Superexchange tunneling conductance in molecular wires

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Abstract
The modified superexchange model is used to derive the expression for nonresonant tunneling conductance mediated by localized and delocalized molecular orbitals associated with the terminal and the interior molecular units respectively. The model is shown to work as long as delocalization of electron density in the chain’s molecular orbitals is sustained during the tunneling. The criteria for reduction of...
the superexchange model of charge tunneling to the flat barrier model are formulated and the parameters of the barrier model (energy gap and effective electron mass) are specified in the terms of inter-site coupling and energy distance from the Fermi level to the delocalized wire's HOMO level. Application of the theory to the experiment shows that the modified superexchange model is quite appropriate to explain the experimental results in case of the nonresonance tunneling conductance in \(-(\text{CH}_2)_N\text{NH}_2\) and \(\text{HOOC-(CH}_2)_N\text{COOH}\) molecular wires.

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*Key words:* molecular wires; nonresonant tunneling; conductance

## 1 Introduction

The use of organic molecules is becoming one of the major strategies in miniaturization of electronic, optoelectronic and spintronic circuit components [1,2,3,4,5,6,7,8]. A significant progress in this direction has been achieved by applying scanning tunneling and atomic force microscopes for monitoring and controlling charge transfer processes in molecular junctions as well as for fabrication of molecular structures with desirable conduction properties [9,10,11,12,13]. A molecular junction where single molecules or self assembled monolayers (SAMs) are embedded between the electrodes can fulfill the functions of molecular wires, diodes, transistors, registers, switches etc. [14,15,16]. A number of factors such as the molecule-electrode couplings, the energy position of molecular orbitals (MOs) relative to the Fermi-levels of the contacts, electronic density of states, conformation mobility of the molecule etc., controls the current-voltage and conductance characteristics of single molecules and molecular compounds. Therefore, the efficiency of the charge transmission
pathways depends strongly on the type of the molecular junction as well as magnitude and polarity of the applied electric field.

The mechanism of formation of the tunneling conductance in the molecular junction "metal - molecule - metal" where a molecule comprises a regular chain anchored to the electrodes through its terminal units is of great importance. These units bind the chains to the metallic surface thus forming the SAM of regular chains. As part of the SAM, each molecule functions as molecular wire and thus can mediate transmission of an electron/hole from one electrode to another. Due molecular wire determining the a distant electron/hole transfer, the specification of the factors that control the wire conductance at different regimes of charge transmission remains the central problems in molecular electronics. One of the working regimes is associated with nonresonant charge tunneling where the MOs of the molecular wire are not occupied by the transferred electron/hole. At such a regime, both the current and the conductance decay exponentially with molecular length \[11,17,18,19,20,21,22,23,24\]. The analysis of conductivity/resistance in molecular wires is mostly performed with the simple flat-barrier Simmons model \[25\]. The model predicts an exponential decrease in the tunneling current and conductance where the attenuation factor \(\beta\) is expressed via two fitting parameters, the effective mass \(m^*\) and the height of rectangular barrier \(\Delta E\). Detail analysis of the Simmons model shows \[17,18,20\] that the choice of the above mentioned fitting parameters, especially \(\Delta E\), depends on the precise voltage region and the chain length. Thus, for molecular junctions, the rectangular barrier model does not have the unified parameters.

The model of superexchange tunneling through a molecular wire provides an alternative approach based on mutual overlap of wave functions of the bridging
interior wire units as well as on the overlap of wave functions of the terminal wire units and the electrodes. This leads to formation of a direct distant coupling between the conductive states of the spaced electrodes. The McConnell’s version of superexchange model [26] was successfully used to describe a distant hole transfer through DNA molecules [27,28,29] as well as combined hopping-tunneling electron transmission in the terminated molecular wires [30]. McConnell model has also been used to analyze the $I/V$ characteristics of alkane chains [20,31]. The model explains the exponential drop of the current with the increase of the wire length, however, it shows discrepancy with the attenuation factor predicted by the barrier model. In the superexchange model, the attenuation factor is determined through the hopping matrix element between the neighboring sites of electron/hole localization in a regular chain, and the energy distance of the Fermi level with respect to position of the localized MO belonging the interior wire unit. This energy distance differs strongly on the barrier height $\Delta E$, which, in case of molecular junction, is assumed to be the gap between the Fermi level and the delocalized HOMO level belonging to the regular range of the wire [18,20].

In this paper, the modified theory of nonresonant superexchange tunneling is used to analyze the dependence of the conductance of the terminated molecular wire on the length of the wire’s regular range. The explicit expressions for the conductance are derived along with the attenuation factor, an important parameter that describes the efficiency of the tunneling across the molecular junction. In limiting cases, the attenuation factor yields two different limits corresponding the Simmons or McConnell models.

The paper is organized as follows. In Section 2, the basic principles of the modified superexchange model are presented and distinct expressions for the
conductance of linear terminated molecular wires are derived. Results concerning the applicability of the model to description of the conductance in specific molecular junctions are given in Section 3. Concluding remarks are presented in Section 4.

2 Theoretical base

We consider molecular junction as a quantum system where a linear molecular wire is attached to the left (L) and the right (R) electrodes, Fig. 1. Bearing in mind the application of the theory to the analysis of the tunneling conductivity in the molecular junctions, where energies of the highest occupied molecular orbitals (HOMOs) are closer to the electrode’s Fermi level compared to the energies of the lowest unoccupied molecular orbitals (LUMOs), only the formation of a superexchange charge transfer with participation of the virtual HOMOs is considered here. We use the tight-binding model where the transferred electron can leave the twofold filled energy level of the HOMO\(_n\) located on the wire unit \(n = (0, 1, \ldots, N, N+1)\). The distance \(l_{nn+1} \equiv l_s\) between the neighboring units is associated with the distance between the sites of main electron localization within the unit. For instance, in the \(N\)–alkane chain, the \(l_s\) refers to the distance between the neighboring C–C bonds. For the sake of definiteness, let us assume that the left electrode is grounded so that the chemical potential of the \(r\)th electrode appears as \(\mu_r = E_F - |e|V\delta_{r,R}, \ (r = L,R),\) where \(E_F\) is the energy of electrode’s Fermi level. In the linear approximation over the bias voltage \(V = (\mu_L - \mu_R)/|e|,\) the energy of an electron on the \(n\)th unit reads \(E_n = E_n^{(0)} - n|e|V,\) where \(E_n^{(0)}\) is the zero bias orbital energy and
Fig. 1. Arrangement of units of a linear molecular wire relative to the attached electrodes L and R. Terminal units are denoted via 0 and N + 1, the units of a regular chain (interior range of the wire) are n = 1, 2, ..., N. Quantities \( \Gamma_L \) and \( \Gamma_R \) are the width parameters characterizing the broadening of respective terminal orbital energies \( E_0 \) and \( E_{N+1} \). Rest explanations in the text.

\( \eta_n \) is the factor that characterizes the Stark shifts of the orbital energies. With the grounded left electrode, this yields \( \eta_{L(R)} = l_{L(R)}/l \) at \( n = 0(N + 1) \) and \( \eta_n = [l_L + l_1 + (n - 1)l_s]/l \) at \( n = 1, 2, ..., N \), with \( l = l_L + l_1 + (N - 1)l_s + l_N + l_R \) being the total interelectrode distance. The electron couplings between the MOs of the neighboring wire units are characterized by the hopping matrix elements \( t_{n,n+1} \). For the interior (regular) part of a molecular wire, we set \( t_{n,n+1} \equiv t_s \) whereas \( t_{0,1} \equiv t_1 \) and \( t_{N,N+1} \equiv t_N \) are used for the terminal units, Fig. 1. Interaction of the chain with the electrodes is provided by its terminal units \( n = 0 \) and \( n = N + 1 \). We consider the LWR systems where orbital energies \( E_0 \) and \( E_{N+1} \) differ from the interior unit energies \( E_n \). Thus, a mixs between the MO belonging the terminal unit and the MO of the nearest interior wire unit is assumed to be so insignificant that the localization of the terminal MOs is conserved during the electron/hole transmission across the wire. As a result, the interaction between the terminal and interior units can be considered as the perturbation. The same refers to the interaction between the terminal MOs and each electronic conduction state of the electrodes [32].
2.1 Tunneling current and conductance

The noted tight binding model has been used to derive distinct expressions for a nonresonant tunneling current $I$ through the terminated molecular wire. From ref. [33], in the framework of tight-binding model, the Landauer-Büttiker approach [34,35,36] gives the following basic (integral) form for the current:

$$I = i_0 \int_{\Delta E_{Rs}}^{\Delta E_{Ls}} d\epsilon T_L(\epsilon - \Delta E_{0s})T_{reg}(\epsilon, N)T_R(\epsilon - \Delta E_{N+1s})$$  \hspace{1cm} (1)

where $i_0 \equiv (|e|/\pi \hbar) \times 1 \text{ eV} \approx 77.3 \mu\text{A}$ is the current unit. In Eq. (1), the integration limits coincide with energy gaps (see also Fig. 2)

$$\Delta E_{rs} = \Delta E_{s}^{(0)} + |e|V[\eta_{c.g.}\delta_{r,L} - (1 - \eta_{c.g.})\delta_{r,R}]$$  \hspace{1cm} (2)

where $\Delta E_{s}^{(0)} = E_F - E_{s}^{(0)} > 0$ is the main transmission energy gap in an unbiased LWR. Eq. (1) shows that the wire transmission function is represented as the product of three functions. Among them

$$T_L(\epsilon - \Delta E_{0s}) = \frac{\Gamma_L}{t_s} \frac{t_1^2}{(\epsilon - \Delta E_{0s})^2 + \Gamma_L^2/4}$$  \hspace{1cm} (3)

and

$$T_R(\epsilon - \Delta E_{N+1s}) = \frac{\Gamma_R}{t_s} \frac{t_N^2}{(\epsilon - \Delta E_{N+1s})^2 + \Gamma_R^2/4}.$$  \hspace{1cm} (4)

refer to the terminal units. In Eqs. (3) and (4), $\Gamma_L$ and $\Gamma_R$ are the width parameters that characterize broadening of the respective terminal energies $E_0$ and $E_{N+1}$ caused by interaction of the levels with the attached electrodes. Quantities

$$\Delta E_{0s} = \Delta E_{0s}^{(0)} + |e|V(\eta_{c.g.} - \eta_L),$$

$$\Delta E_{N+1s} = \Delta E_{N+1s}^{(0)} - |e|V(1 - \eta_{c.g.} - \eta_R).$$  \hspace{1cm} (5)

are the energy distances $\Delta E_{0(N+1)s} = E_{0(N+1)} - E_{c.g.}$ between the terminal levels and the position of the ”center of gravity” of electron density distributed
over the delocalized MOs. The quantity \( \Delta E_{0(N+1)s}^{(0)} = E_{0(N+1)}^{(0)} - E_{s}^{(0)} \) is the unbiased energy distance between MO’s levels of the \( 0(N + 1) \)th terminal unit and the interior unit. As to the transmission function of a regular chain (interior range of the wire) it reads

\[
T_{\text{reg}}(\epsilon, N) = \frac{\sinh^2 \left[ \beta(\epsilon)/2 \right]}{\sinh^2 \left[ (N + 1)\beta(\epsilon)/2 \right]}
\]

where

\[
\beta(\epsilon) = 2 \ln \left[ \left( \epsilon/2|t_s| \right) + \sqrt{\left( \epsilon/2|t_s| \right)^2 - 1} \right], \quad (\epsilon = E - E_{\text{c.g.}} > 0),
\]

is the attenuation factor per one chain unit. It characterizes a decrease of the \( T_{\text{reg}}(\epsilon, N) \) depending on the number of chain units \( N \). Expression (7) exists only if the inequality

\[
2|t_s|/\epsilon < 1
\]

is satisfied at the nonresonant tunneling.

In the integrand of Eq. (1), a voltage dependence is present only in terminal transmission functions. Therefore, the tunneling conductance of a molecular wire, \( g = \partial I/\partial V \), appears as the sum of two contributions:

\[
g = g^{(1)} + g^{(2)}.
\]

Introducing the conductance unit \( g_0 = |e|i_0 = e^2/\pi \hbar = 77.3 \mu S \), for the first contribution one obtains:

\[
g^{(1)} = g_0 \left[ \eta_{\text{c.g.}} T_L(\Delta E_{L0}) T_{\text{reg}}(\Delta E_{Ls}, N) T_R(\Delta E_{LN+1}) \right.
\]

\[
+ (1 - \eta_{\text{c.g.}}) T_L(\Delta E_{R0}) T_{\text{reg}}(\Delta E_{Rs}, N) T_R(\Delta E_{RN+1}) \left. \right].
\]

Here, terminal transmission functions (3) and (4) comprise the gaps

\[
\Delta E_{r0} = \Delta E_{0}^{(0)} + |e|V[\eta_L \delta_{r,L} - (1 - \eta_L) \delta_{r,R}],
\]
Fig. 2. Position of the transmission energy $\epsilon = E - E_{c.g.}$ with respect to the "center of gravity" of electronic density distributed over the delocalized HOMOs. When tunneling energy $E$ enters in window $\mu_L \geq E \geq \mu_R$, than the $\epsilon$ varies in range $[\Delta E_{Rs}, \Delta E_{Ls}]$. Quantity $\Delta E_{r0(N+1)}$ is the energy gap between chemical potential of the $r(= L, R)$th electrode and orbital energy of the $0(N + 1)$th terminal unit. $\Delta E = E - E_H$ is the energy distance between tunneling energy and the HOMO level position $E_H$ for a long $(N \gg 1)$ regular chain. In the pre-resonant tunneling regime, when $E - E_H \ll 2|t_s|$, quantity $\Delta E$ can be referred to the height of the apparent rectangular barrier.

$$\Delta E_{r,N+1} = \Delta E_{N+1}^{(0)} - |e|V[\eta_R \delta_{r,R} + (1 - \eta_R) \delta_{r,L}]$$  \hspace{1cm} (11)$$

whereas the gaps for chain transmission functions (6) are $\Delta E_{rs}$, Eq. (2). The second conductance contribution appears in the integral form:

$$g^{(2)} = (g_0/|e|) \int_{\Delta E_{Rs}}^{\Delta E_{Ls}} d\epsilon T_{\text{reg}}(\epsilon, N) \left[ \frac{\partial T_L(\epsilon - \Delta E_{0s})}{\partial V} T_R(\epsilon - \Delta E_{N+1s}) + T_L(\epsilon - \Delta E_{0s}) \frac{\partial T_R(\epsilon - \Delta E_{N+1s})}{\partial V} \right].$$  \hspace{1cm} (12)$$

The expressions for current and conductance are true for the molecular junctions where charge transmission is formed with participation of the localized and delocalized HOMOs belonging respectively to the terminal and the interior wire units. The energies of the HOMOs are represented in Fig.2 Rigorous analysis shows [33] that the delocalized chain HOMOs can be involved (virtu-
ally) in formation of the superexchange tunneling only if the inequality

$$|\Delta_s/2t_s|S(N) \ll 1$$

is satisfied in the LWR system. In Eq. (13),

$$\Delta_s = |e|V(l_s/l)$$

is the energy drop between identical neighboring units and

$$S(N) = \left( \frac{1}{N+1} \right) \left[ \frac{1}{1 - \cos \left( \frac{\pi}{N+1} \right)} - \frac{1}{1 - \cos \left( \frac{3\pi}{N+1} \right)} \right]$$

$$\times \left[ \frac{1}{\cos \left( \frac{\pi}{N+1} \right) - \cos \left( \frac{2\pi}{N+1} \right)} \right]$$

is the function that depends solely on the number of chain units. If the inequality (13) is satisfied, then energies of the delocalized HOMOs are given by equation

$$\mathcal{E}_\nu = E_{c.g.} - 2|t_s|\cos \left( \frac{\pi \nu}{N+1} \right), \quad (\nu = 1, 2, \ldots, N),$$

with

$$E_{c.g.} = E_{s}^{(0)} - |e|V\eta_{c.g.}$$

being the energy position of the "center of gravity" of the electron density for the delocalized HOMOs. It should be particularly emphasized that the Stark shift is identical for each energy level related to the delocalized orbitals.

### 2.2 Explicit expressions for a conductance

Reading form for the first conductance contribution follows from Eq. (10) taking into account Eqs. (3), (4), (6) and the relation

$$\cosh \left[ \beta(\epsilon)/2 \right] = \epsilon/2|t_s|.$$
This yields

\[
g^{(1)} = g_0 \left[ \eta_{c.g.} \left( \frac{\Gamma_L \Gamma_R}{\Delta E_{Ls}^2} \right) \frac{t^2_1 t^2_0 \Phi(\beta_L, N)}{(\Delta E_{L0}^2 + \Gamma_L^2/4)(\Delta E_{LN+1}^2 + \Gamma_R^2/4)} \right] + (1 - \eta_{c.g.}) \left( \eta_{L/R} \frac{\Gamma_L \Gamma_R}{\Delta E_{Rs}^2} \right) \frac{t^2_1 t^2_N \Phi(\beta_{L/R}, N)}{(\Delta E_{R0}^2 + \Gamma_L^2/4)(\Delta E_{RN+1}^2 + \Gamma_R^2/4)} \right]. \tag{19}
\]

Here, \( \Phi(\beta_{L(R)}, N) \) is the chain attenuation function

\[
\Phi(\beta(\epsilon), N) = \frac{\sinh^2 \beta(\epsilon)}{\sinh^2 [(N+1)(\beta(\epsilon)/2)]} \tag{20}
\]

with attenuation factor (7) taken at \( \epsilon = \Delta E_{rs}, \ (r = L, R) \). Bearing in mind property \( \Phi(\beta(\epsilon), 1) = 1 \), the function (20) becomes a very suitable value to characterize the superexchange tunneling drop dependence on the chain length.

To obtain a reading form for the second conductance contribution, Eq. (12) we employ the approach previously proposed [33] for reduction of the integral form for the current, Eq. (11) to more simple analytic forms. One of them is derived using the so called mean-value (m.v.) approximation. This leads to a nearly identical dependence of the \( I \) on \( V \) and \( N \) as given by basic integral form (1). In our case, in line with the m.v. approximation, the transmission functions \( T_{L(R)}, T_{reg} \) and derivatives \( \partial T_{L(R)}/\partial V \) are substituted for averaged values \( \overline{T_{L(R),}} \), \( T_{reg}(N) \) and \( \overline{\partial T_{L(R)}/\partial V} \), respectively. This reduces Eq. (12) to

\[
g^{(2)} \approx g^{(2)}_{m.v.} \approx 4g_0 \left[ \frac{(\eta_{c,g} - \eta_L)(\Delta \epsilon_0 \Gamma_L/4) t^2_1 t^2_N}{(\Delta E_{L0}^2 + \Gamma_L^2/4)(\Delta E_{R0}^2 + \Gamma_R^2/4)} \chi_{N+1} \right. \]

\[
- \left. \frac{(1 - \eta_{c,g} - \eta_L)(\Delta \epsilon_{N+1} \Gamma_R/4) t^2_1 t^2_N}{(\Delta E_{LN+1}^2 + \Gamma_L^2/4)(\Delta E_{RN+1}^2 + \Gamma_R^2/4)} \chi_0 \right] T_{reg}(N) \tag{21}
\]

where

\[
\chi_{0(N+1)} = \tan^{-1} \left( \frac{2\Delta E_{L0(N+1)}}{\Gamma_L(R)} \right) - \tan^{-1} \left( \frac{2\Delta E_{R0(N+1)}}{\Gamma_L(R)} \right). \tag{22}
\]

With use of expressions [33]

\[
T_{reg}(1) = \frac{t^2_L}{\Delta \epsilon_s^2 - (|\epsilon|V/2)^2}, \tag{23}
\]

11
\[ T_{\text{reg}}(2) = \frac{t_s^2}{4} \left\{ \frac{1}{|e|V t_s} \ln \left[ \frac{\Delta \epsilon_s^2 - (t_s + |e|V/2)^2}{\Delta \epsilon_s^2 - (t_s - |e|V/2)^2} \right] \right\}^{1/(\Delta \epsilon_s - t_s)^2 - (|e|V/2)^2} + \frac{1}{(\Delta \epsilon_s + t_s)^2 - (|e|V/2)^2} \right\}. \] (24)

and

\[ T_{\text{reg}}(N \geq 3) \approx \left( \frac{t_s}{|e|V} \right) \frac{1}{2N - 1} \times \left[ F(\beta_R) e^{-\beta_R[N-1/2]} - F(\beta_L) e^{-\beta_L[N-1/2]} \right], \] (25)

where

\[ F(\beta) = 1 - (2N - 1) \left[ \frac{3}{2N + 1} e^{-\beta} + \frac{3}{2N + 3} e^{-2\beta} + \frac{1}{2N + 5} e^{-3\beta} \right]. \] (26)

we obtain an explicit form for the second conductance contribution. It is important to note that attenuation factors \( \beta_L \) and \( \beta_R \) are identical to those in Eq. (19).

3 Results and discussion

To demonstrate the mechanism of formation of the nonresonant superexchange tunneling conductance, we consider the perfectly symmetric LWR system where the wire is the \( N \)-alkane chain anchored to the gold electrodes via terminal units \( X = \text{–SH, –NH}_2, \text{–COOH} \). The experimental data on high and low conductance of the \( X-(\text{CH}_2)_N-X \) wires as a function of molecular length are well represented in paper [21]. The voltage region covers [-0.4, +0.4] V and the number of \( \text{CH}_2 \) groups is changed from 2 to 12. In such conditions, the orbital energies \( E_0 \) and \( E_{N+1} \) do not enter in resonance with electrodes’s Fermi levels. Besides, transmission gaps in Eqs. (19) and (21) exceed broadenings \( \Gamma_L = \Gamma_R \equiv \Gamma_\ast \). This yields \( \chi_0(N+1) \approx |e|V \Gamma_\ast/[2 \Delta E_{L0(N+1)} \Delta E_{R0(N+1)}] \).

Introducing \( t_\ast \equiv t_1 = t_{N+1} \) along with \( \eta_\ast \equiv \eta_L = \eta_R \) and bearing in mind the
fact that independently on the chemical structure of molecular junction the factor $\eta_{c.g.}$ is equal to $1/2$, for the first conductance contribution one obtains

$$g^{(1)} = \frac{g_0}{2} \left[ \frac{\Gamma^2 t^4}{\Delta E_{L0}^2 \Delta E_{R0}^2 \Delta E_{LN+1}^2} \Phi(\beta_L, N) + \frac{\Gamma^2 t^4}{\Delta E_{R0}^2 \Delta E_{R0}^2 \Delta E_{RN+1}^2} \Phi(\beta_R, N) \right].$$

(27)

The dependence of $g$ on $N$ is concentrated in the terminal gaps [11] and the attenuation functions $\Phi(\beta_{L(R)}, N)$. Because $\Phi(\beta_r, 1) = 1$, the function $\Phi(\beta_R, N)$ is quite suitable for characterization of conductance drop with chain length increase. As to the second contribution, it appears as

$$g^{(2)} \approx g_{m.v.}^{(2)} = g_0|e|V(1 - 2\eta_*) \frac{(\Gamma^2 t^4/t_s^2)}{\Delta E_{L0} \Delta E_{R0} \Delta E_{LN+1} \Delta E_{RN+1}} \times \left[ \frac{\Delta \epsilon_0}{\Delta E_{L0} \Delta E_{R0}} - \frac{\Delta \epsilon_{N+1}}{\Delta E_{LN+1} \Delta E_{RN+1}} \right] T_{reg}(N).$$

(28)

To estimate the numerical weight of $g^{(1)}$ and $g^{(2)}$ in the total conductance $g$ let us refer to the results concerning the application of the modified superexchange model to description of a nonresonant tunneling current through –S–(CH$_2$)$_n$–S– wire. To this end, let us note that the model contains two fundamental parameters, the zero bias gap $\Delta E_{s}^{(0)}$ and the intersite coupling $t_s$ (for alkane chains, parameter $t_s$ is positive so that $t_s = |t_s|$). These parameters determine the most important wire characteristic, attenuation factor $\beta_0 \equiv \beta(\epsilon = \Delta E_{s}^{(0)})$. Strong relation between above parameters is fixed with the basic equality [18]. In the case of molecular wire with $X =$ SH, NH$_2$ and COOH, the $\beta_0$ takes the values 1.02, 0.83 and 0.80 (per CH$_2$ group), respectively [21]. Therefore, corresponding magnitudes for the ratio $\Delta E_{s}^{(0)}/2t_s$ are 1.133, 1.087 and 1.081. The second important relation between parameters $\Delta E_{s}^{(0)}$ and $2t_s$ follows from the condition at which HOMO energy $E_H = \mathcal{E}_{n=N} = E_{c.g.} + 2t_s$ enters in resonance with the Fermi energy of one of the electrodes. At a positive polarity,
this occurs at $V = V_{cr}$ where

$$V_{cr} = \frac{2}{|e|} (\Delta E_s^{(0)} - 2t_s). \quad (29)$$

In HS–(CH$_2$)$_N$–SH wire, the $V_{cr}$ is presumably about 1.5 V. (No conductance peaks are observed outside of 1.5 V [20]). Therefore, using the expressions (18) and (29), one obtains $\Delta E_s^{(0)} \approx 6.3$ eV, $t_s \approx 2.78$ eV. These values have been used in ref. [33] to explain the $I/V$ characteristics of the –S–(CH$_2$)$_N$–S– wire. Our calculations of the contributions $g^{(1)}$ and $g^{(2)}$, which have been presented in Fig. 3a show that in the case of charge tunneling across –S–(CH$_2$)$_N$–S– wire the $g^{(1)}$ exceeds the $g^{(2)}$ significantly, so that $g \simeq g^{(1)}$ (cf. the insertion in Fig. 3b). Physically, this result is explained by the alignment of the terminal energies $E_0$ and $E_{N+1}$ with respect to Fermi levels. In –S–(CH$_2$)$_N$–S– wire, the terminal units are attributed to either sulfur’s lone pair or the binding Au-S orbitals. Each of them does not enter in resonance with Fermi levels. Therefore, the terminal transmission functions (3) and (4) are monotonic in the integration region $\Delta E_{Ls} \geq \epsilon \geq \Delta E_{Rs}$. The similar situation is true for terminal NH$_2$ and COOH units. This is due to the fact that in voltage region [-0.4,+0.4]V the orbital energies $E_0$ and $E_{N+1}$ of these units are positioned below chemical potentials $\mu_L$ and $\mu_R$ (cf. Fig. 2). Thus, bearing in mind that X–(CH$_2$)$_N$–X wires contain same N - alkane chains one can estimate the conductance setting $g \simeq g^{(1)}$.

To specify fundamental parameters $\Delta E_s^{(0)}$ and $t_s$ for the wires X–(CH$_2$)$_N$–X with X = NH$_2$, COOH, one has to take into account the fact that different terminal units can change the energy position of delocalized HOMO level with respect to the Fermi levels [21]37]. Thus, the magnitudes of $\Delta E_s^{(0)}$ and $t_s$ have to be nonidentical for different wires. For the wire with X = SH, the atten-
Fig. 3. Voltage dependence of conduction contributions $g^{(1)}$ and $g^{(2)}$ on the applied voltages (a). Ratio of the contributions shows a minor weight of the $g^{(2)}$ in common $g$ (b). Parameters of the modified superexchange model are the same that have been utilized in ref. [33] for the $-\text{S}-(\text{CH}_2)_N\text{S}$– wire: $\Delta E_* = 3.4 \text{ eV}$, $t_* = 2.5 \text{ eV}$, $\Delta E_s^{(0)} = 6.3 \text{ eV}$, $\Gamma_* = 0.2 \text{ eV}$.

Evaluation factor $\beta_0$ exceeds the similar quantity for the wires with $X = \text{NH}_2$, COOH. Therefore, in line with basic equality (18) one can assume that for the last two wires, the $\Delta E_s^{(0)}$ is smaller in value. We estimate the $\Delta E_2^{(0)}$ comparing the theoretical expression for the current with the experimental $I/V$ characteristics at different number of CH$_2$ units. The theoretical description is based on the mean-value approximation for the current, which reads [33]

$$I_{m.v.} = i_0 |e|V \frac{(\Gamma_* t_*^2 / t_s)^2}{[\Delta E_*^2 - (|e| V \eta_*)^2][\Delta E_s^2 - (|e| V)^2(1 - \eta_*)^2]} T_{reg}(N).$$

(30)
Fig. 4. $I/V$ characteristics of $N$-alkanes terminated with diamine (a) and dicarboxylic-acid anchoring groups. The data points represent the data adopted from experiment [21]. Insertions show the exponential drop of nonresonant tunneling current at the fixed attenuation factor $\beta = \beta_N$ (symbol $N$ indicates the drop per chain unit). The curves are calculated with Eq. (30) at $N = 4, 6, 8, 10$. Calculation parameters are $\Delta E_s = 1.50$ eV, $\Delta E_s^{(0)} = 5.72$ eV, $t_s = 2.60$ eV, $t_s = 2.63$ eV, $\Gamma_s = 0.30$ eV (a) and $\Delta E_s = 1.25$ eV, $\Delta E_s^{(0)} = 6.03$ eV, $t_s = 2.64$ eV, $t_s = 2.79$ eV, $\Gamma_s = 0.09$ eV (b).

Here, $T_{reg}(N)$ being determined by Eqs. (23) - (26). Fig. 4 shows a good fit of Eq. (30) to the data if one sets $\Delta E_s^{(0)} \approx 5.72$ eV, $t_s \approx 2.63$ eV and $\Delta E_s^{(0)} \approx 6.03$ eV, $t_s \approx 2.79$ eV for $\text{H}_2\text{N}-(\text{CH}_2)_N-\text{NH}_2$ and $\text{HOOC}-(\text{CH}_2)_N-\text{COOH}$ molecular wires, respectively. With the same parameters, we achieve
Fig. 5. Attenuation of the nonresonant tunneling conductance with an increase of the number of C-C bonds of $N$-alkanedithiol wire attached to the electrodes through NH$_2$ and COOH groups. The data points represent the data adopted from experiment [21]. Exponential approximation yields the same $\beta = \beta_N$ that of the current (see insertions in Fig.4). Calculations of the $g \simeq g^{(1)}$ with use of Eq. (27). Parameters are the same as in Fig.4.

Note, that for the description of the near-zero bias (z.b.) conductance, a much more simple form for the $g$ exists. This follows directly from Eq. (27) yielding

$$g = g_{z.b.} \simeq g_{\text{unit}} \Phi(\beta_0, N)$$  \hspace{1cm} (31)$$

where

$$g_{\text{unit}} = g_0 \left( \frac{\Gamma_s}{\Delta E_s^{(0)}} \right)^2 \left( \frac{t_s}{\Delta E_s} \right)^4$$  \hspace{1cm} (32)$$

is the conductance through a molecular wire with one bridging unit, and $\Phi(\beta_0, N)$ is the attenuation function (20) with attenuation factor $\beta_0 = \beta(\epsilon = \Delta E_s^{(0)})$. Form (31) refers to the wire where terminal units are coupled via the bridging units. This means that one can not set $N = 0$ in attenuation function $\Phi(\beta_0, N)$ to specify the contact conductance.
For the wire where \( \exp \left[ - (N + 1) \beta(\epsilon) \right] \ll 1 \), the attenuation function \( \Phi(\beta(\epsilon), N) \) appears as

\[
\Phi(\beta(\epsilon), N) \approx \left( 1 - e^{-2\beta(\epsilon)} \right)^2 e^{-\beta(\epsilon)(N-1)}. \tag{33}
\]

It demonstrates a pure exponential drop with \( N \).

At small inter-site coupling \( t_s \), when condition

\[
(2t_s/\epsilon)^2 \ll 1 \tag{34}
\]

is satisfied, the attenuation factor \( (1) \) is reduced to McConnel’s form

\[
\beta(\epsilon) \simeq \beta_{M.C.} = 2 \ln \left( \epsilon/t_s \right). \tag{35}
\]

Another limiting case is realized if property

\[
\Delta E \ll 2t_s \tag{36}
\]

is satisfied for quantity

\[
\Delta E = \epsilon - 2t_s. \tag{37}
\]

Physically, \( \Delta E \) is the energy distance between transmission energy \( E \) and the position of the "the center of gravity" (cf. Fig. 2 and Eq. (17)). When the inequality \( (36) \) is satisfied, one can introduce the effective electron mass \( m^* \) even though the regular chain as a whole may be of finite length \( 33 \). The expression for the mass,

\[
m^* = \hbar^2 / 2t_s l_s^2, \tag{38}
\]

is determined by the intersite coupling \( t_s \) and the distance \( l_s \) between the neighboring sites of electron localization (cf. Fig. 1). Introduction of the effective mass leads to the equality

\[
\exp \left[ - \beta(\epsilon)(N - 1) \right] = \exp (-\beta_B d_s) \tag{39}
\]
where

$$\beta_B = \frac{2}{\hbar} \sqrt{2m^* \Delta E}$$  \hspace{1cm} (40)$$

is the attenuation factor (in Å⁻¹) and \(d_s = l_s(N - 1)\) is the distance (in Å) between the edge chain units \(n = 1\) and \(n = N\). It follows from Eq. (40) that the \(\Delta E\) can be referred to as the height of rectangular barrier of length \(d_s\). Note, however, that such an interpretation can be used only if specific condition (36) exists during a transmission process.

Since near-zero bias tunneling occurs at \(E \approx E_F\), then \(\epsilon \approx \Delta E^{(0)}_s\). This means that \(\Delta E_0 = \Delta E^{(0)}_s - 2t_s \approx 0.46\) eV and 0.45 eV for \(H_2N-(CH_2)_N-NH_2\) and HOOC–(CH₂)ₙ–COOH molecular wires, respectively. As far as the gap \(\Delta E_0\) satisfies the condition (36), it becomes possible to interpret a nonresonant superexchange transmission across \(H_2N(HOOC)-(CH_2)_N-NH_2(COOH)\) molecular wire as a tunneling of an electron with an effective mass \(m^* = 0.85(0.80)m_e\) through a rectangular barrier of the height \(\Delta E_0 = 0.46\ (0.45)\) eV and the length \(d_s = l_s(N - 1)\), \(m_e\) is the elementary electron mass). In line with relation (39), the corresponding zero-bias barrier attenuation factor (40) reads \(\beta_B^{(0)} = \beta_0 l_s^{-1}\). In the biased LWR system, the conductance drop with chain length is determined by the attenuation functions \(\Phi(\beta_L, N)\) and \(\Phi(\beta_R, N)\).

Similarly, with the near-zero bias case, one can express the chain attenuation factor \(\beta_r\), \((r = L, R)\), via the barrier one,

$$\beta_r = l_s \beta_B^{(r)}$$  \hspace{1cm} (41)$$

where

$$\beta_B^{(r)} = \frac{2}{\hbar} \sqrt{2m^* \Delta E_r}.$$  \hspace{1cm} (42)$$

In accordance with Eq. (2) the dependence of the barrier height on the bias
voltage reads
\[ \Delta E_r = \Delta E_0 + (|e|V/2)(\delta_{r,L} - \delta_{r,R}). \] (43)

Thus, in the \( N \)-alkanes terminated by SH, NH\(_4\)\(_2\) and COOH anchoring groups, the analysis of the conductance drop can be also performed using the barrier model, until inequalities (13) and (13) are satisfied at the tunneling transmission. In a barrier model, the height, Eq. (37) and the tunneling effective electron mass, Eq. (38) are expressed via the characteristics of a molecular junction. This is reflected in relation (41) between respective attenuation factors. The relation exists until the inequality
\[ \Delta E_L(R) \ll 2t_s \] (44)

retains its validity during the tunneling charge transmission. However, it is necessary to note that apart from attenuation factors, Eq. (41), additional quantities exist that specify the current and the conductance. For a perfectly symmetric LWR system, they are the following: coupling of the terminal unit to the corresponding chain edge unit \( (t_s) \), MO’s broadening \( (\Gamma_s) \), the voltage division factor \( (\eta_s) \), and the terminal gap \( (\Delta E_s) \). In the case of an ohmic regime, some of these quantities are combined in a single parameter \( g_{unit} \), Eq. (32) characterizing the conductance of an elementary LWR system with the single bridging unit. As follows from Fig. 4, \( g_{unit} \) is about \( 2.5 \cdot 10^{-2}g_0 \) and \( 4 \cdot 10^{-3}g_0 \) for H\(_2\)N–(CH\(_2\))\(_N\)–NH\(_2\) and HOOC–(CH\(_2\))\(_N\)–COOH molecular wires, respectively. The \( g_{unit} \) does not contain the barrier characteristics of a regular chain. Thus, even though the rigorous correspondence, Eq. (41) exists between the attenuation factors, it is more preferable to explain the physics of a tunneling process in the framework of superexchange model.

At given \( V \) and \( N \), the feasibility of the modified superexchange model is
limited by inequality \([13]\). For \(N\)-alkanes with terminal \(\text{NH}_2\) and \(\text{COOH}\) groups where \(t_s \approx 2.7\) eV, the model works at \(N \leq 20\) and \(N \leq 10\) if \(V = 0.1\) V and \(V = 0.4\) V, respectively. Therefore, for instance, the theoretical curves in Fig. 4 that cover the experimental data at \(N = 4\), predict \(I/V\) characteristics at \(N = 6, 8, 10\).

4 Conclusions

The main objective of this study was to obtain explicit expressions for the tunneling conductance in a molecular wire consisting of a regular chain connected to metal electrodes through terminal groups or individual atoms. In the case of a nonresonant electron/hole transmission through such a molecular junction, a temperature independent current and conductance were observed, and their values decay exponentially with increasing length of the wire’s interior range (regular chain). Since the exponential attenuation indicates the tunneling nature of the conductivity in the "electrode-molecular wire-electrode" system, the analysis of experimental current-voltage characteristics and the conductance in the LWR system is most often carried out using the Simmons barrier model by analogy with the "electrode-dielectric-electrode" structures. However, this phenomenological model does not sufficiently reflects the specifics of a current/conductance formation in molecular junctions. The progress in understanding the mechanism of conductivity in the molecular wires is due to McConnel’s model of distant superexchange transfer of electrons/holes. In this model, the current decays exponentially similar the barrier model. At the same time, McConnel’s model has restrictions related to the applicability of the perturbation theory in the parameter that characterizes ratio \([34]\) between
the inter-site coupling $t_s$ and transmission gap $\epsilon$.

In the present paper, the modified model of superexchange tunneling in the version proposed in ref. [33] is used for the description of the nonresonant current through a molecular wire. The model assumes a much more soft relation, Eq. (8) between quantities $t_s$ and $\epsilon$ as in comparison with the model of deep tunneling. This allows one to derive the attenuation factor $\beta(\epsilon)$, Eq. (7) that, in limiting cases, is reduced to that for McConnel’s, Eq. (35) or barrier’s, Eq. (40) models. It is shown that when analyzing the current through molecular wires, the rectangular barrier model can work only in the case of a strong delocalization of an electron/hole in virtual states of a regular chain. It is shown that the delocalization is conserved only if the condition (13) is satisfied at given $V$ and $N$. Besides, the height of apparent zero-bias rectangular barrier $\Delta E$ has to be much less than the doubled parameter of site-site coupling (cf. Eq (36)). In the case of superexchange tunneling mediated by the virtual chain HOMOs, the zero-bias barrier coincides with the energy gap between the Fermi level and the delocalized HOMO level of a long chain. At nonzero bias voltage, this barrier is transformed into two, Eq. (43) that have to satisfy the condition (44). It is important to note that even though a rigorous correspondence is established between the attenuation factors (cf. Eq. (41)), a more complete description of the wire conductance occurs with use of superexchange model. This is due to the superexchange model allowing one to obtain not only the chain attenuation functions $\Phi(\beta_L, N)$ and $\Phi(\beta_R, N)$, but also the factors that specify properties of the elementary molecular wire with a single bridging unit. In Eq. (27), these basic superexchange factors are presented just before functions $\Phi(\beta_L, N)$ and $\Phi(\beta_R, N)$. In the ohmic regime of the tunneling transmission, these superexchange factors reduce to the $g_{\text{unit}}$, 22
Eq. (32).

The analysis of the nonresonance tunneling conductance in \(-(\text{CH}_2)_N\text{NH}_2\) and \(\text{HOOC}-(\text{CH}_2)_N\text{COOH}\) molecular wires shows that the modified superexchange model is quite appropriate to explain the experimental results. In framework of the model, a formation of the conductance is associated with the virtual participation of the localized HOMOs of terminal units \(\text{H}_2\text{N}\) or \(\text{COOH}\) as well as the delocalized chain HOMOs formed from the localized C-C bonds. In the case of ohmic transmission regime, the attenuation of the conductance with length of \(N\)-alkane chain may be interpreted as the process of electron tunneling through a rectangular barrier. The barrier height and width as well as the effective mass of the tunneling electron are determined via the characteristics of the \(N\)-alkane chain. However, such interpretation is possible only for those \(V\) and \(N\) at which principal inequalities (13) and (36) are satisfied.

Present study shows, that the analysis of current and conductance characteristics with use of the modified superexchange model opens new possibilities of understanding the mechanism of tunneling charge transfer processes in linear molecular junctions.

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