Different wavelength oscillations in the conductance of 5*d* metal atomic chains

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Combining *ab initio* and self-consistent parametrized tight-binding calculations we analyze the conductance properties of atomic chains of 5*d* elements like Au, Pt and Ir. It is shown that, in addition to the even-odd parity oscillations characteristic of Au, conduction channels associated with the almost full *d* bands in Pt and Ir give rise to longer periods which could be observed in sufficiently long chains. The results for short chains are in good agreement with recent experimental measurements.

A traditionally idealized textbook example, the atomic linear chain, has recently become an actual system that can be explored experimentally. The formation of atomic chains several (up to 7–8) atoms long has been achieved in recent years using experimental techniques like scanning tunneling microscope and mechanically controllable break junctions.[1] In both cases, evidence has been found of chain formation in the last stages of pulling an atomic contact for certain metallic elements like Au, Pt and Ir. It has been suggested that the stability of the chains for these 5*d* elements as opposed to other metals is related to relativistic effects involving transfer of charge between *sp* and *d* bands.[2]

These atomic chains exhibit, on the other hand, interesting conductance properties. Recent experimental results indicate the presence of conductance oscillations with period $\sim 2a$ (*a* being the interatomic distance) after averaging over many realizations of the chain.[3] While in the case of Au the oscillations are superimposed to an almost constant background of the order of the quantum of conductance $G_0 = 2e^2/h$, in the case of Pt the mean value of the conductance exhibits a continuous decrease from ~ 2.5 to $\sim 1.0 G_0$. On the other hand, for Ir chains the conductance varies between ~ 2.2 and $\sim 1.8 G_0$ with a less clear oscillatory behavior.

Theoretical studies of the conductance of atomic chains have been so far mainly restricted to idealized models[4] or to *ab initio* calculations for light metallic elements like Na, Si or C,[5] but realistic calculations for the actual 5*d* metal chains, in which the role of *d* orbitals is expected to be relevant, are still lacking.[6] From the theoretical point of view even-odd conductance oscillations are already present at the level of simple tight-binding (TB) models for the half-filled case.[4] This is an interference phenomena arising from the commensurability of the Fermi wavelength and the lattice spacing. This behavior has also been observed in more realistic calculations based on *ab initio* methods for Na and C.[5,7] This simple explanation can account qualitatively for the behavior in the case of Au, characterized by a full 5*d* band and a nearly half-filled 6*s* band.

For single atom Pt contacts the value around $2.5 G_0$ has been attributed to the contribution of additional channels associated with the 5*d* orbitals.[8] Thus the observation of oscillations with period 2*a* is not at all obvious in this case and deserves a detailed analysis. The aim of this work is to un-

derstand the possible mechanisms leading to this behavior. We will show that the channels associated with the almost full *d* bands in Pt and Ir exhibit transmission oscillations with longer periods which can be associated with the Fermi wave vector of the bands in the infinite chain.

We shall consider model geometries like the one depicted in Fig. 1 in which the atomic chain is connected to bulk electrodes represented by two semi-infinite fcc perfect crystals grown along the (111) direction. The interatomic distance *a* will be allowed to take larger values than in the relaxed structure of the infinite chain to account for the effect of the applied stress. For simplicity we shall concentrate first on the analysis of the ideal linear geometry, discussing in a second step the effect of possible structural deformations.

A convenient approach to quantum transport calculations in atomic size conductors uses a self-consistent parametrized TB model in which the main features of the bulk band structure are included.[9] This type of calculation has been fruitful to obtain information about the conduction channels in one atom contacts.[10] In the particular case of atomic chains a natural starting point is the band structure of the infinite linear chain whose main properties are discussed below.

The electronic structure and total energy calculations for the infinite chains were performed using the WIEN97 code.[11] This is an implementation of the linearized augmented plane wave method based on density functional theory. For exchange and correlation we have used the local density approximation, with the correlation part as given by Perdew and Wang.[12]
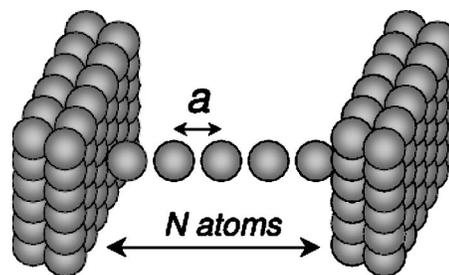

FIG. 1. Model geometry considered for the calculation of the conductance. The electrodes are represented by semi-infinite fcc crystals grown in the (111) direction.
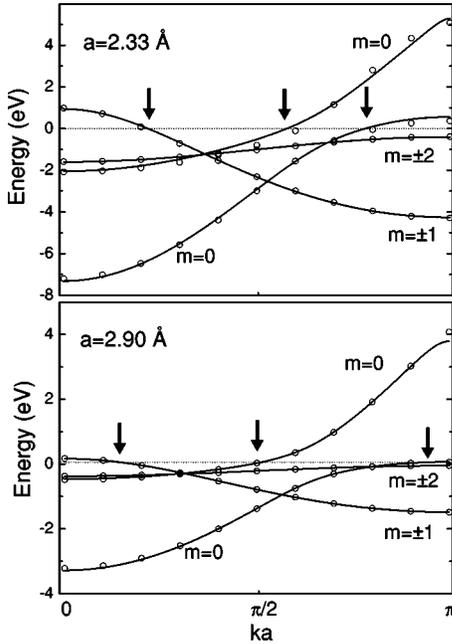
FIG. 2. Band structure of the infinite Pt chain for two different interatomic distances. The symbols and the full lines correspond to the *ab initio* and to the fitted TB bands, respectively. The bands are classified by the quantum number m corresponding to the projection of the angular momentum on the chain axis. The arrows indicate the crossing of the Fermi level for the $m=0$ and the $m=\pm 1$ bands.
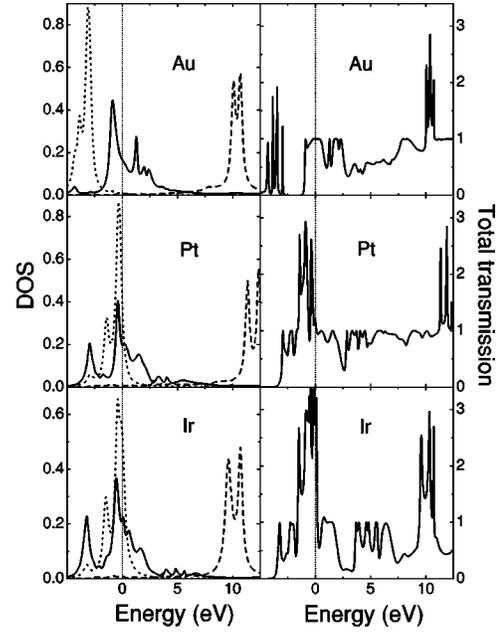

FIG. 3. Local density of states (LDOS) at the central atom and total transmission for Au, Pt and Ir chains with $N=5$ at an intermediate elongation. The LDOS is decomposed in s (full line), d (dotted line) and p dashed line with the same normalization in the three cases.

We will discuss the band structure of the chains taking the case of Pt as a representative example (Au and Ir exhibit a rather similar band structure although displaced with respect to E_F). Figure 2 shows the bands around the Fermi energy for Pt at two different situations with increasing stress: one close to the calculated equilibrium situation ($a=2.33$ Å) and the other corresponding approximately to the maximum stress before breaking the chain ($a=2.90$ Å). The fits of these bands using a Slater-Koster TB scheme are shown as full lines. Several features of this band structure are worth noting: 1) Symmetry considerations allow one to classify the bands according to the projection of the angular momentum along the chain axis m (we take the z axis along the chain direction). 2) Close to the Fermi level there is an almost flat filled twofold degenerate band with d_{xy} and $d_{x^2-y^2}$ ($m=\pm 2$) character. The other partially filled and more dispersing bands have $s-p_z-d_{z^2}$ ($m=0$) and p_x-d_{xz} or p_y-d_{yz} ($m=\pm 1$) character (see the labels in Fig. 2). 3) When the chain is elongated the dispersion of the bands is reduced and a net charge transfer from s to d is observed, tending rather fast to the "atomic" charge configuration $5d^9 6s^1$. As a consequence the upper $m=0$ band with a predominant s character gets closer to the half-filled situation ($k_F a \sim \pi/2$) which, as commented above, would give rise to even-odd conductance oscillations. Notice on the other hand that the $m=\pm 1$ bands cross the Fermi level at a lower wave vector.

In order to describe the electronic properties for a model geometry like the one of Fig. 1 the TB Hamiltonian is written as $\hat{H}=\Sigma h_{i,j,\alpha,\beta}\hat{c}^\dagger_{i,\alpha,\sigma}\hat{c}_{j,\beta,\sigma}=\hat{H}_{\text{chain}}+\hat{V}_L+\hat{V}_R+\hat{H}_R$, where $\hat{H}_{\text{chain}}$ and $\hat{H}_{L,R}$ describe the uncoupled chain and the left and right

electrodes, respectively; $\hat{V}_{L,R}$ being a coupling term between the chain and the electrodes which, in the model geometry of Fig. 1, corresponds to the hopping elements connecting the outermost atoms of the chain and their three nearest neighbors on the electrodes surface. The matrix elements $h_{i,j,\alpha,\beta}$, where i,j and α,β design sites and orbitals, respectively, are taken from the fits to the chain and to the bulk *ab initio* band structure. As a self-consistency condition we impose local charge neutrality by fixing the charge of the d orbitals and sp orbitals within the chain equal to the ones of the infinite chain.[13] The corresponding condition is also imposed on the electrodes surfaces.

Once the TB Hamiltonian has been built the conductance $G(E)=G_0 \text{Tr}[\hat{t}^\dagger(E)\hat{t}(E)]$ of the chain is calculated in terms of the matrix elements of the Green function operator $\hat{G}^r(E)=\lim_{\eta\to 0}[E+i\eta-\hat{H}]^{-1}$ using

$$\hat{t}(E)=2\hat{\Gamma}^{1/2}_L(E)\hat{G}^r_{1N}(E)\hat{\Gamma}^{1/2}_R(E), \qquad (1)$$

where $\hat{\Gamma}_{L,R}$ are the matrix tunneling rates connecting the chain to the leads.[9] The transmission matrix $\hat{t}^\dagger \hat{t}$ can then be diagonalized in order to obtain the transmission eigenchannels and eigenvalues τ_n which characterize completely the linear transport properties of the system.

In order to illustrate the main features and the differences between Au, Pt and Ir, we show in Fig. 3 the density of states and the energy-dependent transmissions for an $N=5$ chain of these metals at an intermediate elongation. As has been shown in previous works,[6] Au chains are characterized by a single conducting channel around the Fermi energy with predominant s character. The transmission of this channel lies
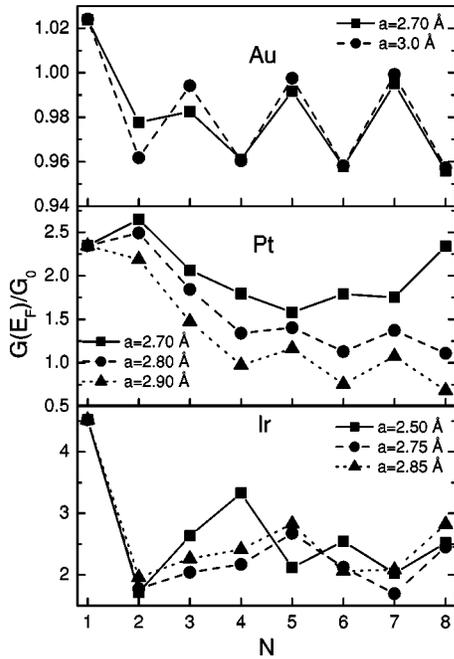
FIG. 4. Evolution of the conductance with N for different values of the interatomic distance a.

FIG. 5. Channel decomposition of the conductance for Pt and Ir as a function N for intermediate elongations. The legends indicate the symmetry of the associated bands in the infinite chain. The dotted lines in the case of Ir correspond to functions of the form $\sim \cos^2(k_{F,i} Na)$ where $k_{F,i}$ is the Fermi wave vector of the associated bands, which help to visualize the oscillatory behavior.

close to one and exhibits small oscillations as a function of energy resembling the behavior in a single band TB model.[4] For odd N charge neutrality provides a strong mechanism for the almost perfect quantization of the conductance, as discussed in Ref. 14 for one atom.

In the case of Pt the contribution from the almost filled $5d$ bands becomes important for the electronic properties at the Fermi energy. There are three conduction channels with significant transmission at E_F: one due to the hibridization of $s-p_z$ and d_{z^2} orbitals, and two almost degenerate with p_x-d_{xz} and p_y-d_{yz} character, respectively. One can naturally associate this channel distribution with the band structure presented in Fig. 2.

The contribution of the $5d$ orbitals is even more important in the case of Ir where a fourth channel related to the lower $m=0$ band exhibits a significant transmission.

Let us analyze the evolution of the conductance with the number of atoms in the chain. We find that this evolution is rather sensitive to the elongation, especially in the case of Pt and Ir (for Au the conductance exhibits small amplitude even-odd oscillations, $\sim 0.04 G_0$, which remain basically unaffected upon stretching). The center panel in Fig. 4 shows the total conductance of Pt chains as a function of N for different interatomic distances. Notice that a slight increase of a from the equilibrium value leads to a global decrease of the conductance with N together with the appearance of even-odd oscillations. For $a=2.9$ Å the total conductance drops from $2.4 G_0$ to around $1 G_0$ for $N>4$, while the oscillations amplitude is of the order of $0.2 G_0$.

A deeper understanding of this behavior can be gathered when analyzing the evolution of the conductance and its channel decomposition for even longer chains. This is illustrated in Fig. 5 for the case of Pt and Ir. As can be observed the decrease of the total conductance of Pt for $N<7-8$ cor-
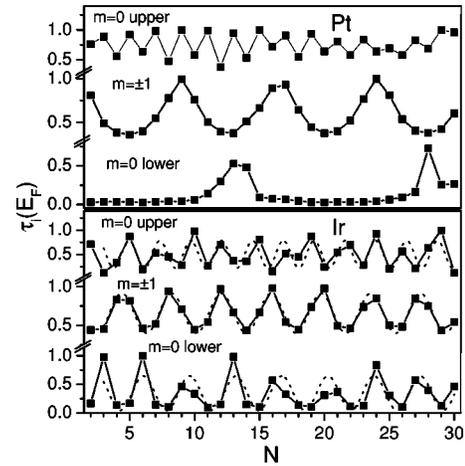
responds actually to a long period oscillation in the transmission of the two nearly degenerate channels associated with the $m=\pm 1$ bands. This period can be related to the small Fermi wave vector of these almost filled d bands, as indicated by the left arrows in Fig. 2. In addition, the upper $m=0$ band crossing the Fermi level is close to half-filling giving rise to the even-odd oscillatory behavior observed in the transmission of the channel with predominant s character. The lower $m=0$ band tends to be completely filled as the chain is elongated and the corresponding channel is nearly closed for short chains. However, for intermediate elongations one can still appreciate a very long period oscillation in its transmission, rising up to $\sim 0.5 G_0$, as can be observed in the upper panel of Fig. 5.

In the case of Ir both the $m=\pm 1$ and the lower $m=0$ are less filled than in Pt leading to four partially open channels. The corresponding values of the Fermi wave vector fix its overall oscillatory behavior as illustrated in the lower panel of Fig. 5.

The results presented so far correspond to the idealized geometry depicted in Fig. 1. Deviations from this situation can arise both from disorder in the atomic positions and possible structural distortions. Previous studies indicate that the relaxed structure for Au chains corresponds to a zig-zag configuration.[15] Our *ab initio* calculations indicate that this is also the case for Pt and Ir, the main effect of the external stress being first to suppress the zig-zag deformation and then to increase the interatomic distances. This deformation has some effect on the band structure, mainly consisting in the breaking of the degeneracies present in the linear case. Although this would affect the results close to the relaxed situation, we have checked that the main conclusions regarding the appearance of long period oscillations associated with the d bands are still valid. On the other hand, molecular dynamics simulations suggest a non-uniform distribution of bond lengths along the chain.[16] We have found that this type of deformation as well as the inclusion of moderate disorder

in the atomic positions do not give rise to qualitative changes in the conductance behavior as long as they remain within the ranges predicted in Ref. 16.

In conclusion we have analyzed the conductance properties of Au, Pt and Ir atomic chains. In addition to the well-understood even-odd parity effects of Au, in metals like Pt and Ir the partially filled $5d$ bands give rise to a more complex oscillatory pattern in which more than a single wavelength can be identified. As a general rule we predict that the transmission corresponding to each conduction channel oscillates as $\sim\cos^2(k_{F,i}Na)$ where $k_{F,i}$ is the Fermi wave vector of the associated band in the infinite chain. In the case of Pt the charge transfer from s to d orbitals that takes place upon stretching leads to a nearly half-filled s band with the consequent even-odd oscillations in the corresponding channel,

while the channels associated with the almost filled d bands exhibit longer period oscillations. The total conductance for short chains ($N<7-8$) exhibits an overall decrease with superimposed even-odd oscillations in qualitative agreement with the experimental results of Ref. 3. In the case of Ir we find four partially open channels with rather similar wavelengths leading to a less clear oscillatory pattern. Our predictions for the channel decomposition could be checked experimentally by similar techniques to the ones used in Refs. 10 and 17. Advances in the fabrication techniques would allow one to test these predictions for longer chains.

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