H₂ dissociation over Au-nanowires and the fractional conductance quantum

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The dissociation of H₂ molecules over stretched Au nanowires and its effect on the conductance are analyzed using a combination of Density Functional (DFT) total energy calculations and nonequilibrium Keldysh-Green function methods. Our DFT simulations reproduce the characteristic formation of Au monoatomic chains with a conductance close to $G_0 = 2e^2/h$. These stretched Au nanowires are shown to be better catalysts for H₂ dissociation than Au surfaces. This is confirmed by the nanowire conductance evidence: while insensitive to molecular hydrogen, atomic hydrogen induces the appearance of fractional conductances ($G \sim 0.5G_0$) as observed experimentally.

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Gold surfaces are chemically inert and regarded as poor catalysts at variance with other metal surfaces. The low reactivity of molecular hydrogen on noble metal surfaces, like Au and Cu, seems to be well understood [1, 2, 3, 4]. Density Functional (DFT) calculations [1] have shown that the dissociation of H₂ on Au or Cu is an activated process: for large molecule-surface distance, $d$, the interaction energy is repulsive with a high barrier of 1.1 eV (around $d = 1.5$ Å), which the molecule has to overcome to move along the reaction path H₂ → H + H and reach the final atomic chemisorption state, with a total adsorption energy ($2.07$ eV per atom [4]) that is less than the H₂ binding energy ($4.75$ eV). Compared to surfaces, small particles are known to be better catalysts. Au is, in particular, considered as an exceptional catalyst when prepared as nanoparticles on a variety of support materials [2]. Understanding this strong catalytic activity is still the subject of an extensive research effort with different possible explanations, including the particle shape or perimeter, support effects and the metal oxidation state [5, 6, 7, 8].

Nanowires are a good example of systems whose size is so small that one can expect their reactivity with molecules to be increased considerably. The formation of metallic nanocontacts has been analyzed in detail thanks to the gentle control of the distance at the atomic scale provided by both the Scanning Tunneling Microscope and the Mecanically Controllable Break Junction [2, 10]. While, in many metallic contacts, the formation of nanowires during the last stages of the stretching, just before the breaking point, is characterized by an atomic dimer geometry (Al is a paradigmatic case [11, 12]), in Au the final geometry seems to be a chain of several atoms between the two electrodes with a conductance close to the conductance quantum unit $G_o = \frac{2e^2}{h}$ [13]. Although the formation and stability of monoatomic Au chains has been addressed by several authors [14, 15, 16], certain relevant aspects—in particular, the changes in the structural and transport properties of the nanocontacts induced by the presence of impurities [17, 18, 19, 20]—are not yet fully understood.

Recently, Csonka et al [21] have analyzed the interaction of H₂ with a breaking gold nanowire and have found new fractional peaks (in units of $G_o$) in the conductance histogram. Moreover, conductance traces in a stretched nanowire demonstrate a reversible transition between fractional and integer conductances, in a time scale of milliseconds or seconds, suggesting successive adsorption and desorption of hydrogen on the chain. These experiments do not show these effects for Cu and Ag, where stable single-atom chains are not formed. This suggests the great importance of the Au chains in the variation of gold conductance in the presence of H₂. Csonka et al [21] have proposed a possible explanation for the observed behaviour in terms of a dimerization effect which has been theoretically predicted for idealized clean Au nanowires [14, 22]. However this dimerization has neither been observed in conductance histogram measurements nor in more complex theoretical simulations [2, 14, 23].

In this Letter, we show that there is, in fact, a strong link between the enhanced reactivity of the stretched monoatomic gold chains and the appearance of the fractional conductance peaks. First, we have simulated the whole deformation process for an Au nanocontact upon stretching, finding the formation and the final breaking of a 4-atom Au chain. The realistic nanocontact configurations, calculated in this way, are then used to investigate whether the new fractional peaks in the conductance are associated with adsorbed molecular or atomic hydrogen. As our analysis suggests that only atomic hydrogen can be responsible for these changes in the nanowire conductance, we have also investigated how the chemical reaction H₂ → H + H is affected by the presence of a freely suspended Au-wire. This simplified model captures the key ingredients in the real nanocontact struc-
FIG. 1: Total energy per unit cell and ball-and-stick structure models (see also Figure 2) for the Au nanowire as a function of the stretching displacement. The inset shows the total differential conductance and channel contribution along the stretching path.

Our calculations show that a stretched Au-nanowire is much more reactive than the Au surfaces, with a small activation barrier, around 0.1 eV, for the H\(_2\) dissociation and larger chemisorption energies. Our results for the nanocontact conductance, combined with the low value we have calculated for the \(\text{H}_2\)-reaction activation barrier, strongly suggest that the molecule dissociates on a Au-nanowire and that the observed fractional conductance upon adsorption of molecular hydrogen is basically due to the atomic hydrogen produced in the reaction.

The inset of figure 1 shows the conductance of the system along the stretching process, as well as the different channels contributing to it. Notice that these results compare well with the experimental evidence [9]. In particular, we reproduce (a) the long conductance plateau associated with the formation of the monoatomic chain (configurations C \(\rightarrow\) I), where the conductance is basically controlled by a single channel associated mostly with the Au s-electrons; and (b) the conductance oscillations during the elongation process. The very good agreement between both our structural and conductance results for the evolution of the Au nanocontact and the experimental evidence provides strong support to the remaining simulations presented in this paper.

In a second step, we have analyzed the nanowire conductance upon the adsorption of molecular and atomic hydrogen. Starting with the different geometries corresponding to the points E, F and G in figure 1, we have analyzed, via our local-orbital DFT code, how molecular and atomic hydrogen are adsorbed on those geometries and, then, how the nanowire conductance is modified according to the new optimized structures (see Figure 2). Molecular hydrogen is weakly adsorbed on all the different nanowires, with energies of around 0.3 eV. Notice that, in all these cases, molecular hydrogen does not penetrate the nanowire too much (see figure 2) and the conductance properties of the nanowire are not affected prac-
tically by the adsorption of molecular hydrogen. In particular, for the three cases shown in figure 2 the nanowire conductance takes the values 1.05 \( G_o \), 1.05 \( G_o \) and 0.95 \( G_o \), respectively. Atomic hydrogen introduces more dramatic changes: in particular, for the cases shown in figure 2 the adsorption energies are 3.3 eV, 3.5 eV and 3.9 eV for the chains with two, three or four atoms in the nanowire, respectively. These values are much larger than the ones found for H adsorbed on a surface (around 2.1 eV) [3, 4]. Moreover, we find significant modifications in the conductance of these three cases, with total values of 0.68 \( G_o \), 0.65 \( G_o \) and 0.55 \( G_o \), respectively. The eigenchannel analysis for all these cases shows that the transport is dominated, as in the clean nanowire, by a channel mostly associated with the Au s-electrons but with a reduced transmitivity. This reduction is related to the significant displacement of the density of states (DOS) to lower energies (particularly evident for the d bands) for the Au atoms bonded to hydrogen that results in a reduction of the total DOS at \( E_F \). The nanowires with three or four atoms have been reanalyzed assuming that two hydrogen atoms are simultaneously adsorbed on the chain: the case of three atoms (case F) presents a conductance of 0.45 \( G_o \), while for a four-atom nanowire (case G) the conductance is 0.2 \( G_o \).

The enhanced reactivity of Au-chains, with respect to Au-surfaces, is due to the change in the Au DOS. Fig. 3b shows this DOS for the atoms of the Au(111)-surface, and for the Au-atoms of the four atom chain in the nanowire: Au-atoms with lower coordination form directional bonds and present a narrower DOS shifted towards the Fermi level. Then, for \( H \) chemisorbed on the chain, its DOS (see fig. 3a) presents a tightly bound state at -7.3 eV below the Fermi level, whereas the DOS for \( H \) on the Au(111)-surface presents a broadened resonance with some contribution from antibonding states just below the Fermi level [1]. Notice that the reactivity of Au chains is further increased by the wire stretching due to a further shift of the Au-bands towards the Fermi level.

It is remarkable that, in the geometries shown in figure 2 neither the molecule nor the atom penetrates the nanowire, breaking the bond between two Au atoms. Recent work by Barnett et al [17] showed that, for an essentially broken Au wire (with \( G \sim 0.02G_o \), a barrierless insertion of the \( H_2 \) molecule into the contact is possible. This would correspond, in our case, to a wire state beyond the configuration I in figure 1 where the conductance is still very close to \( G_o \). They then used this configuration as a starting point for a detailed study of the structure, orientation and stability of the molecule upon compression of the wire. Our approach is different, since we are interested in the wire-H\(_2\) interaction during the chain formation process. We have calculated the energy barriers the molecule experiences when moving from the geometries shown in figure 2 to inserted sites. Our calculations yield values larger than 0.5 eV.

Both the conductance and the total energy results discussed so far support the dissociation of molecular hydrogen in the Au monoatomic chains. As the energetics were discussed in terms of the local orbital code, using the LDA approximation for the exchange-correlation, we have re-analyzed the dissociation mechanism on freely suspended Au-wires, with \( H \) (or \( H_2 \)) adsorbed on them, using CASTEP [28, 29], with a gradient corrected approximation [30] (GGA) for the exchange-correlation functional. This simplified model for the nanowire is dictated by the computational resources needed for this full calculation, but it offers the possibility to discuss the relative contribution of the low dimensionality and the strain in the enhanced reactivity of the nanowire.

We have considered a freely suspended Au wire with six independent atoms per chain and periodic boundary conditions chosen to produce a stretch deformation in order to simulate the breaking process. After relaxing the free wire for each strain condition, we have studied how molecular hydrogen interacts with it: in particular, we have explored the possibility of having the following reaction, \( H_2 \rightarrow H + H \) on the suspended wire. Figure 4 shows this reaction. More...
shows our main results for a wire with a 11% strain in an arbitrary configurational path: the case A in the figure represents the geometry of H₂ interacting with the freely suspended wire; this is a physisorbed state with an adsorption energy of around 0.02 eV. Case B corresponds to an intermediate state in which a H-atom is chemisorbed between two Au-atoms, and the other H is still bonded to the Au-atom on which the molecule was initially physisorbed: this case has an adsorption energy of 0.3 eV; we have found, however, a barrier of 0.1 eV between states A and B. Case C corresponds to the final reaction state, in which the two H are adsorbed between two Au-atoms; the chemisorption energy of this final state is 1.4 eV, but again we find an energy barrier of 0.4 eV between states B and C. The reaction path drawn in figure 4 shows that molecular hydrogen sees an energy barrier of 0.4 eV between states A and B. Case C corresponds to the final reaction state, in which the two H are adsorbed between two Au-atoms; the chemisorption energy of this final state is 1.4 eV, but again we find an energy barrier of 0.4 eV between states B and C. The reaction path drawn in figure 4 shows that molecular hydrogen sees a total barrier of 0.1 eV for the reaction H₂ → H + H on a freely suspended Au-wire. In a Au-surface, the energy barrier for that reaction is around 1.0 eV, and the adsorption energy, with respect to H₂, is negative, around 0.5 eV. These numbers show the extreme importance that a stretched Au-nanowire has in the reactivity of molecular hydrogen: its reaction energy barrier and its chemisorption energy are lowered at least by 1 eV by the nanowire.

In conclusion, stretched Au nanowires are much more reactive with molecular hydrogen than Au surfaces. Our DFT-GGA calculations show that, in a stretched Au nanowire, the activation barrier for H₂ dissociation is very small, around 0.10 eV. Notice that this is a reliable upper bound, as the use of the the GGA approximation (that only partially corrects the gross overestimation of barriers in LDA), the freely suspended wire geometry considered, and the neglect of possible quantum tunneling effects in H tend to overestimate the calculated barrier. This enhanced reactivity can also be expected in the case of Pt, where the formation of chains of several atoms has been also observed. Complementary evidence is given by Csonka et al. for data for the conductance of a stretched Au nanowire with adsorbed molecular hydrogen. Our calculations indicate that only atomic hydrogen can be responsible of the changes observed by those researchers in the nanowire conductance. It is the combination of these two results, our calculated activation barrier and the changes in the nanowire conductance, that strongly suggest that molecular hydrogen dissociates when adsorbed on stretched Au nanowires.

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