
FORMATION OF A TUNNEL CURRENT THROUGH A CHAIN MOLECULE WITH ACTIVE TERMINAL GROUPS

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The tunnel current through a linear chain molecule with active terminal groups has been studied. An expression for the electron current through the molecule has been derived, and the corresponding distance decay parameters have been determined. Sections with a negative differential conductance have been revealed to emerge in the current-voltage characteristic of the molecule in the resonance mode of electron transmission between the electrodes and the terminal groups of the molecule. The current rectification effect has been demonstrated to be a result of nonsymmetric coupling between the terminal groups and the electrodes.

1. Introduction

Nowadays, the main stream of researches in molecular electronics is focused upon elucidating the physical mechanisms which are responsible for charge transmission through molecules [1–5]. Large attention is paid to the development of the theory of electron-transport processes in organic structures which play a role of either active or passive bridges between metal electrodes [6–16]. One of the key factors that influence the formation of a current through the molecular bridge is related to the conditions at contact sections between the electrodes and the molecule (see recent works [17–20]).

In this work, a molecular wire is considered, the terminal groups of which have vacant electron levels located close enough to the Fermi levels of the corresponding electrodes. Unlike the terminal groups, the internal part of the chain has molecular orbitals (MOs) which are located far from the Fermi levels. Therefore, the current through the internal part of the molecule is formed following the tunnel scenario, and the corresponding MOs participate virtually in electron transmission. The terminal groups play another role. They make possible for an electron, being under the action of an external field, to make a resonance jump between the electrode and the corresponding terminal group of the molecule. One can say that it is terminal

groups that play the most active role in the formation of a current through the chain molecule.

We consider a situation that often arises, when the wave functions of both terminal groups of the molecule are weakly mixed with the MOs of the internal chain links. In this case, the states of terminal groups are well localized. At the same time, the one-electron states of the internal part of the chain are strongly delocalized, which gives rise to the “metallization” [21] of the internal part of the molecule. A chain, the links of which are $-(\text{CH}_2)-$ groups with single σ -bonds, can serve as an example of such molecules. The one-electron levels of such a chain are known to be located a few electron-volts higher than the Fermi levels in electrodes. As to active terminal groups, they should either contain π -bonds or form a σ -bond with the electrode, as it occurs with a sulfur atom. (See also work [22], where the influence of terminal atoms O and F, as well as terminal groups $-\text{OH}$ and $-\text{CN}$, on the electron transport through a benzene molecule is studied.)

Making use of the method of nonequilibrium density matrix for quantum-mechanical systems (see works [23, 24]), we have considered the specific features of the formation of a tunnel current through a linear molecular chain with active terminal groups, provided that the action of an external field does not break the delocalization of MOs belonging to the internal part of the molecule. Expressions for the current through such a molecule have been obtained, and the dependence of the current magnitude on the molecular chain length has been analyzed.

2. Model and Theory

In Fig. 1,*a*, the scheme of a linear molecule with active terminal groups (0 and $N + 1$) and a regular internal part that contains N links is depicted. Coupling between the terminal groups and the corresponding adjacent electrodes is characterized by the matrix elements β_{Lk} and β_{Rq} , and between the terminal groups and the

1-st and the N -th link, which belong to the internal part of the chain, by the matrix elements β_1 and β_N , respectively. The matrix element β_c describes a quantum jump of an electron between the neighbor links in the chain. The energy of the n -th active local state of the internal part of the molecule in the electric field is $E_n(V) = E_B + \Delta E_n(V)$, where $\Delta E_n(V)$ is a correction due to the potential difference $V_R - V_L$ applied to electrodes. If $V_L = -eV/2$ and $V_R = eV/2$, the correction looks like

$$\Delta E_n(V) = eV/2 [\eta_L + \eta(2n - N - 1) - \eta_R] \quad (1)$$

for $n = 1, 2, \dots, N$. The energy levels of the 0-th and $(N+1)$ -th terminal groups are $E_0(V) = E_0 - (eV/2)(1 - 2\eta_0)$ and $E_{N+1}(V) = E_{N+1} + (eV/2)(1 - 2\eta_{N+1})$, respectively. In those expressions for level energies, the quantities $\eta = a/\delta$, $\eta_L = \delta_L/\delta \equiv (\delta_0 + a_1)/\delta$, $\eta_R = \delta_R/\delta \equiv (a_N + \delta_{N+1})/\delta$, $\eta_0 = \delta_0/\delta$, and $\eta_{N+1} = \delta_{N+1}/\delta$ were introduced, which characterize the Stark shifts of the levels, and $\delta = \delta_0 + a_1 + (N+1)a + a_N + \delta_{N+1}$ is the electrode-to-electrode distance.

For us, the shift of energy levels with respect to the Fermi levels in the electrodes is of importance. Therefore, let us introduce the energy gaps $\Delta E_{0(N+1)r}(V) = E_{0(N+1)}(V) - \mu_r$, where $r = (L, R)$, which characterize the indicated shifts. Their specific forms are given by the expressions

$$\begin{aligned} \Delta E_{0L}(V) &= \Delta E_0 + \eta_0 eV, \\ \Delta E_{0R}(V) &= \Delta E_0 - (1 - \eta_0) eV, \\ \Delta E_{N+1L}(V) &= \Delta E_{N+1} + (1 - \eta_{N+1}) eV, \\ \Delta E_{N+1R}(V) &= \Delta E_{N+1} - \eta_{N+1} eV. \end{aligned} \quad (2)$$

Here, $\Delta E_0 = E_0 - E_F$ and $\Delta E_{N+1} = E_{N+1} - E_F$ denote the energy distances between the localized electron levels of terminal groups and the Fermi level of electrodes in the absence of applied potential difference. Gaps (2) are illustrated in Fig. 1, b.

The electron Hamiltonian of the molecule looks like

$$\begin{aligned} H_M &= \sum_{n\sigma} [E_n(V) a_{n\sigma}^\dagger a_{n\sigma} - \\ &- \beta_c (a_{n\sigma}^\dagger a_{n+1\sigma} (1 - \delta_{n,N}) + a_{n\sigma}^\dagger a_{n-1\sigma} (1 - \delta_{n,1}))] + \\ &+ \sum_{\sigma} [E_0(V) a_{0\sigma}^\dagger a_{0\sigma} + E_{N+1}(V) a_{N+1\sigma}^\dagger a_{N+1\sigma}]. \end{aligned} \quad (3)$$

Here, the first term includes the summation over the internal links of the molecule, and it is associated with the energy of the chain. At the same time, the next term is associated with the energy of terminal groups in the molecule. In expression (3), $a_{l\sigma}^\dagger$ and $a_{l\sigma}$ are the operators

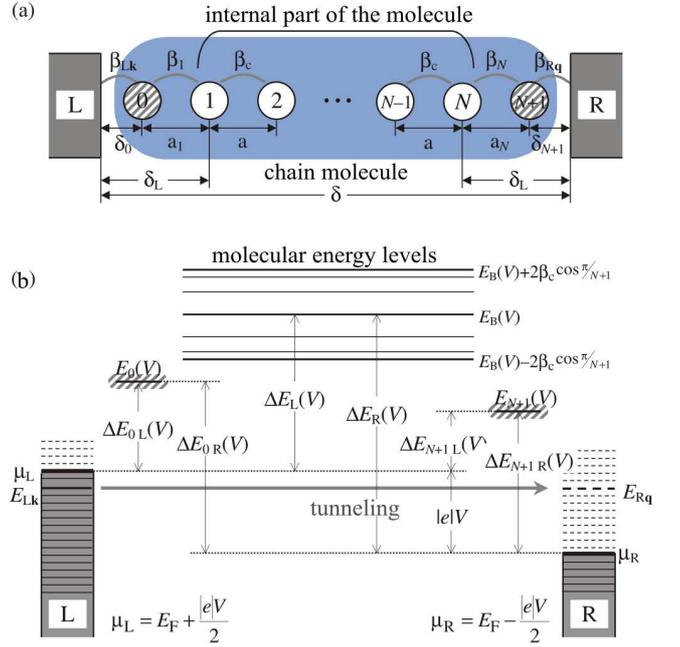


Fig. 1. Structural (a) and energy (b) diagrams of the transport system “L-electrode–molecule–R-electrode” (LMR-system) with active terminal groups 0 and $N+1$ (hatched). See explanations in the text

of creation and annihilation, respectively, of an electron at the terminal and internal links of the molecular chain ($l = 0, 1, \dots, N+1$). The general Hamiltonian of the system “electrode–molecule–electrode” (LMR),

$$H = H_{LR} + H_M + V_{LR-M}, \quad (4)$$

is composed of three terms. The first one defines the electron Hamiltonian of electrodes:

$$H_{LR} = \sum_{r=L,R} \sum_{\mathbf{k},\sigma} E_{r\mathbf{k}\sigma} a_{r\mathbf{k}\sigma}^\dagger a_{r\mathbf{k}\sigma}, \quad (5)$$

where $E_{r\mathbf{k}\sigma}$ stands for the energy of an electron with the spin projection σ and the wave vector \mathbf{k} in the conduction band of the r -th electrode ($r = L, R$). The second term in Eq. (4) is given by expression (3). And the third one,

$$\begin{aligned} V_{LR-M} &= \sum_{n\mathbf{k}|\sigma} \sum_{r=L,R} [\beta_{r\mathbf{k}} a_{r\mathbf{k}\sigma}^\dagger a_{n\sigma} + \beta_{r\mathbf{k}}^* a_{n\sigma}^\dagger a_{r\mathbf{k}\sigma}] \times \\ &\times (\delta_{r,L} \delta_{n,0} + \delta_{r,R} \delta_{n,N+1}) + \sum_{\sigma} [\beta_1 (a_{0\sigma}^\dagger a_{1\sigma} + a_{1\sigma}^\dagger a_{0\sigma}) + \end{aligned}$$

$$+ \beta_N \left(a_{N\sigma}^\dagger a_{N+1\sigma} + a_{N+1\sigma}^\dagger a_{N\sigma} \right) \Big], \quad (6)$$

is the operator of interaction between the molecule and the electrodes. It describes quantum jumps of an electron between the terminal groups of the molecule and the electrodes. In Eqs. (5) and (6), the operators of creation, $a_{r\mathbf{k}\sigma}^\dagger$, and annihilation, $a_{r\mathbf{k}\sigma}$, of an electron in the $\mathbf{k}\sigma$ -state in the r -th electrode were introduced.

Since the interaction between links in the chain is stronger than their interaction with terminal groups, it seems reasonable to diagonalize that part of the molecular Hamiltonian (3) which is associated with the internal part the chain; it is the summand that contains the summation over n . For this purpose, let us consider the influence of the electric field as a perturbation and take into account that the terminal groups interact with the adjacent electrodes more strongly than with the groups at the chain ends. We also take into consideration that the energy levels in the chain are located substantially higher – in comparison with the energy levels of terminal groups – above the Fermi levels in the electrodes. Therefore, the broadening of terminal levels due to the interaction with electrodes is practically not reflected in the broadening of chain levels (for a more detailed discussion concerning the broadening of delocalized molecular levels stemming from the interaction between electrodes and terminal groups, see work [21]).

Taking all the cited circumstances into account, we come to the following expression for the effective Hamiltonian of the molecule, the internal part of which is coupled with delocalized states:

$$H_M^{(\text{eff})} = \sum_{\sigma} \left[\mathcal{E}_0(V) a_{0\sigma}^\dagger a_{0\sigma} + \mathcal{E}_{N+1}(V) a_{N+1\sigma}^\dagger a_{N+1\sigma} + \right. \\ \left. + \sum_{\mu=1}^N E_{\mu}(V) a_{\mu\sigma}^\dagger a_{\mu\sigma} \right]. \quad (7)$$

The symbol μ means one of the delocalized MOs formed as a superposition of localized states of all N internal chain links (the number of MOs is also equal to N).

Hamiltonian (7) is diagonal, and the quantity

$$E_{\mu}(V) = E_B(V) - 2\beta_c \cos \frac{\pi\mu}{N+1} \quad (8)$$

in it defines the energy of the μ -th MO (Fig. 1,b). In Eq. (8), $E_B(V) = E_B + \Delta\varepsilon(V)$, where the quantity

$\Delta\varepsilon(V)$ is the shift of collectivized levels in the regular chain and looks like

$$\Delta\varepsilon(V) = (eV/2) (\eta_L - \eta_R). \quad (9)$$

In addition,

$$\mathcal{E}_{0(N+1)}(V) = E_{0(N+1)}(V) - (i/2)\Gamma_{0(N+1)}(E) \quad (10)$$

is the electron energy at the 0-th ($(N+1)$ -th) terminal group, and

$$\Gamma_{0(N+1)}(E) = 2\pi \sum_{\mathbf{k}} |\beta_{L(R)\mathbf{k}}|^2 \delta(E - E_{L(R)\mathbf{k}}) \quad (11)$$

is the broadening of the level occupied by the transported electron. Formally, the width of a renormalized electron level of the molecule is a function of the tunnel energy E , which the electron possesses when it comes from the electrode into the molecule. But, in the case of metal electrodes, i.e. when the conduction bands of electrodes are large (a few electron-volts), this dependence is so weak that it can be neglected, by assuming $\Gamma_{0(N+1)}(E) \approx \Gamma_{0(N+1)}$ (the wide-band approximation [3, 25]).

A condition, under which Hamiltonian (7) is valid, is the absence of the destruction of delocalized MOs subjected to the action of an external electric field. This condition looks like

$$\zeta_{\mu\mu'} = \zeta \frac{1}{(N+1)^2} \left| \frac{\sin \frac{\pi\mu}{N+1} \sin \frac{\pi\mu'}{N+1}}{\sin \frac{\pi(\mu+\mu')}{2(N+1)} \sin \frac{\pi(\mu-\mu')}{2(N+1)}} \right|^2 \ll 1, \quad (12)$$

where

$$\zeta \equiv \left| \frac{eV}{8\beta_c} \right|^2 \left(\frac{a}{\delta} \right)^2 \quad (13)$$

is a quantity which depends on the magnitude of the applied electric field.

3. Tunnel Current Through the Molecule

Provided the tunnel mechanism of electron transmission through the molecule which is located between electrodes, the current can be calculated on the basis of the expression

$$I = -e (K_{L \rightarrow R} - K_{R \rightarrow L}), \quad (14)$$

where $e = -|e| < 0$ is the electron charge, and $K_{L \rightarrow R}$ ($K_{R \rightarrow L}$) is the tunnel flux of electrons from the left (right) electrode to the right (left) one.

In work [26], it was pointed out that the tunneling is possible by engaging both relaxed and non-relaxed virtual states of the molecule (for which the positions of nuclei are not changed if an excess electron gets into the molecule). Taking into account that the main contribution (up to 98%) to the current through a bridge with highly located energy levels is given by the elastic component [27], the electron tunneling in the system under investigation is associated with the non-relaxed molecular states. Therefore, in the case of a non-magnetic molecule and non-magnetic electrodes, we have

$$K_{L \rightarrow R} = \frac{4\pi}{\hbar} \sum_{\mathbf{k}\mathbf{q}} |T_{R\mathbf{q},L\mathbf{k}}|^2 f_L(E_{L\mathbf{k}} - eV_L) \times (1 - f_R(E_{R\mathbf{q}} - eV_R)) \delta(E_{L\mathbf{k}} - E_{R\mathbf{q}}) \quad (15)$$

for the elastic flux of electrons [21, 28]. Here, $f_r(E_{r\mathbf{k}} - eV_r) = (e^{[(E_{r\mathbf{k}} - \mu_r)/k_B T]} + 1)^{-1}$ is the Fermi function of the electron distribution, and $T_{R\mathbf{q},L\mathbf{k}}$ is the effective matrix element describing the jump of an electron from the state with the wave vector \mathbf{k} in the conduction band of the left electrode to the state with the wave vector \mathbf{q} in the conduction band of the right electrode, provided that the spin projection and the vibration state of the molecule remain invariable. The expression for the reverse flux $K_{R \rightarrow L}$ can be obtained from formula (15), by making the substitution $L \rightleftharpoons R$ in it. On the basis of the obtained diagonal Hamiltonian (7) and following the procedure given in work [8], one can demonstrate that

$$T_{R\mathbf{q},L\mathbf{k}} = \frac{\beta_{L\mathbf{k}} \beta_{R\mathbf{q}}^* \beta_1 \beta_N (-\beta_c)^{N-1}}{(E - \mathcal{E}_0(V))(E - \mathcal{E}_{N+1}(V)) \prod_{\mu=1}^N (E - E_\mu(V))} \quad (16)$$

Taking formulas (11), (15), and (16) into account, expression (14) for the current reads

$$I = I_0 \left(1 - e^{-|\mu_L - \mu_R|/k_B T} \right) \int_{-\infty}^{+\infty} dE T(E, V) \times (f_L(E - eV_L) - f_R(E - eV_R)), \quad (17)$$

where the integrand includes the transmission function

$$T(E, V) = \Gamma_0(E) \Gamma_{N+1}(E) \times \left| (E - E_0(V) + (i/2)\Gamma_0(E)) \times (E - E_{N+1}(V) - (i/2)\Gamma_{N+1}(E)) \right|^{-2} \times \left| \frac{(-\beta_c)^{N-1}}{\prod_{\mu=1}^N (E - E_\mu(V))} \right|^2. \quad (18)$$

In Eq. (17), the quantity $I_0 \equiv |e|/\pi\hbar$ was introduced, which is called a current unit. (If the energy values are measured in terms of electron-volt units and the current values in terms of ampere ones, $I_0 \approx 77.6 \mu\text{A}$.)

Now, let us use the explicit expression for the chain energy levels given by Eq. (8) and the exact equality

$$\frac{(-\beta_c)^{N-1}}{\prod_{\mu=1}^N (E - E_\mu(V))} = -\frac{1}{\beta_c} \frac{\sinh \Lambda(E_B(V) - E)}{\sinh[(N+1)\Lambda(E_B(V) - E)]}, \quad (19)$$

in which

$$\Lambda(\varepsilon) = \ln \left[\frac{\varepsilon}{2\beta_c} + \sqrt{\left(\frac{\varepsilon}{2\beta_c} \right)^2 - 1} \right] \quad (20)$$

is the parameter of the superexchange interaction decay per one chain link. Ultimately, we obtain (in the wide-band approximation) that

$$I(V) = I_0 \frac{\Gamma_0 \Gamma_{N+1}}{\beta_c^2} \beta_0^2 \beta_{N+1}^2 \times \int_{-|e|V/2}^{|e|V/2} \frac{d\varepsilon'}{\left[(\varepsilon' - \Delta E_0(V))^2 + \left(\frac{\Gamma_0}{2} \right)^2 \right]} \times \frac{1}{\left[(\varepsilon' - \Delta E_{N+1}(V))^2 + \left(\frac{\Gamma_{N+1}}{2} \right)^2 \right]} \times \frac{\text{sh}^2 \Lambda(\Delta E_B(V) - \varepsilon')}{\text{sh}^2[(N+1)\Lambda(\Delta E_B(V) - \varepsilon')]} \quad (21)$$

In this expression, the energy gaps

$$\Delta E_0(V) = E_0(V) - E_F = \Delta E_0 + (|e|V/2)(1 - 2\eta_0),$$

$$\Delta E_{N+1}(V) = E_{N+1}(V) - E_F =$$

$$= \Delta E_{N+1} - (|e|V/2)(1 - 2\eta_{N+1}) \quad (22)$$

were introduced, which are distances reckoned from the shifted energy level of either terminal group to the Fermi level of identical electrodes. Gaps (22) are related to gaps (2) by means of the relations $\Delta E_{0L}(V) = \Delta E_0(V) + (\mu_L - E_F)$ and $\Delta E_{N+1R}(V) = \Delta E_{N+1}(V) + (\mu_R - E_F)$.

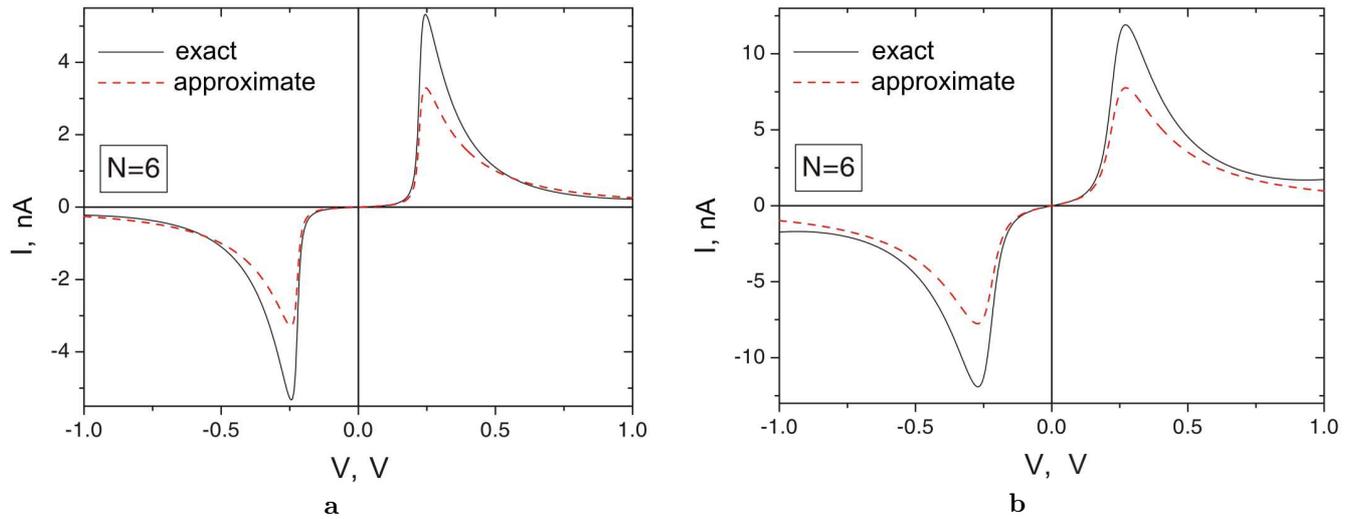


Fig. 2. Current-voltage characteristics of a molecule with two identical active terminal groups characterized by a small (a) and a large (b) level broadening. The tunnel mode of the current formation. Peak values are observed at the resonance, when the electron energy of a terminal group coincides with the Fermi level of either electrode. The results of calculations by the approximate formula (24) (solid curves) and the exact formula (21) (dashed curves) qualitatively correspond to each other. Calculation parameters are $\Delta E_B = 4.5$ eV, $\Delta E_0 = \Delta E_{N+1} = 0.2$ eV, $\beta = 2$ eV, $\beta_0 = \beta_N = 0.5$ eV, $\Gamma_L = \Gamma_R = 0.02$ eV, and $\eta_L = \eta_R = 0.1$

Since the analytical dependences of gaps (22) and the gap

$$\Delta E_B(V) = E_B(V) - E_F = \Delta E_B - (|e|V/2)(\eta_L - \eta_R), \quad (23)$$

where $\Delta E_B = E_B - E_F$, on the parameter V are different, there is no possibility to transform the integral in expression (21), in order that the entire dependence on the external electric field may be concentrated within the integration limits. That is why both the current and the conductance $g(V) = dI(V)/dV$ can be evaluated only numerically.

However, in the approximation of weak influence of the electric field on the superexchange coupling between electrodes, the entire voltage dependence of the current can be gathered in the denominator of the integrand and within the integration limits. Such an influence is contained in the distance factor

$$\frac{\sinh^2 [\Lambda(\Delta E_B(V) - \varepsilon')]}{\sinh^2 [(N + 1)\Lambda(\Delta E_B(V) - \varepsilon')]}$$

If the influence is weak, the argument $\Delta E_B(V) - \varepsilon'$ of this factor can be changed to ΔE_B , so that the distance factor can be removed from the integrand. Then, the expression for the current becomes simpler:

$$I(V) = I_0 \frac{\Gamma_0 \Gamma_{N+1}}{\beta_c^2} \beta_0^2 \beta_{N+1}^2 \frac{\text{sh}^2 \Lambda(\Delta E_B)}{\text{sh}^2 [(N + 1)\Lambda(\Delta E_B)]} \times$$

$$\times \int_{-|e|V/2}^{|e|V/2} \frac{d\varepsilon'}{\left[(\varepsilon' - \Delta E_0(V))^2 + \left(\frac{\Gamma_0}{2}\right)^2 \right]} \times \frac{1}{\left[(\varepsilon' - \Delta E_{N+1}(V))^2 + \left(\frac{\Gamma_{N+1}}{2}\right)^2 \right]}. \quad (24)$$

4. Results of Calculations

As follows from the expressions for the current, the $I - V$ characteristics of the molecule are essentially governed by the widths of the terminal group levels (Γ_0 and Γ_{N+1}), the matrix elements of the electron jump between chain links (β_0 , β_{N+1} , and β_c), and the energy gaps [expressions (22) and (23)]. A comparison of Figs. 2,a and 2,b makes it evident that the peak value of the current grows with increase in the level widths, but, simultaneously, the peak becomes broader as well. Figure 2 also demonstrates that the calculations of the current by the approximate formula (24) and the more exact formula (21) bring about the same result at the qualitative level. This circumstance allows the qualitative analysis of molecular $I - V$ characteristics to be carried out on the basis of a simpler description model. At the same time, the current decay with the increase of the

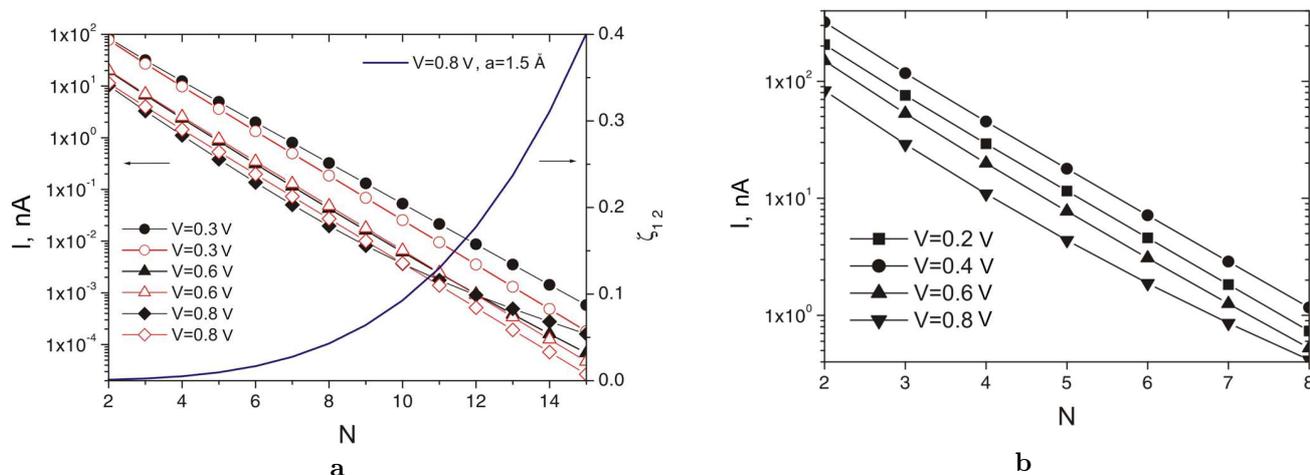


Fig. 3. Dependences of the current I on the number of identical links N in the molecular chain. The molecule is coupled with electrodes through identical active terminal groups. Calculations by the approximate formula (24) (hollow symbols) testify to the exponential current decay with increasing N , whereas calculations by the more exact formula (21) (solid symbols) evidence for a deviation from the exponential law. Calculation parameters are the same as in Fig. 2

molecular chain length turns out sensitive to the model choice.

For the tunnel mechanism of electron transmission, typical is the exponential dependence of the current I on the molecular chain length d , $I \sim \exp(-\beta d)$ [29], where β is the distance decay parameter which depends on both the overlapping between the one-electron wave functions of the neighbor chain links and the energy distance between the MO and the Fermi level. The simple model (24) does not contain any dependence of the distance decay coefficient β on V , and, therefore, this parameter is reduced to the value $\beta = (2/a) \ln \Lambda(\Delta E_B)$ (see Fig. 3,a). At the same time, the more exact model (21) provides such a dependence through either the $\beta_L(V)$ - or the $\beta_R(V)$ -dependence, which are taken in the form

$$\beta_r(V) = \frac{2}{a} \ln \left[\frac{\Delta E_r(V)}{2\beta_c} + \sqrt{\left(\frac{\Delta E_r(V)}{2\beta_c} \right)^2 - 1} \right], \quad (25)$$

$r = (L, R)$. Depending on the V -sign, either of the $\beta_L(V)$ and $\beta_R(V)$ quantities can be larger than the other, and the smallest one should be taken as β . Therefore, one can adopt that

$$\beta = \beta(V) \approx (2/a) \ln \Lambda[\Delta E_B - (|e|V/2)(1 + \eta_L - \eta_R)] \quad (26)$$

at $V > 0$ and

$$\beta = \beta(V) \approx (2/a) \ln \Lambda[\Delta E_B - (|e|V/2)(1 + \eta_R - \eta_L)] \quad (27)$$

at $V < 0$.

Figures 3,a and 3,b demonstrate that the dependences of the distance decay parameter on the chain link number N and the potential difference V become more pronounced for longer chains and at high V -values, which reflects the integral origin of contributions made by tunnel paths in the whole energy range from $E_F - |eV|/2$ to $E_F + |eV|/2$. The deviation is associated with both the dependence $\Lambda(\Delta E_B(V) - \varepsilon')$ of the distance decay coefficient on the tunnel energy and the influence of terminal groups. The effect is stronger for longer chains; in this case, however, condition (12) is no more valid. For Fig. 3,a, the condition $\zeta_{12} \ll 1$ [see condition (12)] defines a restriction that is imposed on the use of expressions obtained for the current. In particular, at $V = 0.8$ V, it is satisfied up to $N = 8 \div 10$. In Fig. 3,b, the dependence $\beta(V)$ weakly manifests itself up to $V = 0.6$ V, but it becomes noticeable, if $V = 0.8$ V and $N > 5$.

If the contacts between the molecule and the electrodes are not identical, the symmetric $I - V$ characteristic transforms into an asymmetric one. Figure 4 illustrates the case where the interaction between the left terminal group and the adjacent electrode is stronger than the similar interaction right

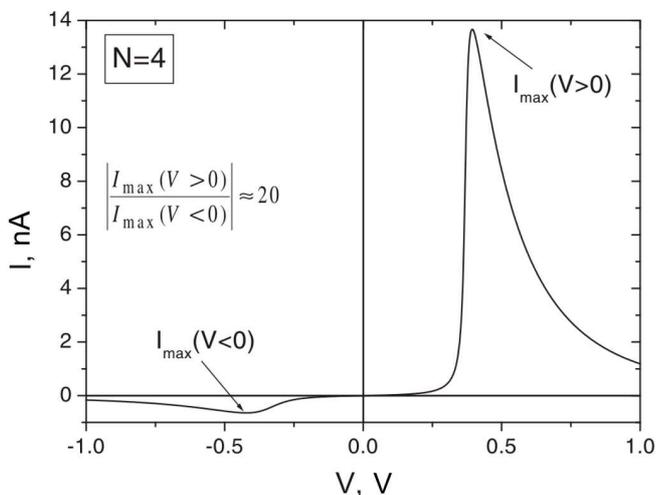


Fig. 4. Effect of current rectification by active terminal groups of the chain molecule. Calculations were carried out by formula (21) with the parameters $\Delta E_B = 4.5$ eV, $\Delta E_0 = 0.3$ eV, $\Delta E_{N+1} = 0.35$ eV, $\beta = 2$ eV, $\beta_0 = 0.4$ eV, $\beta_N = 0.2$ eV, $\Gamma_L = 0.14$ eV, $\Gamma_R = 0.02$ eV, $\eta_L = 0.05$, and $\eta_R = 0.1$

terminal group–electrode. The effect of tunnel current rectification by terminal groups is clearly seen. It becomes especially pronounced at peak current values, when the rectification factor (the ratio between maximal, by absolute value, current values at a positive and a negative potential difference, $|I_{\max}(V > 0)/I_{\max}(V < 0)|$) is equal to 20.

5. Conclusion

The process of formation of a tunnel current through a molecular chain with active terminal groups, which is located between electrodes, has been considered. The internal part of the chain forms a tunnel barrier for electron transport, which retains its rectangular shape as long as condition (12) holds true. In general, the transport process has character of a coherent distant jump.

The presence of active terminal groups has been shown to bring about specific features in the current-voltage characteristics of the molecule, the internal links of which play the role of a bridge between its terminal groups. Owing to the close arrangement of the electron levels of terminal groups and the Fermi levels of electrodes, the tunnel transmission of electrons in the resonance mode through the molecule and the appearance of sections with a negative differential conductance become possible. In addition, if the couplings between the terminal groups in the molecule

and the adjacent electrodes are not identical, there emerges a rectification effect, so that the molecule starts to function as a diode. The availability of active terminal groups also influences the character of current decay as the chain length increases. The effective value of the distance decay parameter becomes dependent on both the applied potential difference and the chain length. This effect has an integral character and is caused by the tunneling of electrons in the energy range from $E_F - |eV|/2$ to $E_F + |eV|/2$.

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ФОРМУВАННЯ ТУНЕЛЬНОГО СТРУМУ ЧЕРЕЗ ЛАНЦЮЖКОВУ МОЛЕКУЛУ З АКТИВНИМИ ПРИКІНЦЕВИМИ ГРУПАМИ

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Резюме

Проведено вивчення тунельного струму через лінійну ланцюжкову молекулу з активними кінцевими групами. Отримано вирази для електронного струму через молекулу та визначено параметри дистанційного затухання струму. Показано, що за рахунок формування режиму резонансної трансмісії між електродами та кінцевими групами молекули у вольт-амперній характеристиці молекули виникають ділянки з негативною диференціальною провідністю. Продемонстровано виникнення ефекту випрямлення струму при несиметричному зв'язку кінцевих груп з електродами.