



이학박사 학위논문

Exchange-correlation energy and spin-valley polarized half/quarter metal phase of multilayer graphene

다층 그래핀의 교환-상관 에너지와 스핀-밸리 분극 절반/사분의 일 금속 위상

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서울대학교 대학원

물리천문학부

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Abstract

Exchange-correlation energy and spin-valley polarized half/quarter metal phase of multilayer graphene

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Single- and multilayer graphene has been one of the most important materials in recent decades. It plays an important role in a research on 2D van der Waals materials and topological materials, and its good physical properties make it interesting for application to devices. The chiral nature of the multilayer graphene leads to an interesting phenomena, such as correlated state caused by electron-electron interactions. Also, it is also very interesting that multilayer graphene has various electronic structures depending on the stacking method and the electronic structure can be changed by various manipulations such as vertical electric fields or strain. The recent discovery of superconductivity and spin-valley polarization state in ABC trilayer graphene. In this thesis, we focus on the polarization state that can appear due to these electron-electron interactions.

First, we analyze the electron-electron interaction depending on the stacking method in multilayer graphene. We calculate exchange self energy, density-density response function, and ground-state energy of multilayer graphene systems. The influence of electron-electron interaction on electrical properties can be understood as competing contributions from intraband exchange, inter band exchange, and correlation. We show that the contribution of interband exchange is strongly suppressed as the chirality J increases.

Second, we theoretically study the spin-valley polarization state recently discovered in the ABC trilayer graphene. A four-fold spin-valley degeneracy of the electronic structure can change into condensed states in some of the four degenerates due to electron-electron interactions. We find a non-interaction wavefunction through self-consistent Hartree calculation and we use it to calculate the ground-state energy considering the exchangecorrelation energy. We demonstrate that the spin-valley polarization states can have a lower ground-state energy compared to that of the normal state and exchange contribution plays a key role in the appearance of the polarized state. Furthermore, we show that the spin-valley polarization phase can be present in AB bilayer graphene and ABCA rhombohedral tetralayer graphene.

On the other hand, we investigate different correlated states, layer polarized, by electron-electron interaction. The layer polarized state of Bernalstacked bilayer graphene has been theoretically predicted and experimentally observed. This state can be explained as a pseudospin model. Benalstacking tetralayer graphene has a heavy-mass band and a light-mass band in the low-energy region. The ground-state configuration is complicated due to the pseudospin doublets and spin-valley degeneracy, but it can be explained using an effective Hund's law. We also study the effect of the stacking method and the response to the vertical electric field. We derive the effective Hamiltonian for alternating twist multilayer graphene and show a step-like feature in the optical conductivity.

Keywords : Mutilayer graphene, exchange-correlation energy, ground-state energy, spin-valley polarized state **Student Number :** 2011-20417

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Chapter 1

Introduction

Multilayer graphene has been studied in recent decades due to the possibility of an electronic device applications and its chiral feature[1–5]. The electronic structure of multilayer graphene is also sensitive to its stacking sequence and can be easily controlled by applying a vertical electric field.

To understand the electronic properties in the presence of electronelectron interactions is a fundamental issue in multilayer graphene. Its chiral feature of multilayer graphene plays an important role in electron-electron interaction[6, 7]. There are layer polarized correlated phase that can occur by electron-electron interaction [8–14]. Recently, spin-valley polarized state has been experimentally observed in rhombohedral ABC trilayer graphene[15– 22] when a vertical electric field is applied. To understand this phenomenon, we analyze the ground-state energy by considering electron-electron interaction.

In Chapter 2, we introduce the rotational transformation of the chiral wavefunction. This method offers computational cost benefits by determining the complex phase of the chiral wavefunction, which is determined by the chiral nature and its hopping network in the minimal model of multilayer graphene. This approach overcomes the high computational cost of electron-electron interaction calculation and enables calculation of the full scope of the thesis. Using this method, we obtain the exchange selfenergy, density-density response function, plasmon dispersion, and finally the ground-state energy of multilayer graphene within the random phase approximation(RPA). We analyze the relationship between electron-electron interaction and chirality by analyzing these results, and we find that the interband contribution is strongly suppressed as the number of layers increases.

In Chapter 3, we show that the four-fold spin/valley degeneracy of the graphene system can be broken and half- or quarter- metal states can appear. Some of the spin-valleys become correlated due to electron-electron interaction, forming a spin-valley polarized state. We calculate the ground-state energy for the four possible pure polarized states within the RPA, and show that the polarized state can have lower energy than the normal state by comparing their ground-state energies.

In Chapter 4, we theoretically studied alternating twist multilayer graphene (ATMG) in the presence of an electric field and obtained a low-energy effective Hamiltion of ATMG up to pentalyer. We also calculate the optical conductivity of ATMG and and determine its characteristic optical spectrum, which includes a step-like feature.

In Chapter 5, we study the spontaneous layer polarized phase due to electron-electron interaction for Benal-stacking multilayer graphene. There are various possible ground-state configurations depending on the direction of the pseudospin of heavy-mass and light-mass bands in which four spin/valleys. We showed that various Hall conductivities can appear depending on these configurations, and that the heavy-mass band and light-mass band pseudospin doublets follow an effective an Hund's rule.

In chapter 6, We conclude this thesis with a summary.

Chapter 2

Stacking dependence of carrier-interactions in multilayer graphene systems

2.1 Introduction

Multilayer graphene has attracted considerable attention recently because of exotic chiral features in its electronic structure and the possibility of future electronic device applications[1–4]. The band structure of a multilayer system is qualitatively dependent on its stacking sequence, opening up the possibility of engineering electronic properties by selecting a desired arrangement. In this chapter we use an approach in which momentumdirection dependent intersite phases determined by the stacking sequence are explicitly exhibited to show that this qualitative dependence is inherited by carrier-carrier interaction phenomena.

Because the number of π -bands in a multilayer graphene system is proportional to the number of layers, and because π -band wavefunctions are not isotropic in momentum space, accurate evaluation of physical quantities which require integrations over momentum space, for example quasiparticle energy spectra and density–density correlation functions, rapidly becomes more difficult as layer number increases. To mitigate this problem and to make the relationship between stacking arrangement and interactions more transparent, we introduce a momentum-direction dependent unitary transformation which makes the single-particle Hamiltonian isotropic. In addition to making accurate many-electron perturbation theory calculations practical for multilayer stacks, this approach facilitates understanding of some qualitative trends in the stacking arrangement dependence of quasiparticle energy spectra, plasmon dispersion and damping, and carrier thermodynamic properties.

2.2 Rotational transformation of multilayer Dirac Hamiltonian

Our calculation is based on the minimal continuum model for multilayer graphene which retains only a Dirac model for hopping within each layer and only nearest-neighbor interlayer hopping. Different stacking sequences are specified by different interlayer near-neighbor arrangements. The Hamiltonians for these minimal models can be made isotropic by multiplying wavefunction components by stacking and momentum-direction dependent phase factors. To illustrate how this transformation works, we consider first the example of Bernal stacked bilayer graphene, in which one sublattice in the first layer (say 1B) is a near neighbor of the opposite sublattice in the second layer (say 2A). The Hamiltonian at finite wavevector kis then expressed in the (1A, 1B, 2A, 2B) basis as

$$\mathcal{H}(\phi_{\mathbf{k}}) = \begin{pmatrix} 0 & \hbar v k e^{-i\phi_{\mathbf{k}}} & 0 & 0 \\ \hbar v k e^{i\phi_{\mathbf{k}}} & 0 & t_{\perp} & 0 \\ 0 & t_{\perp} & 0 & \hbar v k e^{-i\phi_{\mathbf{k}}} \\ 0 & 0 & \hbar v k e^{i\phi_{\mathbf{k}}} & 0 \end{pmatrix}, \quad (2.1)$$

where $k = \sqrt{k_x^2 + k_y^2}$, $\phi_{\mathbf{k}} = \arctan(k_y/k_x)$, v is the bare Dirac velocity, which is related to the nearest-neighbor intralayer hopping amplitude by $t = 2\hbar v/\sqrt{3}a \sim 3 \text{ eV}$ (a = 0.246 nm is the lattice constant), and $t_{\perp} \sim 0.1t$ is the nearest-neighbor interlayer hopping parameter. It is easy to see that the eigenvalues of this Hamiltonian are independent of $\phi_{\mathbf{k}}$ and that all eigenvalues satisfy $\Psi(\phi_{\mathbf{k}}) = (c_{1A}, c_{1B}e^{i\phi_{\mathbf{k}}}, c_{2A}e^{i\phi_{\mathbf{k}}}, c_{2B}e^{2i\phi_{\mathbf{k}}})^{\text{t}} \equiv U(\phi_{\mathbf{k}})\Psi(0)$, where the $\{c_i\}$ depend on k only and can be obtained by diagonalizing \mathcal{H} at $\phi_{\mathbf{k}} = 0$. The locking between intersite phases and momentum direction in these spinors is reminiscent of the properties of spinors in chiral systems and will be referred to below as sublattice pseudospin chirality. The unitary operator $U(\phi)$ is a diagonal matrix whose diagonal components $(1, e^{i\phi}, e^{i\phi}, e^{2i\phi})$ are determined by the bilayer stacking. The phase difference $e^{i\phi}$ between the 1A and 1B components of the wavefunction, and between the 2A and 2B components, comes from the monolayer-like intralayer coupling, whereas the zero phase difference between the 1B and 2A components comes from the momentum-independent interlayer coupling. If we know the wavefunction at a specific angle, we can easily obtain the wavefunction at an arbitrary angle by attaching site-dependent phase factors determined by the stacking sequence.

We can easily generalize from the bilayer case to multilayer graphene with an arbitrary stacking order. Eigenstates at momentum orientation ϕ_k satisfy

$$\Psi(\phi_{k}) = (c_{1A}e^{iP_{1A}\phi_{k}}, c_{1B}e^{iP_{1B}\phi_{k}}, \cdots)^{t} = U(\phi_{k})\Psi(0), \qquad (2.2)$$

where $\mathcal{H}(0)\Psi(0) = \varepsilon \Psi(0)$. $\mathcal{H}(\phi_k) = U(\phi_k)\mathcal{H}(0)U^{-1}(\phi_k)$ has matrix elements

$$\mathcal{H}_{ij}(\phi_{\mathbf{k}}) = \mathcal{H}_{ij}(0)e^{i(P_i - P_j)\phi_{\mathbf{k}}},\tag{2.3}$$

and eigenvalues ε that are independent of ϕ_k . By comparing the matrix elements in Eq. (2.3) with those in the original Hamiltonian, we can determine the phase factor chirality parameters $\{P_i\}$. In general two sites connected by nearest-neighbor interlayer hopping have the same phase and within a layer $P_{\rm B} = P_{\rm A} + 1$. Using these two rules, $\{P_i\}$ is completely determined by the stacking sequence. Figure 2.1 illustrates their application in multilayer structures with up to four layers. We explain below how these band structure properties influence electron-electron interaction physics in multilayer graphene systems.



Figure 2.1: Stacking diagrams and phase factor chirality parameters $\{P_i\}$ for (a) ABC and (b) ABA graphene. (c) Phase factors for all stacking arrangements from monolayers to tetralayers. We have chosen to set the phase factor of the sublattice 1A to zero. These results are for valley K. For valley K' the chirality parameters change sign.

2.3 Exchange self-energy of multilayer graphene

Our goal in this chapter is to address interaction effects in moderate carrier density multilayer graphene systems, which are are weakly correlated two-dimensional Fermi liquids in which electron-electron interaction effects can be reliably addressed using perturbation theory. At leading order the electron self-energy is given by the unscreened exchange contribution:

$$\Sigma_{\rm ex}(\boldsymbol{k},s) = -\sum_{s'} \int \frac{d^2 k'}{(2\pi)^2} V_{\boldsymbol{k}-\boldsymbol{k}'} f_{s',\boldsymbol{k}'} F_{\boldsymbol{k},\boldsymbol{k}'}^{s,s'}, \qquad (2.4)$$

where $f_{s,k}$ is the Fermi function for the band s and wavevector k, $F_{k,k'}^{s,s'} = |\langle s, k | s', k' \rangle|^2$ is a wavefunction overlap factor, and $V_q = 2\pi e^2/\epsilon_0 q$ is the



Figure 2.2: (a) Exchange self-energies and (b) conduction band pseudospin direction (s = +1) for C2DESs with J = 1, 2, 3, 4. Exchange self-energies of (c) the lowest conduction band (s = +1) of ABC trilayer graphene for $n = 10^{11}, 10^{13} \text{ cm}^{-2}$, and (d) the lowest (s = +1) and second lowest (s = +2) conduction bands of ABA trilayer graphene for $n = 10^{12} \text{ cm}^{-2}$. (The bands of the ABA multilayer structures are shown in the inset.) Here $\Sigma_0 = \frac{2e^2k_{\rm F}}{\epsilon_0\pi}$ and we use the effective fine structure constant $\alpha = \frac{e^2}{\epsilon_0\hbar v} = 1$ and momentum cutoff $q_c = 1/a$.

two-dimensional Coulomb interaction. (We note that the Coulomb interaction between layers with the layer separation d is given by $V_q(d) = V_q e^{-qd}$. Due to the small layer separation we approximate $V_q(d) \approx V_q$ for the analytic calculations. The full numerical calculations using $V_q(d)$ do not change the results qualitatively.) It is conventional to absorb the self-energy at the Dirac point ($\mathbf{k} = 0$) in the absence of carriers into the zero of energy.

To understand the consequences for interaction physics of multilayer wavefunction chiral properties, it is instructive to first consider the chiral two-dimensional electron system (C2DES) Hamiltonians[6, 7] that provide a low-energy effective theory of multilayer graphene. The Hamiltonian of a C2DES with the chirality index J is

$$\mathcal{H}_{J}(\boldsymbol{k}) = t_{\perp} \begin{pmatrix} 0 & \left(\frac{\hbar v k e^{-i\phi_{\boldsymbol{k}}}}{t_{\perp}}\right)^{J} \\ \left(\frac{\hbar v k e^{i\phi_{\boldsymbol{k}}}}{t_{\perp}}\right)^{J} & 0 \end{pmatrix}, \qquad (2.5)$$

and yields eigenenergies $\varepsilon_{s,\mathbf{k}} = st_{\perp} (\hbar v |\mathbf{k}|/t_{\perp})^J$, and eigenspinors $|s, \mathbf{k}\rangle = (s, e^{iJ\phi_{\mathbf{k}}})^t / \sqrt{2}$, where $s = \pm 1$ for positive and negative energy states respectively. For a C2DES with the chirality $J, F_{\mathbf{k},\mathbf{k}'}^{s,s'} = \frac{1}{2} [1 + ss' \cos J(\phi_{\mathbf{k}} - \phi_{\mathbf{k}'})] = \frac{1}{2} (1 + ss' \mathbf{n}_{\mathbf{k}} \cdot \mathbf{n}_{\mathbf{k}'})$, where $\mathbf{n}_{\mathbf{k}} = (\cos J\phi_{\mathbf{k}}, \sin J\phi_{\mathbf{k}})$ is the pseudospin direction at \mathbf{k} characterized by the chirality index J. Note that the overlap factor $F_{\mathbf{k},\mathbf{k}'}^{s,s'}$ for a C2DES has the form of Heisenberg interactions between pseudospins with orientation $J\phi_{\mathbf{k}}$ and $J\phi_{\mathbf{k}'}[8]$.

In Fig. 2.2(a) intraband and interband contributions to the conduction band exchange self-energy of a C2DES are plotted. In Fig. 2.2(b) pseudospin chirality is illustrated by plotting the spin-1/2 pseudospin orientation appropriate for two-component spinors. As the chirality increases, the magnitude of each contribution is suppressed because pseudospin orientation changes more rapidly with wavevector. Especially, the interband exchange is suppressed more strongly owing to the contribution from states occupying the infinite sea of negative energies. In Figs. 2.2(c) and (d) we compare C2DES exchange self-energies with those of ABC and ABA graphene multilayers. At low carrier densities in ABC graphene, the relative chiral index of the dominant wavefunction components is 3 and the exchange selfenergy resembles the weak form found in a C2DES with J = 3; as the density increases, interlayer hopping becomes less important, and the exchange self-energy eventually approaches that of a C2DES with J = 1. At low densities, ABA graphene is described[6, 7] by a direct product of chiral gases with J = 1 and J = 2.



Figure 2.3: Loss function $\text{Im}[-\varepsilon(q,\omega)^{-1}]$ of (a) ABC, (b) ABA, (c) ABCA, and (d) ABAB stacked multilayer graphene for $n = 10^{12} \text{ cm}^{-2}$ and $\alpha = 1$ with $\eta = 5 \times 10^{-5} \varepsilon_{\text{F}}$. The thick black lines indicate boundaries of the electron-hole continua and the insets in each panel show the energy band structure. In the ABA structure and in other multilayer structures with mirror symmetry, some interband transitions do not contribute to plasmon Landau damping, as indicated by dotted lines in panel (b).

2.4 Density-density response functions and collective modes of multilayer graphene

Figure 2.3 plots loss functions $\text{Im}[-\varepsilon(q,\omega)^{-1}]$ for several different multilayer graphene structures. Here $\epsilon(q,\omega)$ is the dielectric function which we approximate using the weak coupling random phase approximation (RPA) expression $\epsilon(q,\omega) = 1 - V_q \Pi_0(q,\omega)$, and $\Pi_0(q,\omega)$ is the non-interacting electron density-density response function:

$$\Pi_{0}(\boldsymbol{q},\omega) = g_{\rm sv} \sum_{s,s'} \int \frac{d^{2}k}{(2\pi)^{2}} \frac{f_{s,\boldsymbol{k}} - f_{s',\boldsymbol{k}+\boldsymbol{q}}}{\hbar\omega + \Delta_{\boldsymbol{k},\boldsymbol{k}+\boldsymbol{q}}^{s,s'} + i\eta} F_{\boldsymbol{k},\boldsymbol{k}+\boldsymbol{q}}^{s,s'}, \qquad (2.6)$$

where $g_{sv} = g_s g_v = 4$ is the spin-valley degeneracy, $\Delta_{k,k+q}^{s,s'} = \varepsilon_{s,k} - \varepsilon_{s',k+q}$, $\varepsilon_{s,k}$ is the eigenenergy for the band index s and wavevector k, and η is a positive infinitesimal number. The black thick lines in Fig. 2.3 plot the boundaries of electron-hole continua within which $\text{Im}\Pi_0(q,\omega)$ is non-zero and electron-hole excitations are allowed. When $\epsilon(q,\omega) = 0$, the loss function has a δ -function peak corresponding to plasmon collective excitations. When the plasmon modes enter the electron-hole continuum, they can decay into single electron-hole pairs through the Landau damping process. In multilayer graphene, plasmon modes decay through interband transitions. The shark-fin structures around $\omega = 0$ reflects from the chiral nature of the wavefunctions which lead to suppressed momentum-dependent scattering[23].

2.5 Ground state energy of multilayer graphene

The ground-state energy is the sum of the non-interacting kinetic energy and interaction (exchange-correlation) energies. The exchange-correlation energy can be expressed in terms of the density-density response function[24] by applying the integration-over-coupling-constant method and appealing to the fluctuation-dissipation theorem. The RPA approximation to the exchange-correlation energy is justified in part by the relatively large spin-valley flavor degeneracy $g_{sv} = 4$ which makes the RPA bubble-diagram contributions to the energy more dominant[24]. For technical reasons it is convenient to separate the first-order exchange-correction to the interaction energy and higher order corrections commonly referred to as the correlation energy. The dependence of the exchange and RPA correlation energies on carrier density can then be expressed[25, 26] as integrals along the imaginary frequency

axis:

$$\varepsilon_{\text{ex}} = -\frac{\hbar}{2n} \int \frac{d^2q}{(2\pi)^2} \int_0^\infty \frac{d\nu}{\pi} V_q \delta \Pi_0(q, i\nu), \qquad (2.7)$$

$$\varepsilon_{\text{corr}} = \frac{\hbar}{2n} \int \frac{d^2q}{(2\pi)^2} \int_0^\infty \frac{d\nu}{\pi} \bigg[V_q \delta \Pi_0(q, i\nu) + \ln \bigg| \frac{1 - V_q \Pi_0(q, i\nu)}{1 - V_q \Pi_0(q, i\nu)} \bigg| \bigg],$$

where $\delta \Pi_0(q, i\nu) = \Pi_0(q, i\nu) - \Pi_0(q, i\nu)|_{n=0}$. We use the momentum cutoff $q_c = 1/a$ to remove the ultraviolet divergences in the momentum integrals.

Using these expressions, we find that in terms of the dimensionless coupling constant $\alpha_{\rm F} = e^2/\epsilon_0 \hbar v_{\rm F} = (v/v_{\rm F})\alpha$ where $v_{\rm F}$ is the Fermi velocity, the exchange energy is given by

$$\varepsilon_{\rm ex} = \hbar v_{\rm F} k_{\rm F} C_1 \alpha_{\rm F} = \frac{e^2}{\epsilon_0} k_{\rm F} C_1, \qquad (2.8)$$

and the correlation energy for small $\alpha_{\rm F}$ has the form of

$$\varepsilon_{\rm corr} = \hbar v_{\rm F} k_{\rm F} \left(C_2 \alpha_{\rm F}^2 + \cdots \right), \qquad (2.9)$$

whereas in the strong coupling limit ($\alpha_{\rm F} \gg 1$),

$$\varepsilon_{\rm corr} = \hbar v_{\rm F} k_{\rm F} \left(D_1 \alpha_{\rm F} + D_0 + \cdots \right). \tag{2.10}$$

The coefficients $\{C_i\}$ and $\{D_i\}$ in these expressions have weak density dependence through the response function and the momentum cutoff.

To address multilayers, we first discuss the case of C2DES models whose exchange and correlation energies exhibit a systematic dependence on their chirality index J. As we see from Eq. (2.8) that the exchange energy is approximately proportional to $k_{\rm F}$ irrespective of the interaction strength. The positive value of C_1 for J = 1 reflects the dominance in this case of



Figure 2.4: Comparison between the ground-state exchange energies (left panel) and correlation energies (right panel) of several different multilayer graphene (thick lines) structures and C2DES systems (dotted lines) as a function of carrier density for $\alpha = 0.05$.

interband exchange. For J > 1, the interband contribution is suppressed because of the larger chirality indices and the exchange energy turns negative ($C_1 < 0$). For the correlation energy in the strong coupling limit, we find from Eq. (2.10) that $\varepsilon_{\text{corr}} = (e^2/\epsilon_0)k_{\text{F}}D_1 + J\varepsilon_{\text{F}}D_0 + \cdots$, where ε_{F} is the Fermi energy. Note that $C_1 = -D_1$; thus for $J > 1 \varepsilon_{\text{corr}}$ is positive ($D_1 > 0$), whereas for $J = 1 \varepsilon_{\text{corr}}$ is negative ($D_1 < 0$). In the weak coupling limit, we see from Eq. (2.9) that $\varepsilon_{\text{corr}} \propto v_{\text{F}}k_{\text{F}}a_{\text{F}}^2 \propto k_{\text{F}}^{2-J}$.

Figure 2.4 illustrates these properties of C2DES models and compares these exchange-correlation energy properties with those of multilayer graphene systems. For multilayer graphene, at low densities, the exchange and correlation energies follow those of the largest J C2DES model contained within its low-energy bands because they are responsible for the largest density of states (DOS). For example, for ABA stacking the exchange and correlation energies at low densities follow those of a J = 2 C2DES because a J = 2C2DES has a larger DOS than a J = 1 C2DES. As the carrier density increases, interlayer hopping becomes less important and the exchange and correlation energies begin to approach those of monolayer graphene.

2.6 Summary and Discussion

In this chapter we have exploited the simple dependence of band wavefunctions on momentum orientation to simplify many-electron perturbation theory calculations for multilayer graphene, and to bring out the relationship between stacking sequence and carrier-carrier interaction phenomena in this interesting class of materials. By explicit calculations for a variety of different structures we have shown that the exchange self-energies and related exchange-correlation energy features in multilayer graphene systems follow those of C2DES models at low carrier densities, but cross over to be more similar to those of monolayer graphene as carrier densities increase. The rotational transformation of the chiral wavefunction is very general and can be applied even in the presence of site energy variations or remote hopping terms, unless momentum-dependent hopping terms do not appear in the Hamiltonian. For example, if the remote interlayer hopping term γ_2 is included in the Hamiltonian, it modifies $\{c_i\}$, but not the angular part of the wavefunction in Eq. (2.2).

The model we employ, however, does not include momentum-dependent remote interlayer hopping terms. We also use the weak-coupling RPA in the calculation. Both limit the applicability of our calculations to moderate to high carrier densities, and at very low carrier densities correlations frequently become strong and lead to broken symmetry ground states not
captured by the RPA[27].

Our theory, however, captures important observable effects produced by interactions which strongly depend on the stacking sequences such as plasmon collective excitations and self-energies. The dependence of ground state energies on carrier and spin densities are responsible for renormalized electronic compressibility and spin susceptibility, respectively. For example, the electronic compressibility κ is given by $\kappa^{-1} = n^2 d\mu/dn$, where $\mu =$ $\partial (n\varepsilon_{\rm tot})/\partial n$ is the chemical potential of the interacting system, and $\varepsilon_{\rm tot}$ is the total ground-state energy per particle. In an ordinary parabolic band twodimensional electron system the compressibility famously becomes negative at low carrier densities[28]. In contrast, for a C2DES we find that in the low-density strong-coupling limit, $\kappa_0/\kappa \approx 1 + J(J+2)D_0/2$ with $D_0 > 0$ for J = 1 and $D_0 < 0$ for J > 1. (Here κ_0 is the non-interacting compressibility.) It follows that for a J = 1 C2DES, the electronic compressibility is strongly suppressed by interactions due to the interband exchange contribution and remains positive [25]. For a J > 1 C2DES, the interband exchange contribution is suppressed with the chirality; thus, the electronic compressibility is enhanced by the interactions. Interestingly, we find that for $J \ge 5$, the compressibility can be negative in the low-density limit, suggesting an instability toward other ground states, whereas in the absence of correlation, this occurs for $J \ge 2$. For multilayer graphene, at low carrier densities, the compressibility follows the trend of the corresponding C2DES, but as the carrier density increases, the compressibility follows that of monolayer graphene with suppressed compressibility[29, 30], showing non-monotonic behavior arising from competition between the intraband exchange, interband exchange, and correlation.

In conclusion, our new approach allows us to effectively calculate the quasiparticle and thermodynamic properties of interacting many-body chiral systems. We show that as the chirality increases, the exchange contribution to the single particle energy is suppressed and the correlation contribution increases, indicating that the exchange-correlation is controlled by the stacking arrangement. Our results suggest that correlation effects play a more important role in a system with a large chirality; thus, we expect that rhombohedral graphene with periodic ABC stacking could show exotic interaction-induced phenomena such as ordered states and non-Fermi liquid behavior[27].

Chapter 3

Spontaneous spin-valley polarization in rhombohedral multilayer graphene

3.1 Introduction

Multilayer graphene has recently attracted considerable attention because of its stacking-dependent chiral electronic structure [1–4]. The lowenergy effective theory of multilayer graphene is described by a set of chiral two-dimensional electron systems (C2DESs) determined by the stacking arrangement in which the extra sublattice/layer degrees of freedom, called pseudospin, play an important role [6, 7]. Thus, the electronic structure of multilayer graphene is sensitive to its stacking sequence, which could open the possibility of engineering the electronic properties by tuning the stacking arrangement.

A fundamental issue in multilayer graphene is to understand the electronic properties in the presence of electron–electron interactions. Because of the interplay between the chiral nature of the wave function and electron– electron interactions, various interaction-induced phenomena can occur in multilayer graphene[8–14]. Especially, in rhombohedral multilayer graphene with a periodic ABC stacking arrangement, the low-energy dispersion becomes flatter as the number of layers increases, indicating that the interaction energy becomes dominant over the kinetic energy. Thus, rhombohedral multilayer graphene is an ideal platform to observe interaction-induced phenomena, as seen in recent experiments demonstrating superconductivity and correlated phases [15–22].

In this chapter, we theoretically investigate spontaneous spin-valley polarized states in rhombohedral multilayer graphene in the presence of the Coulomb interaction. In graphene, there are four spin/valley flavors, (\uparrow, K) , (\downarrow, K) , (\uparrow, K') and (\downarrow, K') . In the absence of interactions, electrons occupy the four flavors equally. This spin-valley symmetry could be broken by electron–electron interactions, and we are considering the case that electrons occupy one or some of the flavors. We calculate the exchange-correlation energy varying the carrier density and perpendicular electric field, and obtain the corresponding phase diagram for the spontaneous spin-valley polarization.



Figure 3.1: (a) Schematic picture for the spin-valley polarized states P_2 and P_4 . (b) Shape of the density dependence of the energy and the corresponding tendency toward the spin-valley polarization. When the density dependence of the energy is concave down (up), $E(2n_0) < 2E(n_0)$ ($E(2n_0) > 2E(n_0)$) for a density n_0 as in the left (right) panel, thus the system shows a tendency toward (against) the spontaneous spin-valley polarization.

Figure 3.1(a) shows possible spin-valley polarized states denoted by P_1-P_4 , among which the ground state is determined by comparing the to-



Figure 3.2: Density dependence of (a) the kinetic plus Hartree energy, (b) the exchange plus correlation energy, (c) the total energy in ABC trilayer graphene for $U_{\rm ext} = 0$ (black) and $U_{\rm ext} = 0.05$ eV (red), (d), (e), (f) their first derivatives, and (g), (h), (i) their second derivatives with respect to the density. Note that the second derivatives are related to the electronic compressibility as $\kappa^{-1} = \frac{n^2}{V} \frac{\partial^2 E_{\rm tot}}{\partial n^2}$. The red vertical dashed lines represent the density $n_{\rm M_4} \approx 1.04 \times 10^{12}$ cm⁻² that that fills the Mexican hat structure of the P₄ state when $U_{\rm ext} = 0.05$ eV. Here we use the effective fine structure constant $\alpha = \frac{e^2}{\epsilon \hbar v} = 1$ where ϵ is the effective dielectric constant.

tal energy for each phase. (We will discuss possible intermediate states with unequal flavor concentrations later.) If the density dependence of the energy is concave down (up), the system has a tendency toward (against) the spontaneous spin-valley polarization, as shown in Fig. 3.1(b). This implies that the electronic compressibility κ , which can be expressed as $\kappa^{-1} = n^2 \frac{\partial \mu}{\partial n}$ where n is the carrier density, $\mu = \frac{\partial E_{\text{tot}}}{\partial N}$ is the chemical potential, E_{tot} is the total ground-state energy and N is the total number of particles in the system, has a close connection to the spontaneous spin-valley polarization, thus can be used as a powerful thermodynamic probe of the electron-electron interaction effect.



Figure 3.3: Phase diagrams of (a) AB, (b) ABC and (c) ABCA stacked multilayer graphene. (d), (e) Energy difference between the P_3 and P_4 states for ABC trilayer graphene for (d) $U_{ext} = 0.05$ eV following the white dashed line in (b) and (e) $U_{ext} = 0.1$ eV (solid lines) and $U_{ext} = 0.15$ eV (dasheddot lines) following the white solid and dashed-dot lines in (b), respectively. The insets to (d) show the low-energy conduction band and the Fermi energy of the occupied flavors for the P_3 and P_4 states in the regions (1), (2) and (3) in (b). In (d), these regions are separated by the vertical dashed lines at $n = n_{M_3}$ and $n = n_{M_4}$. Here we use $\alpha = 1.0619$.

3.2 Density dependence of the energies and their derivatives

The ground-state energy is given by the sum of the kinetic, Hartree, exchange and correlation energies.

In the presence of a perpendicular electric field $E_{\rm ext}$, we start from a mean-field band structure including the effect of the Hartree potential self-consistently, taking into account the energy gap opening by $E_{\rm ext}$. Then from this band structure, we obtain the exchange-correlation energy using the integration-over-coupling-constant method within the random phase approximation (RPA). See the detailed derivation in the Chapter B.1.

Figure 3.2 shows the density dependence of the kinetic plus Hartree energy, the exchange plus correlation energy, the total energy, and their first and second derivatives with respect to the density in ABC trilayer graphene for $U_{\text{ext}} = 0$ and $U_{\text{ext}} = 0.05$ eV, respectively, where $U_{\text{ext}} = eE_{\text{ext}}d$ with the interlayer separation d = 3.35 Å.

First, consider the $U_{\text{ext}} = 0$ case. To understand the density dependence of the energies, let us begin with the C2DES as a low-energy effective theory of rhombohedral multilayer graphene. The Hamiltonian of a C2DES with the chirality index J neglecting the electron-electron interactions is of the form

$$\mathcal{H}_{J}(\boldsymbol{k}) = t_{\perp} \begin{pmatrix} 0 & \left(\frac{\hbar v k_{\perp}}{t_{\perp}}\right)^{J} \\ \left(\frac{\hbar v k_{+}}{t_{\perp}}\right)^{J} & 0 \end{pmatrix}, \qquad (3.1)$$

where $k_{\pm} = k_x \pm i k_y$, v is the in-plane Fermi velocity of monolayer graphene and t_{\perp} is the nearest-neighbor interlayer hopping. The eigenenergies of Eq. (3.1) are given by $\varepsilon_{s,k} = st_{\perp} (\hbar v |\mathbf{k}|/t_{\perp})^J$ with $s = \pm 1$ for positive and negative energy states, respectively. For $U_{\text{ext}} = 0$, the Hartree energy is zero and the kinetic energy per particle is given by $\frac{E_{\text{kin}}}{N} = \frac{2}{J+2}\varepsilon_{\text{F}}$ where ε_{F} is the Fermi energy. Since $\varepsilon_{\text{F}} \sim k_{\text{F}}^J$ and $n \sim k_{\text{F}}^2$ where k_{F} is the Fermi wave vector, $E_{\text{kin}} \sim k_{\text{F}}^{J+2} \sim n^{\frac{J+2}{2}}$ is concave up for the density n, thus the kinetic energy does not favor the spin-valley polarization. In contrast, the exchange energy per particle is given by $\frac{E_{\text{ex}}}{N} = C_1 \frac{e^2}{\epsilon_0} k_{\text{F}}$ where C_1 is a coefficient which has weak density dependence with $C_1 < 0$ for $J \ge 2$ ($C_1 > 0$ for J = 1) due to the dominant intraband (interband) exchange interaction [31]. This means that for $J \ge 2$, $E_{\rm ex} \sim -k_{\rm F}^3 \sim -n^{\frac{3}{2}}$ is concave down for n, thus the exchange energy favors the spin-valley polarization. From the power-law dependence, we find that at small carrier densities, the exchange energy is dominant over the kinetic energy thus there is a tendency toward the spin-valley polarization, whereas at large enough densities, the kinetic energy is dominant over the exchange energy thus there is a tendency toward the normal phase.

If we include the correlation effect, the tendency toward the spin-valley polarization is reduced because the correlation energy typically tends to cancel the exchange contribution at low densities [31], and the density dependence of the correlation energy is concave up thus does not favor a spin-valley polarized state. Note that only the exchange contribution to the electronic compressibility κ is negative. Combining all the contributions, κ remains positive, thus ABC trilayer graphene remains in the normal phase for $U_{\text{ext}} = 0$.

For $U_{\text{ext}} \neq 0$, the low-energy spectrum develops the Mexican hat structure. As mentioned, the band structure is obtained self-consistently considering the effect of the kinetic and Hartree energies. As density n increases, the Fermi energy increases changing the Fermi surface from a disk with a concentric hole to a filled disk. Note that the Fermi energy in our approximation corresponds to the first derivative of the kinetic plus Hartree energy with respect to n, thus the second derivative of the kinetic plus Hartree energy remains positive even in the presence of U_{ext} , showing a tendency toward the normal phase. Next, consider the effect of U_{ext} on the density dependence of the exchange contribution. A perpendicular electric field aligns some pseudospins oppositely in the conduction and valence bands along the z direction, thus the exchange contribution increases with n due to the interband contribution up to the induced density corresponding to the oppositely aligned pseudospins, and then decreases with n due to the intraband contribution to the exchange energy, as in the $U_{\text{ext}} = 0$ case. At the same time, the second derivative of the exchange energy decreases more negatively as the pseudospins in the conduction band are aligned along the same direction by the perpendicular electric field. This means that compared to the $U_{\text{ext}} = 0$ case, the density dependence of the exchange energy becomes more concave down and the tendency toward the spin-valley polarization is enhanced. When n crosses $n_{\rm M}$, the density that fills the Mexican hat structure, the (negative intraband) exchange contribution from electrons near k = 0 becomes absent and gives a less negative contribution to the exchange energy, resulting in a jump in the first derivative of the exchange energy [Fig. 3.2(e)]. Note that the correlation contribution typically has an opposite trend of the exchange contribution, reducing the magnitude of the exchange contribution. Overall, the electronic compressibility κ of the system becomes negative for $U_{\text{ext}} \neq 0$ at low densities, thus the system no longer remains in the normal phase, leading to a spin-valley polarized state. At high enough densities, however, the kinetic energy associated with large k becomes dominant and the system eventually undergoes a transition to the normal phase.

3.3 Phase diagram of multilayer graphene

From the density dependence of the energy in the C2DES, we have seen that the exchange energy drives an instability toward the spin-valley polarization. Now let us consider the phase diagram of multilayer graphene as a function of the carrier density and perpendicular electric field. For the exchange-correlation energy in multilayer graphene, we use the rotational transformation of the chiral wave function in which the chiral wave function at an arbitrary angle can easily be obtained analytically from the wave function obtained at one angle, allowing one to effectively calculate the exchange-correlation energy of interacting electrons in multilayer graphene [31]. The phase diagram is then determined by comparing the total energy of each spin-valley polarized phase by varying n and U_{ext} .

Figure 3.3 shows the phase diagrams of AB, ABC, ABCA stacked multilayer graphene. To understand the phase diagrams, let us consider ABC trilayer graphene and see how the band structure evolves following the white dashed line on the phase diagram in Fig. 3.3(b) with a fixed $U_{\text{ext}} = 0.05$ eV. Focusing on the phase boundary between the P₃ and P₄ states, as the Mexican hat structure of the P_3 state is fully filled while that of the P_4 state remains partially filled, the (negative intraband) exchange contribution from electrons near k = 0 becomes absent in the P₃ state, giving a less negative contribution to the exchange energy, as expected from the pseudospin directions at the Fermi energy in the insets to Fig. 3.3(d). This means that just after the Mexican hat structure of the P₃ state is filled, the energy difference between the P_3 and P_4 states, E_{34} , becomes positive, leading to a phase transition from P_3 to P_4 at the critical density n_c^{34} , as indicated by the black arrow in Fig. 3.3(d). As U_{ext} increases, the density that fills the Mexican hat structure (n_{M_3}) increases and the critical density where the phase transition occurs (n_c^{34}) also increases, showing a positive slope in the phase diagram. As we move to the higher density region, the difference between the two densities n_{M_3} and n_c^{34} becomes smaller since the effect of the kinetic plus Hartree energy is dominant over that of the exchange plus correlation energy. Thus, n_{M_3} and n_{c}^{34} eventually occur at the same point, showing a kink structure in the phase diagram. For a high enough U_{ext} above the kink point, the Mexican hat structures of both P₃ and P₄ states are partially filled and E_{34} increases by U_{ext} as shown in Fig. 3.3(e), resulting in the decreased n_{c}^{34} with a negative slope in the phase diagram. Similarly, other phase boundaries in the phase diagram can be explained, exhibiting a similar pattern.

3.4 Discussion

The calculated phase diagram in Fig. 3.3 captures the main feature of the spontaneous spin-valley polarization recently observed by Zhou et al. [15] in rhombohedral trilayer graphene. Depending on the carrier density and the external electric field, various spin-valley polarized states occur with positive slopes of the phase boundaries within the experimentally accessible range, and the overall structure of the phase diagram agrees well with the experiment in the high density and electric field regime where our theory is valid and the interaction-induced spin-valley polarized states are manifested in the experiment. In the experiment by Zhou et al., there occurs intermediate states between the phases (not shown in the calculated phase diagram in Fig. 3.3) because we determined the phase diagram by comparing the total energy of each phase assuming that the occupied flavors have equal concentrations for simplicity. However, an intermediate state with unequal flavor concentrations is also possible near the phase boundaries. For example, between the P1 and P2 states, a state in which two flavors are occupied with unequal concentrations is possible if it has a lower energy compared to those of P1 and P2. In the current calculation where a mean-field band structure obtained from a self-consistent Hartree approximation is used as a noninteracting band, intermediate states tend to appear more dominantly over pure states in the low-field region of the phase diagram compared to the experiment, which could be cured if we include the effect of the exchangecorrelation energy in the band structure beyond the Hartree energy. For details, see the Chapter B.2.

Here we use a minimal model for multilayer graphene including the nearest-neighbor intralayer and interlayer hopping terms only but neglecting the trigonal warping terms and other remote hopping terms so that the energy dispersion is isotropic, which makes the many-electron perturbation theory calculations practical for multilayer stacks through the rotational transformation of the chiral wave function [31]. This approximation cannot describe states induced by the trigonal warping terms near n = 0 and $U_{\text{ext}} = 0$ point, but captures the spontaneous spin-valley polarized phases which is manifested away from that point. We also want to point out that in the experiment by Zhou *et al.* [15], the P₂ state is ferromagnetic that the two flavors with the same spin polarization are occupied, which is not captured in the current calculation because interactions between the flavors are not included. Moreover, this may explain the appearance of the P₃ state in the current calculation. If we treat spin and valley interactions anisotropically, the P₃ state may disappear, as in the experiment. We leave the effect of electron–electron interactions between the flavors open for future work.

In summary, we studied the spin-valley polarization in rhombohedral multilayer graphene, demonstrating that the spin-valley polarization is driven by the exchange interaction between chiral electrons. Our result explains the tendency toward the spin-valley polarized states as the carrier density, the external external field and the number of layers vary in rhombohedral multilayer graphene.

Chapter 4

Electronic structure of biased alternating twist multilayer graphene

4.1 Introduction

The twisted graphene systems have garnered significant attention due to the discovery of superconductivity and correlated insulating states in magic-angle twisted bilayer graphene (TBG) [32, 33]. When two graphene layers are twisted, a new long-period structure known as a moiré superlattice appears, resulting in a unique band structure that is dependent on the twist angle. At magic angles, the Fermi velocity is reduced to zero and nearly flat bands are formed [34], making it an ideal platform for studying the correlation of electrons.

There are many studies such as twisted double-bilayer graphene [35–40] and twisted triple-bilayer graphene [41], and even to other twisted twodimensional material systems [42–45] and revealed interesting phenomena due to interaction such as correlated insulating [37–40, 44] and topological [35] phases.

Among these systems, alternating twist multilayer graphene (ATMG) has been extensively studied both theoretically [46–48] and experimentally [49–52] due to its robust superconductivity observed in bilayer to pentalayer samples and its magic angle moves to larger angles.

In this chapter, we investigate the effect of a vertical electric field on the electronic structure of ATMG. Using first-order degenerate perturbation theory, we derive the low-energy effective Hamiltonian and energy bands, and calculate the optical conductivity of ATMG, revealing a step-like feature arising from the energy shift of Dirac nodes. The chapter is organized with an introduction to the model of ATMG, followed by the analytical derivation of the low-energy effective Hamiltonian and the calculation of the optical conductivity. Finally, we conclude with a discussion of the results.

4.2 Electronic structure of the alternating twist multilayer graphene

4.2.1 Model



Figure 4.1: Schematic illustration of the alternating twist trilayer graphene with a potential difference U.

We use the model of N-layer graphene with with the ℓ -th layer alternating twist multilayer graphene (ATMG) by an angle $\theta_{\ell} = (-1)^{\ell} \theta/2$, as shown in Fig. 4.1. we assume an interlayer potential difference U due to a vertical electric field. The Hamiltonian of ATMG[48] is given by

$$H = \begin{pmatrix} H_{k}^{(1)} & T(\mathbf{r}) & 0 & \cdots \\ T^{\dagger}(\mathbf{r}) & H_{k}^{(2)} & T^{\dagger}(\mathbf{r}) & \cdots \\ 0 & T(\mathbf{r}) & H_{k}^{(3)} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} + V$$
(4.1)

where the diagonal term $H_{\mathbf{k}}^{(\ell)} = \hbar v_0(\mathbf{k} \cdot \boldsymbol{\sigma}_{\theta_\ell})$ is the Hamiltonian of monolayer graphene with $\boldsymbol{\sigma}_{\theta_\ell} = e^{\frac{i}{2}\theta_\ell\sigma_z}\boldsymbol{\sigma}e^{-\frac{i}{2}\theta_\ell\sigma_z}$ rotated by $\pm\theta/2$, $T(\mathbf{r})$ is the interlayer tunneling, and $V = \text{diag}(V^{(1)}\mathbb{I}_2, V^{(2)}\mathbb{I}_2, ..., V^{(N)}\mathbb{I}_2)$ is a on-site potential difference term. We use the intralayer hopping t = -3.1 eV and the Fermi velocity is about $v_0 = \sqrt{3}a|t|/2\hbar \simeq 10^6$ m/s where a = 2.46 Å is the lattice constant.

We set $V^{(\ell+1)} - V^{(\ell)} = U$ by the definition of interlayer potential difference, and $V^{(1)} = -V^{(N)}$ to fix Dirac cone's height to center. The interlayer tunneling term[34] is given by

$$T(\mathbf{r}) = \sum_{j=0,\pm} e^{i\mathbf{q}_j \cdot \mathbf{r}} T^j, \qquad (4.2)$$

where

$$T^{0} = \begin{pmatrix} w' & w \\ w & w' \end{pmatrix}, \ T^{\pm} = \begin{pmatrix} w' & w e^{\pm i 2\pi/3} \\ w e^{\pm i 2\pi/3} & w' \end{pmatrix},$$
(4.3)

 $q_0 = 2k_D \sin(\theta/2)(0, -1)$ and $q_{\pm} = 2k_D \sin(\theta/2)(\pm\sqrt{3}/2, 1/2)$ with the Dirac momentum $k_D = 4\pi/3a$, w' = 0.0939 eV and w = 0.12 eV [36]. We used a model that considered the hopping difference between the AA and AB (BA) regions and out-of-plane relxation [53, 54]. This is given by the result w/=w' of the tunneling term.

We performed calculations for angles greater than 3° . This angle is larger than the $1^{\circ} - 2^{\circ}$ where the magic angle is located, but it is the better condition that our minimal model fits better. At this large angle, the velocity

in the Dirac cone at \bar{K} and \bar{K}' near the two moiré Brillouin zone (mBZ) does not approach zero.

Without the vertical electric field, the system is decomposed into twisted bilayer graphenes and an additional monolayer graphene (only for odd number of layers) band[46]. The property of ATMG is almost similar to that of Bernal stacked multilayer graphene, which decomposition into bilayer graphenes and monolayer graphene (only for odd number of layers). We can analytically obtain the ATMG wavefunction by extending the tBG wavefunction using this property.

Using the first shell model, we first find the wavefunction of twisted bilayer graphene with the rigid model (w = w' = 0.12 eV). This approximation is still valid when the twist angle is large. The Hamiltonian near \bar{K} takes into account only the three neighboring \bar{K}' , is given by

$$\psi_{\lambda,\bar{K}}^{\text{TBG}} = \frac{1}{\sqrt{1+6\alpha^2}} \begin{pmatrix} a_{\lambda} \\ b_{q_{0},\lambda} \\ b_{q_{+},\lambda} \\ b_{q_{-},\lambda} \end{pmatrix}, \qquad (4.4)$$
$$\begin{pmatrix} b_{q_{0},\lambda} \end{pmatrix}$$

$$\psi_{\lambda,\bar{K}'}^{\text{TBG}} = \frac{1}{\sqrt{1+6\alpha^2}} \begin{pmatrix} b_{\boldsymbol{q}_0,\lambda} \\ b_{\boldsymbol{q}_+,\lambda} \\ b_{\boldsymbol{q}_-,\lambda} \\ a_{\lambda} \end{pmatrix}$$
(4.5)

where $\alpha = w/(2v_0k_D\sin(\theta/2))$ is a dimensionless parameter[34] and we use a_λ as a nomalized wavefunction of the nomalized monolayer graphene Hamiltonian, $\hat{k} \cdot \sigma_{\theta_\ell}$ with $\lambda = \pm 1$ is eigenvalue index, and $b_{q_j,\lambda} = -h_j^{-1}T_j^{\dagger}a_\lambda$ with $h_j = \hbar v_0(\mathbf{k} + \mathbf{q}_j) \cdot \sigma_{\theta_\ell}$ [46].

In a similar to Bernal stacked multilayer graphene, the wavefunctions of ATMG is given as the form of linear combination of the wavefunctino of twited biayer graphene. it can be constructed by the following method [46]:

$$\Psi_{r,\lambda}^{(\ell)} = \sqrt{\frac{2\tau}{N+1}} \sin(\ell\theta_r) \,\psi_{r,\lambda}^{\text{TBG}},\tag{4.6}$$

where $\tau = 2 - \delta_{r,n+1}$, $\theta_r = r\pi/(N+1)$ with r = 1, 2, ..., n for even N = 2n or for odd N = 2n + 1 with additional r = (n + 1)-th mode near \bar{K} , and $\psi_{r,\lambda}^{\text{TBG}}$ can be obtained from Eq. (4.4) by changin $\alpha \to t_r \alpha$ and $b_{\lambda} \to t_r b_{\lambda}$ with $t_r = 2\cos\theta_r$. Here, $\Psi_{r,\lambda} = (\Psi_{r,\lambda}^{(1)}, \Psi_{r,\lambda}^{(2)}, ..., \Psi_{r,\lambda}^{(N)})^t$ is a normalized eigenstate of the effective Hamiltonian $H_{\text{eff}} = \hbar v_r(\mathbf{k} \cdot \boldsymbol{\sigma})$ of ATMG with $|\Psi_{r,\lambda}|^2 = 1$, where v_r is a Fermi velocity of the Dirac cone $\Psi_{r,\lambda}$ given by

$$\frac{v_r}{v_0} = \frac{1 - 3t_r^2 \alpha^2}{1 + 6t_r^2 \alpha^2}.$$
(4.7)

The above Eq. (4.7) can be used not only when N is an even number but also when it is an odd number, and in the case of r = n+1, an expression for odd number of layers is obtained.

Here, we introduce a low-energy effective Hamiltonian with a vertical electric field using the first order degenerate perturbation in the first shell model. In the absence of an electric field, the Dirac-cones are layer hybridized. However, when an electric field is applied, Dirac-cones become localized to the a single layer, and the center of Dirac-cone shifts proportionally to the given potential difference U. Therefore the effective Hamiltonian of each Dirac-cone are represented as

$$H_{\text{eff}} = C(\alpha)U + \hbar v^* (\boldsymbol{k} \cdot \boldsymbol{\sigma}), \qquad (4.8)$$

where first term $C(\alpha)U$ is the energy shift of corresponding Dirac-cone, the energy shift is proportional to the interlayer potential U, and v^* is the modified Fermi velocity of the effective Hamiltonian and the Fermi velocity v^* can be represented as a linear combination of v_r .

In the following chapter 4.2.B and 4.2.C, we introduce the effective

Hamiltonian of N = 3 and N = 4 ATMG as examples, and the N = 5 case in Appendix C.1.

4.2.2 *N* = 3

Here, we introduce the detail of the effective Hamiltonian of alternating twist trilayer graphene (AT3G) naer \bar{K} and \bar{K}' of the mBZ. There are two Dirac cones with v_0 and v_1 Fermi velocities at \bar{K} , as shown in Fig. 4.2(a) where v_0 is the Fermi velocity of monolayer graphene. Using Eq. (4.4), we obtain the following normalized wave functions $\Psi_{r,\lambda}$ near \bar{K} in our first shell model:

$$\Psi_{1,\lambda} = \frac{1}{\sqrt{2+24\alpha^2}} \begin{pmatrix} a_{\lambda} \\ 2b_{q_0,\lambda} \\ 2b_{q_+,\lambda} \\ 2b_{q_-,\lambda} \\ a_{\lambda} \end{pmatrix}, \quad \Psi_{2,\lambda} = \frac{1}{\sqrt{2}} \begin{pmatrix} a_{\lambda} \\ 0 \\ 0 \\ 0 \\ -a_{\lambda} \end{pmatrix}.$$
(4.9)

The perturbation \hat{V} is given by $\hat{V} = \text{diag}(-U\mathbb{I}_2, \mathbf{0}_6, U\mathbb{I}_2)$. Then, using the wave functions in Eq. (4.9), we obtain the perturbation matrix is represented as

$$V_{\bar{K}} = \begin{pmatrix} 0 & -U/\sqrt{1+12\alpha^2} \\ -U/\sqrt{1+12\alpha^2} & 0 \end{pmatrix}.$$
 (4.10)

We find the effective Hamiltonian near \bar{K} as

$$H_{\text{eff},\bar{K}}^{(\pm)} = \pm C(\alpha)U + \hbar v^* (\boldsymbol{k} \cdot \boldsymbol{\sigma}), \qquad (4.11)$$

where $C(\alpha) = 1/\sqrt{1+12\alpha^2}$ and $v^* = (v_0 + v_1)/2$ and this result illustrated as the inset of Figs. 4.2 (a) and 4.2 (b).

On the other hand, near $\overline{K'}$, there is a only one Dirac-cone with v_1 , its



Figure 4.2: Band structure of N = 3 ATMG at $\theta = 3^{\circ}$ for (a) U = 0 and (b) U = 0.1 eV. The left and right insets to (a) and (b) represent the schematic band structure near \bar{K} and \bar{K}' . (c) $C(\alpha)$ and (d) v^*/v_0 as a function of twist angle θ for the full numerical calculations (solid line) and the analytical result from the rigid ($\omega = \omega'$) first shell model (dashed line).

wavefunction is given by

$$\Psi_{1,\lambda} = \frac{1}{\sqrt{1+12\alpha^2}} \begin{pmatrix} b_{\boldsymbol{q}_0,\lambda} \\ b_{\boldsymbol{q}_+,\lambda} \\ b_{\boldsymbol{q}_-,\lambda} \\ a_{\lambda} \\ b_{\boldsymbol{q}_0,\lambda} \\ b_{\boldsymbol{q}_+,\lambda} \\ b_{\boldsymbol{q}_-,\lambda} \end{pmatrix}.$$
(4.12)

Then, the perturbation matrix $V_{\bar{K}'}$ vanishes near \bar{K}' , the effective Hamilto-



Figure 4.3: Similar to panels (a)-(c) in Fig. 4.2, but for N = 4 ATMG. If U < 0, the energy shifts are reversed. In panel (d), we show the two Fermi velocities v_{\pm}^* as given in Eq. (4.18) of the positively and negatively shifted Dirac cones illustrated in the inset to (b).

nian is given by

$$H_{\text{eff},\bar{K}'} = \hbar v_1 (\boldsymbol{k} \cdot \boldsymbol{\sigma}). \tag{4.13}$$

In Figs. 4.2, we show (c) the energy shift coefficient $C(\alpha)$ and (d) the modified Fermi velocity v^* and the result of the first shell model (dashed line) and the full numerical result (solid line) agree at large angles.

4.2.3 N = 4

In this section, we introduce the detail of the effective Hamiltonian of alternating twist tetralayer graphene (AT4G) naer \bar{K} and \bar{K}' of the mBZ, like AT3G. The change point is that the number of dirac cones in \bar{K}' is changed and the potential perturbation form is changed. The wavefunction

of AT4G near \bar{K} is given by

$$\Psi_{r,\lambda} = \frac{2}{\sqrt{5(1+6t_r^2\alpha^2)}} \begin{pmatrix} \sin\theta_r \cdot a_\lambda \\ \sin 2\theta_r \cdot t_r b_\lambda \\ \sin 3\theta_r \cdot a_\lambda \\ \sin 4\theta_r \cdot t_r b_\lambda \end{pmatrix}$$
(4.14)

where r = 1, 2 and $b_{\lambda} = (b_{q_0,\lambda}, b_{q_+,\lambda}, b_{q_-,\lambda})^t$. The perturbation is given by $\hat{V} = \text{diag}(-\frac{3U}{2}\mathbb{I}_2, -\frac{U}{2}\mathbb{I}_6, \frac{U}{2}\mathbb{I}_2, \frac{3U}{2}\mathbb{I}_6)$ near \bar{K} . the size of the perturbation matrix $V_{\bar{K}}$ would be 2 × 2 due to two Dirac cones near \bar{K} , and its elements $V_{rr'}$ are given by

$$V_{rr'} = \frac{4U}{N+1} \frac{1 - 6t_r t_{r'} \alpha^2}{\sqrt{(1 + 6t_r^2 \alpha^2)(1 + 6t_{r'}^2 \alpha^2)}}$$
$$\sum_{l=0}^{N/2} \left(2\ell - \frac{N-1}{2}\right) \sin(2\ell+1)\theta_r \sin(2\ell+1)\theta_{r'}$$
$$= \frac{2U}{5} \frac{1 - 6t_r t_{r'} \alpha^2}{\sqrt{(1 + 6t_r^2 \alpha^2)(1 + 6t_{r'}^2 \alpha^2)}} (-3\sin\theta_r)$$
$$\cdot \sin\theta_{r'} + \sin 3\theta_r \sin 3\theta_{r'} + 5\sin 5\theta_r \sin 5\theta_{r'}). \quad (4.15)$$

By diagonalizing $V_{\bar{K}}$, we find the effective Hamiltonian of biased AT4G near \bar{K} as

$$H_{\text{eff},\bar{K}} = C_{\pm}(\alpha)U + \hbar v_{\pm}^{*}(\boldsymbol{k} \cdot \boldsymbol{\sigma}), \qquad (4.16)$$

where

$$C_{\pm}(\alpha) = \frac{1}{2(1+18\alpha^2+36\alpha^4)} [-(1+12\alpha^2-36\alpha^4) \\ \pm \sqrt{(1+12\alpha^2)(1+18\alpha^2+45\alpha^4+108\alpha^6)}] \quad (4.17)$$

and

$$v_{\pm}^{*} = \frac{A_{\pm}^{2}v_{1} + B^{2}v_{2}}{A_{\pm}^{2} + B^{2}}.$$
(4.18)

Here, A_{\pm} and B are mixing coefficients are given by

$$A_{\pm} = 1 + 15\alpha^2 - 36\alpha^4$$

$$\pm \sqrt{5(1 + 12\alpha^2)(1 + 18\alpha^2 + 45\alpha^4 + 108\alpha^6)},$$

$$B = -2(1 + 6\alpha^2)\sqrt{1 + 18\alpha^2 + 36\alpha^4}.$$
(4.19b)

From the above result, we find that the two Dirac cones with the velocities v_1 and v_2 are hybridized with the ratio of A_{\pm} and B, and shifted by $C_{\pm}(\alpha)U$, as schematically illustrated in Fig. 4.3(b).

We confirmed that the modified Fermi velocity of the energy shifted Dirac-cone is given by a linear combination of v_1 and v_2 with the vertical electric field, is shown as Fig. 4.3 (b).

On the other hand, near \overline{K}' , the wavefunctions for two Dirac-cones with the velocity v_1 and v_2 are given by

$$\Psi_{r,\lambda} = \frac{2}{\sqrt{5(1+6t_r^2\alpha^2)}} \begin{pmatrix} \sin\theta_r \cdot t_r b_\lambda \\ \sin 2\theta_r \cdot a_\lambda \\ \sin 3\theta_r \cdot t_r b_\lambda \\ \sin 4\theta_r \cdot a_\lambda \end{pmatrix}.$$
(4.20)

Since $\sin \ell \theta_r = (-1)^r \sin (N + 1 - \ell) \theta_r$, the wavefunction near \bar{K}' can be obtained by flipping two Dirac-cones near \bar{K} . Therefore, the effective Hamiltonian of AT4G near \bar{K}' can be represent as

$$H_{\text{eff},\bar{K}'} = -C_{\pm}(\alpha)U + \hbar v_{\pm}^{*}(\boldsymbol{k} \cdot \boldsymbol{\sigma}), \qquad (4.21)$$

where $C_{\pm}(\alpha)$ and v_{\pm}^* are the same with those near \bar{K} . In detail, our model Hamiltonian of AT4G has a combined symmetry $\hat{\Sigma}\hat{T}$, which can be ex-

pressed as

$$(\hat{\Sigma}\hat{\mathcal{T}})H(\boldsymbol{k})(\hat{\Sigma}\hat{\mathcal{T}})^{-1} = -H(-\boldsymbol{k}), \qquad (4.22)$$

where $\hat{\Sigma}$ is defined as

$$\hat{\Sigma} = \begin{pmatrix} 0 & 0 & 0 & \sigma_x \\ 0 & 0 & -\sigma_x & 0 \\ 0 & \sigma_x & 0 & 0 \\ -\sigma_x & 0 & 0 & 0 \end{pmatrix}.$$
(4.23)

The operator $\hat{\Sigma}$ only changes the valley index $(K \leftrightarrow K')$, while maintaining the mBZ corner $(\bar{K} \rightarrow \bar{K}, \bar{K}' \rightarrow \bar{K}')$ [55]. Meanwhile, the time-reversal operator $\hat{\mathcal{T}}$ changes both the valley index and the mBZ corner points $(K \leftrightarrow$ $K', \bar{K} \leftrightarrow \bar{K}')$. This combined symmetry $\hat{\Sigma}\hat{\mathcal{T}}$ is maintained even when an interlayer potential is present. The effective Hamiltonians between \bar{K} and \bar{K}' are also related as Eq. (4.22).

4.2.4 Arbitrary N

As the layer number N is increased, the size of the perturbation matrix is also proportionally increased and it becomes progressively cumbersome to obtain analytically the effective Hamiltonian of ATMG for a large number of layers in the presence of an applied field even if we use the first shell model. Instead, here want to provide the general behavior patterns of the effective Hamiltonian of biased ATMG for arbitrary N. Tables 4.1 and 4.2 show the summary of the effective Hamiltonian for N = 2 - 8 ATMG in the presence of the interlayer potential difference.

As the layer number N increases, the number of Dirac-cones increases and the size of the perturbation matrix increases proportionally. Analytically obtaining the effective Hamiltonian of an ATMG becomes increasingly complex. Here, we discuss the general pattern of the effective Hamiltonian of ATMG. Tables 4.1 and 4.2 show behavior for N = 2 - 8 ATMG with a vertical electric field.

N		near <i>K</i>		near \overline{K}'	
		Band	H _{eff}	Band	H _{eff}
3	U = 0		$\begin{cases} H^{(0)} = \hbar v_0 (\mathbf{k} \cdot \boldsymbol{\sigma}) \\ H^{(1)} = \hbar v_1 (\mathbf{k} \cdot \boldsymbol{\sigma}) \end{cases}$		$H^{(1)} = \hbar v_1 (\boldsymbol{k} \cdot \boldsymbol{\sigma})$
	<i>U</i> ≠ 0		$H^{(\pm)} = \pm \Delta + \hbar v^* (\mathbf{k} \cdot \boldsymbol{\sigma})$		$H^{(1)} = \hbar v_1 (\boldsymbol{k} \cdot \boldsymbol{\sigma})$
5	U = 0		$\begin{cases} H^{(0)} = \hbar v_0(\boldsymbol{k} \cdot \boldsymbol{\sigma}) \\ H^{(1)} = \hbar v_1(\boldsymbol{k} \cdot \boldsymbol{\sigma}) \\ H^{(2)} = \hbar v_2(\boldsymbol{k} \cdot \boldsymbol{\sigma}) \end{cases}$		$\begin{cases} H^{(1)} = \hbar v_1 (\mathbf{k} \cdot \boldsymbol{\sigma}) \\ H^{(2)} = \hbar v_2 (\mathbf{k} \cdot \boldsymbol{\sigma}) \end{cases}$
	<i>U</i> ≠ 0	$\begin{matrix} \Delta_1 \\ \Delta_1 \\ \downarrow \end{matrix} $	$\begin{cases} H^{(0)} = \hbar v_0^* (\boldsymbol{k} \cdot \boldsymbol{\sigma}) \\ H^{(\pm 1)} = \pm \Delta_1 \\ + \hbar v_1^* (\boldsymbol{k} \cdot \boldsymbol{\sigma}) \end{cases}$		$H^{(\pm)} = \pm \Delta + \hbar v^* (\mathbf{k} \cdot \boldsymbol{\sigma})$
7	U = 0		$\begin{cases} H^{(0)} = \hbar v_0(\boldsymbol{k} \cdot \boldsymbol{\sigma}) \\ H^{(1)} = \hbar v_1(\boldsymbol{k} \cdot \boldsymbol{\sigma}) \\ H^{(2)} = \hbar v_2(\boldsymbol{k} \cdot \boldsymbol{\sigma}) \\ H^{(3)} = \hbar v_3(\boldsymbol{k} \cdot \boldsymbol{\sigma}) \end{cases}$		$\begin{cases} H^{(1)} = \hbar v_1(\boldsymbol{k} \cdot \boldsymbol{\sigma}) \\ H^{(2)} = \hbar v_2(\boldsymbol{k} \cdot \boldsymbol{\sigma}) \\ H^{(3)} = \hbar v_3(\boldsymbol{k} \cdot \boldsymbol{\sigma}) \end{cases}$
	$U \neq 0$	$\begin{matrix} v_2^* \\ v_1^* \\ \Delta_1 \end{matrix} \begin{matrix} v_2^* \\ v_1^* \\ \Delta_2 \end{matrix} \begin{matrix} v_2^* \\ v_2^* \end{matrix}$	$\begin{cases} H^{(\pm 1)} = \pm \Delta_1 \\ +\hbar v_1^*(\boldsymbol{k} \cdot \boldsymbol{\sigma}) \\ H^{(\pm 2)} = \pm \Delta_2 \\ +\hbar v_2^*(\boldsymbol{k} \cdot \boldsymbol{\sigma}) \end{cases}$	$\begin{matrix} \Delta_1 \\ \Delta_1 \\ \Delta_1 \end{matrix} $	$\begin{cases} H^{(0)} = \hbar v_0^* (\boldsymbol{k} \cdot \boldsymbol{\sigma}) \\ H^{(\pm 1)} = \pm \Delta_1 \\ + \hbar v_1^* (\boldsymbol{k} \cdot \boldsymbol{\sigma}) \end{cases}$

Table 4.1: the effective Hamiltonian and the configuration of modified Fermi velocity of ATMG for odd numbers N = 3, 5, 7.

Firstly, for an odd number of layers ATMG, there are (N-1)/2 TBG Dirac-cones with modified Fermi velocity v_r (r = 1, 2, ..., (N-1)/2) near \bar{K} and \bar{K}' , and one additional monolayer-like Dirac cone with v_0 at \bar{K} . We can use these to find the perturbation matrix and find the effective Hamiltonian as shown in Table 4.1. In detail, if there are m Dirac cones at \bar{K} or \bar{K}' ,



Figure 4.4: Schematic picture of the potential differences and energy shift of Dirac cones near \bar{K} and \bar{K}' in the asymptotic limit ($\alpha \rightarrow 0$).

we have m/2 pairs of Dirac-cones shifted by $\pm \Delta_i$ (i = 1, 2, ..., m/2) for even m, whereas we have (m - 1)/2 pairs of Dirac cones plus one Dirac cone without energy shift for odd m. Each pair of Dirac cones has the same effective Fermi velocity. If the number of Dirac-cones is m, there are $\lfloor m/2 \rfloor$ Dirac-cone pairs with the opposite energy shift \pm . If m is odd, there is an additional monolayer-like band with no energy shift.

Secondly, for an even number of layers ATMG, there are N/2 TBG Dirac-cones with modified Fermi velocity v_r (r = 1, 2, ..., N/2) near \bar{K} and \bar{K}' . We can use these to find the perturbation matrix and find the effective Hamiltonian as shown in Table 4.2. However, one side of the pair belongs to



Figure 4.5: Band structure for N = 5-8 ATMG at $\theta = 5^{\circ}$ with U = 0.1 eV. Solid(dashed) lines represent the numerical result of full numerical model (effective Hamiltonian) in the $\alpha \to 0$ limit.

 \bar{K} and the other to \bar{K}' . In detail, there are N/2 Dirac-cones near each \bar{K} or \bar{K}' , we have N/2 pairs of Dirac-cones shifted by $\pm \Delta_i$ (i = 1, 2, ..., m/2), however, one side of the pair belongs to \bar{K} and the other to \bar{K}' . Each pair of Dirac cones has the same effective Fermi velocity.

Lastly, let us consider the effective Hamiltonian of biased ATMG in the asymptotic limit ($\alpha \rightarrow 0$) where the twist angle θ becomes much larger than the first magic angle of ATMG. For the first shell model, $|b_{\lambda}|$ becomes proportional to α , so only monolayer terms a_{λ} of $\Psi_{r,\lambda}$ survive in this limit. Thus, the energy splitting coefficient $C(\alpha)$ of ATMG with arbitrary N at \overline{K} ($\overline{K'}$) can be obtained as odd (even) layer components of \hat{V} , as schematically shown in Fig. 4.4.

Finally, we consider the asymptotic limit ($\alpha \rightarrow 0$) of the effective Hamiltonian of ATMG, corresponding that angle θ becomes much larger.

In this limit, all of Dirac-cone become monolayer-like with the monolayer velocity v_0 . $|b_{\lambda}| \propto \alpha$ and goes zero, a_{λ} is only finite. Thus, the energy shift is obtained as layer component of \hat{V} , as shown in Fig. 4.4. The modified Fermi velocity v^* goes to v_0 , since all Dirac-cones goes a single monolayer term.

Therefore, the effective Hamiltonian can be described as monolayer graphenes with the energy shift described by $C(\alpha \rightarrow 0)U$, which can be obtained in Fig. 4.4. Figure 4.5 shows the band structure of N = 5 - 8 ATMG with U = 0.1 eV at $\theta = 5^{\circ}$ in the asymptotic limit, which agrees with the full numerical for enough large angle.

4.3 Optical conductivity of the alternating twist multilayer graphene

The Kubo formula for the optical conductivity is given by [56]

$$\sigma_{ij}(\omega) = -\frac{ie^2}{\hbar} \sum_{s,s'} \int \frac{d^2k}{(2\pi)^2} \frac{f_{s,\mathbf{k}} - f_{s',\mathbf{k}}}{\varepsilon_{s,\mathbf{k}} - \varepsilon_{s',\mathbf{k}}}$$

$$\times \frac{M_i^{ss'}(\mathbf{k}) M_j^{s's}(\mathbf{k})}{\hbar\omega + \varepsilon_{s,\mathbf{k}} - \varepsilon_{s',\mathbf{k}} + i0^+}, \qquad (4.24)$$

where $i, j = x, y, f_{s,\mathbf{k}} = 1/[1 + e^{(\varepsilon_{s,\mathbf{k}}-\mu)/k_{\rm B}T}]$ is the Fermi distribution function with the band index s and k is wavevector, μ is the chemical potential and $M_i^{ss'}(\mathbf{k}) = \langle s, \mathbf{k} | \hbar \hat{v}_i | s', \mathbf{k} \rangle$ with the velocity operator $\hat{v}_i = \frac{1}{\hbar} \frac{\partial \hat{H}}{\partial k_i}$.

We consider the only real part of the longitudinal conductivity at zero temperature with $\mu = 0$ and $\eta = 5$ meV in Eq. (4.24). In Figs. 4.6 and 4.7, we show the optical conductivity results for AT3G and AT4G with(without) a vertical electric field at the twist angle $\theta = 5^{\circ}$.

With a vertical electric field, the longitudinal conductivity converges to $N\sigma_0$ for low- and high-frequency limits, as shown in Figs. 4.6(c) and 4.7(c) where $\sigma_0 = g_{\rm sv}e^2/16\hbar$ is the optical conductivity of monolayer graphene. In



Figure 4.6: Band structure and the longitudinal conductivity for (a), (c) U = 0 and (b), (d) U = 0.1 eV in N = 3 ATMG at $\theta = 5^{\circ}$. The insets in (b) shows a zoomed in view of the band structure near \overline{K} and $\overline{K'}$. The arrows in the band structure indicate interband transitions corresponding to peaks in the conductivity. In (d), a Drude peak appears at low frequencies due to intraband contributions.

low-frequency region, there are N Dirac-cones, which give $N\sigma_0$. In highfrequency region, since energy for interlayer hopping is neglected, it converges to $N\sigma_0$. In intermediate frequency region, a dominant peak appears around $\hbar\omega \sim 0.9$ eV as indicated by the red arrows.

With a vertical electric field, the conductivity show a step-like feature in low frequency region, in Figs. 4.6(d) and 4.7(d). For AT3G, two Diraccones near \bar{K} are energy shifted and interband transition are forbidden, however, a Dirac-cones at \bar{K}' gives just σ_0 in the low frequency region. For AT4G, two Dirac-cones near \bar{K} are energy shifted and interband transition



Figure 4.7: Same as Fig. 4.6 for N = 4 ATMG.

are forbidden, a Dirac-cones near \overline{K}' is same with \overline{K} in the low frequency region, so only Drude peak appears.

Since these step-like features are related to the interband transition, they are related to the magnitude of the Dirac-cone energy shift Δ . as the frequency increase, the optical conductivity increase by $2\sigma_0$ near $\hbar\omega \sim$ 2Δ and $\Delta_+ + \Delta_-$ and eventually $\sigma \rightarrow N\sigma_0$ like AA-stacked multialyer graphene[57, 58].

4.4 Discussion

We obtain the analytic form of the effective Hamiltonian including the potential difference near \bar{K} and \bar{K}' using the first shell model, and find the modified Fermi velocities. This effective model is valid within $k_c \sim U/\hbar v_0$.

With small angle about the first magic angle $\theta_{M}^{(N)} \leq \theta_{M}^{(\infty)} \approx 2.2^{\circ}$ [46], the first shell model is broken down, so our results agree with the full numerical calculation for twist angle $\theta \gtrsim 2.2^{\circ}$.

In summary, we have studied the effect of the vertical electric field on the low energy effective model of the electronic structure of ATMG, how it affects the optical conductivity. We analytically find the low energy effective Hamiltonian and its modified Fermi velocity near \bar{K} and \bar{K}' for AT3G, AT4G and arbitrary N. we show that the change of the band structure including the energy shift of the Dirac cone makes a step-like feature similar to AA stacking multilayer graphene in the optical conductivity.

N		near \overline{K}		near \overline{K}'	
		Band	H _{eff}	Band	H _{eff}
2	U = 0		$H^{(1)} = \hbar v_1 (\boldsymbol{k} \cdot \boldsymbol{\sigma})$		$H^{(1)} = \hbar v_1 (\boldsymbol{k} \cdot \boldsymbol{\sigma})$
	<i>U</i> ≠ 0		$H^{(-1)} = - \Delta + \hbar v_1 (\mathbf{k} \cdot \boldsymbol{\sigma})$		$H^{(+1)} = + \Delta + \hbar v_1 (\mathbf{k} \cdot \boldsymbol{\sigma})$
4	U = 0		$\begin{cases} H^{(1)} = \hbar v_1 (\mathbf{k} \cdot \boldsymbol{\sigma}) \\ H^{(2)} = \hbar v_2 (\mathbf{k} \cdot \boldsymbol{\sigma}) \end{cases}$		$\begin{cases} H^{(1)} = \hbar v_1 (\boldsymbol{k} \cdot \boldsymbol{\sigma}) \\ H^{(2)} = \hbar v_2 (\boldsymbol{k} \cdot \boldsymbol{\sigma}) \end{cases}$
	<i>U</i> ≠ 0	$\begin{matrix} \Delta_2 \\ \Delta_1 \end{matrix} \\ \begin{matrix} \psi_1^* \end{matrix}$	$\begin{cases} H^{(-1)} = - \Delta_1 \\ +\hbar v_1^*(\boldsymbol{k} \cdot \boldsymbol{\sigma}) \\ H^{(+2)} = + \Delta_2 \\ +\hbar v_2^*(\boldsymbol{k} \cdot \boldsymbol{\sigma}) \end{cases}$	$\begin{vmatrix} \Delta_1 \\ \Delta_2 \end{vmatrix} = \begin{matrix} v_1^* \\ v_2^* \\ v_2^* \end{matrix}$	$\begin{cases} H^{(+1)} = + \Delta_1 \\ +\hbar v_1^*(\boldsymbol{k}\cdot\boldsymbol{\sigma}) \\ H^{(-2)} = - \Delta_2 \\ +\hbar v_2^*(\boldsymbol{k}\cdot\boldsymbol{\sigma}) \end{cases}$
6	U = 0		$\begin{cases} H^{(1)} = \hbar v_1(\boldsymbol{k} \cdot \boldsymbol{\sigma}) \\ H^{(2)} = \hbar v_2(\boldsymbol{k} \cdot \boldsymbol{\sigma}) \\ H^{(3)} = \hbar v_3(\boldsymbol{k} \cdot \boldsymbol{\sigma}) \end{cases}$		$\begin{cases} H^{(1)} = \hbar v_1(\boldsymbol{k} \cdot \boldsymbol{\sigma}) \\ H^{(2)} = \hbar v_2(\boldsymbol{k} \cdot \boldsymbol{\sigma}) \\ H^{(3)} = \hbar v_3(\boldsymbol{k} \cdot \boldsymbol{\sigma}) \end{cases}$
	<i>U</i> ≠ 0	$\begin{matrix} \Delta_2 \\ \Delta_1 \\ \Delta_1 \\ \Delta_3 \end{matrix} \qquad $	$\begin{cases} H^{(-1)} = - \Delta_1 \\ +\hbar v_1^*(\boldsymbol{k}\cdot\boldsymbol{\sigma}) \\ H^{(+2)} = + \Delta_2 \\ +\hbar v_2^*(\boldsymbol{k}\cdot\boldsymbol{\sigma}) \\ H^{(-3)} = - \Delta_3 \\ +\hbar v_3^*(\boldsymbol{k}\cdot\boldsymbol{\sigma}) \end{cases}$	$\begin{matrix} \Delta_3 \\ \Delta_1 \\ \Delta_2 \\ \Delta_2 \end{matrix} \downarrow \begin{matrix} \psi_1^* \\ \psi_1^* \\ \psi_2^* \end{matrix}$	$\begin{cases} H^{(+1)} = + \Delta_1 \\ +\hbar v_1^*(\boldsymbol{k}\cdot\boldsymbol{\sigma}) \\ H^{(-2)} = - \Delta_2 \\ +\hbar v_2^*(\boldsymbol{k}\cdot\boldsymbol{\sigma}) \\ H^{(+3)} = + \Delta_3 \\ +\hbar v_3^*(\boldsymbol{k}\cdot\boldsymbol{\sigma}) \end{cases}$
8	U = 0		$H^{(r)} = \hbar v_r (\mathbf{k} \cdot \boldsymbol{\sigma})$ $(r = 1, 2, 3, 4)$		$H^{(r)} = \hbar v_r (\boldsymbol{k} \cdot \boldsymbol{\sigma})$
	$U \neq 0$	$\begin{matrix} \Delta_4 \\ \Delta_2 \\ \Delta_1 \\ \Delta_3 \end{matrix} \begin{matrix} \psi_4^* \\ \psi_2^* \\ \psi_1^* \\ \psi_1^* \end{matrix}$	$H^{((-1)^r r)} = (-1)^r$ $\cdot \Delta_r + \hbar v_r^* (\mathbf{k} \cdot \boldsymbol{\sigma})$ $(r = 1, 2, 3, 4)$	$\begin{matrix} \Delta_3 \\ \Delta_1 \\ \Delta_2 \\ \Delta_2 \\ \Delta_4 \end{matrix} = \begin{matrix} v_3^*\\ v_2^*\\ v_4^* \end{matrix}$	$H^{((-1)^{r+1}r)} = (-1)^{r+1} \cdot \Delta_r + \hbar v_r^* (\boldsymbol{k} \cdot \boldsymbol{\sigma})$

Table 4.2: the effective Hamiltonian and the configuration of modified Fermi velocity of ATMG for odd numbers N=2,4,6,8.

Chapter 5

Broken sublattice symmetry states in Bernal stacked multilayer graphene

5.1 Introduction

Over the past decade, two-dimensional graphene and multilayer graphene have been studied due to many interesting properties and expectation for device applications[1–5]. In particular, the band dispersion varies depending on the stacking method of single-layer graphene, and the gap opens when a vertical electric field is applied. It gives a lot of interest in being able to tune the system. Multilayer graphene has a structure called Dirac cone at the charge neutral point, and it has the chiral nature in addition to low energy dispersion. This property allows the multilayer graphene system to have strong electron-electron interaction, and shows many body effects[11, 59– 63]. In particular, spontaneous symetry breaking layer polarized states and band gap opening were predicted in bilayer graphene[8] and rhombohedral trilayer graphene[9], and observed experimentally[12, 13]. In addition, the band gap opening of the dirac cone, which has a chiral nature, causes various Hall effects, research on this has also been studied[64–67].

In this chapter, we analyze the possible symmetry breaking groundstates induced by the electron-electron interaction in ABAB Bernal stacking tetralyer graphene. Interestingly, When an electric field below a certain is applied, a correlated state can occur and its band gap does not disappear. We show that the heavy-mass band and light-mass band follow an effective Hund's rule for pseudospinor. These changes can alter the type of Hall conductivity and this change can be observed in experiments. In Bernal-stacked multilayer graphene with more than 6 stacked even layers, but its condensed state can be described qualitatively. On the other hand, graphene with an odd number of layers has a suppressed gap in the odd number of layers.

This chapter is based on the publicated paper [14], in which I participated as a co-author.

5.2 Method

We used the minimal continuum model for multilayer graphene, which only considers nearest-neighbor intralayer and interlayer hopping. The noninteraction Hamiltonian is given by

$$\hat{H}_0 = \sum_{\boldsymbol{k},\xi,\xi'} \hat{c}^{\dagger}_{\boldsymbol{k},\xi} \varepsilon^{(0)}_{\boldsymbol{k},\xi'}(\boldsymbol{k}) \hat{c}_{\boldsymbol{k},\xi'}, \qquad (5.1)$$

where $\varepsilon_{\xi,\xi'}^{(0)}(\mathbf{k})$ is the matrix elements of the non-interacting Hamiltonian for a set of index $\xi = (\sigma, \tau, i)$ for the spin σ , valley τ , sublattice *i*, wavevector \mathbf{k} , and $\hat{c}_{\mathbf{k},\xi}^{\dagger}$ ($\hat{c}_{\mathbf{k},\xi}$) is creation (annihilation) operator. Here, we use the nearest-neighbor intralayer hopping parameter $t_0 = 2.598$ eV, the interlayer hopping parameter $t_1 = 0.377$ eV[68, 69], $v = \sqrt{3}t_0a/2\hbar$ is the Fermi velocity for monolayer graphene and a = 2.46 Å is the lattice constant.

We consider the electron-electron interacion on non-interaction model in the mean-field Hartree-Fock approximation,

$$\hat{H}_{\rm MF} = \hat{H}_0 + \sum_{\boldsymbol{k},\boldsymbol{\xi},\boldsymbol{\xi}'} \hat{c}^{\dagger}_{\boldsymbol{k},\boldsymbol{\xi}} (\varepsilon^{(H)}_{\boldsymbol{\xi},\boldsymbol{\xi}'}(\boldsymbol{k}) + \varepsilon^{(F)}_{\boldsymbol{\xi},\boldsymbol{\xi}'}(\boldsymbol{k})) \hat{c}_{\boldsymbol{k},\boldsymbol{\xi}'}$$
(5.2)

where

$$\varepsilon_{\xi}^{(H)}(\boldsymbol{k}) = \delta_{\xi\xi'} \sum_{\boldsymbol{k}',\xi'} V_{n,n'}(0) \langle c_{\boldsymbol{k}',\xi'}^{\dagger} c_{\boldsymbol{k}',\xi'}, \rangle$$
(5.3)

$$\varepsilon_{\xi,\xi'}^{(F)}(\boldsymbol{k}) = -\delta_{\xi\xi'} \sum_{\boldsymbol{k}'} V_{nn'}(|\boldsymbol{k} - \boldsymbol{k}'|) \langle c_{\boldsymbol{k}',\xi'}^{\dagger} c_{\boldsymbol{k}',\xi} \rangle, \qquad (5.4)$$

where *n* is the layer number index. $V_{nn'}(q) = \frac{2\pi e^2}{\epsilon_r q} e^{-|n-n'|qd}$ is the Coulomb interaction term where d = 3.35 Å is the interlayer distance, *q* is the wavevector size, and ϵ_r is the effective dielectric constant. Eq. 5.4 is the Hartree contributions and Eq. 5.4 is the exchange Fock contributions. Here, the Hartree
contribution reduce to potential differences between the layers in limit at q = 0. We use the dimensionless coupling constant $\alpha \equiv e^2/\epsilon_r \hbar v$. The case of $\alpha = 0.1$ agrees the experimental result in bilayer graphene[59, 62, 63].

Self-consistent Hartree-Fock calculation need heavy computational cost. To solve computational problem, we use the rotational tranformation method[31]. We can find its complex phase analytically using relation between chiral nature and hopping network by the rotational tranformation method in minimal continuum model. Here, We neglect the inter-valley interaction because it is small.

5.3 Gapped phases induced by interaction in Bernal stacked tetralayer graphene

In Bernal stacked tetralayer graphene, a band gap is observed experimentally that indicates there is a symmetry broken state induced by electronelectron interaction.[12, 13]

Here we introduce a sublattice symmetry broken and gapped phase due to electron–electron interaction, and show that it can be described as a pseudospinnor picture. As the electric field increases, the pseudospinnors also flip over and eventually align in the direction of the electric field.

Fig. 5.1 (a) and (c) show that the non-interacting ground state consists of two bands with different masses[6, 7], with no layer polarity and no gap, and all spin/valley flavors are equal. The light-mass band can be represented by an effective two-band model confined to two sublattices (1A and 4B), which can be described as pseudospinors. The heavy-mass band is localized at sublattices (2B and 3A) and can likewise be represented as a pseudospinor. In the absence of an electric field, sublattice symmetry is preserved and the electron densities in the two sublattices are the same, depicted as gray color in Fig. 5.1 (c). Additionally, the pseudospinors have no z-axis component, as shown in the same figure.



Figure 5.1: Electronic band structure and its wavefunction configuration in the K or K' valley for ABAB tetralayer graphene. (a) band stcurues and (c) configuration are case of non-interaction and zero vertical electric field, while (b) and (d) are for the results obtained from self-consistent Hartree-Fock approximation. "Light" and "Heavy" labels indicate the light-mass or heavy-mass bands in the low-energy region. Colored circles indicate the sublattice in which the charge density of the corresponding band is localized. Gray, red, and blue colors represent neutral, positive, and negative local charge densities for the corresponding sublattice, respectively. The up and down direction of the arrows is the direction of the corresponding pseudospinor, which is the same as the charge polarization direction. "×4" and "×2" indicate the number of equal spin/valley flavor.

Considering the electron-electron interaction, the sublattice symmetry broken state appears. It is similar to bilayer graphene[8], but it is more complex because ABAB tetralayer graphene has two low-energy bands. For each spin/valley, the charge densities of the light-mass and heavy-mass bands are layer-polarized, as depicted in Fig. 5.1 (d) with red (blue) circles indicating positive (negative) charge density. The charge density layer-polarized states have a band gap, as depicted in Fig. 5.1 (b). However, the light-mass and heavy-mass bands have opposite polarization directions, its configuration is represented as (\downarrow, \uparrow) or (\uparrow, \Downarrow) in Fig. 5.1 (d).

Between the four spin/valley flavors, two are the same configuration, and the other two are opposite. As a result, the sum is canceled out, and the charge density is not polarized in real space. However, the case of Chern numbers differs from the direction polarization case. The alignment directions of the light-mass band and the heavy mass band are opposite, but the Chern numbers are the same as (+1,+1) or (-1,-1) for each spin/valley flavor. Since the Chern number has an opposite sign in opposite valleys, the sum can no longer be zero. Therefore, different types of Hall conductivities are possible depending on the combination of the four spin/valley flavor, discussed in Appendix D.1.

5.4 Electric field induced "Hund's rule" and Hall effects

When an electric field is applied in a non-interacting system, the direction of charge polarization is aligned with the direction of the electric field and four spin/valley are equal. Even considering the interaction, if a large electric field is applied, the charge polarization should be aligned toward the electric field. Therefore, as the electric field gradually increases, and the direction of the pseudospinor have to be flipped out. Here, the electric field direction is assumed to be upward and the polarization direction is flipped

$ \begin{array}{c c} K_{u} & K'_{u} & K_{d} & K'_{d} \\ \hline E \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\ (E_{c5}, \infty) & -1+1 & +1-1 & -1+1 & +1-1 \\ \hline E \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\ (E_{cb}, E_{c2}) & -1+1 & +1-1 & -1-1 & +1+1 \\ \hline E \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\ [0, E_{cl}) & \downarrow & \uparrow & \uparrow & \uparrow & \uparrow \\ \hline \end{bmatrix} $				
$ \begin{array}{c c} E \\ (E_{c,b},\infty) \\ \hline (E_{c,b},E_{c,2}) \\ \hline (E_{c,b},E_{c,1}) \\ \hline (E_{c,b},E_{c,$	•	<u>K'</u> "		<u>K'</u> d
$ \begin{array}{c c} E \uparrow \\ (E_{cb}, E_{c2}) \\ \hline \hline$	$E \atop (E_{c2},\infty)$		-1 +1	+1 -1
$E \blacklozenge \\ [0, E_{c}) \downarrow \\ \downarrow \uparrow +1 +1 \downarrow \\ \downarrow \uparrow \downarrow +1 +1 \downarrow \\ \hline \downarrow \uparrow \downarrow \\ -1 -1 \downarrow \downarrow \\ -1 -1 \downarrow \downarrow \downarrow \\ -1 -1 \downarrow \downarrow \downarrow \downarrow +1 +1 \downarrow \\ \hline \downarrow \downarrow$	$E \uparrow \\ (E_{cl}, E_{c2})$	€		
	$E \blacklozenge$ [0, E_{ct})			

Figure 5.2: The evolution of the antiferro-state as the vertical electric field increases. In the box, arrows represent the direction, and the numbers indicate the Chern numbers for the light and heavy-mass pseudospinors. The hollow arrow at the top of the box is the configuration for the Hall conductivity for the corresponding spin/valley flavor. The bold number and the arrow in a dashed circle indicate the changes as the electric field increases.

from downward to upward.

In this process, we fixed the number of flipped configurations. The four equal spin/valley flavor is called as ferro-state, the equal two and other two is called antiferro-, and the equal three and the one other is called ferri-state. these name is discussed in bilayer graphene[8]. Therefore, ground-state is antiferro-state and eventually becomes ferro-state for enough large electric field.

In this process, we fix the number of the pseudosipnor that are flipped in the configurations. the state for the four equal spin/valley flavors are referred to as a ferro-state, two equal and the other two are called antiferro-, and three equal and one other is referred to as a ferri-state. These names have been discussed in bilayer graphene [8]. As a result, the ground-state is an antiferro-state and it eventually becomes a ferro-state for a sufficiently large electric field.

If the magnitude of the electric field is small, it remains in the same state as the ground-state, $[(\downarrow, \Uparrow) \times 2, (\uparrow, \Downarrow) \times 2]$. Among the light-mass band and the heavy-mass band, the light-mass band flips first, resulting in the heavy-mass band following. When the magnitude of the electric field reaches the first critical point $E_{c1} = 0.025$ meV/Å, and the polarization direction of the light-mass band is flipped, its configuration becomes $[(\uparrow, \Uparrow) \times 2, (\uparrow, \Downarrow) \times 2]$. When the size of the electric field increases and reaches the second critical point $E_{c2} = 0.879$ meV/Å, and the heavy-mass band is overturned, resulting in four $[(\uparrow, \Uparrow) \times 4]$.

If generalized to consider the case when the number of layers is increased, the pseudospinors are flipped in order of increasing mass, starting with the lightest mass. This "Hund's rule" can apply to ferri-state as well as antiferro- and ferro-state, is discussed in Appendix D.3.

Fig. 5.2 depicts one of the possible configuration combinations. Here, the same spin in the ground-state has the same configuration, valley independently. In this ground-state, the sum of Chern numbers is zero and the charge Hall effect does not occur. However, if contrast is given to the spin sign and valley sign, the sum of the Chern numbers becomes non-zero, spin resolved valley Hall effect occurs, and the system becomes the layer antiferromagnetic (LAF) phase. Other configuration combinations are discussed in Appendix D.1.

5.5 Generalization for number of layers

In Bernal stacked multilayer graphene, the properties are completely different depending on whether the number of layers is odd or even, and this is because it is more difficult for monolayer-like bands to form a gapped state[8]. Due to this property, in the case of odd-numbered layers, there is a tendency for there to be gapless or small gap[7, 70–72]. On the other hand, in the case of even-numbered layers, the gap decreases as the number of layers increases, but the gap is significantly larger than that of a odd-number layers as shown in Fig. 5.3 (a).

Restricting the discussion to even numbers, we can depict a configuration combination as shown in Fig3 (b). Here, antiferro-, ferri-, and ferrostates are all considered.

Flipping order of pseudospinor is the same as the previous discussion from the lightest mass, but the number of flips can be 1 or 2. In the case of bilayers and tetralayer, flip 1 over from the antiferro-state(blue region) goes through the ferri-state (red region) Fig. 5.3 (b). However, in the case of hexalayer, two pseudospinors flipped at once, so the ferri-state does not appear.

The order of flipping the pseudospinor remains the same as discussed previously, starting from the lightest mass. The number of flips can be either one or two. In the case of bilayers, tetralayer and hexalayer, flipping one pseudospinor from the antiferro-state (represented by the blue region) goes through the ferri-state (represented by the red region) as shown in Fig. 5.3 (b). Interestingly, for this ferri-state, the various Hall conductivities all have nonzero values.

5.6 Discussion

We analyzed the layer polarzied gapped state that occurs when the sublattice symmetry is broken by considering the electron-electron interaction in Bernal stacked multilayer graphene. We use the many simplified assumptions, the minimal continuum model, ignoring remote hopping, and not considering correlation energies in interactions. In particular, considering the remote interaction, the chiral nature of multilayer graphene is distorted, so the ground-state gap is expected to be smaller D.4. As the gap decreases, the screening effect becomes more important. In summary, we give a simple picture of the symmetry broken states in Bernal-stacked multilayer graphene by the electron-electron interaction. We analyze the various ground-state configuration combination and gives an estimate of the experimentally measurable Hall conductance.



Figure 5.3: (a) Energy band gap as a function of the number of layers without a vertical electric field. The energy gaps of even (odd) number of layers are colored as red (blue). (b) The configuration combination has lowest total energy with a vertical electric field in an even number of layers. The antiferro-(ferri-, ferro-)states is colored in blue(red, gray). The order of the pseudospins is the mass order of the corresponding bands.

Chapter 6

Conclusion

In this thesis, our focus is on electron-electron interaction induced correlated states in the multilayer graphene systems, such as layer polarized state and spin-valley polarized state by electron-electron interaction.

In multilayer graphene, the complex phase of the wavefunction changes rapidly near the Dirac cone, the chiral nature, the physical quantity changes greatly due to electron-electron interaction. As the chirality increases, the bands flatten out and interactions become increasingly important.

In Chapter 2, we obtain the exchange self-energy and the ground-state energy of multilayer graphene within the random phase approximation(RPA). The exchange self-energy result shows that the positive interband contribution is suppressed as J increases. When J > 1, the intraband contribution becomes larger than the interband contribution and the exchange becomes negative. Negative compressibility is shown to have when $J \ge 5$ in the small n region. This is indirect evidence of a correlated state.

In Chapter 3, we demonstrate that spin-valley polarized states can appear. The exchange plays an important role in formation of a polarized state. When the density is correlated, there is an advantage in terms of exchange energy. When U_{ext} is small, the moment the density fills the empty circle of the Fermi disk(n_{M}), there is a sudden change in the ground-state energy, which leads to a phase transition. However, If U_{ext} is large, the kinetic energy becomes the dominant factor more than exchange.

In Chapter 4, we conduct a theoretical investigation of alternating twist multilayer graphene (ATMG) in the presence of a vertical electric field. We derive the low-energy effective Hamiltonian for ATMG up to pentalayer. We also calculate its optical conductivity. The vertical electric field shifts the energy of the Dirac cones up and down, these shifted Dirac cones make a step-like feature.

In Chapter 5, we study the spontaneous layer polarized phase that arises from electron-electron interaction in Bernal-stacked multilayer graphene. The ground-state configurations depend on the direction of the pseudospin of the heavy-mass and light-mass bands in the four spin/valleys, resulting in various possible Hall conductivities. We demonstrate that the pseudospin doublets of the heavy-mass and light-mass bands follow an effective Hund's rule.

We have studied the effect of electron-electron interaction, including exchange and correlation, by considering the stacking method, vertical electric field in multialyer graphene. Multilayer graphene is a valuable system for exploring correlated states induced by electron-electron interactions and advancing our understanding of their effect on the electronic structure. There are still numerous unresolved questions, which can lead to a deeper understanding.

Appendices

Appendix A

Stacking dependence of carrier-interactions in multilayer graphene systems

A.1 Dynamic polarization function and dielectric function of multilayer graphene.

In this chapter, we present the results of the density-density response function, also known as the dynamic polarization function, and the dielectic function within random phase approximation.

When $\operatorname{Re}[\epsilon(q, \omega)] = 0$, plasmon collective excitation occurs. Fig. 2.3 shows that not only optical plasmons introduced, but also multi-band acoustic and combined plasmons can occur. In case of rhombohedral stacking, there are two plasmon dispersions: the acoustic and optical plasmon, as shown in Fig. A.1 (c) and A.2 (c). One of them above and the others below the electron continuum boundary seen in Fig. A.1 and A.2 (d), and the above one of them is the optical plasmon dispersion and the other is the acoustic plasmon dispersion. However, the acoustic plasmon, with $\omega \propto q^1$, rapidly decays due to the electron-hole continuum caused by intraband transitions, as shown in Fig. 2.3. On the other hand, the optical plasmon, with $\omega \propto q^{1/2}$, avoids the electron-hole continuum as its energy increases rapidly with momentum q.

In Bernal-stacking multilayer graphene, such as ABA trilayer and ABAB tetralayer graphene, there are two or more low-energy bands, resulting in more than two plasmon dispersions as shown in Fig. A.3 (c) and Fig. A.4 (c). The combined plasmon dispersion lies between the optical plasmon and the acoustic plasmon dispersions. However, similar to the acoustic plasmon, it decays due to the electron-hole continuum caused by intraband transitions



Figure A.1: The dynamic polarization function and inverse dielectric function of ABC trilayer graphene are shown in (a) the real part and (b) the imaginary part for a carrier density of $n = 10^{12}$,cm⁻². ((c) the real part and (d) the imaginary part of the dynamic polarization function for $n = 10^{12}$ cm⁻² with $\alpha = 1.0$ and $\eta = 10^{-4} \times E_{\rm F}$.

of the conduction band with the highest velocity. This is why only one plasmon dispersion, the optical, is visible in the Fig. 2.3.

A.2 Weak coupling limit of the correlation energy in multilayer graphene.

In the weak coupling limit, the correlation energy is represented as

$$\varepsilon_{\rm corr} = \hbar v_{\rm F} k_{\rm F} \left(C_2 \alpha_{\rm F}^2 + \cdots \right) \sim v_{\rm F} k_{\rm F} a_{\rm F}^2 \propto \alpha^2 k_{\rm F}^{2-J} \tag{A.1}$$



Figure A.2: Same as Fig. A.1 for ABCA tetralayer graphene.

from Eq. (2.9). Fig A.5 shows that the correlation energy converges its asymptotic line.

A.3 Strong coupling limit of the inverse compressibility of multilayer graphene.

For the correlation energy in the strong coupling limit, we find from Eq. (2.8) and Eq. (2.10) that ground-state energy is given by

$$\varepsilon_{\rm tot} = \varepsilon_{\rm F} + J \varepsilon_{\rm F} D_0 + \cdots$$
 (A.2)



Figure A.3: Same as Fig. A.1 for ABA trilayer graphene.

where ε_F is the Fermi energy. From the fact that $\varepsilon_F \propto k_F^J$ and inverse compressibility $\kappa^{-1} = n^2 d\mu/dn$, we obtain the strong coupling limit asymptotic form, $\kappa_0/\kappa \sim 1 + J(J+2)D_0/2$. Since the strong coupling limit is when n is small and α is large, Fig. A.6 shows that the inverse compressibility converges well to its asymptotic line except for J=2 when n is small. This is because α is not large enough, but as alpha increases, the inverse compressibility of J = 2 converges to the asymptotic line.

As J increases, the value of D_0 decreases and becomes negative for $J \ge 5$. This means that negative compressibility can occur for J > 5 at low density.



Figure A.4: Same as Fig. A.1 for ABAB tetralayer graphene.



Figure A.5: The correlation energy(solid) and its weak coupling limit asymptotic line(dashed), $\hbar v_{\rm F} k_{\rm F} C_2 \alpha_{\rm F}^2$, for J=2,3,4 with $\alpha=0.05$.



Figure A.6: The inverse compressibility of J-chiral gas(solid line) for $J = 2 \sim 7$, and strong coupling limit asymptotic line(dashed line), $1 + J(J + 2)D_0/2$, for strong coupling limit with $\alpha = 1.0$.

Appendix B

Spontaneous spin-valley polarization and intermediate states in rhombohedral multilayer graphene

B.1 Exchange-correlation energy using a self-consistent Hartree band structure

In this chapter, we performed self-consistent Hartree calculations. In the presence of a perpendicular electric field E_{ext} , In the presence of a perpendicular electric field E_{ext} , there is an additional an induced electric field due to electrons charge density localized at each layer. We consider this, we initiate our calculations using a mean-field band structure that takes into consideration the self-consistent Hartree potential.

From the definition of electric potential and Gauss's law,

$$U^{(i)} - U^{(i-1)} = eE^{(i-1,i)}d,$$
(B.1)

$$E^{(i,i+1)} - E^{(i-1,i)} = 4\pi n^{(i)}(-e)/\varepsilon_r$$
(B.2)

$$E^{\text{top}} - E^{\text{bottom}} = 4\pi n(-e)/\varepsilon_r$$
 (B.3)

where $U^{(i)}$ is the potential energy of *i*-th layer, $E^{(i-1,i)}$ is the z-component of the electric field between *i*-th and (i - 1)-th layer, $n^{(i)}$ is the charge density at *i*-th layer, $n = \sum_{i} n^{(i)}$ is the charge density, ε_r is the effective relative permittivity and *d* is the distance between layers.

To distinguish potential energy by external field and potential energy



Figure B.1: A schematic figure for tetralayer graphene. The potential energy of the *i*-th layer is $U^{(i)}$, the charge density at *i*-th layer is $n^{(i)}$, and the magnitude of the vertical electric field between the *i*-th layer and the (*i*-1)-th layer is $E^{(i-1,i)}$.

by charge density induced field, we can defined as

$$(E^{\rm top} + E^{\rm bottom})/2 = E_{\rm ext}, \tag{B.4}$$

then

$$E^{(i-1,i)} = E_{\text{ext}} + E_{\text{ind}}^{(i-1,i)}.$$
 (B.5)

$$U^{(i)} = U^{(i-1)} + E^{(i-1,i)}_{\text{ind}}ed.$$
 (B.6)

where $E_{\text{ext}}ed = U_{\text{ext}}$ and $E_{\text{ind}}^{(i-1,i)}ed$.

The potential applied to each layer is the sum of the external electric potential U_{ext} and the internal electron distribution induced electric potential U_{ind} . This can be represented as

$$U^{(i)} = U^{(i)}_{\text{ext}} + U^{(i)}_{\text{ind}}$$
(B.7)

where i, j are layer indices and $U^{(i)}$ is an electric potential for *i*-th layer.

$$E_{\rm ind}^{\rm top} = -E_{\rm ind}^{\rm bottom} = 2\pi n(-e)/\varepsilon_r,$$
 (B.8)

$$\sum_{i=0}^{N} U^{(i)} = 0.$$
 (B.9)

A self-consistent Hartree solution, $\psi(\mathbf{k})$, satisfies the following equation:

$$(H_{\rm kin} + H_{\rm ext} + H_{\rm ind}) |\psi_s\rangle = \varepsilon_s |\psi_s\rangle \tag{B.10}$$

where s is the band index, $H_{\rm kin}$ is the Hamiltonian of rhombohedral multilayer graphene without the potential for vertical electric field, $H_{\rm ext} = {\rm diag}(U_{\rm ext}^{(1)}\mathbb{I}_2, U_{\rm ext}^{(2)}\mathbb{I}_2, ..., U_{\rm ext}^{(N)}\mathbb{I}_2)$ is a diagonal matrix of the external potential and $H_{\rm ind} = {\rm diag}(U_{\rm ind}^{(1)}\mathbb{I}_2, U_{\rm ind}^{(2)}\mathbb{I}_2, ..., U_{\rm ind}^{(N)}\mathbb{I}_2)$ is a diagonal matrix of the induced potential.

The kinetic energy that takes into account the external potential is given by

$$E_{\rm kin} = g_{\rm sv} \sum_{s} \int \frac{d^2k}{(2\pi)^2} \langle \psi_s | H_{\rm kin} + H_{\rm ext} | \psi_s \rangle f_{s,\boldsymbol{k}}$$
(B.11)

where $f_{s,k}$ is the Fermi distribution function for the band s and wavevector k and $g_{sv} = g_s g_v = 4$ is the spin-valley degeneracy.

The Hartree energy due to the induced potential is given by

$$E_{\text{Hartree}} = g_{\text{sv}} \frac{1}{2} \sum_{s} \int \frac{d^2k}{(2\pi)^2} \langle \psi_s | H_{\text{ind}} | \psi_s \rangle f_{s,\boldsymbol{k}}.$$
(B.12)

Note that Eq. (S8) includes the factor 1/2 to eliminate double counting.

Starting from a mean-field band structure obtained from the self-consistent Hartree approximation, we can obtain the exchange and the RPA correlation energies using the integration-over-coupling constant method as[???]

$$\frac{E_{\text{ex}}}{V} = -\frac{\hbar}{2} \int \frac{d^2q}{(2\pi)^2} \int_0^\infty \frac{d\omega}{\pi} V_q \delta \Pi_0(q, i\omega), \qquad (B.13)$$

$$E_{\text{ex}} = -\frac{\hbar}{2} \int \frac{d^2q}{(2\pi)^2} \int_0^\infty \frac{d\omega}{\pi} V_q \delta \Pi_0(q, i\omega), \qquad (B.13)$$

$$\frac{E_{\rm co}}{V} = \frac{\hbar}{2} \int \frac{d^2q}{(2\pi)^2} \int_0^\infty \frac{d\omega}{\pi} \left[V_q \delta \Pi_0(q, i\omega) + \ln \left| \frac{1 - V_q \Pi_0(q, i\omega)}{1 - V_q \Pi_0(q, i\omega)|_{n=0}} \right| \right]$$

where Π_0 is the noninteracting electron density-density response function given by

$$\Pi_{0}(\boldsymbol{q},\omega) = g_{\rm sv} \sum_{s,s'} \int \frac{d^{2}k}{(2\pi)^{2}} \frac{f_{s,\boldsymbol{k}} - f_{s',\boldsymbol{k}+\boldsymbol{q}}}{\hbar\omega + \varepsilon_{\boldsymbol{k}}^{s} - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}}^{s'} + i\eta} F_{\boldsymbol{k},\boldsymbol{k}+\boldsymbol{q}}^{s,s'}, \qquad (B.15)$$

 $\delta \Pi_0(\boldsymbol{q},\omega) = \Pi_0(\boldsymbol{q},\omega) - \Pi_0(\boldsymbol{q},\omega)|_{n=0}, \text{ and } F^{s,s'}_{\boldsymbol{k},\boldsymbol{k}+\boldsymbol{q}} = \left|\left\langle \psi_{\boldsymbol{k},s}|\psi_{\boldsymbol{k}',s'}\right\rangle\right|^2 \text{ is the wavefunction overlap factor.}$

In spin-valley polarized states, electrons no longer occupy the four spin-valley flavors equally but tend to occupy some of the four flavors, thus each spin-valley flavor needs to be considered separately as

$$g_{\rm sv} \rightarrow \sum_{\xi}$$
 (B.16)

$$f_{s,\boldsymbol{k}} \rightarrow f_{s,\boldsymbol{k}}^{\xi}$$
 (B.17)

where ξ is a spin-valley index. In the case of the P3 state, for example, the density is equally filled for $\xi = 1, 2, 3$ while n = 0 for $\xi = 4$. Accordingly,

the kinetic and Hartree energies are given by

$$E_{\rm kin} \quad \to \quad \sum_{\xi} \sum_{s} \int \frac{d^2k}{(2\pi)^2} \langle \psi_s | H_{\rm kin} + H_{\rm ext} | \psi_s \rangle f_{s,\boldsymbol{k}}^{\boldsymbol{\xi}}, \ (B.18)$$

$$E_{\text{Hartree}} \rightarrow \frac{1}{2} \sum_{\xi} \sum_{s} \int \frac{d^2k}{(2\pi)^2} \langle \psi_s | H_{\text{ind}} | \psi_s \rangle f_{s,\boldsymbol{k}}^{\xi}$$
(B.19)

On the other hand, in the case of exchange and correlation, the expressions (B.13) and (B.14) do not change, but the bare polarization function changes as

$$\Pi_{0}(\boldsymbol{q},\omega) \to \sum_{\boldsymbol{\xi}} \sum_{s,s'} \int \frac{d^{2}k}{(2\pi)^{2}} \frac{f_{s,\boldsymbol{k}}^{\boldsymbol{\xi}} - f_{s',\boldsymbol{k}+\boldsymbol{q}}^{\boldsymbol{\xi}}}{\hbar\omega + \varepsilon_{\boldsymbol{k}}^{s} - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}}^{s'} + i\eta} F_{\boldsymbol{k},\boldsymbol{k}+\boldsymbol{q}}^{s,s'}.$$
(B.20)

In this chapter, we set the energy at n=0 for a given U_{ext} as the zero of energy.

B.2 Intermediate states in the spin-valley polarization phase diagram

In the intermediate state, the occupied flavors can have different densities. We denote the intermediate state between the two pure states $P\xi_1$ and $P\xi_2$ with the mixing ratio r, as $P_{\xi_1\xi_2,r}$ where we assume $1 \le \xi_1 < \xi_2 \le g_{sv}$. We can divide spin-valleys into three groups: two groups with densities n_1 and n_2 , and one group with density $n_3 = 0$. The degeneracy numbers of these groups are ξ_1 , $\xi_1 - \xi_2$, and $g_{sv} - \xi_2$. The densities satisfy $\xi_1 n_1 + (\xi_2 - \xi_1)n_2 = n$ and $n_1 = (n/\xi_1)(1 - r) + (n/\xi_2)r$, $n_2 = (n/\xi_2)r$. This intermediate state starts at the pure polarized sate P_{ξ_1} when r = 0 and eventually changes to the P_{ξ_2} when r = 1. For example, in the case of $P_{12,0.2}$, the densities of each spin-valley can be expressed as $\{n^{\xi}\} = (n_1, n_2, 0, 0)$ where $n_1 = (n/p_1)(0.8) + (n/p_2)(0.2) = 0.9n$ and



Figure B.2: Energy difference between the P34 and P4 states for ABC trilayer graphene for $U_{\rm ext}=0.05~{\rm eV}$

We can determine the mixing ratio r that minimizes the energy for a given U_{ext} and n by searching through different values of r. It greatly increases the computational cost. The rapid change in total energy at (n_{M}) causes the total energy of the intermediate state to always be lower than that of pure polarized states. For example of the intermediate state $P_{34,r}$ between P3 and P4, $n_{\text{M}_{34,r}}$ satisfies $n_{\text{M}_3} \leq n_{\text{M}_{34,r}} \leq n_{\text{M}_4}$ for a given U_{ext} . As the mixing ratio r increases, $n_{\text{M}_{34,r}}$ moves to a larger density and the position of the minimum value of energy of intermediate state moves to a larger density accordingly. The total energy of the pure polarized state P3 increases very rapidly near n_{M_3} and this increase is greater than the change in the minimum of total energy as r increases. In other words, for a given r, intermediate state $P_{34,r}$ has lowest energy among other intermediate states and pure state P3 and P4 at $n = n_{M_{34,r}}$. Figure B.2 show this trend continues when $n_{M_3} < n < n_{M_4}$. In conclusion, pure polarized state P3 has the lowest energy when $n = n_{M_3}$, and P4 has the lowest energy when $n = n_{M_4}$, and there is always an intermediate state $P_{34,r}$ for a certain value of r has a lower energy than P3 and P4 for $n_{M_3} < n < n_{M_4}$

Since this fact applies not only to the intermediate state between P3 and P4 but also to all intermediate states, most areas of state diagram become intermediate states except for the $n_{\rm M}$ point of pure polarized states. As a result, it becomes P1 for $0 \le n < n_{\rm M_1}$, P₁₂ for $n_{\rm M_1} < n < n_{\rm M_2}$, P2 for $n = n_{\rm M_2}$, P₂₃ for $n_{\rm M_2} < n < n_{\rm M_3}$, P3 for $n = n_{\rm M_3}$, P₃₄ for $n_{\rm M_3} < n < n_{\rm M_4}$, and P4 for $n_{\rm M_4} < n$.

This is due to the fact that we use the wavefunction and Fermi surface determined from the self-consistent Hartree calculation for the exchangecorrelation energy calculation. Figures, 3.2 (d) and (f) in the main text show that there is a discontinuity in the slope of the total energy at n_M . These results can be slightly improved by allowing degrees of freedom to the inner and outer radius of the Fermi surface, but this increases the computational cost. In order to completely overcome this problem and obtain the areas of the pure polarized state and the intermediate state, GW calculation is necessary.

Appendix C

Effective model and the optical conductivity of alternating twist pentalayer graphene

C.1 Derivation of the effective Hamiltonian for N = 5 ATMG

In this section, we derive the effective Hamiltonian of alternating twist pentalayer graphene (AT5G) near \bar{K} and \bar{K}' . There are three Dirac cones with the modified Fermi velocity v_0 , v_1 and v_2 near \bar{K} as shown in Fig. C.1(a). The size of the perturbation matrix $V_{\bar{K}}$ is 3×3 . Using Eq. (4.4), the normalized wavefunctions $\Psi_{r,\lambda}$ near \bar{K} is given by

$$\Psi_{r,\lambda} = \frac{2}{\sqrt{6(1+6t_r^2\alpha^2)}} \begin{pmatrix} \sin\theta_r \cdot a_\lambda \\ \sin 2\theta_r \cdot t_r b_\lambda \\ \sin 3\theta_r \cdot a_\lambda \\ \sin 4\theta_r \cdot t_r b_\lambda \\ \sin 5\theta_r \cdot a_\lambda \end{pmatrix}, \quad (C.1a)$$

$$\Psi_{3,\lambda} = \frac{1}{\sqrt{3}} \begin{pmatrix} a_\lambda \\ 0 \\ -a_\lambda \\ 0 \\ a_\lambda \end{pmatrix} \quad (C.1b)$$

with r = 1, 2, where $\hat{V} = \text{diag}(-2U\mathbb{I}_{2\times 2}, -U\mathbb{I}_{6\times 6}, \mathbf{0}_{2\times 2}, U\mathbb{I}_{6\times 6}, 2U\mathbb{I}_{2\times 2})$. Following Secs. 4.2.B and 4.2.C, we find the perturbation matrix $V_{\bar{K}}$ with the elements of $V_{11} = V_{22} = V_{33} = 0$, $V_{12} = V_{21} = -2U(1+9\alpha^2)/\sqrt{3(1+6\alpha^2)(1+12\alpha^2)}$, and $V_{23} = V_{32} = -4U/\sqrt{6(1+6\alpha^2)}$ in the basis of the wavefunctions in Eq. (??). Finally, we obtain the effective Hamiltonian as

$$H_{\text{eff},\bar{K}}^{(0)} = \hbar v_0^* (\boldsymbol{k} \cdot \boldsymbol{\sigma}), \qquad (C.2a)$$

$$H_{\text{eff},\bar{K}}^{(\pm 1)} = \pm C_{\bar{K}}(\alpha)U + \hbar v_1^*(\boldsymbol{k} \cdot \boldsymbol{\sigma}), \qquad (C.2b)$$

where

$$C_{\bar{K}}(\alpha) = 2\sqrt{\frac{1+18\alpha^2+27\alpha^4}{(1+6\alpha^2)(1+18\alpha^2)}},$$
 (C.3)

and

$$v_0^* = \frac{A^2 v_0 + B^2 v_1}{A^2 + B^2}, \quad v_1^* = \frac{B^2 v_0 + A^2 v_1}{2(A^2 + B^2)} + \frac{v_2}{2},$$
 (C.4)

where $A = 1 + 9\alpha^2$ and $B = \sqrt{2(1 + 18\alpha^2)}$, is mixing coefficients.

On the other hand, there are two Dirac cones with the modified Fermi velocities v_1 and v_2 near \bar{K}' as shown in Fig. C.1(a), then the wavefunctions are given by

$$\Psi_{r,\lambda} = \frac{2}{\sqrt{6(1+6t_r^2\alpha^2)}} \begin{pmatrix} \sin\theta_r \cdot t_r b_\lambda \\ \sin 2\theta_r \cdot a_\lambda \\ \sin 3\theta_r \cdot t_r b_\lambda \\ \sin 4\theta_r \cdot a_\lambda \\ \sin 5\theta_r \cdot t_r b_\lambda \end{pmatrix}$$
(C.5)

with r = 1, 2, where the size of $V_{\bar{K}'}$ would be 2×2 with the elements of $V_{11} = V_{22} = 0$ and $V_{12} = V_{21} = -U(1 + 12\alpha^2)/\sqrt{(1 + 6\alpha^2)(1 + 18\alpha^2)}$. We obtain the effective Hamiltonian is given by

$$H_{\text{eff},\bar{K}'}^{(\pm)} = \pm C_{\bar{K}'}(\alpha)U + \hbar v^* (\boldsymbol{k} \cdot \boldsymbol{\sigma}), \qquad (C.6)$$

where

$$C_{\bar{K}'} = \frac{1 + 12\alpha^2}{\sqrt{(1 + 6\alpha^2)(1 + 18\alpha^2)}}$$
(C.7)

and $v^* = (v_1 + v_2)/2$. There is additional monolayer-like band near \overline{K}' like cafe of AT3G. Dirac cone pairs shifted by $\pm C(\alpha)U$, but monolayer-like Dirac-cone does not be shifted.

C.2 Optical conductivity of N = 5 ATMG

In this section, we show the result of the longitudinal conductivity of AT5G with(without) a vertical electric field in Fig. C.2 for U = 0 and U = 0.1 eV at the twist angle $\theta = 5^{\circ}$.



Figure C.1: Similar to panels (a)-(c) in Fig. 4.2, but for N = 5 ATMG. In panel (d), we show the modified Fermi velocities v_0^* and v_1^* given in Eq. (C.4) at \bar{K} and $v^* = (v_1 + v_2)/2$ at \bar{K}' in the inset to (b).

Without a vertical electric field, the longitudinal conductivity goes to $5\sigma_0$ for low- and high-frequency limit as as shown in Fig. C.2 (c). On the other hand, with a vertical electric field, the conductivity shows a step-like feature in low frequency region, as shown in Fig. C.2 (d) starting σ_0 due



Figure C.2: Same as Fig. 4.6 for N = 5 ATMG.

to unshifted monolayer-like Dirac-cone. the conductivity increases twice steps of $2\sigma_0$ due to the forbidden interband transitions by the energy shift of Dirac-cones. However, the second jump is about $1.5\sigma_0$, not exactly $2\sigma_0$. This is because transition energy enters the energy region where the diraccone feature is lost.

Specifically, the conductivity starts with σ_0 from the unshifted Dirac cone at \bar{K} then increases toward $5\sigma_0$ in steps of $2\sigma_0$ when $\hbar\omega \sim 2|\Delta_{\bar{K}}|$ and $2|\Delta_{\bar{K}'}|$, respectively, at which the forbidden interband transitions due to the splitting of Dirac nodes by the applied electric field can occur. Using smaller U or larger θ , the step size $2\sigma_0$ will recover.

Appendix D

Ground-state configurations of broken sublattice symmetry states in Bernal stacked multilayer graphene

D.1 Flavor antiferro states in ABAB tetralyer graphene

Since the charge polarization of the antiferro-state cancels out, there is no Hartree energy cost. Therefore, we can expect the antiferro-state to be the lowest energy state. However, there are several ways to assign antiferrostates to the four spin/valley flavors. We differentiated these into different types of Hall phases[65, 66], layer antiferromagnetic (LAF) phase, quantum spin Hall (QSH) phase and quantum anomalous Hall (QAH) phase. LAF phase is spin contrast state, but its Chern numbers are spin/valley contrast. QSH phase is spin/valley contrast state, but its Chern number are spin contrast state. QAH phase is valley contrast state, but its Chern number are same for each spin/vaelly as shown in Fig. D.1.

Various hall conductivities are observed for different ground-states. We defined the following quantities according to the spin/valley contrast: the spin Hall (SH), valley Hall (VH), charge Hall (CH), and spin resolved valley Hall (SV) and they are represented as



Figure D.1: Schematic picture of the ground-state configuration and corresponding spontaneous Hall effect for LAF, QSH and QAH, which are possible configuration combinations of antiferro-state. For each spin/valley flavor, the arrows in the box indicate the direction of the pseudospin and the numbers is below the boxes are corresponding Chern numbers. The hollow arrows on top of the box indicates the direction of the current in the Hall experiment.

$$\sigma_{\rm SH} = \frac{e^2}{h} (C_{K,\rm u} - C_{K,\rm d} + C_{K',\rm u} - C_{K',\rm d}), \qquad (D.1)$$

$$\sigma_{\rm VH} = \frac{e^2}{h} (C_{K,\rm u} - C_{K,\rm d} + C_{K',\rm u} - C_{K',\rm d}), \qquad (D.2)$$

$$\sigma_{\rm CH} = \frac{e^2}{h} (C_{K,\rm u} - C_{K,\rm d} + C_{K',\rm u} - C_{K',\rm d}), \qquad (D.3)$$

$$\sigma_{\rm SV} = \frac{e^2}{h} (C_{K,\rm u} - C_{K,\rm d} + C_{K',\rm u} - C_{K',\rm d}). \tag{D.4}$$

Figure D.2 shows the various Hall conductivities for three posiible configuration combinations of antiferro-state (LAF, QSH, QAH) for the antiferrostate.

$E_{\rm ext}$	LAF				QSH				QAH			
	SH	VH	CH	SV	SH	VH	CH	SV	SH	VH	CH	SV
E_{c2}	0	0	0	0	0	0	0	0	0	0	0	0
E_{c1}	0	-4	0	4	4	-4	0	0	0	-4	4	0
0	0	0	0	8	8	0	0	0	0	0	8	0
$-E_{c1}$	0	4	0	4	4	4	0	0	0	4	4	0
$-E_{c2}$	0	0	0	0	0	0	0	0	0	0	0	0

Figure D.2: Various Hall conductivities in units of e^2/h for the antiferro states in Bernal stacked tetralayer graphene with a vertical electric field. Here, $E_{c1} = 0.025 \text{ mV/Å}$ and $E_{c2} = 0.879 \text{ mV/Å}$.

D.2 Flavor ferri and ferro states in ABAB tetralyer graphene



Figure D.3: The evolution of ABAB tetralayer graphene with a vertical electric field for (a) assuming ferri-state, and (b) assuming ferro-state. For each spin/valley flavor, the arrows in the box indicate the direaction of the pseudospin and the numbers is below the boxes are corresponding Chern numbers. The hollow arrows on top of the box indicates the direction of the current in the Hall experiment.
The evolution of the ferri-state can be explained according to "the Hund's rule" mentioned in the text. The light-mass pseudospinor flips first, and the heavy-mass pseudospinor flips later in a larger electric field. After all, in a enough large electric field, all pseudospinor are aligned in the direction of the electric field as shown in Fig. D.3.

Interestingly, given any spin/valley contrast, the ferri-state always has a non-zero Chern number and we can expect the Hall conductivity from any quntum Hall experiment. This is why the ferri-state is called "All" state[65– 67]. On the other hand, in the case of the ferro-state, the valley Hall conductivity can be expected only in the ground-state with a low electric field.

E	Ferri					F	Ferro				
	SH	VH	CH	SV		Ľ	\mathbf{SH}	VH	CH	SV	
E_{c2+}^{ferri}	0	0	0	0		E_{c1+}^{ferro}	0	0	0	0	
E_{c1+}^{ferri}	-2	-2	2	2		0	0	8	0	0	
0	-4	4	4	4		$-E_{c1-}^{\text{ferro}}$	0	0	0	0	
$-E_{c1-}^{\text{ferri}}$	-2	6	2	2				58 · · ·		ί	
$-E_{c2-}^{\text{ferri}}$	0	0	0	0							

Figure D.4: Various quantum Hall conductivities in units of e^2/h with a vertical electric field in ABAB tetralayer for the ferri- and ferro-states in Fig. D.3. $E_{c1+}^{\text{ferri}} = 0.019$, $E_{c2+}^{\text{ferri}} = 0.943$, $E_{c1-}^{\text{ferri}} = 0.031$, $E_{c2-}^{\text{ferri}} = 0.815 \text{ meV/Å}$ for the ferri-state. On the other hand, the ferro-state has $E_{c1+}^{\text{ferro}} = 0.013$ and $E_{c1-}^{\text{ferro}} = 0.753 \text{ meV/Å}$.

Fig. D.5 shows the vertical electric field dependence of the total charge polarization for antiferro-, ferri- and ferro-state. Here, the total charge polarization ζ is defined by

$$\zeta = \frac{\frac{3}{2}n_4 + \frac{1}{2}n_3 - \frac{1}{2}n_2 - \frac{3}{2}n_1}{n_4 + n_3 + n + 2 + n_1},$$
 (D.5)

where n_i is the charge density of *i*-th layer. Interestingly, like the magnetic hysteresis curve, there are two solutions depending on the direction



Figure D.5: Total charge polarization ζ according to a vertical electric field for antiferro-state (top), ferri-state (middle), and ferro-state (bottom). ζ is defined in Eq. D.5. The right panel is an enlargement of part of the left panel, which enclosed in a dashed black box. The dashed line is the direction in which the electric field increases starting at a small. The solid line is the direction in which the electric field decreases.

of the electric field increasing and decreasing for the case of ferri-state and ferro-state[8]. Since top and bottom are identical in the ground-state, even if symmetry is broken, there is freedom to choose top and bottom, which is a natural result. system.

D.3 Ground-state configurations for hexalayer graphene

Bernal stacked hexalayer graphene is decomposed as three bilayer graphene has different masses. Considering the electron-electron interaction, a symmetry-

E	F	lavor	I	F	avor	II	Chern Number				
	(1	$\mathbf{n}_{\mathrm{u}}, \mathbf{n}$	u)		$\mathbf{A}_{\mathrm{d}}, \mathbf{A}$	d)	$K_{\rm u}$	$K_{\rm d}$	K'_{u}	$K'_{\rm d}$	
$E_{c3}^{(6)}$	\uparrow	1	1	1	\uparrow	1	1	1	-1	-1	
$E_{c2}^{(6)}$	\uparrow	1	1	1	\uparrow	4	1	-1	-1	1	
$E_{c1}^{(6)}$	1	+	1	1	1	4	3	-1	-3	1	
0	\uparrow	\downarrow	1	\downarrow	1	\downarrow	3	-3	-3	3	
$-E_{c1}^{(6)}$	\downarrow	\downarrow	1	\downarrow	\uparrow	↓	1	-3	-1	3	
$-E_{c2}^{(6)}$	\downarrow	\downarrow	1	\downarrow	\downarrow	+	1	-1	-1	1	
$-E_{c3}^{(6)}$	\downarrow	\downarrow	\downarrow	↓	\downarrow	↓	-1	-1	1	1	

Figure D.6: The configuration of the direction of the pseudospinor and corresponding Chern numbers with a vertical electric field in Bernal stacked hexalayer graphene for the LAF state. The pseudospinor are written in increasing mass order. Here, $E_{\rm c1}^{(6)}=0.017$, $E_{\rm c2}^{(6)}=0.251$, and $E_{\rm c3}^{(6)}=0.281$ meV/Å. The red arrow indicates the flipped pseudospinor.

$E_{\rm ext}$		LA	١F			QS	SH		QAH			
	SH	VH	CH	SV	SH	VH	CH	SV	SH	VH	CH	SV
$E_{c3}^{(6)}$	0	4	0	0	0	4	0	0	0	4	0	0
$E_{c2}^{(6)}$	0	0	0	4	4	0	0	0	0	0	4	0
$E_{c1}^{(6)}$	0	4	0	8	8	4	0	0	0	4	8	0
0	0	0	0	12	12	0	0	0	0	0	12	0
$-E_{c1}^{(6)}$	0	-4	0	8	8	-4	0	0	0	-4	8	0
$-E_{c2}^{(6)}$	0	0	0	4	4	0	0	0	0	0	4	0
$-E_{c3}^{(6)}$	0	-4	0	0	0	-4	0	0	0	-4	0	0

Figure D.7: Various quantum Hall conductivities in units of e^2/h for the antiferro-states in Bernal stacked hexalayer graphene with a vertical electric field.

breaking state appears as in bilayer graphene and tetralayer graphene and the ground state is the antiferro-state. In the ground-state, the direction of the pseudospinors changes as alternating way. In summary, configuration of the ground-state is $[(\downarrow, \uparrow, \downarrow) \times 2, (\uparrow, \downarrow, \uparrow) \times 2]$. Interestingly, its Chern numbers are (+1,+1,+1) or (1,1,1). Fig. D.6 shows the ground-state configurations in the LAF state for hexalayer graphene and its Chern numbers and Fig. D.7 shows the various quantum Hall conductivities for various ground-state configuration combination.

Similarly, we can understand the ground-state configurations of octalayer graphene is $[(\downarrow, \uparrow, \downarrow, \uparrow) \times 2, (\uparrow, \downarrow, \uparrow, \downarrow) \times 2]$ with the Chern numbers (+1,+1,+1,+1) or (1,1,1,1). As the electric field increases, according to "Hund's rule", the pseudospinor with the smallest mass is flipped, and the larger mass gradually is flipped.

D.4 Effect of the remote hopping terms



Figure D.8: The phase diagram for the ground-state configuration of tetralayer graphene on α and γ_2 plane. Here, in the gap dominant region, the ground-state is described by the sublattice symmetry breaking and the effective Hund's rule. The phase diagram for the ground state configuration of tetralayer graphene on α and γ_2 plane.

In even number of layers, the energy gap, which is induced by electronelectron interaction is the dominant scale, the effect of other energy scales , for example remote hopping, is not significant. However, when the size of remote-hopping increases or the strength of interaction, α , decreases, the scale reversal occurs and the ground-state is no longer described as the sublattice symmetry broken state and the "Hund's rule". Fig. D.8 shows the phase diagram between the gap dominant and remote-hopping dominant regions with interaction strength α and next-nearest interlayer hopping γ_2 . Here, the gap (remote-hopping) dominant region denotes a region where the ground state is (not) depicted by the sublattice symmetry breaking and the "Hund's rule". On the other hand, in the remote-hopping dominant region, we cannot explain it that way.

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국문초록

단층 그리고 다층 그래핀은 최근 십수년간 가장 중요한 연구 물질 중 하나였다. 그래핀 시스템은 2D 반 데르 발스 물질에 대한 연구와 위상물 질에 대한 연구에 큰 영향을 끼쳤고, 좋은 물성으로 전자 소자 등의 응용 부분에도 큰 관심을 받았다. 다층 그래핀은 카이랄 전자 구조로 인해 흥미 로운 현상을 보인다. 예를들어 전자-전자 상호작용의 의한 층간 분극 상태 등이 발견되었다. 또 다층 그래핀은 쌓는 방법에 따라 다양한 전자 구조를 갖고, 다양한 조작 수직 전기장이나 당김에 의해서도 전자 구조를 변화 시 킬 수 있다는 점 또한 매우 흥미로운 점이다. 또한 최근에는 ABC 삼중층 그래핀에서 초전도 현상이 발견됨에 따라 다층 그래핀에서의 상호작용 은 중요한 연구 대상이 되고 있다. 본 학위논문에서는 이러한 전자-전자 상호작용에 의해 나타날 수 있는 스핀-벨리 분극 상태에 초점을 맞추어 다룬다.

첫번째로, 우리는 다층 그래핀에서 적층되는 방법에 따른 전자-전자 상호작용을 분석한다. 여러 다른 다층 그래핀 시스템의 자체 에너지, 밀 도-밀도 응답함수, 바닥 상태 에너지를 계산하였다. 전기적 특성에 대한 전자-전자 상호작용의 영향은 밴드내 교환(intra band exchange), 밴드 외 교환(inter band exchange) 그리고 상관관계에 따른 기여도가 경쟁하는 것 으로 이해 할 수 있고, 마름모계로 쌓은 다층 그래핀의 층수와 비례하는 카이랄리티 J가 늘어남에 따라 밴드 외 교환의 영향이 급격하게 줄어드 는 것을 보였다.

두번째로, 최근 ABC 삼중층 그래핀에서 발견된 스핀-벨리 분극 상 태에 대해 이론적으로 설명할 수 있음을 보였다. 사중첩된 스핀-벨리 축퇴 전자구조는 전자-전자 상호작용으로 인하여 네가지 축퇴 중 일부에 응축 된 상태를 가질 수 있다. 우리는 일관성 있는(self-consistent) Hartree 계 산을 통해 상호작용이 없는 바닥 상태를 찾고, 이를 이용하여 교환-상관 에너지를 고려한 바닥 상태 에너지를 계산하였다. 이를 통해 분극 상태

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가 정상 상태(normal state)보다 낮은 바닥 상태 에너지를 가질 수 있음과 교환에너지가 중요한 역할을 하는 것을 보였다. 또 이를 AB 이중층부터 ABCA 마름모계 사중층 다층 그래핀에 적용하여 마찬가지로 스핀-벨리 분극상태가 나타남을 보였다.

한편, 우리는 전자-전자 상호작용에 유도된 다른 상관 상태,층 분극화 를 조사했다. 버널적층된 (Benal-stacked) 두층 그래핀은 층간 분극 상태를 가짐을 이론적으로 예측되었고, 실험적으로 관찰되었다. 이러한 층간 분 극 상태는 유사스피너(pseudospin) 모델로 설명 할 수 있다. 버널 적층된 사중층 그래핀은 무거운 질량의 전자띠와 가벼운 전자띠를 낮은 에너지 영역에서 가진다. 이 두 전자띠의 유사스피너와 사중첩된 스핀-벨리의 자 유도로 인하여 복잡한 양상을 보이는데 이것을 효과적인(effective) 훈트 의 법칙을 통해 설명할 수 있었다. 또한 수직 전기장에 대한 스태킹 방법 및 응답에 미치는 영향을 연구합니다. 교대로 비틀려 쌓은 다층 그래핀에 대해 효과적인 해밀토니안을 유도하고 광전도도에서 계단형 특징을 보여 줍니다.

주요어: 다층 그래핀, 교환상관 에너지, 바닥상태 에너지, 스핀-밸리 편향 상태

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