QUANTUM CONFINED STATES AND ROOM TEMPERATURE SPIN COHERENCE IN SEMICONDUCTOR NANOCRYSTAL QUANTUM DOTS

by

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Quantum Confined States and Room Temperature Spin Coherence in Semiconductor Nanocrystal Quantum Dots

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Abstract

In this thesis we studied the signature of quantum confined electronic structure of CdSe nanocrystal quantum dots (NCQDs) in the electron spin behavior via time resolved Faraday rotation (TRFR) measurement at room temperature. We found that there is a distinction between the optical spin pumping efficiency (SPE) spectrum and the optical absorbance. Although the first peak in the SPE coincides with the band edge absorption peak, the rest of the two spectra show significant distinctions. There is a second peak in the signal from the larger NCQDs 200 meV higher in energy. The SPE diminishes afterwards. In smaller NCQDs there is only one peak in the signal. We model this behavior following a 6-band effective mass approximation spin dependent absorbance calculation. We also investigated the dynamics of the spin signal and the presence of two precessing components in the TRFR signal. We find that the inhomogeneous dephasing is not sufficient to explain the dynamics of both components. We associate one of the components to the spin signal from neutral excitons and the other one to positively charged trions. We describe the data using a magnetic field dependent spin decoherence mechanism that occurs via fluctuation of the exciton energy levels in between the available fine structure states. This model captures the TRFR experiment data on both short and long timescales. Additionally, we developed a NCQD-polymer composite optical waveguide and investigated the optical spin measurement on these structures.
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Chapter 1

Introduction

1.1 Focus of this dissertation

Semiconductor nanocrystal quantum dots (NCQDs) in the strong confinement regime provide a platform for studying electron spin at room temperature. The discrete quantum states of these structures can be addressed optically and the evolution of electron state can be studied by means of different techniques including polarimetry of the photoluminescence and pump-probe measurements. With the recent progress in synthesis of monodisperse NCQDs these structures have proved applicable in different devices e.g. back-light of LCD panels, photovoltaic cells, single photon emitters, LED lighting fixtures, etc. Despite the extensive research, there are several questions still to be answered regarding the electron spin interactions in this medium as well as their photoluminescence properties. We use time resolved Faraday rotation (TRFR) pump-probe measurement to excite spin-polarized charge carriers in NCQDs of different sizes and record their behavior over time. In this thesis we focus on three aspects in optical spin excitation and electron spin dynamics: 1. How exciting different energy levels in the NCQDs with different sizes affects the final spin polarization. 2. What the origin of the two precession frequencies observed in the TRFR signal are. 3. How we can enhance the TRFR signal from these structures or incorporate them in integrated optical devices. In current chapter we review the fundamental properties of NCQDs and the experimental method we use. Each of the following three chapters focuses on
1.2 Quantum energy levels in semiconductor nanocrystal quantum dots

When the dimensions of a semiconductor crystal become small, comparable to the exciton Bohr radius, a transition in electronic energy levels from continuous bands to discrete quantum levels happens. Optical properties of semiconductor crystals strongly depend on the ratio of the crystal radius, $a$, to the Bohr radius of the photo-excited electron-hole pair, $a_B = h^2\epsilon/Me^2$, where $M$ is the reduced mass of the electron-hole pair and $\epsilon$ is the dielectric constant of the semiconductor material. These size dependent properties in nanocrystals with various geometry and material have been investigated extensively in last two decades[1, 2, 3, 4, 5, 6, 7].

The electron and hole quantum energy levels in a spherical nanocrystal in parabolic approximation and by assuming an infinite potential barrier surrounding the nanocrystal when the electron and hole interaction is neglected is the solution to the Hamiltonian $H = \frac{P^2}{2m} + V_e(r_e) + V_h(r_h)$ when $P = \hbar/\iota \nabla; V_e(r_e) = V_h(r_h) = 0$ for $r_i < a$ and $V_e(r_e) = V_h(r_h) = \infty$ for $r_i > a[8]$. The energy levels are

$$E_{l,n} = \frac{\hbar^2 \phi_{l,n}^2}{2m_e h a^2}. \quad (1.1)$$

Where $\phi_{l,n}$ is the $n$th root of the spherical Bessel function of order $l$ and $m_{e,h}$ is the electron and hole effective mass respectively. The energy of the lowest electron and hole levels increases by decreasing the size of the nanocrystal and the band edge of the optical transition can be tuned as desired. For example, in CdSe nanocrystals the first exciton energy level can be increased to 3 eV while the bulk band gap value is 1.8 eV. Therefore, these systems provide quantum confinement effect at room temperature. The Coulomb interaction between the electron and hole should be also taken into account. However, the Coulomb interaction ($\propto 1/a$) increases slower than the quantization energy ($\propto 1/a^2$) and becomes less significant in smaller nanocrystals.
Hence in the strong confinement regime, where \( a \ll a_B \) the electron and holes can be treated independently and the Coulomb interaction energy can be added as a correction. The exciton Bohr radius for bulk CdSe is 5.4 nm.

Typical semiconductor band structure:

![Schematic of simplified semiconductor band structure.](image)

Figure 1-1: Schematic of simplified semiconductor band structure.

Figure 1-1 depicts the typical band structure of a semiconductor close to the Gamma point. In the valence band of the CdSe, the spin orbit split off energy of \( \Delta_{so} = 0.42 \) eV pushes the \( J = 1/2 \) states lower in energy. Also the four-fold degeneracy in the \( J = 3/2 \) states is broken to half by means of the crystal filed energy splitting of \( \Delta_{cr} = 25 \) meV \[^5\]. A so called 6-band effective mass model which includes the interaction of the three hole sub-bands is proven to be adequate for describing the details of the excitation spectra of nanostructures in wide band gap materials like CdSe and CdTe\[^9\;\[^6\]. In this model the interaction between conduction and valence bands are neglected so the electron and holes are treated as separate entities and the Coulomb interaction is added as a perturbative correction. We will show that how the mixing of the three heavy hole, light hole and split-off valence subbands leads to interesting behavior in optical spin pumping. We find that the 6-band picture describes the energy dependence of spin pumping in these structures very well. In chapter \[^3\] we also report the importance of the fine structure of the first excitonic level on the dynamics of the spin signal.
In an actual sample of these NCQDs there exist a distribution of size and shape that depends on the details of the synthesis process. When we are creating excitons in these samples we are addressing the whole ensemble and would have significant broadening in the energy levels. We will study how the ensemble size and shape distribution affects the spin signal characteristic in detail.

1.3 Optical spin pumping

The selection rules for optical excitation in semiconductors allow preferential excitation of electrons and/or holes with a spin projection in a particular direction. This can be utilized for optical spin pumping. A circularly-polarized photon carries a total angular momentum of $\pm \hbar$. Absorption of this photon excites an electron from a particular valence sub-band (heavy hole, light hole, or split-off hole) into the conduction band. Possible transitions between different valence sub-bands and the conduction band with the corresponding relative probabilities are shown in Fig.1-2. The relative probability of the transitions from the hh, lh, and s.o. bands to the c-band are in the ratio of 3:1:2 in bulk [10, 11]. If the photon energy is sufficiently larger than $E_g + \Delta_{SO}$ then all of the transitions can happen. In this case adding up all the relative transitions leads to a total photoexcitation with no particular spin polarization.

In the bulk spin up or spin down electrons can be excited by tuning the energy of the exciting photon and addressing a specific valence band to conduction band transition. For example a photon carrying an angular momentum $+1\hbar$ can excite an electron from the heavy hole sub-band, from a $|J = 3/2, J_z = -3/2\rangle$ state, to the c-band $|J = 1/2, S_z = -1/2\rangle$, creating an electron-hole pair with $|J_{z,h} = +3/2, S_{z,e} = +1/2\rangle$ and spin down in conduction band. Similarly a $+1\hbar$ photon tuned to the lh to cb transition creates an electron-hole pair with $|J_{z,h} = +1/2, S_{z,e} = -1/2\rangle$, a spin up in conduction band (see Fig.1-2 (a)). Here $J_{z,h}$ and $S_{z,e}$ are the v-band and c-band angular momentum projections, respectively. So considering the relative oscillator strength of the transitions the net pumped spin in the c-band can be determined by adjusting the excitation energy. For example, with an excitation energy where the hh
Figure 1-2: Schematic of different valence sub-bands and possible optical transitions to the conduction band via right handded or left handed circularly polarized photon.

and lh bands are excited equally, net spin polarization is still created in the c-band.

One important point is the excitation of virtually two spins, the hole and electron spins, upon optical excitation. The hole spin lifetime is typically much shorter than that of the electrons in bulk semiconductors ($\tau_h < 1$ ps) because the v-band is strongly spin mixed due to spin-orbit coupling in the p-like valence band [12]. Therefore, the total spin of the system on timescales longer than $\tau_h$ is the electron spin in the c-band. We will discuss that our experiments is not sensitive to the time scale of the hole spin lifetime.

In the NCQDs this process is different because each hole state in general is a superposition of the three valence subbands. Moreover, the contribution of each subband in the hole wavefunction depends on the size of the nanocrystal. Also the order of energy levels can change depending on the size. These three points makes the spin pumping very different in nanocrystals. In larger NCQDs these effects might not be substantial but the samples we study in this thesis are in the strong confinement regime with strong valence band mixing [6].

In the case of nanocrystal quantum dots the $J_z$ refers to the projection of the total angular momentum onto the c-axis of the nanocrystal. As described above, absorption of a photon propagating parallel to the crystal c-axis can create an exciton
with total angular momentum of $F = \pm 1$ depending on its helicity. Whereas propagation perpendicular to the c-axis can excite only into the $F = 0$ exciton state.\[13\] In this work we perform all of the measurements on an ensemble of NCQDs that are randomly oriented with respect to the pump light propagation direction. The NCQDs are suspended in a solution, dispersed on a glass substrate, or embedded in a transparent polymer layer. In this case the circularly polarized laser pump creates a superposition of $F = \pm 1$ excitons in the suitably oriented NCQDs. This generates a net spin polarization that we read out. The excitons might be generated at the resonance energy or pumped with shorter wavelengths, higher quantum size levels. We assume that these states rapidly ($< 1 $ ps) decay to the lowest exciton level \[14\] while conserving the spin information or with minimal change in the spin state. We examined pumping exciton with higher pump energies and the fact that the spin dynamics does not show any change pump energy dependence supports this assumption.

### 1.4 Optical spin probing

A photon slightly detuned form a transition energy acquires a phase shift in its electric field when it is in vicinity of that transition. This is the basis of the so called Faraday rotation effect. Assume, as we discussed earlier in section\[1.3\] a $\sigma_+$ photon has created a spin down through a hh to c-band transition. If a linearly polarized laser with slightly less energy than the transition is sent through the vicinity of this transition, it would experience a rotation in the polarization \[15\]. Note that the linearly polarized light is a superposition of left-handed and right-handed circular states of polarization. The rotation in the polarization happens because only the $\sigma_-$ component of this superposition can interact with that energy transition. The $\sigma_+$ interaction is forbidden because of the Pauli blockade.\[16\] This is a quantum non-demolition measurement which keeps the spin state intact. As the energy detuning from the resonant transition is increased this dispersive response falls off linearly, more slowly than absorption, and dominates the linear absorption that might happen. This makes the FR spin probing practical.
We use Faraday effect to measure the magnetization induced by optically pumped spins in an ensemble of NCQDs. The Faraday effect, induced polarization rotation in a linearly polarized probe laser, arises from the difference in the index of refraction $\Delta n$ for right and left circularly polarized light induced by spin polarization. In this case, $\Delta n$ primarily arises from Pauli blocking of optical transitions with selection rules involving circularly polarized light. We actually measure the $\Delta n$ through polarization rotation of linearly polarized light [17, 18].

Faraday effect measurements are sensitive to both electron and/or hole spin. If an $F = +1$ exciton is generated by $\sigma^+$ excitation and then the hole spin is rapidly flipped, the electron spin still blocks that transition or other transitions involving the same electron state for $\sigma^+$ photons. This aspect of Faraday-effect based measurements explains why a spin signal can still be measured well beyond the spin lifetime of the exciton state. Meier and Awschalom have studied the optical probing process in details for similar structures [19].

1.5 CdSe NCQD samples

We performed all of the presented measurements on colloidal solutions of CdSe NCQDs. The solution samples are used as received from NN-Labs with 2mg/mL of CdSe in the toluene. The surface of the nanocrystals are passivated with octadecyl amine and the particles form a colloid suspension in the solvent. Fig. 1-3(a) shows the absorption spectra of the largest size nanocrystals we studied with the band edge absorption peak at 627 nm. The spectra is taken using an ocean optics tungsten halogen light source at room temperature. The absorption spectrum of the same cell filled with toluene is used as reference. Smaller detail of the absorption spectrum is broadened mostly due to size inhomogeneity and also thermal effects in comparison to the spectra taken at low temperature. The red curve in fig.1-3(a) shows the luminescence resulting from excitation at high energies, 490 ± 15 nm. The feature is particularly broad with FWHM around 40 nm. This is mainly because the emission occurs from the entire ensemble. The PLE data shown in fig.1-3(b) is taken with 30 nm excita-
tion width centered at each data point. The data points represent the area under the subsequent PL spectrum. The data is then normalized to the pump intensity as the laser output was different across the spectrum. The PLE data actually does not reveal much more information about the details of the quantum energy levels than the absorbance spectrum. PLE measurement at low temperature has proven to be a reliable method for identifying the different exciton energy levels[9].

Figure 1-3: (a) Absorbance (blue) and photoluminescence (red) spectra of the CdSe NCQD sample A. The horizontal arrows indicate typical wavelength ranges for pump and probe lasers. PL is taken with excitation at 490 ± 15 nm. (b) PLE of sample A

1.6 Charge configurations in NCQDs, exciton and trion

Studies in the intermittency of the fluorescence from individual NCQDs (blinking)[20][21] has revealed that several possible metastable ground state charge configuration exist in these NCQDs. The charge configuration after optical pumping depends on the
initial condition. Here we consider possible optical excitation from three initial ground states, $G_+$ consisting of a single resident hole in the valence band, $G_-$ consisting of a single electron in the conduction band, and $G_0$ consisting of no holes or electrons prior to the optical excitation. After the optical excitation and subsequent rapid energy relaxation, the final state depends on the initial ground state as shown in Fig. 1-4. The $G_-$ ground state results in two electrons and a hole (negative trion, $X^-$), the $G_+$ ground state results in two holes and an electron (positive trion $X^+$), and the $G_0$ ground state results in a neutral exciton $X$. Excitation into the $X$ state results in one of the exciton states shown in Fig. 3-3 (or a linear combination of them). In the $G_+$ case a positively charge exciton is generated. We assume that the two holes pair up and rapidly relax into a spin zero state. So this configuration results into a lone electron spin in the nanocrystal. Similarly, the $X^-$ state results in a pair of electrons in a spin zero state with the single hole comprising the only spin in the system. Our measurements are not sensitive to this fast relaxing hole spin.

It should be noted that the presence of the charged nanocrystal quantum dots and the mechanisms that lead to their specific population and depopulation are unknown. We observe a difference in these populations and their relative fraction in different samples and over the time. The component of the FR data associated with positively charged NCQDs weakened over time in the sample. This might be because of a neutralizing process that happens in the sample over time or the way that surface charge traps alter. So while the data we present in chapter 2 are mostly indicative
of one component the main focus of chapter 3 is how spin dynamics in NCQDs with $X^+$ and $X$ charge configurations differ and result in the two different $g$-factor in the ensemble spin signal.

1.7 Larmor precession and Lande $g$-factor

To study the magnetic field dependence of electron spin dephasing and decoherence we apply a transverse magnetic field $B$, with respect to the excitation direction. This creates a Zeeman splitting between spin up and down states with energy difference $\Delta E_Z = g\mu_B B$ and results in a coherent spin precession at a Larmor frequency

$$\omega = \frac{\Delta E_Z}{\hbar} = \frac{g\mu_B B}{\hbar}.$$  \hspace{1cm} (1.2)

$\mu_B$ is the Bohr magneton, $\hbar$ is Planck’s constant, and $g$ is the effective $g$-factor in the NCQD. The magnetic field creates a superposition of eigenstates for the spin in the NCQD so the state evolves in time with a relative phase accumulating to each eigenstate at a rate proportional to the energy of that eigenstate. For the simple case of a single electron in a transverse magnetic field $B$, for a typical magnetic field of $B \sim 100$ mT, this results in $\omega \sim 10$ GHz.

In case of spins in semiconductors $g$-factor not only takes different effective values for electron and holes that significantly departs from the free electron value of $g_0 = 2.002$, it becomes a tensor with different values with respect to the main symmetry axis of the crystal[25, 26]. For NCQDs these values are further modified by the quantum confinement effects. In chapter 3 we will use the following phenomenological relation to describe how quantum confinement shifts the electron $g$-factor. In principal the theoretical treatment of the electron $g$-factor in NCQDs is involved because of possible crystal symmetry induced anisotropy, the effects of exchange coupling in exciton states, and the possible effects of nanocrystal shape and surface contributions[27].

In the eight-band Kanne model, electron $g$-factor is related to its energy as
\[ g_e(E) = g_0 - \frac{2}{3} \frac{E_p \Delta_{so}}{(E_g + E + \Delta_{so})(E_g + E)}, \]  
\[ (1.3) \]

where \( g_0 \) is the free electron g-factor, \( E_p \) is the Kane energy parameter, \( \Delta_{so} \) is the spin-orbit splitting of the top of the valence band, \( E_g \) is the semiconductor band gap, and the size dependence is introduced via electron energy \( E \). For CdSe \( \Delta_{so} = 0.42 \text{ eV} \), \( E_p = 19.1 \text{ eV} \) and \( E_g = 1.83 \text{ eV} \). So the second term in eq. \( 1.3 \) describes how g-factor decreases with increasing quantum level energy following the size reduction. TRFR data from the initially neutral quantum dots results in a g-factor for excitons. Gupta et al find that \( g_{exc} = (g_e - 3g_h)/2 \) for the quasi-spherical nanocrystals (discussed in chapter 3).

1.8 Spin relaxation mechanisms

The strong interaction of the spin degree of freedom with its surroundings is the major obstacle on the process of exciting a spin in a certain direction and manipulating it coherently. The semiconductor nanocrystals provide the discrete energy levels that can be addressed precisely to selectively excite spins polarized at certain direction. However, the coherence time remains very short and makes the spin manipulation challenging. Some local inhomogeneous effective magnetic fields for example from the nuclei can cause the dephasing of different constituents that make the signal. In the context of this work the decoherence time is the spin state lifetime before it gets randomized by various decoherence and dephasing processes originating from spin-orbit, hyperfine, or exchange interactions. An external magnetic field can cause a dephasing between different spins excited in the ensemble because of the g-factor inhomogeneity. This also drives different members of the ensemble out of phase. Here we refer to it with a distinct characterizing time, dephasing lifetime.

M.I. Dyakonov provides a clear picture of the different spin relaxation processes in semiconductors in Ref. [12]. The relaxation mechanisms can be understood by considering the interaction of a spin with an in time and in space varying magnetic field [30] [12]. These interactions can be identified with two parameters, the precession
frequency of the spin $\omega$ (which is proportional to the field strength) and the correlation time of the randomly fluctuating magnetic field $\tau_B$. This is the time at which the spin observes a relatively constant magnetic field. Consider a spin precessing around the magnetic field lines at a certain direction for a time $\tau_B$ when the magnetic field changes randomly to another value and direction spin starts precessing in a different rate and direction. The initial spin state can be eventually changed via this effective spin scattering phenomena. The quantity $\omega \tau_B$, which represents an angle, defines the strength of the scattering. During time $t$ a total of $t/\tau_B$ scattering event happens. When the scattering is weak, $\omega \tau_B \ll 1$, then the squared angle after time $t$ equals: $(\omega \tau_B)^2(t/\tau_B)$. The time after which this angle equals 1 is defined as the spin relaxation time $\tau_s$

$$\frac{1}{\tau_s} \sim \omega^2 \tau_B.$$  \hspace{1cm} (1.4)

In this case spin relaxation time is much larger than the magnetic field correlation time. In the $\omega \tau_B \gg 1$ case the spin has made many precessions during each field correlation time. This means that its projection transverse to the magnetic field has lost the original direction completely while the longitudinal component is preserved. When the magnetic field changes its direction after time $\tau_B$ the spin information is lost so the relaxation time $\tau_s \sim \tau_B$.

With this general picture various relaxation mechanisms can be understood. In *Elliot-Yaffet Mechanism* spin relaxation happens because of the scattering off the impurities in the lattice or the electric field of the lattice vibrations, phonons. For the impurity case the relaxation happens when the electron approaches the impurity center and the the direction and strength of the field it sees depend on the individual event.

The *Dyakonov-Perel Mechanism* which is usually the dominant effect in bulk III-V and II-VI semiconductors like GaAs, is related to the spin-orbit interaction. An electron experiences an effective fluctuating magnetic field due to electron collisions that redirects its momentum. So the spin relaxation time is proportional to the momentum relaxation time. This case is similar to the weak case above ($\omega_b \tau \ll 1$)
with $\omega$ being the precession frequency of spin around the effective magnetic field which depends on the electron momentum vector (spin-orbit coupling). This mechanism can also be seen in a different but equivalent way. The fluctuating magnetic field produces a fluctuating spin splitting which ultimately causes the decoherence. We use this picture later in chapter 3 to describe a decoherence that happens because of the random fluctuation of electron energy between different fine structure levels.

The exchange interaction between the electron and hole spin can also decohere the spin state. This mechanism is called Bir-Aranov-Pikus relaxation and is dominant in heavily p-doped semiconductors. Similarly, the nuclear spins create a randomly fluctuating field and produces a spin relaxation through hyperfine interaction.

Holes follow a different scenario. Valence band is strongly spin mixed because of the spin-orbit coupling. Therefore, hole loses its spin information quickly. The hole spin lifetime is in order of a few picoseconds\cite{31, 32, 33, 34}. For this reason, we are not able to record signals from lone holes in the measurements we present.

1.9 Time resoved Faraday rotation, experimental method

An optical time resolved pump-probe method is used for time dependent spin excitation and read-out \cite{18, 17, 35, 11}. Both the pump and probe laser pulses are derived from a single supercontinuum fiber laser source (Fianium SC450-8PP). The laser output is divided to two beams via a beam splitter. Then each of them is sent through a pair of short-pass and long-pass continuously graded filters. The filters are mounted on mechanical actuators so the throughput spectrum of the laser could be adjusted up to a few nanometer with a bandwidth as small as $\sim 5$ nm. The laser outputs a pulse train at 80 MHz but the final repetition rate can be reduced down to 1 MHz via its built-in pulse picker. All of the measurements presented here are carried out at 5 MHz. This repetition rate produced the best signal to noise ratio in comparison to higher and lower frequencies. The pump laser is sent through a mechanical delay
The delay line consists of a precision optical track with a retro-reflector mounted atop a sliding stage. The stage is moved through a stepper motor and high precision gearbox. The pump is getting reflected off the retro-reflector twice, by means of a fixed mirror, a quarter wave plate, and a polarizing beam splitter. Therefore, by moving the stage by 1 cm a temporal delay of \( \sim 133 \) ps is produced in between the pump and probe pulses. The delay between the pump and probe arrival time at the sample could be adjusted from \(-0.5\) to \(16\) ns with a resolution of about \(1\) ps. By means of reducing the path length of the pump pulse with respect to the probe pulse we could create the spin polarization and probe it at a later desired time.

Figure 1-5 shows a schematic of the optical set up. The circular polarization of the pump is adjusted using a quarter waveplate and the probe polarization is set vertical using a linear polarizer. The two beams are aligned parallel to each. The beams are sent across the room to make sure they travel parallel to each other. They are then focused into a cuvette which holds the sample solution onto a \(\sim 10\) \(\mu\)m diameter spot. The optical cuvette have \(1.0\) and \(0.5\) mm optical path thickness. In an alternative more efficient scheme we aligned the pump and probe beams on top of each other using a dichroic mirror. In this case, when the two beams take the same path instead of two parallel paths, the overlap volume of the focused pump and probe beams inside the sample is bigger and this enhances the measured signal significantly.

The goal is measurement of the rotation in polarization of the linear probe induced by the spin polarization generated by the pump pulse. The pump beam is blocked by means of long pass filters and/or a mechanical aperture. The probe beam is sent through a half wave plate adjusted at \(22.5^\circ\) from the vertical direction and then a Wollaston prism splits the beam into two beams with perpendicular polarization. The two beams are then focused into two photodiodes of a bridge detector. An Oscilloscope is used for monitoring the RF output of the detector which gives out the subtraction of the two input channels. Using the half wave plate this difference is adjusted to zero. The balanced detector also outputs each of the channels separately. One of these outputs is used to record the total power reaching the detector. This is used in data processing in the LabVIEW routine to find out the actual angle.
Figure 1-5: Schematic of TRFR experimental set-up. The abbreviations in the figure are defined as follows: beam splitter (BS), polarizing beam splitter (PBS), quarter waveplate (QWP), linear polarizer (LP), half waveplate (HWP), Wollaston prism (WP), and retroreflector (RR).

of rotation. The typical size of the Faraday rotation is a few micro-radians so the measurement should be done through a lock-in detection scheme. For this purpose the probe and pump are passed through optical choppers at $f_1 = 7.5$ kHz and $f_2 = 350$ Hz respectively. These modulations are used as reference signal in the two cascaded lock-in detectors. The RF output of the balanced detector is first sent to a low noise amplifier (Stanford Research Systems SR560). This amplifier also has low-pass and long-pass filters which are set at 1 kHz and 10 kHz to let the modulated signal pass only. The output is then fed to the first lock-in detector (Signal Recovery 2765DSP) which is using the $f_1$ as reference with a time constant of 650 $\mu$s. The “Fast X” output of this detector is sent to the input of the second detector. This second lock-in detector is using the slower modulation, $f_2$, as reference and is set at a long time constant, usually 1 sec.

Using the combination of the two sets of long-pass and short-pass filter pairs we can independently select pump and probe beam’s center wavelength and bandwidth. The actual wavelengths depend on the size of the nanocrystals under measurement. But in general the probe is set slightly off the band edge absorption peak at higher wavelength. The selection of the pump wavelength and its consequences is subject of the chapter [2]. For the NCQD sample with mean diameter $a = 6.1$ nm, sample
A, a typical pump and probe wavelength bandwidth are shown in fig. 1-3 on top of the absorbance curve of the sample. The absorbance spectrum is measured using an spectrometer (OceanOptics HR4000) with the sample in the cuvette (1mm thick). The measurements presented for the decoherence discussion in chapter 3 are taken with the same pump and probe spectra. The probe is centered at 660 nm with a width of 30 nm and pump is 50 nm wide and centered at 585 nm. The first absorption peak is at 627 nm.

Figure 1-6: The red curve shows the TRFR data in zero magnetic field. The blue curve shows the TRFR data while a 200mT transverse magnetic field is applied.

Figure 1-6 shows the resultant TRFR scan on sample A with the magnetic field at $B = 200$ mT (blue curve) and $B = 0$ (red curve). The $t = 0$ on the horizontal axis represents the simultaneous arrival of the pump and probe pulses at the sample. At this moment a net spin polarization is initialized in the region of interaction of the pump and the sample. The probe which is sent through the same point in the sample measures the spin state through the Faraday rotation in its polarization. That leads to the large spike at $t = 0$. By moving the retroreflector, the delay between the pump and probe can be swept and the dynamics of the ensemble averaged spin polarization mapped out it time (see fig. 1-6). The data points of these particular measurements are taken by moving the retroreflector a distance equivalent to 10 ps in delay time. Then the data is recorded and averaged over for 3 sec (three times the time constant value of the second lock-in detector) before moving to the next step. The red curve
which decays in a few nanosecond is the projection of the spin polarization onto the propagation direction of the probe pulse. In the presence of a magnetic field (blue curve) the spins precess around the magnetic field lines at Larmor frequency. In this case the projection of the net spin vector onto the probe direction oscillates around zero until it decays. It is noticeable that the spin lifetime is shorter when the magnetic field is present. Also a beating pattern is seen in the signal at around 750 ps. The interpretation of these features is studied in chapter 3 in extensive detail.

The duration of the pulses produced by the utilized laser is longer than what people often use in fast time resolved measurements which is typically in the order of a few hundred femtoseconds \[28\]. As a result the observed TRFR is spread in time by the finite duration of both pump and probe pulses. We measured the duration of the pump and probe pulses using a time-correlated photon counting setup (PicoQuant HydraHarp 400) and found pulse half-width at half maximum \( t_{pump} \approx 40 \text{ ps} \) for the pump pulse and \( t_{probe} \approx 20 \text{ ps} \) for the probe pulse. These values are for the pump and probe pulses with spectral bandwidths shown in fig. 1-6. The measured TRFR is effectively taken by performing a convolution of the signal with a pulse with HWHM \( t_p \approx \sqrt{t_{pump}^2 + t_{probe}^2} \approx 45 \text{ ps} \). We will see that the signal contains features both with timescale long compared to \( t_p \) and features limited in time by \( t_p \).

![Figure 1-7: TRFR data taken with laser repetition rate at 80 MHz.](image)

The parallel alignment of the pump and probe beams and their collimation are of importance and might affect the way the two beams are overlapped and focused.
inside the sample. This can subsequently affect the decay time and the envelope of the FR signal if not adjusted properly. Specially as the retroreflector is moving over a few ten centimeter range to create the more than 4 ns delay presented here. So we must check whether the mechanical motion of the delay line introduces position-dependent errors. To measure this effect, we set the pulse repetition frequency of the laser to $f_{\text{rep}} = 80$ MHz (repetition period $t_{\text{rep}} = 12.5$ ns). This allows us to observe two pump pulses within the motion range of the mechanical delay line. By comparing the two features separated by $t_{\text{rep}}$, we can determine the amount of error. This measurement quantifies a position dependent error of 2.8% per nanosecond. Over the range of interest of several ns, this yields an error of $\sim 10\%$ which can be considered a systematic error in our measurements. The data in Fig.1-7 is noisier than the previous data shown, that is primarily because the laser outputs less energy per pulse at 80 MHz for the same time-averaged power compared to the 5 MHz case.
Chapter 2

Efficiency of optical spin pumping

Spin dynamics and relaxation processes in NCQDs have been subject of previous studies, however the details of the optical spin pumping process presented in this chapter have not been the focus of any prior work. We study how the room temperature optical spin pumping process depends on the pump energy. We find significant difference between the absorption spectrum and the spin pumping efficiency (SPE) spectrum.

2.1 Electronic structure and valence band mixing in CdSe nanocrystals

In this section we calculate the quantum-confined electron and hole wavefunctions using the effective mass approximation with appropriate boundary conditions. The holes are considered to be bound inside the NCQD within an infinite potential well while the electron wavefunction can spread outside the nanocrystal. In general, the electron wavefunction can be written as:

$$\Psi_{l,m}^e(r) = f_{l,m}^e(r) u_{c,S_z}.$$  

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Where \( u_{c,S_z} \) and \( f_{l,m}^c \) are the Bloch and envelope functions in c-band. The subscripts \( l \) and \( m \) denote the quantum numbers for envelope function angular momentum magnitude and its projection. By replacing this form into the Schroedinger equation we can separate radial and angular part of the wavefunction as \( f_{l,m}^c(r) = R_l(r)Y_{l,m}(\Omega) \).

The boundary condition for the interface is that the radial component of the envelope function and its derivative inside and outside the crystal should be matched. The discontinuity of the electron effective mass has also should be taken into account. The probability current conservation is then satisfied by use of the following condition which is solved numerically to find the electron eigenvalues \([2, 42]\).

\[
\left[ 1 + 2f + \frac{E_p}{3} \left( \frac{2}{E + E_g/2} + \frac{1}{E + E_g/2 + \Delta} \right) \right] \frac{\partial}{\partial r} \ln[j_l(k_s r)]|_{r=a}
= \frac{\partial}{\partial r} \ln[K'_l(k_m r)]|_{r=a}. \tag{2.2}
\]

Here \( E_g \) is the semiconductor band gap, \( \Delta \) is the spin-orbit coupling, \( j_l \) is the \( l \)th order spherical Bessel function and \( K'_l(z) = \sqrt{\pi/2}zK_{l+1/2}(z) \) with \( K_{l+1/2} \) being the modified Bessel function. This equation determines electron quantum energy levels. Ekimov, et al\([6]\) determined the radial part of the electron wave function to be spherical and modified Bessel functions for the inside and outside regions respectively. The upper row in fig. 2-1 shows the radial part of the electron wavefunction for the lowest energy level for three different sizes of a spherical CdSe nanocrystal. The electron energy states can be labeled as \( nL_e \), where \( n \) is the principal quantum number, and the \( L \) represents the lowest possible angular momentum quantum number \( l \) via conventional atomic symbols \( S, P, D \), etc. Therefore, the lowest energy level is \( 1S_e \). In fig. 2-1 the vertical offset of zero value of \( R(r) \) is adjusted to show the decrease in the energy of \( 1S_e \) level from smaller to bigger radius \( a \), i.e. smaller confinement.

The hole state wavefunctions can be obtained similarly but it should be summed over all of the possible Bloch components

\[
\Psi_{F,M}^{h,\pm}(r) = \sum_l \sum_{J_s,J} f_{l,m}^{u,\pm}(r) u_{J_s} u_{J,M}, \tag{2.3}
\]
Figure 2-1: The top row shows the ground state electron, $1S_e$, radial wavefunction for three different nanocrystal radii, $a = 2.04, 2.40, 3.05$ nm. The bottom row depicts radial part of two hh wavefunction components, $1S_{3/2}$ and $2S_{3/2}$, (red). The black curves show three different s.o. wavefunction components, $1S_{1/2}$, $2S_{1/2}$, and $3S_{1/2}$. The vertical offsets of the zero value of $R(r)$ show the energy difference on left vertical axes.

with $u_{J_z}$ and

$$f_{l,m}^{e,±} = R_{l,J_z}(r)Y_{l,m}(\Omega)$$

(2.4)

being the Bloch and envelope functions in v-band. The three valence bands in CdSe are labeled by their angular momentum projection along the crystalline main axes, heavy holes $J_z = \pm 3/2$, light holes $J_z = \pm 1/2$, and the split-off holes with $J_z = \pm 1/2$. Equation 2.3 is a simplified representation of eq.[10] in ref. [6]. The band diagram near $\Gamma$ point is depicted in fig. 1-1. In CdSe NCQDs 5S orbitals of Cd form the conduction band the 4P orbitals of Se comprise the valence band so the electrons carry an angular momentum of 1/2 and holes carry a total angular momentum of 3/2 or 1/2.
To describe the complex nature of the valence energy states in semiconductors a notation similar to atomic physics is developed by Lipari et al [43]. In the spherical approximation made here, the ‘total angular momentum’ $F$ which is sum of the angular momenta of the envelope, $L_{\text{env}}$, and the band edge Bloch functions $J$. It is a constant of motion and a \textit{good quantum number} to describe the system. The envelope function number $L_{\text{env}}$ is analogous to the orbital angular momentum number in atomic physics notation. Using the total angular momentum $F$ in analogy to $L - S$ coupling, the eigenstates of the valence band Hamiltonian are denoted as $nL_F$. Where $n$ is the principal quantum number, $L$ is the lowest orbital momentum included in the state. The consequences of each valence band energy state comprising $L_{\text{env}}$ and $L_{\text{env}} + 2$, S-D mixing, will be discussed in more details below.

The hole eigenstates are labeled by $F$ and $M$, a complete set of good quantum numbers. Where $M = J_z + m$ is the projection of $F$. The ± superscript in eq. 2.3 denotes even and odd parity states. For even states $l = F + 1/2$ and $F - 3/2$ and for odd states, $l = F - 1/2$ and $F + 3/2$. In the v-band, the radial part of the envelope function is in general a sum of three spherical Bessel functions $j_l(k_tr)$. $k_t$ is the wavevector in different valence sub-bands, $t = lh, hh, s.o$. The second summation in Eq. 2.3 includes contributions from the three valence sub-bands. With $J = 3/2$, the sum is over $J_z = \pm 3/2, \pm 1/2$ which includes the Bloch functions, $u_{3/2, J_z}$ of the hh and lh sub-bands. With $J = 1/2$, the summation is over $J_z = \pm 1/2$ which includes $u_{1/2, \pm 1/2}$, the Bloch functions for the s.o. sub-band. Similar to the electron part the energies and envelope functions are again determined by imposing the appropriate boundary conditions. The exciton energy levels are calculated by the difference between c-band and v-band energies. The electron-hole Coulomb energy is included empirically, following Ref. 2 as a correction. In Fig. 2-1 two heavy hole wavefunction components (red, lower row) and three split-off hole wavefunction components (dashed black, lower row) are plotted for three different radii of spherical nanocrystals, $a = 2.04, 2.40$ and $3.05$ nm. The zero value of the $R(r)$ axis has been adjusted to match the energy value of each level on the left vertical axis. The red curves show $R_{0,3/2,3/2}$ for the $1S_{3/2}$ and $2S_{3/2}$ states with $M = 3/2$ from top to bottom respectively.
As expected the number of nodes equals $n - 1$. Also increasing the confinement pushes the states away from each other making each level more energetic. The black curve in lower row of fig. 2-1(a)-(c) shows $R_{0,1/2,1/2}$ for the $1S_{1/2}$ and $2S_{1/2}$ and $3S_{1/2}$ states with $M = 1/2$. The shape of these components and how they change in three different sizes are startling and important for the spin pumping discussion that follows. The $1S_{1/2}$ has one node in all three different sizes. How the shape of these components change with size of the nanocrystals is important as it defines the optical transition strength integrals.

Figure 2-2 depicts the calculation results for the first five electron energy levels (blue) and first eight hole (red) energy levels for different radii of CdSe spherical nanocrystals. Note that the energy axis has different scales in electron and hole segments for better contrast between the hole states.

Figure 2-3 shows the calculated exciton energy levels for different sizes of nanocrystals. The energies are calculated as the difference between the subsequent electron and hole levels shown in fig. 2-3 and by introducing the Coulomb interaction as a first order correction following Ref. [9]. The correction is included as $-1.8e^2/\epsilon a$ for the transitions containing $S_e$ states and as $-1.7e^2/\epsilon a$ for transitions from $P_e$, where $\epsilon$ is
Figure 2-3: Calculated exciton energies vs. NCQD radius.

The transitions are labeled using the standard notation \( n_l \). First the v-band state is denoted \( n_l_F \), where \( n \) is the principal quantum number, \( l \) is the lowest orbital momentum included in the state. The c-band state is then denoted \( n_l_c \). Figure 2-3 shows transitions with strength greater than 5% of transition (i) only. The color of the lines in Fig. 2-3 represents \( l \) of the c-band state (blue: S, red: P, and green: D). For all sizes, the lowest energy transition is \( 1S_{3/2}1S_e \), and the next lowest is the \( 2S_{3/2}1S_e \). All of the transitions show decreasing energy with increasing radius, as the quantum confinement is reduced.

These calculations show good agreement with experimental energy level assignments. However the energy values for smaller nanocrystals are not precise. The nonparabolicity of the conduction band is taken account for via the Kane model so the cause of the observed deviation has been implied to be either the breakdown of the effective mass model or an incorrect boundary condition. Also the number of available transitions is large at higher energies which makes the experimental determination of particular states difficult even when the experiment is performed at low temperatures. In this work we are using the theoretical calculations only to understand the underlying mechanism of the optical spin pumping so the small deviation
from the experimental value in smaller and larger quantum dots does not undermine the argument.

## 2.2 Optical transitions

The strength of an optical transition is the probability of a transition from vacuum state to the final exciton state with angular momentum $F$, $\Psi_F$. It can be calculated as below:

$$P = |\langle 0 | e\hat{p} | \Psi_F \rangle|^2. \quad (2.5)$$

Where $e$ is the polarization vector of the absorbed or transmitted light and $\hat{p}$ is the momentum operator. In an equivalent picture a transition induced by right handed or left handed circularly polarized light $\sigma^{\pm}$ can be calculated as the probability of a transition between a hole and an electron state. This is written as:

$$P^{\pm} = |\langle \Psi^h | e^{\pm} \hat{p} | \Psi^e \rangle|^2. \quad (2.6)$$

$e^{\pm} = e_x \pm ie_y$ is the polarization vector of the incident light. The operator $\hat{p}$ acts only on the Bloch functions of the valance band. In the envelope function approximation using the wavefunctions we defined in eq. 2.1 and eq. 2.3 as

$$P_{F,M}^{\pm} = \sum_{l,J,J_z} \int dr f_{l,m}^c(r)f_{l,m}^v(r)|\langle u_{J,J_z} | e^{\pm} \hat{p} | u_{e,S_z} \rangle|^2. \quad (2.7)$$

Figure 2-4 shows the calculated optical transition strength, $P_{F,M}$, vs. radius $a$ as the thickness of the transition lines. We are interested in 1. how the energy levels change with nanocrystal size and compared of each other; 2. how strong is each transition; and 3. what is the origin of the valance band state regarding the hh, lh, and s.o. mixture. These three factors will determine the spin polarization output of the optical excitation at different energies.

The resonant band edge transition $1S_{1/2}1S_e$ is the strongest and then the $1P_{3/2}1P_e$
is the next strongest transition. The overall trend of these energy transitions also stand out in the experimental absorption spectra of the nanocrystal ensembles. Figure 2-5 shows absorption spectra of three samples with the first absorption peaks indicated with vertical lines in fig. 2-4. The $1S_{1/2}1S_e$ makes the first absorption peak in all the three samples. Then there is a significant reduction in the absorbance until the higher energy $nP_x1P_e$ transitions happen.

The transition energies do not all change at the same rate with size of the nanocrystal. For example, the $2S_{1/2}1S_e$ transition crosses other transitions as the NCQD radius changes. For smaller NCQDs, (e.g. sample C, indicated by vertical dashed line (C) in Fig. 2-4), the third-lowest energy transition is $2S_{1/2}1S_e$. At higher energies, four transitions involving holes in $1P_{3/2}$, $1P_{5/2}$, $1P_{1/2}$, and $2P_{3/2}$ states and $1P_e$ electrons emerge. In contrast for larger NCQDs this cluster of $P$ transitions occurs at lower energies than level $2S_{1/2}1S_e$ (e.g. sample A). This change in the order of transitions has significant implications for optical spin pumping of large and small NCQDs.

The fact that the hole wave function, eq. 2.3, is a superposition of $hh$, $lh$, and so sub-bands, represented as the summation over $u_{J,J_z}$, means that e.g. if the transition $1S_{3/2}1S_e$ is driven it is not a transition purely from the $hh$ sub-band to the c-band. In consequence, both c-band spin up and spin down are generated by each circularly po-
larized light polarity. The optical transitions shown in Fig. 2-4 include contributions from all three valence sub-bands, regardless of the c-band spin state they involve. However, to determine the probability of creating a certain c-band spin polarization by a circularly polarized photon we separately consider the oscillator strength of transitions to states with c-band spin up and spin down: $P_{\uparrow}^{\pm} = P^{\pm}(S_z = 1/2)$ and spin down $P_{\downarrow}^{\pm} = P^{\pm}(S_z = -1/2)$. This result is presented in the next section along with the experimental measurements.

2.3 Experimental measurement of spin pumping efficiency

Here we experimentally investigate how outcome of optical spin pumping is different at different pump energies and how it varies for different sizes of NCQDs. For this purpose, we performed a series of TRFR measurements using the experimental setup discussed on section 1.9 on three samples with different nanocrystal sizes. The first absorption peaks of the ensembles are centered at energies $E_{\text{abs}} = 1.94, 2.07, \text{ and } 2.10 \text{ eV}$. They are referred to as sample A, B, and C respectively hereafter. Their corresponding absorption spectra are shown on fig. 2-5. The calculations discussed in section 2.2 relate these $E_{\text{abs}}$ values to mean NCQD radii $a_A = 3.05$, $a_B = 2.40$, and $a_C = 2.04 \text{ nm}$. For a different discussion, which is presented in chapter 3, we measured the size distribution of sample A using transmission electron microscopy (TEM). That measurement confirms this size assignment. TEM measurements also reveal that the NCQD ensemble has a normal size distribution with 10% fractional width. We assume the same width of size distribution for the two other samples.

In these series of TRFR measurements we chose a narrow pump energy width, equal to 20 nm or 30 nm spectral width, and swept the center pump wavelength from the longer wavelength side of the absorption spectrum to the shortest wavelength that was available in the spectrum of the utilized supercontinuum laser. We performed a time resolved measurement at each step. For example, for the largest NCQD size
ensemble, sample A, we performed 23 TRFR scans with pump energy changing from 1.8 to 2.7 eV, in equivalent 20 nm spectral steps, and repeated the time resolved scan each time. The energy value for the 20 nm spectral width is $\Delta E = 60$-100 meV across the energy range studied here. The data taken using sample A at $B = 250$ mT is shown in fig. 2-6.

The probe pulse for these measurements is fixed at an energy slightly less than $E_{abs}$, and has bandwidth $\Delta \lambda = 30$ nm. This setting satisfies the condition discussed
in section 1.4 for spin probing. The probe and pump energy ranges are indicated in Fig. 2-5 with horizontal bars and a horizontal arrow respectively. With this specific fixed probe wavelength range we are always probing the resonant transition. This is a plausible arrangement as the higher energy excitons relax to the lowest energy level in a time scale less than 1 ps [14]. However, with varying the pump energy in such a big range we have to take into account a few points. One is the fact that at each step we had a slightly different amount of power. So before we are able to compare the scans taken at different pump energies we have to examine how the FR signal scales with the pump power. Before this we have to find a way to summarize the scans in one quantity to be able to analyze and compare the data across the pump energy range. Then we would be able to compare the experimental results with our calculation from section 2.4.

Figure 2-7: (a) $\theta(t)$ from sample A for three different $E_p$. (b) shows the same data normalized by $\sigma_s$.

We have to quantify the spin signal and take into account the noise level. The FR signal at time $t$ denoted as $\theta(t)$, a summation of spin signal and a noise term:
\( \theta(t) = s(t) + n(t) \). Assuming that \( n(t) \) is a Gaussian uncorrelated noise with standard deviation \( \sigma_n \), the standard deviation of the signal \( \theta(t) \) is written as

\[
\sigma_\theta = \sqrt{\sigma_s^2 + \sigma_n^2}.
\]  

(2.8)

We determined the noise level \( \sigma_n \) by taking data at times prior to pump pulse arrival. The \( \sigma_s \) is calculated using data from \( t = 0 - 2 \) ns. We use \( \sigma_\theta \), defined above, as a measure of SPE.

If \( \sigma_s \) really measures SPE then the FR signal amplitude should scale with \( \sigma_s \). To evaluate this, three FR scans are taken at different \( E_p \) values, which lie on distinct regions of the absorption spectra. As seen in fig. 2-7(a) the difference in the magnitudes of the signals are considerable. However if we normalize them by \( \sigma_s \) they exactly lie on top of each other (see fig. 2-7(b)). There are two important points in this analysis. First that the three curves exactly follow each other signifies that the spin dynamics are the same while the excitons are initially excited to distinct states. Second that the quantity \( \sigma_s \) is a proper measure of the spin pumping efficiency.

![Figure 2-8: The data points are \( \sigma_s \) as a function of pump power. Blue line is a linear fit.](image)

The utilized laser outputs different powers at different part of its spectrum. Once a new pump wavelength is chosen using the motorized long-pass and short-pass filters, the data is being taken with a slightly different pump power, \( P_{pump} \). To examine how this affects the data we performed the TRFR data at a single pump energy but varied the amount of power. The data points in fig. 2-8 shows the dependence of \( \sigma_\theta \) on \( P_{pump} \). The data closely follows a linear fit which signifies that we can normalize the data by
pump power. The SPE data presented are normalized by $P_{pump}$, which is kept within the linear regime shown in fig. 2-8.

By following the procedure of taking FR data at each pump energy, calculating the $\sigma_\theta$, and normalizing it to the pump power, we generated the SPE data in fig 2-9(a)-(c) for samples (A)-(C). The plot depicts $\sigma_s$ vs. $E_p$. At pump energies with no measurable FR signal, and $\sigma_n > \sigma_\theta$, we set $\sigma_s = 0$. We determined the uncertainty $\Delta \sigma_s$ of the measurements in $\sigma_s$ via the uncertainties $\Delta \sigma_n = \sigma_n/\sqrt{N_n}$ and $\Delta \sigma_\theta = \sigma_\theta/\sqrt{N_\theta}$ where $N_n$ ($N_\theta$) is the number of values used to determine $\sigma_n$ ($\sigma_\theta$). The error-bars in fig 2-9 shows the $\Delta \sigma_n$.

Although onset of the all curves in fig. 2-9 resemble the absorption spectra of the subsequent sample, the SPE spectrum is significantly different from the absorption spectrum in both behavior and nature at higher energies. All samples show a low energy peak that corresponds roughly to $E_{abs}$. Sample A, with the largest NCQD size, shows a second peak approximately 200 meV higher. At higher energies SPE falls off to a low broad plateau. In contrast, in samples B and C no clear second peak is observed in the SPE spectrum, but instead a broad shoulder is seen as $E_p$ is increased. These results can be understood by looking at the spin dependent optical transition strengths of NCQDs and size-dependence of electron and hole energy levels.

2.4 Understanding the SPE data, comparison to the calculations

As discussed earlier the key to interpreting the optical pumping data in these NCQDs is how an admixture of hh, lh, and so valence sub-bands are involved in excitations with different energies. In section 2.2 we developed the method to calculate the spin dependent absorption spectra. The results for $P_{\uparrow}^+(E_p)$ and $P_{\downarrow}^+(E_p)$ is depicted as the blue and red areas in fig 2-9. A normal distribution of NCQD size with a standard deviation of 10% centered at the mean diameter of the sample broadens the individual
Figure 2-9: (a)-(c) show $\sigma_s$ vs. $E_p$ for sample (A)-(C) respectively. The red(blue) regions represent $P_\uparrow (P_\downarrow)$ vs. $E_p$. Labels on $E_p$-axes show important transitions as named in Fig. 2-4.

transition lines to the smooth curves in the figure.

Let’s first follow the experimental data in fig 2-9. The main features are 1- the presence of the first peak in SPE corresponding to the band edge exciton absorption for all three samples and 2- Occurrence of the second peak in the sample (A) but not the other two samples with smaller NCQDs. Let’s compare this behavior with the absorbance spectra in fig. 2-5. Obviously there is a first peak in the absorbance spectra corresponding to the $1S_\ell 2S_{3/2}$ band-edge exciton, a similar peak happens in SPE for all samples. However unlike the SPE absorbance stays significantly strong at higher energies while SPE in fig 2-9 falls off to almost zero at higher energies for all samples.

Now we put everything together and try to understand the data in comparison with the model calculations presented as the filled region in the fig 2-9. The red region subtracted by the blue region is supposed to give the total spin polarization at certain $E_p$. Although we used a very simple picture and neglected contributions form crystal fields, exchange interaction, and surface properties of the particles the calculation
provides a solid physical picture into the experimental results. The resonant transi-
tions at 1.95, 2.05, and 2.15 eV in samples A, B, and C respectively are dominated
by the heavy hole sub-bands and lead to up spins. Clearly $P^+(E_p) - P^+(E_p)$ results
to a peak at these energies. In sample (A) another cluster of transitions (iii-vi) as
labeled on the horizontal axis happens at higher energy. These transitions are also
dominated hh component of the valence band. Therefore they create the second peak
in SPE (see Fig. 2-9(a)). At higher energy, transition (vii) is excited, which is the first
transition to be dominated by lh and s.o. hole components. This transition excites
mainly spin down in the c-band, leading to a sharp drop in the SPE. Note that the
absorption spectra include both of these groups indistinctively and remains high. At
higher energy SPE goes very small values. This is because now the contribution of
both hh and lh-so groups are significant and results in a smaller population of net
spin up. In sample C, the smallest size NCQDs, the ordering of transition (vii) and
the cluster (iii-vi) is reversed. Thus the spectrum shows only the resonant peak and a
small shoulder from the weaker transition (ii) before being cut off by the contribu-
tions from the lh and s.o. sub-band in transition (vii). The intermediate sample B, shows
a broader shoulder, with some spin signal emerging from transition (iii) before the
emerging significance of the lh and s.o. bands reduces the SPE.

\[ P^+(E_p) - P^+(E_p) \] at higher energies result in an additional broad, low peaks in the
SPE at even higher energies. For example, in sample A, the calculation shows a low
peak around 2.55 eV, where we instead observe just a broad shoulder. In all of these
processes exciton will rapidly relax to its ground state and keeps its electron spin
polarization intact. One reason for the absence of the calculated peak at very high
energies might be that the electron spin direction is being lost during the relaxation
process. Also we have not taken into account the shape anisotropy in the ensemble.
The variation in the shape might weaken this higher energy peak.
2.5 Summary and conclusion

In summary, we have studied SPE in three different ensembles of CdSe NCQDs and calculated the expected values. We learned that depending on the contents of the hole state admixture of the three valence subbands the net excited spin polarization can be different at different pump energies. Also because the levels with alike valence subband mix switch their position in energy the SPE is significantly different for samples of distinct sizes of NCQDs. In small NCQDs off resonant pumping leads to weak spin polarization. That is mainly because of the overlap of the three valence subbands. However, in large NCQDs there is peak in SPE $\sim 200$ meV higher than the resonant peak. This peak is coming from a hh dominant transition which in case of smaller NCQDs coincides with lh-so transitions. This investigation provides a complete understanding of the spin pumping processes in these structures and the origin of the difference of SPE and absorbance spectra.
In this chapter we concentrate on understanding the origin of the two oscillating components present in TRFR data of CdSe NCQDs and the pertinent decoherence and dephasing mechanisms. Understanding the spin decoherence and dephasing times in semiconductor structures are of interest in because of its implication for quantum state control and quantum computation. There are primarily two confounding factors that arise in studying the spin decay mechanisms in NCQDs. First, measurements of spin dynamics in NCQD ensembles generally show the sum of two distinct components, we refer here as $S_1$ and $S_2$ components, with different dynamics and decay characteristics. Second, in these ensemble measurements, inhomogeneous dephasing plays a significant role in the decay of the spin signal, particularly in transverse magnetic field $B \neq 0$. These effects must be disentangled in order to accurately measure dephasing and decoherence processes.

Regarding the origin of the decoherence mechanism this chapter focuses on the fine structure of the band edge state $1Se1S_{1/2}$ in comparison to our studies focused on role of different exciton states in last chapter. We know that higher exciton states relax to this ground state in $\sim 1$ ps \cite{44, 32}. The decoherence and dephasing

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mechanisms are affecting the spin while the electron is residing in this state. We also know that the fine structure of this state strongly depends on the size and shape of the nanocrystals. To quantitatively unravel these connections, we measure and study the NCQD ensemble shape and size distributions and their effects on FR spin signal in extensive detail.

3.1 Multiple $g$-factors

![Graphs showing TRFR data and Fourier transforms](image)

Figure 3-1: (a) TRFR data at $B = 200$ mT (blue) and $B = 0$ at (red) room temperature. Inset of (a) is a zoom-in on the beating region of the data. (b) Fourier transform of the data shown in (a). (c) shows the $B = 0$ data in log scale.

Figure 3-1(a) shows a typical FR data set from CdSe NCQDs in transverse magnetic field $B = 200$ mT (blue) and at $B = 0$. The inset shows a zoom in of the same data. A beating pattern and presence of two oscillating frequencies is obvious. Fig.3-1(b) shows Fourier transform of the same data set. The two peaks in the plots are indicative of the two precession frequencies and the components we name...
$S_1$ and $S_2$. The origin of these two components is suggested to be the positively charged trions and neutral excitons in 'quasi-spherical NCQDs' which we will discuss in next sections (for charge configuration see sec 1.6, 37, 28). We will see that the spin dynamics and timescale is different in these two components and the conventional inhomogeneous dephasing and decoherence is not sufficient to address the differences. Fig.3-1(c) shows a semi-logarithmic plot of the data in (a) at $B = 0$ mT. The nonlinear shape of the curve indicates that the FR time trace should have even more than two exponential components.

3.2 Fine structure of exciton states in NCQDs

The spectrum of electron-hole (exciton) states in NCQDs displays significant fine structure splitting (FSS). The FSS of the first exciton energy level and its dependence on size and shape of the nanocrystals has been subject of numerous theoretical and experimental studies. In a spherical nanocrystal with cubic crystal lattice the first electron state $1S_e$ with spin $S = 1/2$ is doubly degenerate and the hole state $1S_{3/2}$ with $J = 3/2$ has a four-fold degeneracy in total giving rise to an eight-fold degenerate exciton level. The crystal asymmetry both in lattice structure and the actual shape as well as the exchange interaction between the hole and electron not only lifts the degeneracy to some extent, it can also change the position of the energy states.

In a cubic structure the crystal field is symmetric for all p-type valence band orbitals. The effects of considering the asymmetry of a hexagonal lattice can be calculated through perturbation theory in the quasicubic model [13]. The crystal field breaks the four-fold degenerate state into two states with $M = 3/2$ and $M = 1/2$. The energy separation depends only on the $\beta$, the effective mass ratio of the light and heavy holes.

$$\Delta_{cr.} = \nu(\beta)\Delta$$

(3.1)

$\Delta_{cr.}$ is the subsequent energy splitting in the bulk semiconductor which equals 25 meV for CdSe. The $M = 3/2$ state has the lower energy.
The nonsphericity of the nanocrystal can be quantified as \( \mu = c/b - 1 \) where \( c \) and \( b \) are the major and minor principal-axes respectively. \( \mu \) is positive for prolate and negative for oblate crystals. A. Efros et al calculate the energy splitting caused by the ellipticity \( \mu \) as below.

\[
\Delta_\mu = 2\mu u(\beta) E_{3/2}(\beta)
\]  

(3.2)

\( E_{3/2} \) is the energy of the hole ground state \( 1S_{3/2} \) for a spherical nanocrystal with radius \( a = (b^2 c)^{1/3} \). \( u(\beta) \) is calculated in Ref. [47]. The combination of \( \Delta_\mu \) and \( \Delta_{cr.} \), which is a function of the effective mass ratio, size, and shape of the nanocrystal accounts for the intrinsic crystal field and the shape anisotropy. In CdSe \( \beta = 0.28 \) and \( u(\beta) \) is negative and the net splitting decreases with size in prolate quantum dots. This exchanges the position of the \( |M| = 3/2 \) and \( |M| = 1/2 \) states in small nanocrystals[5].

![Figure 3-2: The fine structure splitting in the ground exciton state. Levels are labeled with the total angular momentum projection \( F = M + s_z \). Ground state of a neutral quantum dot and five exciton states labeled by their angular momentum projection along the crystal c-axis.](image)

Because of the significant enhancement of the electron and hole wavefunction overlap in the strong confinement regime the electron-hole exchange energy is expected to be bigger than the 0.12 meV of the bulk value[18]. This in turn can farther move the bright and dark exciton levels away from each other. The exchange interaction
interchanges different electron and hole spin states. It can be calculated using a phenomenological Hamiltonian $H_{\text{exch}}$ which acts on the exciton envelope function.

$$H_{\text{exch}} = -\frac{2}{3}\varepsilon_{\text{exch}}(a_0)^3 \delta(r_e - r_h) \sigma \cdot J$$

where $\sigma$ and $J$ are the Pauli matrices for spin-1/2 and spin-3/2 particles, $a_0$ is the lattice constant, and $\varepsilon_{\text{exch}}$ is the exchange strength constant\textsuperscript{48, 49}. In the cubic bulk lattice this energy separates the exciton states with total angular momentum 2 and 1. It creates a fivefold degenerate spin 2 state that is optically inaccessible (dark) and a threefold optically active (bright) state with total angular momentum 1. For the hexagonal lattice this energy splits the fourfold ground state into a singlet and a triplet state. In CdSe $\varepsilon_{\text{exch}} = 450$ meV for $a_{ex} = 5.6$ nm.

![Figure 3-3: FSS of a prolate CdSe QD with $\mu = 0.41$.](image)

So by taking the crystal shape asymmetry, hexagonal lattice field, and the exchange interaction the degeneracy in the lowest-energy exciton level is generally lifted into five energy levels. Figure 3-2 illustrates the ground state of a neutral quantum dot, and the first exciton state ($1S_e 1S_{3/2}$) split into $F = 1$ and 2 levels and eventually into five levels considering all three interactions (on right), labeled by their angular momentum projection $F = M + s_z$ along the crystal c-axis.

We calculate the fine structure of the $1S_e 1S_{3/2}$ exciton following the method of Al
A Efros et al. The full analytical treatment is presented in Ref. [5]. It is basically finding the answer to the eigenvalue problem $det(H - E)$ with $H = H_{exc} + H_{cr}$ using the total exciton wavefunction of the exciton $\Psi_{exc}(r_e, r_h) = \Psi_h(r_h)\Psi_e(r_e)$. The NCQDs are taken to be ellipsoidal with an ellipticity $\mu = c/b - 1$, where $c$ and $b$ are the semi-major and semi-minor axes, respectively. Following the calculations of Ref. [5] the five energy eigenvalues are as follows:

$$\varepsilon^{U,L}_0 = \eta/2 + \Delta/2 \pm 2\eta,$$  \hspace{1cm} (3.4)

$$\varepsilon^{U,L}_1 = \frac{\eta}{2} \pm \sqrt{(2\eta - \Delta)^2/4 + 3\eta^2},$$  \hspace{1cm} (3.5)

$$\varepsilon_2 = -3\eta/2 - \Delta/2,$$  \hspace{1cm} (3.6)

where $\eta$ is a function of nanocrystal size and parameter $\beta$ and $\Delta = \Delta_{\mu} + \Delta_{cr}$. In fig. 3-3 these energy levels for NCQDs with mean radius $a$ and a fixed ellipticity $\mu = 0.41$ are plotted. The five levels are made up of three Kramers doublets, one with $F = \pm 2$ and two with $F = \pm 1$, and two levels with $F = 0$. The superscripts “L” and “U” denote symmetric and anti-symmetric superpositions of the exciton basis states. Figure 3-4(a) depicts how the fine structure changes with the ellipticity $\mu$ for a nanocrystal with fixed $a = 3$ nm. The FSS depends strongly on both NCQD size and shape. Similar to the size dependence case in Fig 3-3 there exist a configuration at which the fine structure effects cancel each other. We will discuss how the size and shape dependence of the FSS contribute to the decoherence and dephasing behavior of spin signal from an ensemble of nanocrystal quantum dots.

The most important feature in Fig. 3-3 and Fig. 3-4(a) is the fact that there are NCQDs with $a$ and $\mu$ value for which the crystal field and shape anisotropy contributions to the FSS cancel each other for the sets of symmetric and anti-symmetric states. In Fig 3-4(a) the label $\mu_{qs}$ indicates the particular subset of NCQD in which this effect happens. An NCQD with this combination of size and shape is referred to as quasi-spherical because the effects that define a unique NCQD axis are canceled, leaving the spherically symmetric electron-hole exchange interaction as the only source of intrinsic FSS.[5] A lone hole in the NCQD also displays strong FSS, which
cancels out at $\mu_{qs}$. The subpopulation of NCQDs at or near $\mu_{qs}$ has been proposed to play an important role in the observed long lived spin dynamics.\textsuperscript{28} This point is the major focus of this chapter and we propose a model based on these phenomena that can well-reproduce our experimental spin data.

We have not considered effects of a magnetic field so far. An applied magnetic field lifts the degeneracy of the three Kramers doublets, resulting in exciton FSS with eight non-degenerate levels. Away from $\mu_{qs}$ where the spacing between the Kramers doublets is large compared with the Zeeman energy, the Zeeman splitting can be treated perturbatively. Near $\mu_{qs}$, however, the addition of a magnetic field mixes the exciton eigenstates yielding two anticrossings of the energy levels. Fig. 3-4(b) and (c) show two branches on energy states where the anticrossing occurs.

Figure 3-4: (a) FSS of a CdSe QD with $a = 3$ nm vs ellipticity. (b) and (c) show the FSS vs ellipticity of the same structure near the quasispherical point in presence of a 0.1 T magnetic field for higher and lower branches.
3.3 Exciton relaxation

Once an $F = \pm 1$ exciton is optically pumped to energies higher than the ground state, it transits to other exciton states with finite probabilities. Unlike the case of bulk material exchange of an optical phonon is not the dominant relaxation mechanism, because the energy level difference between the quantum states is very larger than the typical optical phonon energy. Also the phonon cooling is a slow process $[50]$. Transient grating spectroscopy has provided a tool to measure these transition probabilities in NCQDs.$[31]$ In general, the exciton states have lifetimes on the order of picoseconds. The electron or hole spin may flip with inverse rates $\tau_e \sim 1$ ns and $\tau_h \sim 1$ ps during these transitions.$[44, 32, 51]$ Transitions between exciton states involving a change in both the electron and hole state are also possible, but will be neglected here for simplicity. Though the exciton state is changed on the timescale of $\tau_h$, the electron spin state may persist for a longer time. The measurements presented here are sensitive to both the electron and hole spins regardless of the particular exciton state.

3.4 Simple model for ensemble spin signal

An exciton initially in a coherent state will be randomized after some finite time due to decoherence processes. Furthermore, slowly varying effective magnetic fields (e.g. from the hyperfine interaction with nuclear spins) may cause dephasing in a time averaged measurement.$[52, 53]$ Since the measurements presented here do not distinguish the timescales associated with these decoherence and dephasing processes, we will combine them into a single decay time $\tau$, with the decay described by an exponential function $\exp(-t/\tau)$. Magnetic-field-dependent ensemble averaging effects, such as dephasing due to the inhomogeneity of $g$-factors or inhomogeneity of decoherence times, are not included in $\tau$, and will be discussed separately.

All of our measurement are done on an ensemble of the CdSe NCQDs. Here we develop simple picture of the expected Faraday rotation signal from an NCQD en-
semble. Via optical pumping discussed earlier a spin polarized exciton population is induced in the sample at time $t = 0$. A superposition of exciton eigenstates are generated so the presence of a transverse magnetic field makes the spins to precess at frequency $\omega = g\mu_B B/\hbar$ around the magnetic field lines. Through various possible interactions the spin state is randomized with a characteristic time $\tau$. The time resolved FR measurement yields an exponential decay of the signal. The Voigt geometry Faraday rotation measurement then measures a projection of this spin state onto the probe direction vs. $t$. The rotation signal can be written as

$$\theta(t) = \Theta(t) A \cos\left(\frac{g\mu_B Bt}{\hbar}\right) \exp\left(-\frac{t}{\tau}\right),$$

(3.7)

where $\Theta(t)$ is a step function, and $A$ is the amplitude of the signal at $t = 0$.

Because of the size and shape distribution of NCQDs we expect broadening in all of the optical properties as well as a distribution of different $g$-factors of the charge carriers. We discussed how the $g$-factor depends on the crystal size in section 1.7. When there is a distribution of precession frequencies $\omega$ across the ensemble the spins precess at different frequencies and acquire a different phase at a given time. When the spins get out of phase their resultant spin projection on the probe direction attenuates. This adds another limit on the spin signal lifetime. For NCQDs in a magnetic field $B$, this is caused by a distribution $P(g)$ of $g$-factors. We define $P$ as a normalized probability distribution. Then $P(g)dg$ is the fraction of QDs with $g$-factor in a range $dg$ around the value $g$. The ensemble averaged FR signal can be obtained by integrating Eq. 3.7 over the possible $g$ distribution $P(g)dg$:

$$\langle \theta(t) \rangle = A\Theta(t) \exp(-t/\tau) \int_{-\infty}^{\infty} P(g)dg \cos(\alpha g t),$$

(3.8)

If $P(g)$ is symmetric about a central $g$-factor $g_0$ (i.e. $P(g - g_0)$ is an even function), then it is convenient to make a change of variables from $g$ to $g - g_0$:

$$\langle \theta(t) \rangle = A\Theta(t) \exp(-t/\tau) \int_{-\infty}^{\infty} P(g - g_0)dg \cos(\alpha(g - g_0)t)$$

$$= A\Theta(t) \exp(-t/\tau) \cos(\mu B g_0 t / \hbar) \int_{-\infty}^{\infty} P(g - g_0)dg \cos(\mu B(g - g_0)t / \hbar)$$
\[-A\Theta(t) \exp(-t/\tau) \sin (\mu B g_0 t/\hbar) \int_{-\infty}^{\infty} P(g - g_0) dg \sin (\mu B (g - g_0) t/\hbar)\] (3.9)

The second integral is asymmetric and goes to zero. The integral in the first term is just the Fourier transform \(\hat{P}(\mu B t/\hbar)\) of \(P(g - g_0)\) with respect to \(\alpha\). We rewrite the time dependent FR angle as below:

\[
\langle \theta(t) \rangle = A\Theta(t) \exp(-t/\tau) \cos (\mu B g_0 t/\hbar) \hat{P}(\mu B t/\hbar). \tag{3.10}
\]

Now \(\hat{P}(\mu B t/\hbar)\) represents the decay envelope caused by inhomogeneous dephasing.

Because of the two spin components discussed in sec. 3.1, \(S_1\) and \(S_2\), we have to have a model that includes two independent components similar to eq. 3.10. So the expected FR signal should be written as:

\[
\langle \theta(t) \rangle = \Theta(t) \sum_{n=1,2} A_n \exp(-t/\tau_n) \cos (g_n \mu B t/\hbar) \hat{P}_n(\mu B t/\hbar), \tag{3.11}
\]

where \(n = 1, 2\) refers to the \(S_1\) and \(S_2\) components.

Now the details of the signal behavior over time strongly depends on two terms the exponential decoherence life time \(\tau_n\) and the dephasing envelope \(\hat{P}_n\). In the next section we discuss the possible decoherence mechanisms. Afterwards we will describe how to obtain the correct dephasing envelope from the ensemble’s size and shape distributions.

### 3.5 Size and shape distribution of a CdSe NCQD ensemble

To complete the picture presented for the ensemble spin signal in the previous section we have to determine \(P(g)\), the \(g\)-factor distribution. This can be achieved by measuring the size distribution of the NCQDs in the sample. We also discussed the importance of the NCQD shape in the fine structure of the ground state exciton level. We experimentally measured the size and shape distributions by analyzing a
set of transmission electron microscopy (TEM) images from the sample. An aliquot of the NCQD suspension is drawn from the same sample that used for the optical measurement and prepared by drop casting diluted NCQD solution on a TEM grid. A typical TEM image from sample (A) is shown in Fig. 3-5(a). As discussed above, we consider the NCQDs to be ellipsoidal, with circular cross-section normal to the crystal c-axis. In order to measure the ellipticity \( \mu \), we must identify NCQDs that are lying with the c-axis parallel to the image plane. This can be accomplished with reasonable accuracy by selecting only images where the planes of atoms perpendicular to the c-axis are clearly visible through the atomic layer fringes in the image, as in the NCQD labeled (A) in Fig. 3-5(a) (For contrast, the NCQD labeled (B) is not
suitably oriented.). The major and minor axes of the NCQD are then measured by placing an ellipse on the image (using the software ImageJ) with one axis along the c-axis and adjusting the major and minor axes to match the image (see NCQD (C) in Fig. 3-5(a)).

We have measured the major and minor axes of 182 NCQDs in this sample resulting in the histograms of mean diameter $d$ and ellipticity $\mu$ shown in Fig. 3-5(b) and (c). From these measurements of the size and shape inhomogeneity, we can compare the FR data to models that quantitatively include the effects of ensemble-averaged dephasing and decoherence. These effects were previously accounted for via fitting procedure. This size and shape distribution measurement can be a quantitative evaluation of the previous models. In fig 3-5(c) the red curve is a fit to the following normal distribution.

$$N(\mu) = \frac{N_0}{\sqrt{2\pi}\delta_\mu} \exp\left(-\frac{(\mu - \bar{\mu})^2}{2\delta_\mu^2}\right)$$ (3.12)

with the mean value $\bar{\mu}$ and the standard deviation $\delta_\mu$ resulting to be 0.15 and 0.18 respectively.

### 3.6 Size and shape distribution induced dephasing

In this section we start fitting the TRFR data with the model we described in previous sections. First we convert the measured size distribution to a $g$-factor distribution that defines the inhomogeneous dephasing and then compare the model with the data. We will see that a gID model fails to follow the experimental data.

#### 3.6.1 $g$-factor distribution

In this section we calculate the $g$-factor distribution and the appropriate fit function for the ensemble using the TEM statistics described earlier. In previous works, a normal distribution of $g$-factors arising from non-uniform NCQD size[28] is assumed to create the inhomogeneous dephasing of spins in NCQDs. As we discussed earlier size distribution of the NCQDs result in a distribution of the $g$-factors in the sample.
And the expected dephasing envelope from a $g$-factor distribution $P(g)$ is given by the Fourier transform $\hat{P}(\mu_B B t / \hbar)$. Here we estimate the $P(g)$ from the measured size distribution using Eq. 1.3 for the $S_1$ component and from $g_{exc} = (g_e - 3g_h)/2$ for the $S_2$ component (again, with the size dependence largely arising from $g_e$, and $g_h$ taken to be constant). The widths $\Delta g_{1,2}$ of the $g$-factor distributions for the $S_{1,2}$ components should be related by $\Delta g_2 = \Delta g_1/2$ given the relationship between $g$-factors of the two components.

The electron $g$-factor distribution of NCQDs calculated based on TEM size measurements. The red curves show fits to (a)Normal distribution and (b)Lorentzian distribution . The shaded regions depict the $1/e$ confidence interval for each bin of data, assuming a Poissonian statistics.

Figure 3-6 shows the electron $g$-factor histogram calculated using the TEM size measurements. Now we have to determine the best function to describe this data. In previous studies a normal distribution is assumed. We will see below that a Lorentzian distribution provides a better fit. The two normal and Lorentzian distributions used are as below.

$$P(g) = \exp\left(-\frac{(g - \bar{g})^2}{2\Delta g^2}\right)$$  \hspace{1cm} (3.13)  

$$P(g) = \frac{1}{1 + \left(\frac{g - \bar{g}}{\Delta g}\right)^2}. \hspace{1cm} (3.14)$$

The resultant fits to these two functions are also shown in Fig 3-6(a) and (b) respec-
tively. The fitting process results in $\bar{g} = 1.005$, $\Delta g = 0.043$ for the normal distribution and $\bar{g} = 1.003$, $\Delta g = 0.036$ for the Lorentzian function. The $1/e$ confidence region calculated via $\bar{g} \pm \frac{1}{2} \chi^2(1 + 1/e; 2k)$ for each data point is shown as the shaded area around the fit function. This allows a quantitative comparison of the goodness of the fit. If $P(g)$ is a normal distribution with standard deviation $\Delta g$, as in eq.3.13 the dephasing envelope is:

$$\hat{P}(t) = \int_{-\infty}^{\infty} P(g)dg \cos(\mu_B B g t / \hbar) = \exp \left( -\frac{(\Delta g \mu_B B t)^2}{2\hbar^2} \right), \quad (3.15)$$

which is a Gaussian function with standard deviation $\tau = \hbar / (\Delta B g \mu_B)$. Deriving a similar integral when $P(g)$ is a Lorentzian distribution with HWHM $\Delta g$, the dephasing envelope is the exponentially decaying function below

$$\hat{P}(t) = \exp \left( -\frac{\Delta g B \mu_B t}{\hbar} \right), \quad (3.16)$$

with time constant $\tau = \hbar / (\Delta g B \mu_B)$. The Lorentzian distribution with $\Delta g_1 = 0.036$ provides a better fit than the normal distribution in the Fig. 3-6(b). The normal distribution does not capture the tails of the histogram in Fig. 3-6(a). We should note that the size and shape distribution in a sample of NCQDs is likely dictated by the specific chemical synthesis process used.

### 3.6.2 Modeling TRFR data using the measured g-factor distribution, gID model

Now we can compare the FR data to the model defined in Eq. 3.11. We will try different forms of $P(g)$ that we discussed in previous section and evaluate the results. Before that there are some details that should be added to the eq. 3.11. One comes from the experimental fact that the laser pulses used for the measurements have a finite time duration in the order of a few ten picoseconds. This means that the time evolution recorded by our FR measurement is convoluted with the laser pulse temporal profile. $f_p(t)$ defined as a Gaussian function with HWHM $t_p$ represents this
profile. Also there is a small non-precessing background \( f_{bkg} = a_{bkg} \exp(-t/\tau_{bkg}) + y_{bkg} \) which must be included to achieve a good fit. Such backgrounds have been observed previously, \([37, 54]\) and their origin remains unclear. Adding these modifications, we obtain the model function

\[
\langle \theta(t) \rangle = [\Theta(t)(A_1f_1(t) + A_2f_2(t) + f_{bkg}(t))] * f_p(t), \tag{3.17}
\]

where

\[
f_n(t) = \cos(g_n\mu_B Bt/\hbar)\hat{P}_n(\Delta g_n\mu_B Bt/\hbar) \exp(-t/\tau_n) \tag{3.18}
\]

in which \( \hat{P}_n \) is either exponential or Gaussian decay envelope for each component, \( n = 1, 2 \), corresponding to a Lorentzian or normal \( g \)-factor distribution. The three parameters \( A_n, \Delta g_n, \) and \( \tau_n \) describe the decay envelope, and \( g_n \) describes the coherent dynamics of the \( S_n \) component. The main effect of pulse width \( t_p \) is a broadening of the step that occurs at \( t = 0 \). At \( t \gg t_p \), the effect of \( t_p \) is limited to small changes in the overall amplitude of the signal. We will first focus on exponential \( \hat{P}_n \), which is supported by the measured \( g \)-factor distribution.

There are 12 free parameters in the eq.3.17. One expects that the model with these number of free parameters will be able to capture the experimental data curve. Figure 3-7(a) shows a fit of the FR data at \( B = 200 \) mT to Eq. 3.17 with exponential \( \hat{P}_n \), allowing all parameters in the model to vary in a domain adjacent to previous experimental or theoretical results. Despite the large number of free parameters, the model does not follow the data well. Although the first spike and oscillation is captured as the inset shows the model fails drastically in creating the data at longer times. This is because the short-timescale behavior, \( t \lesssim 0.1 \) ns, is not characterized by the same lifetime as the longer-time behavior, \( t \gtrsim 0.1 \) ns. Such a short timescale feature is generally observed in FR measurements of NCQDs\([28, 55, 37, 54, 40, 56]\) and is typically ignored either by truncating the data for short times, or by taking the Fourier transform which transfers the short time feature into a broad feature in frequency domain, which can then be ignored. Note that in previous work with shorter pulse duration, this feature appears more sharply peaked in time. Therefore,
Figure 3-7: Fits to gID model at $B = 200$ mT: (a) fit to Eq. 3.17 with exponential $\hat{P}_{\alpha}$, (b) fitting result to the same function with data at $t < 0.13$ ns excluded. The solid black curve in (b) is $f_{\text{bg}}(t)$.

it is likely that the width of the short timescale feature seen here is set by the pulse width $t_p$ in our experiment.

Let’s use the same function and this time fit the data without the prominent initial spike. As in Fig. 3-7(b) data only after $t > 0.13$ ns, indicated by the vertical dashed line, is included. The inset shows a zoom-in at longer times. For this time range the model captures many features of the data well, including the shape of the decay envelope and the coherent precession. Although the details are not followed perfectly. However, the main deficiency is clearly that this model does not capture the short-timescale behavior. This again signifies that there are two time scales involved in the spin dynamics. Table 3.1 shows the found through this fitting process.

We have to emphasize that even though we truncated the short timescale data for now, we do attribute it to FR from optically pumped spins, unlike the case in GaAs where a pulse-width-limited feature is attributed to non-linear optical effects that do not arise from optical spin pumping.[57] The non-linear optical effect, e.g. in Ref.[57]
Table 3.1: Fit parameter for the function plotted in 3-7

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$A_1$ (mRad)</th>
<th>$A_2$ (mRad)</th>
<th>$\Delta g_1$</th>
<th>$\Delta g_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>fit value</td>
<td>0.21</td>
<td>0.51</td>
<td>0.087</td>
<td>0.138</td>
</tr>
<tr>
<td>$\tau_1$  (ns)</td>
<td>0.79</td>
<td>$\tau_2$ (ns)</td>
<td>$g_1$</td>
<td>1.15</td>
</tr>
<tr>
<td>$a_{bkg}$ (mrad)</td>
<td>0.041</td>
<td>$\tau_{bkg}$ (ns)</td>
<td>$y_{bkg}$ (µrad)</td>
<td>2.22</td>
</tr>
</tbody>
</table>

do not require an excitation, the feature remains prominent at pump energies within the bandgap. However, in this case, the short timescale spike disappears at pump energies below the bandgap, and in fact scales with pump energy the same as the longer timescale FR signal. So this feature is clearly originating from excited spins.

### 3.6.3 Cross-correlation between the fit parameters

Because the models being used to fit the data here in general have a large number of parameters, we must examine cross-correlations between parameters in the model to ensure that the fitting procedure yields meaningful results. The general fitting scheme we employ is as follows: First, we manually select realistic initial values $\beta_n$ for the $N_p$ model parameters and fit a representative dataset of FR vs. time ($t_j, \theta_j$) with all parameters varied in a non-linear least squares fit to model function $f(\beta_n; t)$. This will provide a starting value for the $\beta_n = \beta_n^0$ that is at least roughly consistent with the data. Then based on [58] we calculate how different two parameters in the model are correlated. To do so we obtain the Jacobian matrix $\hat{J}$ with elements

$$J_{jn} = \frac{\partial f(\beta_n, t_j)}{\partial \beta_n} \bigg|_{\beta_n^0}. \quad (3.19)$$

The correlation matrix $\hat{C}$ is then obtained with matrix elements

$$C_{jk} = \frac{(\hat{J}^T \hat{J})^{-1}_{jk}}{\sqrt{(\hat{J}^T \hat{J})^{-1}_{jj}(\hat{J}^T \hat{J})^{-1}_{kk}}}. \quad (3.20)$$
From the $N_p \times N_p$ elements of $\hat{C}$, we can evaluate the degree of independence of each parameter. If $C_{jk} = \pm 1$ for $j \neq k$, then a small change in $\beta_j$ has the same effect on the model function as a small change in $\beta_k$, and these two parameters would be completely correlated. (By definition, $C_{jj} = 1$.) On the other hand, if a small change in $\beta_j$ alters the model function in a way orthogonal the effect of a small change in $\beta_k$, then the two parameters are completely uncorrelated and $C_{jk} = 0$. If two parameters are highly correlated, then those parameters are not well-determined by the fit. Below, we will disregard the sign of the cross-correlations and use the matrix $|\hat{C}|$ with elements $|C_{jk}|$.

In order to get reliable information from our fitting procedure, we can reparametrize the fit function or hold some parameters constant to reduce cross-correlations, or to isolate cross-correlations in fit parameters that are not of interest.

**3.6.4 A more systematic approach to the gID model fitting process**

Based on the method described on the previous section we now fit the data and try to keep the important physical values in the model as uncorrelated as possible. Calculating the cross correlation gives numerical information on how strongly different parameters influence each other. We will use these correlations to categorize the parameters into independent groups and focus on important parameters properly.

The initially chosen parameters $\beta^0_n$ yield an initial set of values for studying the correlations between parameters. As an example the resulting set of parameters for the fit in fig.3-7(b) are shown in Table 3.1. Figure 3-8(a) depicts the correlation matrix $|\hat{C}|$ calculated for that model curve (In the greyscale black = 1, white = 0). The parameters have been grouped to render the matrix roughly block-diagonal. The parameters that are highly correlated with each other can be split into different groups. The first two groups correspond to the parameters that govern the shape of the decay envelopes. The $S_1$ decay envelope is set by $A_1$, $\tau_1$, and $\Delta g_1$, while the $S_2$ envelope is set mainly by $A_2$, $\tau_2$, and $\Delta g_2$. The pulse width $t_p$ also is correlated with this second group, but with the initial spike excluded from the fit, this parameter has very little
impact on the model function. The other main group of correlated parameters ($A_{bkg}$, $\tau_{bkg}$ and $y_{bkg}$) govern the small non-precessing background (shown for reference as solid curve in Fig. 3-7(b)). Because these background parameters are not of interest for the discussion here, the correlations between them are not of consequence. The remaining two parameters $g_1$ and $g_2$ which give rise to the precession frequencies are highly independent of all the other parameters. This conform to the fact that the g-factors are independent physical parameters independent of other signal parameters.

Figure 3-8: Correlation matrices of fit parameters in gID model. The gray color saturation shows the degree of correlation between the parameters. Black is perfect correlation and white is independence. (a)$|C|$ for the initial model (fit shown in Fig. 3-7(a)) (b)$|C|$ when $t_p$ is fixed and the decoherence and correlation times are combined into $\zeta_n$. (c)$|C|$ after introducing $A_n^* = A_n \exp(\zeta_n t_0)$.

The parameters grouped with the blue dashed square in Fig. 3-8(a) separates the parameters that pertain to the dephasing and decoherence properties. These are the relevant parameters we like to focus on. Although the two subgroups of parameters in this region are strongly correlated, they are very well independent of the other five parameters ($g_1$, $g_2$, and the three background) in the model. There are four main time constants in the model, two decoherence and two dephasing lifetimes ($\hbar/\Delta g_n \mu_B B$). It is unavoidable that the fitting process does not distinguish these times from each other. To decrease the number of parameters and better deal with the cross-correlations between them, for both $S_1$ and $S_2$ components, we can combine
the decoherence and dephasing terms in Eq. 3.17 into one term

\[
\exp(-t/\tau_n) \hat{P}_n(\mu_B Bt/h) = \exp(-\zeta_n t),
\]

(3.21)

where

\[
\zeta_n = 1/\tau_n + \Delta g_n \mu_B B / h.
\]

(3.22)

The two decoherence and dephasing times are now combined into a single parameter, however because of the magnetic field dependence of the dephasing time constant they can be untangled. The other parameter that can be removed from the fitting process is the laser pulse duration. As mentioned in sec. 1.9 we experimentally measured the pump and probe time profile. Also we noticed that its value does not have a significant influence on the model function when this initial value is given. Therefore we set it as \( t_p = 45 \) ps, the approximate measured value.

A new correlation matrix is generated with the new set of combined parameters, the effective decay rates \( \zeta_n \), and with the \( t_p \) taken out. As shown in Fig. 3-8(b) now the number of main parameters are decreased to four. But expectedly the \( a_n \) and \( \zeta_n \) are very correlated. This is mainly because the fitting is being done on the truncated data where the \( t = 0 \) is omitted. At that time scale the difference between a change in these two parameters is greatest. This can be resolved with changing the time origin. By reparameterization \( A^*_n = A_n \exp(\zeta_n t_0) \), with a constant \( t_0 = 0.23 \) ns the correlation reduces greatly. This shifts the point where the exponential is equal to unity to \( t = t_0 \), within the range of the fit. With this change made to both components, the resulting correlation matrix is shown in Fig. 3-8(c). We now see that only the background terms show significant cross-correlations between themselves, and all of the other parameters are highly independent. This independence signifies the physical relevance of all the remaining parameters in describing the data.

So far we focused on the FR data taken at \( B = 200 \) mT which shows strong inhomogeneous dephasing effect. Using the electromagnet in the Voigt geometry we performed the measurement in the magnetic field ranging from \( B = 0 \) to \( B = 200 \) mT. We now perform the least squares fit of eleven datasets to the model described above.
Figure 3-9: Fits to gID model with reduced parameters. The short-timescale data, $t < 0.13$, is truncated. Insets show a close-up and $|\tilde{C}|$ (Matrix elements are ordered as in Fig. 3-8(c)).

With the modifications made to the model now we have nine free parameters, with four of them pertaining to the behavior of interest. Figure 3-9 shows three of these data sets and corresponding fits, with the insets showing a zoom of the long-timescale behavior. Also shown is the correlation matrix for each fit (The order of parameters in the matrix is the same as in Fig. 3-8(c)). All fits show reasonable agreement with the data. The parameters show significant correlation at the lowest magnetic fields. That is not a surprise as the magnetic field dependence of the spin dynamics is less important. At lowest $B$ values the field dependent and oscillation frequency parameters, $g_1$ and $g_2$, become redundant.

We coupled the decoherence and dephasing terms into the parameter $\zeta_n$ to simplify
the model and then use its magnetic field dependence later. Figure 3-10(b)-(e) shows how parameters $A_n$, $g_n$, and $\zeta_n$ vs. $B$, for $B > 40$ mT, the field region at which the parameters are largely uncorrelated. The errorbars are generated using the fit function of MATLAB. They are basically calculated from QR decomposition of the Jacobian matrix (similar to Eq. 3.19). We see that the $A_n$ and $g_n$ are roughly constant which is desirable regarding the fact that they are physical constants of the measurement. The effective decay rates $\zeta_n$ vary linearly with the magnetic field, as indicated by the fits shown in Fig. 3-10(a). From these fits, we can obtain $\tau_1 = 0.89 \pm 0.30$ ns, $\tau_2 = 2.72 \pm 1.79$ ns, $\Delta g_1 = 0.068 \pm 0.03$, and $\Delta g_2 = 0.14 \pm 0.02$.

![Figure 3-10: Fit parameters in gID model](image)

Figure 3-10: Fit parameters in gID model: (a)$\zeta_{1,2}$ (blue,red) vs. $B$ along with linear fits. (b) and (c) show $A_{1,2}$. (d) and (e) depict $g_{1,2}$.

The fits are now reasonably successful regarding how they capture the experimental data. Also the $\zeta_n$ show linear magnetic field dependence, in agreement with the model of gID and $B$-independent decoherence. We had experimentally measured $\Delta g_n$ through the size distribution. The fit values do not agree with them. The $\Delta g_1$ value from the FR data is more than two times bigger than the value form the size distribution.
distribution. It is even worse for the second component. \( \Delta g_2 \) differs by about a factor of 8 whereas it should be \( \Delta g_2 \approx \Delta g_1/2 \). The fits to the gID model result in \( \Delta g_2 \) value significantly larger than \( \Delta g_1 \). There are additional sources of \( g \)-factor inhomogeneity that we have basically neglected because previous studies do not signify their importance. They are structural properties of the NCQDs such as shape anisotropy and surface structure \[59, 27\]. The discrepancy in the value related to the \( S_2 \) component is stronger than what could be lifted by inclusion of those effects. This unexpectedly strong dephasing in the \( S_2 \) component was also observed in Ref. \[28\], with no explanation given. We provide an explanation for the strong dephasing properties of the second component in the next section.

Figure 3-11: Fits to gID model with reduced parameters at \( B = 200 \) mT. The short time data, \( t < 0.13 \) ns, is not included. (a) and (b) are with exponential and Gaussian \( \hat{P}_n \) respectively. Insets show zoom-in at longer times.

In fig.3.13 we observed that the Lorentzian is a better fit so the dephasing should be modeled as an exponential envelope. Let’s use the values of \( \tau_1 \) and \( \tau_2 \) obtained from the fits above (which do not depend on the form of the \( B \)-dependent dephasing) and repeat the fit at \( B = 200 \) mT using Gaussian \( \hat{P}_n \), and compare to the exponential
case. The resulting fit is shown in Fig. 3-11 with $\tau_{1,2}$ fixed, but allowing $\Delta g_{1,2}$ to vary. The exponential dephasing envelope captures the long time behavior much better than the Gaussian case in 3-11 (b). We used fixed values of the decoherence lifetimes and this comparison signifies the importance of using the right dephasing function form and knowledge of the $g$-factor distribution.

The followed a refined fitting process using the $g$-factor induced dephasing model in this section. We minimized the cross correlation of the fit parameters and decreased the number of parameters as possible. However, the gID model fails to follow the data. It fails to predict the first spike. Also the numerical value found for the dephasing parameters are far from what is expected, especially for the $S_2$ component. In the next section we add a magnetic decoherence and dephasing term that in combination with the gID model provides a complete picture for the data.

3.7 Magnetic field dependent decoherence and dephasing

In this section we describe how rapidly fluctuating random splitting arising from transitions between different exciton fine structure causes a relaxation mechanism. Then we compare the FR data to a model that contains this fine structure decoherence (FSD) mechanism for spins in the exciton component $S_2$. We briefly introduced different spin relaxation mechanisms including the Bir-Aronov-Pikus mechanism which roots in exchange interaction and bound holes.\[60\] FSD is similar but with the fluctuating splitting given by a combination of exchange interaction and shape-dependent crystal splitting. The time scale of the transitions between the FSS states in a NCQD is measured at room temperature by Huxter et al.\[51, 44\] to be $\sim 1$ ps$^{-1}$. This time scale might be confusing regarding the fact that we are measuring nanosecond decoherence time for spins. The FR measurement is sensitive to the net spin polarization of both charge carriers regardless of the exciton state. For example, a similar effect arises in GaAs, where the electron spin coherence time is much longer than that of
Long-lived spin coherence is observed via FR even though the optically pumped exciton very rapidly loses coherence. The full analytical treatment of the FSD, the optical excitation and the spin state evolution within the fine structure states is beyond the scope of this experimental study. Here we will present an effective theory that captures the essential physics, and well-describes the data. Furthermore, we will find that the predicted ensemble spin behavior is insensitive to the details of the exciton state dynamics, justifying the simplified model.

3.7.1 Introducing fine structure decoherence

We describe the FSD based on two widely supported assumptions in NCQDs: 1. The NCQD exciton state is randomly varied on short timescales, but without complete loss of spin information, and 2. There exist NCQDs within the ensemble where the exciton FSS approaches zero in zero applied magnetic field. Transient grating measurements\cite{51} that find transition times among exciton states to be $\sim$ ps, and TRFR measurements\cite{28} that show coherent spin behavior persisting for timescales $\sim$ ns strongly support the first assumption. The second assumption refers to the existence of “quasi-spherical” NCQDs, as hypothesized by Gupta et al\cite{28}. In Fig. 3-4(b) and (c), we reviewed that the FSS contains two energy crossings at $\mu = \mu_{qs}$, with the lower (higher) energy crossing corresponding to (anti-)symmetric states. The second assumption refers to existence on an exciton state within the ensemble that is composed of a linear combination of eigenstates near one of these crossings.

Let’s assume that the randomly fluctuating exciton state has the correlation time $\tau_c$. The exciton state alters between the superpositions of different available eigenstates and consequently its energy fluctuates with a root-mean-squared (rms) magnitude $\delta E$. This energy value is obtained from the magnitude of the FSS in that NCQD. For simplicity we assume that $\delta E$ is a function of NCQD ellipticity $\mu$ only, and it increases linearly away from the quasi-spherical point $\mu_{qs}$. As we say when a magnetic field $B$ is present the the crossing at $\mu_{qs}$ becomes an anti-crossing with
splitting $\Delta \propto B$. We write the energy splitting as below.

$$
\delta E = \sqrt{k^2(\mu - \mu_{qs})^2 + \Delta^2} = \sqrt{k^2(\mu - \mu_{qs})^2 + (\gamma B)^2},
$$

(3.23)

where $k$ and $\gamma$ are constants that describe the slope of $\delta E$ vs. $\mu$, and the magnitude of $\delta E$ at the anti-crossing, respectively. Figure 3-12(a) shows $\delta E(\mu)$ at $B = 0$ and at $B \neq 0$ for $k = 2$ meV, $\gamma = 0.1$ meV, and $\mu_{qs} = 0.41$.

![Figure 3-12](image)

Figure 3-12: (a) and (b) show $\delta E$ and $\tau$ vs. ellipticity $\mu$ in the vicinity of $\mu_{qs}$ at $B = 0$ T and $B = 0.2$ T.

A rapidly fluctuating spin splitting causes decoherence of a spin state with an exponential decay envelope. The decoherence rate $1/\tau$ resulting from an isotropic randomly varying splitting with rms magnitude $\delta E$ and correlation time $\tau_c$ can be calculated in the Born-Markov approximation. In the regime where $\tau_c \ll \tau$,

$$
\frac{1}{\tau} \approx \frac{(\delta E)^2\tau_c}{\hbar^2} \left(1 + \frac{1}{(g\mu_B B/\hbar)^2\tau_c^2 + 1}\right).
$$

(3.24)

The results presented here are in the regime where $g\mu_B B/\hbar \ll 1/\tau_c$, so we can simplify

$$
\frac{1}{\tau} \approx \frac{(\delta E)^2\tau_c}{\hbar^2}.
$$

(3.25)
Combining Eq. 3.23 and Eq. 3.25 we obtain an expression for the decoherence rate

\[
\frac{1}{\tau} = \left( \frac{k^2 (\mu - \mu_{qs})^2 + (\gamma B)^2}{\hbar^2} \right)^{\frac{1}{2}} \tau_c.
\] (3.26)

This decoherence time is depicted in fig. 3-12(b) at \( B = 0 \) and \( B \neq 0 \). Its value varies greatly depending on the shape of the NCQD. At \( B = 0 \), \( \tau(\mu_{qs}) = \infty \), and declines like \((\mu - \mu_{qs})^{-2}\). At \( B \neq 0 \), the maximum at \( \mu_{qs} \) is reduced with \( \tau(\mu_{qs}) \propto B^{-2} \) and far from \( \mu_{qs} \), also falls off like \((\mu - \mu_{qs})^{-2}\). At large values of \(|\mu - \mu_{qs}|\) the calculated decoherence time \( \tau < \tau_c \) which is outside the range of validity of Eq. 3.24. These short timescales, however, are below the resolution of the measurements here, and therefore will not significantly affect the comparison of the model to the data.

Now we have to take into account the shape distribution effect of the ensemble. We use the experimental shape distribution data of fig. 3-5(c) fitted by a normal distribution \( P(\mu) \) with mean ellipticity \( \bar{\mu} \) and standard deviation \( \delta_{\mu} \) as below

\[
P(\mu) = \frac{1}{\sqrt{2\pi} \delta_{\mu}} \exp \left( \frac{-(\mu - \bar{\mu})^2}{2\delta_{\mu}^2} \right),
\] (3.27)

Then by integrating the exponential decay with lifetime given by Eq. 3.26 over the distribution \( P(\mu) \) we obtain the ensemble decay envelope

\[
\Gamma_{FSD}(t) = \int_{-1}^{1} \exp \left( -t / \tau(\mu) \right) P(\mu) = \int_{-1}^{1} \exp \left( -t / \tau(\mu) \right) \frac{1}{\sqrt{2\pi} \delta_{\mu}} \exp \left( \frac{-\bar{\mu}^2}{2\delta_{\mu}^2} \right)
\]

\[
\exp \left[ -t \gamma^2 B^2 \tau_c / \hbar^2 \right]
\] (3.28)

The three terms of this equation are plotted in Fig. 3-13, with time on a logarithmic scale axis. We can see that \( \Gamma_{FSD}(t = 0) = 1 \), and then decays to zero as time increases. The first term (blue curve) is non-zero only at short timescales (\( \sim 1 \) ps) and yields a fast decay. The second term (green curve) modifies the first term in short scales before it plateaus to a constant value. If \( \bar{\mu} = \mu_{qs} \) (if the shape distribution is centered at the quasispherical point), then this term is equal to unity. As long as the shape distribution has some amount of weight at the quasispherical point (\(|\bar{\mu} - \mu_{qs}| \lesssim \delta_{\mu} \)),
the second term will change the relative amplitude of the fast decay to the slow decay by a factor on the order of unity. The third term (red curve) describes an exponential decay with a time constant proportional to $1/B^2$. The dephasing term in gID model has a similar term but with an inverse $B$ dependency instead of inverse $B^2$.

Figure 3-13: The three terms of Eq. 3.29 plotted with $\mu_{qs} = 0.41$, $k = 2$ meV, $\gamma = 0.1$ meV, $\delta \mu = 0.179$, and $\bar{\mu} = 0.147$.)

The exponential terms in Eq. 3.29 signify the effect of the NCQDs with $\mu \approx \mu_{qs}$. These nanocrystals involve in the ns-scale spin dynamics. Figure 3-14 depicts the geometry distribution as each black circle represents NCQDs with certain diameter and ellipticity measured via TEM. The curve shows calculated $\mu_{qs}(d)$. The overlap of $\mu_{qs}(d)$ with the measured scatter of $(\mu, d)$ points suggests that we expect NCQDs with long-lived spin coherence to exist within the ensemble. The NCQDs farther from the line in Fig. 3-14 give rise to the observed short-timescale behavior.

Figure 3-14: Black circles indicate measured $d$ and $\mu$ within the ensemble. The curve shows $\mu_{qs}(d)$.  

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### 3.7.2 gID+FSD model

In previous section we introduced a decoherence time that in conjunction with the
g-factor inhomogeneity induced dephasing can describe the lifetime and dynamics of
the $S_2$ component in FR signal. Here we will develop a model function, including the
gID and FSD mechanisms to explain the magnetic-field-dependent decay envelopes.

As discussed above the $S_1$ component is thought to arise from individual electrons
(either in the $X^+$ state or after recombination of the $X^-$ state\cite{37}), so the splittings
due to the hole spin and the electron-hole exchange interaction will not affect the $S_1$
spin signal, and thus the FSD mechanism will not be active in the $S_1$ component.

Therefore, we will model the $S_1$ component using gID and B-independent decoherence:

$$f_1(t) = \cos \left( \frac{g_1 \mu_B B t}{\hbar} \right) \exp \left( -\frac{\Delta g_1 \mu_B B t}{\hbar} \right) \exp \left( -\frac{t}{\tau_1} \right). \quad (3.30)$$

We will model the $S_2$ component, attributed to NCQDs in the $X$ state, using the same
terms as above, with the addition of the FSD ensemble decoherence mechanism:

$$f_2(t) = \cos \left( \frac{g_2 \mu_B B t}{\hbar} \right) \exp \left( -\frac{\Delta g_2 \mu_B B t}{\hbar} \right) \exp \left( -\frac{t}{\tau_2} \right) \Gamma_{\text{FSD}}(t). \quad (3.31)$$

$\Gamma_{\text{FSD}}$ also depends on parameters $\mu$, $\mu_{qs}$, $\delta\mu$, $k$, $\tau_c$, and $\gamma$. We will use the measured
values of $\overline{\mu} = 0.147$ and $\delta\mu = 0.179$ and the calculated value of $\mu_{qs} = 0.409$; the rest
of parameters will be discussed below.

As in the previous section, we must closely examine the model and the resulting fits
to the data to extract meaningful information, given the large number of parameters.
This will be accomplished by studying and reducing the cross-correlations between
parameters in the model, where possible. There are a total of 15 parameters in this
model for which we choose an initial guess and perform a least squares fit to the
dataset at $B = 200$ mT, shown in Fig. 3-15(a).

From Fig. 3-15(a), we see that this model, unlike the model with gID alone, is capable of describing the data over the entire range, including both long- and short-timescale dynamics. Fig. 3-15(b) shows the correlation matrix $|\hat{C}|$ for the fit
Figure 3-15: (a) Fit to the gID+FSD model at $B = 200$ mT. The inset shows a close-up. (b) $|\hat{C}|$ for the parameters used in (a). The parameters that primarily define the dephasing and the decoherence dynamics are enclosed in the dashed box. (c) $|\hat{C}|$ with reduced number of parameters by introducing $\zeta_1$ and $\zeta_2^*$. The fit parameter values in (a) are as follows: $\gamma = 0.09$ meV/T, $g_1 = 1.15$, $g_2 = 1.59$, $k = 4.5$ meV, $\tau_1 = 1.5$ ns, $\tau_2 = 1.08$ ns.

with all parameters varied (Fig. 3-15(a)), with the parameters ordered to make $|\hat{C}|$ roughly block-diagonal. Black (white) indicates completely correlated (uncorrelated) parameters. These parameters are grouped according to which parts of the FR signal they affect. The decay envelope of the $S_1$ component is described by $A_1$, $\tau_1$, and $\Delta g_1$. The short timescale portion of the decay envelope of $S_2$ is described by $A_2$, $k$, $\tau_c$, and $t_p$. The pulse width $t_p$ enters here because the duration of the pump and probe pulses is most prominently seen in the convolution with the very short timescale behavior. The longer timescale decay envelope $S_2$ is mainly given by parameters $\gamma$, $\Delta g_2$, and $\tau_2$, which characterize the random splitting at $\mu = \mu_{qs}$, the gID mechanism, and the B-independent decoherence time, respectively. Again, $g_1$ and $g_2$ describe
The oscillation of the FR signal, and the final three parameters include a small non-precessing background.

The parameters we are primarily interested in here are those pertaining to the dephasing and decoherence envelopes, and are highlighted by the dashed box in Fig. 3-15(b). The remaining parameters describe the spin precession and the background, and are quite un-correlated with the parameters of interest. The high degree of correlation between the parameters that describe the short timescale dynamics ($A_2$, $k$, $\tau_c$, and $t_p$) is inevitable given that the details of the dynamics on these short timescales are below the time resolution of the experiment. Therefore, we cannot ascribe any significance to the specific values of those parameters. Instead, we will fix three of the four ($k$, $\tau_c$, and $t_p$), and only vary $A_2$ in the fits. The values for these three fixed parameters are all in the expected range: $k = 2.1$ meV matches the typical energy scales of FSS, $\tau_c = 1$ ps agrees with exciton transition rates measured in Ref. [31], and $t_p = 41$ ps is close to the value obtained from time-correlated photon counting. This leaves the correlations within the two sets of three parameters defining the longer timescale decay envelopes of the $S_1$ and $S_2$ components. Similar to Sec. 3.6.4, we can combine exponentially decaying terms together by using $\zeta_1$ defined previously, and

$$\zeta_2^* = \frac{1}{\tau_2} + \Delta g_2 \mu_B B/\hbar + \gamma^2 B^2 \tau_c/\hbar^2$$

(3.32)

$\zeta_1$ is a first order in $B$ as the last section, but $\zeta_2^*$ is a second order polynomial in $B$ now that we have added the exponential decay contribution from FSD with decay rate $\propto B^2$. As before we can further reduce correlations between the decay rates and the amplitudes by shifting the zero of the exponential decay, using the parameter $A_2^*$ defined above. The resulting correlation matrix with reduced parameters is shown in Fig. 3-15(c). By making the changes described in the previous paragraph, there are now nine parameters in the model, four of which affect the dephasing and decoherence behavior. The remaining five describe the spin precession dynamics, and a small non-precessing background. Figure 3-16 shows the result of fitting the data to this model at several magnetic fields, and the corresponding correlation matri-
Figure 3-16: Fits of FR data to gID+FSD model with reduced parameters at different magnetic fields. The insets in panels (a), (b), and (c) show a close-up of data and the fits along with $|\hat{C}|$. The insets in (d) are semilog plot of the data and fit along with $|\hat{C}|$. 
ces. From the correlation matrices we can see that the four dephasing/decoherence parameters are highly uncorrelated from the five other parameters, and the four dephasing/decoherence parameters are only partially correlated amongst themselves at $B \neq 0$.

In order to separately extract the different contributions to the decay contained in $\zeta_1$ and $\zeta_2^*$, we fit datasets at 11 magnetic fields from $B = 0$ to $B = 200$ mT. The model captures the short and long timescale dynamics at all magnetic fields, well-reproducing the shape of the decay envelope. This can be seen further in the semi-log plot of the $B = 0$ data and fit in the inset to Fig. 3-16(d). The best-fit parameters are plotted in Fig. 3-17. $A_1$, $A_2$, $g_1$, and $g_2$ do not vary greatly with $B$. By fitting $\zeta_1$ vs. $B$ to a first order polynomial and $\zeta_2^*$ to a second order polynomial, we obtain values for $\tau_1$, $\tau_2$, $\Delta g_1$, $\Delta g_2$, and $\gamma$. The fits are shown in Fig. 3-17(a) with the values obtained listed in Table 3.2.

Figure 3-17: (a)$\zeta_1$ (blue circles) and $\zeta_2^*$ (red squares) vs. $B$ along with linear (dashed blue) and 2nd order polynomial (solid red) fits to them. Panels (b), (c), (d), and (e) show $A_{1,2}$ and $g_{1,2}$ vs $B$ respectively.

The value of $\Delta g_1 = 0.057 \pm 0.009$ and $\Delta g_2 = 0.040 \pm 0.011$ are consistent with
the values found from the TEM measurements. Significantly, these values agree with the expectation that $\Delta g_2 \approx \Delta g_1/2$. The fact that these values of $\Delta g_{1,2}$ are somewhat greater than those from the TEM size measurements suggests that other sources of $g$-factor inhomogeneity are present, e.g. surface structure and shape dependence.\[59, 27\]

Since $\gamma$ arises from Zeeman splitting of degenerate states, we expect $\gamma \sim \mu_B \approx 0.0579$ meV/T. The value $\gamma = 0.098$ meV/T agrees with this expectation. Finally, these measurements provide values of $\tau_1 = 1.69 \pm 0.28$ ns and $\tau_2 = 3.11 \pm 0.47$ ns. These decay times are significantly different from each other, and emphasize that the $S_1$ and $S_2$ components are subject to different $B$-independent dephasing/decoherence processes.

Table 3.2: Fit parameters in the gID+FSD model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_1$</td>
<td>1.69 ± 0.28 ns</td>
</tr>
<tr>
<td>$\tau_2$</td>
<td>3.11 ± 0.47 ns</td>
</tr>
<tr>
<td>$\Delta g_1$</td>
<td>0.057 ± 0.009</td>
</tr>
<tr>
<td>$\Delta g_2$</td>
<td>0.040 ± 0.011</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>0.098 ± 0.001 meV/T</td>
</tr>
</tbody>
</table>

Comparison of the FR data to the two models above demonstrates that the gID model is not sufficient to explain the observed behavior, but the addition of the FSD mechanism well-captures the measured decay envelope. To explain the $B$-dependence of the decay envelope using gID alone, the magnitude of the effect for the $S_2$ component would have to be implausibly large, given both the magnitude of the effect in the $S_1$ component and the prediction from TEM measurements and effective mass theory. On the other hand, the measured NCQD size and shape distribution are consistent with the gID+FSD model, but not with the gID model alone.

Previous FR measurements in NCQDs have observed the short timescale behavior here attributed to FSD.\[54, 28, 37, 40\] In these works, the short-timescale behavior is ignored, typically by eliminating the data at short time. These experiments were performed with shorter pump and probe pulse duration, $t_p \sim 100$ fs to $\sim 1$ ps. Because in the present work the short timescale behavior predicted by FSD is limited by convolution with the pump and probe pulses, the short timescale feature has
smaller amplitude and larger width than in experiments with shorter pulse duration. Figure 3-18 shows the gID+FSD model function (Eq. 3.17 with $f_{1,2}$ as in Eq. 3.30 and Eq. 3.31) plotted with $t_p = 40$ ps, $t_p = 5$ ps, and $t_p = 0.5$ ps. On the nanosecond scale axes on which the FR data is typically plotted, the short timescale feature often appears as a spike with unresolved width. In some previous work, the short timescale feature is plotted off the y-axis scale (inset to Fig. 3-18).

![Figure 3-18: gID+FSD model function with $t_p = 0.5$ ps, $t_p = 5.0$ ps, and $t_p = 40$ ps. Parameter values are from final fit of the previous section with $B = 200$ mT. Inset shows a close-up of the $t_p = 5.0$ ps curve.](image)

3.8 Conclusions

The inclusion of the FSD mechanism in the $S_2$ component but not the $S_1$ component is supported by data in Ref. [37] and Ref. [54]. Both of these results observe spin dynamics in NCQDs that can be tuned to include both the $S_1$ and $S_2$ components, or the $S_1$ component only (by charging the NCQDs electrochemically [37] or by tuning the pump energy [54]). In both cases, the short timescale feature is present if and only if the $S_2$ component is present (see Fig. 2 in Ref. [37], and Fig. 3 in Ref. [54]). The FSD mechanism should also be present in the dynamics of lone holes, or in the $X^-$ state with the electrons in a spin zero configuration. We do not observe long-timescale dynamics reflecting the expected hole $g$-factor, but these states may contribute to the short-timescale signal.
The procedure used to fit the data here allows for the extraction of the zero-field decoherence times \( \tau_1 = 1.69 \pm 0.28 \text{ ns} \) and \( \tau_2 = 3.11 \pm 0.47 \text{ ns} \) with reasonable confidence. The fact that these numbers differ with statistical significance suggests that different mechanisms are ultimately limiting the spin coherence time for the \( S_1 \) and \( S_2 \) components. The \( S_2 \) component, associated with carrier spin dynamics in NCQDs containing an exciton, is clearly not limited by the exciton recombination lifetime \( \tau_X \approx 20 \text{ ns} \). The lifetime of several nanoseconds is consistent with predictions of decoherence and dephasing caused by randomly oriented nuclear spins, which interact with the carrier spins via the hyperfine interaction. We would expect the \( S_1 \) component to also be affected by nuclear spin induced decoherence, but as \( \tau_1 < \tau_2 \), it appears that another mechanism must be further limiting the \( S_1 \) lifetime. If the \( S_1 \) component arises from the electron spin in the \( X^+ \) state, then \( \tau_1 \) would be limited by the non-radiative recombination of the \( X^+ \) state. While the lifetime \( \tau_{X^+} \) of the \( X^+ \) non-radiative recombination is not precisely known, estimates of \( \tau_{X^+} \approx 0.7 \text{ ns} \), are at least of the correct order of magnitude. In negatively charged NCQDs, single electron spins can be initialized by a process involving Pauli blocking of transitions to the \( X^- \) state. In that process, the electron is polarized in the ground state so there is no possibility of spin decay by recombination. While it is possible that some other mechanism could limit the single electron spin lifetime, the fact that we measure \( \tau_1 < \tau_2 \) suggests that the \( S_1 \) component arises from the electron in the \( X^+ \) state, or possibly a combination of \( X^+ \) and single electrons polarized via the \( X^- \) state.

The results here illustrate that to obtain quantitative information about decoherence and dephasing in NCQDs from a fit to a multi-parameter model, there is a need to use a well-defined procedure for fitting the data in which cross-correlations between model parameters are understood. Furthermore, we see that excluding parts of the data in order to improve the quality of the fit, can alter the results, and therefore such fits must be treated with caution.

The FSD mechanism presented here provides a resolution to four separate open questions. First, given the FSS of the exciton ground state in NCQDs, it was un-
clear how exciton spin dynamics should manifest in this ensemble. This led to the hypothesis that only quasi-spherical NCQDs give rise to the observed exciton spin precession. This idea is built into the FSD mechanism in that only excitons near the quasi-spherical point exhibit long-lived spin coherence. Second, FSD correctly reproduces the previously unexplained short timescale feature, here caused by exciton spins in NCQDs away from the quasi-spherical point. Third, FSD accounts for the unexpectedly strong $B$-dependence of the decay of the spin signal for the $S_2$ component. In this model, this arises from the anti-crossing in the FSS near the quasi-spherical point, which has a splitting proportional to $B$. Random fluctuations between the levels near this anti-crossing cause decoherence at a rate $\propto B^2$. The fitting here reveals this parabolic dependence of the decay rate vs. $B$. Fourth, transient grating measurements have shown very short lifetimes for excitons in a particular fine-structure state despite long-lived spin coherence observed in Faraday rotation experiments. This has previously been explained by positing that rapid fluctuations do occur between exciton fine structure states, but without total loss of carrier spin information. In FSD, these rapid fluctuations are the cause of the decoherence of the long-lived carrier spin.

In the discussion of the FSD mechanism here, the exact nature of the fluctuations between different exciton fine-structure states is not discussed. Here, we can avoid this complex issue as the decay envelope predicted by FSD does not depend strongly on these details within the resolution of these measurements, as long as the quasi-spherical point is included somewhere within the inhomogeneous ensemble, and the random splitting becomes large away from it. This allows us to assume a simple form for the distribution of random splittings which allows analytical evaluation of the ensemble decay profile. Future work may shed light on how the details of the time evolution of the exciton state within the manifold of fine structure states affects the spin dynamics.

The time-resolved Faraday rotation measurements, combined with TEM characterization of the ensemble and fitting procedures demonstrated here allow for quantitative analysis of decoherence and dephasing effects in NCQDs. Previously, this
has proven difficult due to the complexity of the observed dynamics, and the ad-hoc nature of the model functions used for fitting. These techniques will allow future experiments that study the room-temperature and low-temperature decoherence and dephasing mechanisms in NCQDs in greater detail, with the possibility achieving more robust spin coherence in these semiconductor nanostructures.

Comparison of the FR data to the two models above demonstrates that the gID model is not sufficient to explain the observed behavior, but the addition of the FSD mechanism well-captures the measured decay envelope. To explain the $B$-dependence of the decay envelope using gID alone, the magnitude of the effect for the $S_2$ component would have to be implausibly large, given both the magnitude of the effect in the $S_1$ component and the prediction from TEM measurements and effective mass theory. On the other hand, the measured NCQD size and shape distribution are consistent with the gID+FSD model, but not with the gID model alone.
Chapter 4

Enhancing Faraday rotation

In this chapter we focus on two methods for enhancing the FR signal and performing the measurement in an optical device that might be incorporated in integrated optical circuits.

4.1 Brewster’s reflectors

The FR angle is practically minuscule. It means that the majority of the linearly polarized probe photons pass through the sample without any change. This unchanged portion of the probe beam does not convey any spin information. We can use a linear polarizer to cancel out this component and send the perpendicular component into a single photodetector. The change in the intensity of this component is a probe of the magnetization in the sample. However, we would lose the benefits of the differential measurement through two balanced photodiodes. The signal to noise ratio would be much smaller also the photodiodes usually require a threshold of input intensity to reach their optimum output signal to noise ratio. So we need an incomplete polarizer to cancel some part of the unrotated beam but keep the perpendicular component intact. A simple piece of glass that is positioned at the Brewster’s angle in front of the beam can perform this modification.
4.1.1 Experimental method and results

Here we demonstrate how a simple set of glass reflectors positioned at the Brewster’s angle in front of the probe beam after the sample can enhance the FR signal. We call them here Brewster reflectors (BRs). This method might be generally used in any optical measurement that is based on detection of a rotation in a linearly polarized laser e.g. Faraday or Kerr rotation. As we studied in previous chapters the typical angle of polarization rotation in these experiments is in the order of a few milliradians or less. Detection of these small variation in polarization caused by a pump pulse is usually carried out using a differential measurement through two cascaded lock-in detectors, one using a reference signal from a modulation on the pump beam and the second one from the probe beam modulation.

![Figure 4-1: Schematic of the Faraday polarization rotation and Brewster’s reflection effect. The out of plane arrows represent the s polarization and the two-headed in plane arrows represents the p polarization](image)

A schematic of the polarization scenario in FR measurement is depicted in Fig 4-1. The red beam indicated with an out of plane arrow is the initially linearly polarized probe. The pump and probe pulsed laser beams that are aligned on top of each other using a dichroic mirror are focused on a cuvette containing colloidal suspension. The out coming probe light acquires a horizontal component after the sample, shown by the two-headed arrow. A set of BRs are positioned here to reflect part of the vertically polarized component. The pump pulse is then blocked with a long pass optical filter. A half wave plate (HWP) is used to rotate the polarization so that a Wollaston prism creates two balanced beams with perpendicular polarizations. The two beams are then sent into two photodetectors. Using the HWP the intensity of these two beams
are balanced when the probe pulse arrives earlier than the pump pulse in the sample.

We stacked up to 15 250-micron-thick glass slides at Brewster’s angle of glass-air interface, 56°, in front of the probe beam after the sample. We used a plastic holder built using a 3d printer. The BRs partially reflect (∼ 15%) the unrotated component of the polarization and hence enlarge the angle of rotation and the measured signal. This method introduces a simple way for enhancing the polarization rotation and might lift the need for complex differential measurements.

To quantify the enhancement, the final polarization state of the probe laser can be calculated as below were [HWP], [BR], and [FR] represent the Jones matrices for the half waveplate, transmission through a BR, and Faraday rotator [67] respectively. \( n \) is the number of BRs in place. Here we neglect unwanted reflection off the surfaces including the glass-air interface inside the BRs and assume perfect HWP and Wollaston prism.

\[
E_{p,f}E_{s,f} = [HWP][BR]^n[FR]E_{p,i}E_{s,i}
\]

(4.1)

\( E_{p,i,f} \) and \( E_{s,i,f} \) represent amplitude of the light electric field in s and p directions before the sample and at the detectors respectively. The recorded polarization rotation can therefore be written as:

\[
\Theta = \frac{E_{p,f}^2 - E_{s,f}^2}{E_{p,f}^2 + E_{s,f}^2}
\]

(4.2)

Figure 4-2 depicts how \( \Theta \) depends on the number of BRs, \( n \), assuming a perfect s polarized input probe and an initial Faraday rotation of 0.1 degrees. In this ideal model the polarization angle reaches 45° by using 40 BRs. While the polarization increases the transmitted power drops as 0.85\(^n\). This reduction in power can potentially decrease the signal to noise ratio (SNR) in the measurement. As the available power becomes insufficient for stimulating enough voltage in the photodetectors the uncorrelated background noise from the detectors and electronics gradually dominate the output. The noise caused by the fluctuation in the actual FR signal might also
be affected by the probe power.

The experiments are performed by measuring the FR signal at zero delay time, when the pump and probe pulse arrive at the same time. The measurement is repeated for different number of glass slides. Fig. 4-3(a) shows the FR angle measured at different number of BRs. The FR angle increases monotonically with $n$ as predicted. The initial probe power into the detectors is 52.7 $\mu$W and it decreases to 0.92 $\mu$W when 15 BRs are used. The SNR, shown in 4-3(b), is calculated as the FR value divided by the standard deviation in the 50 data points taken to create each data point in fig. 4-3(a). The available probe power sets a limit on the number of BRs that can be used. This is because the amount of noise produced by the detectors increases at low laser intensities so the SNR decreases afterward. In fig. 4-3(a) the FR angle increases by about three folds while the SNR stays almost constant. In another set of measurement, we kept the total power reaching the detectors constant at 0.75 $\mu$W level. We started with a small incoming probe power and increased the incoming power after adding each BR so the final power is constant. Fig. 4-3 (c) and (d) depict the result. In this case not only the FR angle increases at each step but we also get an enhancement in SNR.
4.1.2 Conclusion

We demonstrated a simple method for amplifying the FR angle and improving the SNR in Faraday and Kerr rotation measurements by introducing BRs to cancel out the unnecessary polarization component of the probe laser. We observed a linear increase in FR signal as number of reflectors increases. Although our experiment was limited by the available probe laser power, we recorded both enhancement of the FR angle and signal to noise ratio.

4.2 FR measurement on a QD-polymer composite optical waveguide

Optical waveguide and resonators are essential components of integrated optical devices. Their design and fabrication are very well established through standard semiconductor fabrication techniques. Also optical spin measurement and control is a
well-established and powerful way for preparing, reading, and manipulating spins in different media. However, bringing these two fields together for creating an integrated optical spin device remains challenging. In this section we describe the efforts toward performing the FR spin measurement and in general polarization rotation measurement in an optical waveguide. We report the fabrication method and characterization of a QD-Polymer composite optical waveguide and the resultant FR data. Developing an integrable optical device on which these measurements can be performed opens interesting possibilities for creating new sensors as well as possible results toward coherent spin manipulation. T.W. Saucer et al recently reported that an optical ring-resonator with a spin active medium included in the resonator can result in up to six orders of magnitude enhancement in the Faraday rotation [68]. R.G. Beausoleil et al have developed waveguide-resonator structures with embedded nitrogen-vacancy centers in diamond as an scalable method for quantum photonic applications [69, 70]. Here we focus on embedding the NCQDs, investigated in last chapters, in an optical waveguide-resonator device for spin pumping and probing in an ensemble.

4.2.1 QD-polymer waveguide, fabrication method

Coupling optically active quantum structures to optical waveguide resonators is the main challenge in this subject regarding the optical requirement for pumping and probing the spin states, geometry of the device, and the nanoscale precision required for placement of the spin medium in the device. To avoid various complications of this method we fabricate the optical waveguide on a QD-PMMA composite. This is intended to be a proof of concept for ensemble spin measurement. Various challenges remain to be address toward fabrication of a device for single spin or entangled spins measurements.

The optical medium of the waveguide is made of PMMA and NCQD composite. It is fabricated on a thin film of Cytop, an optically clear Fluoropolymer resin with refractive index of $\sim 1.34$, atop a silicon substrate. The waveguides are fabricated following the method of J.K. Poon et al [71]. We first fabricated a series of optical waveguides with different dimensions on PMMA only to examine the efficiency of
such structures and find the optimized geometry. The fabrication process is depicted in fig. 4-4. A 500-Micron thick silicon wafer is diced into 1cm by 1cm dies. The dies are cleaned thoroughly in several steps to remove any external contaminant residue. Any residual substance might create adhesion problems for the thin film layer being deposited on top. A layer of Cytop resin (obtained from Asahi Glass) is then spin coated to create a 4-Micron thick layer. The 4-Micron thickness is obtained via three times of spin-coating and baking of the substrate. After each spin coating step the substrate is backed in three stages 65°C for 60sec, 95°C for 60sec, and 180°C for 20 min. Then the final sample has been baked for 3 hours at 180°C. All of the processes is performed in a cleanroom to avoid any contamination. Prior to spin coating of the PMMA layer a surface modification via O₂ plasma exposure is necessary to make surface less hydrophobic. The plasma treatment rearranges the surface molecules so that the surface-PMMA adhesion improves. For the plasma treatment an RIE chamber is used at 200 mTorr of O₂ at 100W for 30-40 seconds. After spin coating the desired layer of PMMA or QD-PMMA composite another baking at 180°C for 20 minutes is followed to harden the active layer.

![Figure 4-4: The fabrication steps shown on the cross section of the device. (a) shows the different coated layers on Si substrate. (b) depicts the exposed PMMA regions. (c) shows the cross section of the typical waveguide after removal of the exposed PMMA region.](image)

The waveguides are patterned via electron beam lithography. A layer of 15 nm gold is deposited on the PMMA layer via thermal CVD to prevent charge accumulation.
during e-beam exposure. After metal deposition the substrate is cleaved along a 200 Micron deep scratch line scribed on the backside. The device will be made on the cleaved edge. This is necessary because the spincoating is not uniform on entire surface and the outer edges of the die have substantially thinner Cytop or PMMA films. We break the die in the middle and make the device on the center part of the chip. The waveguide pattern is written utilizing a TEScan scanning electron microscope at 30kV. The surface is exposed via 6.00mm working distance with a typical dosage of 350 μC/cm². Subsequently, the Au layer is removed using a gold etchant solution (Sigma Aldrich) and the PMMA is developed by putting in MIBK:IPA(1:3) developer solution for 90s following 20s of IPA immersion. Putting the device in DI water would finally stop the development process. The plasma treatment step is specifically critical for this step. Without exposure to proper plasma power, pressure, and exposure time the PMMA would not stand this chemical step and peal off the Cytop layer.

The same process was followed for fabricating QD-PMMA waveguides. With the NCQDs embedded in PMMA the plasma treatment had to be adjusted for achieving the required adhesion to CYTOP. Also the adhesion critically depends on the concentration of the NCQDs in the PMMA film. Figure 4-5 shows an optical microscope image of a QD-PMMA waveguide with 1 × 1 Micron cross section. The waveguide is located inside the wider groove on two sides of the image. The corner bends have a radius of 25 Microns.

In case of QD-PMMA composite, several trials were necessary for proper adjustment of QD:PMMA concentration. The main issue to resolve was the aggregations of the nanoparticles and adhesion of the layer to Cytop. Aggregates bigger than a few hundred nm specially decreased the light coupling efficiency because of a strong scattering. Including the nanocrystals also decreased adhesion of the composite layer to Cytop and created non-uniform sidewalls. The QD-PMMA solution was prepared as follows: we first centrifuged the NCQDs solution to separate the NCQDs from the solution. For the nanocrystals to precipitate a few ten microliter of Methanol was added to the 200 microliter of NCQD solution in the centrifuge vial. Methanol is
a polar solvent and breaks the bounds keep the nanocrystals suspended in Toluene. The particles precipitate relatively fast, in a few minutes. The rest of the solution is removed from the vial and the vial is left under a fume-hood to dry for a few hours. Then appropriate amount of 7% PMMA in chlorobenzene, depending on the target QD:PMMA ratio, is added to the vials containing the NCQDs. This solution is stirred using a magnetic stirrer for several hours to prevent formation of aggregation and to reach a uniform solution. We started with a filing factor of 1% for NCQD concentration. The volume ratio of the NCQDs in the final dried layer of PMMA is called the filing factor. It turned out that a filling factor of 1% leads to an unreasonably dense QD layer with significant aggregation. We prepared samples with filling factor of 0.5, 0.1, 0.02, and 0.01% for comparison.

4.2.2 The optical characterization of the waveguides and FR measurements

We are using the waveguides for a polarization dependence measurement so it is crucial to know what happens to the polarization once the laser travels through the structure. Another limiting point is amount of light we can couple into and out of the structure, the coupling efficiency. The out-coupled laser intensity from a PMMA waveguide with $1 \times 1.5$ Micron cross section waveguide that is 450Micron
long was about 20% for 600 ± 25 nm wavelength. We prepared a single mode waveguide at the first step however the coupling efficiency was significantly lower. The coupling also strongly depends on the shape of the two input and output facets of the waveguide. Sometimes the PMMA layer was stretched and bent when we were cleaving the sample. For this reason, a visual inspection of the cleaved area was necessary with the purposes of choosing the right sample and position before performing the lithography steps.

For examining the polarization retention properties of the waveguide, we sent a vertically (or horizontally) polarized light into the structure and measured the polarization of the output via a cross-polarizer. About 6% of the light could pass through. This means that the waveguide is slightly birefringent. The birefringence is usually associated with the bends in the waveguide, sharper bends create stronger birefringence. A similar measurement with a linearly polarized light with 45 degrees angle confirms this observation. As expected a circular polarization turns into an elliptical output. To inspect this, we used a linear polarizer in front of the output while a circular polarization is sent in. If the polarization of the out-coupled light is still circular, the linear polarizer should reduce the power to half regardless of its angle. However, the output varies between 30 to 70 percent. The coupling at 660 ± 15 nm is similar but slightly weaker.

The optical set up for FR measurement on the waveguide is exactly the same as the TRFR setup described in 1.9 with the only difference that the pump and probe beams are now traveling in the same path and being focused using a 60x microscope objective on one end of the waveguide. Using the end-fire coupling method the coupled laser light travels through the waveguide and couples back into the same microscope objective. Because of the ~150 Micron separation between the two legs of the waveguides the out-coupled beam is positioned far enough from the incoming beams to be easily gathered and sent towards the detection optics.

The FR measurements on these structures were greatly unsuccessful. Although we observed a big signal originating from arrival of the pump pulse, we could not conclude that it is associated with excited spins in the waveguide. However, we are
Figure 4-6: TRFR data from a QD-PMMA waveguide at 100 mT. Certain that the data is associated with the interaction of the pump pulse with the nanocrystals and consequently a polarization rotation in the probe. In a PMMA only waveguide such signal was not recorded, also the signal magnitude depends on the concentration of the QDs in the waveguide. Figure 4-6 shows a set of data taken from a QD-PMMA waveguide with a filling factor of ∼0.02%, 1 × 1 Micron cross section, and 450 Micron long. A magnetic field of ∼100 mT is applied perpendicular to plane of the waveguide using a permanent magnet positioned beneath the sample. Although there is rise in the signal at zero time delay and the sign of this component changes with the helicity of the circular pump, the rest of the signal does not show a characteristic of CdSe spin signal. Specifically, it is not responsive to the applied magnetic field. Experiments on longer waveguides with smaller filling factors did not generate meaningful results. The time scale of the signal suggests that it is not similar to the transient absorption data.

4.3 Conclusion

We fabricated a series of PMMA and QD-PMMA optical waveguides with different sizes and established a robust fabrication procedure. However, the FR measurement on the samples was not successful. The resultant signal cannot be conclusively related to the excited spin polarization in the NCQDs. There are a few possibilities including...
a combination of FR and transient absorption signal and most likely the nonlinear birefringence property of the waveguide structure.
Chapter 5

Summary and Conclusions

We studied optical spin initialization and read-out in room temperature CdSe NCQDs via pump-probe Faraday rotation measurement. We utilized a supercontinuum laser for both pump and probe beams. This provides the freedom to independently choose the proper pump and probe wavelengths for samples with a wide range of mean nanocrystal sizes. In chapter 2, we presented our investigation on optical spin pumping in three different ensembles with mean particle radii of 3.05, 2.40, and 2.04 nm. We scanned the pump energy across a wide range and measured how resultant spin polarization varies. The band-edge exciton has different energies in these NCQDs and consequently the resonant spin pumping of the first exciton level happens at different energies (see fig. 2-5). Pumping the first exciton level gives rise to the resonant peak in the SPE data in all three samples however they show different behavior for higher pump energies (see fig. 2-9). The difference originates from the composition of the valence band states and size dependence of each exciton energy level. A valence band state is in general a superposition of hh, lh, and s.o. subbands with different states being composed with different weights of each subband. We calculated the valence band mixing for different states and resultant spin polarization. The calculation via a 6-band effective mass model gives an interpretation of the experimental data. After the first peak the three different samples display distinct SPE trends. Sample (A), larger size NCQDs, shows a second peak at 200meV higher in energy and then the signal goes to zero at higher energies. Sample (B), the sample with intermediate
size NCQDs, displays a broad shoulder in SPE before it falls off to zero. The SPE in sample (C), the smallest NCQDs, decays relatively fast after the first peak. The presented calculation follows this data based on the fact that a strong hh transition leads to spin up states and lh+s.o. transitions lead to electrons with spin down. This study provides an understanding of the underlying optical spin pumping mechanism for these structure.

In chapter 3 we studied a different aspect of the electron spin in NCQDs. We focused on dynamics of the spin polarization over time. The presence of multiple spin species with different precession frequencies was observed previously. However, a model that could describe the origin of contrasting dynamics of these components was not defined. We followed the conventional inhomogeneous dephasing model to describe the two observed components by developing a rigorous fitting procedure. However, this model fails to capture the spin data both at short and long timescales. We also experimentally measured the size distribution and the g-factor distribution to make certain that we are using the right set of parameters in the model. The issue to be addressed was the fact that these two components had two completely different dynamics. JA Gupta et al had suggested that one of the components is associated with the electron spin in a positively charged trion and the other one to a neutral exciton. There are studies that confirm this assignment. Although they had hypothesized that the long lifetime behavior in the second component is arising from the 'quasi-spherical' NCQDs, a mechanism capable of capturing this behavior and the prominent sharp spike in the beginning of TRFR scans was missing (for example see fig. 3-7). We developed a semi-empirical model that can fit the data very well and provides insight into the origin of the sharp short timescale as well as the long lived exciton spins. We associate the decoherence properties of the second component partly to a spin decoherence pathway that happens because of exciton state fluctuation in between the available fine structure states. This fluctuation relaxes the spin state similar to the Bir-Aronov-Pikus mechanism. The time scale of this relaxation depends on the how strong the energy fluctuation is. The fine structure itself varies depending on the size and shape of the NCQDs. The result of this model is shown in 3-16 at
different applied magnetic fields. The combination of the magnetic field dependent fine structure decoherence and size dependent inhomogeneous dephasing successfully captures the data in both short and long timescales.

Our efforts in incorporating the NCQDs in more applicable optical devices is presented in chapter 4. First we presented a simple method for enhancing the Faraday rotation measurements by canceling the unrotated polarization component of the probe laser beam. Then we presented a QD-PMMA optical waveguide device for performing FR measurement on a chip. The resultant signal however was not conclusive and cannot be associated with spins signal.

The colloidal nanocrystal quantum dots with the tunable size dependent optical properties and improved chemical stability are currently being integrated in various optical devices. They also provide an easily accessible room temperature system for studying electron spin interactions. In this thesis we investigated some important aspects of spin initialization and relaxation properties that contribute to our understanding of spin phenomena in semiconductor nanostructures.
Bibliography


