Solving rate equations for electron tunneling via discrete quantum states

Edgar Bonet, Mandar M. Deshmukh, and D. C. Ralph
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, NY, 14853
(Dated: March 22, 2022)

We consider the form of the current-voltage curves generated when tunneling spectroscopy is used to measure the energies of individual electronic energy levels in nanometer-scale systems. We point out that the voltage positions of the tunneling resonances can undergo temperature-dependent shifts, leading to errors in spectroscopic measurements that are proportional to temperature. We do this by solving the set of rate equations that can be used to describe electron tunneling via discrete quantum states, for a number of cases important for comparison to experiments, including (1) when just one spin-degenerate level is accessible for transport, (2) when 2 spin-degenerate levels are accessible, with no variation in electron-electron interactions between eigenstates, and (3) when 2 spin-degenerate levels are accessible, but with variations in electron-electron interactions. We also comment on the general case with an arbitrary number of accessible levels. In each case we analyze the voltage-positions, amplitudes, and widths of the current steps due to the quantum states.

PACS numbers: 73.22.-f, 73.23.Hk, 74.80.Bj

I. INTRODUCTION

Nanometer-scale single-electron tunneling transistors can now be fabricated in which electron flow occurs through a discrete spectrum of well-resolved quantum states. This has been achieved in devices incorporating semiconducting quantum dots, metal nanoparticles, and molecules. In a transistor geometry, the source-drain voltage \(V\) and the gate voltage \(V_g\) can be adjusted to achieve the simplest case that electron flow occurs just through a single quantum state. As \(V\) and \(V_g\) are changed, additional excited electronic states may also become energetically accessible for tunneling, providing alternative channels for current flow. In this regime, the tunneling processes can become quite complicated, due to the many combinations of non-equilibrium states that may be excited during tunneling, and the possibility of relaxation between these states.

As long as the tunnel-barrier resistances are much greater than \(h/e^2\) and internal relaxation is negligible, the currents traveling via any number of energetically-accessible states can be analyzed in a sequential-tunneling picture using a rate-equation approach. The general procedure for completing this type of analysis has been outlined previously, for example in Ref. 3,4.

Our purpose in this paper is to present the solutions of this model for selected simple cases important for analyzing experiments on non-magnetic islands, and we describe several previously-unappreciated consequences of the model that explain recent observations. Whenever more than a single (non-spin-degenerate) quantum state is accessible for tunneling, we show that the voltage-positions of the tunneling resonances can become temperature dependent (shifting proportional to \(T\)). For the important case of tunneling via one spin-degenerate quantum state, we derive the full form of the tunneling current as a function of \(V\), \(V_g\), and \(T\). This provides simple exact solutions for the voltage shift, resonance width, and current amplitude, thereby improving upon an approximate approach used previously. When multiple spin-degenerate states participate in tunneling, effects of non-equilibrium excitations and variations in electron-electron interactions can lead to additional shifts and broadening of the tunneling resonances. The computer code which we use for calculating the tunneling current in the general case with an arbitrary number of accessible quantum states is available electronically in both Mathematica and C formats at http://www.ccmr.cornell.edu/~ralph/.

This paper is organized as follows: In section II we review the general procedure for calculating tunneling currents in the rate-equation approach. We discuss the physical assumptions under which this approach is accurate, and we explain our notation. In section III, we solve the simplest non-trivial case, in which current flow occurs by means of tunneling via a single spin-degenerate quantum level. In section IV we then extend this discussion to the case of tunneling via 2 or more spin-degenerate levels, and we describe several experimentally-relevant consequences of the rate-equation model for an arbitrary number of accessible states. In section V, we consider effects of fluctuations in electron-electron interactions that can occur when current flow generates non-equilibrium electronic states, and we explain how these effects can produce additional shifts and can also broaden the measured tunneling resonances.

II. RATE-EQUATION CALCULATIONS OF CURRENT FLOW

We are interested in calculating the tunneling current via a non-magnetic single-electron transistor in the regime where the discrete quantum states in the transistor island are well resolved. The circuit under consideration is shown in Fig. 2 which illustrates the definitions of the bias voltage \(V\) and the gate voltage \(V_g\). We will limit our discussion to the conditions under which the
energy levels are best resolved: (a) $k_B T$ is smaller than the level spacing, (b) the level spacing is much smaller than the Coulomb charging energy of the transistor island $e^2/(2C_S)$, where $C_S$ is the total capacitance of the island, (c) the tunnel barriers have resistances $\gg \hbar/e^2$ so that cotunneling processes may be neglected and the tunneling current is accurately described by lowest-order perturbation theory, and (d) $k_B T$ is larger than the intrinsic lifetime broadening of the quantum states. In parts of the discussion, in order to simplify the notation, we will also assume that electron interactions are sufficiently weak that many-body eigenstates $|\alpha\rangle$ are well-approximated as single Slater-determinants specified by the occupation of a set of single-electron states $i$: $|\alpha\rangle = \{n_i\}$. Our primary goals are to study the effects on current flow of non-equilibrium electronic excitations and electron-electron interactions. Non-equilibrium excitations can be suppressed when the rate of internal relaxation within the transistor island is large compared to the tunneling rate. However, measurements on metal nanoparticles indicate that the relaxation rate is generally comparable to or slower than the tunneling rate in realistic samples. Therefore we will generally neglect internal relaxation effects entirely, limiting ourselves to noting the ways in which internal relaxation will produce qualitative changes to the results.

### A. Energy of the eigenstates

In general, the quantum-mechanical electronic states within the transistor island can be complicated correlated many-electron eigenstates. The energy of any state can be written as a sum of three terms:

$$E = E_C + E_K + E_J,$$

the terms being respectively the electrostatic or “Coulomb” energy, the kinetic energy, and the fluctuations in the electron-electron interactions. Notice that the mean-field contribution of the electron-electron interactions is the same as the electrostatic energy $E_C$. Therefore $E_J$ accounts only for the level-to-level fluctuations in these interactions.

1. **Electrostatic energy**

The electrostatic energy will in general depend on the charge of the island as well as on the applied voltages $V$ and $V_g$. However, what matters for calculations of electronic transport are energy differences as electrons make transitions between the transistor island and the leads. We can select our zero of energy (or, equivalently, the reference electrostatic potential) for convenience, and we will do so in a way that makes the energy of the eigenstates on the island independent of $V$ and $V_g$. The consequence is that the Fermi energies in the leads will shift with $V$ and $V_g$. To be specific, we choose the reference electrostatic potential such that $\sum_k C_k \phi_k = 0$, where $C_k$ and $\phi_k$ are the capacitance of the island to the $k$-th lead and the electric potential of the $k$-th lead, and the sum extends over the three leads. Using this reference, the charge $Q$ in the island is related to its potential $\phi$ by $Q = C_S \phi$. In calculating the energy required for a tunneling transition, we must consider the work done. The tunneling of charges $\delta Q_l$ and $\delta Q_r$ from the island to the left and right leads requires a work

$$\delta W = (\phi_l - \phi)\delta Q_l + (\phi_r - \phi)\delta Q_r$$

and the effective Fermi energies of the leads can be written as $E_{Fl}^e = e\phi_l$, where $e$ is the electron charge, including its sign. To be explicit,

$$E_{Fl}^e = eC_r + eC_g V - eC_g V_g$$

$$E_{Fr}^e = -eC_r + eC_g V - eC_g V_g.$$

Since the charge of the island varies only by multiples of $e$, we can write it as $Q = Q_0 + Ne$ where $Q_0$ is a background charge and $N$ the number of electrons in the island. The electrostatic energy is then

$$E_C = \frac{1}{2C_S} (Q_0 + Ne)^2.$$

This is minimized when $N$ is the integer closest to $-Q_0/e$. Throughout this paper, we will assume that the Coulomb energy is much larger than the level spacing so that only the two lowest-energy values for $N$, namely $N_0$ and $N_1 = N_0 + 1$, are permitted during the process of current flow. This assumption allows us to take the electrostatic energy.
to be proportional to $N$: since $[N - (N_0 + N_1)/2]^2 = 1/4$ is a constant, $E_C$ for $N_0$ or $N_1$ electrons can be rewritten, to within a constant, as

$$E_C = N \frac{e}{C_\Sigma} \left( Q_0 + \frac{N_0 + N_1 e}{2} \right) \quad (6)$$

Notice that Eq. (6) explicitly includes the Coulomb energy which forbids states not having $N_0$ or $N_1$ electrons, but this is implicit in Eq. (3). The condition $N = N_0$ or $N_1$ has therefore to be assumed explicitly when using Eq. (6).

2. Kinetic energy

The kinetic energy of the electrons in the island can be written

$$E_K = \sum_i \epsilon_i^K n_i \quad (7)$$

where $\epsilon_i^K$ is the energy, relative to the Fermi level, of spin-degenerate single-electron quantum state $i$, and $n_i$ is the occupancy of this level (either 0, 1, or 2).

Since $N = \sum_i n_i$, the sum of the electrostatic and kinetic energies is just

$$E_{CK} = \sum_i \epsilon_i n_i \quad (8)$$

where $\epsilon_i$ is defined by

$$\epsilon_i = \epsilon_i^K + \frac{e}{C_\Sigma} \left( Q_0 + \frac{N_0 + N_1 e}{2} \right). \quad (9)$$

Writing the effective energy of the single-electron states in this way allows a simple accounting of the average Coulomb energy in the calculations.

In the absence of variations in electron-electron interactions between electrons in different energy levels, the energy of the island is just $E_{CK}$. With our conventions, the threshold voltages required for the onset of a tunneling process can be pictured with simple energy diagrams, as illustrated in Fig. 2. For example, at $T = 0$, electrons can tunnel from lead $k$ into the island if the island is a $N_0$-electron state and Fermi energy $E_F^{k}$ of lead $k$ is above the energy $\epsilon_i$ of a non-fully occupied level. In the same way, electrons can tunnel out of the island into lead $k$ if the island is in a $N_1$-electron state and $E_F^{k}$ is below the energy of a non-empty state. The onset of the current is associated with the first level available for tunneling, i.e. the lowest-energy non-full level in the $N_0$-electrons ground state or the highest-energy non-empty level in the $N_1$-electrons ground state. As $V$ is ramped for a fixed value of $V_g$, the Fermi energy in a lead can sweep past the energy required to initiate tunneling via an eigenstate, producing a stepwise change in current. The voltage-position, width, and current-amplitude of this step are the quantities that we will analyze. It is important to note that as $V$ is increased, more than one spin-degenerate quantum level can contribute to tunneling even at the initial onset of current flow. One example of this case is illustrated by Fig. 2(a). The first allowed tunneling transition is for an electron to enter the level with energy $\epsilon_d$ from the right electrode. However, after this electron has tunneled in to give a total of $N_1$ electrons on the island, transitions to the left electrode can occur either from the state with energy $\epsilon_d$ or from the lower-energy occupied state depicted in Fig. 2(b). If an electron tunnels out of the lower-energy state, subsequent tunneling transitions from the right electrode can involve either quantum level. Therefore, calculations of current for this situation must include tunneling processes occurring via both levels.

It is possible to have current flow at vanishing $V$ if the Fermi energy of both leads is aligned with the first level available for tunneling. The gate voltage that realizes this condition is called degeneracy point and is defined by

$$V_g^0 = -\frac{C_\Sigma}{e C_g} \epsilon_d \quad (10)$$

where $\epsilon_d$ is the energy of this particular level.

3. Variations in electron-electron interactions

In the presence of variations in electron-electron interactions between electrons in different energy levels, the energy of the island has the extra term

$$E_J = J(\{n_i\}) \quad (11)$$

Eq. (11) can be interpreted as an expansion of the energy of the system around the ground state: the second term is the part of $E$ that is linear in $\{n_i\}$, the first term is the
the energy required to remove an electron from that level.

Notice that this is only defined if \( n_i < 2 \). In the same way, the energy of a non-empty energy level in a \( N_1 \) state can be defined as minus the energy required to remove an electron from that level.

### B. Steady-state occupation probabilities

Because of the influence of the Coulomb charging energy, even in the simplest cases that we will consider the occupation probability for a given many-body state \( |\alpha\rangle = \{n_i\} \) of the particle cannot be factorized as the product of occupancy probabilities for each single-electron level.

Therefore we have to solve the full rate-equation problem where the occupation probability of each many-body state is treated as an independent variable.

The evolution of the occupation probability of state \( |\alpha\rangle \) is given by:

\[
\frac{dP_\alpha}{dt} = \sum_\beta (\Gamma_{\beta \rightarrow \alpha} P_\beta - \Gamma_{\alpha \rightarrow \beta} P_\alpha)
\]  

(13)

where \( \Gamma_{\alpha \rightarrow \beta} \) is the transition rate from state \( |\alpha\rangle \) to state \( |\beta\rangle \).

This can be written in matrix form as

\[
\frac{dP}{dt} = \Gamma \cdot P
\]

(14)

with the following coefficients for the matrix \( \Gamma \):

\[
\Gamma_{\alpha \beta} = \Gamma_{\beta \rightarrow \alpha} \quad \text{if} \quad \alpha \neq \beta
\]

(15a)

\[
\Gamma_{\alpha \alpha} = - \sum_{\beta \neq \alpha} \Gamma_{\alpha \rightarrow \beta}
\]

(15b)

We do not consider cotunneling or internal relaxation in the particle. Therefore, the only states that are coupled together are states that have the same occupancy for all the levels, except one electron difference in one level. Let’s assume that states \( |\alpha\rangle \) and \( |\beta\rangle \) differ only by \( |\beta\rangle \) having one extra electron in level \( i \). Then

\[
\Gamma_{\alpha \rightarrow \beta} = \gamma_i^\prime f(\epsilon_i^\prime - E_i^F) (2 - n_i)
\]

(16a)

\[
+ \gamma_i f(\epsilon_i - E_i^F) (2 - n_i)
\]

\[
\Gamma_{\beta \rightarrow \alpha} = \gamma_i^\prime (1 - f(\epsilon_i^\prime - E_i^F)) n_i
\]

(16b)

\[
+ \gamma_i (1 - f(\epsilon_i - E_i^F)) n_i
\]

where

\[
f(x) = 1/(1 + \exp(x/k_BT))
\]

(17)

### C. Current

Once the occupation probabilities for each state \( |\alpha\rangle \) are determined at given values of \( V \) and \( V_g \), then the current can be calculated either through the right tunnel barrier or through the left barrier. In the steady state these two currents are equal. The current through the left barrier is

\[
I_l = |e| \sum_\alpha \sum_\beta \Gamma_{\alpha \rightarrow \beta} P_\alpha
\]

(18)

where \( \Gamma_{\alpha \rightarrow \beta} \) is the contribution of the left lead to \( \Gamma_{\alpha \rightarrow \beta} \), multiplied by +1 or -1 depending on whether the \( \alpha \rightarrow \beta \) transition gives a positive or negative contribution to the current.

In order to get a feeling of the physics that will come out of this rate-equation model, in the rest of the paper we will consider selected examples that are simple enough to be solved by hand, yet have the basic ingredients of the complete problem.

### III. ONE SPIN-DEGENERATE LEVEL ACCESSIBLE

#### A. General formula

Consider the situation represented in Fig. 3 where only one spin-degenerate energy level, with energy \( \epsilon_1 \), is accessible for tunneling and (on account of the large Coulomb energy) it can be occupied by either zero or one electron, but not two. If we call

\[
f_r = f(\epsilon_1 - E_i^F)
\]

(19a)

\[
f_l = f(\epsilon_1 - E_i^F)
\]

(19b)
the occupation probabilities are for the tunneling-in and tunneling-out transitions. Then, \( C_l = C_t \) and \( \gamma_l = 4 \gamma_r \). The bias voltage is plotted in units of \( k_B T/|e| \). The current is in units of \( |e| \gamma_0 \) where \( \gamma_0 = \gamma_\| \gamma_r / (\gamma_l + \gamma_r) \). The reduced gate voltage \( v_g = |e| C_g (V_g - V_g^0) / C_2 k_B T \) is 0, -3 or -6.

and \( N = 0 \) or \( 1 \) the state with \( N \) electrons, the transition rates are

\[
\begin{align*}
\Gamma_{0 \rightarrow 1} &= 2 \gamma_r f_r + 2 \gamma_l f_l \\
\Gamma_{1 \rightarrow 0} &= \gamma_r (1 - f_r) + \gamma_l (1 - f_l) 
\end{align*}
\]

(20a)

(20b)

for the tunneling-in and tunneling-out transitions. Then, the occupation probabilities are

\[
\begin{align*}
P_1 &= \frac{\Gamma_{0 \rightarrow 1}}{\Gamma_{0 \rightarrow 1} + \Gamma_{1 \rightarrow 0}} = \frac{2 \gamma_r f_r + 2 \gamma_l f_l}{\gamma_r (1 + f_r) + \gamma_l (1 + f_l)} \\
P_0 &= \frac{\Gamma_{1 \rightarrow 0}}{\Gamma_{0 \rightarrow 1} + \Gamma_{1 \rightarrow 0}} = \frac{\gamma_r (1 - f_r) + \gamma_l (1 - f_l)}{\gamma_r (1 + f_r) + \gamma_l (1 + f_l)}
\end{align*}
\]

(21a)

(21b)

and the current through the left lead in the steady state is

\[
I = |e| (\gamma_l (1 - f_l) P_1 - 2 \gamma_l f_l P_0) = 2 |e| \frac{\gamma_r \gamma_l (f_r - f_l)}{\gamma_r (1 + f_r) + \gamma_l (1 + f_l)}. 
\]

(22)

This expression differs from an approximate form used in Ref. 10 to analyze tunneling data.

We can plot the current as a function of the applied voltages by replacing \( f_k \) by their definitions in Eqs. (12) and \( E_k^F \) by the expressions in Eqs. (6). Fig. 4 shows the current steps as a function of the bias voltage when the gate voltage is first equal to the degeneracy point, then is tuned away from it.

B. High bias limit

If the level spacing is very large compared to \( k_B T \), there is an interesting regime in which \( V \) is substantially bigger than \( k_B T / |e| \) yet only one level is involved in the current transport. The limiting current in this case is bias-independent and can be obtained from Eq. (22) by setting \( f_r = 1 \) and \( f_l = 0 \) (positive bias) or \( f_l = 1 \) and \( f_r = 0 \) (negative bias). For these two cases we have respectively:

\[
\begin{align*}
I_+ &= 2 |e| \frac{\gamma_r \gamma_l}{2 \gamma_r + \gamma_l} \\
I_- &= -2 |e| \frac{\gamma_r \gamma_l}{\gamma_r + 2 \gamma_l}. 
\end{align*}
\]

(23a)

(23b)

These expressions give different heights for the positive and negative current steps. Measuring these heights can therefore allow an experimental determination of both \( \gamma_r \) and \( \gamma_l \). Note that this is in contrast with the case in which tunneling occurs through a single level that is not spin degenerate. In that case

\[
I_1^\pm = \pm |e| \frac{\gamma_r \gamma_l}{\gamma_r + \gamma_l} 
\]

(24)

for both bias directions, so that \( \gamma_r \) and \( \gamma_l \) can not be determined separately.

In the limit of barriers with very different tunneling rates (which can be experimentally relevant if the barrier thickness is not well controlled), the current depends only on the smaller \( \gamma \). For example, if \( \gamma_l \gg \gamma_r \), then \( I_+ = 2 |e| \gamma_l \) and \( I_- = -|e| \gamma_r \). The factor of 2 in \( I_+ / I_- \) arises from the difference in the number of spin states accessible for tunneling for the rate-limiting transition across the right barrier.

C. Position and width of the current step

Next we consider the case depicted in Fig. 5 in which \( V_g \) is adjusted away from the degeneracy point so that at the threshold \( V \) for tunneling only the effective Fermi energy in the right electrode is close to \( \epsilon_1 \), while the Fermi energy of the left electrode is at a much lower energy. That is, we will assume \( f_l = 0 \). Using this assumption, after some algebra Eq. (22) becomes

\[
I = I_+ f \left( \epsilon_1 - E_r^F - k_B T \ln \frac{2 \gamma_r + \gamma_l}{\gamma_r + \gamma_l} \right). 
\]

(25)

Even though both spin-states of the quantum level contribute to tunneling, we can see in this expression that the current step has the shape of a simple Fermi function whose width is given by the electron temperature of
the leads. However, at non-zero temperature, the center of the step is shifted relative to its position at zero temperature. The shift is proportional to the temperature, vanishes if $\gamma_r \gg \gamma_l$, and has a maximum value of $k_B T \ln 2$ when $\gamma_r \gg \gamma_l$. Fig. 6 shows the shape of the conductance peak $dI/dV$ in the latter limit for three different temperatures.

There is a simple intuitive explanation of the shift in the limit $\gamma_r \gg \gamma_l$. The current threshold at zero temperature is given by $E_F^r = \epsilon_1$. At non-zero temperatures, when $E_F^r = \epsilon_1$, the Fermi occupancy probability is 1/2 for states in the right lead with energy $\epsilon_1$. In this case the transition rates are dominated by electrons tunneling back and forth from the right lead (since $\gamma_r \gg \gamma_l$):

\begin{align}
\Gamma_{0\rightarrow 1} &= \frac{1}{2} (2\gamma_r) \\
\Gamma_{1\rightarrow 0} &= \frac{1}{2} \gamma_r.
\end{align}

Here the factor 1/2 comes from the Fermi occupancy of the lead and the factor 2 in $\Gamma_{0\rightarrow 1}$ is from the spin degeneracy. This factor is only present for $\Gamma_{0\rightarrow 1}$ because electrons tunneling into the island see two empty states, while an electron tunneling out comes from a given spin state. It follows that when $E_F^r = \epsilon_1$ the probability that the island is in the 1-electron state is exactly two-thirds. Then the rate at which electrons tunnel to the left lead (the rate-limiting process determining the total current) is two-thirds of the maximum value. This can be seen directly in Fig. 6(a), or in Fig. 6(b) by the fact that two-thirds of the current (area under the peaks) lies left of $V - V_0 = 0$. This T-dependent shift in the apparent resonance position has been observed by Deshpande et al.\cite{Deshpande2005}.

**D. Zeeman splitting of the energy level**

In the presence of an applied magnetic field, the two spin states associated with a given orbital level are no longer degenerate, but split to give the energies $\epsilon_i^\pm = \epsilon_1 \pm g\mu_B H / 2$. If we call these states + and −, and $f_i^\pm = f(\epsilon_i^\pm - E_F^l)$, then the transition rates are

\begin{align}
\Gamma_{0\rightarrow \pm} &= \gamma_r f_i^+ + \gamma_l f_i^- \\
\Gamma_{\pm\rightarrow 0} &= \gamma_r (1 - f_i^+) + \gamma_l (1 - f_i^-).
\end{align}

Notice the absence of the factors 2 that were in Eqs. (27) due to the spin degeneracy. The occupation probabilities are

\begin{align}
P_0 &= \frac{1}{1 + \Gamma_{0\rightarrow \pm} / \Gamma_{\pm\rightarrow 0}} \\
P_{\pm} &= \frac{\Gamma_{0\rightarrow \pm}}{\Gamma_{\pm\rightarrow 0}} P_0
\end{align}

and the current through the left lead is

\begin{equation}
I = |e| \gamma_l \left( (1 - f_i^+) P_+ + (1 - f_i^-) P_- + (f_i^+ + f_i^-) P_0 \right)
\end{equation}

Figure 6 shows the effect of the magnetic field on the conductance peak at positive bias for a gate voltage below the degeneracy point (i.e. the case $f_i^\pm = 0$). The peak splits into two subpeaks of different weight. This asymmetry can be understood by noticing that the first subpeak carries a current given by Eq. (23) and the two peaks together give a total current given by Eq. (23).

Then the fraction of the total current carried by the first subpeak is just

\begin{equation}
\frac{I_i^+}{I^+} = \frac{2 \gamma_r + \gamma_l}{2 \gamma_r + 2 \gamma_l}.
\end{equation}

If $\gamma_r \gg \gamma_l$, this ratio is one and the second peak vanishes. On the other hand, if $\gamma_l \gg \gamma_r$, the peak splits into two subpeaks carrying the same current.

**IV. TWO LEVELS ACCESSIBLE**

Next consider the situation pictured in Fig. 8 where two spin-degenerate levels are accessible for tunneling and the number of electrons in these levels is $N = 2$ or 3. Because of Coulomb blockade, no current flow is possible until an electron can tunnel from the right electrode to state 1; however after this happens both states 1 and 2 can contribute to the current even at the initial current onset. Let $(n_1, n_2)$ be the state with $n_1$ electrons in level 1 and $n_2$ electrons in level 2 ($n_1 + n_2 = N$), let $P(n_1, n_2)$ be the probability of state $(n_1, n_2)$, and let $\gamma_i^k$ be the bare tunneling rate of level $i$ across barrier $k$. We will specialize immediately to the interesting case of positive bias (as pictured in Fig. 8) with the right barrier substantially
FIG. 7: Splitting of a conductance peak in a magnetic field. We assume \( f_0^\pm = 0, C_r = C_l, \) and \( \gamma_r = \gamma_l = \gamma. \) At zero temperature and zero field the peak occurs at \( V_0 = 2C_0(V_g - V_0^\delta)/C_2. \) The reduced field \( h = g\mu_B\mu_0H/(2k_BT) \) is 0, 3 or 6.

![Energy diagram for a case with two levels available for tunneling.](image)

FIG. 8: Energy diagram for a case with two levels available for tunneling.

We assume \( \Gamma = \Gamma_{uu} = \Gamma_{cc}. \) At zero temperature and zero field the peak occurs at \( V_0 = 2C_0(V_g - V_0^\delta)/C_2. \) The reduced field \( h = g\mu_B\mu_0H/(2k_BT) \) is 0, 3 or 6.

\[
\begin{pmatrix}
-2f\gamma_2 & 0 & 0 \\
0 & -\gamma_1 - f\gamma_2 & 0 \\
0 & 0 & -2\gamma_1 \\
2f\gamma_2 & \gamma_1 & 0 \\
0 & f\gamma_2 & 2\gamma_1
\end{pmatrix}
\begin{pmatrix}
\gamma_1 + (1 - f)\gamma_2 \\
2\gamma_1 - f\gamma_2 + 2(1 - f)\gamma_2 \\
0 \\
-\gamma_1 - (1 - f)\gamma_2 - 2\gamma_1 \\
0 - 2\gamma_1 - 2(1 - f)\gamma_2 - \gamma_1
\end{pmatrix}
\]

This matrix has the structure

\[
\Gamma = \begin{pmatrix}
\Gamma_{uu} & \Gamma_{uc} \\
\Gamma_{cu} & \Gamma_{cc}
\end{pmatrix}
\]

where \( \Gamma_{uu} \) and \( \Gamma_{cc} \) are diagonal blocks associated respectively with the \( N_0 \)-electron (uncharged) and \( N_1 \)-electron (charged) states. The cross-diagonal blocks are associated with the tunneling-out (\( \Gamma_{uc} \)) and tunneling-in (\( \Gamma_{cu} \)) events. This structure is preserved whatever number of levels are available for tunneling.

In the steady state, the solutions for the occupation probabilities are as follows:

\[
\begin{align*}
P(2, 1) & \ll 1 \\
P(1, 2) & \ll 1 \\
P(2, 0) & = \frac{1}{S} \\
P(1, 1) & = \frac{4fK}{S} \\
P(0, 2) & = \frac{f^2K^2}{S}
\end{align*}
\]

where \( K = \frac{2f\gamma_2}{\gamma_1} \) and \( S = 1 + 4fK + f^2K^2. \)

This inequality will simply be called \( f. \) These conditions correspond to line III in the data of Ref. 8.

Figure 8 shows the available transitions together with the corresponding transition rates. Since \( \gamma_1 \ll \gamma_i \) for \( i = 1, 2, \) the terms having a factor \( 1 - f \) can be neglected.

### A. Rate equation

The rate equation in this case has to describe eight possible transitions between five different states. It is therefore convenient to use the matrix notation of Eq. (14), which gives

\[
\frac{d}{dt} \begin{pmatrix} P(2, 0) \\ P(1, 1) \\ P(0, 2) \\ P(2, 1) \\ P(1, 2) \end{pmatrix} = \Gamma \begin{pmatrix} P(2, 0) \\ P(1, 1) \\ P(0, 2) \\ P(2, 1) \\ P(1, 2) \end{pmatrix}
\]

with

\[
\begin{pmatrix}
\gamma_1 + (1 - f)\gamma_2 \\
2\gamma_1 - f\gamma_2 + 2(1 - f)\gamma_2 \\
0 \\
-\gamma_1 - (1 - f)\gamma_2 - 2\gamma_1 \\
0 - 2\gamma_1 - 2(1 - f)\gamma_2 - \gamma_1
\end{pmatrix}
\]

### B. Current

Since we can neglect the tunneling-out transitions through the right barrier, we can calculate the current as the sum of the contributions of the tunneling-in events through this barrier:

\[
I = \frac{4\gamma_2K + 2\gamma_1^2K^2}{1 + 4fK + f^2K^2}.
\]

In Fig. 10 we compare this expression to the current we would have in the presence of infinitely fast relaxation in the island (state (1, 1) relaxing instantaneously to (2, 0)). In such a case electrons can only tunnel into the higher energy level in the island. Since the tunneling-in of electrons is the rate-limiting process, this situation is equiv-
The main effect of non-equilibrium states as illustrated in Fig. 10 is therefore to shift the current step to lower voltage. Although not exactly a Fermi function, the shape of the step described by Eq. (22) is very close to a Fermi function, shifted by $-1.79k_BT$ and widened by 8.5%. The shift can be understood as follows: When $E^F_r = \epsilon_2$, electrons tunneling to the upper level come from half-full states in the right lead. If the island is in a non-equilibrium state (1, 1) or (0, 2)), electrons can also tunnel to the lower level. Since these electrons come from full states in the lead, the current at $E^F_r = \epsilon_2$ is higher when these states are allowed, hence the shift.

The temperature dependence of the current step and the conductance peak in this two-level-accessible case with $\gamma_l \gg \gamma_r$ is shown in Fig. 11. Although the $T$-dependent shift looks very similar to the result for one level displayed in Fig. 8, the shift in Fig. 11 is of a different nature since it originates from non-equilibrium states. For the one-level-accessible case, there was no shift for positive bias with $\gamma_l \gg \gamma_r$. If we look at the opposite limit with two levels (positive bias $\gamma_l \ll \gamma_r$), the rate equation will be dominated by electrons tunneling back and forth between the right lead and the second level in the island. This situation is very similar to the one-level case and gives the current:

$$I = |e|(2\gamma^l_1 + \gamma^l_2)f(\epsilon_2 - E^F_r - k_BT \ln 2),$$

(36)

where the shift by $k_BT \ln 2$ is explained by the same argument as in the one-level case. The additional level therefore does not produce an additional shift when $\gamma_l \ll \gamma_r$.

If the voltages are tuned so that more than two levels are made available for tunneling-out transitions (by lowering $E^F_r$), or if the tunnel couplings to state 1 are greater than to state 2, then the shifting of the resonance away from the $T = 0$ position in the $\gamma_l \gg \gamma_r$ case will be enhanced beyond what is shown in Fig. 11. This shift will however remain proportional to $k_BT$.

We have also considered the case when $E^F_l$ is very high, so that many levels are accessible for an electron to tunnel into the island across the higher-resistance tunnel barrier, while $E^F_l$ remains fixed slightly below $\epsilon_1$. In such a situation the total tunneling-in transition rate will be proportional to the number of levels available for tunneling-in, and this rate can eventually become greater than the tunneling-out rate which will be roughly constant. In this case, tunneling through the left lead will eventually become the bottleneck process even if $\gamma_l \gg \gamma_r$, which allows one to estimate an average tunneling rate through the lower-resistance barrier even in the case of very asymmetric barriers.
V. TWO LEVELS ACCESSIBLE WITH VARIATIONS IN THE INTERACTIONS

In the presence of variations in electron-electron interactions, the energy thresholds for tunneling are different depending on whether the island is initially in a ground state or in an excited state. For example, in the case described in the previous section, this effect can make the energy required for the $(1,1) \rightarrow (1,2)$ transition different than the $(2,0) \rightarrow (2,1)$ transition. We can account for such variations by assigning a different energy to the upper level in the presence or absence of an excitation in the island. Namely, the energy of the upper level will be $\epsilon_2$ for the $(2,0) \rightarrow (2,1)$ transition and $\epsilon_2' = \epsilon_2 + \delta$ for the $(1,1) \rightarrow (1,2)$ transition. Here $\delta$ is a measure of the strength of the variations. In order to generalize the previous notation, we will call $f = f(\epsilon_2 - E_F^r)$ and $f' = f(\epsilon_2' - E_F^r)$.

The possible transitions are still described by Fig. 9 and the corresponding rate equations are the same as Eqs. (33) but with

$$\Gamma_{(1,1)\rightarrow(1,2)} = f'\gamma_2^r$$  \hspace{1cm} (37a)$$\Gamma_{(1,2)\rightarrow(1,1)} = 2\gamma_2 + 2(1-f')\gamma_2^r$$  \hspace{1cm} (37b)

which gives the current

$$I = |e|^2 \frac{(4\gamma_2^r K + 2\gamma_2^r K^2)f f' + (2\gamma_2^r + 4\gamma_2)ff'}{1 + 4fK + ff'K^2}.$$  \hspace{1cm} (38)

FIG. 12: Current steps for different interaction strengths. We assume $C_l = C_r$, $\gamma_1^r = \gamma_2^r = \gamma_r$, and $\gamma_1 = \gamma_2 = \gamma_r$, with $\gamma_1 \gg \gamma_r$. The “equilibrium” curve assumes infinitely fast relaxation in the island. The other curves assume no relaxation and $\delta/k_B T$ ranging (a) from 0 to -20 and (b) 0 to 6.

VI. CONCLUSIONS

We have solved the rate equations describing electron tunneling via discrete quantum states on a nanoscale island, for selected simple cases, under the assumption that rate for internal relaxation of excited electronic states is slower than the electron tunneling rate. Even the simplest case of tunneling via a single spin-degenerate energy level has some initially-surprising features. The magnitude of the maximum tunneling current can depend on the sign of the applied bias $V$, and the voltage-position of the resonance is temperature-dependent. When two spin-degenerate quantum levels are accessible for tunneling, the behavior is even richer because of the influence of non-equilibrium excitations on the island. The voltage-position of the resonance can undergo strong temperature-dependent shifts even in regimes (e.g., positive bias and $\gamma_I \gg \gamma_r$ noted above) where the one-level resonance positions do not depend on temperature. Understanding the variations in the strength of electron-electron interactions is critical in the non-equilibrium regime with two or more levels accessible. Such variations can produce additional shifts of resonance curves on top of the shifts noted previously, and they can also introduce extra steps into the current-voltage curves.

The methods we have described for determining tunneling currents are applicable to more than two levels, ranging from 0 to -20, and Fig. 12(b) shows $I$-$V$ curves when the non-equilibrium effect increases the tunneling energy. These plots were made for $\gamma_I^r = \gamma_2^r = \gamma_r$, $\gamma_1 \gg \gamma_r$, and $K = 1$. For negative $\delta$, the effect of the variation in electron-electron interactions is to produce an additional shift in the voltage-position of the current step, on top of the shift already described due to the non-equilibrium states. This additional shift is proportional to $|\delta|$ if $|\delta| \ll k_B T$ and becomes a constant on the order of $k_B T$ if $|\delta| \gg k_B T$. A shift of this sort has been observed in Fig. 3(b) of Ref. 8. For positive $\delta$, the effect of non-equilibrium is to produce an extra step in the $I$-$V$ curve at voltages larger than the position of the $\delta = 0$ current step.

As $V$ is increased so that more than two levels become energetically-accessible for tunneling, the ensemble of possible non-equilibrium excitations grows combinatorially, and each combination of excitations can produce a different shift for the tunneling resonance energies. Interactions which depend on the spin state of the island (neglected thus far) can produce further complications. The non-equilibrium excitations can produce a variety of effects depending on the ratio $\gamma_I/\gamma_r$, and on the magnitude of variations in electron-electron interactions. When the interaction-induced shifts are comparable to $k_B T$, they have been observed to produce an effective broadening of the observed conductance peaks.[4] For larger interactions, shifts due to non-equilibrium excitations have been resolved individually.[4]
but the analytic expressions become sufficiently complicated to be of limited usefulness. We have verified numerically that the results for additional levels are qualitatively similar to the two-level case. The computer codes we have used for calculating the general cases are available electronically at [http://www.ccmr.cornell.edu/~ralph/](http://www.ccmr.cornell.edu/~ralph/). These are useful, for instance, in extracting the rate-limiting bare tunneling rates from experimental data in which stepwise increases in current are measured as $V$ and $V_g$ are adjusted, so that the number of states accessible for tunneling increases one-by-one.

### VII. ACKNOWLEDGEMENTS

We thank Piet Brouwer, Abhay Pasupathy, Moshe Schechter, Jan von Delft, and Xavier Waintal for discussions. This work was supported by the NSF (DMR-0071631) and the Packard Foundation.

---

1. R. Ashoori, Nature 379, 413 (1996).
2. D. C. Ralph, C. T. Black, and M. Tinkham, Phys. Rev. Lett. 74, 3241 (1995).
3. D. H. Cobden, M. Bockrath, P. L. McEuen, A. G. Rinzler, and R. E. Smalley, Phys. Rev. Lett. 81, 681 (1998).
4. D. V. Averin, A. N. Korotkov, and K. K. Likharev, Phys. Rev. B 44, 6199 (1991).
5. C. W. J. Beenakker, Phys. Rev. B 44, 1646 (1991).
6. J. von Delft and D. C. Ralph, Physics Reports 345, 61 (2001).
7. O. Agam, N. S. Wingreen, B. L. Altshuler, D. C. Ralph, and M. Tinkham, Phys. Rev. Lett. 78, 1956 (1997).
8. M. M. Deshmukh, E. Bonet, A. N. Pasupathy, and D. C. Ralph, arXiv:cond-mat/0106024 (2001).
9. M. R. Deshpande, J. W. Sleight, M. A. Reed, R. G. Wheeler, and R. J. Matyi, Phys. Rev. Lett. 76, 1328 (1996).
10. L. I. Glazman and K. A. Matveev, JETP Lett. 48, 445 (1988).
11. M. R. Deshpande, J. W. Sleight, M. A. Reed, and R. G. Wheeler, Phys. Rev. B 62, 8240 (2000).
12. M. M. Deshmukh, S. Guéron, E. Bonet, A. N. Pasupathy, S. Kleff, J. von Delft, and D. C. Ralph (2001), submitted to Phys. Rev. Lett.
13. Technically, this is an enthalpy, since the work done by the voltage sources is not taken into account. The real energy of the field in the capacitors is $\frac{Q^2}{2C} + \sum_k \frac{\phi_k^2}{2\gamma_k}$.
14. The case in which one spin-degenerate level is accessible for tunneling, and the Coulomb energy permits an occupation of either 1 or 2 electrons (rather than 0 or 1) can be solved by exactly the same methods: $I = 2e\gamma_r(2 - f_r) + \gamma_l(2 - f_l)$.\[I = 2e\gamma_r(2 - f_r) + \gamma_l(2 - f_l).\]