Electronic Properties of Silicon-Based Nanostructures

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Master of Science

By

Gian Giacomo Guzmán-Verri
B.A., Universidad de Costa Rica, 2004

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We have developed a new unifying tight-binding theory that can account for the electronic properties of recently proposed Si-based nanostructures, namely, Si graphene-like sheets and Si nanotubes. We considered the $sp^3s^*$ and $sp^3$ models up to first- and second-nearest neighbors, respectively. Our results show that the Si graphene-like sheets considered here are metals or zero-gap semiconductors, and that the corresponding Si nanotubes follow the so-called Hamada’s rule. Comparison to a recent ab initio calculation is made.
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A las mujeres de mi vida: Anita,
Caterina, Loredana,
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Chapter 1

Introduction

Richard Feynman was not wrong when he made an invitation to young researchers to a new field of physics during a famous talk that he gave to the American Physical Society on December 29, 1959, at Caltech [1]. Nowadays, this new field has a name: nanophysics. Nanophysics studies the physical properties of all sort of nanomaterials. In order to do this, it combines multiple fields in physics such as classical and quantum mechanics, electromagnetism, thermodynamics, and even quantum field theory. Among all these nanomaterials, the most popular ones are fullerenes, carbon nanotubes (CNT’s) and graphene. Actually, CNT’s are now considered the “hottest” research area in physics, according to a recent report in the Journal Nature [2].

The reason for their success is attributed to the fact that they provide “plenty of room” for potential applications in different areas, for instance:

- in biology, studies have shown that the properties of CNT’s could be used for developing new bio-nanodevices [3],

- in engineering, CNT’s and graphene could be the main components of the next
generation of electronic device due to their unique electronic properties [4],

• in physics, due to the nanoscale of the CNT’s, probes for atomic force microscopy made of these materials, have the capability of improving significantly the resolution of the images currently obtained from this technique [5].

After the first synthesis of CNT’s by Iijima more than a decade ago [6], other types of nanotubes have been predicted and experimentally observed such as GaN, BN, and AlN among others [7, 8, 9, 10]. However, it was not until fairly recent that the most obvious alternative candidate for creating graphene-like sheets and nanotubes was proposed: Si [11]. So far, only a handful of papers have explored the electronic properties of these nanomaterials, moreover, practically all of them correspond to ab initio calculations [11, 12, 13, 14]. In addition, different structures have been proposed, each one with different hybridizations: $sp^2$, $sp^2 − sp^3$ and $sp^3$.

The objective of this project is to apply the tight-binding models, so successfully used to study the electronic properties of graphene and CNT’s [15], to the Si nanostructures that have $sp^2$ and $sp^3$ hybridization. We will refer to this structures as silicene, Si (111), Si hexagonal nanotubes, and Si gear-like nanotubes.

The organization of the present work is the following: the electronic properties of graphene are reviewed in Chapter two; in Chapter three, we review the electronic properties of CNT’s and their chirality dependence; in Chapter four, our results from our tight-binding calculations are presented; finally, our conclusions and suggestions for further research on these materials are given in Chapter five.
Chapter 2

Tight-binding Theory

The tight-binding (TB) model is one of the most successful empirical theories in the study of the solid state properties of materials. Metals, semiconductors, insulators, superconductors and nanomaterials can be studied using this model. The form in which the theory is now presented, was proposed by Slater and Koster in 1954 [16]. The main idea underlying the TB scheme is that the wave function is expressed as a linear combination of atomic orbitals\(^1\). Then, the interaction of the atomic orbitals is represented by the so-called TB parameters, which have to be fitted to experiments or other theories. The TB model has the advantages that its implementation is straightforward and it incorporates the symmetry of the crystal.

In order to gain some physical insight into this theory, we first introduce the TB one-band model. The tight-binding one band model is the simplest model that it is possible to have that includes the basic physics that appear in more elaborate theories. We will take advantage of its simplicity to understand the ideas that are inherent in the

\[^1\text{Formally, the wave function is a linear combination of hybrid orbitals, however, most of the literature refers to them as atomic orbitals. Refer to Appendix A to see the differences between them.}\]
more realistic model that we will use in the present work, \textit{i.e.}, the multiband model.

Finally, we will apply the multiband formalism to two types of bulk materials, namely, GaAs and Si. The latter is of significant importance for the present work in the study of C-based and Si-based nanostructures.

2.1 The Tight-Binding One-band Model

In the present discussion of the one-band model, we follow the approach in Cohen et al. [17] and Feynman et al. [18].

Consider an infinite chain of identical atoms with lattice constant $a$. Since we want to keep the model as simple as possible, we make the following assumptions:

- \textit{All the atoms in the chain are motionless}. In reality, atoms move around their corresponding lattice point due to thermal excitations, for instance.

- \textit{Single electron approximation}. Each electron is under the influence of the attraction and repulsion of the positive atomic nucleii and the other electrons in the solid. By assuming that these interactions are effectively contained a single one, each electron moves independently from all the other electrons and, as a result, it is only affected by a periodic potential $V(r)$ that has the periodicity of the lattice.

- $|v_n\rangle$ is the only allowed state. When the electron is bound to the $n$-th ion, there is only one possible state: $|v_n\rangle$.

- $\langle v_n|v_p\rangle = \delta_{np}$. There is no overlap between the states of different atoms. Furthermore $\{|v_n\rangle\}$ provides an orthonormal basis.
Let us calculate the Hamiltonian in the \( \{ |v_nrangle \} \) representation. On the one hand, the diagonal elements are given by \( E_0 \equiv \langle v_n | H | v_n \rangle \); since all ions are identical, all diagonal elements are equal to \( E_0 \). On the other hand, the non-diagonal elements \( \langle v_n | H | v_p \rangle \), \( (p \neq q) \), are non-zero if they correspond to the nearest-neighbor interaction, in other words,

\[
\langle v_n | H | v_p \rangle = \begin{cases} 
-\gamma, p = n \pm 1, \\
0, \text{otherwise.}
\end{cases}
\] (2.1)

This is known as the first nearest neighbor approximation. Physically speaking, Eq. (2.1) means that an electron located on one atom, can tunnel onto the neighboring atom and \( \gamma \) is called the coupling between neighboring states. The Hamiltonian in the \( \{ |v_nrangle \} \) representation is given in Eq. (2.2). Since there are an infinite number of states \( |v_nrangle \), the dimension of the Hamiltonian matrix is infinite.

\[
H = \begin{pmatrix}
\vdots & \vdots & \vdots & \vdots \\
& E_0 & -\gamma & 0 & 0 \\
& -\gamma & E_0 & -\gamma & 0 \\
& 0 & -\gamma & E_0 & -\gamma \\
& 0 & 0 & -\gamma & E_0 \\
\vdots & \vdots & \vdots & \vdots 
\end{pmatrix}.
\] (2.2)

Hamiltonian diagonalization: An eigenstate of the Hamiltonian would be,

\[
|\varphi_k\rangle = \sum_{q=-\infty}^{\infty} c_q(k) |v_q\rangle = \sum_{q=-\infty}^{\infty} e^{ikqa} |v_q\rangle.
\] (2.3)
The coefficients \( c_q \) are chosen so that \(|\varphi_k\rangle\) satisfies Bloch’s theorem \(^2\). Using Eq. (2.3) in the eigenvalue equation
\[
H |\varphi_k\rangle = E(k) |\varphi_k\rangle,
\]
projected onto \(|v_q\rangle\) gives,
\[
E_0 e^{ikqa} - \gamma \left[ e^{ik(q+1)a} + e^{ik(q-1)a} \right] = E e^{ikqa}
\]
\[
\Rightarrow E(k) = E_0 - 2\gamma \cos ka.
\]

Equation (2.4) is known as the energy dispersion relation or, simply, dispersion relation. Figure 2.1 shows the dispersion relation for the one-band model. Its maximum and minima are equal to \( E_0 + 2\gamma \) at \( k = 0 \) and \( E_0 - 2\gamma \) at \( k = \pm \pi/a \), respectively. The band width is equal to \( 4\gamma \). This dependence of the width on \( \gamma \) is an important result in the one-band model: it says that the width of the band depends on the coupling between two states: the stronger the coupling between the states, the wider the energy band.

\(^2\)Let us show that \(|\varphi_k\rangle\) satisfies the Bloch theorem. The theorem says that \( \varphi_k(x + a) = e^{ika} \varphi_k(x) \), where \( \varphi_k(x) = \langle x |\varphi_k\rangle \). Notice that \( v_q = v_0(x - qa) \), therefore, \( \varphi_k(x) \) can be written as,
\[
\varphi_k(x) = \sum_{q=-\infty}^{\infty} e^{ikqa} v_0(x - qa).
\]

So,
\[
\varphi_k(x + a) = \sum_{q=-\infty}^{\infty} e^{ikqa} v_0(x + a - qa),
\]
\[
= \sum_{q=-\infty}^{\infty} e^{ikqa} v_0(x - [q - 1]a),
\]
\[
= e^{ika} \sum_{q'=-\infty}^{\infty} e^{ikq'a} v_0(x - q'a),
\]
\[
= e^{ika} \varphi_k(x).
\]

Hence, \( \varphi_k(x) \) does obey Bloch’s theorem.
So far, we have found in our one-band model that, for each value of $k$ in the interval $[-\pi/a, \pi/a)$, there is an eigenstate $|\varphi_k\rangle$ of $H$ associated with it. For a chain with an infinite number of ions, $k$ is a continuous variable. In a real solid, however, the lattice is finite, so $k$ will not be continuous anymore. This means that we will have to introduce boundary conditions at the edge of the solid. If we are interested in the physics of the bulk and not of the edge, then we can use the periodic Born-Von Karman (BVK) conditions. Consider a finite linear chain of $N$ ions and length $L$. The BVK conditions require the wave function have the same value at both ends of the chain. This is equivalent to placing an infinite number of identical chains of length $L$ or to make a circular chain. The eigenstate of the Hamiltonian would have the same form, but now they must satisfy
the BVK conditions. This is expressed in expansion coefficients \(c_q\) and, consequently in \(k\),
\[
c_q = e^{ikL} = 1 \Rightarrow k_n = \frac{n 2\pi}{L} \quad (n = 0, \pm 1, \pm 2, \ldots).
\] (2.5)

In principle, the integer number \(n\) can take values up to infinity. However, this is not necessary since \(k\) is required to be in the Brillouin zone. The spacing between two adjacent \(k_n\) values is \(\Delta k = k_{n+1} - k_n = 2\pi/L\), and the length of the Brillouin zone is \(2\pi/a\), therefore, the total number number of states in the Brillouin zone is,
\[
\frac{\text{length of the Brillouin zone}}{\text{spacing between } k_n\text{'s}} = \frac{2\pi/a}{2\pi/L} = \frac{L}{a} = N - 1 \approx N,
\] (2.6)

where we assumed that \(N\) is large. Thus, \(k_n\) is discrete in a finite linear chain of ions, and can take any of the values given by
\[
k_n = \frac{n 2\pi}{L} \quad (n = 0, 1, 2, 3, \ldots, N - 1).
\] (2.7)

As a concluding remark, notice that we only considered one state and, therefore, we obtained only one band. We will see in the following section that if we consider a number \(\mathcal{N}\) of states, then we will obtain a total number of \(\mathcal{N}\) bands.
2.2 The Tight-binding Multiband Model

The present is a review of the work done by Slater and Koster on simplified LCAO method for the periodic potential problem [16]. A Bloch sum is defined as [19]

\[ |b, \alpha, k\rangle = \frac{1}{\sqrt{N}} \sum_{i=1}^{N} e^{ik(\mathbf{R}_i + \tau_b)} |\mathbf{R}_i, b, \alpha\rangle, \]

(2.8)

where\(^3\)

\[ \alpha : \text{atomic orbital label (s, p}_x, p_y, p_z, d, \text{etc)}, \]

\[ b : \text{labels the atoms in a primitive unit cell}, \]

\[ k : \text{wave vector}, \]

\[ \mathbf{R}_i : \text{lattice vector}, \]

\[ \tau_b : \text{position vectors of the atoms in the basis}, \]

\[ N : \text{number of unit cells in the crystal}. \]

The sum extends over the atoms in equivalent positions in all the unit cells of the crystal. Equation (2.8) is called a tight-binding Bloch function or, simply, a Bloch sum.

In general, \(|b', \alpha', k|b, \alpha, k\rangle\) is not equal to zero because the atomic orbitals at different atomic positions are not orthogonal.

The position representation of the kets \(|b, \alpha, k\rangle\) and \(|\mathbf{R}_i, b, \alpha\rangle\) is defined as

\[ \Phi_{b\alpha k}(\mathbf{r}) \equiv \langle \mathbf{r}|b, \alpha, k\rangle, \]

(2.9)

\(^3\text{In the present work, we label } |\mathbf{R}, b, \alpha\rangle \text{ to denote an atomic orbital, and } |\mathbf{R}, b, \beta\rangle \text{ to denote a Löwdin orbitals, which we will define later in this chapter.}\)
\[ \phi_\alpha (\mathbf{r} - \mathbf{R}_{ib}) \equiv (\mathbf{r} | \mathbf{R}_i, b, \alpha), \quad (2.10) \]

where \( \mathbf{R}_{ib} \equiv \mathbf{R}_i + \mathbf{\tau}_b \). Because of the translational symmetry of a lattice, Eq. (2.8) has to satisfy Bloch’s theorem. If \( T^{(k)}(\mathbf{R}) \) denotes the translation operation and we apply it to \( \Phi_{b\alpha k}(\mathbf{r}) \),

\[
T^{(k)}(\mathbf{R})\Phi_{b\alpha k}(\mathbf{r}) = \Phi_{b\alpha k}(\mathbf{r} + \mathbf{R})
= \frac{1}{\sqrt{N}} \sum_i e^{i\mathbf{k} \cdot (\mathbf{R}_i + \mathbf{\tau}_b)} \phi_\alpha (\mathbf{r} + \mathbf{R} - \mathbf{R}_{ib})
= \frac{1}{\sqrt{N}} \sum_i e^{i\mathbf{k} \cdot (\mathbf{R}_i + \mathbf{\tau}_b)} \phi_\alpha (\mathbf{r} - [\mathbf{R}_{ib} - \mathbf{R}])
= e^{i\mathbf{k} \cdot \mathbf{R}} \left[ \frac{1}{\sqrt{N}} \sum_i e^{i\mathbf{k} \cdot \mathbf{R}'_ib} \phi_\alpha (\mathbf{r} - \mathbf{R}'_{ib}) \right]
= e^{i\mathbf{k} \cdot \mathbf{R}} \Phi_{b\alpha k}(\mathbf{r}).
\]

Hence, the Bloch sum satisfies Bloch’s theorem.

The wave function of the crystal \( |n\mathbf{k}\rangle \) is given by a linear superposition of Bloch sums:

\[
|n\mathbf{k}\rangle = \sum_{\alpha, b} c_{n\mathbf{k}}^{\alpha b} |b, \alpha, \mathbf{k}\rangle, \quad (2.11)
\]

and it is also a solution of the time-independent Schrödinger equation; that is,

\[
H |n\mathbf{k}\rangle = E_{nk} |n\mathbf{k}\rangle. \quad (2.12)
\]

The set of \( N \) translations \( T^{(k)}(\mathbf{R}) \) form a cyclic group. Hence, the irreducible representations of the group are one-dimensional and have the form \( e^{i\mathbf{k} \cdot \mathbf{R}} \), where the wave number vector \( \mathbf{k} \) labels the representation. Recall that two basis functions that belong
to two different irreducible representations, say \( T^{(k)}(R) \) and \( T^{(k')} (R) \), are orthogonal to each other; moreover, according to Bloch’s theorem, the Bloch sums \( |b, \alpha, k \rangle \) and \( |b, \alpha, k' \rangle \), are basis functions of \( T^{(k)}(R) \) and \( T^{(k')} (R) \), respectively. Thus, it follows from representation theory, that two Bloch sums with different wave vectors \( k \) and \( k' \), are orthogonal to each other, that is,

\[
(b, \alpha, k'|b, \alpha, k) = 0, \quad k' \neq k.
\] (2.13)

The energy eigenvalues can be found from Eq. (2.12):

\[
E_{nk} = \frac{\langle nk|H|nk \rangle}{\langle nk|nk \rangle} = \frac{\sum_{\alpha, \beta, b, b'} c_{nk}^{\alpha b} c_{nk}^{\beta b'} \bar{H}_{\alpha \beta}^{bb'}(k)}{\sum_{\alpha, \beta, b, b'} c_{nk}^{\alpha b} c_{nk}^{\beta b'} \bar{S}_{\alpha \beta}^{bb'}(k)}
\] (2.14)

where

\[
H_{\alpha \beta}^{bb'}(k) \equiv \langle b, \alpha, k|\hat{H}|b', \beta, k \rangle, \quad S_{\alpha \beta}^{bb'}(k) \equiv \langle b, \alpha', k|b', \beta, k \rangle.
\] (2.15)

\( H_{\alpha \beta}^{bb'}(k) \) and \( S_{\alpha \beta}^{bb'}(k) \) are the matrix elements of the so called energy integral matrix \( H \), and overlap integral matrix \( S \). Now we use the variational approach in order to find the dispersion relation. We minimize \( E_{nk} \) by taking the derivative of Eq. (2.14) with respect to \( c_{nk}^{\alpha b} \).

\[
\frac{\partial E_{nk}}{\partial c_{nk}^{\alpha b}} = \frac{\sum c_{nk}^{\beta b'} H_{\alpha \beta}^{bb'}(k)}{\sum c_{nk}^{\alpha b} c_{nk}^{\beta b'} S_{\alpha \beta}^{bb'}(k)} - \frac{\sum c_{nk}^{\alpha b} c_{nk}^{\beta b'} H_{\alpha \beta}^{bb'}(k)}{\left[ \sum c_{nk}^{\alpha b} c_{nk}^{\beta b'} S_{\alpha \beta}^{bb'}(k) \right]^2} \sum c_{nk}^{\beta b'} S_{\alpha \beta}^{bb'}(k) = 0.
\] (2.16)

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If we multiply Eq. (2.16) by \( \sum c_{\alpha k}^* c_{\beta k} S_{\alpha\beta}^{bb'}(k) \), we find

\[
\sum c_{\alpha k}^* H_{\alpha\beta}^{bb'}(k) \sum_{E_{nk}} c_{\beta k} S_{\alpha\beta}^{bb'}(k) = 0
\]

\[
\Rightarrow \sum c_{\alpha k}^* H_{\alpha\beta}^{bb'}(k) = E_{nk} \sum_{E_{nk}} c_{\alpha\beta} S_{\alpha\beta}^{bb'}(k) = 0,
\]

\[
\Rightarrow Hc - E_{nk}Sc_{nk} = 0,
\]

\[
\Rightarrow (H - E_{nk}S) c_{nk} = 0. \tag{2.17}
\]

If the matrix \((H - E_{nk}S)\) has an inverse, then the solution for Eq. (2.17) is the trivial solution \(c_{nk} = 0\), i.e., there is no wave function since \(|n, k\rangle = 0\). On the other hand, if this matrix does not have an inverse, then we obtain solutions that are different from the trivial one. An equivalent statement for saying that a matrix does not have an inverse is that its determinant is equal to zero, that is,

\[
|H - E_{nk}S| = 0. \tag{2.18}
\]

This equation is known as the secular equation. The explicit dependence on the wave vector \(k\), of the Hamiltonian matrix elements \(H_{\alpha\beta}^{bb'}\) can be obtained from Eqs. (2.8) and (2.15),

\[
H_{\alpha\beta}^{bb'}(k) = \sum_i e^{ik(R_i + \tau' b - \tau' b')} (0, b, \alpha | \hat{H} | R_i, b', \beta) = \sum_i e^{ikR_{a'b'}} E_{\alpha\beta}^{bb'}(R_i).
\]
Let us rewrite the previous equation as a shell summation:

\[(\alpha/\beta)_{bb'} \equiv H_{\alpha\beta}^{bb'}(k) = \sum_{j,l} e^{ik \cdot \delta_j^{(i)}} e_{\alpha\beta}^{bb'}(\delta_j^{(i)}) \]

\[= E_{\alpha\beta}^{bb'}(0) + \sum_{j} e^{ik \cdot \delta_j^{(1)}} e_{\alpha\beta}^{bb'}(\delta_j^{(1)}) + \sum_{j} e^{ik \cdot \delta_j^{(2)}} e_{\alpha\beta}^{bb'}(\delta_j^{(2)}) + \ldots \tag{2.19}\]

The vector \(\delta_j^{(1)}\) corresponds to the position vector of the \(j\)-th first nearest-neighbor (1NN), the vector \(\delta_j^{(2)}\) corresponds to the position vector of the \(j\)-th second nearest-neighbor (2NN) and so on. Figure 2.2 shows the first two shells of a graphene sheet, which in this case correspond to circles instead of spheres. Only the position vectors of the 1NN are shown for the sake of clarity. The atom "0" has three 1NN and six 2NN. All three 1NN vectors \(\delta_j^{(1)} (j = 1, 2, 3)\), have the same magnitude, which corresponds to the radius of the inner circle. In a similar way, all six 2NN vectors, \(\delta_j^{(2)} (j = 1, 2, \ldots, 6)\) have equal magnitude which corresponds to the radius of the outer circle.

### 2.3 Löwdin Orbitals

The Bloch sums are not orthogonal to each other since the atomic orbitals of different atoms are not orthogonal. Nevertheless, this problem is solved by creating new orbitals \(|R, b, \alpha\rangle\) which are linear combinations of the atomic orbitals \(|R, b, \beta\rangle\) [16, 20]:

\[|R, b, \alpha\rangle = \sum_{\alpha} (S^{-\frac{1}{2}})_{\beta\alpha} |R, b, \beta\rangle . \tag{2.20} \]
Figure 2.2: First and second nearest-neighbors in graphene. The inner and outer circles indicate where the 1NN and 2NN are. The vectors $\delta_j^{(1)} (j = 1, 2, 3)$ have all a magnitude equal to the radius of the inner circle.

Here, $\left(S^{-\frac{1}{2}}\right)_{\beta\alpha}$ is the $\beta\alpha$-th matrix element of the reciprocal of the square root of the overlap matrix $S$,

$$S_{\beta\alpha} \equiv \langle R, b, \beta | R, b, \alpha \rangle.$$ (2.21)

These new orbitals are called Löwdin orbitals. The Löwdin orbitals are orthonormal to each other, i.e. [16, 20]

$$\langle R, b, \alpha | R, b, \beta \rangle = \delta_{\alpha\beta}.$$ (2.22)
Now we can write the Bloch sums using the Löwdin orbitals,

\[ |b, \alpha, \mathbf{k}\rangle = \frac{1}{\sqrt{N}} \sum_{i=1}^{N} e^{i \mathbf{k} \cdot \mathbf{R}_i} |\mathbf{R}_i, b, \alpha\rangle \]  

(2.23)

2.4 Spin-orbit Interaction

We now consider spin-orbit interaction (SO) in our Hamiltonian, which we label as \( H_{SO} \). This interaction is local and modifies the band structure qualitatively and quantitatively [19]. Denoting by “↑” and “↓” spin “up” and spin “down”, respectively, a general matrix element of the total Hamiltonian \( H_T \), would be,

\[
\langle b, \alpha, \xi, \mathbf{k} | H_T | b', \beta, \xi', \mathbf{k}\rangle = \langle b, \alpha, \xi, \mathbf{k} | H | b', \beta, \xi', \mathbf{k}\rangle + \langle b, \alpha, \xi, \mathbf{k} | H_{SO} | b', \beta, \xi', \mathbf{k}\rangle \\
= (\alpha/\beta)_{bb'} \delta_{\xi \xi'} + \lambda^{b}_{\alpha \beta} \delta_{bb'} , \ (\xi, \xi' = \uparrow, \downarrow) .
\]

(2.24)

Notice in this equation the new parameter \( \lambda_{\alpha \beta}^{b} \), which is known as the SO coupling. In a theory that we will soon introduce known as the \( sp^3 \) model, there are fourteen SO parameters, nonetheless, in diamond and zincblende structures, for example, it can be shown that they are all related to only one or two of them, respectively [19]. The locality of the SO correction is included in the Kroneker delta \( \delta_{bb'} \), since \( b \) and \( b' \) correspond to different positions of the atoms in the lattice.

2.5 Two-center Approximation

A simplifying assumption often used in CNT’s, and one that will be crucial for us to develop a unifying theory for the Si nanostructures, is the two center approxima-
The potential energy of the whole crystal $V(\mathbf{r})$ is the sum of spherical potentials $v_j(\mathbf{r})$ located on each atom; that is

$$V(\mathbf{r}) = \sum_j v_j(|\mathbf{r} - \delta_j|),$$

(2.25)

where $\delta_j$ is the vector position of the $j$-th atom.\(^4\) By expanding this equation, we find that,

$$(\delta_k, \alpha | V(\mathbf{r}) | \delta_l, \beta) = (\delta_k, \alpha \left\{ \sum_j v_j(|\mathbf{r} - \delta_j|) \right\} | \delta_l, \beta)$$

$$= (\delta_k, \alpha | \{ v_1(|\mathbf{r} - \delta_1|) + ... + v_i(|\mathbf{r} - \delta_i|) + ... + v_l(|\mathbf{r} - \delta_l|) \} | \delta_l, \beta).$$

Since the atomic orbitals and the spherical potentials are centered at different atomic positions, Eq. (2.26) is a linear combination of three-center integrals and two two-center integrals. Here, we make a further approximation: we neglect all the three-center integrals in Eq. (2.26) and retain the two-center integrals only. Hence,

$$(\delta_k, \alpha | V(\mathbf{r}) | \delta_l, \beta) \approx (\delta_k, \alpha | v_i(|\mathbf{r} - \delta_k|) | \delta_l, \beta) + (\delta_k, \alpha | v_l(|\mathbf{r} - \delta_l|) | \delta_l, \beta)$$

(2.26)

Our problem is then reduced to the diatomic molecule problem, in which $\mathbf{r}_k - \mathbf{r}_l$ is the axis of the molecule. We choose the $\delta_k - \delta_l$ axis as the quantization axis since now, our problem has axial symmetry. The integrals $(\delta_k, \alpha | v_i(|\mathbf{r} - \delta_k|) | \delta_l, \beta)$ and $(\delta_k, \alpha | v_l(|\mathbf{r} - \delta_l|) | \delta_l, \beta)$ are known as the two-center parameters. Using the Slater and

\(^4\)Notice that $V(\mathbf{r})$ does not have spherical symmetry even though $v_j(\mathbf{r})$ does.
Koster notation [16] for these parameters, we give some of the energy integrals that will be useful for us in Chapter five.

\[
E_{s,s}(\delta_k) = (ss\sigma),
\]
\[
E_{s,x}(\delta_k) = l(sp\sigma),
\]
\[
E_{x,x}(\delta_k) = l^2(pp\sigma) + \left(1 - l^2\right)(pp\pi),
\]
\[
E_{x,y}(\delta_k) = lm(pp\sigma) - lm(pp\pi),
\]

where \(l, m\) are the direct cosines of \(\delta_k\).

In the present work we will make use of the TCA in the so-called \(sp^3\) and \(sp^3s^*\) models. The terminology \(sp^3\) means that the Bloch function is a superposition of \(s\) and \(p\) orbitals: \(p_x, p_y\) and \(p_z\). The \(sp^3s^*\) model corresponds to a superposition of the previous \(s\) and \(p\) orbitals, and also and extra excited state \(s^*\). Later in the present chapter, we will discuss the band structures obtained from these models when we will apply them to the band structure of Si. In the meantime, it is useful to derive general expressions for the matrix elements of the Hamiltonian. Eventually, we will apply these equations to graphene, Si (111), and nanotubes. From Eq. (2.19) we find that,

\[
(s/s)_{AB} = \sum_j E_{ss}^{AB}(\delta_j) e^{ik\delta_j^{(1)}} = (ss\sigma)^{AB}_1 g_0(k),
\]
\[
(x/x)_{AB} = \sum_j E_{xx}^{AB}(\delta_j) e^{ik\delta_j^{(1)}} = (pp\sigma)^{AB}_1 g_3(k) + (pp\pi)^{AB}_1 g_4(k),
\]
\[
(y/y)_{AB} = \sum_j E_{yy}^{AB}(\delta_j^{(1)}) e^{ik\delta_j^{(1)}} = (pp\sigma)^{AB}_1 g_6(k) + (pp\pi)^{AB}_1 g_4(k),
\]
\[
(z/z)_{AB} = \sum_j E_{zz}^{AB}(\delta_j^{(1)}) e^{ik\delta_j^{(1)}} = (pp\sigma)^{AB}_1 g_{11}(k) + (pp\pi)^{AB}_1 g_{12}(k),
\]
\[ (s/x)_{AB} = \sum_j E^{AB}_{\delta_j} e^{i\mathbf{k}\cdot\mathbf{\delta}_j} = (sp\sigma)^1 g_1(k), \]  

\[ (s/y)_{AB} = \sum_j E^{AB}_{\delta_j} e^{i\mathbf{k}\cdot\mathbf{\delta}_j} = (sp\sigma)^1 g_2(k), \]  

\[ (s/z)_{AB} = \sum_j E^{AB}_{\delta_j} e^{i\mathbf{k}\cdot\mathbf{\delta}_j} = (sp\sigma)^1 g_3(k), \]  

\[ (x/y)_{AB} = \sum_j E^{AB}_{\delta_j} e^{i\mathbf{k}\cdot\mathbf{\delta}_j} = [(pp\sigma)^1 - (pp\pi)^1] g_5(k), \]  

\[ (x/z)_{AB} = \sum_j E^{AB}_{\delta_j} e^{i\mathbf{k}\cdot\mathbf{\delta}_j} = [(pp\sigma)^1 - (pp\pi)^1] g_6(k), \]  

\[ (y/z)_{AB} = \sum_j E^{AB}_{\delta_j} e^{i\mathbf{k}\cdot\mathbf{\delta}_j} = [(pp\sigma)^1 - (pp\pi)^1] g_{10}(k), \]  

\[ (s/s)_{AA} = E^{AA}_{ss}(0) + \sum_j E^{AA}_{\delta_j} e^{i\mathbf{k}\cdot\mathbf{\delta}_j} = E^A_s + (ss\sigma)^2 g_{13}(k), \]  

\[ (x/x)_{AA} = E^{AA}_{xx}(0) + \sum_j E^{AA}_{\delta_j} e^{i\mathbf{k}\cdot\mathbf{\delta}_j} = E^A_p + (pp\sigma)^2 g_{16}(k) + (pp\pi)^2 g_{17}(k), \]  

\[ (y/y)_{AA} = E^{AA}_{yy}(0) + \sum_j E^{AA}_{\delta_j} e^{i\mathbf{k}\cdot\mathbf{\delta}_j} = E^A_p + (pp\sigma)^2 g_{19}(k) + (pp\pi)^2 g_{20}(k), \]  

\[ (z/z)_{AA} = E^{AA}_{zz}(0) + \sum_j E^{AA}_{\delta_j} e^{i\mathbf{k}\cdot\mathbf{\delta}_j} = E^A_p + (pp\sigma)^2 g_{24}(k) + (pp\pi)^2 g_{25}(k), \]  

\[ (s/x)_{AA} = \sum_j E^{AA}_{\delta_j} e^{i\mathbf{k}\cdot\mathbf{\delta}_j} = (sp\sigma)^2 g_{14}(k), \]  

\[ (s/y)_{AA} = \sum_j E^{AA}_{\delta_j} e^{i\mathbf{k}\cdot\mathbf{\delta}_j} = (sp\sigma)^2 g_{15}(k), \]  

\[ (s/z)_{AA} = \sum_j E^{AA}_{\delta_j} e^{i\mathbf{k}\cdot\mathbf{\delta}_j} = (sp\sigma)^2 g_{21}(k), \]  

\[ (x/y)_{AA} = \sum_j E^{AA}_{\delta_j} e^{i\mathbf{k}\cdot\mathbf{\delta}_j} = [(pp\sigma)^2 - (pp\pi)^2] g_{18}(k), \]  

\[ (x/z)_{AA} = \sum_j E^{AA}_{\delta_j} e^{i\mathbf{k}\cdot\mathbf{\delta}_j} = [(pp\sigma)^2 - (pp\pi)^2] g_{22}(k), \]  

\[ (y/z)_{AA} = \sum_j E^{AA}_{\delta_j} e^{i\mathbf{k}\cdot\mathbf{\delta}_j} = [(pp\sigma)^2 - (pp\pi)^2] g_{23}(k), \]
where

\[ g_0(k) = \sum_j e^{ik \delta_{j}^{(1)}} = e^{ik \delta_{1}^{(1)}} + e^{ik \delta_{2}^{(1)}} + e^{ik \delta_{3}^{(1)}} + \ldots, \]

\[ g_1(k) = \sum_j \ell_j^{(1)} e^{ik \delta_{j}^{(1)}} = l_1^{(1)} e^{ik \delta_{1}^{(1)}} + l_2^{(1)} e^{ik \delta_{2}^{(1)}} + l_3^{(1)} e^{ik \delta_{3}^{(1)}} + \ldots, \]

\[ g_2(k) = \sum_j m_j^{(1)} e^{ik \delta_{j}^{(1)}} = m_1^{(1)} e^{ik \delta_{1}^{(1)}} + m_2^{(1)} e^{ik \delta_{2}^{(1)}} + m_3^{(1)} e^{ik \delta_{3}^{(1)}} + \ldots, \]

\[ g_3(k) = \sum_j \left( \ell_j^{(1)} \right)^2 e^{ik \delta_{j}^{(1)}} = \left( \ell_1^{(1)} \right)^2 e^{ik \delta_{1}^{(1)}} + \left( \ell_2^{(1)} \right)^2 e^{ik \delta_{2}^{(1)}} \left( \ell_3^{(1)} \right)^2 e^{ik \delta_{3}^{(1)}} + \ldots, \]

\[ g_4(k) = \sum_j \left\{ 1 - \left( \ell_j^{(1)} \right)^2 \right\} e^{ik \delta_{j}^{(1)}} = \left\{ 1 - \left( \ell_1^{(1)} \right)^2 \right\} e^{ik \delta_{1}^{(1)}} + \left\{ 1 - \left( \ell_2^{(1)} \right)^2 \right\} e^{ik \delta_{2}^{(1)}} + \left\{ 1 - \left( \ell_3^{(1)} \right)^2 \right\} e^{ik \delta_{3}^{(1)}} + \ldots, \]

\[ g_5(k) = \sum_j l_j^{(1)} m_j^{(1)} e^{ik \delta_{j}^{(1)}} = l_1^{(1)} m_1^{(1)} e^{ik \delta_{1}^{(1)}} + l_2^{(1)} m_2^{(1)} e^{ik \delta_{2}^{(1)}} + l_3^{(1)} m_3^{(1)} e^{ik \delta_{3}^{(1)}} + \ldots, \]

\[ g_6(k) = \sum_j \left( m_j^{(1)} \right)^2 e^{ik \delta_{j}^{(1)}} = \left( m_1^{(1)} \right)^2 e^{ik \delta_{1}^{(1)}} + \left( m_2^{(1)} \right)^2 e^{ik \delta_{2}^{(1)}} + \left( m_3^{(1)} \right)^2 e^{ik \delta_{3}^{(1)}} + \ldots, \]

\[ g_7(k) = \sum_j \left\{ 1 - \left( m_j^{(1)} \right)^2 \right\} e^{ik \delta_{j}^{(1)}} = \left\{ 1 - \left( m_1^{(1)} \right)^2 \right\} e^{ik \delta_{1}^{(1)}} + \left\{ 1 - \left( m_2^{(1)} \right)^2 \right\} e^{ik \delta_{2}^{(1)}} + \left\{ 1 - \left( m_3^{(1)} \right)^2 \right\} e^{ik \delta_{3}^{(1)}} + \ldots, \]

\[ g_8(k) = \sum_j n_j^{(1)} e^{ik \delta_{j}^{(1)}} = n_1^{(1)} e^{ik \delta_{1}^{(1)}} + n_2^{(1)} e^{ik \delta_{2}^{(1)}} + n_3^{(1)} e^{ik \delta_{3}^{(1)}} + \ldots, \]

\[ g_9(k) = \sum_j l_j^{(1)} n_j^{(1)} e^{ik \delta_{j}^{(1)}} = l_1^{(1)} n_1^{(1)} e^{ik \delta_{1}^{(1)}} + l_2^{(1)} n_2^{(1)} e^{ik \delta_{2}^{(1)}} + l_3^{(1)} n_3^{(1)} e^{ik \delta_{3}^{(1)}} + \ldots, \]

\[ g_{10}(k) = \sum_j m_j^{(1)} n_j^{(1)} e^{ik \delta_{j}^{(1)}} = m_1^{(1)} n_1^{(1)} e^{ik \delta_{1}^{(1)}} + m_2^{(1)} n_2^{(1)} e^{ik \delta_{2}^{(1)}} + m_3^{(1)} n_3^{(1)} e^{ik \delta_{3}^{(1)}} + \ldots, \]

\[ g_{11}(k) = \sum_j \left( n_j^{(1)} \right)^2 e^{ik \delta_{j}^{(1)}} = \left( n_1^{(1)} \right)^2 e^{ik \delta_{1}^{(1)}} + \left( n_2^{(1)} \right)^2 e^{ik \delta_{2}^{(1)}} + \left( n_3^{(1)} \right)^2 e^{ik \delta_{3}^{(1)}} + \ldots, \]

\[ g_{12}(k) = \sum_j \left\{ 1 - \left( n_j^{(1)} \right)^2 \right\} e^{ik \delta_{j}^{(1)}} = \left\{ 1 - \left( n_1^{(1)} \right)^2 \right\} e^{ik \delta_{1}^{(1)}} + \left\{ 1 - \left( n_2^{(1)} \right)^2 \right\} e^{ik \delta_{2}^{(1)}} + \left\{ 1 - \left( n_3^{(1)} \right)^2 \right\} e^{ik \delta_{3}^{(1)}} + \ldots, \]
\[ g_{13}(k) = \sum_j e^{ik \delta_j^{(2)}} = e^{ik \delta_1^{(2)}} + e^{ik \delta_2^{(2)}} + e^{ik \delta_3^{(2)}} + ..., \]

\[ g_{14}(k) = \sum_j l_j^{(2)} e^{ik \delta_j^{(2)}} = l_1^{(2)} e^{ik \delta_1^{(2)}} + l_2^{(2)} e^{ik \delta_2^{(2)}} + l_3^{(2)} e^{ik \delta_3^{(2)}} + ..., \]

\[ g_{15}(k) = \sum_j m_j^{(2)} e^{ik \delta_j^{(2)}} = m_1^{(2)} e^{ik \delta_1^{(2)}} + m_2^{(2)} e^{ik \delta_2^{(2)}} + m_3^{(2)} e^{ik \delta_3^{(2)}} + ..., \]

\[ g_{16}(k) = \sum_j \left( l_j^{(1)} \right)^2 e^{ik \delta_j^{(1)}} = \left( l_1^{(1)} \right)^2 e^{ik \delta_1^{(1)}} + \left( l_2^{(1)} \right)^2 e^{ik \delta_2^{(1)}} \left( l_3^{(1)} \right)^2 e^{ik \delta_3^{(1)}} + ..., \]

\[ g_{17}(k) = \sum_j \left\{ 1 - \left( l_j^{(2)} \right)^2 \right\} e^{ik \delta_j^{(2)}} = \left\{ 1 - \left( l_1^{(2)} \right)^2 \right\} e^{ik \delta_1^{(2)}} + \left\{ 1 - \left( l_2^{(2)} \right)^2 \right\} e^{ik \delta_2^{(2)}} + \left\{ 1 - \left( l_3^{(2)} \right)^2 \right\} e^{ik \delta_3^{(2)}} + ..., \]

\[ g_{18}(k) = \sum_j l_j^{(2)} m_j^{(2)} e^{ik \delta_j^{(2)}} = l_1^{(2)} m_1^{(1)} e^{ik \delta_1^{(2)}} + l_2^{(2)} m_2^{(1)} e^{ik \delta_2^{(2)}} + l_3^{(2)} m_3^{(1)} e^{ik \delta_3^{(2)}} + ..., \]

\[ g_{19}(k) = \sum_j \left( m_j^{(2)} \right)^2 e^{ik \delta_j^{(2)}} = \left( m_1^{(2)} \right)^2 e^{ik \delta_1^{(2)}} + \left( m_2^{(2)} \right)^2 e^{ik \delta_2^{(2)}} + \left( m_3^{(2)} \right)^2 e^{ik \delta_3^{(2)}} + ..., \]

\[ g_{20}(k) = \sum_j \left\{ 1 - \left( m_j^{(2)} \right)^2 \right\} e^{ik \delta_j^{(2)}} = \left\{ 1 - \left( m_1^{(2)} \right)^2 \right\} e^{ik \delta_1^{(2)}} + \left\{ 1 - \left( m_2^{(2)} \right)^2 \right\} e^{ik \delta_2^{(2)}} + \left\{ 1 - \left( m_3^{(2)} \right)^2 \right\} e^{ik \delta_3^{(2)}} + ..., \]

\[ g_{21}(k) = \sum_j n_j^{(2)} e^{ik \delta_j^{(2)}} = n_1^{(2)} e^{ik \delta_1^{(2)}} + n_2^{(2)} e^{ik \delta_2^{(2)}} + n_3^{(2)} e^{ik \delta_3^{(2)}} + ..., \]

\[ g_{22}(k) = \sum_j m_j^{(2)} n_j^{(2)} e^{ik \delta_j^{(2)}} = m_1^{(2)} n_1^{(2)} e^{ik \delta_1^{(2)}} + m_2^{(2)} n_2^{(2)} e^{ik \delta_2^{(2)}} + m_3^{(2)} n_3^{(2)} e^{ik \delta_3^{(2)}} + ..., \]

\[ g_{23}(k) = \sum_j \left( n_j^{(2)} \right)^2 e^{ik \delta_j^{(2)}} = \left( n_1^{(2)} \right)^2 e^{ik \delta_1^{(2)}} + \left( n_2^{(2)} \right)^2 e^{ik \delta_2^{(2)}} + \left( n_3^{(2)} \right)^2 e^{ik \delta_3^{(2)}} + ..., \]

\[ g_{24}(k) = \sum_j \left\{ 1 - \left( n_j^{(2)} \right)^2 \right\} e^{ik \delta_j^{(2)}} = \left\{ 1 - \left( n_1^{(2)} \right)^2 \right\} e^{ik \delta_1^{(2)}} + \left\{ 1 - \left( n_2^{(2)} \right)^2 \right\} e^{ik \delta_2^{(2)}} + \left\{ 1 - \left( n_3^{(2)} \right)^2 \right\} e^{ik \delta_3^{(2)}} + ..., \]

with

\[ l_j^{(n)} = \frac{\hat{\mathbf{i}} \cdot \delta_j^{(n)}}{\left| \delta_j^{(n)} \right|}, \quad m_j^{(n)} = \frac{\hat{\mathbf{j}} \cdot \delta_j^{(n)}}{\left| \delta_j^{(n)} \right|}, \quad n_j^{(n)} = \frac{\hat{\mathbf{k}} \cdot \delta_j^{(n)}}{\left| \delta_j^{(n)} \right|} \]
2.6 Application to Zinc-blende and Diamond Structures

2.6.1 Zinc-blende

In the following, we use the same convention and notation as Lew Yan Voon [19]. In the LS representation, the Hamiltonian has the form,

\[
H_T(k) = \begin{bmatrix}
    h_{aa}^0 & h_{ac}^0 & O & O \\
    h_{ca}^0 & h_{cc}^0 & O & O \\
    O & O & h_{aa}^0 & h_{ac}^0 \\
    O & O & h_{ca}^0 & h_{cc}^0 \\
\end{bmatrix} + \begin{bmatrix}
    h_{aa}^{so}(\uparrow\uparrow) & O & h_{aa}^{so}(\uparrow\downarrow) & O \\
    O & h_{cc}^{so}(\uparrow\uparrow) & O & h_{cc}^{so}(\uparrow\downarrow) \\
    h_{aa}^{so}(\downarrow\uparrow) & O & h_{aa}^{so}(\downarrow\downarrow) & O \\
    O & h_{cc}^{so}(\downarrow\uparrow) & O & h_{cc}^{so}(\downarrow\downarrow) \\
\end{bmatrix},
\]

(2.31)

Each sub-block matrix in Eq. (2.31) has dimensions equal to the number of orbitals on each atom. We now give the explicit expressions for: \(h_{bb}^0, h_{bc}^0, h_{bb}^{so}(\uparrow\uparrow), h_{bb}^{so}(\uparrow\downarrow)\). For the 20-band 2NN \(sp^3s^*\) model, we have:
\[
\begin{pmatrix}
(s/s)_b & (s/x)_b & (s/y)_b & (s/z)_b & (s/s^*)_b \\
(x/x)_b & (x/y)_b & (x/z)_b & (x/s^*)_b \\
(y/y)_b & (y/z)_b & (y/s^*)_b \\
(z/z)_b & (z/s^*)_b \\
(s^*/s^*)_b
\end{pmatrix}^\dagger = h_{bb}^0,
\] (2.32)

with

\[
(s/s)_b = E_s^b + W_{ss}^b (110) (C_1 C_2 + C_2 C_3 + C_3 C_1),
\]

\[
(x/x)_b = E_p^b + W_{xx}^b (110) C_1 (C_2 + C_3) + W_{xx}^b (011) C_2 C_3,
\]

\[
(y/y)_b = E_p^b + W_{xx}^b (110) C_2 (C_3 + C_1) + W_{xx}^b (011) C_3 C_1,
\]

\[
(z/z)_b = E_p^b + W_{xx}^b (110) C_3 (C_1 + C_2) + W_{xx}^b (011) C_1 C_2,
\]

\[
(s^*/s^*)_b = E_{s^*}^b + W_{s^*s^*}^b (110) (C_1 C_2 + C_2 C_3 + C_3 C_1),
\]

\[
(s/x)_b = iW_{sx}^b (110) S_1 (C_2 + C_3) - W_{sx}^b (011) S_2 S_3,
\]

\[
(s/y)_b = iW_{sx}^b (110) S_2 (C_3 + C_1) - W_{sx}^b (011) S_3 S_1,
\]

\[
(s/z)_b = iW_{sx}^b (110) S_3 (C_1 + C_2) - W_{sx}^b (011) S_1 S_2,
\]

\[
(x/y)_b = -W_{xy}^b (110) S_1 S_2 - iW_{xy}^b (011) S_3 (C_1 - C_2),
\]

\[
(x/z)_b = -W_{xy}^b (110) S_3 S_1 - iW_{xy}^b (011) S_2 (C_1 - C_3),
\]

\[
(y/z)_b = -W_{xy}^b (110) S_2 S_3 - iW_{xy}^b (011) S_1 (C_2 - C_3),
\]

\[
(s/s^*)_b = W_{ss^*}^b (110) (C_1 C_2 + C_2 C_3 + C_3 C_1),
\]

\[
(x/s^*)_b = -iW_{s^*x}^b (110) S_1 (C_2 + C_3) - W_{s^*x}^b (011) S_2 S_3,
\]

\[
(y/s^*)_b = -iW_{s^*x}^b (110) S_2 (C_3 + C_1) - W_{s^*x}^b (011) S_3 S_1,
\]

\[
(z/s^*)_b = -iW_{s^*x}^b (110) S_3 (C_1 + C_2) - W_{s^*x}^b (011) S_1 S_2,
\]

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\[ C_1 = \cos \xi/2, \quad S_1 = \sin \xi/2, \quad \xi = a_0 k_x, \]
\[ C_2 = \cos \eta/2, \quad S_2 = \sin \eta/2, \quad \eta = a_0 k_y, \]
\[ C_3 = \cos \zeta/2, \quad S_3 = \sin \zeta/2, \quad \zeta = a_0 k_z, \]

\[
h_{ac}^0 = \begin{bmatrix}
(s/s)_{ac} & (s/x)_{ac} & (s/y)_{ac} & (s/z)_{ac} & (s/s^*)_{ac} \\
(x/s)_{ac} & (x/x)_{ac} & (x/y)_{ac} & (x/z)_{ac} & (x/s^*)_{ac} \\
(y/s)_{ac} & (y/x)_{ac} & (y/y)_{ac} & (y/z)_{ac} & (y/s^*)_{ac} \\
(z/s)_{ac} & (z/x)_{ac} & (z/y)_{ac} & (z/z)_{ac} & (z/s^*)_{ac} \\
(s^*/s)_{ac} & (s^*/x)_{ac} & (s^*/y)_{ac} & (s^*/z)_{ac} & (s^*/s^*)_{ac}
\end{bmatrix}
\]

\[
= \begin{bmatrix}
V_{ss} g_0 & V_{s0p} g_1 & V_{s0p} g_2 & V_{s0p} g_3 & 0 \\
-V_{s1p} g_1 & V_{xx} g_0 & V_{xy} g_3 & V_{xy} g_2 & -V_{s1p} g_1 \\
-V_{s1p} g_2 & V_{xy} g_3 & V_{xx} g_0 & V_{xy} g_1 & -V_{s1p} g_2 \\
-V_{s1p} g_3 & V_{xy} g_2 & V_{xy} g_1 & V_{zz} g_0 & -V_{s1p} g_3 \\
0 & V_{s0p} g_1 & V_{s0p} g_2 & V_{s0p} g_3 & 0
\end{bmatrix}
\]

where

\[
g_0 = \cos \xi/4 \cos \eta/4 \cos \zeta/4 - i \sin \xi/4 \sin \eta/4 \sin \zeta/4, \]
\[
g_1 = -\cos \xi/4 \sin \eta/4 \sin \zeta/4 + i \sin \xi/4 \cos \eta/4 \cos \zeta/4, \quad \text{(2.35)}
\]
\[
g_2 = -\sin \xi/4 \cos \eta/4 \sin \zeta/4 + i \cos \xi/4 \sin \eta/4 \cos \zeta/4, \]
\[
g_3 = -\sin \xi/4 \sin \eta/4 \cos \zeta/4 + i \cos \xi/4 \cos \eta/4 \sin \zeta/4, \]
\begin{equation}
\begin{bmatrix}
0 & 0 & 0 & 0 & 0 \\
0 & 0 & -i\lambda_1^b & 0 & 0 \\
0 & i\lambda_1^b & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
\end{bmatrix},
\end{equation}

\begin{equation}
\begin{bmatrix}
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & \lambda_1^b & 0 \\
0 & 0 & 0 & -i\lambda_1^b & 0 \\
0 & -\lambda_1^b & i\lambda_1^b & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
\end{bmatrix},
\end{equation}

and

\begin{equation}
\begin{bmatrix}
h_{so}^b(\downarrow\downarrow) = [h_{so}^b(\uparrow\uparrow)]^* \\
h_{so}^b(\downarrow\uparrow) = [h_{so}^b(\uparrow\downarrow)]^\dagger \\
\end{bmatrix}
\end{equation}

As an example of the 2NN \textit{sp}$^3$s$^*$ model in zinc-blende structures, the GaAs band structure is depicted in Fig. 2.3. In this figure, \textit{L}, \textit{\Gamma}, \textit{X}, \textit{U} and \textit{K} are high symmetry points of the Brillouin zone of zinc-blende; explicitly,

\begin{align*}
\text{\textbf{L}} &= \frac{2\pi}{a} [111], \quad \text{\textbf{\Gamma}} = [000], \\
\text{\textbf{X}} &= \frac{2\pi}{a} [100], \quad \text{\textbf{K}} = \frac{2\pi}{a} \begin{bmatrix} 3 & 3 & 0 \\ 4 & 4 & 0 \end{bmatrix},
\end{align*}

where the points are given in terms of the cubic axes [21].
Figure 2.3: Band structure of GaAs. Spin-orbit coupling is included. Tight-binding parameters were taken from Ref. [22].
2.6.2 Diamond

The TB Hamiltonian for diamond can be obtained from the zinc-blende one if we relate the cation to the anion. Unlike zinc-blende, diamond has inversion symmetry \[19\] and, therefore, the cation and anion TB parameters are related as shown in Eq. (2.39) with the exceptions listed in Eq. (2.40). For the 2NN $sp^3s^*$ model, the total number of parameters needed for diamond is 20.

\[
E^c_\alpha = E^a_\alpha, \quad W^c_{\alpha\beta} = W^a_{\alpha\beta} \equiv W_{\alpha\beta}, \quad \lambda^c_i = \lambda^a_i \equiv \lambda, \quad (2.39)
\]

except for

\[
V_{s1p} = V_{s0p}, \quad V_{s*1p} = V_{s*0p}, \quad W^c_{sz}(011) = -W^a_{sz}(011) \equiv -W_{sz}(011), \quad (2.40)
\]

\[
W^c_{s*x}(011) = -W^a_{s*x}(011) \equiv -W_{s*x}(011), \quad W^c_{xy}(011) = -W^a_{xy}(011) \equiv -W_{xy}(011),
\]

In the following, we will compare the band structure of bulk Si, which has diamond structure, using different parameter sets. Our goal is to find the set(s) that reproduces the bands and the effective masses most accurately. Silicon is a semiconductor with an indirect band gap of 1.12 eV. The minimum of the conduction band occurs close to 85% away from the Γ point along the Δ direction \[23\]. More material parameters of Si such as the hole and the electron effective-masses are given in Table 2.2 according to Madelung \[23\]. The parameters $\Delta^L_{5O}$ and $\Delta^L_{5O}$ are the splittings due to the SO coupling.
at the Γ and L points, respectively.

It is was shown by Chadi et al. [24] that a 1NN $sp^3$ TB theory reproduces fairly well the valence bands of bulk Si, nonetheless, it fails to reproduce well the conduction band of Si and any other solid that has diamond structure. This theory wrongly predicts a direct gap. However, in a later publication, using the same model but adding SO coupling, Chadi [25] showed that the TB parameter $\lambda$ in Eq. 2.39 is related to the SO splittings $\Delta_{SO}$ in the form,

$$\Delta_{SO}^\Gamma = \frac{1}{3} \lambda,$$
$$\Delta_{SO}^L = 2 \lambda.$$

After an detailed search, the most accurate parameter sets we found in the literature are the ones corresponding to Klimeck et al. [26], Martins et al. [27], Grosso et al. [28], and Vogl et al [29], respectively. Table 2.1 lists all these parameters. We point out that we do not use the TB parameters from Papaconstantopoulos [30] since those correspond to a $sp^3$ model under the third nearest-neighbor approximation. We reproduce the band structure of bulk Si for each one of these sets in Fig. 2.4. Spin-orbit interaction is included in all the calculations but the one of Vogl et al. [29]. Since the SO coupling is small for Si and it cannot be seen in the figures at the scale that they have been plotted, the labels for the energies at the $L, \Gamma, X$ points correspond the ones without SO interaction.

In the case of the $sp^3s^*$ model proposed by Vogl et al. [29], the indirect gap problem is solved by introducing the $s^*$ orbital. The addition of this extra orbital creates a band

\footnote{There are some typos in the numerical values of $\lambda_{SO}$ (Table 2 of Ref. [26]), $E_{s^*}$, $\lambda_{SO}$, and $\Delta_{SO}$ (Tables I and II of Ref. [27]). See Tables 2.1 and 2.2 for the correct values.}
that “pushes down” the conduction bands, creating a minimum in the $\Delta$ direction. Physically speaking, $s^*$ orbital is intended to represent the $d$-orbitals in an effective manner. Notice that if we were to include the real $d$-orbitals, we will have to add 5 more states to the model, which would end up with a $18 \times 18$ Hamiltonian if SO interaction is neglected [31]. The 1NN $sp^3s^*$ model for Si, is the simplest model with which a somewhat realistic band structure can be computed. However, the conduction band minimum occurs 72% away from $\Gamma$, and the longitudinal effective mass at the $X$ point $m_X^*$ is infinite, which implies that the bands along that direction are flat [32].

If one wishes more accurate bands to reproduce well the, e.g., Si transport properties, then, more complicated models are needed [26]. Examples of more elaborate theories are: the 2NN and the 3NN $sp^3$ model, 1NN $sp^3d^5$ model, and the $sp^3d^5s^*$ [28, 31, 33, 34].

The band structures of Si using Klimeck’s and Martin’s parameters correspond to a 2NN $sp^3s^*$ model. The main difference between them is that the latter includes the nonzero hoppings $W_{s^*s^*}(110)$ and $W_{ss^*}(110)$ in order to “push” away the valence band minimum from 75% to 85% along the $\Delta$ direction [27]. Moreover, using the so-called generic algorithm, the TB parameters were fitted to the experimental Si material ones given by Madelung [23, 26, 27] They are all reproduced here in Table 2.1. We found that both parametrizations do not reproduce well the valence band along the $\Sigma$ direction (c.f. Fig. 2.4) which is relevant to the band structures of Si nanotubes. Moreover, our calculations of the material parameters of Si do not always agree. For instance, $m_{hh}[111] (-0.232 \, m_e)$ and $m_{SO}(-0.044 \, m_e)$ are smaller than their corresponding ones in Martins et al. [27] ($-0.727 \, m_e$ and $-0.239 \, m_e$, respectively), and our $E_L^c (2.431 \, \text{eV})$ is greater than the one in Klimeck et al. [26] (2.186 eV). Using only 1NN in the $sp^3$ model, one finds that bands in this direction are accurate, hence, one expects improvement if
2NN interactions are included. Since this is not the case for Martin’s and Klimeck’s parametrizations, we will not consider them for further calculations.

Grosso’s parametrization corresponds to a TB 2NN $sp^3$ model. In order to check that our $sp^3$ model is correct, we computed the effective masses and compared them to the reported ones. Our results are in good agreement as it is shown in Table 2.2. The discrepancies in the second decimal place in the indirect gap $E_{c}^{\Delta_{min}}$, and the effective mass $m_{lh}^*[111]$, are due to numerical accuracy.

In principle, the 2NN $sp^3$ model contains a total of 14 parameters (two on-site terms, four 1NN and seven 2NN interactions, and one SO coupling). After performing several approximations, the authors end up with only 9 of them [28]. They fitted the remaining parameters to previous band structures obtained by other techniques [35, 36].

As is shown in Fig. 2.4 and Table 2.2, the band structure of Si looks fine and it gives fairly good material parameters when compared to experimental values. The addition of 2NN interactions fixes the direct gap problem of the 1NN $sp^3$ model. The bands are fairly accurate in the $\Sigma$ direction, as well. The position of the indirect band gap is 77% away from $\Gamma$ in the $\Delta$ direction.

In summary, Vogl’s and Grosso’s TB parameter sets reproduce fairly well the valence and conduction bands of bulk Si, though, only the latter parametrization gives fairly good effective masses. Martin’s and Klimeck’s parameter sets, on the other hand, do not give the band structure along $\Sigma$ accurately, which is needed for the nanostructures that we will consider in this work. Therefore, we will choose Vogl’s and Grosso’s TB parameters for calculating the energy bands of these materials.
Figure 2.4: Band structure of Si using different sets of TB parameters. Spin-orbit coupling is included in all band structures but Vogl’s one. Since this effect is small in bulk Si, the notation for labeling the energies at the high symmetry points \( L, \Gamma \) and \( X \), correspond to the one without the coupling. All TB parameters sets are given in Table 2.1.
Table 2.1: Tight-binding parameters for Si in eV. Blank space in the table means that the parameter does not pertain to the model that the author(s) used. In Ref. [28], $E_s$ and $E_p$ are arbitrary, as long as $E_p - E_s = 5.0794$ eV. Therefore, we chose $E_p$ and $E_s$ so that $E(\Gamma'_{25}) = 0$.

<table>
<thead>
<tr>
<th>Klimeck et al. [26]</th>
<th>Martins et al. [27]</th>
<th>Grosso et al. [28]</th>
<th>Vogl et al. [29]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_s$</td>
<td>-4.81341</td>
<td>-4.848054</td>
<td>-4.0497</td>
</tr>
<tr>
<td>$E_p$</td>
<td>1.77563</td>
<td>1.787118</td>
<td>1.0297</td>
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<tr>
<td>$E_s^*$</td>
<td>5.61342</td>
<td>5.608014</td>
<td>-8.2648</td>
</tr>
<tr>
<td>$V_{ss}$</td>
<td>-8.33255</td>
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<td>-8.2648</td>
</tr>
<tr>
<td>$V_{xx}$</td>
<td>1.69916</td>
<td>1.697556</td>
<td>1.7148</td>
</tr>
<tr>
<td>$V_{xy}$</td>
<td>5.29091</td>
<td>5.351079</td>
<td>5.5100</td>
</tr>
<tr>
<td>$V_{sp}$</td>
<td>5.86140</td>
<td>5.822197</td>
<td>4.8152</td>
</tr>
<tr>
<td>$V_{s^*p}$</td>
<td>4.88308</td>
<td>4.864480</td>
<td></td>
</tr>
<tr>
<td>$\lambda$</td>
<td>0.01501</td>
<td>0.014905</td>
<td>0.0147</td>
</tr>
<tr>
<td>$W_{ss}(110)$</td>
<td>0.01591</td>
<td>0.029958</td>
<td>0.0000</td>
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<tr>
<td>$W_{s^<em>s^</em>}(110)$</td>
<td></td>
<td>0.191517</td>
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<td>$W_{ss^*}(110)$</td>
<td>0.007036</td>
<td></td>
<td></td>
</tr>
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<td>$W_{xx}(110)$</td>
<td>0.08002</td>
<td>0.161749</td>
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<td>$W_{xx}(011)$</td>
<td>1.31699</td>
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<td>0.0000</td>
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<tr>
<td>$W_{s^*x}(110)$</td>
<td>-0.00579</td>
<td>-0.095653</td>
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<td>$W_{s^*x}(011)$</td>
<td>0.50103</td>
<td>0.966257</td>
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<td>$W_{xx}(110)$</td>
<td>0.00762</td>
<td>0.037296</td>
<td>1.0576</td>
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<td>$W_{xx}(011)$</td>
<td>-0.10662</td>
<td>-0.132810</td>
<td>-1.4448</td>
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<td>$W_{xy}(110)$</td>
<td>0.55067</td>
<td>0.619876</td>
<td>0.7200</td>
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<tr>
<td>$W_{xy}(011)$</td>
<td>-2.27784</td>
<td>-2.496288</td>
<td>0.0000</td>
</tr>
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</table>
Table 2.2: Material parameters for Si. Energies and effective masses are given in eV and electron rest mass $m_e$, respectively. Blank space mean that the parameter was not provided in the corresponding report.

<table>
<thead>
<tr>
<th></th>
<th>Madelung [23]</th>
<th>Present work</th>
<th>Martins et al. [27]</th>
<th>Present work</th>
<th>Klimeck et al. [26]</th>
<th>Present work</th>
<th>Grosso et al. [28]</th>
<th>Present work</th>
<th>Vogl et al. [29]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta_{\text{min}}$</td>
<td>85%</td>
<td>85%</td>
<td>84.8%</td>
<td>64%</td>
<td>64%</td>
<td>77%</td>
<td>72%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E^{\Delta_{\text{min}}}_\Gamma$</td>
<td>1.124</td>
<td>1.130</td>
<td>1.130</td>
<td>1.117</td>
<td>1.118</td>
<td>1.11</td>
<td>1.12</td>
<td>1.170</td>
<td></td>
</tr>
<tr>
<td>$m^*_Xl$</td>
<td>0.916</td>
<td>0.919</td>
<td>0.916</td>
<td>0.526</td>
<td>0.531</td>
<td>0.51</td>
<td>0.51</td>
<td>0.725</td>
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<tr>
<td>$m^*_Xt$</td>
<td>0.191</td>
<td>0.196</td>
<td>0.191</td>
<td>1.055</td>
<td>1.020</td>
<td>0.20</td>
<td>0.20</td>
<td>1.700</td>
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<td>$E^F_{\Delta}$</td>
<td>2.050</td>
<td>1.990</td>
<td></td>
<td>2.431</td>
<td>2.186</td>
<td>2.41</td>
<td>2.496</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$m^*_{lh}[011]$</td>
<td>0.147</td>
<td>-0.120</td>
<td>-0.148</td>
<td>-0.181</td>
<td>-0.154</td>
<td>-0.20</td>
<td>-0.195</td>
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<tr>
<td>$m^*_{lh}[011]$</td>
<td>0.579</td>
<td>-0.587</td>
<td>-0.574</td>
<td>-0.633</td>
<td>-0.580</td>
<td>-0.52</td>
<td>-0.707</td>
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<tr>
<td>$m^*_{lh}[111]$</td>
<td>0.139</td>
<td>-0.139</td>
<td>-0.148</td>
<td>-0.171</td>
<td>-0.117</td>
<td>-0.18</td>
<td>-0.17</td>
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</tr>
<tr>
<td>$m^*_{lh}[111]$</td>
<td>0.738</td>
<td>-0.232</td>
<td>-0.727</td>
<td>-0.692</td>
<td>-0.692</td>
<td>-0.54</td>
<td>-0.54</td>
<td>-0.252</td>
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</tr>
<tr>
<td>$m^*_{lh}[001]$</td>
<td>0.204</td>
<td>-0.205</td>
<td>-0.204</td>
<td>-0.197</td>
<td>-0.187</td>
<td>-0.25</td>
<td>-0.25</td>
<td>-0.180</td>
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<tr>
<td>$m^*_{lh}[001]$</td>
<td>0.275</td>
<td>-0.293</td>
<td>-0.277</td>
<td>-0.348</td>
<td>-0.348</td>
<td>-0.28</td>
<td>-0.28</td>
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<tr>
<td>$m^*_{SO}$</td>
<td>0.234</td>
<td>-0.044</td>
<td>-0.239</td>
<td>-0.232</td>
<td>-0.247</td>
<td>-0.27</td>
<td></td>
<td></td>
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<tr>
<td>$\Delta_{SO}$</td>
<td>0.045</td>
<td>0.045</td>
<td>0.045</td>
<td>0.045</td>
<td>0.045</td>
<td>0.045</td>
<td>0.044</td>
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<tr>
<td>$\Delta^z_{SO}$</td>
<td>0.030</td>
<td>0.030</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.029</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.6.3 Comments

i. In order to improve the computational accuracy of the calculations, it is convenient to use the following trigonometric identities in Eq. (2.33),

\[
\begin{align*}
\cos x + \cos y &= 2 \cos \left( \frac{1}{2} (x + y) \right) \cos \left( \frac{1}{2} (x - y) \right), \\
\cos x - \cos y &= 2 \sin \left( \frac{1}{2} (x + y) \right) \sin \left( \frac{1}{2} (y - x) \right).
\end{align*}
\]

ii. It is worthwhile to make equivalences between the parameters used here and in other works. This is done in Table 2.3

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Present work</th>
<th>Talwar &amp; Ting [37]</th>
<th>Boykin [22]</th>
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<tbody>
<tr>
<td>$4E_{ax}^{sa}(111)$</td>
<td>$V_{s0p}$</td>
<td>$P_6$</td>
<td>$V_{sa,pc}$</td>
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<tr>
<td>$4E_{sx}^{ca}(111)$</td>
<td>$V_{s0p}$</td>
<td>$P_7$</td>
<td>$V_{s0,pc}$</td>
</tr>
<tr>
<td>$4E_{ax}^{ca}(111)$</td>
<td>$V_{s1p}$</td>
<td>$V_{pa,sc}$</td>
<td></td>
</tr>
<tr>
<td>$4E_{ax}^{ca}(111)$</td>
<td>$V_{s1p}$</td>
<td>$V_{pa,sc}$</td>
<td></td>
</tr>
<tr>
<td>$-4E_{sx}^{c}(011)$</td>
<td>$W_{sx}^{c}(011)$</td>
<td>$-P_{21}$</td>
<td>$-4E_{sc,xc}^{(011)}$</td>
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<tr>
<td>$-4E_{sx}^{c}(011)$</td>
<td>$W_{sx}^{c}(011)$</td>
<td>$-4E_{s0,sc}^{(011)}$</td>
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<tr>
<td>$-4E_{xy}(011)$</td>
<td>$W_{xy}^{c}(011)$</td>
<td>$-P_{23}$</td>
<td>$-4E_{sc,yc}^{(011)}$</td>
</tr>
</tbody>
</table>
Chapter 3

Graphene

Believe it or not, we are all somewhat familiar with graphene. When we use a pencil to write the phone number of the woman (man) we like, thousands of graphene layers are detaching from graphite so that we can record the precious information on a piece of paper. Most likely, we do not think about this while we are writing, however, probably some physicists started doing it recently, because of all the new physics that graphene encloses.

Graphene corresponds to one layer of three-dimensional graphite as the one shown in Fig. 3.2. The carbon atoms are arranged in a honeycomb lattice with an interatomic distance between two C atoms of 1.42Å [15]. Most of its interesting electronic properties (and mysteries) come from the π electrons in its lattice. In the present chapter, we will discuss these properties in further detail.

In this thesis, we discuss graphene as a route towards the nanotubes.
3.1 Recent Findings in Graphene

From the theoretical point of view, graphene has been studied for more than two decades, however, it was not until the late in the year 2005 that a single graphene sheet was observed [38]. This observation has done by Novoselov et al. [38] and from the experimental point of view, it is the most relevant report on this two-dimensional material, so far.

Graphene is unique in the sense that, unlike other materials, it exhibits a linear energy dispersion relation close to the $K$ point of its Brillouin zone, whereas most materials show a parabolic dispersion [39]. Recently, this linear dispersion has been referred as the Dirac cone [40] since the dispersion in the neighborhood of $K$ looks like a cone in the three-dimensional energy dispersion. The electrons close to the point in question obey Dirac’s equation for massless particles\(^1\) rather than Schrödinger’s equation. This explains the term “Dirac cone”. It is common to find in the literature, that these electrons are referred as Dirac massless fermions [38, 41, 42] \(^2\).

From the theoretical point of view, there is consensus that the effective mass of the electrons in the Dirac cone is zero, nevertheless, from the experimental point of view, this is not clear. Novoselov et al. [38] observed the the Dirac cone in a graphene sheet, which provides evidence for the zero-mass interpretation. However, they also measured a non-zero effective mass\(^3\) that the authors define from the well-known Einstein’s equation,

$$E = m^* v^2,$$

where $v$ is the Fermi velocity and it is of the order of $10^6$ m/s [4, 38]. We point out

\(^1\)This equation is also known as Weyl’s equation.
\(^2\)Recently, Zhou et al. [43] reported the first observation of Dirac massless fermions in graphite.
\(^3\)In their report, Novoselov et al. [38] refers to it as the cyclotron mass.
that none of these effective masses agree with the one defined in standard solid state
physics [44],
\[ m^* = \frac{\hbar^2}{d^2 E(k)/dk^2}, \]
for the one-dimensional case. Close to $K$, $E(k) \propto k$ [41], thus, $m^* = \infty$.

To add more confusion, it is not clear why graphene is a conductor. If one looks
only at the dispersion relation and density of states (DOS) of graphene, one would
conclude that it is a zero-gap semiconductor [15]. Nevertheless, further TB and $k \cdot p$
calculations on the transport properties of this material [38, 41, 42, 45, 46], show that
graphene is in fact, a metal. This has been confirmed by recent experiments done by
Novoselov et al. [38] and Berger et al. [4]. The physics of this phenomenon is not clear
either. Ando [41, 45], for example, argues that this anomaly occurs due to what he calls a
topological singularity; Novoselov [38], on the other hand, attributes it to disorder effects
in the graphene sheet. Finally, we mention that there is disagreement between theory
and experiment, as far as the exact electrical conductivity value is concerned. Most
theories predict a value of $e^2/\pi \hbar$ [42, 45], while the measured one is close to $4e^2/h$ [38].

On the application side, it seems to be easier to build coherent electronic devices
using graphene than CNTs [4].

3.2 Graphene Structure

Graphene’s honeycomb lattice is a non-Bravais lattice. It can be constructed in several
forms which, obviously, lead to the same structure. One form is to consider two two-
dimensional hexagonal lattices with lattice constant $a = 2.46\text{Å}$, and superpose one on
the other\(^4\); another form is by taking the two-dimensional hexagonal lattice with the same lattice constant and add a basis of two carbon atoms A and B, separated by the bond distance \(a_{C-C} = a / \sqrt{3} = 1.42\ \text{Å}\). The position of the basis is arbitrary with respect to a point of the hexagonal lattice, thus, we choose to place the A atoms exactly where the lattice points are. Figure 3.2 shows a scheme of this construction.

![Figure 3.1: Construction of the honeycomb lattice. The basis of two C atoms A and B, is added to the two-dimensional hexagonal lattice. The vector \(\mathbf{T}\) is a translational vector of the lattice.](image)

The vectors \(\mathbf{a}_1\) and \(\mathbf{a}_2\) are the basis vectors of graphene as they are shown in Fig. 3.2. In terms of cartesian coordinates \(\{\hat{x}, \hat{y}\}\), these two vectors are given by

\[
\mathbf{a}_1 = \frac{a\sqrt{3}}{2} \hat{x} - \frac{a}{2} \hat{y}, \quad \mathbf{a}_2 = \frac{a\sqrt{3}}{2} \hat{x} + \frac{a}{2} \hat{y},
\]

where the magnitude of both vectors is \(|\mathbf{a}_1| = |\mathbf{a}_2| = a\), and the angle \(\alpha\) between them is

\[
\cos \alpha = \frac{\mathbf{a}_1 \cdot \mathbf{a}_2}{|\mathbf{a}_1| |\mathbf{a}_2|} = \frac{a^2/2}{a^2} = \frac{1}{2} \implies \alpha = 60^\circ.
\]

Furthermore, \(\mathbf{a}_1\) and \(\mathbf{a}_2\) define a unit cell of the graphene with area \(|\mathbf{a}_1 \cdot \mathbf{a}_2| = \frac{a^2}{2} = 3.03\text{Å}^2\).

\(^4\)The same can be done starting with two two-dimensional trigonal lattices, each one with lattice constant \(a\).

\(^5\)Notice that we need to give to the two C atoms different labels because they are not equivalent from the symmetry point of view even though, chemically, they are the same.
This unit cell is shown in Fig. 3.2.

Figure 3.2: (a) Basis vectors and unit cell of graphene. The dark and light dots indicate the A and B inequivalent lattice points. (b) Reciprocal lattice vectors and Brillouin zone of graphene. The Γ, K, M points are high symmetry points.

Once the basis vectors of the real lattice are defined, the expressions

\[ \mathbf{a}_1 \cdot \mathbf{b}_1 = 2\pi, \mathbf{a}_2 \cdot \mathbf{b}_2 = 2\pi, \mathbf{a}_2 \cdot \mathbf{b}_1 = 0, \mathbf{a}_1 \cdot \mathbf{b}_2 = 0, \]

allow us to calculate the reciprocal vectors, labeled as \( \mathbf{b}_1 \) and \( \mathbf{b}_2 \). Substituting Eq. (3.1) in the previous relations, and solving for each of the components, one finds that

\[ \mathbf{b}_1 = \frac{2\pi}{\sqrt{3}a} \hat{x} + \frac{2\pi}{a} \hat{y}, \quad \mathbf{b}_2 = \frac{2\pi}{\sqrt{3}a} \hat{x} - \frac{2\pi}{a} \hat{y} \]  

(3.2)

where \(|\mathbf{b}_1| = |\mathbf{b}_2| = 4\pi / (\sqrt{3}a)\) and the angle \( \beta \) between them is

\[ \cos \beta = \frac{\mathbf{b}_1 \cdot \mathbf{b}_2}{|\mathbf{b}_1||\mathbf{b}_2|} = \frac{-8\pi^2 / 3a^2}{16\pi^2 / 3a^2} = -\frac{1}{2} \Rightarrow \beta = 120^\circ. \]

Figure 3.2(b) shows the reciprocal lattice vectors and its first Brillouin zone. The area of the latter is equal to \(|\mathbf{b}_1 \cdot \mathbf{b}_2| = 8\pi^2 / 3a^2 = 4.35 \text{ Å}^{-2}\). Notice that the reciprocal lattice
corresponds to a rotation by $90^\circ$ of the real honeycomb lattice.

Notice that the unit cell of graphene contains only one point of the hexagonal lattice and two C atoms. The $\Gamma, M, K$ points correspond to high symmetry points and they are given explicitly in Eq. (3.3). We will calculate the energy band dispersion along the perimeter of the triangle formed by these points.

$$\Gamma = (0, 0),$$
$$M = \frac{2\pi}{a} \left( \frac{1}{\sqrt{3}}, 0 \right),$$
$$K = \frac{2\pi}{a} \left( \frac{1}{\sqrt{3}}, \frac{1}{3} \right).$$

### 3.3 Tight-binding Theory of Graphene

We now apply the TB theory in the TCA explained in Chapter one to calculate the band structure of graphene. Carbon shows $sp^2$ hybridization in graphene, consequently, there are one and three electrons that, respectively, form $\pi$ and $\sigma$ bonds between C atoms. The $\pi$ and $\sigma$ bands of graphene, arise from these two bonds. In addition, the $2p_z$ states are associated with the $\pi$ bands and the $2s, 2p_x$, and $2p_y$ states are related to the $\sigma$ bands. Whereas the $\pi$ states are oriented perpendicular to the sheet, the $\sigma$ states lay in the plane of the sheet. In graphene, due to the even and odd symmetry in the mirror plane, the $\pi$ and $\sigma$ bands are not coupled, which allow us to treat them independently.

In the following, we calculate the $\pi$ and $\sigma$ energy bands of graphene using a non-orthogonal TB model within the 1NN approximation. This is a standard treatment and we follow the presentation of Saito et al. [15].

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3.3.1 \( \pi \) bands

As it was mentioned above, the only states that form the \( \pi \) bands are the \( 2p_z \) ones. Since there are two inequivalent lattice points \( A \) and \( B \), the Hamiltonian is \((2 \times 2)\).

In Chapter one, we gave general formulae for computing the Hamiltonian matrix elements using the TCA. According to Eqs. (2.28) and (2.30), we need to specify the position vectors \( \delta^{(i)}_j \), and their corresponding direct cosines \( l, m, n \). From Fig. 3.2, we notice that each C atom has three 1NN, whose position vectors are given by

\[
\begin{align*}
\delta^{(1)}_1 &= \frac{a}{\sqrt{3}} \hat{x} + 0 \hat{y}, \\
\delta^{(1)}_2 &= -\frac{a}{2\sqrt{3}} \hat{x} + \frac{a}{2} \hat{y}, \\
\delta^{(1)}_3 &= -\frac{a}{2\sqrt{3}} \hat{x} - \frac{a}{2} \hat{y}.
\end{align*}
\]

Using Eq. (2.30), we can find the direct cosines,

\[
\begin{align*}
l^{(1)}_1 &= 1, \\l^{(1)}_2 &= l^{(1)}_3 = -\frac{1}{2}, \\
m^{(1)}_1 &= 0, \\m^{(1)}_2 &= -m^{(1)}_3 = \frac{\sqrt{3}}{2}, \\
n^{(1)}_1 &= n^{(1)}_2 = n^{(1)}_3 = 0.
\end{align*}
\]

By substituting Eqs. (3.4) and (3.5) in Eq. (2.28) we find the following Hamiltonian matrix elements,

\[
\begin{align*}
(z/z)_{AA} &= (z/z)_{BB} = E_p, \\
(z/z)_{AB} &= (pp\pi)^{AB} g_{12}(k).
\end{align*}
\]
For the overlapping matrix elements we obtain

\[(z/z)^S_{AA} = (z/z)^S_{BB} = 1,\]
\[(z/z)^S_{AB} = (pp\pi)^{AB}_S g_{12}(k),\]

where \(g_{12}(k)\) is given in Eq. (B.1). In matrix form, the Hamiltonian \(H\), and the overlap matrix \(S\) are

\[
H = \begin{pmatrix} E_p & \gamma_0 g_{12}(k) \\ \gamma_0 g_{12}^*(k) & E_p \end{pmatrix}, \quad S = \begin{pmatrix} 1 & s g_{12}(k) \\ s g_{12}^*(k) & 1 \end{pmatrix}, \quad (3.6)
\]

where \(\gamma_0 \equiv (pp\pi)^{AB}_1\) and \(s \equiv (pp\pi)^{AB}_S\). Substitution of Eq. (3.6) into the secular equation (2.18) allows us to find an analytical energy dispersion \(E(k)\), that is,

\[
E(k) = \frac{E_p \pm \gamma_0 w(k)}{1 + s w(k)}, \quad (3.7)
\]

where

\[
w(k) = \sqrt{|g_{12}(k)|^2} = \sqrt{1 + 4 \cos \frac{\sqrt{3} k_x a}{2} \cos \frac{k_y a}{2} + 4 \cos^2 \frac{k_y a}{2}}. \quad (3.8)
\]

If we set \(E_p = 0\) and neglect the overlap of the \(p_z\) states \((s \approx 0)\) then, Eqn. (3.9) reduces to,

\[
E(k) = \pm \gamma_0 w(k). \quad (3.9)
\]

Figure 3.3 shows the \(\pi\) bands obtained from Eq. 3.9. We notice that the \(\pi\) bands are degenerate at the \(K\) point. Each of the C atoms in the unit cell contributes with one electron and, since there are two electrons per unit cell, this means that the lower \(\pi\) band is full.
Figure 3.3: Energy dispersion relation $E(k)$ for graphene. (a) Three-dimensional energy surface in reciprocal space. (b) $E(k)$ along $K\Gamma M K$ directions. Here, $E_p = 0, \gamma_0 = -3.03$ eV and $s = 0$. 
3.3.2 σ bands

In order to compute the σ bands, we make use of a $sp^2$ TB model. Again, since the $A$ and $B$ points in the honeycomb lattice of graphene are inequivalent, our Hamiltonian matrix is $6 \times 6$. By using Eqs. (3.4), (3.5), and the formulae given in Chapter one [c.f. Eqs. (2.28) and (2.30)], we compute the matrix elements of the Hamiltonian.

\[
(s/s)_{AA} = (s/s)_{BB} = E_s,
\]
\[
(x/x)_{AA} = (y/y)_{AA} = (x/x)_{BB} = (y/y)_{BB} = E_p
\]
\[
(x/s)_{AA} = (y/s)_{AA} = (x/s)_{BB} = (y/s)_{BB} = 0,
\]
\[
(s/s)_{AB} = (ss\sigma)^{AB} g_0(k),
\]
\[
(x/x)_{AB} = (pp\sigma)^{AB} g_3(k) + (pp\pi)^{AB} g_4(k),
\]
\[
(y/y)_{AB} = (pp\sigma)^{AB} g_6(k) + (pp\pi)^{AB} g_4(k),
\]
\[
(s/x)_{AB} = (sp\sigma)^{AB} g_1(k),
\]
\[
(s/y)_{AB} = (sp\sigma)^{AB} g_2(k),
\]
\[
(x/y)_{AB} = [(pp\sigma)^{AB} - (pp\pi)^{AB}] g_5(k).
\]

In a similar fashion, Eq. (3.11) gives the overlap matrix $S$ elements.

\[
(s/s)^S_{AA} = (s/s)^S_{BB} = 1,
\]
\[
(x/x)^S_{AA} = (y/y)^S_{AA} = (x/x)^S_{BB} = (y/y)^S_{BB} = 1
\]
\[
(x/s)^S_{AA} = (y/s)^S_{AA} = (x/s)^S_{BB} = (y/s)^S_{BB} = 0,
\]
\[
(s/s)^S_{AB} = (ss\sigma)^{SB} g_0(k),
\]
\[
(x/x)^S_{AB} = (pp\sigma)^{SB} g_3(k) + (pp\pi)^{SB} g_4(k),
\]
\[
(y/y)^S_{AB} = (pp\sigma)^{SB} g_6(k) + (pp\pi)^{SB} g_4(k).
\]
\[
\begin{align*}
(y/y)_A^B &= (pp\sigma)_S^A g_6(k) + (pp\pi)_S^A g_4(k), \\
(s/x)_A^B &= (sp\sigma)_S^A g_1(k), \\
(s/y)_A^B &= (sp\sigma)_S^A g_2(k), \\
(x/y)_A^B &= [(pp\sigma)_S^A - (pp\pi)_S^A] g_5(k),
\end{align*}
\]

where all the \(g_j(k)\) functions are given in Eq. (B.1). Results for the band structure of graphene are shown in Fig. 3.4. The two-center parameters used for the calculations are listed in Table 3.1. The full Hamiltonian at \(\Gamma\) is given in Eq. (3.12) (including the \(p_z\) sector). If we solve the secular equation [c.f. Eq. (2.18)] at this point, we can find analytical expressions for the energies,

\[
\begin{align*}
E_{p,\pm}(\Gamma) &= E_p \pm 3(pp\pi)_1^{AB}, \\
E_{s,\pm}(\Gamma) &= E_s \pm 3(ss\sigma)_1^{AB}, \\
E_{p,\pm}(\Gamma) &= E_p \pm \frac{3}{2} [(pp\pi)_1^{AB} + (pp\sigma)_1^{AB}], \quad (2.f.d.),
\end{align*}
\]

where 2.f.d. stands for “two-fold-degenerate”.

Finally, we point out that the notation used here differs from the notation in Saito et al. [15]. Table 3.2 shows how the two notations are related.

### 3.4 Effective-mass Theory of Graphene

In this section we will derive in detail the effective-mass model of graphene proposed by Ando [41]. There are several reasons why it is worthwhile examining this theory: (1) it is from the effective-mass approach that the Dirac equation for massless fermions in
\[ H = \begin{pmatrix}
  z_A & z_B & s_A & s_B & x_A & x_B & y_A & y_B \\
  (z/z)_A & (z/z)_B & 0 & 0 & 0 & 0 & 0 & 0 \\
  (z/z)_A & (z/z)_B & 0 & 0 & 0 & 0 & 0 & 0 \\
  s_A & 0 & 0 & (s/s)_A & (s/s)_B & 0 & 0 & 0 \\
  s_B & 0 & 0 & (s/s)_A & (s/s)_B & 0 & 0 & 0 \\
  x_A & 0 & 0 & 0 & 0 & (x/x)_A & (x/x)_B & 0 \\
  x_B & 0 & 0 & 0 & 0 & (x/x)_A & (x/x)_B & 0 \\
  y_A & 0 & 0 & 0 & 0 & 0 & 0 & (x/x)_A & (x/x)_B \\
  y_B & 0 & 0 & 0 & 0 & 0 & 0 & (x/x)_A & (x/x)_B
\end{pmatrix}. \quad (3.12) \]

\[
\begin{align*}
(z/z)_A &= E_p \\
(z/z)_B &= 3(pp\pi)^{AB} \\
(s/s)_A &= E_s \\
(s/s)_B &= 3(ss\sigma)^{AB} \\
(x/x)_A &= E_p \\
(x/x)_B &= \frac{3}{2}[(pp\pi)^{AB} + (pp\pi)^{AB}] 
\end{align*}
\]
Table 3.1: Two-center integral parameters for graphene. (From Ref. [15].)

\[
\begin{array}{|c|c|}
\hline
\text{Parameter} & \text{Value} \\
\hline
E_s & -8.868 \\
E_p & 0 \\
(ss\sigma)^{AB} & -6.769 \\
(sp\sigma)^{AB} & 5.580 \\
(pp\sigma)^{AB} & 5.037 \\
(pp\pi)^{AB} ≡ \gamma_0 & -3.033 \\
(ss\sigma)^{AB}_S & 0.212 \\
(ss\sigma)^{AB}_S & -0.102 \\
(sp\sigma)^{AB}_S & -0.146 \\
(pp\pi)^{AB}_S ≡ s & 0.129 \\
\hline
\end{array}
\]

Table 3.2: Notation used here and in Saito et al. [15].

<table>
<thead>
<tr>
<th>Present work</th>
<th>Saito et al. [15]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta_j^{(1)}$</td>
<td>$\tau_j$</td>
</tr>
<tr>
<td>$g_{12}(\mathbf{k})$</td>
<td>$f(\mathbf{k})$</td>
</tr>
<tr>
<td>$E_s$</td>
<td>$\epsilon_{2s}$</td>
</tr>
<tr>
<td>$E_p$</td>
<td>$\epsilon_{2p}$</td>
</tr>
<tr>
<td>$(ss\sigma)^{AB}$</td>
<td>$\mathcal{H}_{ss}$</td>
</tr>
<tr>
<td>$(sp\sigma)^{AB}$</td>
<td>$-\mathcal{H}_{sp}$</td>
</tr>
<tr>
<td>$(pp\sigma)^{AB}$</td>
<td>$-\mathcal{H}_{\sigma}$</td>
</tr>
<tr>
<td>$(pp\pi)^{AB} ≡ \gamma_0$</td>
<td>$\mathcal{H}_\pi ≡ t$</td>
</tr>
<tr>
<td>$(ss\sigma)^{AB}_S$</td>
<td>$s_{ss}$</td>
</tr>
<tr>
<td>$(ss\sigma)^{AB}_S$</td>
<td>$-s_{sp}$</td>
</tr>
<tr>
<td>$(sp\sigma)^{AB}_S$</td>
<td>$-s_{\sigma}$</td>
</tr>
<tr>
<td>$(pp\pi)^{AB}_S ≡ s$</td>
<td>$s_\pi ≡ s$</td>
</tr>
</tbody>
</table>

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Figure 3.4: Band structure of graphene. We used the TB parameters from Saito et al. [15].

Figure 3.5: Graphene lattice and basis vectors used in the effective-mass theory of graphene.
graphene is derived; (2) it has been applied to study the electronic properties of more complicated structures such as helically coiled nanotubes and nanotube junctions [47, 48, 49]; and (3) it allows one to obtain analytical or semi-analytical expressions for optical and transport properties of CNT’s [41, 50].

Figure (3.5) shows a graphene sheet and the vectors we will use in this section. The position of the 1NN is given by vectors \( \tau_1 = a/(2\sqrt{3})j \), \( \tau_2 = -a/2i - a/(2\sqrt{3})j \), \( \tau_3 = a/2i - a/(2\sqrt{3})j \) where \( a \) is the lattice constant. The vectors \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) are the primitive vectors of the graphene sheet. Following Ando and Tamura et al. [41, 47], we can write the wave function \( \psi(\mathbf{r}) \), as a linear superposition of atomic orbitals \( \phi(\mathbf{r} - \mathbf{R}) \),

\[
\psi(\mathbf{r}) = \sum_{\mathbf{R}_A} \psi_A(\mathbf{R}_A) \phi(\mathbf{r} - \mathbf{R}_A) + \sum_{\mathbf{R}_B} \psi_B(\mathbf{R}_B) \phi(\mathbf{r} - \mathbf{R}_B),
\]

(3.13)

where \( \mathbf{R}_A \) and \( \mathbf{R}_B \) are the position vectors of the lattice points \( A \) and \( B \). Equation (3.13) is the similar to the wave function of graphene using the Bloch functions, however, notice that the coefficients \( \psi_A(\mathbf{R}_A) \) and \( \psi_B(\mathbf{R}_B) \) have not been specified. If we want the wave function in Eq. (3.13) to obey Bloch’s theorem, then we have to make the coefficients equal to \( e^{i\mathbf{k} \cdot \mathbf{R}_n} \). We will not do this at this point, since, as we will see later, the expansion (3.13) is intended to be applied to non-periodic or finite systems such as a finite graphene sheet or a CNT.

Substituting Eq. (3.13) into the time-independent Schrödinger equation, \( H\psi(\mathbf{r}) = \varepsilon \psi(\mathbf{r}) \), we find

\[
\sum_{\mathbf{R}_A} \psi_A(\mathbf{R}_A) H\phi(\mathbf{r} - \mathbf{R}_A) + \sum_{\mathbf{R}_B} \psi_B(\mathbf{R}_B) H\phi(\mathbf{r} - \mathbf{R}_B)
= \varepsilon \sum_{\mathbf{R}_A} \psi_A(\mathbf{R}_A) \phi(\mathbf{r} - \mathbf{R}_A) + \varepsilon \sum_{\mathbf{R}_B} \psi_B(\mathbf{R}_B) \phi(\mathbf{r} - \mathbf{R}_B).
\]

(3.14)
If we multiply by the atomic orbital $\phi^*(r - R_A)$, and integrate over the whole space we obtain,

$$\sum_{R'_A} \psi_A(R'_A) \int \phi^*(r - R_A) H \phi(r - R'_A) \, dr + \sum_{R'_B} \psi_B(R'_B) \int \phi^*(r - R_B) H \phi(r - R'_B) \, dr$$

$$= \varepsilon \sum_{R'_A} \psi_A(R'_A) \int \phi^*(r - R_A) \phi(r - R'_A) \, dr + \varepsilon \sum_{R'_B} \psi_B(R'_B) \int \phi^*(r - R_A) \phi(r - R'_B) \, dr.$$

We can approximate $\int \phi^*(r - R_A) \phi(r - R'_B) \, dr \approx 0$ when we do not take into consideration any overlapping between the $p_z$ orbitals. Moreover, by using the 1NN approximation we can calculate some of the summations

$$\sum_{R'_A} \psi_A(R'_A) \int \phi^*(r - R_A) H \phi(r - R'_A) \, dr \approx \psi_A(R_A) \varepsilon_{2p},$$

where $\varepsilon_{2p} \equiv \int \phi^*(r - R_A) H \phi(r - R'_A) \, dr$ is called the on-site integral, and it is chosen to be equal to zero, i.e., $\varepsilon_{2p} \equiv 0$. Furthermore,

$$\varepsilon \sum_{R'_A} \psi_A(R'_A) \int \phi^*(r - R_A) \phi(r - R'_A) \, dr \approx \varepsilon \psi_A(R_A) \int \phi^*(r - R_A) \phi(r - R_A) \, dr = \varepsilon \psi_A(R_A),$$

$$\varepsilon \sum_{R'_B} \psi_B(R'_B) \int \phi^*(r - R_A) \phi(r - R'_B) \, dr \approx 0,$$

and

$$\sum_{R'_B} \psi_B(R'_B) \int \phi^*(r - R_A) H \phi(r - R'_B) \, dr \approx -\gamma_0 \sum \psi_B(R'_B),$$

where we the atomic orbitals are normalized, i.e., $\int \phi^*(r - R_A) \phi(r - R'_A) \, dr = 1$, and
\[ \gamma_0 \equiv - \int \phi^*(r - R_A) H \phi(r - R'_B) \, dr. \] \gamma_0 \] is called the transfer integral between nearest-neighbors and its value is approximately \(-2.7\) eV [41]. From Fig. (3.5), one finds that \(R_B = R_A + \tau_l\), therefore,

\[ \varepsilon \psi_A(R_A) = \gamma_0 \sum_{l=1}^{3} \psi_B(R_A + \tau_l). \tag{3.15} \]

The second relation between the probability amplitudes \(\psi_A\) and \(\psi_B\), is found by multiplying Eq. (3.14) by \(\phi^*(r - R_B)\):

\[
\sum_{R'_A} \psi_A(R'_A) \int \phi^*(r - R_B) H \phi(r - R'_A) \, dr + \sum_{R'_B} \psi_B(R'_B) \int \phi^*(r - R_B) H \phi(r - R'_B) \, dr
= \varepsilon \sum_{R'_A} \psi_A(R'_A) \int \phi^*(r - R_B) \phi(r - R'_A) \, dr + \varepsilon \sum_{R'_B} \psi_B(R'_B) \int \phi^*(r - R_B) \phi(r - R'_B) \, dr.
\]

One can use the previous definitions and approximations to rewrite this equation in the following manner

\[ \varepsilon \psi_B(R_B) = \gamma_0 \sum_{l=1}^{3} \psi_A(R_B - \tau_l). \tag{3.16} \]

Let us check that we have done things in the appropriate manner. Recall that Eq. (3.13) is a more general expansion than the TB function so, if we set make the coefficients \(\psi_s\) equal to the TB ones, we should obtain the dispersion relation of graphene given in Eq. (3.9). Substituting \(\psi_s \propto c_s(k)e^{i k \cdot R_s} \) \((s = A, B)\) into Eqs. (3.15), and (3.16), we find that

\[
\begin{pmatrix}
0 & f_{AB}(k) \\
f_{AB}^*(k) & 0
\end{pmatrix}
\begin{pmatrix}
c_A(k) \\
c_B(k)
\end{pmatrix} = \varepsilon \begin{pmatrix}
c_A(k) \\
c_B(k)
\end{pmatrix} \tag{3.17}
\]

where \(f_{AB}(k) = \gamma_0 \sum_{l=1}^{3} e^{i k \cdot \tau_l}\). The energy dispersion relation can be obtained from
Eq. (3.17) by calculating its eigenvalues $\varepsilon_{\pm}$. Hence,

$$
\varepsilon_{\pm}(k) = \pm \gamma_0 \sqrt{1 + 4 \cos \left( \frac{k_x a}{2} \right) \cos \left( \frac{\sqrt{3} k_y a}{2} \right) + 4 \cos^2 \left( \frac{k_x a}{2} \right)}.
$$

(3.18)

This energy dispersion relation matches with the previously given in Eq. (3.9).

In order to derive an effective-mass theory, we write the wave function amplitudes $\psi_A$ and $\psi_B$ in Eqs. (3.15) and (3.16) as a linear superposition of envelope functions $F_{[41]}$, that is,

$$
\psi_A(R_A) = e^{iK \cdot R_A} F_{KA}(R_A) + e^{i\eta} e^{iK' \cdot R_A} F_{KA}(R_A),
$$

(3.19)

$$
\psi_B(R_B) = -\omega e^{i\eta} e^{iK_R \cdot R_B} F_{KB}(R_B) + e^{iK' \cdot R_B} F_{KB}(R_B),
$$

(3.20)

where $\omega = e^{2\pi i}$ and $K$ and $K'$ are equivalent Brillouin points in the unit cell. The non-periodic effects in the honeycomb lattice, for instance, CNT boundary conditions, impurities, etc., are taken into consideration in the envelope functions $F$ and the summation on $k^6$. In other words, if we were dealing with a periodic system then, $F = 1$, and the summation on the wave vector is not needed anymore. Equations (3.19) and (3.20) can be rewritten in the following manner,

$$
\psi_A(R_A) = a^\dagger(R_A) F_A(R_A),
$$

(3.22)

In a non-periodic system the wave-number vector $k$, is no longer a good quantum number hence, we have to take all possible wave-vectors into consideration. In other words, the wave function of the system is

$$
\psi(r) = \sum_{n,k} d_{nk} \psi_{nk},
$$

(3.21)

where $\psi_{nk}$ is the wave function of the perfect crystalline lattice and the $d_{nk}$ coefficients are complex numbers. It would be interesting to develop a general non-periodic TB theory since, to the best of our knowledge, there are no reports in the literature of such theory.
\[ \psi_B(R_B) = b^\dagger(R_B)F_B(R_B), \]  

(3.23)

where

\[
a(R_A) = \begin{pmatrix}
e^{iK\cdot R_A} \\
e^{-i\eta e^{-iK\cdot R_B}} \\
e^{-iK\cdot R_B}
\end{pmatrix}, \\
b(R_b) = \begin{pmatrix}
-\omega^{-1}e^{-i\eta e^{-iK\cdot R_B}} \\
e^{-iK\cdot R_B}
\end{pmatrix},
\]  

(3.24)

and

\[
F_A(R_A) = \begin{pmatrix}
F^K_A(R_A) \\
F^{K'}_A(R_A)
\end{pmatrix}, \\
F_B(R_B) = \begin{pmatrix}
F^K_B(R_B) \\
F^{K'}_B(R_B)
\end{pmatrix}.
\]  

(3.25)

Now, using Eqs. (3.22), and (3.23), in Eq. (3.15) we obtain,

\[ \varepsilon a^\dagger(R_A)F_A(R_A) = -\gamma_0 \sum_{l=1}^{3} b^\dagger(R_A - \tau_l)F_B(R_A - \tau_l), \]  

(3.26)

\[ \varepsilon b^\dagger(R_B)F_B(R_B) = -\gamma_0 \sum_{l=1}^{3} a^\dagger(R_A + \tau_l)F_A(R_B + \tau_l). \]  

(3.27)

Next, let us define a real function \( g(R) \) that has the following characteristics,

\[ \sum_{R_A} g(R_A) = \sum_{R_B} g(R_B) = 1, \]  

(3.28)

and

\[ F(R) = \frac{1}{\Omega_0} \int_{\Omega_0} g(r - R)F(r) \, dr, \]  

(3.29)

where \( \Omega_0 \) is the area of the unit cell of graphene and is equal to \( \sqrt{3}/2a^2 \). The function \( g(R) \) is similar to the Dirac delta function \( \delta(r) \); however, its domain is only the area of the 2D graphene unit cell rather than the whole 3D space. We can use this function to rewrite Eqs. (3.26), and (3.27). If we multiply the left hand side (lhs) of Eq. (3.26) by...
\( g(r' - R_A)a(R_A) \) and sum over \( R_A \), we find,

\[
\varepsilon \sum_{R_A} g(r - R_A)a(R_A)a^\dagger(R_A)F_A(R_A) = \varepsilon \sum_{R_A} g(r - R_A)a(R_A)a^\dagger(R_A)F_A(r).
\]

On the other hand, the right hand side (rhs) of Eq. (3.26) becomes

\[
\begin{align*}
-\gamma_0 \sum_{R_A} g(r - R_A) & \sum_{l=1}^{3} a(R_A)b^\dagger(R_A - \tau_l)F_B(R_A - \tau_l) \\
&= -\gamma_0 \sum_{l=1}^{3} \sum_{R_A} g(r' - R_A)a(R_A)b^\dagger(R_A - \tau_l) \\
&\quad \times \left[ F_B(r') - (\tau_l \cdot \frac{\partial}{\partial r'}) F_B(r') + ... \right],
\end{align*}
\]

where we have expanded the envelope function \( F_B(r') \) in a Taylor series. In order to calculate the summations we have to compute the vector products \( a(R_A)a^\dagger(R_A) \) and \( a(R_A)b^\dagger(R_A - \tau_l) \). Using Eq. (3.24) we find

\[
\sum_{R_A} g(r - R_A)a(R_A)a^\dagger(R_A)
= \sum_{R_A} g(r - R_A) \begin{pmatrix} 1 & e^{i(K-K')\cdot R_A}e^{-i\eta} \\ e^{-i(K-K')\cdot R_A}e^{i\eta} & 1 \end{pmatrix}
= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix},
\]

hence

\[
\sum_{R_A} g(r - R_A)a(R_A)a^\dagger(R_A) = \varepsilon F_A(r'),
\]
\[ \sum_{R_{A}} g(r - R_{A}) a(R_{A}) b^{\dagger}(R_{A} - \tau_{l}) \]
\[ = \sum_{R_{A}} g(r - R_{A}) \begin{pmatrix} -\omega e^{i\eta} e^{-iK \cdot \tau_{l}} & e^{-i(K-K') \cdot R_{A}} \\ -\omega e^{i\eta} e^{-iK \cdot \tau_{l}} e^{i(K-K') \cdot R_{A}} & e^{-i(K-K') \cdot \tau_{l}} \end{pmatrix} \]
\[ = \left( \begin{array}{cc} -\omega e^{i\eta} e^{-iK \cdot \tau_{l}} & 0 \\ 0 & e^{-i(K-K') \cdot \tau_{l}} \end{array} \right) \]  

(3.33)

where we have used the result \[ \sum_{R_{A}} g(r' - R_{A}) e^{i(K-K') \cdot R_{A}} = 0 \]. Therefore,

\[ \sum_{l=1}^{3} \sum_{R_{A}} g(r - R_{A}) a(R_{A}) b^{\dagger}(R_{A} - \tau_{l}) F_{B}(r') \]
\[ = F_{B}(r') \begin{pmatrix} -\omega e^{i\eta} \sum_{l=1}^{3} e^{-iK \cdot \tau_{l}} & 0 \\ 0 & e^{-i\eta} \sum_{l=1}^{3} e^{-i(K-K') \cdot \tau_{l}} \end{pmatrix} \]  

(3.34)

By substituting vectors \( K, K' \) and \( \tau_{l} \) we obtain that

\[ \sum_{l=1}^{3} e^{-iK \cdot \tau_{l}} = 0, \quad \sum_{l=1}^{3} e^{-iK' \cdot \tau_{l}} = 0, \]
\[ \sum_{l=1}^{3} e^{-iK \cdot \tau_{l} \cdot \tau_{l}} = \sqrt{3} \omega^{-1} a/2 (i,1), \quad \sum_{l=1}^{3} e^{-iK' \cdot \tau_{l}} = \sqrt{3} a/2 (-i,1). \]

Combining the previous results, Eq. (3.30) can be rewritten in the form

\[ \varepsilon F_{B}(r) = \gamma \begin{pmatrix} e^{i\eta}(\hat{k}_{x'} - i\hat{k}_{y'}) & 0 \\ 0 & e^{-i\eta}(\hat{k}_{x'} + i\hat{k}_{y'}) \end{pmatrix} F_{B}(r), \]  

(3.35)

where \( \gamma = (\sqrt{3}/2)\gamma_{0}a, \ \hat{k}_{x'} = -i \frac{\partial}{\partial x'}, \) and \( \hat{k}_{y'} = -i \frac{\partial}{\partial y'}. \) It turns out that it is convenient to perform a counter-clockwise rotation of our coordinate system (primed coordinates) by

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an angle $\eta$. Once this rotation is performed, Eq. (3.35) changes to

$$\varepsilon \mathbf{F}_A(r) = \gamma \begin{pmatrix} (\hat{k}_x - i\hat{k}_y) & 0 \\ 0 & (\hat{k}_x + i\hat{k}_y) \end{pmatrix} \mathbf{F}_B(r),$$

(3.36)

where $\hat{k}_x \equiv -i \frac{\partial}{\partial x}$, and $\hat{k}_y \equiv -i \frac{\partial}{\partial y}$. By following a similar procedure, one can show that the equation for the envelope function $\mathbf{F}_B(r)$, is

$$\varepsilon \mathbf{F}_B(r) = \gamma \begin{pmatrix} (\hat{k}_x + i\hat{k}_y) & 0 \\ 0 & (\hat{k}_x - i\hat{k}_y) \end{pmatrix} \mathbf{F}_A(r).$$

(3.37)

Equations (3.36), and (3.37) can be written in a more compact form

$$\hat{H}_0 \mathbf{F}(r) = \varepsilon \mathbf{F}(r)$$

(3.38)

where

$$\hat{H}_0 \equiv \gamma \begin{pmatrix} 0 & (\hat{k}_x - i\hat{k}_y) & 0 & 0 \\ (\hat{k}_x + i\hat{k}_y) & 0 & 0 & 0 \\ 0 & 0 & 0 & (\hat{k}_x + i\hat{k}_y) \\ 0 & 0 & (\hat{k}_x - i\hat{k}_y) & 0 \end{pmatrix},$$

(3.39)

$$\mathbf{F}^K(r) \equiv \begin{pmatrix} F^K_A(r) \\ F^K_B(r) \end{pmatrix}, \quad \mathbf{F}'^K(r) = \begin{pmatrix} F'^K_A(r) \\ F'^K_B(r) \end{pmatrix},$$

(3.40)

and

$$\mathbf{F}(r) \equiv \begin{pmatrix} \mathbf{F}^K(r) \\ \mathbf{F}'^K(r) \end{pmatrix}. $$

(3.41)

There is another useful manner of writing the equations that govern the envelope func-
tions $F(r)$; that is,

$$\gamma \left( \hat{k} \cdot \hat{\sigma} \right) F^K(r) = \varepsilon F^K(r),$$
$$\gamma \left( \hat{k}' \cdot \hat{\sigma} \right) F^{K'}(r) = \varepsilon F^{K'}(r),$$

(3.42)

where

$$\hat{\sigma} \equiv (\hat{\sigma}_x, \hat{\sigma}_y), \quad \mathbf{k}' = \begin{pmatrix} \hat{k}_x \\ -\hat{k}_y \end{pmatrix},$$

(3.43)

where $\hat{\sigma}_x$ and $\hat{\sigma}_y$ are the Pauli matrices,

$$\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}.$$  (3.44)

Equation (3.42) is the so-called Weyl equation, which corresponds to the Dirac equation for massless particles.

We have applied this theory to study the electronic properties of helical carbon nanotubes [51].
Chapter 4

Single-walled Carbon Nanotubes

A carbon nanotube is a hollow cylinder made of carbon atoms arranged in a honeycomb lattice. The diameter of the cylinder is of the order of the nanometers and usually their length is much larger than their diameter. The ratio length/diameter is called aspect ratio. For CNT’s it is of the order of $10^4 - 10^6$ [15]. In principle, carbon nanotubes can be made from a graphene sheet. If we roll this sheet and glue the ends of it, we have a single-walled carbon nanotube (SWCNT). A SWCNT is fully determined by the so called chiral vector. Furthermore, SWCNT’s are classified by their chiral vectors: amchair, zig-zag, and chiral tube [52]. The name of the first two names come from the shape of their cross-sectional ring [15]. Each one of these three types of nanotubes exhibit different symmetries that belong to the line groups. Detailed studies of these groups and its connection to the electronic properties of SWCNT’s can be found in Refs. [52, 53, 54, 55, 56]. We will study the chiral vector and the electronic properties of these type of nanotubes and our treatment follows the one in Saito et al. [15].
4.1 Chiral Vector

The vector $OA$ in Fig. 4.1(a) defines the chiral vector $C_h$. This vector can be expressed in the following manner

$$C_h = n\mathbf{a}_1 + m\mathbf{a}_2,$$

(4.1)

where $\mathbf{a}_1, \mathbf{a}_2$ are the basis vectors of graphene given in Eq. (3.1), and $n$ and $m$ are integers with the restriction $0 \leq |m| \leq n^1$.

An armchair nanotube has a chiral vector $C_h = (n,n)$, and a zigzag nanotube corresponds to $C_h = (n,0)$. All other $(n,m)$ vectors correspond to chiral nanotubes.

The magnitude of the chiral vector $C_h$, defines the circumference of its corresponding tube. Let us call this length $L$. In other words,

$$L = |C_h| = a\sqrt{n^2 + m^2 + nm},$$

(4.2)

where $a$ is the the lattice constant of graphene. The diameter $d$ of the CNT is, therefore,

$$d = \frac{L}{\pi}.$$  

(4.3)

Figures 4.1(b),(c) show an armchair and a zig-zag tube with chiral vectors $(3,3)$ and $(5,0)$, respectively. According to Eq. (4.3), the former has a diameter equal to $3\sqrt{3}a/\pi$, and the latter equal to $5a/\pi$. In general, a $(n,0)$ zig-zag nanotube has a diameter $d$ equal to

$$d = \frac{a\sqrt{n^2}}{\pi} = \frac{an}{\pi},$$

Due to the six-fold symmetry of graphene, this restriction is necessary so that a CNT is defined uniquely.
Figure 4.1: Chiral, translational and symmetry vectors of CNT’s. The chiral and translational vectors define the unit cell of a CNT. There are $N$ hexagons and $2N$ atoms within the unit cell. (a) Carbon nanotube with $C_h = (4, 2)$, (b) with $C_h = (3, 3)$, and (c) with $C_h = (5, 0)$. 
and for a \((n, n)\) armchair, it is equal to,

\[
d = \frac{a\sqrt{n^2 + n^2 + n^2}}{\pi} = \frac{\sqrt{3}an}{\pi}.
\]

### 4.2 Chiral Angle

When we fold the graphene sheet to form the nanotube, the orientation of the hexagons with respect to the nanotube axis changes according to the chirality of the tube. This tilt is measured by the so-called chiral angle \(\theta\), which is shown in Fig. 4.1(a). The chiral angle corresponds to the angle between the chiral vector \(\mathbf{C}_h\) and the vector \(\mathbf{a}_1\). Thus, we can find the chiral angle by calculating the scalar product between \(\mathbf{C}_h\) and \(\mathbf{a}_1\),

\[
\cos \theta = \frac{\mathbf{C}_h \cdot \mathbf{a}_1}{|\mathbf{C}_h||\mathbf{a}_1|} = \frac{2n + m}{2\sqrt{n^2 + m^2 + nm}}.
\]

As an example, let us consider the chiral angle of a zig-zag and an armchair tube.

- **Zig-zag tube:** \(\mathbf{C}_h = (n, 0)\)

  \[
  \cos \theta = \frac{2n + 0}{2\sqrt{n^2 + 0^2 + n0}} = \frac{2n}{2n} = 1 \Rightarrow \theta = 0^\circ.
  \]

- **Armchair tube:** \(\mathbf{C}_h = (n, n)\)

  \[
  \cos \theta = \frac{2n + n}{2\sqrt{n^2 + n^2 + n^2}} = \frac{3n}{\sqrt{3}n} = \frac{1}{\sqrt{3}} \Rightarrow \theta = 30^\circ.
  \]

From the restriction \((0 \leq |m| \leq n)\), we see that the zig zag and armchair tubes have the smallest and greatest chiral angles, respectively. In other words, \(0^\circ \leq \theta \leq 30^\circ\). Hence,
for any chiral tube $0^\circ < \theta < 30^\circ$. Consider the $(4,2)$ tube in Fig. 4.1. By substituting $n = 4$ and $m = 2$ in Eq. (4.4), we find $\theta = 19.1^\circ$. This confirms that the $(4,2)$ tube satisfies the restriction on $\theta$.

### 4.3 Translational Vector

In Figs. 4.1(a),(b),(c), the translational vector corresponds to the vector denoted by $\mathbf{T}$. It is orthogonal to the chiral vector $\mathbf{C}_h$, and it is parallel to the nanotube axis. The magnitude of $\mathbf{T}$ is the length along the vector $\mathbf{OB}$ between the origin and the first lattice point of the two-dimensional graphene sheet. In terms of the basis vectors $\mathbf{a}_1$ and $\mathbf{a}_2$, the translational vector is given by

$$\mathbf{T} = t_1 \mathbf{a}_1 + t_2 \mathbf{a}_2, \quad (4.5)$$

where $t_1$ and $t_2$ are integer numbers. These integers can be related to $n$ and $m$ by using the orthogonality between $\mathbf{T}$ and $\mathbf{C}_h$. That is, $\mathbf{T} \cdot \mathbf{C}_h = 0$.

$$\mathbf{T} \cdot \mathbf{C}_h = (t_1 \mathbf{a}_1 + t_2 \mathbf{a}_2) \cdot (n \mathbf{a}_1 + m \mathbf{a}_2)$$

$$= [(2n + m)t_1 + (2m + n)t_2] a_2^2 / 2 = 0, \quad (4.6)$$

$$\Rightarrow \quad \frac{t_1}{t_2} = -\frac{2m + n}{2n + m}. \quad (4.7)$$

We might think at this point that $t_1 = 2m + n$ and $t_2 = -(2n + m)$; however, these components do not give the shortest vector. For example, if $\mathbf{C}_h = (4,2)$ then, $\mathbf{T} = (8, -10)$. The vector $\mathbf{T}$ has the appropriate direction, but not the correct magnitude,
according to the definition of $T$ previously given. In order to shorten it and to keep $t_1, t_2$ integers, we divide by the greatest common divisor (gcd) of 8 and 10, which is 2. Thus, $T = (8, -10)/2 = (4, -5)$. In general,

$$t_1 = \frac{2m + n}{d_R}, \ t_2 = -\frac{2n + m}{d_R}$$

(4.8)

where $d_R$ is the (gcd) of $(2m + n)$ and $(2n + m)$. We can relate $d_R$ to the (gcd) of $n$ and $m$ by repeated use of Euclid’s law². Denoting as $d$ the (gcd) between $n$ and $m$, we obtain

$$d_R = \begin{cases} 
  d & \text{if } (n - m) \text{ is not a multiple of } 3d, \\
  3d & \text{if } (n - m) \text{ is a multiple of } 3d.
\end{cases}$$

(4.9)

The vector $T$ has length,

$$T = \left( t_1^2 + t_2^2 + t_1 t_2 \right)^{1/2} a$$

$$= \frac{a}{d_R} \left[ (2m + n)^2 + (2n + m)^2 - (2m + n)(2n + m) \right]^{1/2}$$

$$= \frac{\sqrt{3}a \sqrt{n^2 + m^2 + nm}}{d_R} = \frac{\sqrt{3L}}{d_R}.$$  

(4.10)

For a zig-zag tube, $d_R = d = n$, thus,

$$T = (1, -2), \ T = \sqrt{3}a \ (\text{zig zag})$$

(4.11)

and for an armchair tube, $d_R = 3d = 3n$. So,

$$T = (1, -1), \ T = a \ (\text{armchair}).$$

(4.12)

²If two integers, $\alpha$ and $\beta$ ($\alpha > \beta$) have a common divisor $\gamma$, then $\gamma$ is also a common divisor of $(\alpha - \beta)$ and $\beta$. 

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We conclude that all zig-zag nanotubes have the same translational vector since its respective \( t_1 \) and \( t_2 \) always have a (gcd). Same occurs for all armchair tubes. Notice that \( T \propto 1/d_R \), hence the magnitude of \( T \) is significantly reduced when \((n, m)\) have a (gcd), as in the two cases just mentioned before.

### 4.4 Unit Cell

The shaded areas in Figs 4.1(a),(b),(c) are the nanotube unit cells. Each cell is defined by the vectors \( C_h \) and \( T \) and its corresponding area is given by \( |C_h \times T| \). Denoting by \( N \) the number of hexagons per the unit cell, it is clear that,

\[
N = \frac{\text{area of the CNT unit cell}}{\text{area of a hexagon}} = \frac{|C_h \times T|}{|a_1 \times a_2|}
\]

\[
= \frac{2}{\sqrt{3}a^2} |mt_1a_2 \times a_1 + nt_2a_1 \times a_2|
\]

\[
= |nt_2 - mt_1| = \frac{|-2n^2 - 2m^2 - 2nm|}{d_R} = \frac{2(n^2 + m^2 + nm)}{d_R}
\]

\[
= \frac{2L^2}{a^2d_R}.
\]

(4.13)

### 4.5 Brillouin Zone

The reciprocal basis vectors can be obtained from the following equations,

\[
C_h \cdot K_1 = 2\pi, \ T \cdot K_1 = 0, \ C_h \cdot K_2 = 0, \ T \cdot K_2 = 2\pi.
\]

(4.14)
Substituting \( \mathbf{C}_h \), \( \mathbf{T} \) and defining the \( \mathbf{K} \) vectors as

\[
\mathbf{K}_1 = \alpha_1 \mathbf{b}_1 + \beta_1 \mathbf{b}_2, \quad \mathbf{K}_2 = \alpha_2 \mathbf{b}_1 + \beta_2 \mathbf{b}_2,
\]  

(4.15)

we substitute them in Eq. (4.14),

\[
\mathbf{K}_1 \cdot \mathbf{C}_h = (\alpha_1 \mathbf{b}_1 + \beta_1 \mathbf{b}_2) \cdot (na_1 + ma_2) = 2\pi(n\alpha_1 + m\beta_1) = 2\pi, \tag{4.16}
\]

\[
\mathbf{K}_1 \cdot \mathbf{T} = 2\pi(\alpha_1 t_1 + \beta_1 t_2) = 0. \tag{4.17}
\]

The components \( t_1, t_2 \) are given in Eq. (4.8). Once we insert them in Eqs. (4.16) and (4.17) we obtain for \( \mathbf{K}_1 \),

\[
n\alpha_1 + m\beta_1 = 1,
\]

\[
(2m + n)\alpha_1 - (2n + m)\beta_1 = 0,
\]

or

\[
\alpha_1 = \frac{2n + m}{2(n^2 + m^2 + nm)} = -\frac{t_2 d_R a^2}{2L^2} = -\frac{t_2}{N},
\]

\[
\beta_1 = \frac{2m + n}{2(n^2 + m^2 + nm)} = \frac{t_1}{N},
\]

\[
\mathbf{K}_1 = \frac{1}{N}(-t_2 \mathbf{b}_1 + t_1 \mathbf{b}_2). \tag{4.18}
\]

and for \( \mathbf{K}_2 \),

\[
\mathbf{K}_2 \cdot \mathbf{C}_h = (\alpha_2 \mathbf{b}_1 + \beta_2 \mathbf{b}_2) \cdot (na_1 + ma_2)
\]
\[ = 2\pi (n\alpha_2 + m\beta_2) = 0, \]
\[ \mathbf{K}_2 \cdot \mathbf{T} = 2\pi (\alpha_2 t_1 + \beta_2 t_2) = 2\pi, \]

or

\[ n\alpha_2 + m\beta_2 = 0, \]
\[ (2m + n)\alpha_2 - (2n + m)\beta_2 = d_R, \]

and

\[ \alpha_2 = \frac{m}{2(n^2 + m^2 + nm)}d_R = m\frac{d_R a^2}{2L^2} = \frac{m}{N}, \]
\[ \beta_2 = -\frac{n}{N}, \]
\[ K_2 = \frac{1}{N}(mb_1 - nb_2). \] (4.19)

The vectors \( \mathbf{K}_1 \) labels discrete points while \( \mathbf{K}_2 \) describes a one-dimensional Brillouin zone. The Brillouin zone for the (4,2) CNT is shown in Fig. 4.2. There are \( N \mathbf{K}_1 \) values,

Figure 4.2: Brillouin zone of SWCNT (corresponding to \( C_h = (4,2) \) case).
\( \mu \mathbf{K}_1 \) \((\mu = 0, N - 1)\). Each one-dimensional first Brillouin zone (FBZ) \(WW'\) along \( \mathbf{K}_2 \) is of length \(2\pi/T\). Since the \( \mathbf{K}_2 \) point separation is inversely proportional to the crystal length \(L_t\), there are discrete points with spacing \(2\pi/L_t\) if \(L_t\) is finite.

The lattice vectors of the reciprocal lattice are:

\[
\mathbf{K}_1 = \frac{1}{N} (-t_2 \mathbf{b}_1 + t_1 \mathbf{b}_2) ; \mathbf{K}_2 = \frac{1}{N} (n_2 \mathbf{b}_1 - n_1 \mathbf{b}_2)
\]

(4.20)

where \( \mathbf{b}_1 \) and \( \mathbf{b}_2 \) are the reciprocal lattice vectors of the graphene sheet. The vectors \( \mathbf{K}_1 \) and \( \mathbf{K}_2 \) for a \((4,2)\) NT are shown in Fig. 4.2. It turns out that \( \mathbf{K}_1 \) and \( \mathbf{K}_2 \) are parallel to the chiral \( \mathbf{C}_h \) and translational \( \mathbf{T} \) vectors, respectively. The Brillouin zone of a CNT corresponds to the line segments \(WW'\) along the \( \mathbf{K}_2 \) direction whose length is equal to \(2\pi/T\). The discrete segments along \( \mathbf{K}_1 \) arise from the periodic boundary conditions on \( \mathbf{C}_h \). Since there are \( N \) lattice points along \( \mathbf{C}_h \), there are \( N \) \( WW' \) segments, each one of them specified by a vector \( \mu \mathbf{K}_1 \) where \((\mu = 0, 1, 2, 3, ..., N - 1)\). Physically, \( \mu \) gives the number of nodes that wave function has in the circumferential direction. In the \((4,2)\) case, \( N = 28 \) and the length of \( WW' \) is \(2\pi/21a\).

### 4.6 Electronic Structure of SWCNT

#### 4.6.1 Energy dispersion of a general CNT and Hamada’s rule

Neglecting the curvature effects, the energy dispersion relation \( E(\mathbf{k}) \) of CNT’s can be found from the one of graphene. Recall that CNT’s are constructed by rolling up a graphene sheet, thus, as a first approximation, we obtain \( E(\mathbf{k}) \) by calculating graphene’s
dispersion relation [see Eq. (3.9)] in the CNT Brilloiun zone, that is,

\[ E_\mu(k) = E_{\text{graph}} \left( \mu K_1 + k \frac{K_2}{K_2} \right), \left( -\frac{\pi}{T} < k < \frac{\pi}{T} \right), \]  

(4.21)

where \( \mu = 0, 1, 2, ..., N - 1 \) and \( K_2 = |K_2| \). The index \( \mu \) is the band index, and each of its values correspond to a cross sectional area of the band structure of graphene. Literally, the vectors \( \mu K_1 + k \frac{K_2}{K_2} \) cut the energy surface in Fig. 3.3(a) into \( N \) parallel slices. If any of these vectors turns out to pass through graphene’s \( K \) point, then the nanotube (NT) will have a zero gap, and if it does not, then there will be a gap. Calculations performed by Dresselhaus et al. [57], show a finite density of states at the Fermi energy for the zero-gap NT’s, thus, they are metals. All remaining tubes are semiconductors. In Fig. 4.3, the solid and the open circles show which NT’s are metals and which are semiconductors, respectively. Most of them (\( \approx 2/3 \)) exhibit semiconducting behaviour.

Figure 4.3: Map of the electronic behaviour of CNT’s. Metallic and semiconducting tubes correspond to solid and open circles, respectively. After Saito et al. [15]

Now we ask the question: given a NT with chiral vector \((n, m)\), is it a metal or a
semiconductor? The answer to this question was given by Hamada et al. [58] and Saito et al. [59]. They found that if \((n - m)\) is a multiple of 3, the NT is a metal, otherwise, it is a semiconductor. Since this is one of the most relevant results in the electronic properties of CNT’s, we will reproduce its derivation following Ref. [52].

The wave vectors \(k\) corresponding to the electronic states in a CNT are given by the condition

\[
k \cdot C_h = 2\pi\mu. \tag{4.22}
\]

If a nanotube is a metal then, for one of the wave vectors, it holds that \(k = K\). The \(K\) point in graphene is located at \((1/3)(b_1 - b_2)\), and the scalar product \(K \cdot C_h = (2\pi/3)(n - m)\). Substitution of this result in Eq. (4.22) yields,

\[
n - m = 3\mu. \tag{4.23}
\]

Since \(\mu\) is an integer, then \(n - m\) must be a multiple of 3. Hereafter, we refer to Eq. (4.23) as Hamada’s rule. For CNT’s with chiral vector \(C_h = (n, n)\), \(n - n = 0\), therefore, all armchair tubes are metals. For CNT’s with chiral vector \(C_h = (n, 0)\), \(n = 3\mu\), hence, zig-zag tubes are metals if \(n\) is a multiple of 3, otherwise, they are semiconductors. Notice that this is the case in the map shown in Fig. 4.3.

4.6.2 Energy dispersion relation of armchair nanotubes

The translational \(T\) and reciprocal \(K_2\) vectors of an armchair CNT are parallel to the \(y\) and \(k_y\) axes, as it is shown in Fig. 4.4(a). On the other hand, the chiral \(C_h\) and reciprocal \(K_1\) vectors (not showed in the figure for the sake of clarity) are parallel to the \(x\) and \(k_x\) axes. Periodic boundary conditions along the circumferential direction, \(i.e.,\)
the $x$ direction, give the allowed wave vectors in the Brillouin zone,

$$k = k_{x,q} \hat{k}_x + k \hat{k}_y$$  \hspace{1cm} (4.24)

where

$$k_{x,q} = \frac{2\pi q}{\sqrt{3}na} \quad (q = 1, 2, ..., N = 2n) .$$  \hspace{1cm} (4.25)

We showed for armchair tubes that, $T = a$ thus, the length of the Brillouin zone is $2\pi/a$. According to Eq. (4.21), we substitute the armchair $k$ vector given in Eq. (4.24), in Eq. (3.9) in order to obtain the armchair NT energy dispersion relation. Hence,

$$E^A_q(k) = \pm \gamma_0 \left\{ 1 + 4 \cos \frac{q \pi}{n} \cos \frac{ka}{2} + 4 \cos^2 \frac{ka}{2} \right\}^{1/2} ,$$

$$\left( -\frac{\pi}{a} < k < \frac{\pi}{a} \right), \quad (q = 1, 2, ..., N = 2n) .$$  \hspace{1cm} (4.26)

The energy bands of a (4, 4) CNT obtained from Eqn (4.26) are shown in Fig. 4.5(a). Carbon nanotube bands are symmetric with respect to the $\Gamma$ point thus, they are plotted only along the $X\Gamma$ direction (the $X$ point corresponds to the edge of the first Brillouin zone). Notice that we have used the zone-folding scheme in order to plot this figure. The Fermi level $E_F$, is at zero and, as mentioned before, the DOS is finite at this point. Therefore, the (4, 4) armchair CNT is a metal, which is in agreement with Hamada’s rule (4.23). The only two energy eigenvalues at the $X$ point are largely degenerate. This result can be found analytically if we evaluate $E^A_q(k)$ at $X$ ($k = \pi/a$),

$$E^A_q(X) = \pm \gamma_0 .$$
Particularly, each of the two eigenvalues of the (4, 4) NT are eight-fold degenerate. For a general \((n, n)\) NT, they are \(2n\) degenerate.

![Diagram](image)

Figure 4.4: Translational and reciprocal vectors of (a) armchair and (b) zig-zag CNT’s.

The crossing of the lowest conduction and highest valence bands in Fig. 4.5(a) occurs at \(k = 2\pi/3a\). This holds true not only for the (4, 4) tube but for any armchair CNT. The band gap closes if we make \(q = n\) in Eq. (4.26), \(E_q^A(k)\) reduces to

\[
1 - 4 \cos \frac{ka}{2} + 4 \cos^2 \frac{ka}{2} = (2 \cos \frac{ka}{2} - 1)^2 = 0,
\]

\[\Rightarrow k = \frac{2\pi}{3a}\]

The direction of the \(K_1\) vector is always the same for all armchair tubes, since it is parallel to \(C_h\). For any \((n, n)\) tube, there is always a segment \(WW'\) of its Brillouin zone.
that passes through the $K$ point of graphene exactly at $k = 2\pi/3a$.

Figure 4.5: Energy dispersion relations for (a) (4, 4) armchair, (b) (8, 0) and (c) (12, 0) zig-zag CNT’s.

### 4.6.3 Energy dispersion relation of zig zag nanotubes

In zig-zag NT’s, the translational $T$ and reciprocal $K_2$ vectors are, respectively, parallel to the $x$ and $k_x$ axes, as it is shown in Fig. 4.4. The former has magnitude $T = \sqrt{3}a$ and the Brillouin zone has length $2\pi/\sqrt{3}a$. The corresponding chiral $C_h$ and reciprocal $K_1$ vectors are along the $-y$ and $-k_y$ directions. Once periodic boundary conditions are applied on the $k$ along the chiral direction, one finds that the allow wave vectors in zig-zag tubes are,

$$k = k\hat{k}_x - k_y q\hat{k}_y$$

(4.27)
where
\[ k_{y,q} = \frac{2\pi q}{na} \quad (q = 1, 2, ..., N = 2n). \] (4.28)

As we did with armchair CNT’s, the energy bands of zig-zag tubes are given by substituting Eq. (4.27) in Eq. (3.9). The dispersion is then,

\[ E^Z_q(k) = \pm \gamma_0 \left( 1 + 4 \cos \frac{\sqrt{3}ka}{2} \cos \frac{q\pi}{n} + 4 \cos^2 \frac{q\pi}{n} \right)^{1/2}, \quad \left( -\frac{\pi}{\sqrt{3}a} < k < \frac{\pi}{\sqrt{3}a} \right), \quad (q = 1, ..., 2n). \] (4.29)

Figure 4.5(b),(c) show the energy bands versus the wave vector \( k \) for the (8,0) and (12,0) zig-zag tubes. While the former NT has a non-zero gap, the latter one does not. According to Hamada’s rule, this has to be the case since 8 is not a multiple of 3 whereas 12 is. For metallic zig-zag CNT’s, i.e., when \( n \) is a multiple of 3, the crossing between the conduction and valence bands is located at \( k = 0 \) (\( \Gamma \)). Similarly to \( (n, n) \) armchair NT’s, this occurs because for all \( (n, 0) \) zig-zag tubes, there is always one \( WW' \) segment of the Brillouin zone, that cuts the \( K \) point of graphene at \( k = 0 \). Assume \( n \) even. Setting \( q = n/2 \) in Eq. (4.29) gives,

\[ E^Z_{q=n/2}(k) = \pm \gamma_0. \]

Therefore, dispersionless bands occur for \( n \) even.

As a final comment, all the results derived previously, hold for CNT with large diameters where curvature effects can be neglected. For small nanotubes, curvature induces a coupling between the \( \pi \) and \( \sigma \) states [15, 52]. This coupling (also called
hybridization) does not open a gap in armchair tubes, hence, they are still metals. Nonetheless, it has been shown that for metallic zig-zag CNT’s, there is a gap opening of the order of the meV [15].

4.7 The Band Gap of Semiconducting CNTs

In the case of CNTs that are semiconductors, we focus our attention on the highest filled and lowest empty bands. The highest occupied valence band and lowest conduction band correspond to

\[
\mu = \frac{1}{3}(N + 1), \quad \mu = \frac{1}{3}(2N - 1) \quad \text{if} \quad d = 3j + 1 \\
\mu = \frac{1}{3}(N - 1), \quad \mu = \frac{1}{3}(2N + 1) \quad \text{if} \quad d = 3j - 1
\]

(4.31)

where \( j \) is an integer. The energy band gap \( E_g \) is given by these values of \( \mu \),

\[
E_g = 2\gamma_0 \text{Min} \omega (kK_2 + \frac{1}{3}(N \pm 1))K_1
\]

(4.32)

where \( \pm \) and \( \text{Min} \omega \) correspond to \( d = j \pm 1 \) and to the minimum value of \( \omega \) with respect to \( k \). Once one minimizes \( w \), one finds that [15]

\[
E_g \approx \frac{|\gamma_0|a_c-c}{L}.
\]

(4.33)

Equation (4.33) shows that the band gap of semiconducting CNTs is dependent only upon their diameters and not upon their chiral angle. This result does not hold for nanotubes with small diamters where curvature has a significant role [57].
Chapter 5

Si-based Nanomaterials

In the present chapter, we derive a new TB theory of novel Si based nanomaterials: silicene, Si (111) and single-walled Si nanotubes (SiNT’s) and study the electronic properties of them. Our results are compared to (a) its C-based counterparts and (b) to previous first-principles calculations performed by Yang et al. [12].

A review of the most relevant works that can be found in the literature of these nanomaterials is provided as well.

5.1 Review of the Electronic and Structural Properties of SiNT’s

Besides CNT’s, there have been predictions and experimental synthesis of other types of tubes such as GaN, BN, AlN, and Si [7, 8, 9, 10, 11]. Different chemical composition of these materials modify the nanotube electronic and structural properties. For example, armchair CNT’s are metals, while BN nanotubes are semiconductors [15]. In this section,
we focus our attention on SiNT’s.

Theoretical studies have predicted that the physical properties of SiNT’s stongly depend on the hybridization of the starting sheet. If we start from a Si graphene-like sheet, which has \(sp^2\) hybridization, and roll it up to form a nanotube, the electronic properties of the resulting tubes would be similar to the CNT ones [11, 12]. On the other hand, if we start with a sheet that shows \(sp^3\) hybridization, like SiH, the resulting nanotubes are all semiconductors [13]. Nevertheless, it is not completely clear which hybridization(s) are actually present in Si-NT’s. Using ab-initio calculations, most groups agree that, among all the possible ones mentioned above, the \(sp^2\) hybridization is the least favorable and, in contrast, the \(sp^3\) hybridization is one of the most favorable because of stability reasons [11, 12, 13, 14]. Fagan et al. [11] and Zhang et al. [13] argued that if Si atoms were to have \(sp^2\) configuration, as in silicene, the cohesive energy per atom in the sheet would have to be greater than its corresponding energy in Si bulk. This implies that the existence of these structures is doubtful, as Seifert et al. [14] stated. This is not, however, the end of the story.

Even though, from the theoretical point of view, there is substantial evidence of SiNT’s having gear-like strutures, experiments cannot completely disregard the presence of \(sp^2\) hybridization [60] due to its inertness to external contaminations.

Since the previous studies are of relevance for the present work, let us now review the most important results of them in more detail.

- The work by Fagan et al. [11] was the first attempt to examine the electronic and mechanical properties of SiNT’s. In order to calculate them, they used an ab-

\[\text{Hereafter we will refer to the sheets showing } sp^2 \text{ and } sp^3 \text{ hybridization, as silicene and Si (111) sheets, respectively. In addition, its corresponding nanotubes will be refered as Si h-NT’s and g-NT’s. The Si (111) sheet corresponds to one Si layer of bulk Si in the [111] direction.}\]
initio technique, namely, density functional theory (DFT). They constructed their nanotubes by wrapping silicene, and, as expected, they concluded that SiNT’s have similar electronic properties as CNT’s, i.e., they follow Hamada’s rule.

As far as mechanic properties are concerned, the authors report cohesive energies of 5.42 eV/atom and 5.46 eV/atom in the silicene sheet and in the nanotubes, respectively. Both energies are greater than the corresponding one in Si bulk (4.63 eV). According to the authors, this explains why it is difficult to produce a Si graphitic sheet. However, they point out that the bending energy (the energy it takes to bend silicene and converted into a nanotube) is $5.46 - 5.42 = 0.04$ eV/atom, which is close to 0.05 eV/atom needed for CNT’s.

• In a later publication, Seifert et al. [14] studied the same properties that Fagan et al. [11] did, but this time using a different model. The authors performed their simulations using a nonorthogonal density-functional tight-binding scheme (DFTB). They emphasized that it is unlikely that Si h-NT’s exist because they are not stable. They argued that other C-based structures such as graphene, CNT’s and fullerenes are stable because C forms strong $\pi$ bonds; silicon, on the other hand, does not.

Their planar sheets are made of either negatively charged Si atoms (Si$^-$) or hydrogen saturated Si atoms (SiH). The purpose of charging or saturating the atoms is to avoid dangling bonds in the sheet. Both Si$^-$ and SiH sheets are semiconductors with a gap of 2.49 eV and 2.50 eV, respectively. The authors labeled the nanotubes made from the SiH sheet SiH-sf and SiH-io according to the orientation of the H atoms. The suffix -sf refers to H atoms bound outside the nanotube
surface, and -io to alternating inside/out (c.f. Fig. 2 in Ref. [14]). Obviously, the nanotubes formed from these sheets, Si\(^{-}\), SiH-sf and Si-io, are all semiconductors. They consider armchair and zig zag tubes, only. The gap-size of these nanotubes shows an interesting behaviour: while the gap of a SiH-sf nanotube decreases as its diameter increases, the gap of Si\(^{-}\) and SiH-io NT’s increases until they reach their corresponding sheet value.

Seifert et al. [14] also found that a flat SiH-sf sheet is not stable, nevertheless, it can easily bend and form small nanotubes. Once the SiH-sf NT’s are formed, only the ones with small diameter are stable since, as their diameter increases, they become unstable. This occurs because when the diameter increases, curvature decreases, and the Si-Si-H bond angle approaches 90\(^{\circ}\), which increases the repulsion between electrons.

On the other hand, SiH-io nanotubes are stable. The strain energy decreases as the diameter increases. Unlike SiH-sf nanotubes, the angle in the Si-Si-H bond approaches 109.5\(^{\circ}\) when the nanotube diameter increases. The angle of 109.5\(^{\circ}\) is the ideal angle for \(sp^3\) hybridization.

• The most in-depth analysis of the SiNT structure has been done Zhang et al. [13]. In this work, the authors investigated other possible structures of SiNTs via Density-Functional Tight-binding Molecular Dynamics simulations (DFTB-MD) and ab-initio calculations [13]. Their results show that SiNT’s can adopt a variety of structures: CNT-like, gear-like, string-bean-like tubes, severe distortion tube, and collapsed tube. The main difference between them is their degree of distortion, being the CNT-like tube the less distorted and the collapsed one the most
distorted one. Among all these types of nanotubes, however, the authors found that the most predominant is the gear-like structure, even though the string-bean-like configuration was more stable. The reason for this to occur is not clear.

As far as the Si g-NT electronic properties are concerned, Zhang et al. [13] found that all armchair tubes are semiconductors whose band gap decreases as the tube diameter increases. For zig zag tubes, there was no clear trend, although, for the few nanotubes considered in their work, they noticed that they follow Hamada’s rule (see Chapter two)\(^2\).

- A few months after Zhang’s publication, Yang et al. [12] achieved similar conclusions about the structural properties of Si g-NT’s, that is, the gearlike geometry is more stable than the hexagonal one. Their calculations were performed using the Vienna Ab initio Simulation Package [12]. This is the only report where the band structure of the starting sheet, \(i.e., \) Si (111), is shown. They considered the energy bands of both Si h-NT’s and g-NT’s. For the Si h-NT’s, they obtained the same results as in CNT’s. However, they found discrepancies with their CNT counterparts. All armchair Si g-NT’s considered in their work are semiconductors with gaps that are inversely propotional to the tube diameter. Zig zag Si g-NT’s are metals if their diameters are small, otherwise, they are semiconductors. The authors attribute the metallicity of the former ones to the \(\sigma - \pi\) coupling.

Yang’s work is of particular importance for the present work since our tight-binding calculations will be compared to the ab-initio ones [12]. We will see that there is good agreement in the band structure of Si (111) and Si h-NT’s, however, our Si

\(^2\)Zhang et al.’s [13] calculations include curvature effects on the band structures, therefore, their zig zag tubes that follow Hamada’s rule have a small gap of the order of the meV.
g-NT band structures differ from theirs.

- So far, the most relevant experimental work on Si NT’s was done by De Crescenzi et al. [60]. The authors reported the synthesis of, presumably, SiNT’s, whose diameters were in the range of $2 - 35$ nm [60, 61]. Furthermore, their findings suggest that SiNT’s posseses $sp^3$ hybridization, although, $sp^2$ hybridization cannot be excluded since their samples were inert to contaminations such as carbon and oxygen.

Regarding the electronic properties of these NT’s, they found that armchair tubes are semiconductors, while chiral tubes seem to be metals. As Perepichka et al. [61] pointed out in his review article, this is surprising since armchair CNT’s are metals, and most chiral tubes are semiconductors.

5.2 A Tight-binding Theory of Si (111)

We now present a new theory of the band structure of a single Si sheet. This theory applies to both the flat Si sheet and the Si (111) layer.

The reason a unifying theory is possible is because the lattice structure of a Si (111) sheet is the same as for silicene except that one set of atoms (e.g., B) is vertically displaced (e.g., down) from the A-plane due to the $sp^3$ bonding. Figure 5.1(a) is a two-dimensional representation of the lattice. The dark atoms are in the $xy$-plane and they correspond to the A atoms; the light ones, on the other hand, correspond to the B atoms. The $z$ axis points towards the reader. The basis vectors of the lattice are $a_1$ and $a_2$ with magnitude $a$ where $a$ is the lattice constant. If we label $d$ the Si-Si bond distance, then $a = d/\sqrt{2}$. The shaded area corresponds to the two-dimensional unit cell...
of Si (111). Notice that the basis vectors and the unit cell of Si (111) have the same form as in the honeycomb lattice of graphene [see Chapter two]. Due to this similarities with graphene, the Brillouin zone of the Si (111) lattice has the same shape as the graphene one shown if Fig. 4.2.

We will see that the choice of this coordinate system facilitates the transition from the Si (111) sheet to the silicene one.

Figure 5.1: Lattice of Si(111). (a) Two-dimensional representation of a Si sheet in the (111) direction where the atoms labeled as A are all in the $xy$ plane ($z_A = 0$) and all the B atoms are located out of the plane $[z = -a/(2\sqrt{6})]$. Notice that the $z$ axis points towards the reader. The vectors $a_1, a_2$ are the two-dimensional unit vectors and the shaded area is the Si (111) unit cell and . (b) First nearest-neighbors of Si(111)

In order to compute the band structure of Si (111), we use a 1NN $sp^3s^*$ and a 2NN $sp^3$ orthogonal tight-binding models. For these two models, we derive their respective $10 \times 10$ and $8 \times 8$ Hamiltonians. These choices were dictated by the availability of good Si parameters which we discussed in Chapter two. Like silicene and graphene, the wavevector $\mathbf{k}$ in the Hamiltonian is two dimensional, however, their $g_j(\mathbf{k})$ functions differ due the $\sigma - \pi$ coupling. Furthermore, we use the TCA in order to approximate the TB parameters. We used Eq. (2.27) in Chapter one to derive the TCA parameters
from the eight Vogl et al. [29] and Grosso et al. [28] bulk parameters\(^3\). The bulk and TCA parameter sets are given in Tables 2.1, and 5.1, respectively. Recall from Chapter one that Vogl’s \(sp^3s^*\) parameters reproduce fairly well the top valence and the lowest conduction bands of bulk Si, but not the effective masses of the conduction one. Grosso’s parameters accomplish, in a satisfactory manner, good bulk bands and most effective masses, as well.

Using Eq. (2.30), we find the matrix elements of the Hamiltonian under the 2NN approximation. The position vectors of the 1NN and 2NN for Si (111) are:

- **First nearest-neighbors**

\[
\begin{align*}
\delta_1^{(1)} &= \frac{a}{\sqrt{3}} \hat{x} + 0 \hat{y} - \frac{a}{2\sqrt{6}} \hat{z}, \\
\delta_2^{(1)} &= -\frac{a}{2\sqrt{3}} \hat{x} + \frac{a}{2} \hat{y} - \frac{1}{2\sqrt{6}} \hat{z}, \\
\delta_3^{(1)} &= -\frac{a}{2\sqrt{3}} \hat{x} - \frac{a}{2} \hat{y} - \frac{1}{2\sqrt{6}} \hat{z}.
\end{align*}
\]  

(5.1)

- **Second nearest-neighbors**

\[
\begin{align*}
\delta_1^{(2)} &= 0 \hat{x} + \hat{y} + 0 \hat{z}, \\
\delta_2^{(2)} &= 0 \hat{x} - \hat{y} + 0 \hat{z}, \\
\delta_3^{(2)} &= \frac{a\sqrt{3}}{2} \hat{x} - \frac{a}{2} \hat{y} + 0 \hat{z}, \\
\delta_4^{(2)} &= -\frac{a\sqrt{3}}{2} \hat{x} + \frac{a}{2} \hat{y} + 0 \hat{z}, \\
\delta_5^{(2)} &= \frac{a\sqrt{3}}{2} \hat{x} + \frac{a}{2} \hat{y} + 0 \hat{z}.
\end{align*}
\]  

(5.2)

---

\(^3\)The actual number of Grosso’s TB parameters is nine since they included SO interaction. We neglect this interaction since it is known to be small (\(\sim\) meV).
\[ \delta^{(2)}_6 = -\frac{a\sqrt{3}}{2} \mathbf{x} - \frac{a}{2} \mathbf{y} + 0 \mathbf{z}. \]

For simplicity, Fig. 5.1(b) only shows the position vectors of the 1NN. Notice that the \( x \)- and \( y \)-components of the 1NN in Si(111) correspond to the ones of graphene. The non-zero \( z \)-components are the vertical displacements of the \( B \) atoms in the Si(111) sheet. In other words, the choice of the coordinate system facilitates the transition from Si (111) and silicene by making the \( z \) component of the position vectors in Eq. (5.1) equal to zero [compare to Eq. (3.4)]. The 2NN coincide for both sheets.

Using Eq. (2.30), the direct cosines would be,

\[ l_1^{(2)} = l_2^{(2)} = 0, \]
\[ l_3^{(2)} = -l_4^{(2)} = l_5^{(2)} = -l_6^{(2)} = \frac{\sqrt{3}}{2}, \]
\[ m_1^{(2)} = -m_2^{(2)} = 1, \quad m_3^{(2)} = -m_4^{(2)} = -m_5^{(2)} = m_6^{(2)} = -\frac{1}{2}; \]
\[ n_1^{(2)} = n_2^{(2)} = n_3^{(2)} = n_4^{(2)} = n_5^{(2)} = n_6^{(2)} = 0. \]  

(5.3)

The matrix elements of the Hamiltonian are given according to Eqs. (2.28) and (2.30),

\[ (s/s)_{AA} = (s/s)_{BB}^* = E_s + (ss\sigma)_{2}^{AA} g_{13}(k) \]
\[ (s/x)_{AA} = -(s/x)_{BB}^* = (sp\sigma)_{2}^{AA} g_{14}(k) \]
\[ (s/y)_{AA} = -(s/y)_{BB}^* = (sp\sigma)_{2}^{AA} g_{15}(k) \]
\[ (s/z)_{AA} = -(s/y)_{BB}^* = 0 \]
\[ (x/x)_{AA} = (x/x)_{BB}^* = E_p + (pp\sigma)_{2}^{AA} g_{16}(k) + (pp\pi)_{2}^{AA} g_{17}(k) \]
\[ (x/y)_{AA} = (x/y)_{BB}^* = [(pp\sigma)_{2}^{AA} - (pp\pi)_{2}^{AA}] g_{18}(k) \]

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\[(x/z)_{AA} = (x/z)_{BB} = 0\]
\[(y/y)_{AA} = (y/y)_{BB} = E_p + (pp\sigma)^{AA}_1 g_{19}(k) + (pp\pi)^{AA}_2 g_{20}(k)\]
\[(y/z)_{AA} = (y/z)_{BB} = 0\]
\[(z/z)_{AA} = (z/z)_{BB} = E_p + (pp\pi)^{AA}_2 g_{25}(k)\]
\[(x/x)_{AB} = (pp\sigma)^{AB}_1 g_3(k) + (pp\pi)^{AB}_1 g_4(k)\]
\[(y/y)_{AB} = (pp\sigma)^{AB}_1 g_6(k) + (pp\pi)^{AB}_1 g_4(k)\]
\[(z/z)_{AB} = (pp\pi)^{AB}_1 g_{11}(k) + (pp\pi)^{AB}_1 g_{12}(k)\]
\[(s/x)_{AB} = - (x/s)_{AB} = (sp\sigma)^{AB}_1 g_1(k)\]
\[(s/y)_{AB} = - (y/s)_{AB} = (sp\pi)^{AB}_1 g_2(k)\]
\[(s/z)_{AB} = - (z/s)_{AB} = (sp\sigma)^{AB}_1 g_8(k)\]
\[(x/y)_{AB} = (y/x)_{AB} = \left[ (pp\sigma)^{AB}_1 - (pp\pi)^{AB}_1 \right] g_5(k)\]
\[(x/z)_{AB} = (z/x)_{AB} = \left[ (pp\sigma)^{AB}_1 - (pp\pi)^{AB}_1 \right] g_9(k)\]
\[(y/z)_{AB} = (z/y)_{AB} = \left[ (pp\sigma)^{AB}_1 - (pp\pi)^{AB}_1 \right] g_{10}(k)\]
\[(s^*/s^*)_AA = (s^*/s^*)_BB = E_{s^*} + (s^*s^*\sigma)^{AA}_2 g_{13}(k)\]
\[(s^*/x)_{AA} = - (s^*/x)_{BB} = (s^*p\sigma)^{AA}_2 g_{14}(k)\]
\[(s^*/y)_{AA} = - (s^*/y)_{BB} = (s^*p\sigma)^{AA}_2 g_{15}(k)\]
\[(s^*/z)_{AA} = - (s^*/y)_{BB} = 0\]
\[(s/s^*)_{AA} = (s/s^*)_{BB} = (ss^*\sigma)^{AA}_2 g_{13}(k)\]
\[(s^*/x)_{AB} = - (x/s^*)_{AB} = (s^*p\sigma)^{AB}_1 g_1(k)\]
\[(s^*/y)_{AB} = - (y/s^*)_{AB} = (s^*p\sigma)^{AB}_1 g_2(k)\]
\[(s^*/z)_{AB} = - (z/s^*)_{AB} = (s^*p\sigma)^{AB}_1 g_8(k)\]
where all the \( g_j(\mathbf{k}) \) functions are given in Eq (B.2). The Hamiltonian, then, has the form

\[
H(\mathbf{k}) = \begin{bmatrix}
h_{AA} & h_{AB} \\
h_{BA} & h_{BB}
\end{bmatrix}
\]  \hspace{1cm} (5.5)

where

\[
h_{AA} = \begin{bmatrix}
(s/s)_{AA} & (s/x)_{AA} & (s/y)_{AA} & 0 & (s/s^*)_{AA} \\
(x/x)_{AA} & (x/y)_{AA} & 0 & (x/s^*)_{AA} \\
(y/y)_{AA} & 0 & (y/s^*)_{AA} \\
\uparrow & (z/z)_{AA} & 0 & (s^*/s^*)_{AA}
\end{bmatrix}, \hspace{1cm} (5.6)
\]

\[
h_{AB} = \begin{bmatrix}
(s/s)_{AB} & (s/x)_{AB} & (s/y)_{AB} & (s/z)_{AB} & (s/s^*)_{AB} \\
(x/s)_{AB} & (x/x)_{AB} & (x/y)_{AB} & (x/z)_{AB} & (x/s^*)_{AB} \\
(y/s)_{AB} & (y/x)_{AB} & (y/y)_{AB} & (y/z)_{AB} & (y/s^*)_{AB} \\
(z/s)_{AB} & (z/x)_{AB} & (z/y)_{AB} & (z/z)_{AB} & (z/s^*)_{AB} \\
(s^*/s)_{AB} & (s^*/x)_{AB} & (s^*/y)_{AB} & (s^*/z)_{ac} & (s^*/s^*)_{AB}
\end{bmatrix}, \hspace{1cm} (5.7)
\]

where the matrix elements correspond to the previously given in Eq. (5.4). The remain-
ing blocks are given by,

\[
h_{BB} = \begin{pmatrix}
(s/s)_{AA}^* & -(s/x)_{AA}^* & -(s/y)_{AA}^* & 0 & (s/s)_{AA}^*

(x/x)_{AA}^* & (x/y)_{AA}^* & 0 & (x/s)_{AA}^*

(y/y)_{AA}^* & 0 & (y/s)_{AA}^*

(z/z)_{AA}^* & (z/s)_{AA}^* & \ast

(s^*/s)_{AA}^*
\end{pmatrix}, \quad (5.8)
\]

and \( h_{BA} = [h_{AB}]^\dagger \). In these equations, \( h_{AA} \) and \( h_{AB} \) correspond to the interaction between \( A - A \) and \( A - B \) lattice points, respectively.

The \( sp^3 \) Hamiltonian at the \( \Gamma \) point is given Eq. (5.9). We find expressions for some of the energies at the point in question\(^4\),

\[
E_{p^+}(\Gamma) = E_p + 3[(pp\sigma)_{2}^{AA} + (pp\pi)_{2}^{AA}] + \frac{1}{3}[4(pp\sigma)_{1}^{AB} + 5(pp\pi)_{1}^{AB}], \quad (2.f.d)
\]

\[
E_{p^-}(\Gamma) = E_p + 3[(pp\sigma)_{2}^{AA} + (pp\pi)_{2}^{AA}] - \frac{1}{3}[4(pp\sigma)_{1}^{AB} + 5(pp\pi)_{1}^{AB}], \quad (2.f.d)
\]

Recall that 2.f.d stands for two-fold degenerate.

In the next section, we explain how this formalism developed for Si (111) can be transferred to silicene.

### 5.3 \( \pi \) and \( \sigma \) Bands in Silicene

The \( \pi \) and \( \sigma \) bands can be obtained from the previous Hamiltonian by making the \( z \)-component of the 1NN equal to zero and substituting the appropriate direct cosines of

\(^4\) Actually, it is possible to find analytic formulae for all energies at the \( \Gamma \) point, though, we chose to reproduce the simplest ones only, since the remaining ones are very elaborate.
\[
\left[
\begin{array}{cccccccc}
  z_A & (z/z)_A^\Gamma & z_B & (z/z)_B^\Gamma & s_A & s_B & x_A & x_B \\
  z_A & (z/z)_A^\Gamma & z_B & (z/z)_B^\Gamma & s_A & s_B & x_A & x_B \\
  z_B & (z/z)_A^\Gamma & s_A & (z/z)_A^\Gamma & s_B & (z/z)_B^\Gamma & x_A & x_B \\
  z_B & (z/z)_A^\Gamma & s_A & (z/z)_A^\Gamma & s_B & (z/z)_B^\Gamma & x_A & x_B \\
  s_A & 0 & (z/s)_A^\Gamma & s_A & (z/s)_A^\Gamma & s_B & (z/s)_B^\Gamma & x_A \\
  s_A & 0 & (z/s)_A^\Gamma & s_A & (z/s)_A^\Gamma & s_B & (z/s)_B^\Gamma & x_A \\
  s_B & (z/s)_B^\Gamma & 0 & (z/s)_B^\Gamma & s_A & (z/s)_A^\Gamma & x_A & x_B \\
  s_B & (z/s)_B^\Gamma & 0 & (z/s)_B^\Gamma & s_A & (z/s)_A^\Gamma & x_A & x_B \\
  x_A & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
  x_A & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
  y_A & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
  y_B & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\end{array}
\right].
\]

(5.9)

\[
(z/z)_A^\Gamma = E_p + 6 (pp\pi)_2^{AA}
\]

\[
(z/z)_B^\Gamma = \frac{1}{3} [(pp\sigma)_1^{AB} + 8 (pp\pi)_1^{AB}]
\]

\[
(z/s)_A^\Gamma = (sp\sigma)_1^{AB}
\]

\[
(s/s)_A^\Gamma = E_s + 6 (ss\sigma)_2^{AA}
\]

\[
(s/s)_B^\Gamma = 3 (ss\sigma)_1^{AB}
\]

\[
(x/x)_A^\Gamma = E_p + 3 [(pp\sigma)_2^{AA} + (pp\pi)_2^{AA}]
\]

\[
(x/x)_B^\Gamma = \frac{1}{3} [4 (pp\sigma)_1^{AB} + 5 (pp\pi)_1^{AB}]
\]
the 1NN position vectors in the $g_j(k)$ functions given in Eq. (2.30). Notice that now the 1NN match to the 1NN of graphene. We point out that the 2NN are the same for both silicene and Si (111) since both are in the sheet plane.

As a result, the $\pi$ and $\sigma$ bands are decoupled, as in graphene. This allow us to consider the bands independently.

For the $\pi$ bands, we recover the $2 \times 2$ Hamiltonian but now, including 2NN interactions,

$$H = \begin{pmatrix} E_p + (pp\pi)^{AA}_{2} g_{25}(k) & \gamma_0 g_{12}(k) \\ \gamma_0 g_{12}^*(k) & E_p + (pp\pi)^{AA}_{2} g_{25}(k) \end{pmatrix}. \quad (5.10)$$

The energy dispersion relation for silicene is found by solving the secular equation $|H - E(k)S| = 0$, (recall that $S$ equals the identity matrix in the orthogonal model).

$$E_{\text{sil}}(k) = E_p + (pp\pi)^{AA}_{2} g_{25}(k) \pm (pp\pi)^{AB}_{1} w(k). \quad (5.11)$$

where $w(k) \equiv \sqrt{|g_{12}(k)|^2}$. The energy dispersion versus the wave vector is shown in Figs. 5.2(c) and 5.2(f). Notice that if we make the 2NN contribution equal to zero, i.e., $(pp\pi)^{AA}_{2} = 0$, we recover graphene’s energy dispersion [see Eq. (3.9)].

For the $\sigma$ bands, the matrix elements of the Hamiltonian correspond to similar ones given in Eq. (5.4) for Si (111), but now the $g_j(k)$ functions correspond to the ones given in Eq. (B.1). This bands are shown in Figs. 5.2(c) and 5.2(f).

By evaluating the Hamiltonian at the $\Gamma$ point, we can obtain analytical formulae for the eigenenergies. Equation (5.12) gives the Hamiltonian at this point, including the $\pi$ sector.

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\[
\begin{pmatrix}
  z_A & zB & sA & sB & xA & xB & yA & yB \\
  (z/z)_{AA}^\Gamma & (z/z)_{AB}^\Gamma & 0 & 0 & 0 & 0 & 0 & 0 \\
  (z/z)_{AB}^\Gamma & (z/z)_{AA}^\Gamma & 0 & 0 & 0 & 0 & 0 & 0 \\
  sA & 0 & 0 & (s/s)_{AA}^\Gamma & (s/s)_{AB}^\Gamma & 0 & 0 & 0 \\
  sB & 0 & 0 & (s/s)_{AB}^\Gamma & (s/s)_{AA}^\Gamma & 0 & 0 & 0 \\
  xA & 0 & 0 & 0 & 0 & (x/x)_{AA}^\Gamma & (x/x)_{AB}^\Gamma & 0 \\
  xB & 0 & 0 & 0 & 0 & (x/x)_{AB}^\Gamma & (x/x)_{AA}^\Gamma & 0 \\
  yA & 0 & 0 & 0 & 0 & 0 & 0 & (x/x)_{AA}^\Gamma \\
  yB & 0 & 0 & 0 & 0 & 0 & 0 & (x/x)_{AB}^\Gamma \\
\end{pmatrix}.
\]

(5.12)

\[
(z/z)_{AA}^\Gamma = E_p + 6(\pi \pi)_{2}^{AA}
\]
\[
(z/z)_{AB}^\Gamma = 3(\pi \pi)_{1}^{AB}
\]
\[
(s/s)_{AA}^\Gamma = E_s + 6(\sigma \sigma)_{2}^{AA}
\]
\[
(s/s)_{AB}^\Gamma = 3(\sigma \sigma)_{1}^{AB}
\]
\[
(x/x)_{AA}^\Gamma = E_p + 3[(\sigma \sigma)_{2}^{AA} + (\pi \pi)_{2}^{AA}]
\]
\[
(x/x)_{AB}^\Gamma = \frac{3}{2}[(\pi \pi)_{1}^{AB} + (\pi \pi)_{1}^{AB}]
\]
By solving the secular equation of the 2NN Hamiltonian, we find that,

\[
E_{p\pm}(\Gamma) = E_p \pm 3(pp\pi)^{AB}_1,
\]

\[
E_{s\pm}(\Gamma) = E_s + 6(ss\sigma)^{AA}_2 \pm 3(ss\sigma)^{AB}_1,
\]

\[
E_{p\pm}(\Gamma) = E_p + 3 \left[ (pp\sigma)^{AA}_2 + (pp\pi)^{AA}_2 \right] \pm \frac{3}{2} \left[ (pp\pi)^{AB}_1 + (pp\sigma)^{AB}_1 \right], \quad \text{(2.f.d.).}
\]

We now proceed to examine all these results. In the following discussion, we compare Si (111) to bulk Si and to graphene. On the one hand, the first comparison clarifies how the bulk Si band structure arises from the Si (111) layer when one adds an infinite number of them parallel to each other. On the other hand, the second comparison shows the effect of going from \(sp^2\) to \(sp^3\) hybridization. Furthermore, we also compare silicene to graphene.

### 5.3.1 Si (111) vs bulk Si

Figure 5.2 show the band structures of bulk Si and Si (111) along the \(K\GammaMK\) directions, respectively\(^5\). The two-center parameters were computed from Vogl et al. [29] and Grosso et al. [28] and they are listed in Table 5.1.

In both cases, there are four electrons on each of the two atoms that are in the

\(^5\)In these figures, the \(K\) point corresponds to the one in graphene and not to the usual one of bulk Si shown in Fig. 2.4. In the crystallographic axes, \(\{i,j,k\}\) graphene’s \(K\) point is given by

\[
K = \frac{2\pi}{a} \left( -\frac{2}{3} i + \frac{2}{3} j \right).
\]

For the \(M\) point, we have that

\[
M = \frac{2\pi}{a} \left( -\frac{1}{3} i + \frac{2}{3} j - \frac{1}{3} k \right).
\]
Table 5.1: Silicon two-center parameters obtained from different sources. Blank spaces correspond to parameters that do not belong to the model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Grosso et al. [28]</th>
<th>Vogl et al. [29]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_s$</td>
<td>-4.0497</td>
<td>-4.2000</td>
</tr>
<tr>
<td>$E_p$</td>
<td>1.0297</td>
<td>1.7150</td>
</tr>
<tr>
<td>$E_{s^*}$</td>
<td></td>
<td>6.6850</td>
</tr>
<tr>
<td>$(ss\sigma)^{1AB}$</td>
<td>-2.0662</td>
<td>-2.0750</td>
</tr>
<tr>
<td>$(sp\sigma)^{1AB}$</td>
<td>2.0850</td>
<td>2.4808</td>
</tr>
<tr>
<td>$(pp\sigma)^{1AB}$</td>
<td>3.1837</td>
<td>2.7163</td>
</tr>
<tr>
<td>$(pp\pi)^{1AB}$</td>
<td>-0.9488</td>
<td>-0.7150</td>
</tr>
<tr>
<td>$(s^*p\sigma)^{1AB}$</td>
<td></td>
<td>2.3274</td>
</tr>
<tr>
<td>$(ss\sigma)^{AA}$</td>
<td>0.0000</td>
<td></td>
</tr>
<tr>
<td>$(sp\sigma)^{AA}$</td>
<td>0.0000</td>
<td></td>
</tr>
<tr>
<td>$(pp\sigma)^{AA}$</td>
<td>0.8900</td>
<td></td>
</tr>
<tr>
<td>$(pp\pi)^{AA}$</td>
<td>-0.3612</td>
<td></td>
</tr>
</tbody>
</table>

primitive cell and each band can be occupied by two electrons per primitive cell [62]. For bulk Si, all bands are singly degenerate in the $MK$ direction, hence, each of the valence bands will accommodate two electrons. Since there are four valence bands, all eight available electrons will fill them and will leave the conduction ones empty.

As is shown in Fig. 5.2, the energies at the $K$ point have been labelled as $K_1, K_2, ..., K_5$ for Si (111). The $K_2$ and $K_5$ energies are singly degenerate and the $K_1, K_3, K_4$ energies are two-fold degenerate. Four electrons will be at $K_1$ and two at $K_2$, thus, we still have two electrons and fourteen states available for them in the conduction band. At $K_2$ and $K_5$, only the $3p_x$ and the $3p_y$ states are coupled and all the states are coupled at the remaining energies. In other words, whereas the eigenvectors of $K_2$ and are linear combinations of $3p_x$ and $3p_y$, only, the eigenvectors of $K_1, K_3, K_4$ linear combinations of $3s, 3p_x, 3p_y, 3p_y, 3p_z$.

In the case of bulk Si, the energies have been labeled as $K'_1, K'_2, ..., K'_5, K''_1, K''_2, ..., K''_5$ (c.f. Fig 5.2). All energies are non-degenerate. The only states that are coupled at $K'_2$ and
Figure 5.2: Band structures of Si (111), rotated bulk Si, and silicene along the \( K \Gamma M K \) directions. The TB and two-centre parameters correspond to Vogl et al. [29] and Grosso et al. [28]. The letters \( K \) and \( K' \) label the energies at the \( K \) point for Si (111) and bulk Si. The energy \( K''_4 \) is not shown for the sake of clarity.
Table 5.2: Energy splittings in the Si (111) when is transformed into its respective bulk.

<table>
<thead>
<tr>
<th>Si (111)</th>
<th>Bulk Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_1$</td>
<td>$K'_1, K''_1$</td>
</tr>
<tr>
<td>$K_2$</td>
<td>$K'_2$</td>
</tr>
<tr>
<td>$K_3$</td>
<td>$K'_3, K''_3$</td>
</tr>
<tr>
<td>$K_4$</td>
<td>$K'_4, K''_4$</td>
</tr>
<tr>
<td>$K_5$</td>
<td>$K'_5$</td>
</tr>
</tbody>
</table>

$K''_5$ are $3p_x$ and $3p_y$. All states are coupled at the remaining energies.

When the Si (111) and the bulk Si band structures are compared, we see how the former is modified when we add an infinite number of Si sheets so that it becomes the bulk band structure. Notice that all degeneracies in Si (111) at the $K$ point are now removed. Indeed, these degeneracies are a reflect of the hexagonal Bravais lattice and are also present in silicene and graphene. Notice how $K_1$ splits into $K'_1$ and $K''_1$, second, $K_3$ into $K'_3$ and $K''_3$, and third, $K_4$ into $K'_4$ and $K''_4$. The removing of the $K_3$ degeneracy turns bulk Si to a semiconductor. All states are coupled in the primed and non primed energies. As far as the $K_2$ and $K_5$ energies are concerned, they are “displaced” to $K'_2$ and $K'_5$, respectively. Table 5.2 summarizes these results.

5.3.2 Si (111) vs graphene

The band structure of Si (111) is shown in Figs. 5.2(a) and 5.2(d). The former was obtained using Vogl’s parameters whereas the latter using Grosso’s ones. In Si (111), the $sp^3$ hybridization causes a coupling between the $\pi$ and the $\sigma$ states. The effect of it is evident in the anticrossing of the originally uncoupled bands in graphene [c.f. Fig. 3.4]. Note, however, that the $\pi$ band is still doubly degenerate at the $K$ point. In graphene, the degeneracy at this point is required by the in-plane symmetry [52]. When we lower
the B atoms in silicene to create the Si (111) sheet [c.f. Fig. 5.3], this symmetry is not removed hence, the \(\pi\) bands are still degenerate at \(K\) in Si (111).

Notice that the TB parameters by Vogl et al. [29] and by Grosso et al. [28] lead to different bands, particularly, close to the \(\Gamma\) point. As the bands approach this point, the curvature of some of them changes. Consider, for instance, the second lowest valence band in Figs. 5.2(a) and 5.2(d). Close to \(\Gamma\), this band has negative curvature in the former figure, while it has positive curvature in the latter one. These differences might be due to 2NN interactions. We computed the band structure of Si (111) using two parameter sets for a \(sp^3\) TB model by Chadi et al. [24]; one of them for 1NN only, and the other one for 1NN plus one 2NN interaction. These results are not presented here, however, we mention that the band without the 2NN interaction has negative curvature, like Fig. 5.2(a), and the band with only one 2NN interaction has positive curvature, like Fig. 5.2(d). Another possible reason for the curvature differences is the sign of the TB parameters. Further calculations on the curvature of the bands at the \(\Gamma\) point are needed in order to determine if it is due to the 2NN interactions or the TB parameters. These calculations will be shown somewhere else.

As far as the eigenstates are concerned, they are different in graphene and Si (111). The \(\pi\) bands in both structures are a good example of this. Whereas the eigenstates of the the \(\pi\) bands in graphene are \(p_z\) orbitals, the eigenstates of the “\(\pi\) bands” in silicene correspond to a linear combination of \(s, p_x, p_y\) and \(p_z\) orbitals. This occurs because in Si (111), the \(\pi\) and \(\sigma\) bands are coupled.

It is known that close to the \(K\) point, graphene shows a linear dispersion [38, 41],

\[
E(p) = \pm \text{const} |k| = \pm \text{const} |\hbar k| = \pm v_0 |p|, \tag{5.13}
\]
where $v_0$ and $p$ are the Fermi velocity and the carrier momentum, respectively. In graphene, it has been measured that $v_0 \approx 10^6$ m/s [38]. The linearity of $E(p)$ is responsible for the electrons to behave as if they were Dirac massless fermions [38, 41].

From Fig 5.2(d) one notices that the dispersion of Si (111) is linear, which would indicate the presence of the Dirac particles. From a linear fitting performed close to the $K$ point, we estimate that $v_0 \approx 10^4$ m/s for the Si (111) sheet, which is two orders of magnitude smaller than in graphene. Hence, Dirac fermions will effectively move slower in a Si (111) sheet than in a graphene-like one. Let us look at the hybridizations of both sheets in order to understand the difference in velocities.

On the one hand, each atom shows $sp^2$ hybridization in graphene. In this hybridization, each atom has a lobe that is perpendicular to the sheet plane (the sheet corresponds to the $xy$-plane and the lobe is oriented along the positive $z$-axis as it is shown in Fig. 5.3(a). All lobes are oriented along the same direction, i.e., the $z$-axis, and, therefore, they form $\pi$ bondings with their 1NN. The $\pi$ bondings are responsible for the conducting character of the sheet.

On the other hand, Si (111) shows $sp^3$ hybridization. Figure 5.3(b) shows that each atom has a lobe that is perpendicular to the sheet, however, neighboring atoms have their lobes pointing in opposite directions, i.e., the positive and negative $z$-axes. Due to the alternating orientation, a lobe that points along the, say, positive $z$-axis, will not form a $\pi$ bonding with its 1NN, but with its 2NN.

Since the $\pi$ bondings in graphene occur between 1NN, the coupling is stronger than in Si (111), where the bondings occur between 2NN. An electron finds it “easier” to tunnel from one atom to the another one when the coupling is stronger. This explains why electrons in graphene move faster than they do in Si (111).
5.3.3 Silicene vs graphene

The silicene band structure is shown in Figs. 5.2(c) and 5.2(f) according to Vogl’s and Grosso’s parametrizations, respectively. Recall that in silicene and in graphene, the \( \pi \) bands are not coupled to the \( \sigma \) bands [c.f. Figs. 3.3 and 3.4]. When we compare the \( \pi \) energy bands of silicene using Vogl’s parameters to the corresponding ones in graphene, we notice that they have a similar form. This occurs because both sheets have the same lattice structure. As far as the \( \sigma \) bands are concerned, the valence bands in silicene have been lowered down therefore, the crossings that occur in graphene between the \( \pi \) and \( \sigma \) bands do not occur in silicene. One could argue that the \( s^* \) conduction band “pushes” down the valence bands not letting them cross with the \( \pi \) bands.

Different results are obtained when we perform the same comparison using Grosso’s parameters. One has to keep in mind that, unlike Vogl’s parametrization, Grosso’s para-
metrization corresponds to a 2NN one. The $\pi$ band maintains the form as in graphene, nevertheless, the $\pi^*$ band changes its curvature as it approaches $\Gamma$ from the $K\Gamma$ and the $M\Gamma$ directions. This change could occur because of the 2NN interactions or because of the signs of the TB parameters. In order to determine which is the case, one has to perform further calculations on the curvature of the band, which will be presented somewhere else. In contrast to Vogl's parameters, the $\pi$ and $\sigma$ valence bands cross. Since there is no $s^*$ band in this model, one could think that the $\sigma$ bands are not repelled from it.

Even though we attributed the differences in the crossings to the presence or not of the $s^*$ state, one could formulate a counter-argument for it: the energy difference between the $s^*$ and valence bands is large, therefore, one would expect that the effect of it is small on the latter. In other words, it is not clear whether there should be crossings between the $\pi$ and $\sigma$ silicene valence bands or not.

Finally, Figs. 5.2(c) and 5.2(f) show that silicene has a linear dispersion close to the $K$ point. By performing a linear fitting, we find that the Fermi velocity $v_0$ in Eq. (5.13), is of the order of $10^5$ m/s for both parametrizations. Compared to graphene ($v_0 \approx 10^6$ m/s), the electrons move slower in silicene. This occurs since the $\pi$ bonds, which are the responsible for conduction in the sheets, are weaker in silicene than in graphene (the distance between two Si atoms in silicene is greater than the distance between two C atoms in graphene).
5.4 Tight-binding Theory of Si Nanotubes

In order to compute the band structures of Si h-NT’s and g-NT’s from silicene and Si (111), we follow the same steps for computing the CNT band structure. First, we impose boundary conditions along the chiral direction. Consequently, the wavevector is quantized along the \( K_1 \) direction, \( i.e., k = kK_2 + \mu K_1 \) \( (\mu = 0, 1, 2, \ldots, N - 1) \).

Second, we make use of the zone folding approximation in order to graph the energy bands of the nanotubes.

5.5 CNT’s vs SiNT’s

5.5.1 CNT’s vs Si h-NT’s

Band structure

The band structures of Si h-NT’s with chiral vectors \((4, 4), (6, 6), (8, 0)\) and \((12, 0)\) are shown in the left-most column of Fig. 5.4. This bands were obtained by substituting the quantized nanotube wave vector \( k \) in Eq. (5.11). In this figure, the dispersion \( g_{25}(k) \), introduced by the 2NN interactions, is hardly noticeable, therefore, the band structure of Si h-NT’s looks very similar to the one of CNT’s in the 1NN approximation. It is due to this similarity, that we neglect the dispersion \( g_{25}(k) \) in the band structure of Si h-NT’s and discuss it as if it were a 1NN approximation only. In the 1NN case, the only difference between the CNT and the Si h-NT band structures is a scaling factor, which corresponds to the transfer integral \( \gamma_0 \) \( (\gamma_0 = -3.033 \text{ eV for C and } \gamma_0 = -0.949 \text{ eV for Si}) \). Whether or not a Si h-NT would be conductor or semiconductor, does not depend on \( \gamma \) but on its symmetries, thus, Si h-NT will follow Hamada’s rule as CNT’s do, \( i.e., \)
if \( n - m \) is a multiple of 3, the nanotube is a metal, otherwise, it is a semiconductor. From Hamada’s rule, we conclude that all armchair Si h-NT’s are conductors \((n = m)\) and zig zag tubes are conductors if \( n \) is a multiple of 3 \((m = 0)\). The band structures for Si h-NT’s shown in Fig. 5.4 confirm this rule.

We proceed to compare the energy band gaps between CNT’s and Si h-NT’s. According to Eq. (4.32) the band gap is given by

\[
E_g = 2\gamma \text{Min}_w \left( k \frac{K_2}{K_2} + \frac{1}{3}(N \pm 1)K_1 \right),
\]

where \( K_1 \) and \( K_2 \) are the reciprocal vectors of graphene and silicene, \( \gamma \) is the transfer integral, \( N \) is the number of hexagons in the nanotube unit cell, \( k \) is the wave vector, and Min\( w \) is the minimum of the graphene dispersion relation \( w \) with respect to \( k \) (see Eq. (3.8)). In particular, for zig zag tubes, the minimum occurs at \( k = 0 \) [15], according to Eq. (4.32), this yields to,

\[
E_g = 2\gamma_0 \sqrt{1 + 4 \cos \frac{\pi q_0}{n} + \cos^2 \frac{\pi q_0}{n}},
\]

where \( q_0 = 1/3(N \pm 1) \) and \( N = 2n \). In Fig. 5.5, we show our results for the band gap of both CNT’s and h-SiNT’s as a function of the diameter. For a given diameter, the band gap \( E_g \) of Si h-NT’s is smaller than the band gap of CNTs. In order to understand this result, we should look to the approximate expression for \( E_g \) derived by Saito et al. and Ando [15, 41],

\[
E_g \sim \frac{|\gamma|}{d}, \quad \gamma = \frac{\sqrt{3}a}{2\gamma_0},
\]

where \( d = L/\pi \) is the nanotube diameter. For a given diameter, \( E_g \) depends only on the
Figure 5.4: Band structures of Si h- and Si g-NT’s according to our calculations and to Yang and Ni [12]. The two-center parameters used in our calculations were taken from Grosso et al. [28].
parameter $\gamma$, which depends on the transfer integral (recall that the transfer integral corresponds to the interaction between neighboring $p_z$ orbitals). Since this interaction is smaller for Si h-NT’s than for CNT’s, the band gap is greater for the latter.

Notice that the $1/d$ dependence in the nanotube band gap is expected. If we let $d \to \infty$, then $E_g \to 0$. The limit $d \to \infty$ corresponds to make a nanotube thicker and thicker, and, therefore, more similar to graphene, which has a zero band gap.

![Graph showing the band gap of CNT’s and Si h-NT’s as a function of their diameters.](image)

**Figure 5.5: Band gap of CNT’s and Si h-NT’s as a function of their diameters**

**Effective masses**

We proceed to compute and to compare the effective masses of Si h-NT’s and CNT’s. By differentiating the band structure of zig zag nanotubes given in Eq. (4.29), we obtain an analytical formula for their effective masses at the $K$ point,

$$m^*_{\pm} = \frac{\hbar^2}{\left. \frac{d^2E}{dk^2} \right|_{k=0}} = \pm \frac{2\hbar^2}{3\gamma_0 a^2} \frac{\cos \frac{\pi q_0}{n}}{\sqrt{1 + 4 \cos \frac{\pi q_0}{n} + \cos^2 \frac{\pi q_0}{n}}}.$$  \hspace{1cm} (5.16)
Equation (5.16) is plotted in Fig. 5.6. First, notice the general trend for Si h-NT’s and CNT’s that the effective masses decrease as the their diameter increases. This occurs because electrons in a Si h-NT (CNT) with large diameter, behave more similar to electrons in silicene (graphene). In other words, if we increase the nanotube diameter, we will see that the electrons start “losing” their masses, until they become Dirac massless fermions. Second, notice that for a given diameter, electrons in Si h-NTs are heavier, in magnitude, than electrons in CNT’s. The top valence band and lowest conduction band are flatter than the corresponding ones in CNT’s, which explains their mass difference.

We point out that the effective-masses can be obtained from $\mathbf{k} \cdot \mathbf{p}$ theory, as well. Ando [41] derived the following dispersion relation for the nanotube band gap,

$$E_{n\pm}(k) = \pm \gamma \sqrt{\kappa(n)^2 + k'^2}, \kappa = \frac{2\pi}{L} \left( n - \frac{\nu}{3} \right), n = 0, \pm 1, \pm 2, ...$$  \hspace{1cm} (5.17)

where $k'$ is the wave vector measured from the $K$ point, $L$ is the magnitude of the chiral
vector and $|\nu| = 1$ for semiconducting nanotubes. Hence, the effective mass of the zig zag tubes is

$$m^*_{\pm} = \frac{\hbar^2}{d^2 E_{0\pm}/dk'^2} \bigg|_{k' = 0} = \pm \frac{2\hbar^2}{3\sqrt{3}\gamma_0 a} \left(\frac{1}{d}\right).$$

(5.18)

This equation confirms what was stated above about the nanotube effective-masses using TB theory: (a) $m^*$ decreases as the $d$ increases since it explicitely depends upon $d^{-1}$; (b) an electron in a Si h-NT would have greater $m^*$ than in a CNT since the product $|\gamma_0 a|$ is smaller in the former ($\approx 3.64$ eVÅ) than the latter ($\approx 7.55$ eVÅ).

### 5.5.2 CNT’s vs Si g-NT’s

The column located in the middle of Fig. 5.4 shows the band structures of Si g-NT’s with chiral vectors $(4,4), (6,6), (8,0)$ and $(12,0)$. The dashed line corresponds to the Fermi level. Notice that for all graphs but the ones in the second column, the Fermi energy is at zero. From this figure, one notices that there is a proliferation of the number of bands in the Si g-NT’s when compared to CNT’s. In CNT’s there is a total of $2N$ bands, where $N$ is the number of hexagons in the CNT unit cell and it is given by Eq (4.13). The factor of 2 comes from the $2 \times 2$ Hamiltonian, and $N$ bands come from the quantisation of the wave vector $k$ along the $K_1$ direction. In Si g-NT’s, there are $8N$ bands; eight from the $8 \times 8$ Hamiltonian, and other $N$ from the same quantazation in $k$. Hence, Si g-NTs have four times the number of bands that CNT’s have. Moreover, there are 4 electrons per Si atom and a total of $2N$ atoms in the g-NT unit cell, hence, there are $4 \times 2N = 8N$ electrons per unit cell. In particular, armchair and zig zag g-NT’s, have $16n$ bands and electrons per unit cell ($N = 2n$). Table 5.3 summarizes some of the general characteristics of the h- and g-NT energy bands.
Table 5.3: General characteristics of the h- and g-NT energy bands. Here, e\(^{-}\) and u.c. refer to electrons and the nanotube unit cell, respectively.

<table>
<thead>
<tr>
<th></th>
<th>h-NT ((sp^2))</th>
<th>g-NT ((sp^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>e(^{-}) per atom</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>atoms per u.c.</td>
<td>2(N)</td>
<td>2(N)</td>
</tr>
<tr>
<td>Number of bands</td>
<td>2(N)</td>
<td>8(N)</td>
</tr>
<tr>
<td>e(^{-}) per u.c.</td>
<td>2(N)</td>
<td>8(N)</td>
</tr>
</tbody>
</table>

After wrapping the Si (111) sheet into a zig-zag g-NT, we find that the (8, 0) tube is a semiconductor with a gap of 0.34 eV, and the (12, 0) is either a metal or a semiconductor of gap zero. The armchair (4, 4) and (6, 6) tubes could be metals or zero gapped semiconductors, as well. In order to completely characterize the electronic behaviour of the last three nanotubes, we need their density of states (DOS), which we did not calculate. However, due to the similarities with CNT’s, we would expect them to have a finite DOS at the Fermi level and thus, to be metals.

Furthermore, Si g-NT’s obey Hamada’s rule like CNT’s do. In order to understand this, we apply a similar reasoning used for CNT’s. We first started with the Si (111) band structure (c.f. Fig. 5.2), which has zero gap at the \(K\) point of its Brillouin zone, second, we sliced the Si (111) bands by quantizing the wavevector \(\mathbf{k}\) along the \(\mathbf{K}_1\) direction, and, third, we used the zone-folding approximation to plot the Si g-NT bands. If any of the “slices” cuts the \(K\) point then, the g-NT is a conductor, if it does not, then it is a semiconductor. In the language of group theory, the degeneracies caused by the vertical and the horizontal mirror plane symmetries in CNT’s are not removed in the gear-like tube.
5.6 Yang and Ni’s Results vs Present Results

5.6.1 Si (111) and silicene

Figure 5.7: Band structures of Si (111) and silicene according to Yang and Ni. [12].

- 1NN $sp^3s^*$ The energy bands of silicene obtained in the present work are shown in Fig. 5.2(c), and the ones by Yang et al. [12] in Fig. 5.7(b). When the two models are compared one notices certain differences. For example, in the neighborhood of the Γ point in Fig 5.2(c), both conduction and valence bands have the opposite curvature with respect to Fig. 5.7(a). Possibly, this difference can be attributed to the 1NN approximation in the $sp^3s^*$ model.

There is agreement in the silicene $\pi$ and the lower $\sigma$ bands, however, this is not the case for the upper $\pi^*$ band, which has opposite curvature. Moreover, there are no crossings between the $\pi$ and $\sigma$ valence bands. As it was discussed previously, this could be happening because of the repulsion from the $s^*$ band or the TB parameters.
• 2NN $sp^3$

Figure 5.2(d) shows good agreement between our and Yang’s et al. [12] findings for Si (111), especially, along the $K\Gamma M$ directions. Close to $\Gamma$, the curvature problem is overcome by including some TCA interactions from 2NN in the Hamiltonian, namely, $(pp\sigma)^{AA}_2$ and $(pp\pi)^{AA}_2$.

Most of the differences occur along the $MK$ direction, for instance, our calculations show that the second-lowest valence band should have the opposite curvature when compared to Yang et al. [12]. The positive curvature of this band comes from the strong repulsion induced by the $p$-like band located above it.

### 5.6.2 Silicon g-NT’s

From the previous comparisons of the Si sheets, we find better agreement between our calculations and the ones by Yang et al. [12] when we use our 2NN $sp^3$ TB model. Hence, we only compare our energy bands obtained from this theory to the ab-initio calculations.

Our Si g-NT energy bands are shown in the second column of Fig. 5.4, and the respective ones computed by Yang et al. [12] are reproduced in the third column of the same figure. We find that all our band structures differ from their work. Whereas all our armchair tubes are metals or zero-gap semiconductors, their corresponding tubes are semiconductors. As it was mentioned before, our zig-zag tubes follow Hamada’s rule, while theirs do not.

The authors argue that in zig zag Si g-NT’s with small diameter, like (8, 0) gaps do not occur because of the $\sigma^* - \pi^*$ coupling. We think that this hypothesis is doubtful, since our theory does include this coupling and it does not close the gap of the small
semiconducting tubes like (8, 0). Furthermore, band gaps tend to open and not to close when couplings are added. A possible explanation for the discrepancy is that the ab initio calculation suffers from the density-functional-theory band gap problem.

These significant differences between the TB and the ab initio bands are quite surprising since both approaches coincide on the band structure of Si (111). We point out, though, that in their report, Yang et al. [12] do not explain the gap openings when the Si (111) sheet is rolled up to form Si g-NT’s [12]. One could think that curvature effects in Yang’s results might open a gap in Si g-NT’s, nonetheless, such a gap should be, at most, of the order of the meV. Consider a CNT and a Si g-NT with the same chirality, for instance, $C_h = (12, 0)$. It is known that the gap opening $\Delta E$ due to curvature in CNT’s, is inversely proportional to it and it is close to 10 meV [15, 52]. The transfer integral $|\gamma|$, can be used as an energy scale for the nanotubes, thus, $\Delta E \sim |\gamma|/d^2$. The ratio between the openings in CNT’s and Si g-NT’s is then given by

$$\frac{\Delta E_{Si}}{\Delta E_{C}} \sim \frac{|\gamma_{Si}|/d_{Si}^2}{|\gamma_{C}|/d_{C}^2} = \frac{|\gamma_{Si}|}{|\gamma_{C}|} \left( \frac{d_{C}}{d_{Si}} \right)^2 \Delta E_C.$$  

According to Eq. (4.3), $d_C = 30 \text{ Å}$ and $d_{Si} = 46 \text{ Å}$, respectively [12, 15]. Substituting $|\gamma_{C}| = 3.033 \text{ eV}, |\gamma_{Si}| = 0.949 \text{ eV}$ and $\Delta E_{C} = 10 \text{ meV}$ [12, 15], we find that

$$\Delta E_{Si} \approx 1 \text{ meV}$$

The band gap in the (12, 0) Si g-NT of Yang et al. [12] [see band structure in the lower right corner of Fig. 5.4] is close to 200 meV so, curvature cannot be responsible for the
whole opening of the gap Yang’s nanotubes.

Our TB scheme, on the other hand, provides an explanation for the gap behaviour in all g-NT’s openings in terms of Hamada’s rule. For example, our (12, 0) Si g-NT has a zero gap since this corresponds to a zig zag tube with \( n \) multiple of 3.
Chapter 6

Conclusions

On the carbon side, the electronic properties of graphene and CNT’s were reviewed in the present work. We pointed out the discrepancies between current theories and recent experiments on the effective masses and on the electronic behaviour of graphene.

On the silicon side, the electronic properties of silicene, Si (111), Si h-NT’s and Si g-NT’s were studied via a TB approach. We derived $sp^3s^*$ and $sp^3$ Hamiltonians up to 1NN and 2NN, respectively.

The comparison between the energy bands of Si (111) and bulk Si, showed that all degeneracies at the $K$ point of Si (111) are removed in its respective bulk. The coupling between each of the Si (111) layers in bulk Si is responsible for the openings.

We compared the band structures of Si (111) and of silicene to the one of graphene. Since all of these materials have in-plane symmetry, the “$\pi$” bands are two-fold degenerate at $K$. We expect Si (111) and silicene to be either semiconductors of band gap zero or metals. Electrons in the neighborhood of the $K$ point should behave as Dirac massless fermions due to the presence of the Dirac cone in both structures. However,
the Fermi velocity $v_0$ in Si (111) ($10^4$ m/s) and in silicene ($10^5$ m/s) are smaller than the one in graphene ($10^6$ m/s). Electron tunnelization between Si atoms is less favorable in Si (111) and silicene than in graphene because the “π” interaction is weaker in the first two materials.

Silicon h-NT’s and Si g-NT’s were compared to CNT’s, as well. The band structure of Si h-NT’s and of CNT’s are similar two each other. Even though we performed calculations including 1NN and 2NN, we found that the effect of the latters on the bands is negligible. This allowed us to make further approximations when discussing and calculating the band gap and effective masses of Si h-NT’s. In the case of zig zag semiconductor Si h-NT’s, the gap is inversely proportional to the tube diameter, as in zig zag CNT’s, nonetheless, for a given diameter, Si h-NT’s will have a smaller gap. The magnitude of the effective masses is also inversely proportional to their diameter, however, for a given diameter Si h-NT’s have greater mass, which makes CNT’s more suitable for transport properties. As far as Si g-NT’s are concerned, we found that they follow Hamada’s rule as CNT’s do, even though they show different hybridizations.

Our calculations for all the Si-based materials considered here were compared to the ab initio calculations performed by Yang et al. [12]. When comparing silicene and Si (111), we found that the 2NN $sp^3$ model is in better agreement with Yang’s band structures than the 1NN $sp^3s^*$ model. For this reason, we chose the $sp^3$ model in order to reproduce the energy dispersions of Si nanotubes.

For Si h-NT’s, our band structures agree with the ones obtained by Yang et al. [12]: they all follow Hamada’s rule. In contrast, they disagree for all Si g-NT’s. Whereas our calculations show that these nanotubes also follow this rule, Yang’s calculations do not. We emphasize that the $\sigma-\pi$ coupling does not close the gap for Si g-NT’s with small
diameters, contrary to the hypothesis of Yang et al [12].

6.0.3 Further work

Since the study of Si-based nanomaterials started with the work of Fagan et al. [11] in the year 2000, this field is relatively new and there is still significant work to be accomplished. To the best of our knowledge, there are no reports on the optical and thermal properties of them.

The symmetries of the Si (111) sheet and Si g-NT’s should be studied in order to achieve better understanding of the band structures of these materials. For example, the group theory of these structures will predict which degeneracies are required by symmetry and which are accidental. Moreover, selection rules for the optical transitions can be derived from such.

Further analysis on the properties of the Dirac massless fermions in Si (111) will provide a better understanding of the electron dynamics in this material. In graphene, the wave function of these fermions is $p_z$-like, in contrast, the wave function of the corresponding fermions in Si (111) is a combination of $s$, $p_x$, $p_y$, and $p_z$ orbitals, which would lead to a different electronic behaviour.

Accurate transport and optical properties can be calculated from this TB model if more accurate TB parameters for bulk Si are available.

Once the physical properties of straight Si nanotubes are understood, one could hypothesize more intricate structures made of Si, for example, Si nanotube junctions or helical Si nanotubes. Carbon nanotube junctions and helical carbon nanotubes have potential applications as logic gates and nanoswitches [63, 64]. If their Si counterparts can be made, it would be useful to know whether they are more suitable for these
applications or not.

Last but not least, more experiments are necessary. The experimental work done so far, have not been able to determine if the hybridization of Si (111) and SiNT’s is $sp^2$, $sp^3$ or a combination of both [60]. More experiments will enlight the path on the structural properties of these fascinating materials.
Appendix A

Atomic and Hybrid Orbitals

Here, we review the atomic and hybrid orbitals of atoms. Both orbitals form a complete set of states in Hilbert space and, therefore, they define one of the infinite number of bases in this space. The hybrid orbitals relevant to this work since they are chosen to be the basis for TB Bloch function. In addition, the eigenstates of the Hamiltonian of a crystal, are discussed in terms of them. Our review follows the one presented by Cohen et al. [17]

Let us consider the wave functions of the hydrogen (H) atom. The corresponding wave functions have the form,

\[
\phi_{n_l m}(r) = R_{n_l}(r)Y_{l m}(\theta, \phi)
\]  

(A.1)

where \( R_{n_l} \) and \( Y_{l m}(\theta, \phi) \) are the radial and the angular function of the H atom.\(^1\) Also, the quantum numbers \( n, l, m \) refer to the energy \( E_n \), the square of the angular momentum \( l(l+1)\hbar^2 \), and the \( z \)-component of the angular momentum \( m\hbar \). These orbitals are known\(^1\) Actually, the \( Y_{l m}(\theta, \phi) \) functions are the spherical harmonics.
as atomic orbitals. Each atomic orbital $\phi_{nlm}(r)$ is a stationary state where the quantum numbers $n, l$ and $m$ are good quantum numbers.

We can construct new stationary states by making a linear superposition of atomic orbitals with the same energy. In other words, we add atomic orbitals that have the same $n$ but different $l$ and $m$. These states are the so-called hybrid orbitals. Obviously, in the case of hybrid orbitals, $l$ and $m$ are not good quantum numbers since they are not well defined anymore. In the following, we provide definitions for the $s$ and $p$ atomic orbitals.

- **$s$ orbitals**

  The $s$ orbitals are the states defined by Eq. (A.1) when $l = 0, m = 0$,

  $$s \equiv \phi_{n00}(r) = R_{n00}(r)\sqrt{\frac{1}{4\pi}}.$$  

  (A.2)

  Since $s$ does not depend on neither $\theta$ nor $\phi$, the state is spherically symmetric as it is shown in Fig. A.1

- **$p$ orbitals**

  If we set $l = 1$ in Eq. (A.1), then $m$ can have the values $m = 0$ and $m = \pm 1$. The atomic orbitals $p_x, p_y$, and $p_z$ are defined as follows,

  $$p_x \equiv \frac{1}{\sqrt{2}}(\phi_{n11}(r) + \phi_{n1-1}(r)) = \sqrt{\frac{3}{8\pi}}R_n(r)\frac{x}{r},$$

  $$p_y \equiv \frac{1}{\sqrt{2}}(\phi_{n11}(r) - \phi_{n1-1}(r)) = \sqrt{\frac{3}{8\pi}}R_n(r)\frac{y}{r},$$

  (A.3)

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\[ p_z \equiv \phi_{n10}(r) = \sqrt{\frac{3}{4\pi}} R_n(r) \cos \theta = \sqrt{\frac{3}{4\pi}} R_n(r) \frac{z}{r}. \]

The angular part of the \( s \) and \( p \) orbitals is depicted in Fig. A.1.

![Figure A.1: Hybrid orbitals \( s, p_x, p_y \) and \( p_z \).](image-url)
Appendix B

Lists of $g(k)$ Functions

In this appendix we give the $g_j(k)$ functions for the graphene, silicene, and Si (111) sheet Hamiltonians within the second-nearest and two-center approximations.

B.1 Graphene and Silicene

\[
\begin{align*}
g_0(k) &= e^{i k \cdot \delta_1^{(1)}} + e^{i k \cdot \delta_2^{(1)}} + e^{i k \cdot \delta_3^{(1)}}, \\
g_1(k) &= e^{i k \cdot \delta_1^{(1)}} - \frac{1}{2} e^{i k \cdot \delta_2^{(1)}} - \frac{1}{2} e^{i k \cdot \delta_3^{(1)}}, \\
g_2(k) &= \frac{\sqrt{3}}{2} \left( e^{i k \cdot \delta_2^{(1)}} - e^{i k \cdot \delta_3^{(1)}} \right), \\
g_3(k) &= e^{i k \cdot \delta_1^{(1)}} + \frac{1}{4} e^{i k \cdot \delta_2^{(1)}} \frac{1}{4} e^{i k \cdot \delta_3^{(1)}}, \\
g_4(k) &= \frac{3}{4} \left( e^{i k \cdot \delta_2^{(1)}} + e^{i k \cdot \delta_3^{(1)}} \right), \\
g_5(k) &= -\frac{\sqrt{3}}{4} \left( e^{i k \cdot \delta_2^{(1)}} - e^{i k \cdot \delta_3^{(1)}} \right),
\end{align*}
\]
\( g_6(k) = \frac{3}{4} \left( e^{ik\delta_2^{(1)}} + e^{ik\delta_3^{(1)}} \right), \)

\( g_7(k) = e^{ik\delta_1^{(1)}} + \frac{1}{4} e^{ik\delta_2^{(1)}} + \frac{1}{4} e^{ik\delta_3^{(1)}}, \)

\( g_8(k) = g_9(k) = g_{10}(k) = g_{11}(k) = 0, \)

\( g_{12}(k) = e^{ik\delta_1^{(2)}} + e^{ik\delta_2^{(2)}} + e^{ik\delta_3^{(2)}} \)

\( g_{13}(k) = e^{ik\delta_1^{(2)}} + e^{ik\delta_2^{(2)}} + e^{ik\delta_3^{(2)}} + e^{ik\delta_4^{(2)}} + e^{ik\delta_5^{(2)}} + e^{ik\delta_6^{(2)}}, \)

\( g_{14}(k) = \frac{\sqrt{3}}{2} \left( e^{ik\delta_3^{(2)}} - e^{ik\delta_4^{(2)}} + e^{ik\delta_5^{(2)}} - e^{ik\delta_6^{(2)}} \right), \)

\( g_{15}(k) = e^{ik\delta_1^{(2)}} - e^{ik\delta_2^{(2)}} - \frac{1}{2} e^{ik\delta_3^{(2)}} + \frac{1}{2} e^{ik\delta_4^{(2)}} + \frac{1}{2} e^{ik\delta_5^{(2)}} - \frac{1}{2} e^{ik\delta_6^{(2)}}, \)

\( g_{16}(k) = \frac{3}{4} \left( e^{ik\delta_3^{(2)}} + e^{ik\delta_4^{(2)}} + e^{ik\delta_5^{(2)}} + e^{ik\delta_6^{(2)}} \right), \)

\( g_{17}(k) = e^{ik\delta_2^{(2)}} + \frac{1}{4} e^{ik\delta_3^{(2)}} + \frac{1}{4} e^{ik\delta_4^{(2)}} + \frac{1}{4} e^{ik\delta_5^{(2)}} + \frac{1}{4} e^{ik\delta_6^{(2)}}, \)

\( g_{18}(k) = \frac{\sqrt{3}}{4} \left( -e^{ik\delta_3^{(2)}} - e^{ik\delta_4^{(2)}} + e^{ik\delta_5^{(2)}} + e^{ik\delta_6^{(2)}} \right) \)

\( g_{19}(k) = e^{ik\delta_2^{(2)}} + e^{ik\delta_3^{(2)}} + \frac{1}{4} e^{ik\delta_4^{(2)}} + \frac{1}{4} e^{ik\delta_5^{(2)}} + \frac{1}{4} e^{ik\delta_6^{(2)}}, \)

\( g_{20}(k) = \frac{3}{4} \left( e^{ik\delta_3^{(2)}} + e^{ik\delta_4^{(2)}} + e^{ik\delta_5^{(2)}} + e^{ik\delta_6^{(2)}} \right), \)

\( g_{21}(k) = g_{22}(k) = g_{23}(k) = g_{24}(k) = 0, \)

\( g_{25}(k) = e^{ik\delta_1^{(2)}} + e^{ik\delta_2^{(2)}} + e^{ik\delta_3^{(2)}} + e^{ik\delta_4^{(2)}} + e^{ik\delta_5^{(2)}} + e^{ik\delta_6^{(2)}}. \)

\[ \text{B.2} \quad \text{Si (111) Sheet} \]

\( g_0(k) = e^{ik\delta_1^{(1)}} + e^{ik\delta_2^{(1)}} + e^{ik\delta_3^{(1)}}, \)

\( g_1(k) = -\frac{2\sqrt{2}}{9} \left( e^{ik\delta_1^{(1)}} - \frac{1}{2} e^{ik\delta_2^{(1)}} - \frac{1}{2} e^{ik\delta_3^{(1)}} \right), \)
\( g_2(k) = \sqrt{\frac{2}{3}} \left( e^{ik} \delta_2^{(1)} - e^{ik} \delta_3^{(1)} \right), \)
\( g_3(k) = \frac{8}{9} \left( e^{ik} \delta_1^{(1)} + \frac{1}{4} e^{ik} \delta_2^{(2)} \right) - e^{ik} \delta_3^{(1)}, \)
\( g_4(k) = \frac{1}{9} \left( e^{ik} \delta_1^{(1)} + 7 e^{ik} \delta_2^{(1)} + 7 e^{ik} \delta_4^{(1)} \right), \)
\( g_5(k) = -\frac{2}{3} \left( e^{ik} \delta_2^{(2)} + e^{ik} \delta_3^{(1)} \right), \)
\( g_6(k) = \frac{2}{3} \left( e^{ik} \delta_2^{(1)} + e^{ik} \delta_3^{(1)} \right), \)
\( g_7(k) = e^{ik} \delta_1^{(1)} + \frac{1}{3} e^{ik} \delta_2^{(1)} + \frac{1}{3} e^{ik} \delta_3^{(1)}, \)
\( g_8(k) = -\frac{1}{3} \left( e^{ik} \delta_1^{(1)} + e^{ik} \delta_2^{(1)} + e^{ik} \delta_3^{(1)} \right), \)
\( g_9(k) = -\frac{2\sqrt{2}}{9} \left( e^{ik} \delta_1^{(1)} - \frac{1}{2} e^{ik} \delta_2^{(1)} - \frac{1}{2} e^{ik} \delta_3^{(1)} \right), \)
\( g_{10}(k) = \frac{1}{3} \sqrt{\frac{2}{3}} \left( e^{ik} \delta_2^{(2)} - e^{ik} \delta_3^{(2)} \right), \)
\( g_{11}(k) = \frac{1}{9} \left( e^{ik} \delta_1^{(1)} + e^{ik} \delta_2^{(1)} + e^{ik} \delta_3^{(1)} \right), \)
\( g_{12}(k) = \frac{8}{9} \left( e^{ik} \delta_1^{(1)} + e^{ik} \delta_2^{(1)} + e^{ik} \delta_3^{(1)} \right), \)
\( g_{13}(k) = e^{ik} \delta_1^{(2)} + e^{ik} \delta_2^{(2)} + e^{ik} \delta_3^{(2)} + e^{ik} \delta_4^{(2)} + e^{ik} \delta_5^{(2)} + e^{ik} \delta_6^{(2)}, \)
\( g_{14}(k) = \frac{\sqrt{3}}{2} \left( e^{ik} \delta_3^{(2)} - e^{ik} \delta_4^{(2)} + e^{ik} \delta_5^{(2)} - e^{ik} \delta_6^{(2)} \right), \)
\( g_{15}(k) = e^{ik} \delta_1^{(2)} + e^{ik} \delta_2^{(2)} + \frac{1}{4} e^{ik} \delta_3^{(2)} + \frac{1}{4} e^{ik} \delta_4^{(2)} + \frac{1}{4} e^{ik} \delta_5^{(2)} - \frac{1}{4} e^{ik} \delta_6^{(2)}, \)
\( g_{16}(k) = \frac{3}{4} \left( e^{ik} \delta_3^{(2)} + e^{ik} \delta_4^{(2)} + e^{ik} \delta_5^{(2)} + e^{ik} \delta_6^{(2)} \right), \)
\( g_{17}(k) = e^{ik} \delta_1^{(2)} + e^{ik} \delta_2^{(2)} + \frac{3}{4} e^{ik} \delta_3^{(2)} + \frac{3}{4} e^{ik} \delta_4^{(2)} + \frac{3}{4} e^{ik} \delta_5^{(2)} + \frac{3}{4} e^{ik} \delta_6^{(2)}, \)
\( g_{18}(k) = \frac{\sqrt{3}}{4} \left( -e^{ik} \delta_3^{(2)} - e^{ik} \delta_4^{(2)} + e^{ik} \delta_5^{(2)} + e^{ik} \delta_6^{(2)} \right), \)
\( g_{19}(k) = e^{ik} \delta_1^{(2)} + e^{ik} \delta_2^{(2)} + \frac{1}{4} e^{ik} \delta_3^{(2)} + \frac{1}{4} e^{ik} \delta_4^{(2)} + \frac{1}{4} e^{ik} \delta_5^{(2)} + \frac{1}{4} e^{ik} \delta_6^{(2)}, \)
\( g_{20}(k) = \frac{3}{4} \left( e^{ik} \delta_3^{(2)} + e^{ik} \delta_4^{(2)} + e^{ik} \delta_5^{(2)} + e^{ik} \delta_6^{(2)} \right), \)
\( g_{21}(k) = g_{22}(k) = g_{23}(k) = 0, \)
$$g_{24}(k) = e^{i k \delta_{1}^{(2)}} + e^{i k \delta_{2}^{(2)}} + e^{i k \delta_{3}^{(2)}} + e^{i k \delta_{4}^{(2)}} + e^{i k \delta_{5}^{(2)}} + e^{i k \delta_{6}^{(2)}}.$$
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