

# Ab Initio Study of the Electronic and Vibrational Properties of 1-nm-Diameter Single-Walled Nanotubes

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## ABSTRACT

The electronic structure, band gap, density of states of the (8,8), (14,0) and (12,3) single-walled carbon nanotubes by the SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) method in the framework density-functional theory (DFT) with the generalized gradients approximation (GGA) were studied. Also, we studied the vibrational properties of the (8,8) and (14,0) nanotubes. Only the calculated relaxed geometry for (12,3) nanotube show significant deviations from the ideal rolled graphene sheet configuration. The electronic transition energies of van Hove singularities were studied and compared with previous results. The calculated band structures, density of states and dispersion curves for all tubes were in good agreement with theoretical and experimental results.

**Keywords:** Carbon Nanotubes; Electronic Structure; Dispersion Curve

## 1. Introduction

Carbon nanotubes can be regarded as graphitic cylinders generated just by rolling one sheet of graphene with a finite width [1]. Also it is known that a nanotube can be metallic or semiconducting depending on their diameter and chirality [2-4]. In recent years, it has attracted great attention in many fields of science and technology because of its novel and unique structural and electronic properties [5]. Nanotubes are promising for applications, such as probes and sensors; tips for atomic force microscopy, gas sensors, biosensors and physical sensors [6].

There has been much theoretical and experimental work on the vibrational and electronic properties of carbon nanotubes. The first theoretical calculation of SWCNT's electronic structure was carried out using zone folding scheme [7,8]. Within this framework, all the armchair nanotubes (n,n) are expected to be metallic, while approximately one third of zigzag (n,0) and chiral (n,m) tubes should be metallic, with remainder being semiconducting [3,4]. The zone-folding scheme in general works reasonably well and has proven immense success in providing physically relevant information on the nature of electronic and vibrational interactions in carbon nano-

tubes [9,10]. However, previous studies show the effects of the  $\sigma$ - $\pi$  hybridization in small diameter SWCNT's on their electronic properties [11,12]. An example of particular importance is the (5,0) nanotube which has been demonstrated by *ab initio* (using local density approximation in the framework of the density-functional theory) and symmetry-adapted non-orthogonal tight-binding calculations to be a metal [12-14] but not a semiconductor with a moderate gap as reported in the previous  $\pi$ -band tight-binding work [2,3].

The phonon dispersion curves over the full Brillouin zone are useful in such fields as the inelastic neutron scattering [15], Second-order Raman spectroscopy [16], double-resonance processes [17-20] and the electron-phonon interactions [21-24]. The calculations of the phonon dispersions have been made using both empirical methods and the accuracy *ab initio* calculations. Initial work on this problem using zone folding and force constant models [9,25-27] shows that the zone-folding method has two shortcomings: the structural relaxation effect has been completely ignored which makes the transferability of the phonon spectra between the graphene and the SWCNT's a serious question and that the vibrational eigenvectors are also different from the graphene to the SWCNT's. The *ab initio* phonon dispersion is

advantageous because such calculations do not depend on any predefined parameter. There are different authors that have reported *ab initio* phonon dispersion of SWCNT's, all using the supercell approach [11,28,29].

One way to study the structural and mechanical properties of carbon nanotubes is by applying hydrostatic pressure. A recent study shows that in DWCNT's the outer tube acts as a protection shield for the inner tube (at least up to 11 GPa) [30,31]. This means that the inner tube retains its properties as single-walled nanotube. In Figures 5 and 6 of Ref. [30], the Raman spectrums of the radial breathing modes (RBM) of the inner and the outer shells of pristine and filled DWCNT's have been observed, respectively. In both in pristine or Te-filled DWCNT's tubes with diameters around 1 nm for the inner tubes of DWCNT's are presented.

In this paper, we present first-principles calculations of the structural, electronic, and vibrational properties of SWCNT's about 1 nm in diameter to address the point mentioned above. We will discuss the relaxed geometry of the (8,8), (14,0) and (12,3) nanotubes comparing it to the ideal cylindrical configuration. We also examine the importance of the detailed structure in discussing electronic properties of nanotubes. Finally, we discuss about phonon dispersion curves for the (8,8) nanotube.

## 2. Computational Method

Our first-principles calculations are based on density functional theory (DFT) employ a numerical-atomic-orbital basis set. We used the package SIESTA *ab initio* simulation package [32]. We worked within the gradient generalized approximation (GGA) as parametrized by Perdew-Burke-Ernzerhof (PBE) [33]. The core electrons were replaced by pseudopotentials of the type Troullier-Martins [34], the valence electrons were described by localized pseudo-atomic orbitals [35]. The valence electrons were described by a double- $\zeta$  polarized basis set with a cutoff radius of 4.99 a.u. for the s and 6.25 for the p and the polarizing d orbitals, as is determined from an energy shift of 50 meV by localization. These values have been tested by M. Machón *et al.* [12]. They found that an increasing of the cutting of the orbitals only produces changes in the total energies less than 0.1 meV/atom and none significant effect neither on the structure nor on the energies of electronic states was observed. The dynamical matrix was found by a finite-difference approach, this is, calculating the Hellman-Feynmann forces for displaced atoms.

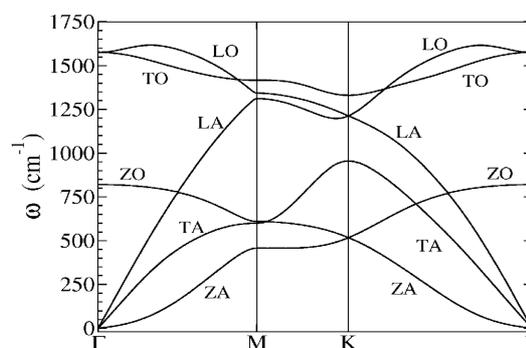
Calculations were performed for the following tubes: (8,8), (14,0) and (12,3). They were all considered as isolated. For that purpose, we used periodic-boundary conditions on supercell geometry with sufficient lateral separation among neighboring tubes. For the purpose of sampling the Brillouin zone in the direction of the tube

axis, as well as for the computation of the force-constant matrix for phonon calculations, we used supercells consisted of five unit cells for the armchair (8,8) tube with 160 atoms and three unit cells for zigzag (14,0) tube with 162 atoms. The supercell length (about 1 nm) in the tube-axis direction is not too different from one another. We are aware that the supercell should be large enough so that the effect of the image displacement is negligible [11].

## 3. Results and Discussion

### 3.1. Dispersion Curve of Graphene

In **Figure 1** we show the phonon frequencies of graphene calculated from first principles. This will serve as a test of accuracy of the calculation method. In general, a good agreement between our calculations and experiment (see Ref. [36]) for the TO, LO and LA branches is found. This shows the accuracy of the basis set used in this work. We optimized the bond length of a graphene sheet in a supercell with the interlayer distance being 10 Å, which can be considered enough to neglect the interlayer interaction. The bond length of graphite obtained by this optimization is 1.437 Å, which is 1.5% higher than the experimental value (1.416 Å) [37]. The small splitting of the LO and LA phonons at the M point equal to 33  $\text{cm}^{-1}$  coincides with the experimental value reported by inelastic x-ray scattering [36]. While, our calculated splitting between TO and LA modes at the K point 118  $\text{cm}^{-1}$  is different from experimental value 71  $\text{cm}^{-1}$ . Other theoretical values have been reported; Pavone *et al.* [38] obtained a splitting of 120  $\text{cm}^{-1}$  and a value of 140  $\text{cm}^{-1}$  by using LDA was also reported [28]. The zone center phonon value 1575  $\text{cm}^{-1}$  is slightly below the experimental values for graphite and grapheme (1582  $\text{cm}^{-1}$ ) measured recently [39]. These differences can be explained by taking into account that other authors have estimated uncertainties of 10  $\text{cm}^{-1}$  for the frequencies higher than 1300  $\text{cm}^{-1}$  [11,40].

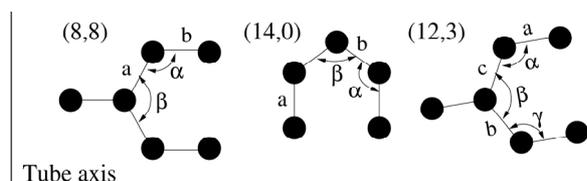


**Figure 1.** *Ab initio* calculations of the phonon dispersion of graphene. We used a supercell with 98 atoms. The mesh cutoff was 350 Ry, with 3321  $k$  points and a 50 meV PAO energy shift.

### 3.2. Geometries and Electronic Band Structure of Nanotubes

The closed distances between atoms on different tubes being as long as 10 Å; to suppress sufficiently the inter-tube interaction. We completely optimized the atomic positions of atoms by using the conjugate-gradient (CG) method. We also optimized the length of the unit cell along the axes of the tubes by changing the lattice constant ( $c$ ) along the tube axis. The atomic positions were relaxed until the forces on the atoms were less than 0.04 eV/Å.

For the relaxed structure we calculated the theoretical lattice constant. In **Table 1** are shown the results of geometry parameters (**Figure 2**) relaxed together with the parameters corresponding to the ideal cylindrical geometry obtained by rolling up the graphene plane. To determine the magnitude of the translation vector ( $T$ ) we used the values 1.44 Å and 1.437 Å for ideal cylindrical geometry and relaxed geometry, respectively. Hence, we find that the lattice constant of the nanotubes in the direction of the tube axis ( $z$ ) changed by less than 0.3% during the relaxation, in agreement with the trend indicated by Machón *et al.* [12]. Also, the bonds and angles in the direction of the tube axis and in the direction of the circumference for the (8,8) and (14,0) nanotubes changed by less than 0.3% with respect to the ideal structure. Nevertheless, the bonds  $c$  and  $a$  for the (12,3) nanotube experience changes by up to 10%. In the (12,3) nanotube the bonds and angles tend to form a perfect hexagon for the relaxed geometry and the sum of their three bond angles is always smaller than 360° for all tubes.



**Figure 2.** Geometry parameters of the 1-nm-diameter nanotubes.

**Table 1.** Geometry parameters for the ideal (i) rolled graphene sheet and for the relaxed (r) configuration. The parameters are defined as in Figure 2.  $T$  is the lattice constant.

	$T$ (Å)	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\alpha$	$\beta$	$\gamma$
(8,8)-R	2.49	1.437	1.436		119.4	120.0	
(8,8)-I	2.49	1.437	1.433		119.3	120.0	
(14,0)-R	4.32	1.436	1.438		120.2	118.5	
(14,0)-I	4.31	1.437	1.435		120.1	118.7	
(12,3)-R	6.59	1.438	1.439	1.436	120.0	120.0	118.7
(12,3)-I	6.59	1.389	1.335	1.597	112.5	115.9	130.0

In **Table 1**, we observe that the values of the relaxed bond lengths are approximately the same for three nanotubes. Imtani & Jindal found three equal bond lengths and three unequal bond angles in the structure of different chiral tubes [41]. It is in agreement with the relaxed bond length for the chiral tube (12,3). However, is in disagreement with calculations obtained by Jiang *et al.* [42], they found three unequal bond lengths in the structure of chiral (4,2) and (9,3) tubes. According to [41], these differences were attributed to the unsatisfactory reproduction of the graphite sheet bond length (1.42 Å) from the beginning. On the other hand, Jiang *et al.* have also found three unequal bond angles in the structure of chiral (4,2) and (9,3) tubes. They obtained a value of  $\beta$  larger than the ideal value and the other two bond angles are smaller. Imtani & Jindal found three unequal bond angles in the structure of different chiral tubes. Our results show bond angles very close to 120° for any nanotubes. We think that these differences could be related to the radius of the nanotubes, *i.e.* our nanotubes do not show effects of confinement.

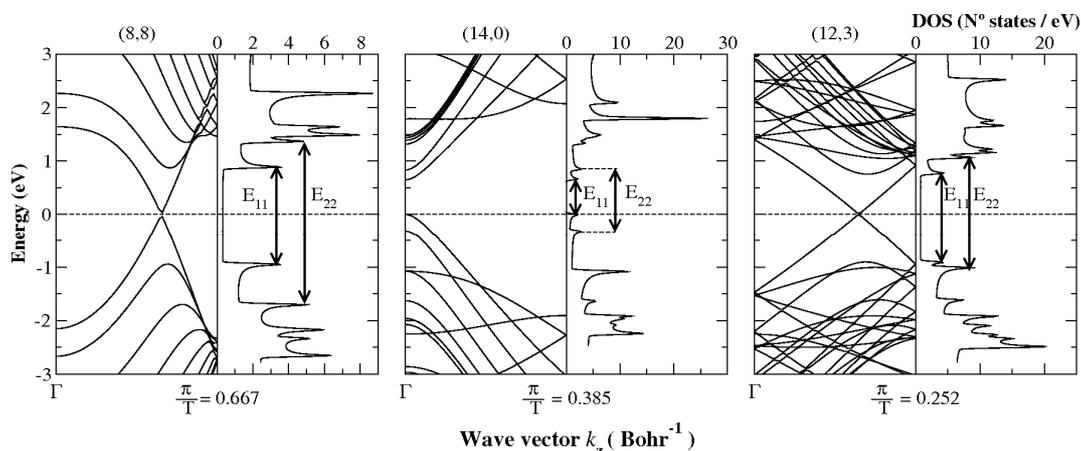
The electronic band structures were calculated using the relaxed geometries obtained above. The band structures obtained are given in **Figure 3**. The density of states for the (8,8) and (12,3) tubes shown a metallic character. This metallic character of both nanotubes is in good agreement with the classification as metal 2p reported by Saito *et al.* [4]. Experimental results also confirm the theoretical predictions about the metallicity of the nanotube (8,8). Ouyang *et al.* [43] have reported the tunneling spectrum of (8,8) nanotubes in bundles and isolated. They have finding a gap-like feature at  $E_F$  that is not present in spectra of the isolated (8,8) armchair, in good agreement with our result. Also, an *ab initio* calculation recent on a armchair (7,7) nanotube (using full potential-linearized augmented plane wave (FP-LAPW) in the GGA approximation) shown that it is a metallic nanotube with zero band gap and with the valence and conduction bands cross each other at the Fermi level [44], just as is observed in **Figure 3** for (8,8) and (12,3) nanotubes.

The nanotube (14,0) is clearly a semiconductor material with a direct energy gap, as expected. This is consistent with previous results obtained from *ab initio* code VASP [45] and with the classification as semiconductor type I given by Saito *et al.* [4].

In the Tight-Binding/Zone-Folding method, the transition energies between van Hove singularities in the electronic density of states is related to the diameter of the tube by

$$E_{ii} = 2n\gamma_0 a_{cc}/d \quad (1)$$

where  $\gamma_0 = 2.9$  eV is the overlapping integral and



**Figure 3.** Calculated electronic band structures and DOS of the relaxed SWCNT's. The Fermi level is at 0 eV. One thousand  $k$  points for (8,8) nanotube and five thousand  $k$  points for (14,0) and (12,3) nanotubes were employed and the mesh cutoff was at 1600 Ry for (8,8) nanotube and at 1200 Ry for (14,0) and (12,3) nanotubes.

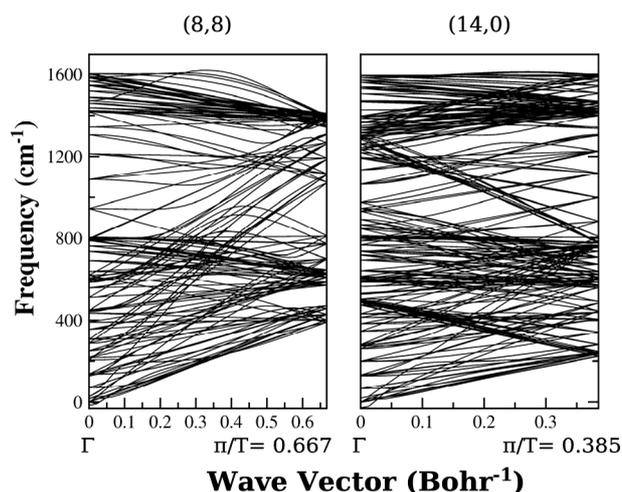
$a_{cc} = 1.437$  Å (Table 1) is the carbon-carbon distance mean of the nanotubes. The integer  $n$  has the values 1, 2, 4, 5 ... for the transitions  $E_{11}$ ,  $E_{22}$ ,  $E_{33}$ ,  $E_{44}$ , of the semi-conducting tubes, respectively, and 3, 6, ... for the transitions  $E_{11}$ ,  $E_{22}$ , of the metallic tubes, respectively [46].

In Table 2 are shown electronic transition energies ( $E_{ii}$ ). In this table is observed that the calculated values for the gap energy ( $E_g$ ) are in good agreement with the previous report. On the contrary, the values for energies  $E_{11}$  and  $E_{22}$  differ from values reported using different techniques. The energies  $E_{ii}$  obtained from Zone-Folding (Z-F) and Resonance Raman Spectroscopy (RRS) are based in Tight-Binding approximation [46,47]. Thus, the differences between our results and those obtained by Z-F or RRS are due to the type of approximation used for calculations of the energies  $E_{ii}$ , i.e. Tight-Binding or Density Functional Theory. On the other hand, they find that the experimental values 1.45 and 2.73 eV for the (8,8) nanotube shown in [43] are below our values. Although, even the approach used is better than those obtained by other methods, it does not reproduce well the valence bands in the electronic band structure. This is a problem inherent in all DFT-based methods.

The Figure 4 shows phonon dispersion curves of (8,8) and (14,0) nanotubes. The phonon-dispersion curve for (10,10) nanotube reported by Ye *et al.* [29] is very similar to the nanotube (8,8). And also, the dispersion curve of (14,0) zigzag tube is in good qualitative agreement with a dispersion curve for the (11,0) nanotube reported in [29]. According to group theory there are eight modes Raman active for an armchair carbon nanotube, with symmetries and number of optically active phonon modes given by [48]:

$$\Gamma(R) = 2A_{1g} \otimes 2E_{1g} \otimes 4E_{2g}, \quad (2)$$

$$\Gamma(IR) = 3E_{1u}. \quad (3)$$



**Figure 4.** Phonon dispersion curves. We have used a supercell with 160 atoms for the (8,8) nanotube and 162 atoms for the (14,0) nanotube. Seventy-five  $k$  points for (8,8) nanotube and fifty  $k$  points for (14,0) and (12,3) nanotubes were employed and the mesh cutoff was at 350 Ry for all nanotubes.

**Table 2.** Energy-gap values and electronic transitions energies values.

	$E_g$ (eV)		$E_{11}$ (eV)		$E_{22}$ (eV)	
	Our	Rep.	Our	Rep.	Our	Rep.
(8,8)	0.00	0.00 <sup>c</sup>	1.84	2.28 <sup>a</sup> 2.22 <sup>b</sup> , 1.45 <sup>d</sup>	3.08	4.56 <sup>a</sup> 2.73 <sup>d</sup>
(14,0)	0.67	0.62 <sup>c</sup>	0.67	0.76 <sup>a</sup>	1.16	1.51 <sup>a</sup>
(12,3)	0.00	0.00 <sup>c</sup>	1.69	2.31 <sup>a</sup> 2.04 <sup>b</sup>	2.08	4.62 <sup>a</sup>

<sup>a</sup>Ref. [46]; <sup>b</sup>Ref [47]; <sup>c</sup>Ref. [4]; <sup>d</sup>Ref. [43]; <sup>e</sup>Ref. [45].

The  $A$  modes are non-degenerate and the  $E$  modes are doubly degenerate.

In Table 3 we have assigned the symmetry of the different modes of vibration calculated to the (8,8) nanotube,

**Table 3. Vibrational modes in zone center for (8,8) nanotubes. R and IR mean Raman-Active and infrared-active.**

Symmetry	Our <i>Ab initio</i> (GGA)	Ref. [29] <i>Ab initio</i> (LDA)	Ref. [54] Tight-Binding	Ref. [49] Exp.
$E_{2g}$ (R)	1603	1593	1698	1609
$A_{1g}$ (R)	1589	1580	1672	1593
$E_{1u}$ (IR)	1583	1574	1683	-
$E_{1g}$ (R)	1568	1561	1668	1567

following the assignment given in [29] taking into account the Equations (2) and (3). In a recent paper presented earlier by Rao *et al.* Raman bands were observed for an isolated nanotube with chirality that are consistent with an ensemble of (8,8), (9,9), (10,10), and (11,11) tubes [49]. They observed seven Raman peaks and failed to detect the lowest frequency mode in the experiment because of the strong Rayleigh scattering back-ground. These values are used for comparison with our calculations. From **Table 3** is clear that in the high frequency region the calculations made with the GGA approximation agree much better with experiment than those using LDA or Tight-binding. It is known that, the LDA and Tight-binding approximations tends to over estimate the high-energy phonons.

In the high-frequency region the phonon dispersions is well reproduced in our calculations. For example, the modes for  $A_{1g}$  symmetry are 1589 and 1593  $\text{cm}^{-1}$  for (8,8) and (14,0) tubes, respectively. These values are just below the highest frequency mode. On the other hand, taking into account that the strongest G band (assigned to  $A_{1g}$  symmetry [50,51]) at about 1590  $\text{cm}^{-1}$  does not depend on the tube diameter and that the G bands of the outer tubes (in pristine DWCNT's) fall in the same spectral range as the  $G^+$  of an isolated semiconducting SWCNT (1589 - 1593  $\text{cm}^{-1}$ ) [30,52,53]. We conclude that our results for the zone-center phonons in the high-frequency region are in very good agreement with the experimental values.

#### 4. Conclusion

We have made a study of DFT as implemented in the code SIESTA, using localized atomic wave functions as a basis set with the GGA, and applied it to the study of SWCNT's about 1 nm in diameter. We found that the structure for (8,8) and (14,0) nanotubes does not show significant change compared with the rolled graphene sheet, while the (12,3) nanotube shows significant change. It has been observed a natural tendency to form regular hexagons that dominates in the later case. Our results predict that the electronic band structure for (8,8) and (12,3) nanotubes has metallic behavior, that is, behaves as metal at 0 K. Whereas the (14,0) nanotube is a semi-

conducting. Also, it is found that the accuracy of the method for predicting the transition energies of Van Hove singularities is insufficient. This is a problem inherent in DFT-based methods because it does not reproduce well the valence bands in the electronic band structure. Finally, we have shown that our results are comparable with the experimental values, this proves that the method used can be quite accurate for the high-energy vibrations because of their reliable description of the chemical bonds.

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