Non-universal behavior of the parity effect in monovalent atomic wires

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We propose a mixed analytical-ab-initio method for the accurate calculation of the conductance in monovalent atomic wires. The method relies on the most general formula for ballistic transport through a monovalent wire, whose parameters can be determined from first-principles calculations. Our central result is the demonstration of the highly non-universal behavior of the conductance, which depends on the fine details of the contacts to the leads. We are therefore able to reconcile a large number of the apparently contradictory results that have recently appeared in the literature.

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In the last two decades transport properties of atomic contacts have been the subject of intensive research (for overviews see Ruitenbeek \cite{1} and Agrait, Yeyati and Ruitenbeek \cite{2}). First experimental evidences of the formation of golden atomic chains have been reported by Yanson et al. \cite{3} and Ohnishi et al. \cite{4}. Experiments on chains of Au, Pt and Ir atoms \cite{4} exhibit electrical conductance oscillations as a function of the wire length and similar oscillations as a function of bias voltage and electrode separation \cite{5, 6}. Rodrigues et al. \cite{7} investigated the energetically preferred orientation of the crystal planes of the wire by the application of high-resolution transmission electron microscopy. Their results show a strong correlation between the atomic arrangement and the conductance.

The above experiments were stimulated by early theoretical predictions of conductance quantization \cite{8, 9} and conductance oscillations \cite{10, 11}. The latter issue generated a sequence of theoretical papers using a variety of techniques \cite{11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23}. Density-functional theory predicted that the conductance of Na atom chains is close to the conductance quantum $2e^2/h$ for odd numbers of atoms, and smaller than this for even numbers of atoms \cite{10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23}. In the literature this is called the even-odd effect. A similar effect was found for other monovalent alkali-metal atoms such as Cs, but an opposite behavior, with a conductance bigger for even numbers of atoms than for odd numbers of atoms, was predicted for noble-metals (Cu, Ag and Au) \cite{13, 14}. The even-odd oscillation of the conductance for atomic wires of Na has also been analyzed using a pseudoatom-jellium model \cite{15}, where it was found that the sign of the effect is sensitive to the lead cone angle. Applying the first-principle recursion-transfer-matrix method Hirose et al. \cite{22} showed that the bonding nature of the atoms at the contact plays a crucial role in determining transport properties. Lee and Kim \cite{17} and Zeng and Claro \cite{18}, studied the effects of symmetries and found that the conductance of atomic chains with mirror symmetry and an odd number of atoms is always equal to the conductance quantum $2e^2/h$.

In the literature various heuristic models have been proposed to interpret physically the results mentioned above: the standing wave model proposed by Emberly et al. \cite{12}, a simple barrier model suggested by Lee et al. \cite{23}, a simplified one-dimensional free-electron model of Sim, Lee et al. \cite{15, 24} and, more recently, a resonant transport model used by Thyesen and Jacobsen to explain the four-atom period oscillation of the conductance for Al wires \cite{21}.

To reconcile the different behaviors observed in the literature and elucidate whether the parity behavior is universal or depends on the fine details of the system, we present in this letter a theoretical scheme which treats electronic structure and transport to the same degree of rigor and interprets results in terms of a simple, but general framework. We use the non-equilibrium Green’s function approach, combined with a rather general, model-free formula, where a derivation requires only two assumptions: i) the existence of a translational invariant region within the atomic chain, ii) the presence of only one conducting channel in the wire, even though many conductance channels are allowed in the leads. We then demonstrate the validity of this formula by comparing with the conductance calculated from ab-initio calculations for different choices of the contacts.

Figure 1 (a) shows atomic chains of physical length $D$, containing a translationally-invariant region of length $d = (n + 1)a$, where $n$ is the number of atoms in that region and $a$ is the lattice constant of the chain. In general, $D > d$ because atoms near the contacts may experience a different electrostatic potential from those in the region of length $d$. To verify this we performed atomistic calculations of the electronic structure of gold and sodium chains using the density functional code SIESTA \cite{25, 26, 27}. Gold and sodium are prototypes of noble and alkali metals, respectively. The external leads used in the simulations are bcc for sodium and fcc for gold, both grown along the (001) direction, and can be terminated with a surface cross-section containing either 4 or 5 atoms. This allows us to perform three separate calculations.
corresponding to three different choices of termination of the left-right leads, which we denote 4-4, 5-5, and 4-5. We also used leads with bigger cross sections and leads grown along (111) for gold and verified that the overall predictions are essentially the same. Figure 1(b) shows the electrostatic potential $V$ as a function of the distance $x$ along the chain of gold. One can see a rapid variation of the potential near the contact and an almost perfect periodic dependence around the middle of the chain in a relatively long translationally invariant segment of length $d$.

The system comprising the translational invariant segment of the atomic chain connected to atoms on the left and right can be characterized by two scattering matrices that couple the left and the right regions to the segment $d$. Using the unitary relations for the scattering matrices and the Landauer-Büttiker formula [28] we find that the conductance (in units of $2e^2/h$) is

$$g = \frac{(1 - r_L^2)(1 - r_R^2)}{1 + r_L^2 r_R^2 - 2r_L r_R \cos(2kd + \Phi_{LR})}, \tag{1}$$

where $\Phi_{LR} = \Phi_L + \Phi_R$ and $\Phi_L(\Phi_R)$, and $r_L(r_R)$ are the phase shifts and magnitudes of reflection amplitudes at left (right) ends of the region $d$ and $k$ is the wavenumber of the transmitting electron. This model-free equation is the most general form of the conductance through a monovalent ballistic atomic chain. Note that in Eq. (1) $r_L, r_R$ and $\Phi_{LR}$ are scalars depending on the details of the coupling of the region $d$ to the leads and the Fermi energy, and are independent of the length $d$ of the chain. Thus, the conductance is a periodic function of the length $d$. As we shall demonstrate, the parameters $r_L^\prime, r_R^\prime$ and $\Phi_{LR}$ can be determined from ab-initio calculations.

We immediately notice two differences between Eq. (1) and the corresponding result obtained from a model based on the simplified one-dimensional free-electron picture [4] and the barrier model [23]. First, $d$ is the length of the translational invariant region of the chain, which is not necessarily equal to $D$. Second, Eq. (1) contains a phase, which is missing from the analysis of Refs. [4,23] and even for a model in which $D = d$, this phase is in general, non-zero. Consequently, the even-odd behavior of the conductance strongly depends on the details of the coupling of the chain to the leads (through the phase shift $\Phi_{LR}$) and this is the reason for the different predictions in the literature [4,10,14,15,23]. It is obvious from Eq. (1) that the conductance $g$ becomes unity when the two leads are identical ($r_L' = r_R'$), and the cosine term is 1. For the simple tight-binding approximation used in, e.g., [23] the dispersion relation is $\varepsilon(k) = \varepsilon_0 + 2\gamma \cos(ka)$, where $\varepsilon_0$ and $\gamma$ are the on-site energy and the hopping energy. For a chain of monovalent atoms the Fermi energy is $\varepsilon_0$ and the Fermi wave number is $k = \pi/(2a)$. Hence, for $\Phi_{LR} = 0$ and for an odd number of atoms $n$, i.e., $d = (n + 1)a$, the conductance is $g = 1$, and is smaller for even $n$, in agreement with [17,18] and the model in [4,23]. However, this prediction is in contrast to the results of [17] for gold wires and [23] for noble-metals, implying that in those cases the phase $\Phi_{LR} \neq 0$.

To obtain the conductance from an ab-initio calculation we used our newly developed code SMEAGOL [24,31], which calculates the density matrix and the transmission coefficients of a two probe device from the Hamiltonian provided by SIESTA using the non-equilibrium Green’s function formalism (NEGF) [23]. In this calculation the main input is the atomic number and atomic positions of the constituents, whereas Eq. (1) is obtained from a model-free scattering approach. The ab-initio calculation yields $g$ as a function of the energy $\varepsilon$ and does not compute $r_L', r_R'$ and $\Phi_{LR}$ directly. To obtain the latter, we compute the ab-initio conductance $g(\varepsilon)$ for a range of $\varepsilon$ and perform a least squares fit to Eq. (1), treating $r_L', r_R', \Phi_{LR}$ and $k(\varepsilon)$ as fitting parameters.

At first sight, it is not obvious that the simplicity of Eq. (1) is sufficient to capture the complexity of an ab-initio calculation. To show the validity of this formula we now determine the parameters in Eq. (1) from atomistic calculations and show that the phase $\Phi_{LR}$ of the asymmetrical system satisfies a simple addition rule in the following sense. For identical leads with a particular choice of contact denoted by $\alpha$ the parameters $r_L^\prime = r_R^\prime$ and $\Phi_{LR}$ obtained from ab-initio calculations will be denoted by $r_{\alpha\alpha}$ and $\Phi_{\alpha\alpha}$, respectively. For a symmetric system with another choice of contact to the leads, say $\beta$, these parameters will be denoted by $r_{\beta\beta}$ and $\Phi_{\beta\beta}$. Equation (1) requires that the conductance of an asymmetrical system with the left-lead contacted as $\alpha$ and the right-lead as $\beta$, is obtained by substituting $r_L^\prime = r_{\alpha\alpha}, r_R^\prime = r_{\beta\beta}$ and $\Phi_{LR} = (\Phi_{\alpha\alpha} + \Phi_{\beta\beta})/2$ into formula (1). Figure 2 shows the predicted conductance of the asymmetrical lead configuration

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**FIG. 1:** (a) Three different couplings of the chain to the leads were studied: the chain coupled to both leads by 4 atoms (case 4-4), the chain coupled to the left and right lead by 4 and 5 atoms, respectively (case 4-5), and the chain coupled to both leads by 5 atoms (case 5-5). (b) The variation of the potential $V$ (in units of Rydbergs) along the Au chain with 18 number of atoms (in units of Å) in the case of the three types of couplings shown in (a).


using the parameters obtained from the two symmetrical cases for Na chains (similar results are obtained for gold). As can be seen in the main panel of the figure the agreement is excellent.

![Graph showing conductance g as a function of length D for Na chains](image)

**FIG. 2:** The main panel shows the conductance \( g \) (in units of \( 2e^2/h \)) obtained from the ab-initio calculations (dots) of Na chains between different leads (4-5) as a function of length of the chain (in units of the number of atoms) for \( \varepsilon = E_F + 0.099 \) eV, and the conductance (solid line) obtained by substituting \( r_L' = r_{44}, r_R' = r_{55} \) and \( \Phi_{LR} = (\Phi_{44} + \Phi_{55})/2 \) in Eq. (1). In the left (right) insets the results of the ab-initio calculations (dots) and the fits of \( g \) (solid line) using Eq. (1) for the 4-4 (5-5) cases are shown yielding the parameters \( r_{44}, \Phi_{44}, \) and \( r_{55}, \Phi_{55} \), respectively.

Figure 3 shows the ab-initio results at the Fermi energy for the conductances of Na and Au chains. One can see that the conductances strongly depend on the material and the type of coupling, demonstrating thus the non-universal behavior of the even-odd effect in these systems. In each case the parity effect is obvious, which means that wavenumber \( k \) in Eq. (1) at the Fermi energy is near to \( \pi/(2a) \). We also compared the predicted \( k(\varepsilon) \) with the band structure obtained from a separate ab-initio calculation on an infinitely-periodic atomic chain. Our results of \( k(\varepsilon) \) from fitting and the ab-initio band structure calculation for an infinite long Na atomic chain are shown in Fig. 4 The good agreement is clearly visible.

The validity of the addition rule for the phases can be checked directly, as is demonstrated in Fig. 5 for sodium wires. One can see from the figure that the agreement is again very good (only close to the Fermi energy the errors of the numerical fit are larger). Similar agreement is also obtained for gold chains, not shown here. We find that there are significant differences in the phase shifts \( \Phi_{LR} \) for different lead-wire configurations. The results shown in Fig. 5 demonstrate that the phase of the even-odd behavior is sensitive to the lead-chain coupling and can be opposite to that which is normally expected.

Equation (1) also explains why the ensemble-averaged conductance of Au wires oscillates with small amplitude, which in most cases is less than about 0.05 in unit of \( 2e^2/h \). Neglecting the sample dependence of the reflection amplitudes \( r_L', r_R \) in formula (1) and assuming a uniform distribution for the phase shift \( \Phi_{LR} \) over the interval \([0, 2\pi]\), one can calculate the ensemble-averaged conductance by integrating formula (1) with respect to \( \Phi_{LR} \) to yield an average conductance, which is independent of the length \( d \) of the chain. Since the experimental result for the average conductance shows a small, but finite amplitude of oscillation, the distribution of the phase \( \Phi_{LR} \) is presumably not exactly uniform, or correlated to sample-dependent reflection amplitudes. This suggests the importance of a sample-dependent statistical analysis of the calculated or measured conductance for a better understanding of the conductance oscillation. We think that formula (1) through the functional form of the conductance can be useful starting point for such an analysis.

In summary, a simple, but model-free formula for the transport through monovalent atomic chains was presented and compared with the results obtained from ab-initio calculations for Au and Na based on the non-equilibrium Green’s function approach. Our results clearly demonstrate that i) Eq. (1) describes accurately the conductance through atomic wires with a variety of contacts provided there is a translationally invariant segment in the chain with one conducting channel and ii)
FIG. 5: The insets show the phase $\Phi_{44}$ and $\Phi_{55}$ (in units of radians) for Na chains. The main figure shows a comparison between the inset with error bars and the average ($\Phi_{44} + \Phi_{55}$)/2 (filled circle with error bars). The energy scale is in units of eV.

the non-universal behavior of the parity effect, which helped us to understand and reconcile the different results observed in the literature.

We believe that the conductance formula (1) derived from the scattering approach, unifies and captures the essential feature of the earlier models [4, 12, 23]. Moreover, as it is known, the resonant assisted transport such as developed in Refs. [15, 21, 24] in general, can be interpreted by the scattering matrix approach (see e.g. Ref. [15] and references therein).

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