Conductance Oscillations in Zigzag Platinum Chains

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Using first principles simulations we perform a detailed study of the structural, electronic, and transport properties of monatomic platinum chains, sandwiched between platinum electrodes. First, we demonstrate that the most stable atomic configuration corresponds to a zigzag arrangement that gradually straightens as the chains are stretched. Second, we find that the averaged conductance shows slight parity oscillations with the number n of atoms in the chain. Additionally, the conductance of chains of fixed n oscillates as the end atoms are pulled apart, due to the gradual closing and opening of conductance channels as the chain straightens.

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The existence of single atom chains was demonstrated some time ago using the scanning tunneling microscope and mechanically controllable break junctions [1] where a quantized conductance close to $G_0 = 2e^2/h$ for gold was measured, in agreement with previous theoretical predictions [2]. Since then, a number of experiments [3,4] and theoretical calculations [5] have proved that the $5d$ elements Au, Ir, and Pt can be used to produce monatomic chains. For gold chains [1], the average distance between conductance peaks was found to be 2.5 Å with the conductance G of the last plateau being very close to G_0. The ensemble-averaged conductance also shows small oscillations around G_0 as the length of the chain increases [4]. For platinum, the average distance between the peaks in the length histograms is about 1.9–2.3 Å [3,4]. In contrast with gold, the conductance is no longer an integer multiple of G_0, but instead decreases from $1.6G_0$ to $1.2G_0$ as the length of the chain increases [4]. In addition, significant conductance oscillations are superimposed on top of this decreasing trend, which have been attributed to a parity effect [4,6]. The rich behavior of platinum compared with gold arises from the larger number of conduction channels at the Fermi energy (E_F) due to the presence of d bands.

To understand the structural, electronic, and transport properties of platinum chains, we have performed a complete series of first principles simulations of platinum chains attached to platinum fcc leads. We have employed our newly developed code SMEAGOL [7,8], which calculates the density matrix and the transmission coefficients of a two probe device using the nonequilibrium Green's function formalism. The scattering potential is calculated self-consistently using the SIESTA implementation of density functional theory [9–11]. We have approximated the exchange and correlation potential by the local density approximation, since we have found that provides a slightly more accurate description of the structural and conducting properties of bulk and infinite platinum chains than generalized gradient approximation [12]. We have not included in our calculations spin polarization, which is relevant only for very stretched chains [13]. Our main result is that the most stable arrangement of platinum chains corresponds to zigzag configurations, which are straightened as the chains are stretched. The conductance decreases from $1.6G_0$ to $1.2G_0$ upon chain stretching, showing slight parity oscillations. Additionally, we also find geometry-induced oscillations as the electrodes are pulled apart. Such oscillations are due to the gradual opening and subsequent closing of transport channels as chains with a fixed number of atoms n are straightened.

We start by discussing the case of infinite platinum chains, which is useful to understand the basic physics of the constriction when a long chain is formed. We use a two-atom unit cell with periodic boundary conditions along the three spatial directions. The cell is large enough along the x and y axes to avoid spurious interactions between the chain in the central unit cell and its images. We simulate two kinds of chains: linear chains, where the atoms are constrained to lie along the z axis, and zigzag chains, where forces are allowed to relax along the three spatial coordinates. We find that zigzag chains are more stable than linear chains, as can be seen from the cohesive energy of Fig. 1(a). The equilibrium distances along the z axis are $d_{z,\mathrm{eq}} = 2.15$ and 2.38 Å for the zigzag and linear chains, respectively. In the zigzag arrangement the Pt-Pt bonds are located in the xz plane and make a 24.8° angle with the z axis. This means that the interatomic distance for the zigzag configuration is $d = 2.37$ Å, which is almost the same as for the linear case. These angles decrease almost linearly as the chains are stretched, and become approximately zero for d_z larger than 2.5 Å. Interestingly, if the distance is reduced below the zigzag minimum, the system falls into another stable configuration with a ladder arrangement.

Figure 1(b) shows the number of open scattering channels $N(E_F)$ at the Fermi energy E_F of an infinite zigzag chain, as a function of d_z. The figure reveals that

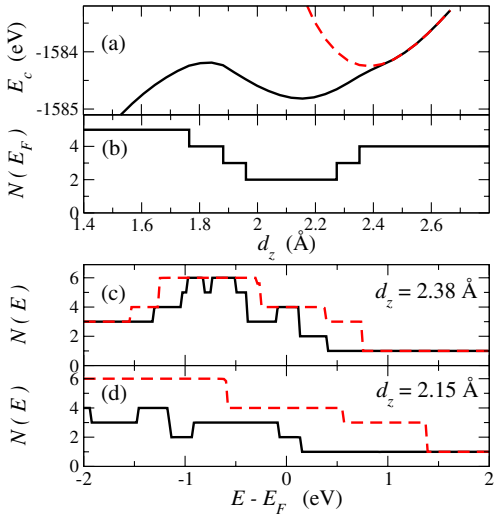

FIG. 1 (color online). (a) Cohesive energy E_c and (b) number of open scattering channels at the Fermi energy $N(E_F)$ of platinum chains as a function of d_z. Number of open scattering channels $N(E)$ as a function of energy E calculated at (c) $d_z = 2.38$ and (d) $d_z = 2.15$ Å for zigzag (solid line) and linear (dashed line) chains.

$N(E_F) = 5$ for small d_z, but decreases to $N(E_F) = 2$ as the chain is stretched beyond 1.95 Å, and maintains that value for quite a large range of distances. For d_z somewhat larger than 2.30 Å, $N(E_F)$ increases in two steps to $4G_0$, and stays constant thereafter until the chain breaks. To understand which channels are opening and closing, we have studied the projected density of states (PDOS) for chains at different stretching. As limiting cases we compared a linear chain at $d_z = 2.38$ with a zigzag chain at $d_z = 2.15$ Å. For the linear chain we find that the d_{xy} and d_{x^2-y2} orbitals are completely filled, while the hybridized s, d_{xz}, d_{yz}, and $d_{z^2-r^2}$ orbitals have all finite weight at E_F, leading to four open channels, as shown in Fig. 1(c). Atoms in zigzag chains at $d_z = 2.38$ Å make small angles with the z axis at this distance, and therefore, the d_z dependence of the PDOS and $N(E_F)$ both look fairly similar to those of the linear chain. In contrast, the number of open channels $N(E)$ as a function of energy E, shown in Fig. 1(d), and the PDOS of zigzag chains at $d_z = 2.15$ Å look rather different from those of the linear chain. The zigzag chain has only two, and not four, open channels at the Fermi energy, corresponding to a mixture of all d orbitals, since now the s orbital is completely filled, while the d_{xy} and $d_{x^2-y^2}$ have moved up in energy. This analysis of infinite chains can explain why in some experiments the conductance increases when the electrodes separate, because there is a gradual transition from a zigzag to a linear configuration upon the stretching of the chain, with the linear chain presenting a larger number of open scattering channels.

This simplified picture cannot explain, however, the features that are present in a real experiment, where the contact to the electrodes and rearrangement of the leads near the surface can decrease the transmission of channels or even close them. To investigate this possibility, we have simulated finite chains of various lengths (between 1 and 5 atoms), attached to fcc platinum leads oriented along the (001) direction (see Fig. 2). The leads are composed of repeated slices of 3×3 atoms and are connected to the chain through a square of 4 atoms, i.e., through the fcc (001) hollow site. In order to get rid of undesirable oscillations in the transmission coefficients, we have used periodic boundary conditions along the xy plane and summed over 12 k points. To treat the contact region self-consistently, three atomic planes of bulk platinum are included in each side of the scattering region [14]. To calculate the most stable configuration for each chain, we perform the relaxation by keeping fixed the bulk Pt leads and relaxing the apexes of the point contact. In this way the relaxation is performed over the chains and the two 2×2 planes forming the hollow site. The ground state energy is therefore calculated as a function of the distance d_z between the outer slices (unrelaxed) as indicated in Fig. 2. In Fig. 3 we plot the cohesion curves for zigzag atomic chains with a number of atoms ranging between 2 and 5.

The ground state energy of the single atom contact (not shown) as a function of distance is a parabola whose minimum is located at the equilibrium distance $d_{z,\mathrm{eq}} = 6.3$ Å. A parabolic dependence is also found when we place two atoms facing each other, with $d_{z,\mathrm{eq}} = 9.1$ Å. However, if we allow the outer planes to move along the x and y directions, these two atoms achieve a zigzag configuration that has a lower energy, as shown in Fig. 3. This zigzag arrangement is actually a local minimum, as in the case of chains of infinite length. For short distances, the atoms at the apex gain energy by forming further chemical bonds to other atoms at the electrodes. The same kind of curves are observed for 3, 4, and 5 atoms, with $d_{z,\mathrm{eq}} = 11.4$, 13.3, and 15.4 Å, respectively. We find that the difference in lengths between chains of n and $n + 1$ atoms lies in the range 1.9–2.1 Å, in very good

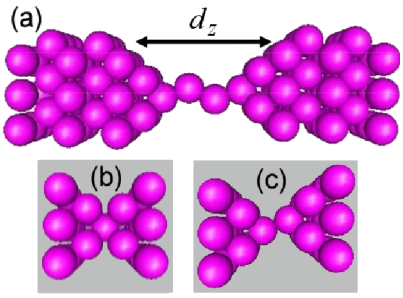

FIG. 2 (color online). The different chains connecting (001) oriented fcc leads studied in this Letter: (a) 4-atom chain, (b) single atom contact, and (c) 2-atom chain. d_z is the distance between leads.

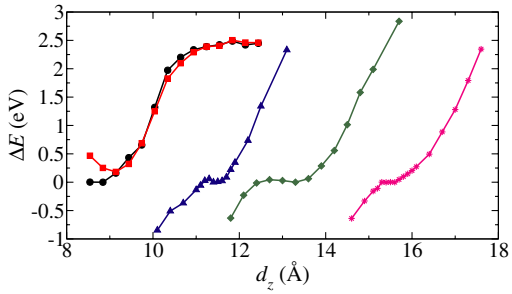

FIG. 3 (color online). Cohesion curves of the chain plus leads systems, for zigzag and linear chains of two atoms (circles and squares, respectively), and zigzag chains containing 3, 4, and 5 atoms (triangles, diamonds, and stars, respectively). All curves have been shifted in energy in order to align the local minima.

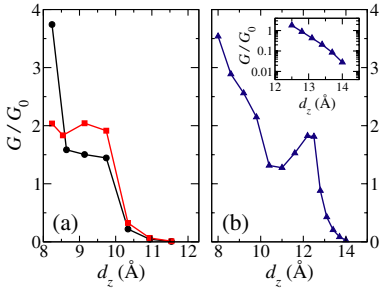

FIG. 4 (color online). Conductance of platinum chains. (a) Two atoms in zigzag or linear arrangement (circles or squares, respectively). (b) Three atoms; in the inset is plotted the tail of the curve in a logarithmic scale that shows the tunneling behavior when the chain breaks.

agreement with experiments [4]. The only configuration that does not fit into this pattern is the single atom contact, whose equilibrium distance is 2.8 Å away from the 2-atom chain. Indeed, the single atom contact does not constitute a chain by itself, since a large number of bonds link the central atom to its neighbors, which must be broken simultaneously in order to snap the chain. In contrast, atomic chains can be topologically characterized as broken by cutting just one single bond, which leads us to ascribe the peaks found in length histograms [4] to chains 2, 3, 4, and 5 atoms long. Figure 3 also indicates that the region of stability of the $(n + 1)$-atom chain begins at a distance where the n-atom chain is very stretched and therefore close to being broken. This fact helps one understand why the first two peaks found in length histograms, which correspond to chains with two or three atoms, are much higher than those attributed to chains of four or five atoms [3,4], because there is a significant probability that an n-atom chain will break before the $(n + 1)$-atom chain forms. At a more detailed level, we also find that the angles between the atomic bonds and the chain axis are small for short chains (9.1° for the 3-atom chain), but increase with the chain length (21.6° for the 4-atom chain). The case of the 5-atom chain is more complicated: the two atoms joining the leads make angles of 36.3°, while those in the middle have angles equal to 16.1°.

Moving to transport, we observe that the single atom contact behaves very differently from any other, with a conductance of about $5.9G_0$ at the equilibrium distance, which decreases almost linearly to $G = 3.5G_0$ until the contact breaks. These values are very different from those of Ref. [6], where the pyramidlike structure of the contact was not included, probably leading to an overestimate of the interatomic distance. For the 2-atom chain we find a conductance of $1.5G_0$ at the equilibrium distance in the zigzag arrangement and a conductance ranging between $1.8G_0$ and $2.0G_0$ in the linear case, as shown in Fig. 4(a). The second value can be associated with the return conductance measured when a contact is made again after the system breaks [6]. We therefore propose that the first configuration established between two atoms should be linear when both tips are brought together.

For larger chains, we obtain a nonmonotonic behavior of the conductance as a function of d_z. When the separation between the leads increases from a compressed configuration, the conductance initially decreases and then exhibits a plateau at around the equilibrium distance. Under further expansion it grows again (for stretching of about 1 Å beyond the equilibrium separation) and finally decreases exponentially. An example is shown in Fig. 4(b), for $n = 3$. This behavior can be understood as follows. For small distances, atoms in the chain are very close to each other, and there is a large number of open channels. As the distance increases, the transmission through many of these channels is reduced and the conductance decreases until a value between $1.0G_0$ and $1.5G_0$ is reached, where the chain has a zigzag configuration. If the chain is stretched further, the conductance increases again, following the evolution from a zigzag to a linear chain, until a small plateau with a conductance of $2G_0$ is formed. Finally, the chain enters the exponential tunneling regime, as shown in the inset of Fig. 4(b), whose onset signals the point where the chain would break or a new atom would enter the chain.

To try to make contact with the experiments of Ref. [4], the conductances of all chains are gathered together in Fig. 5(a). We find clear oscillations with a periodicity equal to the interatomic distance, which have a structural origin. These oscillations are due to the gradual closing and opening of channels, which occurs as the angles between the atomic bonds and the z axis increase and decrease. For a stretched chain, the angles increase if a new atom enters the chain, and subsequently decrease as the chain is further stretched. Moreover, the size of the conductance is linked to the biggest angle subtended by atoms in the middle of the chain. Larger chains tend to have bigger angles and lower conductances. One exception is the 5-atom chain, whose conductance, $1.2G_0$, is slightly bigger than that of the 4-atom chain ($1.0G_0$). This is also easily explained by

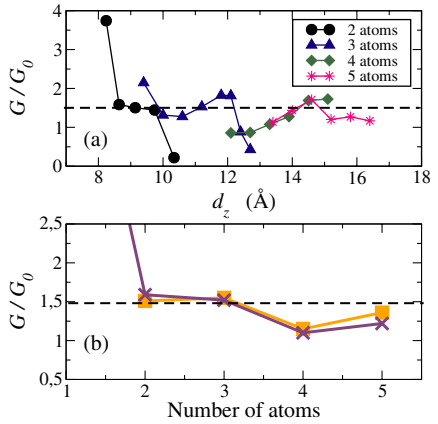

FIG. 5 (color online). (a) Evolution of the conductance of 2, 3, 4, and 5 atom chains as a function of d_z (circles, triangles, diamonds, and stars, respectively). (b) Conductance vs the number of atoms in the chain measured at the equilibrium distance (crosses) and averaged over a range of 2 Å about such distance (squares).

our calculations, since atoms in the middle of the 5-atom chains have a smaller angle than those of 4-atom chains (16.1° versus 21.6°).

The large geometry oscillations of Fig. 5(a) may mask those due to the parity effect, which have a larger periodicity but a smaller amplitude. The experimental conductance curves shown in Ref. [4] are obtained by averaging individual conductance traces over thousands of pulling circles. We therefore expect that this averaging should smooth out short-distance fluctuations, such as the large geometry oscillations discussed above, and uncover parity oscillations that have a longer wavelength. To explore such a possibility, we have plotted in Fig. 5(b) the conductance of each chain, taken at its equilibrium distance. We find that the large geometry oscillations have been completely washed out, leaving only a small oscillation that has a periodicity equal to twice the interatomic distance. To further check the stability of these results, we have also plotted in Fig. 5(b) the conductance of each chain, but now averaged over a range of lengths of about two angstroms around each equilibrium distance. We believe that such a procedure may reproduce the most important features of the experimental averaging of conductance curves. Interestingly, both curves almost overlap. The remaining curve actually shows two peaks, corresponding to chains with three and five atoms. We note that the position of the conductance peaks, the overall shape of the curve, and the magnitude of the conductance are in excellent quantitative agreement with the results of Ref. [4]. In view of the above results, we propose that the geometry oscillations seen in our simulations are averaged over in the experiments by Smit *et al.* [4], leaving only the smaller amplitude, but robust parity oscillations.

In summary, we have shown that monatomic platinum chains have a zigzag structure, both in the case of perfect infinite chains, where the conductance is halved compared to the linear configuration, and the case of chains between two fcc (001) electrodes. We find that atomic chains are composed of at least two atoms, while the single atom contact shows significantly different structural and transport features. Our calculations explain the negative slope in the conductance that is found for larger chains, and accurately reproduce the oscillations given by parity effects found in the experiments of Ref. [4].

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