Master’s Thesis

Few-Particle Effects in Semiconductor Quantum Dots: Spectrum Calculations on Neutral and Charged Exciton Complexes

Kuang-Yu Chang

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Flerpartikeleffekter i halvledarbaserade kvantprickar: beräkningar på neutrala och laddade excitoner
Few-Particle Effects in Semiconductor Quantum Dots: Spectrum Calculations on Neutral and Charged Exciton Complexes

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Sammanfattning
Abstract

It is very interesting to probe the rotational symmetry of semiconductor quantum dots for quantum information and quantum computation applications. We studied the effects of rotational symmetry in semiconductor quantum dots using configuration interaction calculation. Moreover, to compare with the experimental data, we studied the effects of hidden symmetry. The 2D single-band model and the 3D single-band model were used to generate the single-particle states. How the spectra affected by the breaking of hidden symmetry and rotational symmetry are discussed.

The breaking of hidden symmetry splits the degeneracy of electron-hole single-triplet and triplet-singlet states, which can be clearly seen from the spectra. The breaking of rotational symmetry redistributes the weight percentage, due to the splitting of $p_x$ and $p_y$ states, and gives a small brightness to the dark transition, giving rise to asymmetry peaks. The asymmetry peaks of 4X, 5X, and 6X were analyzed numerically. In addition, Auger-like satellites of biexciton recombination were found in the calculation. There is an asymmetry peak of the biexciton Auger-like satellite for the 2D single-band model while no such asymmetry peak occurs for the 3D single-band model. Few-particle effects are needed in order to determine the energy separation of the biexciton main peak and the Auger-like satellite.

From the experiments, it was confirmed that the lower emission energy peak of $X^2$ spectrum is split. The competed splitting of the $X^2$ spectra were revealed when temperature dependence was implemented. However, since the splitting is small, we suggest the $X^2$ peaks are broadened in comparison with other configurations according to single-band models. Furthermore, the calculated excitonic emission patterns were compared with experiments, The 2D single-band model fails to give the correct energy order of the peaks for the few-particle spectra; on the other hand the peaks order from 3D single-band model consistent with experimental data.

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Preface

Background

It has been a great triumph for the semiconductor industry during the last several decades. By making the microchip smaller and smaller, it finally gave rise to nanotechnology. Thanks to the developments of nanotechnology, it is now possible to fabricate nanostructured semiconductor with high quality, namely quantum wells (QWs), quantum wires (QWRs), and quantum dots (QDs). Electrons in these nanostructured devices are quantum confined. Many exciting quantum mechanical effects have been observed, such as quantum Hall effect [1]. From the application point of view, these low-dimensional semiconductor devices have been very interesting for their great potentials in various fields. To be specific, nanosized quantum dots may be used as single photon source, emitting photon one by one, for applications in quantum communication. Moreover, symmetric quantum dot may be used as the source for entangled photon pairs and correlated photons for quantum computation.

Besides quantum mechanical interests, III-V semiconductors have attracted many attentions. GaAs, AlAs, InP, and their ternary alloy, like Al$_x$Ga$_{1-x}$As, have been important in many applications. Different from silicon (VI group) based semiconductors, two general properties for most of III-V semiconductors are the high carrier mobility and the direct band gap. This reason makes III-V semiconductor a better choice for optical device when compared to Si semiconductor.

To combine the optical property of III-V semiconductors and quantum confinement effects of nanosized heterostructured semiconductors, the object of this thesis work is the spectra calculation of pyramidal AlGaAs/GaAs/InGaAs quantum dots, shown in Figure 1. These specific quantum dots are grown by metal organic chemical vapor deposition (MOCVD) technique with highly controlled geometry [2].

![Figure 1](image-url)  

**Figure 1:** Side view of heterostructured AlGaAs/GaAs/InGaAs pyramidal quantum dot. Self-formed quantum dot is located at the top of micrometer-sized pyramid. [3]
Motivations
Since the perfectly symmetric quantum dot is the ideal source for entangled photon pairs [4], it is very interesting to probe the symmetry of quantum dots, in the perspective of quantum computation and quantum optics applications. By controlling the excitation power of photoluminescence, the number of trapped charge carriers in quantum dots can be controlled [5]. Together with effective mass approximation of semiconductor materials (section 2.1.1) and configuration interaction (CI) (chapter 2.2.2), so called few-carrier system can be solved in reasonable time frame without further approximation [6, 7].

Many works have devoted to the spectra prediction with different number of charge carrier [5, 8, 9]. There are two symmetries are usually assumed. One is the symmetry between electron wave function and hole wave function, sometimes referred as hidden symmetry [10]. The other is the rotational symmetry of the quantum dot structure.

However, some features from the experimental data have not yet been explained. We attempt to solve those unexplained mysteries by the breaking of quantum dot symmetries. Therefore, the present thesis is focused on the asymmetry effects on the optical spectra, where the asymmetries are introduced to the confinement potential of quantum dots.

Methods
The calculation procedure can be summarized as follow:

1. Calculate single-particle states according to the selected quantum dot model. It was done by solving the single-particle Schrödinger equation using finite difference equation. (Appendix B).

2. Generate the CI Hamiltonian for few-particle systems (section 2.2.2). The matrix elements were calculated by Fourier convolution. Only Coulomb interactions were considered.

3. Diagonalize the CI Hamiltonians for each few-particle system. The diagonalization procedures were done by Matlab commend `eig`.

4. Generate the spectra according to Fermi golden rule.

All the codes were written in Matlab script. And the calculations were done on Green server of Linkoping University, which is a 74 nodes Linux cluster system. Detail flow diagrams are shown in Appendix D.

Thesis plan

chapter 1 introduces on the physical properties and some essential concepts of semiconductor and quantum dots. Including the energy band, crystal structure, and the concept of quantum dots.

chapter 2 establishes the theoretical background to describe the charge carriers in the quantum dots, which is the path to few-particle effects. Including the effective mass approximation, optical transition, configuration interaction, second quantization formalism, and the dipole operator for optical transition.

chapter 3 describes two models, 2D single-band model and 3D single-band model, that were used in this thesis work. Some results of single-particle calculation are shown.

chapter 4 discusses the calculated results. Includes the neutral exciton spectra and the charged exciton spectra. We focused on the asymmetry effects on the emission spectra.

chapter 5 presents some of the measured spectra of the few-particle configurations, which were obtained from the experiments.
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Chapter 1

Introduction to Semiconductors and Quantum Dots

This chapter introduces some general but essential concepts of semiconductors and quantum dots. We start with the description of the Bloch electrons, which follows by the introductions of energy band and the crystal structure. Then, we introduce the quantum dots and the notations for exciton complexes in quantum dots.

1.1 Electron in Solid

Knowledge of electrons is necessary to understand the properties of material. Not only electric and thermal properties are determined by the behavior of electrons, but also the structure of crystal and molecules, optical properties are depended on the electronic structure [11].

Free electron

To start with, consider the free electron, which is not being attracted by any potential. The Hamiltonian to describe such electron is $\hat{H}_{\text{Free}} = \frac{\mathbf{p}^2}{2m_e}$, where $\mathbf{p} = -i\hbar \nabla$ is the momentum operator. The eigenstates of this Hamiltonian are plane waves, $\psi_k(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}$. Instead of quantum number $(n, l, m)$ in atomic physics, wave vector $\mathbf{k}$ is a good quantum number to identify the energy of each state, namely the dispersion relation

$$E(k) = \frac{\hbar^2}{2m_e}|k|^2.$$ (1.1)

One obtains the empty lattice band structure from Equation (1.1) for any type of crystal structure [12].

---

\(^1\)Wave vector is related to wave length by $|k| = 2\pi/\lambda$
Chapter 1. Introduction to Semiconductors and Quantum Dots

Bloch function
In a solid, the full Hamiltonian can be written as follows:

\[
\hat{H} = \sum_i \frac{p_i^2}{2m_i} + \sum_j \frac{P_j^2}{2M_j} + \frac{1}{2} \sum_{i,i'} \frac{e^2}{4\pi\epsilon_0 |r_i - r_{i'}|} + \frac{1}{2} \sum_{j,j'} \frac{Z_j Z_{j'} e^2}{4\pi\epsilon_0 |R_j - R_{j'}|} - \sum_{i,j} \frac{Z_j e^2}{4\pi\epsilon_0 |R_j - r_i|},
\]

(1.2)

where summation index \(i\) runs through all the electrons while index \(j\) runs through all the nuclei. \(p_i\) and \(r_i\) are the momentum operator and position operator of \(i^{th}\) electron, while \(P_j\) and \(R_j\) are the operators for nuclei. \(Z_j\) is the atomic number of \(j^{th}\) nucleus [13].

However, it is possible to neglect the kinetic energy of the nuclei for the present purpose. The nucleus-nucleus interactions therefore become a constant under such approximation. Furthermore, those moving electrons tend to screen out the embedded positive nuclei by the factor \(e^{-k_s r}\), where \(k_s\) is the Thomas-Fermi screening length [14]. As a result, it is possible to neglect the electron-nucleus attraction terms and rewrite the electron-electron interaction terms as some periodically deformed constant, which is the effective potential of the crystal [15], \(V_{\text{cry}}(r)\).

That is, we have the periodicity

\[V_{\text{cry}}(r + T) = V_{\text{cry}}(r),\]

where \(T\) is the crystal translation vector. Combine all these approximations together, Equation (1.2) takes the form of the Schrödinger equation with a periodic potential, namely

\[\hat{H} \approx \hat{H}_{\text{per}} = \sum_i \frac{p_i^2}{2m_i} + V_{\text{cry}}(r),\]

which can be solved analytically,

\[\hat{H}_{\text{per}}(r) \psi(r) = \left( -\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{cry}}(r) \right) \psi(r) = E \psi(r).\]

(1.3)

The solution is, the Bloch function,

\[\psi(r) = u_k(r) e^{i k \cdot r}.\]

(1.4)

where \(u_k(r)\) has the same periodicity as \(V_{\text{per}}(r)\), i.e \(u_k(r + T) = u_k(r)\) [14]. Electron described by Equation (1.4) is a Bloch electron. It is the fundamental tool to describe electrons in solid. Similar to free electron case, energy for each state can be expressed by \(k\). Therefore, the energy near band edge\(^2\) can be approximated as

\[
\begin{cases}
E_c(k) = E_g + \frac{\hbar^2}{2m_e} |k|^2, \\
E_v(k) = -\frac{\hbar^2}{2m_h} |k|^2,
\end{cases}
\]

(1.5)

where \(m_e^*\) and \(m_h^*\) are the effective masses (see section 2.1.1) of Bloch electrons and holes, while \(E_c\) and \(E_v\) is the energy of conduction band and valence band respectively. For simplicity, Bloch electron is abbreviated as electron throughout this thesis, unless otherwise noted.

\(^2\) From the derivation of nearly free electron model [14], one gets \(E(k) = \Delta E + (1 \pm C) \frac{\hbar^2 k^2}{2m_e},\) where \(C\) is some constant from derivation and \(\Delta E\) is the splitting of energy at band edge.
1.2 Energy Bands

As shown in Figure 1.1, when two atoms come closer to each other, the energy level splits into bonding state, $|\text{Atom}_1\rangle + |\text{Atom}_2\rangle$, and antibonding state, $|\text{Atom}_1\rangle - |\text{Atom}_2\rangle$, e.g. $|s\rangle \rightarrow |s_1\rangle \pm |s_2\rangle$ or $|p\rangle \rightarrow |p_1\rangle \pm |p_2\rangle$, where $s$ and $p$ represent $s$-orbital and $p$-orbital respectively. For the case of GaAs, there are three valence electrons from Ga ($4s^2 4p^1$) and five valence electrons from As ($4s^2 4p^3$). It is sufficient to consider four valence electrons per atom ($4s^2 4p^2$), with slightly deformed crystal potential. The situation is similar in the case of Al$_x$Ga$_{1-x}$As. We may plot the energy levels of four valence electrons as functions of atomic distance (Figure 1.2(a)). Note that the filled orbitals of valence electrons are two bonding state, $|s_1\rangle + |s_2\rangle$ and $|p_1\rangle + |p_2\rangle$. This result can be extended to the case with more atoms, namely solid (Figure 1.2(b)). Single energy level splits into energy band\(^3\). The filled and the empty orbitals become the valence band and the conduction band [12].

Conduction Band

Excited states in the conduction band are the excited electrons. For the present purpose, we concern only the electrons near the lower band edge. As shown in Figure 1.2(b), the conduction band at the lower band edge is rooted from empty $|s_1\rangle - |s_2\rangle$ orbital. It is important to point out the $S$-like property at the lower band edge of conduction band. The spherical symmetry of $S$-like orbital makes the structure of conduction band much simpler than valence band.

Valence Band

Excited states in valence band are the vacancies of electrons. It can be considered as the quasi-particles, holes, which sometimes referred as hole picture. In the hole picture, holes in valence band are positively charged particles with opposite spins of their electron counter parts. Again, we concern only the holes near the upper edge of valence band. As shown in Figure 1.2(b), valence band at the upper band edge is rooted from the filled $|p_1\rangle - |p_2\rangle$ orbital in Figure 1.2(a). There are two things to be considered. The first is the non-isotropic nature of $p$ orbitals, e.g. $p_x$, $p_y$, and $p_z$, which give rise to heavy hole and light hole. The second is the spin-orbit coupling. Since the total angular momentum of $p$-states is nonzero, spin-orbit coupling, $H_{so} \propto \mathbf{S} \cdot \mathbf{L}$, is also nonzero. The spin-orbit term slightly deforms all the bands and gives rise to another split-off band. Figure 1.2(c) shows the schematic band structure of \(^3\)Only direct band gap are considered in this section because the object of present thesis is direct band gap material.

\[\text{Figure 1.1: Numerical illustrations of bonding state and antibonding state. Arbitrary units of distance and energy are used to illustrate the splitting of energy levels as two atoms come closer to each other. Atomic distance between two atom is decreasing from (a) to (c).}\]
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Figure 1.2: Schematic illustration of energy level vary with atomic distance, using tightly bound electron model. (a) Two atoms case, energy levels split as atomic distance decreases from infinite. Dash lines are empty orbitals and solid lines are filled orbitals. (b) Solid case, energy levels split into energy bands (gray region). Band gap and lattice constant are shown as $E_g$ and $a_0$ [12]. (c) Schematic illustration of the band structure near $\Gamma$ point. Electron band, heavy hole band, light hole band, and split-off band are shown. [13].

knowledge of crystal structure is necessary to understand the quantum dots. The crystal structure of GaAs is zinc-blende structure. It can be constructed by diamond structure with two different elements, as shown in Figure 1.3. Each group III element is surrounded by four group V element and vice versa. For the case of ternary alloy, like Al$_x$Ga$_{1-x}$As or In$_x$Ga$_{1-x}$As, Aluminum (indium) takes the place of Ga randomly according to the mole fraction $x$. One important consequence of the ternary alloy is that the band gap depends on the mole fraction. Figure 1.4 shows the relations between band gap and molar fraction for Al$_x$Ga$_{1-x}$As.
1.4 Quantum Dots and Excitons

Semiconductor Quantum Dots
Quantum Dots (QDs), sometimes referred as artificial atoms, is the object of this thesis work. It can be seen as semiconductor device with highly controlled artificial structure. Because the width of band gap is sensitive to the atomic composition of the crystal, it is possible to engineer on the width of band gap in 3-dimensional space.

In principle, the QDs are formed by the heterostructure of materials with different band gaps, which introduce a locally deformed term, $V^{QD}(r)$, to the effective crystal potential in Equation (1.3). The deformed effective potential not only confines the charge carriers, which become localized in QD, but also attracts the other near by free carriers and further traps them in the dot, as shown in Figure 1.5. Therefore, from quantum mechanical point of view, QDs can be seen as a potential trap for charge carriers in the crystal. It is important to mention that the QD confinement potential, in principle, is depending on the structure of QD. However, the structural dependence is not shown in the Figure 1.5 for the clear illustration of the carrier trapping mechanism.

Excitons in Quantum Dots
When one electron is excited across the band gap, one electron in conduction band and one hole in valence band are created. Since electron and hole have opposite charges, they attract each other via Coulomb force. Therefore the electron-hole pair, so called exciton, is formed. This excitation process can be seen as the creation of exciton with an annihilated photon. More importantly, the annihilation of exciton, or the recombination of electron in conduction band and hole in valence band, release the energy of exciton. The energy released by emitting a photon, abbreviated as optical transition, is of main interest in the present thesis. Other forms of the released energies will not be considered.

Excitons trapped in QDs become quantum confined. Moreover, few individual electrons and holes can also be trapped in the QDs, which resulted in various exciton complexes in QDs. Several typical few-particle exciton complexes are shown in the Figure 1.6. They are exci-
Chapter 1. Introduction to Semiconductors and Quantum Dots

Figure 1.5: Schematically illustrates the origin of quantum confinement and the charge carrier trapping or creation mechanism. The structure dependence is not shown in the figure.

ton ($X$), negatively charged exciton ($X^-$), double negatively charge exciton ($X^{2-}$), positively charge exciton ($X^+$), and biexciton ($2X$). Note that the spacial dependence of QD confinement potential is shown in Figure 1.6.

Figure 1.6: Schematically illustrate some few-particle exciton complexes. Spin configurations are illustrated by triangles. Only ground state and first excited state are considered. (a)One exciton state $|X\rangle$. (b)2e1h state $|X^-\rangle$. (c)3e1h state $|X^{2-}\rangle$. (d)1e2h state $|X^+\rangle$. (e)Two excitons state $|2X\rangle$ [3].

The optical properties of exciton in QDs can be determined by the emission intensity (see section 2.1.2). The excitons can be classified into two types, optically active (bright) excitons and optically inactive (dark) excitons. Note that only bright excitons can be created via photon absorption.
Chapter 2

Single- and Few-Particle States

This section establishes the basis of the thesis work. In order to take many particles into account, we need to consider the few-particle states, which are constructed from the single-particle states. We start with the single-particle states, namely the effective mass approximation for quantum dots and the optical transition. Then we introduce the extension of single-particle wave function to few-particle wave function, including the concept of configuration interaction, second quantization formalism, and the dipole operator for exciton radiative decay.

2.1 Single-Particle States

2.1.1 Effective Mass Approximation for Quantum Dots

Since the charged carriers in the QDs are confined, the wave function of charge carriers are multiplied by an localized envelope function. It is sufficient to treat those envelope functions as localized quasi particles.

Effective masses are defined to describe the response of charge carriers in solid under external electric field [14]. Because these charge carriers at the edge of band behave similar compared to free electron. Effective masses are defined as, by Equations (1.5) and (1.1),

\[ \frac{1}{m^*} = \frac{1}{\hbar^2} \nabla_k^2 E_k, \]

for both electron and hole.

Mathematically, QDs are described by the locally deformed effective potential, which can be written as

\[ V_{QD}^{QD}(r) = V_{cry}(r) + V_{QD}^{QD}(r), \]

where \( V_{QD}^{QD} \) is the confinement potential of QD. Therefore the periodic Hamiltonian in Equation (1.3) becomes

\[ \hat{H}\psi(r) = \left( \hat{H}_{per} + V_{QD}^{QD}(r) \right) \psi(r) = E\psi(r). \tag{2.1} \]

Using the definition of effective masses and the QD confinement potential, the excited electron and hole states in QDs can be described by effective Schrödinger equation,

for electron:

\[ \left( -\frac{\hbar^2}{2m_e^*} \nabla^2 + V_{e}^{QD}(r) \right) \chi_e(r) = (E - E_g) \chi_e(r), \tag{2.2a} \]

for hole:

\[ \left( -\frac{\hbar^2}{2m_h^*} \nabla^2 + V_{h}^{QD}(r) \right) \chi_h(r) = E\chi_h(r), \tag{2.2b} \]

where \( \chi_e (\chi_h) \) and \( V_{e}^{QD} (V_{h}^{QD}) \) are the envelope function and confinement potential of the excited electron (hole) in QDs, (see Appendix A.1). Note that for the wave function in QDs, quantum numbers \((n, l, m)\) become good quantum numbers again, back to the notation of
atomic physics. It is because the excited states in QDs are confined in 3 dimensions, analogy to electrons confined around the core of an atom. It is important to point out that only one band in considered using Equation (2.2), because single-band structure is assumed in the derivation in Appendix A.1.

2.1.2 Optical Transitions

In the electron picture, the de-excitation of a excited electron in the conduction band release the energy $\hbar \omega$. The theory of this state transition from initial state $|i\rangle$ to final state $|f\rangle$ is well developed and wildly used in various field of physics (see Appendix A.2).

In principle, we consider the interaction between the oscillating electromagnetic fields and the quantum state, where the electromagnetic field can be treated as a perturbation $\hat{H}'(t)$. This interaction is described by time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |i(t)\rangle = \hat{H}(t)|i(t)\rangle.$$  

The Hamiltonian is the sum of unperturbed system, $\hat{H}_0$, and the perturbation term, $\hat{H}'(t)$, namely, $\hat{H}(t) = \hat{H}_0 + \hat{H}'(t)$. This Hamiltonian allows us to calculate the probability, $I_{fi}$, of the transition from $|i\rangle$ to $|f\rangle$ by

$$I_{fi} = |\langle f| \hat{H}'(t)|i\rangle|^2,$$  \hspace{1cm} (2.3)

where the time dependence of states are omitted. This probability can be interpreted as the emission or absorption intensity.

2.2 Few-Particle States

2.2.1 Notations for Few-Particle System

To begin with, we introduce some notations for the following discussions. The lowercase Greek alphabets are used to describe single-particle states, $|\psi\rangle$ or $|\phi\rangle$, while the capital Greek alphabets are used to describe the few-particle wave functions, $|\Psi\rangle_N = \Psi(r_1, r_2, \ldots, r_N)$ or $|\Phi\rangle_N = \Phi(r_1, r_2, \ldots, r_N)$, where the subscript $N$ denote the number of particles of the system. Similar to Hilbert space for single-particle wave functions, few-particle wave function belongs to Fock space $F$. Further more, $\Phi$ is the Slater determinant generated by single-particle states, namely

$$\Phi(r_1, r_2, \ldots, r_N) = \begin{vmatrix} \phi_1(r_1) & \phi_1(r_2) & \cdots & \phi_1(r_N) \\ \phi_2(r_1) & \phi_2(r_2) & \cdots & \phi_2(r_N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(r_1) & \phi_N(r_2) & \cdots & \phi_N(r_N) \end{vmatrix}.$$  \hspace{1cm} (2.4)

We call $|\Phi\rangle_N$ as noninteracting state because it is constructed directly from $N$ single-particle states, as in Equation (2.4), neglecting all particle interactions. In addition, we use $|\Psi\rangle_N$ to denote the eigenstate of few-particle Hamiltonian (Equation (2.9)), which is also referred to as the interacting state.

---

1. It is annihilation of exciton using hole picture

2. Fock space $F$ is the function space for many particles wave functions. Mathematically, it can be defined by tensor product of single-particle Hilbert spaces $H$, $F_n(H) = \bigoplus_{n=0}^{\infty} S_n H^\otimes n$, where $S_n$ represents the symmetry or antisymmetry of each Hilbert space. It was first defined by V. A. Fock in his German paper, Konfigurationsraum und zweite Quantelung [17].
2.2 Few-Particle States

2.2.2 Configuration Interaction

Configuration interaction (CI) is one of the oldest approach to many body problem in quantum chemistry. It is rather straight forward and perfectly suitable for few-particle cases. Since the noninteracting few-particle wave functions, $\Phi_i(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N)$, form a complete basis of Fock space, the interacting few-particle wave function, $\Psi_{CI}(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N)$, can be expanded in terms of this basis,

$$|\Psi_{CI}\rangle = a_1|\Phi_1\rangle + a_2|\Phi_2\rangle + \cdots = \sum_{i=1} a_i|\Phi_i\rangle,$$

where $|\Phi_i\rangle$ is the $i^{th}$ lowest energy state. By minimizing the energy of CI state, $\langle \Psi_{CI} | \hat{H} | \Psi_{CI} \rangle$, under the constraint that CI state is normalized, $\langle \Psi_{CI} | \Psi_{CI} \rangle = N$, the coefficients $a_i$ of Equation (2.5) can be determined. It can be done by the technique of Lagrange multiplier (see Appendix A.3).

A very useful conclusion from Lagrange minimization procedure of CI is that we have the equation in the form of Schrödinger equation, that is

$$\hat{H}_N|\Psi_{CI}\rangle = E|\Psi_{CI}\rangle. \quad (2.6)$$

Note that $E$ is the Lagrange multiplier, which is also the energy of $|\Psi_{CI}\rangle$.

2.2.3 Second Quantization Formalism

Instead of using spacial variables of $N$ particles for Slater determinant wave function, namely $\Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N)$, it can be represented in a more compact form with second quantization formalism using occupation number,

$$|\Phi\rangle_N = |n_1, n_2, \cdots, n_N\rangle,$$

where $n_i = \{0, 1\}$ is the number of particles in the $i^{th}$ single-particle state $|\phi_i\rangle$. The subscripts $N$ in Equation (2.7) denote the $N$-particle wave function. Further more, antisymmetric nature of electrons (holes) is taken cared of by the creation and the annihilation operators, $\hat{c}_i$ and $\hat{c}_i^\dagger$ ($\hat{h}_i^\dagger$ and $\hat{h}_i$). The notation for vacuum state is $|0\rangle = |0, 0, \cdots, 0\rangle$ (see appendix A.4). From now on, subscript $N$ for N-particle space will be omitted, for simplicity, through out the rest of this thesis.

Figure 1.6 shows some configurations in the QD confinement potential. Second quantization notation can be used to express the configuration in QDs. For example, states in Figure 1.6 can be written as

$$|X\rangle = \frac{1}{\sqrt{2}} | 1, 0, 0, 0 \rangle_e \otimes | 0, 1, 0, 0 \rangle_h = \hat{c}_1^\dagger \hat{h}_1^\dagger (|0\rangle_e \otimes |0\rangle_h),$$

$$|X^-\rangle = | 1, 1, 0, 0 \rangle_e \otimes | 0, 1, 0, 0 \rangle_h = \hat{c}_1^\dagger \hat{c}_1^\dagger \hat{h}_1^\dagger (|0\rangle_e \otimes |0\rangle_h),$$

$$|X^2^-\rangle = | 1, 1, 1, 0 \rangle_e \otimes | 1, 0, 0, 0 \rangle_h = \hat{c}_1^\dagger \hat{c}_1^\dagger \hat{c}_1^\dagger \hat{h}_1^\dagger (|0\rangle_e \otimes |0\rangle_h),$$

$$|X^+\rangle = | 0, 1, 0, 0 \rangle_e \otimes | 1, 1, 0, 0 \rangle_h = \hat{c}_1^\dagger \hat{h}_1 \hat{h}_1^\dagger (|0\rangle_e \otimes |0\rangle_h),$$

$$|2X\rangle = | 1, 1, 0, 0 \rangle_e \otimes | 1, 1, 0, 0 \rangle_h = \hat{c}_1^\dagger \hat{c}_1^\dagger \hat{h}_1^\dagger (|0\rangle_e \otimes |0\rangle_h),$$

where the arrows represent the spin and the subscripts $e$ and $h$ denote the Fock space for electrons and holes respectively.

One useful result from second quantization formalism is that one- and two-particle operators can be elegantly calculated. As shown in appendix A.4, one- and two-particle Hamiltonians for
electrons can be written as
\[ \hat{H}_{1\text{-particle}} = \sum_{i,j} H_{ij} \hat{e}_i^\dagger \hat{e}_j, \] (2.8a)
\[ \hat{H}_{2\text{-particle}} = \sum_{i,j,k,l} H_{ijkl} \hat{e}_i^\dagger \hat{e}_j^\dagger \hat{e}_k \hat{e}_l. \] (2.8b)

where \( H_{ij} = \langle \phi_i | \hat{H} | \phi_j \rangle \), \( H_{ijkl} = \langle \phi_i \phi_j | \hat{H} | \phi_k \phi_l \rangle \), and \( \hat{e}_i^\dagger |0\rangle = |\phi_i\rangle \). Note that the spin vector is implicitly included using this notation. This result can be used to express few-particle Hamiltonian in next section.

### 2.2.4 Few-Particle Hamiltonian

By introducing Coulomb term, \( H_C \) to Equations (2.2), one may obtain the Hamiltonian of few-particle system [18]
\[ \hat{H}_N = \sum_{i=1}^{N} \hat{H}_0(r_i) + \frac{1}{2} \sum_{i \neq j} \hat{H}_C(r_i, r_j), \]

where
\[ \hat{H}_0(r) = -\frac{\hbar^2}{2m^*} \nabla^2 + V_{QD}(r), \]
\[ \hat{H}_C(r_i, r_j) = \left( \frac{1}{4\pi \epsilon_0 \epsilon} \right) \frac{q_i q_j}{|r_i - r_j|}, \]
and \( q_i \) is the charge of \( i_{th} \) particle. Note that \( \epsilon \) is the dielectric function of material, \( (\epsilon = 13.6 \text{ for GaAs}) \). One thing to point out is that \( \hat{H}_C \) is a two-particle operator. Using the hole picture with the second quantization formalism, the Hamiltonian becomes [8]
\[ \hat{H}_N = \sum_i E_i^e \hat{e}_i^\dagger \hat{e}_i + \sum_i E_i^h \hat{h}_i^\dagger \hat{h}_i - \sum_{ijkl} V_{ijkl}^e \hat{e}_i^\dagger \hat{e}_j^\dagger \hat{h}_k \hat{h}_l + \frac{1}{2} \sum_{ijkl} V_{ijkl}^{ee} \hat{e}_i^\dagger \hat{e}_j^\dagger \hat{e}_k \hat{e}_l + \frac{1}{2} \sum_{ijkl} V_{ijkl}^{hh} \hat{h}_i^\dagger \hat{h}_j^\dagger \hat{h}_k \hat{h}_l. \] (2.9)

The first two terms are the single-particle energies of each electron and hole. The third term is the electron-hole Coulomb attraction energies, which runs through each electron-hole pairs. The last two terms are the electron-electron and hole-hole Coulomb repulsion energies. The Coulomb matrix elements in Equation (2.9) are
\[ V_{ijkl}^{eh} = \langle \phi_i^e \phi_k^h | \hat{V}_C | \phi_j^h \phi_l^e \rangle = \left( \frac{1}{4\pi \epsilon_0 \epsilon} \right) \int \int \frac{\phi_i^{e*}(r) \phi_k^{h*}(r') \phi_j^h(r') \phi_l^e(r)}{|r - r'|} d^3r d^3r', \]
\[ V_{ijkl}^{ee} = \langle \phi_i^e \phi_j^e | \hat{V}_C | \phi_k^e \phi_l^e \rangle = \left( \frac{1}{4\pi \epsilon_0 \epsilon} \right) \int \int \frac{\phi_i^{e*}(r) \phi_j^{e*}(r') \phi_k^e(r') \phi_l^e(r)}{|r - r'|} d^3r d^3r', \]
\[ V_{ijkl}^{hh} = \langle \phi_i^h \phi_k^h | \hat{V}_C | \phi_j^h \phi_l^h \rangle = \left( \frac{1}{4\pi \epsilon_0 \epsilon} \right) \int \int \frac{\phi_i^{h*}(r) \phi_k^{h*}(r') \phi_j^h(r') \phi_l^h(r)}{|r - r'|} d^3r d^3r', \] (2.10)

where \( V_C = \left( \frac{1}{4\pi \epsilon_0} \right) \frac{1}{|r - r'|} \) due to the Coulomb interaction, and \( \phi_i \) is the \( i^{th} \) single-particle state. These matrix elements in Equations (2.10) can be calculated by Fourier convolution [19], as shown in Appendix C.1. It can be integrated analytically for the 2D harmonic oscillator QD model. Comparisons between analytical and numerical results are included in appendix C.
2.2 Few-Particle States

2.2.5 Dipole Operator

In general, the intensity of the exciton radiative decay, Equation (2.3), can be solved by integrating a differential equation and the solution is depending on the polarization of the light. However, the case become much simpler under single-band assumption. We can approximate the intensity of radiative exciton decay from \( j^{th} \) single-particle states by

\[
I_j \approx C \left| \int \chi_{e,j}^*(r) \chi_{h,j}(r) dr \right|^2,
\]

where \( C \) is some constant, \( \chi_{e,j}(r) \) and \( \chi_{h,j}(r) \) are the envelope function of recombining electron and hole in \( j^{th} \) single-particle state. Detailed derivation can be found in Appendix A.2. Whether the transition is bright or dark is determined by this transition intensity and the spin arrangement of the exciton.

Using the second quantization formalism, it is convenient to describe the intensity of few-particle radiative decay by dipole operator. Dipole operator can be defined as

\[
\hat{P} = \sum_{j,\sigma} S_j \hat{e}_{j,\sigma} \hat{h}_{j,-\sigma},
\]

which operates on any few-particle state. The summation index \( j \) runs through all the single-particle states while the index \( \sigma \) denote the spin. Note that only opposite spin of electron and hole can recombine. The factor \( S_j \) is defined as the \( j^{th} \) envelope functions integration

\[
S_j = \int \chi_{e,j}^*(r) \chi_{h,j}(r) dr.
\]

For the noninteracting state \( \ket{\Phi} \), \( \langle \Psi | \hat{P} | \Phi \rangle \) adds up the transition amplitudes of all the allowed radiative exciton decays of each electron-hole pair. Therefore, we can write the intensity of the transition form a initial CI state, \( \ket{\Psi_i} = \sum c_{j,i} \ket{\Phi_{j,i}} \), to a final CI state \( \ket{\Psi_f} = \sum c_{j,f} \ket{\Phi_{j,f}} \) as

\[
I_{fi} = \left| \langle \Psi_f | \hat{P} | \Psi_i \rangle \right|^2
\]

\[
\propto \sum_{j,j'} c_{j',f} c_{j,i} \left| \langle \Phi_{f,j'} | \hat{P} | \Phi_{j,i} \rangle \right|^2,
\]

which accumulates the contributions from all the noninteracting states.
Chapter 3

QD Models and Symmetries

This chapter describes the calculation models and the symmetries that is usually assumed for the QDs. There are two models used in the present thesis work, 2D model and 3D model. We start with the introduction of 2D single-band model and 3D single-band model. Then, we discuss the two types of symmetries that we focused on in this thesis work. Most of the efforts were made on 2D single-band model. However, in order to achieve better agreement with experimental results, 3D single-band model was used.

Figure 3.1: Potential profile of 2D single-band model. (a) confinement potential $V_{QD}^e(x,y)$ of electron. (b) confinement potential $V_{QD}^h(x,y)$ of hole. Resolution for both confinement potentials are 1.5 nm.

3.1 2D Single-Band Model

2D single-band model, abbreviated as 2D model, is a rather general model. It can be applied to various QDs system and has been wildly used [8, 9, 20, 21, 22]. For the present purpose, only $s$-shell and $p$-shell are taken into 2D model calculations. The computational resources required by 2D model were relatively small and 2D model is easy to be applied. These reasons make 2D model an ideal tool to gain some insight of the few-particle system in QDs.

The 2D model is based on the fact that the confinement potential of QDs is finite, which
means that the harmonic approximation can be applied. Moreover, confinement in z-direction is stronger than in x- or y-directions, as shown in section 3.2 (QD size in z-direction is 6 nm while in x- and y-directions are 24 nm). Therefore, the confinement potential of holes and electrons can be approximated by 2D harmonic oscillators. However, the energy splitting, $\hbar \omega$, of the oscillator\(^1\), needs to be fitted either by experimental data or by the symmetry requirements.

![Figure 3.2: Single-particle states of electron and hole of 2D-QD Calculation. The notations of basis for each orbital are included. Only spin up states are shown.](image)

**Potential Profile**

The confinement potentials for electrons and holes are determined from the experimental data of energy levels. Essentially, the approximated 2D harmonic oscillator can be written as $V(x, y) = \frac{m\omega^2}{2}(x^2 + y^2)$, where $\hbar \omega$ is the separation of energy levels and $m$ is the effective masses of confined particles. For the present purpose, we have

\[
\begin{align*}
\hbar \omega_e &= 35 \text{ meV}, \\
\hbar \omega_h &= 10 \text{ meV}, \\
m_e^* &= 0.067 m_e, \\
m_h^* &= 0.103 m_e.
\end{align*}
\]

Therefore by fitting the experimental data, the confinement potentials become

\[
\begin{align*}
V^{QD}_e(x, y) &= 5.387 \times 10^{-4}(x^2 + y^2) \text{ eV}, \\
V^{QD}_h(x, y) &= 6.757 \times 10^{-5}(x^2 + y^2) \text{ eV},
\end{align*}
\]

\(^1\)Sometimes effective length, $l_{eff} = \sqrt{\hbar/m\omega}$, of the oscillator is used, which is a quantity to describe the lateral confinement.
where $x$ and $y$ are given in the units of nanometers. Note that these potentials describe the spatial deformations at the top of valence band and the bottom of conduction band. These potentials are visualized in Figure 3.1. It is clearly shown that the confinement potential for electrons is stronger than the one for holes.

**Single-Particle States**

First three single-particle states, $|s\rangle$, $|p_x\rangle$, and $|p_y\rangle$, are taken into CI calculation. The numerical results of these three states are shown in Figure 3.2. Because the confinement potential for electron is stronger, electron is strongly confined while hole is weakly confined. The energy of these states from the numerical calculation are

$$\begin{align*}
E_e^s &= 34.86 \text{ meV}, & E_h^s &= 9.98 \text{ meV}, \\
E_{px}^e &= 96.56 \text{ meV}, & E_{px}^h &= 19.94 \text{ meV}, \\
E_{py}^e &= 96.56 \text{ meV}, & E_{py}^h &= 19.94 \text{ meV}.
\end{align*}$$

(3.2)

It is important to note that the diameter of hole wave functions is about 30 nm, which is too large. The large holes are the consequences of small separation energy value. However, it is still worth to use it as the first approximation.

**Allowed Exciton Recombinations**

It is worth to point out that the wave function integration of the single-particle state, $\langle \chi_e | \chi_h \rangle$, is none zero only if the electron and the hole are in the same orbital. This means that the only possible radiative decays are

$$\langle s_e | s_h \rangle, \quad \langle p_x^e | p_x^h \rangle, \quad \langle p_y^e | p_y^h \rangle.$$

### 3.2 3D Single-Band Model

In order to achieve better agreement with available experimental results, a 3D single-band model (3D model for short) is implemented. For this reason, we focus on the spectra of those few-particle configurations, which are more comparable with experiments. One thing to be noted is that 3D model is specifically fitted with the pyramidal QDs system, which makes 3D model not as general as 2D model. Moreover, it is necessary to take the structure of pyramidal QDs into considerations in order to set up a reasonable 3D model. On the other hand, when carry a 3D model calculation, fit to the experimental data is not needed. The energy separation is uniquely determined by QD structure.

**Structure of Pyramidal QD System**

In general, self-limited QD located at the top of pyramid due to the thickness variation. In addition to the QD, there are two vertical quantum wires (VQWRs) connected to the top and the bottom of the QD. The formation of these quantum structure is attributed to the epitaxial growth during the fabrication procedure.

Detailed pyramid structure information has been obtained from the work done by Zhu et al [23]. For the pyramid used in the present thesis work, the concentration of indium decreased from 20\% at the center to 10\% at the edge in the QD region (shown in Figure 3.3, region I). We model the size of the QD region as 24 nm wide and 6 nm height; the band gap increases quadratically with the concentration as we go farther from the center. At VQWRs regions (region II), the concentration of aluminum is constant 5\%. We model this region as constant potential cylinder with radious 16 nm. At background region (region III) we use the constant band gap 1.923 eV for Al$_x$Ga$_{1-x}$As.
Hole Structure

It is important to note that the pyramidal QDs is grown on the [111] direction (see section 1.3) of GaAs crystal, which is aligned with $z$-direction. Therefore the heavy hole effective mass is heavier in $z$-direction than in $x$- and $y$-directions. It can be derived from $k \cdot p$ theory that

$$m_{hh,z}^* = \frac{1}{\gamma_1 - 2\gamma_3}, \quad \text{and} \quad m_{hh,\perp}^* = \frac{1}{\gamma_1 + \gamma_2},$$

where $\gamma_1 = 6.85$, $\gamma_2 = 2.1$, and $\gamma_3 = 2.9$ [24], are the so called Luttinger parameters, for GaAs. $m_{hh,\perp}$ is the effective mass in any direction in $xy$ plane. Put the values into the formula of effective mass, we have

$$m_e^* = 0.067 \, m_e,$$
$$m_{hh,z}^* = 1.282 \, m_e,$$
$$m_{hh,\perp}^* = 0.106 \, m_e.$$

Note that heavy hole in $z$-direction is more than 10 times heavier than in $x$- and $y$-directions.

Potential Profile

![Diagram of QD structure and 3D model](image)

**Figure 3.3:** Schematic illustration of the QD structure and the 3D model. Three regions are shown by the arrows.

3D model is based on the idealized spatial structure of the QD. As in section 3.2, the cladding VQWRs and Al$_x$Ga$_{1-x}$As background are needed to be considered. To simplify the problem,
we assume that the confinement potentials are constant except for QD region. Moreover, we neglect the concentration variation in \( z \)-direction, meaning that QD confinement potentials can be written in the following form
\[
V(x, y, z) = \frac{1}{2} m \omega^2 (x^2 + y^2) + C,
\]
for some constant \( C = V(0,0,z) \). Together with the experimental data, we set our 3D confinement potential as
\[
V_e(r,z) = \begin{cases} 
0 & r > 30, \ r < 12, \ |z| \leq 3, \ \text{QD} \\
115, & r < 8, \ |z| > 3, \ \text{VQWRs} \\
331, & \text{else where.} \ \text{background}
\end{cases}
\]
for electrons and
\[
V_h(r,z) = \begin{cases} 
0 & r > 50, \ r < 12, \ |z| \leq 3, \ \text{QD} \\
125, & r < 8, \ |z| > 3, \ \text{VQWRs} \\
247, & \text{else where.} \ \text{background}
\end{cases}
\]
for holes, where \( r = \sqrt{x^2 + y^2} \). The energy and length units in Equation (3.3) and (3.4) are given in meV and nm respectively. Note that the band gap energy, \( E_g = 1.345 \) eV, is subtracted from these potentials in order to have zero energy for both electrons and holes when \((x, y, z) = (0, 0, 0)\). These confinement potentials can be visualized in Figure 3.4(b).

**Single-Particle States**

One thing that is needed to be considered is the atomic \( p \)-orbital nature of holes, which leads to heavier hole effective mass in \([1 1 1]\) crystal direction. This non isotropic effective mass gives rise to \( p_z \)-orbital of the envelope function as the first excited hole state, Figure 3.6, while the corresponding first excited electron states remain in \( x \)- and \( y \)-directions, Figure 3.5.

![Figure 3.5: Numerical results of electron orbitals isosurface (a) s electron, (b) \( p_x \) electron and (c) \( p_y \) electron are degenerated first excited states.](image)

The calculated energies of these states for the symmetric QD are
\[
\begin{align*}
E_s^e &= 72.588 \ \text{meV,} \\
E_{p_x}^e &= 109.510 \ \text{meV}, \ \text{and} \\
E_{p_y}^e &= 109.510 \ \text{meV}.
\end{align*}
\]
3.3 Symmetries of Quantum Dots

Allowed Exciton Recombinations
One thing that makes 3D model significantly different from 2D model is that none of the electron wave functions overlap with the hole in $p_z$ orbital, meaning that $\langle \chi_e | \chi_{h,p_z} \rangle = 0$ for $s, p_x,$ and $p_y$ orbitals. Therefore the only allowed optical transitions involve the recombination of a hole in the $s$-shell.

3.3 Symmetries of Quantum Dots

Since the asymmetry effects are the objects of the present thesis work, it is necessary to introduce the symmetries that we focused on. Among the works that devoted to the spectra calculations, two symmetries are usually assumed.

Hidden Symmetry
The first is the symmetry between electron and hole, which resulted in identical single-particle states. We call this symmetry as hidden symmetry, which is also used by other authors [10]. The consequence of hidden symmetry is the symmetric Coulomb matrix elements, namely $V_{ijkl}^{hh} = V_{klji}^{ee}$ and $V_{ijkl}^{eh} = V_{ljki}^{ee}$, meaning that hole-hole and electron-hole interactions are related to electron-electron interaction. This relation simplify the emission spectra significantly because of the cancellations between these interactions.

Rotational Symmetry
The second symmetry is the symmetry in different directions, namely, the rotational symmetry. Under this symmetry we have the degenerate excited states and the angular momentum is conserved. We expect to get more peaks when the rotational symmetry breaks down, due to the splitting of those degenerated excited states.

Level of Symmetry
We expect both of these symmetries (hidden symmetry and rotational symmetry) to be slightly broken for real QDs. To compare with the experimental results, we remove these symmetries one by one. Firstly, we remove the hidden symmetry, in order to fit the energy levels measured from the experiments. Then, we break the rotational symmetry, in order to achieve better agreement with experiment. Note that for 3D model, we discuss only rotational symmetry.
because there is no hidden symmetry if we take \( z \)-direction into account.
Chapter 4

Results and Discussions

We discuss all the results from the calculation in this chapter. The results can be separated into two parts. The first part is the asymmetry effects on neutral exciton complexes, namely $4X$, $5X$, and $6X$. Moreover, Auger-like satellite of $2X$ spectra is discussed. The second part is the charged exciton complexes, $X^+$, $X^-$, $X^{2-}$, $X^{3-}$, $X^{4-}$, and $X^{5-}$, which are compared with experimental data.

Unless otherwise noted, all the emission spectra are generated by the transition from excitonic ground state $(n_e, m_h) \rightarrow ((n - 1)e, (m - 1)h)$, where $n$ and $m$ denote the number of electrons and holes respectively. Note that ground state spectra means that the temperature is absolute zero.

4.1 Notations and Concepts

Before we start, it is worth to introduce some of the notations and concepts that are used for this section.

Hamiltonian

In general, if we use the noninteracting states (see section 2.2.1) to express the few-particle Hamiltonian, it can be divided into two parts. The diagonal part and the nondiagonal part, namely

$$\hat{H} = \hat{H}^d + \hat{H}^n.$$

Note that each of the noninteracting state, $|\Phi\rangle$, is an eigenstate of the diagonal part of the Hamiltonian. We further introduce the eigenvalues of the diagonal Hamiltonian as

$$\hat{H}^d |\Phi\rangle = H^d_{\Phi} |\Phi\rangle,$$

where $|\Phi\rangle$ can be any noninteracting state and $H^d_{\Phi}$ is the related eigenvalue. Note that $H^d_{\Phi}$, which is the summation of all possible energy terms, can be interpreted as the energy of noninteracting state $|\Phi\rangle$. For example, $H^d_X = E^e_s + E^h_s - V_{ss,d}^{eh}$ for noninteracting exciton ground state $|X\rangle$.

Furthermore, we call the truncated Hamiltonian that we used in the 2D and 3D model as full Hamiltonian$^1$ in order to introduce the simplified Hamiltonian, which is used to gain some intuitive understanding of the few-particle system.

$^1$Strictly speaking, full Hamiltonian has to be infinite dimensional under CI calculation
Scattering between States

The Coulomb terms in Equation (2.9) allow the particles to be scattered from one state to another state, e.g. \( \hat{V}_{ijkl}^{eh} = V_{ijkl}^{eh} \hat{e}_i^\uparrow \hat{h}_j^\uparrow \hat{h}_k^\downarrow \hat{e}_l^\downarrow \) moves \( i^{th} \) electron and \( k^{th} \) hole to \( i^{th} \) position and \( j^{th} \) position respectively. This scattering conserves the total spin of electrons and holes separately because the Coulomb matrix elements are zeros for opposite spin in Equation (2.10). For example,

\[
\hat{V}_{6512}^{eh} |s_e^\uparrow, p_x^\uparrow e \rangle \otimes |s_h^\downarrow, p_y^\downarrow h \rangle = |0, 0, 1, 0, 1, 0 \rangle_e \otimes |0, 0, 0, 1, 0, 1 \rangle_h
\]

which can be seen as \( \hat{V}_{6512}^{eh} \) scatters exciton from \( s \)-orbital into \( p_y \)-orbital. Note that all the scattering terms of the Hamiltonian are belonging to the nondiagonal part of the few-particle Hamiltonian.

Coulomb Matrix Elements

Because the Coulomb matrix elements in Equation (2.9) are identical for spin up and spin down, we use the simplified notation for \( V_{ijkl}^{eh} \)

- **Direct interaction:**
  - \( V_{bb,dd}^{hh} = V_{4334}^{hh} = V_{bbbd}^{hh} \)
  - \( V_{ab,dd}^{hh} = V_{1441}^{hh} = V_{abbd}^{hh} \)
- **Exchange interaction:**
  - \( V_{ac,x}^{ee} = V_{1515}^{ee} = V_{acac}^{ee} \)
  - \( V_{bc,x}^{ee} = V_{2321}^{ee} = V_{bcbc}^{ee} \)
- **Scattering:**
  - \( V_{aa,s}^{eh} = V_{2121}^{eh} = V_{aaaa}^{eh} \)

The subscripts \( a, b, \) and \( c \) denote the \( s \)-orbital, \( p_x \)-orbital, and \( p_y \)-orbital for 2D model, while \( b \) denotes the \( p_z \) hole orbital in 3D model. The subscripts \( x \) and \( d \) denote the exchange and direct interactions, while subscript \( s \) denote the scattering terms of the Hamiltonian. Note that the spin orientation defines whether the interaction is direct of exchange. The up scripts \( ee, hh, \) and \( eh \) denote the electron-electron, hole-hole, and electron-hole interactions respectively. The Coulomb matrix elements are listed in table C.2. We use this simplified notations throughout the rest of this thesis, unless otherwise noted.

4.2 Neutral Excitons

4.2.1 Breaking of Hidden Symmetry

It is worth to compare the results with the previous work done by Bare et al [9]. The emission spectra of the symmetric QD in 2D model are shown in Figure 4.1. 4.1(a) shows the spectra with fitted energy levels with experiment (see section 3.1), while 4.1(b) is generated by input the same Coulomb matrix elements as in Bare’s work. Note that the spectra in Figure 4.1(b) perfectly reproduce the one reported by Bare et al (see reference [9] figure 1). The energies are measured from the band gap. The peaks are labeled by total spin of final state for electrons and holes, as labeled in the reference [9].

In general, the emission spectra in Figure 4.1(a) can be divided into two groups. Higher emission energy (more than 70 meV) for \( p \)-shell exciton recombinations and lower emission...
4.2 Neutral Excitons

Figure 4.1: Numerical result of spectra with different number of excitons δ-function are replaced by narrow Lorentzians for better visibility. (a) shows the spectra from the fitted energy level. (b) shows the reproduced spectra from the parameters from Bare at el.

energy (less than 40 meV) for s-shell exciton recombinations. From the first sight, the fitted results (Figure 4.1(a)) are quit different from the previous study (Figure 4.1(b)). First, the 4X spectrum seems to be totally different. Besides, instead of stable p-shell exciton recombination energy for different number of particles in 4.1(b), the spectra in Figure 4.1(a) shows increasing p-shell exciton recombination energies versus number of particles. Finally, the triplet-singlet/singlet-triplet peaks in 3X and 5X spectra split, as illustrated in Figure 4.1(a) by circles.

These differences can be attributed to the breaking of the hidden symmetry. The hidden symmetry refers to the identical envelope function of electron and hole, $\chi_e$ and $\chi_h$, as well as degenerated single particle states (see section 3.3). The Coulomb interactions are then symmetric for electrons and holes. Therefore few-particle energy of a specific state can be dramatically simplified, due to cancellations of Coulomb energies. For example, because the exchange interactions for electrons and holes are symmetric, the energy of 2X triplet-singlet state, $|ts\rangle = |1,0,0,0,0\rangle_e \otimes |1,1,1,0,0\rangle_h$, is identical to singlet-triplet state, $|st\rangle = |1,1,0,0,0\rangle_e \otimes |1,0,1,0,0\rangle_h$, under such symmetry. The notation for singlet-triplet is defined as electrons are singlet while holes are triplet as follow

$$|\text{singlet}^{\uparrow}s\uparrow, \downarrow, p^e_x, p^h_x, p^e_y, p^h_y\rangle = |\text{triplet}^{\uparrow}s\uparrow, \downarrow, p^e_x, p^h_x, p^e_y, p^h_y\rangle.$$

The arrows represent the spin up and spin down state for each particle.

In order to fit with experimental data, confinement potentials of electrons and holes must be

$$E_{ts} = E_{st} \text{ is that } E_p^e - V_{ab,x}^ee = E_p^h - V_{ab,x}^{hh}.$$
Figure 4.2: Illustration of spectra evolve with hole confinement potential. The $r$ value is the ratio between $s$-shell direct Coulomb matrix element, namely $r = V_{ee}^{s}/V_{hh}^{s}$. The fitted values used in the 2D model is $r = 1.491$. The split peaks are emphasized by dashed circles in 3X and 5X spectra. There is a sudden switch of spectra feature in 4X spectra (a) evolution of 3X spectra (b) evolution of 4X spectra (c) evolution of 5X spectra.

adjusted. As shown in Figure 3.2, the envelope function of electrons and holes are significantly different, which breaks the hidden symmetry. However, it is possible to engineer on the confinement potentials numerically to regain such symmetry. By increasing the confinement energy of holes, from $\hbar \omega_{h} = 10$ meV to $\hbar \omega_{h} = 24.7$ meV, we get the ratio $r = V_{hh}^{s}/V_{ee}^{s} \approx 1$. It is clearly shown in Figure 4.2 that the symmetry breaking of Coulomb matrix elements evolves the spectra from Bare’s work (Figure 4.1(b)) to the results fitted with experimental data (Figure 4.1(a)). Specifically, the triplet-singlet/singlet-triplet peak in 3X and 5X spectra splits into two peaks, triplet-singlet peak and singlet-triplet peak, because $E_{p}^{e} - V_{ee}^{x} \neq E_{p}^{h} - V_{hh}^{x}$.

The shift of the $p$-shell exciton recombination energy can be explained by this breaking of hidden symmetry as well. As shown in Figure 4.2, 5X $p$-shell exciton recombination peak evolves from 93 meV to 80 meV, while 3X $p$-shell exciton recombination peak evolves from 93 meV to 75 meV. This difference makes 5X $p$-shell exciton recombination peak having 5 meV higher energy than 3X $p$-shell exciton recombination peak. It is due to that there are more carrier-carrier interactions in the 5X spectra than in the 3X spectra. These interactions cancel each other by the presence of hidden symmetry, which gives rise to the stable $p$-shell exciton recombination energy under hidden symmetry.

For 4X spectra, there is a sudden switch from the Bare’s spectra to the one fitted with experiment; we postpone the explanation to later analysis in next section.

### 4.2.2 Breaking of Rotational Asymmetry

The rotational asymmetry the of QD is introduced to the confinement potential by asymmetry factor $a_{y}$

$$V_{QD}(x, y, a_{y}) = \frac{m^{*} \omega^{2}}{2} (x^{2} + a_{y} y^{2}). \quad (4.3)$$

Because asymmetry is considered as a structural defect, value of $a_{y}$ is the same for both electrons and holes. Some numerical results are shown in Appendix C. Figure 4.4 illustrates how the $|p_{x}\rangle$ and $|p_{y}\rangle$ split.

The spectra of 4X, 5X, and 6X are shown in Figure 4.3. Two features can be observed when asymmetry factor becomes larger. The first is that the blue shift of each peak linearly
4.2 Neutral Excitons

Figure 4.3: Numerical results of asymmetric QD spectra of 4X, 5X, and 6X. $a_y$ is the asymmetry factor, which grows from 1 to 1.13. The asymmetry peaks due to rotational asymmetry are illustrated by the arrows. (a) 4X spectra, there is a sudden switch, as in the discussion of hidden symmetry, when $a_y > 1.09$. (b) 5X spectra, there are paired asymmetry peaks. Not only the intensities but also the splitting separation increased with asymmetry factor. (c) 6X spectra, the intensity of asymmetry peak increased with asymmetry factor.

depends on the asymmetry factor. The second is some extra “asymmetry peaks” at $p$-shell recombinations region show up, illustrated by the tilted arrows in Figures 4.3. These two features need to be explained separately. The reason for blue shift of the peaks is trivial. Because the asymmetry factor adds to the confinement potential, the quantum energy level in $y$-direction is increased by multiplying the asymmetry factor. As a result, the energy increment is linearly depending on asymmetry factor, as listed in Appendix C.3. However, the explanations for asymmetry peaks are less trivial. We discuss the asymmetry peaks case by case in the following sections.

6X Spectra: Increasing Intensity

To explain the asymmetry peaks for the asymmetric QDs, let us focus on the simplest case, 6X $\rightarrow$ 5X spectrum. There are only 3 final noninteracting states for $(e \downarrow, h \uparrow)$ recombination:

\[
|s\rangle = |1, 0, 1, 1, 1, 1\rangle_e \otimes |0, 1, 1, 1, 1, 1\rangle_h = |a\rangle,
|p_x\rangle = |1, 1, 1, 0, 1, 1\rangle_e \otimes |1, 1, 0, 1, 1, 1\rangle_h = |b\rangle,
|p_y\rangle = |1, 1, 1, 1, 1, 0\rangle_e \otimes |1, 1, 1, 0, 1, 1\rangle_h = |c\rangle,
\]

which can be used as a restricted basis for the 5X Hamiltonian. $s (p_x$ and $p_y)$ on the left hand side represents the $s$-orbital ($p_x$-orbital and $p_y$-orbital) recombination.

For 6X case, there are three kinds of scattering processes:

\[
(s, p_x \text{ scattering}) : \hat{V}^{ch}_{ab, s},
(s, p_y \text{ scattering}) : \hat{V}^{ch}_{ac, s},
(p_x, p_y \text{ scattering}) : \hat{V}^{ch}_{bc, s}.
\]

For $|b\rangle$, there are only two scattering terms needed to be considered, namely $\hat{V}^{ch}_{bc, x}$ and $\hat{V}^{ch}_{bc, s}$.

\footnote{The same result can be extended to $(e \uparrow, h \downarrow)$ recombination.
Therefore we have

\[ \hat{H}|b\rangle = (\hat{H}^d + \hat{H}^n)|b\rangle = H^d|b\rangle - (V^{ch}_{bc,s} + V^{ch}_{ba,s})|b\rangle = H^d|b\rangle - V^{ch}_{bc,s}|c\rangle - V^{ch}_{ba,s}|a\rangle, \]

where \( \hat{H}^d|b\rangle = H^d|b\rangle \) as defined in Equation (4.1). Assume that we have the few-particle eigenstate \( |\Psi\rangle = \alpha|a\rangle + \beta|b\rangle + \gamma|c\rangle \), it is possible to solve the coefficients \( \alpha \), \( \beta \), and \( \gamma \) by diagonalizing the simplified Hamiltonian

\[ \hat{H}|\Psi\rangle = (\alpha H^d_a - \beta V^{ch}_{ba,s} - \gamma V^{ch}_{ca,s})|a\rangle + (\beta H^d_b - \gamma V^{ch}_{cb,s} - \alpha V^{ch}_{ac,s})|b\rangle + (\gamma H^d_c - \beta V^{ch}_{cb,s} - \alpha V^{ch}_{ac,s})|c\rangle. \]

That is \( \hat{H} \) can be written as

\[ \hat{H} = \begin{pmatrix} H^d_d & -V^{ch}_{ab,s} & -V^{ch}_{ca,s} \\ -V^{ch}_{ab,s} & H^d_b & -V^{ch}_{cb,s} \\ -V^{ch}_{ac,s} & -V^{ch}_{bc,s} & H^d_c \end{pmatrix}, \tag{4.5} \]

using Equations (4.4) as basis. Note that this Hamiltonian has been significantly simplified from the full 5X Hamiltonian, which is a 36 by 36 matrix.

We have to solve \( \alpha \), \( \beta \), and \( \gamma \) numerically for the eigenstates. But, luckily, when the QD is symmetric, it is possible to derive a simple expression for the state which gives rise to the asymmetry peak. Consider the linear combination \( |\Psi_{a_y}\rangle = \beta|b\rangle - \gamma|c\rangle = \frac{1}{\sqrt{2}}|b\rangle - \frac{1}{\sqrt{2}}|c\rangle \), it is an eigenstate of the simplified Hamiltonian, because \( V^{ch}_{ba,s} = V^{ch}_{ca,s} \) and \( H^d_b = H^d_c \) for the symmetric QD\(^5\),

\[ \hat{H}|\Psi_{a_y}\rangle = \hat{H}^d|\Psi_{a_y}\rangle + \hat{H}^n|\Psi_{a_y}\rangle = \frac{1}{\sqrt{2}} \left( H^d_b|b\rangle - H^d_c|c\rangle \right) + \frac{1}{\sqrt{2}} \left( -V^{ch}_{bc,s}|c\rangle - V^{ch}_{ba,s}|a\rangle + V^{ch}_{cb,s}|b\rangle + V^{ch}_{ca,s}|a\rangle \right) = \left( H^d_b + V^{ch}_{cb,s} \right)|\Psi_{a_y}\rangle. \]

Note that the other two eigenstates turn out to be the final states of s- and p-shell exciton recombination peaks. The transitions to \( |\Psi_{a_y}\rangle \) gives zero emission intensity because \( I \propto |\langle \Psi|\hat{P}|6X\rangle|^2 \), where \( \hat{P} \) is the dipole operator for emission, \( |6X\rangle \) is the six exciton ground state, and \( |\Psi\rangle \) is the 5X final state. For the case of \( |\Psi_{a_y}\rangle = \frac{1}{\sqrt{2}}|b\rangle - \frac{1}{\sqrt{2}}|c\rangle \), we have

\[ |\langle \Psi_{a_y}|\hat{P}|6X\rangle|^2 = \left| \frac{1}{\sqrt{2}} \langle b|\hat{P}|6X\rangle - \frac{1}{\sqrt{2}} \langle c|\hat{P}|6X\rangle \right|^2 = 50\%(\langle b|\hat{P}|6X\rangle|^2 - 50\%\langle c|\hat{P}|6X\rangle|^2 = 0 \]

where \( \langle b|\hat{P}|6X\rangle = \langle c|\hat{P}|6X\rangle \), meaning that the transition to \( |\Psi_{a_y}\rangle \) is forbidden. However, when the asymmetry is introduced to the QD, we have \( H^d_b \neq H^d_c \) and \( V^{ch}_{ba,s} \neq V^{ch}_{ca,s} \). This asymmetry redistribute the weight of each noninteracting state, which contributes to a small intensity to the dark state transition. As the asymmetry factor gets larger, the weight of \( |b\rangle \) gets heavier. For example 73.32% of \( |b\rangle \), 26.65% of \( |c\rangle \), and 0.03% of \( |a\rangle \), when \( a_y = 1.05 \), and we have

\[ |\langle \Psi_{a_y}|\hat{P}|6X\rangle|^2 \approx 73.3\%|\langle b|\hat{P}|6X\rangle|^2 - 26.7\%|\langle c|\hat{P}|6X\rangle|^2 \neq 0. \]

\(^4\)The signs of creation and annihilation operators nicely cancel each other.

\(^5\)The values of Coulomb matrix elements are as shown in Table C.2
4.2 Neutral Excitons

The eigenstates of the simplified Hamiltonian, Equation (4.5), agrees exactly with the full Hamiltonian, meaning that it is sufficient to neglect all other configurations without losing any understanding. This result can be interpreted intuitively that the asymmetry peak origins from the splitting of p-shell, as illustrated in Figure 4.4(b), but the exact position of the asymmetry peak and the intensity can not be explained by this naive picture.

**Figure 4.4:** Schematic illustration of rotational asymmetric 6X radiative decay. Electrons are represented by gray triangles while holes are represented by blank triangles. The direction of each triangle indicates the direction of spin. Note that p_y orbital is the higher energy one. Breaking of rotational symmetry is illustrated by the dashed line. The intuitive explanation for 6X radiative decay is shown by the wavy line.

5X Spectra: Splitting Peaks

The same concept, as 6X spectrum, can be used to explain the asymmetry peaks of 5X spectra. However, it is difficult to obtain a simple intuitive explanation which agrees with the full Hamiltonian. It is because the number of configurations blow up for 4X final states, which increase the number of available scattering processes. The short discussion here is focused on the splitting asymmetry peaks of 5X → 4X spectra.

As shown in Figure 4.3(b), there are paired asymmetry peaks in 5X spectra. When the asymmetry factor increases from \( a_y = 1.05 \) to \( a_y = 1.13 \), not only the intensities of the paired peaks but also the splitting separation increased. The splitting of 5X asymmetry peaks can, again, be attributed to the breaking of hidden symmetry, which leads to splitting of electron-electron exchange interaction and hole-hole exchange interaction. Some typical 4X final states of 5X spectra, after the recombination of a p-shell exciton, are

\[
\begin{align*}
\text{p-shell e-e exchange states} & \begin{cases} \\
|e\uparrow\downarrow, h\uparrow\downarrow⟩ = |1, 1, 1, 0, 0, 1⟩_e ⊗ |1, 1, 1, 0, 0, 1⟩_h, \\
|e\uparrow\uparrow, h\uparrow\uparrow⟩ = |1, 1, 1, 0, 0, 1⟩_e ⊗ |1, 1, 1, 0, 1, 1⟩_h,
\end{cases} \\
\text{p-shell h-h exchange states} & \begin{cases} \\
|h\downarrow\downarrow, e\downarrow\downarrow⟩ = |1, 1, 1, 0, 0, 1⟩_e ⊗ |1, 1, 1, 0, 1, 1⟩_h, \\
|h\uparrow\uparrow, e\uparrow\uparrow⟩ = |1, 1, 1, 0, 1, 1⟩_e ⊗ |1, 1, 1, 0, 1, 0⟩_h,
\end{cases}
\end{align*}
\]

where the arrows denote the direction of p-shell carrier spin. Similar to the case of 6X spectra, the linear combination

\[
|Ψ_{e,x}⟩ = \frac{1}{\sqrt{2}} (|e\uparrow\uparrow, h\uparrow\downarrow⟩ - |e\uparrow\downarrow, h\uparrow\uparrow⟩), \\
|Ψ_{h,x}⟩ = \frac{1}{\sqrt{2}} (|h\downarrow\downarrow, e\downarrow\downarrow⟩ - |h\uparrow\uparrow, e\uparrow\uparrow⟩),
\]

is the final states for the asymmetry peaks. The different energy of these two states, which results in the a paired splitting asymmetry peaks, arise from the asymmetric exchange interaction (also see section 4.2.1). For example, as shown in Appendix C.3, \( V_{bhb}^{ee} = 1.358 \) meV and
$V_{ccbb}^{hh} = 0.930 \text{ meV when } a_y = 1.05$. But, one thing different from the 6X spectra is that the weight of $|\uparrow\uparrow, \uparrow\downarrow\rangle$ and $|\uparrow\uparrow, \downarrow\uparrow\rangle$ do not redistribute when the asymmetry is introduced to the QD. It is because there is no energy difference between these two states, and the scattering term cancels each other. On the other hand, the increasing intensity of 5X asymmetry peaks is contributed by the asymmetric initial 5X states$^6$.

**4X Spectra: Sudden Switch**

![Diagram](image)

**Figure 4.5:** (a) shows the unpolarized 4X ground state. There are three paired electron-electron exchange interaction, while only two paired hole-hole exchange interaction. (b) shows the polarized 4X ground state, which gives rise to sudden switch of 4X spectra.

The sudden switch of 4X $\rightarrow$ 3X spectra appears when the asymmetry factor becomes $a_y \gtrsim 1.09$ in Figure 4.3 and when the ratio of Coulomb interaction becomes $r \gtrsim 1.491$ in Figure 4.2. The reason for the sudden switch is the polarization of orbital wave function. For the weakly deformed QD, a typical 4X ground states is

$$|\Psi_{weak}\rangle = |1,1,1,0,1,0\rangle_e \otimes |1,1,0,1,0,1\rangle_h,$$

as shown in Figure 4.5(a). The spin arrangement of $|\Phi_{weak}\rangle$ is due to Hund’s law, where each orbital of a given shell is half populated by parallel spin electrons before and of the orbital is fully occupied. The Hund’s law can be explained by the exchange interaction between electrons with parallel spins, which lower to total energy of $|\Phi_{weak}\rangle$. On the other hand, a typical 4X ground state of a strongly deformed QD is

$$|\Psi_{strong}\rangle = |1,1,1,1,0,0\rangle_s \otimes |1,1,1,1,0,1\rangle_{py},$$

as shown in Figure 4.5(b), where $p_y$ is the higher energy orbital. The number of available optical transitions is dramatically decreased when the ground state transform from $|\Psi_{weak}\rangle$ to $|\Psi_{strong}\rangle$. This transformation happens only if the energy of $|\Psi_{strong}\rangle$ becomes lower than the energy of $|\Psi_{weak}\rangle$. Intuitively, if we neglect the scattering processes$^7$, this transformation can be seen as the competition between the energy of p-shell and the energy of exchange interaction. For the diagonal energies $H_s^d = \langle \Psi_{strong}|\hat{H}|\Psi_{strong}\rangle$ and $H_w^d = \langle \Psi_{weak}|\hat{H}|\Psi_{weak}\rangle$, we have

$$H_s^d = (2E_1^e + 2E_2^e - 2V_{ee}^{ab,x}) + (2E_1^h + 2E_2^h - 2V_{hh}^{ab,x}) - C_e^s,$$

$$H_w^d = (2E_1^e + E_2^e + E_3^e - V_{ee}^{ab,x} - V_{ee}^{ac,x} - V_{ee}^{cb,x}) + (2E_1^h + E_2^h + E_3^h - V_{hh}^{ab,x} - V_{hh}^{ac,x} - V_{hh}^{cb,x}) + C_e^w,$$

$^6$For 6X spectra, the increasing intensity of asymmetry peak is contributed by the asymmetric final 5X state

$^7$From the numerical point of view, it is reasonable to neglect the scattering terms because the weight percentage of the diagonal term is about 99%.
where $C^{eh}_s$ and $C^{eh}_w$ are the electron-hole Coulomb attraction energies for $|\Psi_{\text{strong}}\rangle$ and $|\Psi_{\text{weak}}\rangle$ respectively. $a$, $b$, and $c$ denote $s$-orbital, $p_x$-orbital, and $p_y$-orbital as in 6X spectra. Note that there are four paired exchange interactions for the electrons of $|\Psi_{\text{strong}}\rangle$, while there are six paired exchange interactions for the electrons of $|\Psi_{\text{weak}}\rangle$. If we define $\Delta E = H_s - H_w$, we can conclude that the sudden switch happens when $\Delta E$ change sign from $\Delta E \geq 0$ to $\Delta E \leq 0$.

It is interesting to point out that as the asymmetry factor becomes larger, the 4X spectra become simpler, which is contrary to our expectation.

### 4.2 Neutral Excitons

#### 4.2.3 Auger-like Satellites: Biexciton

Auger-like satellite refers to the emission signal coming from the exciton radiative decay, which also excites other particle none radiatively. Intuitively, as shown in Figure 4.6, when the exciton $(e \uparrow, h \downarrow)$ recombines a part of the energy is transfered to the other exciton $(e \downarrow, h \uparrow)$, which is excited and jumps to higher orbital.

![Figure 4.6: Schematically illustration of Auger-like emission.](image)

Since the observation of the Auger-like satellite is possible to carry out in the experiment, it is interesting to calculate these Auger-like satellite. For the few-particle configurations, only biexciton has the Auger-like satellite emission, when $s$ and $p$ orbital are taken into account. In addition, since the intensities of Auger-like satellite are expected to be weak, the relative position to other strong peaks is critical to find the Auger-like satellite, we focus ourself on the positions of the Auger-like satellite from the biexciton main emission.

#### Results from 2D Calculations

The calculated Auger-like satellite are shown in Figure 4.7(a). The separation between Auger-like satellite and 2X main emission peak is about 47.50 meV. The intensity is rather small, the intensity ratio $I_{\text{auger}}/I_{\text{main}}$ is about $7.4 \times 10^{-5}$. A concrete explanation for the Auger-like satellite is due to the few-particle effects. To see this, we define some biexciton noninteracting initial states

- 2X ground state: $|g\rangle_{2X} = |1, 1, 0, 0, 0, 0\rangle_e \otimes |1, 1, 0, 0, 0\rangle_h$
- 2 holes excited state: $|hh\rangle_{2X} = |1, 1, 0, 0, 0\rangle_e \otimes |0, 0, 1, 1, 0\rangle_h$
- 1 exciton excited state: $|eh\rangle_{2X} = |1, 0, 0, 1, 0\rangle_e \otimes |0, 1, 1, 0, 0\rangle_h$

and we define $|2X_g\rangle_{CI}$ to be the CI ground state of biexciton configuration. Therefore, for symmetric QD, 2D calculation yields the biexciton CI ground state as

$$\langle 2X_g|2X_g\rangle_{CI} \approx 97.4\% \langle g|g\rangle_{2X} + 1.6\% \langle eh|eh\rangle_{2X} + 0.6\% \langle hh|hh\rangle_{2X}.$$
Figure 4.7: (a) 2D Calculation of Auger-like satellite spectrum for a asymmetric QD, \( a_y = 1.05 \). The separation of Auger-like satellite and the \( 2X \) main emission peak is about 47.50 meV. (b) Schematically illustration of the radiative decay of split Auger-like satellite.

The 1.6% of \( |eh\rangle_{2X} \) component contribute to a small intensity of Auger-like satellite. To estimate the biexciton ground state energy, the small contribution from \( |eh\rangle_{2X} \) and \( |hh\rangle_{2X} \) can be neglected and treat the biexciton ground state as a pure state \( |g\rangle_{2X} \). It is because we concern only the peaks separation, which is determined by the energy separation of final state.

Next, let us define some single exciton final state, which are noninteracting states

\[
\begin{align*}
X \text{ ground state: } & |a\rangle_X = |1, 0, 0, 0, 0, 0\rangle_e \otimes |0, 1, 0, 0, 0, 0\rangle_h \\
\text{ } p_x \text{ excited state: } & |b\rangle_X = |0, 0, 1, 0, 0, 0\rangle_e \otimes |0, 0, 0, 1, 0, 0\rangle_h \\
\text{ } p_y \text{ excited state: } & |c\rangle_X = |0, 0, 0, 0, 1, 0\rangle_e \otimes |0, 0, 0, 0, 0, 1\rangle_h,
\end{align*}
\]

where only \((e \uparrow, h \downarrow)\) exciton is considered. Similar to 6X discussion, we can conclude that only 3 types of scattering are available, meaning that we can write down the simplified Hamiltonian using these three states as basis

\[
\hat{H} = \begin{pmatrix} 
H_d & V_{eh} & V_{eh} \\
V_{eb} & H_b & V_{eh} \\
V_{ec} & V_{eh} & H_c
\end{pmatrix}.
\]

Using the data of rotational symmetric QD, Appendix C.3, instead of the noninteracting ground
state \(|a⟩_X\), we have the exciton CI ground state

\[ |X^1⟩_{CI} \approx 0.9967|a⟩_X + 0.057|b⟩_X + 0.057|c⟩_X, \]

which can be written in the weight percentage

\[ \langle X^1⟩|X^1⟩_{CI} \approx 99.35%|a⟩_X + 0.32%|b⟩_X + 0.32%|c⟩_X. \]

Further more, we have the first excited state, \(|1⟩_{CI}\), and the second excited state, \(|2⟩_{CI}\), as

\[ |1⟩_{CI} \approx -0.0806|a⟩_X + 0.7048|b⟩_X + 0.7048|c⟩_X, \]
\[ |2⟩_{CI} \approx -0.7071|b⟩_X + 0.7071|c⟩_X, \]

Note that \(|2⟩_{CI}\) can be written as \(\frac{1}{\sqrt{2}}(|b⟩_X - |c⟩_X)\), which gives rise to a dark transition. The separation between 2\(X\) main peak and Auger-like satellite is the energy difference between \(|X^1⟩_{CI}\) and \(|1⟩_{CI}\).

One interesting result from 2D calculation is that the Auger-like satellite splits when the rotational asymmetry is introduced to the QD. The asymmetry dependence of the biexciton Auger-like satellites is shown in Figure 4.8. It is again due to the splitting between \(p_x\) orbital and \(p_y\) orbital. As we have done for 6\(X\) emission spectra, one can expect that the asymmetry redistributes the weight percentage of \(|2⟩_{CI}\), which contributes to a small intensity to the dark transition. However, the intensity of the split Auger-like satellite is even weaker than the main Auger-like satellite.

**Results from 3D Calculations**

![Figure 4.9: 3D Calculation of Auger-like satellite spectrum for a symmetric QD.](image)

The result from 3D calculation is shown in Figure 4.9(a). The separation between Auger-like satellite and 2\(X\) main emission is significantly smaller than 2D calculations. For the rotational symmetric QD, the separation is about 16.26 meV. Instead of one exciton been excited in 2D calculations, only one hole been excited after Auger-like emission, as shown in Figure 4.9(b), because the Coulomb matrix elements of 3D model allow only the one hole scattering, \(V_{aaba}^{ch}\) and \(V_{abaa}^{ch}\) (see Table C.4 and C.5). This explains the smaller peaks separation from 2D calculation. Again, let us define some of the biexciton noninteracting states that are needed for biexciton CI ground state

- 2\(X\) ground state: \(|g⟩_{2X}^{3D} = |1, 1, 0, 0, 0, 0⟩_e \otimes |1, 1, 0, 0⟩_h,\]
- two holes excited state: \(|hh⟩_{2X}^{3D} = |1, 1, 0, 0, 0, 0⟩_e \otimes |0, 0, 1, 1⟩_h,\]
- two electrons excited state: \(|ee⟩_{2X}^{3D} = |1, 1, 0, 0, 0, 0⟩_e \otimes |0, 0, 1, 1⟩_h,\]
- one hole excited state: \(|h⟩_{2X}^{3D} = |1, 1, 0, 0, 0, 0⟩_e \otimes |1, 0, 0, 0⟩_h,\]
- two excitons excited state: \(|xx⟩_{2X}^{3D} = |0, 0, 1, 1, 0, 0⟩_e \otimes |0, 0, 1, 1⟩_h,\]
From these states, the 3D calculation gives the weight percentage of biexciton CI ground state, \(|2X_g|^{3D}_{CI}\), as
\[
\langle 2X_g|2X_g|^{3D}_{CI} \rangle = 97.36\%\langle g|g\rangle^{3D}_{2X} + 1.39\%\langle hh|hh\rangle^{3D}_{2X} + 1.23\%\langle ee|ee\rangle^{3D}_{2X} + 0.01\%\langle xx|xx\rangle^{3D}_{2X} + 0.01\%\langle hh\rangle^{3D}_{2X}
\]
Note that only one hole excited component, \(|h\rangle^{3D}_{2X}\), gives rise to the Auger-like satellite, because only \(s\) orbital exciton recombination is allowed.

For the single exciton case, we need to consider only two states
\[
\text{X ground state: } |g\rangle^{3D}_{X} = |1, 0, 0, 0, 0, 0\rangle_e \otimes |0, 1, 0, 0\rangle_h \\
\text{one hole ground state: } |h\rangle^{3D}_{X} = |1, 0, 0, 0, 0, 0\rangle_e \otimes |0, 0, 0, 1\rangle_h,
\]
Therefore the eigenstates of the simplified Hamiltonian,
\[
\hat{H} = \begin{pmatrix} H^d_g & V_{aba} \\ V_{aba} & H^d_h \end{pmatrix},
\]
where \(\hat{H}^d|g\rangle^{3D}_{X} = H^d_g|g\rangle^{3D}_{X}\) and \(\hat{H}^d|h\rangle^{3D}_{X} = H^d_h|h\rangle^{3D}_{X}\), yield the correct energy separation.

### 4.3 Charged Excitons in Rotational Asymmetric QDs

Since the structure of holes in valence band is rather complicated and not fully represented by single-band model, the system of more than two holes is not comparable with experiments. For this reason, we turn ourself to the negatively charged excitons, with SOLELY one hole in the system, and we focus only on the rotational asymmetry.

#### 4.3.1 \(X^{2-}\) Spectra and Temperature Dependence

**Results of 2D Calculations**

Many efforts have been made on the \(X^{2-}\) spectra in order to achieve good agreement with the experimental results (see chapter 5). It was confirmed that there is a stronger peak with relatively high emission energy, while there are a paired weaker peaks at lower emission energy. The splitting of the paired peaks is about 1 meV and the separation between stronger peak and the paired peaks is about 7 meV, which can be explained by electron-electron exchange interactions.

The calculated \(X^{2-}\) spectrum of 2D model from a symmetric QD is shown in the Figure 4.12(a). It is clear that there is a stronger peak at 36.8 meV and a weaker peak at 29.4 meV, but there is no splitting of weaker low-energy peak. The similar spectra were obtained from asymmetric QDs (not shown). Different from 5X and 4X initial states, the \(X^{2-}\) ground state is very sensitive to the symmetry of the QD. As soon as asymmetry is introduced, the \(X^{2-}\) ground state become polarized and leave \(p_y\) orbital empty, for example
\[
|\Psi_1\rangle = |1, 1, 1, 0, 0, 0\rangle_e \otimes |1, 0, 0, 0, 0\rangle_h, \\
|\Psi_0\rangle = |1, 1, 0, 1, 0, 0\rangle_e \otimes |1, 0, 0, 0, 0\rangle_h,
\]
are two possible \(p_x\)-polarized ground states, where the up scripts 1 and 0 represent the spin of final states after the \((e \downarrow, h \uparrow)\) recombination. The sensitivity to the symmetry is because there is only one electron in \(p\) orbital, which leads to no available scattering process. Therefore, there is only one state needed to be considered for the few-particle Hamiltonian.
The initial $X^{2−}$ state is not directly intuitive but, luckily, there are only a few states and scattering processes involved in two-electron final state, therefore the $X^{2−}$ spectra can be understood analytically. The simple conclusion is: this two peaks feature resulted from the energy difference between two-electron triplet states and two-electron singlet state.

Because there is only $s$-shell recombination allowed for $X^{2−}$ spectra, and there is only $(p_x, s)$ scattering allowed for polarized two-electron states, the following four polarized final states can be treated as basis for Hamiltonian

\[
\begin{align*}
|1\rangle &= |1,0,1,0,0,0\rangle_e, \text{ spin: 1} \\
|2\rangle &= |0,1,0,1,0,0\rangle_e, \text{ spin: -1} \\
|3\rangle &= |0,1,1,0,0,0\rangle_e, \text{ spin: 0} \\
|4\rangle &= |1,0,0,1,0,0\rangle_e, \text{ spin: 0}.
\end{align*}
\]

Note that the scattering two-particle operator in this case, e.g. $\hat{V}_{ee}^{4132} = \hat{V}_{abab}$, only change the spin arrangement but the spin is conserved, because the Hamiltonian conserves spin \[\text{(6)}\].

As the analysis for $6X$ spectra, we consider the scattering processes. There is no scattering allowed for $|1\rangle$ and $|2\rangle$ since any other state has different spin. Only $(p_x, s)$ scattering between $|3\rangle$ and $|4\rangle$ is allowed. Combine these facts and we have

\[
\hat{H} = \begin{pmatrix}
H_1^d & 0 & 0 & 0 \\
0 & H_2^d & 0 & 0 \\
0 & 0 & H_3^d & -V_{ee}^{ab,x} \\
0 & 0 & -V_{ee}^{ab,x} & H_4^d
\end{pmatrix} = \begin{pmatrix}
\hat{H}_{\{1,-1\}}^d & 0 \\
0 & \hat{H}_{\{0\}}^d
\end{pmatrix},
\]

where $H_i^d = \langle i | \hat{H} | i \rangle$ is the diagonal energy. $\hat{H}_{\{1,-1\}}^d$ is the $2 \times 2$ diagonal matrix for $|1\rangle$ and $|2\rangle$ while $\hat{H}_{\{0\}}^d$ is the $2 \times 2$ matrix for $|3\rangle$ and $|4\rangle$. The numbers in the curved parenthesis of subscript denote the spin of basis. These diagonal energies can be calculated directly

\[
\begin{align*}
H_1^d &= E_a^e + E_b^e + V_{ee}^{ab,x} - V_{ee}^{ab,x}, \\
H_2^d &= E_a^s + E_b^s + V_{ee}^{ab,x} - V_{ee}^{ab,x}, \\
H_3^d &= E_a^e + E_b^e + V_{ee}^{abba}, \\
H_4^d &= E_a^e + E_b^e + V_{ee}^{abba}.
\end{align*}
\]

8If we apply $(p_y, s)$ scattering, $\hat{V}_{ee}^{6512}$, to the polarized state, $|1,0,1,0,0,0\rangle_e$, we have $\hat{V}_{ee}^{6512}|1,0,1,0,0,0\rangle_e = 0.$
These four diagonal energies can be reduced to two, that is we have the energy for spin 1 and -1, $H^d_{[1,-1]} = H^d = H^d_0$, and the energy for spin 0, $H^d_{[0]} = H^d_0 = H^d_0$. It is fairly easy to calculate the eigenvectors, $|\pm\rangle = \frac{1}{\sqrt{2}} (|3_x\rangle \pm |4_x\rangle)$ and eigenvalues, $E^d_{[0]} = H^d_{[0]} + V^{ee}_{ab,x}$, of $\hat{H}(0)$. Therefore we have the two-electron few-particle states and their energies as

$$|	ext{triplet}\rangle \quad \begin{cases} |1\rangle : H^d_{[1,-1]}, \\ |2\rangle : H^d_{[1,-1]}, \\ |+\rangle : H^d_{[0]} - V^{ee}_{ab,x} = H^d_{[1,-1]}, \end{cases}$$

$$|\text{singlet}\rangle \quad \begin{cases} |-\rangle : H^d_{[0]} + V^{ee}_{ab,x} = H^d_{[1,-1]} + 2V^{ee}_{ab,x}. \end{cases}$$

which are the final states of $X^2$ spectra. The energy difference between triplet states and singlet state is $2V^{ee}_{ab,x} \approx 7$ meV, which is the peaks separation in Figure 4.10(a). Note that exactly the same result can be derived for $p_y$-polarized two-electron states.

Concerning the singlet transition splitting, since the energies of $p_x$ and $p_y$ orbital is different for asymmetric QDs, we expect an additional peak if the transitions to the $|\text{singlet}_y\rangle$ (instead of $|\text{singlet}_x\rangle$) are allowed, where the subscripts $x$ and $y$ represent the $p_x$ polarized final state and $p_y$ polarized final state respectively. Further more, from the experimental point of view, the measurements are usually performed at the temperature $T \approx 5K \sim 25K$. If a initial excited state is close enough to initial ground state, the initial few-particle ground states can be excited by thermal energy $k_BT \approx 0.43$ meV $\sim 2.15$ meV. Put these together, we introduce the temperature dependence to the initial states by Boltzmann population function

$$f(E) = e^{\frac{E-E_g}{k_BT}},$$

where $f(E)$ is the probability of the state with energy $E$ being occupied, and $E_g$ is the ground state energy. The numerical calculation shows, when $a_y = 1.05$, the energy of $p_x$-polarized ground states is 150.627 meV while the energy of $p_y$-polarized states is 151.529 meV. The next excited states energy is 169.532 meV, which can be neglected. For simplicity, let us focus on two initial states, $|\Psi_x\rangle$ and $|\Psi_y\rangle$. The final spin up script is neglected from Equation (4.6) to simplify the notations.

To get an analytical expression for the emission energy, we need to solve the energy of initial states. Unfortunately, we have to solve the energy of these initial state numerically. However, it is possible to neglect the scattering terms because $|\Psi_x\rangle$ and $|\Psi_y\rangle$ are nearly diagonal, the sum of probability weight for all others scattered terms is less than 1%. The diagonal energy, which is relatively easy to calculate, of these states are

$$|\Psi_x\rangle : E_x \approx 2E^e_x + E^h_x + E^h_x + V^{ee}_{aa,d} + 2V^{ee}_{ab,d} - V^{ee}_{ac,x} - V^{eh}_{aa,d} - V^{eh}_{ab,d} - V^{eh}_{ac,x},$$

$$|\Psi_y\rangle : E_y \approx 2E^e_y + E^h_y + E^h_y + V^{ee}_{aa,d} + 2V^{ee}_{ac,d} - V^{ee}_{ab,x} - V^{eh}_{aa,d} - V^{eh}_{ab,d} - V^{eh}_{ac,d}.$$

From Equation (4.8) and (4.7), we can estimate the emission energy.

$$|\Psi^1_x\rangle \rightarrow |\text{triplet}_x\rangle : E^{t_x}_x = E^e_x + E^h_x + V^{eh}_{aa,d} + V^{ee}_{ab,d} - 2V^{eh}_{ac,x} - V^{eh}_{ab,d} - V^{eh}_{ac,d},$$

$$|\Psi^1_y\rangle \rightarrow |\text{triplet}_y\rangle : E^{t_y}_y = E^e_y + E^h_y + V^{eh}_{aa,d} + V^{ee}_{ab,d} - 2V^{eh}_{ac,x} - V^{eh}_{ab,d} - V^{eh}_{ac,d},$$

$$|\Psi^0_x\rangle \rightarrow |\text{singlet}_x\rangle : E^{s}_x = E^e_x + E^h_x + V^{eh}_{aa,d} + V^{ee}_{ab,d} - 2V^{eh}_{ac,x} - V^{eh}_{ab,d} - 2V^{ee}_{ab,x},$$

$$|\Psi^0_y\rangle \rightarrow |\text{singlet}_y\rangle : E^{s}_y = E^e_y + E^h_y + V^{eh}_{aa,d} + V^{ee}_{ab,d} - 2V^{eh}_{ac,x} - V^{eh}_{ab,d} - 2V^{ee}_{ac,x},$$

where the up script 0 and 1 of $|\Psi_x\rangle$ denote the spin of final state, the up script t (s) of $E^t_x$ denotes the triplet (singlet) transition.

From theoretical point of view, the splitting features appear for both singlet transition, $\Delta E^s = E^s_y - E^s_x$, and triplet transition, $\Delta E^t = E^t_y - E^t_x$, when we introduce the temperature
dependence, due to the splitting between $p_y$ orbital and $p_x$ orbital. But interestingly, $\Delta E^s$ can be ten times larger than $\Delta E^t$, because

$$\Delta E^s = (V_{ee ac,d} - V_{eh ac,d} - 2V_{eh ac,x}) - (V_{ee ab,d} - V_{eh ab,d} - 2V_{eh ab,x}),$$

$$\Delta E^t = (V_{ee ac,d} - V_{eh ac,d}) - (V_{ee ab,d} - V_{eh ab,d}),$$

(4.9)

where $\Delta E^t = (V_{ee ac,d} - V_{eh ac,d}) - (V_{ee ab,d} - V_{eh ab,d})$ nearly cancels the difference between $p_y$ orbital and $p_x$ orbital. For example, when $a_y = 1.09$ and $T = 15K$, we have singlet splitting $\Delta E^s = 93.3 \mu eV$ while triplet splitting $\Delta E^t = 6.1 \mu eV$. The spectra with temperature 15K is shown if Figure 4.10. It is clear shown that the splitting of singlet transition is much stronger than triplet transition.

**Results of 3D Calculations**

The $X^{2−}$ spectra from 3D calculations are shown in Figure 4.11. It is clearly shown that not only the singlet transition splits when the rotational asymmetry is introduced to the QD, but also the triplet transition splits. Since the only thing different from 2D calculation is the values of Coulomb matrix elements. If we use Equations (4.9) to estimate the peaks separation, we have

$$\Delta E^s = -19.8 \mu eV,$$

$$\Delta E^t = 36.5 \mu eV.$$  

This means that the cancellation of $\Delta E^t$ in 2D calculations becomes over compensate in 3D model.

**Peak Broadening**

It is important to note that the resolution used to generate the spectra in this section much higher than what can be achieved in most experiments. The high resolution (about 1 $\mu eV$) is used to illustrate the asymmetry effects. In practice, instead of a pair of splitting peaks, we expect an effective broadening of the peaks in the experimental data.

**4.3.2 Negatively Charged Excitons**

The few-particle charged excitons are easy to observed in the experiments, as shown in Figure 5.2. We shortly compare the results from 2D model and 3D model for the few-particle charged
excitons. It is clearly shown in Figure 5.3 that the emission energies of the main emission peak are decreasing with the number of electrons. The results of 2D model (Figure 4.12(a)) shows the emission energy increasing with the number of electron, while the results from 3D model agree with the experimental data (see chapter 5). Some more spectra of charged exciton configurations from both 2D and 3D model are shown in Figure 4.12. In general, the energy order of the peaks form 3D calculations agrees with experiments. These calculated results are similar to the work done by Hartmann [5] for the same pyramidal QD system.

The different peak order between 2D calculation and 3D calculation is due to the structure of hole’s wave functions. As mentioned in chapter 3, in order to fit with the experimentally extracted hole-level spacing, $\Delta E^h \approx 10$ meV, the holes in 2D calculations must be weakly confined in comparison with electrons, Figure 3.2. These weakly confined holes give rise to lower energy separation between initial and final states.

Figure 4.12: Low particle spectra calculated by (a) 2D model and (b) 3D model. spectra measured from band gap $E_g = 1345$ meV. The spectra are arranged in the order of increasing electron number.
Chapter 5

Experiment: Few-particle Spectra

In addition to the calculations, some efforts were devoted to the experimental work. The purpose of the experimental work is to confirm the splitting of low energy emission line of $X^{2-}$, which was first observed by Dufäker et al [25]. Moreover, some few-particle spectra, the configurations with less than two holes, were acquired in order to compare 2D and 3D models.

The measurements were carried out by the $\mu$-PL instrument, as illustrated in Figure 5.1. The sample was cooled by liquid Helium at the temperature about 25K. The laser beam and the camera were focused on a single QD by a microscope objective lens. The emission spectrum was collected by a CCD detector.

Power dependent spectra of two QDs were collected as shown in Figure 5.2. Emission peaks are identified according to the back-hopping mechanism proposed by Hartmann et al [5]. When the excitation power decreased, the QDs become more negatively charged. These results agree with the 3D model calculations. Note that the general features of these spectra are similar for QD1 and QD2. This is because the structure of the pyramidal QD system is well controlled, which gives rise to a consistent energy levels.
The $X^{2-}$ peaks are identified for three QDs, as shown in Figure 5.3. Other than QD1 and QD2 in Figure 5.2, spectrum of QD3 was collected to show the splitting of lower energy peak of $X^{2-}$ emission. The power dependent spectra of QD3 behaves similarly (not shown). As can be seen, the lower energy peak of $X^{2-}$ split for QD2 and QD3, while it remains single peak for QD1.

Figure 5.2: Few-particle spectra of two QDs with decreasing excitation power. Emission peaks are identified according to the work done by Hartmann et al [5]. The spectra are measured from band gap $E_g = 1345$ meV.

Figure 5.3: Experimental data of the splitting lower energy $X^{2-}$ peak. Spectra of three QDs have been collected.
Chapter 6

Summary

Conclusions
Here we draw some conclusions of this thesis work. We have performed the 2D and 3D calculations of the pyramidal QDs. We have focused on the neutral excitons, $4X$, $5X$, and $6X$, to see the effects of hidden symmetry in 2D model. The same spectra, as in the work done by Bare et al, has been generated for QDs with hidden symmetry. It has been shown in section 4.2.1 that when the hidden symmetry breaks down, the $|ts\rangle$ and $|st\rangle$ transition split. Moreover, we have analyzed the Auger-like emission for $2X$ spectrum. The separation of Auger-like satellite was predicted as 47.5 meV from 2D calculation, while it was predicted as 16.3 meV from 3D calculation.

Then, we turned ourselves to the charged excitons, $X^+$, $X^-$, $X^{2-}$, $X^{3-}$, $X^{4-}$, and $X^{5-}$, in order to compare with the experimental results. 3D model shows a better agreement of the emission peak energy order with experimental data, which is similar to the calculated result done by Hartmann. Most of the attention were put on the $X^{2-}$ spectra, with temperature dependence. The analysis reveals that there are two-electron singlet transition (weaker peak) and two-electron triplet transition (stronger peak) of biexciton spectra, which give rise to a stronger peak at higher energy region and a weaker peaks at lower energy region. These two peaks are separated by electron-electron exchange interaction, $2V_{ee}^{ab,x}$. When the temperature is implemented, 2D calculations suggests a broadening of the weaker peak while the stronger peak is not affected. On the other hand, 3D calculations suggests both peaks broaden when the temperature is considered. Moreover, following the observation of Dufäker et al, the splitting of low energy emission line of $X^{2-}$ was confirmed.

Future Works
In order to resolve the split weaker peak of $X^{2-}$ emission spectra, it is possible to include $\mathbf{k} \cdot \mathbf{p}$ calculation with piezoelectric effects. Moreover, the model can be improved, in order to retain the triangular symmetry of the pyramidal QDs.

Experimentally, if it is possible to measure the Auger-like satellite of biexciton, it would be very interesting to see the separation between the Auger-like satellite and the main peak of biexciton, which could imply some clue to further improve the calculation model.
Appendix A

Theoretical Derivations

A.1 Effective Mass Approximation for QDs

This section derives the effective mass approximation of single-band QDs. The derivation and notations mainly follow Davies’s book [16]. There are two assumptions\(^1\) can be made for the single-band model:

1. Only one band contributed to the wave function \(\psi(\mathbf{r})\), namely there is no band mixing.
2. All the Bloch states contribute to the wave function \(\psi(\mathbf{r})\), having small variation in \(\mathbf{k}\) value.

Given that we have a 3-dimensional confinement potential, \(V^{QD}(\mathbf{r})\), of a quantum dot. We can rewrite the Equation (1.3) as

\[
\left(\hat{H}_{\text{per}} + V^{QD}(\mathbf{r})\right) \psi(\mathbf{r}) = E\psi(\mathbf{r}), \tag{A.1}
\]

where \(\hat{H}_{\text{per}}\) is the Hamiltonian for perfect crystal. Solution for Equation (A.1) can be expressed as Fourier expansion

\[
\psi(\mathbf{r}) = \int_{\Omega} \tilde{\chi}(\mathbf{k})\phi_{\mathbf{k}}(\mathbf{r}) \frac{d\mathbf{k}}{2\pi}, \tag{A.2}
\]

since all the \(\phi_{\mathbf{k}}\) form a complete basis of Hilbert space\(^2\). It is important to point out that these solutions are the eigenstates of \(\hat{H}_{\text{per}}\), that is, \(\hat{H}_{\text{per}}\phi_{\mathbf{k}} = E(\mathbf{k})\phi_{\mathbf{k}}\). Moreover, if we concern the wave function around Γ point (\(\mathbf{k} \approx 0\)), from the second assumption \(\phi_{\mathbf{k}}(\mathbf{r})\) can be written as \(\phi_{\mathbf{k}}(\mathbf{r}) \approx u_{\mathbf{k}=0}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}} = \phi_{0}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}\). Combine the Equations (A.1) and (A.2), and the second assumption, we get

\[
\left(\hat{H}_{\text{per}} + V^{QD}(\mathbf{r})\right) \psi(\mathbf{r}) = \left(\hat{H}_{\text{per}} + V^{QD}(\mathbf{r})\right) \int_{\Omega} \tilde{\chi}(\mathbf{k})\phi_{\mathbf{k}}(\mathbf{r}) \frac{d\mathbf{k}}{2\pi}
\approx \phi_{0}(\mathbf{r}) \int_{\Omega} E(\mathbf{k})\tilde{\chi}(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}} \frac{d\mathbf{k}}{2\pi} + V^{QD}(\mathbf{r})\phi_{0}(\mathbf{r}) \int_{\Omega} \tilde{\chi}(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}} \frac{d\mathbf{k}}{2\pi} \tag{A.3}
\]

If we consider electrons near the band edge of conduction band,

\[
E(\mathbf{k}) = E_{g} + \frac{\hbar^{2}}{2m^{*}} k^{2}. \tag{A.4}
\]

---

\(^1\) The results from these assumptions, on impurity for bulk property, have good agreement with experiment results [16].

\(^2\) Hilbert space is the function space for wave functions. Mathematically, Hilbert space is vector space with inner product.
Using the property of Fourier transform\textsuperscript{3} that \[ (k)^nF(k) \mapsto (-i\nabla)^n f(r) \] Substitute Equation (A.4) into Equations (A.3) and perform Fourier transform, we get

\[
\phi_0(r) \left( \frac{\hbar^2}{2m_e} \nabla^2 + V^{QD}(r) \right) \chi(r) = \phi_0(r)E\chi(r),
\]

which can be rewritten as

\[
\left( \frac{\hbar^2}{2m_e} \nabla^2 + V^{QD}(r) \right) \chi(r) = (E - E_0) \chi(r), \tag{A.5}
\]

where \(\chi(r)\) is the Fourier transform\textsuperscript{4} of \(\tilde{\chi}(k)\). The similar result can be derived for holes by changing the energy dispersion relation \(E(k)\).

\section*{A.2 Fermi Golden Rule}

This section devotes to the derivation of time-dependent perturbation theory, also known as Fermi golden rule. The derivation can be divided into two parts, the first part is the general time-dependent perturbation, the second part is to apply the result of first part to the electromagnetic field.

**Time Dependent Perturbation**

Assume that we have some small time-dependent perturbation, \(\hat{H}'(t)\), to the Hamiltonian. We have \(\hat{H} = \hat{H}_0 + \hat{H}'(t)\), namely the time-dependent Schrödinger equation

\[
\hat{H}(t)|\psi(t)\rangle = i\hbar \frac{d}{dt}|\psi(t)\rangle. \tag{A.6}
\]

Given that \(|\phi_i(t)\rangle\) are the eigenstates of \(\hat{H}_0\), we have the expansion \(|\psi(t)\rangle = \sum a_i(t)|\phi_i(t)\rangle\). Therefore Equation (A.6) becomes

\[
\sum (a_i(t)\hat{H}_0|\phi_i(t)\rangle + a_i(t)\hat{H}'(t)|\phi_i(t)\rangle) = i\hbar \left( \sum (a_i(t)\frac{d}{dt}|\phi_i(t)\rangle + \frac{da_i(t)}{dt}|\phi_i(t)\rangle) \right), \tag{A.7}
\]

which can be reduced to

\[
i\hbar \sum \frac{da_i(t)}{dt} |\phi_i(t)\rangle = \sum a_i(t)\hat{H}'(t)|\phi_i(t)\rangle,
\]

because the first term on left hand side cancels the first term on right hand side of Equation (A.7). Note that the time dependence of wave function is simply a phase factor \(e^{-iE}\), where \(E\) is the energy of each non perturbed state. Therefore, together with the orthogonality of wave functions, we can further reduce Equation (A.7) to

\[
\frac{da_f(t)}{dt} = \frac{1}{i\hbar} \sum a_i \langle\phi_f|\hat{H}'|\phi_i\rangle e^{i(E_f - E_i)t},
\]

where \(f\) is any chosen state, which can be interpreted as final state after the perturbation with time \(t\). Therefore the probability density of the chosen final state is

\[
a_f(t) = \frac{1}{i\hbar} \int_0^t \langle\phi_f|\hat{H}'|\phi_i\rangle e^{i(E_f - E_i)t} dt \tag{A.8}
\]

\textsuperscript{3} It may be tricky to generalize 1-dimensional Fourier transform result to 3-dimension, but for this case, \(E(k)\) is parabolic, which means the notation \((-i\nabla)^2\) is still valid.

\textsuperscript{4} By performing Fourier transform, one may obtain \(\int_\Omega \tilde{\chi}(k)e^{ik\cdot r}dk = \chi(r)\)
Electromagnetic Absorption

Now, there are several assumptions to be made for the electromagnetic field:

1. Electromagnetic field does not affected by the charge carrier, meaning that we treat the electromagnetic field classically.

2. The wavelength of electromagnetic wave is much longer then a unit cell of the crystal, meaning that we have the frequency around visible light.

3. The energy of incident electromagnetic wave is weak, which means the perturbation procedure is applicable.

Combine all above assumptions together, we have the electric field as

\[ \mathbf{E}(\mathbf{r}, t) = \frac{2eE_0}{\omega} \cos(\mathbf{K} \cdot \mathbf{r} - \omega t), \]

where \( e \) is the polarization vector of the incident light and \( \mathbf{K} \) and \( \omega \) are the wave vector and angular frequency of electric field respectively. Without lose of generality, we choose the scalar potential to be zero. Furthermore, according to Maxwell equations, \( \mathbf{E} = -\frac{\partial}{\partial t} \mathbf{A} \), we have

\[ \mathbf{A}(\mathbf{r}, t) = \frac{2eE_0}{\omega} \sin(\mathbf{K} \cdot \mathbf{r} - \omega t), \]

where \( \mathbf{A} \) is the vector potential.

The Hamiltonian of electron in the crystal, with an external electromagnetic field, can be written as

\[
\hat{H} = \left( \frac{(\mathbf{p} + q \mathbf{A})^2}{2m} + V_{\text{per}}(\mathbf{r}) \right) \psi(\mathbf{r})
\]

\[
= \frac{p}{2m} + \frac{q}{2m} (\mathbf{A} \cdot \mathbf{p} + p \cdot \mathbf{A}) + \frac{q^2}{2m} A^2
\]

\[
\approx \hat{H}_{\text{per}} + \frac{q}{2m} (\mathbf{A} \cdot \mathbf{p})
\]

\[
= \hat{H}_0 + \frac{qE_0}{m\omega} \sin(\mathbf{K} \cdot \mathbf{r} - \omega t)
\]

because the Coulomb gauge is used, \( \nabla \cdot \mathbf{A} = 0 \), and \( \mathbf{A}^2 \approx 0 \). Therefore we have the perturbation Hamiltonian \( \hat{H}'(t) = \left( \frac{qE_0}{m\omega} \right) \sin(\mathbf{K} \cdot \mathbf{r} - \omega t) \), which gives the transition probability in Equation (A.8) as

\[
|a_f(t)|^2 = \frac{2\pi}{\hbar} \left( \frac{qE_0}{m\omega} \right)^2 |\langle \phi_f | \mathbf{e} \cdot \mathbf{p} | \phi_i \rangle|^2 \delta(E_f - E_i - \hbar\omega).
\]

Note that for QDs, only \( |\langle \phi_f | \mathbf{e} \cdot \mathbf{p} | \phi_i \rangle|^2 \) gives rise to different intensity, because all other factors are the same for all available transitions. This fact leads to

\[
I_{fi} \propto |\langle \phi_f | \mathbf{e} \cdot \mathbf{p} | \phi_i \rangle|^2,
\]

where \( I_{fi} = |a_f(t)|^2 \) is the probability, or intensity, of transition from \( |\phi_f \rangle \) to \( |\phi_i \rangle \).

Single-Band QDs

The transition probability can be further simplified under single-band approximation for interband transition of QDs. Consider the transition across the band gap, namely the creation of annihilation of exciton. Equation (A.9) becomes

\[
I_{fi} \propto \int_{QD} \chi_e^*(\mathbf{r}) u_{e,k}^*(\mathbf{r}) (\mathbf{e} \cdot \mathbf{p}) \chi_h(\mathbf{r}) u_{h,k}(\mathbf{r}) d\mathbf{r}
\]

\[
\approx \left( \sum_{QD} \chi_e^*(\mathbf{r}) \chi_h(\mathbf{r}) \right) \int_{cell} u_{e,k}^*(\mathbf{r}) (\mathbf{e} \cdot \mathbf{p}) \chi_h(\mathbf{r}) u_{h,k}(\mathbf{r}) d\mathbf{r}
\]

\[
\approx C \int_{QD} \chi_e^*(\mathbf{r}) \chi_h(\mathbf{r}) d\mathbf{r}.
\]

where \( \chi_e \) and \( \chi_h \) are the envelope functions of the recombining electron and hole respectively, and \( C = \int u_{e,k}^*(\mathbf{r}) (\mathbf{e} \cdot \mathbf{p}) u_{h,k}(\mathbf{r}) d\mathbf{r} \). In Equation (A.10), the first approximation is due to envelope functions are nearly constant in each unit cell, while the periodic parts of Bloch function \( u_k(\mathbf{r}) \) are not. This means that we can take the envelope functions out of the integration.

40
### A.3 Lagrange Minimization for CI

This section performs the minimization procedure using Lagrange multiplier technique. The derivation in this section is mainly follow Jensen’s book [26]. Minimizing the energy subjected to the constraint, we have the Lagrange function

\[
L = \langle \Psi_{CI} | \hat{H}_N | \Psi_{CI} \rangle - \epsilon (\langle \Psi_{CI} | \Psi_{CI} \rangle - N),
\]

(A.11)

where \( \hat{H}_N \) is the \( N \)-particle Hamiltonian in Equation (2.9) and \( \epsilon \) is the Lagrange multiplier.

Substitute Equation (2.5) into Equation (A.11), we have [26]

\[
L = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} a_i a_j \langle \Phi_i | \hat{H}_N | \Phi_j \rangle - \epsilon a_i a_j \langle \Phi_i | \Phi_j \rangle + \epsilon N.
\]

(A.12)

The zero derivative of Lagrange function with respect to each \( a_i \) gives the minimum subjected to the constraint. Therefore we have

\[
\frac{\partial L}{\partial a_i} = -2a_i \epsilon + 2 \sum_{j=1}^{\infty} a_j \langle \Phi_i | \hat{H}_N | \Phi_j \rangle = 0,
\]

which can be reduced to

\[
\sum_{j=1}^{\infty} a_j \langle \Phi_i | \hat{H}_N | \Phi_j \rangle = a_i \epsilon, \quad \text{for all } a_i.
\]

(A.13)

Equation (A.13) can be expressed in the matrix form

\[
\begin{pmatrix}
H_{11} & H_{12} & \cdots & H_{1j} & \cdots \\
H_{21} & H_{22} & \cdots & H_{2j} & \cdots \\
\vdots & \vdots & \ddots & \vdots & \cdots \\
H_{j1} & H_{j2} & \cdots & H_{jj} & \cdots \\
\vdots & \vdots & \ddots & \vdots & \cdots
\end{pmatrix}
\begin{pmatrix}
a_1 \\
a_2 \\
\vdots \\
a_j \\
\vdots
\end{pmatrix} = \epsilon
\begin{pmatrix}
a_1 \\
a_2 \\
\vdots \\
a_j \\
\vdots
\end{pmatrix},
\]

(A.14a)

\[
\hat{H}_{CI} a = \epsilon a,
\]

(A.14b)

where \( H_{ij} = \langle \Phi_i | \hat{H}_N | \Phi_j \rangle \). That is, the CI state can be obtained by diagonalizing the CI matrix \( \hat{H}_{CI} \) and the Lagrange multiplier is the corresponding energy of each CI state. The important result is that the Lagrange multiplier can be interpreted as the energy of the CI state.

### A.4 One- and Two-Particle Operators

This section focuses on the one-particle and two-particle operator representation using second quantization formalism. The same results can be concluded for electron and hole, only electron is considered for simplicity. Therefore we have the state vector written as \( |\phi\rangle \) instead of \( |\phi\rangle_e \).

**Creation and Annihilation Operators**

Lets start with creation and annihilation operators. In order to express many electron system, creation operators\(^5\) \((\hat{e}_i^\dagger)\) and annihilation operators \((\hat{e}_i)\) are used. They operate as follow

\[
\hat{e}_i^\dagger |n_1, n_2, \cdots, n_i, \cdots\rangle = \begin{cases} 0, & \text{if } n_i = 1, \\ (-1)^{n_i} |n_1, n_2, \cdots, n_i + 1, \cdots\rangle, & \text{if } n_i = 0, \end{cases}
\]

(A.15a)

\[
\hat{e}_i |n_1, n_2, \cdots, n_i, \cdots\rangle = \begin{cases} 0, & \text{if } n_i = 0, \\ (-1)^{n_i} |n_1, n_2, \cdots, n_i - 1, \cdots\rangle, & \text{if } n_i = 1, \end{cases}
\]

(A.15b)

\(^5\) Creation (annihilation) operators for hole are \( \hat{h}_i^\dagger \) (\( \hat{h}_i \)). Note that \((\hat{e}_i)^\dagger = (\hat{e}_i^\dagger)^*\) is the adjoint operator.
where

\[ c_i = \sum_{j=1}^{i-1} n_j, \quad \text{and} \quad a_i = \sum_{j=1}^{i-1} n_j, \]

are used to represent the antisymmetry of electron\(^6\). Combine Equation (2.7) and Equation (A.15), \( N \) particle state \(|\Phi_N\rangle\) can be written as

\[ |\Phi_N\rangle = \left((\hat{e}_1^\dagger)^{n_1}(\hat{e}_2^\dagger)^{n_2} \cdots (\hat{e}_N^\dagger)^{n_N}\right) |0,0,\ldots,0\rangle. \]

The antisymmetry nature of electron is included by

\[ (\hat{e}_i^\dagger \hat{e}_j^\dagger) |\Psi_{N-2}\rangle = -(\hat{e}_j^\dagger \hat{e}_i^\dagger) |\Psi_{N-2}\rangle \]

### Basis Transformation

It is possible to derive basis transformation using second quantization formalism. For single particle Hilbert space, when we express some specific state \(|\psi_{i_0}\rangle = \hat{e}_{i_0}^\dagger |0\rangle\) using the basis \(|\phi_j\rangle = \hat{e}_j^\dagger |0\rangle\), we have

\[ \hat{e}_{i_0}^\dagger |0\rangle = |\psi_{i_0}\rangle = \sum_j \langle \phi_j |\psi_{i_0}\rangle |\phi_j\rangle = \sum_j \langle T_{j\ i_0} \rangle \hat{e}_j^\dagger |0\rangle, \]

where \( T_{j\ i_0} = \langle \phi_j |\psi_{i_0}\rangle \). In other words, creation and annihilation operators can be seen as basis of single particle state, with the transformation

\[ \hat{e}_{i_0}^\dagger = \sum_j \langle T_{j\ i_0} \rangle \hat{e}_j^\dagger. \]  

(A.16)

It is similar for two-particle Fock space, any specific two-particle state \(|\psi_{i_0\ j_0}\rangle = \hat{e}_{i_0}^\dagger \hat{e}_{j_0}^\dagger |0\rangle\) can be expanded in terms of a complete basis \(|\phi_{kl}\rangle = \hat{e}_k^\dagger \hat{e}_l^\dagger |0\rangle\). That is

\[ \hat{e}_{i_0}^\dagger \hat{e}_{j_0}^\dagger |0\rangle = |\psi_{i_0\ j_0}\rangle = \sum_{k,l} \langle \phi_{kl} |\psi_{i_0\ j_0}\rangle |\phi_{kl}\rangle = \sum_{k,l} T_{kl\ i_0\ j_0} \hat{e}_k^\dagger \hat{e}_l^\dagger |0\rangle, \]

where \( T_{kl\ i_0\ j_0} = \langle \phi_{kl} |\psi_{i_0\ j_0}\rangle \). Therefore the similar result is obtained

\[ \hat{e}_{i_0}^\dagger \hat{e}_{j_0}^\dagger = \sum_{k,l} T_{kl\ i_0\ j_0} \hat{e}_k^\dagger \hat{e}_l^\dagger. \]  

(A.17)

### Single-Particle Operators

Using the notation of creation and annihilation operators, single-particle operator or two-particle operator can be considered as scattering between different states. For single particle Hamiltonian \( \hat{H} \) with eigenstate \(|\psi_i\rangle\), we have \( \hat{H} |\psi_i\rangle = E_i |\psi_i\rangle \), where \( E_i \) is the eigenvalue of \(|\psi_i\rangle\). Therefore, in Dirac notation, the Hamiltonian can be written as

\[ \hat{H} = \sum_i |\psi_i\rangle E_i \langle \psi_i| = \sum_i E_i \hat{e}_i^\dagger \hat{e}_i. \]  

(A.18)

\(^6\) For the case that \( i = 1 \), both \( c^i \) and \( a^i \) are zero.
In general, basis transformation, Equation (A.16), may be used for the state that is the eigenstate. Equation (A.18) becomes\footnote{\(T_{j,0}\) is defined orbital integration \(\langle \phi_j | \psi_{i0} \rangle\). Similarly, \(T_{i0j}^*\) is defined as \(\langle \psi_{i0} | \phi_j \rangle\).} \cite{27}

\[
\hat{H} = \sum_i E_i \left( \sum_j T_{ji} \hat{e}_j \right) \left( \sum_k T_{ik}^* \hat{e}_k \right) \\
= \sum_{j,k} \hat{e}_j^\dagger \hat{e}_k \sum_i T_{ji} E_i T_{ik}^* \\
= \sum_{j,k} \hat{e}_j^\dagger \hat{e}_k \sum_i \langle \phi_j | \psi_i \rangle E_i \langle \psi_i | \phi_k \rangle \\
= \sum_{j,k} \langle \phi_j | \hat{H} | \phi_k \rangle \hat{e}_j^\dagger \hat{e}_k \\
= \sum_{j,k} H_{jk} \hat{e}_j^\dagger \hat{e}_k, \tag{A.19}
\]

where \(\hat{H} = \sum_i |\psi_i \rangle E_i \langle \psi_i|\) from Equation (A.18) and \(H_{jk} = \langle \phi_j | \hat{H} | \phi_k \rangle\). Note that one-particle operator depends only on the matrix elements \(H_{jk}\) and paricle operators \(\hat{e}_j^\dagger \hat{e}_k\).

**Two-Particle Operator**

The similar result can be obtained for two-particle operator. It is reasonable to start with Coulomb interaction, \(\hat{H}_C = \frac{1}{|r_i - r_j|}\), its two-particle eigenstates \(|\psi^C_{ij} \rangle = \hat{e}_i^\dagger \hat{e}_j^\dagger |0 \rangle\), and the related eigenvalues \(V^C_{ij}\). Therefore we have the eigenvalue equation \(\hat{H}_C |\psi^C_{ij} \rangle = V^C_{ij} |\psi^C_{ij} \rangle\). Note that all the two-particle eigenstates form a complete basis of two-particle Fock space. In analogy Equation (A.18) we have

\[
\hat{H}_C = \sum_{i,j} V^C_{ij} \langle \psi^C_{ij} | \psi^C_{ij} \rangle = \sum_{i,j} \hat{e}_i^\dagger \hat{e}_j^\dagger \hat{e}_j \hat{e}_i V^C_{ij} \tag{A.20}
\]

By expanding in terms of a general basis \(|\phi_{kl} \rangle\), we obtain

\[
\hat{H}_C = \sum_{i,j} V^C_{ij} \left( \sum_{p,q} T^C_{pqij} \hat{e}_p^\dagger \hat{e}_q \right) \left( \sum_{r,s} T^C_{jirs} \hat{e}_r \hat{e}_s \right) \\
= \sum_{p,q,r,s} \hat{e}_p^\dagger \hat{e}_q^\dagger \hat{e}_r \hat{e}_s \sum_{i,j} T^C_{pqij} T^C_{jirs}^* \\
= \sum_{p,q,r,s} V^C_{pqrs} \hat{e}_p^\dagger \hat{e}_q^\dagger \hat{e}_r \hat{e}_s, \tag{A.21}
\]

where \(V^C_{pqrs} = \langle \phi_{pq} | \hat{H}_C | \phi_{rs} \rangle\) is the Coulomb matrix element.
Appendix B

Finite Difference Equation

Finite difference equations are used to solve single particle Schrödinger equation, which is a second order differential equation.

B.1 1D Case

Although all the QD models are either 2D or 3D cases, 1D finite difference equation contains fundamental concepts, which is necessary to be introduced. By the definition of differentiation, the first derivative of a differentiable function \( f(x) \) is

\[
 f'(x) = \lim_{\delta x \to 0} \frac{f(x + \delta x) - f(x)}{\delta x}.
\]

In order to do the numerical calculation, it is reasonable to introduce a set of uniformly separated\(^1\) finite points \( \{x_i : i = 1 \sim N\} \), where \( N \) is some finite number. We can define \( f_i = f(x_i) \). Therefore, the differentiation can be approximated by

\[
 f'_i = f'(x_i) \approx \frac{f_{i+1} - f_{i}}{\Delta}, \text{ for } 1 \leq i \leq N - 1. \tag{B.1}
\]

Equation (B.1) is the finite difference equation of function \( f(x) \). It can be easily extended to second derivative \( f''(x) \). Second derivative is defined as

\[
 f''(x) = \lim_{\delta x \to 0} \frac{f'(x) - f'(x - \delta x)}{\delta x}.
\]

Insert Equation (B.1) into this definition, it becomes

\[
 f''_i = f''(x_i) \approx \frac{f'_i - f'_{i-1}}{\Delta} = \frac{f_{i+1} - 2f_i + f_{i-1}}{\Delta^2}, \text{ for } 2 \leq i \leq N - 1. \tag{B.2}
\]

Note that \( f_1 \) and \( f_N \) are the boundary condition of \( f(x) \). For Dirichlet condition, \( f_1 = f_N = 0 \).

If we define \( \mathbf{f'} = (f_1', f_2', \cdots, f_N') \) and \( \mathbf{f} = (f_1, f_2, \cdots, f_N) \) it is easier to express Equation (B.2) as matrix form for Dirichlet condition.

\[
 \hat{D}_N \mathbf{f} = \begin{bmatrix}
 -2 & 1 & 0 \\
 1 & -2 & \ddots \\
 \vdots & \ddots & \ddots & 1 \\
 0 & 1 & -2 \\
 \end{bmatrix} \begin{bmatrix}
 f_1 \\
 f_2 \\
 \vdots \\
 f_N \\
 \end{bmatrix} = \begin{bmatrix}
 f_1'' \\
 f_2'' \\
 \vdots \\
 f_N'' \\
 \end{bmatrix}, \quad \text{(B.3)}
\]

\(^1\) Uniformly separated means \( x_i - x_{i-1} = \Delta, \forall i = 2 \sim N \).
where $\hat{D}_N$ is the $N$-dimensional second order differential operator. For the case of Schrödinger equation $-\hbar^2/2m \frac{d}{dx} \psi(x) + V(x) = E\psi(x)$, we have

$$\hat{H}\psi = \begin{pmatrix} -2c + V_1 & c & 0 & & & & \\ c & -2c + V_2 & \ddots & & & & \\ & \ddots & \ddots & c & & & \\ 0 & c & -2c + V_N \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \vdots \\ \psi_N \end{pmatrix} = E \begin{pmatrix} \psi_1 \\ \psi_2 \\ \vdots \\ \psi_N \end{pmatrix},$$

(B.4)

where $c = -\left(\frac{\hbar^2}{2m}\right)$. This equation can be solved by diagonalizing the Hamiltonian $\hat{H}$.

### B.2 2D and 3D Cases

For 2D case, for a two-dimensional differentiable function $f : \mathbb{R}^2 \mapsto \mathbb{R}$. We need only the definition of partial derivative in $x$ and $y$ directions, which is

$$\frac{\partial}{\partial x} f(x,y) = \lim_{\delta x \to 0} \frac{f(x + \delta x, y) - f(x, y)}{\delta x}.$$

For a rectangular domain, the similar procedure as in 1D case can be applied. Consider a four by four grid, define the function values on the grid as $f_i = f(r_i)$, as shown in Figure B.1.

Figure B.1: function grid

The only difference from 1D case is at the boundary. Note that there are twelve boundary values for 2D, instead of two boundary values for 1D. The boundary conditions are summarized in Table B.1.

Therefore, the $16 \times 16$ finite difference matrix can be written as

$$\hat{D}_{xx} = \left(\frac{1}{\Delta x^2}\right) \begin{pmatrix} \hat{D}_4 & 0 \\ 0 & \hat{D}_4 \end{pmatrix},$$

(B.5)

$$\hat{D}_{yy} = \left(\frac{1}{\Delta y^2}\right) \begin{pmatrix} \hat{I}_4 & -2\hat{I}_4 & 0 \\ -2\hat{I}_4 & \hat{I}_4 & 0 \\ 0 & 0 & \hat{I}_4 \end{pmatrix},$$

where $\hat{I}_4$ is the second order differential operator $\partial^2/\partial x^2$.

2All the values are multiplied with $\Delta x^2$ (or $\Delta y^2$) to simplify the notations.
Table B.1: List of Dirichlet boundary conditions for x-direction and y-direction at twelve boundary points in Figure B.1.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta x^2 \frac{\partial^2}{\partial x^2}$</th>
<th>$\Delta y^2 \frac{\partial^2}{\partial y^2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\partial_{xx} f_1$</td>
<td>$-f_1 + f_2$</td>
<td>$\partial_{yy} f_1$</td>
</tr>
<tr>
<td>$\partial_{xx} f_4$</td>
<td>$f_3 - f_4$</td>
<td>$\partial_{yy} f_2$</td>
</tr>
<tr>
<td>$\partial_{xx} f_5$</td>
<td>$-f_5 + f_6$</td>
<td>$\partial_{yy} f_3$</td>
</tr>
<tr>
<td>$\partial_{xx} f_8$</td>
<td>$f_7 - f_8$</td>
<td>$\partial_{yy} f_4$</td>
</tr>
<tr>
<td>$\partial_{xx} f_9$</td>
<td>$-f_9 + f_{10}$</td>
<td>$\partial_{yy} f_{13}$</td>
</tr>
<tr>
<td>$\partial_{xx} f_{12}$</td>
<td>$f_{11} - f_{12}$</td>
<td>$\partial_{yy} f_{14}$</td>
</tr>
<tr>
<td>$\partial_{xx} f_{13}$</td>
<td>$-f_{13} + f_{14}$</td>
<td>$\partial_{yy} f_{15}$</td>
</tr>
<tr>
<td>$\partial_{xx} f_{16}$</td>
<td>$f_{16} - f_{16}$</td>
<td>$\partial_{yy} f_{16}$</td>
</tr>
</tbody>
</table>

where $\hat{D}_4$ is defined in Equation (B.3), and $\hat{I}_4$ is the four-dimensional identity matrix. In general, for N-grid, Equation (B.5) can be written in Matlab script code as

$$D_{xx} = dx^2 \cdot \text{kron(eye(N), Dn(N))},$$
$$D_{yy} = dy^2 \cdot \text{kron(Dn(N), eye(N))},$$

where $dx^2 = \frac{1}{\Delta x^2}$ ($N = 4$ for the case of Figure B.1).

The similar argument can again applied to 3D case. By extending the argument of boundary condition, One may obtain the final result as

$$D_{xx} = dx^2 \cdot \text{kron(eye(N2), Dn(N))},$$
$$D_{yy} = dy^2 \cdot \text{kron(eye(N), kron(Kn(N), eye(N)))},$$
$$D_{zz} = dz^2 \cdot \text{kron(Kn(N), eye(N2))},$$

where $N2 = N^2$. 
Appendix C

Coulomb Matrix Elements

C.1 Coulomb Integral

The Coulomb matrix elements $V_{ijkl}$, are calculated by the integrals in Equation (2.10). The actual calculations were carried out by Fourier convolution [19], with the following definitions:

$$f(r - r') = \frac{1}{|r - r'|} \xrightarrow{F} \tilde{f}(k),$$
$$g(r) = \phi^*_j(r') \phi_k(r') \xrightarrow{F} \tilde{g}(k),$$

where $\tilde{f}(k)$ and $\tilde{g}(k)$ are the Fourier transform of $f(r)$ and $g(r)$ respectively. From the above definition, we have the Fourier convolution $\tilde{C}(k) = \tilde{f}(k)\tilde{g}(k)$. Therefore the Coulomb integral can be written as

$$V_{ijkl}^{ee} = \int \phi^*_i(r)C(r)\phi_l(r)d^3r,$$

where $C(r)$ is the inverse Fourier transform of $\tilde{C}(k)$.

C.2 Comparison with Analytical Results

Because the Harmonic oscillator can be solved analytically, there is a simple analytical expression for each direct and exchange Coulomb matrix element of symmetric QD, as the work done by Warburton et al [21]. We compare those matrix elements are used in the present thesis work with the analytical one. Note that the single particle orbital basis used in Warburton et al are $\{|s\}, |p_-\rangle, |p_+\rangle\}$ instead of $\{|s\}, |p_x\rangle, |p_y\rangle\}$, where $|p_{\pm}\rangle = \frac{1}{\sqrt{2}}(|p_x\rangle \pm i|p_y\rangle)$. In this section, we use $\alpha, \beta, \gamma$ to denote the orbital $s, p_-, \text{and} p_+$ respectively. The values are presented in the unit of $V_{\alpha\alpha d}^{ee}$. For simplicity, the symmetric terms are omitted, for example, we use $(\beta, \beta, \beta, \beta)$ to denote $V_{\beta\beta\beta\beta}^{ee} = V_{\gamma\gamma\gamma\gamma}^{ee}$.

C.3 Tables of Numerical Values

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\footnote{We consider only the electron-electron part because all other paired interactions are similar to electron-electron part}
### Table C.1: The comparison between analytical and numerical results of direct and exchange interactions. The analytical values are obtained from the expression of the work done by Warburton et al, with effective length $l_e = 5.70$ nm and $l_h = 8.60$ nm.

<table>
<thead>
<tr>
<th>$V_{ijkl}^{ee}$</th>
<th>Analytical results</th>
<th>Numerical results</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\alpha, \beta, \beta, \alpha)$</td>
<td>0.750</td>
<td>0.762</td>
<td>1.60 %</td>
</tr>
<tr>
<td>$(\beta, \beta, \beta, \beta)$</td>
<td>0.688</td>
<td>0.697</td>
<td>1.29 %</td>
</tr>
<tr>
<td>$(\alpha, \beta, \alpha, \beta)$</td>
<td>0.250</td>
<td>0.240</td>
<td>-3.96 %</td>
</tr>
<tr>
<td>$(\beta, \gamma, \beta, \gamma)$</td>
<td>0.188</td>
<td>0.174</td>
<td>-7.23 %</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$V_{ijkl}^{hh}$</th>
<th>Analytical results</th>
<th>Numerical results</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\alpha, \beta, \beta, \alpha)$</td>
<td>0.750</td>
<td>0.778</td>
<td>3.75 %</td>
</tr>
<tr>
<td>$(\beta, \beta, \beta, \beta)$</td>
<td>0.688</td>
<td>0.632</td>
<td>1.29 %</td>
</tr>
<tr>
<td>$(\alpha, \beta, \alpha, \beta)$</td>
<td>0.250</td>
<td>0.236</td>
<td>-5.60 %</td>
</tr>
<tr>
<td>$(\beta, \gamma, \beta, \gamma)$</td>
<td>0.188</td>
<td>0.168</td>
<td>-10.53 %</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$V_{ijkl}^{eh}$</th>
<th>Analytical results</th>
<th>Numerical results</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\alpha, \beta, \beta, \alpha)$</td>
<td>0.653</td>
<td>0.670</td>
<td>2.65 %</td>
</tr>
<tr>
<td>$(\beta, \beta, \beta, \beta)$</td>
<td>0.659</td>
<td>0.669</td>
<td>1.56 %</td>
</tr>
</tbody>
</table>

### Table C.2: The numerical values of symmetric QD, $a_y = 1.00$, from 2D model. The notation of Equation (4.2) is used, namely $a = (1, 2)$, $b = (3, 4)$, and $c = (5, 6)$

<table>
<thead>
<tr>
<th>$V_{ijkl}^{ee}$</th>
<th>2D model</th>
<th>$a_y = 1.00$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Direct}$</td>
<td>meV</td>
<td>Exchange and Others</td>
</tr>
<tr>
<td>$(a,a,a,a)$</td>
<td>15.388</td>
<td>(a,b,a,b),(b,a,b,a)</td>
</tr>
<tr>
<td>$(a,b,b,a),(b,a,a,b)$</td>
<td>11.726</td>
<td>(a,c,a,c),(c,a,c,a)</td>
</tr>
<tr>
<td>$(a,c,c,a),(c,a,a,c)$</td>
<td>11.726</td>
<td>(b,c,b,c),(c,b,c,b)</td>
</tr>
<tr>
<td>$(b,b,b,b)$</td>
<td>12.074</td>
<td>(a,a,b,b),(b,b,a,a)</td>
</tr>
<tr>
<td>$(b,c,c,b),(c,b,b,c)$</td>
<td>9.373</td>
<td>(a,a,c,c),(c,c,a,a)</td>
</tr>
<tr>
<td>$(c,c,c,c)$</td>
<td>12.074</td>
<td>(b,b,c,c),(c,c,b,c)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$V_{ijkl}^{hh}$</th>
<th>2D model</th>
<th>$a_y = 1.00$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Direct}$</td>
<td>meV</td>
<td>Exchange and Others</td>
</tr>
<tr>
<td>$(a,a,a,a)$</td>
<td>10.317</td>
<td>(a,b,a,b),(b,a,b,a)</td>
</tr>
<tr>
<td>$(a,b,b,a),(b,a,a,b)$</td>
<td>7.816</td>
<td>(a,c,a,c),(c,a,c,a)</td>
</tr>
<tr>
<td>$(a,c,c,a),(c,a,a,c)$</td>
<td>7.816</td>
<td>(b,c,b,c),(c,b,c,b)</td>
</tr>
<tr>
<td>$(b,b,b,b)$</td>
<td>8.079</td>
<td>(a,a,b,b),(b,b,a,a)</td>
</tr>
<tr>
<td>$(b,c,c,b),(c,b,b,c)$</td>
<td>6.229</td>
<td>(a,a,c,c),(c,c,a,a)</td>
</tr>
<tr>
<td>$(c,c,c,c)$</td>
<td>8.079</td>
<td>(b,b,c,c),(c,c,b,c)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$V_{ijkl}^{eh}$</th>
<th>2D model</th>
<th>$a_y = 1.00$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Direct}$</td>
<td>meV</td>
<td>Exchange and Others</td>
</tr>
<tr>
<td>$(a,a,a,a)$</td>
<td>12.111</td>
<td>(a,b,a,b),(b,a,b,a)</td>
</tr>
<tr>
<td>$(a,b,b,a),(b,a,a,b)$</td>
<td>8.045</td>
<td>(a,c,a,c),(c,a,c,a)</td>
</tr>
<tr>
<td>$(a,c,c,a),(c,a,a,c)$</td>
<td>8.045</td>
<td>(b,c,b,c),(c,b,c,b)</td>
</tr>
<tr>
<td>$(b,b,b,b)$</td>
<td>8.993</td>
<td>(a,a,b,b),(b,b,a,a)</td>
</tr>
<tr>
<td>$(b,c,c,b),(c,b,b,c)$</td>
<td>7.169</td>
<td>(a,a,c,c),(c,c,a,a)</td>
</tr>
<tr>
<td>$(c,c,c,c)$</td>
<td>8.993</td>
<td>(b,b,c,c),(c,c,b,b)</td>
</tr>
</tbody>
</table>

$E_s^{ee}$ 34.856 $E_s^{hh}$ 9.981
$E_{ps}^{ee}$ 69.559 $E_{ps}^{hh}$ 19.943
$E_p^{ee}$ 69.559 $E_p^{hh}$ 19.943
Table C.3: The numerical values of typical asymmetric QD, $a_y = 1.05$, for 2D model. The notation of Equation (4.2) is used, namely $a = (1, 2)$, $b = (3, 4)$, and $c = (5, 6)$

<table>
<thead>
<tr>
<th>$V_{ijkl}^{ee}$</th>
<th>Direct</th>
<th>2D model</th>
<th>$a_y = 1.05$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>meV</td>
<td>Exchange and Others</td>
<td>meV</td>
</tr>
<tr>
<td>(a,a,a,a)</td>
<td>15.478</td>
<td>(a,b,a,b),(b,a,b,a)</td>
<td>3.728</td>
</tr>
<tr>
<td>(a,b,b,a),(b,a,a,b)</td>
<td>11.783</td>
<td>(a,c,a,c),(c,a,c,a)</td>
<td>3.703</td>
</tr>
<tr>
<td>(a,c,c,a),(c,a,a,c)</td>
<td>11.809</td>
<td>(b,c,b,c),(c,b,c,b)</td>
<td>1.358</td>
</tr>
<tr>
<td>(b,b,b,b)</td>
<td>12.122</td>
<td>(a,a,b,b),(b,b,a,a)</td>
<td>3.728</td>
</tr>
<tr>
<td>(b,c,c,b),(c,b,b,c)</td>
<td>9.448</td>
<td>(a,a,c,c),(c,c,a,a)</td>
<td>3.703</td>
</tr>
<tr>
<td>(c,c,c,c)</td>
<td>12.135</td>
<td>(b,b,c,c),(c,c,b,b)</td>
<td>1.358</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$V_{ijkl}^{hh}$</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>meV</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a,a,a,a)</td>
<td>10.379</td>
<td>(a,b,a,b),(b,a,b,a)</td>
<td>2.533</td>
</tr>
<tr>
<td>(a,b,b,a),(b,a,a,b)</td>
<td>7.855</td>
<td>(a,c,a,c),(c,a,c,a)</td>
<td>2.517</td>
</tr>
<tr>
<td>(a,c,c,a),(c,a,a,c)</td>
<td>7.872</td>
<td>(b,c,b,c),(c,b,c,b)</td>
<td>0.930</td>
</tr>
<tr>
<td>(b,b,b,b)</td>
<td>8.118</td>
<td>(a,a,b,b),(b,b,a,a)</td>
<td>2.533</td>
</tr>
<tr>
<td>(b,c,c,b),(c,b,b,c)</td>
<td>6.272</td>
<td>(a,a,c,c),(c,c,a,a)</td>
<td>2.517</td>
</tr>
<tr>
<td>(c,c,c,c)</td>
<td>8.126</td>
<td>(b,b,c,c),(c,c,b,b)</td>
<td>0.930</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$V_{ijkl}^{eh}$</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>meV</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a,a,a,a)</td>
<td>12.183</td>
<td>(a,b,a,b),(b,a,b,a)</td>
<td>2.723</td>
</tr>
<tr>
<td>(a,b,b,a),(b,a,a,b)</td>
<td>8.080</td>
<td>(a,c,a,c),(c,a,c,a)</td>
<td>2.705</td>
</tr>
<tr>
<td>(a,c,c,a),(c,a,a,c)</td>
<td>8.107</td>
<td>(b,c,b,c),(c,b,c,b)</td>
<td>0.917</td>
</tr>
<tr>
<td>(b,b,b,b)</td>
<td>9.031</td>
<td>(a,a,b,b),(b,b,a,a)</td>
<td>2.723</td>
</tr>
<tr>
<td>(b,c,c,b),(c,b,b,c)</td>
<td>7.229</td>
<td>(a,a,c,c),(c,c,a,a)</td>
<td>2.705</td>
</tr>
<tr>
<td>(c,c,c,c)</td>
<td>9.045</td>
<td>(b,b,c,c),(c,c,b,b)</td>
<td>0.917</td>
</tr>
</tbody>
</table>

| $E^s_s$          | 35.285 | $E^h_s$  | 10.104       |
| $E^c_s$          | 69.987 | $E^h_c$  | 20.066       |
| $E^s_p$          | 70.837 | $E^h_p$  | 20.311       |
Table C.4: The numerical values of symmetric QD, $a_y = 1.00$, from 3D model. The notation of Equation (4.2) is used, namely $a = (1,2)$, $b = (3,4)$, and $c = (5,6)$.

<table>
<thead>
<tr>
<th>$V_{ijkl}^{ee}$</th>
<th>3D model</th>
<th>$a_y = 1.00$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct</td>
<td>meV</td>
<td>Exchange and Others</td>
</tr>
<tr>
<td>(a,a,a,a)</td>
<td>35.691</td>
<td>(a,b,a,b),(b,a,b,a)</td>
</tr>
<tr>
<td>(a,b,b,a),(b,a,a,b)</td>
<td>30.836</td>
<td>(a,c,a,c),(c,a,c,a)</td>
</tr>
<tr>
<td>(a,c,c,a),(c,a,a,c)</td>
<td>30.836</td>
<td>(b,c,b,c),(b,c,b,c)</td>
</tr>
<tr>
<td>(b,b,b,b)</td>
<td>31.472</td>
<td>(a,a,b,b),(b,b,a,a)</td>
</tr>
<tr>
<td>(b,c,c,b),(c,b,b,c)</td>
<td>26.648</td>
<td>(a,a,c,c),(c,c,a,a)</td>
</tr>
<tr>
<td>(c,c,c,c)</td>
<td>31.472</td>
<td>(b,b,c,c),(c,c,b,b)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$V_{ijkl}^{hh}$</th>
<th>Special 3D terms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct</td>
<td>meV</td>
</tr>
<tr>
<td>(a,a,a,a)</td>
<td>41.326</td>
</tr>
<tr>
<td>(a,b,b,a),(b,a,a,b)</td>
<td>39.181</td>
</tr>
<tr>
<td>(a,c,c,a),(c,a,a,c)</td>
<td>-</td>
</tr>
<tr>
<td>(b,b,b,b)</td>
<td>38.429</td>
</tr>
<tr>
<td>(b,c,c,b),(c,b,b,c)</td>
<td>-</td>
</tr>
<tr>
<td>(c,c,c,c)</td>
<td>-</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$V_{ijkl}^{eh}$</th>
<th>meV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct</td>
<td>meV</td>
</tr>
<tr>
<td>(a,b,a,a),(a,a,b,a)</td>
<td>38.041</td>
</tr>
<tr>
<td>(a,c,a,a)</td>
<td>32.999</td>
</tr>
<tr>
<td>(b,b,b,b)</td>
<td>31.386</td>
</tr>
<tr>
<td>(c,b,c)</td>
<td>31.386</td>
</tr>
<tr>
<td>(c,c,c)</td>
<td>-</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$E_e$</th>
<th>$E_h$</th>
<th>$E_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_s^e$</td>
<td>72.588</td>
<td>$E_s^h$</td>
</tr>
<tr>
<td>$E_p^e$</td>
<td>109.510</td>
<td>$E_p^h$</td>
</tr>
<tr>
<td>$E_{p_y}^e$</td>
<td>109.510</td>
<td>$E_{p_y}^h$</td>
</tr>
</tbody>
</table>
Table C.5: The numerical values of typical asymmetric QD, $a_y = 1.05$, from 3D model. The notation of Equation (4.2) is used, namely $a = (1, 2)$, $b = (3, 4)$, and $c = (5, 6)$

<table>
<thead>
<tr>
<th>$V_{ijkl}^{ee}$</th>
<th>Direct</th>
<th>meV</th>
<th>3D model</th>
<th>Exchange and Others</th>
<th>meV</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a,a,a,a)</td>
<td>35.713</td>
<td>(a,b,a,b),(b,a,b,a)</td>
<td>7.642</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a,b,b,a),(b,a,a,b)</td>
<td>30.849</td>
<td>(a,c,a,c),(c,a,c,a)</td>
<td>7.614</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a,c,c,a),(c,a,a,c)</td>
<td>30.838</td>
<td>(b,c,b,c),(c,b,c,b)</td>
<td>2.417</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b,b,b,b)</td>
<td>31.462</td>
<td>(a,a,b,b),(b,a,b,a)</td>
<td>7.642</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b,c,b),(c,b,b,c)</td>
<td>26.673</td>
<td>(a,a,c),(c,c,a,a)</td>
<td>7.614</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(c,c,c,c)</td>
<td>31.442</td>
<td>(b,b,c,c),(c,c,b,b)</td>
<td>2.417</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$V_{ijkl}^{hh}$</th>
<th>Special 3D terms</th>
</tr>
</thead>
<tbody>
<tr>
<td>(b,a,a,a),(a,b,a,a)</td>
<td>1.313 (a,b,b),(b,a,b,b)</td>
</tr>
<tr>
<td>(a,a,a,a),(a,a,a,b)</td>
<td>3.8043 (a,b,a,b),(b,a,b,a)</td>
</tr>
<tr>
<td>(c,a,a,c)</td>
<td>32.304 (b,c,b),(c,b,c,b)</td>
</tr>
<tr>
<td>(b,b,b,b)</td>
<td>31.383 (a,a,b),(b,a,b,a)</td>
</tr>
<tr>
<td>(c,b,b,c)</td>
<td>31.391 (a,a,c),(c,a,c,a)</td>
</tr>
<tr>
<td>(c,c,c,c)</td>
<td>- (b,c,b),(c,b,c,b)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$V_{ijkl}^{eh}$</th>
<th>Special 3D terms</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a,b,a,a),(a,a,b,a)</td>
<td>0.782 (b,a,b),(b,b,a,b)</td>
</tr>
</tbody>
</table>

| $E_{es}$ | 72.710 | $E_{eh}$ | 28.280 |
| $E_{es}$ | 109.608 | $E_{hp}$ | 43.213 |
| $E_{ps}$ | 109.794 | $E_{ps}$ | 51 |
Appendix D

Flow Diagrams

This section includes some of the main subroutines flow diagrams. In FlowDiagram and DataStorage the structures of the stored data are shown on the right hand side. On the left hand side, the main loop with input parameters and three subroutines are shown. The three subroutines are getQDD, CI, and getSpectra. A detailed flow diagram of each of these subroutines is shown in the successive pages.

getQDD

Single particle states are calculated in this subroutine, as well as Coulomb matrix elements. The material properties and the symmetry are the input parameters. QDD represents the QD Data, including the second quantized basis and the QD information. QD information means the energies and the wave functions of single particle states, Coulomb matrix elements, and envelope integration of electron-hole recombinations.

CI

Generation of CI Hamiltonian and dipole operators, this subroutine is the core of the calculation in the present thesis. The calculation time for a full Hamiltonian of a single QD is about 10 hours. eN and hN denote the particle configurations, for example (eN, hN) = (3, 1) means the \( X^{2-} \) system.

getSpectra and spectrumPlot

The data of spectra, namely the position and intensity of each peak. The spectrum for each particle configuration of a given QD is plot by spectrumPlot.
INPUT (red):
- Range of asymmetric parameter, min : d : MAX
- Number of considered energy states, energyLevels
- Size of QD (optional) : size_nm
- Grid resolution (optional) : res_nm

Subroutine: getQDD
Data: QDD
Subroutine: CI
Optional input: chargedLevel, maxParticles
Data: CIOUT
Subroutine: getSpectra
Data: Spectra
Subroutine: spectrumPlot

QDD.basis.vectors[eN,hN]=[1,0,0,1,0,1:1,1,0,0,0]
configuration[ith_basis,eN,hN]=[-0.5, -0.5]
QDD.QD[ay].ay
eE(1:energyLevels)
hE(1:energyLevels)
eWF(1:energyLevels)
hWF(1:energyLevels)
Vee
Vhh
dVeh
envelopelIntegral

CIOUT.basis=QDD.basis
CIOUT.QD[ay].ay
H_CI[eN,hN]
E_CI[eN,hN]
WF_CI[eN,hN]
dipoleOP[eN,hN]

Spectra[ay].ay
data[eN,hN].E
.I

FlowDiagram and DataStorage
Subroutine: getQDD

INPUT parameter: \( a y \)
Optional input: size, resolution
Material Data...

generate basis

New particle arrangement

All particle arrangement \((eN,hN)\)?

No

QD calculations

Record data: \( QDD.basis(eN,hN) \)

1. Solve 2D harmonic oscillator
2. Calculate Coulomb matrix elements

Record data: \( QDD.QD(ay) \)

More QD to calculate, \((ay)\)?

Yes

Save Data QDD Data OUTPUT: QDD

No
Subroutine: CI

INPUT: QDD
Optional input: chargedLeve, MaxParticle

Get new QDD.QD(ay)

Charge less then chargeLevel?

Yes

CI matrix calculation

H_Ci: Generate Hamiltonian

no

H_Ci - annihilateOP
createOP

dipoleOP: generate exciton recombination matrix

Diagonalize CI matrix

Dipole operator calculation

Record data:
CIOUT.QD(ay).H_Ci(eN.hN)
CIOUT.QD(ay).E_Ci(eN.hN)
CIOUT.QD(ay).WF_Ci(eN.hN)

More particle arrangement (eN.hN)?

Yes

More QD to calculate, (ay)?

Yes

Save Data: CIOUT
Data OUTPUT: CIOUT

No

No
Subroutine: getSpectra

INPUT: CIOUT

Get new CIOUT.QD{ay}

Generate emitting exciton ground state

Create merged state vectors, initial state and final state

Calculate intensity by $\langle f|P|i\rangle$

If intensity $> \text{cutoff}$

Record data:
Spectra{ay}.data{eN,hN}.E
Spectra{ay}.data{eN,hN}.I

More particle arrangement, {eN,hN}?

Yes

More QD to calculate, {ay}?

Yes

Save Data Spectra
Data OUTPUT: Spectra

No

Yes

No

No
Bibliography


