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Theoretical Calculation of Optical Absorption Spectrum for Armchair Graphene Nanoribbon

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Abstract

The optical absorption spectrum of armchair graphene nanoribbon has been studied using first principle calculation. For this purpose, first we calculate the band structure and therefore the energy gap of A-GNRs by tight- binding model by including the edge deformation due to passivation of edges by hydrogen atoms. Then from single electron approximation, we obtain the real part of conductance and optical absorption of A-GNRs. Results shows that all families of A-GNRs behaves like a semiconductor and by tuning the shape and wide of ribbon one can control the energy gap and optical absorption of A-GNRs for optical applications

1. Intoduction

Graphene is an alternative material to use in low dimensional structures. Recently study of graphene based devices is growing rapidly [1]-[3]. Graphene is single layer of carbon atoms that arranges in honeycomb structure [4]. Graphene nanoribbons (GNRs) have attracted much attention because of their properties and their potential in designing high performance devices [5]-[6]. Graphene nanoribbon is finite- width Graphene strips and has quasi 1D structure. However recently isolated nanometer sized GNRs have been actually synthesized by etching large graphene samples or by CDV growth on suitable patterned surfaces. Optimizing fabrication methods opens vast application areas for GNRs [7]-[9].

Electronic properties of Graphene and GNRs have been studied before [10]-[12]. It shows unique electronic properties and origin of a lot of peculiar phenomena. Also Graphene has remarkable optical properties. Despite of on layer thickness of grahene, it has able to absorb photons from visible to far infrared and terahertz and strength of

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Electronic and optical properties of GNRs strongly depend on the shape of nanoribbon and especially to the width of nanoribbon. The edge shape dictates their classification in Armchair (A) and Zigzag (z) ones, thus determining their band structure and optical absorption. In general, theoretical studies show a metallic behavior for graphen nanoribbon with zigzag edge, but graphen nanoribbon with armchair edge (A-GNRs) has oscillating behavior. According to this behavior A-GNRs are further classified in three distinct families: N=3m, N=3m+1 and N=3m+2, with integer m, where N indicates the number of unit cells across the ribbon width. In addition this classification will be affect on the optical properties especially optical absorption [17]. For study of response in electronic devices like photodetectors optical absorption controlling will be important. In previous works optical absorption in A-GNRs was determined by Density functional theory model. In this paper we want to study the single electron band structure of A-GNRs by tight- binding model, we will calculate the energy gap for different families of A-GNR by considering the edge deformation (the edge carbon atoms of A-GNR are all passive by hydrogen atoms). Finally we will calculate the optical absorption by using the single electron approximation.

2. Theoretical model

Band structure of Armchair GNRs has been studied before in many papers. We follow the work of Zheng et al. (2007) for calculating the band structure and energy gap of A-GNR by tight- binding model [18]. The structure of A-GNR consist two type sub-lattices A and B and therefore there are two type atoms A and B in unit cell (fig 1). For perfect (without considering edge deformation) A-GNR the Hamiltonian of system is:

$$H = \sum_i \varepsilon_i |i\rangle\langle i| - \sum_{\langle i,j\rangle} t_{i,j}\left(|i\rangle\langle j|\right) \tag{1}$$

Where $\langle i , j \rangle$ denotes the nearest neighbor, ε_i on-site energy and $t_{i,j}$ hopping energy of sites i and j. In perfect A-GNR we set $\varepsilon_i=\varepsilon=0$ and $t_{i,j}=t$, by considering the hard wall boundary condition:

$$\phi_A(0) = \phi_B(0) = 0,$$
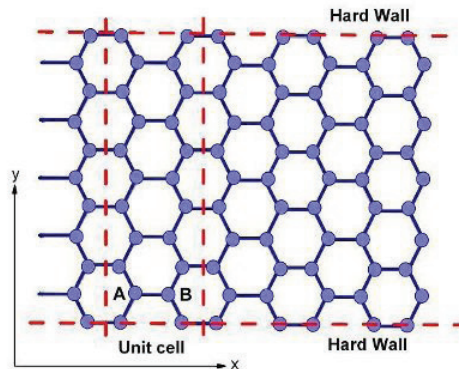$$\phi_A(n+1) = \phi_B(n+1) = 0 \tag{2}$$

Fig 1- structure of armchair grahene nanoribbon, unit cell consist of two type A and B atoms. Hard wall boundary condition used to finding band structure

One can easily obtain band structure and energy gaps of A-GNR by solving the Schrödinger equation. On the other hand every atom on the edge has one dangling bond unsaturated; the characteristics of the C-C bond at the edge can change electronic structure dramatically. In optical transitions, band gap energy plays an important role and edge effects should be considered carefully. We consider that edge atoms passive by hydrogen atoms. The bond lengths between carbon atoms at the edge are predicted to vary about 3-4% when hydrogenated. Correspondingly the hopping integral increase about 12% extracted from analytical tight- binding expression. The Hamiltonian of the A-GNR with edge deformation can be written as:

Where $\delta t_{i,j}$ indicates the variation of transfer integral. For edge atoms $\delta t_{i,j}=\delta t_0=12\%\ t$ and it vary exponentially across the nanoribbon width. In analogy of perfect case, band structure and energy gap of nanoribbon can be calculated by solving the Schrodinger equation.

Now we want to determine the optical absorption spectrum. For this purpose first we should calculate the real part of conductance $\sigma_1(\omega)$ that is directly related to the absorption of incident energy. From perturbation theory for weak fields we have [19]:

$$\sigma_1(\omega)=\frac{2\pi e^2}{m_e^2\omega L}\sum_{n,n',k}\left[f\left(E_{n,k}\right)-f\left(E_{n',k}\right)\right]\left|\langle n,k|P_x|n',k\rangle\right|^2\times\delta\left(E_{n,k}-E_{n',k}-\hbar\omega\right) \qquad (4)$$

Where L is the width of nanoribbon, $f(E_{n,k})$ is the Fermi- Dirac distribution function, P_x is the x component of momentum operator and the factor 2 is for spin degeneracy. Here we assume $f(E_{n,k})=1$ for $E_{n,k}<E_F$ and $f(E_{n,k})=0$ for $E_{n,k}>E_F$. Since the on-site energy is chosen to be zero, the Fermi level $E_F=0$ is zero for A-GNR.

In the presence of an incident laser beam with photon energy $\hbar\omega$, a peak in $\sigma_1(\omega)$ indicate an absorption peak for the photon with the energy $\hbar\omega$. The imaginary part of conductance, $\sigma_2(\omega)$, can be calculated from Kramers- Kronig relations. The absorption spectrum $\alpha(\omega)$ can be calculated from $\sigma_1(\omega)$ by using:

$$\alpha(\omega)=\frac{4\pi}{n_b c}\sigma_1(\omega)$$

Where n_b the refractive index of background material and c is light speed. In other words, starting from $\sigma_1(\omega)$, we can calculate pretty much all the optical properties of graphene nanoribbon, including refraction index and reflectivity.

For calculating the matrix element of momentum $\langle n,k|P_x|n',k\rangle$, we only consider the effect of nearest neighbors, and we use $\langle i|P_x|j\rangle=M\ \hat{e}_{i,j}$, where $M=0.206$ and $\hat{e}_{i,j}$ is unit vector from site i to site j [20]. It should be mentioned that the value of M dose not affect on the shape of $\sigma_1(\omega)$, therefore, the shape of absorption spectrum is independent of the numerical value of M.
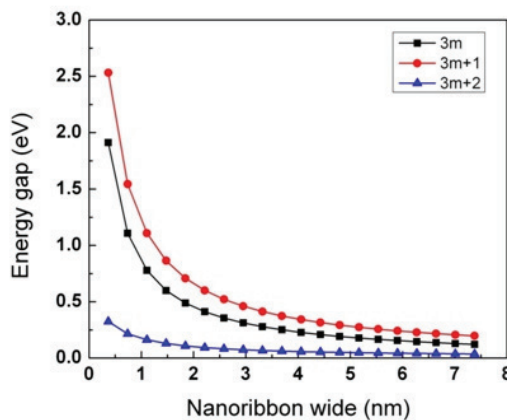

Fig 2- Energy gap of A-GNR for different three families by including the edge deformation (edge atoms passivated by hydrogen).

3. Results and Discussion

First we have calculated the band structure and energy gap for the graphen nanoribbon with armchair edge and by including the edge deformation; we have used the tight- binding model that explained in previous section. There are three distinct families for A-GNRs. For the perfect A-GNRs (without considering edge deformation), in the case of $N=3m+2$, energy gap is zero and A-GNR is metallic, but in other two families energy gap appears and A-GNR classified as a semiconductor structure. The energy gap of $N=3m+1$ case is bigger than $N=3m$ case. By including the edge deformation Hamiltonian to the Hamiltonian of system (deformation is localized near two edges) and by solving the Schrödinger equation we have find the band structure of system. Results show that all A-GNRs become semiconductor. For example we can compare the energy gaps of A-GNRs with $N=8$, 9 and10. For perfect A-GNRs

widths of ribbon. Figure shows the decrease of energy gap by increasing the ribbon width. However to detuning the energy gap of system for optical applications, we should optimize the shape and the width of graphene nanoribbon.

For determining optical absorption spectrum we should obtain real part of conductance for graphene nanoribbon with armchair edge. Band structure in A-GNRs with finite width consist of subbands (for both conduction and valance band), transition between these subbands can lead to a peak in real conductance and therefore in absorption spectrum. Figure 3 shows the band structure and real conductance $\sigma_1(\omega)$ for band edge transitions. Three subfigures belong to N=8, 9 and 10 A-GNRs. various peaks is due to subband transitions ($k=0$) that exists in calculating energy range (0-4 eV). The strength of interband transitions is higher for the smaller energy gaps that belong to the difference of minimum of conduction band and maximum of valance band.

Finally we obtain the optical absorption of A-GNRs with N=8, 9 and 10, that have shown in figure 4. In general, optical absorption has the shape of absorption for quasi 1D system. When energy of incident photon is smaller than energy gap, there is no absorption. For photon energy equal to the energy gap, absorption spectrum has maximum value, and decrease for energies higher than energy gap, until the energy of photon is equal to the second energy gap belong to another subband transition. Results show that one can tune the absorption spectrum in interested energy that will be used in optical device, by choosing a suitable shape for graphene nanoribbon.
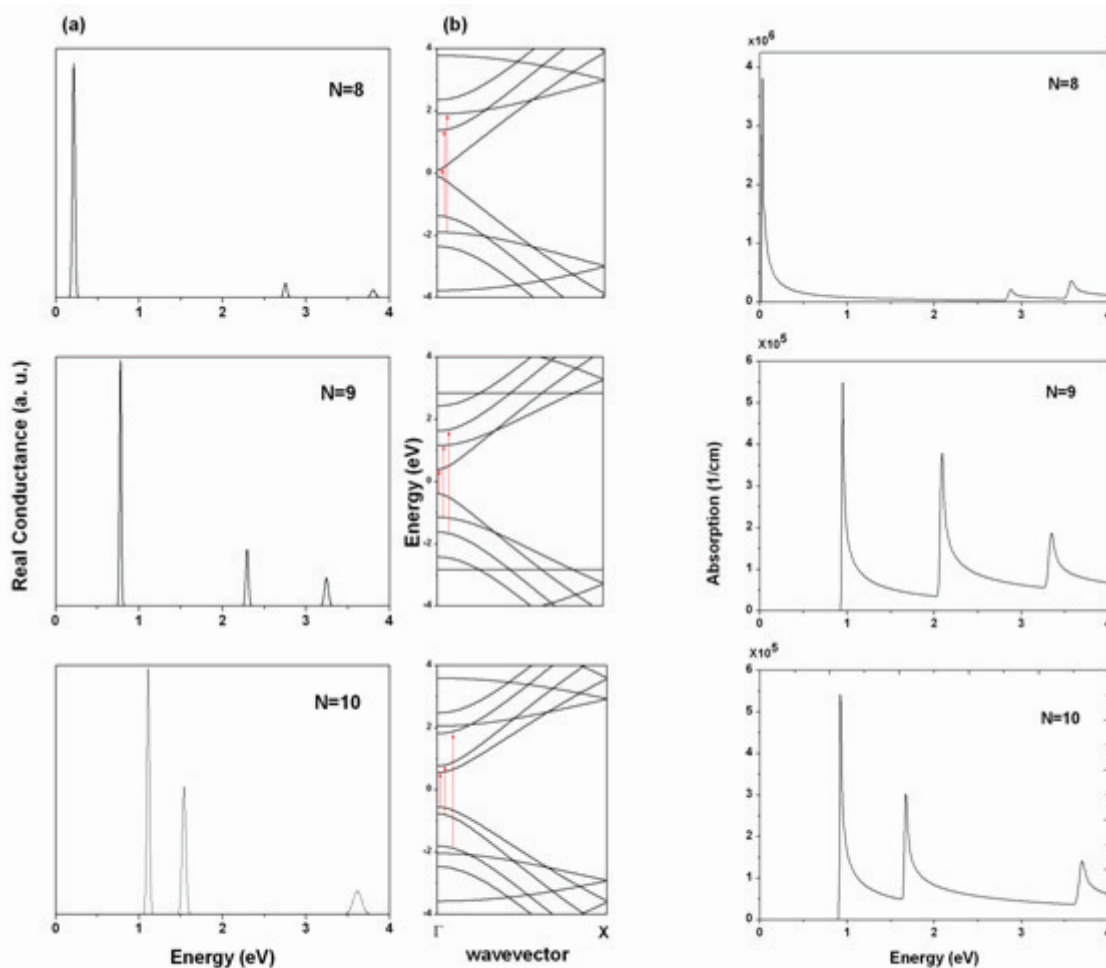

Fig 3- (a) Real conductance of hydrogen passivated A-GNRs: N=8 (1.05 nm wide), N=9 (1.17 nm wide) and N=10 (1.29 nm wide). (b) Band structure of A-GNR that calculates by tight- binding model.

Fig 4- Optical absorption spectra for A-GNRs: N=8, 9, and 10.

binding model for nearest neighbor atoms and by considering the edge deformation, that edge atoms passives by hydrogen atoms. In addition, we calculated the real conductance and absorption spectrum at the presence of incident beam, in single electron approximation, results shows that by varying the shape of nanoribbon especially by changing the width of ribbon, one can tune the optical absorption for optical applications.

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