Vacancy and Coulombic Defects in Graphene

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Experimental Motivation
Recent experiments have probed vacancy and Coulombic defects in graphene using scanning tunneling microscopy. Vacancy defects are created when a single carbon atom is removed from the lattice (figure 1). Coulombic defects are created by placing calcium dimers near a localized point on the graphene sheet (figure 2).

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 Schrödinger 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 have been long sought experimentally but never yet seen in the heavy ion context. In this project we 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.

Results and Conclusions
We find that the Coulomb impurity problem in two dimensions is extremely singular. No matter how weak the charge, at low angular momentum, we find that at every energy the Dirac equation has two competing solutions both of which are sufficiently regular at the origin to be integrable. The ambiguity is resolved by the method of self-adjoint interactions which determines a boundary condition that the solution must obey at the origin (see below).

\[ \psi = \begin{pmatrix} a_1 e^{i \lambda_1 r} + a_2 e^{i \lambda_2 r} \\ b_1 e^{-i \lambda_1 r} + b_2 e^{-i \lambda_2 r} \end{pmatrix} \]  

Close to the origin the competing solutions behave as:

\[ r \psi \propto \psi \sim r^{-\frac{1}{4}} \]  

Here Z is the charge of the impurity and alpha is the fine structure constant. Thus there is a transition in the form of boundary conditions at Z alpha = 1/2 as the exponent transitions from real to pure imaginary. Since alpha in graphene is approximately 2.2, and Z is quantized to be an integer, in practice this means all charged impurities are above this threshold. By way of comparison in three dimensions the Coulomb problem is much less singular. No matter how weak the charge, at low angular momentum, we find transitions that are sufficiently regular at the origin to be integrable. The ambiguity is resolved by the method of self-adjoint interactions which provides quantitative and qualitative insights into impurity bound states that can be compared to experimental data and other more computationally intensive theoretical analyses.

Methods
The electronic structure of graphene can be accurately modeled as a single orbital tight binding model on a honeycomb lattice. The energy momentum dispersion relation for this model is shown in figure 4. Near zero energy the dispersion relation is linear justifying the use of the Dirac equation in describing low energy electronic states.

\[ \alpha_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \alpha_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \]

Using the Dirac equation to model electrons in graphene has proved an extremely fruitful approach. However for analyzing defects it has hitherto been assumed that it is necessary to return to the full lattice model. In this work we propose that defects can still be treated within the continuum Dirac approach as suitable boundary conditions that must be imposed on the Dirac equation at the location of the defect. The appropriate boundary conditions can be determined using the mathematical method of self-adjoint extensions. Only certain boundary conditions are consistent with the self-adjointness of the Dirac Hamiltonian that is required by the fundamental principles of quantum mechanics. Thus the method allows us to construct a model of impurities with one parameter that can be fit to experiment or derived from the underlying lattice model.

Literature References
4. Yang Wang et al., Observing Atomic Collapse Resonances in Artificial Nuclei on Graphene, Science, 10.1126, 1234530, 7 March 2013