Tailoring the Fermi level of the leads in molecular-electronic devices

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(Dated: November 9, 2008)

The dependence of the transport properties on the specific location of the Fermi level in molecular electronics devices is studied by using electrodes of different materials. The zero-bias transport properties are shown to depend dramatically on the elemental composition of the electrodes, even though the shape of the transmission coefficients is very similar. By using alkaline materials it is possible to move the Fermi level from the HOMO-LUMO gap to the LUMO resonance and change dramatically the length dependence of the conductance of molecular wires, which opens the possibility of using molecules with different lengths and very similar conductances in nanoscale circuits. This method shows how to dramatically increase the conductance of molecular devices and alter qualitatively and quantitatively their electronic and transport properties.

PACS numbers: 85.65.+h,73.63.-b,73.40.-c

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When a low-enough voltage is applied to a single molecule bridging two metallic electrodes, the measured electrical conductance \( G \) is governed by the spatial extent of the molecular orbitals, their level broadening \( \Gamma \) due to the contacts and the position of the HOMO (\( E_{H} \)) and LUMO (\( E_{L} \)) levels relative to the Fermi energy (\( E_{F} \)) of the electrodes [13, 14, 15]. This dependence is captured by the Landauer formula, \( G(E_{F}) = \frac{2e^{2}}{h} \int_{-\infty}^{\infty} dE T(E) \left( -\frac{\partial f(E-E_{F})}{\partial E} \right) \), where \( f(E) \) is the zero-bias Fermi distribution in the electrodes and \( T(E) \) is the transmission coefficient for electrons of energy \( E \) passing from one electrode to the other. For synthetic molecules such as oligothiophenes [12] \( \Gamma \ll E_{L} - E_{H} \) and therefore \( T(E) \) exhibits Breit-Wigner [16] or Fano resonances [17] in the vicinity of \( E_{L} \) and \( E_{H} \). For conjugated symmetric molecules with extended wave functions along the backbones, resonant values of \( T(E) \) can be of order of unity and therefore at low-enough temperatures \( G(E_{F}) \approx 2e^{2}/h \) whenever \( E_{F} \) aligns with a resonance. In principle, this high conductance channel could be observable in conjugated single-molecule wires of arbitrary length, provided inelastic scattering is negligible. In practice, for most recently-studied families of molecules the measured conductance is much less than \( 2e^{2}/h \) because \( E_{F} \) lies in the HOMO-LUMO gap. This means a serious handicap from the point of view of molecular circuitry, because the conductance will decrease exponentially as a function of length, and from the point of view of molecular sensing, because the movement of resonances produce by other molecules or environmental changes will have less effect in the middle of the gap. One approach to overcoming this problem is to introduce a third gate electrode, which shifts \( E_{L} \), \( E_{H} \) relative to \( E_{F} \). In what follows we explore an alternative approach based on varying the electrode composition to yield a \( E_{F} \) close to \( E_{H} \) or \( E_{L} \) and consequently high-conductance molecular wires without the need for a gate electrode.

The idea of using alkaline electrodes to tune the work function of electronic contacts is well known in the organic LEDs (OLEDs) community [18, 19, 20]. In this paper, for the first time, we examine the effect of using alkaline electrodes for single-molecule electronics. We present a series of ab-initio calculations based on density functional theory (DFT) [21] and non-equilibrium Green’s functions (NEGF) [22] which determine the effect of tuning \( E_{F} \). We examine two molecules, the archetypal benzene-1,4-dithiol (BDT) molecule that has been the subject of many experiments and theoretical works [2, 23] (see Fig. (1)), and a longer molecule (namely 1,4-bis[4- (acetylsulphonyl)phenylethynyl]-2,6-dimethoxybenzene (molecule R3, shown in Fig. (1)) [24] made of three aromatic rings, with the middle ring slightly twisted by the effect of oxygen-related side groups. We also examine molecules R5, R7 and R9 with 5, 7 and 9 aromatic rings, obtained by doubling, tripling and quadrupling the number of phenyl rings in molecule R3, respectively.

THEORETICAL METHOD

We use the Smegol code, [9] which interfaces NEGF to the SIESTA code [26] and obtains self-consistently the den-
density matrix and the transmission coefficients. We employ a basis set that includes polarization orbitals (SZP), which is good enough in this case [27]. To approximate the exchange and correlation we use the local density approximation (LDA) [28], which works relatively well for organic molecules and noble or alkali metals. The real-space grid is defined by a plane-wave cutoff of 200 Ry. The leads are made of slices of fcc (gold) or bcc (alkali) lattices grown along the (001) direction, with 16 atoms per slice and periodic boundary conditions along the directions perpendicular to the transport axis, \( x \) and \( y \). The system is also made periodic along \( z \) to avoid surface effects. The scattering region includes the molecule and five and six slices of the electrodes on the left and right parts of the unit cell, respectively. Each transport calculation has around 250 atoms.

**PRELIMINARY CALCULATIONS**

To evaluate how the Fermi level aligns relative to the molecular levels we first calculate the energy states of the leads and each molecule separately. Since in SIESTA the energy origin is arbitrary [29] it is necessary to use a common reference to compare the levels of different calculations. For this purpose we use a hydrogen molecule 10 Å away from the slab or molecule, whose bonding orbital is taken as reference. The results are shown in Fig. 2. As can be seen, all Fermi levels of the slabs sits inside the HL gap of the BDT. The Fermi level is smallest for gold and increases through the alkali metals from Li to Cs. In the molecules, the HL gap is smaller in R3 than in BDT, as expected, and decreases as the number of rings increases towards R9. These results suggest that the conductance of molecular wires will change dramatically if gold is replaced by alkali leads. However, they describe only isolated molecules and do not include bonding to the surface and charge transfer. After coupling to the slabs the molecular states will broaden into transmission resonances and the LUMO will shift upwards in energy towards \( E_F \), due to charge transfer onto the molecule [15]. To understand these effects we now perform complete transport calculations.

Since in most of these systems it is not exactly known where the molecule would attach on the surface, it is necessary first to determine the most stable bonding configuration. We achieve this by calculating the energy as a function of the distance between a S-C\(_6\)H\(_4\)-SH molecule and a slab made of 4 layers of fcc Au or bcc Li, Na, K, R or Cs grown along the (001) direction, as a function of the distance between the free sulphur atom and the surface. The results can be seen in Fig. 3. The same calculation was repeated for various positions, which include top, bridge and a 4-atoms hollow configuration. In the hollow configuration, steric interactions between some of the atoms of the molecule and the surface atoms on the corners of the square can give different energies. We also computed then the case where the molecule was rotated 45 degrees along the axis perpendicular to the surface, but the results were practically the same.

We found that in all cases the most stable configuration corresponds to the hollow position. For short distances, however, the bridge can become the most favorable bonding configuration in the case of alkali leads. Its cohesive curve shows also two minima, as opposed to the one-minimum curves of other configurations. The second minimum appears when the...
surface.

and decreases the interaction between the molecule and the
ening of the parabola in the cohesion curve from Li to Cs,
surface atoms, something which is manifested by the broad-
also affect the transport properties and could be detected in the
configuration undergoes a transition between the hollow and
sulphur atom crosses the line between both surface atoms and
goes deep into the surface. We expect then that the bonding
energies, which correspond to less bounded electrons. In some
cases the molecule acted also as an impurity reducing the total
transmission between the leads. As a consequence, it was not
easy to clearly distinguish the molecular contribution from the
electrode contribution. For that reason, our attention moved to
the R3 molecule, for which the electrodes are far enough.

ALKALI VS. GOLD ELECTRODES

We first simulated the benzene molecule between gold elec-
trodes and obtained the well known result that the Fermi level
is close to the HOMO resonance [30, 31]. When gold was re-
placed by Li, however, the LUMO resonance moved towards
the Fermi level and the conductance increased, as can be seen
in Fig. 4. This was expected from the results of Fig. 2 due to the change in position of the Fermi level relative to
the molecular orbitals. The same trend was also found for
the other alkali metals. However, for the heavier alkali ele-
ments K, Rb and Cs there was direct transport between the
electrodes even in the absence of the molecule. This effect
was produced by the reduction of the distance between the
leads due to the penetration of the molecule in the surface for
large lattice constants and the increasing electronic delocal-
ization of the outer electrons as the atomic number increases
in these elements. This can be clearly seen in the lower panels
of Fig. 4 where the direct transmission increases for high en-
ergies, which correspond to less bounded electrons. In some
cases the molecule acted also as an impurity reducing the total
transmission between the leads. As a consequence, it was not
easy to clearly distinguish the molecular contribution from the
electrode contribution. For that reason, our attention moved to
the R3 molecule, for which the electrodes are far enough.

Fig. 5 shows the transport properties of the R3 molecule
between gold and alkali leads. As can be seen, the transmis-
sion coefficients are very similar in all cases and are charac-
terized by the presence of two main resonances, correspond-
ing to the HOMO and LUMO orbitals, and a large HL gap.
In the case of gold, the Fermi level sits in the middle of the
HL gap, which produces a very small zero-bias conductance.
However, for the alkali elements the Fermi level moves to the
LUMO resonance and dramatically increases the value of the
conductance [32]. The increase of the conductance can also be
seen by plotting on real space the density of states (DOS) on an energy interval of 0.2 eV around the Fermi level, as shown in Fig. 1. In the gold case the DOS of the leads does not penetrate into the molecule and electrons have to tunnel between both surfaces. When \( E_F \) moves towards the LUMO, DOS appears also in the molecule and makes it metallic.

We found that the conductance increases from Li to K, but
after that it decreases towards Cs. Such non-trivial behav-
ior can be explained by taking into account the movement

sulphur atom crosses the line between both surface atoms and
goes deep into the surface. We expect then that the bonding
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FIG. 3: Energy of a S-C\(_2\)H\(_4\)-SH molecule on top of a surface of fcc
gold (a) and bcc lithium (b), sodium (c), potassium (d), rubidium (e)
and cesium (f), as a function of the distance between the free sulphur
and the surface for various configurations.

TABLE I: Total charge gained by the molecule after connecting it to
the electrodes obtained from the Mulliken populations.

|         | Au | Li | Na | K  | Rb | Cs |
|---------|----|----|----|----|----|----|
| \( \Delta Q \) (e) | 0.45 | 0.63 | 0.88 | 1.15 | 1.24 | 1.34 |

Fig. 4: Transmission coefficients of a BDT molecule between fcc
gold (a) and bcc lithium (b), sodium (c), potassium (d), rubidium (e)
and cesium (f). The dash-dotted line shows the difference between
the transmission curves with and without molecule.

FIG. 4: Transmission coefficients of a BDT molecule between fcc
gold (a) and bcc lithium (b), sodium (c), potassium (d), rubidium (e)
and cesium (f). The dash-dotted line shows the difference between
the transmission curves with and without molecule.
of the Fermi level, charging effects and changes arising from bonding to different surfaces. As the alkali atomic number increases, the LUMO resonance moves downwards (see Fig. 5) but as it starts to cross the Fermi energy, the charge on the molecule increases and the intralevel repulsion moves the states upwards again [15]. The total amount of charge transferred to the molecule increases with the atomic number of the alkali elements, as can be seen in Table (I), which is expected due to the increasing electronegativity and delocalization. At the same time, the lattice constant of the contact increases with the atomic number and therefore the space in the hollow position becomes larger, which reduces the coupling between the contact sulphur atom and the surface and decreases the width of the LUMO resonance. The first effect increases the conductance from Li to K, whereas the second decreases it towards Cs.

We therefore expect a dramatic increase of the conductance if gold electrodes were replaced by alkali leads. Based on our calculations we predict that gold is one of the worst possible choices for high-conductance molecular nanowires, since the conductance decreases exponentially as the length of the nanowire increases.

From Fig. 5 it is possible to deduce some general properties which can help to understand the influence of various factors. For example it is noticeable that while the LUMO resonances in all cases have a similar width, the HOMO resonance is very sharp when the molecule is coupled to the alkali leads, as compared to the gold case, and its width decreases with the atomic number of the alkali element. This arises because the LUMO is delocalized along the molecule (see Fig. 1) and it is better coupled to the contacts, whereas the HOMO is localized in the middle of the molecule and is sensitive to any change in the coupling. Since the coupling to the alkali leads is smaller than the coupling to gold and decreases from Li to Cs, the width of the HOMO resonance is much smaller in the former and becomes sharper as the atomic number increases.

Additional information on the electronic structure and its influence on the transport properties can be obtained by analyzing the projected density of states (PDOS), which we show in Figs. 6 and 7 for the Au and Na configurations corresponding to Fig. 5. In both cases the transmission resonances associated with the HOMO and LUMO orbitals coincide with features in the PDOS of the C and S atoms related to the p−1 orbitals, which are perpendicular to the transport direction and make on the molecular backbone the delocalized states near the Fermi level. Such orbitals penetrate into the molecule and generate the channels associated with the resonances. In the case of gold there is an additional p1 contribution on the S near the HOMO, due to the strong interaction with the surface atoms that move these orbitals up in energy, but it does not go inside the molecule because it almost disappears in the C atom. The small transmission in the HL gap is produced by the absence of C states in this region, even though there are S states generated by hybridization with the surface states. The density of states of gold and sodium is finite in all the energy window and is mainly due to the s orbitals. Notice we plot the density of states per atom, so even in regions where it looks relatively small it has a finite contribution which allows the formation of a conductance channel, like for example in Fig. 6 between 0.5 and 1 eV.

LENGTH DEPENDENCE

The fact that the Fermi energy is close to the LUMO resonance opens the possibility of having non-exponential dependence of the conductance as a function of the molecular length, provided the Fermi level for longer molecules is still close enough. Such a possibility would allow the use of molecular wires with various lengths to connect different parts of a nanoscale circuit with almost no change in the conduc-
tance. We checked this possibility by using longer molecules with the same central unit and more benzene rings. To ensure that only the length was varied and no additional effects were introduced, the rings were made coplanar with the outer ones and the same number was added on both sides. The lengths of such molecules, which we call R5, R7 and R9, were 3.4, 4.7 and 6.1 nm, respectively.

It is well known that as the molecular length increases, the HL gap decreases due to the higher electronic delocalization along the molecule. The HL gap and the relative position of the HOMO and LUMO of all molecules can be seen in Fig. (2). However, as the HL gap decreases, the value of the transmission coefficients inside the gap decreases due to the larger separation between the electrodes. This implies again that, if the Fermi level sits inside the gap, the conductance will decrease exponentially as a function of the molecular distance. In Fig. (8) we show the transmission coefficients around the Fermi energy as a function of the distance for gold (a) and sodium electrodes (c). As can be seen in Figs. (8)(a) and (b), which are plotted on a logarithmic scale, the transmission at the Fermi level decreases exponentially when the molecules are contacted to gold. Such exponential behavior has a beta of 0.16 Å⁻¹ and indeed proves that the quantum transport is in the tunnelling regime. As the molecular size increases, the LUMO resonance moves downwards and all conductance decreases and a position that increases slightly with the molecular length. The reduction of the width can be explained by taking into account that the weight of the LUMO decreases at the edges of the molecule and therefore the coupling between this orbital and the contacts tend to decrease as the length increases (the same, but more pronounced, happens to the HOMO orbital). The upwards movement of the LUMO resonance looks counterintuitive, since the LUMO width grows the orbitals move downwards, but it can be explained by the upwards shift of the levels produced by the additional charge on the molecule.

FIG. 7: Projected density of states on the first C atom, the S atom and the Na electrodes for a R3 molecule in the same configuration as in Fig. (5) (b).

FIG. 8: Length dependence of the transmission coefficients and low bias conductance for molecules between gold electrodes ((a) and (b), respectively), and molecules between sodium electrodes ((c) and (d), respectively).

CONCLUSIONS

The long-term goal of using high-conductance molecular wires as interconnects in sub-10 nm electronics requires that HOMO or LUMO resonances coincide with the Fermi energy of metallic electrodes so that the conductance does not decrease exponentially and all nanoscale electronic elements are connected with almost the same conductance. The pinning of the Fermi level at the LUMO is also important from the point of view of sensing, since the effect produced by other molecules or environmental changes, which is manifested mainly by movements of the resonances, will be much higher. In this paper we have shown that by analogy with current technology used in OLEDs, this can be achieved by using alkali metals instead of the more commonly used gold.

We thank Ian Sage for useful discussions. VMGS thanks...
the EU network MRTN-CT-2004-504574 for a Marie Curie grant, the EPSRC and the DTI.

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