

Nonuniversal 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 nonuniversal 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 Ruitenbeek¹ and Agraït, Yeyati, and Ruitenbeek²). The first experimental evidence of the formation of gold atomic chains has been reported by Yanson *et al.* and by Ohnishi *et al.*³ Experiments on chains of Au, Pt, and Ir atoms⁴ exhibit electrical conductance oscillations as a function of the wire length and similar oscillations as a function of bias voltage and electrode separation.^{5,6} Rodrigues *et al.*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 quantization⁸ and conductance oscillations.^{9,10} The latter issue generated a sequence of theoretical papers using a variety of techniques.^{11–23} 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.^{10,15,16,20} 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 the 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).²³ The even-odd oscillation of the conductance for atomic wires of Na has also been analyzed using a pseudoatom-jellium model,¹⁹ where it was found that the sign of the effect is sensitive to the lead cone angle. Applying the first-principles recursion-transfer-matrix method Hirose *et al.*²² showed that the bonding nature of the atoms at the contact plays a crucial role in determining transport properties. Lee and Kim¹⁷ and Zeng and Claro¹⁸ 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 $2e^2/h$. Recently, the electron correlations of atomic chains have been studied using the density matrix renormalization group algorithm and it was shown that the amplitude of the length-dependent

oscillations of the conductance depends on the electron density in the chain.²⁴

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.*,¹² a simple barrier model suggested by Lee *et al.*,²³ the simplified one-dimensional free-electron model of Smit *et al.*,⁴ the Friedel sum rule and charge neutrality of Sim and co-workers,^{15,25} and, more recently, the resonant transport model used by Thygesen and Jacobsen to explain the four-atom period oscillation of the conductance for Al wires.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 paper 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 nonequilibrium Green's function approach, combined with a rather general, model-free formula, where the derivation requires only two assumptions: (i) the existence of a *translationally invariant* region within the atomic chain, and (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.^{26–28} 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 four or five atoms.

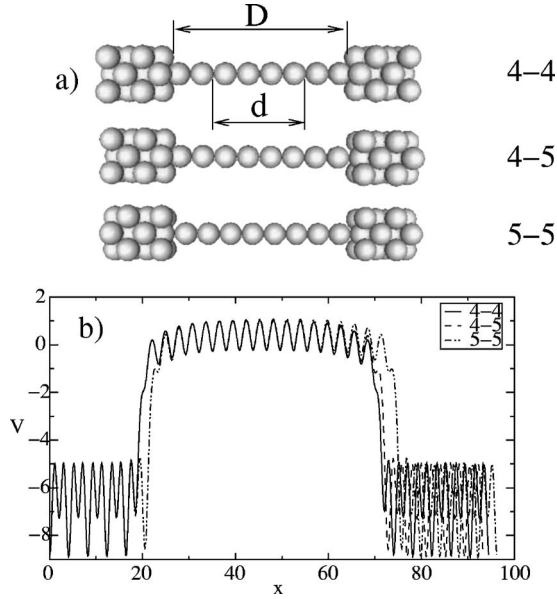


FIG. 1. (a) Three different couplings of the chain to the leads were studied: the chain coupled to both leads by four atoms (case 4-4), the chain coupled to the left and right leads by four and five atoms, respectively (case 4-5), and the chain coupled to both leads by five atoms (case 5-5). (b) The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

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 translationally 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 formula²⁹ we find that the conductance (in units of $2e^2/h$) is

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

where $\Phi_{LR} = \Phi_L + \Phi_R$, Φ_L (Φ_R) and r_L' (r_R') are the phase shifts and magnitudes of reflection amplitudes at the left (right) ends of the region d , and k is the wave number 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 (1) r_L' , r_R' , and Φ_{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' , r_R' , and Φ_{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 picture⁴ and the barrier model.²³ First, d is the length of the translationally 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 and 23 and even for a model in which $D=d$, this phase is in general nonzero. 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 Φ_{LR}) and this is the reason for the different predictions in the literature.^{4,10,12,18,19,23} 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., Ref. 30, the dispersion relation is $\varepsilon(k) = \varepsilon_0 + 2\gamma \cos(ka)$, where ε_0 and γ are the on-site energy and the hopping energy. For a chain of monovalent atoms the Fermi energy is ε_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 Refs. 17 and 18 and the model in Refs. 4 and 23. However, this prediction is in contrast to the results of Ref. 12 for gold wires and Ref. 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 code SMEAGOL,^{31,32} 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.³³ 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 ε and does not compute r_L' , r_R' , and Φ_{LR} directly. To obtain the latter, we compute the *ab initio* conductance $g(\varepsilon)$ for a range of ε and perform a least-squares fit to Eq. (1), treating r_L' , r_R' , Φ_{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 Φ_{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 α the parameters $r_L' = r_R'$ and Φ_{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 β , 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 α and the right lead as β , is obtained by substituting $r_L' = r_{\alpha\alpha}$, $r_R' = r_{\beta\beta}$, and $\Phi_{LR} = (\Phi_{\alpha\alpha} + \Phi_{\beta\beta})/2$ into formula (1). Figure 2 shows the predicted conductance of the asymmetrical lead configuration using the parameters obtained from the two symmetrical cases for Na chains (similar results are obtained

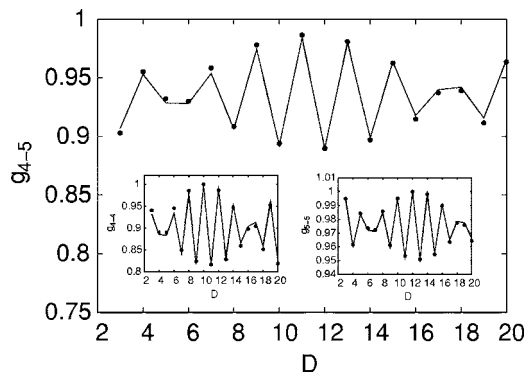


FIG. 2. The main panel shows the conductance g (in units of $2e^2/h$) obtained from the *ab initio* calculations (dots) of Na chains between different leads (4-5) as a function of length of the chain (in units of the number of atoms) for $\varepsilon = E_F + 0.099$ eV, and the conductance (solid line) 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} , Φ_{44} , and r_{55} , Φ_{55} , respectively.

for gold). As can be seen in the main panel of the figure the agreement is excellent.

Figure 3 shows the *ab initio* results at the Fermi energy for the conductances of Na and Au chains. One can see that the phase of the conductance oscillations strongly depends on the material and the type of coupling, demonstrating thus the nonuniversal behavior of the even-odd effect in these systems. In each case the parity effect is obvious, which means that the wave number 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.

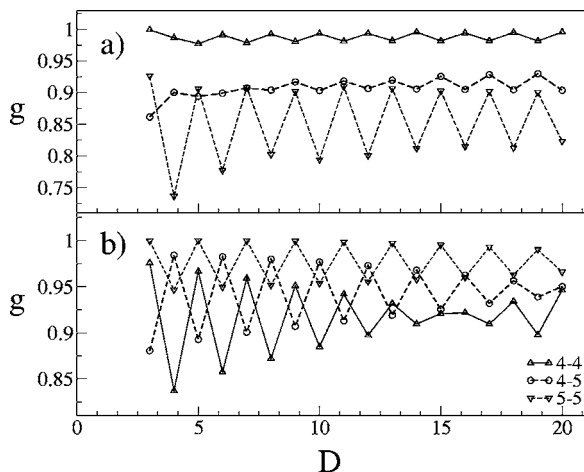


FIG. 3. The conductance (in units of $2e^2/h$) obtained from atomistic simulations for Au (a) and Na (b) atomic chains at energy $\varepsilon = E_F$ as a function of length of the chain D (in units of the number of atoms) for the three different choice of contacts shown in Fig. 1(a).

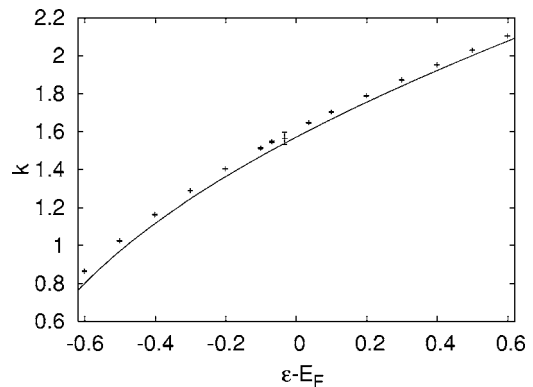


FIG. 4. The energy–wave number relation obtained with help of formula (1) (+ sign and error bars) and dispersion relation calculated using SIESTA (solid line) for an infinite Na atomic chain. The energy and the wave number are in units of eV and the inverse of the lattice constant, respectively.

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 are the errors of the numerical fit larger). Similar agreement is also obtained for gold chains, not shown here. We find that there are significant differences in the phase shifts Φ_{LR} for different lead-wire configurations. The results shown in Figs. 5 and 3 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 wires⁴ 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 Φ_{LR} over the interval $[0, 2\pi]$, one can calculate the ensemble-averaged conductance by integrating formula (1) with respect to Φ_{LR} , to yield an average conductance, which is independent of the length d of the chain.

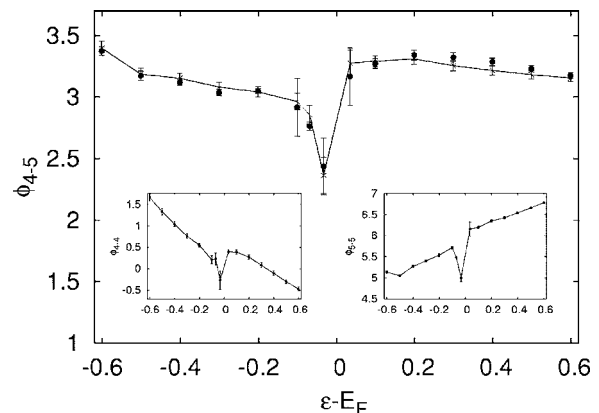


FIG. 5. The insets show the phase Φ_{44} and Φ_{55} (in units of radians) for Na chains. The main figure shows a comparison between Φ_{45} (\times sign and line with error bars) and the average $(\Phi_{44} + \Phi_{55})/2$ (filled circle with error bars). The energy scale is in units of eV.

Since the experimental result for the average conductance shows a small but finite amplitude of oscillation, the distribution of the phase Φ_{LR} is presumably not 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 a 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 nonequilibrium Green's function approach. Our results clearly demonstrate (i) that 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) the nonuniversal behavior of the parity effect due to the sensitive geometry dependence of the phase, 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, and 25, in general can be interpreted by the scattering matrix approach (see, e.g., Ref. 34 and references therein).

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