Electronic Properties of Graphene Nanoribbons Coupled with Organic Molecules

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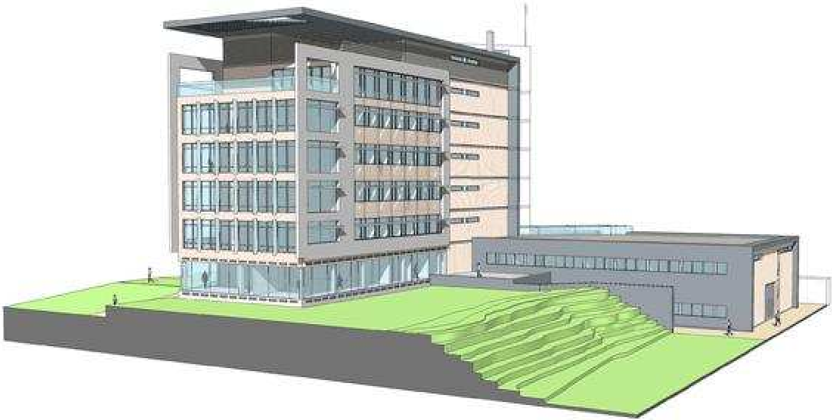


Current works

1. Scarpa, F., Adhikari, S. and Gil, A. J., ”The bending of single layer graphene sheets: Lattice versus continuum approach”, Nanotechnology, accepted.
2. Chowdhury, R., Wang, C. Y. and Adhikari, S., ”Low-frequency vibration of multiwall carbon nanotubes with heterogeneous boundaries”, Journal of Physics D: Applied Physics, accepted.
3. Chowdhury, R., Rees, P., Adhikari, S., Scarpa, F., and Wilks, S.P., ”Density functional simulations of silicon doped ZnO”, Physica B: Condensed Matter, accepted.
4. Scarpa, F., Adhikari, S. and Wang, C. Y., ”Nanocomposites with auxetic nanotubes”, International Journal of Smart and Nanomaterials, accepted.
5. Chowdhury, R., Adhikari, S. and Mitchell, J., ”Vibrating carbon nanotube based bio-sensors”, Physica E: Low-dimensional Systems and Nanostructures, 42[2] (2009), pp. 104-109.
6. Scarpa, F., Adhikari, S. and Wang, C. Y., ”Mechanical properties of non reconstructed defective single wall carbon nanotubes”, Journal of Physics D: Applied Physics, 42 (2009) 142002 (6pp).
7. Scarpa, F., Adhikari, S. and Phani, A. Srikanth, ”Auxeticity in single layer graphene sheets”, International Journal of Novel Materials, accepted.
8. Wang, C. Y., Li, C. F., and Adhikari, S., ”Dynamic behaviors of microtubules in cytosol”, Journal of Biomechanics, 42[9] (2009), pp. 1270-1274.
9. Tong, F. M., Wang, C. Y., and Adhikari, S., ”Axial buckling of multiwall carbon nanotubes with heterogeneous boundary conditions”, Journal of Applied Physics, 105 (2009), pp. 094325:1-7.
10. Scarpa, F., Adhikari, S. and Phani, A. Srikanth, ”Effective mechanical properties of single graphene sheets”, Nanotechnology, 20[1-2] (2009), pp. 065709:1-11.
11. Scarpa, F. and Adhikari, S., ”Uncertainty modelling of carbon nanotube terahertz oscillators”, Journal of Non-Crystalline Solids, 354[35-39] (2008), pp. 4151-4156.
12. Scarpa, F. and Adhikari, S., ”A mechanical equivalence for the Poisson’s ratio and thickness of C-C bonds in single wall carbon nanotubes”, Journal of Physics D: Applied Physics, 41 (2008) 085306 (5pp).

Outline of the present talk

1. **Introduction**
   - Bio-nano sensors
   - Graphene Nanostructure
2. **CNT based mass sensor**
3. **Computational methodology for Graphene**
4. **Energy states of system**
   - Graphene ribbons: Two probe system
   - Coupled system: Two probe system
5. **Transmission spectrum of System**
   - Graphene ribbons
   - Coupled System
6. **Summary**

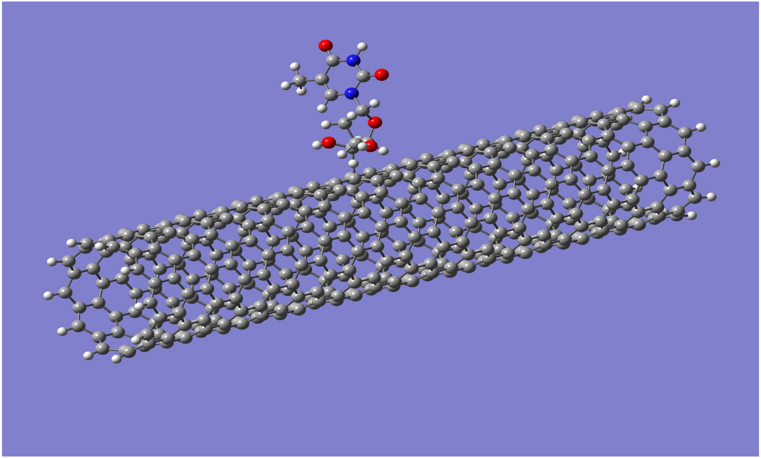
Bio-nano sensors

- Several approaches have been proposed for bio nano sensors.
- The development of nano-bio sensors has been driven by the experimental evidence that biological entities such as proteins, enzymes, bacteria can be immobilized either in the hollow cavity or on the surface of carbon nanotubes and Graphene sheets (GRs). Significant attempts are being made for the use of CNTs & GRs as superior biosensor materials in the light of successful fabrication of various electroanalytical nano devices, modified by external biological agents.
- These devices have shown promising sensitivities required for such applications as antigen recognition, enzyme-catalyzed reactions, and DNA hybridizations.
- In this talk two approaches, namely a carbon nanotube based approach and a graphene based approach will be discussed.

Graphene Nanostructure

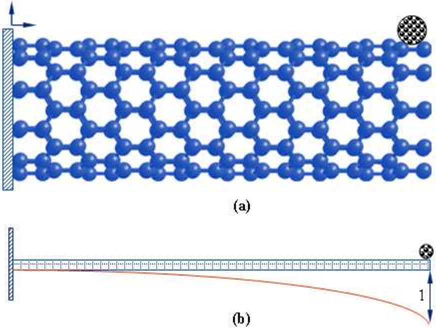
- Scanning probe microscopy of graphene ribbons revealed bright stripes along its edges, suggesting a large density of states at edge near Fermi level.
- The electronic properties of graphene nanoribbons (GNRs) are defined by their quasi-one-dimensional electronic confinement and the shape of the ribbon ends.
- This indicates remarkable applications in graphene-based devices. However, due to their planner structure, some of the properties seem to be easier to manipulate than carbon nanotubes.
- In particular, different quantization rules have been predicted for pure graphene ribbons with zigzag (ZGNRs) and armchair (AGNRs) edge-shaped.

CNT with bio-molecule



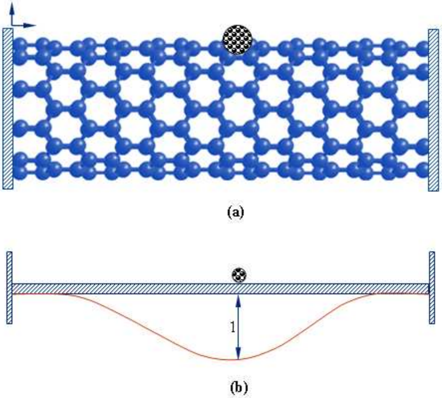
CNT (10,0) with attached bio molecule (DeOxy Thymidine with Free Residue).

Cantilevered nanotube resonator



Cantilevered nanotube resonator with an attached mass at the tip of nanotube length: (a) Original configuration; (b) Mathematical idealization. Unit deflection under the mass is considered for the calculation of kinetic energy of the nanotube.

Bridged nanotube resonator



Bridged nanotube resonator with an attached mass at the center of nanotube length: (a) Original configuration; (b) Mathematical idealization. Unit deflection under the mass is considered for the calculation of kinetic energy of the nanotube.

Sensor equations

- After some algebra (Physica E, 2009) The value of the added mass can be obtained as

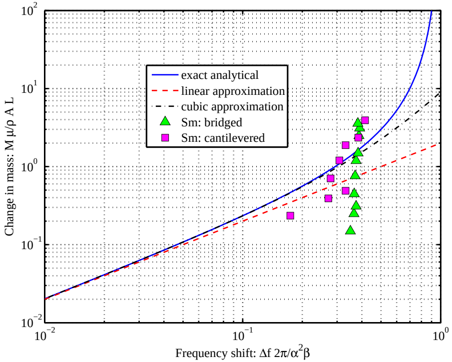
$$M = \frac{\rho A L}{\mu} \frac{\left(\alpha^2 \beta\right)^2}{\left(\alpha^2 \beta - 2\pi \Delta f\right)^2} - \frac{\rho A L}{\mu} \tag{1}$$

  This is in general a nonlinear relationship.
- Using the linear approximation, the value of the added mass can be obtained as

$$M \approx \frac{\rho A L}{\mu} \frac{2\pi \Delta f}{\alpha^2 \beta} \tag{2}$$

- The nondimensional constant α depends on the boundary conditions and μ depends on the location of the mass. For a cantilevered SWCNT with a tip mass $\alpha^2 = \sqrt{140/11} = 3.5675$, $\mu = 140/33 = 4.2424$ and for a bridged SWCNT with a mass at the midpoint $\alpha^2 = \sqrt{6720/13} = 22.7359$, $\mu = 35/13 = 2.6923$.

Validation

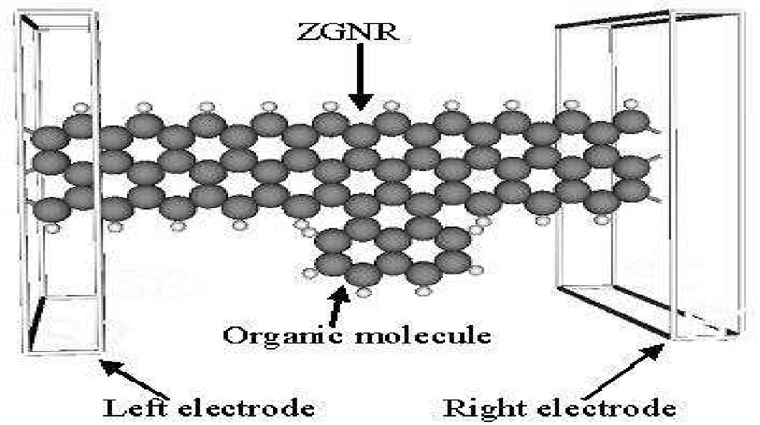


The general relationship between the normalized frequency-shift and normalized added mass of the bio-particles in a SWCNT. Relationship between the frequency-shift and added mass of bio-particles obtained from direct simulation are also presented here to visualize the effectiveness of

Graphene Nanostructure

- Electronic properties are used for a possible sensing device
- This type of structures seem to be useful to describe, qualitatively, the effects on the transport properties of ZGNR when organic molecules attached to the ribbon edges.
- The energy states and transmission of the ZGNR suggests that ZGNR can be used as a spectrograph sensor device.
- Additionally, significant effect of doping on these quasi-one dimensional system can be observed in the transmission spectrum.
- Based on these results, one may propose an extended and more detailed study of these nanostructures acting as nano-sensor devices.

Coupled system: Two probe system



Zigzag nanoribbons and linear polyaromatic hydrocarbons such as Naphthacene, as the organic molecules.

Computation

- Electronic structures and geometry relaxations are calculated by using SIESTA code.
- Functional used : local-density approximation (LDA).
- Basis set : Double-ζ plus polarization.
- Energy cut-off : 300 Ry.
- Force tolerance : 0.001 eV/Å.

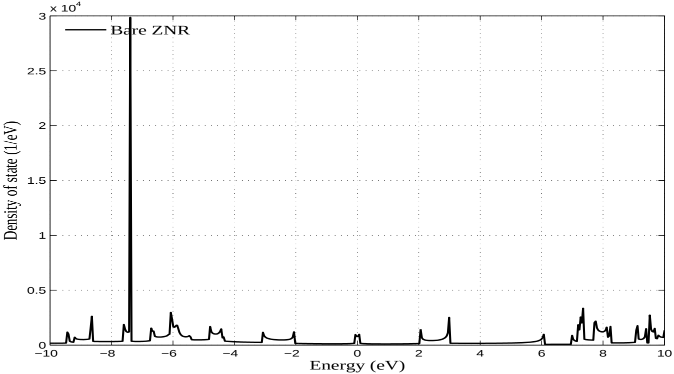
System studied

- Bare zigzag nanoribbon:
  1. Undoped ZGNR
  2. Boron doped at center of the ribbon
  3. Boron doped at edge of the ribbon
  4. Nitrogen doped at center of the ribbon
  5. Nitrogen doped at edge of the ribbon
- Zigzag nanoribbon with attached organic-fragment (Naphthacene):
  1. Undoped coupled system
  2. Boron doped at center of the coupled system
  3. Boron doped at edge of the coupled system
  4. Nitrogen doped at center of the coupled system
  5. Nitrogen doped at edge of the coupled system

Response calculated

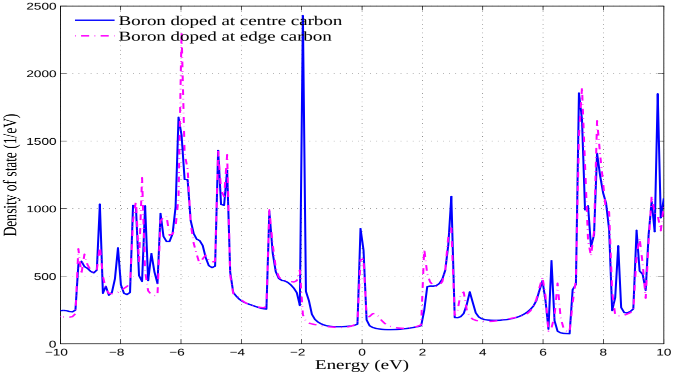
- Total energy.
- Density of States.
- Transmission spectrum.
- Current-Voltage (I-V) characteristics: A derived quantity from transmission.

Density of States (DOS) of Bare ZGNR



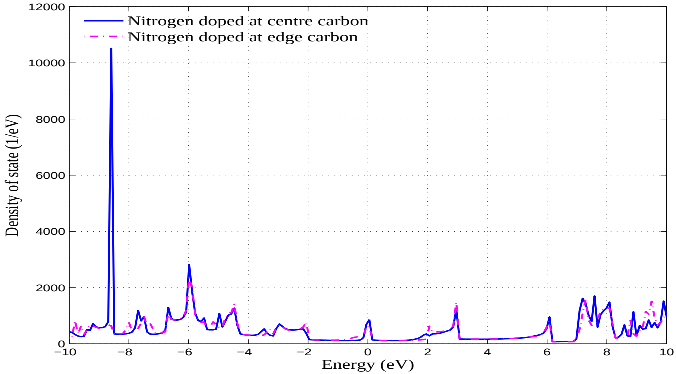
There is one DOS peak in labeled at -7.8 eV from the Fermi level. Total energy of the system = -8996.4489 eV.

DOS of Boron doped Bare ZGNR



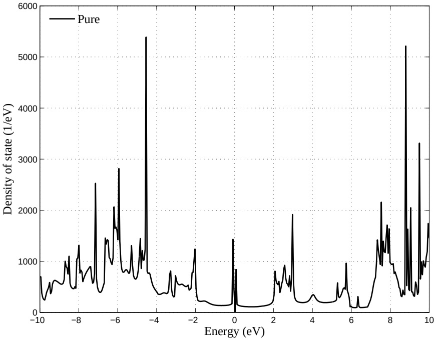
Doping shifts the DOS peak at -1.9 eV and -6.0 eV from the Fermi level for central and edge doping, respectively, compared to undoped system. Total energy of the system: $Boron_{Edge} = -8918.6167eV$, $Boron_{Central} = -8914.0341eV$.

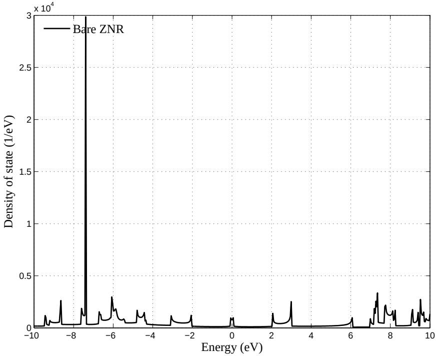
DOS of Nitrogen doped Bare ZGNR



Doping shifts the DOS peak at -7.5 eV from the Fermi level for central doping, compared to undoped system. Total energy of the system: $Nitrogen_{Edge} = -9110.8388eV$, $Nitrogen_{Central} = -9113.4977eV$.

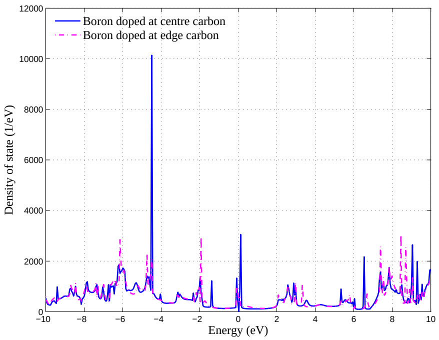
Comparison of DOS of Undoped Coupled System with Bare ZGNR

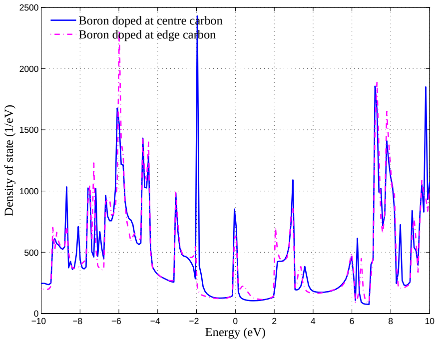




There are two DOS peaks in undoped ZNRs labeled at -4.5 eV and 8.3 eV from the Fermi level. Total energy of the coupled system = -9965.3414 eV. Total energy of the bare system = -8996.4489 eV.

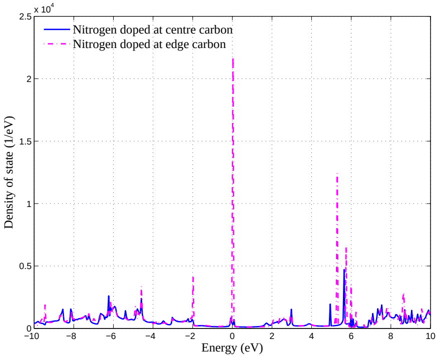
Comparison of DOS of Boron doped Coupled System with Bare ZGNR

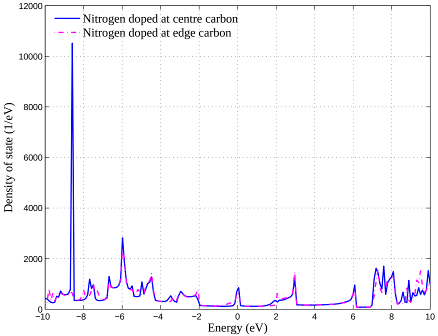




Same peak is observed at -4.5 eV from the Fermi level, compared to undoped coupled system. Total energy of the system: $Boron_{Edge} = -9886.7513eV$, $Boron_{Central} = -9884.2640eV$.

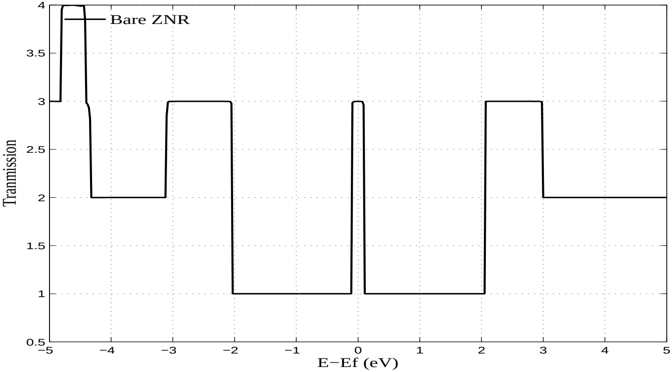
Comparison of DOS of Nitrogen doped Coupled System with Bare ZGNR





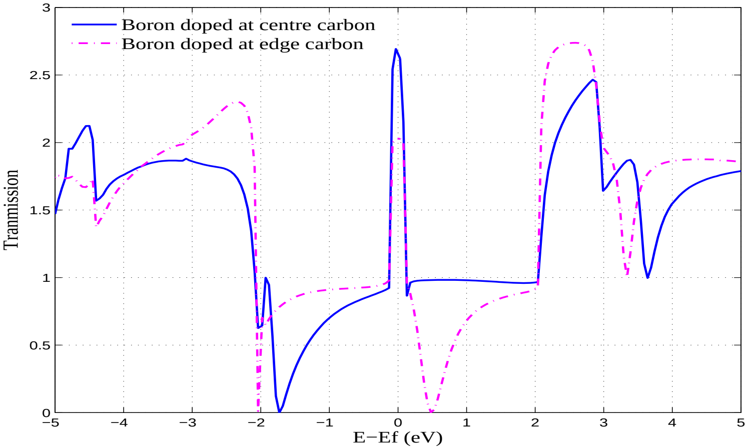
For nitrogen doped system, sharp peak is observed at the Fermi level, compared to bare ZGNR. This could make significant effect on conductance.

Transmission of Bare ZGNR



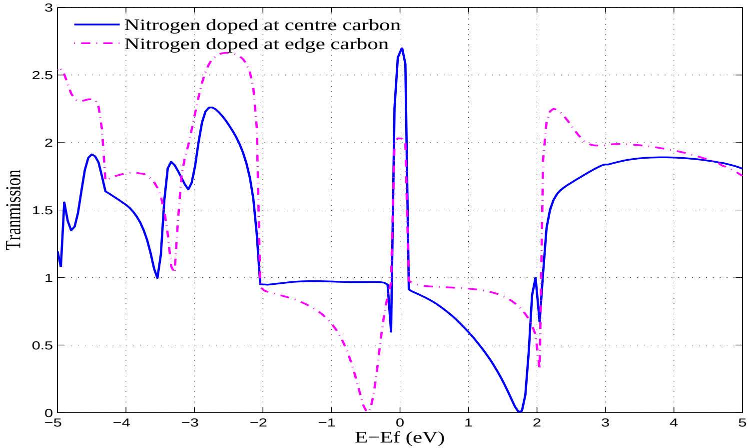
Note the asymmetry around the Fermi energy, especially for the edge doping case. This will have a significant influence on the current voltage characteristics and thus enables to develop high-fidelity sensing devices.

Transmission of Boron doped Bare ZGNR



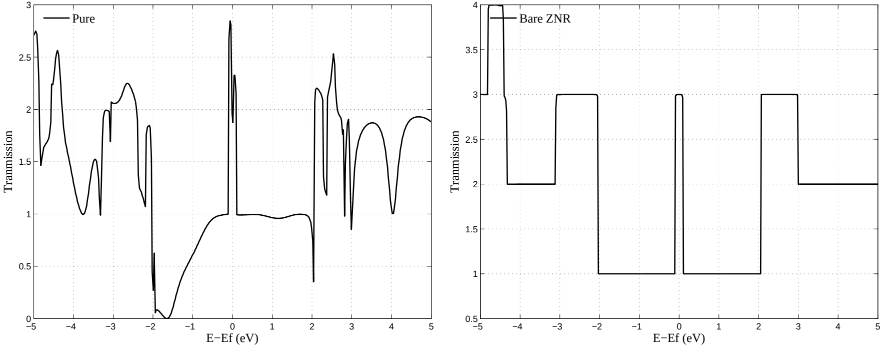
Central doping reduces the transmission across the ribbon. Further reduction in transmission observed due to edge doping.

Transmission of Nitrogen doped Bare ZGNR



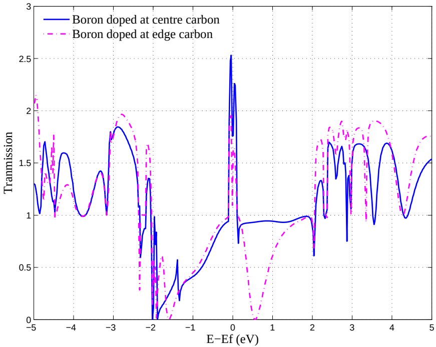
Similar features are observed for nitrogen doping to the bare ZGNR. Central doping reduces the transmission across the ribbon. Further

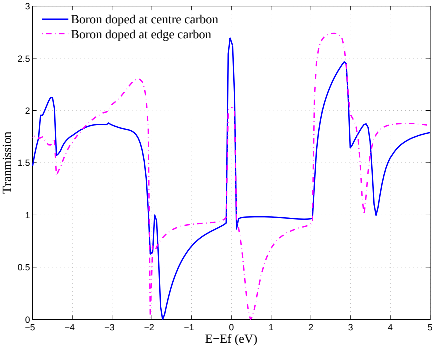
Comparison of transmission of Undoped Coupled System with Bare ZGNR



Attaching organic fragments reduces the transmission at Fermi level, which affects conductance of the system.

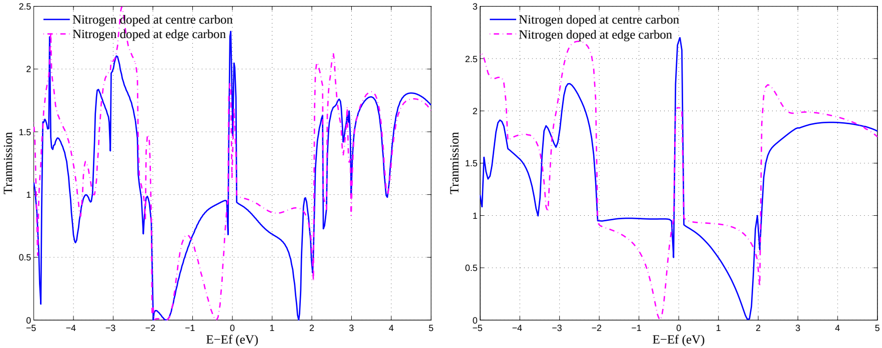
Comparison of transmission of Boron doped Coupled System with Bare ZGNR





Similar features are observed for doped coupled system as observed in undoped system.

Comparison of transmission of Nitrogen doped Coupled System with Bare ZGNR



Similar features are observed for doped coupled system as observed in undoped system.

Summary of results

1. The type of coupled system seem to be useful to describe, the effects on the transport properties of GNR when organic molecules attached to the ribbon edges.
2. The energy states and transmission of the ZGNR suggests that ZGNR can be used as a spectrograph sensor device.
3. Significant effect of doping on these quasi-one dimensional system can be observed in the transmission spectrum.
4. Based on these results, one may propose an extended and more detailed study of these nanostructures acting as nano-sensor devices.
5. A systematic analysis following this line may be useful to determine the type and concentration of foreign entities which could be detected with these kinds of structures.

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