Electronic Properties of Graphene Nanoribbons Coupled with Organic Molecules

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Outline of the present talk

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   - 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.
Introduction

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

\[ M = \frac{\rho Al}{\mu} \frac{\left(\alpha^2 \beta\right)^2}{\left(\alpha^2 \beta - 2\pi \Delta f\right)^2} - \frac{\rho Al}{\mu} \] (1)

This is in general a nonlinear relationship.

Using the linear approximation, the value of the added mass can be obtained as

\[ M \approx \frac{\rho Al \cdot 2\pi \Delta f}{\mu \cdot \alpha^2 \beta} \] (2)

The nondimensional constant \( \alpha \) depends on the boundary conditions and \( \mu \) 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 \( \alpha^2 = \sqrt{6720/13} = 22.7359 \), \( \mu = 35/13 = 2.6923 \).
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 analytical formulas.
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.
Electronic structures and geometry relaxations are calculated by using SIESTA code.

- Functional used: local-density approximation (LDA).
- Basis set: Double-$\zeta$ 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.
There is one DOS peak labeled at -7.8 eV from the Fermi level. Total energy of the system = -8996.4489 eV.
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: $Boron_{Edge} = -8918.6167\text{ eV}$, $Boron_{Central} = -8914.0341\text{ eV}$. 
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:

\[
\text{Nitrogen}_{\text{Edge}} = -9110.8388 \text{eV}, \quad \text{Nitrogen}_{\text{Central}} = -9113.4977 \text{eV}.
\]
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:

\[ Boron_{\text{Edge}} = -9886.7513\text{ eV}, \quad Boron_{\text{Central}} = -9884.2640\text{ eV}. \]
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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