

## Nonlinear Electron Current through a Short Molecular Wire

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The voltage and the temperature behavior of inelastic interelectrode current mediated by a short molecular wire is analyzed within a nonlinear kinetic approach that accounts for strong Coulomb repulsion between transferring electrons. When the coupling to the heat bath occurs via high-frequency vibration modes we predict a generally nonlinear current-voltage characteristics (an Ohmic behavior at small voltage, rising towards saturation and being followed by an abrupt decrease at large voltage) and a bell-shaped current response vs temperature at not too large temperatures.

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Molecular wires refer to especially tailored molecular nanostructures whose spatial and energetic properties promote a distant electron transfer (ET) between two microelectrodes [1–5]. These molecular systems are able to exhibit various nonlinear features such as, e.g., a threshold behavior, rectification, or a blockade characteristic. As such, these structures form the ideal candidates possessing the potential to construct novel molecular electronic devices such as a few-molecule transistor. In recent years, much emphasis has been placed on the study of *elastic* [1–6] and *inelastic* [2,7–10] ET processes mediated by a molecular wire including as well ET processes that are controlled by external magnetic [6,7] and time-dependent [11] fields. There exist molecular nanostructures [12] where the ET process is mediated by incoherent hopping events. In those cases the role of Coulomb repulsion will prominently rule the transport when the molecular wire is synthesized to be of small length, typically of 25–40 Å in size. Our primary objective with this work is to study the physics of an inelastic *hopping* interelectrode electron current in a *short* molecular wire where the presence of a strong Coulomb repulsion between transferring electrons causes a nonlinear current characteristics. We restrict ourself to a physical situation where the energy separation between the lowest unoccupied molecular orbital (LUMO) levels of each wire unit and the Fermi level is much less than the corresponding energy distance between the Fermi level and the highest occupied molecular orbital (HOMO) levels. In this case, the thermal activation of an electron from the Fermi level to the LUMO level is much more effective than the corresponding activation of a hole to the Fermi level; consequently, a hole transport is not essential.

*Theoretical model.*—To start, we model the molecular nanostructure by a linear molecular wire (MW) composed of  $N$  units that are divided by spacers (S) and bridging groups (B), Fig. 1a. The bridging groups form the superexchange electron couplings  $V_{nn\pm 1}$  between the neighboring wire units. It is well known from the theory of bridge-assisted ET [13] that for a weak site-to-site superexchange coupling  $V_{nn'}$  the coherent effects in ET play a

minor role. The ET between two sites  $n$  and  $n'$  then assumes a nonadiabatic character. The corresponding quantum transfer rates (denoted by  $g_n$  and  $r_n$  in Fig. 1a) follow from a Golden rule calculation. The same situation holds for the site electrode, and electrode-site transfer rates, i.e.,  $\chi_{a,b}$  and  $\chi_{-a,-b}$ , respectively. In a *short* molecular wire the Coulomb repulsion is shown to inhibit statistically the appearance of an additional extra electron if the length of molecular wire does not exceed 40 Å and, additionally, the wire is surrounded by a nonpolar medium (with a dielectric constant  $\epsilon = 3 - 5$ ).

The physics of Coulomb repulsion thus reduces the number of possible configuration wire states to two types only, one *without* and one *with* a single transferring electron inside the wire. Statistically, the working states are characterized by the weight  $W_0$  to find the whole wire in

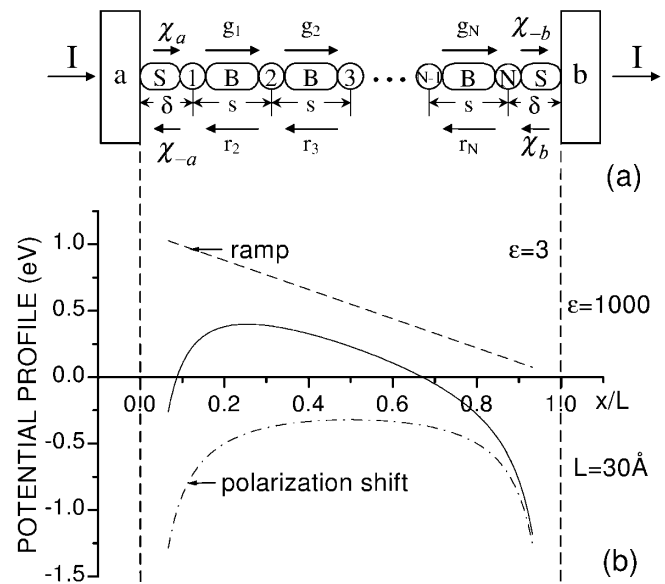


FIG. 1. (a) Linear molecular wire embedded between the microelectrodes. (b) Electrostatic profile (solid line) formed by the ramp (dotted line) and the polarization image potential (dashed line).

the *open* state and the weights  $W_n$ , ( $n = 1, 2, \dots, N$ ) for  $N$  *singly occupied* wire states, respectively. The interelectrode electron current through the short wire is then governed by a nonlinear kinetic process that involves just these two classes of wire configuration weights. The remaining wire states that statistically involve two, three, or more transferring electrons occupying the wire can be referred to as blocking states.

*Nonlinear kinetic approach to molecular wire current.*—As far as a Coulomb repulsion allows only a single electron transfer across the wire, we can work with averaged site occupancies  $P_n \leq 1$ , ( $n = 1, 2, \dots, N$ ). The working configuration weights can be written as  $W_0 \equiv \prod_{n=1}^N (1 - P_n)$  and  $W_n = P_n \prod_{j \neq n}^N (1 - P_j)$ . In the absence of a magnetic field, the current related to any fixed electron spin projection is given by  $I = -e\dot{N}_a = e(\chi_a W_0 - \chi_{-a} W_1)$  where  $e$  is the value of electron charge, and  $\dot{N}_a = -\dot{N}_b$  is the time variation of the number of electrons which are capable of being transferred through a molecular wire from electrode  $a$  to electrode  $b$ . To specify  $W_0$  and  $W_n$  we have derived (by use of a density matrix method [14]) a set of coupled nonlinear quantum kinetic equations for the site occupancies  $P_n$ , reading [15]

$$\begin{aligned} \dot{P}_1 &= -(\chi_{-a} + g_1)P_1 \prod_{j \neq 1} (1 - P_j) + \chi_a \prod_j (1 - P_j) \\ &\quad + r_2 P_2 \prod_{j \neq 2} (1 - P_j), \\ \dot{P}_n &= -(g_n + r_n)P_n \prod_{j \neq n} (1 - P_j) \\ &\quad + g_{n-1} P_{n-1} \prod_{j \neq n-1} (1 - P_j) \\ &\quad + r_{n+1} P_{n+1} \prod_{j \neq n+1} (1 - P_j), \quad (n \neq 1, N), \\ \dot{P}_N &= -(\chi_{-b} + r_N)P_N \prod_{j \neq N} (1 - P_j) + \chi_b \prod_j (1 - P_j) \\ &\quad + g_{N-1} P_{N-1} \prod_{j \neq N-1} (1 - P_j). \end{aligned} \quad (1)$$

Our focus is on the stationary current when  $\dot{N}_a$  assumes a constant. By use of the stationary condition  $\dot{P}_n = 0$ , and by invoking the auxiliary quantities  $U_n := P_n/(1 - P_n)$ ; i.e.,  $P_n = U_n/(1 + U_n)$ , the set (1) assumes a *linear*, inhomogeneous system of equations for the set  $\{U_n\}$  of the form  $\mathbf{A}U = C$ , which can be solved iteratively to yield

$$\begin{aligned} U_1 &= \frac{1}{\chi_{-a}} (-J + \chi_a), \\ U_{n+1} &= \frac{1}{r_{n+1}} (-J + g_n U_n), \end{aligned} \quad (2)$$

where the particle flow through the wire

$$J = \frac{1}{\text{Det}} (\chi_a g_1 \cdots g_{N-1} \chi_{-b} - \chi_b r_N \cdots r_3 r_2 \chi_{-a}) \quad (3)$$

is given in terms of the determinant  $\text{Det}$  of the corresponding matrix  $\mathbf{A}$ .

Casting the interelectrode current into the form

$$I = eW_0 J, \quad \left( W_0 = \prod_{n=1}^N [1/(1 + U_n)] \right), \quad (4)$$

we can formally consider  $W_0$  as a transmission factor. It is this very dependence on  $W_0$  which characterizes the physics at work in a *short* molecular wire.

Equations (2)–(4) describe single-electron hopping ET across a short molecular wire. We next discuss the current-voltage (-temperature) dependence for the case of a regular wire with identical units. The specification of the transfer rates is obtained for a molecular wire model where the coupling to a heat bath occurs effectively via an active vibrational mode of frequency  $\omega_0$  [16]. For this case the theory of nonadiabatic ET [5,11,13,17] yields the rates [13,17]:  $r_{n+1} = \exp[-(E_n - E_{n+1})/k_B T] g_n$ ,

$$\begin{aligned} g_n &= \alpha_0 \Phi_{\nu_n}, \\ \Phi_{\nu_n} &= \exp \left[ -S \coth \frac{\hbar \omega_0}{2k_B T} \right] \left[ \frac{1 + n_B(\omega_0)}{n_B(\omega_0)} \right]^{\nu_n/2} \\ &\quad \times I_{|\nu_n|} (2S \sqrt{n_B(\omega_0) [1 + n_B(\omega_0)]}). \end{aligned} \quad (5)$$

Next, we specify the transfer rates  $\chi_{a,b}$  and  $\chi_{-a,-b}$ . The latter ones are determined by transitions between the terminal local level and the quasicontinuous band spectrum. Here, the phononless transitions, i.e.,  $\nu = 0$ , yield the main contribution, i.e., with  $\chi_{a,b} = \exp[-\Delta E_{a,b}/k_B T] \chi_{-a,-b}$  one obtains

$$\chi_{-a,-b} = \chi_0 [1 - n_F(\Delta E_{a,b})] \Phi_0. \quad (6)$$

In (5) and (6),  $\alpha_0$  and  $\chi_0$  denote voltage and temperature independent constants;  $n_B(\omega_0) = [\exp(\hbar \omega_0/k_B T) - 1]^{-1}$  and  $n_F(\Delta E_{a,b}) = [\exp(\Delta E_{a,b}/k_B T) + 1]^{-1}$  are Bose and Fermi distribution functions, respectively.  $T$  is the temperature,  $\Delta E_a = E_1 - E_F - eV$ ,  $\Delta E_b = E_N - E_F$  with  $V$  being the applied voltage bias.  $E_F$  is the Fermi-level energy;  $\nu_n := (E_n - E_{n+1})/\hbar \omega_0$  with  $E_n$  being the energy of the transferring electron which occupies the  $n$ th wire unit;  $S = \lambda/\hbar \omega_0$  ( $\lambda$  is the reorganization energy); and  $I_{|\nu_n|}(z)$  denotes the modified Bessel function.

The hopping mechanism of the underlying nonadiabatic ET implies that the transferring electron is localized within a molecular wire. Therefore, a spatially varying electrostatic potential [4,10] acts on the transferring electron. It consists of the sum of the polarization image-force potential at the electrodes and the linear ramp across the metal electrode, i.e.,  $E_n = E_0 + E^{(i)}(x_n) + eV(1 - x_n/L)$  where  $E_0$  is the energy of the unperturbed LUMO level,  $E^{(i)}(x_n)$  is the polarization shift [2,10] at the site of electron localization  $x_n = \delta + (n - 1)s$  [ $\delta$  and  $s$  are the distances indicating the electron localization,  $L = 2\delta + (N - 1)s$  is the wire length, cf. Fig. 1].

*Discussion of main result.*—The current (4) is caused by the competition between the transfer rates which form a particle flow  $J$  and a blocking transmission factor  $W_0$ .

To specify the voltage and temperature dependence of the rates (and thus the current) we refer to values for the parameters  $\lambda$  and  $\omega_0$  that characterize common ET in rigid molecular systems [13,16].

*Voltage dependence.*—Let the temperature be held fixed. The analysis shows that for the case that the site-electrode distance  $\delta$  is comparable with the site-site distance  $s$ , cf. Fig. 1a, and with a symmetric form of polarization shift  $E^{(i)}(x_n)$ , cf. Fig. 1b, the current-voltage (-temperature) characteristic is similar both with a local shift  $E^{(i)}(x_n)$  or an averaged polarization shift, i.e.,  $\bar{E} = \frac{1}{N} \sum_{n=1}^N E^{(i)}(x_n)$ . In the latter case, however, the rates (5) become equal, i.e.,  $g_1 = g_2 = \dots = g_{N-1} := \alpha$ ,  $r_N = r_{N-1} = \dots = r_2 := \beta$ ,  $\nu_n := \nu = eVs/L\hbar\omega_0$  implying  $U_{n+1} = \frac{1}{\beta}(-J + \alpha U_n)$ , with

$$J = \frac{\chi_a \zeta_a - \chi_b \zeta_b \gamma^{N-2}}{(1 - \gamma^{N-1})/(1 - \gamma) + \zeta_a + \zeta_b \gamma^{N-2}}, \quad (7)$$

where  $\gamma = \beta/\alpha = \exp(-eVs/Lk_B T)$ ,  $\zeta_a = \alpha/\chi_{-a}$ ,  $\zeta_b = \beta/\chi_{-b}$ . Figure 2a supports this conclusion for a wide range of the bias voltage. The further discussion and interpretation uses this simplified version. At small bias voltage  $V$ , when  $\gamma \approx 1$ , yielding  $\zeta_b \approx \zeta_a$ , all occupancies become identical, i.e.,  $P_n \approx (1 + e^d)^{-1}$ , with  $d = \Delta E/k_B T$  and  $\Delta E = E_0 - E_F + \bar{E}_i$ . As a consequence, we find that the voltage behavior of the current assumes an *Ohmic law*, i.e.,  $I = GV$  where the conductance is with  $\zeta := \alpha_0/\chi_0$  given by

$$G = \frac{e^2 \chi_0 \Phi_0}{k_B T} \left( \frac{1}{1 + e^{-d}} \right)^N \frac{e^{-d}}{2(1 + e^{-d}) + \zeta^{-1}(N-1)}. \quad (8)$$

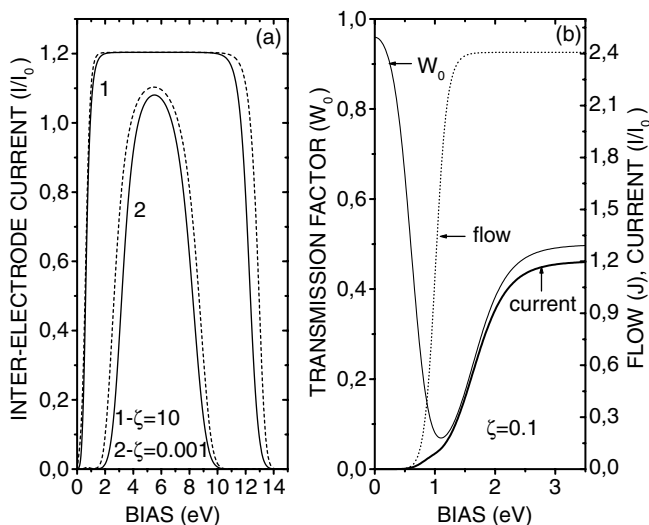


FIG. 2. Molecular wire current  $I$  (in units  $I_0 = e\chi_0 \times 10^{-6}$ ) vs voltage bias  $V$  at room temperature  $T = 300$  K for  $N = 4$ ,  $L = 30$  Å,  $\delta = 5$  Å,  $S = 20$ ,  $\omega_0 = 500$  cm $^{-1}$ , i.e.,  $\lambda = 1.25$  eV. (a) Calculations with (2), (3) (solid lines) and (2), (7) (dashed lines). (b) Dependence of transmission  $W_0$ , and flow  $J$  (in units  $\chi_0 \times 10^{-6}$ ) ruling the current  $I$  for  $E_0 - E_F = 0.68$  eV.

*Size dependence.*—Let  $\exp(-d) \ll 1$ . This condition yields a small electron population on the wire units; thus, the role of Coulomb repulsion is minor. In this case the transmission factor,  $W_0 \approx 1$ , is maximal so that the conductance (8) depends mainly on the number of wire units  $N$  via the factor  $[2 + \zeta^{-1}(N-1)]^{-1}$ . When  $\zeta$  is small, this factor reduces to  $\zeta/(N-1)$ , i.e., the conductance of the molecular wire becomes proportional to the inverse wire length. A similar Ohmic regime has also been predicted for a single electron donor-acceptor ET mediated by a bridge with a *large* number of bridge units [9]. For our case of a *short* molecular wire, this Ohmic regime corresponds to the specific condition that  $\zeta \ll N-1$ .

*Current dependence.*—When the voltage bias increases the factor  $\kappa := \exp(-\Delta E_a/k_B T) = \exp(-[\Delta E - eV(\delta/L)]/k_B T)$  which controls the delivery rate  $\chi_a$  for an electron from the Fermi sea to the first unit increases as well. This in turn causes the current to rise. At large  $V$ , when  $\gamma \ll 1$ , (7) reduces to  $J \approx \chi_a \zeta_a / (1 + \zeta_a)$ . For  $\zeta_a \gg 1$ , it simplifies to  $J \approx \chi_a \sim n_F(\Delta E_a)$ . Therefore, upon observing that with  $\kappa \gg 1$ , i.e.,  $n_F(\Delta E_a) \approx 1$ , one finds that all quantities, the flow  $J$ , the transmission  $W_0$ , and the current  $I$  saturate, cf. Fig. 2b. Notably, the length of the saturation plateau shortens with decreasing  $\zeta$ . At very small  $\zeta$ , the plateau crosses over into a peak (curve 2 in Fig. 2a). Physically, the appearance of the plateau corresponds to the switch-on of a resonance mechanism for tunneling from the electrode to the terminal wire unit. It occurs at voltages when  $\Delta E_a \leq 0$ , i.e., when the electrode-site bias  $eV\delta/L$  exceeds the effective gap  $\Delta E$ . At very large  $V$ , when  $\nu \gg 1$ , the current formally exhibits a sudden drop which is due to the limiting electron-phonon coupling for multiphonon processes as encoded with the corresponding Franck-Condon factor in the Jortner model.

*Temperature dependence.*—Next, let the voltage bias be held at a fixed value. The temperature behavior of the current is then controlled by the parameter  $\kappa$  for the delivery rate, the intersite parameter  $\gamma$ , as well as by the factor  $\exp(-\hbar\omega_0/k_B T)$  and  $\nu$ , which all specify the transfer rates. Figure 3 depicts the frequency effect: at the fixed reorganization energy  $\lambda$ , the ET process is much more effective if the coupling to the bath occurs with a high-frequency vibration mode; e.g., at room temperature,  $T = 300$  K, the difference in currents comprises 2 orders of magnitude for  $\omega_0 = 1000$  cm $^{-1}$  and  $\omega_0 = 2000$  cm $^{-1}$ , respectively. At high frequencies, the current-temperature dependence assumes a bell-shaped behavior. It can be explained as follows: for  $eV\delta/L < \Delta E$ , i.e.,  $\Delta E_a > 0$ , and the first energy level of the transferring electron being positioned above the Fermi level the factor  $\kappa$  is at low temperature far too small to provide an ample population of the wire with transferring electrons. Thus, both the inner site occupancies and the resulting current are small. With increasing temperature the occupancies  $P_n$ , the flow  $J$ , and the current  $I$  rise as well. The rise of occupancies, however, causes the transmission factor  $W_0$  to decrease. A bell-shaped behavior in an intermediate

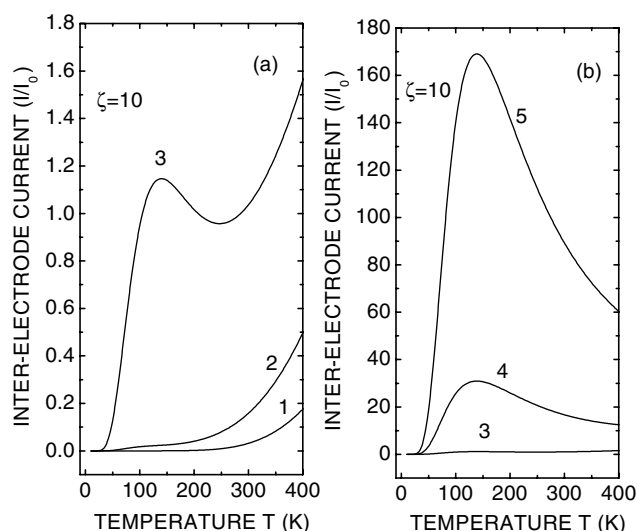


FIG. 3. Interelectrode current  $I$  from (2), (7) (in units  $I_0$ ) vs temperature  $T$  at a fixed voltage  $eV = 0.01$  eV for  $N = 4$ ,  $L = 30$  Å,  $\delta = 5$  Å,  $E_0 - E_F = 0.48$  eV,  $\lambda = 1.25$  eV. The lines are calculated for (a) 1 ( $\omega_0 = 500$  cm $^{-1}$ ), 2 ( $\omega_0 = 700$  cm $^{-1}$ ), and 3 ( $\omega_0 = 1000$  cm $^{-1}$ ); (b) 3 ( $\omega_0 = 1000$  cm $^{-1}$ ), 4 ( $\omega_0 = 1500$  cm $^{-1}$ ), and 5 ( $\omega_0 = 2000$  cm $^{-1}$ ).

temperature regime thus reflects the competition between the delivery process for an electron from the electrode onto the adjacent terminal unit and the repulsion effect induced by the transferring electrons. The bell-shaped behavior, however, is not universal; a moderate bath oscillator frequency can cause a monotonic current-temperature characteristic, cf. Fig. 3a.

**Conclusions.**— In this work we have elucidated the characteristics of an inelastic (hopping) ET through a short molecular wire. The basic expressions for the particle flow  $J$  and transmission factor  $W_0$  follow from the stationary solution of the corresponding set of nonlinear quantum kinetic equations for the site occupancies  $P_n$  (1). In this way, all transfer rates displayed in Fig. 1a become defined in terms of the microscopic site-electrode and site-site electron couplings, as well as the vibrational structure of the thermal environment. The effect of Coulomb repulsion is accounted for in a nonlinear kinetic manner via a transmission factor. The Coulomb inhibition is most effective when the transmission factor  $W_0$  assumes a small value. At fixed temperature, an Ohmic behavior can appear at small bias voltages, cf. Fig. 2b. At strong bias, however, one can observe a saturation or rather a broad peak behavior, cf. Fig. 2a. The situation changes for a fixed voltage: For a high vibrational frequency of the bath mode one can find an intermediate decrease of the current with increasing temperature. The current-voltage and the temperature-voltage characteristics depend substantially on the form of the transfer rates and the parameters specifying those rates. The results of the present work relate to a model where the hopping process occurs due to a coupling with a high-frequency vibration mode.

Independently on the specific form of rate constants, the bell-shaped behavior of the current has its origin mainly in the transmission factor  $W_0$ . Therefore, in virtue of the strong nonlinearity caused by the Coulomb repulsion between the transferring electrons in a short wire, the current can be controlled externally upon varying not only the voltage but also the temperature. Apart from its potential for molecular electronics the nonlinear processes dealt with in this work do impact other transport schemes such as the charge transfer in low-dimensional systems including strongly anisotropic single crystals, doped polymers, supramolecular compounds, and even transport in ion channels.

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