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Theoretical investigation of electronic bandgaps of semiconducting single-walled carbon nanotubes using semi-empirical self-consistent tight binding and *ab-inito* density functional methods

Manish K Niranjan

Department of Physics; Indian Institute of Technology, Hyderabad, TS, 502285, India

E-mail: manish@iith.ac.in

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Abstract

We perform a comprehensive theoretical study of electronic band gaps of semiconducting single-walled carbon nanotubes (SWNTs) with different sets of chiral indices using semi-empirical tight binding and density functional (DFT) based *ab-initio* methods. In particular, self-consistent extended Huckel (EH-SCF) and self-consistent Slater Koster (SK-SCF) tight binding models are used as semi-empirical methods, whereas the DFT based LDA-1/2 and Tran-Blaha (TB09) meta-GGA schemes are used as *ab-initio* methods. The calculations are performed for 1) (*n, m*) chiral SWNTs for which experimental optical gaps have been reported 2) (9, 0), (12, 0) and (15, 0) 'metallic' zigzag SWNTs for which small bad gaps have been reported 3) Pairs of SWNTs having same diameters but different chiral angles 4) (*n,* 0) zigzag SWNTs with $10 \leqslant n \leqslant 30$. From the comparison of bands gaps of tubes with same diameter, the electronic band gaps are found to vary with chiral angles with opposing trend as compared to that reported for experimental optical band gaps. This result may be expected to have important implications for self-energy corrections and/or exciton binding energies and their dependence on chiral angles. The hopping parameter γ_0 obtained from fitting EH-SCF and SK-SCF bandgap data, is found to be in good agreement with that obtained from fitting experimental data. In general, the band gap values of SWNTs computed using semi-empirical EH-SCF and SK-SCF methods are quite close (within ~ 5%) to those computed using DFT-based LDA-1/2 and TB09 meta-GGA methods. The results suggest that self-consistent semi-empirical methods can be expected to provide similar accuracy in results as that expected from more computationally challenging *ab-intio* DFT based LDA-1/2 and TB09 meta-GGA methods.

1. Introduction

Carbon nanotubes (CNTs) are highly promising materials for technological applications due to their novel electronic, optical, and mechanical properties [1–4]. In particular, CNTs are very attractive for potential applications in nanoelectronics and energy storage devices in the form of nanoscale electronic components such as 1D quantum wires, nanotransistors, optical switches etc Usually, the single-walled carbon nanotubes (SWNTs) exhibit semiconducting or metallic properties which in turn depend on their diameters and chiral angles [1, 2]. The electronic properties of SWNTs are known to critically depend on chiral indices $(n,\ m)$ (where n and m are integers). In general, a SWNT of diameter $d_t = a_{c-c}\sqrt{3(n^2 + \mathrm{nm} + \mathrm{m}^2)}/\pi$ (where a_{c-c} is the nearest neighbor carbon-carbon distance) and chiral angle $\theta = arctan(\sqrt{3}\,m/(2n + m))$ can be formed by rolling up a single graphite sheet along the chiral vector $\vec{C}_h = (n\vec{a}_1 + m\vec{a}_2)$ having chiral indices $(n,\ m)$. The simple zone-folding tight-binding model predicts that the SWNTs are metallic when $n - m = 3l$ (where l is an integer) due to bands crossing the Fermi level. In case of $n - m \neq 3l$, the SWNTs are predicted to be semiconducting with energy gaps of ~0.5 eV [1–3]. Thus, the armchair $(n,\ n)$ SWNTs are expected to be metallic. On the other hand, zigzag $(n,\ 0)$ SWNTs are expected to be semiconducting provided $n \neq 3l$ (where l

is an integer). However, in recent years, small finite band gaps ($\leqslant$0.08 eV) have been reported for (9, 0), (12, 0) and (15, 0) zigzag SWNTs grown on Au(111) substrates [5]. The electronic band gap of a CNT is an important parameter in that it critically influences its transport properties. Thus for novel CNT based device applications, the control of the electronic band gap is highly desirable. The experimental measurement of the electronic band gaps of 1D wires such as CNTs are generally nontrivial and challenging as the observed optical band gap energies include contributions of exciton binding energies [6, 7]. The exciton binding energies can be significant for the nanotubes with smaller diameters. Usually theoretical models are required to estimate exciton energies since direct measurements of these energies are generally difficult [8, 9].

In last two decades, the electronic structures and band gaps of select SWNTs have been studied theoretically using formalisms such as *ab-inito* density functional theory (DFT) and semi-empirical zone-folding tight-binding (TB) method [1–3]. However, the band gaps computed within DFT framework and using local density (LDA) and generalized gradient (GGA) approximations for the exchange-correlation (xc) functional are generally underestimated significantly. Improved estimates of band gaps of few select SWNTs have also been reported using *GW* approximation wherein many-body self-energy operator is expressed as the product between electronic Green's function (G) and the screened Coulomb interaction (W) [6, 10–13]. Though *GW* scheme usually provides band gap estimates with good accuracy, the method is hugely expensive computationally. Furthermore, care in calculations is required in order to obtain converged results [14]. The band gaps of few select SWNTs computed using DFT framework and hybrid xc-functionals have also been reported. Some of these functionals are B3LYP [15], HSE [16], TPSSh [17] etc, wherein a fraction of Hartee-Fock exact exchange is combined with different flavors of correlation functionals. Like the *GW* scheme, the hybrid functional schemes are highly expensive computationally, although they usually provide reasonably accurate predictions of electronic structures. In addition to DFT-based first-principles approaches, the electronic structures and band gaps of few select SWNTs have also been computed using semi-empirical tight binding models wherein only adjustable parameters are required and fitted to first-principles calculations or experimental results [18, 19]. However, only simple tight binding such as graphite, sp^3 and sp^3s^* models have been considered to best of our knowledge [1, 2, 18, 19]. One of the major drawbacks of these models is that the charge (potential) distribution in the system remains non-self-consistent.

The semi-empirical methods are mainly advantageous due to their low computational cost. This factor becomes significantly important when the systems such as CNTs consist very large number of atoms. Further, semi-empirical methods can provide quite accurate results when used within the domain of their application. On the other hand, *ab-initio* methods are more predictive as compared to semi-empirical methods and usually do not require prior experimental data. However, *ab-intio* density-functional theory (DFT) based approaches, in particular those based on *GW* or hybrid functional schemes, can be extremely demanding in terms of computational requirements, for systems with very large number of atoms.

In this article, we perform a comprehensive as well as comparative study of electronic band gaps of several semiconducting SWNTs using semi-empirical as well as *ab-inito* approaches. Within semi-empirical domain, we employ self-consistent extended Huckel (EH-SCF) tight binding method [20, 21] and self-consistent Slater-Koster tight binding method (SK-SCF) [22]. The EH-SCF model can be viewed as an extension of non-selfconsistent extended Huckel method wherein charge rearrangement and resulting Hartree potential is treated self-consistently. Likewise, the SK-SCF method can be viewed as extension of standard non-self-consistent Slater-Koster tight binding method. The SK-SCF method is based on the expansion of the Kohn-Sham total energy in DFT formalism, to a second order with respect to charge density fluctuations. We also compute band gaps of SWNTs within *ab-initio* density functional framework using (1) Tran Blaha meta-GGA xc-functional [23, 24] and (2) LDA-1/2 method [25, 26]. These schemes are significantly less expensive computationally as compared to *GW* and/or hybrid functional schemes. Further, excellent agreement between the experimental band gaps and those computed using these methods have been reported for a wide range of semiconductors. In the TB09 meta-GGA xc-functional scheme, the exchange potential has the explicit dependence on the electron kinetic energy. In case of LDA-1/2 (or DFT-1/2) method, the DFT self-interaction error is corrected by defining an atomic self-energy potential that cancels the electron-hole self-interaction energy. The atomic self-energy potential is defined as the difference between the potential of the neutral atom and that of a charged ion which results from the removal of its charge between 0 and 1 electrons. In this article, we perform the study of electronic band gaps of SWNTs with different sets of chiral indices using aforementioned semi-empirical and *ab-inito* methods. In particular, we consider (1) ($n.m$) chiral semiconducting SWNTs with reported experimental optical gaps (2) zigzag (9, 0), (12, 0) and (15, 0) 'metallic' SWNTs for which small band gaps have been reported experimentally (3) pairs of SWNTs with different chiral angles but having same diameters (4) (n, 0) zigzag SWNTs with diameter more than 1.0 nm and $10 \leqslant n \leqslant 30$. Our results suggest that self-consistent semiempirical (SK-SCF and EH-SCF) methods can be expected to provide electronic band gap estimates of CNTs with similar accuracy as that expected from *ab-intio* DFT based LDA-1/2 and TB09 meta-GGA methods. In particular, the band gap estimates of SWNTs obtained using semiempirical EH-SCF and SK-SCF methods are

found to be within ~5% of those obtained using *ab-intio* DFT-based (LDA-1/2 and TB09 meta-GGA) methods. The results also suggest that electronic band gaps may vary with chiral angles with reverse trend as compared to that reported for experimental optical band gaps. Furthermore, as discussed later, the small band gaps of 'metallic' (9, 0), (12, 0) and (15, 0) zigzag SWNTs computed semi-empirical (EH-SCF and SK-SCF) methods and *ab-initio* (LDA, GGA, LDA-1/2 and TB09 meta-GGA) methods are found to be in good agreement with the experiments.

The article is organized as follows. In section 2, the computational methodology is presented. The results and discussions are presented in section 3. Finally, the concluding remarks are given in section 4.

2. Computational methodology

The semi-empirical calculations are performed using self-consistent extended Huckel model (EH-SCF) [20, 21] and self-consistent Slater-Koster density-functional tight binding model (SK-SCF) [22, 27] as implemented in Atomistix Toolkit [28]. The Cerda-Hückel basis set parameters optimized to target values of the band dispersion of bulk diamond obtained with DFT-*GW* method [29] are used in EH-SCF model [28]. The matrix elements are described in terms of overlapping between the Slater orbitals on each site. The Slater-Koster type parameters from Hotbit consortium are used in SK-SCF model [30] and a numerical function is used to describe the distance-dependence of the matrix elements. In both semi-empirical models, a two-center approximation is used to parametrize the non-self-consistent part of the tight-binding Hamiltonian. Thus, the matrix elements depend on the distance between two atoms and remain independent of other atomic positions.

The *ab-intio* density functional calculations [31] are performed using scheme based on nonorthogonal pseudoatomic orbitals (PAOs) [32] basis set as implemented in the Atomistix Toolkit [28]. The Kohn-Sham wavefunctions are expanded using a basis of double-ζ PAOs including polarization functions (DZP). The ionic cores are described using the Troullier-Martins norm-conserving pseudopotentials [33]. In order to obtain better accuracy in the bang gap estimates of SWNTs, the Tran-Blaha (TB09) meta-GGA xc-functional [23, 24] is used. The magnitude of the *c*-parameter of TB09 scheme is adjusted so that the computed band gap of bulk diamond is matched to the experimental value. The improved band gaps of SWNTs are also obtained using LDA-1/2 [25, 26] scheme and using optimized parameters as provided in Atomistix Toolkit. The SWNTs with axis along [001] direction are simulated using supercells consisting appropriate number of vacuum layers in [100] and [010] direction. The $1 \times 1 \times N$ Monkhorst–Pack *k*-point meshes are used for the Brillouin zone sampling (where $N > 12$).

3. Results and discussion

We study and compute the electronic band gaps of different types of SWNTs using semiempirical (SK-SCF, ET-SCF) and *ab-initio* DFT based (LDA-1/2, TB09 meta-GGA xc-functional) methods. The tight-binding as well as DFT based LDA (GGA) approximations provide estimates of single-particle excitation energies. However, in one-dimensional (1D) systems such as SWNTs, significant difference between many-particle and single-particle electronic band gaps can arise due to strong many-body electron-electron interactions. Despite this shortcoming, the tight binding models are capable of capturing the primary features of the electronic structures of SWNTs. Furthermore, a fraction of many-body effects is usually included in the tight binding models through their fitted parameters. The many-body effects result in the modification of single-particle energies through self-energy corrections. In addition, many-body electron-hole interactions lead to bounded excitons which are revealed in optical transitions [8, 34–37]. However, it has been shown that self-energy corrections and excitonic effects, which are of the order of ~0.5–1.0 eV, tend to cancel each other. This results in significant reduction in difference between single-particle electronic and many-body optical band gaps [38–40]. Thus, partially due to this cancellation effect, the magnitude of band gaps obtained from early scanning tunnelling spectroscopy (STS) experiments [41, 42] and electronic structure calculations [43, 44] have been found to be quite similar to those obtained from optical experiments [45]. Further, recent experimental STS study has shown that observed band gaps of SWNTs on metal substrates are generally the reduced many-body gaps due to screening of many-body interactions by metal substrate [45]. On the basis of two-photon experiments, it has been suggested that after accounting for many-body self-energy corrections, the single-quasiparticle gap (E_{11} in eV) as s function of tube diameter (d_t in *nm*) may be expressed as [8]:

$$E_{11} = E_0 + \Delta E = \frac{1.11}{0.11 + d_t} + \frac{0.34}{d_t} \tag{1}$$

where, the E_0 and $\Delta E \sim \frac{0.34}{d_t}$ in equation (1) are approximately single-particle and the many-body self-energy contributions to the gap respectively. Further, on the basis of optical measurements, it has been suggested that

$E_0 \sim \frac{1.11}{0.11 + d_t}$ and $\Delta E \sim \frac{0.34}{d_t}$ are the measure of optical gap and lowest exciton binding energy respectively [44]. The excitons with significant electron-hole binding energy in the excited states arising due to many-body interactions are important in one dimensional systems such as SWNTs [46–48]. Using a simple zone-folding tight-binding (TB) model, the single-particle electronic band gap (E_{11}^{TB} in eV) of SWNTs may be shown to vary with nanotube diameter (d_t in nm) as [1, 2]:

$$E_{11}^{TB} = 2\gamma_0 a_{c-c}/d_t \tag{2}$$

where γ_0 is the hopping integral between the first-nearest carbon neighbors, $a_{c-c} = 1.42$ Å is the distance between neighboring carbon atoms. A magnitude of 2.5 eV to 2.9 eV for γ_0 has been suggested in the various published reports [3, 41, 49]. For instance, $\gamma_0 = 2.7 \pm 0.1$ eV has been suggested from the scanning tunnelling microscopy and spectroscopy measurements on individual SWNTs [41]. Further, a theoretical estimate of $\gamma_0 = 2.5$ eV has been suggested for a single graphene sheet [48]. As can be seen in equation (2), the simple zone-folding tight-binding model does not predict the dependence of the band gap on chiral angle (θ) of the nanotube. However, it has been shown that the weak dependence of the optical band gap on the chiral angle of the tube with chiral indices (n, m) may be expressed as [36]:

$$E_{11}^{op} = \frac{1.163}{0.147 + d_t} + \frac{A_{1(2)}\cos(3\theta)}{d_t^2} \tag{3}$$

Where $A_1 = -0.0880$ eV if $(n - m) mod\ 3 = 1$ and $A_2 = +0.0458$ eV if $(n - m) mod\ 3 = 2$. A slightly modified form of equation (3) has been reported in [7]. As discussed in following sections, the dependence of band gaps on chiral angles in our calculations is captured due to the application of self-consistency in tight binding models which is not considered in simple zone-folding tight binding model.

3.1. (*n, m*) Chiral nanotubes

We first consider a set of 34 chiral nanotubes for which experimental band gaps have been reported. Figure 1 shows the atomic structure of chiral SWNTs with indices (15, 4) and (10, 9). The magnitude of chiral vector (diameter) for (15, 4) and (10, 9) SWNTs are 7.39 nm (1.36 nm) and 7.02 nm (1.29 nm) respectively. The number of atoms in one unit cell are 1204 and 1084 for (15, 4) and (10, 9) tubes respectively. The electronic band gaps of SWNTs computed using semi-empirical EH-SCF and SK-SCF as well as reported experimental optical band gaps are listed in table 1. As mentioned earlier, the computed single-particle electronic gaps are expected to be smaller than the experimental optical gaps since many-body interactions are not fully accounted in tight-binding based semi-empirical models. As can be seen in table 1, the band gap estimates computed using EH-SCF and SK-SCF models are smaller by ~0.2–0.3 eV and are in qualitative agreement with average magnitude of lowest exciton binding energy (~0.3–0.4 eV) reported for SWNTs [36, 45]. By fitting data (see table 1) for tubes having diameters greater than 1.0 nm with analytical expression for band gap in equation (2), the computed value of hopping parameter γ_0 comes out to be 2.77 eV and 2.57 eV for EH-SCF and SK-SCF models respectively. These values are in good agreement with reported value $\gamma_0 = 2.7 \pm 0.1$ eV which is obtained from fitting experimental band gap data [41].

Next we study the dependence of SWNTs band gaps on chiral angles. The computed difference in electronic band gaps (δE) of seven pairs of SWNTs with same diameter but different chiral angles are shown in table 2. The band gaps are calculated using semi-empirical (EH-SCF and SK-SCF) and DFT based *ab-initio* (TB09 meta-GGA and LDA-1/2) methods. Table 2 also shows reported experimental optical band gaps as well as estimates obtained using equation (3). It may be noted from results presented in table 2 that the computed absolute values of band gap differences (δE) are in reasonable agreement with experimental values. However, the computed δE values are positive whereas experimental values are negative. These results suggest that constants $A_1(A_2)$ in equation (3) have plus (minus) signs respectively in case of electronic band gaps as compared to minus (plus) signs as in case optical band gaps. Thus the dependence of electronic band gap on chiral angles may exhibit opposite trend as compared to that in case of optical band gaps.

3.2. 'Metallic' (3 m, 0) Zigzag SWNT ($m = 3, 4, 5, 6, 7$)

Next we study the band gaps of zigzag SWNTs with chirality indices ($3m$, 0) (where m is a integer). Figure 1(c) shows the (21, 0) zigzag SWNT with diameter 1.64 nm and chiral vector 0.43 nm. As discussed earlier, the simple (sp^3) or zone-folding tight-binding model predicts that zigzag ($3m$, 0) SWNTs should be metallic with high electrical conductivity [43, 44, 50]. However, small energy gap may still result in these zigzag ($3m$, 0) and some other chiral SWNTs due to finite curvature which in turn modifies the overlap of π-orbitals. Recently, on the basis of low-temperature atomically resolved scanning tunneling microscopy, it has been reported that 'metallic' zigzag SWNTs with indices (9, 0), (12, 0) and (15, 0) are small-gap semiconductors with energy band gaps 0.080 eV, 0.042 *eV* and 0.029 *eV* respectively [5]. We have computed the electronic gaps of these SWNTs using semi-empirical and *ab-initio* methods. As shown in table 3 the band gaps of (9, 0), (12, 0) and (15, 0) zigzag SWNTs computed using semi-empirical EH-SCF (SK-SCF) models are 0.11 eV (0.11 eV), 0.07 eV (0.06 eV) and

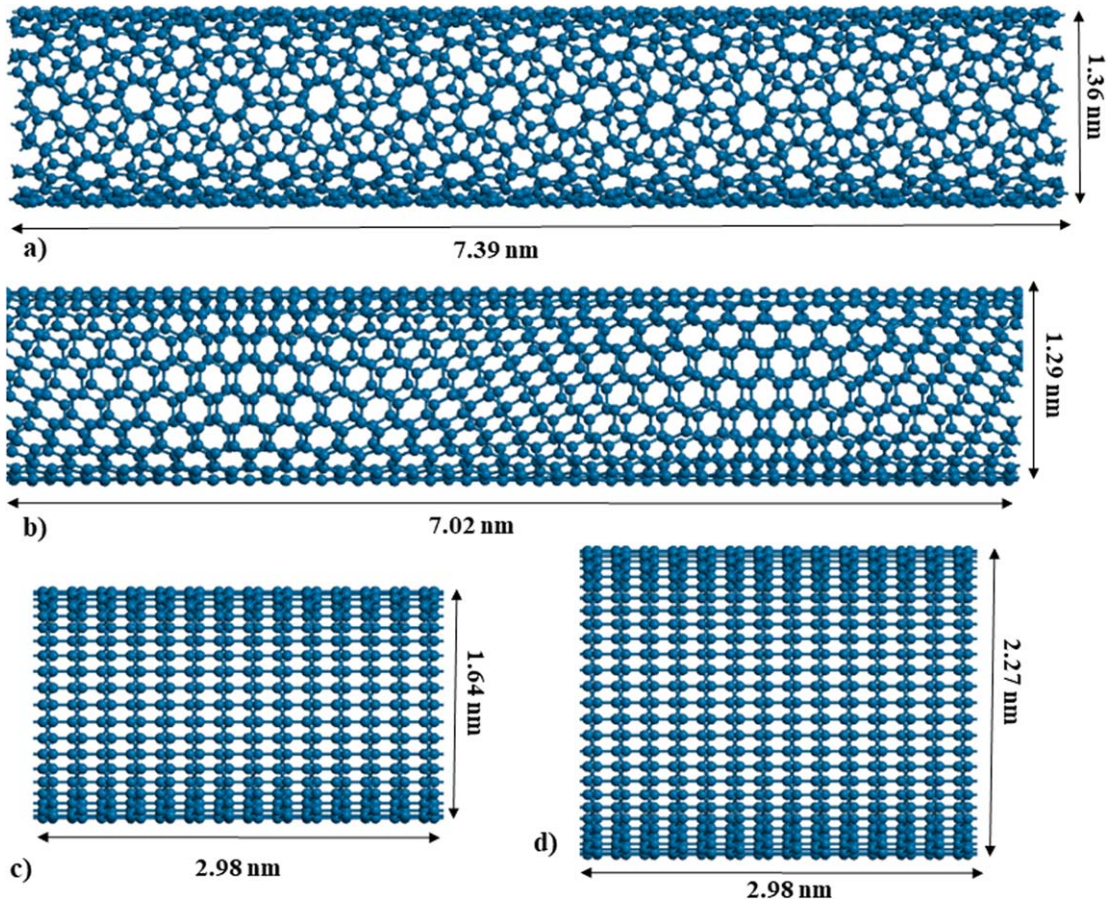

Figure 1. Single walled carbon nanotubes (SWNTs) with chiral indices (a) (15, 4) (b) (10, 9) (c) (21, 0) (d) (29, 0). The length shown is equal to 1 $\times$ C_h for (15, 4) and (10, 9) SWNTs and 7 $\times$ C_h for (21, 0) and (29, 0) SWNTs respectively (where C_h is the chiral vector). The number of carbon atoms in single unit cell of (15, 4), (10, 9), (21, 0) and (29, 0) SWNTs are 1204, 1084, 84 and 116 respectively.

0.05 eV (0.04 eV) respectively. As can be seen, these band gap values computed using semi-empirical self-consistent tight-binding models are in good agreement with experiments. Further, as listed in table 3, the band gaps computed using LDA (PBE-GGA) xc-functionals are 0.084 eV (0.093 eV), 0.052 eV (0.058 eV) and 0.035 eV (0.039) eV. The computed LDA and GGA values are also in good agreement with experimental values. It may be noted that the band gap values computed using LDA and GGA for (9, 0), (12, 0) and (15, 0) zigzag SWNTs are in much better agreement with experiments than those reported in earlier *ab-inito* studies. Previous LDA (PBE-GGA) based studies have reported band gaps 0.024 eV (0.030 eV) for (9, 0), 0.002 eV (0.010 eV) for (12, 0), and 0.00 eV (0.00 eV) for (15, 0) SWNTs [51–53]. Using DFT based B3LYP hybrid functional studies, the computed band gaps for (9, 0), (12, 0) and (15, 0) SWNTs were found to be 0.079 eV, 0.041 eV and 0.036 eV respectively [53], in good agreement with experiments. However, as mentioned earlier, the hybrid functional studies are usually very expensive computationally, in particular for systems having large number of atoms. Table 3 also shows the band gap results computed using DFT based LDA-1/2 and TB09 meta-GGA xc-functional methods. As stated earlier, the TB09 meta-GGA and LDA-1/2 methods are much less expensive computationally as compared to *GW* or hybrid functional methods. The computed band gaps are slightly higher than the experimental values (see table 3). Nevertheless, both methods show that (9, 0), (12, 0) and (15, 0) SWNTs are semiconducting with low band gaps. Further, the semi-empirical EH-SCF and SK-SCF methods provide band gap estimates of SWNTs with similar accuracy as compared to band gaps computed with *ab-initio* TB09 meta-GGA and LDA-1/2 methods. The band gaps of $(3m,\ 0)$ zigzag SWNTs listed in table 3 vary with diameter (d_t) as $\sim 1/d_t^2$ in accordance to the model suggested by Ouyang *et al*, [5]. According to this model the small energy gaps of 'metallic' zigzag tubes should scale as $\sim A_0/d_t^2$ with $A_0 = 3\gamma_0 a_{c-c}^2/4$ where γ_0 is tight binding transfer matrix element and $a_{c-c} = 0.142$ nmis the distance between nearest neighbor carbon atoms. It has been suggested that finite curvature of the nanotube reduces the overlap between nearest-neighbor π-orbitals resulting in a shift of Fermi wave vector $(\vec{k}_F)$ from the first Brillouin zone corner (K-point) of a 2D graphene sheet. In case of 'metallic' zigzag $(3m,\ 0)$ SWNTs, the Fermi wave vector moves away from the K-point along the circumferential direction in a way that the allowed one-dimensional sub-band $\vec{k}$ no longer passes through Fermi wave vector which results in a small band gap opening [5].

Table 1. Electronic band gaps (in eV) of chiral *(n, m)* SWNTs computed using semiempirical self-consistent SK-SCF and EH-SCF methods. d_t (in nm) is the diameter.

(n, m)	d_t (nm)	SK-SCF	EH-SCF	Exp.[a]
(5, 4)	0.612	1.218	1.289	1.488
(6, 4)	0.683	1.051	1.141	1.42
(6, 5)	0.747	0.999	1.067	1.272
(9, 1)	0.747	0.891	0.992	1.359
(8, 3)	0.772	0.896	0.986	1.300
(9, 2)	0.795	0.943	1.003	1.088
(7, 5)	0.818	0.886	0.960	1.212
(8, 4)	0.829	0.910	0.974	1.114
(7, 6)	0.883	0.844	0.910	1.105
(9, 4)	0.903	0.780	0.854	1.126
(11, 1)	0.903	0.832	0.894	0.982
(10, 3)	0.924	0.817	0.879	0.992
(8, 6)	0.953	0.765	0.832	1.058
(9, 5)	0.963	0.782	0.844	0.997
(12, 1)	0.982	0.696	0.765	1.059
(11, 3)	1.000	0.695	0.761	1.036
(8, 7)	1.018	0.731	0.792	0.979
(12, 2)	1.027	0.735	0.794	0.901
(10, 5)	1.036	0.689	0.752	0.992
(11, 4)	1.054	0.717	0.776	0.904
(9, 7)	1.088	0.672	0.732	0.937
(10, 6)	1.097	0.685	0.742	0.898
(13, 2)	1.105	0.627	0.687	0.949
(12, 4)	1.130	0.624	0.682	0.924
(9, 8)	1.154	0.644	0.700	0.877
(13, 3)	1.154	0.655	0.711	0.828
(11, 6)	1.170	0.615	0.670	0.887
(12, 5)	1.185	0.636	0.692	0.829
(15, 1)	1.216	0.571	0.623	0.87
(10, 8)	1.224	0.599	0.652	0.828
(13, 5)	1.261	0.564	0.616	0.837
(10, 9)	1.290	0.575	0.626	0.797

[a] Ref. [36]

Table 2. Electronic band gap differences (in eV) of *(n, m)* SWNTs having same diameters but different chiral angles computed using semi-empirical, self-consistent (SK-SCF and EH-SCF) methods; DFT-based (LDA, PBE-GGA, LDA-1/2 and TB09 meta-GGA) methods.

	SK-SCF	EH-SCF	LDA	GGA	LDA-1/2	TB09- m-GGA	Exp.[a]	equation (3)
$E_{(6,5)} - E_{(9,1)}$	+0.108	+0.075	+0.094	+0.090	+0.091	+0.108	−0.087	−0.104
$E_{(11,1)} - E_{(9,4)}$	+0.051	+0.041	+0.073	+0.061	+0.053	+0.068	−0.144	−0.139
$E_{(13,0)} - E_{(8,7)}$	+0.009	+0.008					—	−0.075
$E_{(10,6)} - E_{(14,0)}$	+0.058	+0.054					—	−0.031
$E_{(13,3)} - E_{(9,8)}$	+0.011	+0.011	+0.018	+0.016	+0.013	+0.016	−0.049	−0.050
$E_{(11,7)} - E_{(14,3)}$	+0.040	+0.041					—	−0.048
$E_{(11,9)} - E_{(15,4)}$	+0.019	+0.020					—	−0.016

[a] [36].

3.3. Semiconducting $(n, 0)$ Zigzag SWNTs ($n \neq 3m$)

Next, we compute the band gaps of semiconducting $(n, 0)$ zigzag SWNTs (where $n \neq 3m$ is a integer). Figure 1(d) shows the (29, 0) zigzag SWNT with diameter 2.27 nm and chiral vector 0.43 nm. The computed electronic band gaps of $(n, 0)$ nanotubes with $10 \leqslant n \leqslant 30$ are listed in table 4. The estimated band gap values using EH-SCF method are slightly higher by ~0.03–0.05 eV than those estimated using SK-SCF method. Further the band gap values computed using *ab-initio* LDA-1/2 method are lower by ~0.02–0.08 eV than those obtained using semi-empirical SK-SCF and EH-SCF methods. On the other hand, the band gap values computed using *ab-initio* TB09 meta-GGA method are slightly higher by 0.02–0.08 eV than those obtained using EH-SCF and SK-SCF methods. It may be noted that bandgap values computed using *ab-initio* LDA-1/2 and TB09 meta-GGA

Table 3. Electronic band gaps (in eV) of zigzag 'metallic' (3*m*, 0) SWNTs computed using semiempirical, self-consistent (SK-SCF and EH-SCF methods); DFT-based (LDA, PBE-GGA, LDA-1/2 and TB09 meta-GGA) methods.

(3m, 0)	SK-SCF	EH-SCF	LDA	GGA	LDA-1/2	TB09-m-GGA	Exp.[a]
(6, 0)	0.18	0.00	0.00	0.00	0.00	0.00	—
(9, 0)	0.110	0.117	0.084	0.093	0.118	0.141	0.080
(12, 0)	0.066	0.078	0.053	0.058	0.076	0.078	0.042
(15, 0)	0.043	0.056	0.036	0.039	0.051	0.056	0.029
(18, 0)	0.031	0.032	—	—	—	—	—
(21, 0)	0.016	0.018	—	—	—	—	—

[a] Ref. [5].

Table 4. Electronic band gaps (in eV) of zigzag semiconducting (n, 0) SWNTs (where $n \neq 3m$) computed using semiempirical, self-consistent (SK-SCF and EH-SCF) methods; DFT-based (LDA, PBE-GGA, LDA-1/2 and TB09 meta-GGA) methods.

(n, 0)	SK-SCF	SCF-ETH	LDA-1/2	TB09 m-GGA
(10, 0)	0.95	1.04	0.93	1.07
(11, 0)	0.86	0.94	0.84	0.96
(13, 0)	0.740	0.800	0.721	0.825
(14, 0)	0.628	0.689	0.607	0.692
(16, 0)	0.603	0.657	0.590	0.675
(17, 0)	0.524	0.572	0.507	0.582
(19, 0)	0.508	0.556	0.497	0.573
(20, 0)	0.450	0.490	—	—
(22, 0)	0.438	0.480	—	—
(23, 0)	0.394	0.429	—	—
(25, 0)	0.385	0.421	—	—
(26, 0)	0.350	0.382	—	—
(28, 0)	0.343	0.376	—	—
(29, 0)	0.315	0.344	—	—

methods are quite close and are within ~0.02 eV to those obtained using semi-empirical (SK-SCF and EH-SCF) methods. In order to extrapolate band gap of tubes with larger diameter, we fit the data shown in tables 1 and 4 for tubes with diameter greater than 1.0 nm, with simple relation $E_{11} = a/d_t$. The computed value of parameter a is found to be 0.795 and 0.729 eV-nm using EH-SCF and SK-SCF respectively. The computed value of a is smaller than that suggested from fitting experimental optical bandgap data (~1 eV).

4. Conclusion

Electronic band gaps of semiconducting single-walled carbon nanotubes (SWNTs) with different sets of chiral indices are investigated using semi-empirical tight binding and density functional (DFT) based *ab-initio* methods. The self-consistent extended Huckel (EH-SCF) and self-consistent Slater-Koster (SK-SCF) tight binding schemes are used as semi-empirical methods, whereas DFT based LDA-1/2 and Tran Blaha (TB09) meta-GGA schemes are used as *ab-initio* methods. The electronic bad gaps are calculated for four different sets of SWNTs viz. (1) (n, m) chiral nanotubes for which experimental optical gap data is available 2) ($3m$, 0) 'metallic' zigzag nanotubes ($m = 3, 4, 5$) for which small band gaps have been reported (3) nanotubes with same diameter but different chiral angles 4) ($n \neq 3m$, 0) zigzag semiconducting nanotubes with diameter greater than 1 *nm* and $10 \leqslant n \leqslant 30$. The results suggest that the electronic band gaps of SWNTs vary with chiral angles with opposing trend as compared to that reported for experimental optical band gaps. This in turn suggest interesting implications for exciton binding energy dependence on chiral angles. By fitting data obtained using EH-SCF and SK-SCF methods and to the equation (zone-folding tight binding model) $E_{11}^{TB} = 2\gamma_0 a_{c-c}/d_t$, the hopping parameter γ_0 is computed to be 2.77 eV and 2.57 eV respectively. These computed values of γ_0 are in good agreement with that obtained from fitting experimental data ($2.7 \pm 0.1\ eV$). The electronic band gaps obtained using semi-empirical ET-SCF and SK-SCF methods are found to be smaller by ~0.2–0.3 eV than reported experimental optical gaps. The low band gaps of 'metallic' (9, 0), (12, 0) and (15, 0) zigzag nanotubes computed using semi-empirical (EH-SCF, SK-SCF) and *ab-initio* (LDA-1/2, TB09 meta-GGA) schemes are found to be in good agreement with the experimental values. Moreover, the band gaps of these 'metallic' zigzag

SWNTs computed using *ab-intio* LDA and GGA-PBE xc-functional methods are found to be in excellent agreement with experiments and may be partially attributed to cancellation of errors in both LDA and GGA. Overall, the electronic band gaps computed using semiempirical EH-SCF and SK-SCF methods are found to be within ~5% to those computed using DFT-based LDA-1/2 and TB09 meta-GGA methods. The results suggest that self-consistent semi-empirical methods can be expected to provide accuracy comparable to that expected from more computationally expensive *ab-intio* DFT based LDA-1/2 and TB09 meta-GGA schemes.

ORCID iDs

Manish K Niranjan https://orcid.org/0000-0002-4417-5107

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