

Inelastic fingerprints of hydrogen contamination in atomic gold wire systems

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Abstract. We present series of first-principles calculations for both pure and hydrogen contaminated gold wire systems in order to investigate how such impurities can be detected. We show how a single H atom or a single H₂ molecule in an atomic gold wire will affect forces and Au-Au atom distances under elongation. We further determine the corresponding evolution of the low-bias conductance as well as the inelastic contributions from vibrations. Our results indicate that the conductance of gold wires is only slightly reduced from the conductance quantum $G_0 = 2e^2/h$ by the presence of a single hydrogen impurity, hence making it difficult to use the conductance itself to distinguish between various configurations. On the other hand, our calculations of the inelastic signals predict significant differences between pure and hydrogen contaminated wires, and, importantly, between atomic and molecular forms of the impurity. A detailed characterization of gold wires with a hydrogen impurity should therefore be possible from the strain dependence of the inelastic signals in the conductance.

1. Introduction

In the late 1990s it was discovered that gold can form free-standing single-atomic wires [1]. It was first observed in molecular dynamics simulations of the formation of an atomic point contact [2, 3], and soon after also demonstrated experimentally [4, 5]. One of two popular techniques is typically used for creating such atomic gold wires. By utilizing the mechanical control of a scanning tunneling microscope (STM) to first contact a gold surface with a gold tip and next slowly withdraw the tip such that the gold bridge thins out, it may lead to the formation of a chain of single atoms [4]. The other method is based on the mechanically controllable break-junction (MCBJ) consisting of a macroscopic gold wire mounted on a flexible substrate, which is bent until the wire breaks and exposes clean fracture surfaces [5]. By controlling the bending it is possible to repeatedly form contacts and (in some cases) to pull chains several atoms long.

These ultimate thin metallic wires are interesting for several reasons. They are nearly ideal realizations of the perfectly transmitting one-dimensional conductor, and have a conductance close to the quantum $G_0 = 2e^2/h$ due to a single transmission channel. Also their mechanical and chemical properties are very different from that of bulk gold due the low coordination of chain atoms. Further, these wires allow for studying various fundamental quantum phenomena that are excellent for bench-marking new theoretical models and schemes.

While gold is usually perceived as an inert material it is known that low coordinated atoms—e.g., around surface step edges—are more chemically active [6, 7, 8]. Consequently it is expected that atoms arranged in a wire geometry (with only two nearest neighbors) may be

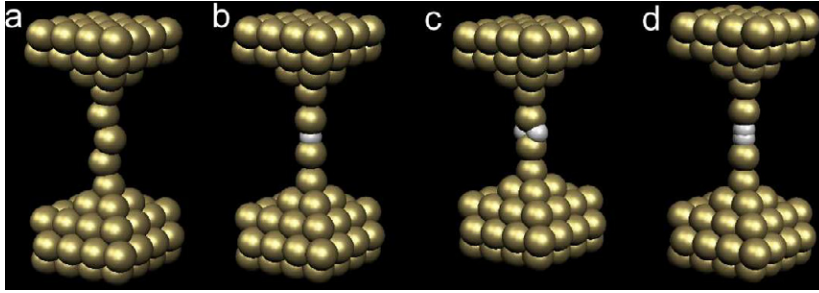


Figure 1. (Color online) Supercells modeling (a) pure gold wires and wires contaminated with (b) an H atom or (c-d) an H₂ molecule. The characteristic electrode separation L is measured between the second-topmost surface layers.

strongly reactive and hence prone to contamination. Indeed, a substantial amount of work has addressed issues related to the incorporation of various impurities in atomic gold wire systems [7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20]. One motivation for some of these studies was the anomalously large Au-Au distances (as long as 4 Å) which were directly observed by Ohnishi et al. [4] using transmission electron microscopy (TEM). To account for this observation researchers have therefore proposed that various light-weight impurities could be present in the wire, because these are difficult to detect with TEM due to their low contrast. Bahn et al. [7, 8] investigated the interaction of the diatomic molecules CO, N₂, and O₂ with an infinite gold wire model employing density functional theory (DFT), and suggested that oxygen is a likely candidate to form stable wires with Au-Au distances of more than 3.8 Å. Later Novaes et al. [11, 14] and Legoas et al. [9, 15, 16] examined several other impurity candidates with DFT and disputed whether H or C in fact is the most realistic contaminant accounting for the long bond length. Independently, Skorodumova and Simak also presented DFT-based calculations of gold wires with hydrogen that showed long Au-Au distances [12].

Beside these structural considerations the implications of hydrogen on the electronic transport properties of atomic gold wires have also been addressed both theoretically [13, 20] and experimentally [10, 17]. Whereas these studies generally provide evidence that hydrogen adsorbs on the wire and possibly dissociates, the details of the atomic arrangement are still not yet fully understood. For instance, conclusive evidence is missing of whether the atomic or the molecular form of hydrogen is the preferred configuration.

In a similar way that molecular hydrogen in a platinum contact has been characterized by means of vibrational spectroscopy [21, 22], we here present for the first time theoretical predictions for the inelastic conductance signals of atomic gold wires influenced by the presence of hydrogen. We consider a setup with either a single H atom or a single H₂ molecule incorporated in the middle of a short gold wire suspended between bulk gold electrodes. For comparison we also present the inelastic transport calculations for a pure gold wire system, for which the inelastic signals have previously been investigated [23, 24]. We find that by studying the inelastic signals of the gold wire formation in a hydrogen atmosphere it is possible—under certain conditions which we describe—to detect specific vibrational modes related to hydrogen. In particular, our results further suggest how to differentiate between atomic and molecular configurations.

2. Theory

To calculate the inelastic transport properties of some atomic-scale junction we have developed a scheme based on a combination of DFT and non-equilibrium Green's functions (NEGF) [25]. The structural properties are studied using the standard DFT SIESTA package [26] and the elastic conductance calculated with TRANSIESTA [27]. The vibrations are determined by diagonalizing the dynamical matrix extracted from finite differences and the inelastic contribution to the conductance evaluated according to the method presented in Ref. [28].

We consider the periodic supercell representations shown in Fig. 1. The electrodes are

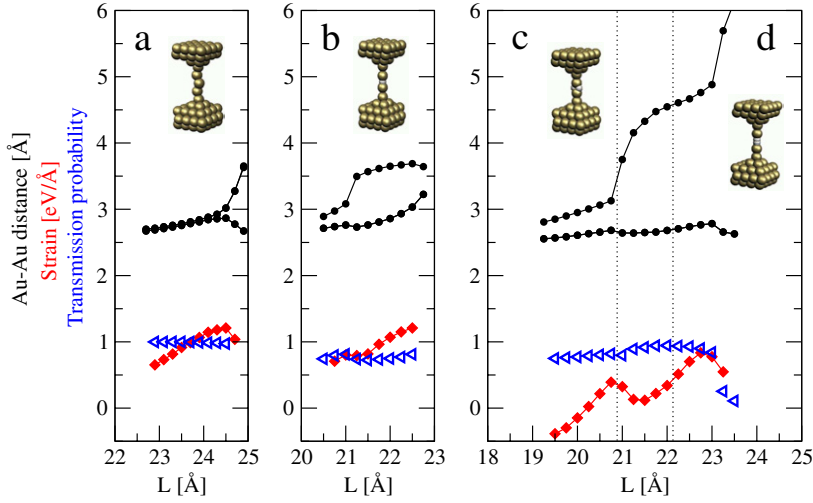


Figure 2. (Color online) Mechanical and electronic properties of (a) pure gold wires and wires contaminated with (b) an H atom or (c-d) an H₂ molecule. Black dots indicate the Au-Au distances between wire atoms (in units of Å), red squares the external force on the supercell (in units of eV/Å), and blue triangles the elastic transmission probability at the Fermi energy.

modeled by a slab containing five Au(100) atomic layers in a 4×4 representation, and the gold wire is suspended between two pyramidal bases that connects to the electrode surfaces. The characteristic electrode separation L is measured between the second-topmost surface layers since we relax both the wire, the pyramids, and the first surface layers (which hence deviates on the decimals from the bulk values). The pure gold wire setup contains 5 wire atoms, from which we generate the contaminated structures by replacing the middle Au atom by either a single H atom or a single H₂ molecule. The corresponding calculations with SIESTA are performed using a single-zeta plus polarization (SZP) basis set for the Au atoms and a split-valence double-zeta plus polarization (DZP) basis set for the H atoms (determined using a confining energy of 0.01 Ry), the generalized gradient approximation (GGA) for the exchange-correlation functional, a cutoff energy of 200 Ry for the real-space grid integrations, and the Γ -point approximation for the sampling of the three-dimensional Brillouin zone. The interaction between the valence electrons and the ionic cores are described by standard norm-conserving pseudo-potentials.

3. Results

We relax the supercells under varying electrode separation L to characterize the junction as it is mechanically manipulated. The resulting Au-Au distances between the wire atoms are shown in Fig. 2 with black dots. For the pure Au wire the bond lengths gradually increase from around 2.67 Å at $L = 22.70$ Å (the zigzag wire depicted in Fig. 1a) to 2.86 Å at $L = 24.30$ Å; beyond this point the wire dimerizes and break. When a hydrogen impurity is introduced the adjacent Au-Au bond becomes slightly longer than the rest. With a single H atom in a short wire the impurity prefers to sit to the side. As the wire is elongated to around $L = 21.50$ Å the impurity moves into the center of the wire (Fig. 1b) resulting in an Au-Au distance larger than 3.6 Å. With H₂ in a short wire the impurity sits in a transverse configuration, cf. Fig. 1c. At $L = 21.00$ Å it begins to tilt under elongation and reaches a straight Au-H-H-Au bridge configuration around $L = 22.00$ Å, cf. Fig. 1d. This crossover region is marked in Fig. 2c-d by dotted vertical lines. Just before breaking the Au-Au distance becomes as large as 4.9 Å.

By studying how the total energy changes as the electrode separation increases we can numerically evaluate the force on the supercell. This is indicated in Fig. 2 by red squares. We generally find that it requires an external restoring force to prevent contraction of the wires. However, for the short H₂ configurations this force is negative indicating the existence of a stable situation around $L = 20.00$ Å. From these curves we get an idea of the break force—defined as the maximal force under the elongation process—which is of the order 1.2 eV/Å for the pure and single H contaminated systems, but noticeably lower in the H₂ case (around 0.8 eV/Å).

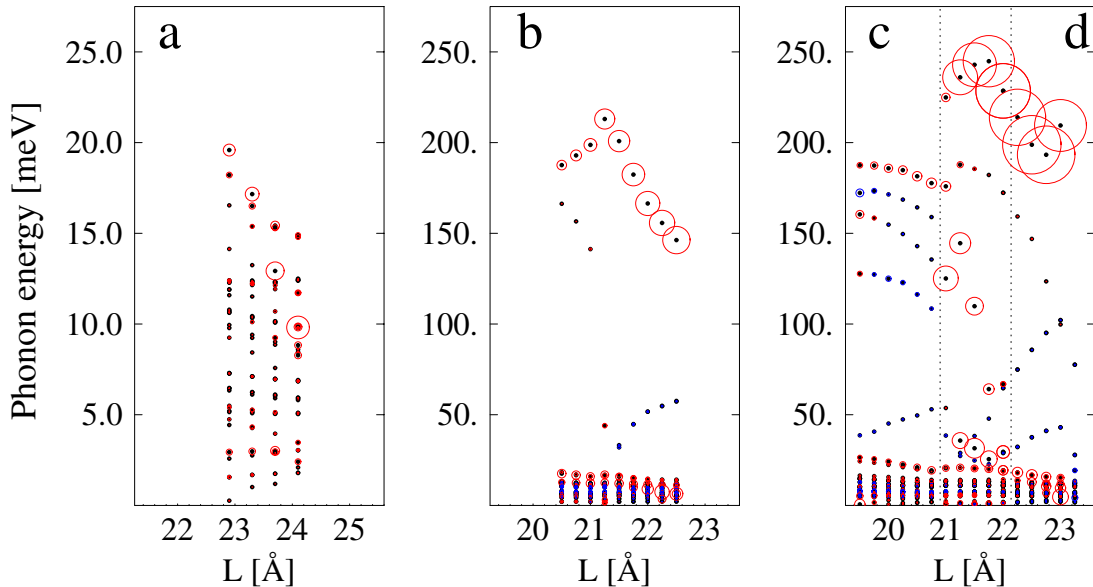


Figure 3. (Color online) Inelastic signals in the nonlinear conductance for (a) pure gold wires and wires contaminated with (b) an H atom or (c-d) an H₂ molecule. The black dots mark vibrational modes at the corresponding threshold voltages. The surrounding red (blue) circles represent with their area the conductance decrease (increase) as observed in an experiment.

The elastic transmission probability at the Fermi energy $T(\varepsilon_F)$, which describes the low-temperature zero-bias conductance via $G = G_0 T(\varepsilon_F)$, is also shown in Fig. 2 with blue triangles. Whereas the pure Au wire has a conductance of $(0.98-1.00)G_0$ depending on the length, the case of a single H atom lowers the conductance to $(0.73-0.81)G_0$ and an H₂ molecule the conductance to $(0.76-0.94)G_0$. In an experiment it may thus be difficult to differentiate among these configurations based on a measurement of the zero-bias conductance only.¹

If one instead investigates the inelastic signals we find significant differences between the systems. Our results from a vibrational analysis are summarized in Fig. 3 for which all the atoms in the contact between the surface layers were considered to be active. The existence of a vibrational mode is marked with a black dot at the vibrational threshold and a corresponding decrease (increase) in the conductance is indicated with the area of a surrounding red (blue) circle. The pure gold wires have phonon energies in a region comparable with the phonon density of states in bulk gold, i.e., up to around 25 meV. A single dominant conductance decrease is seen in Fig. 3a. This signal, caused by the alternating bond length (ABL) longitudinal phonon [23, 24], strengthens with elongation of the wire while the mode frequency softens.

This picture is changed by the presence of light-weight impurities, as seen from Fig. 3b-d, because they contribute to the vibrational spectrum with new modes that lie well above the gold phonon band. With a single H atom our calculations predict a significant inelastic signal in the range 150-220 meV corresponding to movement of the impurity along the wire axis. Comparatively, in the case of H₂ we have one inelastic signal around 180-250 meV due to the internal H₂ stretch mode, but find further two active modes in the range 25-150 meV occurring only when the H₂ molecule appears in a tilted configuration (marked by the dotted lines in Fig. 3c-d). These additional modes have a transverse component and are unambiguous indications for the H₂ configuration.

¹ We note that our findings are slightly different from that of Ref. [20], but differs significantly from Ref. [13] that ascribes less than $0.25 G_0$ to a gold wire contaminated with an H atom or an H₂ molecule.

4. Conclusions

It may experimentally be difficult to determine if an atomic gold wire contains a hydrogen impurity without measuring the inelastic signals. We find that the low-bias conductance and the break force of the chains are generally very similar for both pure and H or H₂ contaminated wires, cf. Fig. 2. However, the inelastic conductance signals enable us to separate the different geometries from each other. In a pure gold wire there is generally one dominant inelastic conductance decrease which strengthens in magnitude and decreases in threshold voltage as the wire is elongated. This signal is caused by the ABL longitudinal phonon. Similar signals (below 25 meV) can also be seen for the hydrogen-contaminated wires (Fig. 3b-c) reflecting that active modes involving the gold atoms survive. On the other hand, hydrogen induces new inelastic signals at much higher phonon energies. In the case of a single H atom (H₂ molecule) our calculations predict a signal approximately at 150 (200) meV just before the wire breaks. Another diversity discussed above is the fact that two additional active modes may be detectable if H₂ sits in a tilted configuration. These differences can possibly be used to differentiate between the H and H₂ configurations.

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