Modified superexchange model for electron tunneling across the terminated molecular wire

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The explicit expressions for a nonresonant tunneling current mediated by the bridging units of the molecular wire embedded between the metallic electrodes, are derived. The specific regimes of the charge transmission controlled by nonresonant and resonant participation of terminal’s energy levels are studied, and the role of energy position of delocalized orbitals in formation of a distant superexchange electrode-electrode coupling is clarified. 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 (LUMO) level. Special attention is paid to derivation of explicit analytic expressions for the tunneling current using different approximations. It is shown that if terminal units play barrier’s role in the charge transmission process, the best correspondence with the observed current-voltage characteristics is achieved with the simplest Gauss and the mean-value explicit forms. This is supported by comparison of the theory with experimental data concerning the current-voltage characteristics of N-alkanedithiol chain.

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I. INTRODUCTION

The use of tunnel and atomic force microscopes to study charge transport processes in molecular compounds, as well as to create molecular structures with specified conductive properties has revealed wide possibilities to utilize these structures as basic elements of molecular electronics, optoelectronics and spintronics [1–15]. Of great importance is the mechanism of formation of the nonresonant interelectrode current in the molecular junction “left electrode - molecular wire - right electrode” (LWR system) where a molecular wire comprises a regular chain anchored to the electrodes through its terminal units. In the nonresonant charge transmission regime, where the MOs of the wire is not occupied by the transferred electrons/holes, the current decays exponentially with an increase in the molecular length [16, 22].

Analysis of I – V characteristics of molecular wires is mainly performed with the simple flat-barrier Simmons model [24]. The model predicts an exponential decrease in the tunneling current where 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 [16, 17, 19] that a choice of the above mentioned fitting parameters, especially \( \Delta E \), depends on the precise voltage region and chain length. Thus, for molecular junctions, the rectangular barrier model does not have the uniform 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 and the overlap between the terminal wire units and the electrodes; this gives rise to formation of a direct distant coupling between the conductive states of the spaced electrodes. The development of the superexchange model originates from pioneer McConnell’s paper [24] on donor-acceptor transfer of an electron through the chain of aromatic free radicals. Later the model was expanded for the analysis of distant donor-acceptor electron transport through various types of organic bridging structures and protein chains (see examples in refs. 25–30). McConnell’s version of superexchange model [24] was used to describe a distant hole transfer through DNA molecules [31, 33], to analyze the I – V characteristics of alkane chains [19, 34], and to study the combined hopping-tunneling electron transmission in the terminated molecular wires [35]. The model explains an exponential drop of a current with the wire length but there is a discrepancy in the attenuation factor predicted by the barrier model. In the superexchange model, the attenuation factor is determined through both the hopping matrix element between the sites of electron/hole localization on the neighboring units of a regular chain and the energy distance of the Fermi level with respect to position of the localized molecular orbitals (MOs) belonging the interior wire unit. This energy distance differs strongly on barrier height \( \Delta E \), which, in the 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 [17, 18].

In this paper, the theory of nonresonant electron/hole superexchange tunneling is modified to derive explicit expressions for the current through a molecular junction. Within this modified model, the expression for attenuation factor \( \beta \) yields two different limits corresponding either the flat-barrier or McConnell’s models. The paper is organized as follows. In Section II, the tight binding model is used to derive a modified form for the nonresonant superexchange tunneling current along with its explicit analytic forms. Results concerning the applicability of the modified superexchange model to description of experimental data in the terminated molecular
wires are presented in Section III. Concluding remarks concentrate the attention on the explicit forms for the tunneling current as well as on corresponding the modified superexchange model to the superexchange model of a deep tunneling and the barrier model.

II. MODEL AND BASIC EQUATIONS

We consider a molecular junction as the quantum LWR system where a linear molecular wire is attached to the left (L) and the right (R) electrodes, Fig. 1.

A. Hamiltonian

The standard form for the Hamiltonian of molecular junction reads

$$H = H_E + H_M + V_{E-M}$$

(1)

where

$$H_E = \sum_{r=L,R} \sum_{k,\sigma} E_{r k \sigma} a_{r k \sigma}^\dagger a_{r k \sigma}$$

(2)

is the Hamiltonian of electrodes with $E_{r k \sigma}$ being the energy of an electron with the $r$th spin projection in the $k$th conduction band state of the $r$th electrode. Operators of creation and annihilation of an electron in the single-electron band state $k$ are denoted through $a_{r k \sigma}^\dagger$ and $a_{r k \sigma}$, respectively. For a molecular Hamiltonian, we use the tight-binding model where the transferred electron can leave the twofold filled energy level of the highest occupied molecular orbital (HOMO)$_n$ or occupy an empty energy level of the lowest unoccupied molecular orbital (LUMO)$_n$ located on the wire unit $n = (0,1,...N,N+1)$. The distance $l_{n,n+1}$ defines the distance between the neighboring units is associated with that of between the sites of main electron localization within the unit. For instance, in the (–CH$_2$–)$_N$ alkane chain, the $l_s$ refers to a distance between the neighboring C–C bonds. With introduction of the creation operator $c_{n\sigma}^+$ and the annihilation operator $c_{n\sigma}$ of an electron on the $n$th wire unit, the molecular Hamiltonian can be represented in the following form

$$H_M = \sum_{n=0}^{N+1} \sum_{\sigma} [E_n c_{n\sigma}^+ c_{n\sigma}$$

$$+(1 - \delta_n,N+1) t_{n,n+1} (c_n^+ c_{n+1\sigma} + c_{n+1\sigma}^+ c_n)$$

(3)

In Eq. (3), $E_n$ is the energy of an electron on the $n$th unit in the presence of the bias voltage $V = (\mu_L - \mu_R) / |e|$ where $|e|$ is the absolute value of electron charge. For definiteness sake, the left electrode is assumed to be grounded so that chemical potential of the $r$th electrode appears as

$$\mu_r = E_F - |e| V \delta_{r,R}, \quad (r = L,R)$$

(4)

with $E_F$ being the energy of electrode’s Fermi level. Introducing the zero bias orbital energy $E_n^{(0)}$, in a linear approximation over the $V$, one obtains

$$E_n = E_n^{(0)} - \eta_n |e| V.$$  

(5)

Here, the Stark shifts are characterized by the factors $\eta_n$ (1) - (6), refer to a typical LWR systems where the termi-

tion across the wire.

B. The wire transmission function

Because about 98% of tunneling current is concentrated in the elastic component, we consider formation of the nonresonant tunneling current associated exclusively with this component. According to the

FIG. 1: Arrangement of units of a linear molecular wire relative to the attached electrodes L and R. Explanation in the text.
Landauer–Büttiker approach [37, 39], the elastic tunneling current is given by expression

$$I = \frac{|e|}{\pi \hbar} \int_{\mu_R}^{\mu_L} dE T(E, V).$$  \hspace{1cm} (7)

Here, \( T(E, V) = \text{tr} \left[ G(E) \hat{\Gamma}^{(L)}(E) \hat{G}^+(E) \hat{\Gamma}^{(R)}(E) \right] \) is the transmission function of a molecular junction where \( G(E) = (E - H_M)^{-1} \) is the Green operator with \( H_M = H \) + \( \Sigma_L(E) + \Sigma_R(E) \) being the modified molecular Hamiltonian. The modification is caused by molecule-electrodes interaction [6] and is included in the self-energy operators \( \Sigma_r(E) \). The latter specify also the width operators \( \Gamma_r(E) = 2 \text{Im} \Sigma_r(E) \). In the lowest order of perturbation in the molecule-electrodes interaction [6], only the diagonal elements of the operator \( \Sigma_r(E) \) are important for specification of the \( \Gamma_r(E) \) and \( \hat{G}(E) \) (see more details in refs. [40, 41]). Therefore, one can set \( \Gamma_r^{(\nu\nu)}(E) \approx \delta_{\nu\nu} \Gamma_r^{(\nu)}(E) \) and \( G_r^{(\nu\nu)}(E) \approx \delta_{\nu\nu} (E - \varepsilon_\nu + (i/2) [\Gamma_r^{(\nu)}(E) + \Gamma_r^{(\nu)}(E)])^{-1} \) where \( \varepsilon_\nu \) is the eigenvalue of the molecular Hamiltonian \( H_M \) and \( \Gamma_r^{(\nu)}(E) = \Gamma_r(E) \delta_{r,L} \left[ U_{\nu0}^2 + \delta_{r,R} U_{\nu N+1} \right] \) is the transmission function of a regular chain. Below, the explicit analytic form for the \( T_{\text{reg}}(E, N) \) is derived for the molecular wires where chain MOs conserve their delocalization.

Delocalization of the transferred electron/hole over the interior wire range occurs at weak bias voltages \( V \) or/and at strong site-site couplings \( t_s \). At \( V = 0 \), the transform-matrix \( \hat{U}^{(\text{reg})} \) is determined by its elements \( U_{\nu n}^{(\text{reg})} = [2/(N + 1)]^{1/2} \sin [\pi \nu/(N + 1)] \). Perturbation caused by the applied bias voltage is concentrated in the values \( \lambda_{\nu \nu'} = -|e| V \sum_{\nu n=1}^N \eta_n U_{\nu n}^{(\text{reg})} U_{\nu' n}^{(\text{reg})} \). Here, the diagonal elements \( \lambda_{\nu \nu'} = -|e| V \eta_\nu \), determine Stark’s shift of the “center of gravity” for electron density distributed over each delocalized MO. Position of the “center of gravity” is defined by the voltage division factor

$$\eta_{\nu \text{c.g.}} = [L + l_1 + l_s(N - 1)/2]/l.$$  \hspace{1cm} (11)

The off-diagonal elements,

$$\lambda_{\nu \nu'} = -|e| V \left( \frac{t_s}{l} \right) \left[ \frac{1 - (-1)^{\nu + \nu'}}{2(N + 1)} \right] \times \left[ \frac{1}{1 - \cos \left( \frac{\nu - \nu'}{N + 1} \right)} \right]$$

\hspace{1cm} (12)

characterize the transitions between the delocalized MOs. Therefore, value

$$\varepsilon_\nu = E_{\nu \text{c.g.}} - 2|t_s| \cos \left( \frac{\pi \nu}{N + 1} \right), \hspace{1cm} (\nu = 1, 2, \ldots N),$$  \hspace{1cm} (13)

can be referred as to energy of the delocalized MO, i.e. \( \text{HOMO}_{\text{reg}}, (\text{HOMO -1})_{\text{reg}}, \ldots \text{ or LUMO}_{\text{reg}}, \text{(LUMO+1)}_{\text{reg}} \ldots \) if only the inequality \( \zeta_{\nu \nu'} \equiv |\lambda_{\nu \nu'}/(\varepsilon_\nu - \varepsilon_{\nu'})| \ll 1 \) is held for \( \nu' \neq \nu \). Dependence of the \( \varepsilon_\nu \) on the bias voltage is comprised in Stark’s shift of the “center of gravity”:

$$E_{\nu \text{c.g.}} = E_{\nu}^{(0)} - |e| V \eta_\nu.$$  \hspace{1cm} (14)

It should be particularly emphasized that the shift is identical for each energy level related to the delocalized MO. The estimations show that among values \( \zeta_{\nu \nu'} \) the greatest are \( \zeta_{\pm 1 \pm 1} \) (even \( N \)), \( \zeta_{\pm 1 \pm 1} \) (odd \( N \)), and
Inequality (15) shows that the energy drop between the function $S(N)$ and the function \( S_{n.s.} \) of the number of chain units \( N \). Thus, the form (12) is valid if
\[
\zeta = |\Delta s/2s| S(N) \ll 1.
\]
Inequality (15) shows that the energy drop between the identical neighboring units,
\[
\Delta s = |e| V(l_s/l),
\]
and the function
\[
S(N) = \left( \frac{1}{N+1} \right)^2 \frac{1 - \cos \left( \frac{\pi}{N+1} \right)}{1 - \cos \left( \frac{3\pi}{N+1} \right)}
\times \left[ \cos \left( \frac{\pi}{N+1} \right) - \cos \left( \frac{2\pi}{N+1} \right) \right]
\]
are those quantities that control an impact of the chain length on applicability of the model of the delocalized MOs even though \( V 
eq 0 \). Note that the function \( S(N) \) depends solely on the number of chain units, Fig. 2 and, thus, is identical for any regular chain.

If inequality (15) is true then substitution the \( E_{\nu} \), Eq. (13) for the Eq. (10) yields (see also [42])
\[
T_{\text{reg}}(\epsilon, N) = \frac{\sin^2 \left[ \beta(\epsilon)/2 \right]}{\sinh^2 \left[ (N+1)\beta(\epsilon)/2 \right]}.
\]
Here,
\[
\beta(\epsilon) = 2\ln \left[ (\epsilon/2|t_s|) + \sqrt{(\epsilon/2|t_s|)^2 - 1} \right]
\]
is the attenuation factor (per chain unit) that characterizes a decrease of the chain transmission function depending on the number of chain units \( N \). In Eq. (19), one has to substitute \( \epsilon = E - E_{c.g.} > 0 \) or \( \epsilon = E_{c.g.} - E > 0 \) if electron tunneling is mediated by the delocalized HOMOs or LUMOs, respectively. Below, for the purpose of definiteness, let us set \( \mu_L \geq \mu_R \), whereby tunneling energy \( E = E_{\text{tun}} \) lies mainly within the voltage window \( \mu_L \geq E \geq \mu_R \). This means that for the HOMO pathway the transmission occurs in the range
\[
\Delta E_{Ls} \geq \epsilon \geq \Delta E_{Rs}.
\]
Here, \( \Delta E_{rs} = \mu_r - E_{c.g.} \) is the energy gap between the Fermi level of the \( r \)th electrode and the energy, Eq. (14) associated with the "center of gravity" for the HOMOs (cf. Fig. 3). The explicit form for the gaps is
\[
\Delta E_{rs} = \Delta E_{s}^{(0)} + |e| V [\eta_{c.g.} \delta_{r,L} - (1 - \eta_{c.g.}) \delta_{r,R}]
\]
where quantity \( \Delta E_{s}^{(0)} = E_F - E_{s}^{(0)} > 0 \) is the main energy gap in an unbiased LWR. Since the energies of delocalized HOMO (LUMO) are arranged below (above) the Fermi levels, then, along with the condition (20), the inequality
\[
\epsilon > 2|t_s|
\]
has to be satisfied at the nonresonant tunneling.

If \( \exp[-(N+1)\beta(\epsilon)] \ll 1 \), then the dependence of the \( T_{\text{reg}}(\epsilon, N) \) on the number of chain units appears in the form
\[
T_{\text{reg}}(\epsilon, N) \simeq (t_s/\epsilon)^2 \]
\[
\times [\delta_{N,1} + (1 - \delta_{N,1})(1 - e^{-2\beta(\epsilon)})^2 e^{-\beta(\epsilon)(N-1)}].
\]
At small site-site coupling \( t_s \), when
\[
(2t_s/\epsilon)^2 \ll 1,
\]
Eq. (20) reduces to
\[
T_{\text{reg}}(\epsilon, N) \simeq (t_s/\epsilon)^{2N}.
\]
This expression reflects a superexchange version of the deep electron tunneling originally proposed by Mc Connell for description of distant donor-acceptor electron transfer mediated by a molecular chain \[24\]. The corresponding attenuation factor reads

$$\beta(\epsilon) \simeq 2 \ln (\epsilon / |t_s|) . \quad (26)$$

This result has also been received in ref. \[43\]. Another limiting case happens when the energy gap between the transmission energies \(\epsilon\) and the energy \(E_H = E_{c-g} + 2|t_s|\), (cf. Fig. [3]), is small in comparison with the \(2|t_s|\), i.e., at

$$\Delta \epsilon = \epsilon - 2|t_s| \ll 2|t_s| . \quad (27)$$

In this case, following the approach that has been earlier derived for description of the donor-acceptor electron transfer through the protein chains \[26\], one can introduce the effective electron mass

$$m^* = \hbar^2 / 2|t_s| l_s^2 . \quad (28)$$

Here, \(l_s\) is the distance between the sites of electron localization on the neighboring units of a regular chain, Fig. [1]. [Compare a standard definition of the effective electron mass, \(1/m^* = (1/\hbar^2)(\partial^2 E / \partial k^2)\), based on expansion of the band energy of an infinite chain, \(E = E(k)\), around the zero wave vector \(k = 0\).] Using definition \[25\] one obtains

$$T_{reg}(\epsilon, N) \simeq (1/4) e^{- (2/\hbar) \sqrt{2 m^* \Delta \epsilon} d} , \quad (29)$$

where \(\Delta \epsilon\) is given by Eq. \[27\] (see also Fig. [3]). The quantity \(d = (N - 1)/l_s\) is the distance between the sites of electron localization on the edge chain units \(n = 1\) and \(n = N\), Fig. [1]. Formal introduction of an effective mass with Eq. \[25\] is independent of the chain length and, thus, is quite suitable for comparison of the superexchange model with a barrier model.

Due to inequality \[27\], expression \[29\] reflects the preresonant regime of tunneling transmission. Such a regime mimics a tunneling through a rectangular barrier of the \(\Delta \epsilon\) height, but it is well to bear in mind that similar interpretation is true at very specific condition determined by Eq. \[27\].

### C. Explicit forms for the current

Our aim is to obtain the distinct expressions that could be acceptable to describe the \(I - V\) characteristics of molecular wires containing regular bridging chains. To this end, let us introduce the current unit \(i_0 \equiv (|e| / \pi \hbar) \times 1 \text{eV} \approx 77, 3 \mu \text{A}\) and rewrite expression \[7\] in the form

$$I = i_0 \int_{-|e|V/2}^{+|e|V/2} d\xi T(\xi, V) . \quad (30)$$

Here, the wire transmission function

$$T(\xi, V) = T_L(\Delta \epsilon_0 - \xi) T_{reg}(\Delta \epsilon_s - \xi, N) T_R(\Delta \epsilon_{N+1} - \xi) \quad (31)$$

appears as the product of partial components

$$T_L(\Delta \epsilon_0 - \xi) = \frac{\Gamma_L}{t_s} \frac{t_s^2}{(\Delta \epsilon_0 - \xi)^2 + \Gamma_L^2 / 4} , \quad (32)$$

$$T_R(\Delta \epsilon_{N+1} - \xi) = \frac{\Gamma_R}{t_s} \frac{t_s^2}{(\Delta \epsilon_{N+1} - \xi)^2 + \Gamma_R^2 / 4} , \quad (33)$$

In the last expression, the \(\beta\) - factor is given by Eq. \[19\] at \(\epsilon = \Delta \epsilon_s - \xi\). If superexchange electron tunneling is mediated by the HOMOs, then a voltage dependence is concentrated in the quantities

$$\Delta \epsilon_0 = \Delta \epsilon_0^{(0)} - (|e|V/2)(1 - 2 \eta_L) , \quad \Delta \epsilon_{N+1} = \Delta \epsilon_{N+1}^{(0)} + (|e|V/2)(1 - 2 \eta_R) , \quad (34)$$

and

$$\Delta \epsilon_s = \Delta \epsilon_s^{(0)} - (|e|V/2)(1 - 2 \eta_{c.g.}) . \quad (35)$$

The transmission functions exhibit a specific voltage behavior dependently on position of the gaps \[34\] and \[35\] relative to energy window

$$-|e|V/2 \leq \xi \leq |e|V/2 . \quad (36)$$

At nonresonant tunneling, the gap \(\Delta \epsilon_s\) remains always outside this window. Moreover, at perfectly symmetric molecular junction, i.e. \(\eta_{c.g.} = 1/2\), it becomes independent of the \(V\) so that \(\Delta \epsilon_s = \Delta \epsilon_0^{(0)}\). As to the rest gaps, they can enter in the energy window either at \(V > 0\) (gap \(\Delta \epsilon_0\)) or at \(V < 0\) (gap \(\Delta \epsilon_{N+1}\)). In a LWR system where \(\Delta \epsilon_0 > |e|V/2\), the \(T(\xi, V)\) increases smoothly with \(\xi\). It is not the case if \(\Delta \epsilon_0 < |e|V/2\) where \(T(\xi, V)\) manifests the presence of a peak at \(\xi = \Delta \epsilon_0\) associated with the partial component \(T_L(\Delta \epsilon_0 - \xi)\). This circumstance allows one to express the current, Eq. \[30\] with three possible explicit forms.

1. Zero Gauss approximation

The simplest form is associated with zero Gauss approximation, when \(T(\xi, V)\) is taken at the middle of the integration limits, i.e. \(\xi = 0\). This yields

$$I \approx I_G = i_0 |e|V T_L(\Delta \epsilon_0) T_{reg}(\Delta \epsilon_s, N) T_R(\Delta \epsilon_{N+1}) , \quad (37)$$

Introducing the current mediated by a single bridging unit,

$$I_G(1) = i_0 |e|V \frac{\Gamma_L \Gamma_R t_s^2}{\Delta \epsilon_0^2[\Delta \epsilon_0^2 + \Gamma_L^2/4][\Delta \epsilon_{N+1}^2 + \Gamma_R^2/4]} , \quad (38)$$
one obtains
\[ I_G = I_G(1) \Phi(\beta_s, N). \]  
(39)

Distant behavior of current \( I_G \) is comprised in the chain attenuation function
\[ \Phi(\beta_s, N) = \frac{\sinh^2 \beta_s}{\sinh^2 [(N + 1)(\beta_s/2)]}. \]  
(40)

that is equil to unit at \( N = 1 \). Corresponding attenuation factor \( \beta_s \) is given by Eq. (19) at \( \epsilon = \Delta \varepsilon_s \). For a chain where \( \exp \left[-(N + 1)\beta_s\right] \ll 1 \), the drop appears as
\[ \Phi(\beta_s, N) \approx (1 - e^{-2\beta_s})^2 e^{-\beta_s(N-1)}. \]  
(41)

2. Mean-value approximation

To obtain the second explicit form for the current, we employ the mean-value (M.V.) approximation, whereby the transmission functions \[ (32) \] and \[ (33) \] are substituted for averaged values \( \bar{T}_{L(R)} \) and \( T_{reg} \), respectively. Thus,
\[ I_{M.V.} = i_0 |e|V \bar{T}_L \bar{T}_{reg}(N) \bar{T}_R \]  
(42)

where
\[ \bar{T}_L = \frac{2t^2_s}{t_s |e|V} \left[ \tan^{-1}\left( \frac{2\Delta E_{L0}}{\Gamma_L} \right) - \tan^{-1}\left( \frac{2\Delta E_{R0}}{\Gamma_L} \right) \right]. \]  
(43)

and
\[ \bar{T}_R = \frac{2t^2_s}{t_s |e|V} \left[ \tan^{-1}\left( \frac{2\Delta E_{L,N+1}}{\Gamma_R} \right) - \tan^{-1}\left( \frac{2\Delta E_{R,N+1}}{\Gamma_R} \right) \right]. \]  
(44)

Averaging is performed within the window \[ (32) \]. Voltage dependence of each function \( \bar{T}_r \), \( (r = L, R) \), is deduced in terminal gaps \( \Delta E_{rn} = \mu_r - E_n \) that read
\[ \Delta E_{r0} = \Delta E_{0}^{(0)} + |e|V[\eta_L \delta_{r,L} - (1 - \eta_L) \delta_{r,R}], \]

\[ \Delta E_{rN+1} = \Delta E_{N+1}^{(0)} - |e|V[\eta_R \delta_{r,R} + (1 - \eta_R) \delta_{r,L}], \]  
(45)

Note the abrupt behavior of \( \bar{T}_r \) in the vicinity of those \( V \) where the gaps \( \Delta E_{rn} \) change their sign. If \( |\Delta E_{rn}| \gg \Gamma_r \), then for estimation of the \( \bar{T}_r \), one can use the approximation
\[ \tan^{-1}\left( \frac{2\Delta E_{rn}}{\Gamma_r} \right) \approx \frac{\pi}{2} \left( \frac{\Delta E_{rn}}{\Gamma_r} - \frac{\Gamma_r}{\pi \Delta E_{rn}} \right). \]  
(46)

The expressions for \( \bar{T}_{reg}(N) \) with \( N = 1 \) and \( N = 2 \) bridging units are respectively
\[ \bar{T}_{reg}(N = 1) = \frac{t_s^2}{\Delta \varepsilon_s^2 - (|e|V/2)^2}; \]  
(47)

\[ \bar{T}_{reg}(N = 2) = \frac{t_s^2}{4 \left\{ (\Delta \varepsilon_s - t_s)^2 - (|e|V/2)^2 \right\} + \frac{1}{|e|V/2} \ln \left[ \frac{\Delta \varepsilon_s^2 - (t_s + |e|V/2)^2}{\Delta \varepsilon_s^2 - (t_s - |e|V/2)^2} \right]. \]  
(48)

When the number of chain units exceeds 2, then with a high degree of precision,
\[ \bar{T}_{reg}(N \geq 3) \approx \frac{t_s}{\Gamma_s} \frac{1}{2N - 1} \times \left[ F(\beta_R)e^{-\beta_R[N-1/2]} - F(\beta_L)e^{-\beta_L[N-1/2]} \right] \]  
(49)

where
\[ F(\beta) = 1 - (2N - 1) \left\{ \frac{3}{2N + 1} e^{-\beta} + \frac{3}{2N + 3} e^{-2\beta} \right\} + \frac{1}{2N + 5} e^{-3\beta}. \]  
(50)

Voltage dependence of quantity \( \bar{T}_{reg}(N \geq 3) \) is concentrated in the corresponding attenuation factors \( \beta_L \) and \( \beta_R \) determined by the Eq. (19) with \( \epsilon = \Delta E_{L(R)s} \), Eq. (35).

At a near-bias voltage, above expressions reduce to
\[ \bar{T}_{reg}(N = 1) \approx \left( \frac{t_s}{\Delta E_s^{(0)}} \right)^2, \]
\[ \bar{T}_{reg}(N = 2) \approx \frac{t_s}{\sqrt{(\Delta E_s^{(0)})^2 - 4t_s^2}} \times \left( \frac{(2t_s)^3}{(\Delta E_s^{(0)})^3 + (\Delta E_s^{(0)})^2 - 4t_s^2} \right)^3; \]  
(51)

and
\[ \bar{T}_{reg}(N \geq 3) \approx \frac{t_s(1 - e^{-\beta_0})^3}{\sqrt{(\Delta E_s^{(0)})^2 - 4t_s^2}} e^{-\beta_0[N-1/2]}. \]  
(52)

Quantity \( \beta_0 \) is the zero-bias attenuation factor for a regular chain. Its general and McConnel's forms are given by respective Eqs. (19) and (26) at \( \epsilon = \Delta E_s^{(0)} \).

If, independently of a bias voltage magnitude, the terminal energies \( E_0 \) and \( E_{N+1} \) remain below the Fermi level of electrodes, then the gaps \[ (32) \] are positive independently of the polarity. This simplifies expressions for \( \bar{T}_r \) yielding
\[ I \approx I_{M.V.} = i_0 |e|V \left[ \frac{\Gamma_L \Gamma_R}{t_s^2} \Delta E_{L0} \Delta E_{L,N+1} \Delta E_{R0} \Delta E_{R,N+1} \right] \times \bar{T}_{reg}(N). \]  
(53)
3. Terminal unit approximation

If at certain bias voltages, the gaps (33) fall within energy window (36), then the terminal transmission functions (32) exhibit a maximum at $\xi = \Delta \varepsilon_{0(N+1)}$. This corresponds to the transmission process at which the tunneling energy $E$ enters in resonance with the respective energies $E_0$ and $E_{N+1}$ of terminal units. The third possible explicit version for the tunneling current supposes that the transmission functions of a regular chain as well as one of the terminal units are extracted from the integral (30) at $\xi = \Delta \varepsilon_0$ or $\xi = \Delta \varepsilon_{N+1}$ depending on the voltage polarity. A similar simplification could be referred to the terminal unit approximation (T.U.) that appears in the form

$$I \approx I_{T.U.} = i_0|e|V [\mathcal{T}_L \mathcal{T}_{reg}(\Delta E_{0s},N)\mathcal{T}_R(\Delta E_{0N+1}) \Theta(V)$$

$$+T_L(-\Delta E_{0N+1})T_{reg}(\Delta E_{N+1s},N)\mathcal{T}_R(\Theta(-V))].$$

(54)

Here, energy gaps

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

and

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

(55)

(56)

coincide with the energy distances between the terminal HOMO or HOMO$_{N+1}$ levels and the position of “center of gravity” of interior wire units, Fig. 5. As to an energy distance $\Delta E_{0N+1} = E_0 - E_{N+1}$ between the terminal levels, it reads

$$\Delta E_{0N+1} = E_{0}^{(0)} - E_{N+1}^{(0)} + |e|V(1 - \eta_l - \eta_R).$$

(57)

[If tunneling is mediated by the LUMOs, one can use Eqs. (54) - (56) with substitution $\Delta E_{ns}$ for $\Delta E_{0n} = E_s - E_n$. Note now that in line with Eqs. (13), (14) and (16) one can set $T_{L(R)} \approx (\pi t_{1(N)}/t_s)|e|V$. This yields

$$I_{T.U.} = i_0 \pi \left\{ \frac{\Gamma_R t_1^2 t_N^2}{\Delta E_{0s}^2[\Delta E_{0s}^2 + (\Gamma_R/2)^2]} \Phi(\beta_{0s},N) \Theta(V)$$

$$- \frac{\Gamma_L t_1^2 t_N^2}{\Delta E_{N+1s}^2[\Delta E_{N+1s}^2 + (\Gamma_L/2)^2]} \Phi(\beta_{N+1s},N) \Theta(-V) \right\}. $$

(58)

The chain attenuation function $\Phi(\beta_{0(N+1)s},N)$ is given by Eq. (19). The expression for the corresponding attenuation factor $\beta_{0(N+1)s}$ follows from Eq. (19) at $\epsilon = \Delta E_{0(N+1)s}$.]

III. RESULTS AND DISCUSSION

The modified model of superexchange tunneling under consideration works in much more soft condition (22) as opposed to the condition (24) valid for the deep tunneling. There are two kinds of basic physical parameters, that specify the model: the transmission gaps and the couplings. Among the gaps, the main are $\Delta E_{Rs}$ and $\Delta E_{Rs}$ (see definition (25) and Fig. 3). Nonresonant superexchange tunneling occurs at the condition (22). Since the transmission energy $\epsilon$ enters in the window (20), then at positive polarity ($\mu_L > \mu_R$) the noted condition reads $\Delta E_{Rs} > 2|t_s|$. When $V$ exceeds a critical voltage

$$V_{RH} = \frac{\Delta E_{s}^{(0)} - 2|t_s|}{|e|(1-\eta_{c.g.})},$$

(59)

the gap $\Delta E_{RH} = \Delta E_{Rs} - 2|t_s|$ becomes negative and, thus, charge transmission occurs at the resonant regime. Physically, $V_{RH}$ is the value at which chemical potential of right electrode $\mu_R$ and the energy $E_{c.g.} = E_{c.g.} + 2|t_s|$ (cf. Fig 3). Along with critical voltage (59), there exists the second critical voltage,

$$V_{R0} = \frac{\Delta E_{0}^{(0)} - |e|(1-\eta_L)}{|e|(1-\eta_L)}.$$

(60)

Expression (60) results from the condition that the gap $\Delta E_{00}$, Eq. (15) vanishes at $V = V_{R0}$. Realization of the precise nonresonant tunneling regime is controlled by relations between above critical voltages. If $V_{R0} > V_{RH}$, then transmission energy $E$ is not able to enter in resonance with energy $E_0$ related to the 0th terminal unit and, thus, this unit plays an inactive (bridging) role in the tunneling. This case is presented in Fig 3. It is not the case if $V_{R0} < V_{RH}$. Now, at $V = V_{R0}$, a specific resonant transmission becomes possible via the localized HOMO of the 0th unit and, thus, the role of this unit becomes active in the nonresonant tunneling through a regular range of the wire. (At the negative polarity, a similar conclusion refers to terminal unit $n = N + 1$).

The theory establishes a correspondence between the pair of basic parameters of the modified superexchange model (zero bias gap $\Delta E_{0}^{(0)}$ and inter-site coupling $t_s$) from one side and the pair of observable values (zero bias attenuation factor $\beta_0$ and critical voltage $V_{RH}$) from another side. Using definition (19) at $\epsilon = \Delta E_{0}^{(0)}$ and expression (59) one arrives to relations

$$\Delta E_{s}^{(0)} = |e|V_{RH} \frac{(1 - \eta_{c.g.}) \cosh (\beta_0/2)}{2 \sinh^2 (\beta_0/4)}$$

(61)

and

$$|t_s| = \frac{|e|V_{RH} \frac{1 - \eta_{c.g.}}{4 \sinh^2 (\beta_0/4)}}$$

(62)

which clarify essentially the analysis of charge transmission processes.

Below, to demonstrate the mechanism of formation of the nonresonant tunneling current in molecular junctions, we consider the simplest case of perfectly symmetric LWR system. In such a system,

$$\Delta E_{N+1}^{(0)} = \Delta E_{0}^{(0)} \equiv \Delta E_s,$$
It tunneling meets difficulties in its application to analyze McConnel’s model. Therefore, the model of deep ratio is in contradiction with condition (24) of applicability, and (66) reduce to ∆s = 2|ts| cos (π/(N + 1)).

A. Bridging role of terminal units

As an example, let us consider a tunneling across the N- alkanedithiol chain anchored to gold contacts via sulfur atoms. To simplify the analysis, we omit non principal details attributed to the differences between the actual bond lengths between backbone atoms and introduce the average bond length ̂n. This means that in accord with the Fig. 1 one has to set lL ≈ l1 ≈ ls ≈ lN ≈ lR ≈ ̂n. Thus,

l ≈ (N + 1)̂n,

ηs = 1/(N + 3).

Due to the property I(−V) = −I(V), it is quite sufficient to consider the I − V characteristics at the positive polarity only. Actual geometric position of a sulfur atom relative to surface gold atoms is unknown a priori. Therefore, electrode-molecule couplings may noticeably differ relative to surface gold atoms is unknown a priori. There-

Thus, electrode’s Fermi level is not exactly known. Therefore, actual geometric position of localized and delocalized orbitals with respect to electrode’s Fermi level is not exactly known. Therefore, we pay a particular attention to a semi-phenomenological estimation of the fitting parameters with the use of relations (61) and (62). For instance, the following correspondence,

∆Es(0) = 2|ts| cos (β0/2),

exists between the zero bias gap and intersite coupling. In the case of deep tunneling, a similar correspondence follows from Eq. (20) and appears in the form

∆Es(0) = |ts| exp (β0/2).

For a typical value β0 = 1 per CH2 unit, relations (65) and (66) reduce to ∆Es(0) ≈ 2.27 ts and ∆Es(0) ≈ 1.65 ts, respectively. [In alkane chains, the coupling ts is positive, so that |ts| = ts]. In both models, ∆Es(0)/ts ~ 1. This ratio is in contradiction with condition (24) of applicability of McConnel’s model. Therefore, the model of deep tunneling meets difficulties in its application to analyze I − V characteristics in N-alkane’s wires.

An approximate estimation of hopping integral ts can be performed using comparison of the HOMO energies of alkane chains [44] with zero bias energies Es(N) = E0. The latter are given by the Eq. (13) at V = 0 and reads

Es(N) = E0 + 2|ts| cos (π/(N + 1)).

As a result, approximation of Es(N) by Eq. (67) is more and less adequate only for the chains with N ≥ 6. In this case, the fitting parameters can be taken as Es(0) ≈ −12.84 eV and ts ≈ 2.97 eV. For short chains, the correlations modify strongly both Es(0) and ts. Thus, the uncertainty exists in specification of coupling ts and, owing to relation (65), in finding the basic zero bias gap ∆Es(0). For instance, the same magnitude for the attenuation factor, β0 = 1 per C-C bond, is obtained at ∆Es(0) = 3.86, 4.99, 7.04 eV if ts = 1.71, 2.23, 3.12 eV, respectively. The uncertainty is removed if one knows critical voltage VRH wherein resonance tunneling is switched on through chain’s delocalized orbitals of a long chain. Therefore, both basic parameters of superexchange model, ∆Es(0) and ts, can be simultaneously estimated with the use of expressions (61) and (62). The experimental results show that in N- alkanedithiols, the ohmic I−V characteristics are held at |V| ≈ 0.1-0.5 V [17, 19–21] and no conductance peaks are observed outside of 1.5 V [19]. Thus, one can suppose that nonresonant tunneling occurs in voltage region V < 1.5 V so that one can set VRH = 1.5 V. Substituting this magnitude and ηc.g. = 1/2 in Eqs. (61) and (62), one can see that value β0 ≈ 1 is obtained at ∆Es(0) ≈ 6.3 eV and ts ≈ 2.78 eV. Value 2.78 eV does not contradict data presented in ref. [44]. Moreover, a direct calculation of tight binding parameters in graphene shows that for neighboring carbon atoms ts ≈ 2.74 eV [45]. For comparison, the magnitudes of Au-Au and Au-S site-couplings are tAu−Au ≈ 2eV and tAu−S ≈ 2.65 eV, respectively [48]. It follows from the recent results of quantum-chemical calculations of orbital energies in oligoethylene glycol chains [13] that in the (CH2CH2O) unit, energy of sulfur lone pair orbitals are positioned about 2.9 eV above energy of the C-C bonding orbital so that we can set E0 = 6.3 eV and E0 = 2.9 eV. Now it becomes possible to specify zero bias energy gaps between the Fermi level and the energy levels of both delocalized HOMOs as well as localized lone pair orbitals. They are ΔEs(0) ≈ 6.3 eV and ΔEs(0) ≈ 3.4 eV, respectively. [Obviously, for the bonding single or triple Au-S orbitals, the ∆Es(0) exceeds 3.4 eV]. At V ≠ 0, the zero bias gaps are transformed into those given by Eqs. (53) and (55).
FIG. 4: Attenuation of the nonresonant tunneling current with an increase of the number of C-C bonds of N - alkanedithiol molecular wire. Due to a monotonic behavior of total and partial transmission functions (cf. the insertions), the mean-value distinct form for the current, Eq. (42) and (68) is in a good correspondence with the numerical data generated by the more exact basic integral form, Eq. (30). For bias voltages $V = 0.1$, 0.5 and 1 V, the applicability of the model is limited by the unit numbers $N < 20$, 9 and $N < 6$, respectively. Calculation parameters are $\Delta E_s = 3.4$ eV, $t_s = 2.50$ eV, $t_s = 2.78$ eV, $\Gamma_s = 0.2$ eV.

duces to the form

$$I_{M.V.} = i_0 |e|V \frac{(\Gamma_s t_s^2/t_s)^2}{\Delta E_s^2 - (|e|V/2)^2(1 - \eta_s)^2} \times T_{reg}(N)$$  

with $T_{reg}(N)$ specified by Eqs. (47) - (49). It is important to notice that at small voltages (up to 0.2 V), the simplest Gauss approximation,

$$I_G = i_0 |e|V \left[ 2\frac{\Gamma_s t_s^2/\Delta E_s(0)}{\Delta E_s^2 - (|e|V/2)^2(1 - \eta_s)^2} \right]^{1/2} \Phi(\beta_0, N),$$

provides a similar magnitude of the current as the mean-value approximation. In Eq. (69), due to the fact that $\Delta \epsilon_s = \Delta E_s(0)$ (cf. definition (35)), one obtains $\beta_s = \beta_0$. Thus, function $\Phi(\beta_0, N)$ is identical to $\Phi(\beta_s, N)$, Eq. (40). As a result, the dependence of attenuation factor $\beta_0$ on the bias voltage vanishes. Moreover, as inequality (27) is satisfied at $\epsilon = \Delta E_s(0)$, one can introduce the effective mass, Eq. (28). This allows one to represent the attenuation factor (per C-C unit) in the form

$$\beta_0 = \frac{2}{\hbar} \sqrt{2 m^* \Delta E_s \pi}$$

where $\Delta E = \Delta E_s(0) - 2t_s \approx 0.74$ eV. For $\pi = 1.3$ Å, the estimation of effective mass yields $m^* \approx 0.8 m_e$, where $m_e$ is the elementary electron mass. Analogously, one can introduce attenuation factors $\beta_L$ and $\beta_R$ that characterize a decrease of $T_{reg}(N)$, Eq. (49). They read

$$\beta_r = \frac{2}{\hbar} \sqrt{2 m^* \Delta E_r \pi}$$

where $\Delta E_r = \Delta E_s - 2t_s$, Fig. 3. Bearing in mind Eq. (49), this yields

$$\Delta E_r = \Delta E + (|e|V/2)(\delta_{r,L} - \delta_{r,R}).$$

Recollect now that the model where superexchange tunneling is mediated by the delocalized MOs works until perturbation caused by a bias voltage, does not destroy the delocalization. Condition (15) shows that at $t_s = 2.78$ eV and $V = 0.1$ V the delocalization is well maintained for $N \leq 20$ whereas at $V = 1.5$ V it is broken at $N > 5$. Fig. 5 shows good correspondence between the theory and the experiment for those alkane chains where, at precise bias voltages, inequality (15) is satisfied. Moreover, the theory is able to explain why the rectangular barrier model is works at low biases but meets difficulties in its application to long chains.

**B. Active role of terminal units**

Let us assume that in the LWR - system, a regular range of the wire binds to electrodes through specific terminal units whose localized HOMOs are not far from the
Fermi levels of the electrodes. It is supposed that at certain voltages, terminal unit’s energy \(E_0\) (at \(V > 0\)) or \(E_{N+1}\) (at \(V < 0\)) can enter in a local resonance with the respective electrode’s Fermi level. This means that at each polarity, there exists two transmission bias regions. At the positive polarity, these regions are \(0 \leq V < V_{R0}\) and \(V_{R0} \leq V < V_{RH}\) where critical voltages are given by the expressions (59) and (60). Fig. 6 illustrates the behavior of nonresonant tunneling current as a function of the number of chain units in both noted regions. The case of a perfectly symmetric molecular junction is considered and the chain superexchange parameters, \(\Delta E_s^0\) and \(t_s\), are chosen identical to those for the alkane chain. This allows one to use the same limitation for the applicability of the theory of superexchange tunneling mediated by the delocalized chain HOMOs. Transmission regime in the region \(V < V_{R0}\) (Fig. 6a) is identical to the regime that controls a nonresonant tunneling with participation of the bridging terminal units (Fig. 4a). This is due to the fact that at \(V = 0.1\) V, terminal energy \(E_0\) is below the \(\mu_R\) and, thus, the peak of terminal transmission function \(T_L(\xi)\), Eq. (32) lies outside the integration region of the basic expression for the current, Eq. (30). Therefore, owing to a monotonic behavior of the total wire transmission function \(T(\xi, V)\) in energy window (36) (see the insertions to Fig. 6a), both the zero Gauss and mean-value approximations give, in fact, the identical results with basic integral expression for a current, Eq. (30) while the edge-unit approximation shows significant deviation. Situation changes essentially in region \(V > V_{R0}\) where the peak of the \(T_L(\xi)\) enters in energy window (36) (cf. the insertions to Figs. 6b,c). Here, the best attenuation of the nonresonant tunneling current with an increase of the number of C-C bonds of \(N\) - alkanedithiol wire attached to the electrodes through active terminal units. The mean-value approximation form is in the best correspondence with the basic integral one. The zero Gauss and terminal-unit explicit forms work well in voltage regions \(V < V_{R0}\) and \(V > V_{R0}\), respectively. The superexchange parameters of the chain are the same as in Fig. 4. The remaining parameters are \(\Delta E_s = 0.4\) eV, \(t_s = 0.74\) eV, \(\Gamma_s = 0.03\) eV. Theory works at \(N \leq 20\) (at \(V = 0.1\) V, (a)), \(N \leq 8\) (at \(V = 0.7\) V, (b)) and \(N \leq 6\) (at \(V = 1.0\) V, (c)).
coincidence with the basic integral expression belongs to the explicit mean-value and terminal-unit forms. For a symmetric LWR - system, the terminal-unit form for the current reads

\[ T_{T.U.} = i_0 \Gamma \frac{(t_s^4/t_s^2)}{\Delta E_s(\Delta E_{s+1} + \Gamma_s^2)} \times \left[ \Phi(\beta_{0s}, N)\Theta(V) - \Phi(\beta_{N+1s}, N)\Theta(-V) \right]. \] (73)

As to Gauss's approximation, it leads to great disagreements with others (in Fig. 6c the Gauss approximation is omitted).

IV. CONCLUSIONS

The main result of this paper is to obtain explicit formulas for analyzing tunnel volt-ampere characteristics of a linear molecular wire. It is assumed that the mixing of localized orbitals of terminal units of wire with delocalized orbitals of the inner range wire (regular chain) is weak. Under such conditions the origin of the inter-electrode superexchange coupling is associated with the overlap of localized electronic wave functions of terminal wire units as with band electronic wave functions of adjacent electrodes, and with delocalized wave functions of a regular chain. The superexchange coupling supposes that wire's orbital states are not populated by the transferred electron/hole and therefore participate in formation of the interelectrode superexchange coupling in a virtual way. The mechanism of superexchange tunneling through localized and delocalized orbitals remains stable only if the condition (15), in which the delocalization of the orbitals of a regular chain is not destroyed by the bias voltage, is satisfied. Received explicit expressions for the nonresonance tunneling current show that under an ohmic regime of charge transmission, it is convenient to analyze the current dependence on the number of chain units using the simplest expression for the current obtained in the zero Gauss approximation, Eq. (69). Applicable to a perfectly symmetric molecular wire the expression for the current reduces to Eq. (69), from which it follows that the factor of exponential attenuation of the current is independent of the applied voltage until delocalization of the orbitals of the regular chain is conserved. A more accurate mean-value approximation makes it possible to analyze volt-ampere characteristics of a molecular wire not only for ohmic regime (where there is a coincidence with the results of the Gauss approximation), but also outside the ohmic regime.

Comparison with experimental data (Fig. 5) shows that for the alkane chain, a good agreement between theoretical and experimental volt-ampere characteristics is carried out at all those chain lengths at which the electric field does not destroy delocalization of orbitals. This result reflects one of the principal differences between the modified superexchange model from the model of a "deep" superexchange tunneling. The latter is based on the overlapping of the wave functions of localized orbitals belonging the terminal and regular wire units. Therefore, in the "deep" tunneling model, the damping factor (20) corresponds to one of the limiting cases of the expression (19) derived in the framework of the modified superexchange model.

Another important result of the modified superexchange model is that when the condition (27) is satisfied, the attenuation factor (19) is transformed into a form used in the phenomenological barrier model (see expressions (70) - (72)). Thus, the modified superexchange model establishes the limit of applicability of the barrier models for the analysis of current-voltage characteristics of the molecular chains, and also connects the parameters of the barrier model (the effective tunneling mass of an electron, height and width of the barrier) with the characteristics of the molecular chain.

The role of terminal units in a distant nonresonance tunneling is determined by the position of the terminal energy levels with respect to the Fermi levels of the adjacent electrodes. If the orbital energies of terminal units are positioned from the Fermi levels about several electron volts, then the terminal units perform a role of the bridging structures, creating the tunnel barriers between the terminal units and the adjacent electrodes. If, however, the energy gaps between the terminal orbital energies and Fermi levels are such that, with the experimentally achievable bias voltages the orbital energies enter in local resonance with the chemical potentials of the electrodes, then terminal units begin to play an active role. This role appears in the enhancement of the distant nonresonant tunneling current by the inclusion of local resonant transmission processes between the electrodes and adjacent terminal units (compare the magnitudes of the current in Figs. 4 and Fig. 6 at V = 0.7 V and V = 1 V).

In general, it can be said that the use of the modified superexchange model has less restrictions on conditions of applicability in comparison with the model of "deep" tunneling or the model of rectangular barrier (which most often used for the analysis of tunneling currents through molecular chains). Explicit formulas of the modified superexchange models have well-defined physical ranges of their applicability and therefore are convenient for clarifying the peculiarities of the formation not only of the tunnel current, but also the conductivity and the resistance in different types of molecular wires.

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