

Vacancy and Coulombic Defects in Graphene

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## Abstract

Graphene is a new material with remarkable electronic properties. The electronic motion is confined to flat sheets and is governed by the Dirac equation rather than the familiar Schrdinger equation more commonly used in solid state physics. Defects in graphene are of fundamental interest as well as for potential applications. The electronic structure of defects in graphene has recently been probed experimentally by scanning tunneling measurements. Near vacancy defects a quasi-bound state has been found near zero energy with a long power law tail. Near charged defects in graphene, bound states are found that are analogous to predicted bound states in relativistic heavy ions. Such states that have been long sought experimentally but never yet seen in the heavy ion context. In this project we aim to show that impurities in graphene can be mathematically modeled by solving the Dirac equation with suitable boundary conditions that are determined by the mathematical method of self-adjoint extensions. These methods are expected to provide quantitative and qualitative insights into impurity bound states that can be compared to experimental data and other more computationally intensive theoretical analyses.

## Chapter 1

## Introduction

Lattice impurities in graphene are challenging to model for a number of reasons. First and foremost, computational requirements of solving a single lattice defect problem using traditional solid state density functional calculations are enormous due to the many body problem associated with the electron-electron interactions and the electron-ion interactions. In addition, near defects in pure graphene lattices, both geometric and potential distortion can occur. In vacancy states, for example, Jahn-Teller distortion causes the atomic distances and hopping parameters between vacancies and adjacent carbon atoms to deform. Nanda et al. showed that the traditional equilateral triangular structure surrounding a vacancy was deformed around the vacancy site, breaking the degeneracy in the vacancy bound states (see figure 1.1) [4].


Figure 1.1: Vacancy Graphene Impurity
Shows a graphene lattice with a single vacancy defect and illustrates the effects of Jahn-Teller distortion. Notice the symmetry breaking due to the modified lattice parameters near the vacancy[4].

Further complications arise when graphene is coupled with another pure 2D material (such as hexagonal boron nitride as a neutral ground), hybridizing vacancy states with the coupled lattice. It was long thought that the various defect problems in graphene would require us to move away from the convenient analytic solutions found through the Dirac equation and instead return to a discretized lattice model analysis. As such, many approaches to this problem include using the tight binding model along with density functional calculations to determine the energies and wave functions near the imperfections [1],[3],[5],[6],[9],[12],[13]. For long range interactions, typically Green's function calculations are used to extend the results near the imperfections to the rest of the lattice. In our analysis, we hope to return to modeling electronic motion using the Dirac equation, representing the defects as modified boundary conditions using the method of self-adjoint extensions.

## Chapter 2

## Experimental Motivation

A number of experiments have been performed that involve creating and studying impurities in monolayer graphene or similar bilayer structures (such as graphene coupled with hexagonal boron nitride to reduce charge inhomogeneity). The local density of states near impurities in graphene has been studied using scanning probe microscopy to measure the local electron current. Levitov et al. found that divalent and trivalent charge impurity systems create an ideal system for observing the atomic resonance states, where the Dirac fermion wave functions are best described through BohrSommerfeld quantization of collapsing trajectories and Klein tunneling [3]. Levitov et al. additionally predicted the formation atomic collapse resonances near charge impurities in bilayer graphene [3]. An experimental group, Crommie et al. used an STM tip to place calcium dimers in a localized area on a single sheet of graphene coupled to hexagonal boron nitride. The hexagonal boron nitride acts simply to reduce inherent charge inhomogeneity in the graphene, allowing for a pristine study of the calcium charge impurities. Crommie et al. observed the aforementioned formation of atomic resonance states using $\mathrm{dI} / \mathrm{dV}$ spectroscopy to measure the local density of states near calcium dimers inserted onto graphene-hexagonal boron nitride bilayer lattices (see figure 2.1)[13].


Figure 2.1: LDOS for Calcium Dimer Defects
Shows the placement of calcium dimers on a graphene lattice and the formation of a bound state in the $\mathrm{dI} / \mathrm{dV}$ spectrum. As you can see, the resonance peak increases the closer the STM tip was placed in relation to the dimers[13].

Another group, M.M Ugeda et al. measured the local density of states near vacancy defects in graphene using the same $\mathrm{dI} / \mathrm{dV}$ spectroscopy (see figure 2.2). They found the formation of a quasiresonant bound state near the center of the vacancy. Additionally, they measured a characteristic inverse r squared power law tail away from the center of the impurity (see figure 2.3).


Figure 2.2: LDOS for Vacancy Defect
Shows a dI/dV plot over a vacancy defect, identifying the local quasi-resonant bound state near the vacancy (red) when compared to the base graphene spectrum (black) [6].


Figure 2.3: LDOS Decay for Vacancy Defect
Shows a plot of the maximum density of states for positions near the vacancy. There is an interesting inverse r squared power law tail. Note the axis is merely for scale, the vacancy is centered around the $3-4 \mathrm{~nm}$ position. [6].

Theoretical groups including Pereira et al., and Islamoglu et al. used the tight binding model along with density functional calculations and various nearest neighbor approximations to model localized and de-localized states in graphene with lattice impurities [6],[12],[9]. Their results yield a wealth of information, however the calculations themselves are computationally intensive and relatively inflexible with respect to introducing new fields (such as a magnetic field). It has been shown through DFT calculations that using boundary conditions to model defects predicts the existence of resonant bound states through Klein tunneling [3],[13]. We hope to reproduce the experimental results using a more accessible model by examining the electronic motion with the Dirac equation and using the method of self-adjoint extensions.

Studying these impurities yeilds a wealth of useful information concerning fundamental physics and the possible engineering applications of defected graphene. Most notably, graphene can provide an excellent examination of heavy ion physics since the Dirac analysis modifies the electronic fine structure constant, allowing for relatively small charges to interact like heavy ions (this will be shown in the methods). Additionally, it has been suggested that vacancy defects in graphene can allow for low temperature hydrogen storage through the use of the quasi-bound states. It was also theorized that multilayer sheets of graphene could act a non-metallic ferro magnets (since the quasi-bound states additionally generate a small magnetic moment)[4], [6].

## Chapter 3

## Methods

### 3.1 Dirac Fermions in Graphene

Electronic motion in graphene is unique mainly because of the Dirac-like nature of the electrons. Typically, when one uses the Dirac equation to describe fermionic motion, one thinks of particles that travel near the speed of light. However, in graphene, the electrons are not considered relativistic, but they are Dirac-like since their dispersion relation is linear in momentum (figure 1).


Figure 3.1: Graphene Dispersion Relation
Shows a slice of the energy band of graphene. Notice the linear energy momentum spectrum near the mini Dirac point [10].

We can observe this phenomenon mathematically by examining the band structure of graphene given below.

$$
\begin{equation*}
E= \pm \gamma \sqrt{1+4 \cos \frac{\sqrt{3} k_{x} a}{2} \cos \frac{k_{y} a}{2}+4 \cos ^{2} \frac{k_{y} a}{2}} \tag{3.1}
\end{equation*}
$$

In the above equation, gamma refers simply to the interaction integral between successive lattice points in the tight binding model. Its experimentally derived value is given as

$$
\begin{equation*}
\gamma \sim 2.7 \mathrm{eV} \tag{3.2}
\end{equation*}
$$

The band structure is quite complicated (figure 2), but what is most interesting is the lack of a band gap at certain points within lattice k space.


Figure 3.2: Graphene Band Structure
Shows the band structure of graphene. Notice how the conduction and valence band touch at 6 points in k-space denoted mini Dirac points[2].

These points are known as mini Dirac points (since electronic motion is Dirac-like near these points) and are given below.

$$
\begin{equation*}
K=\left( \pm \frac{2 \pi}{\sqrt{3} a}, \pm \frac{2 \pi}{3 a}\right), K^{*}=\left(0, \pm \frac{4 \pi}{3 a}\right) \tag{3.3}
\end{equation*}
$$

From the above expression for the mini Dirac points, it may or may not be obvious that the six Dirac points are not independent. If you remember for introductory solid state physics, lattice k-space is periodic, and it turns out there are 2 distinct mini Dirac points and the other 4 can expressed as the original 2 plus some periodic k -space term. Interestingly, near these k space points, the band structure reduces to a simple linear dispersion relation:

$$
\begin{equation*}
E \propto \pm \gamma|k| \tag{3.4}
\end{equation*}
$$

Since electrons are intrinsically promoted to the conduction band through contact points between the valence band and the conduction band, it can be argued that the electrons that dominate electronic properties exist near the Dirac points in k space. Since a linear dispersion relation is achieved near the Dirac points, we have a justification for using the Dirac equation as an analytic approach to modeling electronic motion in graphene (with some parameter subtleties that will be discussed in the next section).

### 3.2 The 2D Dirac Equation in Graphene

The most general form of the Dirac equation simply asserts that energy must be treated on equal footing with both momentum and mass (rest energy). The general formulation is given by the succinct expression (with $c$ and $\hbar$ set equal to 1 ):

$$
\begin{equation*}
(\vec{\alpha} \cdot \vec{p}+\beta m) \psi=E \psi \tag{3.5}
\end{equation*}
$$

The matrices $\alpha$ and $\beta$ have anti commutation restrictions so that

$$
\begin{equation*}
\left\{\alpha_{i}, \alpha_{j}\right\}=2 \delta_{i, j} \text { and }\left\{\alpha_{i}, \beta\right\}=2 \tag{3.6}
\end{equation*}
$$

In three dimensions, the matrices $\alpha$ and $\beta$ are denoted by the famous gamma matrices (in the Dirac representation) and the Dirac equation becomes:

$$
\begin{gather*}
i \hbar \gamma^{\mu} \partial_{\mu} \psi-m c \psi=0  \tag{3.7}\\
\gamma^{0}=\left(\begin{array}{cc}
I_{2} & 0 \\
0 & -I_{2}
\end{array}\right), \gamma^{i}=\left(\begin{array}{cc}
0 & \sigma_{i} \\
-\sigma_{i} & 0
\end{array}\right) \tag{3.8}
\end{gather*}
$$

As a construct of the matrices used in the Dirac equation, the wave functions have 4 distinct spinor components. In graphene, we want to take advantage of this form of the Dirac equation since there are two distinct mini Dirac points (we can consider each set of 2 spinors representative of the 2 mini Dirac points). However, the dimensionality of the system in our model reduces to 2 since the electrons are essentially confined to a single plane. Additionally, in the analysis presented in this paper, we reduce the number of spinor components to 2 , which serves to reduce the complexity of the problem. When we perform the full calculation, however, we will need to use the 4 spinor form of the Dirac equation. Keep in mind throughout the analysis of the problems, that our 2 spinor analysis is not physical, but done so that we can formulate a set of tools necessary for tackling the full 4 component problem.

With this in mind, an appropriate choice of $\alpha$ and $\beta$ matrices is given:

$$
\alpha_{1}=\left(\begin{array}{ll}
0 & 1  \tag{3.9}\\
1 & 0
\end{array}\right), \alpha_{2}=\left(\begin{array}{cc}
0 & -i \\
i & 0
\end{array}\right), \beta=\left(\begin{array}{cc}
1 & 0 \\
0 & -1
\end{array}\right)
$$

An important point to note about using the Dirac equation in graphene is the modification of the speed of light. We are considering the relativistic analog of these Dirac fermions, but in reality they are not considered relativistic in nature. When formulating the Dirac equation for relativistic particles, the speed of light is important because it serves as the slope in the linear dispersion relation of a photon. However, in graphene, the slope of the dispersion is not equal to the speed of light, it is actually equal to the crystal velocity (which translates to the Fermi velocity in graphene). We need to remember we are using the Dirac equation only as a model for electronic motion in graphene, so it's necessary to adjust the parameters of the model so that we reproduce the same physics described by the Dirac equation. As such, we need to adjust the speed of light so it matches the Fermi velocity, which is well-known in graphene to be:

$$
\begin{equation*}
\nu_{F} \sim \frac{c}{300} \tag{3.10}
\end{equation*}
$$

This has the overall effect in our calculations of modifying the fine structure constant. Typically, when examining the hydrogen atom example and similar situations, the fine structure constant is $\sim \frac{1}{137}$. However, the structure constant is defined as $\alpha \sim \frac{e^{2}}{4 \pi \epsilon_{0}} \frac{1}{\hbar c}$. Since the speed of light is decreased by a factor of 300 , the fine structure constant for graphene is:

$$
\begin{equation*}
\alpha_{\text {graphene }} \sim \alpha_{\text {hydrogen }} * 300 \sim 2.1898 \tag{3.11}
\end{equation*}
$$

### 3.3 Self-Adjoint Extensions: a General Theory

The method of self-adjoint extensions involves analyzing the conditions needed for an operator to be self-adjoint. In the most general terms, we require the following inner product expression involving the desired operator:

$$
\begin{equation*}
(\phi, A \psi)=(A \phi, \psi) \tag{3.12}
\end{equation*}
$$

The inner product expression corresponds to an integral of dimension equal to the dimensionality of our physical system (can be volume, area, etc...). When evaluating the 3 dimensional spherical problem for example, our inner product expression becomes:

$$
\begin{align*}
\int_{a}^{b} \phi^{*}(\mathrm{H} \psi) \mathrm{d} \tau & =\int_{a}^{b}\left(\phi^{*} \mathrm{H}^{\dagger}\right) \psi \mathrm{d} \tau  \tag{3.13}\\
\int_{r_{1} \theta_{1} \phi_{1}^{*}}^{\int_{2} \theta_{2} \phi_{2}^{*}} \phi^{*}(\mathrm{H} \psi) \mathrm{r}^{2} \sin \theta \mathrm{~d} r d \theta d \phi^{*} & =\iint_{r_{1} \theta_{1} \phi_{1}^{*}}^{r_{2} \theta_{2} \phi_{2}^{*}} \int^{*}\left(\phi^{*} \mathrm{H}^{\dagger}\right) \psi r^{2} \sin \theta \mathrm{~d} r d \theta d \phi^{*} \tag{3.14}
\end{align*}
$$

The operator need not be scalar or single dimensional. In practice the operator can be as complicated as a differential matrix operator (as in the Dirac examples) or as simple scalar quantities. We typically integrate over all space evaluating in the spherical coordinates for example, $r \in[0, \infty]$, $\theta \in[0, \pi]$, and $\phi \in[0,2 \pi]$, however the power of this method allows us to pick and choose our boundary conditions [7]. In problems that can effectively be determined with the method of self-adjoint extensions, the equality typically reduces to a conglomeration of surface terms and integral terms such that

$$
0=\left.\left(F\left(x^{\mu}\right)+G\left(x^{\mu}\right)\right)\right|_{x_{1}^{\mu}} ^{x_{2}^{\mu}}+\int_{x_{1}^{\mu}}^{x_{2}^{\mu}} \mathrm{H}\left(\mathrm{x}^{\mu}\right) \mathrm{d} \Omega
$$

Note here $x^{\mu}$ is an expression for the characteristic coordinate system $F\left(x^{\mu}\right)$ and $G\left(x^{\mu}\right)$ can contain wave function components, derivatives, etc...

In order for an operator to be what we call formally self-adjoint, we need all terms to vanish except for the surface boundaries so that:

$$
\begin{equation*}
\text { Formal Self-Adjoincy: } \int_{x_{1}^{\mu}}^{x_{2}^{\mu}} \mathrm{H}\left(\mathrm{x}^{\mu}\right) \mathrm{d} \Omega=0 \tag{3.16}
\end{equation*}
$$

An operator is considered rigorously self-adjoint if both the integral and surface terms vanish.

$$
\begin{equation*}
\text { Rigorous Self-Adjoincy: }\left.\left(F\left(x^{\mu}\right)+G\left(x^{\mu}\right)\right)\right|_{x_{1}^{\mu}} ^{x_{2}^{\mu}}+\int_{x_{1}^{\mu}}^{x_{2}^{\mu}} \mathrm{H}\left(\mathrm{x}^{\mu}\right) \mathrm{d} \Omega=0 \tag{3.17}
\end{equation*}
$$

In the problems we have examined, the method of self-adjoint extensions requires us to formulate a family of boundary conditions to force rigorous self-adjoincy of the characteristic Hamiltonian. Of course it's always easier to view an example, so in the next sections I will derive two examples to show the general procedure used in the method of self-adjoint extensions: the canonical particle in a box and the 1 D relativistic particle.

### 3.4 Example 1: 1D Schrödinger Particle in a Box



Figure 3.3: Particle in a Box
The canonical particle in box describing an electron wave function confined within two infinite potential barriers [11].

To give a simple example, we can examine the particle in a box solutions using the method of selfadjoint extensions. This problem is very familiar to anyone who has studied some level of quantum mechanics, but we will see that self-adjoint extensions can give us unique results, allowing us to explore the possible solutions more fully. In our examination of self adjoint extensions, we first aim to identify the Hamiltonian and characteristic wave functions. The Hamiltonian and self-adjoint condition as given by (3.13) gives us the following wave function restrictions.

$$
\begin{gather*}
H=-\nabla^{2}  \tag{3.18}\\
\int_{a}^{b} \phi^{*}\left(-\nabla^{2} \psi\right) \mathrm{d} x=\int_{a}^{b}\left(-\nabla^{2} \phi^{*}\right) \psi \mathrm{d} x \tag{3.19}
\end{gather*}
$$

Using integration by parts, we see formal adjoincy is immediately satisfied and our self-adjoint condition reduces to a selection of surface terms.

$$
\begin{equation*}
\left.\left(\phi^{*} \nabla \psi-\psi \nabla \phi^{*}\right)\right|_{a} ^{b}=0 \tag{3.20}
\end{equation*}
$$

Of course, the particle in a box wave functions solutions are well-known to be sinusoidal terms.

$$
\begin{equation*}
\psi=A \sin (k x)+B \cos (k x) \tag{3.21}
\end{equation*}
$$

An examination of the self-adjoint condition found by formulating two possible wave functions and inserting them into the self-adjoint conditions gives us interesting results based on the boundary conditions. Let's say for ease of example we send the second boundary out to infinity (infinity large
box) so that we can ignore the behavior of the wave function near the edge. This allows to examine the single boundary condition (typically taken at the origin). This gives a somewhat simplified condition:

$$
\begin{equation*}
\phi^{*}(0) \nabla \psi(0)=\psi(0) \nabla \phi^{*}(0) \tag{3.22}
\end{equation*}
$$

Let's take a moment here to think about the power of this analysis. Typically, we are quick to discard certain solutions based our idea of what the boundary conditions are whether they are Neumann, Dirichlet, or Cauchy boundary conditions, we use them to restrict our analysis. This is certainly a reasonable analysis, but this restricts the conditions we can impose on the wave functions since we are fixing the self-adjoint condition based on a single boundary condition. However, the power of self-adjoint extensions allows us recognize an entire family of conditions. To see this, we formulate linear boundary relations such that:

$$
\begin{align*}
\phi & =\lambda \nabla \phi  \tag{3.23}\\
\psi & =l \nabla \psi \tag{3.24}
\end{align*}
$$

Interestingly enough, when we impose these boundary conditions on the wave functions, we find that the self-adjoint condition will be satisfied as long as $\lambda=l$ where $\lambda, l \in \Re$. This is pretty remarkable considering that normally we would have a single self-adjoint condition if using the canonical boundary condition analysis. However, with the method of self-adjoint extensions, we are able to formulate an entire family of conditions that lead to self-adjoint Hamiltonians. In practice, we could tune these self-adjoint parameter to match different wave function requirements near the origin. One last really interesting point is an examination of the momentum operator using self-adjoint extensions. I will leave it up to the reader if you choose to read the derivation (See Appendix 6.2), but essentially one can prove that the Schrödinger momentum operator is NOT self-adjoint since there is a lack of unique surface terms. It's interesting to think that self-adjoint extensions can so well described Hamiltonian conditions, yet the basic momentum operator is not rigorously self-adjoint. It shows the power of this method in describing quantum mechanical situations and physical observables. See Appendix 6.1 for a full discussion and derivation of the particle in a box problem.

### 3.5 Example 2: 1D Relativistic Dirac Free Particle



Figure 3.4: 1D Relativistic Particle
The canonical use of the Dirac equation is to model the behavior of a fermion moving near the speed of light

Now that we've warmed up our self-adjoint analysis muscles, we are able to examine an example that begins to take on the characteristics of the problem we intend to solve in graphene. When examining the self-adjoint conditions of Dirac Hamiltonians, we use the same analysis as with the particle in a box case, but our Hamiltonian and wave functions are now matrix operators. We define our Hamiltonian using a suitable choice of $\alpha$ and $\beta$ matrices as discussed in the methods section (equation 3.5-6) such that:

$$
H_{\text {dirac }}=\left(\begin{array}{cc}
0 & m-\nabla_{x}  \tag{3.25}\\
m+\nabla_{x} & 0
\end{array}\right)
$$

If we first like to examine the solutions, we find sinusoidal wave functions. Both spinor components contain the same basic functions such that:

$$
\begin{equation*}
\psi=\binom{a_{1} \sin \left(\sqrt{E^{2}-m^{2}} x\right)+a_{2} \cos \left(\sqrt{E^{2}-m^{2}} x\right)}{b_{1} \sin \left(\sqrt{E^{2}-m^{2}} x\right)+b_{2} \cos \left(\sqrt{E^{2}-m^{2}} x\right)} \tag{3.26}
\end{equation*}
$$

Which is exactly what we expect. The solution to this problem is basically the same as the particle in the box except we have two spinor components and the self-adjoint condition will be different as we shall see. The self-adjoint condition simplifies to surface terms encompassed by:

$$
\begin{equation*}
\left.\left(-\phi_{1}^{*} \psi_{2}+\phi_{2}^{*} \psi_{1}\right)\right|_{a} ^{b}=0 \tag{3.27}
\end{equation*}
$$

Where 1 and 2 denote the spinor component and $\phi$ and $\psi$ denote two distinct Eigen functions. Once again, ignoring the second boundary, setting the boundary $a$ at the origin and presuming linear boundary conditions such that:

$$
\begin{gather*}
\phi_{1}(a)=\lambda \phi_{2}(a)  \tag{3.28}\\
\psi_{1}(a)=l \psi_{2}(a) \tag{3.29}
\end{gather*}
$$

We find an entire family of boundary conditions such that $\lambda, l \in \Re$. The aim of this example was to introduce the reader to the procedure for analyzing self-adjoint conditions on Dirac operators, where we begin to see the use of differential matrix operators. These operators seem quite complicated, but in practice the self-adjoint condition necessarily reduces to an examination of surface boundary terms that we can eliminate by imposing linear wave function relations. For a full analysis and thorough discussion of the Dirac problem, see Appendix 6.3.

### 3.6 Self-Adjoint v. Hermitian Operator

Before moving on to the results, I would like to discuss a subtlety in our defintions of self-adjoint operators versus what is commonly referred to as Hermitian operators. In elementary quantum mechanics, one typically thinks of a Hermitian operator as one that is "equal to its own conjugate transpose", which is also known as the adjoint of an operator. However, this definition lacks depth because the difference between self-adjoint and Hermitian is more subtle. In our definition of self adjoint operators, we came up with two defintions: formally self-adjoint and rigorously self-adjoint (equations 3.16-17). A Hermitian operator is formally self-adjoint up to a set of surface terms. When we examined self-adjoint operators we asserted that a rigorously self-adjoint operator is one in which
the surface term vanish AND the boundary conditions on the Eigen functions are the same for both Eigen functions. However the elimination of the surface terms in a Hermitian operator does NOT require that the wave functions boundaries be the same. A fine example of a Hermitian operator that is not self-adjoint is the quantum mechanical momentum operator (see Appendix 6.2). In the self-adjoint extension analysis of momentum, we see that the surface terms will vanish as long as one of the wave functions vanish at the boundaries, not necessarily both.

## Chapter 4

## Objectives

The objectives for our research are all directed towards solving the graphene defect problems, however we studied a multitude of problems in order to work up to the full graphene analysis. Not all the objectives were directly relevant to studying graphene, but relevant to adapting tools needed to solve to defect problems. As such, I will list the problems we solved in working up to graphene problem, but only two will be presented in our results since they are most relevant to graphene. The others are presented in appendices.

1. Examine the method of self-adjoint extensions in the context of analyzing common quantum mechanical problem
(a) self-adjoint extensions of the 1D Schrödinger Hamiltonian (Appendix 6.1)
(b) self-adjoint extensions of the 1D Schrödinger momentum (Appendix 6.2)
(c) self-adjoint extensions of the 1D Dirac Hamiltonian (Appendix 6.3)
2. Examine the 2 dimensional radial problems
(a) self-adjoint extensions of the 2D radial Schrödinger Hamiltonian (Appendix 6.4)
(b) self-adjoint extensions of the 2D radial Dirac, 2 spinor Hamiltonian (Appendix 6.5)
3. Examination of the 2 dimensional radial problems with Coulombic impurities
(a) self-adjoint extensions of the 2D radial Schrödinger Coulombic Hamiltonian (Results 5.1, Appendix 6.6)
(b) self-adjoint extensions of the 2D radial Dirac, 2 spinor Coulombic Hamiltonain (Results 5.2, Appendix 6.7)

## Chapter 5

## Results

The goal of our project was to model defects in graphene including vacancies and Coulombic defects using the 2D Dirac equation and the method of self-adjoint extensions. We solved two distinct problems that prepare us for a full study of each type of the defects, namely the 2D, 2 spinor Dirac problem and the 2D, 2 spinor Dirac problem with a Coulombic impurity. I will discuss the results in two parts: the 2D, 2 spinor Dirac problem warming up to the vacancy problem and the $2 \mathrm{D}, 2$ spinor Dirac Coulombic problem warming up to the Coulombic defect problem.

### 5.1 2D, 2 Spinor Radial Dirac Problem

As a prelude, I want to mention I will give the abbreviated derivation in this section and highlight the main results. If the reader is interested in the full derivation and discussion, see Appendix 6.6.

To start our analysis, we want to identify the solution to the 2D radial Dirac equation. As would be expected for radial problems, the full solutions contain Bessel functions of the first and second kind, along with angular momentum channels in the form of phase factors. In practice, we set the angular momentum channel equal to 0 because we are interested in problems without angular spin. The solutions also depend on the energy range we are examining. We have two cases where $E>m$ and $E<m$ and our redefined independent variable is $s=\sqrt{E^{2}-m^{2}} r$. The full solutions were found to be either Bessel functions or modifies Bessel functions:
$E>m$

$$
\begin{equation*}
\psi=\binom{a_{0} J_{l}(s)+a_{1} Y_{l}(s)}{i a_{0} \sqrt{\frac{E-m}{E+m}} J_{l+1}(s)+i a_{1} \sqrt{\frac{E-m}{E+m}} Y_{l+1}(s)} \tag{5.1}
\end{equation*}
$$

Where J is the Bessel function of the first kind and Y is the Bessel function of the second kind.
In the limit of small $\mathrm{s}, l=0$

$$
\begin{equation*}
\psi=\binom{a_{0}\left(1-\frac{s^{2}}{4}\right)+a_{1}\left(\log \left(\frac{s}{2}\right)+\gamma\right)}{i \sqrt{\frac{E-m}{E+m}}\left(a_{0} \frac{s}{2}-a_{1}\left(\frac{2}{s}\right)\right) e^{i \theta}} \tag{5.2}
\end{equation*}
$$

$E<m$

$$
\begin{equation*}
\psi=\binom{a_{0} I_{l}(s)+a_{1} K_{l}(s)}{i a_{0} \sqrt{\frac{E-m}{E+m}} I_{l+1}(s)+i a_{1} \sqrt{\frac{E-m}{E+m}} K_{l+1}(s)} \tag{5.3}
\end{equation*}
$$

Where K is the modified Bessel function of the first kind and I is the modified Bessel function of the second kind.

In the limit of small s, $l=0$

$$
\begin{equation*}
\psi=\binom{a_{0}\left(1+\frac{s^{2}}{4}\right)-a_{1}\left(\log \left(\frac{s}{2}\right)+\gamma\right)}{i \sqrt{\frac{E-m}{E+m}}\left(a_{0} \frac{s}{2}+a_{1}\left(\frac{2}{s}\right)\right) e^{i \theta}} \tag{5.4}
\end{equation*}
$$

Before using the method of self-adjoint extensions, I want to note that both cases have functions of the same order, only differing in some coefficient signs. As such, the self-adjoint analysis will be the same for both cases, so I will only examine one case. Keeping the analysis general for now, we find the following equality must hold true for a self-adjoint Hamiltonian.

$$
\begin{equation*}
\left(\phi, H_{\text {dirac }} \psi\right)=\left(\phi, H_{\text {dirac }} \psi\right)+\left.s\left(\phi_{2}^{*} \psi_{1}-\phi_{2}^{*} \psi_{1}\right)\right|_{a} ^{b} \tag{5.5}
\end{equation*}
$$

We can formulate two Eigen functions to use in our self-adjoint analysis, $\phi$ and $\psi$ such that

$$
\begin{align*}
& \psi=\binom{\psi_{1}}{\psi_{2}}=\binom{a_{0}\left(1-\frac{s^{2}}{4}\right)+a_{1}\left(\log \left(\frac{s}{2}\right)+\gamma\right)}{i \sqrt{\frac{E-m}{E+m}}\left(a_{0} \frac{s}{2}-a_{1}\left(\frac{2}{s}\right)\right) e^{i \theta}}  \tag{5.6}\\
& \phi=\binom{\phi_{1}}{\phi_{2}}=\binom{c_{0}\left(1-\frac{s^{2}}{4}\right)+c_{1}\left(\log \left(\frac{s}{2}\right)+\gamma\right)}{i \sqrt{\frac{E-m}{E+m}}\left(c_{0} \frac{s}{2}-c_{1}\left(\frac{2}{s}\right)\right) e^{i \theta}} \tag{5.7}
\end{align*}
$$

Now, if we take a look at the solutions, we see that the most divergent term will be of order $\frac{1}{s}$. Unfortunately, this is a problem for our self-adjoint analysis. In order to properly analyze solutions with self-adjoint extensions, we need to ensure that normalization is possible. The basic definition for normalization requires that the probability kernel diverges less that $\frac{1}{r}$. Unfortunately, the full wave function we derived is not normalizable under these restrictions, so in order to force self-adjoincy of the Hamiltonian, we need to drop the components of the wave functions that diverge by applying specific boundary conditions so that diverging components vanish. While this may seem like this method in not fruitful in examining graphene defects, we are quite hopeful about solving the graphene problem because we are using the 2 spinor Dirac equation in order to gain the necessary tools to examine the full problem. Our next steps in solving the problem is to re-analyze the problem using the 4 component Dirac equation.

### 5.2 2D, 2 Spinor Radial Dirac Problem with a Coulombic Impurity

As a prelude, I want to mention I will give the abbreviated derivation in this section and highlight the main results. If the reader is interested in the full derivation and discussion, see Appendix 6.7.

When examining the Coulombic impurity problem, we have a similar equation as in the 2 D radial problem, but with a Coulombic potential. We take a similar formalism so that we have separable solutions with $r$ and $\theta$ components and phase factor angular momentum channels (we take to $l=0$ angular momentum channel). In addition, we are looking at bound states of the Hamiltonian so that $E<m$. With these in mind, we formulate the final wave function solution.

$$
\begin{equation*}
\psi=\binom{\frac{1}{\sqrt{\rho}} \sqrt{m+E} \rho^{\gamma}\left(a_{0} M\left(\gamma-\frac{\lambda E}{\sqrt{E^{2}-m^{2}}}, 1+2 \gamma ; \rho\right)+a_{1} U\left(\gamma-\frac{\lambda E}{\sqrt{E^{2}-m^{2}}}, 1+2 \gamma ; \rho\right)\right)}{-\frac{i}{\sqrt{\rho}} \sqrt{m-E} \rho^{\gamma}\left(b_{0} M\left(\gamma-\frac{\lambda E}{\sqrt{E^{2}-m^{2}}}, 1+2 \gamma ; \rho\right)+b_{1} U\left(\gamma-\frac{\lambda E}{\sqrt{E^{2}-m^{2}}}, 1+2 \gamma ; \rho\right)\right)} \tag{5.8}
\end{equation*}
$$

M refers to the confluent hypergeometric function of the 1st kind, U is the confluent hypergeometric function of the second kind. $\lambda$ is the charge impurity coefficient.

$$
\begin{equation*}
\gamma=\sqrt{\frac{1}{4}-\lambda^{2}} \tag{5.9}
\end{equation*}
$$

When examining the final solution, we see a formulation for the conditions needed for a self-adjoint Hamiltonian. Remember we require proper normalization so that the probability kernel diverges less than $\frac{1}{r}$. In order have proper normalization, we require the following:

$$
\begin{equation*}
\sqrt{\frac{1}{4}-\lambda^{2}}<\frac{1}{2} \tag{5.10}
\end{equation*}
$$

This requires that $\lambda>0$, which essentially requires that the Coulombic impurity have nonzero charge. This leads to three cases for the value of $\lambda$. Noting that

$$
\lambda=Z \frac{e^{2}}{4 \pi \epsilon_{0}} \frac{1}{\hbar c} \quad c=1.0 \times 10^{6} \mathrm{~m} / \mathrm{s} \text { in graphene }
$$

$$
\begin{equation*}
\lambda=\frac{300}{137} Z \tag{5.11}
\end{equation*}
$$

$\lambda=0$
Only the non-divergent solution is normalizable and self-adjoint extensions is invalid.
$0<\lambda<\frac{1}{2}$
This corresponds to the case where $0.23>Z>0$, which is not very physical since $Z$ is integer quantized for any Coulombic impurity. Mathematically, however, we can see both solutions are normalizable and self-adjoint extensions is needed to determine boundary conditions.
$\lambda \geq \frac{1}{2}$
This corresponds to the case $Z>0.23$, which describes all physical charge impurities since $Z>1$ for any non zero charge impurity. In this case the power exponent is imaginary, but both solutions are still normalizable and we must examine the self-adjoint condition to determine boundary conditions.

Performing our self-adjoint analysis, we found that self-adjoint extensions allows us to discover a family of boundary conditions only if $0<\lambda<\frac{1}{2}$. However this is not physical since Z must be an integer. Therefore, self-adjoint extensions does not work well to describe the 2D, 2 spinor Dirac Coulombic Hamiltonian problem. Unfortunately, this means the 2D, 2 spinor Dirac equations does not accurately model the graphene wave functions for integer charge impurities. However, we shouldn't
be discouraged since the full graphene problem requires the use of the 4 spinor component Dirac equation. We are hopeful that 4 spinor equivalent of the Dirac equation will give us conditions for self-adjoint Hamiltonian extensions that more closely resemble the experiment conditions. This problem is extremely helpful in formulating the tools we will need to solve the final 4 spinor Dirac equation with a Coulombic impurity.

## Chapter 6

## Conclusions

To summarize our research goals, we aimed to model electronic motion within graphene near vacancy and charge defects using the Dirac equation and the method of self-adjoint extensions. Our method included using the 2 dimensional, 2 spinor component Dirac equation as a simplified model for electronic motion. We found that self-adjoint extensions does not provide us with a family of boundary conditions in either physical case due normalization requirements and physical constraints. For the vacancy problem, our wave functions are not part of the Sobolev space for the regime near the origin. More specifically, the divergent component of the wave function is not even a member of $L^{2}$ norm space, which means it must be killed off with boundary terms (thereby making self-adjoint analysis unnecessary) [7]. For the charge defects, we found a regime where self-adjoint extensions is needed to examine the boundary terms, but this regime is unphysical since it corresponds to a charge quantization between 0 and 1 . The problem with the analysis is the "slow" speed of light in graphene, which increases the fine structure constant by a factor of $\sim 300$, increasing the effect of the charge quantization in determining the divergence of the wave functions. While our 2 spinor 2D analysis did not yield physical results, we are hopeful that the method of self-adjoint extensions may yet yield significant results if we examining the 4 spinor component wave function form of the Dirac equation in graphene. It's encouraging that there is still some range of $Z$ values that allow for self-adjoint extensions in the 2 spinor component problem and we are hopeful the 4 spinor component will yield a greater range for self-adjoint analysis. Interestingly enough, the 4 spinor component is a more realistic description of the graphene fermions. When we look at the energy band of graphene, we saw the existence of 6 Dirac points, but only 2 of those points were independent. This implies that we are required to use the four component spinor form of the Dirac equation for graphene. In the next steps of our research, we aim to continue our analysis of defects in graphene using the tools we learned from the 2 spinor Dirac case to examine the problem using the 4 component Dirac form.

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## Appendices

"SAE" = self-adjoint extensions

### 6.1 SAE for 1D Schrödinger Hamiltonian

To begin a self-adjoint analysis for the 1D Shrödinger problem, we first need to identify the Hamiltonian and the conditions for self-adjoincy. In 1 dimension, the Hamiltonian is simply given by:

$$
\begin{equation*}
H=-\nabla^{2}=-\frac{d^{2}}{d x^{2}} \tag{6.1}
\end{equation*}
$$

Whose solutions are found by examining the equality $-\nabla^{2} \psi=E \psi=k^{2} \psi$. Clearly the solutions are of the form:

$$
\begin{gather*}
\psi=A \sin (k x)+B \cos (k x) \text { for positive energy unbound states }  \tag{6.2}\\
\psi=A e^{-k x}+B e^{+k x} \text { for negative energy bound states } \tag{6.3}
\end{gather*}
$$

Examining the condition for self-adjoint extensions, we see the following equality must hold true:

$$
\begin{align*}
\left(\phi, \nabla^{2} \psi\right) & =\left(\nabla^{2} \phi, \psi\right)  \tag{6.4}\\
\int_{a}^{b} \phi^{*}\left(\nabla^{2} \psi\right) \mathrm{d} x & =\int_{a}^{b}\left(\nabla^{2} \phi^{*}\right) \psi \mathrm{d} x \tag{6.5}
\end{align*}
$$

Using integration by parts, we see the expression simplifies to surface terms, proving formaladjoincy of the 1D Schrödinger Hamiltonian.

$$
\begin{gather*}
\left.\phi^{*} \nabla \psi\right|_{a} ^{b}-\int_{a}^{b} \nabla \phi^{*} \nabla \psi \mathrm{~d} x=\left.\psi \nabla \phi^{*}\right|_{a} ^{b}-\int_{a}^{b} \nabla \phi^{*} \nabla \psi \mathrm{~d} x  \tag{6.6}\\
\left.\left(\phi^{*} \nabla \psi-\psi \nabla \phi^{*}\right)\right|_{a} ^{b}=0 \tag{6.7}
\end{gather*}
$$

The utility of self-adjoint extensions allows us to achieve self-adjoincy of the Hamiltonian by choosing boundary conditions. For example, we could choose any range of boundary conditions listed below. For ease of example, lets take the second boundary go to infinity, where the wave functions needs to vanish, so we can examine the effect of a single boundary condition.

## Neumann Boundary Conditions

Neumann boundary condition requires we define the derivative at the boundary. For a self-adjoint Hamiltonian, we expect the condition imposed on $\psi$ must be the same as the condition imposed on $\phi$

$$
\begin{gather*}
\nabla \psi(a)=\alpha, \nabla \phi(a)=\beta  \tag{6.8}\\
\phi^{*}(a) \alpha=\psi(a) \beta^{*} \tag{6.9}
\end{gather*}
$$

The wave functions and their derivatives for positive energy, propagating particle was found to be:

$$
\begin{align*}
\psi & =a_{1} \sin (k x)+a_{2} \cos (k x)  \tag{6.10}\\
\phi & =b_{1} \sin (k x)+b_{2} \cos (k x)  \tag{6.11}\\
\nabla \psi & =a_{1} k \cos (k x)-a_{2} k \sin (k x)  \tag{6.12}\\
\nabla \phi & =b_{1} k \cos (k x)-b_{2} k \sin (k x) \tag{6.13}
\end{align*}
$$

for $a=0$, examining boundary conditions at the origin.

$$
\begin{gather*}
\psi=a_{2}  \tag{6.14}\\
\phi=b_{2}  \tag{6.15}\\
\nabla \psi=a_{1} k=\alpha  \tag{6.16}\\
\nabla \phi=b_{1} k=\beta \tag{6.17}
\end{gather*}
$$

The self-adjoint condition gives us restrictions on the above wave function coefficients through $a_{2} \alpha=b_{2} \beta^{*}$ so that $a_{2} a_{1}=b_{2} b_{1}$. We know that according to normalization the coefficient terms must be equal and so $\alpha$ must equal $\beta$ and real for the Hamiltonian to be self-adjoint. The canonical situation is where we define $\alpha=\beta=0$. This immediately shows that if we restrict $\nabla \psi(0)=0$, then $\nabla \phi^{*}(0)=0$ must be true, immediately leading to self-adjoint extensions forced through boundary conditions.

## Dirichlet Boundary Conditions

Dirichlet boundary condition requires we define the wave function the boundary. For a selfadjoint Hamiltonian, we expect the condition imposed on $\psi$ must be the same as the condition imposed on $\phi$

$$
\begin{gather*}
\psi(a)=\alpha, \phi(a)=\beta  \tag{6.18}\\
\nabla \phi(a) \alpha=\nabla \psi(a) \beta \tag{6.19}
\end{gather*}
$$

The wave functions and their derivatives for positive energy, propagating particle was found to be:

$$
\begin{align*}
\psi & =a_{1} \sin (k x)+a_{2} \cos (k x)  \tag{6.20}\\
\phi & =b_{1} \sin (k x)+b_{2} \cos (k x)  \tag{6.21}\\
\nabla \psi & =a_{1} k \cos (k x)-a_{2} k \sin (k x)  \tag{6.22}\\
\nabla \phi & =b_{1} k \cos (k x)-b_{2} k \sin (k x) \tag{6.23}
\end{align*}
$$

for $\mathrm{a}=0$, examining boundary conditions at the origin.

$$
\begin{gather*}
\psi=a_{2}=\alpha  \tag{6.24}\\
\phi=b_{2}=\beta  \tag{6.25}\\
\nabla \psi=a_{1} k  \tag{6.26}\\
\nabla \phi=b_{1} k \tag{6.27}
\end{gather*}
$$

The self-adjoint condition gives us restrictions on the above wave function coefficients through $a_{1} \alpha=b_{1} \beta^{*}$ so that $a_{2} a_{1}=b_{2} b_{1}$. We know that according to normalization the coefficient terms must be equal and so $\alpha$ must equal $\beta$ and real for the Hamiltonian to be self-adjoint. The canonical situation is where we define $\alpha=\beta=0$. This immediately shows that if we restrict $\psi(0)=0$, then $\phi^{*}(0)=0$ must be true, immediately leading to self-adjoint extensions forced through boundary conditions.

## Linear Boundary Conditions

A more common and more general approach to finding a family of self-adjoint extensions is to propose a linear relation between wave functions and their derivatives. We postulate (again at the given boundary condition) that:

$$
\begin{equation*}
\psi(a)=\lambda \nabla \psi(a) \text { and } \phi(a)=l \nabla \phi(a) \tag{6.28}
\end{equation*}
$$

The self-adjoint condition now becomes:

$$
\begin{align*}
\phi^{*}(a) \nabla \psi(a) & =\psi(a) \nabla \phi^{*}(a)  \tag{6.29}\\
\phi^{*}(a) \lambda \psi(a) & =\psi(a) l^{*} \phi^{*}(a) \tag{6.30}
\end{align*}
$$

Remember the goal of self-adjoint extensions is to find boundary conditions that require the same constraint for each wave function. Well, clearly as long as $\lambda=l^{*}$ then this condition will be met. That means for this choice of boundary conditions, we find an entire family of self-adjoint extensions such that $\lambda, l \in \Re$. The method of self-adjoint extensions is an extremely powerful tool that can uncover a wealth of information about even simple examples such as this 1D Schrödinger equation that is otherwise unavailable with a simple boundary condition analysis.

### 6.2 SAE for 1D Schrödinger Momentum

The method of self-adjoint extensions can be applied to any give operator and it's an interesting exercise to go through the mechanics of the self-adjoint extensions on momentum operator given as $\hat{p}=-i \hbar \nabla_{x}$ in one dimension (denoted as x ). Exacting the conditions of self-adjoint extensions on momentum, we see the following condition emerges:

$$
\begin{gather*}
(\phi, \hat{p} \psi)=(\hat{p} \phi, \psi)  \tag{6.31}\\
-i \hbar \int_{a}^{b} \phi^{*}(\nabla \psi) \mathrm{d} x=i \hbar \int_{a}^{b}\left(\nabla \phi^{*}\right) \psi \mathrm{d} x  \tag{6.32}\\
\left.\phi^{*} \psi\right|_{a} ^{b}-\int_{a}^{b} \nabla \phi^{*} \psi \mathrm{~d} x=-\int_{a}^{b}\left(\nabla \phi^{*}\right) \psi \mathrm{d} x  \tag{6.33}\\
\phi^{*}(a) \psi(a)=0 \tag{6.34}
\end{gather*}
$$

According to the above condition, the momentum operator will be self-adjoint if either the $\phi(a)$ or $\psi(a)$ are 0 , but this is problem because it requires no constraints on the complementary wave function. Imagine we set $\phi(a)=0$, the condition will be met regardless of the behavior of $\psi(a)$. But this is not consistent with a self-adjoint operator. In order for it to be self adjoint, we require both wave functions to have the same condition imposed on them, so momentum in the 1D Schrödinger problem is not a self-adjoint operator! This is an excellent example of the utility of self-adjoint extensions in determining the physical operators in quantum mechanics. Clearly momentum is not consistent with physical observables, however, the energy spectrum (as was shown in Appendix 6.1) is completely physical under a certain family of boundary conditions.

### 6.3 SAE for 1D Dirac Free Particle Hamiltonian

An examination of the self-adjoint extensions of the Dirac Hamiltonian is more complex due to the existence of 2 spinor components, but it is instructive to go through the derivation of a 1 D relativistic particle. The Hamiltonian for a 1D Dirac is found taking a suitable choice of matrices in the Dirac equation given in 1D and 2D as:

$$
\begin{equation*}
(\vec{\alpha} \cdot \hat{p}+\beta m) \psi=E \psi \tag{6.35}
\end{equation*}
$$

Before I define the choice of matrices, I want to mention that we have a number of suitable choices for $\alpha$ and $\beta$ matrices. As I mentioned earlier in this paper, the available matrices in 1 dimension are the Pauli spin matrices, but that leaves 3 possible matrices for the two we require. Each choice of matrices will lead to slightly different self-adjoint conditions, but they yield the same wave functions and are in effect only rotation representations of each other. I will go through the derivation with a few different choices in matrices to illustrate this.

## Choice 1

$$
\begin{gather*}
\alpha_{1}=\left(\begin{array}{cc}
0 & -i \\
i & 0
\end{array}\right), \beta=\left(\begin{array}{ll}
0 & 1 \\
1 & 0
\end{array}\right)  \tag{6.36}\\
H_{d i r a c}=\left(\begin{array}{cc}
0 & m-\nabla_{x} \\
m+\nabla_{x} & 0
\end{array}\right) \tag{6.37}
\end{gather*}
$$

First, solving the Eigen vector problem, we can find the spinor component solutions quite easily.

$$
\begin{gather*}
\Psi=\binom{\eta(x)}{\xi(x)}  \tag{6.38}\\
\left(m-\nabla_{x}\right) \xi(x)=E \eta(x)  \tag{6.39}\\
\left(m+\nabla_{x}\right) \eta(x)=E \xi(x) \tag{6.40}
\end{gather*}
$$

Which lead to nice decoupled second order differential equations for $\xi$ and $\eta$.

$$
\begin{align*}
& -\nabla_{x}^{2} \xi=\left(E^{2}-m^{2}\right) \xi  \tag{6.41}\\
& -\nabla_{x}^{2} \eta=\left(E^{2}-m^{2}\right) \eta \tag{6.42}
\end{align*}
$$

Which has the expected solutions for a 1D particle:

$$
\begin{align*}
& \xi=a_{1} \sin \left(\sqrt{E^{2}-m^{2}} x\right)+a_{2} \cos \left(\sqrt{E^{2}-m^{2}} x\right)  \tag{6.43}\\
& \eta=b_{1} \sin \left(\sqrt{E^{2}-m^{2}} x\right)+b_{2} \cos \left(\sqrt{E^{2}-m^{2}} x\right) \tag{6.44}
\end{align*}
$$

The coefficients in the spinor components are indeed dependent since their solutions originate from coupled differential equations. We can find some relations by examining the original coupled equations. Equations 6.39-40 give:

$$
\begin{gather*}
\left(m-\nabla_{x}\right)\left(a_{1} \sin \left(\sqrt{E^{2}-m^{2}} x\right)+a_{2} \cos \left(\sqrt{E^{2}-m^{2}} x\right)\right)=  \tag{6.45}\\
E\left(b_{1} \sin \left(\sqrt{E^{2}-m^{2}} x\right)+b_{2} \cos \left(\sqrt{E^{2}-m^{2}} x\right)\right)  \tag{6.46}\\
m a_{1}+a_{2} \sqrt{E^{2}-m^{2}}=E b_{1}  \tag{6.47}\\
m a_{2}-a_{1} \sqrt{E^{2}-m^{2}}=E b_{2} \tag{6.48}
\end{gather*}
$$

And the second coupled differential equation gives us:

$$
\begin{gather*}
\left(m+\nabla_{x}\right)\left(b_{1} \sin \left(\sqrt{E^{2}-m^{2}} x\right)+b_{2} \cos \left(\sqrt{E^{2}-m^{2}} x\right)\right)=  \tag{6.50}\\
E\left(a_{1} \sin \left(\sqrt{E^{2}-m^{2}} x\right)+a_{2} \cos \left(\sqrt{E^{2}-m^{2}} x\right)\right)  \tag{6.51}\\
m b_{1}-b_{2} \sqrt{E^{2}-m^{2}}=E a_{1}  \tag{6.52}\\
m b_{2}+b_{1} \sqrt{E^{2}-m^{2}}=E a_{2} \tag{6.53}
\end{gather*}
$$

If we guess an Ansatz for the constants $a_{1}=b_{1}=1$ (which is not normalized, but chosen for ease of calculations), we can easily find $a_{2}$ and $b_{2}$. In fact, right from the above equations, we can see that $a_{2}=\frac{E-m}{\sqrt{\left(E^{2}-m^{2}\right)}}$ and $b_{2}=\frac{m-E}{\sqrt{\left(E^{2}-m^{2}\right)}}$. Clearly, it's easy to pick out some consistent relation between Eigen function components, however, we need to examine the self-adjoint conditions on the spinor components to find the entire family of allowed boundary conditions. We perform a self-adjoint analysis using the familiar method.

$$
\begin{equation*}
\left(\phi, H_{\text {dirac }} \psi\right)=\left(H_{\text {dirac }} \phi, \psi\right) \tag{6.54}
\end{equation*}
$$

Here, we define two wave functions:

$$
\begin{gather*}
\phi=\binom{\phi_{1}(x)}{\phi_{2}(x)}, \psi=\binom{\psi_{1}(x)}{\psi_{2}(x)}  \tag{6.55}\\
\int_{a}^{b}\left(\phi_{1}^{*}, \quad \phi_{2}^{*}\right)\binom{\left(m-\nabla_{x}\right) \psi_{2}}{\left(m+\nabla_{x}\right) \psi_{1}} \mathrm{~d} x=\int_{a}^{b}\left(\left(m-\nabla_{x}\right) \phi_{2}^{*} \quad\left(m+\nabla_{x}\right) \phi_{1}^{*}\right)\binom{\psi_{1},}{\psi_{2}} \mathrm{~d} x  \tag{6.56}\\
\int_{a}^{b}\left(\phi_{1}^{*}\left(\mathrm{~m}-\nabla_{\mathrm{x}}\right) \psi_{2}+\phi_{2}^{*}\left(\mathrm{~m}+\nabla_{\mathrm{x}}\right) \psi_{1}\right) \mathrm{d} x=  \tag{6.57}\\
\int_{a}^{b}\left(\left(\mathrm{~m}-\nabla_{\mathrm{x}}\right) \phi_{2}^{*} \psi_{1}+\left(\mathrm{m}+\nabla_{\mathrm{x}}\right) \phi_{1}^{*} \psi_{2}\right) \mathrm{d} x \tag{6.58}
\end{gather*}
$$

Eliminating the similar terms, the integrals simplify:

$$
\begin{align*}
& \int_{a}^{b}\left(-\phi_{1}^{*} \nabla_{\mathrm{x}} \psi_{2}+\phi_{2}^{*} \nabla_{\mathrm{x}} \psi_{1}\right) \mathrm{d} x=  \tag{6.59}\\
& \int_{a}^{b}\left(-\nabla_{\mathrm{x}} \phi_{2}^{*} \psi_{1}+\nabla_{\mathrm{x}} \phi_{1}^{*} \psi_{2}\right) \mathrm{d} x \tag{6.60}
\end{align*}
$$

Using integration by parts to examine the surface terms, we see the Hamiltonian is formally self-adjoint.

$$
\begin{gather*}
\left.\left(-\phi_{1}^{*} \psi_{2}+\phi_{2}^{*} \psi_{1}\right)\right|_{a} ^{b}-\int_{a}^{b}\left(-\nabla_{\mathrm{x}} \phi_{1}^{*} \psi_{2}+\nabla_{\mathrm{x}} \phi_{2}^{*} \psi_{1}\right) \mathrm{d} x=  \tag{6.61}\\
\int_{a}^{b}\left(-\nabla_{\mathrm{x}} \phi_{2}^{*} \psi_{1}+\nabla_{\mathrm{x}} \phi_{1}^{*} \psi_{2}\right) \mathrm{d} x  \tag{6.62}\\
\left.\left(-\phi_{1}^{*} \psi_{2}+\phi_{2}^{*} \psi_{1}\right)\right|_{a} ^{b}=0 \tag{6.63}
\end{gather*}
$$

To fulfill the self-adjoint conditions, I first make the simplifying choice to send the upper bound to infinity and note that the wave function disappears at infinity. Therefore, we are only concerned with boundary conditions at the lower bound. I define linear relations between the spinor components such that:

$$
\begin{gather*}
\phi_{1}(a)=\lambda \phi_{2}(a)  \tag{6.64}\\
\psi_{1}(a)=l \psi_{2}(a)  \tag{6.65}\\
\lambda^{*} \phi_{2}^{*}(a) \psi_{2}(a)=\phi_{2}^{*}(a) l \psi_{2}(a) \tag{6.66}
\end{gather*}
$$

Therefore, the self-adjoint condition will hold true as long as $\lambda^{*}=l$, which requires that $\lambda, l \in \Re$. This gives us a family of self-adjoint conditions between the wave function components.

## Case 2

For the second case, I will choose the following matrices:

$$
\begin{gather*}
\alpha_{1}=\left(\begin{array}{cc}
1 & 0 \\
0 & -1
\end{array}\right), \beta=\left(\begin{array}{ll}
0 & 1 \\
1 & 0
\end{array}\right)  \tag{6.67}\\
H_{\text {dirac }}=\left(\begin{array}{cc}
-i \nabla_{x} & m \\
m & i \nabla_{x}
\end{array}\right) \tag{6.68}
\end{gather*}
$$

The choice of matrices does not change the inherent physics in the problem, but we can easily solve the Eigen vector problem again.

$$
\begin{gather*}
\Psi=\binom{\eta(x)}{\xi(x)}  \tag{6.69}\\
-i \nabla_{x} \eta(x)+m \xi(x)=E \eta(x)  \tag{6.70}\\
m \eta(x)+i \nabla_{x} \xi(x)=E \xi(x) \tag{6.71}
\end{gather*}
$$

Which lead to nice decoupled second order differential equations for $\xi$ and $\eta$.

$$
\begin{align*}
& -\nabla_{x}^{2} \xi=\left(E^{2}-m^{2}\right) \xi  \tag{6.72}\\
& -\nabla_{x}^{2} \eta=\left(E^{2}-m^{2}\right) \eta \tag{6.73}
\end{align*}
$$

Which of course has the same solution as case 1 .

$$
\begin{align*}
& \xi=a_{1} \sin \left(\sqrt{E^{2}-m^{2}} x\right)+a_{2} \cos \left(\sqrt{E^{2}-m^{2}} x\right)  \tag{6.74}\\
& \eta=b_{1} \sin \left(\sqrt{E^{2}-m^{2}} x\right)+b_{2} \cos \left(\sqrt{E^{2}-m^{2}} x\right) \tag{6.75}
\end{align*}
$$

Now, we can perform a similar self-adjoint analysis on the second case Dirac Hamiltonian.

$$
\begin{equation*}
\left(\phi, H_{\text {dirac }} \psi\right)=\left(H_{\text {dirac }} \phi, \psi\right) \tag{6.76}
\end{equation*}
$$

Here, we define two wave functions:

$$
\begin{gather*}
\phi=\binom{\phi_{1}(x)}{\phi_{2}(x)}, \psi=\binom{\psi_{1}(x)}{\psi_{2}(x)}  \tag{6.77}\\
\int_{a}^{b}\left(\phi_{1}^{*}, \quad \phi_{2}^{*}\right)\binom{-i \nabla_{x} \psi_{1}+m \psi_{2}}{m \psi_{1}+i \nabla_{x} \psi_{2}} \mathrm{~d} x= \\
\int_{a}^{b}\left(i \nabla_{x} \phi_{1}^{*}+m \phi_{2}^{*}, \quad m \phi_{1}^{*}-i \nabla_{x} \phi_{2}^{*}\right)\binom{\psi_{1},}{\psi_{2}} \mathrm{~d} x  \tag{6.78}\\
\int_{a}^{b}\left(\phi_{1}^{*}\left(-\mathrm{i} \nabla_{\mathrm{x}}^{*} \psi_{1}\right)+\mathrm{m} \phi_{1}^{*} \psi_{2}+\phi_{2}^{*}\left(\mathrm{~m} \psi_{1}+\mathrm{i} \nabla_{\mathrm{x}} \psi_{2}\right)\right) \mathrm{d} x=  \tag{6.79}\\
\int_{a}^{b}\left(\mathrm{i} \nabla_{\mathrm{x}} \phi_{1}^{*}+\mathrm{m} \phi_{2}^{*}\right) \psi_{1}+\left(\mathrm{m} \phi_{1}^{*}-\mathrm{i} \nabla_{\mathrm{x}} \phi_{2}^{*}\right) \psi_{2} \mathrm{~d} x \tag{6.80}
\end{gather*}
$$

Eliminating the similar terms, the integrals simplify:

$$
\begin{gather*}
\int_{a}^{b}\left(-\mathrm{i} \phi_{1}^{*} \nabla_{\mathrm{x}} \psi_{1}+\mathrm{i} \phi_{2}^{*} \nabla_{\mathrm{x}} \psi_{2}\right) \mathrm{d} x=  \tag{6.81}\\
\int_{a}^{b}\left(\mathrm{i} \nabla_{\mathrm{x}} \phi_{1}^{*} \psi_{1}-\mathrm{i} \nabla_{\mathrm{x}} \phi_{2}^{*} \psi_{2}\right) \mathrm{d} x \tag{6.82}
\end{gather*}
$$

Using integration by parts to examine the surface terms, we see the Hamiltonian is formally self-adjoint.

$$
\begin{gather*}
\int_{a}^{b}\left(\nabla_{\mathrm{x}}\left(\phi_{1}^{*} \psi_{1}-\phi_{2}^{*} \psi_{2}\right) \mathrm{d} x=\right.  \tag{6.83}\\
\left.\left(\phi_{1}^{*} \psi_{1}-\phi_{2}^{*} \psi_{2}\right)\right|_{a} ^{b}=0 \tag{6.84}
\end{gather*}
$$

To fulfill the self-adjoint conditions, I first make the simplifying choice to send the upper bound to infinity and note that the wave function disappears at infinity. Therefore, we are only concerned with boundary conditions at the lower bound. I define linear relations between the spinor components such that:

$$
\begin{gather*}
\phi_{1}(a)=\lambda \phi_{2}(a)  \tag{6.85}\\
\psi_{1}(a)=l \psi_{2}(a)  \tag{6.86}\\
\lambda^{*} l \phi_{2}^{*}(a) \psi_{2}(a)=\phi_{2}^{*}(a) \psi_{2}(a)  \tag{6.87}\\
\lambda^{*} l=1 \tag{6.88}
\end{gather*}
$$

We can see from the self-adjoint conditions that $\lambda$ and $l$ must mutually cancel to one, but in order for self-adjoint, $\lambda=l$. From this, we can guess that $\lambda$ and $l$ must be of the form $\lambda=l=e^{i n \theta}$ for some arbitrary number $n \in \Re$.

### 6.4 SAE for 2D Radial Schrödinger Hamiltonian

An example that more closely resembles the vacancy problem is that of the 2 dimensional Schrödinger problem. We start by formulating the Hamiltonian in radial coordinates:

$$
\begin{gather*}
-\nabla^{2} \psi=E \psi  \tag{6.89}\\
-\left(\frac{1}{r} \frac{\partial}{\partial r}\left(r \frac{\partial \psi}{\partial r}\right)+\frac{1}{r^{2}} \frac{\partial^{2} \psi}{\partial \theta^{2}}\right)=E \psi  \tag{6.90}\\
-\frac{\partial^{2} \psi}{\partial r^{2}}-\frac{1}{r} \frac{\partial \psi}{\partial r}-\frac{1}{r^{2}} \frac{\partial^{2} \psi}{\partial \theta^{2}}=E \psi \tag{6.91}
\end{gather*}
$$

We postulate separation of variables, specifically so that $\psi=f(r) e^{i l \theta}$.

$$
\begin{gather*}
-\frac{\partial^{2} f}{\partial r^{2}}-\frac{1}{r} \frac{\partial f}{\partial r}+\frac{l^{2} f}{r^{2}}=E \psi  \tag{6.92}\\
\frac{\partial^{2} f}{\partial r^{2}}+\frac{1}{r} \frac{\partial f}{\partial r}+E f-\frac{\left(l^{2}\right) f}{r^{2}}=0 \tag{6.93}
\end{gather*}
$$

Making the change of variable to $E=k^{2}$ and $s=k r$ so that the differential equation becomes the Bessel equation.

$$
\begin{equation*}
\frac{\partial^{2} f}{\partial s^{2}}+\frac{1}{s} \frac{\partial f}{\partial s}+f-\frac{\left(l^{2}\right) f}{s^{2}}=0 \tag{6.94}
\end{equation*}
$$

Whose solutions are Bessel functions of the first and second kind. Taking the $l=0$ channel, since we expect physical situations to have no overall momentum.

$$
\begin{gather*}
\psi(r, \theta)=\left(a_{0} J_{l}(s)+b_{0} Y_{l}(s)\right) e^{i l \theta}  \tag{6.95}\\
\psi(r, \theta)=\left(a_{0} J_{0}(s)+b_{0} Y_{0}(s)\right) \tag{6.96}
\end{gather*}
$$

Now that we have the analytic solution for the wave functions, we can start our self adjoint analysis.

$$
\begin{equation*}
\int_{a}^{b} \phi^{*}\left(\frac{1}{\mathrm{r}} \frac{\partial}{\partial \mathrm{r}}\left(\mathrm{r} \frac{\partial \psi}{\partial \mathrm{r}}\right)+\frac{1}{\mathrm{r}^{2}} \frac{\partial^{2} \psi}{\partial \theta^{2}}\right) \mathrm{rd} r=\int_{a}^{b}\left(\frac{1}{\mathrm{r}} \frac{\partial}{\partial \mathrm{r}}\left(\mathrm{r} \frac{\partial \phi^{*}}{\partial \mathrm{r}}\right)+\frac{1}{\mathrm{r}^{2}} \frac{\partial^{2} \phi^{*}}{\partial \theta^{2}}\right) \psi \mathrm{r} \mathrm{~d} r \tag{6.97}
\end{equation*}
$$

Of course since we are dealing with the $l=0$ channel, the angular terms vanish. In addition, I ignored the angular part of the integral since the only effect it has is to introduce a $2 \pi$ constant, which can be omitted.

$$
\begin{gather*}
\int_{a}^{b} \phi^{*} \frac{1}{\mathrm{r}} \frac{\partial}{\partial \mathrm{r}}\left(\mathrm{r} \frac{\partial \psi}{\partial \mathrm{r}}\right) \mathrm{rd} r=\int_{a}^{b} \frac{1}{\mathrm{r}} \frac{\partial}{\partial \mathrm{r}}\left(\mathrm{r} \frac{\partial \phi^{*}}{\partial \mathrm{r}}\right) \psi \mathrm{r} \mathrm{~d} r  \tag{6.98}\\
\int_{a}^{b} \phi^{*} \frac{\partial}{\partial \mathrm{r}}\left(\mathrm{r} \frac{\partial \psi}{\partial \mathrm{r}}\right) \mathrm{d} r=\int_{a}^{b} \frac{\partial}{\partial \mathrm{r}}\left(\mathrm{r} \frac{\partial \phi^{*}}{\partial \mathrm{r}}\right) \psi \mathrm{d} r \tag{6.99}
\end{gather*}
$$

Using integration by parts, we see the expressions simplifies to surface terms, proving formaladjoincy of the 1D Schrödinger Hamiltonian.

$$
\begin{equation*}
\left.\left(\phi^{*} r \frac{\partial \psi}{\partial r}-\psi r \frac{\partial \phi^{*}}{\partial r}\right)\right|_{a} ^{b}=0 \tag{6.100}
\end{equation*}
$$

Postulating two possible wave functions to examine self-adjoint extensions:

$$
\begin{align*}
\psi(r, \theta) & =\left(a_{0} J_{0}(s)+b_{0} Y_{0}(s)\right)  \tag{6.101}\\
\phi(r, \theta) & =\left(c_{0} J_{0}(s)+d_{0} Y_{0}(s)\right) \tag{6.102}
\end{align*}
$$

Again, we are sending the second boundary to infinity and ignoring the upper bound terms. Our first boundary is going to be examined near the origin (since our physical impurities are at the origin). The small r limit wave functions are given and are inserted into the self-adjoint conditions:

$$
\begin{align*}
& \psi(r, \theta)=\left(a_{0}\left(1-\frac{s^{2}}{4}\right)+b_{0}\left(\gamma+\log \frac{s}{2}\right)\right)  \tag{6.104}\\
& \phi(r, \theta)=\left(c_{0}\left(1-\frac{s^{2}}{4}\right)+d_{0}\left(\gamma+\log \frac{s}{2}\right)\right) \tag{6.105}
\end{align*}
$$

Notice in the low $s$ limit (remember also s is synonymous with r multiplied by some constant), each term contains some constant factor ( $\gamma$ is the Euler-Mascheroni constant), so we can actually group $b_{0} \gamma$ into $a_{0}$ and $d_{0} \gamma$ into $c_{0}$. When we insert this form of the wave functions into the self-adjoint condition, we find the expressions reduces to the following:

$$
\begin{equation*}
0=d_{0} a_{0}^{*}-b_{0}^{*} c_{0}+\text { terms that vanish as s goes to } 0 \tag{6.107}
\end{equation*}
$$

Therefore, when we take the lower bound goes to zero, our self-adjoint condition becomes:

$$
\begin{equation*}
0=d_{0} a_{0}^{*}-b_{0}^{*} c_{0} \tag{6.108}
\end{equation*}
$$

Asserting the linear boundary conditions we have used previously we find the final self-adjoint
condition.

$$
\begin{gather*}
a_{0}=\lambda b_{0}  \tag{6.110}\\
c_{0}=l d_{0}  \tag{6.111}\\
d_{0} b_{0}^{*} \lambda^{*}=b_{0}^{*} d_{0} l  \tag{6.112}\\
\lambda^{*}=l \tag{6.113}
\end{gather*}
$$

Now, we have found the entire family of self-adjoint extensions to the 2D Schrödinger radial Hamiltonian. Namely, the wave functions will allow self-adjoint Hamiltonian as long as $\lambda, l \in \Re$.

### 6.5 SAE for 2D Radial Schrödinger Coulombic Hamiltonian

An example that more closely resembles the Coulombic defect problem is that of the 2 dimensional Schrödinger problem. We start by formulating the Hamiltonian in radial coordinates:

$$
\begin{gather*}
-\nabla^{2} \psi+V(r) \psi=E \psi  \tag{6.114}\\
-\left(\frac{1}{r} \frac{\partial}{\partial r}\left(r \frac{\partial \psi}{\partial r}\right)+\frac{1}{r^{2}} \frac{\partial^{2} \psi}{\partial \theta^{2}}\right)-\frac{\alpha}{r} \psi=E \psi  \tag{6.115}\\
-\frac{\partial^{2} \psi}{\partial r^{2}}-\frac{1}{r} \frac{\partial \psi}{\partial r}-\frac{1}{r^{2}} \frac{\partial^{2} \psi}{\partial \theta^{2}}-\frac{\alpha}{r} \psi=E \psi \tag{6.116}
\end{gather*}
$$

We postulate separation of variables, specifically so that $\psi=f(r) e^{i l \theta}$.

$$
\begin{gather*}
-\frac{\partial^{2} f}{\partial r^{2}}-\frac{1}{r} \frac{\partial f}{\partial r}+\frac{l^{2} f}{r^{2}}-\frac{\alpha}{r} \psi=E \psi  \tag{6.117}\\
\frac{\partial^{2} f}{\partial r^{2}}+\frac{1}{r} \frac{\partial f}{\partial r}+E f-\frac{\left(l^{2}\right) f}{r^{2}}-\frac{\alpha}{r} f=0 \tag{6.118}
\end{gather*}
$$

First, guessing an Ansatz of $f(r)=e^{-\gamma r} \eta(r)$, we can plug this into our previous expression and determine the equation for $\eta$. We also want to note that we are concerned with bound particles, meaning the energy is less than zero (which leads to the exponential decay Ansatz else, it would be a plane wave for unbound states. This is supposed to give a similar example to the bound vacancies we studied). With our bound state energy notation, the equation becomes:

$$
\begin{gather*}
\eta(r)^{\prime \prime}+\eta(r)^{\prime}\left(\frac{1}{r}-2 \gamma\right)+\eta(r)\left(\gamma^{2}-E+\frac{\alpha}{r}-\frac{l^{2}}{r^{2}}-\frac{\gamma}{r}\right)=0  \tag{6.119}\\
\text { Of course choosing } E=k^{2}=\gamma^{2}  \tag{6.120}\\
\eta^{\prime \prime}+\eta^{\prime}\left(\frac{1}{r}-2 k\right)+\eta\left(\frac{\alpha}{r}-\frac{l^{2}}{r^{2}}-\frac{\gamma}{r}\right)=0 \tag{6.121}
\end{gather*}
$$

Now, making another Ansatz and a variable change such that $\rho=2 k r$ and $\eta(\rho)=\rho^{\beta} \xi(\rho)$.

$$
\begin{gather*}
\eta^{\prime \prime}(\rho)+\eta^{\prime}(\rho)\left(\frac{1}{\rho}-1\right)+\eta\left(\frac{\alpha}{2 k \rho}-\frac{l^{2}}{\rho^{2}}-\frac{1}{2}\right)=0  \tag{6.122}\\
\text { Inserting our Ansatz with } \xi \text {, we find we can eliminate }  \tag{6.123}\\
\text { the unwanted term (in this case the } \frac{1}{\rho^{2}} \text { term). }  \tag{6.124}\\
\xi^{\prime \prime}+\xi^{\prime}\left(\frac{2 \beta+1}{\rho}-1\right)+\frac{\xi}{\rho^{2}}\left(\beta^{2}-l^{2}\right)+\frac{\xi}{\rho}\left(\frac{\alpha}{2 k}-\beta-\frac{1}{2}\right)=0 \tag{6.125}
\end{gather*}
$$

Naturally, we choose $\beta=l$ and our differential equation reduces to the well-known Kummer's equation! Therefore, we can immediately write down the analytic solution as confluent hypergeometric functions.

$$
\begin{equation*}
\xi^{\prime \prime}+\xi^{\prime}\left(\frac{2 l+1}{\rho}-1\right)+\frac{\xi}{\rho}\left(\frac{\alpha}{2 k}-l-\frac{1}{2}\right)=0 \tag{6.126}
\end{equation*}
$$

When we compare this to the well-known Kummer's equation, we can determine the summation coefficients:

$$
\begin{equation*}
x y^{\prime \prime}+y^{\prime}(b-x)-y a=0 \tag{6.127}
\end{equation*}
$$

clearly, we have the expression that $b=2 l+1$ and $a=\frac{1}{2}+l-\frac{\alpha}{2 k}$. With these, coefficients, we can acquire the desired quantized energy expression by examining the quantization of the confluent hypergeometric function coefficients. Let's say we want $a$ to be quantized. We choose $a$ such that:

$$
\begin{equation*}
a=\frac{1}{2}+l-\frac{\alpha}{2 k}=-n \tag{6.128}
\end{equation*}
$$

Note that we need to make a few distinctions before suggesting the energy spectrum. First, we need to note that I omitted the factor of $1 / 2$ that appears in the kinetic operator. In effect this will make $\alpha$ contain a factor of 2 AND that actual value for the parameter $\gamma=2 \sqrt{2} k$ which means in our expressions for the coefficient $a$, we have the following expression.

$$
\begin{gather*}
\frac{\alpha}{\sqrt{2}\left(l+n+\frac{1}{2}\right)}=k  \tag{6.129}\\
E=\frac{-13.6\left(Z^{2}\right)}{2\left(n+l+\frac{1}{2}\right)^{2}} e V \tag{6.130}
\end{gather*}
$$

For our circumstance, $l=0$ and this recovers an expression similar to the familiar hydrogen atom energy spectrum! (remember to note that the parameter $n$ does not refer to energy level as we typically think of it because the n index starts at 0 . Therefore, our $n$ is $n_{\text {hydrogen }}+1$, which index starts at 1 . Note also that this differs in that the base scale starts of at $1 / 2$ instead of 1 .

$$
\begin{equation*}
E=-13.6 e V \frac{Z^{2}}{2\left(n+\frac{1}{2}\right)^{2}} \tag{6.131}
\end{equation*}
$$

Note that this energy expression is found by restricting the parameters of the confluent hypergeometric function. For the method of self-adjoint extensions, the energy expression will not be equal to equation 6.133. Now, after all this work, we are ready to write down the final radial Schrödinger wave function. In its full form, it is given below.

$$
\begin{equation*}
\Psi_{n, l}(r, \theta)=e^{-\rho / 2} \rho^{l}\left(a_{0} M(-n, 2 l+1, \rho)+b_{0} U(-n, 2 l+1, \rho)\right) \tag{6.132}
\end{equation*}
$$

Here $M$ and $U$ are the aforementioned hypergeometric functions of the first and second kind respectively. Now that we have the analytic solution for the wave functions, we can start our self adjoint analysis. We define two separate wave functions:

$$
\begin{align*}
& \psi_{n}(r, \theta)=e^{-\rho / 2}\left(a_{0} M(-n, 1, \rho)+b_{0} U(-n, 1, \rho)\right)  \tag{6.133}\\
& \phi_{n}(r, \theta)=e^{-\rho / 2}\left(c_{0} M(-n, 1, \rho)+d_{0} U(-n, 1, \rho)\right) \tag{6.134}
\end{align*}
$$

Interestingly enough, the self-adjoint analysis is not changed by the introduction of a Coulombic potential since it's a scalar term identical on both sides of the condition.

$$
\begin{equation*}
\int_{a}^{b} \phi^{*}\left(\frac{1}{\mathrm{r}} \frac{\partial}{\partial \mathrm{r}}\left(\mathrm{r} \frac{\partial \psi}{\partial \mathrm{r}}\right)+\frac{1}{\mathrm{r}^{2}} \frac{\partial^{2} \psi}{\partial \theta^{2}}+\frac{\alpha \psi}{\mathrm{r}}\right) \mathrm{rd} r=\int_{a}^{b}\left(\frac{1}{\mathrm{r}} \frac{\partial}{\partial \mathrm{r}}\left(\mathrm{r} \frac{\partial \phi^{*}}{\partial \mathrm{r}}\right)+\frac{1}{\mathrm{r}^{2}} \frac{\partial^{2} \phi^{*}}{\partial \theta^{2}}+\frac{\alpha \phi^{*}}{\mathrm{r}}\right) \psi \mathrm{r} \mathrm{~d} r \tag{6.135}
\end{equation*}
$$

Of course since we are dealing with the $l=0$ channel, the angular terms vanish. In addition, I ignored the angular part of the integral since the only effect it has is to introduce a $2 \pi$ constant, which can be omitted.

$$
\begin{gather*}
\int_{a}^{b} \phi^{*} \frac{1}{\mathrm{r}} \frac{\partial}{\partial \mathrm{r}}\left(\mathrm{r} \frac{\partial \psi}{\partial \mathrm{r}}\right) \mathrm{r} \mathrm{~d} r=\int_{a}^{b} \frac{1}{\mathrm{r}} \frac{\partial}{\partial \mathrm{r}}\left(\mathrm{r} \frac{\partial \phi^{*}}{\partial \mathrm{r}}\right) \psi \mathrm{r} \mathrm{~d} r  \tag{6.136}\\
\int_{a}^{b} \phi^{*} \frac{\partial}{\partial \mathrm{r}}\left(\mathrm{r} \frac{\partial \psi}{\partial \mathrm{r}}\right) \mathrm{d} r=\int_{a}^{b} \frac{\partial}{\partial \mathrm{r}}\left(\mathrm{r} \frac{\partial \phi^{*}}{\partial \mathrm{r}}\right) \psi \mathrm{d} r \tag{6.137}
\end{gather*}
$$

Using integration by parts, we see the expressions simplifies to surface terms, proving formaladjoincy of the 2D Schrödinger Hamiltonian with a Coulombic potential.

$$
\begin{equation*}
\left.\left(\phi^{*} r \frac{\partial \psi}{\partial r}-\psi r \frac{\partial \phi^{*}}{\partial r}\right)\right|_{a} ^{b}=0 \tag{6.138}
\end{equation*}
$$

Again, we are sending the second boundary to infinity and ignoring the terms. Our first boundary is going to be examined near the origin (since our physical impurities are at the origin). The small $\rho$ limit wave function is actually quite complicated an involves quite a bit of limit analysis since the linearity between the independent hypergeometric functions breaks down when $l=0$. N.N.Lebedev gives an excellent account of the procedure in "Special Functions and Applications". I will give a brief overview here. The quantization of the b coefficient in the second hypergeometric functions leads to a new expression:

$$
\begin{align*}
& U(a, n+1 ; z)=\frac{(-1)^{n+1}}{\Gamma(a-n)} \sum_{k=0}^{\infty} \frac{(a)_{k} z^{k}}{(n+k)!k!} \\
& \times(\Psi(a+k)-\Psi(1+k)-\Psi(n+1+k)+\log (z)) \\
&+\frac{1}{\Gamma(a)} \sum_{k=0}^{n-1} \frac{(-1)^{k}(n-k-1)!(a-n)_{k}}{k!} z^{k-n} \tag{6.139}
\end{align*}
$$

In the previous equation, the symbol $\Psi$ refers to the logarithmic derivative of the gamma function.

The previous equation looks quite daunting, but in the limit of small $\rho$ (remember in the previous equation $\rho$ will take the place of $z$ ), the equation can be reduced to various terms of $\rho$. In addition, remember we set $n=0$ since that is the analog of angular momentum channel, which we set to 0 . Also, it's important to note that the above expression actually requires the restriction that the coefficient $a$ in the hypergeometric functions is positive [8]. If you remember from our previous expression, we set $a$ so that it will always be negative to allow for positive energy indexes, but self-adjoint analysis requires we use the convention that $a>0$. In practice, we can determine a new energy expression based on self-adjoint parameters. The reason we need to require $n<0$ has to do with the behavior of the second hypergeometric function. When $n>0$ a degeneracy occurs and the second function reduces to some constant times the first hypergeometric function. This is unacceptable in our selfadjoint analysis because we need the log terms to allow for the imposition of self-adjoint boundary conditions. Else, the self-adjoint condition would be satisfied independent of any conditions on the wave function. If we return to our solution, in the limit of small $\rho$ it simplifies.

$$
\begin{equation*}
\psi=a_{0}+a_{1} \rho^{2}+a_{2} \log (\rho)+a_{3} \rho^{2} \log (\rho) \tag{6.140}
\end{equation*}
$$

Now, we can postulate two wave functions for the self-adjoint analysis.

$$
\begin{align*}
\phi & =a_{0}+a_{1} \rho^{2}+b_{0} \log (\rho)+b_{1} \rho^{2} \log (\rho)  \tag{6.141}\\
\psi & =c_{0}+c_{1} \rho^{2}+d_{0} \log (\rho)+d_{1} \rho^{2} \log (\rho) \tag{6.142}
\end{align*}
$$

Notice in the low $\rho$ limit (remember also $\rho$ is synonymous with r multiplied by some constant), each term contains some constant factor and some factor dependent on $\rho$ and $\log (\rho)$. When we insert this form of the wave functions into the self-adjoint condition, we find the expression reduces to the following:

$$
\begin{equation*}
0=d_{0} a_{0}^{*}-b_{0}^{*} c_{0}+\text { terms that vanish as } \rho \text { goes to } 0 \tag{6.143}
\end{equation*}
$$

Therefore, when we take the lower bound goes to zero, our self-adjoint condition becomes:

$$
\begin{equation*}
0=d_{0} a_{0}^{*}-b_{0}^{*} c_{0} \tag{6.144}
\end{equation*}
$$

Asserting the linear boundary conditions we have used previously we find the final self-adjoint condition.

$$
\begin{gather*}
a_{0}=\lambda b_{0}  \tag{6.145}\\
c_{0}=l d_{0}  \tag{6.146}\\
d_{0} b_{0}^{*} \lambda^{*}=b_{0}^{*} d_{0} l  \tag{6.147}\\
\lambda^{*}=l \tag{6.148}
\end{gather*}
$$

Now, we have found the entire family of self-adjoint extensions to the 2D Schrödinger radial Hamiltonian. Namely, the wave functions will allow self-adjoint Hamiltonian as long as $\lambda, l \in \Re$.

### 6.6 SAE for 2D, 2 Spinor Dirac Hamiltonian

To start an analysis of the vacancy defects in graphene, we attempt to model the vacancy as a boundary condition found through self-adjoint extensions. First, we need to solve the 2D radial problem to determine the spinor components. Looking at the Dirac formulation presented in the methods section we choose a suitable choice of $\alpha$ and $\beta$ such that

$$
\begin{gather*}
(\vec{\alpha} \cdot \vec{p}+\beta m) \psi=E \psi  \tag{6.149}\\
\alpha_{1}=\left(\begin{array}{ll}
0 & 1 \\
1 & 0
\end{array}\right), \alpha_{2}=\left(\begin{array}{cc}
0 & -i \\
i & 0
\end{array}\right), \beta=\left(\begin{array}{cc}
1 & 0 \\
0 & -1
\end{array}\right) \tag{6.150}
\end{gather*}
$$

With this choice of matrices in mind, our 2D Dirac radial Hamiltonian takes the form:

$$
H_{D}=\left(\begin{array}{cc}
m & e^{-i \theta}\left(-i \frac{\partial}{\partial r}-\frac{1}{r} \frac{\partial}{\partial \theta}\right)  \tag{6.151}\\
e^{i \theta}\left(-i \frac{\partial}{\partial r}+\frac{1}{r} \frac{\partial}{\partial \theta}\right) & -m
\end{array}\right)
$$

As was mentioned earlier in the results, we formulate separable solutions consisting of a radial component and an angular momentum channel.

$$
\begin{equation*}
\psi=\binom{\eta(r) e^{i l \theta}}{\xi(r) e^{i(l+1) \theta}} \tag{6.152}
\end{equation*}
$$

When we plug our desired wave functions into the previous Hamiltonian form, we find two coupled differential equations.

$$
\begin{gather*}
i \frac{\partial}{\partial r} \xi+i \frac{l+1}{r} \xi+(E-m) \eta=0  \tag{6.153}\\
i \frac{\partial}{\partial r} \eta-i \frac{l}{r} \eta+(E+m) \xi=0 \tag{6.154}
\end{gather*}
$$

These two coupled differential equations lead the nice decoupled equations for each spinor component. In addition, we can make the simplifying substitution that $\gamma^{2}=E^{2}-m^{2}$ and $s=\gamma r$. Note one subtlety occurs with respect to the sign of $\gamma^{2}$. If $E>m$ then $\gamma^{2}$ is positive, however if $E<m$, then $\gamma^{2}<0$. As such, we also have two cases for solutions. I will solve both solutions for sake of completion.

Case 1: $\gamma^{2}>0$ :

$$
\begin{gather*}
\frac{\partial^{2}}{\partial s^{2}} \eta+\frac{1}{s} \frac{\partial}{\partial s} \eta+\left(1-\frac{l^{2}}{s^{2}}\right) \eta=0  \tag{6.155}\\
\frac{\partial^{2}}{\partial s^{2}} \xi+\frac{1}{s} \frac{\partial}{\partial s} \xi+\left(1-\frac{(l+1)^{2}}{s^{2}}\right) \xi=0 \tag{6.156}
\end{gather*}
$$

Which you may recognize as none other than the Bessel equations! This means we can immediately write down the solutions for both spinor components using Bessel functions of the first and second kind.

$$
\begin{gather*}
\eta=a_{0} J_{l}(s)+a_{1} Y_{l}(s)  \tag{6.157}\\
\xi=b_{0} J_{l+1}(s)+b_{1} Y_{l+1}(s) \tag{6.158}
\end{gather*}
$$

Taking the zeroth order angular momentum channel, the full Dirac wave function is given:

$$
\begin{equation*}
\psi=\binom{a_{0} J_{0}(s)+a_{1} Y_{0}(s)}{\left(b_{0} J_{1}(s)+b_{1} Y_{1}(s)\right) e^{i \theta}} \tag{6.159}
\end{equation*}
$$

When examining vacancies in graphene, we want to look at the $s \ll 1$ limit. In this limit, the Bessel functions simplify to the lowest order in $s$ (noting $\gamma$ in this expression is the Euler Mascheroni constant):

$$
\begin{equation*}
\psi=\binom{a_{0}\left(1-\frac{s^{2}}{4}\right)+a_{1}\left(\log \left(\frac{s}{2}\right)+\gamma\right)}{\left(b_{0} \frac{s}{2}-b_{1}\left(\frac{2}{s}\right)\right) e^{i \theta}} \tag{6.160}
\end{equation*}
$$

Case 2: $\gamma^{2}<0$ :

$$
\begin{gather*}
\frac{\partial^{2}}{\partial s^{2}} \eta+\frac{1}{s} \frac{\partial}{\partial s} \eta-\left(1+\frac{l^{2}}{s^{2}}\right) \eta=0  \tag{6.161}\\
\frac{\partial^{2}}{\partial s^{2}} \xi+\frac{1}{s} \frac{\partial}{\partial s} \xi-\left(1+\frac{(l+1)^{2}}{s^{2}}\right) \xi=0 \tag{6.162}
\end{gather*}
$$

Which you may recognize as the modified Bessel equations (which is in slight contrast to the previous case)! This means we can immediately write down the solutions for both spinor components using modified Bessel functions of the first and second kind.

$$
\begin{gather*}
\eta=a_{0} I_{l}(s)+a_{1} K_{l}(s)  \tag{6.163}\\
\xi=b_{0} I_{l+1}(s)+b_{1} K_{l+1}(s) \tag{6.164}
\end{gather*}
$$

Taking the zeroth order angular momentum channel, the full Dirac wave function is given:

$$
\begin{equation*}
\psi=\binom{a_{0} I_{0}(s)+a_{1} K_{0}(s)}{\left(b_{0} I_{1}(s)+b_{1} K_{1}(s)\right) e^{i \theta}} \tag{6.165}
\end{equation*}
$$

When examining vacancies in graphene, we want to look at the $s \ll 1$ limit. In this limit, the modified Bessel functions simplify to the lowest order in $s$ (noting $\gamma$ in this expression is the Euler Mascheroni constant):

$$
\begin{equation*}
\psi=\binom{a_{0}\left(1+\frac{s^{2}}{4}\right)-a_{1}\left(\log \left(\frac{s}{2}\right)+\gamma\right)}{\left(b_{0} \frac{s}{2}+b_{1}\left(\frac{2}{s}\right)\right) e^{i \theta}} \tag{6.166}
\end{equation*}
$$

## Self-Adjoint Analysis

First, I want to point out that the actual form of the Bessel functions and modified Bessel functions are essential equal. Both wave functions contain terms proportional to $s, \log (s), \frac{1}{s}$, so the self-adjoint analysis is essentially the same for both cases $\left(\gamma^{2}<0\right.$ and $\left.\gamma^{2}>0\right)$.

Returning to the rigorous self-adjoint condition, we have the following integral inequality.

$$
\left.\begin{array}{c}
\int_{a}^{b}\left(\phi_{1}^{*} e^{-i l \theta}, \quad \phi_{2}^{*} e^{-i(l+1) \theta}\right)\left(\begin{array}{cc}
m & e^{-i \theta}\left(-i \frac{\partial}{\partial r}-\frac{l}{r} \frac{\partial}{\partial \theta}\right) \\
e^{i \theta}\left(-i \frac{\partial}{\partial r}+\frac{l}{r} \frac{\partial}{\partial \theta}\right) & -m
\end{array}\right)\binom{\psi_{1} e^{i l \theta}}{\psi_{2} e^{i(l+1) \theta}} \mathrm{r} d r \\
=\int_{a}^{b}\left(\left(\begin{array}{cc}
m & e^{-i \theta}\left(-i \frac{\partial}{\partial r}-\frac{l}{r} \frac{\partial}{\partial \theta}\right) \\
e^{i \theta}\left(-i \frac{\partial}{\partial r}+\frac{l}{r} \frac{\partial}{\partial \theta}\right) & -m
\end{array}\right) \phi_{2} \phi_{1} e^{i(l+1) \theta}\right.
\end{array}\right)^{\dagger}\binom{\psi_{1} e^{i l \theta}}{\psi_{2} e^{i(l+1) \theta}} \mathrm{r} d r .
$$

The integral equation simplifies down to a surface term:

$$
\begin{equation*}
\left(\phi, H_{\text {dirac }} \psi\right)=\left(\phi, H_{\text {dirac }} \psi\right)+\left.s\left(\phi_{1}^{*} \psi_{2}-\phi_{2}^{*} \psi_{1}\right)\right|_{a} ^{b} \tag{6.169}
\end{equation*}
$$

When we write down the possible wave functions for $\eta$ and $\xi$ we write out the two functions.

$$
\begin{align*}
& \psi=\binom{a_{0}\left(1-\frac{s^{2}}{4}\right)+a_{1}\left(\log \left(\frac{s}{2}\right)+\gamma\right)}{\left(b_{0} \frac{s}{2}-b_{1}\left(\frac{2}{s}\right)\right) e^{i \theta}}  \tag{6.170}\\
& \phi=\binom{c_{0}\left(1-\frac{s^{2}}{4}\right)+c_{1}\left(\log \left(\frac{s}{2}\right)+\gamma\right)}{\left(d_{0} \frac{s}{2}-d_{1}\left(\frac{2}{s}\right)\right) e^{i \theta}} \tag{6.171}
\end{align*}
$$

Now, if we take a look at the solutions, we see that the most divergent term will be of order $\frac{1}{s}$. Unfortunately, this is a problem for our self-adjoint analysis. In order to properly analyze solution with self-adjoint extensions, we need to ensure that normalization is possible. The basic definition for normalization requires that the probability kernel diverges less than $\frac{1}{r}$. Unfortunately, the full wave function we derived is not normalizable under these restrictions, so in order to force self-adjoincy of the Hamiltonian, we need to drop the components of the wave functions that diverge by applying specific boundary conditions so that diverging components vanish. While this may seem like this method does not give us any more insight into the graphene vacancy problem, we are quite hopeful about solving the graphene problem because graphene actually requires the use of the 4 spinor component wave function, which may allow for self-adjoint extensions. Our next steps in solving this problem is to re-analyze the problem using the 4 component Dirac equation.

### 6.7 SAE for 2D, 2 Spinor Radial Dirac Coulombic Hamiltonian

In our examination of defects in graphene, we attempt to model the electronic motion using the 2D Dirac equation (since the electrons are confined within a 2D lattice). Our formulation in 2D with a radial potential is given:

$$
\begin{gather*}
(\vec{\alpha} \cdot \vec{p}+\beta m) \psi-\frac{\lambda}{r} \psi=E \psi  \tag{6.172}\\
\alpha_{1}=\left(\begin{array}{ll}
0 & 1 \\
1 & 0
\end{array}\right), \alpha_{2}=\left(\begin{array}{cc}
0 & -i \\
i & 0
\end{array}\right), \beta=\left(\begin{array}{cc}
1 & 0 \\
0 & -1
\end{array}\right) \tag{6.173}
\end{gather*}
$$

With this choice of matrices, our complete Dirac Hamiltonian becomes:

$$
H_{D}=\left(\begin{array}{cc}
m-\frac{\lambda}{r} & e^{-i \theta}\left(-i \frac{\partial}{\partial r}-\frac{1}{r} \frac{\partial}{\partial \theta}\right)  \tag{6.174}\\
e^{i \theta}\left(-i \frac{\partial}{\partial r}+\frac{1}{r} \frac{\partial}{\partial \theta}\right) & -m-\frac{\lambda}{r}
\end{array}\right)
$$

With this Hamiltonian in mind, we hope to eliminate the angular components. As is common in these Dirac problems, we guess a wave function with an angular phase factor.

$$
\begin{equation*}
\psi=\binom{f(r) e^{i l \theta}}{i g(r) e^{i(l+1) \theta}} \tag{6.175}
\end{equation*}
$$

When we plug our desired wave functions into the previous Hamiltonian form, we find two coupled differential equations.

$$
\begin{gather*}
\frac{\partial}{\partial r} g+\frac{l+1}{r} g+\left(m-\frac{\lambda}{r}-E\right) f=0  \tag{6.176}\\
\frac{\partial}{\partial r} f-\frac{l}{r} f+\left(m+\frac{\lambda}{r}+E\right) g=0 \tag{6.177}
\end{gather*}
$$

It may not be obvious how to reduce these equations to something recognizable, but there are a few tricks we can employ. To begin, we can imagine that these equations will be more easy to solve if they are similar as possible, allowing for a simple decoupling of the equations, so we can make our first Ansatz in the aim of replicating the $l$ term in each equation. We guess:

$$
\begin{equation*}
f(r)=\frac{f}{\sqrt{r}}, g(r)=\frac{g}{\sqrt{r}} \tag{6.178}
\end{equation*}
$$

Inserting these expressions into the decoupled equations, we gain a reduction in the $l$ term in equation by $1 / 2$.

$$
\begin{gather*}
\frac{\partial}{\partial r} g+\frac{l+\frac{1}{2}}{r} g+\left(m-\frac{\lambda}{r}-E\right) f=0  \tag{6.179}\\
\frac{\partial}{\partial r} f-\frac{\left(l+\frac{1}{2}\right)}{r} f+\left(m+\frac{\lambda}{r}+E\right) g=0 \tag{6.180}
\end{gather*}
$$

In an attempt to remove the powers of $E$ and $m$ in the equations, we guess the following:

$$
\begin{equation*}
g=-G \sqrt{m-E}, f=F \sqrt{m+E} \tag{6.181}
\end{equation*}
$$

Inserting into the equations and substituting for $\rho=r \sqrt{m^{2}-E^{2}}$.

$$
\begin{align*}
\frac{\partial}{\partial \rho} G+\frac{l+\frac{1}{2}}{\rho} G & =\left(\frac{1}{2}-\frac{\lambda}{\rho} \frac{\sqrt{m+E}}{\sqrt{m-E}}\right) F  \tag{6.182}\\
\frac{\partial}{\partial \rho} F-\frac{\left(l+\frac{1}{2}\right)}{\rho} F & =\left(\frac{1}{2}+\frac{\lambda}{\rho} \frac{\sqrt{m-E}}{\sqrt{m+E}}\right) G=0 \tag{6.183}
\end{align*}
$$

Before I go on, the reason we are taking the next step is to avoid decoupling these equations through straight substitution. Notice how there are terms that go $1 / \rho$, which will lead to ugly terms when differentiating in the substitution. With that in mind, we make the next choice of function substitution.

$$
\begin{equation*}
h_{1}=F+G, h_{2}=F-G \tag{6.184}
\end{equation*}
$$

Which yield the following differential equations found by adding and subtracting the above two equation respectively:

$$
\begin{align*}
\rho \frac{\partial}{\partial \rho} h_{1}-\frac{1}{2} \rho h_{1}+\frac{\lambda E}{\sqrt{m^{2}-E^{2}}} h_{1} & =\left(l+\frac{1}{2}\right) h_{2}-\frac{\lambda m}{\sqrt{m^{2}-E^{2}}} h_{2}  \tag{6.185}\\
\rho \frac{\partial}{\partial \rho} h_{2}+\frac{1}{2} \rho h_{2}-\frac{\lambda E}{\sqrt{m^{2}-E^{2}}} h_{2} & =\left(l+\frac{1}{2}\right) h_{1}+\frac{\lambda m}{\sqrt{m^{2}-E^{2}}} h_{1} \tag{6.186}
\end{align*}
$$

Eliminating $h_{1}$ we can acquire the second order differential equation for $h_{2}$.

$$
\begin{equation*}
\rho^{2} \frac{\partial^{2}}{\partial \rho^{2}} h_{2}+\rho \frac{\partial}{\partial \rho} h_{2}+\frac{1}{2} \rho h_{2}=\frac{1}{4} \rho^{2} h_{2}-\rho \frac{\lambda E}{\sqrt{m^{2}-E^{2}}} h_{2}+\left(\left(l+\frac{1}{2}\right)^{2}-\lambda^{2}\right) h_{2} \tag{6.188}
\end{equation*}
$$

Now that we a single decoupled differential equation, we can make the simplifying variable substitution $\gamma=\sqrt{\left(l+\frac{1}{2}\right)-\lambda^{2}}$. Making another function substitution $h_{2}=\rho^{\gamma} \xi$. The differential equation becomes:

$$
\begin{equation*}
\rho \frac{\partial^{2}}{\partial \rho^{2}} \xi+((1+2 \gamma)-\rho) \frac{\partial}{\partial \rho} \xi-\left(\gamma-\frac{\lambda E}{\sqrt{m^{2}-E^{2}}}\right) \xi=0 \tag{6.189}
\end{equation*}
$$

Which is the confluent hypergeometric equation! Finally after all this work, we found a familiar differential equation! We will come back to an expression of the full solution later, but now we can examine the self-adjoint condition. For normalization requirements, we need the polar integral kernel to diverge less than $1 / r$. Since the most divergent term in the wave functions is $\psi \propto \rho^{-\frac{1}{2}-\sqrt{\frac{1}{4}-\lambda^{2}}}$. The integral kernel's most divergent term is there for $I \propto \frac{1}{{ }_{r} \sqrt{\frac{1}{4}-\lambda^{2}}}$. Therefore, for self-adjoincy to be possible, we require the following conditions on our wave function:

$$
\begin{equation*}
\sqrt{\frac{1}{4}-\lambda^{2}}<\frac{1}{2} \tag{6.190}
\end{equation*}
$$

From this inequality, we have three distinct conditions on $\lambda$.

## Case 1

$$
\begin{equation*}
\lambda=0, \text { only the } \rho^{\gamma} \text { solution is normalizable } \tag{6.191}
\end{equation*}
$$

## Case 2

$$
\begin{equation*}
0<\lambda<\frac{1}{2} \tag{6.192}
\end{equation*}
$$

both solution are normalizable and SAE is needed to determine boundary conditions
Case 3

$$
\begin{equation*}
\lambda \geq \frac{1}{2} \tag{6.193}
\end{equation*}
$$

both solutions are noramlizable and SAE is needed to determine boundary conditions
Now, we need to bring back the units for $\lambda$, since we set $c=\hbar=1$. Our condition on $\lambda$ becomes:

$$
\begin{gather*}
\lambda=Z \frac{e^{2}}{4 \pi \epsilon_{0}} \frac{1}{\hbar c}  \tag{6.194}\\
c=1.0 \times 10^{6} \mathrm{~m} / \mathrm{s} \text { in graphene }  \tag{6.195}\\
\lambda=\frac{300}{137} Z  \tag{6.196}\\
Z_{\text {transition }}=0.23 \tag{6.197}
\end{gather*}
$$

Since $Z$ is an integer, than any charge impurity is above the critical value and we need self-adjoint extensions to determine the boundary conditions. Now for our self-adjoint analysis, we return to the initial self-adjoint condition:

$$
\begin{equation*}
\left(\phi, H_{\text {dirac }} \psi\right)=\left(H_{\text {dirac }} \phi, \psi\right) \tag{6.198}
\end{equation*}
$$

Here, we define two wave functions:

$$
\begin{equation*}
\phi=\binom{F(r) e^{i l \theta}}{i G(r) e^{i(l+1) \theta}}, \psi=\binom{f(r) e^{i l \theta}}{i g(r) e^{i(l+1) \theta}} \tag{6.199}
\end{equation*}
$$

$$
\begin{gather*}
\int_{a}^{b}\left(F^{*} e^{-i l \theta},-i G^{*} e^{-i(l+1) \theta}\right)\left(\begin{array}{cc}
m-\frac{\lambda}{r} & e^{-i \theta}\left(-i \frac{\partial}{\partial r}-\frac{l}{r} \frac{\partial}{\partial \theta}\right) \\
e^{i \theta}\left(-i \frac{\partial}{\partial r}+\frac{l}{r} \frac{\partial}{\partial \theta}\right) & -m-\frac{\lambda}{r}
\end{array}\right)\binom{f e^{i l \theta}}{i g e^{i(l+1) \theta}} \mathrm{r} d r \\
=\int_{a}^{b}\left(\left(\begin{array}{c}
m-\frac{\lambda}{r} \\
e^{i \theta}\left(-i \frac{\partial}{\partial r}+\frac{l}{r} \frac{\partial}{\partial \theta}\right)
\end{array} \begin{array}{c}
e^{-i \theta}\left(-i \frac{\partial}{\partial r}-\frac{l}{r} \frac{\partial}{\partial \theta}\right) \\
-m-\frac{\lambda}{r}
\end{array}\right) i G e^{i(l+1) \theta}\right)^{i l \theta}\binom{f e^{i l \theta}}{i g e^{i(l+1) \theta}} \mathrm{r} d r  \tag{6.200}\\
\int_{a}^{b}\left(\left(\mathrm{~F}^{*} \frac{\partial}{\partial \mathrm{r}} \mathrm{~g}-\mathrm{G}^{*} \frac{\partial}{\partial \mathrm{r}} \mathrm{f}\right)+\mathrm{F}^{*}\left(\left(\mathrm{~m}-\frac{\lambda}{\mathrm{r}}\right) \mathrm{f}+\frac{\mathrm{l}+1}{\mathrm{r}} \mathrm{~g}\right)+\mathrm{G}^{*}\left(\frac{\mathrm{l}}{\mathrm{r}} \mathrm{f}-\left(\mathrm{m}+\frac{\lambda}{\mathrm{r}}\right) \mathrm{g}\right)\right) \mathrm{r} d r= \\
\int_{a}^{b}\left(\left(\mathrm{f} \frac{\partial}{\partial \mathrm{r}} \mathrm{G}^{*}-\mathrm{g} \frac{\partial}{\partial \mathrm{r}} \mathrm{~F}^{*}\right)+\mathrm{F}^{*}\left(\left(\mathrm{~m}-\frac{\lambda}{\mathrm{r}}\right) \mathrm{f}+\frac{\mathrm{l}}{\mathrm{r}} \mathrm{~g}\right)+\mathrm{G}^{*}\left(\frac{\mathrm{l}+1}{\mathrm{r}} \mathrm{f}-\left(\mathrm{m}+\frac{\lambda}{\mathrm{r}}\right) \mathrm{g}\right)\right) \mathrm{r} d r \tag{6.201}
\end{gather*}
$$

Which thankfully reduces to the simple expressions:

$$
\begin{equation*}
\left(\phi, H_{\text {dirac }} \psi\right)=\left(\phi, H_{\text {dirac }} \psi\right)+\left.r\left(F^{*} g-G^{*} f\right)\right|_{a} ^{b} \tag{6.202}
\end{equation*}
$$

Now that we have conditions on the wave functions, we need to find solutions that we can easily examine. We have already found the analytic solution to the problem, but we can find a much simpler expression if we examine the original equations and look at small $r$ solutions.

$$
\begin{gather*}
\frac{\partial}{\partial r} g+\frac{l+1}{r} g+\left(m-\frac{\lambda}{r}-E\right) f=0  \tag{6.203}\\
\frac{\partial}{\partial r} f-\frac{l}{r} f+\left(m+\frac{\lambda}{r}+E\right) g=0 \tag{6.204}
\end{gather*}
$$

For our analysis, we look for low r solutions of the form:

$$
\begin{align*}
& g=a_{0} r^{\alpha}+a_{1} r^{\alpha+1}+\ldots  \tag{6.205}\\
& f=b_{0} r^{\alpha}+b_{1} r^{\alpha+1}+\ldots \tag{6.206}
\end{align*}
$$

Plugging these guesses into the characteristic equations, we find equations constraining the coefficients in varying powers of r . I will abbreviate the substitution and list the relevant equations (which are easy to inspect by eye).

$$
\begin{gather*}
\alpha a_{0}+(l+1) a_{0}-\lambda b_{0}=0  \tag{6.207}\\
(\alpha+1) a_{1}+(l+1) a_{1}-\lambda b_{1}+(m-E) b_{0}=0  \tag{6.208}\\
(\alpha+2) a_{2}+(l+1) a_{2}-\lambda b_{2}+(m-E) b_{1}=0 \tag{6.209}
\end{gather*}
$$

$$
\begin{gather*}
\alpha b_{0}-l b_{0}+\lambda a_{0}=0  \tag{6.210}\\
(\alpha+1) b_{1}-l b_{1}+\lambda a_{1}+(m+E) a_{0}=0  \tag{6.211}\\
(\alpha+2) b_{2}-l b_{2}+\lambda a_{2}+(m+E) a_{1}=0 \tag{6.212}
\end{gather*}
$$

Examining the two equations with zeroth order coefficients, we find restrictions for $\alpha$ that are consistent with our previous results:

$$
\begin{gather*}
(\alpha+l+1)(l-\alpha)=\lambda^{2}  \tag{6.213}\\
\alpha=-\frac{1}{2} \pm \frac{1}{2} \sqrt{l^{2}-\lambda^{2}}  \tag{6.214}\\
\alpha=-\frac{1}{2} \pm \gamma \tag{6.215}
\end{gather*}
$$

Now that we have the power term in r, we actually have both independent solutions, one for $+\gamma$ and one for $-\gamma$. We can write down the wave functions with the two solutions.

$$
\begin{align*}
& g=a_{0} r^{-\frac{1}{2}+\gamma}+a_{1} r^{-\frac{1}{2}+\gamma+1}+\ldots+c_{0} r^{-\frac{1}{2}-\gamma} a+c_{1} r^{-\frac{1}{2}-\gamma+1}+\ldots  \tag{6.216}\\
& f=b_{0} r^{-\frac{1}{2}+\gamma}+b_{1} r^{-\frac{1}{2}+\gamma+1}+\ldots+d_{0} r^{-\frac{1}{2}-\gamma} a+d_{1} r^{-\frac{1}{2}-\gamma+1}+\ldots \tag{6.217}
\end{align*}
$$

Remember those equations we found previously to determine the coefficients? Well, we can use those to determine the relations between each of the coefficients. Just a quick note, the equations are given with a and $b$ coefficients, but it is equally valid for $c$ and $d$ coefficients, we just need to remember that the equations with a and b coefficients corresponds to $\alpha=-\frac{1}{2}+\gamma$ and the equations with c and d coefficients correspond to $\alpha=-\frac{1}{2}-\gamma$. With these in mind, we can write the relations:

$$
\begin{align*}
& b_{0}=\frac{\left(l+\frac{1}{2}+\gamma\right)}{\lambda} a_{0}  \tag{6.218}\\
& d_{0}=\frac{\left(l+\frac{1}{2}-\gamma\right)}{\lambda} c_{0} \tag{6.219}
\end{align*}
$$

Returning to the self-adjoint condition and defining a series of wave functions to lowest non vanishing order:

$$
\begin{align*}
g & =a_{0} r^{-\frac{1}{2}+\gamma}+\ldots+c_{0} r^{-\frac{1}{2}-\gamma} a+\ldots  \tag{6.220}\\
f & =b_{0} r^{-\frac{1}{2}+\gamma}+\ldots+d_{0} r^{-\frac{1}{2}-\gamma} a+\ldots  \tag{6.221}\\
G & =A_{0} r^{-\frac{1}{2}+\gamma}+\ldots+C_{0} r^{-\frac{1}{2}-\gamma} a+\ldots  \tag{6.222}\\
F & =B_{0} r^{-\frac{1}{2}+\gamma}+\ldots+D_{0} r^{-\frac{1}{2}-\gamma} a+\ldots \tag{6.223}
\end{align*}
$$

Entering the self-adjoint condition:

$$
\begin{align*}
&\left.r\left(F^{*} g-G^{*} f\right)\right|_{a} ^{b}=0 \\
& \qquad 0=r^{-2 \gamma}\left(D_{0}^{*} c_{0}-C_{0}^{*} d_{0}\right)+\left(B_{0}^{*} c_{0}+D_{0}^{*} a_{0}-C_{0}^{*} b_{0}-A_{0}^{*} d_{0}\right) \\
&+ \text { terms vanishing for low r } \tag{6.224}
\end{align*}
$$

Noting the trend of coefficient dependencies, we examine the effect of these on the self-ajoincy condition.

$$
\begin{align*}
b_{0} & =\frac{\left(l+\frac{1}{2}+\gamma\right)}{\lambda} a_{0}  \tag{6.225}\\
d_{0} & =\frac{\left(l+\frac{1}{2}-\gamma\right)}{\lambda} c_{0}  \tag{6.226}\\
B_{0} & =\frac{\left(l+\frac{1}{2}+\gamma\right)}{\lambda} A_{0}  \tag{6.227}\\
D_{0} & =\frac{\left(l+\frac{1}{2}-\gamma\right)}{\lambda} C_{0} \tag{6.228}
\end{align*}
$$

Inserting these expressions into the self-adjoint conditions, we see two conditions emerge.

$$
\begin{gather*}
\frac{\left(\gamma-\gamma^{*}\right)}{\lambda} C_{0}^{*} c_{0}=0  \tag{6.229}\\
\frac{\left(\gamma+\gamma^{*}\right)}{\lambda}\left(A_{0}^{*} c_{0}-C_{0}^{*} a_{0}\right)=0 \tag{6.230}
\end{gather*}
$$

Note both conditions must be satisfied for self-adjoincy of the Hamiltonian. This also shows we have two distinct cases one being when $\gamma$ is real and another when $\gamma$ is imaginary. We have already determined the conditions on the Coulombic potential for these two circumstances (see beginning of proof).

Case 1: $\gamma \in \Re$ When $\gamma$ is real, our conditions simplify to the final form:

$$
\begin{equation*}
\frac{2 \gamma}{\lambda}\left(A_{0}^{*} c_{0}-C_{0}^{*} a_{0}\right)=0 \tag{6.231}
\end{equation*}
$$

Like previous examples, we postulate linear relations between coefficients.

$$
\begin{equation*}
a_{0}=\alpha c_{0} \text { and } A_{0}=\beta C_{0} \tag{6.232}
\end{equation*}
$$

Which yields our desired self-adjoint condition:

$$
\begin{gather*}
C_{0}^{*} \beta^{*} c_{0}-C_{0}^{*} \alpha c_{0}=0  \tag{6.233}\\
\beta^{*}=\alpha  \tag{6.234}\\
\beta=\alpha \text { as long as } \alpha, \beta \in \Re \tag{6.235}
\end{gather*}
$$

Case 2: $\gamma \in \Im$
When $\gamma$ is imaginary, our conditions simplify to the final form:

$$
\begin{equation*}
\frac{2 \gamma}{\lambda} C_{0}^{*} c_{0}=0 \tag{6.236}
\end{equation*}
$$

Which requires that we set either $c_{0}$ or $C_{0}$ equal to zero. This is a problem for proving selfadjoincy because the main condition we require is that all sets of wave functions must have the same restriction on them. However, when set either $c_{0}$ or $C_{0}$ we eliminate the need to force conditions on the complementary wave function. This means there are no self-adjoint conditions possible when $\lambda \in \Im$. Unfortunately, this shows that for any Coulombic impurity $Z>0$, we are unable to use self-adjoint conditions to define the boundary conditions. However, we are hopeful that the full 4 spinor component form of the 2D Dirac equation may yield the desired self-adjoint solutions.

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