Conductance oscillations in zigzag platinum chains - suppression of parity effects

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Using first principles simulations we perform a detailed study of the structural, electronic and transport properties of monoatomic 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. Secondly, we find that the conductance at equilibrium atomic spacing does not oscillate with the number of atoms n in the chain, but instead decreases almost monotonically with n. In contrast, the conductances of chains of fixed n oscillate 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 (STM) and mechanically-controllable break junctions (MCBJ) [1, 2] where a quantized conductance close to $G_0 = 2\,e^2/h$ for gold was measured, in agreement with previous theoretical predictions [3]. Since then, a number of experiments [4, 5] and theoretical calculations [6] have proved that the 5d elements Au, Ir and Pt can be used to produce monoatomic chains. The chain length is usually obtained from MCBJs [2] by measuring the distribution of lengths of the last conductance plateau over a large number of contact-breaking cycles. These length histograms typically show three or four equally-spaced peaks indicating the lengths at which the chains break [4, 5]. For gold chains [1, 2], 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 [5]. Although the actual structure of these chains (zigzag vs straight chains) is still a matter of debate [7, 8], both the integer conductance and the small dispersion in the conductance distribution were attributed to the monovalency of this metal.

For platinum, the average distance between the peaks in the length-histograms is about 1.9-2.3 Å [4, 5], and it is not known whether the structural configuration is linear or zigzag. In contrast with gold, the conductance is no longer an integer multiple of G_0, but instead decreases from 1.6 G_0 to 1.2 G_0 as the length of the chain increases [5]. In addition, significant conductance oscillations are superimposed on top of this decreasing trend, which have been attributed to a universal, even-odd parity effect associated with chains of fixed atomic spacing, but varying numbers of atoms [5, 9]. 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 and although the use of simple models is appealing, the origin of conductance oscillations remains to be established.

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 [11, 12], which calculates the density matrix and the transmission coefficients of a two probe device using the non-equilibrium Green's Function formalism (NEGF) [13]. The system is divided into a left- and a right-hand side current-carrying lead and a central scattering region [14]. The scattering potential is calculated self-consistently using the SIESTA implementation of density functional theory [15, 16, 17]. Our main result is that the most stable arrangement of platinum chains corresponds to zigzag configurations, that are straightened as the chains are stretched, leading to a conductance, which decreases from 1.6 G_0 to 1.2 G_0 upon chain stretching. The conductance also oscillates as the electrodes are pulled apart due to the gradual opening and subsequent closing of transport channels as chains of a fixed number of atoms n are straighten. This geometry-induced oscillation is distinct from the even-odd parity effect proposed in [5], which applied to chains of fixed interatomic spacing, but different n.

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 cubic cell, large enough along the x and y axes to avoid spurious intra-chain interactions and periodic boundary conditions along z. 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. In agreement with previous theoretical simulations of gold [7] we find that zigzag chains are more stable than linear chains, as it 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 degrees 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

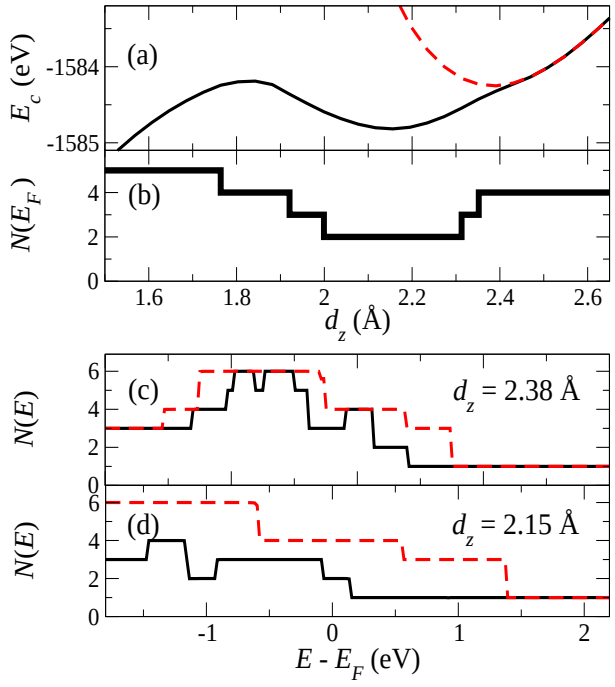

FIG. 1: (a) Cohesive energy E_c and (b) number of open scattering channels $N(E_F)$ of platinum chains as a function of d_z. $N(E)$ as a function of energy E calculated at (c) $d_z = 2.38$ and (d) $d_z = 2.15$ Å for zigzag (solid line) and linear (dashed line) chains.

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, similar to that predicted by Sen et al. [18].

Fig. 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 $N(E_F) = 5$ 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 2.25 Å, $N(E_F)$ increases in two steps to 4 G_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 $d_{x^2-y^2}$ 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 make small angles with the z-axis at this distance and therefore, the d_z-dependence of the PDOS and $N(E_F)$ look both 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 chains. 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 larger number of open scattering channels.

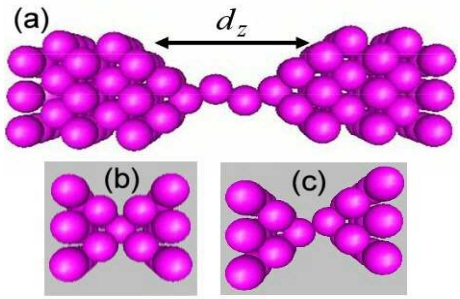

FIG. 2: The different atomic chains connecting (001) oriented fcc leads studied in this paper: (a) Four-atoms chain, (b) single atom contact and (c) 2-atom chain. d_z is the distance between leads.

This simplified picture cannot however explain all 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, a number of atomic planes of bulk platinum are included in the scattering region, until the chosen degree of convergence is obtained.

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 chain and the two 2×2 planes forming the hollow site. The total free energy is therefore calculated as a function of the distance d_z between the outer slices (unrelaxed) as indicate in figure 2. In Fig. 3 we plot the cohesion curves for zigzag atomic chains with a number of atoms ranging between 2 and 5.

The free 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 lo-

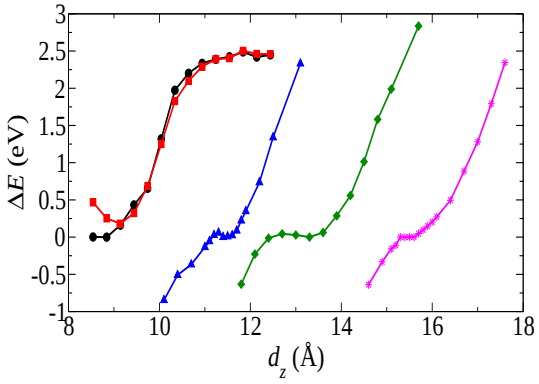

FIG. 3: Cohesion curves of the chain plus leads systems, for zigzag and linear chains of two atoms (circles and squares, respectively), and zigzag chains containing 3, 4 and 5 atoms (triangles, diamonds and stars, respectively). All curves have been shifted in energy in order to make the local minimum coinciding with the zero value and allow a better comparison. d_z is the distance between leads. Lines have been added to guide the eye.

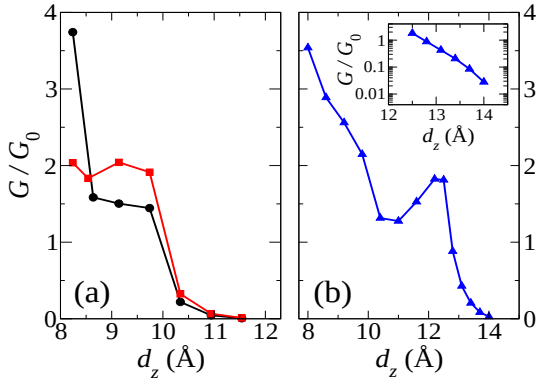

FIG. 4: Conductance of platinum monoatomic chains. (a) 2 atoms in a zigzag or linear arrangement (circles or squares, respectively). (b) 3 atoms; in the inset is plotted the tail of the curve in a logarithmic scale, that clearly shows the tunneling behavior when the chain breaks.

cal 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 agreement with experiments [5]. The only configuration which does not fit into this pattern is the single atom contact, whose equilibrium distance is 2.8 Å away from the two-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. This leads us to ascribe the peaks found in length histograms [5] to chains 2-, 3-, 4- and 5-atoms long. Fig. 3 also indicates that the region of stability of the $(n+1)-$atom chain begins at a distance where the the $n-$atom chain is very stretched and therefore close to being broken. This fact helps understand why the first two peaks found in length-histograms, that correspond to chains with two or three atoms, are much higher than those attributed to chains of four or five atoms [4, 5], 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 degrees for the 3-atom chain), but increase with the chain length (21.6 degrees for 4-atom chain). The case of the 5-atom chain is more complicated: the two atoms joining the leads make angles of 36.3 degrees, while those in the middle have angles equal to 16.1 degrees.

Moving to transport, we observe that the single atom contact behaves very differently from any other, with a conductance of about 5.9 G_0 at the equilibrium distance, which decreases almost linearly to $G = 3.5\,G_0$ until the contact breaks. These values are very different from those of reference [9], where the pyramid-like structure of the contact was not included leading to an overestimate of the interatomic distance. For the 2-atom chain we find a conductance of 1.5 G_0 at the equilibrium distance in the zigzag arrangement and a conductance ranging between 1.8 and 2.0 G_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 [9]. 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 non-monotonic 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 1.0 and 1.5 G_0 is reached, when 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 2 G_0 is formed. Finally, the chain enters the exponential tunneling regime, as shown in the inset to Fig. 4 (b), whose onset signals the point where the chain would break or a new atom would enter the chain.

In Fig. 5 (a) we plot the conductance as a function of the number of atoms in the chain, computed at the equilibrium distance. The values for $n > 2$ range between 1.6 and 1.0 times G_0, which is significantly smaller than that of the monatomic contact. These conductances decrease almost monotonically as a function of n and do not clearly show the

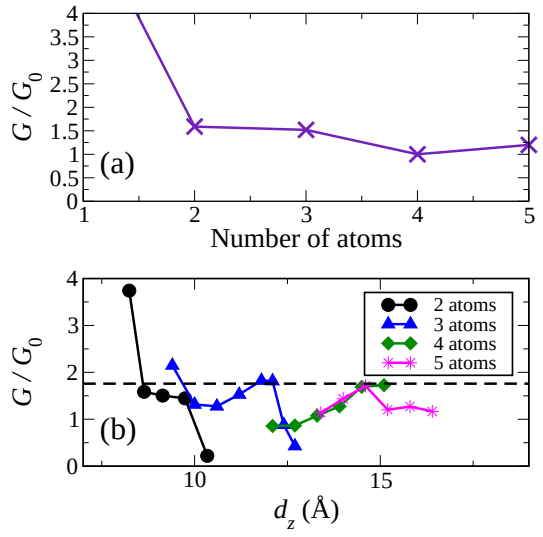

FIG. 5: (a) Conductance vs. the number of atoms in the chain for the equilibrium distance. (b) Evolution of the conductance of 2-, 3-, 4- and 5-atoms chains as a function of d_z (circles, triangles, diamonds and stars, respectively).

suggested parity effect discussed in [5].

To obtain oscillations, we return to the behavior of G as a function of distance, for fixed n. As shown in Fig. 4, the conductance indeed oscillates as chains of fixed n are stretched, primarily due to the closing and opening of channels as the angles between the atomic bonds and the z-axis decrease. To compare with experiment, we plot in Fig. 5(b) the conductance of all chains together as a function of distance. The average conductance measured in the experiments of [5] are obtained by sampling these curves with an unknown sampling probability, which depends on temperature, voltage and presumably external noise sources. Since the combined curves shown in Fig. 5(b) display clear oscillations, the resulting ensemble averaged conductance will also oscillate with distance.

In view of the above results, we propose that the oscillations seen in the experiments by Smit et al. [5] are not primarily due to parity effects, but instead have a structural origin. Oscillations in the conductance are mainly due to the gradual closing and opening of channels as the angles between the atomic bonds and the z-axis increase and decrease. For a stretched chain, such angles increase if a new atom enters the chain, and subsequently decrease as the chain is further stretched. Moreover we link the size of the conductance 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, 1.2 G_0, is slightly bigger than that of the four-atom chain (1.0 G_0). This is also easily explained by our calculations, since atoms in the middle of the 5-atoms chains have a smaller angle than those of four atoms chains (16.1^0 versus 21.6^0). Our calculations do not rule out that electronic interference may affect the conductance of platinum chain but this seems not to be the dominant effect.

In summary, we have shown that monoatomic 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. We have been able to explain the negative slope that is found for larger chains. We propose that conductance oscillations are not given by parity effects but rather to gradual opening and closing of channels as chains are elongated.

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