Band Gap and DOS in Multi-layer Graphene Systems

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Abstract. Graphene is a single layer of carbon atoms arranged in a hexagonal honeycomb lattice, characterized by sp2 hybridization. It is a nanomaterial known for its excellent thermal and electrical conductivity, making it ideal for the next generation of faster, thinner electronic devices. Notably, in 2018, researchers discovered that when two graphene layers are twisted at a specific “magic angle,” the material exhibits superconductivity at low temperatures, which arises from strong electron correlations in flat electronic bands. The unique properties of graphene, such as high electron mobility, tensile strength, and transparency, make it a promising material for various applications including flexible electronics, quantum computing, and advanced sensors. The material's potential to revolutionize industries like energy, electronics, and healthcare emphasizes the need for further research into its electronic behavior and stacking configurations. In this paper, we explore the multi-layer graphene systems with AB and ABC stacking, and their electronic properties including band structures and density of state (DOS). By applying tight-binding model to these systems, we conclude that both the band gaps and energy difference between DOS peaks can be widen by increasing the displacement fields.

Keywords: Graphene, superconductivity, tight-binding model.

1. Background

1.1. Graphene

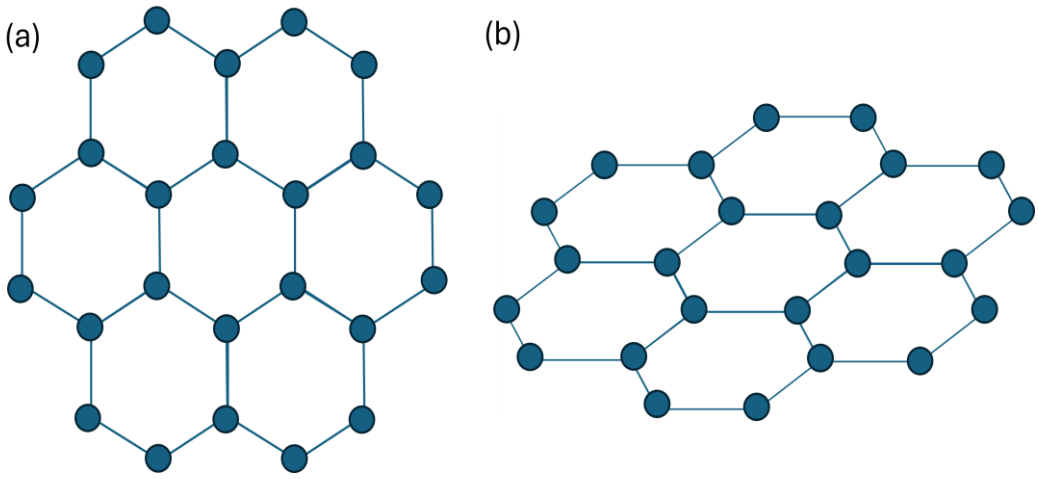

Fig 1. Top/Front view of the honeycomb lattice structure in single-layer graphene. (a) Top view. (b) Front view.

Graphene is an allotrope of carbon, which consists of a single layer of atoms arranged in a honeycomb lattice structure, whose top and front views are shown in Fig.1. The carbon atoms of graphene form a hexagonal honeycomb lattice with sp2 hybridized orbitals in a planar thin film, with a thickness equivalent to the diameter of one carbon atom. Graphene is a nano material with excellent thermal and electrical conductivity, with a resistivity (about $10-6\Omega \cdot$ cm) lower than copper or silver. Therefore, this material can be used to develop a new generation of electronic devices that are thinner and conduct electricity faster. Its special superconductivity under certain condition also encourages us to have further research on this material.

1.2. Stacking Methods

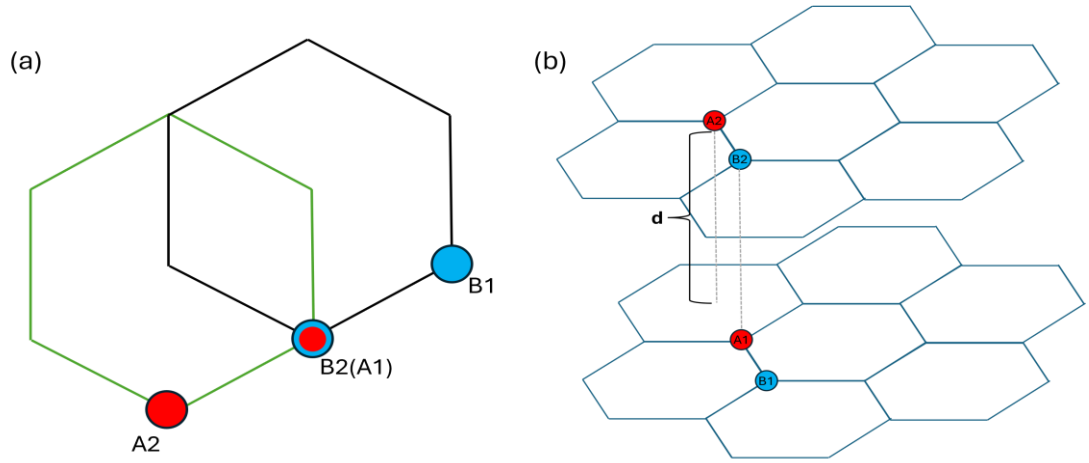

Fig 2. (a) Top view of the unit cell in AB stacked graphene.
(b) Front view of the AB stacked graphene, with A_i and B_i (i =1, 2) representing the four atoms in one unit cell while d is the inter-layer distance.

Multi-layer graphene refers to the graphene system consists of several single-layer graphene, which stacks in specific arrange. The idea of the stacking method is introduced via the AB bilayer graphene case in this paper. The term AB refers to shifting one of the graphene layers in the direction along one-third of the translation vector. Each unit cell of AB bilayer graphene consists of four atoms, Ai and Bi (i = 1, 2). As shown in Fig.2, we could construct the unit cell with four atoms paralleled, which is so called basis in condensed matter physics. Held by van der Waals forces in the z direction, the arrangement of hexagonal graphene sheets will form different sequences and therefore stacked graphene. ABC-stacked graphene, another graphene system with layer number up to three, will be also studied in this report. All the configurations of stacked graphene show some unique electronic behavior that can be significant for both study and industrial applications.

1.3. Superconductor

Can graphene be a superconductor? Graphene is not naturally a superconductor. However, in 2018, scientists at the Massachusetts Institute of Technology discovered that, under the right conditions, graphene could become a superconductor if one piece of graphene were laid on top of another piece and the layers were twisted to a specific angle—1.08 degrees—creating twisted bilayer graphene. This special angle is known as magic angle. This graphene is so called twisted bilayer graphene. [1]

People will wonder why the superconductivity happens with two twisted layers. This behavior lies in the interaction between the electronic bands. At the magic angle, there will be a flat band where we can find strong electron correlations, resulting in superconductivity with a low temperature around several Kelvin.

1.4. Improtance

Based on the above discussion, we learn that the electronic bands in graphene will be worth deeply studying, which will help us understand the mechanism behind this behavior. In addition, as multi-layers of carbon atoms arranged in a two-dimensional honeycomb lattice with specific stacking methods, graphene is highly important due to its exceptional properties and versatile applications. It is one of the strongest and most flexible materials known, with a tensile strength surpassing that of steel. Graphene's high electron mobility and zero-bandgap semiconductor nature make it ideal for high-speed electronics and potential quantum computing. Its excellent thermal conductivity and optical transparency (absorbing only about 2.3% of light) are valuable for heat management and transparent conductive films in touchscreens and solar cells. Additionally, graphene's chemical stability and versatility have led to its use in flexible electronics, energy storage, composite materials, biomedical applications, water purification, and advanced sensors. These unique characteristics,

combined with its potential to revolutionize multiple industries, including electronics, energy, and healthcare, underscore graphene's significance in both fundamental research and practical applications.

2. Numerical Methods

2.1. Bohr Model

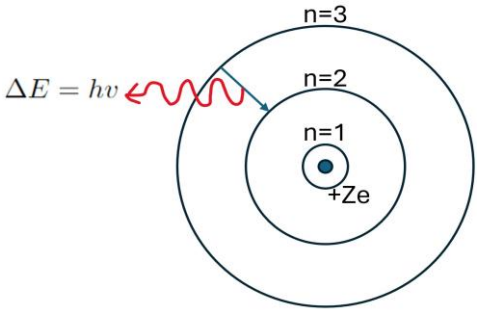

Fig 3. Bohr atom model with the number of protons equal to Z. The nucleus is surrounded by electron orbit n=1, 2, 3...

The plum pudding model of J J Thomson is the first scientific model to study the internal structure of atom. This model distributes the electrons uniformly inside the atom while the positive charges will be just like the plums inserted into it. Compared with this original model, the Bohr model[2] was more successful. This model suggests that the atom consists of a dense and small nucleus and is surrounded by the electrons running in a circle, as shown in Fig. 3. We can find that this structure is very similar to that of the Solar System. The nuclear is analogous to the sun while the electrons are like the surrounding planets. One thing to mention is that the attraction force between the nuclear and electrons is electrostatic force instead of gravity. Furthermore, the quantum mechanism[3] will help us understand the electron state as a wave instead of pure particles.

2.2. Tight-Binding Model

A "tight-binding model"[4] in solid-state physics is a method for calculating the electronic band structure of a material by approximating the electron wave functions as a superposition of localized atomic orbitals, essentially assuming electrons primarily reside around individual atoms and only have a small probability of "hopping" to neighboring sites due to quantum tunneling; it's closely related to the Linear Combination of Atomic Orbitals (LCAO) method used in chemistry, offering a simplified way to analyze electronic properties of a crystal structure by focusing on nearest neighbor interactions.

Based on the tight-binding model, we can construct the hamiltonian matrix for graphene systems. Let's take AB graphene as an example:

$$H_{AB} = \begin{bmatrix} -\frac{\Delta_1}{2} + \delta & -\gamma_0 f(\mathbf{k}) & \gamma_4 f^*(\mathbf{k}) & \gamma_1 \\ -\gamma_0 f^*(\mathbf{k}) & -\frac{\Delta_1}{2} & -\gamma_3 f(\mathbf{k}) & \gamma_4 f^*(\mathbf{k}) \\ \gamma_4 f(\mathbf{k}) & -\gamma_3 f^*(\mathbf{k}) & \frac{\Delta_1}{2} & -\gamma_0 f(\mathbf{k}) \\ \gamma_1 & \gamma_4 f(\mathbf{k}) & -\gamma_0 f^*(\mathbf{k}) & \frac{\Delta_1}{2} + \delta \end{bmatrix} \quad (1)$$

Where $f(\mathbf{k}) = e^{-\frac{ik_y a}{\sqrt{3}}} + 2e^{\frac{ik_y a}{2\sqrt{3}}} \cos\left(\frac{k_x a}{2}\right)$ with a = 0.246 nm. γ_0 describes the nearest neighbor hopping amplitude between the atoms within the same layer, γ_i (i=1, 3, 4) refers to the interlayer hopping parameters whose values are referred to the article and discussed in the following two tables. δ is the on-site potential term that only exists at sites A_1 and B_2, which have neighbors in the adjacent layers. The following are two tables of parameters about γ_i, for AB and ABC graphene:

Table 1. Minimal tight-binding parameters in AB graphene, expressed in eV.

Parameters (eV)	γ_0	γ_1	γ_3	γ_4	δ
	3.16	0.381	0.380	0.140	0.022

Explanation for Table 1: The tight-binding model assumes that the electronic wavefunctions in AB graphene can be approximated as a linear combination of atomic orbitals. The Hamiltonian matrix H_{AB} includes terms that represent the hopping between nearest-neighbor carbon atoms, as well as on-site energies. The parameter γ_0 represents the main hopping integral, while other γ_i parameters [5] describe additional hopping processes and their respective energies.

Table 2. Minimal tight-binding parameters in ABC graphene, expressed in eV.

Parameters (eV)	γ_0	γ_1	γ_2	γ_3	γ_4	γ_5	δ
	3.10	0.370	-0.032	0.300	0.040	0.050	0.040

Explanation for Table 2: the tight-binding parameters differ slightly, reflecting the different stacking sequence. The parameter γ_0 remains the primary hopping integral, but the presence of γ_2 and γ_5 indicates the influence of next-nearest neighbor interactions and interlayer coupling, respectively. These parameters are crucial for accurately describing the electronic structure and predicting the material's properties.

After constructing all the Hamiltonian, we can obtain the eigenvalues with given momentum **k** in the first Brillouin zone (BZ) [6], which is a uniquely defined primitive cell in the reciprocal space. To be specific, we will choose momentum along high-symmetric path in the first BZ, which helps us learn more about the band structure of graphene systems.

3. Results

In this article, we apply the tight-binding model to AB and ABC graphene systems given different electric displacement fields' Δ_1. Based on the comparison between the band gaps with different Δ_1 [5, 7], we could further analyze the electronic band structures and density of state (DOS) in graphene systems, which may provide predictions for experiments.

3.1. AB graphene

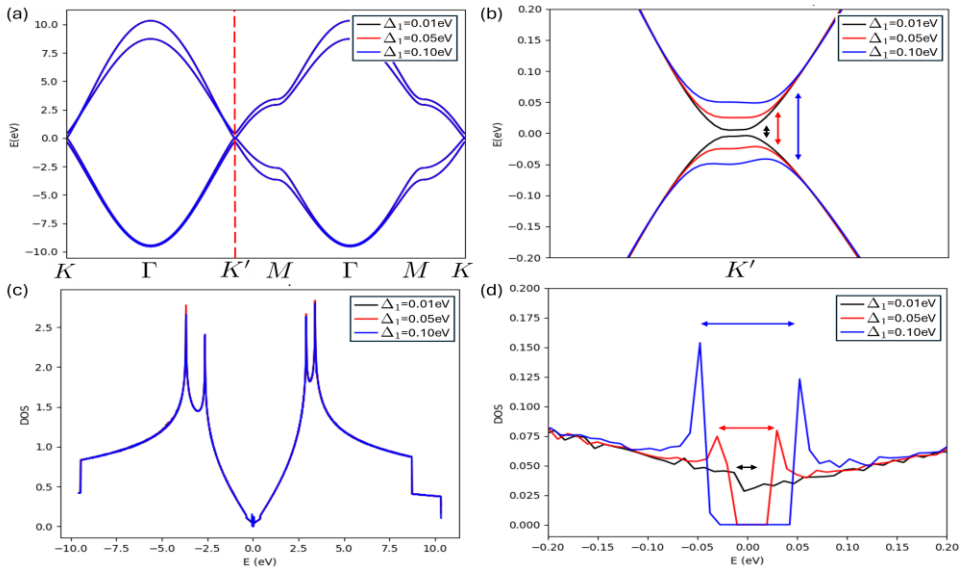

Fig 4. Band and DOS in AB graphene with different displacement field Δ1 =0.01eV, 0.05eV, 0.1eV. (a) The band structure in AB graphene along high-symmetry path. (b) K-point band structure. (c) The density of state in AB graphene. (d) DOS near the fermi energy of graphene systems.

As shown in Figure 4, the band structures and DOS of AB graphene vary with the displacement field Δ_1. However, the influnce on the band structures will be small as displayed in Figure 4 (a). Three band structures given different displacement fields seem to overlap totally with each other. If we focus on the K-point band structure instead of the total pictures, we will further find that the band gaps, represented by the double arrows in Figure 4 (b), will be widen as the Δ_1 increases. Similar to band structures, DOS shows distinct peaks corresponding to the allowed energy levels. To be specific, DOS peaks will appear near the fermi energy level. The energy difference between two peaks in Figure 4 (d) will be close to the band gaps. This demonstrates the sensitivity of the electronic properties to the interlayer interaction. To increase the accuracy of the calculation, we choose five hundred moment **k** between two high symmetric points, like *K* and Γ. The same for DOS calculations, we choose $N_k = 4000 \times 4000$ **k** points within the first BZ, and we set the energy difference in the x-axis to $e_{step} = 0.01eV$.

3.2. ABC graphene

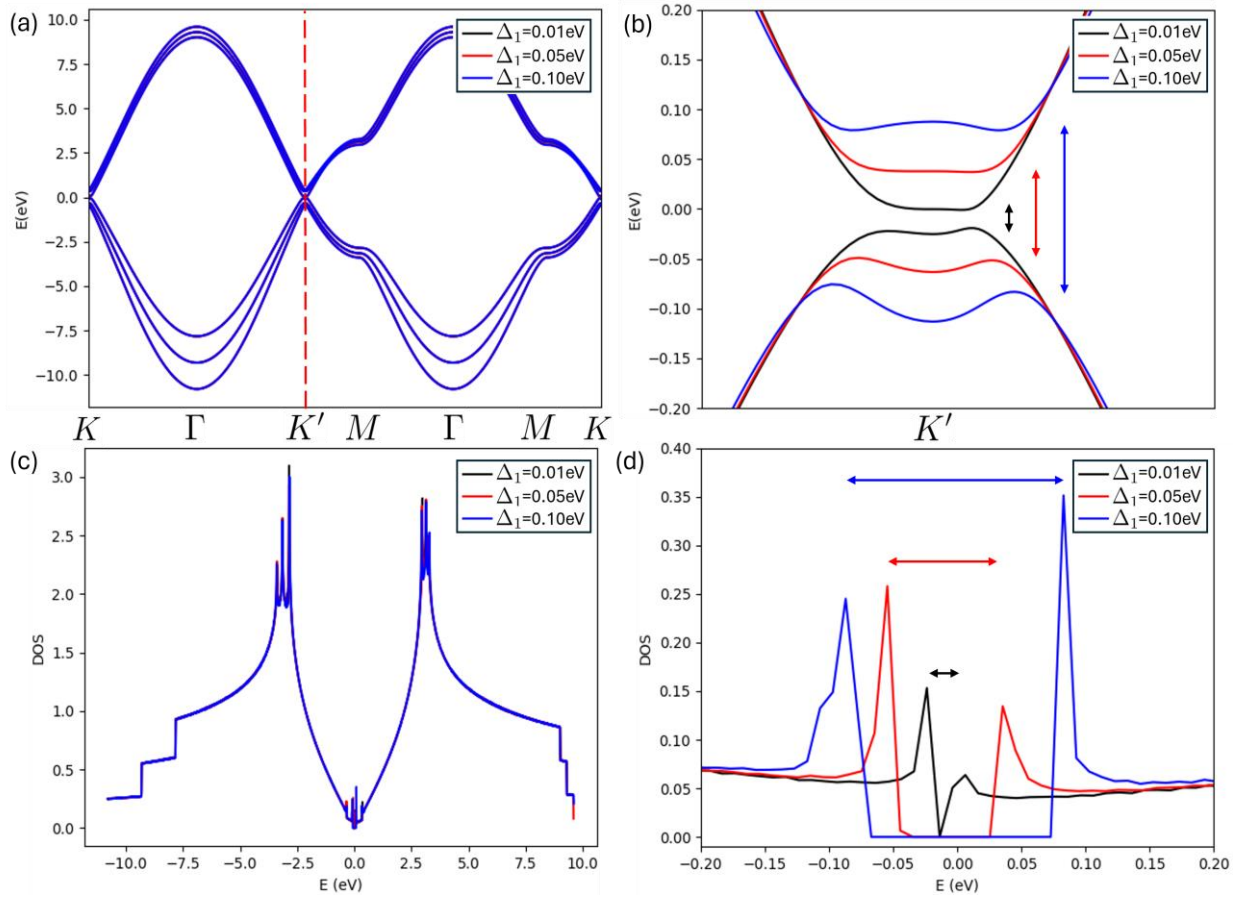

Fig 5. Band and DOS in ABC graphene with different displacement field Δ1 =0.01eV, 0.05eV, 0.1eV. (a) The band structure in ABC graphene along high-symmetry path. (b) K-point band structure. (c) The density of state in ABC graphene. (d) DOS near the fermi energy of graphene systems.

Similar to AB graphene, the electronic properties of ABC graphene, as depicted in Figure 5, also exhibit dependence on Δ_1. One interesting difference is that there will be more DOS peaks in ABC graphene systems. The differences in the band structure and DOS between AB and ABC graphene highlight the impact of the stacking sequence on the material's electronic behavior. In ABC graphene systems, the band gaps, represented by the double arrows in Figure 5 (b), will be widen when increasing the displacement fields.

4. Discussion

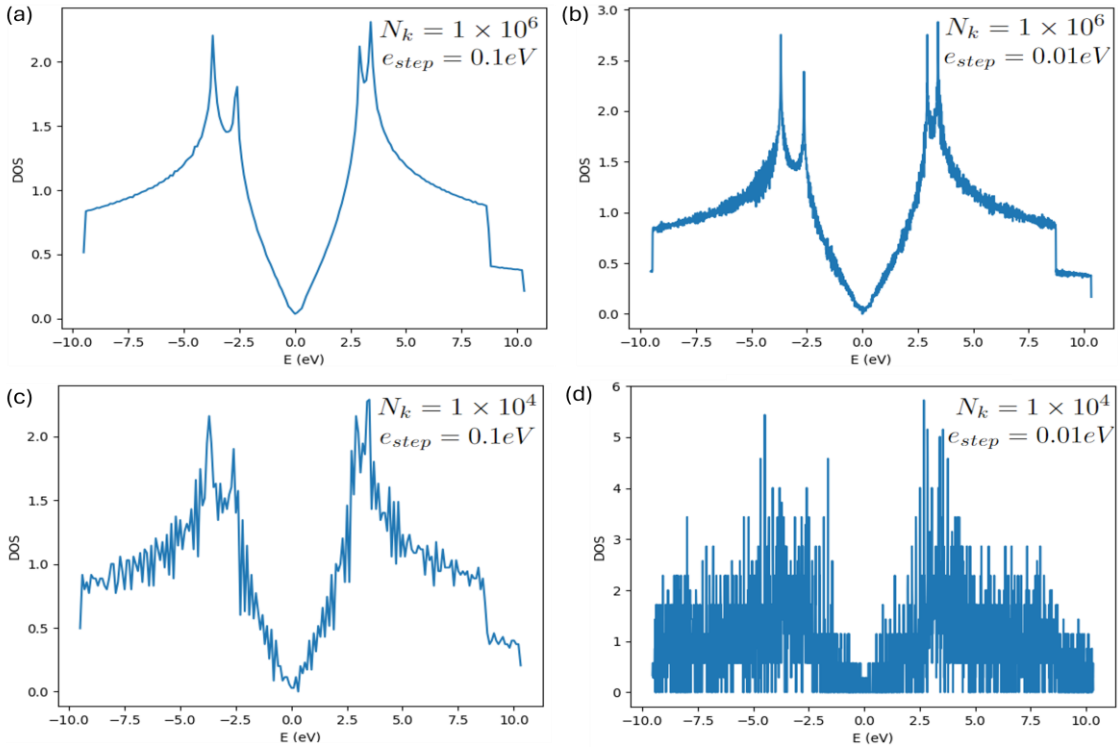

Fig 6. DOS in AB graphene given displacement field Δ_1 =0.01eV, but calculated with different number of k points N_k and band distance e_{step}. (a) N_k =1×10^6, e_{step} =0.1eV. (b) N_k =1×10^6, e_{step} =0.01eV. (c) N_k =1×10^4, e_{step} =0.1eV. (d) N_k =1×10^4, e_{step} =0.01eV.

The accuracy of the DOS calculation in AB graphene is influenced by the number of k points Nk and the energy step size estep. As seen in Figure 6, we compare the DOS in AB graphene with certain displacement field Δ1 = 0.01eV but different Nk and estep. We find that increasing Nk and decreasing estep will lead to a smoother and more accurate DOS curve. However, we should find suitable Nk for specific estep. This is particularly important for capturing the fine details of the electronic structure, such as the positions and widths of the DOS peaks.

5. Conclusion

This study investigates the band gap and density of states (DOS) in multi-layer graphene systems, specifically AB and ABC stackings, under various displacement fields Δ_1. The results showed that the electronic properties, including the band structure and DOS, are sensitive to Δ_1 and the stacking configuration. The most interesting point is the band gap will be wider with increased displacement fields. The tight-binding model is applied to and effective in predicting these properties, providing a theoretical basis for the design of novel graphene-based electronic devices. Our future work could focus on exploring the effects of additional factors, such as strain and doping, on the electronic properties of multi-layer graphene.

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