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2008 J. Phys.: Condens. Matter 20 022203

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Conformation dependence of molecular conductance: chemistry versus geometry

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Received 31 August 2007, in final form 26 October 2007

Published 6 December 2007

Online at stacks.iop.org/JPhysCM/20/022203

Abstract

Recent experiments by Venkataraman *et al* (2006 *Nature* **442** 904) on a series of molecular wires with varying chemical compositions revealed a linear dependence of the conductance on $\cos^2 \theta$, where θ is the angle of twist between neighbouring aromatic rings. To investigate whether or not this dependence has a more general applicability, we present a first-principles theoretical study of the transport properties of this family of molecules as a function of the chemical composition, conformation and the contact atom and geometry. If the Fermi energy E_F lies within the HOMO–LUMO (highest occupied molecular orbital–lowest unoccupied molecular orbital) gap, then we reproduce the above experimental results. More generally, however, if E_F is located within either the LUMO or the HOMO states, the presence of resonances destroys the linear dependence of the conductance on $\cos^2 \theta$ and gives rise to non-monotonic behaviour associated with the level structure of the different molecules. Our results suggest that the above experiments provide a novel method for extracting spectroscopic information about molecules contacted to electrodes.

(Some figures in this article are in colour only in the electronic version)

Single-molecule electronics poses many fundamental challenges for chemistry, physics and engineering, partly because a molecule attached to metallic electrodes is a quantum object that lives between the traditional disciplines of chemistry and physics. Challenges also arise, because many electrical properties of single-molecule devices are exponentially sensitive to changes in the environment and to details of the contact to electrodes. As a consequence, experiments using mechanically-controlled break junction techniques (MCBJ) [1] and scanning tunnelling microscopy (STM) [2, 3] yield broad distributions of measured transport properties, corresponding to slightly different attachments of molecules and in some cases, to environmental fluctuations [4, 5]. Given these sensitivities, it is remarkable that systematic experimental studies can yield clear trends associated with generic molecular features. One such example is a study of the effect of tilting the angle of contact between the long axis of a molecular wire and the plane of the locally-flat electrode [6]. Other examples are studies of

single-molecule electron transport as a function of molecular conformation [7–10].

While both of the above studies reveal that geometry plays an important role in controlling electron transport through single molecules, the experiments of [9] contain an even stronger suggestion, namely that for the set of molecules studied, changes in chemical composition are irrelevant. In these experiments, each molecule in the chosen series, (see figure 1), possessed two phenyl rings linked by a single carbon-carbon bond. Different chemical groups on the molecules caused the static angle of twist θ to vary from molecule to molecule. The highest conjugation and therefore the highest conductance is expected when the two rings lie in the same plane (i.e. $\theta = 0$). However, when the rings are rotated relative to each other, the overlap between the π orbitals decreases and the electrical conductance follows a $\cos^2 \theta$ law. This simple dependence on geometry is remarkable, since different chemical side groups were used to produce different angles.

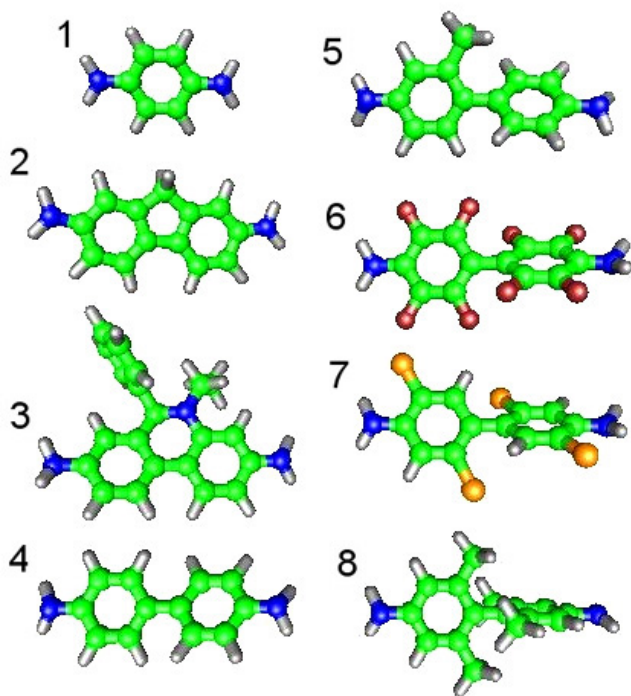


Figure 1. GGA-relaxed configurations of all molecules studied in this work capped with NH_2 . The dark vertex in the backbone of molecule 3 corresponds to N and the side groups of molecules 6 and 7 (other than H) correspond to F and Cl atoms, respectively.

In other words, it appears that chemistry is irrelevant and geometry is everything.

In this article, we aim to understand whether or not the dominance of geometry over chemistry can be widely expected or if this is a peculiar property of the set of molecules measured. Close inspection of the measured conductances in [9] reveals that they do not follow a perfect $\cos^2 \theta$ law and it is of interest to understand these deviations. The influence of the chemical composition can be separated in two parts. On the one hand, different atoms or molecular groups can be attached to the aromatic rings to produce a desired angle. These include hydrogen atoms, alkanes, other aromatic chains, nitrogen, fluorine and chlorine atoms. Such groups define the ground-state angle θ , which can vary between 0 and almost 90° . On the other hand, it is also possible to employ different end atoms, which attach the molecules to the leads. In the experiments, Venkataraman *et al* [9, 11] used molecules capped with either thiol (SH) or amino groups (NH_2) and found that nitrogen termination gave more reproducible results.

In what follows, we present a theoretical analysis of the structural configurations and transport properties of a series of molecules shown in figure 1, with thiol or amino end-groups. Results were obtained using the SIESTA implementation of DFT [12], which employs norm-conserving pseudopotentials and linear combinations of atomic orbitals¹. To treat

¹ We employed double zetas and polarization orbitals (DZP) to perform the structural relaxations. However, due to the fact that the transmission coefficients and the value of the conductance at the Fermi level converge very fast with the basis set we used a single-zeta (SZ) to obtain the transport characteristics, but we also made some tests with DZP. The real space grid was defined with a plane wave cutoff of 200 Ryd. The coordinates were relaxed until all forces were smaller than $0.02 \text{ eV } \text{\AA}^{-1}$.

exchange and correlation we used the generalized gradient approximation (GGA) [13], but we also made some tests with the local density approximation (LDA) [14], which allowed us to check the influence of the energy functional on structural and transport properties². Transport properties were calculated with the SMEAGOL code [15], which is interfaced to SIESTA and self-consistently computes the charge density, the electron-transmission coefficients and the I - V characteristics³.

To find the most stable structure we started from a twisted configuration, with an angle between 0 and 90° , and then allowed the molecule to freely relax. Since the presence of local minima could have prevented the rings from rotating to the most stable configuration, we used various initial angles to ensure that we reached the absolute minimum. $\theta = 0$ corresponds to a meta-stable configuration for most of the molecules. For other starting angles we found that the molecules always relaxed to the most stable configuration. Table 1 shows the ground-state angles calculated with LDA and GGA. Both functionals give similar results, although in most cases the LDA underestimates the angle. Both sets of results compare well with previous GGA values, computed in [9]. Table 1 also shows the dependence of θ on the end-groups and reveals that the end group can change θ by up to 15%.

We used the relaxed conformation of the pristine molecule as a starting point to compute the transport characteristics between fcc (111) gold electrodes. We assumed that the protecting hydrogens of the amino and thiol groups were lost when the molecules were attached and the angle between the molecule and the surface was 90° . We carefully determined the distance between the molecule and the gold leads by studying the energy as a function of the distance of a simplified molecule composed of a benzene attached to only one N or S on top of a (111) gold slab made of 5 layers⁴. With this distance and the molecule in its ground-state conformation⁵, we calculated the transmission coefficient $T(E)$ for electrons of energy E passing through the device.

The transmission coefficients of all molecules between gold (111) electrodes computed with GGA are shown in

² The optimized molecular geometries can be slightly different depending on the exchange-correlation functional, with the LDA/GGA tending to underestimate/overestimate distances and angles. However, the general shape of the transmission coefficients around the Fermi level and the zero-bias conductance are very similar in both cases.

³ The system was divided in three parts: left lead, right lead and extended molecule (molecule plus part of the leads modified by the presence of the molecule and the surfaces). The unit cell of the leads was made of three slices of fcc gold grown along (111) with 9 atoms per slice. We also used periodic boundary conditions and 4 k -points along the perpendicular directions to avoid spurious peaks and gaps in the transmission coefficients.

⁴ This approach is based on the assumption that the most important part in the molecule which determines the contact distance is that which is closest to the surface, i.e. the contact atom and the atom attached to it, which in all these molecules is the same. The rest of the molecule can also produce some differences, but since in all cases the central one or two rings are aromatic and therefore electronically very similar, such differences are expected to be rather small. Apart from that, we also found that the conductance around the Fermi level does not change when the distance between the molecule and the surface is slightly modified [16].

⁵ We have verified with molecule 1 that the transmission coefficients are practically identical when the coordinates of the isolated molecule are relaxed in the presence of the electrodes. This agrees with a previous work of Stokbro *et al* [17].

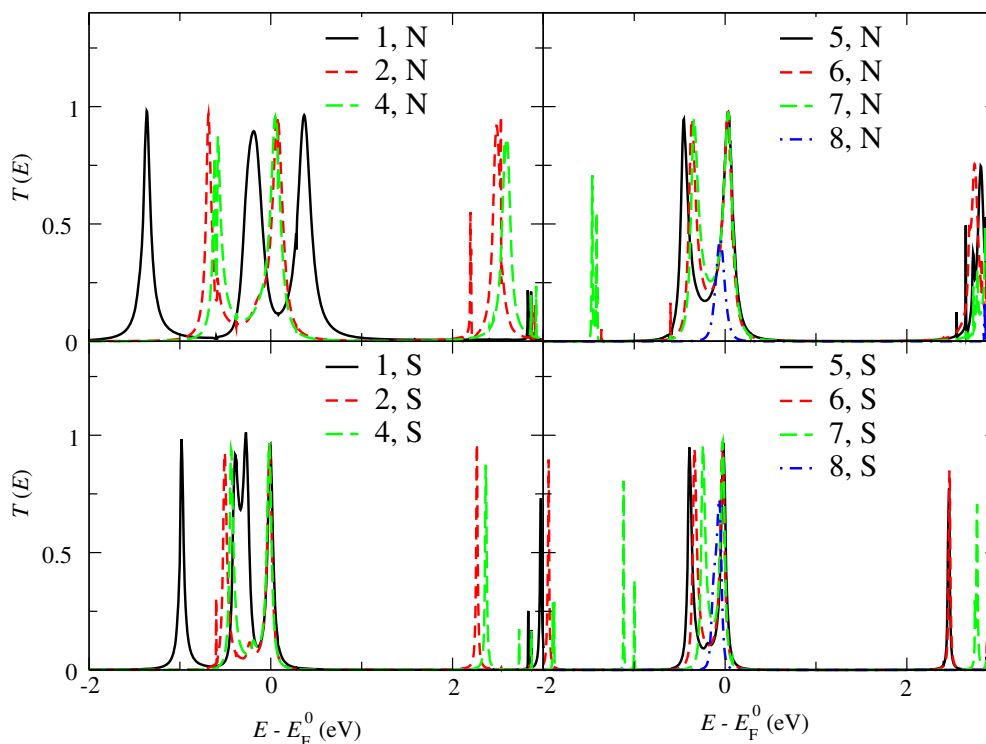


Figure 2. Transmission curves for molecules 1–8 between gold leads contacted by a surface gold adatom.

figures 2 and 3.⁶ We found that nitrogen termination hole dopes the system, compared to the thiol termination, since the former moves the HOMO closer to the computed Fermi energy $E_F = 0$. We also studied two possible contact geometries, namely a hollow position (figure 3), where the contact atom sat on top of a 3-atoms hollow of the (111) surface, and a top position (figure 2), where a gold adatom was placed on top of the hollow position and in contact with the molecule. By comparing both contact configurations, we found that the top position produces a much weaker coupling [18], which is manifested in figure 2 by a series of sharp Breit–Wigner resonances of height equal to unity. In the hollow position, figure 3, the coupling is much stronger and the resonances are merged and smeared out. Note also that in the top configuration the Fermi level is much closer to the HOMO as a consequence of the reduction of the charge transfer in this case, which moves the molecular resonances upwards. The use of LDA and/or DZP changes the height and shape of the LUMO peak, but gives a similar value for the $T(E)$ at the Fermi energy and almost the same HOMO peak.

Close inspection of the structure of $T(E)$ reveals information about the molecular states. Figure 2 shows the evolution of the peaks in the top configuration as θ increases and reveals that both HOMO peaks, which initially are clearly separated, move together and eventually merge for angles close to 90° . The overall effect is a movement of the molecular

⁶ Molecule 3 overlaps strongly along the perpendicular directions with molecules of adjacent unit cells due to its large transversal size. This affects dramatically the transmission curves and produces deviations from the expected behaviours. For this reason we have decided not to include the transport results of this molecule.

Table 1. Angles between rings calculated using LDA and GGA.

| Molecule | Amines | | Thiols | |
|----------|--------|------|--------|------|
| | LDA | GGA | LDA | GGA |
| 2 | 0.0 | 0.0 | 0.0 | 0.0 |
| 3 | 15.6 | 14.9 | 14.7 | 15.7 |
| 4 | 29.4 | 31.5 | 30.4 | 30.9 |
| 5 | 44.1 | 52.5 | 43.2 | 46.8 |
| 6 | 50.4 | 57.6 | 50.8 | 49.3 |
| 7 | 54.0 | 61.2 | 62.5 | 62.8 |
| 8 | 87.6 | 89.5 | 89.4 | 88.1 |

HOMO to lower energies [19], which increases the charge on the molecule as it crosses the Fermi level. This behaviour is reminiscent of bonding and antibonding states with a coupling matrix element, which depends on the overlap between the π conjugated states of both rings⁷. From the same figure, it is also clear that the width of the resonances does not decrease as the angle changes, which means that the couplings to the leads (the Γ matrices) are the same for all molecules and the observed changes have an intramolecular origin. In the hollow configuration, figure 3 shows that $T(E)$ is characterized by the presence of two broad peaks associated with HOMO and LUMO levels. As θ increases, the width of the HOMO decreases, which is again due to the fact that the splitting between bonding and antibonding states, within the HOMO peak, decreases with increasing θ . In this case the charge on the

⁷ Despite the fact that the HOMOs on both aromatic rings are bonding orbitals their interaction gives rise to an splitting that produces a higher (antibonding) and a lower (bonding) molecular orbitals.

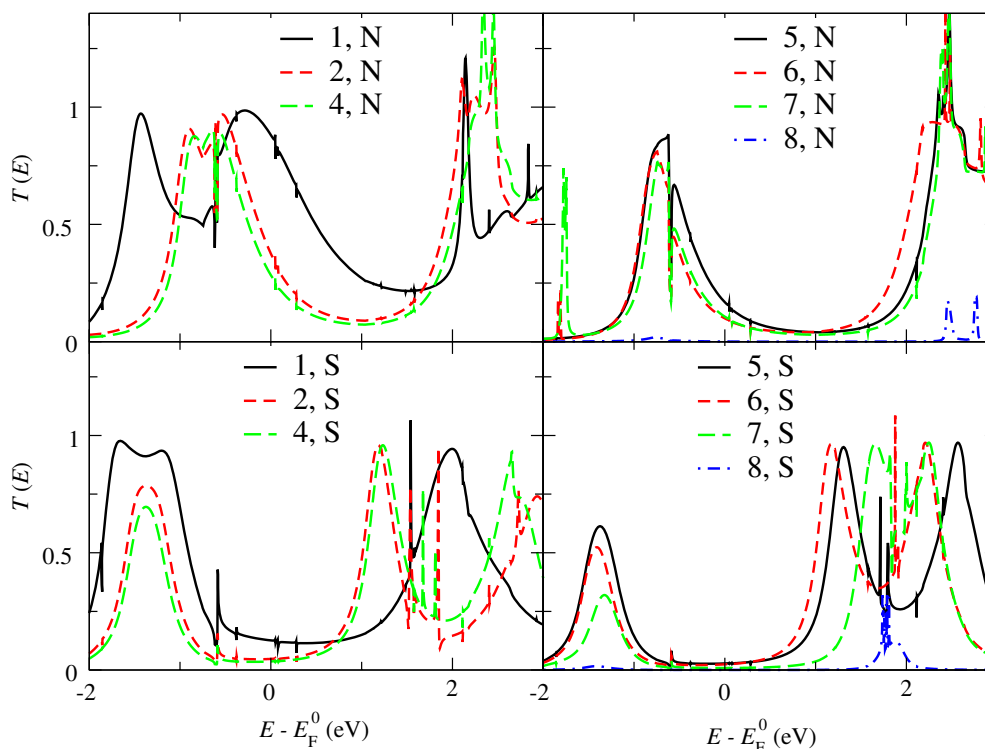


Figure 3. Transmission curves for molecules 1–8 between gold leads contacted by a three-atoms hollow site.

molecule does not change as much as in the top configuration, because the HOMO does not cross the Fermi level. Therefore the number of electrons on the molecule remains constant.

Having examined $T(E)$ for a range of energies, we now turn to the low-voltage, low-temperature conductance $G(\theta) = G_0 T(E_F, \theta)$, where $G_0 = 2e^2/h$, E_F is the Fermi energy and for ease of notation we have now made the dependence of the transmission coefficient on θ explicit. In figures 2 and 3, the zero of energy is chosen to coincide with the computed Fermi energy E_F . In an experiment, the actual Fermi energy may differ from E_F for a number of reasons, including the presence of a dielectric environment, such as air or water [4, 5]. Furthermore, even in the absence of environmental effects, differences can arise from the absence of self-interaction corrections in the exchange–correlation functional [20].

Our first observation is that when the Fermi energy is inside the HOMO–LUMO gap, the conductance is approximately a linear function of $\cos^2 \theta$, in agreement with the experiments of [9]. This result is illustrated in figure 4(a), which shows a comparison between experimental results for the normalized conductance $\bar{G} = G(\theta)/G(0)$ and theoretical results⁸, obtained in the hollow configuration, for both N and S couplings. (In the experimental curve we also use our GGA-computed angular values.) As can be seen the, agreement with

⁸ The disagreement between theory and experiments comes mainly from an incorrect determination of the contact geometry [21] and coupling distances [16] and can also be amplified by the experimental environment [4, 5]. But since the highest resistance and therefore the main transport characteristics are determined by what happens in the central molecular region, the qualitative behaviour and general trends generated by intramolecular changes are correctly described by theory.

the experimental curve is rather good. Note that in this regime, chemistry comes into play by moving some points out of the straight line, in the case of molecules 6 and 7, where depending on the angle, the conductance is lower than expected due to the downward movement of states produced by the highly electronegative side groups F and Cl.

Figure 4(b) shows plots of $T(E, \theta)$ obtained in the top configuration, for several values of E . Again we find a linear dependence on $\cos^2 \theta$, when the Fermi energy sits in the HOMO–LUMO gap. If these curves are normalized to the $\theta = 0$ value, as shown in the inset of figure 4(b), all of them sit on top of each other, which indicates the robustness of the linear dependence inside the HOMO–LUMO gap.

In contrast with the above behaviour, when E approaches either the HOMO or the LUMO orbitals, the θ dependence of the molecular resonances destroys the linear behaviour and $T(E, \theta)$ can even become non-monotonic. This is illustrated in figure 4(c) for the case of N bonding to a top site, which also shows that in this case $T(E, \theta)$ depends sensitively on E . Similar behaviour is found in the hollow configuration or when N is substituted by S as the bonding atom. This implies that by gating [22] the molecules, the measured θ dependence could be tuned to be either linear or non-monotonic, depending on the value of E . Note that in the non-monotonic regime the influence of chemistry becomes extremely important due to dramatic changes produced by movements of resonances originated by the side groups. This suggests a new method to extract molecular spectroscopic information and distinguish between chemical and conformational changes.

In summary, we have studied the transport properties of a series of molecular wires as a function of their

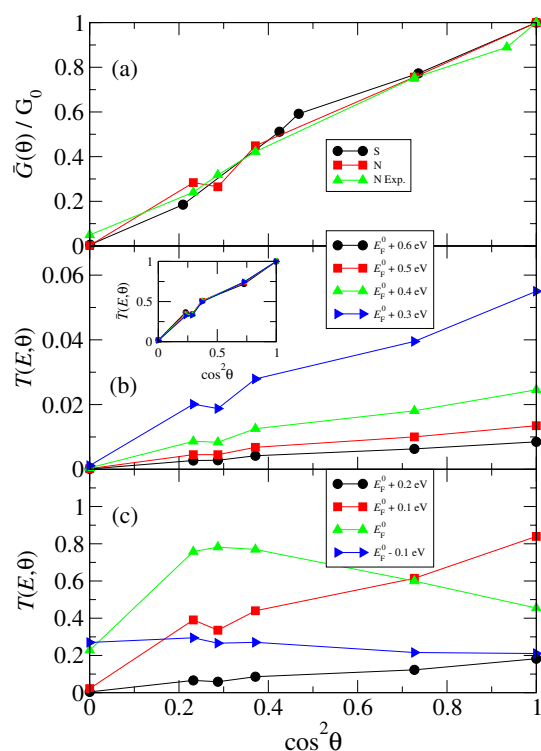


Figure 4. (a) Zero-bias conductance in the hollow configuration, for sulfur contact (circles), nitrogen contact (squares) and values from [9] (triangles). All cases have been normalized to the $\theta = 0$ value. (b) and (c) Computed low-bias $T(E, \theta)$ as a function of electron energy E and $\cos^2 \theta$, for the top configuration and nitrogen contact. The inset shows the curves of graph (b) normalized to the $\theta = 0$ value.

conformal, chemical and contact configuration. We find that geometry is the dominant factor when the Fermi level sits inside the HOMO–LUMO gap but when the Fermi level approaches either the HOMO or LUMO resonances, chemistry comes into play, because the chemical composition of the pristine molecules causes the positions of the HOMO and LUMO resonances to differ from molecule to molecule. This result shows that experiments such as those in [9] yield important spectroscopic information about molecules in contact with electrodes, since the experimentally-measured linear dependence on $\cos^2 \theta$, allows one to conclude that the Fermi energy in these experiments lies in the HOMO–LUMO gap.

We thank Ian Sage and Martin Bryce for useful discussions and the NWGrid for computing resources. We acknowledge

financial support from the European Commission, Qinetiq, and the British Engineering and Physical Sciences Research Council, Department of Trade and Industry, Royal Society, and Northwest Regional Development Agency.

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