GATE ELECTRIC FIELD CONTROL OVER THE TUNNEL CONDUCTIVITY OF A MOLECULE

YE.V. SHEVCHENKO, E.G. PETROV

Bogolyubov Institute for Theoretical Physics, Nat. Acad. of Sci. of Ukraine
(14b, Metrolohichna Str., Kyiv 03680, Ukraine; e-mail: shevchenko@bitp.kiev.ua)

The role of a gate potential on the formation of a tunnel current in the system "electrode–molecule–electrode" has been studied in the configuration where the interior part of the molecule is a linear bridge with strongly delocalized molecular orbitals, the energies of which are assumed to be well separated from both the Fermi levels of electrodes and the electron levels of molecular end groups. It has been shown that the electric potential of the gate electrode governs the molecular conductivity by shifting the electron levels of the bridge. Hence, the current-voltage characteristics of such a molecular device can be controlled in a wide range of bias voltages.

1. Introduction

First researches of conduction properties of organic nanostructures – such as nanowires, carbon nanotubes, molecular monolayers, and individual nanomolecules – have been started more than 30 years ago [1, 2]. Nowadays, owing to the prospects of the development of molecular nanoelectronic devices, those researches attract a special attention [3–7]. A few basic theoretical approaches to the description of the charge transport through a molecule or a molecular wire have been formed. These are the formalism of nonequilibrium Green's function [8–10], the method of nonequilibrium density matrix for open quantum-mechanical systems [11,12], and the simulation of molecular properties in the framework of the density functional theory [13–15]. Experiments and numerical simulations show that molecular conductors reveal a rich spectrum of properties. In particular, they can be characterized by a negative differential resistance; moreover, they can serve as current switches and rectifiers [8, 16, 17]. The special attention is paid to the simulation of rectifying properties of the "electrode–molecule–electrode" system [19, 22–25]. Today, monomolecular devices which behave like a diode [26], a transistor [27], or a memory cell [28, 29] can be fabricated. Owing to the novel technique aimed at measuring the conductivity of molecular nanoobjects with the help of a double-tip scanning tunneling microscope combined with a scanning electron microscope [30], it became possible to directly study currents that pass through a molecule.

A system, in which a molecule is affected by a control (gate) electrode, is of considerable interest. This electrode is capable of changing the level arrangement of those molecular orbitals (MOs) which participate in the charge transfer. Therefore, it plays, like a contact between the molecule and the electrodes, a substantial governing role at the electron transmission [18,21,23]. In this work on the basis of the results obtained earlier for the elastic electron transport through saturated carbon chains with two terminal groups [31–33], the influence of a gate potential on the current-voltage characteristics of the electrode–molecule–electrode (EME) system is studied.

2. Model and Basic Relations

In Fig. 1, the diagram of a molecular device that is functioning as a transistor is depicted. The device consists of a linear molecule, the right (R) and left (L) electrodes, and the gate (G) electrode, the field of which influences the internal regular part of the molecule. The molecule is a chain composed of $N + 2$ units. The terminal units, the 0-th and the $(N + 1)$-th ones, are in contact with electrodes L and R, respectively. The remaining part of the molecule is a regular bridge (B) which consists of N internal units of the molecule. Owing to the strong non-diagonal interaction between adjacent units of the bridge (the corresponding parameter is β_c), its electron MOs are strongly delocalized. The energy of an excess electron on the bridge MOs is high in comparison with the corresponding energies in the terminal units and the Fermi levels of electrodes. Therefore, the probability of finding an electron on the bridge can be regarded as infinitesimally small. The gate electrode G affects, by its potential V_G, the arrangement of energy levels of bridge MOs, but does not practically change the energy of electrons that arrive at the terminal units of the molecule in the course of charge transmission. The gate electrode is also assumed to be well insulated from the molecule, so it
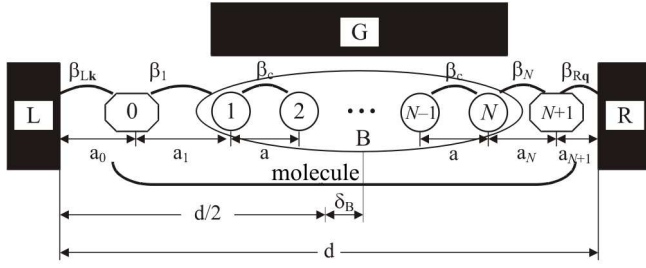
Fig. 1. Block diagram of a molecular transistor composed of the transport system electrode–molecule–electrode and an additional electrode G

does not participate directly in the charge transmission through the molecule. The interaction of terminal units of the molecule with the $\mathbf{k}$-th level of the adjacent electrode is characterized by the parameters $\beta_{L\mathbf{k}}$ and $\beta_{R\mathbf{k}}$, and with the 1-st and the N-th unit by the parameters β_1 and β_N, respectively.

The EME system under consideration is similar to that studied earlier in work [31]. However, the EME system additionally includes now the gate electrode which should be taken into account, when constructing the system Hamiltonian. Using the results of works [31–33] for the model of broad electrode bands, we obtain the following diagonalized Hamiltonian of the EME system:

$$H = H_{LR} + H_M^{(\text{eff})}. \tag{1}$$

Here, the electrode Hamiltonian looks like

$$H_{LR} = \sum_{r=L,R} \sum_{\mathbf{k},\sigma} E_{r\mathbf{k}\sigma} a_{r\mathbf{k}\sigma}^\dagger a_{r\mathbf{k}\sigma}, \tag{2}$$

where $E_{r\mathbf{k}\sigma}$ is the energy of an electron with the spin projection σ and the wave vector $\mathbf{k}$ which belongs to the conduction band of the r-th $(r = L, R)$ electrode; and $a_{r\mathbf{k}\sigma}^\dagger$ and $a_{r\mathbf{k}\sigma}$ are the creation and annihilation operators of this state, respectively.

The second term in Eq. (1) is the effective Hamiltonian of the molecule

$$H_M^{(\text{eff})} = \sum_\sigma \Big[\varepsilon_0(V) a_{0\sigma}^\dagger a_{0\sigma} + \varepsilon_{N+1}(V) a_{N+1\sigma}^\dagger a_{N+1\sigma} +$$

$$+ \sum_{\mu=1}^N \varepsilon_\mu(V, V_G) a_{\mu\sigma}^\dagger a_{\mu\sigma} \Big], \tag{3}$$

where $a_{\lambda\sigma}^\dagger$ and $a_{\lambda\sigma}$ $(\lambda = 0, 1, \ldots, N+1)$ are the creation and annihilation operators, respectively, of an electron
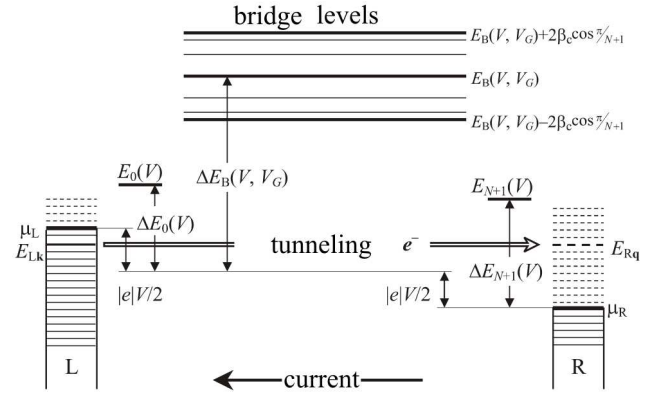

Fig. 2. Electron energy diagram of a molecular transistor with delocalized bridge molecular orbitals. μ_L and μ_R are the chemical potentials of the left and right electrodes, respectively

with spin projection σ on the λ-th molecular orbital. The MO energies of terminal groups look as follows:

$$\varepsilon_{0(N+1)} = E_{0(N+1)}(V) - \frac{i}{2} \Gamma_{0(N+1)}. \tag{4}$$

Here, $E_0(V)$ and $E_{N+1}(V)$ are the energies of an excess electron, which is located on the 0-th and the $(N + 1)$-th unit of the molecule, respectively (Fig. 2). Those energies depend on the electric potential difference V applied between electrodes L and R. Below, we assume that the potentials of the right and left electrodes are equal to $V/2$ and $-V/2$, respectively. Then

$$E_0(V) = E_0 + \frac{|e| V}{2} (1 - 2\eta_0),$$

$$E_{N+1}(V) = E_{N+1} - \frac{|e| V}{2} (1 - 2\eta_{N+1}), \tag{5}$$

where $|e|$ is the elementary charge, and E_0 and E_{N+1} are the corresponding electron energies at $V = 0$. The quantities η_0 and η_{N+1} make allowance for the geometric positions of the end molecular units with respect to their adjacent electrodes, with $\eta_{0(N+1)} = a_{0(N+1)}/d$ (see Fig. 1).

The quantities Γ_0 and Γ_{N+1} are the broadenings of MO levels, which the transported electron is located on. The broadening results from the interaction with electrodes L and R. In the approximation of the wide conduction band of a metal, those quantities do not depend on the energy of a tunneling electron E [8], we have

$$\Gamma_{0(N+1)} \approx \Gamma_{0(N+1)}(E) =$$

$$= 2\pi \sum_{\mathbf{k}} \left| \beta_{L(R)\mathbf{k}} \right|^2 \delta \left(E - E_{L(R)\mathbf{k}} \right). \tag{6}$$

The energy of every μ-th MO of the internal part of the molecule ($\mu = 1, 2, \ldots, N$) looks like

$$\varepsilon_\mu(V, V_G) = E_B(V, V_G) - 2\beta_c \cos \frac{\pi\mu}{N+1}, \qquad (7)$$

where $E_B(V, V_G)$ is the energy of an electron on a separate unit of the bridge in the absence of delocalization. This quantity depends not only on the interelectrode potential difference V, but also on the gate potential V_G:

$$E_B(V, V_G) = E_B - |e| V \eta_B - |e| V_G. \qquad (8)$$

In Eq. (8), η_B is a deviation of the bridge "center" from the mid-point of the distance between the electrodes, $\eta_B = \delta_B/d$, and E_B is the electron energy at zero potentials.

Hamiltonian (3) can be used, if the external electric field V does not destroy the delocalization of the bridge MOs. This is possible, provided that the following condition is satisfied [33]:

$$\left| \frac{eV}{8\beta_c} \right|^2 \left(\frac{a}{d} \right)^2 \frac{1}{(N+1)^2} \left| \frac{\sin \frac{\pi}{N+1} \sin \frac{2\pi}{N+1}}{\sin^3 \frac{3\pi}{2(N+1)} \sin^3 \frac{\pi}{2(N+1)}} \right| \ll 1. \qquad (9)$$

3. Controlled Tunnel Current

With the gate electrode, the EME system is a molecular transistor. Since the energy levels of the bridge MOs are located rather far from the electrode Fermi levels, the dominant mechanism of current flow through this molecular transistor is the tunnel electron transfer by means of the superexchange mechanism [31]. Under condition (9) in the case of a non-magnetic molecule and non-magnetic electrodes, we obtain the following expression for the current:

$$I(V, V_G) = I_0 \frac{\Gamma_0 \Gamma_{N+1}}{\beta_c^2} \beta_0^2 \beta_{N+1}^2 \times$$

$$\times \int_{-\frac{|e|V}{2}}^{\frac{|e|V}{2}} \frac{d\varepsilon'}{\left[(\varepsilon' - \Delta E_0(V))^2 + \left(\frac{\Gamma_0}{2} \right)^2 \right]} \times$$

$$\times \frac{1}{\left[(\varepsilon' - \Delta E_{N+1}(V))^2 + \left(\frac{\Gamma_{N+1}}{2} \right)^2 \right]} \times$$

$$\times \frac{\sinh^2 \Lambda(\Delta E_B(V, V_G) - \varepsilon')}{\sinh^2 \left[(N+1) \Lambda(\Delta E_B(V, V_G) - \varepsilon') \right]}, \qquad (10)$$

where the quantity

$$\Lambda(\varepsilon) = \ln \left[\frac{\varepsilon}{2\beta_c} + \sqrt{\left(\frac{\varepsilon}{2\beta_c} \right)^2 - 1} \right] \qquad (11)$$

characterizes the superexchange coupling between terminal units 0 and $N+1$ of the molecule. In Eq. (10), the current unit $I_0 \equiv |e|/(\pi\hbar) \approx 77.6 \ \mu$A was introduced, and all energy quantities are reckoned from the Fermi level E_F of electrodes at $V = 0$:

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

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

$$= \Delta E_{N+1} - \frac{|e| V}{2} (1 - 2\eta_{N+1}),$$

$$\Delta E_B(V, V_G) = E_B(V, V_G) - E_F =$$

$$= \Delta E_B - |e| V \eta_B - |e| V_G. \qquad (12)$$

The quantities ΔE_0 and ΔE_{N+1} stand for the energy gaps between the Fermi levels in the electrode and in the corresponding terminal unit in the molecular chain, and ΔE_B is the gap between the Fermi level in electrodes and the energy of an electron transferred along the bridge units without taking the delocalization into account and at $V = 0$.

In expression (10) obtained for the tunnel current, the gate characteristics are included into the parameter $\Lambda(\Delta E(V, V_G) - \varepsilon)$. One can see that, owing to the presence of the bridge, the gate electrode potential considerably affects the effective superexchange interaction which is formed between the terminal molecular groups and, hence, the tunnel current. As follows from Fig. 3, the current dependence on the gate potential is exponential-like, with the deviations from the exponential law becoming larger both when the length of the molecule grows and when the width of the energy gap that separates the bridge from the terminal units of the molecular chain and the electrodes diminishes (this occurs, when the positive potential of the gate increases). As a result of such a monotonous dependence, the additional electrode in the EME system turns out to be a
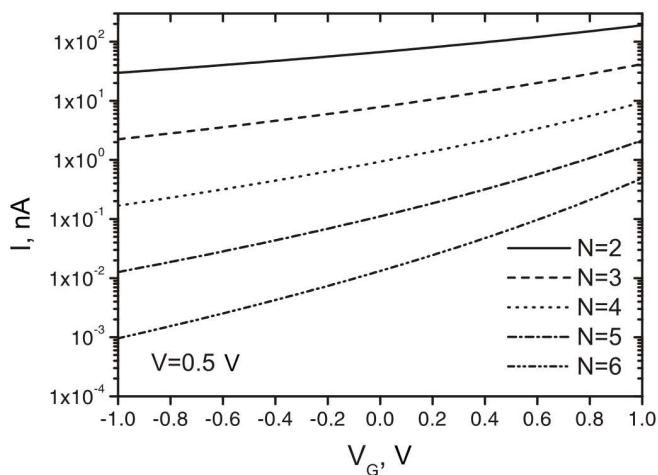
Fig. 3. Dependences of the tunnel current through a molecular transistor on the gate potential. Calculations were carried out by formulas (10)–(12) with the parameter values $\Delta E_B = 5$ eV, $\Delta E_0 = \Delta E_{N+1} = 0.3$ eV, $\beta_c = 1.5$ eV, $\beta_0 = \beta_{N+1} = 0.4$ eV, $\Gamma_0 = \Gamma_{N+1} = 0.4$ eV, $\eta_B = 0$, $\eta_0 = \eta_{N+1} = 0.15$
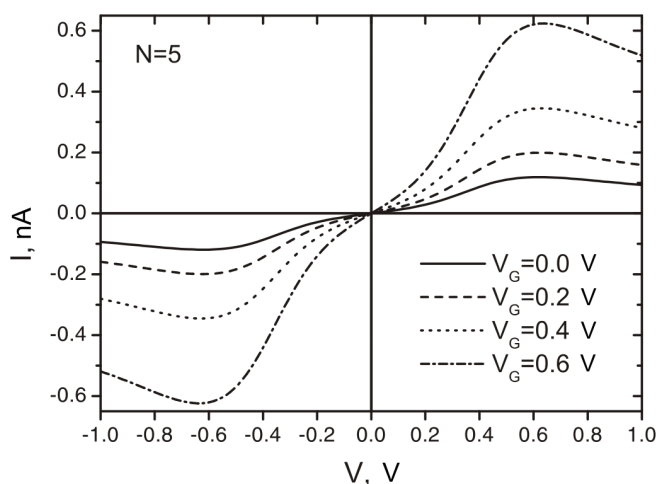

Fig. 4. Influence of the gate potential on the shape of current-voltage characteristics of a molecule mounted in between the electrodes. Calculations were carried out by formulas (10)–(12) with the same parameter values as in Fig. 3

control device for the current value within the range of several orders of magnitude (Fig. 4).

For the system under examination, the influence of the electric field produced by electrodes L and R on the superexchange coupling between electrodes is assumed to be weak. Therefore, the parameter κ of current attenuation with increase in the distance, which is the key characteristic of the tunnel current damping according to the law $I \sim \exp(-\kappa d)$, can be described by the simple
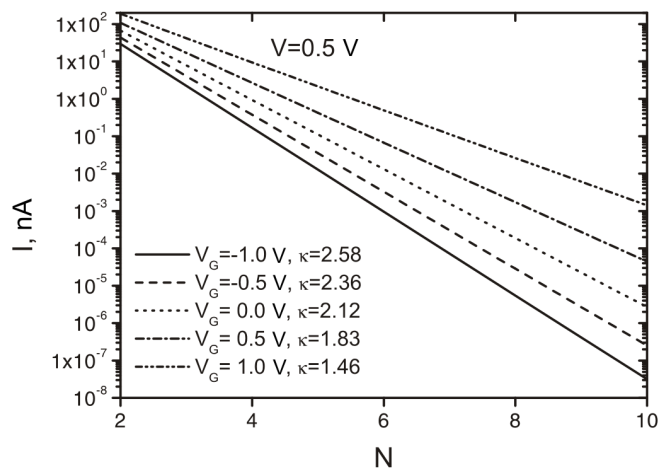
Fig. 5. Effect of a distance damping reduction of the tunnel current through the molecule at the growth of the gate potential. Calculations were carried out by formulas (10)–(12) with the same parameter values as in Fig. 3

expression

$$\kappa = \frac{2}{a}\Lambda(\Delta E_B(V_G)). \tag{13}$$

It is evident that the gate potential, which directly influences the energy of electron levels in the bridge, modifies the attenuation factor by changing the tunnel barrier amplitude $\Delta E_B(V_G)$. This effect is clearly demonstrated in Fig. 5: the higher the potential V_G, the closer is the bridge energy (8) to the Fermi levels of electrodes and the more slowly the current decreases with increase in the molecule length.

4. Conclusion

In this work, a model of molecular transistor is proposed, which is the electrode–molecule–electrode system, where the linear molecule contains terminal groups that contact directly with corresponding electrodes, and the internal regular part consists of N identical units. The chemical composition of internal units is such that the state of an excess electron in those units is strongly delocalized, with the lower level being located far from both the electron energy level on the Fermi surfaces of electrodes and the energy of the excess electron in the terminal groups. Such a situation becomes possible, if the internal units of the chain are composed of atoms which are connected with one another by saturated (unary) chemical bonds (for instance, CH_2 groups) or by alternating unary and ternary bonds. Bridges consisting of five- or six-membered rings connected by saturated bonds are

also possible [26]. The remoteness of the energy of an electron in the internal molecular units results in that the electron is transferred from one electrode to another owing to the superexchange (tunnel) mechanism, when the tunnel barrier is mainly formed by internal units of the linear molecule. Provided that condition (9) is satisfied, the electric field of the gate changes only the height of this barrier rather than its shape. The barrier height variation leads to an appreciable (by several orders of magnitude) change of the tunnel current. Hence, the gate governs the current through the linear molecule, and the molecule itself plays the role of a nanomolecular transistor.

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РЕГУЛЮВАННЯ ТУНЕЛЬНОЇ ПРОВІДНОСТІ
МОЛЕКУЛИ ЕЛЕКТРИЧНИМ ПОЛЕМ ЗАТВОРА

Є.В. Шевченко, Е.Г. Петров

Р е з ю м е

Розглянуто вплив потенціалу затворного електрода на формування тунельного струму в системі "електрод–молекула–електрод", в якій внутрішня частина молекули являє собою лінійний місток із сильно делокалізованими молекулярними

орбіталями, що енергетично добре відокремлені як від рівнів Фермі електродів, так і від електронних рівнів термінальних груп молекули. Показано, що потенціал затворного електрода, зсуваючи розташування електронних рівнів містка, дозволяє

змінювати провідність молекули. Завдяки такому зсуву можливо керувати вольт-амперними характеристиками молекулярного пристрою в широкому діапазоні різниць потенціалів, що прикладаються.