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Electron transport through single molecular wires

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Using a scattering technique combined with density-functional theory, a computational study of electron transport through two recently synthesized molecules is presented. The effect of connecting the molecules to gold electrodes is studied by iteratively increasing the number of gold layers, treated self -consistently as part of the molecule.

Key words: *molecular wires; single molecule; transport*

1. Introduction

Molecular electronics, in the sense of electronic devices whose active region consist of a few molecules or even a single molecule, has been proposed at the conceptual level for many years [1]. A typical molecular device consists of a metal–molecule –metal junction, formed between macroscopic electrodes and a single organic molecule or a monolayer of molecules. To form a reliable molecular junction, a gap of the length of the active molecule has to be formed between the electrodes.

At the moment, various techniques are used to probe the properties of single molecule junctions. These are scanning probe [2], break junctions [3, 4], and electro migration [5] methods. While these techniques provide convenient laboratory tools for probing single molecular junctions, it is unlikely that they will be employed for the large-scale production of devices. One possible way forward is to employ longer molecules than benzene dithiol or nitroamine, which were measured by Reed et al. [3, 4], since longer molecules would impose less stringent requirements on the contact lithography. In this paper, we theoretically investigate the equilibrium transport properties of two such recently synthesized molecules [6] (Fig. 1), which are approximately 4 nm and 7 nm in length. These structures are soluble fluorenone-based

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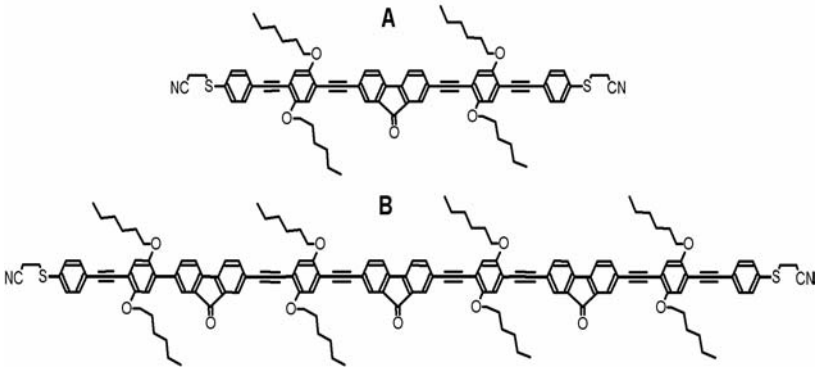

Fig. 1. Two rigid-rod conjugated molecules (A and B) approximately 4 and 7 nm in length, which have protected terminal thiol groups

molecular wires, which are suitable for single molecule device fabrication and could serve as building blocks in the construction of other molecular wires with precise conjugation lengths.

2. Theoretical method

One of the most important features in modelling a molecular device is the interface between the molecule and electrode surface. A systematic approach, therefore, has to be developed to ensure that the effects of the interface are included as part of the calculation.

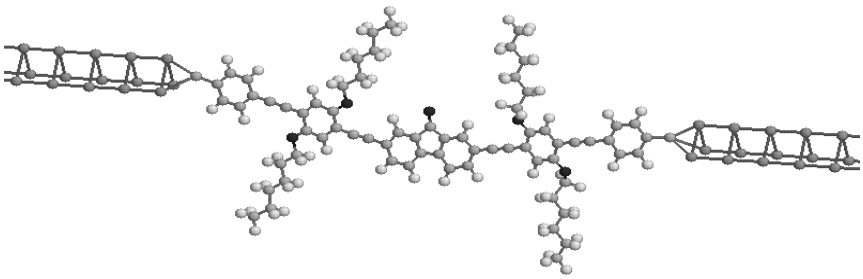

Fig. 2. Molecule A extended to include the surface of the gold lead

The structure of a molecule transport calculation can be broken down into three parts. The first is the structure of the lead, the second is the molecule, and the third is the interface between the surface of the leads and the end of the molecule. A hierarchical theoretical consisting of three stages approach is used here to calculate transport through a molecule contacted between two semi-infinite leads. The first stage is calculating the relaxed geometry of the molecule. This, in principle, could be achieved using any first principles quantum chemistry code. Here we use the density

functional theory code SIESTA [7], combined with a super cell approach. We use the local density approximation as parameterised by Perdue and Zinger [8], non-local norm-conserving pseudopotentials [9], and valence electrons described by a single -zeta basis set. This stage of the calculation also gives useful information about the energetics of the isolated molecule.

One of the main problems in such calculations is correctly modelling the contact region between the molecule and the two leads. Both of the molecules studied here have terminal protected thiol groups, which are known to bond well with gold electrodes. In these calculations, the contact region consists of three gold atoms arranged in an equilateral triangle, to which the sulphur atom covalently bonds. To accurately determine the bonding between the surface of the gold lead and the end of the molecule self consistently, the molecule is extended to include several layers of the gold leads at each of its ends (Fig. 2). One unknown with these new molecules is the optimal distance between the sulphur atom and the surface of the lead. It is found by minimization with respect to the total energy. This parameter is varied for one of these molecules, so as to investigate the effect of changing the coupling strength.

Once the relaxed structure has been calculated, the tight binding Hamiltonian for this extended molecule and contacts can be extracted using the SIESTA code. The final stage in the approach is to utilize this material-specific Hamiltonian in a transport calculation, using single electron, scattering codes [10] developed at Lancaster. This technique determines the quantum-mechanical scattering matrix of a phase coherent region connected to ideal external reservoirs. At zero temperature, the zero-bias conductance is given by the Landauer–Büttiker [11] formula

$$G(E)=\frac{2e^2}{h}T(E_F)$$

where $T(E_F)$ is the total transmission coefficient evaluated at an energy of $E = E_F$.

In what follows, the contact region of the extended molecule consists of triangular layers of three gold atoms, with triangular leads whose cross-section also contains a triangle of three gold atoms (Fig. 2). This allows for a simple continuation between the semi-infinite leads and the ends of the molecule. Our results clearly demonstrate that a non self-consistent treatment of the contacts can yield erroneous results for $T(E)$. By increasing the number of gold atoms that are self-consistently included as a part of the molecule contacts, however, the conductance across the molecule is found to converge, due to the fact that charge transfer effects at the gold-molecule interface decay over a small number of slices into the bulk gold lead.

3. Results

The first molecule, A, that we investigate is shown in Fig. 1. After computing the optimal geometry of its structure, its length was found to be approximately 36.93 Å. This is in good agreement with a S–S length of 37.4 Å determined by X-ray diffrac-

tion [6]. The iterative process of increasing the number of gold atoms in the contact region, until transmission through the molecule converges, can be seen in Figs. 3a and b. In Figure 3a, transmission through molecules containing 2, 3, and 4 layers in the contact region is shown, and while there are small differences in most of the transmission peaks, there is a large difference in the magnitude of the HOMO peak. Figure 3b shows that transmission through 5 layers is identical to transmission through 6 layers. Therefore, transmission through the molecule in this case has converged after including 5 layers of gold.

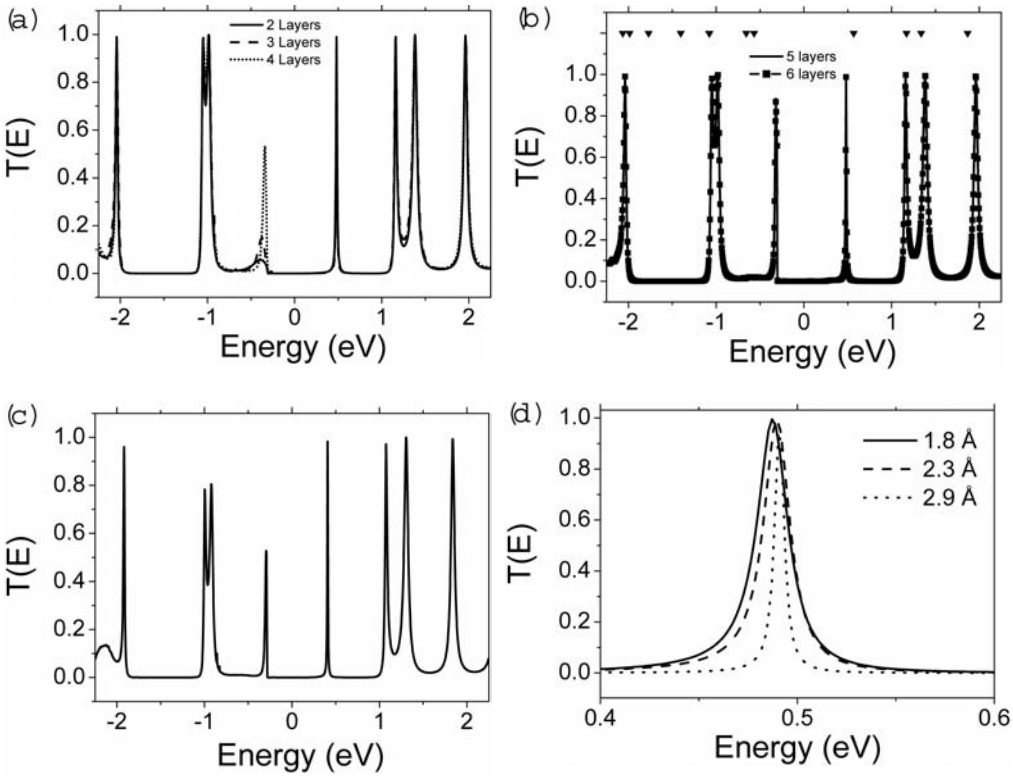

Fig. 3. Transport through molecule A for a contact region of: 2, 3, and 4 slices (a), and 5 and 6 slices (b). Transmission through molecule A with methyl replacing side groups and 6 slices of self-consistently treated gold (c). Variation in the Au–S contact distance (d)

A closer inspection of the zero bias conductance computed for molecule A (Fig. 3b) shows that it has resonant peaks on each side of the Fermi energy (0 eV) and shows a conducting gap of approximately 0.8 eV. This behaviour is typical of transport through a system with discrete energy levels and weakly connected to external reservoirs. To show this more clearly, the energy levels of the isolated molecule, predicted using SIESTA, are represented by the small triangles in Fig. 3b. Conductance shows a resonance peak for the HOMO (Highest Occupied Molecular Orbital) level at approximately 0.32 eV below the Fermi energy, and the LUMO (Lowest Unoccupied

Molecular Orbital) peak is 0.48 eV above the Fermi energy. Therefore, this predicts a conducting gap of approximately 0.8 eV, which is smaller than the predicted gap of the isolated molecule (SIESTA energy levels show a gap of 1.1 eV). One of the reasons for this is the interaction between the molecule and gold leads, which causes the molecular levels to broaden and shift.

Both of the molecules studied here contain complex side groups (Fig. 1), mainly to aid the solubility of these long structures. These groups, however, greatly increase the number of atoms in the molecule. In the case of longer molecules such as B, this will cause the computation time to increase significantly. These side groups can be replaced by methyl without altering the electronic properties of the molecule, simplifying the structure of a long molecular wire. The transmission plot for molecule A with methyl replacing the original side groups is shown in Fig. 3c, showing identical positions for the resonant peaks and only a slight change in the magnitude of the HOMO peak. Therefore, in dealing with the second molecule B, we further consider only the structure with the original side groups replaced by methyl. For this structure, such a substitution reduces the number of atoms in the molecule by 120.

As mentioned previously, the sulphur-gold distance at the lead surface is an unknown parameter, found by minimising the total energy with respect to this distance. In the case of molecule A, this was found to be 2.1Å. Figure 3d shows the effect that altering this distance has on the LUMO resonance in the transmission. Due to symmetry, a weakening of the coupling strength causes the width of the transmission resonances to decrease, and causes no change in the magnitude of the transmission peak.

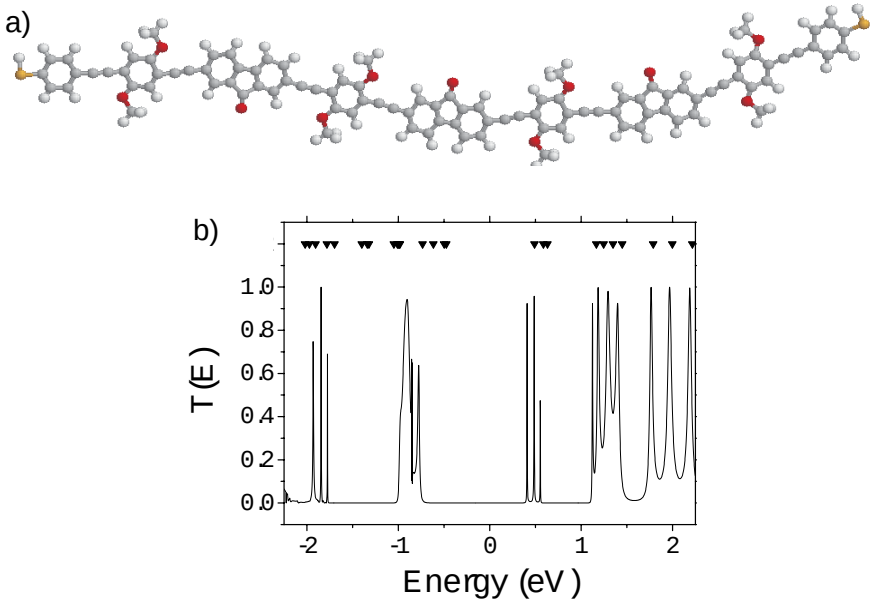

Fig. 4 Optimised geometry for molecule B (a) and zero bias transmission through molecule B with 6 slices of gold (b)

The second molecule, B (Fig. 1), is much longer than molecule A and is partly formed by doubling molecule A. An interesting feature of this molecule is that it has various metastable configurations and, depending on the initial orientation of various parts of the molecule, its length can vary between approximately 68 Å and 74 Å. Using the configuration predicted to be the most stable (i.e., minimises the energy), SIESTA predicts a S–S length of 72.3 Å. The geometry of this structure can be seen in Fig. 4a. Therefore, this molecule would allow the electrode gap to be increased to approximately 7.5 nm.

The computed transmission through this structure can be seen in Fig. 4b, along with the energy levels predicted by SIESTA for the isolated molecule. In this case, the HOMO peak is positioned at approximately –0.7 eV, and there are three peaks close together at the LUMO level, at approximately 0.4 eV. Therefore, for this much longer molecule, formed by effectively doubling the size of molecule A, the conducting gap has increased to approximately 1.1 eV. This is comparable to the gap of the molecule, which SIESTA predicts to be 1 eV.

4. Conclusions

A hierarchical, theoretical approach has been employed to calculate the transport properties of recently synthesized molecular wires, whose relatively long lengths offer the technical advantage of increasing the electrode gap. A method has been described and implemented to accurately include the effect of the molecule-lead interface in the calculations. In the present paper, we have confined our calculations to the transmission coefficient $T(E)$ and stable molecular geometries. In order to build a single molecule device that could perform some basic electronic function, an understanding of finite bias effects is also required. The calculations presented here provide a starting point to understanding such effects, which may take the form of charge or conformation changes in the molecule.

References

[1] AVIRAM A., RATNER M.A., Chem. Phys. Lett., 29 (1974), 277.
[2] GITTENS D., BETHELL D., SCHIFFRIN D., NICHOLS R., Nature, 408 (2000), 67.
[3] REED M., ZHOU C., MULLER C., BURGIN P., TOUR J., Science, 278 (1997), 252.
[4] CHEN J., REED M.A., RAWLETT A.M., TOUR J.M., Science, 286 (1999), 1550.
[5] PARK H., LIM A., ALIVISATOS A., PARK J., MCEUEN P., Appl, Phys, Lett., 75 (1999), 301.
[6] WANG C., BATSANOV A., BRYCE M., SAGE I., Org. Lett., 6 (2004), 2181.
[7] SOLER J.M., ARTACHO E., GALE J.D., GARCÍA A., JUNQUERA J., ORDEJÓN P., SÁNCHEZ-PORTAL D., J. Phys.: Condens. Matter, 14 (2002), 2745.
[8] PERDEW J.P., ZUNGER A., Phys. Rev. B, 23 (1981), 5048.
[9] TROULLIER N., MARTIN J.L., Phys. Rev. B, 43 (1991), 1993.
[10] SANVITO S., LAMBERT C.J., JEFFERSON J., BRATKOVSKY A., Phys. Rev. B, 59 (1999), 11936.
[11] BUTTIKER M., IMRY Y., LANDAUER R., PINHAS S., Phys. Rev. B, 31 (1985), 6207.

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