Tight-Binding Approach to Electronic Structure of Carbon Nanotubes

BY

SHU-KIN LOK

A Thesis Presented to
The Hong Kong University of Science and Technology
In Partial Fulfillment
of the Requirements for
the Degree of Master of Philosophy
in Physics

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List of Publications in Preparation

1. *Tight binding calculation of the band structure and optical properties of single wall carbon nanotubes*, S. K. Lok, B. S. Wang, and W. K. Ge

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Abstract

The electronic structure and optical properties of single-wall carbon nanotubes (SWCN’s) have been studied using a nearest-neighbor empirical tight-binding model. Hybridization of the $\sigma$, $\pi$, $\pi^*$ and $\sigma^*$ states of the graphene network is shown to be as important as zone-folding effects in determining the metallicity of small radius carbon nanotubes. The energy dispersion relations are further used to calculate the imaginary part of the dielectric function, which can be directly related to the experimental absorption spectrum.
Chapter 1

Introduction

It is well known that two crystalline allotropes of carbon exist in nature: graphite and diamond. In 1985, a new form of carbon, fullerene $C_{60}$, was discovered by three chemists, Harry Kroto, Robert Curl and Richard Smalley [1]. They were awarded the Nobel Prize in chemistry in 1996 for their discovery. Five years later, after the discovery of $C_{60}$, a discussion with Huffman and M. S. Dresselhaus at a carbon-carbon composites workshop [2], stimulated Smalley to speculate about the existence of carbon nanotubes of dimension comparable to $C_{60}$. These conjectures were later followed up in August 1991 by an oral presentation at a fullerene workshop in Philadelphia by Dresselhaus [3] on the symmetry proposed for carbon nanotubes capped at either end by fullerene hemispheres, with suggestions on how zone folding could be used to examine the electron and phonon dispersion relations of such structures. In late 1991, Iijima [4] reported the experimental observation of multiple-shell graphitic nanotubes in the graphite electrodes under a DC arc discharge. It was this work which bridged the gap between experimental observation and theoretical framework of carbon nanotubes in relation to fullerenes and as theoretical examples of 1D systems. Since then, the research on carbon nanotubes has progressed rapidly, and a comprehensive theoretical study of their physical properties is essential before they can be synthesized in industrial production.

1.1 Atomic nature of carbon

Being the lightest element in column IV of the periodic table, carbon-based materials exhibit unique physical and chemical properties in many ways. While other
group IV elements such as Si, Ge and Sn have primarily $sp^3$ hybridization, carbon has many more allotropic forms such as graphite, diamond, carbon fibers, fullerenes and carbon nanotubes. The reason why carbon assumes so many structural forms is that a carbon atom can form several distinct types of valence bonds, where the chemical bonds refer to the hybridization of orbitals by physicists.

A carbon atom has six electrons which occupy $1s^2$, $2s^2$ and $2p^2$ atomic orbitals in the ground state. Four outermost shell electrons, which occupy the $2s^2 2p^2$ orbitals, can have their wave functions mix with each other so as to enhance the binding energy of C atom with its neighboring atoms. The mixing of $s$ and $p$ orbitals is called hybridization, and there are three possible hybridizations that occur in carbon: $sp$, $sp^2$ and $sp^3$ as shown in Figure 1.1 [5].

![Figure 1.1: Schematic presentation of (a) $sp^1$, (b) $sp^2$ and (c) $sp^3$ bonding hybridizations. The unshaded lobes denote strong bonds and the shaded lobes denote weak bonds.](image)

In $sp$ hybridization, a linear combination of the $2s$ orbital and one of the $2p$ orbitals of a carbon atom, for example $2p_x$, is formed. From the two electron
orbitals of a carbon atom, two hybridized \( sp \) orbitals, denoted by \( |sp_a\rangle \) and \( |sp_b\rangle \) are expressed by the linear combination of \( |2s\rangle \) and \( |2p_x\rangle \) wavefunctions of the carbon atom,

\[
|sp_a\rangle = \frac{1}{\sqrt{2}} \left( |2s\rangle + |2p_x\rangle \right) \\
|sp_b\rangle = \frac{1}{\sqrt{2}} \left( |2s\rangle - |2p_x\rangle \right)
\] (1.1)

In \( sp^2 \) hybridization, the \( 2s \) orbital and two \( 2p \) orbitals, for example \( 2p_x \) and \( 2p_y \), are hybridized. The corresponding \( sp^2 \) hybridized orbitals \( |sp_i^2\rangle (i = a, b, c) \) are made from \( 2s, 2p_x \) and \( 2p_y \) orbitals as follows:

\[
|sp_a^2\rangle = C_1 |2s\rangle - \sqrt{1-C_2^2} |2p_y\rangle \\
|sp_b^2\rangle = C_2 |2s\rangle + \sqrt{1-C_2^2} \left\{ \frac{\sqrt{3}}{2} |2p_x\rangle + \frac{1}{2} |2p_y\rangle \right\} \\
|sp_c^2\rangle = C_3 |2s\rangle + \sqrt{1-C_3^2} \left\{ -\frac{\sqrt{3}}{2} |2p_x\rangle + \frac{1}{2} |2p_y\rangle \right\}
\] (1.2)

where \( C_1 = C_2 = 1/\sqrt{3} \) and \( C_3 = -1/\sqrt{3} \). These three orbits are elongated and arranged in the same plane with an angle of 120° to each other.

In \( sp^3 \) hybridization the \( 2s \) orbit and three \( 2p \) orbits are mixed with each other. The corresponding hybridized orbitals consist of the linear combinations of \( 2s, 2p_x, 2p_y \) and \( 2p_z \) as follows:

\[
|sp_a^3\rangle = \frac{1}{2} \{ |2s\rangle + |2p_x\rangle + |2p_y\rangle + |2p_z\rangle \} \\
|sp_b^3\rangle = \frac{1}{2} \{ |2s\rangle - |2p_x\rangle - |2p_y\rangle + |2p_z\rangle \} \\
|sp_c^3\rangle = \frac{1}{2} \{ |2s\rangle - |2p_x\rangle + |2p_y\rangle - |2p_z\rangle \} \\
|sp_d^3\rangle = \frac{1}{2} \{ |2s\rangle + |2p_x\rangle - |2p_y\rangle - |2p_z\rangle \}
\] (1.3)

These four hybridized orbitals form tetragonal bonding to the four nearest neighbor atoms.
Chapter 2

Lattice Structure and Brillouin Zone of Carbon Nanotubes

As a new form of carbon atom, the structure of carbon nanotubes is very different from the usual crystal, which has primarily the translational symmetry as its symmetry group. This chapter introduces the lattice structure and Brillouin zone of a single-wall carbon nanotube (SWCN).

2.1 Lattice Structure and Parameters

A SWCN can be visualized as a conformal mapping of a two dimensional graphitic lattice onto the surface of a cylinder with typical diameter < 2 nm. Three examples of single-wall carbon nanotubes (SWCN’s) are shown in Figure 2.1 [6].

The primary classification of a carbon nanotube is as either achiral (symmorphic) or chiral (non-symmorphic). An achiral carbon nanotube is defined by a carbon nanotube whose mirror image has an identical structure to the original one. There are only two cases of achiral nanotubes; armchair and zigzag nanotubes, as are shown in Figure 2.1 (a) and (b), respectively. Chiral nanotubes exhibit a spiral symmetry whose mirror image cannot be superposed on to the original one.

In Figure 2.2, the two dimensional graphene sheet is shown. A SWCN is formed by rolling the honeycomb sheet so that points $O$ and $A$ coincide (and points $B$ and $B'$ coincide). Thus, we can specify the structure of a SWCN by the vector $C_h$ (Figure 2.2), which is called the chiral vector. The chiral vector $C_h$ can be expressed by the real space unit vectors $a_1$ and $a_2$ (Figure 2.2):

$$C_h = n a_1 + m a_2 \equiv (n, m), \ (n, m \text{ are integers, } 0 \leq |m| \leq n) \quad (2.1)$$
Figure 2.1: Typical examples of carbon nanotubes: (a) armchair, (b) zigzag and (c) chiral nanotubes.

The condition for \(0 \leq |m| \leq n\) does not lead to loss of generality because of the hexagonal symmetry of the honeycomb lattice. Moreover, with the definition of the chiral vector \(C_h\), an armchair nanotube correspond to the case of \(n = m\), and a zigzag nanotube corresponds to the case of \(m = 0\). All other \((n, m)\) chiral vectors corresponds to chiral nanotubes.

Once the chiral vector \(C_h\) for a nanotube is given, all the other parameters of that nanotube can be determined by \((n, m)\). The circumferential length \(L\) and the diameter \(d_t\) are given by

\[
L = |C_h| = a\sqrt{n^2 + m^2 + nm}, \quad d_t = L/\pi
\]

(2.2)

where \(a = |a_1| = |a_2| = 1.44\text{Å} \times \sqrt{3} = 2.49\text{Å}.\) The angle between the vectors

\(^1\)The C-C bond lengths of graphite and nanotube are 1.42Å and 1.44Å, respectively.
Figure 2.2: The two dimensional graphene sheet. A nanotube is constructed by rolling the graphene sheet so that points $O$ and $A$ coincide, and points $B$ and $B'$ coincide. $\overrightarrow{OA}$ and $\overrightarrow{OB}$ define the chiral vector $C_h$ and the translational vector $T$ of the nanotube, respectively.

$C_h$ and $a_1$ is called the chiral angle $\theta$ (Figure 2.2), and is given by

$$
\cos \theta = \frac{2n + m}{2\sqrt{n^2 + m^2 + nm}}
$$

(2.3)

In Figure 2.2, $\overrightarrow{OB}$ has defined the translational vector $T$, which is parallel to the nanotube axis and is normal to the chiral vector $C_h$, and is expressed as:

$$
T = t_1a_1 + t_2a_2 \equiv (t_1, t_2)
$$

(2.4)

We can obtain the expression for $t_1$ and $t_2$ by imposing the requirement that vector $T$ corresponds to the first lattice point of the 2D graphene sheet. Thus, we have

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

(2.5)

where $d_R$ is the greatest common divisor of $(2m + n)$ and $(2n + m)$. The unit cell of the nanotube is defined by the vectors $C_h$ and $T$, and the number of carbon
atoms in each unit cell of the nanotube is $2N$, with

$$N = \frac{2n^2 + m^2 + nm}{d_R}$$  \hspace{1cm} (2.6)

The symmetry vector $\mathbf{R}$ (Figure 2.2) is defined as the site vector having the smallest component in the direction of $\mathbf{C}_h$, and is expressed as:

$$\mathbf{R} = pa_1 + qa_2 \equiv (p, q)$$  \hspace{1cm} (2.7)

where $p$ and $q$ do not have a common divisor except for unity, and satisfy the condition

$$t_1q - t_2p = 1, \quad (0 < mp - nq \leq N)$$  \hspace{1cm} (2.8)

### 2.2 Unit Cell and Brillouin Zones

The unit cell for a carbon nanotube in real space is given by the rectangle generated by the chiral vector $\mathbf{C}_h$ and the translational vector $\mathbf{T}$, as shown in Figure 2.2. In Figure 2.3, we show the reciprocal lattice vectors, $\mathbf{K}_1$ and $\mathbf{K}_2$ for a

![Diagram](image)

Figure 2.3: The Brillouin zone of a carbon nanotube is represented by the line segment $WW'$ which is parallel to $\mathbf{K}_2$. The vectors $\mathbf{K}_1$ and $\mathbf{K}_2$ are reciprocal lattice vectors corresponding to $\mathbf{C}_h$ and $\mathbf{T}$, respectively.

$\mathbf{C}_h = (4, 2)$ chiral nanotube. Expressions for the reciprocal lattice vectors $\mathbf{K}_2$ along the nanotube axis and $\mathbf{K}_1$ in the circumferential direction are obtained
from the relation $\mathbf{R}_i \cdot \mathbf{K}_j = 2\pi \delta_{ij}$, where $\mathbf{R}_i$ and $\mathbf{K}_j$ are, respectively, the lattice vectors in real and reciprocal space. In fact, since nanotubes are 1D materials, only $\mathbf{K}_2$ is a reciprocal lattice vector, and $\mathbf{K}_1$ gives discrete $k$ values in the direction of $\mathbf{C}_h$. Using Equations 2.5, 2.6 and the relations

\[
\begin{align*}
\mathbf{C}_h \cdot \mathbf{K}_1 &= 2\pi, \quad \mathbf{T} \cdot \mathbf{K}_1 = 0 \\
\mathbf{C}_h \cdot \mathbf{K}_2 &= 0, \quad \mathbf{T} \cdot \mathbf{K}_2 = 2\pi 
\end{align*}
\] (2.9)

we get expressions for $\mathbf{K}_1$ and $\mathbf{K}_2$:

\[
\begin{align*}
\mathbf{K}_1 &= \frac{1}{N} ( -t_2 \mathbf{b}_1 + t_1 \mathbf{b}_2 ) , \quad \mathbf{K}_2 = \frac{1}{N} ( m\mathbf{b}_1 - n\mathbf{b}_2 ) 
\end{align*}
\] (2.10)

where $\mathbf{b}_1$ and $\mathbf{b}_2$ are the reciprocal lattice vectors of 2D graphite (see Figure 3.1). The first Brillouin zone of this 1D material is the line segment $WW'$ as shown in Figure 2.3. Since $N\mathbf{K}_1 = -t_2 \mathbf{b}_1 + t_1 \mathbf{b}_2$ corresponds to a reciprocal lattice vector of 2D graphite, two wave vectors which differ by $N\mathbf{K}_1$ are equivalent. Since $t_1$ and $t_2$ do not have a common divisor except for unity, none of the $N-1$ vectors $\mu\mathbf{K}_1$ (where $\mu = 1, \cdots, N-1$) are reciprocal lattice vectors of 2D graphite. Thus the $N$ wave vectors $\mu\mathbf{K}_1$ ($\mu = 0, \cdots, N-1$) give rise to $N$ discrete $k$ vectors, as indicated by the $n = 28$ parallel line segments in Figure 2.3, which arise from the quantized wave vectors associated with the periodic boundary conditions on $\mathbf{C}_h$. The length of all the parallel lines in Figure 2.3 is $2\pi/|\mathbf{T}|$ which is the length of the 1D first Brillouin zone.
Chapter 3

Theory

Since the band structures of graphite and $C_{60}$ calculated with the tight binding model [8] are essentially identical to those from the \textit{ab initio} local-density calculation [9], and it only needs a few parameters in the model, thus we use Slater-Koster [10] tight-binding model to calculate the electronic structure of carbon nanotube. In this chapter, we first introduce the basic theory that underlies the mode, and calculate the band structure for graphite, which is important for understanding the electronic structure of carbon nanotubes in further discussion.

3.1 Tight Binding Calculation

Because of the translational symmetry of the unit cells in the direction of the lattice vectors, $\vec{a}_i$ ($i = 1, \cdots, 3$), any wavefunction of the lattice, $\Psi$, should satisfy Bloch’s theorem

$$T_{\vec{a}_i} \Psi = e^{i \vec{k} \cdot \vec{a}_i} \Psi, \quad (i = 1, \cdots, 3)$$

(3.1)

where $T_{\vec{a}_i}$ is a translational operation along the lattice vector $\vec{a}_i$, and $\vec{k}$ is the wave vector. There are many possible functional forms of $\Psi$ which satisfy Equation 3.1, in this paper, we choose the $j$-th atomic orbital in the unit cell as basis states in which the wave function is expanded. A tight binding Bloch function $\Phi_j(\vec{k}, \vec{r})$ is given by,

$$\Phi_j(\vec{k}, \vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i \vec{k} \cdot \vec{R}} \varphi_j(\vec{r} - \vec{R}), \quad (j = 1, \cdots, n)$$

(3.2)

Here $\vec{R}$ is the position of the atom and $\varphi_j$ denotes the atomic wavefunction in state $j$. The number of atomic wavefunctions in the unit cell is denoted by $n$.  

9
and we have \( n \) Bloch functions in the solid for a given \( \vec{k} \). To form \( \Phi_j(\vec{k}, \vec{r}) \) in Equation 3.2, the \( \varphi_j \)'s in the \( N \ (\sim 10^{24}) \) unit cells are weighted by the phase factor \( \exp(i\vec{k} \cdot \vec{R}) \) and are then summed over the lattice vectors \( \vec{R} \) of the whole crystal.

It is clear that Equation 3.2 satisfies Equation 3.1 since

\[
\Phi_j(\vec{k}, \vec{r} + \vec{a}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \varphi_j(\vec{r} + \vec{a} - \vec{R})
\]

\[
= e^{i\vec{k} \cdot \vec{a}} \frac{1}{\sqrt{N}} \sum_{\vec{R}-\vec{a}} e^{i\vec{k} \cdot (\vec{R} - \vec{a})} \varphi_j(\vec{r} - (\vec{R} - \vec{a}))
\]

\[
= e^{i\vec{k} \cdot \vec{a}} \Phi_j(\vec{k}, \vec{r})
\]

(3.3)

where we use the periodic boundary condition for the \( M = N^{-1/3} \) unit vectors in each \( \vec{a}_i \) direction,

\[
\Phi_j(\vec{k}, \vec{r} + M\vec{a}_i) = \Phi_j(\vec{k}, \vec{r}) \quad (i = 1, \ldots, 3)
\]

(3.4)

which is consistent with the boundary condition imposed on the translation vector \( T_{M\vec{a}_i} = 1 \). From this boundary condition, the phase factor appearing in Equation 3.2 satisfies \( \exp(ikMa_i) = 1 \), from which the wave number \( k \) is related by an integer \( p \),

\[
k = \frac{2p\pi}{Ma_i}, \quad (p = 0, 1, \ldots, M - 1), \quad (i = 1, \ldots, 3)
\]

(3.5)

In three dimension, the wave vector \( \vec{k} \) is defined for the \( x \), \( y \) and \( z \) directions, as \( k_x \), \( k_y \) and \( k_z \). Thus \( M^3 = N \) wave vectors exist in the first Brillouin zone, where \( k_i \) can be considered as continuum variables.

The eigenfunctions in the solid, \( \Psi_j(\vec{k}, \vec{r}) \) \((j = 1, \ldots, n)\), where \( n \) is the number of Bloch wavefunctions, are expressed by a linear combination of Bloch functions \( \Phi_{j'}(\vec{k}, \vec{r}) \) as follows:

\[
\Psi_j(\vec{k}, \vec{r}) = \sum_{j'=1}^{n} C_{jj'}(\vec{k}) \Phi_{j'}(\vec{k}, \vec{r})
\]

(3.6)
where \( C_{ij}(\vec{k}) \) are coefficients to be determined. Since the function \( \Psi_j(\vec{k}, \vec{r}) \) should also satisfy Bloch’s theorem, the summation in Equation 3.6 is taken only for the Bloch orbitals \( \Phi_j(\vec{k}, \vec{r}) \) with the same value of \( k \).

The \( j \)-th eigenvalue \( E_j(\vec{k}) \) \((j = 1, \cdots, n)\) as a function of \( \vec{k} \) is given by

\[
E_j(\vec{k}) = \frac{\langle \Psi_j | H | \Psi_j \rangle}{\langle \Psi_j | \Psi_j \rangle} = \frac{\int \Psi_j^* H \Psi_j \, d\vec{r}}{\int \Psi_j^* \Psi_j \, d\vec{r}}
\tag{3.7}
\]

where \( H \) is the Hamiltonian of the solid. Substituting Equation 3.6 into Equation 3.7 and making a change of subscripts, we obtain the following equation

\[
E_j(\vec{k}) = \frac{\sum_{j,j'=1}^n C_{ij}' C_{ij} \langle \Phi_j | H | \Phi_{j'} \rangle}{\sum_{j,j'=1}^n C_{ij}' C_{ij} \langle \Phi_j | \Phi_{j'} \rangle} = \frac{\sum_{j,j'=1}^n H_{jj'}(\vec{k}) C_{ij}' C_{ij}}{\sum_{j,j'=1}^n S_{jj'}(\vec{k}) C_{ij}' C_{ij}}
\tag{3.8}
\]

where the integrals over the Bloch orbitals, \( H_{jj'}(\vec{k}) \) and \( S_{jj'}(\vec{k}) \) are called transfer integral matrices and overlap integral matrices, respectively, which are defined by

\[
H_{jj'}(\vec{k}) = \langle \Phi_j | H | \Phi_{j'} \rangle, \quad S_{jj'}(\vec{k}) = \langle \Phi_j | \Phi_{j'} \rangle \quad (j = 1, \cdots, n)
\tag{3.9}
\]

When we fix the values of the \( n \times n \) matrices \( H_{jj'}(\vec{k}) \) and \( S_{jj'}(\vec{k}) \) in Equation 3.9 for a given \( \vec{k} \) value, by variational principle, the coefficient \( C_{ij}' \) is optimized so as to minimize \( E_j(\vec{k}) \). It is noted that the coefficient \( C_{ij}' \) is also a function of \( \vec{k} \), and therefore \( C_{ij}' \) is determined for each \( \vec{k} \). When we take a partial derivative for \( C_{ij}' \) while fixing the other \( C_{ij}, C_{ij}', \) and \( C_{ij} \) coefficients, we obtain zero for the local minimum condition as follows,

\[
\frac{\partial E_j(\vec{k})}{\partial C_{ij}'} = \frac{\sum_{j,j'=1}^n H_{jj'}(\vec{k}) C_{ij}'}{\sum_{j,j'=1}^n S_{jj'}(\vec{k}) C_{ij}'} - \frac{\sum_{j,j'=1}^n H_{jj'}(\vec{k}) C_{ij}'}{\left( \sum_{j,j'=1}^n S_{jj'}(\vec{k}) C_{ij}'^2 \right)^2} \sum_{j'=1}^n S_{jj'}(\vec{k}) C_{ij'} = 0
\tag{3.10}
\]
or more simply,

\[ \sum_{j'=1}^{n} H_{j j'}(\vec{k}) C_{i j'} = E_{i}(\vec{k}) \sum_{j'=1}^{n} S_{j j'}(\vec{k}) C_{i j'} \]  

(3.11)

Defining a column vector,

\[ C_{i} = \begin{pmatrix} C_{i1} \\ \vdots \\ C_{in} \end{pmatrix} \]  

(3.12)

Equation 3.11 is expressed by

\[ H C_{i} = E_{i}(\vec{k}) S C_{i} \]  

(3.13)

For eigenfunction to be non-zero, we have

\[ \text{det} |H - E_S| = 0 \]  

(3.14)

where Equation 3.14 is called the secular equation. It is customary to choose the scale of the basis states such that they are normalized; that is, \( S_{j j} = 1 \). Moreover, we shall assume that the basis states are orthogonal: \( S_{j j'} = 0 \) (\( j \neq j' \)). This may in fact not be true, however, the corrections can largely be absorbed in the parameters of the theory [11]. Therefore Equation 3.14 is further simplified as

\[ \text{det} |H - E I| = 0 \]  

(3.15)

where \( I \) is the identity matrix. The one-electron energy eigenvalues \( E_{i}(\vec{k}) \) are obtained by solving the secular Equation 3.15. The actual procedure of the tight binding calculation is as follows:

1. Specify the unit cell and unit vectors, \( \vec{a}_i \). Specify the coordinates of the atoms in the unit cell and select \( n \) atomic orbitals which are considered in the calculation.

2. Specify the Brillouin zone and the reciprocal lattice vectors, \( \vec{b}_i \). Select the high symmetry directions in the Brillouin zone, and \( \vec{k} \) points along the high symmetry axes.

3. For the selected \( \vec{k} \) points, calculate the transfer matrix, \( H_{ij} \).
4. For the selected \( \vec{k} \) points, solve the secular Equation 3.15 and obtain the eigenvalues \( E_i(\vec{k}) \) \((i = 1, \ldots, n)\) and the coefficients \( C_{ij}(\vec{k}) \).

In applying these calculational approaches to real systems, the symmetry of the problem is considered in detail on the basis of a tight-binding approach and the transfer matrix elements are often treated as parameters selected to reproduce the band structure of the solid obtained either experimentally or from first principles calculations. Both extrapolation methods such as \( \vec{k} \cdot \vec{p} \) perturbation theory or interpolation methods using the Slater-Koster approach are commonly employed for carbon-related systems [12].

### 3.2 Electronic Structure of Graphite

In Figure 3.1 we show (a) the unit cell and (b) the Brillouin zone of two dimensional graphite as a dotted rhombus and shaded hexagon, respectively, where \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) are unit vectors in real space, and \( \mathbf{b}_1 \) and \( \mathbf{b}_2 \) are reciprocal lattice vectors. By selecting the first Brillouin zone as the shaded hexagon, the highest symmetry is obtained for the Brillouin zone of 2D graphite. The three high symmetry points \( \Gamma, K \) and \( M \) are defined as the center, the corner and the edge, respectively. As we know that the \( \pi \) energy bands are covalent and are the most important for determining the solid state properties of graphite, we consider only \( \pi \) energy bands for 2D graphite.

Two Bloch functions, constructed from atomic orbitals for the two inequivalent carbon atoms at A and B in Figure 3.1 are given by

\[
\Phi_j(r) = \frac{1}{\sqrt{N}} \sum_{R_\alpha} e^{ikR_\alpha} \varphi_j(r - R_\alpha), \quad (\alpha = A, B)
\]

where the summation is taken over the atom site coordinate \( R_\alpha \) for the A or B carbon atoms in the solid.

The \( (2 \times 2) \) matrix Hamiltonian, \( H_{\alpha\beta}, \ (\alpha, \beta = A, B) \) is obtained by substituting
Figure 3.1: (a) The unit cell and (b) Brillouin zone of two dimensional graphite are shown as the dotted rhombus and the shaded hexagon, respectively. $a_i$ and $b_i$, ($i = 1, 2$) are unit vectors and reciprocal lattice vectors, respectively.
Equation 3.16 into Equation 3.9. When $\alpha = \beta = A$

$$H_{AA}(r) = \frac{1}{N} \sum_{R,R'} e^{ik(R-R')} \langle \varphi_A(r-R') | H | \varphi_A(r-R) \rangle$$

$$= \frac{1}{N} \sum_{R=R'} e^{2\pi p} + \frac{1}{N} \sum_{R=R'+a} e^{\pm ika} \langle \varphi_A(r-R') | H | \varphi_A(r-R) \rangle$$

$$= \epsilon_{2p} + \text{(terms equal to or more distant than } R = R' \pm 2a)$$

$$= \epsilon_{2p} + \text{(terms equal to or more distant than } R = R' \pm 2a)$$

(3.17)

When we consider only nearest-neighbor interactions, then there is only an integration over a single atom in $H_{AA}$ and $H_{BB}$, and thus $H_{AA} = H_{BB} = \epsilon_{2p}$. For the off-diagonal matrix element $H_{AB}(r)$, the largest contribution to $H_{AB}(r)$ arises when atom A and B are nearest neighbors. Thus, in the summation over $R'$, we obtain

$$H_{AB} = t(e^{ik\vec{R}_1} + e^{ik\vec{R}_2} + e^{ik\vec{R}_3})$$

$$= tf(k)$$

(3.18)

where the $t$ is the transfer integral

$$t = \langle \varphi_A(r-R) | H | \varphi_B(r-R \pm a/2) \rangle$$

(3.19)

and $f(k)$ is a function of the sum of the phase factors of $e^{ik\vec{R}}$ ($j = 1, \cdots, 3$). Using the $x$, $y$ coordinates of Figure 3.1, $f(k)$ is given by:

$$f(k) = e^{ik_x a/\sqrt{3}} + 2e^{-ik_x a/2\sqrt{3}} \cos \left( \frac{k_y a}{2} \right)$$

(3.20)

Solving the secular equation $\det |H_E I| = 0$ for

$$H = \begin{pmatrix} \epsilon_{2p} & tf(k) \\ tf(k)^* & \epsilon_{2p} \end{pmatrix}$$

(3.21)

we obtain the energy dispersion relation as:

$$E_{g2D}(k_x, k_y) = \pm t \left\{ 1 + 4 \cos \left( \frac{\sqrt{3}k_x a}{2} \right) \cos \left( \frac{k_y a}{2} \right) + 4 \cos^2 \left( \frac{k_y a}{2} \right) \right\}^{1/2}$$

(3.22)
Chapter 4

Electronic Structure of Single-Wall Nanotubes

Usually, the diameter of the carbon nanotube, \( d_t \sim \) several nm, is much larger than the nearest-neighbor distance between two carbon atoms, \( a_{c-c} = 1.44\text{Å} \), in nanotube, thus we can derive the electronic structure of carbon nanotubes by simply zone-folding from that of 2D graphite. However, as the diameter grows smaller and smaller, we have to take account of the curvature effect. In this chapter, we first show how to obtain the energy band of nanotubes by the zone-folding effect, and then introduce the curvature effect in our model.

4.1 Zone-Folding of Energy Dispersion Relations

The electronic structure of a single-wall nanotube can be obtained simply from that of 2D graphite if the nanotube’s diameter is not very small. By using periodic boundary conditions in the circumferential direction denoted by the chiral vector \( C_h \), the wave vector associated with the \( C_h \) direction becomes quantized, while the wave vector associated with the direction of the translational vector \( T \) (or along the nanotube axis) remains continuous for a nanotube of infinite length. Thus the energy bands consist of a set of 1D energy dispersion relations which are cross sections of those for 2D graphite.

When the energy dispersion relations of 2D graphite, \( E_{g2D} \) (Equation 3.22) at line segments shifted from \( WW' \) by \( \mu K_1 \) \((\mu = 0, \cdots, N - 1)\) are folded so that the wave vectors parallel to \( K_2 \) coincide with \( WW' \) as shown in Figure 4.1 [6], \( N \) pairs of 1D energy dispersion relations are given by

\[
E_\mu(k) = E_{g2D}\left(k\frac{K_2}{|K_2|} + \mu K_1\right), \quad (\mu = 0, \cdots, N - 1, \text{ and } -\frac{\pi}{T} < k < \frac{\pi}{T})
\]  

(4.1)
corresponding to the energy dispersion relations of a single-wall carbon nanotube. The $N$ pairs of energy dispersion curves given by Equation 4.1 correspond to the cross sections of the 2D energy dispersion surface, where cuts are made on the lines of $k_2 |K_2| + \mu K_1$. If for a particular $(n,m)$ nanotube, the cutting line passes through a $K$ point of the 2D Brillouin zone (Figure 3.1), where the $\pi$ and $\pi^*$ energy bands of 2D graphite are degenerate by symmetry, the 1D energy band has a zero energy gap.

The condition for obtaining a metallic energy band is that the ratio of the length of the vector $Y \vec{K}$ to that of $K_1$ in Figure 4.1 is an integer. Since the vector $Y \vec{K}$ is given by

$$Y \vec{K} = \frac{2n + m}{3} K_1$$

the condition for metallic nanotube is that $(2n + m)$ or equivalently $(n - m)$ is a multiple of 3.
4.2 Our Model

As the diameter of nanotube become comparable to the nearest-neighbor distance between two carbon atoms, we have to take account of the effect of curvature in calculating the energy dispersion relations. In the previous calculation, we simply assume that the $2p_z$ orbitals, which is responsible for the $\pi$ band, of the two nearest carbon atoms are perpendicular to the graphene sheet (see Figure 4.2 (a)), and parallel to each other. However, in reality, when graphene sheet rolls up to form a cylinder, the two $2p_z$ orbitals form an angle between them (see Figure 4.2 (b)). Thus, to include this effect in those nanotubes with small diameter, we have to start from very beginning to reconstruct the Hamiltonian.

Let us consider an atomic site $\vec{r}_i^\alpha$ on the cylindrical surface of a nanotube as shown in Figure 4.3. We define the translational operator $\hat{T}(\vec{r}_i^\alpha)$ and rotational operator about $y$ axis, $\hat{R}(\psi_i^\alpha)$, as

\[
\hat{T}(\vec{r}_i^\alpha)f(\vec{r}) = f(\vec{r} - \vec{r}_i^\alpha) \\
\hat{R}(\psi_i^\alpha)f(\psi) = f(\psi - \psi_i^\alpha)
\]  

(4.3)

also, we define $\vec{c}_i$ $(i = 1, \cdots, 3)$ to be the vectors pointing from a reference atom $O$ to its nearest atom sites on an unrolled graphene sheet as shown in Figure 4.4 (a). The reference atom $O$ is mapped to an arbitrary point $O'$ on the cylindrical nanotube surface in Figure 4.4 (b), and the vectors $\vec{c}_i$ $(i = 1, \cdots, 3)$ in Figure 4.4 (a) are mapped to the corresponding vectors $\vec{d}_i$ $(i = 1, \cdots, 3)$ in Figure 4.4 (b), respectively.

Now there are four atomic orbitals per carbon atom, $2s$, $2p_x$, $2p_y$ and $2p_z$. We thus have eight Bloch orbitals in the 2 atom unit cell for unrolled graphene sheet, resulting in an $8 \times 8$ Hamiltonian matrix. The Bloch orbitals consisting of A and B atoms are given by

\[
\Phi_j^\alpha(\vec{r}) = \frac{1}{\sqrt{N}} \sum_i e^{ik\cdot\vec{r}_i^\alpha} \hat{T}(\vec{r}_i^\alpha) \hat{R}(\psi_i^\alpha) \varphi_j(\vec{r}), \quad (\alpha = A, B)
\]  

(4.4)

where the summation is taken over the atom site $i$ for the A or B carbon atoms in the solid. The $\varphi_j$'s are the atomic orbitals for the free atom: $2s^A$, $2p_x^A$, $2p_y^A$, $2p_z^A$. 18
Figure 4.2: The side view of p orbitals for (a) the unrolled graphene sheet, and (b) rolled graphene sheet. The shading denotes the positive amplitude of the wavefunction.
2p^A, 2s_B, 2p^B, 2p_y, 2p_z. Then the matrix elements coupling the same atoms (for example A and A) can be expressed by a 4×4 small matrix which is a sub-block of the 8×8 matrix. Within the nearest-neighbor site approximation, the small Hamiltonian matrix is a diagonal matrix as follows,

\[
H_{AA} = \begin{pmatrix}
\epsilon_{2s} & 0 & 0 & 0 \\
0 & \epsilon_{2p} & 0 & 0 \\
0 & 0 & \epsilon_{2p} & 0 \\
0 & 0 & 0 & \epsilon_{2p}
\end{pmatrix}
\]  \hspace{1cm} (4.5)

where

\[
\epsilon_{2s} = \langle 2s | H | 2s \rangle, \quad \epsilon_{2p} = \langle 2p_x | H | 2p_x \rangle = \langle 2p_y | H | 2p_y \rangle = \langle 2p_z | H | 2p_z \rangle
\]  \hspace{1cm} (4.6)

For matrix elements between the A and B atoms, from Eq.(4.4)

\[
\langle \Phi_j^A | H | \Phi_{j'}^B \rangle = \frac{1}{N} \sum_{i,i'}^N e^{i\vec{k} \cdot (\vec{r}_i^A - \vec{r}_i^B)} \langle \hat{T}(\vec{r}_i^A) \hat{R}(\psi_i^A) \varphi_j(\vec{r}) | H | \hat{T}(\vec{r}_{i'}^B) \hat{R}(\psi_{i'}^B) \varphi_{j'}(\vec{r}) \rangle
\]

\[
= \sum_{i=1}^3 \langle \varphi_j(\vec{r}) | H | \hat{T}(\vec{a}_i) \hat{R}(\psi_i) \varphi_{j'}(\vec{r}) \rangle
\]  \hspace{1cm} (4.7)
Figure 4.4: Conformal mapping of (a) $O$ point and vectors $\vec{c}_i$ $(i = 1, \cdots, 3)$ on an unrolled graphene sheet to (b) $O'$ point and vectors $\vec{d}_i$ $(i = 1, \cdots, 3)$ on a real cylindrical nanotube surface, correspondingly.
where

\[ u_i = e^{ik_i} \hat{e}_i, \quad (i = 1, 2, 3) \quad (4.8) \]

and \( \psi_i \ (i = 1, \cdots, 3) \) are the azimuthal angles of the corresponding vectors \( \vec{d}_i \ \ (i = 1, \cdots, 3) \). In last step of Eq.(4.7), we make the use of the nearest-neighbor site approximation. The various off-site matrix elements are listed as follows:

1. \( \varphi_j = 2s^A, \varphi_j' = 2s^B \)

\[ \langle \varphi_j(\vec{r}) | H | \tilde{T}(\vec{d}_i) \tilde{R}(\psi_i) \varphi_j'(\vec{r}) \rangle = \langle 2s^A | H | 2s^B \rangle \]

\[ = V_{ss} \quad (4.9) \]

2. \( \varphi_j = 2s^A, \varphi_j' = 2p^B_\lambda; \quad (\lambda = x, y, z) \)

\[ \langle \varphi_j(\vec{r}) | H | \tilde{T}(\vec{d}_i) \tilde{R}(\psi_i) \varphi_j'(\vec{r}) \rangle = \langle 2s^A | H | 2p^B_\lambda \rangle \]

\[ = (2\tilde{p}^B_\lambda \cdot \hat{d}_i) V_{spa}, \quad (i = 1, 2, 3) \quad (4.10) \]

where \( \hat{d}_i = \frac{\vec{d}_i}{|\vec{d}_i|} \) is the unit vector of \( \vec{d}_i \), and \( 2\tilde{p}^B_\lambda \) is the unit vector in the direction of \( |2p^B_\lambda| \) orbital at atom site \( \vec{d}_i \)\(^1\).

3. \( \varphi_j = 2p^A_\gamma, \varphi_j' = 2s^B; \quad (\gamma = x, y, z) \)

\[ \langle \varphi_j(\vec{r}) | H | \tilde{T}(\vec{d}_i) \tilde{R}(\psi_i) \varphi_j'(\vec{r}) \rangle = \langle 2p^A_\gamma | H | 2s^B_i \rangle \]

\[ = - (2\tilde{p}^A_\gamma \cdot \hat{d}_i) V_{spa}, \quad (i = 1, 2, 3) \quad (4.11) \]

the negative sign arises from the fact that \( \vec{d}_i \) is now pointing from a \( p \) orbital to a \( s \) orbital.

4. \( \varphi_j = 2p^A_\gamma, \varphi_j' = 2p^B_\lambda; \quad (\gamma, \lambda = x, y, z) \)

\[ \langle \varphi_j(\vec{r}) | H | \tilde{T}(\vec{d}_i) \tilde{R}(\psi_i) \varphi_j'(\vec{r}) \rangle = \langle 2p^A_\gamma | H | 2p^B_\lambda \rangle \quad (4.12) \]

\(^1\)The \( p \) orbitals behave like a vector, \((x, y, z)\), in which we mean a wavefunction \( C_x |p_x\rangle + C_y |p_y\rangle + C_z |p_z\rangle \), where \( C_x^2 + C_y^2 + C_z^2 = 1 \), is another \( p \) wavefunction whose direction of positive amplitude is the direction \((C_x, C_y, C_z)\). Thus, we can assign a unit vector \( \vec{p} \) to a \( p \) orbital.
\[
\begin{align*}
&= (2\hat{\rho}_a^A \cdot \hat{d}_i)(2\hat{\rho}_\lambda^{B_i} \cdot \hat{d}_i)V_{pp\sigma} \\
&+ \left[ 2\hat{\rho}_a^A \cdot 2\hat{\rho}_\lambda^{B_i} - (2\hat{\rho}_a^A \cdot \hat{d}_i)(2\hat{\rho}_\lambda^{B_i} \cdot \hat{d}_i) \right] V_{pp\pi} \\
&(i = 1, 2, 3)
\end{align*}
\]

Thus, once the various transfer integral matrix elements are known, we can calculate the energy band structure for the carbon nanotubes. We used the first nearest neighbor parameters proposed in Reference [7] for graphite, and listed in Table 4.1.

<table>
<thead>
<tr>
<th>Transfer integral matrices</th>
<th>(\epsilon_{2s})</th>
<th>(\epsilon_{2p})</th>
<th>(V_{ss\sigma})</th>
<th>(V_{sp\sigma})</th>
<th>(V_{pp\sigma})</th>
<th>(V_{pp\pi})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy (eV)</td>
<td>-7.3</td>
<td>0.0</td>
<td>-4.30</td>
<td>4.98</td>
<td>6.38</td>
<td>-2.66</td>
</tr>
</tbody>
</table>

Table 4.1: The values of the Slater-Koster parametrized transfer integral matrices for graphite.

### 4.3 Results and Discussion

We have calculated the electronic structure of the zigzag nanotubes \(C_h = (n, 0)\) for \((n = 5, \cdots, 9)\) using our model, and plot the results in Figure 4.7 (b)–4.11 (b). We also plot the energy bands with only the zone folding effect in Figures 4.7 (a)–4.11 (a) for comparison. The values of the energy band gaps calculated by our model are listed in Table 4.2.

<table>
<thead>
<tr>
<th>Nanotubes ((n, 0))</th>
<th>((5, 0))</th>
<th>((6, 0))</th>
<th>((7, 0))</th>
<th>((8, 0))</th>
<th>((9, 0))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy band gaps (eV)</td>
<td>1.432</td>
<td>0.287</td>
<td>0.937</td>
<td>1.338</td>
<td>0.131</td>
</tr>
</tbody>
</table>

Table 4.2: The values of energy band gaps calculated by our model for nanotubes \((n, 0)\) \((n = 5, \cdots, 9)\).

As we have discussed in Section 4.1, the bonding and antibonding \(\pi\) bands are degenerate at the \(K\) point in the Brillouin zone of a graphene sheet in Figure 4.1. Therefore, if a vertical line crosses the \(K\) point, namely, if \(n - m\) is a multiple of 3 the nanotube is a metal as shown in Figure 4.8 (a) and 4.11 (a). However, in our model, we found that the degenerate point is actually moved from the \(K\) point to the position shown by open circles in Figure 4.5 (the right-most circle is
denote as $K'$). The nanotube thus becomes a narrow-gap semiconductor, not a metal, as shown in Figure 4.8 (b) and Figure 4.11 (b).

Figure 4.5: The first Brillouin zone of a graphite sheet (dashed lines), and the wave vectors allowed by the periodic boundary condition along the circumference for (6,0) (solid lines). Open circles show the points where the bonding and the antibonding $\pi$ bands are degenerated in the nanotube (the right-most one is denoted as $K'$).

Moreover, we plot the ratio $\Gamma K' / \Gamma K$ for nanotube $(n,0)$ ($n = 5, \cdots, 9$) in Figure 4.6. When diameter of nanotube increases, the cylindrical surface become flatter, and as a result, the curvature effect that we have discussed in Section 4.2 reduces. As a limiting case, when diameter approach to infinite, we recover the graphene sheet, and the shifted degenerate point $K'$ approach to the original $K$ point as indicated by the decreasing of ratio $\Gamma K' / \Gamma K$ in Figure 4.6.
Figure 4.6: The ratio $\Gamma K'/\Gamma K$ for nanotube $(n,0)$ ($n = 5, \cdots, 9$).

Figure 4.7: The band structure of carbon nanotube $(5,0)$ calculated by (a) zone-folding for the $\pi$ band of 2D graphite, and (b) our model.
Figure 4.8: The band structure of carbon nanotube \((6, 0)\) calculated by (a) zone-folding for the \(\pi\) band of 2D graphite, and (b) our model.

Figure 4.9: The band structure of carbon nanotube \((7, 0)\) calculated by (a) zone-folding for the \(\pi\) band of 2D graphite, and (b) our model.
Figure 4.10: The band structure of carbon nanotube (8,0) calculated by (a) zone-folding for the π band of 2D graphite, and (b) our model.

Figure 4.11: The band structure of carbon nanotube (9,0) calculated by (a) zone-folding for the π band of 2D graphite, and (b) our model.
Chapter 5

Optical Properties

Optical studies of solids probe the details of the electronic structure. The central property is the response of the solid to some external electromagnetic field or mechanical force. In this chapter we introduce the complex dielectric function, which connects the microscopic interaction processes between the elementary excitations with photons and the macroscopic effect of absorption, reflection, and dispersion. Moreover, the differences of the selection rule for the interband transitions in case of polarization of electric field perpendicular and parallel to the nanotube’s axis are explained also.

5.1 Basic Theory

The effect of a radiation field on the crystal electronic states can be studied using standard quantum mechanical methods. From standard classical mechanics we know that the kinetic energy of a system of $N$ electrons

$$
\sum_{i=1}^{N} \frac{p_i^2}{2m}
$$

has to be replaced, in the presence of an electromagnetic field, by the expression

$$
\sum_{i=1}^{N} \left[ \frac{1}{2m} \left( p_i + \frac{eA(r_i, t)}{c} \right)^2 \right],
$$

where $e$ is the absolute value of the electron charge, $A$ is the vector potential of the electromagnetic field, and the scalar potential $V$ has been taken as zero without loss of generality because of the arbitrariness in the gauge. Furthermore
we can now neglect non-linear effects by disregarding the term in $A^2$. We then find that the interaction Hamiltonian of electrons in a radiation field is given by the expression

$$H_{eR} = \frac{e}{mc} \sum_{i=1}^{N} A\left(r_i, t\right) \cdot p_i.$$  \hspace{1cm} (5.1)

The effect of a radiation field on the crystal states can be studied by treating $H_{eR}$ as a time dependent perturbation term on the electronic states of the crystal. This time dependent term will cause electrons to make transitions between occupied bands and empty bands. From the transition probability rate, the relationship between the electronic structure and the phenomenological optical constants can be derived.

From elementary quantum mechanics we know that, to first order in perturbation theory, the probability per unit time that a perturbation of the form $\mathcal{L} e^{\pm i\omega t}$ induces a transition from the initial state $|i\rangle$ of energy $E_i$ to the final state $|f\rangle$ of energy $E_f$ is

$$P_{i \rightarrow f} = \frac{2\pi}{\hbar} |\langle f | \mathcal{L} | i\rangle|^2 \delta (E_f - E_i \mp \hbar \omega).$$  \hspace{1cm} (5.2)

The above relation has the interpretation that a perturbation $\mathcal{L} e^{-i\omega t}$ induces transitions with absorption of a quantum energy $\hbar \omega$, while a perturbation $\mathcal{L} e^{i\omega t}$ gives rise to emission of a quantum energy $\hbar \omega$. Since the perturbation must be real we have the sum of both absorption and emission terms, but the choice of initial and final states in Eq.(5.2) selects out the term to be considered. If the initial state is the ground state, the emission term vanishes. Thus only the absorption term needs to be considered in discussing the optical excitation spectrum of a crystal in the ground state.

We now calculate the contribution to the optical constants due to a couple of valence and conduction bands. The ground state of the electronic system can be written as a Slater determinant

$$\Psi_o = A \left\{ \psi_{vk_1}(r_1) \alpha(1) \psi_{vk_1}(r_2) \beta(2) \ldots \psi_{vk_{1}s_l}(r_n) \ldots \psi_{vk_N}(r_{2N}) \beta(2N) \right\},$$

where $A$ is the antisymmetrizing operator, $N$ is the number of unit cells, $v$ refers to a specific valence band, $\alpha$ and $\beta$ are the spin eigenfunctions, and $s_l$ is a spin
index indicating either $\alpha$ or $\beta$. A trial excited state, in which the conduction wave function $\psi_{ck, sf}$ replaces the valence wave function $\psi_{ck, s}$, can be written as

$$\Psi' = A \left\{ \psi_{ck_1} (r_1) \alpha (1) \psi_{ck_2} (r_2) \beta (2) \ldots \psi_{ck_f} (r_n) \beta (2N) \right\}$$

We need the matrix elements of the operator $H_{eR}$ between the ground state and the excited states. Since $H_{eR}$ is a sum of one-particle operators, the non-vanishing matrix elements connect the ground state $\Psi_o$ with states $\Psi'$ having only one electron which is excited. Thus

$$\langle \Psi' | H_{eR} | \Psi_o \rangle = \frac{e}{mc} \langle \psi_{ck_f} | A \cdot p | \psi_{ck_s} \rangle$$

$$= \frac{e}{mc} \delta_{s_i, s_f} \langle \psi_{ck_f} | A \cdot p | \psi_{ck_i} \rangle.$$

For radiation of a given frequency $\omega$ the vector potential $A$ can be written as

$$A(r, t) = A_o e^{i(\eta \cdot r - \omega t)} + c.c., \quad (5.3)$$

where $e$ is the polarization vector in the direction of the electric field, $\eta$ is the wave vector of the radiation, and c.c. indicates the complex conjugate of the previous term.

We shall only consider the effect of the first term in Eq.(5.3) which gives rise to the absorption.

The transition probability per unit time Eq.(5.2) now becomes

$$P_{ck_i \rightarrow ck_f} = \frac{2\pi}{\hbar} \left( \frac{e A_o}{mc} \right)^2 \delta_{s_i, s_f} \left| \langle \psi_{ck_f} | e^{i\eta \cdot r} e \cdot p | \psi_{ck_i} \rangle \right|^2 \delta (E_f - E_i \mp \hbar \omega), \quad (5.4)$$

which is the basic expression for computing optical constants in the frequency region of interband transitions.

To obtain the number of transitions $W(\omega)$ per unit time per unit volume induced by light of frequency $\omega$, we must sum Eq.(5.4) over all possible states in the unit volume, i.e. we must sum over $k_i$, $k_f$, the spin variable $s$, and over the band indices $v$ (occupied) and $c$ (empty).

$$W(\omega) = \frac{2\pi}{V \hbar} \left( \frac{e A_o}{mc} \right)^2 \sum_{v, c, k_i, k_f} 2 \left| \langle \psi_{ck_f} | e^{i\eta \cdot r} e \cdot p | \psi_{ck_i} \rangle \right|^2 \delta (E_f - E_i \mp \hbar \omega), \quad (5.5)$$
where $V$ is the crystal volume. The summations of $k_i$ and $k_f$ are over the first Brillouin zone and the factor of 2 arises from the integration of spin variables.

Optical properties can be described in terms of the complex dielectric function $\varepsilon = \varepsilon_1 + i\varepsilon_2$ or the complex refractive index $N = n + ik$, where $n$ is the ordinary refractive index and $k$ is known as the extinction coefficient. The optical constants $\varepsilon$ and $N$ are connected by the relation $\varepsilon = N^2$, and the absorption coefficient $\alpha$ depends on the above optical constants via

\begin{equation}
\alpha = \frac{2k\omega}{c},
\end{equation}

\begin{equation}
\alpha = \frac{\omega}{nc^2},
\end{equation}

The average energy density $u$ in a medium of a radiation field described by the vector potential Eq.(5.3) is related to the optical constants through the relation

\[ u = \frac{n^2 A_o^2 \omega^2}{2\pi c^2}. \]

It is also known that the radiation in the medium propagates with velocity $c/n$. The absorption coefficient is by definition the energy absorbed per unit time per unit volume divided by the energy flux

\[ \alpha (\omega) = \frac{\hbar \omega W(\omega)}{u (c/n)}, \]

where $\hbar \omega W(\omega)$ is the energy absorbed per unit volume and time, and the product $u (c/n)$ of the energy density by the velocity of propagation in the medium is the energy flux. Using Eq.(5.7)

\[ \varepsilon_2 (\omega) = \frac{2\pi \hbar c^2 W(\omega)}{A_o^2 \omega^2}. \]

This is the basic expression which connects the band structure with the optical properties. The quantum expression for $\varepsilon_1 (\omega)$ can be obtained using the dispersion relation of Kramers-Kronig

\[ \varepsilon_1 (\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \omega' \varepsilon_2 (\omega') \frac{1}{\omega'^2 - \omega^2} d\omega', \]

where $P$ indicates the principal part.
5.2 Dielectric Function of Carbon Nanotube Bundles

We shall confine ourselves to bundles [13] made up of parallel, identical, and single-shell or multi-shell nanotubes to begin with. The optical properties are studied within the independent nanotube approximation [14, 15, 16]; that is, the optical excitations are the superposition of those from all the independent nanotubes. This approximation is reasonable since the intertube separation is much larger than the C-C bond length. For convenience, the nanotubes are assumed to be located in accord with a triangular lattice [17, 13, 18] with the lattice constant $d$; thus the bundle has a density of one nanotube per $(2r + d)^2$. Within the independent nanotube approximation, how the nanotubes are arranged is not important, only their density is relevant here. The dielectric function, thus, essentially depends on single nanotube excitations and, within the relaxation-time approximation [19] is given by[20]:

$$
\varepsilon(\omega) = \varepsilon_o - \frac{16\pi e^2}{\sqrt{3}\omega(2r + d)^2} \sum_{\mu,\mu'} \int_{1st \ BZ} dk \frac{1}{2\pi} \frac{\omega_{vc}(\mu, \mu', k)}{\omega_{vc}(\mu, \mu', k) + i\Gamma} \left\{ \frac{1}{\omega - \omega_{vc}(\mu, \mu', k) + i\Gamma} - \frac{1}{\omega + \omega_{vc}(\mu, \mu', k) + i\Gamma} \right\}^2
$$

(5.11)

The interband transition energy is denoted as $\omega_{vc}(\mu, \mu', k) = E_{\mu',k}^c - E_{\mu,k}^v$. The back ground dielectric constant $\varepsilon_o = 2.4$ is taken from graphite [21]. $\Gamma$ is the energy width due to various de-excitation mechanisms, and is treated as a parameter in the calculations. The velocity matrix element $|\langle \Psi_{k,\mu'}^c | \mathbf{e} \cdot \mathbf{p} / m | \Psi_{k,\mu}^v \rangle|$ is calculated in Appendix A. The value of lattice constant $d$ is set to 13.7Å [23]. Similar approximations have been successfully applied in evaluating optical spectra of graphite [19] and graphite intercalation compounds (GIC’s) [24].

5.3 Selection Rules

Before we calculate the dielectric function in detail for carbon nanotubes, there exist some selection rules which greatly simplify the calculation. Let’s consider the
transition from state $|\Psi_{k,\mu}^v\rangle$ to state $|\Psi_{k',\mu'}^v\rangle$, where $c$, $v$ indicate the conduction band and valence band, respectively, $k$, $k'$ are the wave vectors (in case of carbon nanotube, they’re scalars), and $\mu$, $\mu'$ are the angular momenta for the subbands. The matrix element
\[
\langle \psi_{ck'} | e^{i\eta \cdot r} \cdot p | \psi_{ck} \rangle.
\]
in Eq.(5.5) is now written as
\[
\langle \Psi_{k',\mu'}^v | e^{i\eta \cdot r} \cdot p | \Psi_{k,\mu}^v \rangle. \tag{5.12}
\]
The function $\Psi_{k',\mu'}^v$ belongs to the irreducible representation of the translation group (along cylindrical $y$-axis of nanotubes) with $k'$. The function $\Psi_{k,\mu}^v$ as well as its derivative $e \cdot p \Psi_{k,\mu}^v$, belongs to the irreducible representation with $k$, and $e^{i\eta \cdot r}$ belongs to the irreducible representation of vector $\eta_y$, where $\eta_y$ is the component of $\eta$ along the cylindrical $y$-axis. Since the product of the irreducible representation $k$ by the irreducible representation $\eta_y$ is the irreducible representation $k + \eta_y$, from group theory, the matrix element of Eq.(5.12) is zero unless
\[
k' = k + \eta_y + q |K_2| \tag{5.13}
\]
where $q$ is an integer, and $|K_2|$ is the length of reciprocal lattice vector $K_2$ in Figure 2.3. The above equation expresses the conservation of momentum in a periodic medium. For typical photon energies of the order of an electron volt
\[
|\eta| \approx 2\pi/10^4 \text{Å}^{-1}.
\]
The range of variation of $k$ (and $k'$) is $2\pi/a$ with $a$ of the order of a few angstroms, and so for all practical purposes we can neglect the radiation propagation vector $\eta$ in Eq.(5.12). Furthermore, since $k$ and $k'$ are confined to the first Brillouin zone, we may write
\[
k = k' \tag{5.14}
\]
However, the selection rule for $\mu$ and $\mu'$ is more complicated. For the case of polarization vector parallel to cylindrical axis of nanotube, $e_||$, the matrix element is written as
\[
\langle \Psi_{k,\mu'}^v | p_y | \Psi_{k,\mu}^v \rangle \tag{5.15}
\]
where \( p_y \) is the moment operator along cylindrical axis. The function \( \Psi_{k,\mu'}^c \) belongs to the \( \mu' \)th row of the irreducible representation of translation group (along cylindrical axis) with \( k \), and the derivative \( p_y \Psi_{k,\mu}^v \), belongs to the \( \mu \)th row of the irreducible representation with \( k \). Thus we have non-zero matrix element with

\[
\mu = \mu'
\]  

(5.16)

For the case of polarization vector perpendicular to cylindrical axis, \( e_\perp \), the matrix element is written as

\[
-i\hbar \left\langle \Psi_{k,\mu'}^c \left| \sin \phi \frac{\partial}{\partial r} + \cos \phi \frac{\partial}{r \partial \phi} \right| \Psi_{k,\mu}^v \right\rangle,
\]  

(5.17)

where \( \phi \) is the azimuthal angle, and \( r \) is the distance from cylindrical axis. From the rotational symmetry of the nanotube, we know that the functions \( \frac{\partial}{\partial r} \Psi_{k,\mu}^v \) and \( \frac{\partial}{r \partial \phi} \Psi_{k,\mu}^v \) both belong to the irreducible representation of the rotation group with \( \mu \), and function \( \Psi_{k,\mu'}^c \) belongs to the irreducible representation with \( \mu' \). Expressing \( \sin \phi = (e^{i\phi} - e^{-i\phi})/2i \), and \( \cos \phi = (e^{i\phi} + e^{-i\phi})/2 \) we readily see that the selection rule follows

\[
\mu = \mu' \pm 1.
\]  

(5.18)

### 5.4 Results and Discussion

We have calculated the imaginary part \( \varepsilon_2 \) of dielectric function for nanotube \((5,0)\) with polarization of electric field parallel and perpendicular to the nanotube axis in Figure 5.1 and 5.2, respectively. Together, the experimental result of the absorption spectrum for nanotube \((5,0)\) is also plotted in Figure 5.3[25].

Compare Figure 5.1 with 5.3, we have a qualitative agreement between the curves for \( \Gamma = 0.05 \) eV in Figure 5.1 and 0 degree in Figure 5.3. However, we can’t obtain satisfactory result in the case of \( e_\perp \) when we compare the graph in Figure 5.2 and the curve for 90 degree in Figure 5.3. As the experimental result in Figure 5.3 suggest, the intensity of spectrum in \( e_\perp \) is much smaller than the one in \( e_{||} \), on the contrary, we obtain a larger value of \( \varepsilon_2 \) in \( e_\perp \) case. Such discrepancy
may be arisen from the approximation we have been made for the calculation of dipole matrix elements, which is discussed in Appendix A, besides, we can’t give a reasonable explanation.

Figure 5.1: The imaginary part $\varepsilon_2$ of dielectric function for nanotube $(5,0)$ in the $e_\parallel$ case at several different energy widths.
Figure 5.2: The imaginary part $\varepsilon_2$ of dielectric function for nanotube (5,0) in the $e_\perp$ case at several different energy widths.

Figure 5.3: The experimental result of the absorption spectrum for nanotube (5,0) at the different polarization of electric field. 0 and 90 degree curves corresponding to parallel and perpendicular case.
Chapter 6

Conclusions

The physical properties of single-wall carbon nanotubes has been studied theoretically. We used the empirical tight-binding model in the calculation of the electronic structure of carbon nanotubes. On the basis of “zone-folding” of the two dimensional Brillouin zone for graphite, we introduced the effect of curvature, due to the cylindrical shape of nanotube in reality, by considering the hybridization of the graphitic $\sigma$, $\pi$, $\pi^*$ and $\sigma^*$ states in detail.

Since the hybridization effect is significant in the small diameter carbon nanotubes, we have calculated electronic structure for nanotubes $(n,0)$ $(n = 5, \cdots, 9)$. Of note is that there is a shift of the degeneracy of bonding and antibonding $\pi$ bands from the $K$ point in the Brillouin zone of graphite, as a result, we obtain a narrow-gap semiconductor for $(6,0)$ and $(9,0)$, even though they satisfy the metallic condition $n - m = 3q$. Moreover, we also plotted the ratio of this shift in degeneracy point for $(n,0)$ $(n = 5, \cdots, 9)$, and as predicted by our model, we obtain a decreasing value of the ratio when we increase $n$. It is a direct consequence of less curvature effect in large diameter nanotube.

The energy dispersion relations are further used to calculate the imaginary part of the dielectric function of $(5,0)$ nanotube. Since the selection rules are different for the polarizations of electric field parallel or perpendicular to the nanotube axis, we carried out the calculation in both cases. In the case of $e_{parallel}$, our result agrees qualitatively with the experimental one. However, in the case of $e_{perp}$, the numerical result doesn’t have a good agreement with the experimental one. On the contrary, we obtained a higher magnitude of $\varepsilon_2$ in $e_{perp}$ case, which is suggested to be far smaller than the one in $e_{parallel}$ case by the experimental data. So far, we can’t give a reasonable explanation to this discrepancy.
Appendix A

Velocity Matrix Elements

To calculate the velocity matrix element \( \langle \Psi_{k,\mu'}^c | \mathbf{e} \cdot \mathbf{p} / m | \Psi_{k,\mu}^v \rangle \), we express the moment operator \( \mathbf{p} \) as

\[
\mathbf{p} = \frac{m}{i\hbar} [\mathbf{r}, H]
\]

and we obtain the expression

\[
\langle \Psi_{k,\mu'}^c | \frac{\mathbf{e} \cdot \mathbf{r}}{m} | \Psi_{k,\mu}^v \rangle = \frac{\mathbf{e}}{i\hbar} \langle \Psi_{k,\mu'}^c | [\mathbf{r}, H] | \Psi_{k,\mu}^v \rangle
\]

\[
= \frac{\mathbf{e}}{i\hbar} \left\{ \langle \Psi_{k,\mu'}^c | \mathbf{r} H | \Psi_{k,\mu}^v \rangle - \langle \Psi_{k,\mu'}^c | H \mathbf{r} | \Psi_{k,\mu}^v \rangle \right\}
\]

\[
= \frac{(E_{k,\mu}^v - E_{k,\mu'}^c)}{i\hbar} \langle \Psi_{k,\mu'}^c | \mathbf{e} \cdot \mathbf{r} | \Psi_{k,\mu}^v \rangle
\]

\[
= -\frac{\omega_{vc}(\mu, \mu', k)}{i\hbar} \mathbf{e} \cdot \langle \Psi_{k,\mu'}^c | \mathbf{r} | \Psi_{k,\mu}^v \rangle
\]

(A.2)

where \( \omega_{vc}(\mu, \mu', k) = E_{\mu',k}^c - E_{\mu,k}^v \) is the interband transition energy, and \( \langle \Psi_{k,\mu'}^c | \mathbf{r} | \Psi_{k,\mu}^v \rangle \) will be called the “dipole term” [22].

At first sight, there are seven distinct dipole matrix elements, represented schematically in Figure A.1. One is on-site, while the others are off-site. (More precisely, there is a set of off-site dipole matrix elements for each order of nearest neighbors included.) These matrix elements are special because any dipole term can be written as a linear combination of them, in a manner analogous to the Slater-Koster two-center integral formulas for Hamiltonian matrix elements[10].

On closer inspection it is seen that the matrix elements denoted by (d) and (e) in Figure A.1 are actually equal, for \( x_{\mu} = y_{\mu} \). Also, the assumption of orthogonal tight-binding forces (b), (c), and (d) to be zero. This is because the origin may be translated to the mid-point, where the integrals are zero by parity. Thus, we are left with three special dipole matrix elements, one on-site(a), and
Figure A.1: Various dipole matrix elements between $s$ and $p$ atomic like states. The first (a) is on-site, while the rest are off-site. The arrow indicates the direction of the vector $r$, which gives a non-vanishing contribution to the matrix element.

two off-site (f), (g). We use the values proposed in Reference [22] for these dipole matrix elements.
Bibliography


[25] The experimental result is provided by Dr. Zikang Tang.