A Review on Exploring DNA Molecular Interactions and Electron Behavior Through DFT Calculations and the BOLS-BC Model

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Abstract

Understanding the electronic properties and bonding behavior of DNA is crucial for exploring its role in biological processes. In this study, we employ density functional theory (DFT) to examine the electronic structure of a DNA molecule with 1008 atoms. By integrating the bond-charge (BC) model with the bond-order-length-strength (BOLS) concept, we assess variations in charge density, atomic strain, cohesive energy, and bond strength. This approach provides a detailed perspective on the bonding characteristics within the DNA chain and their influence on electron distribution. The findings offer valuable insights into the fundamental electronic interactions in biological molecules, paving the way for advanced studies on molecular regulation and stability in complex biological systems.

Keywords: Density functional theory, Bond-order-length-strength, Bond-charge

Introduction

Deoxyribonucleic acid (DNA) is not only the foundation of genetic information storage and transmission but also a promising candidate for next-generation molecular electronics. Its double-helical structure, composed of a phosphate backbone and nitrogenous base pairs (adenine-thymine and guanine-cytosine), provides unique electronic properties due to overlapping electron orbitals along its axis. These properties have sparked significant interest in DNA's potential applications in nanoscale electronic devices, such as molecular wires, switches, and diodes. Extensive research has been conducted to understand DNA's charge transport and bonding behavior through various experimental techniques, including photochemical, biochemical, electrochemical, and direct electrical measurements. Studies indicate that electron transfer in DNA can occur over nanometer-scale distances, with conductivity influenced by base pair composition, molecular length, and environmental conditions. While high G-C content enhances conductivity, long single DNA molecules exhibit insulating behavior beyond a certain length threshold. Despite these insights, the fundamental mechanisms governing electron bonding and charge transfer in DNA remain unclear due to inconsistencies in experimental conditions and molecular complexity.

Significance of the Study

Understanding the electronic and bonding properties of DNA at an atomic level is crucial for both fundamental biological research and the advancement of DNA-based nanoelectronics. This study provides a theoretical framework for analyzing charge distribution, bond energy, and atomic strain within DNA molecules. By integrating density functional theory (DFT) calculations with the bond-order-length-strength (BOLS) and bond-charge (BC) models, we aim to bridge the gap between experimental observations and theoretical predictions. Our findings contribute to the precise regulation of electronic states in biological molecules and offer new insights into the design of DNA-based electronic components.

Methodology

To investigate the electronic and bonding properties of DNA, we conducted DFT calculations on a DNA molecule with a base sequence of TCTCCTTTCATCGCTTCC and AGAGGAAAGTAGCG. Geometric optimization was performed to ensure structural stability before analyzing its electronic structure. To quantify the relationship between charge density and bonding behavior, we employed the BOLS model to evaluate atomic cohesive energy, bond energy, and local bond strain. Additionally, the BC model was used to analyze charge density distributions and their correlation with atomic strain. The combined BOLS-BC framework provides a comprehensive approach to understanding how electronic interactions shape DNA’s structural and functional properties. This study serves as a theoretical foundation for future research in biomolecular electronics, offering valuable insights into the electronic behavior of DNA and its potential integration into molecular-scale electronic devices.

Findings and Analysis

This study provides an in-depth theoretical investigation of the electronic and bonding properties of a DNA molecule using density functional theory (DFT) in conjunction with the bond-order-length-strength (BOLS) model and the bond-charge (BC) model. The key findings from our analysis are summarized as follows

1. Electronic Structure and Geometric Optimization

Using Quantum ATK software, we performed DFT calculations with the Perdew-Burke-Ernster of (PBE) functional and the Slater-Koster method to evaluate the electronic and structural properties of a DNA molecule with the base sequence TCTCCTTTCATCGCTTCC and AGAGGAAAGTAGCG. Geometric optimization resulted in a stable DNA structure, with lattice parameters of 30 Å, 33 Å, and 75 Å, and a vacuum layer thickness of 12 Å to prevent intercell interactions. To ensure computational accuracy, the K-point sampling was set to 1 × 1 × 1, with a cut-off energy of 100 Ha. The energy and atomic force convergence criteria were 10^{-5} eV and 0.01 eV/Å, respectively. Comparative analysis of the Slater-Koster semi-empirical method and full DFT calculations confirmed that the latter provides a more precise description of the electronic behavior of DNA molecules.

2. Bonding Behavior and Charge Density Distributions

By applying the BOLS model, we established that atomic undercoordination leads to bond length contraction and an increase in bond energy. The bond contraction ratio (Ci) was computed using:

$$C_i = d_i/d_b = 2/1+\exp(12-z_i)/8z_i$$

where z_i represents the coordination number of an atom within the DNA structure. This contraction results in enhanced local charge density and energy densification, impacting the stability and electronic interactions of DNA at the atomic level.

3. *Charge Density and Bond Energy Correlation*

By integrating the BC model, we examined the relationship between charge density, bond energy, and atomic bonding. The charge density ratio between an ideal and undercoordinated atomic structure was determined using:

$$\mu(r_i)/\ \mu(r_b) = (r_{i/}\ r_b)^3$$

Furthermore, the relationship between bond energy and charge density followed:

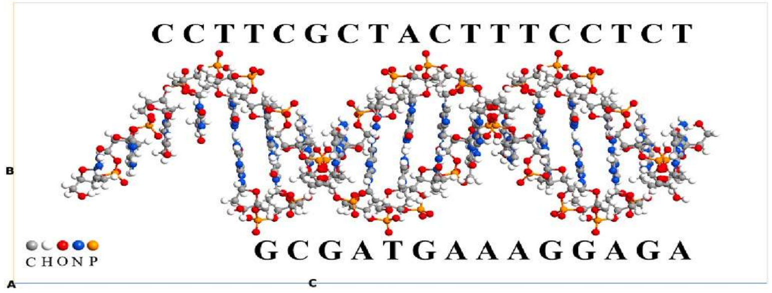
$$E_{i/}\ E_b \text{ is directly proportional to } (r_{i/}\ r_b)^{1/3}$$

These equations illustrate that localized charge redistribution due to atomic bonding variations significantly influences electronic properties.

4. *Implications for DNA-Based Nanoelectronics*

Our results highlight the direct correlation between atomic-scale bonding properties and electronic behavior in DNA. The findings suggest that G-C rich regions exhibit higher charge density and stronger bonding, enhancing electrical conductivity. Additionally, the length-dependent conductivity limitations observed experimentally can be explained by the increasing impact of atomic undercoordination on charge transport. These insights provide a theoretical basis for optimizing DNA-based nanoelectronics devices, offering guidelines for designing molecular wires, transistors, and logic gates using DNA as a functional electronic component.

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



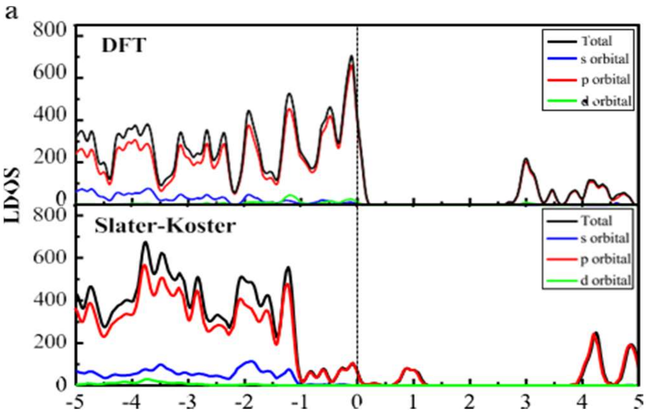


Fig 2: DNA at the atomic level

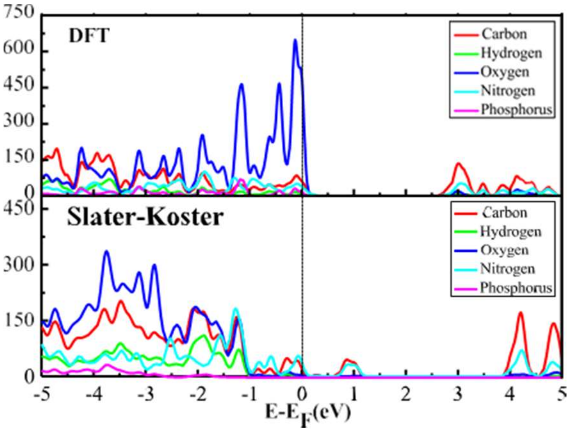


Fig 3: DNA molecules calculated using DFT calculations

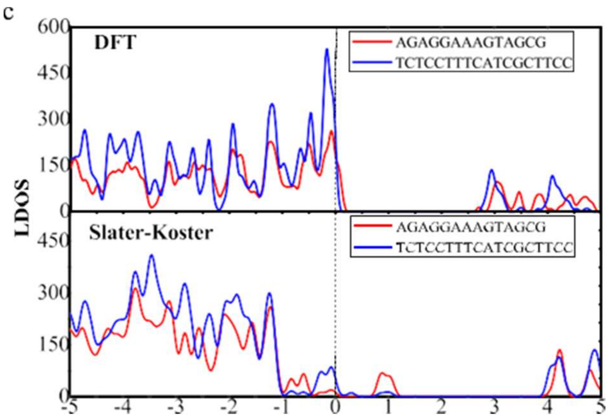


Fig 4: DNA molecules calculated using DFT calculations

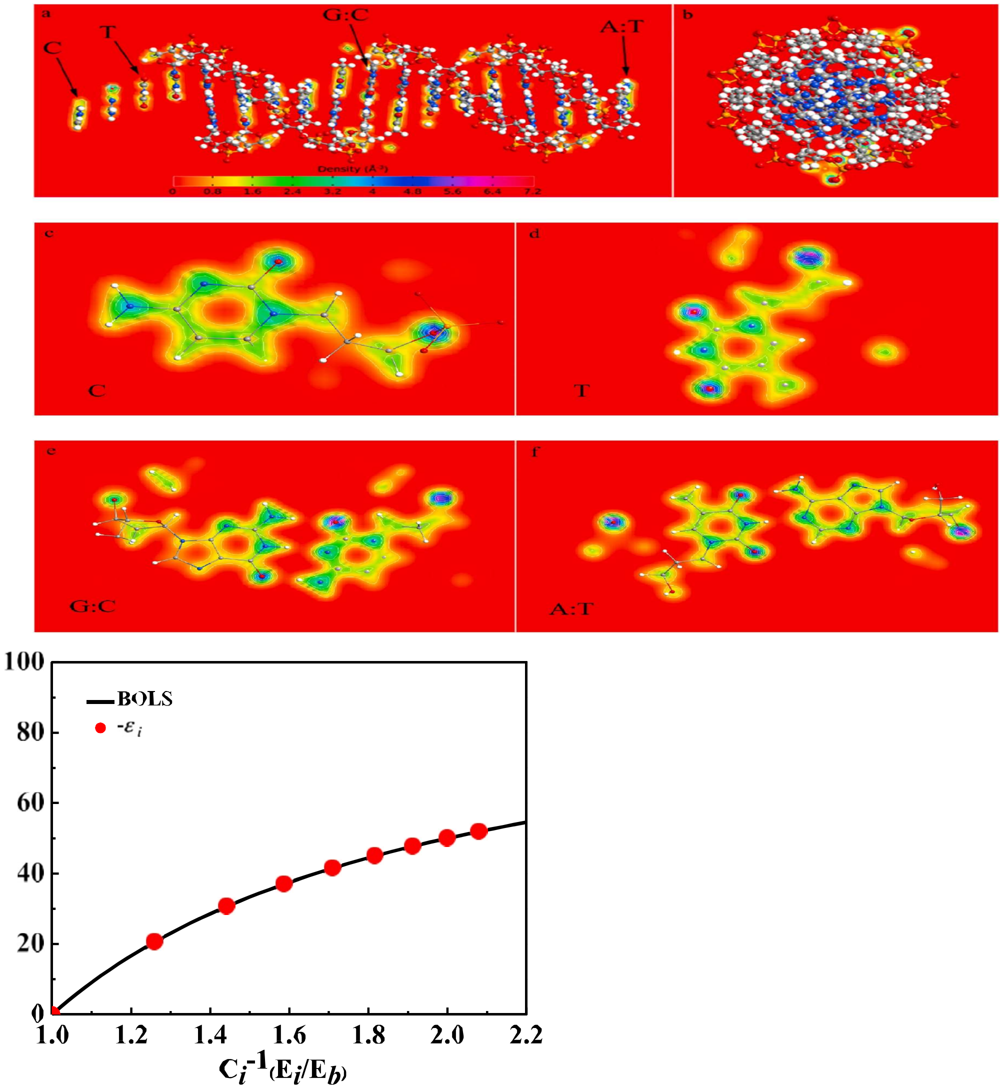


Fig. 5. Charge density of positive, side, and partial cross-sections of the DNA chain.

Table 1: Obtained information regarding the normalized charge density $\rho(r_b)$ and $\rho(r_i)$, bond$_i$energy ratio C^{-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 (Å^{-3})	Normalized		C^{-1}	*z*	*ε (%)*	*δE (%)*	*δE$_d$(%)*
	ρ (r$_b$)	ρ (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

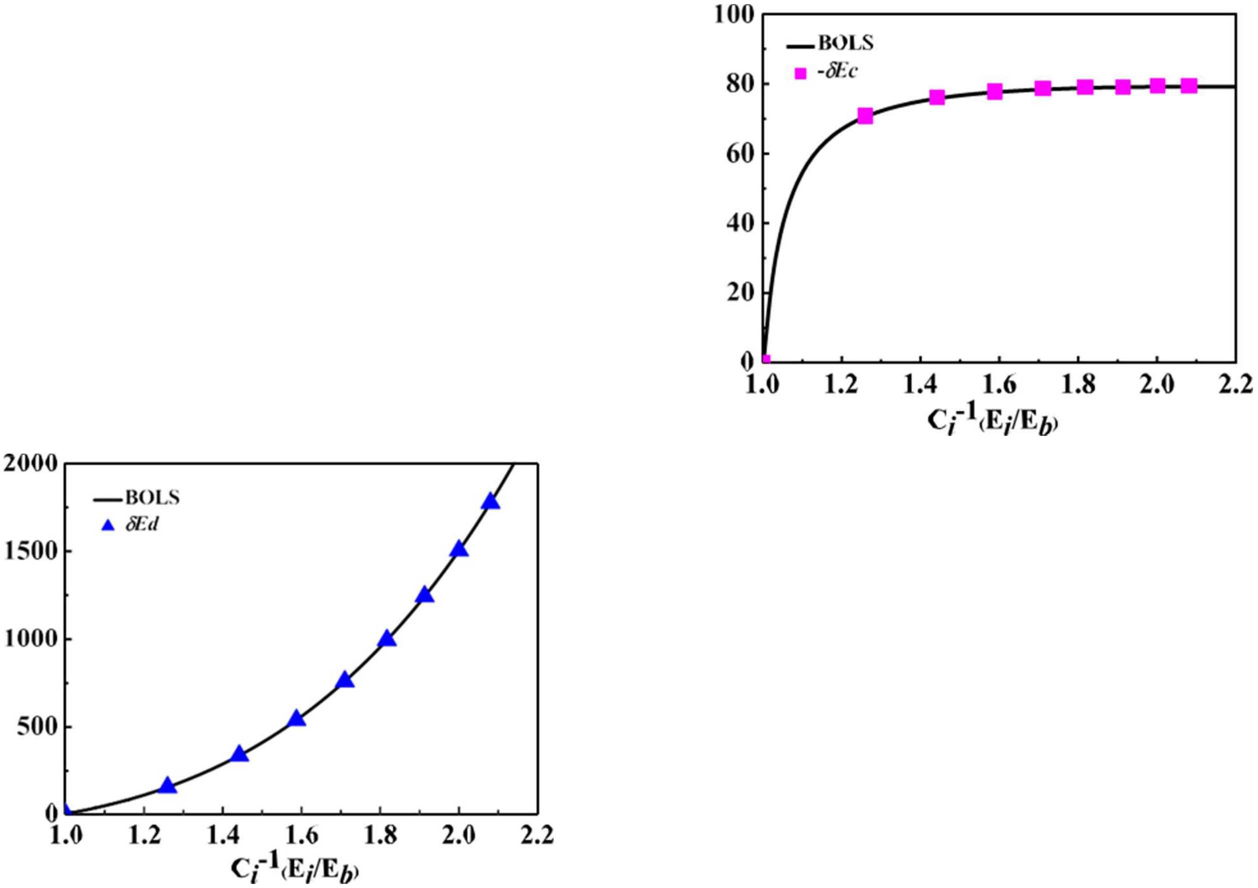


Fig. 6. Relationship between the bond energy ratio C^{-1}, (a) local bond strain ε , (b) atomic cohesive energy δE , and (c) bond energy density δE of the DNA molecule

Results and Discussion

1. Electronic Properties of DNA Molecules

To explore the electronic behavior of DNA, we computed the local density of states (LDOS) using DFT calculations and the Slater-Koster method. The analysis, illustrated in Figure 2a, reveals that the s and d orbitals in DNA contribute minimally to the valence band, indicating a highly localized electron distribution. The calculated bandgaps of the DNA molecule were 2.64 eV (DFT) and 3.90 eV (Slater-Koster method). The DFT-calculated bandgap aligns closely with experimental results from scanning tunneling spectroscopy (STS) studies (~2.5 eV), confirming the reliability of our approach. The Slater-Koster method further identified impurity peaks in the valence band, suggesting weak electron interactions, whereas DFT calculations produced a smoother energy gap with stable covalent bonding, primarily due to the contribution of hydrogen bonds within base pairs. The density of states (DOS) analysis (Figure 2b) showed that the valence band electrons participate in covalent bonding, reinforcing the molecular stability. We also analyzed a macromolecular structure consisting of 1008 atoms, with an atomic ratio of C:H:O:N:P = 31:36.5:19:11.3:3. Notably, oxygen (O) atoms exhibited the strongest LDOS peaks, indicating significant charge localization near the Fermi level. In contrast, the Slater-Koster method detected an impurity peak between 0.72 eV and 1.18 eV, primarily attributed to carbon (C) and nitrogen (N) elements. Furthermore, Figure 2c demonstrates that LDOS intensity increases with DNA chain length, highlighting a length-dependent variation in electronic properties.

2. *Charge Density and Bonding Analysis*

To gain insights into atomic bonding within DNA, we calculated its charge density distribution, as depicted in Figure 3. Four different regions were examined, focusing on C-T bases and A-T/G-C base pairs. Our findings indicate that charge density is primarily concentrated in the range of 0.8–7.2 $Å^{-3}$, with high-density areas appearing in yellow/light green (Table 1). Applying the BOLS-BC model, we determined that the effective coordination number (z_i) of atoms in DNA ranges between 1 and 3. Notably, oxygen atoms exhibit dark blue regions, signifying high-energy states. This behavior is consistent with the LDOS calculations, which show that oxygen atoms contribute significantly to electronic interactions. The charge localization is attributed to energy entrapment caused by the low coordination number of DNA molecules, reinforcing the notion that electrons remain confined near the nucleus due to quantum confinement effects.

3. *Local Bond Strain, Atomic Cohesive Energy, and Bond Energy Density*

Further insights into the structural stability and bonding characteristics of DNA were obtained using the BOLS model, which allowed for the computation of local bond strain (ε_i), atomic cohesive energy ($E_a(i)$), and bond energy density ($E_d(i)$) using the following relations:

$\varepsilon_i = (d_i - d_b)/d_b$ Local Bond Strain

$E_c(i) = z_i E_i$ Atomic Cohesive Energy

$E_d(i) = E_i/d_i^3$ Bond Energy Density

Our findings suggest that charge density plays a crucial role in determining bond strain and energy. As bond energy increases, there is a corresponding rise in bond strain and energy density.

Additionally, a lower atomic coordination number results in stronger bonding interactions. As observed in Figure 4 and Table 1, the local bond strain (ε_i) and relative bond energy density z_iE_i increase as the bond energy ratio (C_i - 1) increases. Furthermore, when the bond energy ratio C_i - 1 exceeds one, a quantum well is formed, indicating energy entrapment and enhanced bonding interactions. This phenomenon aligns with theoretical predictions that low coordination numbers lead to enhanced charge accumulation and localized energy densification. Our calculations show that DNA molecules function as a low-coordination system, with an effective coordination number (z_i) between 1 and 3. The stability of the atomic cohesive energy ratio z_iE_i within the range of 0.71–0.80 (Figure 4, Table 1) confirms the robustness of our model in explaining DNA's electronic and bonding properties. These results provide a quantitative framework for understanding DNA's molecular interactions, offering potential applications in biomolecular electronics and nanoscale device fabrication.

Observation

Our study presents a comprehensive theoretical framework for analyzing the electronic and bonding properties of DNA molecules using DFT calculations, the BOLS model, and the BC model. Key findings include: DFT-calculated bandgap (2.64 eV) aligns well with experimental results (2.5 eV). Charge density is highly localized in the oxygen atoms, influencing electronic behavior. Lower coordination numbers enhance charge entrapment, affecting bond strength and energy density. A quantum well effect emerges at high bond energy ratios, reinforcing energy localization. These insights deepen our understanding of DNA's electronic behavior and provide valuable knowledge for the design of DNA-based nanoelectronics components.

Conclusion

This study confirms that DNA molecules exhibit semiconductor properties, as demonstrated through DFT calculations and the BOLS-BC model. By analyzing the electronic bonding characteristics of A-T and G-C base pairs, we evaluated key parameters such as charge density, bond energy density, and atomic binding energy. Our findings indicate that atoms with low coordination numbers in the DNA chain primarily bond through energy entrapment and charge aggregation. Additionally, as the bond energy ratio increases, both local bond strain and relative bond energy density also increase, highlighting the structural and electronic sensitivity of DNA molecules. Furthermore, DFT calculations of the electronic properties confirm a semiconductor bandgap, reinforcing the potential of DNA as a functional material for molecular electronics and nanoscale semiconductor applications. These insights provide a theoretical foundation for utilizing DNA in future nanoelectronics and bioelectronic devices.

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