Examining the Information Content of Voltage-Dependent, Two-Dimensional Conductance Histograms

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I. Introduction

In nanometer-scale systems in which quantum mechanical effects are crucial, the study of the conductance of a single molecule is a topic that has undergone significant *recently* ~~recent~~ advances. This area of research has garnered excitement due to potential applications in areas such as molecular electronics, photovoltaic technologies, and thermo-electrics. It is popularly hoped that a better understanding into the realm of molecular conductance properties will *ultimately* lead to the replacement of electronic components with ~~in the ultimate case~~ single molecules, allowing for dramatic size reduction *in electronic devices*. An application could thus be in creating smaller circuit components for the placement of more transistors in processor chips, resulting eventually in increased processing power for both industrial and personal uses. Moore's law expects the miniaturization of circuits to the atomic level in ten or twenty years, and molecular circuitry is the next logical step for present-day technological innovation. However, current challenges exist in finding the most efficient way to measure the molecular conductance experimentally, and also in the analysis of the physical factors contributing to the property.

In contrast with conventional electronics, molecular systems do not have precisely *[handwritten: not needed?]* measurable physical properties. The workings of quantum electron transport as well as small changes in particular parameters contribute to variation in tests. The molecule can be thought of as a collection of channels *where* there are a finite number of channels within the molecular system that can be used for transmission of electron charges. These channels have varying states of

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conductance ranging from zero (closed) to one (open). A conductance of zero means no electron transport, while a value of one means 100% chance of transport. The quantum of conductance, G_0, is defined

$$G_0 = \frac{2e^2}{h} \tag{1}$$

Quantum Conductance

where e is the electron charge and h is Planck's constant, is the constant associated with a channel that has a conductance of one. That is, the "one" indicates a channel conductance of one quantum of conductance. The conductance of the single molecule is then the sum of all the constituent conductances of the channels. Note that because of the variation in conductance of a single channel, total conductance of the molecule is not necessarily an integer multiple of the quantum.

The variability of the limited number of channels due to physical junction contact differences then creates significant uncertainty in stating an official value for conductance. The electric properties of a single molecule have also been repeatedly shown to be highly dependent on (currently?) electrode contact geometry. As there is no way to consistently replicate the arrangement for each measurement, methods such as the mechanically controllable break junction (MCBJ) and the scanning tunneling microscope (STM) break junction have been employed in order to make large amounts of measurements for study. The general break junction method essentially involves pulling a contact, which can be the tip of a scanning microscope among other things, away from the substrate and monitoring current.

When applying the break junction method

Eventually, only a single molecule will cling to the tip, and further retraction will result in the circuit breaking. The measured current all the way down to the single molecule can thus theoretically be determined, yielding the conductance value.

Conductance Histograms

Large amounts of data are necessary to account for the variations in contact geometry, so conductance histograms, as shown in Figure 1, are a common way for experimental studies to characterize the conductance of the system. Experimental techniques, such as STM or MCBJ, are performed thousands of times to generate large amounts of conductance data, and the properties are then be determined statistically. After compiling the data into the histogram, there is much debate on how ~~analysis should be done on it, but~~ In general, the peak is ~~interpreted as~~ the "expected" conductance. Extensive work has been done in modeling the line shape of the histogram using distributions such as double beta, log-normal, normal, and Lorentzian. The peak width depends on chemistry and structure of the molecule, especially on electrode contact geometry.
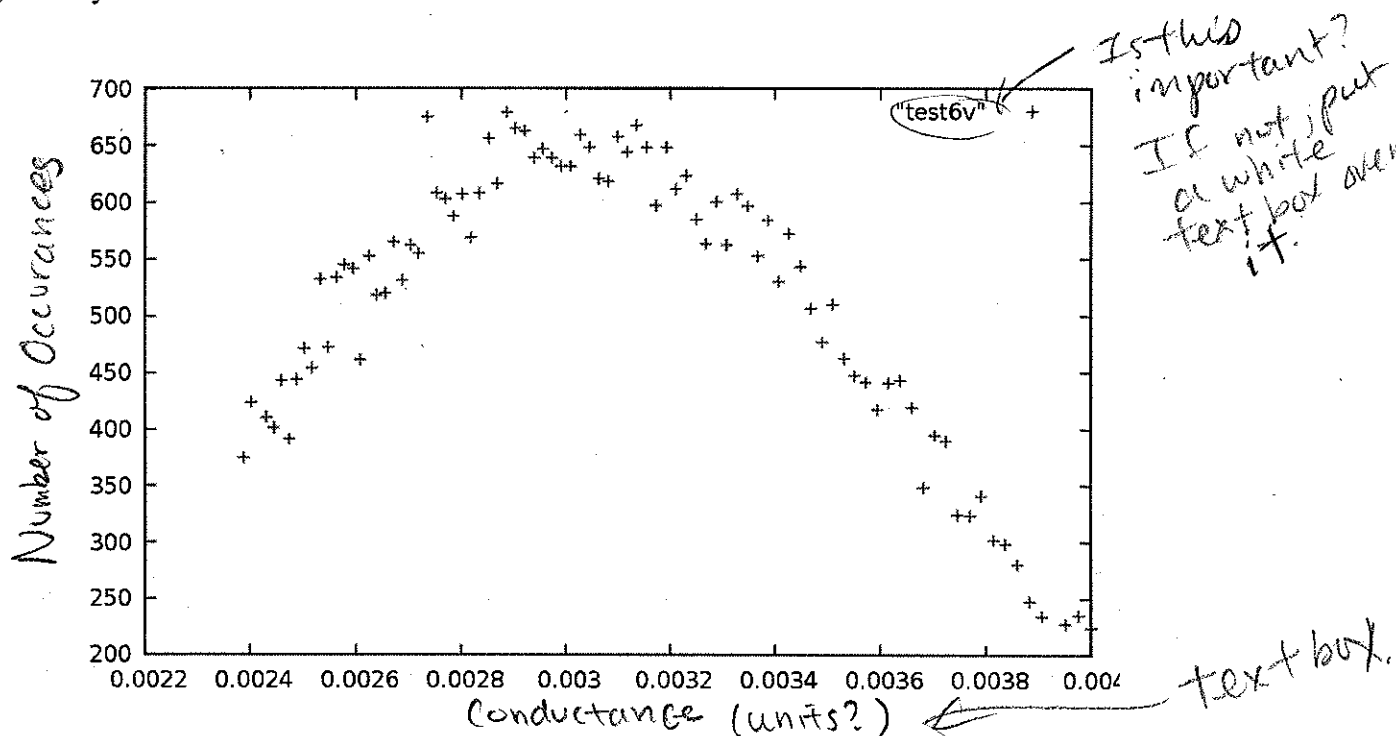
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Figure 1. A typical one-dimensional conductance histogram, with conductance on the x-axis and number of occurrences on the y-axis. ~~Note the peaking, here at around 0.003.~~

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Developments in 2011 by S. Guo et al. involved a new experimental method that gave a new [*different?*] dimension to the conductance analysis with measurements of current-voltage, conductance-voltage, and transition voltage histograms. The addition of the voltage, or *bias*, factor still confirmed conductance for alkanedithiols and biphenyldithiol, at least at low values. In the new [*molecules commonly used in testing*] [*conductance?*] [*you say this later...*] technique, when a step is detected as the tip is moving away from the substrate, the tip is held still and voltages are swept for one cycle, meaning a range of voltages is applied and the variation in current data recorded. This allows the creation of I-V (current-voltage) and (G-V) (conductance-voltage) graphs for each step, giving a two-dimensional view on the information of the step. The researchers' method confirmed values from literature at low biases but showed unexpected results for higher biases, which remain an open question. They also revealed that variation in molecular conductance is primarily due to contact resistance rather than changes in energy level alignment.

The field of study is ready for in-depth study on the effects of a high applied bias to the molecular system. In contrast to traditional conductance histograms which use an axis of conductance values versus an axis of number of times observed, two-dimensional G-V histograms relate voltage to conductance while preserving the frequency of the conductance using contour shading. [*In this research?*] An attempt is made to relate the additional physical parameter of bias voltage to its effects on changes in conductance data, along with the other meaningful physical information previously studied in the analytical model developed by P. D. Williams and M. G. Reuter such as the energy of the electron, the channel energy, the channel-electrode coupling, and the Fermi level.

II. Methods

Voltage-Dependent Electron Transport

Used in this project as a basis for mathematical calculation is the Landauer-Büttiker-Imry coherent scattering theory for electron transport. In this project, the key quantity is the transmission function,

$$T(E) = \frac{\Gamma^2}{(E-\varepsilon)^2 + \Gamma^2} \tag{2}$$

where E is the energy of the electron, ε is the channel energy, Γ is the channel-electrode coupling (assuming channel couples symmetrically to both electrodes), and T is the transmission of the electron. The current is then given by

$$I(V) = \frac{2e}{h} \int_{-\infty}^{\infty} dE\, T(E;V) \left[f_L(E;V) - f_R(E;V) \right] \tag{3}$$

where I is the current, V is the applied bias, ~~e is the electron charge, h is Planck's constant~~, and f_L and f_R are the Fermi functions of the left and right electrodes respectively. $T(E)$, in principal, depends on V which makes it possible to relate the transmission and thus conductance to the bias in this model.

For simplicity, this model is assumed to be operating at zero temperature, which eliminates any inelastic effects, allowing for use of the Landauer-Büttiker-Imry formalism. In this limited-temperature case,

$$f_L(E;V) \to \Theta(-E + E_F + \eta eV) \tag{4}$$

$$f_R(E;V) \to \Theta(-E + E_F + (\eta - 1)eV) \tag{5}$$

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where Θ is the Heaviside step function, E_F is the Fermi energy of the system, and $0 \leq \eta \leq 1$ controls the relative voltage drop at each of the electrode-channel interfaces. As written, $\eta = 0$ means all voltage drops at the right electrode and $\eta = 1$ means all voltage drops at the left. $\eta = 0.5$ would then indicate symmetric voltage drops, which are special points of interest for generalizations since this project aims to fit a symmetric histogram. Then, from Equation (3),

$$I(V) = \frac{2e}{h} \int_{-\infty}^{\infty} dE\, T(E;V) \left[\Theta(-E + E_F + \eta eV) - \Theta(-E + E_F + (\eta - 1)eV) \right]$$

$$= \frac{2e}{h} \int_{E_F+(\eta-1)eV}^{E_F+\eta eV} dE\, T(E;V) \tag{6}$$

Finally, looking at the differential conductance, $g(V)$,

$$g(V) \equiv \frac{\partial}{\partial V} I(V)$$

$$= \frac{2e}{h} \int_{-\infty}^{\infty} dE \left\{ \frac{\partial}{\partial V} T(E;V)[\Theta(-E + E_F + \eta eV) - \Theta(-E + E_F + (\eta - 1)eV)] \right.$$

$$\left. + T(E;V)[\eta e \delta(-E + E_F + \eta eV) + (1 - \eta)e\delta(-E + E_F + (\eta - 1)eV)] \right\}$$

$$= \frac{2e^2}{h} [\eta T(E_F + \eta eV; V) + (1 - \eta)T(E_F + (\eta - 1)eV; V)]$$

$$+ \frac{2e}{h} \int_{E_F+(\eta-1)eV}^{E_F+\eta eV} dE\, \frac{\partial}{\partial V} T(E;V) \tag{7}$$

And in the limit $V \to 0$, a common expression is verified:

$$g(0) = \frac{2e^2}{h} T(E_F; 0) \tag{8}$$

which, substituting the quantum of conductance,

$$g(0) = G_0 T(E_F; 0) \qquad (9)$$

gives the basic equation used for calculating conductance at zero-bias and zero temperature.

Implementation into Code – Simulating Conductance Data

Equation (7) provides the differential conductance through a system with a particular level energy (ε), coupling strength (Γ), and bias drop symmetry (η). In real experiments, each time the measurement is taken, these values change slightly due to the aforementioned quantum effects, and to simulate this effect, each of these parameters is considered to be a randomized variable. Each simulated experimental measurement is created from a statistical distribution (the normal distribution is used for simplicity): ε comes from a normal distribution with mean ε_0 and standard deviation δ_ε and Γ comes from a normal distribution with mean Γ_0 and standard deviation δ_Γ. The many experiments are then simulated (in this project, one million runs are simulated each time for an significant distribution) by choosing sets of parameters and calculating conductances by plugging into the derived equation (7). ~~Screenshot 1 in the appendix~~ *Appendix 1* shows the equation implemented into the code with voltage-independent functions.

The code written uses standard input to enter a series of values for the mentioned variables into the simulator program. One of the inputs specifies the model, since three different models of varying complexity are included in the program. The simplest model, the "i" model, neglects a mathematically complicated integral (the latter part of Equation (7)) and generates voltage-independent conductance data, that is, ε does not depend on V. The "s" model attempts to utilize the integral by making ε linearly dependent on V, allowing the integral to be solved. The "d" model is the most complex and involves two conductance "sites", as if there were two molecules linked together between the electrodes. It essentially involves shifting the two ε values for the

two sites in opposite directions, both linearly related to V, and hence solves the integral in a different way from the "s" model. Our full array of self-explanatory inputs is depicted in Table 1, and screenshot 2 of the Appendix 2 gives more context. After the simulator outputs a list of paired voltage and conductance data, a binner is used to organize the raw data into a format that can be drawn as a two-dimensional histogram. An example of some of the data is shown in Table 2. This data is then stored into a data file named with the parameters for graphing, as shown in screenshot 3 of the Appendix 3. Finally, OriginPro (company) was used to visualize the two-dimensional histograms.

Table 1. Definitions of the parameters prompted for while running the simulator.

Parameter	Definition
model	Model "i", "s", or "d"
n	Number of trials
EF	Fermi level (eV)
depsilon	Standard deviation in site level energy (eV)
epsilon0	Average site level energy (eV)
dgamma	Standard deviation in the coupling (eV)
gamma0	Average coupling for one electrode (eV)
Vmin	Lower bound of the applied bias range (eV)
Vmax	Upper bound of the applied bias range (eV)
eta	Relative voltage drop for one electrode

Table 2. The data file generated takes the form of bias, conductance, relative probability of occurrence. Binning changes one million runs into ten thousand of these data sets.

| Bias (V)	Conductance	Probability	Bias (V)	Conductance	Probability	Bias (V)	Conductance	Probability
-1.98E+00	-3.19E+00	0.00E+00	-1.86E+00	-2.47E+00	9.29E-01	3.00E-01	-2.69E+00	9.61E-01
-1.98E+00	-3.18E+00	0.00E+00	-1.86E+00	-2.45E+00	9.21E-01	3.00E-01	-2.68E+00	9.42E-01
-1.98E+00	-3.17E+00	0.00E+00	-1.86E+00	-2.48E+00	9.14E-01	3.00E-01	-2.65E+00	9.42E-01
-1.98E+00	-3.16E+00	0.00E+00	-1.86E+00	-2.46E+00	8.91E-01	3.00E-01	-2.70E+00	9.02E-01
-1.98E+00	-3.15E+00	0.00E+00	-1.86E+00	-2.44E+00	8.76E-01	3.00E-01	-2.67E+00	9.02E-01
-1.98E+00	-3.14E+00	0.00E+00	-1.86E+00	-2.49E+00	8.65E-01	3.00E-01	-2.71E+00	9.01E-01
-1.98E+00	-3.13E+00	0.00E+00	-1.86E+00	-2.50E+00	8.31E-01	3.00E-01	-2.66E+00	8.54E-01
-1.98E+00	-3.12E+00	0.00E+00	-1.86E+00	-2.43E+00	8.26E-01	3.00E-01	-2.63E+00	8.07E-01
-1.98E+00	-3.11E+00	0.00E+00	-1.86E+00	-2.42E+00	7.82E-01	3.00E-01	-2.73E+00	8.01E-01
-1.98E+00	-3.10E+00	0.00E+00	-1.86E+00	-2.41E+00	7.37E-01	3.00E-01	-2.64E+00	7.95E-01

III. Results
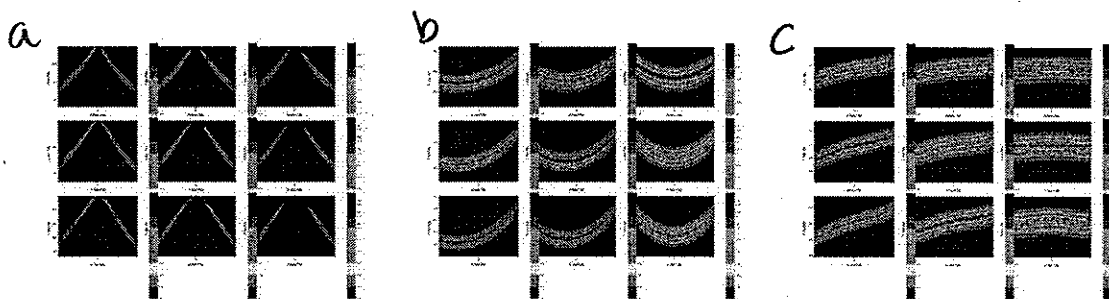
Figure 2. Two-dimensional conductance histograms for the d model with varying values for ε (particular level energy) ~~from left to right,~~ a) -3 eV, b) -6.5 eV, and c) -10 eV.
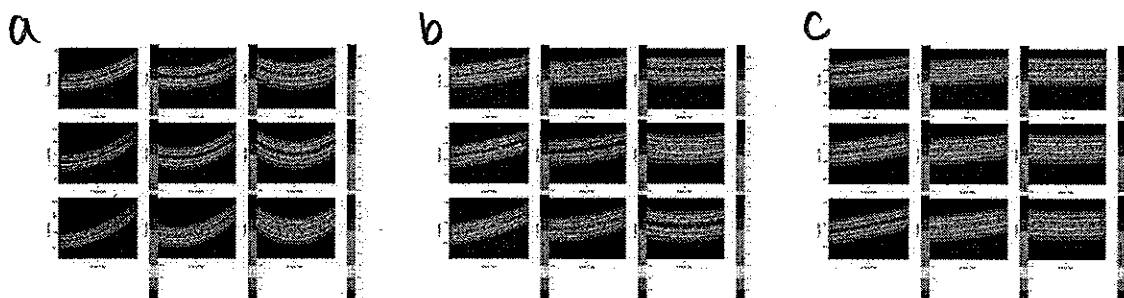

Figure 3. Two-dimensional conductance histograms for the i model with varying values for Γ (coupling strength) ~~from left to right,~~ a) -3 epV, b) -6.5 eV, and c) -10 eV.
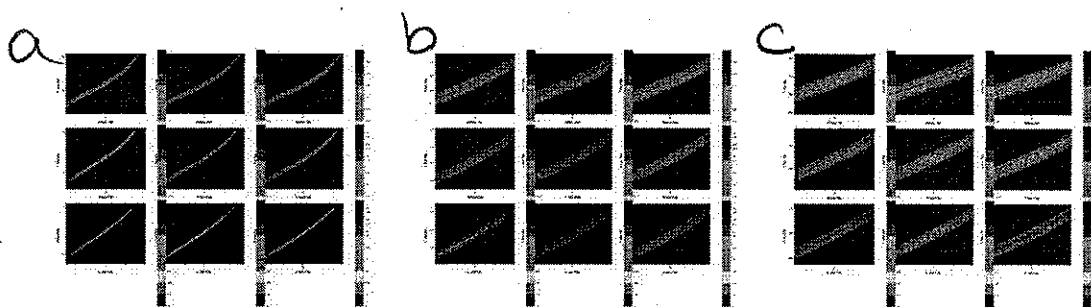

Figure 4. Two-dimensional conductance histogram for the s model with varying values for ε (particular level energy) ~~from left to right,~~ a) -3 eV, b) -6.5 eV, and c) -10 eV.