Effects of mutual arrangements in the optical response of carbon nanotube films

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Abstract

We study the electronic band-structure of single-wall carbon nanotube, isolated and in bundles, by means of a tight-binding model for general carbon structures. We show how the single-electron volume-to-conduction excitation energies vary as a function of the nanotube diameter and mutual arrangement.

Specifically, we evaluate the density of states of an isolated nanotube and of a bundle of the same material. The lateral dispersion affects the density of states, with a rounding and splitting of the Van-Hove singularities characteristic of nanotubes. We also investigate the same effects for a stack of crossing nanotubes representative of a disordered configuration, as opposed to the well-ordered parallel bundle, comparing the resulting electronic structure and density of states of the two configurations.

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1 Introduction

Carbon is common element that in nature is mostly found in three well known and widely studied allotropic form: graphite, diamond, amorphous carbon. There is, however a fourth form in which carbon can rearrange: fullerenes; they include buckyballs, carbon nanotubes, carbon nanobuds and nanofibers.

Carbon nanotubes (CNs) were discovered in 1991 by the Japanese physicist Iijima [1], that in 2002 was awarded the Benjamin Franklin medal for his studies in this research field. After this discovery the physics of CNs has rapidly evolved into a new field of research: theoretical and experimental studies in different field such optics and mechanics have focused on both the fundamental physical properties and the potential applications of nanotubes.

The interest in these objects has been sparked by the exceptional properties of those nano-sized objects combined with the relative simplicity of theoretical investigations due to the relatively limited number of atoms and the comparably electron-electron interactions, which make even ab-initio calculations possible. CNs are promising nanodevice with relevance for electrical and thermal interconnections in sensors and other micro- and nanodevices and for light-capture.

The CN structure can be single-walled or multi-walled, respectively referred to as SWCN and MWCN, the former being a hollow cylinder of nanometric diameter, the last being a series of concentric cylinders, see Fig. 1.

Figure 1: Single-wall carbon nanotube (SWNT) compared to a multi-wall carbon nanotube (MWNT).
In the present work we focus on SW carbon nanotubes, and in particular on their optical properties when arranged in bundles. Basing our efforts on a previously developed tool to perform tight-binding (TB) calculations on carbon-only materials we compute band-structure, density of states (DOS) and joint density of states (JDOS) of metallic and semiconducting CN in several mutual arrangements. We plan to address specifically the role of spatial ordering of SWNT in films of CNs.

![Figure 2: STM image of a carbon nanotube. The red clear objects are individual carbon atoms, with dark hexagonal holes between atoms.](image)

## 2 Carbon Nanotubes

One of the main features of CNs is that they are substantially one-dimensional systems: we can see a CN as a single graphene layer, i.e a sheet of carbon arranged in a honeycomb structure, rolled up to form an effectively 1D object, because of its large length to diameter ratio: the former being of µm the latter being of nm.

Because the microscopic structure of CNs is closely related to graphene, CNs are usually labeled in terms of the graphene lattice vectors; indeed this relation to graphene allow us to derive several properties of CNs . Figure. 3 shows the graphene lattice. The unit cell is spanned by the two vectors

\[
\mathbf{a} = a \left( \frac{\sqrt{3}}{2}, \frac{1}{2} \right)
\]

\[
\mathbf{b} = a \left( 0, 1 \right)
\]

where the lattice spacing \( a = |\mathbf{a}| = |\mathbf{b}| \) for graphene equals \( \sqrt{3} a_{\text{CC}} = 2.46126 \ \text{Å} \) with \( a_{\text{CC}} = 1.421 \ \text{Å} \) the carbon-carbon bond length. In carbon nanotubes, the
Figure 3: The honeycomb lattice of graphene. The hexagonal unit cell contains two carbon atoms. The chiral vector determining the structure of a carbon nanotube is given by \( \mathbf{C} \), and its length gives the circumference. The chiral angle is denoted by \( \theta_0 \), with \( \theta_0 = 0 \) corresponding to zigzag nanotubes and \( \theta_0 = \pi/6 \) to armchair nanotubes.

The graphene sheet is rolled up in such a way that the chiral vector \( \mathbf{C} \) becomes the circumference of the tube. This vector \( \mathbf{C} \), which is usually denoted by the pair of integers \( (n_1, n_2) \), such that \( \mathbf{C} = n_1 \mathbf{a} + n_2 \mathbf{b} \) defines uniquely a specific tube. It is shown below that many properties, and in particular the electronic bandstructure, vary dramatically with the chiral vector, even for tubes with similar diameter.

The direction of the chiral vector is identified by the chiral angle

\[
\cos \theta_0 = \frac{2n_1 + n_2}{2 \sqrt{n_1^2 + n_1 n_2 + n_2^2}}. \tag{3}
\]

Tubes of the type \( (n_1, 0) \) \( (\theta_0 = 0) \), see Fig. 3, are called zig-zag nanotubes because they exhibit a zig-zag pattern along the circumference; \( (n_1, n_1) \) tubes are called armchair for a similar reason, and their chiral angle is \( \theta_0 = 30^\circ \). Both, zig-zag and armchair CN are achiral tubes, in contrast to general chiral \( (n_1, n_2) \) tubes with \( n_1 > n_2 > 0 \).

The geometry of the graphene lattice and the chiral vector of the CN determine all of its structural properties, namely diameter, 1D repeated unit cell, and the number of carbon atoms in the basis. The diameter of the CN is of course proportional to the length of the chiral vector

\[
d = \frac{|\mathbf{C}|}{\pi} = \frac{a_{CC}}{\pi} \sqrt{n_1^2 + n_1 n_2 + n_2^2}. \tag{4}
\]
The smallest graphene lattice vector \( \mathbf{a} \) perpendicular to \( \mathbf{C} \) defines the translational period \( a \) along the CN axis. In general, the translational period \( a \) is determined by the chiral indices \((n_1, n_2)\) by

\[
a_{1D} = \frac{2n_2 + n_1}{nR} a + \frac{2n_1 + n_2}{nR} b
\]

and

\[
|a_{1D}| = \frac{\sqrt{3(n_1^2 + n_1n_2 + n_2^2)}}{nR} a_{CC}
\]

where \( n \) is the g.c.d of \((n_1, n_2)\), \( R=3 \) if \( \frac{(n_1-n_2)}{3n} \) is integer, and \( R=1 \) otherwise. Equation (5) and (6) provide the nanotube unit cell length.

The number of carbon atoms in the unit cell can be calculated from the area \( S_t = a_{1D} \cdot \mathbf{C} \) of the cylinder surface and the area \( S_g \) of the exagonal graphene unit cell. The ratio of these two quantities gives the number \( q \) of graphene hexagons in the nanotube unit cell

\[
q = \frac{S_t}{S_g} = \frac{2(n_1^2 + n_1n_2 + n_2^2)}{nR}
\]

Since the graphene unit cell contains two carbon atoms, there are

\[
n_c = 2q = \frac{4(n_1^2 + n_1n_2 + n_2^2)}{nR}
\]

carbon atoms in the unit cell of the CN. In the special case of achiral tubes, \( q = 2n, n_c = 4n_1 \).

### 2.1 The tight-binding method

The tight binding model is a simple technique for solving the problem of the adiabatic motion of the electron in the field provided by the nuclei, considered as fixed. Electron-electron correlation are treated at a mean field level, thus solving an effective one electron Hamiltonian. The total \( N \)-electron wavefunction is the Slater determinant of the \( N/2 \) lowest-energy single-electron eigen-functions, occupied by two appropriate-spin electrons. The corresponding total energy is given by

\[
E_{TOT} = \sum_i 2\epsilon_i.
\]

The corresponding single-electron wave functions are expanded on the basis of the atomic orbitals; this set happens to be non orthogonal since wave functions centered to different atoms generally overlap. However our model is implemented in order to remove this non-orthogonality: we switch to a orthogonal basis which possess the same symmetry properties of the original one, as explained in details in Ref [17]. This method is known as the Löwdin [19] method. Our TB implementation is capable to account for metallic states by using a suitable function.
for the electron occupancies around the Fermi energies \[9\]. The adopted TB parameterization for carbon is the one of Ref. \[10\].

### 2.2 Zone-folding approximation

The so-called *zone-folding* approximation helps us understanding the CN bandstructure in terms of the graphene one; furthermore this approach is the simplest one capable to explain the metallic or semiconducting nature of nanotubes. One should be aware that this simplified point of view completely neglects the effects related to the cylindrical geometry, i.e. the curvature of the nanotube wall. The graphene structure is stabilized by two kinds of bonds, due to the planar \(sp^2\) hybridization of \(2s\) \(2p\) valence orbitals of carbon: the \(2s\), \(2p_x\) and \(2p_y\), which are located in the sheet plane, combine to form in-plane \(\sigma\) bonding and \(\sigma^*\) antibonding ”orbitals”. These extended levels are in fact crystalline band states, and responsible of most of the binding energy of the graphene sheet.

The \(p_z\) orbitals give origin to two delocalized \(\pi\) bonding/anti-bonding conduction bands which cross the Fermi level at singular points \(K\) located at the edge of the BZ, in the vicinity of which the dispersion relation is approximately linear, which give rise to the conical bands of Fig. 4. Near these points, two of which are inequivalent, electrons behave as relativistic particles, described by the Dirac equation for spin \(-\frac{1}{2}\) particles, and called Dirac fermions for this reason. The six corners are called Dirac points.

When the graphene layer is rolled up to form a CN the wave vector perpendicular to the nanotube axis, \(k_{\perp}\), is quantized. The reciprocal lattice vector of the nanotube, \(k_{\parallel}\), is parallel to the nanotube axis and still takes continuous values, see Fig. 5(a).

Therefore, the allowed \(k\)-points for the nanotube are just parallel slices of the
graphene Brillouin zone (allowed lines), i.e. those vectors that fulfill the condition \( \mathbf{k} \cdot \mathbf{C} = 2\pi m \), where \( \mathbf{C} \) is the chiral vector introduced above, and \( m \) is an integer. A fundamental result, which was first pointed out by Hamada et al. [15] and Saito et al. [16], states that a tube is a metal if \( n_1 - n_2 \) is an integer multiple of three.

\[
\mathbf{k} \cdot \mathbf{C} = 2\pi m = 2\pi \left\lfloor \frac{1}{3}(n_1 - n_2) \right\rfloor \quad (9)
\]
or equivalently if \( 3m = n_1 - n_2 \).

### 2.3 Electronic density of states

The density of states (DOS) for the electronic band-structure can give a rough initial idea about the response of the electron to an electromagnetic perturbation. This picture is only approximate because the DOS neglects entirely the dipole matrix elements between initial and final states, and electron-electron correlation effects. The density of states is known to depend dramatically on the dimensionality of a system. For parabolic bands, as found in all crystals near the Brillouin-zone center and edges, the DOS rises as the square root of energy in 3D case, it exhibits a discontinuous function in 2D solids, and it diverges as the inverse of the square root of energy in 1D:

\[
\text{DOS}(\epsilon) = \sum_{j \in \text{bands}} \int_{BZ} \delta(\epsilon - \epsilon_j(k)) \, dk. \quad (10)
\]

Isolated CN are one-dimensional crystals. Thus we expect several \( E^{-\frac{1}{2}} \) singularities for the DOS. This is confirmed by some early ab-initio and TB calculations for both achiral and chiral tubes. In graphene the density of states at \( \epsilon_F \) vanishes, because we have to integrate over the 2D Brillouin zone. In one-dimensional nanotubes a similar linear shape of the bands leads to a finite and approximatively constant DOS at the Fermi level. Semiconducting nanotubes instead have vanishing DOS within a finite gap. In both cases a sequence of discontinuity arises. To the extent that the band-structure is symmetrical above and below the Fermi energy, the Van-Hove singularity energies are approximately \( \pm E_1, \pm E_2, \) etc. in order of increasing energy distance away from the Fermi level, which is set at 0 for simplicity. As the \( \pm E_i \) singularities are related to stationary points at the same \( \mathbf{k} \) in the 1D BZ, the accumulation of particularly intense vertical (in \( \mathbf{k} \)-space) optical transition involving single electron excitation from the filled \( -E_i \) level to the empty \( +E_i \) level gives rise to prominent peaks in the optical absorption spectra. The \( -E_i \rightarrow E_i \) peaks are commonly referred to as \( E_{ii} \) transitions in the CN literature. For the present thesis we implement the calculation of the electronic DOS, and JDOS in a TB code previously developed in Refs. [9, 20].
Figure 5: The one-dimensional wave-vectors $k$ in the BZ of graphene as bold lines for (a) metallic and (b) semiconducting CNs. $K$ and $K'$ label the two inequivalent Dirac points. (c) Band structure for the (6,6) conducting CN. (d) Band structure for the (8,4) semiconductor CN.
These transitions depend of course on the detailed band-structure of the CN, but it is possible to identify general trends. In particular a clear correlation of the $E_{ii}$ transition to the diameter was identified \[6\].

In order to see how our model predict this singularity we have performed band-structure calculation based on 15 k-points in the Brillouin zone, and we investigate the $E_{11}$ gap for CN from (4,0) up to (16,0).

We start from an ideal structure generated using the software of Ref. \[7\] for CN small enough to have $n_1 + n_2 \leq 15$. For larger tubes we use the code of Ref. \[8\]; We set the C-C bond length to $\alpha_{CC} = 1.4210$ Å, not far from the one we found relaxing tube (6,6). For each CN we perform a full structural relaxation, by minimizing the total TB energy. We take metallic occupancies into account, where relevant, as discussed in Ref. \[9\].

We sample the 1D BZ with a mesh of 15 k-points, that using symmetries, see Ref. \[9\], become effectively 8 k-points. Finally we perform band-structure calculations on the relaxed structure. The length of the repeated cell is however left unrelaxed, therefore a small residual longitudinal strain is possible. We investigate 13 different carbon nanotubes. Table 1 reports the results for all these CNs: chirality, number of atoms, diameter and energy gap as obtained from band analysis, and excitation energy determined experimentally \[18\].

The resulting band gaps obtained from relaxed structures are compared to experiments in Fig. 7. The $E_{11}$ transitions follows the general trend $\propto 1/d$ \[11\].

Figure 6: The Kataura plot. $E_{11}$ transition (black stars), $E_{33}$ transition (black open squares) and $E_{44}$ transition (filled squares) \[14\].
<table>
<thead>
<tr>
<th>Chirality</th>
<th>Diameter [Å]</th>
<th>Carbon Atoms per unit cell</th>
<th>$E^{Exp}_{11}$ [eV]</th>
<th>$E^{T_{11}}_{cor}$ [eV]</th>
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<tr>
<td>(4,0)</td>
<td>3.34</td>
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<td>1.20</td>
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<td>0.71</td>
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<td>(6,0)</td>
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<td>24</td>
<td>2.12</td>
<td>2.31</td>
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<tr>
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<td>0.71</td>
<td>0.66</td>
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<td>28</td>
<td>0.68</td>
<td>0.74</td>
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<td>0.42</td>
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<td>(14,0)</td>
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<tr>
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<td>60</td>
<td>0.98</td>
<td>0.95</td>
</tr>
<tr>
<td>(16,0)</td>
<td>12.50</td>
<td>56</td>
<td>0.32</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Table 1

The properties of a few CNs obtained from a TB calculation on a relaxed structures. The experimental energies are taken from Ref. [18].
Figure 7: $E_{11}$ transition energies: the diamond shows our TB results for CN of Tab. 11 while the circles are taken from Ref. 18.

3 Nanotube Bundles

After analyzing the properties of a single CN we move on to analyze a bundle of nanotubes. Actual bundles are held together by the weak van der Waals intertube interactions; the distance between the nanotubes in the bundle varies only within a small range between 3.3 and 3.4 Å, with little or no chiral-angle or diameter dependence.

A bundle of CN is different from an isolated nanotube in two aspects. Firstly, a nanotube bundle (or rope) usually consists of a mixture of nanotubes of different chirality and slightly different diameter. Secondly, the bundling also changes the nanotube properties due to tube-tube interaction. Even a perfect crystal of exactly equal CN behaves differently from an isolated CN.

Putting metallic, e.g armchair, nanotubes in a bundle the symmetry is reduced: the valence and the conduction bands in the absence of symmetry belong
Figure 8: (a) A portion of (6,6) CN bundle we considered. (b) A lateral vision of a portion of the same bundle.
Figure 9: Fully relaxed total energy of a single (6,6) nanotube as a function of the length of the cell in z periodic direction.

Figure 10: Total energy of the bundle of (6,6) CN as a function of the CN inter-distance.
(a) The path in the Brillouin zone we select for our band calculation of the CN bundle.

(b) Band structure of an isolated (6,6) CN.

(c) Band dispersion of the (6,6) CN bundle with intertubule distance of 2 Å.

Figure 11
to the same group representation; they will therefore repel and open a small gap near the Fermi level [13]. In the present situation we report the band-structure of a (6,6) CN and compare it to the corresponding bundle. The primitive cell of the (6,6) contains 24 carbon atoms. Its diameter is ≃ 4.08 Å. We have performed a band-structure calculation for the single CN taking a 1D cell whose size is found by minimizing the total energy at each cell length, with each calculation fully relaxed. We use a similar $k$-point mesh in the Brillouin zone. This relaxation is illustrated in Fig. 9. The optimal cell length, obtained by a parabolic fit of the 2.46-2.48 Å data is 2.4620 Å, to compare with the theoretical cell length of 2.46124 Å, consistent with $a_{CC} = 1.4208$ Å.

The simulation of the bundle is realized by 1 CN per cell in an hexagonal lattice to represent an infinite bundle, a portion of which is shown in Fig. 8. To estimate the size of the unit cell for the bundle, we consider intertubule distances from 2.6 Å to 1.5 Å in steps of about 0.1 Å. For each separation we compute the total relaxed energy, in order to find an optimal separation that we find near 2 Å. This result is an artifact of the adopted TB method, see Sec. 2.1, whereas real bundles have CN at a significantly larger mutual separation. To perform the band calculation we follow a simple path in the Brillouin zone with $k_x$ and $k_y$ fixed to zero, see Fig. 11(a).

Figure 11(c) shows the electronic band-structure along $\Gamma - A$ for the bundle of (6,6) CN. We note that, compared to the band of the isolated CN, Fig. 11(b), a gap of ≈ 0.5 eV seems to open at the Fermi level, caused by tube-tube interaction. The higher valence and conduction bands, which are both two-fold degenerate in isolated nanotubes, split due to the symmetry lowering. For most bands this splitting is quite small, and hardly visible in the figure; the two non-degenerate bands that are highlighted in Fig 11(c), however, are strongly split in the bundle (0.5 eV energy difference at $\Gamma$). In the isolated tube they form the doubly degenerate $m = \pm 3$ bands, as highlighted in Fig. 11(b), but as $|m| = 3$ belong to different representations their degeneracy is immediately lifted in the bundle. It is important to note that this gap is strictly related to the path we choose in the BZ, and in fact as we look at the DOS, see Fig. 12, we can note that no gap opens at the Fermi energy, so that the behaviour of the bundle remains metallic.

3.1 Electronic joint density of states

The joint density of states (JDOS) is defined as the number of electronic states in the conduction and valence band that are separated vertically (in $k$ space) by
Figure 12: Electronic density of states (DOS) in a (6,6) CN metallic bundle (bold blue line) compared with the DOS of an isolated (6,6) tube (black line). Note that with respect to the isolated tube the Van Hove singularities are broadened and several of them split into of two peaks. The distance between the tube is 2 Å, significantly smaller than the experimental one, due to a deficiency in the description of disperse forces in the TB adopted model.
a given energy, and is proportional to the optical absorption function:

\[ JDOS(\epsilon) = \sum_{j \in \text{full}} \int_{\text{BZ}} dk \delta(\epsilon - \epsilon_j(k) - \epsilon_i(k)). \]  

(11)

Figure 13 shows the JDOS of the (6,6) CNs bundle compared to that of an isolated (6,6) CN: note that the first Van-Hove singularity, \( E_{11} \) peak, in the bundle is broadened with respect to the isolated CN, and that it is lowered in energy.

### 3.2 Bundles of crossing nanotubes

In Sec. 3 we have considered only a bundle in which CNs were arranged regularly. However, CNs in nature are frequently found in disordered conformations. To see how mutual arrangement of CNs affects their optical properties we consider a primitive cell constituted by two CNs arranged as in Fig. 14(a); the cell is a simple tetragonal one and has length in \( z \)-direction of 20.34064 Å, while along \( x \) and \( y \) of 14.77212 Å.

To perform band-structure calculations we follow the paths shown in Fig. 14(b). Figure 16 illustrates the obtained bands structure, and Fig. 17 shows the corresponding DOS. We can argue that even in case of crossing CN the bundle maintains its metallic character, i.e. the symmetry is not broken; we can indeed see that at 0 eV the DOS remains finite like in Fig. 12.
Figure 14: (a) Lateral view for the primitive cell. (b) The 3D primitive cell of the bundle is formed by two orthogonal (6,6) CNs.

Figure 15: The BZ path to track the bands in case of crossing tubes.
Figure 16: Bands obtained for two crossing orthogonal (6,6) CNs. The BZ path illustrated in Fig. 15.

Figure 17: Electronic density of states for the crossing bundle. Small regular oscillations are consequence of the finite mesh of $k$-points we choose in the reduced 3-D BZ ($\approx 4100$) and would vanish if the mesh was infinitely dense, as the definition of DOS requires. In order to account for the different number of atom per cell the bundle DOS (blue line) is scaled by 24/288 (number of atom per cell for the isolated CN with respect to crossing CNs).
4 Discussion and Conclusion

We applied a modified computer code to isolated CNs and compare the resulting DOS and JDOS to a similar calculations made for nanotubes in a bundle; we find that the CN-CN interaction splits and deforms the bands near the Fermi energy, thus affecting the DOS and the JDOS.

We also consider a bundle of orthogonal crossing CNs, as representative of a disordered structure. The corresponding DOS reveals that the bundle maintains its metallicity, and that the Van-Hove singularities are not broadened with respect to the isolated CN, unlike in the parallel bundle. An obvious limitation of the TB model affects the present work: the short range cutoff (2.6 Å) implies complete neglect of the van der Waals interaction between tubes, that is actually what is keeping the CN together in bundles. Additionally, CN bundles in nature are made of CNs of several different diameters, an aspect which in this thesis we leave completely unexplored. Future work is needed to address the issues discussed above.
References


