

Green function of conjugated oligomers: the exact analytical solution with an application to the molecular conductance

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Abstract

The exact analytical expression of the Green function of oligomers $M-M-\dots-M$ and $M_1-M_2-M_1-\dots-M_2-M_1$, where M , M_1 , and M_2 are monomers of arbitrary π electronic structure described by the tight-binding Hamiltonian, is derived for the first time. This result makes possible to address relevant spectral and electron transport properties of large linear molecules on the basis of realistic exactly solvable models. The power of the approach is exemplified by obtaining a number of explicit relations between the transport related quantities, in particular, through molecule tunneling decay constant, and the molecular electronic structure for a wide family of potential molecular wires. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Green function; Conjugated oligomers; Molecular conductance

1. Introduction

Much attention has recently been paid to the application of Green function method in calculations of spectroscopic and electron transport related quantities for polyatomic molecules [1–12]. For instance, the Green function technique has been extensively used for a perturbative description of bridge-mediated electron transfer between donor and acceptor [2], as well as for obtaining model exact analytical expressions of the electronic factor in the intramolecular electron-transfer rate [4] and linear-response molecular conductance [5]. However, mostly, the Green function approach has been used for the development of efficient schemes to compute the electronic factor [3,7–9] and molecular conductance [10–12].

The reported analytical treatments of long-distance electron transfer/transmission across molecules have been essentially restricted to the molecular chain modeled by a linear sequence of one-site one level subunits coupled via a constant nearest-neighbor hopping integral [1,4,5]. This model is known to give a single band of one electron states, that is nothing else but 1-D metal. On the other hand, the molecules tried in electrical measurements as

molecular wires [11–15] are inherently either dielectrics or semiconductors but not metals. Moreover, as it is evidenced experimentally, 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. For these reasons, the above mentioned model of molecular chain, though useful, is not adequate to reproduce the performance of real molecular wires. To take into account the molecular band gap, a more sophisticated model has recently been proposed [16] that refers to CH- and SN-chains. A far more reach variety of linear organic molecules can be approached analytically by the Green function technique.

To describe the electrical properties of metal–molecular–metal heterojunctions, the Green function of the molecule spanned between metal electrodes has to be found with account to the molecule–metal interaction [5,10,17]. The perturbation of molecular levels can be included by a proper definition of the self-energy operator. An important point to note is that the effect of molecule–metal interaction is taken into account not in a perturbative manner but exactly [17]. Thereby, the problem to solve is finding the resolvent of a complex (because of adding self energy to the molecular Hamiltonian) hermitian matrix of the same order as the matrix of non-perturbed molecular

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Hamiltonian. By further redefinition of the self energy the electron–phonon interaction as well as charging effects can also be included into consideration, at least approximately [12,17]. In all the applications mentioned (and many others, e.g., in the chemisorption theory [18]), the knowledge of unperturbed molecular Green function greatly facilitates calculations. The formal reason for the simplification is that provided the molecular Green function is known the problem of inverting the matrix of the order determined by the basis set of the molecule is reduced to the order determined by the number of atoms interacting with the metal. The latter is usually much less than the total number of atoms in the molecule. For instance, it can be taken as small as two [5,10–12].

Furthermore, the unperturbed Green function matrix elements referred to the end binding sites of the molecule (which connects/bridges electrodes in metal–molecular heterojunctions or donor and acceptor in donor–bridge–acceptor systems) determine the through-molecule tunneling rate [4,5,19,20]. In particular, from the Green function expression the tunneling decay constant can be deduced. By using the latter quantity, the charge transmitting abilities of different molecules can be compared with a clear reference to the molecular electronic structure. Otherwise, the estimate of the tunneling decay constant, not to mention a detailed analysis of molecular conductance, requires a large volume of computational work. In view of the system complexity, this kind of calculations is usually performed on the basis of approximate semi-empirical methods [10,21,22] with much uncertainty left with regard to their accuracy. It makes therefore advisable a comparison with rigorous exact results which can be obtained in the framework of simplified but realistic tight-binding models.

The conjugated oligomers are considered to be the most likely candidates to act as molecular wires [10–15]. They possess a number of other potentials for molecular electronics [23]. The relevant Green functions are known only for the simplest finite linear sequences of repeating units, such as simple tight-binding chains with constant [24] and alternating [6,25] value of hopping integral. The purpose of this paper is to give the exact analytical solution of the Green function problem for two broad families of conjugated oligomers covered by structural formulas M–M–...–M (oligomers of polyene, polythiophene, polyparaphenylene, etc.) and M₁–M₂–M₁–...–M₂–M₁ (oligomers of polyaniline, polyparaphenylenevinylene, etc.). As an illustration, the solution obtained is then used to describe the molecular tunnel conductance of metal–molecular heterojunctions.

2. Green function of M-oligomers

In one-electron approximation, the π electron Hamiltonian of linear conjugated molecules M–M–...–M (M-

oligomers), where M denotes a monomer of arbitrary chemical structure can be represented as

$$\hat{H}^{\text{OM}} = \sum_{n=1}^N \hat{H}_n^{\text{M}} + \hat{V}, \quad (1)$$

where \hat{H}_n^{M} is the Hamiltonian operator of the n th monomer, N is the number of monomers in the molecule, and \hat{V} is the energy operator of inter-monomer interaction,

$$\hat{V} = \beta_{\text{int}} \sum_{n=1}^N \left[|(n+1)_{\alpha_1}\rangle \langle n_{\alpha_r}| + |(n-1)_{\alpha_r}\rangle \langle n_{\alpha_1}| \right]. \quad (2)$$

In Eq. (2), $|0_{\alpha_r}\rangle = |(N+1)_{\alpha_1}\rangle = 0$, the ket $|n_{\alpha}\rangle$ has its usual meaning of the π orbital of the α th atom in the n th monomer, β_{int} is the energy of resonance π electron transfer (hopping integral) between the neighboring sites (denoted as α_r and α_1 , respectively) of the n th and $(n+1)$ th monomers. Since the further derivation is not restricted to the particular form of operator \hat{H}_n^{M} its form will not be specified at this stage.

To find the Green function for the Hamiltonian defined in Eqs. (1) and (2), it is convenient to use the Dyson equation

$$\hat{G}^{\text{OM}}(E) = \hat{G}^{\text{O}}(E) + \hat{G}^{\text{O}}(E) \hat{V} \hat{G}^{\text{OM}}(E), \quad (3)$$

which in the matrix representation reads (henceforth, the indication of explicit dependence of the Green function on electron energy E is omitted)

$$G_{n_{\nu}, m_{\mu}}^{\text{OM}} = \delta_{n,m} G_{\nu, \mu}^{\text{M}} + \beta_{\text{int}} \left[G_{\nu, \alpha_1}^{\text{M}} G_{(n-1)_{\alpha_r}, m_{\mu}}^{\text{OM}} + G_{\nu, \alpha_r}^{\text{M}} G_{(n+1)_{\alpha_1}, m_{\mu}}^{\text{OM}} \right], \quad (4)$$

$$G_{0_{\alpha_r}, m_{\mu}}^{\text{OM}} = 0, \quad G_{(N+1)_{\alpha_1}, m_{\mu}}^{\text{OM}} = 0, \quad (5)$$

where $G_{\nu, \mu}^{\text{M}} = \langle \nu | (E\hat{I} - \hat{H}_n^{\text{M}})^{-1} | \mu \rangle$ is the matrix element of the monomer Green function operator; indexes n and m take all possible values from 1 to N , while indexes ν and μ identify the location of atoms within the monomer. In particular, setting in Eq. (4) $\nu = \alpha_1$, α_r , and $\mu = \alpha_1$, α_r , we obtain four equations for the matrix elements referring to the binding sites of monomers.

Finding the solutions to Eqs. (4) and (5) is substantially simplified by using the dispersion relation between the energy E and quasi-impulse ξ of electron in M-oligomers that has the form [26]

$$2\cos \xi = f(E), \quad f(E) = \left(\beta_{\text{int}} G_{\alpha_1, \alpha_r}^{\text{M}} \right)^{-1} (1 - G_{\Delta}^{\text{M}}), \quad (6)$$

where

$$G_{\Delta}^{\text{M}} \equiv \beta_{\text{int}}^2 \left[G_{\alpha_1, \alpha_1}^{\text{M}} G_{\alpha_r, \alpha_r}^{\text{M}} - \left(G_{\alpha_1, \alpha_r}^{\text{M}} \right)^2 \right]. \quad (7)$$

Representing the Green function matrix elements appeared in Eq. (4) for $\nu = \alpha_1$, α_r , and $\mu = \alpha_r$, as a superposition of incident and reflected waves and exploiting Eq.

(6), after some lengthy but straightforward algebra we arrive at the following expressions of $G_{n_{\alpha_1}, m_{\alpha_1}}^{O_M}$ and $G_{n_{\alpha_r}, m_{\alpha_r}}^{O_M}$

$$G_{n_{\nu}, m_{\alpha_1}}^{O_M} = \left(\beta_{\text{int}}^2 G_{\alpha_1, \alpha_r}^M D_M \sin \xi \right)^{-1} \times \begin{cases} \beta_{\text{int}} G_{\alpha_1, \alpha_1}^M \sin \xi (N+1-m) \\ \quad \times [\sin \xi (n-1) - \beta_{\text{int}} G_{\alpha_1, \alpha_r}^M \sin \xi (n-2)], & \text{if } \nu = \alpha_1, \\ \beta_{\text{int}}^2 G_{\alpha_1, \alpha_1}^M G_{\alpha_r, \alpha_r}^M \sin \xi (N+1-m) \sin \xi n, & \text{if } \nu = \alpha_r, \\ n < m, \\ \beta_{\text{int}} G_{\alpha_1, \alpha_1}^M [\sin \xi (m-1) \\ \quad - \beta_{\text{int}} G_{\alpha_1, \alpha_r}^M \sin \xi (m-2)] \sin \xi (N+1-n), & \text{if } \nu = \alpha_1, \\ [\sin \xi (m-1) - \beta_{\text{int}} G_{\alpha_1, \alpha_r}^M \sin \xi (m-2)] \\ \quad \times [\sin \xi (N-n) - \beta_{\text{int}} G_{\alpha_1, \alpha_r}^M \sin \xi (N-1-n)], & \text{if } \nu = \alpha_r, \\ n \geq m. \end{cases} \quad (8)$$

The expressions of matrix elements $G_{n_{\alpha_r}, m_{\alpha_r}}^{O_M}$ can be found in a similar way,

$$G_{n_{\alpha_r}, m_{\alpha_r}}^{O_M} = \begin{cases} \frac{G_{\alpha_r, \alpha_r}^M \sin \xi (N-n) - \beta_{\text{int}} G_{\alpha_1, \alpha_r}^M \sin \xi (N-n-1)}{\beta_{\text{int}} G_{\alpha_1, \alpha_r}^M \sin \xi} \\ \quad \times \frac{\sin \xi m}{D_M}, & \text{if } n > m, \\ n \leftrightarrow m, & \text{if } n \leq m. \end{cases} \quad (9)$$

In Eqs. (8) and (9), a new notation is introduced

$$D_M = \sin \xi N - \beta_{\text{int}} G_{\alpha_1, \alpha_r}^M \sin \xi (N-1). \quad (10)$$

If the electron energy satisfies Eq. (6), the solutions to equation $D_M = 0$ determine the eigenvalues of quasi-impulse ξ in M-oligomers [26].

The equations represented above give the exact explicit expression for any component of the M-oligomer Green function operator \hat{G}^{O_M} in terms of the matrix elements of monomer Green function operator \hat{G}^M . In Section 3, they are used to derive the Green function for another wide class of linear organic compounds with a somewhat more complex structure, $M_1-M_2-M_1-\dots-M_2-M_1$, called here for brevity (M_1-M_2) -oligomers.

3. Green function of (M_1-M_2) -oligomers

The (M_1-M_2) -oligomers can be considered as M-oligomers, $M = M_1-M_2$, where at the chain end M is substituted by M_1 . The molecular Hamiltonian is now conveniently represented as

$$\hat{H}^{O_{M_1-M_2}} = \sum_{n=1}^{N-1} \hat{H}_n^{M_1-M_2} + \hat{V} + \beta_{\text{int}} |(N-1)_{\alpha_r}\rangle \langle N_{\alpha_1}| + \hat{H}_N^{M_1}, \quad (11)$$

where operator \hat{V} is defined in Eq. (2) with N replaced by $N-1$; all the other notations have already been introduced.

The matrix elements of operator $\hat{G}^{O_{M_1-M_2}}(E) = (E\hat{I} - \hat{H}^{O_{M_1-M_2}})^{-1}$ can be found from

$$G_{n_{\nu}, m_{\mu}}^{O_{M_1-M_2}} = G_{n_{\nu}, m_{\mu}}^0 + \beta_{\text{int}} \left[G_{n_{\nu}, (N-1)_{\alpha_r}}^0 G_{N_{\alpha_1}, m_{\mu}}^{O_{M_1-M_2}} + G_{n_{\nu}, N_{\alpha_1}}^0 G_{(N-1)_{\alpha_r}, m_{\mu}}^{O_{M_1-M_2}} \right], \quad (12)$$

where $G_{n_{\nu}, m_{\mu}}^0 = \langle n_{\nu} | (\hat{I}E - \hat{H}^{O_M} - \hat{H}_N^{M_1})^{-1} | m_{\mu} \rangle$ and operator \hat{H}^{O_M} is given by Eq. (1) with N replaced by $N-1$, and M by M_1-M_2 .

For the Green function matrix elements referred to the end atoms of the (M_1-M_2) -oligomer, it follows from Eq. (12)

$$G_{1_{\alpha_1}, N_{\alpha_r}}^{O_{M_1-M_2}} = \beta_{\text{int}} \frac{G_{\alpha_1, \alpha_r}^{M_1} G_{1_{\alpha_1}, (N-1)_{\alpha_r}}^{O_M}}{1 - \beta_{\text{int}}^2 G_{\alpha_1, \alpha_1}^{M_1} G_{(N-1)_{\alpha_r}, (N-1)_{\alpha_r}}^{O_M}},$$

$$G_{1_{\alpha_1}, 1_{\alpha_1}}^{O_{M_1-M_2}} = \frac{G_{1_{\alpha_1}, 1_{\alpha_1}}^{O_M} - G_{\alpha_1, \alpha_1}^{M_1} G_{\Delta}^{O_M}}{1 - \beta_{\text{int}}^2 G_{\alpha_1, \alpha_1}^{M_1} G_{(N-1)_{\alpha_r}, (N-1)_{\alpha_r}}^{O_M}},$$

$$G_{N_{\alpha_r}, N_{\alpha_r}}^{O_{M_1-M_2}} = \frac{G_{\alpha_r, \alpha_r}^{M_1} - G_{(N-1)_{\alpha_r}, (N-1)_{\alpha_r}}^{O_M} G_{\Delta}^{M_1}}{1 - \beta_{\text{int}}^2 G_{\alpha_1, \alpha_1}^{M_1} G_{(N-1)_{\alpha_r}, (N-1)_{\alpha_r}}^{O_M}} \quad (13)$$

where G_{Δ}^M is defined in Eq. (7), and

$$G_{\Delta}^{O_M} = \beta_{\text{int}}^2 \left[G_{1_{\alpha_1}, 1_{\alpha_1}}^{O_M} G_{(N-1)_{\alpha_r}, (N-1)_{\alpha_r}}^{O_M} - \left(G_{1_{\alpha_1}, (N-1)_{\alpha_r}}^{O_M} \right)^2 \right]$$

$$= \frac{\sin \xi (N-1) - \beta_{\text{int}} G_{\alpha_1, \alpha_r}^M \sin \xi N}{\sin \xi (N-1) - \beta_{\text{int}} G_{\alpha_1, \alpha_r}^M \sin \xi (N-2)}. \quad (14)$$

The dispersion relation for (M_1-M_2) -oligomers has the form of Eq. (6), where M is of course a compound monomer M_1-M_2 . It may be instrumental to use the Green function components of monomers M_1 and M_2 which have a more simple structure than those of the compound monomer. For this purpose one can use the following expressions for the matrix elements of operator $\hat{G}^{M_1-M_2}$

$$G_{\alpha_1, \alpha_r}^{M_1-M_2} = \beta_{\text{int}} \frac{G_{\alpha_1, \alpha_r}^{M_2} G_{\alpha_1, \alpha_r}^{M_1}}{1 - \beta_{\text{int}}^2 G_{\alpha_1, \alpha_1}^{M_2} G_{\alpha_r, \alpha_r}^{M_1}},$$

$$G_{\alpha_1, \alpha_1}^{M_1-M_2} = \frac{G_{\alpha_1, \alpha_1}^{M_1} - G_{\alpha_1, \alpha_1}^{M_2} G_{\Delta}^{M_1}}{1 - \beta_{\text{int}}^2 G_{\alpha_1, \alpha_1}^{M_2} G_{\alpha_r, \alpha_r}^{M_1}},$$

$$G_{\alpha_r, \alpha_r}^{M_1-M_2} = \frac{G_{\alpha_r, \alpha_r}^{M_2} - G_{\alpha_r, \alpha_r}^{M_1} G_{\Delta}^{M_2}}{1 - \beta_{\text{int}}^2 G_{\alpha_1, \alpha_1}^{M_2} G_{\alpha_r, \alpha_r}^{M_1}}. \quad (15)$$

Expressed in terms of the matrix elements of Green function operators \hat{G}^{M_1} and \hat{G}^{M_2} function $f(E)$ in the dispersion relation for (M_1-M_2) -oligomers takes the form

$$f(E) = \frac{1}{\beta_{\text{int}}^2 G_{\alpha_1, \alpha_r}^{M_1} G_{\alpha_1, \alpha_r}^{M_2}} \left[1 - \beta_{\text{int}}^2 \left(G_{\alpha_1, \alpha_1}^{M_1} G_{\alpha_r, \alpha_r}^{M_2} + G_{\alpha_r, \alpha_r}^{M_1} G_{\alpha_1, \alpha_1}^{M_2} \right) + G_{\Delta}^{M_1} G_{\Delta}^{M_2} \right]. \quad (16)$$

For applications, it is also useful to have the expressions of the components of (M_1-M_2) -oligomer Green function as functionals of ξ and matrix elements of operators \hat{G}^{M_1} and \hat{G}^{M_2} . Making use of Eqs. (8), (9) and (14) in Eq. (13), and taking into account the relations (15) and (16) one can find

$$G_{1_{\alpha_1}, N_{\alpha_r}}^{O_{M_1-M_2}} = \frac{G_{\alpha_1, \alpha_r}^{M_1} G_{\alpha_1, \alpha_r}^{M_2} \sin \xi}{G_{\alpha_1, \alpha_r}^{M_2} \sin \xi N + G_{\alpha_1, \alpha_r}^{M_1} G_{\Delta}^{M_2} \sin \xi (N-1)}, \quad (17)$$

$$G_{1_{\alpha_1}, 1_{\alpha_1}}^{O_{M_1-M_2}} = \frac{G_{\alpha_1, \alpha_1}^{M_1} G_{\alpha_1, \alpha_1}^{M_2} \sin \xi N + G_{\alpha_1, \alpha_1}^{M_1} G_{\alpha_1, \alpha_1}^{M_2} \sin \xi (N-1)}{G_{\alpha_1, \alpha_r}^{M_2} \sin \xi N + G_{\alpha_1, \alpha_r}^{M_1} G_{\Delta}^{M_2} \sin \xi (N-1)}, \quad (18)$$

$$G_{N_{\alpha_r}, N_{\alpha_r}}^{O_{M_1-M_2}} = \frac{G_{\alpha_r, \alpha_r}^{M_1} G_{\alpha_r, \alpha_r}^{M_2} \sin \xi N + G_{\alpha_r, \alpha_r}^{M_1} G_{\alpha_r, \alpha_r}^{M_2} \sin \xi (N-1)}{G_{\alpha_1, \alpha_r}^{M_2} \sin \xi N + G_{\alpha_1, \alpha_r}^{M_1} G_{\Delta}^{M_2} \sin \xi (N-1)}. \quad (19)$$

It is worth noting that as in the case of M-oligomers, for the given kind of linear molecules the bilinear combination of Green function matrix elements

$$\beta_{\text{int}}^2 \left[G_{1_{\alpha_1}, 1_{\alpha_1}}^{O_{M_1-M_2}} G_{N_{\alpha_r}, N_{\alpha_r}}^{O_{M_1-M_2}} - \left(G_{1_{\alpha_1}, N_{\alpha_r}}^{O_{M_1-M_2}} \right)^2 \right] = \frac{G_{\Delta}^{M_1} G_{\alpha_1, \alpha_r}^{M_2} \sin \xi N + G_{\alpha_1, \alpha_r}^{M_1} \sin \xi (N-1)}{G_{\alpha_1, \alpha_r}^{M_2} \sin \xi N + G_{\alpha_1, \alpha_r}^{M_1} G_{\Delta}^{M_2} \sin \xi (N-1)}, \quad (20)$$

which is an analogue of Eq. (14), has poles of the same order as that of the Green function itself.

4. Molecular tunnel conductance

The ohmic conductance of a molecule that connects two metal pads is determined by the Green function of the whole system [5,10] (consisting of the source and drain electrodes and the molecule itself) which is taken at the Fermi energy E_F . Under the assumption that the electrodes can be modelled by a semi-infinite 3-D cubic lattice with the nearest-neighbor electron-transfer interaction and that

the molecule [M- or (M_1-M_2) -oligomer] is coupled electronically with metal pads only via its end atoms, it can be shown that the molecular conductance is given by

$$g = \frac{8e^2}{h} \left| \left\langle 1_{\alpha_1} \left| \frac{\text{Im} \Sigma_1(E_F) \text{Im} \Sigma_r(E_F)}{E_F \hat{I} - \hat{H}^{O_M} - \hat{\Sigma}_1(E_F) - \hat{\Sigma}_r(E_F)} \right| N_{\alpha_r} \right\rangle \right|^2, \quad (21)$$

where the self energy operator $\hat{\Sigma}_1(E_F) + \hat{\Sigma}_r(E_F)$, which takes into account the interaction between molecule and metal pads, is defined as $\langle \nu | \hat{\Sigma}_{1(r)}(E_F) | \mu \rangle = \delta_{\nu, \mu} \delta_{\nu, 1_{\alpha_1}(N_{\alpha_r})} \beta_{1(r)}^2 G(E_F)$, $\beta_{1(r)}$ is the molecule-metal coupling constant, and $G(E_F)$ is the surface diagonal matrix element of the Green function operator for a free electron in semi-infinite cubic lattice. In this simplest model of metal-molecule-metal heterojunction, the shift and broadening of molecular levels that interact with metal are determined by the real and imaginary parts of product $\beta_{1(r)}^2 G(E_F)$. Eq. (21) has been used to examine the molecular wire properties modeled by chains with a constant [5] and alternating [27] value of the hopping integral.

According to experimental data [11–15], the Fermi energy is usually far from the molecular levels and the metal-molecule interaction is weak. Hence, to estimate the molecular conductance in the first approximation, one can use Eq. (21) with the Green function of bare molecule, i.e.,

$$g = \frac{8e^2}{h} \text{Im} \Sigma_1(E_F) \text{Im} \Sigma_r(E_F) \left[G_{1_{\alpha_1}, N_{\alpha_r}}^{O_M}(E_F) \right]^2. \quad (22)$$

This expression makes apparent the fact that, in addition to the effective metal-molecule coupling constants $\text{Im} \Sigma_1(E_F)$ and $\text{Im} \Sigma_r(E_F)$, the molecular electronic structure and particularly, the width of the band gap, and the relative position of the Fermi energy with respect to the molecular levels play a decisive role in determining the efficiency of the through band gap electron transmission between metal electrodes.

The gross structure of the one-electron spectrum of conjugated oligomers is described by Eq. (6). In particular, it determines the boundaries of allowed (real values of ξ in the interval $[0, \pi]$) and forbidden (complex values of ξ , $\xi = \pm i\delta$ or $\xi = \pi \pm i\delta$) zones and also the dispersion relations $E(\xi)$ and $E(\delta)$ that correspond to these zones. The band boundaries determine the energy intervals of delocalized electron states of the oligomer. The number of such states in the band is proportional to the molecular length, that is to the number of monomers. It follows from Eq. (6) that the band boundaries which correspond to $\xi = 0$ and to $\xi = \pi$ are determined by equations $f(E) = 2$ and $f(E) = -2$, respectively.

In the case of periodic boundary conditions, the band gaps would be free of electron states. The chain ends, however, play the role of defects. Under certain conditions specified below, even in ideal oligomers consisting of identical monomers, there exist in-gap (local) electron levels. Strictly speaking, approximation (22) is not valid, if the Fermi energy is near in-gap states. Therefore, whether or not the local levels are present in the molecular spectrum is an important question to answer.

The presence or absence of in-gap states, as well as the band joining, band degeneracy and other important features of the gross structure of oligomer electron spectrum

can be overseen at the monomer level by examining the monomer Green function properties. In particular, the π electron spectrum of M-oligomers does not contain in-gap states, if [26]

$$|\beta_{\text{int}} G_{\alpha_l, \alpha_r}^M| < 1 \quad (23)$$

at energies that satisfy equation

$$G_{\alpha_l, \alpha_l}^M G_{\alpha_r, \alpha_r}^M = 0, \quad (24)$$

the solution to which may exist within the band gap energy intervals only.

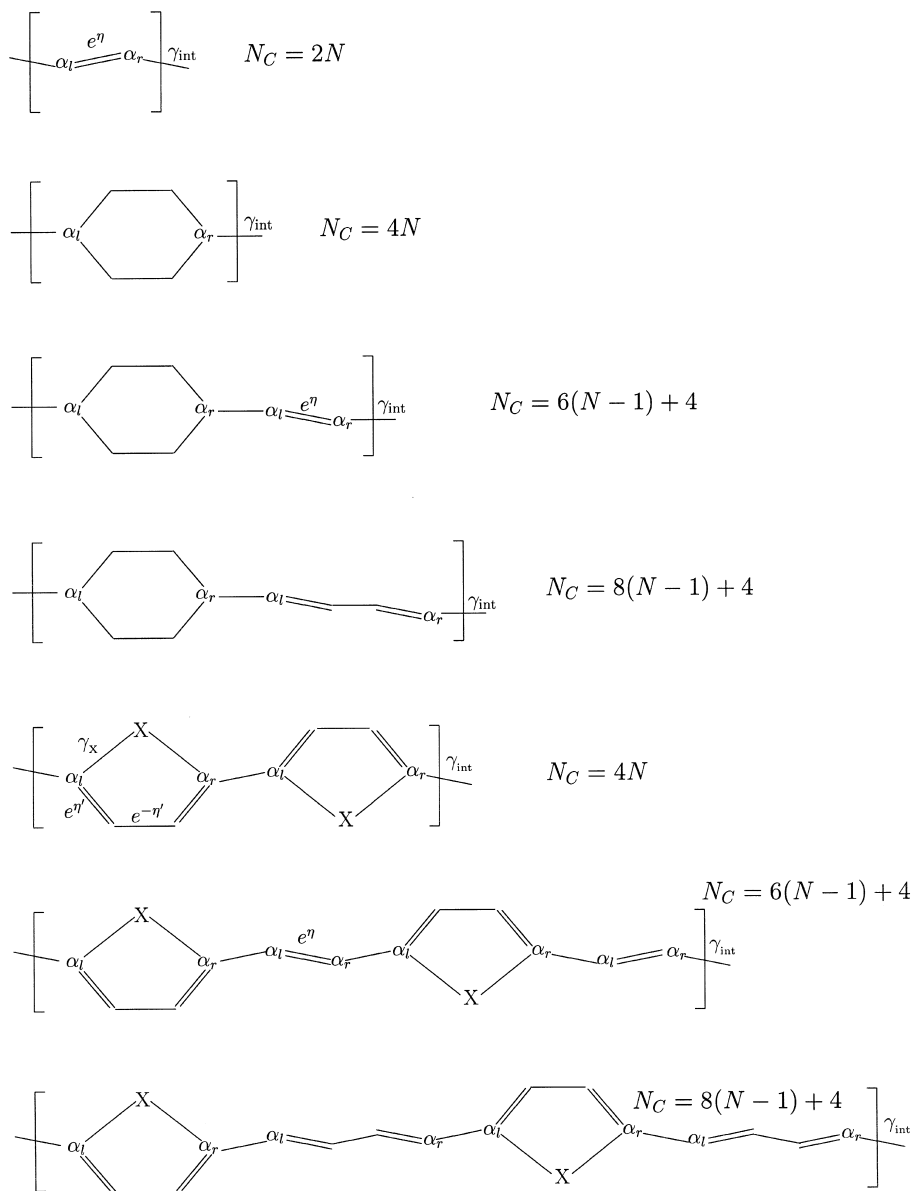


Fig. 1. Examples of chemical structure of conjugated oligomers (from top to bottom): $M = C_2H_2$; $M = C_6H_4$; $M_1 = C_6H_4$, $M_2 = C_2H_2$; $M_1 = C_6H_4$, $M_2 = C_4H_4$; $M = C_4H_2X$; $M_1 = C_4H_2X$, $M_2 = C_2H_2$; $M_1 = C_4H_2X$, $M_2 = C_4H_4$. X denotes heteroatom, for instance, S. Oligomers of comparable length have the same number of carbons in row (N_C). N and $N - 1$ indicate the number of monomers M and M_1 - M_2 in M- and $(M_1$ - $M_2)$ -oligomers, respectively.

An extension of this result to the case of (M_1-M_2) -oligomers leads to the following condition:

$$\left| \frac{G_{\alpha_1, \alpha_r}^{M_1}}{G_{\alpha_1, \alpha_r}^{M_2}} G_{\Delta}^{M_2} \right| < 1 \quad (25)$$

at the energies determined by

$$(G_{\alpha_r, \alpha_r}^{M_2} - G_{\alpha_r, \alpha_r}^{M_1} G_{\Delta}^{M_2})(G_{\alpha_1, \alpha_1}^{M_2} - G_{\alpha_1, \alpha_1}^{M_1} G_{\Delta}^{M_2}) = 0, \quad (26)$$

which ensures the absence of in-gap states in the (M_1-M_2) -oligomer spectrum.

Obviously, the through band gap electron tunneling is substantially dependent on whether the in-gap levels exist or not. In what follows we restrict our consideration by the assumption that, in the respective cases, inequalities (23) and (25) are valid.

To calculate the molecular tunnel conductance given by Eq. (22), one needs only the expression of the Green function matrix element, $G_{1_{\alpha_1}, N_{\alpha_r}}^{O_M}$ or $G_{1_{\alpha_1}, N_{\alpha_r}}^{O_{M_1, M_2}}$. As explained above, these must be taken at energies within the band gap, where $|f(E)|/2 > 1$. According to Eq. (6), the imaginary part of quasi-impulse is then related to the electron energy as

$$\delta = \ln \left(|f(E)|/2 + \sqrt{[f(E)/2]^2 - 1} \right), \quad (27)$$

where the choice of the sign in front of the square root accounts to condition (23) [or Eq. (25)].

For complex values of $\xi = \pi \pm i\delta$ and $\xi = \pm i\delta$ Eq. (8) for $n = N$ and $m = 1$, and Eq. (17) give

$$G_{1_{\alpha_1}, N_{\alpha_r}}^{O_M} = \frac{(\mp 1)^N G_{\alpha_1, \alpha_r}^M \sinh \delta}{\sinh(\delta N) \pm \beta_{\text{int}} G_{\alpha_1, \alpha_r}^M \sinh[\delta(N-1)]}, \quad (28)$$

and

$$G_{1_{\alpha_1}, N_{\alpha_r}}^{O_{M_1, M_2}} = \frac{(\mp 1)^N G_{\alpha_1, \alpha_r}^{M_1} G_{\alpha_1, \alpha_r}^{M_2} \sinh \delta}{\sinh(\delta N) \mp G_{\alpha_1, \alpha_r}^{M_1} G_{\Delta}^{M_1} \sinh[\delta(N-1)]}, \quad (29)$$

respectively, where the upper sign corresponds to $\xi = \pi \pm i\delta$, and the lower sign corresponds to $\xi = \pm i\delta$ ($\delta > 0$).

The above expressions determine the molecular tunnel conductance in the case of weak molecule–metal coupling [28]. Also, as mentioned in Section 1, Eqs. (28) and (29) can be used for estimating the electronic factor in the non-adiabatic oligomer-mediated electron transfer rate [19,20]. The strict proof of these relations is given here for the first time.

Under the condition $\exp(\delta N) \gg 1$, Eqs. (28), (29) and (22) recover the exponential dependence of the tunnel conductance on the oligomer length with the pre-exponential factor and the tunneling decay constant explicitly

related to the molecular electronic structure. Specifically, we have (in units $2e^2/h$)

$$g = g_0 g_0^{\text{mol}} e^{-2\delta N}, \quad (30)$$

where $g_0 = 4 \text{Im} \Sigma_1(E_F) \text{Im} \Sigma_r(E_F) / \beta_{\text{int}}^2$, and factors

$$g_0^{\text{mol}} = \frac{4 \sinh^2 \delta}{\left([\beta_{\text{int}} G_{\alpha_1, \alpha_r}^M]^{-1} \pm e^{-\delta} \right)^2} \quad (31)$$

and

$$g_0^{\text{mol}} = \frac{4 \left(\beta_{\text{int}} G_{\alpha_1, \alpha_r}^{M_2} \sinh \delta \right)^2}{\left(G_{\alpha_1, \alpha_r}^{M_2} / G_{\alpha_1, \alpha_r}^{M_1} \mp G_{\Delta}^{M_2} e^{-\delta} \right)^2} \quad (32)$$

multiplied by $\exp(-2\delta N)$ represent a purely molecular contribution into the conductance of metal–molecular heterojunctions based on M- and (M_1-M_2) -oligomers, respectively. In Section 5, we specify further this contribution in the particular case of aromatic-ring based oligomers without (M-oligomers) and with C_2H_2 or C_4H_4 group ((M_1-M_2) -oligomers) between the five- and six-membered rings, C_4H_2X and C_6H_4 , see Fig. 1 where X stands for heteroatom.

5. Tunnel conductance of aromatic-ring based oligomers

For the monomers in focus the Green function matrix elements G_{α_1, α_r}^M and $G_{\alpha_1, \alpha_1}^M = G_{\alpha_r, \alpha_r}^M$, and bilinear combination G_{Δ}^M calculated in the tight-binding approximation take the form

$$\beta_{\text{int}} G_{\alpha_1, \alpha_r}^M = \frac{\gamma_{\text{int}}}{D_M} \begin{cases} e^{\eta}, & M = C_2H_2, \\ e^{\eta}, & M = C_4H_4, \\ 2 \cosh \eta', & M = C_6H_4, \\ e^{\eta} (E - \varepsilon_X) \\ + \gamma_X^2 (E^2 - e^{-2\eta'}), & M = C_4H_2X, \end{cases}$$

$$\beta_{\text{int}} G_{\alpha_1, \alpha_1}^M = \frac{\gamma_{\text{int}}}{D_M} \begin{cases} E, & M = C_2H_2, \\ E (E^2 - e^{2\eta} - \gamma_{\text{int}}^2), & M = C_4H_4, \\ E [E^2 - 2 \cosh(2\eta') - 1], & M = C_6H_4, \\ E (E - \varepsilon_X) [E^2 - 2 \cosh(2\eta')] \\ - \gamma_X^2 (E^2 - e^{-2\eta'}), & M = C_4H_2X, \end{cases}$$

$$\gamma_{\text{int}}^{-1} G_{\Delta}^M = \frac{\gamma_{\text{int}}}{D_M} \begin{cases} 1, & M = C_2H_2, \\ E^2 - \gamma_{\text{int}}^2, & M = C_4H_4, \\ (E^2 - e^{2\eta'}) (E^2 - e^{-2\eta'}) \\ \times [E^2 - 2 \cosh(2\eta') + 1]^{-1}, & M = C_6H_4, \\ (E - \varepsilon_X) (E^2 - e^{-2\eta'}), & M = C_4H_2X, \end{cases} \quad (33)$$

where

$$D_M = \begin{cases} E^2 - e^{2\eta}, & M = C_2H_2, \\ (E^2 - e^{2\eta})^2 - E^2 \gamma_{\text{int}}^2, & M = C_4H_4, \\ [E^2 - 2 \cosh(2\eta') + 1] (E^2 - 4 \cosh^2 \eta'), & M = C_6H_4, \\ (E^2 + E e^{-\eta} - e^{2\eta'}) [(E - \varepsilon_X) \\ \times (E^2 - E e^{-\eta} - e^{2\eta'}) - 2 \gamma_X^2 (E^2 - e^{-\eta})], & M = C_4H_2X. \end{cases} \quad (34)$$

Table 1

Minimal conductance in units $2e^2/h$, $g_{\min}/g_0 = g_0^{\text{mol}}(\delta_{\max})e^{-2\delta_{\max}N}$, and maximal resistance in units $h/(2e^2) \approx 12.9 \text{ k}\Omega$, $R_{\max} = g_0/g_{\min}$ calculated for oligomers listed in Fig. 1 (represented in the same order as in Fig. 1). The Fermi energy corresponds to the maximum of tunneling decay constant δ_{\max} within the HOMO–LUMO gap Δ_{HL} . The oligomer length is indicated as $N_{\text{C}} = 16, 20, 22$, and 28 , N_{C} is the number of C atoms in row, see Fig. 1. The parameters of the molecular electronic structure are: for polyene $\eta = 0.1333$ [30a,30b], and $\eta = 0.1$ in all other cases; for $M = \text{C}_6\text{H}_4$ $\eta' = 0$, $\gamma_{\text{int}} = 0.92$, and for $M = \text{C}_4\text{H}_2\text{S}$ $\eta' = 0.1$, $\gamma_{\text{int}} = 1$; $\gamma_{\text{X}} = 0.38$, $\varepsilon_{\text{X}} = 0.25$ [31]; $\beta = -3.757 \text{ eV}$ [30a,30b]

Oligomer	$g_0^{\text{mol}}(\delta_{\max})$	δ_{\max}	$\Delta_{\text{HL}} \text{ (eV)}$	$g_{\min} (\times 10^{-2})$				$R_{\max} (\times 10^2)$				
				16	20	22	28	16	20	22	28	
(M)												
$M = \text{C}_2\text{H}_2$	1	0.27	2.0	1.4	0.48	0.28	0.06	0.71	2.08	3.57	16.7	
$M = \text{C}_6\text{H}_4$	1	0.78	3.4	0.20	0.04			5	25			
$M = \text{C}_4\text{H}_2\text{S}$	1	0.56	2.0	1.1	0.35			0.91	2.86			
(M_1 – M_2)												
$M_1 = \text{C}_6\text{H}_4$												
$M_2 = \text{C}_2\text{H}_2$	1.5	0.98	2.7	0.43		0.06		2.33		16.7		
$M_2 = \text{C}_4\text{H}_4$	2.2	1.18	2.4		0.19		0.02		5.26		50	
$M_1 = \text{C}_4\text{H}_2\text{S}$												
$M_2 = \text{C}_2\text{H}_2$	1.5	0.77	1.9	1.5		0.32		0.67		3.13		
$M_2 = \text{C}_4\text{H}_4$	2.2	0.97	1.9		0.66		0.94		1.5		1.06	

The notations appeared in Eqs. (33) and (34) have the following meaning. The hopping integrals associated with double and single C–C bonds in the polyene chain and between the rings are denoted as βe^η and $\beta e^{-\eta}$, respectively. Similarly, $\beta e^{\eta'}$ and $\beta e^{-\eta'}$ distinguish double and single C–C bonds within aromatic rings. $\beta \varepsilon_{\text{X}}$ is the heteroatom site energy, $\beta \gamma_{\text{X}}$ is the hoping integral of C–X bond, and $\gamma_{\text{int}} = \beta_{\text{int}}/\beta$. All energies are in units β , and the electron site energy at carbon is taken as the reference point. Further details on the monomer Hamiltonians used to obtain the above relations are given in [26,29].

It can be seen from the dispersion relations (6) and (16) [they are simplified considerably by using Eqs. (33) and (34)] that in the case of aromatic ring based oligomers function $f(E)$ may have singularities at some energies and, hence, the tunneling decay constant δ may go to infinity. Physically, this means that such oligomers can act as nearly ideal switches provided the Fermi energy is properly tuned.

If the properties of the monomer Green function are such that $f(E)$ has no singularities, the tunneling decay constant remains finite, and its maximal value δ_{\max} within the given band gap is reached at the extremum of this function, where $f'(E) = 0$. Table 1 represents the values of δ_{\max} for oligomers shown in Fig. 1.

It is of interest to find the expression of the decay constant at the energies which are solutions to Eqs. (24) and (26). In the case of alternant, all carbon oligomers, within the HOMO–LUMO (highest occupied molecular orbital–lowest unoccupied molecular orbital) gap such a solution corresponds to the extremum of $f(E)$ at $E = 0$. At the energies which satisfy Eq. (24) for M-oligomers and Eq. (26) for (M_1 – M_2)-oligomers, the expression of tunneling decay constant takes an especially simple form

$$\delta = \ln |\beta_{\text{int}} G_{\alpha_1, \alpha_r}^{\text{M}}|^{-1} \quad (35)$$

and

$$\delta = \ln \left| \frac{G_{\alpha_1, \alpha_r}^{\text{M}_1} G_{\Delta}^{\text{M}_2}}{G_{\alpha_1, \alpha_r}^{\text{M}_2}} \right|^{-1}, \quad (36)$$

respectively. To recall, the case of $|\beta_{\text{int}} G_{\alpha_1, \alpha_r}^{\text{M}}| > 1$ and $|G_{\alpha_1, \alpha_r}^{\text{M}_1} (G_{\alpha_1, \alpha_r}^{\text{M}_2})^{-1} G_{\Delta}^{\text{M}_2}| > 1$ is excluded of the consideration.

Finally, using in Eqs. (35) and (36) the above given explicit expressions of $G_{\alpha_1, \alpha_r}^{\text{M}}$ and G_{Δ}^{M} for alternant oligomers one gets

$$\delta_{\max} = \begin{cases} 2\eta, & M = \text{C}_2\text{H}_2, \\ 4\eta, & M = \text{C}_4\text{H}_4, \\ \ln\{2\cosh\eta'[2\cosh \\ \times (2\eta') - 1]/\gamma_{\text{int}}\}, & M = \text{C}_6\text{H}_4, \\ \ln\{2\cosh\eta'[2\cosh \\ \times (2\eta') - 1]/\gamma_{\text{int}}\} + 2\eta, & M_1 = \text{C}_6\text{H}_4, M_2 = \text{C}_2\text{H}_2, \\ \ln\{2\cosh\eta'[2\cosh \\ \times (2\eta') - 1]/\gamma_{\text{int}}\} + 4\eta, & M_1 = \text{C}_6\text{H}_4, M_2 = \text{C}_4\text{H}_4. \end{cases} \quad (37)$$

The maximal value of the tunneling decay constant (37) can be easily estimated by using the known data: the value of η is close to 0.1 [30a,30b]; this same value is characteristic for parameter η' in the heterocyclic rings [31] while C–C bonds within phenyl ring are nearly equal to each other, i.e., $\eta' \approx 0$; and expected values of γ_{int} are close to unity. As an example, for oligomers of polypara-phenylenevinylene these data yield the value of dimensional tunneling decay constant in the middle of the gap $\kappa_{\max} = 0.306 \text{ \AA}^{-1}$ ($\kappa_{\max} = 2\delta_{\max}N/L$, L is the oligomer length in \AA). For this estimate, a commonly accepted geometry was assumed, namely: the length of $M_1 = \text{C}_6\text{H}_4$, $M_2 = \text{C}_2\text{H}_2$, and C–C bond between M_1 and M_2 was taken to be equal to 2.78, 1.32, and 1.48 \AA , respectively; and the angle between double and single C–C bonds was set to be 120° . The estimated value of κ_{\max} is in a good

agreement with that calculated by Magoga and Joachim [21] 0.278 \AA^{-1} , and also by Larsson et al. [22] 0.303 \AA^{-1} . It is also consistent with the value of 0.2 \AA^{-1} which is considered as a typical characteristic of linear conjugated molecules in the bridge-mediated electron transfer [32].

6. Conclusion

The exact solution of the Green function problem for M-oligomers described by the tight-binding Hamiltonian represents the central result of the paper. In the solution found, the matrix elements of the oligomer (linear macromolecule) Green function are explicitly expressed in terms of monomer Green function. The calculation of the latter quantity is a far more easy task. As is demonstrated in the above illustrative examples, in many cases of interest, it can be found in an analytical form.

A number of physical properties can be conveniently described if the Green function of the system is known. The solution found makes the π electronic structures of two families of conjugated oligomers covered by formulas $M-M-\dots-M$ and $M_1-M_2-M_1-\dots-M_2-M_1$ available for a comprehensive Green function analysis. Actually, due to early works of Sandorfy [33], and Pople and Santry [34], with an appropriate choice of the system parameters, the same type of Hamiltonian, as that has been used here, is also applicable for the description of σ electrons. The formal analogy between π and σ electron system has recently been used for a comparison of the electron-transmitting abilities of conjugated and saturated carbon chains [27]. Furthermore, by the standard methods, the knowledge of M-oligomer Green function can be extended to the case of molecular chains with side and/or end groups whose Green functions are to be found separately. For instance, the Green function of oligomers terminated by arbitrary end groups can be obtained essentially in the same way as it has been derived above for (M_1-M_2) -oligomers.

In this work, the knowledge of the Green function has been used to examine the electron tunneling through the molecular band gap. So far, the molecular tunnel conductance has been studied mostly by numerical methods. For a number of conjugated oligomers, the tunneling decay constant has been calculated on the basis of the extended Hückel model [21]. It is not our intention to make a detailed comparison with these and similar results but rather to notice an obvious advantage of the analytical definition given in Eq. (27). Firstly, this and subsidiary equations derived make equally simple the estimate of the tunneling decay constant at any energy within the band gap. This is a useful application of the theory in view of uncertainty with regard to the relative position of the Fermi energy which in numerical models is usually fixed [21,22]. Secondly, the analytical expression of the tunneling decay constant establishes the relationship between the through band gap tunneling efficiency and the parameters

of molecular Hamiltonian which determine the details of electronic structure such as band gap, valence and conduction band widths, the full width of the π electron spectrum, etc. Unfortunately, the values of the Hamiltonian parameters are not strictly defined in the microscopic sense. However, on the basis of available experimental and theoretical data, they can reasonably be chosen to investigate the qualitative trends in molecular conductance.

To summarize, for broad families of conjugated oligomers the exact analytical expression of the full Green function matrix is derived. Although this result has a number of other potentials, its presentation is primarily addressed to modeling metal–molecular heterojunctions by both analytical and computational means. Its use seems to be especially helpful for the understanding of electrical properties of long oligomers consisting of monomers with nontrivial chemical structure. A particular problem is the dependence of current–voltage characteristics on the number of monomers in the wire. The work aimed to examine this issue is now in progress.

Acknowledgements

This work was supported in part by grants from the Dutch Science Foundation (NWO) and Royal Swedish Academy of Sciences.

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