

Landauer theory, inelastic scattering, and electron transport in molecular wires

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(Received 16 July 1999)

In this paper, we address the topic of inelastic electron scattering in mesoscopic quantum transport. For systems where only elastic scattering is present, Landauer theory provides an adequate description of transport that relates the electronic current to single-particle transmission and reflection probabilities. A formalism proposed recently by Bonča and Trugman facilitates the calculation of the one-electron transmission and reflection probabilities for *inelastic* processes in mesoscopic conductors connected to one-dimensional ideal leads. Building on their work, we have developed a self-consistent procedure for the evaluation of the non-equilibrium electron distributions in ideal leads connecting such mesoscopic conductors to electron reservoirs at finite temperatures and voltages. We evaluate the net electronic current flowing through the mesoscopic device by utilizing these nonequilibrium distributions. Our approach is a generalization of Landauer theory that takes account of the Pauli exclusion principle for the various competing elastic and inelastic processes while satisfying the requirement of particle conservation. As an application we examine the influence of elastic and inelastic scattering on conduction through a two site molecular wire with longitudinal phonons using the Su-Schrieffer-Heeger model of electron-phonon coupling.

I. INTRODUCTION

The role of inelastic scattering in electron transport through mesoscopic systems is a topic of current theoretical and experimental interest. Recent experiments have revealed the importance of the electron-phonon interaction in transport measurements performed on certain mesoscopic systems. In particular inelastic scattering effects have been observed directly in scanning tunneling microscopy (STM) measurements of the differential conductance of molecules adsorbed on metallic substrates.¹⁻³ Theoretically the effects of inelastic scattering on electron transport through mesoscopic semiconductor devices have been investigated by a variety of methods ranging from Green's function techniques⁴⁻⁶ to the Fermi golden rule.⁷ Some theoretical models have also been proposed to elucidate the effects of molecular vibrations on electron tunneling through molecules contacted by an STM.⁸⁻¹⁰ Recent work has provided a method for calculating the electronic current at finite temperatures for electrons tunneling through a one-dimensional conductor in the presence of phonons.¹¹ These approaches have yielded valuable insights into the behavior of specific systems.

In the absence of inelastic scattering and electron correlations, Landauer theory¹² provides a general framework for calculations of the electronic current through mesoscopic conductors that are coupled to ideal single- or multichannel quasi-one-dimensional leads. It relates the electronic current to the transmission probability for an electron incident from the source lead to scatter elastically through the conductor and into the drain. The transmission probability is found by solving the single-electron quantum scattering problem.

When inelastic processes such as phonon emission and absorption are considered, electron scattering becomes a many-body phenomenon involving electrons and the various excited phonon states of the system. A nonperturbative ap-

proach has been proposed by Bonča and Trugman for treating this scattering problem for a system consisting of a mesoscopic conductor (which supports the phonon modes) coupled to two single-channel ideal leads that act as the electron source and drain.¹³ Their method approximates the many-body problem by a multichannel single-electron scattering problem, which can be solved exactly. Here each channel corresponds to a different vibrational quantum state of the mesoscopic conductor. Using their approach it is possible to determine the transmission and reflection probabilities for all inelastic and elastic scattering events that an electron may suffer in the conductor as it goes from the source to the drain. This method has been applied to study the effects of phonons on electron transmission through one-dimensional conductors where the electron-phonon coupling has been modelled using the Holstein Hamiltonian^{14,15,11} and the Su-Schrieffer-Hieger (SSH) Hamiltonian.^{16,17}

The present paper is complementary to the above theoretical work. Its purpose is to generalize the Landauer theory of electrical conduction to mesoscopic systems with electron-phonon scattering, assuming that the latter is described accurately within the multi-channel single-electron scattering approach of Bonča and Trugman.¹³ I.e., given the Bonča-Trugman¹³ solution of the inelastic scattering problem, our objective is to calculate the electric current by appropriately generalizing Landauer theory.

When transport in a many-electron system is described in terms of one-electron scattering processes, the Pauli exclusion principle needs to be considered since in general electrons involved in different transitions may compete to occupy the same final state. In treatments of transport based on the Boltzmann equation, if the electron scattering is elastic, this competition has no effect because of a mutual cancellation of terms.¹⁸ However such a cancellation does not occur when scattering is inelastic.¹⁹ In Landauer theory scattering

is assumed to be elastic and the electronic current is carried by electrons that occupy single-particle scattering states that extend across the mesoscopic conductor from the source to the drain. These scattering states are orthogonal to each other.²⁰ Because of this orthogonality, if an electron populates one of these scattering states it does not compete with any of the other filled scattering states. Thus in Landauer theory (as in the elastic case of the Boltzmann equation) the Pauli exclusion principle for the final states in the scattering processes does not play a role in the determination of the electronic current.

In our generalization of Landauer theory that includes inelastic scattering, this is no longer true: Different scattering processes can send electrons to the same outgoing state and the Pauli principle plays an important role in determining the occupations of the outgoing channels. In the Boltzmann treatment of inelastic scattering the Pauli principle is applied to the nonequilibrium one-electron distribution function for the system since transport is an inherently nonequilibrium phenomenon. Here we apply an analogous principle: In our extension of Landauer theory the Pauli exclusion principle is applied to the nonequilibrium electron distributions in the *outgoing* channels of the scattering process and these distributions must be determined selfconsistently. Since some processes may be excluded because of the Pauli principle, overall particle conservation is another consideration that must be taken into account when trying to generalize Landauer theory to include inelastic scattering.

We have developed a practical method for determining these nonequilibrium electron distributions for a class of mesoscopic systems. These systems are similar to those considered by Bonča and Trugman¹³ in that they consist of a mesoscopic conductor, which is attached to two single-mode ideal leads, which act as a source and drain, and phonons are assumed to be present only on the conductor and not on the ideal leads. We consider scattering processes which change the conductor's phonon state or leave it unchanged. Each of these processes contributes to the nonequilibrium electron distribution. We determine each contribution selfconsistently (i.e., in the presence of the other processes that can occur) in terms of the transmission and reflection probabilities for the given process and the Fermi functions that describe the incoming electron distributions in the left and right leads. Included in this self-consistent method is the constraint of particle conservation. We do not however include cumulative effects of the current on the phonon distribution in the conductor; i.e., we assume that the conductor is in contact with a heat bath. With the nonequilibrium electron distribution determined we then evaluate the current flowing through this system for finite temperatures and bias voltages.

As an application of the above theoretical approach we calculate the electronic current as a function of voltage for a two site molecule. The molecule has two single-particle molecular energy levels through which electrons from the leads can resonantly tunnel. It also has two longitudinal phonon modes that can be excited. A Su-Schrieffer-Heeger (SSH) Hamiltonian is used to represent the electron-phonon coupling. For our model system one of the phonon modes is chosen to have an energy equal to the gap between the two electronic energy levels. Because of this, electrons which are resonant with the higher energy level can emit a phonon and

be resonant with the lower level. Such a process is found to be highly transmitting. When the voltage is high enough that there is a sufficient number of electrons in the left lead that can undergo this process, we find that the current in the right lead due to elastically scattered electrons is reduced significantly due to competition with these inelastically scattered electrons. Thus we find that the mutual exclusion between the scattered electrons that make up the nonequilibrium distribution in the drain lead can have important consequences for the electronic current flowing through the molecule.

In Sec. II, we describe the class of systems that we study and explain how the scattering states are calculated. In Sec. III, we present our generalization of the Landauer theory and our method for calculating the nonequilibrium electron distribution and associated electronic currents. We then apply our methodology to a simple model for a two-site molecular chain and calculate its current-voltage characteristics in Sec. IV. Our conclusions are summarized in Sec. V.

II. INELASTIC SCATTERING IN ELECTRON TRANSPORT THROUGH A MESOSCOPIC CONDUCTOR

In the absence of inelastic scattering and electron correlations, electron transport through a mesoscopic conductor can be described in terms of the probability $T(E, V)$ that a single electron with energy E scatters through the conductor from the source to the drain at an applied bias voltage V .¹² When phonons (or vibrational modes) of the conductor are considered, an electron entering from the source can suffer inelastic collisions by absorbing or creating phonons before entering the drain. Each of these processes can be described by its own transmission probability. If we assume that the source and drain are single-mode leads, which are free from phonons, we can characterize the above single-electron scattering process by a transmission probability $T_{L \rightarrow R}^{\alpha, \alpha'}(E, E')$. This describes an electron that enters from the left lead (L) with energy E , suffers inelastic collisions on the conductor, which change the phonon population on the conductor from α to α' , and then scatters into the right lead (R) with energy E' . Similarly, an electron incident from the left lead can suffer a collision and be reflected back into the left lead. This is characterized by a reflection probability $R_L^{\alpha, \alpha'}(E, E')$. Elastic scattering processes are included with α'_L being equal to α . For all processes the total energy is conserved, so E' plus the net energy of all of the created and destroyed phonons is equal to E . We now describe a method for calculating these transmission and reflection probabilities for a mesoscopic structure.

A schematic of our model for the mesoscopic conductor, which consists of a source (left) and a drain (right) lead attached to a one-dimensional conductor/wire is depicted in Fig. 1. We assume that the leads are ideal and that they only have one electronic channel. Phonons are considered to be only on the conductor and not on the ideal leads. An electron flows through the wire under an applied bias V . We assume that the voltage drop only occurs at the interface between the wire and the leads with the left lead held at $-V/2$ and the right lead held at $+V/2$. We solve the transport problem by solving Schrödinger's equation for the many-body wave function of the electron-phonon system from which we extract the transmission and reflection coefficients mentioned

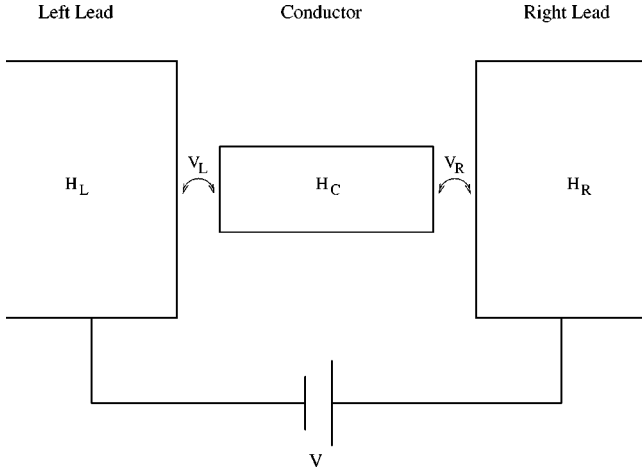


FIG. 1. A schematic of our model for a one-dimensional mesoscopic conductor. The conductor bridges two one-dimensional ideal leads. The applied bias voltage is V . The Hamiltonians of the individual elements making up the system are labeled.

above. These will be used in the calculation of the nonequilibrium electron distributions and the current, which follows in the next section.

The Hamiltonian H of this system can be split up into the Hamiltonians for the isolated systems consisting of the left lead H_L , the right lead H_R , and the conductor H_C . It also includes the coupling between the wire and the left and right leads, V_L and V_R respectively. Thus we write,

$$H = H_L + H_R + H_C + V_L + V_R. \quad (1)$$

We treat each of the above Hamiltonians in the tight-binding approximation. We model the wire using a set of orthogonal atomic orbitals $\{|i\rangle\}$. Each atomic state has an energy e_i with a corresponding creation operator b_i^\dagger , which creates an electron in that state. In our Hamiltonian for the wire an electron can hop from orbital i to all nearest-neighbor orbitals j , and this is governed by the hopping parameter $t_{i,j}^0$ for the equilibrium configuration of atoms. The wire also has a discrete set of vibrational modes, each characterized by a frequency ω_k . The phonons on the wire are described by the state $|\alpha\rangle = |\{n_k\}\rangle$, where $\{n_k\}$ is the set of mode occupation numbers. A phonon in mode k is created by the operator a_k^\dagger . To first order in phonon creation/destruction operators the electron-phonon interaction is given by $\gamma_{i,j}^k$, and this governs the process of an electron hopping from site i to site j and exciting or de-exciting a phonon in mode k . The Hamiltonian of the N -site wire that we consider is,

$$H_C = \sum_{i=1}^N e_i b_i^\dagger b_i + \sum_{i \neq j} t_{i,j}^0 (b_i^\dagger b_j + \text{H.c.}) + \sum_k \sum_{i \neq j} \times \gamma_{i,j}^k (a_k^\dagger + a_k) (b_i^\dagger b_j + \text{H.c.}) + \sum_k \hbar \omega_k a_k^\dagger a_k.$$

The leads are modelled as a chain of atoms each with a single-atomic orbital $|n\rangle$, where n labels the site. For the left lead n ranges from $-\infty$ to -1 . On the right lead n ranges from 1 to ∞ . On the left lead an electron is created on site n by the operator c_n^\dagger . The site energy is given by $\epsilon_L = \epsilon + eV/2$. Electrons can hop to nearest-neighbor sites and this

is controlled by the hopping parameter β_L . Similarly, on the right lead an electron can exist on site n in an orbital with energy $\epsilon_R = \epsilon - eV/2$. The nearest-neighbor hopping is controlled by the parameter β_R . Since we assume that there are no phonons on the leads the Hamiltonians for the left and right leads are given by

$$H_L = \epsilon_L \sum_{n=-\infty}^1 c_n^\dagger c_n + \beta_L \sum_{n=-\infty}^1 (c_n^\dagger c_{n-1} + \text{H.c.})$$

$$H_R = \epsilon_R \sum_{n=1}^{\infty} c_n^\dagger c_n + \beta_R \sum_{n=1}^{\infty} (c_n^\dagger c_{n-1} + \text{H.c.}).$$

The wire is coupled to the leads via V_L and V_R . We assume that only the sites on the leads directly adjacent to the wire are coupled to the wire. Electrons can hop from these lead sites to any site j on the wire and this is governed by $w_{-1,j}$ for the left lead and $w_{1,j}$ for the right lead. We take the electron-phonon interaction between the leads and the wire to first order. This allows for electrons from the leads to hop onto the wire and excite a phonon in mode k . This electron-phonon interaction is given by $\Gamma_{-1,j}^k$ for the left lead and $\Gamma_{1,j}^k$ for the right lead. Thus the coupling potentials are,

$$V_L = \sum_{j=1}^N w_{-1,j}^0 (c_{-1}^\dagger b_j + \text{H.c.}) + \sum_k \sum_{j=1}^N \Gamma_{-1,j}^k (a_k^\dagger + a_k) \times (c_{-1}^\dagger b_j + \text{H.c.})$$

$$V_R = \sum_{j=1}^N w_{1,j} (c_1^\dagger b_j + \text{H.c.}) + \sum_k \sum_{j=1}^N \Gamma_{1,j}^k (a_k^\dagger + a_k) \times (c_1^\dagger b_j + \text{H.c.}).$$

We now determine the scattering wave function from Schrödinger's equation, $H|\Psi^\alpha\rangle = E|\Psi^\alpha\rangle$, where α labels the initial phonon state on the conducting wire. The wavefunction describes the many-body system consisting of a single electron and the phonons. As shown by Bonča and Trugman, the scattering process can be represented graphically.¹¹ The power of this representation is in that the many-body problem can be viewed as a multichannel single-electron scattering problem. The α' channel in either the left or the right leads corresponds to an electron propagating in the single-electron mode of that lead with the wire being in its α' phonon state. A scattering process that changes the phonon state from $|\alpha\rangle = |\{n_k\}\rangle$ to $|\alpha'\rangle = |\{n'_k\}\rangle$ can then be represented graphically as an electron incident from the α channel and then scattering into the α' channel. Figure 2 shows a graphical representation of the scattering channels for a simple single site wire described by the above Hamiltonian. An electron incident in the α channel in the left lead can scatter elastically or inelastically into any of the outgoing channels in the left and right lead. Channels are connected horizontally by the electron hopping part of the Hamiltonian whereas they are connected vertically by the electron-phonon interaction.

With this picture in mind, we now write explicit forms for the wave function on the left lead (L), right lead (R), and the wire conductor (C). We assume that the wire is initially in

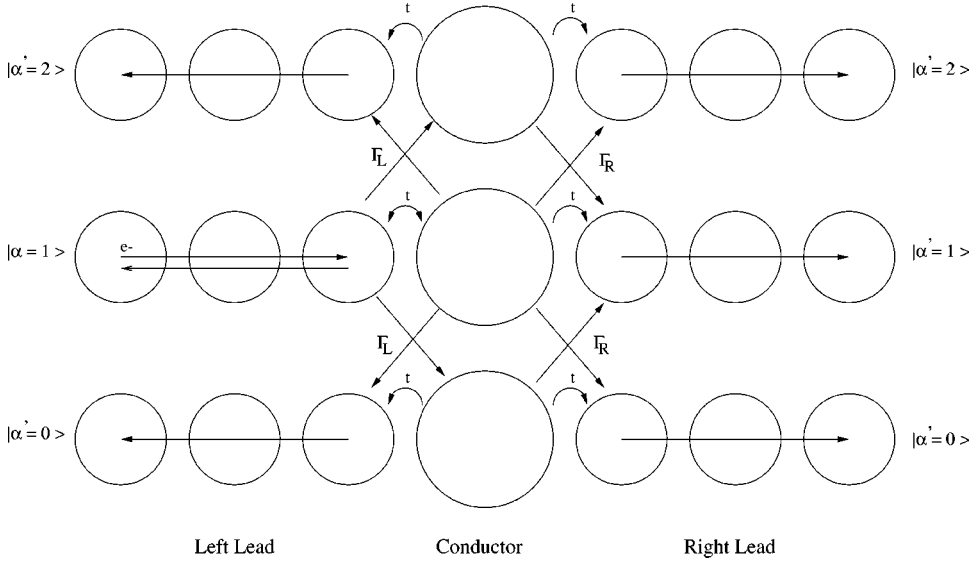


FIG. 2. A graphical representation of the inelastic scattering problem for a single site wire with first order electron-phonon coupling between the leads and the wire. Each phonon state of the wire along with the Bloch state of the electron in a lead can be visualized as a separate scattering channel. Scattering channels are connected horizontally by the electron hopping parameters t and β , while they are connected vertically by the electron-phonon interaction Γ, γ . An electron is initially incident in the α channel and can scatter into any of the other channels.

the phonon state $|\alpha\rangle$ and that there is a rightward propagating electron in a Bloch mode $\sum_n e^{iny^\alpha} |n\rangle$ with energy E in the left lead. The electron can then be reflected elastically or inelastically into any of the other channels in the left lead and propagate in a new Bloch mode with energy E' in the left lead with the wire in a new phonon state $|\alpha'\rangle$. Thus, the wavefunction on the left lead will consist of the initial state plus a sum over all possible reflected states with some unknown coefficients $r_{\alpha',\alpha}$. On the wire the wave function will be a linear combination of the product of the atomic orbitals with all of the different phonon states. On the right lead the electron can be transmitted into any of the outgoing channels and propagate in a Bloch state with an energy E' , leaving the wire in a phonon state $|\alpha'\rangle$. Thus the wave function on the right lead will be a sum over all transmitted states with coefficients $t_{\alpha',\alpha}$ to be determined. Thus, we have

$$|\Psi^\alpha\rangle_L = \sum_{n=-\infty}^{-1} e^{iny^\alpha} |n\rangle \otimes |\alpha\rangle + \sum_{\alpha'} r_{\alpha',\alpha} \times \sum_{n=-\infty}^{-1} e^{-iny^{\alpha'}} |n\rangle \otimes |\alpha'\rangle \quad (2)$$

$$|\Psi^\alpha\rangle_C = \sum_{\alpha'} \sum_{j=1}^N u_j^{\alpha',\alpha} |j\rangle \otimes |\alpha'\rangle \quad (3)$$

$$|\Psi^\alpha\rangle_R = \sum_{\alpha'} t_{\alpha',\alpha} \sum_{n=1}^{\infty} e^{iny^{\alpha'}} |n\rangle \otimes |\alpha'\rangle \quad (4)$$

with

$$|\Psi^\alpha\rangle = |\Psi^\alpha\rangle_L + |\Psi^\alpha\rangle_C + |\Psi^\alpha\rangle_R. \quad (5)$$

The total energy of the system is conserved, so $E = E' + \sum_k (n'_k - n_k) \hbar \omega_k$, where E' is the energy of the scattered electron. $y^{\alpha'}$ corresponds to the reduced wave vector of an electron propagating with energy E' and is determined from the condition $E' = \alpha_{L/R} + 2\beta_{L/R} \cos(y^{\alpha'})$ depending on whether it is in the left or right lead.

Inserting the above wave function into Schrödinger's equation $H|\Psi^\alpha\rangle = E|\Psi^\alpha\rangle$ yields a system of linear equations that can be solved numerically for the $t_{\alpha',\alpha}$, $r_{\alpha',\alpha}$, and the $u_j^{\alpha',\alpha}$ at each energy E . For our particular model based on single-channel leads we then determine the transmission and reflection coefficients for each inelastic channel using,

$$T_{L \rightarrow R}^{\alpha,\alpha'}(E, E') = \left| \frac{v_R^{\alpha'}}{v_L^{\alpha}} \right| |t_{\alpha',\alpha}|^2 \quad (6)$$

$$R_L^{\alpha,\alpha'}(E, E') = \left| \frac{v_L^{\alpha'}}{v_L^{\alpha}} \right| |r_{\alpha',\alpha}|^2 \quad (7)$$

where $v_L^{\alpha'}$ and $v_R^{\alpha'}$ are the velocity of the electron in the α' channel of the left or right lead, respectively.

We then solve the corresponding problem for electrons incident from the right lead to determine $T_{R \rightarrow L}^{\alpha,\alpha'}(E, E')$ and $R_R^{\alpha,\alpha'}(E, E')$. We now proceed to show how these quantities are used to calculate the nonequilibrium electron distribution and current for the above system.

III. NONEQUILIBRIUM ELECTRON DISTRIBUTIONS AND THE EVALUATION OF THE ELECTRONIC CURRENT

As mentioned in the introduction, when calculating the current using Landauer theory the Pauli exclusion principle for final states does not play a role; scattered electrons do not compete with each other. A complication that arises when inelastic scattering processes are considered is that electrons can now compete with other electrons that are scattered to the same final state; the Pauli principle becomes important. For instance, for the system discussed in Sec. II, an electron that suffers an inelastic collision that puts it into a final state with energy E' in the drain competes with all other scattered electrons that can occupy that final state (as shown in Fig. 3). The likelihood that this state is unoccupied in the drain is $[1 - f(E')]$, where $f(E')$ is the nonequilibrium electron distribution function in the drain. Using the equilibrium electron distribution (Fermi function) here is not correct since we are

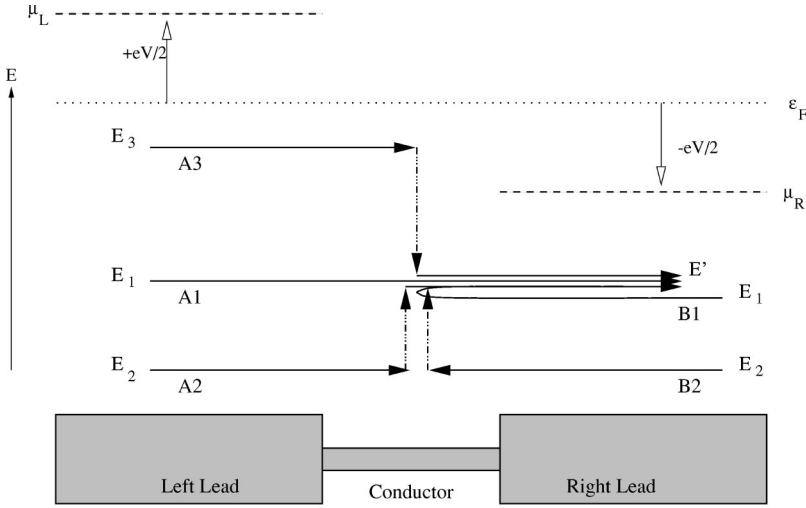


FIG. 3. A schematic of the various elastic and inelastic scattering processes that can occur within the mesoscopic conductor that contribute to the rightward propagating electron distribution in the right lead. The applied bias voltage is V . The electrochemical potentials of the two leads under this applied bias are labeled μ_L and μ_R for the left and right leads, respectively. They share a common Fermi energy labeled by ϵ_F . Scattering processes originating in the left lead are labeled A1-A3, and for those originating in the right lead, they are labeled B1-B2.

discussing transport, an inherently nonequilibrium phenomenon. We will now explain how to determine this nonequilibrium distribution for the model presented in Sec. II.

Figure 3 depicts the processes we are considering for electrons that scatter from various initial states with differing energies E to the same final state at energy E' in the right lead. Some assumptions must be made about which processes can compete with each other. To be consistent with Landauer theory we assume that elastic scattering processes do not compete with other elastic scattering processes (these correspond to those processes, which both begin and end at energy E' labeled A1 and B1 in Fig. 3). With this assumption an electron that is elastically scattered from the source to the drain at energy E' does not compete with an electron that is elastically reflected back into the drain at the same energy (process B1). However, elastically scattered electrons can compete with all electrons that can be inelastically scattered to the same final state. The inelastically scattered electrons correspond to those electrons that start at various energies E labeled A2, A3, and B2 in Fig. 3. We also assume that inelastically scattered electrons compete with all other scattered electrons that start in a different initial electron state (i.e., electrons undergoing process A2 compete with electrons suffering processes A1, A3, B1, and B2).

At a given final scattered energy E' , we consider the following contributions to the non-equilibrium rightward moving electron distribution in the right lead: elastically scattered electrons transmitted from the left lead $(f_{+,el}^{\alpha,\alpha'})^R(E')$, inelastically scattered electrons transmitted from the left lead $(f_{+,in}^{\alpha,\alpha'})^R(E')$ (the final phonon state is α'), elastically scattered electrons that originate in the right lead and are reflected back into the right lead $(f_{-,el}^{\alpha,\alpha'})^R(E')$, and inelastically scattered electrons which start in the right lead and are reflected back into the right lead $(f_{-,in}^{\alpha,\alpha'})^R(E')$. [The (+) denotes transmitted electrons, the (-) reflected electrons and the R signifies that these are the distributions in the right lead.]

To determine the contribution to the nonequilibrium distribution in the right lead that is due to transmitted electrons we must first consider the distribution of electrons incident from the left lead. As in Landauer theory, we assume that this distribution is given by the equilibrium electron distribution

function that exists deep in the left lead. This is the Fermi function for the left lead $F_L(E) = 1/\{\exp[(E - \mu_L)/kT] + 1\}$ where the electrochemical potential is $\mu_L = \epsilon_F + eV/2$ with ϵ_F being the common Fermi energy of the two leads and V the applied bias voltage. An electron incident with energy E from the left lead can then scatter elastically or inelastically into the final state with energy E' with a transmission probability $T_{L \rightarrow R}^{\alpha,\alpha'}(E, E')$. (Elastic scattering corresponds to $\alpha = \alpha'$ and $E = E'$.) Because we now have a number of processes that can place electrons into this same final state the Pauli exclusion principle must be considered. To incorporate this into our determination of the distribution function we must then consider the probability that this state is unoccupied by competing electrons in the drain. For the distribution due to elastically scattered electrons, this probability will be determined by the non-equilibrium electron distributions of the inelastically transmitted and reflected electrons, according to the above assumptions. It is given by $[1 - \sum_{\alpha'} (f_{+,in}^{\alpha,\alpha'})^R(E') - \sum_{\alpha'} (f_{-,in}^{\alpha,\alpha'})^R(E')]$. For the distribution of a specific inelastic transmitting process, the probability that the state in the right lead is unoccupied by competing electrons is determined by the distributions due to all other scattering processes. It is given by $[1 - (f_{+,el}^{\alpha,\alpha'})^R(E') - (f_{-,el}^{\alpha,\alpha'})^R(E') - \sum_{\alpha'} (f_{-,in}^{\alpha,\alpha'})^R(E') - \sum_{\beta \neq \alpha'} (f_{+,in}^{\alpha,\beta})^R(E')]$. The transmitted electron distributions will be proportional to the product of the above probabilities with F_L and with the respective transmission probability T . We define the appropriate proportionality constant for electrons incident from the left lead with energy E , to be $c(E)$. This proportionality constant will be determined by imposing the constraint of particle conservation. Combining the above considerations we arrive at the following expressions for the contributions to the nonequilibrium electron distribution due to elastically and inelastically transmitted electrons:

$$(f_{+,el}^{\alpha,\alpha'})^R(E') = c(E') F_L(E') T_{L \rightarrow R}^{\alpha,\alpha'}(E', E') \times \left[1 - \sum_{\alpha'} (f_{+,in}^{\alpha,\alpha'})^R(E') - \sum_{\alpha'} (f_{-,in}^{\alpha,\alpha'})^R(E') \right] \quad (8)$$

$$\begin{aligned}
(f_{+,in}^{\alpha,\alpha'})^R(E') = & c(E) F_L(E) T_{L \rightarrow R}^{\alpha,\alpha'}(E, E') \left[1 - (f_{+,el}^{\alpha,\alpha})^R(E') \right. \\
& - (f_{-,el}^{\alpha,\alpha})^R(E') - \sum_{\alpha'} (f_{-,in}^{\alpha,\alpha'})^R(E') \\
& \left. - \sum_{\beta \neq \alpha'} (f_{+,in}^{\alpha,\beta})^R(E') \right]. \quad (9)
\end{aligned}$$

Similarly for the contributions to the nonequilibrium electron distribution in the right lead due to elastically and inelastically *reflected* electrons, we must consider the distribution of incident electrons given by the Fermi function $F_R(E) = 1/\{\exp[(E - \mu_R)/kT] + 1\}$ for the right lead where $\mu_R = \epsilon_F - eV/2$. Those electrons which are incident with energy E can be inelastically or elastically reflected into the final state with energy E' with a probability $R_R^{\alpha,\alpha'}(E, E')$. Again we take into account the competition for the occupation of this state using the Pauli principle. For elastically reflected electrons the probability that this state is unoccupied is the same as that for elastically transmitted electrons. For inelastically reflected electrons the probability that the state is unoccupied is determined by all distributions due to different scattering processes. It is given by $[1 - (f_{+,el}^{\alpha,\alpha})^R(E') - (f_{-,el}^{\alpha,\alpha})^R(E') - \sum_{\alpha'} (f_{+,in}^{\alpha,\alpha'})^R(E') - \sum_{\beta \neq \alpha'} (f_{-,in}^{\alpha,\beta})^R(E')]$. Again, the reflected electron distribution will be proportional to the product of the above probabilities with R and F_R . For electrons incident from the right lead with energy E , the proportionality constant is $d(E)$. Based on these considerations we write the nonequilibrium distributions in the right lead due to elastically and inelastically scattered electrons as

$$\begin{aligned}
(f_{-,el}^{\alpha,\alpha'})^R(E') = & d(E') F_R(E') R_R^{\alpha,\alpha'}(E', E') \\
& \times \left[1 - \sum_{\alpha'} (f_{+,in}^{\alpha,\alpha'})^R(E') - \sum_{\alpha'} (f_{-,in}^{\alpha,\alpha'})^R(E') \right] \quad (10)
\end{aligned}$$

$$\begin{aligned}
(f_{-,in}^{\alpha,\alpha'})^R(E') = & d(E) F_R(E) R_R^{\alpha,\alpha'}(E, E') \left[1 - (f_{+,el}^{\alpha,\alpha})^R(E') \right. \\
& - (f_{-,el}^{\alpha,\alpha})^R(E') - \sum_{\alpha'} (f_{+,in}^{\alpha,\alpha'})^R(E') \\
& \left. - \sum_{\beta \neq \alpha'} (f_{-,in}^{\alpha,\beta})^R(E') \right]. \quad (11)
\end{aligned}$$

Similarly a system of equations is set up for the nonequilibrium electron distributions in the left lead, $(f_{+,el}^{\alpha,\alpha})^L$, $(f_{+,in}^{\alpha,\alpha'})^L$, $(f_{-,el}^{\alpha,\alpha})^L$, and $(f_{-,in}^{\alpha,\alpha'})^L$. [Here, (+) signifies transmitted electrons from the right lead to left lead, (−) refers to reflected electrons in the left lead, and (L) denotes that all these distributions are in the left lead.]

The last consideration we must impose is particle conservation. Particle conservation requires that the total incoming current be equal to the sum of the total transmitted current plus the total reflected current. This will allow us to determine the constants of proportionality for both the left and right leads. For the left lead we apply the following equality:

$$\begin{aligned}
F_L(E) = & (f_{+,el}^{\alpha,\alpha})^R(E) + (f_{-,el}^{\alpha,\alpha})^L(E) + \sum_{\alpha'} (f_{+,in}^{\alpha,\alpha'})^R(E') \\
& + \sum_{\alpha'} (f_{-,in}^{\alpha,\alpha'})^L(E'). \quad (12)
\end{aligned}$$

This equality²¹ expresses that the incident electron distribution is equal to the sum over all transmitted and reflected electron distributions that arise from that incident channel. Since all of the transmitted and reflected distributions originated from the same incident channel, they all involve the same proportionality constant $c(E)$. Inserting the expressions for the f 's into Eq. (12) allows us to solve for $c(E)$. This yields,

$$c(E) = \frac{1}{A_{el} + A_{in} + B_{el} + B_{in}}, \quad (13)$$

where

$$\begin{aligned}
A_{el} = & T_{L \rightarrow R}^{\alpha,\alpha}(E, E) \left[1 - \sum_{\alpha'} (f_{+,in}^{\alpha,\alpha'})^R(E) - \sum_{\alpha'} (f_{-,in}^{\alpha,\alpha'})^R(E) \right] \\
A_{in} = & \sum_{\alpha'} T_{L \rightarrow R}^{\alpha,\alpha'}(E, E') \left[1 - (f_{+,el}^{\alpha,\alpha})^R(E') - (f_{-,el}^{\alpha,\alpha})^R(E') \right. \\
& \left. - \sum_{\beta} (f_{-,in}^{\alpha,\beta})^R(E') - \sum_{\beta' \neq \alpha'} (f_{+,in}^{\alpha,\beta'})^R(E') \right] \\
B_{el} = & R_L^{\alpha,\alpha}(E, E) \left[1 - \sum_{\alpha'} (f_{+,in}^{\alpha,\alpha'})^L(E) - \sum_{\alpha'} (f_{-,in}^{\alpha,\alpha'})^L(E) \right] \\
B_{in} = & \sum_{\alpha'} R_L^{\alpha,\alpha'}(E, E') \left[1 - (f_{+,el}^{\alpha,\alpha})^L(E') - (f_{-,el}^{\alpha,\alpha})^L(E') \right. \\
& \left. - \sum_{\beta} (f_{+,in}^{\alpha,\beta})^L(E') - \sum_{\beta' \neq \alpha'} (f_{-,in}^{\alpha,\beta'})^L(E') \right].
\end{aligned}$$

Similarly, $d(E)$ can be determined by applying a similar equality for the distributions originating from the right lead. This yields,

$$d(E) = \frac{1}{C_{el} + C_{in} + D_{el} + D_{in}}, \quad (14)$$

where

$$\begin{aligned}
C_{el} = & T_{R \rightarrow L}^{\alpha,\alpha}(E, E) \left[1 - \sum_{\alpha'} (f_{+,in}^{\alpha,\alpha'})^L(E) - \sum_{\alpha'} (f_{-,in}^{\alpha,\alpha'})^L(E) \right] \\
C_{in} = & \sum_{\alpha'} T_{R \rightarrow L}^{\alpha,\alpha'}(E, E') \left[1 - (f_{+,el}^{\alpha,\alpha})^L(E') - (f_{-,el}^{\alpha,\alpha})^L(E') \right. \\
& \left. - \sum_{\beta} (f_{-,in}^{\alpha,\beta})^L(E') - \sum_{\beta' \neq \alpha'} (f_{+,in}^{\alpha,\beta'})^L(E') \right]
\end{aligned}$$

$$D_{el} = R_R^{\alpha,\alpha}(E, E) \left[1 - \sum_{\alpha'} (f_{+,in}^{\alpha,\alpha'})^R(E) - \sum_{\alpha'} (f_{-,in}^{\alpha,\alpha'})^R(E) \right]$$

$$D_{in} = \sum_{\alpha'} R_R^{\alpha,\alpha'}(E, E') \left[1 - (f_{+,el}^{\alpha,\alpha})^R(E') - (f_{-,el}^{\alpha,\alpha})^R(E') \right. \\ \left. - \sum_{\beta} (f_{+,in}^{\alpha,\beta})^R(E') - \sum_{\beta' \neq \alpha'} (f_{-,in}^{\alpha,\beta'})^R(E') \right].$$

The above self-consistent system of nonlinear equations must be solved iteratively to determine the unknown distributions f , and the unknown proportionality constants $c(E)$ and $d(E)$. For an initial trial solution, we let the f 's take on the following values,

$$(f_{+,el}^{\alpha,\alpha})^R(E) = \frac{F_L(E) T_{L \rightarrow R}^{\alpha,\alpha}(E, E)}{T_{L \rightarrow R}^{\alpha,\alpha}(E, E) + R_L^{\alpha,\alpha}(E, E)}$$

$$(f_{-,el}^{\alpha,\alpha})^R(E) = \frac{F_R(E) R_R^{\alpha,\alpha}(E, E)}{T_{R \rightarrow L}^{\alpha,\alpha}(E, E) + R_R^{\alpha,\alpha}(E, E)}$$

$$(f_{+,el}^{\alpha,\alpha})^L(E) = \frac{F_R(E) T_{R \rightarrow L}^{\alpha,\alpha}(E, E)}{T_{R \rightarrow L}^{\alpha,\alpha}(E, E) + R_R^{\alpha,\alpha}(E, E)}$$

$$(f_{-,el}^{\alpha,\alpha})^L(E) = \frac{F_L(E) R_L^{\alpha,\alpha}(E, E)}{T_{L \rightarrow R}^{\alpha,\alpha}(E, E) + R_L^{\alpha,\alpha}(E, E)}$$

$$(f_{\pm,in}^{\alpha,\alpha'})^R(E) = 0$$

$$(f_{\pm,in}^{\alpha,\alpha'})^L(E) = 0.$$

Using this initial guess for the f 's, we evaluate the constants of proportionality $c(E)$ and $d(E)$ from Eqs. (13) and (14). With these determined, we then evaluate a new set of f 's from Eqs. (8)–(11) using these c 's and d 's and the old f 's. We then iterate until the f 's have converged.

With the nonequilibrium electron distributions thus determined we proceed to evaluate the electronic current flowing through the wire for an applied voltage V and at a given temperature T . At a given energy E the current, $(\delta i_+)^R$, flowing in an energy interval δE due to rightward propagating transmitted electrons in the right lead is given by the charge $-e$ times the velocity $v_R(E)$, times the density of states $dg(E)/dE$, times the electron distribution for transmitted rightward propagating electrons in the right lead $(f_{+,tot})^R(E) = (f_{+,el}^{\alpha,\alpha})^R(E) + \sum_{\alpha'} (f_{+,in}^{\alpha,\alpha'})^R(E)$. Thus, we can write (including a factor of 2 for spin)

$$(\delta i_+)^R = -\frac{2e}{h} (f_{+,tot})^R(E) \delta E, \quad (15)$$

where in one dimension the density of states cancels the velocity factor. The total current due to rightward propagating transmitted electrons in the right lead is found by integrating Eq. (15), yielding,

$$(i_+)^R(V) = -\frac{2e}{h} \int dE (f_{+,tot})^R(E). \quad (16)$$

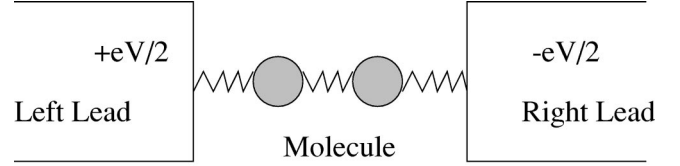


FIG. 4. A schematic of our two-site molecular wire. We model the longitudinal vibrations of the molecule using a nearest-neighbor ball and spring model. The two atoms of the molecule are coupled by an effective spring coupling k , while they are coupled to the leads with a spring coupling K .

Similarly, the total current in the left lead due to transmitted leftward propagating electrons is given by,

$$(i_+)^L(V) = \frac{2e}{h} \int dE (f_{+,tot})^L(E), \quad (17)$$

where $(f_{+,tot})^L(E) = (f_{+,el}^{\alpha,\alpha})^L(E) + \sum_{\alpha'} (f_{+,in}^{\alpha,\alpha'})^L(E)$. The net current flowing through the mesoscopic conductor is then

$$i_{tot}(V) = (i_+)^R(V) + (i_+)^L(V). \quad (18)$$

IV. APPLICATION TO A DIATOMIC MOLECULE

We now proceed to apply the above formalism to a simple molecular wire system. It consists of two identical one-dimensional leads, which are attached to the left and right ends of a two-atom chain. Figure 4 shows a schematic of our system. Each atom making up the molecule has just one atomic orbital, so the isolated two-atom molecule has two discrete electronic energy levels. When this molecule is coupled to the leads, incident electrons with energies that roughly coincide with the energy of either of these two states will be favorably transmitted. In the absence of phonons we expect two strong peaks in the transmission spectrum at the energies of the two molecular levels. When longitudinal phonons on the molecule are considered we expect interesting physics to occur when one of the phonon energies corresponds to the energy gap between the two energy levels of the molecule. When an electron is incident at an energy corresponding to the higher molecular level it can emit a phonon and drop to the lower electronic energy level. This process should have a significant transmission probability because the electron will be resonant with the higher energy level and then also with the lower energy level. (Processes where phonons are created and the electron is not resonant with either of the two molecular energy levels will not be strongly transmitting). If we assume that the leads' Fermi energy lies between the two molecular energy levels, we expect the following behavior for the nonequilibrium electron distributions: For low voltages and temperatures, the nonequilibrium electron distribution in the drain will be dominated by resonant electrons elastically scattered through the lower energy level and elastically reflected electrons. As the voltage increases the electrochemical potential in the left lead rises while it decreases in the right lead. Eventually, at sufficiently high voltages there will be electrons in the left lead with enough energy to undergo the inelastic scattering process mentioned above. The nonequilibrium electron distribution in the drain will then have a significant contribution

due to these inelastically scattered electrons. These inelastically scattered electrons will compete with elastically scattered electrons that are transmitted through the lower energy state. This competition between electrons due to the Pauli principle will play an important role in determining the current of this two site system at higher voltages.

We have chosen the following set of tight-binding parameters for the system described above. On the leads, the site energy is $\epsilon = -10$ eV and the nearest-neighbor hopping energy is $\beta_L = \beta_R = -2$ eV. For the molecule, the two atoms have the same site energy $e_1 = e_2 = -10.0$ eV and the hopping energy is $t_{1,2} = -0.15$ eV. The coupling of the left lead to the first molecular site is $w_{-1,1} = -0.2$ eV and the coupling of the second molecular site to the right lead is $w_{2,1} = -0.2$ eV. We use the SSH Hamiltonian to model the vibrational modes of the molecule and electron-phonon coupling as is discussed in the Appendix: Our vibrational model of the molecule has two longitudinal phonon modes with energies $\hbar\omega_1 = 0.24$ eV and $\hbar\omega_2 = 0.33$ eV. The electron-phonon (e-p) couplings on the chain are $\gamma_{1,2}^1 = 0.0$ eV and $\gamma_{1,2}^2 = -0.24$ eV. The e-p couplings between the leads and the chain are $\Gamma_{-1,1}^1 = 0.12$ eV, $\Gamma_{-1,1}^2 = 0.12$ eV, $\Gamma_{2,1}^1 = -0.12$ eV and $\Gamma_{2,1}^2 = 0.12$ eV. We assume that the system is at a temperature of $T = 77$ K.

For the transport calculation, the initial phonon state $|\alpha\rangle = |\{n^k\}\rangle$ is taken to be the average phonon distribution on the chain for temperature T , with $n^k = 1/\{\exp[\hbar\omega_k/(k_B T)] - 1\}$. We approximate each average mode occupation number n^k by the nearest integer. At the temperature of interest, $|\alpha\rangle = |\{n_1, n_2\}\rangle = |\{0, 0\}\rangle$. The other phonon states that we include in the calculation are those obtained by taking all $n_i = 0, \dots, N_{max}$ where $N_{max} = 2$.

In Fig. 5(a), the total transmission probability found by summing over all outgoing channels (solid line) is shown along with the transmission probability in the absence of phonons (dashed line). (These transmission probabilities were calculated for 0 V applied across the molecule. We emphasize that they are the *one-electron* transmission probabilities defined in Sec. II and do not reflect the effects of the Pauli principle discussed in Sec. III. The latter is taken into account in the calculated nonequilibrium distributions and currents presented later in this section). In the absence of phonons the two strong resonant tunnelling peaks are seen. With the inclusion of phonons, there are extra peaks due to the creation of phonons. The two resonant peaks are shifted because the inclusion of vibrations alters the hopping between sites, which in turn shifts the energies at which electrons are resonant. In Fig. 5(b), the transmission probability for elastically scattered electrons is shown. The elastic spectrum shows two strong peaks at the molecular energy levels. It also has other smaller peaks which are due to the interaction of the electrons with virtual phonons.

Figure 6 shows the inelastic one-electron transmission probability for three of the inelastic channels vs the energy E of the incident electron state. The first graph, Fig. 6(a) is for the process where a phonon with $\hbar\omega_1 = 0.24$ eV is created on the molecule. The peak labeled A corresponds to an electron emitting this phonon and dropping into the lower resonant molecular energy level at -10.26 eV. The peak labeled B corresponds to resonant tunnelling through the higher mo-

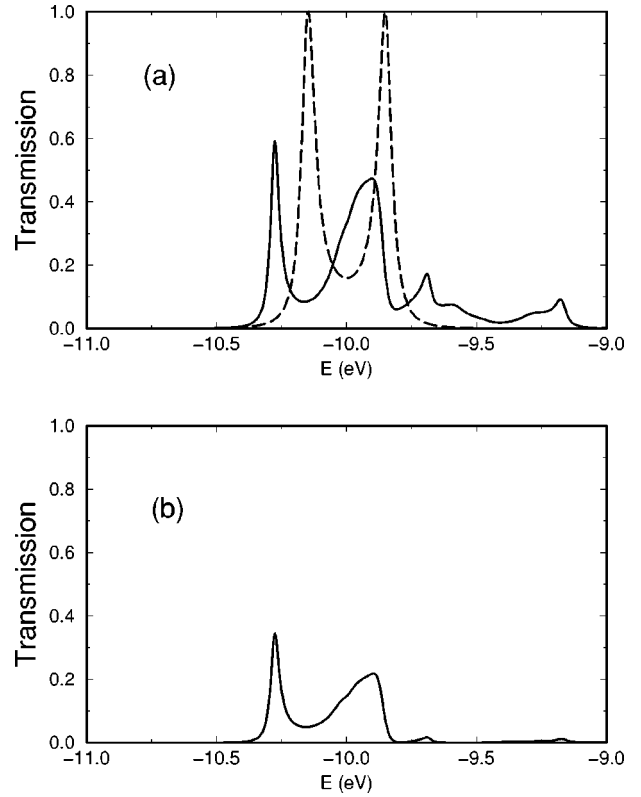


FIG. 5. (a) Total transmission probability as a function of energy E of the incident electron for the two site molecule. The dashed curve corresponds to the transmission probability in the absence of phonons. The solid curve is with the inclusion of longitudinal phonons in the calculation at a temperature of $T = 77$ K. (b) The transmission probability for the elastic scattering channel of the two site. Both graphs are at $V = 0$ molecule.

lecular energy level after the creation of this phonon. The two tunnelling peaks C and D at the energies of the molecular resonant states correspond to an electron entering the resonant molecular energy levels prior to emitting the same phonon. The second graph, Fig. 6(b) corresponds to the creation of a single excitation of the second phonon mode with energy $\hbar\omega_2 = 0.33$ eV, equal to the molecular energy level gap. As discussed previously, we expect electrons with energies incident on the higher energy molecular state to be strongly transmitting and this process corresponds to the peak labeled A in this graph. Graph (c) is for the process where a single excitation is created in both phonon modes. The transmission probability of this process is essentially the superposition of Figs. 6(a) and 6(b), with an overall reduction in amplitude because this corresponds to a higher order process.

We now proceed to calculate the nonequilibrium electron distributions from the calculated one-electron transmission and reflection coefficients using the method presented in Sec. III. We take the Fermi energy of the leads to be $\epsilon_F = -10$ eV. The nonequilibrium distributions play an important role in the calculation of the current because of the Pauli principle. For instance, the presence of inelastically transmitted or back-scattered electrons can result in a significant suppression of the elastically transmitted current. In this system, as mentioned above, the process whereby an electron creates a phonon with energy $\hbar\omega_2$ and is then at resonance with the

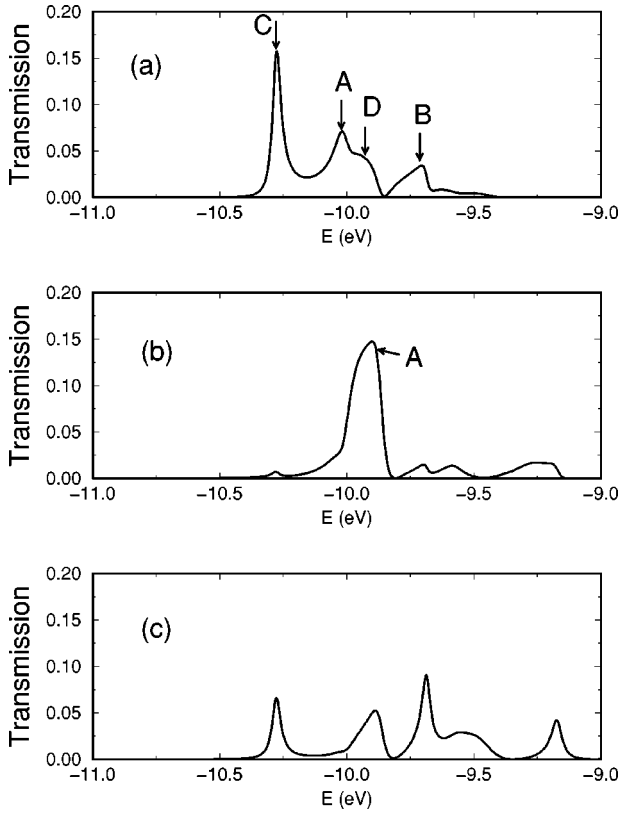


FIG. 6. Transmission probabilities for three of the inelastic scattering channels of the two site molecule. (a) Scattering from the initial state $|\alpha\rangle = |0,0\rangle$ to $|\alpha'\rangle = |1,0\rangle$. (b) Scattering from the initial state $|\alpha\rangle = |0,0\rangle$ to $|\alpha'\rangle = |0,1\rangle$. (c) Scattering from the initial state $|\alpha\rangle = |0,0\rangle$ to $|\alpha'\rangle = |1,1\rangle$. All graphs were calculated at $T = 77$ K and $V = 0$.

lower electronic resonant tunnelling state, is strongly transmitting in the inelastic spectrum at $E = -9.9$ eV. At low voltages there are not very many of these particular inelastic processes occurring since there are not many electrons with this energy incident from the left lead, and the final electron states for the transitions are almost fully occupied by competing elastic processes. At higher voltages (greater than 0.55 V) there is a significant number of these processes and the nonequilibrium distribution $f_{+,in}^{\alpha,\alpha'}(E)$ where α' corresponds to the phonon state $\{n_k'\} = \{0,1\}$ is significant. As the voltage increases further, the total distribution due to inelastically scattered electrons continues to grow as more processes become energetically favorable. The total nonequilibrium Fermi distribution for all of the transmitted elastically scattered electrons is shown in Fig. 7(a) for 0.5 V (solid line) and 1 V (dashed line). Figure 7(b) shows the corresponding distribution for inelastically transmitted electrons. It highlights how this distribution function increases as more inelastic processes become energetically favorable. It also shows that there is a significant presence of inelastically scattered electrons in the drain for energies around -10.25 eV. At this energy, elastically scattered electrons are also particularly strongly transmitting and the dip in the distribution of the inelastically scattered electrons at this energy is due to the presence of these elastically scattered electrons in the drain. This is labeled “A” in Fig. 7(b).

These nonequilibrium distributions are now used to evalu-

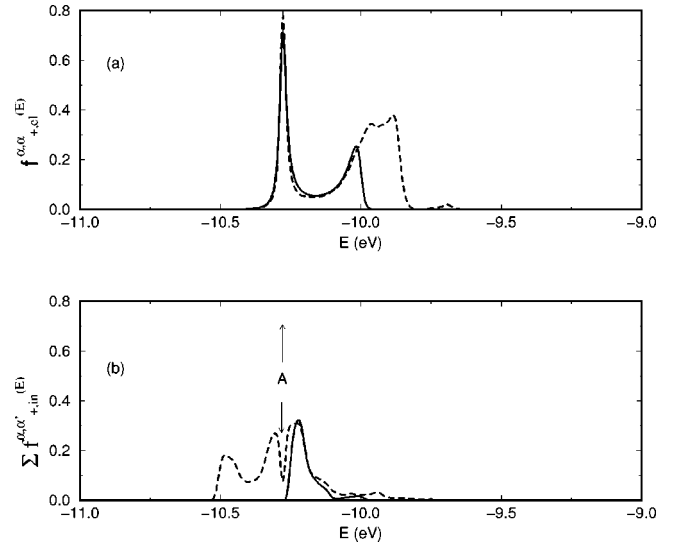


FIG. 7. Nonequilibrium electron distributions in the right lead for the two site molecule. (a) Total nonequilibrium electron distribution for transmitted elastically scattered electrons at 0 V (dashed curve) and 1 V (solid curve). (b) Total nonequilibrium electron distribution for transmitted inelastically scattered electrons at 0.5 V (solid curve) and 1 V (dashed curve). The position labeled “A” shows how there is a dip in the inelastic distribution due to the sharp rise in the elastic distribution at that energy E .

ate the current flowing through the two atom molecule. In Figs. 8(a) and 8(b) we show the total rightward flowing current that is elastically and inelastically transmitted through the molecule, evaluated using our method.

We also show (dotted lines) the corresponding currents evaluated assuming instead that the nonequilibrium distribution of electrons in the drain that appears in the Pauli exclusion factor is replaced simply by the equilibrium Fermi func-

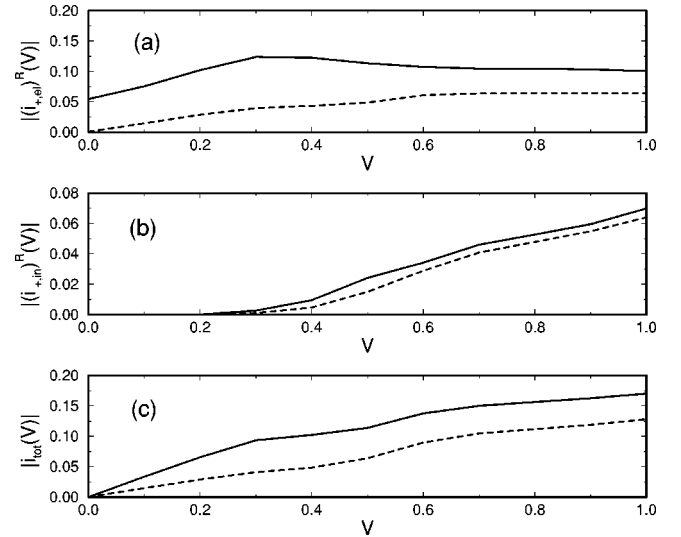


FIG. 8. (a) Total rightward flowing electronic current in the right lead due to elastically transmitted electrons. (b) Total rightward flowing electronic current in the right lead due to inelastically transmitted electrons. (c) The net electronic current flowing through the two-site molecule. The solid curves are calculated from the nonequilibrium electron distribution and the dashed curves are calculated using Eq. (19). The current is in units of $2e^2/h eV$.

tion in the right lead. For transmitted elastically scattered electrons this simplified expression for the current is

$$i_{el}^+ = -\frac{2e}{h} \int dE T_{L \rightarrow R}^{\alpha, \alpha}(E, E) F_L(E) [1 - F_R(E)]. \quad (19)$$

For models that do *not* include electron-phonon interactions, the *net* current through the molecule obtained in this way is the same¹¹ as is obtained from Landauer theory, although the factor $[1 - F_R(E)]$ does not appear in the latter as was explained in the introduction. However, if electron-phonon interactions are present, approximating the effects of the Pauli principle in this way does not account for competition between elastic and inelastic processes which (at higher voltages) inject electrons into states that are unoccupied according to the equilibrium distribution. This approximation (even at low voltages) also violates particle conservation when electron-phonon interactions are present.

By using the nonequilibrium distributions described in Sec. III these effects are properly taken into account and current is conserved. All of this is reflected in the graphs: In Fig. 8(a) initially the solid curve (the present result) shows significantly more elastic current (as expected from Landauer theory), and then eventually the elastic current is reduced due to the presence of transmitted inelastically scattered electrons in the normally unoccupied states of the drain. The total current flowing through the molecule as a function of voltage is shown in Fig. 8(c). The larger total current exhibited by the solid curve is a manifestation of current conservation in the present formalism. The dashed curve falls below the solid curve because the approximations used to calculate it do not conserve current.

V. CONCLUSIONS

We have shown that to generalize Landauer theory to include the effects of inelastic scattering, it is necessary to calculate selfconsistently the nonequilibrium contributions to the electron distribution in the source and the drain leads. We have developed a method for determining these nonequilibrium distributions and applied it to a simple model. The model was based on single-channel ideal leads attached to a mesoscopic conductor. Phonons were only considered on the conductor. The nonequilibrium distributions were determined solely in terms of the Fermi functions of the left and right leads and the transmission and reflection probabilities for the various one-electron elastic and inelastic scattering processes considered. We showed how to properly take account of the Pauli exclusion principle and particle conservation in the calculation of the nonequilibrium electron distribution. We applied our approach to a two site molecule. One of the phonons had an energy that corresponded to the molecular energy level gap. For this system we found that the details of the nonequilibrium electron distribution had an important role in the determination of the current. At higher voltages we found that the distribution in the right lead due to inelastically scattered electrons began to compete significantly with elastically scattered electrons because of the Pauli exclusion principle. We found that this competition resulted in a reduction of the elastically scattered current at higher voltages.

ACKNOWLEDGMENT

This work was supported by NSERC.

APPENDIX

To find the vibrational modes of a molecule the atoms and bonds may be modelled by a set of balls and springs. For our model, we consider chainlike molecules, and represent the chain as a set of balls with effective springs connecting nearest-neighbor atoms. The longitudinal displacement from equilibrium of the i th atom with mass m_i in the molecule is given by the coordinate q_i . We assume that each atom only interacts with its nearest neighbors via an effective spring coupling $V_{i,j}$. The molecule has a discrete set of longitudinal normal modes which vibrate with a particular frequency ω_k and have atomic displacements given by $q_i^k = d_i^k \exp(-i\omega_k t)$. These normal modes satisfy the familiar eigenvalue problem,

$$\sum_j V_{i,j} d_j^k = \omega_k^2 m_i d_i^k \quad (A1)$$

where for our model, the sum over j is just over the nearest neighbors of atom i . Solving this equation yields the eigenfrequencies and eigenvectors for the longitudinal normal modes.

The problem is canonically quantized by assuming $[q_i, p_j] = i\hbar \delta_{i,j}$, where p_j is the conjugate momentum to q_j . We transform into normal mode operators Q_k and P_k by writing $q_i = \sum_k d_i^k Q_k$ and $p_i = \sum_k d_i^k m_i P_k$. It is easily verified that $[Q_k, P_{k'}] = i\hbar \delta_{k,k'}$. Performing second quantization on these operators gives,

$$Q_k = \sqrt{\frac{\hbar}{2\omega_k}} (a_k + a_k^\dagger) \quad (A2)$$

$$P_k = i \sqrt{\frac{\hbar \omega_k}{2}} (a_k^\dagger - a_k), \quad (A3)$$

where a_k^\dagger and a_k are creation and destruction operators for the normal mode (or phonon) with frequency ω_k , respectively.

The effects of longitudinal vibrations on the electronic properties of the molecule can be taken into account by using the Su-Schreiffer-Hieger (SSH) model.¹⁶ In it, the nearest-neighbor hopping parameter $t_{i,j}$ between two neighboring atomic sites is expanded to linear order in terms of their atomic displacements from equilibrium. This gives,

$$t_{i,j} = t_{i,j}^0 - \alpha_{i,j} (q_i - q_j) \quad (A4)$$

where $t_{i,j}^0$ is the hopping parameter at $q = q_i = q_j = 0$ and $\alpha_{i,j} = (dt_{i,j}/dq)_{q=0}$. (Note $\alpha_{j,i} = -\alpha_{i,j}$.)

By using the above expression for q_i in terms of the Q_k 's, and writing them in their second quantized form, this gives $t_{i,j}$ as,

$$t_{i,j} = t_{i,j}^0 - \alpha_{i,j} \sum_k (d_i^k - d_j^k) \sqrt{\frac{\hbar}{2\omega_k}} (a_k + a_k^\dagger). \quad (A5)$$

This defines the mode dependent electron-phonon coupling, $\gamma_{i,j}^k$ as,

$$\gamma_{i,j}^k = \alpha_{i,j} \sqrt{\frac{\hbar}{2w_k}} (d_i^k - d_j^k) \quad (\text{A6})$$

in terms of the known quantities $\alpha_{i,j}$, ω_k and the d^k 's.

We now proceed to evaluate the eigenfrequencies and eigenvectors of the longitudinal modes for our two atom molecule attached to two semi-infinite leads. The atoms in the leads are assumed fixed in their static positions. The effective spring coupling between the leads and the nearest-neighbor atoms on the molecule is given by $K = 180 \text{ eV/\AA}^2$. The effective spring coupling between the two atoms of the molecule is $k = 90 \text{ eV/\AA}^2$. Each atom of the molecule has a mass $m = 13 \text{ A.M.U.}$ Solving the eigenvalue problem using the above parameters we find two phonon

modes with energies of $\hbar\omega_1 = 0.24 \text{ eV}$ and $\hbar\omega_2 = 0.33 \text{ eV}$. The corresponding eigenvectors are $d_1^1 = 0.054 \text{ \AA}$, $d_2^1 = 0.054 \text{ \AA}$, and $d_1^2 = 0.054 \text{ \AA}$, $d_2^2 = -0.054 \text{ \AA}$.

In the SSH model the electrons are coupled to the phonons via the parameter $\alpha_{i,j}$. The nearest-neighbor coupling between the leads and the molecule and between the two sites on the molecule is assumed to be $\alpha_{i,j} = 25 \text{ eV/\AA}$ for i to the right of j . This gives the couplings between the first site on the molecule and the left lead as $\Gamma_{1,-1}^1 = \Gamma_{1,-1}^2 = 0.12$. The couplings between the right lead and the second site on the molecule are $\Gamma_{1,2}^1 = -0.12$ and $\Gamma_{1,2}^2 = 0.12$. The electron-phonon couplings on the molecule are $\gamma_{2,1}^1 = 0$ and $\gamma_{2,1}^2 = -0.24$.

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²¹Here each initial phonon configuration is treated separately because Eq. (12) expresses electron conservation in the scattering process, and electron conservation should apply separately for every initial phonon state of the conductor and every incident electron state.