

Coulomb blockade in molecular quantum dots

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Received 9 July 2005; accepted 27 August 2005

Abstract: The rate-equation approach is used to describe sequential tunneling through a molecular junction in the Coulomb blockade regime. Such device is composed of molecular quantum dot (with discrete energy levels) coupled with two metallic electrodes via potential barriers. Based on this model, we calculate nonlinear transport characteristics (conductance-voltage and current-voltage dependences) and compare them with the results obtained within a self-consistent field approach. It is shown that the shape of transport characteristics is determined by the combined effect of the electronic structure of molecular quantum dots and by the Coulomb blockade. In particular, the following phenomena are discussed in detail: the suppression of the current at higher voltages, the charging-induced rectification effect, the charging-generated changes of conductance gap and the temperature-induced as well as broadening-generated smoothing of current steps.

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Keywords: Molecular electronics, molecular quantum dot, rate equation, Coulomb blockade, transport

PACS (2006): 73.23.-b, 73.23.Hk, 85.65.+h

1 Introduction

Molecular-scale electronic devices are of growing interest among scientists and engineers due to their potential in becoming active components for future nanocircuits, namely: interconnects, switches, diodes, transistors, dielectrics, photovoltaics, memories and others [1–4]. Recent advances in experimental techniques has made it possible to fabricate such

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junctions, composed of single molecules (or molecular layers) attached to two (or more) electrodes [5–11]. From an applied point of view, it is desirable to be able to control the way the molecule-to-electrodes couple and eventually connect individual devices into a properly working integrated circuit. On the other hand, for scientific researchers, it is important to understand and appropriately model transport at a molecular scale. Until now, a number of theoretical models have been proposed for calculating transport characteristics through molecular junctions in different transport regimes, using parametric as well as first-principles theories.

A molecule itself represents quantum dot with discrete energy levels, at least an order of magnitude smaller than semiconductor quantum dots, which is important from the viewpoint of further miniaturization of electronic devices. Usually the molecular contact with the electrodes is suggested to be weak and molecular quantum dots (MQDs) can be treated as electrically isolated from metallic electrodes (with a large electron density of states) via potential barriers [5–7]. Under the influence of bias voltage, the current will flow through the system. However, the number of electrons on the molecular island can change in discrete units by tunneling through potential barriers; however, the charge is transferred through energetically accessible molecular states (conducting channels). Therefore, the shape of transport characteristics is determined by the combined effect of the electronic structure of molecular quantum dots and by Coulomb interactions between electrons.

Let us consider the situation, when one spin-degenerate level is coupled via two tunnel barriers with capacitances C_1 and C_2 to the source and drain electrodes. The stored electrostatic energy of this capacitor is expressed as: $U = e^2/(2C)$ (where e is an electron charge, while $C = C_1 + C_2$ is the total capacitance of the system). This charging energy is usually very small compared to the thermal energy $E_T = k_B T$ (where: k_B is Boltzmann constant, while T is an absolute temperature), and the Coulomb blockade phenomenon can be fully neglected. In this case, the self-consistent field (SCF) method is sufficient to describe transport. However, the capacitance in molecular junctions can reach the value of $C \sim 10^{-19}$ F [6] which corresponds to $U \sim 1$ eV, making single-electron tunneling observable even at room temperature ($E_T \sim 1/40$ eV). Moreover, it is clear that the charging energy U is influenced mainly by the extent of the electronic wavefunction. Generally, the more localized wavefunction of the level, the smaller value of the U -parameter.

One of the present work's objectives is to study the transport characteristics of the metal/MQD/metal junction in the Coulomb blockade (CB) regime within the frames of the proposed model. Obtained results will be compared to the results suitable for the case of the SCF regime [12]. The origin of the Coulomb blockade is due to a small electric capacitance of a small-area junction; its electrostatic energy is changed considerably even when a single electron occupies the molecular island. In our calculations, we restrict ourselves to the situation in which internal relaxation processes inside the molecular island are negligible, as relaxation rates are slower than electron transfer rates [13]. Further simplification stems from the assumption that tunnel barriers have resistances much larger

than the quantum of resistance $h/(2e^2) \approx 12.9 \text{ k}\Omega$ (or equivalently conductances much smaller than quantum of conductance $2e^2/h \approx 77.5 \text{ }\mu\text{S}$). In this case, all the cotunneling processes can be neglected and the current is accurately described by lowest-order perturbation theory. In these conditions, transport can be analyzed in the sequential-tunneling picture using a rate-equation approach [7, 14–17]. In other words, the current flowing through the device is a strict consequence of sequential electron transition, whereby the molecular quantum dot is successively charged and discharged by the tunneling process.

2 Description of the model

2.1 Energy of the eigenstates

For one spin-degenerate level, the state can be occupied by zero, one or two electrons (with opposite spins). Multi-electron energy for this system can be written as a function of the number of electrons [18]:

$$E(N) = \varepsilon N + \frac{U}{2} (N - N_{eq})^2, \quad (1)$$

The first term of the above Eq. 1 is associated with kinetic energy, while the second term is the electrostatic energy stored in the capacitor formed by the conducting level and the electrodes [4]. The electrostatic energy term can be obtained from the relation $Q^2/(2C)$ by noting that $Q = e(N - N_{eq})$ denotes an amount of charge stored in the mentioned capacitor (N_{eq} being the equilibrium number of electrons occupying the particular energy level) and taking into account charging energy defined as $U = e^2/(2C)$. Our simplified treatment neglects electron-electron interactions between electrons occupying different energy levels. This assumption can be adequate when separation between particular energy levels is large ($\sim \text{eV}$), and the coupling with the electrodes is orders of magnitude smaller ($\sim 0.01 \text{ eV}$) to avoid overlapping effects.

However, of importance for transport calculations, are energy differences since electrons make transitions between MQD and the electrodes. Such differences are determined independently for every energy level ε_i taking into consideration its location relatively to Fermi energy ε_F (or equivalently different values of N_{eq}). Here we can distinguish three different situations: (1) $\varepsilon_i < \varepsilon_F$ hence $N_{eq} = 2$ and therefore $\varepsilon_i^+ = E(2) - E(1) = \varepsilon_i - U/2$ and $\varepsilon_i^- = E(1) - E(0) = \varepsilon_i - 3U/2$, (2) $\varepsilon_i = \varepsilon_F$ hence $N_{eq} = 1$ and therefore $\varepsilon_i^+ = E(2) - E(1) = \varepsilon_i + U/2$ and $\varepsilon_i^- = E(1) - E(0) = \varepsilon_i - U/2$, (3) $\varepsilon_i > \varepsilon_F$ hence $N_{eq} = 0$ and therefore $\varepsilon_i^+ = E(2) - E(1) = \varepsilon_i + 3U/2$ and $\varepsilon_i^- = E(1) - E(0) = \varepsilon_i + U/2$.

2.2 Determination of probabilities

Every level of the molecular system i has different probabilities to be occupied by an exact number of electrons: zero P_{0i} , one P_{1i} or two P_{2i} , respectively. All these occupancy probabilities must add up to one (normalization), since there cannot be more than two

electrons located on one spin-degenerate level (due to Pauli exclusion principle), hence:

$$P_{0i} + P_{1i} + P_{2i} = 1. \quad (2)$$

For this situation, we can write down the rate equation that describes four possible transitions among three different states (for details see the Appendix):

$$\frac{d}{dt} \begin{pmatrix} P_{0i} \\ P_{1i} \\ P_{2i} \end{pmatrix} = \begin{bmatrix} -\gamma_{0 \rightarrow 1}^i & \gamma_{1 \rightarrow 0}^i & 0 \\ \gamma_{0 \rightarrow 1}^i & -(\gamma_{1 \rightarrow 0}^i + \gamma_{1 \rightarrow 2}^i) & \gamma_{2 \rightarrow 1}^i \\ 0 & \gamma_{1 \rightarrow 2}^i & -\gamma_{2 \rightarrow 1}^i \end{bmatrix} \begin{pmatrix} P_{0i} \\ P_{1i} \\ P_{2i} \end{pmatrix}. \quad (3)$$

Here we limit ourselves to steady state conditions, where all the relaxation processes associated with coupling are neglected and therefore all the occupation probabilities are time-independent quantities. Since the left hand side of Eq. 3 is equal to zero, we have to deal with a homogeneous set of three equations. Eliminating the central equation and taking advantage of normalization defined by Eq. 2, we obtain:

$$\begin{bmatrix} \gamma_{0 \rightarrow 1}^i & -\gamma_{1 \rightarrow 0}^i & 0 \\ 0 & \gamma_{1 \rightarrow 2}^i & -\gamma_{2 \rightarrow 1}^i \\ 1 & 1 & 1 \end{bmatrix} \begin{pmatrix} P_{0i} \\ P_{1i} \\ P_{2i} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}. \quad (4)$$

It is easy to solve Eq. 4 and express the occupation probabilities with the help of the proper transition rates between analyzed states:

$$P_{0i} = \frac{\gamma_{1 \rightarrow 0}^i \gamma_{2 \rightarrow 1}^i}{\gamma_{1 \rightarrow 0}^i \gamma_{2 \rightarrow 1}^i + \gamma_{0 \rightarrow 1}^i (\gamma_{1 \rightarrow 2}^i + \gamma_{2 \rightarrow 1}^i)}, \quad (5a)$$

$$P_{1i} = \frac{\gamma_{0 \rightarrow 1}^i \gamma_{2 \rightarrow 1}^i}{\gamma_{1 \rightarrow 0}^i \gamma_{2 \rightarrow 1}^i + \gamma_{0 \rightarrow 1}^i (\gamma_{1 \rightarrow 2}^i + \gamma_{2 \rightarrow 1}^i)}, \quad (5b)$$

$$P_{2i} = \frac{\gamma_{0 \rightarrow 1}^i \gamma_{1 \rightarrow 2}^i}{\gamma_{1 \rightarrow 0}^i \gamma_{2 \rightarrow 1}^i + \gamma_{0 \rightarrow 1}^i (\gamma_{1 \rightarrow 2}^i + \gamma_{2 \rightarrow 1}^i)}. \quad (5c)$$

2.3 Transition rates and formula for the current

To obtain the occupation probabilities from Eqs. 5, we have to know the transition rates that can be determined by assuming a specific model for the coupling with reservoirs. Using Fermi golden-rule arguments we can express them as follows:

$$\gamma_{0 \rightarrow 1}^i = \frac{2}{\hbar} \int_{-\infty}^{+\infty} d\varepsilon [\Gamma_{1i} f_1 + \Gamma_{2i} f_2] D_i^-, \quad (6a)$$

$$\gamma_{1 \rightarrow 0}^i = \frac{1}{\hbar} \int_{-\infty}^{+\infty} d\varepsilon [\Gamma_{1i}(1 - f_1) + \Gamma_{2i}(1 - f_2)] D_i^-, \quad (6b)$$

$$\gamma_{1 \rightarrow 2}^i = \frac{1}{\hbar} \int_{-\infty}^{+\infty} d\varepsilon [\Gamma_{1i}f_1 + \Gamma_{2i}f_2] D_i^+, \quad (6c)$$

$$\gamma_{2 \rightarrow 1}^i = \frac{2}{\hbar} \int_{-\infty}^{+\infty} d\varepsilon [\Gamma_{1i}(1 - f_1) + \Gamma_{2i}(1 - f_2)] D_i^+. \quad (6d)$$

Here Γ_{1i} and Γ_{2i} are parameters describing the strength of the coupling, while $f_1 = f(\varepsilon - \mu_1)$ and $f_2 = f(\varepsilon - \mu_2)$ are Fermi distribution functions for electrons in source and drain electrodes defined by electrochemical potentials $\mu_1 = \varepsilon_F + eV/2$ and $\mu_2 = \varepsilon_F - eV/2$. Furthermore, D_i^+ and D_i^- are densities of states contributing information regarding the availability of electrons with energies ε_i^+ and ε_i^- (defined in subsection 2.1), respectively. Here we assume that such densities have the shape of a Lorentzian curve:

$$D_i^\pm = \frac{1}{\pi} \frac{\Gamma_i}{(\varepsilon - \varepsilon_i^\pm)^2 + \Gamma_i^2}, \quad (7)$$

where: $\Gamma_i = (\Gamma_{1i} + \Gamma_{2i})/2$. However, in case of extremely weak coupling $\Gamma_i \rightarrow 0$, the density of states becomes Dirac delta functions $D_i^\pm \approx \delta(\varepsilon - \varepsilon_i^\pm)$; and since we limit ourselves to a weak-coupling case, we will use this approximation throughout this paper (except subsection 3.3, where the influence of broadening on transport characteristics will be discussed).

Since every level (conducting channel) contributes independently to the current flowing through the device, a general formula for that current can be written as a sum over all accessible energy levels i as (for details see the Appendix):

$$I = \frac{2e}{\hbar} \sum_i \int_{-\infty}^{+\infty} d\varepsilon \Gamma_{1i} \left[P_{2i}(1 - f_1) D_i^+ + \frac{P_{1i}}{2} [(1 - f_1) D_i^- - f_1 D_i^+] - P_{0i} f_1 D_i^- \right]. \quad (8)$$

3 Results and discussion

For the fabrication of molecular devices, different types of nanowires are possible to provide. The most popular types are organic molecules [1], where conduction is due to π -conjugated molecular orbitals. In particular, linear carbon-atom chains containing up to 20 atoms connected at the ends to metal atoms have been synthesized [19] and recognized as ideal one-dimensional wires [20]. As an example, we have studied a linear chain containing 12 carbon atoms weakly connected to the metal electrodes at the ends. Since only π -electrons are involved in the conduction process, an initial electronic structure of the molecule is obtained through the use of Hückel Hamiltonian (with orthogonal atomic basis set of states) in the procedure of diagonalization [12] (“bare” energy levels are given in eV: ± 0.603 , ± 1.773 , ± 2.840 , ± 3.743 , ± 4.427 , ± 4.855). For further calculation we also

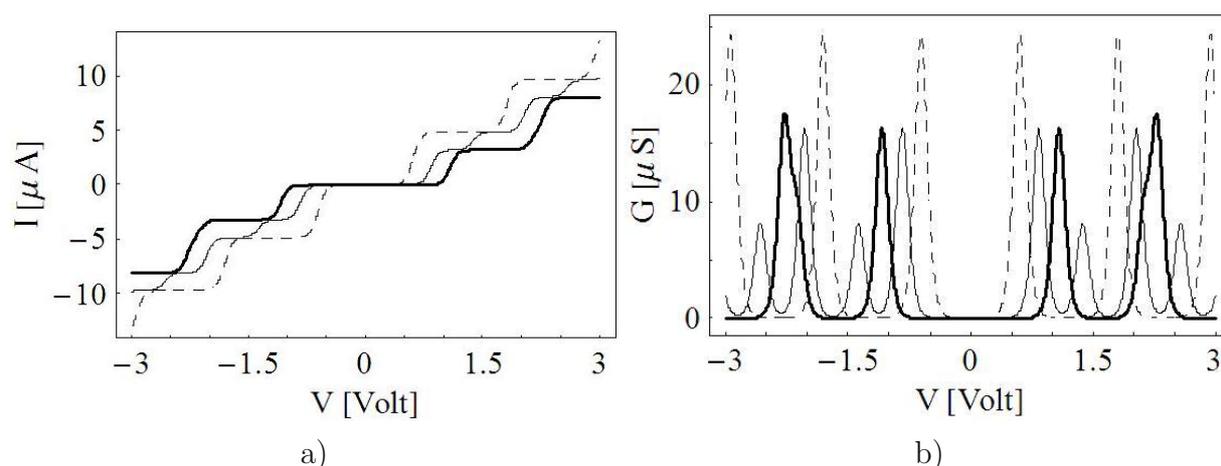


Fig. 1 Results for linear chain of 12 carbon atoms for symmetric coupling to the electrodes ($\Gamma_1 = 0.02 = \Gamma_2$) and different values of charging: $U = 0$ (broken line), $U = 0.25$ (thin solid line) and $U = 0.5$ (thick solid line): (a) current-voltage $I(V) = -I(-V)$ and (b) conductance-voltage $G(V) = G(-V)$ characteristics. Temperature: $k_B T = 1/40$ eV.

assume realistically that the Fermi level of unbiased electrodes is closer to the LUMO level ($\varepsilon_F = 0.3$) [21].

3.1 Charging-induced effects

Fig. 1 presents transport characteristics of a 12-atom nanowire connected symmetrically to two metallic electrodes at room temperature. For the case of $U = 0$, our CB model accurately reproduces the results obtained with the help of the generalized Breit-Wigner formula for $U = 0$ [12]. However, for $U > 0$, we observe the richer structure of such characteristics than with the SCF approach. Particularly, selected additional steps in the I-V dependences and some additional peaks in the conductance spectra are documented. This is a direct consequence of Coulomb interactions into the molecular system. The distance between these additional and main peaks in the G-V functions is $V = 2U/e$, and they appear in the direction outside the conductance gap (CG). Of course, for the case of symmetric coupling, we obtain symmetric transport characteristics (there is no physical reason for different behaviour).

One of the most important results is associated with the actual suppression of the current at higher voltages (or equivalently partition of conductance peaks) due to the Coulomb blockade, where the jump-like character of the I-V curve is still evident. In the SCF regime we observe smoothing of I-V curves due to Coulomb interactions, whereby the suppression of the current is possible only for extremely large U -parameter (while the current staircase is invisible in this case). This suppression is a desirable effect from a theoretical point of view as it can partially explain discrepancies between calculated and experimentally obtained current values (differences of two-three orders of magnitude) [21]. So far this divergence was closely connected to some coupling effects, such as: the atomic-

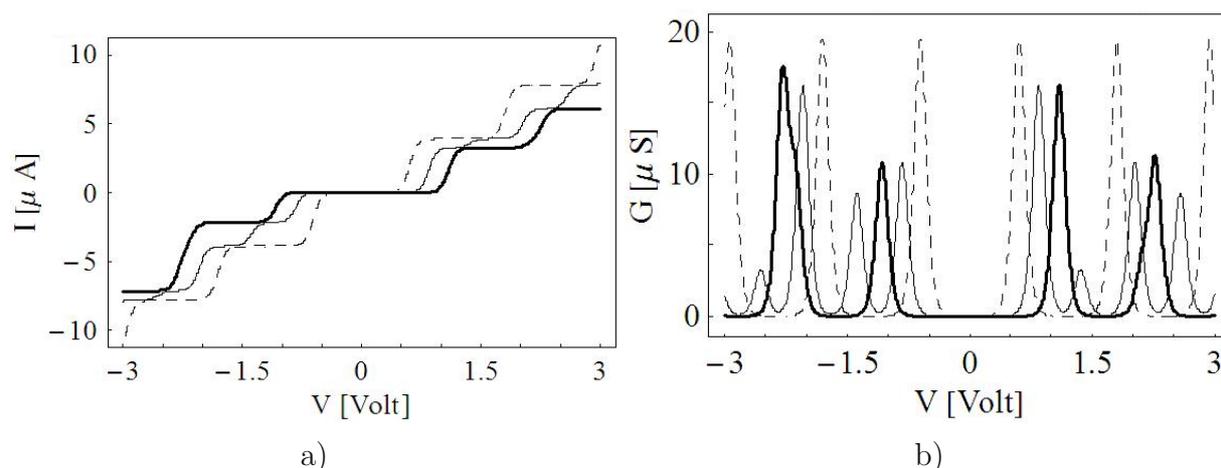


Fig. 2 Results for linear chain of 12 carbon atoms for asymmetric coupling to the electrodes ($\Gamma_1 = 0.01 = 4\Gamma_2$) and different values of charging: $U = 0$ (broken line), $U = 0.25$ (thin solid line) and $U = 0.5$ (thick solid line): (a) current-voltage $I(V) \neq -I(-V)$ and (b) conductance-voltage $G(V) \neq G(-V)$ characteristics. Temperature: $k_B T = 1/40$ eV.

scale contact geometry, the nature of molecule-to-electrodes coupling (chemisorption or physisorption) or even the changes of surface properties due to adsorption of the molecular layer. However, here we show that also the Coulomb blockade phenomenon can reduce the current at the molecular scale. Among the other factors that can alter the value of the current flowing through the molecular junction one can also enumerate: some thermal effects (hot electrons and vibrational coupling) or local disorder in the electrodes near the contacts (electron localization).

On the other hand, charging enters the picture of conductance only at higher voltages, similarly as in the SCF regime. However, here we observe a charging-induced increase of the conductance gap for $U > 0$, whereby the mentioned gap strongly depends on the value of the U -parameter. It should be noted that it is also possible to reduce the CG quantity, assuming that the charging parameter is negative $U < 0$ (this choice can be justified by a strong electron-phonon interaction in the molecular quantum dot [22] or by certain purely chemical arguments as in mixed valence complexes [23]). The total conductance gap in the CB regime is given through the relation: $4(|\varepsilon_F - \varepsilon_{LUMO}| - \Delta + U/2)$ (where: $\Delta \sim 4k_B T + \Gamma_1 + \Gamma_2$). Here we should remind the reader that in the SCF limit, the CG quantity does not change upon charging [12, 24] and is expressed as follows: $4(|\varepsilon_F - \varepsilon_{LUMO}| - \Delta)$. Furthermore, it should be noted that some state-of-art first-principles calculations overestimate the conductance gap in comparison to the experimental data [21]. Here we indicate that the Coulomb blockade phenomenon has a great influence on the determination of the CG quantity.

In Fig. 2 we plot the transport characteristics for a 12-atom nanowire connected asymmetrically to two metallic electrodes at room temperature. In the enclosed pictures we can see that there is no possibility to generate an asymmetric transport dependence in the absence of the Coulomb blockade (for $U = 0$), although the molecule-to-electrodes

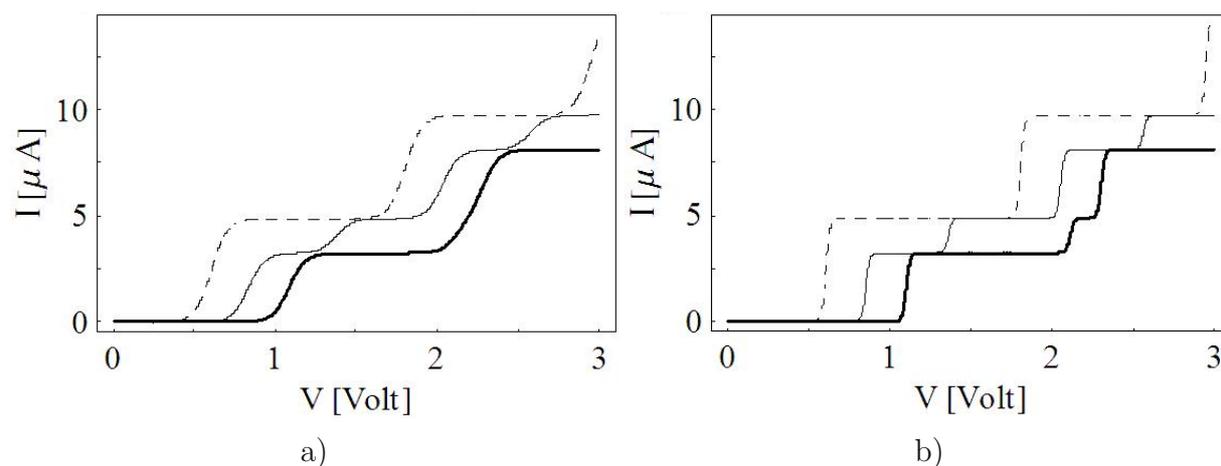


Fig. 3 Current-voltage $I(V) = -I(-V)$ characteristics for linear chain of 12 carbon atoms for symmetric coupling to the electrodes ($\Gamma_1 = 0.02 = \Gamma_2$) and different values of charging: $U = 0$ (broken line), $U = 0.25$ (thin solid line) and $U = 0.5$ (thick solid line): (a) temperature $k_B T = 1/40$ eV, (b) temperature $k_B T = 1/170$ eV.

coupling is asymmetric. This conclusion coincides with the SCF results [12, 24]. For $U > 0$ we can observe a charging-induced rectification effect, whereby the magnitude of the current depends on the polarity of applied bias (for higher voltages). Generally, the larger U -parameter, the stronger asymmetry in I-V dependence and the higher voltages should be applied to be able to observe a diode-like behaviour (since the conductance gap increases with an increase in charging energy). Such a rectification effect has been demonstrated in a number of experiments involving monolayer and multilayer films as well as in single molecule type junctions and STM measurements [8, 9]. Within our model, this behaviour is explained as a combined effect of asymmetric coupling to the reservoirs and the Coulomb blockade phenomenon.

3.2 Temperature-induced effects

Fig. 3 documents I-V dependences of a 12-atom nanowire connected symmetrically to two metallic electrodes at two different temperatures: room temperature ($k_B T = 1/40$ eV) and liquid nitrogen ($k_B T = 1/170$ eV), respectively. A significant temperature-induced smoothing of I-V curves (or equivalently broadening of conductance peaks) is observed; however, this effect is not as essential in the SCF transport regime. In this case, approximate current steps (or conductance peaks) can even merge due to the mentioned phenomenon (compare the curves for $U = 0.5$). Additionally, the temperature-generated shifting of resonances (current steps or conductance peaks) [17] should be noted. However, this effect seems to be negligibly small for MQD-based junctions within a reasonable range of model parameters.

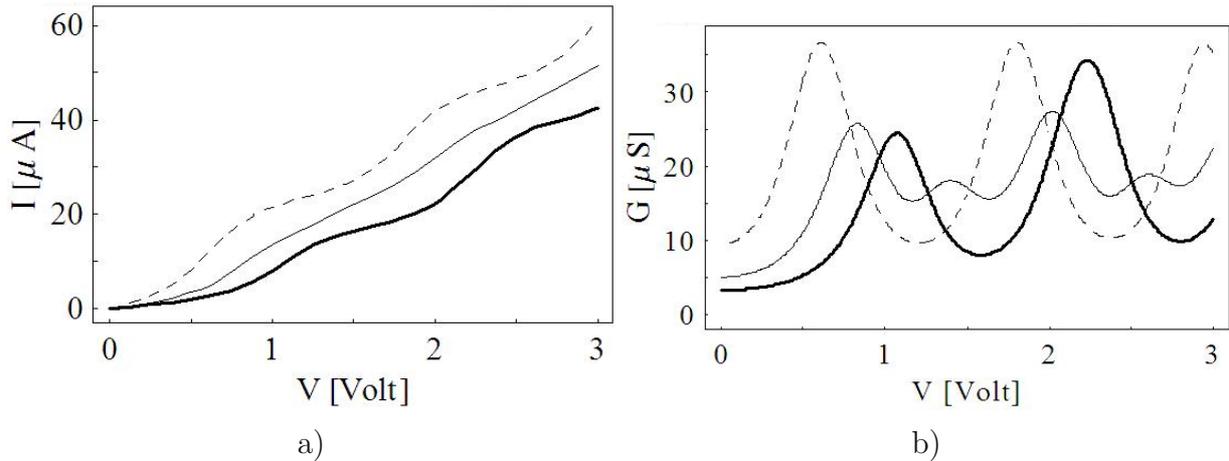


Fig. 4 Results for linear chain of 12 carbon atoms for symmetric coupling to the electrodes ($\Gamma_1 = 0.1 = \Gamma_2$) and different values of charging: $U = 0$ (broken line), $U = 0.25$ (thin solid line) and $U = 0.5$ (thick solid line): (a) current-voltage $I(V) = -I(-V)$ and (b) conductance-voltage $G(V) = G(-V)$ characteristics. Temperature: $k_B T = 1/40$ eV.

3.3 Broadening-induced effects

In Fig. 4 we show transport characteristics of a 12-atom nanowire connected symmetrically to two metallic electrodes at room temperature. Now we will analyze a stronger coupling, whereby the broadening of energy levels can not be neglected (in our model this effect is taken into account by Lorentzian densities of states). As expected, with an increase in the strength of the coupling to the electrodes, we observe an increase in values of the current flowing through the device. Also significant broadening-induced smoothing of I-V curves (or equivalently extending of conductance peaks) is observed similar to the SCF transport regime. However, we should keep in mind that this model is not well justified regarding very strong coupling. Nevertheless, we have shown here how the broadening due to the coupling with reservoirs can be included into the rate-equation theory and some possible effects associated with this broadening.

4 Conclusions

In this work we have used a simplified model based on a rate-equation approach to study the qualitative changes of transport characteristics in molecular devices in the Coulomb blockade regime. We have found a few interesting effects, such as, the suppression of the current at higher voltages, a charging-induced rectification effect, charging-generated changes of conductance gaps and the overall structures of transport characteristics. We have focused our attention especially on the differences and similarities between obtained results in the CB transport regime and those obtained in the SCF transport regime. Finally, temperature-induced as well as broadening-generated smoothing of current steps were also confirmed.

Acknowledgment

The author is very grateful to Gloria Platero for many interesting discussions.

Appendix

Here we present a standard rate-equation approach to transport via discrete energy states [7, 14–17]. This was used in section 2 to develop the presented model. The time evolution of the occupation probability of the arbitrary state $|\alpha\rangle$ is given through the so-called master equation:

$$\frac{dP_\alpha}{dt} = \sum_{\beta} (\gamma_{\beta \rightarrow \alpha} P_\beta - \gamma_{\alpha \rightarrow \beta} P_\alpha). \quad (\text{A1})$$

Presented below (A2) is the stationary state limit, where all the probabilities are time-independent $dP_\alpha/dt = 0$, hence:

$$\sum_{\beta} \gamma_{\beta \rightarrow \alpha} P_\beta = \sum_{\beta} \gamma_{\alpha \rightarrow \beta} P_\alpha. \quad (\text{A2})$$

Moreover, the summation over all the probabilities must be equal to one (normalization):

$$\sum_{\alpha} P_\alpha = 1. \quad (\text{A3})$$

Once the master equation for the individual probabilities is solved, the current flowing through the device can be calculated from the following formula:

$$I_q = e \sum_{\alpha, \beta} (\pm) \gamma_{\alpha \rightarrow \beta}^q P_\alpha, \quad (\text{A4})$$

where $q = L, R$ denotes the contact (left and right, respectively) and the sign of the q -term of transition rate $\gamma_{\alpha \rightarrow \beta}^q$ depends on whether the transition $\alpha \rightarrow \beta$ gives a positive (plus) or negative (minus) contribution to the current.

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