

Hydrogen 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 theory (DFT) total energy calculations and nonequilibrium Keldysh-Green function methods. Our DFT simulations reproduce the characteristic formation of Au monatomic 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 are regarded as poor catalysts at variance with other metal surfaces. The low reactivity of molecular hydrogen on noble metal surfaces, such as Au and Cu, seems to be well understood [1–4]. Density functional theory (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 in order to move along the reaction path $H_2 \rightarrow H + H$ and reach the final atomic chemisorption state, with a total adsorption energy (2.07 eV per atom [4]), which is less than the H₂ binding energy (4.75 eV). Compared to surfaces, small particles are known to be better catalysts. In particular, Au is considered an exceptional catalyst when prepared as nanoparticles on a variety of support materials [5]. 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 [5–8].

Nanowires are a good example of systems whose small size enhances their reactivity with molecules considerably. The formation of metallic nanocontacts has been analyzed in detail thanks to the delicate control of distance at the atomic scale, provided by the scanning tunneling microscope and the mechanically controllable break junction [9,10]. In many metallic contacts, the formation of nanowires, during the last stages of the stretching prior to the breaking point, is characterized by an atomic dimer geometry (Al is a paradigmatic case [11,12]). In the case of 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 $G_0 = \frac{2e^2}{h}$ [13]. Although the formation and stability of monatomic Au chains has been addressed by several authors [14–16], certain relevant aspects—in particular, the changes in the structural and transport properties of the nanocontacts induced by the presence of impurities [17–20]—are not yet fully understood.

Recently, Csonka *et al.* [21] analyzed the interaction of H₂ with a breaking gold nanowire and found new fractional peaks (in units of G_0) 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 behavior, in terms of a dimerization effect, which has been theoretically predicted for idealized clean Au nanowires [14,22]. However, this dimerization has not been observed in conductance histogram measurements or in more complex theoretical simulations [9,16,23].

In this Letter, we show that there is, in fact, a strong link between the enhanced reactivity of the stretched monatomic Au chains and the appearance of the fractional conductance peaks. First, we simulated the whole deformation process, during the stretching of a Au nanocontact, finding the formation and the final breaking of a 4-atom Au chain. The realistic nanocontact configurations, calculated in this way, were then used to investigate whether the new fractional peaks in the conductance were associated with adsorbed molecular or atomic hydrogen. As our analysis suggested that only atomic hydrogen can be responsible for these changes in the nanowire conductance, we also investigated how the chemical reaction $H_2 \rightarrow H + H$ is affected by the presence of a freely suspended Au wire. This simplified model captures the key ingredients in the real nanocontact structure and provides a natural playground to explore the influence of the low dimensionality and the strain in the different steps of the dissociation process. These 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 H₂ dissociation and larger chemisorption energies. Our results for the

nanocontact conductance, combined with the low value we have calculated for the 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.

Our calculations for stretched Au nanowires were performed using a fast local-orbital DFT-LDA (local-density approximation) code (FIREBALL2004 [24]), which offers a very favorable accuracy versus efficiency balance, if the basis of excited pseudoatomic orbitals [25] is chosen carefully. The electrical conductance of the Au nanocontacts was calculated, at each point of the deformation path (see Refs. [11,12] for details), using a Keldysh-Green function approach based on the first-principles tight-binding Hamiltonian obtained from the FIREBALL code.

First, we analyzed the formation of a Au nanowire obtained by stretching a thick Au wire having four layers, with three atoms in each layer, sandwiched between two (111)-oriented metal electrodes as shown in Fig. 1 (configuration *A* represents the initial relaxed configuration). We used a supercell approach, where periodic boundary conditions along different directions were introduced: parallel to the surface we considered a 3×3 periodicity, while in the perpendicular direction we artificially joined the last layers of both electrodes (see Refs. [11,12]). Figure 1 shows the total energy of the system as a function of the stretching displacement [26]: notice the energy jumps associated with the irreversible deformations and the structural rearrangements the wire has during this process. This figure (see also Fig. 2) shows several snapshots for different geometries corresponding to the labels in the energy curve. Our DFT simulations reproduced the characteristic

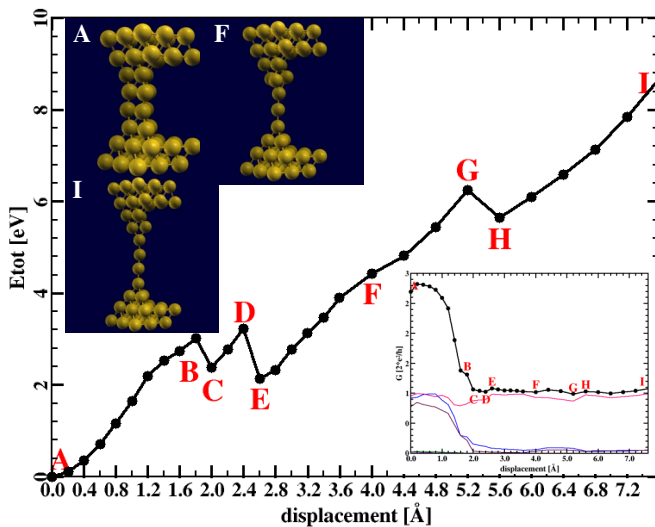


FIG. 1 (color online). Total energy per unit cell and ball-and-stick structure models (see also Fig. 2) for the Au nanowire as a function of the stretching displacement. The inset shows the total differential conductance and channel contribution along the stretching path.

formation of Au monatomic chains (with up to four atoms) found in the experiments. Similar results were recently obtained using parametrized tight-binding molecular dynamics [27].

The inset of Fig. 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 monatomic 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 Letter.

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 Fig. 1, we analyzed, via our local-orbital DFT code, how molecular and atomic hydrogen were adsorbed on those geometries and, then, how the nanowire conductance was modified according to the new optimized structures (see Fig. 2). Molecular hydrogen was weakly adsorbed on all the different nanowires, with energies of around 0.3 eV. Notice that, in all these cases, molecular hydrogen did not penetrate the nanowire too much (see Fig. 2) and the conductance properties of the nanowire were practically unaffected by the adsorption of molecular hydrogen. In particular, for the three cases shown in Fig. 2, the nanowire conductance took the values $1.05G_0$, $1.05G_0$, and $0.95G_0$, respectively. Atomic hydrogen introduced more dramatic changes: in particular, for the cases shown in Fig. 2, the adsorption energies were 3.3, 3.5, and 3.9 eV for the chains with two, three, and four atoms in the nanowire, respectively. These values were much larger than those found for H adsorbed on a surface (around 2.1 eV) [1,4]. Moreover, we found significant modifications in the conductance of these three cases, with total values of $0.68G_0$, $0.65G_0$, and $0.55G_0$, respectively. The eigenchannel analysis for all these cases revealed that the transport was dominated, as in the clean nanowire, by a channel mostly associated with the Au s electrons, but with a reduced transmittivity. 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 were reanalyzed assuming that two hydrogen atoms were simultaneously adsorbed on the chain: the case of three atoms (case *F*) had a conductance of $0.45G_0$, while for a four-atom nanowire (case *G*) the conductance was $0.2G_0$.

It is remarkable that, in the geometries shown in Fig. 2, neither the molecule nor the atom penetrates the nanowire,

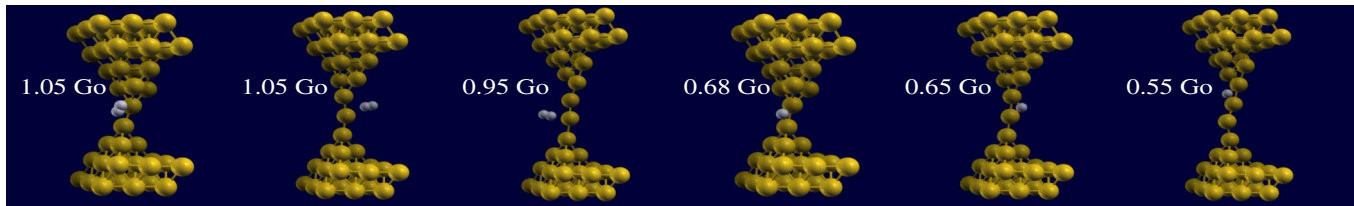


FIG. 2 (color online). Ball-and-stick structure models and total conductance for the adsorption of molecular (first three structures) and atomic hydrogen on different nanowire geometries (corresponding to the points E , F , and G in Fig. 1).

breaking the bond between two Au atoms. Recent work by Barnett *et al.* [17] showed that, for an essentially broken Au wire (with $G \sim 0.02G_0$), 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 Fig. 1, where the conductance is still very close to G_0 . 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 calculated the energy barriers the molecule experienced when moving from the geometries shown in Fig. 2 to inserted sites. Our calculations yielded values larger than 0.5 eV.

The enhanced reactivity of Au chains, with respect to Au surfaces, was due to the change in the Au DOS. Figure 3(b) 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. For H chemisorbed on the chain, the DOS [see Fig. 3(a)] has a tightly bound state at -7.3 eV below the Fermi level, whereas the DOS for H on the Au(111) surface

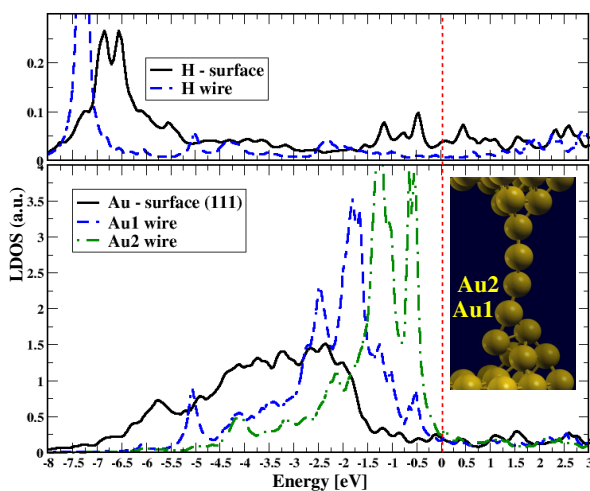


FIG. 3 (color online). (a) Density of states (DOS) for H chemisorbed on the Au(111) surface (solid line) and on the Au nanowire (dashed line). (b) Comparison of the DOS for topmost atoms in the Au(111) surface and for Au atoms in the four-atom chain of the nanowire (see inset).

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.

Both the conductance and the total energy results, discussed so far, support the dissociation of molecular hydrogen on the Au monatomic chains. As the energetics were discussed in terms of the local-orbital code, using the LDA for the exchange correlation, we reanalyzed 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 (GGA) [31] for the exchange-correlation functional. This simplified model for the nanowire was 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 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 studied how molecular hydrogen interacted with it: in particular, we explored the possibility of having the following reaction: $H_2 \rightarrow H + H$ on the suspended wire. Figure 4 depicts 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 H_2 interacting with the freely suspended wire; this was a physisorbed state with an adsorption energy of around 0.02 eV. Case B corresponds to an intermediate state in

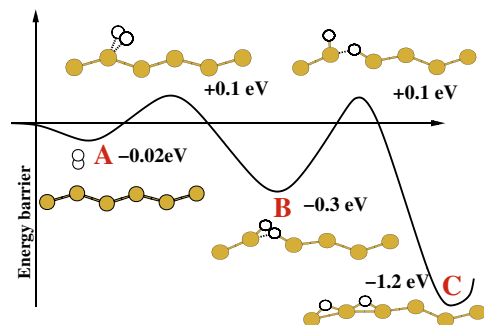


FIG. 4 (color online). Energetics of the H_2 dissociation on a stretched Au nanowire along an arbitrary configurational path.

which a H atom was chemisorbed between two Au atoms, and the other H was still bonded to the Au atom on which the molecule was initially physisorbed: this case had an adsorption energy of 0.3 eV; we found, however, a barrier of 0.1 eV between states *A* and *B*. Case *C* corresponds to the final reaction state, in which the 2 H were adsorbed between two Au atoms; the chemisorption energy of this final state was 1.4 eV, but again an energy barrier of 0.4 eV was found between states *B* and *C*. The reaction path, drawn in Fig. 4, shows that molecular hydrogen sees a total barrier of 0.1 eV for the reaction $H_2 \rightarrow H + H$ on a freely suspended Au wire. On a Au surface, the energy barrier for that reaction is around 1.0 eV, and the adsorption energy, with respect to H_2 , is negative, around 0.5 eV. These numbers show the great importance of the stretched Au nanowire in the reactivity of molecular hydrogen: its reaction energy barrier and its chemisorption energy are lowered at least by 1 eV by the nanowire. Notice that the reduced dimensionality of the nanowire (compared to the surface) is not enough to induce this high reactivity, as shown by similar calculations for a nonstrained chain, where we found an initial bound state for the molecule with energy -0.10 eV and quite large barriers (~ 0.5 eV) for the dissociation.

In conclusion, stretched Au nanowires are much more reactive with molecular hydrogen than Au surfaces. Our DFT-GGA calculations showed that, in a stretched Au nanowire, the activation barrier for H_2 dissociation was very small, around 0.10 eV. Notice that this is a reliable upper bound, since the use of the GGA approximation only partially corrects the gross overestimation of barriers in LDA; the freely suspended wire geometry, and the neglect of possible quantum tunneling effects in H, also 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 also been observed [32]. Complementary evidence is given by Csonka *et al.* [21] data for the conductance of a stretched Au nanowire with adsorbed molecular hydrogen. Our calculations indicate that only atomic hydrogen can be responsible for 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, which strongly suggest that molecular hydrogen dissociates when adsorbed on stretched Au nanowires.

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