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Theoretical study of electron transport along self-assembled graphitic nanowires

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Abstract. Electron transport through stacks of polyaromatic hydrocarbons is studied theoretically using the Landauer formalism. The polyaromatic hydrocarbons can be synthesized in many different sizes and can form molecular stacks with a varying number of molecules and with a rather strong π -overlap along the stack. This allows for a large flexibility in the nanostructure of these materials and makes it possible to study the variation in the conductance with a number of different factors: a near-linear increase in the conductance as a function of the number of atoms in the individual molecule is observed. Furthermore, the conductance drops exponentially with the number of molecules in the stacks, from which it follows that an increase in the intermolecular hopping results in an increase in the conductance which is proportional to the intermolecular hopping to the power of $2(N - 1)$, where N is the number of molecules in the stack.

1. Introduction

Macromolecular structures exhibit an amazingly wide range of electronic properties, ranging from metallic behaviour of some carbon nanotubes to semiconducting unsaturated hydrocarbons and insulating large-band-gap saturated hydrocarbon chains like polyethylene. Furthermore, most unsaturated hydrocarbon structures can be doped by means of charge transfer from a dopant. This further increases the possibilities of altering the electronic properties on the molecular scale, which is of interest as regards the possibility of switching the electronic properties. Also the formation of supermolecular structures is of great interest for tuning the electronic properties at the nanometre scale.

Molecular electronics has shown an enormous development during the last decade. At the level of individual molecules, there is a lot of ongoing activity, in particular using scanning probe microscopy as a technique to measure the conductance through individual molecules [1]. One class of molecules with a particularly large flexibility in terms of the size of the molecules, and as regards the possibility of doping and of forming supermolecular structures is the polyaromatic hydrocarbons (PAH); see figure 1. PAH can be synthesized in many different sizes, from single benzene units up to systems with 30–40 benzene units connected in the form of graphite flakes. Several studies on synthesis [2] and characterization [3–6] of PAH have been published recently. Contacting a PAH molecule on a graphite surface with a STM tip enabled Stabel *et al* [7] to measure the conductance through a single PAH molecule. Derivatives of the PAH with alkyl side chains replacing some of the hydrogens on the edge of the carbon flakes have also been synthesized [2]. Adding side chains makes the molecule soluble, and in

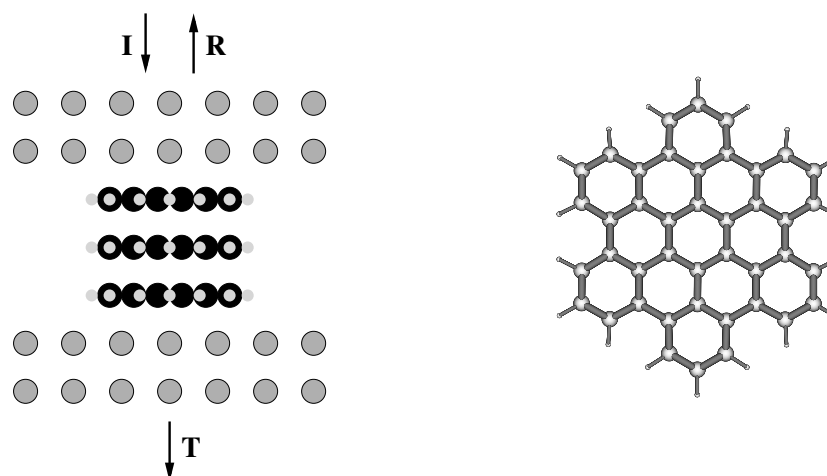


Figure 1. Left: a schematic view of the orientation of the contacts (grey circles) and a stack of three PAH molecules (black); the figure is not drawn to scale. The arrows symbolize the incoming (I), reflected (R) and transmitted (T) current. The geometry of $C_{42}H_{18}$ is shown on the right.

a certain temperature range [4] they form liquid crystals in which the planar graphitic flakes of the molecule stack on top of each other while the alkyl chains are molten and this insulates the π -electron systems of the different stacks from each others. This situation is very interesting for molecular wire (or nanowire) applications since electron transport can only occur along the π -stacks and the liquid crystal could be seen as many independent parallel nanowires.

The aim of this study is to investigate the electron transport along single stacks of PAH molecules. Using a simple one-electron tight-binding Hamiltonian combined with the Landauer formula, the conductance is calculated as a function of various parameters such as the size of the molecules, the number of molecules in a stack and the intermolecular interaction. Section 2 of this article introduces the model used to describe the electronic properties of the molecules and the method used to calculate the conductance. The results are presented and discussed in section 3 and a summary of the results is given in section 4.

2. Methodology

The conductance is calculated from the many-channel Landauer formula [8,9]

$$G = \frac{e^2}{\pi\hbar} \text{Tr}(t(E)t(E)^\dagger) \quad (1)$$

where $t(E)$ represents the amplitudes for electron transmission between the metallic channels for an electron with energy E . In the results presented below the prefactor is excluded, giving a dimensionless conductance, which is identical to the transmission probability denoted here by $T(E)$.

The conductance through a single PAH molecule or a stack of molecules connected by two metallic lattices on the top and bottom of the molecular structure is studied; see figure 1. To calculate the conductance, the Hamiltonians for the molecule and the metallic contacts have to be specified as well as the coupling between these parts.

The Hamiltonian of the molecule is described within the tight-binding (T.B.) approximation which only treats the π -electron system. The restriction to treating only the π -system

is well justified as has been shown repeatedly [10]. By choosing the on-site energy of the carbon atoms to be zero, the energy offset is determined. The intramolecular interactions are restricted to electron hopping between nearest-neighbour (n.n.) atoms only. The values of the hopping term, $t_{l',l}$, are calculated from a simple exponential relation with the C–C bond lengths $R_{l',l}$:

$$t_{l',l} = t_0 e^{-\alpha(R_{l',l} - R_0)} \quad (2)$$

where R_0 is the reference bond length, which is fixed to 1.40 Å for the systems discussed here. The values of the constants used were $\alpha = 2.5 \text{ \AA}^{-1}$ and $t_0 = -2.5 \text{ eV}$; these values have been shown to give good agreement for other conjugated systems. To obtain realistic values of $R_{l',l}$ in equation (2), the semi-empirical MNDO method [11] was used to calculate the geometry of single planar molecules without side chains. The intermolecular interaction is taken as a constant, t^\perp , connecting corresponding atoms on adjacent PAH molecules (see the discussion about stacking in section 3). The interaction used here is $t^\perp = 0.3 \text{ eV}$ which is close to that used for graphite [10], even though the intermolecular distances in the PAH stacks are approximately 5–10% larger than the interlayer separation in graphite [4].

Transmission through individual molecules or stacks of PAH involves the coupling between the metal contacts and the molecule as well as the transport along the molecular stacks. Here the focus is on the molecular properties and the interaction of the PAH. Therefore, the metal contacts are described in a simple way by cubic T.B. lattices. The lattice properties are described by a lattice parameter $a = 2.83 \text{ \AA}$, hopping t_l and an on-site energy ϵ_l . To obtain a finite number of equations, a finite lattice ($N \times N$) in the directions parallel to the metal surface is used (with hard boundary conditions). The coupling between the molecule and the two contacts is described with the same exponential dependence as the intramolecular interaction (see equation (2)) except that the coupling is not restricted to nearest neighbours. Note that the interaction between the contact and molecule is quite weak (see section 3) since the distance between the metal contacts and the stack of PAH is approximately twice the C–C bond lengths in the molecules.

The calculation of the transmission amplitudes is done in a similar way to that described by Cerdá *et al* [12]. By dividing the system into three parts, the two metal surfaces and the molecule, the wavefunction of the metal parts can be written as a linear combination of the known stationary solutions for in the metals. Special care is taken to include the closed decaying channels in the metal contacts. To obtain the transmission amplitude, an *ansatz* with unit flux incoming from one contact and unknown reflected and transmitted amplitudes is made. The Hamiltonians and interactions between the contacts and molecule give a set of linear equations for the transmittance and reflection amplitudes which was solved numerically using the Green function of the molecule. For details of this approach we refer the reader to Paulsson [13].

3. Results and discussion

The use of the Landauer formula together with a T.B. type of Hamiltonian has repeatedly proven valuable for calculating the conductance of conjugated molecular systems. This method requires fitting of some of the theoretical parameters in order to obtain quantitative results. Especially important is the strength of the interaction between the metal contacts and the molecule. Moreover, the results of this study have been checked to ensure that they are qualitatively unaffected by changes in the parameters that are not accessible from comparison with experimental data. Changes in the distance between the contacts and the closest molecule affect the size of the transmission while preserving the qualitative behaviour. In the results

shown below, this distance was set to 3 Å. The orientation of the PAH molecule relative to the metallic lattices, i.e. rotations around the normal of the planes, as well as the lattice parameter of the contacts were found to have negligible effects on the conductance. In the T.B. description of the contacts, the hopping between the metal atoms was set to $t_m = -2.5$ eV. Increasing this parameter decreases the density of states in the metal since its bandwidth increases; the decreasing density of states leads to a decrease in the conductance without affecting the qualitative behaviour. The size of the metallic lattice used was $11 \times 11 = 121$ atoms for which the conductance has converged for all molecules included in this study. Two different ways of stacking the PAH stacks were studied: A–A stacking in which the identical carbon atoms of consecutive molecules in the stack appear exactly on top of each other; and A–B–A–B stacking, which corresponds to the ordering of the basal planes in graphite. A–A stacking gives a larger effective interaction in the stacks than the A–B–A–B stacking. However, apart from this quantitative difference, the results are essentially identical for both types of stacking and only the A–A case is shown in the figures below.

One way of tuning the conductance of the PAH stacks is by varying the size of the molecule. In figure 2 the conductance through three different molecules, $C_{42}H_{18}$, $C_{60}H_{22}$ and $C_{84}H_{26}$, is shown. The decrease of the band gap when the size of the molecule is increased is clearly seen as a shift of the resonance tunnelling peaks towards the centre of the gap in the transmission spectra. Note that for the PAH molecules the band gap varies as $\simeq E_0/\sqrt{N}$ [14], where N is the number of benzene units in the molecule and E_0 is the band gap of benzene. The band gap thus decreases very slowly with increasing size of the molecules. Transmission at $E = 0$ is therefore a tunnelling process which leads to an exponential decrease of the conductance with increasing number of molecules in the stack. The asymmetry of the transmission spectra reflects the fact that the effective interaction between the contacts and the molecule depends on the wavefunctions of the molecular orbitals. The higher-energy molecular orbitals change phase between adjacent sites in the molecule more rapidly than the lower-energy molecular orbitals. The effective interaction with an atom in the contact will thus be lower for higher

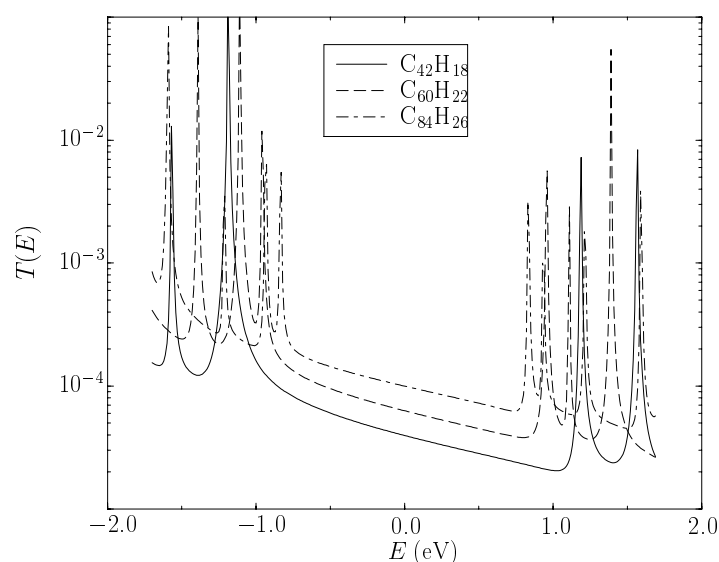


Figure 2. A log plot of the transmission as a function of energy for $C_{42}H_{18}$, $C_{60}H_{22}$ and $C_{84}H_{26}$. $E = 0$ corresponds to the Fermi energy of the neutral molecule.

energies since the atom interacts with sites of the molecule with different phases. This in turn results in lower transmission.

The conductance through the $C_{42}H_{18}$ molecule (with side chains) has been measured by Stabel *et al* [7]. In the experiment the current–voltage (I – V) characteristic of a single molecule on a graphite surface contacted with a STM tip was measured. The Fermi energy of an uncharged PAH is in our model $E = 0$. Placing a molecule on a surface can result in a charge transfer between the surface and molecule, which would change the Fermi energy of the molecule [15]. Negligible charge transfer is expected on graphite since the molecule is very similar to the surface. The turn-on voltage of the large non-linearity in the experiment corresponds well to the calculated band gap of 2.4 eV. However, charge transfer is also expected when large voltages are applied over the contacts. Large charge transfers will not only change the Fermi energy but also invalidate the tight-binding model used here; therefore only the linear low-voltage limit at around $E = 0$ will be discussed below. Comparing the experimental low-voltage conductance, where no charge transfer is expected, with our calculated data shows that the measured conductance is between one and two orders of magnitude lower than the calculated one. This discrepancy is due to the fact that our contacts do not describe a STM tip. The strength of interaction between the tip and the molecule is usually lower than that between the substrate and the molecule. In our work we have not made any effort to simulate this asymmetry in the coupling strength, which results in a lower total contact resistance as compared to the experimental value and therefore also a larger conductance.

Increasing the size of the molecule gives a wider area for electron transmission through the molecule. In a classical picture the current increases linearly with the area of the molecule. However, this study is quite far from this limit. Examining the dependence of the conductance as a function of the number of atoms in the PAH molecule shows that the increase is slightly larger than linear. In figure 3 the logarithm of the transmission versus the number of carbon atoms in the molecule is shown. The best linear fit to the data points has a slope of 1.28.

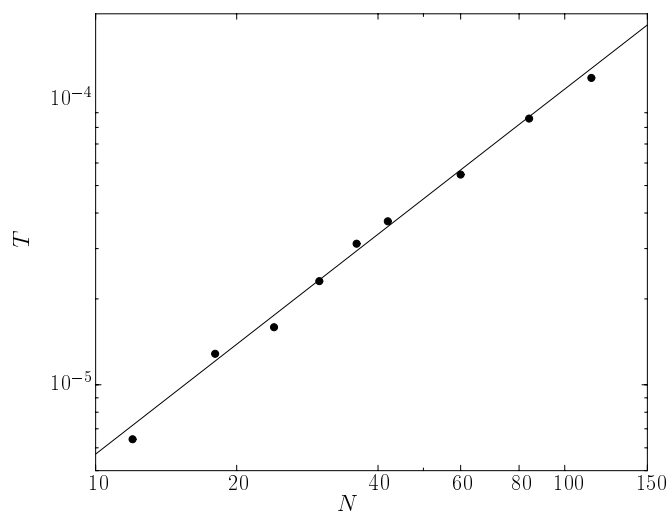


Figure 3. A log–log plot of the calculated transmission at $E = 0$ as a function of the size of the molecule. A best fit is shown as the full line; the slope of the line is 1.28.

The increase of the transmission as the size of the molecule is increased can be separated into two contributions which are described below. Theoretically the transmission can be seen as going through different channels, i.e. the eigenstates of the stack. Increasing the number

of atoms in the PAH molecule increases the number of channels. Studying the transmission through several different channels shows that the resulting transmission is determined by the interference effects of the channels. If the channels add up in phase—constructive interference—the transmission amplitude will increase linearly with the number of channels. Since the conductance is proportional to the absolute square of the transmission amplitude, constructive interference will give an increase in the conductance which is proportional to the square of the number of atoms. In contrast, destructive interference will give a transmission amplitude of zero. In this study many different channels are open in the metallic contacts connecting the molecule to the electron reservoirs; e.g. at $E = 0$ there are 81 open metallic bands. The phase change for a path of the electron through the molecule depends on the electronic properties of the molecule together with the effective coupling of the molecule to the metallic contacts, which in turn depends on the wavefunction of the channel in the metal. Thus the phase differences between different paths will vary depending on the channel used in the metallic lead. Therefore the interference effects will in this case, with many open channels in the metals, average out and give an increase of the conductance that is almost linear with the number of channels. The averaging effect was confirmed in numerical calculations using channels with random phase difference. Interference in the transmission has been studied in previous work by us [16] and the averaging is clearly shown in the work by Magoga and Joachim [17]. Another factor to consider is the variation in the band gap with the size of the molecule. As described above, the band gap decreases slowly when the molecular size is increased. Moving eigenstates (of the isolated molecule) closer to the Fermi energy increases the transmission through these states giving an additional small increase in transmission (at $E = 0$) as the size of the molecule is increased.

Calculations using different values of the strength of the interaction (t^\perp) between the PAH molecules shows that this parameter has a strong influence on the size of the transmission. The intermolecular hopping is exponentially dependent on the intermolecular distances and the ordering and overlap of the PAH in the stacks. Therefore it is sensitive to changes in several different factors, e.g. the type of side chains [4], temperature and type of substrate used. This is quite interesting as regards possible applications, since small changes in the environment of the stacks could give large changes in the conductance. In appendix A the theoretical dependence of the transmission probability on the intermolecular interactions in the non-resonant tunnelling limit is examined. Perturbation theory using t^\perp as the expansion parameter shows that the transmission probability behaves as $T \sim (t^\perp)^{2(N-1)}$ to the lowest order in t^\perp . Here N is the number of molecules in the stack and $N - 1$ therefore equals the number of intermolecular hoppings in the molecule. Note that the interaction, i.e. distance, between the contacts and molecules is not changed.

The transmission through stacks with two to five $C_{42}H_{18}$ molecules with intermolecular hopping strength between 0.05 and 1.0 eV was calculated; some of the data are shown in figure 4. As can be seen, the theoretical prediction is confirmed in the low- t^\perp limit. However, at the estimated strength of hopping between the PAH molecules $t^\perp = 0.3$ eV, the transmission starts to deviate from the lowest-order approximation. When more molecules are added to the stacks the numerical results, at $t^\perp = 0.3$ eV, show an increasing deviation from the lowest-order theoretical result giving a stronger t^\perp -dependence.

4. Summary and conclusions

The conductance through stacks of PAH has been studied using the Landauer formalism. Increasing the size of the molecule increases the conductance. This increase is composed of a small contribution from the decrease of the band gap together with the more important increase

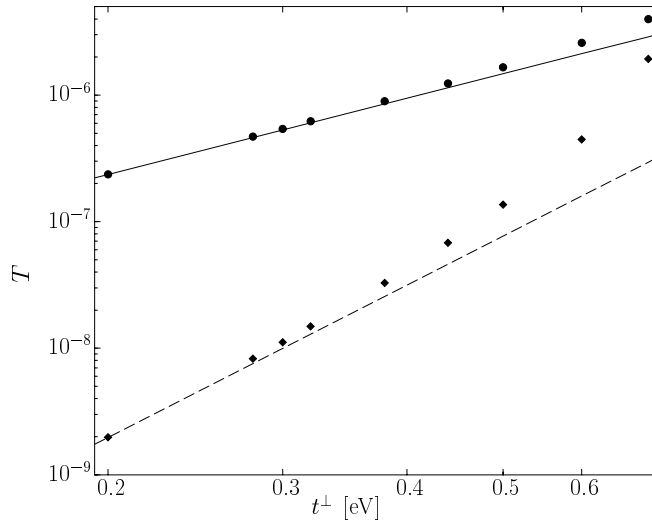


Figure 4. A log–log plot of the transmission versus hopping strength (t^\perp) for stacks of two and three $C_{42}H_{18}$ molecules. The solid line and dashed line correspond to the theoretical low- t^\perp limit with slopes of 2 (two molecules) and 4 (three molecules) respectively.

of the area of the molecule. The interference effect in the transmission through the molecule shows averaging, causing a nearly linear relation between the area, i.e. the number of carbon atoms in the molecule, and the conductance. The conductance through stacks of PAH is very sensitive to changes in the intermolecular coupling (t^\perp). In the low- t^\perp limit the transmission increases as $(t^\perp)^{2(N-1)}$ where N is the number of molecules. The numerical results show that for realistic values of t^\perp the conductance through stacks of PAH is slightly more sensitive to changes in t^\perp than this relation indicates. In this article we have pointed out the various possibilities for tuning the conductance of stacks of PAH. These types of stack are relatively easy to make and it would be possible, first, to experimentally verify the results presented here and, at a later stage, to develop large-area self-assembled structures of these stacks for nanoelectronics applications. For example, the strong non-linearity in the conductance versus intrastack intermolecular hoppings can be utilized in a 2-D pressure sensor with nm spatial resolution (cf. reference [18]).

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Appendix A. The weak-interaction limit

In the non-resonant tunnelling limit, the transmission amplitude is proportional [19,20] to

$$t_{nm} \sim \langle \psi_n | T_2 G_s T_1 | \psi_m \rangle \quad (\text{A.1})$$

where t_{nm} is the amplitude for transmission from channel m to n in the contacts, $G_s = (E - H_s)^{-1}$ is the Green function of the stack, $T_{1,2}$ the interaction between the molecule and the two contacts, and $\psi_{n,m}$ the wavefunctions corresponding to the channels m and n

respectively. The Dyson equation is used to expand the Green function of the stack with the interaction matrix between the PAH molecules (t) as the perturbation:

$$G_s = G_m + G_m t G_m + G_m t G_m t G_m + \dots \quad (\text{A.2})$$

where G_m is the Green function of the unperturbed molecule. In the T.B. approximation the matrix t only connects adjacent molecules. Therefore the lowest-order contribution to the transmission—see equation (A.1)—is the term with $N - 1$ number of t where N is the number of molecules in the stack. In our case $t_{nm} \sim (t^\perp)^{(N-1)}$ since t is the identity matrix times t^\perp .

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