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Conductance manipulation at the molecular level

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Abstract. Using a tight-binding model we have studied the electronic transmission through a C_{60} molecule sandwiched between a metal surface and a metal (scanning tunnelling microscope) tip. By simulating compression of C_{60} we have interpreted an experimental study of the variation of the conductance through a C_{60} molecule with an applied external pressure. We found that the observed increase in conductance cannot be explained in terms of the changes in the electronic structure of the C_{60} molecule alone. Effects related to the metal/molecule contact, i.e. the strength of the metal/ C_{60} interaction and the shape of the molecular orbitals in the tip, are in fact more important for the conductance. In view of this we discuss the importance of interference effects in the tip/molecule coupling.

1. Introduction

The development of molecular wires for electronic applications is an area of rapidly growing interest [1, 2]. Like in conventional solid-state electronics, control of two-terminal electric conduction by a third (external) signal is central in this type of application. So far, however, most studies have been focused on the understanding of how details in the molecular electronic structure affect the conduction along the wires [3–7]. There are several aspects of the molecular electronic structure which are of importance in this context—for instance, the distribution of the energy levels, in particular the size of the energy gap, the length of the molecules, and localization properties of the electronic states. Clearly, if the molecule supports extended states, the resistance will be very low when the Fermi energies of the metal contacts align with these energy levels. If, instead, the Fermi energy lies in an energy gap, the electronic transport is via a tunnelling process. In this case, the conduction depends crucially on the size of the gap, the strength of the coupling between the molecule and contacts, as well as on the length of the molecular system. For instance, it has been shown that the conductance drops exponentially with increasing molecular length [4, 8].

Another factor of importance for the conduction is the electronic coupling between the molecule and the metallic contacts. This aspect of the molecular device is less well studied. Gold contacts have been used experimentally as well as in theoretical modelling of the metal/molecule/metal structures [1, 2, 7, 9]. Some experimental studies also use copper and an STM tip of tungsten to make contact with the molecule [10]. Studies of metal/molecule contacts in the case of polymer light-emitting diodes (LEDs) have revealed the importance of the position of the Fermi energy relative to the valence and conduction bands of the

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semiconducting polymer [11]. A low-work-function metal, like Ca, has far better electron injection properties than, for instance, Al, since the Fermi energy of the low-work-function metal is close to the conduction band edge of the polymer. Therefore, polymer LEDs usually use different metals for the electron and hole injecting contacts [12]. With a suitable choice of contact material(s) in the metal/(single) molecule/metal devices, the energy of the injected electrons can possibly be tuned to energies for which the switching properties of a given molecular material are most efficient.

For given values of the Fermi energy of the metal contacts and the metal/molecule coupling strength it is evident that the energies of the molecular orbitals, in particular the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbitals, are of central importance for the conductivity across the molecular wire. Therefore, control of the conductivity through the molecule would be possible if the energies of the MOs could be varied. A very interesting example is the observation of varying conductance through a single C₆₀ molecule that is distorted by an external pressure [10]. Monolayers of C₆₀ molecules on copper are contacted with a STM tip (tungsten). The tip is approaching the surface and in this way compressing a single molecule. The distortions of the compressed molecule result in a reduction of the HOMO–LUMO energy separation. The current through the C₆₀ molecule was shown to increase by approximately two orders of magnitude when the C₆₀ molecule was compressed [10]. However, as shown here, the increase caused by the reduction in the HOMO–LUMO gap can only account for a negligible part of the increase; the major effect is caused by a change in the coupling between the metal and molecule.

In the papers by Joachim *et al* [13,14] the conductance through a C₆₀ molecule sandwiched between a gold surface and a STM tip is calculated using the extended Hückle molecular orbitals approximation. The calculations of the conductance for the compressed molecule are in agreement with experiments. Linear $I(V)$ characteristics obtained experimentally at low bias voltages are explained from the lack of molecular orbitals around the Fermi energy.

In this paper we focus on three aspects of the increase of the conductance: the compression of the molecule, the description of the molecule/contact coupling especially at a point of high symmetry and the strength of this coupling. We present a tight-binding model that accounts for the compression of the C₆₀ molecule. The model, which is described in section 2, involves optimization of the geometries of the compressed molecule, calculation of hopping integrals from the optimized geometry and, by using a Green function technique, calculation of the conductance through the molecule. Results from the conductance calculations are presented in section 3 followed by a summary and description of the outlook for this type of approach in section 4.

2. Methodology

The conductance is calculated from the many-channel Landauer formula [15, 16]:

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

where $t(E)$ represents the amplitude for electron transmission between the metallic channels for an electron with energy E . In the results presented below we have excluded the prefactor; this results in a dimensionless conductance, which is identical to the transmission probability.

To calculate the conductance we have to specify the Hamiltonians for the molecule and the metallic contacts as well as the coupling between these parts. The Hamiltonian of the molecule is described within the tight-binding approximation. It only treats the π -electron system with a basis of orthogonal atomic orbitals. Calculations of the conductance by Chavy

et al [17] show that the main part contributing to the conductance comes from the π -electrons and only a very small part from the σ -electrons. The restriction to treating only the π -system is therefore well justified. The intermolecular interactions are restricted to electron hopping between nearest-neighbour (n.n.) atoms only:

$$H = \sum_{l',l \in (\text{n.n.})} |l'\rangle t_{l',l} \langle l| + \text{h.c.} \quad (2)$$

The values of the hopping term, $t_{l',l}$ constitute a crucial parameter in this study since they will change as a result of the geometrical changes caused by compression of the molecule. Here we adopt a simple exponential relation between the value of the hopping integral $t_{l',l}$ and the C–C bond length $R_{l',l}$

$$t_{l',l} = t_0 e^{-\alpha(R_{l',l} - R_0)}. \quad (3)$$

R_0 is the reference bond length, which is fixed at 1.40 Å for the C_{60} system discussed here. It is important to use realistic values of $R_{l',l}$ in equation (3). We have used the semi-empirical AM1 method [18] to calculate the geometry of the C_{60} molecule. First, the equilibrium structure of C_{60} is determined. The icosahedral symmetry results in hexagon planes facing each other on opposite sides of the carbon cage. The distance between such hexagons was optimized to 6.52 Å. To simulate compression, we fixed this distance at 5.52 Å instead, and let all other geometrical parameters adjust to this deformed structure. The largest individual change in a bond length relative to the equilibrium structure was 0.043 and the increase in total energy was 171.0 kcal mol⁻¹. We have also studied compression in other directions by fixing the distance between opposite pentagons, single bonds, double bonds and atoms but with qualitatively the same results as in the hexagon case; however, in this paper we will only discuss the case with the hexagons since a simpler model was used for the metal surface in the other cases.

Using the optimized bond lengths for the undistorted C_{60} , which were optimized to 1.464 Å and 1.385 Å for the long and shorts bonds, respectively, we determine t_0 and α (see equation (3)) by adjusting these parameters to fit the experimentally obtained gap and bandwidth energies [19]. We found that the values $t_0 = -2.5$ eV and $\alpha = 2.0$ Å⁻¹ reproduced quite well the electronic spectrum of C_{60} . The gap between the HOMO and the LUMO is 2.2 eV and the total width of the π -electronic structure 13.1 eV. These values are close to the experimental values of 2.3 eV and 14–15 eV, for the band gap and π -bandwidth, respectively, obtained from photoemission studies [19] of solid C_{60} .

Transmission through the C_{60} involves the coupling between the metal contacts and the molecule as well as the transport through the molecular system. Here the focus is on the changes in the molecular properties and in the coupling to the tip. Therefore, the metal surface is described in a simple way as a cubic tight-binding lattice. The lattice properties are described by a hopping t_l and an on-site energy ε_l . To get a finite number of equations we use a finite lattice (10 × 10) in the directions parallel to the metal surface (with hard boundary conditions). The metal tip is modelled by a 1D metallic wire, using the same hopping t_l and ε_l as for the metal surface.

The coupling between the molecule and the two contacts is described in terms of hopping between the top/bottom hexagons of the C_{60} molecule and the atoms of the metal contacts. To have a realistic model of the metal surface we want to model a metal surface with many open channels for transport. We studied various different ways of connecting the molecule to the surface but there were very small differences in the calculated transmission spectrum; thus we only present results for the coupling between the molecule and the surface as described by figure 1. The value of the hopping were t_{lm} for the atoms on top of each other and $t_{lm}/2$ for the other bonds.

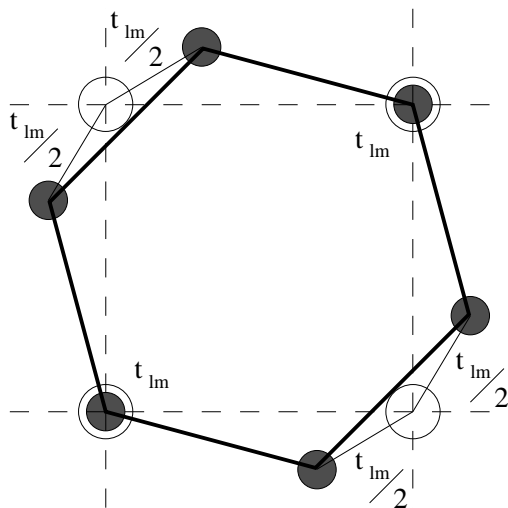


Figure 1. Coupling between the C_{60} molecule and the metal surface. Large circles: the atoms of the surface; and grey circles: the atoms of the bottom hexagon of the molecule. The coupling strength is indicated by t_{lm} and $t_{lm}/2$.

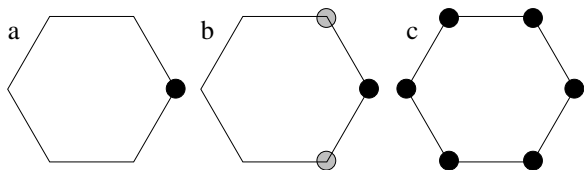


Figure 2. The three different ways of coupling the C_{60} molecule and the metal tip used in this work. Black circle: coupling t_{lm} ; and grey circle: coupling $t_{lm}/2$.

Three different ways of connecting the STM tip to the hexagon on top of the C_{60} were studied; see figure 2. The end site of the 1D wire modelling the STM tip is coupled to the atoms of the hexagon, with a coupling strength of t_{lm} for the black circles and $t_{lm}/2$ for the grey circles. The three different of coupling geometries shown in figure 2 could be considered as an approximate way of simulating different structures and/or orientations of the tip relative to the top hexagon of the C_{60} molecule. In a simulation of the measured conductance, the best fit is probably obtained for a combination of these three (or more) cases. The aim of the present study is, however, to point out the effects of using different contact geometries and we will therefore discuss the results for the various cases separately.

The calculation of the transition amplitudes is done following Credá *et al* [20]. By dividing the system into three parts, the metal surface, the molecule and the metal tip, we can write the wavefunction of the metal parts as a linear combination of the known stationary solutions for the metals, with special care taken to include the closed decaying channels in the metal surface. To obtain the transmission amplitude we formulate an *ansatz* with unit flux incoming from the tip and unknown reflected and transmitted amplitudes. The Hamiltonians and the coupling give a set of linear equations for the transmittance and reflection amplitudes which were solved numerically using the Green function of the molecule. For details of this approach we refer the reader to Paulsson [21].

3. Results and discussion

The dimensionless conductance, $T(E)$, is calculated as a function of the (Fermi) energy of the electron which is emitted from the metal contact into the molecule. It is assumed here that the applied electric field is small, which is necessary in order for our model to be valid. In this situation, we can assume that the variations in E correspond to changes in the Fermi energy

of the metal contacts. A given Fermi energy could, in our simple model, be obtained for a variety of combinations of the parameter ε_l and the band filling (k_F). We have studied the conductance as a function of E (or E_F) when E is related to ε_l (with k_F fixed) as well as for E related to k_F (with ε_l fixed). This corresponds to moving the metallic bands (k_F fixed) or varying the band filling (ε_l fixed). For bandwidths of the metals greater than or of the order of the molecular band width, i.e., for $t_l \gtrsim t_0$ the differences between these two cases are small in the energy range $\pm t_0$ around the centre of molecular electronic band. The differences found are mostly caused by finite-size effects of the lattice that we have used to model the surface. The data shown here are for the case of fixed k_F where there are no finite-size effects. Note that for Fermi energies outside the C_{60} HOMO–LUMO gap the molecule will be charged, which most probably will affect the conductance properties in a way that cannot be described by a simple tight-binding Hamiltonian; however, since the size of the conductance inside the gap is controlled by the resonances outside the gap, we have chosen to plot an energy range including the resonances outside the gap. Also the Fermi level of most metals that are used in this context [11] fall in the energy region of the electronic gap of C_{60} . The results presented below are for the case of $t_l = -2.0$ eV, $\varepsilon_l = E$ (the centre of the conduction band of the metal aligns with the energy of the incoming electron) and the lattice size is 10×10 . We have also used different values of the parameter t_l . The main effect of this is an overall increase in the conductance as t_l decreases, which is understood from the fact that the density of states in the metal contacts increases with decreasing t_l .

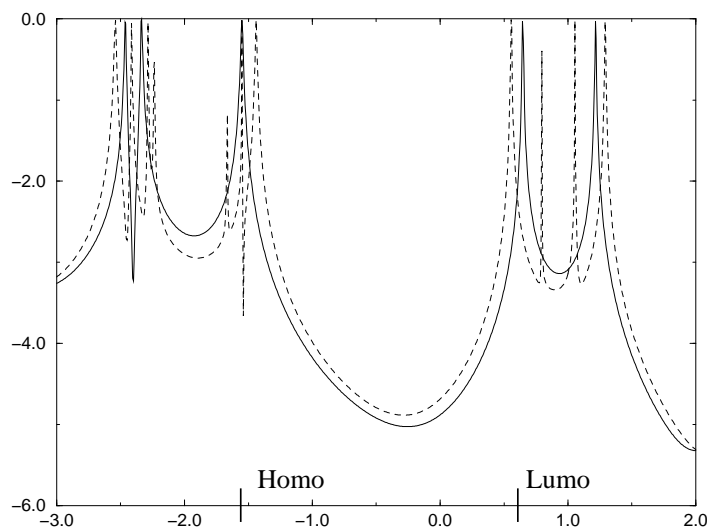


Figure 3. The logarithm of the dimensionless conductance for C_{60} : ground state (solid curve); compressed by 1 Å (dashed curve). The tip is contacted with the molecule as in figure 2(a).

$T(E)$ is shown in figure 3 for C_{60} in its equilibrium state (solid curve) and compressed by 1 Å (dashed curve). The data presented in figure 3 correspond to the case for which the tip couples to one site of the C_{60} molecule (see figure 2(a)), and the molecule/metal hopping is in these calculations set to $t_{lm} = -0.3$ eV.

The effect of distorting the C_{60} molecule is observed as a shift in the conductance peaks into the band-gap region of the undistorted system. From the calculations it is seen that the fivefold-degenerate HOMO level at -1.55 eV of the uncompressed molecule is split as a result of the compression into a doubly degenerate level at -1.66 eV, one unaffected at -1.55 eV

and a doubly degenerate level at -1.44 eV. In the same way, the threefold-degenerate LUMO at 0.65 eV is split into a doubly degenerate level at 0.56 eV and one level at 0.79 eV. Around the new eigen-energies, the increase in the conductance is large, up to a factor of 100. In the mid-gap region, however, the conductance of the compressed structure is only weakly enhanced as compared to the uncompressed structure. At -0.55 eV the gain is only 1.34 times. Clearly, this small increase of the conductance due to the change of the geometry of the C_{60} cannot explain the experimental results that showed an increase of approximately two orders of magnitude [10].

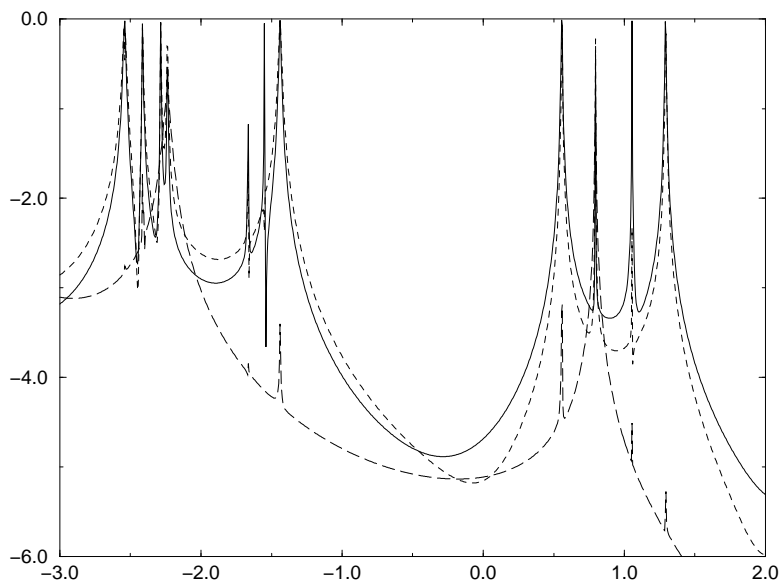


Figure 4. The logarithm of the dimensionless conductance for the compressed C_{60} ; solid, dashed and long-dashed curves correspond to coupling from the tip to one, three and six atoms of the molecule as described in figures 2(a), 2(b) and 2(c), respectively.

One important factor related to the conductance through a molecule is how the tip contacts the molecule. To investigate the effect of the contact geometry we have calculated the conductance for three different cases (see section 2). The calculated conductance through the compressed C_{60} is shown in figure 4 for the three cases, contact from the tip to one atom in the molecule (solid curve), three atoms (dashed curve) and all six atoms (long-dashed curve), respectively. The cases of contacting one and three atoms show the same qualitative behaviour; transmission resonances occur at levels associated with the HOMO and LUMO. However, when the tip contacts all six atoms in the top hexagon of the C_{60} molecule the resonances at the HOMO levels and the lowest LUMO level at 0.56 eV disappear almost entirely. Exactly the same behaviour occurs in the case of the uncompressed molecule. We believe that the small peaks in the figure are caused by deviations from the ideal symmetry of the molecule induced by tiny numerical errors in the geometry optimization of the compressed C_{60} molecule. We calculated the coupling matrix element connecting the tip and molecular orbitals for the compressed molecule for the case of coupling to all atoms in the top hexagon of the C_{60} molecule. This matrix element is almost zero for the HOMO and the two LUMO levels at 0.56 eV showing that the suppression of the resonance tunnelling is caused by destructive interference at the tip/molecule coupling. This interference effect clearly shows the importance of the tip/molecule interaction in calculations of the conductance through a molecule, especially

at symmetry points.

An STM tip of the type used in the experiment of Joachim and Gimzewski [10] cannot contact totally symmetrically with the C_{60} molecule. The suppression of the resonance peaks in the conductance will not be as complete as in the results obtained here (figure 4, long-dashed curve). The coupling between the tip and molecule is a combination of the three cases shown in figure 4 and the conductance spectrum would therefore be a mixture of the three curves. Another factor that has not been investigated is the possibility of several open channels for transport in the tip which should also be considered in a realistic model of the tip/molecule interaction. This lies, however, outside the scope of this work, in which we try to point out the effects of using different contact geometries.

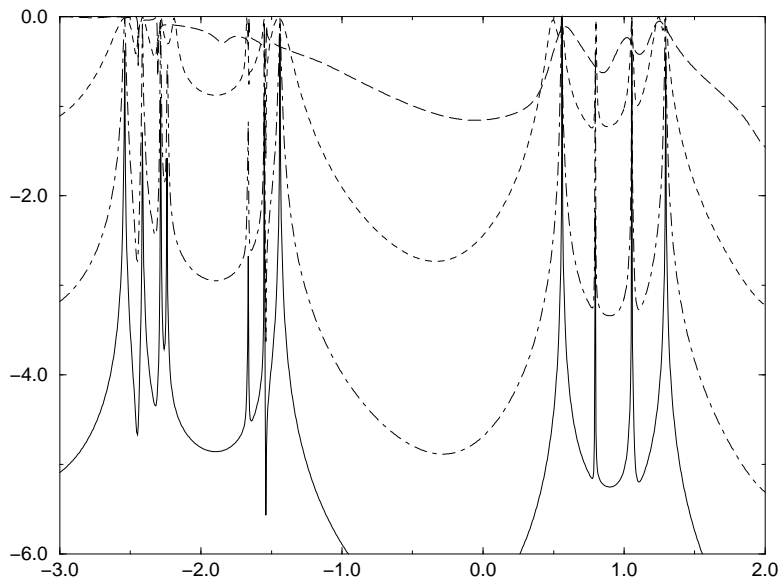


Figure 5. The logarithm of the dimensionless conductance for the compressed C_{60} ; $t_{lm} = 0.1, 0.3, 1.0$ and 3.0 eV for the solid, dot-dashed, dashed and long-dashed curves, respectively.

Since the STM tip is pressed onto the C_{60} molecule, the electronic coupling both at the tip/molecule interface and at the molecule/surface interface is likely to increase. To investigate the effect of changes in this coupling strength we performed calculations with $t_{lm} = -0.1, -0.3, -1.0$ and -3.0 eV. The results are shown in figure 5 (solid, dot-dashed, dashed and long-dashed curves, respectively). The increase of the conductance behaves as t_{lm}^4 for the lower values of the hopping, as can be expected in the gap from simple considerations [20]. For large coupling strength, i.e. $t_{lm} = -3.0$ eV, the interactions between the contacts and molecule are so strong that the molecule loses its identity. The energy spectrum is broadened and shifted; the conduction can no longer be considered as resonance tunnelling through eigenstates of the isolated molecule. This large coupling is however unrealistic for the system considered here.

Unfortunately, at this level of theory we are unable to determine quantitatively how large the increase of t_{lm} due to compression actually is. Assuming that a relation similar to equation (3) is valid also for the metal/molecule hopping, an increase in t_{lm} by a factor of 3.33, such as that between the middle curves shown in figure 5, corresponds to a decrease in the distance between the tip and the C_{60} molecule by 0.60 \AA and an increase of the conductance of 123 times. Such a change of the metal-to-molecule distance is quite realistic when the STM tip is pressed onto the C_{60} molecule. It is notable that the conductance increase as a result of

this effect is considerably higher than that resulting from distorting the C₆₀ molecule, and this represents the major factor governing the change in the conductance through the molecule.

4. Summary and conclusions

The electron transmission through uncompressed and compressed C₆₀ molecules has been discussed. In the case of compressed C₆₀, the effect of the compression on the electronic structure of the molecule is quite small and cannot explain the large increase in conductivity that was observed experimentally, about 100 times. We argue here that the main part of the increase in conductivity comes from the increased metal/molecule coupling which increases the conductance as t_{lm}^4 .

Interference effects associated with the tip/molecule contact have been shown to affect the conductance spectra; destructive interference for the highly symmetrical C₆₀ molecule removes some of the resonant tunnelling peaks in the conductance. The study of interference effects in other systems would be very interesting, especially in molecules that allow for long separated paths for the wavefunction. Distortions of the molecule lead to changes in the interference pattern, which can cause large shifts in, for instance, the energy corresponding to the destructive interference. This type of feature should be further investigated in the context of tunnelling through single molecules.

Acknowledgments

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