Understanding atomic bonding and electronic distributions of a DNA molecule using DFT calculation and BOLS-BC model

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ABSTRACT

Deoxyribonucleic acid (DNA) is an important molecule that has been extensively researched, mainly due to its structure and function. Herein, we investigated the electronic behavior of the DNA molecule containing 1008 atoms using density functional theory. The bond-charge (BC) model shows the relationship between charge density and atomic strain. Besides, the model mentioned above is combined with the bond-order-length-strength (BOLS) notion to calculate the atomic cohesive energy, the bond energy, and the local bond strain of the DNA chain. Using the BOLS-BC model, we were able to obtain information on the bonding features of the DNA chain and better comprehend the associated properties of electrons in biological systems. Consequently, this report functions as a theoretical reference for the precise regulation of the electrons and the bonding states of biological systems.

1. Introduction

Deoxyribonucleic acid (DNA), is an essential component of life and is regarded as the cornerstone of a new generation of electronic devices [1]. In biology, DNA is responsible for the storage and transmission of genetic information. It consists of a phosphate backbone and four nitrogen-containing bases, namely adenine (A), cytosine (C), guanine (G), and thymine (T). Among them, the A base is only paired with the T base, and the G base is always paired with the C base [2]. Several electron orbitals in the base are very overlapped with each other along the long axis of DNA [1], which makes the DNA molecule have an excellent conductive structure.

In recent years, researches on the electron transport properties and bond energy properties of the DNA chain have received extensive attention. Charge transport in DNA chain has been studied by photo-chemical [3–6], biochemica [7,8], electrochemical [9,10], and direct electrical measurements [11–13]. Such as the experiments by Barton et al. have shown that electron transfer in DNA can span distances of several nanometers [14]. Dulic et al. studied electronic transport in short DNA chain under dry conditions and observed that the electrical con-ductivity of DNA molecules increased with the increase of the content of

G-C base pairs in the DNA chain [15]. The experiment of A. J. Storm et al. concluded that: DNA at the single-molecule scale is insulating at length scales larger than 40 nm [16]. It shows that the conductivity of DNA chain decreases with the increase of length, which is limited by the length of DNA.

The unique electrical properties of DNA molecules promise to become the construction module of electronic devices in the future [17, 18]. For example, the experimental results of Zhang et al. show that the thymine base holds great potential applications in designing a multi-functional spin molecular device [19]. Ilya et al. gave a study on the electron transport properties of adenine-thymine DNA base pairs. The results show that it exhibits significant conductance under low voltage bias, which provides a method for using a single DNA molecule to construct wires, switches and diodes [20]. It makes DNA molecules have a wide application prospect in electronic devices.

However, in experiments, the electrical conductivity of DNA chain is greatly affected by the experimental environment, and the mechanism of charge transfer in DNA chain and the properties of electron bonding has not been elucidated so far. In this study, we designed DNA chain molecules with reasonable length and stable structure through geo-metric optimization to study the electronic and atomic bonding

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properties of DNA molecules to obtain the regularity of base pairs in the DNA chain. We used density functional theory (DFT) calculations [21] to study the DNA chain with base sequences of TCTCCTTTCATCGCTTCC and AGAGGAAAGTAGCG. (Fig. 1 depicts the bases that are arranged from right to left). In particular, we evaluated the charge density distribution of the G-C and A-T base pairs in the double-stranded DNA molecules. In this study, we used the bond-order-length-strength (BOLS) notion [22] and the bond-charge (BC) model [23] to obtain the quantitative relationship between charge density and bond energy, thereby providing theoretical calculations for the study of local bond strain, atomic cohesion energy, and the bond energy density of DNA molecules.

2. Principles and methods of calculation

2.1. DFT calculation and Slater-Koster method

All the structural relaxation and electronic properties of the DNA chain with the TCTCCTTTCATCGCTTCC and AGAGGAAAGTAGCG sequences were calculated using QuantumATK. The simulation mentioned above utilized the Slater-Koster method and the Perdew-Burke-Ernzerhof (PBE) model [24] of DFT calculations to analyze the bonding, energetics, and electronic properties of the DNA chain. The geometric optimization yielded a stable DNA structure, as shown in Fig. 1.

The lattice parameters for A, B, and C are 30, 33, and 75 Å, respectively ($\alpha = \beta = \gamma = 90°$). We selected a vacuum layer with a thickness of 12 Å to eliminate the interaction between two adjacent cells. The K-point sampled at $1 \times 1 \times 1$, and the cut-off energy set to 100 Ha. In this calculation, energy and atomic force converge to 10^{-5} eV and 0.01 eV/Å, respectively. We also compared the differences of the Slater-Koster semi-empirical method and DFT method to compute the electronic properties of DNA molecules.

2.2. BOLS-BC notion

2.2.1. BOLS notion

According to the BOLS notion [26], the atomic undercoordination number shortens the bond length between atoms and enhances the chemical bond energy. Consequently, the bond length between the under-coordinated atoms decreases from the bulk value (d_b) to $d_i = C_i d_b$, whereas the bond energy increases from the bulk zero standard (E_b) to $E_i = C_i^m E_b$. Here, C_i is the coefficient of bond contraction, and d_i is the bond length of the atom. E_i represents the single bond energy, and the subscript i is the atomic layer number. E_b represents the single bond energy of the ideal crystal, and the subscript b represents the bulk atoms. m is the bond parameter that determines the relationship between the bond energy and the bond length of a particular substance. In most scenarios, $m = 1$. The chemical bond shrinkage results in a localized bond charge and the densification of energy density. The following equation represents the BOLS notion:

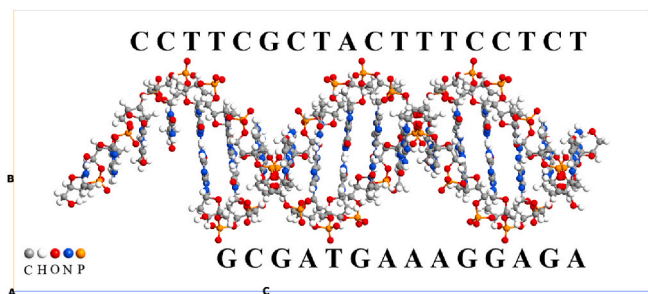$$C_i = d_i / d_b = 2 / \{1 + \exp[(12 - z_i) / (8z_i)]\} \text{ (bond contraction ratio)} \quad (1)$$

Fig. 1. Molecular geometry of the duplex DNA molecule.

where, z_i is the coordination number of an atom in the ith atomic layer.

2.2.2. BCE model

In theory, we contact DFT calculations to extend the existing BOLS theory to clarify the relationship between electronic charge and atomic bonding. Eq. (2) establishes the relationship between the Bohr radius and the charge density:

$$\frac{\rho(r_i)}{\rho(r_b)} = \frac{r_i^{-3}}{r_b^{-3}} = \frac{r_b^3}{r_i^3} \quad (2)$$

where, r_i and $\rho(r_i)$ are the Bohr radius and the charge density of a crystal with surface defects, respectively. r_b and $\rho(r_b)$ are the Bohr radius and charge density of an ideal crystal.

$$C_i^m = \frac{E_i}{E_b} \propto \left(\frac{1/d_i}{1/d_b}\right)^m \cong \frac{1/r_i}{1/r_b} \quad (3)$$

$$\frac{E_i}{E_b} \propto \sqrt[3]{\frac{\rho(r_i)}{\rho(r_b)}} \quad (4)$$

When an atom participates in bonding, the atomic orbitals overlap, and the ratio of d_b to d_i is an exact multiple of the Bohr radius. From this, the coefficient of bond contraction (C_i) can be calculated. Eqs. (3) and (4) explains the relationship between the charge density and the chemical bond (energy and length) according to the BOLS theory. Based on the BOLS-BC model, the functional relationship among the Bohr radius, bond energy, and charge density is obtained by dimensional analysis and unit conversion.

3. Results and discussion

3.1. Electronic property

To study the properties of the electrons in the DNA chain, we calculated the local density of states (LDOS) of the DNA molecules, as shown in Fig. 2a. The calculated results show that the s and d orbitals in the DNA molecule marginally contribute to the valence band electrons, indicating that the electrons are highly localized on the s and d orbitals.

The energy gaps of the DNA molecules are 2.64 and 3.90 eV when determined using the DFT calculation and the Slater-Koster method. Shapir, E. et al. applied scanning tunneling spectroscopy (STS) to determine the bandgap of the DNA molecule (2.5 eV) [25]. The bandgap (2.64 eV) calculated using DFT is consistent with the experimental results.

The Slater-Koster method confirms the presence of a few impurity peaks in the valence band and a weak electron interaction. The energy gap calculated using DFT is flat; there is no impurity peak, and the covalent bonds of the electrons in the valence band is secure, which is primarily due to the contribution of the hydrogen bonds of the bases. Several of the electrons in the valence band form covalent bonds. We analyzed the density of states (DOS) diagram of each atom, as shown in Fig. 2b.

We calculated a macromolecular structure with a total atomic number of 1008 and an atomic ratio of C:H:O:N:P = 31:36.5:19:11.3:3. The proportion of the H element is the largest, whereas that of the P element is the smallest. In the LDOS calculated using the DFT calculation, we find that the O atom produces the strongest peak, and the electrons in the O atom are localized near the Fermi surface. However, in the LDOS calculated using the Slater-Koster method, we were able to identify an impurity peak at ~0.72–1.18 eV, mainly comprised of C and N elements. Fig. 2c depicts the LDOS diagrams of two single molecular chains: TCTCCTTTCATCGCTTCC and AGAGGAAAGTAGCG. The results show that the intensity of the LDOS peak increases as the length of the
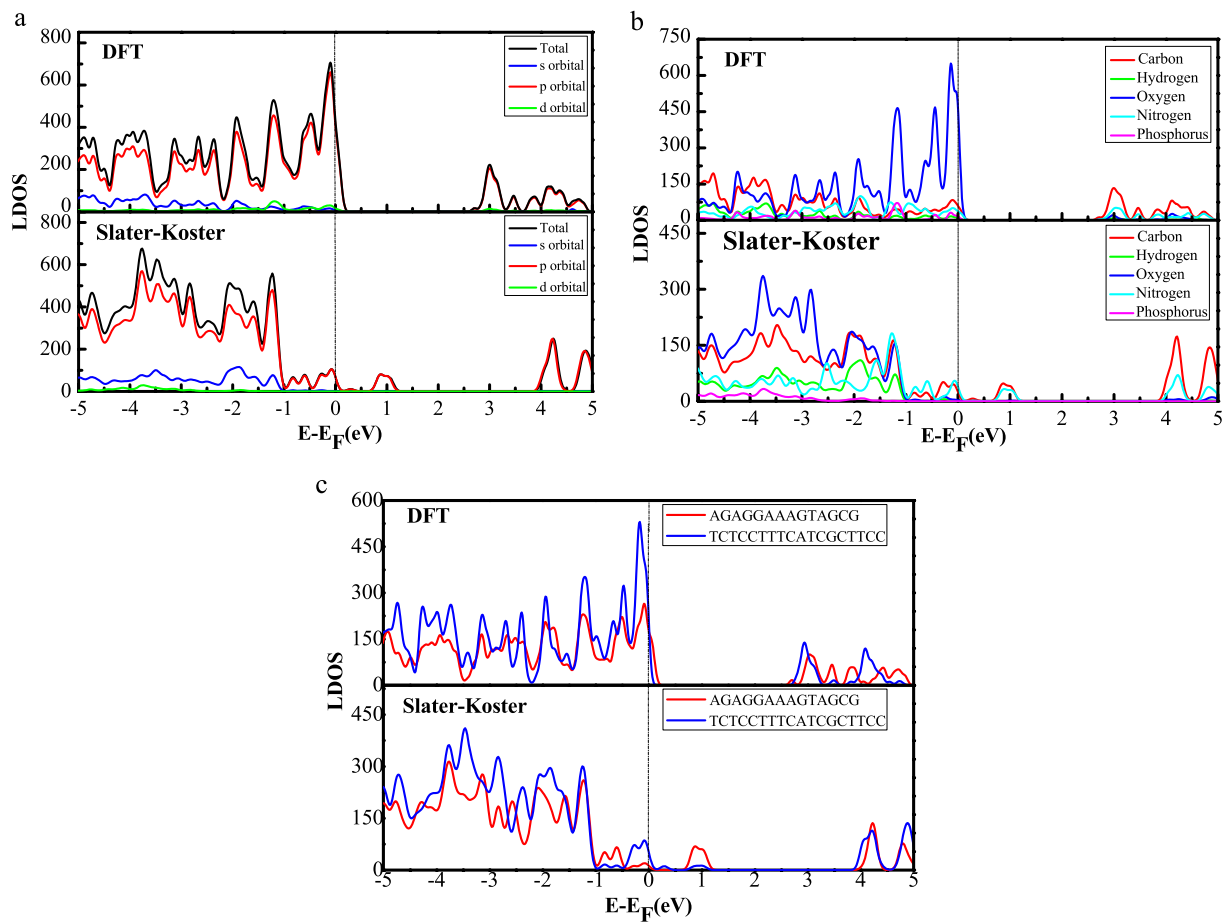
Fig. 2. LDOS (a),(b),(c) of DNA molecules calculated using DFT calculations with a PBE function and a Slater-Koster semi-empirical method.

DNA chain increases.

3.2. Electronic density analysis

To obtain the bonding information between the atoms of the DNA chain, we calculated the charge density of the DNA molecule, as shown in Fig. 3. To calculate the charge density, we selected four different positions, as shown in Fig. 3a. The bases C and T and the bonding processes of the base pairs A-T and G-C were calculated and analyzed. We confirmed that the charge density between atoms is mainly concentrated in the 0.8–7.2 $Å^{-3}$ range, indicated by the yellow/light green color, as shown in Table 1.

We use the BOLS-BC model formula to calculate and find that the number of effective coordination numbers of atoms in the DNA chain is between 1 and 3, And observed that there are several dark blue regions near the oxygen atoms. It exhibits a higher energy state, which is consistent with the energy change of the O atom in the calculated LDOS. This phenomenon is due to the fact that the DNA molecules are formed by the accumulation of bases and typically have a low coordination number z_i. This region of the electron density is very high, and the electrons are trapped around the nucleus. This is due to the energy entrapment and charge accumulation caused by the low coordination effect of the atom.

3.3. Local bond strain ε_z, atomic cohesive energy $E_c(i)$, and bond energy density $E_d(i)$

Additional information on the chemical bond parameters, such as the local bond strain ε_z, the atomic cohesive energy $E_c(i)$, and the bond energy density $E_d(i)$, can be obtained using the BOLS theoretical calculation:

$$\begin{cases} \varepsilon_i = (d_i - d_b)/d_b & \text{(local bond strain)} \\ E_c(i) = z_i E_i & \text{(atomic cohesive energy)} \\ E_d(i) = E_i/d_i^3 & \text{(bonding energy density)} \end{cases} \quad (5)$$

The position of each atom determines the charge density and the energy density distribution between orbitals. A high energy density results in a high bond strain and high bond energy. The lower atomic coordination number causes the corresponding bond energy stronger. As shown in Fig. 4 and Table 1, the local bond strain ($\varepsilon_i = C_i - 1$) and the relative bond energy density ($\delta E_d(z) = (E_i/d_i^3)/(E_b/d_b^3) - 1 = C^{-m-3} - 1$) increase with increasing bond energy ratio (C_i^{-1}). This effect is caused by the reduction of the coordination number of the atoms. The calculated results show that a quantum well is formed when bond energy ratio C_i^{-1} is greater than one. It is thereby indicating that the formation of the interatomic bond is mainly caused by energy entrapment and chemical bond enhanced. Based on the BOLS-BC model combined with the DFT calculations, an increase in the charge density is expected to result in an increase in the local bond energy, local bond strain ε_i, and relative bond energy density δE_d. Table 1 shows that the DNA molecule is a low coordination system, with an effective atomic coordination number z_i of 1–3. When the $\delta E_c(z) = z_i E_i/z_b E_b$ is stabilizes in a specific range of values 0.71–0.80, as is shown in Fig. 4 and Table 1. Quantitative information on the BOLS-BC model facilitates the comprehension of the chemical bond properties of a DNA molecule.

4. Conclusion

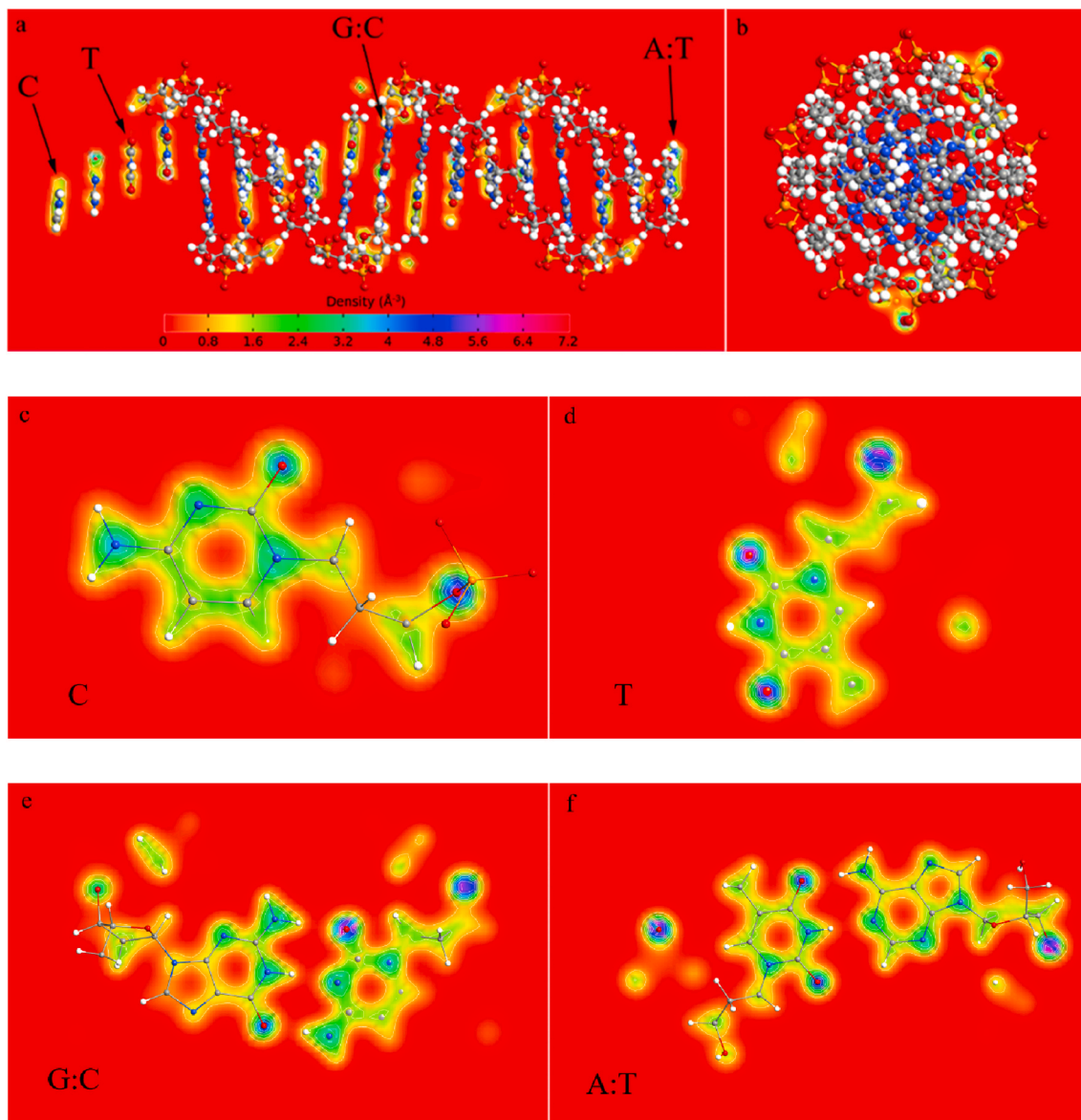We systematically studied the atomic bond and electronic behavior

Fig. 3. Charge density of positive, side, and partial cross-sections of the DNA chain.

Table 1
Obtained information regarding the normalized charge density $\rho(r_b)$ and $\rho(r_i)$, bond energy ratio C_i^{-1}, atomic coordination number z_i, local bond strain ε_i (%), relative atomic cohesive energy δE_c (%), and the relative bond-energy density δE_d (%) from Eq. (5).

Density ($\mathring{A}^{-3}$)	Normalized		C_i^{-1}	z_i	ε_i (%)	δE_c (%)	δE_d(%)
	$\rho(r_b)$	$\rho(r_i)$					
0.800	0.022	0.022	1.000	12.000	0.000	0.000	0.000
1.600	0.022	0.044	1.260	2.759	20.630	71.029	151.984
2.400	0.022	0.067	1.442	1.977	30.664	76.237	332.675
3.200	0.022	0.089	1.587	1.663	37.004	78.000	534.960
4.000	0.022	0.111	1.710	1.487	41.520	78.811	754.988
4.800	0.022	0.133	1.817	1.372	44.968	79.230	990.272
5.600	0.022	0.156	1.913	1.289	47.724	79.454	1239.052
6.400	0.022	0.178	2.000	1.226	50.000	79.569	1500.000
7.200	0.022	0.200	2.080	1.176	51.925	79.617	1772.075

of the DNA molecule chain by using DFT calculations and the BOLS-BC model. Besides, we studied the electronic bonding properties of the A-T and G-C base pairs. The charge density, bond energy density, and atomic binding energy of the DNA chain are calculated using the BOLS-BC model. The results show that the bonding mode of atoms with low

coordination numbers in the DNA chain is mainly due to energy entrapment and charge aggregation. In addition, the local bond strain and the relative bond energy density increase as the bond energy ratio increases. DFT calculations of the relevant electronic properties show that the DNA chain demonstrate a semiconductor bandgap, indicating
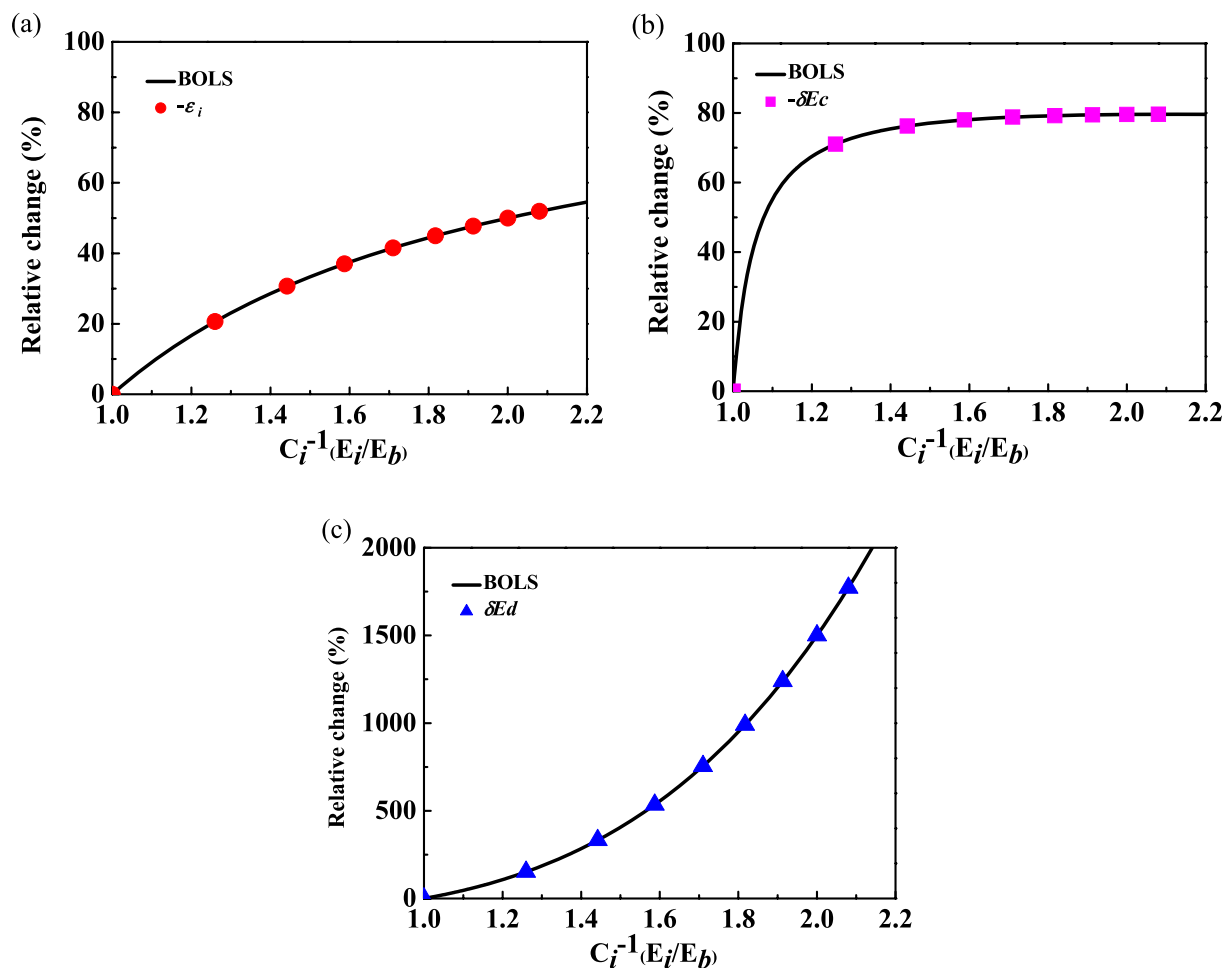
Fig. 4. Relationship between the bond energy ratio C_i^{-1}, (a) local bond strain ε_i, (b) atomic cohesive energy δE_c, and (c) bond energy density δE_d of the DNA molecule.

that the DNA molecules have semiconductor properties.

CRediT authorship contribution statement

Anlin Deng: performed calculations and wrote the paper. **Hanze Li:** performed calculations and wrote the paper. **Maolin Bo:** Formal analysis, developed BOLS-BC modelling and analysis. **ZhongKai Huang:** revised the paper. **Lei Li:** and. **Chuang Yao:** Formal analysis, Data curation, performed data analysis. **Fengqin Li:** performed calculations and wrote the paper. All authors read and contributed to the manuscript.

Declaration of competing interest

We declare that we have no conflict of interest.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.bbrep.2020.100804.

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