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, New York 14853
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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 the 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 two spin-degenerate levels are accessible, with no variation in electron-electron interactions between eigenstates, and (3) when two 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.

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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.[1–3] 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 the current flow. In this regime, the tunneling processes can become quite complicated, due to the many combinations of nonequilibrium 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 Refs. 4–6. Our purpose in this paper is to present the solutions of this model for selected simple cases important for analyzing experiments on nonmagnetic 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 nonequilibrium excitations and variations in electron-electron interactions can lead to additional shifts and broadening of the tunneling resonances. The computer code that 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.[19]

This paper is organized as follows: In Sec. 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 Sec. III, we solve the simplest nontrivial case, in which current flow occurs by means of tunneling via a single spin-degenerate quantum level. In Sec. IV we then extend this discussion to the case of tunneling via two 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 Sec. V, we consider effects of fluctuations in electron-electron interactions that can occur when current flow generates nonequilibrium 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 nonmagnetic 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. 1, 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_BT is smaller than the level spacing, (b) the level spacing is much smaller than the Coulomb-charging energy of the transistor island $e^2/(2C_\Sigma)$, where C_Σ is the total capacitance of the island, (c) the tunnel barriers have resistances $\gg h/e^2$ so that cotunneling processes may be neglected and the tunneling current is accurately described by lowest-order perturba-

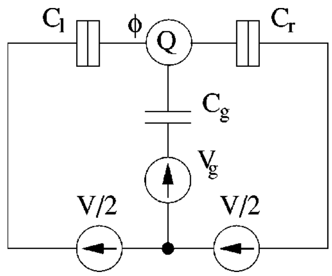

FIG. 1. Circuit schematic defining the bias voltage V, the gate voltage V_g, and the capacitances C_l, C_r, and C_g. ϕ and Q are the potential and the total charge of the island.

tion theory, and (d) k_BT 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: $|\alpha\rangle=\{n_i\}$. We neglect many-body effects associated with Fermi-edge singularities in electrodes with low-electron densities[7] and effects of coupling to phonons or local degrees of freedom, which can produce additional features in tunneling characteristics.[8–10] Under these approximations, the temperature enters our calculation only through the Fermi functions in the electrodes.

Our primary goals are to study the effects on current flow of nonequilibrium electronic excitations and electron-electron interactions. Nonequilibrium excitations can be suppressed when excited electronic states return back to the ground state at a rate that is fast compared to the electron 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.[11,12] 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

$$E=E_C+E_K+E_J, \tag{1}$$

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 $\Sigma_k C_k\phi_k=0$, where C_k and ϕ_k are the capacitance of the island to the kth lead and the electric potential of the kth lead, and the sum extends over the three leads. Using this reference, the charge Q in the island is related to its potential ϕ by $Q=C_\Sigma\phi$. In calculating the energy required for a tunneling transition, we must consider the work done. The tunneling of charges δQ_l and δQ_r from the island to the left and right leads requires a work

$$\delta W=(\phi_l-\phi)\,\delta Q_l+(\phi_r-\phi)\,\delta Q_r \tag{2a}$$

$$=\phi_l\delta Q_l+\phi_r\delta Q_r+\frac{1}{C_\Sigma}Q\,\delta Q \tag{2b}$$

$$=\delta\left(\phi_lQ_l+\phi_rQ_r+\frac{Q^2}{2C_{g\Sigma}}\right), \tag{2c}$$

where Q_k is the total charge that has tunneled into lead k [Note $\delta Q=-(\delta Q_l+\delta Q_r)$.]. From Eq. (2) it follows that the electrostatic energy[17] of the island is

$$E_C=\frac{Q^2}{2C_\Sigma} \tag{3}$$

and the effective Fermi energies of the leads can be written as $E_k^F=e\phi_k$, where e is the electron charge, including its sign. To be explicit,

$$E_l^F=+e\,\frac{2C_r+C_g}{2C_\Sigma}V-e\,\frac{C_g}{C_\Sigma}V_g, \tag{4a}$$

$$E_r^F=-e\,\frac{2C_l+C_g}{2C_\Sigma}V-e\,\frac{C_g}{C_\Sigma}V_g. \tag{4b}$$

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

$$E_C=\frac{1}{2C_\Sigma}(Q_0+Ne)^2. \tag{5}$$

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 $[N-(N_0+N_1)/2]^2=\frac{1}{4}$ is a constant, E_C for N_0 or N_1 electrons can be rewritten, to within a constant, as

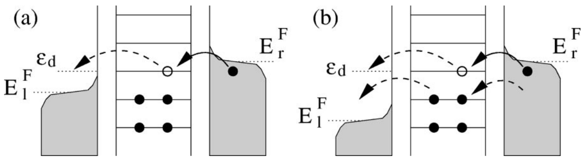

FIG. 2. Energy diagrams for the single-electron transistor. The island is represented by a set of discrete energy levels and the leads by continua of levels. Filled dots in the island stand for electrons present in an N_0-electron ground state. The empty dot is an extra electron that tunnels onto the island to give an N_1-electron state. The transition marked with a solid arrow is the one that determines the initial threshold for starting current flow. The transitions marked by dotted arrows then also contribute to the total current. (a) When the Fermi energy of the right lead is swept past the first level available for tunneling at energy ϵ_d, current can tunnel through this level. (b) For a slightly lower gate voltage and higher bias voltage, two levels contribute to tunneling even at the initial onset of current flow.

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

Notice that Eq. (5) explicitly includes the Coulomb energy that forbids states not having N_0 or N_1 electrons, but this is implicit in Eq. (6). 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 as

$$E_K = \sum_i \epsilon_i^K n_i, \tag{7}$$

where ϵ_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 $N=\Sigma_i n_i$, the sum of the electrostatic and kinetic energies is just

$$E_{CK} = \sum_i \epsilon_i n_i, \tag{8}$$

where ϵ_i is defined by

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

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_k^F of lead k is above the energy ϵ_i of a nonfully 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_k^F is below the energy of a nonempty state. The onset of the current is associated with the first level available for tunneling, i.e. the lowest-energy nonfull level in the N_0-electrons ground state or the highest-energy nonempty 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 the 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(b). The first-allowed tunneling transition is for an electron to enter the level with energy ϵ_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 ϵ_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 the 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

$$V_g^0 = -\frac{C_\Sigma}{eC_g}\epsilon_d, \tag{10}$$

where ϵ_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,[11] the energy of the island has the extra term

$$E_J = J(\{n_i\}). \tag{11}$$

Equation (1) 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 mean-field contribution of the quadratic part and $J(\{n_i\})$ is defined to be the rest. The net effect of the $J(\{n_i\})$ term is to produce shifts in the energy thresholds for tunneling that depend on the actual state of the particle. For instance, the effective energy level ϵ_i' for adding an election to level i starting with the N_0-electron state $\{n_j\}$ is

$$\epsilon_i' = \epsilon_i + J(\{n_j+\delta_{ij}\}) - J(\{n_j\}). \tag{12}$$

Notice that this is only defined if $n_i<2$. In the same way, the energy of a nonempty 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

Owing to 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[4,5]

$$\frac{dP_\alpha}{dt}=\sum_\beta (\Gamma_{\beta\to\alpha}P_\beta-\Gamma_{\alpha\to\beta}P_\alpha), \tag{13}$$

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

This can be written in matrix form as

$$\frac{d\mathbf{P}}{dt}=\mathbf{\Gamma}\cdot\mathbf{P} \tag{14}$$

with the following coefficients for the matrix $\mathbf{\Gamma}$.

$$\Gamma_{\alpha\beta}=\Gamma_{\beta\to\alpha}\quad \text{if}\quad \alpha\neq\beta \tag{15a}$$

$$\Gamma_{\alpha\alpha}=-\sum_{\beta\neq\alpha}\Gamma_{\alpha\to\beta}. \tag{15b}$$

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 us assume that states $|\alpha\rangle$ and $|\beta\rangle$ differ only by $|\beta\rangle$ having one extra electron in level i. Then

$$\Gamma_{\alpha\to\beta}=\gamma_i^l f(\epsilon_i'-E_l^F)(2-n_i)+\gamma_i^r f(\epsilon_i'-E_r^F)(2-n_i), \tag{16a}$$

$$\Gamma_{\beta\to\alpha}=\gamma_i^l[1-f(\epsilon_i'-E_l^F)]n_i+\gamma_i^r[1-f(\epsilon_i'-E_r^F)]n_i \tag{16b}$$

where

$$f(x)=1/[1+\exp(x/k_BT)] \tag{17}$$

is the Fermi function corresponding to the temperature in the leads and γ_i^l and γ_i^r are the bare tunneling rates between level i and each of the leads. Here ϵ_i' is the energy needed to add an electron to state $|\alpha\rangle$ in level i. It includes the contribution of the interaction term.

The steady-state occupation probabilities can be found by iterating Eq. (14) with a discrete timestep dt to find the probabilities for which $d\mathbf{P}/dt=0$. This is equivalent to finding the eigenvector $\mathbf{P}_0$ of $\mathbf{\Gamma}$ associated with the eigenvalue zero.

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[4,5]

$$I_l=|e|\sum_\alpha\sum_\beta \Gamma^l_{\alpha\to\beta}P_\alpha, \tag{18}$$

where $\Gamma^l_{\alpha\to\beta}$ is the contribution of the left lead to $\Gamma_{\alpha\to\beta}$, multiplied by $+1$ or -1 depending on whether the $\alpha\to\beta$ 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.

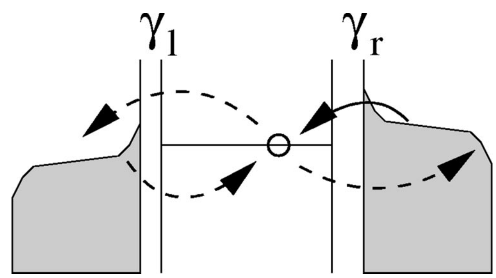

FIG. 3. Energy diagram with one level available for tunneling.

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 ϵ_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.[18] If we call

$$f_r=f(\epsilon_1-E_r^F) \tag{19a}$$

$$f_l=f(\epsilon_1-E_l^F) \tag{19b}$$

and $N=0$ or 1 the state with N electrons, the transition rates are

$$\Gamma_{0\to1}=2\gamma_r f_r+2\gamma_l f_l \tag{20a}$$

$$\Gamma_{1\to0}=\gamma_r(1-f_r)+\gamma_l(1-f_l) \tag{20b}$$

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

$$P_1=\frac{\Gamma_{0\to1}}{\Gamma_{0\to1}+\Gamma_{1\to0}}=\frac{2\gamma_r f_r+2\gamma_l f_l}{\gamma_r(1+f_r)+\gamma_l(1+f_l)} \tag{21a}$$

$$P_0=\frac{\Gamma_{1\to0}}{\Gamma_{0\to1}+\Gamma_{1\to0}}=\frac{\gamma_r(1-f_r)+\gamma_l(1-f_l)}{\gamma_r(1+f_r)+\gamma_l(1+f_l)} \tag{21b}$$

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

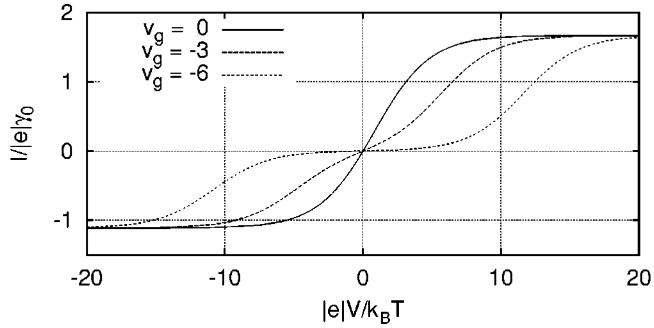

FIG. 4. Current profiles as a function of the bias voltage for the case of a single spin-degenerate level accessible for tunneling, for three different gate voltages. We assume $C_r = C_l$ and $\gamma_l = 4\gamma_r$. The bias voltage is plotted in units of $k_BT/|e|$. The current is in units of $|e|\gamma_0$, where $\gamma_0 = \gamma_l\gamma_r/(\gamma_l+\gamma_r)$. The reduced gate voltage $v_g = |e|C_g(V_g - V_g^0)/C_\Sigma k_BT$ is $0, -3$ or -6.

$$I = |e|[\gamma_l(1-f_l)P_1 - 2\gamma_l f_l P_0] = 2|e|\frac{\gamma_r\gamma_l(f_r - f_l)}{\gamma_r(1+f_r)+\gamma_l(1+f_l)}. \tag{22}$$

This expression differs from an approximate form used in Ref. 13 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. (19) and E_k^F by the expressions in Eqs. (4). Figure 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_BT, there is an interesting regime in which V is substantially bigger than $k_BT/|e|$ 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,[14]

$$I_+ = 2|e|\frac{\gamma_r\gamma_l}{2\gamma_r+\gamma_l} \tag{23a}$$

$$I_- = -2|e|\frac{\gamma_r\gamma_l}{\gamma_r+2\gamma_l}. \tag{23b}$$

These expressions give different heights for the positive and negative current steps. Measuring these heights can, therefore, allow an experimental determination of both γ_r and γ_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

$$I_1^{\pm} = \pm|e|\frac{\gamma_r\gamma_l}{\gamma_r+\gamma_l} \tag{24}$$

for both bias directions,[14] so that γ_r and γ_l cannot be determined separately.

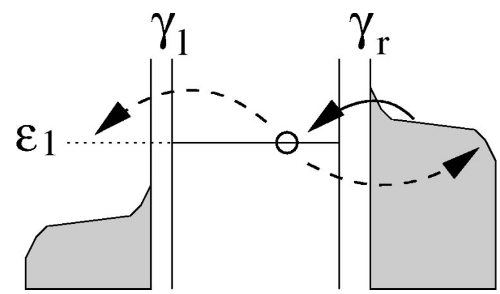

FIG. 5. Energy diagram with one level available for tunneling and $V_g < V_G^0$. Since E_l^F is substantially below ϵ_1, electrons can tunnel into the island only from the right lead.

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 γ. For example, if $\gamma_l \gg \gamma_r$, then $I_+ = 2|e|\gamma_r$ 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 ϵ_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

$$I = I_+ f\left(\epsilon_1 - E_r^F - k_BT\ln\frac{2\gamma_r+\gamma_l}{\gamma_r+\gamma_l}\right). \tag{25}$$

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 a nonzero temperature, the center of the step is shifted relative to its position at zero temperature. The shift is proportional to the temperature, vanishes if $\gamma_l \gg \gamma_r$, and has a maximum value of $k_BT\ln 2$ when $\gamma_r \gg \gamma_l$. Figure 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 $E_r^F = \epsilon_1$. At nonzero temperatures, when $E_r^F = \epsilon_1$, the Fermi occupancy probability is $\frac{1}{2}$ for states in the right lead with the energy ϵ_1. In this case the transition rates are dominated by electrons tunneling back and forth from the right lead (since $\gamma_r \gg \gamma_l$)

$$\Gamma_{0\to1} = \tfrac{1}{2}(2\gamma_r) \tag{26a}$$

$$\Gamma_{1\to0} = \tfrac{1}{2}\gamma_r. \tag{26b}$$

Here the factor $\frac{1}{2}$ comes from the Fermi occupancy of the lead and the factor 2 in $\Gamma_{0\to1}$ is from the spin degeneracy. This factor is only present for $\Gamma_{0\to1}$ because electrons tun-

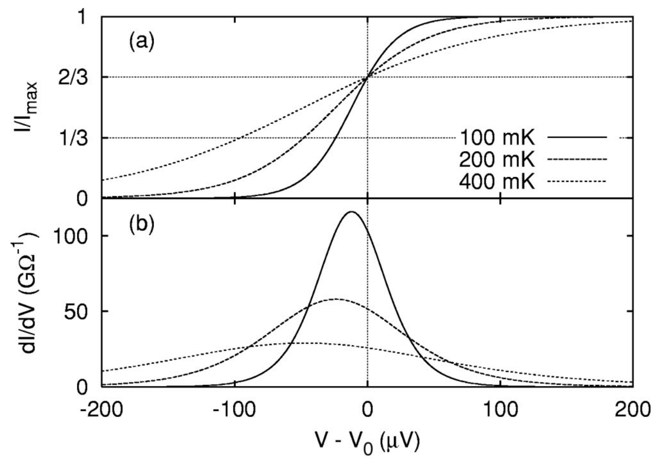

FIG. 6. (a) Current step and (b) conductance peak at positive bias and negative gate voltage for three different temperatures. We assume $C_r = C_l$, $\gamma_l = 50$ MHz Ref. 12 and $\gamma_r \gg \gamma_l$. The peak occurs at $V_0 = 2C_g(V_g - V_g^0)/C_\Sigma$ at zero temperature and shifts from this position by an amount $2k_BT \ln 2/|e|$ at nonzero temperature.

neling into the island see two empty states, while an electron tunneling out comes from a given spin state. It follows that when $E_r^F = \epsilon_1$ the probability that the island is in the one-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 Figs. 6(a), or in 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.*[15]

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 $\epsilon_1^\pm = \epsilon_1 \pm g\mu_B\mu_0 H/2$. If we call these states $+$ and $-$, and $f_k^\pm \equiv f(\epsilon_1^\pm - E_k^F)$, then the transition rates are

$$\Gamma_{0\to\pm} = \gamma_r f_r^\pm + \gamma_l f_l^\pm \tag{27a}$$

$$\Gamma_{\pm\to 0} = \gamma_r(1 - f_r^\pm) + \gamma_l(1 - f_l^\pm) \tag{27b}$$

Notice the absence of the factors 2 that were in Eqs. (20) due to the spin degeneracy. The occupation probabilities are

$$P_0 = \frac{1}{1 + \dfrac{\Gamma_{0\to +}}{\Gamma_{+\to 0}} + \dfrac{\Gamma_{0\to -}}{\Gamma_{-\to 0}}} \tag{28a}$$

$$P_\pm = \frac{\Gamma_{0\to\pm}}{\Gamma_{\pm\to 0}} P_0 \tag{28b}$$

and the current through the left lead is

$$I = |e|\gamma_l[(1 - f_l^+)P_+ + (1 - f_l^-)P_- - (f_l^+ + f_l^-)P_0]. \tag{29}$$

Figure 7 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 $f_l^\pm = 0$). 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. (24) 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

$$\frac{I_1^+}{I_+} = \frac{2\gamma_r + \gamma_l}{2\gamma_r + 2\gamma_l}. \tag{30}$$

If $\gamma_r \gg \gamma_l$, this ratio is one and the second peak vanishes.[14] On the other hand, if $\gamma_l \gg \gamma_r$, the peak splits into two subpeaks carrying the same current.

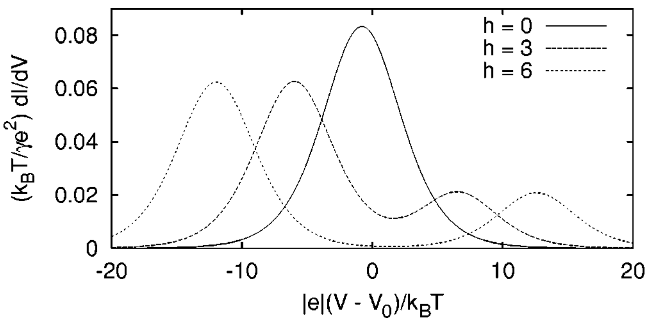

FIG. 7. Splitting of a conductance peak in a magnetic field. We assume $f_l^\pm = 0$, $C_r = C_l$, and $\gamma_r = \gamma_l = \gamma$. At zero temperature and zero field the peak occurs at $V_0 = 2C_g(V_g - V_g^0)/C_\Sigma$. The reduced field $h = g\mu_B\mu_0 H/(2k_BT)$ is 0, 3, or 6.

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. Due to the Coulomb blockade, no current flow is possible until an electron can tunnel from the right electrode to state 2; 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 γ_i^k be the bare tunneling rate of the level i across the barrier k. We will specialize immediately to the

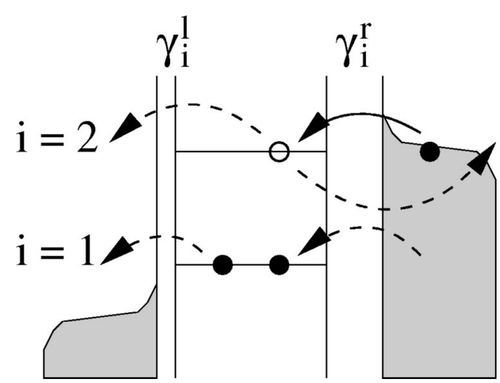

FIG. 8. Energy diagram for a case with two levels available for tunneling.

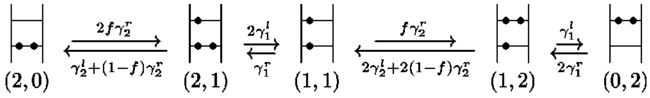

FIG. 9. Available transitions for the situation described in Fig. 8.

interesting case of positive bias (as pictured in Fig. 8) with the right barrier substantially thicker than the left barrier, so $\gamma_i^l \gg \gamma_j^r$ for i, $j \in \{1,2\}$. (Note that this is opposite to the inequality considered in Fig. 6.) To simplify further, we will also look only at the current onset at positive bias for a large negative gate voltage, i.e., we will assume $f(\epsilon_1 - E_l^F) = f(\epsilon_2 - E_l^F) = 0$ and $f(\epsilon_1 - E_r^F) = 1$. For this case, $f(\epsilon_2 - E_r^F)$ will simply be called f. These conditions correspond to line III in the data of Ref. 12.

Figure 9 shows the available transitions together with the corresponding transition rates. Since $\gamma_i^r \ll \gamma_i^l$ 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

$$\frac{d}{dt}\begin{pmatrix} P(2,0) \\ P(1,1) \\ P(0,2) \\ P(2,1) \\ P(1,2) \end{pmatrix} = \mathbf{\Gamma} \begin{pmatrix} P(2,0) \\ P(1,1) \\ P(0,2) \\ P(2,1) \\ P(1,2) \end{pmatrix} \tag{31a}$$

with

$$\Gamma = \left(\begin{array}{ccc|cc} -2f\gamma_2^r & 0 & 0 & \gamma_2^l + (1-f)\gamma_2^r & 0 \\ 0 & -\gamma_1^r - f\gamma_2^r & 0 & 2\gamma_1^l & 2\gamma_2^l + 2(1-f)\gamma_2^r \\ 0 & 0 & -2\gamma_1^r & 0 & \gamma_1^l \\ \hline 2f\gamma_2^r & \gamma_1^r & 0 & -\gamma_2^l - (1-f)\gamma_2^r - 2\gamma_1^l & 0 \\ 0 & f\gamma_2^r & 2\gamma_1^r & 0 & -2\gamma_2^l - 2(1-f)\gamma_2^r - \gamma_1^l \end{array}\right). \tag{31b}$$

This matrix has the structure

$$\Gamma = \begin{pmatrix} \Gamma_{uu} & \Gamma_{uc} \\ \Gamma_{cu} & \Gamma_{cc} \end{pmatrix} \tag{32}$$

where Γ_{uu} and Γ_{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 (Γ_{uc}) and tunneling-in (Γ_{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:

$$P(2,1) \ll 1, \quad P(1,2) \ll 1, \tag{33a}$$

$$P(2,0) = \frac{1}{S}, \quad P(1,1) = \frac{4fK}{S}, \quad P(0,2) = \frac{f^2K^2}{S}, \tag{33b}$$

where $K = \gamma_1^l \gamma_2^r / \gamma_2^l \gamma_1^r$ and $S = 1 + 4fK + f^2K^2$.

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

$$\frac{I}{|e|} = 2f\gamma_2^r P(2,0) + (f\gamma_2^r + \gamma_1^r) P(1,1) + 2\gamma_1^r P(0,2)$$

$$I = |e| \frac{(4\gamma_2^r K + 2\gamma_1^r K^2) f^2 + (2\gamma_2^r + 4\gamma_1^r) f}{1 + 4fK + f^2K^2}. \tag{34}$$

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-

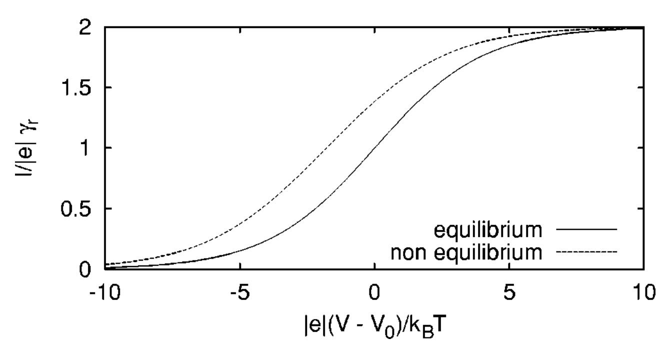

FIG. 10. Shift of the current step by nonequilibrium in the two-levels-accessible case. We assume $\gamma_1^l = \gamma_2^l = \gamma_l$ and $\gamma_1^r = \gamma_2^r = \gamma_r$, with $\gamma_l \gg \gamma_r$. The step occurs at $V_0 = 2C_g(V_g - V_g^0)/C_\Sigma$ at zero temperature. The "equilibrium" curve assumes infinitely fast relaxation in the island. The "nonequilibrium" curve assumes no relaxation.

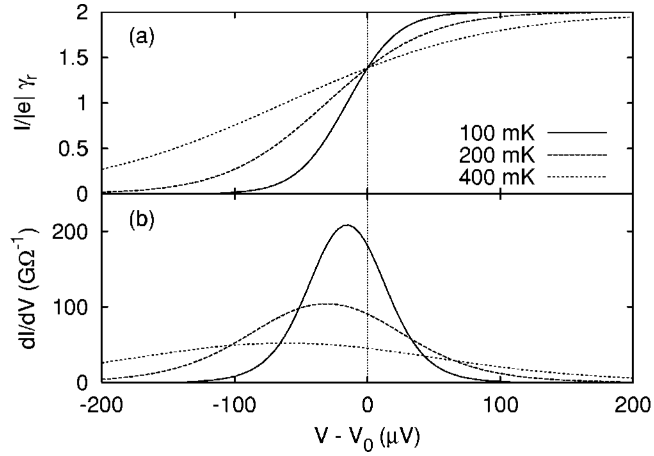

FIG. 11. Dependence of (a) the current step and (b) the conductance peak on the temperature in the two-levels-accessible case in the presence of nonequilibrium. We assume $\gamma_1^l = \gamma_2^l = \gamma_l$ and $\gamma_1^r = \gamma_2^r = \gamma_r$, with $\gamma_l \gg \gamma_r$ and no relaxation in the island.

limiting process, this situation is equivalent to the case of Eq. (22) when only one level is accessible for tunneling, and the current would just be

$$I_{\text{equilibrium}} = 2|e|\gamma_2^r f(\epsilon_2 - E_r^F). \tag{35}$$

The main effect of nonequilibrium states as illustrated in Fig. 10 is, therefore, to shift the current step to a lower voltage. Although not exactly a Fermi function, the shape of the step described by Eq. (34) 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 $E_r^F = \epsilon_2$, electrons tunneling to the upper level come from half-full states in the right lead. If the island is in a nonequilibrium 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 $E_r^F = \epsilon_2$ 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 displayed in Fig. 11. Although the T-dependent shift looks very similar to the result for one level displayed in Fig. 6, the shift in Fig. 11 is of a different nature since it originates from nonequilibrium 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

$$I = |e|(2\gamma_1^l + \gamma_2^l) f(\epsilon_2 - E_r^F - k_BT \ln 2), \tag{36}$$

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_l^F), 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_r^F 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_l^F remains fixed slightly below ϵ_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 preceding section, this effect can make the energy required for the $(1,1) \to (1,2)$ transition different than the $(2,0) \to (2,1)$ 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 ϵ_2 for the $(2,0) \to (2,1)$ transition and $\epsilon_2' = \epsilon_2 + \delta$ for the $(1,1) \to (1,2)$ transition. Here δ is a measure of the strength of the variations. In order to generalize the previous notation, we will call $f = f(\epsilon_2 - E_r^F)$ and $f' = f'(\epsilon_2' - E_r^F)$.

The possible transitions are still described by Fig. 9 and the corresponding rate equations are the same as Eqs. (31) but with

$$\Gamma_{(1,1)\to(1,2)} = f' \gamma_2^r \tag{37a}$$

$$\Gamma_{(1,2)\to(1,1)} = 2\gamma_2^l + 2(1 - f')\gamma_2^r, \tag{37b}$$

which gives the current

$$I = |e| \frac{(4\gamma_2^r K + 2\gamma_1^r K^2) f f' + (2\gamma_2^r + 4\gamma_1^r) f}{1 + 4fK + ff'K^2}. \tag{38}$$

Figure 12(a) shows the current step for the case that the energy required for the tunneling transition is decreased by nonequilibrium (negative δ) for various values of δ/k_BT ranging from 0 to -20, and Fig. 12(b) shows I-V curves when the nonequilibrium effect increases the tunneling energy. These plots were made for $\gamma_1^r = \gamma_2^r = \gamma_r$, $\gamma_l \gg \gamma_r$, and $K = 1$. For negative δ, 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 nonequilibrium states. This additional shift is proportional to $|\delta|$ if $|\delta| \ll k_BT$ and becomes a constant of the order of k_BT if $|\delta| \gg k_BT$. A shift of this sort has been observed in Fig. 3(b) of Ref. 12. For positive δ, the

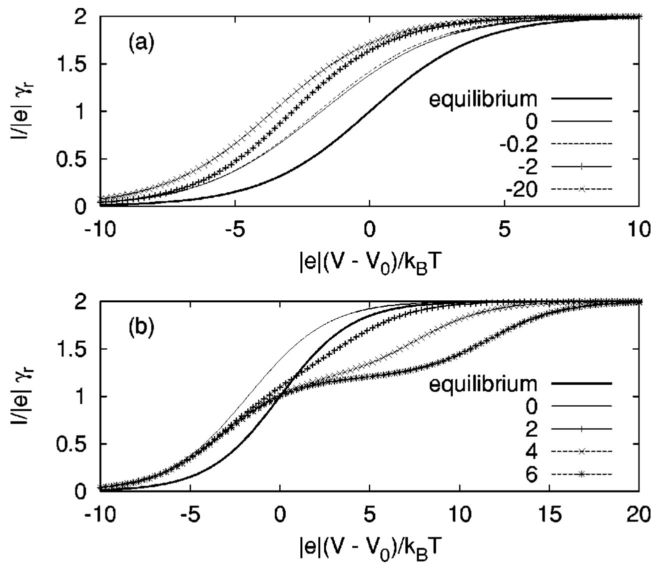

FIG. 12. Current steps for different interaction strengths. We assume $C_l = C_r$, $\gamma_1^l = \gamma_2^l = \gamma_l$, and $\gamma_1^r = \gamma_2^r = \gamma_r$, with $\gamma_l \gg \gamma_r$. The "equilibrium" curve assumes infinitely fast relaxation in the island. The other curves assume no relaxation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

effect of nonequilibrium 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 nonequilibrium excitations grows combinatorically, and each combination of excitations can produce a different shift for the tunneling resonance energies. Interactions that depend on the spin state of the island (neglected thus far) can produce further complications. The nonequilibrium excitations can produce a variety of effects depending on the ratio γ_l/γ_r and on the magnitude of variations in electron-electron interactions. When the interaction-induced shifts are comparable to k_BT, they have been observed to produce an effective broadening of the observed conductance peaks.[12] For larger interactions, shifts due to nonequilibrium excitations have been resolved individually.[11,16]

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 nonequilibrium excitations on the island. The voltage position of the resonance can undergo strong temperature-dependent shifts even in regimes (e.g., positive bias and $\gamma_l \gg \gamma_r$ noted above) where the one-level resonance positions do not depend on the temperature. Understanding the variations in the strength of electron-electron interactions is critical in the nonequilibrium 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, 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.[19] These are useful, for instance, in extracting the rate-limiting bare tunneling rates from experimental data in which stepwise increases in the current are measured as V and V_g are adjusted, so that the number of states accessible for tunneling increases one by one.[12]

ACKNOWLEDGMENTS

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[17] 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 $Q^2/2C_\Sigma + \Sigma_k (C_k/2)\phi_k^2$.

[18] The case in which one spin-degenerate level is accessible for tunneling, and the Coulomb energy permits an occupation of either one or two electrons (rather than 0 or 1) can be solved by exactly the same methods: $I = 2e[\gamma_r \gamma_l (f_l - f_r)]/[\gamma_r(2 - f_r) + \gamma_l(2 - f_l)]$.

[19] See web site http://www.ccmr.cornell.edu/~ralph/projects/set/