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# TOWARDS A THEORY OF ELECTRICAL TRANSPORT THROUGH ATOMIC AND MOLECULAR JUNCTIONS

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Present trends in the miniaturization of electronic devices suggest that ultimately single atoms and molecules may be used as electronically active elements in a variety of applications. In this context, there is an obvious request for a theory that can elucidate the transport mechanisms at the single-molecule scale, and in turn help in the future engineering of molecular devices. We present here a candidate to such a theory, which based on the combination of quantum chemistry methods and Green functions techniques. Our main goal in this work is to show how the electronic structure of single atoms and molecules controls the macroscopic electrical properties of the circuits in which they are used as building blocks. In particular, we review our work on three basic problems that have received a special experimental attention in the last years: (i) the conductance of a single-atom contact; (ii) the conductance of a hydrogen molecule; and (iii) the current through single organic molecules.

*Keywords:* Molecular electronics; Atomic contacts; Single-molecule junctions

## 1. INTRODUCTION

The recent advances in nanofabrication have triggered the hope that electronic devices can be shrunk down to the single molecule scale (Aviram and Ratner, 1998; Joachim *et al.*, 2000). In fact, it has been already shown that single molecules can perform functions analogous to those of the key components of today's microelectronics such as switches (Collier *et al.*, 1999; Gao *et al.*, 2000; Reed *et al.*, 2001), rectifiers (Metzger, 1999) and electronic mixers (Chen *et al.*, 1999). In view of these achievements one can get the impression that *molecular electronics* is about to replace the traditional microelectronics based on the silicon technology. However, the future of this new field depends crucially on our understanding of the transport mechanisms in single-molecule junctions, and at this stage there are still very basic problems which remain unsolved. Thus for instance, from the experimental side it is difficult to achieve an unambiguous contact to a single molecule, and in many cases the measurements

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are not reproducible. On the theoretical side the situation is even more unsatisfactory. In this field there are notorious differences between different theories, not to mention the discrepancies between theory and experiment.

In this context it is worth revising some of the emerging concepts in molecular electronics. There are many different mechanisms that in principle can control the current at the single molecule scale. However, in addition to generic principles of nanoscale physics, e.g. Coulomb blockade, the chemistry and geometry of the molecular junction emerge as the fundamental tunable characteristics of molecular circuits. In this article we shall review our efforts to understand the electronic transport in atomic and molecular junctions. Our main goal is to show how the electronic structure of individual atoms and molecules determines the macroscopic electrical properties of the circuits in which they are embedded. Making use of a combination of quantum chemistry methods and nonequilibrium Green functions techniques, we shall describe the electronic transport in some of the most basic situations. To be precise, we study three examples of special experimental interest: (i) the conductance of single-atom contacts; (ii) the conductance of a hydrogen molecule; and (iii) the current through simple organic molecules.

The rest of the article is organized as follows. In Section 2 we shall describe the theoretical formalism used to compute the different results in this work. Section 3 is devoted to the analysis of the conductance of single-atom contacts. In Section 4 we study the conductance of a hydrogen molecule. In Section 5 we shall investigate the current through simple organic molecules. Finally, in Section 6 we present a brief summary of the main conclusions of this work. The impatient readers who want to get a quick idea about the content of this work are recommended to jump directly to this last section.

## 2. THEORETICAL APPROACH

In order to analyze the electrical current in atomic and molecular junctions we use a combination of quantum chemistry calculations and nonequilibrium Green functions techniques. This type of approach has become quite popular and nowadays it is used by many authors (Joachim *et al.*, 1995; Kemp *et al.*, 1996; Datta *et al.*, 1997; Emberly and Kirczenow, 1998; Yaliraki *et al.*, 1999; Ventra *et al.*, 2000; Damle *et al.*, 2001; Palacios *et al.*, 2001; Taylor *et al.*, 2001; Brandbyge *et al.*, 2002; Heurich *et al.*, 2002), and this section is devoted to its brief description.

Our approach starts with a description of the electronic structure of a molecular junction, like the one shown schematically in Fig. 1(a), which is based on the following Hamiltonian

$$\hat{H} = \hat{H}_L + \hat{H}_R + \hat{H}_C + \hat{V}. \tag{1}$$

Here, $\hat{H}_C$ describes the "central cluster" of the system, which contains the molecule plus part of the leads (see Fig. 1), $\hat{H}_{L,R}$ describe the left and right electrode respectively, and $\hat{V}$ gives the coupling between the electrodes and the central cluster. Since the current is mainly controlled by the narrowest part of the system, the electronic structure of the central cluster must be resolved in detail. We do this within the density functional theory (DFT) approximation, unless the opposite is stated. The DFT calculations have been performed with the code GAUSSIAN98 (Frisch *et al.*, 1998). The left and

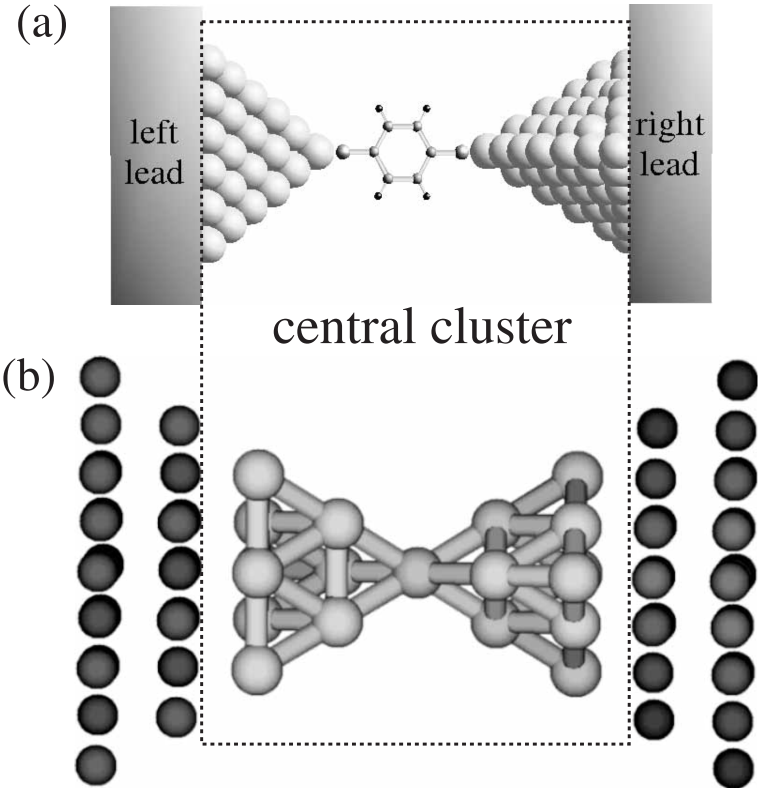

FIGURE 1 (a) Schematic representation of a single-molecule contact. Notice that ''the central cluster'' consists of the molecule plus part of the metallic leads; (b) single-atom contact consisting of a fcc structure with bulk interatomic distances grown along the (111) direction. The blue atoms represent the bulk atoms used to model the reservoirs.

right reservoirs are modeled as two perfect crystals of the corresponding metal using the tight-binding parameterization of Papaconstantopoulos (1986) or Mehl and Papaconstantopoulos (1996). The inclusion of part of the leads in the *ab initio* calculation is an important ingredient that assures the correct description of the molecule–electrodes coupling, the charge transfer between the molecule and the leads and therefore the lineup of the molecular levels relative to the metal Fermi level. The Fermi level is set naturally by the highest occupied molecular orbital (HOMO) for a sufficiently large number of metallic atoms in the central cluster.

In order to obtain the current for a constant bias voltage, $V$, between the leads, we make use of nonequilibrium Green functions techniques. Since the Hamiltonian of Eq. (1) does not contain inelastic interactions, one can show that the current adopts the usual form of the Landauer formula (for a detailed derivation of the following expressions see Cuevas, 1999)

$$I = \frac{2e}{h}\int_{-\infty}^{\infty} d\epsilon\, \mathrm{Tr}\{\hat{t}\hat{t}^{\dagger}\}[f(\epsilon - eV/2) - f(\epsilon + eV/2)], \tag{2}$$

where $f$ is the Fermi function and $\hat{t}$ is the energy and voltage dependent transmission matrix given by

$$\hat{t}(\epsilon, V) = 2\,\hat{\Gamma}_L^{1/2}(\epsilon - eV/2)\hat{G}_C^r(\epsilon, V)\hat{\Gamma}_R^{1/2}(\epsilon + eV/2). \tag{3}$$

The scattering rate matrices are given by $\hat{\Gamma}_{L,R} = \mathrm{Im}(\hat{\Sigma}_{L,R})$, where $\hat{\Sigma}_{L,R}$ are the self-energies which contain the information of the electronic structure of the leads and their coupling to the central cluster. They can be expressed as $\hat{\Sigma}_{L,R}(\epsilon) = \hat{v}_{CL,R} g_{L,R}(\epsilon)\hat{v}_{L,RC}$, $\hat{v}$ being the hopping matrix which describes the connection between the central cluster and the leads. $g_{L,R}$ are the Green functions of the uncoupled leads, which we assume to be the bulk Green functions of the corresponding metal. Finally, the central cluster Green functions are given by

$$\hat{G}_C(\epsilon, V) = \left[\epsilon\hat{1} - \hat{H}_C - \hat{\Sigma}_L(\epsilon - eV/2) - \hat{\Sigma}_R(\epsilon + eV/2)\right]^{-1}. \tag{4}$$

In this work we shall mostly concentrate on the analysis of the transport in the linear regime, in which the low temperature conductance is given by $G = G_0 \mathrm{Tr}\{\hat{t}\hat{t}^\dagger\} = G_0 \sum_i T_i$, where $G_0 = 2e^2/h$ is the quantum of conductance and the $T_i$s are the transmission eigenvalues at the Fermi energy $E_F$. As it will become clear in the next sections, the analysis of the current in terms of *conduction channels*, defined as eigenfunctions of $\hat{t}\hat{t}^\dagger$, provides a deep understanding of the electronic transport.

## 3. THE CONDUCTANCE OF A SINGLE ATOM

What determines the electrical conduction in the simplest imaginable circuit, namely a one-atom contact between two metallic banks? Or in other words, what is the conductance of a single atom? This is the basic question which we address theoretically in this section. Our main goal is to show that the properties of such a contact are mainly determined by the nature of the atom.

Using simple experimental techniques such as the scanning tunneling microscope (STM) or the so-called mechanically controllable break junctions (MCB), it is possible to gently break a metallic contact to form a wire of atomic dimensions. Indeed, the diameter of these nanowires can be easily reduced to a single atom. These atomic-size contacts have been extensively studied in the last decade, and they have turned out be an ideal test-bed for concepts from mesoscopic physics. The activity in this field has been recently summarized in an excellent review by Agraït *et al.* (2003), and we refer the reader to this work for more details about these systems.

The most satisfactory answer to the question posed at the beginning of this section has been given by Cuevas and coworkers (Cuevas *et al.*, 1998a,b; Scheer *et al.*, 1998), and the rest of this section is devoted to review their ideas. Following Cuevas *et al.* (1998a) we analyze the current through a single-atom contact making use of the orthogonal tight-binding parametrization of Papaconstantopoulos (1986), which is known to reproduce the electronic structure of bulk materials. This means that we use the bulk hoppings to construct also the Hamiltonian matrix elements of the atomic constrictions ($H_C$ in Eq. (1)). Here the basis is formed by 9 orbitals, namely the *s*, *p*, and *d* orbitals

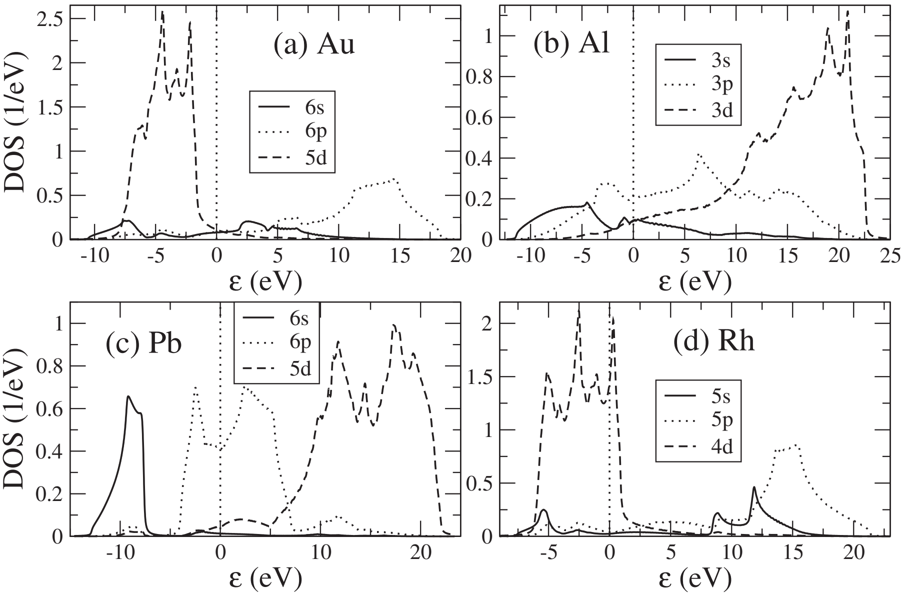

FIGURE 2 Bulk DOS as a function of energy for Au, Al, Pb and Rh. The DOS is projected into the *s*, *p*, and *d* bands around the Fermi energy, which is set to zero and it is indicated with a vertical dotted line.

which give the main contribution to the bulk density of states (DOS) around the Fermi energy. It is important to remark that we include hopping elements up to second neighbors. The final ingredient of the model is the local charge neutrality that typical metallic elements must exhibit. We impose it in the tight-binding approximation by means of a self-consistent variation of the diagonal Hamiltonian matrix elements.

In this work we analyze the following four metals: Au, Al, Pb, and Rh. We have chosen these materials to cover a broad range of valences and orbital structures. As a reference the bulk DOS of these metals is shown in Fig. 2. We have computed the transmission and its decomposition into channels for the structure shown in Fig. 1(b), and the results can be seen in Fig. 3. The main findings are the following. The Au contact has a conductance close to $G_0$, which is largely dominated by a single channel. In the case of Al the total transmission at the Fermi energy is also close to 1, but there are three channels with a significant contribution. In the Pb contact the transmission is also formed by three channels, but the conductance has a value of $2.34\,G_0$. Finally, in the case of the transition metal Rh the conductance is composed of 5 channels giving a total transmission of 1.68.

Let us now discuss the origin of these results. In order to understand what controls the number of channels we now make two assumptions that simplify the model. First, we consider only nearest neighbor interactions. Second, we reduce the size of the basis, $N_{orb}$, in such a way that we only consider the *s* band for monovalent metals such as the alkali and noble metals, the *s* and *p* bands for metals such as Al or Pb, and the *s* and *d* bands for transition metals. One can easily check that these two approximation give reasonable results. The maximum number of channels is determined by the dimension of $\hat{t}\hat{t}^{\dagger}$, which can be arbitrarily large depending on the size of the central cluster. However, the actual number of conducting channels (those with a nonvanishing

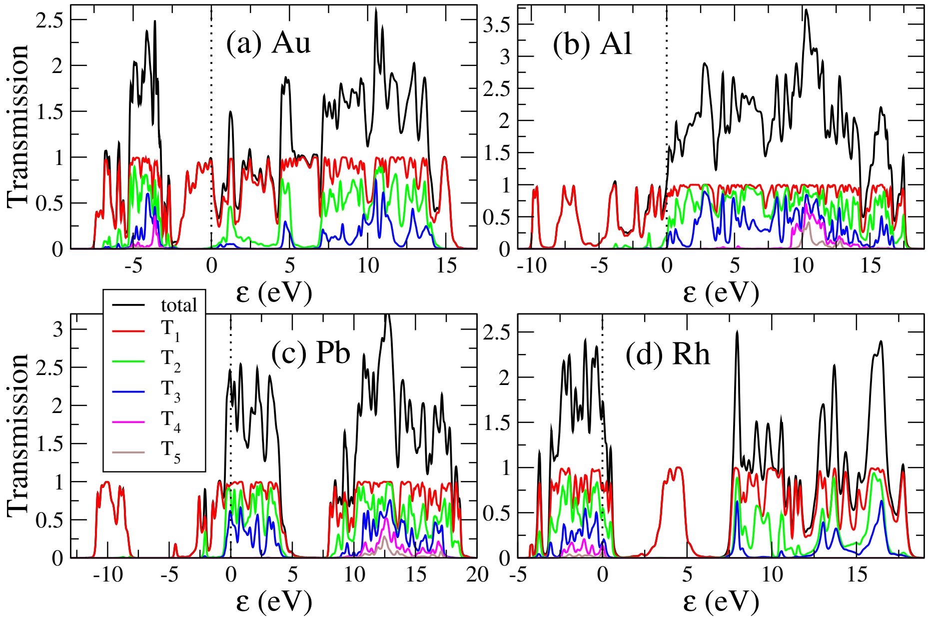

FIGURE 3 Transmission and channel decomposition as a function of energy of the structure shown in Fig. 1(b) for four metals: Au, Al, Pb, and Rh. The Fermi energy is set to zero and it is indicated with a vertical dotted line. For simplicity the channels are ordered according to the transmission value, and not according to their character. The total transmission and the transmission coefficients at the Fermi energy are the following. (a) Au: $T_{\text{total}} = 0.97$, $T_1 = 0.95$, and $T_2 = 0.02$. (b) Al: $T_{\text{total}} = 1.046$, $T_1 = 0.817$, $T_2 = 0.208$, $T_3 = 0.019$, $T_4 = 0.002$. (c) Pb: $T_{\text{total}} = 2.345$, $T_1 = 0.959$, $T_2 = 0.798$, $T_3 = 0.588$, $T_4 = 2 \times 10^{-5}$. (d) Rh: $T_{\text{total}} = 1.680$, $T_1 = 0.784$, $T_2 = 0.523$, $T_3 = 0.167$, $T_4 = 0.142$, $T_5 = 0.060$, $T_6 = 10^{-4}$.

transmission eigenvalue $T_i$) are limited by the number of orbitals in the narrowest section of the neck ($N_{\text{orb}}$ when having a single-atom contact). This fact can be shown by the following simple argument. As the division between central cluster and leads is somewhat arbitrary, one could always redefine the leads for the geometry of Fig. 1(b) in such a way that the new central cluster consists of only the central atom. Then, the new scattering rate matrices $\hat{\Gamma}_{L,R}$ have a dimension of just $N_{\text{orb}}$ and the new transmission matrix would only admit $N_{\text{orb}}$ eigenmodes. Current conservation along each conducting channel ensures that the nonvanishing eigenvalues $T_i$ are the same, no matter where the transmission matrix is calculated.

The above simple argument already gives us a rule of thumb to estimate the maximum number of relevant conduction channels in a one-atom contact. Thus, for monovalent metals such as the noble and alkali metals, one expects a single channel, for an *sp*-like metal like Al or Pb, this number should be typically four, while for a transition metal like Rh (having a negligible weight of *p* orbitals at $E_F$) this number would be of order six. Indeed, comparing the results of Fig. 3 and the estimation of this simple rule we see that there is a slight deviation in the case of the *sp*-like metals, where the actual number of channels is three instead of four, and in the case of the transition metal Rh, where there are five channels instead of six. Indeed, the simple rule should be taken as an upper bound. The actual number of conducting channels can be smaller as some of the channels can carry no current due to symmetry considerations. Thus, for instance the analysis of the character of the channels reveals that in the case of the *sp*-like metals the dominant channel is essentially a symmetric combination of the *s* and $p_z$ orbitals of the central atom, where *z* is the transport direction. The antisymmetric combination of these two orbitals gives rise to a channel that is closed because it is orthogonal to the incoming metal states. In the same way, in the case of transition metals the *s* and $d_{z^2}$ orbitals combine to give a widely open channel (symmetric combination) and a closed channel (antisymmetric combination).

So in short, the analysis above suggests that one can easily estimate the conductance of a single-atom contact just using the information of the number of valence orbitals and the chemical valence. It is worth stressing that the predictions about the number of channels of this tight-binding model have been confirmed so far by all the experiments that have tested the individual channels (Scheer *et al.*, 1997, 1998; van de Brom and van Ruitenbeek, 1999; Ludoph *et al.*, 1999; Ludoph and van Ruitenbeek, 1999). It is also important to remark that this model explains in a natural way the typical conductance values observed in the different materials. It explains not only the differences between the different classes of metals: monovalent metals (alkali and noble metals), *sp*-like metals, transition metals, etc, but also the differences between the metals of the same class. Thus for instance, within the transition metals the model predicts a simple hierarchy. The highest conductance should be exhibited by V, Nb, and Ta (with 5 valence electrons), since for them the Fermi level lies in the middle of the *d* band. The conductance and in particular the transmissions of the fourth and fifth channels should diminish towards the column of Pd and Pt, since in this case the Fermi lies in the edge of the *d* band. Indeed, this is precisely what is observed in the conductance histograms (Agraït *et al.*, 2003). For the *sp*-like metals, Pb, Al, Zn, Cd, etc, there is a huge difference between Pb, with 4 valence electrons, and the other materials, with 2 or 3 valence electrons. The conductance of Pb is much higher due to the position of the Fermi energy, well inside the *p* band.

## 4. THE CONDUCTANCE OF A HYDROGEN MOLECULE

In this section we discuss the electrical conduction through an individual hydrogen molecule. The results described here are based on our recent work Heurich *et al.* (2003). As we mentioned in the introduction, at this stage of the development of the field of molecular electronics one can hardly find any satisfactory agreement between theory and experiment. In this context the measurement of the conductance of an individual hydrogen molecule reported by Smit *et al.* (2002) provides a valuable opportunity to analyze the emerging concepts on the electrical conduction in single-molecule devices in the perhaps simplest possible system. In Smit *et al.* (2002) it was shown that a single hydrogen molecule can form a stable molecular bridge between platinum contacts. In contrast to results for organic molecules (Reed *et al.*, 1997; Kergueris *et al.*, 1999; Reichert *et al.*, 2002), this bridge has a conductance close to one quantum unit, carried by a single channel. This result belies the conventional wisdom because the closed-shell configuration of $H_2$ results in a huge gap between its bonding and antibonding states, making it a perfect candidate for an insulating molecule.

Before describing the results of our DFT calculations, it is very instructive to discuss our prejudices and naive expectations based on a toy model for the conduction through a hydrogen molecule. We describe $H_2$ with a two-sites tight-binding model, see Fig. 4(a).

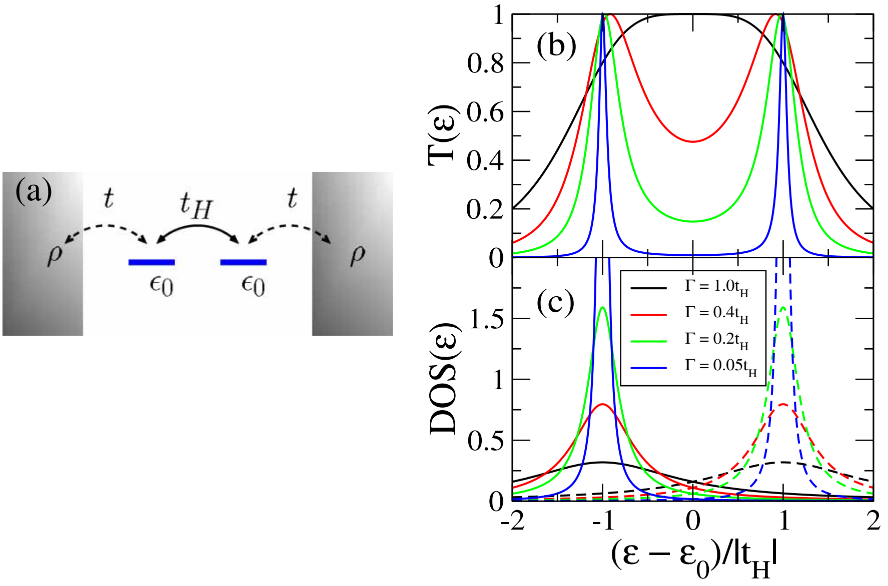

FIGURE 4 (a) Schematic representation of the toy model described in the text. (b) and (c) Transmission and DOS projected into the bonding (solid lines) and antibonding (dashed lines) states *vs* energy for different values of the scattering rate Γ.

In this scheme $\epsilon_0$ represents the 1*s* energy level of H and $t_H$ is the hopping connecting the H atoms. This hopping is simply related to the splitting between the bonding ($\epsilon_+$) and the antibonding state ($\epsilon_-$) of the molecule, namely $\epsilon_\pm = \epsilon_0 \pm t_H$, and its value is $\sim -12$ eV. The molecule is coupled symmetrically to the leads with a single hopping $t$. Within this model the total transmission as a function of energy is given by

$$T(\epsilon) = \frac{4\Gamma^2 t_H^2}{\left[(\epsilon - \tilde{\epsilon}_+)^2 + \Gamma^2\right]\left[(\epsilon - \tilde{\epsilon}_-)^2 + \Gamma^2\right]}. \tag{5}$$

Here, $\tilde{\epsilon}_\pm = \epsilon_0 \pm t_H + t^2 \mathrm{Re}\{g^a\}$ are the renormalized molecular levels, $g^a(\epsilon)$ being the advanced Green function which describes the local electronic structure of the leads. The scattering rate Γ, which determines the broadening of the molecular levels, is given by $\Gamma(\epsilon) = t^2 \mathrm{Im}\{g^a\} = \pi t^2 \rho$, where $\rho(\epsilon)$ is the LDOS of the Pt contacts. For the sake of simplicity, let us assume that Γ is energy independent and that the levels are not renormalized ($\tilde{\epsilon}_\pm = \epsilon_\pm$). In Fig. 4(b) we show the transmission as a function of energy for different values of Γ in units of $t_H$. We also show in Fig. 4(c) the corresponding DOS projected into the bonding and antibonding states of $H_2$, which are given by $\rho_\pm = \Gamma/\pi\{(\epsilon - \tilde{\epsilon}_\pm)^2 + \Gamma^2\}$ respectively. Taking into account the huge value of $t_H$, one naively expects the curve for $\Gamma = 0.05\, t_H$ to represent the relevant situation. Assuming that $H_2$ remains neutral, the bonding state is occupied by two electrons and $E_F = \epsilon_0$. In this simple picture $H_2$ would be insulating, in clear disagreement with the observations of Smit *et al.* (2002).

Let us now see if the full DFT calculations can resolve this puzzle. In the last section we learned that a single-atom contact of transition metal such as Pt sustains

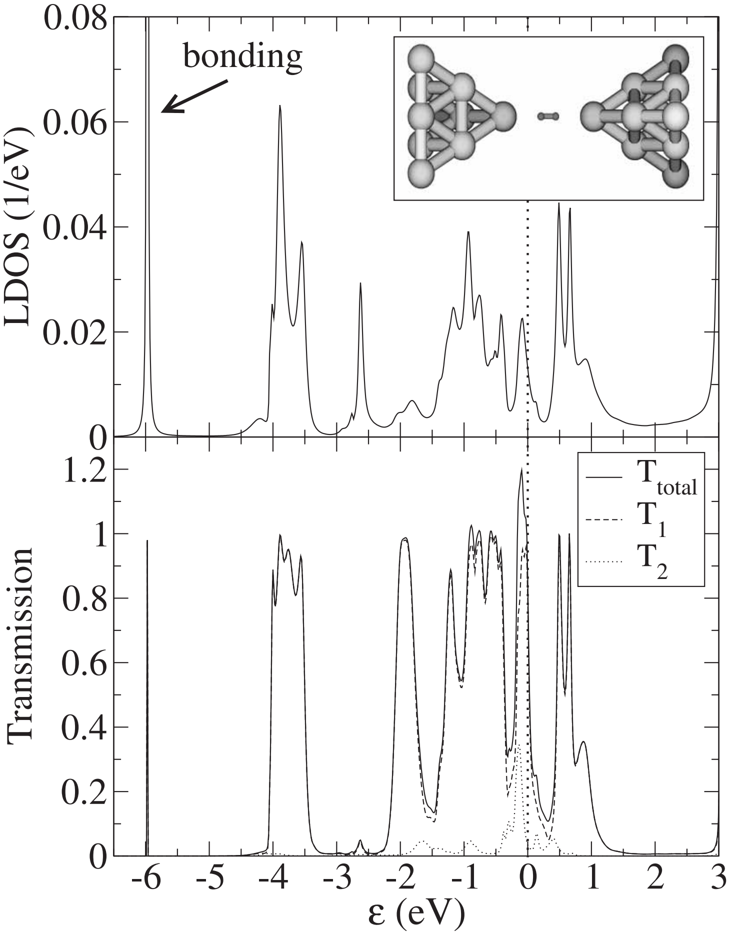

FIGURE 5 Transmission and LDOS projected into one of the H atoms as a function of energy for the Pt–$H_2$–Pt structure, the central cluster of which is shown in the inset. At $E_F$ $T_1 = 0.83$ and $T_2 = 0.03$. The H–H and Pt–H distances are 0.8 and 2.1 Å respectively. We use the cc-pVDZ basis set for H.

five conduction channels. Following the experiment of Smit *et al.* (2002), we now study how the presence of $H_2$ modifies the conduction. Usually the lack of knowledge of the precise geometry of the molecular junction complicates the comparison between theory and experiment. However, in Smit *et al.* (2002) the presence of $H_2$ was identified by means of the signature of its vibrational modes in the conductance. This information establishes clear constraints on the geometries realized in the experiment. In this sense, we only consider configurations which are compatible with the observed vibrational modes. The most probable configuration is shown in the inset of Fig. 5, where the $H_2$ is coupled to a single Pt atom on either side (top position). In this geometry the vibrational mode of the center of mass motion of $H_2$, which is the one seen in the experiment, has an energy of 55.6 meV, lying in the range of the experimental values (see Heurich *et al.*, 2002 for the technical details about the basis sets and functional used in the DFT calculations). In Fig. 5 we also show the transmission and the LDOS projected into the orbitals of one of the H atoms. The total transmission at the

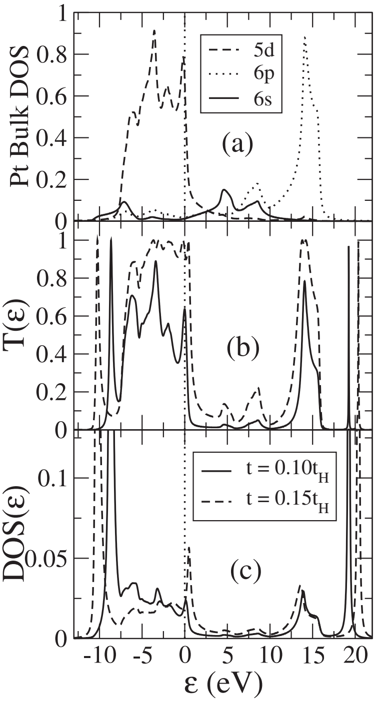

FIGURE 6 (a) Bulk DOS of the Pt reservoirs. (b) and (c) Transmission and LDOS projected into one of the H atoms for two values of the hopping $t$, assuming that the leads are modeled by Pt bulk atoms, $t_H = -12$ eV and $\epsilon_0 = 9$ eV. Fermi energy is set to zero and it is indicated with a vertical dotted line.

Fermi energy is $T_{\text{tot}} = 0.86$ and it is largely dominated by a single channel, in agreement with experimental results. We would like to draw the attention to the following two features in the LDOS: (i) the bonding state of the molecule appears as a peak at $\sim$6 eV below $E_F$ and the antibonding state, not shown in Fig. 5, is located at $\sim$18 eV above $E_F$. (ii) around the Fermi energy the gap between the molecular states is filled due to the strong hybridization with the Pt leads, which is indeed the mechanism behind the high conductance of this molecule.

How can we understand these results in simple terms? In other words, what ingredients were missing in the toy model presented above? Our DFT calculations indicate that there are two main ingredients missing in this simple argument. First, H forms a bond with Pt by sharing electrons. The DFT calculations show that every H atom donates $\approx$0.12 e to Pt. This implies that the Fermi level lies closer to the bonding state. With this charge transfer the transmission raises significantly, but it is not yet sufficient to reproduce the DFT results. Thus, a large broadening ($\Gamma$) of the bonding state is still needed. As suggested by the DFT calculations, this is provided by the good Pt–$H_2$ coupling and the large DOS around the Fermi energy coming from the $d$ band of Pt. We test this idea assuming that $g^a$ is the bulk Green function of Pt. The Pt bulk DOS is shown in Fig. 6(a). We also show in Fig. 6(b) and (c) the transmission and the LDOS projected into one of the H atoms for two values of the coupling to the leads $t$. One can see that for realistic values of $t \approx 1$–2 eV, the transmission at $E_F$ can now indeed reach values close to one. Therefore, we conclude that *the high conductance of* $H_2$ *is due to the charge transfer between* $H_2$ *and the Pt leads and the strong hybridization between the bonding state and the d band of Pt*. This mechanism is not exclusive of Pt and it must also operate in other transition metals, as it was shown experimentally for Pd (see Smit *et al*., 2002).

The above analysis has been performed for a particular geometry and a legitimate question is whether we can be sure that this is the geometry realized in the experiment. In principle, there are other configurations compatible with the vibrational modes analysis. However, based on the channel analysis performed in the experiment many geometries can be ruled out. For more details about this point we refer the reader to Heurich *et al*. (2003).

## 5. CURRENT THROUGH SIMPLE ORGANIC MOLECULES

Since the pioneering experiment of Reed and coworkers (Reed *et al*., 1997) many different organic molecules have been investigated experimentally. Most of these molecules consist of a few benzene rings forming a short wire, which is terminated by thiol groups. This means in practice that the molecules are attached to gold electrodes by means of a stable covalent bond between sulfur and gold. These molecules have usually $\pi$ delocalized orbitals, which make them in principle ideal building blocks for molecular circuits (Tour *et al*., 1998). There are many different interesting observations such as negative differential conductance (Chen *et al*., 1999), which still, by-and-large, beg theoretical explanation. In this section we concentrate ourselves on the answer to

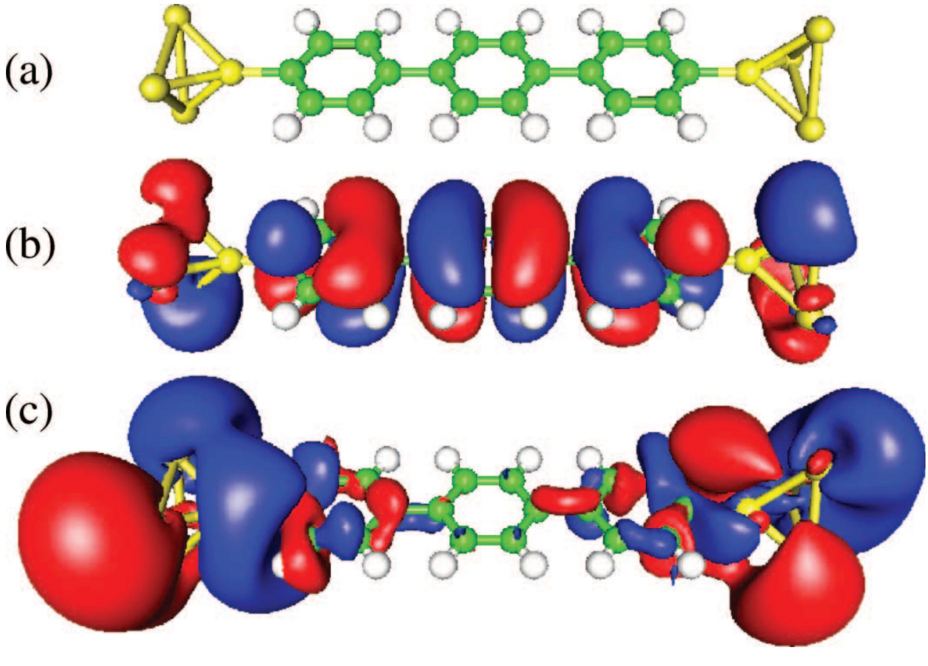

FIGURE 7 (a) Organic molecule analyzed in this work connected to three gold atoms in the hollow position. Color codes: C (green), H (white), S (yellow), Au (gold). (b) Charge density of the HOMO of the central cluster. (c) Charge density of the LUMO of the central cluster.

the following question: why is the low bias conductance of these molecules much lower than in the hydrogen case?

As a example we consider the molecule shown in Fig. 7(a). It consists of three benzene rings terminated by a thiol group on each side. The S atoms are attached to three Au atoms in the hollow position and the Au–S distance is 2.37 Å. For this molecule, as for many of this type, the work function of gold lies inside the HOMO–LUMO gap, which usually means that there is not a significant charge transfer between the metal and the molecule. This is confirmed by the Mulliken population analysis of the central cluster. Thus, the question of whether this molecular junction is highly conductive or not reduces to the question of whether the coupling to the gold electrodes is strong enough to fill the HOMO–LUMO gap. In the DFT calculation we have used the B3LYP functional (Becke, 1993), the LANL2DZ basis (Hay and Wadt, 1985) for the atoms of the molecule and the basis set of Christiansen *et al.* (Ross *et al.*, 1990) for the Au atoms. In Fig. 8 we show both the transmission through the molecule and

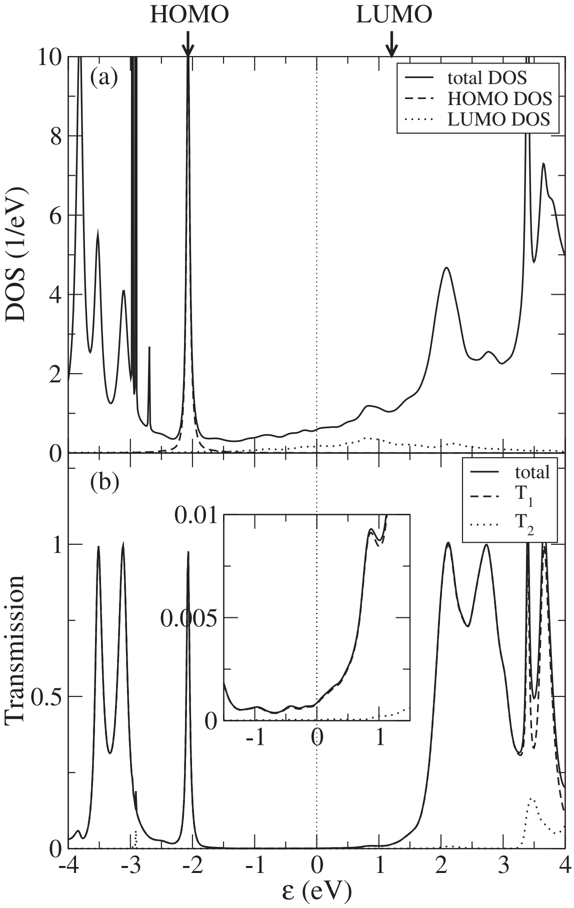

FIGURE 8 (a) Total DOS and DOS projected into the HOMO and LUMO of the central cluster of the molecular junction shown in Fig. 7(a). (b) Corresponding zero bias transmission *vs* energy. The inset show a blow up of the region around the Fermi energy. Notice that the transmission is largely dominated by a single channel. The Fermi energy has been set to zero.

the density of states of the central cluster. Notice that the transmission at the Fermi energy is $8.2 \times 10^{-4}$, which reproduces the general trend observed in these molecules (Reed *et al.*, 1997; Kergueris *et al.*, 1999; Reichert *et al.*, 2002). The reason for this low transparency can be understood with the analysis of the density of states. In Fig. 8(b) we show the DOS projected into the HOMO and LUMO of the central cluster. We see that the HOMO has a width of $\sim 0.3\,\mathrm{eV}$ and only its tail reaches the Fermi level. Thus, although this molecular orbital has an extended character, see Fig. 7(b), it does not give a large contribution to the low bias conductance. The LUMO is broader due to its stronger coupling to the leads, see Fig. 7(c). However, it does not give either a large contribution at the Fermi energy. So in short, *we can conclude that this molecule does not conduct very well at low bias because its hybridization with the metallic electrodes is not strong enough to fill its HOMO–LUMO gap*. Finally, it is important to remark that although we have paid special attention to the contribution of the HOMO and LUMO, there are many other levels close to the Fermi energy, which give at least a similar contribution to the current. This seems to be a common feature of many of these organic molecules (Heurich *et al.*, 2002).

## 6. CONCLUSIONS

In this work we have analyzed theoretically the electronic transport through atomic and molecular junctions. The main conclusion is that the set of our results illustrate clearly how the electronic structure of single atoms and molecules determines the macroscopic current of the circuits in which they are used as building blocks. Below, we summarize the main conclusions of the different sections.

*Single-atom contacts* The ensemble of the experimental and our theoretical results show unambiguously that the conduction channels in an atomic contact are determined by the orbital electronic structure and the local atomic environment around the neck region. In particular, for the case of one-atom contacts the conduction channels are determined by the chemical nature of the central atom. As a simple rule, we could say that the number of active channels corresponds to the number of valence orbitals of such atom. Our calculations, in agreement with the experimental results, predict the presence of three conducting channels for *sp*-like metals like Al or Pb. For transition metals like Pt, we expect the presence of five conduction modes due to the contribution of *d* orbitals. In the case of simple metals such as alkali or noble metals, we expect the presence of a single conducting channel due to the contribution of the *s* band.

*Conductance of a hydrogen molecule* We have presented a theory for the conductance of a hydrogen bridge between Pt contacts explaining the experimental observations of Smit *et al.* (2002). We have shown that the conduction mechanism consists of two main ingredients. First, the catalytic activity of platinum is responsible for a significant charge transfer between $H_2$ and the Pt contacts, which moves the bonding state of the molecule towards the Fermi energy. Then, the strong hybridization with the *d* band of the Pt leads provides a large broadening of the bonding state, finally allowing for a high transmission. Our analysis of this ideal test system illustrates that ingredients such as charge transfer and the electronic structure of the metallic contacts are essential for the proper description of the electrical conduction in single-molecule devices.

*Current through simple organic molecules* We have studied the transport through a simple organic molecule consisting of three benzene rings terminated by thiol groups. We have shown that the low conductance exhibited by this type of molecules in the low voltage regime is due to the following reason. The hybridization between the molecular orbitals and the metallic states is not strong enough to fill the HOMO–LUMO gap, and the current proceeds then through the tails of the closest levels to the Fermi energy.

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