Properties of Type-II ZnTe/ZnSe Submonolayer Quantum Dots Studied via Excitonic Aharonov-Bohm Effect and Polarized Optical Spectroscopy

Haojie Ji
Graduate Center, City University of New York
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by

Haojie Ji

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This manuscript, Properties of Type-II ZnTe/ZnSe Submonolayer Quantum Dots Studied via Excitonic Aharonov-Bohm Effect and Polarized Optical Spectroscopy, by Haojie Ji, has been read and accepted for the Graduate Faculty in Physics in satisfaction of the dissertation proposal requirements for the degree of Doctor of Philosophy.

__________________________  ________________________________
Date  Professor Igor L. Kuskovsky  
       Chair of Examining Committee

__________________________  ________________________________
Date  Professor Igor L. Kuskovsky  
       Executive Officer

Professor Carlos Meriles ________________________________

Professor Vinod M. Menon ________________________________

Professor Lev Murokh ________________________________

Dr. Dmitry Smirnov ________________________________

Supervisory Committee

THE CITY UNIVERSITY OF NEW YORK
Abstract

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By

Haojie Ji

Adviser: Professor Igor L. Kuskovsky

In this thesis I develop understanding of the fundamental physical and material properties of type-II ZnTe/ZnSe submonolayer quantum dots (QDs), grown via combination of molecular beam epitaxy (MBE) and migration enhanced epitaxy (MEE). I use magneto-photoluminescence, including excitonic Aharonov-Bohm (AB) effect and polarized optical spectroscopy as the primary tools in this work.

I present previous studies as well as the background of optical and magneto-optical processes in semiconductor nanostructures and introduce the experimental methods in Chapters 1 - 3.

In Chapter 4 I focus on the excitonic AB effect in the type-II QDs. I develop a lateral tightly-bound exciton model for ZnTe/ZnSe type-II QDs, using analytical methods and numerical calculations. This explained the magneto-PL observation and allowed for establishing the size and density of the QDs in each sample based on the results of PL and magneto-PL measurements. For samples with larger QDs, I observe behaviors that fall between properties of quantum-dot and quantum-well-like systems due to increased QD densities and their type-II nature. Finally, the decoherence mechanisms of the AB excitons are investigated via the temperature dependent studies of the magneto-PL. It is
determined that the AB exciton decoherence is due to transport-like (acoustic phonon) scattering of the electrons moving in the ZnSe barriers, but with substantially smaller magnitude of electron-phonon coupling constant due to relatively strong electron-hole coupling within these type-II QDs.

In Chapter 5 I discuss the results of circularly polarized magneto-PL measurements. A model with ultra-long spin-flip time of holes confined to submonolayer QDs is proposed. The $g$-factor of type-II excitons was extracted from the Zeeman splitting and the $g$-factor of electrons was obtained by fitting the temperature dependence of the degree of circular polarization (DCP), from which $g$-factor of holes confined within ZnTe QDs was found. It is shown that it is about three times larger than that of bulk ZnTe.

In Chapter 6 I study the optical anisotropy in QDs. I show that all samples exhibit such an effect, and explain it based on non-spherical shape of the QDs. Numerical calculation is applied to calculate degree of linear polarization, and estimate the aspect ratio. The exciton anisotropic exchange splitting is calculated from the magnetic field dependence of the DCP.

In the last two chapters I show my achievement on the growth of ZnO nanorods as a core for type-II 1D systems and propose an outlook for future research on the type-II semiconductor heterostructures.
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Chapter 1

Introduction

1.1. Motivation

Progress in fabrication of semiconductor heterostructures at the ‘nano’ scale has opened up numerous opportunities both for fundamental research and for new applications, giving rise to novel optoelectronic devices. Quantum wells (QWs), nanowires (NWs), quantum rings (QRs), and quantum dots (QDs) are among the most important building blocks of the heterostructure-based devices as these lower dimensional structures are capable of modifying the density of states and band alignments of the semiconductors which can be engineered as per requirement. Therefore, the understanding of underlying fundamental physical phenomena in such structures is very important for future progress.

Based on the band alignment, semiconductor heterostructures are generally divided into two groups: type-I heterostructures, where electrons and holes are located in the same material, which has lower potential for both of them, and type-II heterostructures, where one of the materials has lower potential for electrons while the other has lower potential for holes, leading to spatial separation of the charge carriers (for more details see section 1.2.1). Because of the Coulomb interaction, these electrons and holes are bound in pairs, forming spatially indirect, type-II, excitons. Due to the less overlap of the charge carriers’ wavefunction, these excitons generally have recombination lifetimes longer than that in the type-I excitons. In addition, the energies and the recombination
oscillator strength of type-II excitons are sensitive to the carrier densities [1] as well as the external electric and magnetic fields [1, 2], which are substantial advantages for novel device applications.

Among type-II semiconductor heterostructures, ZnSe layers with ZnTe sub-monolayer QD multilayers have attracted a lot of interest due to its suitable band structure, which can be tuned to interact with light in a large wavelength range, from near ultraviolet (UV) to infrared [2-4]. For ZnTe QDs embedded in ZnSe barriers, the photo-generated holes and electrons are located within the QDs and in the barriers, respectively (detail discussion will be given in section 4.1) [2, 3]. Along with the fact that ZnTe can be easily doped p-type [5, 6], this structure has practical applications in photodetectors [5] and photovoltaic devices [6].

Using a combination of molecular beam epitaxy (MBE) and migration enhanced epitaxy (MEE), the ZnTe/ZnSe sub-monolayer QDs are grown without the formation of wetting layers, which might be a key to improvements in device performance [5, 6]. For all the device applications, the morphology, size, and density of QDs are critical parameters, since they determine optical anisotropy, the discrete energy levels, the oscillator strength of type-II excitons, and the degree of light absorption. However, due to the low contrast between the ZnTe submonolayer QDs and ZnSe barriers, it is very difficult to characterize the structure by transmission electron microscopy. In this case, indirect methods are required to finely probe the morphology, size and density of the submonolayer QDs.

These Type-II QDs exhibit a fundamentally intriguing effect that can be observed in the magnetic field – excitonic Aharanov-Bohm (AB) effect. An electric dipole moving in
a magnetic field can acquire a topological phase, which can be observed via optical emission of radially polarized excitons in nanostructures with suitable ring-like geometry [7-11]. This is a so-called excitonic AB effect, and can present itself as a transition between different angular momentum states of the excitons [11]. Detail calculation and discussion about excitonic AB effect will be given in section 2.2. It has recently inspired greater interest in quantum information related applications for the possibility of storage and manipulation of light and excitons in QRs and disk-like type-II QDs with externally applied magnetic and electric fields [12-14]. The excitonic AB effect has been observed in terms of the oscillation in the PL intensity and the excitonic energy for QR systems [12, 15-18] and type-II QDs [2, 19-21].

In addition, in recent years there has been intense interest in manipulating electron and hole spin states in semiconductor QDs for application in spintronics and quantum information processing [22-26]. For these applications, the confinement of the wavefunction of the charge carriers in QDs plays a key role in the enhancement of Zeeman splitting [27, 28] and the prolongation of spin-flip time [29, 30]. These effects have been reported for electrons in several material systems [31-35]. For holes confined in QDs, theoretical studies have predicted that its spin-flip time can be even longer than that of confined electrons [36-38]. Along with the enhancement of the Zeeman splitting due to the quantum confinement, holes in QDs have attracted more attention as the carriers for spin based applications. However, experimental results of g-factors or spin-flip time of holes in QD systems are rarely reported.

Towards understanding the underlying physics as well as the material properties of the ZnTe/ZnSe submonolayer nanostructures, we have studied the optical, magneto-
optical and polarized-optical properties of this QD system. We applied numerical calculations for the excitonic AB effect, the shape elongation and the g-factor of holes in the type-II QDs.

Type-II core-shell 1D nanostructures have the similar ring-like geometry as the QDs. However, the excitonic AB effect has not been reported in this type of structures. Therefore, we are interested in ZnO based core-shell nanorods as the candidate for excitonic AB effect, for ZnO has wide bandgap of 3.3 eV and can form type-II band alignment with several II-VI semiconductors, including ZnTe and ZnSe. We applied the Au catalyzed vapor-liquid-solid (VLS) process to grow vertical aligned ZnO nanorod arrays on sapphire substrates since it is a well-established growth method and sapphire is transparent to visible and near UV light. We also achieved growth of vertical aligned ZnO nanorod arrays. We report and discuss our results till date.

This thesis is divided into three main parts. In Chapters 1 to 3 we discuss the relevant background information. In Chapters 4 to 7 we present the experimental results, analysis and numerical calculations. In Chapter 8 we discuss some unresolved issues with future scopes of research.

1.2. Semiconductor nanostructures

1.2.1. Semiconductor heterostructures

A heterojunction is formed when two dissimilar semiconductors are joined adjacent to one another and heterostructures are formed from single or multiple heterojunctions. Heterostructures give rise to the possibilities of confining electronic states in lower dimensional systems. Via changing the material combination, composition and geometry,
one can engineer the properties of semiconductor devices or create new functions. Heterostructure-based electronic devices are widely used in many areas of daily human activities such as telecommunication systems and light-emitting diodes. At larger scales, solar cells incorporating heterostructures are used extensively in both space and terrestrial programs [39]. Semiconductor heterostructures can also be used for electronic devices such as transistors, optical and photonic components such as waveguides and microresonators [40-42], and optoelectronic devices such as laser diodes and photodetectors [43-46].

To analyze the wavefunction of charge carriers in heterostructures, one usually solves Schrödinger equations in each component of the heterojunction, with the effective mass, the bandgap and the Fermi level being a function of position. The discontinuity in either the conduction or the valence bands can be treated by a constant potential term in the Schrödinger equation. The electronic properties which depend largely on the band offsets and on the bulk properties of the constituting materials may abruptly change at the interface.

Based on the band alignment, semiconductor heterostructures are generally divided into two types: type-I heterostructures (Fig. 1.1(a)), where electrons and holes are located in the same material, which has lower potential for both of them, and type-II heterostructures (Fig. 1.1(b) and (c)), where one of the materials has lower potential for electrons while the other has lower potential for holes, leading to spatial separation of the charge carriers. Because of the Coulomb interaction, these electrons and holes are bound in pairs, forming spatially indirect, so-called type-II, excitons. We note here that this “indirectness” is only in the real space, while in k-space excitons are still direct, if the
underlying materials are direct band gap semiconductors. In this case the radiative recombination can still be in high efficiency since no phonons assistance is required. The electric field across the interface created due to the spatial separation of the electron and hole results in band bending at the interface of the heterojunction, which is dependent on the carrier density (and thus the excitation intensity) [4]. The band bending model is equivalent to a capacitor model which considers a capacitor formed at the interface due to accumulation of electron and hole on different sides. In this thesis we apply the band bending model as following. At higher carrier densities the band bending effect is enhanced, which manifests itself as a blue shift in the PL emission energy, due to the increase in the energy separation of the electron and hole energy levels. Moreover, the carrier recombination lifetimes are also expected to be carrier density dependent. Since the band bending effectively ‘pushes’ both the charge carriers closer to the barrier, it enhances the overlap of the e-h wavefunctions. The larger the overlap of the e-h wavefunctions, the stronger is the oscillator strength and consequently at higher carrier densities (higher excitation intensity), the decay time is reported to be shorter than at lower carrier densities in, for example, Ref. 4 and references therein. Thus, both PL and TRPL are predicted and reported to be excitation intensity dependent, which are considered hallmarks for type-II heterostructures. Detail discussion and examples are given in section 1.3.3.
Figure 1.1. Band alignment of semiconductor heterostructures showing (a) type-I, (b) type-II, with core material as potential well for electrons, and (c) type-II, with core material as potential well for holes.

1.2.2. Quantum confinement

Nowadays with the progress in nano-fabrication it is possible to produce lower dimensional systems and confine charge carrier states. The electronic properties which depend on the density of states change as a function of the dimensionality of these heterostructures as shown in Fig. 1.2 (a) for bulk, and (b), (c) and (d) for QWs, quantum wires (QWRs) and QDs, where the confinement is in one, two and three dimensions, respectively.

Figure 1.2. Density of states $N(E)$ for (a) bulk semiconductor (3D), (b) quantum well (2D), (c) quantum wire (1D), and (d) quantum dot (0D). [47]
A three-dimensional bulk material can be modelled as an infinite crystal along all three dimensions. Within an effective mass approximation [48], the energy of ‘free’ electrons with an effective mass $m_e$, in bulk solids scales with the square of the wave vector, $k$, in the three dimensions. In wide band gap semiconductors and for a small $k$ near the $\Gamma$ point, the dependence is approximately parabolic,

$$E = \frac{\hbar^2}{2m_e} \left( k_x^2 + k_y^2 + k_z^2 \right) = \frac{\hbar^2 k^2}{2m_e}, \quad (1.1)$$

$$N(E) = \frac{dN}{dE} = \frac{dN}{dk} \frac{1}{dk} \alpha k^2 \frac{1}{k} = k \propto \sqrt{E}.$$  

When one (QW-case) or two (QWR-case) of the three dimensions are reduced to order of nano-scales, charge carriers are confined along those one or two dimensions which results in corresponding quantization of the $k$ vectors and modification of density of states and energy distribution. For example, in QW with thickness $L_z$,

$$E = \frac{\hbar^2}{2m_e} \left( k_x^2 + k_y^2 + k_z^2 \right) = \frac{\hbar^2 k^2}{2m_e} + \frac{\hbar^2}{2m_e} \left( \frac{2\pi n}{L_z} \right)^2, \quad n = 1, 2, 3..., \quad (1.3)$$

$$N(E) = \frac{dN}{dE} = \frac{dN}{dk} \frac{1}{dk} \alpha k^2 \frac{1}{k} = const.$$  

When the charge carriers are confined in all the three dimensions (QD-case); each individual state can be represented by a point in the $k$-space. As a consequence, the energy bands converge to atom-like discrete energy states, which lead to the emergence of delta function peaks in the electronic density of states.

We’d like to mention disk-like QD here since it’s similar to our actual system. The vertical confinement is much stronger than the lateral ones. The overall density of states behavior approaches the QW case, while the fine structure (at each energy level created
by vertical confinement) is discrete due to the weak lateral confinement. Its density of states diagram looks like Fig. 1.2(d) overlaid onto each stage in Fig. 1.2(b).

In bulk semiconductors, the valence band has six-band degeneracy at the band edge. Due to the spin-orbit interaction, holes in the angular momentum states $\left| \frac{1}{2}, \pm \frac{1}{2} \right\rangle$ have the energy splitting $\Delta$ from the holes in $\left| \frac{3}{2}, \pm \frac{3}{2} \right\rangle$ (heavy hole) and $\left| \frac{1}{2}, \pm \frac{1}{2} \right\rangle$ (light hole), forming so called split off band, as shown in Fig. 1.3 [40]. The heavy hole and light hole states have different energy dispersions which can be expressed by using the effective mass approximation,

$$E_{hh, lh} = \frac{\hbar^2}{2m_{hh, lh}} \left( k_x^2 + k_y^2 + k_z^2 \right),$$  \hspace{1cm} (1.5)

where $m_{hh} > m_{lh}$. With the confinement, the ground state of light hole will have higher energy than that of the heavy hole. Therefore, in most semiconductor nanostructures, the lowest energy state of hole are heavy hole state. However, strain within the heterostructures can affect the energies of the heavy hole and light hole bands. The splitting between them may increase, decrease or even reverse depending on the type and strength of the strain.

**Figure 1.3.** Energy dispersions of the hole states.
1.2.3. Excitons in semiconductor nanostructures

Exciton is a ‘quasiparticle’ described as an electron and hole pair bound together through attractive Coulomb interaction. An exciton can move through the crystal and can transport energy; it does not transport charge because it is electrically neutral. There are two types of excitons that can be formed in non-metallic solids, namely Wannier-Mott excitons [49] and Frenkel excitons [50, 51]. Frenkel excitons generally occur in organic crystals where the electron-hole interaction is strong (binding energy ~ 100 to 300 meV) and the exciton size (the Bohr radius ~ 10 Å) is on the order of the unit cell. The concept of Wannier-Mott excitons is generally valid for inorganic semiconductors, which have high dielectric constants that reduce the Coulomb interaction between the electron and hole due to screening. The Wannier-Mott excitons have a larger size (Bohr radius of the order of tens of lattice constants, typically ~ 30 - 100 Å) and smaller binding energies (~ 1 - 30 meV). The Wannier-Mott excitons can be viewed as an effective hydrogen atom with the positive charge establishing the coordinate reference frame in which the negative charge with reduced mass $\mu = \left( \frac{1}{m_e} + \frac{1}{m_h} \right)^{-1}$ moves. Similarly to the spectrum of the hydrogen atom, the total exciton energy is quantized to

$$E_n(k) = E_{\text{gap}} + \frac{\hbar^2 K^2}{2(m_e + m_h)} - \frac{Ry^*}{n^2}, \quad \text{(1.6)}$$

where the second term is the kinetic energy in the center of mass approximation with $K$ standing for the wave-vector of the exciton; $Ry^*$ is the Rydberg constant for the exciton defined by $Ry^* = \frac{\mu e^4}{2\hbar^2 e^2}$. The radiative recombination of the exciton is allowed only when $K = 0$, in which case the exciton is localized (so-called bound exciton) due to doping, defects or structure confinement.
In nanostructures, the exciton (for type-I heterostructure) or one of the electron and hole (for type-II heterostructure) have a component of the wave vector quantized for each direction of confinement. When the exciton Bohr radius is comparable to the dimensions of the system, the binding energy of exciton is modified. Due to the structural dependence of the confinement energies of the charge carriers, as well as that of the Coulomb potential between electron and hole, the total exciton energy is structural dependent. For type-I systems the binding energy increases with the enhancing of confinement, since the Coulomb interaction gets enhanced with more overlapping of the charge carriers’ wavefunction. For type-II systems, however this can be inverted due to the spatial separation of electron and hole. In this case the barrier plays an important role in the overlapping of the charge carriers’ wavefunction, and therefore, the binding energy [1, 4]. Excitonic wavefunctions and energies need to be calculated numerically for specific material systems and confinement potentials. More detailed, self-consistent calculations involving addressing of Coulomb interaction, complexity of band structures and anisotropic effects require high computational capabilities, while some commercial solutions such as COMSOL and MATLAB can be helpful.

1.3. Optical process in semiconductors

Optical studies constitute some of the most important methods of determining the band structures and material properties of semiconductors.

1.3.1. Absorption

In bulk semiconductor with a simple band structure direct intraband optical transitions are forbidden by the momentum and energy conservation laws
\[ k' = k + q, \quad \frac{\hbar^2 k'^2}{2m} = \frac{\hbar^2 k^2}{2m} + \hbar \omega, \quad (1.7) \]

because they cannot be satisfied simultaneously. Here \( k, k' \) are the electron wave vectors in the initial and final states, and \( q, \omega \) are the light wave vector and frequency. The intraband absorption can only occur by absorption of a photon and simultaneous scattering by “third particle”, e.g., a phonon, another free carrier or a static defect [52].

In an interband optical absorption process, the radiation field transfers an electron from the occupied valence band to the unoccupied conduction band. In other words, the photon absorption is followed by the generation of an electron-hole pair.

If \( I(x) \) is the light intensity at position \( x \) within the material and \( \delta I \) is the change in the light intensity in the small elemental volume of thickness \( \delta x \) at \( x \), then \( \delta I \) will depend on the number of photons arriving at this volume and the thickness they pass

\[ \delta I = -\alpha I \delta x, \quad (1.8) \]

where \( \alpha \) is the absorption coefficient of the semiconductor, whose magnitude depends on the photon energy. Integration of the above equation yields the Beer-Lambert law, which reveals that the transmitted intensity decreases exponentially with the thickness:

\[ I(x) = I_0 \exp(-\alpha x), \quad (1.9) \]

For interband absorption, the absorption coefficient \( \alpha \) increases rapidly with the photon energy \( \hbar \nu \) above the band gap \( E_g \). The band gap can thus been obtained via linear fit using the following equation [53] with \( B \) as a constant,

\[ (\alpha \hbar \nu)^2 = B \left( \hbar \nu - E_g \right). \quad (1.10) \]

Strength of band edge absorption depends on whether the valence band maximum and the conduction band minimum occur at the same point in the Brillouin zone.
Semiconductors whose fundamental absorption edge involves a direct transition (same $k$ value) are said to have a direct absorption edge. Otherwise the absorption edge is said to be indirect. Diamond, Si, Ge, AlAs, AlSb, SiC and GaP have indirect absorption edges, while GaAs, GaSb, InP, GaN, InAs, InSb, and all the II-VI semiconductors have direct absorption edges. Optical transitions across an indirect bandgap are not allowed by the momentum conservation condition so that such transitions need to involve phonons (although they are orders of magnitude weaker than direct transitions). Hence they can be observed only when their energy is below that of all the direct transitions.

Excitonic absorption contributes below the band gap via the bound states or the continuum states [48]. The bound states are quantized as Eq. 1.6. In the continuum states, excitons can be considered to be ionized into free electrons and free holes but their wavefunctions are still modified by their Coulomb attraction. In the two-particle picture introduced in Ref. [48], optical absorption is the conversion of a photon into an exciton; conservation of energy and wavevector requires that this process must occur at the point where the photon dispersion curve intersects the exciton dispersion curves, forming degenerate, ‘coupled’ states of an exciton with a photon, which is known as an exciton-polariton. If one takes the assumption that whenever a photon is converted into an exciton it will lose its energy completely inside the medium via exciton damping processes, then the rate of dissipation of energy from the photon field is completely determined by the rate of conversion of photons into excitons. The contributions to the imaginary part of the dielectric function due to exciton absorption consist of two parts: one arising from the bound states and the other from the continuum. Detail calculations have been developed in Ref. [48]. As a result, the exciton effect enhances the absorption coefficient both above
(continuous enhancement and approaching a non-zero constant at the bandgap) and below (independent absorption lines) the bandgap.

1.3.2. Photoluminescence

Luminescence, or fluorescence, is an efficient tool to study the excited electronic states in solids. Since the luminescence intensity is determined both by the population of the excited states and the optical-transition probabilities, luminescence, in many cases, offers an advantage in analyzing the fine structure of excited states, which does not show up in absorption or reflection spectra. Moreover, it provides the possibility to investigate the kinetics of population and relaxation of the excited states [52]. The luminescence induced by the optical excitation is so called photoluminescence (PL). In semiconductors, the PL spectrum is mainly determined by the oscillator strength and lifetime of the radiative states with the energies lying close to the fundamental absorption edge. Depending on the character of the radiative transition, one distinguishes between intrinsic, extrinsic and exciton luminescence. Intrinsic, or band-to-band, luminescence is connected with the recombination of free electrons and holes. Extrinsic or impurity luminescence originates from the radiative recombination of free electrons with holes bound to acceptors, or of free holes with bound-to-donor electrons, the so-called bound-to-free emission, as well as from radiative donor-acceptor recombination and optical transitions between the levels of the same impurity center. Exciton luminescence appears due to the recombination of free, impurity-bound or localized excitons.

In undoped semiconductors, the photon absorption results in an excess electron concentration $\Delta n$, equal to the excess hole concentration $\Delta p$. The time dependence of the excess carrier concentration is governed by the rate equation [52]
\[
\frac{d\Delta n}{dt} = -\frac{\Delta n}{\tau},
\]  

where \(\tau\) is the carrier lifetime which represents the average time a carrier spends in the given band before recombination. The carrier lifetime is usually dependent on carrier concentration and applied external electric or magnetic fields.

The radiative processes are also accompanied by non-radiative recombination processes such as thermalization, successive emission of phonons, and the Auger processes wherein the recombination energy is transferred to a third carrier. The effective recombination time is given by

\[
\tau_{\text{eff}}^{-1} = \tau_{\text{rad}}^{-1} + \tau_{\text{non-rad}}^{-1}.
\]  

\(\tau_{\text{eff}}\) can be measured via time-resolved PL. As discussed in Ref. 4, the non-radiative lifetime decreases with increasing temperature in an exponential dependence

\[
\tau_{\text{non-rad}} \propto \exp\left(\frac{E_{\text{act}}}{k_B T}\right),
\]

while the radiative lifetime is generally time independent (exception may occur under specific geometry). Therefore, usually \(\tau_{\text{rad}}\) dominates at lower temperature while \(\tau_{\text{non-rad}}\) dominates at higher temperature.

In the case of excitonic transitions, the overlap integral of electron and hole wavefunctions directly relate to the probability of recombination and is commonly termed as the ‘oscillator strength’, usually defined as

\[
f \propto \int \langle \psi_e | \psi_h \rangle^2 dr \quad [52].
\]

We note that any kind of change in the confinement of the wavefunctions generally deals with the modulation of the oscillator strength and therefore affects the lifetime and efficiency of the luminescence.
1.3.3. Optical process in type-II nanostructures

The spatial separation of electrons and holes at the interface in type-II heterostructures results in tunability of the optical properties since the quantum mechanical tunneling at abrupt interfaces allows for effective overlapping of their wavefunctions. The extent of overlap governs the exciton oscillator strengths and the optical transition matrix elements $M_{ij} = c_i c_j \langle \psi(e) \mid \psi(h) \rangle$, which determine the optical properties of the systems, including the decay dynamics.

The electric field created due to the spatial separation of the $e$ and $h$ results in band bending at the interface of the heterojunction which is dependent on the carrier density (and thus the excitation intensity). At higher carrier densities the band bending effect is enhanced which manifests itself as an increase in the PL emission energy, due to the increase in the energy separation of the $e-h$ energy levels. The bandgap and band offsets do not change with the band bending, as shown in Fig. 1.4, while the band bending pushes up the electron level through confinement and pushes down the hole level through the hump in valence band. This is observed as a characteristic blue shift from the PL of type-II structures [54-56] when the excitation intensity is increased. An example is shown in Fig. 1.5 for ZnTe/ZnSe stacked QDs [4].
**Figure 1.4.** Band bending due to the electric dipole across the interface of type-II heterostructure.

**Figure 1.5.** PL plot showing experimental observation of signature blue shift in type-II ZnTe/ZnSe QDs. The green closed circles show the behavior of the ‘green’ band PL which is dominated by QD emission [4].
In addition to possessing naturally longer carrier recombination lifetimes (in comparison to that in type-I heterostructures) due to spatial separation of the photogenerated e and h, another optical signature of type-II heterostructures is that the carrier recombination lifetimes are also expected to be carrier density dependent [54]. The stronger the band bending, the larger is the overlap of the carrier wavefunctions and the stronger is the oscillator strength. Consequently at higher carrier densities via high excitation intensity, the decay of PL is faster than at lower carrier densities, as shown in Fig. 1.6 for ZnTe/ZnSe stacked QD system [57]. Thus both cw PL and TRPL are predicted and reported to be excitation intensity dependent, which are considered hallmark for type-II heterostructures.

![Image](image-url)

**Figure 1.6.** Time dependence of PL intensity for different excitation intensities for type-II ZnTe/ZnSe QDs [57].
1.3.4. Optical anisotropy

In zinc blende semiconductor QDs, the pure bright exciton states $|+1\rangle$ and $|-1\rangle$ are circularly polarized (detail selection rules for it will be discussed in section 2.3.3). If there is a lowering of confinement symmetry, it will lead to the valence band mixing between heavy hole and light hole states [58-60], which are originally separated due to confinement. In consequence, the two degenerate circularly polarized states will mix and form nondegenerate linearly polarized states $\frac{1}{\sqrt{2}}(|+1\rangle \pm |-1\rangle)$, the emissions from which are polarized along the [110] and [1$\overline{1}$0] crystal directions, respectively [61, 62]. The energy splitting between the linearly polarized states is a so-called doublet fine structure [62, 63]. The linearly polarized emission and the doublet fine structure have been observed and studied in self-assembled InAs [62, 63], InP [64, 65], CdTe [66], and CdSe QDs [67]. Three main origins of confinement symmetry lowering have been proposed [62]: (i) structural elongation of the QDs [63, 65, 68, 69], (ii) anisotropic strain relief or defects [62, 70], and (iii) anisotropic interface bond alignment [61, 71].

Microscopic defects such as dislocations have been recognized to cause the optical anisotropy. For example, linear polarization of bound exciton luminescence in ZnSe reflects an anisotropic strain relief of the ZnSe lattice resulting from different densities of $\alpha$ and $\beta$ type misfit dislocations [72]. The analysis of the linearly polarized luminescence has been exploited to identify light absorption below the band gap in the p-type doped regions in ZnSe based laser structures. By comparing not preferentially polarized luminescence associated with point defects with the strongly linearly polarized Y luminescence in thin ZnSe films it has also been demonstrated, that $60^\circ \alpha$ dislocations play an important role in the relaxation process of thin ZnSe layers [72]. Besides that, an
asymmetric density of dislocations at the interface, the incorporation of oriented defects, and an asymmetric relaxation of the residual strain in thin ZnSe layers have been revealed as different origins of the linearly polarized luminescence [72].

The anisotropic effects in the in-layer excitonic properties of semiconductor multilayered structures have been attributed to differences between the top and bottom interfaces of each layer. These differences are probably related to the growth process, which may yield different material intermixing, step density and orientation, and local stress for the two kinds of interfaces. The anisotropy mechanism includes the disordered material near the interfaces, which arises from differences in the degree of chemical disorder between the interfaces. It also includes the presence of oriented interfacial roughness and the existence of potential fields across the layers induced by differences in between the bottom and top interfaces of each layer [73].

For the case of QD heterostructures, while most device concepts assume highly symmetric dots, it is experimentally well established that self-assembled semiconductor QDs often grow in a highly anisotropic manner. The low symmetry of the dots naturally induces quantum interference between linear and circular polarized photon states. Time resolved experiments would result in quantum beats in the polarization, while, under the steady-state conditions, a net conversion results [74].
Chapter 2

Magneto-Optical Process in Semiconductors

In this chapter we will introduce different effects of magnetic field on semiconductors, including the Landau levels, diamagnetism, Zeeman Effect, and the Aharonov-Bohm (AB) effect. We will discuss the excitonic AB effect and the Zeeman Effect in detail.

2.1. Effects of magnetic field on semiconductors

Magnetic fields quantize the energy states of the conduction bands and the valence bands in semiconductors. In high magnetic fields, the quantization of energy states in semiconductors becomes very prominent and the radius of the cyclotron motion of conduction electrons or the electron wavefunction extension is much reduced. The quantization of the electronic states and the modification of the electronic wavefunction cause many new phenomena.

2.1.1. Landau levels for free electrons

When a semiconductor is placed in a magnetic field $B_z$, the electron motion in the $z$-direction is not affected, but motion components in the transverse direction result in a periodic circular motion with angular frequency (called the cyclotron frequency):

$$\omega_c = \frac{eB}{m^*c},$$

where $m^*$ is the effective mass of electron. Same discussion can be applied to a free hole, with the difference in effective mass. These orbits are quantized and the allowed transverse energies become
\[ E_n = \hbar \omega_c \left( n + \frac{1}{2} \right) = \frac{e\hbar B_z}{mc} \left( n + \frac{1}{2} \right). \quad (2.1) \]

In semiconductors, the simplest approach to treat energy bands and Landau levels within the framework of the \( k \cdot p \) approximation is the two band model with a single conduction and valence band and relatively small band gap, in which case the effect of other bands is considered to be negligibly small in comparison to the mixing of the two bands. The energy of the Landau levels express the non-parabolicity of the energy band at higher \( k \) values. Such two-band model works on narrow band gap material and nondegenerate conduction and valence bands. In semiconductors with wide band gap and degenerate valence bands, complicated calculations, taking in account of the interband matrix element of the momentum operator and spin orbit interactions, are required to obtain the Landau energy levels [75].

2.1.2. Landau levels and diamagnetism for excitons

As discussed in the previous chapter, the problem of exciton states in magnetic fields can be reduced to a fundamental problem of a hydrogen atom in magnetic fields. The total Hamiltonian [75] is

\[ H = \frac{\hbar^2}{2m^*} \left( \frac{\nabla \cdot e \vec{A}}{i} + \frac{e \vec{A}}{\hbar} \right)^2 - \frac{e^2}{4\pi \varepsilon_0 r} + gJ \mu_B B. \quad (2.2) \]

The first term is the canonical kinetic energy; the second term is the Coulomb interaction; the last term is the Zeeman energy. Taking the symmetric gauge, and assuming that magnetic field is parallel to the \( z \)-axis, we obtain

\[ \vec{B} \parallel z, \quad \vec{A} = B \left( \frac{y}{2}, \frac{x}{2}, 0 \right), \quad (2.3) \]
and

\[ H = \frac{p^2}{2m} + \frac{\omega_c}{2} L_z + \frac{1}{8} m^* \omega_c^2 (x^2 + y^2) - \frac{e^2}{4\pi\varepsilon_0 r} + gJ \mu_B B. \]  

(2.4)

It is not possible to obtain a solution for Hamiltonian in Eq. 2.4 analytically, because the magnetic field has a cylindrical symmetry while the Coulomb energy has spherical symmetry. Therefore, various approximate solutions were derived in different range of magnetic field relative to the Coulomb interaction. The characteristic energy representing the intensity of magnetic field is the energy of the cyclotron motion, \( \hbar \omega_c \), while that for the Coulomb interaction is the effective Rydberg energy

\[ R_y^* = \frac{m^* e^4}{32\pi^2 \hbar^2 e^2 \varepsilon_0^2}, \]

which is the binding energy. A parameter is defined as

\[ \gamma = \frac{\hbar \omega_c}{2} / R_y^* = \frac{16\pi^2 \hbar^2 e^2 \varepsilon_0^2}{m^* e^3} B. \]  

(2.5)

When \( \gamma \ll 1 \), the system is almost hydrogen atom-like and the magnetic field is regarded as a small perturbation. When \( \gamma \gg 1 \), the system is almost Landau level-like, and the Coulomb interaction is regarded as a small perturbation. For \( \gamma \approx 1 \), the two perturbation should be treated with an equal weight so that the problem is more complicated.

When the magnetic field is weak so that \( \gamma \ll 1 \), the terms involving magnetic field can be treated as perturbations acting on a hydrogen atom-like state. In this case, \( L_z \) can be commutated with the Hamiltonian, so it is a good quantum number. For an \( s \) state, \( \langle L_z \rangle = 0 \), so that apart from the Zeeman term, the only term which is related to magnetic field is

\[ \frac{1}{8} m^* \omega_c^2 (x^2 + y^2). \]

Taking this term as a perturbation, one can calculate a first order perturbation energy for the ground state,
\[ \Delta E_{1s} = \langle 1s | \frac{1}{8} m^* \omega_r^2 \left( x^2 + y^2 \right) | 1s \rangle = \frac{4\pi e^2 \varepsilon_r^2 \hbar^4}{e^2 m^*} B^2 = \sigma B^2, \quad (2.6) \]

When the effect of magnetic field is much larger than that of the Coulomb interaction, \( \gamma \gg 1 \), the latter effect is considered to be a small perturbation to the magnetically formed energy states. To calculate the energy levels in such a situation, the adiabatic approximation is often used, for which in the x-y plane, only the magnetic field effect is taken into account and the Coulomb interaction is considered in the z-component.

\[ \Delta E_{N} = \left( N + \frac{1}{2} \right) \hbar \omega_c + E_{\text{Coulomb}}^{(z)}. \quad (2.7) \]

For \( \gamma \rightarrow \infty \), the states tend to Landau level-like, so that their magnetic dependence tends to be proportional to \( B \). This is in contrast to the \( B^2 \) dependence in the case of weak field limit.

In quantum wells and superlattices, excitons should have a nearly two-dimensional character. For a two dimensional hydrogen atom (see e.g., Ref. [76]),

\[ a = \frac{a_B}{2}, \quad E_{\text{Coulomb}} = -4 \text{Ry}. \quad (2.8) \]

This indicates that in a two-dimensional space, electrons move in a smaller orbit around the proton in comparison to the three-dimensional case, so that the Coulomb binding energy is four times larger. The diamagnetic shift is proportional to \( \langle x^2 + y^2 \rangle \), so that it should be smaller in a 2D space,

\[ \Delta E_{1s} (2D) = \frac{3}{16} \sigma B^2 = \frac{3}{16} \Delta E_{1s} (3D). \quad (2.9) \]
2.2. Excitonic Aharonov-Bohm effect

In addition to the above mentioned effects, another fundamental effect, the excitonic Aharonov-Bohm effect, can be observed in semiconductor systems of specific geometry.

2.2.1. Aharonov-Bohm effect for charged particles

In 1959 Aharonov and Bohm showed that the vector potential can affect the quantum behavior of a charged particle even in regions where the field is zero [77]. The AB effect is a purely quantum mechanical effect, the experimental proof of which is achieved by Caprez, etc. in 2007 [78]. It reveals the physical reality of electromagnetic potentials. There are different manifestations of the AB effect. Here as an ideal case, we consider a charged particle with mass \( m \) and charge \( q \) constrained to move over a circular orbit with radius \( R \), within which there is an infinitely long solenoid with radius \( a \) less than \( R \) (Fig. 2.1). Therefore, there is no magnetic field at the particle’s trajectory, while the vector potential \( \vec{A} \) exists.

![Figure 2.1. A charged particle moving around an infinitely long solenoid.](image)
The Schrodinger equation in the cylindrical co-ordinates with the polar angle as only variable

\[
\frac{1}{2m} (\hat{p} - qA)^2 \psi = E \psi . 
\] (2.10)

Choosing the convenient gauge, the vector potential is given by

\[
A_\rho = A_z = 0; A_\phi = \frac{\Phi}{2\pi R} .
\] (2.11)

Here \( \Phi = \pi a^2 B \) is the magnetic flux through the solenoid. Equation (2.10) becomes

\[
\frac{1}{2mR^2} \left( -i\hbar \frac{\partial \psi}{\partial \phi} - q \frac{\Phi}{2\pi} \right)^2 \psi = E \psi .
\] (2.12)

The continuity of the wavefunction, \( \psi(\phi) = \psi(\phi + 2\pi) \) gives solutions of the form

\( \psi_l = e^{il\phi} , l = 0, \pm1, \pm2, \ldots \). And the corresponded energy eigenvalues are

\[
E_l = \frac{\hbar^2 l^2}{2mR^2} , \text{ for } \Phi = 0 ,
\] (2.13)

and

\[
E_l = \frac{\hbar^2}{2mR^2} \left( l - \frac{\Phi}{q / \hbar} \right)^2 , \text{ for } \Phi \neq 0 .
\] (2.14)

Thus, the existence of magnetic flux through the trajectory of the charged particle splits the degenerate angular momentum states of the particle. In particular, positively charged particle will have angular momentum positive while negatively charged particle will have angular momentum negative for lower energy states.

As a consequence of Eq. 2.14, for a charged particle orbiting around a solenoid, the kinetic angular momentum \( \mathbf{K} = \mathbf{r} \times m\mathbf{v} \) can change with increasing magnetic flux. This is because the Hamiltonian corresponding to the kinetic energy of the particle is not a
conserved quantity for time dependent flux. On the contrary the canonical angular momentum is conserved, which is indeed the total angular momentum of the system, that is, the kinetic angular momentum plus the electromagnetic angular momentum \( \mathbf{L} = \mathbf{K} + \mathbf{M} \). In varying the flux of the solenoid we effectively change the kinetic angular momentum of the charged particle as well as the electromagnetic angular momentum of the field, while the total angular momentum is conserved [79, 80]. The spectrum of the Hamiltonian is determined by the kinetic angular momentum and the AB effect is just a consequence of the quantization of the canonical angular momentum that does not depend upon the flux.

### 2.2.2. Excitonic Aharonov-Bohm effect

Theoretically it was predicted that the AB phase can as well be acquired by an electric dipole moving in a magnetic field, which can be observed via optical emission of radially polarized excitons in nanostructures with suitable ring-like geometry [7-11]. This is so-called excitonic AB effect.

![Figure 2.2](image.png)

**Figure 2.2.** Schematic diagram showing electron-hole motion in nanoring [11].
Here we introduce the excitonic model in nanoring discussed in Ref. 11. Assuming the radial wavefunctions of electron and hole are strongly localized on two concentric rings with different radii, $R_e$ and $R_h$ (Fig. 2.2). The Hamiltonian describing the angular wave function $\psi(\theta_e, \theta_h)$ is

$$
\hat{H}_{exc} = -\frac{\hbar^2}{2m_e R_e^2 \partial^2 / \partial \theta_e^2} - \frac{i\hbar \omega_e}{2} \frac{\partial}{\partial \theta_e} - \frac{\hbar^2}{2m_h R_h^2 \partial^2 / \partial \theta_h^2} + \frac{i\hbar \omega_h}{2} \frac{\partial}{\partial \theta_h} + \frac{m_e \omega_e^2 R_e^2 + m_h \omega_h^2 R_h^2}{8} + u_e |\theta_e - \theta_h|,
$$

(2.15)

where $\omega_{e,h} = \frac{|e|B}{m_{e,h}c}$ are the cyclotron frequencies of the particles, $B$ is the normal magnetic field, and $u_e$ is the Coulomb potential averaged over the radial coordinate involving the radial wavefunctions.

Depending on the strength of the e-h coupling, different observations are predicted. In small QRs, the quantization due to kinetic motion is much stronger than the Coulomb interaction, and the picture is basically that of single particles. This limit corresponds to $R_{e,h} < a_0^*$, where $a_0^*$ is the effective Bohr radius in the semiconductor. Since the electron and hole move independently, the exciton spectrum is given by

$$
E_{exc} = E_g + \frac{\hbar^2}{2m_e R_e^2} \left( \frac{L_e}{\Phi_e} - \frac{\Phi_e}{\Phi_0} \right)^2 + \frac{\hbar^2}{2m_h R_h^2} \left( \frac{L_h}{\Phi_h} - \frac{\Phi_h}{\Phi_0} \right)^2,
$$

(2.16)

where $E_g$ is the magnetic field-independent term which includes the band-gap energy. $L_e$ and $L_h$ represent the angular momenta of electron and hole. The magnetic field $B$ enters Eq. 2.16 through the magnetic fluxes $\Phi_{e,h} = \pi R_{e,h}^2 B$, which describe the quantum phase accumulating in the wave function of each particle as it travels along the ring. And
$\Phi_0 = h/e$ is the flux quantum. In this case, as the field increases, the ground state $(L_e, L_h) = (0, 0)$ changes successively in favor of other states: $(0,+1), (-1,+1), (-1,+2)\ldots$, producing a sequence of ground state total angular momentum values of $L = L_e + L_h = 0,1,0,1$ and so on. Thus, multiple oscillations in both energy and intensity of excitonic emission are expected.

In large QRs, where $R_{e,h} \ll a_0^*$, the angular motion becomes strongly correlated as the particles form a tightly-bound exciton and move together around the ring. The tightly-bound exciton spectrum takes the form

$$E_{exc} = E_g + \frac{\hbar^2}{2MR_0^2} \left( L + \frac{\Delta \Phi}{\Phi_0} \right)^2,$$

where $E_g$ is the field independent ground state energy of the exciton; $R_0 = (R_e + R_h)/2$; $M = (m_eR_e^2 + m_hR_h^2)/R_0^2$; $L = L_e + L_h$ is the total angular momentum of the exciton; $\Delta \Phi = \pi(R_e^2 - R_h^2)B$ is the net magnetic flux through the area between the electron and hole trajectories. In this case, as the field increases, the ground state of exciton changes successively from $L = 0$ to -1, -2, -3 and so on. In this case, single oscillation in intensity of exciton emission is expected to be observed.

For ZnTe/ZnSe submonolayer QDs, the holes are located inside the QDs while the electrons are outside the QD boundary. The QD radius (~15 nm [81]) is much larger than the effective Bohr radius (~2.5 nm [82]). Therefore, the exciton behaviours are similar to the tightly-bound exciton model of Ref. 11.

We’d like to mention another approach of excitonic AB effect introduced in Ref. [12, 83] for narrow type-I QRs. Different from the approach for type-II system, in the type-I
approach the electron and hole have the same orbits. Based on a model with a short-range attraction potential between an electron and a hole, the energy spectrum of an exciton oscillates on the term of \( \cos \left( \frac{2\pi \Phi}{\Phi_0} \right) \). The origin of the effect is explained the finite probability for electron and hole, created by a photon at the same point, to tunnel in the opposite directions and meet each other on the opposite side of the ring [83].

### 2.2.3. Decoherence of Aharonov-Bohm excitons

The quantum phase coherence, needed for the appearance of the AB Effect is conserved only during a finite time, \( \tau_D \), called the decoherence time. The quantum coherence can be lost when the investigated system or its parts interact with the environment via inelastic and/or irreversible processes. This environment usually consists of thermal excitations of the lattice (phonons), impurities with internal degrees of freedom, and other charge carriers. When this type of decoherence dominates, the characteristic decoherence length, \( L_D \), is directly proportional to the decoherence time [84-86]. Phase coherence can also be lost in the situation when multiple scattering events lead to the diffusive regime of transport. In this case, the characteristic phase-breaking length is proportional to the square root of the dephasing time [84].

The amplitude of the AB oscillations, which reflects the degree of coherence, is expected to decrease due to interaction with environment. The broadly defined decoherence rate, \( \tau_D^{-1} \), can thus be extracted from temperature dependence of the AB oscillation amplitude. According to the pioneering works [86, 87], the main decoherence
mechanisms in mesoscopic systems are the electron-phonon (e-ph) and electron-electron (e-e) interactions, with the temperature dependence of the decoherence rate given by

$$\tau_D^{-1} = \tau_{ee}^{-1} + \tau_{eph}^{-1} = aT^n + bT^3,$$

(2.18)

where generally $n = 2/3$ [86, 87] for nanowires and $n = 1$ for Aharonov-Bohm rings (e.g., Refs. [88-90] and references therein) in diffusive regime; in the ballistic one channel regime the dephasing length and thus time was shown to behave as $T^{-1}$ (e.g., Refs. [91, 92]) . In both cases the dephasing time is expected to diverge at $T \to 0$; however, in many actual experiments starting from Ref. [93] (for reviews, see Refs. [94, 95] and references therein), the dephasing time saturates at very low temperatures.

2.3. Zeeman effects in semiconductor nanostructures

In recent years there has been intense interest in manipulating electron and hole spin states in semiconductor nanostructures and QDs for application in spintronics and quantum information processing [22-26]. For these applications, the confinement of the wavefunction of the charge carriers plays a key role in the enhancement of Zeeman splitting [27, 28] and the prolongation of spin-flip time [29, 30]. These effects have been reported for electrons in several material systems [31-35]. For holes confined in QDs, theoretical studies have predicted that its spin-flip time can be longer than confined electrons [36-38]. Along with the enhancement of the Zeeman splitting due to the quantum confinement, holes in QDs have attracted more attention as the carriers for spin based applications. However, experimental results of $g$-factors or spin-flip time of holes in QD systems are rarely reported.
2.3.1. Nonlinearity and enhancement of Zeeman splitting

Experimental results have been reported for two features that give critical tests of the understanding of Zeeman splittings in nanostructures. (i) In QDs the Zeeman splittings of excitons are approximately linear in $B$, but the associated $g$ factors depend strongly on the structure size [27, 96]. (ii) Exciton Zeeman splittings in QWs have strong (well-width-dependent) nonlinear dependences on the magnetic field $B$, even becoming negative in narrow wells [28, 31, 97].

In Ref. [28], a standard six-band $k\cdot p$ effective-mass Kane-Luttinger Hamiltonian of the band-edge carrier states, which includes the coupling of the light-hole and heavy-hole valence bands and also their coupling with the conduction band, is used for the electron and hole Zeeman splittings and $g$ factors. In Faraday geometry where the magnetic field is parallel to the growth direction, the dispersion of an electron ($i = e$) or hole ($i = h$) in the QW plane up to order of $k_{\parallel}^2$ is

$$E_i(k_{\parallel}) = E_i(k_{\parallel} = 0) + \frac{\hbar^2 k_{\parallel}^2}{2m_{\text{eff}}^{(i)}} + \frac{\mu_0 B}{2} \left[ g_{00}^i + g_{20}^i + (g_{22}^i + g_{32}^i + g_{42}^i) k_{\parallel}^2 \right], \quad (2.19)$$

where $k_{\parallel}$ is the parallel wave vector; the first index of each of the $g_{ij}$ labels the order of perturbation theory, and the second the power of $k_{\parallel}$.

Equation 2.19 accounts for the observed size dependences of the $g$ factors in dots and for the observed nonlinearities of the spin splitting with $B$ in quantum wells. The spin splitting is given by the last term in Eq. 2.19 where the $k_{\parallel}^2$ terms arise from mixing of the subband states of the quantum well potential. In quantum dots and wires the carrier functions are confined, and the dominant term in $\langle k_{\parallel}^2 \rangle$ at small $B$ is $\langle k_{\parallel}^2 \rangle \sim 1/L^2$, where $L$ is the lateral size. This gives a size dependence to the $g$ factor in quantum dots and wires.
In a quantum well in magnetic field, $\langle k^2 \rangle \sim \hbar \omega_c \sim B$, where $\omega_c$ is the cyclotron frequency.

In this case, in effect, the carrier is “localized” in a Landau state, and then these contributions to the last term in Eq. 2.19 giving nonlinear dependences of the splitting on $B$. An example of nonlinear Zeeman splitting in QWs is shown as Fig. 2.3 [28].

![Figure 2.3](image.png)

**Figure 2.3.** Experimental spin splittings and theoretical calculations (solid lines) as functions of the magnetic field along the growth direction for varying In$_{0.10}$Ga$_{0.90}$As/GaAs quantum well sizes indicated in the legend. [28]

### 2.3.2. Longer spin-flip time

There are two main spin relaxation mechanisms for electron spins in semiconductors: the phonon assisted spin flips mediated by spin-orbit coupling [29, 30, 98] and the hyperfine interaction with surrounding nuclear spins [99-101]. In Ref. [102], Khaetskii and Nazarov have shown that the localized character of the electron wave functions in the
QD’s suppresses the most effective intrinsic spin-flip mechanisms related to the absence of inversion symmetry in zinc blende semiconductors. This leads to an unusually low rate of spin-flip transitions. The spin-flip processes due to the spin-orbit interaction is the main source of the spin flips for the 3D and 2D electron states in the GaAs-type crystal without an inversion center. Besides, in such a polar-type crystal one finds a strong coupling of electrons to the bosonic environment via the piezoelectric interaction with acoustic phonons. The combination of these two mechanisms provides an effective spin-lattice relaxation of free carriers. However, the spin-lattice relaxation for the electron localized in the QD is much less effective [102]. In this case, the hyperfine interaction between the electron spin and the nuclear spins leads to the strongest decoherence effect [38].

Since the valence band has $p$ symmetry, the hyperfine interaction of holes with lattice nuclei is suppressed with respect to that of the conduction band (electrons) [37]. Thus the potentially slower relaxation due to phonons is expected to dominate. Hole spin relaxation has been studied in bulk semiconductors [103] and in quantum wells [104, 105]. There, relaxation typically occurs by elastic phonon processes mediated by spin-orbit coupling and gives rapid rates on the order of ps and ns, respectively, due to strong phonon scattering of holes. In dots, on the other hand, the hole states are discrete, and thus phonon induced scattering involves inelastic processes [36]. Therefore hole spin relaxation could be slow in QD’s, and holes might become attractive candidates as carriers of quantum information.
2.3.3. Zeeman splitting in ZnSe/ZnTe QDs

In the type-II ZnTe/ZnSe QDs, holes are confined in ZnTe QDs while electrons are located in ZnSe barrier. The g-factor of electrons in bulk ZnSe is positive, ~1.1 [106]. For holes confined in QDs, as discussed in Chapter 1, the ground state of light hole will have higher energy than that of the heavy hole. Since our QDs have their thickness much smaller than the lateral size [107], the energy levels are mostly modified by vertical confinement, approaching the QW case. Therefore, we solved a 1D Schrödinger equation for the hole in the submonolayer QD, and the splitting between light and heavy hole levels is more than 200 meV for our QD thickness between 0.5 to 1 nm, as shown in Fig. 2.4. Therefore, at low temperature and under low excitation, the holes in QDs are heavy holes [2, 81], with spin \( J_z = \pm \frac{3}{2} \).

![Figure 2.4](image.png)

**Figure 2.4.** Solutions for light and heavy hole energy levels in ZnTe/ZnSe submonolayer QDs with varying thickness.
Considering the above facts, there are three possible Zeeman splitting patterns for ZnTe/ZnSe QDs based on the sign and magnitude of the heavy hole $g$-factor, as shown in Figs. 2.5 (a), (b) and (c). The Zeeman splitting are $g_e \mu_B B$ and $g_{hh} \mu_B B$ for electron and hole, respectively. Because of the optical selection rule, electron with spin +1/2 can only recombine with hole with spin -3/2 to emit $\sigma^-$ polarized photon, while electron with spin -1/2 can only recombine with hole with spin +3/2 to emit $\sigma^+$ polarized photon. If the heavy hole $g$-factor is negative, as in Fig. 2.5 (a), then the $\sigma^-$ polarized emission has higher energy than the $\sigma^+$ polarized emission. If the heavy hole $g$ factor is positive, there are two cases. In the case of $g_{hh} < g_e$, as in Fig. 2.5 (b), the $\sigma^-$ polarized emission has higher energy than the $\sigma^+$ polarized emission. In the case of $g_{hh} > g_e$, as in Fig. 2.5 (c), the $\sigma^+$ polarized emission has higher energy than the $\sigma^-$ polarized emission. The Zeeman splitting patterns involving light holes are shown in Fig. 2.5 (d), (e) and (f) for reference since they might be important for the excitons in ZnSe barrier.

**Figure 2.5.** Energy levels of heavy hole excitons Zeeman splitting in ZnTe/ZnSe QDs for (a) $g_{hh} < 0$, (b) $0 < g_{hh} < g_e$, and (c) $0 < g_e < g_{hh}$, and of light-hole excitons for (d) $g_{lh} < -g_e < 0$, (e) $-g_e < g_{lh} < 0$, and (f) $g_{lh} > 0$. 
Chapter 3

Experimental Methods

In this chapter we first introduce the growth procedure of ZnTe/ZnSe submonolayer quantum dots and the growth parameters of the six samples we are going to study. Then we will introduce the optical characterization methods and setups including photoluminescence (PL), linearly polarized PL, time-resolved PL, magneto-PL and circularly polarized magneto-PL. After that, we will give a brief introduction of secondary ion mass spectroscopy and high resolution x-ray diffraction.

3.1. Growth of ZnTe/ZnSe submonolayer quantum dots

Multilayered Zn-Se-Te structures with sub-monolayer insertion of ZnTe were grown on (001) GaAs substrates by a combination of Molecular Beam Epitaxy (MBE) and Migration Enhanced Epitaxy (MEE) in a Riber 2300 system, under the leadership of Prof. Maria Tamargo at the City College of CUNY. Prior to the growth of the QD layers, an undoped ZnSe buffer layer was grown at optimum growth temperature of 270 °C. After the buffer layer growth, the multilayers were grown. Ten monolayers (10 MLs) thick ZnSe spacer (barrier) were grown by opening the Zn and Se shutters together, after which the Se shutter was closed to produce a Zn-terminated surface. Then all shutters were closed to desorb excess Zn from the surface. The Te shutter was opened for 5 seconds to deposit Te onto the Zn-terminated surface. This was followed by closing of all shutters followed by opening of the Zn shutter to produce another Zn terminated surface. We note
that Te (Zn) was deposited without Zn (Te), which enhances surface diffusion. Since a very small Te flux is used during the deposition, only a fraction of a Te monolayer (submonolayer) is formed, which leads to formation of type-II QDs. The lack of full ZnTe monolayers is also supported by monitoring the RHEED oscillations during the growth. This procedure was repeated one time (single-cycled) or three times (triple-cycled), before the Se shutter was again opened to start the next growth sequence. The whole cycle was repeated for between 100 and 200 times. The overall thickness of the samples is ~ 500 to 600 nm. Fig. 3.1(a) and (b) demonstrate the shutter sequence during the growth procedure and a schematic sample structure, respectively.

![Figure 3.1](image.png)

**Figure 3.1.** Schematic diagram for (a) shutter sequence for sample growth, and (b) sample structure.

The Te effusion cell temperature and the number of QD growth cycles (single or triple) were chosen as the varied parameters which determine the size and density of the ZnTe submonolayer QDs. Six samples were grown in two sets. For set I (sample A, B, C), sample A and sample C had the same Te effusion cell temperature while they were
single-cycled and triple-cycled, respectively. Sample B was triple-cycled and had Te effusion cell temperature lower than sample C. For set II (sample D, E, F), samples D and E were triple-cycled while sample F was double-cycled, named in increasing Te effusion cell temperature. The growth parameters, the average Te concentrations obtained via SIMS and the compressive strain were listed in Table 1 for the six samples. We notice here the Te effusion cell temperature and the average Te concentration of sample F are much higher than those of the other samples. Meanwhile, the crystal axes [110] and [110] of sample F was marked after its growth.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Set I</th>
<th>Set II</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A(D55)</td>
<td>B(D53)</td>
</tr>
<tr>
<td>Number of QD growth cycles</td>
<td>single</td>
<td>triple</td>
</tr>
<tr>
<td>Te effusion cell temperature (°C)</td>
<td>$T_1+6$</td>
<td>$T_1$</td>
</tr>
<tr>
<td>Te flux $\times$ Number of cycles ($10^{-7}$ torr)</td>
<td>2</td>
<td>3.9</td>
</tr>
<tr>
<td>Te concentration ($10^{19}$ cm$^{-3}$)</td>
<td>2.82</td>
<td>6.11</td>
</tr>
<tr>
<td>Strain (Compressive)</td>
<td>$3\times10^{-3}$</td>
<td>$4\times10^{-3}$</td>
</tr>
</tbody>
</table>

Table 1. Sample information with varied growth parameters and Te concentrations.
3.2. Photoluminescence

Photoluminescence is a very useful optical technique used to investigate electronic properties of materials. The method employs the measurement of emitted light as a function of wavelength (photon energy) when the sample is irradiated with photon beam of energy higher than the band gap of the material. The PL spectra can deliver information about a variety of states; such as energy band extrema, free excitons, bound excitons associated with impurities and defects, and charged excitons. To analyze PL spectra, the identification of the origin of the light emission is necessary.

For most PL measurements, as the schematic diagram shown in Fig. 3.2, the 351 nm emission line from an Ar-ion laser was used for excitation. The excitation intensity was varied over 4 orders of magnitude using neutral density filters (NDF). The PL emission was detected by a TriVista SP2 500i Triple monochromator coupled to a thermo-electrically cooled photomultiplier tube (PMT) and a photon counting system. An ARS closed cycle refrigerating system was used for low temperature and temperature dependent measurements from 7 to 300 K for cw, time resolved, and linearly polarized PL measurements.
3.3. Linearly polarized photoluminescence

Linearly polarized PL is the technique to investigate the polarization property of the PL emission from the samples. The linear polarization of the PL emission gives information of anisotropy in the samples, which may related to QD morphology, strain relief, defects, and so on.

A schematic diagram of linearly polarized PL setup is shown in Fig. 3.3. A 405-nm diode laser combined with a linear polarizer and a quarter-wave plate was used to excite the samples with right-handed circularly polarized laser. The emission was focused into a fiber coupled to an Ocean Optics high resolution solid state spectrometer. Samples were kept in an ARS Inc. temperature-variable closed-cycle refrigerating system, allowing for
measurements at 7.5 K. A linear polarizer on a rotation mount was placed in front of the collecting fiber to analyze the linear polarization of the PL.

![Schematic diagram of linearly polarized PL setup.](image)

**Figure 3.3.** Schematic diagram of linearly polarized PL setup.

### 3.4. Time-resolved photoluminescence

Time-resolved PL is the technique employed to investigate the decay dynamics which can lead to the determination of the lifetime of the excited $e$-$h$ pair. The PL lifetime is an average time for the carriers to remain in the excited state after photo-excitation and before emitting a photon. TRPL is measured by exciting luminescence from a sample with a pulsed source of excitation, and then measuring the subsequent decay in the PL emission as a function of time. The 337 nm line of a N$_2$ pulsed laser (the 4 ns pulse width; 30 Hz repetition rate) was used for excitation, while a 500 MHz Tektronix TDS 654C oscilloscope was used for data recording, as the schematic diagram shown in Fig. 3.4.
3.5. Magneto-photoluminescence and circularly polarized magneto-photoluminescence

External effects such as magnetic fields can lead to observation of modified PL emission as per corresponding changes in energy levels (which govern the optical properties) in the system. PL and polarized PL can be performed in the presence of external magnetic field (magneto-PL). When the magnetic field is applied parallel or perpendicular to the propagation vector of the incident electromagnetic wave, which is the growth direction (z-axis) of the sample, the arrangement is called the Faraday or the Voigt configuration, respectively.

Magneto-PL measurements were performed in the Faraday and Voigt geometries within a Cryo Industries of America, Inc. 9 T superconducting magnet at Queens College (QC), and in the Faraday geometry within a 18 T superconducting magnet in the National
High Magnetic Field Laboratory (NHMFL). Both the magnets were outfitted with fiber optic probes, used for excitation and collection of the PL. The PL was excited by a 405-nm diode laser and detected with an Ocean Optics high-resolution solid-state spectrometer (QC and NHMFL) or a single grating spectrometer equipped with a thermoelectrically cooled CCD detector (NHMFL). The experimental temperature is fixed to 7.5 K by vaporizing liquid helium (QC) or varies between 0.36 K to 30 K in a $^3$He cryostat (NHMFL). The circular polarization of the PL was analyzed by a circular polarizer consisting of an achromatic quarter wave plate and a linear polarizer. The $\sigma^+$ and $\sigma^-$ circularly polarized PL components were selected by reversing the polarity of the magnetic field. A schematic diagram of circularly polarized magneto-PL setup is shown in Fig. 3.3.

![Schematic diagram of circularly polarized magneto-PL setup.](image)

**Figure 3.5.** Schematic diagram of circularly polarized magneto-PL setup.
3.6. **Secondary ion mass spectroscopy**

Secondary ion mass spectrometry (SIMS) is a technique that can determine elemental, isotopic, or molecular composition of a specimen, to great accuracy. The sample is subjected to a focused primary ion beam and the ejected secondary ions are collected and analyzed. The secondary ions are then accelerated, focused (by extraction lens), and analyzed by a mass spectrometer to determine the composition of the system. The bombarding primary ion beam produces monoatomic and polyatomic particles of sample material and resputtered primary ions, along with electrons and photons. The secondary particles carry negative, positive, and neutral charges and they have kinetic energies that range from zero to several hundred eV, as shown in Fig. 3.6. Primary beam species useful in SIMS include Cs\(^+\), O\(_2\)^+, O\(^+\), Ar\(^+\), and Ga\(^+\) at energies between 1 and 30 keV. Primary ions are implanted and mix with sample atoms to depths of 1 to 10 nm. SIMS measurements on our samples were done by EVANS Analytical Group at their lab in Sunnyvale, CA. The measured Te concentrations in the samples are listed in Table 1.

![Figure 3.6. Schematic diagram of SIMS measurement [47].](image)
3.7. High resolution x-ray diffraction

A typical High resolution x-ray diffraction (HRXRD) setup consists of X-ray synchrotron radiation source, beam conditioners (collimated and monochromatic beam is obtained with the help of beam conditioners) on incident and diffracted beam side, a sample stage which is capable of movement in different directions (tilt and rotation for precise placement of sample) and detector. The technique is widely used for structural characterization of epitaxial layers to determine thickness and composition as well as to evaluate strain and relaxation within a given layer of a multilayer structure. This technique can be understood simply by reducing the Laue equation to Bragg’s law. Bragg’s law gives the condition for coherent and incoherent scattering from the lattice sites in a crystal structure. Bragg diffraction occurs when an electromagnetic radiation with wavelength comparable to atomic spacing is incident upon a crystalline sample, are scattered by the underlying atoms and undergo constructive interference. A schematic diagram of HRXRD setup is shown in Fig. 3.7.

The HRXRD measurements were carried out at Beamline X20A at the National Synchrotron Light Source at the Brookhaven National Laboratory. All measurements were performed using monochromatic synchrotron radiation at 8 keV, with a double-crystal Ge (111) monochromator. To enhance the angular resolution, a Si (111) analyzer was placed in front of the detector.
Figure 3.7. Schematic diagram of HRXRD measurement [47].
Chapter 4

Optical Studies and Excitonic Aharonov-Bohm Effect in Stacked Type-II ZnTe/ZnSe Submonolayer Quantum Dots

In this chapter we first introduce a lateral tightly-bound exciton model for excitonic Aharonov-Bohm (AB) effect in the type-II quantum dots (QDs) to calculate the magnetic field value of the AB oscillation peak as a function of the QD stack radius. Based on the results of PL and magneto-PL measurements, we find out the distribution of the sizes of QDs and calculated the density of QDs in each sample. By comparing the samples with different QD sizes and densities, we discuss the observation of tuning between quantum-dot and quantum-well-like behaviors. We also study the temperature effects on the AB oscillation to investigate the decoherence mechanism of the type-II excitons.

4.1. Excitonic Aharonov-Bohm effect in type-II ZnTe/ZnSe submonolayer quantum dots

Due to high vertical correlation between the multilayers, the submonolayer QDs form vertical stacks [2, 108]. The ZnSe spacers between the QD layers were about 3.0 nm thick, much smaller than the lateral separation between QDs [109]. Because of the vertical confinement, the electrons, which are located in the ZnSe barrier, have their wave function “pushed” to the side of the stacked QDs [2]. The estimated radius of the stacked
QDs in our previous study is about 9 - 11 nm [2, 3, 109], which is much larger than the free exciton Bohr radius in ZnTe (4.6 nm) and ZnSe (2.8 nm) [82]. Under such conditions, according to the discussion in Ref. [11] and [110], within the QD plain, the Coulomb interaction between electron and hole is much stronger than the quantization due to kinetic motion. Therefore, we apply a lateral tightly-bound exciton model in the type-II ZnTe/ZnSe stacked submonolayer QDs, the schematic diagram of which is shown in Fig. 4.1. The hole is strongly localized on a circular trajectory inside the QD, while the electron is strongly localized on a trajectory outside the QD. The angular motions of the hole and the electron are strongly correlated as they move together along the side of the QD, forming a well-defined dipole. In this model, we can separate the wavefunctions of electron and hole in the radial direction, which can be obtained by solving the following single-particle equations in the effective mass approximation:

\[
\begin{align*}
-\frac{\hbar^2}{2m_e} & \frac{1}{r_e} \frac{\partial}{\partial r_e} \left( r_e \frac{\partial}{\partial r_e} \right) + \frac{\hbar^2}{2m_e} \frac{l_e^2}{r_e^2} + V_e(r_e) - \frac{e^2}{2\varepsilon} \int \frac{\left| \psi_e(r_h) \right|^2}{|r_e - r_h|} r_h \; dr_h \psi_e(r_e) = E_e \psi_e(r_e) , \\
-\frac{\hbar^2}{2m_h} & \frac{1}{r_h} \frac{\partial}{\partial r_h} \left( r_h \frac{\partial}{\partial r_h} \right) + \frac{\hbar^2}{2m_h} \frac{l_h^2}{r_h^2} + V_h(r_h) - \frac{e^2}{2\varepsilon} \int \frac{\left| \psi_h(r_e) \right|^2}{|r_e - r_h|} r_e \; dr_e \psi_h(r_h) = E_h \psi_h(r_h) ,
\end{align*}
\]

where \( m_e \) and \( m_h \) are the effective electron and hole masses, respectively. \( l_e \) and \( l_h \) are the angular momentum quantum numbers of electron and hole, respectively. For the ground states, \( l_e = l_h = 0 \). \( V_e(r_e) \) and \( V_h(r_h) \) are the confinement potentials for electron and hole, respectively:

\[
V_e(r_e) = \begin{cases} 
V_e, & r_e < R \\
0, & r_e > R
\end{cases} , \tag{4.2a}
\]

\[
V_h(r_h) = \begin{cases} 
0, & r_h < R \\
V_h, & r_h > R
\end{cases} . \tag{4.2b}
\]
where $V_e$ and $V_h$ are the conduction band offset and valence band offset between ZnTe and ZnSe, respectively. $R$ is the radius of the stacked QDs.

![Figure 4.1](image)

Figure 4.1. Schematic diagram of lateral tightly-bound exciton in type-II ZnTe/ZnSe stacked submonolayer QDs.

We use COMSOL to solve the equations self-consistently via an iterative procedure. As an example, Fig. 4.2(a) shows the ground state radial probability densities of electron and hole for QD stack radius $R = 13.5$ nm, from which we obtain the trajectory radii of both charge carriers. Thus, we obtain the dependence of electron and hole trajectory radii on the QD stack radius, plotted in Fig. 4.2(b). The result shows that for QDs with large lateral size ($R > 9$ nm), the trajectory radii of electron and hole increase linearly with the QD stack radius. In particular, the trajectories of electron and hole are $\sim 6.5$ nm outside and $\sim 4.4$ nm inside the QD boundary, respectively. This behavior of excitons in stacked submonolayer type-II QDs is similar as that in spherical type-II QDs calculated in Ref. [110]. In addition, the calculation using COMSOL gives the lateral confinement energy of holes $\sim 1.7$ meV, much smaller than the $\sim 9.7$ meV exciton binding energy. This confirms the validity of the lateral tightly-bound exciton model.
Figure 4.2. (a) The ground state radial probability densities of electron and hole for QD stack radius $R = 13.5 \text{ nm}$ . The dashed lines present the potential barriers at the QD boundary for electron and hole due to the conduction band offset and valence band offset between ZnTe and ZnSe. (b) Trajectory radii of electron and hole as functions of QD stack radius. The dotted lines are for eye guidance.

As calculated in Ref. [11], for lateral tightly-bound excitons in ring-like geometry, the spectrum in magnetic field takes the form

$$E_{\text{exc}} = E_{\text{exc}0} + \frac{\hbar^2}{2MR_0^2} \left( L + \frac{\Phi}{\Phi_0} \right)^2,$$

(4.3)

where $E_{\text{exc}0}$ is the field independent ground state energy of the exciton; $R_0 = (R_e + R_h)/2$; $M = (m_e R_e^2 + m_h R_h^2)/R_0^2$; $L = L_e + L_h$ is the total angular momentum of the exciton; $\Phi = \pi (R_e^2 - R_h^2)B$ is the net magnetic flux through the area between the electron and hole trajectories, referring to the schematic diagram in the inset of Fig. 4.3(a); and $\Phi_0 = \hbar/e$ is the flux quantum.

The exciton energy as a function of net magnetic flux over flux quantum is plotted in Fig. 4.3(a) for angular momentum states $L = 0$, $L = -1$ and $L = -2$. At such a magnetic field that $\Phi = \Phi_0 / 2$, the ground state of exciton transits from $L = 0$ state to $L = -1$ state. This cross of angular momentum states leads to the oscillation of exciton ground-state...
energy and change in the PL intensity due to optical selection rules [11]. Experimentally, a peak of the PL emission from the type-II excitons occurs at the first angular momentum transition (see Ref. [111, 112] and references therein). According to Eq. (4.3), the magnetic field value of the AB oscillation peak is determined by the area \( \pi(R^2 - R_0^2) \), which is dependent on the QD stack radius. Therefore, we calculated the magnetic field value of the AB oscillation peak as a function of the QD stack radius, plotted as Fig. 4.3(b), based on which, we can finely probe the lateral sizes of ZnTe QDs from the experimentally observed AB oscillation peaks.

![Figure 4.3](image)

**Figure 4.3.** (a) The exciton energy as a function of net magnetic flux over flux quantum for the first three angular momentum states. Inset shows the 2-D schematic diagram of tightly-bound exciton and the area for the net magnetic flux \( \Phi \). (b) The magnetic field value of the AB oscillation peak as a function of the QD stack radius.

### 4.2. Determination of the size and density of ZnTe/ZnSe submonolayer quantum dots

The normalized PL spectra at 7.5 K of all six samples are shown in Fig. 4.4. It is apparent that each spectrum consists of several bands, and the relative intensities of these bands depend on Te flux used during growth. Detailed optical analysis of multiple
samples (see Ref. [4, 113, 114] and references therein) revealed that PL of the QDs (generally seen as broad ‘green bands’ with peak energy < 2.6 eV) is convoluted with the blue emission (energy > 2.6 eV) from excitons bound to Te\(_{\geq 2}\) isoelectronic centers (ICs) within the ZnSe barriers [4]. With the increase of Te concentration, the PL spectrum changes gradually from IC dominated emission (sample A) to QD dominated emission (sample F), indicating the increase of QD density.

![Normalized photoluminescence spectra at 7.5 K of the samples.](image)

**Figure 4.4.** Normalized photoluminescence spectra at 7.5 K of the samples.

Considering confinement of holes in ZnTe QDs one can estimate energy levels of the holes from the peak position of the green bands, which are determined via fitting the spectra with Gaussian peaks (listed in Table 2). For this we interpolated the band parameters of ZnTe/ZnSe taken from Ref. [57] based on 50 percent of Te fraction within QDs [3]. The obtained energy levels, measured from the top of the valence band of ZnSe\(_{0.5}\)Te\(_{0.5}\), are 0.58 eV for sample A, 0.46 to 0.48 eV for samples B, C, D and E, and 0.30 eV for sample F. Since the lateral size of the sub-monolayer QDs is much larger
than their thickness, the energy level of holes is mostly determined by the confinement in
the growth direction. We therefore numerically solve the Schrodinger equation for a hole
in one dimensional quantum well in order to correlate the energy level of holes and the
thickness of QDs. Using this approach, we determined the average thicknesses of QDs
for all the samples, listed in Table 2.

To estimate the lateral size of the type-II exciton and confirm the validity of the
lateral tightly-bound model to the real system, we looked at the diamagnetic shift of the
PL emission energy of sample F, through the magnetic field dependence of its normalized
PL spectra shown in Fig. 4.5. The dashed line is a parabolic fit to Eq. 2.6, which gives the
exciton size $\rho_{ex} = 6.5$ nm, much smaller than the QD sizes, but close to the trajectory
separation (~10 nm) between electron and hole as shown in Fig. 4.2 (b). Therefore, the
fitting of diamagnetic shift confirms that in our system the type-II excitons are tightly-
bound so that their sizes are smaller than the QD sizes.

![Figure 4.5. Contour plot of normalized PL spectra of sample F under different magnetic fields at 1.6 K.](image-url)
The normalized integrated PL intensities of the six samples as functions of applied magnetic field are shown in Fig. 4.6. The AB peak is observed for each of the samples. The magnetic field value of AB peaks decreases with increasing Te concentration. We use the magnetic field value of AB peaks (shown in Fig. 4.6) and the curve in Fig. 4.3 (b) to obtain the average QD stack radius in each sample, listed in Table 2. The electron trajectory radii are estimated as 6.5 nm outside the QD boundary.

![Figure 4.6](image)

**Figure 4.6.** Normalized integrated photoluminescence intensity as a function of the magnetic field for the samples.

We further quantitatively estimate the area density of QDs, \( n_{QD} \), as

\[
n_{QD} = \frac{N_{Te}}{N_A} \left( \frac{h_L}{h_{QD}} \right) \frac{1}{\pi R^2 x}
\]  
(4.4)
where, $N_{Te}$ is the average Te concentration, as measured by SIMS; $N_A$ is the volumetric atomic density of ZnTe, which is $3.52 \times 10^{22}$ cm$^{-3}$ [115]; $h_l$ and $h_{QD}$ are the average thicknesses of the one spacer layer and the QDs, respectively; $R$ is the average radius of the QD stacks; and $x \approx 0.5$ is the Te fraction within QDs. The results of the calculation are listed in Table 2, along with the average distances between the centers of QDs as estimated from the area densities.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Green band peak position (eV)</th>
<th>QD Thickness (nm)</th>
<th>QD stack radius (nm)</th>
<th>QD Area density ($\times 10^9$ cm$^{-2}$)</th>
<th>Average distance between QD centers (nm)</th>
<th>Electron trajectory radius (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A(D55)</td>
<td>2.62</td>
<td>0.4</td>
<td>13.4</td>
<td>2.13</td>
<td>216.7</td>
<td>19.9</td>
</tr>
<tr>
<td>B(D53)</td>
<td>2.51</td>
<td>0.5</td>
<td>14.9</td>
<td>2.99</td>
<td>183.0</td>
<td>21.4</td>
</tr>
<tr>
<td>C(D54)</td>
<td>2.50</td>
<td>0.5</td>
<td>15.2</td>
<td>4.80</td>
<td>144.3</td>
<td>21.7</td>
</tr>
<tr>
<td>D(D50)</td>
<td>2.52</td>
<td>0.5</td>
<td>14.1</td>
<td>2.09</td>
<td>219.0</td>
<td>20.6</td>
</tr>
<tr>
<td>E(D51)</td>
<td>2.50</td>
<td>0.5</td>
<td>15.0</td>
<td>3.09</td>
<td>179.9</td>
<td>21.5</td>
</tr>
<tr>
<td>F(D47)</td>
<td>2.34</td>
<td>1.1</td>
<td>20.3</td>
<td>8.50</td>
<td>108.5</td>
<td>26.8</td>
</tr>
</tbody>
</table>

Table 2. Size and density of QDs in all samples.

The average thickness of QDs, the average QD stack radius and the area density of QDs as functions of Te concentration in the samples are plotted in Fig. 4.7. Both the size and the density of QDs increase with more Te concentration in the samples. As the Te concentration increases by 25 times from sample A to sample F, the average thickness of
QDs increases by 3 times; the average QD stack radius increases by 50%; and the density of QDs increases by 4 times.

**Figure 4.7.** The average thickness of QDs, the average QD stack radius and the area density of QDs as functions of Te concentration in the samples.

To investigate the lateral size distribution of QDs, we spectrally analyzed the AB peak of PL intensity for samples A, B, C and F. For different emission energies, we studied the corresponding emission intensities as functions of magnetic field and locate the magnetic field value of the AB peaks. Based on the curve in Fig. 4.3 (b), which gives a one-to-one mapping between the AB transition field and the radius of the QD stack, we obtained the dominating QD radii corresponding to the emission energies across the PL
spectra for the four samples, shown in Fig. 4.8. In single-cycled sample A, which has smallest Te concentration, QDs have a uniform radius of about 13.4 nm, giving the smallest lateral size of ZnTe submonolayer QDs in this particular ZnTe/ZnSe multilayer system. In sample F, the one with highest Te concentration, QD radius varies gradually across the PL spectrum, with the largest variation (from 18.6 to 20.9 nm) among the four samples. In sample B and C, the QD radii take several particular values, confirming the vertical correlation and stacking nature of the submonolayer QDs. Thus, we correlated the spectral dependence of QD radius to the spectral dependence of PL emission intensity for sample B and C, and investigated the distribution of QDs in each presenting radius value, shown in Fig. 4.9. Sample B has its QDs 62.3% in radius 14.1 nm and 16.6% in radius 15.1 nm, while sample C has its QDs 10.8% in radius 14.1 nm and 86.6% in radius 15.1 nm. With higher Te flux during growth and higher Te concentration, sample C has more QD stacks distributing in the larger radius set than sample B has, though they have the same presenting values of QD stack radius.
Figure 4.8. QD radii (circular dots) corresponding to different emission energies, overlaid over the spectra (solid lines) of (a) sample A; (b) sample B; (c) sample C; (d) sample F.

Figure 4.9. Percentage distribution of QDs in the presenting radius values for sample B and sample C.
4.3. Tuning between quantum-dot and quantum-well-like behaviors

In QD based heterostructures, with increasing QD density, it is expected that the QDs would start to coalesce, forming quantum-well-like layer, which would change the electronic properties of the samples. For type-II QDs, and for the ZnTe/ZnSe system in particular, where the electrons are located in the barriers, the wavefunctions of charge carriers can start to strongly overlap much earlier than the onset of physical QD coalescence. Thus, type-II QD layers can start behaving like quantum wells (QWs) at much lower densities than those required for the formation of real QW layers, with obvious consequences for device performance.

We compare the separation between QDs to the electron trajectory radius listed in Table 2 for samples D, E and F. For samples D and E, the average distances between QDs are about one order of magnitude larger than the electron trajectory radius, so that the electrons bound to different QDs are not affected by each other. For sample F, the average distance between QDs is about four times the electron trajectory radius. Therefore, it is possible that some electrons bound to neighboring QDs may have their wavefunctions overlap, leading to QW-like properties of the multilayers.

To further investigate this, we study the temperature dependent TRPL to extract the excitonic PL lifetimes and exciton binding energies. Fig. 4.10 shows the excitonic PL lifetimes at low temperature across the spectra of the three samples. For samples D and E, at the higher energy side, the PL has relatively short lifetimes (~60 ns), since the emission is dominated by ICs. At the lower energy side, the PL lifetimes of all three sample approach similar values around 95 ns; these values give the lifetimes of excitons bound to type-II ZnTe QDs at low temperature. We next consider emission at a photon
energy of 2.45 eV, which is within the emission region associated with QDs, and find that the PL lifetime in sample F is ~52 ns, which is much shorter than that (~95 ns) for both sample D and sample E. We suggest that this is one of the effects of the overlapping of electron wavefunctions in sample F. Indeed, because of the vertical confinement in the multilayers with stacked QDs, electrons prefer to be located in the barrier on the side of QDs, instead of above/below as for a single ideal QD. In sample F, because some of the electron wavefunctions start to overlap, a fraction of electrons might be located in the barrier region above/below the QDs, forming excitons like those in QW multilayers. Since the thickness of the sub-monolayer QDs is much smaller than their lateral size, these QW-like excitons have much stronger electron and hole wavefunctions overlap, and therefore, shorter lifetimes. In addition, due to vertical confinement, the electrons located above/below QDs have higher energies than those located on the side of QDs. They contribute more on the higher energy side of the PL spectrum. Therefore, the excitonic lifetimes on the high energy side is shorter than those on the low energy side of sample F.
Figure 4.10. Excitonic photoluminescence lifetimes (circular dots) at different photon energies, overlaid over corresponding spectra (solid lines): (a) Sample D; (b) Sample E; (c) Sample F.

We further consider the photon energy of 2.36 eV, which is only related to emission from QDs, for samples E and F, to study the dependence of excitonic PL lifetimes on temperature. Results are shown in Fig. 4.11. Within the temperature region below ~120 K, the excitonic lifetimes increase with increasing temperatures, which is a signature of radiative recombination in type-II QDs [4]. As the temperature rises, the bound excitons are ionized, while the holes are still confined within the QDs, lowering the average overlap of wavefunctions of electrons and holes, which results in a longer lifetime of excitons undergoing radiative recombination. When temperature is higher than 120 K, the non-radiative processes of hole ionization [4] start to dominate. Thus, the excitonic lifetimes decrease with increasing temperatures in the high temperature region. It was argued in Ref. [4] that under such conditions the temperature dependence of a type-II
excitonic lifetime, \( \tau \), can be fitted with the following formula proposed in Ref. [4], modified from Ref. [116],

\[
\frac{1}{\tau} = \frac{1}{\tau_{r0}} \left[ 1 - C \exp(-\varepsilon_b / k_B T) \right] + \frac{1}{\tau_{nr0}} \exp(-\varepsilon_a / k_B T)
\]

(4.5)

where \( C \) is a constant; \( k_B \) is the Boltzmann constant; \( \tau_{r0} \) and \( \tau_{nr0} \) are the radiative and non-radiative excitonic lifetimes at \( T = 0 \) K, respectively; \( \varepsilon_b \) is the exciton binding energy; and \( \varepsilon_a \) is the non-radiative activation energy. The fitting parameters with errors are listed in Table 3. We notice that the exciton binding energy in sample F is comparably larger than that in sample E, which is in conflict with the larger lateral QD sizes in sample F, if one assumes that in both samples electrons are located only at the ‘side’ of all QDs. This conflict, however, reveals the fact that in sample F with high density of QDs, because of the overlapping of electron wavefunctions, a portion of the electrons move to the barrier above/below QDs, creating QW-like excitons which have stronger electron-hole overlap, and therefore, larger binding energies.

Figure 4.11. Excitonic photoluminescence lifetimes as a function of temperature at 2.36 eV for sample E (red circles) and sample F (blue squares); dash lines are fittings to Eq. 4.5.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Exciton Binding Energy (meV)</th>
<th>$\tau_{r0}$ (ns)</th>
<th>Non-radiative Activation Energy (meV)</th>
<th>$\tau_{nr0}$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>6.9 ± 0.3</td>
<td>93 ± 4</td>
<td>118 ± 10</td>
<td>0.10 ± 0.05</td>
</tr>
<tr>
<td>F</td>
<td>9.1 ± 0.9</td>
<td>99 ± 5</td>
<td>88 ± 5</td>
<td>1.2 ± 0.2</td>
</tr>
</tbody>
</table>

Table 3. Fitting parameters of the 2.36 eV type-II excitons for sample E and F.

4.4. Temperature effect on the Aharonov-Bohm oscillations

The PL intensity as a function of magnetic field at different experimental temperatures for samples A and F is shown in Fig. 4.12. The amplitude of the AB peak of PL intensity does decrease with increasing temperature, as expected. We further plotted the magnitude of the AB peak as a function of experimental temperature in Fig. 4.13 for sample A and F.
The magnitude of the AB peak as a function of temperature for the two samples is shown in Fig. 4.13. For analyses of the data we take into account that the electron travels over longer distances outside of the dot than the confined hole and its probability to be scattered is much larger. Correspondingly, the magnitude of the AB peak decreases exponentially with the electron path length $L$: $\Delta I_{AB} \propto \exp[-L/L_D]$, where $L_D$ is the coherence length. We also assume here that the ballistic regime is applied as the electron path around the QDs is relatively small ($< 160$ nm), so that the coherence length is proportional to the decoherence time. In this case,
\[ \Delta I_{AB} \propto \exp \left( -\frac{t_0}{\tau_D} \right), \]  
(4.6)

where \( t_0 \) is time exciton ‘spends’ on the orbit before recombining radiatively or non-radiatively, corresponding to an average lifetime of the electrons \( \sim 100 \text{ ns} \) as measured by the PL decay. Therefore, using Eq. (2.18), the experimental data are analyzed with help of the following expression

\[ \Delta I_{AB} = \Delta I_{AB}(0) \cdot \exp\left[-At_0T - bt_0T^3\right]. \]  
(4.7)

The result of fitting experimental data to Eq. (4.7) is shown in Fig. 4.12 (b) for sample F (red dashed line); the best fit was obtained for \( At_0 = 0.04 \text{ K}^{-1} \) and \( bt_0 = 9.2 \times 10^{-5} \text{ K}^{-3} \). Assuming \( t_0 = 100 \text{ ns} \), we get \( A = 4 \times 10^{-4} \text{ ns}^{-1}\text{K}^{-1} \) and \( b = 9.2 \times 10^{-7} \text{ ns}^{-1}\text{K}^{-3} \). It should be emphasized that the latter parameter is much smaller than approximately \( 5 \times 10^{-3} \text{ ns}^{-1}\text{K}^{-3} \) obtained after introducing of ZnSe parameters into the corresponding expression of Ref. [117], where the electron-phonon effects on decoherence were addressed. We attribute that to the strong electron-hole coupling. Even in the situation when only the moving electron is scattered, the whole electron-hole system emits or absorbs phonons which diminishes such energy exchange.

Figure 4.13. Magnitude of the AB peak as a function of the temperature for (a) sample A and (b) sample F. The dashed line is the fit to Eq. (4.7) for sample F.
Chapter 5

Long Spin-Flip Time and Large Zeeman Splitting of Holes in Type-II ZnTe/ZnSe Submonolayer Quantum Dots

In this chapter we will show the results of circularly polarized magneto-PL measurements. To explain observed relative intensities and energy positions of the $\sigma^+$ and the $\sigma^-$ emissions, a model with ultra-long spin-flip time of holes confined to submonolayer QDs is proposed. The $g$-factor of electrons, located in ZnSe barriers, was obtained from fitting the temperature dependence of the degree of circular polarization within this model. The $g$-factor of the QD-bound type-II excitons was extracted from the Zeeman splitting, from which $g$-factor of holes in ZnTe QDs was calculated and found about three times larger than that in bulk ZnTe. Tight-binding calculations were employed to understand the origin of such an increase.

5.1. Zeeman energy splitting of the type-II exciton

Fig. 5.1 (a) shows the PL spectra at 0.36 K of $\sigma^+$ and $\sigma^-$ polarized emission at magnetic field of 18 T. It is apparent that the intensity of $\sigma^+$ polarized emission is much higher than that of $\sigma^-$ polarized emission. To show the energy difference between $\sigma^+$ and $\sigma^-$ polarized emissions, we plot the normalized $\sigma^+$ and $\sigma^-$ PL for selected values of magnetic field at $T=0.36$ K in Fig. 5.1 (b). As expected, at $B = 0$ T the differently
polarized lines coincide, while with applied magnetic field, the spectrum of $\sigma^+$ polarized emission shifts to higher energy while that of the $\sigma^-$ polarized emission shifts to lower energy. Therefore, we observed relatively rare case when $\sigma^+$ polarized emission with higher energy shows higher emission intensity, which we will discuss below.

We start from the energy relation between $\sigma^+$ and $\sigma^-$ polarized emissions. A schematic diagram of the Zeeman splitting of the electrons’, holes’ and excitons’ spin states which coincide with the energy shift of $\sigma^+$ and $\sigma^-$ polarized emission is shown in Fig 5.1(c), taking into account that the $g$-factor of electrons in ZnSe is positive [106], and the ground state of holes confined in ZnTe QDs is heavy hole state [2, 81], with spin $J_z = \pm \frac{3}{2}$. Based on optical selection laws, the bright exciton with $J_z = -1$ consists of a spin-up electron and a spin-down hole whose recombination will emit a $\sigma^-$ photon, while that with $J_z = +1$ consists of a spin-down electron and a spin-up hole whose recombination will emit a $\sigma^+$ photon. Therefore, since the spin-up excitons have higher energy than spin-down ones, the $g$-factor of the excitons is positive. This requires the $g$-factor of the heavy holes in ZnTe QDs be positive and larger than the $g$-factor of electrons in ZnSe, since the energy splitting between the $\sigma^+$ and the $\sigma^-$ polarized spectra can be expressed as [118]

$$E_{\sigma^+} - E_{\sigma^-} = g_{hh}\mu_B B - g_e\mu_B B = g_X\mu_B B,$$

(5.1)

where $g_{hh}$, $g_e$, and $g_X$ are the $g$-factors of heavy holes, electrons and the type-II excitons; $\mu_B$ is the Bohr magneton and $B$ is the magnetic field applied in the Faraday geometry.
Figure 5.1. (a) PL spectra at 0.36 K of $\sigma^+$ and $\sigma^-$ polarized emission under magnetic field 18 T. (b) Normalized PL spectra under different magnetic field at 0.36 K. $\sigma^+$ is shown in blue while $\sigma^-$ is shown in red. (c) Zeeman splitting of the ground states of electron, hole and exciton. The double-arrrows indicate the spin states associated with $\sigma^+$ and $\sigma^-$ polarized emission, which are corresponding to the $J_Z = +1$ and $J_Z = -1$ excitons, respectively.

To find out the value of g-factor of excitons in Eq. 5.1, we plot the peak energy splitting between $\sigma^+$ and $\sigma^-$ polarized spectra as a function of magnetic field at different temperatures in Fig 5.2(a). It is surprising that the splitting at lower temperatures is much larger than that at higher temperatures since the g-factors should not have strong temperature dependence [119]. We attribute this experimental observation to the multiple-band nature of the PL spectra [109].

As an example, we fitted the polarized PL spectra of 18 T at 0.36 K with two Gaussian bands in Fig. 5.2(b). The peak energy differences of corresponding Gaussian bands of $\sigma^+$ and $\sigma^-$ emission are ~2 meV, same as those for the polarized spectra at 30.5 K.
as shown in Fig. 5.2(c). However, since the DCP, defined as \( \frac{I_{\sigma^+} - I_{\sigma^-}}{I_{\sigma^+} + I_{\sigma^-}} \), of the Gaussian band with higher energy is larger than that of the Gaussian band with lower energy, the overall \( \sigma^+ \) spectrum is effectively shifted to higher energy. Therefore, the energy splitting of the polarized spectra at 0.36 K is effectively enhanced. At higher temperature, the DCPs of the multiple bands are small. The contribution of their difference to the peak energy splitting is negligible. In this case, the peak energy splitting between \( \sigma^+ \) and \( \sigma^- \) polarized spectra at higher temperatures such as 26.3 K and 30.5 K, where the magnetic field dependences of peak energy splitting coincide as shown in Fig. 5.2(a), is purely related to the Zeeman splitting of the spin states. Thus, we use Eq. 5.1 to fit the magnetic field dependence of peak energy splitting between \( \sigma^+ \) and \( \sigma^- \) polarized spectra at 30.5 K. This fitting gives \( g_x = 1.9 \).

**Figure 5.2.** (a) Peak energy splitting between \( \sigma^+ \) and \( \sigma^- \) polarized spectra as a function of magnetic field at different temperatures. The dashed lines are linear fits. (b) and (c) PL spectra of \( \sigma^+ \) and \( \sigma^- \) polarized emission under magnetic field 18 T at 0.36 and 30.5 K, respectively. The dashed lines are fittings with two Gaussian bands.
5.2. Long spin-flip time of the confined holes

The origin of the difference in the intensities of $\sigma^+$ and $\sigma^-$ polarized emission can be the difference in recombination oscillator strength of $\sigma^+$ and $\sigma^-$ polarized emission or the distribution of excitons in $J_z = +1$ and $J_z = -1$ states. As discussed above, $J_z = -1$ exciton state has lower energy than $J_z = +1$ one. If the excitons follow the Boltzmann distribution to the two states, the $J_z = -1$ state is higher occupied than the $J_z = +1$ state, reversed to the intensity relationship between $\sigma^-$ polarized and $\sigma^+$ polarized emission. Therefore, to explain our observation of positive DCP it requires the ratio of the recombination oscillator strengths of these two emissions larger than seven, which is physically unrealistic. Meanwhile, with increasing temperature, the inversion of the occupation of the spin states which originates from the Boltzmann distribution becomes weaker. In the case here, the population of $J_z = -1$ excitons decreases while that of $J_z = +1$ excitons increases with increasing temperature. Therefore, the DCP at higher temperature must be larger than that at lower temperature, which does not agree with the experimental observation shown in Fig. 5.2(b) and 5.2(c).

The discussion above reveals two facts of the exciton spin states. First, the excitons have their spin-flip time longer than their recombination lifetime so that they do not follow Boltzmann distribution to the two spin states. Thus, the type-II excitons in ZnTe/ZnSe QDs have spin-flip time ultra-long, and as long as 100 ns [109]. This must be attributed to the suppression of spin-flip of the holes confined in QDs. Indeed, it is predicted theoretically [36-38] that holes confined in QDs can have very long spin-flip time because of the suppression of hyperfine interaction of holes with lattice nuclei with respect to that of electrons, the invalidation of elastic phonon for spin flip due to the
discrete hole states, and the spin-orbit mixing being inhibited by the motional quantization of holes in QDs.

The second fact is that initially there are more type-II excitons formed with $J_z = +1$ than those with $J_z = -1$. To understand this fact, we note that the laser used in the experiment was not circularly polarized so that the photo-generated charge carriers are initially equally distributed in their spin states. Since the spin-flip time of electrons in ZnSe barrier is short [109, 120], the electron spin states are thus assumed in the thermal equilibrium before the type-II excitons are formed. Therefore, the electron spin states populations follow the Boltzmann distribution. As for holes, since they are scattered into the QDs with assistance of phonons, their spin states are assumed to be equally occupied before the formation of type-II excitons. Therefore, initially there are more type-II excitons formed with $J_z = +1$ than those with $J_z = -1$. Furthermore, with increasing temperature, the Boltzmann distribution of the electron spin states approaches equally distribution so that the difference in the population of $J_z = +1$ and $J_z = -1$ excitons decreases. Therefore, the DCP should decrease with increasing temperature, which agrees with the experimental observation.

5.3. Fitting the g-factor of electrons

Using the above discussed model, since the distribution of exciton spin states is dominated by the distribution of electron spin states, the DCP can be expressed as [121, 122]
\[ DCP = \frac{1 - \exp\left(\ln(r) - \frac{\Delta E}{kT}\right)}{1 + C_s + \exp\left(\ln(r) - \frac{\Delta E}{kT}\right)} \]  

(5.2)

where \( \Delta E = g_e \mu_B B \) is the energy splitting of the electron spin states; \( k \) is the Boltzmann constant and \( T \) is the temperature; \( r \) is the ratio of recombination oscillator strengths of \( \sigma^+ \) and \( \sigma^- \) polarized emission; \( C_s \) is a constant that includes contribution from spin-flip time and structural anisotropy [121]. As an example, we use data for 10 T magnetic field to plot the DCP as a function of temperature in Fig. 5.3(a), and fit it employing Eq. 5.2. The fitting gives \( g_e = 1.0 \pm 0.1, \ C_s = 0.26 \pm 0.04 \), and \( r = 1.1 \pm 0.1 \). We applied the same fitting procedure to DCPs obtained for the magnetic fields higher than 8 T, where the anisotropic splitting is mostly overcome by the Zeeman splitting; the fitting parameters are consistent for different magnetic field, as shown in Figs. 3(b)-(d). The small ratio of recombination oscillator strength agrees with the proposed model of long spin-flip time for holes in ZnTe submonolayer QDs, so that the large DCP is largely related to the distribution in the exciton spin states. We notice that the fitted electron g-factor decrease with increasing magnetic field. This is due to the increasing contribution to PL from the anisotropic dark states of which the emission is not circularly polarized [123].
Figure 5.3. (a) Temperature dependence of DCP at 10 Tesla. The line is fitted to Eq. 5.2. (b) - (d). The fitting parameters for the temperature dependence of DCP at different magnetic fields, fitted to Eq. 5.2. Lines are for eye guidance.

5.4. Enhancement of the $g$-factor of holes

As defined in Eq. 5.1, the $g$-factor of heavy holes in QDs can be calculated as $g_{hh} = g_x + g_c = 2.9$. This value is more than three times larger than the hole $g$-factor in bulk ZnTe ($g_{hh} = 6\kappa + \frac{27}{2} \alpha = 0.85$, using the formula in [118] and the Luttinger parameters in [124]). As discussed in Ref. [28], the confinement of hole wavefunction can enhance the Zeeman splitting by inducing admixture of the subband states. To distinguish the contribution from wavefunction confinement and other origins, such as local strain, to the enhancement of heavy hole $g$-factor, we cooperate with Dr. Garnett W.
Bryant in Quantum Measurement Division and Joint Quantum Institute of NIST, working on numerical calculation of the Zeeman splitting of heavy holes in ZnTe/ZnSe QDs using the parameters reported in Refs. [57, 81, 109]. The calculation is still ongoing so that we plan to discuss the experimental and calculation results in our future publications.

In summary, via investigating circularly polarized magneto-PL of type-II submonolayer ZnTe/ZnSe QDs, we observed the evidence of long spin-flip time (>>100 ns) of type-II excitons in submonolayer QDs. Through quantitatively analysis of Zeeman energy splitting and temperature dependence of DCP, we obtained $g$-factors of the type-II excitons, electrons and heavy holes. The $g$-factor of holes in QDs is enhanced, of which the origins are under investigation.
Chapter 6

Optical Anisotropy in ZnTe/ZnSe Submonolayer Quantum Dots

In this chapter we will show the observation of linearly polarized photoluminescence for ZnTe/ZnSe submonolayer quantum dots (QDs). The ratio of heavy-light hole mixing is calculated through analysis of the degree of linear polarization (DLP). Combined with the magnetic field dependence of degree of circular polarization (DCP), the energy of anisotropic exchange splitting is obtained for type-II excitons in this system. The comparison of the spectral dependence of DLP between four QD samples indicates that the optical anisotropy is mostly related to the structure elongation of ZnTe QDs. Numerical calculation is applied to estimate the aspect ratio of the elongated QDs from the DLPs. At the end, the optical anisotropy is compared to the anisotropic x-ray diffraction pattern.

6.1. Linear polarization of photoluminescence

We did linearly polarized photoluminescence on samples A, C, E and F. Among them, the crystal axes are marked only on sample F.

The PL spectra of sample F polarized along the [110] and [1\overline{1}0] axes are shown in Fig. 6.1(a), while the PL intensity as a function of the angle between axis of the linear polarizer and the [110] axis is shown in Fig 6.1(b). The PL emission polarized along the
[110] axis is the strongest while that along the [1\bar{1}0] axes is the weakest. The DLP, defined as $\frac{I_{[110]} - I_{[\bar{1}10]}}{I_{[110]} + I_{[\bar{1}10]}}$, is about 0.18.

![Figure 6.1](image)

**Figure 6.1.** (a) The photoluminescence emission of sample F polarized along [110] and [1\bar{1}0] crystal axes. (b) The integrated intensity of the photoluminescence of sample F as a function of the angle between axis of the linear polarizer and the [110] crystal axis.

### 6.2. Light-heavy mixing and anisotropic exchange splitting

Since the PL spectrum is broad and consists of multiple bands [113], the doublet fine structure cannot be resolved from the linearly polarized spectra. To obtain the value of the anisotropic exchange splitting, we studied the DCP of the PL as a function of the magnetic field for sample F. Without the magnetic field, due to the doublet fine structure, the PL emission is linearly polarized instead of circularly polarized. While magnetic field increases, the Zeeman splitting gradually increases, and eventually dominates the anisotropic exchange splitting, resulting in decreased mixing between the $|+1\rangle$ and $|-1\rangle$ excitonic states. Thus the DCP will increase with the increasing magnetic field. The DCP as a function of the square of magnetic field is shown in Fig. 6.2. To analyze these results, we follow Refs. [61, 123], where the magnetic field dependence of the DCP is discussed.
in terms of completion among the Zeeman splitting, the anisotropic exchange splitting and the bright/dark exciton relaxation; such a dependence can be described by the following expression [123]

\[ DCP(B) = \frac{B^2}{B^2 + B_1^2} \left[ P_0^0 + \tilde{P}_c^0 \frac{B^2}{B^2 + B_2^2} \right] , \]  

(6.1)

where the effective magnetic fields \( B_1 = \frac{\Delta E}{\Delta E_{\text{Zeeman}} / B} \) and \( B_2 = \frac{d^{1/2} \Delta E_2}{\Delta E_{\text{Zeeman}2} / B} \) stand for the ratio between anisotropic exchange splitting (\( \Delta E \) and \( \Delta E_2 \)) and Zeeman splitting of the bright and the dark excitonic states, respectively; \( d >1 \) is a constant; \( P_0^0 \) and \( \tilde{P}_c^0 \) are constants. Constant \( P_0^0 \) can be related to the ratio of light-heavy hole mixing, \( \gamma \), using the formula \( P_0^0 = \left(1 - \gamma^2 / 3\right) / \left(1 + \gamma^2 / 3\right) \) introduced in Ref. [59].

The values of \( \gamma \) can be deduced from the DPL according to the following relation [58, 59]:

\[ DLP = 2 \kappa \gamma / \left(1 + \kappa^2 \gamma^2 \right) , \]  

(6.2)

where \( \kappa = 1 / \sqrt{3} \) measures the difference in strength between light hole and heavy hole radiative coupling. Thus, from the DLP we calculated the overall ratio of light-heavy hole mixing in sample D is \( \sim 0.16 \). Therefore, \( P_0^0 \) is \( \sim 0.98 \) for sample F. We have demonstrated in Chapter 5 that \( \Delta E_{\text{Zeeman}} \) in our system is determined only by the electron Zeeman splitting, and therefore is given by \( g_e \mu_B B \) (here \( g_e \) is the electron \( g \)-factor and \( \mu_B \) is the Bohr magneton). Fitting our data, shown as open circles in Fig. 6.2, to Eq. 6.1 gives \( B_1 = 3.8 \) T and \( B_2 = 14 \) T, which translates to the anisotropic exchange splitting of \( \Delta E_1 = 0.22 \) meV for bright excitons, and \( \Delta E_2 = 0.81 \) meV for dark excitons. These values of
anisotropic exchange splitting are comparable to those reported for CdTe and CdSe QDs (0 - 0.5 meV, see Refs. [66, 67] and references therein).

![Figure 6.2](image)

**Figure 6.2.** The degree of circular polarization as a function of the square of magnetic field for sample F. The dashed line is fitted to Eq. 6.1.

### 6.3. Spectral dependence of degree of linear polarization

Next we discuss origin of the observed optical anisotropy. Ivchenko and Nestoklen [71] have discussed that the optical anisotropy of type-II heterostructures CA/C'A' can come from anisotropic interface bond alignment, since the relative contributions of the $p_x$- and $p_y$-orbitals to the valence-band function near the interface C-A' or C'-A differ substantially. However, for the ZnTe/ZnSe QD system, the interface can only be Te-Zn-Se. Therefore, the interfacial symmetry lowering is not the cause of the optical anisotropy in our samples.

To distinguish the contribution from the anisotropic strain relief or defects and the QDs structure elongation to the optical anisotropy, we investigated the spectral dependence of $DLP$ for the four samples, as plotted in Fig. 6.3, overlaid with their
normalized PL spectra at 7.5 K. There are several facts in the spectral dependence of DLP suggesting that instead of anisotropic strain relief or defects, it is the QDs structure elongation which dominates to the optical anisotropy. First, for all the samples, the QD related PL emission is more linearly polarized than the IC related PL emission. This agrees with the spectral analysis of the anisotropic exchange splitting for sample F, shown in Fig. 6.4, fitted from spectral magnetic field dependence of DCP. Second, the QD emission dominated PL spectrum of sample F has the highest DLP among the samples, correlated to the highest Te concentration and the highest QD density in this sample. In addition, sample C and E have close Te concentration, similar PL spectrum and similar spectral dependence of DLP, while sample C has the lowest strain and sample E has the highest strain among four samples. Along with the two similar ‘humps’ in the spectral DLP of samples C and E which are correlated with the stack nature of ZnTe QDs [2, 108], it indicates that the optical anisotropy in the samples is mostly related to the structure elongation of the ZnTe QDs instead of the anisotropic strain relief or defects in ZnSe barrier.
Figure 6.3. Spectral dependence of the degree of linear polarization for all samples overlaid over corresponding normalized spectra (dashed lines).

Figure 6.4. Anisotropic exchange splitting at different emission energy for sample F, overlaid over PL spectrum.
6.4. Calculation of the aspect ratio of elongated dots

To estimate lateral shape anisotropy of the QDs, we applied the theory developed in Refs. [68, 69], where the degree of linear polarization of interband transitions is defined by

\[
DLP = \frac{\left| \langle \Psi_e | \hat{p}_x | \Psi_h \rangle \right|^2 - \left| \langle \Psi_e | \hat{p}_y | \Psi_h \rangle \right|^2}{\left| \langle \Psi_e | \hat{p}_x | \Psi_h \rangle \right|^2 + \left| \langle \Psi_e | \hat{p}_y | \Psi_h \rangle \right|^2},
\]

(6.3)

where \( \Psi_e \) and \( \Psi_h \) are the ground states of electrons and holes, respectively. The \( p_x \) and \( p_y \) orbitals are chosen to align along the long and short axes of the dots, which are the [110] and [1\( \overline{1} \)0] axes, respectively.

The ground state of the holes can be written as \( | \Psi_h \rangle = \psi_h^x | s \rangle + \psi_h^y | x \rangle + \psi_h^y | y \rangle + \psi_h^z | z \rangle \), where \( \psi_h \)'s are the envelop functions. Considering that \( \left| \langle \Psi_e | \hat{p}_x | \Psi_h \rangle \right|^2 = P_0 \left| \langle \psi_e^x | \psi_h^x \rangle \right|^2 \),

we have

\[
DLP = \frac{\left| \psi_h^x \right|^2 - \left| \psi_h^y \right|^2}{\left| \psi_h^x \right|^2 + \left| \psi_h^y \right|^2},
\]

(6.4)

here \( \left| \psi_h^x \right|^2 \) and \( \left| \psi_h^y \right|^2 \) represent the probability of a hole in the \( p_x \) and \( p_y \) orbitals, respectively.

Since \( \psi_h^x = \langle x | \Psi_h \rangle \) and \( \psi_h^y = \langle y | \Psi_h \rangle \), we use the analytic solution of a two-dimensional hydrogen atom in Ref. [76] to rewrite

\[
\langle x | (x_0, y_0) = (x-x_0) \exp \left( -\frac{km_{h(ZnTe)} e^2}{2\varepsilon_r(ZnTe) \hbar^2} \sqrt{(x-x_0)^2 + (y-y_0)^2} \right),
\]

(6.5a)
\[
<y|(x_0, y_0) = (y - y_0) \exp \left(-\frac{km_{h(ZnTe)}}{2E_{r(ZnTe)}h^2} \sqrt{(x - x_0)^2 + (y - y_0)^2} \right). 
\]
\[
(6.5b)
\]
so that
\[
\psi_h^*(x_0, y_0) = \iint (x - x_0) \exp \left(-\frac{km_{h(ZnTe)}}{2E_{r(ZnTe)}h^2} \sqrt{(x - x_0)^2 + (y - y_0)^2} \right) \Psi_h(x, y) dx dy , 
\]
\[
(6.6a)
\]
\[
\psi_h^*(x_0, y_0) = \iint (y - y_0) \exp \left(-\frac{km_{h(ZnTe)}}{2E_{r(ZnTe)}h^2} \sqrt{(x - x_0)^2 + (y - y_0)^2} \right) \Psi_h(x, y) dx dy , 
\]
\[
(6.6b)
\]
and
\[
DLP = \iint \psi_h^*(x, y) \psi_h^*(x, y) dx dy - \iint \psi_h^*(x, y) dx dy - \iint \psi_h^*(x, y) dx dy + \iint \psi_h^*(x, y) dx dy . 
\]
\[
(6.7)
\]
We use COMSOL to calculate the ground state wavefunction of holes \( \Psi_h \) confined in an elliptical ZnTe QD and use MATLAB to integrate DLP from Eqs. 6.5, 6.6 and 6.7, the code of which is listed in Appendix A. The constants and parameters are listed in Table 4. The calculations were done for two sizes of QDs with areas of \( a \times b = 412 \) and \( = 228 \) nm\(^2\) (here \( a \) and \( b \) are the major and minor axis of the ellipse, respectively), which correspond to the average lateral size of sample F and samples C and E [81], respectively. The results in terms of the aspect ratio \( \beta = a / b \) are shown in Fig. 6.5 (a).

Comparing with the spectral results of DLP shown in Fig. 6.3, we conclude that the aspect ratio of the QDs in sample F ranges from 1.2 to 1.4, while the aspect ratio of the QDs in samples C and E range from 1.1 to 1.2 and from 1.05 to 1.1, respectively. In addition, as discussed in Ref. [107, 109], QDs in sample F are thicker than those in samples C and E, and in the PL spectra the emission with lower energy is from thicker.
QDs. Thus, our experiment and calculation results suggest that the thicker QDs have larger aspect ratios.

To further investigate the ratio of heavy-light hole mixing in different samples and its relation to the QD size, we plot the $DLP$ as a function of $\gamma$ calculated from Eq. 6.2 in Fig. 6.5 (b). Comparing with the spectral results of $DLP$, we find out that the ratio of heavy-light mixing ranges from 0.04 to 0.26 in various samples, with larger (thicker) QDs having stronger heavy-light hole mixing. This conclusion agrees with the discussion in Ref. [58] that the ratio of heavy-light hole mixing is inversely proportional to the energy separation between the heavy hole and light hole ground state, based on the facts that smaller QDs have stronger confinement for holes which leads to larger energy separations between heavy and light holes.

<table>
<thead>
<tr>
<th></th>
<th>$h$</th>
<th>$m_0$</th>
<th>$k$</th>
<th>$e$</th>
<th>$eV$</th>
</tr>
</thead>
<tbody>
<tr>
<td>constants</td>
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<td>$9.109 \times 10^{-31}$</td>
<td>$8.987 \times 10^{9}$</td>
<td>$1.602 \times 10^{-19}$</td>
<td>$1.602 \times 10^{-19}$</td>
</tr>
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<td>$m_e^*$</td>
<td>$0.122 m_0$</td>
<td>$0.45 m_0$</td>
<td>$10.3$</td>
<td>$0.3 eV$</td>
<td>$0$</td>
</tr>
<tr>
<td>$m_h^*$</td>
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<td>$0.32 m_0$</td>
<td>$8.6$</td>
<td>$0$</td>
<td>$0.7 eV$</td>
</tr>
</tbody>
</table>

Table 4. Constants and parameters for calculation of DLP.
Figure 6.5. (a) Calculated DLP as a function of aspect ratio of the elongated QDs with larger lateral size (squares) and smaller lateral size (circles) as described in text. The inset shows a lateral elongated QD with aspect ratio $\beta = a / b$. (b) DLP as a function of the ratio of heavy-light hole mixing calculated from Eq. 6.2.

6.5. Comparison to x-ray diffraction

The evidence of elongation of QDs is also observed in x-ray diffraction (XRD) measurements for sample F [125]. Diffuse scattering corresponds to the average ensemble of illuminated dots and is sensitive to dot shape and size distribution as well as to the density contrast between dots and surrounding matrix. The inset of Fig. 6.6(a) shows periodic satellite SL peaks observed in the $q_z$ scan along (004) orientation for sample F. Specific trajectories in reciprocal space have been recorded to measure the in-plane map around the (004) SL(-1) peak. A set of rocking curves along 360° has been merged to obtain proper $q_x - q_y$ map as shown in Fig. 6.6(a). The SL(-1) peak was specifically chosen for this analysis as it is well separated from both the substrate and ZnSe buffer layer Bragg peaks but still has high enough signal strength to obtain reliable data. Also, satellite peaks exhibit combined characteristics of the overall SL and thus erratic contributions from individual layers can be avoided. The width $\Delta q_x$ shows periodic oscillations as a function of azimuthal angle $\phi$; hence in-plane RSM presents a strong
anisotropy in the diffuse scattering signal (Fig. 6.6(a)), which follows the same anisotropic axes as the linear polarized PL.

A set of different QD configurations has been computed, as shown in Fig. 6.7 (a) through (c), in order to reproduce the experimental results. It was observed that QD size distribution presenting centro-symmetric shapes leads to centro-symmetric diffuse scattering pattern. Ellipsoid dots with random orientation lead also to a similar feature. Only an assembly of elongated ellipsoidal QDs with definite orientation explains the experimental signal. Thus, ellipsoidal QDs elongated along [110] axis with varied in-plane aspect ratios (i.e. $b/a$, as shown in Fig. 6.7 (d)) were used for the purpose of simulating the anisotropy of in-plane reciprocal space map. The simulations as shown in Fig. 6.6 (b) present clear evidence of the anisotropically shaped QDs elongated along [110] orientation and the best match with the experimental data was obtained for the QD aspect ratio of $1.3 \pm 0.05$, perfectly agreeing with the aspect ratio obtained from DLP for sample F. Moreover, the axis of polarization and the asymmetric shape of the $\omega - \phi$ scan shows excellent correlation (Fig. 6.8) further confirming the presence of the elongated QDs, preferentially orientated along [110] direction.

In summary, we studied the optical anisotropy of the type-II ZnTe/ZnSe submonolayer QDs. The anisotropic exchange splittings extracted from the field dependence of DCP agree with the DLP of PL emission, giving a value of about $200 \mu$eV. Through analysis of spectral dependence of DLP in four QD samples, we propose that the optical anisotropy is mostly related to structure elongation of the ZnTe QDs, instead of the anisotropic strain relief and defects in ZnSe barrier or any interfacial symmetry lowering. We calculated the aspect ratios of the QDs in samples C, E and F, which shows
thicker QDs are more elongated. In addition, the elongation of QDs agrees with the anisotropy observed in XRD measurements.

**Figure 6.6.** (a) In-plane reciprocal space map around satellite SL(-1) of (004) Bragg peak depicting clear anisotropic shape. Inset: \(\omega-2\theta\) scan along (004) showing periodic satellite SL peaks. The arrow indicates the specific satellite peak under investigation. (b) Simulated rocking curves as a function of azimuthal angle for a known size dispersion of elongated QDs.
Figure 6.7. (a) - (c) Simulated RSMs of QDs with various shapes and orientations, the insets show the corresponding QD configuration. (d) Schematic diagram of the disc-shaped embedded SML QDs elongated along [110] orientation.

Figure 6.8. Plot showing correlation between the width of rocking curve and the intensity of linearly polarized PL emission as a function of azimuthal angle $\phi$. 
Chapter 7

ZnO Nanorods

In this chapter we will introduce the background about ZnO 1-D nanostructures. We will show our achievement on the growth of ZnO nanorods and the characterization of it using scanning electron microscope (SEM) and optical measurement.

7.1. ZnO 1-D nanostructures

In recent years, tremendous effort has been devoted to the growth of ZnO nanostructures. ZnO possesses outstanding physical properties including a wide direct band gap of 3.3 eV, high excitonic binding energy of 60 meV, and high thermal and chemical stabilities which promise a range of applications in diverse areas such as UV lasing, field emission displays, resonators, and sensors [126]. ZnO nanostructures of various morphologies are required for different applications. For example, well-aligned nanorods appear to be best suited for field emitters and UV/white light emitting devices and nanowires appear optimally suited for applications as interconnects in nanoelectronic circuits and sensors. Understanding the growth process, and developing methods to control the morphology in a reasonably straightforward manner are vital aspects for commercial fabrication of ZnO nanostructures with various desired morphologies.

ZnO nanostructures have been prepared using various techniques such as vapor phase transport (VPT) chemical vapor deposition (CVD) [127, 128], metal-organic CVD [129], and chemical solution methods [130]. Among these techniques, the VPT method has been
used extensively for growing ZnO nanostructures on metal catalyzed substrates, most commonly using Au as the catalyst.

Based on ZnO 1-D nanostructures, the type-II ZnO/ZnSe [131, 132] and ZnO/ZnTe [133] core-shell nanowires have been synthesized for photovoltaic and especially, solar cell applications.

### 7.2. Growth of ZnO nanorods

We set up a CVD system (the picture of which is shown in Fig. 7.1) for the growth of vertical aligned ZnO nanorods. A quartz tube working as the growth chamber is placed inside a three zone furnace which can be heated up to 1200 ºC. The right end of the quartz tube is connected to the gas flow input system which can control the flow rate of nitrogen, argon, and oxygen separately between 0.9 to 200 sccm. The left end of the quartz tube is connected to an adjustable valve and a vacuum pump which give control of the growth chamber pressure between 4.2 Torr and atmosphere pressure.

![Figure 7.1. Picture of the CVD system.](image)
We used the VPT growth method and the corresponding vapour-liquid-solid (VLS) growth process is briefly described as following. The a-plane sapphire wafers coated with 1 nm, 2 nm and 4 nm Au layer were placed in the left zone as substrate. The 2:1 (in weight) mixture of ZnO and graphite powder was placed in the middle zone as source. The chamber was first pumped to 4.2 Torr with argon flow input to create Ar rich environment. Then the argon and oxygen flow rate were set to 50 sccm and 0.9 sccm, respectively. And the pressure was set to 18 Torr. All the three zones were heated up to 900 ºC in twenty minutes. The furnace was then turned off immediately after reaching 900 ºC. At 900 ºC, Zn vapour was released via the chemical reaction

$$\text{ZnO}(s) + C(s) \rightarrow \text{Zn}(v) + \text{CO}(v)$$

and was transported to the substrate by argon flow. At the same time, the Au thin layer on the substrate melted into nanosized droplet and absorbed the incoming Zn vapour to form Au-Zn alloy, as shown in the schematic diagram in Fig. 7.2. The Au-Zn alloy was then oxidized by the oxygen flow, leading to supersaturation of ZnO. Thus, ZnO was precipitated out at the solid-liquid interface while Au-Zn alloy stays on the top, forming vertical ZnO nanorods.

![Figure 7.2. Schematic diagram of VLS growth process.](image-url)
7.3. SEM imaging and optical characterization

We use scanning electron microscope (SEM) to study the morphology of the ZnO nanorod array grown using 4 nm, 2 nm and 1 nm Au coatings. The SEM images are shown in Fig. 7.3. The diameters of the nanorods are similar in the three samples, while the density of nanorods increases with thicker Au coating. We think it is because the size of Au droplets does not depend on the thickness of Au coating while the density of Au droplets does.

![SEM images of ZnO nanorods](image)

**Figure 7.3.** SEM images of ZnO nanorods grown using (a) 4 nm, (b) 2 nm, and (c) 1 nm Au coatings.

We studied the room temperature absorption and excitation dependent PL spectra of the ZnO nanorods grown with 1 nm Au coating, shown in Fig. 7.4. The absorption spectrum gives the band edge absorption at about 3.2 eV at room temperature. The PL spectra of the ZnO nanorods consist of two bands. The blue emission at about 3.25 eV is
from the ZnO free excitons while the broad green emission is from surface states and dislocations. At lower excitation intensity, the emission from surface states and dislocations dominates, while the emission from free excitons dominates at higher excitation intensity.

**Figure 7.4.** Room temperature (a) absorption spectrum and (b) excitation dependent PL spectra normalized to the 3.25 eV peak of the ZnO nanorods grown with 1 nm Au coating.
Chapter 8

Outlook

8.1. Multiple oscillation features in the magneto-photoluminescence

Besides the AB peak, there are multiple oscillation features in the magneto-PL intensity. As seen in Fig. 4.5, the most permanent feature is the initial intensity drop at the zero field for all samples. We are still not sure about the cause of these initial drops. Based on the temperature dependence of magneto-PL shown in Fig. 4.11, the decrease of amplitude of initial drop with increasing temperature is faster than that of the AB peak. This suggests that the initial drops and the AB peaks have different origins.

For sample A, with lowest Te concentration, extra oscillation features (as peaks) show up at 0.7 and 1.8 T at experimental temperature lower than 2 K, as seen in Fig. 4.11 (a). The same peaks are also observed in sample D at low temperature, but not in the other samples with higher Te concentrations. The spectral analysis for samples A and D at 0.4 K, as shown in Fig. 8.1, reveals that these peaks are emission energy dependent and are most permanent for the blue bands, especially for the “sharp lines” related to IC bound excitons.
For sample F, with highest Te concentration, an extra oscillation peak at 0.16 T shows up for all experimental temperature, shown in Fig. 4.11(b). The temperature dependence of this peak is similar to the AB peak. Fig. 8.2 shows the spectral analysis of magneto-PL intensity for sample F at 0.3K. The emission energy dependences of this extra peak and of the AB peak are similar, while that of the initial drop is much different. The observations above suggest that this extra peak may have origins closely related to AB peak.

**Figure 8.1.** PL intensity as a function of magnetic field at experimental temperature 0.4 K for different emission energies of (a) sample A and (b) sample D.

**Figure 8.2.** PL intensity as a function of magnetic field at experimental temperature 0.3 K for different emission energies of sample F.
We run the magnetic field up to 14 T for sample E and 31 T for sample F in NHMFL. Fig. 8.3 shows the PL intensity as a function of magnetic field at different temperatures for samples E and F. At magnetic field above 8 T, both samples have long range oscillations which are temperature dependent. Roughly speaking, at low temperatures (T < 7.5 K), the PL intensity decreases with increasing magnetic field. At temperature from 7.5 K to 20 K, there is a hump of intensity at magnetic field around 12 T. At temperature above 20 K, all magnetic field dependent oscillations vanish. We propose that these long range oscillations may relate to the brightening of dark states at high magnetic field, for which a quantative model need to be built up.

![Figure 8.3](image.png)

**Figure 8.3.** PL intensity as a function of magnetic field at different temperatures for (a) sample E and (b) sample F.

### 8.2. Magneto-photoluminescence at Voigt geometry

We studied magneto-PL at Voigt geometry under different excitation intensities for samples A and F. The PL intensity as a function of magnetic field at Voigt geometry under two excitation intensities for sample A and under four excitation intensities for sample F are plotted in Fig. 8.4 (a) and (b), respectively, both overlaid over their magneto-PL at Faraday geometry. The PL intensity as a function of magnetic field at
Voigt geometry with two sample orientations under two excitation intensities for sample F is plotted in Fig. 8.4 (c). At Voigt geometry, the PL intensity increases with increasing magnetic field, opposite to that at Faraday geometry. For sample F, the magneto-PLs for magnetic field parallel to [110] and [1-10] axes behave differently, which must be related to the anisotropic QD shape discussed in Chapter 6. For the magneto-PL at Voigt geometry of sample A, there is a small peak at 2.07 T, the same field value for the oscillation peak at Faraday geometry. This suggests that the peaks at both geometries may have the same origins, which are related to the nature of isoelectronic centres. However, the causes of the increase of intensity at Voigt geometry, the origins of the 2.07 T peaks, and the relation between the anisotropy behaviour in magneto-PL and the elongation of QDs are still under investigation.
Figure 8.4. Magneto-PL at Voigt geometry for (a) sample A, (b) sample F (both overlaid over that at Faraday geometry), and (c) sample F in two orientations.
8.3. Nonlinear Zeeman effect

We did circularly polarized magneto-PL up to 31 T at 1.6 K for sample F at NHMFL. The Zeeman energy splitting between $\sigma^+$ and $\sigma^-$ polarized spectra as a function of magnetic field is shown in Fig. 8.5. It behaves nonlinearly. As discussed in Chapter 2, the mixing of the bands will lead to a parallel wave vector dependence of the Zeeman splitting, $\Delta E_{\text{Zeeman}} = \mu_0 B (g_0 + g_2 k_\parallel^2)$. Due to vertical confinement and cyclotron orbits, $\langle k_\parallel^2 \rangle \sim \hbar \omega_c \sim B$, so that $\Delta E_{\text{Zeeman}} = \mu_0 g_0 B + \mu_0 g_4' B^2$. However, the experimental data cannot be fitted with parabolic function. In Ref. [28], the dispersion is expressed up to the order of $k_\parallel^2$. If we take $k_\parallel^4$ term into account, the Zeeman splitting will be expressed as

$$\Delta E_{\text{Zeeman}} = \mu_0 B (g_0 + g_2 k_\parallel^2 + g_4 k_\parallel^4) = \mu_0 g_0 B + \mu_0 g_2' B^2 + \mu_0 g_4' B^4. \quad (8.1)$$

The experimental data shown in Fig. 8.5 fits well with Eq. 8.1, indicating that the $k_\parallel^4$ term is not negligible in the dispersion. A quantitative model is needed to understand the nonlinear Zeeman splitting.

**Figure 8.5.** Peak energy splitting between $\sigma^+$ and $\sigma^-$ polarized spectra as a function of magnetic field at 1.6 K for sample F. The line is fitted to Eq. 8.1.
8.4. Outlook for future research

Besides the projects mentioned above, there are more experiments and studies for further understanding the complicate mechanism in ZnTe/ZnSe submonolayer QDs.

1) PL (cw and time-resolved) studies in the presence of electric field parallel or normal to the growth direction of ZnTe/ZnSe QDs. This may give the possibility of extraction of information about the symmetry of the system as a lack of symmetry can cause a permanent dipole in the system which can exhibit opposite behaviour for positive and negative applied field. We would like to try electro-PL at higher fields as more prominent effects are expected at higher fields.

2) Combining electric field with magnetic field (in Faraday configuration) on QD samples to investigate the effect on the AB oscillation.

3) Studying the linear polarization of PL under different excitation intensity and different temperatures.

4) Resonantly exciting QDs with circularly polarized laser to study the time-resolved circular polarization of PL, without and with magnetic field.

5) Measuring the circular polarization and linear polarization of PL as a function of magnetic field under Faraday and Voigt geometries.

6) Based on the ZnO nanorod arrays grown, synthesizing ZnO/ZnSe(Te) core/shell nanorods. Studying optical and magneto-optical properties of the core/shell nanostructures.
Appendix

A. Matlab code for calculating degree of linear polarization as a function of aspect ratio

Following are the code for the calculation discussed in Chapter 6, section 6.4.

```matlab
model = mphload('aspect ratio study.mph'); % load model
%ModelUtil.showProgress(true); % display the progress bar
%model.material('mat1').propertyGroup('def').set('thermalconductivity', [k{n} '0' '0' '0' k{n} '0' '0' '0' k{n}]); % this is the line I noted in the 'preprocessing', it's modified on every loop
model.study('std1').run; % solve for electron and hole
el_wave = mpheval(model, 'e'); % extract and store data
el_norm = mphint2(model, 'e*conj(e)', 'surface');
solution = mphsolinfo(model, 'soltag', 'sol1');
el_eigen = solution.solvals;

ho_wave = mpheval(model, 'h');
ho_norm = mphint2(model, 'h*conj(h)', 'surface');
solution = mphsolinfo(model, 'soltag', 'sol2');
ho_eigen = solution.solvals;

for i = 1:81
    for j = 1:81
        Wave_h(i,j) = mphinterp(model, 'h', 'coord', [i-41; j-41]); % i stand for y-axis, j stand for x-axis, from -40 to 40 nm, 1 nm step
    end
end

bata = 1.102; % bata = 10^(-9) * (k * m_h * e^2) / (ebs_r * hbar^2)
Pha_X = 0;
Pha_Y = 0;
for i = 1:81
    for j = 1:81
        Px(i,j) = 0;
        Py(i,j) = 0;
        for k = 1:81
            for l = 1:81
                Px(i,j) = Px(i,j) + (l-j) * exp(-bata * sqrt((k-i)^2 + (l-j)^2)) * Wave_h(k,l);
                Py(i,j) = Py(i,j) + (k-i) * exp(-bata * sqrt((k-i)^2 + (l-j)^2)) * Wave_h(k,l);
            end
            Pha_X = Pha_X + Px(i,j)^2;
            Pha_Y = Pha_Y + Py(i,j)^2;
        end
    end
end

Deg_LP = (Pha_X-Pha_Y)/(Pha_X+Pha_Y);

ModelUtil.remove('model') % remove model because it will be reloaded on every loop
```
B. Determination of effective masses and g-factors of electrons and holes in bulk ZnSe and ZnTe

We use following Luttinger valence-band parameters to determine the effective masses and g-factors of holes in bulk ZnSe and ZnTe (see Refs. [124], [134] and references therein).

<table>
<thead>
<tr>
<th></th>
<th>$\gamma_1$</th>
<th>$\gamma_2$</th>
<th>$\gamma_3$</th>
<th>$\kappa$</th>
<th>$q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSe</td>
<td>4.3</td>
<td>0.6</td>
<td>1.34</td>
<td>0.64</td>
<td>0.02</td>
</tr>
<tr>
<td>ZnTe</td>
<td>3.96</td>
<td>0.86</td>
<td>1.39</td>
<td>0.14</td>
<td>0.001</td>
</tr>
</tbody>
</table>

We use the formulas $m_{hh}^* = m_0 / \left( \gamma_1 - 2\gamma_2 \right)$ and $m_{lh}^* = m_0 / \left( \gamma_1 + 2\gamma_2 \right)$ for the effective masses of heavy and light holes [135].

We use the formulas $g_{hh} = 6\kappa + \frac{27}{2} q$ and $g_{lh} = 2\kappa + \frac{1}{2} q$ for the g-factors of heavy and light holes [118].

Therefore, the effective masses and g-factors of electrons and heavy/light holes in bulk ZnSe and ZnTe are listed below (see Refs. [57], [106] and references therein).

<table>
<thead>
<tr>
<th></th>
<th>$m_e^*/m_0$</th>
<th>$m_{hh}^*/m_0$</th>
<th>$m_{lh}^*/m_0$</th>
<th>$g_e$</th>
<th>$g_{hh}$</th>
<th>$g_{lh}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSe</td>
<td>0.16</td>
<td>0.32</td>
<td>0.18</td>
<td>1.15</td>
<td>4.11</td>
<td>1.29</td>
</tr>
<tr>
<td>ZnTe</td>
<td>0.122</td>
<td>0.45</td>
<td>0.18</td>
<td>-0.40</td>
<td>0.85</td>
<td>0.28</td>
</tr>
</tbody>
</table>
Bibliography


[53] F. Urbach, Phys Rev. 92, 1324 (1953).


