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Transactions F: Nanotechnology

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Research Note

First-principles study of strain-induced charge polarization in a molybdenum disulfide monolayer

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Received 7 June 2016; received in revised form 24 September 2016; accepted 8 April 2017

KEYWORDS

Molybdenum disulfide;
Charge polarization;
Piezoelectric;
Electrostatic potential.

Abstract. In the presence of elastic planar strain distributions, electronic properties of molybdenum disulfide (MoS_2) monolayer are investigated within Density Functional Theory (DFT) calculations as implemented in SIESTA package. Three types of planar strain are considered with some different intensity values, and uniaxial strain along the armchair and zigzag directions as well as biaxial strain. We present a systematic study of the strained MoS_2 monolayer by focusing on the calculation of Total Density Of State (TDOS), Partial Density Of State (PDOS), electron charge density, and electrostatic potential using post processing tools. In most cases, the states due to Mo atoms have dominant association in the TDOS close to the Fermi level of MoS_2 monolayer under strain. As a consequence of the strain, S atom takes electron from Mo atom and becomes negatively charged. In addition, the tensile and compressive strains introduce the charge polarization in two opposite directions per three types of strain for both sheets, which is in line with the experimental study. As another important result, the strain-induced charge polarization is proportional to the intensity value of strain.

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1. Introduction

MoS_2 single-layer, as one of transition metal dichalcogenide (TMD) monolayers (novel two dimensional honeycomb semiconductors), is composed of three layers with hexagonal symmetry, in which each Mo atom is covalently bonded with equal distances with three S atoms in up-layer and three S atoms in down-layer. It has been focused on due to remarkable properties, including sizable direct band gap [1], tunable electronic properties, high coherence length [2], easy fabrication [3-5], and high surface to volume ratio [6,7]. Also, It shows a high on/off current ratio and mobility when a hafnium oxide (high k dielectric) is used

as a gate dielectric [8], allowing applications in the next-generation nano-devices. In addition, defect-free MoS_2 monolayer and MoS_2 monolayer in the presence of single S-vacancy as well as single Mo-vacancy do not exhibit any magnetic properties [9]. However, magnetism is found in the MoS_2 monolayer when the monolayer is doped by some transition metal atoms [10] and nonmagnetic elements [11], in which the induced local magnetism can be controlled via geometrical distortions [12].

The electronic properties of MoS_2 monolayer can be manipulated by means of applying strain [13-18] and external electric and magnetic fields [19]. For example, the biaxial planar tensile strain induces direct to indirect band gap transition in MoS_2 monolayer [13,15]. Also, it exhibits semiconductor-metal transition upon the biaxial planar tensile strain about 11% [13,14]. Moreover, the biaxial and uniaxial tensile and compres-

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sive strains modulate longitudinal and transverse effective masses of both electron and hole [14,18]. On the other hand, both experimental and theoretical studies have reported piezoelectricity in two-dimensional MoS₂ monolayer [20,21]. The observed piezoelectricity causes MoS₂ monolayer to be a potential candidate for piezotronics. In order to provide deep understanding of strain-induced charge polarization as well as electrostatic potential, a systematic study is presented on the electronic properties of the strained MoS₂ single-layer [22–26].

In the earlier work, we calculated the tunable electronic and magnetic properties of an MoS₂ monolayer with vacancies under elastic planar strain at the level of Density Functional Theory (DFT) [9]. Here, we provide theoretical observations of induced charge polarization as well as the electrostatic potential due to the elastic mechanical deformations in the 2D MoS₂ monolayer in details. All calculations are performed using DFT implemented in SIESTA package based on norm-conserving pseudopotentials to describe the electron-ion interaction and numerical atomic orbital basis set for the expansion of the single-particle Kohn-Sham wave functions.

The outline of this paper is as follows. Technical details of DFT calculations for the MoS₂ monolayer system are briefly provided in Section 2. Also, various configurations are introduced. In Section 3, the influence of the elastic planar strain on the electronic properties is investigated. The last section of the paper is allocated to a brief discussion and conclusion of the findings.

2. Computational details

The type and intensity dependence of strain on the electronic properties of an MoS₂ monolayer is theoretically investigated by focusing on the piezoelectric charge polarization. For this reason, the structural relaxation and electronic structure calculation are performed based on the DFT implemented in the SIESTA package [27,28], which uses the numerical atomic orbitals as the basis set and Troullier-Martin type norm-conserving pseudopotentials [29]. Also, Perdew-Burke-Ernzerhof (PBE) functional form of Generalized Gradient Approximation (GGA) for the exchange-correlation approximation, which generates excellent results for TMD materials [13], has been used. Mo and S atoms are described by $5s^1 4d^5$ and $3s^2 3p^4$ valence electrons plus the corresponding pseudo-potential ion charges, respectively.

We aim to study the effect of various tensile and compressive planar strain distributions on electronic properties of MoS₂ single-layer. For this reason, we have considered three types of strain distribution for the system, namely, uniaxial (asymmetrical) strain

distribution along the armchair direction as shown in the right panel of Figure 1(a), uniaxial (asymmetrical) strain distribution along the zigzag direction as shown in the right panel of Figure 1(b), and the symmetrical (biaxial) strain distribution as shown in the right panel of Figure 1(c). Also, the directions of three types of strain have been depicted from the viewpoint of charge density in Figure 1. The tensile and compressive planar strains, $\epsilon\%$, along the special direction can be modeled by increasing and decreasing the lattice constant from a to $a(1+\epsilon)$ and $a(1-\epsilon)$, respectively. After the SIESTA calculations, the results are post-processed using the `pdosxml`, `denchar`, and `plrho` utilities of SIESTA to calculate the Partial Density Of States (PDOS), the charge density distribution, and the electrostatic potential, respectively.

3. Results and discussions

In order to investigate the electronic properties of the MoS₂ monolayer under different strain distributions, at first, we have represented the Total Density Of States (TDOS) of a pristine MoS₂ layer in Figure 2(a). The calculations have been done on the rectangular unit cell of MoS₂ single-layer with the lattice constant $5.55 \times 3.20 \times 20.00$ in unit of angstrom, which contains six atoms, while the rectangular supercell of MoS₂ single-layer has been used with the lattice constant $5.55 \times 6.40 \times 20.00$ in unit of angstrom to plot the electrostatic potential. The spacing distance along z direction is considered to be 20.00 Å to avoid mirror interactions between the single layers. Double ζ -plus-polarization basis set, plane wave cutoff of 190 Ry, and $9 \times 15 \times 1$ Monkhorst-Pack k -point sampling of the Brillouin zone are determined by the total energy convergence tests within 0.01 meV. However, the grid is increased to $24 \times 42 \times 1$ k -points for density-of-state calculations. Besides these, maximum absolute forces over atoms are better than 0.004 eV/Å in all cases. Also, all geometry optimizations and electronic structure calculations are performed corresponding to the above considerations. The lattice constant and the band gap of the optimized pristine MoS₂ monolayer are obtained 3.20 Å and 1.51 eV, respectively, which are in agreement with the reported theoretical results [30]. In all calculations, the curves have been plotted with the fixed values of $\epsilon = \pm 2\%$, $\pm 5\%$, and $\pm 12\%$ when the strain is applied. The mechanical deformations with the considered strength values are at the elastic mechanical deformation range for the MoS₂ single-layer [13].

The TDOS of an MoS₂ single-layer and its Projected Density Of States (PDOS) on the Mo and S atoms have been plotted at various intensity values of strain in Figure 1(a)-(c). It is seen that the MoS₂ single-layer nearly exhibits the same electronic

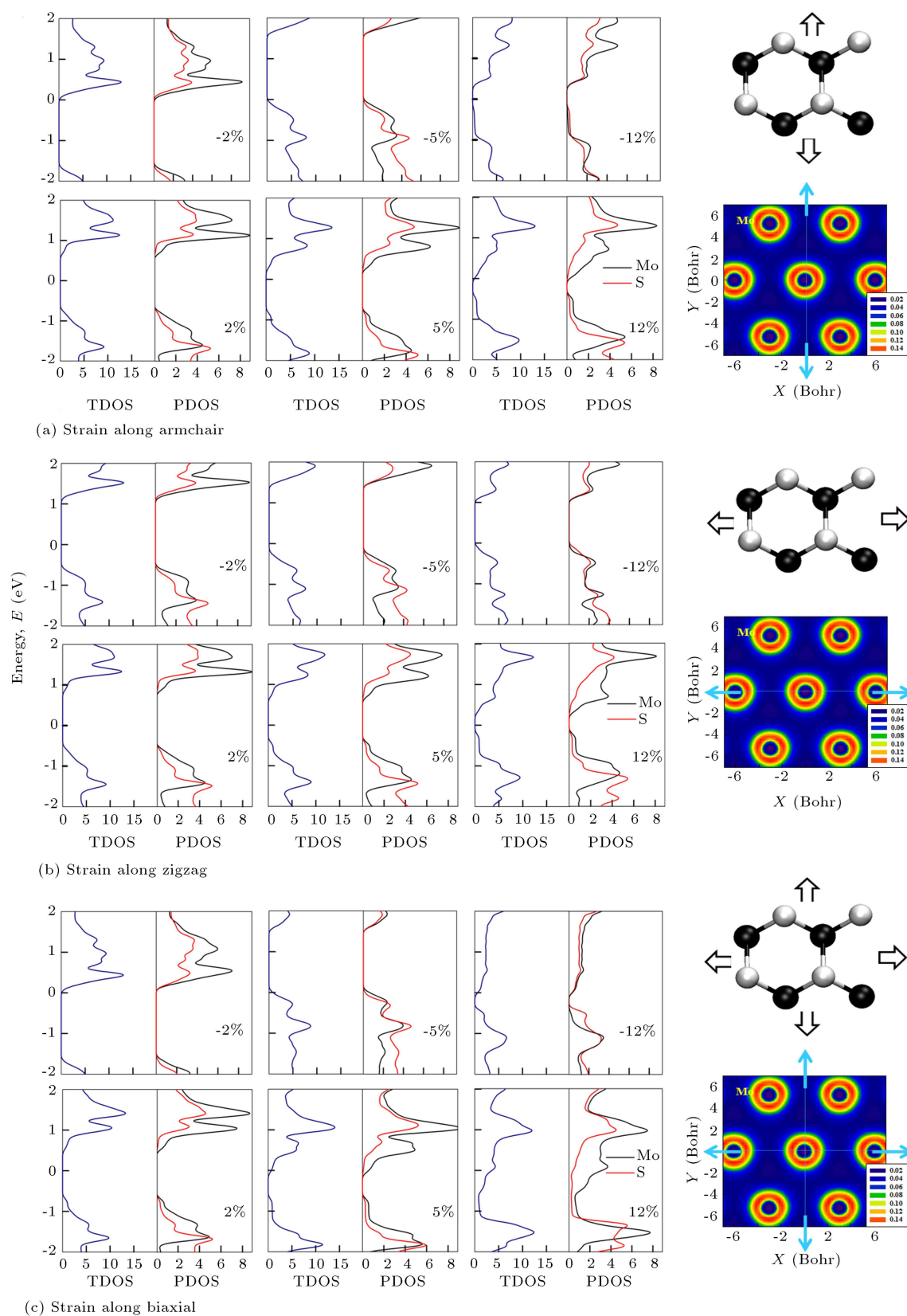


Figure 1. The dependence of the total density of states and the partial density of states on the S and Mo atoms as a function of energy for MoS₂ monolayer under (a) the uniaxial strain along the armchair, (b) the uniaxial strain along the zigzag direction, and (c) the biaxial strain. The schematic top view of a supercell including 12 atoms and the electron charge density of Mo-Mo layer are shown in the right panel of the figure.

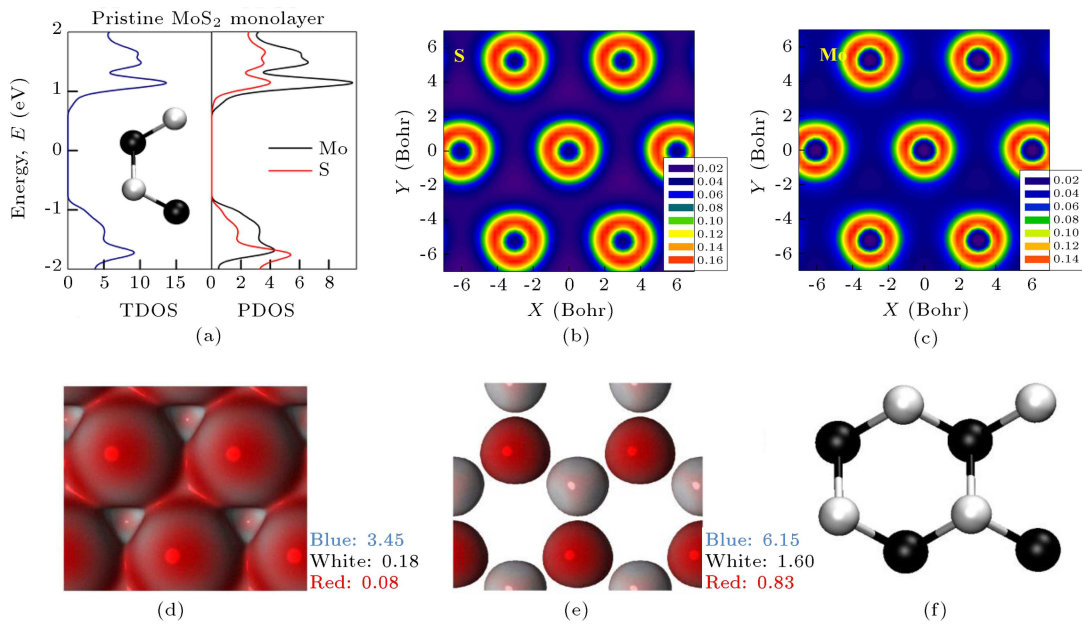


Figure 2. (a) The dependence of the total density of states as well as the partial density of states as a function of energy. The inset figure shows the hexagonal unit cell of the structure. (b) The contour plots of electron charge density of S-S sheet and (c) Mo-Mo sheet. (d) The electrostatic potential maps per isosurface of the electron density in three dimensions with the isovalues of 0.02 electrons/bohr³ and (e) 0.1 electrons/bohr³ of the pristine molybdenum disulfide monolayer. (f) Schematic representation of a rectangular supercell including 12 atoms from top view. The units of the electron density and the potential are electrons/bohr³ and Ry, respectively.

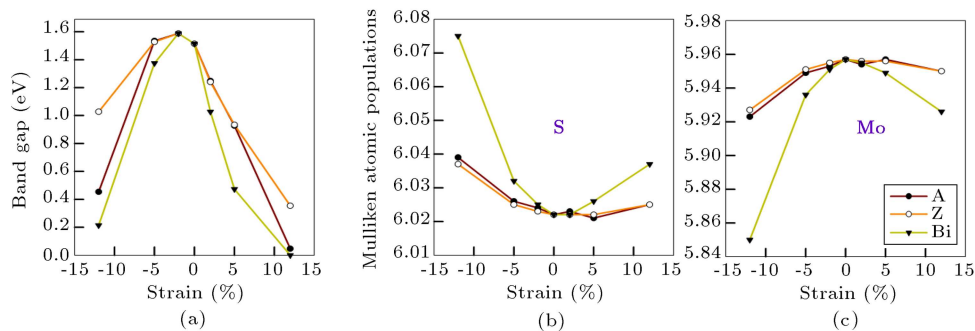


Figure 3. (a) The dependence of the band gap. Mulliken atomic population of (b) S atom and (c) Mo atom as a function of three types of strain upon the MoS₂ monolayer.

properties under both of the uniaxial strains, while it is affected more due to the biaxial strain. As it is observed, the band gap of MoS₂ single-layer is highly sensitive to the type and strength of strain distributions. This can be found quantitatively in Figure 3(a), which is explained in the next paragraph. Besides these, the PDOSs generally indicate that the states due to the Mo atoms have dominant association of TDOSs near the Fermi level in most cases. Also, the introduced metallic states upon the tensile biaxial strain mostly originate from the Mo atoms. The semiconductor-metal transition due to the biaxial strain is in agreement with the work of Ghorbani-Asl et al. [13].

Figure 3(a) shows the band gap evolution of MoS₂ monolayer versus the intensity value of strain. In

particular, one can observe that the band gap decreases upon the tensile symmetrical strain; ultimately, the MoS₂ single-layer exhibits the metallic behavior under the tensile biaxial strain $\varepsilon = 12\%$, whereas the compressive biaxial strain of $\varepsilon = -2\%$ at first causes the band gap to increase; but, the increase in the compressive strain causes the band gap to decrease, of which the trend is in agreement with the theoretically reported works [16,17]. Figure 3(b) and (c) shows the charge evolution of S and Mo atoms upon three types of strain, which is estimated using the Mulliken population analysis. As a consequence of the strain, S atom takes electron from Mo atom and becomes negatively charged. At the same time, the compressive strain induces larger partial charge changes than the tensile strain does. Also, the biaxial

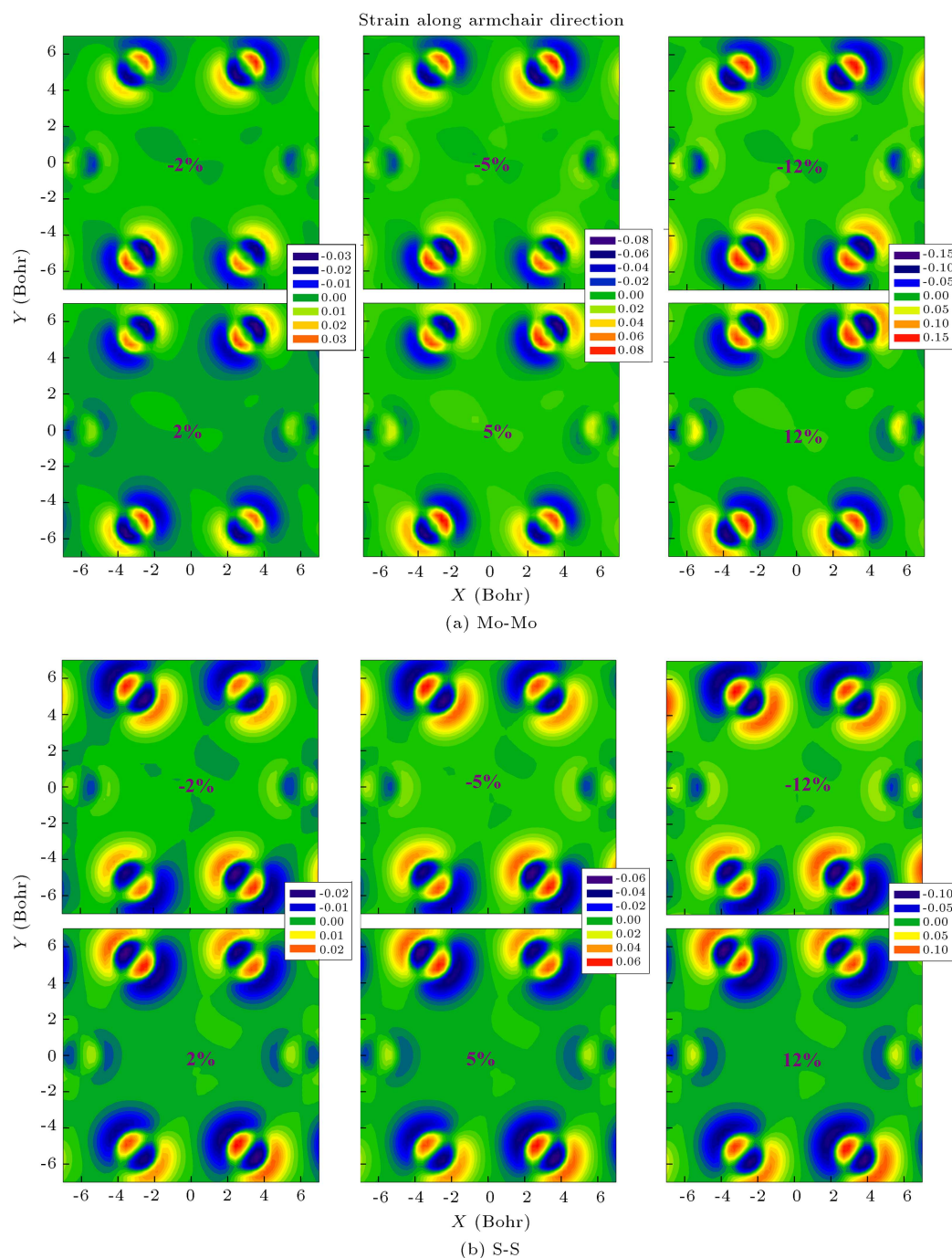


Figure 4. The contour curves for electron charge density difference of (a) Mo-Mo sheet and (b) S-S sheet in MoS₂ monolayer in the presence of the strain along the armchair direction. The charge density is in the unit of electrons/bohr³.

mechanical deformation causes the atomic charge to change much more than uniaxial ones.

In order to further qualitatively elucidate the charge changes due to the applied strain, we provide the contour curves for electron charge density difference. These curves are plotted for S-S and Mo-Mo sheets of these configurations in unit of electrons/bohr³ as shown in Figures 4-6. Here, the electron charge density difference is obtained by subtracting the electron charge density of the strained MoS₂ monolayer from that of

pristine MoS₂ monolayer. To show exact position of atoms, the contour plots of electron charge density of S-S as well as Mo-Mo sheets are plotted in Figure 2(b) and (c), respectively, in which the reference of Mo-Mo and S-S sublattices has been considered on Mo and S atoms, respectively. Therefore, the charge density figures as well as charge density difference figures of S-S sublattice in comparison with those of Mo-Mo sublattice have about 2 bohr displacements. In order to explore the charge polarization calculation of the

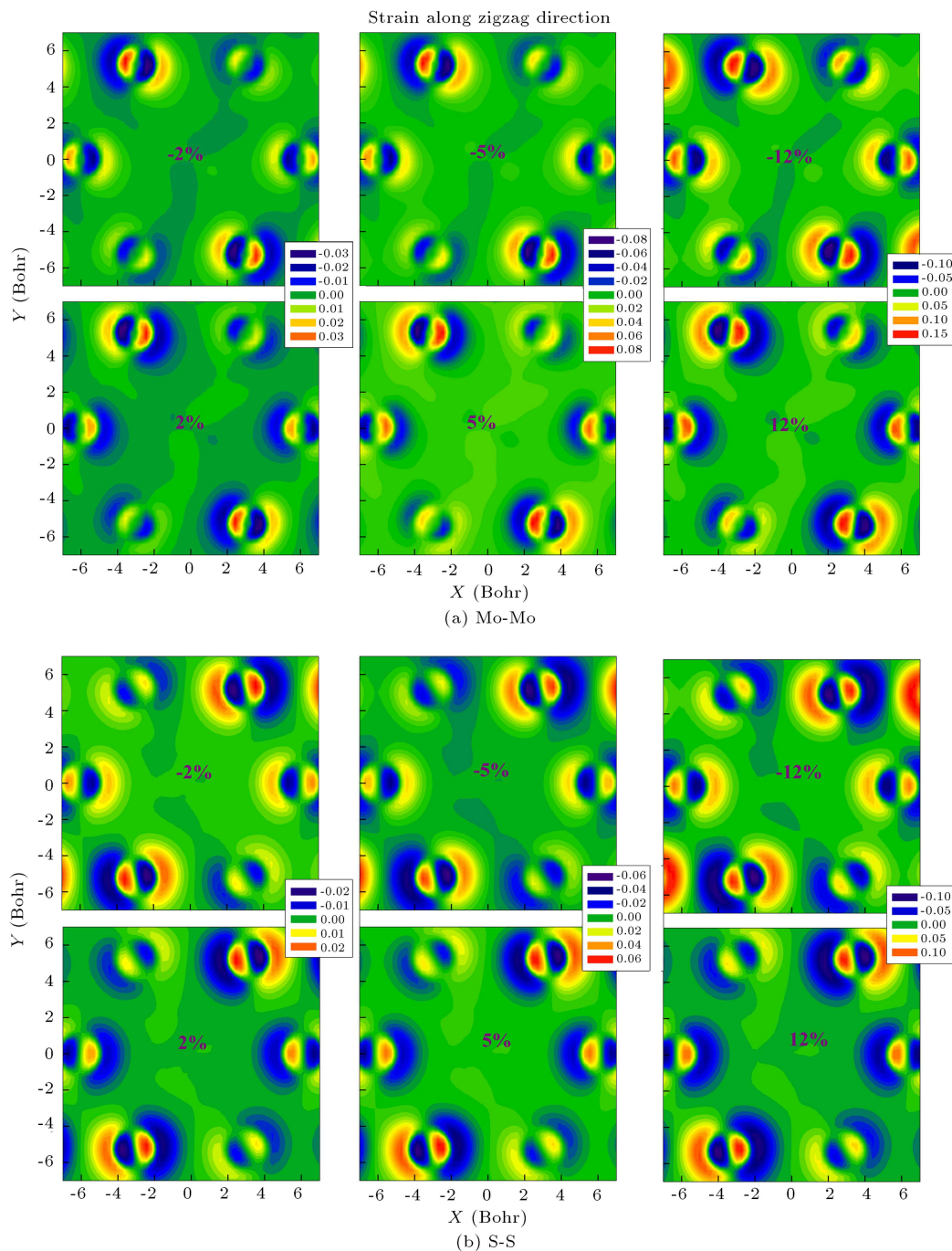


Figure 5. The contour curves for electron charge density difference of (a) Mo-Mo sheet and (b) S-S sheet in MoS₂ monolayer in the presence of the strain along the zigzag direction. The charge density is in the unit of electrons/bohr³.

system, let us consider 3D lattice of MoS₂ monolayer including alternating anions and cations. The first thing to point out is that there is not any Mo ion as center of inversion symmetry, which means that there is no similarity, when one sits on each Mo ion and looks at top along each Mo-S bond length and then looks at its opposite direction. Therefore, the MoS₂ monolayer is polar. Polarization is defined as the dipole moment per unit area, which is measured using Sawyer-Tower circuit experimentally [31]. Hence, the change of charge

polarization is computed at the edge of the MoS₂ unit cell according to the figures. The figures clearly show that the strain significantly affects the electron distribution. The planar strain generally causes Mo atom to donate more charge to S atom, which makes the system polarize. One observes that the tensile and compressive strains induce the charge polarization in two opposite directions per three types of strains for both sheets, which is in line with the experimental study [20]. Thus, strain can asymmetrically modulate the conductance

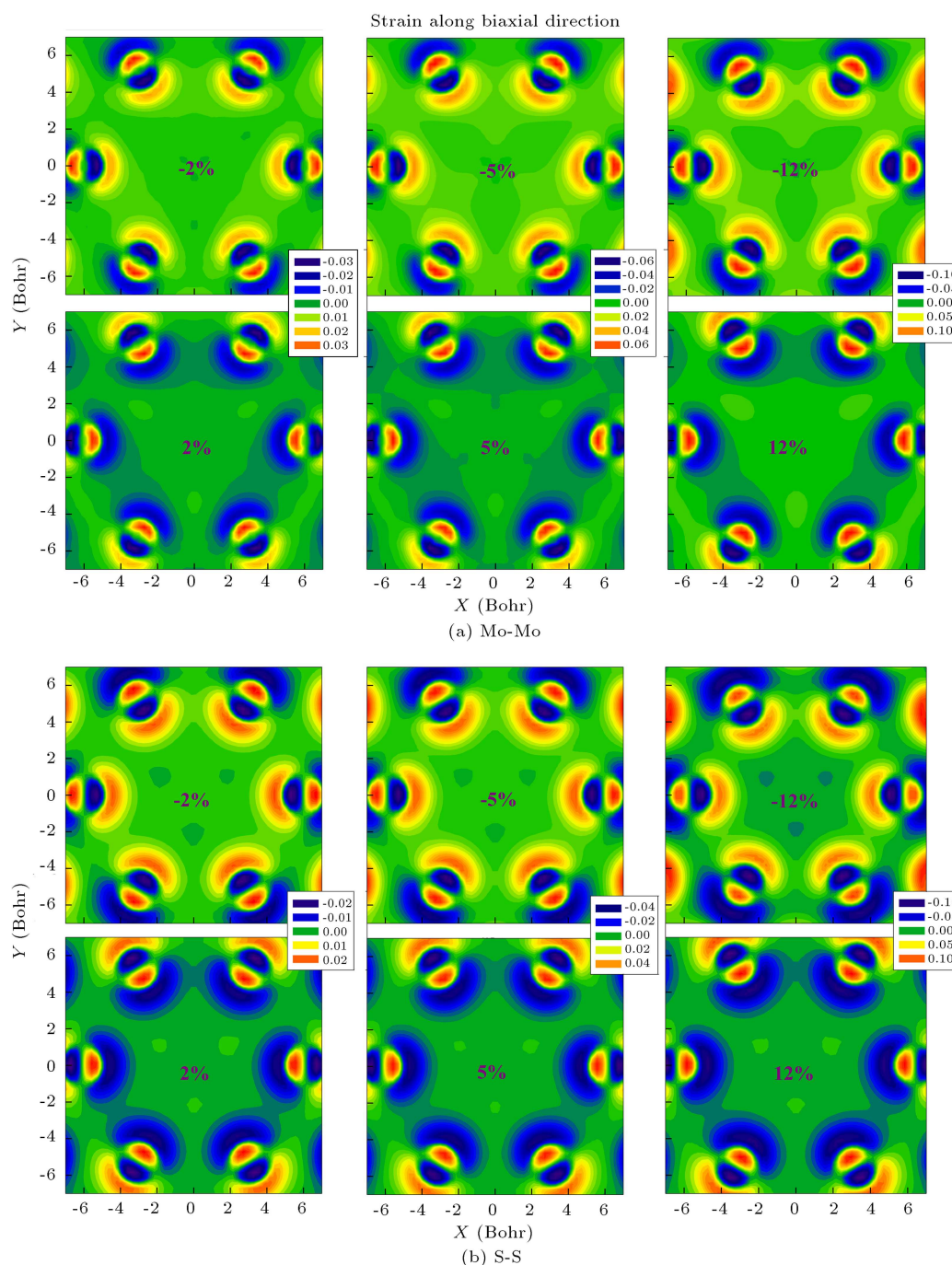


Figure 6. The contour curves for electron charge density difference of (a) Mo-Mo sheet and (b) S-S sheet in MoS_2 monolayer in the presence of the biaxial strain. The charge density is in the unit of electrons/bohr³.

of an MoS_2 single-layer. As another important result, the strain-induced charge polarization is proportional to the intensity value of strain.

In order to gain insight into induced potential due to the piezoelectric charge polarization, we draw the electrostatic potential in the studied configurations using *plrho* code. By the way, an isosurface of the electron density is plotted in three dimensions. Then, this isosurface is colored according to the electrostatic potential of the supercell by red, white, and blue

corresponding to the minimum, mean, and maximum values of the saturation range, respectively. Here, the supercell is composed of one unit cell along the armchair direction and two unit cells along the zigzag direction (see Figure 2(f)). As it is expected from the studied charge polarization, Mo atom possesses higher potential than S atom does. Therefore, the strain-induced potential drop is created between Mo-Mo and S-S sheets. Also, there is not any difference between the potential drop of Mo atom and S atom in up-layer and S

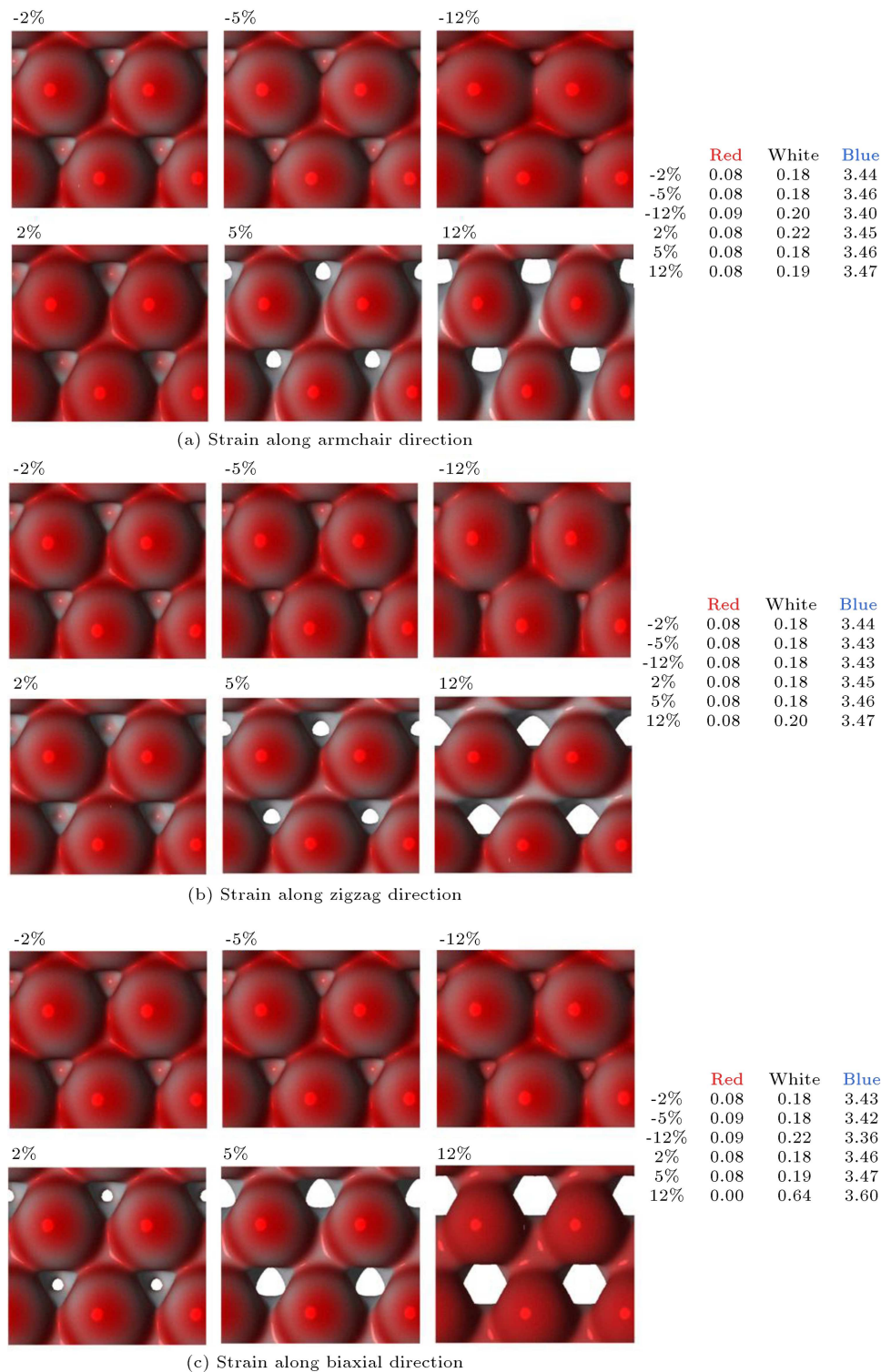


Figure 7. Top views of the electrostatic potential of MoS₂ monolayer in the presence of the stain along the armchair direction, the zigzag direction, and the biaxial strain per 0.02 electrons/bohr³ isovalue electron density. The unit of the potential is Ry.

atom in down-layer. Thus, in order to obviously figure out the strain-induced potential due to three types of planar strain, the electrostatic potential maps of the strained MoS₂ supercell are plotted in Figure 7(a)-(c) from top view. To determine the exact atomic position

from potential point of view, the electrostatic potential maps of pristine MoS₂ monolayer are presented per two different isovalues of 0.02 and 0.1 electrons/bohr³ in Figure 2(d)-(e), which correspond to the interstitial and atomic regions, respectively. To investigate the

potential changes due to strain in all cases, the iso-surface of the electron density with isovalue of 0.02 electrons/bohr³ is plotted. Figures show that the compressive strain causes the electrostatic potential of interstitial regions to drop in the S sheet. In other words, the electrostatic potential difference between interstitial and atomic regions decreases when the compressive strain increases. In contrast, the potential rise occurs in the interstitial regions in the S sheet due to the tensile strain. These results confirm that the S atom takes more partial charge due to the compressive strain in comparison to the tensile one.

4. Concluding remarks

Electronic properties of the MoS₂ monolayer under planar tensile and compressive strains were calculated using the DFT calculations. As a consequence of the strain, S atom took electron from Mo atom and became negatively charged. Besides these, the compressive strain induced larger partial charge changes than the tensile strain did. Also, strain could significantly cause the system to polarize. Moreover, the tensile and compressive strains induced the charge polarization in two opposite directions. Finally, the strain-induced charge polarization was proportional to the intensity value of strain.

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