Ab initio calculation of stable structures of a Na atomic chain under bias voltages

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Abstract

The stable geometries of a three-atom Na chain connected to two semi-infinite jellium electrodes are studied under bias voltages by performing ab initio force calculations within the density functional theory. At a low bias voltage of 0.01 V, the stable geometry is found to be symmetric, while it becomes asymmetric for higher bias voltages. The displacements of Na atoms in the chain are proportional to the applied bias voltages up to 1 V, while their behavior changes drastically above 1 V. These results can be understood from the behavior of charges induced by the applied voltage. It is also found that the structural relaxation due to the bias voltage also affects the potential drop along the chain and the current–voltage characteristics of the chain.

1. Introduction

Properties of atomic chains bridging two electrodes have attracted much attention of both experimental and theoretical researchers. Ohnishi et al. [1] succeeded in producing a single atomic chain of four gold atoms suspended between two electrodes. The stable structure in a linear chain-shape was found to persist for as long as two minutes in their experiment, observed from transmission electron microscopy. Quantized conductance in steps of $2e^2/h$, where $e$ is the electron charge and $h$ is Planck’s constant, was simultaneously observed in their experiment. Another leading experiment by Yanson et al. [2] also reported the quantized conductance while pulling out a gold chain one-atom thick and at least four atoms long, though the atomic structure cannot be directly imaged in their experiment.

Despite their seemingly simple structures and the above precise experiments, stable structures of Au atomic chains arouse much controversy. Ohnishi et al. [1] reported that the Au–Au distance in the observed chain was anomalously long. On the other hand, all of the reported theoretical calculations so far, which adopted various methods, suggest that the Au chain breaks before reaching such suspended geometries [3–6]. To explain the experimental observation, a few explanations have been proposed, such as that some of atoms in the chain is spinning [4], and that lighter atoms are inserted between Au atoms [7]. Even among experiments there exists a discrepancy: Kizuka et al. [8] reported similar experiments as those of Ohnishi et al., but in his experiments the Au–Au interatomic distance was much shorter and the conductance of single atomic chain was measured to be zero.

Stimulated by the above situation and various experiments on quantum point contacts, atomic chains of other species have also aroused much interests. Here we would like to point out that Na atomic chains have attracted particular interest as one of the simplest model systems. Although a Na atomic chain more than one-atom long has not been experimentally fabricated yet (excluding Na point contact [9], Na nanowire bridge [10,11] experiments), a possibility of three-atom-long Na chains has been demonstrated theoretically [12]. Theoretical calculations also revealed various interesting properties of Na atomic chains, such as quantized conductance [13–15], anomalous dependence of resistance on length [13], even–odd behavior of...
conductance [14], and negative differential conductance [15]. However, almost all of them neglected structural relaxation of the chains: only in Ref. [15], the central two or three atoms in the Na atomic chain are relaxed at zero bias while the two end atoms are kept frozen. Judging from the situation of studies on Au chains, the analysis and discussion of the stable structure must be necessary to gain insight into the true physical origins of properties in the case of Na atomic chains. In particular, structural relaxation due to the applied bias voltage and induced electric currents must be clarified. Although the existence of such relaxation is naturally expected, this has not been clarified yet in the case of the Na chain. Further, even in the case of other chains only few theoretical studies, tight-binding calculation for an Au chain [16] and ab initio calculations for Au [17] and Si [18] chains, have been reported very recently.

This paper presents a theoretical study on the stable structure of a Na atomic chain by using ab initio force calculations within the framework of the density functional theory. The objective is to clarify the stable structure of atomic chains under applied bias voltages. An emphasis is placed on the discussion of bias dependence of the stable structure of the Na atomic chain. Effects of structural relaxation on the conductance of the atomic chain are also studied.

2. Method

The theoretical framework of the present study is based on a self-consistent density functional method, developed by our group [19,20] to calculate the electronic structure and transport properties under electric fields. This method computes the electron wavefunctions by solving the Kohn-Sham equation straightforwardly as boundary-value problems. Exchange and correlation effects are included in the density functional formalism within the local-density approximation. The whole system, consisting of semi-infinite electrodes and nanostructures, is divided into three regions. At the boundaries of these regions, continuation conditions of wavefunctions are utilized so as to eliminate unknown transmission and reflection coefficients. The effects of coherent currents under electric fields or bias voltages are explicitly included in this method. In order to determine the stable structure of an atomic chain, it is necessary to evaluate forces acting on atoms in the chain and to relax the positions of atoms according to the forces. For this purpose, we have implemented modules to calculate forces according to Hellmann-Feynman theorem [21] into the main program developed by our group [19,20]. Prior to the force calculation, the electronic density, together with the effective potential, should be determined self-consistently with an adequate accuracy (10^{-9} in our calculation). It is noted that our method to calculate forces is similar to those adopted in Refs. [17,18], except that their methods are based on the Green’s function while ours are the continuation of wavefunctions, and that Ref. [17] adopts atomic orbitals as basis set and thus has to consider the Pulay force [22] in addition to the Hellmann-Feynman force.

The model used in our study is the same as that used by Lang [13]: a three-atom Na chain connecting two semi-infinite jellium 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 [23], which is successful in studying the structure properties of bulk Na crystal [24], liquid Na [25], Na cluster [26], 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 Na-surface bond length defined from the center of a Na nucleus to the edge of the adjacent electrode is taken as 3 bohr, and the Na–Na bond length 7 bohr, which is the bonding distance in bulk Na. In structural optimization, the spacing of the two jellium electrodes is fixed to 20 bohr. The mesh size \( h \) in the direction normal to the electrode surface, the cutoff energy for plane wave expansion in the lateral directions and the number of sampling \( k \) points are set to be 0.2 bohr, 2.2 Ry and 36, respectively.

3. Results and discussion

3.1. Bias voltage dependence of stable structure

The stable structure of the three-atom Na chain under a low bias voltage of 0.01 V is shown in Fig. 1. Here, we chose the value of 0.01 V because the same value is used in the experiment of conductance measurement of the Au atomic chains [27]. In order to check the stability of the structure shown in Fig. 1, we displace an atom in the Na chain from its stable position by 0.2 bohr in different directions, as shown in Fig. 2. The displaced atom experiences a force in the order of \( 10^{-3} \) a.u. (= atomic unit) toward its stable position, while other atoms are in equilibrium (i.e. forces are in the order of \( 10^{-4} \) a.u. or less). Therefore, we can say that the structure shown in Fig. 1 is stable. As can be seen in Fig. 1, this stable structure is linear and symmetric, and the distances between neighboring Na atoms are smaller than that in bulk Na. The smaller spacing in our Na atomic chains than bulk Na can be understood.

Fig. 1. Calculated stable structure of a three-atom Na chain between two jellium electrodes \((r_s = 2)\) at the bias voltage of 0.01 V. The values of bonding lengths shown in the figure are given in bohr. Note that the voltage of the left electrode is negatively biased in our model.
from the fact that the coordination number of atoms in the chain is less than that in the bulk solid, so the bond length will be shortened in order to form stronger chemical bonding.

Next we study the effect of bias voltages on the stable structure of the three-atom Na chain when high bias voltages up to 2 V are applied. The stable geometry at 0.01 V is used as the initial geometry to perform structural relaxation. The calculated displacements of atoms due to the applied bias voltages are summarized in Fig. 3. The most notable feature seen here is that stable structures of the chain become asymmetric. The move trend of Na atoms in the chain under the bias voltage less than 1 V is the same as that of Au atoms in a three-atom Au chain calculated by ab initio method [17]: the two atoms adjacent to jellium electrodes move toward the \(-z\) direction (from the right to the left), while the middle one toward \(+z\); which is the same direction as that of the electron flow. Todorov et al. [16] also reported a similar move trend for a four-atom Au chain by a tight-binding method, in which the two atoms adjacent to electrodes would move toward the negatively biased electrode, and the two central atoms toward the other direction. However, the move trend of atoms in the three-atom Si chain [18] is quite different: all the atoms move opposite to the electron flow, including the middle atom. Another notable feature seen in Fig. 3 is that all the atomic displacements are proportional to the applied bias voltage up to 1 V. The existence of the linear response regime is expected, but our calculation have revealed for the first time for the Na chain up to what strong voltages the linear response holds. As far as we know, there are two other calculations for the dependence of atomic displacements on the applied bias voltages for Au [17] and Si [18] chains. In the case of the Au chain, the linear response regime holds up to about 0.7 V, and thus comparable to our case of Na. On the other hand, in the case of the Si chain, the dependence of displacements on the bias voltage is not clearly shown, but seems much more complicated than our case of the Na chain, judging from a complicated behavior of forces acting on Si atoms. This discrepancy between Si and Na may be attributed to the different atomic species. When the bias voltage exceeds 1 V, behavior of the displacements changes drastically. In particular, the displacement of the middle atom becomes smaller as the bias voltage increases. It should be noted that the linear geometry is confirmed to be stable against displacement of atoms in the direction perpendicular to the chain. As for the distinct difference in behavior between the regime below 1 V and above 1 V, we will try to clarify it in the following.

3.2. Charge-density analysis

Fig. 4 shows the contour map of the electron distribution for the applied bias voltage of 0.01 V. Reflecting the symmetric geometry at this bias voltage, the electron distribution is symmetric within numerical errors. Formation of chemical bonds between adjacent atoms is also seen in Fig. 4 from the electron distribution in the interatomic region. Fig. 5(a) and (b) show the induced charge distribution defined as the electron density differences between the bias voltages of 0.5 and 0.01 V, and between those of 1 and 0.5 V, respectively. In the contour maps of Fig. 5(a) and (b), the three Na atoms are located at the stable positions for 0.01 and 0.5 V, respectively. It is noted that the difference of electron density is calculated using the electron density distributions in the stable positions of the Na chain from those for the bias voltage of 0.01 V. A positive value means a shift toward the right electrode. The move trend of individual Na atoms in the chain for bias voltages below 1 V is shown in the left-upper corner. Note that in our model, the direction of the electron flow is in the \(z\) direction (from the left to the right).
structures at corresponding bias voltages. In Fig. 5(a), positive charge is induced, i.e. electron density decreases, between the left and the middle atoms, while negative charge is induced, i.e. electron density increases, between the middle and the right atoms. Since Na ionic cores have positive charges, the induced charges produce forces to move the left and the right atoms toward the $-z$ direction. For the middle atom, both of the induced positive and negative charges act to move it toward the $+z$ direction. The fact that the contour maps in Fig. 5(a) and (b) are very similar to each other is consistent with the linear response of atomic displacements seen in Fig. 3 up to 1 V. Small discrepancy between Fig. 5(a) and (b) may be due to the difference in the atomic positions and bias voltage difference ($0.5 - 0.01 V = 0.49$ vs. $1.0 - 0.5 V = 0.5 V$).

The distribution of the induced charge around the middle atom seen in Fig. 5 is quite similar to that reported by Brandbyge et al. [17] for the three-atom Au chain at 1 V, though the distribution near the electrodes seems a little more complex in their case than ours. In a word, we can describe the behavior of the induced charge around the middle atom as a formation of an induced dipole. Since the formation of the dipole makes it possible to screen the effects of the applied bias voltages with minimal charge transfer, such a behavior is considered to be reasonable in the linear response regime. Occurrence of a similar kind of dipole formation is known in other phenomena such as alkali atom adsorption on surface [28].

In Fig. 6, we plot the induced charge distributions defined as the electron density differences between (a) 1 and 0.01 V, and (b) 2 and 1 V. Remarkable discrepancy seen between Fig. 6(a) and (b) suggests that the behavior of the induced charge in the regime above 1 V is completely different from that in the regime below 1 V. We can understand the behavior above 1 V as follows. The induced charge distribution like Fig. 6(b) is unfavorable in the regime of small bias voltages because this cannot be accomplished by local charge redistribution and needs charge transfer between a longer distance. On the other hand, the induced charge distribution like Fig. 6(a) becomes unfavorable as the bias voltage increases, because of the increase of the Coulomb repulsion energy due to the localized induced charge. Judging from the fact that the maximum of the induced charge is much smaller in Fig. 6(b) than that in Fig. 6(a), the induced charge distribution like Fig. 6(b) is considered to be more favorable when the bias voltage is sufficiently large.

3.3. Shift of effective potential

Fig. 7 shows the potential drop at 1 V bias, i.e. the difference of effective potential at 1 and 0.01 V when the atoms are fixed at the stable positions of 0.01 V. It is clearly seen that the potential drop is not uniform, and is mainly concentrated between the left and the middle atoms. This result is consistent with those reported by
Brandbyge et al. [17] for Au atomic chains, Tsukamoto and Hirose [15] for Na atomic chains, and Furuya et al. [20] for Al atomic chains.

Fig. 8 shows the bias voltage dependence of the shift of effective potentials at atomic positions of the Na chain, measured from the potentials at respective atomic positions for the bias voltage of 0.01 V. The Na atomic chain is at the stable geometries of the corresponding bias voltages in the case of Fig. 8(a), while it is fixed at the stable geometry of 0.01 V in Fig. 8(b). First, we can see that the potential shift is largest at the middle atom. Similar ‘overshoot’ of the potential shift is seen in the calculation by Tsukamoto and Hirose [15] for a Na chain, though the model of their chain is different from ours. On the other hand, the order of the potential shift is in accordance with that of atomic positions for Al chains in the calculation by Furuya et al. [20] It is worth noting that the concentration of the potential drop along the chain between the left and the middle atoms mentioned before is also seen in Fig. 8.

Comparing Fig. 8(a) and (b), we can also see notable differences between the cases of relaxed atomic geometries and those fixed at the one for 0.01 V. First, the values of potential shifts monotonically decrease as the bias voltage increases in the fixed geometries, while the behavior of the potential shifts in the regime above 1 V is complicated in the relaxed geometries. It should be noted that similar but more complicated behavior of the potential shift was reported for Al4 and Al5 chains [20]. The behavior of the potential shift in the relaxed one must be correlated with the change of the induced charge distribution in the same regime mentioned in Section 3.2. Next, in general the degree of the localization of the potential drop is more significant in the relaxed geometries (Fig. 8(a)) than in the fixed ones (Fig. 8(b)): in particular, the potential shift at the left atom position is always smaller in Fig. 8(a) than in Fig. 8(b). This seems reasonable, considering the fact that the distance between the left and the middle atoms becomes larger after the relaxation.

A few mechanisms of the above behaviors of the potential shifts have been proposed. Tsukamoto and Hirose [15] attributed this to the gathering and back-scattering of electron flows accompanied by the geometrical transition from the wide three-dimensional electrode to the narrow one-dimensional chain, like the *vena contracta* effect known in hydrodynamics. This, however, cannot explain the complicated behavior seen in Fig. 8(a). On the other hand, Furuya et al. [20] speculated that the mechanism may be similar to that of nonlinear current–voltage characteristics seen in semiconductor superlattice [29]. This may explain the complicated behavior above 1 V in Fig. 8(a), but cannot explain that the localization of the potential drop is seen even at low bias voltages. Further, we do not have evidences sufficient to support the above mechanisms. Thus, it remains as a future task to clarify the mechanism of the behavior of the potential shifts.

3.4. Effects of relaxation on currents

The calculated current–voltage (I–V) characteristics are shown in Fig. 9 for both initial and relaxed geometries. We can see distinct difference of the currents between the two geometries for the region above 1 V. This can be expected
from the different behavior of the potential shifts between the two geometries. The difference in the currents, however, is less remarkable than that in the potential shifts, though it cannot be neglected in the case that quantitative estimation of currents is desired. It is worth mentioning that similar behavior in the $I$–$V$ curve with and without the effect of structural relaxation is reported for a three-atom Si chain from ab initio theoretical calculation [18].

We can also see common features of $I$–$V$ characteristics between the two geometries. First, the conductance in the low bias voltage region below 0.1 V is nearly $G_0 = \frac{2e^2}{h}$, as reported by previous calculations [14,15]. Second, conductances ($\langle I/V \rangle$) in the bias voltage region above 0.1 V are smaller than those in the region below 0.1 V. Similar behavior is seen in previously tight-binding [30] and ab initio [31] results for Au atomic chains. It can be reasonable, considering the facts that the number of conduction channel of the Au and Na chains is one [32] and that transmission probability through the channel can be less than unity: the change of potential involved by the applied bias voltage decreases the transmission probability of wave functions which transmit almost completely in the case of zero bias voltage. Non-uniform potential drop in the chain, which has been pointed out by several calculations [15,20,31], may enhance this decrease. Here, it should be noted that the deviation of the conductance from the quantized value itself is not surprising. Conductances of atomic chains and atomic point contacts have been found to be sensitive to their structures and interface geometries, as shown by a few theoretical studies [13,14,33] and indicated by the experimental fact that the peaks of the conductance histogram of the atomic point contacts at the quantized values are not very sharp. It is also worth mentioning that dissipation processes in atomic chains, such as the excitation of the atomic vibrations by the electrons traversing the chain [34], have not been considered in our calculation. The effects of such processes, however, are small, as seen in, for example, the measurement of the conductance of a H$_2$ molecule bridging Pt electrodes [35], and can be expected from the extremely short length of our atomic chain, which must be shorter than the mean free path.

It is also noted that the decrease in conductance while increasing bias voltages is also reported in experiments [36,37]. However, the decrease in experiments is just the decrease of peak heights in conductance histogram, and not the shift of the conductance peaks to lower values. In this sense, we cannot say that our results correspond to experiments well. To clarify the origin of the decrease of conductance in experiments, further theoretical studies are needed.

4. Conclusions

We have analyzed bias voltage dependence of the stable structure of a three-atom Na chain connecting two jellium electrodes by performing ab initio force calculation within the density functional theory. At a low bias voltage of 0.01 V, the stable geometry is found to be symmetric, while it becomes asymmetric for higher bias voltages. The displacements of Na atoms in the chain are proportional to the applied bias voltages up to 1 V, while their behavior changes drastically above 1 V. These results can be understood from the behavior of charges induced by the applied voltage. It is also found that the structural relaxation due to the bias voltage also affects the potential drop along the chain and the current–voltage characteristics of the chain. Our results suggest that the effects of structural change due to the applied voltages cannot be negligible. Therefore, it is desirable to take account of such structural change in studying interesting issues concerning nanostructures under applied electric fields or bias voltages, such as the anomalous atomic spacing in Au atomic chains and the conductance oscillation due to the chain length mentioned in Section 1.

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