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Empirical Equation of Tight Binding Model Parameter to Calculate Bandgap of Semiconducting Single Wall Carbon Nanotube

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***Abstract*— Both Mod 1 and Mod 2 type Semiconducting single wall carbon nanotubes over a wide diameter range are studied separately to find their band gap trend. For accurate calculation of their band gaps, modification of nearest-neighbor hopping parameter of the tight-binding model is proposed by considering it as a function of nanotube chiral index and mod value. A simple empirical equation for the nearest-neighbor hopping parameter is presented to produce band gaps of these nanotubes that agree well with simulated data. Empirical data are also compared with experimental data and found to be in excellent agreement with it after adding a flat correction.**

***Index Terms*—Carbon nanotube, band gap, nearest-neighbor hopping parameter, tight-binding model, chiral index.**

I. Introduction

The tight-binding (TB) model of π-bands of graphene using the zone-folding approximation has been widely used for modeling single-wall carbon nanotube (SWCNT) due to its simplicity, low computational cost, and good qualitative agreement with experimental results [1]. Initially, to study the electronic structure of SWCNT in the TB approximation, most authors took into account only the first neighboring interactions for hopping and overlap for simplicity of the model. The band structure of SWCNT from improved TB model, which include up to third-nearest-neighbor interaction and overlap [2] was found to be good agreement with the result from first principle ab-initio calculations [1]. Nevertheless, TB model with the nearest-neighbor approximation can correctly predict the first optical transition energy, though the higher transition energies are strongly overestimated [2].

TB model with the nearest-neighbor approximation can provide a simple way to calculate band gap of semiconducting SWCNT, despite its failure in the overall quantitative predictions of the electronic energies [1, 2]. The expression for the band gap [3] of semiconducting SWCNT with chirality (n,m) is :

$$E_g = 2\gamma_0 a_{cc} / d_t \quad (1)$$

where γ_0 is the nearest-neighbor hopping parameter, $a_{cc} = 1.42$ Å is carbon-carbon bond length, and d_t is nanotube diameter in nm, given by $d_t = \sqrt{3\left(n^2 + nm + m^2\right)} a_{cc} / \pi$.

A SWCNT with chirality (n, m) is metallic if $\mathrm{mod}(n-m,3) = 0$, whereas $\mathrm{mod}(n-m,3) = 1$ or 2 represents semiconducting [4]. This relation is always found true except for SWCNT with very small diameter, where curvature effect dominates its properties [5]. It is also observed from Kataura plot [6] that band gap of semiconducting nanotube decreases in general with the increase of its diameter.

The band gap of mod 2 semiconducting SWCNT is always found higher than that of mod 1 type with similar or comparable diameter [6, 7]. Though this observation is explainable within zone-folding picture, it has an apparent contradiction with (1) if γ_0 is assumed as a constant. In most of the earlier literatures, γ_0 was taken merely as a fitting parameter without having any dependency on nanotube structure. $\gamma_0 = 2.7$ was chosen as best fitting value [1,2] though values ranging from 2.5 to 3.0 are also found in other literatures [7, 8]. Later, correction of γ_0 was proposed by many authors to include curvature effect [3, 8, 9]. They include the effect of CNT diameter on $\boldsymbol{\gamma_0}$ and do not consider the effect of chirality**.** So, their equations give same $\boldsymbol{\gamma_0}$ for two SWCNTs with same diameter but different chirality. Subsequent works revealed that beside curvature or diameter effect, CNT chirality also has effect on the value of $\boldsymbol{\gamma_0}$ [7, 10, 11]. But, most importantly, those who discussed chirality effect on $\boldsymbol{\gamma_0}$, they mainly meant the effect of chiral angle on $\boldsymbol{\gamma_0}$ [7, 10, 11], not directly the chiral indices (n, m).

In our perception, classifying semiconducting SWCNT in mod 1 and mod 2 originates from chirality (n, m), not from diameter or chiral angle. So, γ_0 should have some direct

dependency on combination of chiral index (n, m) rather than diameter directly. Considering this, we are motivated to find a simple empirical equation for γ_0 in terms of its chirality (n, m) and mod value, which can reflect the precise behavior of semiconducting SWCNT as mod 1 or mod 2 type. The contribution of our work is that we expressed the chirality effect on γ_0 directly in terms of chiral indices (n, m) through a simple equation without any need of including CNT diameter or chiral angle. This can reduce much computational complexity in calculating band gap of semiconducting SWCNT while giving acceptable accuracy.

Our objective in this paper is to extend and strengthen the capacity of Eqn 1 to calculate the band gap of semiconducting SWCNT with good accuracy by proposing a chirality dependent simple empirical equation for the nearest-neighbor hopping parameter (γ_0) over a wide diameter range.

II. Methods and Results

We considered total 211 samples of zigzag and chiral semiconducting SWCNTs. 108 samples were mod 1 type and 103 samples were mod 2 type with diameter ranging from 0.8 nm to around 5.5 nm and chiral index from (7, 5) to (71, 0). All possible combinations of chirality from (7, 5) to (20, 19) for semiconducting SWCNTs were taken continuously, and after this, only random chiral indices were considered up to (71, 0) to see the general trend of data at large diameters. For mod 1 type, 63 from its 108 samples have continuous chiral indices from (7, 6) to (20, 19) and rest 45 are random samples from (21, 5) to (70, 0). Similarly, for mod 2 type, 59 from its 103 samples have continuous chiral indices from (7, 5) to (20, 18) and rest 44 are random samples from (21, 4) to (71, 0). In case of random samples, both zigzag and chiral SWCNTs were considered. In our diameter range, the lowest diameter comes from (7, 5) tube which is 0.82 nm and the highest diameter comes from (71, 0) tube which is 5.56 nm.

The diameter and band gap of each of the SWCNT is calculated using Virtual NanoLab (VNL), which is a graphical user interface of The Atomistix ToolKit (ATK) simulation software by Quantumwise [12] that offers a rich set of powerful tools for investigating and analyzing the properties of nanostructures. It provides built in tools for analyzing SWCNT properties as well.

The Atomistix ToolKit (ATK) simulation software is available in two packages: ATK-SE and ATK-DFT. The ATK-SE (ATK - Semi-Empirical) program can model the electronic properties of closed and open quantum systems using both self-consistent and non-self-consistent tightbinding models. The implemented tight-binding model is based on the extended-Hückel model. ATK-SE program closely follows the implementation presented in [13, 14], where details mathematical formalism behind this model can also be found.

The Extended-Hückel Model provides a description of the electronic structure of the valence electrons of molecules and solids. The key parameter in the self-consistent loop is the density matrix. For open systems, the density matrix is calculated using non-equilibrium Green's functions, while for closed or periodic systems it is calculated by diagonalization of the Hamiltonian. The Density matrix defines the electron density and the electron density sets up an electrostatic potential, i.e. the Hartree potential. The Hartree potential is obtained by solving the Poisson equation in real space.

Basis Parameters in Extended-Hückel model are:

{The basis orbitals, The ionization potential for each of the given orbitals, The on-site Hartree shift, The number of valence electrons used to determine the neutral state, The Wolfsberg-Helmholtz constant, The energy level of vacuum} along with Slater Orbital Parameters: { Principal quantum number , Angular momentum, Slater coefficients, Weights}

For calculating CNT bandstructure, the required value of Hückel basis parameters are found from [14] which were derived by fitting Hückel Basis Parameters to a reference band structure of a graphene sheet calculated with DFT-LDA.

The Atomistix ToolKit-Density Functional Theory (ATK-DFT) program can model the electronic properties of closed and open quantum systems with Density Functional Theory models using numerical basis sets. The key parameter in the self-consistent loop is the density matrix. For open systems, the density matrix is calculated using non-equilibrium Green's functions, while for closed or periodic systems it is calculated by diagonalizing the Kohn-Sham Hamiltonian. The Density Matrix defines the electron density, and the electron density sets up an effective potential, i.e. the Hartree and exchange-correlation potential. From the effective potential, the Kohn-Sham Hamiltonian is obtained. ATK-DFT program closely follows the implementation presented in [15] and supported by [16], where details mathematical formalism behind this model can also be found.

ATK has 3 different types of basis functions: Confined Orbital, Analytical Split and Polarization Orbital. The basis orbitals have a number of parameters that determines the shape of the orbitals. ATK comes with a number of pre-build basis sets for each element which are: Single Zeta, Double Zeta, Single Zeta Polarized, Double Zeta Polarized and Double Zeta Double Polarized. The default basis set is Double Zeta Polarized.

ATK uses following parameters to generate the basis set orbitals which are used to solve the Kohn-Sham equations:

{The size of the basis set (Default: Double Zeta Polarized), The separation between the points used for the radial representation of the numerical orbitals (Default: 0.001*Bohr), The confinement radius of the numerical

orbitals (Default: 0.01*Rydberg), The inner radius of the soft confinement potential (Default: 0.8), The softness of the confined potential (Default: 40.0*Rydberg), Defines the net charge of that atom when generating basis orbitals (Default: 0.0) and The matching radius of an analytical orbital which splits the first zeta orbital into a double zeta basis (Default: 0.15) }. For our purpose of calculating the diameter and band gap of each of the SWCNT, we used graphical user interface (Virtual NanoLab) of ATK-SE package which is based on extended-Hückel model as described before. The ATK-SE package is chosen instead of ATK-DFT package because of its availability and faster computation process. Any DFT based program (first principle method) is usually expensive and requires heavy and lengthy computation which is dependent on high speed processor. Moreover the graphical user interface (Virtual NanoLab) of ATK-SE package shows numerical value of band gap in a separate window along with graphical representation but that of of ATK-DFT package only showed graphical representation. So, if bandgap is calculated from graphical representation of band structure, there may be some observation error from viewer's side. Theoretically ATK-DFT program should give better result than ATK-SE program because of proven higher accuracy of first principle method. But, since the Hückel parameters used in ATK-SE program have been fitted to the correct band structure, so this program also can give a correct band structure of semiconductors including CNTs with much faster computation than DFT. These are the reasons of choosing ATK-SE package for our calculation. It is worth mentioning here that diameter of SWCNT is directly calculated from chiral index (n, m) using the formula mentioned earlier and so calculated value of diameter is not dependent on any simulation software package. Using VNL of ATK-SE package, we recorded simulator generated values of band gaps and diameters for all our 211 samples of SWCNTs.

To find suitable value of $\boldsymbol{\gamma_0}$ to reproduce VNL simulated data from (1), at first we assigned a constant value 2.7 to $\boldsymbol{\gamma_0}$ which was preferred in many earlier works [1, 2]. We calculated band gaps for all 211 samples from (1) using γ_0=2.7 and compared that with VNL generated bandgaps. It was observed that γ_0 =2.7 always overestimate the result for mod 1 type and it always underestimate the result for mod 2 type over the full range with high error for some specific chiralities. The observations have been summarized in Table I**.**

Table I shows that performance with γ_0 = 2.7 is very poor in the case of zigzag or close to zigzag tubes specially for lower diameters. So, we cannot accept γ_0 = 2.7 for calculating band gap from (1). In fact, no single constant value for $\boldsymbol{\gamma_0}$ is acceptable because in that case (1) gives similar bandgap for both mod 1 and mod 2 types for similar diameter. But, it was mentioned earlier that the band gap of mod 2 type has to be always higher than that of mod 1 type for comparable diameter.

Then, we proceed with two different constant values of $\boldsymbol{\gamma_0}$ for mod-1 and mod-2 to reproduce VNL generated data from (1). As band gap of mod 2 type is higher than that of mod 1 type for comparable diameter, so the chosen value of $\boldsymbol{\gamma_0}$ for mod 2 type should be higher than that for mod 1 type. We assigned 2.5 & 2.6 to $\boldsymbol{\gamma_0}$ for mod 1 type and 2.8 & 2.9 to $\boldsymbol{\gamma_0}$ for mod 2 type. We then calculated band gaps of our samples for these four cases using (1) and compared each of them with

TABLE I: OBSERVED ERROR FOR CHIRAL AND ZIGZAG TUBES FOR Γ_0=2.7.

0.8 nm $\leq d_t \leq$ **5.5 nm**	**MOD 1 Type**	**MOD 2 Type**
Maximum %error ($\%\lvert\Delta E\rvert$) for zigzag (n, 0) tubes and chiral tubes with $n >> m$	15.1%	12.32%
Maximum % error ($\%\lvert\Delta E\rvert$) for chiral tubes with $n \approx m$	< 5%	< 5%

TABLE II: OBSERVED ERROR FOR MOD 1 TYPE (WITH Γ_0=2.5 & 2.6) AND MOD 2 TYPE (WITH Γ_0=2.8 & 2.9) CHIRAL AND ZIGZAG TUBES.

0.8 nm $\leq d_t \leq$ **5.5 nm**	**MOD 1 Type**		**MOD 2 Type**	
	γ_0 **=2.5**	γ_0 **=2.6**	γ_0 **=2.8**	γ_0 **=2.9**
$\%\lvert\Delta E\rvert$ for chiral tubes (n,m) where m =n - 1, n - 4 or n/2 (mod1) m =n - 2 or n - 5 (mod 2)	>5%	<5%	<5%	>7.6%
$\%\lvert\Delta E\rvert$ for zigzag or zigzag-like tubes, i.e. (n, m) with m = 0 or $n >> m$	<5%	>10.8%	>9.1%	<5%

VNL simulated data. The observation is summarized in Table II. After analyzing the result, it is clear that two separate constant value of γ_0 for mod 1 type(2.5 or 2.6) and mod 2 type (2.8 or 2.9) also failed to generate close replica of VNL data within tolerable error margin as they could not show uniform behavior to all type of nanotube chiralities. So, any constant value of $\boldsymbol{\gamma_0}$ produces good result for one kind of chirality, but poor result for another kind of chirality. This strongly suggests that the value of hopping parameter $\boldsymbol{\gamma_0}$ should have some dependency on chiral index (n, m) of SWCNT so that its value varies according to chiral combination and remove above discrepancies. This also suggests that two different sets of $\boldsymbol{\gamma_0}$ is required for mod 1 and mod 2 type for best reproduction of simulated data using (1).

In this context, we need to find such an empirical equation for γ_0, which can generate values of γ_0 depending on both CNT mod value and chirality (n, m). Based on above experiences with any constant γ_0 , the arrangement of the parameters in our desired empirical equation should be such that it can generate suitable γ_0 for every single chirality without making any discrepencies. After scruitinizing some earlier attempts for more accurate calculation of bandgap using tight binding model, we found that some authors proposed the dependency of band gap on an extra term added to (1). Some of them made this term proportional to cos3θ (θ is the SWCNT chiral angle) [7, 9], some proposed it proportional to $1/R^2$ (R is SWCNT radius, i.e. $d_t/2$) [3, 17] and some considered it proportional to both i.e. $\cos3\theta/R^2$ [10, 18]. We carefully investigated those proposals and simplified the relation used by them in terms of chiral index n & m. As γ_0 is proportional to E_g.dt from (1), we derived from the simplified relation that the variation of γ_0 can be made proportional to a term *1/(2n-m)* [Appendix-1].

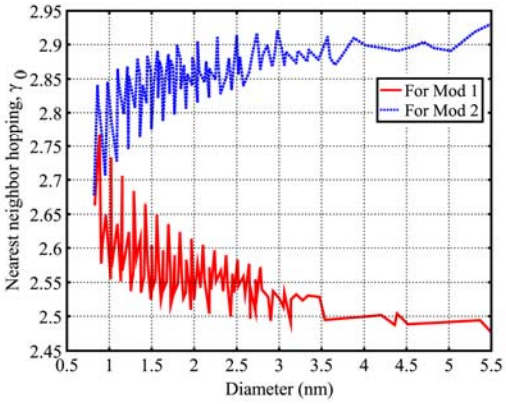

Fig. 1. Empirical value of nearest-neighbor hopping parameter (γ_0) as plotted against nanotube diameter (d_t). Solid line (red) is for mod 1 type semiconducting SWCNT and dotted line (blue) is for mod 2 type semiconducting SWCNT. γ_0 varies from 2.48 to 2.76 for mod 1 type and from 2.68 to 2.93 for mod 2 type.

We found a simple combination of chiral index *1/(2n-m)* to express γ_0, which leads to show the dependency of band gap directly on chiral index. By intelligently arranging mod value and other constants around this extracted term, we find following empirical equation for γ_0 to meet our requirement.

$$\gamma_0 = 10a_0\left\{1+\frac{k-1}{5}+\frac{(-1)^{k-1}}{2n-m}\right\} \qquad (2)$$

Where a_0 is graphene lattice constant ($=\sqrt{3}a_{cc}=0.246$ nm) and $k=\mathrm{mod}(n-m,3)$. k is 1 for mod 1 type SWCNT and 2 for mod 2 type SWCNT. It can be noted that, $10a_0$ = 10*0.246 =2.46 ≈ 2.5, which is the lowest limit of the value of γ_0 as we mentioned earlier. So, $10a_0$ term sets the lowest limit for γ_0 and a small value proportional to 1/(2n-m) is always added to it to generate suitable γ_0 for any (n, m) tube. Putting the value of k in (2) gives following individual expression for γ_0 for mod 1 and mod 2 type:

$$\gamma_0 = 10a_0\left\{1.0+\frac{1}{2n-m}\right\} \qquad (3)$$

$$\gamma_0 = 10a_0\left\{1.2-\frac{1}{2n-m}\right\} \qquad (4)$$

Equation (3) and (4) generate values of γ_0 depending on chiral indices (n, m) for mod 1 and mod 2 types SWCNT, respectively. Generated γ_0 was found to be varied continuously over a set ranging from a minimum value of around 2.5 to a maximum value of around 3.0.

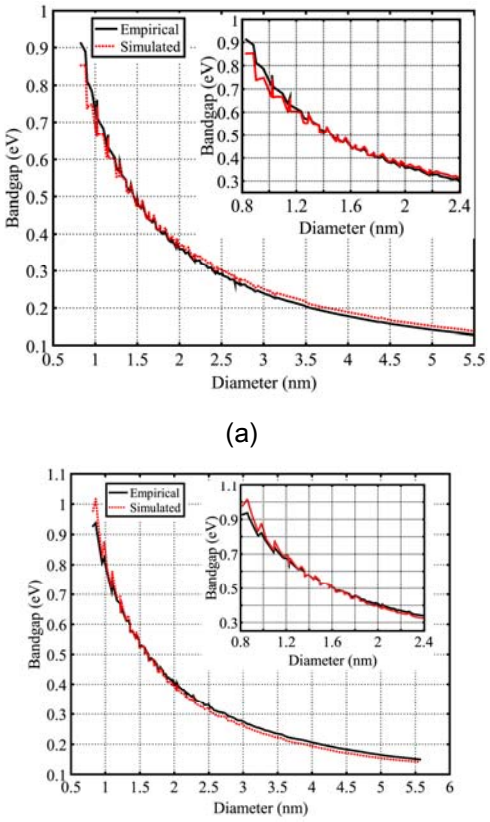

Fig. 2. Energy band gap (E_g) with respect to nanotube diameter (d_t). Solid line (black) represents empirical data from (2) and dotted line (red) represents simulated data from Virtual NanoLab (VNL) of Quantumwise. (a) For mod 1 type semiconducting SWCNT. Inset: Enlarged plot for diameter ranging from 0.8 nm to 2.4 nm for mod 1 type. (b) For mod 2 type semiconducting SWCNT. Inset: Enlarged plot for diameter ranging from 0.8 nm to 2.4 nm for mod 2 type.

Figure 1 shows the plot of γ_0 vs d_t for both mod 1 and mod 2 types, from which we can see that γ_0 varies from 2.48 to 2.76 for mod 1 and from 2.68 to 2.93 for mod 2. This agrees with most of the literatures that always selected γ_0 within this range (but as a constant). When we calculate the band gap from (1) for any semiconducting SWCNT, using γ_0 generated from (2), the result was found to be in excellent agreement with band gaps found from VNL simulation.

The plots of band gap (E_g) versus nanotube diameter (d_t) for mod 1 and mod 2 are shown in Fig. 2. Slightly higher deviation for initial lower diameters and better matching for increasing diameters is visible from these graphs. Enlarged portion of the plot (inset) for Mod 1 and Mod 2 show how excellently empirical data from our equation are tracing the VNL simulated data point by point, specially at the large middle part of the curve. For diameter above 2.0 nm, the empirical data is always around 0.01 eV lower than VNL data for mod 1 type, whereas it is around 0.01 eV higher than VNL data for mod 2 type. This means, for diameter above 2.0 nm, both mod 1 and mod 2 maintain a constant deviation of only around 0.01 eV from VNL simulated data.

TABLE III. DEVIATION OF EMPIRICAL DATA FROM VNL DATA FOR MOD 1 AND MOD 2 SEMICONDUCTING SWCNT.

0.8 nm $\le d_t \le$ 5.5 nm	**Mod 1**	**Mod 2**
Maximum positive deviation ($+\Delta E$)	0.013 eV	0.079 eV
Maximum negative deviation ($-\Delta E$)	0.072 eV	0.015 eV
Average ($\lvert\Delta E\rvert$)	0.013 eV	0.013 eV
$\%\lvert\Delta E\rvert$	3.49%	3.61%

After comparing band gap for each sample from VNL simulation with that from our empirical equation, it is observed that for every kind of chirality, our equation produces better result than using any constant value for γ_0 that we tried initially. We also observed that our equation can clearly differentiate between two CNTs with same diameter but different chiral indices by generating two different γ_0, and consequently two different bandgaps for them from (1).

The overall comparison between the empirical data and VNL simulated data is summarized in Table III for total 211 experimental samples. Table III shows that average absolute deviations for both mod 1 and mod 2 types are very low (≈ 0.012 eV). We observed that, the maximum and minimum deviations for both type reduce drastically for increasing diameters, i.e. highly improved performance. For example, from our calculation we find that, maximum negative deviation for mod 1 which is 0.072 eV for $d_t \approx 0.8$ nm, reduces to 0.02 eV for $d_t > 1.2$ nm, which further reduces to around 0.01 ev or below for all $d_t > 1.4$ nm. Similarly, Maximum positive deviation for mod 2, which is 0.079 eV for $d_t \approx 0.8$ nm, reduces to 0.02 eV for $d_t > 1.2$ nm, which further reduces to around 0.01 ev or below for all $d_t > 1.4$ nm. This observation gives us hints that though we carried our analysis for SWCNTs with diameter up to 5.5 nm, but this equation may be applied for nanotubes of any higher diameters with this very small constant deviation from simulated data.

III. COMPARISON WITH EXPERIMENTAL VALUE OF BAND GAP

We compared VNL generated bandgaps for our samples of SWCNTs with experimentally found band gaps from different sources [19, 20, 21, 22]. It is observed that VNL generated band gaps underestimate the experimental value with a constant difference of about .21 eV for both mod 1 and mod 2 cases. This may be due to the limitation of semi-empirical model used by ATK-SE package. So, if all VNL data are raised by adding this correction of .21 eV, it was then found be a close replica of the experimental band gaps value.

TABLE IV. COMPARISON BETWEEN EXPERIMENTAL VALUE OF BAND GAP AND CALCULATED BAND GAP FROM OUR EMPIRICAL EQ (2) AFTER ADDING THE CORRECTION:

SWCNT chiral index (n, m)	**Band gap (E_g) (from Experiments)**	**Bandgap (E_g) [from Empirical Eq(2) + .21 ev (correction)]**
Mod 1		
(8,4)	1.12	1.12188
(7,6)	1.11	1.099106
(9,5)	0.997	0.993731
(8,7)	0.979	0.971046
(12,2)	0.901	0.921194
(11,4)	0.904	0.909671
(10,6)	0.898	0.892977
(9,8)	0.877	0.875948
(12,5)	0.829	0.830076
(10,9)	0.797	0.800816
Mod 2		
(12,1)	1.059	1.032803

SWCNT chiral index (n, m)	Band gap (E_g) (from Experiments)	Bandgap (E_g) [from Empirical Eq(2) + .21 ev (correction)]
(11,3)	1.036	1.011597
(10,5)	0.992	0.983234
(9,7)	0.937	0.920876
(13,2)	0.949	0.94236
(12,4)	0.924	0.921005
(11,6)	0.887	0.889233
(15,1)	0.87	0.879636
(10,8)	0.841	0.847376
(13,5)	0.835	0.848461

We added this correction and found the resultant data a true reflection of experimental data. As our empirical equation followed VNL data , so same correction needs to be added to our equation also, i.e. after calculating band gap E_g from (1) using empirical γ_0 given by (2), following correction has to be added to E_g flatly to reflect the true experimental value,

$$E_g = 2\gamma_0 a_{cc} / d_t + 0.21 \text{ eV} \quad (5)$$

Interestingly, after adding this correction, we found that the calculated values of band gaps from (5) using our empirical γ_0 reflected experimental data more closely than the VNL data.

Table IV compares experimental value of band gap and calculated value of band gap from our empirical Eq (2) for 10 mod 1 type and 10 mod 2 type SWCNTs after adding the .21 ev correction. Table IV shows that after adding the correction, band gaps calculated from our empirical equation excellently become almost a replica of experimental data.

IV. Conclusions

From our analysis, in summery, we can say that band gap of a large range of semiconducting nanotubes can be calculated with good accuracy using tight-binding model of SWCNT with the nearest-neighbor approximation if the nearest-neighbor hopping parameter γ_0 is taken as a chirality (n, m) and mod(n-m, 3) dependent parameter rather than a constant or nanotube diameter dependent parameter. We also showed, there should be two different sets of γ_0 for mod 1 and mod 2 semiconducting SWCNT and presented an empirical equation to generate that two sets of γ_0. Calculated band gap using that equation of γ_0 was found to be in good agreement with VNL simulated data. Finally, it was observed that by adding a flat correction of .21 eV, our empirical equation can excellently predict experimental data.

V. Appendix

A. Derivation of the Empirical Equation

H. Yorikawa and S. Muramatsu proposed in their work [18] that band gap of SWCNT has a part which is proportional to $cos(3\theta)/R^2$ where θ and R are radius and chiral angle of SWCNT respectively. In our work, we tried to simply this term to express it as a linear combination of nanotube chiral index *n* & *m*. Our objective was to find an empirical equation directly in terms of chiral index to generate γ_0 which will be used to calculate band gap of semiconducting SWCNT.

For a (n, m) tube with chiral angle θ,

$$Cos\theta = (2n+m)/\left(2\sqrt{n^2+nm+m^2}\right). \quad (A1)$$

As, $\cos 3\theta = 4\cos^3\theta - 3\cos\theta$, after simplifying we get,

$$Cos3\theta = \left(\frac{2n+m}{2\sqrt{n^2+nm+m^2}}\right)\left\{\frac{(n+2m)(n-m)}{n^2+nm+m^2}\right\} \quad (A2)$$

Now, CNT diameter,

$$d_t = a_0\sqrt{\left(n^2+nm+m^2\right)}/\pi \quad (A3)$$

So, radius, $R = d_t/2 = a_0\sqrt{\left(n^2+nm+m^2\right)}/2\pi$ (A4)

Since E_g is proportional to $cos(3\theta)/R^2$ as suggested by [18], and γ_0 is proportional to $E_g * d_t$ as seen from (1), so γ_0 is proportional to $cos(3\theta)/R$. From (A2) and (A4), the expression of the $cos(3\theta)/R$ is

$$\frac{\cos 3\theta}{R} = \left\{\frac{(2n+m)(n+2m)(n-m)}{\left(n^2+nm+m^2\right)^2}\right\}\pi/a_0 \quad (A5)$$

Here, the highest power of n and m in nominator is 3, whereas highest power of n and m in denominator is 4. As the power of n & m in denominator is lagged by 1 than nominator, the above ratio Cos 3θ / R can be approximately made proportional to a term 1/(a.n ± b.m) where a & b are arbitrary constants to best suit the ratio. So, we can write

$$\frac{(Cos3\theta)}{(R)} \propto \left\{\frac{1}{\text{an} \pm \text{bm}}\right\} \quad (A6)$$

Constants a & b can be found by trial and error method to best suit the above ratio for different nanotubes. After trial and error, we found a = 2 and b = -1 as best fitting integer value. So,

$$\frac{(Cos3\theta)}{(R)} \propto \left\{\frac{1}{2\text{n} - \text{m}}\right\} \quad (A7)$$

This right side term is the core term that determined the shape of our empirical equation. It is the term that played the main role of adjusting proper value for γ_0 to generate the correct band gap value for SWCNT of any chirality. We formulated our final empirical equation using this term by suitably arranging other terms and constants around it in a logical manner to best fit the target data. For example, the term a_0 comes in the empirical equation to balance same term in (A5) and the multiplying factor 10 comes to set the lowest limit of the accepted range of γ_0 which is around 2.5 [as $10a_0$ = 10*.246 =2.46 ≈ 2.5]. Higher band gap value for mod 2 is ensured by incorporating the dependency of band gap on mod value k. All the terms and constants are arranged intelligently in this way from which we finally formulated following empirical equation:

$$\gamma_0 = 10a_0\left\{1+\frac{k-1}{5}+\frac{(-1)^{k-1}}{2n-m}\right\}$$

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