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An analytic approach to the conductance and I – V characteristics of polymeric chains

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Abstract

Electron transport is studied in a molecular device made of two semi-infinite leads connected by a molecule. Both the molecule and the leads are described within the tight-binding model. Using a transfer matrix method, the transmission is calculated, taking into account a finite potential difference between the leads. In several interesting cases, such as some oligomeric chains of arbitrary length, the use of the transfer matrix method allows us to obtain explicit results for the transmission for finite bias voltage. From our transmission results, we obtain the current–voltage characteristics for short molecular chains and discuss a dependence of the current on the coupling between the molecules and the leads.

1. Introduction

One of the central issues of molecular electronics is a relation between the electronic structure of a molecule and the current–voltage (or I – V) characteristics of a molecular device [1]. Much effort has been made to develop *ab initio* methods for the calculation of the conductance of relatively simple structures such as carbon chains [2] and benzene dithiolate [3, 4]. It is however desirable, and sometimes sufficient, to be able to explain the I – V characteristics of the device in terms of an approach based on a simple parametric model, especially in the case of bigger molecules which are difficult to study with the *ab initio* methods. Such semi-empirical approaches based on the extended Hückel method [5–7] or a single-band tight-binding model [8] have recently been applied to analyse the conductance and localization of states in polymeric chains.

In the present paper we use an analytic approach based on the tight-binding model and the transfer matrix method [9, 10] to derive the transmission in the molecular device for a finite difference of the potential in the leads. We study the effects of dimensionality of the leads, comparing the results for one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) leads as well as leads of finite width. The method is applied to calculate the transmission as well as the I – V characteristics of some oligomeric chains.

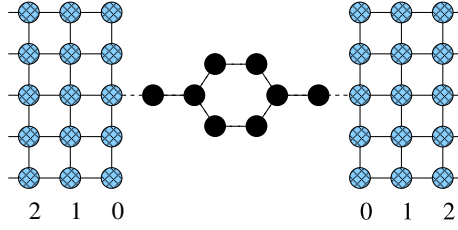


Figure 1. A schematic picture of a molecule connecting two leads. The dark circles represent atoms of the molecule; the light circles show atoms of the leads. In this example the 2D leads have widths of $N = 5$ lattice units. Numbers in the figure refer to the consecutive layers of the atoms of the source and drain electrodes (see equation (1)).

2. Transmission as a function of bias voltage

The device that we want to describe is defined as a system of two semi-infinite leads joined to a molecule (see figure 1). The single-band tight-binding model of the device is defined with the one-particle Hamiltonian

$$\mathcal{H} = \sum_{\mu; j=0}^{j=\infty} (a_{\mu j}^\dagger t_\mu a_{\mu j+1} + \text{h.c.}) + \sum_{\mu; j=0}^{j=\infty} a_{\mu j}^\dagger H_\mu a_{\mu j} + c^\dagger H_c c + \sum_{\mu} (a_{\mu 0}^\dagger W_\mu c + \text{h.c.}). \quad (1)$$

In equation (1), $a_{\mu j}$ is an N^{D-1} -dimensional vector of electron annihilation operators for D -dimensional hypercubic leads and N is the width of the lead in atomic units. The index μ takes value $\mu = 1$ for the source and $\mu = 2$ for the drain lead and j denotes the position of the atoms in the direction parallel to the axes of the leads. c is an L -dimensional vector of electron operators for the molecule, where L is the number of atomic sites in the molecule.

The first two terms of equation (1) describe the electron hopping along (t_μ) and across (H_μ) the leads, respectively. Additionally, the diagonal elements of the matrices H_μ represent the site energy terms, which include the constant potential in the leads, $U_1 = -U_2 = U/2$. By assumption, $(N^{D-1} \times N^{D-1})$ -dimensional matrices t_μ , H_μ are independent of the site index j .

All details of the connection of the molecule to the leads, which are included in the $(N^{D-1} \times L)$ -dimensional matrices W_1 and W_2 , will be specified below.

We calculate the conductance of the device with the help of the scattering formalism [11], which allows us to obtain the current flowing through the device from the transmission function \mathcal{T} as

$$\mathcal{I} = \frac{2e}{h} \int d\omega \mathcal{T}(\omega, U) [f(\omega - \mu_1) - f(\omega - \mu_2)] \quad (2)$$

where f denotes the Fermi distribution function and $\mu_v = \mu - eU_v$. In order to calculate the transmission we use the transfer matrix method (see [10, 13] and the appendix for the details). The transmission can be readily represented in terms of the parameters of our Hamiltonian (see also [11])

$$\mathcal{T} = \text{tr}[(Q_1 - Q_1^\dagger)G_c(Q_2^\dagger - Q_2)G_c^\dagger]. \quad (3)$$

Above, G_c denotes the Green function of the molecule, which includes the terms Q_μ , describing the coupling of the molecule to the leads:

$$G_c = \left(\omega I - H_c - \sum_{\mu} Q_\mu \right)^{-1} \quad (4)$$

where I denotes the unit matrix. The coupling terms are related to the Green functions of the perfect leads [13], multiplied by the matrices W_μ :

$$Q_\mu = W_\mu^\dagger S_\mu \Lambda_\mu S_\mu^\dagger W_\mu / t_\mu. \quad (5)$$

The matrices S_μ are given by: $S_\mu = 1$, for $D = 1$;

$$(S_\mu)_{\alpha\beta} = \sqrt{\frac{2}{N+1}} \sin\left(\frac{\pi\alpha\beta}{N+1}\right), \quad \alpha, \beta = 1, \dots, N$$

for $D = 2$; and

$$(S_\mu)_{\vec{\alpha}\vec{\beta}} = \frac{2}{N+1} \sin\left(\frac{\pi\alpha_1\beta_1}{N+1}\right) \sin\left(\frac{\pi\alpha_2\beta_2}{N+1}\right),$$

$$\vec{\alpha} = (\alpha_1, \alpha_2), \quad \vec{\beta} = (\beta_1, \beta_2), \quad \alpha_{1,2}, \beta_{1,2} = 1, \dots, N$$

for $D = 3$. The $(N^{D-1} \times N^{D-1})$ -dimensional diagonal matrices Λ_μ include eigenvalues of the transfer matrices for the leads, corresponding to the propagating outwards and evanescent waves in the leads [13]. The matrices Λ_μ are defined in terms of diagonal matrices P_μ :

$$\Lambda_\mu = P_\mu \pm \sqrt{P_\mu^2 - I}, \quad (6)$$

which include eigenvalues of the matrices $(2t_\mu)^{-1}(\omega I - H_\mu)$ on the diagonals:

$$P_\mu = \frac{\omega - U_\mu}{2t_\mu}, \quad \text{for } D = 1;$$

$$(P_\mu)_{\alpha\alpha} = \frac{\omega - U_\mu}{2t_\mu} - \cos\left(\frac{\pi}{N+1}\alpha\right), \quad \text{for } D = 2;$$

$$(P_\mu)_{\vec{\alpha}\vec{\alpha}} = \frac{\omega - U_\mu}{2t_\mu} - \cos\left(\frac{\pi}{N+1}\alpha_1\right) - \cos\left(\frac{\pi}{N+1}\alpha_2\right), \quad \text{for } D = 3.$$

Note that the transmission matrix depends both on the energy ω of the incident electron and (via the matrices Λ_μ) on the difference of the applied bias voltage U .

So far we have not specified the details of connection of the molecule to the leads. In general, the distinction between the leads and the molecule is a matter of choice, especially if one wants to take into account variation of the potential and electron density in the leads close to the junction. Such considerations are important for self-consistent computations, as described in [12]. In this paper we restrict ourselves to analytic treatment and assume a very simple model of the junction in which the leads are connected to the molecule through a single atomic site each (see figure 1). In this case the lead-to-molecule hopping matrices have only one non-zero element:

$$(W_1)_{\alpha\beta} = w_1 \delta_{\alpha 1} \delta_{\beta p}, \quad (W_2)_{\alpha\beta} = w_2 \delta_{\alpha L} \delta_{\beta p}$$

where we assume that the p th atom of the 0th layer of the left (right) lead is connected to 1st (L th) atom of the molecule. The transmission coefficient can now be rewritten as

$$T(\omega, U) = \text{tr}(\tau \tau^\dagger) = 4 \text{Im } q_1(\omega) \text{Im } q_2(\omega) |\tau_c|^2, \quad (7)$$

where

$$\tau_c = \frac{[g_c(\omega)]_{1L}}{\{1 - q_1(\omega)[g_c(\omega)]_{11}\}\{1 - q_2(\omega)[g_c(\omega)]_{LL}\} - q_1(\omega)q_2(\omega)[g_c(\omega)]_{1L}[g_c(\omega)]_{L1}} \quad (8)$$

$$q_\mu(\omega) = \frac{w_\mu^2}{t_\mu} [S_\mu \Lambda_\mu(\omega) S_\mu^\dagger]_{pp}, \quad g_c = (\omega I - H_c)^{-1}. \quad (9)$$

All the information concerning the molecule is now contained in the Green function of an *isolated* molecule, g_c , whereas the lead–molecule coupling is included in the functions q_μ .

In a number of interesting cases the coupling functions q_μ may be explicitly obtained.

$q_\mu = (w_\mu^2/t_\mu)\Lambda_\mu$ for $D = 1$;

$$q_\mu = \frac{w_\mu^2}{t_\mu} \frac{2}{N+1} \sum_{\alpha=1}^{\alpha=N} \sin^2\left(\frac{\pi}{N+1} p\alpha\right) (\Lambda_\mu)_{\alpha\alpha}, \quad \text{for } D = 2; \quad (10)$$

and

$$q_\mu = \frac{w_\mu^2}{t_\mu} \frac{4}{(N+1)^2} \sum_{\alpha_1, \alpha_2=1}^{\alpha_1, \alpha_2=N} \sin^2\left(\frac{\pi}{N+1} p_1\alpha_1\right) \sin^2\left(\frac{\pi}{N+1} p_2\alpha_2\right) (\Lambda_\mu)_{\alpha\alpha}, \quad \text{for } D = 3, \quad (11)$$

where the choice of the sign in equation (6) should correspond to the physically appropriate (i.e. evanescent and outgoing) scattered solutions. In the limit of infinitely wide stripes ($D = 2$ and $N \rightarrow \infty$), the sum in equation (10) may be replaced by an integral and one finds

$$\text{Im } q_\mu(\omega) = \theta(1 - |\omega_\mu|/2) \frac{2w_\mu^2}{\pi t_\mu} [(1 + |\omega_\mu|/2)\mathcal{E}(k_\mu) - |\omega_\mu|\mathcal{K}(k_\mu)] \quad (12)$$

$$\text{Re } q_\mu(\omega) = \text{sgn}(\omega_\mu) \frac{w_\mu^2}{\pi t_\mu} [\pi|\omega_\mu|/2 + (1 - |\omega_\mu|/2)\mathcal{K}(1 - k_\mu) - (1 + |\omega_\mu|/2)\mathcal{E}(1 - k_\mu)] \quad (13)$$

$$\omega_\mu = \frac{\omega - U_\mu}{2t_\mu}, \quad k_\mu = \left(\frac{1 - |\omega_\mu|/2}{1 + |\omega_\mu|/2}\right)^2$$

where \mathcal{K} , \mathcal{E} are the complete elliptic integrals of the first and the second kind, respectively. For several other 2D and 3D structures of the leads, the corresponding limiting formulae can be also deduced from the known lattice Green functions [17].

With the help of equation (8) we can draw some general conclusions concerning the dependence of the transmission on the energy of the electron and the bias voltage. For a weak coupling of the molecule to the leads ($w_\mu \ll t_\mu$), the energy dependence of the denominator in equation (8) can be neglected when compared to unity, except in the vicinity of the resonances, which coincide with eigenvalues of the molecular Hamiltonian, H_c . The total transmission $\mathcal{T}(\omega, U)$ is almost everywhere very small (i.e. of the order of $w_1^2 w_2^2 / t_1 t_2 \Delta(\omega)^2$, where $\Delta(\omega)$ is the distance to the nearest molecular energy level) except at the resonances, where it approaches unity. In this limit the experiment would show well resolved molecular energy structure. The voltage dependence of the transmission depends mostly on the behaviour of the product $\text{Im } q_1 \text{Im } q_2$, which has a maximum for $U_1 = U_2$, decreases with increase of $|U_1 - U_2|$ and vanishes for $|U_1 - U_2| = 2D(t_1 + t_2)$.

With increase of the value of the lead–molecule coupling, the energy dependence of the denominator in equation (8) has to be taken into account. The resonances gain a substantial width and may even merge. The voltage dependence of the denominator in equation (8) becomes important. The increase of $|U_1 - U_2|$ allows us to see the resonances more clearly again (see below).

We exemplify the above-discussed general energy dependence of the transmission using the tight-binding model of a two-atom molecule with hopping t_c between the atoms and the lead–molecule coupling $w_1 = w_2 = w$. We assume identical leads with $t_1 = t_2 = t$ and consider the limit of zero bias voltage, $U_1 = U_2 = 0$, when $q_1 = q_2 = q$. The energy spectrum of the isolated molecule consists of two levels, $\varepsilon_\pm = \pm t_c$, and the relevant elements of the Green

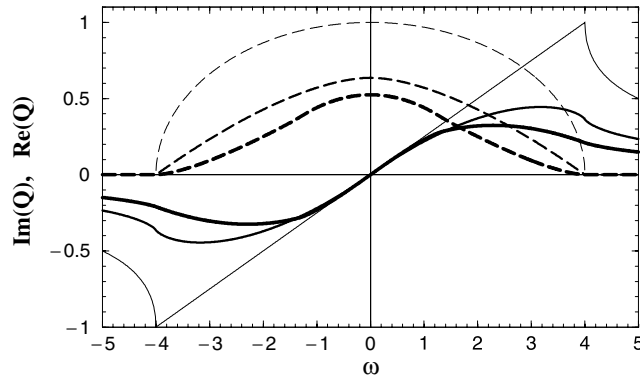


Figure 2. The Green function q_1 (equations (12), (13), multiplied by the factor t_1/W_1^2) as a function of energy ω . Here and in other figures the energy is given in units of the hopping t_1 . Solid curves—real parts of q_1 ; broken curves—imaginary parts of q_1 . Thick, intermediate width and thin curves correspond to $D = 3$ (with t_1 scaled by a factor of $2/3$), $D = 2$ and $D = 1$ (scaled by a factor of 2), respectively. The results for $D = 3$ and $D = 1$ were scaled for easier comparison with $D = 2$ leads.

function are: $[g_c(\omega)]_{11} = [g_c(\omega)]_{22} = \omega/(\omega^2 - t_c^2)$ and $[g_c(\omega)]_{12} = [g_c(\omega)]_{21} = t_c/(\omega^2 - t_c^2)$. From equations (7), (8) we obtain

$$\mathcal{T}(\omega) = \frac{(2t_c \operatorname{Im} q)^2}{[(\omega + \operatorname{Re} q)^2 - t_c^2 + (\operatorname{Im} q)^2]^2 + (2t_c \operatorname{Im} q)^2}. \quad (14)$$

For a weak lead-to-molecule coupling w , the transmission given by equation (14) exhibits two maxima given by solutions of the equation

$$\omega = -\operatorname{Re} q(\omega) \pm \sqrt{t_c^2 - (\operatorname{Im} q(\omega))^2} \quad (15)$$

where the transmission is complete. With increasing w , the widths of the corresponding peaks in \mathcal{T} increase and the peaks approach zero. For $\operatorname{Im} q(0) > t_c$ (i.e. for $w > w_0 = \sqrt{\pi t t_c}/2$ for infinitely wide 2D leads), equation (15) can no longer have real solutions and the transmission exhibits a single broad peak centred at $\omega = 0$. The transmission at the maximum in this strong-coupling limit decreases with increasing w . As a result, it can be concluded that the transmission at $\omega = 0$ is not a monotonic function of the coupling strength [15] and reaches a maximum value $\mathcal{T}(0) = 1$ for $w = w_0$.

The results (10)–(13) can be used to verify some other analytical approaches used to study transmission through molecular devices. In the particular case of 1D leads, a result formally equivalent to the Newns–Anderson (NA) model [16] is obtained (to mimic the bandwidth of the 2D leads with the 1D result we have to double the transfer integral of the leads).

Some qualitative differences can be noted between the results obtained using the NA model and those found for the true 2D and 3D leads (see figure 2). The coupling function q computed for 2D leads is a considerably better approximation of the 3D case than the NA model.

In all the cases, $\operatorname{Im} q$ is a smooth function of electron energy ω . This is very unlike the behaviour of the density of states (DOS) functions of bulk 1D, 2D and 3D lattices, which have inverse square root (for $D = 1$), logarithmic (for $D = 2$) and square root (for $D = 3$) singularities. The replacement of $\operatorname{Im} q$ with the DOS function of the bulk, as proposed recently in [14], would be justified if the molecule interacted in the same way with all states of the continuum of both leads [15]. The latter assumption is however incompatible with the nearest-neighbour tight-binding model of the molecule–lead hopping.

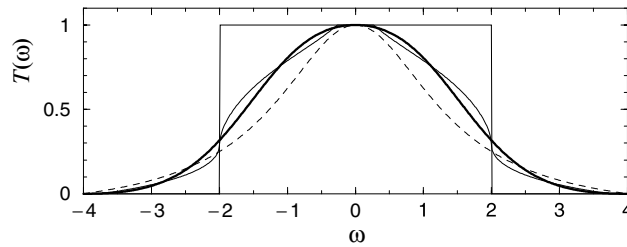


Figure 3. Transmission T as a function of energy of the transmitted electron for a single atom with $E_m = 0$ for different leads and zero bias voltage in the strong-coupling case ($t_1 = t_2 = w_1 = w_2$). Thick solid curve—infinitely wide 2D leads; thin solid curve—stripes of width $N = 5$; thin rectangular line—1D leads; broken curve NA model (i.e. 1D leads with $t_1 \rightarrow 2t_1$).

In order to estimate the effect of the structural details of the leads on the transmission itself, the simplest possible case of a one-atom molecule was analysed in more detail. In this case the Green function is $g_c = 1/(\omega - E_m)$, where E_m is the energy of the molecular level. In figure 3 we present the transmission as a function of electron energy for stripes of different widths. One may note there that the results for $N = 5$ already quantitatively approach the $N = \infty$ limit fairly well and are better in this respect than the NA model predictions over almost the whole energy range.

3. Transmission of a polymeric chain

The molecular data enter the expression for the transmission via the elements of the molecular Green function g_c . The calculation of g_c may in many cases be facilitated by the use of the transfer matrix method. Let us consider a molecule which starts and ends with a single bond, with a hopping t_c corresponding to this bond. Using a tight-binding model for this molecule we can write an eigenstate of the molecule in the form $\Psi_c = \gamma c^\dagger |0\rangle$. We can write a relation between the amplitudes of the two boundary pairs in the form

$$\begin{bmatrix} \gamma_L \\ \gamma_{L-1} \end{bmatrix} = T(\omega) \begin{bmatrix} \gamma_2 \\ \gamma_1 \end{bmatrix} \quad (16)$$

which defines a (2×2) -dimensional transfer matrix T for the isolated molecule. The Green function elements may be obtained directly from the transfer matrix:

$$[g_c]_{1L} = [g_c]_{L1} = \frac{-t_c}{t_c^2 T_{22} - \omega_1 \omega_L T_{11} + t_c \omega_1 T_{21} - t_c \omega_L T_{12}}, \quad (17)$$

$$[g_c]_{LL} = (T_{11} \omega_1 / t_c + T_{12}) [g_c]_{1L}, \quad [g_c]_{11} = (T_{11} \omega_L / t_c - T_{21}) [g_c]_{1L} \quad (18)$$

where $\omega_\alpha = \omega - E_\alpha$ and E_α is a site energy at the site α . For a purely 1D chain, the transfer matrix can always be found as a product of the intermediate transfer matrices, which are obtained from recurrence equations relating amplitudes at the neighbouring pairs of sites along the chain. In the case of more complicated polymeric systems, composed of complex molecular subunits connected with single carbon bonds, the local hopping matrices are not in general reversible and the intermediate transfer matrices cannot be defined directly from the recurrence equations. Such an oligomeric chain may be written schematically as

$$(1)-(2)\mathcal{O}_1(3)-(4)\mathcal{O}_2(5)-\dots-(L-2)\mathcal{O}_{L/2-1}(L-1)-(L)$$

where \mathcal{O}_n denotes n th oligomer subunit and numbers in parentheses are indices of atoms linking neighbouring oligomers. Here we first eliminate the coefficients γ of internal oligomeric coordinates, obtaining effective ω -dependent hopping t_ω and site energy E_ω for linking sites.

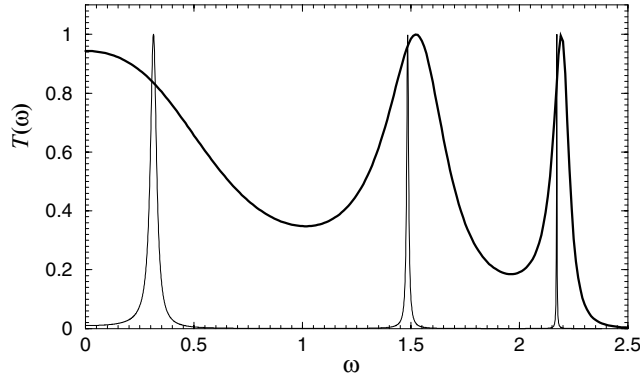


Figure 4. Transmission $T(\omega) = T(-\omega)$ as a function of electron energy ω (for zero bias voltage) for a model of one benzene ring ($M = 1$) connected to 2D leads by means of symmetrically attached bridging atoms. Thick solid curve—the strong molecule-to-leads coupling ($w_\mu = t_\mu$); thin solid curve—the weak-coupling case ($w_\mu = 0.2t_\mu$).

The system of M identical subunits is very similar to a dimerized 1D chain where the hopping alternates along the chain between the values t_c and t_ω and the site energy is constant, $E = E_\omega$ (except the first and the last sites, connected to the leads, where $E = 0$). The transfer matrix is given by

$$T(\omega) = T_1(\omega)^M = \begin{bmatrix} \tilde{\omega}^2/t_\omega t_c - t_\omega/t_c & -\tilde{\omega}/t_\omega \\ \tilde{\omega}/t_\omega & -t_c/t_\omega \end{bmatrix}^M, \quad \tilde{\omega} = \omega - E_\omega. \quad (19)$$

We apply the procedure outlined above to an oligomeric chain of M benzene rings, known as polyparaphenylene. The effective site energy and hopping parameters are given by

$$\tilde{\omega} = \frac{\omega(\omega^2 - 3t_c^2)}{\omega^2 - t_c^2}, \quad t_\omega = \frac{2t_c^3}{\omega^2 - t_c^2}. \quad (20)$$

The elements of the transfer matrix and the necessary elements of the Green function can be explicitly obtained for arbitrary M in terms of the eigenvalues of $T_1(\omega)$:

$$\lambda_\pm(\omega) = p_\omega \pm \sqrt{p_\omega^2 - 1}, \quad p_\omega = \frac{(\omega^2 - t_c^2)(\omega^2 - 5t_c^2)}{4t_c^4} \quad (21)$$

and the corresponding eigenvectors.

In figures 4, 5 we present the transmission as a function of energy for the chains composed of $M = 1$ and 3 benzene rings for zero bias voltage for strong ($w_\mu = t_\mu = t_c$) and weak ($w_\mu = 0.2t_\mu = 0.2t_c$) lead-to-molecule coupling.

For $M = 1$ our model mimics the benzene-1, 4-dithiolate molecule¹, which was studied extensively with *ab initio* methods [3, 4]. Within our one-band tight-binding model we obtain eight non-degenerate energy levels in this system. The transmission, however, shows only five (for strong coupling) to six (weak-coupling case) peaks. It is obvious that the central maximum, observed for strong coupling for $\omega = 0$, is a result of the merging of the two levels closest to $\omega = 0$. More mysterious is the absence of the peaks corresponding to the eigenvalues located at $\omega = \pm t_c$. These eigenvalues are present already for the benzene ring and are not perturbed by symmetrical attachment of two extra bonds. The absence of these states in the

¹ We neglect here the difference between the site energies of carbon and sulphur atoms.

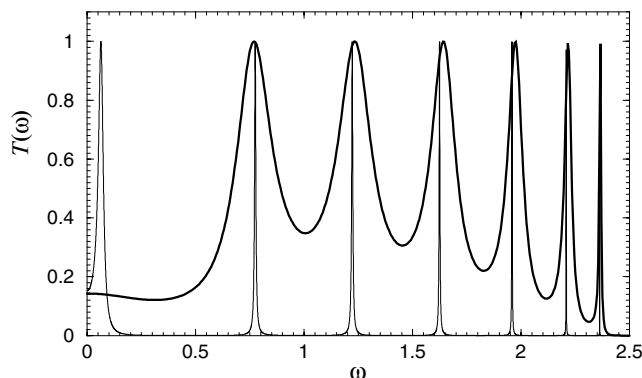


Figure 5. As in figure 4, but for $M = 3$.

transmission may be explained using a spectral representation of the Green function:

$$[g_c(\omega)]_{nm} = \sum_{\lambda} \frac{\phi_{\lambda}^*(n)\phi_{\lambda}(m)}{\omega - \lambda} \quad (22)$$

where $\phi_{\lambda}(n)$ is the amplitude of the molecular eigenstate λ at site n . Within the tight-binding method each eigenstate is a linear combination of (orthogonal, by assumption) atomic states. If a given eigenstate does not change after adding new sites to the molecule, the atomic states of these new sites do not contribute to this eigenstate. As a result the amplitude of the eigenstate at the new sites vanishes and the corresponding eigenvalue does not give rise to a pole of g_c at these sites.

On adding more benzene rings to the system we observe a gradual decrease of the transmission in the region near $\omega = 0$ (figure 5). This region eventually (for $M \rightarrow \infty$) transforms into a gap of an infinitely long polymer. From equation (21) we find that only for $-1 + \sqrt{2} < |\omega/t_c| < 1 + \sqrt{2}$ are the eigenvalues of $T(\omega)$ complex. In this way we determine the boundaries of a continuum of the extended states in the polymer chain studied in the $M \rightarrow \infty$ limit.

Within the gap and in the limit of weak lead-to-molecule coupling, there are still two peaks located approximately at $\omega_{\pm}/t_c = \pm 2^{-M-1}$. For $\omega \approx \omega_{\pm}$ the molecule behaves as a simple two-level system discussed in the previous section, with an effective hopping $\sim 2^{-M-1}t_c$ between the two atoms. Note that in the present case the threshold coupling w_0 decreases with increasing M like $\sim 2^{-(M-1)/2}$. The residues of $[g_c]_{1L}$ at these peaks decrease like $\sim 2^{-M-1}$ and they quickly become unimportant for the transmission in a large chain for $|\omega/\omega_{\pm}| > 1$.

Transmission for $|\omega/t_c| < -1 + \sqrt{2}$ can be discussed in terms of tunnelling. $T(\omega)$ for $\omega \approx 0$ decreases exponentially with the number of benzene rings in the chain. The reason for this is obvious from equations (17), (19). Within the gap region, the behaviour of $T(\omega)$ for large M is dominated by the highest of the eigenvalues, $\lambda_+ > 1$: $T(\omega) \sim |\lambda_+(\omega)|^M$. As a result, the numerator of τ_c decreases exponentially with M and the transmission decreases as

$$T(\omega) \sim \exp(-M\gamma), \quad \gamma = 2 \ln |\lambda_+(\omega)| = -2 \ln |\lambda_-(\omega)|.$$

As correctly noted in [6], the ‘damping factor’ γ is not related in a simple way to the energy distance from the continuum (in the present case $\Delta(\omega) = t_c(\sqrt{2} - 1) - \omega$). This contradicts the WKB-type estimates [5] obtained ignoring the internal energetic structure of the component oligomers.

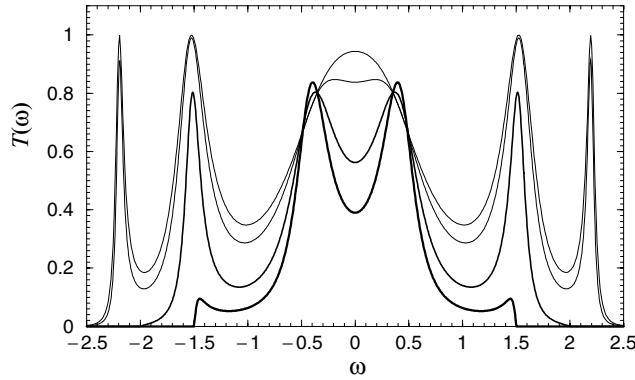


Figure 6. Transmission as a function of energy for several values of bias voltage U , for the model of a single benzene ring connected to 2D leads by means of symmetrically attached bridging atoms for the strong-coupling case ($eU/t_1 = 0, 2, 4, 5$: the width of the lines increases with voltage).

4. I - V characteristics of the polymeric chain

Comprehensive analysis of the transmission spectrum allows us to discuss now the bias dependence of the transport through the device including the polymeric chain. Using equations (8), (17), (19) we are able now to compute the transmission for a finite voltage $U = U_1 - U_2$.

In figure 6 we present results obtained for a system with a single benzene ring ($M = 1$) for several voltage values. The vanishing of the peripheral peaks from the transmission and the overall suppression of the transmission are consistent with the reduction of overlap of the spectral densities of the leads, $\text{Im } q_1(\omega)$, $\text{Im } q_2(\omega)$ with increasing U . However, this decrease is not at all uniform. The broad unresolved maximum near $\omega = 0$ splits into a pair of peaks with increasing bias voltage and the peak positions also slightly depend on U .

Transmission at the peaks is no longer perfect (unlike in the $U = 0$ case) and the relative decrease of \mathcal{T} is smaller at the peaks than it is in the valleys. The reduction of the transmission at the peaks can be most easily understood using the case of a one-atom molecule, with molecular energy E_m . In this case one can obtain an upper boundary for the transmission:

$$\mathcal{T}(\omega, U) = \frac{4 \text{Im } q_1 \text{Im } q_2}{(\omega - E_m - \text{Re } q_1 - \text{Re } q_2)^2 + (\text{Im } q_1 + \text{Im } q_2)^2} \leq 1 - \left(\frac{\text{Im } q_1 - \text{Im } q_2}{\text{Im } q_1 + \text{Im } q_2} \right)^2. \quad (23)$$

As follows from equation (23), the transmission is smaller than unity for any ω in the case of any inequivalence of the leads. A particular case of this inequivalence is the finite bias voltage (with the exception of the special case of $E_m = 0$ for $\omega = 0$ when $\text{Re } q_1 = -\text{Re } q_2$ and $\text{Im } q_1 = \text{Im } q_2$ for arbitrary U).

Figures 7, 8 present the results of our computations of the current as a function of bias voltage for strong ($w_\mu = t_\mu$, figure 7) and weak ($w_\mu = 0.2t_\mu$, figure 8) coupling of the molecule to the leads. These results were obtained with the transmission calculated for a finite bias voltage, in the integrand of equation (2). In our analysis we assumed [18] that the Fermi level lies at $\mu = 0$ (i.e. in the middle of the HOMO–LUMO gap of the isolated molecule).

In computations of the I - V characteristics of the molecular devices, the U -dependence of the transmission is often neglected [4, 7]. We include the results following from this approximation in figures 7, 8 for comparison. One can see that the neglect of the U -dependence of \mathcal{T} leads to a noticeable overestimation of the current for high voltages. The relative error

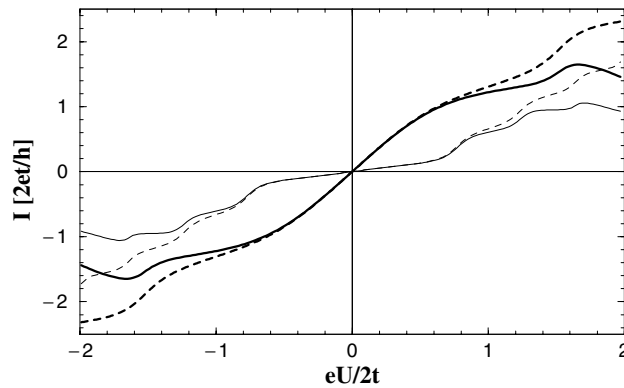


Figure 7. I - V characteristics for the molecules with one (thick curves) and three (thin curves) benzene rings connected to 2D leads by means of symmetrically attached bridging atoms for strong molecule-to-leads coupling, $w_\mu = t_\mu = t$. Solid curves: results computed by taking into account a reduction of transmission for the finite bias voltage; broken curves: results obtained with $T(\omega, U = 0)$ in equation (2).

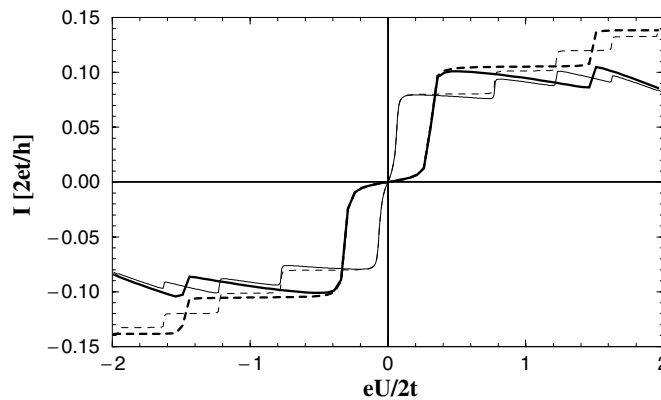


Figure 8. As figure 7, but for weak coupling, $w_\mu = 0.2t_\mu = 0.2t$.

of the approximation increases slightly with decreasing coupling strength. One can speculate that the neglect of the U -dependence of the transmission can at least partly account for the disagreement between some experimental results and the theory (see, e.g. [7], figure 10).

Figures 7 and 8 show the dependence of the I - V characteristics on the coupling strength. In the strong-coupling case the current is a fairly smooth function of voltage as a result of the sizable linewidth of the transmission peaks. In the weak-coupling case the peaks are very narrow and the I - V dependence resembles a stepwise function.

For the intermediate range of voltage and in the strong-coupling case, the current decreases with increasing number of benzene rings in the polymer chain. The decrease of the current is less significant in the weak-coupling case.

With decreasing U , the linear response limit is approached, where the current is proportional to the voltage:

$$\mathcal{I}(U) = \frac{2e^2}{h} T(\mu, 0)U \quad (24)$$

i.e. \mathcal{I} is directly related to the value of transmission at $\omega = \mu$. It has been shown in the

previous section that the transmission of the polymer chain for $\omega \approx 0$ can be explained by analogy to the behaviour of a two-level system (see section 2, equation (14)) with effective hopping, $t_{eff} \sim t_c \times 2^{-M-1}$. For a given value of the molecule-lead coupling, the effective hopping decreases with increasing number of benzene rings in the chain. For M large enough, the two peaks located near $\omega = 0$ merge into a single maximum, with $\mathcal{T} \approx 1$, resulting in a maximum value of the current for a given (small) voltage, $\mathcal{I} = (2e^2/h)U$. Still further increase of M would reduce both the transmission peak and the current in the small- U limit. The above-discussed evolution with M is seen in figure 8 for small U . For $M = 1$, the device is effectively deep in the weak-coupling limit with well resolved peaks. For $M = 3$, the peaks located near $\omega = 0$ begin to merge and the current approaches values typical of the strong-coupling limit.

In order to obtain an estimate of the voltages and the currents in the usual units for these quantities we take $t_c = 2.5$ eV—a value typical of π -electron compounds [19]. With this value of $t_c = t_1 = t$ as our energy unit, we have $U = 10$ V for $eU/2t = 2$, an upper limit of our computations presented in figures 7, 8. This is a factor of 2 more than the experimental limit usually reached in molecular devices; see, e.g. [20]. For $t = 2.5$ eV, our unit current (i.e. $\mathcal{I} = 2et/h$) corresponds to $\mathcal{I} \approx 400$ μ A, which is a value comparable to the results of some *ab initio* calculations [3]. Experimental peak values of current are usually much smaller (about 3–5 orders of magnitude; see, e.g. [7, 21]), which suggests that the weak-coupling limit (see figure 8) describes most experimental data better. In the weak-coupling limit the computed current is very sensitive to the value of the coupling and varies like $\sim w^4$. This may give a possible explanation for the large scatter of the experimental data, with peak values of the current varying in the range 1 nA–1 μ A, depending on the molecules studied.

It should be remembered, however, that the present theoretical models do not take into account several effects which are likely to have significant impact on both the experimental values of current and the overall shape of the I - V curve. Among the most important ones, incoherent scattering due to phonons and the influence of random interactions with solvent particles (which are always present in break junction experiments) should be considered [7].

5. Concluding remarks

In our paper, the tight-binding model was used to describe the transmission in a molecular device for finite potential difference between the leads. We neglected all effects of electron correlations as well as inelastic scattering, whereas all processes of coherent scattering were treated exactly for a given geometry of the molecules and the leads.

For a wide class of polymeric chains it is possible to derive an analytical formula for the transmission $\mathcal{T}(\omega)$ for a finite bias voltage U . Our results may be used to study I - V characteristics of molecular devices using oligomers as bridging molecules. We found that the increase of the voltage leads to a non-uniform reduction of $\mathcal{T}(\omega)$. This shows the limitations of a rough modelling of the effects of U by a simple shift of the energy variable in the transmission function [4, 7].

In fact, the effects of finite bias voltage may be far more complicated in real systems than in our non-self-consistent model. For instance, we completely neglected a possible change of the electronic structure of the molecule in the electric field (i.e. Stark effect). The *ab initio* computations [3] showed that this effect may be important, especially in asymmetric molecules. Within the scheme presented, such effects can be modelled by assuming phenomenological forms of the potential drop within the molecule [16].

The results obtained here are based on the simple tight-binding model with one orbital per atom for both the molecule and the attached leads. This approximation has the usual

drawbacks of the π -electron theory of carbon-based molecules and neglects all details of the electronic structure beyond the close vicinity of the HOMO–LUMO energy levels. Including more orbitals per atom is possible within the conceptual framework used here and one could work out a multi-band extension of the transfer matrix approach for oligomeric chains of arbitrary length. In such a case our results should approach the ones obtained with the help of extended Hückel theory [5–7].

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Appendix

In this appendix we briefly present basic principles for solving the scattering problem for our molecular device with the help of the transfer matrix method. The molecule bridging between the two perfect semi-infinite leads may be considered by analogy with a defect in a single, infinite multichannel lead. Our solution is valid for hypercubic leads for $D = 1, 2, 3$, where the matrix t_μ describing hopping between the consecutive layers of the leads may be written as a unit matrix multiplied by a number (hopping parameter).

An electron with energy ω travelling in the lead may be described with a help of a stationary wavefunction

$$\Psi = e^{-i\omega t} \sum_j a_{\mu j}^\dagger \gamma_{\mu j} |0\rangle \quad (\text{A.1})$$

where the N^{D-1} -dimensional column vector γ_j ($j = 0, \dots, \infty$), includes electron amplitudes of the atoms in the j th layer of the lead, and the 0th layer is in contact with the molecule. The index μ refers here to the position ‘ahead of’ ($\mu = 1$) and ‘behind’ ($\mu = 2$) the defect.

A stationary solution of the Schrödinger equation for amplitudes $\gamma_{\mu j}$ in the leads may be written in a compact form using a transfer matrix:

$$\begin{bmatrix} \gamma_{\mu j+1} \\ \gamma_{\mu j} \end{bmatrix} = \begin{bmatrix} t_\mu^{-1}(\omega - H_\mu) & -I \\ I & 0 \end{bmatrix}^j \begin{bmatrix} \gamma_{\mu 1} \\ \gamma_{\mu 0} \end{bmatrix} = S_\mu^{-1} \begin{bmatrix} \Lambda_\mu^j & 0 \\ 0 & \Lambda_\mu^{-j} \end{bmatrix} S_\mu \begin{bmatrix} \gamma_{\mu 1} \\ \gamma_{\mu 0} \end{bmatrix}. \quad (\text{A.2})$$

In the second equality of equation (A.2), we reduced the transfer matrix to a diagonal form with a help of a similarity transformation defined with a $(2N^{D-1} \times 2N^{D-1})$ -dimensional matrix S_μ . In the case of the hypercubic lattices the matrix S_μ may be explicitly derived and written in a block-matrix form as follows:

$$S_\mu = \begin{bmatrix} S_\mu & S_\mu \\ S_\mu \Lambda_\mu^{-1} & S_\mu \Lambda_\mu \end{bmatrix}. \quad (\text{A.3})$$

The matrices S_μ are made up of eigenvectors of matrices H_μ and satisfy the relation

$$t_\mu^{-1}(\omega I - H_\mu) S_\mu = S_\mu (\Lambda_\mu + \Lambda_\mu^{-1}). \quad (\text{A.4})$$

The explicit formulae for $(N^{D-1} \times N^{D-1})$ -dimensional matrices S_μ are presented in section 2.

The solutions for the amplitudes in the leads depend on the boundary amplitudes $\gamma_{\mu 1}$, $\gamma_{\mu 0}$. To relate the amplitudes of incident, reflected and scattered electron waves on either side of the obstacle, we remove the amplitudes corresponding to atoms of the molecule from the Schrödinger equation by a procedure of elimination. Note that in this procedure we do not need to define explicitly a transfer matrix corresponding to the defected region, as is usually done

in applications of the transfer matrix method to the scattering problem in disordered systems (see e.g. [10, 13]). The calculations, which are otherwise similar to the ones presented in the literature [10, 13], lead to the formula for the transmission given in equation (3).

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