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Incoherent charge transport through molecular wires: interplay of Coulomb interaction and wire population

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Abstract

The influence of Coulomb interaction on the electron transport through molecular wires is studied in the regime of incoherent tunneling. In the limit of strong Coulomb repulsion, the current for spinless electrons is determined. It is shown that the voltage profile along the wire crucially influences the dependence of the current on the wire length. Upon inclusion of the spin degree of freedom one finds a blocking effect which depends both on the *interaction strength* and on the *population* of the wire. For finite Coulomb interaction, the temperature dependence of the blocking is studied and it is shown that several regimes with different blocking strength may exist.

Keywords: Molecular wire; Electron transfer; Coulomb interaction

1. Introduction

In the last few years, considerable progress towards an electronics based on single molecules has been made [1]. Nanotubes [2,3], fullerenes [4,5], and organic molecules [6–9] have been contacted and current–voltage characteristics were measured. These experimental successes are accompanied by a vast body of theoretical studies [10] which mostly concentrate on coherent transport through the molecules. However, relaxation processes on the molecule may lead to incoherent transport [11–13] and some of the experimental data may be interpreted in this sense [5,8].

In the coherent regime, Coulomb interaction may give rise to interesting effects in the current–voltage characteristics [14,15]. However, the additional charge due to the coupling to the electrodes is often small [16] and then charging effects should be weak. In contrast, for incoherent transport, electrons are temporarily localized on the wire and thus the influence of Coulomb interaction becomes more significant. Recently, this problem of incoherent transport in the presence of Coulomb interaction has been addressed by Petrov et al. [12,13] in the framework of a nonlinear quantum kinetic statistical many-body approach in mean-field approximation in the limit of very strong Coulomb interaction. In the present paper we will instead employ a description based on master equations which allows us to elucidate the role of the electron spin, finite Coulomb interaction, and finite temperature.

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We start in Section 2 by introducing a generic model for the molecular wire and discussing the voltage profile across the wire. Assuming that relaxation processes on the wire units are much faster than the time scale for tunneling between different units, a description in terms of rate equations for the electronic state of the wire is then adequate. The limit of strong Coulomb repulsion, which will be considered in Section 3, allows us to restrict the calculation to the lowest unoccupied molecular orbitals (LUMOs) and to neglect excitations to higher levels. In particular, this implies that temperature is sufficiently low so that the Coulomb interaction exceeds the thermal energy. In Section 4 we will include the spin degree of freedom for the electrons which had been neglected in Section 3. In this context the blocking of spin channels due to Coulomb interaction will be discussed in detail. Finally, in Section 5 we relax the requirement of strong Coulomb interaction and study the different regimes arising from the interplay between Coulomb repulsion and thermal fluctuations.

2. Model for a molecular wire

In this paper, we will focus on generic properties of incoherent charge transport through a molecular wire. The model for the wire will consequently be kept as simple as possible: a linear array of N identical wire units numbered consecutively from left to right is joined by $N-1$ identical molecular bridges denoted by "M". In order to apply a voltage and to pass a current through the wire, the setup shown in Fig. 1 is used where two contacts "C" connect the wire to the electrodes marked by "L" and "R".

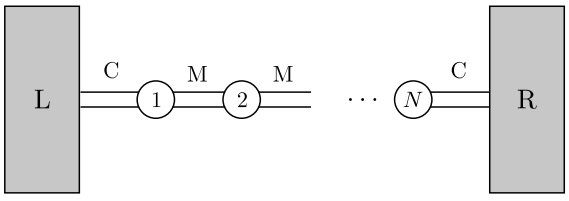

Fig. 1. The molecular wire is modeled by identical wire units represented by circles which are joined by identical molecular bridges "M". Two contacts "C" provide the connection to the left and right electrodes denoted by "L" and "R", respectively.

Except for Section 5, we will confine the discussion to the case of strong Coulomb interaction. This prevents the wire from being charged with more than one electron. Neglecting spin for the moment, the wire will then always be found in one of $N+1$ states: either the wire is in its ground state and all wire units are neutral, or exactly one of the units is charged by an additional electron. We will denote these states by "0" for a neutral wire or the number of the unit $i = 1, \ldots, N$ which carries an extra charge.

Since we are interested in the current across the molecule beyond linear response, we also need to specify the voltage drop along the wire. In principle, this requires the solution of the coupled Schrödinger and Poisson equations of the electrode–molecule–electrode system [17], which in itself presents a formidable task that we will not try to tackle. Instead, we will use the simple model proposed in [7,16], which views the two electrodes as parallel plates forming a capacitor with the molecule in between acting like a dielectric.

Within this picture one obtains a potential profile where the applied voltage V drops partially by $\eta_L V$ and $\eta_R V$ at the left and right contact, respectively, and decreases linearly by $\eta_M V$ along the wire. The condition $\eta_L + \eta_M + \eta_R = 1$ ensures that we have accounted for the full voltage drop. This situation is shown in Fig. 2 where we have fixed the electrochemical potential in the left electrode at zero energy. The dashed lines at energy $\mathscr{E}$ indicate the position of the LUMOs in the absence of an applied voltage. The actual levels represented by the full lines at energies

$$E_i = \mathscr{E} - \eta_L eV - \eta_M \frac{i-1}{N-1} eV \tag{1}$$

are shifted according to the local voltage, thereby displaying the voltage profile.

The current through the wire is governed by the energy differences between neighboring sites

$$\Delta E_M = E_i - E_{i+1} = \eta_M \frac{eV}{N-1} \tag{2}$$

and between the electrochemical potentials in the electrodes and the adjacent wire units

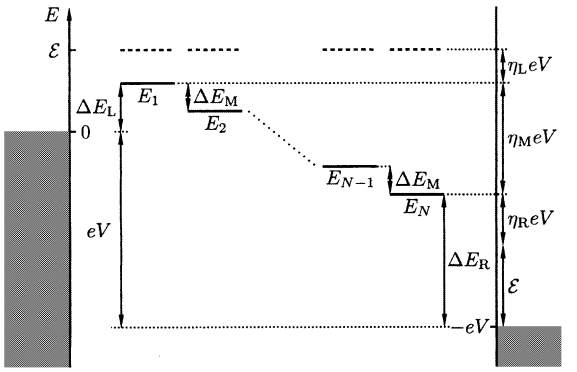

Fig. 2. The energies of the LUMOs of the wire units are depicted as dashed lines at energy $\mathscr{E}$ above the electrochemical potential in the left electrode. An external voltage V shifts the levels to the positions marked by the full lines. The energy differences ΔE_{L}, ΔE_{M}, and ΔE_{R} are defined in Eqs. (2)–(4). η_{L}, η_{M}, and η_{R} denote the fractions of the total applied voltage which drop across the left contact, the wire, and the right contact, respectively.

$$\Delta E_{\mathrm{L}} = -E_1 = \eta_{\mathrm{L}} eV - \mathscr{E}, \tag{3}$$

$$\Delta E_{\mathrm{R}} = E_N + eV = \eta_{\mathrm{R}} eV + \mathscr{E}. \tag{4}$$

Particularly at very low temperatures the current depends strongly on the energy differences (2)–(4). If one of these energy differences is negative, the absence of thermally activated processes will lead to a suppression of the current. This situation is depicted in Fig. 2 where $\Delta E_{\mathrm{L}} < 0$. If, on the other hand, the energy levels of the molecular sites lie between the electrochemical potentials in the two electrodes, a current may flow even at zero temperature. Apart from Section 5, we will always have the latter situation in mind when discussing zero temperature results.

In the following, the electrochemical potential $-eV$ in the right electrode is assumed to lie lower in energy, thereby favoring transport from left to right, which we will denote as forward direction. Furthermore, we specialize the voltage profile to the two limiting cases depicted in Fig. 3. Within *model A* the voltage is constant along the molecule and drops by equal amounts at the two contacts ($\eta_{\mathrm{L}} = \eta_{\mathrm{R}} = 1/2$, $\eta_{\mathrm{M}} = 0$). In contrast, in *model B* the entire voltage drops linearly along the molecule ($\eta_{\mathrm{L}} = \eta_{\mathrm{R}} = 0$, $\eta_{\mathrm{M}} = 1$).

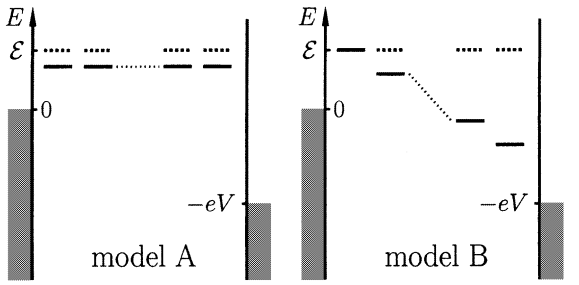

Fig. 3. The positions of the energy levels are shown for models A (left) and B (right) of the voltage drop across the system.

3. Current for spinless electrons in the presence of strong Coulomb interaction

3.1. Master equation and tunneling rates

The incoherent electron transport through an individual wire shall be described as sequential tunneling events of an electron between the electrodes and the end units of the wire or between adjacent wire units. The dynamics is then modeled in terms of a Markovian master equation. Fig. 4 shows the possible transitions between the $N+1$ different wire states. The arrows over the corresponding tunneling rates Γ indicate the direction of transport for a geometry depicted in Fig. 1, while the subscripts L, M, and R correspond to the left contact, a molecular bridge, and the right contact, respectively.

In order to determine the average current through the wire, we will need the probabilities $p_i(t)$ to find the system in one of the states $i = 0, \ldots, N$. Since these constitute the only

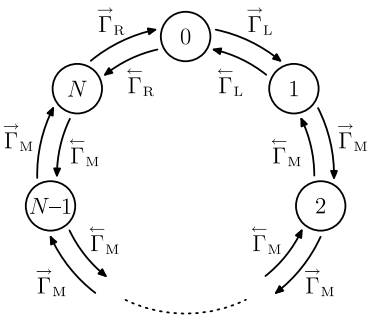

Fig. 4. Transitions between the $N+1$ states of the wire occur either by tunneling between adjacent wire units or between the end units of the wire and one of the two electrodes.

possible states, the probabilities should satisfy the normalization condition

$$\sum_{i=0}^{N} p_i(t) = 1. \tag{5}$$

The dynamical evolution of the probabilities due to the incoherent transitions depicted in Fig. 4 is determined by the master equation

$$\dot{p}_0(t) = -\left(\vec{\Gamma}_{\mathrm{L}} + \overleftarrow{\Gamma}_{\mathrm{R}}\right)p_0(t) + \overleftarrow{\Gamma}_{\mathrm{L}}p_1(t) + \vec{\Gamma}_{\mathrm{R}}p_N(t), \tag{6}$$

$$\dot{p}_1(t) = -\left(\vec{\Gamma}_{\mathrm{M}} + \overleftarrow{\Gamma}_{\mathrm{L}}\right)p_1(t) + \vec{\Gamma}_{\mathrm{L}}p_0(t) + \overleftarrow{\Gamma}_{\mathrm{M}}p_2(t), \tag{7}$$

$$\vdots$$

$$\dot{p}_i(t) = -\left(\vec{\Gamma}_{\mathrm{M}} + \overleftarrow{\Gamma}_{\mathrm{M}}\right)p_i(t) + \vec{\Gamma}_{\mathrm{M}}p_{i-1}(t) + \overleftarrow{\Gamma}_{\mathrm{M}}p_{i+1}(t) \quad (i = 2, \ldots, N-1), \tag{8}$$

$$\vdots$$

$$\dot{p}_N(t) = -\left(\vec{\Gamma}_{\mathrm{R}} + \overleftarrow{\Gamma}_{\mathrm{M}}\right)p_N(t) + \overleftarrow{\Gamma}_{\mathrm{R}}p_0(t) + \vec{\Gamma}_{\mathrm{M}}p_{N-1}(t). \tag{9}$$

From a solution of these equations, the average currents through the left and right contacts

$$I_{\mathrm{L}}(t) = e\left(\vec{\Gamma}_{\mathrm{L}}p_0 - \overleftarrow{\Gamma}_{\mathrm{L}}p_1\right), \quad I_{\mathrm{R}}(t) = e\left(\vec{\Gamma}_{\mathrm{R}}p_N - \overleftarrow{\Gamma}_{\mathrm{R}}p_0\right), \tag{10}$$

and through the molecular bridge between units i and $i+1$

$$I_{\mathrm{M},i}(t) = e\left(\vec{\Gamma}_{\mathrm{M}}p_i - \overleftarrow{\Gamma}_{\mathrm{M}}p_{i+1}\right) \tag{11}$$

can be obtained. We will be particularly interested in the stationary case where the probabilities p_i become time-independent. Then, all currents (10) and (11) will be equal, i.e.

$$I = I_{\mathrm{L}} = I_{\mathrm{R}} = I_{\mathrm{M},i}, \tag{12}$$

thereby ensuring current conservation.

As can be seen from Eqs. (6)–(9), the stationary probabilities p_i depend only on ratios of transition rates. We therefore introduce the "backward–forward" ratios

$$\gamma_{\mathrm{M}} = \frac{\overleftarrow{\Gamma}_{\mathrm{M}}}{\vec{\Gamma}_{\mathrm{M}}}, \quad \gamma_{\mathrm{L}} = \frac{\overleftarrow{\Gamma}_{\mathrm{L}}}{\vec{\Gamma}_{\mathrm{L}}}, \quad \gamma_{\mathrm{R}} = \frac{\overleftarrow{\Gamma}_{\mathrm{R}}}{\vec{\Gamma}_{\mathrm{R}}}, \tag{13}$$

and the "branching" ratios

$$\zeta_{\mathrm{L}} = \frac{\vec{\Gamma}_{\mathrm{M}}}{\vec{\Gamma}_{\mathrm{L}}}, \quad \zeta_{\mathrm{R}} = \frac{\vec{\Gamma}_{\mathrm{M}}}{\vec{\Gamma}_{\mathrm{R}}}. \tag{14}$$

The latter two relate molecular properties to contact properties and therefore depend on the microscopic details. The ratios (13), on the other hand, combine backward and forward rates at the same contact or bridge. In order to ensure thermodynamic equilibrium they are given by Boltzmann factors at inverse temperature $\beta = 1/k_{\mathrm{B}}T$

$$\gamma_{\mathrm{M}} = \mathrm{e}^{-\beta\Delta E_{\mathrm{M}}}, \quad \gamma_{\mathrm{L}} = \mathrm{e}^{-\beta\Delta E_{\mathrm{L}}}, \quad \gamma_{\mathrm{R}} = \mathrm{e}^{-\beta\Delta E_{\mathrm{R}}}, \tag{15}$$

where the energy differences have been introduced in Eqs. (2)–(4). Since all energy differences have to sum up to the difference in electrochemical potential between left and right electrodes, i.e.

$$\Delta E_{\mathrm{L}} + (N-1)\Delta E_{\mathrm{M}} + \Delta E_{\mathrm{R}} = eV, \tag{16}$$

the "backward–forward" ratios obey the relation

$$\gamma_{\mathrm{L}}\gamma_{\mathrm{M}}^{N-1}\gamma_{\mathrm{R}} = \mathrm{e}^{-\beta eV}. \tag{17}$$

3.2. Stationary solution

In the following, we will restrict ourselves to the stationary case. Together with the ratios (13) and (14), the master equation (6)–(9) then turns into

$$-(\zeta_{\mathrm{R}} + \gamma_{\mathrm{R}}\zeta_{\mathrm{L}})p_0 + \gamma_{\mathrm{L}}\zeta_{\mathrm{R}}p_1 + \zeta_{\mathrm{L}}p_N = 0, \tag{18}$$

$$-(\zeta_{\mathrm{L}} + \gamma_{\mathrm{L}})p_1 + p_0 + \gamma_{\mathrm{M}}\zeta_{\mathrm{L}}p_2 = 0, \tag{19}$$

$$\vdots$$

$$-(1+\gamma_{\mathrm{M}})p_i + p_{i-1} + \gamma_{\mathrm{M}}p_{i+1} = 0 \quad (i = 2, \ldots, N-1), \tag{20}$$

$$\vdots$$

$$-(1+\gamma_{\mathrm{M}}\zeta_{\mathrm{R}})p_N + \gamma_{\mathrm{R}}p_0 + \zeta_{\mathrm{R}}p_{N-1} = 0. \tag{21}$$

Out of these $N+1$ equations only N are linearly independent, so that the normalization condition (5) is needed to determine the $N+1$ stationary probabilities p_i.

It is convenient to start with the "molecular" part (20), which takes on the form of a two-step recursion relation and can thus readily be solved in terms of the two probabilities p_1 and p_N leading to

$$p_i = \frac{1-\gamma_M^{N-i}}{1-\gamma_M^{N-1}} p_1 - \frac{\gamma_M^{N-1}-\gamma_M^{N-i}}{1-\gamma_M^{N-1}} p_N \quad (i = 1,\ldots,N). \tag{22}$$

Inserting this result into Eqs. (19) and (21) and making use of the normalization (5), one finds for the probability for a neutral wire

$$p_0 = \Bigg[1 + \Bigg\{(\gamma_M^N - 1)(\zeta_L\gamma_R + \zeta_R) + N(e^{-\beta eV} - 1) + \frac{\gamma_M^N - 1}{\gamma_M - 1}(1 - \gamma_L\gamma_R)\Bigg\} \Big/ \{\gamma_L(\gamma_M^{N-1} - 1) + (\gamma_M - 1)(\zeta_L + \zeta_R\gamma_L\gamma_M^{N-1})\}\Bigg]^{-1}, \tag{23}$$

while the probability for an electron on site i may be expressed in terms of p_0 as

$$p_i = \frac{e^{-\beta eV} - 1 + [(\gamma_M - 1)(\zeta_L\gamma_R + \zeta_R) + 1 - \gamma_L\gamma_R]\gamma_M^{N-i}}{\gamma_L(\gamma_M^{N-1} - 1) + (\gamma_M - 1)(\zeta_L + \zeta_R\gamma_L\gamma_M^{N-1})} p_0. \tag{24}$$

3.3. Stationary current

The stationary solution (23) and (24) allows to calculate from any of the expressions (10) and (11) the average current (12). The resulting expression can be cast into the form

$$I = e\frac{1 - e^{-\beta eV}}{\frac{c_L}{\vec{\Gamma}_L} + \frac{c_M}{\vec{\Gamma}_M} + \frac{c_R}{\vec{\Gamma}_R}}, \tag{25}$$

where we have introduced the abbreviations:

$$c_L = 1 + \frac{e^{-\beta eV}}{\gamma_L}\frac{1 - 1/\gamma_M^N}{1 - 1/\gamma_M}, \tag{26}$$

$$c_M = \gamma_L\frac{1-\gamma_M^{N-1}}{1-\gamma_M} + (\gamma_L\gamma_R - 1)\frac{1-\gamma_M^N}{(1-\gamma_M)^2} + N\frac{1 - e^{-\beta eV}}{1-\gamma_M}, \tag{27}$$

$$c_R = \frac{e^{-\beta eV}}{\gamma_R} + \frac{1-\gamma_M^N}{1-\gamma_M}. \tag{28}$$

The current changes its sign when the applied voltage is reversed and at the same time forward and backward rates as well as left and right contacts are interchanged. This can be verified by noting that under these changes the coefficients (26)–(28) are transformed according to $c_L/\vec{\Gamma}_L \to e^{\beta eV}c_R/\vec{\Gamma}_R$, $c_R/\vec{\Gamma}_R \to e^{\beta eV}c_L/\vec{\Gamma}_L$, and $c_M/\vec{\Gamma}_M \to e^{\beta eV}c_M/\vec{\Gamma}_M$.

Further insight into the result (25)–(28) can be gained by discussing several special cases. An important limit, which will be particularly relevant in the discussion of the following sections, is a wire consisting only of one unit and no bridges. Then, the current simplifies to

$$I = e\frac{\vec{\Gamma}_L\vec{\Gamma}_R - \overleftarrow{\Gamma}_L\overleftarrow{\Gamma}_R}{\vec{\Gamma}_L + \overleftarrow{\Gamma}_L + \vec{\Gamma}_R + \overleftarrow{\Gamma}_R} \tag{29}$$

containing forward and backward contributions. For positive energy differences ΔE_L and ΔE_R, the backward rates vanish at zero temperature and one is left with the familiar result

$$I = e\frac{\vec{\Gamma}_L\vec{\Gamma}_R}{\vec{\Gamma}_L + \vec{\Gamma}_R} \tag{30}$$

for an sequential incoherent process with rates $\vec{\Gamma}_L$ and $\vec{\Gamma}_R$.

For more than one wire unit it is instructive to compare the two models for the voltage profile introduced in Section 2. We start by considering *model A* where the voltage drops only across the contacts. As a consequence, the forward and backward rates on the molecule are equal and we have $\gamma_M = 1$. In this case, the coefficients (26)–(28) become

$$c_L = 1 + \frac{e^{-\beta eV}}{\gamma_L}N, \tag{31}$$

$$c_M = \gamma_L(N-1) + (1 + e^{-\beta eV})\frac{N(N-1)}{2}, \tag{32}$$

$$c_R = \frac{e^{-\beta eV}}{\gamma_R} + N, \tag{33}$$

which is consistent with Eqs. (29) and (30) for $N = 1$. For long wires, the current scales like $1/N^2$ with the number of wire units. Since forward and backward tunneling rates on the wire are equal, the electron has equal probability for tunneling in

forward and backward direction. The length dependence of the current can therefore be understood in terms of a random walk where the average time to diffuse across a wire of length N is proportional to N^2.

For *model B*, where the voltage drops entirely along the wire, the same argument holds provided the thermal energy is much larger than the energy difference between adjacent sites, $k_{\mathrm{B}}T \gg \Delta E_{\mathrm{M}}$. At low temperatures, however, the situation differs qualitatively since the backward rates are negligibly small. In order to obtain a finite current even in the limit of zero temperature, we assume that $\Delta E_{\mathrm{L}},\ \Delta E_{\mathrm{R}} > 0$. At zero temperature, Eqs. (25)–(28) then yield

$$I = e\frac{1}{\frac{1}{\vec{\Gamma}_{\mathrm{L}}} + \frac{N-1}{\vec{\Gamma}_{\mathrm{M}}} + \frac{1}{\vec{\Gamma}_{\mathrm{R}}}}, \tag{34}$$

which reduces to (30) for $N = 1$. For a long wire, the current now decreases linearly with the number of units or, equivalently, with the length of the wire. In this sense, for model B the wire resembles an ohmic resistor.

The comparison of models A and B demonstrates that the dependence of the current on the wire length at low temperatures may provide qualitative information about the voltage drop across the molecule. In any case, however, incoherent transport leads to an algebraic length dependence of the current in clear contrast to the exponential dependence characteristic for coherent transport [10].

4. Blocking of spin channels by strong Coulomb interaction

So far, we have ignored the spin degree of freedom of the electrons. In this section, we will take the spin into account but, due to the strong Coulomb interaction, there will be not more than one electron present on the wire. Furthermore, we will assume that the two spin directions are equivalent and that no spin flips occur.

Inclusion of the electron spin increases the number of possible wire states to $2N + 1$. The wire can now either be neutral (with probability $p_0(t)$) or there can be an extra electron with spin up or down at site $i = 1, \ldots, N$ (with probability $p_{\uparrow,i}(t)$ and $p_{\downarrow,i}(t)$, respectively). The possible transitions between the different states are depicted in Fig. 5. We emphasize that, like in Section 3, all rates are to be understood as rates per spin direction. In the presence of a magnetic field, the two spin directions would no longer be equivalent and the rates would have to be distinguished by a spin index.

A comparison of Figs. 4 and 5 shows that the two molecular parts are independent of the spin direction and correspond to the molecular part in the spinless case. The only difference lies in the coupling to the neutral state "0". This motivates to introduce the total probability $p_i(t) = p_{\uparrow,i}(t) + p_{\downarrow,i}(t)$ for an electron on site i irrespective of its spin. The resulting master equation including the normalization condition is of the same form as Eqs. (5) and (6)–(9) in the spinless case. The only difference consists in a factor of 2 by which the rates $\vec{\Gamma}_{\mathrm{L}}$ and $\vec{\Gamma}_{\mathrm{R}}$ describing the charging of the wire have to be multiplied. For these rates, the spin degree of freedom leads to an additional process

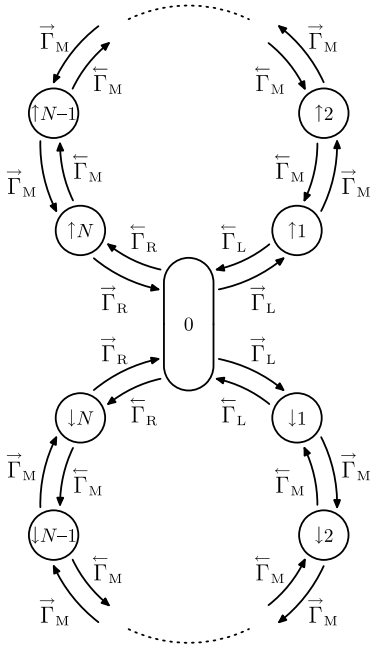

Fig. 5. The situation depicted in Fig. 4 is generalized to include the electron spin. The two rings corresponding to the two spin directions are joined via the neutral state "0" of the molecule.

allowing to occupy the wire. This is not the case for an electron leaving the wire. In this case, the spin is fixed and the corresponding rates $\overleftarrow{\Gamma}_{\mathrm{L}}$ and $\overrightarrow{\Gamma}_{\mathrm{R}}$ are not doubled.

The appearance of a factor of 2 may also be understood in terms of the density of states in the electrodes which enters the tunneling rates. For tunneling of electrons onto the wire the number of initial states is increased by the spin degree of freedom thereby leading to an effective doubling of the density of states. On the other hand, for tunneling into the electrodes the density of final states is not increased since the spin is determined by the electron leaving the wire.

Taking into account the factor of 2 in the tunneling rates that populate the wire, one finds for the average current

$$I = e\left(2\overrightarrow{\Gamma}_{\mathrm{L}}p_0 - \overleftarrow{\Gamma}_{\mathrm{L}}p_1\right). \tag{35}$$

Here, the probability p_1 implicitly contains a factor of 2 since the electron contributing to the backward current may carry either spin up or down. Making the required modifications of the rates $\overrightarrow{\Gamma}_{\mathrm{L}}$ and $\overleftarrow{\Gamma}_{\mathrm{R}}$, the current (25)–(28) turns into

$$I = e\frac{1-\mathrm{e}^{-\beta eV}}{\frac{c_{\mathrm{L}}}{\overrightarrow{\Gamma}_{\mathrm{L}}} + \frac{c_{\mathrm{M}}}{\overrightarrow{\Gamma}_{\mathrm{M}}} + \frac{c_{\mathrm{R}}}{\overrightarrow{\Gamma}_{\mathrm{R}}}}, \tag{36}$$

where the coefficients now are given by

$$c_{\mathrm{L}} = \frac{1}{2} + \frac{\mathrm{e}^{-\beta eV}}{\gamma_{\mathrm{L}}}\frac{1-1/\gamma_{\mathrm{M}}^{N}}{1-1/\gamma_{\mathrm{M}}}, \tag{37}$$

$$c_{\mathrm{M}} = \frac{\gamma_{\mathrm{L}}}{2}\frac{1-\gamma_{\mathrm{M}}^{N-1}}{1-\gamma_{\mathrm{M}}} + (\gamma_{\mathrm{L}}\gamma_{\mathrm{R}}-1)\frac{1-\gamma_{\mathrm{M}}^{N}}{(1-\gamma_{\mathrm{M}})^2} + N\frac{1-\mathrm{e}^{-\beta eV}}{1-\gamma_{\mathrm{M}}}, \tag{38}$$

$$c_{\mathrm{R}} = \frac{\mathrm{e}^{-\beta eV}}{2\gamma_{\mathrm{R}}} + \frac{1-\gamma_{\mathrm{M}}^{N}}{1-\gamma_{\mathrm{M}}}. \tag{39}$$

We remark that due to the mutual blocking of the electrons one does not obtain an overall factor of 2 in the current relative to the spinless case (25)–(28). Instead, the current shows a more intricate influence of the spin degree of freedom.

The mechanism of blocking is particularly transparent if the wire consists of only one site, i.e. $N = 1$. We restrict ourselves to the case of zero temperature where, as in the derivation of Eq. (30), all backward rates vanish. Then the current (36) simplifies to read

$$I = 2e\frac{\overrightarrow{\Gamma}_{\mathrm{L}}\overrightarrow{\Gamma}_{\mathrm{R}}}{2\overrightarrow{\Gamma}_{\mathrm{L}} + \overrightarrow{\Gamma}_{\mathrm{R}}}. \tag{40}$$

This result has to be compared with the case where the two spin directions lead to independent transport channels so that the expression (30) is multiplied by a factor of 2 yielding the current

$$I_0 = 2e\frac{\overrightarrow{\Gamma}_{\mathrm{L}}\overrightarrow{\Gamma}_{\mathrm{R}}}{\overrightarrow{\Gamma}_{\mathrm{L}} + \overrightarrow{\Gamma}_{\mathrm{R}}}. \tag{41}$$

The effect of blocking due to the Coulomb interaction is quantified by the ratio of the current (40) in the presence of Coulomb repulsion and the current (41) in the absence of interaction, i.e.

$$\frac{I}{I_0} = \frac{1+\eta}{1+2\eta}. \tag{42}$$

The blocking is completely determined by the ratio

$$\eta = \frac{\overrightarrow{\Gamma}_{\mathrm{L}}}{\overrightarrow{\Gamma}_{\mathrm{R}}} \tag{43}$$

of the rates through the left and right contacts and varies between 1 for $\overrightarrow{\Gamma}_{\mathrm{L}} \ll \overrightarrow{\Gamma}_{\mathrm{R}}$ and 1/2 for $\overrightarrow{\Gamma}_{\mathrm{L}} \gg \overrightarrow{\Gamma}_{\mathrm{R}}$ as shown in Fig. 6.

This dependence on η can be understood in terms of the average population of the wire which here is given by p_1. From the stationary solution of the master equation for the case with spin and $N = 1$ one obtains

$$p_1 = \frac{2\eta}{1+2\eta}. \tag{44}$$

The blocking effect on the current (42) may therefore be directly related to the average population of the wire by

$$\frac{I}{I_0} = 1 - \frac{p_1}{2}. \tag{45}$$

For small η, or equivalently $\overrightarrow{\Gamma}_{\mathrm{L}} \ll \overrightarrow{\Gamma}_{\mathrm{R}}$, the wire is depleted almost immediately after it has been populated. The average population of the wire therefore is very small and the passage of another

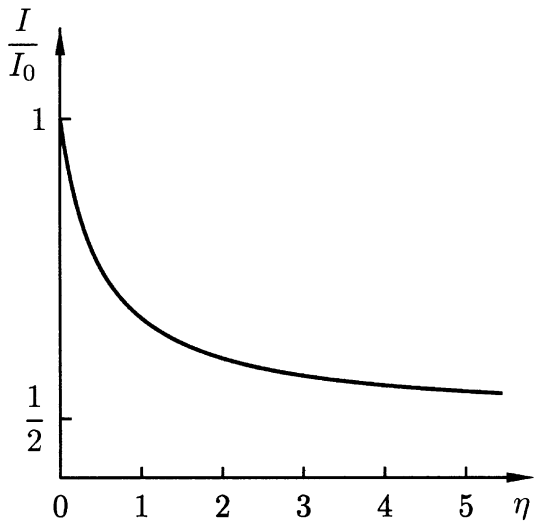

Fig. 6. The current suppression (42) due to Coulomb interaction is plotted as a function of the ratio η of the tunneling rates in the left and right contacts.

electron is almost never blocked. In the opposite case of large η, or $\vec{\Gamma}_{\rm L} \gg \vec{\Gamma}_{\rm R}$, the right contact represents a bottleneck which leads to a sizable average population of the wire and therefore to the blocking of transport.

This result clearly shows that inclusion of the spin degree of freedom does not necessarily lead to a doubling of the current as would be the case in the absence of Coulomb interaction on the wire. Apart from the interaction strength, the average population of the wire plays a decisive role and blocking is strongest when the right contact increases the population by acting as a bottleneck.

5. Temperature dependence of blocking

The calculation of the current–voltage characteristics presented so far was based on the assumption that at any given time there is at most one extra electron on the wire. Although it is straightforward to generalize the rate equations (6)–(9) to more than one electron by extending the state space, in general one has to solve the rate equations numerically.

Some insight into the validity of the limit of strong Coulomb interaction can be gained by allowing a second electron on the wire. Then, an analytical treatment is still possible if we restrict the length of the wire to one site, i.e. $N = 1$. We will assume that this very site may be occupied by at most two electrons of opposite spin. Then, there exist four different wire states, $|0\rangle$, $|\uparrow\rangle$, $|\downarrow\rangle$, and $|\uparrow\downarrow\rangle$, which correspond to no electron, one electron with spin up or down, and two electrons, respectively. The energies of these four states are schematically shown in Fig. 7 where we allow for an interaction energy U if two electrons are present on the wire. By changing both, the temperature as well as the one-electron energy $\mathscr{E}$ relative to the left electrochemical potential, we may choose the levels which are relevant for the transport through the wire.

The discussion in the last section has shown that the effect of blocking is most pronounced when the tunneling rates through the right contact are much smaller than through the left one. We therefore shall concentrate on this limit. Then, the master equation for the probabilities p_n of being in a state with $n = 0,\ 1$, or 2 electrons depends only on the rates through the left contact. These tunneling rates may be identified by the change of the number of electrons. For example, $\Gamma_{2\to1}$ refers to the backward rate through the left contact with initially two electrons on the molecule. With this notation the master equation reads:

$$\dot{p}_0(t) = -2\Gamma_{0\to1}p_0(t) + \Gamma_{1\to0}p_1(t), \tag{46}$$

$$\dot{p}_1(t) = -(\Gamma_{1\to0} + \Gamma_{1\to2})p_1(t) + 2\Gamma_{0\to1}p_0(t) + 2\Gamma_{2\to1}p_2(t), \tag{47}$$

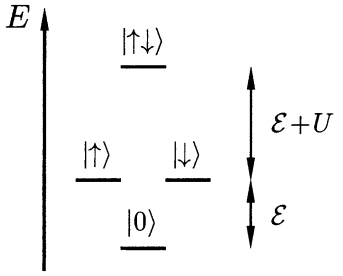

Fig. 7. Many-particle states for one site with $n = 0,\ 1$, and 2 electrons. Δ is the one-particle energy of the states $|\uparrow\rangle$ and $|\downarrow\rangle$ and U is the Coulomb interaction energy between the electrons occupying the site.

$$\dot{p}_2(t) = -2\Gamma_{2\to1}p_2(t) + \Gamma_{1\to2}p_1(t) \tag{48}$$

with the normalization condition

$$p_0(t) + p_1(t) + p_2(t) = 1. \tag{49}$$

The rates $\Gamma_{0\to1}$ and $\Gamma_{2\to1}$ are each multiplied by a factor of 2, thereby accounting for the two spin directions possible in these processes. The probability p_1 of finding one electron of arbitrary spin on the wire implicitly contains a factor of 2 in the same sense as was discussed after Eq. (35).

If the probabilities are calculated from the master equations (46)–(48), thereby neglecting tunneling through the right contact, the current has to be evaluated at that contact. We will assume that the electrochemical potential in the right electrode is so low that the forward rates $\vec{\Gamma}_R$ through the right contact are approximately independent of the occupation of the molecular site and that backward rates may be neglected. Then, the stationary current is obtained as

$$I = e\vec{\Gamma}_R(p_1 + 2p_2), \tag{50}$$

where the factor of 2 accounts for the two spin directions available when one of two electrons is leaving the molecule.

Solving the master equations (46)–(48) in the stationary limit, we obtain from (50) for the current

$$I = e\vec{\Gamma}_R \frac{1 + \frac{\Gamma_{1\to2}}{\Gamma_{2\to1}}}{1 + \frac{\Gamma_{1\to0}}{2\Gamma_{0\to1}} + \frac{\Gamma_{1\to2}}{2\Gamma_{2\to1}}}. \tag{51}$$

In order to study the effect of blocking, we have to compare this current with the current I_0 in the absence of Coulomb interaction. In this case $\Gamma_{1\to2} = \Gamma_{0\to1}$ and $\Gamma_{2\to1} = \Gamma_{1\to0}$ and we find

$$I_0 = e\vec{\Gamma}_R \frac{1 + \frac{\Gamma_{0\to1}}{\Gamma_{1\to0}}}{1 + \frac{\Gamma_{1\to0}}{2\Gamma_{0\to1}} + \frac{\Gamma_{0\to1}}{2\Gamma_{1\to0}}}. \tag{52}$$

This result still depends on temperature and on the energy $\mathscr{E}$ of the one-electron level relative to the left electrochemical potential.

The ratio I/I_0 depends only on rate ratios which, as in Section 3.1, may be expressed in terms of Boltzmann factors. For single occupation of the molecule, we have

$$\frac{\Gamma_{0\to1}}{\Gamma_{1\to0}} = e^{-\beta\mathscr{E}}. \tag{53}$$

Double occupancy costs the additional interaction energy U, so that

$$\frac{\Gamma_{1\to2}}{\Gamma_{2\to1}} = e^{-\beta(\mathscr{E}+U)}. \tag{54}$$

The blocking due to Coulomb interaction is then described by

$$\frac{I}{I_0} = 1 - \frac{1 - e^{-\beta U}}{e^{\beta\mathscr{E}} + 2 + e^{-\beta(\mathscr{E}+U)}}. \tag{55}$$

Fig. 8 depicts this result as a function of $k_BT/|\mathscr{E}|$ for $U/|\mathscr{E}| = 2$ and 2000. The full lines correspond to the case, where the one-electron energy lies below the left electrochemical potential, i.e. $\mathscr{E} < 0$. The dashed line refers to the opposite case with $\mathscr{E} > 0$. As a function of temperature, we can distinguish three different regimes.

In the limit of zero temperature, one finds for $\mathscr{E} < 0$, and $U > -\mathscr{E}$ an interaction induced reduction of the current by a factor of 1/2. This is the blocking discussed already in Section 4. For $\mathscr{E} + U < 0$, double occupancy is possible even in the zero temperature limit and no blocking occurs. As can be seen from the dashed lines in Fig. 8, blocking is also absent for $\mathscr{E} > 0$. In this case, the current as well as the occupation of the molecule

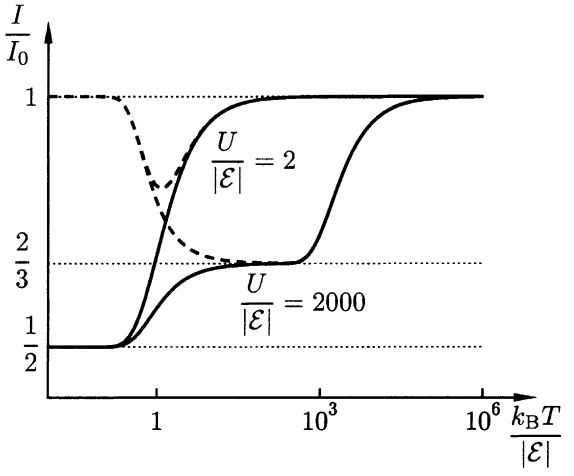

Fig. 8. The current (51) through the wire normalized with respect to the current (52) in the absence of Coulomb interaction is plotted as a function of the temperature T in units of $|\mathscr{E}|$ for $U/|\mathscr{E}| = 2$ and 2000. For each value of $U/|\mathscr{E}|$, a full line and a dashed line are shown, corresponding to $\mathscr{E} < 0$ and $\mathscr{E} > 0$, respectively.

approach zero exponentially for low temperatures. In analogy to the reasoning presented in Section 4, blocking thus becomes ineffective.

For $U \gg |\mathscr{E}|$, a second regime appears at intermediate temperatures $|\mathscr{E}| \ll k_B T \ll U$. For $U/|\mathscr{E}| = 2000$, Fig. 8 indeed shows a clear plateau at a blocking factor of 2/3. This can be attributed to the fact that for $k_B T \gg |\mathscr{E}|$ the backward rate $\Gamma_{1\to 0}$ is of the order of the forward rate $\Gamma_{0\to 1}$. This reduces the population of the molecule and therefore blocking is less effective than at lower temperatures.

The reduction by a factor of 2/3 can be understood even without recourse to Eq. (55). For equal forward and backward rates, the probabilities for an empty wire or a wire occupied with one electron of given spin are equal, leading to probabilities $p_0 = 1/3$, $p_1 = 2/3$ and $p_2 = 0$. From Eq. (50) one therefore finds $I = (2/3)e\vec{\Gamma}_R$. In the absence of Coulomb interaction, double occupancy is allowed and one finds all four possible states with equal probability leading to $p_0 = 1/4$, $p_1 = 1/2$ and $p_2 = 1/4$. This yields the current $I_0 = e\vec{\Gamma}_R$, and thus the blocking factor reads $I/I_0 = 2/3$.

Finally, in the high-temperature regime, where $k_B T \gg |\mathscr{E}|, U$, the thermal energy is much bigger than the interaction energy U so that the latter becomes irrelevant. Therefore, the Coulomb interaction can no longer lead to blocking of the electronic transport.

6. Conclusions

The influence of Coulomb interaction on incoherent electronic transport through a molecular wire has been found to be multifaceted. In the regime of strong Coulomb interaction, the current of spinless electrons shows an algebraic dependence on the wire length characteristic for incoherent transport. It was found, however, that this length dependence varies as a function of the voltage profile across the system. At low temperatures a $1/N^2$ behavior indicates the absence of a voltage drop along the molecule while in the presence of a voltage drop a $1/N$ behavior is expected.

Inclusion of the spin degree of freedom in the absence of Coulomb interaction leads to an increase of the current by a factor of 2. Coulomb interaction, on the other hand, should lead to a reduction of the current. It was found that this blocking effect not only depends on the interaction strength but also on the average population of the wire and thus on the tunneling rates (cf. Fig. 6).

For finite Coulomb interaction, the amount of blocking also depends on temperature. Between the limits of suppression of the current by a factor of 2 at zero temperature and the absence of blocking at high temperatures an intermediate regime may exist. There, Coulomb interaction prohibits double occupancy. Nevertheless the current is only reduced by a factor of 2/3 (cf. Fig. 8). This is a consequence of the competition between backward and forward rates, which equally populates the two one-electron levels.

As a final remark, we mention that even though we have restricted ourselves to electronic transport, the approach presented here is also applicable to hole transport. Depending on the situation, holes may be the dominant charge carriers; the results presented above may easily be adapted to this case. On the other hand, if both, holes and electrons, contribute to the transport, an extension similar to the one presented in Section 4, where spin is included, becomes necessary.

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References

[1] C. Joachim, J.K. Gimzewski, A. Aviram, Nature 408 (2000) 541.
[2] T.W. Ebbesen, H.J. Lezec, H. Hiura, J.W. Bennett, H.F. Ghaemi, T. Thio, Nature 382 (1996) 54.
[3] S.J. Tans, M.H. Devoret, H.J. Dai, A. Thess, R.E. Smalley, L.J. Geerligs, C. Dekker, Nature 386 (1997) 474.
[4] C. Joachim, J.K. Gimzewski, R.R. Schlittler, C. Chavy, Phys. Rev. Lett. 74 (1995) 2102.
[5] D. Porath, Y. Levi, M. Tarabiah, O. Millo, Phys. Rev. B 56 (1997) 9829.

[6] M.A. Reed, C. Zhou, C.J. Muller, T.P. Burgin, J.M. Tour, Science 278 (1997) 252.
[7] S. Datta, W. Tian, S. Hong, R. Reifenberger, J.I. Henderson, C.P. Kubiak, Phys. Rev. Lett. 79 (1997) 2530.
[8] C. Kergueris, J.-P. Bourgoin, S. Palacin, D. Esteve, C. Urbina, M. Magoga, C. Joachim, Phys. Rev. B 59 (1999) 12505.
[9] J. Reichert, R. Ochs, D. Beckmann, H.B. Weber, M. Mayor, H.V. Löhneysen, cond-mat/0106219.
[10] For a review see e.g. A. Nitzan, Ann. Rev. Phys. Chem. 52 (2001) 681.
[11] D. Segal, A. Nitzan, W.B. Davis, M.R. Wasielewski, M.A. Ratner, J. Phys. Chem. B 104 (2000) 3817.
[12] E.G. Petrov, P. Hänggi, Phys. Rev. Lett. 86 (2001) 2862.
[13] E.G. Petrov, V. May, P. Hänggi, this issue.
[14] V. Mujica, M. Kemp, A. Roitberg, M. Ratner, J. Chem. Phys. 104 (1996) 7296.
[15] G. Treboux, J. Phys. Chem. B 104 (2000) 9823.
[16] W. Tian, S. Datta, S. Hong, R. Reifenberger, J.I. Henderson, C.P. Kubiak, J. Chem. Phys. 109 (1998) 2874.
[17] V. Mujica, A.E. Roitberg, M. Ratner, J. Chem. Phys. 112 (2000) 6834.