Chirality (n, m) Dependence of Band Gap of Semiconducting SWCNT

G. R. Ahmed Jamal[1], Non-member

ABSTRACT

Experimental band gap energies of 208 semiconducting single-wall carbon nanotubes (n, m) from 0.4 nm to 3 nm are analyzed by dividing them in mod (n-m, 3) =1 and 2 types. Effects of nanotube curvature and chirality (n, m) on their band gap energies are closely investigated. An exponential empirical relation of band gap of SWCNTs with its diameter and chiral index (n, m) is devised for both mod 1 and mod 2 type semiconducting SWCNTs. The proposed empirical relation enables the simplest tight binding model to predict band gap of all semiconducting SWCNTs with higher accuracy. Calculated empirical values of band gap energies closely match with experimental data with less than 1% average absolute error over the full diameter range. The proposed empirical relation greatly improves simple tight binding model and removes its quantitative and qualitative failure in predicting band gap of semiconducting SWCNTs.

Keywords: Carbon nanotube, band gap, tight-binding model, nearest-neighbor hopping parameter, chiral index, mod value.

1. INTRODUCTION

Semiconducting single-wall carbon nanotubes (SWCNT) have already emerged as a promising candidate for molecular electronics and photovoltaic applications including solar cell. Any application of semiconducting SWCNTs is primarily related to proper information about its bandgap. Hence, accurate estimation of its bandgap energy is necessary before selecting a SWCNT (n, m) for specific application. The tight-binding (TB) model of π-bands of graphene using the zone-folding approximation has been widely used for modelling single-wall carbon nanotube (SWCNT) due to its simplicity, low computational cost, and good qualitative agreement with experimental results [1-5]. Initially, to study the electronic structure of SWCNT, authors took into account only the first neighboring interactions for hopping and overlap to simplify the TB model [5]. Later, extended TB model was proposed considering up to third-nearest-neighbors interaction and overlap [1, 2] and resultant band structure of SWCNT was found to be in good agreement with ab-initio (first-principles) calculations [1-3]. Nevertheless, TB model with the nearest-neighbor approximation still provides the simplest way for qualitative description of electronic band structure of SWCNT, especially for higher diameter tubes [2, 3].

The one-dimensionality of the nanotubes gives rise to a set of subbands instead of one wide electronic energy band, the so called van Hove singularities (vHS) in the nanotube Density of States (DOS) [4, 6]. The energy difference between the first van Hove singularities is the lowest optical transition energy and it is the bandgap of a SWCNT [4, 6].

A SWCNT (n, m) will be metallic or mod 1 & mod 2 type semiconducting if mod(n-m, 3) = 0, 1 and 2, respectively [5]. This relation is always found true except for SWCNT with very small diameter, where curvature effect dominates its properties [3]. Hence, around two third of the SWCNTs are semiconducting and one third are metallic.

Considering approximately linear dependence of wave vector on the TB model given electronic band structure near Fermi level, the interband transition energy between the first VHSs, hence the band gap (E_g) of semiconducting SWCNT is given by [4, 7]:

$$E_g = \frac{2\gamma_0 a_{cc}}{d_t} \tag{1}$$

where γ_0 is the nearest-neighbor hopping parameter, Å is carbon-carbon bond length, is nanotube diameter in nm, given by $d_t = \frac{\sqrt{3(n^2+nm+m^2)}a_{cc}}{\pi}$ This inverse proportional trend of bandgap of SWCNT with its diameter is also observed from Kataura plot [8] and other optical spectroscopic experiments [9].

Equation (1) gives a simple way to calculate bandgap of semiconducting SWCNTs, but, it fails to give accurate qualitative and quantitative prediction of them. The basic tight-binding model badly underestimates the apparent scatter arising from chiral variations at a given diameter. These chiral variations in experimental bandgap energy are at least twice as large as predicted by the tight-binding model for tube diameters of 1.5 nm or less. It is also noticed that the tight-binding model (with γ_0 = 2.90 eV) underestimates bandgap energies by up to 25% relative to the experimental values [10]. For example, simple TB model predicted bandgap for (11, 0) tube, having diameter 0.873 nm, is 0.956 ev which deviates by 20%

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[1]The authors is with Bangladesh University of Engineering and Technology, Dhaka, Bangladesh, e-mail: iqbal.gra@gmail.com

from experimentally reported value of 1.191 ev. Its quantitative failure is more prominent for lower diameter tubes [3]. A constant Îş0 cannot bring the simple TB model predictions into accord with the experimental bandgap energies.

Equation (1) also fails to reflect some specific tendencies of transition energies observed from various optical spectroscopic experiments. It is observed that the mod 1 type semiconducting SWCNTs have smaller bandgaps than mod 2 type semiconducting SWCNTs with comparable diameter [9]. This observation is not reflected through Eq. (1) as it gives comparable values of bandgaps for comparable diameters with any constant γ_0, irrespective of mod type.

Above mentioned disagreements of Eq. (1) with experimental results are attributed to many factors. The first factor is nanotube 'curvature effect' induced σ-π rehybridization and de-localized π bond orbitals and corresponding band structure deviation from simple π-orbital graphene picture [1, 3, 11, 14]. The second factor is 'chirality effect' that originates from individual nanotube chirality and responsible for some unique features of each tube [14]. The third factor is 'trigonal warping effect' [15] that arises from both curvature and chirality. The fourth factor is many body effect or self-energy and exitonic effect [16].

Many authors [10, 13, 15, 17-20] tried to improve Eq. (1) to give better prediction of experimental observations. Some of them proposed to add extra terms with (1) to reflect curvature effect (in terms of d_t) and chirality effects (in terms of chiral angle, θ) [13, 14, 18-20]. Some proposed to take γ_0 as a curvature (d_t) and chirality dependent parameter instead of a constant so as to include these effects in γ_0 [10, 14, 15]. Though their improved equations give better picture than its basic form but those also failed to predict experimental values accurately. Consequently, empirical relation became necessary and Weisman et al. [10, 17] came up with a model independent empirical equation to predict bandgaps of semiconducting SWCNTs.

One common factor in all the above mentioned theoretical and empirical models or equations is, they expressed chirality effect always in the form of a specific term cos (3θ) [18-20] and did not consider any other combination of chiral indices. Though the empirical equation proposed by weisman el al. [10] is effective enough to reflect experimental data but it requires some computational efforts due to inclusion of chiral angle, fractional terms and fractional powers. Moreover, their approach totally ignored basic TB model derived Eq. (1), as they proposed model independent empirical equations.

The overall issues can be alternatively addressed if curvature, chirality and other effects are included in γ_0 empirically, so that the basic form of Eq. (1) remains intact. In fact, γ_0 was considered as a fitting constant only in earlier works [1], though no one proposed any fixed value for it. Most of the authors used $\gamma_0 = 2.9$, while different values ranging from 2.5 to 3 or greater are also reported in literatures [14, 15]. Idea of a constant γ_0 is not appreciated now and some authors [14] later discussed possible dependency of γ_0 on nanotube structure. So an approach of relating γ_0 with nanotube structure is quite justified and will be more effective to improve the TB model calculation of bandgap energies. As classifying semiconducting SWCNTs in mod 1 and mod 2 types originates from chirality (n, m), not from chiral angle, so chirality effect can be reflected through a suitable combination of chiral index instead of chiral angle. A properly designed model of γ_0 can directly relate bandgap with nanotube chirality (n, m), which can be used to calculate bandgap energies of any semiconducting SWCNTs with higher accuracy.

2. METHOD

All the semiconducting SWCNTs in between theoretically possible minimum and maximum diameter range were considered. Theoretical calculations based on energetics considerations have shown that diameter of a freestanding SWCNT should be at least 0.4 nm large to afford strain energy and at most about 3.0 nm large to maintain tubular structure and prevent collapsing [5, 21]. Total 208 semiconducting SWCNTs were found within this range, comprising both zigzag and chiral tubes. After dividing them according to their mod value, 107 mod 1 type and 101 mod 2 type semiconducting SWCNTs were found.

Values of bandgap energies (eV) corresponding to all these semiconducting SWCNTs were recorded from various reports on optical spectroscopic experiments [7, 9, 10, 17, 22]. Recorded data showed that band gaps of mod 2 types are higher than that of mod 1 types for comparable diameters, as expected. In order to reflect this phenomenon, it is better to propose and formulate γ_0 for mod 1 and mod 2 separately. It will help to find and address unique trend of both groups more precisely.

In order to devise separate γ_0 for these two groups, bandgaps of mod 1 and mod 2 semiconducting SWCNTs were studied separately to reveal their specific trends with diameter, chiral index and mod value. It was observed that even within a particular mod type though the band gaps decrease in general with increasing diameter, but this decreasing follows continuous nonliear ups and downs. It is noticeable up to 80% of the total diameter range. After investigating those sharp ups and downs more closely, it was found that their rise and down trend is very sensitive to a specific chiral index combination (n+2m). Though mod 1 type and mod 2 types were studied separately, this sensitiveness to (n+2m) term is commonly observed for each group. This important finding enables to reflect chirality effect in terms of this

(n+2m) term for better tracing of experimental data. Now, 'curvature effect' and 'trigonal warping effect' need to be addressed.

'Curvature effect' arised from nanotube curvature and is the dominant effect for lower diameter tubes. It is the main cause of quantitative deviation of Eq. (1) from experimental results. Fortunatey, expressing 'curvature effect' is comparatively easy and less ambiguous. As diameter d_t is fully responsible for tube curvature, so suitable inclusion of d_t term can reflect this effect. 'Trigonal warping effect' is another significant effect that also depends on d_t. Hence, intelligent placing of d_t term in our empirical equation can account both the effects.

Rest other effects like many body effect or self-energy and exitonic effect will be adjusted within numerical fitting parameters. Any pre-defined or specific term cannot be included to account these effects as the nature and amount of these effects are still being discussed in literatures and also much disputed.

After setting all necessery tools to devise our empirical equation, as a last step, all the previous theoretical and empirical efforts [10, 13, 15, 17-20] of predicting transition energies were re-examined to avoid their shortcomings. Finally, combining all these in depth observations over this wide range of data with the insights found from earlier equations, a smart format to predict experimental data was designed. Accordingly, following two empirical expressions were formulated for nearest-neighbor hopping parameter γ_0, separately for mod 1 and mod 2 types, so as to use it for predicting bandgaps of semiconducting SWCNTs correctly.

γ_0 to calculate E_g (for mod 1 type):

$$\gamma_0 = 3.8exp\left(\frac{d_t - 3.2}{n + 2m}\right) \tag{2}$$

γ_0 to calculate E_g (for mod 2 type):

$$\gamma_0 = 3.8exp\left(\frac{d_t - 1.9}{n + 2m}\right) \tag{3}$$

Equations (2) and (3) generate values of γ_0 for mod 1 and mod 2 types SWCNTs, depending on their d_t and (n+2m) terms to reflect experimental results.

3. RESULT

Bandgaps of all 208 semiconducting SWCNTs were calculated from Eq. (1) using empirical γ_0 from (2) and (3). The calculated bandgaps excellently match with experimental data from lowest diameter (0.4 nm) to highest diameter (3 nm). Bandgap values from Eq. (1) using a constant value of $\gamma_0 = 2.9$ were also calculated, which is conventionally used. The resultant value highly differed from experimental values of bandgaps, as expected.

The plots of bandgaps vs d_t for both mod 1 and mod 2 types are shown in Fig.1 (a) and (b). The

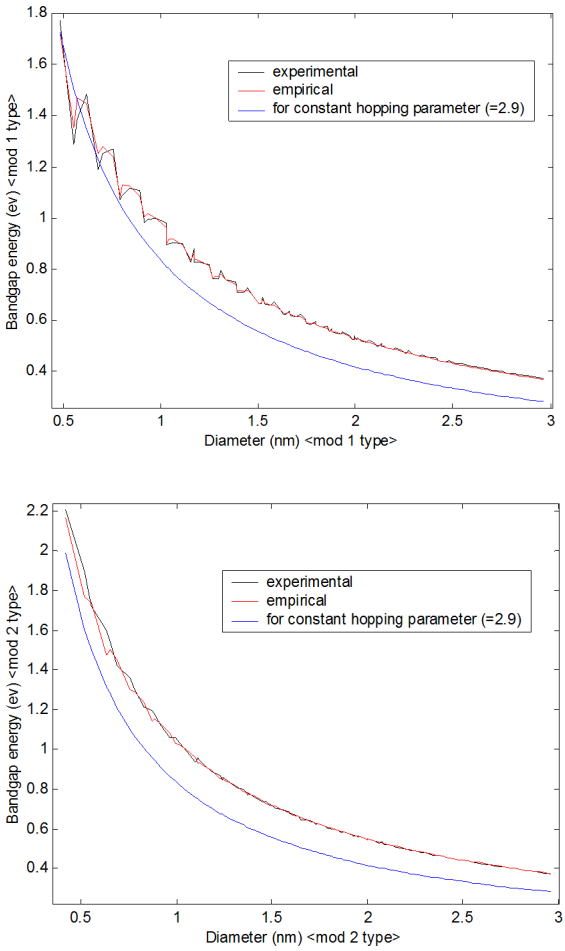

Fig. 1: *Plot of bandgap (E_g) vs diameter (d_t) for experimental (black), empirical (red) and constant γ_0 of a)mod 1 and b)mod 2 type semiconducting SWCNTs.*

good agreement between experimental and empirical curves over the full diameter range for both mod types is clearly reflected from this figure. The deviation of the curve for $\gamma_0 = 2.9$ from both experimental and empirical curves shows how erroneous it will be to use such constant value for γ_0 in order to calculate bandgap of SWCNTs.

The overall comparison between the empirical data and experimental data is summarized in Table 1. It is reflected from Table 1 that average absolute errors ($|\Delta E|$) and % average absolute errors ($\%|\Delta E|$) of empirical values from experimental values of E_g are negligible. Average absolute errors for E_g over full diameter range are 0.008 eV and 0.009 eV for mod 1 and mod 2 types, respectively. Corresponding percentage average absolute errors are 1.09% and 0.94% for mod 1 and mod 2 types, respectively. Moreover, $|\Delta E|$ and $\%|\Delta E|$ reduces more for increasing diameters as represented in Table 1. So, the proposed empirical relation between bandgap and chiral index (n, m) of all semiconducting SWCNTs through the expres-

Table 1: *The average and variation of irradiation and ambient temperature in rainy season*

Diameter (d_t)	MOD 1 TYPE		MOD 2 TYPE	
	Avg $\|\Delta E\|$	*Avg* $\%\|\Delta E\|$	*Avg* $\|\Delta E\|$	*Avg* $\%\|\Delta E\|$
0.4 nm $\leq d_t \leq$3nm	0.008	1.09%	0.009	0.94%
0.6 nm $\leq d_t \leq$3nm	0.007	0.99%	0.008	0.87%
0.8 nm $\leq d_t \leq$3nm	0.006	0.91%	0.005	0.72%
1 nm $\leq d_t \leq$3nm	0.005	0.84%	0.004	0.61%
1.5 nm $\leq d_t \leq$3nm	0.004	0.79%	0.002	0.45%

sion of γ_0 enables Eq. (1) to predict band gap energies of semiconducting SWCNTs with higher accuracy. Especially, it gives acceptable level of accuracy from lower to higher diameters and hence strengthens nearest neighbour tight binding model which is commonly accused for being highly inaccurate in lower diameter tubes.

4. CONCLUSION

In summary, effect of chirality on bandgaps of semiconducting SWCNTs was investigated. It was observed from the plots of experimental bandgaps that variation of bandgaps with chirality is related to a term (n+2m), a simple linear combination of chiral index. Based on this observation, two effective empirical equations of nearest neighbor tight binding model hopping parameter (γ_0) for mod 1 and mod 2 type semiconducting SWCNTs were presented in order to relate bandgap with chirality. The proposed empirical γ_0 is expressed in terms of (n+2m), d_t and other numerical parameters to reflect chirality effect, curvature effect and trigonal warping effect. This empirical γ_0 strengthens nearest neighbor TB model and enables it to predict bandgaps of semiconducting SWCNTs with higher accuracy. Bandgap Eg for all semiconducting SWCNTs were calculated within nanotube diameter range 0.4 to 3 nm using proposed empirical γ_0 and resultant values showed good agreement with experimental values with less than 1% average absolute error. The proposed empirical relation of bandgap with chirality highly improved quantitative calculation of nanotube bandgap from TB model by keeping its basic form intact, as only one of its parameter was modified.

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G. R. Ahmed Jamal received his B.Sc and M.Sc. degree in Electrical and Electronic Engineering from Bangladesh University of Engineering and Technology (BUET), Dhaka, Bangladesh in 2003 and 2012, respectively. At present, he is pursuing his Ph.D degree in the same institute. He is also working as Asst. Professor in the Department of Electrical and Electronic Engineering, University of Asia Pacific, Dhaka, Bangladesh since 2012. His current research interest includes Carbon Nanotechnology and Photovoltaic cells.