

Thermoelectric voltage switching in gold atomic wire junctions

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We explore the thermoelectric properties of gold atomic chains bridging gold electrodes by means of *ab initio* and semiempirical calculations, and heuristic reasoning. We predict the thermoelectric voltage induced by a temperature difference across such junctions to oscillate, repeatedly changing sign, as a function of the number of atoms N making up the atomic chain. We also predict the amplitude of the oscillations to be proportional to N for long atomic chains. Further, we predict the thermoelectric voltage to change sign, in some cases, if the junction is stretched without changing N . Our predictions apply regardless of whether regular or irregular electrode grain boundaries are present and whether the electrodes are symmetric or asymmetric. Our findings may pave the way to the realization of new mechanically controllable voltage switches, enabling direct conversion of heat into electricity in energy harvesting applications.

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I. INTRODUCTION

In the past two decades, the formation, evolution, and breaking of gold atomic chains that bridge a pair of electrodes have been the subject of many experimental and theoretical studies, motivated by their fundamental scientific interest and potential applications as the narrowest possible conducting wires for nanoscale electronic devices [1–10]. The electric current through such atomic chains can be measured in scanning tunneling microscopy experiments [11,12]. Also, mechanically controlled break junctions can be used to form a gold atomic chain between two gold clusters. In this way, atomic chains up to 2 nm long have been fabricated in ultra-high vacuum [1,13,14]. The production of very thin suspended gold nanowires, as thin as a linear atomic chain with 4–10 atoms has also been reported [15–18]. Moreover, molecular dynamics simulations of stretched gold nanowires have shown that the number of atoms in monatomic chains is a function of temperature and that there is an optimal temperature for creation of long atomic chains [19].

The length of these atomic chains can be estimated experimentally from the length of the last conductance plateau [2,3,14]. An oscillatory dependence of the conductance with the length of gold atomic chains has been reported by Smit *et al.* [2], suggesting a dependence on whether the number of atoms in the chain is even or odd and originating from interference effects in the electron wave functions. However, Vardimon *et al.* [3], carried out conductance and shot noise measurements, and inferred, consistent with theory [9], that the conductance oscillations of gold atomic chains during stretching are mainly related to variations in bond angles (and hence in orbital overlaps) as the chain undergoes transitions between zigzag and linear atomic configurations.

The conductance properties of gold atomic chains have also been investigated theoretically by means of extended Hückel theory [4], classical molecular dynamics simulations combined with a tight-binding approximation [7], and *ab initio* calculations [5,8–10]. It was shown that the conductance of gold atomic wires is close to $1g_0 = 2e^2/h$ for wires with different lengths [4,5]. In addition, the gold chains are characterized by a single conducting channel around the Fermi energy with predominant half-filled s character, giving rise to the even-odd conductance oscillation with the number of atoms in the chain due to quantum interference [5] or conductance oscillations due to bond angle and bond length changes during elongation of zigzag atomic chains. [9] A similar mechanism involving changing bond angles has been proposed by us to account for variation of the conductances of molecular junctions bridging gold electrodes in response to their elongation under tensile stress [20]. In the present paper, we study the effects of both mechanisms, those of quantum interference by varying the number of atoms in the chain while keeping the average interatomic spacing fixed, and those due to variation of bond angles and bond lengths by stretching the atomic chains while keeping the number of atoms in them fixed. We find both mechanisms to influence the conductance.

On the other hand, the thermoelectric properties of atomic and molecular junctions are particularly interesting for developing high-efficiency energy-conversion devices [21–32]. Owing to the advances in experimental techniques developed to study the thermoelectric properties of atomic and molecular bridges [21,27,33,34], much progress has been achieved in understanding and controlling electron and heat transport properties of atomic contacts [28,32]. Recently, it has been demonstrated that the thermopower of metallic atomic-size contacts can differ qualitatively from that in the macroscopic limit [35], such that few-atom gold and platinum junctions exhibit opposite signs in their thermopower, unlike bulk structures. This difference is due to the discreteness of the energy levels responsible for transport in atomic junctions

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($6s$ orbitals for gold and $5d$ orbitals for platinum) [35,36] and the tunability of their properties by external factors such as pressure and electrostatic gates [27]. A sign change of the thermoelectric voltage has also been reported in helicene molecular junctions with an on/off ratio of more than three orders of magnitude [37].

More recently, we have reported bipolar thermoelectric voltage generation in few-atom gold contacts, achieved by controlling electronic quantum interference through the application of mechanical force [29]. Despite its potential importance for energy conversion nanoelectronics, the present-day understanding of the relationship between the polarity change of thermoelectric voltage and the junction length or the number of atoms in atomic chains bridging two metal electrodes and also the role of the atomic layer structures within the electrodes of atomic-sized junctions require further investigation.

To shed light on this issue, in this paper the atomic chain length-dependence of the electron transmission probability and thermoelectric voltage of gold atomic wire junctions with regular and irregular electrode grain boundaries are explored theoretically by means of density functional theory (DFT) calculations and a semiempirical tight-binding method based on the extended Hückel theory [38–40]. A heuristic interpretation of the numerical results is also provided. The junction length is varied either by adding atoms to the atomic chain, bridging two electrodes or by imposing tensile strains while keeping the number of atoms in the chain fixed. We present our theoretical analysis of thermoelectric effects in structures consisting of a few hundreds of atoms ranging from 225 (three-layer electrodes and a single Au atom in between) to 607 (six-layer electrodes bridged by a 21-atom chain). Our electrical and thermal transport calculations show that the thermoelectric voltages of these atomic wire junctions exhibit regular oscillations (with successive sign changes and growing amplitude) as the number of atoms in the atomic chain is increased. Furthermore, we demonstrate that the polarity of the thermoelectric voltage can be controlled mechanically by applying a tensile strain.

The paper is organized as follows. In Sec. II, we outline the computational details of the energy optimization of atomic junctions and of the electrical and thermal transport calculations. In Sec. III, we discuss the results for junctions with differing numbers of atoms in the chains bridging the electrodes, the influence of electrodes with differing numbers of atomic layers, and also the effect of regular and irregular grain boundaries. In addition, we present our results for the influence of mechanical strain on the total energy, transmission probability, and thermoelectric voltage for typical junctions. Finally, in Sec. IV, we conclude this work with a general discussion of the results.

II. THEORY

A. Modeling the structures

In the models that we consider here, the electrodes are represented by a pair of atomic clusters with up to several hundred gold atoms and are bridged by atomic chains ranging from 1 to 21 gold atoms that form the junction. The positions of the gold atoms in the atomic chain and in its immediate vicinity were estimated by minimizing the total energy of the

system, computed within DFT using the GAUSSIAN 16 package with the PBE1PBE functional and Lanl2DZ pseudopotentials and basis sets [41,42]. The gold atoms of the electrodes that are further from the junction are fixed during the relaxations and are assumed to have the geometrical configuration of the ideal fcc lattice in the crystal direction $\langle 111 \rangle$ with nearest-neighbor distance 2.88 \AA .

For our studies of the dependence of the thermoelectric voltage on the number N of atoms in the atomic chain, we constructed the chains atom by atom, increasing the separation of the atomic clusters representing the electrodes by 2.497 \AA each time that an atom was added to the chain and then relaxing the structure as described above. For our studies of dependence of the thermoelectric voltage on the tensile strain in the junction, we started with the structures obtained as above for the studies of the N -dependence and then increased the separation between the electrodes in small steps, relaxing the positions of the gold atoms in the chain and in its immediate vicinity, while holding the other atoms of the electrodes frozen.

Our DFT calculations directed at finding the energetically favorable location of the tip atom on the surface of each gold electrode reveal that the hollow site configuration is the most stable, compared to the top and bridge sites. This result was obtained not only for a single Au atom on the surface of gold electrodes, but also for each gold atomic chain in contact with electrodes. Further, the surface structure did not change drastically during the optimization process, indicating that, of the electrode atoms, only those in the vicinity of the tip atoms need to be included in optimizing the geometry of the gold nanojunctions. To determine how many neighbors of the tip atom of each electrode should be considered unfrozen in the energy minimization, we have optimized the first atomic layer of each electrode plus tip atom, while only the positions of the surrounding (outermost) atoms in the layer were fixed.

In Fig. 1(a), we show a side view of a single electrode consisting of six atomic layers in which all orbitals belonging to the sixth layer are connected to one-dimensional (1D) leads. The optimized structure of the tip atom (marked by a red ring) and the atomic arrangement in the first layer are also shown in Fig. 1(b). The bond length between tip and its immediate (electrode) neighbors was found to be 2.74 \AA , which is less than in plane Au-Au bond length. It is clear that, although all the interior atoms in the layer are free to move, the positions of the three immediate neighbors of the tip atom have changed slightly and it is energetically favorable for these atoms to move out of the plane towards the tip atom. For this layer, we found at most 0.022 \AA atomic displacement in the plane and 0.34 \AA out of the plane.

B. Thermoelectric calculations

To investigate the effects of the gold clusters (electrodes) and atomic chain sizes in the aforementioned nanojunctions on the thermoelectric properties, we first calculate the electron transmission probabilities \mathcal{T} through the device (atomic chain and electrodes) at the Fermi energy E_F . To do this, we attached a large number of semi-infinite quasi-1D ideal leads representing electron reservoirs to the valence orbitals of the atoms in the outer layer of each of the gold clusters that represent the two electrodes, as in previous work on

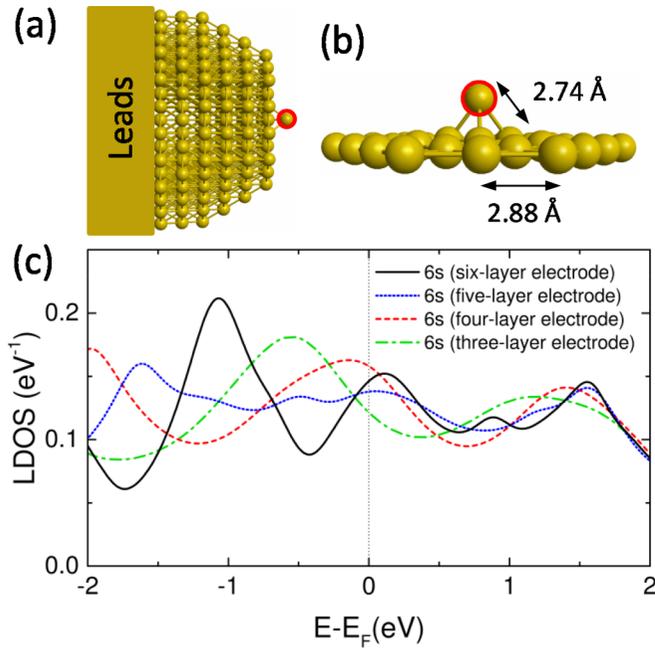


FIG. 1. (a) The side view of a six-layer electrode in contact with semi-infinite leads. (b) Optimized geometry of the tip atom and the first layer of the electrode. The red circle denotes the tip atom. (c) Calculated local density of states of tip 6s orbital in the vicinity of Fermi energy for three-, four-, five-, and six-layer electrodes, obtained by extended Hückel semiempirical calculations.

transport through nanostructures [20,43–48]. In the present model, the boundaries between these ideal leads and the gold clusters may be viewed as electrode grain boundaries that play a role in the thermoelectric behavior of experimental devices [29]. The role of such grain boundaries, which can be regular or irregular in our model, will be discussed in the next section. The electron transmission probability $\mathcal{T}(E)$ through the system, within Landauer theory [38], is related to the conductance via $g(E_F) = g_0 \mathcal{T}(E_F)$, and can be written as

$$\mathcal{T}(E_F) = \sum_{\alpha, \beta} |t_{\beta\alpha}(E_F)|^2 \frac{v_\beta}{v_\alpha}. \quad (1)$$

Here $t_{\beta\alpha}$ is the transmission amplitude through the entire device and α (β) is the electronic state of a carrier with velocity v_α (v_β) in the electron source (drain) leads.

On the other hand, it is known that if a temperature difference ΔT is imposed between two electrodes bridged by a nanoscale junction, the thermoelectric voltage ΔV between the electrodes (with no electric current flowing through the junction) is given by [49]

$$\Delta V = \frac{\pi^2 k_B^2 T}{3e} \frac{1}{\mathcal{T}(E)} \left. \frac{\partial \mathcal{T}(E)}{\partial E} \right|_{E=E_F} \Delta T, \quad (2)$$

where k_B and e are the Boltzmann constant and the electron charge, respectively, and $\mathcal{T}(E)$ is the electron transmission probability at energy E through the device that includes the atomic wire and both electrodes. Note that Eqs. (1) and (2) are valid provided that the electron transmission probability varies smoothly in the range $|E - E_F| < k_B T$ [as will be seen below in Fig. 2] and that the temperature difference

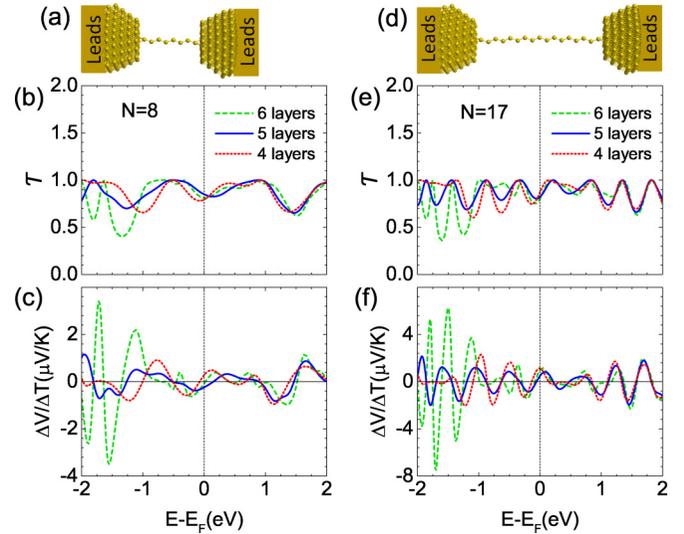


FIG. 2. (Optimized gold atomic wire junctions consisting of (a) $N = 8$ and (d) $N = 17$ atoms with five-layer electrodes in contact with semi-infinite leads. (b), (e) Calculated Landauer electron transmission probabilities and (c), (f) thermoelectric voltages versus electron energy E around the Fermi energy for four-, five-, and six-layer electrodes at a mean temperature of 27 K. Note that the thermopower or Seebeck coefficient S is related to the quantities shown here by $S = -\Delta V / \Delta T$.

ΔT between the electrodes is much smaller than the mean temperature T . In addition, it should be mentioned that the above equations do not include electron-electron interactions beyond mean field theory, or electron-phonon interactions, i.e., phonon drag. In macroscopic metallic wires, the phonon drag contribution to the thermopower is important at low temperatures, primarily due to the interaction of electrons with long wavelength acoustic phonons [50]. However, for metallic atomic point contacts, the phonon drag contribution is believed to be suppressed [36,50]. Also, because gold atomic chains are 1D single-channel electronic systems, absorption of long wavelength acoustic phonons by electrons is expected to be suppressed in them due to energy and crystal momentum selection rules. Consequently, the role of electron-phonon interactions will not be discussed further in the present work. Here we focus on the electron contribution to the coherent transport within the Landauer formalism [27].

When an electron traverses the device, it is scattered multiple times from the surfaces of the electrodes as well as from grain boundaries and also from the boundaries between the atomic wire and electrodes. Consequently, the thermoelectric voltage ΔV given by Eq. (2) can be affected by all of these structural details as well as the electron energy and ΔT [34]. In this context, it is worth mentioning that, in experiments, other defects such as dislocations and vacancies that the electrodes may contain can also play a role in the thermoelectric properties of devices.

III. RESULTS AND DISCUSSION

The electronic states of the tip atoms influence electron conduction through the gold nanojunctions. Transport

experiments on Au chains have shown that among the gold atomic valence orbitals that include $5d$, $6s$, and $6p$ states, the electronic density of states around the Fermi energy is dominated by $6s$ orbitals, indicating that the conduction channel is mainly a single $6s$ band [1,35,51]. In Fig. 1(c), the $6s$ orbital-tip density of states is depicted for single electrodes consisting of different numbers of atomic layers. We see that although the local density of states changes as the number of layers in the gold electrode increases from three to six, the change is not significant at Fermi energy.

We will now consider atomic chains with different numbers N of gold atoms sandwiched between two gold electrodes, each of which may contain different numbers of atomic layers. All the atomic wire junctions (i.e., the two electrodes and the atomic wire in between) are optimized in the same way as described in Sec. II A. In Fig. 2, we have depicted the transmission probability and thermoelectric voltage versus electron energy, E , for the wire junctions with $N = 8$ and $N = 17$ and four- to six-layer electrodes. The peaks in the electron transmission probability \mathcal{T} are due to organ pipelike electron standing waves forming in the device and giving rise to transmission resonances [4,29,52]. We see that the number of oscillations in \mathcal{T} and $\Delta V/\Delta T$ increases as the number of atoms in the atomic chain is increased. Indeed, the number of transmission resonances at which $\mathcal{T}(E) = 1$ (in the energy range shown) increases when more atoms are added to the chain.

The underlying reason for this is that for a longer atomic chain, a smaller change in the electron de Broglie wavelength (corresponding to a smaller change in the electron energy E) is sufficient to switch the device between adjacent electronic standing wave resonances, i.e., between adjacent peaks of $\mathcal{T}(E)$ in Figs. 2(b) and 2(e). This can be understood intuitively by analogy with the acoustic resonances of a pipe, which obey the resonance condition $L = n\lambda/2$ where L is the effective length of the resonator, λ is the resonant wavelength, and n is an integer. The difference between the wavelengths λ and λ' of two consecutive resonances can then be written as $\Delta\lambda = \lambda - \lambda' = \frac{\lambda\lambda'}{2L}$. Thus, for large L , the difference between the energies of two consecutive resonances is $\Delta E \approx \frac{\partial E}{\partial \lambda} \Delta\lambda \approx \frac{\partial E}{\partial \lambda} \frac{\lambda_{\text{dB}}^2}{2L}$, where λ_{dB} is the electron de Broglie wavelength at the Fermi level. Thus, for large numbers N of atoms in the atomic chain, $\Delta E \propto 1/N$.

This behavior of the electron transmission probability $\mathcal{T}(E)$ in turn affects the quantity $\Delta V/\Delta T$. Importantly, the fact that oscillations in $\mathcal{T}(E)$ become more closely spaced in energy E with increasing number N of atoms in the chain results in an increase in $\frac{\partial \mathcal{T}(E)}{\partial E}$ with increasing N that is reflected in an increase in the thermoelectric voltage ΔV given by Eq. (2). In particular, if $\mathcal{T}(E)$ can be regarded as sinusoidal and the amplitude of the oscillations in $\mathcal{T}(E)$ is not sensitive to N [as can be seen by comparing Figs. 2(b) and 2(e)], then $\frac{\partial \mathcal{T}(E)}{\partial E}$ is inversely proportional to the energy spacing between the peaks of $\mathcal{T}(E)$. Then our result $\Delta E \propto 1/N$ obtained above translates into the amplitude of the oscillations of $\Delta V/\Delta T$ being directly proportional to the number N of gold atoms in the chain for large N . This heuristic prediction is consistent with the increase in the amplitude of the oscillations of $\Delta V/\Delta T$ by approximately a factor of 2 from Fig. 2(c) [$N = 8$] to Fig. 2(f)

[$N = 17$]; note the factor 2 difference between the vertical scales of the two figures. It is further supported strongly by the systematic studies of the dependence of the thermoelectric voltage on the number of atoms N in the atomic chains that will be presented below.

In the case of $N = 8$, as the number of atomic layers in the electrodes increases from 4 to 6, $\Delta V/\Delta T$ changes from positive to almost zero to negative values at Fermi energy [see Fig. 2(c)]. This behavior is totally different than that for the case of $N = 17$, where $\Delta V/\Delta T$ is positive at the Fermi energy for all three sizes of the electrodes [see Fig. 2(f)]. These results suggest that the sign of the thermoelectric voltage can be affected by the number of layers in electrodes as well as by the number of atoms in the chain.

To better understand the role of N and the number of atomic layers in the electrodes, we have shown in Fig. 3 the quantities \mathcal{T} and $\Delta V/\Delta T$ at the Fermi energy as a function of the number of chain atoms N in wire junctions with different electrodes. It is evident that both quantities oscillate as N changes. However, while the amplitude of the oscillations of \mathcal{T} is insensitive to N , the amplitude of the oscillations of $\Delta V/\Delta T$ increases proportionally to N for larger values of N , as was predicted heuristically above. Although for small and moderate N the amplitude of oscillations of the thermoelectric voltage are irregular in the structures with three-layer electrodes [see Fig. 3(d)], they become rather regular if more atomic layers are included in the electrode structures [see Figs. 3(a)–3(c)]. Nevertheless, small deviations from regular oscillations in transmission probabilities occur for the short junction lengths with $N = 1 - 3$. Indeed, the nature of atomic chains in such nanojunctions manifests itself for $N \geq 4$. This result makes sense because, in all of the wire junctions, the first and the last atoms of the chain are bonded to the electrodes through three atomic bonds, while the other chain atoms make only a single bond with their neighbor atoms. Importantly, the sign of the thermoelectric voltage oscillates between positive and negative values with N , regardless of the number of atomic layers in the electrodes. The sign changes in the thermoelectric voltage with increasing numbers of layers or chain atoms reveal an important property of gold atomic junctions and suggest a potential application as a perfect voltage switch. In other words, the polarity of the voltage can be switched by elongation of the junction. In the junction with five-layer electrodes, the oscillations of $\Delta V/\Delta T$ between positive and negative values versus N are almost symmetric, while there is a shift towards more positive values for the junctions with four- and also six-layer electrodes [see Figs. 3(a) and 3(c)], which can be attributed to the quantum interference of electrons in the electrodes.

Sign differences of the thermoelectric voltage have been observed previously in atomic-scale and molecular junctions. For instance, amine-terminated molecular junctions have positive thermoelectric voltages, whereas pyridine-terminated molecular junctions exhibit negative values of their thermoelectric voltages [53]. However, the oscillatory characteristics of $\Delta V/\Delta T$ with increasing amplitudes and the polarity changes for long atomic chain junctions predicted here have not been reported previously. Also, it has been observed that gold atomic-sized contacts have an average negative thermopower, whereas platinum contacts present a positive

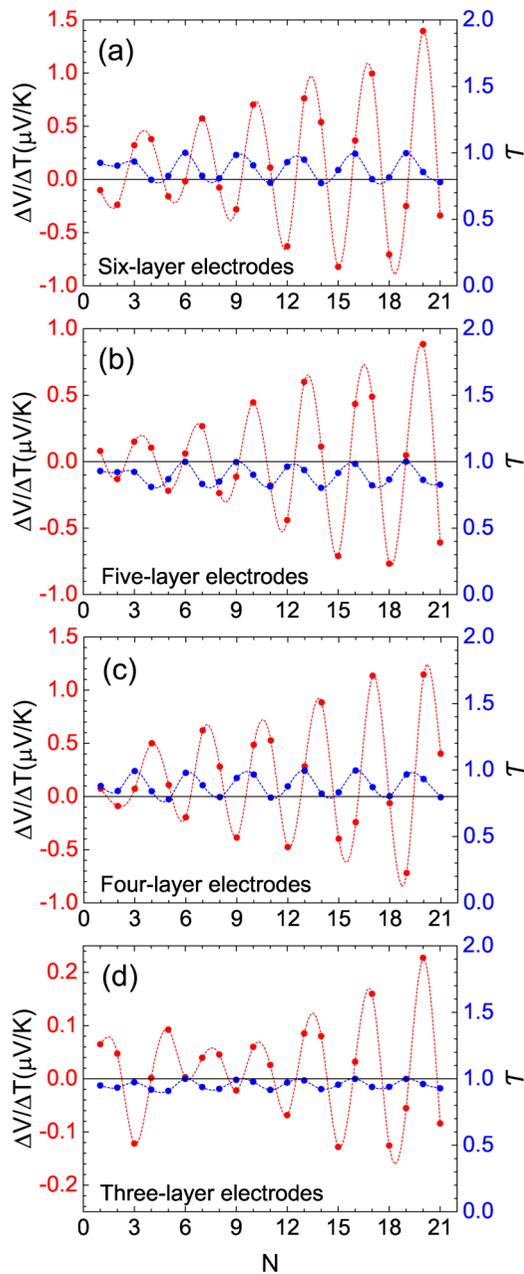


FIG. 3. Calculated electron transmission probabilities \mathcal{T} (blue dots) and thermoelectric voltages $\Delta V/\Delta T$ (red dots) at the Fermi energy versus the number of gold atoms N in the wire junctions bridging the two electrodes, each consisting of (a) six, (b) five, (c) four, and (d) three gold atomic layers at a mean temperature of 27 K. Dotted lines are guides to the eye.

thermopower [35]. By contrast, we have shown that both positive and negative polarities of the thermoelectric voltage can be generated in an atomic wire junction. This feature improves the feasibility of realizing voltage switches based on nanowire junctions.

In the structures that we have considered so far, the interfaces between the ideal leads and electrodes that can be regarded as representing crystal grain boundaries were regular and the two electrodes had the same number of atomic layers. In Fig. 4(a), however, we have depicted the electron trans-

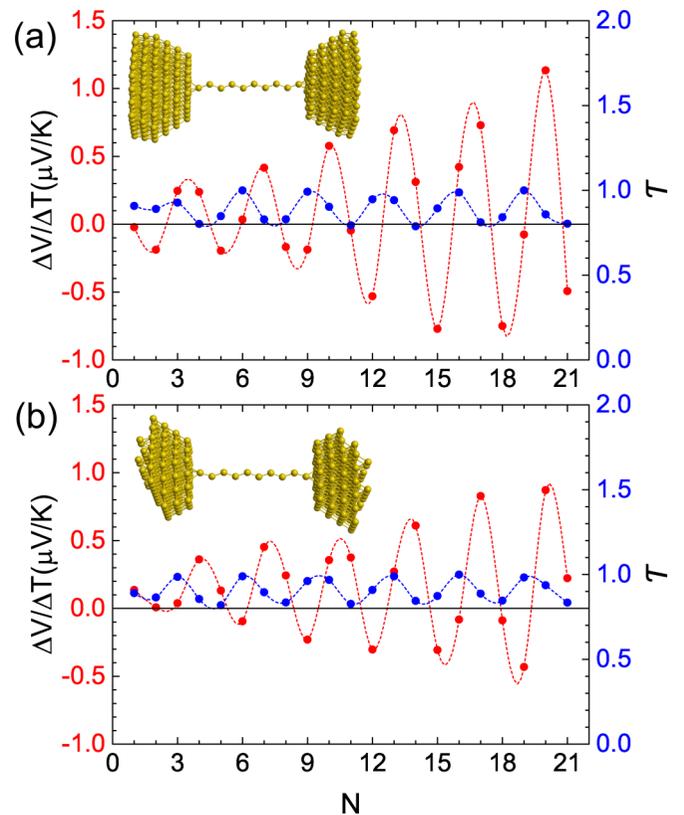


FIG. 4. Calculated electron transmission probabilities \mathcal{T} (blue dots) and thermoelectric voltages $\Delta V/\Delta T$ (red dots) at the Fermi energy versus the number of gold atoms N in the wire junctions between (a) a six-layer electrode at left and a five-layer electrode at right with regular grain boundaries and (b) five-layer electrodes with irregular grain boundaries at a mean temperature of 27 K. The insets show two typical gold atomic junctions with $N = 10$. The semi-infinite leads are not shown here. Dotted lines are guides to the eye.

mission probability and thermoelectric voltage for the wire junctions with different electrodes, i.e., a six-layer electrode at left and a five-layer electrode at right. We see that the oscillations in both \mathcal{T} and $\Delta V/\Delta T$ are still regular and the amplitude of thermoelectric oscillations increases nearly linearly with N as the number of atoms N in the chain is increased. Moreover, the oscillations of $\Delta V/\Delta T$ are almost symmetric with respect to the zero line. This suggests that switching to gold atomic wire junctions with electrodes having differing numbers of atomic layers and regular grain boundaries does not affect the sign change mechanism of thermoelectric voltage. In the case of irregular grain boundaries, however, the amplitude of the oscillations of $\Delta V/\Delta T$ decreases somewhat and the thermoelectric voltage becomes skewed to positive values as shown in Fig. 4(b). Nevertheless, the regularity of the oscillations, the growth of their amplitude with increasing N and the occurrence of sign changes of $\Delta V/\Delta T$ are, for the most part, not affected by the irregular grain boundaries.

Cortes-Huerto *et al.* [19] have shown that the growth of monatomic chains can stop if the contact tips become symmetric because the system requires more energy to remove one gold atom from the contacts and add it to the chain than that needed for bond breaking within the chain. We note, however,

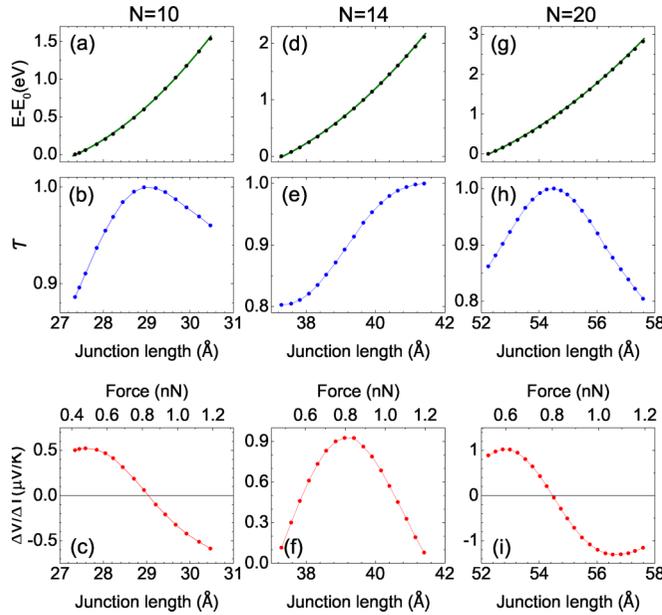


FIG. 5. Calculated [(a), (d), and (g)] total energies, [(b), (e), and (h)] electron transmission probabilities, and [(c), (f), and (i)] thermoelectric voltages at the Fermi energy versus the junction length in the wire junctions with five-layer electrodes and regular grain boundaries at a mean temperature of 27 K. The top axis in (c), (f), and (i) shows the force required for elongation of the junction. The green curves show the fitted results, while the blue and red lines are guides to the eye. E_0 represents the total energy at zero strain.

that, although in this study the atomic junctions extend along $\langle 111 \rangle$ crystal direction, the gold clusters do not have the same symmetry and thus, it is expected that long atomic chains may form before the junctions rupture. Although long atomic chains with up to 21 atoms may not have been realized experimentally at this time, our *ab initio* calculations and semiempirical extended Hückel model suggest that such long chains can be formed between two atomic-size contacts and should have interesting properties. This may motivate experimentalists to make such long atomic chains and measure their transport characteristics.

The response of thermoelectric properties to variable tensile strains, however, is of great importance for both scientific understanding and potential applications such as atomic-sized switches and high-performance energy conversion devices [28,54,55]. In this context, we have also investigated the effect of junction elongation in the structures with atomic chains having fixed numbers of atoms, specifically, chains with $N = 10$, $N = 14$, and $N = 20$. As shown in Figs. 5(a), 5(d), and 5(g), by increasing the tensile strain, the total energy of all structures increases quadratically, until the chains rupture. On the other hand, the magnitude of mechanical force required to elongate the junctions can be obtained as the derivative of the total energy with respect to the junction length. For this purpose, precise quadratic fits to the total energy diagrams in the range of elongation lengths are employed [see the green curves in Figs. 5(a), 5(d) and 5(g)].

Although the transmission probability increases initially with junction elongation in all structures [see Figs. 5(b), 5(e) and 5(h)], it may reach its maximum value and decrease

again (see Figs. 5(b) and 5(h)). This behavior manifests itself as a sign change of the thermoelectric voltage as shown in Figs. 5(c) and 5(i). In other words, when the transmission probability passes its maximum value, the sign of thermoelectric voltage switches from positive to negative [see Figs. 5(c) and 5(i)]. However, such a maximum does not exist for the structure with $N = 14$. Indeed, in Fig. 5(e), the transmission probability increases with junction length until the chain ruptures. We see that if the chains bridging the electrodes support the external strains, both \mathcal{T} and $\Delta V/\Delta T$ can show partial oscillations. In Figs. 5(c), 5(f) and 5(i) we have also shown the range of forces required for elongation of the junctions. Interestingly, the maximum mechanical force does not exceed 1.2 nN, irrespective of the chain length. In this respect, Rubio *et al.* [56] showed experimentally that the force required to break one single bond in the chain is 1.5 nN, which is larger than the maximum value 1.2 nN in this study. This suggests that junction elongations similar to those shown in Fig. 5 can be achieved experimentally and thus the sign changes of the thermoelectric voltage predicted in Figs. 5(c) and 5(i) should be observable.

To demonstrate that our theory is able to reproduce the results of experimental conductance measurements, we compare the oscillations of the transmission probabilities versus N in Figs. 3 and 4 with the evolution of the conductance versus chain length in Refs. [2] and [3]. According to the experimental results, shown for Au in Fig. 2 of Ref. [2] and also in Fig. 1(d) of Ref. [3], the conductance of the last plateau with values $\sim 1g_0$ shows oscillations in the process of elongating the gold atomic chain and the electric conductance changes by about 10–15%. This result is in good agreement with our theory in which the transmission probability (g/g_0) of the gold wire junctions versus N shows oscillations and its value varies by about 10–20% (see \mathcal{T} versus N in Figs. 3 and 4). We also find modulation of g/g_0 by 10–20% when the junction is stretched without changing N (as in Fig. 5), again in agreement with the experiments.

Previously reported calculations of Vega *et al.* [5] for finite Au chains obtained an oscillatory behavior of the conductance due to a single conducting channel around the Fermi energy with predominant s character, which is in good agreement with our results for \mathcal{T} versus N in Figs. 3 and 4. Furthermore, as we mentioned above, the variation of conductance with chain length in our theory is in good agreement with experiments [2,3], whereas the conductance oscillations in the theory of Vega *et al.* [5] exhibit smaller amplitudes $\sim 0.04g_0$, suggesting that our modeling may be more realistic. However, the amplitudes of the conductance oscillations in the simulations of Tavazza *et al.* [9] were similar to those found in the present work.

Using an analytic approach to study transport in a 1D atomic chain with one orbital per site as a model of a single channel wire we have also shown that the transmission probability and thermoelectric voltage (see Appendix) exhibit regular oscillations due to the quantum interference effects in the electron wave functions originating from electron scattering from the barriers between the N -atom central chain and the electrodes. Comparing the aforementioned results obtained by combining DFT and extended Hückel parameters with those given in Fig. 6, we conclude that the details of the

bonding between the electrodes and the atomic chain, of the atomic arrangements in the electrodes, and of the multiple valence orbitals of each gold atom which are all absent in the simplified 1D model studied analytically in Appendix, result in significant deviations of the oscillations from simple even-odd oscillatory behavior with the length of atomic chains.

Vardimon *et al.* [3] argued that the conductance oscillations of gold atomic chains that they observed experimentally were due to increasing conductance as zigzag chain structures were straightened by stretching followed by decreasing conductances when an additional gold atom was pulled out of a contact and added to the chain. Tavazza *et al.* [9] found similar behavior theoretically and proposed that a gradual decrease of the conductance can occur due to increasing interatomic bond lengths. Our results for the conductance in Figs. 5(b), 5(e) and 5(h) where the atomic chains are stretched while holding the number of atoms in the chains fixed, agree well with these previous experimental and theoretical findings. However, to observe the regular oscillations of the conductance and thermoelectric voltage due to quantum interference effects that we predict and are shown in Figs. 3 and 4, it is necessary to separate them experimentally from the effects due to formation and straightening of zigzag chain structures and variation of interatomic bond lengths that mask them in the conductance data of Vardimon *et al.* [3]. This might be achieved by measuring the conductances and thermoelectric voltages *only* of junctions with atomic chains having equal average interatomic spacings but different numbers of gold atoms, as in our calculations whose results are reported in Figs. 3 and 4. However, an alternative approach that may be less challenging experimentally is to measure the conductances and thermoelectric voltages for atomic chains having different numbers of gold atoms N but subjected to the *same* value of the applied tensile force. Thus all of the studied atomic chains would have similar bond angles and bond lengths, and any observed dependence of the conductance and thermoelectric voltage on N would be due primarily to quantum interference, as in Figs. 3 and 4.

Finally, we note that although some details of the results that we have presented for the thermoelectric voltage depend on the exact size and geometry of the contacts in our simulations, the important aspects of our results are reasonably robust, considering that we are dealing with nanoscale systems and phenomena affected by quantum interference. The robust features that we found are as follows: In all cases, for electrodes with more than three atomic layers, we found regular oscillations of the thermoelectric voltage with the amplitude of the oscillations growing linearly with the number of atoms in the chain. Also, for electrodes with more than three atomic layers, the period of the oscillations was almost the same in all cases and the amplitude of the oscillations (for equal numbers of atoms in the chains) varied from system to system by less than a factor of two. This robustness suggests that experiments studying thermoelectricity of gold atomic chains may succeed in finding interesting results despite the presence of defects such as disordered grain boundaries in the contacts close to the atomic chain. However, further theoretical studies with statistical analysis of the results for large numbers of different sample geometries would be of interest.

IV. CONCLUSION

In summary, using a combination of *ab initio* and semiempirical calculations, we have presented a systematic exploration of the response of the thermoelectric voltage of gold atomic wire junctions to changes of the junction's length. The junction's length was varied in two ways: (i) By successively adding single gold atoms to the atomic chain bridging two gold clusters, and (ii) by stretching the chain mechanically by applying a tensile stress which increases the Au-Au bond lengths and Au-Au-Au bond angles between atoms of the chain while keeping the number of atoms in the chain fixed. Our results predict that both the electron transmission probability through the junction and the thermoelectric voltage should exhibit an oscillatory behavior in response to adding more atoms to the atomic chain bridging the electrodes. We predict the amplitude of the oscillations of the thermoelectric voltage to increase in proportion to the number of atoms in the atomic chain for long atomic chains, based on our numerical results and on heuristic reasoning. Similar behavior is also predicted if a variable tensile strain is imposed, provided that the atomic chain junction supports the applied external force.

Our findings show that whether the junction elongation is imposed by adding extra gold atoms to the atomic junction or by external strain, a polarity change in thermoelectric voltage can be achieved in the atomic metallic chains. This feature may enable direct conversion of thermal energy into electricity and designing mechanically controllable voltage switches [29].

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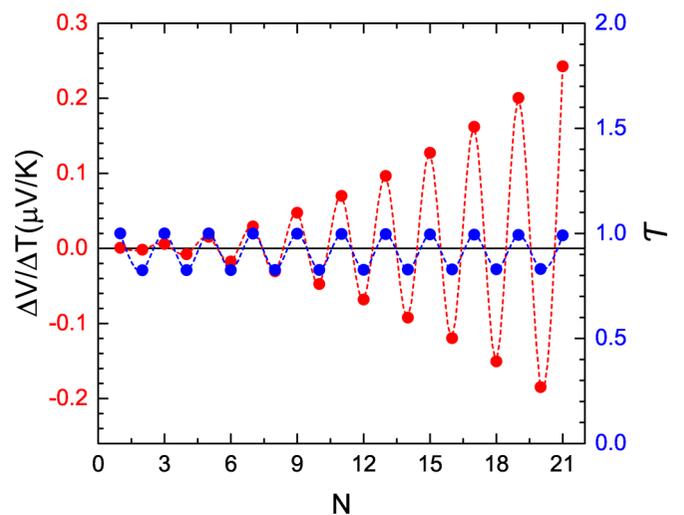


FIG. 6. Calculated electron transmission probabilities \mathcal{T} (blue dots) and thermoelectric voltages (red dots) at $E = 0$ versus the number of gold atoms N in a single channel wire at a mean temperature of 27 K. Dotted lines are guides to the eye.

APPENDIX: ANALYTICAL CALCULATION FOR TRANSPORT THROUGH A SINGLE-CHANNEL WIRE

The transmission function $\mathcal{T}(E)$ for a single-channel wire can be calculated analytically by means of the transfer-matrix formalism. We consider an infinite linear chain with lattice constant a described by a nearest-neighbor single-orbital tight-binding model with on-site energy ϵ_0 and the hopping integrals γ . To show the evolution of $\mathcal{T}(E)$ versus the number of chain atoms N , we assume the hopping parameter to be 0.8γ between sites $l = 0$ and $l = 1$ and also between $l = N$ and $l = N + 1$. This means that the incoming electrons from left region (electrode) can be partially transmitted to the right ($l \geq N + 1$) and partially reflected back into the left region ($l \leq 0$) due to the electron scattering from sites $1 \leq l \leq N$ acting as a junction. The electron wave function can be written

as $|\Psi\rangle = \sum_l \psi_l |l\rangle$, where $|l\rangle$ represents the single atomic orbital at site l . The Schrödinger equation for the coefficient ψ_l at site l is given by

$$(\epsilon_0 - E)\psi_l + \gamma_{l,l+1}\psi_{l+1} + \gamma_{l,l-1}\psi_{l-1} = 0, \quad (\text{A1})$$

where E is the electron energy. Within the transfer matrix framework, Eq. (A1) can be expressed as

$$\begin{pmatrix} \psi_{l+1} \\ \psi_l \end{pmatrix} = \begin{pmatrix} \frac{E-\epsilon_0}{\gamma_{l,l+1}} & -\frac{\gamma_{l,l-1}}{\gamma_{l,l+1}} \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \psi_l \\ \psi_{l-1} \end{pmatrix} = T_l(E) \begin{pmatrix} \psi_l \\ \psi_{l-1} \end{pmatrix}. \quad (\text{A2})$$

Here, $T_l(E)$ connects the coefficients of the wave function at site $l + 1$ and l to those at l and $l - 1$. Therefore, the transfer matrix $P(E)$ connecting the sites $l = -1, 0$ to the sites $l = N + 1, N + 2$ can be obtained from

$$\begin{pmatrix} \psi_{N+2} \\ \psi_{N+1} \end{pmatrix} = \prod_{l=N+1}^0 T_l(E) \begin{pmatrix} \psi_0 \\ \psi_{-1} \end{pmatrix} = P(E) \begin{pmatrix} \psi_0 \\ \psi_{-1} \end{pmatrix}. \quad (\text{A3})$$

The coefficients of wave function for $l \geq N + 1$ and $l \leq 0$ are plane waves with wave vector $ka = \cos^{-1}(\frac{E-\epsilon_0}{2\gamma})$. Therefore, the incoming and outgoing scattering waves within the electrodes are given by $\psi_{N+2} = \tau e^{ika(N+2)}$, $\psi_{N+1} = \tau e^{ika(N+1)}$, $\psi_0 = 1 + r$, and $\psi_{-1} = e^{-ika} + r e^{ika}$ where τ and r are the amplitudes of transmitted and reflected wave functions. Using Eq. (A3), the analytical form of transmission probabilities $\mathcal{T}(E) = |\tau|^2$ for the single-channel wire can be given by

$$\mathcal{T}(E) = \frac{4 \sin^2(ka)}{[P_{12} - P_{21} + (P_{11} - P_{22}) \cos(ka)]^2 + (P_{11} + P_{22})^2 \sin^2(ka)}. \quad (\text{A4})$$

Therefore, the energy derivative of transmission probability, $\partial\mathcal{T}/\partial E$, and hence the thermoelectric voltage can be easily computed for this single-channel wire. The results for \mathcal{T} and $\Delta V/\Delta T$ are shown in Fig. 6 with the parameters $\epsilon_0 = 0.05$ eV and $\gamma = -2.5$ eV.

As can be seen in Fig. 6, this simple analytic model reproduces qualitatively the behavior obtained from the more detailed numerical DFT and extended Hückel-based approach presented in the main text of this paper. Namely, constant amplitude conductance oscillations that are periodic in the chain length N , and regular oscillations of the thermoelectric voltage whose amplitude increases with N .

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