The effect of stretching or buckling behavior on the charge distribution of C, Si, P and S single atom chains

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Abstract
We used the semi-empirical quantum calculations to simulate the structural evolution of the isolated one-dimensional linear atomic chains of C, Si, S and P in the process of stretching and compression. The effects of stretching or buckling behavior on the charge distribution of C, Si, P and S single atom chains were studied. Our results show that the C and Si atomic chains tend to form stable linear structures, in which the charges are odd-evenly oscillated. For the first time we theoretically predict that S and P atoms can form stable curved chain structures. At the beginning of the elastic compression range, the linear atom chains of C and Si have a metastable transition state, that is, there is a bending point at which the chain’s binding energy suddenly reduces a little then increases with further compression. The charges in the chains are locally uneven and symmetrically distributed, and the number of charges fluctuates in the chains. The charge gain or loss of each C or Si atom is stable during compression, while change slightly during stretching.

1. Introduction

With the development of nanoscience and nanotechnology, the microminiaturization of some electronic devices is also developed rapidly. When the size of the device is reduced to the electron average free path size, the electron transport process will produce many new quantum phenomenons [1–5]. At present, the use of single molecules to construct different functional nanodevices has become a hotspot in nanoelectronics research [6–8]. Many researchers have conducted extensive studies on the electron transport phenomena of various linear nanostructures [9–11]. Mechanical properties belong to the most basic physical properties of materials, and the imagination of excellent mechanical properties of nanomaterial’s could date back to 1959. Feynman foresaw the development of nanotechnology in the report ‘There’s Plenty of Room at the Bottom’, and pointed out that it is a different relationship between the various types of forces applied to the material and the characteristic dimensions of material [12]. This was a new concept that was confirmed in the development of MEMS and devices in the 1980 s [13, 14]. And at the nanoscale, these effects are bound to become even more pronounced, so it is not hard to imagine that the material size reduced to the nanometer scale will achieve more excellent mechanical properties.

Single-atom chains are the extreme bottom-structure of materials. In recent years, some research had been made thoroughly on the electronic transport properties of Cu, Au, Si, Al, C, SiC and other metal or non-metallic atomic chains [15–21]. Mikhailovskij et al [22] successfully stretched a carbon chain containing more than a dozen atoms from carbon fibers using a field emission microscope; Jin et al [23] bombarded graphene with an electron beam to obtain carbon atom-length carbon chains. Up to date, isolated silicon, sulfur and phosphorus atom chains have not been reported from experiments. With the development of techniques such as scanning tunneling microscopy (STM) and mechanically controllable cleave junction (MCBJ), it is possible to design and fabricate smaller isolated silicon atom chains. Senger et al [24–28] calculated the structure and conductivity of Si and other atomic chains, and found that Si chain structure is stable and show a metal conductivity property, and
Liu et al. [29] calculated the properties of electron transport through linear silicon atomic chain. Fujimori et al. [30] researched the conducting properties of sulfur chains inside carbon nanotubes. Qiao et al. [31] researched geometric stability and electronic structure of infinite and finite phosphorus atomic chains. In view of a large number of experimental and theoretical studies, the effect of stretching or buckling behavior on the charge distribution of C, Si, P and S single atom chains are rarely reported. In this paper, we used the semi-quantum method to calculate the effect of stretching or buckling behavior on the charge distribution of C, Si, P and S single atom chains, which may be help to understand these materials and provides possible guidance for future experiments.

2. Calculation methods

Our calculation is based on the semi-quantum method in the software package MOPAC (Molecular Orbital Package) [32]. MOPAC is a general-purpose, semi-empirical molecular orbital program for the study of chemical reactions involving molecules, ions and linear polymers. MOPAC can be used to study chemical molecules structure and chemical reactions of semi-empirical molecular orbital approximation. The Hamiltonian functions MNDO, MIVDO/3, AM1 PM3 and PM7 are applied for the calculation of the valence orbit electrons of the molecule to obtain the molecular orbital, generated heat and the corresponding optimized geometric conﬁguration [33, 34]. It uses self-consistent field (SCF) method to optimize the molecule’s structure and electron’s density from minimum energy optimization. The electrostatic repulsion and exchange stabilization are key factors in calculation process. In SCF calculation of MOPAC, the structural parameters, including the distance between atoms \(d\), the charge \(q\) of atoms in the atomic chain and the total energy \(E\) of the system [35, 36], are taken into consideration.

In order to test the validity of MOPAC, we use VASP [37, 38], an electronic structure computing and quantum mechanics—molecular dynamics simulation package, along with MOPAC to calculate the charge distribution of carbon atom chain (C10). The charges of carbon atom chain (C10) from MOPAC and those from VASP are shown in figure 1(a). Figure 1(a) indicates that four C atoms have slightly different negative charges, on the contrary other six C atoms have different positive charges due to their covalent bonding, which can be linearly fitted. These two computational methods show a good degree of consistency. These calculations suggested that MOPAC is feasible software to calculate the charge distribution for atomic chains. Compared with precise first-principles calculations, the semi-classical quantum MOPAC can be greatly time-effective. Since the two softwares are based on different principles, there is a slight deviation for the calculated structures and charges, but the overall trend is same.

In this paper, the one-dimensional single-atom chain models of C, Si, P and S was obtained, and their most stable structure (with the lowest binding energy) of four kinds of atomic chains was optimized. The initial stable structures of the four single atom chains used in the calculation are shown in figure 1(b). C and Si atom chains are linear, P and S atom chain have the curve shape. In order to simulate the atomic chains during compression and extension, the PM7 Hamiltonian functions in MOPAC were used to calculate optimized binding energy and charge distribution.

Figure 1. Comparison of charges from MOPAC with VASP for carbon atom chain (C10) (a) and the initial stable structures of the four single atom chains (b).
3. Results and discussions

3.1. Mechanical properties

3.1.1. Carbon and silicon atomic chains

In our structure optimization, carbon atom chains and silicon atom chains can be regarded as linear elastic strings having bending stiffness. The compression processes are divided into two stages under axial compressive stress. In the first stage, the atomic chain is an elastic chain. The entire energy of the chain maintains almost quadratic parabola curve along with slight extension, which is an important feature of the material undergoes linear elastic deformation. Under compression, the distance between atoms is reduced, the interaction between atoms increases, the energy of the system gradually increases, and the stability decreases. However, when the compressive amount of the C atom chain increases up to \( \Delta d = 0.02 \) Å, and the compressive force of the Si atom chain increases up to \( \Delta d = 0.25 \) Å, the interaction force between the atoms is further enhanced, and the C and Si atom chains lost their linear stability and begin to bend. At the turn points, the total energy suddenly reduces. This is because when they bend, the system’s energy is released, forming a metastable state. As the compression increases continually, the chains bend more and their energies increase further. This is the second stage, which is a curved elastic period \((\Delta L/L < 6\%)\). The details are shown as below.

Ten C, Si, P or S atoms are used to construct four types of isolated atomic chains for simulation. We optimized their original structures, and then the relative energy change \( \Delta E \) are obtained with the variation of compressive or extensive displacement \( \Delta d \). C and Si single atomic chains’ data are shown in Figure 2.

When \( \Delta d < 0 \), the Si and C atom chains are in the compressed state. The \( \Delta E - \Delta d \) curve in Figure 2 shows that the compressed C or Si isolated single atom chains experience two stages, namely, linear stage and bending stage with a bending point between them. In the linear stage, with the increase of the compression displacement \( \Delta d \), the relative energy change \( \Delta E \) increases, and the atomic chain is always in the linear structure. At the bending points, the relative energy change has a jump with the increase of the displacement \( \Delta d \). For 10 carbon atom chain in Figure 2(a), at the bending point and the \( \Delta E \) is \( 2 \times 10^{-5} \) eV, all much smaller than those in the silicon chain \((\Delta d \approx 0.25 \) Å and \( \Delta E \approx 0.1 \) eV) in Figure 2(b) at the bending point. This means that C atoms chain is easier to start bending than Si atoms chains. Comparing the values of \( \Delta E/\Delta d \), approximately \( 0.25 \) eV/Å for C chain and \( 0.0725 \) eV/Å for Si chain, we find that C chain is harder to be compressed than Si chain.

When \( \Delta d > 0 \), the Si and C atom chains are in the tensile state. With the \( \Delta d \) continuing to increase, \( \Delta E \) increases. This instability increases obviously with the variation of stretching displacement \( \Delta d \). Comparing the value of \( \Delta E/\Delta d \), approximately \( 4 \) eV/Å for C chain and \( 1 \) eV/Å for Si chain, we find that C chain is also harder to be extended than Si chain. Generally speaking, Si atoms chain is easier to change shape than Si atoms chain.

3.1.2. Phosphor and sulphur atomic chains

We optimized the original linear structure for two types of chains of P and S elements and found that P and S isolated atom chains are possibly stable. Their relative energy change \( \Delta E \) curves are obtained with the variation of compressive or stretching displacement \( \Delta d \). S and P single atom chains’ data with 10 atoms are shown in
\[ \Delta d = 0 \text{ and } \Delta E = 0 \] indicate that the most stable P or S single atom chain structure is in the 'M' shape or the 'U' shape, respectively. The \( \Delta E = \Delta d \) curve in figure 3 also shows that the S and P monatomic chains begin to deform at the beginning of stretching and compression, this is due to their non-linear structural mechanical properties.

When \( \Delta d < 0 \), the S and P atom chains are in the compressed state. With the same compression amount (for example, \( \Delta d = 1.5 \, \text{\AA} \)), the relative energy change (\( \Delta E = 0.01 \, \text{eV} \)) for P atom is much smaller that of \( \Delta E = 0.05 \, \text{eV} \) for S atom chain. S atom chain has larger elasticity and compressive strength. Because S and P chains' stable structure are curved, they do not have the bending points.

When \( \Delta d > 0 \), the S and P atom chains are in the tensile state. With variation of the stretching displacement \( \Delta d \), the variation of the relative energy change (\( \Delta E \)) of the S atom chain is larger than that of the P atom chain, which again indicates that the S atom chain has larger tensile strength and elasticity. In addition, the energy curve of the P atom chain is approximately symmetric from left to right during the whole process, \( \Delta d = \pm 1.5 \, \text{\AA} \) and \( \Delta E \approx 0.01 \, \text{eV} \), which indicates that the compressive strength and tensile strength of the P atom chain are approximately equal. However, the energy curve of the S atom chain on the right side during stretching process is obviously steeper than that on the left side during the compression. This indicates that the compressive strength of S chain is lower than tensile strength. Comparing above four types of atom strains, P and S chains are much softer than C and Si chains.

3.2. Charge distribution

3.2.1. Charge distribution in Carbon atomic chains with different length

In order to further explore the electronic properties of carbon atoms, we study the charge distribution in atomic chains. Figures 4(a)–(f) and (g)–(k) show the charge distribution of even number atomic chains and odd number atomic chains, respectively. In carbon chains, atoms have left-right symmetry in regard to the center and alternating distribution positive and negative electronic charge (\( +|e| \) and \( -|e| \)). Figures 5(a) and (b) show the relationship between atomic charge transfer's absolute value and the distance to atomic chain's center. The terminal atoms forming dangling bonds (1.286 Å) always show positive charge, about +0.47 \( |e| \) (in figure 5). And the atoms close to terminal show the largest negative charge, about −0.795 \( |e| \) (in figure 5).

The calculated data indicated that charge distribution is very different between the odd and even atomic chains. Firstly, in even number atomic chain, as the distance to the center decreases, there is an oscillation but the oscillation is damped almost to zero at the center (figures 4(a)–(f) and 5(a)). The charge transfer of the carbon atoms at the center has the least charge, average 0.07 \( |e| \). Secondly, if the number of atoms in the carbon chain is \( 2n \), namely, it is a multiple of 2 but not a multiple of 4 (e.g., \( n = 2m + 1 \)); \( m = 1, 2, 3 \ldots \) the two atoms in the middle of the carbon chain have positive charge in figures 4(d)–(f). If it is a multiple of 4 (e.g., \( n = 2m, m = 1, 2, 3 \ldots \)), the two atoms in the middle of the carbon chain have negative charge in figures 4(a)–(c). However, in odd number atomic chain, as the distance to the center decreases, the oscillation is also obvious but with smaller damping (figures 4(g)–(k) and 5(b)). It can be seen that the atom charge transfer lies in 0.55 − 0.61 apart from the first and the second terminal atoms. These regular patterns do not change with increasing length, whether in an odd number atomic chain or in an even number atomic chain.
3.2.2. Charge distribution in atomic chains under stress

Ten C, Si atoms chains are selected to optimize their electron gain and loss with the variation of compressive or stretching displacement $\Delta d$. Si and C single atom chains’ data are shown in figure 6. In figure 6(a), when $\Delta d < 0$, the C atom chains are in the compressed state. $C_4$, $C_7$, $C_2$ and $C_9$ atom gain the electrons and other atoms alternately lose electrons, from the center to ends, gaining and losing electrons of the C atomic chains slowly increases. When $\Delta d > 0$, C atom chain is in the tension state. Comparing to compression, losing electrons of $C_1$, $C_{10}$ gradually increase and losing electrons of $C_4$, $C_7$ gradually reduce. The electron gains and losses of other atoms remain constant during stretching and compression.

The electron gain or loss of 10 silicon atom chain is shown in figure 6(b). When $\Delta d < 0$, gaining and losing electrons ($\Delta q$) of Si atom chains is stable in the initial stage of compression, when $\Delta d = -0.25$ Å (bending point), the $\Delta q - \Delta d$ curve appears a fluctuation point, and this means that fluctuating points ($\Delta q - \Delta d$) is corresponding to the bending point ($\Delta E - \Delta d$). The curve of electrons gaining and losing of Si has a slight fluctuation with the compressive displacement ($\Delta d$). When $\Delta d < -0.25$ Å, the atomic chain is in the bending state then the $\Delta q - \Delta d$ curve has been in a steady state. In addition, $Si_1$ and $Si_{10}$, $Si_5$ and $Si_6$, $Si_1$ and $Si_{10}$ always get electrons and other atoms alternately lose electrons, from the center to ends, gaining and losing electrons of

Figure 4. Charge distribution in atomic C chains with even number atoms (a)–(f) and odd number atoms (g)–(k).

Figure 5. The absolute value of charge transfer with distance to the center in even number atomic chains (a) and odd number atomic chains (b).
the Si atomic chains slowly increase. When $\Delta d > 0$, the Si atom chains are in the tension state, gaining electrons of $C_1, C_{10}, C_3, C_8$ gradually increase, and losing electrons of $C_4, C_7, C_2, C_9$ gradually reduce. Compared with the state of compression, gaining electrons of $C_1, C_6$ is always constant, indicating that these two atoms in the middle are affected very little by extension.

Ten S or P atoms chain is selected for simulating their charge distribution, as shown in figure 7. Ten phosphor atoms chain’s charge distribution is shown in figure 7(a). From $\Delta d = -1.5$ Å to 1.5 Å, the charge of $P_1$ and $P_{10}, P_2$ and $P_9, P_3$ and $P_7$ are almost unchanged. Charge of $P_5$ and $P_6$, and charge of $P_3$ and $P_8$ reduces in the process of tensile and compression. When $\Delta d < 0$, the charges of $P_5$ and $P_6$ reduces by 0.04, while charge of $P_3$ and $P_8$ increases by 0.05 compared with that at $\Delta d = 0$. When $\Delta d > 0$, the charges of $P_5$ and $P_6$ increase by 0.04, while the charges of $P_3$ and $P_8$ reduce by 0.05 compared with that at $\Delta d = 0$. Ten sulfur atoms chain is shown in figure 7(b). From $\Delta d = -1.5$ Å to 1.5 Å, the charge of $S_1$ and $S_{10}, S_2$ and $S_9$, and $S_3$ has little change in the process of tensile and compression. The charge of $S_4$ and $S_8$ increases at first then decreases as $\Delta d$ increases. On the contrary, the charge of $S_1$ and $S_2$ decreases at first then increases as $\Delta d$ increases. Our results suggest that the charge in isolated C, Si, P and S single atom chain is unevenly distributed, and the mechanical shape change has little effect on the charge distribution.

Figure 6. The electron gain and loss of C (a) and Si (b) single atomic chains with compressing and stretching displacement ($\Delta d$).

Figure 7. The electron gain and loss of S (a) and P (b) single atomic chains with compressing and stretching displacement ($\Delta d$).
4. Conclusions

The semi-empirical quantum calculation method is used to study the effect of stretching or buckling behavior on the charge distribution of C, Si, P and S single atom chains. The main conclusions are: (1) C or Si atoms form linear atomic chains (ground-state geometry), and we predicted that S and P can form curved chains. (2) In the process of compression and stretching, C and Si chains have a metastable transition state (bending point). (3) Charge is unequally distributed in these atomic chains. (4) The charge gain or loss of each C or Si atom in the chain is stable during compression, while charge slightly during stretching. Compression and extension can slightly affect charge distribution in S and P atoms chains.

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References

[1] Svižhenko A, Leu P W and Cho K 2015 Effect of growth orientation and surface roughness on electron transport in silicon nanowires Phys. Rev. B 75 125417
[2] Amorim E P M et al 2007 Short linear atomic chains in copper nanowires Nanotechnology 18 145701
[3] Lin Z Z and Ning X J 2011 Controlling the electronic properties of monatomic carbon chains Euro. Phys. Lett. 95 47012
[4] Yu J X, Hou Z W and Liu X Y 2015 Stability of conductance oscillations in carbon atomic chains Chin. Phys. B 24 067307
[5] Owens F J 2015 Electronic structure of phosphorene nanoribbons Solid. State. Commun. 223 57–9
[6] Lang N D 1997 Anomalous dependence of resistance on length in atomic wires Phys. Rev. Lett. 79 1357–60
[7] Li A Y et al 2006 TiNi monatomic chains stabilized by alloying: a first-principles study Chin. Phys. Lett. 23 182–5
[8] Thijssen W H A et al 2008 Formation and properties of metal–oxygen atomic chains New J. Phys. 10 033005
[9] Wang B et al 2001 Novel structures and properties of gold nanowires Phys. Rev. Lett. 86 2046
[10] Li A Y, Li R Q, Zhu Z Z and Wen Y H 2005 Structural stabilities and electronic structures of Ti atomic chains Phys. E 30 138–42
[11] Lin Y S, Li A Y and Zhu Z Z 2004 Atomic and electronic structures of Zr atomic Chin. Phys. Lett 21 1791–4
[12] Kerr I and Bassi G 2004 Not that much room? Nanotechnology, networks and the politics of dancing Health. Law. J. 12 103
[13] Luo J K and Lin M 2006 MEMS based digital variable capacitors with a high- k dielectric insulator Sensor. Actuat. A-Phys. 132 139–46
[14] Da Silva E Z et al 2004 Theoretical study of the formation, evolution, and breaking of gold nanowires Phys. Rev. B 73 115411
[15] Okamoto M and Takayanagi K 1999 Structure and conductance of a gold atomic chain Phys. Rev. B 60 7808–11
[16] Lee S S et al 2002 Structural and electronic properties of the quasi-one-dimensional metallic chains of the Au–induced facets on the Si(512) surface Phys. Rev. B 66 115317
[17] Sen P et al 2001 Structure of aluminum atomic chains Phys. Rev. B 64 195420
[18] Wallis T M, Nilius N and Ho W 2002 Electronic density oscillations in gold atomic chains assembled atom by atom Phys. Rev. Lett. 89 236802
[19] Moses J et al 1997 Quantized conductance of Si atomic wires Phys. Rev. B 56 R4351–4
[20] Liu F T et al 2013 Electron transport through a silicon atomic chain Chin. Phys. Lett. 30 067302
[21] Shin D W et al 2007 Size dependence of the electronic structure of copper nanoclusters in SiC matrix Chem. Phys. Lett. 422 543–6
[22] Mikhailovskij I M and Wanderka N 2001 Structure and conductance of a gold atomic chain Phys. Rev. B 64 115317
[23] Jia C et al 2009 Viewpoint: deriving carbon atomic chains from graphene Phys. Rev. Lett. 102 203501
[24] Senget R T et al 2005 Atomic chains of group–IV elements and III–V and II–VI binary compounds studied by a first-principles pseudopotential method Phys. Rev. B 72 75419
[25] Tongay S et al 2004 Ab initio electron transport calculations of carbon based string structures Phys. Rev. Lett. 93 136404
[26] Ohnishi H, Kondo Y and Takayanagi K 1998 Quantized conductance through individual rows of suspended gold atoms Nature 395 780–3
[27] Kizuka T 2008 Atomic configuration and mechanical and electrical properties of stable gold wires of single–atom width Phys. Rev. B 77 155401
[28] Yanson A L et al 1998 Formation and manipulation of a metallic wire of single gold atoms Nature 395 783–5
[29] Liu F T et al 2014 Calculation of the properties of electron transport through linear silicon atomic chain J. Lanzhou Univ. 50 284–8
[30] Fujimoto T et al 2013 Conducting linear chains of sulphur inside carbon nanotubes Nat. Commun. 4 2162
[31] Qiao J S, Zhou L W and Ji W 2017 Geometric stability and electronic structure of infinite and finite phosphorus atomic chains Chin. Phys. B 26 036803
[32] Stewart J I 1990 MOPAC: a semiempirical molecular orbital program J. Comput. Aid. Mol. Des. 4 1–105
[33] Banmoke T O 2006 Calculation of the arhenius parameters for the pyrolysis of some alkyl vinyl ethers using mopac J. Appl. Sci. 6 631–4
[34] Dutra J D L et al 2013 Sparkle/PM7 lanthanide parameters for the modeling of complexes and materials J. Chem. Theory. Comput. 9 3333–41
[35] Hohenstein E G et al 2015 An atomic orbital-based formulation of the complete active space self-consistent field method on graphical processing units J. Chem. Phys. 142 224103
[36] Shun Q et al 2006 Structural Stabilities and Electronic Structures of Ga Atomic Chains Chin. Phys. Lett. 19 219–22
[37] Kresse G and Furthmüller J 1996 Efficiency of ab initio total energy calculations for metals and semiconductors using a plane-wave basis set Comp. Mater. Sci. 6 15–50
[38] Kresse G and Furthmüller J 1996 Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set Phys. Rev. B 54 11169–86