Band gap of graphene nanoribbons calculated using Huckel molecular orbital theory

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Abstract—**In this paper, a new model based on Huckel molecular orbital theory is developed and used to calculate the band gap of graphene nanoribbons, which are stripes of etched graphene. Band gaps of graphene nanoribbons with different edge structures and widths are calculated to reveal physical properties. The proposed model well captures the band gap characteristics of graphene nanoribbons without intensive calculations. The understanding of the band gap properties of grapheme nanoribbons allows for various electronic and photonic applications.**

Index Terms—**Band gap, Electronics, Graphene, Molecular orbital.**

I. INTRODUCTION

Graphene consists of billions of carbon atoms joined in a hexagonal lattice, like a honeycomb structure that is only one atom thick. Often called a magic material, graphene is extremely thin, mechanically strong, transparent and flexible [1]. Most remarkably, because the delocalized p electrons in graphene behave like massless particles with incredible mobility in two dimensions, graphene is highly attractive for various electronic and photonic applications, such as high frequency transistors, logic transistors and photodetectors [2].

However, graphene has a zero band gap which can lead to many challenges in real applications, since a band gap is required for obtaining the basic electric logic states (on or off) in logic transistors and the carrier extraction in photodetectors [3]. To open a band gap in graphene, one approach is to etch or pattern graphene into stripes: graphene nanoribbons (GNRs) [4]. GNRs keep the favorable properties of graphene sheets but have effective band gaps useful for various electronic and photonic applications. Therefore, it is very important to understand the band structure of GNRs before we are able to fine-tune their band gaps and make them suitable for different devices.

The band gap of GNRs has shown to be closely related to their edge structure and width, since a change in these parameters imposes different boundary conditions on the molecular orbital wave function [1]. GNRs have two kinds of edge structures: armchair-shaped edge and zigzag-shaped edge [3]. By convention, the width of armchair GNRs is determined by the number of dimer lines (Wa) across the ribbons, whereas the width of zigzag GNRs is determined by the number of zigzag chains (Wz). We can calculate the actual width Wa and Wz using the C-C bond length in graphene which is 1.42 Å [5]. Perpendicular to the direction of the width, GNRs repeat their geometric structures, forming one-dimensional periodic structures.

Many theoretical studies have been conducted to

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investigate the relationship between the band gap of GNRs and their edge structures and widths. Among them, tight binding model (TB) and density function theory (DFT) have been most widely used to calculate the band gap [3], [5], [6], [7]. Comprehensive as those methods are, they can be computationally expensive, especially for systems with over two hundred atoms [6].

In this paper, Huckel molecular orbital theory (HMO) is used to calculate the band gap of GNRs and examine how the band gap changes with the width and edge structure. It provides a quick estimation of the GNR band gap since the calculation can be performed more easily than TB and DFT. The results agree with the experimental band gap values as well as theoretical ones based on the TB and DFT model.

II. MATERIALS AND METHODS

2.1 Application of Huckel molecular orbital theory

The model is constructed based on Linear Combination of Atomic Orbitals (LCAO). We can express the GNR molecular orbitals as a linear combination of carbon atomic orbitals. Applying the variational principle to find coefficients that minimize the expected energy and plugging in the LCAO wavefunction, we get a homogeneous system of linear simultaneous equations with respect to the coefficients c_i of atomic orbitals. Using Huckel theory, we assume the overlap integral S is negligible. Since all carbon atomic orbitals in GNRs are identical, every Coulomb integral can be denoted as α. In addition, all adjacent orbitals have the same resonance integral β whereas the non-adjacent ones have zero integral [8].

Therefore, the system of equations becomes:

$$(\alpha - E)c_1 + \beta c_2 + \cdots = 0$$

$$\beta c_1 + (\alpha - E)c_2 + \cdots = 0$$

$$\cdots$$

The band gap E can thus be calculated from the systems of equations.

2.2. Band gap and width

Infinite one-dimensional GNRs can be approximated by ring structures with a very large radius, because when the number of atoms of a ring becomes very large, its curvature approaches zero. This approximation has the advantage of avoiding edge phenomena which do not exist in GNRs extending infinitely in one dimension.

An armchair GNR of given width Wa can then be treated as a "band" with width Wa and length L that is sufficiently large, except that the top and bottom of the "band" are connected. With this model, we label the carbon atomic orbitals in an armchair GNR row by row following the convention of counting the dimer lines (Fig. 1). The system of equations can thus be solved if we assign α to entries corresponding to

atomic orbitals and β to those corresponding to adjacent orbitals.

Here a = -10.7 eV, which is the carbon atomic energy in p orbital, and b = -1.58 eV, which is the resonance integral [9].

MATLAB is used to construct matrix A, solve for its eigenvalues and calculate the band gap.

The same methods of modeling the infinite GNRs and labelling the atomic orbitals are applied to find the matrix A for zigzag GNRs. Again, MATLAB completes the calculation of the band gap.
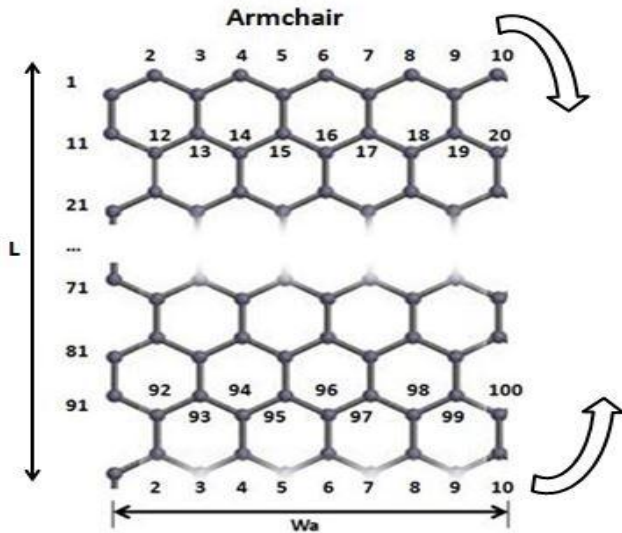

Fig. 1: Orbital labeling in an armchair GNR with Wa=10 atoms and L=10 atoms.

III. RESULTS AND DISCUSSION

3.1. GNRs with armchair edge structure

After calculating the band gaps of an armchair GNR with a range of width, we can plot the results to give a clear picture of the relationship we are interested in. Fig.2 shows the band gap of an armchair GNR with respect to its width. First, the plot suggests that the band gap decreases with an increase in width. In addition, it reveals that the variation in band gap of armchair GNR can be classified into three groups based on Wa, the number of dimer lines along the width [7]: if Wa = 3n or Wa = 3n+1(n is a positive integer), the GNR is semiconducting with a maximum band gap of 1.3 eV; if Wa = 3n+2, it shows the metallic property with a zero band gap. In other words, armchair GNRs can be separated into three groups with a hierarchy of gap size given by

$$\Delta E_{3n} \geq \Delta E_{3n+1} > \Delta E_{3n+2} = 0.$$

The results obtained based on Huckel theory are then compared with those calculated by TB and DFT models (Fig. 3) [7]. It is interesting to see that Fig.2 from our calculation is extremely similar to the plot made from the TB model, with both showing a decreasing trend of band gap with increasing width and the same hierarchy of gap size among three groups of armchair GNRs. This is due to the fact that the TB model is closely related to LCAO [10]. However, more differences are
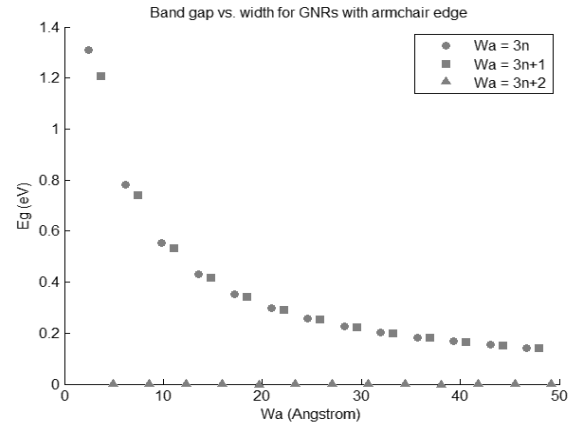

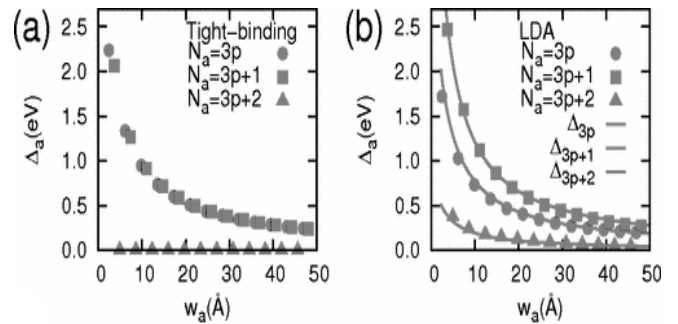Fig. 2: Band gap of armchair GNRs with respect to width

Fig. 3: Band gap of armchair GNRs with respect to width from (a) TB calculations and (b) DFT calculations by Son et al. [7]

seen between our results and those based on DFT. According to the results from DFT, there is still a decreasing trend of the band gap, but Wa = 3n+2 group of armchair GNRs are suggested to be semiconducting with a non-zero band gap. Moreover, the gap size hierarchy changes, which becomes $\Delta E_{3n+1} > \Delta E_{3n} > \Delta E_{3n+2} \neq 0$ [11].

3.2. GNRs with zigzag edge structure

Fig.4 shows the band gap of a zigzag GNR with respect to its width. Similar to that of armchair GNRs, the band gap of zigzag GNRs decreases with increasing width. However, the band gap approaches zero much faster as the ribbon widens, and there are no classified gap size groups as in armchair GNRs. The results are qualitatively consistent with calculations using the TB model and DFT [2], [7].
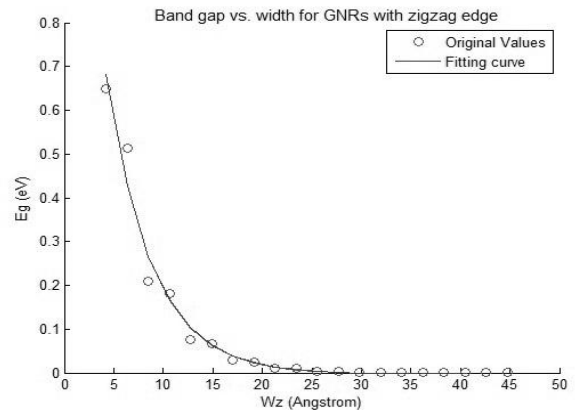

Fig. 4: Band gap of zigzag GNRs with respect to width

3.3. Band gap and edge structure

As shown in Fig.2 and Fig.4, with the same ribbon width, armchair GNRs in both 3n and 3n+1 groups have greater band gaps than zigzag GNRs. Armchair GNRs in the 3n+2 group have zero band gap for all widths, but since the band gap of zigzag GNRs approaches zero as soon as the width is greater than 25 $\overset{\circ}{A}$, both 3n+2-type armchair GNRs and zigzag GNRs are predicted to have metallic properties because of their zero band gap.

3.4. Quantitative accuracy

Compared with the TB and the DFT models, the new model provides a good qualitative estimation of the relationship between band gap, width and edge structure. To examine the quantitative accuracy of the Huckel model, we compare the experimental value of the band gap of n=13 armchair GNR, and the theoretically calculated values based on three models.

Scanning tunneling microscopy and spectroscopy reveal that n = 13 armchair GNR has a band gap of 1.4 eV [1]. Since the resonance integral β in carbon varies from 0.4 eV - 2.6 eV [9], using the Huckel molecular orbital theory, the maximum band gap we can get is approximately 0.67 eV. On the other hand, the TB model leads to an estimation of the band gap that is about 0.78 eV [11]. DFT predicts $E_g = \frac{\alpha}{W}$, in which W is the GNR width and a=0.2-1.5eVnm [12].

Since $W_{n_a=13} \approx 1.5nm$, the predicted value Eg = 0.13 - 1 eV. We can see that the band gap calculated by the new model is comparable to the results from TB and DFT models.

IV. CONCLUSIONS

Based on Huckel molecular orbital theory, a new model is developed in order to obtain qualitative understanding of the band gap of GNRs with respect to their width and edge structure. The band gap in both armchair and zigzag GNRs decreases with increasing width, but zigzag GNRs do not have gap size groups as armchair GNRs do. Besides, two of the three groups of armchair GNRs (3n,3n+1,3n+2) have band gaps greater than zigzag GNRs.

In terms of quantitative analysis of GNR band gap, density function theory provides accurate estimates, but can lead to computationally expensive calculations [6]. On the other hand, the model based on Huckel molecular orbital theory gives a simpler and more efficient way of obtaining comparably good quantitative results.

The dependence of GNR band gap on its width and edge pattern suggests that we are able to make use of the conducting and semiconducting abilities of GNRs by modifying their structures [13], [14], [15], [16]. Calculations based on the Huckel molecular orbital theory provides insight into the electronic property of GNRs and enhances the understanding of the ways to tailor the band gaps of GNPs to various useful applications, such as graphene electrodes and transistors [2].

ACKNOWLEDGMENT

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