Modeling Physical Information of Molecular Wires Using Conductance Histograms

1 Introduction

The exploration into electron transport of molecular systems has become an active topic in the world of quantum physics and electronics [5]. This research plays heavily into the future development of new technologies such as photovoltaic, thermo-electrics, and molecular electronics, and raises fundamental questions into the differences in conventional electronics versus quantum electronics. One way these quantum systems are vastly different from conventional electronics is on the quantum scale, where there are discreet channels for electron flow and limits to the conductance in the channel [6]. These channels can be likened to a city block, where getting across a city can involve many different paths using different streets and different directions. Each of these unique combinations of streets and paths would be similar to a single channel within these quantum systems. Each of these channels are unique and independent of each other.

Compared to conventional electronics in which there are no channels, molecular systems have a finite number of channels through which the electrons can travel [3]. Within each channel, there is a probability that describes how likely it is that an electron will travel from electrode to the other. So these systems are made up of both the individual channels, and the physical aspects that affect them. If a channel is closed, it is said to have a conductance of 0 and if the channel is open, the conductance is 1; meaning if an electron enters the channel,

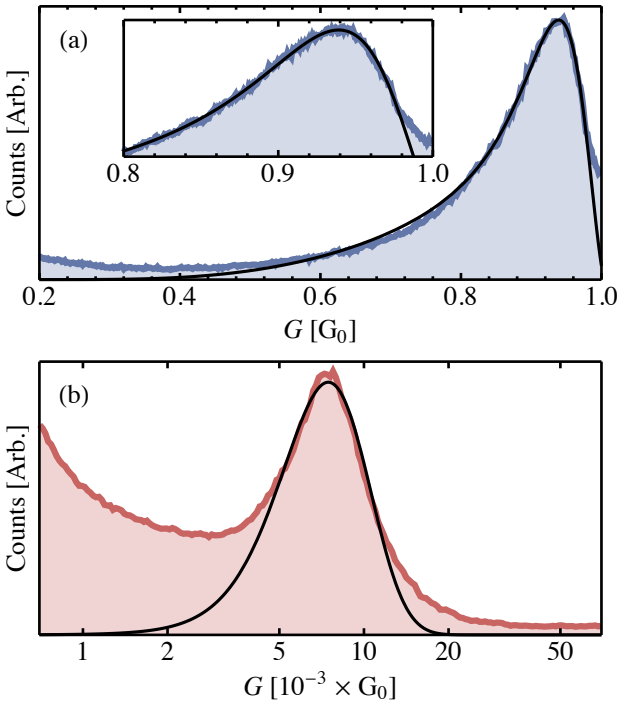

Figure 1: This is the experimental data using a Gold point contact. Where the peaks of the histogram occur is said to be the system's single-molecule conductance. This histogram plots the times a conductance is measured versus actual conductance of the single channel.

it has a 100 percent probability of traveling across the electrodes [6]. In order to understand what quantum properties are affecting these systems, more research must be done into the area.

Currently, when scientists run experiments on these nano-scale conductors, it is not known how to hold the molecular aspects constant in order to evaluate the outcomes of these tests. Between each test, the way the molecule channel couples to the electrode can vary. These uncontrollable variables make the tests highly irreproducible and difficult to analyze [4]. This also raises the question of how to measure the physical aspects that, to date, cannot be controlled. Likewise, the properties that influence these channels and create optimal conductors are very hard to measure and hold constant. In order to get around the problems raised by this process, scientists order the outcomes in histograms, and have concluded that these conductances organize into single-channel peaks as seen in Figure 1 [4].

Scientists currently know that the shape of these peaks say something about the chemistry of the system, but very little research into the area has been done. Currently, it is possible to simulate these peaks using a given set of parameters. Currently it is know how to predict the peak of the histogram, but is it possible to better interpret the experimental parameters by analyzing the data within the peak of the conductance histogram. In order to extract the parameters that affect the conductance histogram, the model devised must be able to solve an inverse problem in which the total amount of data and outcomes are known, but the actual input variables are unknown. Also, the model devised should be able to relate to physical data that affects the tests. Presently, analysis over the data or line shapes has not been done. The only analysis done has been over empirical models that were used to describe the data. So the model devised must be able to estimate what values and physical information are affecting the line shapes of single-channel peak histograms. Therefore the primary point of this research is to understand what fundamental physics is affecting the outcome of these conductances. If it is possible to understand these fundamental processes, then new, groundbreaking work can be done into fields dealing with quantum electron transport.

2 Background

2.1 The Need For Conductance Histograms

Conductance histograms are a useful tool when analyzing electron transport through molecular or quantum systems. The experimental measurements recorded from these systems are highly irreproducible and require special statistical analysis to interpret [4]. Experimental results have proven the sensitivity of conductance to change in the molecule- electrode interface [4]. In each experimental histogram, the x-axis is the measured conductance and the y-axis is number of times observed, or approximately the probability of observation.

Even though much progress has been made into understanding single channel conductance, it is hard to determine all the variables associated with this process. Therefore, in

past experiments scientists have a hard time determining the microscopic details, such as coupling strength and channel's energy, surrounding the molecule-electrode interfaces, or even control them.

2.2 How Conductance Histograms are Used

Scientists conventionally use the mode, or sometimes mean, of the conductance histogram's peak to infer the single-molecule conductance [4]. The peak of the histogram is called the single-molecule conductance. The width of this peak is attributed to the chemistry and structure of the molecule and how it conducts these electrodes. Depending on the geometry of the molecule, the conductance can vary greatly [4]. The geometry of the molecule can determine the path by which the electron travels to the opposite electrode. The more possible paths an electron can take, the wider the variance of the histogram. In this work, the line shapes of the peaks of the conductance histograms are explored because of the information that could be contained in the lines shapes [4]. Primarily, from this peak two cases of electron transport mechanism, either resonant or non-resonant tunneling can be found. All of this information through these systems is then quantized, meaning that there is a specific number of channels by which the electrons can flow through the system [6]. Each one of these channels has a well-defined probability that an electron can successfully make it from one electrode to another [6][3]. The total (zero-bias) conductance is given by

$$G = G_0 T(E_F) \tag{1}$$

where $T(E_F)$ is the total of all transmission probabilities through all channels, E_F is the Fermi Energy,

$$(G_0) = \frac{2e^2}{h} \tag{2}$$

is the quantum of conductance, where e is the electron charge, and h is Planck's constant [6][3]. The conductance is viewed as the probability that the electron will make it across the

system to the electrodes, and subsequently conductance is equal to transmission [**?**]. The conductance through any channel is limited to $0 \leq G \leq G_o$ [6].

Recently, there has been new research into the single channel peaks of the histograms because its believed relevant data can still be extracted [4]. These peaks not only show what is believed to be the "expected conductance" through a system, but also the conduction mechanism (resonant vs. non resonant tunneling) [6]. This line shape formed by the histogram also relates to the probability density function (PDF) for measuring the conductance through system and the line shape of a one-channel peak can be described by a "double beta" distribution, log-normal distribution, normal distribution, and Lorentzian distributions, but these fitting parameters have no physical significance to the system [2][6]. In these PDF's $0 \leq \upsilon \leq 1$ pertains to the transport in the resonant tunneling, and $\upsilon > 1$ for the non-resonant case. When finding the total peak, it is the sum of the two different cases for the two mechanisms [6].

2.3 Landauer-Imry Theory

In the Landauer- Imry theory, transmission in these quantum systems can be viewed as conductance. Landauer and Imry developed Equation 1. In this transmission function, three primary details affect the transmission, as seen in Figure 2.

1. The coupling site energy to the left and right electrode, called Γ_L and Γ_R respectively, determines how the molecule couples to the electrodes.

2. The Fermi Energy of the electrodes is E_F.

3. The energy of the channel, ϵ, determines whether the channel created will be resonant or non-resonant, meaning that the energy of the conductor roughly equals the energy of the electrode.

In the system, the Fermi energy can best be described as the energy of the electrodes, as measured by the electron occupation of each electrode.

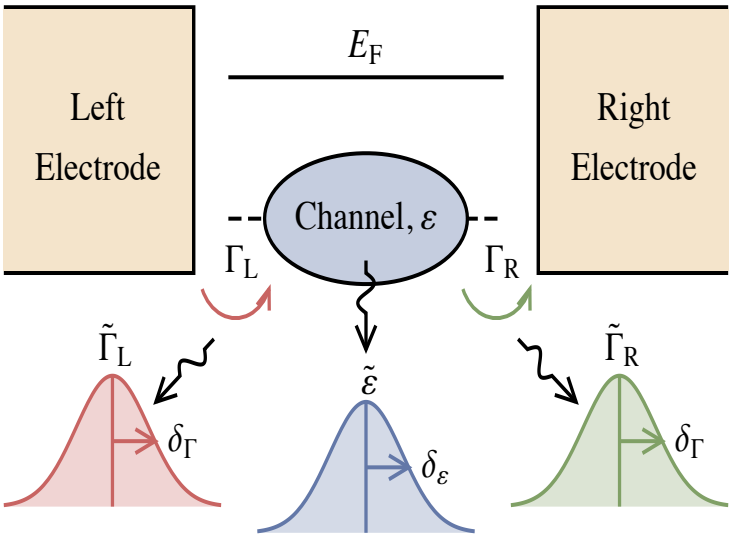

Figure 2: In the schematic, the conductor forms a channel while sandwiched between two electrodes. In order to simulate experimental uncertainty, these values are each treated as random variables with their own probability distribution; having a mean value of $\tilde{\Gamma_L}$ and standard deviation of δ_L.

In the cases evaluated, it is assumed that $\Gamma_L \geq 0$ and $\Gamma_R \geq 0$. Therefore, the transmission in this case would be [3],

$$T(E) = \frac{4\Gamma_L\Gamma_R}{4(E_F - \epsilon)^2 + (\Gamma_L + \Gamma_R)^2} \tag{3}$$

The purpose of modeling the conductance histograms is to see how these variables will affect the system. If these variables can be measured and understood, then a better understanding of these systems can be developed. A single- channel system with two electrodes, in the broadest case requires these three parameters to model the electron transport [6]. If the Fermi Energy and Epsilon are not close to each other, then the test is considered to be "non-resonant," as seen in cases 2 and 3. If $(E_F \approx \epsilon)$ then the transport is "resonant" as seen in case 1 of Figure 2.

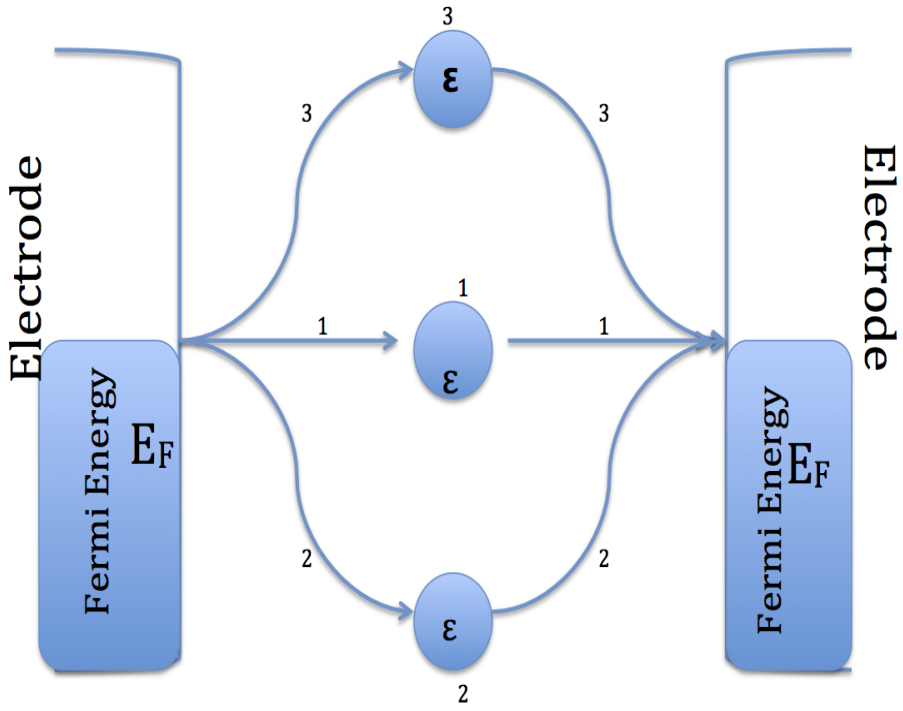

Figure 3: This shows the interaction of the Fermi Energy with the energy level, ϵ, of the molecule or atom creating the channel. If the Fermi Energy and Epsilon are not close to each other, then the test is considered to be "non-resonant," as seen in cases 2 and 3. If $(E_F \approx \epsilon)$ then the transport is "resonant" as seen in case 1.

2.4 Resonant Tunneling

In the resonant tunneling case for electron transport, the electron enters the system when the energy of the molecule energy (ϵ) equals the Fermi Energy of the electrode. The Fermi level or energy is the electron occupation on the two electrodes as seen in Figure 2, case 1. The lower the Fermi Energy of an electrode, the fewer electrons occupy the electrodes in any state. With resonant tunneling, the electron has a much higher chance of making it through the channel. The channel is considered to be open when it is at resonance. When the channel is open, the measured conductance will be the greatest and equal to the quantum of conductance, which was equation 2 [6]. For future research, scientists can look into certain materials that match the Fermi Energy of the electrodes in order to create more efficient quantum conductors.

2.5 Non-resonant Tunneling

In the non-resonant case, the energy of the molecular channel is off the Fermi Energy of the electrode, meaning that the ϵ does not equal E_F. In Figure 3, cases 2 and 3 are both non-resonant cases. In case 3, the energy of the conductor is above the Fermi energy. In case 2, the conductor's energy is less than the Fermi energy of the electrode. When this is the case, there is more scattering of the electrons. Because of the increased probability for scattering, the conductance values measured will be less than resonant case. Also, the conductance measured will not be the same as the quantum of conductance as in resonant tunneling. The channels are not considered open, and will have a much lower measured conductance. The non-resonant cases can been seen in Figure 3 with the examples 2 and 3. In these cases, the transmission values will be lower than if the system was at resonance.

3 Methods

In order to evaluate these conductance histograms and their cases (resonance versus non-resonance), first a model was made using probability theory which gave an integral [2]. This integral was then evaluated and simplified, and parameters were extracted for the different resonant and non-resonant cases. This model was then validated and then applied to experimental data. So in theory, this model will be able to extract important details and information from the line shapes of these conductance histograms.

In order to first start the analysis of the conductance histograms, a model is created using probability theory. This model gave the integral,

$$\hat{G}(g) = \int_{-\infty}^{\infty} d\epsilon \int_{0}^{\infty} d\Gamma \hat{P}_{\epsilon} \hat{P}_{\Gamma}(\Gamma) \delta \left(\frac{\Gamma^2}{(E_F - \epsilon)^2 + \Gamma^2} - g \right) \tag{4}$$

and when was evaluated found that, in the end, the probability density function only has one free parameter, $c \equiv \frac{\Gamma_0}{\delta_\epsilon}$. Therefore the final equation after evaluation for the at resonance case is,

$$\hat{G}(g) \approx \frac{1}{\sqrt{2\pi g^3 (1-g)}} c \exp\left(-c^2 \frac{1-g}{2g}\right) \tag{5}$$

This equation is used to create the control histograms. In the non-resonance case, the statistical integral is evaluated to be,

$$\hat{G}(g) = \frac{c}{\sqrt{8\pi g (1-g)^3}} \exp - \frac{(c\sqrt{g} - d\sqrt{1-g})^2}{2(1-g)} \tag{6}$$

and in this case there is two free parameters, $c \equiv \frac{|E_F - \epsilon|}{\delta_\Gamma}$ and $d \equiv \frac{\Gamma_0}{\delta_\Gamma}$. These two parameters will be used when evaluating the histograms.

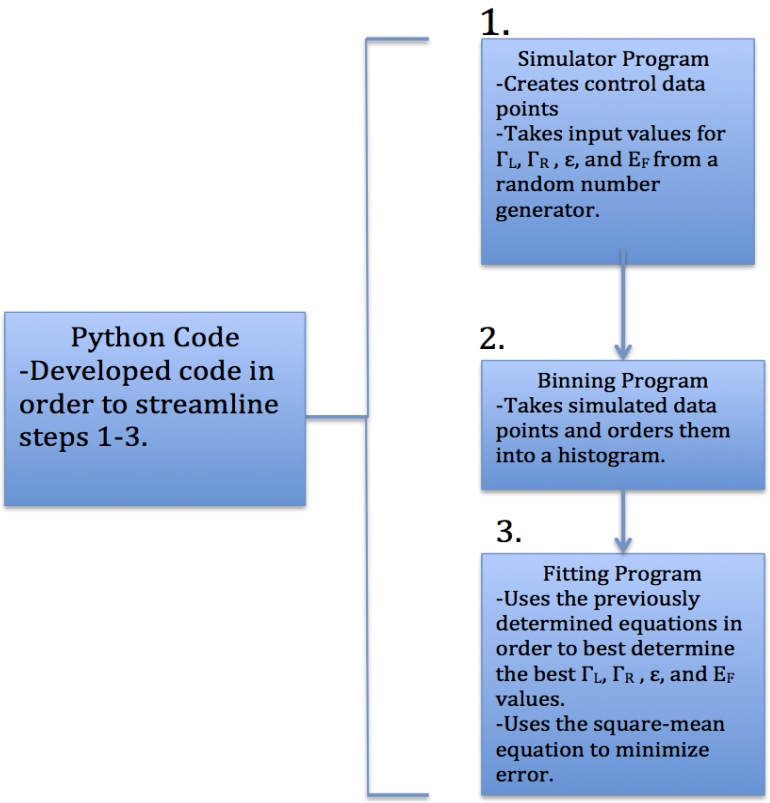

Figure 4: the chart shows the control experiment set up used to validate the fitting program. The python script was used to streamline the process over hundreds of tests.

3.1 Validation

In order to validate that the equations used to model the histograms are valid, a control experiment must be devised. First a program was written that simulated control histograms where the input values of $\Gamma_L, \Gamma_R, \epsilon$, and E_F are all known. This program had to use a random number generator in order to simulate the experimental uncertainty, as seen in Figure 2. This program simulated several hundred data points, and from here this data was then sent to a binning program that organized the simulated data points into a conductance histogram in which the input values were known. From here, the fitting program was fitted to the histogram. This program used equations 5 and 6 for the different scenarios in which the

simulated data could be at resonance or off-resonance. The fitting program used the root mean square equation,

$$\sum_i (P_i - P(g_i, c)^2) \tag{7}$$

to minimize the the difference between the input values P_i and the fitting function $P(g_i, c)$, with parameters c. When Equation 6 was minimized, the output mean values of the parameters were measured.

In figure 3, the python script was written in order to streamline the whole process of testing hundreds of conductance histograms.

3.2 Application

After the fitting program was validated, it has been applied to experimental data. So far the fitting has worked and provided much insight into the way the two couplings Γ_L and Γ_R react in the system.

4 Results and Discussion

After running the evaluation program, it was concluded that the this fitting program is feasible. After getting the results from the validation, the input values for Γ, ϵ, and E_F were plotted against the output values for the fitting program as seen in figure 4.

4.1 Resonant Fitter

let me know if I need to add some background on asymmetric versus symmetric In figure 4, case (a) is the symmetric model with fitting parameter c. The fitting program is able to predict the values practically spot on. Therefore the symmetric fitter is very reliable. In case (b), this is the asymmetric case with parameter c, when $\Gamma_L \neq \Gamma_R$, this case breaks down when $\Gamma_R \approx \Gamma_L$, as indicated by the red dots. This fitter breaks down because the values

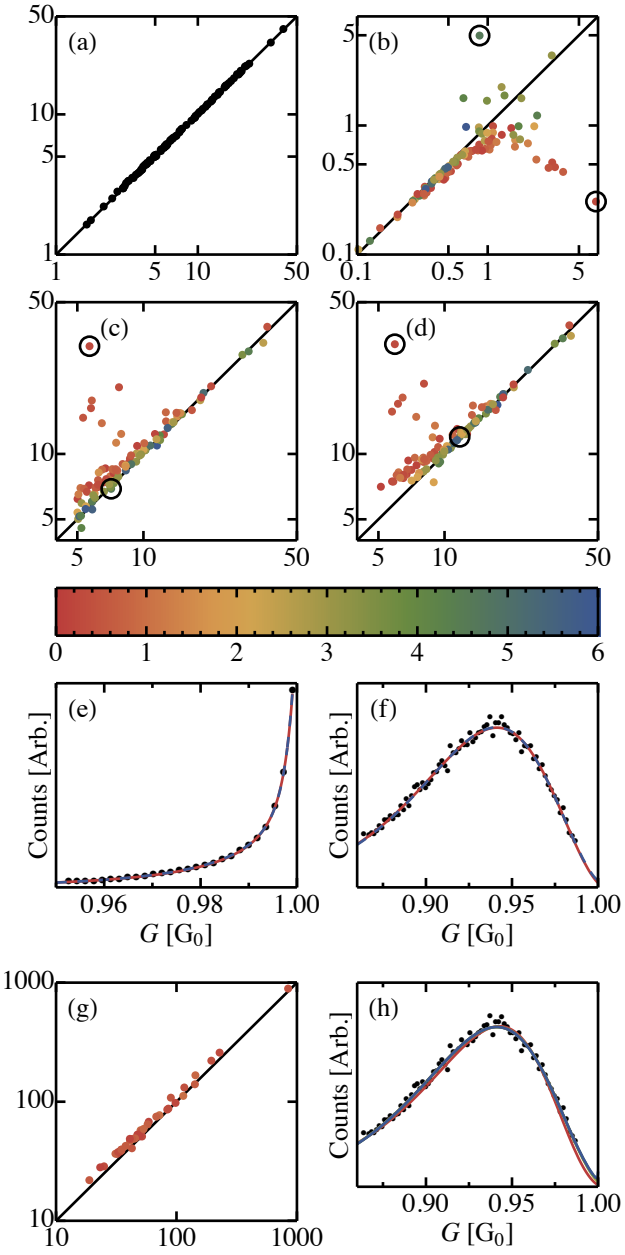

Figure 5: This is the resonant case histograms with the plotted values taken from the fitting program plotted against the actual input values. The bottom graphs are the graphs of the circled outliers in order to examine what was happening. The shading in this figure represents $| \Gamma_L - \Gamma_R |$

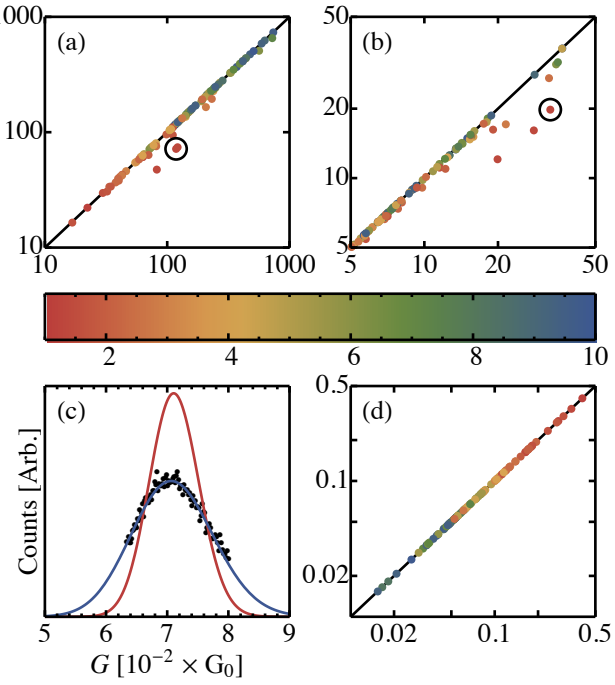

Figure 6: This is the non- resonant case histograms with the plotted values taken from the fitting program plotted against the actual input values. The bottom left graph (c) is the graphs of the circled outliers in order to examine what was happening. The shading in this figure represents $\mid E_F - \epsilon_0 \mid \gg 0$.

are starting to approach the symmetric case and so the asymmetric fitter cannot perform as well. Case (c) is the asymmetric fitter finding $Gamma_L$, and it is very accurate except when fitting close to the symmetric case. Case (d) is the same as case (c) except (d) plots the $Gamma_R$. In order to explore what was happening at these red- dot cases in (b), (c), and (d) these histograms were examined in cases (e), (f), and (h). In each case, the fitting function is represented by the blue line and the model fit is represented by the red line. In each histogram, both the blue and red line match up, but the Γ values are tough to determine because it is so near the symmetric case. Also the green dots are cases in which the E_F and ϵ values start to approach the non-resonant case, so the fitter begins to have trouble fitting. Here it would probably be best to apply the non- resonant fitter. So in summary, the fitter does work, but if the conditions start to approach another type of model then the fitter begins to break down.

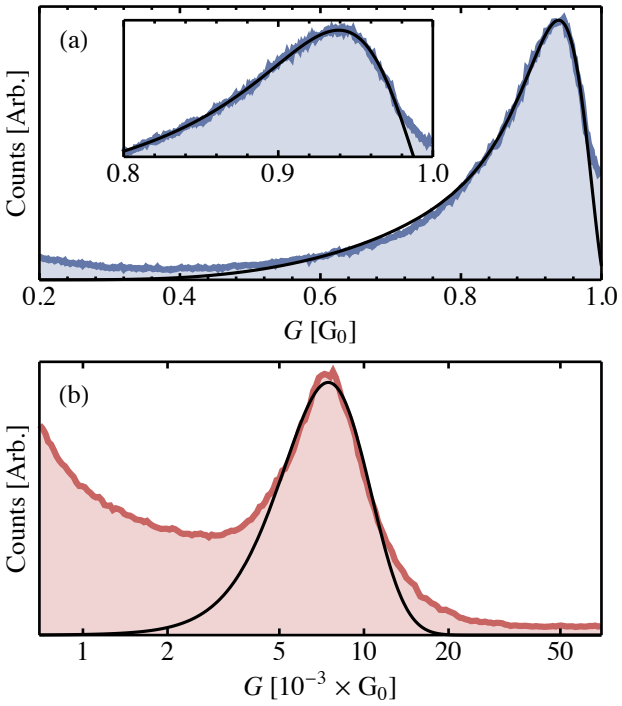

Figure 7: This is the experimental data using a Gold point contact (resonant) and benzene-diamine conductor (non-resonant). In both cases, the fitting program works exceptionally well. From fitting this data, it new data was determined in the way the conductors couple with the two electrodes.

Yes, this is the same histogram as in Figure 1 because I still need to get a sample histogram for figure 1 so I used this one in the meantime.

4.2 Non-resonant Fitter

In figure 5, case (a) is the c parameter extracted out of the non-resonant model. All of the bad fits are red in color because in the derivation of the model it was assumed that $\mid E_F - \epsilon_0 \mid \gg 0$ and in these cases this difference between E_F and ϵ was not great enough. So in these cases, the derived model begins to break down. Case (c) shows how the red line (input parameters) are not even matching with data, but the fitting program is working. So in this case the model is bad because the derivations made bad approximations. In case (d), it is interesting to note though that parameters $\frac{d}{c}$ which means the parameters are working.

4.3 Experimental Data

After receiving some data from Latha Venkataraman, the fitting program was used on them. In figure 6, the top graph (a) is a gold-point contact (resonant). The values extracted were that $\Gamma_1 = 7.43$ and $\Gamma_R = 11.5$ and $c = 0.281$. Interestingly enough, the right coupling seems to be about 150% greater than the left. This is the first time this information has been know to the scientific community. In the bottom graph (b), benzenediamine (non-resonant) was used as the conductor. In this case the values extracted were $c = 64.7$ and $d = 5.79$. The initial hill at the beginning of this graph is background signal from the vacuum tunneling. This fitting program has already proved valuable in determining actual values from experimental data.

5 Conclusion

So from determining the model from heavy statistical analysis, an equation was used to model these histograms. After the fitting program was validated, it was applied to experimental

data. In this analysis, more was learned about the way that the conductors couple with electrodes. Because this model was developed, future research into the area of quantum conductances will be much more useful and applicable. This work has never been done and can tell the scientific community much more into the physical details motivating quantum conductances. This research can be then used in ground-breaking areas such as thermo-electrics, photo-voltaics, and molecular electronics.

References

[1] Büttiker, Imry, Landauer, and Pinhas. Generalized many-channel conductance formula with application to small rings. *Phys Rev B Condens Matter*, 31(10):6207–6215, May 1985.

[2] S. Ghahramani. *Fundamentals of Probabilty*. Prentice- Hall, Upper Saddle River, NJ, USA, 2nd edition, 2000.

[3] Rolf Landauer; Yoseph Imry. Conductance viewed as transmission. *Reviews of Modern Physics*, 71(2):306–312, 1999.

[4] Matthew G Reuter, Mark C Hersam, Tamar Seideman, and Mark A Ratner. Signatures of cooperative effects and transport mechanisms in conductance histograms. *Nano Lett*, 12(5):2243–8, May 2012.

[5] J.C. Cuevas; E. Sheer. *Molecular Electronics*. World Scientific, 2010.

[6] Matthew G. Reuter; Patrick D. Williams. Extracting physical information from the line shapes of single- channel peaks in conductance histograms. 2012.