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Polaronic transport through molecular quantum dots. Charging-induced NDR and rectification

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The polaronic transport through molecules weakly connected to metallic electrodes in the nonlinear response regime has been studied. Molecule itself is treated as a quantum dot with discrete energy levels, its connection to the electrodes is described within the wide-band approximation, while the charging is incorporated by means of the self-consistent potential. Non-perturbative computational scheme, used in this work, is based on the Green's function theory within the framework of polaron transformation. This method transforms the many-body electron-phonon interaction problem into a one-body multi-channel single-electron scattering problem with occupation of polaron levels calculated in a self-consistent way. In particular, three different phenomena are discussed in detail resulting from charging in polaronic transport via discrete quantum states: the suppression of the current at higher voltages, negative differential resistance (NDR effect), and rectification.

Key words: *polaronic transport; decoherence; molecular quantum dot; negative differential resistance (NDR); rectification*

1. Introduction

Electronic conduction through molecular junctions composed of molecules sandwiched between electrodes is of great importance because of their potential to become future electronic devices [1]. The current–voltage characteristics (*I–V* spectra) of such nanojunctions were measured experimentally and negative differential resistance (NDR effect) [2–4] as well as rectifying behaviour [5–8] were reported. Suggested possible mechanisms for NDR involve charging and/or conformational changes [9–13], while the dominant factors in inducing rectification are some geometric asymmetry in the molecular junction and in the electrostatic potential spatial profile [14–17]. Anyway, transport characteristics are usually discussed in the context of simple tunnelling through existing energy levels (molecular orbitals).

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Since molecules involved in the conduction process can be thermally activated to vibrations (phonon modes are excited), their transport properties should be strongly affected by electron-phonon interactions in the case when an electron spends enough time on the molecule. The contact time τ_c of the conduction electron with the molecule can be estimated by a straightforward generalization of the uncertainty principle: $\tau_c \approx \hbar\beta L/\Delta E_G$ ($\beta \approx 1$ Å^{-1}) is the structure-dependent decay length of the electron transfer process, L is the length of the molecular bridge, while ΔE_G is the excitation gap between the injection energy and the isolated bridge frontier orbital energy. The above dependence has important physical implications. For short bridges with large gaps (σ-bonded systems), the contact time $\tau_c \sim$ fs is far too short for significant vibronic coupling. For longer bridges with smaller gaps (π-type systems), the contact time $\tau_c \sim$ ps is of order of magnitude comparable to vibrational period. In the latter case, the vibronic coupling can be strong enough to lead to polaronic transport through molecular bridge, where the electronic virtual excitations of polaron states create conduction channels.

This paper is devoted to the question of polaronic transport through molecules weakly connected to the electrodes in the nonlinear response regime. The molecule itself is treated as a quantum dot with discrete energy levels, the molecule–metal couplings are described within the wide-band model, while the charging is incorporated by means of the mean-field approximation. Here we show that NDR and rectification can occur also in the case of polaronic transport due to the charging effects.

2. Model and method

Let us consider the simplest possible situation in which the molecular quantum dot is represented by one spin-degenerate electronic level coupled to a single vibrational mode (primary mode) while being also connected to two reservoirs of non-interacting electrons. The Hamiltonian of the whole system can be written in the form:

$$H = \sum_{k\in\alpha} \varepsilon_k c_k^+ c_k + \sum_{k\in\alpha} \left(\gamma_k c_k^+ c_j + h.c. \right) + \varepsilon_j c_j^+ c_j + \Omega d^+ d - \lambda \left(d + d^+ \right) c_j^+ c_j \qquad (1)$$

where: ε_j and ε_k are the energies of electronic states on the molecular bridge and in the reservoirs (with momentum k), γ_k is the strength of the molecule-reservoir coupling, G is the phonon energy, λ is the electron-phonon interaction parameter, $\alpha = L, R$ stands for the left and right reservoir. c_k, c_j, d and their adjoints are annihilation and creation operators for electrons in the bridge level and in the reservoirs, and for the primary phonon mode, respectively.

We apply the so-called polaron transformation [18–21] where the electron states are expanded into the direct product states composed of single-electron states and m-phonon Fock states: $|j,m\rangle = c_j^+(d^+)^m|0\rangle/\sqrt{m!}$, $|k,m\rangle = c_k^+(d^+)^m|0\rangle/\sqrt{m!}$ ($|0\rangle$ denotes the vacuum state). This method maps exactly the many-body hole-phonon interaction problem into a one-body multi-channel scattering problem. After eliminating the reservoir degrees of freedom, we can present the effective Hamiltonian of the reduced molecular system as:

$$H_{\text{eff}} = \sum_{m,\alpha}\left(\varepsilon_j^m + \Sigma_\alpha^m\right)|j,m\rangle\langle j,m| - \sum_m \lambda^m\left(|j,m\rangle\langle j,m+1| + |j,m+1\rangle\langle j,m|\right) \tag{2}$$

where: $\varepsilon_j^m = \varepsilon_j + U_{SCF} + m\Omega$, $\lambda^m = \lambda\sqrt{m+1}$, $\Sigma_\alpha^m = -i\Gamma_\alpha^m/2$ is the self-energy in the wide-band approximation, while $\Gamma_\alpha^m = 2\pi\,|\gamma_\alpha^m|^2\,\rho_\alpha$ is the so-called linewidth function with $\gamma_\alpha^m(\equiv\gamma_k)$ as the strength of the coupling between the mth conduction level and the α electrode described by density of states ρ_α. Particular energy levels are redefined with the help of the self-consistent potential $U_{SCF} = UQ_j^m$, in order to take into account the charging effects, where the U parameter represents the on-level Hubbard -type interaction constant, while the occupation of particular channels (polaron levels) can be computed as:

$$Q_j^m = \frac{2}{\pi}\int_{-\infty}^{+\infty} d\varepsilon \frac{f_L^m(\varepsilon)\Gamma_L + f_R^m(\varepsilon)\Gamma_R}{4\left(\varepsilon - \varepsilon_j^m\right)^2 + \left(\Gamma_L + \Gamma_R\right)^2} \tag{3}$$

where $f_\alpha^m(\varepsilon) = \left(1 + \exp\left(\beta(\varepsilon + m\Omega - \mu_\alpha)\right)\right)^{-1}$ is the Fermi function. Here the electrochemical potentials are given as: $\mu_L = \varepsilon_F + \eta eV$, $\mu_R = \varepsilon_F - (1-\eta)eV$, ε_F denotes the Fermi energy, V is applied bias, while the voltage division factor is $\eta = 1/2$. Since the potential U_{SCF} is determined by the occupation Q_j^m, while Q_j^m depends on U_{SCF} – both quantities are recalculated in the self-consistent procedure. Index m numbers the particular channels and their accessibility before scattering is determined by an appropriate weight factor:

$$P_m = \left[1 - \exp(-\beta\Omega)\right]\exp(-m\beta\Omega)$$

where $\beta = 1/k_B\theta$, with θ being the device working temperature. In practice, the maximum amount of phonon quanta excited on each site is restricted to a finite number $m = m_{\max}$ because of the numerical efficiency.

Choosing an appropriate matrix element of the molecular Green function defined as: $F(\varepsilon) = (J\varepsilon - H_{\text{eff}})^{-1}$, where J is the unit matrix, we can define the transmission probability of each possible transition, where an electron incoming from the left reservoir (channel m) can suffer inelastic collisions by absorbing or emitting phonons before outgoing to the right reservoir (channel n):

$$T_{m,n}(\varepsilon) = \Gamma_L\Gamma_R\,|F_{m+1,n+1}(\varepsilon)|^2$$

The electrical current flowing through the system is given by:

$$I = \frac{e}{\pi\hbar}\int_{-\infty}^{+\infty} d\varepsilon \sum_{m,n} T_{m,n}(\varepsilon)\left(P_m f_L^m(\varepsilon)\left(1 - f_R^n(\varepsilon)\right) - P_n f_R^n(\varepsilon)\left(1 - f_L^m(\varepsilon)\right)\right) \tag{4}$$

3. Results and discussion

Figure 1 presents the current–voltage dependences obtained for the symmetric anchoring case, i.e. the strength of the molecule–electrode connections is the same at both ends. We have chosen the following parameters of the model (given in eV): $\varepsilon_j = 0$ (the reference energy of the LUMO level), $\varepsilon_F = -1$, $\Omega = 1$, $\lambda = 0.5$, $\rho_L^{-1} = \rho_R^{-1} = 20$ (both electrodes are made of the same material), while the temperature of the system is set at $\theta = 300$ K ($\beta = 40$ eV^{-1}). Maximum number of allowed phonons $m_{\max} = 4$ is used to obtain the results with accuracy better than 2% for all the chosen parameters.

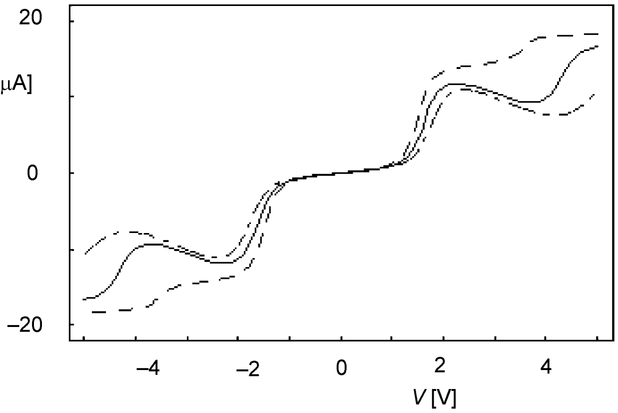

Fig. 1. Current–voltage characteristics for a molecular quantum dot symmetrically connected with two reservoirs ($\gamma_L = \gamma_R = 0.5$ V) for three different charging parameters: $U = 0$ (dashed line), $U = 2$ eV (solid line) and $U = 4$ eV (dashed-dotted line)

The I–V function reveals the well-known staircase-like structure. When we neglect the vibronic coupling, only one current step positioned at $V_0 = 2|\varepsilon_j - \varepsilon_F|/e$ (= 2 V) is expected. However, in the presence of a strong electron-phonon coupling, two current steps in the I–V dependence are observed due to the polaron formation. Using the formula for polaron energies it is possible to deduce the positions of the main conductance peak $V \approx V_0 - 2\lambda^2/(e\Omega)$ (= 1.5 V) and a one phonon side peak $V \approx V_0 - 2\Omega/e - 2\lambda^2/(e\Omega)$ (= 3.5 V). The height of the latter peak as associated with the first excited state of a polaron is much smaller than that of the former peak which corresponds to the polaron ground state.

In the case of a non-zero charging parameter, we also observe two current steps but their positions are shifted towards higher biases. Moreover, inclusion of extremely large values for U results in suppression of the current at higher voltages. Surprisingly, the charging-induced smoothing of the *I–V* curves (or equivalently the charging-induced broadening of the *G–V* function) is negligibly small. This conclusion stands in contradiction to the results obtained in the absence of phonons (see the paper by Walczak in [17]). Besides, after the first current step the NDR effect is documented (the differential conductance reaches negative values). Here we can formulate the following general conclusion: the higher is the value of the *U* parameter, the stronger NDR effect is observed. It is important to note that NDR cannot be generated by only one of the two considered interactions being combined effect of both polaron formation and charging.

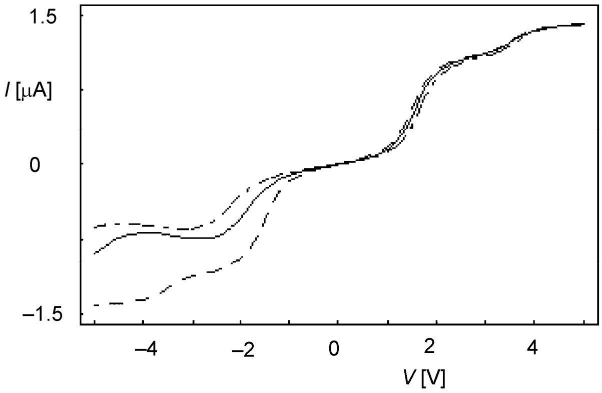

Fig. 2. Current–voltage characteristics for a molecular quantum dot asymmetrically connected with two reservoirs ($10\gamma_L = \gamma_R = 1$ eV) for three different charging parameters: $U = 0$ (dashed line), $U = 2$ eV (solid line) and $U = 4$ eV (dashed-dotted line)

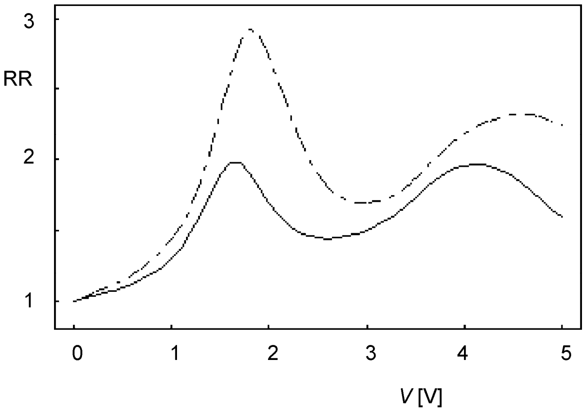

Fig. 3. Rectification ratios (RR) as functions of bias voltages for molecular quantum dot asymmetrically connected with two reservoirs ($10\gamma_L = \gamma_R = 1$ eV) for two different charging parameters: $U = 2$ eV (solid line) and $U = 4$ eV (dashed-dotted line)

In Figure 2, we plot transport characteristics for the asymmetric anchoring case, i.e. for the strength of the molecule–electrode connections being different at both ends. This situation can be realized experimentally by adjusting the molecule–electrode bond length or by linking the molecule with two electrodes with the help of different anchoring groups. Since the magnitude of the current flowing through the system is approximately proportional to the square of the smaller coupling γ parameter, the current in this case is lower.

Our calculations indicate that the *I–V* dependence is symmetric in the absence of charging (for $U = 0$). The rectification effect, in which the magnitude of the junction current depends on the bias polarity, is observed for the case of non-zero charging energy parameter (for $U > 0$). Within our model, this rectifying behaviour for higher voltages is due to a combined effect of asymmetric connections with the electrodes and charging itself. It is easy to draw the following general conclusion: asymmetry in transport characteristics increases with increasing the value of the U parameter.

To quantify the asymmetry of the *I–V* curve, we plot the rectification ratio $RR(V) = |I(V)/I(-V)$ in Fig. 3. Here we show that for the chosen set of model parameters, the junction rectifies with factor $1 < RR < 2$ for $U = 2$ eV and $1 < RR < 3$ for $U = 4$ eV. The oscillatory character of the RR quantity as a function of bias voltage is a direct consequence of the staircase-like structures of the *I–V* dependences.

4. A concluding remark

In summary, it should be mentioned that recently Galperin et al. presented a “pure” polaron model where all the charging effects are omitted [22]. They have suggested that polaronic mechanism can be responsible for NDR and hysteretic/switching behaviour in molecular junctions. In their model, the self-consistency is associated with the energy of the resonant level shifted by polaron formation that in turn depends on the electronic occupation in that level. Here, in contrast, we describe a slightly different approach to polaronic transport, where the self-consistency is related to the energy of polaron level shifted by charging energy that in turn depends on the electronic occupation in that level.

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