TIGHT-BINDING BASED MODELLING OF GRAPHENE ANTIDOT STRUCTURES

PROJECT WRITTEN

BY

RENÉ PETERSEN 9. Semester Nano-Physics Student aauprojects@repetit.dk

January 2, 2009

SUPERVISOR: Ph. D., Professor, Thomas Garm Pedersen

AALBORG UNIVERSITY FACULTY OF ENGINEERING AND SCIENCE INSTITUTE OF PHSYSICS AND NANOTECHNOLOGY

Abstract

Graphene is a two dimensional carbon sheet in which the carbon atoms are situated in a hexagonal lattice. It is the building block of graphite which consists of many layers of graphene. Graphene has been only recently discovered [1][2] and its discovery has brought with it a large research interest both theoretically and experimentally. Graphene has shown superior properties with electron mobilities on the order of $200000 \ cm^2/(Vs)$ and it holds good promise in the electronics industry. Graphene is not a semiconductor though, but a semimetal. If graphene is to be fully exploited in the electronic industry a way to make graphene semiconducting has to be found. By making a periodic array of holes in the graphene layer (graphene antidot lattice) theoretical predictions show that a gap opens up at the Γ point in the Brillouin zone [3], and that this bandgap is tunable by varying the hole size and separation. In this work the band structure of graphene antidot lattices will be calculated using a third nearest neighbour tight binding model. Based on these calculations the absorption spectra of a number of graphene antidot lattices will be calculated. Finally, the effect of excitons will be included. The results will be compared to those of a first nearest neighbour only model.

Preface

Together with software used for calculations this report is the product of the 9th semester project period at Aalborg University, Denmark. It has been written by René Petersen, nanophysics student at Aalborg University. The software has been written in C++ using the Intel Math Kernel Library (Intel MKL) version 10.0.4.023 for numerical operations and the Intel C++ compiler version 10.1.025.

Throughout the text vectors are typeset as a, matrices as \hat{A} and operators as \hat{A} . Most of the time matrices are written in uppercase and vectors in lowercase.

The first chapter provides an introduction to the properties of graphene and to current research activities. The "Tight Binding Theory" chapter provides information on the tight binding method which is used throught this work for modelling. In "Optical Properties of Semiconductors" a fundamental result for the susceptibility of quantum wells is derived and the result is further analyzed. In the chapter "Implementation and Results" the details of the actual implementation is presented along with the results obtained. "Discussion and Conclusion" closes this work with a discussion and a conclusion. The appendices provide additional information on chosen topics which are either not essential for understanding this work, or did not fit naturally into the flow of the text.

A version with colors can be found online at "http://www.repetit.dk/files/projects/p9.pdf"

René Petersen, January 2, 2009

Contents

1	Introduction 5							
	1.1	The Discovery of Graphene	5					
	1.2	Purpose of the Project	7					
2	\mathbf{Tig}	Tight Binding Theory						
	2.1	Tight Binding Theory	8					
	2.2	Approximations in Tight Binding	11					
	2.3	Graphene Two Band Model	11					
3	Opt	Optical Properties of Semiconductors						
	3.1	Theoretical Framework	14					
	3.2	Optical Properties	18					
	3.3	Excitonic Effects	20					
4	Implementation & Results							
	4.1	Setting up the Lattice Geometry	23					
	4.2	Graphene Antidot Band Structure	25					
	4.3	Effective Mass Calculation	27					
	4.4	Optical Spectra	30					
	4.5	Excitonic Effects	33					
5	Discussion and Conclusion 30							
A	Identities							
	A.1	Momentum Operator	38					
	A.2	Dirac-Delta Function	39					
в	The	Closure Relation and Projection Operator	41					
С	C Triangle Integration Method							
D Solving Laguerre's Differential Equation								

Chapter 1

Introduction

1.1 The Discovery of Graphene

Graphene is a two dimensional one atom thick planar sheet of sp^2 bonded carbon atoms densely packed in a honeycomb structure. It is the building block of graphite, which consists of planes of graphene stacked on top of each other. Carbon nanotubes and fullerenes can be thought of as a rolled up graphene sheet, so that graphene constitutes the basic building block of many carbon allotropes. Graphene has shown superior electrical and mechanical properties with a mobility on the order of 200000 cm²/(Vs) [4] and a Youngs Modulus of 500 GPa. For comparison, silicon has an electron mobility of $1350 \text{ cm}^2/(\text{Vs})$ and carbon nanotubes has a Youngs Modulus of 1000 GPa. The high mobility makes ballistic transport over distances on the order of micrometers possible [4].



Figure 1.1: (a) Graphene flakes placed on an SiO_2 wafer and viewed in an optical microscope. Monolayers can be found by searching for flakes which show the weakest contrast and examining them by AFM. (b) A TEM image of graphene layers hanging freely on a scaffold of gold wires. [5]

Graphene is probably the best theoretically studied carbon allotrope. It is the starting point for

all calculations on carbon nanotubes and fullerenes. It is therefore quite ironic that only until recently it was believed that graphene was impossible to synthesize. According to the Mermin-Wagner theorem, long range order in two dimensions are theoretically impossible [2]. Since graphene is a two dimensional crystal it should therefore not exist, and several attempts to synthesize graphene have failed. This is because thermal fluctuations at growth temperatures tend to twist and crumble otherwise flat nanometer scale graphene crystallites into stable 3D structures like nanotubes or fullerenes. In 2005 though, a group from Manchester University used a different and quite naive approach to the production of graphene [1]. By simply rubbing a 3D layered crystal against another solid surface they found that among the resulting flakes some single layer flakes were unexpectedly always found. The identification of the monolayers among the other flakes produced was done by optical microscopy. By placing the flakes on top of an oxidized silicon wafer the monolayers became visible because even the monolayers add up sufficiently to the optical path length so that the interference color changes with respect to the bare substrate. This can be seen in Fig. 1.1. These results show that graphene does in fact exist and is quite easy to produce, and they have triggered an enormous research activity.

Another and possibly even simpler method for graphene production is tape peeling. By putting a thin graphite sample onto adhesive tape, folding the tape back onto the graphite, so that the graphite becomes sandwiched in between, peeling the tape apart and repeating the process some 5-10 times, graphene layers can be produced [2]. The graphene layers can be subsequently transferred onto a silicon dioxide surface for identification and characterization.

In a simple nearest neighbour model graphene is a semimetal with zero overlap between valence and conduction bands. Graphene is peculiar in the respect that the bands are linear near the Kpoints at the corners of the Brillouin zone. In Fig. 1.2 the band structure of graphene is shown and the right part of the figure shows the linearly dispersive bands. This linear dispersion closely resembles the Dirac spectrum for massless fermions which is given by $E = c\hbar k$ where $k = |\mathbf{k}|$. The linear dispersion in graphene near the K points is given by $E = v_F \hbar k$ so that the Fermi velocity $v_F \approx 10^6$ plays the role of the speed of light. For these reasons the K points are also called the Dirac points.



Figure 1.2: The band structure of graphene. The left part shows the whole band structure and the left part shows the linear dispersion around the dirac points. [6]

The surface to volume ratio of graphene is very large. Every atom is exposed on the surface and all atoms are therefore available for interaction with nearby molecules. This makes graphene very sensitive to changes in the local environment and its use as a sensor device is obvious.

The properties of graphene are metallic. If graphene is to be used as the main ingredient

in future transistors instead of silicon, a method to make graphene semiconducting has to be found. Inspired by the knowledge of carbon nanotubes (CNTs), the so called graphene nanoribbons (GNRs) have recently become an active area of research [7]. GNRs are unfolded carbon nanotubes and it is therefore reasonable to expect them to have some properties in common. Due to confinement of the electrons in CNTs some CNTs become semiconducting. When a CNT is unrolled the electrons are still confined to a small planar sheet and this causes some GNRs to be semiconducting too. In [7] and [8] it is demonstrated that the band gap of GNRs can be tuned by adjusting the GNR width. This opens up possibilities for using GNR in electronic and optical applications.

Another approach to making graphene semiconducting is to introduce an additional periodic perturbation into the lattice. This can be done by making a periodic array of holes in the graphene sheet [9] [3]. Due to this additional potential a gap opens up at the Γ point in the Brillouin zone. This gap can be tuned by adjusting the hole diameter and separation. In [9] and [3] a simple tight binding model with nearest neighbour interactions and no overlap of atomic wavefunctions has been used to determine electronic band structures and absorption spectra of a number of graphene antidot lattices.

1.2 Purpose of the Project

In this project the aim is to set up a tight binding model which includes up to third nearest neighbours and overlap. Based on this tight binding model the bandstructure of graphene antidot lattices will be calculated and the results will be used to calculate the optical absorption of antidot lattices. In the model used excitonic effects are not included. These effects are treated separately using the Wannier model.

Chapter 2

Tight Binding Theory

2.1 Tight Binding Theory

The tight binding (TB) method is a method used for calculation of electronic band structures of solids. It is an LCAO (linear combination of atomic orbitals) approach to determining the total wavefunction of the crystal, similar to the LCAO approach used for example when calculating energy levels in atoms. The idea in the LCAO approach is that the complicated unknown wavefunction can be written as a linear combination of relatively simple known wavefunctions. For example, in determining the wavefunction of atoms with Z > 1 the wavefunction is expanded in terms of hydrogenic orbitals which can be obtained analytically. The problem is then a matter of customizing the orbitals to the specific situation and determining the weighing coefficient of each of the hydrogenic orbitals. The last problem can be easily solved by using for example the Hartree-Fock method.

Several variants of TB exists ranging from ab-initio (from first principles) to semi-empirical methods. TB can be viewed as the counterpart to the nearly free electron model for which the plane wave basis is the most suited in describing the delocalized nature of the electrons. TB is used for description of electrons which are tightly bound to the nucleus and therefore the plane wave basis is not suitable. The wavefunction is instead expressed in terms of the wavefunctions of the localized orbitals which then constitutes the basis. In semi-empirical TB an explicit expression for the localized orbitals is not needed, only the matrix elements are needed.

The wave function with band index j is expressed as

$$\Psi_{j\boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{\sqrt{U}} \sum_{p}^{N} \sum_{lmn}^{U} b_{lmn,j}^{p}(\boldsymbol{k}) \left| \varphi^{p}, \boldsymbol{R}_{lmn}^{p} \right\rangle$$
(2.1)

where the first summation runs over all atoms of the unit cell (N) which may or may not be of the same type, and the second summation runs over all unit cells of the crystal (U). $\mathbf{R}_{lmn}^p = l\mathbf{a}_1 + m\mathbf{a}_2 + n\mathbf{a}_3 + \mathbf{r}_p$ is the position of atom p in the unit cell lmn, where r_p describes the atom position within the unit cell . $|\varphi^p, \mathbf{R}_{lmn}^p\rangle$ is the atomic orbital of type p centered at position \mathbf{R}_{lmn}^p . Now, according to the Bloch theorem [10] the wavefunction ψ of an electron in a periodic potential can be written as

$$\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}u_n(\boldsymbol{r},\boldsymbol{k}) \tag{2.2}$$

Since, in Eqn. 2.1 for a particular choice of p, the sum over lmn runs over atoms of the same type separated by $\mathbf{R}_{lmn} = l\mathbf{a}_1 + m\mathbf{a}_2 + n\mathbf{a}_3$, a vector of the lattice, this particular sum can be written as a Bloch function associated with atom p. Thus, a total of N Bloch functions exist, each given by

$$\Phi_{\boldsymbol{k}}^{p}(\boldsymbol{r}) = \frac{1}{\sqrt{U}} \sum_{lmn}^{U} e^{i\boldsymbol{k}\cdot\boldsymbol{R}_{lmn}^{p}} |\varphi^{p}, \boldsymbol{R}_{lmn}^{p}\rangle$$
(2.3)

By writing $b_{lmn}^{p}(\mathbf{k}) = c^{p}(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{R}_{lmn}^{p}}$ where $c^{p}(\mathbf{k})$, is the weight of the *p*'th Bloch function in the total wavefunction, Eqn. 2.1 can be written as

$$\Psi_{j\boldsymbol{k}}(\boldsymbol{r}) = \sum_{p}^{N} c_{j}^{p}(\boldsymbol{k}) \Phi_{\boldsymbol{k}}^{p}(\boldsymbol{r})$$
(2.4)

The wavefunction has now been reexpressed in a basis of Bloch functions. In order to determine the coefficients $c_j^p(\mathbf{k})$ and the energies corresponding to each wavefunction, the wavefunction is inserted into the Schrödinger Equation (SE)

$$\hat{H}\Psi_{j\boldsymbol{k}}(\boldsymbol{r}) = E_j(\boldsymbol{k})\Psi_{j\boldsymbol{k}}(\boldsymbol{r})$$
(2.5)

By using Eqn. 2.4 one gets

$$\sum_{p}^{N} c_{j}^{p}(\boldsymbol{k}) \hat{H} \Phi_{\boldsymbol{k}}^{p}(\boldsymbol{r}) = E_{j}(\boldsymbol{k}) \sum_{p}^{N} c_{j}^{p}(\boldsymbol{k}) \Phi_{\boldsymbol{k}}^{p}(\boldsymbol{r})$$
(2.6)

Premultiplying by $\Phi_{k}^{p'*}$ and integrating over all space gives

$$\sum_{p}^{N} c_{j}^{p}(\boldsymbol{k}) \langle \Phi_{\boldsymbol{k}}^{p'} | \hat{H} | \Phi_{\boldsymbol{k}}^{p} \rangle = E_{j}(\boldsymbol{k}) \sum_{p}^{N} c_{j}^{p}(\boldsymbol{k}) \langle \Phi_{\boldsymbol{k}}^{p'} | \Phi_{\boldsymbol{k}}^{p} \rangle$$
(2.7)

Each particular choice of p' gives a new equation, so that there will be as many equations as there are atoms in the unit cell. This can be formulated as a generalized matrix problem

$$\hat{\mathsf{H}} \cdot \boldsymbol{c}_j = E_j(\boldsymbol{k}) \hat{\mathsf{S}} \cdot \boldsymbol{c}_j \tag{2.8}$$

The matrix \hat{H} contains the matrix elements of the \hat{H} operator and the matrix \hat{S} contains the overlap matrix elements. Both matrices are of dimension $N \times N$. The matrix elements can be

determined by inserting the expressions for $\Phi_{\mathbf{k}}^{p}$ and $\Phi_{\mathbf{k}}^{p'}$, given by Eqn. 2.3, into the expression for the matrix elements. One obtains then

$$\langle \Phi_{\boldsymbol{k}}^{p'} | \hat{H} | \Phi_{\boldsymbol{k}}^{p} \rangle = \frac{1}{U} \sum_{l'm'n'}^{U} \sum_{lmn}^{U} e^{i\boldsymbol{k} \cdot (\boldsymbol{R}_{lmn}^{p} - \boldsymbol{R}_{l'm'n'}^{p'})} \langle \varphi^{p'}, \boldsymbol{R}_{l'm'n'}^{p'} | \hat{H} | \varphi^{p}, \boldsymbol{R}_{lmn}^{p} \rangle$$
(2.9)

$$\langle \Phi_{\boldsymbol{k}}^{p'} | \Phi_{\boldsymbol{k}}^{p} \rangle = \frac{1}{U} \sum_{l'm'n'}^{U} \sum_{lmn}^{U} e^{i\boldsymbol{k} \cdot (\boldsymbol{R}_{lmn}^{p} - \boldsymbol{R}_{l'm'n'}^{p'})} \langle \varphi^{p'}, \boldsymbol{R}_{l'm'n'}^{p'} | \varphi^{p}, \boldsymbol{R}_{lmn}^{p} \rangle$$
(2.10)

Both sums in each matrix element run over every unit cell of the crystal. If one choses a particular set of values of l'm'n' and then executes the other sum over lmn, it gives the same as if another set of values of l'm'n' had been chosen due to the periodicity of the crystal. It does not matter which value is chosen and all choices of l'm'n' give the same contribution to the matrix element, so that the matrix element contains U equal terms. Thus, l' = 0, m' = 0 and n' = 0 can be chosen and the factor of $\frac{1}{U}$ is annihilated

$$\hat{\mathsf{H}}_{pp'} = \langle \Phi_{\boldsymbol{k}}^{p'} | \, \hat{H} \, | \Phi_{\boldsymbol{k}}^{p} \rangle = \sum_{lmn}^{U} e^{i\boldsymbol{k} \cdot \left(\boldsymbol{R}_{lmn}^{p} - \boldsymbol{R}_{000}^{p'}\right)} \, \langle \varphi^{p'}, \boldsymbol{R}_{000}^{p'} | \, \hat{H} \, | \varphi^{p}, \boldsymbol{R}_{lmn}^{p} \rangle \tag{2.11}$$

$$\hat{\mathsf{S}}_{pp'} = \langle \Phi_{\boldsymbol{k}}^{p'} | \Phi_{\boldsymbol{k}}^{p} \rangle = \sum_{lmn}^{U} e^{i\boldsymbol{k} \cdot \left(\boldsymbol{R}_{lmn}^{p} - \boldsymbol{R}_{000}^{p'}\right)} \langle \varphi^{p'}, \boldsymbol{R}_{000}^{p'} | \varphi^{p}, \boldsymbol{R}_{lmn}^{p} \rangle$$
(2.12)

From these equations the matrix elements can in principle be obtained and the eigenvalue problem solved for each value of \boldsymbol{k} within the first Brillouin Zone (BZ) in order to obtain the band structure. However, if one does not have explicit expressions for the wavefunctions another approach has to be taken. One way is to use the tight binding method to calculate certain properties of the structure in question treating the matrix elements as fitting parameters. The calculation can then be fitted to experimental data (empirical tight binding) or to other more accurate calculations.

One task still remains for Eqn. 2.4 to represent a physical wave function. The function has to be normalized, i.e., one must require that the function obeys

$$\langle \Psi_{j\boldsymbol{k}} | \Psi_{j\boldsymbol{k}} \rangle = \sum_{p,p'}^{N} c_j^p(\boldsymbol{k})^* c_j^{p'}(\boldsymbol{k}) \langle \Phi_{\boldsymbol{k}}^p | \Phi_{\boldsymbol{k}}^{p'} \rangle = \sum_{p,p'}^{N} c_j^p(\boldsymbol{k})^* c_j^{p'}(\boldsymbol{k}) \hat{\mathsf{S}}_{pp'} = 1$$
(2.13)

Or in matrix form

$$\boldsymbol{c}_{j}^{\dagger} \cdot \hat{\boldsymbol{\mathsf{S}}} \cdot \boldsymbol{c}_{j} = 1 \tag{2.14}$$

which constitutes the normalization condition for the eigenvectors. The eigenvector and the overlap matrix are of course all k dependent.

2.2 Approximations in Tight Binding

In the equations above no approximations are made. The crystal wave function is written as a linear combination of atomic orbitals, but this is not an approximation since the atomic orbitals constitute a complete set. The expressions for the matrix elements though, contain as many terms as there are unit cells in the crystal, i.e., infinitely many. But since the interaction between atoms decreases rapidly when the distance between them increases, contributions to the matrix elements from atoms separated by more than a few nearest neighbour distances can be neglected. Often only nearest neighbours are included in the calculation but of course one is free to choose the number of nearest neighbours to include.

Another approximation which is frequently made is to completely ignore the overlap and simply put the overlap matrix equal to the unit matrix. In this way the matrix problem to be solved becomes

$$\hat{\mathsf{H}} \cdot \boldsymbol{c}_j = E_j(\boldsymbol{k})\boldsymbol{c}_j \tag{2.15}$$

i.e., a standard eigenvalue problem which is easier and faster to solve. This approximation is valid if the overlap matrix elements are small, i.e., if the atomic orbitals are strongly localized.

In the case of graphene it is the π electrons which are most interesting. This is because the π electrons are free to move in contrast to the other electrons which participate in covalent bonding and are therefore strongly localized. The π electrons therefore constitute the major contribution to the electrical and the optical properties of graphene. Therefore, in Eqn. 2.1, the sum over p would be a sum over π orbitals only.

2.3 Graphene Two Band Model

By applying the TB model in its simplest version to pure graphene a simple model which shows the most important features of graphene can be made. In this model the overlap is ignored and only nearest neighbour interactions are considered. The graphene lattice consists of two interpenetrating triagonal sublattices which are called A and B in the following. Atoms belonging to the A lattice are also identified as A and similar for atoms belonging to the B lattice. Each atom has three nearest neighbours of the other type, i.e., an A atom has three nearest neighbours which are B atoms. In Fig. 2.1(a) a graphene sheet is shown. The red atoms constitute the A sublattice and the blue atoms constitute the B sublattice. The set of lattice vectors shown is the set belonging to the A sublattice. A similar set belongs to the B sublattice. The shaded box shows the two atom unit cell of the graphene lattice. The total graphene sheet can be described as a triagonal lattice with a two atom basis. The lattice vectors of the graphene lattice is given by

$$a_1 = \left(\frac{\sqrt{3}}{2}, \frac{1}{2}\right) a_0, \qquad a_2 = \left(\frac{\sqrt{3}}{2}, -\frac{1}{2}\right) a_0$$
 (2.16)

where $a_0 = 2.46$ Å is the graphene lattice constant. Since there are two atoms in the unit cell, there are two Bloch functions. One for the A atoms and one for the B atoms. Thus, the matrix elements of the Hamiltonian matrix are given by



Figure 2.1: (a) a graphene lattice and the two atom unit cell in graphene. Atoms belonging to different sublattices are colored in different colors. (b) the Brillouin zone of graphene. The shaded area is the irreducible BZ.

$$\langle \Phi^A | \hat{H} | \Phi^A \rangle = \langle \Phi^B | \hat{H} | \Phi^B \rangle = E_0 \tag{2.17}$$

$$\langle \Phi^A | \hat{H} | \Phi^B \rangle = \langle \Phi^B | \hat{H} | \Phi^A \rangle^* = \gamma_{01} \left[e^{i \boldsymbol{k} \cdot \boldsymbol{r}_1} + e^{i \boldsymbol{k} \cdot \boldsymbol{r}_2} + e^{i \boldsymbol{k} \cdot \boldsymbol{r}_3} \right] = \gamma_{01} f_1(\boldsymbol{k})$$
(2.18)

where \mathbf{r}_i are the vectors which connect an A or B atom with its nearest neighbours. The transfer integral $\gamma_{01} = \langle \varphi^A(\mathbf{r}) | \hat{H} | \varphi^B(\mathbf{r} - \mathbf{r}_i) \rangle$ is the same for all i since all nearest neighbours obviously lie in the same distance from the center atom. The vectors \mathbf{r}_i are given by

$$\boldsymbol{r}_1 = (\frac{1}{2\sqrt{3}}, \frac{1}{2})a_0, \qquad \boldsymbol{r}_2 = (\frac{1}{2\sqrt{3}}, -\frac{1}{2})a_0, \qquad \boldsymbol{r}_3 = (-1, 0)a_0$$
(2.19)

and the exponential factor $f_1(\mathbf{k})$ in Eqn. 2.18 is therefore found to be

$$f_1(\mathbf{k}) = e^{-ik_x a_0/\sqrt{3}} + 2e^{ik_x a_0/(2\sqrt{3})} \cos(k_y a_0/2)$$
(2.20)

In order to calculate the band structure the reciprocal lattice vectors has to be known. These are calculated from the requirement that $e^{i\boldsymbol{a}_i\cdot\boldsymbol{b}_j} = 2\pi\delta_{ij}$ from which it follows that $\boldsymbol{a}_i\cdot\boldsymbol{b}_j = 2\pi\delta_{ij}$. The reciprocal lattice vectors are found to be

$$\boldsymbol{b}_1 = \left(\frac{1}{\sqrt{3}}, 1\right) \frac{2\pi}{a_0}, \qquad \boldsymbol{b}_2 = \left(\frac{1}{\sqrt{3}}, -1\right) \frac{2\pi}{a_0}$$
 (2.21)

From the reciprocal lattice vectors the first Brillouin zone can be constructed. This is done by constructing the Wigner-Seitz cell from the reciprocal lattice vectors. The first Brillouin zone

is shown in Fig. 2.1(b). The band structure is calculated by evaluating the eigenvalues of the Hamiltonian matrix for \mathbf{k} values on the path $\Gamma - M - K - \Gamma$. Setting $E_0 = 0$ (it only causes a shift of the eigenvalues) the eigenvalues are given by

$$\begin{vmatrix} -E & -\gamma f_1(\mathbf{k}) \\ -\gamma f_1^*(\mathbf{k}) & -E \end{vmatrix} = E^2 - \gamma^2 \left| f(\mathbf{k}) \right|^2 = 0$$
(2.22)

so that the eigenvalues are given by $E(\mathbf{k}) = \pm \gamma |f_1(\mathbf{k})|$. From this it is seen that if $|f_1(\mathbf{k})| = 0$ for some \mathbf{k} there will be no band gap. $|f_1(\mathbf{k})|^2$ is given by

$$|f_1(\mathbf{k})|^2 = 1 + 4\cos^2\left(k_y \frac{a_0}{2}\right) + 4\cos\left(k_y \frac{a_0}{2}\right)\cos\left(k_x \frac{\sqrt{3}a_0}{2}\right)$$
(2.23)

The K point in reciprocal space lies at $(\frac{2\pi}{\sqrt{3}a_0}, \frac{2\pi}{3a_0})$ and inserting this into the expression for $|f_1(\mathbf{k})|^2$ one gets

$$|f_1(\mathbf{K})|^2 = 1 + 4\cos^2\frac{\pi}{3} + 4\cos\frac{\pi}{3}\cos\pi = 0$$
(2.24)

so that the bands meet in the K point. This point is called the Dirac Point. By doing a second order expansion of the expression for the energy around the K point further properties of graphene can be derived[6], i.e., putting $\mathbf{k} = \mathbf{K} + \mathbf{q}$ where $|\mathbf{q}| \ll \mathbf{K}$ and using the addition formulas for $\cos x$ one obtains

$$E(\boldsymbol{q}) \approx v \left| \boldsymbol{q} \right| \tag{2.25}$$

where $v = \sqrt{3\gamma a_0/2}$. In the usual case one has $E(\mathbf{q}) = |\mathbf{q}|^2/(2m) = v(\mathbf{q})|\mathbf{q}|$ so that the velocity depends on the wavevector \mathbf{q} . In the case of graphene in the vicinity of the \mathbf{K} point the velocity does not depend on the wavevector. The velocity of electrons near the \mathbf{K} point is equal to the Fermi velocity $v_F = 10^6 m/s[6]$ so that, still near the \mathbf{K} point,

$$E(\boldsymbol{q}) \approx v_F |\boldsymbol{q}| \tag{2.26}$$

The impact of this result is that the velocity of electrons near the Dirac point does not depend on energy or momentum, but is equal to the Fermi velocity. The Fermi velocity in graphene is $\sim c/100$, where c is the speed of light.

Chapter 3

Optical Properties of Semiconductors

3.1 Theoretical Framework

In order to describe the optical response of a material harmonic time dependent perturbation theory can be used. The fundamental result of time dependent perturbation theory is

$$X(\omega) = -\sum_{m,n} f_{nm} \frac{\langle \varphi_m | \hat{H}_1 | \varphi_n \rangle \langle \varphi_n | \hat{X} | \varphi_m \rangle}{E_{mn} - \hbar \omega - i\hbar\Gamma}$$
(3.1)

where \hat{H}_1 is the perturbation, \hat{X} is the response observable, $f_{nm} = f(E_n) - f(E_m)$ is the fermi function, $E_{mn} = E_m - E_n$ is the transition energy and Γ is the broadening. The optical properties of a material is determined by its response to an electric field. This is quantified by the electric susceptibility which is determined by the relation $P(\omega) = \varepsilon_0 \chi_e(\omega) E(\omega)$ where Pis the polarizability, E is the electric field and χ_e is the electric susceptibility. In general the susceptibility may be a tensor since the polarization is not necessarily in the same direction as the electric field. If it is assumed that the material is isotropic though, P and E are parallel. If both are chosen to lie along the z-axis so that $E = E\hat{z}$ and $P = P\hat{z}$, the susceptibility is given by $\chi_e(\omega) = P/(\varepsilon_0 E)$.

In Eqn. 3.1 the perturbation is given by $\hat{H}_1 = -\mathbf{E} \cdot \mathbf{d}$ where $\mathbf{d} = -e\mathbf{r}$ is the electric dipole moment operator. Thus, $\hat{H}_1 = eEz$. The response is the dipole moment density given by $-ez/\Omega$. Inserting this into Eqn. 3.1 and dividing by the electric field and ε_0 to obtain the susceptibility one gets

$$\chi(\omega) = \frac{e^2}{\varepsilon_0 \Omega} \sum_{m,n} f_{nm} \frac{|\langle \varphi_m | \, z \, |\varphi_n \rangle|^2}{E_{mn} - \hbar \omega - i\hbar\Gamma}$$
(3.2)

The position matrix element can be reformulated as a momentum matrix element by exploiting the fact that the momentum operator can be expressed in terms of the commutator between the Hamilton operator and the position operator (see App. A)

$$\frac{im}{\hbar}[\hat{H}, \mathbf{r}] = \hat{\mathbf{p}} \tag{3.3}$$

The matrix element of the commutator is

$$\langle \varphi_m | [\hat{H}, \mathbf{r}] | \varphi_n \rangle = \langle \varphi_m | \hat{H} \mathbf{r} | \varphi_n \rangle - \langle \varphi_m | \mathbf{r} \hat{H} | \varphi_n \rangle$$
(3.4)

By using the closure relation (see App. B) (inserting \hat{I} between \hat{H} and r) and exploiting the orthonormality of the φ_i 's and the fact that they are eigenfunctions of \hat{H} with eigenvalue E_i one obtains

$$\langle \varphi_m | \left[\hat{H}, \mathbf{r} \right] | \varphi_n \rangle = \langle \varphi_m | \, \hat{H} \mathbf{r} \, | \varphi_n \rangle - \langle \varphi_m | \, \mathbf{r} \hat{H} \, | \varphi_n \rangle = E_{mn} \, \langle \varphi_m | \, \mathbf{r} \, | \varphi_n \rangle \tag{3.5}$$

where $E_{mn} = E_m - E_n$ and therefore (taking only the z component)

$$\langle \varphi_m | \, z \, | \varphi_n \rangle = -\frac{i\hbar}{mE_{mn}} \, \langle \varphi_m | \, \hat{p}_z \, | \varphi_n \rangle \tag{3.6}$$

The expression for the susceptibility then becomes

$$\chi(\omega) = \frac{\hbar^2 e^2}{\varepsilon_0 m^2 \Omega} \sum_{m,n} f_{nm} \frac{|\langle \varphi_m | \, \hat{p}_z \, | \varphi_n \rangle|^2}{E_{mn}^2 (E_{mn} - \hbar \omega - i\hbar\Gamma)}$$
(3.7)

In this expression the summations over m and n are over all valence band states and all conduction band states. In a crystal there will be many conduction and valence band states each indexed by a different value of k. All these states in a particular conduction or valence band are denoted collectively by c' and v' respectively, so that v' = 1 denotes all the states of different k belonging to this particular valence band. The summation above can be split as follows

$$\sum_{m,n} = \sum_{m \in v'} \sum_{n \in v'} + \sum_{m \in c'} \sum_{n \in c'} + \sum_{m \in c'} \sum_{n \in v'} + \sum_{m \in v'} \sum_{n \in v'} \sum_{n \in c'}$$
(3.8)

For the first two summations the occupation factor f_{nm} is practically zero. The two summations correspond to the contribution to the susceptibility from excitations from a valence band to another valence band and from a conduction band to another conduction band respectively. The probability of these transitions is very low at moderate temperatures. Using $E_{mn} = -E_{nm}$ and $f_{nm} = -f_{mn}$ and exchanging the indices in the last summation (so that m runs over conduction band states and n runs over valence band states) one obtains

$$\chi(\omega) = \frac{2\hbar^2 e^2}{\varepsilon_0 m^2 \Omega} \sum_{m \in c'} \sum_{n \in v'} \frac{f_{nm} \left| \langle \varphi_m \right| \hat{p}_z \left| \varphi_n \rangle \right|^2}{E_{mn} \left[E_{mn}^2 - \hbar^2 (\omega + i\Gamma)^2 \right]}$$
(3.9)

Since photons carry only negligible momentum the wave vector is not changed significantly in the excitation process. All excitations will therefore be between states of equal k. Extracting now the summation over all k which is contained implicitly in c' and v'

$$\chi(\omega) = \frac{2\hbar^2 e^2}{\varepsilon_0 m^2 \Omega} \sum_{m \in c} \sum_{n \in v} \sum_{\mu, \nu} \sum_{\mathbf{k}'} \frac{f_{nm}^{\mu\nu}(\mathbf{k}') \left| \langle \varphi_m^{\mu}(\mathbf{k}') \right| \hat{p}_z \left| \varphi_n^{\nu}(\mathbf{k}') \rangle \right|^2}{E_{mn}^{\mu\nu}(\mathbf{k}') \left[(E_{mn}^{\mu\nu}(\mathbf{k}'))^2 - \hbar^2 (\omega + i\Gamma)^2 \right]}$$
(3.10)

where $m \in c$ and $n \in v$ (c and v without the primes) now run only over all valence and conduction bands and the (continous) state summation lies in the sum over \mathbf{k}' . The prime on \mathbf{k}' signifies that the summation also covers spin. The additional summation over μ and ν is a summation over quantized states. In a bulk crystal there will be no quantized states, but in a 2D (quantum well), 1D (quantum wire) or 0D (quantum dot) material the confinement of the electrons leads to quantized states in the confined directions. In these cases the \mathbf{k} summation runs over the continous states in the extended direction. In a 0D material there are no continous states and therefore no \mathbf{k} summation. In the following only 2D materials are treated. In this case the states φ_m^{μ} and φ_n^{ν} may be taken to be

$$|\varphi_m^{\mu}\rangle = \sqrt{\frac{1}{\Omega}} \sin\left(\frac{\mu\pi x}{d}\right) u_m(\boldsymbol{r}, \boldsymbol{k}) e^{i\boldsymbol{k}\cdot\boldsymbol{r}} |\sigma\rangle$$
 (3.11)

$$|\varphi_n^{\nu}\rangle = \sqrt{\frac{1}{\Omega}} \sin\left(\frac{\nu\pi x}{d}\right) u_n(\boldsymbol{r}, \boldsymbol{k}) e^{i\boldsymbol{k}\cdot\boldsymbol{r}} |\sigma\rangle$$
(3.12)

Thus, for the confined states the result for an electron confined by an infinite potential is used. This makes sense if d, the thickness in the confined direction, is only a few lattice constants. If the width of the quantum well is only one or two lattice constants this approximation is not necessary because it is in fact not an approximation. In graphene, for instance, the perpendicular states are known to be π orbitals. In this case there is no additional summation over the quantized states. This is the case treated in the following.

Since the quantum well is large in the extended directions the k states are closely spaced so that the k summation can be written as an integral. In this case one obtains for the susceptibility (supressing the k dependence from now on)

$$\chi(\omega) = \frac{4\hbar^2 e^2}{\varepsilon_0 m^2 d(2\pi)^2} \sum_{m \in c} \sum_{n \in v} \iint_{\text{BZ}} \frac{f_{nm} \left| \langle \varphi_m \right| \hat{p}_z \left| \varphi_n \rangle \right|^2}{E_{mn} \left[(E_{mn})^2 - \hbar^2 (\omega + i\Gamma)^2 \right]} d^2k \tag{3.13}$$

where the extra factor of two stems from the spin summation $(\sum \mathbf{k}' \rightarrow 2\sum \mathbf{k})$ and d is the width of the quantum well. The absorption of the material is given by the imaginary part of the susceptibility. In the expression above the only contribution to the imaginary part comes from the denominator

$$\operatorname{Im}\left[\frac{1}{(E_{mn})^2 - \hbar^2(\omega + i\Gamma)^2}\right] = \operatorname{Im}\left[\frac{1}{[E_{mn} - \hbar(\omega + i\Gamma)][E_{mn} + \hbar(\omega + i\Gamma)]}\right]$$
(3.14)

Splitting the fraction into partial fractions according to

$$\frac{1}{\left[E_{mn} - \hbar(\omega + i\Gamma)\right]\left[E_{mn} + \hbar(\omega + i\Gamma)\right]} = \frac{A}{E_{mn} - \hbar(\omega + i\Gamma)} + \frac{B}{E_{mn} + \hbar(\omega + i\Gamma)}$$
(3.15)

the constants A and B can thus be determined (more than one solution exists) and they are given by $A = 1/(2E_{mn})$ and $B = 1/(2E_{mn})$. Therefore, after some algebra

$$\operatorname{Im}\left[\frac{1}{(E_{mn})^2 - \hbar^2(\omega + i\Gamma)^2}\right] = \frac{1}{2E_{mn}}\left[\frac{\hbar\Gamma}{(E_{mn} - \hbar\omega)^2 + \hbar^2\Gamma^2} - \frac{\hbar\Gamma}{(E_{mn} + \hbar\omega)^2 + \hbar^2\Gamma^2}\right] (3.16)$$

As the broadening Γ tends to zero in the above expression the last term on the right hand side goes to zero and only the first term persists. For this term one gets (App. A)

$$\frac{1}{2E_{mn}} \lim_{\Gamma \to 0} \left[\frac{\hbar\Gamma}{\left(E_{mn} - \hbar\omega\right)^2 + \hbar^2\Gamma^2} \right] = \frac{\pi}{2E_{mn}} \delta(E_{mn} - \hbar\omega)$$
(3.17)

Since this expression vanishes whenever $E_{mn} \neq \hbar \omega$ one can make the substitution $E_{mn} \rightarrow \hbar \omega$ in the fraction outside the delta function so that

$$\frac{\pi}{E_{mn}}\delta(E_{mn}-\hbar\omega) \to \frac{\pi}{\hbar\omega}\delta(E_{mn}-\hbar\omega)$$
(3.18)

The final expression for the quantum well susceptibility, under the assumption that only the lowest quantized states contribute, is then given by

$$\chi(\omega) = \frac{e^2}{2\pi\varepsilon_0 m^2 \omega^2 d} \sum_{m \in c} \sum_{n \in v} \iint_{\text{BZ}} f_{nm} |P_{mn}|^2 \,\delta(E_{mn} - \hbar\omega) d^2k \tag{3.19}$$

where $P_{mn} = \langle \varphi_m | \hat{p}_z | \varphi_n \rangle$. The relationship between the complex conductivity and the complex susceptibility is given by $\tilde{\sigma} = -id\varepsilon_0 \omega \chi(\omega)$ so that the imaginary part of the susceptibility is related to the real part of the conductivity as

$$\sigma = \operatorname{Re}\left[\tilde{\sigma}\right] = d\varepsilon_0 \omega \operatorname{Im}\left[\chi(\omega)\right] \tag{3.20}$$

Finally, the real conductivity is

$$\sigma(\omega) = \frac{e^2}{2\pi m^2 \omega} \sum_c \sum_v \iint_{\text{BZ}} f_{vc} |P_{cv}|^2 \,\delta(E_{cv} - \hbar\omega) d^2k \tag{3.21}$$

17

3.2 Optical Properties

The integral in Eqn. 3.21 is taken over the first Brillouin zone and the sum runs over all valence band states (v) and all conduction band states (c). $|P_{vc}|^2$ is the squared momentum matrix element (optical matrix element). Note that if $|P_{vc}|^2 = 1$ the integral represents the joint density of states so that the momentum matrix elements play the role of a weighing function. The momentum matrix element is given by

$$P_{vc} = \langle \Psi_{vk} | \, \hat{\boldsymbol{p}} \, | \Psi_{ck} \rangle \cdot \hat{\boldsymbol{x}} \tag{3.22}$$

Since photons carry negligible momentum, the momentum matrix element is taken between states of equal \boldsymbol{k} . The valence and conduction band states are not known analytically though, only the numerical value of the Hamilton matrix elements are known. The momentum matrix elements can be expressed in terms of the Hamilton matrix elements by exploiting the fact that the $\hat{\boldsymbol{p}}$ operator can be expressed as a commutator relation between \hat{H} and \boldsymbol{r} (see App. A).

Therefore, the determination of the momentum matrix elements is now a matter of determining matrix elements of the commutator $[\hat{H}, \mathbf{r}]$. Thus,

$$\langle \Psi_{v\boldsymbol{k}} | \left[\hat{H}, \boldsymbol{r} \right] | \Psi_{c\boldsymbol{k}} \rangle = \sum_{p}^{N} \sum_{p'}^{N} c_{v}^{p'}(\boldsymbol{k})^{*} c_{c}^{p}(\boldsymbol{k}) \left\langle \Phi_{\boldsymbol{k}}^{p'} | \left[\hat{H}, \boldsymbol{r} \right] | \Phi_{\boldsymbol{k}}^{p} \right\rangle$$

$$= \sum_{p}^{N} \sum_{p'}^{N} c_{v}^{p}(\boldsymbol{k})^{*} c_{c}^{p'}(\boldsymbol{k}) \sum_{lmn}^{U} \left\langle \varphi^{p'}, \boldsymbol{R}_{000}^{p'} | \left[\hat{H}, \boldsymbol{r} \right] | \varphi^{p}, \boldsymbol{R}_{lmn}^{p} \right\rangle e^{i\boldsymbol{k} \cdot \left(\boldsymbol{R}_{000}^{p'} - \boldsymbol{R}_{lmn}^{p} \right)}$$
(3.23)

where one of the sums over all lattice vectors has annihilated the 1/U factor as it was argued earlier. The problem has now been reduced to evaluating the matrix element of $[\hat{H}, r]$ between the localized atomic states. Writing out the matrix element

$$\langle \varphi^{p'}, \boldsymbol{R}_{000}^{p'} | \left[\hat{H}, \boldsymbol{r} \right] | \varphi^{p}, \boldsymbol{R}_{lmn}^{p} \rangle = \langle \varphi^{p'}, \boldsymbol{R}_{000}^{p'} | \left. \hat{H} \boldsymbol{r} \right| \varphi^{p}, \boldsymbol{R}_{lmn}^{p} \rangle - \langle \varphi^{p'}, \boldsymbol{R}_{000}^{p'} | \boldsymbol{r} \hat{H} | \varphi^{p}, \boldsymbol{R}_{lmn}^{p} \rangle \quad (3.24)$$

To evaluate the matrix elements on the right hand side the closure relation is used (see App. B), that is, the matrix elements are rewritten according to[11]

$$\langle \varphi^{p'}, \boldsymbol{R}_{000}^{p'} | \hat{H} \boldsymbol{r} | \varphi^{p}, \boldsymbol{R}_{lmn}^{p} \rangle = \langle \varphi^{p'}, \boldsymbol{R}_{000}^{p'} | \hat{H} \hat{I} \boldsymbol{r} | \varphi^{p}, \boldsymbol{R}_{lmn}^{p} \rangle = \sum_{l''m''n''} \sum_{p''} \langle \varphi^{p'}, \boldsymbol{R}_{000}^{p'} | \hat{H} | \varphi^{p''}, \boldsymbol{R}_{l''m''n''}^{p''} \rangle \langle \varphi^{p''}, \boldsymbol{R}_{l''m''n''}^{p''} | \boldsymbol{r} | \varphi^{p}, \boldsymbol{R}_{lmn}^{p} \rangle$$
(3.25)

If for example tight binding is used, the matrix elements of the Hamilton operator are known. Therefore, what is left in determining the momentum matrix elements is the evaluation of the matrix elements of r. Considering first the case when p'' = p, i.e., the two states are of the same type and are separated by a lattice vector, and looking only at the x-component of the matrix element

Figure 3.1: Two atomic orbitals centered at x (\mathbf{R}) and x'' (\mathbf{R}''). The orbitals are symmetrically distributed with respect to the vertical line passing through the midpoint x_M so that their product is an even function. The line shown is an odd function so that the integral over the product of the three vanishes.

here x_M is the midpoint between the two orbitals. This scenario is illustrated in Fig. 3.1. The function $x - x_M$ is a line which passes through the midpoint and it is an odd function of x. Since the two orbitals are the same, their product is an even function. Thus, the integrand is an odd function of x so that the first integral above vanishes. In the second integral x_M is simply a constant and goes outside the integral so that the final result, generalized to three dimensions and neglecting overlap, is

$$\langle \varphi^{p}, \boldsymbol{R}^{p}_{l^{\prime\prime}m^{\prime\prime}n^{\prime\prime}} | \boldsymbol{r} | \varphi^{p}, \boldsymbol{R}^{p}_{lmn} \rangle = \boldsymbol{R}^{p}_{lmn} \delta_{\boldsymbol{R}^{p}_{l^{\prime\prime}m^{\prime\prime}n^{\prime\prime}}, \boldsymbol{R}^{p}_{lmn}}$$
(3.27)

since when $\mathbf{R}_{lmn}^p = \mathbf{R}_{l''m''n''}^p$ the midpoint collapses and $\mathbf{R}_M = \mathbf{R}_{lmn}^p$. Of course, it does not matter if it is $\mathbf{R}_{l''m''n''}^p$ or \mathbf{R}_{lmn}^p which is multiplied onto the delta function. In the case where $p'' \neq p$ one gets simply

$$\langle \varphi^{p^{\prime\prime}}, \boldsymbol{R}^{p^{\prime\prime}}_{l^{\prime\prime}m^{\prime\prime}n^{\prime\prime}} | \boldsymbol{r} | \varphi^{p}, \boldsymbol{R}^{p}_{lmn} \rangle = \langle \varphi^{p^{\prime\prime}}, \boldsymbol{0} | \boldsymbol{r} | \varphi^{p}, \boldsymbol{0} \rangle \, \delta(\boldsymbol{R}^{p}_{l^{\prime\prime}m^{\prime\prime}n^{\prime\prime}} - \boldsymbol{R}^{p}_{lmn}) = \boldsymbol{d}_{pp^{\prime\prime}} \delta_{\boldsymbol{R}^{p}_{l^{\prime\prime}m^{\prime\prime}n^{\prime\prime}}, \boldsymbol{R}^{p}_{lmn}}$$
(3.28)

which is zero if p'' = p since the integrand then is the product of an odd and an even function. The r matrix element is therefore

$$\langle \varphi^{p^{\prime\prime}}, \boldsymbol{R}^{p^{\prime\prime}}_{l^{\prime\prime}m^{\prime\prime}n^{\prime\prime}} | \boldsymbol{r} | \varphi^{p}, \boldsymbol{R}^{p}_{lmn} \rangle = (\boldsymbol{R}^{p}_{lmn} \delta_{pp^{\prime\prime}} + \boldsymbol{d}_{pp^{\prime\prime}}) \delta_{\boldsymbol{R}^{p}_{l^{\prime\prime}m^{\prime\prime}n^{\prime\prime}}, \boldsymbol{R}^{p}_{lmn}}$$
(3.29)

Using this result and Eqn. 3.25 in Eqn. 3.23 the final result for the momentum matrix element is

λī

$$\langle \Psi_{v\boldsymbol{k}} | \, \hat{\boldsymbol{p}} \, | \Psi_{c\boldsymbol{k}} \rangle = \frac{im}{\hbar} \sum_{p,p'}^{N} c_v^p(\boldsymbol{k})^* c_c^{p'}(\boldsymbol{k}) \times$$

$$\sum_{lmn}^{U} \left(\boldsymbol{R}_{lmn}^p - \boldsymbol{R}_{000}^{p'} \right) \langle \varphi^p, \boldsymbol{R}_{lmn}^p | \, \hat{H} \, | \varphi^{p'}, \boldsymbol{R}_{000}^{p'} \rangle e^{i\boldsymbol{k} \cdot (\boldsymbol{R}_{000}^{p'} - \boldsymbol{R}_{lmn}^p)} \quad (3.30)$$

In the formula for the conductivity it is the absolute square of the momentum matrix element which is needed. This is given by $(p_x \hat{\boldsymbol{x}} + p_y \hat{\boldsymbol{y}})^* \cdot (p_x \hat{\boldsymbol{x}} + p_y \hat{\boldsymbol{y}}) = |p_x|^2 + |p_y|^2$. In graphene the minimum conductivity (zero frequency limit) is given by $\sigma_0 = e^2/(4\hbar)$ [9]. Normalizing the conductivity to the graphene minimum conductivity (DC-conductivity) and going to the low temperature limit where $f_{nm} \approx 1$ one gets for the conductivity

$$\frac{\sigma(\omega)}{\sigma_0} = \frac{2}{\pi\hbar\omega} \sum_{v,c} \iint_{\text{BZ}} |P'_{vc}|^2 \,\delta\left[E_{cv}(\boldsymbol{k}) - \hbar\omega\right] dk_x dk_y \tag{3.31}$$

where $|P_{vc}|^2 = \frac{m^2}{\hbar^2} |P'_{vc}|^2$. The integration has to be done numerically since the momentum matrix elements are only known numerically. It can be done by brute force by simply stepping through alot of k points but this is slowly convergent. Instead a more intelligent triangle integration method is adapted. The principle of the method is to split the 2D irreducible BZ into small triangles and then apply a linearization of energies and momentum matrix elements inside this triangle. The method is described in more detail in App. C.

3.3 Excitonic Effects

An exciton in a semiconductor is created when an electron is excited from a valence band to a conduction band thus leaving a hole in the valence band. The electron is negatively charged and the hole is positively charged so that there will be an effective attraction between the two. The exciton is the bound state of the electron and the hole and this particle moves through the crystal. The exciton resembles the hydrogen atom since it is a positive charge and a negative charged which are bound together.

Since graphene is a two dimensional material excitonic effects are expected to be strong. This is because electrons and holes are confined in space to the same plane and this causes a larger overlap of their wavefunctions. When including excitonic effects in the calculation of optical spectra of semiconductors peaks will be seen below the band gap of the structure. This is due to the fact that additional energy levels are introduced, namely those of the bound states of the electron and hole. These bound states can be shown to obey an equation similar to the equation for the hydrogen atom, namely the so called Wannier equation [12]

$$\left(E_g - \nabla^2\right)\Psi_{\rm exc}(\boldsymbol{r}) - \frac{2}{r}\Psi_{\rm exc}(\boldsymbol{r}) = E_{\rm exc}\Psi_{\rm exc}(\boldsymbol{r})$$
(3.32)

The energies here are given in units of the effective Rydberg and distances are given in units of the effective Bohr radius

$$\operatorname{Ry}^{*} = \frac{\hbar^{2}}{2m_{eh}a_{B}^{2}}, \qquad a_{B}^{*} = \frac{4\pi\varepsilon\varepsilon_{0}\hbar^{2}}{m_{eh}e^{2}}$$
(3.33)

where m_{eh} is the reduced effective mass given by $m_{eh} = m_e^* m_h^* / (m_e^* + m_h^*)$. Thus, the unit of energy and the unit of distance depend on the actual system since 1) the effective mass is dependent on the band structure and 2) the value of ε may vary. These units are called natural exciton units. The Wannier equation is valid for both 3D, 2D and 1D materials provided that the corresponding laplace operator and the correct value of E_g is used. In 2D for example, if the 3D value of E_g is used one has to explicitly take into account the modification of the band gap due to the additional confining potential.

Similarly to the hydrogen atom the bound state solutions correspond to solutions with negative energy, i.e., those states for which $E_g > E_{\text{exc}}$. It is these bound states which give rise to the discrete absorption peaks below the band gap. Solutions of positive energy, $E_{\text{exc}} > E_g$ correspond to unbound continous states and it is these continous states which give rise to the continous absorption spectrum above the band gap. For the bound states the above equation can be solved by methods similar to those used to solve the equation for the hydrogen atom, even though the present problem is 2D. It can be shown that only the s-type eigenstates are relevant for the optical spectra and therefore it is only necessary to solve the equation for the states with no angular dependence. The 2D Laplace operator in polar coordinates is given by

$$\nabla^2 = \frac{d^2}{dr^2} + \frac{1}{r}\frac{d}{dr} + \frac{1}{r^2}\frac{d^2}{d\theta^2}$$
(3.34)

For the angle independent s-type states the last operator vanishes. The Wannier equation then takes the form

$$\left(\frac{d^2}{dr^2} + \frac{1}{r}\frac{d}{dr} + \frac{2}{r} - \alpha^2\right)\Psi(r) = 0$$
(3.35)

where $\alpha^2 = E_g - E_{\text{exc}}$ so that α is real for the bound states. In order to solve this equation one first examines the behaviour for $r \to \infty$. In this case one gets

$$\frac{d^2\psi_{\infty}}{dr^2} = \alpha^2\psi_{\infty} \tag{3.36}$$

with the solution $\psi_{\infty} = c_1 e^{-\alpha r} + c_2 e^{\alpha r}$. For the function to be normalizable $c_2 = 0$, and therefore $\psi_{\infty} = c_1 e^{-\alpha r}$. Writing the total exciton wavefunction as $\Psi(r) = \psi(r)\psi_{\infty}(r)$ and inserting this into Eqn. 3.35 the following differential equation for $\psi(r)$ is obtained

$$r\frac{d^2\psi}{dr^2} + (1 - 2\alpha r)\frac{d\psi}{dr} + (2 - \alpha)\psi = 0$$
(3.37)

This differential equation can be transformed into the Laguerre equation by introducing the transformation $\rho = 2\alpha r$. Under this transformation the differential operators behave as

$$\frac{d}{dr} \Longrightarrow (2\alpha) \frac{d}{d\rho}, \qquad \frac{d^2}{dr^2} \Longrightarrow (2\alpha)^2 \frac{d^2}{d\rho^2}$$
 (3.38)

Thus, applying the transformation to Eqn. 3.37 gives

$$\rho \frac{d^2 \psi}{d\rho^2} + (1-\rho) \frac{d\psi}{d\rho} + n\psi = 0$$
(3.39)

where the constant n is given by

$$n = \frac{2 - \alpha}{2\alpha} = \frac{2 - \sqrt{E_g - E_{\text{exc}}}}{2\sqrt{E_g - E_{\text{exc}}}}$$
(3.40)

from which it follows that

$$\alpha^2 = E_g - E_{\text{exc}} = \frac{1}{(n + \frac{1}{2})^2} \tag{3.41}$$

The solution to Eqn. 3.39 is a Laguerre polynomial $L_n(x)$, where *n* is a non-negative integer or zero (n = 0, 1, ...) (see App. D). Therefore, expressing again the functions in terms of *r* instead of ρ , the solution to the 2D Wannier equation Eqn. 3.35 is given by

$$\Psi(r) = c_1 L_n(2r\alpha) e^{-\alpha r} = c_1 L_n\left(\frac{2r}{n+\frac{1}{2}}\right) e^{-r/(n+\frac{1}{2})}$$
(3.42)

with the corresponding energies given by

$$E_{\rm exc} = E_g - \frac{1}{(n + \frac{1}{2})^2} \tag{3.43}$$

Chapter 4

Implementation & Results

4.1 Setting up the Lattice Geometry

In order to apply the TB method the coordinates of the atoms within the unit cell have to be known. In this section it is shown how to generate the geometry of the antidot lattice. For the purpose of illustrating the setup of the unit cell geometry, i.e., to find the coordinates of the atoms in the unit cell, unit cells without holes in them will be considered first. The introduction of holes into the unit cells is simple and is discussed as the last point.

To determine the coordinates of the atoms in the unit cell the lines which bound the unit cell are first defined. These lines are shown in the left part of Fig. 4.1 and they are labelled L1 to L6. The shaded area is the unit cell to be constructed and the white area is the graphene sheet. To create the unit cell geometry one simply checks all points among a set of points which is certain to contain the whole unit cell. If the point lies inside the structure defined by the lines, it belongs to the unit cell. Any point can be transformed into the first quadrant (left part of Fig. 4.1) by taking the absolute value of x and y. Therefore it is enough to check if the transformed point lies within the area bounded by the x and y axes and the two lines L1 and L2 in order to determine if the point belongs to the unit cell.

The lines are defined in terms of the unit cell size. The size of the unit cell is defined by the edge length, L, and the edge length is expressed in terms of the number of hexagons on the unit cell edge. For example, the dark structure shown in the left part of the figure has an edge length of L = 2. The actual length of the unit cell edge in Ångstrøms is given by La_0 where a_0 is the graphene lattice constant. The lines L1 and L2 are defined by

L1:
$$y = -\frac{x}{\sqrt{3}} + La_0$$
 (4.1)

L2:
$$x = \frac{\sqrt{3}L}{2}a_0$$
 (4.2)

The condition for a point (x, y) being inside the unit cell then becomes

$$|x| < \frac{\sqrt{3}L}{2}a_0$$
 and $|y| < -\frac{x}{\sqrt{3}} + La_0$ (4.3)

23



Figure 4.1: The left figure shows a single unit cell in a graphene sheet. The unit cell is the bounded by the six lines L1-L6. The size of the unit cell is specified by the distance d which is given in units of second nearest neighbour distances. In the right figure the primitive translation vectors are shown.

With the position of the atoms within the unit cell specified, it still remains to specify the lattice. This is illustrated in the right part of Fig. 4.1. The lattice vectors are chosen as shown, and they are given by

$$a_1 = \left(\frac{\sqrt{3}}{2}, \frac{3}{2}\right) La_0, \qquad a_2 = \left(\frac{\sqrt{3}}{2}, -\frac{3}{2}\right) La_0$$
(4.4)

No single atom is shared between two or more unit cells. Each atom in the crystal belongs to one and only one unit cell. This is important because in the TB model it must be specified which types of atom each atom interacts with. Each atom in the unit cell is given a unique number but if the atom is shared among several unit cells it is unclear which type of atom it is. In order to avoid these complications the unit cells are chosen as shown.

In order to calculate the band structure it is necessary to know the reciprocal lattice vectors. They can be calculated by the requirement that $e^{i\boldsymbol{a}_i\cdot\boldsymbol{b}_j} = \delta_{ij}$ from which it follows the $\boldsymbol{a}_i\cdot\boldsymbol{b}_j = 2\pi\delta_{ij}$. By exploiting this relationship (for example by setting it up as a matrix equation) the reciprocal lattice vectors are found to be

$$\boldsymbol{b}_{1} = \left(\frac{1}{\sqrt{3}}, \frac{1}{3}\right) \frac{2\pi}{La_{0}}, \qquad \boldsymbol{b}_{2} = \left(\frac{1}{\sqrt{3}}, -\frac{1}{3}\right) \frac{2\pi}{La_{0}}$$
(4.5)

The first Brillouin zone for the antidot lattice is similar to the Brillouin zone for pure graphene, except that it is smaller, and is therefore not shown here. The introduction of holes into the unit cell is simply a matter of removing atoms from the middle of the unit cell. To create a circular hole atoms with coordinates which satisfy $x^2 + y^2 < (Ra0)^2$, where R is the hole radius given in terms of a_0 (R need not be an integer), are removed. The hole radius is thus expressed in terms of a_0 just as the edge length. In Fig. 4.1 two antidot lattices are shown.



Figure 4.2: Antidot lattices $\{10,4\}$ and $\{10,5\}$. The $\{10,4\}$ antidot lattice in unphysical because of the dangling bonds which will quickly relax to form another geometry near the hole.

4.2 Graphene Antidot Band Structure

In this section the band structures of various graphene antidot lattices are shown. In order to calculate these band structures the theory described in Sec. 2.1 is used. The central point is the calculation of the matrix elements, Eqn. 2.11 and Eqn. 2.12, which in the case of graphene or graphene antidot lattices specializes to

$$\hat{\mathsf{H}}_{pp'} = \sum_{lmn}^{U} e^{i\boldsymbol{k} \cdot \left(\boldsymbol{R}_{lmn}^{p} - \boldsymbol{R}_{000}^{p'}\right)} \left\langle \pi(\boldsymbol{r} - \boldsymbol{R}_{000}^{p'}) \right| \hat{H} \left| \pi(\boldsymbol{r} - \boldsymbol{R}_{lmn}^{p}) \right\rangle$$
(4.6)

$$\hat{\mathsf{S}}_{pp'} = \sum_{lmn}^{U} e^{i\boldsymbol{k}\cdot\left(\boldsymbol{R}_{lmn}^{p} - \boldsymbol{R}_{000}^{p'}\right)} \left\langle \pi(\boldsymbol{r} - \boldsymbol{R}_{000}^{p'}) | \pi(\boldsymbol{r} - \boldsymbol{R}_{lmn}^{p}) \right\rangle$$
(4.7)

where π is an atomic π orbital. In graphene the π orbitals are oriented perpendicular to the plane of the carbon atoms, and it is the electrons in these orbitals which are the most loosely bound. It is therefore those which contribute most significantly to the conduction current and to the optical properties of graphene. As it can be seen from the above formulas, in order to evaluate the matrix elements, the overlap and \hat{H} matrix element between π orbitals is needed. These parameters can be obtained from ab-initio calculations or by fitting the TB model to more accurate models. In [13] the parameters have been calculated up to third nearest neighbour by fitting to a more accurate quasi particle model. They are given as[13]

$$\begin{array}{ll} \gamma_1 = -3.4416\,\mathrm{eV} & \gamma_2 = -0.7544\,\mathrm{eV} & \gamma_3 = -0.4246\,\mathrm{eV} \\ s_1 = 0.2671 & s_2 = 0.0494 & s_3 = 0.0345 \end{array}$$

where γ_i is the \hat{H} matrix element and s_i the overlap matrix element between π orbitals up to third nearest neighbour. For example, if the length of $\mathbf{R}_{000}^{p'} - \mathbf{R}_{lmn}^{p}$ equals the first nearest neighbour distance, the matrix element $\langle \pi(\mathbf{r} - \mathbf{R}_{000}^{p'}) | \pi(\mathbf{r} - \mathbf{R}_{lmn}^{p}) \rangle$ equals γ_1 . From these matrix elements and the geometry of the antidot lattice the tight binding problem can be solved and the band structure calculated.

In Fig. 4.3(a) the band structure of a $\{5,3\}$ antidot lattice calculated with only nearest neighbour interactions and without overlap is shown. The bandgap of this structure is $\approx 2.0 \text{ eV}$. In Fig. 4.3(b) the result of a calculation with nearest neighbour interactions and overlap is shown, the bandgap of this structure is $\approx 1.7 \text{ eV}$. The expected behaviour of including the overlap can be predicted by a simple analysis. When including only nearest neighbour interactions the Hamilton and overlap matrices are related by a simple one-to-one correspondence to the same matrix \hat{A} such that $\hat{S} = s_1 \hat{A} + \hat{I}$ and $\hat{H} = \gamma_1 \hat{A} + E_0 \hat{I}$. The generalized eigenvalue problem Eqn. 2.8 then takes the form

$$\left[\gamma_1 \hat{\mathsf{A}} + E_0 \hat{\mathsf{I}} - s_1 E \hat{\mathsf{A}} - E \hat{\mathsf{I}}\right] \cdot \boldsymbol{c} = \boldsymbol{0}$$
(4.8)

Gathering similar terms on each side one obtains the standard eigenvalue problem

$$\hat{\mathsf{A}} \cdot \boldsymbol{c} = \frac{E - E_0}{\gamma_1 - sE} \boldsymbol{c} \tag{4.9}$$

If overlap is neglected one has

$$\hat{\mathsf{A}} \cdot \boldsymbol{c} = \frac{E_{\mathrm{NO}} - E_0}{\gamma_1} \boldsymbol{c} \tag{4.10}$$

where $E_{\rm NO}$ is the eigenvalue without overlap. Therefore

$$\frac{E - E_0}{\gamma_1 - s_1 E} = \frac{E_{\rm NO} - E_0}{\gamma_1} \tag{4.11}$$

Solving for E one gets

$$E(E_{\rm NO}) = \frac{E_{\rm NO}}{1 + s_1(E_{\rm NO} - E_0)/\gamma_1}$$
(4.12)

If all energies are measured in units of $|\gamma_1|$ (dividing the equation by $|\gamma_1|$ and remembering that γ_1 is negative so that $\gamma_1 = -|\gamma_1|$) one gets

$$\epsilon(\epsilon_{\rm NO}) = \frac{\epsilon_{\rm NO}}{1 + s_1(\epsilon_0 - \epsilon_{\rm NO})} \tag{4.13}$$

where $\epsilon_0 = -E_0/|\gamma_1|$ and $\epsilon_{\rm NO} = -E_{\rm NO}/|\gamma_1|$. This provides a simple relationship between the band structure without overlap and the band structure with overlap. It can be seen that the constant ϵ_0 (E_0) no longer plays the simple role of shifting the energies up or down.

Another key point is that the band structure is no longer symmetric about the bandgap as it was when overlap was neglected. This can be easily seen from Eqn. 4.13 since changing the sign of $\epsilon_{\rm NO}$ does not simply imply a change of sign in ϵ . This has the impact that the curvature

of the highest valence band and the curvature of the lowest conduction band are generally not the same. Since the effective electron and hole masses are coupled to the curvature of the bands, the effective masses of electrons and holes are no longer the same.

Differentiating the above expression with respect to $\epsilon_{\rm NO}$ yields

$$\frac{d\epsilon}{d\epsilon_{\rm NO}} = \frac{1 + s_1\epsilon_0}{(1 + s\epsilon_0 - s_1\epsilon_{\rm NO})^2} \tag{4.14}$$

The denominator of this expression is always positive and it is a monotonically decreasing function of $\epsilon_{\rm NO}$ in the range of interest. Thus, the derivative is monotonically increasing (apart from the singularity). This means that the bands below zero of energy are compressed and the bands above zero of energy are expanded. Also, $\epsilon(\epsilon_{\rm NO})$ is negative for $\epsilon(\epsilon_{\rm NO}) < 0$ and positive for $\epsilon(\epsilon_{\rm NO}) > 0$ so that bands preserve their sign after inclusion of overlap.

In Fig. 4.3(a) and Fig. 4.3(b) it is seen that it is mostly the valence bands which are influenced by the overlap. The valence bands are compressed while the conduction bands are hardly changed. This corresponds well with the analysis given above since in the region E = -3.0 eVto E = 0 eV, $E(E_{\text{NO}})$ can be well approximated by a straight line of the form $E(E_{\text{NO}}) = E_{\text{NO}}$.

In Fig. 4.3(c) the band structure of a $\{5,3\}$ antidot lattice is shown taking into account third nearest neighbour interactions and overlap. Now both the valence bands and the conduction bands are heavily changed by the additional interactions. The band gap is not changed substantially by the additional interactions and overlap.

Fig. 4.4 show the band structure of a $\{10,1\}$ antidot lattice for both a nearest neighbour and third nearest neighbour calculation. Here it is to be noticed that the structure has several features which resemble the band structure of pure graphene. The band gap of the $\{10,1\}$ antidot lattice is only about 0.11 eV so that the band gap approaches the graphene value of 0 eV as the disturbance due to the holes gets smaller. Another feature to notice is that the top valence band and the bottom conduction band obeys a nearly linear dispersion which is also a feature of pure graphene.

In Fig. 4.5 the band structure of a $\{10,5\}$ antidot lattice is shown. The band gap increases and the band dispersions again become parabolic near the Γ point.

4.3 Effective Mass Calculation

The effective mass of an electron in a band can be determined from the relation

$$m_n^* = \hbar^2 \left(\frac{d^2 E_n}{dk^2}\right)^{-1}$$
(4.15)

where n designates the particular band. For optical and electrical applications the highest valence band and the lowest conduction band are the most important. Furthermore, since optical excitations at energies of the same magnitude as the band gap will drive electrons from the valence band to the conduction band at the Γ point, and since potential doping will introduce electrons into the conduction band and/or holes into the valence band at the Γ point, it this point which is the most interesting. In this point the bands are approximately parabolic and the curvature can therefore be determined by fitting a parabola to the band structure.



Figure 4.3: The band structure of (a) a $\{5,3\}$ antidot lattice with no overlap and only nearest neighbours taken into account and (b) a $\{5,3\}$ antidot lattice with nearest neighbour interactions and overlap and (c) a $\{5,3\}$ antidot lattice with third nearest neighbour interactions and overlap. It is seen that the band structure is no longer symmetric about the bandgap when overlap is included.

This fit can be easily made by linear regression methods. The goal is to fit a function of the form $f(x, a) = ax^2$ to the conduction band and the valence band in the Γ point, by adjusting the fitting parameter a. The quality of the fit is described by a least square function

$$S(x,a) = \sum_{i}^{N} r_{i}^{2} = \sum_{i}^{N} [y_{i} - f(x_{i},a)]^{2}$$
(4.16)

where *i* runs over N points near the band extremum. In this calculation N = 5. Obviously, the fit is the best when the function S(x, a) is a minimum, and this happens when $\frac{\partial S}{\partial a} = 0$. Thus

$$\frac{\partial S}{\partial a} = 2\sum_{i}^{N} \left[y_i - f(x_i, a) \right] \frac{\partial f}{\partial a} = 0$$
(4.17)

and upon inserting $f(x, a) = ax^2$ one obtains

$$a = \left(\sum_{i}^{N} y_{i} x_{i}^{2}\right) / \left(\sum_{i}^{N} x_{i}^{4}\right)$$

$$(4.18)$$

With the fitting parameter a determined the curvature of the band is easily obtained and is simply given by 2a. Thus, the effective mass of an electron in the conduction band or a hole in the valence band is given by

$$m_e^* = \frac{\hbar^2}{2a_c}, \qquad m_h^* = -\frac{\hbar^2}{2a_v}$$
 (4.19)



Figure 4.4: Band structures of a $\{10,1\}$ antidot lattice. (a) calculated with only nearest neighbour interactions (b) calculated with third nearest neighbour interactions and overlap. Both structures have clear similarities to the band structure of pure graphene.

where the minus sign in the expression for the hole mass is there because the curvature of the valence band is negative. From the electron mass and the hole mass the reduced effective exciton mass μ can be calculated

$$\mu = \frac{m_e^* m_h^*}{m_e^* + m_h^*} \tag{4.20}$$

In Tbl. 4.3 the electron and hole effective masses, the exciton reduced mass and the band gap magnitude are listed for a number of different antidot lattices. The ratio μ/E_g is also shown. All masses are given in units of electron masses. Some of the antidot lattices are not in the list because they are not physical. For example, dangling bonds are not permitted because they will quickly form new bonds and possible crumple the graphene sheet (see Fig. 4.1).

When taking a look at the last column of the table it is seen that the ratio between the reduced mass and the bandgap is on the same order of magnitude for almost all the structures. In particular, for structures with small hole diameters the ratios are nearly equal. For example, for the $\{3,1\}$ structure the ratio is $0.06972 \,\mathrm{eV}^{-1}$. For $\{4,1\}$ it is $0.06497 \,\mathrm{eV}^{-1}$. This suggest that the reduced effective mass might be approximately proportional to the bandgap for these structures.

Another feature to be noticed is that for large unit cells with small holes the effective masses become quite small. For $\{10,1\}$, $\{11,1\}$ and $\{12,1\}$ the effective electron and hole masses are on the order of 0.01. Also, the electron and hole masses are nearly equal and become closer to each other as the ratio of removed atoms to total number of atoms decreases. This is exactly



Figure 4.5: Band structures of a $\{10,5\}$ antidot lattice. (a) calculated with only nearest neighbour interactions (b) calculated with third nearest neighbour interactions and overlap.

what must be expected because the structure must resemble more closely the properties of pure graphene when the ratio of removed electrons to total electrons approaches zero.

4.4 Optical Spectra

The conductivity of a graphene sheet can be calculated from Eqn. 3.31. The sum over valence and conduction states has to include all bands with transition energies allowing for excitation by a photon of frequency ω somewhere in the irreducible Brillouin zone. Thus, if the conductivity between 0 eV and 1 eV is calculated, there is no need to include bands with $v \to c$ transition energies larger than 1 eV. In the calculations only excitation from valence bands to conduction bands are considered. In principle an excitation from a valence band to a conduction band would allow for a subsequent $v \to v$ excitation. This effect is assumed to be small due to rapid relaxation, so that valence states are nearly always occupied, and due to the photons carrying negligible momentum. Intraband transitions are ignored with the same argument.

The integration has to be done over the complete first Brillouin zone. But since the transition energies repeat themselves through the 12 irreducible BZs it is only necessary to do the integration over one irreducible zone. The momentum matrix elements however, are not invariant through the 12 irreducible zones and therefore the symmetrized matrix element $|P_{vc}|^2 = \left(|P_{vc}^x|^2 + |P_{vc}^y|^2\right)/2$ is used. Eqn. 3.31 then takes the form

AD-Lattice	m_e	m_h	μ	E_q	μ/E_g
{3,1}	0.14491	0.13285	0.06931	0.99408	0.06972
{4,1}	0.08314	0.07748	0.04011	0.61732	0.06497
{4,2}	0.25259	0.20371	0.11277	1.025510	0.10996
{5,1}	0.05232	0.04964	0.02547	0.41846	0.06087
{5,2}	0.17637	0.13034	0.07495	0.76228	0.09832
{5,3}	1.00956	0.35812	0.26435	1.808690	0.14615
{6,1}	0.03551	0.03416	0.01741	0.30119	0.05781
{6,2}	0.11630	0.08935	0.05053	0.55527	0.09100
$\{6,3\}$	0.27218	0.18858	0.11140	1.102170	0.10107
{7,1}	0.02556	0.02484	0.01260	0.22662	0.05559
{7,2}	0.07963	0.06148	0.03469	0.42673	0.08130
$\{7,3\}$	0.14819	0.11926	0.06608	0.76363	0.08653
$\{7,5\}$	0.26034	0.35423	0.15006	1.408590	0.10653
{8,1}	0.01926	0.01885	0.00953	0.17643	0.05399
{8,2}	0.05931	0.04900	0.02683	0.34012	0.07889
$\{8,3\}$	0.09683	0.08291	0.04466	0.56913	0.07848
$\{8,5\}$	0.27774	0.23249	0.12656	0.91297	0.13862
$\{8,6\}$	0.24129	0.47132	0.15959	1.015950	0.15708
$\{9,1\}$	0.01504	0.01479	0.00746	0.14114	0.05283
$\{9,2\}$	0.04507	0.03829	0.02070	0.27829	0.07439
$\{9,3\}$	0.06930	0.06132	0.03253	0.44455	0.07318
$\{9,5\}$	0.30484	0.16858	0.10855	0.69616	0.15593
$\{9,6\}$	0.24446	0.30778	0.13625	0.62483	0.21805
$\{10,1\}$	0.01208	0.01192	0.00600	0.11542	0.05199
$\{10,2\}$	0.03541	0.03085	0.01649	0.23235	0.07096
$\{10,3\}$	0.05246	0.04741	0.02490	0.35885	0.06939
$\{10,5\}$	0.34937	0.12968	0.09458	0.57730	0.16382
$\{10,6\}$	0.24468	0.22890	0.11826	0.44964	0.26302
$\{10,7\}$	0.23169	0.65769	0.17133	0.40883	0.41908
{11,1}	0.00990	0.00979	0.00492	0.09611	0.05122
{11,2}	0.02833	0.02487	0.01324	0.19715	0.06717
{11,3}	0.04127	0.03785	0.01974	0.29685	0.06651
$\{11,5\}$	0.22978	0.10343	0.07133	0.48323	0.14760
{11,6}	0.24776	0.19788	0.11002	0.35860	0.30679
{11,7}	0.22017	0.38739	0.14038	0.27993	0.50150
$\{12,1\}$	0.00828	0.00821	0.00412	0.08125	0.05072
{12,2}	0.02346	0.02121	0.01114	0.16953	0.06570
$\{12,3\}$	0.03341	0.03100	0.01608	0.25027	0.06425
{12,5}	0.17581	0.08464	0.05713	0.40811	0.13999
{12,6}	0.24448	0.13207	0.08575	0.30141	0.28449
$\{12,7\}$	0.20711	0.44281	0.14111	0.21503	0.65623

Table 4.1: m_e : effective electron masses (units of m_e), m_h : effective hole masses (units of m_e), μ : reduced effective exciton mass (units of m_e), E_g : energy gap size (eV), μ/E_g : ratio between reduced mass and bandgap (eV⁻¹)

$$\frac{\sigma\left(\omega\right)}{\sigma_{0}} = \frac{12}{\pi\hbar\omega} \sum_{v,c} \iint_{\text{Irr. BZ}} \left(\left|P_{vc}^{x}\right|^{2} + \left|P_{vc}^{y}\right|^{2}\right) \delta\left[E_{cv}(\boldsymbol{k}) - \hbar\omega\right] dk_{x} dk_{y}$$
(4.21)

where the extra factor of 12 stems from the fact that the integration is now only over the irreducible zone. For the numerical integration the triangle integration method described in App. C is used. Each side of the triangular irreducible BZ is partitioned into n = 65 pieces giving a total of 4096 triangles or 2145 k-points. The number of triangles can be calculated from No. Triangles = $(n-1)^2$ and the number of k-points from No. k-Points = n(n+1)/2. In all of the following graphs 10000 points were used along the energy interval from $0 \,\mathrm{eV}$ to $4 \,\mathrm{eV}$. In Fig. 4.6(a) and Fig. 4.6(b) the spectra of a $\{5,1\}$ and a $\{5,3\}$ antidot lattice are shown. The blue curve is with only nearest neighbour interactions and no overlap and the red curve is with three nearest neighbours interactions and overlap. The conductivity is zero below the band gap and rises sharply when the energy becomes large enough to excite the electrons from the top of the highest valence band to the bottom of the lowest conduction band in the Γ point. The peaks in the spectrum correspond to high absorption at the corresponding photon energies. When the calculation is made with 3NN and overlap the band gap decreases in both the $\{5,1\}$ structure and the $\{5,3\}$ structure, although the decrease for the $\{5,1\}$ structure is almost not noticeable. For the $\{5,3\}$ 3NN spectrum the absorption decreases rapidly at around 2.1 eV. This can be explained by looking at the band structure for the $\{5,3\}$ structure in Fig. 4.3(c). A relatively wide band exists between 1.3 eV and 1.8 eV where there are no allowed states. In the 1NN calculation without overlap, Fig. 4.3(a) this band is much narrower.

In Fig. 4.6(c) to Fig. 4.6(f) the spectra of antidot lattices $\{10,1\}$, $\{10,3\}$, $\{10,5\}$ and $\{10,7\}$ are shown. In all the spectra the band gap decreases in the 3NN calculation, just as it was the case for $\{5,1\}$ and $\{5,3\}$, except for $\{10,1\}$ where a slight increase in band gap is observed.

When the hole diameter is small the spectra bear similarities to the spectrum of pure graphene. For the $\{5,1\}$ and $\{10,1\}$ lattices the conductivity approaches unity after the onset of absorption for low energies (low frequencies). This corresponds to the pure graphene case where the DC conductivity is exactly σ_0 . Thus, in the limit of small perturbations due to the holes, the spectra resemble those of pure graphene just as the band structure showed to do. For high energies or for structures with large holes the resemblance to pure graphene disappears.

The peaks are very sharp in the calculations but in a true experiment absorption at such pronounced energies will not be seen in the spectrum. There will be some broadening of the peaks due to thermal fluctuations and imperfections in the crystal. To account for this, the broadening can be introduced by convolution with a Gaussian function

$$f(\omega) = \frac{1}{\Gamma\sqrt{\pi}} e^{-(\omega-\omega')^2/\Gamma^2}$$
(4.22)

where the front factor is a normalization. Convolution can be viewed as a way to "merge" two functions. The convolution of two functions f and g is given by

$$[f * g](\omega) = \int_{-\infty}^{\infty} f(w)g(\omega - w)dw$$
(4.23)

where * denotes the convolution operation. In Fig. 4.7 the convolution of the $\{5,3\}$ and $\{10,5\}$ antidot lattices with a Gaussian function is shown. The broadening is set to $\hbar\Gamma = 0.025 \text{ eV}$. The sharp peaks are not present in these spectra and the fine structure in the spectra has been blurred by the convolution operation. These spectra more closely resemble what would be seen in a realistic experiment.

4.5 Excitonic Effects

In the optical spectra presented in the previous section no excitonic effects were included. Inclusion of excitonic effects results in absorption below the band gap due to additional energy levels introduced as a result of the attraction between the electron and the hole. The energy of an exciton in the bound state is given by Eqn. 3.35 and is restated here

$$E_n = E_g - \frac{\text{Ry}^*}{(n+\frac{1}{2})^2}$$
 $\text{Ry}^* = 13.6 \,[eV] \,\frac{\mu}{\varepsilon^2}$ (4.24)

Thus, the exciton energy levels are located between $E = E_g$ and $E = E_g - 4$ Ry^{*}. In order to calculate the value of the effective Rydberg Ry^{*}, the effective exciton masses found in Tbl. 4.3 are needed together with the dielectric constant. The calculation of the dielectric constant is itself a quite complicated task. Its value depend on the details of the surrounding medium. If graphene is placed in air on a silicon dioxide substrate however, it can be assumed that the effective dielectric constant is given by the average of the dielectric constants of air and SiO₂, $\varepsilon = (\varepsilon_{\text{SiO}_2} + \varepsilon_{\text{air}})/2 = 2.5$. The effective Rydberg for antidot lattices {5,1}, {5,3}, {10,1}, {10,3}, {10,5} and {10,7} are given below

$$\begin{array}{ll} Ry^*_{\{5,1\}} = 55 \, \mathrm{meV} & Ry^*_{\{5,3\}} = 574 \, \mathrm{meV} & Ry^*_{\{10,1\}} = 13 \, \mathrm{meV} \\ Ry^*_{\{10,3\}} = 54 \, \mathrm{meV} & Ry^*_{\{10,5\}} = 205.0 \, \mathrm{meV} & Ry^*_{\{10,7\}} = 371.0 \, \mathrm{meV} \end{array}$$

The quite large magnitudes of the effective Rydbergs show that excitonic effects are indeed of importance in graphene antidot lattices. Some of the values are, however, so large that the difference $E_g - 4Ry^*$ becomes negative, which cannot be true. The dielectric constant has been introduced in a rather arbitrary way and it has a large impact on the value of the effective Rydberg so that this might be an explanation.



Figure 4.6: Normalized conductivity spectra for (a) $\{5,1\}$, (b) (5,3), (c) $\{10,1\}$, (d) $\{10,3\}$, (e) $\{10,5\}$ and (f) $\{10,7\}$ graphene antidot lattices. The blue spectra are calculated with only nearest neighbour interaction and no overlap, and the red spectra are calculated with three nearest neighbours and overlap. (NO: no overlap)



 $\label{eq:Figure 4.7: Conductivity spectra of (a) \{5,3\} \ and \ (b) \ \{10,5\} \ antidot \ lattices \ with \ broadening \ of \ 25 \ meV.$

Chapter 5

Discussion and Conclusion

In this project a tight binding model has been applied in order to model graphene antidot lattices. The band structure has been calculated for a number of different antidot lattices, and the effect of including overlap and up to third nearest neighbour interactions in the calculations has been investigated. The effective electron and hole masses have been determined and used to find the reduced excition masses. Finally, the optical properties of graphene antidot lattices have been studied and the effect of including excitons in the calculations have been treated in a somewhat arbitrary way.

The goal of the project was to investigate the differences between a tight binding model with only nearest neighbour interactions and no overlap, and a model with overlap and up to third nearest neighbour interactions included. This goal has been fulfilled. It is clear from the bandstructures presented in the last chapter that the additional interactions and the overlap have a large impact. The large impact is due to the quite large values of the transfer integrals γ_2 and γ_3 and the overlap integrals s_1 , s_2 and s_3 . It has been shown that the band gap can be tuned by adjusting the hole diameter and the separation of the holes. A clear connection between the diameter, separation and band gap has not been found. It seems however, that for a constant separation and increasing hole diameter, the band gap first increased and then starts to decrease (Tbl. 4.3).

The absorption of some graphene antidot structures has been calculated in both the simple first nearest neighbour tight binding model and the third nearest neighbour model. When the removed atoms to total number of atoms (total number before any are removed) ratio is small, the two models do not differ significantly for low energies. This means that the two models can be expected to give similar results for pure graphene in the low energy (low frequency) limit. For higher energies though, discrepancys are found. This trend becomes particularly pronounced when the ratio of removed atoms to total number of atoms becomes larger. For some structures the differences are so significant that the spectrum is hardly recognizable.

Finally, the effect of excitons has been touched upon. It has been shown that this effect is large in graphene. This was expected since graphene is a two dimensional material, so that electrons and holes are confined to a plane, and this causes a large overlap of their wave functions. Therefore excitons cannot be ignored. In this work however, excitons have not been properly treated and a more rigorous treatment must be made in order to fully account for the effects of excitons. Excitons will also influence the continuum spectrum and not only introduce discrete energylevels below the band gap.

From the results obtained in this work it can be concluded that a tight binding model for graphene antidot lattices, based on only first nearest neighbour interactions with overlap excluded, is not enough for an accurate description of the structures. More accurate models must be used and the three nearest neighbour model is a step in this direction. Furthermore, it can be concluded that excitons play a major role in the optical spectra of graphene antidot structures, and an accurate description has to take excitons fully into account.

Appendix A

Identities

A.1 Momentum Operator

The momentum operator can be expressed in terms of the commutator between \hat{H} and \boldsymbol{r} , this will now be shown. In the single particle case one gets

$$[\hat{H}, \mathbf{r}]\psi = \hat{H}(\mathbf{r}\psi) - \mathbf{r}\hat{H}\psi = \frac{-\hbar^2}{2m}\left(\nabla^2 \mathbf{r}\psi - \mathbf{r}\nabla^2\psi\right)$$
(A.1)

where $\hat{H} = \frac{-\hbar^2}{2m} \nabla^2 + V(\mathbf{r})$ was used in the last step. To evaluate this it is necessary to evaluate $\nabla^2 \mathbf{r} \psi$. Writing it out explicitly

$$\nabla^2 \boldsymbol{r} \psi = \left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}\right) \left(\psi x \hat{\boldsymbol{x}} + \psi y \hat{\boldsymbol{y}} + \psi z \hat{\boldsymbol{z}}\right)$$
(A.2)

Now, there are three equivalent terms on the right hand side and they are of the form $\frac{d^2}{dx^2}(\psi x \hat{x} + \psi y \hat{y} + \psi z \hat{z})$. Evaluating one of these terms one obtains

$$\frac{d^2}{dx^2}\left(\psi x \hat{\boldsymbol{x}} + \psi y \hat{\boldsymbol{y}} + \psi z \hat{\boldsymbol{z}}\right) = \frac{d}{dx} \left(\psi \hat{\boldsymbol{x}} + x \frac{d\psi}{dx} \hat{\boldsymbol{x}} + y \frac{d\psi}{dx} \hat{\boldsymbol{y}} + z \frac{d\psi}{dx} \hat{\boldsymbol{x}}\right)$$
(A.3)

$$= \left(2\frac{d\psi}{dx} + x\frac{d^2\psi}{dx^2}\right)\hat{\boldsymbol{x}} + y\frac{d^2\psi}{dx^2}\hat{\boldsymbol{y}} + z\frac{d^2\psi}{dx^2}\hat{\boldsymbol{z}}$$
(A.4)

Similar expression are obtained from the other terms. Adding these three terms together gives

$$\nabla^{2} \boldsymbol{r} \psi = x \left(\frac{d^{2} \psi}{dx^{2}} + \frac{d^{2} \psi}{dy^{2}} + \frac{d^{2} \psi}{dz^{2}} \right) \hat{\boldsymbol{x}} + y \left(\frac{d^{2} \psi}{dx^{2}} + \frac{d^{2} \psi}{dy^{2}} + \frac{d^{2} \psi}{dz^{2}} \right) \hat{\boldsymbol{y}} + z \left(\frac{d^{2} \psi}{dx^{2}} + \frac{d^{2} \psi}{dy^{2}} + \frac{d^{2} \psi}{dz^{2}} \right) \hat{\boldsymbol{z}} + 2 \frac{d\psi}{dx} \hat{\boldsymbol{x}} + 2 \frac{d\psi}{dy} \hat{\boldsymbol{y}} + 2 \frac{d\psi}{dz} \hat{\boldsymbol{z}} \quad (A.5)$$

The first three terms contain the laplacian of ψ and the last three terms together constitute the gradient of ψ . Thus, all together the final result is

$$\nabla^2 \boldsymbol{r} \psi = 2\boldsymbol{\nabla} \psi + \boldsymbol{r} \nabla^2 \psi \tag{A.6}$$

The commutator is then

$$[\hat{H}, \mathbf{r}]\psi = \frac{-\hbar^2}{m} \nabla \psi \tag{A.7}$$

Since the momentum operator is given by $\hat{\boldsymbol{p}} = -i\hbar\boldsymbol{\nabla}$ it is seen that

$$\frac{im}{\hbar}[\hat{H}, \mathbf{r}] = \hat{\mathbf{p}}$$
 (A.8)

This derivation generalizes to the many particle case as well. In this case the potential depends on all electron coordinates and the kinetic energy term is a sum of ∇_i^2 where each ∇_i^2 operates on the coordinates of the i'th particle.

A.2 Dirac-Delta Function

In order to evaluate the left hand side of the expression Eqn. 3.17 one first rewrites it in an equivalent form

$$\lim_{\Gamma \to 0} \left[\frac{\hbar \Gamma}{\left(E_{mn} - \hbar \omega \right)^2 + \hbar^2 \Gamma^2} \right] \Longrightarrow \lim_{a \to 0} \left[\frac{a}{x^2 + a^2} \right]$$
(A.9)

Looking now at the integral from $-\infty$ to ∞ and taking the limit after the integral has been made

$$\lim_{a \to 0} \int_{-\infty}^{\infty} \frac{a}{x^2 + a^2} dx \tag{A.10}$$

The corresponding indefinite integral can be evaluated by substituting as follows

$$\cos\theta = \frac{a}{\sqrt{x^2 + a^2}}, \quad \sin\theta = \frac{x}{\sqrt{x^2 + a^2}} \tag{A.11}$$

The constant a and the variables x and θ are thought of as sides and angle in some imaginary triangle. Therefore

$$\int \frac{a}{x^2 + a^2} dx = \int \frac{1}{x} \cos \theta \sin \theta dx \tag{A.12}$$

The differential dx can be re-expressed in terms of $d\theta$ by considering

$$\frac{d\cos\theta}{dx} = \frac{d\cos\theta}{d\theta}\frac{d\theta}{dx} = -\sin\theta\frac{d\theta}{dx} = -\frac{ax}{(x^2 + a^2)^{(3/2)}}$$
$$= \frac{-a}{\sqrt{x^2 + a^2}}\frac{x}{\sqrt{x^2 + a^2}}\frac{1}{\sqrt{x^2 + a^2}} = -\cos\theta\sin\theta\frac{1}{\sqrt{x^2 + a^2}} \quad (A.13)$$

which comes from differentiating the first of Eqn. A.11. The differential $d\boldsymbol{x}$ is therefore given by

$$-\sin\theta \frac{d\theta}{dx} = -\cos\theta \sin\theta \frac{1}{\sqrt{x^2 + a^2}} \implies dx = \frac{\sqrt{x^2 + a^2}}{\cos\theta} d\theta$$
(A.14)

And finally

$$\int \frac{1}{x} \cos \theta \sin \theta dx = \int \frac{\sqrt{x^2 + a^2}}{x} \sin \theta d\theta = \int d\theta = \theta + C$$
(A.15)

Dividing $\sin \theta$ by $\cos \theta$ one obtains the expression $\tan \theta = x/a$ so that $\theta = \arctan(x/a)$ and therefore

$$\int \frac{a}{x^2 + a^2} dx = \arctan\left(\frac{x}{a}\right) + C \tag{A.16}$$

The integral in Eqn. A.10 can now be evaluated

$$\int_{-\infty}^{\infty} \frac{a}{x^2 + a^2} dx = \pi \tag{A.17}$$

Now, for $a \to 0$ the integrand in Eqn. A.17 approaches a delta function, but the integral from $-\infty$ to ∞ still has to be equal to π so that

$$\lim_{a \to 0} \left[\frac{a}{x^2 + a^2} \right] = \pi \delta(x) \tag{A.18}$$

and finally

$$\lim_{\Gamma \to 0} \left[\frac{\hbar \Gamma}{\left(E_{mn} - \hbar \omega \right)^2 + \hbar^2 \Gamma^2} \right] = \pi \delta(E_{mn} - \hbar \omega)$$
(A.19)

Appendix B

The Closure Relation and Projection Operator

The closure relation is derived in a simple manner by writing the ket $|\psi\rangle$ in a certain orthonormal basis $|\varphi\rangle$ [14]

$$|\psi\rangle = \sum_{n} c_n |\varphi_n\rangle \tag{B.1}$$

Taking the inner product of $|\psi\rangle$ with $|\varphi_m\rangle$

$$\langle \varphi_m | \psi \rangle = \sum_n c_n \langle \varphi_m | \varphi_n \rangle = c_m$$
 (B.2)

Inserting this in Eqn. B.1

$$|\psi\rangle = \sum_{n} \langle \varphi_{n} |\psi\rangle |\varphi_{n}\rangle = \sum_{n} |\varphi_{n}\rangle \langle \varphi_{n} |\psi\rangle$$
(B.3)

from where it is seen that

$$\sum_{n} |\varphi_n\rangle \langle \varphi_n| = \hat{I} \tag{B.4}$$

The operator given by Eqn. B.4 is thus the unit operator. This relation can be used when the basis constitutes a complete orthonormal set or it can be used approximately when the basis constitutes an approximately complete orthonormal set . It should be noted that the operator $\hat{P}_n = |\varphi_n\rangle \langle \varphi_n|$ is a projection operator. It transforms any vector $|\psi\rangle$ into a vector with magnitude $\langle \varphi_n | \psi \rangle$ pointing in the direction of $|\varphi_n\rangle$.

Appendix C

Triangle Integration Method

The triangle integration method is used to approximate integrals over the 2D irreducible Brillouin zone. The principle is to divide the irreducible zone into smaller triangles and apply a linearization of energy and the function to be integrated. The goal is to approximate an integral of the form

$$S(\omega) = \iint F(\mathbf{k})\delta\left[E_{cv}(\mathbf{k}) - \hbar\omega\right] dk_x dk_y \tag{C.1}$$

Dividing the irreduzible BZ into smaller triangles the integral can be rewritten into

$$S(\omega) = \sum_{N\Delta} \iint_{\Delta} F(\mathbf{k}) \delta \left[E_{cv}(\mathbf{k}) - \hbar \omega \right] dk_x dk_y$$
(C.2)



Figure C.1: The triangle element used for the triangle integration method. The line \mathbf{k}_a to \mathbf{k}_b is the line along which $E_{cv}(\mathbf{k}) - \hbar \omega = 0$.

where the sum is over all the small triangles. Now, the integrand vanishes everywhere except along the line where $E_{cv}(\mathbf{k}) - \hbar\omega = 0$. Therefore the integral is essentially a single integral along the line on which $E_{cv}(\mathbf{k}) - \hbar\omega = 0$ and it can can be rewritten by using an identity for delta functions [15]

$$S(\omega) = \sum_{N\Delta} \int_{l} \frac{F(\boldsymbol{k})}{|\boldsymbol{\nabla}_{k} E_{cv}(\boldsymbol{k})|} dl$$
(C.3)

When applying the linearization of energies inside all of the small triangles the k-gradient of the energy becomes independent of k and the denominator can be taken outside the integral. Thus

$$S(\omega) \approx \sum_{N\Delta} \frac{1}{|\boldsymbol{\nabla}_k E_{cv}(\boldsymbol{k})|} \int_l F(\boldsymbol{k}) dl$$
(C.4)

Applying the linearization of $F(\mathbf{k})$ as well, the evaluation of the integral becomes a simple matter of integrating a linearly varying function along a straight line. In order to determine the start and end points of the integration line l one solves $E_{cv}(\mathbf{k}) - \hbar\omega = 0$. The transition energies, k-points and function values at the corners of the triangle are labelled E_i , k_i and F_i respectively. The energies are assumed to be ordered according to $E_0 \leq E_1 \leq E_2$. For the case where $E_0 \leq \hbar\omega \leq E_1$ one gets for \mathbf{k}_a and \mathbf{k}_b

$$\boldsymbol{k_a} = \boldsymbol{k}_0 + (\boldsymbol{k}_1 - \boldsymbol{k}_0) \frac{\hbar\omega - E_0}{E_{10}}, \quad \boldsymbol{k}_b = \boldsymbol{k}_0 + (\boldsymbol{k}_2 - \boldsymbol{k}_0) \frac{\hbar\omega - E_0}{E_{20}}$$
 (C.5)

where $E_{ij} = E_i - E_j$. A different expression for k_a is obtained for the case when $E_1 \leq \hbar \omega \leq E_2$, namely

$$\boldsymbol{k}_{a} = \boldsymbol{k}_{1} + (\boldsymbol{k}_{2} - \boldsymbol{k}_{1}) \frac{\hbar\omega - E_{1}}{E_{21}}$$
(C.6)

Since the integrand in Eqn. C.4 is linearly varying the integral can be easily evaluated and therefore

$$S(\omega) \approx \sum_{N\Delta} \frac{l}{2 \left| \boldsymbol{\nabla} E_{cv}(\boldsymbol{k}) \right|} \left[F(\boldsymbol{k}_a) + F(\boldsymbol{k}_b) \right]$$
(C.7)

The gradient is the slope of the plane $E_{cv}(\mathbf{k})$ which can be expressed in terms of the values at the corners. All other quantities can also be expressed in terms of the values at the corners of the triangle. Therefore $S(\omega) = \sum S_{\Delta}(\omega)$ with

$$S_{\Delta}(\omega) = \frac{2A_{\Delta}(\hbar\omega - E_0)}{E_{10}E_{20}} \left[F_0 + \frac{\hbar\omega - E_0}{2} \left(\frac{F_{10}}{E_{10}} + \frac{F_{20}}{E_{20}} \right) \right]$$
(C.8)

for the case $E_0 \leq \hbar \omega \leq E_1$ and

$$S_{\Delta}(\omega) = \frac{2A_{\Delta}(E_2 - \hbar\omega)}{E_{21}E_{20}} \left[F_2 + \frac{\hbar\omega - E_2}{2} \left(\frac{F_{21}}{E_{21}} + \frac{F_{20}}{E_{20}} \right) \right]$$
(C.9)

for the case $E_1 \leq \hbar \omega \leq E_2$. A_{Δ} is the triangle area.

Appendix D

Solving Laguerre's Differential Equation

In this appendix it will be shown how to solve the Laguerre differential equation. This differential equation has the following form

$$\rho \frac{d^2 R}{d\rho^2} + (p+1-\rho) \frac{dR}{d\rho} + qR = 0$$
 (D.1)

The solution can be obtained by writing it as a Maclaurin series (the Taylor expansion about $x_0 = 0$)

$$R(\rho) = \sum_{n=0}^{\infty} a_n \rho^n \tag{D.2}$$

and determining the coefficients. Plugging the series solution into the equation one obtains

$$0 = \rho \sum_{n=0}^{\infty} a_n n(n-1)\rho^{n-2} + (p+1-\rho) \sum_{n=0}^{\infty} a_n n\rho^{n-1} + q \sum_{n=0}^{\infty} a_n \rho^n$$
(D.3)

$$=\sum_{n=0}^{\infty}a_nn(n-1)\rho^{n-1} + (p+1)\sum_{n=0}^{\infty}a_nn\rho^{n-1} - \sum_{n=0}^{\infty}a_nn\rho^n + q\sum_{n=0}^{\infty}a_n\rho^n$$
(D.4)

In the first and the second summation the lower bound can be shifted to n = 1 without changing the equation. This is because the term with n = 0 vanish for both sums. Using then an obvious identity for summations

$$\sum_{n=p} a_n F(n) = \sum_{n=p-q} a_{n+q} F(n+q)$$
(D.5)

the equation becomes

$$0 = \sum_{n=0}^{\infty} a_{n+1}n(n+1)\rho^n + (p+1)\sum_{n=0}^{\infty} a_{n+1}(n+1)\rho^n - \sum_{n=0}^{\infty} a_nn\rho^n + q\sum_{n=0}^{\infty} a_n\rho^n$$
(D.6)

$$=\sum_{n=0}^{\infty} \left\{ a_{n+1} \left[n(n+1) + (n+1)(p+1) \right] + a_n \left[q - n \right] \right\} \rho^n$$
(D.7)

$$= \sum_{n=0}^{\infty} \left\{ a_{n+1}(n+p+1)(n+1) + a_n(q-n) \right\} \rho^n$$
(D.8)

Since all terms in the sum are linearly independent, one must require all coefficients to vanish for the equation to be fulfilled for all ρ . Thus

$$a_{n+1}(n+p+1)(n+1) + a_n(q-n) = 0$$
(D.9)

from which one obtains the recursive equation for the coefficients

$$a_{n+1} = -\frac{q-n}{(n+p+1)(n+1)}a_n \tag{D.10}$$

From this equation all coefficients can be calculated if a_0 is known. a_0 can be viewed as an integration constant, and it has to be determined by applying appropriate boundary conditions to the obtained solution. Thus, since a_0 is specified by the specific problem in question, the recursion relation above gives all the coefficient of the Maclaurin series. The series terminate only if q is a non-negative integer or zero, since then $n_{\max} = q$ and $a_{n_{\max}+1} = 0$ and so are all subsequent coefficients. It is a requirement that the series terminates in order for it to represent normalizable solutions. This can be seen by letting n go to infinity in Eqn. D.10 and obtain

$$a_n^{\infty} = \frac{1}{n!} a_0 \tag{D.11}$$

This is the recursion formula for the exponential function e^r which cannot be normalized. Thus, it is a requirement that the series terminates. The first few coefficients from Eqn. D.10, all expressed in terms of a_0 , are

$$a_1 = -\frac{q}{p+1}a_0$$
(D.12)

$$a_2 = \frac{(q-1)q}{2(p+2)(p+1)}a_0 \tag{D.13}$$

$$a_3 = -\frac{(q-2)(q-1)q}{3 \cdot 2 \cdot (p+3)(p+2)(p+1)}a_0$$
(D.14)

From this it can be deduced that the expression for the coefficients a_n is given by

$$a_n = (-1)^n \frac{q!}{n!(p+1)_n(q-n)!} a_0 \tag{D.15}$$

Here the symbol $(x)_n$ denotes the rising factorial (Pochhammer symbol), $(x)_n = x(x+1) \dots (x+n-1)$. Using this expression for the coefficients in the Maclaurin series gives the following solution to Eqn. D.1

$$R(r) = a_0 \sum_{n=0}^{q} (-1)^n \frac{q!}{n!(p+1)_n(q-n)!} \rho^n = a_{0\ 1} F_1(-q, 1+p, r)$$
(D.16)

where $_1F_1$ is a confluent hypergeometric function. In the special case where p = 0 the function reduces to the Laguerre polynomium and so, for p = 0, still with n being a positive integer for the series to terminate, the solution to Eqn. D.1 is

$$R(r) = a_0 \sum_{n=0}^{q} (-1)^n \frac{q!}{(n!)^2 (q-n)!} \rho^n = a_0 L_q(r)$$
(D.17)

since $(1)_n = n!$.

Bibliography

- K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, and A. K. Geim. Two-dimensional atomic crystals. *Proc. Natl. Acad. Sci USA*, 102:10451, 2005.
- [2] A. K. Geim and K. S. Novoselov. The rise of graphene. Nat. Mat., 6:183, 2007.
- [3] T. G. Pedersen, C. Flindt, J. Pedersen, N. A. Mortensen, A. P. Jauho, and K. Pedersen. Graphene antidot lattices: Designed defects and spin cubits. *Phys. Rev. Lett.*, 100:136804, 2008.
- [4] Xu Du, Ivan Skachko, Anthony Barker, and Eva Y. Andrei. Approaching ballistic transport in suspended graphene. Nat. Nanotechnol., 3:491, 2008.
- [5] Andrey K. Geim and Allan H. MacDonald. Graphene: Exploring carbon flatland. *Phys. Today*, 2007.
- [6] A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim. The electronic properties of graphene. arxiv.org:0709.1163v2 [cond. mat], 2008.
- [7] Vernica Barone, Oded Hod, and Gustavo E. Scuseria. Electronic structure and stability. Nano. Lett., 6:2748–2754, 2008.
- [8] Melinda Y. Han, Barbados Özyilmaz, Yanbo Zhang, and Philip Kim. Energy band-gap engineering of graphene nanoribbons. *Phys. Rev. Lett.*, 98:206805, 2007.
- [9] T. G. Pedersen, C. Flindt, J. Pedersen, A. P. Jauho, N. A. Mortensen, and K. Pedersen. Optical properties of graphene antidot lattices. *Phys. Rev. B*, 77:245431, 2008.
- [10] C. Kittel. Introduction to Solid State Physics. John Wiley and sons, 2003. 0-471-41526-X.
- [11] T. G. Pedersen, Kjeld Pedersen, and Thomas Brun Kristensen. Optical matrix elements in tight-binding calculations. *Phys. Rev. B*, 63:201101, 2001.
- [12] H. Haug and S. W. Koch. Quantum Theory of the Optical and Electronic Properties of Semiconductors. World Scientific, 2005.
- [13] A. Grüneis, C. Attaccalite, L. Wirtz, H. Shiozawa, R. Saito, T. Pichler, and A. Rubio. Tight-binding description of the quasiparticle dispersion of graphite and few-layer graphene. *Phys. Rev. B*, 78:205425, 2008.
- [14] B. H. Bransden and C. J. Joachain. Quantum Mechanics. Pearson, 2000.
- [15] wikipedia.org. wikipedia.org. http://wikipedia.org.