# Four-Atom Period in the Conductance of Monatomic Al Wires

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We present first-principles calculations based on density functional theory for the conductance of monatomic Al wires between Al(111) electrodes. In contrast to the even-odd oscillations observed in other metallic wires, the conductance of the Al wires is found to oscillate with a period of four atoms as the length of the wire is varied. Although local charge neutrality can account for the observed period, it leads to an incorrect phase. We explain the conductance behavior using a resonant transport model based on the electronic structure of the infinite wire.

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Metallic chains of single atoms represent the ultimate limit of the miniaturization of electrical conductors. Apart from possible technological applications such as interconnects in molecular electronics, the simple structure of these monatomic wires makes them an ideal test ground for developing and validating our understanding of electron transport on the nanometer length scale. The conductance of monatomic wires has been investigated theoretically by several authors using a number of different techniques [1–6]. Lang was the first to study the dependence of the conductance on the number of atoms in the wire. In 1997 he found that the conductance of a chain of Na atoms between jellium electrodes oscillates with a period of two atoms as the length of the chain is varied [1], and the following year Lang and Avouris observed the same behavior for chains of C atoms [2]. This even-odd effect was also found in Na wires by Tsukamoto and Hirose [3] using a method similar to that of Lang, and by Sim *et al.* [4] who combined cluster density functional theory (DFT) calculations with the Friedel sum rule to obtain the conductance. Recently, the even-odd oscillations have been confirmed experimentally for Au, Pt, and Ir by means of the mechanically controlled break junction [7].

The fact that a large number of metals of rather distinct character exhibit the even-odd effect has led to the suggestion that this is a universal feature of atomic wires [7]. In this Letter we present calculations based on DFT showing that the conductance of monatomic Al wires varies in an oscillatory manner as the number of atoms in the wire is changed. In contrast to the even-odd effect, however, the oscillation has a period of four atoms. Based on a resonant transport picture we show that local charge neutrality can account for the observed 4-atom period. For long wires, however, we find that the occupancy of molecular resonant states and thus the net charge located on the wire is determined by the position of the discrete energy spectrum of the free wire relative to the Fermi level of the neutral, infinite wire. In general, these two effects compete in determining the phase of the conductance oscillation. In the case of Al we find that the latter effect dominates for wires containing more than three atoms, whereas charge neutrality is important for shorter wires. By relating the electronic structure of the free wire to that of the infinite wire, we arrive at a simple picture for the position of the free wire valence resonances which accounts for the conductance both qualitatively and quantitatively. In this picture the filling factor of the infinite wire determines the period of the conductance oscillation: a half-filled band implies the even-odd effect while a filling factor of 0.25 leads to a 4-atom period.

We represent the combined electrode-wire system in a supercell containing the wire itself together with seven $3 \times 3$ sections of the (111) planes in bulk aluminum. An example of such a supercell is shown in Fig. 1. Periodic boundary conditions are imposed on the supercell in the directions perpendicular to the wire axis, and for the DFT calculations also in the parallel direction. The calculational procedure consists of two main steps. (i) A realistic wire configuration is found by relaxing the ion positions as well as the electrode-electrode distance as determined by the length of the supercell. During the relaxation the wire is constrained to be linear and ions below the surface layer are fixed in the bulk crystal structure. These simulations were performed within DFT using a plane-wave based pseudopotential code [8] with an energy cutoff of 15 Ry for the plane-wave expansion. The ion cores are replaced by ultrasoft pseudopotentials [9] and to treat exchange and correlation we use

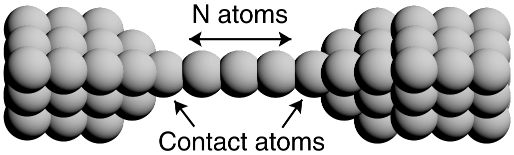

FIG. 1. The $N = 3$ wire connecting Al(111) electrodes via a 3-atom basis. This structure constitutes the supercell in the DFT calculations and forms the scattering region in the conductance calculations.

the PW91 functional by Perdew and Wang [10]. The bond lengths in the wires lie in the range 2.36–2.50 Å with the shorter bond lengths achieved closer to the center of the wire. For the longer wires the bond lengths vary less and approach a value of 2.39 Å, which is also found for the infinite wire. No dimerization is found in accordance with previous results for infinite linear Al chains [11]. Concerning the magnetic properties, Ayuela *et al.* have found that an infinite linear Al chain has a nonmagnetic ground state for interatomic distances smaller than 2.7 Å [12]. Finally, it should be mentioned that the formation of zigzag structures and Peierls distortions in infinite Al wires was recently investigated by Ono and Hirose [13]. (ii) The self-consistent effective potential generated by the DFT code is used as input to the Green function transport code described in detail in Ref. [14]. The effective potential of the supercell forms the scattering region in the transport problem while the potential in the semi-infinite leads is obtained from a DFT bulk calculation. In this way the scattering region and the leads are treated on an equal footing taking their full atomic and electronic structure into account. The conductance is calculated from the Green function of the scattering region, which is represented in terms of a system-independent basis set containing wavelets of compact support. All conductance calculations have been converged with respect to the size of the basis set. Because of the limited size of the supercell in the directions perpendicular to the wire, the two-dimensional Brillouin zone is sampled by eight special **k** points, both in the transport and the DFT calculations.

In Fig. 2 we have plotted the calculated conductance of Al wires containing 1–9 atoms and attached to the (111) surface either directly or via a 3-atom basis. We regard an atom as part of the wire if it has a coordination number of 2; see Fig. 1. With this convention the wire couples to the electrodes via a single atom which we refer to as the contact atom. The conductance oscillates with a period of four atoms taking values in the range $0.5G_0$ to $1.7G_0$. The oscillation amplitude increases approximately 10% when the 3-atom basis is used as contact to the electrodes, but otherwise no difference is found between the two geometries.

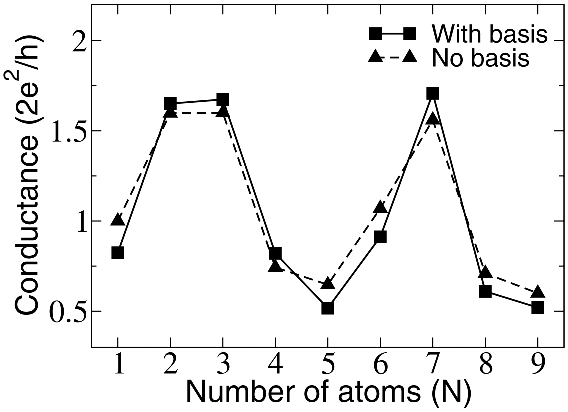

FIG. 2. Calculated conductance as a function of wire length with and without a 3-atom basis as contact to the electrodes.

We can gain some information about the current carrying states by studying the eigenchannel resolved conductance [15], as shown in Fig. 3 for $N = 3$. The valence configuration of atomic Al is $3s^2 3p$, which for the infinite wire leads to a fully occupied $\sigma$ band and a degenerate $\pi$ band with filling factor $f = 0.25$. Three channels contribute to the total conductance: two similar $\pi$ channels and a single $\sigma$ channel. The two $\pi$ channels constitute the main part of the conductance, while the $\sigma$ channel is a tunneling channel whose contribution decays exponentially with the wire length from $\sim 0.2G_0$ at $N = 1$ to $\sim 10^{-4}G_0$ at $N = 9$.

To understand the origin of the conductance oscillations we first relate the conductance to the electronic structure of the wire. When a free $N$-atom wire is connected to bulk electrodes, the molecular orbitals on the wire hybridize with extended states in the electrode. As a result of this mixing, the $n$th energy level of the free wire is broadened into a resonance described by the projected density of states [16]

$$\rho_n(\varepsilon) = \frac{\pi^{-1}\Delta_n(\varepsilon)}{[\varepsilon - \varepsilon_n - \Lambda_n(\varepsilon)]^2 + \Delta_n^2(\varepsilon)}. \quad (1)$$

For each molecular level, the coupling to the electrodes defines a unique orbital, the group orbital, which is located on the contact atoms. In terms of the group orbital we can write $\Delta_n(\varepsilon) = \pi|V_n|^2\rho_{c,n}(\varepsilon)$, where $V_n$ is the matrix element coupling the $n$th molecular level with its corresponding group orbital and $\rho_{c,n}$ is the projected density of states for the group orbital in the absence of the wire. For simplicity we shall not distinguish between the group orbitals and thus we set $\rho_{c,n} = \rho_c$. If we furthermore neglect interference between the different

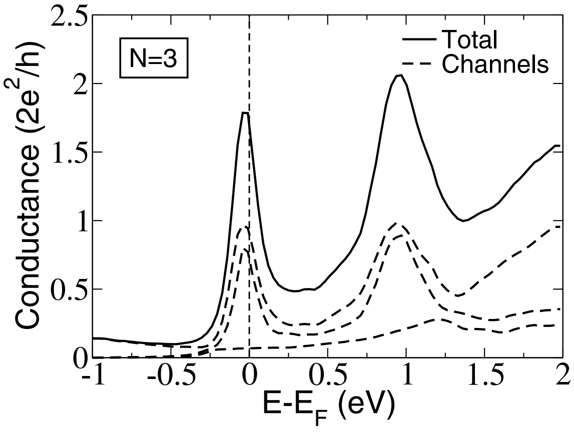

FIG. 3. Eigenchannel resolved conductance for the $N = 3$ wire shown in Fig. 1. The two similar $\pi$ channels together with the $\sigma$ channel are indicated by the dashed lines, while the solid line shows the total conductance.

molecular levels, we obtain a simple expression for the conductance

$$G = \frac{2e^2}{h} \sum_n \pi^2 |V_n|^2 \rho_c(\varepsilon_F) \rho_n(\varepsilon_F), \tag{2}$$

where the sum extends over all molecular levels. From this expression we expect the position of the resonances relative to the Fermi level of the electrodes to be a crucial parameter for the conductance.

Thus far, local charge neutrality has been considered the main cause of the even-odd oscillations in monovalent wires [4,5,7]. In the case of Al, the degeneracy of the $\pi$ orbitals and the fact that each Al atom provides one electron to the $\pi$ system implies that local charge neutrality would cause oscillations in the conductance with a period of four atoms [17]. The resulting phase of the oscillation would, however, be incorrect. The maxima (minima) occur for half-filled (filled) resonances which should correspond to $N = 2, 6, \ldots$ ($N = 4, 8, \ldots$). These numbers are off by one atom as compared to Fig. 2. Consequently, charge neutrality alone cannot account for the conductance of the Al wires. At this point it is interesting to notice that different results have been obtained for the phase of the conductance oscillation in Na wires. As opposed to Tsukamoto and Hirose and Sim *et al.*, Lang [1] has found a higher conductance for even-numbered than for odd-numbered Na chains. Calculations by Havu *et al.* [5] for Na wires between jellium cones show that it is possible to change the phase of the conductance oscillation from even-odd to odd-even by varying the lead opening angle.

To explain the behavior of the conductance, we need to examine more closely the position of the resonances relative to the Fermi level of the electrode-wire-electrode system. As a first step in this direction we consider a linear chain of $N$ sites coupled by nearest neighbor hopping. The Hamiltonian is

$$H = \sum_{i=1}^{N} \varepsilon_0 c_i^\dagger c_i + \sum_{i=1}^{N-1} t(c_{i+1}^\dagger c_i + c_i^\dagger c_{i+1}), \tag{3}$$

where $c_i$ annihilates an electron at site $i$. The eigenvalues, $\varepsilon_n^N$, of $H$ can be expressed in terms of the band structure of the infinite chain of coupled sites, $\varepsilon(k)$, as follows:

$$\varepsilon_n^N = \varepsilon\left(\frac{n\pi}{N+1}\right), \qquad n = 1, \ldots, N, \tag{4}$$

where we have set the intersite distance to 1. Although the above relation is only strictly valid for the model Hamiltonian (3), we can still use it to estimate the spectrum of a free $N$-atom wire in terms of the band structure of the infinite wire. Assuming $\rho_c(\varepsilon)$ to be constant, the $n$th resonance of the $N$-atom wire becomes a Lorentzian of width $\Delta_{N,n} = \pi |V_{N,n}|^2 \rho_c$. Since we are only interested in resonances close to the Fermi energy, it is reasonable to assume an energy independent coupling, $V_{N,n} = V_N$. Furthermore, the extended nature of the eigenstates of the free wire causes $|V_N|^2 \propto 1/N$, which implies a corresponding decrease in the resonance width as the wire length increases, $\Delta_N \propto 1/N$. In Fig. 4 we have illustrated in $k$ space the evolution of the discrete spectrum of a free wire as a function of the wire length. For each eigenvalue we have indicated the width of the corresponding resonance. The eigenvalues are converted to energy via the valence band of the infinite wire and relation (4).

To determine the position of the Fermi level in the electrode-wire-electrode system we note that in the limit of a long wire the net charge per wire atom must vanish and consequently the band filling $f$ must approach that of the infinite wire. Since the Fermi level is fixed by the macroscopic electrodes this argument fixes the Fermi level for wires of any length. We emphasize the difference between this picture and that based on charge neutrality. Whereas the former inherits the molecular levels and the Fermi level from the neutral infinite wire, the latter assumes that the molecular levels somehow adjust to the Fermi level in order to ensure charge neutrality of the coupled finite wire. In Fig. 4 we have indicated the Fermi level for the Al wire by a vertical line at $k = \pi/4$ corresponding to $f = 0.25$. As $N$ increases the resonances move down through the Fermi level in a systematic fashion. The coincidence of the Fermi level with the center of a resonance is a periodic event of period four starting at $N = 3$. Like the local charge neutrality, this picture explains the observed period of the conductance oscillation but in addition it provides information about the actual position of the resonances. The first maximum (minimum) is predicted to occur at $N = 3$ ($N = 5$), which indeed gives the correct phase as compared to Fig. 2.

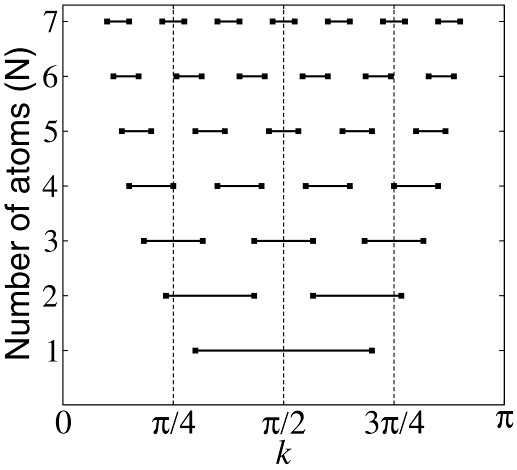

FIG. 4. Evolution in $k$ space of the discrete spectrum of a free $N$-atom wire. The interatomic distance in the wire is set to 1. The horizontal lines symbolize the width of the corresponding resonance formed when the free wire is coupled to electrodes.

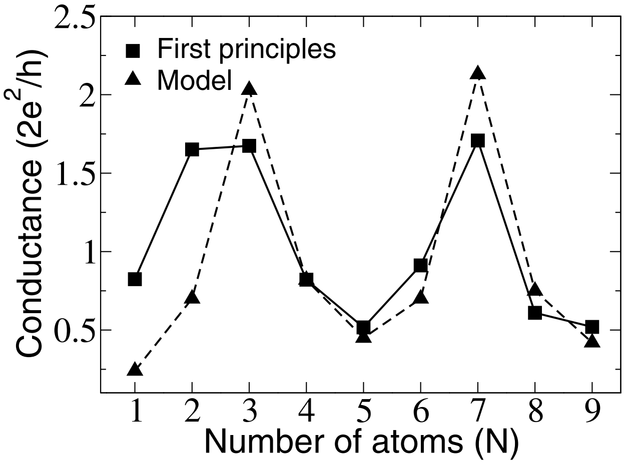

FIG. 5. The conductance of Al wires as calculated from first principles (solid line) and a simple model (dashed line).

The vertical line at $k = \pi/2$ indicates the position of the Fermi level for metals with a half-filled valence band such as Na, Au, and C. Clearly, our model accounts for the even-odd behavior observed in these wires.

According to the filling of $\pi$ resonances as predicted by Fig. 4, the $N$-atom Al wire should hold approximately $N - 1$ valence electrons. For short wires the electrostatic potential from the missing electron drags the resonances down in energy thereby increasing the occupancy. The resulting position of the resonances must be determined self-consistently and will in general lead to an occupation somewhere between $N - 1$ and $N$. For short wires the simple picture is therefore modified by a charge-neutralization process which tends to shift down the phase of the conductance oscillation by one atom. This effect explains the relatively high conductances found for $N = 1, 2$ as compared to $N = 5, 6$.

To test our simple model quantitatively we have used it to reproduce the first-principles results. We use Eq. (2) for the conductance and assume a Lorentzian shape of the projected density of states. The molecular levels given in Eq. (4) are obtained via the $\pi$ band of the infinite Al wire calculated within DFT. From the first resonance in Fig. 3 we read off $\Delta_{N=3} = 0.15$ eV as the half width at half maximum. Because of the $1/N$ scaling, all resonance widths then follow from $\Delta_{N=3}$. The result of the model is seen in Fig. 5 together with the first-principles calculation, repeated here for convenience. Except for the shortest wires ($N = 1, 2$), where charge transfer as well as conduction through the $\sigma$ channel is important, the model gives a good description of the conductance with an average deviation of less than 15%. The fact that the model gives values above $2G_0$ is a consequence of the neglected interference between different molecular levels. Finally, we note that the $1/N$ dependence of the resonance width together with the $1/N$ dependence of the resonance spacing implies the existence of conductance oscillations also for longer wires. This is in agreement with previous results in Ref. [18].

In summary, our calculations show that in contrast to the even-odd effect the conductance of monatomic Al wires oscillates with a 4-atom period as the number of atoms in the wire is varied. This behavior is explained by combining a resonant transport picture with the electronic structure of the free Al wire. By relating the electronic structure of a free wire to the valence band of the infinite wire, we find that the period of oscillation is determined by the filling factor of the valence band of the infinite wire. For long wires (> 4 atoms) a simple model based on these ideas was shown to reproduce the first-principles conductances, while for short wires the simple picture is modified by charge transfer and tunneling effects.

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