

# Analytical model of molecular wire performance: A comparison of $\pi$ and $\sigma$ electron systems

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The exact closed expression of zero-temperature Ohmic conductance for heterojunctions of the type three-dimensional (3D) metal/molecule/3D metal is obtained. It is specified further in explicit forms to examine electrical transport across self-assembled monolayers of linear molecules with conjugated and saturated carbon-carbon bonds. The focus is at the role of thiol head groups in functioning of polyenes and alkanes as charge transmitters between metal pads. Both tunneling and resonance tunneling across linear hydrocarbons without and with one and two end groups have been studied as a function of the Fermi energy, strength of the metal-molecule coupling, and the molecular length. Regarding the linear-response ballistic conductance of the given type of heterostructures the predictions are: pseudoresonances in the through-molecule transmission spectrum, which are generated by sulfur end groups in the band gap of the carbon chain, and suppression of the resonance and pseudoresonance tunneling by the asymmetry of the electronic structure of the system. These and other results of the paper provide a guidance for the electrical-transport spectroscopy experiments. [S0163-1829(99)05815-4]

## I. INTRODUCTION

Electrical transport in self-assembled monolayers of organic molecules and different kinds of metal-molecular heterostructures is the subject of a considerable experimental<sup>1-17</sup> and theoretical<sup>18-27</sup> interest. The atomic resolution and reproducibility of measurements have been achieved on alkanethiol monolayers on gold.<sup>4,5</sup> A clear distinction between conducting properties of saturated and conjugated linear molecules has been documented experimentally.<sup>11</sup> There are several reports on presumably single-molecule electrical characterization.<sup>13-16,27</sup> These are a few examples of recent impressive progress in the field that now is commonly called "molecular electronics."

A persistent theoretical effort has been aimed at the understanding of the relationship between the electronic structure of the molecules used in molecular-metal heterostructures and their observed properties. However, this ultimate goal is yet far from being achieved.<sup>20-25</sup> Because of the complexity of the system, numerical studies of the metal-molecule junctions, where molecules act as charge transmitters, are usually based on semiempirical methods<sup>20,23-25,27</sup> with much uncertainty left regarding their accuracy. At the one-particle level, there have been few attempts to attack the problem by means of analytical<sup>18,19,26</sup> or "semianalytical"<sup>21,24</sup> modeling. In most of them the electronic structure of molecules spanned between metal pads has been described by the tight-binding Hamiltonian of the chain of one-site one-level subunits coupled via the nearest-neighbor hopping integrals. This model is known to give a single band of one-electron states, that is nothing else but one-dimensional (1D) metal. However, the molecules tried in electrical measurements are inherently either dielectrics or semiconductors, but not metals. Moreover, as it is evidenced experimentally<sup>3-5,11,13-16,27</sup> the Fermi energy of metals used to contact these molecules falls somewhere within the band

gap of the molecular spectrum. Under such conditions, the molecular electron states from both valence and conduction bands are expected to contribute the electron tunneling across molecules connecting two metals. Obviously, the above-mentioned model of molecular chain, though useful, cannot be recognized as a realistic one.

Furthermore, all analytical results on the molecular conductance that have been obtained thus far refer to 1D heterojunctions, where the metal pads are mimicked by semi-infinite tight-binding chains.<sup>18,19,26</sup> Such a simplification is also often used in numerical studies.<sup>21,22,24</sup> The relevance of predictions of 1D models to the real systems has to be questioned at the least. The 3D model of metal pads, which is used here, removes the above-mentioned weakness of previous approaches.

For the reliability and control of electrical contacts in metal-molecular heterojunctions, the organic molecules are usually functionalized by thiol groups from one or both ends of the molecule.<sup>2-7,9,11-15</sup> However, the role of sulfur end groups in determining the electron transmitting abilities of the molecules used (or considered potentially) as molecular wires is recognized but not understood.

Hence, the use of a realistic Hamiltonian to describe molecules spanned between metal pads, an explicit account for the presence of sulfur at the metal-molecule interface, and the use of a 3D model for metals are distinctive advantages of the present analytical modeling of the molecular conductance.

The paper is organized as follows. Section II represents the molecular Hamiltonian that enables us to treat  $\pi$  and  $\sigma$  electron systems on the equal formal basis. In Sec. III we briefly discuss the origins of in-gap states in end-substituted polyenes and alkanes. A closed form of the exact solution of the scattering problem, which determines zero-temperature linear-response conductance of metal-molecular heterojunctions is obtained in Sec. IV. It is specified in an explicit analytical form for the structures, where electrical contact

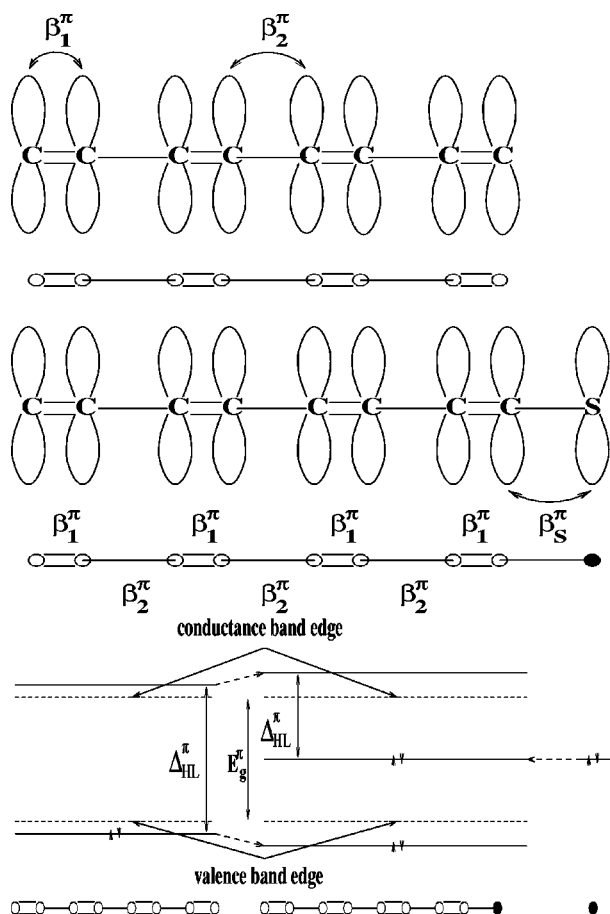


FIG. 1. Schematic representation of the  $\pi$  electronic structure of polyene chains without and with thiol end group and their tight-binding equivalents. In the lower part: the position of HOMO and LUMO levels in unsubstituted (left) and end-substituted (middle) polyenes.

between metals is due to a conjugated or saturated carbon chain with or without thiol end groups. Section V proceeds with a detailed discussion of electron transmitting properties of polyene, alkane, polyenethiol/dithiol, and alkanethiol/dithiol chains. The main findings of the paper are summarized in Sec. VI.

## II. MODEL MOLECULAR HAMILTONIAN

In polyenes  $C_NH_{N+2}$  the nature of the  $\pi$  band gap is still open to question. It can be attributed to the C-C bond alternation (Pierls instability)<sup>28,29</sup> or to electron-electron correlation<sup>30</sup> or, most likely, to both these effects. The bond-length alternation in polyenes is evidenced experimentally.<sup>31,32</sup> Therefore, to the least, two parameters must be used to distinguish the  $\pi$  electron transfer-resonance interaction between the carbons bonded via shorter (double) and longer (single) C-C bonds (see Fig. 1). The corresponding hopping integrals will be denoted as  $\beta_1^\pi = \beta^\pi \exp(\eta^\pi)$  and  $\beta_2^\pi = \beta^\pi \exp(-\eta^\pi)$  ( $\eta^\pi > 0$ ), respectively.

The standard  $\pi$  electron Hamiltonian with the alternating value of the nearest-neighbor resonance integral<sup>28</sup> gives two bands of one-electron states, one valence band ( $v$ ), and one conduction band ( $c$ ). The width of these bands is equal to  $\Delta E_v^\pi = \Delta E_c^\pi = 2|\beta_2^\pi|$ ; the band gap  $E_g^\pi = 2|\beta_1^\pi - \beta_2^\pi|$ . The po-

sition of the valence and conduction bands is symmetrical with respect to the  $\pi$ -electron site energy at carbon atom, the Coulomb integral  $\alpha_C^\pi$ .

The band gap between  $\sigma$  electron bands is known to be considerably larger than the  $\pi$  band gap. This basic distinction in the electronic structure of  $\pi$  and  $\sigma$  systems can be understood in terms similar to those just introduced above. The  $\sigma$  electrons, which are usually described by  $sp^3$  hybrids in saturated compounds and by  $sp^2$  hybrids in conjugated compounds, are strongly localized within the respective covalent bonds. However, the picture of completely localized  $\sigma$  electrons fails to explain charge transfer and other observed properties of  $\sigma$  systems.<sup>33</sup> Therefore, it was suggested that, similar to  $\pi$  electrons,  $\sigma$  electrons are delocalized in polyatomic molecules, i.e., they also can be transferred along the molecule, though such transfer is less efficient than in the case of  $\pi$  conjugation. A simple model that accounts for this effect, ‘‘C approximation,’’ was introduced by Sandorfy<sup>34</sup> (a sophisticated development of this model was given by Hoffmann,<sup>35</sup> and by Pople and Santry<sup>36</sup>). It neglects all interactions between carbon atoms as well as between carbons and hydrogens except those which are responsible for a strong electron transfer between two  $sp^3$  ( $sp^2$ ) hybrids that form covalent bonds between adjacent carbons and a weak electron transfer between two  $sp^3$  ( $sp^2$ ) hybrids of the same carbon directed along covalent bonds with its neighbor carbons. The model of  $\sigma$  systems just cited is shown in Fig. 2, where in analogy with  $\pi$  systems the corresponding resonance integrals are indicated as  $\beta_1^\sigma = \beta^\sigma \exp(\eta^\sigma)$  and  $\beta_2^\sigma = \beta^\sigma \exp(-\eta^\sigma)$ ,  $\eta^\sigma > 0$ . The formal equivalence between the models of  $\pi$  and  $\sigma$  systems noticed by Sandorfy is used here for a comparison of the charge-transfer properties of conjugated and saturated linear hydrocarbons. In this connection, it should be mentioned that in the model of polyenes the number of carbons  $N$  in the chain is equal to twice the number of double bonds ( $N_d$ ), which are characterized by a larger hopping integral  $\beta_1^\pi$  (Fig. 1). For an alkane chain  $C_NH_{2N+2}$  the number of bonds characterized by  $\beta_1^\sigma$  is equal to  $N-1$  (Fig. 2).

The models of  $\pi$  and  $\sigma$  systems represented above can be further extended to account for the end substituents. Conceptually, within the tight-binding formalism one can picture, say, the  $\pi$  electronic structure of end-heterosubstituted polyenes as a result of the interaction between the  $2p_z$  orbital of the end carbon with next to it the heteroatom lone orbital, as shown in Fig. 1. The one-electron states of end-heterosubstituted polyenes (hybridized molecular orbitals) can be found from the stationary Schrödinger equation with the Hamiltonian where the heteroatom-diagonal matrix element and the heteroatom-carbon  $pp\pi$  matrix element differ from the respective matrix elements for the carbon backbone. Namely,

$$\hat{H}^\pi = \alpha_S^\pi (|S_l\rangle\langle S_l| + |S_r\rangle\langle S_r|) + \beta_S^\pi (|S_l\rangle\langle 1_l| + |S_r\rangle\langle N_r| + \text{H.c.}) + \sum_{n=1}^{N_d} \{ \hat{H}_n + \beta_2^\pi [ |(n+1)_l\rangle\langle n_r| + |(n-1)_r\rangle\langle n_l| ] \}, \quad (1)$$

where

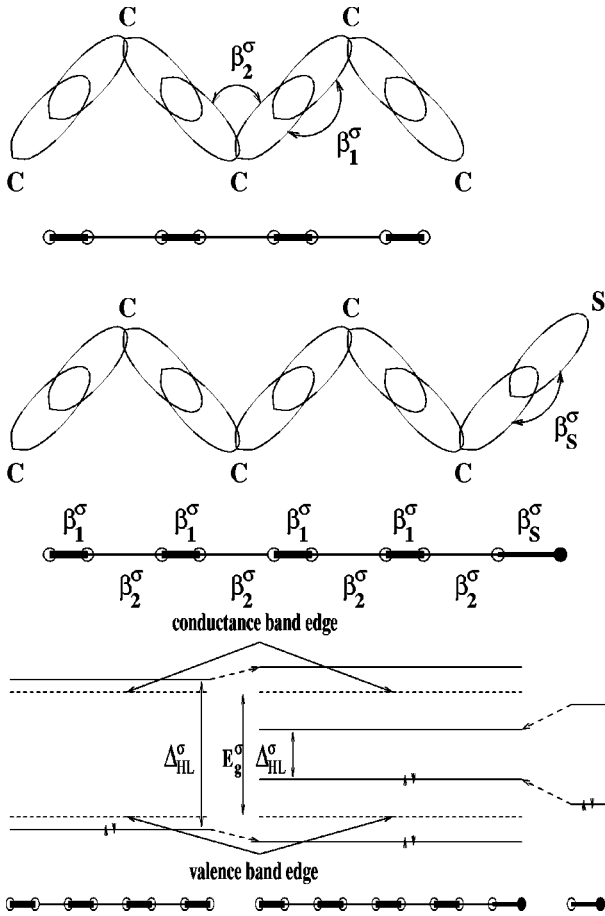


FIG. 2. Schematic representation of the  $\sigma$  electronic structures of alkane chains without and with thiol end group and their tight-binding equivalents (Sandorfy's C approximation). In the lower part: the position of HOMO and LUMO levels in unsubstituted (left) and end-substituted (middle) alkanes, see text.

$$\hat{H}_n = \alpha_C^\pi (|n_l\rangle\langle n_l| + |n_r\rangle\langle n_r|) + \beta_1^\pi (|n_l\rangle\langle n_r| + \text{H.c.}), \quad (2)$$

$|0_r\rangle = |(N+1)_l\rangle = 0$ ,  $\text{ket}|n_{l(r)}\rangle$  has the meaning of the  $2p_z$  atomic orbital of the  $n_{l(r)}$ th C atom, while  $|S_{l(r)}\rangle$  refers to the sulfur orbital,  $\alpha_S^\pi$  and  $\beta_S^\pi$  are the Coulomb energy and resonance integral for sulfur, and  $N_d = N/2$ . Note that with  $|S_l\rangle = |S_r\rangle = 0$  Eqs. (1) and (2) are completely identical to the electronic part of the Su-Schrieffer-Heeger Hamiltonian<sup>29</sup> for polyene with  $N$  carbons and double C-C bonds at the molecule ends. The tight-binding chains with  $N=8$ ,  $|S_l\rangle = |S_r\rangle = 0$ , and  $|S_l\rangle = 0$  are shown in upper and lower parts of Fig. 1, respectively.

As is explained above, if we replace in Eqs. (1) and (2) the superscript  $\pi$  by  $\sigma$ ,  $\hat{H}^\pi \rightarrow \hat{H}^\sigma$ , the Hamiltonian operator  $\hat{H}^\sigma$  can be used to describe saturated hydrocarbons with heterosubstituents at one or both ends of the molecule. Thereby, the number of carbons in the chain is related to  $N_d$  as  $N = N_d + 1$  (see Fig. 2). In what follows, Hamiltonians  $\hat{H}^\pi$  and  $\hat{H}^\sigma$  are used for calculations of ohmic molecular conductance. However, at first it is instructive to have a look at the  $\pi$  ( $\sigma$ ) electronic structure of the molecules under consideration, particularly at the effect of thiol end groups on the energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).

### III. EFFECT OF END GROUPS ON HOMO-LUMO GAP

A likely effect of the attachment of end groups to the carbon chain with alternating C-C bonds is the appearance of in-gap levels.<sup>37–40</sup> As a result the HOMO-LUMO gap of the unsubstituted chain can be substantially modified. In the context of the electron transfer it is of particular importance that in-gap states are preferably localized near the chain ends. Therefore, their contribution into the electron transmitting ability of the molecule is not the same as that of the in-band wavelike states. Below we briefly describe the above-mentioned changes. The aim is to facilitate the understanding of the role of thiol end groups in determining the molecular conductance of  $\pi$  and  $\sigma$  electronic structures. A detailed discussion of the end substitution effects on the  $\pi$  electronic structure of polyenes is given in Refs. 37–40.

#### A. Conjugated systems

The parameters of Hamiltonian (1) for polyenes  $\beta^\pi = -3.757$  eV and  $\eta^\pi = 0.1333$  ( $\beta_1^\pi = -4.33$  eV,  $\beta_2^\pi = -3.29$  eV,  $\beta_2^\pi/\beta_1^\pi = 0.77$ ), were deduced by Kohler<sup>41</sup> from high-resolution spectroscopy experiments. These parameters quantitatively reproduce the values of the  $\pi \rightarrow \pi^*$  transition frequency for unsubstituted and end-substituted polyenes with three to seven double bonds. The model also behaves reasonably in the infinite chain limit giving the band gap  $E_g^\pi = 4|\beta^\pi| \sinh \eta^\pi = 2$  eV. According to these data the  $\pi$  bandwidth,  $\Delta E_{c(v)}^\pi = 2|\beta^\pi| \exp(-\eta^\pi) = 6.58$  eV, is more than three times larger than the band gap; that evidences a strong delocalization of  $\pi$  electron states over the entire molecule.

The S-C bond of the thiol group with the carbon chain is appreciably longer than C-C bonds. Therefore, the hopping integral  $|\beta_S^\pi|$  is substantially smaller than  $|\beta^\pi|$ . The theoretical and experimental estimates of this parameter<sup>42–44</sup> give the value about 0.4–0.7 in units of  $\beta^\pi$ . Furthermore, it is assumed that the attachment of the thiol group to the polyene chain has little effect on its equilibrium geometry. Then, in zero approximation the substitution effect can be considered as a result of weak interaction between the polyene  $\pi$  system and the lone pair of electrons that models sulfur as shown in Fig. 1.

If the energy of the isolated sulfur level falls in the middle of the polyene  $\pi$  band gap, i.e.,  $\alpha_S^\pi = \alpha_C^\pi$ , the  $\pi$  electron spectrum of  $\alpha$  thiopolyene will contain the local level just in the center of the gap. The HOMO and LUMO levels of the unperturbed polyene are shifted equally and in the opposite directions (see Fig. 1). In such a case, the HOMO-LUMO gap of  $\alpha$  thiopolyene is half the unperturbed HOMO-LUMO gap plus the above-mentioned shift, which increases with the increase of  $|\beta_S^\pi|$ .

In the presence of two end groups, the unperturbed HOMO and LUMO levels are shifted additionally. Besides, the two sulfur levels split due to the interaction through the carbon bridge. These two effects nearly cancel each other. This and other predictions of the model regarding the relative position of HOMO and LUMO levels in polyene, polyethiol, and polyenedithiol chains are in a reasonable agreement with modified neglect of differential overlap (MNDO) calculations of the energy of the first singlet  $\pi \rightarrow \pi^*$  transition.

### B. Saturated systems

The respective properties of  $\sigma$  systems are pronouncedly distinctive. According to early estimates the ratio  $\beta_2^\sigma/\beta_1^\sigma$  is around 0.3, with  $\eta^\sigma=0.54$ ,  $\beta_2^\sigma/\beta_1^\sigma=0.3396$ . That is very close to the value 0.34 suggested by Yoshizumi.<sup>45</sup> Setting  $\beta^\sigma$  equal to  $\beta^\pi$  one obtains  $E_g^\sigma=8.515$  eV,  $\Delta E_{c(v)}^\sigma=4.379$  eV,  $\beta_1^\sigma=-6.447$  eV, and  $\beta_2^\sigma=-2.189$  eV. The value of  $|\beta_1^\sigma|$  practically coincides with that given in Ref. 36,  $\beta_1^\sigma=-6.5$  eV. A larger value of  $|\beta_2^\sigma|$  than that found by Pople and Santry,  $\beta_2^\sigma=-1.1$  eV,<sup>36</sup> is taken intentionally to account for C-H  $\sigma$  bonds, which contribute to the electron transfer between two hybridized orbitals attached to the same carbon atom<sup>36</sup> but are ignored in the C approximation. The reported values of the band gap in  $n$  paraffins (about 9 eV) provide an additional support to our choice of the  $\sigma$  system parameters.

The accepted model of  $\sigma$  systems implies that unlike the case of  $\pi$  systems, the attachment of the thiol group to the end of the saturated carbon chains has to be modeled by the interaction  $\beta_2^\sigma$  (and not  $\beta_3^\sigma$ ) between the host chain and a two-level, two-center system, as shown in Fig. 2. When separated from the chain the position of these two levels with respect to the  $\sigma$  band gap is determined by the difference between sulfur and carbon Coulomb integrals  $\alpha_S^\sigma-\alpha_C^\sigma$  and hopping integral  $\beta_{S-C}^\sigma$ . If  $\alpha_S^\sigma=\alpha_C^\sigma$  (such a choice is quite reasonable since the Mulliken electronegativities for carbon and sulfur are equal<sup>46</sup>) the energy difference between the levels of the isolated two-center system is equal to  $2|\beta_{S-C}^\sigma|$ . As a result of the interaction the initial HOMO and LUMO levels of the unsubstituted chain are repelled and become HOMO-1 and LUMO+1 levels in the end-substituted chain. The new HOMO and LUMO levels fall in the band gap. This is in contrast with the  $\pi$  system, where the LUMO level is, most likely, in the conduction band. Another important distinction is that, since the values of  $|\beta_{S-C}^\sigma|$  and  $|\beta_{C-C}^\sigma|$  are considerably smaller than  $|\beta_1^\sigma|$ , the position of HOMO and LUMO levels in  $\alpha$  thiolalkanes is mostly determined by the interaction of sulfur with the end carbon. The contribution from the rest of the carbon chain is comparatively small. The HOMO-LUMO gap is then controlled by  $\beta_{S-C}^\sigma$  and can be roughly estimated as  $2|\beta_{S-C}^\sigma|$ . For the same reason the effect of the chain length quickly saturates with the increase of  $N$ . One can expect, therefore, that one or two thiol groups attached to the ends of not a very short alkane chain ( $N>6$ ) will lead to nearly the same effect on the position of HOMO and LUMO levels.

With  $\alpha_S^\sigma=\alpha_C^\sigma$  and  $\beta_{S-C}^\sigma/\beta_{C-C}^\sigma=0.6$  the values of the HOMO-LUMO gap for unsubstituted and end-substituted alkanes predicted by the C model are in a reasonable quantitative agreement with MNDO calculations of the energy of the first singlet transition in alkanes with  $N=8, 10, 12$  (about 10 eV),  $\alpha$ -thiolalkanes, and  $\alpha,\omega$ -dithiolalkanes (about 4 eV).

Thus, a considerable reduction of the HOMO-LUMO gap due to the attachment of thiol end groups is expected in both conjugated and saturated carbon chains. This effect is relatively stronger in  $\sigma$  systems. For the parameters of Hamiltonians  $\hat{H}^\pi$  and  $\hat{H}^\sigma$  specified above, one and two thiol end groups generate one and two in-gap levels in the  $\pi$  system, but two and four in-gap levels in the  $\sigma$  system. The question

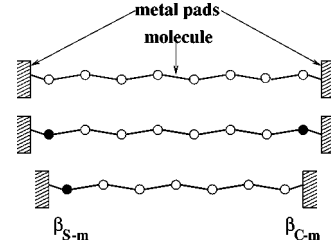


FIG. 3. Connections of molecular chains to the metal: through carbon (unfilled circle, coupling constant  $\beta_{C-m}$ ), through sulfur (filled circle, coupling constant  $\beta_{S-m}$ ).

how the in-gap states affect the molecular resistance is to be answered in subsequent sections.

### IV. EXACT EXPRESSION FOR OHMIC CONDUCTANCE

The role of thiol end groups in determining the conductance/resistance of molecular wires can be exposed most straightforwardly by comparing conducting properties of molecular chains without and with end groups. In what follows, the chain consisting of  $N$  carbons and described by Hamiltonian  $\hat{H}^\pi$  or  $\hat{H}^\sigma$  is supposed to be linked to the metal surfaces either through the carbon or sulfur end atom. Three different connections between the molecule and metal pads are then possible, as shown in Fig. 3: through carbon end atoms, through carbon at one end and sulfur at the other, and through sulfur head group at both ends. These are, of course, simplified but reasonable and experimentally sound models.

The sulfur end group tends to form a chemical bond with, e.g., the Au substrate.<sup>3-7</sup> The electron transfer between carbon and metal can be due to through-space tunneling as, e.g., in scanning tunnel microscope (STM) measurements of the resistance of self-assembled monolayers of alkanethiols on gold.<sup>4,5</sup> Both types of metal-molecule contacts, the chemical with sulfur and physical with carbon, are modeled here by a single-coupling constant denoted below as  $\beta_{S-m}$  and  $\beta_{C-m}$ , respectively. Also, for simplicity both metal surfaces are considered as an abrupt ending of an ideal cubic lattice described in the tight-binding nearest-neighbor approximation. Thus, to mimic the free-electron dynamics in metal pads, only two additional parameters are needed. These are the electron site energy on atoms of the metal, and the energy of electron-resonant transfer between the metal atoms  $L$ . Unlike previous attempts of physical modeling of metal-molecular heterostructures<sup>18,21,22,24,26</sup> we do not treat metal pads as 1D chains.

For the model of metal-molecular heterostructure specified above the zero-temperature linear-response ballistic conductance  $g$  is determined by the transmission coefficient calculated at the Fermi energy,<sup>47,48</sup>  $g=(2e^2/h)T(E_F)$ . There are many equivalent methods for finding  $T(E_F)$ ; see, e.g., Ref. 49 and references therein. The exact solution of the corresponding scattering problem by the Green function method<sup>50</sup> yields

$$T(E_F)=4\frac{A_l^T(E_F)A_r^T(E_F)}{D(E_F)}[G_{l,r}^{OM}(E_F)]^2, \quad (3)$$

where

$$\mathcal{D}(E_F) = |[1 - A_l(E_F)G_{l,l}^{OM}(E_F)][1 - A_r(E_F)G_{r,r}^{OM}(E_F)] - A_l(E_F)A_r(E_F)[G_{l,r}^{OM}(E_F)]^2|^2. \quad (4)$$

In Eqs. (3) and (4),  $G_{\nu,\mu}^{OM}(E_F) = \langle \nu | \hat{G}^{OM}(E_F) | \mu \rangle$ ,  $\nu, \mu = l, r$ , represents the components of dimensionless (multiplied by factor  $\beta = \beta^{\pi(\sigma)}$ ) Green function operator  $\hat{G}^{OM}(E_F) = \beta(E_F \hat{I} - \hat{H}^{OM})^{-1}$ , which are referred to the molecule binding sites:  $l = S_l$  or  $1$  ( $r = S_r$  or  $N$ ) if from the left (right) the chain described by Eq. (1) is terminated by atom S or C;  $\hat{H}^{OM}$  is the Hamiltonian of the molecule spanned between metal electrodes; and  $A_{l(r)}(E_F) = A_r^R(E_F) + iA_l^I(E_F) = [\beta_{l(r)}^2/(\beta L)][G^m(E_F)]$ . In the latter equality,  $\beta_{l(r)}$  takes the value of  $\beta_{S-m}$  or  $\beta_{C-m}$  depending on whether the S or C atom is at the molecule end, and the quantity  $L^{-1}G^m(E_F)$  is the surface-diagonal matrix element of the Green-function operator for a free electron in a semi-infinite cubic lattice.

Expression (3) can be represented in an equivalent form, which makes apparent connections with previous studies of the molecular conductance<sup>14,18,20,27</sup>

$$T = 4 \sum_l^I(E_F) \sum_r^I(E_F) |\langle l | [E_F \hat{I} - \hat{H}^{OM} - \hat{\Sigma}(E_F)]^{-1} | r \rangle|^2, \quad (5)$$

where the self-energy operator  $\hat{\Sigma}(E_F) = \hat{\Sigma}_l(E_F) + \hat{\Sigma}_r(E_F)$  is defined as<sup>49</sup>  $\langle \nu | \hat{\Sigma}_{l(r)}(E_F) | \mu \rangle = \delta_{\nu,\mu} \delta_{\nu,l(r)} \beta A_{l(r)}(E_F)$ . Its real and imaginary parts determine the shift and broadening of molecular levels as a result of the molecule interaction with metal pads. In this connection it is interesting to note that equation  $\mathcal{D}(E) = 0$  with real values of  $A_l$  and  $A_r$  gives the energy eigenvalues of a molecule whose electron on-site energies of the  $l$ th and  $r$ th atoms are perturbed (shifted) by  $A_l$  and  $A_r$ , respectively.

The definition of the transmission coefficient given above requires the knowledge of functions  $G_{\nu,\mu}^{OM}(E_F)$  and  $G^m(E_F)$ . For a typical molecular wire, a linear sequence of monomers in conjugation, the exact analytical expressions of matrix elements  $G_{\nu,\mu}^{OM}(E_F)$  in terms of the monomer Green functions have been found recently.<sup>51</sup> In the particular case of polyene-type chains considered here the necessary matrix elements will be specified below. With regard to the metal Green function it is assumed that the real part of  $G^m(E_F)$  is equal to zero. In the framework of the given model, this means that the conduction band in the metal is half filled. Hence, the quantities  $A_l(E_F)$  and  $A_r(E_F)$  will be treated as effective coupling constants proportional to the local density of states on the metal surface  $-\pi^{-1} \text{Im}[G^m(E_F)]$ ; an assumption that is often used in practical calculations.<sup>18,27</sup> Under such a simplification Eq. (4) takes the form

$$\mathcal{D}(E_F) = [1 + A_l^I A_r^I G_{\Delta}^{OM}(E_F)]^2 + [A_l^I G_{l,l}^{OM}(E_F) - A_r^I G_{r,r}^{OM}(E_F)]^2 + 4A_l^I A_r^I [G_{l,r}^{OM}(E_F)]^2, \quad (6)$$

where

$$G_{\Delta}^{OM}(E_F) = G_{l,l}^{OM}(E_F)G_{r,r}^{OM}(E_F) - [G_{l,r}^{OM}(E_F)]^2. \quad (7)$$

Equations (3) and (6) have clear physical implications. They show, in particular, that the through molecular-wire

transmission without backscattering, i.e., the maximal conductance per one electronic channel  $g = 2e^2/h$  can be attained only in symmetric metal-molecular heterostructures, where  $A_l = A_r$  and  $G_{l,l}^{OM}(E_F) = G_{r,r}^{OM}(E_F)$ . For such structures the condition of resonant transmission reads

$$[G_{l,l}^{OM}(E_F)]^2 - [G_{l,r}^{OM}(E_F)]^2 = -(A_l^I)^{-2}. \quad (8)$$

In the case of asymmetric systems (different metals or/and coupling constants, or/and not centrosymmetric molecules) Eq. (8) cannot be fulfilled simultaneously with equation  $A_l^I G_{l,l}^{OM}(E_F) = A_r^I G_{r,r}^{OM}(E_F)$  at one and the same energy. In STM measurements of the molecular conductance one has to deal with asymmetric rather than symmetric heterojunctions. This is a likely reason for a molecular resistance much larger than  $h/(2e^2) \approx 13k\Omega$  which has been reported so far.<sup>13,14,27</sup> In conventional double-barrier structures the suppressing effect of asymmetry on the resonant tunneling has been discussed by Ricco and Azbel.<sup>52</sup>

For  $A_l^I, A_r^I < 1$  and far from the resonances (and pseudo-resonances, see below) in the electron transmission

$$T^0(E_F) = 4A_l^I A_r^I [G_{l,r}^{OM}(E_F)]^2 \ll 1. \quad (9)$$

The above formula relates the electronic factor in the bridge-mediated donor-acceptor electron transfer rate<sup>53-56</sup> to the molecular-wire conductance.

Now we turn to a more specific discussion of three types of oligomers  $O_M$ , which can be described by Hamiltonian  $\hat{H}^{\pi}$  ( $\hat{H}^{\sigma}$ ) defined in Eqs. (1) and (2). These are an unsubstituted polyene (alkane) chain  $O_M = C_N$  in which case in Eq. (1)  $|S_l\rangle = |S_r\rangle = 0$ ; and end-substituted chains with two ( $O_M = SC_N S$ ) and one ( $O_M = SC_N$ ) thiol end groups. In the latter case, in Eq. (1) either  $|S_l\rangle = 0$  or  $|S_r\rangle = 0$ . Since for the model at hand the formal expressions of the transmission coefficient for the  $\pi$  and  $\sigma$  electronic systems are identical, there is no need in  $\pi/\sigma$  labeling of the corresponding Green functions and coupling constants. However, we retain this labeling for the system parameters.

### A. $C_N$ chains

In this case the expression of  $T(E_F)$  is considerably simplified

$$T(E_F) = 4 \frac{A_C^2}{\mathcal{D}(E_F)} [G_{1,N}^{CN}(E_F)]^2, \quad (10)$$

where  $A_C = A_l^I = A_r^I = [\beta_{C-m}^2/(\beta L)] \text{Im}[G^m(E_F)]$ ,

$$\mathcal{D}(E_F) = [1 + A_C^2 G_{\Delta}^{CN}(E_F)]^2 + 4A_C^2 [G_{1,N}^{CN}(E_F)]^2, \quad (11)$$

and<sup>39</sup>

$$G_{1,N}^{CN}(E_F) = \frac{e^{\eta\pi(\sigma)}}{D_{C_N}(E_F)} \sin \xi, \quad (12)$$

$$G_{1,1}^{CN}(E_F) = G_{N,N}^{CN}(E_F) = \frac{E_F}{D_{C_N}(E_F)} \sin(\xi N_d), \quad (13)$$

$$G_{\Delta}^{C_N}(E_F) = \frac{e^{2\eta^{\pi(\sigma)}}}{\mathcal{D}_{C_N}(E_F)} \{ (E_F^2 - e^{2\eta^{\pi(\sigma)}}) \times \sin(\xi N_d) - \sin[\xi(N_d + 1)] \}, \quad (14)$$

$$\mathcal{D}_{C_N}(E_F) = (E_F^2 - e^{2\eta^{\pi(\sigma)}}) \sin(\xi N_d) - \sin[\xi(N_d + 1)]. \quad (15)$$

In the above equations  $\xi$  has the meaning of the dimensionless wave vector of electron in the molecular chain described by Hamiltonian (1). This quantity is related to the Fermi energy by the dispersion relation<sup>40</sup>

$$2 \cos \xi = E_F^2 - 2 \cosh(2\eta^{\pi(\sigma)}). \quad (16)$$

If  $E_F$  falls in the valence- or conduction-band energy interval,  $\xi$  is real. In the  $\pi(\sigma)$  band gap, see Figs. 1 and 2 [or outside of the  $\pi(\sigma)$  bands] the wave vector acquires complex values  $\xi = \pi \pm i\delta$  (or  $\xi = \pm i\delta$ ) with<sup>55,56</sup>

$$\delta(E_F) = \ln \frac{1}{2} \{ |2 \cosh(2\eta^{\pi(\sigma)}) - E_F^2| + \sqrt{[2 \cosh(2\eta^{\pi(\sigma)}) - E_F^2]^2 - 4} \}. \quad (17)$$

### B. $SC_N S$ chains

Under the assumption that both coupling constants are equal, the transmission spectrum of the  $SC_N S$  chain is described by Eq. (10) with  $A_C$  replaced by  $A_S = [\beta_{S-m}^2 / (\beta L)] \text{Im}[G^m(E_F)]$ , and  $G_{\nu,\mu}^{C_N}(E_F)$  referred to the chain end sites 1 and  $N$  replaced by  $G_{\nu,\mu}^{SC_N S}(E_F)$  referred to the end sites  $S_l$  and  $S_r$ . The Green function of the  $SC_N S$  chain can be readily expressed in terms of the  $C_N$ -chain Green function.<sup>51</sup> For the matrix elements of interest we have

$$G_{S_l, S_l}^{SC_N S}(E_F) = G_{S_r, S_r}^{SC_N S}(E_F) = \frac{E_F - \varepsilon_S^{\pi(\sigma)} - (\gamma_S^{\pi(\sigma)})^2 G_{1,1}^{C_N}(E_F)}{\mathcal{D}_{SC_N S}(E_F)}, \quad (18)$$

$$G_{S_l, S_r}^{SC_N S}(E_F) = \frac{(\gamma_S^{\pi(\sigma)})^2 G_{1,N}^{C_N}(E_F)}{\mathcal{D}_{SC_N S}(E_F)}, \quad (19)$$

$$G_{\Delta}^{SC_N S}(E_F) = \frac{1}{\mathcal{D}_{SC_N S}(E_F)}, \quad (20)$$

$$\mathcal{D}_{SC_N S}(E_F) = [E_F - \varepsilon_S^{\pi(\sigma)} - (\gamma_S^{\pi(\sigma)})^2 G_{1,1}^{C_N}(E_F)]^2 - (\gamma_S^{\pi(\sigma)})^4 [G_{1,N}^{C_N}(E_F)]^2, \quad (21)$$

where  $\beta \varepsilon_S^{\pi(\sigma)} = \alpha_S^{\pi(\sigma)} - \alpha_C^{\pi(\sigma)}$ , and  $\beta \gamma_S^{\pi(\sigma)} = \beta_S^{\pi(\sigma)}$ .

As discussed in Sec. III, the sulfur end groups can produce in-gap states in the  $\pi(\sigma)$  electronic spectrum. Correspondingly, the Green function of the  $SC_N S$  chain has poles in the originally forbidden zone of the  $C_N$  chain. Such poles may or may not give rise to new resonancelike peaks in the transmission spectrum (see below). The full spectrum of  $\pi(\sigma)$  states in the polyene (alkane) dithiol chain is deter-

mined by the solutions to equation  $\mathcal{D}_{SC_N S}(E) = 0$  the explicit form of which has been found earlier.<sup>40</sup>

### C. $SC_N$ chains

In the case of  $SC_N$  chains Eqs. (3), (6), and (7) take the form, respectively,

$$T(E_F) = 4 \frac{A_S A_C}{\mathcal{D}(E_F)} [G_{S_l, N}^{SC_N}(E_F)]^2, \quad (22)$$

$$\mathcal{D}(E_F) = [1 + A_S A_C G_{\Delta}^{SC_N}(E_F)]^2 + [A_S G_{S_l, S_l}^{SC_N}(E_F) - A_C G_{N, N}^{SC_N}(E_F)]^2 + 4 A_S A_C [G_{S_l, N}^{SC_N}(E_F)]^2, \quad (23)$$

and

$$G_{\Delta}^{SC_N}(E_F) = \frac{G_{N, N}^{C_N}(E_F)}{\mathcal{D}_{SC_N}(E_F)}, \quad (24)$$

where

$$G_{S_l, S_l}^{SC_N}(E_F) = \frac{1}{\mathcal{D}_{SC_N}(E_F)}, \quad (25)$$

$$G_{N, N}^{SC_N}(E_F) = \frac{(E_F - \varepsilon_S) G_{N, N}^{C_N}(E_F) - (\gamma_S^{\pi(\sigma)})^2 G_{\Delta}^{C_N}(E_F)}{\mathcal{D}_{SC_N}(E_F)}, \quad (26)$$

$$G_{S_l, N}^{SC_N}(E_F) = \frac{\gamma_S^{\pi(\sigma)} G_{1, N}^{C_N}(E_F)}{\mathcal{D}_{SC_N}(E_F)}, \quad (27)$$

$$\mathcal{D}_{SC_N}(E_F) = E_F - \varepsilon_S^{\pi(\sigma)} - (\gamma_S^{\pi(\sigma)})^2 G_{1,1}^{C_N}(E_F). \quad (28)$$

For  $\pi$  systems, the components of the  $C_N$  Green function above are defined in Eqs. (12), (13), (14), and (15). For  $\sigma$  systems, the equivalent tight-binding carbon chain contains an odd number of sites (see Fig. 2). In such a case the expressions of matrix elements  $G_{\nu,\mu}^{C_N}(E_F)$  for a chain with the odd number of sites change<sup>39</sup>

$$G_{1,1}^{C_N}(E_F) = \frac{e^{-2\eta^{\pi(\sigma)}}}{\mathcal{D}_{C_N}(E_F)} \{ \sin(\xi N_d) + e^{2\eta^{\pi(\sigma)}} \sin[\xi(N_d + 1)] \}, \quad (29)$$

$$G_{N, N}^{C_N}(E_F) = G_{1,1}^{C_N}(E_F, \eta^{\pi(\sigma)} \rightarrow -\eta^{\pi(\sigma)}),$$

$$G_{1, N}^{C_N}(E_F) = \frac{\sin \xi}{\mathcal{D}_{C_N}(E_F)}, \quad (30)$$

$$G_{\Delta}^{C_N}(E_F) = \frac{E_F \sin(\xi N_d)}{\mathcal{D}_{C_N}(E_F)}, \quad \mathcal{D}_{C_N}(E_F) = E_F \sin[\xi(N_d + 1)], \quad (31)$$

whereas dispersion relation (16) remains unchanged.

The exact analytical expressions of  $T(E_F)$  obtained above determine the ohmic conductance of molecular heterojunc-

tions, where two identical metal electrodes are coupled electronically via a chain  $C_N$ , or  $SC_NS$ , or  $SC_N$ . These model expressions enable one to examine the effects of thiol end group(s) on the electron-transmitting abilities of molecular wires. They are also useful for the understanding of the main trends in the molecular conductance dependence on the wire length, respective position of the Fermi energy, strength of molecule-to-metal coupling, etc.

As it has been shown recently<sup>40</sup> with minor modifications, the present model can be extended to cover end groups of arbitrary chemical structure. It is also an advantage of this simple physical model proved to be useful in many other applications<sup>28,33,57</sup> that the electron-transport properties of  $\pi$  and  $\sigma$  systems can be conveniently compared. In the next section we discuss the specific role of sulfur end groups in the functioning of conjugated and saturated carbon chains as charge transmitters.

## V. DISCUSSION

In the electron transmission due to tunneling or resonant tunneling, as discussed in the preceding section, the energy is conserved. For such processes it is usually expected that if the Fermi energy is properly tuned to a molecular state, the electron can be transmitted without any reflection. As it is proved in Eqs. (3) and (6), this can be the case only in the symmetric systems. In principle, the strong asymmetry, e.g., a great difference in coupling constants can completely destroy the resonance structure of the transmission spectrum.

For a symmetric system one would expect the function  $T(E_F)$  to contain as many resonance peaks as the number of molecular electronic states. This expectation is supported by the model of a molecular wire built up of one-level subunits coupled via the nearest-neighbor electron-resonance transfer interaction<sup>18</sup> and similar ones.<sup>24–26</sup> An important point to notice is that in the models cited, all one-electron states are bandlike and thus, current carrying. As it is shown above, see also Refs. 39 and 43, it is likely that the spectrum of end-substituted polyenes and alkanes contains in-gap electronic levels. It will be seen below that these levels do not give rise to resonances in the true sense, but may lead to resonancelike peaks in the transmission spectrum. In such a case the presence of end groups will have a significant effect on the linear-response conductance of molecular wires connecting source and drain electrodes. The regularities of the through molecular-wire transmission, which are common for the  $\pi$  and  $\sigma$  electron systems, will be at focus in the forthcoming illustrative examples.

To visualize the end effects on the linear-response conductance, the dependence  $T(E_F)$  was calculated for two values of metal-to-molecule coupling constant  $A_{C(S)} = 0.1$  and 0.6. Dashed and solid lines in Figs. 4–6 correspond to the smaller and larger values of the coupling constants, respectively. The choice of  $A_C$  and  $A_S$  has been made on the basis of a simple consideration that suggests that  $\beta_{C-m} < L, \beta$ , and  $\beta_{S-m} \sim L < \beta$ , so that  $A_C < A_S$ . Both values  $A_{C(S)}$  seem to be equally reasonable at this level of the description and both are used just for comparison of end effects on the performance of conjugated and saturated carbon chains as molecular wires.

The calculations of  $T(E_F)$  for the  $\pi$  systems were per-

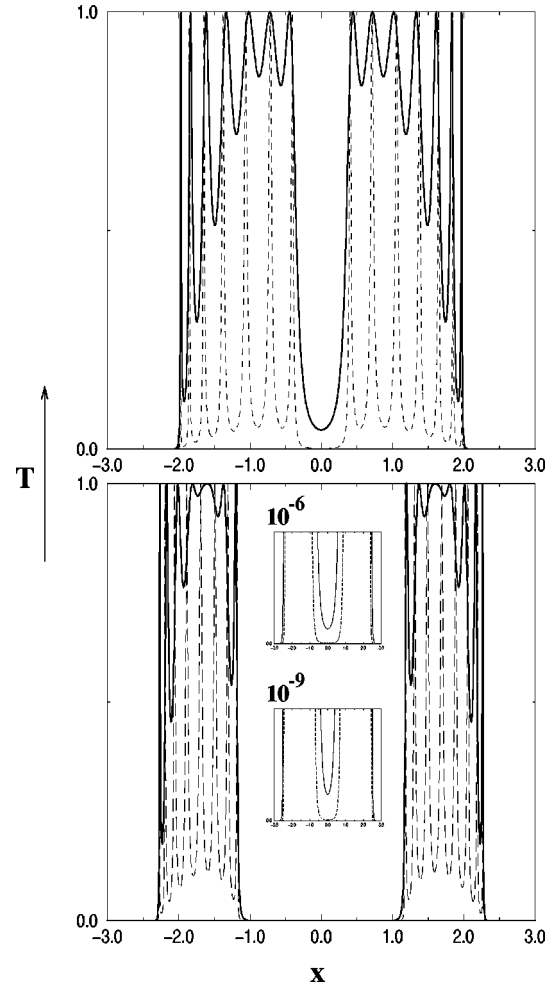


FIG. 4. Transmission spectrum of unsubstituted polyene (up) and alkane (down) chains with the number of carbons  $N=14$  and  $N=9$ , respectively. Dashed curves ( $A_C=0.1$ ) and solid curves ( $A_C=0.6$ ) are calculated from Eq. (10) with  $\eta^\pi=0.1333$ ,  $\eta^\sigma=0.54$ . Insets show the in-gap energy dependence of  $T$ ,  $x=(E_F - \alpha^\sigma)/\beta$ , for alkane chains with  $N=9$  (up) and  $N=12$  (down). For this and next figures the minimal and maximal values of  $T$  in the band gap are indicated in Table I.

formed with  $N=14$  for the  $C_N$  chain, and  $N=12$  for  $SC_N$  and  $SC_NS$  chains. In the case of  $\sigma$  systems we used  $N=9$  for an unsubstituted chain, and  $N=7$  for saturated chains with sulfur end groups. A larger value of  $N=12$  has also been used for calculating dependences  $T(E_F)$  represented in lower inserts of Figs. 4–6. In all figures the Fermi energy is scaled to  $\beta$  and is counted from the value of the Coulomb integral  $\alpha^\pi$  or  $\alpha^\sigma$  depending on the reference to the  $\pi$  or  $\sigma$  system.

### A. Conductance of $C_N$ -based junctions

Figure 4 displays the transmission spectrum determined by Eq. (10) for conjugated (up) and saturated (down)  $C_N$  chains. One can see that within the  $\pi$  and  $\sigma$  bands the resonance structure of the transmission coefficient as a function of energy is similar qualitatively and quantitatively. As expected the increase of the strength of metal-to-molecule coupling leads to the shift and broadening of resonances, very much similarly in both systems. It appears therefore, that with an appropriate choice of the metal work function plac-

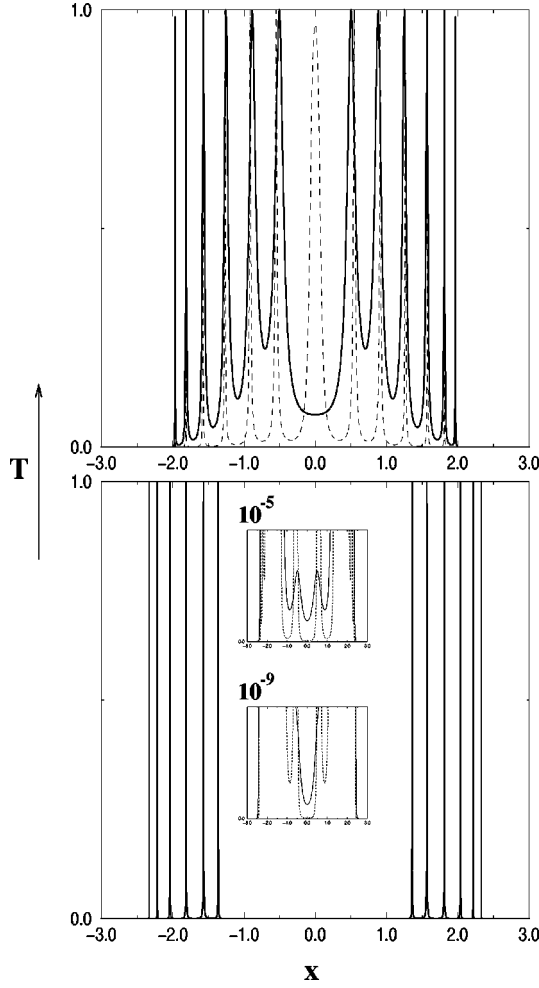


FIG. 5. Transmission spectrum of substituted polyene (up) and alkane (down) chains with two thiol end-groups and the number of carbons  $N=12$  and  $N=7$ , respectively;  $A_S=0.1$  (dashed curves),  $A_S=0.6$  (solid curves),  $\varepsilon_S^{\pi(\sigma)}=0$ ,  $\gamma_S^{\pi(\sigma)}=0.6$ , and same values of  $\eta^{\pi(\sigma)}$  as in Fig. 4. Insets show the in-gap energy dependence of  $T$  for substituted alkane chains with  $N=7$  (up) and  $N=12$  (down).

ing the Fermi energy in the  $\sigma$  band, the saturated carbon chain can perform the electron-transmitting function as efficiently as conjugated molecules. Hence, the efficiencies of electron pathways through  $\pi$  and  $\sigma$  systems in bridge-mediated donor-acceptor electron transfer, which are often opposed to each other,<sup>58,59</sup> seem to be a matter of the position of donor and acceptor levels rather than the domination of  $\pi$  or  $\sigma$  electronic structure of the bridge. The latter just determines the electron group velocity, which is, of course, much larger in  $\pi$ -conjugated systems.

In the band-gap energy interval, however, the electron tunneling capabilities of  $\pi$  and  $\sigma$  states differ dramatically (see Fig. 4 and Table I). In accordance with Eqs. (9) and (12) except the values of  $E_F$  close to the band edges and/or small  $N$ , the behavior of the transmission coefficient as a function of energy is described by the dependence

$$T^0(E_F) = 16A_C^2 \frac{e^{2\eta^{\pi(\sigma)}} \sinh^2[\delta(E_F)]}{(e^{\delta(E_F)} - e^{-2\eta^{\pi(\sigma)}})^2} e^{-\delta(E_F) l^{\pi(\sigma)}}, \quad (32)$$

where  $l^\pi=N$ ,  $l^\sigma=2(N-1)$  for  $\pi$  and  $\sigma$  systems, respectively, and  $\delta(E_F)$  is defined in Eq. (17). To recall, the equi-

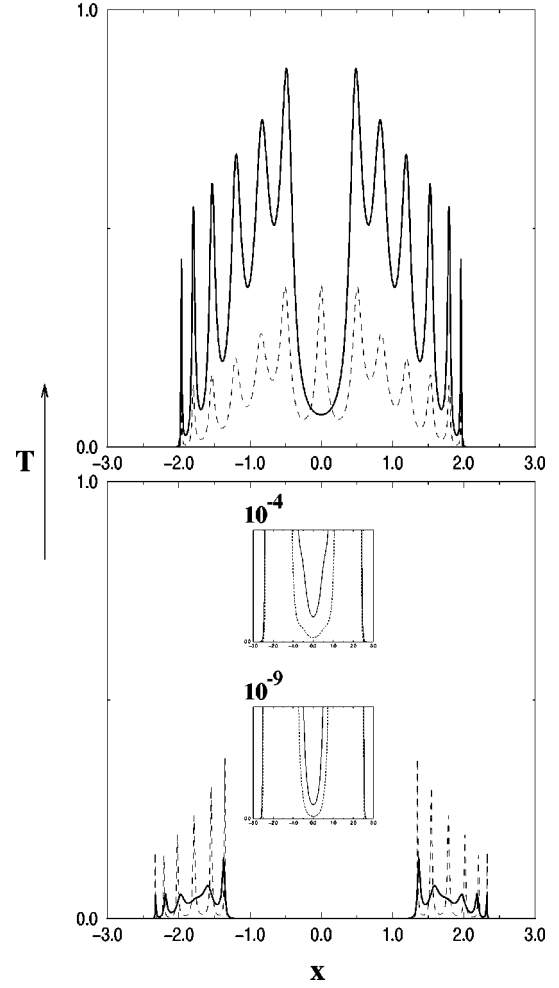


FIG. 6. Transmission spectrum of substituted polyene (up) and alkane (down) chains with one thiol end-group;  $A_S=0.6$ ,  $A_C=0.1$  (dashed curves),  $A_C=0.6$  (solid curves), and same values of other parameters as in Fig. 5.

librium geometry of the unsubstituted conjugated  $C_N$  chain is supposed to be aromatic, i.e., with double C-C bonds at the ends. This precludes the appearance of in-gap states.<sup>39)</sup> The minimal value of  $T(E_F)$   $T_{min}$  corresponds to the middle of the gap, where function  $\delta(E_F)$  reaches its maximum. The maximal tunneling constant  $\delta_m^{\pi(\sigma)}$  defined as  $T_{min}=T(E_F=\alpha^{\pi(\sigma)}) \sim e^{-\delta_m^{\pi(\sigma)} N}$  is then equal to  $\delta_m^\pi=2\eta^\pi$  and  $\delta_m^\sigma=4\eta^\sigma$ . For the parameters of  $\pi$  and  $\sigma$  systems used in these calculations see Sec. III,  $\delta_m^\pi=0.267$  and  $\delta_m^\sigma=2.16$ . Importantly, the value of  $T_{min}$  is given by Eq. (32) at  $E_F=\alpha^{\pi(\sigma)}$  for  $C_N$  chains but not for  $SC_N S$  and  $SC_N$  chains. The exponential dependence (32) with the same definition of the tunneling decay constant, but with another preexponential factor, remains valid for  $SC_N S$  and  $SC_N$  chains. The corresponding preexponential factors can easily be obtained from the expressions of  $G_{S_l, S_r}^{SC_N S}(E_F)$  and  $G_{S_l, N}^{SC_N}(E_F)$  found above.

Joachim and Vinuesa<sup>24</sup> have reported roughly twice smaller values of  $\delta_m^\pi=0.12$  and  $0.13$  deduced from numerical calculations for two different models of the polyene-to-metal connection. (We emphasize that *the value of the tunneling constant is entirely determined by the electronic*



TABLE I. Values of the transmission coefficient at its minima  $T_{min}$  and maxima  $T_{max}$  within the band gap (in parentheses, the values of  $T_{min}$  that are not in the midgap). These are obtained for  $\eta^\pi=0.1333$ ,  $\eta^\sigma=0.54$ ,  $\varepsilon_S^{\pi(\sigma)}=0$ , and  $\beta_S^{\pi(\sigma)}=0.6$ . Each pair of lines corresponds to the smaller (upper row) and larger value of the coupling constant; for  $SC_N$   $A_S=0.6$ , and  $A_C=0.1$  and  $A_C=0.6$  in upper and lower rows, respectively.

$\pi$ system			$\sigma$ system		
$C_{14}$	$SC_{12}$	$SC_{12}S$	$C_9$	$SC_7$	$SC_7S$
$1.2 \times 10^{-3}$	$(6.3 \times 10^{-2})$		$T_{min}$		
$4.4 \times 10^{-2}$	$7.4 \times 10^{-2}$	$7.4 \times 10^{-2}$	$3.7 \times 10^{-9}$	$1.5 \times 10^{-6}$	$2.5 \times 10^{-7} (2.7 \times 10^{-6})$
			$1.3 \times 10^{-7}$	$8.7 \times 10^{-6}$	$8.9 \times 10^{-6} (2.0 \times 10^{-5})$
			$T_{max}$		
	$3.7 \times 10^{-1}$	$9.7 \times 10^{-1}$			$1.1 \times 10^{-3}$
					$3.2 \times 10^{-5}$
$C_{22}$	$SC_{20}$	$SC_{20}S$	$C_{12}$	$SC_{12}$	$SC_{12}S$
$1.5 \times 10^{-4}$	$(1.4 \times 10^{-2})$	$(6.1 \times 10^{-3})$	$T_{min}$		
$5.3 \times 10^{-3}$	$9.0 \times 10^{-3}$	$9.0 \times 10^{-3}$	$5.6 \times 10^{-12}$	$3.1 \times 10^{-11}$	$5.0 \times 10^{-12} (1.8 \times 10^{-9})$
			$2.0 \times 10^{-10}$	$1.9 \times 10^{-10}$	$1.8 \times 10^{-10}$
			$T_{max}$		
	$5.3 \times 10^{-2}$	$2.8 \times 10^{-1}$			$8.3 \times 10^{-8}$

structure of the molecular wire, so that it is independent of end effects.) On the other hand, the dimensional tunneling constant  $\kappa_m^\pi = a^{-1} \delta_m^\pi$ , where  $a$  is the average distance between carbons in polyene along the molecular axis, inferred from the same (extended-Hückel-molecular-orbital-method) calculations by Magoga and Joachim<sup>25</sup> is  $\kappa_m^\pi = 0.187 \text{ \AA}^{-1}$ . The latter value is much closer to ours obtained with  $a = 1.235 \text{ \AA}$ ,<sup>60</sup>  $\kappa_m^\pi = 0.216 \text{ \AA}^{-1}$ , but it is in an obvious conflict with the values of  $\delta_m^\pi$  ( $\gamma$  in their notations) found by Joachim and Vinuesa. Our result also agrees well with the general trend for the electron transfer mediated by conjugated bridges  $\kappa_m^\pi = 0.2 \text{ \AA}^{-1}$ .<sup>53</sup>

To notice, for a number of conjugated oligomers such as oligomers of polyparaphenylene, polythiophene, and many others, the value of the tunneling constant in comparison with  $\kappa_m^\pi$  is within a factor less than 2.<sup>61</sup> For instance, with the same parameters as used above we have obtained for phenylethylenes  $\kappa_m^\pi = 0.306 \text{ \AA}^{-1}$ .<sup>51,61</sup> This value practically coincides with  $\kappa_m^\pi = 0.305 \text{ \AA}^{-1}$  (Larsson *et al.*<sup>23</sup>) and it is reasonably close to  $\kappa_m^\pi = 0.278 \text{ \AA}^{-1}$  (Magoga and Joachim<sup>25</sup>), both inferred from numerical calculations.

Setting the length of C-C bond in the alkane chain equal to  $1.47 \text{ \AA}$ , and  $\angle CCC = 120^\circ$  we obtain  $\kappa_m^\sigma = a^{-1} \delta_m^\sigma = 1.7 \text{ \AA}^{-1}$ . This seems to be the largest estimate reported thus far for saturated bridges:  $0.6-1 \text{ \AA}^{-1}$ ,<sup>53</sup> and  $0.6-1.5 \text{ \AA}^{-1}$ .<sup>59</sup> The reason for a larger value of the tunneling constant obtained here might be a larger distance in energy of the tunneling electron from the valence and conduction band states. This energy must be scaled in units of the characteristic electron-resonance transfer energy, as has been shown in the pioneering McConnell work.<sup>62</sup> Unfortunately, although of crucial importance, the corresponding data are almost never stated clearly. That makes impossible a sensible comparison of numerical results reported with the predictions of this analytical model. It has to be also emphasized that smaller values of the tunneling constant make it difficult to obtain agreement with the established values of the band gap and hopping integrals for alkanes that were used in our estimate of  $\delta_m^\sigma$ .

We stress that a huge difference in the tunneling probabilities across the conjugated and saturated carbon chains refers only to the case of  $E_F$  in the forbidden zone. For the Fermi energies close to the midgap only the  $\pi$  systems can work as efficient electron transmitters for distances as long as tens of  $\text{\AA}$ . For instance, due to a small value of tunneling constant  $\delta_m^\pi$  (for a number of other conjugated oligomers the values of  $\delta_m^\pi$  are found in Ref. 61), the tunneling probability across the midgap of conjugated  $C_N$  chain with  $N=14$  is  $\approx 0.044$  for  $A_C=0.6$ . In the case of a shorter chain  $N=12$ , with saturated C-C bonds such probability is more than eight orders smaller (see Table I).

According to Eqs. (17) and (32) the tunneling capability of linear molecules can be evaluated if both the band gap and the width of the bands nearest to the gap are known. The handbook formula for the tunneling probability through a rectangular barrier of thickness  $l$ ,  $T(E_F) \sim \exp\{-[2\hbar^{-1}\sqrt{2m^*(V-|E_F|)}]l\}$ , contains two adjustable parameters, the barrier height  $V$  and the electron effective mass  $m^*$ , and therefore, it can be quite successfully used for such a purpose.<sup>56</sup> However, a frequent reference to the band gap associated with the barrier height as the only factor determining the through-molecule tunneling probability<sup>5,20</sup> is unjustified and can be misleading.

It is worth noting that due to a much greater difference in values of the transmission coefficient for the in-gap and in-band energies, the  $\sigma$  electron systems seem to be potentially much better switchers than the  $\pi$  electron systems. Certain conjugated oligomers can also act as nearly ideal switchers but in very narrow energy intervals.<sup>56</sup> In contrast, saturated carbon chains are open/closed for transmitting electrons in comparatively wide energy intervals.

### B. Conductance of $SC_N$ S- and $SC_N$ -based junctions

The presence of thiol end groups used to contact organic molecules to Au substrate<sup>2-7,9,11-15,27</sup> affect the molecular transmission spectrum both qualitatively and quantitatively. Thereby, the symmetry of the substitution appears to play a significant role.

Figure 5 exhibits the effect of thiol end groups on the transmission spectrum of centrosymmetric metal-molecular heterostructures. Calculated for the same values of the coupling constant as in Fig. 4, the dependences  $T(E_F)$  show, in the present case, a much sharper resonance structure, particularly, in the transmission spectrum of the  $\sigma$  system. This observation can be easily explained by noting that the coupling of the carbon chain to the metal is now mediated by an additional weak interaction  $\beta_S$ .

In addition to the above-mentioned distinction between end-substituted and unsubstituted carbon chains, the transmission spectra of  $SC_NS$  chains contain a qualitatively new feature, resonancelike peaks within the band-gap energy interval. For the smaller value of coupling constant such peaks are present in the upper and lower curves, which represent the  $\pi$  and  $\sigma$  systems, respectively. The central peak in the upper figure, as well as the peaks shown in inserts, have, in fact, two maxima, which are not resolved in the given scale. The appearance of these maxima is nothing else but a signature of the in-gap states generated by the end groups as discussed in Sec. III.

For the larger coupling constant there are no in-gap peaks in the transmission spectrum of the conjugated and saturated  $SC_NS$  chains with  $N=12$  (solid curves in upper figure and in lower insert of Fig. 5). But they are present in the shorter  $\sigma$  system (see upper inset of the same figure). Such a behavior of in-gap resonancelike peaks is distinctive from in-band (true) resonances. The latter can be shifted and broadened/narrowed by changing the length of the chain and/or the coupling constant but they do not disappear if the system parameters are changed. In contrast, the peaks of the transmission associated with in-gap states of the chain disappear with the increase of coupling constant and/or chain length. To distinguish the in-gap resonancelike features from the true resonances in the transmission spectrum the use of the term ‘‘pseudoresonance’’ seems to be relevant to the case.

From Eq. (3) the conditions of the appearance and disappearance of pseudoresonances in terms of analytical relations between the system parameters can be derived. (Physically similar conditions of the existence of in-gap states in end-substituted polyenes have been obtained earlier.<sup>39,40</sup>) Such an analysis, however, goes far beyond the scope of this paper and will be reported elsewhere. Here, we only mention that the disappearance of pseudoresonances with the increase of the chain length (as illustrated by solid lines in insets of Fig. 5) has to be expected. Indeed, these features are genetically connected with the in-gap local states whose overlap decreases with the increase of  $N$  and hence, eventually, this leads to the pseudoresonance disappearance.

In the case of the  $SC_N$  chain represented in Fig. 6, a new factor comes into play, the system asymmetry. As was pointed out above, this factor suppresses the resonance structure of dependence  $T(E_F)$ . In particular, the effect reveals itself as a substantial reduction of the central peak intensity in the  $\pi$ -system transmission spectrum and ‘‘killing’’ pseudoresonances in the  $\sigma$ -system transmission spectrum. The latter effect can be accompanied by a considerable increase of the value of  $T$  in the midgap. For smaller coupling constants, the increase of  $T_{min}$  is an order of magnitude or even greater (see Table I). Also, all the resonances are lowered and broadened in comparison with the transmission spectrum

of the  $SC_NS$  chain. It is noticeable that the system asymmetry has a stronger effect on tunneling in the case of the  $\sigma$  electronic structure.

The quantitative difference in the probabilities of tunneling through  $C_N$ ,  $SC_NS$ , and  $SC_N$  chains is illustrated by data represented in Table I. These data show that the presence of thiol end groups leads to a substantial increase of the tunneling probability. For instance, with the values of the transmission coefficient in the midgap obtained for dodecanethiol molecule ( $C_{12}H_{26}S$ ) one obtains the molecular resistance about  $4 \cdot 10^5 \text{ G}\Omega$  for  $A_C=0.1$ , and  $6 \cdot 10^4 \text{ G}\Omega$  for  $A_C=0.6$ . The resistance of (shorter) carbon chains without thiol group  $C_{12}$  is larger (see Table I).

Schönenberger *et al.*<sup>5</sup> observed the atomic resolution in the scanning tunneling microscope images of dodecanethiol monolayers on gold at a resistance that is two orders lower,  $500 \text{ G}\Omega$ . This seemingly large divergence with the experiment can easily be removed by assuming a somewhat stronger metal-molecule coupling. Another reason for the divergence can be that the actual position of the Fermi energy is shifted towards either of the bands. This factor can be particularly important in the case of stronger coupling (see insets in Fig. 6). Finally, a partial penetration of the STM tip into the monolayer that diminishes the actual tunneling length also cannot be excluded. With the present uncertainty in the knowledge of the above-mentioned factors, the estimate obtained seems to be satisfactory. In any case, it is evident that the electron transmitting properties of molecular wires cannot be understood without taking into account the role of end groups used for their attachment to metal.

Another important message of the above analysis is that in the presence of end groups, even in the band gap interval the electric transport in molecular wires cannot be adequately described in terms of the electron transfer-rate calculations, that is on the basis of approximation (9). The correct estimate of the conductance of metal-molecular heterojunctions requires the use of Eq. (3) or (5), or their analogues.

The values of molecule-to-metal coupling constants and the position of the equilibrium Fermi energy with respect to the molecular levels considered here as the model parameters are shown to lead to diverse estimates of the molecular ohmic conductance. Thus, the relationship between the molecular electronic structure and its electron-transfer capability can properly be understood only under the condition that the factors mentioned are known. In practice, this is quite a formidable task. A semiphenomenological estimate of these and other factors, which may affect the through-molecule electron transmission, such as electron coupling to the molecular vibrations, charging effects, and the applied voltage drop division across the heterojunction have been recently discussed by Tian *et al.*<sup>27</sup>

## VI. CONCLUSION

The results of the paper have been singled out throughout the discussion. Here we just emphasize the main points of the paper.

An analytically tractable model of metal-molecular heterojunctions is formulated on the basis of the established molecular Hamiltonians that reproduce essentials of the electronic structure of real conjugated and saturated molecules.

For this purpose the well known<sup>33</sup> but rarely used C approximation, which was introduced by Sandorfy<sup>34</sup> to describe linear hydrocarbons with saturated C-C bonds, has been exploited. The model is formally equivalent to the standard Su-Schrieffer-Heeger-Hückel-type Hamiltonian for a carbon chain with alternating C-C bonds, and hence enables a straightforward comparison of the electron transport abilities of  $\pi$  and  $\sigma$  electron systems. It has been also extended to examine the role of thiol end groups in the electronic conduction of conjugated and saturated linear molecules.

As opposed to quite a recent statement that the solution of the scattering problem, which determines the linear-response ballistic conductance of the system 1D metal/polyene/1D metal, cannot be obtained analytically,<sup>24</sup> such a solution has been found for the system 3D metal/molecule/3D metal, where the molecule has been specified as a polyene/alkane chain with and without end groups but, in fact, it can be an arbitrary conjugated oligomer described in the tight-binding nearest-neighbor approximation. For the given type of metal-molecular heterostructures, the exact explicit dependence of the ohmic conductance on the Fermi energy, strength of the metal-molecule coupling, and other characteristic parameters of the system is presented for the first time.

In view of a great complexity of the system to be treated even at the semiempirical level, not to mention accurate *ab initio* calculations, it is especially attractive that the dependence of heterojunction conductance on the Fermi energy is accessible within seconds. Hence, the role of the main factors that govern electrical current across molecular wires can be quickly evaluated in detail. The fully analytical analysis can also be readily performed. A deep insight into the underlying physics of the molecular conductance is thus gained. The mathematically rigorous results derived in the present consideration suggest a firm basis for a test of the accuracy of numerical models, which otherwise can be compared only with, probably, better but also approximate calculations and so on. In particular, computational “discoveries” such as, e.g., the possibility of negative values of the tunneling constant and its dependence on the end effects,<sup>24</sup> have been disproved.

The exact expression of the linear-response conductance (3) represents the central result of this paper. It describes the

ohmic tunnel current and the resonant transmission of electrons through the molecule spanned between metal electrodes. Similar to conventional double-barrier structures (DBS) with identical barriers, in symmetric molecular heterojunctions the transmission coefficient reaches its maximal possible value at certain energies. Equation (8) relates the energies of the resonance transmission to the molecular electronic structure and the strength of the molecule-to-metal coupling. The explicit form of this equation is given for the case of metal electrodes connected by a polyene/alkane chain with and without sulfur head groups. This equation is also applicable for other molecules. It establishes an analytical relationship between the number and position of resonances in the transmission spectrum and the molecular electronic structure whenever the Green function of the latter is known. The exact explicit expression of the Green function has recently been found for a number of conjugated oligomers of the type  $M-M-\dots M$  and  $M_1-M_2-M_1-\dots-M_2-M_1$ .<sup>51</sup>

While there is an apparent similarity between the resonance tunneling in symmetric molecular heterojunctions discussed here, and which is well known in DBS, see, e.g., in Refs. 49 and 63, there is no analogy in DBS to the pseudo-resonance tunneling. The physical origin of the phenomenon is shown to be connected with the in-gap states that are preferably localized near the ends of the molecule. The role of these states (associated with the sulfur end groups) in determining the molecular wire conductance has been proven to be of significance and discussed in many details in the particular context of metal-molecular heterojunctions based on thiol- and dithiopolyenes, and thiol- and dithiolalkanes. In asymmetric metal-molecular heterojunctions, the suppression of the resonances and pseudo-resonances by the system asymmetry has been predicted.

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