

Electron-Electron Interactions in Optical Properties of Graphene Quantum Dots

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Abstract

In this thesis, I present a theory of electron-electron interactions in optical properties of graphene and transition metal dichalcogenides (TMDCs), two dimensional nanostructures with a hexagonal lattice.

We start our discussion with electron-electron interactions in artificial rings for which the strength of interactions can be varied and exact results can be obtained. The artificial rings are described by the extended Hubbard model and solved using an exact diagonalization method in real and Fourier space of configurations. Exact and analytical results for charged rings are obtained in the limit of very strong interactions. For the quadruple quantum dot ring and the artificial benzene ring, we find that chirality leads to the appearance of a topological phase and an effective gauge field that determines the ground state character with varied interaction strength. For the charged artificial benzene ring, our numerical results show a transition from a degenerate to a non-degenerate ground state with increasing strength of Coulomb interactions. We show that the artificial gauge and the transition in the ground state can be detected as changes in the optical absorption spectrum.

In the second part of the thesis, the electronic and optical properties of colloidal graphene quantum dots (CGQD) consisting of many benzene rings are determined. The CGQDs are described by the combination of tight binding, mean field Hartree Fock (HF) and Configuration Interaction methods. The single particle properties are described through the tight binding method based on the p_z carbon orbitals. Screened Coulomb interactions between electrons, including direct, exchange, and scattering matrix elements, are calculated using Slater p_z orbitals. HF ground states corresponding to semiconductor, Mott-insulator, and spin-polarized phases are obtained as a function of the strength of the screened interaction versus the tunnelling matrix element. The many-body ground and excited states in the semiconducting phase are constructed as a linear combination of a finite number of electron-hole pair excitations from the HF ground state (GS). The Hamiltonian is constructed in the subspace of multi-pair HF excitations to obtain the low energy, many body states by exact diagonalization using the Lanczos method.

The degeneracy of the valence- and conduction-band edges of 3-fold rotationally sym-

metric CGQDs is shown to lead to a characteristic exciton and bi-exciton spectrum. The low-energy exciton spectrum is predicted to consist of two bright-singlet exciton states corresponding to two circular polarizations of light and a lower-energy band of dark singlets and dark triplets. The robustness of the bright degenerate singlet pair against correlations in the many-body state is demonstrated as well as the breaking of the degeneracy by the lowering of symmetry of the CGQD. Band edge biexciton energies and binding energies are predicted, and two degenerate exciton (X) states and a corresponding biexciton (XX) state are identified for the generation of an XX-X cascade. The Auger coupling of XX and excited X states is determined and our theoretical results are compared with experimental absorption and non-linear transient absorption spectra.

In the third and final part of the thesis, we replace the two non-equivalent carbon atoms of the graphene hexagonal lattice with a heavy transition-metal atom M, (e.g. Mo or W) and a dimer X_2 (e.g. S). The bandstructure of a monolayer MX_2 is calculated using density functional theory (DFT). It is shown that a direct gap opens up at all K points of the Brillouin zone and strong spin orbit coupling leads to spin splitting of the valence and conduction bands and emergence of valley dependent optical selection rules. Finally, the magnetoluminescence experiments on a monolayer WS_2 emitting circularly polarized light upon its excitation by unpolarized light are described. The emission of polarized light in zero magnetic field is explained by the possibility of formation of a valley polarized 2D electron gas in unintentionally doped WS_2 .

Dedicated to Çito, Mr. Butters and Knuckles...

Declaration

The main body of this thesis contains excerpts from a number of publications, and soon-to-be submitted manuscripts that I have worked on as a Ph.D. student under the supervision of Dr. Pawel Hawrylak. The list below presents detailed information on the publications and manuscripts that are relevant for this thesis;

1. Isil Ozfidan, Anna H. Trojnar, Marek Korkusinski and Pawel Hawrylak, “*Geometry, chirality, topology and electron - electron interactions in the quadruple quantum dot molecule*”, Solid State Communications, Volume 172:15-19, 2013
2. Isil Ozfidan, Marek Korkusinski, Alev Devrim Guclu, John A. McGuire and Pawel Hawrylak, “*Microscopic theory of the optical properties of colloidal graphene quantum dots*”, Phys. Rev. B, 89(8):085310, 2014.
3. Isil Ozfidan, Marek Korkusinski and Pawel Hawrylak, “*Theory of biexcitons and biexciton-exciton cascade in graphene quantum dots*”, Phys. Rev. B., 91(11):115314, 2015.
4. Tom Scrace, Yu-Tsung Tsai, Biplob Barman, Lars Schweidenback, Athos Petrou, George Kioseoglou, Isil Ozfidan, Marek Korkusinski, and Pawel Hawrylak, “*Magnetoluminescence and valley polarized state of two-dimensional electron gas in WS_2 monolayer*”, Nature Nanotech., Advanced Online Publication, 11 May 2015, doi: 10.1038/nnano.2015.78
5. Isil Ozfidan, Milos Vladislavljevic, Marek Korkusinski and Pawel Hawrylak, “*Electron-electron interactions and optical properties of artificial benzene ring*”, Submitted for publication
6. Cheng Sun, Florian Figge, Isil Ozfidan, Marek Korkusinski, Xin Yan, Liang-shi Li, Pawel Hawrylak and John A. McGuire, “*Dirac fermion biexcitons confined in colloidal graphene quantum dots*” Nano Lett. 15(8):5472-5476 (2015)

7. Isil Ozfidan, Marek Korkusinski, Pawel Hawrylak, “*Electronic properties and electron electron interactions in graphene quantum dots*”, Phys. status solidi - Carbononics Special Issue, Under review
8. Isil Ozfidan, Marek Korkusinski, Pawel Hawrylak, “*Theory of optical properties of graphene quantum dots*”, Phys. status solidi - Carbononics Special Issue, Submitted for publication

Except for the articles 4 and 6 and parts of 7 and 8, I have carried out all the calculations and derivations in full detail collaborating with my co-workers as described in the list of authors. The manuscripts 4 and 6 contain both theoretical and experimental results. The experiments were carried out by our collaborators named in the list of authors, while I took part in the theoretical calculations and analysis. Manuscripts 7 and 8 are review papers that introduce, in addition to my work, previous work that was done in our group.

Chapter 3 is written based on articles 1 and 5. Chapter 4 is made out of the material out of articles 2,3,5. Finally, article 4 is relevant for chapter 5.

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Abbreviations

2D	Two-dimensional
2DEG	Two dimensional electron gas
ABR	Artificial benzene ring
CB	Coulomb blockade
CGQD	Colloidal graphene quantum dot
CI	Configuration interaction
CVD	Chemical vapor deposition
DD	Two doubly occupied dots
DFT	Density functional theory
FT	Fourier transform
GNR	Graphene nanoribbons
GQD	Graphene quantum dot
GSA	Genetic search algorithm
HF	Hartree Fock
HGH	Hartwigsen-Goedecker-Hutter
LDA	Local density approximaition
LQQD	Linear quadruple quantum dot
MF	Mean field
NN	Nearest neighbor
NNN	Next nearest neighbor
QQD	Quadruple quantum dot
SB	Spin blockade
sc	Self-consistent

SOC	Spin orbit coupling
tb	Tight binding
THz	TeraHertz
TMDC	Transition metal dichalcogenide
TQD	Triple quantum dot
UV	Ultra Violet
X	Exciton
XX	Biexciton

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Chapter 1

Introduction

Before the isolation of graphene it was long believed that strictly two-dimensional (2D) materials were thermodynamically unstable and consequently would not exist.^{1,2} Indeed suspended graphene is not perfectly flat but is rippled.³ Yet it is still 2D and is one of the most intensively studied materials. In fact it is a celebrity and its fame is not restricted to academia. It has become a household name in the last couple of years with articles published in popular news outlets all around the world. Based on Google search statistics, interest in graphene has increased 500% since 2006. If you look at Google trends for the search query “graphene”, you can see a spike in October 2010. That spike corresponds to the Nobel prize that was awarded to A. Geim and K. Novoselov “*for groundbreaking experiments regarding the two-dimensional material graphene*”. Thanks to their work in 2004,⁴ graphene has the distinction of being the first 2D material that has been produced, isolated, identified and characterized. Since then, there is a great interest in the whole class of 2D materials like monolayers of BN, MoS₂, WS₂, etc.

Although graphene’s fame came after its isolation and the Nobel prize, the theoretical work on it dates back to 1947 when Wallace⁵ at NRC Canada studied the electronic properties of a single layer of graphite-graphene. Wallace showed that graphene, with its peculiar linear electronic band dispersion at low energies is a lot more than just a 2D material. (1) It is a semimetal, with zero energy band gap and zero density of states at the Fermi level. (2) The low energy excitations in graphene can be described as massless Dirac fermions. The spin and speed of light in the Dirac Hamiltonian representing these fermions are replaced by sublattice-*pseudospin* and the Fermi velocity, respectively. (3) Conservation of *pseudospin* in graphene leads to the absence of backscattering that is responsible for ballistic transport, and plays a crucial role in Klein tunnelling where an electron incident on a one-dimensional barrier is perfectly transmitted.

In addition to its peculiar electronic properties, with its flexibility and strength, graphene

is a promising candidate for future engineering applications.⁶ There have already been efforts to fabricate graphene field effect transistors as it has high carrier mobility at room temperatures.⁷ Due to the transparency and high conductivity of graphene, it can be used for flexible displays with low power consumption.⁸ Graphene quantum dots (GQD) can be used in printed electronics as conductive ink as well as for chemical sensing because of the high area per unit volume ratio.^{9,10} Moreover, GQDs can be used as photodetectors or for light harvesting applications.^{11–13} Thanks to the tunable band gap, tunable magnetism, and tunable optical transitions of GQDs, one day there could be all-carbon nano-circuits that can perform processing, storage and communications.¹⁴

Expanding on our earlier work on graphene nanostructures and Transition metal dichalcogenides (TMDCs),^{8,14–24} in this thesis I describe the optical properties of colloidal graphene quantum dots and monolayer TMDCs with hexagonal lattice, and compare calculations with experimental data obtained from our collaborators.

1.1 Fabrication Methods of Graphene Nanostructures

Graphite, stacked-up graphene layers, is the most stable form of carbon found in nature. The challenge is breaking the van der Waals forces to separate graphite into its layers to obtain the single atom-thick, 2D graphene. After Wallace, electronic properties of graphite were further investigated and there were theoretical and experimental works on separating layers of graphite through intercalation.^{25–34}

The Nobel prize was awarded for graphene that was isolated through micromechanical exfoliation.⁴ This technique is implemented as follows: Using a scotch tape, flakes of graphite are peeled off from bulk graphite, overcoming the van der Waals forces keeping them together. These flakes are then deposited on a SiO_2 substrate and the regions of the sample that contain only a single layer of graphene are identified through optical microscopy. It is a simple method for isolating high-quality samples for research purposes, yet does not allow for sample sizes that are large enough for engineering applications.

After isolation of graphene by Geim and Novoselov through mechanical exfoliation, other methods to synthesize graphene are being developed. For example, another approach is the graphite oxide exfoliation. Graphite is chemically modified to produce graphite oxide and is dispersed in a solvent for thermal, chemical or electrochemical reduction of oxygen groups. This method produces low quality graphene samples with decreased mobility but with high flexibility and stiffness.^{35–40}

To obtain graphene in a controlled manner, chemical vapor deposition (CVD) is commonly used to produce graphene on wafers, suitable for mass production. The CVD technique works as follows: A metal sheet (e.g. Ni, Cu) is exposed to a carbon containing

gas mixture at high temperatures, allowing for carbon to diffuse into metal. Upon cooling, carbon atoms segregate to the surface of the metal, forming graphene layers. Then the graphene layers are transferred onto an insulating substrate for characterization. It was shown that the number of graphene layers in this method can be controlled by changing the thickness of the metal substrate and the growth time.^{41–43}

Epitaxial growth on SiC surfaces is yet another promising technique for mass production of graphene. Heating a SiC wafer, graphitization of the upper layers results in formation of a single to few-layer graphene on its surfaces.^{44–46}

Properties of graphene can be modified by confining, for example, in one dimension resulting in graphene nanoribbons (GNR). There are top-down and bottom-up approaches in reaching this confinement. In top-down methods one can reach confinement by 'cutting' and 'etching' of graphene. For example, graphene can be patterned into ribbons by use of electron-beam lithography and an etching mask, through Joule heating and electron beam irradiation,^{47–50} by unzipping of carbon nanotubes,⁵¹ or through cage-opening of Fullerenes.^{52–54}

The semiconducting properties of confined graphene systems, especially their band gap, are directly related to their size and edge character. However, top-down methods result in a mixture of edges and sizes thus cannot reach the chemical precision required. Well-defined GNRs can be produced through bottom-up approaches which include chemical^{55–57} and synthetic⁵⁸ procedures as well as CVD.⁵⁹

By confining graphene in two directions one can obtain graphene quantum dots (GQD). At this scale, bottom-up approaches become more suitable since the number of carbon atoms in a quantum dot is rather small compared to that of a sheet. There are recent efforts in producing finite sized GNRs based on surface assisted^{60,61} and solution mediated^{62,63} cyclodehydrogenation. In surface assisted methods, non-planar polyphenylene precursors are built up from small molecules on metal single-crystal surfaces such as Cu(111), Au(111) or Ag(111). In solution based methods, the monomers are polymerized through various reaction methods to obtain polymer precursors. In both methods, polyphenylene precursors are cyclodehydrogenated, that is graphitized and planarized, to obtain GQDs. The GQDs obtained on metal surfaces are easier to characterize yet are limited by the metal surface itself, while in solution based processes the molecules may form bonds hindering the planarization of polymers.⁶³

There has been substantial amount of work done on avoiding such interactions between polymers to create stabilized graphene quantum dots. Such colloidal graphene quantum dots (CGQD) obtained by a step-wise organic synthesis method have been reported and their optical properties were extensively studied.^{64–72} The stabilization in these studies is achieved through creating a three-dimensional cage around graphene flakes. The attraction

between flakes is reduced by the increased distance between them due to twisting of the “cage” from the plane of the graphene. This way the solubility of larger sized GQDs is increased which leads to stable CGQDs containing up to 200 carbon atoms.

Still, for larger sized graphene quantum dots, top-down approaches are more suitable even though they require multiple steps and make precise control of the size and morphology of the quantum dots difficult. Hydrothermal, solvothermal, electrochemical, microwave-assisted cutting, controlled cutting using Ni nanoparticles, nanolithography, exfoliation or shearing are some of the top-down approaches that are utilized.⁵³

1.2 Engineering Electronic Properties of Graphene

Development of various fabrication methods allows for engineering of the electronic, optical and magnetic properties of graphene by controlling the size, shape, edge character, number of layers, impurities and screening.^{14,73}

Size: Scaling of the band gap with the size of the quantum dot from nanometer to submicron agrees very well with that of confined Dirac electrons and holes. As will be discussed in the next chapter, the band gap scales inversely with the size of the graphene quantum dots or the square root of the number of carbon atoms.^{14,14,74,75}

Interactions: The relativistic nature of carriers in graphene plays a crucial role in many-body effects. Unlike for non-relativistic electrons, the ratio of kinetic energy to Coulomb energy does not depend on the average interparticle separation. It is controlled by the screening and as a result the electronic properties of graphene are greatly affected by the surrounding material. In the semimetallic state of graphene, interactions result in renormalization of Fermi velocity depending on the screening by the substrate.⁷⁶ There have been numerical calculations, from Monte-Carlo to Hubbard model, suggesting a transition from the semi-metallic to a Mott-insulating phase with increasing interaction strength among electrons that is tuned by the environment.^{77–80}

Edge: In addition to the size of graphene flakes, their edges also play an important role in determining their electronic and optical properties. A honeycomb lattice can be terminated in two distinct ways; either by creating armchair or zigzag edges as depicted in Fig.1.1. Through bottom-up approaches one can also create mixtures of the two as has been demonstrated for CGQDs.

Sublattice Symmetry: The sublattice symmetry is the difference in the numbers of carbon atoms on the two sublattices of the graphene that depends on the shape and edge character of GQDs. For example, a triangular GQD with zigzag edges will have unequal number of carbon atoms belonging to different sublattices, breaking the sublattice symmetry, while hexagonal GQDs with armchair edges will have equal numbers of carbon atoms

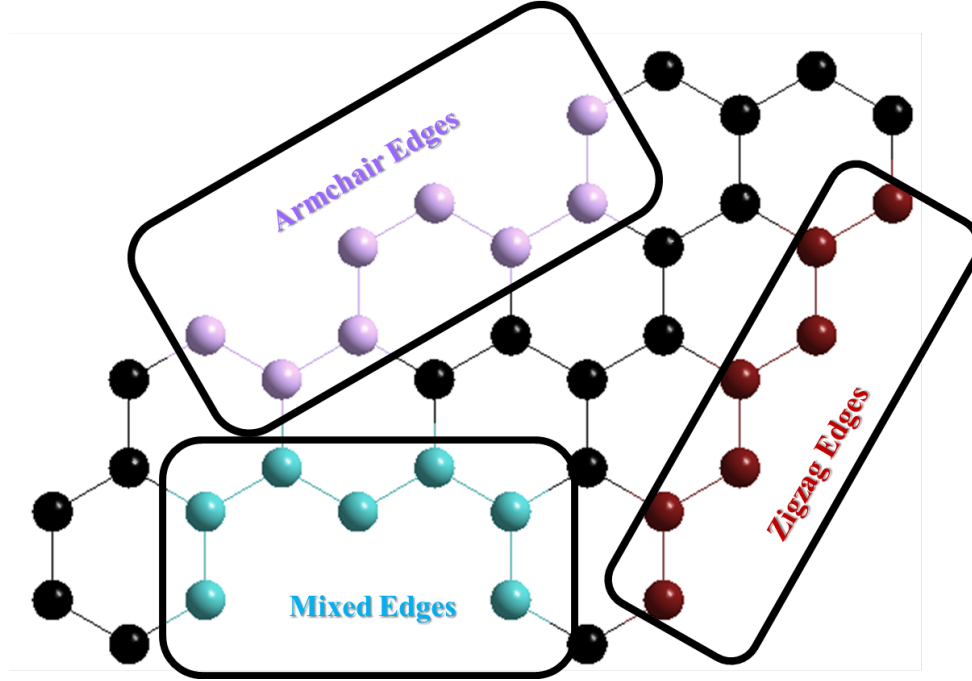


Figure 1.1: Armchair, zigzag and a mixed edge depicted on a sample flake

in their sublattices, preserving the sublattice symmetry. Thus we can further characterize dots according to whether the sublattice symmetry is broken or not. It is an important factor that leads to formation of zero energy levels.^{15,21,81–97}

1.3 2D Semiconductors with Hexagonal Lattice

TMDCs are made of a transition metal element M (such as Mo, W. etc.) and a chalcogen X (such as S, Se, etc.) with the chemical formula MX_2 . They have a layered structure, each layer consisting of three planes in the form X-M-X, with the metal atom sandwiched between the two chalcogen atoms as shown in Fig.1.2. As depicted in Fig.1.2, monolayer MoS_2 and WS_2 are 2D materials with a hexagonal lattice, where the two non-equivalent carbon atoms of graphene were replaced by Mo (W) and a S dimer.^{98,99}

Although the structure and optical properties of WX_2 were studied in the 1960s by Frindt et al. at Simon Fraser University, BC, Canada,^{100–102} it wasn't until the identification of graphene that the transition metal dichalcogenides (TMDC) have started to attract serious attention.^{24,24,98–100,103–144} Unlike graphene which is a semimetal, these materials have a band-gap. Bulk TMDCs have an indirect band-gap and their single layers are shown to be direct band gap semiconductors with gaps in the visible range at all K and K' points of the Brillouin zone.^{99,109,111,139} This direct gap in monolayers results in strong photoluminescence which makes TMDCs suitable for optoelectronic and photonic

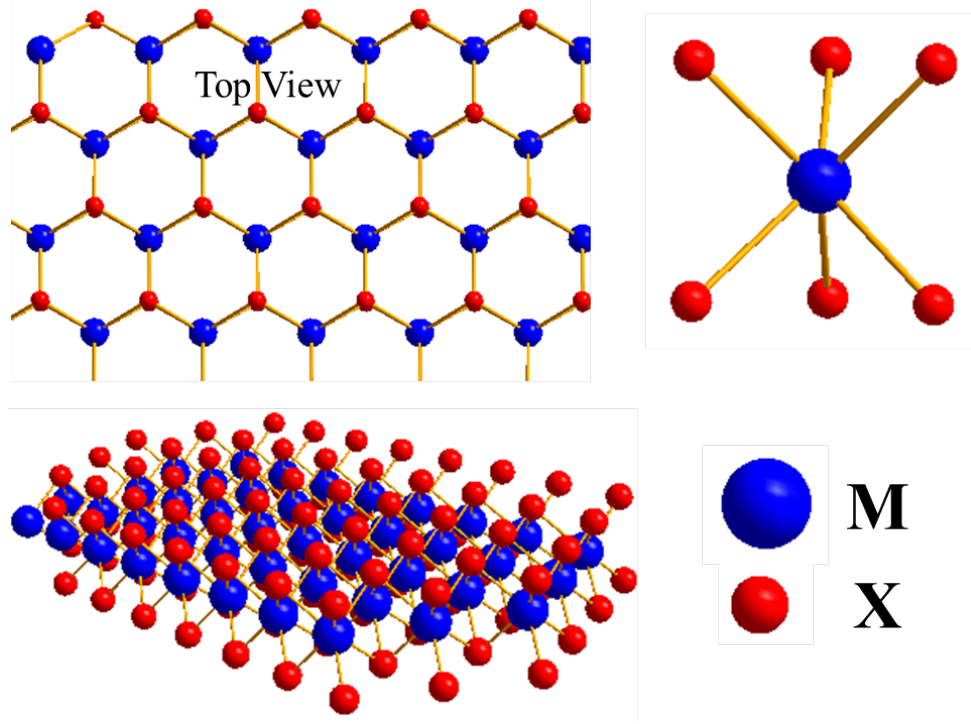


Figure 1.2: Structure of monolayer TMDCs with chemical formula WS_2

applications.^{139,145–148}

Just as for graphene, there are both bottom-up and top-down approaches for synthesizing TMDCs. Most methods rely on the same techniques that have been developed for graphene. For example, a monolayer of TMDC can be peeled off through micromechanical cleavage using an adhesive tape,^{118,121,126,127,135,149} and there have also been studies¹⁵⁰ on separating monolayers of TMDC's through intercalation since the 1980's.¹¹³ Like for graphene, chemical vapor deposition has been demonstrated to be one of the scalable approaches for growing monolayer MoS_2 's,^{151,152} and there are also bottom-up wet chemical approaches for synthesizing monolayers of TMDCs.

In bulk or TMDCs with an even number of layers that have inversion symmetry and time-reversal symmetry, the degeneracy of the energy levels for the spins is preserved. However a monolayer of TMDC lacks inversion symmetry that results in breaking of this degeneracy. In addition, TMDCs exhibit strong spin-orbit coupling due to heavy transition metal atoms leading to spin splitting of hundreds of meV in the valence band.^{105,120,140,143,153,154} Breaking of the degeneracy along with the spin splitting introduces valley degrees of freedom and valley-dependent optical selection rules which makes TMDCs suitable for spintronics and valleytronics.

Similar to graphene, bandstructure of TMDCs is not their only exciting property. With great mechanical flexibility and large carrier mobility, they can be used in many practical

applications. Already, monolayer TMDC field effect transistors and logic circuits have been demonstrated.^{126,127,145,155}

1.4 Thesis Outline

In this thesis I describe the role of electron-electron interactions in the optical properties of graphene quantum dots. In order to understand graphene, composed of benzene rings, I start with the analysis of carbon rings; a quadruple quantum dot molecule (QQD) and an artificial benzene ring (ABR). The bulk of the thesis describes graphene quantum dots and at the end I discuss the work done on WS_2 using *ab initio* DFT methods.

In chapter 2, I outline the methods and models I used throughout this thesis, from the single particle tight binding method to mean field Hartree-Fock, and density functional theory to exact configuration interaction.

Chapter 3 is dedicated to quantum rings, the QQD and the ABR. This chapter is a detailed description of the work published on the QQD¹⁵⁶ and the manuscript on the ABR which is currently under review.

In chapter 4, I describe the electronic properties of colloidal graphene quantum dots and describe excitons and biexcitons. This chapter is a combination of three papers. The first one concentrates on electronic properties of CGQDs and describes excitons along with the absorption spectrum of these dots.¹⁵⁷ The second one¹⁵⁸ outlines the theory of biexcitons, while the third paper is a collaborative paper that studies transient absorption experiments and stability of biexcitons in CGQDs, both theoretically and experimentally.¹⁵⁹

Finally, chapter 5 presents the results of DFT calculations of the bandstructure of MoS_2 and WS_2 , and the collaborative work done on a single layer of WS_2 . In this chapter I also explain the optical properties of MX_2 and describe the magnetoluminescence experiments that were conducted by our collaborators.¹³⁴

Chapter 2

Methods

In this chapter, I will discuss the tools and models that allow us to study electronic properties of carbon rings and graphene quantum dots. I will start by explaining the tight binding method and the single particle properties of graphene, bilayer graphene and graphene quantum dots. Next will be the introduction of the mean field and configuration interaction methods applicable to many-electrons. The second part of this chapter will concentrate on the excited states obtained in the configuration interaction step that are accessible through absorption/emission of radiation.

In quantum dots the electrons and holes are confined in every direction leading to discretization of the energy levels. We can obtain these single particle energy levels using the tight-binding approximation in which we only consider a single electron moving in the effective potential of the quantum dot.

In a charge neutral graphene quantum dot with one electron per orbital, there are many ways of placing N electrons on N orbitals. If we take electrons to be non-interacting, the Hamiltonian can be separated for each electron that would allow for each configuration to be expressed as a Slater determinant of electrons on localized p_z orbitals. The many body eigenstates of the non-interacting, N electron graphene quantum dot can be expressed as a linear combination of these configurations. Each linear combination can be reduced to a single Slater determinant by appropriately rotating the basis of p_z orbitals to obtain single particle orbitals as in a tight-binding approximation. Then, the ground state of N non-interacting electrons can be written as a single Slater determinant, created by placing N electrons on the lowest N single-particle orbitals.

However, in a many-electron problem there are electron-electron interactions that one needs to take into account. Turning on the interactions, there will be a competition between minimizing the kinetic energy versus minimizing the interactions between electrons.

A simple theory for approximating the ground state energy of an interacting system is called the Hartree-Fock theory. It is based on the assumption that the ground state

of an interacting, many body system can be expressed as a single Slater determinant via replacing the electron-electron interaction term in the Hamiltonian by the interaction of an electron with the density of electrons. This way, just as for the non-interacting system, the Hamiltonian becomes separable and the basis of single particle orbitals can be rotated to obtain quasiparticle Hartree-Fock orbitals. The Hartree-Fock Hamiltonian will capture kinetic, direct and exchange energy contributions to the ground state energy.

In general, the exact wavefunction of an interacting system cannot be expressed as a single Slater determinant. This is due to the correlations among electrons that cannot be described with a mean-field approach. In order to account for these correlations we need a linear combination of many body configurations. In the Configuration Interaction method (CI), a basis of Slater determinants is created through excitations out of the HF ground state. Solving the CI-Hamiltonian, the exact ground state of the fully-correlated system is written as a linear combination of configurations out of HF orbitals.

For small structures with several electrons, an exact ground state can be obtained by creating all possible excitations out of the HF ground state. However the number of configurations grows factorially with the number of states and electrons in hand, making the configuration interaction method very computationally expensive. Then one needs to truncate the CI-space to obtain a *good* approximation to the correlated ground state energy.

2.1 Tight-Binding Description of Electronic Properties of Graphene

I will now describe how the tight binding method was applied to describe the electronic properties of graphene by Wallace in 1946.⁵ I'll be following his derivation until we obtain the Dirac cones, the linear dispersion of quasiparticles close to the K points of the Brillouin zone, in the graphene band structure.

Graphene is made out of carbon atoms, each atom having six electrons. Two of the six electrons that occupy the $1s$ orbital are tightly bound core electrons, and do not contribute to the mechanical/electronic properties of carbon-based materials (Fig.2.1(a)). A carbon atom in graphene has three nearest neighbours to which it is connected through 3 of the remaining four valence electrons occupying $2s$, $2p_x$, $2p_y$ orbitals hybridized in the form of sp^2 σ bonds, as depicted in Fig.2.1(b). These 3 electrons are responsible for the mechanical/structural properties of graphene. The remaining valence electron occupies the $2p_z$ orbital orthogonal to the surface of a graphene sheet, as shown in Fig.2.1(c). Hybridized $2p_z$ orbitals form the π bonds responsible for the electronic properties of graphene.

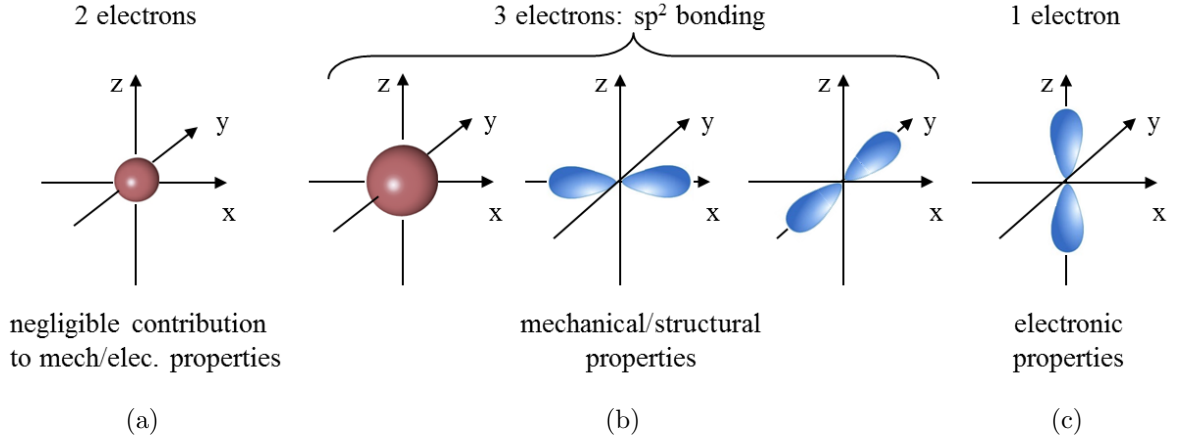


Figure 2.1: The lowest orbitals for the six electrons of a carbon atom. (a) Two electrons that occupy the $1s$ orbital are tightly bound to the nucleus, (b) three valence electrons form the sigma bonds between nearest neighbour carbon atoms, (c) one valence electron occupies each p_z orbital forming π bonds.

In graphene, carbon atoms are arranged in a honeycomb lattice. The unit cell of a honeycomb lattice contains two atoms, A and B, that form triangular Bravais sublattices as shown in Fig.2.2(a). The primitive unit vectors within each sublattice, connecting the unit cells, are the vectors $\vec{a}_{1,2}$ shown in Fig.2.2(b), while $|\vec{\delta}_i| = |(0, a)| = 1.42 \text{ \AA}$ connects the nearest neighbour atoms;

$$\begin{aligned}
 \vec{a}_1 &= \frac{a}{2} \begin{pmatrix} -\sqrt{3}, 3 \end{pmatrix}, \\
 \vec{a}_2 &= \frac{a}{2} \begin{pmatrix} \sqrt{3}, 3 \end{pmatrix}, \\
 \vec{\delta}_2 &= \frac{a}{2} \begin{pmatrix} \sqrt{3}, -1 \end{pmatrix}, \\
 \vec{\delta}_3 &= \frac{a}{2} \begin{pmatrix} -\sqrt{3}, -1 \end{pmatrix}.
 \end{aligned} \tag{2.1}$$

The corresponding reciprocal vectors of the honeycomb lattice $\vec{b}_{1,2}$ are obtained as

$$\begin{aligned}
 \vec{b}_1 &= \frac{2\pi}{3a} \begin{pmatrix} -\sqrt{3}, 1 \end{pmatrix}, \\
 \vec{b}_2 &= \frac{2\pi}{3a} \begin{pmatrix} +\sqrt{3}, 1 \end{pmatrix},
 \end{aligned} \tag{2.2}$$

satisfying $\vec{b}_{1(2)} \cdot \vec{a}_{2(1)} = 0$ and $\vec{b}_{1(2)} \cdot \vec{a}_{1(2)} = 2\pi$. As depicted in Fig.2.2(c), the first Brillouin zone of the hexagonal lattice is also a hexagon. The center of the hexagon corresponds to the Γ point and each corner is a K point.

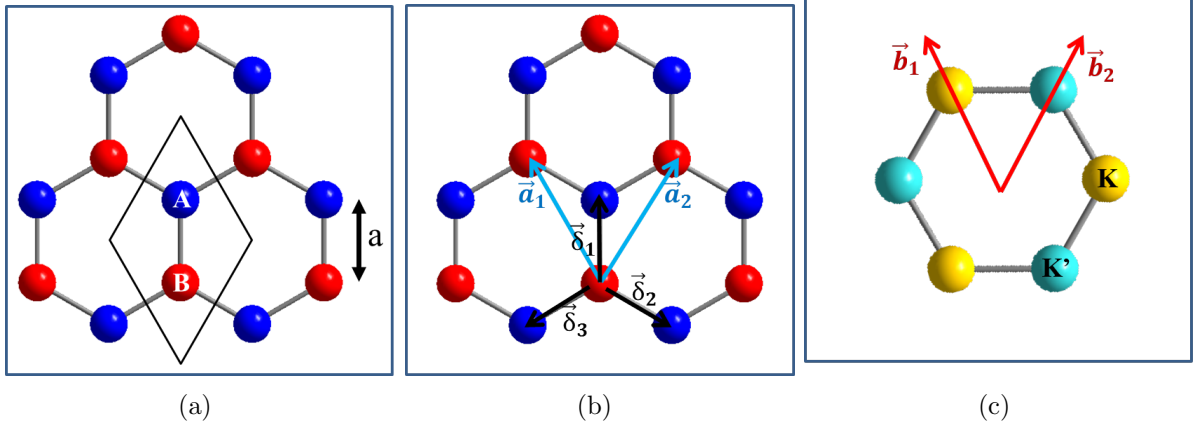


Figure 2.2: Honeycomb lattice of graphene. (a) Parallellogram highlights the unit cell. A and B are the two atoms in the unit cell distinguished by blue and red colors. (b) Unit vectors and vectors connecting NN atoms. (c) First Brillouin zone in the reciprocal space of graphene is also a hexagon. The cyan and yellow represent the location of K and K' points

2.1.1 Tight Binding Model - One Electron Hamiltonian

Single particle properties of graphene can be obtained through the tight binding (tb) approximation. The Hamiltonian for a single electron, under the influence of A- and B-sublattices of carbon atoms has the following form:

$$H(\vec{r}) = \frac{p^2}{2m} + \sum_{R_A} V^A(\vec{r} - \mathbf{R}_A) + \sum_{R_B} V^B(\vec{r} - \mathbf{R}_B), \quad (2.3)$$

where p is the electron momentum, m is the mass of an electron and $V^{A(B)}(\vec{r} - \mathbf{R}_{A(B)})$ is the atomic potential on site $\mathbf{R}_{A(B)}$ due to A(B)-type carbon atom.

2.1.1.1 Bulk Graphene

Exploiting the translational symmetry of graphene, the electron wavefunction on each sublattice can be expanded in terms of localized p_z orbitals, $\phi_z(\vec{r} - \mathbf{R})$, using Bloch's theorem:

$$\begin{aligned} \psi_{\mathbf{k}}^A(\vec{r}) &= \frac{1}{\sqrt{N_s}} \sum_{\mathbf{R}_A} e^{-i\mathbf{k} \cdot \mathbf{R}_A} \phi_z(\vec{r} - \mathbf{R}_A), \\ \psi_{\mathbf{k}}^B(\vec{r}) &= \frac{1}{\sqrt{N_s}} \sum_{\mathbf{R}_B} e^{-i\mathbf{k} \cdot \mathbf{R}_B} \phi_z(\vec{r} - \mathbf{R}_B), \end{aligned} \quad (2.4)$$

where k is the wavevector, $e^{-i\mathbf{k}\cdot\mathbf{R}_A}$ are the expansion coefficients, $\phi_z(\vec{r}-\mathbf{R}_B)$ are p_z orbitals localized on lattice sites $\mathbf{R}_B$, and N_s is the number of carbon atoms in each sublattice. We can then construct orthogonal total electron wavefunctions as

$$\begin{aligned}\Psi_{\mathbf{k}}(\vec{r}) &= A_{\mathbf{k}}\psi_{\mathbf{k}}^A(\vec{r}) + B_{\mathbf{k}}\psi_{\mathbf{k}}^B(\vec{r}), \\ \langle\Psi_{\mathbf{k}}|\Psi_{\mathbf{k}'}\rangle &= \delta_{k,k'},\end{aligned}\tag{2.5}$$

or express them as two-component spinors,

$$\Psi_{\mathbf{k}}(\vec{r}) = \begin{pmatrix} A_{\mathbf{k}} \\ B_{\mathbf{k}} \end{pmatrix}.\tag{2.6}$$

Acting with the Hamiltonian Eq.2.3 on the spinors given in Eq.2.6 and assuming orthogonal p_z orbitals we have

$$\begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix} \begin{pmatrix} A_{\mathbf{k}} \\ B_{\mathbf{k}} \end{pmatrix} = E_{\pm}(\mathbf{k}) \begin{pmatrix} A_{\mathbf{k}} \\ B_{\mathbf{k}} \end{pmatrix},\tag{2.7}$$

and we can calculate the eigenvalues as $E_{\pm} = H_{AA} \pm |H_{AB}|$ since $H_{AA} = H_{BB}$ and $H_{AB} = H_{BA}^*$. In evaluation of these terms, because we are using a nearest neighbour approximation, three-center integrals will be neglected. Then the only non-zero contributions to the diagonal terms will be the kinetic and the on-site energies of p_z orbitals such that

$$\begin{aligned}H_{AA} &= \langle\psi_k^A|H|\psi_k^A\rangle \\ &= \frac{1}{N_s} \sum_{\mathbf{R}_A} \int d\vec{r} \phi_z^*(\vec{r}-\mathbf{R}_A) \left(\frac{p^2}{2m} + V(\vec{r}-\mathbf{R}_A) \right) \phi_z(\vec{r}-\mathbf{R}_A) \\ &= \epsilon.\end{aligned}\tag{2.8}$$

Similarly, the off-diagonal terms are obtained as,

$$H_{BA} = \frac{1}{N_s} \sum_{\langle\mathbf{R}_A, \mathbf{R}_B\rangle} e^{i\mathbf{k}\cdot(\mathbf{R}_A-\mathbf{R}_B)} \int d\vec{r} \phi_z^*(\vec{r}-\mathbf{R}_B) V(\vec{r}-\mathbf{R}_B) \phi_z(\vec{r}-\mathbf{R}_A).\tag{2.9}$$

The integral is a constant, defined as the hopping element, t . Expanding the summation around a site A, summing over all of its three nearest neighbors, the off-diagonal term is rewritten as,

$$H_{BA} = t \frac{1}{N_s} \sum_{\langle\mathbf{R}_A, \mathbf{R}_B\rangle} e^{i\mathbf{k}\cdot(\mathbf{R}_A-\mathbf{R}_B)}$$

$$= t \frac{1}{N_s} \sum_{\mathbf{R}_A} \left[e^{i\mathbf{k} \cdot \vec{\delta}_1} + e^{i\mathbf{k} \cdot \vec{\delta}_2} + e^{i\mathbf{k} \cdot \vec{\delta}_3} \right]. \quad (2.10)$$

Now carrying the summation over all A-atoms and inserting Eq.2.1 into Eq.2.10, we simplify the off-diagonal elements to obtain:

$$\begin{aligned} H_{BA} &= t \left[e^{i\mathbf{k} \cdot (0,a)} + e^{i\mathbf{k} \cdot a(\sqrt{3},-1)/2} + e^{i\mathbf{k} \cdot a(-\sqrt{3},-1)/2} \right] \\ &= t \left[e^{ik_y a} + e^{-ik_y a/2} 2 \cos \left(\sqrt{3} k_x a/2 \right) \right] \\ &= t f(\mathbf{k}). \end{aligned} \quad (2.11)$$

Using the above obtained off-diagonal element in Eq.2.7, and utilizing the identity $2 \cos^2(x) - 1 = \cos(2x)$, the eigenvalues are rewritten as,

$$E_{\pm}(\mathbf{k}) = \epsilon \pm t \left[3 + 2 \cos \left(\sqrt{3} k_x a \right) + 4 \cos \left(\sqrt{3} k_x a/2 \right) \cos \left(3 k_y a/2 \right) \right], \quad (2.12)$$

corresponding to the following spinors at every $\mathbf{k}$,

$$\Psi_{\mathbf{k}}(\vec{r}) = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \mp \exp(-i\theta_{\mathbf{k}}) \end{pmatrix}, \quad (2.13)$$

$$\exp(-i\theta_{\mathbf{k}}) = \frac{f(\mathbf{k})}{|f(\mathbf{k})|}. \quad (2.14)$$

States with negative energy form the valence band while the positive energy states form the conduction band as depicted in Fig.2.3.

Effective Mass Model and Dirac Fermions

From Eq.2.12, at the K and K' points the eigenvalues of both holes and electrons are obtained as zero: $E(K)_+ = E(K)_- = E(K')_+ = E(K')_- = 0$, setting $\epsilon = 0$. We can write the Hamiltonian around these zero points to demonstrate why the K points are called the Dirac points. Starting with the off-diagonal element,

$$H_{BA} = t \left(e^{i\mathbf{k} \cdot \vec{\delta}_1} + e^{i\mathbf{k} \cdot \vec{\delta}_2} + e^{i\mathbf{k} \cdot \vec{\delta}_3} \right), \quad (2.15)$$

working around the K-points $\mathbf{k} \rightarrow \mathbf{K} + \mathbf{q}$, where $|\mathbf{q}| \ll |\mathbf{K}|$, and approximating $\exp(i\mathbf{q} \cdot \vec{\delta}_i) \rightarrow 1 + i\mathbf{q} \cdot \vec{\delta}_i$, it can be rewritten as

$$H_{BA} = t \sum_i e^{i(\mathbf{K} + \mathbf{q}) \cdot \vec{\delta}_i}$$

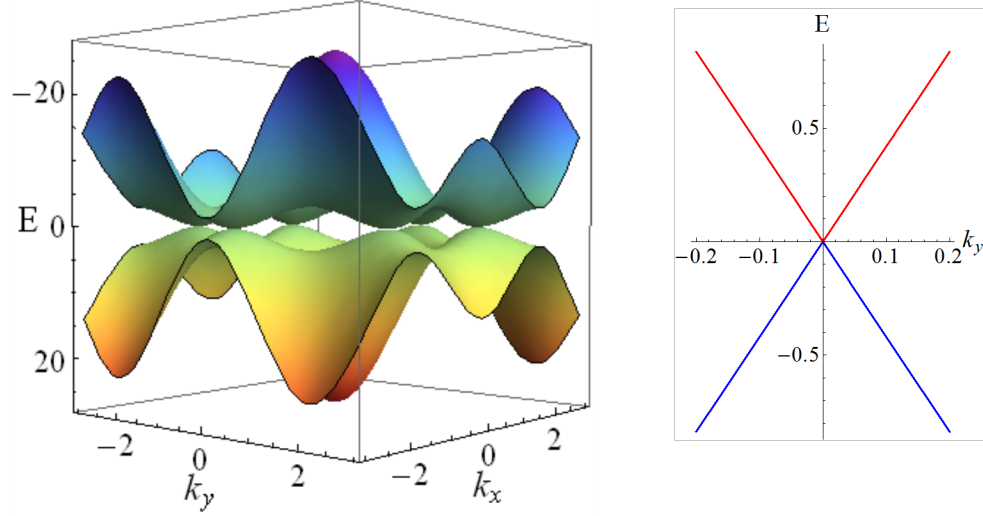


Figure 2.3: (a) Graphene tight binding bandstructure. (b) Cross section of the band structure at $k_x = \frac{4\pi}{3a\sqrt{3}}$

$$= t \left(\sum_i e^{i\mathbf{K} \cdot \vec{\delta}_i} + i \sum_i e^{i\mathbf{K} \cdot \vec{\delta}_i} \mathbf{q} \cdot \vec{\delta}_i \right). \quad (2.16)$$

Using Eq.2.1 and Eq.2.2, the first sum will be evaluated to give zero, and the second sum can be expanded as

$$\begin{aligned} H_{BA} &= ite^{i\mathbf{K} \cdot \vec{\delta}_1} \left(\mathbf{q} \cdot \vec{\delta}_1 + \mathbf{q} \cdot \vec{\delta}_2 e^{-i\mathbf{K} \cdot \vec{a}_1} + \mathbf{q} \cdot \vec{\delta}_3 e^{-i\mathbf{K} \cdot \vec{a}_2} \right) \\ &= ite^{i\mathbf{K} \cdot \vec{\delta}_1} \left(\mathbf{q} \cdot \vec{\delta}_1 (1 + e^{-i\mathbf{K} \cdot \vec{a}_1} + e^{-i\mathbf{K} \cdot \vec{a}_2}) - \mathbf{q} \cdot \vec{a}_1 e^{-i\mathbf{K} \cdot \vec{a}_1} - \mathbf{q} \cdot \vec{a}_2 e^{-i\mathbf{K} \cdot \vec{a}_2} \right) \\ &= -ite^{i\mathbf{K} \cdot \vec{\delta}_1} \left(\mathbf{q} \cdot \vec{a}_1 e^{-i\mathbf{K} \cdot \vec{a}_1} + \mathbf{q} \cdot \vec{a}_2 e^{-i\mathbf{K} \cdot \vec{a}_2} \right). \end{aligned} \quad (2.17)$$

For example using the K point $(4\pi/3a\sqrt{3}, 0)$ to evaluate the exponents, the off-diagonal term can be simplified to

$$H_{BA} = \frac{-3|t|a}{2} (q_x + iq_y). \quad (2.18)$$

Then the effective Hamiltonian takes on the form of a Dirac Hamiltonian for relativistic massless fermions, with the speed of light replaced by the Fermi velocity $v_F = 3|t|a/2\hbar$;

$$H_K = iv_F \sigma \cdot \nabla. \quad (2.19)$$

The eigenenergies and eigenvectors of these Dirac fermions around a K-point will then be

$$E_{\pm}(q) = \pm v_F |\mathbf{q}|,$$

$$\Psi_K(\mathbf{q}) = \frac{1}{\sqrt{2}} \begin{pmatrix} \exp(-i\theta_{\mathbf{q}}/2) \\ \mp \exp(+i\theta_{\mathbf{q}}/2) \end{pmatrix}, \quad (2.20)$$

where $\theta_{\mathbf{q}}$ is the angle of $\mathbf{q}$ measured from the q_x axis giving $\exp(-i\theta_{\mathbf{q}}) = (q_x + iq_y)/|\mathbf{q}|$. Same calculation, done around the K'-point $(-4\pi/3a\sqrt{3}, 0)$ will result in the same eigenvalues with eigenfunctions,

$$\Psi_{K'}(\mathbf{q}) = \frac{1}{\sqrt{2}} \begin{pmatrix} \exp(i\theta_{\mathbf{q}}/2) \\ \pm \exp(-i\theta_{\mathbf{q}}/2) \end{pmatrix}. \quad (2.21)$$

Let us consider an electron with momentum q_x , propagating along the x-direction on one of the Dirac cones. The angle it makes with the x axis is evaluated as $\theta_{\mathbf{q}} = 0$ resulting in the following wavefunction:

$$\Psi_{K'}(\mathbf{q}) = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}. \quad (2.22)$$

Now if we adiabatically move this electron on the constant energy circle in the Dirac cone and return to where it began, the angle and the wavefunction become $\theta_{\mathbf{q}} = 2\pi$ and

$$\Psi_K(\mathbf{q}) = \frac{1}{\sqrt{2}} \begin{pmatrix} \exp(-i2\pi/2) \\ -\exp(i2\pi/2) \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} \exp(-i\pi) \\ -\exp(i\pi) \end{pmatrix}, \quad (2.23)$$

respectively. As can be seen the electron acquires a phase of π called the Berry's phase, as it is brought back to the starting point.

So far we were only concentrating on a single valley. Now let us write a Hamiltonian that describes both valleys with the following basis $(A_K, B_K, A_{K'}, B_{K'})$;

$$H = -v_F \begin{pmatrix} \sigma \cdot \vec{p} & 0 \\ 0 & \sigma^* \cdot \vec{p} \end{pmatrix}, \quad (2.24)$$

where, as described before, $A(B)_{K(K')}$ are the amplitudes of the wavefunction on sublattice A(B) in a given valley K(K') and $\sigma = \sigma_x, \sigma_y$ is the Pauli matrix. Looking at the above Hamiltonian, we can see that the valleys have opposite handedness. That is the electron wavefunctions in K valley are the eigenstates of the right-handed chirality operator, $(\sigma \cdot \vec{p})$ while the electron wavefunctions in the K' valley are eigenfunctions of the left-handed chirality operator $(\sigma^* \cdot \vec{p})$.

2.1.1.2 Bilayer Graphene

Stacking two graphene sheets on top of one another, we can create bilayer graphene. Depending on the way these two layers are arranged, we expect to see different electronic

properties. The two most obvious ways of stacking are arranging all A(B)-atoms above B(A)-atoms, *AB-stacking* (Bernal stacking), or A(B)-atoms above A(B)-atoms, namely *AA stacking*, as depicted in Fig.2.4(a) and Fig.2.4(b), respectively. One can also rotate the layers with respect to one another and obtain Moire patterns.¹⁶⁰ In this thesis, I won't discuss the Moire patterns and I will only introduce the AB stacked bilayer graphene depicted in Fig.2.4(a).

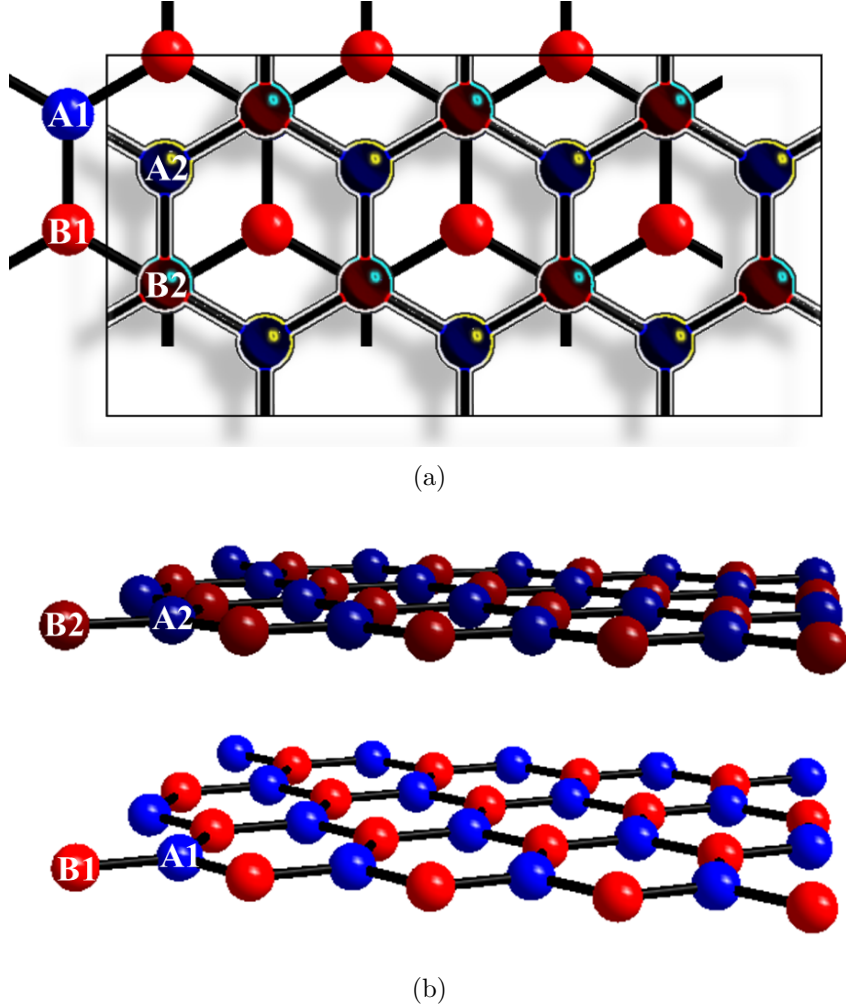


Figure 2.4: a) Bilayer graphene, AB stacking viewed from top, b) AA stacking viewed from the side

Just like we did for a single graphene layer in Eq.2.6, we can express the electronic wavefunctions as spinors. For the case of a bilayer, there are two sublattices A1 and B1 for layer 1 and another two in the second layer A2 and B2. Then we can write a

four-component spinor,

$$\Psi_{\mathbf{k}}(\vec{r}) = \begin{pmatrix} A1_{\mathbf{k}} \\ B1_{\mathbf{k}} \\ A2_{\mathbf{k}} \\ B2_{\mathbf{k}} \end{pmatrix}, \quad (2.25)$$

and create the Hamiltonian in this basis. If we only assume hopping between atoms right above one another, then except for the hopping element $\langle \psi_k^{B2} | H | \psi_k^{A1} \rangle = t_{\perp}$ that couples the two layers, the tight-binding Hamiltonian will be block diagonal capturing the single layer properties in each block;

$$\begin{pmatrix} \epsilon & tf(\mathbf{k}) & 0 & t_{\perp} \\ tf(\mathbf{k})^* & \epsilon & 0 & 0 \\ 0 & 0 & \epsilon & tf(\mathbf{k}) \\ t_{\perp} & 0 & tf(\mathbf{k})^* & \epsilon \end{pmatrix} \begin{pmatrix} A1_{\mathbf{k}} \\ B1_{\mathbf{k}} \\ A2_{\mathbf{k}} \\ B2_{\mathbf{k}} \end{pmatrix} = E(\mathbf{k}) \begin{pmatrix} A1_{\mathbf{k}} \\ B1_{\mathbf{k}} \\ A2_{\mathbf{k}} \\ B2_{\mathbf{k}} \end{pmatrix}. \quad (2.26)$$

We can obtain the eigenvalues diagonalizing this Hamiltonian and plot the bandstructure around one of the K-points. For the case of no coupling between the layers, we would see two degenerate cones at every K-point, one for each layer. However, due to the coupling between the layers, there is only one cone with a zero-gap and the other conduction/valence band pair is pushed up/down as depicted in Fig.2.5(a). Moreover, we see that the fermions around K-points acquired mass as the bands are now parabolic.

Now let's try to describe the AB stacked bilayer graphene using an effective mass model. At the K and K' points the electrons on different sublattices in each layer are decoupled, and the interlayer coupling connects the (A1, B2) pairs only, forming the high energy bands. Ignoring the weak coupling between the (A2, B1) pairs, the low energy states can be described by the following Hamiltonian,

$$H_L = -\frac{1}{2m} \begin{pmatrix} 0 & (\mathbf{p}^*)^2 \\ \mathbf{p}^2 & 0 \end{pmatrix}, \quad (2.27)$$

where $\mathbf{p} = p_x + ip_y = |p|e^{i\theta_p}$. The above Hamiltonian accounts for the hopping between the non-dimer sites through the interlayer hopping between the dimer pair, giving a mass to the chiral electrons $m = t_{\perp}/2v_F^2$ where v_F is the Fermi velocity of electrons in monolayer graphene. The corresponding wavefunction representing the non-dimer, low-energy (A2, B1) pair takes the following form:

$$\psi = \frac{1}{\sqrt{2}} \begin{pmatrix} \exp(i\theta_p) \\ \mp \exp(-i\theta_p) \end{pmatrix} e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}. \quad (2.28)$$

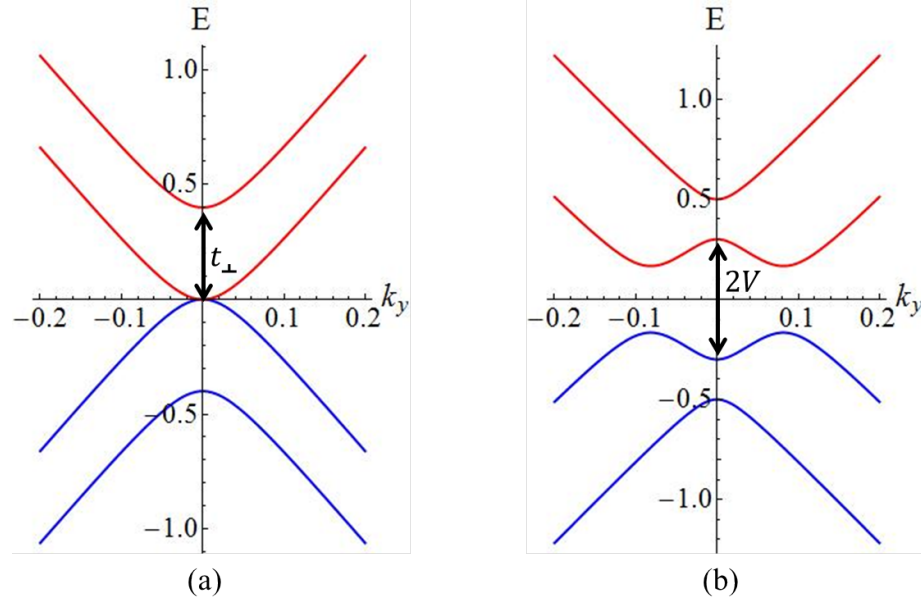


Figure 2.5: Bilayer bandstructure around a K-point $(4\pi/3\sqrt{3}, 0)$ (a) without and (b) with perpendicular electric field corresponding to a potential $V = 0.3\text{eV}$. The parameters are taken to be $t_\perp = 0.4\text{ eV}$, $t = -2.8\text{ eV}$ and $a = 1$

Now for a 2π rotation at a constant energy surface around a Dirac cone, the pseudospin winds 2π , twice as quick compared to a monolayer of graphene.¹⁶¹ The low energy band represented by this spinor becomes approximately linear, $E = vp$, for high momenta, while for low momenta it is quadratic $E = p^2/2m$.

The interesting aspect of bilayer graphene is the possibility of opening of a bandgap by applying a perpendicular electric field. One can create a potential difference of $2V$ between the layers such that the diagonal elements for the top and bottom layers become $\epsilon + V$ and $\epsilon - V$, respectively. The bandstructure of bilayer graphene under an applied field is shown in Fig.2.5(b).²²

2.1.1.3 Graphene Quantum Dots

Now that we discussed the single particle properties of bulk graphene and bilayer graphene, we can introduce confinement and study graphene quantum dots. I will concentrate on three distinct structures; a hexagonal flake with armchair edges with preserved sublattice symmetry (Fig.2.6(a)), a zigzag edged triangle with broken sublattice symmetry (Fig.2.6(b)) and finally a bilayer of the armchair edged flake as depicted in Fig.2.6(c).

The hexagonal graphene flake that is depicted in Fig.2.6(a) is made out of 42 carbon atoms, with 21 of them belonging to the A-sublattice and the remaining 21 to the B-sublattice. Using the tight binding Hamiltonian, we obtain the single particle energy

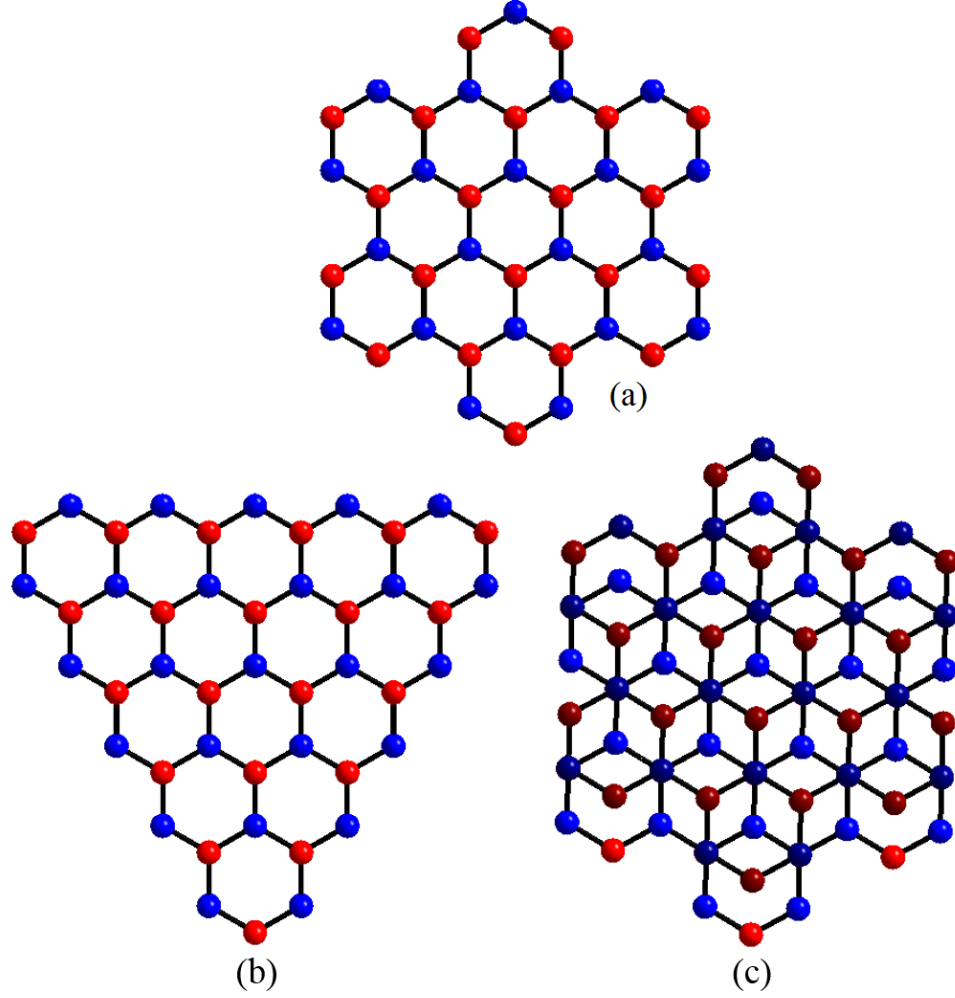


Figure 2.6: (a) Hexagonal quantum dot with armchair edges, (b) triangular quantum dot with zigzag edges, (c) AB stacked bilayer graphene quantum dot with hexagonal shape and armchair edges

levels. As depicted in Fig.2.7(a and b), the single particle energy levels of this hexagonal flake are discretized and there is a non-zero band-gap. The triangular flake with zigzag edges has 46 carbon atoms. 25 of them belong to the A-sublattice while only 21 are in the B-sublattice. The breaking of the sublattice symmetry leads to the zero energy levels in Fig.2.7(a and c). The number of zero energy levels is equal to the difference in the number of carbon atoms in the two sublattices. As for the bilayer, we see a similar band structure to that of a single layer hexagon; no zero energy levels due to preserved sublattice symmetry and a band-gap.

Unlike a sheet of graphene where the electron wavelength can approach infinity, in a graphene quantum dot the longest electron wavelength is limited by the size of the quantum dot. Since the momentum of electrons is inversely proportional to the wavelength, $k \propto 1/\lambda$,

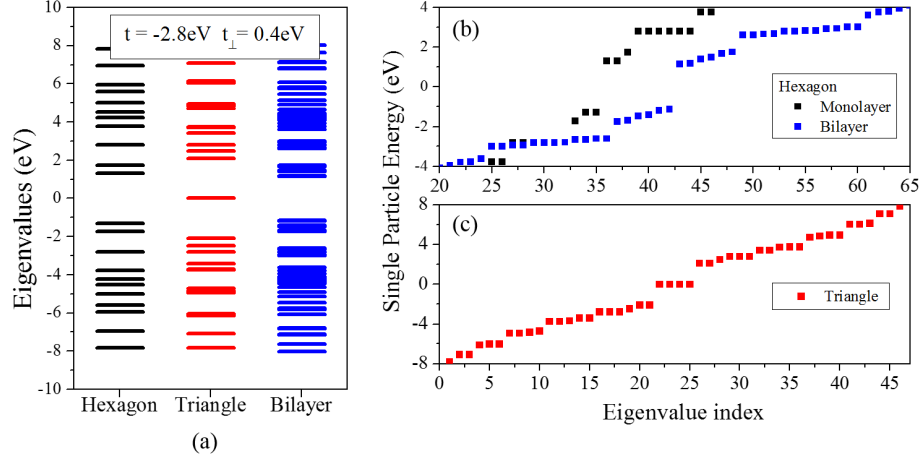


Figure 2.7: Energy levels of graphene quantum dots with Fermi level at $E=0$ eV

combined with the linear dispersion of energy with momentum $E \propto p$ leads to the opening of a size dependent band-gap $E_{gap} \propto k_{min} \propto 1/\lambda_{max}$. When $\lambda \rightarrow \infty$ as in bulk graphene, the gap closes and graphene becomes a gapless material.

We can see the shape and edge dependence of the gap in graphene quantum dots in Fig.2.8(a). The band-gap of the hexagonal, armchair edged flakes has a $1/\sqrt{N} \propto 1/\lambda$ dependence. In contrast to the hexagonal armchair graphene dots, the hexagonal structures with zigzag edges have a band-gap rapidly decreasing with the number of atoms. This is explained by the presence of localized states at the zigzag edges.¹⁶² Finally, for the triangular dots with zigzag edges, the band-gap is defined as the energy difference between the lowest conduction band and the highest valence band after and before the degenerate zero energy levels.²² We again see a Dirac like band-gap that follows the power law $E_{gap} \propto 1/\sqrt{N}$, since the localized edge states that were also present in the hexagonal flakes with zigzag edges constitute the zero energy levels in the triangular flake.

For bilayer graphene, the low energy band evolves between a linear and a quadratic dispersion relation depending on momenta. As a result we expect different energy quantizations in these two regimes. The evolution of the band-gap with the size for AB stacked hexagonal armchair bilayer quantum dot is depicted in Fig.2.8, and is compared with monolayer hexagonal armchair graphene quantum dot. We see the two regimes corresponding to different dispersion relations. The band-gap at the high momenta, small size regime does not perfectly follow a $\frac{1}{\sqrt{N}}$ possibly because the gap is affected by the high energy bands that were shown in Fig.2.5. As we increase the size and move towards the parabolic dispersion regime, we see a change in the evolution of the band-gap towards a $\frac{1}{N}$ dispersion relation.

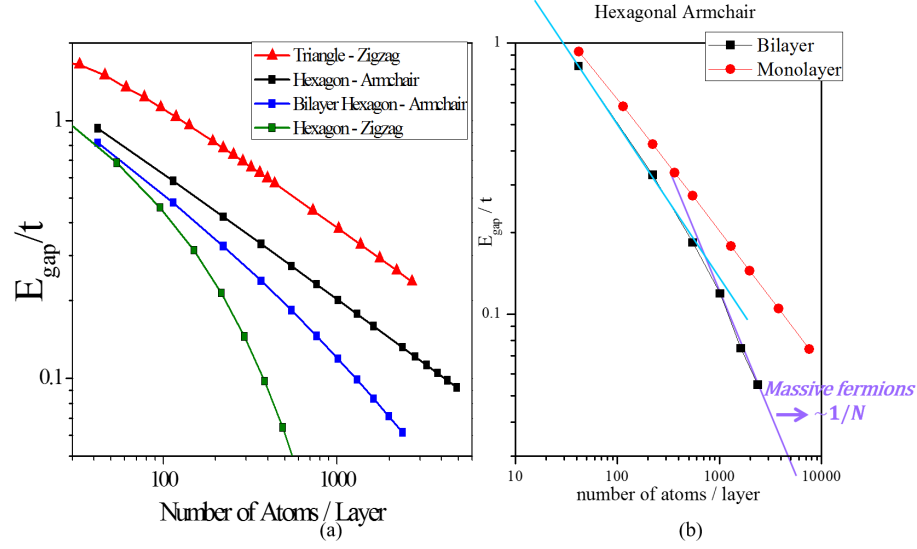


Figure 2.8: (a) Evolution of the band-gap energy of single layer graphene quantum dots with different shape and edge character²²(b) Evolution of the band-gap energy with the size of the flakes for hexagonal armchair mono- and bi-layer graphene quantum dots

2.1.2 Many Body Hamiltonian

Single particle description is a good starting point for describing the electronic properties of materials at a mean-field level. However, electronic, optical and magnetic properties are determined by electron-electron interactions. Thus we need to consider quantum dots with more than one electron. Before complicating the calculations drastically where all electrons interact with one another, I'll start with a simpler case in which there are N , non-interacting electrons.

Starting with the operator $h_i(\vec{r}) = p_i^2/2m + \sum_{R_A, R_B} V(\vec{r} - \mathbf{R})$ for each electron, which describes the kinetic and potential energy of electron i , the Hamiltonian of an N electron system can be expressed as

$$H = \sum_i^N h_i. \quad (2.29)$$

Although at first sight the corresponding N electron wavefunctions are expected to be products of single-electron wavefunctions, we have to remember that electrons are fermions and many-electron wavefunctions must be anti-symmetric. A correctly anti-symmetrized wavefunction describing N , non-interacting electrons can be obtained using the Slater

determinant,

$$\Phi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\vec{r}_1) & \phi_2(\vec{r}_1) & \cdots & \phi_N(\vec{r}_1) \\ \phi_1(\vec{r}_2) & \phi_2(\vec{r}_2) & \cdots & \phi_N(\vec{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\vec{r}_N) & \phi_2(\vec{r}_N) & \cdots & \phi_N(\vec{r}_N) \end{vmatrix}. \quad (2.30)$$

For graphene, $\phi_i(\vec{r}_j)$ corresponds to localized p_z orbitals on each carbon atom, $\phi_z(\vec{r}_j - \mathbf{R}_i)$.

2.1.2.1 Second Quantization

Although at the single particle level the real space description is manageable, as we introduce more and more electrons, it becomes harder and harder to keep track of what is happening in a many body system. Thus, I will now briefly introduce the occupation number formalism, *second quantization*, using the field operators,

$$\begin{aligned} \Psi(\vec{r}) &= \frac{1}{\sqrt{N}} \sum_i c_i \phi_z(\vec{r} - R_i), \\ \Psi^+(\vec{r}) &= \frac{1}{\sqrt{N}} \sum_i c_i^+ \phi_z^*(\vec{r} - R_i). \end{aligned} \quad (2.31)$$

They describe adding/removing an electron at position $\vec{r}$ within the p_z orbital basis, where N is the total number of orbitals. c_i, c_i^+ represent annihilation, creation of an electron on a p_z orbital located at R_i , respectively, and satisfy the anticommutation rules for fermionic creation/annihilation operators:

$$\begin{aligned} \{c_i, c_j\} &= \{c_i^+, c_j^+\} = 0, \\ \{c_i, c_j^+\} &= \delta_{ij}. \end{aligned} \quad (2.32)$$

Starting with the Hamiltonian given in Eq.2.3 for a single electron, we can find its matrix elements by acting on it from both sides with a field operator and expanding in terms of creation/annihilation operators:

$$\begin{aligned} \int d\vec{r} \Psi^+(\vec{r}) H \Psi(\vec{r}) &= \frac{1}{N} \int d\vec{r} \sum_{i,j} c_i^+ \phi_z^*(\vec{r} - R_i) H c_j \phi_z(\vec{r} - R_j) \\ &= \sum_{i,j} \frac{1}{N} \int d\vec{r} \phi_z^*(\vec{r} - R_i) H \phi_z(\vec{r} - R_j) c_i^+ c_j \\ &= \sum_{i,j} H_{ij} c_i^+ c_j. \end{aligned} \quad (2.33)$$

The final expression that is written in terms of the creation/annihilation operators is the single particle Hamiltonian Eq.2.3 in second quantization form.

We can also introduce a short-hand *ket* notation of a Slater determinant:

$$\Phi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \langle \vec{r} | \phi_1, \phi_2, \dots, \phi_N \rangle, \quad (2.34)$$

which represents N electrons placed on orbitals $\{1..N\}$. Using this notation, to ensure the wavefunctions are antisymmetric, we have to be careful in keeping the orbital ordering the same throughout a calculation or changing the sign whenever there is an interchange of any two columns such that

$$|\phi_1, \phi_2, \dots, \phi_N\rangle = -|\phi_2, \phi_1, \dots, \phi_N\rangle. \quad (2.35)$$

This shorthand notation ties perfectly with the second quantization. Starting with vacuum, $|0\rangle$, we can create an electron in orbital i , $|\phi_i\rangle$:

$$c_i^+|0\rangle = |\phi_i\rangle, \quad (2.36)$$

and remove it afterwards with the operator c_i :

$$c_i|\phi_i\rangle = |0\rangle. \quad (2.37)$$

The ground state of a non-interacting N electron quantum dot will be a linear combination of configurations Φ , Eq.2.34:

$$|GS_{NI}\rangle = \sum_i A_i |\phi_\alpha, \phi_\beta, \dots \phi_{N/2}\rangle_i, \quad (2.38)$$

where $|\phi_\alpha, \phi_\beta, \dots \phi_{N/2}\rangle_i$ is a configuration with $N/2$ atoms in occupation representation. We have already shown that by diagonalizing the single-particle Hamiltonian in Eq.2.33, the single-particle orbitals can be obtained. Defining operators $a_i^+(a_i)$ as creating/annihilating an electron on a single particle orbital i the N electron, non-interacting ground state can also be obtained by placing N electrons in the lowest $N/2$ single particle levels:

$$|GS_{NI}\rangle = \prod_i^{N/2} a_{i\uparrow}^+ a_{i\downarrow}^+ |0\rangle, \quad (2.39)$$

where NI stands for non-interacting. Rotating from p_z orbital basis to single particle orbital basis allows us to express the ground state of a non-interacting N electron quantum dot as a single Slater determinant.

Now let us allow electrons to interact with one another. The interaction among electrons is introduced through the Coulomb potential between each pair V_{e-e} and the total Hamiltonian is expressed as

$$H = \sum_{i=1}^N \left[\frac{p_i^2}{2m} + \sum_j V_{ion}(\vec{r}_i - \mathbf{R}_j) \right] + \frac{1}{2} \sum_{i,j,i \neq j}^N V_{e-e}(\vec{r}_i - \vec{r}_j). \quad (2.40)$$

This Hamiltonian for interacting electrons can be cast into second quantization form using the field operators as we did for the single particle Hamiltonian. We will start with the single-particle part separating its components:

$$H_{1e} = \int d\vec{r} \Psi^\dagger(\vec{r}) \left(\frac{p^2}{2m} + V_{ion}(\mathbf{R}_i) + V_{ion}(\mathbf{R}_j) \right) \Psi(\vec{r}) + \int d\vec{r} \Psi^\dagger(\vec{r}) \sum_{k \neq i,j} V_{ion}(\mathbf{R}_k) \Psi(\vec{r}), \quad (2.41)$$

where I used a short-hand notation for the ionic potential localized at R_k such that $V_{ion}(\vec{r} - \mathbf{R}_k) = V_{ion}(\mathbf{R}_k)$. Expanding the field operators in terms of p_z orbitals and creation / annihilation operators, and writing out the on-site terms separately we get:

$$\begin{aligned} H_{1e} &= \sum_i \frac{1}{N} \left[\int d\vec{r} \phi_i^* \left(\frac{p^2}{2m} + V_{ion}(\mathbf{R}_i) \right) \phi_i c_i^\dagger c_i + \sum_{k \neq i} \int d\vec{r} \phi_i^* V_{ion}(\mathbf{R}_k) \phi_i c_i^\dagger c_i \right] \\ &\quad + \sum_{i \neq j} \frac{1}{N} \left[\int d\vec{r} \phi_i^* \left(\frac{p^2}{2m} + V_{ion}(\mathbf{R}_i) + V_{ion}(\mathbf{R}_j) \right) \phi_j c_i^\dagger c_j \right. \\ &\quad \left. + \sum_{k \neq i,j} \int d\vec{r} \phi_i^* V_{ion}(\mathbf{R}_k) \phi_j c_i^\dagger c_j \right] \\ &= \sum_i \epsilon_i c_i^\dagger c_i + \sum_{i,j} t_{ij} c_i^\dagger c_j + \sum_{i,j,k \neq i,j} V_{ijk}^{ion} c_i^\dagger c_j \\ &= \sum_i \epsilon_i c_i^\dagger c_i + \sum_{i,j,k \neq i,j} (t_{ij} + V_{ijk}^{ion}) c_i^\dagger c_j \\ &= \sum_i \epsilon_i c_i^\dagger c_i + \sum_{i,j} \tau_{ij} c_i^\dagger c_j, \end{aligned} \quad (2.42)$$

where τ_{ij} is the hopping element that includes the nearest neighbor hopping and all remaining ionic interactions. So far we have been hiding the information about spin within the indices i, j . However, for the interaction part the spin information will be needed. Thus from now on we will explicitly specify the spin of the electrons being treated, such that $i \rightarrow (i, \sigma)$ where $\sigma = \uparrow / \downarrow$ is the spin of the electron. Now let us write the two body

interaction term in Eq.2.40 in second quantization:

$$\begin{aligned}
H_{ee} &= \frac{1}{2} \int \int d\vec{r} d\vec{r}' \Psi^\dagger(\vec{r}) \Psi^\dagger(\vec{r}') V^{ee}(\vec{r} - \vec{r}') \Psi(\vec{r}') \Psi(\vec{r}) \\
&= \frac{1}{2} \sum_{ijkl\sigma\sigma'} \frac{1}{N^2} \int \int d\vec{r} d\vec{r}' \phi_{i\sigma}^\dagger \phi_{j\sigma'}^\dagger V^{ee}(\vec{r} - \vec{r}') \phi_{k\sigma'} \phi_{l\sigma} c_{i\sigma}^\dagger c_{j\sigma'}^\dagger c_{k\sigma'} c_{l\sigma} \\
&= \frac{1}{2} \sum_{ijkl\sigma\sigma'} \langle ij|V|kl \rangle c_{i\sigma}^\dagger c_{j\sigma'}^\dagger c_{k\sigma'} c_{l\sigma}.
\end{aligned} \tag{2.43}$$

Re-combining the one and two body parts of the Hamiltonian Eq.2.40, in second quantization it takes the following form:

$$H = \sum_{i,\sigma} \epsilon_i c_{i\sigma}^\dagger c_{i\sigma} + \sum_{i,j,\sigma} \tau_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \frac{1}{2} \sum_{ijkl\sigma\sigma'} \langle ij|V|kl \rangle c_{i\sigma}^\dagger c_{j\sigma'}^\dagger c_{k\sigma'} c_{l\sigma}. \tag{2.44}$$

ϵ_i correspond to onsite energies of electrons, which are taken to be equal for all sites. τ_{ij} is the effective hopping element and $\langle ij|V|kl \rangle$ is the two body scattering element.

2.1.2.2 Two Body Scattering Elements

The two body Coulomb matrix elements $\langle ij|V|kl \rangle$ written explicitly are

$$\langle ij|V|kl \rangle = \int \int d\vec{r} d\vec{r}' \phi_{i\sigma}^\dagger \phi_{j\sigma'}^\dagger \frac{e^2}{\kappa |\vec{r} - \vec{r}'|} \phi_{k\sigma'} \phi_{l\sigma}, \tag{2.45}$$

where, as mentioned before, ϕ_i are the p_z orbitals localized on site- i and the interactions are screened statically by κ . In order to numerically calculate this integral, we need to know the form of the p_z orbitals. A good approximation to carbon p_z orbitals is the Slater p_z ¹⁶³ orbital,

$$\phi_i(\vec{r}_i) = \sqrt{\frac{\xi^5}{32\pi}} z \exp\left(\frac{-\xi r_i}{2}\right), \tag{2.46}$$

with $\xi = 3.14$.¹⁶

The two body element represents the interaction of two electrons occupying sites k and l that scatter and end up on sites j and i as a result of this event (Fig.2.9). Up to and including second nearest neighbour sites, we calculate all possible scattering matrix elements as given in Table 2.1. For electrons that are further apart than that, we only include the direct terms, approximating the electrons as two point-charges.¹⁶

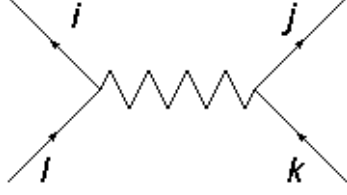


Figure 2.9: Feynman Diagram of two body Coulomb interaction term $\langle ij|V|kl\rangle$.

$\langle ij V kl\rangle$	eV
$\langle 11 V 11\rangle$	16.522
$\langle 12 V 21\rangle$	8.640
$\langle 13 V 31\rangle$	5.333
$\langle 11 V 12\rangle$	3.157
$\langle 12 V 31\rangle$	1.735
$\langle 12 V 12\rangle$	0.873
$\langle 22 V 13\rangle$	0.606

Table 2.1: Coulomb matrix elements calculated using Slater orbitals for graphene taking $\kappa = 1$. 1,2 and 3 indicate onsite, nearest and next nearest sites of a lattice on a hexagon respectively.¹⁶

2.1.2.3 Configuration Interaction Method

Configuration interaction is an exact method for solving many body problems, provided that we use the full space of configurations. Assuming we have M states and $N_\uparrow + N_\downarrow$ electrons, the number of configurations are calculated as

$$N_{conf} = \binom{M}{N_\uparrow} \binom{M}{N_\downarrow}. \quad (2.47)$$

Different S_z subspaces do not mix with one another by the Hamiltonian given in Eq.2.44. Then, for $S_z = (N_\uparrow - N_\downarrow) \times 1/2$, the Hamiltonian will be a $N_{conf} \times N_{conf}$ matrix.

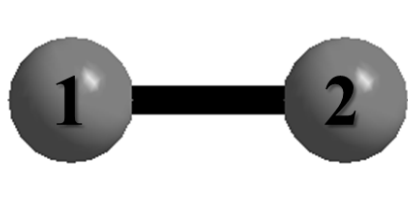


Figure 2.10: A two-atom system

Since the creation of many body configurations is an integral part of this thesis, I will introduce the procedure using a simple 2-site model that is depicted in Fig.2.10. Let us assume that each ball represents a carbon atom with a single orbital and an electron per orbital. In this 2 electron, 2-site model there are in total two electrons ($N_\uparrow + N_\downarrow = 2$) occupying the p_z orbitals of the two carbon atoms ($M = 2$).

I will now discuss all possible configurations of the two electrons. Due to Pauli exclusion principle we cannot place electrons with the same spin onto the same orbital. Then, we

can only have two spin-polarized configurations with $S_z = \pm 1$;

$$\begin{aligned} c_{1\uparrow}^+ c_{2\uparrow}^+ |0\rangle &= |1_{\uparrow}, 2_{\uparrow}\rangle, \\ c_{1\downarrow}^+ c_{2\downarrow}^+ |0\rangle &= |1_{\downarrow}, 2_{\downarrow}\rangle, \end{aligned} \quad (2.48)$$

where $1_{\uparrow}$ symbolizes an up electron placed on the first orbital. We can flip the spin of one electron in each spin-polarized configuration to obtain two $S_z = 0$ configurations,

$$\begin{aligned} c_{1\uparrow}^+ c_{2\downarrow}^+ |0\rangle &= |1_{\uparrow}, 2_{\downarrow}\rangle, \\ c_{1\downarrow}^+ c_{2\uparrow}^+ |0\rangle &= |1_{\downarrow}, 2_{\uparrow}\rangle. \end{aligned} \quad (2.49)$$

Now that we have two electrons with opposite spin, we can also place them on the same orbital to obtain two doubly occupied $S_z = 0$ configurations,

$$\begin{aligned} c_{1\uparrow}^+ c_{1\downarrow}^+ |0\rangle &= |1_{\uparrow}, 1_{\downarrow}\rangle, \\ c_{2\uparrow}^+ c_{2\downarrow}^+ |0\rangle &= |2_{\uparrow}, 2_{\downarrow}\rangle, \end{aligned} \quad (2.50)$$

making sure that we always place an electron onto the second orbital first and a down electron before an up electron.

For this 2-site model we have

$$N_{conf} = \binom{2}{2} \binom{2}{0} = 1, \quad (2.51)$$

configurations in the $S_z = \pm 1$ subspaces and

$$N_{conf} = \binom{2}{1} \binom{2}{1} = 4 \quad (2.52)$$

configurations in the $S_z = 0$ subspace. The Hamiltonian will be a block diagonal 6×6 matrix, with two 1×1 blocks for $S_z = \pm 1$ and a 4×4 block representing the $S_z = 0$ subspace:

$$H = \begin{pmatrix} [1 \times 1] & 0 & 0 \\ 0 & [1 \times 1] & 0 \\ 0 & 0 & \begin{bmatrix} 4 \times 4 \end{bmatrix} \end{pmatrix}. \quad (2.53)$$

Since the computationally most expensive part of the Hamiltonian Eq.2.44 is the nested summations over i, j, k, l indices in the two body term, I will concentrate on that and

try to reduce the computational cost through decreasing the sum over the indices. The interaction term,

$$V = \frac{1}{2} \sum_{ijkl\sigma\sigma'} \langle ij|V|kl\rangle c_{i\sigma}^+ c_{j\sigma'}^+ c_{k\sigma'} c_{l\sigma}, \quad (2.54)$$

can be divided into four to give:

$$\begin{aligned} V = & \frac{1}{2} \left(\sum_{i>j,k>l,\sigma\sigma'} \langle ij|V|kl\rangle c_{i\sigma}^+ c_{j\sigma'}^+ c_{k\sigma'} c_{l\sigma} \right. \\ & + \sum_{i<j,k>l,\sigma\sigma'} \langle ij|V|kl\rangle c_{i\sigma}^+ c_{j\sigma'}^+ c_{k\sigma'} c_{l\sigma} \\ & + \sum_{i>j,k<l,\sigma\sigma'} \langle ij|V|kl\rangle c_{i\sigma}^+ c_{j\sigma'}^+ c_{k\sigma'} c_{l\sigma} \\ & \left. + \sum_{i<j,k<l,\sigma\sigma'} \langle ij|V|kl\rangle c_{i\sigma}^+ c_{j\sigma'}^+ c_{k\sigma'} c_{l\sigma} \right). \end{aligned} \quad (2.55)$$

Using fermionic commutation rules in the last three terms to obtain $c_{i\sigma}^+ c_{j\sigma'}^+ = -c_{j\sigma'}^+ c_{i\sigma}^+$ and $c_{k\sigma'} c_{l\sigma} = -c_{l\sigma} c_{k\sigma'}$ we get

$$\begin{aligned} V = & \frac{1}{2} \left(\sum_{i>j,k>l,\sigma\sigma'} \langle ij|V|kl\rangle c_{i\sigma}^+ c_{j\sigma'}^+ c_{k\sigma'} c_{l\sigma} \right. \\ & - \sum_{i<j,k>l,\sigma\sigma'} \langle ij|V|kl\rangle c_{j\sigma'}^+ c_{i\sigma}^+ c_{k\sigma'} c_{l\sigma} \\ & - \sum_{i>j,k<l,\sigma\sigma'} \langle ij|V|kl\rangle c_{i\sigma}^+ c_{j\sigma'}^+ c_{l\sigma} c_{k\sigma'} \\ & \left. + \sum_{i<j,k<l,\sigma\sigma'} \langle ij|V|kl\rangle c_{j\sigma'}^+ c_{i\sigma}^+ c_{l\sigma} c_{k\sigma'} \right). \end{aligned} \quad (2.56)$$

Now changing the indices $i \leftrightarrow j$ in the second and last, and $k \leftrightarrow l$ in first two terms along with $\sigma \leftrightarrow \sigma'$ we obtain

$$\begin{aligned} V = & \frac{1}{2} \left(- \sum_{i>j,l>k\sigma\sigma'} \langle ij|V|lk\rangle c_{i\sigma}^+ c_{j\sigma'}^+ c_{k\sigma} c_{l\sigma'} \right. \\ & - \sum_{i<j,l>k\sigma\sigma'} \langle ij|V|lk\rangle c_{i\sigma}^+ c_{j\sigma'}^+ c_{k\sigma} c_{l\sigma'} \\ & + \sum_{i>j,k<l,\sigma\sigma'} \langle ij|V|kl\rangle c_{i\sigma}^+ c_{j\sigma'}^+ c_{k\sigma'} c_{l\sigma} \\ & \left. + \sum_{i<j,k<l,\sigma\sigma'} \langle ij|V|kl\rangle c_{i\sigma}^+ c_{j\sigma'}^+ c_{k\sigma'} c_{l\sigma} \right). \end{aligned} \quad (2.57)$$

The Coulomb matrix element $\langle ij\sigma\sigma'|V|l\sigma'k\sigma\rangle$ in the first term and similarly the one in the second term is non-zero only if $\sigma = \sigma'$. Moreover one can show that $\langle ji|V|kl\rangle = \langle ij|V|lk\rangle$ and $\langle ji|V|lk\rangle = \langle ij|V|kl\rangle$ simply using the definition of Coulomb elements, which will reduce our expression to

$$V = \sum_{i>j,k>l,\sigma\sigma'} (\langle ij|V|kl\rangle - \langle ij|V|lk\rangle\delta_{\sigma\sigma'}) c_{i\sigma}^+ c_{j\sigma'}^+ c_{k\sigma'} c_{l\sigma}. \quad (2.58)$$

2.1.2.4 Hubbard Model

The Hubbard model is one of the simplest models for treating interacting systems. The *Hubbard U* model has only three terms; on site energy, site to site hopping and on-site interactions. Since one cannot place same spin electrons on the same orbital, the interaction part of the Hamiltonian reduces to

$$V = \frac{1}{2} \sum_{i\sigma} \langle ii|V|ii\rangle c_{i\sigma}^+ c_{i\bar{\sigma}}^+ c_{i\bar{\sigma}} c_{i\sigma}, \quad (2.59)$$

where $\bar{\sigma}$ symbolizes the opposite-spin of σ . Assuming all on-site interactions are the same $\langle ii|V|ii\rangle = U$, the Hubbard U Hamiltonian takes the following form:

$$H_{Hubb} = \sum_{i\sigma} \epsilon_i c_{i\sigma}^+ c_{i\sigma} - |t| \sum_{\langle ij\rangle\sigma} c_{i\sigma}^+ c_{j\sigma} + \sum_{i=1}^N U n_{i\uparrow} n_{i\downarrow}, \quad (2.60)$$

where $n_{i\sigma} = c_{i\sigma}^+ c_{i\sigma}$ is the number operator. Now let us work on the two electron two site model. I will demonstrate the calculation of a diagonal element, two off-diagonal elements and eventually construct the Hamiltonian matrix.

Since the tunneling term moves an electron from an orbital to its nearest neighbour it only appears in calculation of the off-diagonal matrix elements. Then the diagonal matrix element of the $|1_\downarrow, 2_\uparrow\rangle$ configuration is calculated as;

$$\begin{aligned} \langle 2_\uparrow, 1_\downarrow | H | 1_\downarrow, 2_\uparrow \rangle &= \langle 2_\uparrow, 1_\downarrow | \left[\sum_{i\sigma} \epsilon_i c_{i\sigma}^+ c_{i\sigma} + \sum_i U n_{i\uparrow} n_{i\downarrow} \right] | 1_\downarrow, 2_\uparrow \rangle, \\ &= \langle 2_\uparrow, 1_\downarrow | [\epsilon_1 c_{1\downarrow}^+ c_{1\downarrow} + \epsilon_2 c_{2\uparrow}^+ c_{2\uparrow}] | 1_\downarrow, 2_\uparrow \rangle, \\ &= \epsilon_1 + \epsilon_2, \end{aligned} \quad (2.61)$$

where I have used the fact that $n_{1\uparrow} = n_{2\downarrow} = 0$ for configuration $|1_\downarrow, 2_\uparrow\rangle$. Let us now look at the off diagonal term between the configurations $|1_\downarrow, 2_\uparrow\rangle = c_{1\downarrow}^+ c_{2\uparrow}^+ |0\rangle$ and $\langle 2_\uparrow 2_\downarrow| = c_{2\uparrow}^+ c_{2\downarrow}^+ |0\rangle$

and simplify to obtain,

$$\begin{aligned}
\langle \circ, \uparrow\downarrow | H | \downarrow, \uparrow \rangle &= \langle 0 | c_{2\downarrow} c_{2\uparrow} \left[-|t| \sum_{ij\sigma} c_{i\sigma}^+ c_{j\sigma} \right] c_{1\downarrow}^+ c_{2\uparrow}^+ | 0 \rangle \\
&= -|t| \langle 0 | c_{2\downarrow} c_{2\uparrow} c_{2\downarrow}^+ c_{1\downarrow}^+ c_{1\downarrow}^+ c_{2\uparrow}^+ | 0 \rangle \\
&= -|t| \langle 0 | c_{2\downarrow} c_{2\uparrow} c_{2\downarrow}^+ c_{2\uparrow}^+ | 0 \rangle \\
&= -|t| \langle 0 | c_{2\downarrow} (1 - c_{2\downarrow}^+ c_{2\uparrow}) c_{2\uparrow}^+ | 0 \rangle \\
&= -|t| \langle 0 | c_{2\downarrow} c_{2\uparrow}^+ | 0 \rangle + |t| \langle 0 | c_{2\downarrow} c_{2\downarrow}^+ c_{2\uparrow} c_{2\uparrow}^+ | 0 \rangle \\
&= 0 + |t| \langle 0 | c_{2\downarrow} c_{2\downarrow}^+ | 0 \rangle \\
&= +|t|.
\end{aligned} \tag{2.62}$$

The sign change happened because, according to our convention, a down spin is placed before an up spin within the same orbital. Now let us look at the element between the same doubly occupied configuration and $|1_\uparrow, 2_\downarrow\rangle$:

$$\begin{aligned}
\langle \circ, \uparrow\downarrow | H | \uparrow, \downarrow \rangle &= \langle 0 | c_{2\downarrow} c_{2\uparrow} \left[-|t| \sum_{ij\sigma} c_{i\sigma}^+ c_{j\sigma} \right] c_{1\uparrow}^+ c_{2\downarrow}^+ | 0 \rangle \\
&= -|t| \langle 0 | c_{2\downarrow} c_{2\uparrow} c_{2\uparrow}^+ c_{1\uparrow}^+ c_{1\uparrow}^+ c_{2\downarrow}^+ | 0 \rangle \\
&= -|t| \langle 0 | c_{2\downarrow} c_{2\uparrow} c_{2\uparrow}^+ c_{2\downarrow}^+ | 0 \rangle \\
&= -|t| \langle 0 | c_{2\downarrow} c_{2\downarrow}^+ | 0 \rangle \\
&= -|t|.
\end{aligned} \tag{2.63}$$

In this evaluation there was no sign change because the down electron in the second orbital was already placed before the up electron. The Hamiltonian with the configurations ordered as $|1_\uparrow, 2_\uparrow\rangle, |1_\downarrow, 2_\downarrow\rangle, |1_\uparrow, 2_\downarrow\rangle, |1_\downarrow, 2_\uparrow\rangle, |1_\uparrow, 1_\downarrow\rangle, |2_\uparrow, 2_\downarrow\rangle$ takes on the following form:

$$H = \begin{pmatrix} \epsilon_1 + \epsilon_2 & 0 & 0 & 0 & 0 & 0 \\ 0 & \epsilon_1 + \epsilon_2 & 0 & 0 & 0 & 0 \\ 0 & 0 & \epsilon_1 + \epsilon_2 & 0 & -|t| & -|t| \\ 0 & 0 & 0 & \epsilon_1 + \epsilon_2 & |t| & |t| \\ 0 & 0 & -|t| & |t| & 2\epsilon_1 + U & 0 \\ 0 & 0 & -|t| & |t| & 0 & 2\epsilon_2 + U \end{pmatrix}. \tag{2.64}$$

Since we take the on-site energies of electrons to be the same ($\epsilon_1 = \epsilon_2 = \epsilon$) for every site and conserve the number of electrons, including the on-site term of the Hamiltonian given in Eq.2.44 affects all of the diagonal elements in the same way, shifting the energy spectrum by 2ϵ .

The first two configurations given for the 2-electron system do not couple with any other configuration due to total spin conservation. Because of that, they are already eigenvectors of the Hamiltonian. Setting $\epsilon_1 = \epsilon_2 = 0$, their eigenvalues are zero. The remaining four couple to give one spin-triplet ($S = 1, S_z = 0$) corresponding to an eigenvalue of 0 irrespective of t and U , and three spin-singlets with energies U and $1/2(U \pm \sqrt{16t^2 + U^2})$. In the non-interacting limit, $U \rightarrow 0$, the Hamiltonian reduces to a tight-binding Hamiltonian, and the spin-singlet eigenvalues of the two electrons reduce to $\{0, -2t, +2t\}$. In the strongly interacting regime $t \ll U$, using a Taylor expansion, up to first order, the energies of the two-electron, spin-singlets become $\{U, U + 4t^2/U, -4t^2/U\}$.

Extended Hubbard Model

In addition to the on-site interaction term, the Extended Hubbard Model includes direct interaction terms $\langle ij|V|ji\rangle$ between electrons such that the Hamiltonian takes the following form:

$$H_{Hubb} = \sum_{i\sigma} \epsilon_i c_{i\sigma}^\dagger c_{i\sigma} - |t| \sum_{\langle ij \rangle \sigma} c_{i\sigma}^\dagger c_{j\sigma} + \sum_{i=1}^N U n_{i\uparrow} n_{i\downarrow} + \frac{1}{2} \sum_{ij} \langle ij|V|ji\rangle \varrho_i \varrho_j. \quad (2.65)$$

Here $\varrho_i = n_{i\downarrow} + n_{i\uparrow}$ is the charge density on site i that can take on the values $(0, 1, 2)$. It functions to explicitly include the summation over spin-indices σ, σ' . As a result, the direct interaction term only appears on the diagonals of Eq.2.64, for the singly occupied configurations of the two-electron, two-site model.

2.1.3 Mean Field Methods

As mentioned before, the size of the configuration space increases factorially with the number of sites and eventually becomes unsolvable with today's computational tools. There are approximation methods to solve these numerically unsolvable models. Mean field methods reduce the many body problem into a one body problem assuming that the particles interact with the *mean field* of the other electrons. It is accomplished by replacing the interaction term in the Hamiltonian by an effective mean field term. In most mean field calculations the electron density is used to calculate this effective term.

In real space, the probability of finding a single electron in a volume element $d\vec{r}$ is $|\psi_{a\sigma}(\vec{r})|^2 d\vec{r}$ where $|\psi_{a\sigma}(\vec{r})|^2$ is the probability distribution.¹⁶⁴ Since these wavefunctions have to be normalized, integrating over the whole space, one expects $\int d\vec{r} |\psi_{a\sigma}(\vec{r})|^2 = 1$. If we want to see the bigger picture, the probability of finding any electron at any volume element, we can use the density $\rho(\vec{r})$ such that the probability of finding an electron in

volume element $d\vec{r}$ is now $\rho(\vec{r})d\vec{r}$;

$$\rho(\vec{r}) = \sum_{a,\sigma}^{N_{el}} |\psi_{a\sigma}(\vec{r})|^2, \quad (2.66)$$

where a runs over the occupied orbitals. We can translate this to second quantization by expanding $b_{a\sigma}^+$, the creation operator of an electron with wavefunction $\psi_{a\sigma}(\vec{r})$, in terms of localized creation operators;

$$b_{a\sigma}^+ = \sum_i k_{ai}^* c_{i\sigma}^+. \quad (2.67)$$

Then expressing the density in second quantization,

$$\begin{aligned} \hat{\rho} &= \sum_a^{N_{el}} b_{a\sigma}^+ b_{a\sigma} \\ &= \sum_a^{N_{el}} \sum_i k_{ai}^* c_{i\sigma}^+ \sum_j k_{aj} c_{j\sigma} \\ &= \sum_a^{N_{el}} \sum_{i,j} k_{ai}^* k_{aj} c_{i\sigma}^+ c_{j\sigma}, \end{aligned} \quad (2.68)$$

we obtain the density matrix elements $\rho_{jk} = \sum_a^{N_{el}} \sum_{i,j} k_{ai}^* k_{aj}$. In most mean-field theories, one starts with a *trial* density that is updated self consistently until a convergence is reached.

2.1.3.1 The Variational Principle

The Variational principle states that the ground state energy calculated from a trial wavefunction will be an upper bound to the exact ground state energy. This has big implications for self-consistent methods, since it guarantees that as long as the energy is getting lower, we are getting closer to the actual ground state. Mathematically, let's say we start with a guess-function of Ψ for the ground state, then its energy will be given as

$$E[\Psi] = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \geq E_0, \quad (2.69)$$

where E_0 is the true ground state. The equality holds only if $\Psi = \Psi_0$ where Ψ_0 is the true ground state wavefunction.

2.1.3.2 Mean Field Hartree Fock Approximation

The mean-field Hartree Fock Hamiltonian is obtained from the microscopic Hamiltonian given in Eq.2.44 using the ansatz:

$$\begin{aligned} c_{i\sigma}^+ c_{j\sigma'}^+ c_{k\sigma'} c_{l\sigma} &\approx c_{i\sigma}^+ \langle c_{j\sigma'}^+ c_{k\sigma'} \rangle c_{l\sigma} + \langle c_{i\sigma}^+ c_{l\sigma} \rangle c_{j\sigma'}^+ c_{k\sigma'} \\ &- c_{i\sigma}^+ c_{k\sigma'} \langle c_{j\sigma'}^+ c_{l\sigma} \rangle \delta_{\sigma\sigma'} - \langle c_{i\sigma}^+ c_{k\sigma'} \rangle c_{j\sigma'}^+ c_{l\sigma} \delta_{\sigma\sigma'}. \end{aligned} \quad (2.70)$$

In this expression $\langle c_{j\sigma'}^+ c_{k\sigma'} \rangle$ corresponds to the density matrix element ρ_{jk} . The interaction part, H_{ee} , of the Hamiltonian (Eq.2.44) is rewritten using the above ansatz to give:

$$\begin{aligned} H_{ee}^{HF} &= \frac{1}{2} \sum_{ijkl\sigma\sigma'} \langle ij|V|kl \rangle [c_{i\sigma}^+ \langle c_{j\sigma'}^+ c_{k\sigma'} \rangle c_{l\sigma} + \langle c_{i\sigma}^+ c_{l\sigma} \rangle c_{j\sigma'}^+ c_{k\sigma'}] \\ &- \frac{1}{2} \sum_{ijkl\sigma\sigma'} \langle ij|V|kl \rangle [\langle c_{i\sigma}^+ c_{k\sigma'} \rangle c_{j\sigma'}^+ c_{l\sigma} \delta_{\sigma\sigma'} + c_{i\sigma}^+ c_{k\sigma'} \langle c_{j\sigma'}^+ c_{l\sigma} \rangle \delta_{\sigma\sigma'}], \end{aligned} \quad (2.71)$$

where the first term represents the direct and the second term represents the exchange interaction. First, replacing $i\sigma \leftrightarrow j\sigma'$ in both terms and $l\sigma \leftrightarrow k\sigma'$ in only the direct term, then using the fact that $\langle ij|V|kl \rangle = \langle ji|V|lk \rangle$ we can write the mean-field Hamiltonian as

$$\begin{aligned} H^{HF} &= \sum_{i,\sigma} \epsilon_i c_{i\sigma}^+ c_{i\sigma} + \sum_{i,j,\sigma} \tau_{ij} c_{i\sigma}^+ c_{j\sigma} \\ &+ \sum_{i,j,k,l,\sigma,\sigma'} (\langle ij|V|kl \rangle - \langle ij|V|lk \rangle \delta_{\sigma\sigma'}) \langle c_{j\sigma'}^+ c_{k\sigma'} \rangle c_{i\sigma}^+ c_{l\sigma}. \end{aligned} \quad (2.72)$$

Diagonalizing the mean field Hamiltonian using a *trial* density matrix, we will obtain a set of eigenfunctions and eigenenergies that are used to calculate a new density matrix which will be fed back into the Hamiltonian for another round of diagonalization. By updating the Hamiltonian matrix self consistently, the ground state energy will finally converge. Upon convergence, the final diagonalization procedure will give the Hartree-Fock *quasiparticle* states. Defining the operators $b_{x\sigma}^+/b_{x\sigma}$ creating/annihilating an electron on a Hartree-Fock quasiparticle level x , with eigenvalue ε_x , Eq.2.72 is rewritten as

$$H_{HF} = \sum_{x\sigma} \varepsilon_{x\sigma} b_{x\sigma}^+ b_{x\sigma}. \quad (2.73)$$

The Slater determinant describing the HF ground state of a quantum dot with N-electrons is obtained by placing N electrons on the lowest N/2 quasiparticle levels as depicted

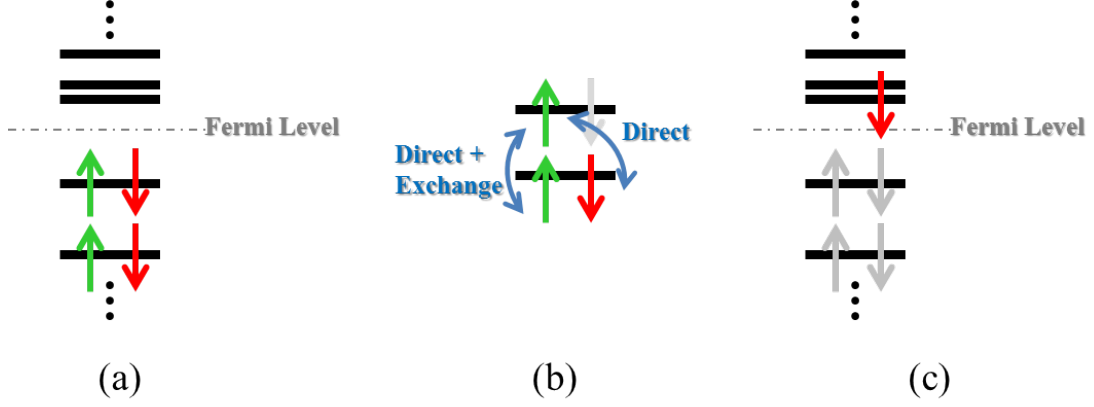


Figure 2.11: (a) Hartree Fock ground state. (b) Direct and exchange interaction of an electron with electrons of a doubly occupied state. (c) electron placed on a HF level feels the presence of a filled valence band

in Fig.2.11(a):

$$|GS_{HF}\rangle = \prod_{x=1}^{N/2} b_{x\uparrow}^+ b_{x\downarrow}^+ |0\rangle. \quad (2.74)$$

HF eigenvalues, corresponding to the quasiparticle states, include the interaction of an electron with all other electrons filling up the valence band. The total interaction energy carried by each HF quasiparticle level is the *self energy*. If an electron is placed in a quasiparticle orbital x , its self energy is expressed as $\Sigma(x, \sigma)$ and explicitly calculated as

$$\Sigma(x, \sigma) = \sum_{i=1}^{N/2} [2\langle ix|V|ix\rangle - \langle ix|V|ix\rangle]. \quad (2.75)$$

The 2 in front of the direct term is due to double occupancy of each orbital; one up and one down electron, and the lack of 2 in front of the exchange term is due to the fact that only electrons with the same spin will have an exchange interaction as depicted in Fig.2.11(b). Thus an electron placed on a HF level x feels the presence of all electrons occupying the valence band (Fig.2.11(c)).

2.1.3.3 Mean Field Hubbard Model

We can use the same ansatz as in Eq.2.70 to obtain a mean-field Hubbard Hamiltonian. The on-site interaction term of the mean-field Hamiltonian given in Eq.2.72 can be written

as

$$\begin{aligned}
H_{ee-on-site}^{MF} &= \sum_{i,\sigma,\sigma'} (\langle ii|V|ii\rangle - \langle ii|V|ii\rangle \delta_{\sigma\sigma'}) \langle c_{i\sigma'}^+ c_{i\sigma'} \rangle c_{i\sigma}^+ c_{i\sigma} \\
&= \sum_{i,\sigma,\sigma'} (\langle ii|V|ii\rangle - \langle ii|V|ii\rangle \delta_{\sigma\sigma'}) \langle n_{i\sigma'} \rangle n_{i\sigma} \\
&= \sum_{i,\sigma} \langle ii|V|ii\rangle \langle n_{i\bar{\sigma}} \rangle n_{i\sigma} \\
&= U \sum_{i,\sigma} \langle n_{i\bar{\sigma}} \rangle n_{i\sigma},
\end{aligned} \tag{2.76}$$

since the terms in the parenthesis cancel each other when $\sigma = \sigma'$. Because we only include on-site interactions between electrons in Hubbard U Hamiltonian, we should treat the electron-ion interactions the same and use the bare t_{ij} element (not τ) ignoring the remaining electron-ion interactions in Eq.2.42.

For the extended Hubbard model, in addition to the on-site element, we include the nearest neighbor direct interaction term;

$$H_{ee-Direct}^{MF} = V \sum_{ij,\sigma} (\langle n_{j\uparrow} \rangle + \langle n_{j\downarrow} \rangle) c_{i\sigma}^+ c_{i\sigma}. \tag{2.77}$$

We also need to reintroduce the corresponding electron-ion interactions that were ignored in the mean-field Hubbard U model. One can do so by calculating electron-electron interactions with respect to deviations from charge neutrality at every site by replacing the mean density $\langle \rho_j \rangle = \langle n_{j\uparrow} \rangle + \langle n_{j\downarrow} \rangle$ with $\langle \rho_i \rangle - 1$.

2.1.3.4 Density Functional Theory

The Density Functional Theory (DFT) has its roots in the Thomas-Fermi Model¹⁶⁵ which is based on the relation between particle density and the many body wavefunctions, such that the ground state energy can be expressed as a functional of the ground state density. Working with the Thomas-Fermi model, Hohenberg and Kohn theorized¹⁶⁶ that the external potential is a unique functional of the density. This allowed the expression of the expectation value of the Hamiltonian in terms of density;

$$E[\rho] = T[\rho] + V_{ext}[\rho] + V_{ee}[\rho], \tag{2.78}$$

with an external potential functional described as

$$V_{ext}[\rho] = \int \hat{V}_{ext}\rho(\vec{r})d\vec{r}. \quad (2.79)$$

Although the form of the external potential is known, the kinetic and the electron-electron interaction functionals are unknown. To solve this problem, Kohn and Sham¹⁶⁷ introduced the idea of non-interacting electrons, each moving under the influence of an effective potential $\hat{V}_{eff}$:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + \hat{V}_{eff}(\vec{r})\right)\psi_i^{KS}(\vec{r}) = \epsilon_i\psi_i^{KS}(\vec{r}), \quad (2.80)$$

which yield $\rho(\vec{r})$ given that:

$$\sum_{i=1}^N |\psi_i^{KS}(\vec{r})|^2 = \rho(\vec{r}). \quad (2.81)$$

The ψ_i^{KS} are the Kohn-Sham orbitals and the effective potential includes the external potential, the Hartree potential and the exchange correlation potential giving:

$$\hat{V}_{eff} = V_{ext} + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|}d\vec{r}' + V_{xc}(\vec{r}). \quad (2.82)$$

This way, the problem of an unknown kinetic and electron-electron interaction terms is reduced to an unknown exchange correlation functional which is much smaller compared to the former. Since the main focus of this thesis is not DFT, I will not give detailed descriptions of various exchange correlation functionals. I will introduce my computational details in Chapter 5.

2.1.4 Tight Binding - Hartree Fock - Configuration Interaction Method

We can use the wavefunctions obtained from the tight-binding procedure to calculate the trial density matrix needed for the mean-field Hartree-Fock Hamiltonian (MF-HF). Starting with the tight binding density, self-consistently updating the MF-HF Hamiltonian we can converge to the HF ground state. We can then introduce the correlations that were ignored in the HF level by going back to Eq.2.44 and rewriting it in HF basis by replacing real space operators $c_{i\sigma}^+$ with HF operators $b_{x\sigma}^+$ as in Eq.2.67:

$$c_{i\sigma}^+ = \sum k_{ix\sigma}^* b_{x\sigma}^+. \quad (2.83)$$

First, we need to express the real space terms τ_{ij} and $\langle ij|V|kl\rangle$ in terms of the HF operators. Inserting Eq.2.67 into Eq.2.73 we get:

$$\begin{aligned} H_{HF} &= \sum_{x,\sigma} \varepsilon_{x,\sigma} \sum_i k_{xi\sigma} c_{i\sigma}^+ \sum_l k_{xl\sigma}^* c_{l\sigma} \\ &= \sum_{i,l,\sigma} \sum_x \varepsilon_{x,\sigma} k_{xi\sigma} k_{xl\sigma}^* c_{i\sigma}^+ c_{l\sigma}, \end{aligned} \quad (2.84)$$

which is equal to the starting mean field Hamiltonian described in terms of real-space operators given in Eq.2.72. Since all onsite energies are equal we can set $\varepsilon_i = 0$ to obtain the equality:

$$\begin{aligned} \sum_{i,j,\sigma} \tau_{ij} c_{i\sigma}^+ c_{j\sigma} + \sum_{ijkl\sigma\sigma'} (\langle ij|V|kl\rangle - \langle ij|V|lk\rangle \delta_{\sigma\sigma'}) \langle c_{j\sigma'}^+ c_{k\sigma'} \rangle c_{i\sigma}^+ c_{l\sigma} \\ = \sum_{i,l,\sigma} \sum_x \varepsilon_{x,\sigma} k_{xi\sigma} k_{xl\sigma}^* c_{i\sigma}^+ c_{l\sigma}. \end{aligned} \quad (2.85)$$

Rearranging this equality, we obtain the hopping element;

$$\begin{aligned} \tau_{il} + \sum_{j,k,\sigma'} (\langle ij|V|kl\rangle - \langle ij|V|lk\rangle \delta_{\sigma\sigma'}) \langle c_{j\sigma'}^+ c_{k\sigma'} \rangle &= \sum_x \varepsilon_{x,\sigma} k_{xi\sigma} k_{xl\sigma}^*, \\ \tau_{il} &= \sum_x \varepsilon_{x,\sigma} k_{xi\sigma} k_{xl\sigma}^* - \sum_{j,k,\sigma'} (\langle ij|V|kl\rangle - \langle ij|V|lk\rangle \delta_{\sigma\sigma'}) \langle c_{j\sigma'}^+ c_{k\sigma'} \rangle \\ \tau_{il} &= \sum_x \varepsilon_{x,\sigma} k_{xi\sigma} k_{xl\sigma}^* - V_{il\sigma}^{MF}, \end{aligned} \quad (2.86)$$

where we introduced the mean-field interaction term,

$$V_{il\sigma}^{MF} = \sum_{j,k,\sigma'} (\langle ij|V|kl\rangle - \langle ij|V|lk\rangle \delta_{\sigma\sigma'}) \langle c_{j\sigma'}^+ c_{k\sigma'} \rangle. \quad (2.87)$$

Inserting Eq.2.86 into the microscopic Hamiltonian given in Eq.2.44 we obtain:

$$H = \sum_{i,l,\sigma} \left(\sum_x \varepsilon_{x\sigma} k_{xi\sigma} k_{xl\sigma}^* - V_{il\sigma}^{MF} \right) c_{i\sigma}^+ c_{l\sigma} + \frac{1}{2} \sum_{i,j,k,l,\sigma\sigma'} \langle ij|V|kl\rangle c_{i\sigma}^+ c_{j\sigma'}^+ c_{k\sigma'} c_{l\sigma}. \quad (2.88)$$

For now, while working on the single particle part, I will name $\frac{1}{2} \sum \langle ij|V|kl\rangle c_{i\sigma}^+ c_{j\sigma'}^+ c_{k\sigma'} c_{l\sigma} \rightarrow V_{ee}$ and use Eq.2.83 to rotate the single particle part from real-space to HF basis,

$$H = \sum_{i,l,\sigma} \left(\sum_x \varepsilon_{x\sigma} k_{xi\sigma} k_{xl\sigma}^* - V_{il\sigma}^{MF} \right) \sum_{x'} k_{ix'\sigma}^* b_{x'\sigma}^+ \sum_y k_{ly\sigma} b_{y\sigma} + V_{ee}$$

$$\begin{aligned}
&= \sum_{i,l,\sigma} \sum_{x',y} \left(\sum_x \varepsilon_{x\sigma} k_{ix'\sigma}^* k_{ly\sigma} k_{xi\sigma} k_{xl\sigma}^* - k_{ix'\sigma}^* k_{ly\sigma} V_{il\sigma}^{MF} \right) b_{x'\sigma}^+ b_{y\sigma} + V_{ee} \\
&= \sum_{x',y,\sigma} \left(\sum_x \varepsilon_{x\sigma} \sum_i |k_{ii}|^2 \delta_{x,x'} \sum_l |k_{ll}|^2 \delta_{y,x} \right) b_{x'\sigma}^+ b_{y\sigma} \\
&\quad - \sum_{x',y,\sigma} \sum_{il} (k_{ix'\sigma}^* k_{ly\sigma} V_{il\sigma}^{MF}) b_{x'\sigma}^+ b_{y\sigma} + V_{ee} \\
&= \sum_{x,\sigma} \varepsilon_{x\sigma} b_{x\sigma}^+ b_{x\sigma} - \sum_{x',y,\sigma} \sum_{i,l} k_{ix'\sigma}^* k_{ly\sigma} V_{il\sigma}^{MF} b_{x'\sigma}^+ b_{y\sigma} + V_{ee}. \tag{2.89}
\end{aligned}$$

Following the same basis-transformation for the interaction part V_{ee} , in the HF basis the CI-Hamiltonian Eq.2.44 takes the following form:

$$H = \sum_{x\sigma} \varepsilon_{x\sigma} b_{x\sigma}^+ b_{x\sigma} + \frac{1}{2} \sum_{x,y,z,r\sigma\sigma'} \langle xy|V|zr\rangle b_{x\sigma}^+ b_{y\sigma'}^+ b_{z\sigma} b_{r\sigma'} - \sum_{xy\sigma} V_{xy\sigma}^{MF} b_{x\sigma}^+ b_{y\sigma}. \tag{2.90}$$

Now let us concentrate on the mean-field term $H^{MF} = \sum_{xy\sigma} V_{xy\sigma}^{MF} b_{x\sigma}^+ b_{y\sigma}$ and further simplify the mean-field interaction element,

$$\begin{aligned}
V_{xy\sigma}^{MF} &= \sum_{i,l} k_{ix\sigma}^* k_{ly\sigma} V_{il\sigma}^{MF} \\
&= \sum_{i,l} k_{ix\sigma}^* k_{ly\sigma} \sum_{j,k,\sigma'} (\langle ij|V|kl\rangle - \delta_{\sigma\sigma'} \langle ij|V|lk\rangle) \langle c_{j\sigma'}^+ c_{k\sigma'} \rangle. \tag{2.91}
\end{aligned}$$

The density matrix $\langle c_{j\sigma'}^+ c_{k\sigma'} \rangle$, can be explicitly evaluated with respect to the ground state given in Eq.2.74 as

$$\begin{aligned}
\langle c_{j\sigma'}^+ c_{k\sigma'} \rangle &= \langle GS | c_{j\sigma'}^+ c_{k\sigma'} | GS \rangle \\
&= \langle GS | \sum_z^N k_{jz\sigma'}^* b_{z\sigma'}^+ \sum_r^N k_{kr\sigma'} b_{r\sigma'} | GS \rangle \\
&= \sum_{z,r}^N k_{jz\sigma'}^* k_{kr\sigma'} \langle GS | b_{z\sigma'}^+ b_{r\sigma'} | GS \rangle \\
&= \sum_{z,r}^{N_{fermi}} k_{jz\sigma'}^* k_{kr\sigma'} n_{z\sigma'}^{gs} \delta_{rz} \\
&= \sum_z^{N_{fermi}} k_{jz\sigma'}^* k_{kz\sigma'} n_{z\sigma'}^{gs}. \tag{2.92}
\end{aligned}$$

It can be put back into the mean field term to fully rotate it into the HF-basis to obtain:

$$\begin{aligned}
V_{xy\sigma}^{MF} &= \sum_{i,l} k_{ix\sigma}^* k_{ly\sigma} \sum_{j,k,\sigma'} (\langle ij|V|kl\rangle - \delta_{\sigma\sigma'} \langle ij|V|lk\rangle) \sum_z^{N_{fermi}} k_{jz\sigma'}^* k_{kz\sigma'} n_{z\sigma'}^{gs} \\
&= \sum_{z,\sigma'}^{N_{fermi}} n_{z\sigma'}^{gs} \sum_{i,l,j,k} k_{ix\sigma}^* k_{jz\sigma'}^* k_{kz\sigma'} k_{ly\sigma} (\langle ij|V|kl\rangle - \delta_{\sigma\sigma'} \langle ij|V|lk\rangle) \\
&= \sum_{z,\sigma'}^{N_{fermi}} n_{z\sigma'}^{gs} (\langle xz|V|zy\rangle - \delta_{\sigma\sigma'} \langle xz|V|yz\rangle). \tag{2.93}
\end{aligned}$$

Electron-Hole Language

So far we have been working in the electron language only. But with the size of the quantum dot, the number of electrons also increases and dealing with all of the electrons that fill up the valence band becomes cumbersome. Instead, we can concentrate on the deviations from the HF ground state. If an electron is moved from the valence band to the conduction band, there will be a hole left behind. Then, concentrating on only the conduction band electrons and the holes left in the valence band, the interaction term V_{ee} can be rewritten in the electron-hole language. In this language, we can divide the interaction term V_{ee} into four; First is the electron-electron interaction term, for which I only mean the interaction of electrons that occupy the conduction band $V_{ee,c}$. The second term will be the interaction of holes in the valence band $V_{ee,v}$. The third term is the interaction between electrons and holes $V_{e,c;e,v}$ and finally the fourth term is the scattering term that turns an electron(hole) into a hole(electron) $V_{ee,s}$. Within the electron-hole language, we will ignore the scattering term. When divided into the above described terms, V_{ee} is written as follows:

$$\begin{aligned}
V_{ee} &= V_{ee,v} + V_{ee,c} + V_{e,c;e,v} \\
V_{ee} &= \frac{1}{2} \sum_{xyzr\sigma\sigma'} \langle xy|V|zr\rangle b_{x\sigma}^+ b_{y\sigma'}^+ b_{z\sigma'} b_{r\sigma} \\
&\quad + \frac{1}{2} \sum_{x'y'z'r'\sigma\sigma'} \langle x'y'|V|z'r'\rangle b_{x'\sigma}^+ b_{y'\sigma'}^+ b_{z'\sigma'} b_{r'\sigma} \\
&\quad + \sum_{xy'z'r\sigma\sigma'} (\langle xy'|V|z'r\rangle - \delta_{\sigma,\sigma'} \langle xy'|V|zr'\rangle) b_{x\sigma}^+ b_{y'\sigma'}^+ b_{z'\sigma'} b_{r\sigma}, \tag{2.94}
\end{aligned}$$

where I used x, y, z, r for valence, x', y', z', r' for conduction band states. Now, we will rearrange the operators in these terms so that some will cancel each other out. Let us start with the fermionic operators in $V_{ee,v}$ (similarly for $V_{ee,c}$). Using the fermionic

commutation rules we can rearrange these operators as

$$\begin{aligned}
b_{x\sigma}^+ b_{y\sigma'}^+ b_{z\sigma'} b_{r\sigma} &= b_{x\sigma}^+ (\delta_{zy} - b_{z\sigma'} b_{y\sigma'}^+) b_{r\sigma} \\
&= \delta_{zy} b_{x\sigma}^+ b_{r\sigma} - b_{x\sigma}^+ b_{z\sigma'} b_{y\sigma'}^+ b_{r\sigma} \\
&= \delta_{zy} b_{x\sigma}^+ b_{r\sigma} - (\delta_{xz} \delta_{\sigma\sigma'} - b_{z\sigma'} b_{x\sigma}^+) (\delta_{yr} \delta_{\sigma\sigma'} - b_{r\sigma} b_{y\sigma'}^+). \tag{2.95}
\end{aligned}$$

Now multiplying the contents of the two parentheses,

$$\begin{aligned}
&= \delta_{zy} b_{x\sigma}^+ b_{r\sigma} - (\delta_{xz} \delta_{\sigma\sigma'} \delta_{yr} \delta_{\sigma\sigma'} - \delta_{yr} \delta_{\sigma\sigma'} b_{z\sigma'} b_{x\sigma}^+ \\
&\quad - \delta_{xz} \delta_{\sigma\sigma'} b_{r\sigma} b_{y\sigma'}^+ + b_{z\sigma'} b_{x\sigma}^+ b_{r\sigma} b_{y\sigma'}^+) \\
&= \delta_{zy} b_{x\sigma}^+ b_{r\sigma} - (\delta_{xz} \delta_{\sigma\sigma'} \delta_{yr} \delta_{\sigma\sigma'} - \delta_{yr} \delta_{\sigma\sigma'} b_{z\sigma'} b_{x\sigma}^+ \\
&\quad - \delta_{xz} \delta_{\sigma\sigma'} (\delta_{ry} - b_{y\sigma'}^+ b_{r\sigma}) + b_{z\sigma'} (\delta_{xr} - b_{r\sigma} b_{x\sigma}^+) b_{y\sigma'}^+, \tag{2.96}
\end{aligned}$$

and renaming some of the indices before regrouping the terms, $V_{ee,v}$ becomes:

$$V_{ee,v} = \sum_{xr\sigma} (\langle xy|V|yr\rangle - \delta_{\sigma\sigma'} \langle xy|V|ry\rangle) b_{x\sigma}^+ b_{r\sigma} + \frac{1}{2} \sum_{xyzr\sigma\sigma'} \langle xy|V|zr\rangle b_{z\sigma'} b_{r\sigma} b_{x\sigma}^+ b_{y\sigma'}^+. \tag{2.97}$$

Similarly, I can rearrange the operators of $V_{e,c;e,v}$ using the fermionic commutation rules,

$$\begin{aligned}
b_{x\sigma}^+ b_{y'\sigma'}^+ b_{z'\sigma'} b_{r\sigma} &= b_{y'\sigma'}^+ b_{x\sigma}^+ b_{r\sigma} b_{z'\sigma'} \\
&= b_{y'\sigma'}^+ (\delta_{xr} - b_{r\sigma} b_{x\sigma}^+) b_{z'\sigma'} \\
&= b_{y'\sigma'}^+ b_{z'\sigma'} \delta_{xr} - b_{y'\sigma'}^+ b_{r\sigma} b_{x\sigma}^+ b_{z'\sigma'}, \tag{2.98}
\end{aligned}$$

and replace $z' \rightarrow y'$, $y' \rightarrow x'$ in the first term to obtain:

$$\begin{aligned}
V_{e,c;e,v} &= \sum_{zx'y'\sigma\sigma'} (\langle zx'|V|y'z\rangle - \delta_{\sigma\sigma'} \langle zx'|V|zy'\rangle) b_{x'\sigma'}^+ b_{y'\sigma'} \\
&\quad - \sum_{xy'z'r\sigma\sigma'} (\langle xy'|V|z'r\rangle - \delta_{\sigma\sigma'} \langle xy'|V|rz'\rangle) b_{y'\sigma'}^+ b_{r\sigma} b_{x\sigma}^+ b_{z'\sigma'}. \tag{2.99}
\end{aligned}$$

Putting all this back into Eq.2.90, the single particle terms in $V_{ee,v}$ and $V_{e,c;e,v}$ cancel the mean field term $H^{MF} = \sum_{xy\sigma} V_{xy\sigma}^{MF} b_{x\sigma}^+ b_{y\sigma}$. Then the CI-Hamiltonian Eq.2.90 becomes:

$$\begin{aligned}
H_{QD} &= \sum_{\alpha=0,\sigma}^N \varepsilon_{\alpha\sigma} b_{\alpha\sigma}^+ b_{\alpha\sigma} \\
&\quad + \frac{1}{2} \sum_{x'y'z'r'\sigma\sigma'} \langle x'y'|V|z'r'\rangle b_{x'\sigma}^+ b_{y'\sigma'}^+ b_{z'\sigma'} b_{r'\sigma}
\end{aligned}$$

$$\begin{aligned}
& + \frac{1}{2} \sum_{xyzr\sigma\sigma'} \langle xy|V|zr\rangle b_{z\sigma'} b_{r\sigma} b_{x\sigma}^+ b_{y\sigma'}^+ \\
& - \sum_{xy'z'r\sigma\sigma'} (\langle xy'|V|z'r\rangle - \delta_{\sigma\sigma'} \langle xy'|V|rz'\rangle) b_{y'\sigma'}^+ b_{r\sigma} b_{x\sigma}^+ b_{z'\sigma'}. \quad (2.100)
\end{aligned}$$

All of this was to separate the treatment of electrons of the valence and the conduction band. To complement that I will now introduce the hole operator $h_{p\bar{\sigma}} = b_{p\sigma}^+$ to rewrite the CI-Hamiltonian in the electron-hole language as

$$\begin{aligned}
H &= \sum_{x'\sigma} \varepsilon_{x'} b_{x'\sigma}^+ b_{x'\sigma} + \sum_{x\sigma} \varepsilon_{x\sigma} h_{x\sigma} h_{x\sigma}^+ \\
&+ \frac{1}{2} \sum_{x'y'z'r'\sigma\sigma'} \langle x'y'|V|z'r'\rangle b_{x'\sigma}^+ b_{y'\sigma'}^+ b_{z'\sigma'} b_{r'\sigma} \\
&+ \frac{1}{2} \sum_{xyzr\sigma\sigma'} \langle zr|V|xy\rangle h_{x\sigma}^+ h_{y\sigma'}^+ h_{z\sigma} h_{r\sigma} \\
&- \sum_{xy'z'r\sigma\sigma'} (\langle xy'|V|z'r\rangle - (1 - \delta_{\sigma\sigma'}) \langle xy'|V|rz'\rangle) b_{y'\sigma}^+ h_{r\sigma'}^+ h_{x\sigma} b_{z'\sigma'}. \quad (2.101)
\end{aligned}$$

Especially for a subspace that contains the ground state and single pair excitations, this Hamiltonian will help reduce the complexity of the problem and aid in visualisation of the solution.

2.2 Optical Properties

As illustrated earlier in this chapter, the band-gap of graphene quantum dots can be controlled by size, edge and shape engineering. One can tune the band-gap from THz to UV, allowing GQDs to be used in multitudes of photonics applications. In order to understand the optical properties of GQDs we need to introduce light-matter interactions in the single particle Hamiltonian. The single particle Hamiltonian that describes an electron moving in an ionic potential,

$$H_o = \frac{\vec{p}^2}{2m} + \sum_i V_{ion}(R_i), \quad (2.102)$$

in the presence of an electromagnetic field becomes:

$$H = \frac{(\vec{p} - q\vec{A})^2}{2m} + \sum_i V_{ion}(R_i). \quad (2.103)$$

Here $\vec{A}$ is a vector potential that satisfies the Coulomb Gauge. Expanding the first term, the Hamiltonian is written as

$$H = \frac{\vec{p}^2}{2m} + \sum_i V_{ion}(R_i) - \frac{q}{2m} (\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p}) + q^2 \frac{A^2}{2m}. \quad (2.104)$$

The first two terms of this Hamiltonian are nothing but the single particle Hamiltonian H_o . Then the light-matter interactions can be described by the interaction Hamiltonian,

$$H_{int} = -\frac{q}{2m} (\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p}) + q^2 \frac{A^2}{2m}. \quad (2.105)$$

Within the weak field approximation, we will neglect the contributions from the second term with A^2 . Rewriting $q \rightarrow -e$ as the charge of an electron, the interaction term becomes:

$$H_{int} = \frac{e}{m} \vec{A} \cdot \vec{p}, \quad (2.106)$$

where we have used the fact that $\vec{p} = -i\hbar\vec{\nabla}$ and $(\vec{\nabla} \cdot \vec{A}) = (\vec{A} \cdot \vec{\nabla})$ in Coulomb Gauge ($\vec{\nabla} \cdot \vec{A} = 0$).

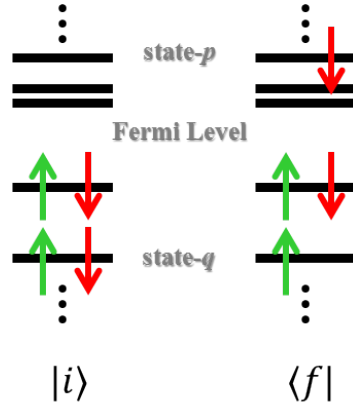


Figure 2.12: Initial and final states after absorption of a photon of energy $E_f - E_i$.

2.2.1 Absorption/Emission

The absorption/emission spectrum is obtained from Fermi's golden rule:

$$A(\omega) = \sum_{i,f} W_i |\langle f | H_{int} | i \rangle|^2 \delta(E_f - E_i \pm \omega), \quad (2.107)$$

where E_i, E_f are, respectively, the energies of the initial and the final state participating in the excitation process, $-\omega(+\omega)$ is the energy of the absorbed (emitted) photon and W_i is the occupation probability of the initial state. We can evaluate the term $\langle f|H_{int}|i\rangle$ by writing out a vector potential that satisfies the Coulomb gauge for a plane wave propagating along $\vec{k}$,

$$\vec{A} = A_0 \hat{e} \left[e^{i\vec{k}\cdot\vec{r}-i\omega t} + e^{-i\vec{k}\cdot\vec{r}+i\omega t} \right], \quad (2.108)$$

where $\hat{e}$ is the polarization of the light. We see that the term with $e^{-i\omega t}$ is responsible for absorption while the term with $e^{+i\omega t}$ is responsible for emission.

Concentrating on absorption, we can expand the matrix elements of the interaction Hamiltonian as

$$\begin{aligned} \langle f|H_{int}|i\rangle &= \langle f|\vec{A} \cdot \vec{p}|i\rangle \frac{e}{m} \\ &= \frac{e}{m} A_0 \hat{e} \langle f|e^{i\vec{k}\cdot\vec{r}} \cdot \vec{p}|i\rangle. \end{aligned} \quad (2.109)$$

Within the dipole approximation, assuming the wavelength of the light absorbed during the transition is much greater than the size of the molecule, we can approximate $e^{i\vec{k}\cdot\vec{r}} \simeq 1$ so that Eq.2.109 becomes:

$$\langle f|H_{int}|i\rangle = \frac{e}{m} A_0 \hat{e} \langle f|\vec{p}|i\rangle. \quad (2.110)$$

Using $[\hat{H}_0, \hat{r}] = -\frac{i\hbar}{m} \hat{p}$ we can rewrite the interaction Hamiltonian as

$$\begin{aligned} \langle f|H_{int}|i\rangle &= \frac{e}{m} A_0 \hat{e} \left(-\frac{m}{i\hbar}\right) \langle f|\hat{H}_0 \vec{r} - \vec{r} \hat{H}_0|i\rangle \\ &= i \frac{e}{\hbar} A_0 \hat{e} \langle f|E_f \vec{r} - \vec{r} E_i|i\rangle \\ &= i(\omega_{fi}) A_0 \hat{e} \cdot \langle f|e\vec{r}|i\rangle \\ &= i(\omega_{fi}) A_0 \hat{e} \cdot \vec{d}(f, i), \end{aligned} \quad (2.111)$$

where $\vec{d}(f, i) = \langle f|e\vec{r}|i\rangle$ is the dipole element that is evaluated in the basis of atomic p_z orbitals $\phi(\vec{r}-\vec{R}_i)$ and $\omega_{fi} = (E_f - E_i)/\hbar$. We can evaluate the dipole element in real-space starting with,

$$\langle f|\vec{r}|i\rangle = \int d\vec{r} \phi^*(\vec{r} - \vec{R}_f) \vec{r} \phi(\vec{r} - \vec{R}_i). \quad (2.112)$$

Replacing $\vec{r} \rightarrow \vec{r} + \vec{R}_f$ on right hand side, we get:

$$\begin{aligned} \langle f|\vec{r}|i\rangle &= \int d\vec{r} \phi^*(\vec{r})(\vec{r} + \vec{R}_f) \phi(\vec{r} - (\vec{R}_i - \vec{R}_f)) \\ &= \int d\vec{r} \phi^*(\vec{r}) \vec{r} \phi(\vec{r} - (\vec{R}_i - \vec{R}_f)) \end{aligned}$$

$$+\vec{R}_f \int d\vec{r} \phi^*(\vec{r}) \phi(\vec{r} - (\vec{R}_i - \vec{R}_f)). \quad (2.113)$$

The first term is non-zero only if $f \neq i$. In the evaluation of the second term, we only include nearest and next nearest neighbouring f, i terms and arrive at the following expression

$$\langle f | \vec{r} | i \rangle = D(\hat{R}_i - \hat{R}_f) \delta_{\langle fi \rangle} + d(\hat{R}_i - \hat{R}_f) \delta_{\langle\langle fi \rangle\rangle} + \vec{R}_i \delta_{fi}, \quad (2.114)$$

where the coefficients $D = \int d\vec{r} \phi_z^*(\vec{r}) \vec{r} \phi_z(\vec{r} - \vec{R}_{\langle fi \rangle}) = 0.343542$ a.u. and $d = \int d\vec{r} \phi_z^*(\vec{r}) \vec{r} \phi_z(\vec{r} - \vec{R}_{\langle\langle fi \rangle\rangle}) = 0.0873$ a.u. are computed using the Slater-type p_z orbitals for nearest-neighbour (NN, $\langle i, j \rangle$) and next-nearest-neighbour (NNN, $\langle\langle i, j \rangle\rangle$) orbitals, respectively and $\hat{R}_i$ are unit vectors. We can now look at the dipole element between N-electron configurations. Typically for absorption, the initial state will be that of a lower number of pair excitations, while the final one will have a higher number. To generalize the derivation let us study the configurations created in the HF basis. We can define the polarization operator $\hat{P}^+ = \sum_{pq\sigma} d(p, q) b_{p\sigma}^+ b_{q\sigma}$ that creates a single pair excitation by moving an electron from HF level q to HF level p while annihilating a photon as depicted in Fig.2.12. Since the quasiparticle states are linear superpositions of atomic orbitals as in Eq.2.67, the dipole element $d(p, q)$ can be expanded in terms of the real space orbitals to be rewritten as

$$\begin{aligned} d(p, q) &= e \langle p | \vec{r} | q \rangle \\ &= \sum_{l=1}^N \sum_{j=1}^N k_{p,l}^* k_{q,j} \langle l | e \vec{r} | j \rangle. \end{aligned} \quad (2.115)$$

2.2.2 Excitations

In order to be able to calculate the absorption spectrum, we need the correlated ground and excited states. As mentioned before, the HF ground state is only the ground state for the mean field Hamiltonian. Once we rotate the full Hamiltonian into the HF basis, we obtain the non-diagonal Hamiltonian given in Eq.2.90. This Hamiltonian acts on the basis of excitations, and it is diagonalized to obtain the correlated ground and excited states. In this section I will explain how one can create excitations out of the ground state, calculate the energy of these excitations and finally obtain correlated ground and excited states that are expressed as linear combinations of configurations.

Excitations (Fig.2.13) are created from the HF ground state $|GS_{HF}\rangle$ and classified according to the number of electron-hole pairs as depicted in Fig.2.14. Keeping the total number of electrons constant and conserving the total projection of spin, we generate single-pair excitations, $|m \uparrow, n \uparrow\rangle = b_{m\uparrow}^+ b_{n\uparrow} |GS\rangle$, where the HF orbital m lies in the conduction band, and the HF orbital n - in the valence band. We can also create single-

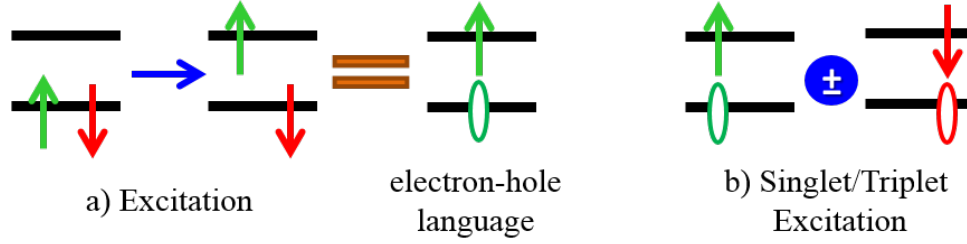


Figure 2.13: a) Spin excitation. The spin up electron is moved from the valence band to the conduction band. Also shown in electron-hole language in the last column. b) Spin singlet/triplet excitations (+/-), depicted in electron-hole language.

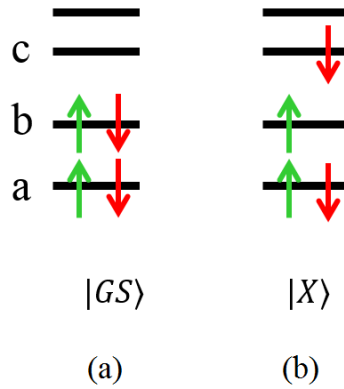


Figure 2.14: (a) Hartree Fock ground state configuration of four electrons on four HF quasiparticle levels (b) a single pair excitation out of the HF ground state

pair excitations for spin down quasiparticles the same way.

2.2.2.1 Vertex Corrections

We have already derived the configuration interaction Hamiltonian in electron and electron-hole languages in Eq.2.90 and Eq.2.101, respectively. These Hamiltonians are written in the basis of configurations that are created out of the HF quasiparticle levels. In order to obtain the correlated ground and excited states we would need to calculate every matrix element of the Hamiltonian by acting with it on every configuration. We can calculate the energies of the configurations with respect to the HF ground state energy that we have already calculated in the MF-HF step.

The two-site, two-electron model is not large enough to properly describe the CI Hamiltonian. For that reason, let us work with a 4-site, 4-electron model and calculate the diagonal elements of the ground state and an excited state. I will demonstrate the same calculation twice, (1) assuming that levels shown in Fig.2.14 are single particle levels ob-

tained from the tight binding Hamiltonian, (2) assuming the levels are HF quasiparticle levels.

(1). Starting with the first assumption, the configurations created out of these levels will be described by the following Hamiltonian:

$$H = \sum_{i\sigma} \epsilon_{i\sigma} c_{i\sigma}^+ c_{i\sigma} + \sum_{i>j, k>l, \sigma\sigma'} (\langle ij|V|kl\rangle - \langle ij|V|lk\rangle \delta_{\sigma\sigma'}) c_{i\sigma}^+ c_{j\sigma'}^+ c_{k\sigma'} c_{l\sigma}, \quad (2.116)$$

where ϵ_i are the single particle energies obtained from the tight-binding Hamiltonian, $c_{i\sigma}^+$ are creation operators acting on single particle orbitals i and $\langle ij|V|kl\rangle$ represent the interactions between electrons on single particle levels. The energy of the ground state depicted in Fig.2.14(a) is calculated as

$$\begin{aligned} \langle GS|H|GS\rangle &= \epsilon_{a\uparrow} + \epsilon_{a\downarrow} + \epsilon_{b\uparrow} + \epsilon_{b\downarrow} \\ &+ \langle aa|V|aa\rangle \\ &+ 2\langle ab|V|ba\rangle - \langle ab|V|ab\rangle + 2\langle ab|V|ba\rangle - \langle ab|V|ab\rangle \\ &+ \langle bb|V|bb\rangle. \end{aligned} \quad (2.117)$$

Using the definition of self energy (Eq.2.75) and the fact that spin up and down eigenvalues are degenerate, the ground state energy is expressed as

$$\langle GS|H|GS\rangle = 2\epsilon_a + 2\epsilon_b + \Sigma(a) + \Sigma(b), \quad (2.118)$$

where $\Sigma(a) = \langle aa|V|aa\rangle + 2\langle ab|V|ba\rangle - \langle ab|V|ab\rangle$ and $\Sigma(b) = \langle bb|V|bb\rangle + 2\langle ab|V|ba\rangle - \langle ab|V|ab\rangle$. Similarly, the energy of the excited state shown in Fig.2.14(b) is calculated as

$$\begin{aligned} \langle X|H|X\rangle &= \epsilon_{a\uparrow} + \epsilon_{a\downarrow} + \epsilon_{b\uparrow} + \epsilon_{c\downarrow} \\ &+ \langle aa|V|aa\rangle \\ &+ 2\langle ab|V|ba\rangle - \langle ab|V|ab\rangle \\ &+ 2\langle ac|V|ca\rangle - \langle ac|V|ac\rangle \\ &+ \langle bc|V|cb\rangle. \end{aligned} \quad (2.119)$$

Using $\Sigma(c) = 2\langle ac|V|ca\rangle - \langle ac|V|ac\rangle + 2\langle bc|V|cb\rangle - \langle bc|V|bc\rangle$ the diagonal matrix element of the Hamiltonian corresponding to the single excitation shown in the Fig.2.14(b) becomes:

$$\langle X|H|X\rangle = \epsilon_{a\uparrow} + \epsilon_{a\downarrow} + \epsilon_{b\uparrow} + \epsilon_{c\downarrow} + \Sigma(a) + \Sigma(c) - \langle bc|V|cb\rangle + \langle bc|V|bc\rangle. \quad (2.120)$$

Combining the two, the energy of the excited state with respect to the ground state is

obtained as

$$\langle X|H|X\rangle - \langle GS|H|GS\rangle = (\epsilon_{c\downarrow} + \Sigma(c)) - (\epsilon_{b\downarrow} + \Sigma(b)) - \langle bc|V|cb\rangle + \langle bc|V|bc\rangle. \quad (2.121)$$

Adding self energies, we end up over counting the interactions between the down electrons on orbital b and orbital c . The terms $-\langle bc|V|cb\rangle + \langle bc|V|bc\rangle$ that correct this over-counting are called the *vertex corrections*.

(2). Now let us do the same calculation, this time assuming these orbitals are HF orbitals with energies ε_x . The configurations shown in Fig.2.14 obey the Eq.2.90 Hamiltonian with $b_{x\sigma}^+$ creating a HF quasiparticle on HF orbital x . Then the diagonal element of the Hamiltonian corresponding to the ground state energy is expressed as follows:

$$\begin{aligned} \langle GS|H|GS\rangle &= \varepsilon_{a\uparrow} + \varepsilon_{a\downarrow} + \varepsilon_{b\uparrow} + \varepsilon_{b\downarrow} \\ &\quad + \langle aa|V|aa\rangle \\ &\quad + 2\langle ab|V|ba\rangle - \langle ab|V|ab\rangle + 2\langle ab|V|ba\rangle - \langle ab|V|ab\rangle \\ &\quad + \langle bb|V|bb\rangle \\ &\quad - V_{aa\uparrow}^{MF} - V_{aa\downarrow}^{MF} - V_{bb\uparrow}^{MF} - V_{bb\downarrow}^{MF}. \end{aligned} \quad (2.122)$$

Since we are calculating the diagonal elements, only summations obeying δ_{xy} are non-zero in the mean field term. For our four electrons on four sites model we explicitly write the mean-field elements $V_{xx\sigma}^{MF}$, as

$$\begin{aligned} V_{xx\sigma}^{MF} &= \langle xa|V|ax\rangle - \delta_{\sigma\uparrow}\langle xa|V|xa\rangle \\ &\quad + \langle xa|V|ax\rangle - \delta_{\sigma\downarrow}\langle xa|V|xa\rangle \\ &\quad + \langle xb|V|bx\rangle - \delta_{\sigma\uparrow}\langle xb|V|xb\rangle \\ &\quad + \langle xb|V|bx\rangle - \delta_{\sigma\downarrow}\langle xb|V|xb\rangle. \end{aligned} \quad (2.123)$$

Using this expression we can calculate every mean field term appearing in Eq.2.122 as

$$\begin{aligned} V_{aa\downarrow}^{MF} &= \langle aa|V|aa\rangle \\ &\quad + 2\langle ab|V|ba\rangle - \langle ab|V|ab\rangle, \\ V_{aa\uparrow}^{MF} &= \langle aa|V|aa\rangle \\ &\quad + 2\langle ab|V|ba\rangle - \langle ab|V|ab\rangle, \\ V_{bb\uparrow}^{MF} &= 2\langle ba|V|ab\rangle - \langle ba|V|ba\rangle \\ &\quad + \langle bb|V|bb\rangle, \\ V_{bb\downarrow}^{MF} &= 2\langle ba|V|ab\rangle - \langle ba|V|ba\rangle \end{aligned}$$

$$+\langle bb|V|bb\rangle. \quad (2.124)$$

Finally, adding it all up,

$$\begin{aligned} \langle GS|H|GS\rangle &= \varepsilon_{a\uparrow} + \varepsilon_{a\downarrow} + \varepsilon_{b\uparrow} + \varepsilon_{b\downarrow} \\ &\quad + \langle aa|V|aa\rangle \\ &\quad + 2\langle ab|V|ba\rangle - \langle ab|V|ab\rangle + 2\langle ab|V|ba\rangle - \langle ab|V|ab\rangle \\ &\quad + \langle bb|V|bb\rangle \\ &\quad - 2\langle aa|V|aa\rangle - 2\langle bb|V|bb\rangle - 8\langle ab|V|ba\rangle + 4\langle ab|V|ab\rangle, \end{aligned} \quad (2.125)$$

and collecting the terms, the diagonal matrix element of the Hamiltonian corresponding to the ground state, in terms of HF quasiparticle levels is calculated as

$$\begin{aligned} \langle GS|H|GS\rangle &= 2\varepsilon_a + 2\varepsilon_b \\ &\quad - \langle aa|V|aa\rangle - 2\langle ab|V|ba\rangle + \langle ab|V|ab\rangle \\ &\quad - \langle bb|V|bb\rangle - 2\langle ab|V|ba\rangle + \langle ab|V|ab\rangle, \\ \langle GS|H|GS\rangle &= 2\varepsilon_a + 2\varepsilon_b - \Sigma(a) - \Sigma(b). \end{aligned} \quad (2.126)$$

Following the same steps for the excited state we can write the matrix element as

$$\begin{aligned} \langle X|H|X\rangle &= \varepsilon_{a\uparrow} + \varepsilon_{a\downarrow} + \varepsilon_{b\downarrow} + \varepsilon_{c\uparrow} \\ &\quad + \langle aa|V|aa\rangle + 2\langle ab|V|ba\rangle - \langle ab|V|ab\rangle \\ &\quad + 2\langle ac|V|ca\rangle - \langle ac|V|ac\rangle \\ &\quad + \langle bc|V|cb\rangle \\ &\quad - V_{aa\uparrow}^{MF} - V_{aa\downarrow}^{MF} - V_{bb\downarrow}^{MF} - V_{cc\uparrow}^{MF}. \end{aligned} \quad (2.127)$$

Again, using Eq.2.123 to calculate the mean-field terms,

$$\begin{aligned} V_{aa\downarrow}^{MF} &= \langle aa|V|aa\rangle \\ &\quad + 2\langle ab|V|ba\rangle - \langle ab|V|ab\rangle, \\ V_{aa\uparrow}^{MF} &= \langle aa|V|aa\rangle \\ &\quad + 2\langle ab|V|ba\rangle - \langle ab|V|ab\rangle, \\ V_{bb\downarrow}^{MF} &= 2\langle ba|V|ab\rangle - \langle ba|V|ba\rangle \\ &\quad + \langle bb|V|bb\rangle, \\ V_{cc\uparrow}^{MF} &= 2\langle ca|V|ac\rangle - \langle ca|V|ca\rangle \end{aligned}$$

$$+2\langle cb|V|bc\rangle - \langle cb|V|cb\rangle, \quad (2.128)$$

the matrix element for the excited state becomes:

$$\begin{aligned} \langle X|H|X\rangle &= 2\varepsilon_a + \varepsilon_b + \varepsilon_c \\ &\quad - \langle aa|V|aa\rangle - 4\langle ab|V|ba\rangle + 2\langle ab|V|ab\rangle - \langle bb|V|bb\rangle \\ &\quad - \langle bc|V|cb\rangle + \langle cb|V|cb\rangle, \\ \langle X|H|X\rangle &= 2\varepsilon_a + \varepsilon_b + \varepsilon_c \\ &\quad - \Sigma(a) - \Sigma(b) - \langle bc|V|cb\rangle + \langle cb|V|cb\rangle. \end{aligned} \quad (2.129)$$

Collecting the terms that make up the self energies, the Hamiltonian matrix element for the excited state with respect to the ground state energy is written as

$$\langle X|H|X\rangle - \langle GS|H|GS\rangle = \varepsilon_c - \varepsilon_b - \langle bc|V|cb\rangle + \langle cb|V|bc\rangle. \quad (2.130)$$

This is the same expression as Eq.2.121 since HF quasiparticle energies already include self energies.

There is a simpler way of calculating the matrix elements for single particle excitations. I will outline these steps below for a system with N electrons. As described in section 2.1.3.2, the $S_z = 0$ ground state is obtained by filling up the valence band with up and down electrons Eq.2.74. Using the definition of self energy Eq.2.75, the ground state $|GS\rangle$, energy can be expressed as

$$E_{GS} = \sum_{x=0}^{N/2} (2\varepsilon_x - \Sigma(x)). \quad (2.131)$$

The 2 in front of the quasiparticle energy accounts for up and down spins occupying each valence orbital. Since each HF orbital energy already includes interactions with all other electrons occupying the valence band, just by adding up the eigenvalues of these levels we would be over counting the interactions. To avoid the over counting we subtract a self energy per orbital in the equation above.

As depicted in Fig.2.13(a), if we take an electron from a valence state (n, σ) where $n < N/2$ and excite it to a level $m > N/2$ such that,

$$|SE\rangle = b_{m,\sigma}^+ b_{n,\sigma} |GS\rangle = |m\sigma; n\sigma\rangle, \quad (2.132)$$

the energy of this new configuration will be obtained by following these steps:

1. Starting with the ground state energy E_{GS} , and HF ground state configuration,

2. we remove the energy of the electron in HF orbital n to obtain $E_{GS} - (\varepsilon_n)$.
3. Then add the energy of an electron in HF orbital m that makes the total energy $E_{GS} - (\varepsilon_n) + (\varepsilon_m)$.

Now we need to correct the over counting. In step 3), by including the HF quasiparticle energy ε_m , we end up including the interaction between the electrons on $(n, \sigma) - (m, \sigma)$ orbitals. The terms emerging from the interaction of these electrons are actually not present as the electron in (n, σ) has been removed. Since they have the same spin, we have a direct + an exchange interaction $\langle mn|V|nm\rangle - \langle mn|V|mn\rangle$ that we need to remove to correct the total energy calculation. Then the energy of a spin-excitation becomes:

$$E_{SE} = E_{GS} - \varepsilon_n + \varepsilon_m - (\langle mn|V|nm\rangle - \langle mn|V|mn\rangle). \quad (2.133)$$

As shown in Fig.2.13(b), a spin singlet/triplet excitation is obtained as

$$|S/T\rangle = \frac{(b_{m\uparrow}^+ b_{n\uparrow} \pm b_{m\downarrow}^+ b_{n\downarrow})}{\sqrt{2}} |GS\rangle, \quad (2.134)$$

where $+$ and $-$ sign corresponds to a singlet (S) and a triplet (T), respectively. The energies of these excitations are obtained as

$$\langle S/T|H|S/T\rangle = \frac{1}{2} (\langle b_{n\uparrow} b_{m\uparrow}^+ | H | b_{m\uparrow}^+ b_{n\uparrow} \rangle + \langle b_{n\downarrow} b_{m\downarrow}^+ | H | b_{m\downarrow}^+ b_{n\downarrow} \rangle \pm 2 \langle b_{n\downarrow} b_{m\downarrow}^+ | H | b_{m\uparrow}^+ b_{n\uparrow} \rangle). \quad (2.135)$$

The terms $1/2 \langle b_{n\uparrow} b_{m\uparrow}^+ | H | b_{m\uparrow}^+ b_{n\uparrow} \rangle$ and $1/2 \langle b_{n\downarrow} b_{m\downarrow}^+ | H | b_{m\downarrow}^+ b_{n\downarrow} \rangle$ are spin excitations whose energy contributions are calculated as Eq.2.133, giving:

$$E_{GS} + \varepsilon_m - \varepsilon_n - \langle mn|V|nm\rangle + \langle mn|V|mn\rangle. \quad (2.136)$$

Then the cross term $\pm \langle b_{n\downarrow} b_{m\downarrow}^+ | H | b_{m\uparrow}^+ b_{n\uparrow} \rangle$ separates the singlet from the triplet level. When we act with the Hamiltonian Eq.2.90 on the cross term, only the Coulomb term survives as others are single particle operations. The contribution emerging from the Coulomb term is derived as

$$\begin{aligned} \langle b_{n\downarrow} b_{m\downarrow}^+ | H | b_{m\uparrow}^+ b_{n\uparrow} \rangle &= \langle b_{n\downarrow} b_{m\downarrow}^+ | \langle ij|V|kl\rangle b_{i\sigma}^+ b_{j\bar{\sigma}}^+ b_{k\bar{\sigma}} b_{l\sigma} | b_{m\uparrow}^+ b_{n\uparrow} \rangle, \\ &= \langle nm|V|nm\rangle \langle b_{n\downarrow} c_{m\downarrow}^+ | b_{n\uparrow}^+ b_{m\downarrow}^+ b_{n\downarrow} b_{m\uparrow} | b_{m\uparrow}^+ b_{n\uparrow} \rangle, \\ &= \langle nm|V|nm\rangle \langle b_{n\downarrow} b_{m\downarrow}^+ | b_{m\downarrow}^+ b_{n\downarrow} b_{n\uparrow}^+ b_{m\uparrow} | b_{m\uparrow}^+ b_{n\uparrow} \rangle, \\ &= \langle nm|V|nm\rangle = \langle mn|V|mn\rangle. \end{aligned} \quad (2.137)$$

When all is added, the energy of a singlet/triplet excitation becomes:

$$E_{S/T} = E_{GS} + \varepsilon_m - \varepsilon_n - \langle mn|V|nm\rangle + \langle mn|V|mn\rangle \pm \langle mn|V|mn\rangle, \quad (2.138)$$

where the $-$ -sign for the triplet states cancels out the exchange contribution. The off diagonal terms between singlets(triplets) looks similar to the vertex corrections that appear in the diagonal terms only with different indices, such that they are given as

$$\langle S/T|H|S'/T'\rangle = -\langle n'm|V|m'n\rangle + \langle n'm|V|nm'\rangle \pm \langle n'm|V|nm'\rangle. \quad (2.139)$$

This way, instead of going through all possible terms in calculating the Hamiltonian matrix, we already know which entries in the matrix are non-zero, as well as their values. The above method gets more complicated once we include more than one-pair excitations.¹⁶⁸

Brillouin's Theorem

The Brillouin's Theorem states that the single pair excitations do not mix with the HF ground state¹⁶⁴ such that

$$\langle GS_{HF}|H(b_{a\sigma}^+b_{p\sigma}|GS_{HF})\rangle = 0, \quad (2.140)$$

where the exciton is defined as removing an electron in the valence band orbital p and creating it in the conduction band orbital a . Using the microscopic Hamiltonian written in terms of HF-states as given in Eq.2.90, I can expand the above matrix element to show that it actually is zero. Using $|GS_{HF}\rangle \rightarrow |0\rangle$ and assigning a certain spin to the excited electron $b_{a\sigma}^+b_{p\sigma}|0\rangle \rightarrow b_{a\uparrow}^+b_{p\uparrow}|0\rangle$ we have

$$\begin{aligned} & \langle 0| H (b_{a\uparrow}^+b_{p\uparrow}|0\rangle) \\ &= \langle 0| \left[\sum_{xy\sigma} (\varepsilon_x \delta_{xy} - V_{xy\sigma}^{MF}) b_{x\sigma}^+ b_{y\sigma} + \frac{1}{2} \sum_{xyzr\sigma\sigma'} V_{xyzr} b_{x\sigma}^+ b_{y\sigma'}^+ b_{z\sigma'} b_{r\sigma} \right] b_{a\uparrow}^+ b_{p\uparrow}|0\rangle. \end{aligned} \quad (2.141)$$

In order to make the derivation easier to follow, I will divide the Hamiltonian into two; the single particle part H_1 and the two body part H_2 and work on them separately, only to show that eventually they cancel each other out. Starting with H_1 , we can expand it

to obtain

$$\begin{aligned}
\langle 0 | H_1 b_{a\uparrow}^+ b_{p\uparrow} | 0 \rangle &= \langle 0 | \sum_{xy\sigma} (\varepsilon_x \delta_{xy} - V_{xy\sigma}^{MF}) b_{x\sigma}^+ b_{y\sigma} b_{a\uparrow}^+ b_{p\uparrow} | 0 \rangle \\
&= \langle 0 | \sum_{xy\sigma} (\varepsilon_x \delta_{xy} - V_{xy\sigma}^{MF}) \delta_{ya} \delta_{xp} \delta_{\sigma\uparrow} | 0 \rangle \\
&= \langle 0 | (-V_{pa\uparrow}^{MF}) | 0 \rangle \\
&= -\langle 0 | \sum_{z\sigma'} n_{z\sigma'} (\langle pz | V | za \rangle - \delta_{\uparrow\sigma'} \langle pz | V | az \rangle) | 0 \rangle. \tag{2.142}
\end{aligned}$$

Now working with H_2 , there are four different combinations of the quasiparticle operators that are non-zero when acting on the exciton:

$$\begin{aligned}
\langle 0 | H_2 b_{a\uparrow}^+ b_{p\uparrow} | 0 \rangle &= \frac{1}{2} \sum_{xyzr\sigma\sigma'} V_{xyzr} b_{x\sigma}^+ b_{y\sigma'}^+ b_{z\sigma'} b_{r\sigma} b_{a\uparrow}^+ b_{p\uparrow} | 0 \rangle \\
&= \langle 0 | \frac{1}{2} \sum_{z\sigma'} V_{pzza} b_{p\uparrow}^+ b_{z\sigma'}^+ b_{z\sigma'} b_{r\uparrow} b_{a\uparrow}^+ b_{p\uparrow} | 0 \rangle \\
&\quad + \langle 0 | \frac{1}{2} \sum_{z\sigma'} V_{zpa z} b_{z\sigma'}^+ b_{p\uparrow}^+ b_{a\uparrow} b_{z\sigma'} b_{a\uparrow}^+ b_{p\uparrow} | 0 \rangle \\
&\quad + \langle 0 | \frac{1}{2} \sum_{z\uparrow} V_{pza z} b_{p\uparrow}^+ b_{z\uparrow}^+ b_{a\uparrow} b_{z\uparrow} b_{a\uparrow}^+ b_{p\uparrow} | 0 \rangle \\
&\quad + \langle 0 | \frac{1}{2} \sum_{z\uparrow} V_{zpa z} b_{z\uparrow}^+ b_{p\uparrow}^+ b_{z\uparrow} b_{a\uparrow} b_{a\uparrow}^+ b_{p\uparrow} | 0 \rangle. \tag{2.143}
\end{aligned}$$

This expansion can be simplified using the fermionic commutation rules to obtain the following expression:

$$\langle 0 | H_2 b_{a\uparrow}^+ b_{p\uparrow} | 0 \rangle = \langle 0 | \sum_{z\sigma'} n_{z\sigma'} (\langle pz | V | za \rangle - \delta_{\uparrow\sigma'} \langle pz | V | az \rangle) | 0 \rangle, \tag{2.144}$$

which cancels with H_1 , leading to

$$\langle 0 | H (b_{a\uparrow}^+ b_{p\uparrow} | 0 \rangle) = \langle 0 | H_1 + H_2 (b_{a\uparrow}^+ b_{p\uparrow} | 0 \rangle) = 0. \tag{2.145}$$

2.2.2.2 Excitons (X)

Although we derived the energies of single pair excitations in section 2.2.2.1, and provided the expressions for the off-diagonal terms that are responsible for the correlations among the electron-hole pairs, we haven't discussed the implications of the diagonal or off-diagonal terms. I will now describe single pair excitations $|i\sigma; j\sigma\rangle$ and their bound states, the

excitons $|X\rangle$,

$$|X_m\rangle = \sum A_{ij}^{(m)} b_{i\sigma}^+ b_{j\sigma} |GS_{HF}\rangle = \sum A_{ij}^{(m)} |i\sigma; j\sigma\rangle. \quad (2.146)$$

As mentioned previously, electron-hole pairs interact and become correlated, excited states. Thus, simply adding the energies of the quasi-electron and the quasi-hole becomes insufficient in representing the true energetics of these excited states. Even before the inclusion of correlations among the pair-excitations, the attraction between the electron and the hole results in bound quasiparticles. Whatever the configuration is, a singlet or a triplet, there is the direct interaction between the electron and the hole that makes the exciton a bound particle. In addition to the direct interaction, the exchange among an electron and a hole for singlets separates the singlet and triplet energies. Having the energies of the individual pairs (diagonal terms), we include pair-correlations (off-diagonal terms) to form correlated electron-hole pairs; the *excitons* with energies $E_X = \varepsilon_e + \varepsilon_h - \Delta_B$. Here Δ_B represents the binding energy of the exciton while $\varepsilon_{e(h)}$ is the quasi-electron(hole) energy.

When populated with equal numbers of up and down electrons, the Hartree-Fock ground state is a total spin $S = 0$ -state. Since photons conserve the total spin, a single photon can only access the singlet states. Thus at a single photon/pulse fluence level, an absorption spectrum can only give the absorption strength of the dipole allowed singlet excitons.

2.2.2.3 Biexcitons (XX)

Biexcitons are created via double electron-hole pair production. Removing two electrons from the valence band and moving them to the conduction band by leaving two holes behind, we obtain the biexcitons $|p\sigma_1, m\sigma_2; q\sigma_1, n\sigma_2\rangle = b_{p\sigma_1}^+ b_{m\sigma_2}^+ b_{q\sigma_1} b_{n\sigma_2} |GS_{HF}\rangle$. Just as in excitons, the electrons and holes attract one another. However this time, due to the higher number of quasiparticles, there are more pair-interactions one would need to consider.

The configuration-interaction step of creating correlated ground and excited states involves creating a basis set that includes the HF ground state, $|GS_{HF}\rangle$, and selected number of excitations. In this basis of configurations, the matrix of the Hamiltonian (Eq.2.90 or Eq.2.101) is constructed and diagonalized numerically. As a result of this process, one obtains correlated eigenstates of the form:

$$\begin{aligned} |\Phi_\nu\rangle &= k_0^\nu |GS_{HF}\rangle + \sum_{mn\sigma} k_{mn}^{\nu(1)} |i\sigma; j\sigma\rangle \\ &+ \sum_{pmqn} \sum_{\sigma_1\sigma_2} k_{pmqn}^{\nu(2)} |p\sigma_1, m\sigma_2; q\sigma_1, n\sigma_2\rangle + \dots \end{aligned} \quad (2.147)$$

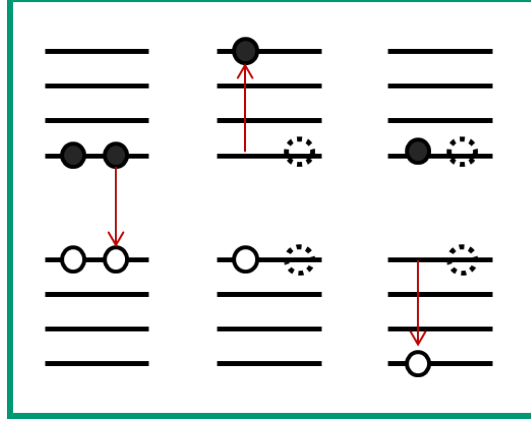


Figure 2.15: Figure depicting Auger recombination process. One of the electron-hole pairs recombines to give the excess energy to the electron or the hole exciting them to become excited excitons

In particular, the HF ground state itself is now corrected by contributions from multi-pair excitations. Although all states are going to be combinations of many excitation pairs, if there is a clear winner (i.e. a configuration with the greatest coefficient k), I will be naming that correlated state after it.

2.2.2.3.1 Biexciton Binding While calculating the exciton binding energy, I compared the energy of the exciton itself with the sum of the two quasiparticle (HF electron and a HF hole) energies. For the case of biexcitons, I will do the same, but this time my quasiparticles will be excitons themselves. Then, the energy of a biexciton can be given as $E_{XX} = E_{X_1} + E_{X_2} + \Delta_{XX}$ where E_{X_i} are the energies of the excitons forming the biexciton and Δ_{XX} is the biexciton binding energy.

2.2.2.3.2 Auger Coupling A biexciton lives in the space of excitons, some of which have similar energies as its energy. This means that even if a pure-biexciton configuration is the most probable configuration in a state, (thus allowing me to name the state after it), the state can have significant contributions from excitons.

Auger recombination is a non-radiative process in which a biexciton is converted into an excited exciton as figuratively explained in Fig.2.15. Starting with a biexciton, one of the electron-hole pairs can recombine and give the excess energy to the remaining electron (hole), exciting it to a higher (lower) conduction (valence) band, creating excited excitons. This process may decrease the lifetime of the biexciton, making it short-lived or even not detectable.

2.2.2.4 Multi Excitons

As we include more and more electron-hole pairs, the CI subspace will grow factorially. Since the CI Hamiltonian is a two body interaction Hamiltonian, N-pair excitations within a ± 2 -pair range will interact with one another directly. For example, a 3-pair exciton will have first order contributions from a range of 1-pair to 5-pair excitations only. Beyond that, all other N-pair excitations will have second or higher order contribution to the energy of a 3-pair exciton. As a result, for weakly interacting electrons the ground state, exciton and biexciton energies will not be greatly affected by presence of excitations beyond 4-pair.

For strongly interacting electrons however, interactions can no longer be considered as perturbations. Thus, excitations interact with one another strongly and higher order excitations become important in determining the correlated ground state.

2.3 Numerical Methods

As emphasized before, the Hartree Fock method is only a coordinate transformation, and if one were able to include all possible excitations at the configuration interaction step, one would obtain the true ground state. The justification of restricting the CI subspace is the small strength of the electron-electron interactions compared to mean field interactions.

2.3.1 Genetic Search Algorithm

Unlike the ground state of a weakly interacting electron system, in a strongly interacting system, the ground state is degenerate. As a result, both Hubbard and Hartree Fock approximations, while converging self consistently, may fall into local minima instead of the global minimum (the lowest energy level within the approximation). In order to avoid that, I have implemented a genetic search algorithm (GSA). The GSA is only executed at the mean-field Hubbard level. The density matrix obtained from the mean-field Hubbard calculation is used as an input for the mean-field Hartree Fock approximation.

I start with a randomly generated density matrix for up and down electrons. If the spin up and down densities are not equal (unlike the weakly interacting regime), then there is a degenerate counterpart of each Slater determinant; exchanging the densities of up and down electrons will result in the same eigenvalue. This may cause a problem if in each step my search results in opposite spin densities. In order to avoid that, after the generation of random density matrices for up and down electrons,

1. I set the first element of the spin up density matrix to 1 (which will be corrected within the iterative scheme). This way the system is forced to remain within the proximity of a certain global minimum.

2. I run the self-consistent Hubbard algorithm 6 times starting with 6 different initial density matrix guesses for spin up and down electrons, using a larger convergence parameter compared to my overall convergence parameter.
3. After the generation of the 6 converged density matrices, I take the two lowest energy guesses and create an average of the two densities to use it as an input for the next run.
4. Until I obtain three such ground state energy - density matrix pairs that are equal (within the convergence window) in energy, I keep searching while removing the one(s) that doesn't match the lowest energy one.

2.3.2 Lanczos Method

In the configuration interaction step, the number of configurations and the size of the Hamiltonian increases factorially. For large matrices, that is $N_{conf} > 10^5$, storing all the elements of the Hamiltonian matrix becomes challenging. More importantly, even if one can store such large matrices, common linear algebra packages become unusable.¹⁶²

Most of the time, we are only interested in a limited window of eigenvalues. In fact, throughout this thesis I only study the ground state and low energy excitations around the band-gap. Thus, creating a full set of eigenvalues and eigenstates and storing them becomes unnecessary. Iterative methods are suitable for such tasks in which one is concentrating on a certain window of eigenvalues. Exploiting the fact that I only need low lying levels, I implemented the Lanczos method to tackle large matrices. The advantage of the Lanczos method is that it reduces the need to store the whole Hamiltonian since it is based on matrix-vector multiplication.

Diagonalizing a Hamiltonian is equivalent to rotating it into a diagonal matrix. Since tridiagonal matrices are a lot easier to solve, instead of rotating to a diagonal matrix (which is the task in hand) we will start with rotating the Hamiltonian into a tridiagonal matrix:

$$W^{-1} \begin{pmatrix} h_{11} & h_{12} & h_{13} & \cdots \\ h_{21} & h_{22} & h_{23} & \cdots \\ h_{31} & h_{32} & h_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} W = \begin{pmatrix} \alpha_1 & \beta_1 & 0 & \cdots \\ \beta_1 & \alpha_2 & \beta_2 & \cdots \\ 0 & \beta_2 & \alpha_3 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}, \quad (2.148)$$

where W is a unitary matrix made out of orthogonal column vectors $\mathbf{w}_i$,

$$W = (\mathbf{w}_1, \mathbf{w}_2, \mathbf{w}_3, \cdots). \quad (2.149)$$

Then multiplying Eq.2.148 from left by the matrix W and expanding its terms, we can

rewrite it as

$$\begin{pmatrix} h_{11} & h_{12} & h_{13} & \cdots \\ h_{21} & h_{22} & h_{23} & \cdots \\ h_{31} & h_{32} & h_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} (\mathbf{w}_1, \mathbf{w}_2, \mathbf{w}_3, \cdots) = (\mathbf{w}_1, \mathbf{w}_2, \mathbf{w}_3, \cdots) \begin{pmatrix} \alpha_1 & \beta_1 & 0 & \cdots \\ \beta_1 & \alpha_2 & \beta_2 & \cdots \\ 0 & \beta_2 & \alpha_3 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}.$$

This equality gives us a set of equations. Let's start with the first one. Acting with the Hamiltonian on the first, randomly generated, normalized column vector $\mathbf{w}_1$ will give us

$$H\mathbf{w}_1 = \mathbf{w}_1\alpha_1 + \mathbf{w}_2\beta_1. \quad (2.150)$$

Multiplying the above equation from left by $\mathbf{w}_1^*$, and using the orthogonality of the vectors $\mathbf{w}_i^*\mathbf{w}_j = \delta_{ij}$, we can obtain the first unknown element of the tridiagonal matrix;

$$\begin{aligned} \mathbf{w}_1^*H\mathbf{w}_1 &= \mathbf{w}_1^*\mathbf{w}_1\alpha_1 + \mathbf{w}_1^*\mathbf{w}_2\beta_1 \\ \mathbf{w}_1^*H\mathbf{w}_1 &= \alpha_1. \end{aligned} \quad (2.151)$$

Knowing α_1 , I can substitute it back in Eq.2.150 to obtain

$$H\mathbf{w}_1 - \mathbf{w}_1\alpha_1 = \mathbf{w}_2\beta_1. \quad (2.152)$$

Although at first sight it is not obvious, since β_1 is just a scalar value, it is the normalization constant of an un-normalized vector $\bar{\mathbf{w}}_2 = \mathbf{w}_2\beta_1$. Then, rewriting the above equation, I can obtain the two remaining unknowns,

$$\beta_1 = |\bar{\mathbf{w}}_2| = |H\mathbf{w}_1 - \mathbf{w}_1\alpha_1|, \quad (2.153)$$

and

$$\mathbf{w}_2 = \frac{\bar{\mathbf{w}}_2}{|\bar{\mathbf{w}}_2|} = \frac{H\mathbf{w}_1 - \mathbf{w}_1\alpha_1}{\beta_1}. \quad (2.154)$$

I can follow the same steps for the next equation. Let's start by explicitly writing it down:

$$H\mathbf{w}_2 = \mathbf{w}_1\beta_1 + \mathbf{w}_2\alpha_2 + \mathbf{w}_3\beta_2. \quad (2.155)$$

This time I don't have to start with a randomly generated vector, since I obtained $\mathbf{w}_2$ in the previous step. Moreover, although there are more terms on the right hand side, the number of unknowns is the same as for the first equation. Let's multiply the above equation from left with $\mathbf{w}_2^*$ to obtain α_2 as $\mathbf{w}_2^*H\mathbf{w}_2 = \alpha_2$. With that knowledge, I can

rearrange the above equation, to find the normalization constant β_2 just as I did for the previous case:

$$\beta_2 = |\bar{\mathbf{w}}_3| = |H\mathbf{w}_2 - \mathbf{w}_1\beta_1 - \mathbf{w}_2\alpha_2|, \quad (2.156)$$

and obtain the next unknown vector as

$$\mathbf{w}_3 = \frac{|H\mathbf{w}_2 - \mathbf{w}_1\beta_1 - \mathbf{w}_2\alpha_2|}{\beta_2}. \quad (2.157)$$

Following the steps above, I can obtain all elements of the tridiagonal matrix such that

$$\begin{aligned} \alpha_k &= \mathbf{w}_k^* H \mathbf{w}_k, \\ \beta_k &= |H\mathbf{w}_k - \mathbf{w}_{k-1}\beta_{k-1} - \mathbf{w}_k\alpha_k|, \end{aligned} \quad (2.158)$$

and the eigenvectors along the way,

$$\mathbf{w}_{k+1} = \frac{H\mathbf{w}_k - \mathbf{w}_{k-1}\beta_{k-1} - \mathbf{w}_k\alpha_k}{\beta_k}. \quad (2.159)$$

The advantage of this process lies within the fact that I only need to create a tridiagonal matrix that is much smaller than my original Hamiltonian yet sufficiently large to converge the lowest eigenenergies that I am interested in. One thing that we have to add into this process is the orthogonalization of the vectors. Otherwise from the above process, the eigenvectors will not be orthogonal which will render the whole process useless. Each time I obtain a vector, I orthogonalize it to the previous ones through Gram-Schmidt orthogonalization.

Due to the form of the Hamiltonian, which only includes single particle and two particle operators, the Hamiltonian matrix ends up being very sparse. That combined with the fact that I only need to find and store the non-zero Hamiltonian matrix elements for the Lanczos method improves the speed and reduces the resource requirements of my calculations significantly.¹⁶²

Chapter 3

Interactions and Artificial Gauge in Artificial Carbon Rings

Single^{169,170}, double,^{171–173}, triple^{174–179} quadruple quantum dot molecules and artificial benzene rings have been demonstrated experimentally^{180–182} and extensively studied theoretically.^{156,183–196,196–206} The interest in these artificial molecules is mainly driven by the fact that one can control the number of electrons on each quantum dot and tune the interactions by means of gates. This tunability allows one to reach regimes that are not accessible by regular molecules. The prospect of having single molecular devices is important both for reducing the size of electronic circuits and improving their efficiency while expanding the fields of application. Developing quantum circuits using artificial molecules, one can have the freedom to tune them according to the needs of the systems of interest.

In this chapter, I will present the work we have done on the quadruple quantum dot (QQD) molecule and the artificial benzene ring (ABR). For both structures, the extended Hubbard model is used.

3.1 Quadruple Quantum Dot Molecule

Motivated by the experimental work on quadruple quantum dots, I will now provide a detailed theory of the electronic properties of a quadruple quantum dot molecule as a function of the number of electrons N , the geometry and the physical parameters such as inter-dot tunnelling, energy bias, and intra- and inter-dot Coulomb interactions. I will primarily focus on the charged QQD (one electron away from half-filling) where chirality, topology, and Fermi statistics play an important role in determining its electronic properties.

The QQD structure can be implemented in a lateral gated AlGaAs/GaAs heterostruc-

ture.^{180,181,183} For example, a metallic gate with four openings can be deposited on the surface of the heterostructure to deplete the two-dimensional electron gas (2DEG) at the AlGaAs/GaAs hetero-interface as shown in Fig.3.1. Electrostatic fields created due to the openings in the gate are translated into local potential minima in the plane of the 2DEG, confining electrons. Thus the four openings represent lateral quadruple quantum dots. The lateral confinement results in a quantized energy spectrum in each dot i , of which in this work we only retain the lowest energy level E_i , assuming one spin-degenerate orbital per dot. The voltage on the main metallic gate and additional gates, not shown in Fig.3.1, can be tuned to control the number of electrons confined in the QQD. The confining potentials in the QQD can be approximated as a sum of four Gaussians. The inter-dot tunnelling and hence the geometry of the QQD can be controlled by additional gate voltages without significantly altering the confinement energies E_i .

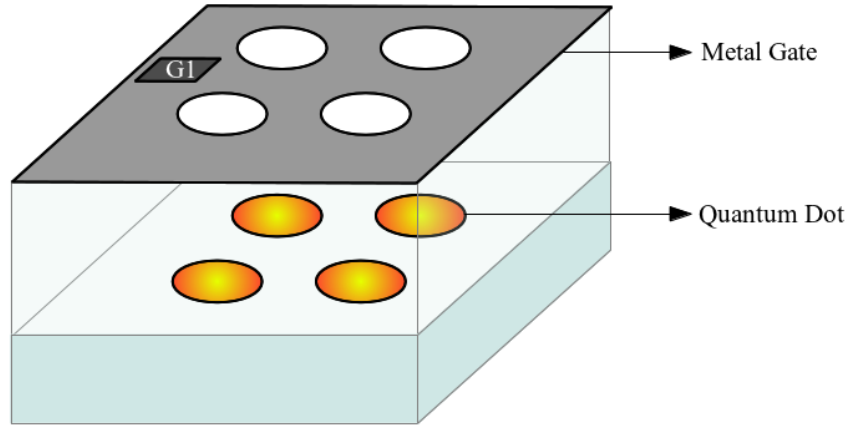


Figure 3.1: (a) A schematic cross-sectional view of the four-dot lateral gated device.

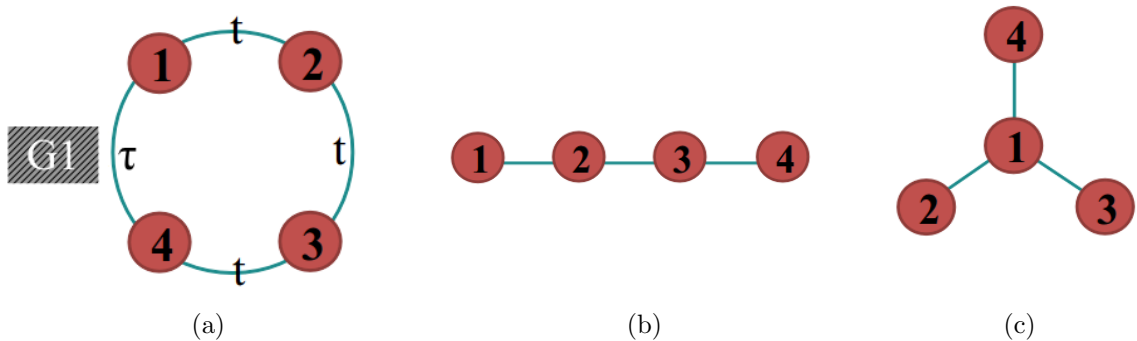


Figure 3.2: The dots can be arranged in ring geometry (a), linear geometry (b), or triangular geometry (c). Reprinted from Ref.¹⁵⁶

We will consider three possible geometrical configurations of the four quantum dots

as shown in Fig.3.2. If we only consider nearest neighbour (NN) tunnelling, we can go from a ring geometry to a linear quadruple quantum dot geometry (LQQD) by inserting a gate (G1 in Fig.3.1) between dots 1-4. Applying a high negative voltage increases the tunnelling barrier and prevents electrons from tunnelling from dot 1 to dot 4. Similarly, one can remove tunnelling between dots 2 and 3 and end up with two capacitively coupled pairs of quantum dots as studied in Ref. 180. A triangular configuration,¹⁹³ i.e., three dots arranged in the corners of an equilateral triangle that are equidistant to a central dot, can also be obtained by tuning the tunnelling between the dots in order to obtain the equivalent schematic representation shown in Fig.3.2(c).

In this work, electronic properties of QQD in a given geometry are described by the extended Hubbard model (Eq.2.65) retaining the NN interactions V_{ij} , and NN tunnelling matrix elements t_{ij} , between dots with one spin-degenerate orbital per dot.^{183,186} . With a single energy level per dot, up to $N_e = 8$ electrons can occupy the quadruple quantum dot molecule.

Single Particle Levels in Fourier Space

The site representation of the Hamiltonian is applicable to all QQD geometries. However, for the ring geometry we can also express the Hamiltonian in the Fourier space by using the Fourier transformed creation/annihilation operators,

$$a_{\kappa_i}^+ = \frac{1}{\sqrt{4}} \sum_{j=1}^4 e^{i\kappa_i(j-1)} c_j^+, \quad (3.1)$$

where a_{κ}^+ is the creation operator in the Fourier space and $\kappa_i = \{0, \pi/2, -\pi/2, \pi\}$ are the allowed wavevectors. Any κ that lies outside of the Brillouin zone $[0, 2\pi]$ is translated back into the zone by the reciprocal lattice vectors $(2\pi)n$ where $n = 1, 2, \dots$. If the dots are identical and on resonance, i.e., $E_i = E$, $U_i = U$, $V_{ij} = V$, then using Eq.3.1 in Eq.2.65 we can represent the Hamiltonian in Fourier space as

$$\hat{H} = \sum_{\sigma, i} \varepsilon_{\kappa_i} a_{\kappa_i \sigma}^+ a_{\kappa_i \sigma} + \frac{1}{2} \sum_{ijkl, \sigma \sigma'} \langle \kappa_i \kappa_j | \mathcal{V}_{ee} | \kappa_k \kappa_l \rangle a_{\kappa_i \sigma}^+ a_{\kappa_j \sigma'}^+ a_{\kappa_k \sigma'} a_{\kappa_l \sigma}. \quad (3.2)$$

Here, ε_{κ_i} is the energy of the molecular state

$$\varepsilon_{\kappa_i} = E - 2|t| \cos \kappa_i, \quad (3.3)$$

and the Coulomb matrix element is evaluated as

$$\langle \kappa_i \kappa_j | \mathcal{V}_{ee} | \kappa_k \kappa_l \rangle = \frac{U + 2V \cos(\kappa_l - \kappa_i)}{4} \delta(\kappa_i + \kappa_j, \kappa_k + \kappa_l). \quad (3.4)$$

We see that the total wavevector κ_{tot} is a good quantum number under Coulomb scattering in a ring geometry since the Fourier transform (FT) diagonalizes the single-particle Hamiltonian and the Coulomb two body matrix elements conserve the total wavevector κ up to the reciprocal vector.

Starting with the vacuum, $|0\rangle$, for a given number of electrons, N_e , we form all possible configurations, $|\alpha\rangle = \prod_{i=1,N} c_{i\sigma}^+ |0\rangle$, and construct the Hamiltonian matrix, Eq.2.65, by computing matrix elements $\langle\alpha'|H|\alpha\rangle$ in the space of configurations in either real or Fourier space. The QQD Hamiltonian matrix is block diagonal according to the total spin S of the configurations since S is a good quantum number, satisfying $[\hat{H}, \hat{S}] = 0$. I will diagonalize each total spin block separately to obtain the eigenvalues and eigenvectors of the Hamiltonian in each total spin subspace.

3.1.1 Single Particle Properties

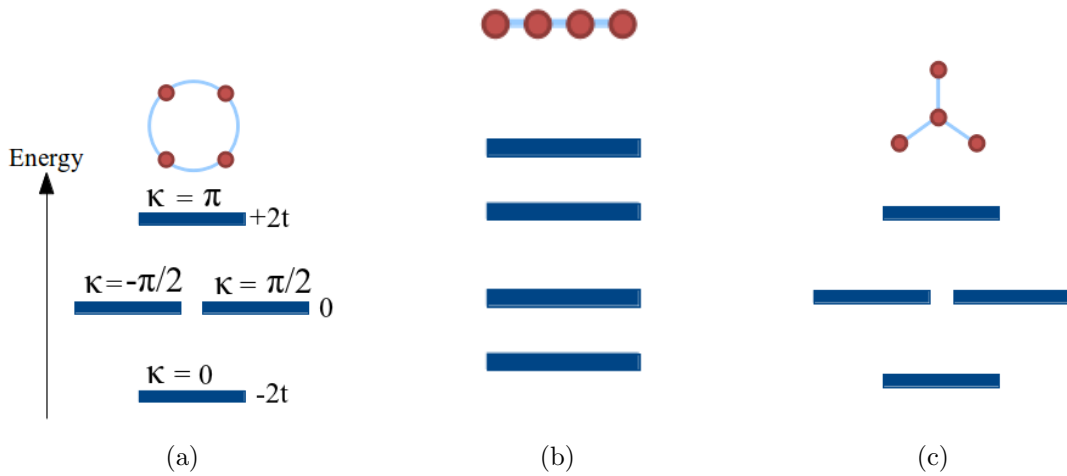


Figure 3.3: Single-particle energy spectrums of ring, linear, and triangular geometries, respectively.

For $N_e = 1$ electron, the basis consists of four orthogonal states $\{|1\rangle, |2\rangle, |3\rangle, |4\rangle\}$ where $|i\rangle = c_i^+ |0\rangle$ represents a configuration with a single electron on dot i . The diagonal elements of the Hamiltonian are the on-site energies of single electrons $\langle i | \hat{H} | i \rangle = E_i$. The off-diagonal elements $\langle i | \hat{H} | j \rangle = -t_{ij}$ correspond to the tunneling element for the nearest neighbor elements $\langle i, j \rangle$.

Let us now start with the ring and linear geometries. When all dots are on resonance, i.e., with $E_1 = E_2 = E_3 = E_4 = E_0$ and with tunneling matrix elements $t_{12} = t_{23} = t_{34} = t$

and $t_{14} = \tau$, the Hamiltonian takes the following form:

$$\hat{H}_{1e} = \begin{bmatrix} 0 & -t & 0 & -\tau \\ -t & 0 & -t & 0 \\ 0 & -t & 0 & -t \\ -\tau & 0 & -t & 0 \end{bmatrix}, \quad (3.5)$$

where for simplicity I took $E_0 = 0$.

For a ring geometry, tunneling from dot 1 to dot 4 is identical to any other tunneling process and $\tau = t$. Its one-electron energy spectrum shown in Fig.3.3(a) is symmetric around a doubly degenerate energy level $E = 0$, with ground and the highest excited level energies of $\pm 2t$. Following Eq.3.1, the Fourier-transformed single-particle molecular orbitals are expressed as:

$$|\kappa_i\rangle = \frac{1}{\sqrt{4}} \sum_j^4 e^{i\kappa_i(j-1)} |j\rangle, \quad (3.6)$$

where $|j\rangle$ represents a dot and $|\kappa_i\rangle$ represents a Fourier-transformed orbital with energy, Eq.3.3. The occupation probability of each dot is equal $\{1/4, 1/4, 1/4, 1/4\}$ at every level of the single-particle energy spectrum. The ground and the highest excited states in the one electron spectrum shown in Fig.3.3(a) correspond to $\kappa = 0$ and $\kappa = \pi$, respectively, while the two degenerate excited levels are the $\kappa = \pi/2$ and $\kappa = -\pi/2$ states.

As in the case of the triple dot,¹⁸⁵ the degeneracy of two levels is an outcome of the geometry. In the limit of a linear quadruple dot molecule where $\tau = 0$, the degeneracy is lifted and the energy spectrum of the molecule consists of four energy levels, $\{(1 \pm \sqrt{5})t/2, (-1 \pm \sqrt{5})t/2\}$, as shown in Fig.3.3(b). Unlike the ring geometry, the occupation probability of each dot is different for each orbital; it is higher at the central two dots for the highest and the lowest energy levels $\{P_-, P_+, P_+, P_-\}$ while it is higher on the outer two for the central energy levels $\{P_+, P_-, P_-, P_+\}$ where $P_{\pm} = (5 \pm \sqrt{5})/20$.

Effects of geometry are also seen in the case of the triangular QQD. Even though the energy levels of the triangular geometry $E = \{0, 0, \pm\sqrt{3}t\}$ possess the same kind of symmetry as the ring geometry as shown in Fig.3.3(c), the spacing of the levels and the occupation probabilities of the dots at each level differs. In the ground state and the highest excited energy level, the probability of occupation of the central dot is higher (0.5) than that of the outer dots (0.166). On the other hand, in the degenerate levels, the occupation probability density is localized on the outer dots decoupling the central dot from the outer dots.

3.1.2 Electron - Electron Interactions

3.1.2.1 Two Electrons

The two-electron Hamiltonian can be expressed in real and Fourier space, both of which can reveal different aspects of electronic properties of the system. Working in real space highlights the importance of topology and Fermi statistics for two-electrons/holes confined in a QQD.

As mentioned before, the Hamiltonian is block diagonal according to total spin. For triplet configurations, because we only have two electrons, it is enough to study only the spin polarized system. The configurations are constructed by taking all possible permutations of two electrons on two different quantum dots since electrons with parallel spins cannot occupy the same quantum dot as a consequence of the Pauli exclusion principle. In total there are six triplet configurations. By defining a two electron triplet configuration as $|ij\rangle_T = c_{i\downarrow}^+ c_{j\downarrow}^+ |0\rangle$ where subscript T denotes a triplet, the two electron triplet basis is constructed as $\{|13\rangle_T, |24\rangle_T, |12\rangle_T, |14\rangle_T, |23\rangle_T, |34\rangle_T\}$. In the ring QQD geometry, the first two are the *antipodal configurations* $\{|13\rangle_T, |24\rangle_T\}$ that are created by placing two electrons on antipodal dots and the remaining four are the *NN states* with two electrons residing on NN dots.

An electron cannot directly tunnel between two antipodal dots since we only include NN tunnelling in our Hamiltonian. As a result, the off-diagonal elements between the NN basis configurations $\{|12\rangle_T, |14\rangle_T, |23\rangle_T, |34\rangle_T\}$ vanish. Similarly, the off-diagonal element between the antipodal states $\{|13\rangle_T, |24\rangle_T\}$ will be zero. The energy of NN configurations includes the kinetic energy of two electrons $E_i + E_j$ and the direct Coulomb interaction V_{ij} between them while the antipodal configurations have only kinetic energy since the two electrons on antipodal dots do not interact via the NN Coulomb interaction.

In order to evaluate the matrix elements between antipodal and NN states ${}_T\langle i'j'|\hat{H}|ij\rangle_T$, we apply the Fermionic anticommutation rules. For example, the tunneling matrix element between $|13\rangle_T$ and $|12\rangle_T$ is evaluated as

$$\begin{aligned}\langle 13|\hat{H}|12\rangle &= \langle 0|c_{3\uparrow}c_{1\uparrow}|(-t_{32}c_{3\uparrow}^+c_{2\uparrow})|c_{1\uparrow}^+c_{2\uparrow}^+|0\rangle \\ &= -t_{32}.\end{aligned}\tag{3.7}$$

Tunneling of an electron from dot 2 to dot 3 in the presence of an electron in dot 1 does not change the sign of the tunneling matrix element. However, the tunneling matrix element acquires a phase $e^{i\pi}$ when an electron tunnels between dots 1 and 4 in the presence of

another electron. This can be shown by evaluating the matrix element

$$\begin{aligned}
 \langle 13|\hat{H}|34\rangle &= \langle 0|c_{3\uparrow}c_{1\uparrow}|(-t_{14}c_{1\uparrow}^+c_{4\uparrow}^+)c_{3\uparrow}^+c_{4\uparrow}^+|0\rangle \\
 &= +t_{14}\langle 0|c_{3\uparrow}c_{1\uparrow}|(c_{1\uparrow}^+c_{4\uparrow}^+)|c_{4\uparrow}^+c_{3\uparrow}^+|0\rangle. \\
 &= +t_{14} = -e^{i\pi}t_{14}.
 \end{aligned} \tag{3.8}$$

On resonance, with $E_0 = 0$, the triplet Hamiltonian matrix for two electrons can be written explicitly as

$$\hat{H}_T = \begin{bmatrix} 0 & 0 & -t & -t & -t & -e^{i\pi}t \\ 0 & 0 & -e^{i\pi}t & -t & -t & -t \\ -t & -e^{-i\pi}t & V & 0 & 0 & 0 \\ -t & -t & 0 & V & 0 & 0 \\ -t & -t & 0 & 0 & V & 0 \\ -e^{-i\pi}t & -t & 0 & 0 & 0 & V \end{bmatrix}. \tag{3.9}$$

In a triple-dot (TQD) molecule,^{183,185} every pair of electrons has NNs and there are only 3 possible configurations. Thus the motion of a pair can be compared to that of a single electron. However, in a ring QQD there are NN and antipodal pairs of electrons and as a consequence the motion of a pair of electrons is different than that of a single electron. Upon tunnelling of an electron, NN electron pairs separate and become antipodal while the antipodal pairs become NN. This process increases the number of states compared to a single electron motion and distinguishes the 6×6 triplet Hamiltonian from that of a single electron.

By diagonalizing the Hamiltonian, Eq.3.9, we find that the symmetric triplet energy spectrum consists of three equally spaced, doubly degenerate energy levels at $((-Q+V)/2, V, (Q+V)/2)$ where $Q = \sqrt{16t^2 + V^2}$. The eigenvectors that depend on the energy V are associated with hidden symmetry of the Hubbard model as discussed by C.N. Yang in Ref.207 and later on in the text. This also means that the Hamiltonian can be further simplified by projecting out these exact eigenstates.

To demonstrate the importance of geometry and statistics, we now investigate the singlet Hamiltonian. The singly-occupied singlet configurations are obtained from the basis of six triplet states by properly anti-symmetrizing the configurations after flipping the spin of one electron, e.g., $|12\rangle_S = \frac{1}{\sqrt{2}}(c_{1\uparrow}^+c_{2\downarrow}^+|0\rangle - c_{1\downarrow}^+c_{2\uparrow}^+|0\rangle)$. The singlet and triplet Hamiltonians turn out to be identical except for the tunneling matrix elements between dots 1 and 4 which do not acquire the phase $e^{i\pi}$. Hence the total spin of a pair of electrons, triplet or singlet, differentiates tunneling of the pair. With energies measured from E_0 , the energy levels of the singly-occupied singlet states are obtained as $\{(-Q'+V)/2, 0, (Q'+V)/2, V, V, V\}$, where $Q' = \sqrt{32t^2 + V^2}$.

If the Coulomb matrix element V is turned off (which can be controlled by an external gate), $V = 0$, the energy gap between the ground state of the triplet and the singly occupied singlet state becomes proportional to the tunneling element as

$$\frac{-Q + V}{2} - \frac{-Q' + V}{2} = 2t(\sqrt{2} - 1). \quad (3.10)$$

For small V , $t > V$, there is a correction proportional to V^2/t , yet the singly occupied singlet remains the ground state. Finally, for $V \gg t$, the energy gap between the singly occupied singlet and triplet states becomes smaller but the singlet remains the overall ground state at all times. This shows that tunneling alone, a single particle process, distinguishes the triplet and singly occupied singlet states.

The singlet subspace also includes four doubly occupied states with two anti-parallel electrons on each dot. The diagonal element of these configurations includes the on-site interaction term, $2E_i + U_i$ on dot i and the only non-zero matrix elements between the doubly occupied and singly occupied singlet states correspond to $\langle ii|\hat{H}|i(i+1)\rangle_S = -\sqrt{2}t_{i(i+1)}$. Perturbatively, in the strong coupling limit where $U \gg V > |t|$, the singlet ground state is calculated as

$$E^S \approx \frac{-Q' + V}{2} - \frac{8t^2}{(2U - V + Q') \left(\frac{Q'}{Q' - V} \right)}. \quad (3.11)$$

The first term emerges from the singly occupied singlet interactions. The second term is the superexchange correction E_{sxc} and it arises from the mixing of singly and doubly occupied configurations. For future reference, we will express the singlet ground state as $E^S \approx \frac{-Q' + V}{2} - E_{sxc}^{(2)}$. In this limit the singlet ground state energy can be written in terms of the triplet ground state energy as

$$E^S = E^T - \frac{Q' - Q}{2} - E_{sxc}^{(2)}. \quad (3.12)$$

Since $Q' \geq Q$, the ground state of the two electron system is always a spin singlet.

In the limit of $t_{14} = 0$, the QQD becomes a linear molecule (LQQD) and the singly occupied singlet and the triplet Hamiltonians become indistinguishable. Unlike in the ring, in a LQQD the tunnelling element alone does not distinguish the triplet and singlet ground states. Only the inclusion of doubly occupied configurations breaks the degeneracy of the singlet and triplet singly occupied eigenstates.

Let us now compute the two electron spectrum in Fourier space. The two-electron molecular states, $|\kappa_1\kappa_2\rangle$, can be classified according to their total wavevector $\kappa_{tot} = \kappa_1 + \kappa_2$. Subspaces $\kappa_{tot} = 0$ and $\kappa_{tot} = \pi$ each have only one triplet configuration $|\pi/2, -\pi/2\rangle$ and

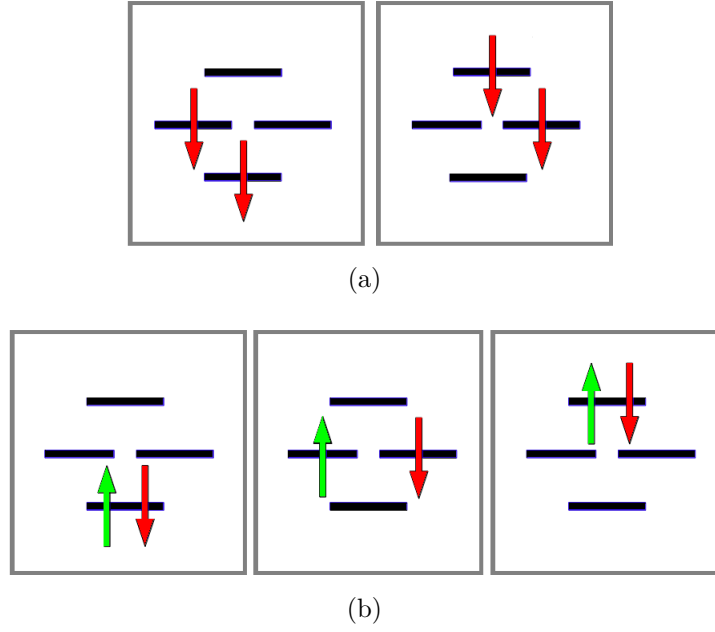


Figure 3.4: The two $\kappa_{tot} = \pi/2$ triplet configurations (a) and the three $\kappa_{tot} = 0$ singlet configurations (b) in Fourier space arising in a two-electron QGD in the ring geometry. The central singly occupied configuration must be properly symmetrized.

$|0, \pi\rangle$ respectively. I will now show how one would calculate the energy of the triplet configuration $|0, \pi\rangle$ in Fourier space.

$$\begin{aligned}
\langle 0, \pi | \hat{H} | 0, \pi \rangle &= \langle 0, \pi | \varepsilon_{\kappa_0} a_{\kappa_0}^+ a_{\kappa_0} | 0, \pi \rangle + \langle 0, \pi | \varepsilon_{\kappa_\pi} a_{\kappa_\pi}^+ a_{\kappa_\pi} | 0, \pi \rangle \\
&\quad + \langle 0, \pi | \langle \kappa_0 \kappa_\pi | V | \kappa_\pi \kappa_0 \rangle a_{\kappa_0}^+ a_{\kappa_\pi}^+ a_{\kappa_\pi} a_{\kappa_0} | 0, \pi \rangle \\
&\quad + \langle 0, \pi | \langle \kappa_0 \kappa_\pi | V | \kappa_0 \kappa_\pi \rangle a_{\kappa_0}^+ a_{\kappa_\pi}^+ a_{\kappa_0} a_{\kappa_\pi} | 0, \pi \rangle \\
&= \varepsilon_{\kappa_0} + \varepsilon_{\kappa_\pi} + \langle \kappa_0 \kappa_\pi | V | \kappa_\pi \kappa_0 \rangle - \langle \kappa_0 \kappa_\pi | V | \kappa_0 \kappa_\pi \rangle \\
&= \varepsilon_{\kappa_0} + \varepsilon_{\kappa_\pi} + \left(\frac{U + 2V \cos(0)}{4} \right) - \left(\frac{U + 2V \cos(\pi)}{4} \right) \\
&= -2|t| + 2|t| + \left(\frac{U + 2V}{4} \right) - \left(\frac{U - 2V}{4} \right) \\
&= V.
\end{aligned} \tag{3.13}$$

Calculating the diagonal element of the configuration $|\pi/2, -\pi/2\rangle$, we will obtain the same eigenvalue. Since these two configurations are all alone in their subspaces, they do not interact with any other configuration and their energies do not get modified. Thus, these configurations correspond to the doubly degenerate, $E = V$, level in the triplet spectrum. Previously in real space basis we showed that the triplet ground state is doubly degenerate. In Fourier space, these degenerate states correspond to a total wavevector $\kappa_{tot} = \pm\pi/2$.

Their eigenvalues can be obtained from the degenerate $\kappa_{tot} = \pm\pi/2$ Hamiltonians written as

$$H_{\kappa=\pm\pi/2}^T = \begin{bmatrix} -2t + \frac{V}{2} & \frac{V}{2} \\ \frac{V}{2} & 2t + \frac{V}{2} \end{bmatrix}, \quad (3.14)$$

in the basis $\{|0, \mp\pi/2\rangle, |\pm\pi/2, \pi\rangle\}$ shown in Fig.3.4(a). Once diagonalized, it will give the degenerate highest and lowest energy levels in the triplet spectrum, $\{(\pm Q + V)/2\}$.

Just as the triplet Hamiltonian, the 10×10 singlet Hamiltonian, once written in the configuration basis becomes block diagonal according to the total wavevector $\kappa_{tot} = \{0, -\pi/2, \pi/2, \pi\}$. The lowest energy singlet configuration is obtained by placing electrons with antiparallel spins onto the lowest energy molecular orbital $|\kappa_0\rangle$. As a result, we expect a total wavevector $\kappa_{tot} = 0$ as the ground state of the singlet configurations. Therefore, instead of a 10×10 basis, the ground state of the singlet subspace can be obtained by working in the 3×3 , $\kappa_{tot} = 0$ subspace written in the basis of $\{|0, 0\rangle, |\pi/2, -\pi/2\rangle_S, |\pi, \pi\rangle\}$ states shown in Fig.3.4(b). Setting $E_0 = 0$, the lowest kinetic energy configuration $|0, 0\rangle$, has an energy of $-4t$ coming from the kinetic energies of the orbitals and a Coulomb term $(U + 2V)/4$ from Eq.3.4 due to electron electron interactions. If we measure energies of all configurations with respect to $|0, 0\rangle$ then the 3×3 , $\kappa_{tot} = 0$ Hamiltonian is obtained as

$$H_{\kappa_{tot}=0}^{S=1/2} = \begin{bmatrix} 0 & \frac{U}{2\sqrt{2}} & \frac{1}{4}(U - 2V) \\ \frac{U}{2\sqrt{2}} & \frac{U-2V}{4} + 4t & \frac{U}{2\sqrt{2}} \\ \frac{1}{4}(U - 2V) & \frac{U}{2\sqrt{2}} & 8t \end{bmatrix}. \quad (3.15)$$

Examining the diagonal elements of this matrix, we see that moving two electrons from state $|0, 0\rangle$ to $|\pm\pi/2, \mp\pi/2\rangle$ requires twice the energy between two molecular levels and a change in Coulomb energy between electrons on the same versus different molecular levels; $4t + (U - 2V)/4$. Similarly, moving two electrons from state $|0, 0\rangle$ to $|\pi, \pi\rangle$ without separating the pair, requires the energy of $8t$ in total; $4t$ for each electron.

In addition to the 3×3 $\kappa_{tot} = 0$ subspace, the full singlet space contains degenerate 2×2 $\kappa = \pm\pi/2$ and 3×3 $\kappa = \pi$ Hamiltonians. The eigenenergies of these subspaces are calculated as $(U + V \pm \sqrt{16t^2 + (U - V)^2})/2$ and $\{0, U, V\}$ for $\kappa_{tot} = \pm\pi/2$ and $\kappa_{tot} = \pi$, respectively.

We see that the calculations in Fourier space are simpler and lead to analytical results. However, they do not identify the phase change upon tunneling across the last link of the QCD ring in the triplet subspace.

C. N. Yang Pairing

Following C.N. Yang,²⁰⁷ we shall now consider the possibility of singlet pairing in our

QQD. Let's consider the Yang operator

$$\eta_m^+ = \frac{1}{2\sqrt{2}} \sum_{l=1}^4 (-1)^l (c_{l\downarrow}^+ c_{l+m\uparrow}^+ + c_{l+m\downarrow}^+ c_{l\uparrow}^+), \quad (3.16)$$

that creates a pair of electrons in a singlet configuration. We now focus on two of them, η_0^+ creating a combination of doubly-occupied configurations, and η_1^+ , which creates a linear combination of nearest-neighbor singlet pairs.

In the limit of $V = 0$, the following commutation relation holds exactly:

$$[H, \eta_0^+] = (2E_0 + U)\eta_0^+. \quad (3.17)$$

This enables us to generate systematically the eigenstates of the Hamiltonian in this limit for two, four, six, and eight electrons by applying the operator η_0^+ repeatedly. Specifically, the exact eigenstate for two electrons in our QQD, $\eta_0^+|0\rangle = \frac{1}{\sqrt{2}} \sum_{l=0}^4 (-1)^l c_{l\downarrow}^+ c_{l\uparrow}^+ |0\rangle$, is composed of the doubly occupied real-space configurations only and has the energy of U with $E_0 = 0$. In the Fourier space the pairing operator assumes the form $\eta_0^+ = \sum_k c_{k\downarrow}^+ c_{\pi-k\uparrow}^+$.

The operator η_1^+ is of particular interest in the limit of $U = \infty$, that is, when the doubly-occupied configurations are excluded. In this case, and in particular for the quadruple-dot system, we find another exact commutation rule:

$$[H, \eta_1^+] = [2E_0 + (N + 1)V]\eta_1^+, \quad (3.18)$$

where N is the number of electrons already existing in the system before application of the Yang operator. Since the doubly-occupied configurations are excluded, in this limit we can generate only the two-electron and the four-electron eigenstate by applying the operator η_1^+ to the vacuum state $|0\rangle$ once and twice, respectively. Let us look at the two-electron singlet, $\eta_1^+|0\rangle = \frac{1}{2\sqrt{2}} \sum_{l=0}^4 (-1)^l (c_{l\downarrow}^+ c_{l+1\uparrow}^+ + c_{l+1\downarrow}^+ c_{l\uparrow}^+)$. As found previously in diagonalizing the Hamiltonian, Eq.3.9, the energy of this eigenstate is equal to V . Note that this state is a linear combination of nearest neighbor pairs.

In the case of finite U and V the two commutation relations discussed above do not hold. In spite of that, the analysis presented in this Section indicates the existence of states with energies equal precisely to U and V , respectively, that is, the paired states $\eta_0^+|0\rangle$ and $\eta_1^+|0\rangle$ are eigenstates of the system. This is understandable considering the fact that in the real-space representation, the Coulomb interactions appear on the diagonals only. The term V is simply inactive for the state $\eta_0^+|0\rangle$ and the same is true for the term U for the state $\eta_1^+|0\rangle$, that is, in these two cases the system behaves as if it was in the appropriate limit, in which the Yang operators generate exact eigenstates.

3.1.2.2 Underdoped QQD

3.1.2.2.1 Three Electron Spectrum in Real Space We can further demonstrate the importance of topology by investigating the three-electron system. I will classify the three electron states according to their total spin, $S = 3/2$ or $S = 1/2$. Three spin-polarized electrons, corresponding to $S = 3/2$, can be distributed on four dots by placing each on a different dot and leaving one empty. These configurations can be thought of as placing a quasi-hole on a single dot in a half-filled spin polarized QQD. Then, a state with three electrons on dots 1, 2, and 3, belonging to the $S = 3/2$ subspace, can be represented as $|123\rangle_{3/2}$ or equivalently placing a quasi-hole on dot 4 as $|4_{qh}\rangle_{3/2}$. As a result, the four possible spin-polarized configurations are represented as follows: $\{|123\rangle_{3/2} = |4_{qh}\rangle_{3/2}, |124\rangle_{3/2} = |3_{qh}\rangle_{3/2}, |134\rangle_{3/2} = |2_{qh}\rangle_{3/2}, |234\rangle_{3/2} = |1_{qh}\rangle_{3/2}\}$. Since no two electrons with parallel spins can occupy the same dot, we find that the $S = 3/2$ quasi-hole Hamiltonian is the same as the single-electron Hamiltonian with a quasi-hole energy of $E_H = 2V + 3E_0$ for dots prepared on resonance:

$$\hat{H}_{\pm} = \begin{bmatrix} E_H & -t & 0 & -t \\ -t & E_H & -t & 0 \\ 0 & -t & E_H & -t \\ -t & 0 & -t & E_H \end{bmatrix}. \quad (3.19)$$

The energy spectrum of the $S = 3/2$ hole is then obtained as $(E_H - 2t, E_H, E_H + 2t)$ where the level E_H is doubly degenerate. Looking at the spectrum we see that the motion of a quasi-hole in a spin-polarized system is the same as that of a single electron in an empty QQD except for the E_H due to the presence of the electrons.

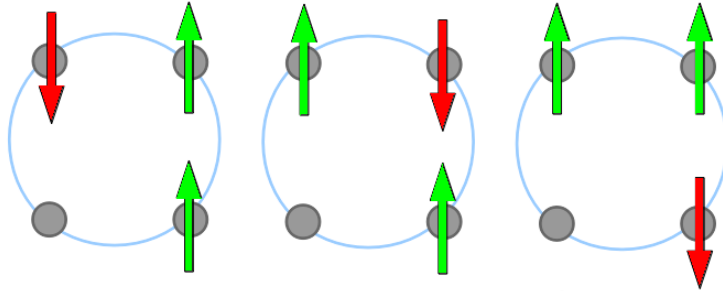


Figure 3.5: Singly occupied configurations within the $|123\rangle$ subspace contributing to the chirality states $|123_{\pm}\rangle$. The minority spin, down spin shown in red, propagating within the subspace

Let us now turn to the spin-depolarized subspace with $S = 1/2$ where there are two electrons with parallel spin that are anti-parallel to the spin of the third electron. Then

singly occupied configurations can be constructed by taking the $S = 3/2$ basis vectors, flipping the spin of one electron,^{183,185,188} and permuting the position of the minority spin within the same quasi-hole subspace (as shown in Fig.3.5 for $|123\rangle = |4_{qh}\rangle$). By properly symmetrizing the resulting configurations we will obtain two degenerate $S = 1/2$ and one excited $S = 3/2$ state from each $S = 3/2$ quasi-hole configuration.

As for two electrons, let's start by setting $U \rightarrow \infty$ and concentrate on the singly-occupied $S = 1/2$ states. We can define the chirality states that are eigenvectors of the chirality operator, $\hat{\chi}_{ijk} = (\hat{\mathbf{S}}_i \times \hat{\mathbf{S}}_j) \cdot \hat{\mathbf{S}}_k$,^{183,185,188,208} and the Hamiltonian in this limit can be diagonalized using the chirality eigenstates,

$$|ijk\rangle_{\pm} = \frac{1}{\sqrt{3}} \sum_{d=\{i,j,k\}} e^{\pm i2\pi(d-1)/3} |d_m\rangle. \quad (3.20)$$

Here, $|d_m\rangle = s_d^- c_{i\uparrow}^+ c_{j\uparrow}^+ c_{k\uparrow}^+ |0\rangle$ where d is the position of the minority spin, s_d^- is the spin lowering operator at site d , and i, j, k takes on the values $\{1, 2, 3, 4\}$ for $i \neq j \neq k$ since we are working with singly occupied states. For example, chiral states $|123\rangle_{\pm} = |4_{qh}\rangle_{\pm}$ are written explicitly as $|123\rangle_{\pm} = c_{1\downarrow}^+ c_{2\uparrow}^+ c_{3\uparrow}^+ |0\rangle + e^{\pm i2\pi/3} c_{1\uparrow}^+ c_{2\downarrow}^+ c_{3\uparrow}^+ |0\rangle + e^{\pm i4\pi/3} c_{1\uparrow}^+ c_{2\uparrow}^+ c_{3\downarrow}^+ |0\rangle$. These degenerate states can be visualized as a minority spin moving either to the left or to the right, generating a spin current, as shown in Fig.3.5. Within this subspace, the Hamiltonian can be block diagonalized into two 4×4 matrices $\hat{H}_{\pm}$, each corresponding to a definite *chirality*,

$$\hat{H}_{\pm} = \begin{bmatrix} E_H & -t & 0 & -e^{\pm i2\pi/3}t \\ -t & E_H & -t & 0 \\ 0 & -t & E_H & -t \\ -e^{\mp i2\pi/3}t & 0 & -t & E_H \end{bmatrix}. \quad (3.21)$$

The above Hamiltonian of the hole attached to chiral three-spin states resembles that of the hole attached to the spin polarized $S = 3/2$ three-electron states, Eq.3.19, except for the phase $e^{\pm i2\pi/3}$ attached to the tunneling element t_{14} . Hence a quasi-hole in a spin unpolarized $S = 1/2$ configuration acquires this phase upon tunnelling between dots 1 and 4. On resonance, the energy spectrum of these singly occupied configurations is calculated as $\{E_H - \sqrt{3}t, E_H - t, E_H + t, E_H + \sqrt{3}t\}$. We see that the chirality related phase, $\pm i2\pi/3$, effectively reduces t_{14} , increases the ground state energy and lifts the degeneracy in the spectrum of the hole attached to the $S = 3/2$ three-spin state.

3.1.2.2.2 Three-Electron Spectrum in Fourier Space Fourier transformed (FT) $S = 3/2$ real space configurations will diagonalize the $S = 3/2$ Hamiltonian. This is

not the case for the $S = 1/2$ subspace. Because of the phase $e^{i2\pi/3}$ attached to the t_{14} hopping element, a simple FT of the $S = 1/2$ chiral states does not diagonalize the Hamiltonian, Eq.3.21. However, one can do so by adding a phase $e^{-in\phi/4}$ in front of each state $|n_{qh}\rangle$, where in this case $\phi/4 = (2\pi/3)/4 = \pi/6$. Then the eigenstates of the $S = 1/2$ Hamiltonian in Fourier space are expressed as

$$|\chi_\kappa\rangle_{1/2} = \sum_n e^{i\kappa n} e^{i\pi n/6} |n_{qh}\rangle_\pm. \quad (3.22)$$

The chirality of the three-electron complex results in an effective gauge field leading to a phase accumulated by the hole moving on the ring. This phase affects the ground state energy of the hole. For singly occupied configurations, the energy of the ground state for both $S = 3/2$ and $S = 1/2$ configurations can be expressed as $E = E_H - 2t\cos(\phi/4)$, where $\phi = 0$ for $S = 3/2$ state and $\phi = \pm 2\pi/3$ for the two $S = 1/2$ chiral states.

The analysis both in real space and Fourier space so far did not include the doubly occupied configurations. In fact, the $S = 1/2$ space contains 12 doubly occupied configurations that mix with the chirality- $\pm$ states. As a result, chirality is no longer conserved and the 20×20 Hamiltonian can no longer be block diagonalized according to chirality. However, if we work in the Fourier space and distinguish the configurations according to their total wavevector, the Hamiltonian can be block diagonalized into four 5×5 matrices through the use of Eq.3.2. The doubly degenerate ground state of the $S = 1/2$ subspace can be obtained by diagonalizing the $\kappa_{tot} = \pm\pi/2$ subspaces which are made out of the doubly occupied $\{|0_\uparrow, 0_\downarrow, \frac{\pm\pi}{2}_\uparrow\rangle, |\frac{\pm\pi}{2}_\uparrow, \frac{\pm\pi}{2}_\downarrow, \frac{\mp\pi}{2}_\uparrow\rangle, |\frac{\pm\pi}{2}_\uparrow, \pi_\uparrow, \pi_\downarrow\rangle\}$, and the singly occupied $|0, \frac{\mp\pi}{2}, \pi\rangle$ basis vectors that are depicted in Fig.3.6 for $\kappa_{tot} = \pi/2$.

As shown in Fig.3.6(a), the state with the lowest kinetic energy $-4t$, has two antiparallel electrons at the molecular state $\kappa = 0$ and one at $\kappa = \pm\pi/2$. There are three states with zero kinetic energy. Two are obtained from the linear combination of the singly occupied states $|0, \pm\pi/2, \pi\rangle$ (one shown in Fig.3.6(b)), and the third one is the doubly occupied state with electrons occupying the degenerate molecular levels $|\pm\pi/2, \pm\pi/2, \mp\pi/2\rangle$ as shown in Fig.3.6(c). Finally, the state with the highest kinetic energy, $E = 4t$, depicted in Fig.3.6(d) has two electrons on the $\kappa = \pi$ state and one electron in one of the degenerate molecular states. Setting $E_0 = 0$, the Hamiltonian describing the $\kappa_{tot} = \pm\pi/2, S = 1/2$

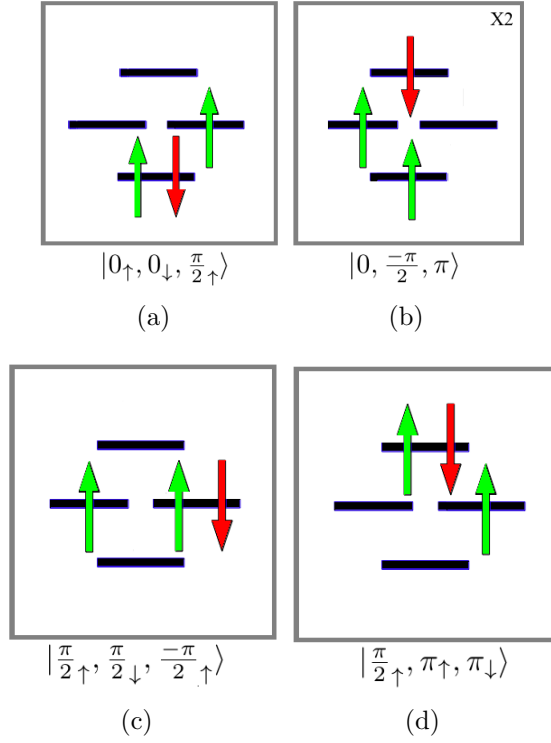


Figure 3.6: $\kappa_{tot} = \pi/2$ configurations. In this three electron subspace there are two singly occupied configurations obtained by changing the position of the minority spin in the configuration $|0, -\frac{\pi}{2}, \pi\rangle$ shown in (b).

subspace is obtained as

$$\hat{H}_{\kappa=\pm\pi/2}^{1/2} = \begin{bmatrix} -4t + \frac{U}{2} + \frac{3V}{2} & -\frac{U-4V}{4\sqrt{2}} & \sqrt{\frac{3}{32}}U & -\frac{U}{4} & \frac{-U+2V}{4} \\ -\frac{U-4V}{4\sqrt{2}} & \frac{3U}{4} + V & 0 & -\frac{U}{2\sqrt{2}} & \frac{U-4V}{4\sqrt{2}} \\ \sqrt{\frac{3}{32}}U & 0 & \frac{3U}{4} + 2V & 0 & \sqrt{\frac{3}{32}}U \\ -\frac{U}{4} & -\frac{U}{2\sqrt{2}} & 0 & \frac{U}{2} + 2V & \frac{U}{4} \\ \frac{-U+2V}{4} & \frac{U-4V}{4\sqrt{2}} & \sqrt{\frac{3}{32}}U & \frac{U}{4} & 4t + \frac{U}{2} + \frac{3V}{2} \end{bmatrix}, \quad (3.23)$$

for the basis vectors ordered as $\{|0_{\uparrow}, 0_{\downarrow}, \frac{\pm\pi}{2}_{\uparrow}\rangle, |0, \frac{\mp\pi}{2}, \pi\rangle_1, |0, \frac{\mp\pi}{2}, \pi\rangle_2, |\frac{\pm\pi}{2}_{\uparrow}, \frac{\pm\pi}{2}_{\downarrow}, \frac{\mp\pi}{2}_{\uparrow}\rangle, |\frac{\pm\pi}{2}_{\uparrow}, \pi_{\uparrow}, \pi_{\downarrow}\rangle\}$. Compared to the lowest kinetic energy configuration $|0_{\uparrow}, 0_{\downarrow}, \frac{\pm\pi}{2}\rangle$, in addition to the energy needed to move two electrons from the $\kappa = 0$ level to the degenerate shell, the doubly occupied state picks up a $V/2$ term from the exchange interaction between these degenerate levels and the singly occupied states have an additional $(U \pm 2V)/4$ Coulomb term at the diagonal.

3.1.2.2.3 Spin Transition

I will now demonstrate Nagaoka's ferromagnetism²⁰⁹ for a QQD in a ring geometry in the strong coupling limit, $U \gg V > t$. If the dots are on resonance, the $S = 1/2$ ground state can be perturbatively calculated from the 20×20 real-space Hamiltonian as

$$E_{1/2}^S \approx E_{3/2}^S + t(2 - \sqrt{3}) - \frac{2t^2}{U + \sqrt{3}t} - \frac{3t^2}{U + \sqrt{3}t - 2V}. \quad (3.24)$$

Compared to the $S = 3/2$ ground state energy $E_{3/2}^S = E_H - 2t$, the energy of this level increases by $(2 - \sqrt{3})t$ but decreases with the superexchange contribution $E_{sxc}^{(3)} = \frac{2t^2}{U + \sqrt{3}t} + \frac{3t^2}{U + \sqrt{3}t - 2V}$. As a result, by manipulating the tunnelling and the on-site Hubbard repulsion, we can tune the ground state of the three electron system between the total spin $S = 3/2$ and $S = 1/2$ states. If $E_{sxc}^{(3)} > (\sqrt{3} - 2)t$ then the ground state has a total spin $S = 1/2$. By increasing the onsite repulsion or decreasing the tunnelling matrix element we can reverse the equality and induce a transition from $S = 1/2$ to a $S = 3/2$ ground state as seen in the phase diagram given in Fig.3.7. This figure depicts the stability of the $S = 1/2$ and $S = 3/2$ phases as a function of V/t and U/t upon exact diagonalization of the full Hamiltonian as well as the perturbative solution.

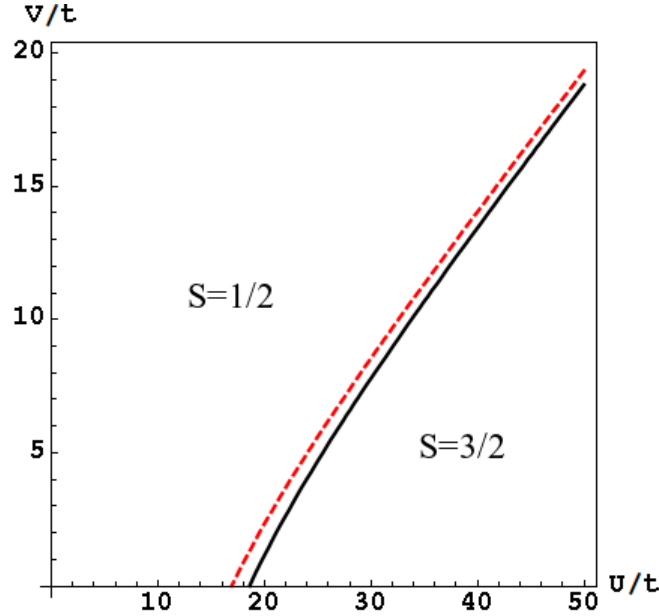


Figure 3.7: Ground state phase diagram showing the dependence of the total spin of the ground state on U/t and V/t . The black line is the exact and the red dashed line is the perturbative solution separating the two total spin domains of the ground state. The $S = 3/2$ ($S = 1/2$) state is the ground state to the right (left) of the black line. Reprinted from Ref.¹⁵⁶

In LQQD, the configurations with electrons on both dots 1 and 4 lose the nearest-

neighbor Coulomb repulsion term V from their corresponding diagonal element in the Hamiltonian. Furthermore, losing the tunnelling element t_{14} , the phase factor disappears due to this change in geometry and the $S = 3/2$ and the singly occupied $S = 1/2$ Hamiltonians become indistinguishable.

As mentioned before, the LQQD cannot be expressed in the Fourier space and the 20×20 $S = 1/2$ Hamiltonian that includes double occupancy cannot be block-diagonalized. Upon its numerical diagonalization, we see that the ground state of the LQQD is always spin unpolarized. Therefore it is not possible to tune the ground state of the three-electron LQQD molecule between the $S = 1/2$ and $S = 3/2$ states by varying Coulomb interaction or the tunnelling matrix elements.

3.1.2.3 Charge Neutral QQD

The half-filled QQD molecule approximated by the Heisenberg model has been studied by Scarola and DasSarma¹⁹⁴ and Mizel and Lidar¹⁹⁵ and the molecule was investigated in the Hubbard model by, e.g., Lobos and Aligia,¹⁹¹ Nisikawa and Oguri¹⁹² and Brum and Hawrylak.¹⁹⁰ I will summarize these results here for completeness.

In the half-filled QQD containing $N_e = 4$ electrons (or 4 holes), there is only one way of placing four spin-polarized electrons on four dots, that is by placing an electron on each dot, $c_{1\uparrow}^+ c_{2\uparrow}^+ c_{3\uparrow}^+ c_{4\uparrow}^+ |0\rangle$. Then the $S = 2, S_z = 2$ subspace contains only one configuration with the energy $E_{S=2} = \sum E_i + V_{12} + V_{23} + V_{34} + V_{14}$.

There are four singly occupied configurations with $S_z = 1$ that can be obtained by flipping one electron in the spin polarized system, permuting the minority spin and properly symmetrizing the resulting configurations using the FT as

$$|\phi_g\rangle = \sum_d e^{ig(d-1)} |d_m\rangle. \quad (3.25)$$

Here, d_m represents the position of the minority spin just as in Eq.3.20 such that $|d_m\rangle = s_d^- c_{1\uparrow}^+ c_{2\uparrow}^+ c_{3\uparrow}^+ c_{4\uparrow}^+ |0\rangle$. Out of these four symmetrized configurations, the configuration with $g = 0$ belongs to the $S = 2$ subspace, while the remaining three configurations with $g = \{\pi/2, \pi, 3\pi/2\}$ belong to the $S = 1$ subspace.

Placing two antiparallel spins on the same dot, within the $S_z = 1$ subspace we can also create doubly occupied configurations. For each doubly occupied quantum dot, the remaining two spin-polarized electrons can occupy three dots in only three ways as depicted in Fig.3.8. Since there are four dots that can be doubly occupied, in total there are $4 \cdot 3 = 12$ doubly occupied configurations in the $S = 1$ subspace. Due to the double occupancy, these states acquire a U term in their diagonal element of the Hamiltonian. The doubly occupied states mix with the singly occupied FT configurations and the ground state of the 15×15

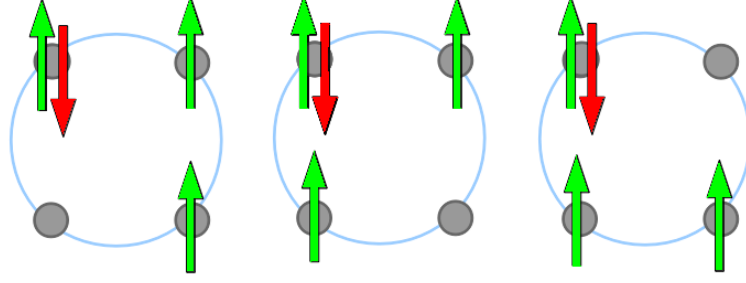


Figure 3.8: Three possible configuration of spin-polarized two electrons if the first dot is doubly occupied

Hamiltonian is approximated as $E_{S=1} = 4V - \frac{16t^2}{3(U-V)}$.

The $S = 0$ subspace contains two configurations with single occupancy. Starting with two pairs of electrons with antiparallel spins in the $S_z = 0$ subspace, there are six possible ways of distributing these four electrons onto four dots without double occupancy. After proper symmetrization of these six singly occupied $S_z = 0$ configurations, there will be one configuration with total spin $S = 2$, three configurations with $S = 1$, and the remaining two will belong to $S = 0$. In addition to the singly occupied configurations, there are 12 doubly occupied configurations that can be obtained from the 12 doubly occupied states mentioned in the $S = 1$ subspace. By flipping the spin of one of the alone electrons and properly symmetrizing these states one can obtain the $S = 0$ doubly occupied configurations. These doubly occupied states come at a cost of U .

With 4 electrons, we can have two pairs of electrons occupying the same dot, creating the *two doubly occupied dots (DD)*. They can also be thought of as taking the spin polarized two-electron states and adding antiparallel electrons on previously occupied dots. As a result, these configurations acquire a $2U$ on-site interaction. Then the full $S = 0$ subspace includes two singly occupied configurations, 12 doubly occupied configurations, and six DD configurations.

When dots are prepared on resonance, in the strong coupling limit where $U \gg V > t$, if we neglect the effects of the DD configurations on the ground state, perturbatively the $S = 0$ ground state energy can be approximated as $E_{S=0} = 4V - \frac{(8+2\sqrt{3})t^2}{U-V}$. Comparing the $S = 0, 1, 2$ ground state energies, we can deduce that the ground state of the four-electron system is always a total spin $S = 0$.

If we work in the Fourier space, the 20×20 $S = 0$ and 15×15 $S = 1$ Hamiltonians can be block diagonalized according to the total wavevector of the configurations as shown for $N_e = 2, 3$ before. Then the $S = 0$ ground state can be found by diagonalizing a 6×6 Hamiltonian matrix, and the $S = 1$ ground state can be found by solving the 4×4 Hamiltonian instead.

At half-filling we can map the low energy spectrum of the Hubbard Hamiltonian onto a Heisenberg Hamiltonian that is given as

$$\hat{H}_{Heis} = \sum_{\langle i,j \rangle, i < j} J_{ij} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j, \quad (3.26)$$

where J_{ij} are the exchange matrix elements. The exchange matrix element is defined in terms of the gap between the ground levels of the different total spin subspaces that is calculated as $E_1 - E_0 = J$. Similarly, the gap between the ground states of the $S = 1$ and $S = 2$ subspaces is found as $E_2 - E_1 = 2J$. Using the perturbatively obtained ground state energies on resonance, J is approximated as $J = \frac{8}{3} \frac{t^2}{U-V}$ in the strong interaction regime ($U \gg t$). The lowest band energies calculated by both Heisenberg and Hubbard models are shown in Fig.3.9.

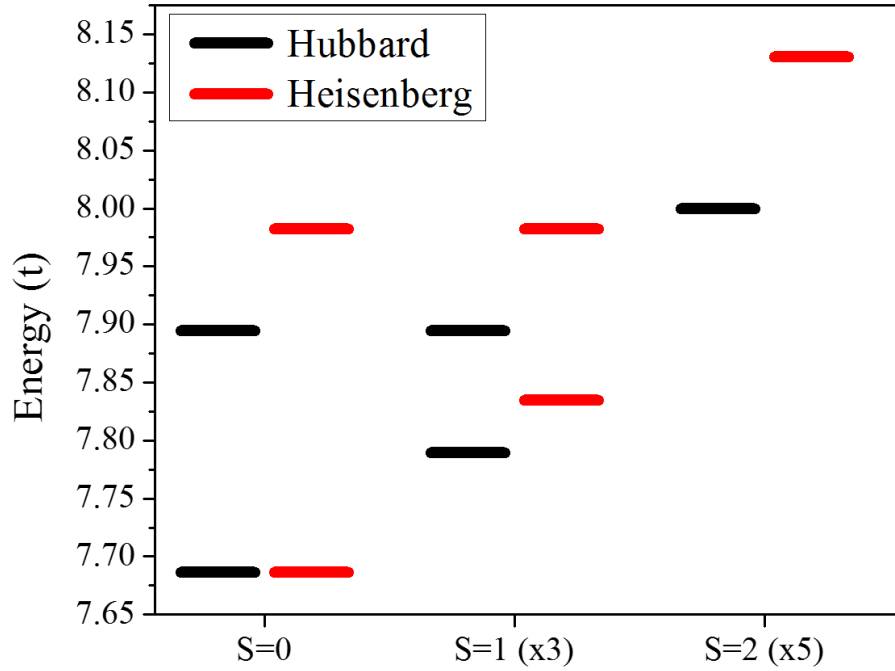


Figure 3.9: Lowest energy spectrum of the half-filled case of QQD calculated by Hubbard (black) and Heisenberg (red) models using $V = 2t$ and $U = 20t$.

As we tune the QQD into a linear molecule by screening the interactions between dots 1 and 4 and blocking the tunnelling, the energy of the $S = 2$ subspace reduces to $3V + 4E$. Perturbatively, the ground state energy of the $S = 1$ subspace is calculated as $3V - \frac{4}{3} \frac{t^2}{U} - \frac{4}{3} \frac{t^2}{U-2V}$. Again, by neglecting the mixing with the DD configurations, the ground state energy of the $S = 0$ subspace is approximated as $3V - (2 + \sqrt{3})t^2(\frac{1}{U} + \frac{1}{U-2V}) - \frac{2t^2}{U-V}$. Since $2 + \sqrt{3} > 4/3$, we clearly see that the ground state of the LQQD is always a total spin $S = 0$ state. If we include the corrections arising from the interactions with DD

configurations, the energy of $S = 0$ ground state will be lowered, further increasing the gap between the $S = 0$, $S = 1$ ground states.

3.1.2.4 Capacitively Coupled Pair of Double Dots

Recently, Shulman *et al.*¹⁸⁰ reported entanglement in two capacitively coupled double quantum dots with two electrons each. Each double dot was biased so that only two states in each dot were relevant, the singlet and triplet $(1, 1)$ configurations. These states are treated as the logical coded qubit states. In the Hubbard treatment of each molecule it is apparent that the singlet state has admixtures of the doubly occupied configurations $(2, 0)$ and $(0, 2)$ which can be tuned by biasing the molecule. On the other hand, the triplet $(1, 1)$ configuration cannot have such admixtures. As a result, the singlet and triplet configurations differ by their charge distribution, which creates the possibility of capacitive coupling with another molecule and allows to generate an entangled state of the two coded qubits.

A simpler system, in which the capacitive coupling is even more apparent, involves a QQD in a ring topology as in Fig.3.2(b), only without the tunneling coupling between dots 1 and 4 as well as 2 and 3. We place one electron in the double dot built out of dots 1 and 2, and another electron in the double dot created by dots 3 and 4. The logical states of each of such coded qubits are identified by the position of the electron in either the left or the right dot. The interdot tunneling rotates each qubit, while the electron-electron interactions provide the coupling between qubits (favors the antipodal configurations) and lead to the formation of entangled states. This system is formally equivalent to the exciton in a vertically coupled double-dot molecule studied by Bayer *et al.* in Ref. 210.

3.1.2.5 One to Three Holes

For a QQD with a single orbital per dot the maximum number of electrons is $N_e^{max} = 8$. Populating the levels with $N_e = 7$ electrons can be interpreted as creating a single hole. Just like a single electron, the hole can be placed on any dot. Starting with the fully occupied QQD $|\nu\rangle = \prod c_{i\uparrow}^+ \prod c_{j\downarrow}^+ |0\rangle$, we can define the operator $h_{i\sigma}^+$ to create a hole with spin σ on the i th dot as $h_{i\sigma}^+ |N_e = 8\rangle = c_{i\sigma} |\nu\rangle$. Due to electron-hole symmetry, the off-diagonal elements t_{nm} of the Hamiltonian will transform as $t_{nm} \rightarrow -t_{nm}$. Since the single-particle spectrum is fully symmetric, the energy spectrum of a $N_h = N$ number of holes will always be the same as $N_e = N$ electrons, but all energy levels will be shifted up in energy because of the additional terms in the diagonal elements of the Hamiltonian (the self energy of the holes). It is interesting to note that the Yang operators discussed in Section 3.1.2.1 apply equally well to the two holes creating exact paired singlet eigenstates.

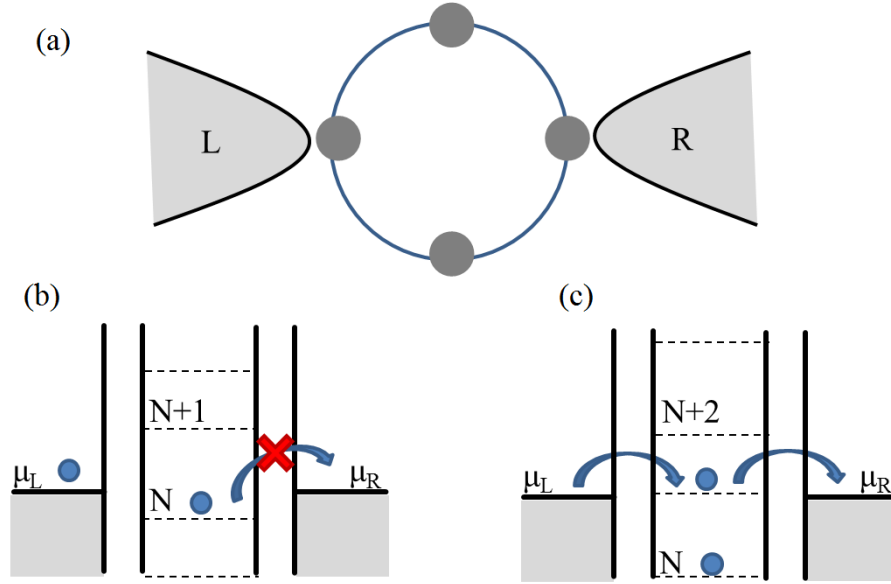


Figure 3.10: (a) Tunnel junction model: the QQD molecule weakly coupled to the leads. (b) Electrons are not allowed to tunnel through the QQD when the chemical potentials are not on resonance. (c) Electron allowed to tunnel through the QQD, creating a current across the leads.

3.1.3 Charging Diagram and Coulomb and Spin Blockade

Now that we have the exact ground state energies, $E_{GS}(N_e)$, of the $N_e = \{1, \dots, 8\}$ electrons and their perturbative approximations, we can construct the charging diagram for the quadruple quantum dot molecule.

Using an external gate potential V_g one can align the chemical potential $\mu(N_e, V_g) = E_{GS}(N_e) - E_{GS}(N_e - 1)$ of the QQD to the chemical potential of the leads, μ_L , for a given number of electrons N_e (Fig.3.10(a)) by controlling E_0 which is taken to be the same for all dots. Once $\mu(N_e, V_g) = \mu_L$, an electron can flow through the QQD as depicted in Fig.3.10(c). For other voltages V_g , current is blocked resulting in Coulomb blockade (CB)(Fig.3.10(b)). Furthermore, to add an electron, the total spin S_i of the initial N_e electron QQD and final total spin S_f of the $N_e + 1$ electron QQD cannot differ by more than the spin of a single electron, $s = 1/2$. If the difference is greater, the spin blockade (SB) prevents current from flowing.^{169,170}

The Coulomb blockade peaks as a function of the gate voltage V_g for $U = 30, V = 4, t = 1$ are shown in Fig.3.11. The amplitude of the peaks correspond to the total spin, S , of the ground state of the N_e electron system at given gate voltages. Dashed lines are used at the $N_e = 3(5)$ system to indicate spin blockade for the given set of parameters. For these parameters the ground state of the 3 electron and 5 electron (3(5) hole) state

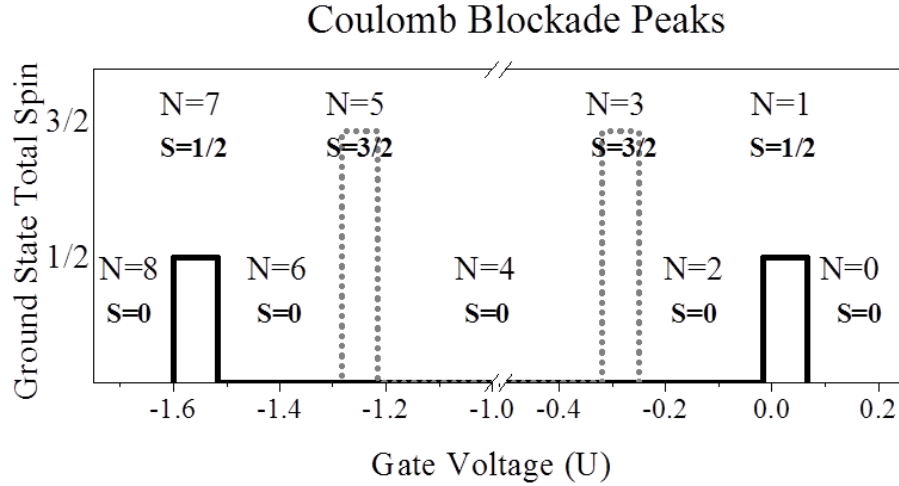


Figure 3.11: Charging diagram of the quadruple quantum dot on resonance in ring geometry as a function of total number electrons and gate voltage for the following parameters $U = 30, V = 4, t = 1$. The peak locations indicate the gate voltage required (in terms of U) to add the next electron. The amplitude of the peaks corresponds to the total spin of the ground state of the N_e electron system. Dashed lines indicate spin blockade. Reprinted from Ref.¹⁵⁶

has spin $S = 3/2$ in ring geometry while they are spin $S = 1/2$ in linear geometry.

The first peak from the right in Fig.3.11 corresponds to the gate voltage allowing for the addition of the first electron. Assuming $\mu_L = 0$, the first electron can enter the molecule when the condition $\mu_L = 0 = E_{GS}(1) - E_{Vac} = (E_0 - 2t) - 0$ is satisfied. Then the first peak is observed at the energy $E_0 = 2t$ which can be used to measure the tunneling matrix element t . In order to be able to extract the values of U and V , the remaining CB peak spacings can be calculated using the perturbative solutions of the ground state energies given in the text.

The second electron enters the dot when $E_{GS}(2) - E_{GS}(1) = 0$. Using the perturbative solution to the ground state of the two-electron system, we can find the gate voltage (or the onsite chemical potential of the dots which are on resonance),

$$\left(2E_0 - \frac{Q' - V}{2} - E_{sc}^{(2)}\right) - (E_0 - 2t) = 0$$

$$E_0 \approx -2t + \frac{Q' - V}{2} + E_{sc}^{(2)}. \quad (3.27)$$

For the chosen values of U, V and t , the total spin of the $N_e = 3$ ring QD is $S = 3/2$ while for both $N_e = 2$ and $N_e = 4$ the total spin is $S = 0$. The difference in total spin $\Delta S = 3/2$ is greater than the spin of a single electron hence it results in a zero-amplitude CB peak. Then for sufficiently strong interactions, the SB can be used to detect the spin

polarized state of the QQD in the ring geometry. One can also use high source and drain spectroscopy to measure excited states and detect the $S = 3/2$ and $S = 1/2$ gap which is directly related to the gauge field threading the ring as discussed above.

Going from three to four electrons, one should expect a SB as the four electron ground state is always $S = 1/2$ and for the chosen values of U, V and t the three-electron ground state is $S = 3/2$.

Since the five-electron ground state has a total spin $S = 3/2$, one would expect a SB, coming from the $S = 1/2$ four electron ground state. Looking at the Fig.3.11 it is important to note that to build a five-electron state, we must have at least one doubly occupied quantum dot. This is important for the weakly interacting system in which there is no spin blockade. As a result of the double occupancy, there is a large energy gap between the gate voltage required to add the 4th electron and the 5th electron.

3.2 Artificial Benzene Ring

Benzene is the building block of most carbon based components, including graphene. The artificial benzene ring, in addition to being a candidate for quantum circuits, is an important structure to study as it might allow us to understand the properties of real benzene rings and how they can be modified by engineering at the nanoscale.

There has been extensive theoretical work on benzene rings addressing different phenomena such as quantum tunnelling in vertically coupled rings,¹⁹⁶ inelastic co-tunnelling in double, triple and sextuple quantum dot molecules,¹⁹⁹ electron localization,²⁰⁰ conductance,²⁰¹ transport,²⁰² quantum interference²⁰³ and Coulomb blockade.²⁰⁴ Moreover the optical properties of benzene have been of interest to materials scientists as they are building blocks of polycyclic aromatic hydrocarbons.²⁰⁵

There have been experiments for realization of artificial graphene or honeycomb structures as a platform to study Dirac fermions and topological phases in addition to their general electronic properties.^{211–213} The realization of core-multishell nanowires that allows for carrier confinements close to the surface of the nanowire led to theoretical proposals and experimental realizations of electron confinement in flat hexagonal rings.^{200,206}

Motivated by these experiments and theoretical interest, I will now provide a theory of electronic and optical properties of an artificial benzene ring (ABR) molecule described as a function of the number of electrons N_e , and physical parameters such as inter-dot

tunnelling, and Coulomb interactions.

An artificial benzene ring structure can be realized inside a nanowire.²⁰⁰ Because of the crystalline structure of most semiconductors, their nanowires possess a hexagonal shape. The core-multishell nanowires are made to have different material compositions along the radial direction. The multishell structure allows for confinement of a two-dimensional electron gas (2DEG) in a hexagonal ring closer to the surface of the nanowire instead of its at center. Exploiting the polygonic shape of the ring and using gates, one can confine the electrons of the 2DEG to the six corners of the hexagon, creating six artificial dots as depicted in Fig.3.12. Tunnelling between the dots and Coulomb interactions can be tuned by changing the size of the structure to modify the distance between the dots. After its construction, the interactions can be altered electronically by changing the gate potentials or adding electrodes to individually control the interactions among specific dots.^{197,200,206,214–217} The advantage of such a system is its tunability when compared to natural benzene.

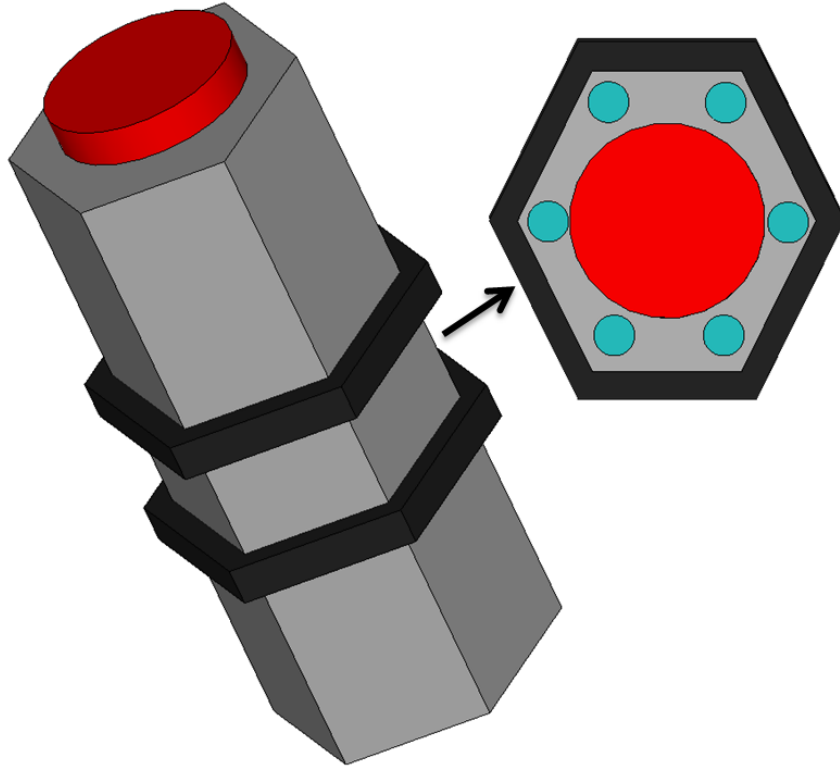


Figure 3.12: (a) confining 2D electron gas in a nanowire. Proposed model for realization of an artificial benzene ring by confining electrons on 6 corners of a hexagonal nanowire

Just as the QQD, the benzene molecule will be assumed to have one spin-degenerate orbital per quantum dot, with the whole molecule containing up to $N_e = 12$ electrons. We can work in the Fourier space using a Fourier transform of the real-space creation/annihilation

operators to obtain,

$$a_{\kappa_i}^+ = \frac{1}{\sqrt{6}} \sum_{j=1}^6 e^{i\kappa_i(j-1)} c_j^+, \quad (3.28)$$

where this time $\kappa_i = \{0, \pm\pi/3, \pm2\pi/3, \pi\}$ are the 6 allowed wave-vectors. Transforming the extended Hubbard Hamiltonian, Eq.2.65, we once again obtain Eq.3.2. However, this time the energy of each molecular state and the Coulomb matrix elements between molecular states are expressed as $\epsilon_{\kappa_i} = E - 2|t| \cos \kappa_i$ and

$$\langle \kappa_i \kappa_j | \mathcal{V}_{ee} | \kappa_k \kappa_l \rangle = \frac{U + 2V \cos(\kappa_l - \kappa_i)}{6} \delta(\kappa_i + \kappa_j, \kappa_k + \kappa_l), \quad (3.29)$$

respectively.

3.2.1 Single Particle Properties

In real space representation, the Hamiltonian matrix for a single electron tunnelling between 6 dots is written as

$$\hat{H} = \begin{bmatrix} 0 & t & 0 & 0 & 0 & \tau \\ t & 0 & t & 0 & 0 & 0 \\ 0 & t & 0 & t & 0 & 0 \\ 0 & 0 & t & 0 & t & 0 \\ 0 & 0 & 0 & t & 0 & t \\ \tau^* & 0 & 0 & 0 & t & 0 \end{bmatrix}, \quad (3.30)$$

where we only include NN tunnelling and τ represents the tunnelling between dot 1 and dot 6. For a benzene ring where dot 1 and dot 6 are connected as depicted in Fig.3.13(a), $\tau = t$. Whereas if we wanted to study a chain of 6 dots, then there would be no tunnelling between these dots, giving $\tau = 0$. In the molecular basis, the 6x6 one electron Hamiltonian matrix with each basis vector containing an electron on a different molecular state is already diagonal¹⁵⁶ with eigenvectors and eigenenergies corresponding to $\{|1\rangle, |2\rangle, |3\rangle, |4\rangle, |5\rangle, |6\rangle\}$ and $\{-2t, -t, -t, t, t, +2t\}$, respectively for $|i\rangle = a_i^+ |0\rangle$ which is depicted in Fig.3.13(b). Each of these molecular states can also be expressed in terms of κ as described in Eq.3.28.

3.2.2 Underdoped Artificial Benzene

Similar to the QQD, the underdoped ABR has lots of exciting properties. Charging the half-filled system with an electron or a hole, the total spin projections of $S_z = \{5/2, 3/2, 1/2\}$ can be obtained. In the underdoped QQD, the unpolarized state con-

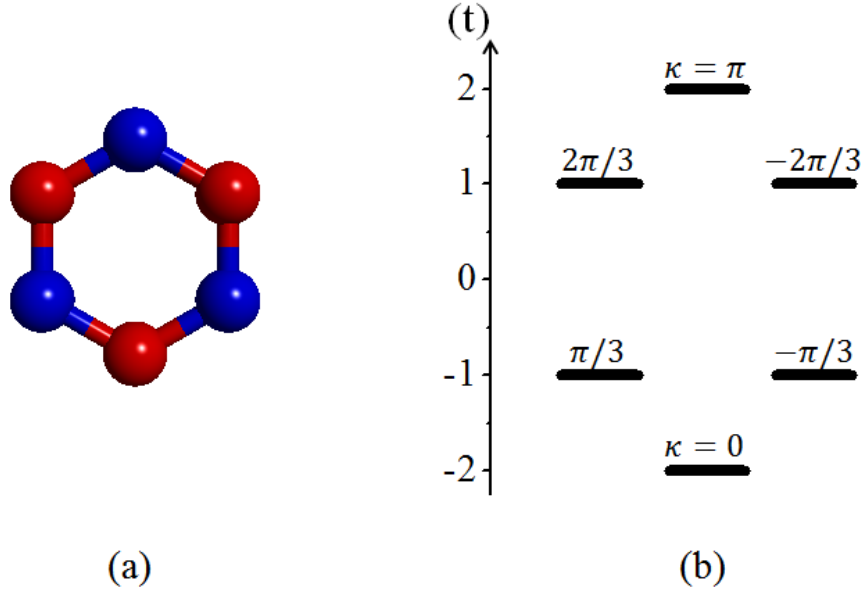


Figure 3.13: (a) The ABR structure (b) one-electron spectrum labelled with Fourier basis indices

tained two total spin states $S = \{1/2, 3/2\}$. For the underdoped ABR, $S_z = 1/2$ contains three possible total spin states $S = \{5/2, 3/2, 1/2\}$. How topology and electron-electron interactions differentiate those states will be described below.

Concentrating on the $N_e = 5$ case, we can analytically describe the energy spectrum at the two extrema; when interactions are so strong that double occupancy is not allowed, $U = \infty$, and when the electrons are not interacting, $U = 0$. For the strongly interacting regime, we restrict ourselves to work in the real-space description of the ABR, since the hopping element can be considered as a perturbation as compared to interactions, $U \gg t$. However, for the $U = 0$ regime where the hopping term is dominant and U is a perturbation, we will be working in Fourier space.

Very Strong Interactions: $U \rightarrow \infty$

We will classify the $N_e = 5$ ABR by total S_z and study each S_z separately.

$S_z = 5/2$: In the maximally spin polarized subspace, $S_z = 5/2$, in which there are no minority spins, the $N_e = 5$ spin-polarized electrons will be distributed on 6 dots, placing each on a different dot and leaving one empty. The five electron configurations obtained this way can be thought as placing a quasi-hole on a single dot in the half-filled system

such that

$$|h_m\rangle = \prod_{i \neq m}^6 c_{i\downarrow}^+ |0\rangle, \quad (3.31)$$

where m represents the position of the quasi-hole, or the removed electron. Just like the QQD¹⁵⁶ or the TQD,¹⁸⁵ the Hamiltonian for a hole in a spin polarized half filled system and that of a single electron (Eq.3.30) are the same, resulting in the same spectrum, shifted in energy by $5E$ due to the electrons residing on 5 quantum dots.

$S_z = 3/2$: The $S_z = 3/2$ configurations are obtained by flipping the spin of an electron in each hole-state of the $S_z = 5/2$ subspace leading to;

$$|j_{h_m}\rangle = c_{j\uparrow}^+ c_{j\downarrow} |h_m\rangle, \quad (3.32)$$

where $|h_m\rangle$ is the $S_z = 5/2$ hole state as defined in Eq.3.31 and j is the index of the flipped electron. We can do a Fourier transform on the minority spin that hops among the 5 filled states of a quasi-hole state $|h_m\rangle$ acquiring a phase of ξ upon each hopping event leading to $|\xi, h_m\rangle = \sum_j e^{i \cdot j \cdot \xi} |j_{h_m}\rangle$ where $\xi = 2\pi/5 * \{0, 1, 2, 3, 4\}$. Upon this rotation, the Hamiltonian becomes block diagonal in ξ , such that each block is made out of configurations with the hole in one of the 6 dots, feeling the minority spin chirality ξ . Each one of the five 6x6 blocks looks exactly like the single-particle Hamiltonian, Eq.3.30, with the artificial gauge field $e^{i\xi}$ emerging for the hole tunnelling between quantum dots one and six within the chirality space of ξ , making $\tau = te^{i\xi}$,

$$\hat{H} = \begin{bmatrix} 0 & t & 0 & 0 & 0 & te^{i\xi} \\ t & 0 & t & 0 & 0 & 0 \\ 0 & t & 0 & t & 0 & 0 \\ 0 & 0 & t & 0 & t & 0 \\ 0 & 0 & 0 & t & 0 & t \\ te^{-i\xi} & 0 & 0 & 0 & t & 0 \end{bmatrix}. \quad (3.33)$$

The chirality Hamiltonians, Eq.3.33, can be analytically diagonalized by realizing that the hole acquires a phase of $\phi_\xi = \xi/6$ every time it tunnels from one dot to another within each minority spin chirality- ξ subspace. Then the eigenvectors, $|\alpha, \xi\rangle$, and eigenvalues of each subspace can be obtained as

$$|\alpha, \xi\rangle = \frac{1}{6} \sum_m^6 e^{i \cdot m \cdot \phi_\xi} e^{i \cdot m \cdot \alpha} |\xi, h_m\rangle, \quad (3.34)$$

and $E_{\alpha, \xi} = 2t \cos(\alpha + \phi_\xi)$, respectively for $\alpha = 2\pi/6 * \{0, 1, 2, 3, 4, 5\}$.

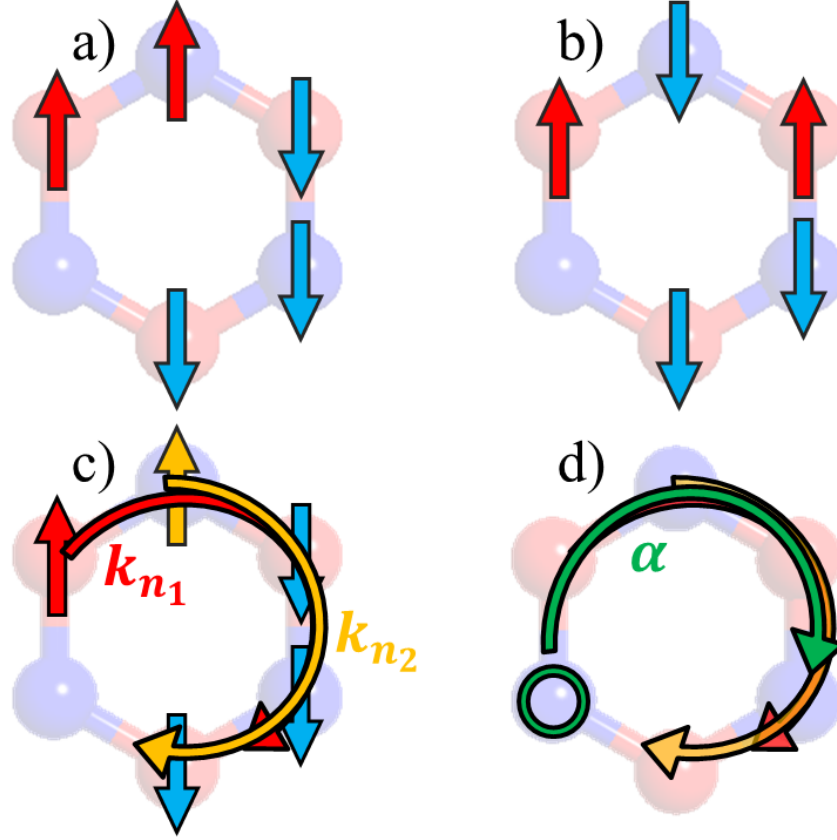


Figure 3.14: (a) and (b): Permutation configurations for two minority spin, $S_z = 1/2$, in 5 electron ABR. For a quasi-hole on the lower left dot, (a) two adjacent minority spins together (b) two minority spins separated by a majority spin. (c) Figure depicting a spin-current state with the beating of minority spin phases k_{n1} and k_{n2} (d) Hole tunnelling under the influence of spin-current-chirality

3.2.2.1 $S_z = 1/2$; Permutation

Flipping two spins in each $S_z = 5/2$ quasi-hole configuration, we can obtain the $S_z = 1/2$ subspace. Without aiming to separate these states in terms of their total spin, one can think of flipping two adjacent spins or two spins that are separated. For example, starting with the $|h_6\rangle$ state as defined in Eq.3.31, two spins can be flipped to give $|A_1^6\rangle = |c_{1\uparrow}^+ c_{2\uparrow}^+ c_{3\downarrow}^+ c_{4\downarrow}^+ c_{5\downarrow}^+\rangle$ and $|B_1^6\rangle = |c_{1\uparrow}^+ c_{2\downarrow}^+ c_{3\uparrow}^+ c_{4\downarrow}^+ c_{5\downarrow}^+\rangle$ as depicted in (a) and (b) of Fig.3.14 respectively, where the superscript represents the position of the quasi-hole and the subscript represents the configuration-index. Applying a permutation operator $\hat{P}$, which acts on the occupied states to permute the electrons on the occupied dots, $\hat{P}|A_1^6\rangle = |A_2^6\rangle = |c_{1\downarrow}^+ c_{2\uparrow}^+ c_{3\uparrow}^+ c_{4\downarrow}^+ c_{5\downarrow}^+\rangle$, we obtain 4 other permutation of $|A_1^6\rangle$ and $|B_1^6\rangle$. The A^h and B^h vectors are non-interacting thus the Hamiltonian can be separated into two non-interacting subspaces of vectors A and B. Just as in the $S_z = 3/2$ case, we can take the Fourier transform

of the five $A^h(B^h)$ states to obtain the two-spin-chirality states differentiated by the phase $\varphi = 2\pi/5 * \{0, 1, 2, 3, 4\}$, and obtain the subspaces for a quasi-hole tunnelling under the two-spin-chirality. Upon rotation, one can see that A and B subspaces are degenerate, and their 6x6 Hamiltonians are the same as Eq.3.30 with $\tau = te^{i\varphi}$.

Although the permutation operator provides an easy to understand description of the quasi-hole and chirality dynamics, the states obtained by this method are not eigenvectors of the total spin operator $\hat{S}$.

3.2.2.2 $S_z = 1/2$; Spin Current

In order to obtain the eigenstates of the total spin operator, let us introduce the spin-current operator $\hat{J}_n$. The spin-current operator takes an electron from an $S_z = 5/2$ quasi-hole state $|h_m\rangle$, flips its spin and shuffles it around the occupied dots, adding a phase of e^{ik_n} each time the electron tunnels (completely ignoring the unoccupied orbital, and consequently its index) such that

$$\hat{J}_n = \sum e^{ik_n j} c_{j\uparrow}^+ c_{j\downarrow}, \quad k_n = \frac{2\pi}{5}n, \quad n = \{1, 2, 3, 4, 5\}. \quad (3.35)$$

When acting on the state $|h_6\rangle = |\uparrow\uparrow\uparrow\uparrow\uparrow \cdot\rangle$ with the spin-current operator where $\cdot$ is a placeholder for the unoccupied orbital, one will get:

$$\begin{aligned} \hat{J}_1 |\uparrow\uparrow\uparrow\uparrow\uparrow \cdot\rangle &= e^{ik_1} |\downarrow\uparrow\uparrow\uparrow\uparrow \cdot\rangle + e^{i2k_1} |\uparrow\downarrow\uparrow\uparrow\uparrow \cdot\rangle + e^{i3k_1} |\uparrow\uparrow\downarrow\uparrow\uparrow \cdot\rangle \\ &+ e^{i4k_1} |\uparrow\uparrow\uparrow\downarrow\uparrow \cdot\rangle + e^{i5k_1} |\uparrow\uparrow\uparrow\uparrow\downarrow \cdot\rangle. \end{aligned} \quad (3.36)$$

For the $S_z = 1/2$ subspace however, one needs to apply two spin current operators onto a spin polarized $|h_m\rangle$ state;

$$\hat{J}_{n_2} \hat{J}_{n_1} = \sum_j \sum_l e^{i(jk_{n_1} + lk_{n_2})} c_{l\downarrow}^+ c_{l\uparrow} c_{j\downarrow}^+ c_{j\uparrow}. \quad (3.37)$$

Since all indices (k_{n_1}, k_{n_2}) and j, l can take on 5 different values, there are $5 \times 5 = 25$ possible spin-current states (k_{n_1}, k_{n_2}) and 25 configurations (j, l) . However, this cannot be true since we start with 10 states only and this is merely a rotation of basis.

Out of the 25 (j, l) configurations, 5 are non existent since $c_{l\downarrow}^+ c_{l\uparrow} c_{j\downarrow}^+ c_{j\uparrow} |\cdot\rangle = 0$ when $j = l$, and the remaining 20 are actually 10 since $c_{l\downarrow}^+ c_{l\uparrow} c_{j\downarrow}^+ c_{j\uparrow} = c_{j\downarrow}^+ c_{j\uparrow} c_{l\downarrow}^+ c_{l\uparrow}$, which takes care of the excess configurations problem.

Now let's look at the spin-current states and try to resolve the excess spin-current state problem. One can right away see that $\{k_{n_1}, k_{n_2}\} = \{k_{n_2}, k_{n_1}\}$, which will get rid of 10 out of these 25 spin-current states leaving us with only 15 to work with. Getting

rid of the 5 non-existent (j, l) configurations in the previous step had made these states non-orthogonal which now requires re-orthogonalization. Along this process we will have a chance of getting rid of the 5 extra spin-current states of the remaining 15.

I will first start by grouping the spin-current states $\{k_{n_1}, k_{n_2}\}$ according to their *total spin current*, which I will define as $k_{tot} = k_{n_1} + k_{n_2}$.

$\times 2\pi/5$	$k_{n_1} + k_{n_2} = 1$	$k_{n_1} + k_{n_2} = 2$	$k_{n_1} + k_{n_2} = 3$	$k_{n_1} + k_{n_2} = 4$	$k_{n_1} + k_{n_2} = 5$
	$\{1,5\}$	$\{2,5\}$	$\{3,5\}$	$\{4,5\}$	$\{5,5\}$
	$\{3,3\}$	$\{1,1\}$	$\{4,4\}$	$\{2,2\}$	$\{1,4\}$
	$\{2,4\}$	$\{3,4\}$	$\{1,2\}$	$\{1,3\}$	$\{2,3\}$

Applying the S^2 operator to these states, one can see that all states with $\{k_{n_1}, 5\}$ belong to the $S = 3/2$ subspace except for $\{5, 5\}$ which is the only state with $S = 5/2$. However, when the S^2 operator is applied to the remainder of the states, we see that they are not eigenfunctions of the total S operator. Further investigation of these states also shows that although the spin-current states that belong to different total-spin-current subspaces are orthogonal, within each total-spin-current subspace they are not. The states with no definite spin can be orthogonalized using the Gram-Schmidt method:

$$|k_{tot}, 1/2, h_m\rangle = |1_{k_{tot}}^{h_m}\rangle - \langle 1_{k_{tot}}^{h_m} | 3/2_{k_{tot}}^{h_m} \rangle |3/2_{k_{tot}}^{h_m}\rangle, \quad (3.38)$$

where $|k_{tot}, 1/2, h_m\rangle$ is the newly obtained orthogonal $S = 1/2$ state in the $\{h_m, k_{tot}\}$ subspace and $|1_{k_{tot}}^{h_m}\rangle$ is the non-orthogonal, spin-undefined state that we had before. Upon orthogonalization, one can see that the orthogonalized, previously undefined-spin states are actually the same state and that it is an eigenstate of the total spin operator with an eigenvalue $1/2$. This way we obtain 10 spin current states, 5 of which belong to the $S=1/2$ subspace, 4 to $S=3/2$ and 1 to the $S=5/2$ subspaces. Let us name these states as $|k_{tot}, S, h_m\rangle$ where S stands for total spin $S = \{1/2, 3/2, 5/2\}$. The total-spin-current can take on the values $k_{tot} = \{0, 2\pi/5, 4\pi/5, -4\pi/5, -2\pi/5\}$ and h_m denotes the position of the hole (the unoccupied orbital). As outlined before, the higher-spin states do not require re-orthogonalization. For either k_{n_1} or $k_{n_2} = 5$, they are given as

$$|k_{tot}, S, h_m\rangle = \frac{1}{N_{k_{n_1}, k_{n_2}}} \sum_n e^{ik_{tot}n} [(e^{ik_{n_1}} + e^{ik_{n_2}}) |A_n^h\rangle + (e^{i2k_{n_1}} + e^{i2k_{n_2}}) |B_n^h\rangle], \quad (3.39)$$

where the normalization factor

$$N_{k_{n_1}, k_{n_2}} = \begin{cases} 2\sqrt{10} & k_{n_1} = k_{n_2} \\ \sqrt{15} & k_{n_1} \neq k_{n_2} \end{cases},$$

is obtained from

$$N^2 = 10D_{k_{n_1}, k_{n_2}} \\ \text{with } D_{k_{n_1}, k_{n_2}} = \left[2 + \cos\left(\frac{2\pi}{5\Delta k}\right) + \cos\left(\frac{4\pi}{5\Delta k}\right) \right], \quad (3.40)$$

and the configurations $|A_n^h\rangle$ and $|B_n^h\rangle$ are given as

$$\begin{aligned} |A_1^6\rangle &= |\uparrow\uparrow\downarrow\downarrow\downarrow\cdot\rangle & |B_1^6\rangle &= |\uparrow\downarrow\uparrow\downarrow\downarrow\cdot\rangle \\ |A_2^6\rangle &= |\downarrow\uparrow\uparrow\downarrow\downarrow\cdot\rangle & |B_2^6\rangle &= |\downarrow\uparrow\downarrow\uparrow\downarrow\cdot\rangle \\ |A_3^6\rangle &= |\downarrow\downarrow\uparrow\uparrow\downarrow\cdot\rangle & |B_3^6\rangle &= |\downarrow\downarrow\uparrow\downarrow\uparrow\cdot\rangle \\ |A_4^6\rangle &= |\downarrow\downarrow\downarrow\uparrow\uparrow\cdot\rangle & |B_4^6\rangle &= |\uparrow\downarrow\downarrow\uparrow\downarrow\cdot\rangle \\ |A_5^6\rangle &= |\uparrow\downarrow\downarrow\downarrow\uparrow\cdot\rangle & |B_5^6\rangle &= |\downarrow\uparrow\downarrow\downarrow\uparrow\cdot\rangle \end{aligned} \quad \text{Upon obtaining all total spin states by do-}$$

ing the above rotation for each hole position (unoccupied orbital), the Hamiltonian can be divided into ten 6x6 blocks for a hole moving in a certain total-spin-current, total-spin $\{k_{tot}, S\}$ pair:

$$H = \begin{bmatrix} 0 & t & 0 & 0 & 0 & te^{ik_{tot}} \\ t & 0 & t & 0 & 0 & 0 \\ 0 & t & 0 & t & 0 & 0 \\ 0 & 0 & t & 0 & t & 0 \\ 0 & 0 & 0 & t & 0 & t \\ te^{-ik_{tot}} & 0 & 0 & 0 & t & 0 \end{bmatrix}. \quad (3.41)$$

Just looking at the above block, which depends on k_{tot} , we can deduce that the energy spectrum will be doubly degenerate. This Hamiltonian, for the hole dressed by the total-spin-current, can be diagonalized by the following eigenstates in which the hole acquires one-sixth of the total phase $\phi_{k_{tot}} = k_{tot}/6$, upon going from one orbital to another;

$$|\chi_{k_{tot}, S}^\alpha\rangle = \frac{1}{6} \sum_m^6 e^{i\cdot m \cdot \phi_{k_{tot}}} e^{i\cdot m \cdot \alpha} |k_{tot}, S, h_m\rangle, \quad (3.42)$$

where $\alpha = \frac{2\pi}{6}\{0, 1, 2, 3, 4, 5\}$ identifies the eigenfunctions within the 6x6 subspace that correspond to eigenvalues $E_{\alpha, k_{tot}} = 2t \cos(\alpha + \phi_{k_{tot}})$. The ground state in the strongly interacting regime belongs to the $k_{tot} = 0$ subspace. Since each subspace is doubly degenerate for $U \rightarrow \infty$, the ground state is also doubly degenerate with one state coming from $S = 1/2$ and another from the $S = 5/2$ subspace.

As we move on to a weakly interacting system, the interaction strength becomes weaker than the kinetic energy of the electrons, $U \ll t$. Thus working in the Fourier-space, where the interactions are treated as perturbations, would simplify our discussion considerably.

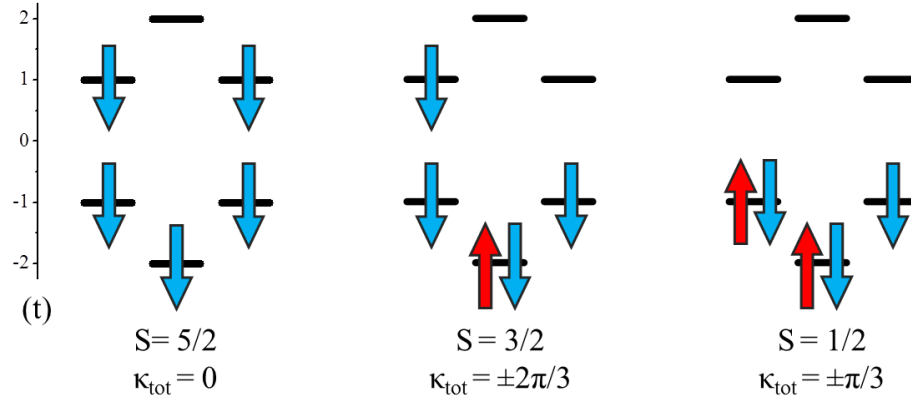


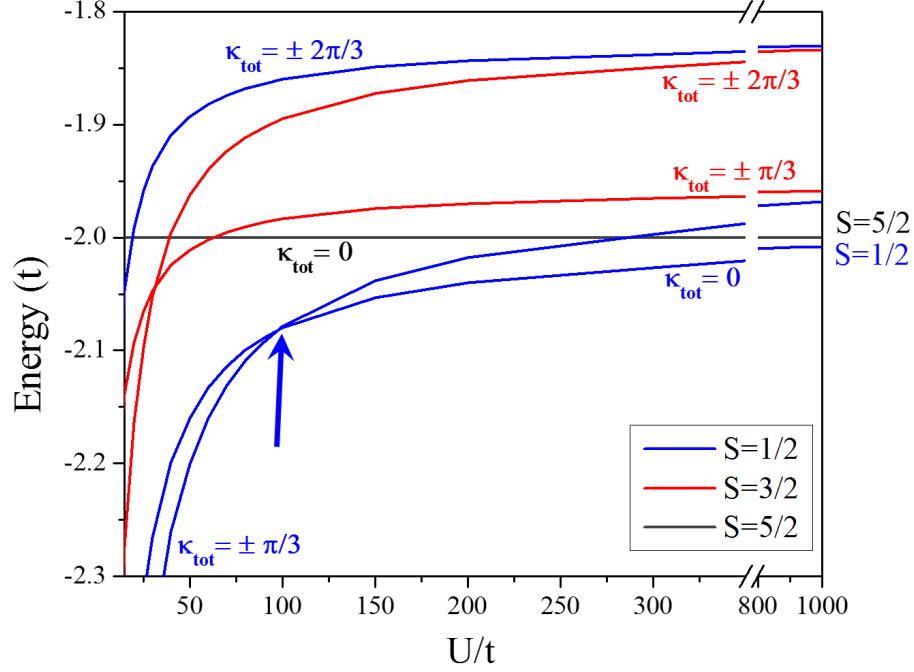
Figure 3.15: Non-interacting limit, ground states for different total spin S and their corresponding κ_{tot} . The $S = 3/2$ and $S = 1/2$ states are degenerate

Weakly Interacting Electrons: $U \rightarrow 0$

At the non-interacting limit, $U \rightarrow 0$, just by placing electrons on the single particle levels, we can obtain their eigenvalues by adding up their single particle energies, since there are no off-diagonal terms connecting these configurations. For example, the lowest energy $S = 5/2$ state is obtained by placing a single electron on each one of the lowest 5 levels, adding upto $E_{5/2}^{GS} = -2t + (-t) + (-t) + t + t = -2t$ and $\kappa_{5/2}^{GS} = 0 + \pi/3 + -\pi/3 + 2\pi/3 - 2\pi/3 = 0$ as depicted in Fig.3.15. The figure also depicts one of the lowest $S = 3/2$ configurations with $\kappa_{tot} = 2\pi/3$ and energy $E_{3/2}^{GS} = -5t$ whose degenerate pair can be obtained by moving the down electron from single particle level $2\pi/3$ to $-2\pi/3$. Similarly, lowest energy $S = 1/2$, $\kappa_{tot} = \pi/3$ configuration is depicted in Fig.3.15. With its degenerate pair, they are the ground state of the underdoped ABR in the non-interacting limit.

Intermediate Interactions: $0 < U < \infty$

While the ground state is still the degenerate $\kappa_{tot} = \pm\pi/3, S = 1/2$ pair, as depicted in Fig.3.16, as we turn on and increase the interactions the ground state of the $S = 3/2$ subspace becomes $\kappa = \pm\pi/3$. Next, with increasing interaction strength, the crossing between the degenerate $\{S = 3/2, \kappa_{tot} = \pm\pi/3\}$ states and the lowest $\{S = 5/2, \kappa_{tot} = 0\}$ state changes the total spin order. As we keep increasing the interaction strength, the ground state of the ABR loses its degeneracy as it becomes a $S = 1/2, \kappa = 0$ state, changing the phase character of the true ground state of the whole system. At $U = \infty$, the $S = 1/2$ ground state approaches the $\{S = 5/2, \kappa_{tot} = 0\}$ state eventually becoming degenerate as predicted and derived in the $U \rightarrow \infty$ section.

Figure 3.16: Evolution of the lowest levels of 5 electron-ABR for $V=0$

3.2.2.3 Absorption

To capture the transitions of the ground state we can study the optical properties of the ABR with varying interaction strength, starting with the Fermi's Golden rule given in Eq.2.107.¹⁵⁷ Since we are working in different representations (real and Fourier space) we should derive the optical selection rules in both spaces. Let us start by rewriting the dipole element obtained in section 2, Eq.2.114,

$$\langle l | \vec{\varepsilon} \cdot \vec{r} | j \rangle = D \vec{\varepsilon} \cdot (\vec{R}_j - \vec{R}_l) \delta_{lj} + \vec{\varepsilon} \cdot \vec{R}_l \delta_{lj}. \quad (3.43)$$

Since we have a hexagonal structure, the magnitude of all the vectors connecting the center of the hexagon with the localized QD orbitals is the same and their directions vary by an angle of $2\pi/6$ as depicted in Fig.3.17. As a result, the dot product between the polarization and the vector pointing from the center to each atom can be simplified as

$$\varepsilon_{\pm} \cdot \vec{R}_m = |R| e^{\pm i m 2\pi/6}, \quad (3.44)$$

where $\pm$ in polarization represents the handedness and m depends on which atom one is pointing towards and it can take on the values $\{0, \dots, 5\}$.

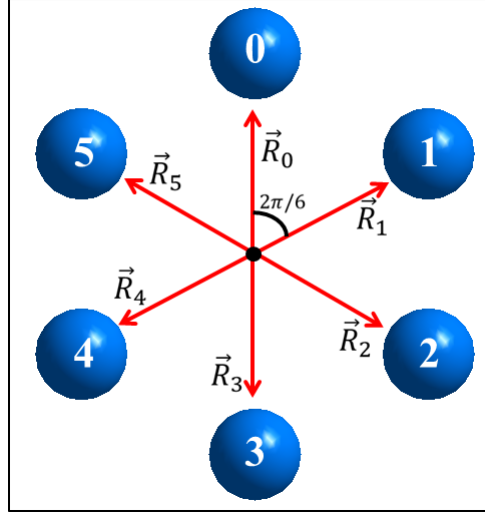


Figure 3.17: Distance from the center of the benzene ring to each quantum dot is the same

$U \rightarrow \infty$: Real-Space

In order to determine the absorption spectrum between total-spin-current states, we have to start with the dipole element between configurations $|A_n^{h_m}\rangle$ and $|B_n^{h_m}\rangle$. For convenience, I will generalize their names as $|C_n^h\rangle$ where C stands for configuration (for both A and B). Let's go back to Fermi's golden rule and look at the matrix element of the polarization operator between two configurations;

$$\begin{aligned}
 \langle C_{n1}^{h1} | P^+ | C_{n2}^{h2} \rangle &= \langle C_{n1}^{h1} | \sum_{i,j,\sigma} d(i,j) c_{i\sigma}^+ c_{j\sigma} | C_{n2}^{h2} \rangle \\
 &= \sum_{i,j} d(i,j) \langle C_{n1}^{h1} | c_{i\sigma}^+ c_{j\sigma} | C_{n2}^{h2} \rangle \\
 &= \sum_{\langle i,j \rangle} D \vec{\varepsilon} \cdot (\vec{R}_j - \vec{R}_i) \langle C_{n1}^{h1} | c_{i\sigma}^+ c_{j\sigma} | C_{n2}^{h2} \rangle \\
 &\quad + \sum_i \vec{\varepsilon} \cdot \vec{R}_i \langle C_{n1}^{h1} | c_{i\sigma}^+ c_{i\sigma} | C_{n2}^{h2} \rangle.
 \end{aligned} \tag{3.45}$$

If both configurations are the same, then the first term is zero while the second term becomes

$$\begin{aligned}
 \langle C_{n1}^{h1} | P^+ | C_{n1}^{h1} \rangle &= \sum_i \vec{\varepsilon} \cdot \vec{R}_i \langle C_{n1}^{h1} | c_{i\sigma}^+ c_{i\sigma} | C_{n1}^{h1} \rangle \\
 &= \sum_i \vec{\varepsilon} \cdot \vec{R}_i \\
 &= -e^{\pm i h_1 2\pi/6},
 \end{aligned} \tag{3.46}$$

since $\sum_{j=1}^6 e^{ij2\pi/6} = 0$ and the only element missing in the above summation is the one that belongs to the hole (the empty orbital). If we look at the same hole but different configuration such that $h_1 = h_2$ and $n_1 \neq n_2$ we get zero since a single-body polarization operator cannot exchange the positions of two spins;

$$\langle C_{n1}^{h1} | P^+ | C_{n2}^{h1} \rangle = 0 \quad n_1 \neq n_2. \quad (3.47)$$

Any configuration (A or B) can be connected to only 2 others since there are only two electrons, one from the left and one from the right that can hop on to the unoccupied orbital. Then, keeping the position of the hole different for two configurations, the second term in Eq.3.45 becomes zero,

$$\sum_i \vec{\varepsilon} \cdot \vec{R}_i \langle C_{n1}^{h1} | c_{i\sigma}^+ c_{i\sigma} | C_{n2}^{h2} \rangle = 0 \quad \text{if } h1 \neq h2. \quad (3.48)$$

Except for $h_1 = \{1, 6\}$, each configuration will be connected to $n_2 = n_1$ and $h_2 = h_1 \pm 1$ while for $h_1 = 1$ the term with $h_2 = h_1 - 1$ will go to $n_2 = n_1 + 1$ and for $h_1 = 6$ the opposite happens; $h_2 = h_1 + 1$ will go to $n_2 = n_1 - 1$:

$$\begin{aligned} \langle A_5^5 | P^+ | A_5^6 \rangle &= (\uparrow \downarrow \downarrow \downarrow \cdot \uparrow) P^+ (\uparrow \downarrow \downarrow \downarrow \uparrow \cdot) \neq 0, \\ \langle A_5^1 | P^+ | A_1^6 \rangle &= (\cdot \uparrow \downarrow \downarrow \downarrow \uparrow) P^+ (\uparrow \uparrow \downarrow \downarrow \cdot) \neq 0, \\ \langle A_5^6 | P^+ | A_4^1 \rangle &= (\uparrow \downarrow \downarrow \downarrow \uparrow \cdot) P^+ (\cdot \downarrow \downarrow \downarrow \uparrow \uparrow) \neq 0. \end{aligned} \quad (3.49)$$

The change in index n does not affect the final result and regardless of what h_1 is, the dipole element between configurations becomes

$$\begin{aligned} \sum_{\langle i, j \rangle} D \vec{\varepsilon} \cdot (\vec{R}_j - \vec{R}_i) \langle C_{n1}^{h1} | c_{i\sigma}^+ c_{j\sigma} | C_{n2}^{h2} \rangle &= D \vec{\varepsilon} \cdot (\vec{R}_{h1} - \vec{R}_{h2}) \\ &= D(e^{ih_1 2\pi/6} - e^{ih_2 2\pi/6}). \end{aligned} \quad (3.50)$$

Lastly, the dipole element between an A and a B configuration will always be zero since they are not connected by the NN dipole element. From above derivations for the dipole element between configurations we see that there is a selection rule on the hole index; $h_2 = h_1$ or $h_2 = h_1 \pm 1$;

$$\Delta h = h_2 - h_1 = \{0, \pm 1\}. \quad (3.51)$$

Now let's go up a step and look at the dipole elements between the $|k_{tot}, S, h_m\rangle$ states. Simply for visual reasons I will rename them as $|k_{tot}, S, h_m\rangle = |S_{k_{tot}}^{h_m}\rangle$ during the discussion of the dipole moments between these states. We don't need to look at the cross terms,

$\langle A|\varepsilon \cdot \vec{r}|B\rangle$ emerging in the evaluation of the dipole element since they will automatically be zero as shown above. For simplicity I won't be looking at the dipole elements between the re-orthogonalized $S = 1/2$ states and only concentrate on the dipole elements among the higher-spin states. However the same derivation can be applied to the Gram-Schmidt orthogonalized $S=1/2$ states to obtain the same selection rules. Ignoring the cross-terms, we can expand the elements as

$$\begin{aligned} \langle S_{k_{tot}}^{h_1} | \varepsilon \cdot \vec{r} | S_{k_{tot}}^{h_2} \rangle &= \sum_{n_1} \sum_{n_2} e^{-ik_{tot}^1 n_1} e^{ik_{tot}^2 n_2} \times \\ &\quad \left[(e^{-ik_1^1} + e^{-ik_2^1})(e^{ik_1^2} + e^{ik_2^2}) \langle A_{n_1}^{h_1} | \vec{\varepsilon} \cdot \vec{r} | A_{n_2}^{h_2} \rangle \right. \\ &\quad \left. + (e^{-2ik_1^1} + e^{-2ik_2^1})(e^{2ik_1^2} + e^{2ik_2^2}) \langle B_{n_1}^{h_1} | \vec{\varepsilon} \cdot \vec{r} | B_{n_2}^{h_2} \rangle \right], \end{aligned} \quad (3.52)$$

where $k_{tot}^1 = k_1^1 + k_2^1$ and $k_{tot}^2 = k_1^2 + k_2^2$. Once simplified, the above equation takes the following form using the notation $|C\rangle$ for the A and B configurations,

$$\begin{aligned} \langle S_{k_{tot}}^{h_1} | \varepsilon \cdot \vec{r} | S_{k_{tot}}^{h_2} \rangle &= \frac{1}{10D_{k_1, k_2}} 10D_{k_1, k_2} \langle C_{n_1}^{h_1} | \varepsilon \cdot \vec{r} | C_{n_2}^{h_2} \rangle \delta(k_{tot}^1 - k_{tot}^2) \\ &= e^{iF(h_1)k_{tot}^2} \langle C_{n_1}^{h_1} | \varepsilon \cdot \vec{r} | C_{n_2}^{h_2} \rangle \delta(k_{tot}^1 - k_{tot}^2). \end{aligned} \quad (3.53)$$

The function F is there since for $h_1 = \{1, 6\}$ we have $n_2 = n_1 \pm 1$. It is defined as

$$F(h_1) = \begin{cases} 0 & \text{if } h_1 \neq 1, 6 \\ +1 & \text{if } h_1 = 1 \\ -1 & \text{if } h_1 = 6 \end{cases}.$$

In addition to the conservation of the total spin and the selection rules on the hole positions, we derive a rule on conservation of the total spin-current, such that

$$\begin{aligned} \Delta h &= h_2 - h_1 = \{0, \pm 1\}, \\ \Delta k_{tot} &= k_{tot}^1 - k_{tot}^2 = 0, \\ \Delta S &= S_1 - S_2 = 0. \end{aligned} \quad (3.54)$$

The above selection rules restrict us within the 6x6 total-spin-current subspaces.

Finally we can look at the dipole elements between the total-spin-current eigenvectors,

$$\langle \chi_{k_{tot}}^{\alpha_1} | P^+ | \chi_{k_{tot}}^{\alpha_2} \rangle = \sum_{h_1} \sum_{h_2} e^{-ih_1 \phi_{k_{tot}}} e^{-ih_1 \alpha_1} e^{ih_2 \phi_{k_{tot}}} e^{ih_2 \alpha_2} \langle S_{k_{tot}}^{h_1} | \vec{\varepsilon} \cdot \vec{r} | S_{k_{tot}}^{h_2} \rangle. \quad (3.55)$$

Using the selection rule on the hole indices, we have

$$\begin{aligned}
\langle \chi_{k_{tot}}^{\alpha_1} | \vec{\epsilon} \cdot \vec{r} | \chi_{k_{tot}}^{\alpha_2} \rangle &= \sum_{h_1} e^{-ih_1(\phi_{k_{tot}} + \alpha_1)} e^{ih_1(\phi_{k_{tot}} + \alpha_2)} \langle S_{k_{tot}}^{h_1} | \vec{\epsilon} \cdot \vec{r} | S_{k_{tot}}^{h_1} \rangle \\
&+ \sum_{h_1} e^{-ih_1(\phi_{k_{tot}} + \alpha_1)} e^{i(h_1+1)(\phi_{k_{tot}} + \alpha_2)} \langle S_{k_{tot}}^{h_1} | \vec{\epsilon} \cdot \vec{r} | S_{k_{tot}}^{h_1+1} \rangle \\
&+ \sum_{h_1} e^{-ih_1(\phi_{k_{tot}} + \alpha_1)} e^{i(h_1-1)(\phi_{k_{tot}} + \alpha_2)} \langle S_{k_{tot}}^{h_1} | \vec{\epsilon} \cdot \vec{r} | S_{k_{tot}}^{h_1-1} \rangle. \quad (3.56)
\end{aligned}$$

Before simplifying the above equation one has to be really careful and remember that there is a h_m dependence in the dipole element between the total spin-current configurations $|S_{k_{tot}}^{h_m}\rangle$. After some algebra, the above equation becomes

$$\langle \chi_{k_{tot}}^{\alpha_1} | P^+ | \chi_{k_{tot}}^{\alpha_2} \rangle = \frac{1}{6} \sum_{h_1} e^{ih_1(\alpha_2 - \alpha_1 \pm 2\pi/6)} [1 + C e^{-ik_{tot}\delta(h_1,6)} + C^* e^{ik_{tot}\delta(h_1,1)}], \quad (3.57)$$

where $C = D(1 - e^{i2\pi/6})$.

Although it looks like there is a selection rule, $\alpha_2 = \alpha_1 \pm 1$ on the total-spin-current eigenvector index, it is destroyed by the fact that there is hole-position dependency in $\delta(h_1, 1), \delta(h_1, 6)$ inside the brackets. However, for the ground state where $k_{tot} = 0, \alpha = 0$, those terms become zero and as a result only $\alpha_2 = \alpha_1 \pm 1$ transitions become allowed. Moreover, since the energies of $\alpha = 1$ and $\alpha = 5$ states are degenerate, we see a single peak in the absorption spectrum as shown in Fig.3.18(d).

U = 0

The dipole elements between molecular states are calculated by writing them out explicitly in terms of the atomic orbitals. For light that is circularly polarized $\hat{\epsilon}_{\pm}$, the dipole element between molecular states becomes

$$\langle \kappa_j | \hat{\epsilon}_{\pm} \cdot \vec{r} | \kappa_i \rangle = \frac{1}{6} \sum_{p,q}^6 e^{i(\kappa_i q - \kappa_j p)} \langle p | \hat{\epsilon}_{\pm} \cdot \vec{r} | q \rangle. \quad (3.58)$$

We can open up the sum and retain the same site, δ_{pq} , and nearest neighbor, $\delta_{\langle pq \rangle}$, elements since we are only including up to nearest neighbor interactions. Then the above equation takes the following form:

$$\begin{aligned}
\langle \kappa_j | \epsilon_{\pm} \cdot \vec{r} | \kappa_i \rangle &= \frac{1}{6} \sum_p [e^{i(\kappa_i(p-1) - \kappa_j p)} \epsilon_{\pm} \cdot D(\vec{R}_{p-1} - \vec{R}_p) \\
&+ e^{i(\kappa_i p - \kappa_j p)} \epsilon_{\pm} \cdot \vec{R}_p]
\end{aligned}$$

$$+e^{i(\kappa_i(p+1)-\kappa_j p)}\epsilon_{\pm} \cdot D(\vec{R}_{p+1} - \vec{R}_p)]. \quad (3.59)$$

Collecting the R_i terms that identify the position of the carbon atoms as shown in Fig.3.17 we get

$$\begin{aligned} \langle \kappa_j | \epsilon_{\pm} \cdot \vec{r} | \kappa_i \rangle &= \frac{1}{6} \sum_p [\epsilon_{\pm} \cdot \vec{R}_p e^{ip(\kappa_i - \kappa_j)} (1 - 2D \cos(\kappa_i)) \\ &\quad + \epsilon_{\pm} \cdot \vec{R}_{p-1} D e^{ip(\kappa_i - \kappa_j)} e^{-i\kappa_i} \\ &\quad + \epsilon_{\pm} \cdot \vec{R}_{p+1} D e^{ip(\kappa_i - \kappa_j)} e^{i\kappa_i}]. \end{aligned} \quad (3.60)$$

For clockwise and counterclockwise polarized light we can use Eq.3.44 and get rid of the products to obtain

$$\begin{aligned} \langle \kappa_j | \epsilon_{\pm} \cdot \vec{r} | \kappa_i \rangle &= \frac{1}{6} \sum_p |R| [e^{ip(\kappa_i - \kappa_j \pm \pi/3)} (1 - 2D \cos(\kappa_i)) \\ &\quad + D e^{ip(\kappa_i - \kappa_j \pm \pi/3)} e^{-i(\kappa_i \pm \pi/3)} \\ &\quad + D e^{ip(\kappa_i - \kappa_j \pm \pi/3)} e^{i(\kappa_i \pm \pi/3)}], \end{aligned} \quad (3.61)$$

which, once simplified, gives

$$\langle \kappa_j | \epsilon_{\pm} \cdot \vec{r} | \kappa_i \rangle = \frac{|R|}{6} \left[\sum_m e^{ip(\kappa_i - \kappa_j \pm \pi/3)} \right] [1 - 2D(\cos(\kappa_i) - \cos(\kappa_i \pm \pi/3))]. \quad (3.62)$$

If we collect all the terms outside of the summation under the constant $C(\kappa_i)$ which is κ_i dependent, the dipole element between molecular levels can simply be expressed as

$$\langle \kappa_j | \epsilon_{\pm} \cdot \vec{r} | \kappa_i \rangle = C(\kappa_i) \delta_{\kappa_i - \kappa_j \pm \pi/3}. \quad (3.63)$$

The above expression is non-zero only if $\kappa_i - \kappa_j = \pm \pi/3$. Only the molecular states within different rotational subspaces (Fig.3.13(b)) can be coupled by light.

3.2.2.4 Detecting Transition in GS of ABR

The transition from a degenerate $\kappa = \pm \pi/3$ ground state to a non degenerate $\kappa = 0$ angular momentum ground state can be captured in the absorption spectrum using the selection rules on angular momentum. We have already derived the selection rules on angular momentum and know that photons conserve the total spin of the system.

In $U = 0$ regime, the absorption is solely dictated by the single particle level selection rules since the Fourier-space levels are non-interacting. Starting on either one of the

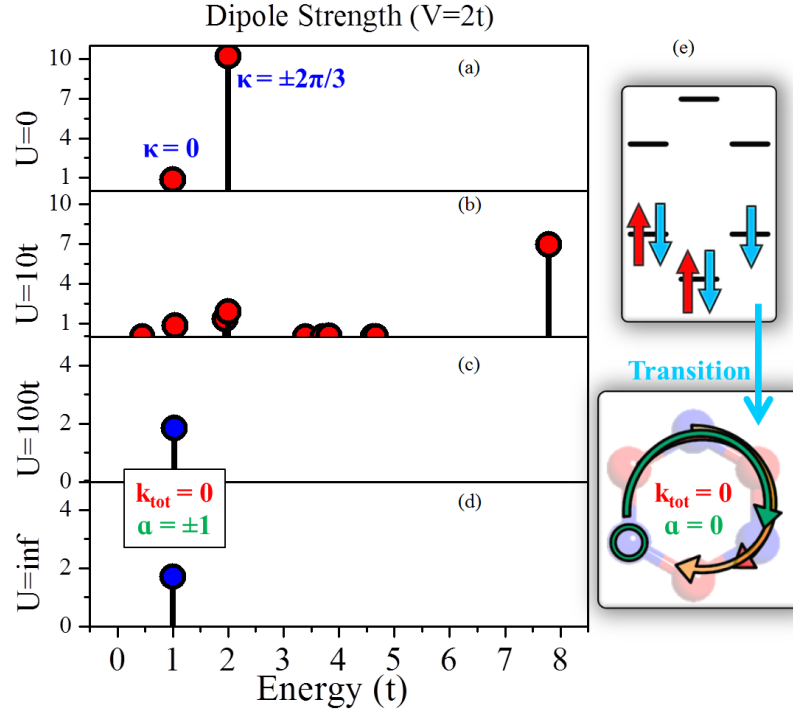


Figure 3.18: Absorption spectrum of the ABR with changing U at constant $V=2t$ (a) Absorption spectrum at $U=0$ where the use of the Fourier representation is appropriate. We can see the k_{tot} dictated selection rules (b) Absorption spectrum at $U=10t$ where the ground state is still degenerate $\kappa = \pm\pi/3$. (c) Absorption spectrum at $U=100t$ in which the ground state is now $\kappa = 0$ and a real space representation is necessary as the Fourier configurations are now highly correlated. U is sufficiently large that we see the $U \rightarrow \infty$ selection rules. (d) Absorption spectrum at $U \rightarrow \infty$. (e) Figure depicting the ground state in Fourier space, before the ground state transition happens, and in real space, after the ground state transition.

$\kappa_{tot} = \pm\pi/3, S = 1/2$ states, an electron from orbital $\kappa = 0$ can be excited to the singly-occupied molecular orbital $\kappa = \mp\pi/3$ via a photon with energy t . For the cost of $2t$, either one of the electrons in the doubly occupied $\kappa = \pm\pi/3$ orbitals can be moved to $\kappa = \pm2\pi/3$. Likewise, moving an electron from the singly occupied $\kappa = \mp\pi/3$ to $\kappa = \mp2\pi/3$ will cost an energy of $2t$. In the non-interacting regime, other transitions are not allowed due to optical selection rules, leading to an absorption spectrum shown in Fig.3.18(a).

Use of Fourier space is convenient only if the interactions can be considered as perturbations. As they get stronger, the configurations created in the Fourier basis become highly correlated and a real-space description becomes necessary for a clear understanding. Fig.3.18(e) depicts the main configuration in the ground state of a weakly interacting charged ABR and its transition to a non-degenerate total-spin-current state as we ap-

proach $U \rightarrow \infty$. In between the two extrema the ground state transition happens around $U > 95t$.

Starting with the non-interacting charged ABR, as we introduce interactions, we see the emergence of multiple peaks in the low energy spectrum since doubly occupied levels are not separated in energy from the singly occupied configurations. However, as we keep increasing the interaction strength, these peaks shift to much higher energies even at $U = 10t$ as depicted in Fig.3.18(b). Right after the transition point, where the interactions are already $U \gg t$, we see the single peak signature of the non-degenerate ground state (Fig.3.18(c)).

3.2.3 Charge Neutral Artificial Benzene

Placing 6 electrons on the ABR, S_z can take on the following values $S_z = \{0, 1, 2, 3\}$ with $S_z = 3$ being the spin-polarized case. Regardless of the effective on-site, U/t or the Coulomb, V/t , interaction term, the ground state of the charge neutral ABR remains as a total spin $S = 0$ state with 6 electrons occupying the lowest 3 molecular orbitals adding up-to a $\kappa_{tot} = 2 * 0 + 2 * \pi/3 + 2 * (-\pi/3) = 0$.

Chapter 4

Colloidal Graphene Quantum Dots

As introduced previously, colloidal graphene quantum dots have been studied extensively by Li and co-workers^{65–68,70}. Concentrating on the synthesis of CGQDs with 132,168 and 170 atoms, Li et al. confirmed the number of atoms in each dot using mass spectroscopy, while the symmetry of the flakes was inferred through the solution chemistry and infrared vibrational spectra. Two flakes, one containing 132 carbon atoms, called the C132 and another containing 168 called the C168 are depicted in Fig.4.1. C132 is obtained by cutting out the upper corner of C168 while C170, the flake with 170 carbon atoms is obtained by adding 2 atoms to C168.

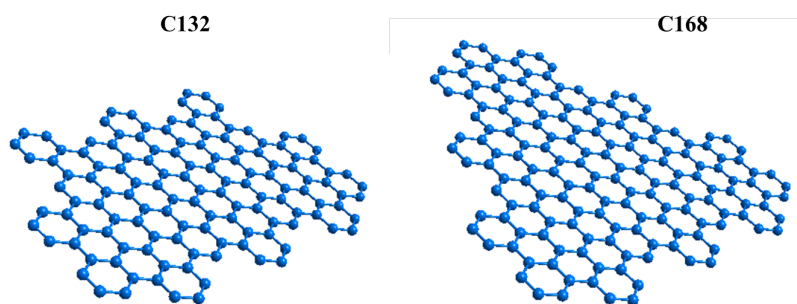


Figure 4.1: Graphene quantum dots with 132 and 168 atoms. Reprinted from Ref.¹⁵⁷.

Since the CGQDs are suspended in solution, whose dielectric constant can be tuned, the electronic properties of CGQDs depend on the strength of the Coulomb interactions as well as their size and shape. Indeed, their optical absorption spectra reveal a clear dependence of the position of the absorption edge on the number of atoms.^{65,66,68,70} The fluorescence and phosphorescence spectroscopy⁷⁰ show existence of a gap between emission and absorption spectra that is interpreted as the energy difference between the singlet and triplet exciton states. The excitonic states of C168 in vacuum was recently analyzed theoretically by Schumacher²¹⁸ using the time-dependent DFT approach. The numerical

simulation revealed the existence of a bright singlet exciton doublet in a band of dark triplet and singlet states.

Here in this chapter I will present a microscopic theory of the electronic and optical properties of colloidal graphene quantum dots with 168 and 132 atoms using the $tb + HF + CI$ approach.

4.1 Electronic Properties

In Eq.2.42 we had embedded the ionic potential into the hopping element. These screened electron-ion interactions $\sum_k V_k$ due to positive ions lead to the scattering matrix elements $\langle i | \sum_k V_k | j \rangle$ from orbital $|i\rangle$ to $|j\rangle$. In this work, we approximate the screened electron-ion interactions V_k by the electron-electron Coulomb elements $\langle i | V_k | j \rangle = -\langle ik | V | kj \rangle$. This way, except for the hopping element, all electron-ion interactions are screened the same way as the electron-electron interactions. Setting on-site energies to zero, Eq.2.44 is rewritten as

$$\hat{H} = \sum_{i,l=1}^N \sum_{\sigma} [t_{il} - \sum_{k \neq i,l} \langle ik | V | kl \rangle] c_{i\sigma}^{\dagger} c_{l\sigma} + \frac{1}{2} \sum_{i,j,k,l} \sum_{\sigma,\sigma'} \langle ij | V | kl \rangle c_{i\sigma}^{\dagger} c_{j\sigma'}^{\dagger} c_{k\sigma'} c_{l\sigma}. \quad (4.1)$$

In this chapter we restrict the tunneling matrix t_{il} to nearest neighbor (NN), $t_{\langle il \rangle} = t$, and next-nearest neighbor (NNN), $t_{\langle\langle il \rangle\rangle} = t_2$, tunneling. Also it is important to note that the positive charge scattering term depends on atomic index and is different for the edge and interior atoms of the CGQD. The last term in Eq.4.1 describes the screened electron-electron interactions via the Coulomb matrix elements $\langle ij | V | kl \rangle$. They are assumed to be screened by the effective dielectric constant κ with contributions from both the σ electrons of graphene and the solvent in which the dots are suspended. As a result, the Hamiltonian contains two energy scales, the hopping matrix elements t and the Coulomb interactions screened by the effective dielectric constant κ . The two energy scales determine the electronic properties of CGQDs.

4.1.1 Single Particle Properties

Single particle properties of CGQDs are obtained by solving the tight-binding Hamiltonian. Fig.4.2 depicts the single particle spectrum of C168 and, for comparison, an armchair edged 168 atom triangular dot and a zigzag edged triangular dot with 166 atoms.

As expected from a structure with broken sublattice symmetry, the triangular dot with zigzag edges has a zero energy band.¹⁶ On the other hand, C168 and the armchair edged structure with 168 atoms have very similar energy level spectrum and do not have zero energy levels. Their band-gaps are very similar since the gap depends on the size of the

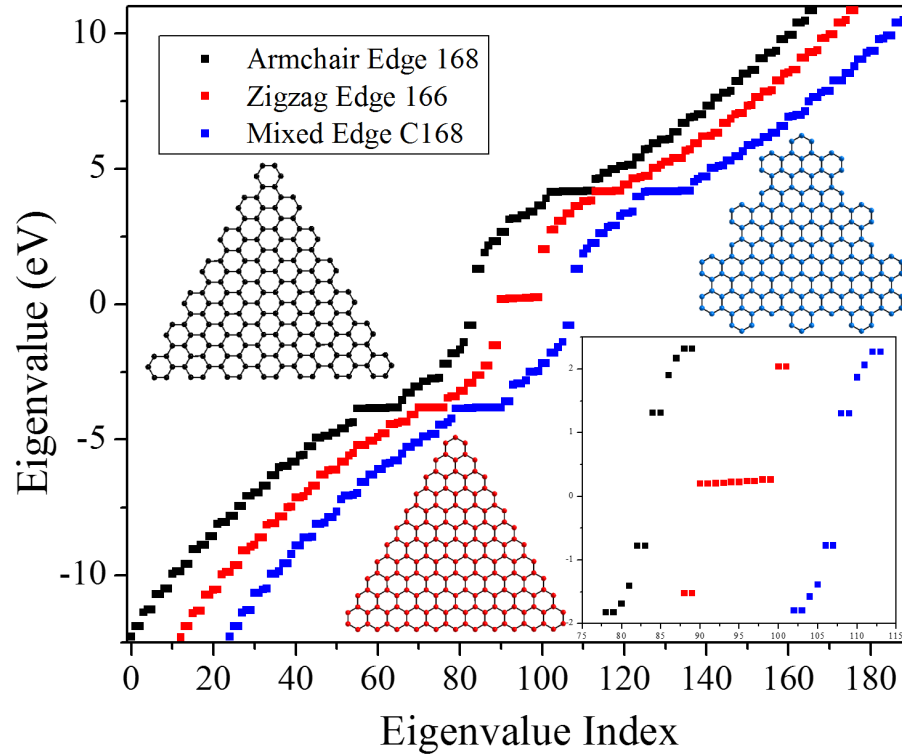


Figure 4.2: Single particle energy spectrum of C168, triangular armchair edged 168 atom flake and a triangular zigzag edged 166 atom flake. The inset shows a close up of the levels around the band edge

flake, and they both have a degenerate band edge (conduction band minimum and valence band maximum). The zigzag edged dot, except for its zero-energy band also possesses these degeneracies in its energy spectrum. In contrast, we do not observe the degeneracies for C132 whose single particle energy levels are depicted in Fig.4.3. Although we do observe the widening of the bandgap due to increased confinement, in C132 we lose the degenerate band edge.

4.1.1.1 C3 Symmetry

The degeneracy of the levels arises from the 3-fold rotational symmetry of graphene quantum dots. Lets examine the C168 flake to understand the origin of this degeneracy. We can define 3 symmetry axes as shown in Fig.4.4. The three symmetry axes, shown in red, divide the CGQD into three segments, A,B, and C, with 56 atoms each. There are mirror symmetries about these axes, and 3-fold rotational symmetry through the triple axis. We will now assign atomic indices j_β ($\beta = A$) to atoms in segment A and to their equivalent counterparts in segments B and C.

We can now define a rotation operator $\hat{R}$ that maps j_A onto one of its *rotationally*

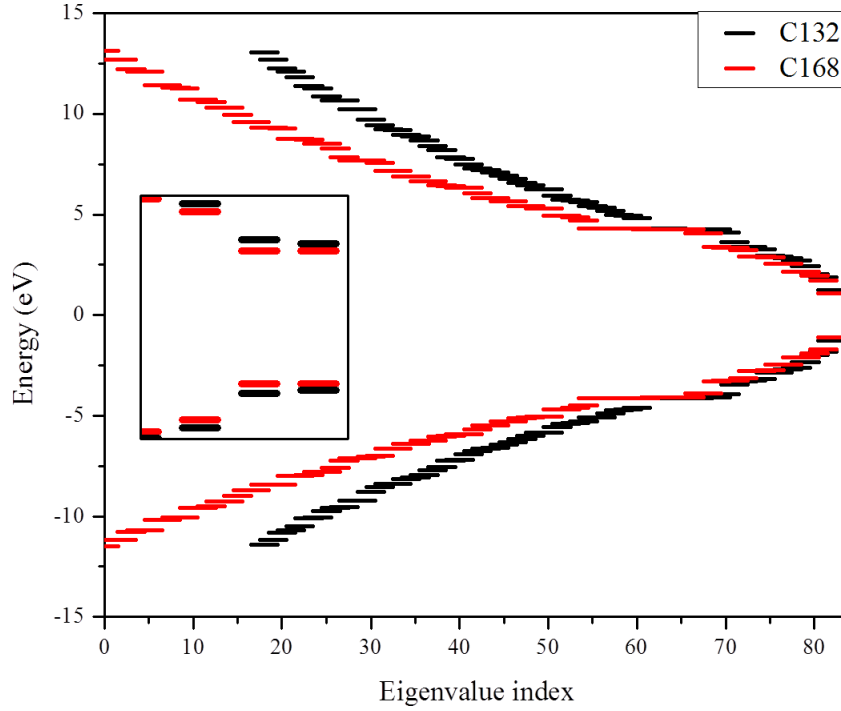


Figure 4.3: Single particle energy spectrum of C168 in comparison to C132 plotted for $t = -4.2\text{eV}$ $t_2 = -0.1\text{eV}$. The inset shows the band edge spectrum and the non-degenerate nature of the C132 levels. Energies normalized with respect to the Fermi level.

equivalent atoms j_B adding a phase of $e^{i\alpha}$. Since we have three segments, applying the rotation operator onto a certain orbital should bring me back to it such that

$$\begin{aligned}\hat{R}|j_A\rangle &= e^{i\alpha}|j_B\rangle ; \hat{R}|j_B\rangle = e^{i\alpha}|j_C\rangle ; \hat{R}|j_C\rangle = e^{i\alpha}|j_A\rangle, \\ \hat{R}\hat{R}\hat{R}|j_A\rangle &= e^{i(\alpha+\alpha+\alpha)}|j_A\rangle = |j_A\rangle,\end{aligned}\tag{4.2}$$

requiring $\alpha = \{m \times 2\pi/3\}$ where $m = \{0, 1, 2\}$. The vectors that are invariant under these rotations can be divided into three subspaces. These invariant vectors are created out of the rotationally equivalent atoms by connecting them with an m -dependent phase

$$\Psi_j^m = \frac{1}{\sqrt{3}} \sum_{\beta=0}^2 e^{i\cdot\beta\cdot m\cdot 2\pi/3} |j_\beta\rangle,\tag{4.3}$$

where I assigned numbers to segments $\beta = \{A, B, C\} = \{0, 1, 2\}$. This way we separate our states according to index m , which is equivalent to angular momenta projections. They can also be expressed as $m = \{-1, 0, 1\}$ instead of $m = \{0, 1, 2\}$. These invariant

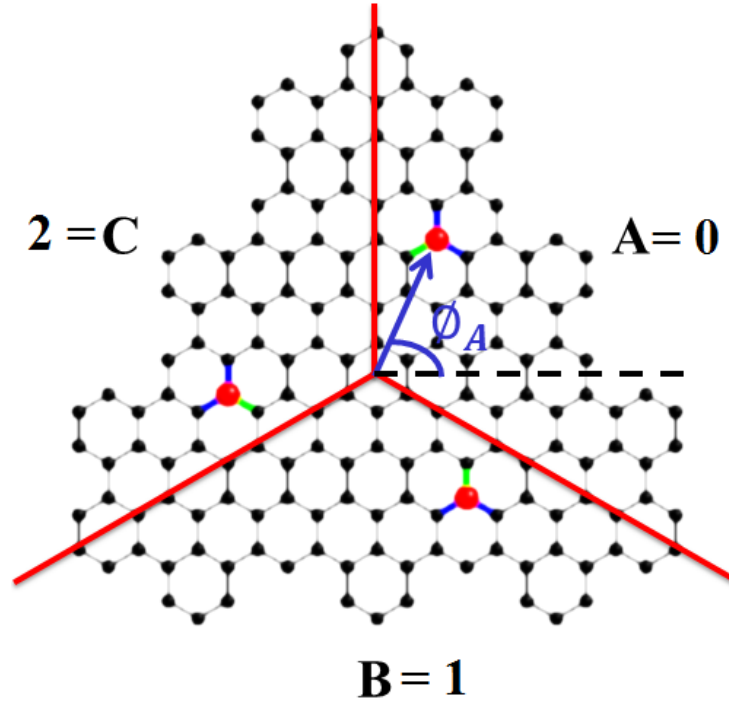


Figure 4.4: Graphene quantum dot with 168 atoms exhibiting all point symmetries of the graphene sheet. The three symmetry axes are shown in red. Reprinted from Ref.¹⁵⁷.

vectors are explicitly written as

$$\begin{aligned}
 \Psi_j^0 &= \frac{1}{\sqrt{3}} (|j_A\rangle + |j_B\rangle + |j_C\rangle), \\
 \Psi_j^1 &= \frac{1}{\sqrt{3}} (|j_A\rangle + e^{i2\pi/3}|j_B\rangle + e^{-i2\pi/3}|j_C\rangle), \\
 \Psi_j^{-1} &= \frac{1}{\sqrt{3}} (|j_A\rangle + e^{-i2\pi/3}|j_B\rangle + e^{i2\pi/3}|j_C\rangle).
 \end{aligned} \tag{4.4}$$

Once separated into angular momentum blocks, we can diagonalize each block to obtain angular momentum separated single particle eigenvectors and energies with eigenvalue index ν and quantum number m , $|\nu, m\rangle$. The degeneracy arises from the $m = 1, 2$ vectors which are complex conjugates of one another since $e^{i2\cdot 2\pi/3} = e^{-i2\pi/3}$ and $(e^{-i2\pi/3})^* = e^{i2\pi/3}$, as seen from Eq.4.4.

The rotational symmetry is not specific to the C168 molecule. Any flake with 3-fold rotational symmetry will have the above described features and its single particle eigenstates can be characterized according to the quantum number m . The most prominent and important feature (at least within the context of this thesis) is the degeneracy of the lowest conduction and the highest valence energy levels. In fact, the Fourier transformed states of the ABR are the building blocks of this degeneracy.

The valley degeneracy of graphene is somewhat similar to degeneracies in the 3-fold rotational flakes. It is due to the fact that the first Brillouin zone of a hexagonal lattice is also hexagonal and has a 3-fold rotational symmetry. This symmetry links K points together with a phase of $2\pi/3$, as well as the K' points with a phase of $-2\pi/3$ generating two distinct but degenerate subspaces, just like the $m = \pm 1$ subspaces in C3 symmetric dots. That is, instead of eigenfunctions that were generated from combinations of atomic orbitals, this time the eigenfunctions in k-space are generated from combinations of 3- $K(K')$ wavefunctions with the same phase relation.

4.1.1.2 Optical Selection Rules

Since the degeneracy can be traced all the way to the ABR, the optical selection rules that we have derived in the previous chapter for ABR can be applied to the 3-fold rotational symmetric graphene quantum dots, specifically C168.

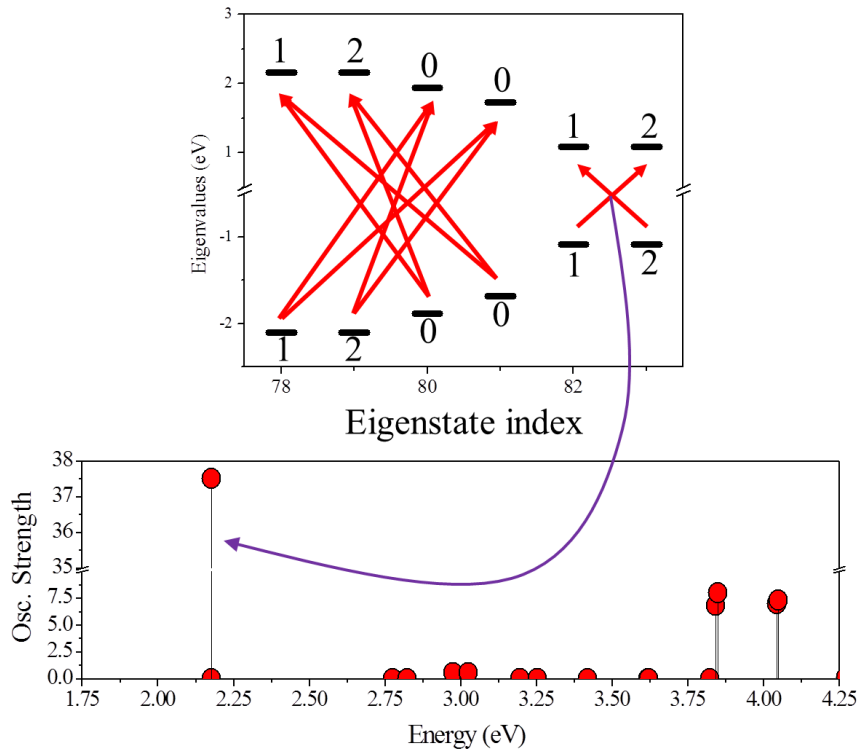


Figure 4.5: a) The tight-binding energy levels of C168 with $t = -4.2\text{eV}$, $t_2 = -0.1\text{eV}$. Shown are only a few levels around the Fermi level. Red lines between valence and conduction band levels show the allowed transitions. b) Oscillator strengths of transitions within the window of 6 valence and 6 conduction band levels. The strongest line around 2.17eV corresponds to transitions between the degenerate conduction band minimum and valence band maximum, while the second set of transitions are due to transitions between higher lying $m=0$ and $m=1,2$ levels.

Expanding the rotationally invariant eigenvectors $|\nu, m\rangle$ in terms of localized orbitals, Eq.4.3, following Eq.3.63 and assuming circular polarization of light $\epsilon_{\pm}$, we find that the dipole elements between eigenstates $|\nu, m\rangle$ satisfy the selection rule:

$$\langle \nu', m' | \vec{\epsilon} \cdot \vec{r} | \nu, m \rangle = \delta_{m', m \pm 1} C_{m, m', \nu, \nu'}, \quad (4.5)$$

where C is a constant determined numerically.

Arrows in Fig.4.5(a) show the optically allowed transitions while Fig.4.5b depicts all possible transition energies along with their dipole strength between 6 valence and 6 conduction band states. We see indeed that the selection rule $\delta_{m', m \pm 1}$ is satisfied and all vertical transitions $\Delta m = 0$ are dark. The transitions with $\Delta m = \pm 1$ correspond to circularly polarized light with $\sigma = \pm 1$ polarizations, in analogy to semiconductor quantum dots.²¹⁹ Fig.4.5b shows the oscillator strength as a function of transition energy. The lowest-energy peaks correspond to allowed band edge transition while the rest are due to transitions among higher order valence and conduction band levels. However, we have to be careful in interpreting the lack of oscillator strength since for some transitions it's simply due to the weak overlap of the wavefunctions and is unrelated to the symmetry.

Now that we have the single particle eigenstates and energies of CGQDs, we can fill up the valence band with electrons to obtain a charge neutral quantum dot. However as soon as the interactions are turned on, these electrons will start interacting and renormalize the single particle energy levels. As a first step, we will start with the self-consistent Hartree Fock approach. By minimizing the ground state energy we obtain the quasiparticle energy levels as well as the interactions between them. Once we obtain the HF ground state and HF quasiparticles, we will construct multi-pair excitations, build the CI Hamiltonian matrix in the space of configurations and diagonalize the Hamiltonian to obtain the correlated ground and excited states of the dot. Let us start with Hartree Fock.

4.1.2 Hartree Fock Phase Diagram

One of the central topics in condensed matter physics is the interactions between quasiparticles. In graphene, understanding interactions of Dirac fermions and the nature of the possible ground states remains challenging.^{76,77,79,220–230} Unlike in metals where the ratio of the Coulomb energy to the kinetic energy is proportional to the average distance between electrons, r_s , in graphene this ratio is independent of density and proportional to $1/v_F\kappa$ where v_F is the Fermi velocity and κ is the dielectric constant.⁷⁷ Several theoretical predictions include insulating ground states^{77,79,228} and excitonic instabilities for strongly interacting electrons in graphene.^{77,227,229,230} On the other hand, many experimental observations can be explained based on the noninteracting model of Dirac fermions²²⁰;

electron-electron interactions appear to lead only to renormalization of the Fermi velocity^{76,222–224,226} of Dirac fermions consistent with weak electron-electron interactions in a semimetallic state.²²¹ There are a few experimental reports of excitonic signatures in graphene.^{225,231} The Hartree Fock method is the first step that I will take towards understanding the properties of the interacting ground state of CGQDs.

The HF quasi-particle energy levels of C168 with $\kappa = 5.0$, $t = -4.2\text{eV}$ and $t_2 = -0.1\text{eV}$ are shown in Fig.4.6. We can clearly see the widening of the band-gap, although not drastic due to the weak nature of interactions ($\kappa = 5.0$). As we increase the interaction strength, both the band-gap and other electronic properties such as the breaking of electron-hole symmetry (asymmetric valence and conduction bands) and the change in the electron bandwidth becomes more prominent.

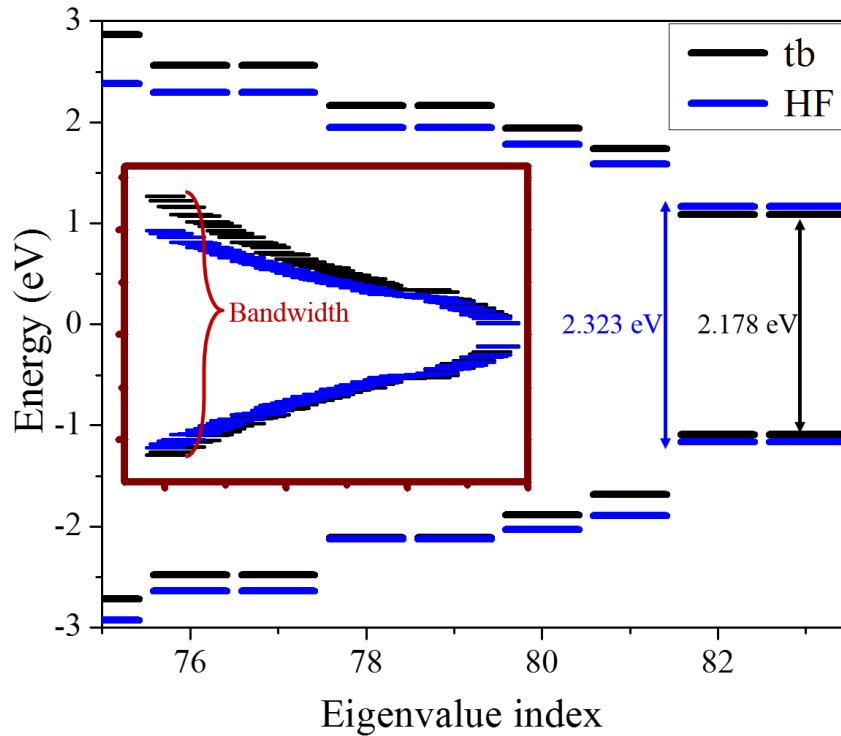


Figure 4.6: The self-consistent Hartree-Fock and tight-binding energy levels for C168 for $\kappa = 5$, $t = -4.2\text{ eV}$, $t_2 = -0.1\text{eV}$. The main figure shows the levels around the Fermi level and the levels are normalized to Fermi level. The inset shows the full spectrum.

Phase diagrams

The ground state energy depends strongly on the strength of screening and the amplitude of the hopping term. Previous work on the ground state properties of graphene^{78,79,232,233} suggest that for strong Coulomb interactions, or small values of κ , there exists a transition from a semi-metallic, weakly-interacting phase to a Mott-insulating, strongly correlated phase. Let us examine C168 phase diagrams along with the NN density element for the

spin-unpolarized ground state that are depicted in Fig.4.7. This figure shows two phase diagrams; one with $t = -2.0$ eV, another with $t = -4.0$ eV and the evolution of the NN density element for $t = -4.0$ eV.

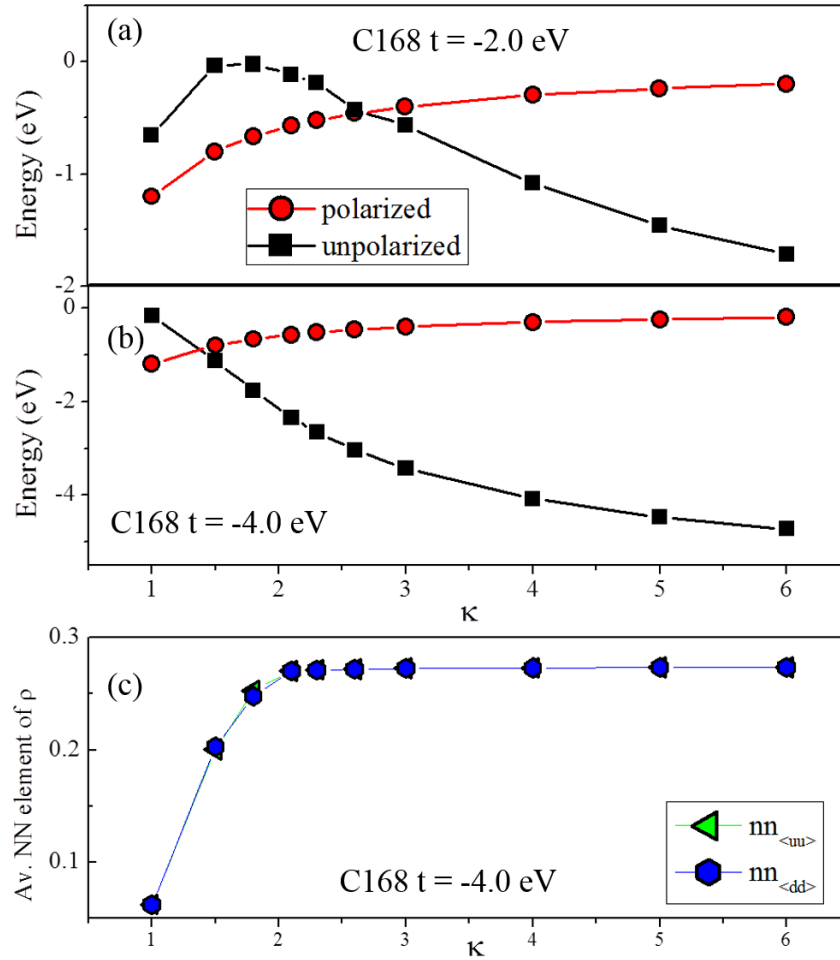


Figure 4.7: Phase diagram of C168 at $t = -4.0$ eV and $t = -2.0$ eV, $t_2 = -0.1$ eV. (a) Ground state energy of the spin polarized and spin unpolarized C168 and (b) the nearest-neighbor up-spin density matrix element of the spin unpolarized C168 as a function of screening strength κ calculated with Hubbard U and HF approaches

Since the important factor determining the electronic properties is the ratio of kinetic to potential energy, that is the ratio of t/U or κt , for $t = -4.0$ eV the transition to a spin-polarized HF ground state does not happen until $\kappa = 1.4$. Weaker $t = -2.0$ eV means that interactions can overpower the kinetic term at larger $\kappa = 2.6$. The NN density matrix element averaged over all NN pairs for the spin-unpolarized ground state as a function of κ is depicted in Fig.4.7(c). The NN density matrix element shows the probability of having two electrons with the same spin on nearest neighbor orbitals. For large κ , the value of the NN density matrix element $\rho_\sigma = 0.26$ is equal to the one obtained for bulk graphene

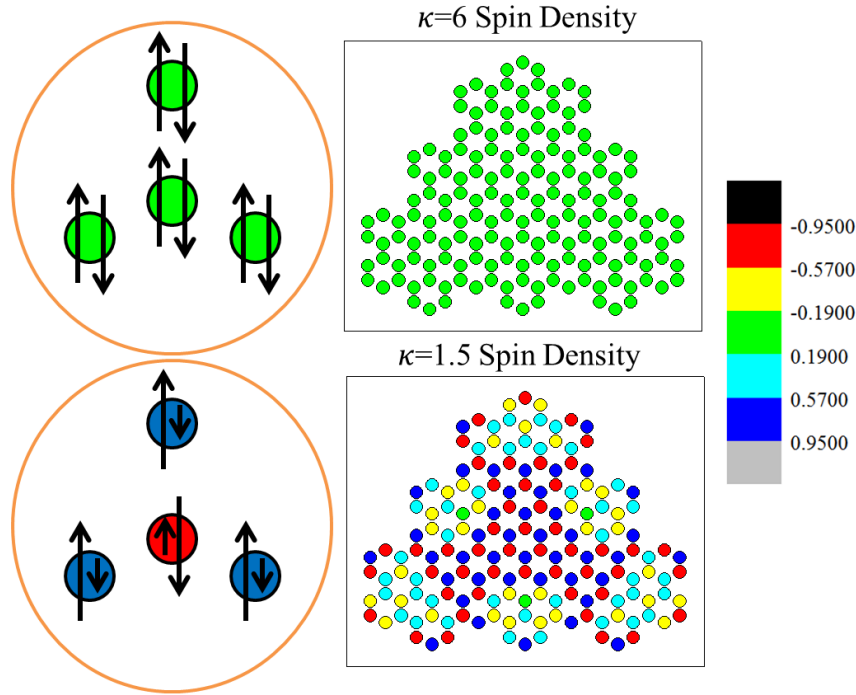


Figure 4.8: Spin density for C168 at $t = -4.0\text{eV}$, $t_2 = -0.1\text{eV}$. When $\kappa = 6.0$ probability of finding up and down electrons on each carbon atom is the same. For $\kappa = 1.5$ we see the spin density slowly turning into a checker board pattern where certain type of spin prefers a certain sublattice which looks like an antiferromagnetic, Mott insulator phase

via HF.¹⁸ However, local values of the NN density element, especially around the edges, deviates from that of the bulk. Decreasing κ , we see the onset of a phase change at around $\kappa = 1.8$, before such transition is apparent in the ground state energies.

Looking at the spin density ($\rho_{i\uparrow} - \rho_{i\downarrow}$) plots given in Fig.4.8, we see that the spin-unpolarized ground state at $\kappa = 6.0$ departs from the semiconducting state and becomes a Mott-insulator at $\kappa = 1.5$ with spins separated onto different sublattices, i.e.: spin up electrons on A sublattice and spin down electrons on B sublattice. Although this transition may be an artifact of the Hartree-Fock approximation, it provides the motivation to examine the strongly interacting regime.

I will now discuss the phase diagram of the C132 molecule as a function of κ for a given t . Fig.4.9 shows the evolution of the HF, Hubbard U and the extended Hubbard + exchange (Hubbard U+V+X) ground state energies for the spin-polarized, $S_z = 66$, and the spin unpolarized, $S_z = 0$, C132 as a function of κ for $t = -3.0\text{ eV}$. With the Hubbard U model, the spin-polarized ground state energy never changes. This is expected, since the only interaction term, U, is avoided in the spin-polarized case due to Pauli exclusion principle. The spin-unpolarized ground state energy increases yet its energy remains lower

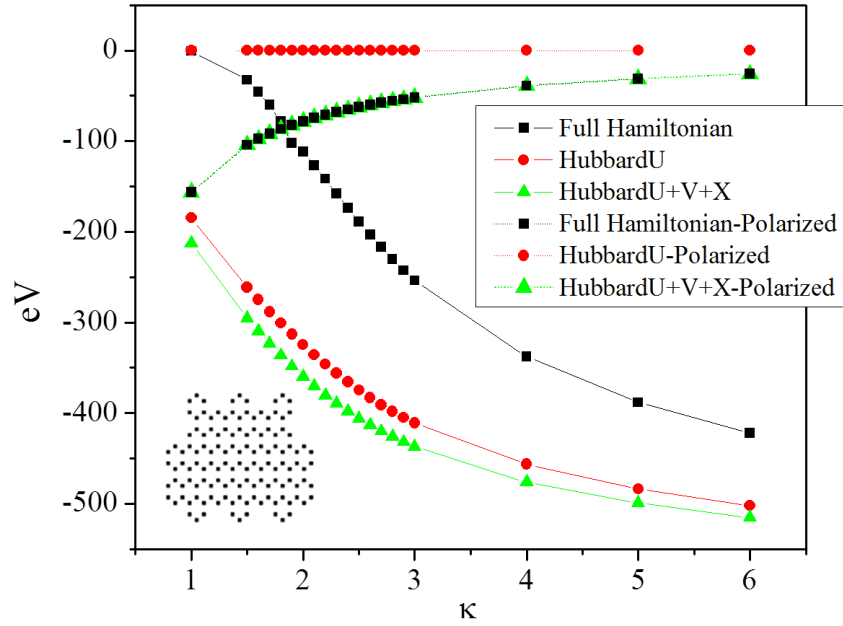


Figure 4.9: Phase diagram of C132 at $t = -3.0\text{eV}$, $t_2 = -0.1\text{eV}$. Ground state energy of the spin polarized and spin unpolarized C132 calculated with Hubbard U, Hubbard U+V+X and HF approaches

than that of the spin polarized state as we tune U up to $\sim 16.5\text{ eV}$ ($\kappa = 1.0$). Introduction of exchange and direct interactions reduce the overall energy of both the spin-polarized and unpolarized ground states yet at $\kappa = 1.0$ the spin-unpolarized state remains the ground state.

Unlike Hubbard U and Hubbard U+V+X, as discussed for C168, the HF Hamiltonian predicts a phase change with increasing interaction strength for C132. At around $\kappa = 2.3$, which corresponds to $U \sim 7.2\text{eV}$, the spin-polarized ground state has a lower energy compared to that of the spin-unpolarized state.

4.2 Optical Properties in Semiconductor Phase

For the rest of this chapter, I will be working in the semiconductor phase, keeping $\kappa/t > 1$. Starting with the HF ground state, we can create excitations out of it by moving HF quasiparticles from the valence to the conduction band. The ground state along with the excitations will then make up the CI-subspace from which the correlated ground and excited states are obtained. With this information, we can calculate the absorption spectrum and compare with the experiments to extract κ and t .

From now until the calculation of the absorption spectrum, the figures will have different κ and t values to depict the robustness of the level ordering with changing parameters

(remaining within the semiconductor phase). As soon as we get to a point where the data can be compared with the experiment, I will depict how κ and t affects the spectrum and determine the values that allow me to reproduce the experiments.

4.2.1 Excitons

Starting with the ground state, moving a single electron from the valence band to the conduction band will leave a hole in the valence band. The electron and the hole attraction will lower the energy of the excitation. In addition to this intrinsic effect, the electron-hole pairs will interact with one another and their resulting linear combinations will be the excitons. The excitons can be thought of as quasiparticles.

4.2.1.1 Excitons at the Band Edge

Now let's look into some of these excitations created at the C168 band edge, since it is a good platform to understand the optical selection rules as well as the electron-hole pair interactions.

The HF ground state $|GS_{HF}\rangle$ is obtained by filling up the valence band with 84 up and 84 down electrons as depicted in Fig.4.10(a). As explained in chapter 2, interactions among these electrons are already included in their self-energies. There are eight ways (four for each spin) of creating electron-hole pairs $|p, q\rangle = b_{p\uparrow}^+ b_{q\uparrow} |GS_{HF}\rangle$ at the band edge, without flipping the spin of the electron. Taking an electron from the $m = 1$ valence band and moving it directly up, to an $m = 1$ conduction band, a $\Delta m = (1) - (1) = 0$ electron-hole pair is created. Similarly taking an electron from the $m = 2$ valence band and moving it up to a $m = 2$ conduction band will result in a $\Delta m = 0$ pair as depicted in Fig.4.10(b). Overall, at the band edge there are four such pairs; two for each spin. None of the four can be created by means of absorption of light since $\Delta m = 0$ excitations are not optically active. Sending a σ^+ polarized light, a spin up/down electron from the $m = 1$ valence band can be excited to the $m = 2$ conduction band creating a $\Delta m = (2) - (1) = +1$ pair. Similarly a σ^- polarized light can move a spin up/down electron from the $m = 2$ valence band to the $m = 1$ conduction band resulting in $\Delta m = (1) - (2) = -1$ pairs as depicted in Fig.4.10(c). Energy of each of these pairs is calculated as given in Eq.2.133.

The 8×8 electron-hole pair subspace can be block diagonalized according to Δm . The $\Delta m = 0$ subspace will then contain 4 pairs while $\Delta m = \pm 1$ will each have 2 pairs. Within each subspace we can create linear combinations of these configurations to create the singlet and triplet pair states further reducing the size of each space that we have to work with. For example the $\Delta m = 1$ configuration for spin up and spin down can be combined to give non-interacting singlet and triplet states.

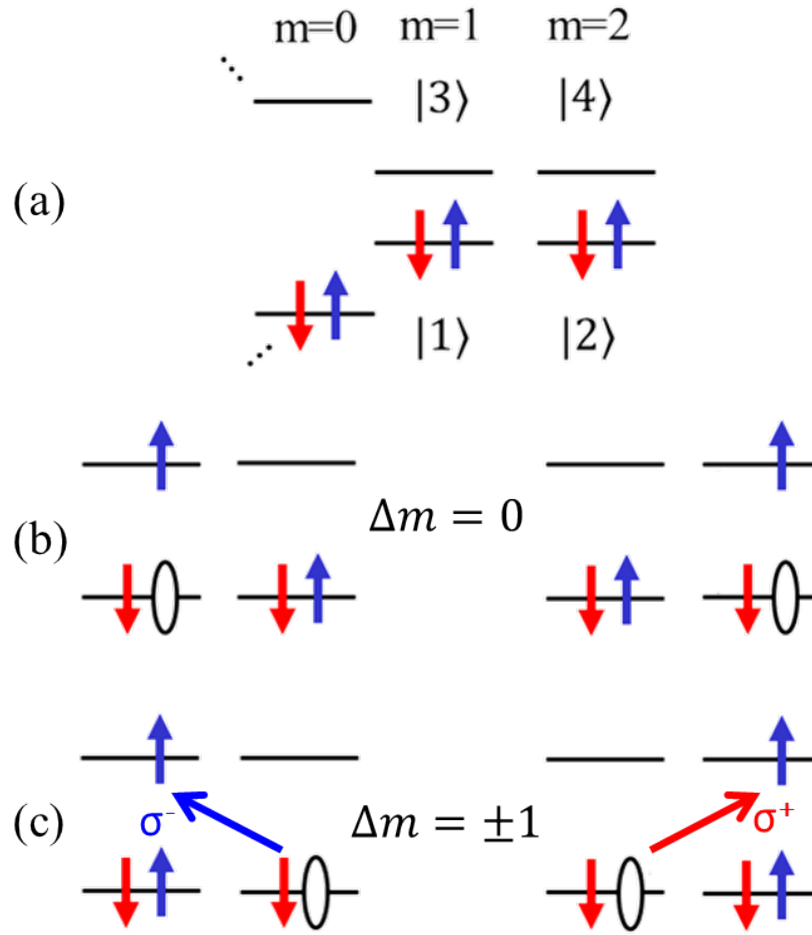


Figure 4.10: (a) The HF ground state $|GS_{HF}\rangle$. (b) Single-pair excitation with total angular momentum $\Delta m = +1$ and $\Delta m = -1$. (c) Single-pair excitations from $|GS_{HF}\rangle$ with total angular momentum, $\Delta m = 0$. Reprinted from Ref.¹⁵⁷.

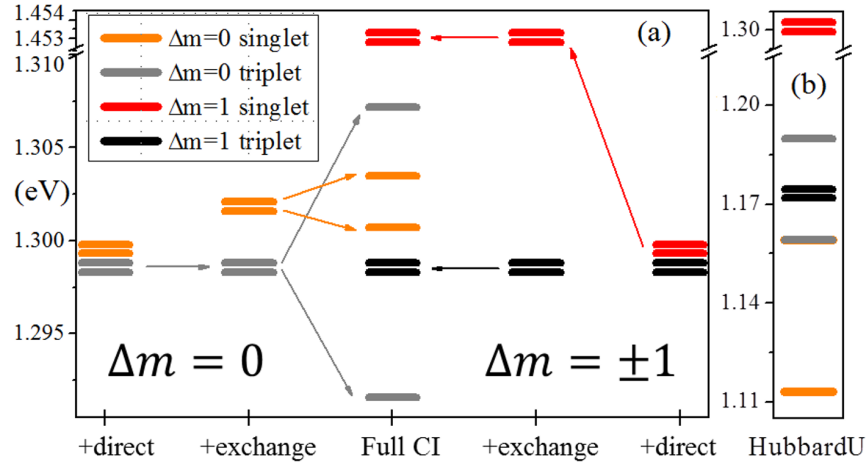


Figure 4.11: (a) Evolution of singlet-triplet splitting with the inclusion of different interactions in C168 for $t = -3.0\text{eV}$, $t_2 = -0.1\text{eV}$ and $\kappa = 5$ starting with the HF ground state. The black lines are $\Delta m = \pm 1$ triplets, red are $\Delta m = \pm 1$ singlets while $\Delta m = 0$ triplet and singlet levels are shown in gray and orange. Left section shows the evolution of $\Delta m = 0$ excitons while the right section shows the evolution of $\Delta m = \pm 1$ excitons. The middle section depicts all Δm levels after CI calculations. (b) starting with the Hubbard U ground state, the singlet-triplet splitting after CI. Reprinted from Ref.¹⁵⁷.

We can understand the importance of interactions by analyzing step by step the evolution of the energies until we obtain the excitons. We will turn on different interactions one by one and examine their effects on the level ordering. Whether singlet or triplet, each pair will have a direct electron-hole interaction correction to its energy. The far left and right columns in Fig.4.11(a) depicts the energies of $\Delta m = 0$ and $\Delta m = \pm 1$ pairs after the inclusion of self energies and direct interaction corrections. Now, if we turn on the exchange interaction that is present for singlets but not for triplets we will get the singlet triplet separation as depicted in the second columns from right and left in Fig.4.11(a). This was the last step for the $\Delta m = \pm 1$ states since each total-spin subspace contains a single state. For the $\Delta m = 0$ states, each total spin subspace has 2 interacting pairs as given in Eq.2.139. Due to lack of exchange, which reduces the strength of interactions, the triplet states push one another stronger compared to singlets as shown in the middle column of Fig.4.11(a). As a result, at the band edge, there are two bright degenerate singlet exciton states and a band of dark excitons composed of two orbitally dark singlets and four dark triplets at lower energies.

By comparing Fig.4.11(a) obtained from HF quasiparticles and Fig.4.11(b) obtained from Hubbard U quasiparticles, we see that the separation of the degenerate bright singlets from the forest of dark singlet and triplets is robust. However, the ordering of the levels in the dark region changes from Hubbard U to HF due to the inclusion of exchange interactions which drives the lowest excited state from a singlet to a triplet.

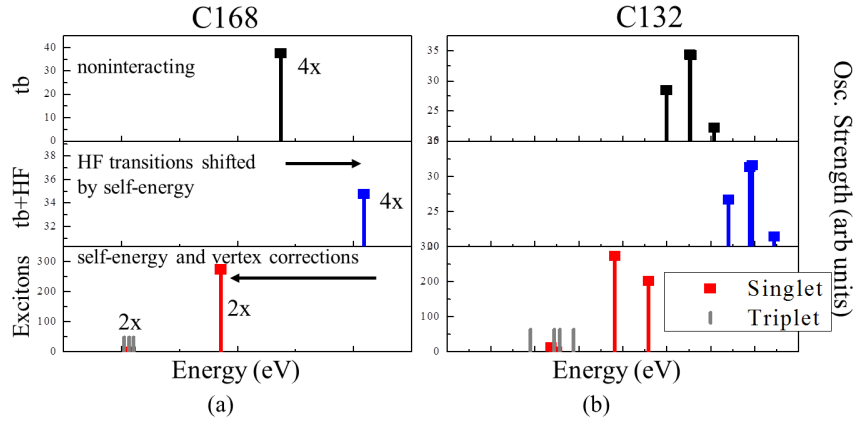


Figure 4.12: Evolution of absorption spectrum of C168 and C132 with increasing accuracy of approximations from tb to $tb+HF$ to $tb+HF+CI$. The energy axis values are not shown since the qualitative shifts are independent of the value of t or κ for GQDs in semiconductor regime.

Fig.4.12 shows the evolution of the low-energy excitonic spectrum associated with the degenerate band edge states for C168, and the non-degenerate band edge for C132. The topmost panel shows the absorption spectrum of the noninteracting CGQDs. The second panel shows the absorption in the $tb+HF$ approximation. The self-consistent HF approach protects the rotational invariance of the $m = \{0, 1, 2\}$ subspaces but blue-shifts the energy gap due to differences in self-energy of the electron and a hole, as expected for C168. For C132 however, due to lack of degeneracy and rotational invariance none of the peaks are degenerate (although each shares the same energy with a dark triplet) and we can distinguish all four possible excitation energies for the $tb+HF$ approximation. The third panel of Fig.4.12 shows the band-edge exciton spectrum calculated from the HF ground state. We see that the inclusion of electron-hole attraction, exchange and electron-hole correlations red-shifts the absorption spectrum and separates in energy the singlet and triplet excitons. The two bright excitons remain degenerate for C168, and the band of dark singlet and triplet exciton states appears at lower energy. For C132, all singlets are optically active since we cannot classify the excitons according to angular momentum, although the two within the triplet band have weaker oscillator strength compared to the higher energy two.

4.2.1.2 Beyond Band Edge

The two conduction and the two valence band states at the band edge allowed us to discuss the important structure of the band edge excitons. The exact energies of these levels however are modified by scattering into higher (lower) energy states of the conduction (valence)

band. In order to extract the proper κ and t values, states beyond the band edge should be included in our calculations. Thus, the absorption spectra that will be discussed in this section are calculated by constructing the CI-Hamiltonian in a larger basis, consisting of 690 single electron-hole pairs and 172155 double electron-hole pairs. Although biexcitons do not appear in the absorption spectrum, double electron-hole pairs are included since they will modify the energies of the exciton levels. The details of these numbers will be explained later in this chapter. Below I will discuss how the absorption depends on the tunnelling matrix element and on screening of electron-electron interactions.

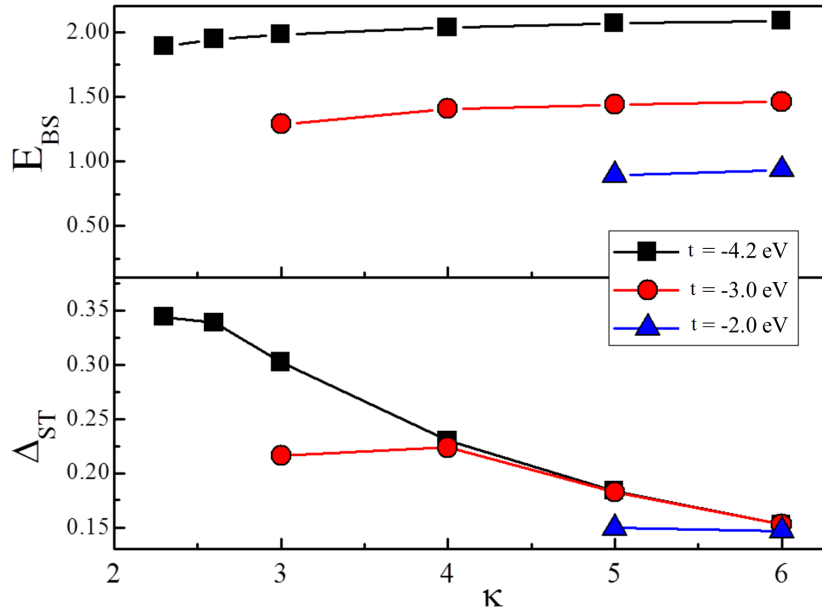


Figure 4.13: Position of the bright degenerate singlet and the bright-singlet–dark-triplet separation as a function of κ . Reprinted from Ref.¹⁵⁷.

The two most prominent features of the band edge spectrum are the location of the bright singlets and the bright singlet - dark triplet band energy separation. I will now discuss the evolution of these two features as a function of t and κ in the semiconducting phase. Fig.4.13 presents the results of the calculated energy of the bright degenerate singlets, and $\Delta_{S/T}$; the bright singlet - lowest triplet separation as a function of t and κ . We see that the energy of the bright singlets weakly depends on κ but varies with tunneling matrix element t from ~ 1 eV for $t = -2$ eV to ~ 2 eV for $t = -4.2$ eV. The bright-singlet–dark-triplet separation $\Delta_{S/T}$ is due to electron-electron interactions and is influenced by the dielectric constant κ rather than the hopping element t . For $t = -4.2$ eV, $\Delta_{S/T}$ varies from 0.15 eV for $\kappa \sim 6$ to 0.35 eV at $\kappa \sim 2$.

Fig.4.14(a) shows the measured⁷⁰ and calculated absorption spectra for $\kappa = 5.0$ and $t = -4.2$ eV. The absorption peaks for theory were plotted with a gaussian broadening in

the left column while the right column shows the calculated singlet exciton peaks separated according to Δm . I am excluding the triplet excitons in this picture since we are interested in addressing excitons optically. We see that the measured absorption spectra show an absorption threshold around $E = 1.6$ eV, a peak at $E = 2.1$ eV and a reduced absorption strength up until $E = 3.1$ eV. Although the two lowest-energy singlet states are orbitally optically dark,^{72,157,218} coupling to phonons should yield the absorption shoulder at 1.7 eV.²³⁴ The pronounced peak at 2.1 eV is associated with the doubly degenerate band-edge bright singlet excitons and my choice of parameters was dictated by this association and the reduced absorption strength at higher photon energies.

Assuming that the peak around the absorption threshold is due to the dark singlets, which were activated by breaking of symmetry due to, e.g., charge and spin fluctuations in the surrounding fluid, my choice of parameters lead to a significantly underestimated bright singlet dark triplet splitting when compared with experiment. The main reason for such discrepancy may be the static treatment of screening, independent of the length scale.

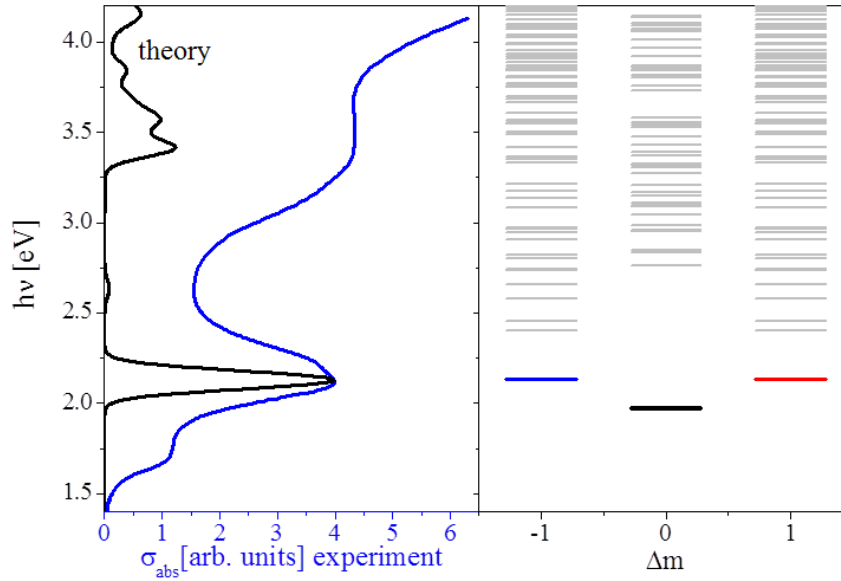


Figure 4.14: (a) Experimental (blue) and theoretical (black) absorption cross section of C168. (b) Calculated singlet exciton states separated according to angular momentum Δm . Gray lines show higher-energy single-exciton states.

In all results presented beyond this point $t = -4.2$ eV, $t_2 = -0.1$ eV and $\kappa = 5$ parameters will be used.

4.2.2 Biexcitons

Excitations are not restricted to single electron-hole pairs. We can move multiple electrons from the valence band to the conduction band creating many electron-hole pairs as long as we provide the sufficient energy and the photon fluence. In this section, I will concentrate on biexcitons in CGQDs.

4.2.2.1 Biexcitons at the Band Edge

Without flipping the spin of an electron, there are 18 biexciton configurations that can be generated at the band edge. Fig.4.15 groups these configurations according to their $\Delta m = m_{1c} + m_{2c} - m_{1v} - m_{2v}$. Here the subscripts are used to specify the angular momentum of the valence band state the electron was taken from and the conduction band state that it has been moved to. In order to be able to distinguish the momentum

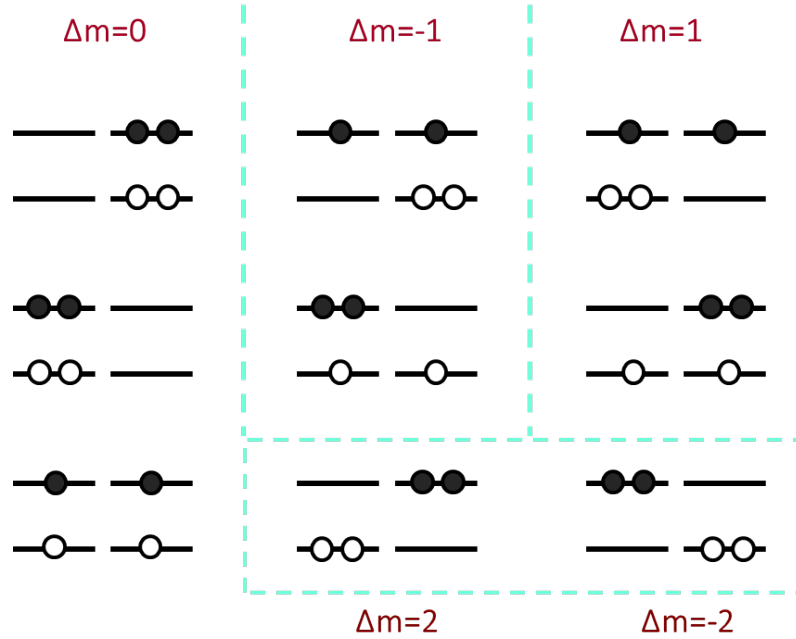


Figure 4.15: XXs at the band edge grouped according to their Δm

of an electron-hole pair from that of an exciton, let us express the Δm of excitons and biexcitons as Δm_X and Δm_{XX} , respectively. An important thing to note in Fig.4.15 is the placement of $\Delta m_{XX} = \pm 2$ XXs. As long as we restrict ourselves to work at the band edge, we can keep such a labelling convention. However, as soon as we include a $m = 0$ quasiparticle level, such characterization becomes invalid and the $\Delta m_{XX} = \pm 2$ configurations map onto $\Delta m_{XX} = \mp 1$. This is due to the fact that $m = 1, 2$ alone does not make up a complete subspace to link $\Delta m_{XX} = \pm 2$ states to $\Delta m_{XX} = \mp 1$ states. Fig.4.16(a)

shows all band edge excitons and XXs color coded according to their spin-character. Since we are interested in optically addressing the Xs and XXs it is enough to concentrate on the singlets that are isolated and shown in Fig.4.16(b). The XX states are classified according to the single-exciton states from which they are primarily derived. Lets start with the

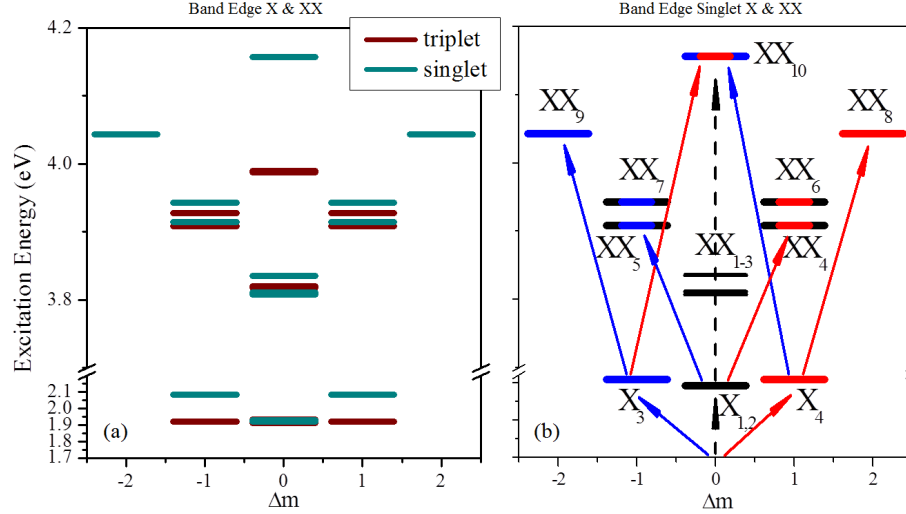


Figure 4.16: Band edge excitons and biexcitons separated by Δm . (a) Both singlet and triplet excitations. (b) Singlet excitons and biexcitons at the band edge measured from ground state energy. Dipole-allowed electronic transitions, corresponding to $\Delta m = \pm 1$, are labeled with solid arrows. $\Delta m = +1$ corresponds to $\sigma+$ photon polarization (red arrow) and $\Delta m = -1$ corresponds to $\sigma-$ photon polarization (blue arrow). Dipole-allowed electronic transitions, corresponding to $\Delta m = \pm 1$, from the ground state and from the lowest singlet exciton states are shown respectively by solid red and blue arrows. The biexcitons are color coded according to their exciton content.

$\Delta m_{XX} = 0$ biexcitons (XXs). In Fig.4.15 they are shown in the first column. We have already shown that in order to be able to optically address a level we need an electron-hole pair that occupies opposite angular momentum states across the band-gap. The first two $\Delta m_{XX} = 0$ XXs do not abide that since both holes and electrons occupy $m = 1$ ($m = 2$) levels. The third state however represents all configurations with its carriers on different band edge states. We can take two electrons from different valence levels and move them across the band-gap, without changing their positions (placing them on to a conduction band state with the same m) to create dark XXs, or exchanging their positions to create bright XXs. Since all configurations in the $\Delta m = 0$ XXs subspace interact with one another, every correlated XX state will be a mixture of all configurations. In Fig.4.16 these XX states are shown in the central column. Out of the four $\Delta m_{XX} = 0$, band edge, singlet XXs, only XX_{10} is optically addressable. I will discuss XX_{10} (HXX) later in the chapter.

Moving on to $\Delta m_{XX} = \pm 1$ XXs, describing either one will suffice, since the same physics applies to the other subspace if we change the polarization of the light. The following discussion excludes the $\Delta m_{XX} = \pm 2$ XXs. As depicted in Fig.4.15, the $\Delta m_{XX} = \pm 1$ configurations are derived from a dark and a bright band edge exciton. As a result, if the dot can be prepared in either one of the dark excitons (by means of pumping at high energy followed by phonon assisted relaxation), the XX_4 - XX_7 states can be optically addressed as will be discussed later.

A $\Delta m_{XX} = \pm 2$ biexciton at the band edge has both electron-hole pairs on the same conduction and valence band states with opposite angular momentum - m 's. They can be addressed optically absorbing two photons with the same polarization from the ground state.

4.2.2.2 Beyond Band Edge

In the previous section we discussed the XX spectrum at the band edge. Let us now discuss how this spectrum changes when electrons and holes can scatter into excited orbitals.

Due to the size of our configuration space, we need to restrict the number of HF quasiparticle states taken into account. Since Auger processes contribute to lifetime and content of XXs, we should make sure to include all excited excitons that may couple strongly to the band edge XXs while restricting the CI-space. In order to do so the CI subspace is chosen to include all HF states that may contribute to an Auger coupling between an excited exciton (X^*) and a band-edge XX. As explained before, starting with a band-edge biexciton, one of the electron-hole pairs can recombine giving the excess energy to the remaining electron-hole pair, exciting the electron up, or the hole down, by an energy equivalent to the band-gap, E_g . Thus, we need to include all HF states within the window of $3E_g$ from the center of the band-gap to capture Auger coupling of the band-edge XXs to excited X^* states.

The $3E_g$ CI window corresponds to 15 valence and 23 conduction band states for the parameters that we are using. Even though one can technically create up to 30 electron-hole pair configurations within this window, even to create a $3X$ configuration, we need at least three times the band-gap energy, which is significantly greater than the energy range that we are interested in. Thus, in this section I will restrict the maximum number of excitations to two. Then the CI-subspace for that is used for the remainder of this chapter includes the ground state, 690 excitons and 172155 biexcitons.

4.2.2.2.1 Biexciton Binding Experimentally, the biexciton binding energy is extracted from the emission spectra of XXs and Xs and it is defined as $E_b^{XX} = E_{ext}^{X_1} + E_{ext}^{X_2} - E_{ext}^{XX}$ where the subscript *ext.* signifies that the energies are measured with re-

spect to the ground state. The first two terms are the energies of the two constituent excitons, counted separately, while the third term is the energy of the biexciton complex. The sign of E_b^{XX} can be positive or negative, corresponding to excitons attracting (binding) or repelling (unbinding) each other, respectively. It is also an indicator of degree of correlation, which is measured by the number of two-electron-hole configurations contributing to the XX state. The binding energies of the band-edge XXs are calculated as follows

$\Delta_{XX_{1-3}}$	54 – 78 meV
$\Delta_{XX_{4,5}}$	145 meV
$\Delta_{XX_{6,7}}$	104 meV
$\Delta_{XX_{8-9}}$	165 meV
$\Delta_{XX_{10}}$	52 meV

We can also investigate the effects of size and shape by computing binding energies for different shapes of CGQDs. Calculations on small systems, restricted to the band edge have shown that the binding energy increases inversely with the size of the C_3 symmetric quantum dots. However, as soon as we break the C_3 symmetry, even if we increase the quantum dot size, the binding energies of both the lowest and the highest XX increase significantly. The sign of the binding energy, determining whether the XX is bound or not, does not seem to be affected by the size or the shape of the quantum dot.

4.2.2.2.2 Transient Absorption Although the two lowest-energy singlet states, $X_{1,2}$ (or collectively LX) are orbitally optically dark we can access those states in a transient absorption experiment.^{72,157,218} I will now report on such experiments that were done on C168 and compare them with our results.

In the experiments⁷², C168 in toluene was excited at 3.1 eV and probed with a broadband continuum. Focusing on long delays, when the system has cooled to the lowest energy singlet excitons, the transitions from LX to higher-energy single-exciton (X^*) and XX states were measured through absorption of the probe pulse. The measured absorption spectra at $t=100$ ps from LX to higher lying excitations is depicted as blue circles in Fig.4.17.

To identify the source of the spectral features in the experimental TA spectrum, we calculate the differential absorption spectrum $-(\alpha_{X_{1,2}} - \alpha_{GS})$, which is the difference between the absorption of LX and that of the ground state shown by the black curve in Fig. 4.17. The absorption spectrum is compared with the excited exciton X^* and biexciton XX energies shown in the upper panel of Fig. 4.17. The induced absorption at ~ 1.95 eV is primarily due to the $LX \rightarrow XX_{4-7}$ transition which involves addition of a bright $X_{3,4}$ exciton observed in the linear absorption spectrum at $E = 2.1$ eV. The peaks before 1.95 eV that

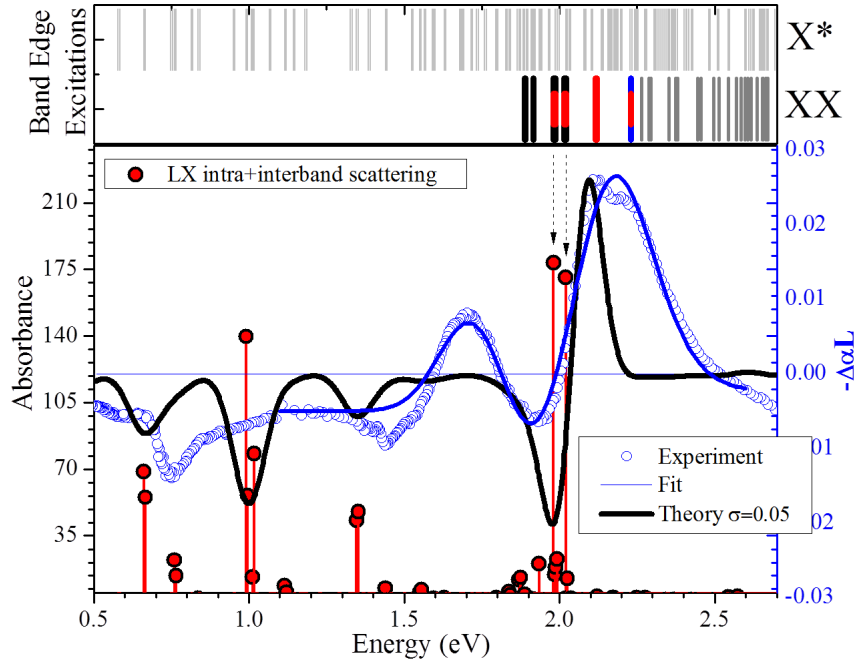


Figure 4.17: Experimental and theoretical absorption spectra from lowest singlet exciton state. Blue circles indicate measured $-\Delta\alpha L(t = 100 \text{ ps})$ for C168. Blue curve is a fit to the experimental data.¹⁵⁹ The red bars indicate calculated transitions from the states $X_{1,2}(\text{LX})$ accounting for intra+interband transitions. The black line is the theoretically calculated, Gaussian-broadened $-\Delta\alpha = -(\alpha_{1,2} - \alpha_0)$ assuming equally populated $X_{1,2}$ states. Top panel shows singlet excitons (light gray), band-edge excitons (color corresponding to Fig. 4.16) and higher XXs (dark gray) accessible from $X_{1,2}$.

are seen both in experiment and theory can be attributed to intraband transitions. The calculated biexciton binding energy $\Delta_{\text{XX}_{4,5}} = 104 - 145 \text{ meV}$ is close to the experimentally fitted value of $0.17 \pm 0.01 \text{ eV}$.

4.2.2.2.3 Auger Processes and Spectral Function

In order to understand the Auger processes between the highest band-edge XX and the highly excited excitons, we need to examine the spectral function of the biexciton interacting with the excited exciton states. The band-edge biexcitons are immersed in an excited exciton sea and the spectral function will help us understand how *pure* these biexcitons are.

Its calculation involves two steps. First, one needs to calculate separately the eigenstates and eigenvalues of the mixed system (GS+X+XX) and the eigenstates and eigenvalues of the system, in which only the configurations with two electron hole pairs are included (the 'conserved' system). After exact diagonalization of the Hamiltonian for the

mixed system we obtain the eigenfunctions in the form of Eq.2.147;

$$\begin{aligned}
 |\Phi_\nu\rangle &= k_0^\nu |GS_{HF}\rangle + \sum_{mn\sigma} k_{mn}^{\nu(1)} |i\sigma; j\sigma\rangle \\
 &+ \sum_{pmqn} \sum_{\sigma_1\sigma_2} k_{pmqn}^{\nu(2)} |p\sigma_1, m\sigma_2; q\sigma_1, n\sigma_2\rangle + \dots
 \end{aligned} \tag{4.6}$$

As for the conserved system with two-pair excitations, the exact diagonalization procedure produces the following eigenfunctions:²³⁵

$$|XX\rangle_\eta = \sum_{pmqn} \sum_{\sigma_1\sigma_2} k_{pmqn}^\eta |p\sigma_1, m\sigma_2; q\sigma_1, n\sigma_2\rangle. \tag{4.7}$$

We restrict both bases in the same manner by including all X and XX within the window of $3 \times E_g$. In the end, we have the eigenstates and eigenenergies of the mixed system, $|\Phi_\nu\rangle$, E_ν and that of the conserved system $|XX_\eta\rangle$, E_η .

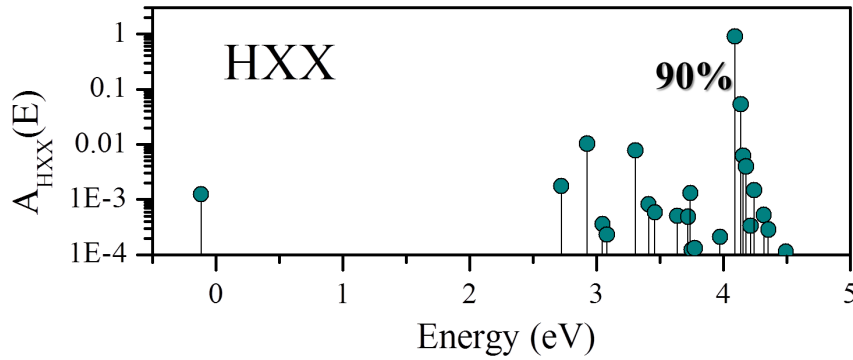


Figure 4.18: Spectral function of the highest biexciton state HXX (XX_{10}). The highest peak at 90% corresponds to HXX

In order to quantify the degree of mixing between a biexciton state $|XX\rangle_\nu$ and the rest of the excitations we introduce the spectra function, $A_{\eta,XX}(\nu)$, that is given as

$$\begin{aligned}
 A_\eta(E) &= \sum_\nu |\langle XX | \Phi_\nu \rangle|^2 \delta(E_\nu - E), \\
 &= \sum_\nu \left| \sum_{pmqn} \sum_{\sigma_1\sigma_2} (k_{pmqn}^\eta)^* k_{pmqn}^{\nu(2)} \right|^2 \delta(E_\nu - E).
 \end{aligned} \tag{4.8}$$

This function is the projection of a conserved biexciton state, XX_η , onto the states of the mixed system.²³⁵ In the weak XX-X coupling limit, the spectral function will approach $A_\eta(E_\nu) \rightarrow 1$ for E_ν corresponding to the eigenstate that is mainly composed of XX_η in the mixed system. As an example, the spectral function of the HXX state ($\eta = 18$) of the

conserved system is shown in Fig.4.18. The highest $A_{HXX}(E_\nu)$ peak with a value of 0.90 corresponds to the energy of HXX in the mixed state. The size of this peak tells us that HXX is coupled weakly to the excited excitons in the mixed system and is expected to be stable against Auger recombination. The inverse of the width of the spectral function defines the Auger lifetime. However, as in semiconductor nanocrystals,²³⁵ the calculated Auger lifetime using the width is significantly higher than the experimentally measured value.⁷² The origins of this discrepancy remain to be determined.

4.2.2.2.4 XX-X Cascade

The opening of an energy gap due to size quantization in graphene, a semimetal, makes graphene quantum dots similar to semiconductor quantum dots but without the spin-orbit coupling.^{14–21,74,85,87–90,236–246} Strong spin-orbit coupling in semiconductor quantum dots is responsible for the existence of two degenerate interband optical transitions and, at first sight, two degenerate exciton states. The cascade between a biexciton and two degenerate exciton levels in semiconductor quantum dots has been proposed as a method for the generation of entangled photon pairs.^{247–250} However, it became clear that the degeneracy of the two exciton levels is removed by the electron-hole anisotropic exchange interaction,^{219,251–257} destroying photon entanglement. On the other hand, the advantage of using semiconductor quantum dots is the existence of a well defined, unique biexciton state. By contrast, as described before, graphene quantum dots¹⁵⁷ with 3-fold rotational symmetry exhibit robust, degenerate exciton states and could potentially replace semiconductors in entangled photon generation if a well defined biexciton level could be found.

Starting with either one of the bright exciton configurations, X_3 or X_4 , there are only two ways to create a biexciton state: by creating an electron hole pair with $\Delta m = 1$ on a $(m = 1) - (m = 2)$ valence-conduction pair or with $\Delta m = -1$ on a $(m = 2) - (m = 1)$ pair. I feel the need to stress that it is not the total Δm_{XX} of the system, but that of the excited electron-hole pairs that needs to be $\Delta m \neq 0$ to couple to light. For example, if we start with a $\Delta m_X = 1$ exciton, it can absorb light to become a $\Delta m_{XX} = 2$ or a $\Delta m_{XX} = 0$ biexciton.

As explained before, the lowest $\Delta m_{XX} = 0$ band of biexciton states do not radiatively couple to any of the exciton states nor the ground state. Next, the set of $\Delta m_{XX} = \pm 1$ biexcitons emit only to dark singlet excitons, thus they are not candidates for a cascade. In the end, at the band edge, there are only three states that emit to bright excitons, which are the $\Delta m_{XX} = \pm 2$ biexcitons and the highest energy $\Delta m_{XX} = 0$ biexciton. In emission, the $\Delta m = \Delta m_X - \Delta m_{XX}$ determines the polarization of the emitted photon; for $\Delta m = \pm 1$, the emitted photon will have a $\sigma^\mp$ polarization.

In the XX-X cascade, both electron-hole pairs of the biexciton recombine, each emitting

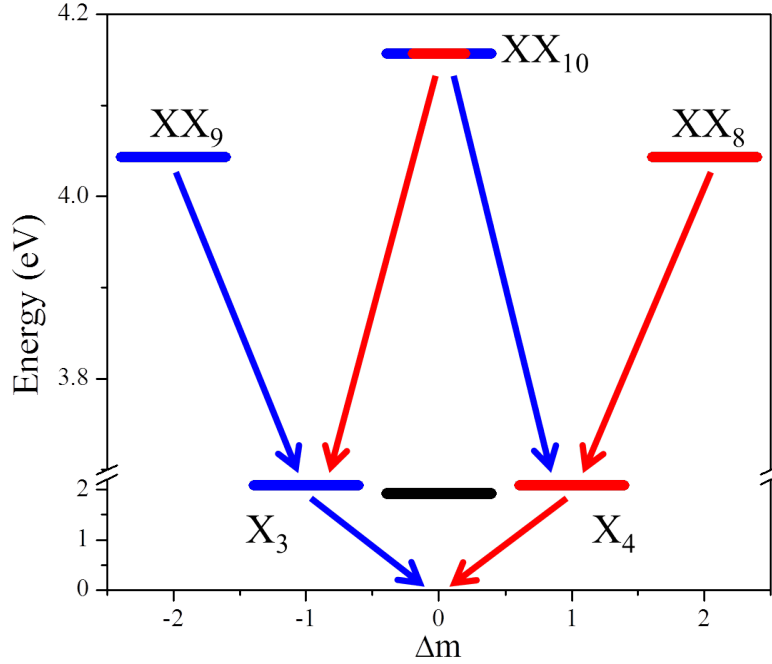


Figure 4.19: Band edge excitons and biexcitons showing possible XX-X cascade routes.

a photon. Fig.4.19 depicts two possible paths of recombination as candidates for the XX-X cascade in these CGQDs. If we prepare the C_3 symmetric graphene quantum dot in the state of XX_{10} the entangled Bell-state of the two photons generated in its radiative recombination will be

$$|\psi\rangle = \frac{1}{\sqrt{2}} (|\sigma^- \sigma^+\rangle + |\sigma^+ \sigma^-\rangle). \quad (4.9)$$

Starting from the XX_{10} state, one can choose either the left or the right path emitting a σ^+ or σ^- polarized photon. The second photon emitted in this process will have polarization opposite to the first photon.

If the CGQD is prepared in a superposition of the XX_8 and XX_9 , the photons emerging from the recombination process will be polarization entangled and their two-photon Bell state will be expressed as

$$|\psi\rangle = \frac{1}{\sqrt{2}} (|\sigma^- \sigma^-\rangle + |\sigma^+ \sigma^+\rangle). \quad (4.10)$$

If, on the other hand, the CGQD is prepared in a state with a specific angular momentum, $\Delta m_{XX} = 2$ or $\Delta m_{XX} = -2$, then the state of the photons will collapse to a certain polarization, $p = \pm$, $|\psi\rangle = |\sigma^p \sigma^p\rangle$ and the entanglement will be destroyed.

Chapter 5

2D Semiconductors with Hexagonal Lattice

In this chapter I will briefly introduce transition metal dichalcogenides (TMDCs) and the results of my studies on 2D TDMCs. As discussed in the introductory chapter, TMDCs can be obtained by replacing the two carbon atoms in the unit cell of graphene by a transition metal element and a Sulfur dimer. Different from graphene, however, TMDCs have a non-zero band-gap. In fact, going from bulk to monolayer, TMDCs become direct gap materials.^{99,117,121,135} The existence of a direct band-gap in these materials makes them suitable for optoelectronic applications. Thus, it is important to understand their electronic and optical properties.^{99,108,109,111,112,114,139} Part of this work was prepared in support of experiments that are published.¹³⁴

5.1 Electronic Properties - Band Structure

Bulk MoS_2 is an indirect gap semiconductor (1.2 eV) with its valence band maximum at the Γ point and conduction band minimum between the Γ and K points.²⁵⁸ As the number of layers is decreased, the Γ point goes down in energy and the conduction band minimum goes up in energy. For a single layer, both of its valence band maximum and conduction band minimum are found at the Brillouin zone (BZ) edges K and K' points, creating a direct gap material with two distinct valleys.¹²¹ The results of DFT calculations using the VASP package without spin-orbit coupling¹, shown in Fig.5.1, depict the evolution of the bandstructure from bulk to a monolayer. We see in Fig.5.1 that bulk MoS_2 has an indirect gap. When MoS_2 is thinned down to bilayer, the gap is still indirect. However, a single layer has a direct band-gap at K points. As explained previously, this transition

¹Spin-orbit coupling was not included in VASP due to problems with our computational resources.

is not unique to MoS₂ but is observed in other MX₂'s as well. We can resolve the orbital

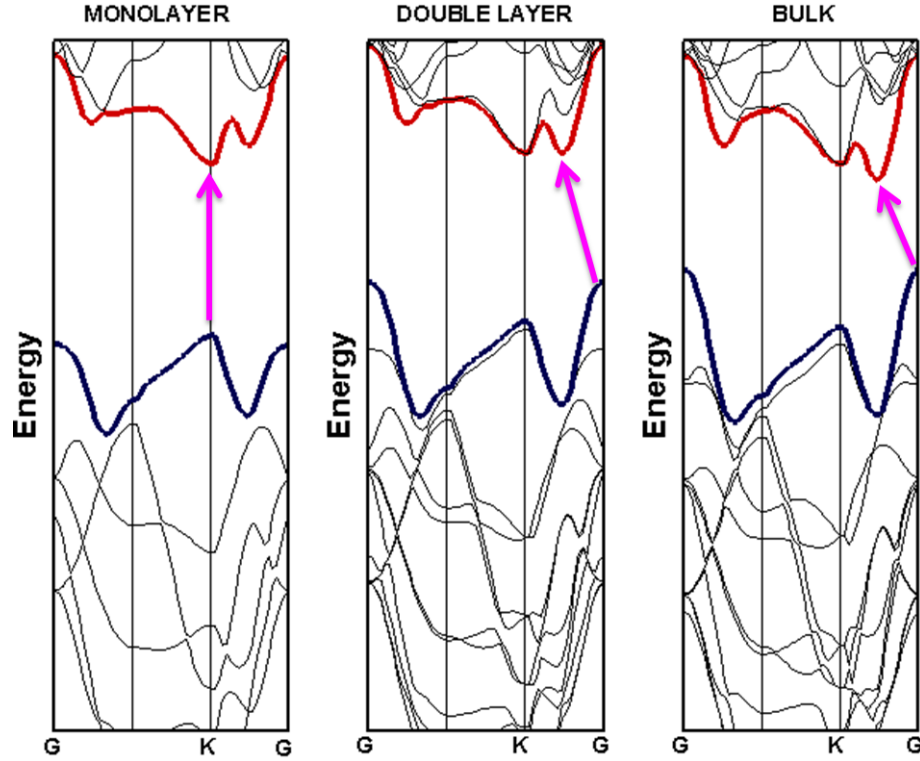


Figure 5.1: Evolution of the band-gap of MoS₂. Band structure calculated using VASP without the inclusion of spin-orbit coupling

spectrum of the top of the valence and bottom of the conduction band to better understand the contributions from each element to the band-gap. Both MoS₂ and WS₂ have the same orbitals contributing to their conduction band minimum and valence band maximum at the K point, since the 5*f* orbitals in W are lower in energy than its 4*d* orbitals. Fig.5.2 shows which orbitals of W and S contribute to the conduction and valence band extrema at K-points. The valence band maximum at the K point is mainly composed of the W *d_{xy}* and *d_{x²-y²}* and S *p_y* and *p_x* orbitals while the conduction band minimum originates from W *d_{z²}* and S *p_y* and *p_x* orbitals. The *d_{xy}* and *d_{x²-y²}* are even orbitals with angular momentum projections $m = \pm 2$ while the W *d_{z²}* orbital, which is also even, has an angular momentum projection of $m = 0$. Similarly, we can see that the S *p_x* and *p_y* orbitals are also even, symmetric about the *xy* plane, corresponding to angular momentum projections of $m = \pm 1$. Although it seems like these 5 orbitals would capture the physics of WS₂ around the Fermi level, we do have to consider contributions from the Γ point, especially at the valence band, since in energy it is very close to K-points. The Γ point is composed of hybridized S *p_z* and W *d_{z²}* orbitals. These orbital compositions are also true for MoS₂. Then to characterize the bands around the Fermi level of a MS₂ (M=Mo or W), we

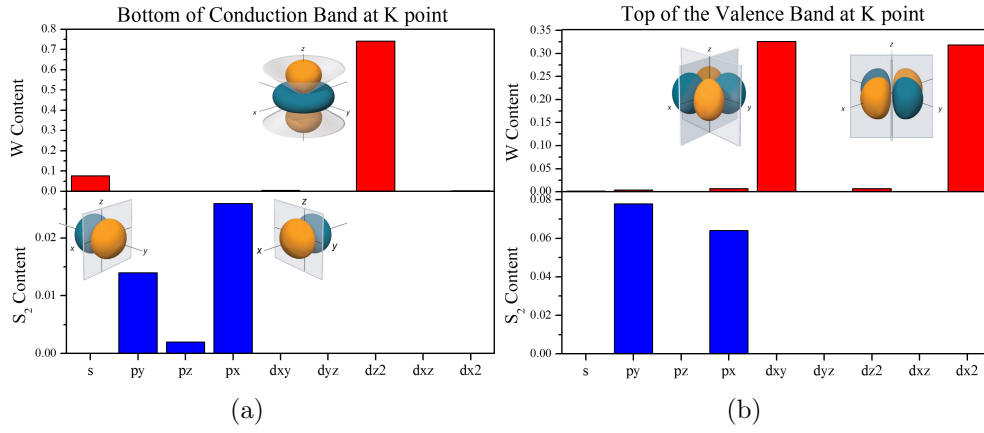


Figure 5.2: Conduction band minimum and valence band maximum W and S orbital contents of the K point in Monolayer WS₂. The shape of the orbitals are shown beside the peaks

need^{116,259}:

$$\begin{aligned}
 M_{3d_{z^2}} & & |m_d = 0\rangle, \\
 M_{3d_{x^2-y^2}} - iM_{3d_{xy}} & & |m_d = -2\rangle, \\
 M_{3d_{x^2-y^2}} + iM_{3d_{xy}} & & |m_d = 2\rangle,
 \end{aligned}$$

orbitals of M and,

$$\begin{aligned}
 S_{2p_x} - iS_{2p_y} & & |m_p = -1\rangle, \\
 S_{2p_x} + iS_{2p_y} & & |m_p = 1\rangle, \\
 S_{2p_z} & & |m_p = 0\rangle,
 \end{aligned}$$

orbitals from each S atom in the unit cell. We can reduce the number of orbitals one needs to consider by combining the two S atoms to make a dimer. In a single layer MS₂, the S atoms are symmetric about the M atom. We construct the symmetric orbitals for the S₂-dimer through linear combinations; $1/\sqrt{2}(|m_p = \pm 1\rangle_{S_1} + |m_p = \pm 1\rangle_{S_2})$ of the even and $1/\sqrt{2}(|m_p = 0\rangle_{S_1} - |m_p = 0\rangle_{S_2})$ of the odd sulfur orbitals. Within the basis of these orbitals, one can write an effective Hamiltonian to describe the band structure of a single layer MS₂ around the Fermi level. This is one of the major differences between transition metal compounds and graphene. We were able to write a 2x2 Hamiltonian to approximate the bandstructure of graphene. As for TMDCs, one needs at least a 6x6 Hamiltonian to capture the bandstructure around the Fermi level.

Since we are interested in the direct gap, one can exploit the symmetry properties

of K and K' points in order to reduce the size of the 6x6 Hamiltonian and determine which basis functions contribute to the valence band maximum and the conduction band minimum at the K and K' points.^{116,259} At the K point, the conduction band minimum originates from $m_d = 0, m_p = -1$ orbitals while valence band maximum is composed of $m_d = 2, m_p = 1$ orbitals. The K' point has contributions from the complex conjugates of the basis functions at the K-point.

Being made out of heavy transition-metals, TMDCs exhibit strong spin-orbit coupling. Thus it is important to include spin-orbit coupling into our calculations to better capture the band structure and understand electronic and optical properties of these materials. Fig.5.3 shows the spin-orbit coupled band structure of two TMDCs, MoS₂ and WS₂. Unlike graphene, both MoS₂ and WS₂ have broken inversion symmetry due to their non-centrosymmetric lattice structure. Due to time reversal symmetry, the electrons with opposite spins will have the same energy at opposite K points, that is $E_{\uparrow}(\vec{k}) = E_{\downarrow}(-\vec{k})$. Time reversal symmetry ensures that at every point in momentum space there is a *Kramers's doublet*. Due to the lack of inversion symmetry however, the spin degeneracy cannot be restored and as a result, in monolayer-MoS₂ and WS₂, valley and spin are coupled.¹²⁰

Since W atoms are heavier than Mo, the splitting of the valence band due to spin-orbit coupling is much greater in WS₂. The band-gaps of both of these materials, calculated using ABINIT, shown in Fig.5.3 are lower than the experimentally measured band-gaps.^{121,135,260} However, in DFT, LDA pseudopotentials are known to underestimate the band-gap. Nevertheless, the predicted spin-orbit splitting of the valence band of 0.42eV and 0.135 eV for WS₂ and MoS₂, respectively, are in agreement with previous theoretical and experimental work.^{112,125,261,262}

5.2 Optical Properties

The non-equivalency of K and K' points of TMDCs leads to valley dependent optical selection rules as depicted in Fig.5.4 for MS₂ (M=Mo, W). At the K point, the only allowed transition will be between the M orbital in the conduction band ($|m_d = 0\rangle$) and the S2 orbital in valence band ($|m_p = 1\rangle$), allowing only a certain polarization, σ^- . At the K' point, the transition will be between the M orbital in the conduction band $|m_d = 0\rangle$ and the S2 orbital in VB with $|m_p = -1\rangle$, allowing only for σ^+ polarized light absorption/emission. When we introduce the spin-orbit interaction, the spin up and down energies for each band realign according to the following spin-orbit interaction Hamiltonian,

$$\hat{H}_{SOC} = \Delta_{SO} \mathbf{L} \cdot \mathbf{S}. \quad (5.1)$$

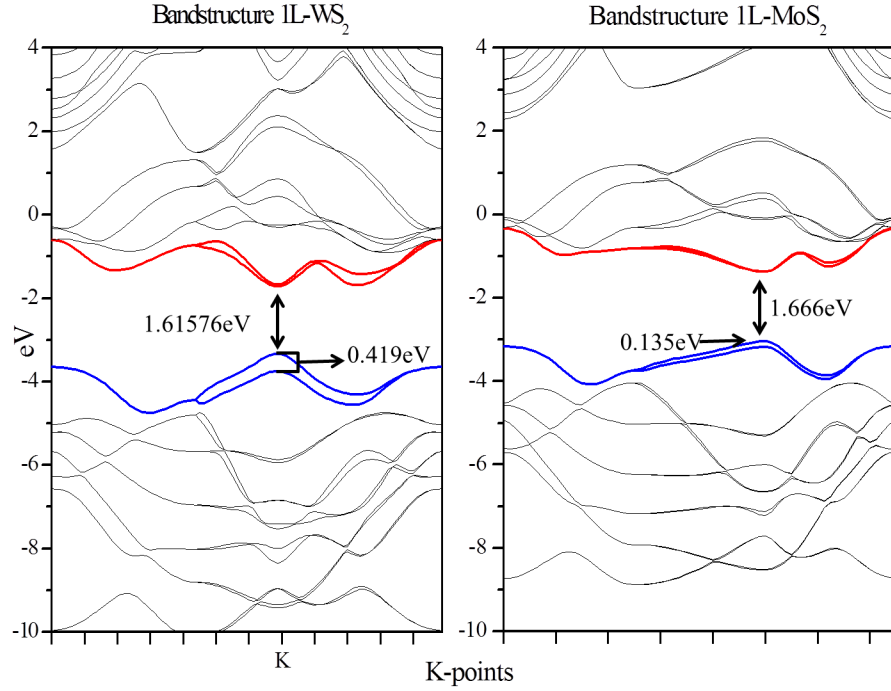


Figure 5.3: spin-orbit coupled bandstructure of Monolayer MoS₂ and WS₂ calculated using LDA-HGH(Local density approximation-Hartwigsen-Goedecker-Hutter) potentials within the ABINIT package

The resulting ordering of the levels depends on the signs of $\mathbf{L}$ and $\mathbf{S}$. Let us look at the K-point. In the conduction band the coupling is dictated by the S2 orbital with $m_p = -1$. Then, the energy of the down spin will increase and the spin up energy will decrease. In the valence band however, angular momenta of both m_d and m_p orbitals are positive. This will result in opposite ordering of spin when compared to the conduction band. The spin up electron band will move up in energy while the spin down moves down. Although this description is adequate for MoS₂ as shown in Fig.5.4(a), it is suggested that the splitting in the conduction band of TMDCs is dictated by two main contributions. The first-order contribution comes from the S2 orbitals as described above while the second order contribution is proposed to be due to coupling to other bands containing $m_d = \pm 1$ orbitals of M.²⁶³ In WS₂, because the W atom is a lot heavier compared to Mo, the second order contribution overpowers the first order contribution coming from the S atoms and changes the sign of Δ_{SO} in the conduction band. As a result, through DFT and k.p calculations, the spin-ordering of the CB of WS₂ was shown to flip compared to that of MoS₂ as depicted in Fig.5.4(b).^{263–265}

Since K and K' points are located at the edges of BZ, they are far away from one another which considerably suppresses the magnitude of intervalley coupling. This leads to valley degrees of freedom for carriers in K, K' points which can be thought as pseudospin.^{105,120,143}

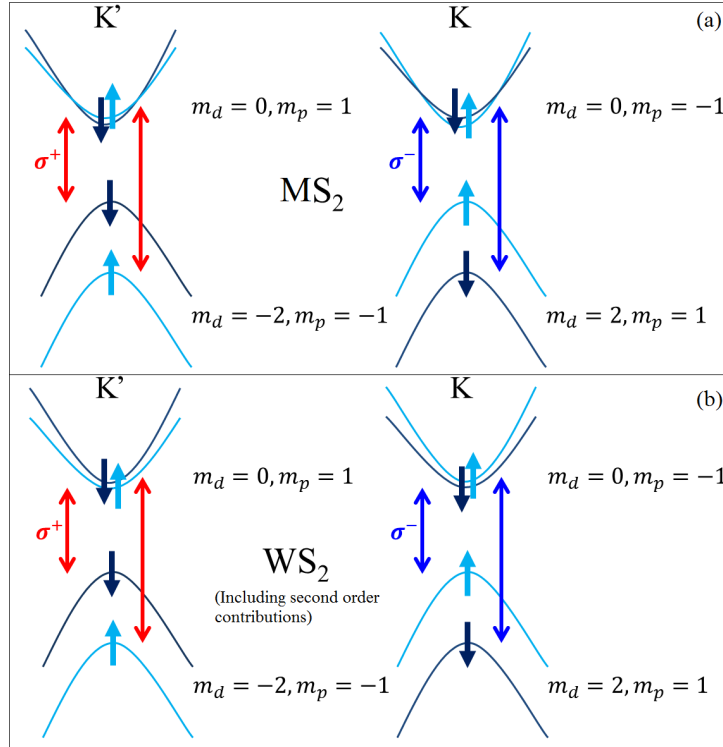


Figure 5.4: Schematic illustration of the level ordering and valley dependent optical selection rule due to spin-orbit coupling and broken inversion symmetry in MoS_2 and WS_2 . (a) MS_2 where M is the transition metal element. For MoS_2 , this picture holds even after the inclusion of second order contribution from $m_d = \pm 1$. (b) Ordering of the levels for WS_2 after the inclusion of second order contributions. Note that the spin-ordering of the conduction band is different for the two.

One can detect the pseudospin by exciting these materials with circularly polarized light. This way, the photons will only be absorbed in one valley. For example, if we excite a monolayer of WS_2 with σ^- polarized light, we would only populate the K valley (Fig.5.4). In an ideal system where there is zero inter-valley coupling, and an electron-hole pair created at the K valley will recombine to emit a σ^- polarized light. However, there are imperfections in any system which, in this case, will lead to non-zero intervalley scattering and a need to quantify polarization. The degree of circular polarization of the emitted light is measured by

$$P = \frac{I_+ - I_-}{I_+ + I_-}, \quad (5.2)$$

where I_+ and I_- are the intensities of σ^+ and σ^- polarized light respectively.

Based on the above discussion, excitation with unpolarized light should result in absorption in both valleys, followed by emission of σ^+ and σ^- polarized light in equal intensities, leading to emission of unpolarized light. I will now explain the experimental work that was done by our collaborators, in which they observe spontaneously circularly

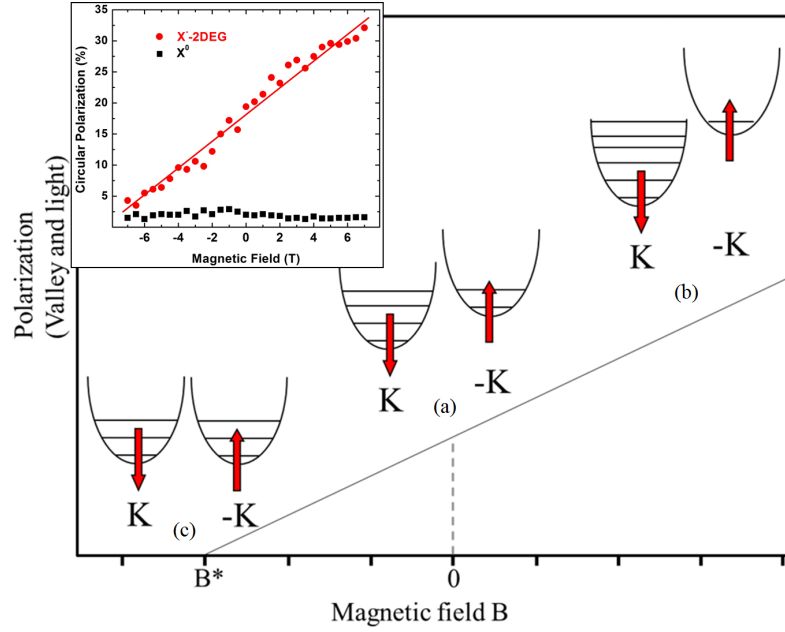


Figure 5.5: Schematic illustration of spontaneous valley polarization at (a) $B=0$ due to e-e interactions, (b) increasing, (c) or decreasing with B due to Zeeman energy and locking of spin and (K, -K) valley states. The red line shows both the valley polarization and light polarization as a function of B . Inset is the experimental data depicting the spontaneous polarization¹³⁴. Reprinted from Ref.¹³⁴.

polarized light emission from single layer- WS_2 excited by linearly polarized light.¹³⁴

Exciting monolayer WS_2 using 2.54 eV linearly polarized light and excitation power density of $2.04 \times 10^2 \text{ W/cm}^2$, Scrase et.al.¹³⁴ observed a strong photoluminescence emission at 2.014 eV, below the neutral exciton (X^0) energy at 2.053 eV, associated with valence hole recombination with a 2D electron gas (2DEG) formed in the sample due to inhomogeneities. Thus this negatively charged exciton (trion), X^- , must be considered in the presence of extra electrons distributed over different valley and spin states.

The experimental data depicting the polarization of emission from X^0 and X^- as a function of magnetic field applied along the normal to the sample plane is given in the inset of Fig.5.5 along with its schematic illustration. In the experiment, they observe very weak polarization of X^0 that changes little with magnetic field (black data points) while the X^- feature exhibits a strong dependence on the magnetic field (red data points). Even at $B=0$, X^- feature emits circularly polarized light with polarization up to 19%. The polarization of light increases(decreases) with increasing(decreasing) magnetic field strength B , at a rate of 2% per Tesla. The coexistence of X^0 and X^- suggests that there are puddles of 2DEG with different densities.¹³⁴

The spontaneous polarization of emitted light can potentially be understood by valley spin locking and spontaneous valley polarization of the 2DEG in WS_2 (Fig.5.5). In the

presence of a 2DEG, electrons can occupy both valleys with densities n_K and $n_{K'}$. The total density $n = n_K + n_{K'}$ can be expressed in terms of the interparticle distance r_s as $n = 1/\pi(r_s)^2$, where the distance is expressed in terms of effective Bohr radius. Just as the polarization of light, we can define valley polarization of electrons as $\zeta = (n_K - n_{K'})/n$.

Neglecting formation of Landau levels, the total energy per particle is written as a sum of the kinetic E_k , exchange E_x , correlation E_c , and Zeeman energies E_z as²⁶⁶

$$E_{tot}(r_s, \zeta, B) = E_k(r_s, \zeta) + E_x(r_s, \zeta) + E_c(r_s, \zeta) + E_z(\zeta, B). \quad (5.3)$$

We assume that the direct interaction is cancelled by the interaction with the positive background. Moreover, since the spins are locked to opposite valleys, there is no exchange interaction between opposite valleys. Now let's start with the kinetic energy term. For parabolic dispersion in each valley, we can write the kinetic energy in terms of effective Rydberg's as $\varepsilon(\vec{k}) = k^2$ and calculate the total density in a single valley as

$$n_K = \frac{k_{max}^2}{4\pi}. \quad (5.4)$$

The maximal energy, at the Fermi level, in terms of the density becomes

$$\varepsilon_{max} = 4\pi n_K. \quad (5.5)$$

Then the total kinetic energy, which is the sum of energies from each valley $E_k(r_s, \zeta) = T_K + T_{K'}$, can be calculated as

$$\begin{aligned} E_k(r_s, \zeta) &= \int_0^{\varepsilon_{maxK}} \varepsilon g(\varepsilon) d\varepsilon + \int_0^{\varepsilon_{maxK'}} \varepsilon g(\varepsilon) d\varepsilon \\ &= 2\pi A(n_K^2 + n_{K'}^2), \end{aligned} \quad (5.6)$$

where $g(\varepsilon)$ is the density of states. Now we can express the total energy in terms of r_s and ζ using the expression for valley polarization and the total density. n_K and $n_{K'}$ can be expressed in terms of total density n and valley polarization ζ as

$$\begin{aligned} n_K &= n \frac{1 + \zeta}{2}, \\ n_{K'} &= n \frac{1 - \zeta}{2}, \end{aligned}$$

which can be used to write the total energy as

$$E_k(r_s, \zeta) = 2\pi A(n_K^2 + n_{K'}^2)$$

$$\begin{aligned}
&= 2\pi A \left(\frac{n}{2}\right)^2 [(1+\zeta)^2 + (1-\zeta)^2] \\
&= \pi A n^2 (1+\zeta^2) \\
&= \frac{1+\zeta^2}{r_s^2}.
\end{aligned} \tag{5.7}$$

Similarly the exchange term per particle is calculated as

$$E_x(r_s, \zeta) = -\frac{4\sqrt{2}}{3\pi} \frac{1}{r_s} [(1-\zeta)^{3/2} + (1+\zeta)^{3/2}]. \tag{5.8}$$

Within Hartree-Fock approximation, that is neglecting the correlation energy, and expressing the Zeeman energy per particle in terms of the valley polarization such as

$$E_z(\zeta, B) = -\frac{g^* \mu_\beta B}{2} \zeta, \tag{5.9}$$

where g^* is the effective band g-factor and μ_β is the Bohr magneton, we have an explicit expression for the total energy per particle in terms of r_s and ζ ;

$$E_{tot}(r_s, \zeta, B) = \frac{1+\zeta^2}{r_s^2} - \frac{4\sqrt{2}}{3\pi} \frac{1}{r_s} [(1-\zeta)^{3/2} + (1+\zeta)^{3/2}] - \frac{g^* \mu_\beta B}{2} \zeta. \tag{5.10}$$

Just looking at the above equation, we can right away deduce that valley polarization costs kinetic energy but gains exchange and Zeeman energy. We can calculate the total energy per particle in a valley polarized $\zeta = 1$ and unpolarized $\zeta = 0$ state as

$$E_{tot}(r_s, \zeta = 1, B) = \frac{2}{r_s^2} - \frac{16}{3\pi r_s} - \frac{g^* \mu_\beta B}{2}, \tag{5.11}$$

$$E_{tot}(r_s, \zeta = 0, B) = \frac{1}{r_s^2} - \frac{8\sqrt{2}}{3\pi r_s}, \tag{5.12}$$

respectively, and use the difference between these energies, ΔE_{tot} , to probe the character of the ground state. Defining

$$\begin{aligned}
\Delta E_{tot}(r_s, B) &= E_{tot}(r_s, \zeta = 1, B) - E_{tot}(r_s, \zeta = 0, B) \\
&= \frac{1}{r_s^2} - \frac{8(2-\sqrt{2})}{3\pi r_s} - \frac{g^* \mu_\beta B}{2},
\end{aligned} \tag{5.13}$$

we see that negative ΔE_{tot} indicates a valley polarized ground state while a valley-unpolarized ground state is expected for positive ΔE_{tot} .

When $B=0$ the valley polarized state is the ground state provided that $\frac{1}{r_s} < \frac{8(2-\sqrt{2})}{3\pi}$ or equivalently for $r_s \geq 2$ (when correlations are included, for valley polarized groundstate

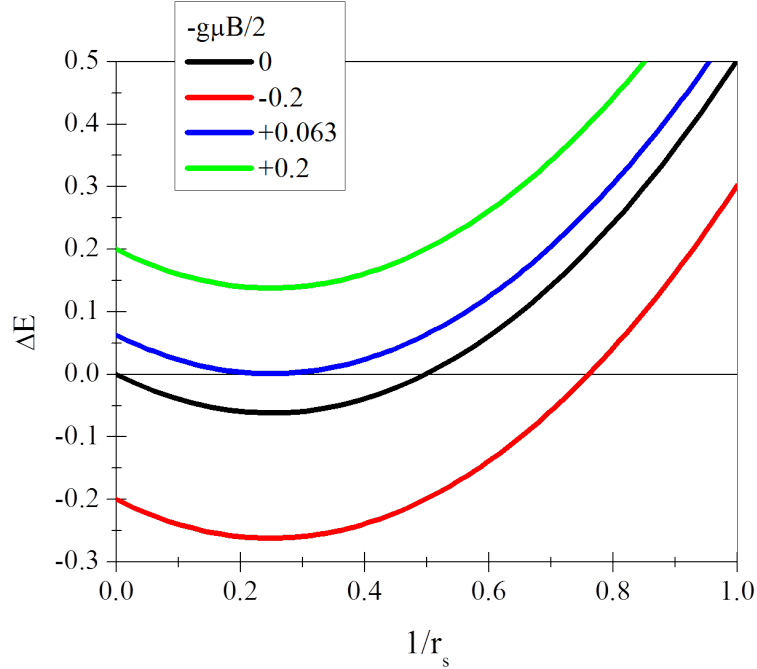


Figure 5.6: Energy difference per electron, ΔE (in effective Ry) between valley polarized and valley unpolarized states as a function of $\frac{1}{r_s}$ (in effective Bohr radius). Negative ΔE points to a valley polarized state is the groundstate.

$r_s > 25.5$ is needed^{266,267}). The dependence of ΔE on r_s is plotted as the black curve in Fig.5.6.

Increasing the magnetic field allows for a valley polarized ground state in a greater range of densities as shown with the red curve in Fig.5.6 while reversing the magnetic field reduces that range. At a critical value of magnetic field, $B=B^*$, satisfying $g^*\mu_\beta B^*/2 = -0.063\text{Ry}$ there is a single value of r_s for which a valley-polarized state is the ground state, as depicted by the blue curve. Beyond that, for lower values of B , the ground state is always valley unpolarized as shown by the green curve.

Thus the schematic description of light polarization vs magnetic field shown in Fig.5.5 also represents the valley polarization with magnetic field strength. At zero magnetic field, due to valley polarization, the population symmetry of the two valleys is spontaneously broken which translates into the polarization of the emitted light. Similar calculations accounting for the correlation energy²⁶⁶ and disorder²⁶⁷ were reported previously. Spin polarized droplets in quantum dots²⁶⁸ and spin polarized ground states in electronic puddles have also been studied previously.^{269,270}

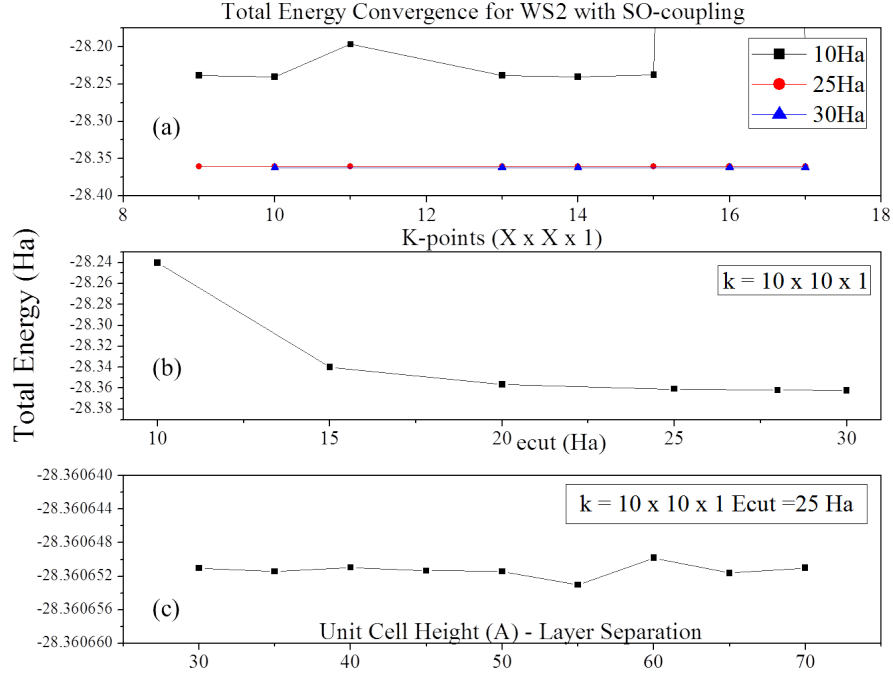


Figure 5.7: Total energy convergence tests for WS₂ with spin orbit coupling. Energy vs (a) k-points (b) energy cutoff (c) unit cell size (vacuum)

5.3 Computational Details

Density Functional Theory calculations were carried out by VASP and ABINIT. Both were used for calculations without spin orbit coupling (SOC) and only ABINIT was used for calculations including SOC. The local density approximation (LDA)-Hartwigsen-Goedecker-Hutter (HGH) potentials were used for calculations including SOC and convergence tests were done with respect to k-points, cutoff energy and vacuum size for single layer MS₂ (Fig. 5.7). For the bulk and bilayer-MS₂, because the inclusion of van der Waals forces is particularly important, unit cell length convergence tests were done with and without van der Waals interactions as depicted in Fig. 5.8. HGH potentials are relativistic LDA potentials that capture the spin-orbit coupling.^{271,272} SOC splits up orbitals with $l > 0$ into spin up and spin down orbitals lifting their degeneracy according to the total angular momentum $j = l \pm 1/2$. Within ABINIT, this is done through adding a spin-orbit term to the usual pseudopotential projectors. The total pseudopotential is divided into local, V_{loc} , and non-local $V_l(r, r')$ parts and SOC only affects the latter. By taking a weighted average of the $l \pm 1/2$ channels and combining with the local part, the relativistic scalar $V_l^{SR}(r, r')$ term, and taking the difference of the two channels, the SOC term $\Delta V_l^{SO}(r, r')$ of the potential is obtained.^{271–273} As a result, for the SOC calculations, the basis functions are two component plane waves and the size of the Hamiltonian quadruples.

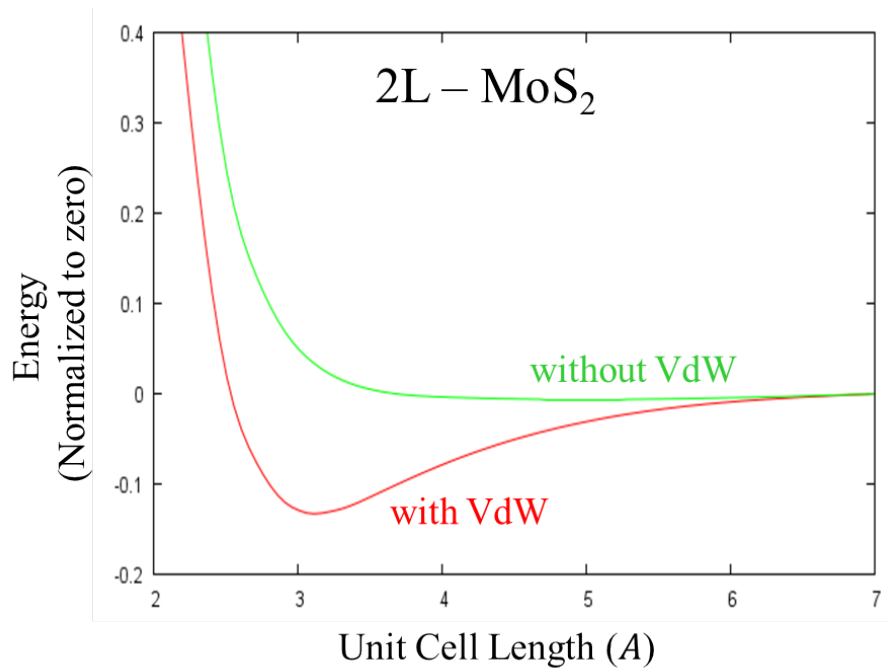


Figure 5.8: Convergence of the unit cell length with and without van der Waals interactions included for bilayer MoS₂. Spin-orbit coupling is not included

Chapter 6

Conclusion

In this thesis, I presented a selection of results obtained in my studies of two-dimensional materials. The detailed knowledge and understanding of these materials is important because of their potential in shaping future technology. It is essential to understand and characterize these materials to be able to take advantage of them.

In chapter 2, I started with the band structure of graphene, bilayer graphene and graphene quantum dots and outlined their well known electronic properties. Then, the theoretical tools that are utilized to describe the electron-electron interaction effects in these low-dimensional materials are introduced.

Starting small, in chapter 3 I concentrated on the quadruple quantum dot molecule (QQD) and the artificial benzene ring (ABR) using the extended Hubbard model. Both of these systems, due to their size, are exactly solvable. That means that without constricting the configuration space, we can know exactly how the electrons behave when they are forced to live together in these confined spaces (QQD and ABR). Already at this level, the emergence of gauge fields and phase transitions in the ground state of charged systems are predicted. For the case of the ABR the optical selection rules that arise due to the symmetry of a benzene ring are identified. In this chapter, the methodology that can be extended to larger quantum dots is developed.

Increasing the number of benzene rings, in chapter 4 I described graphene quantum dots. Although the number of atoms and the size of the system remains countable and measurable, starting with this chapter, mean field approximations had to be introduced as the configuration space becomes too large. In this chapter, we applied our methods to predict the optical properties of colloidal graphene quantum dots that are studied experimentally. Using HF I determined the phase diagram of CGQDs as a function of the strength of the Coulomb interactions. After the re-introduction of the selection rules due to 3-fold rotational symmetry I moved on to study their optical properties. The theory of excitons in colloidal graphene quantum dots is developed and the absorption

spectrum is calculated and compared with that of the experiments. This allowed us to extract the screening of Coulomb interactions by the environment, tunneling matrix elements, as well as to establish the significant role of self-energy and vertex excitonic corrections in the renormalization of the singlet and triplet excitonic spectrum. Going beyond excitons, creating biexcitons, the characteristic band-edge exciton and biexciton spectrum was determined. The absorption spectrum from the lowest exciton to both excited exciton states and biexcitons is computed successfully and compared with transient absorption experiments. Finally, a biexciton and two degenerate, bright exciton levels that could be used for generation of entangled photon pairs through a biexciton-exciton cascade are identified.

In chapter 5 I replaced the two non-equivalent carbon atoms in graphene with a transition metal element and a sulfur dimer. I specifically studied MoS_2 and WS_2 in chapter 5. These emerging materials provide what graphene can't as a bulk: a band gap and a strong spin orbit coupling that leads to additional degrees of freedom. This time using Density Functional Theory (DFT), the electronic properties of bulk to monolayer TMDCs are briefly outlined and the magnetoluminescence experiments on WS_2 are explained, in which the monolayer- WS_2 sample emits circularly polarized light upon being excited with unpolarized light. We explained this phenomenon by the possibility of a valley polarized 2D electron gas in WS_2 even at zero magnetic field.

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