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THEORETICAL STUDY OF CARBON NANOTUBES ADSORBED ON THE SILICON (100) SURFACE
AND
EXPLORATIONS ON THE MODULATION OF CONDUCTANCE FOR METALLIC CARBON NANOTUBES

BY

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Abstract

We present the first *ab initio* study of semiconducting carbon nanotubes adsorbed on the unpassivated Si(100) surface. A dramatic reduction of the semiconducting gap for these hybrid systems as compared with the electronic gaps of their isolated constitutive components was found. This is caused by the changes in the electronic structure as the surface reconstructs due to the tube’s proximity, the concomitant electronic charge transfer from the nanotubes, and the band hybridization with silicon and carbon states resulting in the appearance of states within the energy gap of the formerly isolated nanotube. It is determined that semiconducting nanotubes exhibit weaker adsorption energies and remain at a greater distance from the Si(100) surface as compared to metallic nanotubes of similar diameter; this may be useful for the solid-state separation of metallic and semiconducting nanotubes. The electrostatics and band alignment of carbon nanotubes adsorbed in the fully passivated Si(100) surface have also been investigated. Spectral data indicate a relative displacement, depending on the type of doping, of the surface’s band edges from those of adsorbed nanotubes, and this is confirmed by the *ab initio* calculation of semiconducting nanotubes on the Si(100):H-2×1 surface. A markedly different spatial charge redistribution occurs depending on the dopant specie involved. Finally, and in a different direction, we calculate the effects of a longitudinal electrostatic perturbation on a metallic carbon nanotube to demonstrate conductance modulation. The external modulation would be screened in bulk metals but occurs in nanotubes because of their quasi two-dimensional shape allowing electrons to interact with nearby charges. This modulation is determined by the strength of the self-consistent potential and its periodicity over shorter or longer distances. We employ the zero temperature single-particle Green’s function transport approach in the empirical tight-binding approximation to quantify the conductance.
I want to thank my wife Isabel del Barco for her enduring support and my son Salvador for his love and company. Additional thanks go to my mother, Luz María Lopez for never-ending encouragement.

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LIST OF ABBREVIATIONS

STM  Scanning Tunnelling Microscope
UHV  Ultra High Vacuum
DCT  Dry-contact Technique
SWNT Single Wall Carbon Nanotube
DFT  Density Functional Theory
SIESTA Spanish Initiative for Electronic Simulations with Thousands of Atoms
VASP Vienna Ab-initio Software Package
MP  Monkhorst-Pack
XC  Exchange-Correlation potential
LDA  Local Density Approximation
GGA  General Gradient Approximation
DOS  Density of States
PDOS Projected Density of States
HOES Highest Occupied Electronic State
LUES Lowest Unoccupied Electronic State
GCD(m,n) Greatest Common Divisor of m and n
Part I

*Ab initio* study of single wall carbon nanotubes adsorbed in the Si(100) surface
CHAPTER 1

Introduction

The purpose of this work is the theoretical characterization of semiconducting single-wall carbon nanotubes on the Si(100) surface. The Si(100) surface has been the subject of thorough studies over the years[10, 41, 16, 54] – it is perhaps one of the most studied surfaces, serving as a reference case: the cited articles are not meant to be a representative sample – and besides it can be customarily fabricated out of silicon wafers. The motivation for our efforts is a seminal experimental paper by Albrecht and Lyding where the feasibility of depositing carbon nanotubes from solid phase into semiconductor surfaces was demonstrated[1]. This technique has been appropriately called dry-contact transfer (DCT). Before then, nanotubes have been either directly grown into surfaces by plasma deposition techniques or incorporated in by liquid samples. A comparison between liquid deposition and the DCT method is exemplified in Fig. 1.1 where the cleanness of the interface between nanotubes and surface after DCT deposition of nanotubes is to be contrasted with the resulting interface as nanotubes are deposited from liquid sample. This technological advance has been seen by us and others as the motivation to model these systems with \textit{ab initio} techniques, as the promise of direct comparison between theory and experiment arises.

A detailed description of the interaction between “soft” and inorganic matter is a subject in its early stages of development. Nevertheless, it can be argued it has fundamental importance in bridging physics, biology and chemistry. Graphitic carbon has served as a model system for soft matter[50]: The graphitic planes display strong bonds, while the inter-plane forces are weak (of a van der Waals character). A carbon nanotube can be thought of as a seamless rolled-up graphitic plane. The bonds between carbon atoms in the nanotube are of covalent nature but as it turns out, the equilibrium atomic configuration of nanotubes deposited on the unpassivated, semiconducting Si(100) surface, is dependent on the electronic character of the nanotubes involved (semiconductor or metallic). Due to the extensive work on metallic nanotubes on this surface, most of our work deals with semiconductor, chiral nanotubes. Despite the limitations of density functional theory to account for van der Waals interactions, our results indicate that a metallic carbon nanotube (a 1-D metal) on top of the unpassivated, highly reactive Si(100) surface (2-D semiconductor) has different adsorption characteristics in comparison with a semiconducting nanotube of similar diameter (a 1-D semiconductor) on this same surface. The versatility of carbon enters into play and, when the tube is metallic, covalent bonds between carbon and surface silicon atoms are formed. In contrast, when the nanotube’s chirality makes it a semiconductor, the distance between the closest surface silicon atoms and carbon atoms is about 1 Å greater in comparison to the bond distance in silicon carbide. This suggests a van der Waals type of interaction between the 1-D semiconductor
Figure 1.1 Comparison in degree of contamination during deposition of a carbon nanotube on a semiconductor surface: (a) STM current image showing an isolated SWNT spanning a contaminated H-Si(100) surface following ambient deposition in solution. (b) Topographic and (c) current images of a SWNT deposited via dry-contact transfer (DCT) onto a UHV-prepared hydrogen passivated Si(100) surface. The SWNT axis is aligned with the Si dimer rows; identification of SWNT-Si registration was enabled by the ultra clean DCT process. (Image courtesy of Peter M. Albrecht.)
in proximity of the 2-D semiconducting surface, a characteristic trait of soft-condensed matter. In this direction, the limitations of exchange-correlation potentials in DFT have been pointed out along with a variety of alternative approaches, most of them semiempirical[50, 44, 12] yet a consensus on the way to proceed has not been reached to date. Interestingly, analytical expressions for van der Waals-included functionals call for a force law dependent, not on $r^{-6}$ (a “standard” van der Waals term), but on the electronic character and dimensionality of the materials involved. No analytical calculation for a 1D metal or semiconductor on top of a semiconductor surface was performed, though[12].

The main results of this first Part of the Thesis were obtained with the local density approximation (LDA) to DFT. LDA tends to consistently overestimate binding energies, while the general gradient approximation is known to underestimate them. The values presented in here can then be considered as upper bounds for those energies[55, 44, 45]. Due to commensurability constraints, the work to date by others has been focused to metallic nanotubes on the Si(100) surface, both monohydride and unpassivated. In this Part we describe the comprehensive work performed in order to characterize semiconducting nanotubes adsorbed in this surface. Manifestations of the electrostatic differences might also be the different polarizabilities found for semiconducting and metallic nanotubes[32, 27], as well as the experimental separation of nanotubes depending on their electronic character in liquid sample[28, 58]. The specific phenomena described in this Part of the Thesis has not been reported by others to date. It might lead to an improved mechanism for the separation of nanotubes in solid phase according to their electronic properties.

The first part of this Thesis is divided in four Chapters. In Chapter 2 we provide an example of the steps required to build reliable pseudopotentials and basis functions for use in determining new materials. Finding properties for those systems that match reliable published results is determinant for further results to be accurate. In Chapter 3 we present the work performed by other groups on metallic carbon nanotubes adsorbed on this surface. Chapters 4 and 5 contain the main results of this work: In Chapter 4 a comprehensive description of semiconducting nanotubes of varying diameters and chiralities adsorbed on the unpassivated, undoped Si(100) surface, is given. This study is complemented with an additional metallic nanotube of similar diameter. In Chapter 5 a study of the role of dopants in the adsorption of semiconducting carbon nanotubes on the monohydride passivated Si(100) surface is presented.
CHAPTER 2

Preliminaries on density functional calculations with numeric atomic orbitals

In this Chapter the steps necessary to compute physical properties of condensed matter within the density functional theory (DFT)\cite{26} SIESTA code\cite{56} are summarized. An authoritative and up-to-date account of density functional theory and of the methods to be employed in this work can be found in R. M. Martin’s book\cite{35}. The process of describing properties for new materials has to pass checks for accurately describing the properties of known solid-state systems and in this Chapter we build up the necessary knowledge required to construct the system of interest: a carbon nanotube in close proximity of a semiconductor surface. The results provided in this Chapter thus should help assess the overall care on which the main results of the Thesis build upon. We construct simple systems to test pseudopotentials and basis sets, and after a satisfactory check with published work is made we proceed to describe the (mostly) geometrical constructions required in order to properly account for

- a silicon surface, both with and without hydrogen passivation,
- single wall carbon nanotubes (SWNTs).

At variance with plane-wave density functional codes where the only free parameter is the so-called cutoff energy, describing the number of plane waves to be utilized on a given first principles calculation, SIESTA employs numeric pseudo-atomic orbitals\cite{53} (node-less, valence orbitals), and so a careful construction of the atomic basis is required. A tentative checklist to which we adhere consists on enforcing the following steps:

1. Constructing a pseudopotential.

2. With the pseudopotential built, relaxing forces on a reference structure to obtain lattice constants, basis vectors and electronic band structures comparable with published work.

3. Using a variational algorithm additional fine-tuning of the basis can be achieved.

These steps are further described and exemplified in this Chapter, along with the extensions required to construct a slab to represent the silicon Si(100) surface as well as carbon nanotubes.
2.1 Pseudopotential generation

Pseudopotentials in SIESTA are built with the aid of the *atom* program by Norman Troullier and Jose Luis Martins[61] and currently maintained by Alberto Garcia. It comes bundled with the SIESTA code.

The program’s basic capabilities are[15]:

- All-electron DFT atomic calculations for arbitrary electronic configurations.
- Generation of ab-initio pseudopotentials (several flavors).
- Atomic calculations in which the effect of the core is represented by a previously generated pseudopotential. These are useful to make sure that the pseudopotential correctly reproduces the all-electron results for the valence complex.

This pseudopotential generation code will provide results for *isolated, single atoms*, so a high degree of freedom in choosing parameters exists. The following is a sample file for an all-electron calculation:

```
ae Silicon
n=Si c=pbr # Symbol, XC flavor, { |r|s}
 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0
3 4 # norbs_core, norbs_valence
3 0 1.00 1.00 # 3s2
3 1 1.00 1.00 # 3p2
3 2 0.00 0.00 # 3d0
4 3 0.00 0.00 # 4f0
```

The fist line indicates the type of calculation that is being performed. The options are *ae*: all-electron, *pg*: pseudopotential generation or *pe*: pseudopotential generation with core correction. The second word in this line indicates the atomic species, but it is not mandatory.

In the next line, the atomic symbol is input, as well as the exchange-correlation ‘flavor’ of the calculation:

- **Local density approximation:**
  - *ca*: Ceperley-Alder
  - *wi*: Wigner
  - *hl*: Hedin-Lundqvist
  - *gl*: Gunnarson-Lundqvist

- **General gradient approximation:**
  - *pb*: Perdew, Burke, and Ernzerhof

The next character is a flag to perform the calculation relativistically. The options are:
• \(s\): Spin-polarized calculation, non-relativistic
• \(r\): Relativistic (polarized) calculation
• (blank): Non-polarized (spin ignored), non-relativistic calculation.

The following line with a collection of zeros is not well-documented, but it is left for compatibility purposes. Then the numbers of core and valence orbitals are indicated. In the next lines the occupation of the valence orbitals, per spin channel, are entered.

The pseudopotential file is very similar to the all-electron input file, as can be readily seen in the next sample input file:

```
# Pseudopotential generation for Silicon
pg Silicon
  tm2 3.0
n=Si c=pbr  # Symbol, XC flavor, \(|r|s\)
  0.0 0.0 0.0 0.0 0.0 0.0 0.0
3 4  # norbs_core, norbs_valence
  3 0 1.00 1.00  # 3s2
  3 1 1.00 1.00  # 3p2
  3 2 0.00 0.00  # 3d0
  4 3 0.00 0.00  # 4f0
  1.80 1.80 1.80 1.80
  # rc(s) rc(p) rc(d) rc(f) rcore_flag rcore
```

The additional lines are related to the algorithm to compute the pseudopotential, in this case written by Troullier and Martins[61] \((tm2)\) and the radius (3.0 Bohrs) where a logarithmic derivative is computed in order to compare results from pseudopotential and all-electron calculations. The last line has the atomic radius (in Bohrs) after which the pseudopotential and the all-electron radial parts should match. The radial part of the wavefunction for the calculations with the input files given in this section are shown in Fig. 2.1.

### 2.2 Physical properties of reference systems

Once a suitable pseudopotential has been built, the computation of physical properties for reference systems is in place. Lattice constants with the pseudopotentials we have constructed are given in Table 2.1. As the systems to work with are carbon nanotubes on silicon surfaces, we describe here the properties of bulk silicon in the diamond structure and a single graphitic plane, also known as graphene. A carbon nanotube can be constructed by rolling up a graphene sheet. Finally, we present band structures of silicon slabs with two close-in-total-energy surface reconstructions. Those surfaces will be employed in Chapter 4 as the substrate into which carbon nanotubes will be deposited.

#### 2.2.1 Bulk silicon

Bulk silicon has the diamond structure. The lattice vectors are

\[
a_1 = a(1/2, 1/2, 0) \quad a_2 = a(0, 1/2, 1/2) \quad a_3 = a(1/2, 0, 1/2),
\]

\(2.1\)
Radius (Bohrs)

Figure 2.1 (a-d) Radial part of the pseudo-atomic wave function for an isolated silicon atom; note the zero occupation of $d$ and $f$ orbitals. e) The associated radial part of the charge density (arb. units).

Table 2.1 Lattice constants obtained with our bases, to exemplify the flexibility of our basis set. Unless otherwise stated, results are within LDA.

<table>
<thead>
<tr>
<th>Element</th>
<th>Theoretical estimate (Å)</th>
<th>This work (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (Diamond)</td>
<td>3.570†</td>
<td>3.486</td>
</tr>
<tr>
<td>C (Graphite)</td>
<td>$a$ 2.450‡</td>
<td>$a$ 2.448</td>
</tr>
<tr>
<td></td>
<td>$c$ 6.500‡</td>
<td>$c$ 6.516</td>
</tr>
<tr>
<td>Si (Diamond)</td>
<td>5.430†</td>
<td>5.401</td>
</tr>
<tr>
<td></td>
<td>5.457* (GGA)</td>
<td>5.469 (GGA)</td>
</tr>
</tbody>
</table>

†From Ref. [4].
‡From Ref. [23].
§Ref. [34]
and the basis vectors are

\[ b_1 = (0,0,0) \quad b_2 = a(1/4, 1/4, 1/4), \quad (2.2) \]

with \( a \) taken from Table 2.1. The conventional cubic cell of the diamond lattice[4] is drawn in Fig. 2.3a). For bulk silicon in the diamond structure, an electronic gap of 0.652 eV and a lattice constant of 5.469 Å are found, the latter is off by 0.2% from a value recently reported within GGA with the VASP code[34]. The radial part of the numeric atomic orbitals from a pseudopotential calculation and the associated band structure for silicon in the diamond structure are depicted in Fig. 2.2. Similar tests were performed for graphene, for which we only present the optimum geometrical configurations in later subsections.

### Building the (100) surface

Since the late '70s Chadi, Cohen, Northrupp and others[10, 20] were among the first to study the (100) surface of silicon. Here we indicate the necessary steps required to successfully build it. The Miller indexes define the normal directions to a given surface[4]. In our case

\[ [100] \equiv 1a_1 + 0a_2 + 0a_3 = a_1. \quad (2.3) \]

The (100) surface is the plane normal to the \([100]\) crystallographic direction. In Fig. 2.3b) we have rotated the vector \( a_1 \) from the diamond lattice so that it is collinear with the vertical (\(z-\)axis). A further rotation in the plane perpendicular to this axis helps align the new lattice vectors with the \(x-\) and \(y-\) axis. Refer to Fig. 2.3b) for details. The new unit cell has lattice vectors:

\[ a'_1 = (a', 0, 0) \quad a'_2 = (0, a', 0) \quad a'_3 = (0, 0, a), \quad (2.4) \]

and a basis with four atoms at positions:

\[ v'_1 = (0, 0, 0) \quad v'_2 = (a'/2, 0, a/4) \quad v'_3 = (a'/2, a'/2, a/2) \quad v'_4 = (0, a'/2, 3a/4) \quad (2.5) \]

with \( a' = a/\sqrt{2} \). The reconstructed surface presents a dimer structure, and this structure “buckles” in order for it to remain semiconducting (a non-passivated symmetric dimer structure happens to be metallic[20]). This buckling makes the unit cell increase its size by a factor of four. Furthermore, this buckling structure forms what appears as a “crossed” structure between consecutive dimers in the \(x-z\) plane, as seen in Fig. 2.3c). In Fig. 2.3c) we depict a planar view of the \(p(2\times2)\) reconstructed surface with six silicon monolayers and a dihydride layer passivating two silicon dangling bonds per silicon atom. The \(c(4\times2)\) reconstructed surface structure is formed by inverting the buckling direction in the next consecutive dimer along the \(x-\)direction, and makes the unit cell to increase to \(4\times2\) the size of the cell in Fig. 2.3b), hence its name. The \(p(2\times2)\) and \(c(4\times2)\) reconstructed surfaces are very close in energy, with a difference in our calculations of less than 4meV/Å². The \(c(4\times2)\) reconstruction is the best candidate for the lowest energy surface. When forming the monohydride surface structure the dimer becomes symmetric. Yet, due to the hydrogen passivation this buckled structure shows a gap close to 1 eV. Structures in Fig. 2.3(c-d) are obtained from a fully-relaxed structure with maximum atomic forces less than 0.02 eV/Å. More details are provided in Chapters 4 and 5.
Figure 2.2 I) The radial part of the GGA pseudopotential employed of particular relevance is subplot I.c) where the $d$ orbital has been promoted to a non-zero occupation. II) The band structure obtained with the GGA pseudopotential for bulk Silicon compares very well with other calculations and published results.
Figure 2.3 Geometry of a) bulk silicon in the diamond structure; b) unit cell (without surface reconstruction) necessary to form the (100) surface; c) side view of the p(2×2) reconstructed surface in a slab with six silicon monolayers; d) side view of a Si(100)-H:2×1 reconstructed surface slab (monohydride passivated upper surface) with ten silicon monolayers.
Figure 2.4  a) The geometry of a graphene plane: It is formed by a ‘honeycomb’ lattice, with two atoms (A and B) per unit cell –the diamond-shaped shaded area. The basis vectors, $a_1$ and $a_2$ form a 60° angle. b) As an example, the unit cell for a (9,3) SWNT (with 156 atoms in its unit cell) is built from a graphene sheet: The perimeter of the tube is defined by the vector $C_h = ma_1 + na_2$ and its length $L$ is the shortest distance perpendicular to the perimeter that makes the lattice periodic in the direction parallel to $l_1$ and $l_2$. c) By matching the lines $l_1$ and $l_2$ a 3-dimensional structure is created: In this case the unit cell of a (9,3) SWNT.

2.2.2 Graphene and single wall carbon nanotubes

Graphene is a single graphitic plane. It has received a great deal of attention recently as the experimental means to produce single planes have been recently achieved\cite{63}. Its lattice is hexagonal with a lattice constant $a = 2.46$ Å, and hence has two atoms denoted by A and B on its unit cell and separated by a distance $a_C = a/\sqrt{3}$ as depicted in Fig. 2.4a). The two lattice vectors $a_1$ and $a_2$ form an angle of 60°, while the vector $b$, joining basis vectors A and B is parallel to the vector $a_1 + a_2$ and of magnitude $a_C$. This description of the lattice and basis vectors avoids the use of a co-ordinate axis and thus is very general. The band structure along high symmetry points is shown in Fig. 2.5. At the Fermi level the bands cross at a single point, the $K$ point in the hexagonal Brillouin zone, making graphene a zero-gap semiconductor.

Carbon nanotubes

The material presented in this section is taken mainly from Saito and Dresselhaus\cite{51}. The chiral vector $C_h$ defines univocally a carbon nanotube:

$$C_h = ma_1 + na_2 \equiv (m,n), \tag{2.6}$$

with $m$ and $n$ integers. A tube with indexes $m = n$ is customarily called armchair while a tube with one index equal to zero is referred to as zig-zag. A zig-zag or armchair SWNT is sometimes given the generic name of achiral. Any other tube with indexes different from the ones here considered is chiral. This has to do with the magnitude of the chiral angle $\theta_c$ defined the following way:

$$\theta_c \equiv \acos \left( \frac{C_h \cdot a_1}{|C_h||a_1|} \right) = \frac{2n + m}{2\sqrt{n^2 + m^2 + mn}}. \tag{2.7}$$
Figure 2.5 The band structure of graphene, a single graphitic plane from first principles within LDA. It is a zero-gap semiconductor with linear dispersion about $\sim \pm 2$ eV around the Fermi level.

Therefore, any nanotube with chiral angle other than $0^\circ$ or $30^\circ$ is a chiral SWNT. The radius $R$ of the carbon nanotube is given by the magnitude of the chiral vector, divided by $2\pi$:

$$R = \frac{a\sqrt{m^2 + n^2 + mn}}{2\pi}. \quad (2.8)$$

The translation vector $T$ is parallel to the nanotube axis and is normal to the chiral vector $C_h$ in the unrolled honeycomb lattice. It is expressed in terms of the lattice vectors $a_1$ and $a_2$ as:

$$T = t_1a_1 + t_2a_2, \quad (2.9)$$

with $t_1 = (2n + m)/\text{GCD}(2m + n, 2n + m)$ and $t_2 = -(2m + n)/\text{GCD}(2m + n, 2n + m)$. $\text{GCD}(i, j)$ is the greatest common divisor of integers $i$ and $j$. The length of the nanotube’s unit cell, a parameter of utmost importance when generating supercells to match the underlying surface slab’s length, is the length of vector $T$:

$$L = |T| = \sqrt{12}\pi R/\text{GCD}(2m + n, 2n + m).$$

The number of carbon atoms on a given nanotube unit cell is given by:

$$N = 2\frac{|C_h \times T|}{|a_1 \times a_2|} = 4\frac{m^2 + n^2 + mn}{\text{GCD}(2m + n, 2n + m)}. \quad (2.10)$$

We now move on to describe the electronic properties of graphene and carbon nanotubes. The Brillouin zone for the honeycomb lattice is a hexagon, rotated by $30^\circ$ with respect to the orientation
Figure 2.6  LDA band structure of a semiconducting and a metallic carbon nanotube around the Fermi energy (denoted by the zero in energy).

of hexagons with positions of carbon nearest neighbors in configuration space. The lattice vectors in the reciprocal lattice are given by:

\[ b_1 = \frac{2\pi}{a}(1/\sqrt{3}, 1) \quad b_2 = \frac{2\pi}{a}(1/\sqrt{3}, -1) \]  

(2.11)

We present in Fig. 2.5 the electronic band structure of graphene along high symmetry directions. There exist six \( K \) points in the Brillouin zone. In those, the Fermi level is defined by the crossing point between bands with a linear dispersion (\( E \propto |k| \)). For a carbon nanotube the unit cell is defined by a rectangle of sides \( R_1 \equiv C \) and \( R_2 \equiv T \). The basis vectors in reciprocal space have to satisfy the usual orthogonality rule:

\[ R_i \cdot K_j = 2\pi \delta_{ij}. \]  

(2.12)

It turns out[51] that \( K_1 \) and \( K_2 \) can be expressed in terms of the vectors of the graphene reciprocal lattice the following way:

\[ K_1 = \frac{2}{N}(-t_2 b_1 + t_1 b_2) \quad K_2 = \frac{2}{N}(n b_1 - m b_2). \]  

(2.13)

Since \( N K_1 / 2 \) corresponds to a reciprocal lattice vector, two wavevectors differing by this amount are equivalent. The \( N / 2 \) wavevectors give rise to \( N / 2 \) bands. The condition for obtaining a metallic carbon nanotube is that \( 2m + n \) (or equivalently, \( m - n \)) is a multiple of 3. An illustration of this fact is provided in Fig. 2.6. There exists a \( 1/R \) dependence of the electronic gap of semiconducting nanotubes, as obtained from a tight-binding calculation[36]:

\[ E_g = \frac{|\gamma_\pi| a_C}{R}. \]  

(2.14)

This empirical relation breaks down for nanotubes with radius \( R \) less than five angstroms, as can be seen in Fig. 2.7[38]. In Chapters 6 and 7 we will employ \( \gamma_\pi = -2.7 \text{ eV}[51] \). A description of the electronic structure for carbon nanotubes within the \( \pi \) orbital tight binding approach is deferred
Figure 2.7 The $1/R$ rule overestimates the electronic gap for semiconducting carbon nanotubes when their radius is less than 5 Å. From Ref. [38].

2.3 Electronic structure of the surface slab

By placing periodic copies of the surface reconstructions we constructed superlattices to allow for commensurate semiconducting nanotubes to be deposited on top, providing for at least ten angstroms of separation between nanotube images. The reader should be aware of the fact that while the $(n,n)$ SWNTs have a length on its unit cell of $\sqrt{2}a/3$ to within 3%, it turns out the shortest semiconducting nanotube commensurate with the surface has a length (to within less than 2%) equal to $2\sqrt{2}a$. Here $a$ is the length of the unit cell of silicon diamond. Therefore rather large supercells are required to study these semiconductor-semiconductor systems. Particularly expensive are the force relaxation cycles. The band structures for the supercells with the surface reconstructions employed in this work are shown in Fig. 2.8. In those graphs, the $\Gamma-J'$ ($\Gamma-J$) direction is parallel to the supercell’s short (long) side. The first valence bands are localized in the surface, and so they are not present in the monohydride reconstruction of the surface. This gives an electronic gap close to 1eV in such a case.

In this Chapter we have provided the background necessary to construct the Si(100) surface slabs and carbon nanotubes. We need to remind the reader that the results from DFT in Chapters 4 and 5 are based on the LDA. In the next Chapter we describe in general terms related work on this subject by others, and present our main findings in Chapters 4 and 5.
Figure 2.8 LDA band structure of a) a $3 \times 2$ superlattice with the $p(2 \times 2)$ reconstructed dimer structure and b) a $2 \times 2$ superlattice with the $c(4 \times 2)$ reconstruction of the dimer structure. Those superlattices will eventually allow for the deposition of commensurate carbon nanotubes with more than 10 Å in separation between nanotube images.
CHAPTER 3

Single wall carbon nanotubes on the Si(100) surface: current status of theoretical work

Concurrent to the experimental work developed at the Beckman Institute, briefly described in Chapter 1[1], W. Orellana, R. Miwa and A. Fazio described the physics involved in the adsorption of a metallic (6,6) carbon nanotube on the unpassivated Si(100) surface[42, 43]. In a nutshell, they determined that when the nanotube axis is parallel and on top of the dimer row trench the system minimizes its energy[43]. Then, they rotated the nanotube about its axis to further increase the adsorption energy whenever the nanotube’s chiral axis aligns with the silicon dimer atoms. In this configuration the electronic structure of the hybrid system remains metallic. They also found the creation of bonds between surface silicon atoms and carbon atoms in the nanotube. Their results are reprinted in Fig. 3.1.

As the work by Abrecht and Lyding was first performed on monohydride silicon surfaces, the Brazilian team lead by A. Fazio moved into modelling the same (6,6) single wall carbon nanotube on completely- and partially-passivated substrates. Due to the passivation of the surface bonds, the nanotube is now physisorbed in the surface, and it does not form covalent bonds. Nevertheless, once some hydrogen atoms are removed in a periodical fashion (and this perhaps relate to our model described in Chapter 7) a feeble gap is opened and the hybrid system becomes semiconducting. This result might occur only for this nanotube and no further work on general \((m,n)\) nanotubes on this surface has been reported. Furthermore, no discussion on the feasibility of experimentally producing the hydrogen removal pattern has been provided. This makes the results of Fig. 3.2 appear as an isolated case with little future for applications. It is here where a close collaboration between experimental and theoretical teams fructify. We have learned about the experimental possibilities and have thus modelled systems that close resemble them. Results appear in Chapters 4 and 5.

Concurrently to our work, to be presented in the following Chapters, additional results on metallic nanotubes have been published. Short-diameter \((5,5)\) and \((3,3)\), with an appreciable degree of hybridization due to their curvature have been placed in stepped surfaces and partially H-depassivated surfaces. The current trend from other teams has primary focused in determining geometries where very small gaps for the hybrid systems can be opened for metallic nanotubes adsorbed on the Si(100) surface, partially passivated or unpassivated. Those geometries are just too particular and no study has been made to determine if the effects described can be of any
Figure 3.1 The pioneering work by Orellana et al.\cite{42, 43} consisted on finding out that \((n,n)\) – metallic– carbon nanotubes are commensurate to within 3\% with respect to the underlying surface with a length of 7.638 Å. They determined the best geometrical configuration for a (6,6) SWNT adsorbed parallel to the direction defined by the bottom of the silicon dimer row. The hybrid system forms bonds and remains metallic.
Figure 3.2  By removing hydrogen in a particular periodic configuration a slight gap appears. Due to the inherent periodicity along the SWNTs axis, it is not clear if this effect will arise for non-periodic, selectively H-depassivated silicon and therefore it might be hardly applicable. From Ref. [37].
Figure 3.3 A (3,3) nanotube with a 4.05 Å diameter is shown adsorbed on top of a single H-depassivated silicon row on an otherwise H-passivated Si(100) surface. Front and side views are shown. The band structures depicted are taken from a sequence of electronic properties at varying distances from the optimum adsorption separation, in order to visualize the band hybridization process. A gap is opened; it is unclear if only due to the strong out-of-plane hybridization of the nanotube due to the bonds it forms with silicon atoms and its rather small diameter. From Ref. [30].

general use or even reproducible with current experimental methods. It appears as something obvious to us the following: to have a robust semiconducting hybrid system, one should rather study semiconducting nanotubes adsorbed on the Si(100) surface. This gap would not be limited to a nanotube with a fixed chirality or geometrical disposition, providing a general trend, more easily to be verified by experiment, and besides, of real use in applications. Additional physics brought by the interaction between 1D and 2D semiconductors comes also to enrich this study, as discussed in Chapter 1. The description of my work provides the content of the next two Chapters.
Figure 3.4 A short-diameter, (5,5) carbon nanotube with a diameter of 6.75 Å: This diameter is below the 8 Å limit in Fig. 2.7 and therefore strong out-of-plane hybridization is expected. This hybridization helps open a gap in the configuration shown in the first ball and stick model. In all other configurations, and particularly at terrace edges the systems still remains metallic. From Ref. [8].
CHAPTER 4

*Ab initio* study of semiconducting carbon nanotubes adsorbed on the Si(100) surface

We present the first *ab initio* study of semiconducting carbon nanotubes adsorbed on the unpasivated Si(100) surface. Despite the usual gap underestimation in density functional theory, a dramatic reduction of the semiconducting gap for these hybrid systems as compared with the electronic gaps of both their isolated constitutive components has been found. This is caused by the changes in the electronic structure as the surface reconstructs due to the tube’s proximity, the concomitant electronic charge transfer from the nanotubes, and the band hybridization with silicon and carbon states resulting in the appearance of states within the energy gap of the formerly isolated nanotube. Furthermore, it is determined that semiconducting nanotubes exhibit weaker adsorption energies and remain at a greater distance from the Si(100) surface as compared to metallic nanotubes of similar diameter. This effect may be useful for the solid-state separation of metallic and semiconducting nanotubes.

4.1 Introduction

First-principles studies illustrating the effect of technologically relevant semiconductor surfaces such as InAs[25], GaAs[24] and Si(100) on the electronic properties of single-wall carbon nanotubes (SWNTs) have been published recently. In the case of Si(100), the study was focused on determining the lowest-energy structural configuration and modifications to the electronic structure of a metallic (6,6) SWNT as a result of its interaction with this surface. This calculation was performed for a nanotube in the proximity to an either clean[42, 43] or selectively hydrogen-passivated[37] Si(100) surface where the nanotube axis was parallel to the trench between adjacent Si dimer rows. Remarkably, there have been no studies of this system for *semiconducting* tubes, in different geometrical configurations, nor on the dependence of the properties of the hybrid system against nanotube diameter. These are relevant issues to be addressed, as experimental techniques permitting the ultra-clean deposition of SWNTs onto doped Si(100) and other semiconductor surfaces in ultra-high vacuum (UHV) at room temperature have been reported[1, 2, 49]. As contaminant-free atomistic manipulation becomes more feasible, the promise of molecular systems with tunable electronic and mechanical properties becomes a reality.

It is clear that near-term applications for carbon nanotubes in electronic and opto-electronic devices would benefit from their integration with conventional semiconductor platforms such as
Si or GaAs. In this direction, rectifying carbon nanotube-silicon heterojunction arrays have been demonstrated[62], and semiconductor heterostructures of GaAs/AlAs and GaAs/MnAs have been used as electrical contacts to individual SWNTs[21]. Recent experiments[59] showing the existence of two preferential directions for the growth of SWNTs on silicon surfaces indicate that there is a non-negligible interaction between the SWNT and its substrate. One relevant issue which remains to be addressed is the nature of the mechanical and electronic properties of the semiconductor-nanotube interfaces.

The subject of this work is the interaction between the unpassivated Si(100) surface and semiconducting carbon nanotubes using density functional theory (DFT)[18]. Those studies are complemented with additional calculations on metallic nanotubes of comparable diameter. We study nanotubes that are in parallel or perpendicular orientations relative to the Si dimer row direction. We have found a striking and somewhat counter-intuitive reduction of the semiconducting gaps for these hybrid systems which are composed of two semiconductors. The nanotubes presented in this study have diameters between 5 and 12 Å. This work was comprehensive in order to find robust properties on these hybrid systems; in particular those independent of diameter and chirality as experiments do not have fine control of these variables yet.

Section 4.2 discusses the theoretical approximations employed and the structural configurations considered in this study. In Section 4.3 we show the resulting atomic configurations of the combined Si(100)-SWNT system, which have marked trends depending on the original electronic character of the SWNTs involved (metallic or semiconducting). Results from Voronoi and Hirshfield population analysis[14] are also provided and show electronic charge being transferred from the nanotubes to the silicon slab. The resulting band structures at equilibrium, as well as the projected density of states (PDOS) over the atomic species involved are reported also. The PDOS indicates a clear hybridization of the bands between surface and nanotube states. This hybridization is further confirmed by depicting wavefunctions near the electronic gaps. Finally, we present the change in energy prior to the force minimization procedure, as the nanotubes are rotated about their axes in close proximity to the Si(100) surface. Conclusions are presented in Section 4.4.

**4.2 Methods**

Our calculations in the local density approximation[26] (LDA) were performed with the SIESTA code[56]. The exchange-correlation potential employed is the one parameterized by Perdew and Zunger[46] based on the Ceperley-Alder data[9]. Core electrons are replaced by norm-conserving Troullier-Martins pseudopotentials[61]. For greater variational freedom, a double-ζ basis set for s and p orbitals, and a single-ζ basis set for d orbitals was constructed using the prescription of Junquera et al[22]. To ensure the flexibility in our basis sets, their parameters were optimized by means of the simplex algorithm [47] on graphite and diamond for the carbon basis, while the silicon basis was optimized only in the diamond structure. As the hydrogen atoms only served to passivate dangling bonds, the hydrogen basis was not optimized. As shown in Table 2.1, the lattice constants obtained from the optimized bases compare well with previous theoretical estimates. We use the p(2×2) reconstruction of the Si(100) surface for calculations involving semiconducting SWNTs. The gap obtained is of 0.235 eV. In all cases a slab with six silicon monolayers with a height of 7.81 Å was employed. The bottommost layer is hydrogen(H)-passivated forming a dihydride arrangement. The SWNTs will be placed in proximity of the uppermost unpassivated layer. The area of the unit cell is \( L \times L \) with \( L = 7.639 \) Å. The vacuum region in the vertical
Table 4.1 Carbon nanotubes with length in their unit cell commensurate within 2% to the Si(100) surface’s supercell. In bold, the respective values for the (6,6) SWNT previously studied by Orellana et al[42, 43, 37].

<table>
<thead>
<tr>
<th>Nanotube</th>
<th>Diameter (Å)</th>
<th>Length (Å)</th>
<th>DFT Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(6,2)</td>
<td>5.657</td>
<td>15.391</td>
<td>0.860</td>
</tr>
<tr>
<td>(8,4)</td>
<td>8.302</td>
<td>11.294</td>
<td>0.945</td>
</tr>
<tr>
<td>(12,4)</td>
<td>11.314</td>
<td>15.391</td>
<td>0.699</td>
</tr>
<tr>
<td>(9,3)</td>
<td>8.486</td>
<td>15.391</td>
<td>0.000</td>
</tr>
<tr>
<td>(6,6)</td>
<td>8.153</td>
<td>2.465</td>
<td>0.000</td>
</tr>
</tbody>
</table>

The direction is fixed in order to provide at least 10 Å separation between periodic images when the SWNTs are in place.

Since we are interested in trends that could complement both experimental work in this area and published theoretical results on metallic SWNTs on this surface the SWNTs chosen satisfy the following criteria:

1. They are semiconducting.
2. Their diameter is of the order of 10 Å.
3. They are commensurate with the underlying surface.

While \((n,n)\) (metallic) SWNTs happen to be commensurate to within 3% with the underlying Si(100) surface[42], the shortest commensurate semiconducting SWNT, of indexes \((3n,n)\) –and \(3n – n \neq 3q\) with \(q\) integer– would be 15.391 Å long. The large unit cell sizes involved in calculations have deterred researchers from performing calculations in this system with semiconducting nanotubes. Table 4.1 lists the nanotubes studied, their diameters, lengths as well as their DFT gaps. Tables with chiral indexes \((2n,n)\) are 11.294 Å long, so a supercell constructed out of two nanotube unit cells is required in this case to meet the surface’s supercell length. Thus the slab supercells required for calculations involving both the surface and semiconducting nanotubes have surface areas equal to \(3L \times 2L\) or \(3L \times 3L\), depending on the length of the SWNT, its diameter and the surface reconstruction employed. This choice leaves more than 10 Å between nanotube images. In order to test the accuracy of our calculations against published results[42, 43], benchmark calculations on a chiral metallic SWNT interacting with c(4x2) reconstructed Si(100) surface were performed. The surface gap in this case is equal to 0.223 eV. The c(4x2) reconstruction minimizes the total energy the most and therefore is the best candidate for the surface reconstruction[16]. The metallic (9,3) SWNT is comparable in diameter to the (6,6) SWNT studied extensively by Orellana et al[42, 43, 37]. Due to the surface reconstruction used and the requirement for the nanotube images to be separated by at least 10 Å this required an even larger, \(4L \times 2L\) area for the underlying surface. This benchmark calculation is also used to assess the effect of chirality and the exchange-correlation approximation; LDA in this work and GGA previously[42, 43, 37].

4.3 Results

Figure 4.1 shows hybrid structures with maximum residual forces less than 0.02 eV/Å. The relevant geometric parameters are the minimum distance \(D\) between the SWNT and the dimer trench, the
Table 4.2 Averaged displacement (over the unit cell) in the z-direction (Å) of silicon atoms closest to the nanotube; c.f. Fig. 4.1. \(\langle h_1 \rangle - \langle h_4 \rangle\) refer to the parallel configuration and \(\langle h_5 \rangle\) to the tubes in the perpendicular configuration.

<table>
<thead>
<tr>
<th>Nanotube</th>
<th>(6,2)</th>
<th>(8,4)</th>
<th>(12,4)</th>
<th>(9,3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\langle h_1 \rangle)</td>
<td>0.15</td>
<td>0.11</td>
<td>0.03</td>
<td>0.14</td>
</tr>
<tr>
<td>(\langle h_2 \rangle)</td>
<td>-0.18</td>
<td>-0.29</td>
<td>-0.41</td>
<td>-0.44</td>
</tr>
<tr>
<td>(\langle h_3 \rangle)</td>
<td>0.20</td>
<td>0.15</td>
<td>0.09</td>
<td>0.43</td>
</tr>
<tr>
<td>(\langle h_4 \rangle)</td>
<td>-0.05</td>
<td>-0.06</td>
<td>-0.04</td>
<td>0.00</td>
</tr>
<tr>
<td>(\langle h_5 \rangle)</td>
<td>-0.13</td>
<td>-0.26</td>
<td>-0.16</td>
<td>-0.36</td>
</tr>
</tbody>
</table>

vertical atomic displacements \(\langle h_i \rangle\) resulting from the reconfiguration of the silicon atoms closest to the SWNT, and the azimuthal rotation angle \(\phi\). We want to emphasize the shorter bond lengths between the carbon and silicon atoms when the metallic tubes are involved, as well as a marked distortion of the nanotube, emphasized by the inner (red) circle. In comparison, semiconducting tubes are in equilibrium farther away from the surface and do not change their circular profile, as evidenced by the (green) inner circle perfectly matching the nanotubes’ perimeters. To contrast with published work[42, 43], due to chirality the metallic nanotube in either configuration studied showed only seven bonds of varying lengths (2.03–2.27 Å in the parallel configuration and 2.02–2.15 Å in the perpendicular configuration). For the semiconducting nanotubes, the shortest distance between carbon and silicon atoms turned out to be 2.62 Å and 2.87 Å for the (6,2) tube in the parallel and perpendicular configuration, respectively. All the semiconducting tubes with larger diameters had their carbon atoms more than 2.84 Å away from the closest surface silicon atom and in most cases more than 1 Å above the distance in the C–Si bond of silicon carbide. This is indicative of a weaker bonding for semiconducting nanotubes adsorbed on the Si(100) surface. For chiral nanotubes, the optimal geometrical configuration can not be known \textit{a priori}, but it has to come out after a sweeping through all angles \(\phi\); this angular dependence is not as pronounced for semiconducting SWNTs. A detailed discussion follows.

### 4.3.1 Optimized atomic configurations

An equivalent plane-wave cutoff of 200 Ry was used to calculate the charge density on the real-space grid. To obtain the optimal configuration of these systems, we used a grid with a single \(k\)-point (the \(\Gamma\)-point), except for the (6,2) nanotube, where a \(2 \times 2 \times 1\) Monkhorst-Pack[39] (MP) grid was already employed for obtaining the relaxed structures. The adsorption energies were then calculated with a \(2 \times 2 \times 1\) MP grid.

**Distance from the SWNTs to the silicon surface and surface reconfiguration**

Total energies for the hybrid SWNT-Si(100) system with the SWNTs listed in Table 4.1 were calculated as a function of the distance from the nanotubes to the bottom of the the dimer trench. The optimal distance \(D\) is reached when the total energy is at the global minimum. While holding the bottom hydrogen layer fixed, the hybrid structures were relaxed by a conjugate-gradient method to minimize the residual forces until they no longer exceeded 0.02 eV/Å. We also calculated the optimal distance \(D\) for (8,8) and (10,10) SWNTs for a fixed angle \(\phi\) in order to visualize and
Figure 4.1 SWNTs on the Si(100) surface in two configurations: parallel over the dimer trench, (a)-(b) and perpendicular to the Si(100) surface dimer trench, (c)-(d). D is the distance from the bottom of the SWNT to the bottom of the Si(100) surface dimer trench obtained in the total energy minimization. The vertical displacements $\langle h_i \rangle$ involved in the surface reconfiguration and $\phi$, the angle of rotation of the SWNT about its axis, are also indicated. An evident ‘squashing’ effect—an elongation along the z-direction—can be observed for the (9,3) nanotube but it was not present in any semiconducting nanotube. Semiconducting SWNTs stay at distances farther apart in comparison with the metallic SWNT of similar diameter. Note that for chiral tubes, a rotation $\phi$ about their axis and a displacement $\Delta l$ (not shown) along the nanotube’s axis, are linearly dependent. To minimize the cell size, a p(2×2) surface reconstruction was employed when placing semiconducting nanotubes, and the c(4×2) surface reconstruction for the (9,3) nanotube.
Semiconducting

Metallic

Figure 4.2 Distance $D$ from the bottom of the dimer trench to the lowest carbon atom as a function of nanotube diameter for fixed $\phi$. Semiconducting SWNTs parallel to the dimer trench will be closer to the underlying surface by about 0.5 Å as compared to semiconducting SWNTs in the perpendicular configuration for this diameter range. Notice a more pronounced diameter dependence and an overall smaller distance to the surface for metallic SWNTs. Dashed lines are drawn as a guide to the eye to facilitate the visualization of trends.

distinguish trends between semiconducting and metallic SWNTs. No relaxation procedure was performed on the latter tubes. Under relaxation those distances would decrease slightly, but the trend indicated here will stand. It should also be mentioned that the trend obtained in Fig. 4.2 for metallic tubes remained the same when the c(4$\times$2) reconstructed surface was replaced by a p(2$\times$2) reconstructed surface. This means that the distinct trends observed in Fig. 4.2 are due to the different electronic character of the nanotubes involved, and not to the surface reconstruction employed. This is stressed in Fig. 4.3, where the structural configuration of the (9,3) tube and the p(2$\times$2) reconstructed surface with maximum residual forces down to 0.02 eV/Å, appears extremely similar to the one found for this nanotube on the c(4$\times$2) reconstructed surface. The diameter of the nanotube as well as its electronic character (metallic, semiconducting) are the determining factors on the relative distance between the nanotube and the surface. As the nanotube diameter increases, the distance $D$ from the SWNTs to the bottom of the dimer trench also increases asymptotically towards 5.52 Å, which is the limiting distance from the bottom of the Si dimer trench to a graphene plane (nanotube diameter $\rightarrow\infty$), indicated by the gray line in Fig. 4.2. In order to obtain the separation between the surface and the graphene plane, we constructed silicon surface of area $4L \times L$. A graphene surface can be placed on top in which the vector $\mathbf{v} \equiv \mathbf{a}_1 + \mathbf{a}_2$ is perpendicular to the dimer trench, with a 3% elongation of the graphene plane in both perpendicular directions ($\mathbf{a}_1$ and $\mathbf{a}_2$ are the graphene lattice vectors). We then found a minimal energy by varying the separation between the graphene plane and the relaxed surface. The results in Fig. 4.2 show that metallic nanotubes exhibit a stronger diameter dependence on their optimal distance to the surface’s slab. This dependence of $D$ on the nanotube’s diameter is overlooked in previous work[42]. In previous work,
Figure 4.3 The properties of the hybrid system do not depend on the underlying surface reconstruction as evidenced by the (9,3) nanotube on the p(2 × 2) reconstructed surface. The distance between the nanotube and surface is very close to that found for this nanotube on the c(4 × 2) reconstructed surface, see Fig. 4.2. Notice also the vertical elongation appearing again and the overall structural similarity to the structure presented in Fig. 4.1.

the same distance to the surface was used for the (6,6) SWNT and a tube of 100 Å in diameter, in an attempt to explain experimental results of multiwalled SWNTs on H-passivated surfaces[17]. We speculate that the adsorption energy of nanotubes on an H-passivated surface should be lower than the one corresponding to an unpassivated surface, because the dangling bonds of the silicon surface are hydrogen passivated. This effect is worthy of further investigation, and we touch upon it in the next Chapter. For the semiconducting nanotubes studied the diameter dependence is not as marked. Yet, Fig. 4.2 shows that a semiconducting SWNT in the perpendicular configuration will be about 0.5 Å farther away from the silicon surface in comparison with its equilibrium distance in the parallel configuration, in accordance with experimental observation[3]. The electronic properties of the Si(100) surface are closely related to its atomic configuration. Table 4.2 gives the average vertical displacements \( \langle h_i \rangle \) that the silicon atoms closer to the SWNT undergo due to the proximity of the SWNT. The Si(100) surface in the proximity of the SWNT is subject to a striking atomic reconfiguration. For a given SWNT the amount of surface reconfiguration is always greater in the parallel case. This is consistent with the fact that tubes in the parallel configuration stay closer to the surface (Fig. 4.2) and therefore interact more strongly than in the perpendicular case. We have to stress here that after atomic relaxation the semiconducting nanotubes undergo almost no structural change but remain very stiff. This is not the case for the metallic nanotube, as previously indicated.
Table 4.3 Charge density \( (e/\AA^3) \) at the bonds between nanotube carbon and surface silicon atoms. Notice the smaller density for all studied semiconducting SWNTs in comparison with the bond densities for the metallic nanotube.

<table>
<thead>
<tr>
<th>Nanotube:</th>
<th>(6,2)</th>
<th>(8,4)</th>
<th>(12,4)</th>
<th>(9,3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parallel</td>
<td>0.235</td>
<td>0.175</td>
<td>0.120</td>
<td>&gt;0.370</td>
</tr>
<tr>
<td>Perpendicular</td>
<td>0.155</td>
<td>0.130</td>
<td>0.115</td>
<td>&gt;0.370</td>
</tr>
</tbody>
</table>

Relative strength of the C-Si bonds

With the goal of visually expressing the varying strengths of bonds formed between carbon and silicon atoms for the metallic and semiconducting SWNTs, we show in Fig. 4.4 charge density isosurfaces for the (9,3) and (8,4) SWNTs. Results for the remaining nanotubes can be found in Table 4.3. Very dense bonds can be seen for the (9,3) SWNT in either configuration with the 0.37 \( e/\AA^3 \) isosurface. The charge density isosurfaces show that the C–Si bonds are as strong as the Si–Si and C–C bonds in the surface and the nanotube, respectively, as can be inferred from the similar width. In order to understand the varying strengths of the bonds and the role of chirality on bond formation, refer to Fig. 4.1b, depicting the (9,3) SWNT in the parallel configuration. In this figure, surface dimers are located in the \( (x,z) \) plane. For the shortest bond (2.03 \( \AA \)) the relative coordinates of the involved carbon and silicon atoms are \( (\Delta x, \Delta l, \Delta z) = (-1.00, -0.23, 1.75) \AA \). The second closest carbon atom to a surface silicon atom has relative coordinates equal to \( (0.99, 0.35, 1.76) \AA \), giving a bond length of 2.05 \( \AA \). Although the cartesian projections \( |\Delta x| \) and \( \Delta z \) are very similar in both cases, chirality breaks the mirror symmetry with respect to a plane formed by the SWNT axis and the bottom of the dimer trench once all bonds are considered (recall that only seven –instead of eight– bonds were formed), but it also shifts the carbon atoms by varying distances \( \Delta l \), according to their positions in the SWNT unit cell. Contrast this to the more symmetric configurations previously studied for the (6,6) SWNT in which pairs of bonding atoms have the same \( \Delta l \) and a similar value for \( |\Delta x| \) for all bonds due to mirror symmetry. For the (8,4) SWNT we had to lower the density to 0.175 \( e/\AA^3 \) to identify bond formation in the parallel configuration. Lower density through bonds will reflect the weaker adsorption energies found for semiconducting SWNTs. Notice that this isosurface does not form bonds in the perpendicular configuration. It is at the lower 0.130 \( e/\AA^3 \) density when a single isosurface connecting the nanotube and slab can be seen. This is about a third of the density present in the strongest C–Si bond for the metallic SWNT. In conclusion, bond formation will be weaker for semiconducting SWNTs, and the weakest bond occurs for semiconducting SWNTs in the perpendicular configuration. These results are consistent with all findings of previous subsections.

Amount of charge transferred to the silicon slab

The results from Voronoi and Hirshfield deformation density charge analysis[14] are summarized in Table 4.4. Because of the way they are defined, the results from those methods are independent of the numerical orbital basis, and they are also more meaningful physically: The Voronoi deformation density charge for a given atomic nucleus, for instance, is the absolute charge defined in the volume defined by all the points closer to that atomic nucleus than to any other nuclei. In all instances, the charge is transferred from the nanotube to the slab, and the magnitude of the charge transferred is larger when the tubes are parallel and on top of the dimer trench.

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Figure 4.4 Charge density isosurface plots to visualize the relative strengths of C–Si bonds. Values of the densities associated with each isosurface are shown. The strongest bond occurs for the metallic SWNT.

Table 4.4 Amount of electronic charge per unit length (e/Å) transferred from the SWNT to the slab from the Voronoi (Hirshfield) deformation density analysis.

<table>
<thead>
<tr>
<th>Nanotube</th>
<th>Parallel</th>
<th>Perpendicular</th>
</tr>
</thead>
<tbody>
<tr>
<td>(6,2)</td>
<td>+0.052 (+0.046)</td>
<td>+0.033 (+0.029)</td>
</tr>
<tr>
<td>(8,4)</td>
<td>+0.055 (+0.049)</td>
<td>+0.035 (+0.033)</td>
</tr>
<tr>
<td>(12,4)</td>
<td>+0.072 (+0.065)</td>
<td>+0.035 (+0.031)</td>
</tr>
<tr>
<td>(9,3)</td>
<td>+0.064 (+0.083)</td>
<td>+0.058 (+0.043)</td>
</tr>
</tbody>
</table>
Table 4.5  Electronic gaps (in eV) for the hybrid systems composed of semiconducting nanotubes on Si(100) surface. We also include the (9,3) tube for completeness.

<table>
<thead>
<tr>
<th>Nanotube:</th>
<th>(6,2)</th>
<th>(8,4)</th>
<th>(12,4)</th>
<th>(9,3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parallel</td>
<td>0.099</td>
<td>0.008</td>
<td>0.033</td>
<td>0.000</td>
</tr>
<tr>
<td>Perpendicular</td>
<td>0.083</td>
<td>0.013</td>
<td>0.040</td>
<td>0.000</td>
</tr>
</tbody>
</table>

4.3.2  Ab initio electronic properties of the hybrid Si(100)-SWNT system

Band structures and densities of states

In order to have reliable band structures a stringent force relaxation was performed. As mentioned in Section 4.3.1, the atomic positions were subject to a force minimization procedure with a single \( k \)-point (the \( \Gamma \) point), with the exception of the (6,2) SWNT, where a \( 2 \times 2 \times 1 \) MP grid was employed. The relaxed atomic positions from this calculation were then used in computing the band structures and PDOS. The band structures were obtained with a \( 4 \times 4 \times 1 \) MP grid, while the PDOS was computed from at least a \( 12 \times 12 \times 1 \) MP \( k \)-point grid (for example, the results for the (12,4) nanotube in the parallel configuration were obtained with a \( 24 \times 12 \times 1 \) MP grid), using the converged self-consistent charge density obtained from the calculation with a \( 4 \times 4 \times 1 \) MP grid. The band structures and PDOS are depicted in Fig. 4.5. In all the plots shown in this figure the SWNT was placed parallel to the \( \Gamma - J' \) direction. For the PDOS a Gaussian smearing of 10 meV half-height width and 300 sampling points in the \((-1,1)\) eV energy interval were employed. The Gaussian smearing is in most cases smaller than the electronic gaps obtained from the band structures. The choice of Gaussian smearing is consequent with the \( k \)-point sampling employed. In particular, a finer Gaussian smearing requires a concurrent finer mesh and it is beyond our computational capabilities. The PDOS is computed with a finer mesh, independently from the band structure calculation and indicates the contribution of each atomic species to the band structure. The two columns in Fig. 4.5 correspond to the relaxed hybrid system in either the parallel or perpendicular configurations. The most salient feature from Fig. 4.5, as the band structures indicate, is the dramatic reduction of the gap for the hybrid systems composed of semiconducting nanotubes (with gaps of at least 699 meV when isolated) and the Si(100) surface (with a gap bigger than 200 meV). The biggest gap found occurred for the system involving the (6,2) nanotube, and is equal to 83 meV. Refer to Table 4.5 for a comprehensive list of the electronic gaps. The projected densities of states in Fig. 4.5 indicate a contribution from the carbon orbitals to the band structure at energy values where the gap of isolated tubes is expected, highlighted by the arrows on the carbon PDOS (note the different scales for each species in the PDOS). We believe this reduction of the gap for the hybrid system with respect to the gaps of its constituent subsystems will occur even when more accurate quasiparticle (e.g. GW) calculations and experimental data are in place. Notice that, despite the strong structural modification observed for the metallic tube (Figs. 4.1b and 4.1d), this is insufficient in this case to open a gap in either configuration; refer particularly to Fig. 4.6 where we zoomed the band structure about the Fermi level in the parallel case, to better appreciate this fact. The reader might appreciate the existence of a single band above the Fermi energy for the system involving the (8,4) SWNT in the perpendicular configuration. The PDOS indicates a couple of dips and the density at those dips is not equal to zero. The discrepancy here only comes due to the insufficient number of \( k \)-points employed. This system has the largest number of atoms, and we are certain a calculation with a finer mesh will result in a flatter PDOS in the region of interest,
Figure 4.5 Ab initio band structures and projected densities of states for SWNTs in different alignments with respect to the Si(100) surface. The first column shows the band structures and PDOS when SWNTs are aligned on top and parallel to the dimer trench, while the second column depicts band structures when the nanotubes are perpendicular to the dimer trench. Those results are obtained after atomic relaxation was performed. The ab initio results show a drastic reduction of the semiconducting gap for the hybrid system composed of semiconducting tubes and the Si(100) surface and a high degree of band hybridization. The different positions for the $J, J'$ points reflects the difference in size of the unit cells considered. The band structures involving the metallic nanotube (in blue) show no gap opening at the Fermi level. The band structures are calculated with a $4 \times 4 \times 1$ MP grid, while the PDOS was obtained with at least a $12 \times 12 \times 1$ MP grid. Arrows indicate the contribution to the band structure from carbon atoms in the vicinity of the Fermi level.
but we did not pursue further calculations due to their expensive nature. In the same note, the computational cost involved in computing a PDOS for the zoomed bands, which requires a finer smearing and a correspondingly increased number of $k$-points, prevents us from performing such calculation. Nevertheless we are certain of the accuracy of the band structure, and therefore of the accuracy of the electronic gaps for the hybrid system with a (8,4) tube adsorbed. Experimentally, the gaps for the nanotubes could be obtained accurately on the inert H-passivated substrate, prior to hydrogen depassivation; the surface gap can be measured by a host of experimental techniques. The dramatic reduction of the gap in this hybrid system as well as the distinct structural trends for semiconducting and metallic nanotubes are the main findings of our investigations. Recently[8] a gap opening for the small-diameter and achiral (5,5) nanotube was found in the perpendicular configuration. Due to a lesser symmetry in chiral tubes, which translates in longer bond lengths and a more complex atomic reconstruction and band hybridization, this effect is not seen in the (9,3) nanotube reported on this paper, and certainly more systematic studies would be required to address such a rather interesting effect; particularly with regards to knowing if it is robust enough to be observed in other nanotubes. Our work indicates that any semiconducting nanotube on this semiconductor surface results in a hybrid system with a gap smaller from that of the isolated constituent subsystems.

**Highest occupied, and lowest unoccupied electronic states for the Si(100)-SWNT system**

Wavefunctions for electronic states at the $\Gamma$-point that are just below and above the Fermi energy –the ($\Gamma$-point) Highest Occupied and Lowest Unoccupied Electronic States (HOES/LUES)– are depicted in Fig. 4.7. From those plots we observe that the electrons responsible for metallicity are either (a) extended over both the SWNT and the silicon slab; (b) predominantly over the silicon slab or (c) confined to the SWNT. We also found an instance –the (12,4) SWNT in the parallel configuration– in which the wavefunction is localized at the interface between the nanotube and the surface. In most cases involving the semiconducting nanotubes a more pronounced contribution from the nanotube to the HOES is seen in contrast with a more surface-like LUES. Those findings can be understood in terms of the relative contributions to the band structure from the carbon and silicon orbitals as seen from the PDOS in Fig. 4.5.
Figure 4.7 Wavefunctions depicting Γ-point states right below (highest occupied electronic state) and above (lowest unoccupied electronic state) the Fermi energy. The hydrogen bottom layer is not shown.
Table 4.6 Adsorption energies per unit length (eV/Å) after full relaxation has been achieved. Notice the lower adsorption energies obtained for semiconducting nanotubes. For the (12,4) tube (in bold) the perpendicular configuration turns out to be the most favorable.

<table>
<thead>
<tr>
<th>Nanotube:</th>
<th>(6,2)</th>
<th>(8,4)</th>
<th>(12,4)</th>
<th>(9,3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parallel</td>
<td>0.20</td>
<td>0.18</td>
<td>0.11</td>
<td>0.63</td>
</tr>
<tr>
<td>Perpendicular</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.60</td>
</tr>
</tbody>
</table>

4.3.3 Adsorption energies

Adsorption energies on the Si(100) surface for the carbon nanotubes in this study are presented in Table 4.6. The adsorption energies are obtained as the difference between the total energies in the relaxed hybrid structures and those of the fully relaxed tubes and surface in the same supercell separated by 10 Å. Notice the constant adsorption energy for semiconducting nanotubes in the perpendicular configuration, and the decreasing adsorption energy with increasing diameter for semiconducting tubes in the parallel configuration. These two trends meet for a tube with diameter in between the (8,4) and (12,4) nanotubes, after which a semiconducting tube in the perpendicular configuration has a stronger adsorption energy. This is stressed by the bold font in Table 4.6.

In order to determine the best angular ‘starting’ structure a chiral nanotube has to be rotated about its axis. Chirality precludes a highly symmetric configuration, potentially with the lowest energy, from being easily visualized. The energies as a function of $\phi$ with no atomic relaxation were obtained, and the difference of those energies with respect to the energy of a system where the tubes and surface are 10 Å apart are reported (this is called the energy gain and it is not an adsorption energy as the structures are not fully relaxed). The results are shown in Fig. 4.8, where the lower curves (red squares) refer to SWNTs in the perpendicular configuration. The upper curves (blue triangles) refer to the SWNTs in the parallel configuration. For our chiral tubes, the range of angles is given by $(0, 2\pi /\text{GCD}(m, n))$, where GCD$(m, n)$ is the greatest common divisor of $m$ and $n$. This range gives the maximum angular freedom that the nanotubes will have before the position of their carbon atoms becomes periodic. Notice the almost complete independence on $\phi$ for this energy for all semiconducting tubes, due to their weaker bonding as compared with metallic nanotubes. The (6,2) nanotube with the smallest studied diameter shows the most pronounced oscillations. This is due to its close proximity to the Si(100) surface that can greatly modify its energy as carbon and silicon atoms are brought closer to each other as a result of the tube’s rotation about its own axis. The distinctive trend for the metallic tube indicates an optimal configuration in which an extra bond (for a total of eight bonds) might form when full relaxation is performed. All the previous results shown in this paper were obtained at $\phi = 0.0$. Despite the fact that the metallic tube might not be in optimal angular configuration, our results are the first to date to show distinctively different trends for semiconducting and metallic nanotubes. In fact, once the metallic tube is in its optimal configuration, the trends provided here will only be accentuated. In the previously studied cases[42, 43, 37], the highly symmetric atomic arrangement of the achiral (6,6) SWNT with respect to the underlying surface silicon atoms results in optimal angular configurations in which $\text{D}$ is a function of $\phi$. We consider that in a more general setting, chirality precludes such a highly symmetric configuration from occurring: the relative position of carbon atoms closest to the surface with respect to surface silicon atoms becomes a complicated function of the chiral angle. In Fig. 4.8 we observe a small energy dependence per unit length (of the order of 100 meV/Å) against the tube’s angle of rotation $\phi$. This justifies the angular sweeping at fixed $\text{D}$ for our chiral
SWNTs.

It is also apparent from Fig. 4.8 that the metallic nanotube displays an energy dependence on the angle of rotation twice as large as the semiconducting SWNTs. This is consistent with the fact that metallic tubes stay closer to the surface in comparison to semiconducting nanotubes of the same diameter. This could also be influenced by the different surface reconstruction we employed. The prominent difference in the adsorption energies presented in Table 4.6 suggests a mechanism for the separation between semiconducting and metallic nanotubes in solid phase over this diameter range, provided they are always adsorbed in configurations with the greatest energy gain. Experimental techniques for nanotube separation to date rely on the chemistry and dipole moments of samples in solution[28, 58].

4.4 Conclusions

We have studied semiconducting SWNTs adsorbed on the Si(100) surface. We used the results from the (9,3) SWNT, which compare well to previous published results for metallic SWNTs[42, 43] as a test bed for our choice of exchange-correlation potential and surface reconstruction. Semiconducting SWNTs of the diameter range studied are placed at an almost constant distance to the surface. Those tubes are 0.5 Å closer to the surface when they are above and aligned with the trench between adjacent dimer rows, in comparison with any other configuration in which the trench and the tube axis do not align. We found a weak angular dependence on the adsorption energy of the system, and we believe this dependence will be further lowered as the length of the nanotube’s unit cell increases, due to the loss of symmetry in the relative positions of the carbon atoms in the SWNT closest to the Si(100) surface atoms. For the (9,3) SWNT, we found in agreement with published work[42, 43] that it remains metallic in either configuration, but the weak angular dependence tells us it will remain at an almost fixed height $D$, independent of its angular orientation. We also found a smaller adsorption energy for semiconducting SWNTs in comparison to metallic SWNTs of similar diameter, consistent with weaker bonding.

The electronic properties of these hybrid systems will vary in a qualitative way according to the relative orientation of the SWNT (parallel, perpendicular) with respect to the surface, but we find from our calculations that the system composed of semiconducting tubes on the semiconducting Si(100) surface displays dramatically smaller gaps in comparison with the isolated semiconducting systems that compose it, in both studied configurations. This reduction of the semiconducting gap can be ascribed to the modification of the band structure due to the surface reconfiguration, electronic charge transfer from the nanotubes and the resulting band hybridization from carbon states at energies where the gap appears for isolated tubes, as the PDOS indicates. The HOES for the hybrid systems can be extended, located predominately over either the silicon slab or the SWNT, or be localized at the interface between the SWNT and the Si(100) forming a one-dimensional conduction channel. In contrast, the LUES tend to be more localized towards the surface when semiconducting nanotubes are brought into proximity. Currently, experimental results on this system are starting to emerge[3]. We hope that the results provided in this paper motivate further experimental work in the area, as the properties described in here might be useful for electronic as well as opto-electronic applications.

Systematic studies as the one presented here are truly necessary in order to assess robust properties of this hybrid system against properties that might appear for a given choice of chiral angles.
Figure 4.8 Energy gain vs. axial rotation, prior to the relaxation cycle and at fixed height. Red squares show results in the parallel configuration, while the blue triangles correspond to the perpendicular configuration. \( \mathcal{G} \equiv \text{GCD}(m,n) \). The results shown here help identify the best angular configuration for chiral nanotubes, which can not be known \textit{a priori}. The largest adsorption energies occur for tubes parallel to the trench. The energy dependence on angle of rotation is more marked as the nanotube diameter is decreased, since is brought in closer proximity with the surface. The metallic nanotube shows the most pronounced energy dependence.
and geometrical configuration. In our case, the gap reduction appears for both configurations, and the bonding lengths are found to be consistently larger for semiconducting nanotubes in comparison with metallic ones. This implies a reduced absorption energy for semiconducting nanotubes on this surface. In turn, this might serve to mechanically attach metallic nanotubes and release semiconducting ones by suitable heating under dry conditions[28, 58].
CHAPTER 5

The effect of dopants in the supporting substrate

5.1 Introduction

Isolated carbon nanotubes can be metallic or semiconducting depending on chirality\cite{52, 51}. In many instances their properties can be modified when in close proximity of molecules\cite{55, 31} or surfaces\cite{42, 43, 37, 25, 8, 6}. Until recently, as we discussed in previous Chapters, due to size constraints related to superlattice commensurability, theoretical work has been focused on achiral metallic nanotubes in both Si(100) and other undoped semiconducting surfaces\cite{42, 43, 37, 25, 8, 30}. We have undertaken the first \textit{ab initio} study of semiconducting nanotubes on the unpassivated Si(100) surface, finding different adsorption trends depending on the electronic character (metallic, semiconducting) of the nanotubes involved. Within the inherent underestimation of electronic gaps in density functional theory (DFT), we also reported an additional and dramatic reduction of the electronic gap on those hybrid systems due in great part to the surface reconstruction when the nanotube is in proximity to the surface slab\cite{6}. New physics arises as the adsorption energies and bond lengths suggest a weak, van der Waals-like interaction between semiconducting nanotube and slab, despite the dangling bonds present on unpassivated Si(100) surfaces. New functionals, most of them semi-empirical, are nowadays proposed to account for this kind of interaction but no consensus has been reached yet\cite{50, 44, 12}. With the aid of DFT in the Ceperley-Adler\cite{9} version of the local density approximation (LDA), an upper limit to the adsorption energies and reliable atomic and electronic structures can be obtained\cite{55, 44}. From the experimental counterpart, the dry-contact technique has proved to allow for a very clean deposition of nanotubes on surfaces, with almost no ambient contamination\cite{1, 49, 2}. Those surfaces are routinely doped, contributing to the richness of the physics involved and perhaps also relevant for device implications. In spite of those remarkable advances, experimental characterization of carbon nanotubes with the techniques to be here further described remains a challenging task so that a combined experimental and theoretical approach is now provided. Topographic and electronic characterizations of semiconducting carbon nanotubes are presented on both \textit{p}- and \textit{n}-type degenerately doped silicon wafers, treated in advance so as to have their surface dangling bonds hydrogen-passivated. This data is accompanied with \textit{ab initio} band structures and densities of states for a semiconducting carbon nanotube in doped monohydride-passivated silicon slabs from fully relaxed structures resembling as much as possible experimental configurations. Arguably, the study of semiconducting nanotubes on realis-
tic surfaces is more relevant than the already extensive study of metallic nanotubes in the Si(100) surface (passivated or unpassivated), particularly as semiconducting nanotubes are currently the basis for carbon nanotube-based nano-scale devices. The results to be presented here are general as they do not depend on the orientation of the nanotubes on the surface (due to the small interaction) as well as their chirality and diameter. The theoretical tools and approximations used in this letter are those of previous Chapter[6].

5.2 Experimental details

We work with degenerately doped, \( n \)– and \( p \)–type silicon wafers, with arsenic and boron dopants, respectively. The wafers are subject to heating at 700 K to remove surface contamination. Afterwards hydrogen is injected into the chamber to passivate dangling bonds. Due to its small atomic mass (about one third from that of a silicon atom), boron can easily migrate from the bulk to the surface under heating, while arsenic (more than twice as heavy as silicon) might be harder to diffuse. When the surface has been passivated an applicator is introduced which stamps HiPCo carbon nanotubes from solid powder, with typical results as shown in Fig. 5.1. Room temperature scanning tunnelling microscopy is performed \( i \) to determine the topography of the H-passivated silicon surface and to locate isolated single wall carbon nanotubes, Fig. 5.1a) and \( ii \) to acquire current vs. voltage \( I/V \) measurements to identify the electronic character of the nanotubes adsorbed 5.1b) and to be later related to density of states from density functional calculations. The \( I/V \) data are recorded on the surface in regions separated by at least 20 Å from nanotubes, as well as on top
Figure 5.2  a) Geometry of the studied system. The (12,4) SWNT is 11.314 Å in diameter and 15.391 Å long. In red, the location of the dopant atom is shown. b) The band structure of the isolated (12,4) SWNT. c) Relative band shift between nanotube and slab states from first principles calculations: The band structure of an isolated, semiconducting (12,4) carbon nanotube (reference); band structure and projected density of states for a reference geometry with both the semiconducting slab and nanotube included in the supercell and forces fully relaxed with phosphorus (n-type) and boron (p-type) surface slabs. In all plots in part c) the 0 of the energy was set to the mid-gap of the nanotube states.
Table 5.1 Amount of charge transferred from a (12,4) SWNT to the silicon slab and adsorption energy per unit length. Data on the first two rows are taken from previous Chapter[6]. Notice the lower adsorption energies in comparison with the unpassivated case, as well as the change in opposite directions on the transferred charge depending on dopant specie (in bold font).

<table>
<thead>
<tr>
<th>Surface configuration</th>
<th>Charge transfer (e/Å)</th>
<th>Adsorption energy (eV/Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unpassivated, undoped parallel</td>
<td>0.072</td>
<td>0.111</td>
</tr>
<tr>
<td>Unpassivated, undoped perpendicular</td>
<td>0.035</td>
<td>0.149</td>
</tr>
<tr>
<td>Mono-H, n−doped</td>
<td>0.016 (−0.007)</td>
<td>0.069</td>
</tr>
<tr>
<td>Mono-H, undoped</td>
<td>0.023</td>
<td>0.068</td>
</tr>
<tr>
<td>Mono-H, p−doped</td>
<td>0.027 (+0.004)</td>
<td>0.068</td>
</tr>
</tbody>
</table>

Figure 5.3 a) Total charge for the undoped, passivated Si(100) surface plus the adsorbed (12,4) SWNT b) Charge difference, integrated over the y−direction when phosphorous (n−type) and boron (p−type) dope the slab.

of deposited carbon nanotubes. The band offsets are more easily discerned by means of the $dI/dV$ curves, numerically obtained. The data presented in Fig. 5.1 are representative of all the samples prepared. This deposition process is highly reproducible. The $dI/dV$ characteristics change depending on the location where the trace is taken. The band edges of the semiconducting nanotubes stay aligned at ±0.5 eV, indicating a diameter of about 20 Å from the $1/R$ rule, c.f. Eq. (2.14), to be confirmed by the topographic image.

5.3 Density functional theory calculations

We make use of the SIESTA code[56], and employ an optimized basis with thirteen numerical orbitals per atom for silicon and carbon species, and non-optimized bases[22] for hydrogen (five numerical atomic orbitals) as well as phosphorous and boron (the $n$− and $p$−dopant, respectively with thirteen atomic orbitals as well). Standard DZP bases were employed for the dopant species. The local density approximation to density functional theory is used[55]. This approximation is ideal for the application as it does not underestimate binding energies, in contrast to the general
gradient approximation and thus provides a reliable upper limit for adsorption trends. Although it has been shown that six silicon monolayers are enough to accurately describe carbon nanotubes on the Si(100) surface we have chosen to employ ten silicon monolayers to further lower the dopant concentration and to place the dopant atoms sufficiently away from the upper surface. Additional physics brought up by dopant-induced surface defects is therefore not accounted for in the theoretical model. The bottommost silicon monolayer is hydrogen passivated in a dihydride arrangement, while the uppermost is mono-hydride passivated, forming a \(2 \times 1\) arrangement. It is in the upper surface where carbon nanotubes will be deposited. The hydrogen passivated silicon slab has 312 atoms and a volume of 5015.84 Å³ in its unit cell (the complete system, with a (12,4) nanotube included has 520 atoms). Substitution of a single silicon atom by a dopant atom yields a dopant density of \(1.99 \times 10^{20}/\text{cm}^3\), well within degenerate doping. Despite the inherent periodic placement of the dopant species (they are located in the same position on each unit cell), this approximation is good to describe the experimental data, as will be shown below. The so-called quantum confinement effect yields a gap of 968 meV for the H-passivated slab with variations of a few meVs once dopant species are in place. The vertical separation between the lowest carbon atom to the closest hydrogen layer surface is, in all cases 2.20±0.01 Å and the vertical separation between the nanotube and the uppermost silicon layer is equal to 3.62±0.02 Å. A stringent force relaxation was performed for the cell containing the (12,4) nanotube and the slab, with the only constraint of leaving fixed the bottommost hydrogen atoms, until maximum forces were less than 0.02 eV/Å. The charge is computed on the Voronoi cells, defined as the closest volume to any particular nuclei. By explicitly defining a boundary between atoms, this method avoids the inherent inaccuracy present in Mulliken electronic population analysis, where charge is assigned to an atom in function of the occupation of its atomic orbitals, no matter how extended they are. Results are given in Table 5.1, along with the magnitude of the adsorption energy, which turns out to be less than one half the computed value for this nanotube on an unpassivated surface, c.f. Table 4.6. The Voronoi analysis indicates that more electronic charge is transferred to the slab if it is \(n\)—doped, less charge if \(p\)—doped, with the undoped slab as the intermediate case. Thus the dopant species produce a relative charge dipole when compared to the unpassivated system.

5.4 Discussion

Despite statistical variations in the width of the gap from experiment, the experimental trends for band edge alignments are reproduced by the first-principles calculation as can be seen in Fig. 5.2. The effect of added dopants is to rigidly shift the electronic bands related to the slab from those of SWNT character in opposite directions, depending on the dopant species involved. In order to know the absolute energy shifts, a method similar to that of Resta and coworkers can in principle be employed. One should have in mind that in the region where the nanotube is present there exist vacuum regions that will bias the determination of a 2-D average potential. An alternative solution is presented in Fig. 5.3a), where the total (ionic plus electronic) charge density is presented, integrated over the \(y\)—direction –this average was performed over 152 fixed values of \(y\). The charge difference in the optimized atomic geometry with dopant atom are given in Fig. 5.3b), where a dipole moment is observed that changes sign according to the dopant involved, confirming the result on Table 5.1. It is interesting to notice that upon hydrogen desorption the charge assigned to the dangling bonds will depend on the doping of the slab.

An experimental-theoretical description of SWNT on partially depassivated and doped sub-
5.4 Conclusions

Dopant species add to the already rich electrostatics involved in the adsorption of carbon nanotubes into semiconductor surfaces. A single hydrogen layer prevents the electronic states of the carbon nanotube from shifting along with the band structure of the surface slab. This experimental observation is corroborated by a state-of-the-art \textit{ab initio} calculation in force-relaxed structures with hundreds of atoms on its unit cell. As a macroscopic manifestation of the lone rigid shift of the electronic bands associated to the surface, a dipole moment is created between nanotube and surface which shifts sign according to the type of dopant involved (\textit{n}- or \textit{p}-type). We are currently testing the electrostatic effects caused by partial hydrogen removal on the degenerately doped Si(100) surface, c.f. Fig. 5.4. Results will be given elsewhere.
Part II

Studies of conductance on nanotubes: Green’s function method on a tight binding basis
CHAPTER 6

Introducing lattice Green’s functions

The non-equilibrium Green’s function transport formalism is a theoretical framework currently used for the computation of conductance in nanoscale devices[11]. The basic algorithm is described in this Chapter, and we leave an application of it for Chapter 7. The mathematics presented here indicate the general framework to be followed, despite our use of a first-neighbor tight binding basis, and therefore they can be used as a guide for improved models (for instance, using a numerical orbital basis). Let $H$ be a tight-binding Hamiltonian, its associated Green’s function is formally defined the following way:

$$(H - E) \times G = I,$$

or:

$$G(r, r'; E) = [H(r, r') - E\delta_{r, r'}]^{-1}.$$  \hspace{1cm} (6.1)

Equation (6.1) has divergencies at the eigeenergies of the Hamiltonian operator, which are usually dealt with by adding a small complex part to the denominator. In this chapter we obtain an analytical expression for the Green’s function of a (5,5) carbon nanotube, and a tight-binding expression to be solved numerically for a Green’s function in a finite spatial region. This second case of Green’s functions are employed for studies of electron transmittance in molecular systems, an example of which will be presented in Chapter 7.

6.1 Time-independent lattice Green’s functions for a (5,5) SWNT

Bloch’s theorem

Let $U(r)$ be the potential at position $r$. Lattice periodicity implies[4, 35] $U(r + R_j) = U(r)$, where $R_j$ is a translation of the Wigner-Seitz lattice. The translation operator $\hat{T}_{R_j} \equiv e^{-\frac{i}{\hbar}\hat{P} \cdot R_j}$ satisfies the following relations:

$$[\hat{T}_{R_j}, \hat{H}] = 0,$$

$$[\hat{T}_{R_j}(\hat{P}), \hat{T}_{R_j}^\dagger(\hat{P}')] = 0,$$  \hspace{1cm} (6.2a)

where $\hat{H}$ is a lattice Hamiltonian, and we make the dependence on $\hat{P}$ of the translation operator in (6.2b) explicit. Condition (6.2a) implies that the eigenvectors of the lattice Hamiltonian are those of
the translation operator. Now we let $|\Psi\rangle$ be a solution of the eigenvalue problem $(\hat{H} - E)|\Psi\rangle = 0$ and find an explicit expression for it. First $\hat{T}_{R_j}|\Psi\rangle = e^{i\hat{P} \cdot R_j}|\Psi\rangle = C_{R_j}|\Psi\rangle$. By employing the definition of the translation operator we have $\hat{T}_{R_j}|r\rangle = |r + R_j\rangle$, and since $\Psi(r) \equiv \langle r|\Psi\rangle$ we obtain $\Psi(r + R_j) = C_{R_j}\Psi(r)$. On the other hand, $\langle k|\hat{T}_{R_j}^\dagger|\Psi\rangle = e^{ik \cdot R_j}\langle k|\Psi\rangle = C_{R_j}\langle k|\Psi\rangle$, and so $C_{R_j} = e^{i\hat{P} \cdot R_j}$. This way

$$\Psi_{n,k}(r + R_j) = e^{ik \cdot R_j}\Psi_{n,k}(r) \quad \text{(Bloch’s theorem).} \quad (6.3)$$

The wavefunction

$$\Psi_{n,k}(r) = \frac{1}{\sqrt{\Omega}} e^{ik \cdot r} \sum_j u_{j,n,k}(r) \quad (6.4)$$

$(\Omega$ is the volume of the Wigner-Seitz cell) with the additional condition

$$u_{j,n,k}(r + R_j) = u_{j,n,k}(r), \quad (6.5)$$

satisfies Bloch’s theorem, Eq. (6.3).

**Eigensolutions for the (5,5) SWNT**

We now concentrate on the specifics for obtaining wave vectors for a (5,5) SWNT, aiming to obtain an analytical expression for the Green’s function.

![Figure 6.1](image)

**Figure 6.1** a) Our implementation of the tight-binding Hamiltonian matrix for the (5,5) SWNT, as well as its related Green’s function, is based upon knowledge of connections between nearest atoms. Invariant translations along $z$ occur within two rings (horizontal dotted lines). Two consecutive rings constitute the Wigner-Seitz unit cell. We denote atoms in the graphene A-sublattice by squares and atoms in the B-sublattice by circles. b) The (5,5) SWNT.

The unit cell of graphene has a basis with two atoms and is shown in Fig. 2.4 where we explicitly differentiated the two atoms (A and B) conforming the unit cell. The lattice possesses a basis as a result of the symmetry breaking that occurs by a translation between nearest neighbors. The atoms belonging to different sublattices within the Wigner-Seitz cell are separated by a distance $a_{C-C}$ (also recall that $a = \sqrt{3}a_{C-C}$). In order to obtain a (5,5) SWNT we wrap the graphene lattice along the direction defined by $5a_1 + 5a_2$. With the atom labelling proposed in Fig. 6.1a) we have
a one-to-one way to distinguish the sublattice an atom belongs to and its spatial position. If we employ cylindrical coordinates the atoms are located at:

\[ r(p, q) = \left( r, \phi_q(p), \frac{a}{2}p \right), \] (6.6)

with

\[ r = \frac{15}{2\pi}a_{C-c}, \] (6.7a)

\[ p \in \left\{ 1, \ldots, \frac{2L}{a} \right\}, \] (6.7b)

and

\[ \phi_q(p) \in \left\{ \begin{array}{ll}
0, & \frac{2\pi}{15}, \frac{2\pi}{5}, \frac{8\pi}{15}, \frac{4\pi}{5}, \frac{14\pi}{15}, \frac{6\pi}{5}, \frac{4\pi}{5}, \frac{8\pi}{15}, \frac{26\pi}{15} \\
\frac{29\pi}{15}, \frac{11\pi}{5}, \frac{7\pi}{5}, \frac{23\pi}{15}, \frac{9\pi}{5}, \frac{17\pi}{15}, \frac{7\pi}{5}, \frac{15\pi}{5}, \frac{3\pi}{5}, \frac{\pi}{5} & \text{for odd } p,
\end{array} \right. \] (6.7c)

This labelling can be further expressed by the following rule:

\[ (p + q) \mod 2 \left\{ \begin{array}{ll}
0 & \text{The atom belongs to the A-sublattice (circles)}, \\
1 & \text{The atom belongs to the B-sublattice (squares)}. \end{array} \right. \] (6.8)

A first step towards an explicit form of (6.4) for the (5,5) SWNT is the following:

\[ \Psi(r) = \frac{1}{\sqrt{10 \times P}} e^{ipka/2+m\phi_q(p)} \left[ u((p+q)\mod 2) \delta_{(p+q)\mod 2, 0} + u((p+q)\mod 2) \delta_{(p+q)\mod 2, 1} \right] |p, q\rangle, \] (6.9)

In (6.9) we have made the following explicit substitutions, valid for the (5,5) SWNT:

- We express \( \Omega \) by the product of 10 circumferential lattice sites times the number of rings, which we denote by \( P: \Omega = 10 \times P \) (\( P = 2 \) for a single unit cell of the (5,5) SWNT);
- The ‘envelope’ phase factor is written on the discrete lattice, \( k \cdot r = pka/2 + m\phi_q(p) \), and so are the basis functions \( |p, q\rangle \);
- By virtue of (6.8), condition (6.5) is automatically enforced.

In order to obtain \( u(0) \), \( u(1) \) we solve the eigenvalue problem with (6.9) and the lattice Hamiltonian:

\[ \hat{H} \equiv \sum_{p,q} \left\{ |p, q\rangle \langle p, q| + \sum_{p', q'} |p, q\rangle \gamma_{\pi}(p', q') \langle p', q'| \right\}. \] (6.10)

In Eq. (6.10) \( |p', q'\rangle \) is a basis vector denoting a nearest neighbor to the atom located at point \( (p, q) \). An atom at position \( (p, q) \) has nearest neighbors \( (p', q') \) at the neighboring rings, \( p - 1 \) and \( p + 1 \) —connecting to atoms labelled \( (p - 1, q) \) and \( (p + 1, q) \), respectively. The actual coordinates can be obtained from (6.7b) and (6.7c). An atom at \( (p, q) \) also connects to another atom on its own ring in two non-equivalent ways:

- By increasing \( \phi \) by \( \frac{2\pi}{15} \) (connecting to point \( (p, q + 1) \)), if the atom belongs to the A-sublattice \( [(p + q)\mod 2 = 0] \).
By decreasing $\phi$ by $\frac{2\pi}{15}$ (connecting to point $(p, q - 1)$, if the atom belongs to the B-sublattice $[(p + q) \text{mod} 2 = 1]$.

By writing $(\hat{H} - E) \Psi = 0$ explicitly we decompose the lattice Hamiltonian into sets of pairs of the form (each row for a given sublattice):

$$
(\varepsilon - E)e^{ik \cdot r(p, q)} u(0) - \gamma_p e^{-ik \cdot r(p, q + 1)} \left[ e^{ik \cdot r(p + 1, q)} + e^{ik \cdot r(p - 1, q)} + e^{ik \cdot r(p, q + 1)} \right] u(1) = 0
$$

$$
(\varepsilon - E)e^{ik \cdot r(p, q + 1)} u(1) - \gamma_p e^{-ik \cdot r(p, q)} \left[ e^{ik \cdot r(p + 1, q + 1)} + e^{ik \cdot r(p - 1, q + 1)} + e^{ik \cdot r(p, q)} \right] e^{ik \cdot r(p, q)} u(0) = 0
$$

Previous equation can be expressed as the eigenvalue problem:

$$
\begin{pmatrix}
\varepsilon - \gamma_p e^{-ik \cdot r(p, q + 1)} [e^{ik \cdot r(p + 1, q + 1)} + e^{ik \cdot r(p - 1, q + 1)} + e^{ik \cdot r(p, q)}]
\end{pmatrix} u(0) = E 
\begin{pmatrix}
\varepsilon e^{ik \cdot r(p, q)} u(0)
\end{pmatrix} u(1)
$$

We further assign to $\gamma_p$ the value $-2.7 \text{eV}[51]$. We also have $k \equiv (0, m, k)$ with $k \in [-\pi/a, \pi/a]$, and $m \in [-4, \ldots, 5]$.

We are ready to solve for $u(0)$ and $u(1)$. The only remaining thing to realize is that the phase differences can be written in a way to reduce the problem in real space into a $2 \times 2$ subspace, containing only $u(0)$ and $u(1)$:

$$
(\varepsilon - E) e^{ik \cdot r(p, q)} u(0) - \gamma_p e^{-ik \cdot r(p, q + 1)} \left[ e^{ik \cdot r(p + 1, q)} + e^{ik \cdot r(p - 1, q)} + e^{ik \cdot r(p, q + 1)} \right] e^{ik \cdot r(p, q + 1)} u(1) = 0
$$

$$
(\varepsilon - E) e^{ik \cdot r(p, q + 1)} u(1) - \gamma_p e^{-ik \cdot r(p, q)} \left[ e^{ik \cdot r(p + 1, q + 1)} + e^{ik \cdot r(p - 1, q + 1)} + e^{ik \cdot r(p, q)} \right] e^{ik \cdot r(p, q)} u(0) = 0
$$

Previous equation can be expressed as the eigenvalue problem:

$$
\begin{pmatrix}
\varepsilon - \gamma_p e^{-ik \cdot r(p, q + 1)} [e^{ik \cdot r(p + 1, q + 1)} + e^{ik \cdot r(p - 1, q + 1)} + e^{ik \cdot r(p, q)}]
\end{pmatrix} u(0) = E 
\begin{pmatrix}
\varepsilon e^{ik \cdot r(p, q)} u(0)
\end{pmatrix} u(1)
$$

We finally rewrite the $2 \times 2$ vector in a more convenient way:

$$
\begin{pmatrix}
e^{ik \cdot r(p, q)} u(0)
e^{ik \cdot r(p, q + 1)} u(1)
\end{pmatrix}
e^{ik \cdot r(p, q)} \begin{pmatrix}u(0)\end{pmatrix} u(1)
$$

Notice that, by pairing up the coordinates in the process (6.11-6.13) we have restricted $q$ to belong to the $A-$sublattice. With this understanding, we express the system’s wavefunction, (6.9) for the lattice:

$$
\Psi_{k, m}(p, q) = \frac{e^{ik \cdot r(p, q)}}{\sqrt{10P}} \begin{pmatrix}u(0)\end{pmatrix} u(1)
$$

$q$ belongs to the $A-$sublattice.

We now place explicit expressions for the phase differences for a (5,5) SWNT in order to solve for $u(0)$ and $e^{ik \cdot [r(p, q + 1) - r(p, q)]} u(1)$ in (6.12). First, $k \cdot [r(p, q + 1) - r(p, q)] = \frac{2\pi}{15} m$. Then an explicit
expression for (6.12) is:

\[
\begin{pmatrix}
   \epsilon - E & -\gamma \frac{e^{-\frac{\pi}{5} \cos \left(\frac{1}{2} ka\right)}}{\epsilon - E} \\
   -\gamma \frac{e^{-\frac{\pi}{5} \cos \left(\frac{1}{2} ka\right)}}{\epsilon - E} & \epsilon - E
\end{pmatrix}
\psi_{k,m}(p,q) = \begin{pmatrix} 0 \\ 0 \end{pmatrix}
\] (6.14)

The eigenvalues of system (6.14) are:

\[
E(k,m) = \epsilon \mp \gamma \frac{e^{-\frac{\pi}{5} \cos \left(\frac{1}{2} ka\right)}}{\epsilon - E} \sqrt{1 + 4 \cos \left(\frac{1}{2} ka\right) \left[\cos \left(\frac{1}{2} ka\right) + \cos \left(\frac{\pi m}{5}\right)\right]}
\]

In order to account for the ± sign, we introduce the variable \( s \), which acquires the values \(-1, +1\). Then redefine the eigenenergies of the system the following way:

\[
E_s(k,m) \equiv \epsilon + s \gamma \frac{e^{-\frac{\pi}{5} \cos \left(\frac{1}{2} ka\right)}}{\epsilon - E} \sqrt{1 + 4 \cos \left(\frac{1}{2} ka\right) \left[\cos \left(\frac{1}{2} ka\right) + \cos \left(\frac{\pi m}{5}\right)\right]}
\] (6.15)

Notice, \( E_{-s}(k,m) = -E_s(k,m) \), \( E_s(-k,m) = E_s(k,m) \), and \( E_s(k,-m) = E_s(k,m) \).

We are ready to obtain \( u(0) \) and \( u(1) \). We recall that the normalization of the overall wave function is made over all sites, so we make \( u(0) = 1 \). We then find \( u(1) \) which satisfies (6.14):

\[
e^{2\pi i/15}u(1)_{k,m,s} = -s \frac{e^{\frac{\pi}{5} \cos \left(\frac{1}{2} ka\right)}}{\sqrt{1 + 4 \cos \left(\frac{1}{2} ka\right) \left[\cos \left(\frac{1}{2} ka\right) + \cos \left(\frac{\pi m}{5}\right)\right]}}
\] (6.16)

From (6.16) we see

\[
\begin{align*}
u(1)_{k,m,-s} &= -u(1)_{k,m,s} \\
u(1)_{-k,m,s} &= u(1)_{k,m,s} \\
u(1)_{k,-m,s} &= (u(1)_{k,m,s})^*.
\end{align*}
\]

The Berry’s phase \( \theta(k,m) \) in \( e^{i\theta(k,m)} = \frac{e^{\frac{\pi}{5} \cos \left(\frac{1}{2} ka\right)}}{\sqrt{1 + 4 \cos \left(\frac{1}{2} ka\right) \left[\cos \left(\frac{1}{2} ka\right) + \cos \left(\frac{\pi m}{5}\right)\right]}} \) is shown in Fig. 6.1a). For \( m = 0, 5 \) we have \( \text{Im}[e^{2\pi i/15}u(1)_{k,m,s}] = 0 \), hence \( \theta(k,0) = \theta(k,5) = 0 \). We finally have an expression for the eigensolutions of the lattice Hamiltonian, namely:

\[
\Psi_{k,m,s}(p,q) = \begin{pmatrix} 1 \\ -se^{i\theta(k,m)} \end{pmatrix} \frac{e^{i\phi(p,k)/2+mp_q}}{\sqrt{10P}}.
\] (6.17)
We stress again that $q$ has been restricted to belong to the $A-$sublattice. In particular:

$$
\phi_q(p) \in \begin{cases} 
\{0, \frac{2\pi}{5}, \frac{4\pi}{5}, \frac{6\pi}{5}, \frac{8\pi}{5}\} & \text{for odd } p, \\
\{\frac{\pi}{5}, \frac{3\pi}{5}, \frac{\pi}{5}, \frac{9\pi}{5}\} & \text{for even } p.
\end{cases} \quad (6.18)
$$

**Analytical lattice Green’s function for the (5,5) SWNT**

The equation to solve is:

$$
(\hat{H} - E)G((p, q); (p', q'); E) = \begin{pmatrix} 1 & 0 \\
0 & 1 \end{pmatrix} \delta_{p,p'} \delta_{q,q'}.
$$

We use (6.16-6.18) to write the system’s eigenvectors in matrix form:

$$
\begin{pmatrix} \Psi_{k,m,-1}(p, q) \\
\Psi_{k,m+1}(p, q) \end{pmatrix} = \begin{pmatrix} 1 & 1 \\
e^{i0(k,m)} & -e^{i0(k,m)} \end{pmatrix} \frac{e^{i[pka/2+m\phi_q(p)]}}{\sqrt{10P}}.
$$

We write:

$$
G((p, q); (p', q'); E) = \sum_{m=-4}^{5} \int_{-\pi a}^{\pi a} dk \left( \Psi_{k,m,-1}(p, q) \Psi_{k,m+1}(p, q) \right) A_{k,m}(p', q'; E).
$$

In order to find the coefficients $A_{k,m}(p', q'; E)$, we multiply (6.19) on both sides by $\begin{pmatrix} \Psi_{k',m',-1}(p, q) \\
\Psi_{k',m'+1}(p, q) \end{pmatrix}$ and sum over $p, q$:

$$
\sum_{p=1}^{P} \sum_{q=1}^{5} \left( \Psi_{k',m',-1}(p, q) \Psi_{k',m'+1}(p, q) \right)^\dagger \left( \hat{H} - E \right) G((p, q); (p', q'); E) = \left( \Psi_{k',m',-1}(p', q') \Psi_{k',m'+1}(p', q') \right)^\dagger.
$$

Operating $\hat{H} - E$ to the left we get:

$$
\left( \Psi_{k',m',-1}(p', q') \Psi_{k',m'+1}(p', q') \right)^\dagger \left( \hat{H} - E \right) = \frac{e^{-i[pka/2+m\phi_q(p)]}}{\sqrt{10P}} \times
$$

$$
\begin{pmatrix}
e^{-E + b^*(k',m')e^{-i0(k',m')}} b(k',m') + (E-E)e^{-i0(k',m')}
e^{-E - b^*(k',m')e^{-i0(k',m')}} b(k',m') - (E-E)e^{-i0(k',m')}
\end{pmatrix},
$$

where we define $b(k, m) \equiv -\gamma_p \left[ 2e^{-\frac{2\pi m}{5}} \cos \left( \frac{j}{2}ka \right) + 1 \right]$. Then,

$$
\sum_{p=1}^{P} \sum_{q=1}^{5} \left( \Psi_{k',m',-1}(p', q') \Psi_{k',m'+1}(p', q') \right)^\dagger \left( \hat{H} - E \right) G((p, q); (p', q'); E) =
$$

$$
\frac{1}{10P} \sum_{m=-4}^{5} \int_{-\pi a}^{\pi a} \frac{1}{2}dk \left( \begin{pmatrix}
e^{-E + b^*(k',m')e^{-i0(k',m')}} b(k',m') + (E-E)e^{-i0(k',m')}
e^{-E - b^*(k',m')e^{-i0(k',m')}} b(k',m') - (E-E)e^{-i0(k',m')}
\end{pmatrix}
\begin{pmatrix}
e^{i0(k,m)} \\
- e^{i0(k,m)}
\end{pmatrix} A_{k,m}(p', q'; E) \sum_{p=1}^{P} e^{ip(k-k')/2} \sum_{q=1}^{5} e^{i(m-m')\phi_q(p)}
$$

51
The sum over \( q \) can be easily performed, and yields\(^1 \) \( 5 \delta_{m,m'} \). The sum over \( p \) can be expressed in the form:

\[
\sum_{p=1}^{P} e^{\frac{\alpha}{2}(k-k') api} = \begin{cases} 
P & \text{if } k = k' \\
1 - e^{\frac{1}{2}(k-k')api} & \text{if } k \neq k'
\end{cases}
\]  

(6.23)

In the understanding that we are modelling bands within the SWNT, \( k \) and \( k' \) are to be thought of as continuous variables. Then care must be taken when handling the case \( k \neq k' \).

---

\(1\)When \( m = m' \) we get \( \sum_{q=1}^{5} = 5; \) for \( m \neq m' \) we have:

\[
\sum_{q=1}^{5} e^{i(m-m')q} = \begin{cases} 
1-e^{i(m-m')/2x} & = 0 \\
1-e^{i(m-m')/2x}/5 & = 0 \\
1-e^{i(m-m')/2x}/5 & = 0 \\
1-e^{i(m-m')/2x}/5 & = 0 \\
1-e^{i(m-m')/2x}/5 & = 0
\end{cases}
\]

for odd \( p \)

for even \( p \)
reservoirs, connected through a sparse lattice Hamiltonian: \( A \). A finite-sized system will exhibit a spectrum of discrete eigenenergies. Consider now the following integral expression:

\[
\lim_{P \to \infty} \int_{-\frac{P}{a}}^{\frac{P}{a}} \frac{f(k) dk}{\sin \left[ \frac{1}{4} (k-k') a \right]} f(k') = \frac{4\pi}{a} f(k),
\]

for any continuous function on \( k, f(k) \). Then (6.22) finally becomes (we drop the primes on \( k', m' \)):

\[
\begin{pmatrix}
\epsilon - E - \gamma_k \sqrt{1 + 4 \cos \left( \frac{1}{2} k a \right) \cos \left( \frac{1}{2} k a \right)} \\
0
\end{pmatrix}
\begin{pmatrix}
A_{k,m}(p', q'; E) = \\
\sqrt{\frac{P}{10}} a \frac{\epsilon - i0(k,m) E}{E - i0(k,m)} e^{-i \frac{p' k a}{2 + m \Phi_q(p')}}
\end{pmatrix}
\]

This way (using (6.15)):

\[
A_{k,m}(p', q'; E) = \sqrt{\frac{P}{10}} a \frac{\epsilon - i0(k,m) E}{E - i0(k,m)} e^{-i \frac{p' k a}{2 + m \Phi_q(p')}}
\]

and

\[
G((p,q),(p',q'); E) = \frac{a}{40\pi} \sum_{m=-4}^{5} \int_{-\frac{P}{a}}^{\frac{P}{a}} dk \left( \frac{1}{E - i0(k,m) E} + \frac{1}{\epsilon + i0(k,m) E} \right) \left( \frac{e^{-i0(k,m) E}}{E - i0(k,m) E} + \frac{1}{E - i0(k,m) E} \right)
\]

The analytical expression for \( G^R((p,q),(p', q'); E) = G((p,q),(p', q'); E + i\Delta) \), with \( \Delta \to 0_+ \), will be used in the next Chapter.

### 6.1.1 Calculating the conductance with Datta’s procedure

A finite-sized system will exhibit a spectrum of discrete eigenenergies. Consider now the following (sparse) lattice Hamiltonian:

\[
\begin{pmatrix}
H_{L,L} & H_{L,C} & 0 \\
H_{C,L} & H_{C,C} & H_{C,R} \\
0 & H_{R,C} & H_{R,R}
\end{pmatrix}.
\]  

In (6.25) \( H_{L,L} \) and \( H_{R,R} \) are sections of the Hamiltonian describing the (perhaps infinite) electron reservoirs, connected through \( H_{L,C} \) and \( H_{R,C} \) to a finite, central region with Hamiltonian \( H_{C,C} \). Since in Eq. (6.25) opposite reservoirs do not directly connect with each other but only through the central section of the tube (this is, we neglect long-range interactions between reservoirs), we have made \( H_{L,R} = H_{R,L} = 0 \). Then (6.1) is written as:

\[
\begin{pmatrix}
H_{L,L} + i \frac{\Gamma(L,L)}{2} - E \delta_{L,L} \\
H_{C,L} & H_{C,C} - E \delta_{C,C} \\
0 & H_{R,R} + i \frac{\Gamma(R,R)}{2} - E \delta_{R,R}
\end{pmatrix}
\begin{pmatrix}
0_{L,R} \\
0_{C,R} \\
0_{R,R}
\end{pmatrix} = \begin{pmatrix}
\delta_{L,L} & 0_{L,C} & 0_{L,R} \\
0_{C,L} & \delta_{C,C} & 0_{C,R} \\
0_{R,L} & 0_{R,C} & \delta_{R,R}
\end{pmatrix}.
\]

(Subscripts are left to stress dimensionality of section matrices). \( \delta_{i,j} \) represents an identity matrix of dimensions \( i \times i \). We seek a consistent solution for \( G_{C,C}^R \) on previous system of equations. From
the second column on the r.h.s. of Eqn. (6.26) we obtain:

\[
\begin{bmatrix}
H_{L,L} + \frac{i}{2} \Gamma(L,L) - E \delta_{L,L}
\end{bmatrix}
\begin{bmatrix}
G^R_{L,C} + H_{L,C} G^R_{C,C} = 0_{L,C}
\end{bmatrix},
\]

(6.27a)

\[
H_{C,L} G^R_{L,C} + (H_{C,C} - E \delta_{C,C}) G^R_{C,C} + H_{C,R} G^R_{R,C} = I_{C,C},
\]

(6.27b)

\[
\begin{bmatrix}
H_{R,R} + \frac{i}{2} \Gamma(R,R) - E \delta_{R,R}
\end{bmatrix}
\begin{bmatrix}
G^R_{L,C} + H_{L,C} G^R_{C,C} = 0_{L,C}.
\end{bmatrix}
\]

(6.27c)

From (6.27a) and (6.27c) we can write:

\[
G^R_{L,C} = - \left[ H_{L,L} + \frac{i}{2} \Gamma(L,L) - E \delta_{L,L} \right]^{-1} H_{L,C} G^R_{C,C} \]

(6.28a)

\[
G^R_{R,C} = - \left[ H_{R,R} + \frac{i}{2} \Gamma(R,R) - E \delta_{R,R} \right]^{-1} H_{R,C} G^R_{C,C} \]

(6.28b)

From the first entry on the first column of (6.26), r.h.s., and the last entry on its third column we find:

\[
\left[ H_{L,L} + \frac{i}{2} \Gamma(L,L) - E \delta_{L,L} \right]^{-1} = G^R_{L,L} [I_{L,L} - H_{L,C} G^R_{C,L}]^{-1} \]

(6.29a)

\[
\left[ H_{R,R} + \frac{i}{2} \Gamma(R,R) - E \delta_{R,R} \right]^{-1} = G^R_{R,R} [I_{R,R} - H_{R,C} G^R_{C,R}]^{-1} \]

(6.29b)

respectively. We have used Planck constant here so that \( \Gamma \hbar \) has units of energy (\( \Gamma \) are broadening rate factors, the inverse of the lifetime of the electrons at reservoirs; they provide a non-zero probability for electron tunneling to (from) the central region). The submatrices \( G^R_{L,L}, G^R_{R,R}, G^R_{C,L} \) as well as \( G^R_{C,R} \) are obtained analytically for the (5,5) SWNT from (6.24); the lattice Hamiltonian for the SWNT is also known. Analicity of Green’s functions at boundaries is what allows band emulation in a finite-sized matrix systems. By substituting (6.28-6.29) into (6.27b) we finally obtain

\[
G^R_{C,C} = [H_{C,C} - E \delta_{C,C} + \Sigma_L + \Sigma_R]^{-1}.
\]

(6.30)

In previous expression we have used:

\[
\Sigma_L \equiv - H_{C,L} G^R_{L,L} [I_{L,L} - H_{L,C} G^R_{C,L}]^{-1} H_{L,C},
\]

(6.31a)

\[
\Sigma_R \equiv - H_{C,R} G^R_{R,R} [I_{R,R} - H_{R,C} G^R_{C,R}]^{-1} H_{R,C}.
\]

(6.31b)

Expressions obtained throughout this Chapter will be employed in Chapter 7.
CHAPTER 7

Conductance modulation on metallic carbon nanotubes by remote charges

7.1 Introduction

The high quantum conductance of metallic Single–Wall Carbon Nanotubes (SWNTs), in the absence of defects or interconnects, is promising for applications. It has been demonstrated that vacancies, configurational defects [29, 19] and mechanical deformations lower the conductance of a pristine tube. All-metallic SWNT circuits would have the best performance if one would be able to modulate their conductance without recourse to structural modifications. SWNTs are cylinders created by rolling a graphene sheet; i.e., quasi-one dimensional entities, in contrast to 3D metallic systems. Therefore, a perturbation placed along a SWNT implemented –e. g., by a molecule or surface potential with given periodicity [1]– will alter the electronic properties of an isolated tube. We propose in this Chapter some conditions that will lead to the modulation of conductance by the creation of local gaps in a metallic SWNT. We recently suggested the possibility of conductance modulation in metallic SWNTs by local gates [48], and have also been exploring symmetry properties that are involved in gap creation [33]. We consider a periodic oscillation of the self-consistent potential for the conduction electrons along the length of an infinite SWNT and a perturbation of a finite section of the tube that also shows similar conductance modulation[7]. The three factors involved are:

1. The strength of the self-consistent-potential induced by the remote charges.
2. The length of the unit cell of the superlattice.
3. The total number of unit cells of the superlattice that are in proximity to the SWNT.

7.2 Model and Methods

We consider a neutral SWNT and focus on the perturbation caused by excess charges alternating in sign placed onto equally spaced rings. The charge is uniformly distributed on a given ring of radius $2r$, where $r$ is the SWNT radius (Fig. 7.1(a)). A typical magnitude of the excess charge we use is $|q| = 2.5e$. We choose an axially symmetric potential to model the effect caused by the variation of the potential along the SWNT. The resultant redistribution of the $\pi$–electrons caused by the external potential $\phi(r)$ induces an electrostatic Coulomb potential that counteracts the external potential. As one can see in Fig. 7.1(b), the self-consistent potential oscillates within the gated region and ex-
Figure 7.1  a) A metallic, (5,5) SWNT placed in an electrostatic potential $\phi(r)$ originating from axial-symmetric rings of radius $2r$, where $r$ is the SWNT radius. A charge of magnitude $|q|$ alternating in sign is placed on consecutive rings. b) The change in potential energy, $-e\phi(r)$, caused by the external rings alone (dashed line) and the resulting potential energy after self-consistent rearrangement of $\pi$-electrons (within Hartree-Fock theory), for 5 pairs (left) and 20 pairs (right) of rings, using $|q| = 2.5e$. Twice the distance between equally spaced rings defines the superlattice length $L$ which here is four times the SWNT lattice constant, $L = 4L_0$. $L_0 = a$ and $a = \sqrt{3}a_{C-C}$ where $a_{C-C} = 1.44$ Å is the distance between nearest carbon atoms.
hibits long tail-ends. The total self-consistent potential is naturally more uniform than the external potential $\phi(r)$ given by the dashed line in Fig. 7.1(b). However, the screening is far from complete. This oscillation period plays a crucial role for the modulation of conductance. We employ and combine single-particle Green’s functions, a modified tight-binding Hamiltonian and also use the Kronig-Penney model to capture the elementary physics involved in the conductance modulation. We account for the effect of charge redistribution [13] within the Hartree-Fock approximation assuming charge equilibrium for the remote rings. The $\pi$-electrons that are responsible for electron transport are modelled by using the empirical nearest-neighbor tight-binding approach [51]:

$$\langle r | \Psi_{n_0} \rangle = \sum_i C_{n_0}^i \Phi_\pi(r - r_i). \quad (7.1)$$

Here $\{r_i\}$ represent the positions of the SWNT carbon atoms. $\Phi_\pi(r - r_i)$ are atomic orbitals for the $\pi$-electrons. The nearest-neighbor tight-binding approximation reproduces the characteristics of $\pi$-electrons fairly well. The Hamiltonian in this approximation is given by:

$$\hat{H}_0 = \sum_{\langle ij \rangle} \gamma_\pi \hat{c}_i^\dagger \hat{c}_j, \quad (7.2)$$

where $\gamma_\pi = -2.7eV$ is the hopping integral [51], and $\langle ij \rangle$ indicates that the sum is performed only for neighboring sites $i$ and $j$. The coefficients $C_{n_0}^i$ are determined by the eigenvectors $|\Psi_{n_0}\rangle$ of $H_0$ according to (7.1). Full details are given in Chapter 6. (We sort the eigenvectors in order of their energy levels $E_{n_0}$). However, because charge neutrality is locally violated, one must modify the Hamiltonian (7.2) and we follow a procedure described in [13]. For our basis, the Coulomb kernel is:

$$U_{ij,kl} = \delta_{ij} \delta_{kl} \times \begin{cases} \frac{1}{r_{ik}} & i \neq k \\ U_0 \quad \text{(in our units, }eU_0 = 14.6 V) & i = k \end{cases} \quad (7.3)$$

($r_{ik} = |r_i - r_k|$). For our perturbation—an external potential energy of magnitude $-e\phi(r)$—the SWNT as a whole remains neutral (the total number of $\pi$-electrons for a given spin $n_{CN}$ is well-defined once the length of the SWNT to be modelled has been chosen), but a local redistribution of charge occurs. We assume that the charge distribution of the remaining atomic electrons (both core and $\sigma$ electrons which we refer to as background charge) is not modified by the external field, which holds provided the field is small. Then the relative change of the charge with respect to the unperturbed tube is related to the density matrix:

$$\delta \rho_{ij} = -2e \left[ \sum_{n=1}^{n_{CN}} \langle r_i | \Psi_n \rangle \langle \Psi_n | r_j \rangle - \sum_{n_0=1}^{n_{CN}} \langle r_i | \Psi_{n_0} \rangle \langle \Psi_{n_0} | r_j \rangle \right] = -2e \left[ \sum_{n=1}^{n_{CN}} C_{n}^i (C_{n}^j)^* - \sum_{n_0=1}^{n_{CN}} C_{n_0}^i (C_{n_0}^j)^* \right].$$

We now calculate both $\delta \rho_{ij}$ and $\{|\Psi_n\rangle\}$ self-consistently within the Hartree-Fock approximation as a solution of the following Hamiltonian (Einstein’s summation rule implied):

$$\hat{H} = \hat{H}_0 + \left( -e\phi_e(i) \delta_{i,j} + eU_{ij,kl}^{HF} \delta \rho_{kl} \right) \hat{c}_i^\dagger \hat{c}_j. \quad (7.4)$$

Where:

$$eU_{ij,kl}^{HF} \delta \rho_{kl} = e \left( U_{ij,kl} - \frac{1}{2} U_{il,kj} \right) \delta \rho_{kl} = \sum_{i \neq k} \delta_{ij} e \delta \rho_{k,k} \frac{e}{r_{ik}} - \frac{e}{2} \delta \rho_{ij}. \quad (7.5)$$
Figure 7.2  a) Dispersion relation for the two bands \((E_{+5,0}, E_{-5,0})\) crossing at the Fermi level \((E = 0)\) for a \((5,5)\) SWNT. A small, periodic perturbation along the SWNT will cause, according to the Kronig-Penney model, forbidden gaps for electronic motion at the regions where folding occurs. b) For a field with the periodicity given in Fig. 7.1, folding would occur at the energies shown. c) For comparison purposes, we also show the dispersion relation for a superlattice length \(L\) equal to \(6L_0\). A \((5,5)\) SWNT placed in this superlattice would become a semiconductor.

In previous equation, the term \(-e\delta\rho_{ij}/2r_{ij}\) runs for \(j \neq i\). For \(-e\phi(r_j) \rightarrow 0\) the positive and negative charges balance and \(\delta\rho_{ij} \rightarrow 0\). This reduces the Hamiltonian (7.4) to the familiar case, (7.2).

For \(\phi(r)\) produced by a periodic arrangement of rings (Fig. 7.1(a)), the self-consistent potential energy exhibits a few oscillations with period \(L\) equal to twice the spacing between rings. We consider here a \((5,5)\) nanotube. However, the following argument applies to any metallic SWNT, provided modifications to the dispersion relation and analytical Green’s functions are made.

The eigenvalues of \(H_0\) for an unperturbed \((5,5)\) SWNT are given by Eq. (6.15):

\[
E_{s,0}(k,m) = s\gamma \pi \sqrt{1 + 4 \cos \left(\frac{1}{2}ka\right) \left[\cos \left(\frac{1}{2}ka\right) + \cos \left(\frac{\pi m}{5}\right)\right]}
\]

where the extra zero in \(E_{s,0}\) is meant to indicate that the eigenergies are those of a nanotube for which the electrostatic perturbation has not been set up; \(k\) is the wavevector along the length of the SWNT, \(m\) is the (quantized) circumferential wavevector and \(s = \pm 1\) (sometimes referred to as ‘pseudospin’) arises from orthogonality of the two wavefunctions belonging to different sublattices for the hexagonal lattice. For the \(E_{s,0}(k,5)\) bands, which are the most important for transport, we need to modify Eq. (6.15) so that the energies are monotonic functions of \(k\). We depict them in Fig. 7.2(a), which shows the two bands present close to the Fermi level. There are more bands present in the gray zone, but they are not displayed because they are not relevant for the discussion. For this region conductance is equal to \(2G_0\), where \(G_0 = \frac{2e^2}{h}\) is the quantum of conductance.

Consider first an infinitely long SWNT embedded in a superlattice created by an infinite array of equally-spaced rings. The self-consistent potential would then be periodically oscillating and this would induce according to the Kronig-Penney model a folding of the bands. We show the effect in
the dispersion relation in Fig. 7.2. Vertical lines in Fig. 7.2(a) indicate the zone folding as a result of a perturbation which decreases the size of the Brillouin zone by a factor of four. In Fig. 7.2 (b) we show the modified band structure. Bold horizontal lines show forbidden energy regions for the electrons of a given band. Since there are two bands and folding does not occur simultaneously for both of them for the same value of energy, we expect in this case the conductance to be lowered at most by $1G_0$. The reason for this modulation is that for a vicinity of the $k$-points where folding occurs, a mini-gap develops. This gap-opening is equivalent to a lowering of the density of states (DOS), and this suppression of the DOS results in the modulation of the conductance. For large enough $|V|$ ($|V|$ is the strength of the self-consistent potential), an overlap of two gaps and further suppression of the conductance becomes possible. Also, a perturbation with periodicity that equals a multiple of $3L_0$ will fold the bands at the Fermi point, where the two bands cross: We show the modified band structure for a self-consistent potential with periodicity $6L_0$, $\sim 1.5nm$ in Fig. 7.2(c). Such a perturbation will create a gap for both bands and as a result the conductance at the Fermi point will be zero.

Previous argument can be applied when the length of the CNT unit lattice ($L_0$) is commensurate with twice the spacing between rings ($L$): $nL_0 = mL$ for $n$ and $m$ integers. The Kronig-Penney model can not be used if the periods of the CNT lattice and the lattice for the rings are incommensurate. For a finite system, we believe that even an incommensurate potential will alter the dispersion of the CNT charge carriers in certain regions in $k$-space corresponding to the Fourier component of the potential. This translates into conductance modulation at certain values of energy. Since a strong modulation of conductance requires a long section in which the local density of states is suppressed, one must consider a finite length potential that is long enough or strong enough. This indicates the relation between the modulating effect and the size of the unit cell for the superlattice.

We now describe the effects of a small number of rings around a metallic SWNT. We use the approach of Datta [11] to calculate the electron transport properties. We obtain the relative decrease in conductance in the (5,5) SWNT in terms of zero-temperature single particle Green’s functions. The Green’s function we use is given by Eq. (6.30) where $H$ is defined by Eq. (7.4). $H_{CL}$ and $H_{CR}$ are the submatrices in the Hamiltonian connecting the section under study (C) and semi-infinite, unperturbed sections of the (5,5) SWNT at its left (L) and right (R) (which we call hereafter “leads”). $H_{LC} = H_{CL}^T$ and $H_{RC} = H_{CR}^T$. For the (5,5) SWNT, $\Sigma_{L,R}$ are nonzero only for the submatrices of dimensions 10 $\times$ 10 which are located at the positions where our finite tube is in contact with the leads. $G^{R}_{LL}$, $G^{R}_{RR}$, $G^{R}_{CL}$ as well as $G^{R}_{CR}$ are also 10 $\times$ 10 matrices. Further symmetry for the (5,5) SWNT allows to have orthogonal wavefunctions within a unit cell having two carbon atoms. This allows one to obtain the aforementioned $G^R$-submatrices in terms of the $2 \times 2$ matrix, c.f. Eq. (6.24):

$$G^R((p,q),(p',q');E) = \frac{a}{10\pi} \sum_{m=-4}^{5} \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} M(k,m) \text{Exp} \left[ i \mathbf{k} \cdot (\mathbf{r} - \mathbf{r}') \right] dk,$$

where the matrix $M(k,m)$ carries the information required by orthogonality of wavefunctions in a
They correspond to a unit lattice of length 4. In Fig. 7.3(b) we show the conductance modulation for 50 pairs of rings as those shown in Fig. 7.1(a).

### 7.3 Results and conclusions

In Fig. 7.3(b) we show the conductance modulation for 50 pairs of rings as those shown in Fig. 7.1(a). They correspond to a unit lattice of length 4L0. The self-consistent potential is caused by a charge |q| = 2.5e on each ring and applied to a (5,5) SWNT of length 200L0. A significant suppression of the conductance can be seen at four values of energy which are determined by the energies at which band-folding occurs. These have been given in Fig. 7.2(b) and are shown for comparison in Fig. 7.3(c). They clearly agree even though now the perturbation is of finite length. For an unperturbed (5,5) SWNT, the conductance in this energy range is equal to 2G0 since there are two conduction channels present (Fig. 7.3(a)). In our results, the transmission varied from 2 to 1.8 and shows a number of low amplitude dips and heights in the transmittance that increases linearly with the length of the SWNT. Because the goal of our work is to investigate the major suppression of the conductance due to the periodic self-consistent potential, we did not further investigate this low amplitude structure or attempt to remove it by thermal averaging.

A clear suppression of conductance at the energy points calculated within the Kronig-Penney model can be seen. Unlike the case of heterojunctions created by nanotubes of different chiralities, in this case there is no mismatch between the quantized component of the wavevector. This means...
Figure 7.3  a) Conductance as obtained with our method for an unperturbed (5,5) SWNT of length \( \sim 50 \text{nm} \). b) Modulation of conductance for 50 pairs of rings, \( |q| = 2.5e \) and spacing between rings given in Fig. 7.1. c) Dip positions agree with values predicted by the Kronig-Penney model. Besides additional interference, only one conduction channel is at most suppressed.
that the conductance is high and close to the nominal value $2G_0$ for energy regions apart from the folding energies. We finally mention that we have observed in our calculations a logarithmic dependence between the length to which the perturbation is applied (for fixed external potential) and conductance, and similarly a logarithmic dependence between conductance modulation and the magnitude of $q$ (for a fixed length).

A recent follow-up on this model calculations was provided in Ref. [57] where co-doping was added to a (5,5) carbon nanotube to open a gap. Their results are based on an *ab initio* numeric orbital approach. Main results are shown in Fig. 7.4.

In conclusion, we have shown the possibility of conductance modulation in metallic SWNTs by applying a longitudinal periodic electrostatic perturbation along a section of finite size. We remark the fact that any metallic tube (independent of its actual chirality) is being placed in the proximity of a structure as the one we have described, its conductance can be modulated. Furthermore, since the electrostatic potential that we consider does not have any components along the circumference, no mismatch between wavefunctions in the gated region and the free tube arises, as it is usually the case for metal-semiconducting junctions. This keeps the value of the conductance close to that of a free, ballistic, metallic SWNT in regions comprising energies other than the ones where bending occurs.
APPENDIX A Matlab scripts

A.1 Script to read *.band files
The only required changes are to change the path to the actual file (instead of filename.bands). The vertical range in the axis can also be modified at will.

%script to read bands SIESTA-file
%Salvador Barraza-Lopez. University of Illinois
%First clear off all previous data
clc
clear
file='filename.bands'; fid=fopen(file);
%===============================================
%a) Header info
tline = fgetl(fid);
FermiE= sscanf(tline,'%f')
%ignore second and third lines
tline = fgetl(fid); tline = fgetl(fid);
%Number of bands, nspin, nkpoints:
tline = fgetl(fid);
A=sscanf(tline,'%f');
Nbands=A(1) Nspins=A(2) Nkpoints=A(3) clear A;
%===============================================
%b) Collecting data to plot bands
Nlines=ceil(Nbands/10) for i=1:Nkpoints
  for j=1:1
tline = fgetl(fid);
A=sscanf(tline,’%f’);
  for k=1:10
    Band(i,(j-1)*10+k)=A(k+1);
  end
end
for j=2:Nlines-1
tline = fgetl(fid);
A=sscanf(tline,’%f’);
  for k=1:10
    Band(i,(j-1)*10+k)=A(k);
  end
end
%We omit the last line
tline = fgetl(fid);
end
%===============================================
%closing input file; plotting results
fclose(fid);
Bands=plot(Band) set(Bands,'Color','red') axis([1
Nkpoints ... FermiE-12 FermiE+12])

A.2 Sample script to read *.PDOS files

clc
clear
%file='E:\Salva\9SPRING2006\84tube\per\84per5.PDOS'
%file='E:\Salva\9SPRING2006\93tube\par\Si_c42_nt93.PDOS'
file='E:\Salva\9SPRING2006\Hpassivated124\Undoped.PDOS';
fid=fopen(file);
tline = fgetl(fid);
text= sscanf(tline,'%c');
if text=='<pdos>' disp('Reading PDOS file') else disp('Format
error in input file') end tline = fgetl(fid);
text= sscanf(tline,'%c');
if text=='<nspin>1</nspin>' disp('One spin component') else
disp('Two spin components not yet implemented') end
tline = fgetl(fid);
text= sscanf(tline,'%c');
n=size(text,2); norbitals=0; for j=1:n-23
num=text(n-11-j)*10^(0)-48; norbitals=norbitals+num*10^(j-1); end
norbitals
tline = fgetl(fid);
text= sscanf(tline,'%c');
if text>-10.0 disp('this is a number') end
counter=1; tline = fgetl(fid);
text= sscanf(tline,'%f');
if text>-10.0 Energy(counter,1)=text;
counter=counter+1;
while text>-10.0 tline = fgetl(fid);
text= sscanf(tline,'%f');
if text>-10.0
Energy(counter,1)=text;
counter=counter+1;
end
counter=counter-1; disp('The number of energy values is')
counter disp('on the interval (eV)') Energy(1), Energy(counter)
% We will get four rows of data
% a) H atoms
% b) S
% c) C
% d) Sum
PDOS=zeros(counter,4); warnindex=0; atmcounter=0; for
orbitalindex=1:norbitals orbitalindex
  for i=1:3
    tline = fgetl(fid);
  end
  tline = fgetl(fid);
  text= sscanf(tline,'%c');
  n=size(text,2);
  if n==13 text(14)=' ';
  end
  text2=' species="H" ';
  text3=' species="Si" ';
  text4=' species="C" ';
  if text==text2 % ignore coordinates
    atmcounter=atmcounter+1
    for i=1:7
      tline = fgetl(fid);
    end
    for i=1:counter
      tline = fgetl(fid);
      PDOS(i,1) = PDOS(i,1)+sscanf(tline,'%f');
      if PDOS(i,1)<0 disp('Warning'), warnindex=warnindex+1;
      end
    end
  elseif text==text3
    atmcounter=atmcounter+1
    for i=1:7
      tline = fgetl(fid);
    end
    for i=1:counter
      tline = fgetl(fid);
      PDOS(i,2) = PDOS(i,2)+sscanf(tline,'%f');
      if PDOS(i,2)<0 disp('Warning'), warnindex=warnindex+1;
      end
    end
  elseif text==text4
    atmcounter=atmcounter+1
    for i=1:7
      tline = fgetl(fid);
    end
    for i=1:counter
      tline = fgetl(fid);
      PDOS(i,2) = PDOS(i,2)+sscanf(tline,'%f');
      if PDOS(i,2)<0 disp('Warning'), warnindex=warnindex+1;
      end
    end
  end
end
elseif text==text3
  atmcounter=atmcounter+1
  for i=1:7
    tline = fgetl(fid);
  end
  for i=1:counter
    tline = fgetl(fid);
    PDOS(i,2) = PDOS(i,2)+sscanf(tline,'%f');
    if PDOS(i,2)<0 disp('Warning'), warnindex=warnindex+1;
    end
  end
elseif text==text4
  atmcounter=atmcounter+1
  for i=1:7
    tline = fgetl(fid);
  end
end
for i=1:counter
    tline = fgetl(fid);
    PDOS(i,3) = PDOS(i,3)+sscanf(tline,'%f');
    if PDOS(i,1)<0 disp('Warning'), warnindex=warnindex+1;
    end
end
for i=1:2
    tline = fgetl(fid);
    text= sscanf(tline,'%c');
    end
end
%closing input file
fclose(fid);

%===============================================
subplot(4,1,3) plotH=plot(Energy,PDOS(:,1)), axis([Energy(1)...\nEnergy(counter) 0 2]); set(plotH,'Color','green') subplot(4,1,1)
plotSi=plot(Energy,PDOS(:,2)), axis([Energy(1) Energy(counter)...
040]); set(plotSi,'Color','blue') subplot(4,1,2)
plotC=plot(Energy,PDOS(:,3)), axis([Energy(1) Energy(counter) 0...
20]); set(plotC,'Color','black') for j=1:counter for k=1:3
    PDOS(j,4)=PDOS(j,4)+PDOS(j,k); end
end subplot(4,1,4)
plotD=plot(Energy,PDOS(:,4)), axis([Energy(1) Energy(counter) 0...
60]); hold on, set(plotD,'Color','red')
REFERENCES


Author’s Biography

Salvador Barraza-Lopez was born in Mexico City in 1977. He is the second of two sons. His parents are Fernando Barraza and Luz María López. He studied High school in Vocacional 9 of Instituto Politécnico Nacional (IPN) where his interest in science was born. He continued his education in Escuela Superior de Física y Matemáticas-IPN, graduating in 2001.

Salvador has been recipient of the following awards: First place in the Mexican Olympiad of Physics in 1995 and funded in part for graduate studies from Conacyt (Mexico). In 1999 he went to work in the Laboratory of Dr. Paul Kwiat, then at Los Alamos National Laboratory, where he performed experimental work in classical and quantum optics. Two peer-reviewed publications came out of an eight-month stay.

He is married to Isabel del Barco and has a son, Salvador Barraza-del Barco. Starting in late 2006 he is scheduled to begin a Postdoctoral position in the Department of Physics at Virginia Tech.