Stability of conductance oscillations in monatomic sodium wires

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(Received 5 April 2006; published 25 October 2006)

We study the stability of conductance oscillations in monatomic sodium wires with respect to structural variations. The geometry, the electronic structure, and the electronic potential of sodium wires suspended between two sodium electrodes are obtained from self-consistent density functional theory calculations. The conductance is calculated within the framework of the Landauer-Bütttiker formalism, using the mode-matching technique as formulated recently in a real-space finite-difference scheme [Phys. Rev. B **70**, 195402 (2004)]. We find a regular even-odd conductance oscillation as a function of the wire length, where wires comprising an odd number of atoms have a conductance close to the quantum unit $G_0=e^2/\pi\hbar$, and even-numbered wires have a lower conductance. The conductance of odd-numbered wires is stable with respect to geometry changes in the wire or in the contacts between the wire and the electrodes; the conductance of even-numbered wires is more sensitive. Geometry changes affect the spacing and widths of the wire resonances. In the case of odd-numbered wires the transmission is on-resonance, and hardly affected by the resonance shapes, whereas for even-numbered wires the transmission is off-resonance and sensitive to the resonance shapes. Predicting the amplitude of the conductance oscillation requires a first-principles calculation based upon a realistic structure of the wire and the leads. A simple tight-binding model is introduced to clarify these results.

DOI: 10.1103/PhysRevB.74.165416 PACS number(s): 73.63.−b, 73.40.−c, 71.15.−m, 85.35.−p

I. INTRODUCTION

Recent progress in fabricating conductors of atomic dimensions has stimulated a large number of experimental and theoretical studies on these nanoscale devices.[1] Conductors whose cross section contains only a small number of atoms are commonly called "atomic wires." Clear evidence that the fundamental limit of a one atom cross section can be reached, has been presented for gold atomic wires.[2,3] Over the last decade the electronic transport in atomic wires made of various metals has been characterized in great detail experimentally.[4–9] Such wires have conductances of the order of the quantum unit $G_0=e^2/\pi\hbar$, so the description of their transport properties, as well as of their atomic and electronic structures, requires a full quantum-mechanical treatment.[10]

Simple theoretical schemes have been proposed, in which the atomic wire is described by a jellium[11] or a tight-binding model.[12] At present a first-principles approach based on density functional theory (DFT) gives the most advanced description of the geometry and electronic structure of atomic wires. Several theoretical methods that combine the Landauer-Büttiker formalism with DFT, have been developed in order to solve the quantum transport problem in terms of scattering amplitudes.[13–18] Alternatively, a Green's function formalism is commonly used for solving the transport problem.[19–31] Both these approaches are, in fact, completely equivalent in the case of noninteracting electrons.[32]

Atomic wires that have a cross section of just one atom, so-called "monatomic" wires, are the ultimate examples of quasi-one-dimensional systems. Here the effects of a reduced dimensionality are expected to be most pronounced. *A priori* the existence of monatomic wires is not obvious. Such free-standing one-dimensional structures might be unstable because of the low coordination number of the atoms in the wire. Molecular dynamics simulations based upon an effective medium model[33] or a tight-binding model[24,34] have been used to study the stability of a wire as a function of its elongation. Since such simulations use highly simplified interatomic potentials, they aim at providing a qualitative understanding of the wire formation. A more quantitative description can be provided by first-principles DFT calculations,[35–39] but then only relatively small systems can be handled. A multitude of different structures has been studied, such as dimerized, zigzag, and helical wires.[40–45]

One of the most striking features of monatomic wires is the nonmonotonic behavior of the conductance as a function of the number of atoms in the wire.[46,47] Such a behavior has been predicted by Lang for wires consisting of monovalent atoms.[47] His model assumes a chain of atoms suspended between two planar semi-infinite jellium electrodes. The conductance predicted by this model is much lower than the quantum unit, which disagrees with experiments on monovalent atomic chains.[2,4,6] However, the model can be modified in a simple way by adding a basis consisting of three atoms on top of the jellium electrodes.[48] This reduces the charge transfer between the wire and leads and it reduces spurious reflections at the wire-electrode interfaces. The conductance of a one-atom wire is then close to the quantum unit, in agreement with experiment.

From the Friedel sum rule it can be shown that the conductance of an atomic chain consisting of monovalent atoms exhibits a regular oscillation with respect to the number of atoms in the chain.[49] Moreover, assuming mirror reflection and time-reversal symmetries together with local charge neutrality of the wire, the conductance of wires with an odd number of atoms is expected to be very close to the quantum unit.[50] The period of the conductance oscillation then equals two atoms. This has been confirmed in conductance calculations for wires connected to jellium leads via an atomic basis.[51]

The oscillating behavior of the conductance as a function of the wire length has been observed experimentally in gold wires,[8] and a small parity effect has recently been found in silver wires.[52] Oscillations have also been observed in wires consisting of atoms with a higher valency.[2,53]

Since the discovery of the parity effect in wires of monovalent atoms there has been a discussion on how sensitive the conductance oscillation is to the geometry of the wire and the contacts. The general arguments given in Ref. 49 suggest that the conductance for odd-numbered wires should always be higher than for even-numbered ones, provided that the wires are locally charge neutral. For a sodium wire connected to (artificial) fcc sodium electrodes the charge transfer has been estimated and it is found to be rather small.[54] Conductance calculations based upon a scattering approach have recently been performed for short sodium wires attached to sodium electrodes with a more realistic bcc structure.[17,55] The phase of the conductance oscillation obtained in these calculations, is consistent with that found in the jellium electrode calculations.[49,51]

Other studies predict however that the conductance oscillation found in wires of monovalent atoms is very sensitive to the geometry. Even the phase of the oscillation can be reversed such that even-numbered wires have a larger conductance than odd-numbered ones.[31,56–58] Using the Friedel sum rule to calculate the conductance of a wire connected to jellium electrodes it has been found that the phase of the conductance oscillation is reversed if the jellium leads become sufficiently sharp.[57] This has not been confirmed by later calculations using a scattering approach to calculate the conductance, which give results that are consistent with Lang's findings for planar jellium electrodes.[29,47]

From strictly one-dimensional linear combination of atomic orbitals DFT (LCAO-DFT) calculations, i.e., sodium chains coupled to one-dimensional metallic leads, it has been argued that there is a critical distance between the wire and the leads where the conductance oscillation changes its phase and even-numbered chains become more conductive than odd-numbered ones.[56] A change of phase has also been predicted to occur upon elongating the wire by adding atoms. In short wires the odd-numbered chains then have the higher conductance and in long wires the even-numbered ones have the higher conductance. Similar effects have also been claimed recently for particular atomic configurations in calculations using three-dimensional leads.[31,58]

In conclusion, some of the results that appeared in the literature regarding the even-odd conductance oscillation in monatomic wires seem to be contradictory. In this paper we present the results of conductance calculations for monatomic sodium wires in order to investigate the effect of the wire geometry and the wire-lead coupling on the conductance oscillation. Since sodium has a simple electronic structure, a sodium wire is one of the simplest examples of an atomic wire. As such it is an important reference system for studying wires with a more complicated electronic structure, and it can be used as a system for benchmarking theoretical and computational techniques. We perform first-principles conductance calculations based on the mode-matching technique[17] on sodium wires suspended between sodium electrodes, while systematically varying the atomic configuration of the wire and that of the wire-lead contacts. The entire system consisting of the wire and the semi-infinite electrodes is treated fully atomistically.

We find that the parity effect, i.e., the even-odd conductance oscillation, is very robust with respect to changing the structure of the wire and to varying the strength of the coupling between the wire and the leads. In the conductance of long wires we find no tendency to a phase change in the even-odd oscillation. The conductance is analyzed using the electronic levels of free-standing wires in order to interpret the parity effect in terms of transmission resonances. In addition, we analyze our first-principles results using a simple tight-binding model. In particular, we show that local charge neutrality of the sodium wires provides a strong constraint on the phase of the conductance oscillation for all atomic structures considered. In absence of a significant charge transfer between the wire and the leads, a transmission resonance is pinned at the Fermi energy for wires containing an odd number of atoms, which leads to a conductance close to one quantum unit. Obtaining quantitative values for the conductance, particularly for even-numbered wires, requires well-converged first-principles calculations using a realistic structure of the wire and the leads.

The structure of this paper is as follows. In Sec. II we discuss the geometry of infinite and finite sodium wires. The even-odd oscillation of the conductance is discussed in general terms in Sec. III. We investigate the effects on the conductance of varying the wire geometry and the contacts between wire and leads in Sec. IV. Current-voltage characteristics are analyzed in Sec. V. In Sec. VI we compare our results to those obtained in previous studies. A summary and conclusions are presented in the last section. The important technical detail of **k**-point sampling is discussed in Appendix A.

II. STRUCTURE OF SODIUM WIRES

In this section we investigate possible structures of sodium monatomic wires by DFT total energy calculations in combination with geometry optimizations. DFT total energies are calculated with the PW91 generalized gradient approximation (GGA) functional[59] and the projector augmented wave (PAW) method,[60,61] as implemented in the Vienna *ab initio* Simulation Package (VASP).[62–64] We use a standard frozen core PAW potential and a plane wave basis set with a kinetic energy cutoff of 24 Ry. A Methfessel-Paxton smearing is applied in integrations over the Brillioun zone with a smearing parameter σ=0.1 eV. First we discuss the structure of the infinite wire, and then that of finite wires connected to bcc sodium electrodes.

A. Infinite wires

An orthorhombic supercell is used with cell parameters perpendicular to the wire direction equal to 17 Å. Parallel to the wire the cell parameter is optimized using 24 **k** points to sample the Brillouin zone along the wire direction for a cell containing two atoms.

First we consider a linear wire geometry; the optimized Na-Na bond length is given in Table I. We have checked that

TABLE I. Na-Na nearest neighbor bond length (in a_0) for sodium wires, bulk sodium, and the sodium dimer, compared to all-electron calculations and to experiment. For the zigzag chain also the bond angle is given.

	This work	All electron	Experiment
Linear	6.30		
Zigzag	6.85 (57°)		
Bulk	6.88	6.90 (Ref. 65)	6.91 (Ref. 66)
Dimer	5.88	5.85 (Ref. 67)	5.82 (Ref. 68)

a symmetry breaking in the form of a Peierls distortion is negligible for Na-Na bond lengths near the equilibrium interatomic distance, which agrees with calculations on other monatomic wires.[41,42] Only for sodium wires that are stretched to interatomic distances larger than $6.91a_0$ a Peierls distortion takes place, accompanied by a metal-insulator transition. In order to test the accuracy of the calculations we have also calculated the optimized Na-Na bond length in bulk sodium and in the sodium dimer. The accuracy is found to be better than 1% as compared to the experimental values, see Table I.

One-dimensional chains are often unstable with respect to a deformation in the transverse direction, which results in a zigzag structure. A linear conformation is preferred if the interatomic distance exceeds a critical value.[41] Indeed we find that a sodium wire with a zigzag structure has a lower energy; its geometry is presented in Table I. It is in reasonable agreement with the one obtained in a previous DFT local-density approximation (DFT-LDA) calculation.[69] A bond angle of $\sim 60^{\circ}$ is typically found also in other monatomic wires.[45] Upon stretching the wire a transformation from a zigzag to a linear geometry takes place as soon as the interatomic distance in the linear wire becomes $\gtrsim 6.5a_0$. In Ref. 41 a zigzag structure has been found in gold and copper wires, whereas in potassium and calcium wires it exists only under compression. The stability of the zigzag geometry has, therefore, been related to the presence of directional d bonds in gold and copper. However, our results show that a sodium wire behaves similarly, which suggests that the occurrence of a zigzag geometry is not a result of d bonds only.

Whereas the lowest energy structure is paramagnetic, in Ref. 69 two additional local minima have been found corresponding to ferromagnetic structures with magnetic moments $\sim 0.02\mu_B$ and $0.12\mu_B$, respectively. Our lowest energy (zigzag and linear) structures are always paramagnetic. A magnetic ordering occurs for zigzag structures when the Fermi level crosses two energy bands instead of just one band, but the magnetism disappears rapidly as soon as the wire is stretched sufficiently. Small magnetic moments have also been found in calculations on gold wires.[69] No trace of magnetic effects has been observed in recent conductance measurements performed in magnetic fields.[70] Since both experiment and theory favor nonmagnetic structures, we will only consider nonmagnetic sodium wires in the following.

B. Finite wires

In this section we discuss the structure of a finite monatomic sodium wire suspended between two electrodes. A reasonable approach is to study the structure of the wire near its equilibrium geometry, which corresponds to the most stable chemical bonding. We use the equilibrium geometry of the infinite linear wire as a starting point for finite wires. The electrodes consist of bulk Na in the (001) orientation. To calculate the structure we use a periodic supercell that consists of a slab of five layers of sodium for the electrodes. On top of each electrode surface an apex atom is placed in a hollow site and a linear wire bridges the two apex atoms as shown in Fig. 1. We use a $12\times12\times4$ **k**-point sampling of the supercell. During the geometry optimization the atoms in the wire, the apex atoms, and the atoms in the top surface layer are allowed to relax.

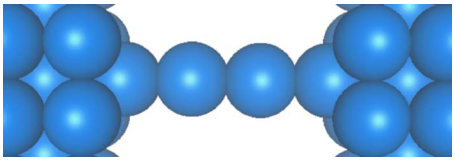

FIG. 1. (Color online) Supercell representing a two atom sodium wire between two sodium leads terminated by (001) surfaces. The wire is connected to electrodes via an apex atom placed on top of each electrode in a hollow site.

The results of the geometry optimization for wires of different lengths are given in Table II. We will discuss the most prominent features of the wire geometries starting from the electrodes. All structures have mirror symmetry with respect to a plane through the center of the wire, parallel to the electrode surface. We emphasize that this symmetry is not forced upon the system, but is the result of the geometry optimization. The top layer of the electrode relaxes slightly outwards; the distance between the top two layers, L1-L2 $\sim 4.03a_0$, is somewhat larger than the bulk value $3.99a_0$. The distance between the apex atom and the surface L1-A decreases with the length of the wire, which indicates a growing bond strength. The distance between the apex atom and the first atom of the wire A-1 is always larger than the maximum bond length between atoms in the wire. This indicates that bonding within the wire is stronger than bonding to the electrodes. For gold wires the opposite has been found, i.e., the A-1 distance is shorter than the average bond length.[37]

Focusing upon the interatomic distances between atoms in the wire, Table II clearly shows that even-numbered wires exhibit dimerization, i.e., an alternation between short and long bonds. A similar tendency is found in odd-numbered chains, but they have a topological defect, i.e., a "kink," in the center of the wire. The average bond length of $\sim 6.40a_0$ in even and in odd-numbered wires is larger than the optimized bond length of $6.30a_0$ in the infinite wire. The infinite chain does not show a dimerization until the average bond length is larger than $\sim 6.91a_0$ (see the previous section). This strongly suggests that dimerization in finite chains is enforced by their boundaries. A qualitatively similar behavior has also been found in finite gold wires.[37]

Since dimerization of a finite wire is associated with its bonding to the electrodes, one needs to check how sensitive the dimerization pattern is to the connection between wire and electrode. We have performed calculations on larger lateral supercells, and have also made the connection more

TABLE II. Optimized bond lengths (in a_0) for a Na wire suspended between Na electrodes. The columns indicate the number of atoms in a wire. The row labels $i-j$ indicate the distance between the i'th and j'th atom in a wire; $\bar{d}$ is the average bond length. A-1 indicates the distance between the apex atom and the wire, L1-A the distance between the apex atom and the surface layer, and L1-L2 the distance between the two top layers of the electrode. The in-plane Na-Na distance in the top layer is given in the bottom row.

Bonds	1	2	3	4	5	6	7	8	9
1-2		6.35	6.45	6.34	6.41	6.34	6.41	6.33	6.37
2-3			6.45	6.46	6.45	6.45	6.43	6.44	6.44
3-4				6.34	6.45	6.36	6.41	6.37	6.40
4-5					6.41	6.45	6.41	6.45	6.42
5-6						6.34	6.43	6.37	6.42
6-7							6.41	6.44	6.40
7-8								6.33	6.44
8-9									6.37
$\bar{d}$		6.35	6.45	6.38	6.43	6.39	6.42	6.39	6.41
A-1	6.53	6.59	6.51	6.54	6.49	6.51	6.47	6.48	6.46
L1-A	3.72	3.64	3.60	3.58	3.52	3.52	3.45	3.43	3.38
L2-L1	4.03	4.03	4.02	4.03	4.02	4.03	4.02	4.06	4.02
In-plane	8.17	8.19	8.20	8.23	8.23	8.25	8.26	8.26	8.31

graduate by putting a base of four atoms between the electrode surface and the apex atom. These structural variations give essentially the same bonding pattern in the wires, i.e., even-numbered wires are dimerized, and odd-numbered wires additionally have a kink in the center. The distance A-1 between apex atom and wire stays larger than the interatomic distances in the wire. These distances can be modified by stretching or compressing the wire, but the dimerization pattern is robust. In conclusion, the optimized wire structures presented in Table II can be considered as typical structures that are formed by sodium finite chains suspended between two semi-infinite electrodes.

III. CONDUCTANCE OSCILLATION

Our calculations of the conductance are based on the mode-matching technique and we use a real-space finite-difference representation of the Kohn-Sham Hamiltonian and the wave functions.[17] As a first step, the one-electron self-consistent potentials of the bulk leads and the scattering region containing the wire are obtained from DFT calculations. Subsequently the scattering problem is solved at the Fermi energy by matching the modes in the leads to the wave function in the scattering region. The conductance G can be expressed in terms of normalized transmission amplitudes $t_{n,n'}$ using the Landauer-Büttiker formula[71]

$$G = G_0 \sum_{n,n'} |t_{n,n'}|^2, \tag{1}$$

where n and n' label the right-going modes in the left and right leads, respectively, and $G_0 = e^2/\pi\hbar$. An efficient implementation of a high-order finite-difference scheme for solving the scattering problem is discussed in Ref. 17.

In more detail, the one-electron potentials of the leads and the scattering regions are extracted from two DFT calculations for bulk bcc sodium and for the supercell shown in Fig. 2, respectively. For these calculations we use a local Troullier-Martins pseudopotential[72] with a core radius $r_c = 2.95a_0$; only the $3s$ electrons of sodium are treated as valence electrons. All plane waves are included up to a kinetic energy cutoff of 16 Ry. We use 32^3 **k** points to sample the Brillouin zone (BZ) of the cubic bcc unit cell of bulk sodium. In our supercell calculations, 8^2 **k** points are used to sample the lateral BZ in case of a 2×2 supercell, and 6^2 **k** points in case of a 3×3 supercell. In all cases a Methfessel-Paxton smearing with $\sigma=0.1$ eV is applied. Total energies are converged to within 5×10^{-7} Hartrees.

One assumes that the leads outside the scattering region are perfectly crystalline bulk material. So at the edges of the scattering region, the potential should join smoothly to the potentials of the bulk leads. We have checked that this is the case. Enlarging the scattering region by including two extra atomic layers in each lead changes the results reported for the conductance only by $\sim1.5\%$ for even-numbered wires

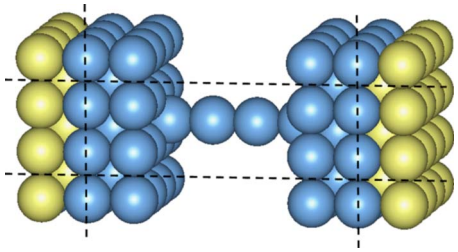

FIG. 2. (Color online) Structure of an atomic wire consisting of two sodium atoms between two sodium leads terminated by (001) surfaces. The boundaries of the supercell are indicated by dashed lines. Bulk atoms are indicated by yellow (light gray) balls and atoms in the scattering region by blue (dark gray) balls, respectively.

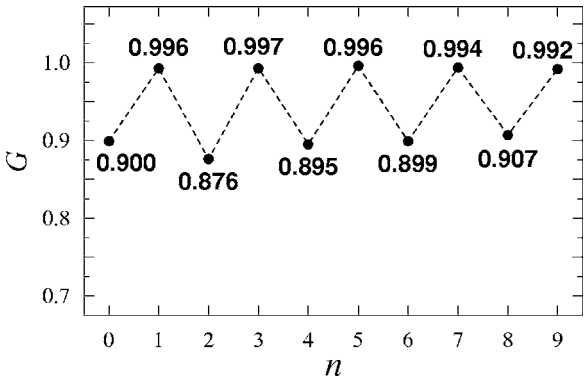

FIG. 3. Conductance (in units of G_0) as a function of the number of atoms in the atomic chain. All atomic bond lengths in the system are equal to the bulk value $d=6.91a_0$.

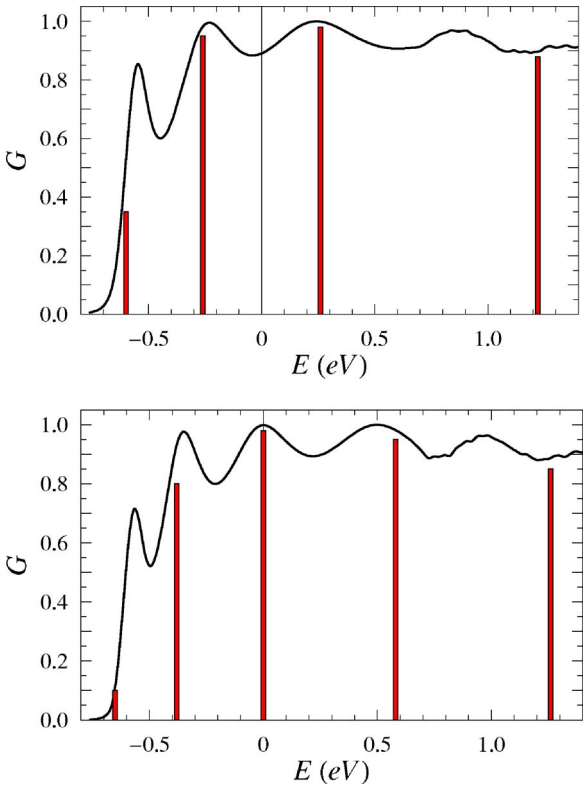

FIG. 4. (Color online) Conductance (in units of G_0) as a function of energy for monatomic wires consisting of four (top figure) and five (bottom figure) atoms. The red (gray) bars correspond to the energy levels of free-standing wires. $E=0$ corresponds to the Fermi level.

and $\lesssim 0.5\%$ for odd-numbered wires. The Fermi energy is extracted from the bulk calculation.[73] The only parameters in calculating the conductance within the mode-matching finite-difference scheme are the order N of the finite-difference approximation of the kinetic energy (i.e., the second derivative) and the spacing $h_{x,y,z}$ between the real-space grid points. We use $N=4$ and $h_{x,y,z}=0.80a_0$; for details and convergence tests we refer to Ref. 17. The total transmission is averaged over the $\mathbf{k}_\parallel$-point grid of the lateral BZ of the supercell. To calculate the transmission it is important to apply a proper $\mathbf{k}_\parallel$-point sampling. This will be discussed in Appendix A. Most calculations are done for a 2×2 lateral supercell. Enlarging the supercell changes the conductance only marginally as will be discussed in Sec. IV B.

The electron transport in the crystalline leads is ballistic, i.e., an electron goes through the leads without any scattering. The transport properties of a monatomic wire suspended between two leads depend upon three factors; the number of atoms in the chain, the geometry of the wire, and the contact between wire and leads. In Sec. IV we will discuss how these factors influence the conductance. In the present section we will analyze the conductance of monatomic sodium wires in a reference geometry, where all Na-Na bond lengths are chosen to be equal to the bulk value $6.91a_0$, see Table I. As in the previous section we attach a finite atomic wire to the leads via two apex atoms, which then have a coordination number 5. All atoms in the wire have a coordination number 2.

A. First-principles calculations

The calculated conductance as a function of the number of atoms in the atomic chain is given in Fig. 3. Since a sodium atom has valence one, both the infinite sodium chain and bulk sodium have a half-filled band, and the infinite wire has one conducting channel at the Fermi level.[74] The conductance of the infinite chain is then equal to the quantum unit G_0, and the conductance of finite wires is $\leqslant G_0$. As can be observed in Fig. 3 the conductance exhibits a regular oscillation as a function of the number of atoms in the wire. The conductance is very close to G_0 for odd-numbered wires, and for even-numbered wires it is $\sim 10\%$ lower. Such a behavior of the conductance in atomic-sized conductors is very different from Ohmic behavior in macroscopic conductors; it expresses the quantum nature of the electron transport at the nanoscale.

In order to interpret the even-odd oscillation we have calculated the conductance as a function of energy for wires of different length. The results for monatomic wires consisting of four and five atoms are shown in Fig. 4. Resonant peaks in the conductance can be clearly identified. Qualitatively they correspond to energy levels of a free-standing Na wire, which are shifted and broadened into resonances by the interaction of the wire with the leads. To illustrate this, the calculated energy levels of free-standing wires of four and five atoms are shown as bars in Fig. 4. The levels are sufficiently close to the resonant energies to warrant an interpretation of the conductance in terms of a transmission through levels of the wire. As is clearly observed in Fig. 4, the Fermi level is in between two resonant peaks for a four atom wire and right on top of a resonance for a five atom wire. By calculating the conductance as a function of energy for wires of different length it can be shown that this observation can be generalized. The Fermi level is between resonances for even-numbered wires and on top of a resonance for odd-numbered wires.

An intuitive picture of the transmission through the energy levels is then presented by Fig. 5. Odd-numbered wires have a highest occupied molecular orbital (HOMO) that is

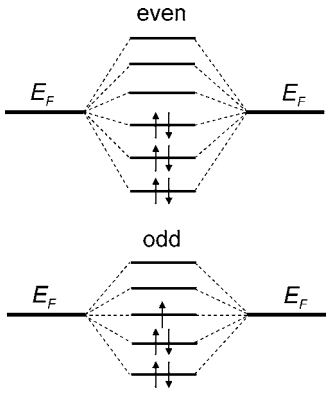

FIG. 5. Energy levels for odd- and even-numbered wires. The Fermi level is in the middle of the HOMO-LUMO gap for even-numbered wires, and it aligns with the HOMO level for odd-numbered wires.

half filled. Perfect transmission through this state takes place if the Fermi level aligns with the HOMO. In even-numbered wires the HOMO is completely filled and separated by a gap from the LUMO (lowest unoccupied molecular orbital) level. The Fermi level is then in the HOMO-LUMO gap. The position of the Fermi level with respect to the HOMO level causes the off and on resonant behavior of the conductance as a function of the wire length, which is causing a regular even-odd oscillation of the conductance. In the next section we will study this intuitive model in somewhat more detail by means of a simple tight-binding model.

B. Tight-binding model

To support the intuitive picture presented in the previous section we use a simple tight-binding model as shown in Fig. 6, in which the leads are modeled as quasi-one-dimensional systems described by effective parameters. Here ε_0, β are the on-site energies and nearest neighbor hopping coefficients of the leads, and ε_0', β' are the corresponding parameters of the wire. The coupling between the left (right) electrode and the atomic chain is given by the hopping coefficient β_c (β_c').

If the system has mirror symmetry, the coupling is symmetric, i.e., $\beta_c=\beta_c'$. The leads and the chain are made of the same material (sodium). If one assumes that all atoms are neutral (local charge neutrality), then it is not unreasonable to set $\varepsilon_0=\varepsilon_0'$. The conductance can be calculated analytically for this model by the mode-matching technique.[32] The modes can be labeled by a wave number k in 1D Brillouin zone of the leads. The familiar relation $E=\varepsilon_0+2\beta\cos(ka)$ gives for a half-filled band the Fermi energy $E_F=\varepsilon_0$ and the Fermi wave

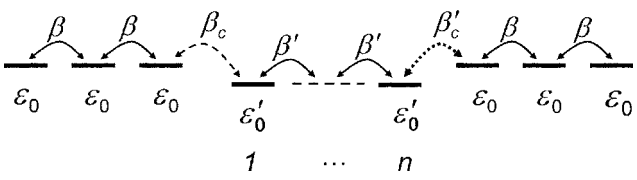

FIG. 6. Tight-binding representation of the n-atomic wire attached to two semi-infinite one-dimensional leads.

number $k_F=\pi/2a$. The parameter β can be used as a scaling parameter. In the following all energy parameters $\varepsilon_0, \varepsilon_0', \beta', \beta_c, \beta_c'$ are in units of β. The conductance of a wire at the Fermi energy consisting of n atoms is given by

$$G = G_0, \quad n \text{ odd}$$

$$= G_0 \frac{4\beta_c^4/\beta'^2}{[1+\beta_c^4/\beta'^2]^2}, \quad n \text{ even}. \tag{2}$$

The conductance for odd-numbered wires is equal to the quantum unit, and it is smaller than the quantum unit for even-numbered wires (unless $\beta_c^2=\beta'$). This corresponds to the situation shown in Fig. 5.

It is instructive to study some other consequences of the tight-binding model. If $\Delta\varepsilon=\varepsilon_0-\varepsilon_0'\neq 0$ then a charge transfer will take place between the leads and the wire. The conductance calculated at the Fermi energy for a one-site wire ($n=1$) and a two-site wire ($n=2$) become, respectively,

$$G = G_0 \frac{4\beta_c^4}{\Delta\varepsilon^2 + 4\beta_c^4}, \tag{3}$$

$$G = G_0 \frac{4\beta_c^4\beta'^2}{[\beta_c^4 + (\beta'+\Delta\varepsilon)^2][\beta_c^4 + (\beta'-\Delta\varepsilon)^2]}. \tag{4}$$

According to Eq. (3) a nonzero $\Delta\varepsilon$ suppresses the transmission through a one-site wire. The transmission is shifted "off resonance" and the conductance becomes smaller than the quantum unit. However, the coupling between wire and lead also causes a broadening of the resonance, which is proportional to β_c. This broadening partially compensates for the decrease of the conductance. If the coupling is sufficiently strong, i.e., $4\beta_c^4 \gg \Delta\varepsilon^2$, then the conductance is again close to the quantum unit. In the limit of weak coupling, i.e., $4\beta_c^4 \ll \Delta\varepsilon^2$, the conductance goes to zero with decreasing β_c for any nonzero $\Delta\varepsilon$. The conductance as a function of β_c is shown in Figs. 7(a) and 7(b) for two different values of $\Delta\varepsilon$.

The conductance of a two-site wire, see Eq. (4), behaves qualitatively different as a function of the coupling strength β_c. In the weak coupling limit, i.e., $\beta_c^4 \ll (\beta' \pm \Delta\varepsilon)^2$, corresponding to $\beta_c<1$ in Fig. 7(a), the conductance goes to zero with decreasing β_c and the decrease is faster than for a one-site wire. Note that this only holds for $\Delta\varepsilon \ll \beta'$. If $\Delta\varepsilon \sim \beta'$ then the conductance decreases more slowly with decreasing β_c for a two-site wire than for a one-site wire, see the range $\beta_c<1$ in Fig. 7(b). If the coupling between wire and lead is strong, i.e., $\beta_c^4 \gg (\beta' \pm \Delta\varepsilon)^2$, corresponding to $\beta_c>1$ in Figs. 7(a) and 7(b), then the conductance always decreases with increasing β_c. This is due to a phenomenon called "pair annihilation" of resonances,[50] which happens if the resonance widths become larger than the spacing between the resonances. In a one-site wire this cannot happen, since there is only one resonance. Between the strong and weak coupling regimes there is a value of β_c (close to 1) where the conductance of a two-site wire is equal to the quantum unit, see Figs. 7(a) and 7(b).

The conductance of longer wires, i.e., $n>2$, can be interpreted along the same lines. For small $\Delta\varepsilon$, the odd-numbered

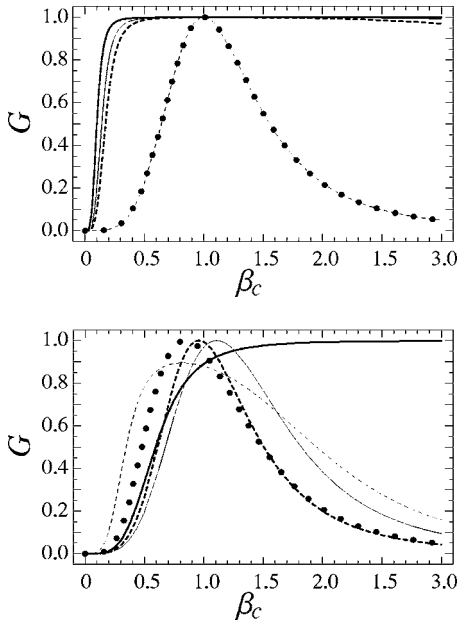

FIG. 7. (a) Conductance (in units of G_0) at the Fermi energy as a function of β_c (in units of β) for wires with $n=1$ (thick solid line), 2 (large dots), 3 (thin solid), 4 (thin dashed), and 5 (thick dashed) atoms; $\Delta\varepsilon=0.02$; $\beta'=1$, (b) As (a) with $\Delta\varepsilon=0.7$; $\beta'=1$.

wires resemble the one-site wire and the even-numbered wires resemble the two-site wire, as shown in Fig. 7(a). For a very large range of coupling strengths β_c one obtains an even-odd oscillation in the conductance of a nearly constant amplitude. The conductance of odd-numbered chains is close to the quantum unit and that of even-numbered chains is smaller by an amount that depends upon the coupling between wire and lead. Apparently, this is the case that corresponds to the results of our first-principles calculations, see Fig. 3.

If $\Delta\varepsilon$ becomes larger, the conductance of all wires as a function of β_c becomes qualitatively similar to that of the two-site wire, see Fig. 7(b) (except the one-site wire, of course). The amplitude and even the phase of the conductance oscillation as a function of the wire length then strongly depends upon the coupling β_c of the wire to the lead. For instance, if $\beta_c \lesssim 0.7$ in Fig. 7(b), the conductance of even-numbered wires is higher than that of odd-numbered wires and all conductances are smaller than the quantum unit. Note that if $\Delta\varepsilon$ is significant, it will be accompanied by a significant charge transfer between wire and leads. Whether this situation occurs can be studied by self-consistent first-principles calculations.

IV. STABILITY OF CONDUCTANCE OSCILLATION

First-principles calculations on a reference geometry give a regular even-odd oscillation of the conductance as a function of the wire length, as discussed in the previous section. The odd-numbered wires have the highest conductance, close to the quantum unit G_0. The simplified tight-binding model suggests that the geometry might influence the amplitude and even the phase of the conductance oscillation. In

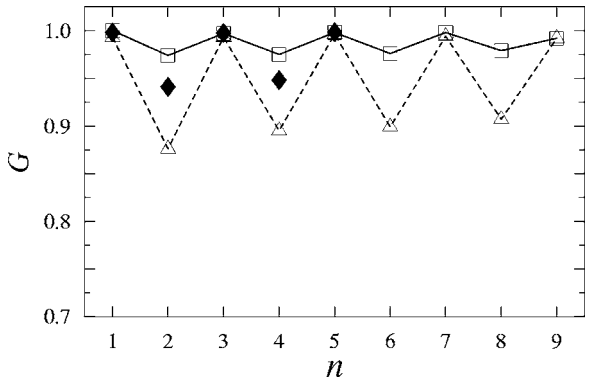

FIG. 8. Conductance (in units of G_0) as a function of the number of atoms in the wire. The triangles correspond to stretched wires with $d=6.91a_0$, squares to compressed wires with $d=5.82a_0$, and diamonds to wires with $d=6.30a_0$.

Sec. II we have shown that monatomic sodium wires can have a linear, zigzag, or dimerized geometry, depending upon the boundary conditions. In this section we study the influence of the wire geometry upon the conductance. In particular, we focus on the question of whether the phase of the even-odd conductance oscillation is robust to modifications of the wire geometry.

A. Tension or compression of linear wires

We consider a uniform tension or compression of the wire. As in the previous section the Na-Na distance between atoms in the wire is kept at a uniform value d and the distance d_c between the apex atom and the wire is equal to d. As reference we use the results shown in Fig. 3 where $d=6.91a_0$, which corresponds to the bond length in bulk sodium. If we take the equilibrium bond length $d=6.30a_0$ of the infinite linear wire as a characteristic bond length, then $d=6.91a_0$ corresponds to a wire under tension, i.e., a stretched wire. A wire with $d=5.82a_0$, which corresponds to the equilibrium bond length of a Na_2 molecule, is a wire under compression.

The results of first-principles calculations of the conductance as a function of the wire length for $d=5.82a_0$, $6.30a_0, 6.91a_0$ are presented in Fig. 8. In all cases the conductance exhibits a regular even-odd oscillation and the conductance of the odd-numbered wires is close to the quantum unit. The conduction of the even-numbered wires is smaller than the quantum unit and it depends only weakly on the number of atoms in the wire. According to the tight-binding analysis in Sec. III B, this suggests that the charge transfer between wire and lead, represented by $\Delta\varepsilon$ in Eqs. (3) and (4), is very small, see Fig. 7(a).

The amplitude of the oscillation decreases with decreasing d. Two opposing effects influence the conductance if we decrease the interatomic spacing d in the wire. Firstly, the spacing between the resonant levels increases. In tight-binding terms the parameter β' increases, which tends to decrease the conductance of even-numbered wires, see Eq. (2). Secondly, since $d_c=d$, the resonances become broader if we decrease the distance between the wire and the lead.

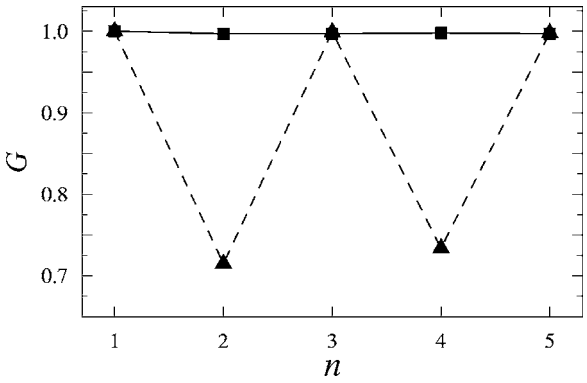

FIG. 9. Conductance (in units of G_0) as a function of the number of atoms in the wire. The triangles correspond to wires with $d=5.82a_0$ and $d_c=6.91a_0$ and the squares to wires with $d=6.91a_0$ and $d_c=5.82a_0$.

Again in tight-binding terms the parameter β_c increases, which tends to increase the conductance of even-numbered wires, cf. Eq. (2).[75] According to Fig. 8 the effect of the resonance broadening upon the conductance is larger than the effect of increased resonance spacing.

One can strengthen this analysis by varying the interatomic distance d in the wire, and the distance d_c between the apex atom and the wire independently. Figure 9 shows the calculated conductance for a wire with $d<d_c$, i.e., $d=5.82a_0$ and $d_c=6.91a_0$. The conductance oscillations are quite large, which can be attributed to the increased resonance spacing discussed in the previous paragraph. A small d results in a large spacing between the resonant levels of the wire. Therefore, the transmission of even-numbered wires, which is off resonance at the Fermi level, is low, whereas the transmission of odd-numbered wires stays on resonance and is high.

If we calculate the conductance for a wire with $d>d_c$, i.e., $d=6.91a_0$ and $d_c=5.82a_0$, we see in Fig. 9 that the conductance oscillation is strongly suppressed. It can be attributed to the resonance broadening. If the coupling between the wire and the lead is strong, the resonances of the wire are wide. The transmission in even-numbered wires is then relatively high, whereas the transmission in odd-numbered wires stays close to the quantum unit. Figure 9 shows that in the case of a strong coupling between wire and lead the amplitude of the even-odd oscillation in the conductance can become very small. According to the tight-binding model, Eq. (2), this happens if $\beta_c^4/\beta'^2 \approx 1$. Note that such a strong coupling is less likely for sodium monatomic wires with optimized geometries, because the results discussed in Sec. II indicate that $d<d_c$. According to Ref. 37 $d>d_c$ in gold monatomic chains, which might explain the small amplitude of the conductance oscillation found experimentally in gold wires.[8]

In conclusion, stretching or compressing the wire changes the amplitude of the conductance oscillation, but it preserves its phase and the value of the conductance for odd-numbered wires, which is close to unity.

B. Contact geometry

The coupling between the wire and the leads could be influenced by the detailed geometry of the two contacts between the wire and the leads.[49] Since the geometries of the wire-lead contacts are not known from experiment, it makes sense to study the sensitivity of the calculated conductances to these geometries. So far in our calculations we have modeled both contacts by one apex atom placed in a hollow site on the (001) surface in a 2×2 lateral supercell. A more "gradual" contact is formed by a five atom pyramid placed on (001) surface, as is shown in Fig. 10. This requires using (at least) a 3×3 supercell. To check that the size of the supercell does not influence the results, we have also done calculations for a 3×3 supercell with one apex atom contacts. The calculated conductances are shown in Fig. 11. The conductance of monatomic sodium wires seems to be relatively insensitive to the contact geometry. At the same time it shows that the results obtained with the 2×2 supercell are converged.

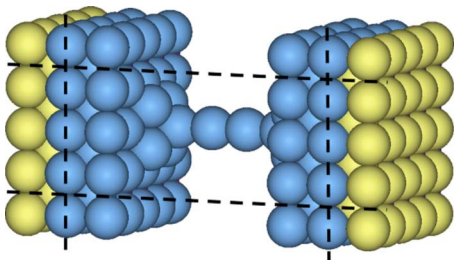

FIG. 10. (Color online) Structure of an atomic wire consisting of two sodium atoms between two sodium leads terminated by (001) surfaces. The atomic wire is connected to each surface via a five atom pyramid. The boundaries of the 3×3 supercell are indicated by dashed lines. Bulk atoms are indicated by yellow (light gray) balls and atoms in the scattering region by blue (dark gray) balls, respectively.

Another way of modifying the contacts is to remove the apex atoms and position the first and the last atom of the wire on top of an atom in the (001) surface layer. The calculated conductances are shown in Figs. 12(a) and 12(b) for the interatomic distances $d=d_c=6.91a_0$ and $d=d_c=5.82a_0$, respectively. The results obtained with these "direct" wire-surface contacts look very similar to the ones obtained with

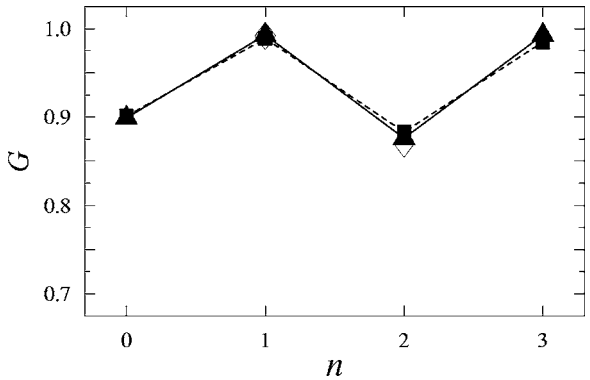

FIG. 11. Conductance (in units of G_0) as a function of the number of atoms in the atomic wire. Squares refer to the 3×3 supercell with five atom pyramid contacts, diamonds to the 3×3 supercell with one apex atom contacts, and triangles to the 2×2 supercell with one apex atom contacts.

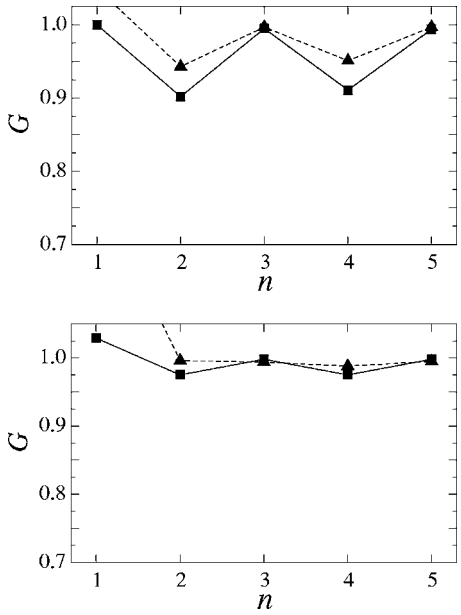

FIG. 12. (a) Conductance (in units of G_0) as a function of the number of atoms in the atomic wire with interatomic distance $d=d_c=6.91a_0$. The triangles (dashed line) correspond to "direct" contacts between wire and leads. The squares (solid line) correspond to a direct contact at one end of the wire and a one apex atom contact at the other end. (b) As (a) with $d=d_c=5.82a_0$.

one apex atom contacts, see Fig. 8. The amplitude of the even-odd oscillation is somewhat smaller for the direct coupling. According to the analysis presented in Sec. IV A this indicates a stronger coupling between wire and leads, or in tight-binding terms, a larger β_c, cf. Eq. (2). Note that the conductance of one-atom wires in Figs. 12(a) and 12(b) is higher than G_0 due to direct tunneling between the electrodes.

One can also break the symmetry and use a direct contact between the wire and one of the leads, and a one apex atom contact between the wire and the other lead. The calculated conductances are given in Figs. 12(a) and 12(b). A comparison with symmetric direct contacts and symmetric one apex atom contacts, see Fig. 8, shows that the phase of the even-odd conductance oscillation is the same and the amplitude is in between that of the two symmetric cases. It means that, besides the already mentioned stronger coupling between wire and lead for the direct contact, this symmetry breaking has little effect on the conductance.

We conclude that varying the geometries of the contacts between wire and leads does not have a large effect on the regular even-odd oscillation of the conductance.

C. Wire geometry: zigzag wires and dimerization

In Sec. II we studied the geometry of infinite zigzag chains. In principle, a structural zigzag deformation could modify the conductance of a finite monatomic wire.[49,76] Figure 13 shows the calculated conductance of a wire with one apex atom contacts and bond lengths $d=d_c=6.91a_0$ to which a zigzag distortion pattern is applied with an amplitude corresponding to 15% of the bond length. Compared to straight

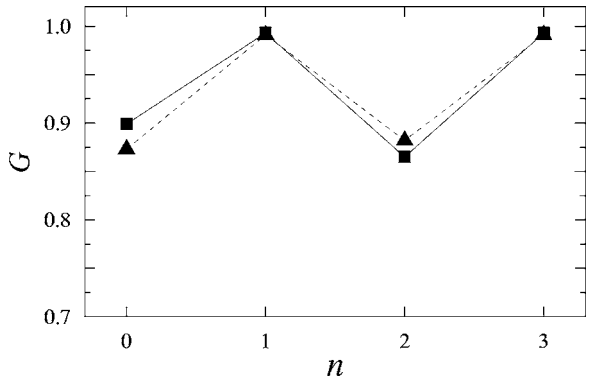

FIG. 13. Conductance (in units of G_0) as a function of the number of atoms in the atomic wire. Dashed line and filled rectangles correspond to zigzag wires; straight line and filled squares to linear wires with $d=6.91\ a_0$.

wires, the conductance of zigzag even-numbered wires changes by $\lesssim 3\%$, whereas the conductance of odd-numbered wires is hardly affected at all. Such small effects are in line with results reported previously.[49,76]

According to the results obtained in Sec. II finite straight wires with equidistant atoms can spontaneously break their symmetry by dimerization. The conductance of optimized broken symmetry structures is discussed in the next section. Here we study the influence of an excessive symmetry breaking. We apply a regular dimerization pattern to the wire, which consists of an alternation between long and short bonds with bond lengths $d=6.91a_0$ and $d=5.82a_0$, respectively. Continuing this pattern into the contacts this means that even-numbered wires have short $d_c=5.82a_0$ contacts to both leads, whereas odd-numbered wires have one short $d_c=5.82a_0$ contact and one long $d_c=6.91a_0$ contact. The results are shown in Fig. 14.

This curve can be analyzed using the tight-binding model introduced in Sec. III B. Assuming charge neutrality, i.e., $\Delta\varepsilon=0$, we need to generalize Eq. (2) to the case where the coupling β_c to the left and β_c' to the right leads are different. In addition, dimerization in the wire leads to an alternation of

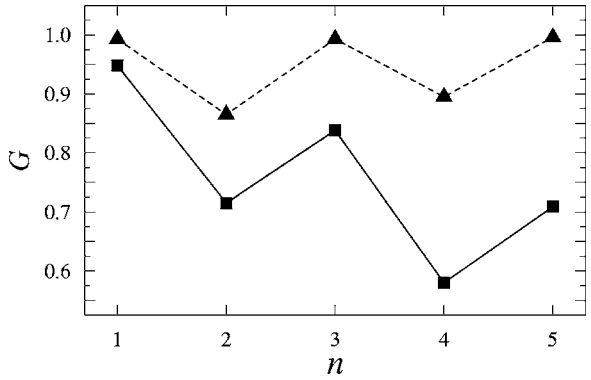

FIG. 14. Conductance (in units of G_0) as a function of the number of atoms in the atomic wire. The squares correspond to dimerized wires with alternating bond lengths of $6.91a_0$ and $5.82a_0$; as a reference, the triangles correspond to wires with a uniform bond length $6.91a_0$.

two hopping coefficients β' and β''. The conductance of an n-atomic wire is then given by

$$G = G_0 \frac{4\left(\frac{\beta_c}{\beta_c'}\right)^2 \left(\frac{\beta''}{\beta'}\right)^{n-1}}{\left[1 + \left(\frac{\beta_c}{\beta_c'}\right)^2 \left(\frac{\beta''}{\beta'}\right)^{n-1}\right]^2}, \quad n \text{ odd}$$

$$= G_0 \frac{4\left(\frac{\beta_c \beta_c'}{\beta'}\right)^2 \left(\frac{\beta''}{\beta'}\right)^{n-2}}{\left[1 + \left(\frac{\beta_c \beta_c'}{\beta'}\right)^2 \left(\frac{\beta''}{\beta'}\right)^{n-2}\right]^2}, \quad n \text{ even}. \tag{5}$$

One notices from Eq. (5) that even the shortest odd-numbered wire, $n=1$ has a conductance smaller than the quantum unit if $\beta_c \neq \beta_c'$. This is observed in our first-principles results, where the conductance of the $n=1$ wire is $0.95G_0$, see Fig. 14. Furthermore, Eq. (5) shows that the conductance of both even-numbered and odd-numbered wires decreases as a function of increasing n if $\beta' \neq \beta''$. Also this is clearly observed in our first-principles calculations. Dimerization of an infinite wire creates a gap in the density of states, so, in general, one expects that the conductance drops as a function of the wire length. A decreasing conductance for longer wires has been observed experientially for platinum, but its nature has not been clarified yet.[8]

Finally, although the conductance for even- and odd-numbered wires decreases as a function of wire length, its even-odd oscillation is preserved. Assuming $\beta''/\beta' = \beta_c/\beta_c' = x$ for odd-numbered wires and $\beta''/\beta' = \beta_c/\beta = \beta_c'/\beta' = y$ for even-numbered wires the tight-binding model, Eq. (5), can be fitted to the first-principles results. This yields the parameter ratio's $x \approx 0.81$ and $y \approx 0.76$ for the odd- and even-numbered dimerized wires presented in Fig. 14.

D. Optimized geometry

In previous sections we studied the influence of the structure of a monatomic wire upon its conductance by varying interatomic distances corresponding to values ranging from the Na dimer $5.82a_0$ to the Na bulk $6.91a_0$ values. In this section we discuss the conductance for wires with optimized geometries, which were obtained in Sec. II. Figure 15 shows the results from the first-principles calculations. As a reference, it also shows the results for wires with equidistant atoms corresponding to the geometry of an infinite wire.

It can be observed that the amplitude of the conductance oscillation for wires with optimized geometry is larger than for the reference wires. This results from a slight decoupling of the wire from electrodes, since for the optimized wires $d_c > \bar{d}$, see Table II and the discussion in Sec. IV B. As can be seen from Fig. 15, the phase of the even-odd conductance oscillation is also observed for optimized geometries. Moreover, despite the presence of a topological defect in the center of the odd-numbered wires, the conductance of odd-numbered wires is close to the quantum unit. This is actually predicted by the tight-binding model for any odd-numbered wire whose geometry has mirror symmetry with respect to a plane through the center and perpendicular to the wire, provided $\Delta\varepsilon = 0$.

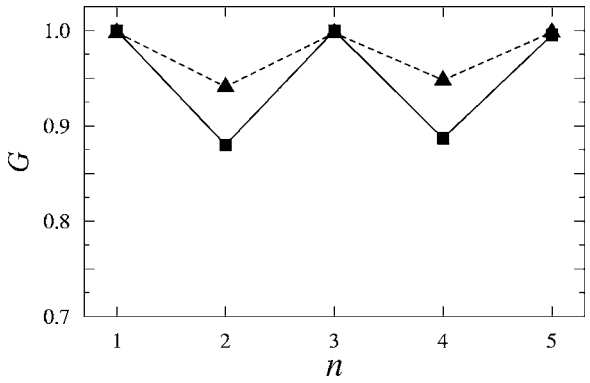

FIG. 15. Conductance (in units of G_0) as a function of the number of atoms in the atomic wire. The triangles correspond to linear wires with $d=6.30a_0$ and the squares to wires with optimized geometry.

One might expect the conductance for even-numbered wires to decrease with the length of the wire, due to the effect of dimerization as discussed in the previous section. This does not show in Fig. 15, because the dimerization in the optimized geometry is much weaker. Therefore, the effect will show up only in wires that are much longer.

V. BEYOND LINEAR RESPONSE

In the linear response regime the current and therefore the conductance are fully determined by the electrons at the Fermi energy. If a finite bias V is applied then the current is given by

$$I = G_0 \int_{E_F - V/2}^{E_F + V/2} T(E,V) dE, \tag{6}$$

where the transmission coefficient $T(E,V)$ depends on the energy of the electron E and the voltage V. The differential conductance is defined as $G(V) = dI/dV$.

In this section we discuss some of the consequences of a finite bias. We make the approximation $T(E,V) \approx T(E)$, which is valid for a relatively small voltage in the limit that the electronic structure of the wire is not changed by the voltage. Examples of transmissions as a function of energy are given in Fig. 4 for atomic wires with the "reference" geometry $d = d_c = 6.91a_0$. The corresponding I-V curves, calculated from Eq. (6), are given in Fig. 16. From the I-V curves we calculate the differential conductance and the second derivative of the conductance, which are also presented in Fig. 16.

The conductance varies by less than 5% for biases up to $\sim \pm 0.2$ V, which one might call the linear response regime. The conductance decreases monotonically for odd-numbered wires and it increases monotonically for even-numbered wires for biases up to ~ 0.5 V. The oscillating behavior of the conductance at higher biases results from the resonant peaks in the transmission. At biases larger than ~ 0.5 V the non-self-consistent procedure probably becomes increasingly inaccurate.[51]

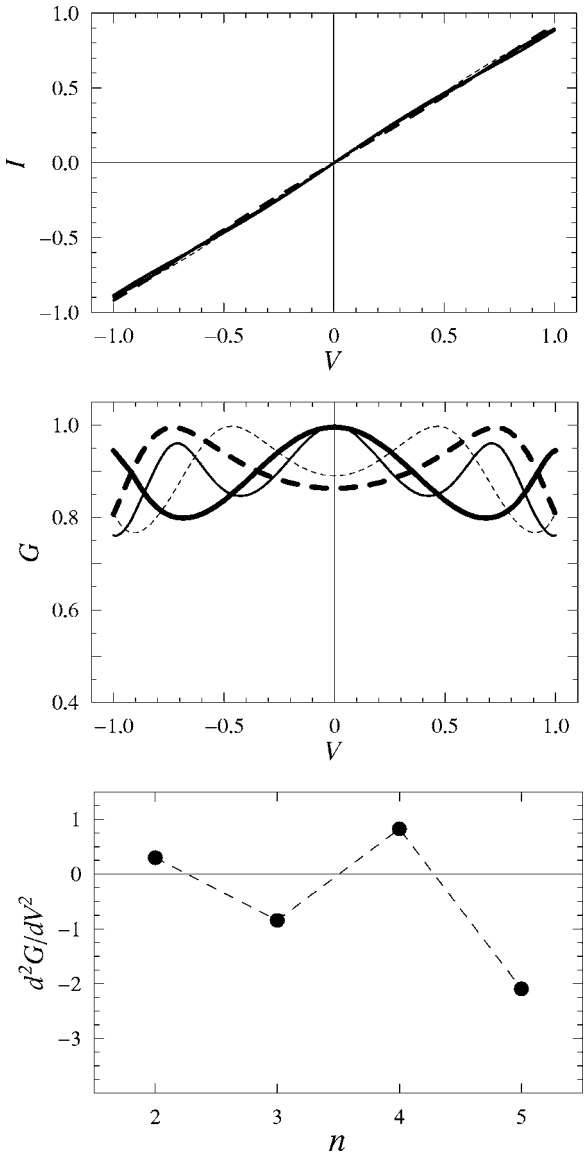

FIG. 16. Current-voltage characteristics for two (thick dashed line), three (thick line), four (thin dashed line), and five (thin line) atomic wires with $d=d_c=6.91a_0$. The top, middle, and bottom figures contain I-V curves, the differential conductance $G(V)=dI/dV$ as a function of V, and the second derivative of the conductance $d^2G(0)/d^2V$ as a function of the number of atoms, respectively.

An important characteristic of the conductance curve that can be measured experimentally is its second derivative at the Fermi energy. If the transmission near the Fermi energy $E_F=0$ is approximated by a polynomial function $T(E)=T(0)+T(0)''E^2$, then the differential conductance is $G(V)=G_0[T(0)+T(0)''V^2/4]$. In Sec. III we interpreted the even-odd conductance oscillation of the conductance in terms of switching between off- and on-resonance behavior. If this is true then the second derivative of the conductance $d^2G/d^2V=T(0)''/2$ must be positive for even-numbered wires and negative for odd-numbered wires at the Fermi energy, as shown in Fig. 16. At the same time the first derivative is zero.

VI. DISCUSSION

In this section we compare our results to those obtained in previous studies. The oscillating behavior of the conductance of monatomic sodium wires was first suggested from calculations using planar jellium electrodes.[47] The conductance of both even- and odd-numbered wires is then significantly lower than the quantum unit and the conductance of even-numbered wires is larger than that of odd-numbered ones. Both of these features are likely to be artifacts of using jellium electrodes, since adding atomic bases between wire and jellium leads reverses the phase of the conductance oscillation and makes the conductance of odd-numbered wires approach the quantum unit.[48,51] Calculations using tip-shaped jellium electrodes predict that the phase of the conductance oscillation critically depends upon the sharpness of the tips,[57] although this effect is disputed in recent calculations.[29]

Using atomistic electrodes with a bulk structure our calculations show that the conductance has a regular even-odd oscillation, in which the conductance of the odd-numbered wires in optimized structures is close to the quantum unit and that of even-numbered wires is approximately 10% lower. Only the latter is modified substantially if the geometry of the wire or the contacts between wire and electrodes are changed within reasonable bounds. Apparently jellium electrodes cause reflections of electrons trying to enter the wire, which results in the artifacts discussed above. The amplitude of the conductance oscillation we find, is smaller by ~67% than that obtained using jellium electrodes plus atomic bases. This would indicate that atomic bases do not completely remove the reflections caused by the jellium electrodes.

Calculations based upon one-dimensional metal electrodes predict that it is possible to change the phase of the conductance oscillation by varying the coupling between the wire and the electrodes.[56] We did not observe such an effect for three-dimensional atomistic electrodes. In a recent calculation it is found that the conductance of odd-numbered wires decreases sharply with increasing wire length, and even the phase of the conductance oscillation can be reversed in long wires.[31] This is not confirmed by our calculations, where the conductance of odd-numbered wires stays close to the quantum unit and the phase of the oscillation is stable. Experiments on the even-odd conductance oscillation in monovalent gold wires do not reveal a decrease of the conductance in odd-numbered wires, and the conductance stays close to the quantum unit.[8]

Other studies seem to indicate that the phase of the even-odd conductance oscillation does not depend very sensitively upon the structure of the electrodes, since the same phase is observed in calculations using bcc electrodes oriented in the (111) direction,[49] and in calculations using electrodes with an artificial fcc structure.[54] The amplitude of the oscillation is much more sensitive, however. A previous study on sodium wires suspended between sodium electrodes gives an amplitude of only 1%, which is an order of magnitude smaller than what we find using similar geometries.[55] Although we do not know what the cause of this difference is, we observe that the amplitude of the even-odd conductance oscillation is sensitive to the one-electron potential used in solving the scattering problem. This potential is obtained from a self-consistent

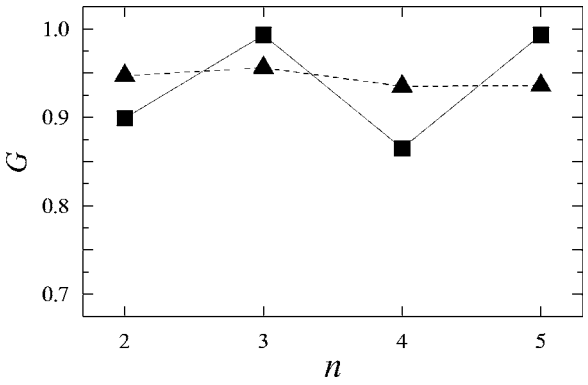

FIG. 17. Conductance (in units of G_0) as a function of the number of atoms in the atomic wire. Triangles and squares correspond to using a potential obtained from a total energy calculation with energy convergence criterion set to $\Delta E=2\times10^{-5}$ and 5×10^{-7} Hartrees, respectively.

electronic structure calculation. Such calculations frequently use a convergence criterion applied to the total energy. However, since a variational principle does not apply to the one-electron potential, the convergence criterion should be much stricter in order to converge the potential.

As an illustration, Fig. 17 shows the conductance of sodium wires calculated from a potential obtained with the usual energy convergence criterion, compared to one obtained with a stricter energy convergence criterion. We have checked that the result does not change anymore if the convergence criterion is even made stricter. This figure clearly shows that changes in the potential that are caused by small charge transfers can markedly influence the amplitude of the even-odd conductance oscillation.

VII. SUMMARY AND CONCLUSIONS

We have performed first-principles calculations to study the stability of even-odd conductance oscillations in a sodium monatomic wire with respect to structural variations. An infinite sodium wire can be linear and consists of equidistant atoms or dimers of atoms, or it can have a zigzag structure, depending upon the tension or compression applied to the wire. The geometry of finite sodium wires, suspended between two sodium electrodes, is influenced by boundary effects. Wires comprising an even or odd number of atoms are dimerized, but odd-numbered wires have a topological defect in the center.

In the linear response regime the conductance is determined by the electrons at the Fermi energy. The conductance of sodium wires shows a distinct even-odd oscillation. The odd-numbered wires have a conductance close to the quantum unit $G_0=e^2/\pi\hbar$ and even-numbered wires have a lower conductance. This oscillation is remarkably robust, as we show by systematically varying the structure of the wires and the geometry of the contacts between the wires and the electrodes. The phase of the oscillation is not affected by these structural variations, i.e., odd-numbered wires have a higher conductance than even-numbered ones. Moreover, odd-numbered wires have a conductance close to the quantum unit, unless the structural deformation of the wire becomes very large and the contact to the left lead is markedly different from that to the right lead. The conductance of even-numbered wires is much more sensitive to the wire geometry. Increasing the interatomic distances in the wire and/or strengthening the contacts between wire and leads increases the conductance of even-numbered wires; increasing the asymmetry between the interatomic distances or between left and right contacts decreases the conductance.

These results can be interpreted on the basis of resonant transmission. For odd-numbered wires the Fermi energy coincides with a resonance in the transmission, whereas for even-numbered wires the Fermi energy is between two resonances. Changing the geometry of the wire or the contacts affects the spacing between the resonances and their widths and therefore it affects the conductance of even-numbered wires; decreasing the spacing and/or increasing the widths increases the conductance.[75] Since for odd-numbered wires the Fermi level is pinned at a resonance, their conductance is affected much less by changing the wire geometry.

We have formulated a simple tight-binding model to analyze these results. It shows that the even-odd conductance oscillation is stable with respect to structural variations, unless the on-site energies for atoms in the wire are substantially different from the on-site energies of atoms in the leads. Note that a large difference in on-site energies is necessarily accompanied by a significant charge transfer between the wire and the leads. The results of the first-principles calculations demonstrate that this is not the case. For wires with equidistant atoms that have mirror symmetry with respect to a plane perpendicular to the wire, Eq. (2) shows that if all on-site energies are identical, the conductance of odd-numbered wires is one quantum unit, whereas that of even-numbered wires is determined by the ratio of the wire-lead coupling and the atom-atom coupling within the wire. Breaking the mirror symmetry, Eq. (5) shows that the conductance of odd-numbered wires becomes smaller than one unit. The symmetry breaking has to be large, however, in order to have a sizable effect on the conductance.

We have also calculated the current-voltage characteristics of sodium wires in the low bias regime. The differential conductance clearly shows a nonmonotonic behavior. In particular, the second derivative of the conductance has an alternating sign as a function of the number of atoms in the wire; even-numbered wires have a positive second derivative and odd-numbered wires a negative one. This effect can be ascribed to the resonant nature of the transmission. It could be used to establish the resonant behavior of the even-odd conductance oscillation experimentally.

Comparison to other work shows that simple jellium electrodes do not reproduce the even-odd conductance oscillation correctly. Using atomic bases yields the correct phase of the oscillation. The conductance of odd-numbered wires is rather stable with respect to varying the atomic structure, but that of even-numbered wires is sensitive to structural details and the quality of the one-electron potential.

ACKNOWLEDGMENTS

This work was financially supported by the "Nederlandse

Organisatie voor Wetenschappelijk Onderzoek (NWO)" via the research programs of "Chemische Wetenschappen (CW)" and the "Stichting voor Fundamenteel Onderzoek der Materie (FOM)," and by "NanoNed," a nanotechnology programme of the Dutch Ministry of Economic Affairs. Part of the calculations were performed with a grant of computer time from the "Stichting Nationale Computerfaciliteiten (NCF)."

APPENDIX A: $\mathbf{k}_\parallel$-POINT SAMPLING

In this Appendix we discuss the effect of $\mathbf{k}_\parallel$-point sampling on the conductance. In modeling a conductor between two semi-infinite electrodes one usually assumes a supercell geometry in the lateral direction. The scattering region then consists of a periodic array of parallel wires, and the lateral supercell must be chosen large enough to prevent an interaction between these wires. To limit the computational demands the supercell is chosen as small as possible, without a significant loss of accuracy. According to the results obtained in Sec. IV B, using a 2×2 supercell is already sufficient for the Na system discussed here. We average the conductance over the 2D Brillouin zone (BZ)

$$G = \frac{1}{N_\parallel}\sum_{\mathbf{k}_\parallel} G_{\mathbf{k}_\parallel}, \tag{A1}$$

where $N_\parallel$ is the number of $\mathbf{k}_\parallel$ points used for the BZ sampling. Calculating the conductance for an infinitely large supercell would include contributions from off-diagonal transmission amplitudes between different $\mathbf{k}_\parallel$. From our results we conclude that their contribution is small as compared to the contribution of the diagonal terms $G_{\mathbf{k}_\parallel}$ already for a 2×2 supercell.

The calculated conductance $G_{\mathbf{k}_\parallel}$ as a function of $\mathbf{k}_\parallel$ for four and five atomic wires is shown in Fig. 18. The dispersion of the conductance is relatively small around the Fermi energy, which means that using a coarse $\mathbf{k}_\parallel$ grid to calculate the conductance in the linear response regime is reasonable. The results discussed in sections have been obtained using a 6×6 grid in the BZ (6 $\mathbf{k}_\parallel$ points in the irreducible BZ). Figure 18 shows that even sampling the BZ with a single $\mathbf{k}_\parallel$ point can give a reasonable result. This can be accidental, however, since the figure also demonstrates that the dispersion is quite large both for energies lower and for energies higher than the Fermi energy. Especially for higher energies a single $\mathbf{k}_\parallel$ point is clearly insufficient for calculating the conductance. This regime becomes important if current-voltage characteristics are calculated, because such calculations require an integration over a wide energy range. The large dispersion at higher energies is related to an increased number of van Hove singularities in the leads. This suggests that $\mathbf{k}_\parallel$-point sampling can be important for leads containing atoms with a valency higher than 1, because the number of van Hove singularities is then usually also higher due to a more complicated band structure.[77]

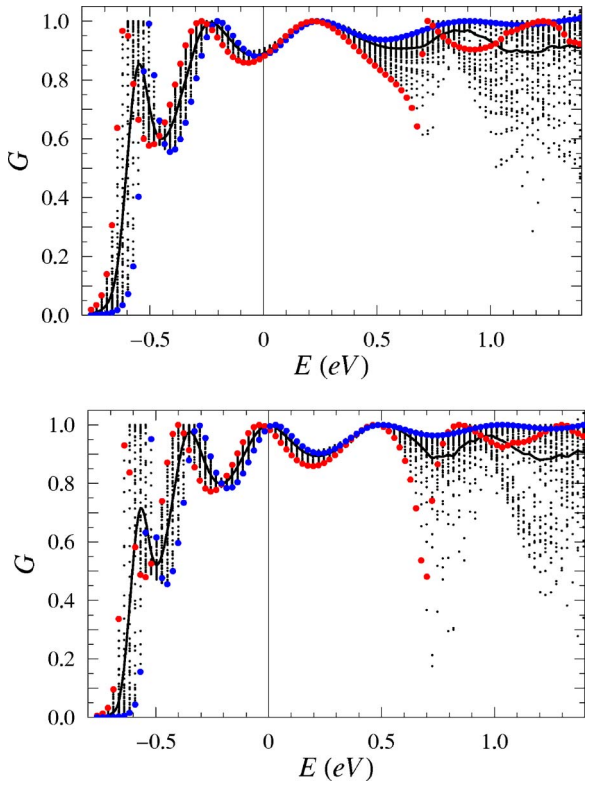

FIG. 18. (Color online) Conductance (in units of G_0) as a function of energy for four (top) and five (bottom) atomic wires. The dots correspond to the conductance for various $\mathbf{k}_\parallel$ points of a 20×20 grid in the BZ ($55\mathbf{k}_\parallel$ points in the irreducible BZ). The thick line is the averaged conductance. The red (light gray) and blue (dark gray) dots correspond to $\mathbf{k}_\parallel=(0,0)$ and (0.5,0.5), respectively.

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[73] We follow the procedure outlined in Ref. 17. to define the Fermi energy for the conductance calculations. In connecting the leads to the scattering region the average potential of the bulk leads is aligned to the average potential in the middle of the supercell slab. The Fermi energies of bulk sodium and of the supercell are measured relative to their respective average potentials. If the slab is sufficiently thick, this procedure ensures an alignment of the Fermi energies of the bulk leads and of the scattering region.

In our calculations we have found a numerical difference between the bulk and supercell Fermi energies in the range 1–15 meV. We have verified explicitly that the conductance is not sensitive to a shift of ~20 meV of the Fermi energy, see, e.g., Fig. 18.

[74] The Fermi level can cross two energy bands for a strongly deformed chain with a zigzag structure. In this case the chain has two conducting channels.

[75] This conclusion is based on an additional assumption that resonances around the Fermi level are not annihilated by a strong coupling between the wire and the leads. Otherwise, the conductance for even-numbered wires decreases if we increase the coupling parameter β_c by decreasing the distance between the wire and the lead.

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