Electronic dynamics in low-dimensional materials

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**ELECTRONIC DYNAMICS IN
LOW-DIMENSIONAL MATERIALS**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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**ELECTRONIC DYNAMICS IN
LOW-DIMENSIONAL MATERIALS**

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Summary

In this work, electronic dynamics in low-dimensional systems are studied. The main objective of this work is to understand the role of electronic structures along confined dimensions in low-dimensional materials. To achieve the goal, graphene saddle point excitons, σ band excitons in graphene multilayer structures, scaling law of many-body interactions in carbon nanotubes and graphene nanoribbons are studied as object systems.

This research establishes an analytic model describing the role of electronic structures perpendicular to the quasi-2D material plane, and demonstrating the importance of this role. The finite thickness of electron wave function is found to be key factor in correctly determining the binding of excitons while the inter-layer coupling also plays significant role in layered structures. This quasi-2D nature also leads to a non-hydrogenic exciton spectrum which should be general for all quasi-2D materials. This work also correlates the geometry with scaling behavior of quasi-1D systems. It is demonstrated that the distinct power law behavior between ZCNTs and AGNRs should be attributed to the geometry difference.

The results of this research imply that electronic structures along confined dimensions in low-dimensional materials are fundamental to their electronic dynamics including excitonic properties. The models established in this work are potentially applicable in general low-dimensional materials.

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Abbreviations

AGNR	Armchair graphene nanoribbon
BLG	Bi-layer graphene
BSE	Bethe-Salpeter equation
CNT	Carbon nanotube
GNR	Graphene nanoribbon
HOPG	Highly ordered pyrolytic graphite
LCAO	Linear combination of atomic orbitals
MLG	Multi-layer graphene
MWNT	Multi-walled nanotube
RPA	Random phase approximation
SLG	Single-layer graphene
SWNT	Single-walled nanotube
TF	Thomas-Fermi
THz	Tera-Hertz
TLG	Tri-layer graphene
TMDC	Transition metal dichalcogenide
ZCNT	Zigzag carbon nanotube

Chapter 1

Introduction

This chapter presents the motivation of the dissertation, objective to be achieved in this work and an overview of the structure of the whole thesis, including introductions to each chapter.

1.1 Motivations

Low-dimensional systems, where particles are confined and have less degrees of freedom, have long been attractive. The term low-dimensional material refers to those with nanoscale or atomic scale in some dimensions, including atomically-thick layer materials, quasi-one-dimensional materials, and nano-particles. In these low-dimensional materials electrons are confined in some dimensions, yet they are not strictly low dimensional systems since in these dimensions they still have finite size. Therefore, they are sometimes referred to as quasi-n-dimensional (quasi-nD) materials.

Electronic dynamics and many-body interactions play important roles in low dimensional materials due to weakened screening and they are closely related to the optical and electronic properties of these systems. And it has been found that there are strong correlations between the size of these quasi-nD materials and their properties. In layer materials such as graphene, layer number and arrangement have been shown fundamental to their electronic structures[1], and extensive researches have been conducted to study how they affect the electronic dynamics. In quasi-1D and quasi-0D materials, such as nanotubes, nanoribbons, nanowires and quantum dots, there are also correlations found between their properties and sizes in those confined dimensions.

However, beside the size effects, there are still some gaps in understanding the role of electronic structures in confined dimensions and it will be interesting and fundamental to understand how their electronic structure in those confined dimensions determines the electronic dynamics in quasi-nD materials. Particularly in quasi-2D structure the electron wave function is actually three dimensional (3D) and it is yet to be studied how this 3D nature affect the electron interactions. Similarly in quasi-1D materials, the role of geometry in the other two dimensions is also fundamental to understanding the electronic dynamics. Therefore, models describing these effects are needed.

In this work, graphene, carbon nanotubes (CNTs) and graphene nanoribbons

(GNRs) are chosen as the object system since they are closely related as members of sp^2 carbon material family. And graphene, as a representative quasi-2D material, has zero band gap yet significant excitonic effects are found which imply strong electron-electron interactions. Moreover, although the Dirac Fermion in graphene has been extensively studied, analytic studies of electronic states beyond Dirac cone, which have strong many-body effects, are rarely conducted. The quasi-1D CNTs and GNRs are similar in the sense of band structures, yet their structures belong to two different typical geometries, say cylinder and flat plain and their properties are found different in some aspects. Therefore, they are suitable for researches on electronic dynamics in low-dimensional materials.

1.2 Objectives

Herein, the objective of this work focuses on building and applying models specifically describing the roles of electronic structure in confined dimensions and how they determine the electron interaction and electronic dynamics in quasi-2D and quasi-1D materials.

According to the above goal, a model describing effective many-body interaction is built with electronic structure in confined dimensions included. Then the model is employed to study excitons from the saddle point of π bands in graphene, excitons from degenerate σ bands around Γ point, and distinct many-body behaviors in zigzag CNTs (ZCNTs) and armchair GNRs (AGNRs) arising from their different geometry.

To study the importance of electronic structure perpendicular to graphene plane, we are going to construct a real space Schrödinger type two-body equation based on effective mass approximation and Bethe-Salpeter equation, and apply this model to simulate the π band saddle point excitons in graphene. The 3D nature of π band wave function is to be included in the model. Then we will solve the excitonic states, study the properties and physics of them and discuss the importance of their structure perpendicular to graphene plane. The results will

also be compared with experiments to validate the model.

Then we are going to apply the model to the parabolic degenerate σ bands around Γ point for further confirmation of our model. In addition to the σ band electronic structure in a single layer, the inter-layer interaction in layered structure will also be included into the model of many-body interaction. Layer number dependence of excitonic properties and exciton spectrum structure will be studied in details and compared with experimental results.

For comparison between ZCNTs and AGNRs, a modified effective mass description of them will be constructed based on graphene model and their respective geometry, and the many-body effect including self-energy and exciton binding energy will be studied based on the model. The functional difference of band structure and power-law scaling behavior of excitons will be compared. And the correlation between geometry difference and property difference will be discussed.

1.3 Dissertation overview

The thesis addresses the electronic dynamics in low-dimensional materials, and contains 7 chapters.

Chapter 1 provides a rationale for the research and outlines the goals and scope.

Chapter 2 reviews the literature concerning sp^2 carbon material family and many-body effects in low-dimensional materials. Brief introduction to sp^2 carbon material family will be given first. Then previous theoretical and experimental studies of many-body effects in quasi-2D and quasi-1D materials, including graphene, CNTs and GNRs, will be reviewed. Based on the reviews, open questions to be answered will be proposed.

Chapter 3 discusses theoretical methods to be employed in this thesis, including tight-binding model, effective mass description, random phase approximation, Bethe-Salpeter equation and GW self-energy.

Chapter 4 provides the two-body model of saddle point excitons in graphene π bands, with the effect from π band 3D wave function included as parameters. By solving the excitonic Hamiltonian, energy levels and wave functions of excitons are obtained in both single layer graphene and bilayer graphene. The obtained excitonic states are compared with experiments, and the importance of the band dependent parameter in correctly determining the excitonic states is discussed.

Chapter 5 shows the excitonic states arising from σ bands in graphene. Symmetry, degeneracy and other properties of bands involved in these excitons are discussed. Layer dependence of σ excitons in multilayer graphene is studied, compared with experiments and then discussed. The excitonic spectrum is presented and compared with conventional 2D hydrogenic model to illustrate the role of σ band electronic structure along the direction perpendicular to graphene plane. The potential application of this model to explain properties in other quasi-2D materials will also be discussed.

Chapter 6 demonstrates the geometry difference between ZCNTs and AGNRs and how this difference leads to distinct power-law scaling behavior of many-body effects. First modified effective descriptions of band structures and many-body interactions in ZCNTs and AGNRs are derived. Then the self-energy correction of band gaps and effective masses are calculated using the model. With effective mass and interactions obtained, the binding energies of excitons are calculated using variational methods. The scaling behavior of band gaps, effective masses and binding energies are presented and discussions on the role of geometry are provided.

Chapter 7 summarizes the achievements and highlights of this thesis and proposes future work recommendations based on the results. The models are potentially applicable to other quasi-2D and quasi-1D systems including transition metal dichalcogenides, nano wires and nano particles. Inclusion of frequency dependence into the model is also possible and could be used to study the tera-Hertz (THz) properties of low-dimensional systems, which has wide range of application in scientific research and engineering.

Chapter 2

Literature Review

In this chapter, literatures in related fields, including sp^2 carbon family and many-body effects of them, are reviewed. Introduction to sp^2 carbon family materials are presented and current gap in research of related field are concluded into open questions to be answered in this thesis.

2.1 Overview of sp^2 Carbon Material Family

Low-dimensional system is an important topic in material research society, especially nanoscience and technology area. Huge efforts have been dedicated to nano-particles[2], nano-wires[3] and thin films[4], which exhibit dramatic properties in comparison with traditional bulk materials. In addition to these nano-sized systems, there are some materials which are intrinsically low-dimensional, with size of atomic scale, including graphene, carbon nanotube, graphene nanoribbon, fullerene, boron nitride, transition metal dichalcogenide (TMDC), black phosphorous, MXene and so on. sp^2 carbon material family is among the earliest members of this group and attracts lots of researchers and experts studying their properties, as seen from the citation times of paper by Iijima who found carbon nanotube[5] and the graphene review paper by Geim and Novoselov[6].

2.1.1 Graphene

Graphene is basically a flat atomic monolayer of carbon atoms, which form a two-dimensional, tightly packing into a honey-comb lattice. This is the basis for the building block of other sp^2 graphitic carbon materials Figure 2.1, such as Fullerenes (0D) when wrapped up, Carbon Nanotubes (1D) via rolling and Graphite (3D) when layers of graphene are stacked together.

Figure 2.1 Graphene as a building block for fullerenes, carbon nanotubes and graphite. Reprinted by permission from Macmillan Publishers Ltd: *Nature Materials*. The rise of graphene, copyright 2007.

Graphene is noted for its high crystal quality, which allows charge carriers to travel long distances (ballistic transportation of thousands of units in inter-atomic distances) with little or no scattering[6]. As monolayer graphene is difficult to obtain, due to separation and isolation issues, there was very little experimentation done until 2004[7]. Yet ever since its mass production and high quality fabrication realized experimentally, it attracts huge interests from research society and studies on graphene cover topics including theories and applications in electronic, electrical, thermoelectric, optical, mechanical, quantum hall effect, and other fields. Its peculiar properties including massless Dirac Fermion type quasi-particle energy dispersion and atomic thickness, as shown in Figure 2.2, makes it promising in real applications including flexible and portable devices.

Figure 2.2. Atomic structure and band structure of graphene.

In addition to those states formed from carbon atomic orbitals, in graphene there is a group of states called image-potential states[8,9]. These states arise from the image-potential effects and are localized outside the graphene plane. There are numerous such states in graphene between Fermi level and carbon-originated conduction bands. Since their effective masses equal to free electrons' and they have almost perfect parabolic energy dispersion, they are sometimes referred to as nearly free electron states.

Graphene is a highly symmetric system, so the symmetry of its electronic states

is important in determining many properties, including allowed optical transitions, symmetry of excitonic states etc. In Kogan and collaborators' work [10], they analyzed the detailed symmetry of graphene electronic states along high symmetry path Γ -K-M- Γ , as given in Figure 2.3.

Figure 2.3 Ab initio band structure and symmetry of graphene electronic states along high symmetry path Γ -K-M- Γ . Reprinted figure with permission from E. Kogan, V. U. Nazarov, V. M. Silkin, and M. Kaveh, *Physical Review B*, 89, 165430, 2014. Copyright 2014 by the American Physical Society.

From Figure 2.3 we can find the symmetry of some important states in graphene. For example, at the Dirac point, electronic states are of group D_{3h} and both conduction and valence π bands realize the E'' representation. At M point, the saddle-like π conduction band realizes the B_{1u} and valence band realizes the B_{2g} representation of D_{2h} group. At Γ point, electronic states belong to D_{6h} group which is similar to benzene. The even and odd image potential states realize the A_{1g} and A_{2u} representations respectively. The doubly degenerate σ bands, consisting of p_x and p_y orbitals, have the symmetry of E_{1u} and E_{2g} respectively. This symmetry analysis is important in determining the excitonic properties, as will be shown in other chapters.

Graphene nanoribbons are graphene cut into narrow straps, as illustrated in Figure 2.5. Unlike CNTs, GNRs are cut from graphene so there are dangling bonds at the edges, so it is reactive and can be easily terminated by other atoms. A common termination form is hydrogen-passivated GNR, where hydrogen atoms are connected to edge carbon atom through sp^2 bond.

Figure 2.4 Structure of H-passivated and bare zigzag graphene nanoribbons

Since GNRs are confined systems, their properties are also closely related to their sizes, or equivalently their width. Like in CNTs, the width and chiralities determine the band gap of GNRs, hence a lot of other properties[11-13]. Due to the confinement, Coulomb interactions are very strong since electron-hole distance becomes very small, therefore many-body effects are pronounced in GNRs. In narrow GNRs, the binding energy of exciton can be even as much as 1~2 eV, which has been proven both numerically[14,15] and experimentally[16].

2.1.2 Carbon nanotubes

The first person who found carbon nanotubes (CNTs) experimentally was Sumio Iijima in 1991[5]. As named, they are tube-like nanostructure formed of carbon lattices with sp^2 bond and hexagonal structure similar to graphene. The single isolated tube shaped structure is also known as single-walled nanotubes (SWNTs). With several tubes with different diameters nesting into each other, they form a more complicated structure called multi-walled nanotubes (MWNTs).

CNTs' diameters are usually several nanometers, making them natural quasi-one-dimensional structures, compared to nanowires whose lattice structures are supercells of their parent bulk materials.

Due to the confined structure, carbon nanotubes exhibit some exotic properties compared to bulk materials. For example, their energy gaps vary from zero to several eVs with different diameters and chiralities[17]. Electronic transport through CNTs behavior like that there is no scattering, which is often referred to as ballistic transport[18]. Excitons in CNTs are also interesting since they exist even in metallic ones[19].

2.2 Electronic properties and many-body effects of sp^2 carbon material family

2.2.1 Band structures

As shown in previous section, the low-energy dispersion of quasi-particles in graphene, say the massless Dirac Fermions, dominates some of the behaviors in graphene and leads to many interesting properties due to its difference from traditional semiconductors where quasi-particles are generally massive and have parabolic energy dispersion. The massless band structure around K/K' point, often referred to as Dirac cone, is also observable in graphene's derivative, graphene nanoribbons (GNRs) and carbon nanotubes (CNTs).

Due to the family-like relation between these two types of derivatives and

graphene, their electronic structures can also be approximately obtained as a confined graphene system[20]. This is done by solving the Dirac equation of graphene with certain boundary conditions. In GNRs, the boundary condition requires vanishing amplitude of wave function beyond the edge of GNR. And in CNTs, the boundary condition requires periodicity of wave function around the tube. These two types of boundary conditions results in quantized momentum along the direction perpendicular to the axis of CNTs and GNRs, therefore only those solutions with certain momentum exist and the graphene π bands break into quantized subbands, like what happens in other quantum confined systems. The band structures of CNTs can be approximated using the so-called zone-folding description based on graphene band structure.

Figure 2.5 Zone folding approximation of GNR and CNT band structure. The dashed lines indicate allowed momenta for GNR/CNT.

Since in this zone-folding description, the allowed momentum depends on the how CNT rolls up from graphene, the band structures also depend on it. We may describe the rolling or cutting using a vector $\mathbf{L} = n\mathbf{a} + m\mathbf{b}$, where $\mathbf{a}$ $\mathbf{b}$ are graphene lattice vectors. In CNT this vector $\mathbf{L}$ is along the circumference. The cutting lines in zone-folding approximation is perpendicular to $\mathbf{L}$. When $n=m$, the allowed cutting lines in Figure 2.6 are parallel to K-K' path, so these Dirac points are both on these lines. This corresponds to the armchair CNTs (ACNTs) which are all gapless and metallic. When $m=0$, the allowed cutting lines are perpendicular to K-K' path, and only when $n=3p$ where p is also an integer, the CNTs are metallic. This corresponds to the zigzag CNTs (ZCNTs). CNTs in all other cases are said to be chiral and only those with $n-m=3p$ are metallic as shown in Figure 2.7.

Figure 2.6 Low energy band structure of (7,0), (8,0), (9,0) zigzag CNTs respectively.

For GNRs, we may also solve the Hamiltonian in similar manner. However, due to the existence of edge states, and different boundary conditions, zigzag GNRs (ZGNRs), which share the same $\mathbf{L}$ with ACNTs, cannot be simply described

using zone-folding method[11]. Meanwhile, those semiconducting armchair GNRs (AGNRs) which are similar to ZCNTs, can be well described using this method and zone-folding approximation is valid. Yet according to *ab initio* calculations, those metallic AGNRs actually have a small band gap due to the edge effect, which means there are no metallic AGNRs at all.

2.2.2 Many-body effects in graphene

Excitons in graphene are very tricky. Since graphene is gapless and no quantum confinement is induced like in GNRs and CNTs, it is expected that excitonic effects are weak. However, strong excitonic effects are found in graphene, both theoretically and experimentally.

By solving Bethe-Salpeter equation numerically Yang et al find a large excitonic shift of M point excitation peak around 0.6 eV[21] and it is later confirmed experimentally in the optical absorption spectra[22-24]. This exciton however, is interpreted as a resonance with broad peak using Fano model[25] which describes a discrete state resonating in a background continuum. Yang also proposed a narrow resonant excitonic peak around 12.5 eV[26] which arises from the parallel π^* and σ bands along Γ -K direction and lies beside the single-particle continuum. In addition to these resonant excitons which involve low-energy π bands in graphene, there is one narrow and pronounced excitonic peak arising from $\sigma \rightarrow \sigma^*$ transitions at 8.3eV for single-layer and 9.6eV for bi-layer graphene, as proposed by Trevisanutto et al[27]. Different from resonant excitons involving π bands, this σ exciton is narrow, isolated and results in vanishing $\sigma \rightarrow \sigma^*$ oscillator strengths at higher energy region where single-particle band-to-band transitions lay. The existence of such narrow exciton peak is supported by later experiments by Santoso et al[28] searching for graphene excitons. They measured the optical conductivity of epitaxial multi-layer graphene on SiC with ultraviolet-vacuum ultraviolet reflectrometry and spectroscopic ellipsometry, and found an isolated pronounced excitonic peak for few-layer graphene at room temperature. A controversy appears however, in the layer-number dependence of the peak position. In this experiment, the exciton peak position remains almost unchanged

for graphene thinner than 22 layers, while the BSE result shows that there is a shift around 1eV between single- and bi-layer graphene.

2.2.3 Graphene nanoribbon and carbon nanotube

The optical properties of quasi-one-dimensional (quasi-1D) sp² carbon materials, particularly carbon nanotubes (CNTs) and graphene nanoribbons (GNRs), is known to be dominated by excitonic effects according many-body models [14,29-33], two-photon excitation spectroscopy measurements on CNTs[34,35] and reflectance difference spectroscopy characterization on GNRs[16]. Due to the confinement and weak screening effect, excitons are even observed in the absorption spectrum of metallic ones[36].

Since both CNTs and GNRs have variable sizes, say diameters and widths respectively, it is interesting to study how their many-body properties depend on their sizes.

In conventional confined systems, a typical behavior is that the exciton binding energy scales with the system size. For example in quantum dots, if we use the simplest effective mass model by solving an interacting electron-hole pair in a confined quantum dot, the binding energy is proportional to inverse of the dot size, say

$$E_b \propto \frac{1}{R} \quad (2.1)$$

However, in real systems, this scaling is usually sublinear[37], which means

$$E_b \propto \frac{1}{R^{1-\delta}} \quad (2.2)$$

where δ is often greater than zero.

Interestingly, by solving excitons in CNTs, it is found that in CNTs, the binding energy has the following scaling behavior[29]

$$E_b \propto R^{\alpha-2} m^{\alpha-1} \varepsilon^{-\alpha} \propto \frac{1}{R} \quad (2.3)$$

In this case, full many-body effects are included, yet the scaling is so perfect that it significantly differs from conventional systems. It has been shown[38] that there is a logarithmic correction to this linear scaling, yet it is much smaller and the dominant behavior is still linear.

Due to the similarity between CNTs and GNRs, it is naturally expected that excitons in GNRs also have this perfect scaling. However, ab initio results by solving Bethe-Salpeter equation oppose to this expectation. By solving excitons in AGNRs[33], it is found that the scaling with width W is

$$E_b \propto W^{(\alpha-2)\xi} m^{\alpha-1} \varepsilon^{-\alpha} \propto \frac{1}{W^\gamma} \quad (2.4)$$

where γ is 0.60, 0.73 and 0.55 for three families of AGNRs. This, similar to conventional quantum confined systems, is a sublinear scaling. It is also found that the scaling of quasi-particles effective mass in AGNRs is also nonlinear, which is different from ZCNTs.

These differences are unexpected since AGNRs and ZCNTs band structures are similar, and the only difference is geometry. It will be interesting to further understand these differences.

2.3 Open Questions

According to the above reviews, there are several open questions to be answered.

The first one is that, why the resonant exciton at saddle point has such a large binding energy? To answer this question, the physics of this saddle point exciton need to be understood. Beside numerical calculations done in literatures, no analytic work has been done to this region. Therefore, to address this problem we will first establish an approach to describe electron-hole interactions in quasi-2D materials, and apply it to graphene saddle point.

The second question is why σ excitons have strong binding even in multi-layer graphene? This question can also be answered using the model developed for first question, with inter-layer coupling included.

The third question, what is the role of geometry in determining the scaling behavior of AGNRs and ZCNTs? Detailed analysis of electron-hole interactions' functional forms is needed to resolve this problem.

Chapter 3

Methodology

This chapter introduces the background and some basic information about tight-binding model and effective mass approximation, as well as many-body effects in random phase approximation, GW approximation and Bethe-Salpeter equation. These theoretical methods and models are to be employed in this thesis.

3.1 Tight-binding model and effective mass approximation

Due to the variety of graphene family, a lot of *ab initio* numerical researches have been conducted on their various properties. However, when we need some insight of the origin of exotic properties and behaviors, an analytical or semi-analytical method will give further details. Furthermore, if we could construct a functional description of electron-electron interactions, the role of each parameters and factors will be intuitively understood.

In this work we employ the effective mass description to simulate the behavior of electron interactions in graphene family since it gives simple and analytical form of both wave functions, energy dispersions and many-body interactions. This effective mass description will also help to convert equations from momentum space into real space, in which interactions are more intuitive since they are similar to classical theories.

3.1.1 Tight-binding model and its application in graphene

The band structure of graphene σ and π bands have been explicitly studied before, where linear combination of atomic orbitals (LCAO) by Painter and Ellis [39] and tight-binding model by Saito, Dresselhaus and Dresselhaus [40] have successfully reproduced the band structure with carbon 2s and 2p orbitals.

Tight-binding model is a model assuming that electrons are tightly localized around the atom, so the electron wave function remains identical to atomic orbitals. With this assumption, the wave function of an electronic state in a system can be written as superposition of atomic orbitals.

$$\psi(r) = \sum_S \sum_n b_{S,n} \phi_{S,n}(r) \quad (3.1)$$

In a lattice structure due to the translational invariant requirement for Bloch states, the wave function with momentum k should be written as

$$\psi(r) = \sum_{\text{unitcells}} \sum_S e^{ikR_S} \sum_n b_{S,n,k} \phi_{S,n}(r) \quad (3.2)$$

If we write the linear combination of same atomic orbital in same site of each unitcell $\varphi_{S,n,k}(r) = \sum_{\text{unitcells}} e^{ikR_S} \phi_{S,n}(r)$, the total wave function can be written as

$$\psi(r) = \sum_S \sum_n b_{S,n,k} \varphi_{S,n,k}(r). \quad (3.3)$$

Then by evaluation the matrix elements of Hamiltonian operator between wave functions of different states, we may obtain the matrix form of Hamiltonian.

$$H = \begin{pmatrix} H_{11} & \cdots & H_{1n} \\ \vdots & \ddots & \vdots \\ H_{n1} & \cdots & H_{nn} \end{pmatrix} \quad (3.4)$$

The diagonal elements of this matrix are called on-site energy, since they correspond to the Hamiltonian of an atomic orbital itself. The off-diagonal elements of this matrix are called hopping energy, since they correspond to the energy required for an electron to hop from one atomic orbital to another.

In the model of graphene, the 2s and 2p_x, 2p_y orbitals are hybridized into sp² orbitals that forms the graphene σ bands, whose Hamiltonians are given by

$$\begin{aligned} H &= \begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix} \\ H_{AA} = H_{BB} &= \begin{pmatrix} \mathcal{E}_{2s} & & \\ & \mathcal{E}_{2p} & \\ & & \mathcal{E}_{2p} \end{pmatrix} \\ H_{AB} = H_{BA}^\dagger &= \begin{pmatrix} H_{ss}(p_1 + p_2 + p_3) & H_{sp}\left(-p_1 + \frac{p_2}{2} + \frac{p_3}{2}\right) & \frac{\sqrt{3}}{2}H_{sp}(-p_2 + p_3) \\ H_{sp}\left(p_1 - \frac{p_2}{2} - \frac{p_3}{2}\right) & -H_s\left(p_1 + \frac{p_2}{4} + \frac{p_3}{4}\right) + \frac{3}{4}H_p(p_2 + p_3) & \frac{\sqrt{3}}{4}\sqrt{3}(H_p + H_s)(p_2 - p_3) \\ \frac{\sqrt{3}}{2}H_{sp}(p_2 - p_3) & \frac{\sqrt{3}}{4}(H_p + H_s)(p_2 - p_3) & H_p\left(p_1 + \frac{p_2}{4} + \frac{p_3}{4}\right) - \frac{3}{4}H_s(p_2 + p_3) \end{pmatrix} \\ p_j &= \text{Exp}\left[i\vec{a}_j \cdot \vec{k}\right] \end{aligned} \quad (3.5)$$

With parameters from Ref [40], the tight-binding band structure of graphene is given below in Figure 3.1.

Figure 3.1 Upper: Band structure of graphene π bands in first Brillouin zone. Lower: Band structure of graphene sp^2 bands along high symmetry path K- Γ -M-K

3.1.2 Effective mass Hamiltonian of graphene

With $\mathbf{k}\cdot\mathbf{p}$ effective mass approximation[41], one may expand the cellular part of a Bloch wave function at small $\mathbf{k}$ as

$$u_n(\mathbf{k}) = \sum_{n'} C_{nn'}(\mathbf{k}) u_{n'}(0) \quad (3.6)$$

In the case when contributions from other bands are neglected due to symmetry or large energy difference, only those in the same degenerate subspace are kept thus

$$\psi_{nj}(\mathbf{k}, \mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{j'}^g C_{nj'}^{j'}(\mathbf{k}) u_n^{j'}(0, \mathbf{r}) \quad (3.7)$$

Then the single-particle Hamiltonian H_0 and eigenfunction $\psi_{nj} = u^T P(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}}$ are matrices which satisfy

$$H_0(\mathbf{k}) P(\mathbf{k}) = P(\mathbf{k}) \Lambda(\mathbf{k}) \quad (3.8)$$

with

$$\begin{aligned} u &= [u_n^1(0, \mathbf{r}), u_n^2(0, \mathbf{r}), \dots, u_n^g(0, \mathbf{r})]^T \\ P(\mathbf{k}) &= \begin{bmatrix} C_{n1}^1(\mathbf{k}) & \dots & C_{ng}^1(\mathbf{k}) \\ \vdots & \ddots & \vdots \\ C_{n1}^g(\mathbf{k}) & \dots & C_{ng}^g(\mathbf{k}) \end{bmatrix} \\ \Lambda(\mathbf{k}) &= \text{diag}(E_{n1}(\mathbf{k}), E_{n2}(\mathbf{k}), \dots, E_{ng}(\mathbf{k})) \end{aligned} \quad (3.9)$$

Applying this model to the massless band around K/K' point, the $\mathbf{k}\cdot\mathbf{p}$ effective mass model of Dirac Fermions is obtained. Since at each Dirac point, there is a double degeneracy, the overall Hamiltonian is a two-dimensional massless Dirac Hamiltonian with two valleys, say

$$H_k = \gamma \begin{pmatrix} 0 & k_x - ik_y & 0 & 0 \\ k_x + ik_y & 0 & 0 & 0 \\ 0 & 0 & 0 & k_x + ik_y \\ 0 & 0 & k_x - ik_y & 0 \end{pmatrix} \quad (3.10)$$

Solving this Hamiltonian, we obtain the wave functions and energy dispersions of π bands near Dirac point K as follows

$$\begin{aligned} \psi_s(k, r) &= \text{Exp}[ik \cdot r] \begin{pmatrix} \text{Exp}[-i\theta_k] \\ s \end{pmatrix} \\ \varepsilon_{sk} &= s\gamma|k| \end{aligned} \quad (3.11)$$

Here θ_k is the direction angle of momentum k while $s = \pm 1$ correspond to conduction/valence bands respectively.

Considering the parabolicity of σ bands around Γ point and π bands around M point, a second-order $k \cdot p$ effective mass model will be a good description of them.

By solving the tight-binding model we found that the highest σ and lowest σ^* bands at Γ point are both doubly degenerate and their wave functions at Γ point where $k=0$ are simple linear combination of p_x/p_y orbitals on two carbon sites, say $\psi_{\sigma^*}^{x/y}(k=0, r) = \Phi_{x/y}^A - \Phi_{x/y}^B$, $\psi_{\sigma}^{x/y}(k=0, r) = \Phi_{x/y}^A + \Phi_{x/y}^B$. The other two σ bands are further away from Fermi level and are linear combinations of carbon 2s orbitals $\Phi_{2s}^A \pm \Phi_{2s}^B$. Therefore within the $k \cdot p$ approximation, the effective mass Hamiltonians are matrices and their Bloch functions around Γ point can be constructed as combination of $\psi_{\sigma^*/\sigma}^{x/y}(k=0, r)$ considering the fact that other σ bands are over ten eVs away, which means the involving σ bands have vanishing 2s character. This is also validated by symmetry group analysis of graphene by Kogan, Nazarov, Silkin and Kaveh [10]. Given the symmetry group of these bands, E_{2g} and E_{1u} of D_{6h} group respectively, we use the method of invariance[41] and obtain the single particle effective mass Hamiltonian for electrons and holes in σ bands as

$$\begin{aligned}
H_0^h(p) &= \alpha_h I_2 (p_x^2 + p_y^2) + \beta_h [\sigma_3 (p_x^2 - p_y^2) - \sigma_1 2p_x p_y] \\
H_0^e(p) &= \alpha_e I_2 (p_x^2 + p_y^2) + \beta_e [\sigma_3 (p_x^2 - p_y^2) + \sigma_1 2p_x p_y]
\end{aligned} \tag{3.12}$$

with $I_2 = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$, $\sigma_1 = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$ and $\sigma_3 = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$. The corresponding eigenvalues are $E_h^\pm = (\alpha_h \pm \beta_h)k^2$ and $E_e^\pm = (\alpha_e \pm \beta_e)k^2$ so these parameters can be obtained from ab initio band structure. The corresponding wave functions are written as linear combinations of $\psi_{\sigma^*/\sigma}^{x/y}(k=0, r)$. To simplify, we may instead use complex orbital and change the basis to $u_h^\pm(r) = \Phi_\pm^A - \Phi_\pm^B$, $u_e^\pm(r) = \Phi_\pm^A + \Phi_\pm^B$ with $\Phi_\pm = \Phi_x \pm i\Phi_y$. Then the Hamiltonians become

$$\begin{aligned}
H_0^h(p) &= \begin{bmatrix} \alpha_h I_2 (p_x^2 + p_y^2) & \beta_h (p_x + ip_y)^2 \\ \beta_h (p_x - ip_y)^2 & \alpha_h I_2 (p_x^2 + p_y^2) \end{bmatrix} \\
H_0^e(p) &= \begin{bmatrix} \alpha_e I_2 (p_x^2 + p_y^2) & \beta_e (p_x + ip_y)^2 \\ \beta_e (p_x - ip_y)^2 & \alpha_e I_2 (p_x^2 + p_y^2) \end{bmatrix}
\end{aligned} \tag{3.13}$$

The π bands at M point is non-degenerate so the effective mass Hamiltonian is trivially

$$H_0^M(p) = \frac{p_x^2}{2\mu_x^M} + \frac{p_y^2}{2\mu_y^M} \tag{3.14}$$

where $\mu_{x/y}^M$ are effective masses to be obtained from simple LDA-DFT band structure.

3.1.3 Effective mass description of other sp^2 materials

Solving the Dirac Hamiltonian for ZCNTs, we may assume that the wave function has similar form to graphene's, for example around K valley,

$$\psi_{s,n}(k, r) = \exp[i\kappa_l \cdot x] \exp[ik \cdot z] F_{s,n,k}$$

The coordinate x is around the tube while z is along the axis. Since the system is periodic for x with a period of circumference $C = 2\pi R = N \frac{a}{2}$, it is required that if x goes the tube once, the amplitude of on-site orbital remains unchanged. From previous discussion we see that in the case of ZCNTs x is parallel to K/K' path, so the tight-binding basis $u^{A/B}(r)$ is superposition of on-site atomic orbital with pre-factor $\exp(iKx)$. Therefore, the on-site amplitude is proportional to $\exp[i(\kappa_l + K)x]$. Then the periodicity requires $\exp[i(\kappa_l + K)C] = 1$. With this we have the quantized allowed momentum k_n . Substituting this into the Dirac Hamiltonian we obtain the wave function for subbands in ZCNTs as

$$\begin{aligned} \psi_{s,l}(k) &= \sqrt{\frac{\delta(\rho - R)}{2LC}} \exp\left[\frac{i\kappa_l C\theta}{2\pi} + ikz\right] \begin{pmatrix} b_l(k) \\ s \end{pmatrix} \\ &= \sqrt{\frac{\delta(\rho - R)}{2LC}} \exp\left[i\left(l \mp \frac{\nu}{3}\right)\theta + ikz\right] \begin{pmatrix} b_l(k) \\ s \end{pmatrix} \end{aligned} \quad (3.15)$$

with energy dispersion

$$E_{s,l}(k) = sv_F \sqrt{\kappa_l^2 + k^2} \quad (3.16)$$

The momenta are given by $\kappa_l = \mp \frac{2\pi}{C} \left(l + \frac{\nu}{3}\right)$, $b_l(k) = \frac{\kappa_l \mp ik}{\sqrt{\kappa_l^2 + k^2}}$. The sign $\mp$ are for K and K' valley respectively. The parameters $\nu = 0, \pm 1$ are family parameters such that the chirality number $N = 3p + \nu$ where p is integer. When $\nu = 0$, $\kappa_l = 0$ is allowed so there is a pair of massless conduction/valence bands. In other cases however, all bands are massive with gap depending on the circumference or

radius equivalently.

For AGNRs with chirality number n , the boundary conditions require vanishing amplitude beyond the edge. Therefore, if we label the A-B dimers in an AGNR unitcell from 1 to n , then the amplitude on site 0 and site $n+1$ should be vanishing. To realize this condition, K and K' valley are no longer decoupled. By mixing them together, the total amplitude on site 0 is

$$\Phi^{A/B} = F_K^{A/B} + F_{K'}^{A/B} \quad (3.17)$$

While on site $n+1$

$$\Phi^{A/B} = F_K^{A/B} \exp(iKx) + F_{K'}^{A/B} \exp(iK'x) \quad (3.18)$$

Solving these two conditions, we obtain the subbands in AGNR as

$$E_{s,l}(k) = sv_F \sqrt{\kappa_l^2 + k^2}$$

$$\psi_{s,l}(k) = \sqrt{\frac{\delta(y)}{4L\tilde{W}}} \exp[ikz] \begin{pmatrix} b_l(k) \exp[i\kappa_l x] \\ s \exp[i\kappa_l x] \\ -b_l(k) \exp[-i\kappa_l x] \\ s \exp[-i\kappa_l x] \end{pmatrix} \quad (3.19)$$

with $\kappa_l = -\frac{\pi}{\tilde{W}} \left(l + \frac{\tilde{v}}{3} \right)$, $b_l(k) = \frac{\kappa_l - ik}{\sqrt{\kappa_l^2 + k^2}}$. Here the effective width $\tilde{W} = (N+1) \frac{a}{2}$

and family parameter $\tilde{v} = N+1-3p$. By using effective width and family parameter, we find subbands in AGNRs and ZCNTs are almost identical in spite that there is valley mixing in AGNRs.

3.2 Many-body interaction

In simplest description of electronic states in a system, electrons can be treated as quasi-particles with energy dispersion determined by solving the eigenstates in the presence of potentials generated by ions and a mean-field by other electrons. With this, each electron is considered as a single particle moving freely without

interaction with other electrons. This description is valid approximation when electron-electron interaction is weak, for example when electric screening is very strong. However, when electron-electron interaction is not negligible, many-particle picture should be included. The effect of such electron-electron interaction is called many-body effects.

3.2.1 Screening effect by random phase approximation

With many electrons existing in the system, it is naturally expected that when an electric potential field is induced into a system, these electrons will move and screen the field.

As shown in Fig 1, in classic view, electrons move in bulk system to screen electric field. Electrons in metal are delocalized and they can accumulate around a point charge to almost completely screen the potential generated. Therefore, it is usually expected that Coulomb interaction is weak in metals. In semiconductor and insulators however, electrons are bound and the screening effect is finite. The resulting screened potential is only weakened by a factor called relative permittivity.

Delocalized Electrons

Localized Electrons

Figure 3.2 Electrons moves in system to screen external fields. In metals, electrons are delocalized so they move freely and screening is stronger. In semiconductors and insulators, electrons are bound and screening effect is local.

In microscopic view, one can derive the screening effect in a self-consistent manner, which is shown to be equivalent to the random phase approximation (RPA)[42]. It is the first order approximation of the response of a system to an external perturbation. In the language of Feynman diagram, it is the simple bubble diagram as shown below.

Figure 3.3 Feynman diagram representing the random phase approximation.

The wave-like lines are photons while solid lines are electrons.

In this approximation the photon from the total electric potential generates an electron-hole pair which in response generates a new induced potential due to change of charge density. This forms a self-consistent equation between external potential, induced potential and total potential,

$$\phi^{tot}(\mathbf{r}) = \phi^{ext}(\mathbf{r}) + \phi^{ind}(\mathbf{r}) \quad (3.20)$$

As described above, the induced potential arises from charge density perturbation which can be expressed as sums of electron-hole pair. To calculate the density perturbation, we make use of the density matrix method. In this description, the many-body system can be described using a density matrix operator

$$\hat{\rho} = \sum f_n |n\rangle \langle n| \quad (3.21)$$

where f_{nk} is the occupation number of state $|nk\rangle$ which satisfies Dirac-Fermi distribution and the matrix elements of this operator are simply $\rho_{mn} = \delta_{mn} f_m$. In this description, expectation value of any operator $\hat{A}$ can be written as

$$\langle \hat{A} \rangle = \text{tr}(\rho A) \quad (3.22)$$

Since the equation of motion of this density matrix is

$$i\hbar\dot{\rho} = [H, \rho] \quad (3.23)$$

while $H = H_0 + \phi^{tot}$ is the perturbed Hamiltonian, in the first order approximation we have

$$[H_0, \delta\rho] + [\phi^{tot}, \rho] = 0 \quad (3.24)$$

Solving this equation we have

$$\langle m | \delta\rho | n \rangle = \frac{f_m - f_n}{E_m - E_n} \langle m | \phi^{tot} | n \rangle \quad (3.25)$$

On the other hand, the density perturbation in density matrix description is

$$n^{ind}(\mathbf{r}) = \sum_{mn} \langle m | \delta\rho | n \rangle \psi_m(\mathbf{r}) \psi_n^\dagger(\mathbf{r}) \quad (3.26)$$

So the induced potential is

$$\phi^{ind}(\mathbf{r}) = \sum_{mn} \frac{f_m - f_n}{E_m - E_n} \langle m | \phi^{tot} | n \rangle \langle n | V_C(\mathbf{r} - \hat{r}) | m \rangle \quad (3.27)$$

In 3D lattice system, the wave functions of electronic states are Bloch type

$$\psi_k(\mathbf{r}) = e^{ik \cdot \mathbf{r}} u(\mathbf{r}) \quad (3.28)$$

Then cellular part of wave function $u(\mathbf{r})$ is oscillating much faster than the plane wave part $e^{ik \cdot \mathbf{r}}$ when k is small. Therefore, if we expand a potential in plane wave, say

$$\phi(\mathbf{r}) = \sum_q e^{iq \cdot \mathbf{r}} \phi(q) \quad (3.29)$$

Then its matrix element is approximately

$$\langle m, k+q | \phi | n, k \rangle \cong \phi(q) \langle m, k+q | e^{iq \cdot r} | n, k \rangle \quad (3.30)$$

With this, we may express the induced potential as

$$\phi^{ind}(\mathbf{r}) = \sum_q e^{iq \cdot \mathbf{r}} \phi^{tot}(q) V_c(q) \sum_{mnk} \frac{f_{m,k+q} - f_{n,k}}{E_{m,k+q} - E_{n,k}} \left| \langle m, k+q | e^{iq \cdot r} | n, k \rangle \right|^2 \quad (3.31)$$

Then we obtain the self-consistent equation in momentum space

$$V_{eff}^{3D}(\mathbf{r}) = V^{scr}(\mathbf{r}) I_g \quad (3.32)$$

The polarization function is defined as

$$\Pi(q) = \sum_{mnk} \frac{f_{m,k+q} - f_{n,k}}{E_{m,k+q} - E_{n,k}} \left| \langle m, k+q | e^{iq \cdot r} | n, k \rangle \right|^2 \quad (3.33)$$

In systems with lower dimensions, the self-consistent equation is a little different.

In 2D case, the Bloch function has the form

$$\psi_k(\rho) = \exp(ik \cdot \rho) u(k, \rho, z) \quad (3.34)$$

And the expansion of bare Coulomb potential is

$$V_c(\mathbf{r} - \mathbf{r}', z - z') = \sum_q \exp[iq \cdot (\mathbf{r} - \mathbf{r}')] \frac{2\pi e^2}{q} \exp(-|q||z - z'|) \quad (3.35)$$

In this case the effect of z is often neglected since the system is usually thin, and the difference in exponential part is trivial compared to the $1/q$ factor. And the polarization function remains unchanged.

For quasi-one-dimensional (quasi-1D) systems like GNRs and CNTs, the Fourier expansion of bare Coulomb potential is

$$r_1 \approx 2749 \text{ \AA} \quad (3.36)$$

In this case it diverges logarithmically so the finite size effect cannot be neglected

as in 2D case. In this case, we assume one can write the Bloch function of quasi-1D system as

$$\psi_m(k_m, \mathbf{r}) = \frac{\exp[ik_m z]}{\sqrt{L}} \xi(m, \boldsymbol{\rho}) F_{mk_m} \quad (3.37)$$

which is true in the case of subband in quantum well, GNRs and CNTs as shown in previous section. Then the Coulomb matrix element is

$$\langle n, k | V_C(r - \hat{r}) | m, k + q \rangle = 2e^2 \int \xi^\dagger(n, \boldsymbol{\rho}) \xi(m, \boldsymbol{\rho}) K_0(|q||\boldsymbol{\rho} - \boldsymbol{\rho}'|) d\boldsymbol{\rho} \quad (3.38)$$

Then the self-consistent equation can be written in the form

$$\begin{aligned} \phi_{ij}^{tot}(q) - \sum_{mn} v_{ijmn}(q) \Pi_{mn}(q) \phi_{mn}^{tot}(q) &= \phi_{ij}^{ext}(q) \\ \phi_{mn}^{tot}(q) &= \int \xi_m^\dagger(m, \boldsymbol{\rho}) \xi_n(n, \boldsymbol{\rho}) \phi^{tot}(q, \boldsymbol{\rho}) d\boldsymbol{\rho} \\ v_{ijmn}(q) &= 2e^2 \int \xi_i^\dagger(i, \boldsymbol{\rho}) \xi_j(j, \boldsymbol{\rho}) K_0(|q||\boldsymbol{\rho} - \boldsymbol{\rho}'|) \xi_m(m, \boldsymbol{\rho}') \xi_n^\dagger(n, \boldsymbol{\rho}') d\boldsymbol{\rho} d\boldsymbol{\rho}' \\ \Pi_{mn}(q) &= \frac{f_{m,k+q} - f_{n,k}}{E_{m,k+q} - E_{n,k}} \left| \mathbf{F}_{m,k+q}^\dagger \cdot \mathbf{F}_{n,k} \right|^2 \end{aligned} \quad (3.39)$$

This lead to a matrix-like RPA equation

$$\phi^{tot} = (\mathbb{I} - v\Pi)^{-1} \phi^{ext} \quad (3.40)$$

where $\mathbb{I}$ is the identity matrix.

3.2.2 GW approximation

In many-body context, the electron-electron interaction induces a self-energy correction to the quasi-particle's energy. With this effect, the quasi-particle band structure will be corrected from single-particle dispersion obtained in mean field. The self-energy Σ can be obtained to the first order approximation, called GW approximation[43]. In this approximation the self-energy is written as

$$\Sigma(r, r', \omega) = \frac{i}{2\pi} \int e^{-i\omega'0^+} G(r, r', \omega - \omega') W(r, r', \omega') d\omega' \quad (3.41)$$

where W is the screened interaction that can be evaluated from dynamic RPA, and G is the real space Green's function which can be written as

$$G(r, r', \omega) = \sum_{nk} \frac{\psi_{nk}(r) \psi_{nk}^\dagger(r')}{\omega - s_n E_{nk} + i0^+ s_n} \quad (3.42)$$

Using the above equation and RPA, the expectation value of self-energy is

$$\begin{aligned} & \langle nk | \Sigma(s_n E_{nk}) | nk \rangle \\ &= \frac{i}{2\pi} \int d\omega' e^{-i\omega'0^+} \sum_q \sum_m w_{m-n, m-n}(q, \omega') \frac{|F_{mk+q, nk}|^2}{s_n E_{nk} - \omega' - s_m E_{mk+q} + i0^+ s_m} \end{aligned} \quad (3.43)$$

Here E_{nk} is the single-particle energy and $|F_{mk+q, nk}|^2$ is the overlapping between wave functions. If the dynamic effect in screening is neglected, which is often a good approximation called screened Hartree-Fock or static RPA[44], the self-energy can be written in a simpler form

$$\langle nk | \Sigma(s_n E_{nk}) | nk \rangle = - \sum_q \sum_m w_{m-n, m-n}(q, 0) |F_{mk+q, nk}|^2 \quad (3.44)$$

Here the summation on m only goes over all occupied states, say the valence bands. Since this self-energy has k dependence, it is expected that it will affect both the band gap and the effective mass.

3.2.3 Bethe-Salpeter equation

In many-body method, the excitons can be described as excited states of a system and the excitation energies can be obtained using the so called Bethe-Salpeter equation (BSE)

$$\left[E_c(k) - E_v(k) + \Delta\Sigma \right] A_{cv}(k) - \sum_{c'v'k'} K_{cc'vv'}^d(k, k') A_{c'v'}(k') = \Omega A_{cv}(k) \quad (3.45)$$

Here the exchange term is neglected since it is only important to the singlet-triplet splitting of excitons while the binding energy of exciton is dominated by the direct interaction $K_{cc'vv'}^d$. It is calculated as

$$K_{c_i c_j v_m v_n}^d = - \int \psi_{c_i}^\dagger(\mathbf{r}') \psi_{c_j}(\mathbf{r}') W(\mathbf{r}', \mathbf{r}) \psi_{v_m}(\mathbf{r}) \psi_{v_n}^\dagger(\mathbf{r}) d\mathbf{r}' d\mathbf{r} \quad (3.46)$$

where $W(\mathbf{r}', \mathbf{r})$ is the screened Coulomb interaction.

Assuming conduction/valence bands have degeneracy of g_c/g_v , the BSE becomes

$$\sum_{c'v'} \left\{ \left[E_{c'}(\mathbf{k}) \delta_{cc'} - \delta_{vv'} E_{v'}(\mathbf{k}) + \Delta\Sigma \right] \delta_{kk'} + \sum_{i'ij'k'} C_{c'}^{i'*}(\mathbf{k}) C_c^i(\mathbf{k}') C_{v'}^{j'}(\mathbf{k}) C_v^{j'*}(\mathbf{k}') V_{i'ij'j}^{\text{scr}}(\mathbf{k} - \mathbf{k}') \right\} A_{c'v'}(\mathbf{k}') = \Omega A_{cv}(\mathbf{k})$$

$$V_{i'ij'j}^{\text{scr}}(\mathbf{k} - \mathbf{k}') = - \int d\mathbf{r}^3 d\mathbf{r}'^3 u_c^{i'}(\mathbf{r})^* u_c^i(\mathbf{r}) u_v^{j'}(\mathbf{r}') u_v^j(\mathbf{r}')^* e^{i(\mathbf{k} - \mathbf{k}')(\mathbf{r}' - \mathbf{r})} V^{\text{scr}}(\mathbf{r}', \mathbf{r}) \quad (3.47)$$

with V^{scr} being the screened Coulomb interaction. For simplicity we employ a new label $|t\rangle = |cv\rangle$ with dimension $g = g_c g_v$ such that

$$A(\mathbf{k}) = \text{vec} \left(\begin{bmatrix} A_{c_1 v_1}(\mathbf{k}) & \cdots & A_{c_1 v_{g_v}}(\mathbf{k}) \\ \vdots & \ddots & \vdots \\ A_{c_{g_c} v_1}(\mathbf{k}) & \cdots & A_{c_{g_c} v_{g_v}}(\mathbf{k}) \end{bmatrix} \right) = \left[A_{t_1}(\mathbf{k}), A_{t_2}(\mathbf{k}), \dots, A_{t_g}(\mathbf{k}) \right]^T \quad (3.48)$$

Then the BSE reduces to the matrix form

$$\begin{aligned} & \left[\Lambda_c(\mathbf{k}) \otimes I_{g_v} - I_{g_c} \otimes \Lambda_v(\mathbf{k}) + \delta \Sigma \right] A(\mathbf{k}) + \\ & \sum_{\mathbf{k}'} P_{eh}(\mathbf{k})^\dagger V_{eh}^{\text{scr}}(\mathbf{k} - \mathbf{k}') P_{eh}(\mathbf{k}') A(\mathbf{k}') = \Omega A(\mathbf{k}) \end{aligned} \quad (3.49)$$

where $P_{eh} = P_c \otimes P_v$. Here $\otimes$ denotes the Kronecker product[45]. Based on the properties of Kronecker product, we have the following relation

$$\left[P_c \otimes P_v \right]^\dagger \left[H_c \otimes I_{g_v} - I_{g_c} \otimes H_v \right] \left[P_c \otimes P_v \right] = \Lambda_c \otimes I_{g_v} - I_{g_c} \otimes \Lambda_v \quad (3.50)$$

With this the BSE becomes

$$\begin{aligned} & \left[H_c(\mathbf{k}) \otimes I_{g_v} - I_{g_c} \otimes H_v(\mathbf{k}) \right] P_{eh}(\mathbf{k}) A(\mathbf{k}) + \\ & \sum_{\mathbf{k}'} V_{eh}^{\text{scr}}(\mathbf{k} - \mathbf{k}') P_{eh}(\mathbf{k}') A(\mathbf{k}') = \Omega P_{eh}(\mathbf{k}) A(\mathbf{k}) \end{aligned} \quad (3.51)$$

which describes an eigenvalue problem on the wave function

$$\Psi(\mathbf{k}) = P_{eh}(\mathbf{k}) A(\mathbf{k}).$$

Chapter 4

π Band Saddle Point Exciton in Graphene and Bilayer Graphene

In this chapter, a real-space Hamiltonian for exciton is developed based on Bethe-Salpeter equation. The electron-hole interaction in this model has band dependence. By applying this model on graphene saddle point exciton, binding energies are obtained and the results imply that the band dependence is fundamental to correctly solving the saddle point exciton problem.

4.1 Introduction

Graphene, as a gapless quasi-2D material, is usually expected to be metallic. However numerous experiments and numerical results indicate strong excitonic effects in graphene, which is in contrast to usual 3D metals. Therefore, it is a desirable object to study the electronic dynamics in quasi-2D materials.

Analytic models of low-energy π bands in graphene have been extensively studied in past decades, known as the Dirac cone that can be described using Dirac equation. However due to the vanishing density of states around Dirac cone, excitonic effects are expected to be prominent beyond this region. The van Hove singularities, where density of states diverges, are expected to be candidature region where excitons form.

Above the Dirac cone, the first van Hove singularity is the saddle point of π bands around M point in Brillouin zone, and strong resonant exciton has been found in this region in both experiments[22-24] and numerical simulations[21,46]. Yet it is still an open question why this exciton is so strong, around half eV, compared to tens of meV for excitons in bulk materials. Hence we need to build a real-space model describing the electron hole interaction between π bands around M point.

4.2 Real-space excitonic Hamiltonian

To construct the real-space excitonic Hamiltonian including both effective-mass kinetic term and effective potential, approximation of the BSE in momentum space is taken. Starting from the scissor operator approximation, we replace the quasi-particle energy by the sum of k-dependent single-particle kinetic terms and a constant band gap correction. The exchange term in the interaction kernel is neglected since it's much smaller than the attractive direct term which dominates the binding strength. Then a stationary exciton is the eigenstate of the following momentum space equation

$$\left[E_c(k) - E_v(k) + \Delta \right] A_{cv}(k) - \sum_{c'v'k'} K_{cc'vv'}^d(k, k') A_{c'v'}(k') = \Omega A_{cv}(k) \quad (4.1)$$

Taking the $k \cdot p$ effective mass approximation[41], the above equation can be transformed into a matrix equation of dimension $g = g_c g_v$, g_c/g_v being the conduction/valence bands degeneracy

$$\left[H_c(k) \otimes I_{g_v} - I_{g_c} \otimes H_v(k) \right] \Psi(k) + \sum_{k'} V_{eh}^{scr}(k-k') \Psi(k') = \Omega \Psi(k) \quad (4.2)$$

$$V_{ijj'}^{scr}(k-k') = \int dr^3 dr'^3 u_c^{i'}(r)^* u_c^i(r) V^{scr}(r', r) u_v^{j'}(r') u_v^j(r')^* e^{i(k-k')(r'-r)}$$

Its Fourier transform is

$$\left[H_c(\hat{p}) \otimes I_{g_v} - I_{g_c} \otimes H_v(\hat{p}) + V_{eff}^{scr}(r) \right] \Psi(r) = \Omega \Psi(r) \quad (4.3)$$

with $V_{eff}^{scr}(r)$ being the Fourier counterpart of $V_{eh}^{scr}(q)$. This is exactly the Schrödinger-type equation describing the relative motion of an electron-hole pair interacting via an effective potential $V_{eff}(r)$ [47-49] determined by the matrix elements $V_{ijj'}^{scr}(q)$. Noticing that the bases functions $u_n^{j'}(0, r)$ have cellular periodicity and the screened Coulomb interaction can be expanded as

$$V^{scr}(r', r) = \sum_q \frac{V_q}{\varepsilon(q)} e^{iq(r-r')} \quad (4.4)$$

So the expression for small k and k' is

$$V_{ijj'}^{scr}(k-k') = \int dr^3 dr'^3 u_c^{i'}(r)^* u_c^i(r) u_v^{j'}(r') u_v^j(r')^* \frac{V_{k-k'}}{\varepsilon(k-k')} \quad (4.5)$$

In 3D case, $V_q = -\frac{1}{L^3} \frac{4\pi e^2}{q^2}$ so the matrix is simple and diagonal

$$V_{ijj'}^{scr}(q) = -\delta_{ii'} \delta_{jj'} \frac{1}{L^3} \frac{4\pi e^2}{\varepsilon(q)|q|^2} \quad (4.6)$$

which means the effective potential is simply the screened Coulomb

$$V_{eff}^{3D}(r) = V^{scr}(r) I_g.$$

However in quasi-2D systems like graphene and TMD, the momentum k is 2D

vector so we need to expand the Coulomb term as $V_q = -\frac{1}{L^2} \frac{2\pi e^2}{q} e^{-|qz|}$. Then

$$V_{ij'j}^{scr}(q) = -\frac{1}{L^2} \frac{2\pi e^2}{\varepsilon(q)q} \int dr^3 dr'^3 u_c^{i'}(r)^* u_c^i(r) u_v^{j'}(r') u_v^j(r')^* e^{-q|z-z'|} \quad (4.7)$$

and it reminds us of the Coulomb terms between sub-bands in quantum wells

$V(q) = -\frac{1}{L^2} \frac{2\pi e^2}{\varepsilon(q)q} \int dz dz' |\xi_c(z)|^2 |\xi_v(z')|^2 e^{-q|z-z'|}$ with $\xi(z)$ being the sub-band envelope functions[50].

To determine the real-space expression of $V_{\text{eff}}^{2D}(r)$, we evaluate the matrix elements for σ and π bands in graphene respectively, written as a modified 2D Coulomb potential

$$V_{ij'j}^{scr}(q) \equiv -\frac{1}{L^2} \frac{2\pi e^2}{\varepsilon(q)} \frac{W(q)}{q} \quad (4.8)$$

with $W(q)$ plotted in Figure 4.1.

Figure 4.1 Effective potential regularization for σ and π bands in graphene.

A reasonable approximation of $W(q)$ would be the exponential function

$$V_{ijj}^{\text{scr}}(q) \cong -\frac{1}{L^2} \frac{2\pi e^2}{\varepsilon(q)q} \exp[-qD_{ijj}] \quad (4.9)$$

considering that the Coulomb matrix elements decay much faster as the momentum transfer q increases[51]. D_{ijj} is chosen such that the $W(q)$ agrees with the integral to the first order of q , which is a good fitting at small q

$$D_{ijj} = \int dr^3 dr'^3 |z - z'| u_c^{i'}(r)^* u_c^i(r) u_v^{j'}(r') u_v^j(r')^* \quad (4.10)$$

The above equation shows that D_{ijj} is closely related to the effective thickness of involving bands and can be understood as the average distance between electron and hole along z axis.

If the dielectric function is q -independent $\varepsilon(q) = \varepsilon$, the Fourier transform of this effective potential is the soft-core Coulomb potential often referred to as Ohno potential[52]

$$V_{\text{eff}}^{2D}(r)_{i'ijj} = -\frac{e^2}{\varepsilon \sqrt{r^2 + D_{i'ijj}^2}} \quad (4.11)$$

This Ohno potential is commonly used as Coulomb energy between atomic orbitals [29,53,54] yet in that case, no distinction can be made between p_z and $p_{x/y}$ orbitals since their on-site Coulomb energy should be the same. It has also been used to describe e-h interaction in graphyne[55] empirically with the parameter adjusted to fit numerical results. Our model here clearly gives the physical definition of this Ohno parameter $D_{i'ijj}$ and screening effect will also be included into this parameter as to be given below.

As plotted in Figure 4.2, this Ohno potential approaches a finite value at small distance, which is the result of the finite extension of wave function perpendicular to the atomic plane. It is similar to the interaction between two wave-packets with finite size, and differs from both bare Coulomb between two point charges, which diverges as $1/r$ at small distance, and screened Coulomb potential in 2D system which diverges logarithmically[56].

Figure 4.2 Real space strength of effective Ohno potential.

By Fourier transforming the approximation given in Figure 4.1, we obtained the real-space form of the effective e-h interaction between σ electrons and between π electrons, as plotted in the inset of Figure 4.2. We can clearly see that interaction between σ electrons is much stronger than that between π electrons.

It's been shown that the dielectric function has the form $\varepsilon(q) = 1 + r_0 q$ in both quasi-2D[57] and strict 2D[56] systems, with $r_0 = \varepsilon d / 2$ and $r_0 = 2\pi\alpha_{2D}$ respectively. With such q-dependent dielectric function, the close form of Fourier transform of $V(q) = \frac{2\pi e^2}{\varepsilon(q)} \frac{\text{Exp}[-qD]}{q}$ is difficult to find. However, an approximation V_{eff}^{2D} which agrees with it in both short range and long range is possible. Since $V^{2D}(q) \xrightarrow{q \rightarrow 0} -\frac{2\pi e^2}{q}$, the long range behavior of screened potential is similar to bare Coulomb $V^{2D}(r) \xrightarrow{r \rightarrow 0} -\frac{e^2}{r}$. Around $r \rightarrow 0$, it goes to a finite value

$$V^{2D}(0) = -2\pi e^2 \int \frac{\exp[-qD_0]}{q(1+r_0q)} \frac{dq^2}{(2\pi)^2} = -\frac{e^{D/r_0} \text{Ei}\left[-\frac{D_0}{r_0}\right]}{r_0} \quad (4.12)$$

And

$$\left. \frac{\partial V^{2D}(r)}{\partial r} \right|_{r=0} = 2\pi e^2 \left. \frac{\partial}{\partial r} \int \frac{\exp[-qD_0]}{(1+r_0q)} \exp[-i\mathbf{q} \cdot \mathbf{r}] \frac{dq^2}{(2\pi)^2} \right|_{r=0} = 0 \quad (4.13)$$

So it still behaves like an Ohno potential with modified parameter

$$V_{\text{eff}}^{2D}(r) = \frac{e^2}{\sqrt{r^2 + D_{\text{eff}}^2}}, D_{\text{eff}} = \frac{r_0 e^{-D_0/r_0}}{\text{Ei}\left[-\frac{D_0}{r_0}\right]} \quad (4.14)$$

If the screening is Thomas-Fermi type, say $\varepsilon(q) = 1 + \frac{q_{TF}}{q}$, the screened potential

is

$$V(q) = 2\pi e^2 \frac{\exp[-qD_0]}{q + q_{TF}} = 2\pi e^2 \frac{\exp[-qD_0]}{q} - 2\pi e^2 \frac{\exp[-qD_0]}{q \left(1 + \frac{q}{q_{TF}}\right)} \quad (4.15)$$

Using the results above, we may approximate this potential in real-space with

$$V_{\text{eff}}^{\text{TF}}(r) = \frac{e^2}{\sqrt{r^2 + D_0^2}} - \frac{e^2}{\sqrt{r^2 + D_{\text{TF}}^2}} \quad (4.16)$$

where $D_{\text{TF}} = \frac{1}{q_{TF}} \frac{e^{-D_0 q_{TF}}}{\text{Ei}[-D_0 q_{TF}]}$. Its asymptotic form at large r is

$$V_{\text{eff}}^{\text{TF}}(r) \approx e^2 \frac{D_{\text{TF}}^2 - D_0^2}{2r^3}.$$

4.3 π band saddle point exciton in graphene and bilayer graphene

Combining the $\mathbf{k}\cdot\mathbf{p}$ effective mass description of bands in graphene with our effective mass excitonic Hamiltonian, we solved the model exciton around the saddle like M point of π bands. Inserting the tight-binding wave functions constructed from carbon p orbital with effective nuclear charge[58], we obtain the parameters $D_0^\pi = 0.930\text{\AA}$. This difference is directly attributed to the different extension of p_z and $p_{x/y}$ orbitals along z axis since the wave functions of π bands are combination of p_z orbitals while those of σ bands are $p_{x/y}$ orbitals.

To employ the real-space exciton Hamiltonian in graphene, we first obtain the band parameters from LDA-DFT calculation as $\mu_x^M = 0.094m_0$, $\mu_y^M = -0.933m_0$. m_0 being the free electron mass. With these parameters, we may solve the excitonic Schrödinger equations numerically. The kinetic part of Hamiltonian is

$$H_0^M(p) = \frac{p_x^2}{2\mu_x^M} + \frac{p_y^2}{2\mu_y^M} \quad (4.17)$$

Figure 4.3 π band energy dispersion around M point shows saddle-like surface.

As shown in Figure 4.1, the solid blue line represents the direction with positive effective masses, while the dashed blue line shows the direction along which effective masses are negative.

Since M point is a saddle point, as shown in Figure 4.1, the masses have opposite sign and the solutions to the attractive two-body problem are not discrete bound

states. Considering the fact that the negative mass is much larger than the positive one, we follow Velicky and Sak [59] and Kane's [60] method by separating the problem into one bound problem and one scattering problem

$$\begin{aligned} \left[\frac{p_x^2}{2\mu_x^M} - V_{\text{eff}}^{\text{scr}}(x, y) \right] \varphi(x, y) &= \mathcal{E}_n(y) \varphi(x, y) \\ \left[\frac{p_y^2}{2\mu_y^M} + \mathcal{E}_n(y) + \frac{1}{2\mu_y^M} \int \left| \frac{\partial \varphi(x, y)}{\partial y} \right|^2 dx \right] \phi(y) &= E_n \phi(y) \end{aligned} \quad (4.18)$$

The first equation describes a 1D bound state problem while the second one lead to a delocalized scattering state with a total wave function $\Psi(x, y) = \varphi(x, y)\phi(y)$.

As discussed, there's no discrete bound state of saddle point exciton near M point, so we may not define a binding energy for this resonant exciton. However, the binding energy of the 1D bound state can be a measure of the Coulomb interaction strength. Using the parameters obtained, we numerically solve the 1D Schrödinger equation

$$\left[\frac{p_x^2}{2\mu_x^M} - V_{\text{eff}}^{\text{scr}}(x, 0) \right] \varphi(x, 0) = \mathcal{E}_n \varphi(x, 0) \quad (4.19)$$

for both single-layer graphene (SLG) and bilayer graphene (BLG) and obtained the binding energy $\mathcal{E}_n$ for first three excited states with n being the number of nodes. The binding energies and parities are shown in Table 4.I.

TABLE 4.I. Binding energies of first three 1D bound states around M point

	$\mathcal{E}_n$ (eV)		Parity
	SLG	BLG	
n=0	-0.73	-0.44	Even
n=1	-0.062		Odd
n=2	-0.035		Even
Exp. [22]	~-0.58	~-0.4	
GW-BSE[26]	-0.60	-0.45	

As analyzed in previous chapters, at M point the symmetry of π conduction/valence band realized the B_{1u}/B_{2g} representation of D_{2h} group. And the in-plane dipole momentum operator $\hat{x}$ and $\hat{y}$ have the symmetry of B_{3u} and B_{2u} respectively. From the product table we see that $B_{3u} \times B_{1u} \times B_{2g} = A_g$ and $B_{2u} \times B_{1u} \times B_{2g} = B_{1g}$. Therefore, for light with dipole x, the exciton whose envelop realizing symmetry A_g will be active, while for light with dipole y, the exciton whose envelop realizing symmetry B_{1g} will be active. However, for envelop with symmetry B_{1g} , the amplitude at zero distance vanishes, so although formally active, it will be difficult to observe compared to A_g exciton since the oscillation strength is proportional to the envelop amplitude at zero distance[60]. Therefore $n=0, 2$ states are expected to be bright and observable. The real-space wave functions and amplitudes along x axis are plotted in Figure 4.2.

Figure 4.4 Exciton wave functions and Amplitudes along positive mass direction of M saddle point

Inspecting our results we find that the $n=0$ states agree well with both experiments and *ab initio* GW-BSE calculation, and its amplitude at $r=0$ is much greater than $n=2$ state so we expect it to be the excitonic state observed.

To evaluate the importance of parameter D in this work, we again calculated the binding energy by manually tuning D in a wide range and solve the first several 1D bound states. The results are plotted in Figure 4.3.

Figure 4.5 Parameter dependence of saddle point exciton binding energy.

From the calculated results it can be seen that as D decreases, the binding energy of state $n=0$ diverges fast, while other states varies less. The solution of 1D Ohno problem has been studied numerically recently by Gebremedhin and Weatherford [61], where the nodeless ground state ($n=0$) has even parity and the eigenvalue approaches negative infinity as the potential evolves Ohno to hard Coulomb potential. This is further confirmed by our results. This means such state is extremely sensitive to the parameter D controlling the effective potential and only when the short range part of the interaction is regularized and no longer diverges as $1/r$ at small r , the existence of such nodeless state can be found. Therefore the

existence of such states is important evidence of the short range regularization of Coulomb interaction. If we only include the non-local screening effect, without the Ohno-type regularization, the binding energy obtained becomes 1.03 eV which is almost twice that from experiments and GW-BSE calculation. This supports the importance of the Ohno-type effective potential which naturally arises from the quasi-2D nature of graphene. The above model also explains the strong saddle point excitonic effect as the 1D nature of bound state along positive mass direction.

4.4 Conclusion

In this chapter, we established a general approach to construct effective mass Schrodinger equation for excitons in quasi-2D materials. The electron-hole interaction in this model is described using an effective potential derived from Bethe-Salpeter equation and the effects of wave function's finite expansion perpendicular to 2D plane are included as a parameter. The results obtained agree almost perfectly with previous experiments and numerical simulations. And discussions imply that inclusion of the finite expansion perpendicular to 2D plane is fundamental to correctly calculation saddle point excitons' binding energies in quasi-2D materials. This supports our claim that the electronic structures along confined dimensions are important to the electronic dynamics in low-dimensional materials.

Chapter 5

σ Exciton in Graphene and Its Multilayer Structures

This chapter models the layer-dependence of dielectric screening in layered structures including graphene multilayer. The screening is combined with model obtained in last chapter to solve the σ exciton in graphene multilayer. This work also finds an exotic exciton spectrum that differs from hydrogenic model.

5.1 Introduction

As an extension to the work in previous chapter, the effective potential with band dependence is applied in multi-layer graphene to solve the σ band excitons. In layered structure like multi-layer graphene, an important feature that differs from single atomic layer is that there are both intra-layer and inter-layer interactions, and both should be included into the screening effect. Therefore in addition to the effective mass model and band-dependent potential derived in previous chapter, a model describing screening in layered structure should be included. As reviewed before, previous studies have established models for screening in layered systems, yet the models either neglected the layer distance, or consider infinite/semi-infinite systems only. Here we first derive a model for screening in finite layered system, then apply the model to calculate σ excitons in multi-layer graphene.

5.2 σ excitons in graphene

5.2.1 Symmetry analysis of graphene σ states

Beside the π band analyzed in previous chapter, more van Hove singularities exist in energy range further from Fermi level. At Γ point, the highest valence bands are σ bands consisting of carbon p_x/p_y orbitals, with symmetry of representation E_{2g} . The degeneracy of these two bands leads to large density of states and they are ideal hole-provider in formation of exciton.

As seen in the ab initio band structure, the first several van Hove singularities above Fermi level arise from the image-potential states. The symmetry of them, as given by [10], are A_{1g} and A_{2u} respectively. Since the in-plane dipole momentum operator has the symmetry of E_{1u} representation, according to product table of D_{6h} group $E_{2g} \times A_{1g} \times E_{1u} = B_{1u} + B_{2u} + E_{1u}$, $E_{2g} \times A_{2u} \times E_{1u} = B_{1g} + B_{2g} + E_{1g}$ none of which contains A_{1g} representation. Therefore, optical excitations with in-plane polarization are forbidden between σ valence bands and these image-potential states. And the only active exciton

arising from such electron-hole pairs are p-like with vanishing amplitude at small electron-hole distance. Therefore, it can be expected that they are not good electron-provider for exciton formation.

Meanwhile, the p_x/p_y conduction bands, with symmetry of E_{1u} representation, are good candidature for exciton formation. Since $E_{1u} \times E_{2g} \times E_{1u} = A_{1g} + A_{2g} + E_{2g}$, optical transition is allowed in this case. And s-like excitonic states become bright. Thus we expect that there will be strong excitonic effects between p_x/p_y σ conduction and valence bands.

It is also interesting to notice that, although the $2s$ $2p_x$ $2p_y$ orbitals are expected to form sp^2 hybridized orbitals with degenerate energy like in benzene, in the case of graphene they actually split into two groups even at Γ point. The p orbitals actually are closer to Fermi level than s orbitals and the energy difference is quite large. This implies that although the bonds in graphene are expected to be sp^2 and similar to benzene, they are actually pretty different.

5.2.2 Layer dependent dielectric screening in multilayer graphene

To construct the effective potential in multilayer graphene, we need to extend our model works to layered structures. The inter-layer or inter-tube screening is found important for many-body behaviors in low dimensional systems [62,63]. Following Visscher and Falicov [63] we consider multilayer graphene or graphite as a stack of single layers, while taking into account the real band structure instead of simple 2D electron gas model. Consider a stack of N 2D layers separated by interlayer distance d , all of which have the same 2D polarizability α_{2D} . The Poisson equation with a point charge in the first layer is

$$\nabla_{\rho,z}^2 \phi(\rho, z) = -4\pi e \delta(\rho, z) - \sum_n^N 4\pi \alpha_{2D} \nabla_{\rho}^2 \phi(\rho, z_n) \delta(z - z_n). \quad (5.1)$$

The 3D Fourier transform is

$$(q^2 + k_z^2)\phi(q, k_z) = 4\pi e - 4\pi\alpha_{2D} \sum_n^N q^2 e^{-ik_z z_n} \int \frac{dk'}{2\pi} \phi(q, k') e^{-ik' z_n} \quad (5.2)$$

The 2D Fourier component in each layer can be defined as an inverse Fourier transform $\phi_n(q) = \int \frac{dk'}{2\pi} \phi(q, k') e^{-ik' z_n}$, so a Fourier transform of the self-consistent equation is given as

$$\phi_n(q) = 2\pi e \frac{e^{-q|z_n|}}{q} - 2\pi\alpha_{2D} q \sum_m^N \phi_m(q) e^{-q|z_n - z_m|} \quad (5.3)$$

Solving this equation we obtain the total potential generated in the first layer

$$\phi_n(q) = \frac{2\pi e}{q} \frac{1}{1 + 2\pi\alpha_{2D} q \frac{\sinh[N\zeta]}{\sinh[N\zeta] - e^{-qd} \sinh[(N-1)\zeta]}} \equiv \frac{2\pi e}{\varepsilon(q)q} \quad (5.4)$$

with $\cosh[\zeta] = \cosh[qd] + 2\pi\alpha_{2D} q \sinh[qd]$. To determine the appropriate α_{2D} , we take the limit $d \rightarrow 0$, say neglecting the finite thickness of the system, and arrive at $\varepsilon(q) = 1 + N2\pi\alpha_{2D} q$. Meanwhile, if we consider a one-layer 2D system, its static dielectric function has the form $\varepsilon(q) = 1 + 2\pi q \chi^{\text{RPA}}$ and the definition of χ^{RPA} is given by Stern[64] as the polarizability in random phase approximation (RPA) with $g_s=2$ be the spin degeneracy.

$$\chi^{\text{RPA}}(q) = -\frac{e^2 g_s}{q^2 A} \sum_{ss'k} \frac{f_{s,k} - f_{s',k+q}}{E_{s,k} - E_{s',k+q}} \left| \langle sk | e^{-iqr} | s'k+q \rangle \right|^2 \quad (5.5)$$

These two expressions for dielectric function should be consistent so we have

$$\alpha_{2D}(q) = \frac{\chi^{\text{RPA}}(q)}{N} \quad (5.6)$$

The summation indices s/s' run over all bands. For multi-layer graphene and graphite, we may simplify the above equation by partitioning these bands into two groups: π bands near K/K' point, and high energy bands. The contribution

from the latter one, which mainly arises from σ bands, is obtained for graphite by measuring the complex dielectric function[65]. They have contribution of $\delta\epsilon = 1.4$ per 2 layers to the total static dielectric constant and in 3D case, it has the RPA expression

$$\delta\epsilon = -\frac{4\pi e^2 g_s}{q^2 A L_c} \sum_{ss'k} \frac{f_{s,k} - f_{s',k+q}}{E_{s,k} - E_{s',k+q}} \left| \langle sk | e^{-iqr} | s'k + q \rangle \right|^2 \quad (5.7)$$

where $L_c = 2d$ is the graphite lattice constant. Then we could approximate their contribution to the polarizability per layer with $\delta\chi = \frac{1}{2} \frac{\delta\epsilon L_c}{4\pi} = \frac{\delta\epsilon d}{4\pi}$. Assuming this value to be universal for both graphene and graphite, we may rewrite the polarization for multilayer graphene as

$$\chi^{\text{RPA}}(q) = N \frac{\delta\epsilon d}{4\pi} - \frac{e^2 g_s g_v}{q^2} \sum_{ss'k} \frac{f_{s,k} - f_{s',k+q}}{E_{s,k} - E_{s',k+q}} \left| \langle sk | e^{-iqr} | s'k + q \rangle \right|^2 \quad (5.8)$$

where the indices s/s' run over π bands near K/K' point only. Using the electronic structure of multilayer graphene[66-68] we obtain the static RPA dielectric function of intrinsic N-layer graphene

$$\chi^{\text{RPA}}(q) = N \frac{\delta\epsilon d}{4\pi} + \frac{e^2}{\pi\gamma q^2} \sum_{n=1}^N \left[t_n + \frac{3q^2 - 4t_n^2}{2q} \tan^{-1} \frac{q}{2t_n} - \sqrt{q^2 - 4t_n^2} \tan^{-1} \frac{\sqrt{q^2 - 4t_n^2}}{2t_n} - 2t_n \ln \frac{\sqrt{q^2 + 4t_n^2}}{q} \right] \quad (5.9)$$

with $\gamma = 6.46 \text{ eV} \cdot \text{\AA}$, $t_{\perp} = 0.39 \text{ eV}$ and $t_n = \left| \frac{t_{\perp}}{\gamma} \cos \left[\frac{n\pi}{N+1} \right] \right|$.

Then we may obtain the dielectric function for single and multi-layer graphene.

For single layer graphene, it has a simple form $\epsilon(q) = 1 + \frac{e^2 \pi}{2\gamma} + \frac{\delta\epsilon d}{2} q$, so the

effective potential has the Ohno form

$$V_{\text{eff}}^{2D}(r) = \frac{e^2}{\epsilon_{bg} \sqrt{r^2 + D_{\text{eff}}^2}} \quad (5.10)$$

$$D_{\text{eff}} = \frac{r_0 e^{-D_0/r_0}}{\text{Ei}\left[-\frac{D_0}{r_0}\right]}, \quad r_0 = \frac{\delta\epsilon d}{2\epsilon_{bg}}, \quad \epsilon_{bg} = 1 + \frac{e^2\pi}{2\gamma}$$

For multi-layers, it is quite complicated. Examining the behavior of α_{2D} we see

that for $q \ll \frac{t_{\perp}}{\gamma}$

$$\alpha_{2D}(q) \xrightarrow{q \rightarrow 0} \frac{\delta\epsilon d}{4\pi} + \begin{cases} \frac{1}{N} \left(\csc \frac{\pi}{2N+2} - 1 \right) \frac{e^2 t_{\perp} \ln 4}{\gamma^2} \frac{1}{q^2} & \text{even } N \\ \frac{1}{N} \left(\cot \frac{\pi}{2N+2} - 1 \right) \frac{e^2 t_{\perp} \ln 4}{\gamma^2} \frac{1}{q^2} & \text{odd } N \end{cases} \quad (5.11)$$

Therefore at small q

$$\zeta(q) \xrightarrow{q \rightarrow 0} \cosh^{-1} \left[1 + 2\pi d \begin{cases} \frac{1}{N} \left(\csc \frac{\pi}{2N+2} - 1 \right) \frac{e^2 t_{\perp} \ln 4}{\gamma^2} & \text{even } N \\ \frac{1}{N} \left(\cot \frac{\pi}{2N+2} - 1 \right) \frac{e^2 t_{\perp} \ln 4}{\gamma^2} & \text{odd } N \end{cases} \right] \quad (5.12)$$

So the dielectric function has a $\frac{1}{q}$ singularity at small q

$$\epsilon(q) \xrightarrow{q \rightarrow 0} 1 + \frac{2\pi \sinh[N\zeta(0)]}{\sinh[N\zeta(0)] - \sinh[(N-1)\zeta(0)]} \times \left[\frac{\delta\epsilon d}{4\pi} q + \begin{cases} \frac{1}{N} \left(\csc \frac{\pi}{2N+2} - 1 \right) \frac{e^2 t_{\perp} \ln 4}{\gamma^2} & \text{even } N \\ \frac{1}{N} \left(\cot \frac{\pi}{2N+2} - 1 \right) \frac{e^2 t_{\perp} \ln 4}{\gamma^2} & \text{odd } N \end{cases} \right] \quad (5.13)$$

The leading terms of dielectric function has the form of Thomas-Fermi screening

$\epsilon(q) \sim 1 + \frac{q_{TF}(N)}{q}$ at small q with layer-number dependent Thomas-Fermi

wavevector $q_{TF}(N)$. For larger $q > \frac{t_\perp}{\gamma}$, it approaches the form for single layer graphene asymptotically. This is because the inter-layer screening decays exponentially, which becomes unimportant for larger q .

This means the long-range part of the screened potential behaves like Thomas-Fermi screened, which is asymptotically $\sim 1/r^3$, while the short-range part is similar to the screened Coulomb in strict 2D dielectric, which approaches a finite value at small distance. With asymptotic behavior of long-range and short-range screening discussed above, an approximation $V_{\text{eff}}^{\text{scr}}$ with layer-number dependence can still be found for multi-layer graphene as

$$V_{\text{eff}}^{\text{scr}}(r) = \frac{e^2}{\epsilon_{bg} \sqrt{r^2 + D_1^2}} - \frac{e^2}{\epsilon_{bg} \sqrt{r^2 + D_2^2}} \quad (5.14)$$

5.3 σ exciton binding strength in single-layer and multi-layer graphene

Using tight-binding model to write the wave function of σ bands around Γ point, we obtain the band-dependent parameter $D_0^\sigma = 0.405A$. Substituting this value into the effective potential obtained, with layer-number dependent screening included, we obtain the effective potential for σ band excitons.

For the effective mass Hamiltonian of σ bands around Γ point, we employ DFT-LDA simulation to obtain the effective mass parameters as $\alpha_h = -\frac{2.29}{2m_0}$,

$$\beta_h = -\frac{0.70}{2m_0}, \quad \alpha_e = \frac{1.85}{2m_0} \quad \text{and} \quad \beta_h = -\frac{1.31}{2m_0} \quad \text{respectively.}$$

The corresponding kinetic energy operators for electrons and holes are

$$\begin{aligned}
H_0^e(p) &= \begin{bmatrix} \alpha_e I_2 (p_x^2 + p_y^2) & \beta_e (p_x + ip_y)^2 \\ \beta_e (p_x - ip_y)^2 & \alpha_e I_2 (p_x^2 + p_y^2) \end{bmatrix} \\
H_0^h(p) &= \begin{bmatrix} \alpha_h I_2 (p_x^2 + p_y^2) & \beta_h (p_x + ip_y)^2 \\ \beta_h (p_x - ip_y)^2 & \alpha_h I_2 (p_x^2 + p_y^2) \end{bmatrix}
\end{aligned} \tag{5.15}$$

vHamiltonian for σ excitons around Γ point is pretty complicated so we employ a variational trial function to find the ground exciton state for σ bands. Examining the Hamiltonian $H_{ex} = H_c(p) \otimes I_{g_v} - I_{g_c} \otimes H_v(p) + V_{eff}^{scr}(r)$, we find that the angular and radial part of eigenfunction can be separated and written as

$$\begin{aligned}
\Psi_l(r) &= e^{il\theta} (\varphi_1(r), e^{i2\theta} \varphi_2(r), e^{-i2\theta} \varphi_3(r), \varphi_4(r))^T \\
&= \text{diag}(e^{il\theta}, e^{i(l+2)\theta}, e^{i(l-2)\theta}, e^{il\theta}) \Psi_l(r)
\end{aligned} \tag{5.16}$$

and for each quantum number l there is a radial Schrodinger equation

$$H_l \Psi_{n,l}(r) = E_{n,l} \Psi_{n,l}(r) \tag{5.17}$$

Using the radial part of 2D hydrogenic orbitals $\varphi_{n,l}(r)$ as the variational trial function such that

$$\Psi_l^t(r) = (A_1 \varphi_{|l|,l}(B_1 r), A_2 \varphi_{|l+2|,l+2}(B_2 r), A_3 \varphi_{|l-2|,l-2}(B_3 r), A_4 \varphi_{|l|,l}(B_4 r)) \tag{5.18}$$

For each l the energy of the lowest state has upper bound

$$E_{0,l} \leq \langle \Psi_l^t | H_l | \Psi_l^t \rangle \tag{5.19}$$

so $E_{0,l}$ can be approximated with the lower bound of $\langle \Psi_l^t | H_l | \Psi_l^t \rangle$. The Hamiltonian leads to degeneracy of states with opposite sign of l and the approximated values of some $E_{0,l}$ are given in Table 5.I. Taking into account the layer-dependent screening effect, the ground excitonic state is also obtained for multilayer graphene, given in Table 5.II. We found that σ exciton is pretty robust even in thicker multilayer graphene, and it is greater than room temperature

(~26meV) even in graphene as thick as 50 layers. As discussed earlier this chapter, for finite q the interlayer screening decays exponentially as distance increases, so the screening from further layers is much weaker than neighbor layers. Meanwhile, since the Ohno parameter D is smaller for σ exciton, the Coulomb matrix element decays more slowly as q increases. This explains the existence of exciton in thick multilayer graphene in our model and experiments [28].

TABLE 5.I. σ exciton binding energies for selected quantum number l .

l	$E_{0,l}$ (eV)
0	-0.51
± 1	-0.12
± 2	-0.48
± 3	-0.083
± 4	-0.026
± 5	-0.016

TABLE 5.II. σ exciton binding energies in multilayer graphene with different layer number N .

Layer Number N	$E_{0,0}$ (eV)
1	-0.51
2	-0.07
3	-0.07
10	-0.05
50	-0.05

However in real systems, the above model might overestimate the screening in few-layer graphene. First, the indirect interlayer coupling lead to the so called trigonal warping in multi-layer graphene [69-71]. This warping effect leads to four massless Dirac cones instead of massive bands around Fermi level. The DOS around Fermi level becomes vanishing in this case, and XF Wang et al[72] have shown that the dielectric function approaches a finite value ~105 in BLG instead of TF-like $1/q$ divergence at small q .

In addition, a finite gap opening has been found in graphene due to spin-orbit coupling and curvature[73,74], and substrate-graphene interaction[75]. According to ARPES measurements of epitaxial few-layer graphene on SiC[75], finite gaps are found for graphene grown on substrates, due to graphene-substrate interaction. For single-, bi- and tri-layer epitaxial graphene on SiC, the gap found are 0.26eV, 0.14eV and 0.066eV respectively. To calculate the effect of finite gap, we start from the effective mass model of gapped single-layer graphene[76] and bi-layer graphene[70]. For intrinsic single-layer graphene with a finite gap Δ , the static dielectric function in RPA is obtained by Pyatkovskiy[76] as

$$\begin{aligned} \varepsilon^{\text{RPA}}(q) &= \varepsilon_{\text{sub}} + \frac{e^2}{\gamma^2 q} \left(\Delta + \frac{\gamma^2 q^2 - \Delta^2}{\gamma q} \arcsin \frac{\gamma q}{\sqrt{\gamma^2 q^2 + \Delta^2}} \right) \\ &\approx \begin{cases} \varepsilon_{\text{sub}} + \frac{4}{3} \frac{e^2}{\Delta} q & q \rightarrow 0 \\ \varepsilon_{\text{sub}} + \frac{\pi e^2}{2\gamma} & q \rightarrow \infty \end{cases} \end{aligned} \quad (5.20)$$

Using the effective 2-band Hamiltonian of gapped bilayer graphene given by McCann[70], we obtain that for small q ,

$$\varepsilon^{\text{RPA}}(q) \approx \varepsilon_{\text{sub}} + e^2 \left(\frac{5\sqrt{t_{\perp}^2 + \Delta^2}}{3\Delta^2} + \frac{4}{3\Delta} - \frac{1}{3\sqrt{t_{\perp}^2 + \Delta^2}} \right) q \quad (5.21)$$

And the dielectric function at large q , which is dominated by higher energy dispersions, should be unchanged since the gap only affect the low-energy band structure. Since the band structure of trilayer graphene is equivalent to a bilayer with parameter with parameter $\gamma_1 \rightarrow \sqrt{2}\gamma_1$, plus a single layer[69], we may approximate the dielectric function with the above equations. Taking into account the effect from high energy bands and inter-layer screening, they all have the following form of screening

$$\varepsilon(q) \approx \begin{cases} \varepsilon_{\text{sub}} + r_1 q + \frac{\delta\varepsilon d}{2} q & q \rightarrow 0 \\ \varepsilon_{\text{sub}} + \frac{\pi e^2}{2\gamma} + \frac{\delta\varepsilon d}{2} q & q \rightarrow \infty \end{cases} \quad (5.22)$$

where $\varepsilon_{sub} = \frac{1+\varepsilon_{SiC}}{2} \approx 5.5$, $r_1 \approx 74\text{\AA}$ for SLG, $r_1 \approx 633\text{\AA}$ for BLG and $r_1 \approx 2749\text{\AA}$ for trilayer. Since the screening parameter r_1 is pretty large here, we need to consider its effect on the long range potential. Considering that $r_1 \gg D_{eff}$, $\frac{\delta\varepsilon d}{2}$, the long range potential is dominated by the screening effect, so for large r

$$V(r) \approx \frac{\pi e^2}{2r_1} \left[H_0 \left(\frac{\varepsilon_{sub} r}{r_1} \right) - Y_0 \left(\frac{\varepsilon_{sub} r}{r_1} \right) \right] \approx \frac{e^2}{5.5r} \left(1 - \frac{r_1^2}{5.5^2 r^2} \right) \quad (5.23)$$

And at small r , it still approaches the finite value $\frac{e^2}{\varepsilon_{bg} D_{eff}}$. Then we may empirically approximate them with

$$\begin{aligned} V_{eff}^{SLG}(r) &\approx \frac{e^2}{9.15\sqrt{r^2 + D_{eff}^2}} + \frac{e^2}{13.8\sqrt{r^2 + 30.1^2}} \\ V_{eff}^{BLG}(r) &\approx \frac{e^2}{9.02\sqrt{r^2 + D_{eff}^2}} + \frac{e^2}{14.1\sqrt{r^2 + 261^2}} \\ V_{eff}^{TLG}(r) &\approx \frac{e^2}{9.01\sqrt{r^2 + D_{eff}^2}} + \frac{e^2}{14.1\sqrt{r^2 + 1133^2}} \end{aligned} \quad (5.24)$$

With these effective potential, the calculated binding energy for σ excitons are 158 meV for SLG, 133 meV for BLG and 130 meV for trilayer graphene respectively. They are plotted in Figure 5.1 together with data in Table 5.II.

Figure 5.1 Layer number dependence of σ excitons binding energies in multi-layer graphene.

We see that in this case the binding energy is not so sensitive to r_1 , as long as there is a finite gap. The reason is that the gap size only affects non-leading terms of the effective potential.

From the above results we see that the finite gap further regularizes the screening at small q from TF-like to insulator-like for both single-layer and bi-layer graphene. Since the band structure of multi-layer graphenes are analogues of single- and bi-layer graphene[69], we would expect that the existence of finite gap will also modify the Thomas-Fermi type long-range screening in multi-layer graphene. However, since the penetration depth of x-ray into HOPG is only 87 Å [77], around 26 layers at most, the effect of substrate in thicker graphene becomes insignificant in the layers that can be reached by x-ray, and the screening on excitons detected will be similar to that of suspended graphene. For thinner graphene however, substrate-induced gap should be considered. And since for finite gap, the gap size only affects the non-leading term of long range potential, the overall binding is not quite dependent on gap size. This explains why the excitonic peaks in thinner epitaxial graphene shift little as layer number increases,

while for thicker epitaxial graphene the peak gradually merge into the inter-band transition peaks, as illustrated in Figure 5.2.

Figure 5.2 Mechanism of photon detection for multi-layer graphene with different thickness.

5.4 Exotic exciton spectrum

From previous symmetry analysis we see that the p_x/p_y σ conduction bands and valence bands around Γ point realizes the E_{1u} and E_{2g} representation of group D_{6h} respectively. Meanwhile, the in-plane dipole operator has the symmetry E_{1u} . From the product table we see that $E_{1u} \times E_{2g} \times E_{1u} = A_{1g} + A_{2g} + E_{2g}$. Therefore the excitonic states whose envelop function are s -like will be bright while p -like will be dark. Inspecting the symmetry of the excitonic states, we note that $l=0$ and $l=\pm 2$ excitons, which have majorly $1s$ -like character, are dipole active to light with in-plane polarization. This large binding energies $\sim 0.5\text{eV}$ of bright σ excitons is smaller than *ab initio* [27] and experimental [28] results. However, it is still remarkable in such gapless system and much greater than common semiconductors.

Inspecting the fine structure of energy levels, we found it noticeable that the binding energies of these bright excitons are only about four times that of $l=\pm 1$ and $l=\pm 3$ which have $2p$ -like character. Such excitonic spectra significantly

deviate from standard 2D hydrogenic spectra[78] where $1s$ state has 9 times the energy of $2s/2p$ state.

For further understanding of such deviation, we solved a two-body Schrödinger equation with the average electron/hole effective mass of σ bands and effective potential with parameters for σ bands. The first several energy levels for such model system, with bare Coulomb potential, bare Ohno potential, non-locally screened Coulomb potential and screened Ohno potential are given in Figure 5.3 in comparison with 2D hydrogenic spectra.

Figure 5.3 Ratio between higher exciton states and 1s state.

The spectra are quite different from 2D hydrogenic spectra. First, energy levels with higher principal quantum numbers are closer to the 1s state. In the spectra of bare Ohno potential, the 1s:2p ratio is around 7.7 and with screening added, this ratio becomes around 7.1. In 2D hydrogenic model however, this ratio should be 9:1. Furthermore, states with higher angular momentum have lower energies, say $E_{2s} > E_{2p}$ and $E_{3s} > E_{3p} > E_{3d}$. Instead of 1:1 in hydrogenic model, the 2p:2s ratio becomes 1.08 and 1.13 for bare and screened Ohno potential respectively. It is in contrast to the usual angular momentum splitting between atomic energy levels.

Such deviations are caused by the regularization of effective potential at small distance, as discussed below. The screening effect, as shown by Cudazzo et al[56], reduces the $1/r$ divergence of Coulomb potential to a logarithmic divergence, and the Ohno effect further regularizes the effective potential to a finite value at $r=0$. From Figure 5.3 we can see that the Ohno-type regularization and nonlocal

screening have comparable contribution to such deviation. As we show in previous chapter, the Ohno-like effective potential induces a significant weakening of Coulomb interaction at small distance. Such weakening is localized and the difference between Coulomb-type potential and our effective potential decays as fast as $\sim 1/r^3$. Therefore, such weakening of potential energy is more effective on states with smaller principal quantum number n , like 1s state, which is much more localized, and the binding energies for states with smaller n are reduced more significantly. And among those states with the same n , states with larger angular quantum number l are more diffusive and have vanishing density at small distance. Therefore, the binding energy reduction of, for example, 2s state is greater than the reduction of 2p state. Such difference results in the unconventional removing of degeneracy between these states. The above explanation is illustrated below in Figure 5.4.

Figure 5.4 Visual illustration of the difference between Coulomb potential and modified effective potential.

To confirm this explanation, we solved the binding energy of several states for different parameter D . The results are plotted in Figure 5.5.

Figure 5.5 Dependence of binding energy ratio on band parameter.

The deviation and splitting becomes greater as the parameter D increases, as plotted in Figure 5.4. Similar behavior has been experimentally observed in tungsten disulphide (WS_2) where the deviation is much larger [79]. This can be expected since WS_2 is much thicker than graphene and the bulk dielectric constant is also greater. Since D is determined by the effective thickness together with 2D polarizability, we can conclude that such exotic behaviors are general for quasi-2D systems including graphene, graphene derivatives and transition metal dichalcogenide.

5.5 Conclusion

By solving the real-space effective mass Schrodinger-type equation with band-dependent effective potential and layer-number dependent screening effect included, we found the correlation between σ excitons binding energies and layer number in multi-layer graphene. In addition, we found an exotic non-hydrogenic excitons spectrum where the energy ratio between higher states and 1s state is greater than expected in 2D hydrogenic model. Degeneracy between states with same principal quantum number is found absent in this case. The results imply that this should be general phenomena in quasi-2D materials.

Chapter 6

Geometry Dependent Scaling Behavior of sp^2 Carbon Nanostructures

In this chapter, the geometry dependence of many-body interaction is studied analytically. The model explains the different scaling behavior in carbon nanotubes and graphene nanoribbons as consequence of their distinct geometry.

6.1 Introduction

To understand the different scaling behaviors in ZCNTs and AGNRs, analysis of many-body interactions in these systems is needed. Specifically, it will help to understand the physics if functional form of correlation between many-body interactions and their respective geometry is given. Hence, in this chapter, we present the functional analysis based on effective mass description to describe the many-body effects in ZCNTs and AGNRs.

6.2 Methodology

6.2.1 Effective mass description of AGNRs and ZCNTs

As discussed in methodology chapter, the wave function, energy dispersion and electronic structures of AGNRs and ZCNTs are pretty similar. For AGNRs, their wave function and energy dispersion can be written as

$$\begin{aligned}\psi_{s,l}(k) &= \sqrt{\frac{\delta(y)}{4L\tilde{W}}} \exp[ikz] \begin{pmatrix} b_l(k) \exp[i\kappa_l x] \\ s \exp[i\kappa_l x] \\ -b_l(k) \exp[-i\kappa_l x] \\ s \exp[-i\kappa_l x] \end{pmatrix} \\ E_{s,l}(k) &= sv_F \sqrt{\kappa_l^2 + k^2} \\ \kappa_l &= -\frac{\pi}{\tilde{W}} \left(l + \frac{\tilde{\nu}}{3} \right), b_l(k) = \frac{\kappa_l - ik}{\sqrt{\kappa_l^2 + k^2}}\end{aligned}\quad (6.1)$$

And for ZCNTs they can be written as

$$\begin{aligned}\psi_{s,l}(k) &= \sqrt{\frac{\delta(\rho - R)}{2LC}} \exp\left[\frac{i\kappa_l C\theta}{2\pi} + ikz\right] \begin{pmatrix} b_l(k) \\ s \end{pmatrix} \\ &= \sqrt{\frac{\delta(\rho - R)}{2LC}} \exp\left[i\left(l \mp \frac{\nu}{3}\right)\theta + ikz\right] \begin{pmatrix} b_l(k) \\ s \end{pmatrix} \\ E_{s,l}(k) &= sv_F \sqrt{\kappa_l^2 + k^2} \\ \kappa_l &= \mp \frac{2\pi}{C} \left(l + \frac{\nu}{3} \right), b_l(k) = \frac{\kappa_l \mp ik}{\sqrt{\kappa_l^2 + k^2}}\end{aligned}\quad (6.2)$$

We see that they are very similar in both functional form and quantization. And they all allow $\kappa_l = 0$ when $\tilde{\nu} = 0$ or $\nu = 0$, which mean they all have gapless metallic families.

The similarity between ZCNTs and AGNRs are illustrated below in Figure 6.1.

Figure 6.1 Similarity between structures of ZCNT and AGNR

However, according to ab initio study, this is not true for AGNRs[12,13]. From both local density approximation and GW calculation, no strictly metallic AGNRs are found. The $3p+2$ families which should have been metallic actually have a small band gap. This unexpected result arises from the edge problem, where the hopping energy towards edge sites is different from its original value t . The modified hopping energy for hydrogen terminated AGNRs are given as

$(1 + \delta)t$ where $\delta = 0.12$. With this the modified band gap for AGNRs are given as[12]

$$\begin{aligned}\Delta_{3p} &\cong t \left(4 \cos \frac{p\pi}{3p+1} - 2 \right) - \frac{8\delta t}{3p+1} \sin^2 \frac{p\pi}{3p+1} \\ \Delta_{3p+1} &\cong t \left(2 - 4 \cos \frac{(p+1)\pi}{3p+2} \right) + \frac{8\delta t}{3p+2} \sin^2 \frac{(p+1)\pi}{3p+2} \\ \Delta_{3p} &\cong \frac{2|\delta|t}{p+1}\end{aligned}\quad (6.3)$$

For large width we find that they become

$$\begin{aligned}\Delta_{3p} &\cong 2\gamma \left(\frac{1}{3} \frac{\pi}{\tilde{W}_{3p}} - \frac{\sqrt{3}\delta}{\tilde{W}_{3p}} \right) \\ \Delta_{3p+1} &\cong 2\gamma \left(\frac{1}{3} \frac{\pi}{\tilde{W}_{3p+1}} + \frac{\sqrt{3}\delta}{\tilde{W}_{3p+1}} \right) \\ \Delta_{3p+2} &\cong 2\gamma \left| \frac{\sqrt{3}\delta}{\tilde{W}_{3p+2}} \right|\end{aligned}\quad (6.4)$$

This seemingly complicated expression can be actually unified into a modified effective mass description by simply replacing the quantized momentum as

$$\kappa_l = -\frac{\pi}{\tilde{W}} \left(l + \frac{\tilde{v}}{3} - \frac{\sqrt{3}\delta}{\pi} \right) \quad (6.5)$$

The forms of wave functions and energy dispersions will remain unchanged except that there is no longer any metallic AGNRs.

In this case, both AGNRs' and ZCNTs' wave functions are still in the same matrix form

$$\psi_m(k_m, \mathbf{r}) = \frac{\exp[ik_m z]}{\sqrt{L}} \xi(m, \rho) \mathbf{F}_{mk_m} \quad (6.6)$$

So the polarizability can be written in a universal form

$$\Pi_{mn}(q) = \sum_k \frac{f_{m,k+q} - f_{n,k}}{E_{m,k+q} - E_{n,k}} \left| \mathbf{F}_{m,k+q}^\dagger \cdot \mathbf{F}_{n,k} \right|^2 \quad (6.7)$$

From the wave function of AGNRs and ZCNTs we see that the wave function overlapping is all written as

$$\left| \mathbf{F}_{m,k+q}^\dagger \cdot \mathbf{F}_{n,k} \right|^2 = \left| \frac{b_m^*(k+q)b_n(k) + s_m s_n}{2} \right|^2 \quad (6.8)$$

And since they share the same functional form of $b_l(k)$ we may evaluate them all together. Summing k over momentum space, we obtain the polarizability in different cases. From the definition we see that the polarizability have the symmetry $\Pi_{mn}(q) = \Pi_{nm}(q)$ and $\Pi_{mn}(q) = \Pi_{mn}(-q)$.

When $\kappa_m = \kappa_n = 0$, the polarizability is constant

$$\Pi_{00}(q) = -\frac{2L}{\pi\gamma} \quad (6.9)$$

When one of them is zero, for example $\kappa_n = 0$

$$\Pi_{m0}(q) = -\frac{2L}{\pi\gamma} \left[1 + \frac{\kappa_m^2}{2q^2} \ln \frac{\kappa_m^2}{\kappa_m^2 + q^2} \right] = -\frac{2L}{\pi\gamma} \frac{1}{2} + \mathcal{O}(q^2) \quad (6.10)$$

When $\kappa_m = \kappa_n \neq 0$

$$\Pi_{mm}(q) = -\frac{2L}{\pi\gamma} \left[1 + \frac{2\kappa_m^2}{q\sqrt{4\kappa_m^2 + q^2}} \ln \frac{\sqrt{4\kappa_m^2 + q^2} - q}{\sqrt{4\kappa_m^2 + q^2} + q} \right] = -\frac{2L}{\pi\gamma} \frac{q^2}{6\kappa_m^2} + \mathcal{O}(q^4) \quad (6.11)$$

When $\kappa_m = -\kappa_n \neq 0$

$$\Pi_{mn}(q) = 0 \quad (6.12)$$

When $\kappa_m \neq \kappa_n \neq 0$

$$\begin{aligned} \Pi_{mn}(q) &= -\frac{2L}{\pi\gamma} \left[1 + \frac{\kappa_m^2 - \kappa_n^2}{4q^2} \ln \frac{\kappa_m^2}{\kappa_n^2} + \frac{(\kappa_m + \kappa_n)^2}{4q^2} \sqrt{\frac{(\kappa_m - \kappa_n)^2 + q^2}{(\kappa_m + \kappa_n)^2 + q^2}} \right] \\ &\quad \times \ln \frac{\kappa_m^2 + \kappa_n^2 + q^2 - \sqrt{(\kappa_m^2 + \kappa_n^2 + q^2)^2 - 4\kappa_m^2 \kappa_n^2}}{\kappa_m^2 + \kappa_n^2 + q^2 + \sqrt{(\kappa_m^2 + \kappa_n^2 + q^2)^2 - 4\kappa_m^2 \kappa_n^2}} \\ &= -\frac{2L}{\pi v_F} \left[\frac{1}{2} - \frac{\kappa_m \kappa_n}{2(\kappa_m^2 - \kappa_n^2)} \ln \frac{\kappa_m^2}{\kappa_n^2} \right] + \mathcal{O}(q^2) \end{aligned} \quad (6.13)$$

These expressions are universal for all AGNRs and ZCNTs.

6.2.2 Geometry dependence of many-body interaction

With polarizability obtained, we then proceed to evaluating the many-body interactions in AGNRs and ZCNTs.

As discussed previously, the bare Coulomb interaction matrix elements are given by

$$v_{ijmn}(q) = 2e^2 \int \xi_i^\dagger(\boldsymbol{\rho}) \xi_j(\boldsymbol{\rho}) K_0(|q||\boldsymbol{\rho} - \boldsymbol{\rho}'|) \xi_m(\boldsymbol{\rho}') \xi_n^\dagger(\boldsymbol{\rho}') d\boldsymbol{\rho} d\boldsymbol{\rho}' \quad (6.14)$$

This expression however, results in quite different behavior of many-body interactions in AGNRs and ZCNTs.

Evaluating this expression in ZCNT, the integration goes over the polar angle. In cylindrical coordinates which suit ZCNT best, the 1D bare Coulomb can be expanded in angular Fourier series as

$$\begin{aligned} \frac{2e^2}{L} K_0(|q||\boldsymbol{\rho} - \boldsymbol{\rho}'|) &= \frac{2e^2}{L} K_0\left(|q| \sqrt{\rho^2 + \rho'^2 - 2\rho\rho' \cos(\theta - \theta')}\right) \\ &= \frac{2e^2}{L} \sum_{l=-\infty}^{\infty} I_{|l|}(|q\rho|) K_{|l|}(|q\rho'|) e^{il(\theta - \theta')} \end{aligned} \quad (6.15)$$

So the bare Coulomb matrix elements in ZCNTs are

$$v_{ijmn}(q) = \delta_{i-j, m-n} \frac{2e^2}{\epsilon_{bg} L} I_{m-n}(|qR|) K_{m-n}(|qR|) \equiv \delta_{i-j, m-n} v_{m-n, m-n} \quad (6.16)$$

Since this Coulomb matrix is diagonal, the self-consistent equation becomes diagonal too

$$\left(1 - v_m(q) \sum_n \Pi_{m+n, n}(q)\right) w_m(q) = v_m^{ext}(q) \quad (6.17)$$

It means the screened Coulomb interactions in ZCNTs are simply

$$\begin{aligned} w_m(q) &= \frac{v_m^{ext}(q)}{\epsilon_m(q)} \\ \epsilon_m(q) &= 1 - v_m(q) \sum_n \Pi_{m+n, n}(q) \end{aligned} \quad (6.18)$$

In AGNRs however, it is totally different. The Coulomb matrix elements are

$$\begin{aligned} v_{ijmn}(q) &= \frac{2e^2}{\epsilon_{bg} L} \int_0^{\bar{W}} \cos[(i-j)x] K_0(|q||x-x'|) \cos[(m-n)x'] dx dx' \\ &= v_{|i-j|, |m-n|}(q) \end{aligned} \quad (6.19)$$

This expression is not diagonal at all. Actually, only when $|i-j| + |m-n|$ is odd will this matrix element be zero. The head of this matrix can be analytically evaluated as

$$\begin{aligned} v_{0,0}(q) &= \frac{2e^2}{\epsilon_{bg} L} \left[-\frac{2}{|Wq|^2} + \frac{2}{|Wq|} K_1(|Wq|) + \pi \left[K_0(|Wq|) \mathbf{L}_{-1}(|Wq|) + K_1(|Wq|) \mathbf{L}_0(|Wq|) \right] \right] \end{aligned} \quad (6.20)$$

Here K_v is the modified Bessel function of the second kind, while $\mathbf{L}_v$ is the modified Struve function. The leading terms of above element is

$$v_{0,0}(q) = \frac{2e^2}{\varepsilon_{bg}L} \left[-\ln(|Wq|) + \frac{3-2\gamma+2\ln 2}{2} + \mathcal{O}(q^2) \right] \quad (6.21)$$

Close forms of other elements are not achieved, yet their leading terms can be found. The leading terms of Bessel functions are

$$K_0(z) = \sum_{j=0}^{\infty} \frac{1}{(j!)^2} \left(\frac{z}{2} \right)^{2j} \left[\mathcal{F}(j+1) - \ln \frac{z}{2} \right] \quad (6.22)$$

The Euler digamma function is $\mathcal{F}(x) = \frac{\Gamma'(x)}{\Gamma(x)}$. Then we evaluate the leading terms and find

$$\begin{aligned} v_{m,m}(q) &= \frac{2e^2}{\varepsilon_{bg}L} \frac{1}{\pi^2} \frac{(-1)^m - 1 + m\pi \text{Si}(m\pi)}{m^2} + \mathcal{O}(q^2) \\ v_{m,n}(q) &= \frac{2e^2}{\varepsilon_{bg}L} \frac{2}{\pi^2} \frac{(-1)^m + 1}{2} \frac{\text{Ci}(m\pi) - \text{Ci}(n\pi) - \ln m + \ln n}{m^2 - n^2} + \mathcal{O}(q^2) \end{aligned} \quad (6.23)$$

Here Si and Ci are sine and cosine integrals respectively.

Using the obtained dielectric function to construct screened Coulomb interaction in many-body picture, we can study the GW self-energy correction and Bethe-Salpeter equation as discussed in previous chapters.

6.3 Scaling behaviors in AGNRs and ZCNTs

6.3.1 Scaling of band gaps and effective masses

As discussed in previous chapters, the static RPA, or screened Hartree-Fock approximation is employed to calculate the self-energy correction as

$$\langle nk | \Sigma(s_n E_{nk}) | nk \rangle = - \sum_q \sum_{m^-} w_{m^-,n,m^-} (q,0) \left| F_{m^-k+q,nk} \right|^2 \quad (6.24)$$

For both ZCNT and AGNR,

$$\left| F_{ms_m k+q, ns_n k} \right|^2 = \frac{1}{2} + s_n s_m \frac{\kappa_m \kappa_n + k(k+q)}{2\sqrt{\kappa_m^2 + (k+q)^2} \sqrt{\kappa_n^2 + k^2}} \quad (6.25)$$

We see that

$$\langle n^+ k | \Sigma(+E_{nk}) | n^+ k \rangle + \langle n^- k | \Sigma(-E_{nk}) | n^- k \rangle = - \sum_q \sum_m w_{m-n, m-n}(q, 0) \quad (6.26)$$

This means it is an overall shift of all bands, so we may subtract it from all self-energy such that the new self-energy correction becomes

$$\langle nk | \Sigma(s_n E_{nk}) | nk \rangle = s_n \sum_q \sum_{m^-} w_{m-n, m-n}(q, 0) \frac{\kappa_m \kappa_n + k(k+q)}{2\sqrt{\kappa_m^2 + (k+q)^2} \sqrt{\kappa_n^2 + k^2}} \quad (6.27)$$

This expression shows electron-hole symmetry of self-energy correction. Since the single-particle band dispersion also has this symmetry, the overall symmetry is preserved.

Evaluating this correction for ZCNTs and AGNRs with different diameter/width, we obtain the scaling behavior of them.

First we plot the circumference dependence of energy gaps for ZCNTs in Figure 6.2. Before including the GW correction, the gaps of semiconducting families 3p+1 and 3p-1 have identical trends while the first gap in metallic family 3p is greater than the other two families. This can be easily seen from the expression that it is three times of semiconducting ones.

However, if we include the GW correction, the gaps become comparable. This is because in metallic ZCNTs, the dielectric function has logarithmical divergence at small momentum, while in semiconducting ones, they approach a finite constant. The leading terms are

$$\begin{aligned} \varepsilon_0^{metallic}(q) &= 1 + \frac{8e^2}{\varepsilon_{bg} \pi \gamma} I_0(Rq) K_0(Rq) + \mathcal{O}(q) \\ \varepsilon_0^{semicon}(q) &= 1 + \mathcal{O}(q^2) \end{aligned} \quad (6.28)$$

Figure 6.2 Circumference dependence of kp effective mass and GW gap of ZCNTs.

Therefore, the screening in metallic ZCNTs is, although not as strong as in higher dimensional metallic systems, stronger than in semiconducting ZCNTs. It is interesting to find that even with GW correction, the gap still scales almost linearly with their radius as shown in the log-log plot in Figure 6.3.

Figure 6.3 Log-log plot of band gap circumference dependence

Similarly, we calculate the effective mass of first massive bands as

$$\begin{aligned} \frac{1}{m_{kp}} &= \frac{1}{\hbar^2} \frac{\partial^2}{\partial k^2} E_{nk} \\ \frac{1}{m_{GW}} &= \frac{1}{\hbar^2} \frac{\partial^2}{\partial k^2} [E_{nk} + \langle nk | \Sigma(E_{nk}) | nk \rangle] \end{aligned} \quad (6.29)$$

The single-particle effective mass and GW effective mass are plotted in Figure 6.4 and the corresponding log-log plot is in Figure 6.5. We see that the effective mass still scales very well with the circumference.

Figure 6.4 Circumference dependence of effective mass of first massive bands in ZCNTs

Figure 6.5 Log-log plot of effective masses in ZCNTs.

In contrast to the cases of ZCNTs, GW corrections in AGNRs do not always scale linearly with the widths. First we calculate the band gaps with and without GW corrections and found that the deviation from linear scaling is not significant, although the band gap enhancement in the small gap $3p+2$ family whose $\tilde{v} = 0$ is much greater than corresponding ZCNT $3p$ family. This is because although small, the band gap is finite in this case so the screening of Coulomb interaction

is not as strong as the case with massless band, and the gap itself is small so the enhancement is much greater than the original kp gap. The linear and log-log plot of band gaps in AGNRs are given in Figure 6.6 and Figure 6.7.

Figure 6.6 Width dependence of band gaps in AGNRs.

Figure 6.7 Log-log plot of width dependence of band gaps in AGNRs.

Then the effective masses of first bands are evaluated using the same techniques as in ZCNTs, as given in Figure 6.8 and Figure 6.9. It is found that different from the cases in ZCNTs, the effective masses significantly deviate from linear scaling

of inverse width. To extract the scaling behavior, we fit them using the following relation

$$m_{GW} = A_{\tilde{v}} R^{\tau} \quad (6.30)$$

The obtained scaling parameter τ is -1.07, -1.07 and -1.29 for family 3p, 3p+1 and 3p+2 respectively.

The above results demonstrate that the effective mass scalings in AGNR deviate from linear scaling significantly while in ZCNTs linear scaling is preserved. Then we proceed to evaluate the deviation of binding energy scaling.

Figure 6.8 Width dependence of effective masses in AGNRs.

Figure 6.9 Log-log plot of effective masses in AGNRs.

6.3.2 Scaling of exciton binding energies

To solve the excitons binding energy, we employ the BSE without exchange effect

$$\begin{aligned} \left[E_c(k) - E_v(k) + \Delta\Sigma \right] A_{cv}(k) - \sum_{c'v'k'} K_{cc'vv'}^d(k, k') A_{c'v'}(k') &= \Omega A_{cv}(k) \\ K_{c_i c_j v_m v_n}^d &= - \int \psi_{c_i}^\dagger(\mathbf{r}') \psi_{c_j}(\mathbf{r}') W(\mathbf{r}', \mathbf{r}) \psi_{v_m}(\mathbf{r}) \psi_{v_n}^\dagger(\mathbf{r}) d\mathbf{r}' d\mathbf{r} \end{aligned} \quad (6.31)$$

The single-particle energy and self-energy can be given to the second order of k . Since the electron-hole symmetry is preserved in our method, and direct interaction is given as screened Coulomb interaction, we can write it as

$$\left[\Delta_{GW} + \frac{k^2}{m_{GW}} \right] A_{cv}(k) + \sum_{c'v'q} W_{cc'vv'}(q) A_{c'v'}(k+q) = \Omega A_{cv}(k) \quad (6.32)$$

The binding energy can be expressed as the difference between excitonic gap and GW gap, so the final equation is

$$\frac{k^2}{m_{GW}} A_{cv}(k) + \sum_{c'v'q} W_{cc'vv'}(q) A_{c'v'}(k+q) = -E_b A_{cv}(k) \quad (6.33)$$

If we assume that only one pair of conduction/valence band is involved, since other bands are energetically far away, we may apply Fourier transform to this equation so that excitons are the stationary states of the following Schrodinger type equation

$$\left[\frac{\hat{P}_z^2}{m_{GW}} + W_{0,0}(\hat{z}) + E_b \right] \psi(z) = 0 \quad (6.34)$$

Here $W_{0,0}(\hat{z})$ is the Fourier transform of 1D screened electron-hole interaction $W_{0,0}(q)$. In ZCNTs, this interaction is simply

$$W_{0,0}(q) = - \frac{\frac{2e^2}{\epsilon_{bg}L} I_0(|qR|) K_0(|qR|)}{1 + \frac{2e^2}{\epsilon_{bg}L} I_0(|qR|) K_0(|qR|) \sum_m \Pi_{mm}(q)} \quad (6.35)$$

From previous sections we see that the polarizability can also be written as $\sum_m \Pi_{mm}(q) = \Pi_0(|qR|)$, therefore in the total screened Coulomb interaction, radius R and momentum q are always coupled, say $W_{0,0}(q) = W(|qR|)$. Then we perform Fourier transformation over q into real space z ,

$$W_{0,0}(z) = \int \exp(iqz) W(|qR|) \frac{dq}{2\pi} = \frac{1}{R} W\left(\frac{z}{R}\right) \quad (6.36)$$

This mean there is a scaling relation between screened Coulomb interaction and radius. As shown in previous section, the effective mass in ZCNT also scales linearly with inverse circumference or equivalently inverse radius, say $m_{GW} = \frac{A_v}{R}$, so the Hamiltonian has the form

$$\left[R \frac{\hat{P}_z^2}{A_v} + \frac{1}{R} W\left(\frac{z}{R}\right) + E_b \right] \psi(z) = 0 \quad (6.37)$$

If we replace z with new scaled coordinate $u = \frac{z}{R}$, $\hat{p}_u = R\hat{p}_z$ the equation becomes

$$\left[\frac{\hat{p}_u^2}{A_v} + W(u) + E_b R \right] \psi(u) = 0 \quad (6.38)$$

Since the Hamiltonian $\hat{H} = -\frac{\hat{p}_u^2}{A_v} + W(u)$ has no radius dependence, its eigen values are R independent. Therefore, $E_b R = \text{const}$. This means in ZCNTs, the excitons binding energy must scale linearly with inverse radius.

It has been shown that there will be a small logarithmic correction[38] to this scaling behavior due to finite width of π bands and energy cut-off. However, the leading term is still the linear one.

In AGNRs however, this scaling behavior is not this perfect since the screening is much more complicated. As discussed in previous section, the dielectric function is a matrix in the case of AGNRs. Since there are finite gaps in all AGNR families, the quantized momenta are nonzero, therefore the polarizability is either

$$\Pi_{mm}(q) = -\frac{2L}{\pi\gamma} \frac{q^2}{6\kappa_m^2} + \mathcal{O}(q^4) \quad (6.39)$$

or

$$\Pi_{mm}(q) = -\frac{2L}{\pi v_F} \left[\frac{1}{2} - \frac{\kappa_m \kappa_n}{2(\kappa_m^2 - \kappa_n^2)} \ln \frac{\kappa_m^2}{\kappa_n^2} \right] + \mathcal{O}(q^2) \quad (6.40)$$

Since only the head of the Coulomb matrix element $v_{0,0}$ has logarithmic divergence, which will be cancelled by the q^2 term in polarizability, the dielectric matrix has very weak momentum dependence. Therefore, we may neglect the momentum dependence by assuming it is constant since excitons are expected to be localized in momentum space.

With above assumption, the screened Coulomb matrix element is

$$W_{0,0}(q) = -\sum_m (\varepsilon^{-1})_{0,m} v_{m,0}(q) \quad (6.41)$$

Similarly, for small q we keep only the leading terms, say constant part, of off-diagonal bare Coulomb matrix elements, then the screened electron-hole Coulomb matrix element is separated into two parts

$$W_{0,0}(q) = -(\varepsilon^{-1})_{0,0} v_{0,0}(q) - \sum_{m>0} (\varepsilon^{-1})_{0,m} v_{m,0}(0) \quad (6.42)$$

Since the first column of dielectric matrix is zero except for the head, it can be shown that $(\varepsilon^{-1})_{0,0} = 1$. Then the Fourier transform of BSE without exchange part becomes

$$\left[\frac{\hat{p}_z^2}{m_{GW}} - v_{0,0}(z) - \delta(z) v_{off} + E_b \right] \psi(z) = 0 \quad (6.43)$$

From the small q expansion of $v_{0,0}(z)$ for ZCNT and AGNR, we see that

$$\begin{aligned} v_{0,0}^{CNT}(q) &= \frac{2e^2}{L} \left(-\ln|qC| + \ln 2 - \gamma_{Euler} + \ln 2\pi + \mathcal{O}(q^2) \right) \\ v_{0,0}^{GNR}(q) &= \frac{2e^2}{L} \left(-\ln|qW| + \ln 2 - \gamma_{Euler} + \frac{3}{2} + \mathcal{O}(q^2) \right) \end{aligned} \quad (6.44)$$

So for small q they only differ as much as a constant. Then we simplify the equation's Fourier transform as

$$\left[\frac{\hat{p}_z^2}{m_{GW}} - v_{0,0}^{CNT}(z) + \delta(z) \left[\ln 2\pi - \frac{3}{2} - v_{off} \right] + E_b \right] \psi(z) = 0 \quad (6.45)$$

Following T. G. Pedersen[80], we use the exponential trial wave function

$$\psi(z) = \frac{1}{\sqrt{\sigma}} \exp\left(-\frac{|z|}{\sigma}\right) \text{ to apply variational method. Then the energy expectation}$$

value is

$$E(\sigma) = \frac{a_B e^2 m_e}{\sigma^2 m_{GW}} + \frac{2e^2}{\sigma} \left(\gamma_{Euler} + \ln \frac{W}{2\pi\sigma} \right) + \frac{1}{\sigma} \left[2e^2 \left(\ln 2\pi - \frac{3}{2} \right) - v_{off} \right] \quad (6.46)$$

Using effective atomic units, it becomes

$$E(\sigma) = \frac{1}{\sigma^2} + \frac{4}{\sigma} \left[\gamma_{Euler} + \ln \frac{W}{\sigma} - \frac{3}{2} - v_{off} \right] \quad (6.47)$$

Since exciton is the stationary state of Hamiltonian, we need to find the stationary point of energy expectation which means the above derivative will be zero or equivalently solving the following equation.

$$1 + \gamma_{Euler} - \frac{3}{2} - v_{off} + \ln \frac{W}{\sigma} + \frac{1}{2\sigma} = 0 \quad (6.48)$$

Then

$$E(\sigma) = -\frac{1}{\sigma^2} - \frac{4}{\sigma} \quad (6.49)$$

Solving the above equation we have the scaling relation between binding energy and width, in effective atomic units.

Figure 6.10 Scaling of family 3p.

Figure 6.11 Scaling of family 3p+1

Figure 6.12 Scaling of family 3p+2

From Figure 6.10-6.12 we see that in effective atomic units, the binding energy scales with inverse width with exponent of 0.87, 0.86 and 0.91 respectively. This significantly differs from the scaling for CNTs whose exponent should be ~ 0.6 [80].

6.3.3 General discussions on geometry dependence of many-body interaction

From the above results and discussion, it can be seen that the major differences between interactions in ZCNTs and AGNRs are the structure of Coulomb matrix elements.

In ZCNTs, the Coulomb matrix elements are diagonal, which means for a potential with given angular period, the period difference between two states involved in the polarization bubble diagram must be the same with the potential's period. This means only certain state pair participate the screening process, as shown in Figure 6.13.

Figure 6.13 State pairs participating in the screening in ZCNTs

In AGNRs however, such selection rule is absent, which means other state pairs can also participate into this polarization and screening process, as illustrated in Figure 6.14.

Figure 6.14 State pairs participating in the screening in AGNRs

To understand the origin of such difference, we provide two explanations: mathematical and physical.

The mathematical explanation comes from the functional form of Coulomb matrix elements. In both ZCNTs and AGNRs, along the axis direction, say z dimension, both systems have translational invariance and the Coulomb matrix elements are proportional to the following integration

$$v_{1234} \propto \int \exp[i(k_1 - k_2)z] V_C(r, r', z - z') \exp[-i(k_3 - k_4)z'] dz dz' \quad (6.50)$$

Due to the translational invariance, we may extract the integration over z' by shifting z such that

$$v_{1234} \propto \int \exp[i(k_1 - k_2)(z + z')] V_C(r, r', z) \exp[-i(k_3 - k_4)z'] dz dz' \quad (6.51)$$

Then the integration over z' is only nonzero if $k_1 - k_2 = k_3 - k_4$ so there is a selection rule on the states participating the polarization.

In ZCNTs, the Coulomb matrix elements are functionally written as

$$v_{mn}(q) = \frac{2e^2}{\epsilon_{bg} L} \int_0^{2\pi} \exp[-im\theta] V_C(|q|, |\theta - \theta'|) \exp[in\theta'] d\theta d\theta' \quad (6.52)$$

Due to the periodicity of system, the wave functions are also periodic in polar angle. Therefore, we may rewrite the above integration by shifting θ such that

$$v_{mn}(q) = \frac{2e^2}{\epsilon_{bg} L} \int_0^{2\pi} \exp[-im(\theta + \theta')] V_C(|q|, |\theta|) \exp[in\theta'] d\theta d\theta' \quad (6.53)$$

Then performing the integration on θ' we see that only when $m=n$ is this integration nonzero. This is due to the orthonormality of complex Fourier basis $\exp(im\theta)$.

The Coulomb matrix elements in AGNRs are

$$v_{mn}(q) = \frac{2e^2}{\epsilon_{bg} L} \int_0^{\bar{W}} \cos[mx] V_C(|q|, |x - x'|) \cos[inx'] dx dx' \quad (6.54)$$

If we assume the 1D Coulomb term also has periodicity along x with period $\bar{W}$, then we may also found that the above equation to be diagonal since the real Fourier basis $(\cos mx, \sin mx)$ is also orthonormal. However, this assumption is not true in nanoribbon which has no periodicity along x , therefore the diagonality is not kept in the case of AGNRs.

From the above discussion, we see that mathematically, the non-diagonality of Coulomb matrix in AGNRs arises from the absent of periodicity of ribbon system along the confined dimension x . And the diagonality of Coulomb matrix in ZCNTs is the consequence of angular periodicity of 2π in cylindrical system. In the other confined dimension, say dimension y in AGNRs and radial dimension r in ZCNTs, the confinement is so rigid that it behaves like a Dirac delta function therefore no integration is needed. Thus this dimension is absent in determining the diagonality of Coulomb matrix.

A physical understanding is related to the conservation of momentum. Along the axis of ZCNTs and AGNRs, particles are free to move and different states have different momentum, so for a potential with momentum q , the responding state pair's momentum difference must equal to this momentum such that the overall momentum is conserved. Therefore, only state pair with momentum difference q participates the screening, as illustrated in Figure 6.15.

Figure 6.15 Bubble diagram for z direction

Similarly in ZCNTs, electrons can move around the tube so eigenstates have different angular momentum around the axis. Then in the polarization process, the angular momentum is also required to be conserved. Thus, the polarization bubble diagram in ZCNTs also has selection rule on angular momentum, as illustrated in Figure 6.16.

Figure 6.16 Bubble diagram for ZCNTs

This selection rule arising from momentum conservation is absent in AGNRs because in AGNRs, all states have zero momentum along x direction. Since in AGNRs, electrons can neither move beyond the boundary, nor move into next period like electrons do in ZCNTs due to absent of periodicity, the eigenstates are required to be standing wave along x direction. Therefore, all states have zero momentum in this direction thus momentum is always conserved, so the conservation of momentum cannot rule out the off-diagonal part of Coulomb matrix.

6.4 Conclusion

In this chapter it is shown that non-diagonal Coulomb matrix is the origin of nonlinear scaling many-body effects in AGNRs. Mathematical and physical explanation of the non-diagonal Coulomb indicates that translational invariance and periodicity is the key to ZCNTs' special linear scaling that differs from usual confined systems.

Chapter 7

Conclusion and Future Work

This chapter summarizes and discusses results obtained in previous chapters and proposes recommendations of future work as extension of current studies.

7.1 Summary and discussion

As proposed in previous sections, the main objective of this thesis is to build and apply models in quasi-2D and quasi-1D materials, describing the role of electronic structures along confined dimensions. For quasi-2D materials, graphene π bands and σ bands are chosen as model systems, while for quasi-1D materials, ZCNTs and AGNRs are selected for comparison. The objective is successfully achieved and there are several important findings, as summarized below.

7.1.1 Excitons in graphene

The goal of the first major work is to build a real space model for electronic dynamics in quasi-2D materials, with electronic structure perpendicular to atomic plane included, and to apply them on graphene π bands to understand the physics of saddle point excitons in graphene.

In this work, the model developed a general approach to effective potential describing the electron-hole interactions in quasi-2D materials, with the wave function of involving bands included as a parameter. Using this model, saddle point exciton of graphene π bands is solved, yielding several energy levels with different symmetry. The resulting exciton binding energies for both single-layer and bi-layer graphene agree almost perfectly with previous experimental and numerical simulation results. By solving excitons for different value of parameter in effective potential, the work demonstrated that inclusion of the finite wave function thickness is key factor to correctly describing the π band saddle point exciton in graphene.

The goal of the second major work is to apply the model to graphene σ bands in single and multi-layer graphene, with inter-layer interaction also included, to understand the strong high-energy excitonic effect and layer-number dependence.

In this work, the band-dependent effective interaction is used to describe the electron-hole interaction in σ band exciton. With inter-layer screening included,

for both intrinsic and gapped multi-layer graphene, layer-number dependence of exciton binding energy is solved. The results explain the controversy between high energy exciton binding energies from previous experiments and numerical simulations. It is also found that the effective interaction, which includes the effect of wave functions' finite thickness, results in a non-hydrogenic 2D excitonic spectrum. Results with different parameters in effective potentials show that such non-hydrogenic spectrum should be general for all quasi-2D materials.

Based on the results above, the model is proven to be successful by correctly reproducing the binding energy and it has been demonstrated in this work that inclusion of the electronic structure perpendicular to 2D plane is key to correctly modeling electronic dynamics in quasi-2D materials.

7.1.2 Geometry dependent scaling behavior in AGNRs and ZCNTs

The goal of the third major work is to study the distinct power-law scaling behavior of many-body effects in ZCNTs and AGNRs, and illustrate the correlation between such distinct behavior and their different geometry.

In this work, the functional difference between many-body interaction in ZCNTs and that in AGNRs are studied by evaluating the dielectric screening in random phase approximation and Coulomb matrix elements. With different many-body interaction, self-energy correction to band gaps and effective masses are calculated for ZCNTs and AGNRs respectively and the scaling with radius/width are found distinct. By using variational method the scaling between exciton binding energy and radius/width is also studied and it is also found that the scaling relation in AGNRs differs from that in ZCNTs. And analysis of functional difference demonstrated that geometry is the determining factor of their distinct behaviors.

The above work demonstrated the fundamental role of geometry in determining the properties and electronic dynamics of quasi-1D materials. And it can be expected that scaling behaviors in other quasi-1D materials are also closely

related to their respective geometries.

7.2 Future works

The above results imply that the electronic properties along confined dimensions are very important to the properties and electronic dynamics in quasi-nD materials. Therefore, it can be expected that they also play fundamental role in other quasi-nD materials, including nanosheets, nanorods, nanowires, quantum dots and nanoparticles. Furthermore, in these works frequency dependence are generally neglected, so we expect that the frequency dependent properties are also correlated to the electronic structure along confined dimensions.

Hence we propose the following future work recommendations.

7.2.1 Tera-Hertz properties of low-dimensional materials

Tera-Hertz (THz) response of materials is an attractive topic since photons in THz range, usually from 0.3 to 3THz, are important radiation sources for researches and applications in many fields including astronomy, imaging, spectroscopy, communication etc. Hence materials for THz photon generators, amplifiers and detectors are much research interests. This requires understanding of materials' response to THz radiation.

A lot of researches have been conducted to find suitable low-dimensional materials for THz research, including graphene[81,82]. Previous models [83] consider graphene as a strict 2D plane and calculate the dielectric function with frequency dependence using random phase approximation

$$\varepsilon^{\text{RPA}}(q) = 1 + \frac{2\pi e^2}{qA} \sum_{ss'k} \frac{f_{s,k} - f_{s',k+q}}{\hbar\omega + E_{s,k} - E_{s',k+q}} \left| \langle sk | e^{-iqr} | s'k + q \rangle \right|^2 \quad (7.1)$$

The resulting dynamic RPA dielectric function has some zeros for certain pair of q and ω . Since the response of an external perturbation is proportional to the

inverse of dielectric function, at those zeros there will be finite response with vanishing perturbation. These zeros of dielectric function, or poles of response are called plasmon, since they correspond to the quantum oscillation of electron-hole plasma system. By finding the zeros of dielectric function one find the plasmon energy dispersion.

The plasmon is important since an external perturbation with q and ω corresponding to plasmon poles will excite strong response from the system. Therefore, if a material has special response to THz photons, say in the energy range of tens of meV, it will be desirable for THz application. Primary results imply that by tuning the carrier density of graphene, it is possible to realize plasmon gain in THz, which means it is potential THz amplifier.

Figure 7.1 Plasmon gain in graphene at THz range.

However the effect of finite thickness, which is very important as discussed in our model, is absent in strict 2D RPA dielectric function. And it is still unclear how this effect changes the THz properties of graphene.

Furthermore, with dynamic effect included, it has been argued that in RPA the dielectric function should have the form

$$\varepsilon(q) = 1 + \frac{2\pi e^2 \sqrt{q^2 - \omega^2 / c^2}}{q^2 A} \sum_{ss'k} \frac{f_{s,k} - f_{s',k+q}}{\hbar\omega + E_{s,k} - E_{s',k+q}} \left| \langle sk | e^{-iqr} | s'k + q \rangle \right|^2 \quad (7.2)$$

And other many-body effect such as phonon-electron interaction are also absent. With both effect included, it is to be studied how graphene's response to THz radiation will be.

If a single layer graphene is expected to be candidature material for THz application, a question naturally arises: how about THz properties in graphene multilayer structures? Since inter-layer coupling is layer-number dependent, as discussed in this work, it will be interesting to study the layer-number dependence of THz response. And it is still unclear whether this inter-layer coupling will help or hinder the THz performance in layered systems.

Meanwhile, it will also be interesting to study the THz response of quasi-1D systems since they are naturally antenna candidature due to their wire-like structure.

7.2.2 Scaling Law in Other Low-Dimensional Materials

In previous chapters we discussed the impact of geometry on the scaling behavior of ZCNTs and AGNRs. From our results we propose that geometry is also fundamental to scaling behaviors in other systems.

As discussed in Chapter 6, we propose that the Coulomb matrix will be diagonal only if in all dimension, the systems are either translational invariant, periodic, or rigidly confined. If that is true, then we can see that in both nanowire and nanosphere, the Coulomb matrices are non-diagonal.

Simply analysis of these systems will show that in these systems, the eigenstate wave functions are standing waves hence the solution of Laplace's equation of certain boundary conditions. For nanowire, the coordinate system of confined dimensions is polar system so they are

$$\psi_{m,n} = e^{in\theta} J_n(k_{m,n}\rho) \quad (7.3)$$

The boundary conditions require $k_{m,n}$ to be selected such that the wave function vanishes at the boundary.

For nanosphere, the coordinate system is spherical so they are spherical harmonics

$$\psi_{n,m,l} = j_n(k_{n,m,l}r) Y_n^m(\theta, \phi) \quad (7.4)$$

Similarly the boundary conditions require $k_{n,m,l}$ to be selected such that the wave function vanishes at the sphere surface.

From the above form we see that the Coulomb matrix is possible diagonal to angular indices. However, the radial parts are to be studied. It can be expected that this will lead to some general scaling law of these low-dimensional systems.

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