

## Bonding, Conductance, and Magnetization of Oxygenated Au Nanowires

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Spin-density-functional calculations of tip-suspended gold chains, with molecular oxygen, or dissociated oxygen atoms, incorporated in them, reveal structural transitions for varying lengths. The nanowires exhibit enhanced strength for both oxygen incorporation modes, and upon stretching tip atoms join the wire. With incorporated molecular oxygen the wire conductance is about  $1(2e^2/h)$ , transforming to an insulating state beyond a critical length. The nanowire conductance with embedded oxygen atoms is low,  $0.2(2e^2/h)$ , and it develops magnetic moments localized on the oxygens and the neighboring Au atoms.

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Metal nanowires (NWs), in particular, gold NWs, have been the topic of continued interest [1,2] since the early description of their formation and properties through molecular dynamics simulations of the elongation of a contact between a Ni tip and an Au surface [3]. Coupled with advances in the field of nanocatalysis [4], focused on the surprising catalytic activity of small gold clusters (in particular, the low temperature oxidation of CO by gold clusters with up to 20–30 atoms), recent investigations explored chemical modifications of gold NWs [5–12].

From experiments on Au NWs it has been concluded [9] that oxygen atoms (rather than molecular oxygen) incorporate and reinforce the wires, thus allowing the drawing of longer gold chains. In experiments at 4.2 K, as well as 40 K, the conductance histogram of the oxygen-incorporated Au suspended chains exhibits a peak at  $1G_0 = 2e^2/h$ , as for bare Au NWs where it corresponds to the last conductance plateau before breaking. A small peak at  $0.1G_0$  has also been recorded at 40 K, but no structural assignment corresponding to this peak was made [9]. A description of the structure underlying the 4.2 and 40 K conductance peak at  $1G_0$  in terms of atomic oxygen incorporation into the Au NW was made [9] following a band-structure calculation of a -Au-O-Au-O- chain [7].

Here we report on first-principles density-functional theory (DFT) calculations of the properties of gold NWs suspended between opposing pyramidal Au tips, with molecular oxygen [mode (i)] or dissociated oxygen atoms [mode (ii)] incorporated in the NWs. We find an enhancement of the NW strength for both modes of oxygen incorporation, and from electronic conductance calculations (using a spin-dependent nonequilibrium Green function technique [13]) we determine that the conductance of mode (i) wires is near  $1G_0$  up to a critical length beyond which the wire transforms into an insulating state. Consequently, the molecular incorporation mode (i) is assigned to the main conductance peak measured in the aforementioned experiments (at both 4.2 and 40 K) [9]. In contrast, the conductance of mode (ii) NWs (dissociative oxygen incorporation) is found to be low (up to  $0.2G_0$ ) with a weak dependence on the wire length, and it may be

associated with the low conductance peak measured only at the higher temperature (40 K). For the ground state of the NWs with atomic oxygen incorporation [mode (ii)] we predict development of magnetic moments localized on the oxygen atoms and the neighboring Au atoms of the NW, originating from hybridization between the gold  $d$  states and the oxygen  $p$  orbitals, with partial charge transfer to the oxygens. On the other hand, in the molecular incorporation mode (i) charge transfer,  $\delta q$ , into the molecule's  $2\pi^*$  orbital quenches the paramagnetism of the free  $O_2$  molecule.

The nature of bonding, structural and chemical changes, forces, and electronic transport in Au NWs formed upon separation of the leads with molecular or atomic oxygen incorporated in the wires, were studied with DFT electronic structure calculations [14] and conductance calculations combining DFT and the nonequilibrium Green function (NEGF) technique [15]. The DFT calculations include the generalized gradient approximation [16], using a plane wave basis (kinetic energy cutoff  $E_{\text{cut}} = 68$  Ry) and pseudoscalar relativistic (for Au) soft pseudopotentials [17].

The electronic and atomic structures of the contact region [comprising the NW and two opposing gold tips of pyramidal shape, see configuration (a) in Fig. 1(a)(ii)] were determined for different values of  $L_0$ . In structural optimizations, all the atoms in the contact region, except for those in the outermost layers (one on each of the tips), were allowed to fully relax for each value of  $L_0$ ; all atoms in the leads connecting to the contact region are held fixed in their bulk positions. We found that changing  $L_0$  expresses itself essentially entirely in the NW region ( $L_{\text{gap}}$ ). These relaxed configurations are subsequently used in the NEGF transport calculations employing semi-infinite fcc (110) leads (consisting of fcc stacked alternating 16- and 9-atom layers) connected through the contact region. In the leads we used an atomic basis with the same orbitals per atom as those used in the pseudopotential construction [17] (with the  $6p$  orbitals added for gold), which are then expanded in a plane wave basis with  $E_{\text{cut}} = 68$  Ry.

Results for the energy changes ( $\Delta E$ ) upon elongation of the distance between the tips ( $\Delta L$ ) for two modes of oxy-

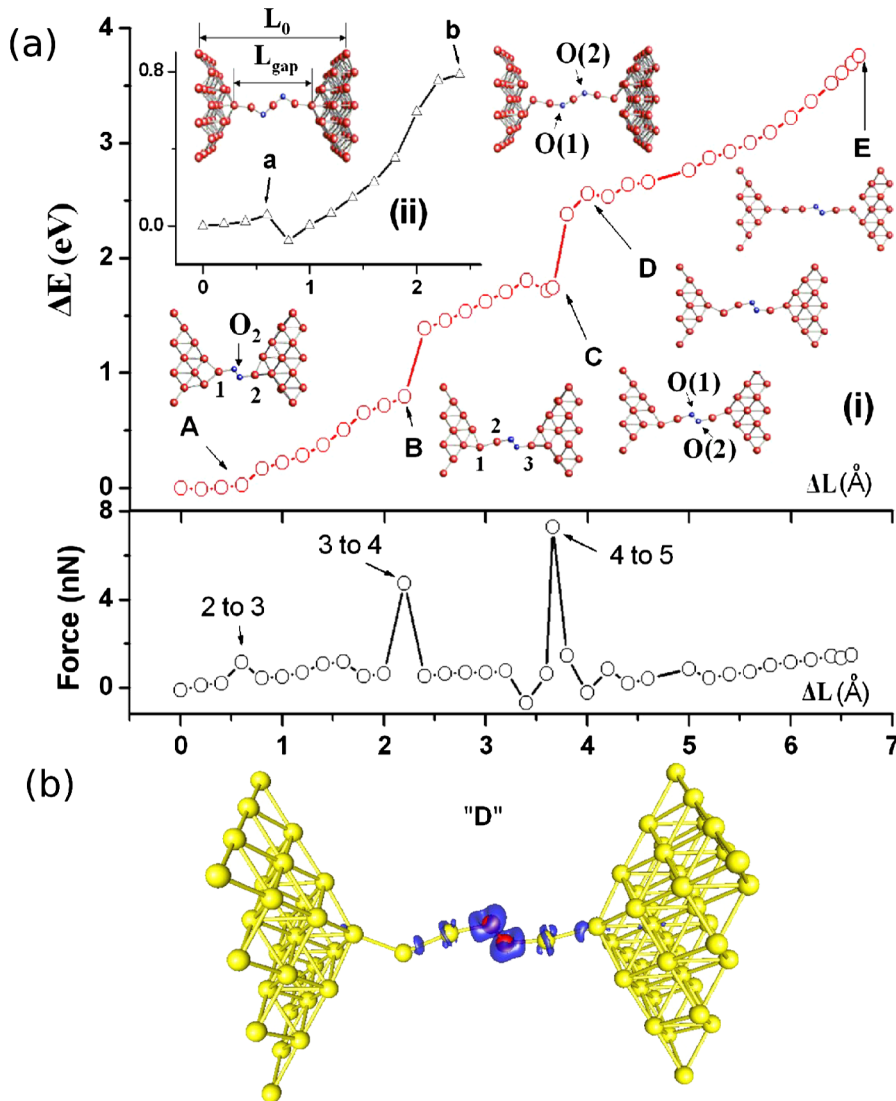


FIG. 1 (color online). (a) Total energy variation versus elongation distance of suspended Au NWs for the molecular (i) and dissociative (ii) oxygen incorporation modes. Selected relaxed atomic configurations are displayed, with the smaller spheres (blue) denoting the oxygen atoms. Bottom panel: the elongation force for mode (i); each of the spikes corresponds to a tip atom joining the NW. The definitions of  $L_0$  (the length of the contact region connecting the two leads) and  $L_{\text{gap}}$  (the NW length) are included in configuration a of (a)(ii). (b) Excess electronic charge distribution on the oxygen molecule embedded in the NW, calculated for state D in (a)(i) as the difference between the charge density of the combined Au NW/O<sub>2</sub> system and the densities of the individual components (i.e., Au NW and O<sub>2</sub> molecule). Excess charge, located mostly on the oxygens, is denoted by shadowed (blue) surfaces. Gold atoms (yellow) and oxygens (red) are located as in configuration D shown in (a).

gen incorporation in the NWs [(i) molecular (O<sub>2</sub>), and (ii) dissociative (atomic)] are given in Fig. 1(a)(i) and (ii), respectively. For the molecular incorporation [18] we start from  $L_0 = 17.19$  Å, where the wire consists of the two Au tip-apex atoms [with a distance  $d_{\text{Au}}(1, 2) = 5.08$  Å] and a slanted O-O molecule [see configuration (A) in Fig. 1(a)(i)], with  $d_{\text{O}(1)-\text{O}(2)} = 1.36$  Å, which is larger by 0.1 Å compared to the internuclear distance in the free molecule (1.25 Å), indicating an activated molecular state; we note that  $d_{\text{O}(1)-\text{O}(2)}$  varies by at most  $\pm 0.02$  Å between configurations A and E shown in Fig. 1(a). Formation of this activated state involves charge transfer  $\delta q$  into the  $2\pi^*$  orbital of the molecule as is the case for gold cluster catalysts (see Chap. 1 in Ref. [4]). From orbital population analysis we find  $\delta q = 1.25e$  for state A and  $\delta q = 1.23$  for state D in Fig. 1(a)(i); the distribution of excess electronic charge accumulated on the adsorbed molecule in state D is shown in Fig. 1(b). The variation of the total energy as the leads are separated is displayed in

Fig. 1(a)(i) together with selected configurations along the stretching path. Similar data corresponding to the dissociative case are shown in Fig. 1(a)(ii), starting from the configuration marked (a) containing 5 Au atoms (including the two tip-apex atoms) and two oxygens [ $L_0 = 20.19$  Å, the length of the wire is 11.7 Å, the distance between neighboring Au atoms 2.61 Å, and the Au-O distance is 2.01 Å].

The total energy change is characterized by a stepwise variation, reflected by the spikes in the force curve versus distance,  $F \equiv -\delta(\Delta E)/\delta(\Delta L)$ , shown for the molecular case in the bottom of Fig. 1(a). The steps reflect structural changes, with each step corresponding to the extraction of an additional Au atom from one of the tips, and its incorporation into the NW; the numbers in the force curve (e.g., “2 to 3”) signify a stretching-induced addition of a gold atom to the wire. This elongation (or “wire-drawing”) mode is a consequence of the stronger Au-O bond compared to the Au-Au bond, resulting in the observed ability

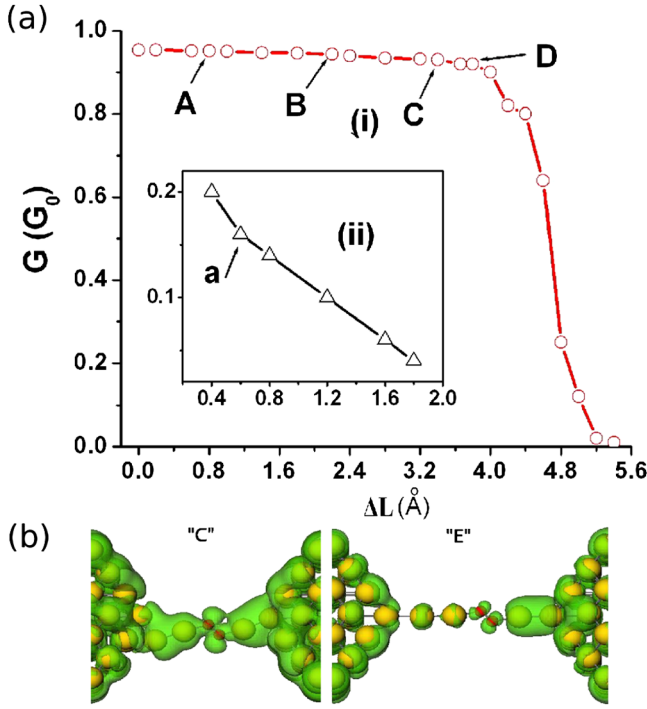


FIG. 2 (color online). (a) Variation of the conductance (in units of  $G_0 = 2e^2/h$ ) of a suspended Au NW with incorporated molecular oxygen, plotted versus the wire elongation. The letters on the curve correspond to the configurations shown in Fig. 1(a). The results for mode (ii) NW are shown in the inset. (b) Isosurfaces [denoted by shadowed regions (green)] of the density of electrons with energy near  $E_F$ ,  $n(\mathbf{r}; E_F)$ , for states C (left) and E (right) of mode (i) oxygenated Au [see also Fig. 1(a)(i)]. In state C (E)  $L_{\text{gap}} = 10.01 \text{ \AA}$  ( $13.71 \text{ \AA}$ ), the average distance between Au atoms is  $2.59 \text{ \AA}$  ( $2.72 \text{ \AA}$ ),  $d_{\text{O}(1)\text{-O}(2)} = 1.36 \text{ \AA}$  ( $1.38 \text{ \AA}$ ),  $d_{\text{Au-O}} = 2.10 \text{ \AA}$  ( $2.24 \text{ \AA}$ ) and  $2.11 \text{ \AA}$  ( $2.05 \text{ \AA}$ ). Note the pronounced structural asymmetry of the 5 Au atom configurations starting from D [Fig. 1(a)(i)]. In the above,  $n(\mathbf{r}; E_F) = \sum_{j,s} [1 - 2|f(j,s) - 0.5|] |\Phi_j, s(\mathbf{r})|^2$ , where  $\Phi_j, s(\mathbf{r})$  and  $f(j,s)$  are, respectively, the Kohn-Sham orbital and the Fermi-Dirac distribution function for energy level  $j$  with spin  $s = \pm \frac{1}{2}$ , and a Fermi temperature  $k_B T_F = 0.014 \text{ eV}$ . Larger spheres (yellow) depict gold atoms, smaller ones (red) correspond to oxygen atoms.

to generate longer wires in the presence of oxygen than for bare gold [9].

The electronic conductance as a function of NW elongation is displayed in Fig. 2(a). The conductance of the mode (i) NW remains high (close to  $1G_0 = 2e^2/h$ ) for most of the wire-drawing process [19], undergoing a sharp transition to a nonconducting state after stage D [see Fig. 1(a)(i) where the distance between the two NW Au atoms at the tips apexes is  $11.68 \text{ \AA}$ , the average distance  $d_{\text{Au-Au}} = 2.6 \text{ \AA}$ ,  $d_{\text{O}(1)\text{-O}(2)} = 1.34 \text{ \AA}$ ,  $d_{\text{Au-O}} = 2.06 \text{ \AA}$ , and  $2.27 \text{ \AA}$ ]. The transition to an insulating wire is illustrated in Fig. 2(b), where the isosurface of the density of electrons with energies near the Fermi level,  $n(\mathbf{r}; E_F)$ , for a conductive state (C) is seen to be extended over the two tips and the NW (including the embedded oxygen molecule), while

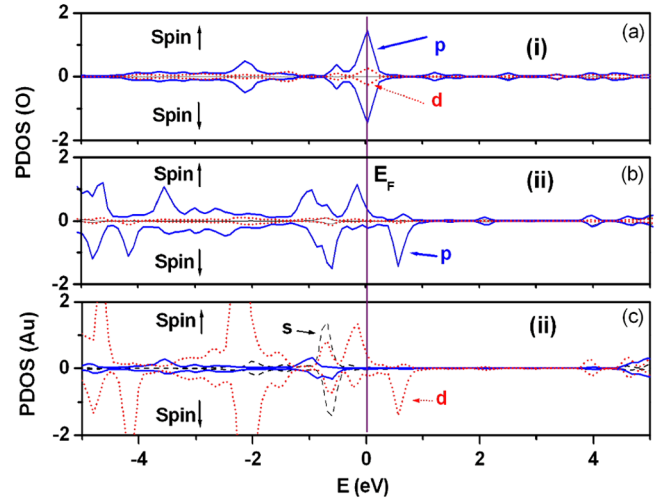


FIG. 3 (color online). Projected densities of states (PDOS, in arbitrary units) on one of the oxygen atoms for (a) mode (i) [corresponding to D in Fig. 1(a)] and (b) mode (ii) [corresponding to configuration a in Fig. 1(a), inset] of the oxygenated Au NWs. (c) PDOS projected on the central Au atom for the mode (ii) NW. The Fermi level is at zero. Solid (blue) lines denote  $p$  states, dotted (red) lines denote  $d$  states, and dashed (black) lines denote  $s$  states.

for an insulating state (i.e. for  $\Delta L > 5 \text{ \AA}$ ) the two tips and the NW appear to be electronically disconnected. For the dissociated case [mode (ii)] the conductance of the wire is low throughout, decreasing monotonically [see inset in Fig. 2(a)]. Consequently, we assign the molecular oxygen incorporation mode as that corresponding to the main peak (at  $1G_0$ ) in the conductance histogram measured (at both 4.2 and 40 K) in Ref. [9], rather than the dissociative mode inferred there. The latter (i.e., dissociative mode) may be associated, instead, with the aforementioned small conductance peak measured [9] only at 40 K.

We examine next the density of states projected either on the oxygen atoms or on selected gold atoms of the NW. In Figs. 3(a) and 3(b) we show the projected density of states (PDOS) on the oxygen atom closer to the left lead for the molecular (i) and dissociative (ii) oxygen incorporation modes [corresponding to the points marked A and a in Fig. 1(a)(i) and (ii), respectively]. Similarly, we show the PDOS on the middle Au atom for the dissociative mode (ii) in Fig. 3(b). For mode (i) the PDOS on the O atom are the same for the two spin directions, with a large contribution from  $p$  states, and a smaller one from Au  $d$  states, at the Fermi level [Fig. 3(a)]. On the other hand, for mode (ii) the symmetry of the PDOS for the two spin directions is broken, and the PDOS at  $E_F$  is significantly reduced, resulting in low conductance. The PDOS on the central Au atom for mode (i) is also found to be symmetric (not shown in Fig. 3), with the main contribution at  $E_F$  coming from  $d$  states (and a smaller one of  $s$  character). The PDOS for mode (ii) is, again, not symmetric for the two spin directions, resulting in a lowering of the PDOS at  $E_F$ ; here

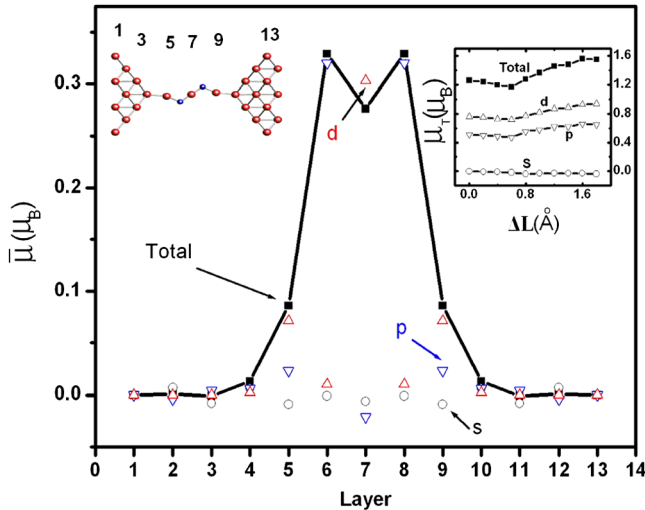


FIG. 4 (color online). Magnetic moments per atom (in Bohr magneton, filled squares) for the different atomic regions (numbered as shown at the upper left corner, with the oxygen atoms denoted as 6 and 8) for configuration (a) [see Fig. 1(a)(ii)] of an Au NW with incorporated atomic oxygen [mode (ii)]. Inset: Total magnetic moments as a function of elongation distance, starting at  $\Delta L = 0$  from configuration (a); see Fig. 1(a)(ii). Up triangles, down triangles, and circles denote the  $d$ ,  $p$ , and  $s$  contributions, respectively.

the main contribution is of  $d$  character, with some  $s$ , and a small  $p$ , contribution [Fig. 3(c)].

From these results we conclude that (a) bonding of oxygen to the Au NW has some covalent character, involving hybridization of the O( $2p$ ) with Au( $5d$ ) and  $6s$ ) orbitals, resulting, as aforementioned, in enhanced strength of the “oxygenated” NW; (b) splitting of the PDOS between the two spin directions causes a reduced population at  $E_F$  for the dissociative mode (ii), correlating with the much lower conductance of these NWs; (c) the broken spin direction symmetry is predicted to result in magnetization of mode (ii) NWs. Indeed, we find significant magnetic moments in the central part of mode (ii) NWs, with strong  $d$  character on the central Au atom and  $p$  character on the oxygens (see Fig. 4); the magnetization exhibits some sensitivity to the stretching (stressing) of the NW (see inset).

In summary, with first-principles DFT calculations we have shown that incorporation of molecular oxygen in tip-suspended Au NWs enhances the nanowire’s cohesive strength via bonding involving charge transfer to the  $2\pi^*$  of the embedded molecule. Structural transitions predicted to occur upon stretching are accompanied by drawing of tip atoms and their incorporation in the NW. The conductance of the nonmagnetic undissociated molecular oxygen-containing wire is calculated to be close to  $1G_0$ , in agreement with experiments (at both 4.2 and 40 K) [9], with a predicted transition to an insulating state beyond a wire length of about 12 Å (see Fig. 2). Incorporation of atomic oxygen is found to result in a low conductance ( $0.2G_0$ ) magnetic NW, with moments localized on the oxygens and

neighboring Au NW atoms. The dissociative mode of the oxygenated Au wire can be associated with the small low conductance peak found experimentally [9] only at 40 K.

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- [18] Choice of the initial configuration followed preliminary explorations that led us to conclude that molecular oxygen incorporation between the two outermost tip atoms [structure A in Fig. 1(a)(i)] is the most likely one to correspond to the measured wire-drawing and transport measurements; see a study of the incorporation of an oxygen molecule into a silver contact by Y. Qi *et al.*, Phys. Rev. Lett. **97**, 256101 (2006).
- [19] Interestingly, a 5-atom bare Au NW, set up with bulk interatomic distances and then fully relax, was found to have a conductance very close to  $1G_0$ . In general, the high conductance of states A–D in Fig. 2(a)(i) is similar to that of the corresponding relaxed suspended bare gold wire.