

Faculteit wetenschappen Departement fysica

# Coulomb impurity in gapped graphene

# Coulomb onzuiverheid in grafeen met een energiekloof

Proefschrift ingediend voor het behalen van de graad van bachelor in de wetenschappen aan de Universiteit Antwerpen door

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# 1 Abstract

Grafeen is een relatief nieuw materiaal met zeer interessante eigenschappen. Een van die eigenschappen is dat de ladingsdragers in grafeen zich gedragen als relativistisch deeltjes in bepaalde punten van het rooster. Dit zorgt ervoor dat het gedrag niet meer beschreven kan worden met de "klassieke" Schrödinger Hamiltoniaan maar moet nu beschreven worden met de zogenaamde Dirac Hamiltoniaan.

Het eerste doel van deze thesis is om te onderzoeken wat het effect is van een geladen onzuiverheid geplaatst in grafeen op de ladingsdragers. Er werd aangetoond worden dat gebonden toestanden toegelaten zijn, maar ook dat voor bepaalde ladingen gebonden toestanden niet mogelijk zijn. De voorwaarden hievoor wordt afgeleid en wat er dan precies gebeurd wordt besproken.

Het tweede doel van deze thesis om de invloed van het elektrische veld op de gebonden toestanden te bestuderen. Met behulp van storingsrekenen zal het effect van een klein lineair elektrisch veld bestudeerd worden. Dit noemt men ook het Stark effect. Dit wordt zowel gedaan in het geval van een niet ontaarde grondtoestand als in het geval van ontaarde niveaus.

# 2 List of symbols

- $v_f$ : Fermi Velocity
- $\triangle$ : effective mass
- E: energy
- $\alpha$ : fine structure constant
- j: angular quantum number
- n: radial quantum number
- $\rho$ :  $2\gamma r$
- $\gamma: \sqrt{\Delta^2 E^2}$
- $\nu$ :  $\sqrt{j^2 \alpha^2}$

# 3 Introduction

#### 3.1 Organization of thesis

In the first part of the thesis an introduction to graphene is given together with the motivation of the thesis. In the second part the effect of a Coulomb impurity placed in gapped graphene is investigated. In the last part the influence of a linear electric field on the bound states of the impurity is studied using perturbation theory.

#### 3.2 Graphene: an introduction

Graphite is a well known material used for centuries. It consists of layers of carbon atoms arranged in a hexagonal lattice. These layers of carbon atoms are bound to each other by the vanderWaals interaction. One layer of carbon atoms is called graphene. Note that this layer is only one atom thick wich makes it quite distinct from graphite.

When graphene was discovered in 2004 by A. Geim and K.S Novoselov it was the start of a huge research wave studying the interesting properties of graphene. Theoretical properties of graphene have been studied since the 40's but for the first time it was possible to conduct experiments on the material. Since 2004 the list of interesting properies of graphene kept expanding making it one of the most studied materials.

#### 3.2.1 The graphene lattice

Graphene has a hexagonal (honeycomb) lattice[14]. The graphene lattice is not a *bravais* lattice, this means that it cannot be created by lineary translating one lattice point. But it can be created by linear translation of two points, meaning that the graphene lattice actually consists of two seperate bravais lattices running through each other. The graphene structure is shown in figure 1.

The two sublattices can be constructed using the vectors  $\mathbf{a_1}$  and  $\mathbf{a_2}$ . These vectors are given by the following coordinates:

$$\mathbf{a_1} = \frac{a}{2} \left( 3, \sqrt{3} \right), \qquad \mathbf{a_2} = \frac{a}{2} \left( 3, \sqrt{3} \right)$$

Each carbon atom is (directly) surrounded by three other carbon atoms. The position of these closest carbon atoms is given by the three vectors  $\delta_1$ ,  $\delta_2$  and  $\delta_3$  with the following coördinates:

$$\delta_{1} = \frac{a}{2} \left( 1, \sqrt{3} \right), \qquad \delta_{2} = \frac{1}{2} \left( 1, -\sqrt{3} \right), \qquad \delta_{3} = \frac{a}{2} \left( -1, 0 \right)$$



Figure 1: The graphene honeycomb lattice consisting of two sublattices, i.e A and B. The vectors  $\mathbf{a_1}$  and  $\mathbf{a_2}$  are the primitive vectors. The vectors  $\delta_1$ ,  $\delta_2$  and  $\delta_3$  donate the nearest neighbouring atoms. The area covered by the dotted line is a unit cell of the lattice.

It is interesting to look at the reciprocal lattice. This can be done by Fourier transforming the lattice in figure 1. Note that the reciprocal lattice is not in real space but in momentum space, because of the Fourier transform. The reciprocal lattice can be constructed using the two vectors  $b_1$  and  $b_2$  given by:

$$\mathbf{b_1} = \frac{2\pi}{3a} \left( 1, \sqrt{3} \right), \qquad \mathbf{b_2} = \frac{2\pi}{3a} \left( 1, -\sqrt{3} \right)$$

In figure 2 the reciprocal lattice is also depicted.



Figure 2: The reciprocal lattice can be constructed using  $\mathbf{b_1}$  and  $\mathbf{b_2}$ . The hexagonals (full lines) form the first brillouin zone, which is actually the primitive cell in reciprocal space. I will show in the next section that the behavior of electrons at the corners of the first brillouin zone i.e K points, is special.

#### 3.2.2 Dispersion relation

The relation between the energy and the wave vector (or momentum) of a particle is called dispersion relation. For example the dispersion relation for a free particle with mass m is given by  $E = \frac{p^2}{2m}$  and for a photon (or any other massless particle)  $E = c \mid p \mid$ .

The dispersion relation in graphene at low energies is given by:

$$E = \pm \nu_F \mid p \mid = \pm \hbar \nu_F \mid k \mid$$

This relation is similar to the relativistic disperison relation of a massless particle except that the speed of light is now replaced by the Fermi velocity of the carriers in graphene. So arround the Brilliouin corners the electrons in graphene behave relativisticly. This is a very interesting property of graphene and has brought many interesting phenomena. For example the form of the Hamiltonian in the Schrödinger equation has to be changed.

The conduction and valance bands touch each other at the Fermi energy (i.e.  $E_f = 0$  in Fig 3).



Figure 3: The band structure in graphene. The points where the negative and positive bands meet are the corners of the brillioun zone. Note that the energy spectrum is linear (for low energies) around these points which causes the relativistic behavior of the electrons in graphene.

#### 3.2.3 Applications of graphene

Although graphene has a rather young age there is a huge variety of (potential) applications. These applications vary from medicine to engineering. A short list of (potential) applications is given below:

**Drug delivery:** It turns out that sheets of graphene can be used as a carpet to deliver drugs. By embedding the drug on the carpet it can be delivered effectively for example for the treatment of cancer. [2]

**Transparant electrodes:** Graphene has a high conductivity and it is transparent due to the fact that it is one atom thick. This makes graphene very usefull as electrodes in for example touchscreens or photovoltaic cells. There exist experiments with OLEDS (organic light emitting diodes) based on graphene.[3]

Water filtration: Recent studies showed that graphene can be used as a filtration system, which is more effective then the traditional membrane filters.[4]

#### 3.3 Graphene: a mathematical description

From the previous section it is known that at the corners of the Brilliouin zone, in graphene the electrons behave relativisticly moving with the Fermi velocity. The purpose of this section is to look into the mathematics and equations behind this peculiar behavior.

#### 3.3.1 Dirac equation

Due to the relativistic behavior a different form of the hamiltonian in the Schrödinger equation has to be used. In order to describe the behavior one must use the Dirac hamiltonian in the Schrödinger equation, this differential equation is given (in the case of a massless particle) as:

$$E\Psi = -iv_F\hbar\left(\sigma_1\frac{\partial}{\partial x} + \sigma_2\frac{\partial}{\partial y}\right)\Psi$$

Where  $\sigma_1$  and  $\sigma_2$  are two of the 3 Pauli matrices,  $-iv_F\hbar\left(\sigma_1\frac{\partial}{\partial x}+\sigma_2\frac{\partial}{\partial y}\right)$  is called the Dirac Hamiltonian and E is the energy. The Pauli matrices are given by:

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

 $\Psi$  is the wave function and due to the fact that the Pauli matrices are 2x2 it's a vector with two components:

$$\Psi = \begin{pmatrix} \psi_a \\ \psi_b \end{pmatrix}$$

The reason that the wave function has two components has to do with the fact that the graphene lattice consists of two sublattices. Note that in this case the expectation value of an operator A is given by the following integral:

$$\left\langle \Psi \right| A \left| \Psi \right\rangle = \int_{V} \Psi^{*} A \Psi dV = \int_{V} \left( \psi_{a}^{*}, \ \psi_{b}^{*} \right) A \begin{pmatrix} \psi_{a} \\ \psi_{b} \end{pmatrix} dV$$

#### 3.3.2 Gapped graphene

Although there are two different sublattices, generated by two atoms, these atoms do not differ in physical space. They are both carbon atoms with the same charge and experiencing the same influence from the other atoms. But one can create a physical difference between the two atoms by applying for example a different electric field to both atoms. The crystal structure of boron-nitride is similar to that of graphene. When graphene is placed on top of a boron nitride layer, the sublattice symmetry in graphene breaks causing an energy gap between the electron and the hole band (see figure 5).



Figure 4: Putting a boron-nitride layer on top of graphene causes a physical difference between the two lattice atoms. This difference breaks the symmetry of the lattice and causes the effective mass of the charge carriers to be non-zero. Picture adopted from [15]



Figure 5: Breaking the symmetry of the lattice causes the effective mass to be non zero and creates a gap i.e.  $2\triangle$  in the dispersion relation. (the dispersion relation on the left is the same as the one shown in figure 3). Picture adopted from [15].

#### 3.3.3 Dirac equation for gapped graphene

In the presence of a mass term  $\triangle$ , the Schrödinger equation with the Dirac Hamiltonian can be written as the following equation:

$$E\Psi = \left(-iv_F\hbar\left(\sigma_1\frac{\partial}{\partial x} + \sigma_2\frac{\partial}{\partial y}\right) + \Delta\sigma_3\right)\Psi.$$

Where  $\sigma_3$  is the third Pauli matrix:

$$\sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

#### 3.4 Gapped graphene with Coulomb impurity

The purpose of this thesis is to investigate what happens when a Coulomb impurity is placed inside graphene.

Similar as the effect of a Boron-nitride substrate an impurity placed in graphene can break the symmetry of the lattice. But note that the position of the impurity will matter: for example when the impurity is placed in the middle of the hexagonal (see figure 6) both atoms will experience the same Coulomb potential and the symmetry will not be broken. The elec-



Figure 6: When a charge is placed in the middle of the lattice (black dot) both base atoms (black box) experience the same electrical field and the symmetry of the lattice is not broken, the effective mass ( $\Delta$ ) is zero. But when a charge is placed for example at one of the base atoms both experience a totally different electric field, the symmetry is broken and all the electrons exhibit an effective mass different from zero.

trons arround the brillioun points will still behave relativisticly but with an effective mass different from zero. But to include the effect of the Coulomb charge the massive Schrödinger equation has to be extended to the following equation:

$$E\Psi = \left(-i\hbar v_F \left(\sigma_1 \frac{\partial}{\partial x} + \sigma_2 \frac{\partial}{\partial y}\right) + \Delta \sigma_3 + I.V(r)\right)\Psi$$

Here V(r) is the potential which in the present case is a Coulomb potential given by:  $-\frac{GZe^2}{r}$ . Note that I is the identity matrix.

#### 3.5 Purpose of the thesis

The main purpose of this thesis is to investigate relativistic electrons bound to an impurity which is placed in graphene with an energy gap. It will be shown that in this region bound states are possible and discrete energy levels will become apparent similar to the case of the well known hydrogen atom. We derive the condition for which bound states are possible. If this condition is not satisfied no bound states are possible and we get the so called "atomic collapse". Special effects caused by the relativistic behaviour will be studied and at the end of the thesis the effect of an external electric field will be studied using perturbation theory.

# 4 The Dirac equation with Coulomb impurity

The behavior of relativistic electrons in a potential field V can be described by the following (stationary) hamiltonian:

$$H = -i\left(\sigma_1 \frac{\partial}{\partial x} + \sigma_2 \frac{\partial}{\partial y}\right) + \Delta \sigma_3 + I.V(r) \tag{1}$$

In this formula  $\sigma_1, \sigma_2, \sigma_3$  are the Pauli matrices,  $\Delta$  is the Dirac mass, V is the potential function and I indicates the identity matrix. Also note that natural units were used, so in this case  $\hbar = v_f = 1$ .

Substituting the exact form of the Pauli matrices and introducing  $V(r) = (-\frac{\alpha}{r}, \alpha > 0)$  equation (1) becomes:

$$H = \begin{pmatrix} \triangle -\frac{\alpha}{r} & -i\frac{\partial}{\partial x} - \frac{\partial}{\partial y} \\ -i\frac{\partial}{\partial x} + \frac{\partial}{\partial y} & -\triangle -\frac{\alpha}{r} \end{pmatrix}.$$
 (2)

A relativistic electron satisfies the Schrödinger equation with the above Hamiltonian, which gives the following eigenvalue problem:

$$H\Psi = E\Psi.$$
 (3)

In this equation  $\Psi$  is the wave function and E the corresponding energy.

Solving (3) and noticing that  $\Psi$  can be written as  $\begin{pmatrix} \psi_a \\ \psi_b \end{pmatrix}$  we obtain the following set of coupled differential equations:

$$\begin{cases} (E - \Delta + \frac{\alpha}{r})\psi_a + (i\frac{\partial}{\partial x} + \frac{\partial}{\partial y})\psi_b = 0\\ (E + \Delta + \frac{\alpha}{r})\psi_b + (i\frac{\partial}{\partial x} - \frac{\partial}{\partial y})\psi_a = 0 \end{cases}$$
(4)

Because we are looking at a steady charge with an orbitting electron one can assume that the problem has radial symmetry. Because we are working in a 2D system we will work with polar coördinates. The transformation formulas for the derivatives in polar coördinates are given by:

$$\frac{\partial}{\partial x} = \cos\theta \frac{\partial}{\partial r} - \frac{1}{r}\sin\theta \frac{\partial}{\partial \theta}$$
(5)

$$\frac{\partial}{\partial y} = \sin\theta \frac{\partial}{\partial r} + \frac{1}{r}\cos\theta \frac{\partial}{\partial \theta}.$$
 (6)

Equations (4) and (5) can be used to rewrite the derivative terms in the set of equations (4). This gives:

$$i\frac{\partial}{\partial x} + \frac{\partial}{\partial y} = (i\cos\theta + \sin\theta)\frac{\partial}{\partial r} + (\cos\theta - i\cos\theta)\frac{1}{r}\frac{\partial}{\partial \theta}$$
(7)

Using Eulers identity twice  $(e^{i\theta} = \cos \theta + i \sin \theta)$  equation (7) reduces to equation (8).

$$i\frac{\partial}{\partial x} + \frac{\partial}{\partial y} = e^{-i\theta} \left( i\frac{\partial}{\partial r} + \frac{1}{r}\frac{\partial}{\partial \theta} \right) \tag{8}$$

A completely analog calculation gives for the other derivative term the formula (9).

$$i\frac{\partial}{\partial x} - \frac{\partial}{\partial y} = e^{i\theta} \left( i\frac{\partial}{\partial r} - \frac{1}{r}\frac{\partial}{\partial \theta} \right) \tag{9}$$

Combining equations (4), (8) and (9) gives the following coupled equations in polar coördinates.

$$\begin{cases} (E - \triangle + \frac{\alpha}{r})\psi_a + e^{-i\theta} \left(i\frac{\partial}{\partial r} + \frac{1}{r}\frac{\partial}{\partial \theta}\right)\psi_b = 0\\ (E + \triangle + \frac{\alpha}{r})\psi_b + e^{i\theta} \left(i\frac{\partial}{\partial r} - \frac{1}{r}\frac{\partial}{\partial \theta}\right)\psi_a = 0 \end{cases}$$
(10)

# 5 Bound states

The functions  $\psi_a$  and  $\psi_b$  depend on r and  $\theta$ . But the coupled equations (10) do not have mixed terms depending on r and  $\theta$ , which allows us to use separation of variables.

#### 5.1 Solving the angular part

The dependence of the equation on  $\theta$  can be filtered out by using a substitution. We use the following substitution:

$$\psi_a = R_a(r)e^{im\theta} \tag{11}$$

$$\psi_b = iR_b(r)e^{i\theta}e^{im\theta} \tag{12}$$

Where  $R_a(r)$  and  $R_b(r)$  are the separated radial parts and  $m \in \mathbb{Z}$ . Plugging equations (11) and (12) in the set of equations (10) gives a new set of coupled equations for the radial part of the wavefunctions:

$$\begin{cases} \left(\frac{\partial}{\partial r} + \frac{m+1}{r}\right) R_b(r) - \left(E - \Delta + \frac{\alpha}{r}\right) R_a(r) = 0\\ \left(\frac{\partial}{\partial r} - \frac{m}{r}\right) R_a(r) + \left(E + \Delta + \frac{\alpha}{r}\right) R_b(r) = 0 \end{cases}$$
(13)

#### 5.2 Solving the radial part

Now the challenge is to solve the set of coupled equations (13). Which is not trivial. A very good and often used technique is to solve the coupled equations (13) in the  $r \to \infty$  and  $r \to 0$  limits, and with the help of the solutions obtained in these limits we solve the general equations.

After taking the limit  $r \to \infty$  equation (13) reduces to:

$$\begin{cases} \frac{\partial R_b(r)}{\partial r} - (E - \Delta) R_a(r) = 0\\ \frac{\partial R_a(r)}{\partial r} + (E + \Delta) R_b(r) = 0 \end{cases}$$
(14)

Decoupling the above equations we obtain:

$$\frac{\partial^2 R_{a/b}(r)}{\partial r^2} + (E^2 - \Delta^2) R_{a/b}(r) = 0.$$
 (15)

This equation has two possible solutions given by  $e^{\pm i\sqrt{E^2-\Delta^2}}$ . Assuming we only consider bound states  $|\Delta| > |E|$  and the fact that the solution should go to zero at infinity, this leaves only one possible solution:

$$e^{-\sqrt{\triangle^2 - E^2}}.$$
 (16)

With this knowledge the solution for  $R_a$  and  $R_b$  can be rewritten.

$$R_a(r) = e^{-\frac{\mu}{2}} H_a(r)$$
 (17)

$$R_b(r) = e^{-\frac{\rho}{2}} H_b(r) \tag{18}$$

where  $\rho = 2\gamma r$  and  $\gamma = \sqrt{\Delta^2 - E^2}$ . The functions  $H_a$  and  $H_b$  have still to be determined.

Substituting equations (17) and (18) back in the set of equations (13) and changing variables from r to  $\rho$  gives the following set of equations in function of  $H_a$  and  $H_b$ :

$$\begin{cases} \left(-\gamma + 2\gamma \left(\frac{m+1}{\rho}\right)\right) H_b(\rho) + 2\gamma \frac{\partial H_b(\rho)}{\partial \rho} - \left(E - \Delta + \frac{2\gamma\alpha}{\rho}\right) H_a(\rho) = 0 \\ \left(-\gamma - 2\gamma \left(\frac{m}{\rho}\right)\right) H_a(\rho) + 2\gamma \frac{\partial H_a(\rho)}{\partial \rho} + \left(E + \Delta + \frac{2\gamma\alpha}{\rho}\right) H_b(\rho) = 0 \end{cases}$$
(19)

Now we consider the limit  $\rho \to 0$  in equation (19) this gives us the following equations:

$$\begin{cases} \frac{\partial H_b(\rho)}{\partial \rho} + \left(\frac{m+1}{\rho}\right) H_b(\rho) - \left(\frac{\alpha}{\rho}\right) H_a(\rho) = 0\\ \frac{\partial H_a(\rho)}{\partial \rho} - \left(\frac{m}{\rho}\right) H_a(\rho) + \left(\frac{\alpha}{\rho}\right) H_b(\rho) = 0 \end{cases}$$
(20)

It is straightforward to see that the solution must be of the form  $\rho^s$  with s a real number. Substituting this gives a new set of equations:

$$\begin{cases} s\rho^{s-1}H_b(\rho) + \frac{m+1}{\rho}\rho^s H_b(\rho) - \alpha r^{s-1}H_a(r) = 0\\ s\rho^{s-1}H_a(\rho) - \frac{m}{r}r^s H_a(\rho) + \alpha \rho^{s-1}H_b(\rho) = 0 \end{cases}$$
(21)

Factoring  $\rho^{s-1}$  out of the equations (21) gives:

$$\begin{cases} (s+m+1)H_b(\rho) - \alpha H_a(\rho) = 0\\ (s-m)H_a(\rho) + \alpha H_b(\rho) = 0 \end{cases}.$$
 (22)

Decoupling equations (22) we arrive at:

$$s^2 + s - m^2 - m + \alpha^2 = 0.$$
(23)

This linear equation has two possible solutions:

$$s = -\frac{1}{2} \pm \frac{1}{2}\sqrt{1 - 4(-m^2 - m + \alpha^2)},$$
(24)

which can be rewritten as:

$$s = -\frac{1}{2} \pm \sqrt{\frac{1}{4} + m^2 + m - \alpha^2} = -\frac{1}{2} \pm \sqrt{\left(m + \frac{1}{2}\right)^2 - \alpha^2}.$$
 (25)

Only the solution with the + sign is physicly possible so the solution can be written as:

$$\rho^{\nu - \frac{1}{2}} \tag{26}$$

where  $\nu = \sqrt{\left(m + \frac{1}{2}\right)^2 - \alpha^2}$ . With this knowledge the solutions  $H_a$  and  $H_b$  can be written as:

$$H_a(\rho) = \sqrt{\Delta + E} \rho^{\nu - \frac{1}{2}} G_a(\rho) \tag{27}$$

$$H_b(\rho) = \sqrt{\Delta - E} \rho^{\nu - \frac{1}{2}} G_b(\rho) \tag{28}$$

where  $G_a$  and  $G_b$  are two functions that have to be determined.

#### 5.2.1 Introducing new variables

Subtituting (27) and (28) in the differential equation (19) gives a new set of coupled equations:

$$\begin{cases} \left(-1+2\left(\frac{m+\frac{1}{2}+\nu}{\rho}\right)\right)G_b(\rho)+2\frac{\partial G_b(\rho)}{\partial\rho}+G_a(\rho)-\frac{\sqrt{\Delta+E}}{\sqrt{\Delta-E}}\frac{2\alpha}{\rho}G_a(\rho)=0\\ \left(-1-2\left(\frac{m+\frac{1}{2}-\nu}{\rho}\right)\right)G_a(\rho)+2\frac{\partial G_a(\rho)}{\partial\rho}+G_b(\rho)+\frac{\sqrt{\Delta-E}}{\sqrt{\Delta+E}}\frac{2\alpha}{\rho}G_b(\rho)=0 \end{cases}$$
(29)

It is still not easy to decouple the above equations. In order to do this we perform one more last substitution. We write  $G_a$  as  $P(\rho) + Q(\rho)$  and  $G_b(\rho)$  as  $P(\rho) - Q(\rho)$ . This gives a new set of differential equations. For the sake of simplicity we ommit  $\rho$  in the functions P and Q:

$$\begin{cases} \left(m + \frac{1}{2} + \nu - \frac{\sqrt{\Delta + E}}{\sqrt{\Delta - E}}\alpha\right)P + \rho\frac{\partial P}{\partial\rho} + \left(\rho - m - \frac{1}{2} - \nu - \frac{\sqrt{\Delta + E}}{\sqrt{\Delta - E}}\alpha\right)Q - \rho\frac{\partial Q}{\partial\rho} = 0\\ \left(-m - \frac{1}{2} + \nu + \frac{\sqrt{\Delta - E}}{\sqrt{\Delta + E}}\right)P + \rho\frac{\partial P}{\partial\rho} + \left(-\rho - m - \frac{1}{2} + \nu - \frac{\sqrt{\Delta - E}}{\sqrt{\Delta + E}}\right)Q + \rho\frac{\partial Q}{\partial\rho} = 0 \end{cases}$$
(30)

We obtain the two following equations by adding and substracting the above equations:

$$\begin{cases} \left(\nu + \frac{\alpha}{2} \left(-\frac{\sqrt{\Delta + E}}{\sqrt{\Delta + E}} + \frac{\sqrt{\Delta - E}}{\sqrt{\Delta + E}}\right)\right) P + \rho \frac{\partial P}{\partial \rho} + \left(-j + \frac{\alpha}{2} \left(-\frac{\sqrt{\Delta + E}}{\sqrt{\Delta - E}} - \frac{\sqrt{\Delta - E}}{\sqrt{\Delta + E}}\right)\right) Q\\ \left(j + \frac{\alpha}{2} \left(-\frac{\sqrt{\Delta + E}}{\sqrt{\Delta - E}} - \frac{\sqrt{\Delta - E}}{\sqrt{\Delta + E}}\right)\right) P - \rho \frac{\partial Q}{\partial \rho} + \left(\rho - \nu + \frac{\alpha}{2} \left(-\frac{\sqrt{\Delta + E}}{\sqrt{\Delta - E}} + \frac{\sqrt{\Delta - E}}{\sqrt{\Delta + E}}\right)\right) Q \end{cases}$$
(31)

The following terms can be simplified as:

$$\frac{\sqrt{\Delta + E}}{\sqrt{\Delta - E}} + \frac{\sqrt{\Delta - E}}{\sqrt{\Delta + E}} = \frac{2\Delta}{\sqrt{\Delta - E}\sqrt{\Delta + E}} = \frac{2\Delta}{\gamma},\tag{32}$$

$$\frac{\sqrt{\triangle + E}}{\sqrt{\triangle - E}} - \frac{\sqrt{\triangle - E}}{\sqrt{\triangle + E}} = \frac{2E}{\gamma}.$$
(33)

Combining equations (31), (32) and (33) gives the following set of equations as function of P and Q:

$$\begin{cases} \left(\rho\frac{\partial}{\partial\rho} + \nu - \frac{\alpha E}{\gamma}\right)P + \left(-j - \frac{\alpha\Delta}{\gamma}\right)Q = 0\\ \left(-j + \frac{\alpha\Delta}{\gamma}\right)P + \left(\rho\frac{\partial}{\partial\rho} - \rho + \nu + \frac{\alpha E}{\gamma}\right)Q = 0 \end{cases}, \tag{34}$$

where  $j = m + \frac{1}{2}$ .

#### **5.2.2** Solving for P and Q

Decoupling the differential equations (34) one can straightforwardly obtain the exact form of  $\nu = \sqrt{j^2 - \alpha^2}$  and  $\gamma = \sqrt{\Delta^2 - E^2}$  which gives the relation:

$$\nu^2 - \left(\frac{\alpha E}{\gamma}\right)^2 = j^2 - \left(\frac{\alpha \Delta}{\gamma}\right)^2.$$
(35)

The decoupled equations with the substitution P + Q and P - Q are given by:

$$\begin{cases} \rho \frac{\partial^2 P}{\partial \rho^2} + (1 + 2\nu - \rho) \frac{\partial P}{\partial \rho} - \left(\nu - \frac{\alpha E}{\gamma}\right) P = 0\\ \rho \frac{\partial^2 Q}{\partial \rho^2} + (1 + 2\nu - \rho) \frac{\partial Q}{\partial \rho} - \left(1 + \nu - \frac{\alpha E}{\gamma}\right) Q = 0 \end{cases}$$
(36)

We investigated the behavior of the solutions at the special points and filtered it out of the solution. This causes P and Q to be a stable series, so it is usefull to try a power series as a solution. Suppose the solutions are given by the following equations:

$$P(\rho) = \sum_{k=0}^{\infty} a_k \rho^k, \qquad (37)$$

$$Q(\rho) = \sum_{k=0}^{\infty} b_k \rho^k.$$
(38)

Substituting (37) in (36) gives:

$$\sum_{k=0}^{\infty} a_k \left( k(k-1)\rho^{k-2} + (1+2\nu)k\rho^{k-2} - k\rho^{k-1} - (\nu-2E)\rho^{k-1} \right) = 0.$$
 (39)

Rewriting equation (39) and raising the index of the  $\rho^{k-2}$  terms by one gives:

$$\sum_{k=0}^{\infty} \left( a_{k+1} \left( k(k+1) + (1+2\nu)(k+1) \right) - a_k \left( k + \nu - \frac{\alpha E}{\gamma} \right) \right) \rho^{k-1} = 0.$$
(40)

This equation is valid for every  $\rho$  so the relationship between  $a_k$  and  $a_{k+1}$  is given by:

$$\frac{a_{k+1}}{a_k} = \frac{k + \nu - \frac{\alpha E}{\gamma}}{(k+1)(k+1+2\nu)}.$$
(41)

In the limit to infinity the coefficients are given by a factorial that causes the series to be unstable except when it's chopped of at a certain index. Let's call this index n. This gives the following condition:

$$n + \nu - \frac{\alpha E}{\gamma} = 0. \tag{42}$$

Rewriting gives us the energy levels:

$$E_{nm} = \Delta \left( 1 + \left( \frac{\alpha}{n + \sqrt{\left(m + \frac{1}{2}\right)^2 - \alpha^2}} \right)^2 \right)^{-\frac{1}{2}}, \qquad (43)$$

where n = 0, 1, 2, ... and  $m = 0, \pm 1, \pm 2, ...$  These are the energy levels we have been looking for. Often  $m + \frac{1}{2}$  is rewritten as j and which takes the values  $\pm \frac{1}{2}, \pm \frac{3}{2}, \pm \frac{5}{2}$  giving the following energy levels:

$$E_{nj} = \Delta \left( 1 + \left( \frac{\alpha}{n + \sqrt{j^2 - \alpha^2}} \right)^2 \right)^{-\frac{1}{2}}.$$
 (44)

If one looks at the equation of  $Q(\rho)$  it's easy to see that an analogue procedure as for  $P(\rho)$  gives a relationship for the coefficients of the Q equation.

$$\frac{b_{k+1}}{b_k} = \frac{k+1+\nu - \frac{\alpha E}{\gamma}}{(k+1)(k+1+2\nu)}$$
(45)

Also this relation is only stable when it's chopped off at a certain (different) index, let's call the index n'. The new index is not independent of the index n, their relationship is given by the following equation:

$$n + \nu - \frac{\alpha E}{\gamma} = n' + 1 + \nu - \frac{\alpha E}{\gamma}$$
(46)

which gives:

$$n' = n - 1. \tag{47}$$

So the solution of Q is chopped off at n-1. The general solution of the equations in (35) are called the confluent hyperbolic functions. This function is the solution of the general differential equation given by [8]:

$$\rho \frac{\partial^2 f(\rho)}{\partial \rho^2} + (b - \rho) \frac{\partial f(\rho)}{\partial \rho} - a f(\rho) = 0.$$
(48)

One of the solutions is given by the following expression (see appendix A):

$$M(a,b,\rho) = \sum_{n=0}^{\infty} \frac{a^{(n)}\rho^n}{b^{(n)}n!}.$$
(49)

Here  $a^{(n)}$  and  $b^{(n)}$  are given by the following recursive relation:

$$a^{(0)} = 1, (50)$$

$$a^{(n)} = a(a+1)(a+2)...(a+n-1).$$
(51)

In the case of the equations in (36) the solutions are given by:

$$P(\rho) = AM(-n, 1+2\nu, \rho),$$
(52)

$$Q(\rho) = BM(-(n-1), 1+2\nu, \rho).$$
(53)

The constant still needs to be determined which will be done in the next section.

**Remark:** The differential equation given in (48) is in fact a second order differential equation. This means there should be in fact two possible solutions. Indeed when solving it, one discovers another solution called  $U(a, b, \rho)$ . But closer inspection of the solution shows that it's not regular at the origin where the  $M(a, b, \rho)$  is regular. This causes it to be not physical and therefore does not need to be considered.

## 6 Total wave function

The constants in the solutions (52) and (53) are not independent. One can derive a relation by substituting (52) and (53) back into the first equation of (34):

$$-\rho \frac{n}{1+2\nu} AM(-n-1,2+2\nu,\rho) + \left(\nu - \frac{\alpha E}{\gamma}\right) AM(-n,1+2\nu,\rho) + \left(-j - \frac{\alpha \Delta}{\gamma}\right) BM(-n+1,1+2\nu,\rho) = 0.$$
(54)

One of the properties of the confluent hypergeometric function was used  $\frac{\partial M(a,b,\rho)}{\partial \rho} = \frac{a}{b} M(a+1,b+1,\rho).$ 

When looking at (54) when  $\rho$  is zero and combining it with (49) it's easy to see that this gives the following relation:

$$\frac{A}{B} = \frac{\left(j + \frac{\alpha \Delta}{\gamma}\right)}{\left(\nu - \frac{\alpha E}{\gamma}\right)}.$$
(55)

Note that from the second equation in (34) another relation can be derived:

$$\frac{A}{B} = -\frac{\left(\nu + \frac{\alpha E}{\gamma}\right)}{\left(-j + \frac{\alpha \Delta}{\gamma}\right)}.$$
(56)

But using the fact that  $\nu^2 - \left(\frac{\alpha E}{\gamma}\right)^2 = j^2 - \left(\frac{\alpha \Delta}{\gamma}\right)^2$  it can be shown that (55) and (56) lead to the same condition.

Combining all the previous results this gives us the two total wave functions and their corresponding energies:

$$\psi_{a}^{(n,j)} = N\sqrt{\Delta + E}e^{im\theta}e^{-\frac{\rho}{2}}\rho^{\nu-\frac{1}{2}}\left[\left(j + \frac{\alpha\Delta}{\gamma}\right)M(-n, 1 + 2\nu, \rho) + \left(\nu - \frac{\alpha E}{\gamma}\right)M(-n + 1, 1 + 2\nu, \rho)\right],$$

$$(57)$$

$$(57)$$

$$(57)$$

$$\psi_{b}^{(n,j)} = iN\sqrt{\Delta - E}e^{i(m+1)\theta}e^{-\frac{\rho}{2}}\rho^{\nu-\frac{1}{2}}\left[\left(j + \frac{\alpha\Delta}{\gamma}\right)M(-n, 1+2\nu, \rho) - \left(\nu - \frac{\alpha E}{\gamma}\right)M(-n+1, 1+2\nu, \rho)\right].$$
(58)

Here N is a normalisation factor and (n, j) are the two quantum numbers and  $m = j - \frac{1}{2}$ . The energy corresponding to these wave functions are of course given by (42). Also note that  $\nu - \frac{\alpha E}{\nu}$  can be rewritten as -n. And after going back to the variable r using the fact that  $\rho = 2\gamma r$  one gets the two following wave functions:

$$\psi_{a}^{(n,j)} = \frac{1}{N}\sqrt{\Delta + E}e^{im\theta}e^{-\gamma r}(2\gamma r)^{\nu - \frac{1}{2}} \left[ \left(j + \frac{\alpha\Delta}{\gamma}\right)M(-n, 1 + 2\nu, 2\gamma r) - nM(-n + 1, 1 + 2\nu, 2\gamma r) \right],$$
(59)  
$$\psi_{b}^{(n,j)} = i\frac{1}{N}\sqrt{\Delta - E}e^{i(m+1)\theta}e^{-\gamma r}(2\gamma r)^{\nu - \frac{1}{2}} \left[ \left(j + \frac{\alpha\Delta}{\gamma}\right)M(-n, 1 + 2\nu, 2\gamma r) + nM(-n + 1, 1 + 2\nu, 2\gamma r) \right].$$
(60)

#### 6.1 Wave function of the n=0 states

An interesting case is of course n = 0. In this case the second part of the wave function in (59) and (60) disappears.  $j + \frac{\alpha \Delta}{\gamma}$  can be rewritten using the fact that  $\gamma = \sqrt{\Delta^2 - E^2}$  to give:

$$\left(j + \frac{\alpha}{\sqrt{1 - \frac{E^2}{\Delta^2}}}\right). \tag{61}$$

Using the exact value of the energy from equation (43) it's easy to show that  $\frac{E^2}{\Delta^2}$  can be rewritten as  $1 - \frac{\alpha^2}{j^2}$ . Using the latter, equation (61) can be rewritten as:

$$(j+|j|). \tag{62}$$

This is a very intresting result! From this it's easy to see that the total wave function becomes zero when j < 0! And for j > 0 the wave functions are given by the relative simple expressions:

$$\psi_{a}^{(0j)} = \frac{1}{N} \sqrt{\Delta + E} e^{im\theta} e^{-\gamma r} (2\gamma r)^{\nu - \frac{1}{2}} (2j), \tag{63}$$

$$\psi_b^{(0j)} = i \frac{1}{N} \sqrt{\Delta - E} e^{i(m+1)\theta} e^{-\gamma} (2\gamma r)^{\nu - \frac{1}{2}} (2j).$$
(64)

We can now conclude that the possible quantum numbers are n = 0, 1, 2, 3, ... if j > 0 and n = 1, 2, 3, ... if j < 0. So every state is degenerate because (n, j) and (n, -j) have the same energy except for the n = 0 states where only (n, j) is allowed.

#### 6.2 Normalization

The wave function is not yet normalized. The normalization factor is given by the following integral:

$$N_{(n,j)}^{2} = \int_{0}^{\infty} \int_{0}^{2\pi} \left( |\psi_{a}^{(n,j)}|^{2} + |\psi_{b}^{(n,j)}|^{2} \right) r dr d\theta.$$
(65)

Note that the r form of the wave functions is used. For the sake of simplicity we look at the  $\rho$  form given by (57) and (58). When this is done the integral changes to:

$$N_{(n,j)}^{2} = \frac{1}{4\gamma^{2}} \int_{0}^{\infty} \int_{0}^{2\pi} \left( |\psi_{a}^{(n,j)}|^{2} + |\psi_{b}^{(n,j)}|^{2} \right) \rho d\rho d\theta.$$
(66)

The angular part of the integral (66) is simply:

$$\int_0^{2\pi} d\theta = 2\pi. \tag{67}$$

The radial part of (66) requires a little bit more work. To solve this it's usefull to look at the following integral:

$$\int_{0}^{\infty} e^{-x} x^{c-1} M(-n, b, x) M(-m, b', x) dx.$$
(68)

This integral can be rewritten using the exact form of the hyperbolic confluent functions in (49):

$$\int_0^\infty \left( \sum_{k=0}^\infty \sum_{l=0}^\infty e^{-x} x^{c-1} \frac{(-n)^{(k)} (-m)^{(l)}}{b^{(k)} {b'}^{(l)} k! l!} x^k x^l \right) dx.$$
(69)

Here n and m are integers, because of this the series will be finite and the integral and summation can be interchanged without any problem! Note that the series will be chopped of at n and m, respectively:

$$\sum_{k=0}^{n} \sum_{l=0}^{m} \frac{(-n)^{(k)} (-m)^{(l)}}{b^{(k)} {b'}^{(l)} k! l!} \left( \int_{0}^{\infty} t^{c+k+l-1} e^{-x} dx \right).$$
(70)

The integral can be recognised as the gamma function [11], note that the gammaf function is given by:

$$\Gamma(x) = \int_0^\infty x^{(t-1)} t^{-x} dx.$$
 (71)

and expression (70) can be rewritten to give:

$$\sum_{k=0}^{n} \sum_{l=0}^{m} \frac{(-n)^{(k)} (-m)^{(l)}}{b^{(k)} {b'}^{(l)} k! l!} \Gamma(c+k+l).$$
(72)

Using the Pochhammers identity [11]  $\Gamma(c+k+l) = (c+k)^{(l)}c^{(k)}\Gamma(c)$  expression (72) can be rewritten to give:

$$\Gamma(c) \sum_{k=0}^{n} \sum_{l=0}^{m} \frac{(-n)^{(k)} (-m)^{(l)} (c+k)^{(l)} c^{(k)}}{b^{(k)} {b'}^{(l)} k! l!}.$$
(73)

Using the fact that  $x^{(n)} = \frac{\Gamma(x+n)}{\Gamma(x)}$  this reduces (73):

$$\Gamma(c) \sum_{k=0}^{n} \sum_{l=0}^{m} \frac{(-n)^{(k)} (-m)^{(l)} (c)^{(k+l)}}{b^{(k)} {b'}^{(l)} k! l!}.$$
(74)

The sum is called the second series of Appel and is written as  $F_2(c; -n, -m; b, b', 1, 1)$  (see appendix A). This gives te following result for the integral[11]:

$$\int_0^\infty \left( e^{-x} x^{c-1} M(-n,b,x) M(-m,b',x) \right) dx = \Gamma(c) F_2(c;-n,-m;b,b',1,1).$$
(75)

Rewriting this relation in terms of the variables in (57) and taking into account the extra  $\rho$  from the surface element in polar coordinates this gives the following usefull relation:

$$\int_{0}^{\infty} \left( e^{-\rho} \rho^{2\nu+1-1} M(-n, 1+2\nu, \rho) M(-m, 1+2\nu, \rho) \right) d\rho =$$

$$\Gamma(c) F_2(1+2\nu; -n, -m; 1+2\nu, 1+2\nu, 1, 1).$$
(76)

It can be proved (see appendix B) that  $F_2(1+2\nu; -n, -m; 1+2\nu, 1+2\nu, 1, 1)$  is given by  $\frac{n!\delta_{mn}}{(1+2\nu)^{(n)}}$  in this case. This makes the solution very simple and reduces relation (76):

$$\int_{0}^{\infty} \left( e^{-\rho} \rho^{2\nu+1-1} M(-n, 1+2\nu, \rho) M(-m, 1+2\nu, \rho) \right) d\rho = \Gamma(1+2\nu) \frac{n! \delta_{mn}}{(1+2\nu)^{(n)}}.$$
(77)

Combining (77) and the exact form of the wave functions in (57) and (58) this gives the following total normalization factor. Note that the mixing terms dissapear due to (77). Thus the normalisation factor squared becomes:

$$N_{(n,j)}^{2} = \frac{4\pi\Gamma(1+2\nu)\Delta}{4\gamma^{2}} \left[ \left(j + \frac{\alpha\Delta}{\gamma}\right)^{2} \frac{n!}{(1+2\nu)^{(n)}} + \left(\nu - \frac{\alpha E}{\gamma}\right)^{2} \frac{(n-1)!}{(1+2\nu)^{(n-1)}} \right]$$
(78)

Using equation (42) equation (78) can be rewritten to give the following simple normalization:

$$N_{(n,j)}^{2} = \frac{4\pi \bigtriangleup \Gamma(1+2\nu)(n-1)!}{4\gamma^{2}(1+2\nu)^{(n-1)}} \left[ \left(j + \frac{\alpha \bigtriangleup}{\gamma}\right)^{2} \frac{n}{(n+2\nu)} + n^{2} \right]$$
(79)

**Remark:** Note that in the case of the n = 0 states the normalistation reduces to  $\frac{\pi}{\gamma^2} j^2 \Delta \Gamma(1+2\nu)$ .

#### 6.3 Energy and wave function plots

#### 6.3.1 Energy levels

In this section a plot of the energy levels is given  $(\frac{E}{\Delta}$  is plotted). The energy levels depend on the two quantum numbers n and m so a 3D plot is given. Note that although the plot is contineous it should be discrete in (n, m). The n quantum number goes from 0 to 4 and the m quantum number goes from -5 to 5. Note that  $\alpha$  was taken to be  $\frac{30}{137}$  (this is done because the pattern is more distinct using a higher charge).



Figure 7: The energy plotted versus the two quantum numbers.

In the next figure a plot of the energy of the ground state in function of the fine structure constant is given:



Figure 8: The energy plotted versus the fine structure constant.

Also a contour plot is given using the same parameters as in the previous picture. The color bar gives the corresponding energy.



Figure 9: A contour plot of the energy levels.

#### 6.3.2 Wave functions

In this section plots are given of a few normalized probability distributions (the absolute square of the wave function). For simplicity the mass ( $\Delta$ ) was taken to be one and the  $\alpha$  was taken to be as example  $\frac{5}{137}$ . Four states are plotted:  $(0, \frac{1}{2}), (1, \frac{1}{2}), (0, \frac{-1}{2})$  and  $(2, \frac{3}{2})$  Also note that only the radial probability densitiy was used.



Figure 10: Plot of the wave functions for the states  $(0, \frac{1}{2})$  and  $(1, \frac{1}{2})$ .



Figure 11: Plot of the wave functions for the states  $(0, -\frac{1}{2})$  and  $(2, \frac{3}{2})$ .

# 7 Critical charge

When looking at the energy levels one can notice that the energy becomes imaginary when  $(m + \frac{1}{2}) < Z\alpha$ . Where Z is the atomic number of the impurity. This of course is physicly impossible and gives a restriction on the charge. Since m = 0 is allowed, this restriction is given by:

$$Z\alpha < \frac{1}{2}.\tag{80}$$

Let's investigate what happens when this condition is not satisfied. When the condition is not satisfied the solution in section 3.2.2 (limit to zero) will become imaginary too. This gives:

$$R(r)_{a/b} = \frac{\rho^{i\sqrt{\alpha^2 - (m + \frac{1}{2})}}}{\sqrt{\rho}}.$$
(81)

Rewriting (81) using natural logarithms gives:

$$R(r)_{a/b} = \frac{e^{\ln \rho^{i\beta}}}{\sqrt{\rho}} = \frac{e^{i\beta\ln\rho}}{\sqrt{\rho}}.$$
(82)

Where  $\beta$  is  $\sqrt{\alpha^2 - (m + \frac{1}{2})}$ . Using Eulers identity and the fact that  $\rho$  is small gives:

$$R(r)_{a/b} = \frac{1 + i \sin\left(\beta \ln \rho\right)}{\sqrt{\rho}}.$$
(83)

Taking the modulus squared gives us more information about the physics behind the equation:

$$|\psi_{a/b}|^2 \propto |R_{a/b}|^2 \propto \frac{1 + (\sin(\beta \ln \rho))^2}{\rho}.$$
 (84)

Where  $\psi_{a/b}$  are the two components of the total wave function  $\Psi$ . Given (81) the total probability integral can be calculated. In a physical situation this integral should converge:

$$\int \left( | R_a |^2 + | R_b |^2 \right) dV.$$
 (85)

Using equation (81) and the volume element in polar coordinates  $dV = \rho d\rho d\theta$  this gives:

$$2\pi \int_0^\infty 2\left(1 + \left(\sin\left(\beta \ln \rho\right)\right)^2\right) d\rho.$$
(86)

In the figure below the function  $1 + (\sin(\beta \ln \rho))^2$  is plotted. It's easy to see that it oscillates really hard arround zero. Notice that the integrand oscillates but is always positive and does not decay to zero for  $\rho \to \infty$  which causes the integral to diverge! Our model breaks down and there are no stable bound states possible!



Figure 12: Plot of the wave function. It is easy to see that it oscillates near zero.

From (80) and the exact value of the fine structure constant  $\alpha = \frac{1}{137}$  the critical charge can be calculated.

$$Z_c = 68, 5$$
 (87)

If the charge of the impurity is larger than 68,5 the model breaks down and the solution is not stable. Notice that this critical charge is independent of the mass term.

**Remark:** In graphene  $\alpha$  has to be replaced by  $\alpha_{eff}$  which also depends on the diëlectric constant of the environment of graphene. This result in a  $\alpha_{eff} > \alpha$  which will decrease  $Z_c$ .

### 7.1 Atomic collapse

We know that for charges above the critical level the model described above breaks down and no stable bound states are possible. But if there are no bound states what will the electron do? To discover this let us first look at the classical atom.

#### 7.1.1 Classical atom

In the classical sence an atom is not stable. Because there is an attraction between the electrons and the nucleus, one could expect that eventually the electron collapses into the nucleus. This is because the electron gradually looses energy due to radiation. This problem is solved by introducing the concept of quantum mechanics.

#### 7.1.2 Bohr atom

The problem of energy loss was solved by quantum mechanics. Here it was discovered that the possible orbits of the electrons are not continous but discrete. The electrons stay "locked" in orbits with a certain energy. Because the electrons are "locked" the radiation loss is no longer an issue anymore.

#### 7.1.3 Situation in graphene

From the previous calculations it's easy to see that when the impurity has a charge larger than 68,5 unit charges, no stable bound states can be found. This means that the electron will not be locked into an orbit arround the impurity but will spiral towards the impurity while losing its energy. This proces is *called atomic collapse*.

This property is unique to graphene and is caused by the fact that the situation is two dimensional and the electron behaves relativisticly. The process of atomic collapse is shown in figure 13.

**Remark:** It turns out that the critical charge can be raised by assuming a finite size point source (this process is called renormalisation). But with this technique the critical charge can only be raised to about 120 unit charges.



Figure 13: When the charge of the nucleus is larger than the critical charge no bounds states are possible, the electron will fall towards the nucleus radiating energy.

#### 7.1.4 Experimentel verification of atomic collapse

In 2013 atomic collapse was for the first time observed in graphene. In the experiment 5 charged calcium dimers (figure 14) were put on top of the graphene lattice[6]. With an AFM it was possible to push several charged dimers close together such that they have a charge far above the critical charge which caused atomic collapse. They also discovered some strange behavior which needs some more investigation: to be continued!



Figure 14: This is an AFM immage of the dimers in graphene. The 5 darker dots are the calcium dimers and the spere arround the dimers is the atomic-collapse electron cloud.

## 8 Comparison with 2D hydrogen atom

In the previous section it was shown that when the lattice is asymmetric, bound states are possible. It's easy to see that the studied case looks a lot like the classical hydrogen atom, there is a heavy charge with orbitting electrons around it with the difference that in this case the electrons are relativistic. Because of that it is interesting to look at the difference between the relativistic case and the non relativistic case.

#### 8.1 Schrödinger equation

In the case of a two dimensional hydrogan atom (using polar coordinates) the Schrödinger equation describing the atom is given by the following equation[13]:

$$\left[-\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2}\right) - \frac{Ze^2}{r}\right]\psi = E\psi$$

When this eigenvalue problem is solved one finds 2 quantum numbers: a principle quantum number n and a quantum number related to the rotation given by l. n can take the values 0, 1, 2, ... and l can take the values 0, 1, 2, ..., n - 1. The value of the energy levels is given by[13]:

$$E_n = -\frac{Z^2}{2\left(n-\frac{1}{2}\right)^2} \frac{m_e e^4}{\hbar^2}$$

The wave function depends on both n and l and the energy is degenerate for all the l quantum numbers. Note that compared to the relativistic hydrogen atom the energy only depends on one of the quantum numbers, and next to that there are more degenerate levels than in the relativistic case. The normalized wavefunctions (radial part) are given by:

$$R_{nl}(r) = \frac{\beta_n}{(2 \mid l \mid)!} \left( \frac{(n+\mid l \mid -1)!}{(2n-1)(n-\mid l \mid -1)!} \right)^{\frac{1}{2}} (\beta_n r)^{\mid l \mid} e^{\frac{-\beta_n r}{2}} M(-n+\mid l \mid +1, 2 \mid l \mid +1, \beta_n r),$$

where M is the same confluent hypergeometric function as in the wave function of the relativistic case. Note that  $\beta_n$  is given by:

$$\frac{2Z}{n-\frac{1}{2}}\frac{m_e e^2}{\hbar^2}$$

On the next page a table is given where the relativistic hydrogen atom is compared to the non relativistic hydrogen atom.

	Classical hydrogen atom	Relativistic hydrogen atom
Quantum numbers	One principle quantum number $n$ and one radial quantum number $l$	One principle quantum number $n$ and one angular quantum number $j$
Quantum number values	$n = 1, 2, 3, \dots$ and $\mid l \mid = 0, 1, 2, \dots, n - 1$	$n = 0, 1, 2, \dots \text{ if } j > 0$ $n = 1, 2, 3, \dots \text{ if } j < 0 \text{ and}$ $ j  = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$
Energy levels	$E_n = -\frac{Z^2}{2\left(n - \frac{1}{2}\right)^2} \frac{m_e e^4}{\hbar^2}$	$E_{nj} =  riangle \left( 1 + \left( rac{lpha}{n+\sqrt{j^2 - lpha^2}}  ight)^2  ight)^{-rac{1}{2}}$
Wave function Radial part	$\begin{split} \psi_{nl} &= e^{il\theta} R_{(nl)} \\ R_{nl}(r) &= \frac{\beta_n}{(2 l )!} \left( \frac{(n+ l -1)!}{(2n-1)(n- l -1)!} \right)^{\frac{1}{2}} (\beta_n r)^{ l } e^{-\frac{\beta_n r}{2}} \\ M(-n+ l +1,2 l +1,\beta_n r) \end{split}$	$\begin{split} \psi_{a}^{(nj)} &= e^{im\theta} R_{a}^{(nj)}, \ \psi_{b}^{(nj)} &= e^{i(m+1)\theta} R_{b}^{(nj)} \\ R_{a}^{(nj)} &= \frac{1}{N}\sqrt{\Delta + E}e^{-\gamma r}(2\gamma r)^{\nu - \frac{1}{2}} \left[ \left( j + \frac{\Delta \Delta}{\gamma} \right) M(-n, 1 + 2\nu, 2\gamma r) \\ &+ nM(-n + 1, 1 + 2\nu, 2\gamma r) \right] \\ R_{b}^{(nj)} &= \frac{1}{N}\sqrt{\Delta - E}e^{-\gamma r}(2\gamma r)^{\nu - \frac{1}{2}} \left[ \left( j + \frac{\Delta \Delta}{\gamma} \right) M(-n, 1 + 2\nu, 2\gamma r) \\ &- nM(-n + 1, 1 + 2\nu, 2\gamma r) \right] \end{split}$
Remarks	Value $\beta_n$ see previous page.	in natural units. To really compare the energies one should rescale the energy to joules, but this is only a scaling factor of course

8.1 Schrödinger equation COMPARISON WITH 2D HYDROGEN ATOM

# 9 Stark effect

Know that we have the proper form of the wave functions and the energy levels it is interesting to look what happens in case of an applied electric field. In this section the effect of a linear electric field on the energy levels and wave functions will be investegated by using perturbation theory.

#### 9.1 Perturbation theory

For the theory behind perturbation theory reference [7] was used.

#### 9.2 Non degenerate perturbation theory

From the above we know that all the states are degenerate except the n = 0 states. So first order non degenerate perturbation theory will be applied on the (0, j) states with the corresponding wave functions  $\Psi^{(0,j)}$ . The application of an electric field can we written as a small perturbation on the hamiltonian:

$$H_{new} = H_{old} + e\epsilon x. \tag{88}$$

The first order correction on the energy due to the electric field  $\epsilon$  is given by [7]:

$$E_{0j}^{(1)} = \langle \Psi^{(0,j)} | x | \Psi^{(0,j)} \rangle.$$
(89)

Because we are working in polar coordinates x can be rewritten as  $r \cos \theta$  and after using the exact form for  $\Psi^{(0,j)}$  equation (89) reduces to the calculation of the following integral:

$$\int_{0}^{2\pi} \cos\theta d\theta \int_{0}^{\infty} \left( |\psi_{a}^{(0,j)}|^{2} + |\psi_{b}^{(0,j)}|^{2} \right) r^{2} dr.$$
(90)

It's easy to see that the angular part of the integral gives zero. This causes the first order correction to be zero. To have an idea of the perturbation due to the electric field on the energy we should look at the second order correction given by:

$$E_{0j}^{(2)} = \sum_{n=0,j'=\frac{1}{2}}^{\infty} \frac{|\langle \Psi^{(n,j')}| r \cos \theta |\Psi^{(0,j)}\rangle|^2}{E_{0j}^{(0)} - E_{nj'}^{(0)}}.$$
(91)

For the matrix element we need to calculate the angular and the radial part.

#### Angular part.

For the angular part we need to look at the following two integrals:

$$\int_{0}^{2\pi} e^{-i(j-\frac{1}{2})+i(j'-\frac{1}{2})} \cos\theta d\theta = \pi \delta_{j,j'-1} + \pi \delta_{j,j'+1}, \tag{92}$$

$$\int_{0}^{2\pi} e^{-i(j+\frac{1}{2})+i(j'+\frac{1}{2})} \cos\theta d\theta = \pi \delta_{j,j'-1} + \pi \delta_{j,j'+1}.$$
(93)

With this knowledge equation (91) can be rewritten to give:

$$\sum_{n=0}^{\infty} \frac{|\langle \Psi^{(n,j-1)} | r \cos \theta | \Psi^{(0,j)} \rangle|^2}{E_{(0,j)}^{(0)} - E_{(n,j-1)}^{(0)}} + \sum_{n=0}^{\infty} \frac{|\langle \Psi^{(n,j+1)} | r \cos \theta | \Psi^{(0,j)} \rangle|^2}{E_{(0,j)}^{(0)} - E_{(n,j+1)}^{(0)}}.$$
 (94)

#### Radial part.

Using the exact form of the wave functions the matrix elements are given by:

$$\pi \left\langle \Psi^{(n,j-1)} \right| r \left| \Psi^{(0,j)} \right\rangle = \frac{\pi}{N} \int_0^\infty \left( R_a^{(n,j-1)} R_a^{(0,j)} + R_b^{(n,j-1)} R_b^{(0,j)} \right) r^2 dr.$$
(95)

The normalization is determined by the two wave functions, so we assume  $N^2 = N_{(n,j-1)}N_{(0,j)}$ . Substituting the exact form of the wave equations this gives the following formula:

$$\frac{2j\pi}{N}\sqrt{\Delta} + E_{(n,j-1)}^{(0)}\sqrt{\Delta} + E_{(0,j)}^{(0)}\int_{0}^{\infty}e^{-(\gamma_{j}+\gamma_{j-1})r}(2\gamma_{j}r)^{\nu_{j}-\frac{1}{2}}(2\gamma_{j-1}r)^{\nu_{j-1}-\frac{1}{2}}\left[\left(j-1+\frac{\alpha\Delta}{\gamma_{j-1}}\right)M(-n,1+2\nu_{j-1},2\gamma_{j-1}r) - nM(-n+1,1+2\nu_{j-1},2\gamma_{j-1}r)\right]r^{2}dr + \frac{2j\pi}{N}\sqrt{\Delta} - E_{(n,j-1)}^{(0)}\sqrt{\Delta} - E_{(0,j)}^{(0)}\int_{0}^{\infty}e^{-(\gamma_{j}+\gamma_{j-1})r}(2\gamma_{j}r)^{\nu_{j}-\frac{1}{2}}(2\gamma_{j-1}r)^{\nu_{j-1}-\frac{1}{2}}\left[\left(j-1+\frac{\alpha\Delta}{\gamma_{j-1}}\right)M(-n,1+2\nu_{j-1},2\gamma_{j-1}r) + nM(-n+1,1+2\nu_{j-1},2\gamma_{j-1}r)\right]r^{2}dr.$$
(96)

This looks awfully complex, but after some rearranging the formula becomes far more workable:

$$\frac{1}{N}2j\pi(A+B)\left(j-1+\frac{\alpha\Delta}{\gamma_{j-1}}\right)\int_{0}^{\infty}e^{-(\gamma_{j}+\gamma_{j-1})r}(2\gamma_{j}r)^{\nu_{j}-\frac{1}{2}}(2\gamma_{j-1}r)^{\nu_{j-1}-\frac{1}{2}}M(-n,1+2\nu_{j-1},2\gamma_{j-1}r)r^{2}dr$$

$$+\frac{1}{N}2jn\pi(B-A)\int_{0}^{\infty}e^{-(\gamma_{j}+\gamma_{j-1})r}(2\gamma_{j}r)^{\nu_{j}-\frac{1}{2}}(2\gamma_{j-1}r)^{\nu_{j-1}-\frac{1}{2}}M(-n+1,1+2\nu_{j-1},r)r^{2}dr$$
(97)

Here A is given by  $\sqrt{(\triangle + E_{(n,j-1)}^{(0)})(\triangle + E_{(0,j)}^{(0)})}$  and B is given by  $\sqrt{(\triangle - E_{(n,j-1)}^{(0)})(\triangle - E_{(0,j)}^{(0)})}$ . Note that the normalization factor can be calculated using the previous results and is given by the following formula:

$$N^{2} = \frac{(\pi)^{2} j^{2} \bigtriangleup^{2} \Gamma(1+2\nu_{j-1}) \Gamma(1+2\nu_{j})}{(1+2\nu_{j-1})^{(n-1)} \gamma_{j}^{2} \gamma_{j-1}^{2}} \left[ \left( j - 1 + \frac{\alpha \bigtriangleup}{\gamma_{j-1}} \right)^{2} \frac{n}{n+2\nu_{j-1}} + n^{2} \right].$$
(98)

This integral in (97) can be calculated numerically for example with mathematica. When n = 0 the integral in (97) reduces to the following integral:

$$\frac{2j\pi(A+B)\left(j-1+\frac{\alpha\Delta}{\gamma_{j-1}}\right)}{N}\int_0^\infty e^{-(\gamma_j+\gamma_{j-1})r}(2\gamma_j r)^{\nu_j-\frac{1}{2}}(2\gamma_{j-1}r)^{\nu_{j-1}-\frac{1}{2}}r^2 dr,\tag{99}$$

with the normelization given by:

$$N^{2} = \frac{\pi^{2} j^{2} (j-1)^{2} \bigtriangleup^{2} \Gamma(1+\nu_{j}) \Gamma(1+2\nu_{j-1})}{\gamma_{j}^{2} \gamma_{j-1}^{2}}.$$
 (100)

The integral in (99) is solved with mathematica and combining the result with (94) the order of magnitude of the effect (the first term) is given by:

$$\left(\frac{2j\pi(A+B)\left(j-1+\frac{\alpha\Delta}{\gamma_{j-1}}\right)}{N}\left((2\gamma_{j})^{\nu_{j}-\frac{1}{2}}(2\gamma_{j-1})^{\nu_{j-1}-\frac{1}{2}}(\gamma_{j}+\gamma_{j-1})^{-2+\nu_{j}+\nu_{j-1}}\Gamma(1+\nu_{j}+\nu_{j-1})\right)\right)^{2}$$
(101)

Note that for  $|\langle \Psi^{(n(j+1))}|r\cos\theta |\Psi^{(0j)}\rangle|^2$  a similar expression, except that j-1 should be changed to j+1. The energy difference in (91) can be calculated using the exact form of the energy levels, it is thus given by:

$$\frac{\Delta\nu_j}{\sqrt{\nu_j^2 - \alpha^2}} - \frac{\Delta\nu_{j-1}}{\sqrt{\nu_{j-1}^2 - \alpha^2}}.$$
(102)

Note that a similer expression is found for the j + 1 terms.

So combining equations (94), (100), (101) and (102) this gives an idea of the order of magnitude of the effect of the applied electric field on the energy shif.

#### 9.3 Degenerate perturbation theory

From section 4.1 only the n = 0 states could be investigated using non degenerate perturbation theory. When a random (n, j) state is investigated degenerate perturbation theory is required because (n, j) and (n, -j) have the same energy.

To investigate the effect of an electric field on the levels (n, j) and (n, -j)(with j > 0) one needs to look at the total (perturbated) hamiltonian of the combined state system. From (88) we know that the perturbated hamiltonian is given by  $e\epsilon x$ . In this case the total hamiltonian is given by the matrix[7]:

$$H = e\epsilon \begin{pmatrix} \langle \Psi^{(n,j)} | r \cos \theta | \Psi^{(n,j)} \rangle & \langle \Psi^{(n,j)} | r \cos \theta | \Psi^{(n,-j)} \rangle \\ \langle \Psi^{(n,-j)} | r \cos \theta | \Psi^{(n,j)} \rangle & \langle \Psi^{(n,-j)} | r \cos \theta | \Psi^{(n,-j)} \rangle \end{pmatrix}.$$
 (103)

The diagonal elements are zero for the same reason that (85) equals to zeros. This gives the following hamiltonian:

$$H = e\epsilon \begin{pmatrix} 0 & \langle \Psi^{(n,j)} | r \cos \theta | \Psi^{(n,j)} \rangle \\ \langle \Psi^{(n,-j)} | r \cos \theta | \Psi^{(n,j)} \rangle & 0 \end{pmatrix}.$$
(104)

The first order correction to the energy can be calculated by solving the following eigenvalue problem:

$$e\epsilon \begin{pmatrix} 0 & \langle \Psi^{(n,j)} | r \cos \theta | \Psi^{(n(-j))} \rangle \\ \langle \Psi^{(n(-j))} | r \cos \theta | \Psi^{(nj)} \rangle & 0 \end{pmatrix} \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix} = E^{(1)} \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix}.$$
(105)

In order to solve the eigenvalue problem we need to look at the determinant of the following matrix:

$$\begin{pmatrix} -E^{(1)} & e\epsilon \langle \Psi^{(n,j)} | r \cos \theta | \Psi^{(n,j)} \rangle \\ e\epsilon \langle \Psi^{(n,-j)} | r \cos \theta | \Psi^{(n,j)} \rangle & -E^{(1)} \end{pmatrix}.$$
 (106)

From the eigenvalues the first correction to the energy can be determined and is given by:

$$E^{(1)} = \pm e\epsilon \sqrt{|\langle \Psi^{(n,j)}| r \cos \theta |\Psi^{(n,-j)}\rangle|^2}.$$
 (107)

So if we find the value of the matrix element in (107) we have the first order correction to the uperturbated energy state  $E_{(n,j)}^{(0)}$ . The matrix element is given by:

$$\int_{0}^{2\pi} e^{-2j\theta} \cos\theta d\theta \int_{0}^{\infty} \left( R_{a}^{(nj)} R_{a}^{(n(-j))} + R_{b}^{(nj)} R_{b}^{(n(-j))} \right) r^{2} dr.$$
(108)

Since for (n, j) and (n, -j) state the  $\gamma$  is the same and it's usefull to go back to the  $\rho$  form of the wave functions. In that case the integral reduces to:

$$\frac{1}{8\gamma^3} \int_0^{2\pi} e^{-2j\theta} \cos\theta d\theta \int_0^\infty \left( R_a^{(nj)} R_a^{(n(-j))} + R_b^{(nj)} R_b^{(n(-j))} \right) \rho^2 d\rho.$$
(109)

The angular part of the intregral is given by  $\pi \delta_{j,\frac{1}{2}}$ . The radial part requires a bit more calculation:

$$\frac{\left(\Delta + E_{(n,j)}^{(0)}\right)}{8\gamma^{3}} \int_{0}^{\infty} e^{-\rho} \rho^{2\nu+1} \left[ \left(j + \frac{\alpha \Delta}{\gamma}\right) M(-n, 1 + 2\nu, \rho) - nM(-n + 1, 1 + 2\nu, \rho) \right] \\
\left[ \left(-j + \frac{\alpha \Delta}{\gamma}\right) M(-n, 1 + 2\nu, \rho) - nM(-n + 1, 1 + 2\nu, \rho) \right] \\
+ \frac{\left(\Delta - E_{(n,j)}^{(0)}\right)}{8\gamma^{3}} \int_{0}^{\infty} e^{-\rho} \rho^{2\nu+1} \left[ \left(j + \frac{\alpha \Delta}{\gamma}\right) M(-n, 1 + 2\nu, \rho) + nM(-n + 1, 1 + 2\nu, \rho) \right] \\
\left[ \left(-j + \frac{\alpha \Delta}{\gamma}\right) M(-n, 1 + 2\nu, \rho) + nM(-n + 1, 1 + 2\nu, \rho) \right] \\
\left[ \left(110\right) \left(110\right) \left(\frac{\alpha \Delta}{\gamma}\right) M(-n, 1 + 2\nu, \rho) + nM(-n + 1, 1 + 2\nu, \rho) \right] \\$$

Note that we can write only one the same  $\nu$ , E and  $\gamma$  because the calculation of  $j^2$  is needed. Rewriting equation (110) gives the following equation:

$$\frac{2\Delta}{8\gamma^3} \int_0^\infty e^{-\rho} \rho^{2\nu+1} \left[ \left( \left( \frac{\alpha\Delta}{\gamma} \right)^2 - j^2 \right) M(-n, 1+2\nu, \rho)^2 + n^2 M(-n+1, 1+2\nu, \rho)^2 \right] d\rho \\ + \frac{4E_{(n,j)}^{(0)} \alpha\Delta}{8\gamma^4} \int_0^\infty e^{-\rho} \rho^{2\nu+1} M(-n, 1+2\nu, \rho) M(-n+1, 1+2\nu, \rho) d\rho.$$
(111)

It's easy to see that the integrals are similar to the ones used in the normalization. Using formula (75) the results of the integrals can be calculated. This gives the following three Appell series we need to calculate

$$F_{2}(2+2\nu;-n,-n;1+2\nu,1+2\nu,1,1)$$

$$F_{2}(2+2\nu;-n+1,-n+1;1+2\nu,1+2\nu,1,1)$$

$$F_{2}(2+2\nu;-n,-n+1;1+2\nu,1+2\nu,1,1)$$
(112)

In reference [12] the following formula is derived:

$$F_2(c+j,-n,-n;c,c;1,1) = \frac{(1)^{(n)}(-1)^j}{c^{(n)}} {}_3F_2(c+n,-j,j+1;c,1;1), \quad (113)$$

where  ${}_{3}F_{2}$  is another hypergeometric series (see appendix A). For the Appell series in (112) the formula reduces to:

$$F_2(2+2\nu, -n, -n; 1+2\nu, 1+2\nu; 1, 1) = \frac{-n!}{(1+2\nu)^{(n)}} F_2(1+2\nu+n, -1, 0; 1+2\nu, 1; 1)$$
(114)

With this knowledge the Appell series can be evaluated:

$$\Gamma(2+2\nu)F_2(2+2\nu;-n,-n;1+2\nu,1+2\nu,1,1) = \frac{n!(1+2\nu+2n)\Gamma(1+2\nu)}{(1+2\nu)^{(n)}},$$
  

$$\Gamma(2+2\nu)F_2(2+2\nu;-n,-n+1;1+2\nu,1+2\nu,1,1) = -\frac{n!\Gamma(1+2\nu)}{(1+2\nu)^{(n-1)}}.$$
(115)

Note that the factor  $\Gamma(1+2\nu)$  is added because of formula (75). Plugging this result back into equation (111) gives (after a bit of rewriting and rearranging) the following result:

$$\frac{2n \bigtriangleup \Gamma(1+2\nu)(n-1)!}{8\gamma^3(1+2\nu)^{(n-1)}} \left[ \left( \left(\frac{\alpha \bigtriangleup}{\gamma}\right)^2 - j^2 \right) \frac{(1+2\nu+2n)}{(n+2\nu)} + n - \frac{4\alpha \ E_{(n,j)}^{(0)} \bigtriangleup}{\gamma} \right]$$
(116)

If the above formula is combined with the result of the angular part and the fact that the wave function should be normalised the final result of the matrix element is given by the following equation:

$$\langle \Psi^{(n,j)} | r \cos \theta | \Psi^{(n,-j)} \rangle = \frac{\frac{\delta_{j\frac{1}{2}}}{4\gamma} \left[ \left( \left( \frac{\alpha \Delta}{\gamma} \right)^2 - j^2 \right) \frac{(1+2\nu+2n)}{(n+2\nu)} + n - \frac{4\alpha \ E^{(0)}_{(n,j)} \Delta}{\gamma} \right]}{\sqrt{\left( \left( j + \frac{\alpha \Delta}{\gamma} \right)^2 \frac{1}{n+2\nu} + n \right) \left( \left( -j + \frac{\alpha \Delta}{\gamma} \right)^2 \frac{1}{n+2\nu} + n \right)}}$$
(117)

Here  $E_{(n,j)}^{(0)}$  is of course the unperturbated energy of the level:  $E^{(0)}$ . Combining equation (107) and the above result the first order correction to the energy.

So the two degenerate energy levels (n, j) and (n, -j) will hybridize and split under the influence of an electric field. Two new states are formed with the following energies:

$$E_1 = E_{(n,j)}^{(0)} + e\epsilon \sqrt{|\langle \Psi^{(n,j)}| r \cos \theta |\Psi^{(n,-j)}\rangle|^2},$$
(118)

$$E_2 = E_{(n,j)}^{(0)} - e\epsilon \sqrt{|\langle \Psi^{(n,j)} | r \cos \theta | \Psi^{(n,-j)} \rangle|^2}.$$
 (119)

**Remark:** note that the above calculation is only non zero for the  $(n, \frac{1}{2})$  states. For the other states second order degenerate perturbation theory is needed. Because of the complexity this will be omitted in this paper.

# 10 Conclusion

In this paper it was shown that bound states are possible in the precence of an impurity placed in graphene. But is was shown that there is a critical charge: any impurity with a charge above this critical charge does not allow bound state this is the phenomena of "atomic collapse". Also a formula for the effect of a linear electric field on the energy levels was calculated and the stark shift was obtained analytically.

# 11 Appendices

In this section we will discuss a couple of results used in the report.

#### 11.1 Appendix A: hypergeometric functions

The hypergeometric function is very important in this paper and a lot of different hypergeometric functions are used. So in this appendix these functions will be put in a broader view.

The most important hypergeometric series is the Kummer series, this is one of the two solutions of the differential equation in (46). This series has the general form:

$$M(a,b,\rho) =_1 F_1(a,b,\rho) = \sum_{n=0}^{\infty} \frac{a^{(n)}\rho^n}{b^{(n)}n!}.$$
(120)

Sometimes the notation  ${}_{1}F_{1}$  is used, the usefullness of this notation will be explained further. The notation  $a^{(n)}$  is called the Pocammer symbol and represents the rising factorial. The recursive relation is given by:

$$a^{(n)} = a(a+1)(a+2)...(a+n-1).$$
(121)

If a is not a negative integer the pochammer symbol can be related to the gamma function using the following idendity:

$$a^{(n)} = \frac{\Gamma(a+n)}{\Gamma(a)},\tag{122}$$

where the gamma function  $\Gamma(x)$  is given by:

$$\int_0^\infty t^{x-1} e^{-x} dx. \tag{123}$$

#### 11.1.1 Generalized hypergeometric series

The hypergeometric function can be extended as follows:

$${}_{p}F_{q}(a_{1}, a_{2}, ..., a_{p}; b_{1}, b_{2}, ..., b_{q}; \rho) = \sum_{n=0}^{\infty} \frac{(a_{1})^{(n)}(a_{2})^{(n)}...(a_{p})^{(n)}\rho^{n}}{(b_{1})^{(n)}(b_{2})^{(n)}...(b_{q})^{(n)}n!}$$
(124)

Now it's clear why the previous notation is so usefull. There are an infinity number of possible hypergeometric functions each with their own set of properties and special cases.

It turns out that these hypergeometric functions are very fundamental and a lot of special functions like Legendre polynomials and the exponential function can be derived as special cases of these hypergeometric functions.

#### 11.1.2 Hypergeometric functions of multiple variables

The hypergeometric functions of one variable (discussed above) can be extendended to more variables. There are certain different ways to do this (they are called the apell series) but in this paper only one generalisation is needed, called the second Appell series. (Here the hypergeometric series is extended to two variables):

$$F(a, b_1, b_2; c_1, c_2; x, y) = \sum_{m=0, n=0}^{\infty} \frac{(a)^{(m+n)} (b_1)^{(m)} (b_2)^{(n)}}{(c_1)^{(m)} (c_2)^{(n)} n! m!} x^m y^n.$$
(125)

#### 11.2 Appendix B: second Appell series[11]

The Appell series  $F_2(1+2\nu, -n, -m; 1+2\nu, 1+2\nu; 1, 1)$  used in the normalisation can be written as:

$$\sum_{k=0}^{n} \sum_{l=0}^{m} \frac{(-n)^{(k)} (-m)^{(l)} (1+2\nu)^{(k+l)}}{(1+2\nu)^{(k)} (1+2\nu)^{(l)} k! l!}.$$
(126)

Using the fact that  $(x)^{(n)} = \frac{\Gamma(x+n)}{\Gamma(x)}$  part of (126) can be rewritten to give:

$$\sum_{k=0}^{n} \frac{(-n)^{(k)}}{k!} \sum_{l=0}^{m} \frac{(-m)^{(l)}(1+2\nu+k)^{(l)}}{(1+2\nu)^{(l)}l!}.$$
(127)

The second part of the equation is given by the hypergeomtric function  $2F_1(-m, 1+2\nu+k; 1+2\nu; 1)$  this gives the following equation:

$$\sum_{k=0}^{n} \frac{(-n)^{(k)}}{k!} 2F_1(-m, 1+2\nu+k; 1+2\nu; 1).$$
(128)

Using the idendity  $_2F_1(-m,b;c;1) = \frac{(c-b)^{(n)}}{c^{(n)}}$  equation (128) reduces to:

$$\sum_{k=0}^{n} \frac{(-n)^{(k)}(-k)^{(m)}}{k!(1+2\nu)^{(m)}}.$$
(129)

The terms only differs from zero if n = m = k so this gives the final solution:

$$\frac{n!\delta_{nm}}{(1+2\nu)^{(n)}}.$$
(130)

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