to average electron

Table 1: Total energy (E_{tot}), relative energy (E_{rel}), and band gap as the relative differences in HOCO and LUCO energy ($\Delta E_{(LUCO-HOCO)}$) of armchair (4,4), (5,5) and (6,6) single walled BNNTs in the presence of external electric field.

| Compound	Field Strength (a.u.)	E_{tot} (a.u.)	E_{rel} (kcal/mol)	E_{LUCO} (eV)	E_{HOCO} (eV)	$\Delta E_{(LUCO-HOCO)}$ (eV)
(4,4) BNNT	0.0000	-1275.53565	0.0	-0.565	-6.677	6.112
	0.0005	-1275.53531	0.2	-0.602	-6.659	6.057
	0.0010	-1275.53009	3.5	-2.312	-6.683	4.371
	0.0012	-1275.52165	8.8	-7.016	-6.701	-0.315
(5,5) BNNT	0.0000	-1594.51233	0.0	-0.312	-6.607	6.295
	0.0005	-1594.51188	0.3	-0.322	-6.615	6.292
	0.0010	-1594.50510	4.5	-1.060	-6.646	5.586
	0.0012	-1594.49378	11.6	-6.122	-6.669	0.546
(6,6) BNNT	0.0000	-1913.47594	0.0	-0.242	-6.576	6.334
	0.0005	-1913.47541	0.3	-0.276	-6.586	6.310
	0.0007	-1913.47397	1.2	-0.292	-6.595	6.304
	0.0010	-1913.46670	5.8	-1.049	-6.619	5.570
	0.0012	-1913.45205	15.0	-6.493	-6.644	0.151
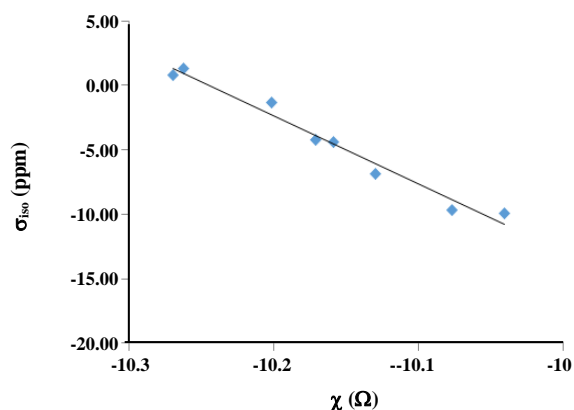
Fig. 6: Isotropic chemical shielding (σ_{iso}) vs. the isotropic total atomic magnetizability ($\chi(\Omega)$) of nitrogen atoms in the ends of armchair (4,4) single-walled BNNT and in the presence of 0.0012 a.u. external electric field.

delocalization index of nitrogen atoms, the average electron delocalization index of boron atoms 0.0009 decreases. Therefore the increase of electron delocalization index of nitrogen atoms in an external electric field lower in the low relative energy is more effective. Also, the energy graph of band gap as relative differences in energy HOCO and LUCO (LUCO-HOCO) vs. average electron delocalization index of nitrogen atoms ($DI_m(N)$) and average electron delocalization index of boron atoms ($DI_m(B)$) in an armchair (4,4) SWBNNT by B3LYP/6-31G(d) computational level are shown in Fig. 10.

As in Figs. 10 (a) and 10 (b) is observed, in order to increase electron delocalization index of nitrogen atoms ($DI_m(N)$) to more minus, energy band gap of BNNT decreased, but on the contrary, the electron delocalization index of boron atoms ($DI_m(B)$) to more positive reduces the energy gap. In this case, exactly the impact of electron delocalization on energy band gap (Fig. 10) as expected converses influence of electron delocalization on relative energy of BNNT (Fig. 9).

CONCLUSIONS

In the present work, we explained how the boron-nitride molecular transistors operate and what controls their performance to explore approaches improving the transistor's performance. Therefore in this research, we report designing a molecular nano-transistor based on armchair (4,4), (5,5) and (6,6) SWBNNTs with the PBC approach using DFT calculations at B3LYP/6-31G(d) without external electric field and also in the presence of external electric fields. When one of these systems is placed between the source, the drain and the gate electrodes as shown in Fig. 1, it behaves like a transistor. The calculation of NMR based on Gauge-Including Atomic Orbitals (GIAO) without PBC approach and electron density analysis based on Quantum Theory of Atoms in Molecules (QTAIM) on armchair (4,4) SWBNNT optimized without the presence of an external electric field and also in the presence of external electric
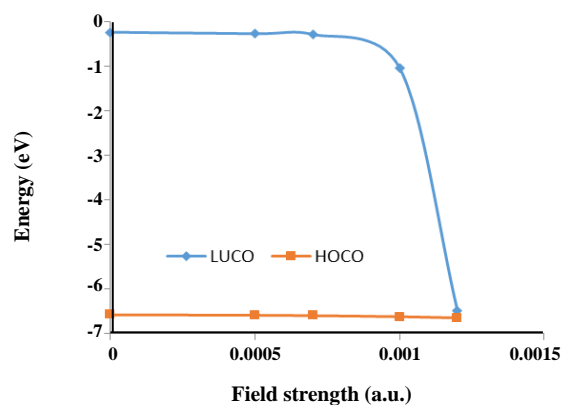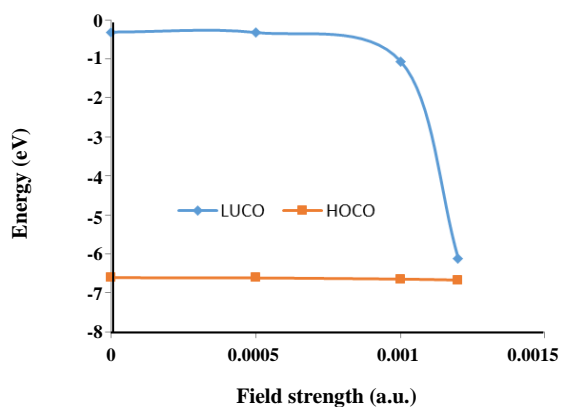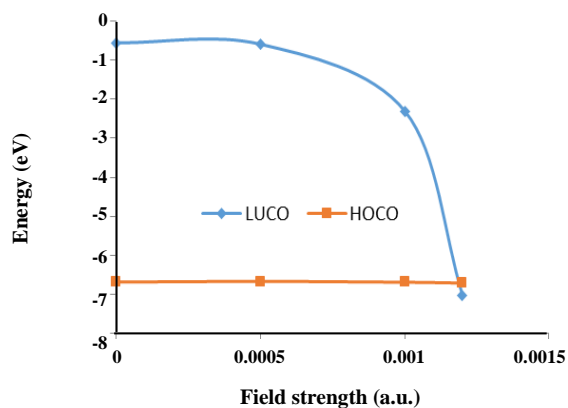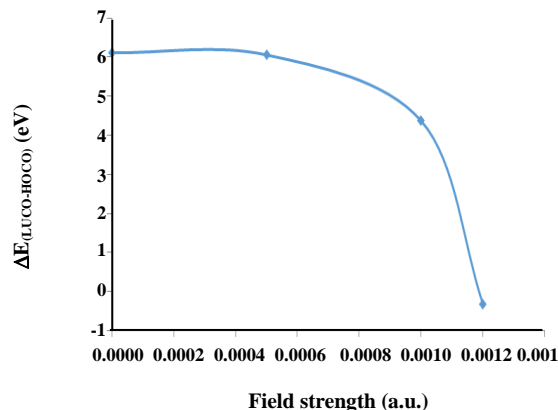
Fig. 8: Energy graph of the relative energy band gap as the difference in energy HOCO and LUCO (LUCO-HOCO) vs. external electric field in an armchair (4,4) single-walled BNNTs.

fields at the same level calculations were carried out. The local minimums second derivative of the total energy (harmonic frequencies) mentioned in the optimized computational level were studied and it was found that all structures are no imaginary frequency.

The linear relationships between isotropic chemical shielding with atomic charge and isotropic total atomic magnetizability in an armchair (4,4) SWBNNT without external electric field and in the presence of 0.0005, 0.0010 and 0.0012 a.u. external electric field are obtained. The obtained linear relationships between isotropic chemical shielding with an atomic charge for boron and nitrogen atoms are inverse each other. Also in this study is shown with increasing the chemical shielding, the total atomic magnetizability is reduced linearly. The inversely linear relationship between the magnetic shielding integration with magnetizability as presented in Equation 1, corresponds.

Also in this research, the relative energy (E_{rel}) and the relative differences in the energy band gap for HOCO and LUCO (LUCO-HOCO) in (4,4),(5,5) and (6,6) BNNTs with the PBC approach without the presence of an external electric field and in the presence of different external electric fields have been studied. According to the results obtained, the armchair (4,4), (5,5) and (6,6) BNNTs without the presence of an external electric field has a band gap (ΔE) about 6 electrons volts. The large LUMO-HOMO gap is often regarded as a molecule stability criterion. More sophisticated treatment of large gaps is seen to occur for systems with high relative

Fig. 7: Energy graph of HOCO and LUCO vs. external electric field in an armchair (a) (4,4),(b) (5,5) and (c) (6,6)single-walled BNNTs.

Table 2: The total energy (E_{tot}), the relative energy (E_{rel}), average electron localization (λ_m(Ω)) and average electron delocalization index (DI_m(Ω)) in nitrogen and boron atoms of armchair (4,4) single-walled BNNT in the presence of an external electric field.

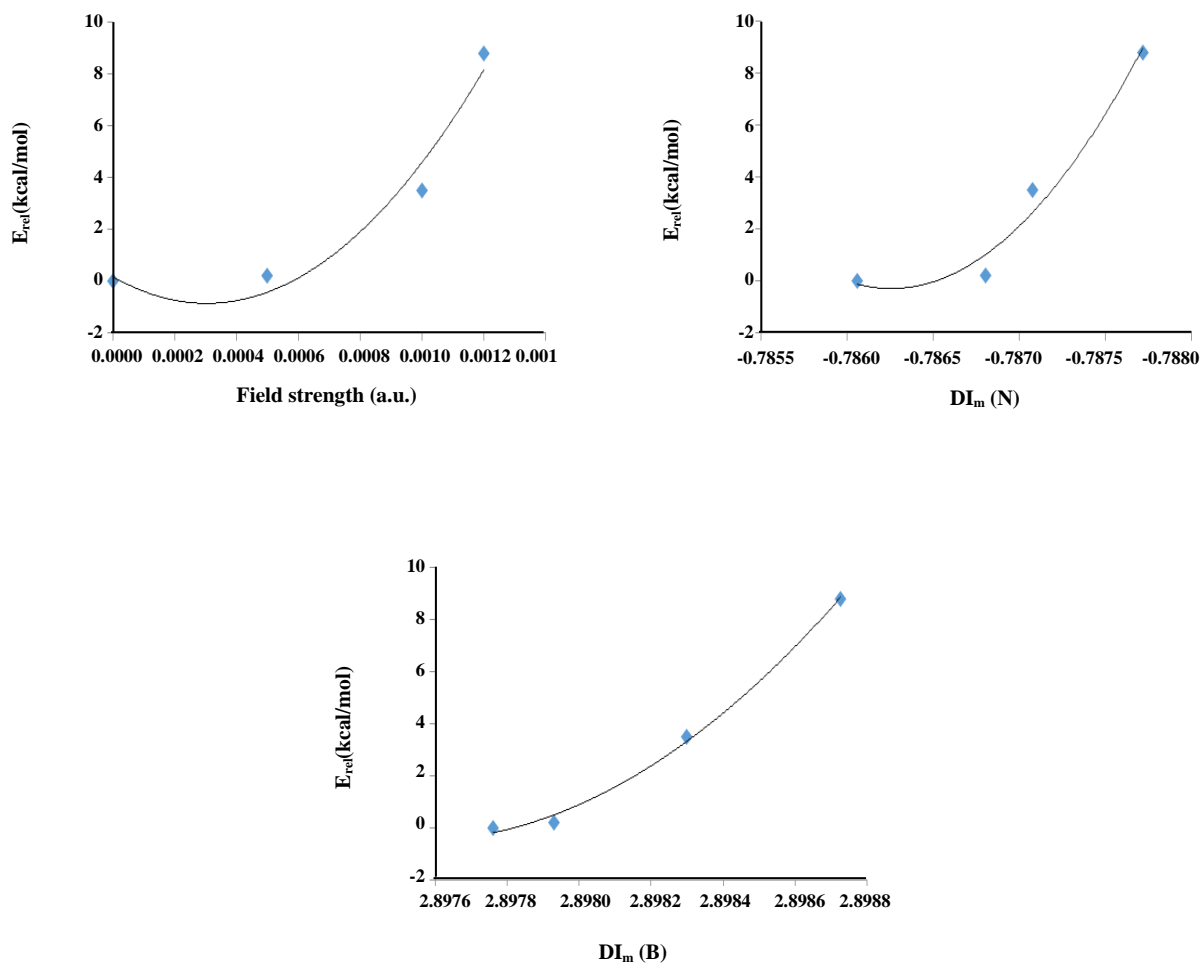| Compound	Field Strength (a.u.)	E_{tot} (a.u.)	E_{rel} (kcal/mol)	$\lambda_m(N)$	$DI_m(N)$	$\lambda_m(B)$	$DI_m(B)$
(4,4) BNNT	0.0000	-1275.53565	0.0	7.7861	-0.7861	2.1022	2.8978
	0.0005	-1275.53531	0.2	7.7868	-0.7868	2.1021	2.8979
	0.0010	-1275.53009	3.5	7.7871	-0.7871	2.1017	2.8983
	0.0012	-1275.52165	8.8	7.7877	-0.7877	2.1013	2.8987

Fig. 9: The relative energy (E_{rel}) against (a) external electric field (b) average electron delocalization index of nitrogen atoms (DI_m(N)) and (c) average electron delocalization index of boron atoms (DI_m(B)) in an armchair (4,4) single-walled BNNT.

stability [9, 17]. The obtained result is shown that with increasing the electric field to 0.0010 a.u., does not change HOCO and LUCO energy. But from 0.0010 a.u. to maximum electric field operable i.e. 0.0012 a.u., immediately LUCO energy is reduced to zero and LUCO-HOCO gap has done equal to zero and therefore BNNTs have done conductive. Also, the results show that increasing of BNNTs diameter has not a great effect on the usable electric field to conduct BNNTs and acting of them as semiconductor channels for nano-diodes and transistors. In this study with increasing of the external electric field, the relative energy of BNNT increases. This situation with reduced energy band gap in higher electric fields corresponds.
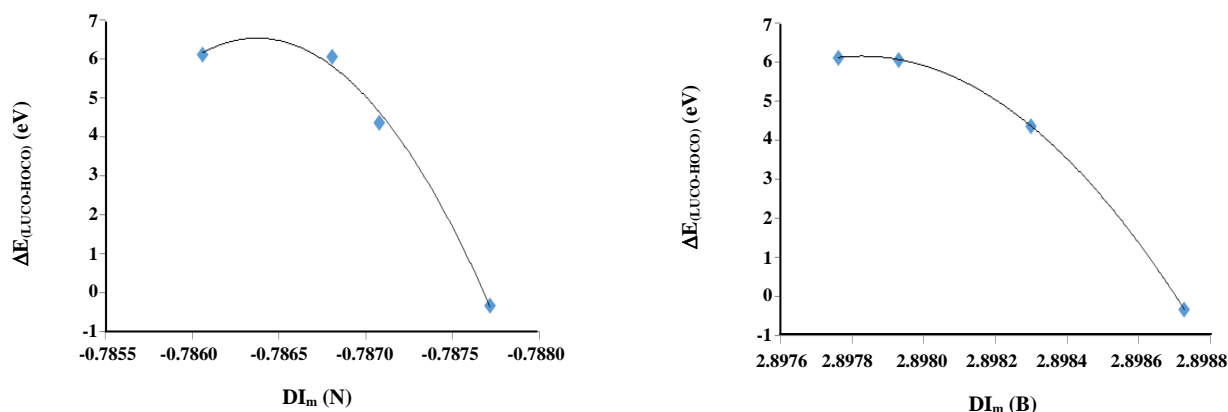
Fig. 10: The energy graph of band gap against (a) average electron delocalization index of nitrogen atoms ($DI_m(N)$) and (b) average electron delocalization index of boron atoms ($DI_m(B)$) in an armchair (4,4) single-walled BNNT.

On the other hand by increasing of average electron delocalization index of nitrogen atoms ($DI_m(N)$), the relative energy of BNNT is decreased, but on the contrary by increasing the average electron delocalization index of boron atoms ($DI_m(B)$), the relative energy increases. The results show that with the increasing of 0.0016 to average electron delocalization index of nitrogen atoms, the average electron delocalization index of boron atoms 0.0009 decreases. Therefore the increase of electron delocalization index of nitrogen atoms is more effective in reducing of relative energy. Also with increasing of average electron delocalization of nitrogen atoms ($DI_m(N)$), energy band gap of BNNT increased, but on the contrary the average electron delocalization of boron atoms ($DI_m(B)$) to reduce the energy gap. In this case, exactly the impact of electron delocalization on energy band gap (Fig. 10) as expected converses influence of electron delocalization on relative energy of BNNT.

Acknowledgments:

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