Effects of structural relaxation on resistance of Na atomic chains

Chunping Hu,* Shinnosuke Furuya, Yoshihiro Gohda, and Satoshi Watanabe
Department of Materials Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan and
CREST, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan
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The resistance of Na atomic chains between two metallic electrodes is studied using an ab initio method within the density functional theory and including the effects of structural relaxation. We have found that the oscillatory behavior of the resistance of Na atomic chains with respect to the number of Na atoms, predicted previously by other groups, becomes much reduced after structural relaxation: Resistances of all the 2-, 3- and 4-atom Na chains become close to the inverse of the conductance unit (12.9 kΩ). Our results suggest that the even-odd parity of conductance may be much weaker than as was expected. [DOI: 10.1380/ejssnt.2003.120]

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I. INTRODUCTION

The even-odd oscillation behavior of conductance of atomic chains is a long-standing controversial topic and attracts much interest from both experimental and theoretical scientists. According to an early calculation on alkali metal atomic chains (Li or Na) by Yamaguchi et al. [1], this even-odd behavior is very robust and should be observable at room temperatures, but all experiments except one [2] didn’t observe such a phenomenon. Another leading theoretical analysis by Lang [3] also reveals the even-odd oscillation of the conductance of Na chains, together with much less conductance of the 1-atom Na chain compared with those of the 2-, 3- and 4-atom Na chains. Successive studies by various groups [4–6] confirmed even-odd parity oscillations in Na atomic chains, but discrepancy is seen among them. Most of them reported that the conductance of an atomic chain oscillates between a perfect quantized conductance unit \( G_0 \) for odd number of atoms in the chain and a conductance smaller than \( G_0 \) for even number of atoms, while two groups reported the opposite behavior [3, 5]. This discrepancy is explained by Havu et al. as due to different geometrical shape of the electrode [5]. Experimentally, Smit et al. [2] observed an oscillatory evolution of conductance for atomic chains of Au, Pt and Ir, and suggested that the even-odd parity is a universal feature of atomic chains. However, the reason why such even-odd oscillations in conductance were not observed in previous experiments [7] (the conductance of Au chains is found to be independent of length) has not been clarified. Moreover, a recent ab initio calculation [8] reported that the conductance of Al atomic chains would oscillate in a period of four atoms, instead of two. It is noted that in most theoretical calculations for Na atomic chains, the effect of structural relaxation is not taken into consideration, whereas such effect is truly existent in atomic chains due to the reduced dimensionality and neighborhood of atomic chains compared with bulk solid, and also due to the existence of currents under applied bias voltages or electric fields [9–11]. Therefore it may be important in clarifying the true physical origin of properties of atomic chains to take account of structural relaxation.

In this Letter, we report the theoretical analysis of the structural relaxation effects on resistance of Na atomic chains. Starting from the geometries adopted by Lang [3], we found an oscillatory behavior in resistance at initial geometries, but the oscillation is much reduced after structural relaxation and close to the ideal value of \( \pi \hbar/e^2 \) (12.9 kΩ). Our results suggest that the even-odd parity feature may be vanished at some stable geometries. This can explain why the even-odd oscillation was not observed in most experiments.

II. METHOD AND MODEL

In the present analysis, we perform ab initio force calculation based on the boundary-matching scattering-state density functional method [12, 13]. Exchange and correlation effects are included within the local density approximation (LDA). Prior to the force calculation, the electronic density, together with the effective potential, is calculated according to the Hellmann-Feynman theorem [14]. This is a standard method, and similar to those used in Refs. [10] and [15]. It is noted that the Pulay force [16] which should be included in the calculations using localized basis sets is not necessary in our method, because wave functions are expanded by plane waves in the directions parallel to the electrode surfaces and calculated in real space for the vertical direction. The force acting on the atom is regarded as zero when it is less than 0.002 Ry/bohr.

The model of atomic chains are the same as those adopted by Lang [3]; atomic chains of one to four atoms connecting two semi-infinite metallic electrodes which have a Wigner-Seitz radius \( r_s \) of 2 bohr. The Na atomic cores are represented using a local empty-core pseudopotential proposed by Ashcroft [17], which has been widely used in studying properties of bulk Na crystal [18], liquid Na [19], Na cluster [20], etc. In our model, the periodic boundary condition is imposed in the directions parallel to the electrode surface, and the size of the surface supercell is \( 12 \times 12 \) (bohr)\(^2\). As the starting geometry, the

*Corresponding author: hu@cello.t.u-tokyo.ac.jp
III. RESULTS AND DISCUSSION

The calculated stable structures of Na chains of one to four atoms under a low bias voltage of 0.01 V are shown by Fig. 1. Here, we choose the value of 0.01 V because the same value is used in the experiment of conductance measurement of the Au atomic chains [21]. As can be seen in Fig. 1, all stable structures of the 2-, 3- and 4-atom chains are linear and symmetric. The linear geometry is confirmed to be stable against displacements of atoms in the direction perpendicular to the chain. The symmetric geometry can be understood from the fact that the bias voltage used in our calculation is sufficiently small so that the effect of bias voltages on structural relaxation can be ignored. It is noted that in all the stable geometries the Na-Na distances are shorter than that in the bulk crystal. Though the Na-Na distance may vary with the electrode spacing, we can say that the bond length in atomic chains is usually smaller than that in bulk crystal, since the optimized Na-Jellium distances are already larger than the equilibrium distance of Na adsorption on Jellium surface [22]. Such structural relaxation can be qualitatively understood from the reduced dimensionality and neighborhood of atomic chains compared with bulk materials: The atoms in the chain are less coordinated than bulk, so the tendency to make strong bondings would shorten the interatomic distances. It is also worth mentioning that in the case of the 4-atom Na chain, the interatomic distances are not equal, i.e. the distance between the two center atoms is smaller than the other interatomic distances. This is not surprising, since the two center atoms are less coordinated than the two atoms adjacent to electrodes.

The resistance of the Na chain is defined as $R \equiv 1/\delta G$, where $\delta G$ is the additional conductance due to the presence of the Na chain. Therefore, $R = V/(J_1 - J_2)$, where $J_1$ and $J_2$ correspond to the electric currents with and without the presence of the Na chain, and $V$ is the applied bias voltages [23]. Figure 2 shows the resistance of the Na chains at the initial and stable geometries as a function of the number of atoms ($n$) in the chain. First, as predicted by Lang [3], the resistance of the 1-atom Na chain is anomalously higher than those of the 2 to 4-atom chains. It is noted that the 1-atom chain is an exceptional case in the sense that the effect of $J_2$ is significant. The resistance estimated by $R = V/J_1$ is nearly $\pi \hbar/e^2$ for the 1-atom case, which is quite different from the one estimated by $R = V/(J_1 - J_2)$, while the effect of $J_2$ is negligible for $n \geq 2$. Second, the oscillation behavior of resistance is also observed in our initial geometry. It is worth mentioning that the calculated resistance of the 5-atom chain at the initial geometry is 12.94 kΩ or less, which confirms the resistance oscillation for $n \geq 2$. Unfortunately, we found that the $n = 5$ case requires more strict computational conditions, such as the number of k points, and thus the structural relaxation has not been done yet. The trend of resistance among the 2- to 4-atom chains is observed, however, is different from Lang’s one. This discrepancy may be due to the different pseudopotentials between his and our calculations. Third, considerable difference of resistances between the initial and stable geometries is seen:
After structural relaxation, the resistances of all the 2-, 3- and 4-atom chains become closer to the ideal value of 12.9 kΩ, i.e., the oscillation behavior of conductance is much reduced. Our result suggests that the even-odd parity is quite sensitive to structures of atomic chains and may be rather weakened or even vanished under stable states, which gives an explanation why the even-odd behavior of conductance was not observed by most experiments.

Figure 3 shows the current density distribution for the 2-atom chain at the initial and stable structures. In Fig. 3(a), the current density between the left electrode and the right atom through the left one is much larger than that between the right atom and the right electrode. In Fig. 3(b), on the other hand, the current density distribution near the right electrode surface is considerably enhanced, and becomes similar to that between the left electrode and the right atom. The amplitude of the average current density also becomes larger (from 0.007 to 0.009 mA/nm$^2$). From the comparison between Figs. 3(a) and (b), we can say that the reflection in the stable chain is much reduced than the initial one. The feature of Fig. 3(b) is consistent with the fact that the resistance of the stable chain is nearly equal to the ideal value of $\pi \hbar/e^2$.

We now briefly address the effect of electrode spacing on the resistance of Na atomic chains. For this purpose, we shorten the electrode spacing for the 4-atom chain by 1.6 bohr. The relaxed bond length between Na atoms is 6.2 bohr, for all interatomic distances. The jellium-atom bonding length is relaxed to 3.4 bohr. The resistance of the 4-atom Na chain at the new stable geometry is found to be 13.2 kΩ, which is again very close to the ideal one. This result, together with the results shown in Figs. 2 and 3, suggests that the resistance of relaxed Na chains may tend to be close to the ideal value. Further investigations would be required to confirm this speculation.

IV. CONCLUDING REMARKS

We analyzed the resistance of Na atomic chains as a function of the chain length by including structural relaxation effects within the framework of the boundary-matching scattering-state density functional method [12]. The even-odd oscillation of resistance found in the initial geometries becomes much reduced after structural relaxation. Our results suggest that the even-odd parity in conductance reported by previous researchers may be much weaker than as was expected.

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