

Electrical conductance of molecular wires

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Received 4 February 1999

Abstract. Molecular wires (MW) are the fundamental building blocks for molecular electronic devices. They consist of a molecular unit connected to two continuum reservoirs of electrons (usually metallic leads). We rely on Landauer theory as the basis for studying the conductance properties of MW systems. This relates the lead to lead current to the transmission probability for an electron to scatter through the molecule. Two different methods have been developed for the study of this scattering. One is based on a solution of the Lippmann–Schwinger equation and the other solves for the t matrix using Schrödinger's equation. We use our methodology to study two problems of current interest. The first MW system consists of 1,4-benzene-dithiolate (BDT) bonded to two gold nanocontacts. Our calculations show that the conductance is sensitive to the chemical bonding between the molecule and the leads. The second system we study highlights the interesting phenomenon of antiresonances in MW. We derive an analytic formula predicting at what energies antiresonances should occur in the transmission spectra of MW. A numerical calculation for a MW consisting of filter molecules attached to an active molecule shows the existence of an antiresonance at the energy predicted by our formula.

1. Introduction

A molecular wire (MW) in its simplest definition consists of a molecule connected between two reservoirs of electrons. The molecular orbitals of the molecule when they couple to the leads provide favourable pathways for electrons. Such a system was suggested in the early 1970s by Aviram and Ratner to have the ability to rectify current [1]. Experimental research on MW has increased over the past few years looking into the possibility of rectification and other phenomena [2–9]. There has also been an increase in the theoretical modelling of MW systems [10–15]. For a comprehensive overview of the current status of the molecular electronics field see [16].

Theoretical studies of the electronic conductance of a MW bring together different methods from chemistry and physics. Quantum chemistry is used to model the energetics of the molecule. It is also incorporated into the study of the coupling between the molecule and the metallic reservoirs. Once these issues have been addressed it is possible to proceed to the electron transport problem. Currently, Landauer theory [17][‡] is used which relates the conductance to the electron transmission probability.

A molecule of current experimental interest as a MW is 1,4-benzene-dithiolate (BDT) [3]. It consists of a benzene molecule with two sulfur atoms attached, one on either end of the benzene ring. The sulfurs bond effectively to the gold nanocontacts and the conjugated π ring provides delocalized

electrons which are beneficial for transport. Two major unknowns of the experimental system are the geometry of the gold contacts and the nature of the bond between the molecule and these contacts. This paper attempts to highlight these important issues by showing how the differential conductance varies with bond strength.

For mesoscopic systems with discrete energy levels (such as MW) connected to continuum reservoirs, the transmission probability displays resonance peaks. Another potentially important transport phenomenon that has been predicted is the appearance of antiresonances [14, 19]. These occur when the transmission probability is zero and correspond to the incident electrons being perfectly reflected by the molecule. We derive a simple condition controlling where the antiresonances occur in the transmission spectrum. We apply our formula to the case of a MW consisting of an 'active' molecular segment connected to two metal contacts by a pair of finite π conjugated chains. In this calculation we show how an antiresonance can be generated near the Fermi energy of the metallic leads. The antiresonance is characterized by a drop in conductance. We find that for this calculation our analytic theory of antiresonances has predictive power.

In section 2, we describe the scattering and transport theory used in this work. Section 2.1 deals with Landauer theory. Section 2.2 outlines a method for evaluating the transmission probability for MW systems. Section 2.3 outlines our derivation of the antiresonance condition. In section 3, we present some calculations on BDT for different lead geometries and different binding strengths. Section 4 describes a numerical calculation for a system

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[‡] For a comprehensive review of Landauer theory and electron transport see [18].

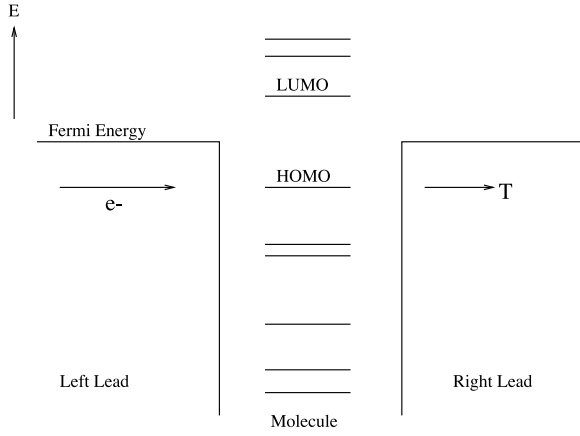


Figure 1. A schematic energy diagram for a MW. The leads couple to the energy levels of the molecule and electrons are incident from the left lead at its Fermi energy. They scatter through the molecule and have a transmission probability, T , to enter the right lead.

displaying antiresonances which are predicted by the formula in section 2. Finally we conclude with some remarks in section 5.

2. Transport theory

2.1. Landauer formula

We consider the transport of electrons through a molecular system by modelling it as a one-electron elastic scattering problem. The molecule acts as a defect between two metallic reservoirs of electrons. An electron incident from the source lead with an energy E , has a transmission probability $T(E)$ to scatter through the molecule into the drain lead. A schematic of the model system is shown in figure 1. By determining the transmission probability for a range of energies around the Fermi energy ϵ_F of the source lead, the finite temperature, finite voltage and Landauer formula can be used to calculate the transmitted current I as a function of the bias voltage, V , applied between the source (left lead) and drain (right lead)

$$I(V) = \frac{2e}{h} \int_{-\infty}^{\infty} dE T(E) \left(\frac{1}{\exp[(E - \mu_s)/kT] + 1} - \frac{1}{\exp[(E - \mu_d)/kT] + 1} \right). \quad (1)$$

The two electro-chemical potentials μ_s and μ_d , refer to the source and drain, respectively. They are defined to be, $\mu_s = \epsilon_F + eV/2$ and $\mu_d = \epsilon_F - eV/2$. The differential conductance is then given by the derivative of the current with respect to voltage.

2.2. t matrix method

We find the transmission probability $T(E)$ used in the Landauer formula, equation (1), by solving the Schrödinger equation directly for the scattered wavefunction of the electron. The electron is initially propagating in a Bloch wave in one of the modes of the source lead. The molecule will reflect some of this wave back into the various modes of the source lead. The molecule is represented by a discrete

set of molecular orbitals (MOs) through which the electron can tunnel. Hence, some of the wave will be transmitted through the molecule and into the modes of the drain lead. By finding the scattered wavefunction it is then possible to determine how much was transmitted, yielding $T(E)$.

We start with Schrödinger's equation, $H|\Psi^\alpha\rangle = E|\Psi^\alpha\rangle$, where H is the Hamiltonian for the entire MW system consisting of the leads and the molecule. $|\Psi^\alpha\rangle$ is the wavefunction of the electron propagating initially in the α th mode of the left lead with energy E . It is expressed in terms of the transmission and reflection coefficients, $t_{\alpha,\alpha'}$ and $r_{\alpha,\alpha'}$ and has different forms on the left lead (L), molecule (M), and right lead (R). The total wavefunction is a sum of these three, $|\Psi^\alpha\rangle = |\Psi_L^\alpha\rangle + |\Psi_M^\alpha\rangle + |\Psi_R^\alpha\rangle$, where

$$|\Psi_L^\alpha\rangle = |\Phi_+^\alpha\rangle + \sum_{\alpha'} r_{\alpha',\alpha} |\Phi_-^{\alpha'}\rangle \quad (2)$$

$$|\Psi_M^\alpha\rangle = \sum_j c_j |\phi_j\rangle \quad (3)$$

$$|\Psi_R^\alpha\rangle = \sum_{\alpha'} t_{\alpha,\alpha'} |\Phi_+^{\alpha'}\rangle. \quad (4)$$

In the above, $|\Phi_\pm^\alpha\rangle$ are forward/backward propagating Bloch waves in the α th mode, and $|\phi_j\rangle$ is the j th MO on the molecule.

We then consider our Hamiltonian in the tight-binding (or Hückel) approximation and use Schrödinger's equation to arrive at a system of linear equations in the unknown quantities, $r_{\alpha',\alpha}$, c_j and $t_{\alpha,\alpha'}$. We solve numerically for the reflection and transmission coefficients for each rightward propagating mode α at energy E in the left lead. The total transmission is then given by

$$T(E) = \sum_{\alpha \in L} \sum_{\alpha' \in R} \frac{v^{\alpha'}}{v^\alpha} |t_{\alpha',\alpha}|^2 \quad (5)$$

where v^α is the velocity of the electron in the α th rightward propagating mode. The sum over α' in the expression for T is over the rightward propagating modes at energy E in the right lead. With $T(E)$ determined the current and differential conductance can then be calculated using equation (1).

2.3. Antiresonance condition

The above section outlined a method for numerically evaluating the transmission probability for a MW system. We now focus on an interesting physical feature of the transmission probability, namely the occurrence of antiresonances. These are characterized by the perfect reflection of electrons incident on the molecule at a certain energy E . The basis of our analysis in this section will be the Lippmann–Schwinger (LS) equation applied to the scattering problem in a highly idealized model. It will lead to an analytic formula for $T(E)$.

Before we proceed further we wish to highlight a problem that arises in most quantum chemistry applications. In studying quantum systems, such as MW, which are composed out of atomic building blocks, it is customary to solve the problem by expressing the electron's wavefunction in terms of the atomic orbitals on the various atoms. A

problem that arises is that these orbitals are not usually orthogonal to each other. Including this nonorthogonality complicates the solution and so it is often neglected. In the analysis that follows we have utilized a transformation which removes the nonorthogonality and allows for a straightforward solution [19]. This transformation leads to an energy-dependent Hamiltonian which will play an important role in determining the presence of antiresonances.

The LS equation we consider has the form

$$|\Psi'\rangle = |\Phi'\rangle + G'(E)W^E|\Psi'\rangle. \quad (6)$$

Here $|\Psi'\rangle$ is the scattered electron wavefunction of the transformed Hamiltonian H^E . W^E couples the molecule to the adjacent lead sites. $|\Phi'\rangle$ is the initial electron state which is a propagating Bloch wave that is confined to the left lead. $G'(E) = (E - H_0^E)^{-1}$ is the Green's function of the decoupled system.

We consider the LS equation in the tight binding approximation and solve for $|\Psi'\rangle$. This gives us the value for Ψ_1 which is the value of the wavefunction on the first atomic site on the right lead. The transmission probability, T is simply $|\Psi_1|^2$. The result is

$$\Psi_1 = \frac{P\Phi'_{-1}}{[(1-Q)(1-R) - PS]} \quad (7)$$

where

$$P = G'_{1,1} \sum_j W_{1,j}^E G'_j W_{j,-1}^E$$

$$Q = G'_{1,1} \sum_j (W_{1,j}^E)^2 G'_j$$

$$R = G'_{1,1} \sum_j (W_{-1,j}^E)^2 G'_j$$

$$S = G'_{1,1} \sum_j W_{-1,j}^E G'_j W_{j,1}^E.$$

The sum over j is over only the MOs. In the above, $W_{1,j}^E = H_{1,j} - ES_{1,j}$ is the energy-dependent hopping element of H^E between the first lead site and the j th MO in terms of the hopping element of the original Hamiltonian H and the overlap S in the nonorthogonal basis. The Green function on the molecule is expanded in terms of its molecular eigenstates and this gives $G'_j = 1/(E - \epsilon_j)$ for the j th MO with energy ϵ_j . $G'_{1,1}$ is the diagonal matrix element of the Green function $G'(E)$ at the end site of the isolated lead.

Antiresonances of the MW occur where the transmission T is equal to zero. These occur at Fermi energies E that are the roots of equation (7), namely

$$\sum_j \frac{(H_{1,j} - ES_{1,j})(H_{j,-1} - ES_{j,-1})}{E - \epsilon_j} = 0. \quad (8)$$

Antiresonances can arise due to an interference between molecular states that may differ in energy, as is seen directly from equation (8). An electron hops from the left lead site adjacent to the molecule onto each of the MOs with a weight $W_{j,-1}^E$. It then propagates through each of the different orbitals and hops onto the right lead with a weight $W_{1,j}^E$. These processes interfere with each other and where they cancel (8) is satisfied and an antiresonance occurs.

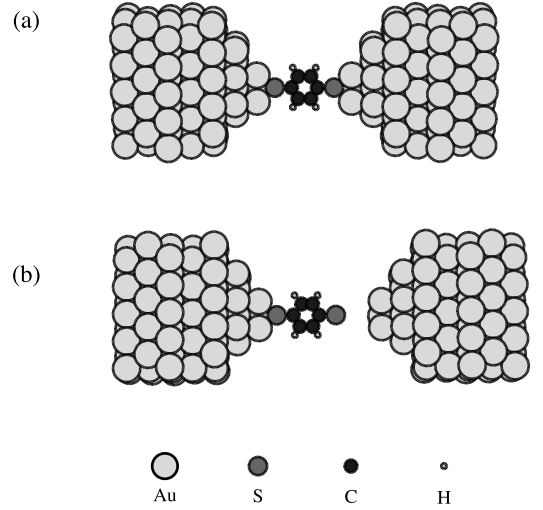


Figure 2. Atomistic diagram of gold (111) leads bonded to a BDT molecule. (a) Case of strong bonding to both leads. (b) Case of weak bonding to one of the leads.

Antiresonances can also arise solely from the nonorthogonality of atomic orbitals. This occurs when only a single MO k couples appreciably to the leads. Equation (8) then becomes $(H_{k,-1} - ES_{k,-1})(H_{1,k} - ES_{1,k}) = 0$. This equation gives two antiresonances. The nonorthogonality of two orbitals can actually stop electron hopping between these orbitals, which blocks electron transport and creates an antiresonance. This is a counterintuitive effect since one would normally expect orbital overlap to aid electron transfer between the orbitals rather than hinder it. Thus, the inclusion of orbital overlap leads to nontrivial physical consequences in the tight binding treatment of MW.

3. Conductance of BDT

For our first application, we apply our t matrix formalism to study the conductance of 1,4-benzene-dithiolate, a MW of recent experimental interest [3]. The molecule consists of a benzene molecule with the hydrogen atoms at the 1 and 4 positions replaced with sulfur atoms. The sulfur atoms act like alligator clips when they bond to the gold leads. We calculate the conductance of the MW geometries shown in figure 2. The gold leads are oriented in the (111) direction. Attached to the molecule are gold clusters which form the tips for the lead. Experimentally it has been found that sulfur atoms preferentially bind over the hollow sites formed on gold surfaces and so for our simulation the BDT molecule is bonded over the hollow site on each tip.

The strength of the bond between the molecule and the gold surface plays an important role in determining the transmission characteristics of the BDT MW. Isolated BDT has a discrete set of MOs with the highest occupied molecular orbital (HOMO) calculated to be around -10.5 eV and the lowest unoccupied molecular orbital (LUMO) found to be around -8.2 eV. These levels when bonded with the leads become part of the continuum of energy states that exist within the metallic reservoirs. For strong bonding they can become significantly altered as their chemical nature becomes mixed with the surface states of the gold tips. For

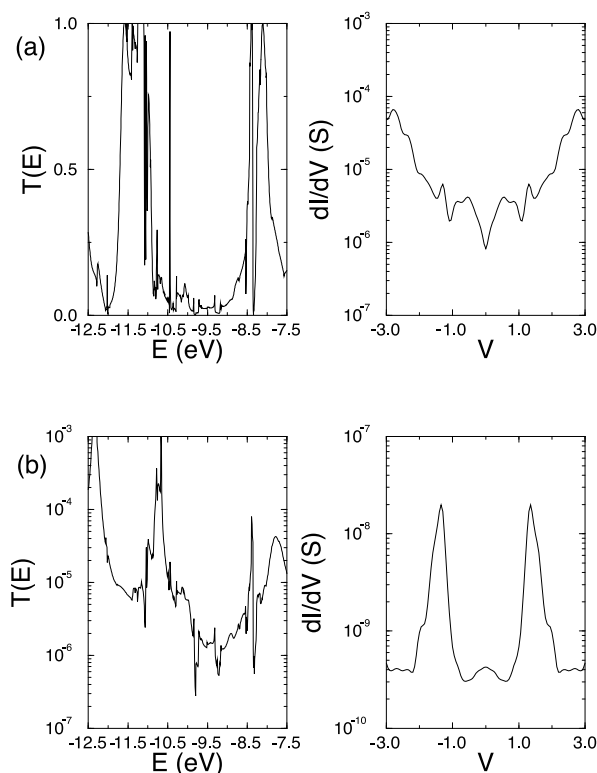


Figure 3. (a) Transmission and differential conductance for BDT bonded to gold (111) leads with strong coupling. (b) Weak coupling case.

weaker bonding the MOs retain the character of the isolated molecule.

We consider strong binding to the (111) leads first. The transmission diagram is shown in figure 3(a). There is strong transmission in the energy regions where the gold tip states have mixed with the molecular states. This occurs most prominently around -11.5 eV, where there exist resonances that can be connected with the HOMO states of the molecule. The HOMO and states around it in the isolated molecule have been mixed and lowered in energy due to the bonding to the lead. The other region of significant transmission is at around -8 eV, which is due to states connected with the LUMO of the BDT. The region in between has resonances that arise from those states that are complex admixtures of gold tip and molecule levels. The differential conductance was calculated with a Fermi level chosen at -10 eV which lies in the HOMO–LUMO gap. The molecule seems to be very conductive when attached strongly to the (111) oriented wide leads.

The magnitude of the conductance found in the above calculation exceeds that found experimentally [3]. We now consider the case of weak binding to see what effect it will have on the transmission. One lead is allowed to bond strongly to the molecule, while the other lead is pulled away from the molecule so as to be at nonbonding distances. The transmission and conductance diagrams for the weak bonding case are shown in figure 3(b). It can be seen that the transmission has gone down significantly in the region between -10.5 and -8 eV. There are also now strong resonances that correspond almost exactly with the isolated

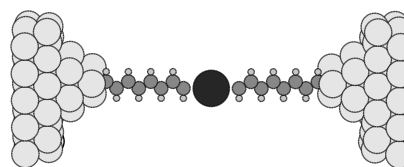


Figure 4. Atomistic diagram of leads attached to filter molecules and active molecule. The filter molecules consist of C_8H_8 chains. The active molecule contains two π levels which interact with the filter molecules. The leads are (111) gold.

molecular levels. The weaker coupling of the molecule to the contacts has lowered the transmission and the conductance. Because there are order of magnitude fluctuations in $T(E)$ the conductance is now quite sensitive to the selection of Fermi energy. Different conductance curves can be obtained if the Fermi energy is chosen to occur on or off resonance.

4. Antiresonance calculations

We now look at a MW system that displays antiresonances that are predicted by the formula derived in section 2. Equation (8) was derived for an idealized MW system where there was only one incident electron mode on the molecule. Thus in designing the MW system for the numerical study we tried to approximate the ideal system as closely as possible. The MW system we suggest consists of left and right π conjugated chain molecules attached to what we will call the ‘active’ molecule. The purpose of these conjugated chains is to act as filters to the many modes that will be incident from the metallic leads. For appropriate energies they will restrict the propagating electron mode to be only π like. This π backbone will only interact with the π orbitals of the molecule if they are bonded in an appropriated fashion.

An atomic diagram of our system is shown in figure 4. The leads are oriented in the (111) direction. The chain molecules are bonded to clusters of gold atoms that form the tips of the leads. The carbon atom nearest to the gold tip binds over the hollow site of the tip. The chains each have eight CH groups, which for the energies considered will only admit a π -like state to propagate along them. This gives rise to the filtering process mentioned above. The active molecule is chosen to have two σ states and two π states. The chain’s π -like orbitals will only couple to the two π states of the active molecule.

The Fermi energy for our gold leads is around -10 eV which lies within the π band. We would like an antiresonance to occur somewhere near this energy. The parameters entering equation (8) (i.e. the molecular orbital energies and their overlaps with the chains) are chosen so that one of the roots of the equation yields a value near -10 eV. The numerically calculated electron transmission probability for this model is shown in figure 5(a); an antiresonance is seen in the plot at the predicted energy of -10.08 eV. The differential conductance at room temperature was calculated using equation (1). Two different conductance calculations are shown in figure 5(b). The solid curve corresponds to a choice of Fermi energy of -10.2 eV. Because it lies to the left of the antiresonance in a region of strong transmission, the conductance is strong at 0 V. It then drops at around

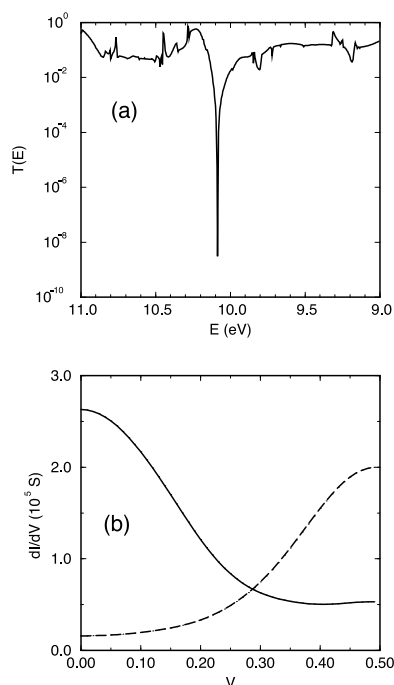


Figure 5. (a) Transmission diagram for an antiresonance molecule displaying a prominent antiresonance at -10.1 eV. (b) Differential conductance for $\epsilon_F = -10.2$ eV (solid curve) and $\epsilon_F = 10.0$ eV (dashed curve).

0.2 V when the antiresonance is crossed. The dashed curve was calculated using a Fermi energy of -10.0 eV. It starts in a region of lower transmission and thus the antiresonance suppresses the increase in current. After 0.2 V the large transmission to the left of the antiresonance is sampled and the current rises sharply. So in both cases the antiresonance has lowered the conductance. It is conceivable to think of utilizing more antiresonances in a narrow energy range to create a more pronounced conductance drop.

5. Conclusions

We have presented a theoretical study of the electrical conductance properties of molecular wires in the context of one-electron theory. A numerical method has been developed for the study of transport in molecular wires which solves for the transmission coefficients using Schrödinger's equation. It allows for the study of multimode leads attached to a molecule. We then proceeded to present a simple analytically solvable model which highlighted the interesting phenomena of antiresonances. A formula was derived that predicts Fermi energies for which a molecule with a given set of molecular energy levels should display antiresonances. It predicts two mechanisms by which antiresonances arise: one due to interference between the molecular orbitals and the other due to a cancellation of the effective hopping parameter.

As an application of our numerical method we studied the conductance of BDT. We examined the role of coupling by considering both the strong and weak regimes. For strong coupling it was found that the MW has regions of strong transmission. These regions occur at energies which differ from the isolated molecule's energy levels because of

state hybridization with the surface states of the gold tips. The conductance found for the strong coupling case was orders of magnitude greater than that found experimentally, although qualitatively it shared common features. In the weak coupling study the transmission displayed resonances at energies corresponding to those of the isolated molecule. The magnitude was also significantly down. This resulted in a conductance curve that was of the magnitude found in the experiment. Future work will need to focus on the electrostatic problem of the molecule within an applied electric field and the consequences of this in the context of Landauer theory, many-electron and possible polaronic effects within the MW.

Using our analytic formula for antiresonances, we were able to predict the occurrence of an antiresonance within a more sophisticated numerical study utilizing a molecule attached bridging a metal wire break junction. The model should also be of interest for future MW work since it introduces the idea of 'filter' molecules. Our numerical studies showed that π conjugated chain molecules act as effective mode filters to electrons incident from the metallic leads. The filter chains in our model reduced the number of propagating modes down to one, which was then coupled to the 'active' molecule. Our formula was derived on the assumption of only a single propagating mode, and for the 'active' molecule considered it was able to successfully predict the energy at which the antiresonance occurred. The antiresonance was characterized by a drop in the differential conductance.

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