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## Electronic and Optical Properties of the Graphene and Boron Nitride Nanoribbons in Presence of the Electric Field

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**Abstract:** In this study, using density functional theory and the SIESTA computational code, we investigate the electronic and optical properties of the armchair graphene nanoribbons and the armchair boron nitride nanoribbons of width 25 in the presence of a transverse external electric field. We have observed that in the absence of the electric field, these structures are semiconductors with a direct energy band gap at  $\Gamma$  point and applying electric field on them causes to change in the band structure, decreasing the band gap and even eliminating the band gap. Increasing the intensity of the applying field on the graphene nanoribbons reduces the distance between the maximum of the highest valence band and the minimum of the lowest conduction band and shifts the convergence of these two bands in K space from the  $\Gamma$  point to the X point. The energy band gap of the boron nitride nanoribbons also has been decreased from 4.46 eV to less than 32.6 meV in presence of a transverse electric field of intensity about 0.30 V/Ang and a semiconductor-metal transition was observed in the presence of the stronger fields.

Next, we investigate the effect of the transverse electric field on the optical properties of both nanoribbons. Of course, in order to study the optical behavior of these systems, we apply only a radiation with the parallel polarization. According to the changes that the electric field makes on the band structure, we observed changes in the location and intensity of the optical graphs peaks. Also with increasing the intensity of the field, we observe a significant increase in the static dielectric constant and the plasmonic behavior of these structures.

**Keywords:** Boron Nitride, Energy Gap, Graphene, Nanoribbons, Optical Properties.

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## 1. INTRODUCTION

When graphene be confined to one dimension, a finite energy band gap appears in its electronic band structure. The resulting structure is called nanoribbon and the value of its energy band gap is depending on the width and chirality of nanoribbon [1, 2]. Similar to graphene, the boron nitride nanoribbons may be formed by cutting the hexagonal sheets or unrolling the nanotubes [3].

The chirality of the nanoribbons depends on the shape of their edges and accordingly they are classified into armchair and zigzag types. The width of the nanoribbons is also specified by the number  $N$  which is number of the zigzag chains or number of the dimer lines in the zigzag or armchair type, respectively. The atoms at the edges of the nanoribbons can be passivated by chemical bonding with the hydrogen atoms. For this purpose, all the carbon atoms on the edges of the graphene nanoribbons are usually attached to the hydrogen atoms [4]. But in the boron nitride nanoribbons, usually only the boron atoms, the nitrogen atoms, or both atoms on the edges are passivated in this way [5].

The investigation of the graphene nanoribbons shows that their armchair types are metallic or semiconductor and the zigzag types are metallic in nature [2, 6].

Also, by changing the width of the semiconductor armchair graphene nanoribbons, the energy band gap exhibits an oscillating behavior [7]. Accordingly, they are classified into three:  $\alpha$ ,  $\beta$  and  $\gamma$  which their width are  $N=5, 8, 11, \dots$ ,  $N=3, 6, 9, \dots$  and  $N=4, 7, 10, \dots$  respectively [2]. The  $\alpha$ -type graphene nanoribbons are metallic and the  $\beta$  and  $\gamma$ -types are semiconductor [8]. Regardless of their chirality and width, the boron nitride nanoribbons are also semiconductor [9-11]. The energy band gap for the zigzag boron nitride nanoribbons, decreases uniformly with increasing the width of nanoribbons and for the armchair type, it exhibits an oscillating behavior [12, 13].

The ability to change and tune the energy band gap of the semiconductor nanoribbons, which is very important in the development of their application, is achieved in various ways such as bending, stretching, doping and applying a transverse electric field [13-22]. However, the use of the electric field is more important and applicable than other methods in tuning the energy band gap. The band structure and the effect of a transverse electric field on it for the  $\beta$  and  $\gamma$  semiconductor graphene armchair nanoribbons have been investigated and elimination of their energy band gap was observed in the presence of a field of intensity  $0.1 \text{ V/\AA}$  [2]. By applying a transverse electric field, The band gap of the zigzag or armchair BN nanoribbons can be reduced and even be closed at a critical field that decreases with increasing ribbon width [20].

Since the energy band gap of the structure undergoes a shift from a finite value to zero in presence of an electric field, which corresponds to the frequency range from ultraviolet to visible, so studying the optical excitations in the electronic structure investigation of these materials is very important. Therefore,

studies have also been conducted focusing on the effect of external electric field on the optical properties of nanoribbons [23-26]. For example, it has been shown that applying the electric field changes feature of the optical absorption graph of graphene nanoribbons [23]. Also utilizing the tight-binding model, the optical properties of zigzag and armchair BN nanoribbons has been studied in presence of the electric field [24].

In light of this introduction, we have investigated the electronic properties of armchair graphene nanoribbons and armchair BN nanoribbons in presence of a transverse external electric field. The widths of these nanoribbons are  $N = 25$  and we have named them AGNR-25 and ABNNR-25 respectively, each of which contains 54 atoms. We have also investigated the effect of the field on the optical behavior of these nanoribbons.

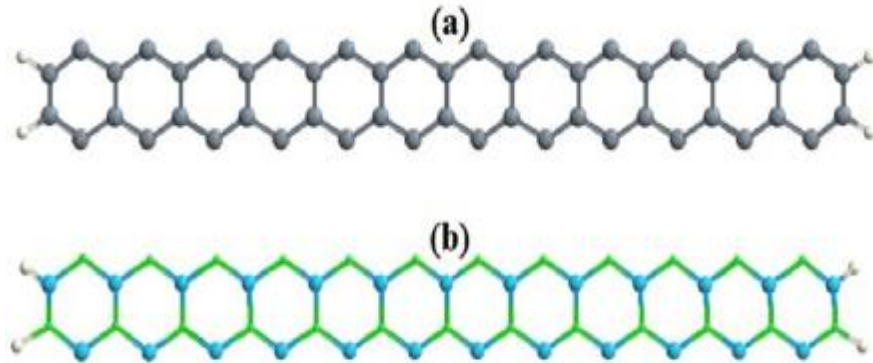
The effect of the electric field on the band gap reduction for  $\beta$  and  $\gamma$  nanoribbons increases with increasing the nanoribbons width, so that weaker fields are needed to close the band gap in wider nanoribbons [2]. That's why we've chosen relatively wide ( $N=25$ ) nanoribbons for study.

The order is that the details of calculations are presented in the first section and in the second part, we analyze the results. Also, the final conclusions have been presented in the end section.

## 2. METHOD AND DETAILS OF CALCULATION

The calculations have been performed using the SIESTA computational code [27]. The Correlation-Exchange Energies have been calculated with (LDA) approximation and the (DZP) base set is used. The nanoribbons are extended along the x-axis and the external electric field is applied in the positive direction of the y-axis. To avoid interactions between adjacent nanoribbons, a vacuum distance of  $10\text{\AA}$  along the z axis is considered. The value of the plane-wave cutoff was considered 450Ry and number of the optimal K points for calculation of the electronic properties was also taken into account equal to  $30 \times 1 \times 1$ . Both structures are so relaxed that the residual forces are less than  $0.01\text{eV/\AA}$ . Of course, relaxation is done only in absence of the electric field.

In the study of the optical properties of these structures, the electric field of radiation has the perpendicular polarization. The optical mesh and the optical broaden are considered  $90 \times 1 \times 1$  and 0.025 respectively. Also, the bond lengths were considered for the AGNR-25 nanoribbons equal to  $1.42\text{\AA}$  [6], and for the ABNNR-25 nanoribbons equal to  $1.44\text{\AA}$  [28]. The images of both structures are presented in Fig. 1.



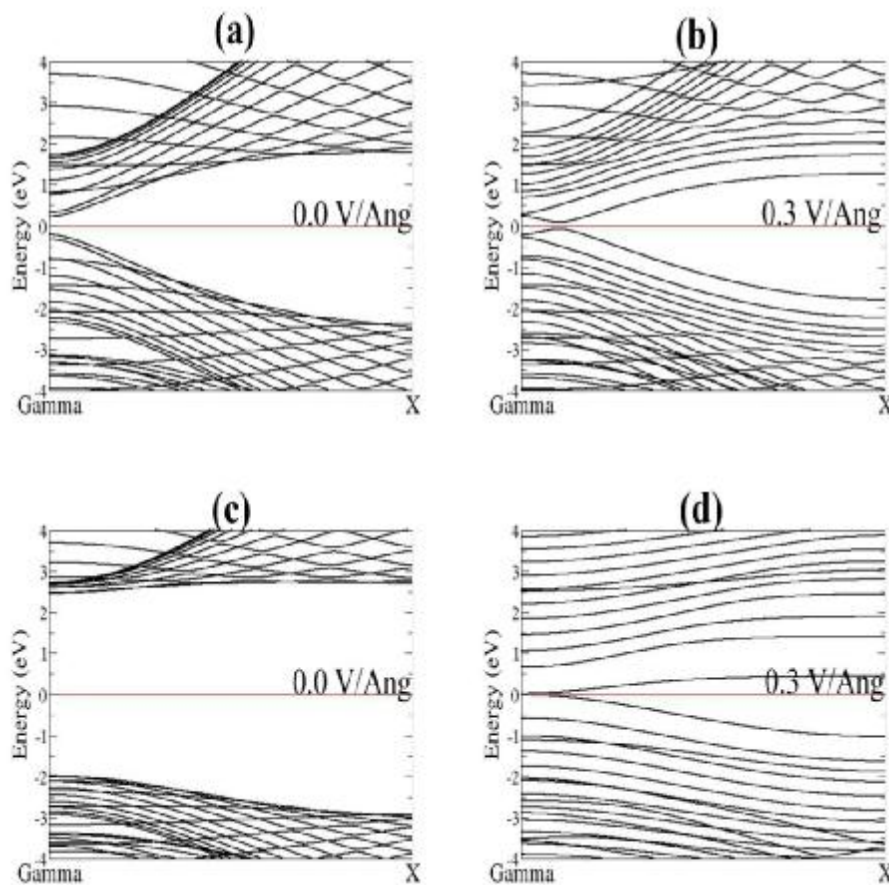
**Fig. 1.** (a): AGNR-25 structure, (b): ABNNR-25 structure.

### 3. RESULTS

#### 3.1 Electronic Properties

The band structure of AGNR-25 and ABNNR-25 in absence and presence of the transverse electric field is presented in Fig. 2. According to Fig. 2(a) and 2(c) in absence of electric field both structures appear as semiconductors with direct energy band gap at the  $\Gamma$  point [29]. We calculated the energy band gap for AGNR-25 equal to 0.4398 eV and for ABNNR-25 equal to 4.457 eV [2]. According to Fig. 2(b) and 2(d), it is observed that applying and increasing the intensity of the field cause to change in the energy dispersion, increase the interband distance and decrease the energy band gap of both structures. Therefore, the band gap of AGNR-25 reduces to 0.1544 eV in presence a field of intensity 0.3 V/Ång.

In Fig. 2 (b), increasing the intensity of the field cause to reduce the distance between the maximum of the highest valence band and the minimum of the lowest conduction band of AGNR-25 and moves converges of two bands in  $K$  space from  $\Gamma$  point to the  $X$  point. Applying of electric field causes to increase the distance between the bands, especially in the vicinity of the Fermi level [30].

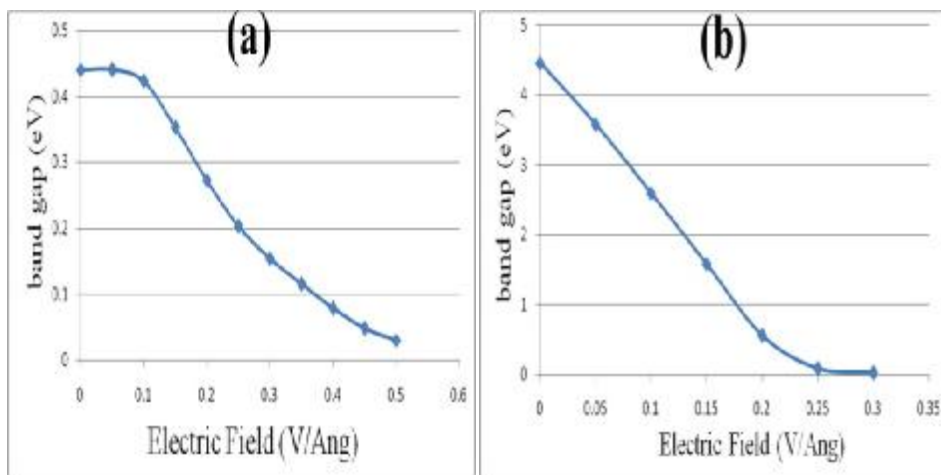


**Fig. 2.** (a), (b): band structure of AGNR-25 and (c), (d): the ABNNR-25 in absence and in presence of a field of intensity 0.3 V/Ang.

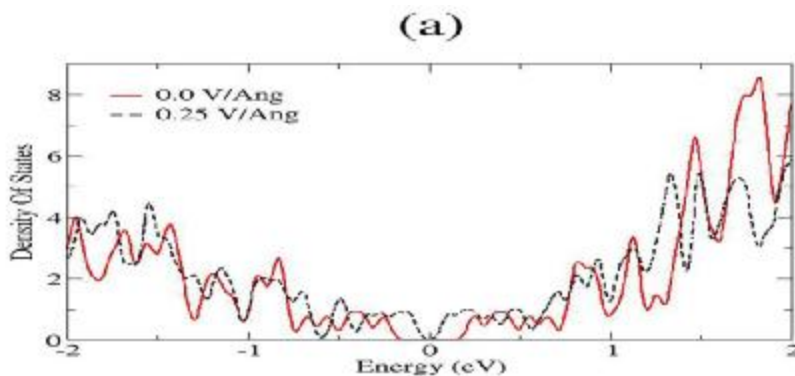
In the ABNNR-25 nanoribbons, HOMO, which contain the  $\pi$  states, are distributed upon N atoms and LUMO, which contain the  $\pi^*$  states, are distributed upon B atoms. Applying a field on the structure causes the electric potential felt by the electrons to be different at two different ends of the nanoribbon, then HOMO tend to edge where its potential is increased and LUMO also tend to edge where its potential is decreased [20].

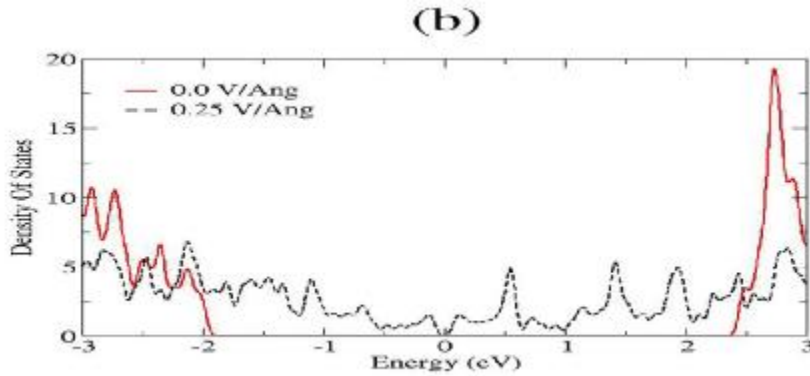
Thus, according to Fig. 2(d), the energy band gap of the structure is reduced from 4.457 eV in absence of the field to less than 32.6 meV in presence of a field of intensity 0.30 V/Ang. **Increasing the intensity of field to above this value will result in a metal-semiconductor transition.**

The graph of the energy band gap value with respect to the field intensity for AGNR-25 and ABNNR-25 are also presented in Fig. 3(a) and 3(b), respectively. As we can see in Fig. 3(a) for the AGNR-25 structure, by increasing the intensity of the field, the value of the energy band gap was increased a small amount about 0.6 meV firstly, then exponentially decreased to zero. In Fig. 3(b) for the ABNNR-25 structure, we also see a linear decrease in the value of the energy band gap with increasing electric field intensity [29].



**Fig. 3.** graph of the energy band gap value with respect to the field intensity for (a): AGNR-25 and (b): ABNNR-25.





**Fig. 4.** Density of states for (a): AGNR-25 nanoribbons and (b): ABNRR-25 nanoribbons in absence and in presence of the electric field.

The densities of states (DOS) in absence and in presence of an electric field with intensity 0.2 V/Ang are separately illustrated for each of the structures in Fig. 4. The positions of the peaks appearing in the DOS graph are related to the energy of the band edge states and the intensity of these peaks is also related to the inverse of the second root of the curvature of the bands.

In the graph of the density of states for AGNR-25, Fig. 4(a), two adjacent peaks of the Fermi energy which appear in absence of the electric field around the energies -0.2493 eV and 0.2493 eV, after applying an electric field of intensity 0.2 V/Ang appear with some displacement at -0.1652 eV and 0.1171 eV. The intensity of the peaks also increases slightly. These changes can be justified by the edge shape of the adjacent bands of the Fermi level in absence and presence of the field. In the graph of the density of states for ABNRR-25, Fig. 4(b), the most noticeable effect of the field is to close the large band gap of this structure. Also, the changes caused by the field in the curvature and energy of the edges of bands has resulted in the displacement of the peaks of DOS and changing their intensity. two adjacent peaks of the Fermi energy which appear in absence of the field around the energies -2.123 eV and 2.495 eV, after applying an electric field of intensity 0.2 V/Ang appear with some displacement around the energies -0.1231 eV and 0.1291 eV.

### 3.2 Optical Properties

In the following, we investigate the optical behavior of the desired nanoribbons. For this purpose, we applied a radiation with parallel polarization whose electric field vector is parallel to the positive direction of the x axis. We investigate the dielectric function and optical absorption coefficient of these structures in absence and in presence of the transverse electric field. The dielectric function

contains useful optical information about the system and includes two real and imaginary parts:

$$\varepsilon(\omega) = \varepsilon_{re}(\omega) + i\varepsilon_{im}(\omega) \quad (1)$$

The imaginary part of the dielectric function,  $\varepsilon_{im}$ , can be defined using momentum matrix elements at the base of the occupied and unoccupied wave functions [31]:

$$e_{im}^{aa}(\omega) = \frac{4p^2}{\Omega\omega^2} \sum_{i \in VB} \sum_{k \in CB} \omega_k |P_{ij}^a|^2 d(\hat{\mathbf{q}}_{kj} - \hat{\mathbf{q}}_{ki} - \omega) \quad (2)$$

The real part of the dielectric function,  $\varepsilon_{re}$ , is also obtained by means of the Kramers–Kronig relation as follows [31]:

$$e_{re}(\omega) = 1 + \frac{4}{p} P \int_0^{\infty} d\omega' \frac{\omega' e_{im}(\omega')}{\omega'^2 - \omega^2} \quad (3)$$

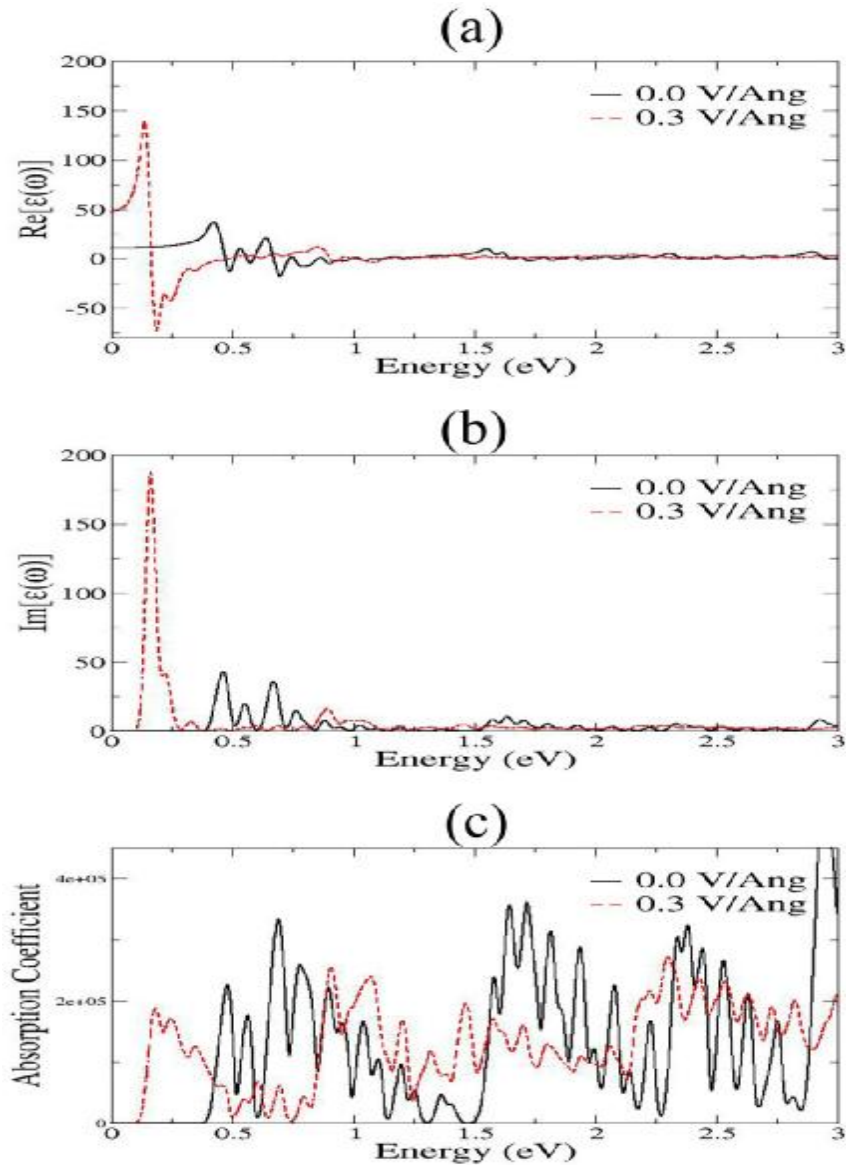
According to the Beer-Lambert law, the intensity of the incident ray in the environment is exponentially attenuated. The absorption coefficient is the distance which by going it, the intensity of radiation reaches to  $e^{-1}$  times its initial value [32]:

$$a = \left( \frac{\sqrt{2}\omega}{c} \right) \frac{e_{im}}{\sqrt{e_{re} + \sqrt{e_{re}^2 + e_{im}^2}}} \quad (4)$$

The graph of the real and imaginary parts of the dielectric function as well as the optical absorption coefficient for the AGNR-25 nanoribbons is presented in Fig. 5. First, in Fig. 5(a), we describe the graph for AGNR-25. The static dielectric function for this structure,  $\varepsilon_{re}(\omega=0)$ , is equal to 11.01. The first peak of the graph also appeared at 0.4225 eV and a negative peak is visible at 0.4875 eV. The value of  $\varepsilon_{re}$  function is zero at the energies 0.4713 eV and 0.5132 eV, and at interval 0.4713 eV < E < 0.5132 eV is negative. It is worth mentioning that at energies in which  $\varepsilon_{re}$  function are negative, the waves are not emitted and we will see the absorption and loss of radiation. The zeroes of the  $\varepsilon_{re}$  function are also associated with the plasmonic excitations of the system [33].

In presence of a field of intensity 0.3 V/Å, the first peak shifts to the lower energy 0.1375 eV and its intensity also increases significantly. Also, the first negative peak shifts to energy 0.1875 eV.





**Fig. 5:** graph of (a): The real part of the dielectric function, (b): The imaginary part of the dielectric function, and (c): Optical absorption coefficient for AGNR-25 structure in absence and presence of the electric field.

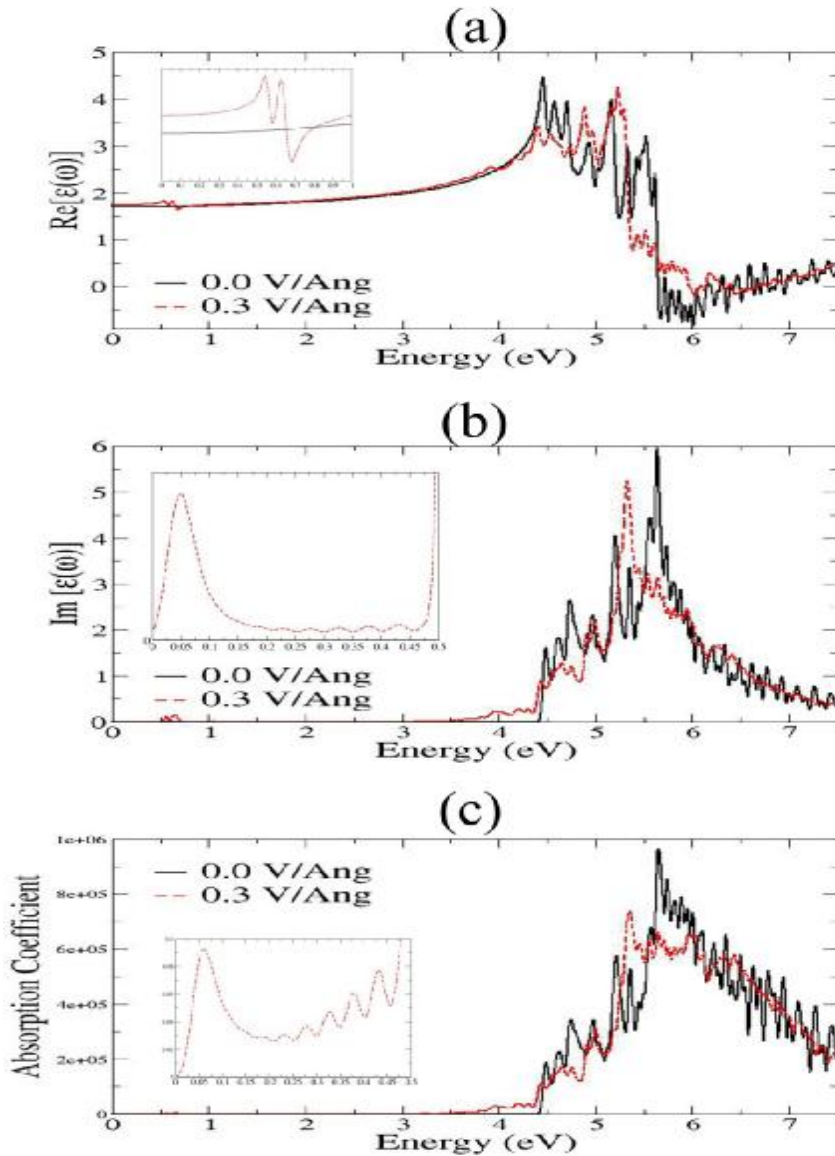
In presence of this electric field, the static dielectric function is enhanced to 47.75 and the energy interval in which the function is negative, also changes to  $0.1681 \text{ eV} < E < 0.4929 \text{ eV}$ .

According to Fig. 5(b), it can be seen that the first and second peaks of  $\epsilon_{im}$  graph in absence of the electric field appear at 0.465 eV and 0.5525 eV respectively.

As a consequence of the decrease of the energy band gap, in presence of the field the first peak shifts to the lower energy 0.165 eV. The intensity of this peak is also increased. The second peak has a red shift too, and appears at energy 0.33 eV, but its intensity decreases. Due to the presence of the field, the distance between the two peaks has increased.

According to Fig. 5(c), the first and second peaks of  $\alpha$  graph in absence of the field appear at 0.4825 eV and 0.5625 eV respectively. The location of the first peak of this graph named optical gap literally. As shown in the diagram, the absorption value is relatively high in the interval of 0.5 eV to 1.0 eV. By applying the field and decreasing the band gap, the first two peaks of this graph are shifted to lower energies 0.1825 eV and 0.2475 eV. The intensity of the first peak is also slightly reduced. In the presence of the field, the distance between the first two peaks decreases and, the absorption value increases relatively from 0.1 V to 0.4 V.

The optical graphs of the ABNNR-25 nanoribbons are presented in Fig. 6. According to Fig. 6(a), the static dielectric function for this structure is equal to 1.706. The first peak of the graph also appears at 4.463 eV and a negative peak is visible at 5.672 eV. The value of  $\epsilon_{re}$  function is zero at the energies 5.649 eV and 5.968 eV, and at interval 5.649 eV  $<E<5.968$  eV is negative. In presence of the field, the first peak shifts to the lower energy 0.5425 eV and its intensity is greatly reduced. Also, the first negative peak shifts to energy 6.032 eV. The static dielectric function is enhanced to 1.746 and the energy interval in which the function is negative, also changes to 5.707 eV  $<E<6.080$  eV.



**Fig. 6:** graph of (a): The real part of the dielectric function, (b): The imaginary part of the dielectric function, and (c): Optical absorption coefficient for ABNNR-25 structure in absence and presence of the electric field.

According to Fig. 6(b), it can be seen that the first and second peaks of  $\epsilon_{im}$  graph in absence of the electric field appear at 4.488 eV and 4.62 eV respectively.

In presence of the field, the first peak shifts to the lower energy 0.05 eV. The intensity of this peak is also increased significantly. The second peak has a red shift too, and appears at energy 0.565 eV. Due to the presence of the field, the distance between the two peaks has increased.

According to Fig. 5(c), the first and second peaks of  $\alpha$  graph in absence of the field appear at 4.49 eV and 4.628 eV respectively. By applying the electric field, the first two peaks of this graph are shifted to lower energies 0.06 eV and 0.1875 eV. The intensity of the first peak is also significantly reduced. Also, In the presence of the field, the distance between the first two peaks decreases.

#### 4. CONCLUSION

In this study, we investigate the electronic and optical behavior of AGNR-25 and ABNNR-25 nanoribbons in presence of an electric field by using density functional theory. If the electric field intensity is large enough, the band gap is almost completely removed. These critical field intensities are 0.5 V/Ang and 0.3 V/Ang for AGNR-25 and ABNNR-25 respectively. Because of the electric field applying, the convergence point of the highest valence band and the lowest conduction band is shifted from  $\Gamma$  point to X point for the AGNR-25. For the ABNNR-25, the semiconductor-metal transition was achieved in the presence of field of intensity 0.3 V/Ang. Increasing the field intensity on the AGNR-25 significantly increased the static dielectric function. But, the presence of the field causes a slight increase in the static dielectric function of the ABNNR-25. Optical band gaps of both system also have undergo a red shift due to the field presence. Finally, displacement of the zeroes of  $\epsilon_{re}$  indicates that the plasmonic behavior of these systems is affected by the electric field. This gap modulation and the resulting changes in the electronic and optical properties promise potential applications in future electronic and optical devices.

#### REFERENCES

- [1] X. Li, X. Wang, L. Zhang, S. Lee, and H. Dai, *Chemically derived, ultrasmooth graphene nanoribbon semiconductors*, science, 319, (2008) 1229-1232.
- [2] H. Raza, and E. C. Kan, *Armchair graphene nanoribbons: Electronic structure and electric-field modulation*, Physical Review B, 77, (2008) 245434.
- [3] H. Zeng, C. Zhi, Z. Zhang, X. Wei, X. Wang, W. Guo, Y. Bando, and D. Golberg, "White graphenes": boron nitride nanoribbons via boron nitride nanotube unwrapping, Nano letters, 10, (2010) 5049-5055.

- [4] Y. Lu, R. Wu, L. Shen, M. Yang, Z. Sha, Y. Cai, P. He, and Y. Feng, *Effects of edge passivation by hydrogen on electronic structure of armchair graphene nanoribbon and band gap engineering*, Applied Physics Letters, 94, (2009) 122111.
- [5] F. Zheng, K.-i. Sasaki, R. Saito, W. Duan, and B.-L. Gu, *Edge states of zigzag boron nitride nanoribbons*, Journal of the Physical Society of Japan, 78, (2009) 074713.
- [6] N. Wang, G. Zhao, X. Liang, and T. Song, "First-principle Studies of armchair graphene nanoribbons." p. 012170.
- [7] F. Ma, Z. Guo, K. Xu, and P. K. Chu, *First-principle study of energy band structure of armchair graphene nanoribbons*, Solid state communications, 152, (2012) 1089-1093.
- [8] S. Behzad, *Thermal properties of biased bilayer graphene and boron nitride nanoribbons*, Physica E: Low-dimensional Systems and Nanostructures, 103, (2018) 338-347.
- [9] M. Topsakal, E. Aktürk, and S. Ciraci, *First-principles study of two- and one-dimensional honeycomb structures of boron nitride*, Physical Review B, 79, (2009) 115442.
- [10] W. Chen, Y. Li, G. Yu, Z. Zhou, and Z. Chen, *Electronic structure and reactivity of boron nitride nanoribbons with stone-wales defects*, Journal of chemical theory and computation, 5, (2009) 3088-3095.
- [11] Y. Wang, Y. Ding, and J. Ni, *Electronic structures of Fe-terminated armchair boron nitride nanoribbons*, Applied Physics Letters, 99, (2011) 053123.
- [12] J. Nakamura, T. Nitta, and A. Natori, *Electronic and magnetic properties of BNC ribbons*, Physical Review B, 72, (2005) 205429.
- [13] A. Du, S. C. Smith, and G. Lu, *First-principle studies of electronic structure and C-doping effect in boron nitride nanoribbon*, Chemical Physics Letters, 447, (2007) 181-186.
- [14] S.-L. Chang, B.-R. Wu, P.-H. Yang, and M.-F. Lin, *Curvature effects on electronic properties of armchair graphene nanoribbons without passivation*, Physical Chemistry Chemical Physics, 14, (2012) 16409-16414.
- [15] S. Jalili, and R. Vaziri, *Curvature effect on the electronic properties of BN nanoribbons*, Molecular Physics, 108, (2010) 3365-3371.

- [16] Y. Lu, and J. Guo, *Band gap of strained graphene nanoribbons*, Nano Research, 3, (2010) 189-199.
- [17] L. Jin, S. Li-Zhong, and Z. Jian-Xin, *Strain effects on electronic properties of boron nitride nanoribbons*, Chinese Physics Letters, 27, (2010) 077101.
- [18] Z. Wang, J. Xiao, and X. Li, *Effects of heteroatom (boron or nitrogen) substitutional doping on the electronic properties of graphene nanoribbons*, Solid state communications, 152, (2012) 64-67.
- [19] T. Nomura, D. Yamamoto, and S. Kurihara, "Electric field effects in zigzag edged graphene nanoribbons." p. 062015.
- [20] Z. Zhang, and W. Guo, *Energy-gap modulation of BN ribbons by transverse electric fields: first-principles calculations*, Physical Review B, 77, (2008) 075403.
- [21] D. Novikov, *Transverse field effect in graphene ribbons*, Physical review letters, 99, (2007) 056802.
- [22] F. Zheng, Z. Liu, J. Wu, W. Duan, and B.-L. Gu, *Scaling law of the giant Stark effect in boron nitride nanoribbons and nanotubes*, Physical Review B, 78, (2008) 085423.
- [23] R. Alaei, and M. Sheikhi, *Optical absorption of graphene nanoribbon in transverse and modulated longitudinal electric field*, Fullerenes, Nanotubes and Carbon Nanostructures, 21, (2013) 183-197.
- [24] F.-L. Shyu, *Electronic and optical properties of boron nitride nanoribbons in electric field by the tight-binding model*, Physica B: Condensed Matter, 452, (2014) 7-12.
- [25] C.-P. Chang, Y.-C. Huang, C. Lu, J.-H. Ho, T.-S. Li, and M.-F. Lin, *Electronic and optical properties of a nanographite ribbon in an electric field*, Carbon, 44, (2006) 508-515.
- [26] H.-C. Chung, C.-P. Chang, C.-Y. Lin, and M.-F. Lin, *Electronic and optical properties of graphene nanoribbons in external fields*, Physical Chemistry Chemical Physics, 18, (2016) 7573-7616.
- [27] J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal, *The SIESTA method for ab initio order-N materials simulation*, Journal of Physics: Condensed Matter, 14, (2002) 2745.
- [28] L. H. Li, and Y. Chen, *Atomically thin boron nitride: unique properties and applications*, Advanced Functional Materials, 26, (2016) 2594-2608.
- [29] C.-H. Park, and S. G. Louie, *Energy gaps and stark effect in boron nitride nanoribbons*, Nano letters, 8, (2008) 2200-2203.

- [30]R. Chegel, and S. Behzad, *Theoretical study of the influence of the electric field on the electronic properties of armchair boron nitride nanoribbon*, Physica E: Low-dimensional Systems and Nanostructures, 64, (2014) 158-164.
- [31]G. Guo, K. Chu, D.-s. Wang, and C.-g. Duan, *Linear and nonlinear optical properties of carbon nanotubes from first-principles calculations*, Physical Review B, 69, (2004) 205416.
- [32]N. Peyghambarian, S. W. Koch, and A. Mysyrowicz, *Introduction to semiconductor optics*, 1993.
- [33]J. D. Sharma, M. Sharma, N. Kumar, and P. Ahluwalia, *Computational study of dielectric function and optical properties of a graphane nano structure containing graphene quantum dot*.p. 012010.

