Electronic structure and dimerization of a single monatomic gold wire

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Abstract

The electronic structure of a single monatomic gold wire is presented for the first time. It has been obtained with state-of-the-art \textit{ab-initio} full-potential density-functional (DFT) LMTO (linearized muffin-tin orbital) calculations taking into account relativistic effects. For stretched structures in the experimentally accessible range the conduction band is exactly half-filled, whereas the band structures are more complex for the optimized structure. By studying the total energy as a function of unit-cell length and of a possible bond-length alternation we find that the system can lower its total energy by letting the bond lengths alternate leading to a structure containing separated dimers with bond lengths of about 2.5 Å, largely independent of the stretching. However, first for fairly large unit cells (above roughly 7 Å), is the total-energy gain upon this dimerization comparable with the energy costs upon stretching. We propose that this together with band-structure effects is the reason for the larger interatomic distances observed in recent experiments. We
find also that although spin-orbit couplings lead to significant effects on the band structure, the overall conclusions are not altered, and that finite Au$_2$, Au$_4$, and Au$_6$ chains possess electronic properties very similar to those of the infinite chain.

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Very recently, single chains of suspended gold atoms have been produced between two [110]-oriented tips in transmission electron microscope (TEM) [1] and in mechanically controllable break-junction (MCB) experiments [2]. In the TEM experiment, conductance measurements were performed simultaneously with electron-microscope images of the atomic-size contact as the tips were separated. Before breaking, the contact consists of a monatomic nanowire made up of four gold atoms and shows a conductance of $2e^2/h$. The MCB experiment, although lacking direct imaging of the systems, gives also evidence of the formation of a monatomic wire upon stretching.

The formation of such a monatomic chain structure for gold and its properties upon stretching were studied theoretically by Sørensen et al. [3] by means of classical molecular-dynamics simulations although for contacts between [100]-oriented tips. More recently, Torres et al. [4] studied the thermodynamical foundations of the spontaneous thinning process as well as the stability of the monatomic gold wire for the [110]-oriented tips using classical many-body force simulations as well as ab-initio local-density (LDA) and generalized-gradient (GGA) density-functional electronic-structure calculations. They found that for bond lengths above 2.8 Å, the system will break into isolated Au$_2$ dimers. However, in the experimental studies, the finite monatomic wire shows an overwhelming stability upon stretching and is stable for bond lengths up to between 3 and 4 Å.

In the present work the problem of the stability of a single monatomic gold
wire is addressed. The electronic structure of the system is presented for the first time and its behaviour upon stretching used to rationalize the whole scenario. In particular we show that, upon stretching, the ordering of the energy levels leads to a situation with one exactly half-filled electronic band so that dimerization (i.e., bond-length alternation) becomes favoured. We show how, as the system is stretched, the energy gain upon dimerization increases, but the nearest-neighbour interatomic distance at equilibrium stays constant at approximately 2.5 Å. Finally, the importance of relativistic effects, not considered in any previous study, is addressed and the results for the infinite chains are compared with similar ones for finite Au$_2$, Au$_4$, and Au$_6$ chains.

We performed full-potential density-functional LMTO (linearized muffin-tin orbital) calculations with a local-density approximation (LDA) on isolated periodic infinite gold chains using the method described in Refs. [5,6]. This method is specifically targeted for isolated, infinite, periodic, helical polymers and chain compounds and have been applied successfully to a wide series of systems [7]. The basis set consists of two sets of $s$, $p$ and $d$ functions on all sites; each function is defined numerically inside non-overlapping atom-centered spheres and in terms of spherical Hankel functions in the interstitial region. The two sets differ mainly in decay constants of the latter. Scalar relativistic (SR) [8] corrections were included in all the calculations presented here; in addition the effects of spin-orbit (SO) couplings were also considered.

For the calculations on the isolated, undimerized gold chain we assume that
the nuclei are lying in the \((x, z)\) plane with the \(z\) axis parallel to the chain axis. 

We use 31 equidistant points in half-part of the first Brillouin zone in order to ensure the appropriate convergence of all the physically relevant quantities and to properly describe the metallicity of the system. We also use the level-broadening scheme described in [9] with an electronic temperature of 0.068 eV \((5 \times 10^{-3}\text{ Ry})\). For the dimerized chain we use 16 points in half-part of the first Brillouin zone.

The structure of the undimerized chain can be described with the single bond length \(a\), whereas the dimerized chain has two alternating bond lengths \(a_1\) and \(a_2\). From these we define an average bond length

\[
\bar{a} = \frac{1}{2}(a_1 + a_2)
\]

(1)

and a dimerization coordinate

\[
\delta = \frac{1}{2}(a_1 - a_2).
\]

(2)

The electronic band structures of a single monatomic gold wire with an interatomic distance of \(a =3.5\ \text{Å}\) are shown in Fig. 1.a. This bond length is representative of those observed experimentally. The system is metallic with a half-filled band of symmetry \(\sigma\). Below this, a broader occupied \(\sigma\) band as well as (doubly degenerate) narrower \(\pi\) and \(\delta\) bands are found. Analyzing the orbitals it turns out that the \(\sigma\) bands have contributions from both 6s and \(5d_{z^2}\) functions, whereas the \(\pi\) and \(\delta\) bands largely are due to \(d\) functions.
Including the spin-orbit (SO) couplings leads to the band structures of Fig. 1.b. Except for the fact that the lower symmetry leads to a splitting of the doubly degenerate bands as well as to avoided crossings between various pairs of bands, the overall picture is not altered and, most important, the occurrence of one exactly half-filled band remains.

Finally, Fig. 1.c shows the energy levels for finite Au\textsubscript{N} chains consisting of \(N = 2, 4,\) and 6 atoms, respectively. In these calculations we set all bond lengths equal to 3.5 Å, but we stress that these do not correspond to the optimized values (for the dimer, the optimized bond length is in fact much shorter, as we shall see below). Instead, they are similar to the ones observed experimentally.

In Fig. 1.c it can be seen that although increasing the number of atoms leads to some broadening of the energy regions spanned by the orbitals, most of the features of the infinite systems are recovered already for these fairly small systems. Most notably, the fact that \(\sigma\) orbitals are those appearing closest to the Fermi level and that \(\pi\) and \(\delta\) orbitals appear at deeper energies is true also for the finite chains. Furthermore, the Fermi energies of the finite systems are very similar to those of the infinite chains.

In Fig. 2 the total energy of the nanowire is shown as a function of the inter-atomic distance \(a\). Empty squares (triangles) indicate values of the cohesive energy for which the relativistic contributions were included up to the SR (SO)
level. At the SR level, an equilibrium distance of about 2.65 Å is predicted together with a total-energy minimum of 1.35 eV/atom in good agreement with the results of the other ab-initio calculations [4]. The inclusion of the SO coupling leads to a reduction of the equilibrium length to 2.55 Å and an increase of the cohesive energy by approximately 0.10 eV/atom. Such contractions due to relativistic effects are often observed (see, e.g., [10]).

In both curves of Fig. 2 the energy values between 2.7 and 2.9 Å are not shown. For these, numerical problems obscured the calculations, i.e., the highest occupied π band for \( k = 0 \) (cf. Fig. 1.a) was lifted to so high energies that it became partly empty. This placed the Fermi level very close to a van Hove singularity in the density of states leading to smaller discontinuities in the total-energy curve. Although the effects were very tiny they were observable. In addition, they show how sensible the system is to external perturbations. Below 2.7 Å the doubly degenerate π band at \( k = 0 \) in Fig. 1.a is lifted even further so that this band is only partially filled and the broad σ band no longer is exactly half-filled.

An exactly half-filled band, as found for \( a \) above 2.9 Å, favours strongly a (Peierls) dimerization. Therefore, in Fig. 3 the energy gain upon dimerization is shown as a function of the dimerization coordinate \( \delta \) for some selected values of the average bond length \( \bar{a} \) that lie in the experimentally accessible region. In contrast to previous calculations [4], we find that the system possess a stable structure consisting of alternating shorter and longer bonds where the shorter
bonds have lengths of about 2.5 Å. Furthermore, by comparing with the total-energy curves of Fig. 2 we see that the energy gain upon dimerization first for $\bar{a}$ about 3.5 Å becomes comparable with the energy costs upon stretching.

Trans polyacetylene (CH)$_x$ is a well-known example of a material that possesses a Peierls dimerization, leading to alternating single and double bonds between the carbon atoms of the backbone. For this, however, both the amplitude of the bond-length alternation as well as the related total-energy gain are much smaller than those observed here for the gold chain [6].

In Fig. 4 we show the band structures for two representative values of $\bar{a}$, and for each case we show them for two values of the dimerization coordinate $\delta$, i.e., a very small one and the optimized value in Fig. 2. The occurrence of a band gap at the Fermi level due to the dimerization is readily recognized for the smaller value of $\delta$. For larger values of $\delta$, at least for the larger values of $\bar{a}$, the highest occupied orbital is no longer derived from the $\sigma$ band crossing the Fermi level for the undimerized structure, but from bands of $\pi$ or $\delta$ symmetry. Moreover, for these larger values of $\bar{a}$, the bands become fairly flat for the optimized structure which indicates that at those distances the electronic interactions between the dimers are only weak. For the sake of comparison we show in the figure also the single-particle energies for the isolated dimer with a bond length of 2.5 Å. These are seen to lie fairly close to the band regions for the optimized structures supporting that this structure essentially consists of weakly interacting Au$_2$ units.
The fact that the nature of the band gap changes from being a direct gap between the two $\sigma$ bands to becoming indirect for larger values of $\delta$ is seen in Fig. 5 that shows the band gap as a function of $\delta$ for different larger values of $\bar{a}$. For smaller values of $\bar{a}$, the above-mentioned fact that the $\sigma$ band no longer is exactly half-filled and that the $\pi$ bands are partly emptied makes the smallest band gap vanishing up till some $\bar{a}$-dependent threshold for $\delta$.

It is remarkable that for the smallest values of the dimerization coordinate $\delta$ all curves lie on top of each other. Assuming that the $\sigma$ band crossing the Fermi level for the undimerized structure can be described with a single Wannier function per atom and that only nearest-neighbour hopping integrals need to be taken into account, the band gap is

$$E_{\text{gap}} = 2|t_1 - t_2|,$$  \hspace{1cm} (3)

where $t_1$ and $t_2$ are the two hopping integrals. These may in turn be assumed to depend linearly on the bond lengths,

$$t_{1,2} = t_0 - \alpha \cdot (a_{1,2} - \bar{a}).$$ \hspace{1cm} (4)

$\alpha$ is an electron-phonon coupling constant. For any average bond length $\bar{a}$ one would expect both $t_0$ and $\alpha$ to depend on $\bar{a}$. However, since Eqs. (3) and (4) imply that

$$E_{\text{gap}} = 4\alpha|\delta|,$$ \hspace{1cm} (5)
we obtain that the electron-phonon coupling constant is independent of $\bar{a}$, at least in the range considered here. Since the tendency towards dimerization largely is determined by the size of the electron-phonon coupling, this result implies that the strength of this tendency is independent of the unit-cell length. Finally, the fact that the curves of Fig. 5 for larger $\delta$ do not lie on the top of each other is due to the above-mentioned change of the nature of the gap.

Experimentally, it is found that the finite chains stay stable up to bond lengths of about 4 Å, after which the chains break. Compared with the systems we have studied here there is a number of differences. First, the experimentally studied systems consist of only about four atoms, but as Fig. 1 shows, already such systems possess electronic properties close to those of the infinite chain. Second, the experimental systems are not isolated but suspended between two tips, which may give further support for studying infinite chains. Third, and more importantly, the experimental systems are not static but subjected both to mechanical (stretching) forces and to electrostatic forces (due to the voltage between the tips). Here, we have only considered the static parts of the mechanical forces, which, however, due to the very different time scales between structural relaxations and the applied forces is justified. On the other hand, the applied electrostatic forces may influence the physically properties since they lead to an overall asymmetric potential along the chain, although the potential is weak (in the 10 meV range).

In total, our results suggest the following for the experimental systems. For a
given structure with a certain average bond length $\bar{a}$ obtained through stretching, the system may attempt to lower its total energy upon structural relaxation. Here, our results show that the overall driving mode for this is to split the system into more or less strongly interacting dimers, although band-structure effects give that this happens first for $\bar{a}$ above around 3 Å. As a competition to this, the system may attempt to relax towards the shorter, optimized, undimerized structure. Although this latter is prohibited by the external mechanical forces, we may still compare the two relaxation modes and, then, first for average bond lengths above about 3.5 Å is the former energetically preferred. Furthermore, due to the external voltage, the dimer-ization mode is weakened. Therefore, we suggest that first when $\bar{a}$ is so large that the energy gain upon the two relaxation modes are comparable, will the system change structure, i.e., split into fairly well separated dimers. This offers thus an explanation for the unusually long average bond lengths that are observed experimentally.

In conclusion we have shown here how it is necessary to analyze the electronic band structures of a single monatomic gold chain in order to gain more understanding into the puzzling problem of its stability. In particular, we have shown that the dimerization is the most relevant structural relaxation that shall be considered for these chains. Furthermore, we have shown that relativistic effects have significant effects on the band structures although, maybe surprisingly, without changing the general picture. To our knowledge, rela-
tivistic effects have not been considered previously for such systems. Finally, we demonstrated that the finite chains have properties very similar to those of the infinite chain.

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Figure 1. (a-b) Electronic energy bands of an infinite, monatomic gold wire and (c) electronic energy levels of some finite linear \( \text{Au}_N \) chains. The interatomic distance for all calculations is set equal to 3.5 Å. In (c), +, ◦, and \( \times \) mark \( \pi \) and \( \delta \) orbitals, empty \( \sigma \) orbitals, and filled \( \sigma \) orbitals, respectively. In (a-b), \( k = 0 \) and \( k = 1 \) represent the center and edge of the first Brillouin zone, respectively, and the vertical dashed lines the Fermi level.

Figure 2. The cohesive energy in eV per atom for a monatomic gold wire with non-alternating bond lengths. Empty squares (triangles) represent results obtained including relativistic contributions up to the SR (SO) level. Lines are drawn as a guide-to-the-eye.

Figure 3. Energy gain upon dimerization for selected unit-cell lengths. The results are shown as a function of the dimerization coordinate \( \delta \), and the different curves are obtained for the different average Au–Au distances \( \bar{a} \) shown in the figure.

Figure 4. Band structures for infinite chains with alternating bond lengths The extra symbols in (b) and (d) represent the single-particle energies for an isolated Au dimer with a bond length of 2.5 Å and using a notation as that of Fig. 1. The values of \( (\bar{a}, \delta) \) in the four panels are (a) (3.0,0.1), (b) (3.0,0.4), (c) (3.6,0.1), (d) (3.6,1.1) in Å.

Figure 5. The smallest band gap between occupied and unoccupied orbitals as a function of the dimerization coordinate \( \delta \) for the same values of \( \bar{a} \) and using the same notation as in Fig. 3. The horizontal dashed line is the value for the isolated \( \text{Au}_2 \) dimer with a bond length of 2.5 Å.
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Figure 2: L. De Maria and M. Springborg, Electronic structure...
Figure 3: L. De Maria and M. Springborg, Electronic structure...
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